Investigation of Phenanthroline Linked Dihydropyrenes as Photochromes

by

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B.Sc. University of Victoria, Victoria B.C., 2007

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

in the Department of Chemistry

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University of Victoria

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Supervisory Committee

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Abstract

Several photochromic dihydropyrenes were designed to test whether the DHP molecule retains its response to light when it is bound to the first row transition metals. DAP 26, NDAP 22 and BDAP 21 were composed of the parent DHP 11, naphthoyl-DHP 38 and the BDHP 12 fragments respectively that were bound via a Sonogashira coupling to the phenanthroline unit through an acetylene linker. A condensation reaction between DHP-imid 29 and BDHP-imid 50 with phenanthroline diketone 28 in the presence of an excess of NH₄⁺OAc⁻ yielded the imidazole functionalized dihydropyrenes DHP-imid 23 and BDHP-imid 24 respectively. PDD 25 which is a [e]pyrazino annelated DHP 11 was obtained from condensation of the DHP-diamine, generated in situ from its dinitro precursor 45, with phenanthroline diketone 28. Compounds 21, 24 and 25 responded reversibly to UV and visible irradiation while also undergoing thermal return. NDAP 22 decomposed upon exposure to UV while being converted from its open to the closed state.

Acac and hfac complexes of BDAP 52-55 and of PDD 60-61 were synthesized by reacting Co(acac)₂(H₂O)₂ 51 and M(hfac)₂ 59 (where M = Co²⁺, Mn²⁺, Ni²⁺) with one equivalent of either BDAP 21 or PDD 25 photochrome respectively. Co(acac)₂(BDAP) 52 and Co(acac)₂(PDD) 60 complexes showed reversible opening and closing under alternative UV and visible irradiation for at least 10 cycles. Mn(hfac)₂(BDAP) 53, Ni(hfac)₂(BDAP) 54 and Co(hfac)₂(BDAP) 55 complexes opened upon exposure to visible light and then closed with heating in the dark. Thermodynamic parameters ΔE_{act}, ΔH‡ and ΔS‡ were determined after fitting the closing rate constant data for each species at 54, 64 and 74 °C (unless stated otherwise) to Arrhenius and Eyring equations.
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List of Numbered Compounds

1. 2. 3.

4. 5.

6.

7.

8.

9.

10.

11.

12.


15. 16.

17. 18. 19.
\[
M(\text{hfac})_2 \quad \text{where } M = \text{Mn}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}
\]
## List of Symbols, Abbreviations and Nomenclature

<table>
<thead>
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<td>A</td>
<td>Absorbance</td>
</tr>
<tr>
<td>b</td>
<td>path length of cell used for UV-vis spectroscopy (1 cm)</td>
</tr>
<tr>
<td>(n)-BuLi</td>
<td>normal butyllithium</td>
</tr>
<tr>
<td>c</td>
<td>concentration (mol L(^{-1}))</td>
</tr>
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<td>cm(^{-1})</td>
<td>inverse centimeters or wavenumbers</td>
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<td>excited state of dimethylidihydropyrene</td>
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<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
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<td>fully deuterated toluene for NMR spectroscopy</td>
</tr>
<tr>
<td>EA</td>
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</tr>
<tr>
<td>(\Delta E_{\text{act}})</td>
<td>activation energy for thermal return reaction</td>
</tr>
<tr>
<td>EM spectrum</td>
<td>electromagnetic spectrum</td>
</tr>
</tbody>
</table>
EtOH  ethanol
ε  extinction coefficient (mol L⁻¹ cm⁻¹)
ΔH‡  enthalpy of activation for thermal return reaction
HETCORR  heteronuclear correlated spectroscopy
ΔHᵢ  enthalpy of formation
¹H NMR  proton nuclear magnetic resonance spectroscopy
HOMO  highest occupied molecular orbital
HRMS  high resolution mass spectroscopy
Hz  Hertz
ΔG‡  Gibb’s free energy for thermal return reaction
IPSO  indolyl phenanthroline spirooxazine
IR (KBr)  infrared spectroscopy in KBr matrix
J  coupling constant (Hz)
K  Kelvin
kcal  kilocalorie
k_calc  calculated rate constant
k_meas  measured rate constant
λ_max  maximum wavelength of absorption
LUMO  lowest unoccupied molecular orbital
m (multiplicity)  multiplet
M  metal or molar
μM  micromolar
MLCT  metal to ligand charge transfer
mmol  millimole
mM  millimolar concentration
mol  mole
mp  melting point
MS  mass spectroscopy
NBS  N-bromosuccinimide
nM  nanomolar concentration
Pd/C  palladium on carbon catalyst
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>Φ</td>
<td>quantum yield</td>
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<tr>
<td>ps</td>
<td>picoseconds</td>
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<td>s</td>
<td>singlet</td>
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<tr>
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<td>spiropyran</td>
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<tr>
<td>ΔS‡</td>
<td>entropy of activation for thermal return reaction</td>
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<td>τ₁/₂</td>
<td>half-life</td>
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<td>Curie or critical temperature</td>
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<td>X-ray</td>
<td>X-ray diffraction analysis of structure</td>
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Acknowledgement

I would like to express my gratitude to Dr. Reginald H. Mitchell for guidance in the progress of this work and for willingness to work with me towards its completion. I appreciate his interest in organic chemistry for just the synthesis itself and for his patience with me as a person. I am thankful to Dr. David J. Berg for helping me finish the work which I had started in graduate school. I would also like to thank Dr. Natia L. Frank for initially accepting me as her graduate student and for her presence during the first two years of this project. I learned how to work on my own and to not need anyone to help me. Special thanks goes to Michelle Paquette for her determination and inspirational work on her own projects when we were working next to each other. Dr. Gabrielle Hager is greatly appreciated for all of the fun and insightful conversations. Doing this work has taught me many things about myself and my life.

I would like to thank Dr. Yun Ling of the University of British Columbia for mass spectrometric analysis. Christine Greenwood of the University of Victoria is acknowledged for running key proton and carbon NMR experiments which were reported in the experimental section of this thesis.

The University of Victoria and the Natural Sciences and Engineering Research Council of Canada are acknowledged for financial support.
To my friend Linda Bos
Chapter One: Introduction and Scope of Thesis

1.1 Introduction to Photochromism

The observation of photoinduced magnetic effects in inorganic molecular materials has led to intense exploration of systems that make optical control of magnetization for molecular electronics and switching devices possible.\textsuperscript{1,1b,2,3} Photoinduced molecular magnetic effects have the potential of being utilized for magneto-optic materials that allow optical switching of the magnetic state for data storage technologies.\textsuperscript{4,5,5b,6}

Striking effects of light irradiation on the magnetic state of molecular systems were first discovered in Co-Fe Prussian blue analogs.\textsuperscript{7} Upon illumination, these materials exhibit dramatic changes in the magnetic state including increased magnetization, linear and nonlinear dynamic susceptibilities, ordering temperature, remanence, and coercivity.\textsuperscript{8} The observed magnetic transition is caused by photochemically or thermally reversible photoinduced charge transfer from one metal center to the other, which leads to an increase in the overall spin state in the sample. However, such metal-centered systems have limitations. The short-lived photoinduced state persists only for several days and only at low temperatures making these systems currently impractical for real-life applications.

Alternative systems with lower optical densities have been explored in spin crossover complexes\textsuperscript{9}, in which excited state trapping of the high-spin state is observed at lower temperatures.\textsuperscript{10,11,12} Hence, in both the Prussian blues and spin crossover systems, photomagnetic effects originate from an excited state of the metal center. Such systems have limitations that arise from facile thermal relaxation to the ground state at temperatures above 100 K or even less. There is therefore great interest in the development of photomagnetic materials that are able to cross over from one spin state to the other and maintain the desired spin configuration at ambient temperature.

The goal for the future is to develop a photon-mode memory which would replace the heating modes that are used in current memory technologies.\textsuperscript{13} For the latter case, the process of writing information involves differential heating of a selected region of a two-
dimensional array of a switchable material with a focused laser. This irradiation must be of sufficient power so that the temperature of the matrix is raised above its critical temperature \( T_c \). As a consequence, the physical properties of this chosen region become altered. These include changes in viscosity, refractive index and reflectivity of the material. The information is subsequently read by using a laser of lesser power, so that the sample is not altered physically again, and measuring the difference between the polarization of the incident and the reflected light. The phenomenon utilized here is generally known as the Kerr effect.\(^{14}\)

Even higher densities for data storage are within reach if photon modes become employed instead of heat. This is because the pixel size, when using organic photochromes for recording, can be reduced to a few and sometimes even to an individual switching molecule. Photochromic molecules can also be ordered into 2D arrays or 3D blocks and a specific unit can be accessed with a simultaneous crossing of two or three laser probes operated at attenuated power. While the intensity of an individual laser is low, it becomes drastically amplified at the location where the beams of several of these are crossed. Upon intersection, the light intensity is enhanced becoming great enough to initiate a photochemical transformation at a precisely chosen location in the material.\(^{15}\)

Herein, a proposal is described for development of a new class of photoresponsive molecular materials which are paramagnetic metal complexes that incorporate photochromic DHP ligands. These metal complexes would couple the changes in electronic structure associated with photoisomerization of dihydropyrene to the spin state dependence of the ligand field in paramagnetic transition metals. It is believed that this strategy can lead to creation of new photoresponsive magnetic materials.

1.2 Classes of Photochromes

Several classes of organic photochromes exist based on key structural variations that determine the type of transformation that is needed to open and close the molecule. They differ from each other in the requirements for the cyclization reaction, their geometries and charge distribution differences between the open and the closed states. The bonds that are broken during photochemical opening and closing events as well as
the relative stability of the open and closed valence isomers define the kind of UV-vis spectra these structures have.

Photoswitching molecules with pale or colorless ground state structures that become subsequently transformed under photo-irradiation into colored and relatively less stable states are classified as positive photochromes. The more deeply colored isomer is the more thermodynamically stable one for the class of negative photochromes. A negative photochrome undergoes a photochemically induced isomerization, transforming itself into a colorless or a pale yellow substance. This colorless product has less thermodynamic stability than the colored starting material and would eventually return to the colored form.\textsuperscript{16}

It is accepted that the photochemical closing event for a conjugated triene goes \textit{via} a concerted 6\pi electrocyclization which is an allowed process in accordance with the Woodward-Hoffmann rules.\textsuperscript{17} The thermal return process is therefore not allowed for a 6\pi electron open cycle and the ring-closing should in theory not proceed in the absence of light. However, it has been observed that some of the photochromes without built-in charges such as diarylethenes, fulgides and dihydropyrenes nevertheless undergo the forbidden dark reaction, resulting in their return to the ground state with time. This thermal return, as predicted by definition of a thermal process, proceeds faster if the surrounding medium temperature is raised. The thermodynamics of this process have been extensively studied in photochromic materials in order to understand the principles that govern this transformation as well as control its occurrence and its rate.\textsuperscript{18}

\subsection*{1.2.1 Diarylethenes}

Irradiation of a \textit{cis}-stilbene 1 closes it to the dihydrophenanthrene 2.\textsuperscript{19,20,21} The subsequent exposure of the reaction mixture to air causes irreversible oxidation of 2 to phenanthrene 3 (Figure 1). When methyl groups are present at positions X and Y of 2, where the new carbon-carbon bond forms during the electrocyclization, the unwanted oxidative decomposition is slowed down and sometimes prevented at lower temperatures so that product 3 does not form. The kinetics of the photoisomerization of stilbenes is described in detail in a review by Waldeck.\textsuperscript{19}
**Figure 1:** Photochemical transformation of *cis*-stilbene 1 to the dihydrophenanthrene 2 followed by the oxidation of product 2 to a fully aromatic phenanthrene 3.

Diarylethenes (DE) belong to a class of switches that usually exhibit positive photochromism. This means that the lowest energy state of the diarylethene is the open structure 4′ (Figure 2) that has a UV-vis profile with shorter wavelength absorptions as labeled with a solid line A in Figure 3, imparting a pale or colorless appearance to this type of substance.

**Figure 2:** Examples of thermally irreversible diarylethenes 4 and 5.

Once a diarylethene is irradiated with the UV light, it undergoes a concerted 6π electrocyclization with bond formation between the two twisted out of plane portions of the molecule giving fused cores analogous to those found in structure 4 (Figure 2). An example of a UV-vis profile of the closed DE is shown in Figure 3 where the spectrum is labeled with a dashed line B. From here and onwards, the plain number, such as 4 for a DE in Figure 2, will be used to designate a closed state of any discussed photochrome and the corresponding primed number such as 4′ will refer to its open counterpart.
Figure 3: General figure showing UV-vis spectra of the open A (colorless) and the closed B (colored) isomer of the diarylethene photochrome type.

The light-driven electrocyclization proceeds only when the aromatic rings with carbon atoms between which the new bond forms are in an anti-parallel conformation with respect to each other\textsuperscript{22,23} as illustrated for molecules 4′ and 5′ in Figure 2. Photocyclization of diarylethenes from this arrangement involves relatively little overall molecular motion. This is a potential advantage in device applications of these dyes since they are more likely to retain photoresponsivity in restrictive media such as polymer matrices and in the solid state. The closed structure of the diarylethene normally has more extensive π-conjugation than the open form does. The UV-vis spectrum of the former is noticeably bathochromically shifted (~550 nm) compared to that of the latter with accompanying intense coloration of the closed compound (Figure 2).

The lifetime of the closed DE structure depends largely on how aromatic the rings are that participate in the electrocyclic rearrangement of the closing event. If these rings are benzenes, which have high resonance energy, then the closed form will return to the ground state open form in the dark more quickly than if these rings were the less aromatic thiophenes or furans. The resonance stabilization energies of the thiophene and furan heterocycles are smaller than those of benzene.\textsuperscript{24,22} Therefore, there is a smaller difference between the energy levels of the open and the closed state of the heterocyclic DE which is thought to lead to a larger barrier of activation for the thermal return process. Irie and coworkers exploited this logic in order to design nearly pure P-type
diarylethene photochromes.\textsuperscript{22} P-type photochromes can be inter-converted between the open and closed states only with light. These molecules, by definition, should not be susceptible towards the forbidden thermal return reactions that occur in the dark, the presence of which characterizes a T-type photochromic system. Molecules shown in Figure 2 remain closed for at least three months while being continuously heated at $80^\circ$C in the absence of light.

Use of a perfluorinated cyclopentene starting material allows for creation of fatigue resistant diarylethene derivatives. Some of these molecules can cycle 10,000 times between the open and closed forms before significant decomposition is noticed by UV-vis.\textsuperscript{15} It is believed that the origin of this property arises from the decreased susceptibility of the fluorinated hydrocarbons to oxidation. The densely packed highly electronegative fluorine atoms insulate the underlying carbon skeleton of the DE from its nucleophilic and electrophilic reactivity with oxidants such as O$_2$.\textsuperscript{25,26,27,28,29,30,31}

The ongoing goal for the synthesis of the diarylethene photochromes for long-term data storage application is to engineer a P-type system which would have highly extended $\pi$-conjugation in its closed state. This would push the absorbance maximum of the closed DE into the near-IR region where the molecule’s state can be probed with a weak diode laser. The synthesis of the P-type diarylethene has been accomplished with a few molecules of this class in which the closed structure exhibited push-pull electronics serving to amplify the dipole moment of the species (Figure 4). This added feature contributed to increasing the $\varepsilon$ and red-shifting the position of the $\lambda_{\text{max}}$ of the closed form 6 to 828 nm as shown in its UV-vis spectrum.\textsuperscript{32,33}

![Figure 4: Push-pull electronics; a closed diarylethene species 6 with $\lambda_{\text{max}}$ at 828 nm.](image)

Incorporation of large electron-rich aromatic substituents into the arms of a diarylethene lowers the energy needed for the allowed transition between its HOMO and
LUMO levels. The size of this gap characterizes the coloration of the conjugated closed state of the photochrome. The undesired outcome of this approach is that DE photochromes become more susceptible towards oxidative degradation in the presence of light as their π surfaces are extended. As the size of the π-system increases, the valence π-electrons are delocalized over larger regions in the overall molecular structure while also becoming much more reactive in comparison to a regular alkene. The closed-ring isomer 6 was also found to be thermally unstable. It returned to its open form 6’ with a \( \tau_{1/2} \) of 186 min at 60°C.\(^2\) Further study and experimentation is necessary in order to circumvent these road-blocks towards the creation of more robust, fatigue resistant and near-IR absorbing P-type diarylethenes.

Diarylethene photochromes with perfluorinated cyclopentene substituents, even when they can be precisely controlled by light, were thought to be not suitable for investigations in this project. Presence of six highly electronegative fluorine atoms, two cyano groups or a maleic anhydride in the backbone of DE reduces the distinction between the subtle differences in the ligand fields of the open and closed structures of this photochrome. This is undesirable since the objective of the current project is to synthesize dyes that have electronically different open and closed geometries with distinguishable effects on the metal center to which they are complexed. The second reason is that DEs tend to lose their inherent photochromism upon coordination to first-row transition metals. In order to explain this observation, it was postulated that the presence of a metal renders the internal conversion of the open to the closed DE inefficient.\(^{34,35,36,37,38}\) It is likely that the metal provides coupling pathways between the newly introduced upper energy levels of metallic origin and the energy levels of the excited state of the open DE.

### 1.2.2 Fulgides

The thermally irreversible fulgide 7/7’ shown in Figure 5 was synthesized by the Heller group\(^{39,40}\) in 1981. The photochromism of this type of molecule works in a similar way to that observed for diarylethenes and so fulgides can be thought of as belonging to a subclass of diarylethenes.
Figure 5: Heller’s thermally irreversible fulgide 7.

For best photochemical properties fulgides need to have an electron-poor moiety such as the maleic anhydride in 7 on one end and a heterocycle with reduced aromaticity compared to a benzene ring on the other side of the molecule. The conjugated triethylene in the heart of a fulgide is where the 6π-electrocyclization reaction occurs for the 7/7′ pair and in its analogues. Introduction of electron-donating and bulky substituents around this ring improved the photochromicity of this type of dye over the next decade, and since then the main focus has been the search for new fulgides.

The positive photochromism of the furyl fulgide along with its typically high extinction coefficients of visible electronic transitions complicates its incorporation into a solid matrix. Surface-limited reactivity of a fulgide that is embedded in a polymer matrix is common since the high absorptivity of the closed state prevents rapid and complete penetration of the photochromic 3D sample with light.\(^{41}\) The electrocyclization process of fulgides obeys the Woodward-Hoffmann rules in P-type systems and is by definition also concerted. These concerted opening and closing events are fast (<20 ps) and proceed without formation of intermediates for the 7/7′ isomers based on results of the laser flash photolysis experiments.\(^{42}\)

The photochemical properties of fulgides are attractive, making their derivatives good candidates for incorporation into metal complexes. This possibility should be explored in future work since very few metal complexes of these photochromes exist.\(^{43,44,45}\) The lengthy synthesis and the unknown effects of having a pendant phenanthroline ligand on the fulgide were some of the reasons why these dyes were not utilized in the current project.
1.2.3 Spirooxazines and Spiropyrans

Spirooxazines (SO) and spiropyans (SP) belong to a class of photochromes that are characterized by the presence of a spiral carbon center in their closed state which restricts electronic communication between the two halves of the molecule as in structure 8 (Figure 6).

![Figure 6: Indolyl spirobenzoxazine (SO) prototype dye shown in its open 8' and closed 8 states.](image)

Spiropyans have only an oxygen heteroatom in the central ring in which the reversible opening and closing occurs. Spirooxazines have an additional nitrogen atom in the opposite position relative to the oxygen of the pyran cycle of 9, converting it into an oxazine ring to get molecule 8 (Figure 7).

![Figure 7: Indolyl spirobenzoxazine (SO) 8 and indolyl spirobenzopyran (SP) 9.](image)

Past studies have shown that incorporation of this extra nitrogen atom into the spiropyran’s framework significantly increases fatigue resistance of the resulting spirooxazine. The spirooxazine in comparison to a spiropyran undergoes more photochemical interconversions before the cycling is finally stopped due to sample decomposition. This is thought to be so because of the slightly higher electronegativity of the nitrogen atom of SO in comparison to the carbon atom that is located in its place in the parent SP 9. The imine bond of the spirooxazines is a less nucleophilic reactant towards atmospheric O₂ making the latter attractive for use in short-term cycling devices such as ophthalmic lenses and soft memories.
The key C\textsubscript{spiro}-O link is cleaved during opening of the SO after UV-promotion of the valence bonding electrons of this bond into the corresponding antibonding orbitals.\textsuperscript{51} Zwitterion 8\textprime differs dramatically in shape and charge distribution along its skeletal backbone from the closed spiroxazine 8. The extended conjugated conformation of 8\textprime forces sterically demanding alterations to take place in the crystal lattice consisting of closed SO. Spirooxazines as a result tend to be poorly reactive towards UV light when they are irradiated in their purely solid state or when they are embedded in a polymer matrix.

Spirooxazines display fast opening and thermal relaxation kinetics in solution.\textsuperscript{52,53} They show positive solvatochromism of the open form which is consistent with better stabilization of the excited state of their open conformation \textit{en route} to the zwitterionic local minimum structure by solvents in the order of increasing dielectric constant.\textsuperscript{54,55} A plethora of synthetic strategies have been developed for making spirooxazines with enhanced photoresponsivity and longer lifetimes of the open form achievable with chemo-gated control.\textsuperscript{56,56b,57,58,59,60,61,62,63,64,65} It has even been shown that some of the crowned spiropyans can cycle between being a positive and a negative photochome upon coordination to a metal.\textsuperscript{66} An additional chemical agent such as a metal ion, a proton or a Lewis acid, which can stabilize the open form of the spiroxazine, increases this dye’s photoresponsivity by changing the equilibrium constant towards production of greater quantities of the zwitterionic form which is in accordance with Le Chatelier’s principle. Consequently, in order to return to the closed SO, which is a process accompanied by the reformation of the C\textsubscript{spiro}-O bond, this additive must be removed by chemical means or by dialysis. The procedures to achieve this have potential to either damage the spiroxazine itself or the matrix in which it is embedded. This is the main reason why chemo-gated SO switches are not popular as cyclical memories while they can work quite well for something like a single-use color test. Gating of the photochromism of the spirooxazines can slow down their thermal return and although effective, more practical ways had to be found for stabilizing the open states of these.
Figure 8: Photoisomerization of indolyl phenanthrolino spiroxazine (IPSO) 10 with UV and visible irradiation.

A simple and convergent synthetic methodology\(^{67}\) was developed for a class of spirooxazines containing aromatic heterocycles capable of binding transition metals in both the closed and open states. Upon irradiation, photoisomerization occurs between the closed spirooxazine form 8 and the open zwitterionic form 8’ (Figure 6). Incorporation of a nitrogen heterocycle, such as phenanthroline that was used for making IPSO 10 (Figure 8), leads to changes in the coordination environment near the bound transition metal. Therefore, there is a possibility of being able to reversibly influence the magnetic properties of the bound metal with the state of the coordinated photochromic ligand. Binding of IPSO 10 to paramagnetic transition metals to form \([M(IPSO)_3]^{2+}\) complexes has been accomplished which allowed investigation of the effect of metal coordination on the thermodynamics and kinetics of spirooxazine photoisomerization, as well as of photoisomerization on the magnetic behavior of the metal-spirooxazine complexes.\(^{67}\)

It has been shown that a series of transition metal-photochrome complexes exhibit significant increases in photoresponsivities and stability in both the closed and open states. The thermal and photochemical equilibria constants depend on the metal, suggesting the existence of strong electronic coupling between the metal center and the photochromic ligand.\(^{68}\) Unfortunately, the spirooxazines as a class of photochromes exhibit rapid thermal relaxation rates due to low energies of activation for the thermal return process (15–20 kcal/mol), giving mixtures of both the open and closed states at thermal equilibria in solution.\(^ {69,70}\) This complicates interpretation of spectroscopic data of metal-spirooxazines and also leads to limited lifetimes of the open form in polymer films at room temperature. Interest therefore developed in the dihydropyrenes 11 as the activation barriers to thermal relaxation are sufficiently high for some derivatives of this class of photochromes to allow for isolation of both the open and closed states at ambient temperature (Figure 9).
1.2.4 Dihydropyrenes

Photochromism in dihydropyrenes was first reported in 1965 by Boekelheide and coworkers.\textsuperscript{71} Dihydropyrenes are predominantly negative photochromes and are commonly classified as tethered diarylethenes. The ground state of the parent DHP 11 is a green molecule which is converted to the pale yellow open CPD 11′ species upon its exposure to visible light (Figure 9). The CPD structure has a UV-vis profile with absorptions mostly in the short wavelength region of the EM spectrum giving the CPD form a pale yellow appearance to the human eye. The CPD 11′ undergoes a 6π-electrocyclization as it is transformed back into its closed DHP isomer 11 when it is irradiated with the UV (254 nm) lamp.

![Figure 9: Photoisomerization of the parent DHP 11/11′ under UV and visible irradiation.](image)

The open and closed variants of the DHP 11 can be obtained separately when the Hoffmann elimination of methyl sulfide in the last step of its synthesis is carried out at different temperatures. Synthesis of DHP 11 at room temperature gives the CPD isomer 11′ which can be isolated and purified by column chromatography yielding a pale yellow solid. But when this reaction is done in refluxing benzene, the starting material undergoes elimination of methyl sulfide followed by the Woodward-Hoffmann forbidden thermal electrocyclization in one pot to afford the closed DHP isomer 11. Both 11 and 11′ are isolable with the former being more thermodynamically stable since the synthetically obtained compound 11′ eventually converts to the closed DHP 11 in the dark. The DHP product 11 shows the visible transitions as illustrated in Figure 10, which because of the large conjugated π system extend well into the visible range (477 nm). Since the closed green DHP 11 is ultimately the final product of all thermal and photochemical transformations that this molecule can undergo, it is categorized as a negative photochrome.
Figure 10: UV-vis spectra of the opened 11′ (blue) and closed 11 (red) DHP molecule in cyclohexane.

The coloration of the flat DHP structure arises from the $\pi \rightarrow \pi^*$ transitions in the visible range with modest extinction coefficients if they are allowed by symmetry. The geometry of the DHP 11 is almost planar with a fully conjugated periphery. Its core element is an [14]-annulene which is stabilized by a large resonance energy. The trans-annular bond is broken during photochemical opening of DHP 11 leading to its structural rearrangement towards 11′. The stepped geometry of the 11′ isomer isolates the smaller aromatic rings from electronically interacting with each other, hence the short-wavelength benzenoid absorptions of the CPD 11′ form (Figure 9 and 10). The geometric changes which accompany the $11 \rightarrow 11'$ transformation require small changes in molecular volume relative to those that are observed for spirooxazines. DHP species do not undergo extensive molecular deformations because the aryl components that are directly involved in the electrocyclization reaction are closely tied by an alkene linker.

There are significant electronic differences between the open and closed dihydropyrene isomers $11'$ and 11 even with fairly small shape differences between them. The $\pi$-electrons in the closed flat annulene are well delocalized over the entire molecular periphery. This circular current induces high magnetic shielding of the internal methyl...
group protons which as a result resonate far upfield (δ -3 to -4) as indicated by the proton NMR spectra of these species relative to methyl groups found in their usual chemical environment (δ 0.9–2). The upfield chemical shift of the internal methyl protons is a signature feature of the closed DHP 11 compound.\textsuperscript{72} This unambiguous assignment was exploited as a probe by the Mitchell group in an attempt to quantify the aromaticity of aromatic rings that were benzannelated to the DHP 11 core.\textsuperscript{73,74} The internal methyl protons of the CPD 11′ appear at δ 0.9–1.5 in the proton NMR spectrum which is closer to the regular chemical shift value for this alkyl group. The planar annulene periphery is interrupted by structural kinks in CPD 11′ and its π-electrons display attenuated reactivity compared to that of the closed DHP 11.

Since DHP 11 and CPD 11′ are ideally poised for the electrocyclic rearrangement, it was expected that the light-initiated opening and closing processes for this species would go with high quantum yields (Φ). Good Φs of 0.4–0.6 were measured only for the photo-closing of the CPD isomers with UV light in cyclohexane. A detailed investigation into the mechanism of the photochemical opening\textsuperscript{75,76} suggested that the CPD isomer 11′ forms from the singlet excited state of DHP 11. This claim was substantiated by addition of a triplet quencher during the opening isomerization experiment and observing that there were no changes in the Φ of CPD 11′ in the presence of O\textsubscript{2}. High-level CASSCF/CASPT2 \textit{ab initio} calculations of the nature of the excited state of the photochemical reaction of DHP suggested that the crossing between the DHP* and CPD*, which is essential for the isomerization to occur, is largely a non-productive process giving mostly the DHP starting material ground state.\textsuperscript{77} Therefore, it was expected that the Φs of the ring-opening of DHP photochromes in solution are low (Φ\textsubscript{vis} was 0.0015 for 11 \rightarrow 11′ in cyclohexane\textsuperscript{76}).

The DHP \rightarrow CPD conversion in the crystalline state was consequently presumed to go forward at a much slower rate than in solution or to not happen at all. This is so because of an inherently low Φ for the opening process combined with having a system that is sterically constrained by its organization into a lattice. The rate of isomerization of an individual DHP unit in a solid depends on the 3D position of this unit and on the state of nearby units within the array. The factors that influence the kinetics of the DHP \rightarrow CPD photo-conversion are the state in which this substance is irradiated, the Φ of the
opening process and the thermodynamic stability of the CPD product in that state. The kinetics of isomerization of any individual DHP switch as a result would deviate from the first order behavior requiring a more complex mathematical treatment for interpretation.

**Figure 11**: Isomerization of BDHP 12 to the open colorless form 12’ with visible light and its return with UV or in the dark.

Much experimental work has been done on dihydropyrenes by the Mitchell group and other investigators in order to understand what factors enhance the Φ of the photo-opening reaction. Benzannelation was one of the most fruitful strategies for achieving this goal. Synthesis of parent BDHP 12 was a key achievement since it was the first of a kind of DHP dye that fully converted to the open form with visible light (Figure 11). Annelation onto the DHP core confers additional resonance stabilization to 12’ by introducing a third benzene ring. The forbidden thermal return reaction of 12 was found to be quite slow with an estimated τ_{1/2} of 7.2 days at 298 K. This is consistent with the additive resonance energy contribution of the three conjugated benzene rings in 12’. It was shown that the tert-butyl substitution as in DHP 11 has little influence on the rate of the 12’ → 12 return process. The unbubylated derivatives of 12 and 12’ were found to only differ by 9.5 kcal/mol in energy, as indicated by the density functional theory calculations, utilizing the B3LYP/G-31G* method, with the closed isomer being slightly more thermodynamically favoured. There is a high enough activation barrier for the thermal return reaction to allow for spectroscopic interrogation of either the open or the closed isomer. BDHP 12 was therefore chosen as the starting structure for this project towards rational design of photochromic DHP-based ligands which were then utilized for binding to metals of interest.
1.3 Effects of Metal Complexation on Photochromic Properties of DHP

To this day there is insufficient experimental evidence to be able to predict whether a chosen DHP molecule would retain its photochromicity after it is bound to a paramagnetic metal. A survey of relevant literature suggests that the photochromicity is retained or lost depending on the mode of binding of the metal to the DHP. The type of metal atom also appears to be an important factor and its choice should be carefully considered in these complexation studies. For example, the η⁶-coordination of photochromic BDHP 12 to a Cr(CO)₃ tripod results in a robust complex 13 that neither opens under prolonged visible irradiation nor decomposes⁸⁰ (Figure 12). The BDHP 12 that is η⁶-bound with its [e]-benzene moiety to Ru(III) which is η⁵-capped by a cyclopentadienide anion on the other side to form a PF₆⁻ salt 14 was shown to be photochromic and electrochromic⁸⁰ (Figure 12).

![Figure 12: Benzo[e]DHP η⁶-coordinated to the Cr(CO)₃ tripod giving a non-photochromic complex 13 and the analogous structure of the photochromic [(BDHP)RuCp]PF₆ salt 14.](image)

A ferrocenyl complex Fe(η⁵-CpDHP)₂ 15, synthesized by reacting two equivalents of LiCpDHP with FeCl₂, was non-photochromic and oxygen sensitive. A closely related ytterbocene Yb(η⁵-CpDHP)₂(THF)₂ 16 was not photochromic either, while the CpDHP starting material that was used for both of these complexation reactions easily underwent reversible opening and closing valence transformations upon its exposure to visible and UV light⁸¹,⁸¹b (Figure 13).
This type of behavior was also true for (BDHP)Fe(CO)$_3$ 17 and (BDHP)[Fe(CO)$_3$]$_2$ 18 complexes that were isolated as intermediates in the synthesis of photochromic BDHP 12 from a reaction of the precursor DHP-furan adduct with Fe$_2$(CO)$_9$ (Figure 14). However, it was concurrently discovered that the heavier metal analogues ($\eta^5$-CpDHP)Re(CO)$_3$ 19 and ($\eta^5$-CpDHP)Ru(Cp*) 20 do photoisomerize (Figure 14).

The findings described above led to a hypothesis that the photochromicity of the metal-bound DHP photochrome depends largely on whether the free DHP is photochromic to begin with and also on the mode of its coordination to the metal. The size and the magnetic state of the metal could also be a critical influence on whether the metal-DHP $\pi$-complex can open and close. Current observations suggest that the $\pi$-coordination to larger transition metals gives mostly photochromic DHP complexes, while the smaller metals such as chromium and iron quench the pathway that leads to the DHP $\rightarrow$ CPD conversion.
1.4 Scope of Thesis

Does binding of the photochromic DHP molecules to small transition metals shut down their photochromic response? To answer this question the first goal was to design and synthesize DHP-based photochromes the structures of which incorporate a phenanthroline component so that they could be complexed to the first row transition metals. Since π-coordination gives largely unpredictable results, we chose to use a σ-donating phenanthroline unit in this investigation as the attachment point between the DHP photochrome and the metal. The bridge between the DHP and the phenanthroline should ideally not break conjugation between these units. This would allow for electronic influence of the open and closed geometry of the DHP via the phenanthroline on the magnetic environment around the metal. Connecting the photoactive DHP at the ortho position of the phenanthroline was expected to give a poor ligand due to anticipated over-crowding at the hexacoordinated metal center.

![Figure 15: Photochromic BDAP 21 and NDAP 22 ligands along with BDHP 12.](image)

Thus BDAP 21 was set as our first synthetic target. BDAP 21 would be created by joining 12 via the acetylene bridge to the meta position of phenanthroline to avoid unwanted steric strain of coordination while maintaining conjugation with 360° of intramolecular twisting (Figure 15). NDAP 22, a variant displaying similar photochromic behavior to 21 where 12 is substituted with a naphthoylated parent DHP 11 was the second target (Figure 15). The kinetics of ring-opening and closing of NDAP 22 were expected to be different from those of 21. The synthesis of BDAP 21 and NDAP 22 molecules will allow for direct comparison of their kinetic and thermodynamic parameters with those of their metal complexes.
The acetylene in 21 allows for full conjugation between phenanthroline and 12 even though the overall structure is not always planar. The imidazole heterocycle that is fused onto the phenanthroline as in structures 23 and 24 does not allow these molecules to be totally planar (Figure 16). Derivatives 24 and 23 would be made to see what the influence of the imidazole substitution is on the photo-opening kinetics of the BDHP 12 and the DHP 11 photochromes (Figure 16).

![Figure 16](image16.png)

**Figure 16**: BDHP 12 used as a building block for photochromic BDHP-imid 24 and DHP 11 for DHP-imid 23 derivatives.

A different approach will be employed in order to make PDD 25 where the phenanthroline is [e]-fused through a 1,4-pyrazine ring to the parent DHP 11. The electronic relay of the state of the switch in this configuration is expected to be intimately recognized by the atomic orbitals of the metal in its coordination site. PDD 25 (Figure 17) is a fully conjugated structure with zero intramolecular rotation in its closed state. It is the ideal candidate for being a photon-gated metal spin state altering device unless the distance for electronic communication between the metal binding pocket and the dihydropyrene is too great.

![Figure 17](image17.png)

**Figure 17**: Photochromic PDD 25 where the DHP 11 is directly annelated to phenanthroline.
To answer the question posed at the beginning of this section, some paramagnetic complexes would be made when the photochromic DHP ligands are in hand. BDAP 21 would be complexed to Co(II), Mn(II), and Ni(II) metals with acac and hfac spectator ligands. The photochromic properties and the rate constants of their photo-opening and closing would be measured and compared to those of free BDAP 21. Complexation of PDD 25 to a cobalt cation that is capped by either two equivalents of hfac or acac ancillaries would also be attempted.

The aim of this report is to give experimental details for synthesis of phenanthroline-based photochromic DHP ligands as well as of their complexes and also to provide a glimpse into possible future applications.
Chapter Two: Synthesis and Characterization of DHP-Phenanthroline Photochromes

2.1 Introduction

Several photochromes were designed to test whether the DHP molecule retains its photochromic properties when it is bound to a paramagnetic metal through a conjugated linker. It was initially reasoned that an acetylene bridge could serve as a strong electronic coupler between the isomerising DHP group and the bidentate ligand, and this strategy gave rise to DAP 26, BDAP 21 and NDAP 22 (Figure 18).

![Figure 18: Structures of target photochromes 21-26.](image)

The parent di-tert-butyl DHP 11 is photochromic with a very small quantum yield (Φ) of ring-opening (0.0015 ± 0.0001). Benzannelation of 11 to create BDHP 12 led to a 28-fold increase in the Φ of ring-opening (0.042 ± 0.002). Then a PDD 25 molecule was envisaged, in which phenanthroline is annelated to the DHP via a 1,4-pyrazine bridge. It was thought that making a system where the electron-rich DHP is annelated to the electron-poor phenanthroline would maximize electronic coupling between the donor-DHP and the acceptor-ligand. It was believed that [e]-annelation through the pyrazine...
bridge would extend the conjugation of the DHP 11 system much like the [e]-benzannelation, leading to an improved ring-opening Φ in PDD 25 relative to 11.

The main design feature of DHP-imid 23 and BDHP-imid 24 was having a photochromic system where the phenanthroline and the DHP portions were joined by a non-linear bridge. What is the influence on the photochemistry of the parent DHP when it is bound to phenanthroline via an imidazole bridge? Simple aromatic systems (eg. Figure 19) with imidazole substituents are known to exhibit fluorescence.\textsuperscript{83} Non-destructible readout of the intensity of near-IR emissions of a photochromic system by reversible switching with UV and visible light is one of the main strategies in development of reliable materials for long-term data storage applications.\textsuperscript{84,85,86,87} The fluorescence of the imidazole is dependent on the steric interactions of the imidazole heterocycle with a substituent at its C\textsubscript{2} position (Figure 19). A planar imidazole linker that is not coplanar with the DHP fragment, because of bay proton interactions, interrupts the overall conjugation in the molecule.

The angle of rotation about the C\textsubscript{2}-phenyl bond as shown in Figure 19 is the most important factor that influences the Φ of fluorescence of the imidazole\textsuperscript{83} 27. The loss in conjugation due to the intramolecular twisting results in a less planarized overall structure and so radiationless motion (instead of the light-emissive relaxation) deactivates the excited state, leading to a low Φ of fluorescence. Perhaps the reversible opening and closing of DHP that is bound to the imidazole can affect the intensity of the emitted light. To address this question it was thus important to devise methodology for joining the ligating phenanthroline to the DHP photochrome via an interlinking imidazole.

The key steps in the synthesis of the photochromes 21-26 were (i) a metal-catalyzed coupling of the DHP fragment with ethynylphenanthroline (21, 22, 26), (ii) a condensation of phenanthroline-5,6-dione 28 with 4,5-diamino-DHP to install the phenanthroline via the [e]-annelated pyrazine ring (25), and (iii) a double condensation of the DHP aldehyde 29 and 50 with the phenanthroline diketone 28 in presence of excess ammonium acetate to give the imidazoles (23, 24). The syntheses were carried out as described in detail below.
2.2 Synthesis of DAP 26

Scheme 1

\begin{center}
\begin{tikzpicture}
\node (n1) at (0,0) {\includegraphics[width=0.8\textwidth]{scheme1.png}};
\end{tikzpicture}
\end{center}

\textit{Reagents and Conditions. (i) CuI, TEA, PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}, TIPS-acetylene, benzene, 90°C for 40 hours, 90% yield; (ii) TBAF/THF, 70% yield; (iii) Compound 30 (1.5 eq), PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}, CuI, TEA, benzene, 55°C, 40 hours, 75% yield.}

The synthetic methodology for coupling the ethynylphenanthroline 30 to the dihydropyrene was first established for the parent di-\textit{tert}-butyl DHP 11 to obtain DAP 26 as shown in Scheme 1. Generation of the ethynylphenanthroline 30 was accomplished by coupling TIPS-acetylene with 3-bromophenanthroline 31\textsuperscript{88} under Sonogashira coupling conditions using Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} and CuI catalysts, followed by removal of the silyl protecting group with TBAF.\textsuperscript{89} The Sonogashira coupling reaction of 31 with TIPS-acetylene in benzene at 90°C for 40 hours yielded 90% of product 32 after purification by column chromatography over silica gel. The terminal alkyne 30 was then generated by deprotection with TBAF in THF at room temperature in 70% yield following column chromatography.

Coupling of the 4-bromo-DHP 33 with 30 was not successful using the PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} catalyst, leading to recovery of starting materials. Aryl iodides are more reactive than the aryl bromides in these types of reactions\textsuperscript{79}, and so iodo-DHP 34 was synthesized and subsequently coupled to 30 under relatively mild Sonogashira\textsuperscript{89} conditions (Scheme 1). DAP 26 was isolated in 75% yield as a brown solid after silica gel chromatography and was characterized by \textit{\textsuperscript{1}H and \textsuperscript{13}C NMR, IR (KBr), UV-vis, EA and MS techniques. Proton NMR spectrum (CDCl\textsubscript{3}) of the product showed
disappearance of the terminal acetylene proton at δ 3.35 and appearance of a new set of resonances for a monosubstituted phenanthroline as well as two singlets for the internal methyl protons at δ -3.82 and δ -3.83. The $^{13}$C NMR spectrum of DAP 26 has two shielded carbon signals at δ 95.4 and δ 92.2 that were assigned to the acetylene functional group. The IR spectrum of a KBr pellet of DAP 26 has a peak at 2186 cm$^{-1}$ for the acetylene C≡C stretch. The HRMS results were satisfactory giving m/z 547.3103 for M+H molecular ion while the calculated mass for M+H was at m/z 547.3113.

2.3 Synthesis of NDAP 22

When a naphthoyl or any other carbonyl group is bound to DHP 11 the ring-opening φ of the parent structure is increased, allowing for observation of formation of the open isomer within a useful time frame for study. The other attractive feature of joining a large aromatic moiety via a carbonyl linkage to the DHP 11 is that the fluorescence emission of the latter can be modulated by opening and closing the switch. The CPD form 11′ is non-fluorescent while the closed DHP 11 exhibits some fluorescence in the visible range due to its greater overall structural planarity (Figure 20) and rigidity which are important for good fluorescence φs. The method of registering fluorescence intensity as a reporter of the state of the DHP is sensitive in the nM concentration regime of the photochrome. This is a significant improvement in the detection limit as compared to monitoring the activity of the switch by UV-vis, which is only useful for substances in mM–μM concentrations.

![Figure 20](image)

**Figure 20**: The closed DHP 11 is flat and the open CPD 11′ state has a stepped geometry.

The presence of a conjugated C=O linker between the DHP 11 and another aromatic system increases the φ of photo ring-opening of the former. In fact, when this carbonyl linker was transformed into a geminally substituted alkene by a Wittig reaction of 35 with a methyl phosphonium salt, the resulting product 36 (Figure 21) was no longer
photochromic. The presence of the alkene was thought to provide a lower energy pathway for non-radiative deactivation of the DHP*.

![Diagram](attachment:image.png)

**Figure 21**: Conversion of 35 to 36 using a Wittig reaction.

The $\lambda_{em}$ in organic molecules is normally bathochromically shifted relative to the $\lambda_{max}$ where the original excitation occurs. This is because of partial energy loss by the system during its internal conversion and nonradiative decay to reach the singlet excited state ($S_1$) prior to relaxation of the molecule to its ground state ($S_0$). This correlation can be manipulated by synthetic modification of the structure to push the $\lambda_{em}$ further into the near-IR frequencies where the changes in absorbance intensity can be registered with a low-intensity red diode laser. This can be achieved in theory by joining larger aromatics through a carbonyl linker to the parent DHP 11 structure.

The large Stokes shift of the $\lambda_{em}$ relative to the corresponding $\lambda_{max}$ of the colored form of the DHP photochrome allows for addressing of either band, with less spectral overlap. This shift is observed because the vibrational relaxation of the excited state of a molecule is faster ($10^{-15}$ s$^{-1}$) than its electronic relaxation to the ground state ($10^{-8}$ s$^{-1}$). The energy of the emitted radiation is therefore smaller than that of which is absorbed with the difference between these corresponding to the vibrational excitation energy. However, there must be a balance between the energy of the $\lambda_{em}$ and the overall molecular stability since DHPs tend to become less stable as their size increases due to rise in their susceptibility to oxidative degradation.

It was hypothesized that joining the phenanthroline acetylene 30 with the photochromic naphthoyl-DHP 38 should provide a product that is also photochromic. The brominated naphthoyl-DHP precursor was obtained from the reaction of 4-naphthoyl-DHP with NBS at -78°C. This reaction gives predominantly the 4,10-brominated product that was isolated from the crude reaction mixture by column chromatography over silica gel. Pure material was obtained on crystallization from hot
hexanes with slow evaporation of the solvent. The best yield of NDAP 22, synthesized by coupling 30 to the 4,10-brominated naphthoyl-DHP\textsuperscript{92} 37 under Sonogashira conditions\textsuperscript{93} (Scheme 2), was obtained by heating the reaction mixture at 60°C for 15 h in dry DMF. The product was purified by column chromatography over silica gel and obtained as an air-stable dark orange solid in 92% yield. NDAP 22 was characterized by \textsuperscript{1}H and \textsuperscript{13}C NMR, UV-vis, IR (KBr), EA and MS techniques.

\textit{Scheme 2\textsuperscript{a}}

\begin{center}
\begin{tikzpicture}
\node at (0,0) (a) {\includegraphics[width=\textwidth]{scheme.png}};
\end{tikzpicture}
\end{center}

\textsuperscript{a}Reagents and Conditions. (i) 1.0 eq. NBS/DMF added to 30 at -78°C \(\rightarrow\) RT, crude 80% yield; (ii) Pd\textsubscript{2}(dba)\textsubscript{3}, P(tBu)\textsubscript{3}, Cs\textsubscript{2}CO\textsubscript{3}, piperidine, DMF, 60°C for 15 hrs, 92% yield.

The \textsuperscript{1}H NMR spectrum (CDCl\textsubscript{3}) of the product did not have a terminal alkyne resonance, while the internal methyl protons appeared at \(\delta\) -3.587 and \(\delta\) -3.616. The IR spectrum of the KBr pellet indicated that NDAP 22 has a substituted acetylene functional group with a 2186 cm\textsuperscript{-1} stretching frequency; an absorption at 1637 cm\textsuperscript{-1} confirmed the presence of a C=O bond of the ketone. The \textsuperscript{13}C NMR spectrum (CDCl\textsubscript{3}) showed unique resonances at \(\delta\) 94.7 and \(\delta\) 92.6 for the alkyne and at \(\delta\) 200.7 for the ketone carbonyl carbons. The HRMS experiment confirmed the composition of 22. The calculated mass for M+H was at \textit{m/z} 701.3532 while this ion was found at \textit{m/z} 701.3542.

\textbf{2.4 Synthesis of BDAP 21}

[e]-Benzannelation of DHP 11 significantly increased the \(\Phi\) of the photochemical ring-opening reaction of this class of dyes\textsuperscript{75}. The UV absorbance spectrum of the closed form of BDHP species 12 has a characteristic broad absorption in the 450–600 nm region of the EM spectrum. The open form 12' has mostly short wavelength absorptions due to
presence of benzene rings. The existence of a broad band at \( \lambda_{520\text{nm}} \) in toluene of the closed BDHP 12, which is well-separated from the benzenoid absorptions of the open BDHP 12', makes it possible to selectively excite the closed state of BDHP with minimal energetic overlap with the tail absorptions of 12'. Thus, a fully opened state of the BDHP 12' is accessible with light.\(^9^1\)

Fixing the double bond on the [e]-side of the DHP 11 by annelating to it a molecule with a higher resonance energy also increases the stability of the open form of the resultant BDHP 12. Upon benzannelation the \( \Delta H_f \), which is the difference between the enthalpy of formation of the closed and the open valence isomers, is reduced and so the thermal conversion rate of \( 12' \rightarrow 12 \) is decreased. The closer the two isomers are in energy, the less favoured is the transition from the less thermally stabilized form to the ground state. The activation energy (\( \Delta E_{\text{act}} \)) associated with the thermal return reaction is increased for the \( 12' \rightarrow 12 \) transformation relative to DHP 11.\(^7^9,^9^4\) This undesired reaction can be slowed down even further or eliminated in some cases in DHP derivatives by cooling the CPD sample on ice.\(^9^5\)

**Figure 22:** A diagram showing the steric interactions between the bay protons of the adjacent benzene rings in the BDHP 12 parent.

To understand the effects of structural modification on the thermodynamics of the transition state, a second factor to consider is the through-space interactions between different parts of the molecule in this transition state. When the DHP molecule is undergoing the geometric transformations from the planar closed DHP annulene to the stepped open geometry of the CPD form, it has to overcome these interactions (Figure 22). These effects are most pronounced at the junction of the DHP core and the fused benzene ring, as in an [e]-annelated structure such as 12, and their extent can be fine-tuned synthetically. Excessive proton bay interactions can destabilize the DHP form enough so that a full CPD \( \rightarrow \) DHP conversion cannot be achieved thermally and
sometimes not even photochemically. Increasing the strain in the DHP relative to the CPD form should theoretically lead to a slower thermal back-reaction of the CPD. But having too much of this strain may also lead to establishment of a photostationary state instead of having a complete conversion between the open and the closed states of a given DHP.

Much effort has been made so far in the direction of creating photochromic materials that exhibit negligible thermal relaxation at room temperature. The goal for long-term memory storage applications is to suppress the unwanted thermal return of the switching dye under ambient conditions. This criterion has been already satisfied for a several of Irie’s diheteroarylethenes and Heller’s early fulgide (Figure 23) and is believed to be a possibility for the class of DHP photochromes once the thermodynamics of the ring-closing reaction are understood better and a suitable structure is optimized. Creating a DHP analogue with a relatively stable open form that can also bind first row transition metals was the motivation behind the design of BDAP 21.

![Figure 23: Examples of two thermally irreversible diarylethenes 4 and 5 and a fulgide 7.](image-url)

The synthesis of BDAP 21 required three more synthetic steps than that of DAP 26 (Scheme 3). The BDHP starting material was brominated at -78°C with 1.0 equivalent of NBS to obtain BDHP-Br in 84% yield. Installation of the acetylene group on the DHP and a subsequent Sonogashira coupling of the product with 3-bromophenanthroline failed and instead yielded dimerization of the ethynyl-DHP – a previously known compound.
**Scheme 3**

```
  12  39  21
  i.   Br   ii.
  N  N  H
```

*Reagents and Conditions.* (i) 1.0 eq. NBS/DMF added to napth-DHP/DCM, -78°C → RT, 84% yield; (ii) Pd$_2$(dba)$_3$, P(tBu)$_3$, Cs$_2$CO$_3$, piperidine, DMF, 65°C for 21 hours, 82% yield.

Therefore, the next obvious step was to try to couple the acetylene with the 3-bromophenanthroline 31 to form 30 and then couple this with the BDHP bromide 38 (Scheme 3). Coupling of phenanthroline acetylene 30 with bromo-BDHP 39 with a Pd$_2$(dba)$_3$ catalyst for 21 hours at 65°C provided the product 21 after column chromatography over silica gel as a dark red solid in 82% yield. The structure of 21 was confirmed by $^1$H and $^{13}$C NMR, UV-vis, IR (KBr), EA and MS experiments. BDAP 21 exhibited resonances in its $^1$H NMR spectrum (CDCl$_3$) due to both structural components with the correct relative integrations. The internal shielded methyl protons appeared at $\delta$ -1.35 and $\delta$ -1.38. The acetylene carbons in the $^{13}$C NMR spectrum were observed at $\delta$ 94.7 and $\delta$ 91.9 together with the shielded internal methyl carbons at $\delta$ 18.2. The IR spectrum of the KBr pellet of 21 showed a well-defined stretch for the C≡C bond at 2186 cm$^{-1}$. The calculated exact mass for M+H of BDAP 21 was at m/z 597.3270 and this molecular ion was found at m/z 597.3263.

### 2.5 Synthesis of PDD 25

The ability to closely affect the magnetic environment around the bound transition metal with the opening and closing of the DHP moiety was thought to be best accomplished by annelation of the 1,10-phenanthroline to the DHP 11 and thus prompted the synthesis of PDD 25. The C5-C6 alkene of the 1,10-phenanthroline was chosen as the bond of fusion between the ligand and the photochrome (Figure 24) since then the
coordination of a metal at the 1,10-phenanthroline nitrogen atoms interferes sterically the least with the DHP unit.

![Diagram](image)

**Figure 24:** The C5-C6 bond where the 1,10-phenanthroline fragment is annelated onto DHP 11 to make PDD 25.

Previous work on a similar pyrazine system gave product 40' (Figure 25) that was not photochromic and decomposed under UV (254 nm) irradiation\(^1\). If there is an acene-like structure embedded in the framework of the closed DHP 40 (red), which is not well stabilized by resonance, then the molecule would prefer to open spontaneously. This was thought to happen because the open conformation 40' is stabilized by an aromatic naphthalene-type of ring (blue) and by the three benzenes of BDHP (Figure 25).

![Diagram](image)

**Figure 25:** Resonance contributors to 40 and 40'.

If there are structural elements that can stabilize the transition state while going from the open to the closed isomer, then the molecule is more likely to undergo this transformation. The biaryl annelated derivative 41', where there are two benzene rings [e]-fused to either side of the DHP 11, has been made previously.\(^5\)
This tetra-aryl species (Figure 26) is most stable in the open form 41' in comparison to the completely delocalized annulene 41 due to the large resonance stabilization contributed by the four independent benzene rings. The green closed structure 41 which is stabilized by a single benzene ring can be observed only for a moment under UV irradiation at -50°C.

**Figure 27:** A proposed mechanism for formation of 40 from 40’ with a 40• biradical as an important resonance contributor.

A version of the DHP molecule without the *tert*-butyl groups was made previously[^91], where one of the [e]-annelating contacts was a pyrazine heterocycle (Figure 27), and was isolated in its open state 40’. Compound 40’ failed to undergo ring closure to yield the DHP 40 under UV irradiation (254 nm), suffering decomposition instead. It was believed that the transannular bond formed momentarily while 40’ underwent the 40’ \(\rightarrow\) 40 transition because the reaction mixture briefly turned dark purple upon its exposure.

[^91]: Please provide the correct citation or reference.
to UV light. These results were rationalized by proposing that the closed structure 40 has a biradical 40• as a major resonance contributor even though the structure of 40 has not been experimentally confirmed.

After excitation with light, the ground state 40′ was proposed to go to 40 which has 40• as its major resonance contributor. The biradical 40• can then either go back to the CPD 40′, following an electronic rearrangement that results in the transannular bond cleavage (Figure 27), or it can decompose. The structure 40• was thought to be stabilized by the highly aromatic [e]-annelated moieties, resulting in fixation of double bonds in the DHP ring. Therefore, the interruption of conjugation by having apical radicals was an expected loss accompanied by reduced aromaticity of the core structure. Because of the high reactivity of biradical 40•, it was anticipated that it would either quickly decompose or that its two separated radicals would recombine to yield 40′.

A radical is formally electron deficient and so an electron-rich substituent is expected to stabilize it. A substituent at the site of the radical can stabilize the unpaired spin by hyperconjugation, by lone-pair participation or by its delocalization onto the π system of the substituent.100,101,102,97 The tert-butyl groups in positions 2 and 7 of the DHP are electron-rich but their C–H bonds are too far away from the radical centers on the dihydropyrene for the hyperconjugative stabilization to be operative.

![Figure 28](image.png)

**Figure 28:** A theoretical structure 42′ that can be photochemically transformed into 42 with a 42• resonance contributor.

With blockage of positions 2 and 7 on the DHP with tert-butyl groups as in 42′, the photochemical reaction does not lead to a stabilized biradical species where the radicals are localized on the annular periphery to allow for further reactivity. If the radicals are formed in the transition state then for a productive photochemical transformation they
must form on the inside of the ring giving an excited state that resembles $42^\bullet$ with the unpaired electrons subsequently recombining to give either $42$ or $42'$ (Figure 28).

If there is a highly aromatic ring [e]-annelated to a given DHP then either its DHP or CPD isomer is more stable when rearrangement of the conjugated double bonds results in external aromatic rings with respect to the core of DHP. The system presented on the left side of Figure 29 illustrates that the masked acene $43$ is only slightly less favoured than its open conformation $43'$.

![Figure 29: Structures of closed 43, open 43', open 25' and closed 25 molecules.](image)

The masked acene (red) $43$ has the same number of full [e]-annelated benzene rings as are [e]-annelated to the CPD 11 to generate structure $43'$ (blue). Both $43$ and $43'$ have a dominant triphenylene (blue) motif that is composed of three fused benzene rings: a superbenzene that is quite stable on its own. Since structure $25$ is akin to that of $43$ it was postulated that the closely related but a less acene-like PDD $25$ would be just as photochemically reversible as compound $43$ is. The tert-butyl groups in positions 2 and 7 would discourage formation of the biradical-type of intermediates that can potentially undergo decomposition, favoring a smoother $25 \rightarrow 25'$ transition. A facile condensation reaction between the amine and carbonyl functional groups offers potential for a simple installation sequence for the pyrazine bridge, and thus, for a straightforward incorporation of the metal-binding phenanthroline unit to create structure $25$.

A much shorter and simpler methodology from what has been previously used by the Mitchell group$^{91}$ was employed to synthesize PDD $25$. Literature precedent exists for a way to introduce two nitro groups at positions 4 and 5 of parent DHP 11 by reaction of the latter with two equivalents of copper nitrate in acetic anhydride.$^{103,104}$ The reduced
diamine product was reported to be unstable towards isolation but it was possible to trap it by addition of a suitable carbonyl electrophile. The salen ligand analogue 44 was made first to see whether the reaction works if a single reactive aldehyde 46 is used as the electrophile. A less reactive phenanthroline diketone 28 was subsequently tested under the same conditions and the experiment successfully provided compound 25 (Scheme 4).

Scheme 4

\[ \text{Reagents and Conditions. (i) Ac}_2\text{O, 2.0 eq. Cu(NO}_3\text{)}_2, 0^\circ\text{C} \rightarrow \text{RT for 90 min, 36\% yield; (ii) H}_2, \text{dry Pd/C 30\%, EtOH 100\%, RT.} \]

The synthesis of PDD 25 commenced with 4,5-(NO\(_2\))\(_2\)-DHP 45 which was made from DHP 11 by reacting it with two equivalents of copper nitrate in acetic anhydride. The reaction did not give yields above 40\% and clean separation of 45 from the mono- and tri-nitrated side products was somewhat difficult, since all nitrated DHP molecules had similar polarities on silica gel in a given solvent mixture. The undesired nitration products were obtained in higher yields when more equivalents of Cu(NO\(_3\))\(_2\) and longer reaction times were used.

The reduction of 45 was accomplished with H\(_2\) gas that was bubbled through the ethanolic reaction solution in presence of a Pd/C 30\% catalyst at room temperature (Scheme 4). The phenanthroline diketone 28 and salicylaldehyde 46 electrophiles were added in separate reactions to trap the diamine intermediate in order to synthesize PDD
25 and DHP-salen 44 respectively. Salicylaldehyde 46 was available commercially while phenanthroline-4,5-dione 28 was made by oxidation of the central aromatic ring of 1,10-phenanthroline with (1:2) HNO$_3$/H$_2$SO$_4$ acid mixture and 1.5 equivalents of KBr at gentle reflux. The trapping agent was added as soon as the starting material 45 was consumed as indicated by TLC.

The condensation reactions between the in situ generated DHP diamine and the added carbonyl compounds were allowed to proceed for 14 h. The DHP-salen 44 was separated from the crude residue by column chromatography over silica gel, and obtained as a dark orange solid. This product was characterized only by $^1$H NMR since the material still contained salicylaldehyde 46 as a major impurity. The $^1$H NMR (CDCl$_3$) revealed 44 to be the desired symmetric DHP molecule as expected, with internal methyl and two alcohol hydrogens appearing at $\delta$ -3.50 and $\delta$ 13.58 respectively. PDD 25 precipitated as a dark green solid from ethanol as the reaction proceeded. Excess of starting material 28 was difficult to remove by chromatography as its polarity resembles that of the product. The solubility of diketone 28 was better in EtOH and so the majority of 25 was separated from the crude reaction mixture by filtration. Column chromatography of crude PDD over silica gel allowed for the isolation of small amounts of clean 25.

PDD 25 was characterized by $^1$H and $^{13}$C NMR, UV-vis, IR (KBr) and HRMS experiments. The proton and carbon NMR spectra (CDCl$_3$) of 25 were greatly simplified due to high structural symmetry of this molecule. The ortho, meta and para hydrogens of the phenanthroline showed up as three nicely resolved sets of doublet of doublets at $\delta$ 9.83, $\delta$ 9.30 and $\delta$ 7.89 while the internal methyl groups appeared at $\delta$ -1.23 as a 6H singlet in the $^1$H NMR spectrum. The UV-vis spectrum (toluene) had a $\lambda_{\text{max}}$ at 449 nm and a weak, broad transition at 600 nm that is responsible for the green color of the closed PDD 25. The calculated exact mass of 25 (M+H) was at $m/z$ 549.3018 while this ion was found at $m/z$ 549.3008.
2.6 Synthesis of DHP-imid 23

The synthesis of the DHP-imid 23 was devised with the intention of making a fluorescent photochrome, because the analogous molecule 47 (Figure 30), where the DHP component is replaced by the phenyl ring, is strongly fluorescent. 106, 107

![Figure 30: Structure of fluorescent phenyl-imidazole-phenanthroline 47.](image)

Pengrong Zhang in the Mitchell group found that linking a phenanthroline unit directly via a single carbon-carbon bond to 11 to form 49 did not improve the photochemistry of the parent DHP 11.

Scheme 5

![Scheme 5](image)

*aReagents and Conditions.* (i) n-BuLi, 1.0 eq., -78°C for 30 min. (ii) -78°C → RT, 40% yield.

Compound 49 was made by reaction of 4-bromo-DHP 33 with n-BuLi at -78°C followed by addition of the dry phenanthroline derivative 48 (Scheme 5). It was postulated that introducing an imidazolyl group between the DHP and phenanthroline components would improve the photochromic behaviour of the DHP 11 by increasing the Φ of its photo-opening.

Bromide 33 was converted to its lithio derivative using 1.0 equivalent of n-BuLi at -78°C, and this was then reacted with dry DMF 81b to give the DHP aldehyde 29 in 78% yield. Aldehyde 29 was subsequently reacted with diketone 28 in presence of excess
ammonium acetate in acetic acid at 80°C for 16 h giving DHP-imid 23 as a yellow solid in 28% yield after silica gel chromatography (Scheme 6). Slow evaporation of an NMR sample of 23 made in CDCl$_3$ gave a brown rod-shaped crystalline material. Product 23 was characterized by $^1$H and $^{13}$C NMR, IR (KBr), EA and HRMS analyses. The internal methyl protons were well separated in the $^1$H NMR spectrum (CDCl$_3$) of this compound due to asymmetry, appearing at δ -3.83 and δ -3.96 while the tert-butyl groups were at δ 1.76 and δ 1.50.

Scheme 6

Reagents and Conditions. (i) n-BuLi, 1.0 eq, -78°C for 30 min, add excess dry DMF -78°C → RT, 78% yield; (ii) 0.75 equiv. of 28, 7 equiv. ammonium acetate, 80°C, 16 hours, 28% yield.

The assignment of the phenanthroline resonances was challenging because of the intramolecular twisting resulting in poor through-space coupling (NOESY) of protons. The imine carbon was at δ 153.5 in the $^{13}$C NMR spectrum, which is a typical value for this functional group. The calculated mass for 23 was at $m/z$ 563.3175 and the obtained mass was at $m/z$ 563.3188 for its M+H ion.

Having the aromatic imine linker between the parent DHP and the phenanthroline in 23 did not give a photochromic product. This result was somewhat anticipated because the DHP-salen 44, where the parent DHP skeleton has free-rotating ortho imines which prefer to be coplanar with the DHP group, is not photochromic either under normal irradiation conditions. Fluorescence measurements were not taken of this material at this time and so whether this property is changed in compound 23, as compared to the fluorescence of the closed DHP 11, is currently unknown. However, compound 23 allowed for synthetic entry into a different type of DHPs that upon benzannelation or substitution could give photochromic products with the desired photochromic properties.
2.7 Synthesis of BDHP-imid 24

The synthesis of the BDHP-imid 24 was done in order to create an imidazole-linked analogue of DHP-imid 23 that exhibited photochromism. A similar route (Scheme 7) was envisioned for its synthesis as was used for obtaining 23. The BDHP aldehyde 50 starting material was made from the corresponding BDHP monobromide 39 by treating the latter with 1.0 equivalent of n-BuLi in dry THF at -78°C, followed by quenching of the generated lithiated species with freshly distilled DMF.\textsuperscript{81b} Aldehyde 50 was isolated as a dark purple solid in 49% yield after column chromatography.

Scheme 7\textsuperscript{a}

![Scheme 7](image)

\textsuperscript{a}Reagents and Conditions. (i) n-BuLi, 1.0 eq., -78°C for 30 min, add excess dry DMF, -78°C → RT, 49% yield; (ii) 0.75 equiv. of 28, 7 equiv. of NH\textsubscript{4}OAc, 80°C for 16 hours, 27% yield.

The reaction of 1.3 equivalents of BDHP-CHO 50 and phenanthroline diketone\textsuperscript{105} 28 with approximately 7 equivalents of ammonium acetate while heating the mixture in acetic acid at 80°C for 16 hours in the dark (Scheme 7) gave the red solid product 24 in 27% yield after column chromatography. BDHP-imid 24 was characterized by \textsuperscript{1}H and \textsuperscript{13}C NMR, UV-vis, IR (KBr) methods. The solution of compound 24 that was made for the NMR experiments was readily bleached under ambient light and so it was stored in a dark cabinet.

The internal methyl protons in the \textsuperscript{1}H NMR spectrum of 24 appeared at δ -1.24 and δ -1.31 which is the expected chemical shift for benzo-annelated DHP compounds. The deshielding compared to the parent DHP is due to reduction in the ring current around the internal methyl substituents of the DHP by the presence of a strongly aromatic [e]-annelated benzene ring. The two distinct signals for the tert-butyl groups were at δ
1.66 and $\delta$ 1.53. The protons on the annular periphery of DHP were assigned with the help of 2D COSY and HETCORR experiments as is the custom while the phenanthroline resonances remained ambiguous. The $^{13}$C NMR spectrum revealed the presence of an imine carbon at $\delta$ 165.0.

2.8 UV-vis Spectroscopy of the DHP Ligands and Their Photoreactivity

Dimethyldihydropyrenes, with several exceptions, belong to a class of negative photochromes. The coloration of the closed DHP arises from the extended $\pi$-conjugation along the flat perimeter of this annulene. The general UV-vis spectra of such species consist of absorptions in the 350–650 nm window in addition to smaller peaks from 680 nm to 700 nm for some derivatives. The pale appearance of the open switch comes from absorptions due mostly to the $\pi \rightarrow \pi^*$ transitions of the benzene rings. These benzenoid bands are in the UV region of the EM spectrum making the CPD form appear colorless.

Gradual transmission of light through crystalline DHP potentially allows for the photo-conversion of the molecules in the entire sample from the closed to the open state, with this reaction not being limited to the surface of the crystal only. This result can rarely be achieved with positive photochromes such as spiropyrans and spirooxazines, which have a pale or colorless stable closed form that is converted with UV irradiation to the intensely colored open state. Because light fails to go through the dark surface of a spirooxazine crystal, high intensity light is required to achieve full conversion of the closed to the open state in the SO solid even if no photostationary equilibria are established. The concentration of the open species and their distribution in a polycrystalline sample made up of positive photochromes therefore depend on the power of the laser and the rate of their thermal return reaction.

A side-effect of using a highly powered light source to initiate photo-conversion on the inside of the crystal is the proportional increase in the rate of competing thermal return reaction arising from the unavoidable heating of the sample by the laser. The effects of UV irradiation on the positive photochromes are reversed faster when the sample solid is heated by the laser and by the release of heat due to the vibronically-coupled relaxation from one state to the other of the neighboring molecules in the lattice.
It was envisaged that the DHP photochromes, which circumvent this issue because of gradual transparency of the sample under visible irradiation, can be switched completely from their closed to the open form in the solid state with a less powerful light source, if photostationary states are avoided and if the Φ of the photo-opening process is good.

BDAP 21 was the first photochrome made in this project that fully converted between its DHP and CPD states in a toluene solution. The naturally slow thermal return and the non-overlapping absorption bands (Figures 31 and 32) of the open and closed forms in toluene and THF allowed for a fast $21 \to 21'$ transition. Benzannelation of the parent DHP led to appearance of an additional broad $\lambda_{\text{max}}$ in the 480–600 nm region of the UV-vis spectrum in toluene with an $\varepsilon$ of 8000 M$^{-1}$ cm$^{-1}$. Irradiation into this band with visible light (>490 nm) at 20°C resulted in complete bleaching of the sample in less than 3 minutes. Longer irradiation times (about 10 minutes) were required to convert closed BDAP 21 molecules into their open $21'$ pale yellow states in a concentrated NMR sample solution.

The position and intensity of the band at 520 nm was such that irradiation with a longer wavelength light (>490 nm) was productive in converting the closed 21 structures to the open $21'$ ones. Also, because this band was due solely to the closed isomer, excitation at that energy led to complete sample bleaching without formation of mixtures at equilibrium. We assume the photochemical conversion to $21'$ went to completion because none of the closed isomer 21 was observed by $^1$H NMR after the lamp was turned off. An isosbestic point was observed at 332 nm as the photochemical conversion of 21 to $21'$ was followed by UV-vis (Figure 33). The presence of such a feature signifies that this transformation proceeds without formation of additional long-lived intermediates for 21.
Figure 31: Overlay of UV-vis spectra of open and closed BDAP 21 in THF

Figure 32: Overlay of UV-vis spectra of open and closed BDAP 21 in toluene
Figure 33: Photochemical ring-opening of BDAP 21 in toluene under visible irradiation (>490 nm) at 293 K, monitored by UV-vis (time shown in seconds).

In contrast to BDAP 21, the irradiation experiments with the uncoordinated DAP 26 (Figure 34) gave no evidence of its ring-opening at room temperature in toluene which is consistent with the photochemical behaviour of the parent DHP 11 compared to BDHP 12. Mechanistic studies of ring-opening of acetylene substituted derivatives of di-tert-butyl DHP showed that attachment of an acetylene leads to a decrease in the Φ of ring-opening by a factor of 3 as compared to the parent 11.\textsuperscript{75,76} Molina Sheepwash in the Mitchell group found that DHP 11 does indeed undergo transient ring-opening reactivity under visible irradiation. The rate of relaxation of the DHP* back to the DHP ground state is much faster than the rate of its transition to the CPD* which is then supposed to go on to make CPD 11’. Therefore the DHP 11 molecule was classified as non-photochromic under normal working conditions.\textsuperscript{75,76}
It was interesting to see if a metal complex of DAP 26 is photochromic and whether the presence of a metal can change the rates of ring opening and closing of this molecule. It is unclear what the role of the metal is in the mechanism of the photochemical isomerization reaction of metal-DHP complexes. The effect of metal binding on the rates of ring opening and closing of DHP-type photochromes is poorly understood to date.\textsuperscript{110,80,78,81a} It is believed that an electronically coupled metal provides low-lying energy levels which allow for the photochemically excited DHP* to decay through an internal conversion back to the DHP ground state instead of undergoing the desired isomerization to the CPD.\textsuperscript{38} One theory suggests that the metal is involved in influencing the probability of the crossing of the CPD* and DHP* as the DHP molecule goes from DHP to the CPD ground state.\textsuperscript{77} An intuitive explanation of the reduced photoresponsivity of metal-DHP complex can also be imagined. A transition metal in this type of complex is a cation and should therefore favour coordination of an electron-rich annulene instead of a metacyclophephane diene via the phenanthroline. The closed DHP would in principle be more stabilized than its open counterpart by a bound positively
charged metal, leading to a less responsive metal complex of a given DHP in comparison to the corresponding unbound photochrome.

A lack of photochemical reactivity in solution was also observed for the DHP-salen 44 and DHP-imid 23 (Figure 35) derivatives. This result was not surprising since the annulene portion of these molecules consists of the parent DHP 11 with a low Φ of conversion to 11'. The pendant fused imidazole phenanthroline π-system of the DHP-imid 23 is out of plane relative to the flat DHP core and contributes little to the extension of conjugation of the parent 11. The DHP-salen 44 showed no photochemical reactivity either even though it contained two sets of additional conjugated imine and benzene functionalities in addition to the DHP 11.

![Figure 35: UV-vis spectrum of the closed DHP-imid 23 in acetone](image-url)
Figure 36: UV-vis spectra of open and closed NDAP 22 in toluene

Figure 37: Photochemical ring-opening of NDAP 22 in toluene with visible light (>490 nm) at 293 K, monitored by UV-vis (time shown in min).
NDAP 22 can be opened to the CPD 22′ by irradiation with visible light (>490 nm). The progress of this photochemical transformation was monitored by UV-vis at 293 K (Figure 37). Due to the presence of a fairly competitive thermal return reaction in naphthoyl-DHP derivatives, the degassed sample solution was irradiated while the cuvette was immersed in a water bath set to 2-3°C. The absorbance value at $\lambda_{427\text{nm}}$ due to the closed form 22 in toluene stopped decreasing after ~8 hours of visible irradiation. A steady state was reached with the NDAP sample in the open state. The 22′/22 ratio at this time was assumed to be the same as that calculated from the relative integrations of the protons of the internal methyl groups in the $^1$H NMR experiment at the time when the intensity of these signals stopped changing under prolonged visible irradiation. The NMR sample of NDAP 22 in CDCl$_3$ was irradiated for 4 hours and 20 minutes at 15°C with visible light (>490 nm). The $^1$H NMR (CDCl$_3$) revealed that the photochemical transformation $22 \rightarrow 22'$ had gone to completion at this time, accompanied by the replacement of the internal methyl protons of 22, found at $\delta$ -3.607 and $\delta$ -3.616, by the new methyl resonances at $\delta$ 1.57 assigned to 22′.

A study of photochromism of PDD 25 in toluene was conducted next to determine whether it is photoresponsive. The $\lambda_{\text{max}}$ for 25 occurs at 449 nm which has a long tailing absorption centered at ~600 nm with a very low $\varepsilon$-value (Figure 38). This band extended well past the region where the orange filter (>490 nm) cuts off the visible irradiation from the source. PDD 25 can be converted from the closed to the open form in toluene (Figure 39), but this transformation does not proceed to completion. A steady state with only 44% of 25′ is reached after 79 hours of continuous visible irradiation of the $^1$H NMR sample (CDCl$_3$) solution with tungsten light (~500 W) at 20°C. These values were determined by taking $^1$H NMR spectra at set time intervals to monitor the relative decrease in intensity of the signals due to the two meta protons on the phenanthroline of 25 at $\delta$ 7.84 as the resonances of the corresponding two meta protons of the open PDD 25′ structure grew in at $\delta$ 7.75. This photostationary state was reached because the light acted unselectively on both DHP 25 and CPD 25′ isomers.
Figure 38: UV-vis spectra of open and closed PDD 25 in toluene at 300 K.

Figure 38 shows the outcome of a similar irradiation experiment carried out with a sample of PDD 25 diluted to concentrations suitable for UV-vis. The 25'/25 ratio of absorbances of PDD at 449 nm before and after the open species reach a photostationary state appears to be much larger than 0.44. The best interpretation of this discrepancy is that the rate and extent of photochemical isomerization for the DHP photochromes used in the present study must depend on concentration of the sample as well as on the type of cell used to collect spectra, the temperature of the surrounding medium, solubility of the open and closed isomers at the concentrations required by the method of investigation employed and, of course, on the time for which the sample is subjected to a specific type of photo-irradiation.
2.9 Rates of Photo-opening of Photochromic DHP Ligands

The rates at which the closed to open state isomerization happens in the NMR (mM) and the UV-vis (μM) samples are presumed to be different because of the concentration effects leading to variable order of response of the active component to light. But the ratio of the open to the closed state should be the same when the steady state plateau for the given transformation is reached if there are no differences in solubility of the two isomers. This is a useful assumption when determination of the extinction coefficients of the absorptions of the open form is not possible since a UV-vis spectrum under the same conditions of the open form alone for the molecule of interest cannot be obtained. The $\varepsilon_{449\text{nm}}$ of the closed PDD 25 was calculated directly from the absorbance value at $\lambda_{449\text{nm}}$ and the sample concentration using the Beer-Lambert relation (equation 1), since the closed state is the most stable state for this molecule and accounts for $\sim100\%$ of the species present before irradiation experiments are started.

$$A = \varepsilon bc$$

equation (1)
The UV-vis absorptions of 25' and 25 have significant spectral overlap. Therefore the electronic transitions that are observed at the photostationary state are not due to any single species, and so none of the absorbance intensities can be used for calculation of the concentration of the open PDD 25' at steady state.

The PDD photochrome 25 has a short synthesis and it seems to be an ideal structure for maximal correlation between 25 or 25' and the magnetic states of the bound transition metal. The downside to 25 is that its photo-conversion is either never complete or there is no way to reliably calculate the amount of 25' at its photostationary state as that ratio depends directly on the method used to obtain the spectral data. This situation arises from there being a large overlap between the absorption maxima originating from the open and the closed states of this DHP. PDD 25 behaves photochemically more like a slightly modified parent DHP 11 rather than a BDHP 12, with the latter having additional bands in the 500–600 nm range in the UV-vis resulting in distinct separation between the absorptions due to the DHP and CPD isomers.

The red BDHP-imid 24 has the expected high energy 422 nm absorption in addition to a transition at 520 nm (Figure 40). The latter is a diagnostic feature of 24 having the BDHP 12 core structure. The transition at 520 nm belongs to the closed BDHP-imid 24 only and can be addressed selectively with visible light (>490 nm) resulting in conversion between the fully open and closed states of this molecule. The 520 nm band disappears completely into the baseline upon exposure of the toluene solution of 24 to visible light, while the absorption at 422 nm decreases significantly in intensity but does not disappear completely (Figure 41).
The $24 \rightarrow 24'$ photoisomerization under visible light goes to completion as determined by UV-vis with the support of $^1$H NMR experiments. The proton NMR gives more information about which species and their relative quantities are present in solution than a UV-vis experiment does. A decay in intensity of up-field peaks at $\delta$ -1.24 and $\delta$ -1.30 of 24 due to shielded internal methyl protons were observed as a new set of resonances, representing the shielded benzylic methyl groups, found at $\delta$ 1.37 and $\delta$ 1.35 of $24'$, grew in at the same rate. During the photochemical opening experiments it was noticed that this transition is faster for the imidazole derivative 24 than it is for BDAP 21 in toluene (Table 1).

The apparent rate constants of the photochemical ring-opening reaction for all synthesized photo-responsive DHP compounds were obtained by measuring the absorbance at a chosen electronic transition for each switch with respect to the time of its exposure to irradiation. A 420 nm filter (unless stated otherwise) was used at the detector to block the effects of the UV light coming from the instrument so that the observed changes in the UV-vis intensities could be approximated by the first-order rate law. The photo-opening reaction of DHP is technically a second order process given that its
kinetics depend on the concentration of the photochrome and on the number of photons needed to achieve conversion. However, because the number of photons used in the present irradiation experiments was usually in excess, the apparent rate constants or the relative efficiencies of ring-opening were approximated by pseudo-first order kinetics. The measured rate parameters for the photochromic DHP compounds are summarized in Table 1.

**Table 1**: Apparent rate constants$^a$ for the photochemical ring-opening of photochromic DHP ligands at 293 K. Irradiation was done with a ~500 W visible light (>490 nm) and the UV-vis spectra were taken with a 420 nm filter at detector (unless stated otherwise).

<table>
<thead>
<tr>
<th>Compound</th>
<th>rate constant of opening (s$^{-1}$)</th>
<th>rate constant of opening rel. to 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>21, BDAP</td>
<td>4.1 (± 0.2) x 10$^{-2}$</td>
<td>15</td>
</tr>
<tr>
<td>24, BDHP-imid</td>
<td>2.4 (± 0.6) x 10$^{-2}$</td>
<td>9</td>
</tr>
<tr>
<td>22, NDAP$^b$</td>
<td>1.9 (± 0.7) x 10$^{-4}$</td>
<td>0.1</td>
</tr>
<tr>
<td>25, PDD</td>
<td>7.0 (± 1.6) x 10$^{-3}$</td>
<td>0.3</td>
</tr>
<tr>
<td>12, BDHP</td>
<td>2.7 (± 1.2) x 10$^{-3}$</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$Errors were determined by measuring the rates of photo-opening at 293 K in triplicate.

$^b$Photo-opening was done at 2-3°C and UV-vis measurements were taken with 455 nm filter at detector.

![Figure 41](image-url): Photochemical opening of BDHP-imid 24 in toluene at 293 K (20°C) with visible light (>490 nm), monitored by UV-vis (time shown in seconds).
Figure 42: Determination of photo-opening rate constant of BDHP-imid 24 at 293 K (20°C) under visible light (>490 nm) in toluene, monitored by UV-vis.

Figure 43: Determination of the rate constant of photo-opening of BDHP 12 in toluene at 297 K under visible irradiation (>490 nm), monitored by UV-vis.
The decay pattern of intensity of a chosen electronic transition in the induction period of the experiment was fitted to a mono-exponential relationship. The apparent rate constant of the photochemical opening of BDAP 21 was $4.1 \pm 0.2 \times 10^{-2}$ s$^{-1}$ as determined from the slope of the negative natural logarithm of absorbance values at 520 nm which were plotted against time (Figure 44). The error in this rate constant was calculated from the standard deviation using three of these measurements taken at 293 K under the same experimental conditions. The same process was monitored for BDHP-imid 24 at 422 nm and the apparent $k$-value was $2.4 \pm 0.6 \times 10^{-2}$ s$^{-1}$ (Figure 42). The data for compound 24 had to be taken every 5 seconds as compared to BDAP 21 which was sampled every 10 seconds since the rate of opening of the former was 1.5 times faster than that of the latter.

![Graph](attachment:image.png)

**Figure 44**: Determination of ring opening rate of BDAP 21 at 293 K in toluene under visible light (>490 nm) by UV-vis spectroscopy.

The apparent rate constant of the photo-opening of 25 at room temperature was significantly smaller than those for the benzannelated derivatives 21 and 24 (Table 1). This rate parameter for NDAP 22 was measured while irradiating the UV-vis sample at 2-3°C in order to slow down the competing thermal back reaction (Figure 46). To make the decay pattern at the 490 nm shoulder for 22 fit the first order relationship as best as
possible a 455 nm instead of the 420 nm filter was used to eliminate the undesired high-energy radiation from the UV-vis instrument. The apparent rate constant of opening of the BDHP 12 was 2.7 (± 1.2) x 10⁻³ s⁻¹ which was 6 and 10 times slower than that for 21 and 24 respectively. In general, attachment of phenanthroline to the BDHP fragment via the acetylene and imidazyl linkages increased the response rate of the resulting DHP species to visible light.

![Graph](image)

**Figure 45**: Ring-opening of PDD 25 with light (>490 nm) in toluene at 297 K to determine the rate constant for this process by UV-vis.
2.10 UV-vis Cycling of the Synthesized DHP Photochromes

Before using any photochrome in data storage applications it is important to know whether the photochrome survives repeated cycles of photo-bleaching with visible light and whether it returns to the original state under UV irradiation. A single full cycle of opening and closing of the photochrome must be run to determine whether the molecule is photochromic in the first place. A truly photochromic compound can be converted from the closed to its open state with light while the reverse transformation must also be possible with light only (P-type), otherwise the compound is termed as thermochromic since the reverse reaction can also proceed by warming the opened molecules in darkness (T-type).²²

Every photochromic DHP compound was subjected to at least 10 full UV-vis cycles which consisted of a photochemical ring-opening reaction, driven by a ~500 W broad-band visible light source (>490 nm), and of a subsequent photochemical closing reaction achieved under UV (254 nm) irradiation. The absorbance intensity at a single chosen maximum was followed as a function of irradiation cycle number in order to see
if the photochemical transformation is reversible or whether the sample decomposes during repeated opening and closing events.

![Figure 47: Photochemical cycling of BDAP 21 in toluene with visible (>490 nm) and UV (254 nm) light at 300 K, monitored by UV-vis.](image)

The BDAP 21 photochrome was subjected to the cycling test first. Figure 47 shows this experiment repeated for 16 cycles without noticeable reduction in the absorbance at $\lambda_{417\text{nm}}$ of the closed state. There was an increase in the $A_{417\text{nm}}$ of the open BDAP 21' with time. This asymmetric change in the UV-vis spectrum can be interpreted as an incomplete $21 \rightarrow 21'$ transition during visible irradiation. The same experiment was repeated in THF in the hopes of seeing a completely reversible cyclical pattern for 21. THF does not absorb light at 254 nm as much as toluene does and so it was anticipated that the ring closing of BDAP 21 would be faster in this solvent.

There was a consistent decrease of the $A_{415\text{nm}}$ for closed 21 and an accompanying increase in the $A_{415\text{nm}}$ for the open BDAP 21' in THF (Figure 48). To rule out the possibility of having a photostationary state, the THF solution of BDAP 21 that went through one UV-vis cycle was heated at 64°C to see whether the absorbance at 415 nm would be restored thermally to its original magnitude.
Figure 48: Photochemical cycling of BDAP 21 in THF with UV (254 nm) and visible (>490 nm) irradiation at 300 K, monitored by UV-vis.

Figure 49: Thermal decay of BDAP 21 observed by UV-vis in THF at 337 K after 1 cycle of visible (>490 nm) and UV (254 nm) irradiation (time shown in min).
Additional decomposition was observed instead as the sample was heated for 1000 s (Figure 49). This result was not unexpected because THF can form peroxides under visible irradiation and these can then be imagined to go on to react with BDAP 21, causing sample decomposition. It was then thought that $A_{415\text{nm}}$ increased for the “open” form of 21 because the decay product of the photo-cycling must have benzenoid absorptions that are very similar to the ones the open state 21’ normally has. The decrease in $A_{415\text{nm}}$ of the closed 21 molecule was attributed to the decrease in concentration of the closed BDAP 21 upon its cyclical exposure to UV light in THF.

![Graph](image.png)

**Figure 50:** Photochemical cycling of PDD 25 in toluene with UV (254 nm) and visible (>490 nm) irradiation at 300 K, monitored by UV-vis.

The UV-vis cycling of PDD 25 in toluene was found to be reversible for ten consecutive cycles at 300 K (Figure 50) which was not true for NDAP 22 (Figure 51). Molecule 22 exhibited photochemical decomposition in toluene which was more pronounced as the UV-vis cycling continued. A fast drop in absorbance at $\lambda_{490\text{nm}}$ of the closed state 22 was accompanied by a fairly non-altered absorbance intensity of the open state 22’ at the same wavelength. This was interpreted to be due to decomposition of NDAP as it was opened from 22 with cycling and this decomposition resulted in products.
that do not have similar absorptions at 427 nm to those of the open state 22'. In contrast, the photo-cycling of BDHP-imid 24 in toluene (Figure 52) gave a reversible change in the absorbance intensities when the process was monitored at $\lambda_{422}\text{nm}$. This switch opened fully within 190 seconds under visible light (>490 nm), taking about 300 seconds to close in toluene under UV irradiation (254 nm).

![Graph](image)

**Figure 51**: Photochemical cycling of NDAP 22 in toluene at 298 K with visible (>490 nm) and UV (254 nm) light, 455 nm filter at detector, monitored by UV-vis.
2.11 Thermal Relaxation of DHP Photochromes

The experiments for determination of the thermal relaxation rates of photochromic compounds are important for learning how quickly the data stored after writing it with light will be lost. In an ideal world, the experimenter would wish to have no thermal decay and no chemical decomposition of the photo-switch at all (!). Unfortunately, all photochromic DHP compounds that were synthesized in the present work eventually relaxed thermally to their more stable DHP states in the dark at room temperature.

The thermal decay for some of the systems takes a very long time and so it was more time-efficient to calculate the rates at 298 K using the Arrhenius equation (2) after finding the faster rates for the same process at elevated temperatures.\(^{97}\) The rates of thermal return were measured at ambient conditions at least once for PDD 25 and NDAP 22 in order to compare the measured values to those that were calculated by extrapolation of the high-temperature data for these using equations (2) and (3). In equation (2), \(k\) is the rate constant for the thermal return reaction, \(R\) is the gas constant, \(\Delta E_{\text{act}}\) is the energy of activation for the thermal return reaction, and \(T\) is the temperature in Kelvin.

**Figure 52:** Photochemical cycling of BDHP-imid 24 in toluene at 298 K with visible (>490 nm) and UV (254 nm) irradiation, recorded by UV-vis.
\[ k = A \exp(-\Delta E_{\text{act}}/RT) \quad \text{equation (2)} \]
\[
\ln(k) = \ln(A) - (\Delta E_{\text{act}}/RT)
\]
\[
-ln(k) = (\Delta E_{\text{act}}/R)(1/T) - \ln(A) \quad \text{equation (3)}
\]

The \(-\ln(k)\) values were plotted against \((1/T)\) to get \(\Delta E_{\text{act}}\) from the slope of the linear fit and the pre-exponential factor, expressed as \(\ln(A)\), from the y-intercept (equation 3).

The thermal return experiments for photochromic molecules were carried out in the UV-vis spectrometer cell that was thermostated at 54, 64 and 74°C (unless stated otherwise). A 420 nm filter was used (455 nm for NDAP 22) to block out the high energy light, originating from the UV-vis instrument, during the data acquisition process. The UV-vis results indicated that the thermal decay of the opened DHPs followed first order kinetics except for those of the NDAP 22 compound. This is reasonable since the reformation of the transannular bond is a unimolecular process in DHP systems. It was suspected that NDAP 22' decomposes during its thermal return to 22, hence the deviation from the pseudo-first order behavior of the \(22' \rightarrow 22\) closing process. The \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\) thermodynamic parameters for the thermal return of 21, 22, 24 and 25 DHPs at 298 K were calculated with the Eyring equation (4) and the rate constants that were experimentally obtained at elevated temperatures. These parameters were also calculated for method validation purposes using the actual rate constants obtained for NDAP 22 and PDD 25 at 298 K.

The Eyring equation relates the rate constant to the Gibb’s free energy of activation for the process (equation 5). The \(k\), \(h\) and \(k\) are the rate, Plank and the Boltzmann constants and \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\) are the enthalpy and the entropy of activation for a given thermal return reaction respectively. The negative values of the natural logarithm of \((k/T)\) ratios were plotted against \((1/T)\) to obtain the desired thermodynamic parameters (equation 6). The slope of the Eyring plot \((\Delta H^\ddagger/R)\) gives the enthalpy of activation \((\Delta H^\ddagger)\) and the y-intercept \((\Delta S^\ddagger/R - 23.73)\) gives the entropy of activation \((\Delta S^\ddagger)\) for the thermal return reaction. Experimentally measured rate constants for the thermal return of photochromic compounds are summarized in Table 2. The rate constants for the thermal return process at 298 K were calculated by using the linear data fitting equation that described the trendline and the \(\tau_{1/2}\) was determined via equation (7).
\[ k = (kT/h)\exp(84.45\{-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT\}) \quad \text{equation (4)} \]

\[ k = (kT/h)\exp\{\Delta G^\ddagger/RT\} = (kT/h)\exp\{((\Delta H^\ddagger - T\Delta S^\ddagger)/RT) \]

\[ \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad \text{equation (5)} \]

\[ k/T = (k/h)\exp\{((\Delta H^\ddagger - T\Delta S^\ddagger)/RT) \]

\[ \ln(k/T) = \ln(k/h) + \{(\Delta H^\ddagger - T\Delta S^\ddagger)/RT\} = \ln(k/h) + \{(\Delta H^\ddagger/RT - \Delta S^\ddagger/R) \}
\]

\[ \ln(k/h) = 23.73 \quad \text{(constant)} \]

\[ -\ln(k/T) = (-\Delta H^\ddagger/R)(1/T) + (\Delta S^\ddagger/R - 23.73) \quad \text{equation (6)} \]

\[ \tau_{1/2} \text{ (298 K)} = (\ln2)/k \quad \text{equation (7)} \]

The \( \Delta E_{\text{act}} \) and the \( \Delta H^\ddagger \) terms are exchangeable when describing the same process going in a given direction along the reaction coordinate. The \( \Delta S^\ddagger \) is a measure of how disordered the molecule is in its transition state, it tells about the extent of structural rearrangement the molecule undergoes in the transition state on its way to a different geometry of the product. A larger positive change in the entropy contributes to decreasing the \( \Delta G^\ddagger \) (equation 5) for the thermal return process. The reaction becomes more favorable in the direction as written when \( \Delta G^\ddagger \) is lowered with a concurrent decrease in the \( \Delta E_{\text{act}} \). For a lower \( \Delta G^\ddagger \) it would take less energy to reach the transition state from the local minimum of the open DHP isomer. The \( \Delta S^\ddagger \) value is expected to be smaller if the geometries of the starting material and the product are similar.

The errors for all measured rate constants and the calculated thermodynamic parameters from these were obtained from the standard deviations for three rate constant measurements at each temperature for each photochrome. With a 420 nm filter (unless stated otherwise) in front of the detector of the UV-vis lamp it was possible to minimize the effects of the high-energy light that triggers the photochemical back-reaction of DHP. The latter is a high \( \Phi \) process (0.1–0.4 in cyclohexane) for dihydropyrenes, adversely affecting the results of the observed thermal return reaction when this pathway is activated. The rates of the thermal return were calculated by the software on the Agilent 89090 UV-vis instrument after automatically fitting the data to an exponential curve for a first-order process.
Table 2: Experimentally measured rate constants\textsuperscript{a} for the thermal return of DHP photochromes in toluene in the dark at 25 (298 K), 54, 64 and 74°C by UV-vis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>k (x 10\textsuperscript{4} s\textsuperscript{-1}) at 54°C</th>
<th>k (x 10\textsuperscript{4} s\textsuperscript{-1}) at 64°C</th>
<th>k (x 10\textsuperscript{4} s\textsuperscript{-1}) at 74°C</th>
<th>k (x 10\textsuperscript{4} s\textsuperscript{-1}) at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>12, BDHP</td>
<td>0.6 ± 0.1</td>
<td>2.0 ± 0.2</td>
<td>5.3 ± 1.4</td>
<td>x</td>
</tr>
<tr>
<td>21, BDAP</td>
<td>3.2 ± 0.2</td>
<td>8.6 ± 0.7</td>
<td>20.7 ± 3.6</td>
<td>x</td>
</tr>
<tr>
<td>25, PDD</td>
<td>19.5 ± 0.7</td>
<td>49.2 ± 4.8</td>
<td>83.6 ± 5.9</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>22, NDAP\textsuperscript{b,c}</td>
<td>9.6 ± 4.7</td>
<td>8.6 ± 3.9</td>
<td>15.8 ± 3.7</td>
<td>0.5 ± 0.5</td>
</tr>
<tr>
<td>24, BDHP-imid</td>
<td>1.3 ± 0.1</td>
<td>3.9 ± 0.2</td>
<td>9.5 ± 0.4</td>
<td>x</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Errors were determined by measuring the rates of thermal return at 25, 54, 64 and 74°C in triplicate. \textsuperscript{b,c} A 455 nm filter was used for measurements done by UV-vis spectroscopy.

Figures 53-60 show that the thermal decay measured by UV-vis of all photochromic ligands fitted to a mono-exponential equation giving a linear relationship between the logarithm of the rate constant and the inverse of temperature at which the rate was measured, with slight deviations from linearity for NDAP 22.

Table 3: Calculated and measured rate constants and τ\textsubscript{1/2} for thermal return of DHP photochromes at 298 K using UV-vis. The calculations were done using thermal return data obtained for the photochromic compounds at 74, 64 and 54°C with equation (7).

<table>
<thead>
<tr>
<th>Compound</th>
<th>k\textsubscript{calc} (x 10\textsuperscript{3} s\textsuperscript{-1})</th>
<th>k\textsubscript{meas} (x 10\textsuperscript{3} s\textsuperscript{-1})</th>
<th>τ\textsubscript{1/2}calc (298 K)</th>
<th>τ\textsubscript{1/2}meas (298 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12, BDHP</td>
<td>0.2</td>
<td>x</td>
<td>5.0 days</td>
<td>x</td>
</tr>
<tr>
<td>12, BDHP\textsuperscript{a}</td>
<td>x</td>
<td>x</td>
<td>7.2 days</td>
<td>x</td>
</tr>
<tr>
<td>21, BDAP</td>
<td>1.1</td>
<td>7.1 x 10\textsuperscript{-1}</td>
<td>17.0 h</td>
<td>27 h</td>
</tr>
<tr>
<td>25, PDD</td>
<td>16.3</td>
<td>6.9 ± 0.8</td>
<td>1.2 h</td>
<td>2.8 h</td>
</tr>
<tr>
<td>22, NDAP\textsuperscript{b}</td>
<td>7.3</td>
<td>5.4 ± 4.5</td>
<td>2.6 h</td>
<td>3.6 h</td>
</tr>
<tr>
<td>24, BDHP-imid</td>
<td>6.3 x 10\textsuperscript{-3}</td>
<td>x</td>
<td>127 days</td>
<td>x</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Parameters measured by other investigators\textsuperscript{79} using UV-vis spectroscopy. \textsuperscript{b} Determined by UV-vis spectroscopy with a 455 nm filter at detector.

Table 4: Thermodynamic parameters ΔE\textsubscript{act}, ΔH\textsuperscript{‡} and ΔS\textsuperscript{‡} calculated at 298 K from the rates of thermal return of photochromes at 74, 64 and 54°C using Arrhenius (2) and Eyring (4) equations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔE\textsubscript{act} (kcal/mol)</th>
<th>ΔH\textsuperscript{‡} (kcal/mol)</th>
<th>ΔS\textsuperscript{‡} (J/molK)</th>
<th>ln(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12, BDHP</td>
<td>24.0</td>
<td>23.4</td>
<td>26.3</td>
<td>27.3</td>
</tr>
<tr>
<td>12, BDHP\textsuperscript{a}</td>
<td>24.6</td>
<td>23.9</td>
<td>16.7</td>
<td>x</td>
</tr>
<tr>
<td>21, BDAP</td>
<td>21.7</td>
<td>21.0</td>
<td>43.3</td>
<td>25.3</td>
</tr>
<tr>
<td>25, PDD</td>
<td>16.5</td>
<td>15.8</td>
<td>94.5</td>
<td>19.1</td>
</tr>
<tr>
<td>22, NDAP\textsuperscript{b}</td>
<td>18.6</td>
<td>18.0</td>
<td>71.0</td>
<td>22.0</td>
</tr>
<tr>
<td>24, BDHP-imid</td>
<td>47.9</td>
<td>47.2</td>
<td>-282.0</td>
<td>64.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Parameters measured by other investigators\textsuperscript{79} using UV-vis spectroscopy. \textsuperscript{b} Determined by UV-vis spectroscopy with a 455 nm filter at detector.
It was important to remember that the rate constants obtained from these experiments are closely related to the type of set-up used in a particular lab. For example, when the 420 nm filter was not used, the thermal return no longer followed first-order kinetics and the observed rate constants were at least three times larger than they should have been. To understand these measurements in a more meaningful way, the collected results were compared to those obtained for BDAP 12 under the same experimental conditions. This was done to get an idea of how behavior of the new photochromes changed with respect to that of the BDHP molecule 12 which has been studied fairly extensively in prior years by the Mitchell and Bohne groups.

There was a relatively large difference of about 35% between the experimentally measured and the extrapolated rate constant for the thermal return for BDAP 21 at 298 K. The calculated rate of $21' \rightarrow 21$ thermal return was $1.1 \times 10^{-5}$ s$^{-1}$ while the measured rate constant at 298 K for the same process was $7.1 \times 10^{-6}$ s$^{-1}$. Large discrepancies between the calculated and the measured rate constants for the thermal return were also observed for PDD 25 and NDAP 22 photochromes (Table 3). This outcome is understandable for 25 and 22 because the lowest temperature at which the measurements for these were taken was 54°C which is 29°C above 298 K. These results are also understandable for NDAP 22 because there are noticeable deviations from linearity in the Arrhenius (2) and Eyring (6) graphs due to suspected decomposition of this compound during the UV-vis experiments. However, these results are less understandable for BDAP 21. BDAP 21 does not decompose with photo/thermal cycling between its open and closed states. There is also virtually no overlap between the absorption bands in the visible range of $21'$ and 21 in toluene. In addition, the lowest temperature at which the thermal return rate was obtained for the $21' \rightarrow 21$ transformation was 34°C with a good linear fit to the Arrhenius (2) graph with an $R^2$ value of 0.9999 (Figure 53). Perhaps the prediction of the rate of the thermal return of DHP species at lower temperature via the Arrhenius equation (2) just does not give reliable results. It is suspected that the experimentally measured rates tell a more realistic story.

$\Delta S^\dagger$ value was found to be the largest for PDD 25 (94.5 J/molK) which was extracted from the extrapolation of the high temperature data of the thermal return for this molecule to ambient conditions. This result can be attributed to the effects of large
stepped core geometry of the open structure 25′ going to the completely flat 25 upon closing. The stepped \(\rightarrow\) flat change also occurs in the transition states of other DHP photochromes. The geometries of closed BDAP 21 and NDAP 22 ligands have additional degrees of freedom because of extra rotations allowed about the acetylene link or about the carbonyl functional group which PDD 25 molecule does not have. However, this reasoning does not explain why the \(\Delta S^\ddagger\) for the thermal return to flat closed BDHP 12 from its corresponding CPD structure 12′ is only 26.3 J/molK as compared to the 94.5 J/molK for PDD 25, while the \(\Delta S^\ddagger\) for BDHP-imid 24 is -282.0 J/molK.

One answer to this question can be that BDHP 12 is a smaller flat molecule in comparison to PDD 25 and so fluctuations between its open and closed states would result in less disorder in the transition state leading to a lower change in entropy during the thermal return. The negative sign of \(\Delta S^\ddagger\) for 24′ \(\rightarrow\) 24 (-282.0 J/molK) contributes to keeping BDHP-imid 24 in the opened state for a longer time once it is converted to 24′ with visible light. The negative sign here also implies that there is less disorder in the transition state for the 24′ \(\rightarrow\) 24 conversion than there is in 24′ itself. This reduces the chances of the thermal conversion of 24′ to the closed 24 molecule. BDHP-imid 24 has less degrees of freedom available to it than either 22 or 21 due to restrictions in its intramolecular rotations. The currently preferred explanation for these large differences in \(\Delta S^\ddagger\) values is that these are naturally subject to large errors due to solvent effects which were not accounted for in the calculations.
**Figure 53**: Arrhenius plot for determination of rate of thermal return of BDAP 21 and $\Delta E_{\text{act}}$ in toluene in the dark by UV-vis.

**Figure 54**: Eyring plot for determination of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the thermal return of BDAP 21 in toluene in the dark at 298 K by UV-vis.
**Figure 55:** Arrhenius plot for determination of Δ$E_{\text{act}}$ and rate of thermal return for PDD 25 at 298 K in toluene by UV-vis.

**Figure 56:** Eyring plot for determination of Δ$H^\dagger$ and Δ$S^\dagger$ for the thermal return of PDD 25 in toluene at 298 K in the dark by UV-vis.
Figure 57: Arrhenius plot for determination of $\Delta E_{\text{act}}$ of the thermal return of NDAP 22 at 298 K in toluene in the dark by UV-vis.

Figure 58: Eyring plot for determination of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the thermal return of NDAP 22 in toluene in the dark at 298 K by UV-vis.
Figure 59: Arrhenius plot for determination of $\Delta E_{\text{act}}$ and rate of thermal return at 298 K for BDHP-imid 24 in toluene by UV-vis.

Figure 60: Eyring plot for determination of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the thermal return reaction of BDHP-imid 24 in toluene in the dark by UV-vis.
BDAP 21 showed complete thermal return from 21’ to the original closed state without decomposition (Figure 61). This transformation was repeated several times to obtain the thermal decay rates for 21’ → 21 at 34, 44, 54, 64 and 74°C. Figure 61 shows the thermal return of BDAP 21 at 54°C in toluene. The bands at 417 nm and 520 nm came back to their initial absorbance values that were recorded for the closed 21 before its exposure to visible light (>490 nm) at 20°C in this experiment. The presence of an isosbestic point at 332 nm signified that the thermal closing of 21’ to 21 proceeded without additional long-lived intermediates.

Figure 62 shows the UV-vis profile for the photochemical ring-opening of PDD 25 to 25’ by the laser using λexc of 488 nm (40 mW). The thermal decay of 25’ to 25 was followed by UV-vis at 298 K and the visual record showed that this transformation was reversible (Figure 63).
Figure 62: Photochemical ring opening of PDD 25 at 298 K (25°C) with a laser beam (488 nm, 40 mW), monitored by UV-vis (time shown in min).

Figure 63: Thermal return of PDD 25’ to 25 at 298 K in toluene in the dark after irradiation with the laser (488 nm, 40mW), monitored by UV-vis (time shown in hours).
Figure 64: Photochemical ring-opening of NDAP 22 in toluene with visible light (>490 nm) at 293 K, monitored by UV-vis (time shown in min).

Figure 65: Thermal return of open NDAP 22’ to closed 22 in toluene at 327 K (54°C) in the dark, monitored by UV-vis (time shown in min).
This experiment was repeated at 25, 54, 64 and 74°C with a 420 nm glass filter blocking out the high-energy light coming from the instrument’s detector, to determine the rate of thermal relaxation of 25′ at 298 K both experimentally and by linear extrapolation. Observation of well-defined isosbestic points at 393, 362, and 313 nm in toluene, as shown in Figures 62 and 63, confirmed that the forward photochemical and the reverse thermal decay reactions proceeded only between the 25 and 25′ species. The calculated and the measured return rates at 298 K were 1.6 x 10^{-4} s^{-1} and 6.9 (± 0.8) x 10^{-5} s^{-1} respectively (Table 3).

The thermal return of open NDAP 22′ to 22 at 54°C after its irradiation with visible light (>490 nm) did not go to completion. The light-driven 22 → 22′ reaction in d₈-toluene went to completion as determined by the proton NMR experiments with no observation of other intermediates. However, it appeared to be that 22′ en route to 22 via the thermal decay generated additional intermediates. This was concluded from the observation of lack of isosbestic points in the spectral overlays presented in Figures 64 and 65 for NDAP 22. These results were substantiated by the outcome of the photochemical cycling experiments (Figure 51), where significant decomposition of 22′ was observed as a function of cycle number of UV irradiation (254 nm). Perhaps this decomposition was not observed by the ¹H NMR experiments because of low sensitivity of this technique to small amounts of impurities.

2.12 Summary

In this chapter, syntheses of the photochromic DHP compounds 21, 22, 24 and 25 were described as well as of those that were the non-photochromic 23 and 26 DHPs. The UV-vis spectra and the photochemical response of these photochromes to UV and visible irradiation were subsequently evaluated. BDAP 21, NDAP 22 and BDHP-imid 24 compounds opened fully without generating photostationary states. PDD 25 gave only 44% of the open form 25′ after subjection of its NMR sample solution to 79 hours of visible irradiation (>490 nm) at 298 K. The photochromic DHP species cycled reversibly in toluene (except for 22) between their closed and open states upon exposure of their UV-vis solutions to alternating UV (254 nm) and visible irradiation (>490 nm, unless stated otherwise).
Thermal return experiments were conducted on 21, 22, 24 and 25 species at 74, 64 and 54°C (unless stated otherwise) in triplicate to approximate the errors for these measurements (Table 2). The rate constants for the thermal ring-closing processes at elevated temperatures for these were used to predict their thermal return rates and ΔE_{act} at 298 K using the Arrhenius relationship (2). Fitting of the thermal data to the Eyring equation (6) allowed for calculation of the thermodynamic parameters ΔS^‡ and ΔH^‡ for the thermal return reactions at room temperature. Since photochrome 25 returned from the open to its corresponding closed state rather quickly, it was possible to measure its actual rate of thermal return at room temperature. Acquisition of reliable rate data for NDAP 22 by UV-vis was difficult due to occasional sample decomposition at high temperatures.
Chapter Three: Preparation & Characterization of DHP-Phenanthroline Metal Complexes

3.1 Introduction

Having completed the synthesis of several photochromic DHP-phenanthroline molecules, we examined whether the introduction of a paramagnetic first-row transition metal into the binding site of phenanthroline would lead to deactivation of the photochemical transformation of the DHP ligand. Co(acac)$_2$(H$_2$O)$_2$ compound (51) was the source of cobalt(II) for preliminary investigations, where acac is short for acetylacetonate. If an equimolar mixture of Co(acac)$_2$(H$_2$O)$_2$ (51) and a DHP-phenanthroline are taken in a weakly coordinating polar solvent such as methanol, the molecules of water become displaced by the bidentate phenanthroline ligand. The forward reaction is primarily entropy driven$^{111}$ and since two molecules of water are lost for each binding phenanthroline, it goes essentially to completion within one hour at room temperature.

The complexation experiments were subsequently extended to the M(hfac)$_2$ series, where hfac is a hexafluorinated derivative of acetylacetonate and M is a first-row transition metal. The objective was to see what the effect is on the photoisomerization reaction of the DHP moiety when an electron-poor hfac ligand is included in the complex. The presence of an electron withdrawing ancillary ligand on the metal should lead to shortening of the ligand-metal contacts resulting in a closer interaction of the metal d-orbitals with the corresponding $\sigma$- and $\pi$-orbitals of phenanthroline.$^{112}$ With this in mind, a spin-active metal complex might be designed with sensitivity of the metal center to changes in the electronic structure of the bound DHP ligand. These differences in the electronic structure of DHP are thought to stem from the consequences of variable delocalization of the diatropic currents in the DHP photochrome when it is opened and closed.$^{73}$

Another attractive reason for choosing hfac ligands is that complexes with these are usually more chemically robust than with their hydrocarbon analogues. Perfluorination of the methyl groups of the acetylacetonate imparts thermal stability to
the overall complex assembly.\textsuperscript{113} It is also known that perfluorination of any component of the complex can stabilize that particular fragment. For example, incorporation of perfluorinated cyclopentenes into the structures of photochromic diarylethenes gave products that were much more stable towards oxidative degradation, which was prominent during photochemical cycling of the hydrocarbon analogues.\textsuperscript{15} Fluorination of the DHP-phenanthroline itself would be expected to reduce the distinction between the ligand field effects of the opened and closed DHP dye that is to be perceived by the metal center of the complex. Thermal stability of the fluorinated complexes, a property that cannot be ignored if they are meant to be used in long-term applications, can be advantageous for building DHP-based photochromic materials with longer shelf-life and reduced fatigue in solution and in polymer matrix media.

The replacement of terminal hydrogens by fluorine atoms in acetylacetonate usually leads to notable differences in solubility between the uncomplexed and fluorinated metal complex which may also be useful in the DHP system. This phenomenon has been employed by chemists for absolute structural elucidation of normally non-crystalline and unstable synthetic intermediates using X-ray crystallography. Incorporation of a single halogen atom into the structure can sometimes make the difficult to handle organic substances more crystalline as well as easier to characterize and purify on larger scales and we hoped that this would apply to our system.

Cobalt metal is magnetically interesting since it exhibits large spin-orbit coupling due to its inherent nuclear anisotropy.\textsuperscript{114} A small change in the ligand field that results from the isomerization of the photochrome, affecting the magnetic orbitals of Co(II), could in principle change the bulk magnetization of the sample.\textsuperscript{115,116} A cobalt complex, where the paramagnetic metal is coordinated to one DHP photochrome and where two semiquinone/catecholates substitute the ancillary acac ligands has potential to provide entry into the next generation of valence tautomeric systems that can be photochemically modulated between their long-lived high and low spin states.\textsuperscript{117,118,119,120,121}

Thus our goal was to synthesize several octahedral complexes combining one equivalent of the corresponding DHP photochrome (BDAP\textsuperscript{21}, NDAP\textsuperscript{22} and PDD\textsuperscript{25}) with two equivalents of either acac or hfac ancillary ligands bound to Co(II), Ni(II) and
Mn(II) metals. Their NMR spectra were recorded, even though the metal centers are paramagnetic, and their photochromicity were investigated.

3.2 Synthesis and UV-vis Spectroscopy of DHP-phenanthroline Complexes

The synthesis of the metal complexes commenced with BDAP 21 as the photochromic ligand of choice because it showed a clean 21 → 21' conversion under visible irradiation. The Co(acac)$_2$(BDAP) complex$^{12}$ 52 was made by first dissolving the metal precursor salt (51) in degassed methanol, and then by adding 1.0 equivalent of BDAP 21 (Scheme 8). The complex 52 precipitated out of solution overnight and was collected by filtration as a red powder in 82% yield; it was characterized by $^1$H NMR, UV-vis, IR (KBr), MS and EA methods.

Scheme 8$^a$

$^a$Reagents and Conditions. (i) MeOH, 1.0 eq. Co(acac)$_2$(H$_2$O)$_2$ 51, add BDAP 21 at RT, 82% yield.

The $^1$H spectrum of the closed complex 52 was obtained in CDCl$_3$. Only 9 out of the 16 aromatic resonances were visible which was not unusual since a paramagnetic metal was present in the complex. The two tert-butyl groups appeared at $\delta$ 0.45 and $\delta$ -0.76 as clean singlets, presumably shielded by the electrons of the paramagnetic metal; the internal methyl protons were also shielded singlets visible at $\delta$ -3.78 and $\delta$ -3.80. The alkane methyl protons were expected to have the best resolution in the NMR spectrum of this species because they are relatively far away from the paramagnetic center, rendering their resonance frequency the least susceptible to broadening.

The UV-vis spectrum of the closed complex 52 looks very similar to that of the unbound closed ligand 21 (Figure 66). Complex 52 has a $\lambda_{\text{max}}$ at 413 nm ($\epsilon_{\text{max}}$ 47300 L mol$^{-1}$ cm$^{-1}$) in toluene while the corresponding transition in BDAP 21 is at 417 nm. The
broad peak at 520 nm ($\epsilon_{\text{max}}$ 10800 L mol$^{-1}$ cm$^{-1}$) found in this complex is also present in BDAP 21 ($\epsilon_{\text{max}}$ 7850 L mol$^{-1}$ cm$^{-1}$).

However, there is a difference in the extent of overlap between these bands. The broad band at 520 nm in the Co(acac)$_2$(BDAP) complex 52 is more like a shoulder rather than a separate local maximum as it appears to be in the UV-vis spectrum of BDAP 21. The bands centered at 413 nm and 520 nm in Co(acac)$_2$(BDAP) 52 are broader with more extensive overlap. The additional transitions in system 52 were attributed to the presence of a metal center and their maxima are most likely located in the region where the bands at 413 nm and 520 nm overlap. The IR spectrum of the KBr pellet of the Co(acac)$_2$(BDAP) complex 52 exhibits the diagnostic acetylene stretch at 2186 cm$^{-1}$ and also a strong absorption at 1588 cm$^{-1}$ that was assigned to the carbonyl stretching modes of the acac ligand. The calculated exact mass for complex 52 was at $m/z$ 853.3416 (M) and it was found at $m/z$ 853.3397.
**Reagents and Conditions.** (i) MeOH, 1.0 eq. of M(hfac)$_2$, add BDAP 21 at RT; 88% (Mn$^{2+}$) 53, 84% (Ni$^{2+}$) 54, 85% (Co$^{2+}$) 55 yield.

In general, the M(hfac)$_2$(phen) complexes are more stable$^{113}$ than their M(acac)$_2$(phen) analogues and so it was anticipated that the BDAP complexes of this type would also exhibit enhanced stability. The three M(hfac)$_2$(BDAP) complexes 53-55 where M was Co(II), Ni(II) and Mn(II) were prepared in the same way as the Co(acac)$_2$(BDAP) complex 52 was, and were isolated in 85, 84, and 88% yields respectively as purple solids with metallic lustres (Scheme 9). They were characterized by $^1$H NMR, UV-vis, IR (KBr), EA and MS experiments. The calculated exact masses for complex 55 was at m/z 1069.2285 for its M+ ion while the found mass for the ionized species (M+) 55 was at m/z 1069.2302 respectively. While exact masses were not obtained for complexes 53 and 54, the elemental analyses for these were satisfactory.

The proton NMR spectra of closed complexes 53-55 were acquired in d$_8$-toluene since they lacked good solubility in CDCl$_3$. All three species had spectra that showed broadening due to the presence of the paramagnetic metal centers. The Mn(hfac)$_2$(BDAP) complex 53 had a peak at $\delta$ -1.13 for the internal methyl protons and at $\delta$ 1.44 representing hydrogens of the two tert-butyl groups. Ni(hfac)$_2$(BDAP) complex 54 had broadened singlets at $\delta$ 1.62 and at $\delta$ 1.45 for the two tert-butyl groups. The internal methyl protons for 54 appeared as two singlets at $\delta$ -1.03 and $\delta$ -1.09. The Co(hfac)$_2$(BDAP) complex 55 had the two tert-butyl groups at $\delta$ 0.82 and at $\delta$ -0.01; both of its internal methyl proton resonances appeared as a broadened singlet at $\delta$ -2.99.

The UV-vis profiles of the hfac complexes 53-55 looked similar, which was expected since the only difference between them was the identity of their metal centers.
The $\lambda_{\text{max}}$ occurred at 417 nm for 53-55 in toluene with a local broad maximum at 518–520 nm. The two absorptions overlapped in energy making their transitions at 520 nm appear as shoulders. The transitions invoked due to presence of the metal are lower in intensity and are usually hidden under the bands of the $\pi \rightarrow \pi^*$ transitions of the nitrogenous ligand. The 417 nm band can be assigned to a $\pi \rightarrow \pi^*$ transition of the DHP ligand and the longer wavelength absorptions can be attributed either to the intraligand $\pi \rightarrow \pi^*$ or to the transitions of the MLCT character. The MLCT transitions for 53-55 appear to be of about the same intensity. While the metals have different electronic configurations, the energy difference between the $T_{2g}$ and $E_g$ levels are not large enough to impact the size of the overall molecular HOMO-LUMO gap.

Figure 67 clearly shows the position of transitions in complexes 53-55 that are due to presence of a metal center. Extinction coefficients of 53-55 species in the 417–425 nm range fluctuate slightly between 45000 and 47800 L mol$^{-1}$ cm$^{-1}$. The extinction coefficients of 53-55 vary even less at the selected shoulder wavelength of 520 nm, fitting between 12200 and 13000 L mol$^{-1}$ cm$^{-1}$. The $\varepsilon_{520\text{nm}}$ in BDAP 21 is 7850 L mol$^{-1}$
cm\(^{-1}\) in toluene, which is two times less than that of either 53-55 metal complex. The MLCT transitions in 53-55 are indistinguishable by the position of their \(\lambda_{\text{max}}\) from the peak for the \(\pi \rightarrow \pi^*\) transition at 520 nm, which is a common feature in the UV-vis spectra of all BDHP-type compounds. Therefore, the MLCT transition in BDAP complexes 53-55 is in the 450–650 nm range of their UV-vis spectra and can be identified by the increased intensity of the 520 nm band upon comparison to the spectrum of the free BDAP 21 recorded at the same concentration.

The IR spectra of the KBr pellets of the hfac complexes show the absorptions due to an acetylene functional group at 2186 cm\(^{-1}\). The conjugated C=O transitions appear at 1637 cm\(^{-1}\) for Co(hfac)\(_2\)(BDAP) 55, and at 1643 cm\(^{-1}\) for Mn(hfac)\(_2\)(BDAP) 53 and Ni(hfac)\(_2\)(BDAP) 54. Complexes 53-55 were crystallized from hot acetone by first cooling the solution followed by slow evaporation of solvent in the dark cabinet. Purple crystals grew as fine needles which were isolated by filtration, washing with cold hexanes or pentane, and gave satisfactory elemental analyses results for 53-55.

The next step was to prepare cobalt acac and hfac complexes with NDAP 22 and PDD 25 and to examine the effect of a paramagnetic metal on the switching properties of these photochromes (Scheme 10).

\textit{Scheme 10\textsuperscript{a}}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{scheme10.png}};
\end{tikzpicture}
\end{center}

\textsuperscript{a}Reagents and Conditions. (i) MeOH, 1.0 eq. of Co(acac)\(_2\)(H\(_2\)O)\(_2\) 51 for 56 and 1.0 eq. of Co(hfac)\(_2\) 58 for 57, add NDAP 22 at RT; 74\% 56, 54\% 57 yield.

The syntheses of the NDAP acac complex 56 and NDAP hfac complex 57 were carried out in a similar manner to the complexes made for the BDAP series 52-55. Equimolar amounts of NDAP 22 and of either Co(acac)\(_2\)(H\(_2\)O)\(_2\) (51) or Co(hfac)\(_2\) 58 were combined
in methanol to generate the Co(acac)$_2$(NDAP) 56 and Co(hfac)$_2$(NDAP) 57 complexes in 74% and 54% yield respectively. The orange products 56 and 57 were individually collected by vacuum filtration and washed with cold methanol to remove unreacted metal salts 58 and NDAP 22 starting material. Analytically pure complexes were obtained by crystallizing them from hot acetone. The cooled solvent was slowly evaporated in the dark yielding crystalline 56 and 57. The Co(acac)$_2$(DAP) complex 59 was also made in 58% yield from Co(acac)$_2$(H$_2$O)$_2$ (51) and DAP 26 for a control experiment, even though the DAP dihydropyrene 26 was determined to be not photochromic itself (Scheme 11).

*Scheme 11*†

![Scheme 11](image)

*Reagents and Conditions.* (i) MeOH, 1.0 eq. of Co(acac)$_2$(H$_2$O)$_2$ 51, add DAP 26 at RT; 58% 59 yield.

The Co(acac)$_2$(NDAP) 56, Co(hfac)$_2$(NDAP) 57 and Co(acac)$_2$(DAP) 59 complexes were characterized by $^1$H NMR, UV-vis, IR (KBr), MS methods. The calculated exact mass for the M+ ion of 56 was at $m/z$ of 957.3678 and found at $m/z$ 957.3704. The four methyl groups of the bound acac ligands in the $^1$H spectrum (CDCl$_3$) of closed Co(acac)$_2$(NDAP) complex 56 appear as a broad singlet at $\delta$ 15.18. The tert-butyl groups were at $\delta$ 0.61 and $\delta$ -0.60 while the internal methyl protons were at $\delta$ -5.95 and $\delta$ -6.00. The $^1$H spectrum of the hfac analogue 57 in CDCl$_3$ had five downfield singlet resonances in addition to several multiplets in the usual aromatic region representing approximately 11 protons. The tert-butyl groups of 57 resonated at $\delta$ 0.54 and $\delta$ -0.01 with the internal methyl protons appearing at $\delta$ -5.48 and at $\delta$ -5.54. These traits are characteristic of these paramagnetic complexes where the aryl protons are the most affected by broadening due to their proximity to the metal center with unpaired spin. The proton NMR spectrum (CDCl$_3$) of complex 59 showed 5 downfield resonances
and 3 resonances in the regular aromatic region. The 12 hydrogen atoms of the two bound acac ligands appeared as a broad singlet at δ 15.12. The two tert-butyl groups were sharp singlets at δ 0.69 and δ -0.49 while the internal methyl protons were at δ -6.15 and δ -6.21.

The shape of the UV-vis spectrum of the parent NDAP ligand 22 is very similar to those of its cobalt acac and the hfac complexes (Figure 68), with enhanced intensity of the 520 nm shoulder absorptions. NDAP 22 has a λ_max at 427 nm in toluene (ε_max 60000 L mol⁻¹ cm⁻¹), a shoulder at 485 nm (ε_max 10500 L mol⁻¹ cm⁻¹) and a weak absorption at a longer wavelength of 685 nm (ε_max 4000 L mol⁻¹ cm⁻¹). The primary λ_max in Co(acac)₂(NDAP) 56 is shifted to 434 nm (ε_max 57000 L mol⁻¹ cm⁻¹) while the other peaks appeared at approximately the same energy as those found for the free NDAP 22 ligand. The Co(hfac)₂(NDAP) 57 complex has λ_max at 423 nm (ε_max 50300 L mol⁻¹ cm⁻¹) while the parent peak of NDAP 22 becomes a broad shoulder centered at about 520 nm (ε_max 13900 L mol⁻¹ cm⁻¹). The ε_683 nm in the UV-vis spectrum of Co(hfac)₂(NDAP) 57 is 5300 L mol⁻¹ cm⁻¹ compared to ε_685 of 4000 L mol⁻¹ cm⁻¹ determined for NDAP 22. This difference is small though noticeable.

The extinction coefficients at the ~488 nm shoulder for 56 and 57 complexes (14100 and 16400 L mol⁻¹ cm⁻¹ respectively) were higher than that of uncomplexed NDAP 22 (10500 L mol⁻¹ cm⁻¹). The extinction coefficients at 415–417 nm and at 685 nm remained relatively unaltered for 56 and 57 when compared to that of compound 22. This result suggests that the MLCT transitions are of substantial intensity for 56 and 57, showing up somewhere in the 488–520 nm shoulder region in toluene.
The MLCT transition is more intense for complex 57 and less so for 56, whereas the transition of NDAP 22 at ~488 nm is probably due only to the intraligand $\pi \rightarrow \pi^*$ electronic transition. Since these transitions are the most intense in the wavelength range where the samples were irradiated (>490 nm), the energy that was absorbed by complexes 56 and 57 must have been mostly dissipated through metal excited state decay back to the closed form. This may explain why the rate of opening of 57 was much slower than that for 56 and even slower than that for free NDAP 22 ligand (Table 1).

The UV-vis spectrum of Co(acac)$_2$(DAP) 59 showed two intense bands at 354 nm ($\varepsilon_{\text{max}} 58000$ L mol$^{-1}$ cm$^{-1}$) and 406 nm ($\varepsilon_{\text{max}} 57300$ L mol$^{-1}$ cm$^{-1}$) in toluene (Figure 69). The band that is normally found at 520 nm appeared for 59 as a broad transition with two local maxima at 483 nm ($\varepsilon_{\text{max}} 16900$ L mol$^{-1}$ cm$^{-1}$) and 507 nm ($\varepsilon_{\text{max}} 17200$ L mol$^{-1}$ cm$^{-1}$). The $\varepsilon_{479 \text{ nm}}$ and $\varepsilon_{501 \text{ nm}}$ for the DAP 26 ligand in toluene are 12500 L mol$^{-1}$ cm$^{-1}$ and 12300 L mol$^{-1}$ cm$^{-1}$ respectively. The MLCT transitions for complex 59 are most likely in the 483–520 nm range since the extinction coefficients for the two bands found there are larger than they are for the uncomplexed ligand 26. The rates of ring-opening of 26 and 59 cannot be compared at a selected wavelength because neither compound opened under
the experimental conditions employed. Therefore, it can only be postulated that these peaks consist of a combination of the $\pi \rightarrow \pi^*$ intraligand and the MLCT energy transfers.

The IR spectrum of the KBr pellet of Co(acac)$_2$(NDAP) 56 showed an absorption at 2192 cm$^{-1}$ for the C=C functional group. For Co(hfac)$_2$(NDAP) 57 it was observed at 2192 cm$^{-1}$ and for Co(acac)$_2$(DAP) 59 it was at 2186 cm$^{-1}$. The conjugated carbonyl stretching modes for Co(acac)$_2$(NDAP) 56, Co(hfac)$_2$(NDAP) 57 and Co(acac)$_2$(DAP) 59 complexes were found at 1588, 1640 and 1588 cm$^{-1}$ respectively.

Lastly, PDD 25 was complexed to cobalt metal with either two equivalents of acac or hfac ancillary ligands to obtain Co(acac)$_2$(PDD) 60 and Co(hfac)$_2$(PDD) 61 complexes (Scheme 12). Phenanthroline diimine dihydropyrene 25 was sparingly soluble in methanol and this property was taken advantage of in the synthesis of Co(acac)$_2$(PDD) 60. The Co(acac)$_2$(H$_2$O)$_2$ (51) starting material was dissolved in degassed methanol followed by addition of 1.0 equivalent of PDD 25 and the solution was left to stir overnight. The green suspension turned into a dark green solution after 15 hours and any unreacted PDD 25 was subsequently removed from the reaction by filtration. The
Co(acac)$_2$(PDD) complex 60 was obtained in 94% yield as a dark green solid upon concentration of the filtrate at reduced pressure.

The Co(hfac)$_2$(PDD) 61 was synthesized from an equimolar mixture of Co(hfac)$_2$ 58 and PDD 25 in degassed methanol (Scheme 12). The Co(hfac)$_2$ salt 58 was dissolved in methanol at first, followed by the addition of the photochromic ligand 25 under inert atmosphere. Solubility of the fluorinated complex 61 was significantly reduced relative to that of Co(hfac)$_2$ 58 and PDD 25 starting materials.

**Scheme 12**

![Scheme 12](image)

*Reagents and Conditions.* (i) MeOH, 1.0 eq. of Co(acac)$_2$(H$_2$O)$_2$ 51 for 60 and 1.0 eq. of Co(hfac)$_2$ 58 for 61, add NDAP 25 at RT; 94% 60, 41% 61 yield.

A slight excess of the Co(hfac)$_2$ 58 reagent was added to avoid having unreacted PDD 25 as an impurity in the isolated product. The reaction mixture was allowed to stir overnight in the dark. Since Co(hfac)$_2$ 58 dissolves easily in methanol, its excess was removed by washing the product with methanol during the filtration of the reaction mixture. The Co(hfac)$_2$(PDD) 61 complex had sparing solubility in methanol and was collected by filtration as a dark green solid in 41% yield. The products 60 and 61 were characterized with $^1$H NMR, UV-vis, IR (KBr), and HRMS experiments. The calculated exact mass for M+ ion of complexes 60 appeared at m/z 805.3164 60 was found at m/z 805.3152. The closed Co(acac)$_2$(PDD) complex 60 was dissolved in CDCl$_3$ for the $^1$H NMR experiment. The 6 different aromatic resonances for 60 were all singlets spanning the δ 52.50–7.48 range. The 12 protons of the four acac methyl groups were represented by a broad singlet at δ 14.58. The two tert-butyl groups which are chemically equivalent were found at δ 1.47, while the internal methyl protons were at δ -0.46. The proton in the α-
position between the two carbonyl carbons of the acac ligand was a singlet of double relative intensity at $\delta$ -16.45.

The closed Co(hfac)$_2$(PDD) complex 61 was observed by $^1$H NMR in d$_8$-toluene. The two different types of phenanthroline protons were resolved singlets at $\delta$ 37.04 and $\delta$ 13.76. The ortho phenanthroline protons were found as a broad singlet at $\delta$ ~85. The three types of aromatic protons of the DHP moiety were singlets at $\delta$ 10.15, $\delta$ 7.85 and $\delta$ 7.54. The tert-butyl protons were at $\delta$ 1.61 and the chemically equivalent internal methyl hydrogens at $\delta$ -0.01. Although the latter are normally more shielded in the DHP species, they were shifted down-field for 61, perhaps because of the electron withdrawing effects of the 12 fluorines on the ancillary hfac ligands. An alternative reason may be that the chemical shifts are dominated by metal paramagnetic effects causing dispersion of the resonances of the PDD 25 that is bound to the metal in complex 61.

The $\lambda_{\text{max}}$ value for PDD 25 was at 449 nm with the $\varepsilon$ of 23800 L mol$^{-1}$ cm$^{-1}$. The $\varepsilon_{453\text{nm}}$ of Co(acac)$_2$(PDD) complex 60 was 49400 L mol$^{-1}$ cm$^{-1}$. This parameter for Co(hfac)$_2$(PDD) 61 at 459 nm reached an even greater value of 67200 L mol$^{-1}$ cm$^{-1}$. The
MLCT transitions for complexes 60 and 61 were hidden or included within the peaks in the 453–459 nm range (Figure 70). The ε at the λ\text{max} for the hfac complex 61 was the largest while its rate of opening was the slowest when compared to those of 25 and 60 under visible light irradiation (>490 nm). Complex 61 must dissipate much of the visible energy that it absorbs while going through nonradiative decay instead of ring-opening.

Table 5: Summary of the chemical shift (δ) values for the internal methyl protons of the closed metal complexes of BDAP 21, NDAP 22 and PDD 25.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Internal Me-H δ (CDCl\text{3})</th>
<th>Internal Me-H δ (d\text{8}-toluene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21, BDAP</td>
<td>-1.35 and -1.38</td>
<td>x</td>
</tr>
<tr>
<td>22, NDAP</td>
<td>-3.59 and -3.62</td>
<td>x</td>
</tr>
<tr>
<td>25, PDD</td>
<td>-1.23</td>
<td>x</td>
</tr>
<tr>
<td>52, Co(acac)\text{2}(BDAP)</td>
<td>-3.78 and -3.80</td>
<td>x</td>
</tr>
<tr>
<td>53, Mn(hfac)\text{2}(BDAP)</td>
<td>x</td>
<td>-1.13</td>
</tr>
<tr>
<td>54, Ni(hfac)\text{2}(BDAP)</td>
<td>x</td>
<td>-1.03 and -1.09</td>
</tr>
<tr>
<td>55, Co(hfac)\text{2}(BDAP)</td>
<td>x</td>
<td>-2.99</td>
</tr>
<tr>
<td>56, Co(acac)\text{2}(NDAP)</td>
<td>-5.95 and -6.00</td>
<td>x</td>
</tr>
<tr>
<td>57, Co(hfac)\text{2}(NDAP)</td>
<td>-5.48 and -5.54</td>
<td>x</td>
</tr>
<tr>
<td>59, Co(acac)\text{2}(DAP)</td>
<td>-6.15 and -6.21</td>
<td>x</td>
</tr>
<tr>
<td>60, Co(acac)\text{2}(PDD)</td>
<td>-0.46</td>
<td>x</td>
</tr>
<tr>
<td>61, Co(hfac)\text{2}(PDD)</td>
<td>x</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

3.3 Photo-opening of the Photochromic DHP-Metal Complexes

Since all of the synthesized DHP complexes were soluble in toluene and because of its high boiling point at 110-111°C, this solvent was chosen for the photochemical ring opening and thermal return studies. One drawback of toluene is that the benzenoid absorptions of the open DHP photochromes occur in the same region as those of the solvent (λ\text{max} at 262 nm as measured in cyclohexane\textsuperscript{123}). Unfortunately, due to the presence of a polar phenanthroline substituent, it was difficult to dissolve all of the DHP ligands and their metal complexes in a single less polar high-boiling solvent that lacked benzenoid absorptions. This was really only a problem during the UV-stimulated closing experiments where the behaviour of the photochrome did not follow first order kinetics because of the competing absorptions by the solvent. The rate of the UV (254 nm) ring-closing of the DHP switch was also very slow in toluene even when the Φ of this transformation is normally quite large (~0.4) in cyclohexane.\textsuperscript{75,76} However, the
measurement of the closing rates of all DHP compounds was not the focus of this project. Our objective was just to see whether the compounds do reversibly close when they are exposed to UV light. Toluene was used for all irradiation experiments to make performance of all photochromes and complexes thereof directly comparable to each other without having to take solvent effects into consideration.

All operations with light sensitive compounds were carried out in the darkened room to avoid premature bleaching of samples. A suitable mass of each complex was dissolved in toluene in a 10 mL volumetric flask to give stock solutions with concentration of approximately $5.0 \times 10^{-4}$ M in analyte. A series of 4-5 standards were prepared of each complex by a 100-fold dilution of their stock solutions. These samples provided UV-vis spectra of the molecules of interest that were superimposed to calculate extinction coefficients at selected maxima and also to determine what concentrations of the latter were suitable for the subsequent kinetic studies.

A typical sample for the photochemical studies was prepared by making a fresh solution from the corresponding stock that was stored in the dark cabinet. A UV-vis
A cuvette with a path length of 1 cm was rinsed and filled with this solution. A stir bar was added if mixing was required during the experiment to ensure sample homogeneity upon data acquisition. The full cuvette was closed with a screw-top lid fitted with a silicone septum. The contents of the sealed cell were then degassed in the dark by bubbling N₂ for 10–15 minutes at room temperature through the solution. Figures 71-78 display the UV-vis spectra of each photochromic complex in its closed state before irradiation and of the corresponding open form after visible light irradiation.

**Figure 72:** UV-vis spectra of open 54' (red) and closed Ni(hfac)₂(BDAP) 54 (blue) in toluene.
The Co(acac)$_2$(DAP) complex 59 was not photochromic and so only the spectrum of its closed form was obtained as shown in Figure 70. The BDAP complexes 52-55 opened within 5 minutes upon their exposure to visible light (>490 nm). A filter cutting off light up to 490 nm was used to block out higher energy wavelengths to avoid invoking competitive photochemical back-reactions and formation of photostationary states when these could be avoided. It was expected that BDAP complexes 52-55 would open fully because the broad peak at approximately 520 nm, assigned to a $\pi \rightarrow \pi^*$ transition belonging to the closed complex, coincided with the non-absorbing regions of the UV-vis spectrum of the complementary CPD form (Figures 71-73). Minimal overlapping of the UV-vis spectra of the open and closed forms in the longer wavelength range allowed for selective irradiation into the band of the closed state leading to full conversion of the dye into its open isomer.
The Co(acac)$_2$(PDD) 60 and Co(hfac)$_2$(PDD) 61 complexes have two strong absorptions in the 430–460 nm region in toluene. Figure 75 shows an overlay of the UV-vis spectra of open 60′ and the closed Co(acac)$_2$(PDD) complex 60. The absorption at 453 nm does not disappear completely when 60 is opened. The persistence of this peak does not necessarily signify that a photostationary state is reached, since it may be due to absorptions of the open Co(acac)$_2$(PDD) complex 60′ only. However, a photostationary state was the likely result here because the diagnostic peaks did not shift when the PDD 25 was opened in this complex assembly.

Figure 76 shows an overlay of the UV-vis spectra of the maximally opened Co(hfac)$_2$(PDD) 61′ and its fully closed complex 61. The absorbance at 459 nm of the open Co(hfac)$_2$(PDD) 61′ is relatively more intense compared to that of the open Co(acac)$_2$(PDD) 60′ at 453 nm (Figures 75 and 76). The open/closed ratios for the Co(acac)$_2$(PDD) 60 and the Co(hfac)$_2$(PDD) 61 complexes must be different at their photostationary states or maybe the absorption at $\lambda_{\text{max}}$ of the open complex 61′ has a greater $\varepsilon$ than that of the open 60′.
Figure 75: UV-vis spectra of open 60' (red) and closed Co(acac)$_2$(PDD) 60 (blue) in toluene.

Little can be inferred about the size of the open/closed ratios or whether they exist for a specific photochrome in the first place without a $^1$H NMR spectrum of the maximally opened state. The extinction coefficients of the absorptions of the open form are not known for either PDD complex. This is because complexes 60 and 61 do not open fully under visible irradiation as determined by $^1$H NMR. Proton spectra of closed 60 and 61 are broadened due to presence of the paramagnetic cobalt metal leading to difficulties in good relative integration of the diagnostic peaks. This is especially true for those protons which are close to the metal center in space or through electronic conjugation. However, an estimate can be made of the open/closed ratio for a given complex based on the difference between the peak heights at a chosen wavelength in the UV-vis spectra of the superimposed “open” and the fully closed forms. This method provides a good guess if the fully open state has absorptions near the baseline at the wavelength of interest.
To prepare an NMR sample, ~5 mg of Co(hfac)$_2$(PDD) 61 was dissolved in d$_8$-toluene. The solution was then degassed with N$_2$ followed by irradiation of the closed tube contents with visible light (>490 nm) for 13.5 hours in a water bath set to ~14°C. The purpose of this experiment was to determine the 61'/61 ratio while this complex is at its photostationary state during irradiation in a UV-vis cuvette. An important assumption made here was that these ratios are equivalent if the irradiation of the sample happens when it is in an NMR tube and in the UV-vis cuvette at the same temperature and at appropriate dilution for either experiment, given that the relative solubility of the isomers and the time of irradiation are not the limiting factors. This assumption is reasonable because a sample of photochromic DHP molecules normally bleaches as the visible irradiation experiment continues, allowing for better permittivity of light through the test solution.

Relative integration of the resolved phenanthroline proton resonances in the mixture of open and closed Co(hfac)$_2$(PDD) complex 61, obtained by visible irradiation (>490 nm) of its NMR solution (d$_8$-toluene), suggested that there was 37% of 61'. Comparison of intensities of internal methyl protons from 61 and alkane methyl protons...
from 61' in the same $^1$H NMR spectrum indicated that the open form 61' accounted for 31% of the total soluble complex concentration. The internal methyl protons on the DHP fragment are further away from the cobalt center than the phenanthroline aromatic protons in the complex and should thus be less affected by paramagnetic broadening. Therefore, the integral values obtained from the shielded methyl groups on the DHP may be more trustworthy.

The relative intensities of absorptions at $\lambda_{459\text{nm}}$ in the overlay of the UV-vis spectra of the closed and the “open” Co(hfac)$_2$(PDD) complex 61 suggest that there is about 40% of 61' in solution at the photo-stationary state (Figure 76). This result is in agreement with the concentration calculations of the open form of this complex based on the quantification done by the $^1$H NMR experiment. This method was subsequently applied to quantification of the open form when the photo-stationary state of the structurally related acac complex 60 was reached. An analogous measurement of the 60'/60 ratio by comparison of the intensities at 453 nm suggested that there is ~67% of the open complex 60' at the photo-stationary state (Figure 75).

Figure 77: UV-vis spectra of the open 56' (blue) and closed Co(acac)$_2$(NDAP) 56 (red) in toluene
NDAP 22 opens fully in toluene under visible irradiation (>490 nm). $^1$H NMR (CDCl$_3$) revealed that the resonances due to the internal methyl protons at $\delta$ -3.59 and $\delta$ -3.62 in 22 are replaced by a new singlet at $\delta$ 1.57 which represents the methyl protons of the shielded benzylic character in the open 22' structure (Figure 78). The UV-vis absorptions of the maximally open NDAP 22 (Figure 78) were not fully replaced by different bands corresponding to 22'; their size merely diminished in comparison to those due to the closed state at the same sample concentration. The open 22' then must have absorptions that extend into the similar wavelengths (~500 nm) as where the $\pi \rightarrow \pi^*$ transitions for the closed 22 molecule occur. This apparent tailing of the spectrum of the open from 22' and the lack of peaks in the $^1$H NMR representing 22' may arise from differences in sensitivities of UV-vis and NMR methods during quantification experiments. The UV-vis technique alone cannot really identify the species in solution. Therefore, it is misleading to assume that there must be an incomplete photochemical 22 $\rightarrow$ 22' conversion if a given absorbance in the UV-vis spectrum of 22 has not disappeared and then been replaced by a transition of a different energy of 21'.

![UV-vis spectra of closed NDAP 22 (red) and open NDAP 22' (blue) in toluene.](image)

**Figure 78:** UV-vis spectra of closed NDAP 22 (red) and open NDAP 22' (blue) in toluene.
Visible irradiation (>490 nm) of the Co(hfac)$_2$(NDAP) complex 57 for 13.5 hours in toluene showed, using $^1$H NMR experiments, that the NDAP 22 ligand does not open in this coordination environment. Another interpretation of this result is that 57 does open but that the amount of 57' formed is very small or that the thermal return of 57' to 57 at 14°C is fast, making determination of the concentration of 57' ineffective by relative integration of chosen proton resonances.

Graphs for the observed apparent rates of opening of the photochromic BDAP 21, NDAP 22 and PDD 25 complexes are shown below in Figures 79-84. The decrease in concentration of the closed species was monitored as a function of time for each complex by UV-vis in the intervals between visible irradiation of the sample. The 420 nm pyrex filter was used for complexes of BDAP 21 and PDD 25 to block out the relatively weak but significant short-wavelength irradiation coming from the instrument during data acquisition. A 455 nm filter of the same quality was used for measurements conducted on NDAP 22 complexes. The induction period of decay of a selected maximum in the UV-vis spectrum of each complex was fitted to a first-order rate law to obtain the apparent rate constant for the photochemical conversion of each closed to its corresponding open state.

![Graph](image_url)

**Figure 79:** Determination of the rate constant for opening of Co(acac)$_2$(BDAP) 52 in toluene at 293 K under visible irradiation (>490 nm) using a 420 nm filter, observed by UV-vis.
Figure 80: Determination of rate constant for opening of Co(hfac)$_2$(BDAP) 55 by UV-vis in toluene under irradiation (>490 nm) at 293 K (20°C) using a 420 nm filter.

Figure 81: Determination of rate constant for ring opening of Mn(hfac)$_2$(BDAP) 53 by UV-vis in toluene under visible irradiation (>490 nm) at 293 K (20°C) using a 420 nm filter.
Figure 82: Determination of the rate constant of ring opening of Ni(hfac)$_2$(BDAP) 54 by UV-vis under visible irradiation (>490 nm) in toluene at 293 K (20°C) using a 420 nm filter.

Figure 83: Calculation of the rate constant for ring opening of Co(acac)$_2$(PDD) 60 in toluene at 293 K (20°C) under visible irradiation (>490 nm) using a 420 nm filter, monitored by UV-vis.
Figure 84: Photochemical opening rate constant determination for Co(hfac)$_2$(PDD) 61 by UV-vis in toluene at 293 K (20°C) under visible irradiation (>490 nm) using a 420 nm filter at record.

Figure 85: Determination of rate constant for opening of Co(hfac)$_2$(NDAP) 57 in toluene at 2-3°C (>490 nm) with a 455 nm filter at the detector, monitored by UV-vis at 500 nm shoulder absorbance.
Table 6: Apparent rate constants\(^a\) of photochemical ring-opening of the photochromic complexes at 293 K (20°C). Irradiation was done with a ~500 W visible light (>490 nm) and the UV-vis measurements taken using a 420 nm filter\(^b\) at the detector.

<table>
<thead>
<tr>
<th>Compound</th>
<th>rate constants for opening (s(^{-1}))</th>
<th>(\tau_{1/2}) of ring-opening</th>
</tr>
</thead>
<tbody>
<tr>
<td>21, BDAP</td>
<td>4.1 (± 0.2) x 10(^{-2})</td>
<td>0.3 min</td>
</tr>
<tr>
<td>22, NDAP(^c)</td>
<td>1.9 (± 0.7) x 10(^{-4})</td>
<td>1.0 h</td>
</tr>
<tr>
<td>25, PDD</td>
<td>7.0 (± 1.6) x 10(^{-4})</td>
<td>17 min</td>
</tr>
<tr>
<td>52, Co(acac)(_2)(BDAP)</td>
<td>1.2 (± 0.1) x 10(^{-2})</td>
<td>0.9 min</td>
</tr>
<tr>
<td>55, Co(hfac)(_2)(BDAP)</td>
<td>1.1 (± 0.1) x 10(^{-2})</td>
<td>1.1 min</td>
</tr>
<tr>
<td>53, Mn(hfac)(_2)(BDAP)</td>
<td>5.8 (± 0.3) x 10(^{-3})</td>
<td>2.0 min</td>
</tr>
<tr>
<td>54, Ni(hfac)(_2)(BDAP)</td>
<td>9.2 (± 0.5) x 10(^{-3})</td>
<td>1.3 min</td>
</tr>
<tr>
<td>60, Co(acac)(_2)(PDD)</td>
<td>2.2 (± 0.5) x 10(^{-4})</td>
<td>53 min</td>
</tr>
<tr>
<td>61, Co(hfac)(_2)(PDD)</td>
<td>9.7 (± 2.3) x 10(^{-3})</td>
<td>2.0 h</td>
</tr>
<tr>
<td>56, Co(acac)(_2)(NDAP)</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>57, Co(hfac)(_2)(NDAP)(^c)</td>
<td>~4.4 x 10(^{-3}) s(^{-1})</td>
<td>4.4 h</td>
</tr>
</tbody>
</table>

\(^a\)Apparent rate constants were estimated by determining rates of photo-opening of the uncomplexed photochromes in triplicate and applying the standard deviations to the rate constants of the metal complexes with each type of ligand. \(^b\)Co(hfac)\(_2\)(NDAP) complex 57 required the use of a filter with a 455 nm cut-off at the detector to minimize the occurrence of the competing photochemical return process. \(^c\)Photochemical opening of NDAP 22 and Co(hfac)\(_2\)(NDAP) 57 were measured at 2–3°C.

A general trend emerged for the apparent rates of opening of NDAP and PDD complexes 56, 57 and 60, 61 respectively. Stimulation of the MLCT transitions by visible light drains the energy from the path leading to productive conversion of the NDAP 22 and PDD 25 from their closed to the opened states while they are bound to the cobalt metal. The presence of the acetylacetonate ligand quenched this transformation to a lesser extent than the hfac ancillary did.

It was noted that BDAP 21 opened 1.5–2 times faster than the metal complexes thereof which was also in agreement with observations made for the NDAP 56-57 and PDD 60-61 derivatives. This is consistent with there being MLCT transitions with relatively high \(\varepsilon\) present for 52-55 and especially for the 60-61 species in toluene (Figures 67 and 70). The \(\tau_{1/2}\) values for opening of BDAP 21 and PDD 25 were comparable to those that were measured for their complexes, corresponding roughly to the magnitudes of the \(\varepsilon\) for their MLCT bands. The bands photo-irradiation into which resulted in the conversion of the bound BDAP 21 to 21' in complexes 52-55 were more intense than the corresponding band observed for free 21. It was observed that the apparent rate of the photochemical conversion of the closed to the open state of a given DHP complex
generally depended on the magnitude of the ε of its MLCT transition. Therefore, the apparent rate constants for opening of complexes 52-55 were understandably smaller in comparison to that of 21. This difference is more pronounced for the apparent opening rate constant of free PDD 25 relative to the rate measurements of its acac and hfac complexes 60-61.

3.4 Thermal Relaxation of the DHP-Metal Complexes

The thermal return rates of all photochromic DHP complexes were measured at 74, 64, and 54°C in degassed toluene in the dark unless stated otherwise. These experiments were done in order to gain knowledge about the thermodynamic parameters such as the energy of activation (ΔE<sub>act</sub>), enthalpy (ΔH<sup>‡</sup>) and the entropy of activation (ΔS<sup>‡</sup>) for their thermal return processes. The experimentally measured rate constants for thermal return at different temperatures for a single complex were incorporated into an Arrhenius equation (3). The plot of negative natural logarithm of the rate constant versus the reciprocal of temperature in Kelvin units gave a straight line, the slope of which provided the ΔE<sub>act</sub> while the y-intercept gave the ln(A) values.

\[-\ln(k) = \frac{(\Delta E_{act}/R)(1/T)}{\ln(A)}\] equation (3)

An attempt was made to estimate the rates of the thermal return of all photochromic DHP complexes at 298 K from these graphs and to calculate the half-lives (τ<sub>1/2</sub>) for these processes using equation (7). These calculated results should be viewed with caution as the extrapolation method is prone to large errors especially when the experimental measurements closest to 298 K were done at the significantly higher temperature of 327 K. This method normally yields errors of ± 0.5 kcal/mol for the ΔE<sub>act</sub>.

\[\tau_{1/2} = \frac{(\ln2)/k}{\ln(A)}\] equation (7)

The Eyring equation (6) was employed to establish a linear relationship between the negative natural logarithm of the k/T ratio with the inverse value of temperature. The slope of this line gave the enthalpy of activation (ΔH<sup>‡</sup>) of the thermal return reaction. The ΔS<sup>‡</sup> parameter was obtained form the y-intercept of the same line which is given by
the $\Delta S^\dagger/R - 23.73$ expression of equation (6). Since the entropy change in the transition state is calculated from the y-intercept which involves substantial extrapolation, the $\Delta S^\dagger$ values that were obtained in this manner were subject to large errors arising from slightest deviations from linearity (equation 6).

$$-\ln(k/T) = (-\Delta H^\dagger/R)(1/T) + (\Delta S^\dagger/R - 23.73)$$

Co(acac)$_2$(PDD) complex 60 showed reversible thermal relaxation following visible (>490 nm) irradiation. Figures 86 and 87 indicate that the photochemical ring-opening and closing of 60 in toluene passes through three isosbestic points at 307, 368 and 393 nm. The thermal return of 60’ to the original absorbance intensities of 60 was allowed to progress at 54°C, going to completion in about 35 min.

Table 7: Experimentally measured rate constants$^a$ for the thermal return of photochromic complexes in toluene in the dark at 54, 64 and 74°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k \times 10^{-4}$ s$^{-1}$; 54°C</th>
<th>$k \times 10^{-4}$ s$^{-1}$; 64°C</th>
<th>$k \times 10^{-4}$ s$^{-1}$; 74°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>52, Co(acac)$_2$(BDAP)</td>
<td>3.1 (± 0.6)</td>
<td>9.0 (± 0.7)</td>
<td>21.5 (± 0.6)</td>
</tr>
<tr>
<td>55, Co(hfac)$_2$(BDAP)</td>
<td>3.2 (± 0.6)</td>
<td>9.0 (± 0.7)</td>
<td>21.4 (± 0.6)</td>
</tr>
<tr>
<td>53, Mn(hfac)$_2$(BDAP)</td>
<td>4.3 (± 0.8)</td>
<td>10.5 (± 0.8)</td>
<td>25.7 (± 0.8)</td>
</tr>
<tr>
<td>54, Ni(hfac)$_2$(BDAP)</td>
<td>3.3 (± 0.6)</td>
<td>8.2 (± 0.7)</td>
<td>23.0 (± 0.7)</td>
</tr>
<tr>
<td>60, Co(acac)$_2$(PDD)</td>
<td>22.5 (± 0.9)</td>
<td>52.2 (± 7.2)</td>
<td>97.9 (± 6.9)</td>
</tr>
<tr>
<td>61, Co(hfac)$_2$(PDD)</td>
<td>30.7 (± 1.2)</td>
<td>70.1 (± 9.6)</td>
<td>120.2 (± 8.5)</td>
</tr>
<tr>
<td>56, Co(acac)$_2$(NDAP)</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>57, Co(hfac)$_2$(NDAP)</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

$^a$Errors for the rate constants for the three types of metal complexes were estimated from the standard deviations in rate constants determined in triplicate of the corresponding uncomplexed photochromes.

It has been established that the Co(acac)$_2$(PDD) complex 60 is thermochromic and photochromic. After visible irradiation of the Co(acac)$_2$(PDD) sample, the $\lambda_{453\text{nm}}$ of 60’ returns to the original absorbance intensity of the fully closed 60 upon heating as well as after exposure of this open isomer to UV light.
Figure 86: Photo-opening of Co(acac)$_2$(PDD) 60 in toluene with visible light (>490 nm) at 293 K, monitored by UV-vis (time shown in minutes).

Figure 87: Thermal return of Co(acac)$_2$(PDD) 60 in toluene at 327 K (54°C) in the dark, monitored by UV-vis (time shown in minutes).
Table 8 shows the experimentally determined rate constants for the thermal return of photochromic DHP complexes at 54, 64 and 74°C. The BDAP series 52-55 were the slowest to come back to their closed states. The rates of thermal return increased approximately three-fold for all BDAP complexes with 10 degree increments of the medium temperature. Substitution of two acac with two hfac ancillary ligands did not significantly alter the rate of closing of the coordinated BDAP 21 photochrome.

Figure 88: Arrhenius plot for determination of rate of thermal return and $\Delta E_{\text{act}}$ of Co(acac)$_2$(BDAP) 52* at 298 K (25°C) in toluene in the dark by UV-vis.
Figure 89: Eyring plot for determination of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of thermal closing of $\text{Co(acac)}_2(\text{BDAP})$ 52' in toluene in the dark at 298 K (25°C) by UV-vis.

The PDD series 60-61 showed faster relative return rates as compared to those measured for complexes 52-55. The rate of the thermal return at 54°C of $\text{Co(acac)}_2(\text{PDD})$ 60 was 22.5 (± 0.9) x $10^{-4}$ s$^{-1}$ which was ~7 times faster than that of $\text{Co(acac)}_2(\text{BDAP})$ 52 that returned at a rate of 3.1 (± 0.6) x $10^{-4}$ s$^{-1}$. These results correlated well with the difference in the thermal return rates for the free BDAP 21 (3.2 (± 0.2) x $10^{-4}$ s$^{-1}$) and PDD 25 (19.5 (± 0.7) x $10^{-4}$ s$^{-1}$) ligands where the latter closed ~6 times faster than the former at 54°C in toluene (Table 2). The rate of thermal return of the Co(hfac)$_2$(PDD) 61 complex was 1.4 times that of the Co(acac)$_2$(PDD) 60 complex, while this difference was not observed for the BDAP series 52-55.
Figure 90: Arrhenius plot for determination of rate of thermal closing and $\Delta E_{\text{act}}$ of Co(hfac)$_2$(BDAP) 61' in toluene in the dark at 298 K (25°C) by UV-vis.

Figure 91: Eyring plot for determination of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of thermal closing at 298 K (25°C) of Co(hfac)$_2$(BDAP) 61' in toluene in the dark by UV-vis.
The $\Delta E_{\text{act}}$ and $\Delta H^\ddagger$ parameters refer to approximately the same quantity and therefore can be exchangeable in the discussion of thermal return kinetics in this report. The molecule with the highest activation energy ($\Delta E_{\text{act}}$) for closing in the dark has the highest enthalpy of activation ($\Delta H^\ddagger$) for this process in the direction as written. The spontaneity of the thermal return process, described by equation (5), depends on the enthalpy ($\Delta H^\ddagger$) and the entropy ($\Delta S^\ddagger$) of activation as well as on the temperature. The complex with the highest activation energy for the thermal return reaction should in principle have the slowest rate of ring closing.

A larger $T\Delta S^\ddagger$ product coupled with a smaller enthalpy of activation ($\Delta H^\ddagger$) makes the $\Delta G^\ddagger$ term more negative and the transformation of the system as written more spontaneous. Table 9 displays the calculated thermodynamic parameters for all of the photochromic complexes.

Table 8: Calculated and measured rate constants$^a$ and $\tau_{1/2}$ for thermal return of the photochromic complexes at 298 K. The calculations were done using thermal return data obtained at 54, 64 and 74°C with equation (7).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$k_{\text{calc}}$ (x 10$^{-5}$ s$^{-1}$) at 298 K</th>
<th>$\tau_{1/2}$ calc (h) at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>52, Co(acac)$_2$(BDAP)</td>
<td>0.9</td>
<td>20.5</td>
</tr>
<tr>
<td>55, Co(hfac)$_2$(BDAP)</td>
<td>1.2</td>
<td>16.7</td>
</tr>
<tr>
<td>53, Mn(hfac)$_2$(BDAP)</td>
<td>2.0</td>
<td>9.5</td>
</tr>
<tr>
<td>54, Ni(hfac)$_2$(BDAP)</td>
<td>1.1</td>
<td>16.9</td>
</tr>
<tr>
<td>60, Co(acac)$_2$(PDD)</td>
<td>18.6 (± 2.2)</td>
<td>1.0</td>
</tr>
<tr>
<td>61, Co(hfac)$_2$(PDD)</td>
<td>38.4 (± 4.5)</td>
<td>0.5</td>
</tr>
<tr>
<td>56, Co(acac)$_2$(NDAP)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>57, Co(hfac)$_2$(NDAP)</td>
<td>seems to decompose upon thermal return</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Errors for the rate constants for the three types of metal complexes were estimated from the standard deviations in rate constants determined in triplicate of the respective uncomplexed photochromes.

\[
\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad \text{equation (5)}
\]

It appears that the fastest thermal return processes are described by the smallest energies and largest entropies of activation. This is rightly so since the consequently derived $\Delta G^\ddagger$ parameters have the appropriately smaller values. Therefore, the thermodynamic data shown in Table 9 are consistent with the relative rate constants that were found using the Arrhenius (equation 2) extrapolation of the corresponding high-temperature data for all of the compounds of interest.
Table 9: Thermodynamic parameters $\Delta E_{\text{act}}$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ calculated at 298 K from the rates of thermal return of metal DHP complexes at 74, 64 and 54°C using Arrhenius (2) and Eyring (4) equations.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta E_{\text{act}}$ (kcal/mol)</th>
<th>$\Delta H^\ddagger$ (kcal/mol)</th>
<th>$\Delta S^\ddagger$ (J/molK)</th>
<th>$\ln(A)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>52, Co(acac)$_2$(BDAP)</td>
<td>23.2</td>
<td>22.5</td>
<td>24</td>
<td>27.6</td>
</tr>
<tr>
<td>55, Co(hfac)$_2$(BDAP)</td>
<td>21.9</td>
<td>21.2</td>
<td>41</td>
<td>25.6</td>
</tr>
<tr>
<td>53, Mn(hfac)$_2$(BDAP)</td>
<td>20.1</td>
<td>19.4</td>
<td>62</td>
<td>23.1</td>
</tr>
<tr>
<td>54, Ni(hfac)$_2$(BDAP)</td>
<td>21.9</td>
<td>21.3</td>
<td>40</td>
<td>25.7</td>
</tr>
<tr>
<td>60, Co(acac)$_2$(PDD)</td>
<td>16.6</td>
<td>15.9</td>
<td>92</td>
<td>19.5</td>
</tr>
<tr>
<td>61, Co(hfac)$_2$(PDD)</td>
<td>14.4</td>
<td>13.8</td>
<td>116</td>
<td>16.6</td>
</tr>
<tr>
<td>56, Co(acac)$_2$(NDAP)</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>57, Co(hfac)$_2$(NDAP)</td>
<td><strong>[25] seems to decompose upon thermal return</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The rates of thermal return of hfac BDAP complexes 53-55 were of the same order of magnitude as the rate of return of the parent acac complex 52. These findings were reflected accordingly among small deviations in the calculated thermodynamic parameters of these. The calculated rate of thermal return of Co(acac)$_2$(PDD) complex 60 was approximately 10 times faster than this rate for the BDAP series 52-55. The $\Delta E_{\text{act}}$ for the thermal back reaction of 16.6 kcal/mol for Co(acac)$_2$(PDD) complex 60 was significantly less than the 23.2 kcal/mol which was found for the Co(acac)$_2$(BDAP) 52. The thermal return of Co(hfac)$_2$(PDD) 61 was about 2 times faster than that of the Co(acac)$_2$(PDD) 60 while the $\Delta E_{\text{act}}$ value was further reduced for this fluorinated PDD species to 14.4 kcal/mol.

It is of interest that noticeably larger positive $\Delta S^\ddagger$ values were found for the PDD complexes 60 and 61. The PDD complexes must experience higher disorder in their transition states, a phenomenon that lowers the $\Delta G^\ddagger$ for their closing in the dark. These increases in $\Delta S^\ddagger$ are thought to arise from the sterically demanding changes happening in the molecular geometry en route from the open $25'$ to the flat and fully conjugated closed $25$. The closing process is not as sterically constrained for BDAP 21 because the accompanying molecular deformations happen mostly in the DHP portion of the photochrome, while the entire molecule has to be transformed from its stepped architecture to the completely planar aromatic architecture for $25' \rightarrow 25$. 
Figure 92: Arrhenius plot for determination of rate of thermal closing and $\Delta E_{\text{act}}$ of Mn(hfac)$_2$(BDAP) 53 in toluene in the dark at 298 K (25°C) by UV-vis.

Figure 93: Eyring plot for determination of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of thermal closing at 298 K (25°C) of Mn(hfac)$_2$(BDAP) 53 in toluene in the dark by UV-vis.
Figure 94: Arrhenius plot for determination of rate of thermal closing and $\Delta E_{\text{act}}$ of Ni(hfac)$_2$(BDAP) 54 in toluene in the dark at 298 K (25°C) by UV-vis.

Figure 95: Eyring plot for determination of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of thermal closing at 298 K (25°C) of Ni(hfac)$_2$(BDAP) 54 in toluene in the dark by UV-vis.
Figure 96: Arrhenius plot for determination of rate of thermal closing and $\Delta E_{\text{act}}$ of Co(acac)$_2$(PDD) 60 in toluene in the dark at 298 K (25°C) by UV-vis.

Figure 97: Eyring plot for determination of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of thermal closing at 298 K (25°C) of Co(acac)$_2$(PDD) 60 in toluene in the dark by UV-vis.
Figure 98: Arrhenius plot for determination of rate of thermal closing and Δ$E_{act}$ of Co(hfac)$_2$(PDD) 61 in toluene in the dark at 298 K (25°C) by UV-vis.

Figure 99: Eyring plot for determination of Δ$H^\ddagger$ and Δ$S^\ddagger$ of thermal closing at 298 K (25°C) of Co(hfac)$_2$(PDD) 61 in toluene in the dark by UV-vis.
Figure 100: Photo-opening of Co(hfac)$_2$(PDD) 61 in toluene with visible irradiation (>490 nm) at 293 K (20°C), monitored by UV-vis (time shown in minutes).

Figure 101: Thermal return of Co(hfac)$_2$(PDD) 61' in toluene in the dark at 327 K (54°C), monitored by UV-vis (time shown in minutes).
Figure 102: Photo-opening of Co(acac)$_2$(BDAP) 52 in toluene with laser (518 nm, 40 mW) at 298 K (25°C), monitored by UV-vis (time shown in seconds).

Figure 103: Thermal return of Co(acac)$_2$(BDAP) 52' in toluene at 327 K (54°C) in the dark, monitored by UV-vis (time shown in hours).
Figure 104: Photo-opening of Ni(hfac)$_2$(BDAP) 54 in toluene under visible irradiation (518 nm, 40 mW) at 298 K (25°C), monitored by UV-vis (time shown in seconds).

Figure 105: Thermal return of Ni(hfac)$_2$(BDAP) 54′ in toluene at 327 K (54°C) in the dark, monitored by UV-vis (time shown in hours).
Figure 106: Photochemical ring opening of Co(hfac)$_2$(BDAP) 55 in toluene at 298 K (25°C) with laser (518 nm, 40 mW), monitored by UV-vis (time shown in seconds).

Figure 107: Thermal return of Co(hfac)$_2$(BDAP) 55' in toluene in the dark at 327 K (54°C), monitored by UV-vis (time shown in hours).
Figure 108: Photochemical opening of Mn(hfac)$_2$(BDAP) 53 in toluene under laser irradiation (518 nm line, 40 mW) at 298 K (25°C), monitored by UV-vis (time shown in seconds).

Figure 109: Thermal return of Mn(hfac)$_2$(BDAP) 53' in toluene in the dark at 327 K (54°C), monitored by UV-vis (time shown in hours).
Figure 110: Photo-opening of Co(acac)$_2$(NDAP) 56 at 293 K (20°C) in toluene under visible irradiation (>600 nm), monitored by UV-vis (time shown in minutes).

Figure 111: Photo-opening of Co(hfac)$_2$(NDAP) 57 in toluene at 2-3°C under visible (>490 nm) irradiation, observed by UV-vis (time shown in minutes).
3.5 Photochemical Cycling of DHP-Metal Complexes

Fatigue resistance is an important property to evaluate for a substance that was designed for use in memory storage applications. Photochemical cycling experiments were conducted in order to determine how stable the DHP complexes were under periodic exposure to visible and UV light. Representative complexes, where Co(acac)$_2$ was bound to either BDAP 21 or PDD 25, were chosen for these photo-cycling experiments. The UV-vis sample was irradiated with visible light (>490 nm) in a water bath set at ~15°C to slow down the competing thermal relaxation during the ring-opening phase. Once most of the molecules in the sample were opened, as indicated by stabilization of the appearance of its UV-vis profile under prolonged illumination, a set of absorbance measurements were taken at 298 K while the sample was irradiated with an Hg pencil UV (254 nm) lamp until the spectra stopped changing once again. The change in the intensity of the selected absorbance was followed as a function of time. This procedure was repeated at least five times to record intensities of the chosen $\lambda_{\text{max}}$ for ten consecutive opening and closing events for each complex.

Co(acac)$_2$(BDAP) 52 and Co(acac)$_2$(PDD) 60 switched reversibly for ten consecutive UV-vis cycles based on the absorbance intensity fluctuations between the $\lambda_{415\text{nm}}$ and $\lambda_{453\text{nm}}$ for 52 and 60 respectively. Complexes 52 and 60 undergo reversible opening and closing processes with little decomposition as illustrated by variations in their $\lambda_{\text{max}}$ absorbance intensities in Figures 112 and 113. While watching the intensity of the absorbance at $\lambda_{415\text{nm}}$ for the closed Co(acac)$_2$(BDAP) 52 in toluene, it was noted that there was a small decrease in this peak’s intensity as the cycling experiment went forward (Figure 113). There was also an accompanying increase in the absorbance at 415 nm but in the open state 52' of the complex. This suggested that there must have been gradual decomposition of the sample with cycling and that the UV-vis spectrum of the decomposition product resembles that of 52'. The dip in the absorbance at 453 nm of Co(acac)$_2$(PDD) 60 in cycle 9 was possibly due to an experimental error since the corresponding absorbance of the open form 60' that was generated in cycle 10 did not increase in proportion (Figure 112). This result can also be rationalized by proposing that the photo-decomposition product of Co(acac)$_2$(PDD) did not resemble either the open or the closed isomer of 60.
Figure 112: Photo-cycling of Co(acac)$_2$(PDD) 60 in toluene with visible (>490 nm) and UV (254 nm) light at 298 K, monitored by UV-vis.

Figure 113: Photo-cycling of Co(acac)$_2$(BDAP) 52 in toluene at 298 K with visible (>490 nm) and UV (254 nm) light, monitored by UV-vis.
3.6 Summary

The objective of Chapter 3 was to present the details of synthesis and characterization of the photochemical properties of some of the first-row transition metal complexes containing the new DHP-phenanthroline BDAP 21, NDAP 22, and PDD 25 ligands. To this end Co(acac)$_2$(BDAP) 52 and M(hfac)$_2$(BDAP) 53-55 complexes where M is Co(II), Mn(II) and Ni(II) metals were made. The apparent rate constants for the opening of BDAP complexes 52-55 at 298 K were between 9.2 x 10$^{-3}$ s$^{-1}$ & 1.2 x 10$^{-2}$ s$^{-1}$, making them effectively identical (Table 6). The UV-vis solutions of these samples were well bleached within a few minutes of their exposure to visible irradiation by wavelengths above 490 nm.

The cobalt PDD complexes 60 and 61 showed incomplete opening leading to photostationary states with 31-37% of the open Co(hfac)$_2$(PDD) 61' in toluene as determined by $^1$H NMR. The UV-vis spectra of 60 and 61 had significant overlap between bands due to presence of both the open and closed PDD 25 that was coordinated to the cobalt center, thus supporting the results of the $^1$H NMR experiments. There were no isolated bands in the UV-vis spectra of either the open or the closed PDD complexes 60-61. Therefore, the UV-vis spectra of the fully opened state of these as well as of the free ligand 25 alone could not be collected. The PDD complexes 60 and 61 opened ~7 times slower than the BDAP analogues 52-55. The thermal closing rates of these were 10 to 20 times faster than those for the BDAP derivatives 52-55, accompanied by appropriate differences in the thermodynamic parameters thereof (Table 9).

Experiments to obtain the apparent rate constants for opening of NDAP 22 under visible irradiation (>490 nm) were carried out at 2-3°C in order to slow down the competitive thermal return process for this species. The kinetics of the photochemical opening reaction were monitored by UV-vis and gave an average apparent rate constant of 1.9 (± 0.7) x 10$^{-4}$ s$^{-1}$ after three consecutive sets of measurements. The opening of Co(hfac)$_2$(NDAP) complex 57 was accomplished under approximately the same experimental conditions giving an apparent rate constant of 4.4 x 10$^{-5}$ s$^{-1}$. Multiple attempts were made to record the rate of return for this complex but no measurements were reported since it was difficult to get reliable results due to the noisy quality of data. Photochemical opening and thermal return of Co(acac)$_2$(NDAP) complex 56 were not
reported due to lack of sample needed to carry out these measurements. It was anticipated that the photochemistry of complex 56 would be akin and slower than that of the free ligand 22.

Chapter Four: Summary and Conclusions

Three different types of photochromic DHP switches were made that incorporated the phenanthroline component for binding to the first row transition metals. The BDAP 21 photochrome was made by interlinking BDHP 12 and the phenanthroline units by the acetylene using a Sonogashira coupling methodology. PDD 25 photochrome resulted from the annelation of DHP 11 to the phenanthroline employing a condensation reaction between phenanthroline diketone105 28 and the in situ generated DHP diamine derived from the air-stable di-nitro-DHP precursor103 45. The imidazole BDHP-imid 24 photochrome was made by condensing the BDHP-CHO aldehyde81b 50 with the phenanthroline diketone105 28 with participation of NH4+OAc− as the nitrogen source.

The photochemistry of the photochromic DHP compounds was studied next. BDAP 21 and BDHP-imid 24 opened fully within 100 seconds under visible irradiation (>490 nm) from a broadband ~500 W tungsten source at 293 K. PDD 25 opened only partially, reaching a photostationary state composed of 44% of the open isomer 25′ as was determined by the 1H NMR experiments. This result was explained by the open and closed forms of PDD 25 having overlapping bands for the electronic transitions in their UV-vis profiles.

The photochromic ligands 21, 22 and 25 were subsequently complexed to Co(II) using acac and hfac as the ancillaries. BDAP 21 was also complexed to Mn(II) and Ni(II) metals. It was found that the complexes with the BDAP 21 ligand undergo a relatively fast photochemical opening reaction giving an apparent rate that was approximately 2/3 of that which was measured for the unbound 21. There was little difference among the apparent rates of the opening of BDAP complexes 52-55 upon replacement of acac with the hfac spectator ligands. The PDD photochrome 25, as well as its acac and hfac complexes 60 and 61, required 70 to 200 min of continuous visible
irradiation (>490 nm) to reach their photostationary states. BDHP-imid 24 exhibited the fastest apparent opening rate, being ~8 times faster than that of the BDHP 12 parent.

The rates of thermal return of the photochromes and their metal complexes were measured at room temperature (298 K) as well as at 54, 64 and at 74°C (unless stated otherwise). The experimentally obtained rates at 298 K were compared to the predicted values calculated by extrapolation of the high temperature rate data using the Arrhenius relationship (2). The high temperature data along with the Eyring equation (4) were used to obtain the thermodynamic parameters $\Delta E_{\text{act}}$, $\Delta S^\ddagger$ and $\Delta H^\ddagger$ for the thermal return reaction of each photochromic compound. The $\tau_{1/2}$ of the thermal return of parent BDHP 12 at 5.0 days, calculated for 298 K from the measured rates at higher temperatures using the Mitchell laboratory set-up, has been surpassed by the performance of BDHP-imid 24.

The PDD complexes 60 and 61 had the fastest rates of return, followed by those of the complexes of BDAP 52-55. It seemed that the thermal return reactivity of each type of synthesized DHP resembled that of its corresponding metal complex. The largest thermal return rate was found for BDHP-imid 24 with the calculated value for $\tau_{1/2}$ of 127 days at 298 K (Table 3). All of the photochromic uncomplexed ligands cycled reversibly at least 10 times when subjected to alternating UV (254 nm) and visible irradiation (>490 nm, unless stated otherwise). Co(acac)$_2$(BDAP) 52 and Co(acac)$_2$(PDD) 60 complexes were also shown to cycle reversibly under these conditions.

The short-term goals of the presented project have been accomplished by successful synthesis of several photochromic DHPs with pendant and annelated phenanthroline moieties. The PDD 25 photochrome had the most promising structure for electronic communication between the bound metal in the ligating pocket of the phenanthroline and the DHP unit. The disadvantage of the structure of PDD 25 was that the UV-vis spectra of its open and closed forms had significant overlap and so a complete $25 \rightarrow 25'$ conversion under visible irradiation was not observed. The UV-vis characteristics of 25 could be improved by decreasing the spectroscopic overlap between the open and closed forms of this molecule. It is known that benzannelation of DHP 11 to obtain BDHP 12 accomplishes this and so it is believed that synthetically replacing the pyrazine bridge with a benzene would likely do the same for the structure of PDD 25.
Once a DHP molecule with satisfactory spectroscopic properties is found, it could be included into a bistable Co(II) semiquinone/catecholate complex (Figure 114). The open and closed states of DHP can potentially stabilize the cobalt center in either its +2 or +3 oxidation state by changing the delocalization of the electron density throughout the molecular skeleton. The opening and closing of the dihydropyrene dye can also affect the redox properties of the bound semiquinone/catecholate ligands. The cobalt complex in its +2 and +3 oxidation states is expected to have a different number of unpaired spins in its electronic configuration. Therefore, the DHP switch can potentially influence the spin state of the electronically bistable metal complex into which it is incorporated. If there is a correlation between the count of unpaired spins of the proposed bistable cobalt complex and the state of the dihydropyrene switch, then it is possible to encode the memories photochemically and read them nondestructively by measuring the system’s magnetic moment.

Figure 114: Proposed structure of the (PBDHP)Co(semiquinone/catecholate) complex
Chapter Five: Experimental Section

5.1 Instrumentation

Melting points were determined on a Gallenkamp melting point apparatus and were reported without corrections. Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer and only the fingerprint bands were reported. The FT-IR spectrometer was calibrated to a polystyrene film standard with all measurements having a resolution of ± 2 cm\(^{-1}\). All UV-vis spectra were recorded on an Agilent 8453 UV-vis Spectroscopy System in toluene (unless specified otherwise). \(^1\)H NMR spectra were recorded on a Bruker AV500 (500 MHz) or on a Bruker AV300 (300 MHz) spectrometer in CDCl\(_3\) (unless specified otherwise). The solvent residual peak was used for internal calibration (δ 7.240 vs. TMS for CHCl\(_3\)). \(^{13}\)C NMR spectra were recorded on a Bruker AV500 (125 MHz), using the solvent peak at δ 77.0 for calibration (unless specified otherwise). Mass spectra were recorded on Bruker Esquire ion trap or Water/Micromass LCT time-of-flight mass spectrometer at the University of British Columbia, Vancouver BC. Exact mass measurements were done on a Water/Micromass LCT time-of-flight mass spectrometer equipped with an electrospray ion source at the University of British Columbia, Vancouver BC. Elemental analyses were performed using an EA1108 elemental analyzer under direction of Dr. Yun Ling (Analytical Manager) at the University of British Columbia, Vancouver BC. All of the solvents used in reactions were purified and distilled according to standard procedures.\(^{124}\) All evaporations were carried out under reduced pressure on a rotary evaporator, or by using a high vacuum oil pump and a dry ice trap. Silica gel, 60 mesh or 60 mesh silica gel, refers to Caledon Laboratory Chemicals silica gel, 60 mesh.

In order to obtain NMR spectra of compounds sensitive to oxygen under visible irradiation, samples were prepared by dissolving the compound in a minimum amount of deuterated solvent. The sample was then filtered through celite, rinsed with sufficient deuterated solvent to make up the correct volume for the measurement followed by bubbling N\(_2\) through the filtrate in the NMR tube for 5–10 minutes. The spectra were acquired after capping the tubes under inert atmosphere. NMR experiments with readily photoisomerizable compounds were obtained by preparing the samples under minimal
ambient light conditions and running the spectra in a dark room. The NMR assignments were made on the basis of COSY/NOESY and HETCORR/HSQC/HMBC experiments for proton and carbon nuclei, respectively. Expanded HSQC/HMBC data sets (with iteration for AA‘XX’ systems) were used to obtain data for the coupling constants \( J \).

Photoisomerizations for the photo-opening and thermal return kinetic studies were performed using the broad band irradiation from a ~500 W tungsten incandescent lamp (or the Spectra-Physics Model 2018 laser, when specified) set at a distance of 10–15 cm from the sample, with a cooling water bath and a plastic filter to block out the higher energy light <490 nm (or <600 nm). All of the DHP compounds that were studied photoisomerized to their CPD forms using a 490 nm cut-off filter placed in the water bath that was between the irradiation source and the sample. The water bath was cooled to 2-3°C with ice to slow down the competitive thermal return reaction of the NDAP ligand 22 as well as of 56 and 57 complexes thereof.

UV closing of the CPD to the DHP form of the selected dihydropyrenes and their complexes was achieved with irradiation by an Hg pencil lamp (254 nm). A 420 nm pyrex filter was used to exclude the short wavelength irradiation coming from the PDA detector source of the UV-vis instrument which triggers the undesired high \( \Phi \) photochemical return of the CPD to DHP isomer. A 455 nm pyrex filter was used for NDAP 22 and its acac and hfac complexes 56 and 57. This was done in an attempt to obtain first-order opening and closing behaviour of the photochromic DHPs and the related complexes.
4-(2’(3’-Phenanthrolinyl)ethynyl)-2,7-di-tert-butyl-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene, BDAP (21)

Tri-tert-butylphosphine (17.0 mg, 84.0 µmol), Pd\(_2\)(dba)\(_3\) (30 mg, 33 µmol), BDHP-bromide\(^{75}\) 39 (0.245 g, 0.517 mmol), ethynyl phenanthroline\(^{89}\) 30 (0.208 g, 1.02 mmol), piperidine (0.1 mL) and Cs\(_2\)CO\(_3\) (0.262 g, 0.804 mmol) were added to dry dimethylformamide (5 mL) under nitrogen in a 10 mL Schlenk tube at room temperature. The solution was degassed with a stream of N\(_2\) and the tube was closed. Reaction was stirred at 65°C for 21 hours in the dark and then cooled to room temperature. The organic layer was diluted with methylene chloride and washed with aqueous KCN solution (50 mL) and then water (50 mL x 3), dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The crude material was purified by column chromatography over SiO\(_2\) with first methylene chloride to collect any unreacted starting material and then with methylene chloride and methanol (95/5) eluant to give the product in 82% yield (0.149 g, 0.249 mmol) as a dark red solid, mp 240–242°C. The dried BDAP 21 was washed with hexanes and then acetonitrile to remove any additional polar and non-polar impurities.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 9.40 (d, \(J = 2.0\) Hz, 1H, H-2”), 9.20 (dd, \(J = 4.3, 1.7\) Hz, 1H, H-9”), 8.75–8.72 (m, 2H, H-9,12), 8.41 (d, \(J = 2.1\) Hz, 1H, H-4”), 8.31 (d, \(J = 0.7\) Hz, 1H, H-3), 8.26–8.24 (m, 2H, H-7”,8), 8.11 (d, \(J = 1.0\) Hz, 1H, H-1), 7.81 (dd, \(J = 11.6, 8.7\) Hz, 2H, H-d,e), 7.65–7.61 (m, 3H, H-10,11,8”), 7.35 (s, 1H, H-6), 7.31 (s, 1H, H-5), 1.57 (s, 9H, tBu-H), 1.49 (s, 9H, tBu-H), -1.35 (s, 3H, 12c-CH\(_3\)), -1.38 (s, 3H, 12d-CH\(_3\)). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 152.6 (C-2”), 150.8 (C-9”), 148.3 (C-2), 146.4, 145.8 (C-7), 144.6, 143.3 (C-12g), 138.2 (C-12h), 137.5 (C-4), 137.2 (C-4”), 136.2 (C-
7″/8), 135.2 (C-12e), 129.7 (C-12f), 129.4 (C-12a), 129.1, 128.2, 127.5 (C-5″/6″), 126.6 (C-10/11), 126.43 (C-5″/6″), 126.36 (C-10/11), 124.87 (C-12/12a), 124.75 (C-12/12a), 123.3 (C-8″), 122.4 (C-5′), 119.6 (C-6), 118.3 (C-1), 117.7 (C-7″/8), 117.4 (C-3), 112.3 (C-12b), 94.7 (C-1′), 91.9 (C-2′), 37.0 (C-12c), 36.2 (C-CH₃), 35.7 (C-13-CH₃), 35.5 (C-12d), 30.8 (C-tBu), 18.2 (12d-CH₃), 18.17 (12c-CH₃). IR (KBr) ν: 2961 (vs), 2862 (m), 2186 (m), 1613 (m), 1473 (m), 1418 (s), 1366 (m), 1253 (m), 1116 (w), 899 (m), 869 (m), 828 (m), 749 (s), 729 (s), 699 (m) cm⁻¹. UV-vis (toluene) λmax (εmax M⁻¹ cm⁻¹) nm: 417 (53600), 520 (7850). LRMS MS m/z 597.2 (M+H). HRMS calcd for C₄₄H₄₀N₂, m/z 597.3270. Found, m/z 597.3263. Anal. Calcd for C₄₄H₄₀N₂: C, 88.55; H, 6.76; N, 4.69. Found: C, 84.45; H, 6.77; N, 4.38.

4-[2′(3″-Phenanthrolinyl)ethynyl]-10-naphthoyl-2,7-di-tert-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene, NDAP (22)

Tri-tert-butylphosphine (5.0 mg, 25 µmol), Pd₂(dba)₃ (8.0 mg, 8.7 µm), naphthoyl-DHP-bromide⁹² 37 (0.127 g, 0.22mmol), Cs₂CO₃ (66 mg, 0.2 mmol), dry piperidine (0.1 mL), and ethynyl phenanthroline⁸⁹ 30 (37 mg, 0.18 mmol) were added to dry dimethylformamide (3 mL) in a 10 mL Schlenk tube under N₂ at room temperature. The solution was degassed with a stream of nitrogen for 10 minutes and then the tube was closed. The mixture was heated at 60°C for 15 hours in the dark. The reaction solution was then cooled to room temperature and transferred into a separatory funnel. The organic layer was diluted with methylene chloride and washed with aqueous KCN (50 mL) and then water (50 mL x 4), dried over Na₂SO₄ and concentrated under reduced pressure to give the crude product. The crude was purified over silica gel eluting with
methylene chloride and methanol (95/5) solvent mixture to give the dark brown solid 22 in 92% yield (0.135 g, 0.193 mmol), mp 180–182°C. $^1$H NMR (500 MHz, CDCl$_3$) δ: 
9.55 (d, $J = 2.1$ Hz, 1H, H-2″), 9.38 (d, $J = 0.8$ Hz, 1H, H-1), 9.24 (d, $J = 0.7$ Hz, 1H, H-9), 9.22 (dd, $J = 4.3$, 1.7 Hz, 1H, H-9″), 8.81 (s, 1H, H-5), 8.67 (s, 1H, H-3), 8.61 (s, 1H, H-6), 8.56 (d, $J = 2.1$ Hz, 1H, H-4″), 8.52 (s, 1H, H-8), 8.47 (d, $J = 8.3$ Hz, 1H, H-c′), 8.27 (dd, $J = 8.1$, 1.8 Hz, 1H, H-7″), 8.07 (d, $J = 8.2$ Hz, 1H, H-c′′), 7.99 (d, $J = 7.9$ Hz, 1H, H-d′), 7.87 (s, 2H, H-5″, 6″), 7.66 (dd, $J = 8.1$, 4.4 Hz, 1H, H-8″), 7.64 (dd, $J = 6.8$, 1.0 Hz, 2H, H-b′), 7.58–7.55 (m, 1H, H-e′), 7.52–7.49 (m, 2H, H-f′, g′), 1.621 (s, 9H, H-tBu), 1.615 (s, 9H, H-tBu), -3.59 (s, 3H, 10c-CH$_3$), -3.62 (s, 3H, 10b-CH$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 200.7 (C=O), 152.7 (C-2″), 151.9 (C-2/7), 150.9 (C-9″), 147.2 (C-2/7), 146.3, 144.9, 140.6 (C-10f), 139.9 (C-i′), 137.9 (C-10e), 137.6 (C-4″), 136.2 (C-7″), 135.8, 134.9, 134.1 (C-j′), 131.8 (C-c′), 131.5 (C-a′), 130.9 (C-10a), 129.20 (C-b′), 129.17, 128.7 (C-d′), 128.2, 127.9 (C-3), 127.75 (C-f′/g′), 127.70 (C-10), 127.6 (C-5″/6″), 126.7 (C-e′), 126.4 (C-5″/6″), 126.1 (C-h′), 125.8 (C-8), 124.8 (C-f′/g′), 124.2 (C-6), 123.4 (C-8″), 121.4 (C-1), 120.6 (C-3″), 120.3 (C-9), 114.1 (C-10d), 94.7 (C-1′), 92.5 (C-2′), 37.0 (C-10c), 36.1 (C-10b), 31.9 (C-tBu), 31.8 (C-tBu), 29.4 (C$_2$-CCH$_3$), 15.5 (10b-CH$_3$), 15.3 (10c-CH$_3$). IR (KBr) ν: 2961 (s), 2186 (m), 1637 (s), 1588 (m), 1506 (m), 1418 (s), 1226 (s), 1193 (m), 1116 (m, 894 (m), 781 (s), 729 (m), 680 (w) cm$^{-1}$. UV-vis (toluene) $\lambda_{\text{max}}$ (ε$_{\text{max}}$ M$^{-1}$ cm$^{-1}$) nm: 368 (36100), 427 (59900), 485 (10500), 685 (3970). LRMS MS $m/z$ 701.3 (M+H). HRMS calcd for C$_{51}$H$_{44}$N$_2$O, 701.3532. Found, 701.3542. Anal. Calcd for C$_{51}$H$_{44}$N$_2$O: C, 87.39; H, 6.33; N, 4.00. Found: C, 84.99; H, 6.42; N, 3.99.
4-[1′(5″,6″-Phenanthrolinyl)imidazyl]-2,7-di-tert-butyl-trans-10c,10d-dimethyl-10c,10d-dihydropyrene, DHP-imid (23)

DHP-CHO\textsuperscript{8ib} 29 (0.149 g, 0.40 mmol), phenanthroline diketone\textsuperscript{105} 28 (83.3 mg, 3.97 mmol), ammonium acetate (0.222 g, 2.85 mmol) and glacial acetic acid (6 mL) were heated at 80°C under N\textsubscript{2} for 16 h in the dark. Then the solution was cooled to room temperature and neutralized to pH 7 with aqueous NaOH and the product was extracted into methylene chloride, washed with water and dried over MgSO\textsubscript{4}. The concentrated crude brown residue was chromatographed over silica gel using methylene chloride and methanol (95/5) mixture as eluant. The solvents were removed under reduced pressure giving the DHP-imid 23 product as a yellow solid in 28% yield (66.0 mg, 0.114 mmol), mp (dec) 270–276°C. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ: 10.31 (s, 1H, H-3), 9.32 (d, J = 7.5 Hz, 1H, H-2″/9″), 9.08 (d, J = 3.0 Hz, 1H, H-4″/7″), 8.99–8.98 (m, 2H, H-5, 4″/7″), 8.86 (d, J = 8.0 Hz, 1H, H-2″/9″), 8.60 (s, 1H, H-1), 8.48–8.44 (m, 3H, H-9, 10, 6/8), 8.05 (s, 1H, H-3″/8″), 1.76 (s, 9H, C\textsubscript{2}-tBu-H), 1.50 (s, 9H, C\textsubscript{7}-tBu-H), -3.83 (s, 3H, 10c-CH\textsubscript{3}), -3.96 (s, 3H, 10b-CH\textsubscript{3}). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) δ: 153.5 (C-1′), 148.7 (C-2), 148.4 (C-4″/7″), 148.0 (C-4″/7″), 146.4 (C-7), 144.6, 138.7 (C-10d), 137.5, 137.1 (C-10a), 136.0 (C-10e), 134.3 (C-10f), 130.9 (C-2″/9″), 129.8 (C-2″/9″), 126.4 (C-5″/6″), 125.2(C-5′/6′), 124.2 (C-9/10), 124.0 (C-9/10), 123.8 (C-3″/8″), 123.1 (C-3″/8″), 122.8 (C-5), 122.0 (C-6), 121.5 (C-1), 120.9 (C-8), 120.4 (C-3), 119.9 (C-4), 36.8 (C\textsubscript{2-CCCH\textsubscript{3}}), 36.0 (C\textsubscript{7-CCCH\textsubscript{3}}), 32.2 (C\textsubscript{2-CCCH\textsubscript{3}}), 31.9 (C\textsubscript{7-CCCH\textsubscript{3}}), 30.8 (C-10b), 29.7 (C-10c), 15.00 (10b-CH\textsubscript{3}/10c-CH\textsubscript{3}), 14.91 (10b-CH\textsubscript{3}/10c-CH\textsubscript{3}). IR (KBr) ν: 2961 (vs), 1717 (w), 1456 (w), 1355 (s), 1231 (s), 1070 (s), 883 (s), 803 (m), 738 (s), 740 (vs), 669 (s) cm\textsuperscript{-1}. 
UV-vis (acetone) \( \lambda_{\text{max}} \) (\( \varepsilon_{\text{max}} \) M\(^{-1}\) cm\(^{-1}\)) nm: 359 (45500), 404 (51300), 479 (10100). Calculated exact mass for M+H ion was at \( m/z \) 563.3175. Found M+H ion at \( m/z \) 563.3188. Anal. Calcd for C\(_{39}\)H\(_{38}\)N\(_4\): C, 83.24; H, 6.81; N, 9.96. Found: C, 82.48; H, 6.82; N, 9.81.

4-([1’(5″,6″)-Phenanthrolinyl]imidazyl]-2,7-di-tert-butyl-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene, BDHP-imid (24)

BDHP-CHO\(^{81b}\) 50 (0.122 g, 0.289 mmol), phenanthroline diketone\(^{105}\) 28 (60.6 mg, 0.288 mmol), ammonium acetate (0.155 g, 2.02 mmol) and glacial acetic acid (5 mL) were heated at 80°C under \( \text{N}_2 \) for 16 hours in the dark. The mixture was then cooled to room temperature, diluted with methylene chloride, washed with \( \text{H}_2\text{O} \) (40 mL x 3) and dried over MgSO\(_4\). The excess solvent was removed under reduced pressure and the crude material was chromatographed over silica gel with methylene chloride and methanol (95/5) solvents. BDHP-imid 24 was obtained as a dark red solid (47.0 mg, 0.078 mmol) in 27% yield, mp 179–181°C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 9.51 (d, \( J = 1.0 \) Hz, 1H, H-1), 9.25 (dd, \( J = 4.5, 2.0 \) Hz, 1H, H-2”/9”), 9.23 (dd, \( J = 4.5, 1.5 \) Hz, 1H, H-2”/9”), 9.02 (dd, \( J = 8.0, 1.5 \) Hz, 1H, H-4”/7”), 8.77 (dd, \( J = 9.0, 1.5 \) Hz, 1H, H-4”/7”), 8.79–8.76 (m, 2H, H-9, 12), 8.41 (d, \( J = 1.0 \) Hz, 1H, H-3), 8.30 (d, \( J = 1.0 \) Hz, 1H, H-8), 8.12 (d, \( J = 1.0 \) Hz, 1H, H-5), 7.81 (dd, \( J = 8.0, 4.5 \) Hz, 1H, H-3”/8”), 7.78 (dd, \( J = 8.0, 4.5 \) Hz, 1H, H-3”/8”), 7.68–7.64 (m, 2H, H-10, 11), 7.53–7.527 (m, 1H, H-6), 1.66 (s, 9H, tBu-H), 1.53 (s, 9H, tBu-H), -1.24 (s, 3H, CH\(_3\)), -1.31 (s, 3H, CH\(_3\)). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 165.0 (C-1’), 151.0 (C-2/7), 149.7 (C-2”/9”), 149.5 (C-2”/9”), 145.9 (C-2/7), 145.2 (C-5”/6”), 144.9 (C-5”/6”), 142.5 (C-12a), 141.3 (C-12e/12h), 138.6 (C-
12e/12h), 138.2, 135.3, 135.1 (C-12g), 129.9 (C-12f), 129.4 (C-9), 128.8 (C-4"/7"), 127.0 (C-10/11), 126.5 (C-10/11), 125.1 (C-9/12), 124.7 (C-9/12), 123.8 (C-3"/4"), 123.6 (C-3"/4"), 123.3, 120.5 (C-6), 120.2 (C-5), 118.4, 118.2 (C-1), 118.1 (C-8), 117.3 (C-3), 115.6 (C-12b), 37.9 (C-12c/C-2-C6H3), 36.7 (C-12c/C-2-C6H3), 35.7 (C7-C6H3), 35.5 (C-12d), 30.9 (C2-C6H3/C7-C6H3), 30.8 (C2-C6H3/C7-C6H3), 18.6 (C2-C6H3), 18.1 (C12d-C6H3). IR (KBr) ν: 2961 (s), 1619 (m), 1560 (m), 1534 (m), 1502 (m), 1476 (m), 1391 (m), 1366 (m), 1342 (m), 1259 (w), 1121 (w), 1061 (s), 1022 (m), 741 (s) cm⁻¹. UV-vis (toluene) λmax (εmax M⁻¹ cm⁻¹) nm: 339 (21100), 351 (20800), 406 (41400), 422 (45700), 520 (7400). Anal. Calcd for C43H40N4: C, 84.28; H, 6.58; N, 9.14. Found: C, 82.18; H, 6.56; N, 6.54.

2,7-Di-tert-butyl-trans-22b,22c-dimethyl-4,17-pyrazino-22b,22c-dihydropyrazino-phenanthrolin[e]pyrene, PDD (25)

Dinitro-DHP 45 (61.0 mg, 0.14 mmol) was dissolved in EtOH (15 mL, 100%). The solution was degassed with a stream of N2 for 10 minutes and Pd/C (30%) catalyst (5 mg) was added to the reaction. Then H2 gas was bubbled through the solution while stirring at room temperature until all of starting material has reacted as determined by TLC (~4 h). When the first reaction has gone to completion, the solution was degassed with nitrogen for 10 minutes and phenanthroline diketone 28 (71.0 mg, 0.34 mmol) was added at room temperature and the second reaction was left to go at room temperature overnight under nitrogen atmosphere. The dark green precipitated product 25 was collected by filtration in a small fritted funnel in 40% yield, mp 270–273°C. 1H NMR (500 MHz, CDCl3) δ: 9.83 (dd, J = 8.0, 1.7 Hz, 2H, H-9), 9.312 (d, J = 1.5 Hz, 2H,
H-22), 9.307 (d, J = 1.8 Hz, 2H, H-7), 7.89 (dd, J = 8.2, 4.4 Hz, 2H, H-8), 7.46 (d, J = 1.3 Hz, 2H, H-1), 7.20 (s, 2H, H-8), 1.59 (s, 18H, C2-tBuH), -1.23 (s, 6H, 22b-CH3).

13C NMR (125 MHz, CDCl3) δ: 152.1 (C-3), 148.1 (C-6b), 145.8 (C-2), 140.5 (C-6), 139.0 (C-4), 137.7 (C-22e), 134.2 (C-22a), 133.5 (C-9), 128.1 (C-6a), 124.2 (C-8), 123.4 (C-7), 123.0 (C-22), 122.6 (C-1), 35.8 (C-22b), 35.6 (C-22b), 30.9 (C-22b), 18.7 (22b-CH3). IR (KBr) ν: 2961 (s), 1621 (w), 1459 (w), 1401 (w), 1366 (s), 1262 (s), 1226 (m), 880 (s), 801 (m), 738 (s), 677 (s) cm⁻¹. UV-vis (toluene) λmax (εmax M⁻¹ cm⁻¹) nm: 343 (17600), 426 (16300), 449 (23800). LRMS MS at m/z 549.2 (M+H). HRMS calcd for M+H was at m/z 549.3018. Found M+H at m/z 549.3008.

4-[2’(3″-Phenanthrolinyl)ethynyl]-2,7-di-tert-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene, DAP (26).

Iodo-DHP79 34 (0.107 g, 0.228 mmol), Pd₂dba₃ (14.0 mg, 15.2 µmol), tri-tert-butylphosphine (13.0 mg, 6.43 mmol), ethynyl phenanthroline89 30 (70.0 mg, 0.342 mmol), Cs₂CO₃ (0.115 g, 0.353 mmol) and dry piperidine (0.1 mL) were dissolved in dry dimethylformamide (4 mL) under nitrogen atmosphere in a 25 mL Schlenk tube at room temperature. The solution was degassed with stream of nitrogen for 10 minutes and the tube was closed. The reaction was heated at 65°C for about 18 hours in the dark and then cooled to room temperature. The organic layer was washed with water (40 mL x 3), dried over MgSO₄ and concentrated under reduced pressure. The crude material was chromatographed over silica gel with methylene chloride and methanol (95/5) mixture as eluant to obtain brown product 26 in 75% yield (93.5 mg, 0.171 mmol), mp 205–207°C. 1H NMR (500 MHz, CDCl₃) δ: 9.55 (d, J = 2.15 Hz, 1H, H-2″), 9.22 (dd, J = 4.3, 1.8 Hz,
1H, H-9″), 9.18 (d, J = 1.1 Hz, 1H, H-4″), 8.69 (s, 1H, H-5), 8.56–8.53 (m, 4H, H-1, 3, 6, 8), 8.47 (dd, J = 11.4, 8.0 Hz, 2H, H-9, 10), 8.27 (dd, J = 8.0, 1.6 Hz, 1H, H-7″), 7.85 (dd, J = 10.1, 8.8 Hz, 2H, H-5″, 6″), 7.65 (dd, J = 8.2, 4.4 Hz, 1H, H-8″), 1.75 (s, 9H, C2-tBu/C7-tBu), 1.68 (s, 9H, C2-tBu/C7-tBu), -3.820 (s, 3H, 10b-C(CH3)3/10c-C(CH3)3), -3.829 (s, 3H, 10b-C(CH3)3/10c-C(CH3)3). 13C NMR (125 MHz, CDCl3) δ: 152.8 (C-3/6), 150.9 (C-9″), 148.1 (C-2/7), 146.7 (C-2/7), 146.4, 144.7, 139.0 (C-1/8), 138.5 (C-10f), 137.4 (C-1/8), 137.2, 136.2 (C-7″), 136.0, 129.1, 128.3, 127.5 (C-10a/10d), 126.5 (C-10a/10d), 125.2 (C-5), 124.6 (C-5″/6″), 123.8 (C-5″/6″), 123.4 (C-8″), 122.5 (C-3/6), 121.8 (C-10e), 121.6, 121.0, 119.6 (C-4″), 113.1 (C-4), 95.4 (C-1′), 92.2 (C-2′), 36.6 (C2-C(CH3)/C7-C(CH3)), 36.2 (C2-C(CH3)/C7-C(CH3)), 32.14 (C2-C(CH3)/C7-C(CH3)), 32.08 (C2-C(CH3)/C7-C(CH3)), 30.8 (C-10b), 29.8 (C-10c), 15.2 (10b-C(CH3)/10c-C(CH3)), 15.0 (10b-C(CH3)/10c-C(CH3)). IR (KBr) v: 2956 (s), 2186 (m), 1588 (m), 1418 (s), 1229 (m), 883 (s), 729 (s), 680 (m) cm⁻¹. UV-vis (toluene) λmax (εmax M⁻¹ cm⁻¹) nm: 356 (50800), 409 (58300), 479 (12500), 501 (12300), 666 (2580). LRMS MS m/z 547.3 (M+H). HRMS calcd m/z for M+H, 547.3113. Found M+H ion at m/z of 547.3103. Anal. Calcd for C₄₀H₃₈N₂: C, 87.87; H, 7.01; N, 5.12. Found: C, 85.12; H, 7.19; N, 4.90.

Cobalt-bis-acetylacetone-(4-[2′(3″-phenanthrolinyl)ethynyl]-2,7-di-tert-butyl-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene), Co(acac)₂(BDAP) 52

Co(acac)₂(H₂O)₂ 51 (28.5 mg, 9.6 x 10⁻² mmol) was dissolved in degassed spectro grade MeOH (10 mL) at room temperature under nitrogen in a 10 mL screw-top vial. When the starting material was completely dissolved, BDAP 21 (52.4 mg, 8.8 x 10⁻² mmol) was added and the reaction was left to stir overnight at RT under N₂ in the dark. The red precipitate was collected by filtration and dried under vacuum giving 82% yield.
of product 52 (61.8 mg, 0.072 mmol), mp 226–228°C. IR (KBr) ν: 2961 (m), 2186 (m), 1588 (vs), 1511 (vs), 1426 (s), 1253 (m), 754 (w) cm\(^{-1}\). UV-vis (toluene) \(\lambda_{\text{max}} (\varepsilon_{\text{max}} \text{ L mol}^{-1} \text{ cm}^{-1})\) nm: 413 (47300), 518 (10800). \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ: 12.60 (s, 1H), 11.60 (s, 1H), 7.76 (dd, 1H \(J = 7.5, 1.8 \text{ Hz}\)), 7.54 (dd, 1H, \(J = 7.5, 2.1 \text{ Hz}\)), 7.01 (s, 1H), 6.92–6.84 (m, 2H), 6.69 (s, 1H), 4.77 (s, 1H), 2.49 (s, 4H), 0.45 (s, 9H), -0.76 (s, 9H), -3.78 (s, 3H), -3.80 (s, 3H). LRMS MS at \(m/z\) 853.3 (M). HRMS \(m/z\) calcld for C\(_{54}\)H\(_{54}\)CoN\(_2\)O\(_4\), 853.3416. Found, 853.3397. Anal. Calcd for C\(_{54}\)H\(_{54}\)CoN\(_2\)O\(_4\): C, 75.95; H, 6.37; N, 3.28. Found: C, 72.98; H, 6.38; N, 3.10.

Manganese-bis-hexafluoroacetylacetone-(4-[2'(3″-phenanthrolinyl)ethynyl]-2,7-di-tert-butyl-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene),

\(\text{Mn(hfac)}_2(\text{BDAP}) \ 53\)

Mn(hfac)\(_2\) (55.2 mg, 0.113 mmol) was dissolved in degassed MeOH (10 mL) at room temperature under nitrogen in a 10 mL vial with a sealable screw-top. Once all of Mn(hfac)\(_2\) was in solution, BDAP 21 (61.2 mg, 0.103 mmol) was added and reaction was left to stir overnight at RT under N\(_2\) in the dark. The shiny purple precipitate was collected by filtration and dried under vacuum to give product 53 in 88% yield (96.4 mg, 0.091 mmol), mp 276–279°C. Part of the mass of complex was crystallized from acetone by slow evaporation to obtain analytically pure sample. IR (KBr) ν: 2961 (w), 2186 (m), 1643 (s), 1500 (s), 1253 (vs), 1201 (vs), 1146 (vs), 795 (w), 661 (w) cm\(^{-1}\). UV-vis (toluene) \(\lambda_{\text{max}} (\varepsilon_{\text{max}} \text{ L mol}^{-1} \text{ cm}^{-1})\) nm: 309 (45000), 417 (45000), 520 (12200). \(^1\)H NMR (300 MHz, d\(_8\)-toluene) δ: 8.71 (s, 2H), 8.38 (s, 2H), 7.52 (s, 3H), 1.44 (s, 18H), 0.46 (s, 4H), -1.13 (s, 6H). LRMS MS \(m/z\) 1065.5 (M\(^+\)). Anal. Calcd for C\(_{54}\)H\(_{42}\)F\(_{12}\)MnN\(_2\)O\(_4\): C, 60.85; H, 3.97; N, 2.63. Found: C, 60.99; H, 3.98; N, 2.72.
Nickel-bis-hexafluoroacetetylactone-(4-[2’(3”-phenanthroinyl)ethynyl]-2,7-di-tert-butyl-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene), Ni(hfac)$_2$(BDAP) 54

Ni(hfac)$_2$ (53.2 mg, 0.112 mmol) was dissolved in degassed MeOH (10 mL) at RT under N$_2$ in a 10 mL vial with a septum in its screw-top lid. When all of starting material dissolved, BDAP 21 (60.1 mg, 0.101 mmol) was added and reaction was left to stir overnight at room temperature in a closed vial in the absence of light. The purple precipitate was collected by filtration and dried under vacuum to afford the product 54 in 84% yield (90.3 mg, 0.0844 mmol), mp 270–272°C. IR (KBr) ν: 2961 (w), 2186 (m), 1643 (s), 1497 (m), 1256 (vs), 1201 (vs), 1146 (vs), 792 (w), 669 (w) cm$^{-1}$. UV-vis (toluene) $\lambda_{\text{max}}$ ($\varepsilon_{\text{max}}$ L mol$^{-1}$ cm$^{-1}$) nm: 316 (49300), 417 (47800), 520 (13000). $^1$H NMR (300 MHz, d$_8$-toluene) δ: 44.34 (s, 1H), 22.46 (s, 1H), 21.59 (s, 1H), 16.13 (s, 1H), 15.88 (s, 1H), 8.76–8.32 (m, 5H), 7.54–7.29 (m, 5H), 1.62 (s, 9H), 1.45 (s, 9H), 0.38 (s, 4H), -1.03 (s, 3H), -1.09 (s, 3H). LRMS MS m/z 1068.5 (M). Anal. calcd for C$_{54}$H$_{42}$F$_{12}$NiN$_2$O$_4$: C, 60.64; H, 3.96; N, 2.62. Found: C, 60.44; H, 3.99; N, 2.72.
Cobalt-bis-hexafluoroacetylacetone-(4-[2′(3″-phenanthrolinyl)ethynyl]-2,7-di-tert-butyl-trans-12c,12d-dimethyl-12c,12d-dihydrobenzo[e]pyrene), Co(hfac)₂(BDAP) 55

Co(hfac)₂ 58 (25.8 mg, 5.45 x 10⁻² mmol) was dissolved in degassed MeOH (10 mL) at RT under N₂ in a 10 mL vial with a septum in its screw-top lid. When all of starting material dissolved, BDAP 21 (31.0 g, 5.2 x 10⁻² mmol) was added and reaction was left to stir vigorously over-night at room temperature in a closed vial in the dark. The purple precipitate was collected by filtration and dried under vacuum to afford the product 55 in 85% yield (47.2 mg, 4.41 x 10⁻² mmol), mp 260–263°C. Crystallization by heating complex in acetone, followed by cooling and slow evaporation of solvent gave analytically pure sample. IR (KBr) ν: 29561 (w), 2186 (m), 1637 (s), 1525 (w), 1256 (vs), 1201 (vs), 1146 (vs), 795 (w), 666 (w), 584 (w) cm⁻¹. UV-vis (toluene) λ_max (ε_max L mol⁻¹ cm⁻¹) nm: 309 (50800), 416 (46400), 518 (12800). ¹H NMR (300 MHz, d₈-toluene) δ: 38.53 (s, 1H), 24.64 (s, 1H), 23.65 (s, 1H), 12.33 (s, 1H), 11.60 (s, 1H), 8.14–7.52 (m, 3H), 5.66 (s, 1H), 5.66 (s, 1H), 3.49 (s, 1H), 0.82 (s, 9H), 0.61 (s, 4H), -0.01 (s, 9H), -2.99 (s, 6H), -23.41 (s, 2H). LRMS MS m/z 1069.5 (M). HRMS calcd for C₅₄H₆₂F₁₂CoN₂O₄ M⁺ m/z 1069.2285. Found, 1069.2302. Anal. Calcd for C₅₄H₆₂F₁₂CoN₂O₄: C, 60.62; H, 3.96; N, 2.62. Found: C, 60.83; H, 3.98; N, 2.65.
Cobalt-bis-acetylacetone-(4-[2′(3″-phenanthrolinyl)ethynyl]-10-naphthoyl-2,7-diter-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene), Co(acac)$_2$(NDAP) 56

Co(acac)$_2$(H$_2$O)$_2$ 51 (24.0 g, 8.1 x 10$^{-2}$ mmol) was dissolved in degassed spectrograde MeOH (10 mL) at room temperature under nitrogen in a 10 mL screw-top vial. When the starting material was completely dissolved, NDAP 22 (49.8 mg, 7.11 x 10$^{-2}$ mmol) was added and the reaction was left to stir overnight at RT under N$_2$ in the dark. The orange precipitate was collected by filtration and dried under vacuum giving 74% yield (50.3 mg, 5.24 x 10$^{-2}$ mmol) of product 56, mp (dec) 220–230°C. IR (KBr) ν: 2961 (m), 2192 (m), 1640 (w), 1588 (vs), 1511 (vs), 1459 (m), 1426 (m), 1407 (m), 1253 (m), 1012 (w), 916 (w), 781 (m), 727 (w) cm$^{-1}$. UV-vis (toluene) $\lambda_{\text{max}}$ ($\varepsilon_{\text{max}}$ L mol$^{-1}$ cm$^{-1}$) nm: 434 (57000), 488 (14100), 685 (5000). $^1$H NMR (300 MHz, CDCl$_3$) δ: 31.82 (s, 1H), 23.79 (d, 1H, $J = 6.00$ Hz), 22.92 (d, 1H, $J = 6.00$ Hz), 15.18 (s, 12H), 12.60 (s, 1H), 11.86 (s, 1H), 7.87–6.63 (m, 12H), 6.02 (s, 1H), 3.31 (s, 7H), 2.65 (s, 7H), 0.61 (s, 9H), -0.60 (s, 9H), -5.95 (s, 3H), -6.00 (s, 3H), -16.87 (s, 2H). Calculated exact mass for C$_{61}$H$_{58}$CoN$_2$O$_5$ M+ m/z 957.3678. Found M+ ion at m/z 957.3704.
Cobalt-bis-hexafluoroacetylaceton-(4-[2'(3'"-phenanthrolinyl)ethynyl]-10-naphthoyl-2,7-di-tert-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene), Co(hfac)$_2$(NDAP) 57

Co(hfac)$_2$ 58 (37.6 mg, 7.93 x 10$^{-2}$ mmol) was dissolved in degassed spectro-grade MeOH (10 mL) at room temperature under nitrogen in a 10 mL screw-top vial. When the starting material was completely dissolved, NDAP 22 (50.5 mg, 7.21 x 10$^{-2}$ mmol) was added and the reaction was stirred overnight at RT under N$_2$ in the dark. The dark orange precipitate was collected by filtration, washed with cold methanol and dried under vacuum, giving 57 in 54% yield (45.3 mg, 3.86 x 10$^{-2}$ mmol), mp 236–238°C. IR (KBr) ν: 2967 (m), 2192 (m), 1640 (vs), 1503 (m), 1429 (m), 1253 (vs), 1201 (vs), 1146 (vs), 894 (w), 781 (m), 666 (m), 584 (m) cm$^{-1}$. UV-vis (toluene) λ$_{\text{max}}$ ($\varepsilon_{\text{max}}$, L mol$^{-1}$ cm$^{-1}$) nm: 355 (38000), 423 (50300), 520 (13900), 683 (5270). $^1$H NMR (300 MHz, d$_8$-toluene) δ: 38.46 (s, 1H), 24.36 (s, 1H), 23.36 (s, 1H), 12.08 (s, 1H), 11.55 (s, 1H), 8.48–7.16 (m, 7H), 6.72–6.32 (m, 4H), 4.20 (s, 1H), 3.83 (s, 1H), 0.54 (s, 9H), -0.01 (s, 9H), -5.48 (s, 3H), -5.54 (s, 3H), -24.18 (s, 2H). Calculated exact mass for C$_{61}$H$_{46}$CoF$_{12}$N$_2$O$_5$ M+ m/z 1173.2547.
Cobalt-bis-acetylacetone-(4-[2'(3''-phenanthrolinyl)ethynyl]-2,7-di-tert-butyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene), Co(acac)₂(DAP) 59

Co(acac)₂(H₂O)₂ 51 (25.0 mg, 8.5 x 10⁻² mmol) was dissolved in degassed spectro-grade MeOH (10 mL) at room temperature under nitrogen in a 10 mL screw-top vial. When the starting material was completely dissolved, DAP 26 (42.1 mg, 7.7 x 10⁻² mmol) was added and the reaction was left to stir overnight at RT under N₂ in the dark. The orange precipitate was collected by filtration and dried under vacuum giving 58% yield (35.8 mg, 4.45 x 10⁻² mmol) of product 59, mp (dec) 230–236°C. IR (KBr) v: 2961 (m), 2186 (m), 1588 (vs), 1514 (vs), 1426 (s), 1253 (w), 1012 (w), 916 (w), 886 (w), 724 (w) cm⁻¹. UV-vis (toluene) λᵒₓₚ (εₕₐₘₓ L mol⁻¹ cm⁻¹) nm: 354 (58000), 406 (57300), 483 (16900), 507 (17200), 669 (2330). ¹H NMR (300 MHz, CDCl₃) δ: 31.64 (s, 1H), 23.70 (d, J = 6.9 Hz, 1H), 22.78 (d, J = 6.9 Hz, 1H), 15.12 (s, 12H), 12.49 (s, 1H), 11.62 (s, 1H), 7.31 (s, 1H), 7.05 (s, 1H), 6.01 (s, 1H), 3.29 (s, 1H), 2.87 (s, 1H), 2.34 (s, 10H), 0.69 (s, 9H), -0.49 (s, 9H), -6.15 (s, 3H), -6.21 (s, 3H), -16.51 (s, 1H). Calculated exact mass for C₅₀H₅₂CoN₂O₄ (M⁺) m/z 803.3259. Found M⁺ ion at m/z 803.3235.
Cobalt-bis-acetylacetone-(2,7-di-tert-butyl-trans-22b,22c-dimethyl-4,17-pyrazino-22b,22c-dihydropyrazinophenanthroline[e]pyrene), Co(acac)\(_2\)(PDD) 60

Co(acac)\(_2\)(H\(_2\)O)\(_2\) 51 (29.3 mg, 9.2 x 10\(^{-2}\) mmol) was dissolved in degassed spectro-grade MeOH (20 mL) at room temperature under nitrogen in a 100 mL 2-neck flask. When the starting material was completely dissolved, PDD 25 (50.5 mg, 9.2 x 10\(^{-2}\) mmol) was added and the reaction was left to stir overnight at RT under N\(_2\) in the dark. PDD 25 has almost no solubility in methanol. The suspension was left to stir overnight and the green solution with much less precipitate on the next day was filtered to remove any unreacted ligand. The filtrate was concentrated under reduced pressure, dried under high vacuum giving 94% yield (69.8 mg, 8.64 x 10\(^{-2}\) mmol) of dark green product 60, mp (dec) 235–245\(^{\circ}\)C. IR (KBr) \(\nu\): 2963 (s), 1608 (s), 1520 (w), 1464 (w), 1439 (w), 1406 (w), 1369 (s), 1254 (m), 1227 (m), 1136 (w), 1080 (w), 888 (w), 816 (w), 738 (m) cm\(^{-1}\). UV-vis (toluene) \(\lambda_{\text{max}}\) (\(\varepsilon_{\text{max}}\) L mol\(^{-1}\) cm\(^{-1}\)) nm: 345 (31300), 431 (32500), 453 (49400), 600 broad (2320). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 52.50 (s, 2H), 31.03 (s, 2H), 14.58 (s, 12H), 13.33 (s, 2H), 9.51 (s, 2H), 7.65 (s, 2H), 7.48 (s, 2H), 1.47 (s, 18H), -0.46 (s, 6H), -16.45 (s, 2H). Calculated exact mass for C\(_{48}\)H\(_{56}\)CoN\(_4\)O\(_4\) (M+) \(m/z\) 805.3164. Found M+ ion at \(m/z\) 805.3152.
Cobalt-bis-hexafluoroacetylacetone-(2,7-di-tert-butyl-trans-22b,22c-dimethyl-4,17-pyrazino-22b,22c-dihydropyrazinophenanthrolino[e]pyrene), Co(hfac)$_2$(PDD) 61

Co(hfac)$_2$ 58 (44.2 mg, 9.3 x 10$^{-2}$ mmol) was dissolved in degassed spectro-grade MeOH (20 mL) at room temperature under nitrogen in a 50 mL 2-neck flask. When the starting material was completely dissolved, PDD 25 (49.3 mg, 9.0 x 10$^{-2}$ mmol) was added and the reaction was left to stir overnight at RT under N$_2$ in the dark. The green precipitate was collected by filtration and dried under vacuum giving 41% yield (37.4 mg, 3.66 x 10$^{-2}$ mmol) of product 61, mp 267–268°C. IR (KBr) ν: 2967 (w), 1648 (s), 1525 (w), 1256 (vs), 1204 (vs), 1146 (vs), 1097 (w), 891 (w), 795 (w), 735 (w), 666 (m), 584 (w) cm$^{-1}$. UV-vis (toluene) $\lambda_{\text{max}}$ ($\varepsilon_{\text{max}}$ L mol$^{-1}$ cm$^{-1}$) nm: 302 (4100), 349 (36400), 435 (40800), 459 (67200). $^1$H NMR (300 MHz, d$_8$-toluene) δ: 37.04 (s, 2H), 13.76 (s, 2H), 10.15 (s, 2H), 7.85 (s, 2H), 7.54 (s, 2H), 1.61 (s, 18H), 0.42 (s, 4H), -0.01 (s, 6H), -22.81 (s, 2H). Calculated mass for C$_{48}$H$_{38}$CoF$_{12}$N$_4$O$_4$ (M+) $m/z$ 1021.2033. Anal. Calcd for C$_{48}$H$_{38}$CoF$_{12}$N$_4$O$_4$: C, 56.42; H, 3.75; N, 5.48. Found: C, 53.79; H, 4.50; N, 7.08.
References


97. Ayub, K. PhD, University of Victoria, 2008.


AVCG3906 51–7/CDCl3 13C/AMB 12/08/09
OVS–93–7 Co(acac)2(DAP) in CDCl3 1H NMR
Co(acac)\(_2\)(NDAP) in CDCl\(_3\) 1H NMR
OVS–93–6 in CDCl3 Co(acac)₂(BDAP) 1H NMR take #2
OVS-77-7 in tol-d8 1H NMR

[Chemical structure image]
OVS-133-6 Co(hfac)_2(PDD) in tol-d8 1H NMR
OVS-85-7 in d8-tol Ni(hfac)2(BDAP) 1H NMR
OVS−79−7 in Tol−d8 1H NMR
OVS−75−7 in tol−d8 1H NMR