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Photochemistry and Photophysics of Highly Ordered Materials in the Solid State: Synthesis and Dynamics of Molecular Rotors, Photodegradation of Bird Feathers, Studies of Photodecarbonylation by Transient Absorption Spectroscopy

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Photochemistry and Photophysics of Highly Ordered Materials in the Solid State:
Synthesis and Dynamics of Molecular Rotors, Photodegradation of Bird Feathers, Studies
of Photodecarbonylation by Transient Absorption Spectroscopy

A dissertation submitted in partial satisfaction of the requirements for the degree
Doctor of Philosophy in Chemistry

By

Melissa Lynn Hughes

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Melissa Lynn Hughes

2015
Abstract of the Dissertation

Photochemistry and Photophysics of Highly Ordered Materials in the Solid State: Synthesis and Dynamics of Molecular Rotors, Photodegradation of Bird Feathers, Studies of photodecarbonylation by Transient Absorption Spectroscopy

By
Melissa Lynn Hughes
Doctor of Philosophy in Chemistry
University of California, Los Angeles, 2015
Professor Miguel A. Garcia-Garibay, Chair

This thesis is presented as three independent sections, all dealing with the interaction of light with organic materials in the solid state. Section 1, consisting of chapters 1 and 2, deals with molecular gyroscopes: a class of amphidynamic materials. Molecular gyroscopes mimic the architecture of their macroscopic namesakes, having a freely rotating component (the rotator) surrounded and shielded by bulky static groups (the stators). Chapter 1 explores the development of a molecular gyroscope which contains the phenyleneethynylene chromophore along its axis of rotation. Chapter 2 discusses the phenyleneethynylene containing molecular gyroscopes with dipolar rotators. Chapter 3 presents a detailed characterization of the photodegradation of bird
feathers. Chapter 4 examines the solid-state photodecarbonylation of tetraphenylacetone by laser flash photolysis. A more in-depth look at the contents of each chapter follows:

**Chapter 1.** Reports the synthesis, crystal structure, solid-state dynamics, and photophysical properties of 6,13-bis(4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzo)pentacene (1), a molecular dirotor with a phenyleneethynylene chromophore. The incorporation of a pentiptycene into the molecular dirotor provides a central stator and a fixed phenylene ring relative to which the two flanking ethynylphenylene rotators can explore various torsion angles; this allows the phenyleneethynylene fluorophore dynamics to persist in the solid state. X-Ray diffraction studies show that molecular dirotor 1 packs so that all the phenyleneethynylene fluorophores adopt a parallel alignment, this is ideal for the development of functional materials. Variable temperature, quadrupolar echo $^2$H-NMR studies show that phenylene rotator flipping has an activation energy of 9.0 kcal/mol and a room temperature flipping frequency of ~2.6 MHz. Lastly, with measurements in solution, glasses and crystals, evidence was obtained that the fluorescence excitation and emission spectra of the phenyleneethynylene chromophores is dependent on the extent of conjugation between the phenylene rings, as determined by their relative dihedral angles.

**Chapter 2.** The molecular gyroscope architecture developed in chapter 1 is further elaborated to include a dipolar rotator. This is the first example of molecular gyroscopes that incorporate both the phenyleneethynylene chromophore and dipolar rotators. While the initial dipolar rotator design lead to molecules which failed to crystalize, a redesigned rotator gave crystals which were isomorphic with those discussed in chapter 1 and therefore retained the desired parallel
alignment. Intriguingly, the optical properties of the dipolar molecular gyroscopes were less variable than those of their nonpolar parent compound.

**Chapter 3.** A study of the photo-induced degradation of bird feathers is performed. Unpigmented turkey feathers and carotenoid pigmented scarlet ibis feathers are aged in ultraviolet light, filtered sunlight, and UV-free museum lighting. Aged feathers are examined and photographed under both visible light and UV light; photo-induced changes that are readily apparent under UV illumination are undetectable under ordinary illumination. Aged feathers are characterized by XPS, FTIR, and fluorescence spectroscopy. Spectral changes caused by light aging are qualitatively similar to previously reported changes in light aged wool spectra and are indicative of increasing concentrations of cystine oxidation products in UV aged feathers. GCMS analysis confirms that the cysteic acid to cystine ratio increases with UV exposure. Pigment concentration decreases with exposure to both visible and UV light and loss of pigment is detectable by analysis of feather extract long before visible changes are observed in feathers.

**Chapter 4.** The first transient absorbance spectra and kinetic data for the photodecarbonylation of a dibenzyl ketone derivative in a microcrystalline suspension are reported. While this class of reaction has been extensively studied under other conditions (solutions, micelles, and in zeolites) the synthetic utility of the solid-state version made it worthy of additional scrutiny. A protocol for the preparation of minimally scattering microcrystalline suspensions of TPA is reported; the crystal packing of these suspensions is similar the bulk powder. Product analysis has shown that while these reactions go cleanly to TPE in the solid state, benzophenone is the major product in solution. The transient absorbance signal for TPA in microcrystalline suspension is slightly (10 nm) red shifted verses the solution spectrum, and the transient lifetimes are significantly longer.
This dissertation of Melissa Lynn Hughes is approved.

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University of California, Los Angeles

2015
To J.T.H., P.S.H., M.M.B., and J.W.B.
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List of Abbreviations

ACN  
Acetonitrile

Ar  
Aryl

ATR  
attenuated total reflectance (IR)

BEPE  
1,2-bis(4-ethynylphenyl)ethyne

BEPEB  
1,4-bis((4-ethynylphenyl)ethynyl)benzene
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>CDCl₃</td>
<td>Deuterochloroform</td>
</tr>
<tr>
<td>Cl</td>
<td>Chloro</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CP/MAS</td>
<td>Cross polarization magic angle spinning (NMR)</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>d</td>
<td>Doublet (NMR)</td>
</tr>
<tr>
<td>d</td>
<td>Deuterium</td>
</tr>
<tr>
<td>DCK</td>
<td>Dicumyl ketone</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DEB</td>
<td>1,4-Diethynyl benzene</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DPM</td>
<td>Diphenyl methyl</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GCMS</td>
<td>Gas chromatography mass spectrometry</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared (spectroscopy)</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin (temperature)</td>
</tr>
<tr>
<td>kcal</td>
<td>Kilocalories</td>
</tr>
<tr>
<td>LFP</td>
<td>Laser flash photolysis</td>
</tr>
</tbody>
</table>
LUMO  lowest unoccupied molecular orbital
m  multiplet (NMR)
M  molar
m/z  mass to charge ratio
MALDI  Matrix-assisted laser desorption/ionization
Me  methyl
MeO  methoxy
MHz  megahertz
min  minute
mp  melting point
Nd:YAG  neodymium-doped yttrium aluminium garnet (laser)
nm  nanometer
NMR  nuclear magnetic resonance spectroscopy
ns  nanoseconds
OD  optical density
Ph  phenyl
ppm  parts per million
PXRD  powder x-ray diffraction
q  quartet (NMR)
RP  radical pair
RT  room temperature
s  singlet (NMR)
SDS  sodium dodecyl sulfate
t       triplet (NMR)
TA      transient absorbance (spectroscopy)
TGA     thermogravimetric analysis
THF     tetrahydrofuran
TLC     thin layer chromatography
TPA     1,1,3,3-tetraphenylacetone
TPE     1,1,2,2-tetraphenylethane
TREPR   time resolved electron paramagnetic resonance (spectroscopy)
UVIVF   ultraviolet induced visible fluorescence
UV-Vis  ultraviolet-visible spectroscopy
XPS     x-ray photoelectron spectroscopy
Å       angstrom
Δ       change
δ       chemical shift (NMR)
Φ       quantum yield
λ       wavelength
τ       excited state lifetime
hv      light
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Publications and Presentations


Chapter 1

Synthesis, Rotational Dynamics, and Photophysical Characterization of a Crystalline Linearly Conjugated Phenyleneethynylene Molecular Dirotor
1.1. Introduction

Recent advances in the fields of functional materials and artificial molecular machines have led to the development of crystalline molecular machinery, which is intended to take advantage of internal molecular motion, and/or chemical reactivity, to influence mechanical properties, electric, magnetic, and/or optical functions in a highly controlled and anisotropic manner.

Over the past few years, our group has emulated the structures of macroscopic gyroscopes as they are useful models for the design of molecules capable of forming amphidynamic crystals with static elements and rapidly moving parts. Like their macroscopic namesakes, molecular gyroscopes consist of a central rotator linked by an axle to two shielding stator groups that are responsible for self assembly of an ordered crystal lattice. The rotational dynamics of these molecules in the solid-state depends on the nature of the stator, the rotator size and symmetry, and the details of the crystal packing.

Using frequency-dependent dielectric spectroscopy as a function of temperature we showed that molecular gyroscopes with rotators bearing a permanent dipole moment can be interfaced with external AC fields. In this study we report a structural motif whose rotational dynamics are expected to allow for the incorporation of optical functions into the bulk crystalline material. Specifically we have modified the common 1,4-diethynylbenzene rotator motif for one that contains two rotators linearly conjugated with a phenyl ring at the center, which is part of a pentiptycene stator. The desired dirotor has a 1,4-bis((4-ethynylphenyl)ethynyl)benzene (BEPEB) chromophore (Figure 1.1.1). Based on the well-known changes in the photophysical properties of these structures as a function of aromatic group planarization and twisting, we expect that changes in conjugation brought about by changes in the orientation of the moving phenylene rotators will result in solid state spectral
shifts that will be useful for the generation of a new class of optical materials. As shown in the top portion of Figure 1.1.1, the chromophore may vary from a fully coplanar 1,4-bis(4-ethynylphenyl)ethynyl)benzene (BEPEB, shown in blue), to structures that have one, or two rings out of conjugation, which result in chromophores analogous to 1,2-bis(4-ethynylphenyl)ethyne (BEPE, shown in purple) and 1,4-diethynyl benzene (DEB, shown in violet).

Figure 1.1.1. Top: Rotation of the phenylene rotators in a phenyleneethynylene molecular dirotor reveals chromophores with varying degrees of π-conjugation; the chromophore may vary from a fully coplanar 1,4-bis((4-ethynylphenyl)ethynyl)benzene (BEPEB, shown in blue) analogue, to a partially conjugated 1,2-bis(4-ethynylphenyl)ethyne (BEPE, shown in purple) analogue, or an unconjugated 1,4-diethynyl benzene (DEB, shown
in violet) analogue. Bottom: An idealized crystal where polar (2,3-difluorophenylene) rotators are able to reorient as a function of an external electric field to change the optical properties of the material.

Linearly conjugated phenyleneethynlenes are remarkable chromophores. Their three aromatic rings experience nearly barrierless rotation in the ground state but have large energy variations as a function of their dihedral angle in the excited state.\textsuperscript{8,9,15} The difference between the ground and excited state rotational potentials is the result of changes in bond order as the single and triple bonds linking the aromatic groups in the ground state acquire the character of an extended cummulene upon electronic excitation. It has been shown that coplanar conformations of 1,4-bis(arylethynyl)benzene display red shifts of ca. 20-30 nm in absorption and emission as compared to “twisted” conformers where the plane of the central ring is twisted with respect to the planes of the rings on the sides.\textsuperscript{8} Elegant studies as a function of temperature by Yang and coworkers with a series of pentaptycene-derived oligo(p-phenyleneethynylene)s with significant intra-chain interactions showed remarkable shifts as the emission changes from an excited state population of mainly twisted conformers at low temperatures, to one that consists of mainly coplanar structures as the temperature increases.\textsuperscript{9} By incorporating two smaller phenylene rotators with one bulky pentaptycene and two shielding trityl groups within the structure of a BEPEB fluorophore, we expect two phenylene rings will preserve some freedom of rotation in the solid state. Figure 1.1.1 (top) shows the suggested pentaptycene structure with two central 2,3-difluorophenylene rotators flanked by two triphenylmethyl stators. The hypothesized changes in excitation energy as a function of planarization for the idealized chromophore are qualitatively expected to resemble the BEPEB, BEPE, and DEB chromophores highlighted in blue, purple and violet, respectively.
Shown in the bottom part of Figure 1.1.1 is an idealized crystal of the desired molecular dirotors. The application of a strong electric field is expected to influence the orientation and torsion angle of the dipolar 2,3-difluorophenylenes in and out of the plane of the pentyptycene central ring. While changes in the direction along the preferred orientation have the potential of breaking a centrosymmetric arrangement in the structure, changes in the orientation of the rotators can affect the conjugation of the chromophore, resulting both in nonlinear optical effects, changes in color (absorption spectra), as well changes in dichroism and birefringence. While this behavior is reminiscent of the function of a liquid crystal,10 suitable stator and rotator combinations in the solid state should lead to essentially barrierless rotation and optical switching at timescales that are only limited by the moment of inertia of the rotator (ca. $10^{-12}$ s), which is six to nine orders of magnitude faster than the time scale required for domain reorientation in a liquid crystal.10 While we have yet to achieve a true inertial rotator, we have previously shown rotation barriers as low as 4.4 kcal/mol, with a room temperature rotation frequency of $\sim$1 GHz.11

In this chapter we report the synthesis, solid-state dynamics, and photophysical properties of the BEPEB molecular dirotor 1 shown in Scheme 1.2.1.1. Compound 1 was synthesized with a meta-methoxy group in each of the two trityl stators in order to increase its solubility. Samples of the isotopologue, $1-d_8$, with deuterated phenylene rotators, were obtained to allow for the determination of the phenylene rotational barrier in the solid state using quadrupolar echo $^2$H-NMR line shape analysis experiments.12,13 We confirmed that the relatively large aspect ratio of the desired molecular structure yields crystals with all the chromophores aligned in the same direction, which is ideal for the preparation of functional materials addressable by external electric fields. In addition, we showed that phenylene rotation is facile at ambient temperature
(298 K) with a phenylene 180° degree jump average frequency of 2.6 MHz. Lastly, we showed that the BEPEB chromophore displays a reasonably strong emission that is homogeneous in a dilute toluene solution at room temperature but becomes highly heterogeneous in a rigid glass at 77 K. Clear evidence for the range of chromophores suggested in Figure 1 was obtained by analyzing the emission spectra as a function of excitation wavelength in the rigid glass, which revealed spectra that are nearly identical to those obtained from simple 1,4-diethynylbenzene (DEB), 1,2-bis(4-ethynylphenyl)ethyne (BEPE), and 1,4-bis((4-ethynylphenyl)ethynyl)benzene (BEPEB). We confirmed that pentiptycene dirotors provide a promising platform for the development of solid-state functional materials with shifting absorption and emission properties with the application of external electric fields.

**1.2. Results and Discussion**

**1.2.1. Synthesis and spectroscopic characterization.** The synthesis of the BEPEB molecular dirotor 1 was accomplished in a convergent manner relying on previously developed procedures. Samples of 3-(m-methoxyphenyl)-3,3-diphenylprop-1-yne 2 were obtained as described recently by our group.\(^\text{14}\) The central 6,13-diethynyl-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene 4 was prepared as reported by Swager and Yang.\(^\text{15}\) As illustrated in Scheme 1.2.1.1, samples of 1-(3-(m-methoxyphenyl)-3,3-diphenylprop-1-ynyl)-4-iodobenzene 3 and its 4-bromo-phenylene deuterated analogue 3-\(d_4\) were prepared via a Pd(0)-catalyzed Sonogashira coupling of 2 with either 1,4-diiodobenzene or 1,4-dibromo- benzene- \(d_4\) in refluxing 2:1 THF:diisopropyl amine. Another Pd(0)-catalyzed coupling reaction using 3 equivalents of 3 or 3-\(d_4\) per equivalent of 4 yielded BEPEB dirotors 1 and 1-\(d_8\), respectively.
Scheme 1.2.1.1.

Key: in 3 and 1 R = 4H, X = I; in 3-d<sub>4</sub> and 1-d<sub>8</sub> R = 4D, X = Br.

In order to have a model chromophores for photophysical studies, 6-((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene 8 and 1,2-bis(4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-
yl)phenyl)ethyne 10 were prepared as shown in Schemes 2 and 3 respectively. To obtain 8, pentiptycene quinone 5 was reacted subsequently with 1-octynyllithium and lithium TMS-acetylide to yield an asymmetrical diol which was immediately re-aromatized with tin(II)chloride and deprotected with potassium hydroxide. The resulting asymmetrical diyne 7 was coupled to 1-(3-(m-methoxyphenyl)-3,3-diphenylprop-1-ynyl)-4-iodobenzene 3 via a Pd(0)-catalyzed Sonogashira reaction. 10 was prepared by a Sonogashira coupling of 2 with 1,2-bis(4-bromophenyl)ethyne 9.

Both the $^1$H and the $^{13}$C NMR spectra of compounds 1, 1-$d_8$, 3, 3-$d_4$, 8, and 10 possess all the signals expected from a mono meta-methoxyphenyl trityl group with chemical shifts that are well conserved across the six structures. In the $^1$H NMR spectrum of 1, a singlet assigned to the methoxy groups is observed at 3.79 ppm, two doublet of doublet of doublets at ca. 6.70 and 6.90 ppm are assigned to the protons that are ortho- and para- to the methoxy group (H3 and H5 in Scheme 1.2.1.1), respectively. A doublet of doublets corresponding to H7 appears at 6.93 ppm and an apparent triplet at 7.23 ppm that is assigned to H4 complete the description of the metha-methoxy phenyl group. The signals corresponding to the protons of the unsubstituted trityl phenyl rings appear as an unresolved multiplet between 7.19 and 7.40 ppm. Hydrogen atoms of the phenylene rotator, labeled H16 and H17 in Schemes 1.2.1.1 – 1.2.1.3, appear as a pair of doublets at 7.65 and 7.74 ppm. Signals corresponding to the pentiptycene moiety appear as a singlet at 5.87 ppm for the bridgehead protons (H23), a doublet of doublets at 6.96 ppm for H26, and the signal for H25 between 7.30 and 7.40 ppm is obscured beneath other aromatic signals between 7.30 and 7.40 ppm. In the assymetric compound 8, the bridgehead protons (H23 and H30) give two distinct signals at 5.83 and 5.82 ppm and the proton signals of the hexyl tail (H35 – H40) are present between 2.76 and 1.01 ppm. In 10, the rotator protons give an apparent
doublet at 7.41 ppm and the pentiptycene signals are absent. All the $^{13}$C NMR spectra matched expectations from their structures. In the case of 1, all 26 non equivalent carbons are accounted for. Notably, the chemical shifts of the four alkyne carbons (C14, C13, C19 and C20) appear at 84.7, 86.5, 96.5 and 97.9 ppm, respectively. The phenylene rotator carbons C16 and C17 occur at 131.5 and 131.7 ppm, respectively however these carbon signals are not observed in deuterated rotators 1-$d_8$ and 3-$d_4$ due to signal splitting caused by deuterium substitution. The pentiptycene bridgehead carbons give signals at 52.2, the quaternary trityl carbons at 56.2 ppm, and the methoxy methyl at 55.1 ppm.

Scheme 1.2.1.2.

Scheme 1.2.1.3.
1.2.2. Crystal Structure. X-Ray diffraction quality single crystals of molecular dirotor \(1\) were obtained by slow evaporation of a saturated 1:4 toluene/dichloromethane (DCM) solution and were used for X-Ray diffraction data acquisition. Diffraction data were obtained with a crystal of \(1-d_8\), after the sample of origin had been shown to have identical PXRD patterns to crystals of natural abundance \(1\). Evaporation of DCM/diethyl ether, DCM/benzene, and DCM/hexane also yielded crystals, but were not of sufficient quality for single crystal X-ray diffraction. Although the crystals obtained from toluene/DCM were shown to include the aromatic solvent (see below), evaporation from pure benzene or toluene yielded no crystals. X-Ray diffraction data acquired at 100 K from the colorless plates obtained from toluene/DCM were solved in the space group \(\overline{P}\bar{1}\) with only one molecular dirotor and four molecules of toluene per unit cell.\(^{16}\) As required by the crystal space group, molecules of \(1\) have a center of symmetry coincident with the one in the triclinic unit cell. As a consequence of this, the two trityl stators have opposing axial chiralities (M and P) and the two phenylene rotators are equivalent (Figure 1.2.2.1). The alkyne
structure deviate significantly from linearity giving 1 an overall S-shape. The torsion angle between rotator phenylenes and the central pentaptycene phenyl ring is 34.2°.

Figure 1.2.2.1. Molecular structure of compound 1 at 100 K with thermal ellipsoids at 50% probability.

Figure 1.2.2.2. Packing diagram of molecular dirotor 1 illustrating the unit cell. Molecules of 1 pack in parallel manner and in layers, with toluene molecules between the layers.

As observed previously for crystals of molecular gyroscopes, which tend to incorporate solvents in the lattice,\textsuperscript{17,18} crystals of 1 include four molecules of toluene per unit cell (Figure
1.2.2.2. The packing coefficient, given by the van der Waals volume of all the molecules in the unit cell in relation to the total volume of unit cell, is 0.71. The unit cell shows that each phenylene rotator is nested in the cleft of the central pentiptycene stator of a neighboring molecule. It is noteworthy that 1 packs in a lamellar fashion, with layers of molecular dirorators separated by channels of toluene molecules, which display a high degree of mobility or disorder as evidenced by their larger thermal ellipsoids. Notably, the toluene channels are adjacent to the phenylene rotators, and may provide a locally “fluid” region in the crystal which may allow for greater phenylene rotational freedom.

The experimental X-ray powder patterns of 1 and 1-\textit{d}_8 are identical to each other but do not have a perfect match to the pattern simulated from the single crystal data (Figure 1.5.23). This may be attributed to the disordered nature and variable content of the toluene clathrate, which tends to escape faster in powder samples. The thermal stability of the crystals was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC shows an endotherm at 458 °C, which is immediately followed by decomposition (Figure 1.5.25). The TGA curve shows the gradual loss of 8% of the total mass between 70 °C and 180 °C, followed by a more rapid loss of an additional 15% of the total mass between 400 °C and 455 °C (Figure 1.5.24). Both are attributed to the escape of toluene from the crystal lattice.

1.2.3. Solid-State Rotational Dynamics of the Phenylene Group. In order to realize the electro-optical response depicted in Figure 1 it will be essential to design molecular and crystal architectures where the phenyl groups are able rotate and to reorient. In order to determine whether or not fast phenylene reorientation is possible within crystals of 1, we decided to use quadrupolar echo \textsuperscript{2}H NMR spectroscopy with samples that had the two phenylene groups \textsuperscript{2}H-labeled. It is well known that static \textsuperscript{2}H NMR is one of the most sensitive probes for dynamics in
the solid state. The $^2\text{H}$-NMR spectrum is dominated by the interaction between the nuclear spin and the electric quadrupole moment at the nucleus.$^{12,13}$ The orientation dependence of the quadrupolar coupling characterizes the spectra; each deuteron provides a doublet with a splitting frequency $\Delta \nu$ that depends on the orientation angle $\beta$ that the C-$^2\text{H}$ bonds make with respect to the external field:

$$\Delta \nu = \frac{3}{4} \left( e^2 q_{zz} Q / h \right) (3 \cos^2 \beta - 1) = \frac{3}{4} \text{QCC} (3 \cos^2 \beta - 1)$$

Here, $Q$ represents the electric quadrupole moment of the deuteron, $e$ and $h$ are the electric charge and Plank’s constant, respectively, and $q_{zz}$ is the magnitude of the principal component of electric field gradient tensor, which lies along the C-$^2\text{H}$ bond. The combination of these quantities is commonly called the quadrupolar coupling constant (QCC). For aromatic C-$^2\text{H}$ bonds, QCC = 180 kHz. The peak separation for static deuterons varies from ca. $\Delta \nu = 270$ KHz when $\beta = 0^\circ$, to $\Delta \nu = 0$ when the C-$^2\text{H}$ bond is at the magic angle $\beta = 54.7^\circ$. In powdered samples, all values of $\beta$ are represented but they are not all equally populated; this gives rise to a collection of doublets in all possible orientations, which collectively give a broad symmetric spectrum with two maxima and two shoulders known as a Pake pattern. When the C-$^2\text{H}$ bonds experience reorientations that reduce the range of their magnetic interactions by dynamic averaging, the shape of the Pake pattern is altered in characteristic ways. It is possible to determine the frequency of the reorientation from ca. $10^4$ to $10^8$ Hz through line shape comparison analysis between experimental and the simulated spectra. Phenylene rotations in solids are typically modeled in terms of a Brownian exchange between degenerate sites related by $180^\circ$ rotation, also known as 2-fold flips. Spectral changes that occur as a result of this 2-fold phenylene flipping have been well studied in the literature,$^{19,20,21}$ and excellent programs for line shape simulation are now readily available.$^{22,23}$
Measurements were carried out using a quadrupolar echo pulse sequence on static crystalline powder samples of 1-$d_8$. Spectra were obtained at 46.07 MHz with a 90° pulse width of 2.5 µs, echo and refocusing delays of 50 µs and 42 µs, respectively, a 5 s delay between pulses, and line broadening of 5000 Hz at temperatures ranging from 170 to 350 K. Some of the data and the best simulations are illustrated in Figure 4. Notably, the experimental spectra were fitted poorly by simulations that assume a single phenylene jump frequency. A good fit required the use of a log-Gaussian distribution model with a width $\sigma = 1.5$, indicating that there is a distribution of activation energies in the sample.\textsuperscript{24} It is likely that different environments form as a result of solvent disorder and/or partial desolvation. An Arrhenius plot of the data using the average 2-fold jumping rate constant (Figure 1.5.22) revealed an activation energy of 9.0 kcal/mol with a pre-exponential factor is $2.4 \times 10^{13}$ s$^{-1}$. The line shape differences between the spectra obtained below 210 K were negligible, indicating that motion at these temperatures reaches the slow exchange regime.
1.2.3.1. Experimental (left) and simulated (right) solid state $^2$H-NMR spectra of 1-$d_8$. Arrhenius analysis of the rate and temperature data resulted in an average activation energy of 9.0 kcal/mol with a pre-exponential factor of $2.4 \times 10^{13}$ s$^{-1}$ (Figure 1.5.22).

1.2.4. Photophysics. It is well known that the fluorescence of phenyleneethynylenes depends both on the degree of coplanarity between the aromatic rings and the extent of fluorophore aggregation.\textsuperscript{8,9,25,26,27} Theoretical and experimental studies have been performed on these systems to determine the magnitude and the nature of the contribution of planarization. It has been found that when freedom of rotation is allowed and aggregation minimized (\textit{i.e.} a dilute solution in a non-viscous solvent), the excitation band is heterogeneously broadened while the emission
spectrum is vibrationally resolved and relatively narrow. The broadness of the absorption spectrum is determined by a large distribution of phenylene rotamers and the well-resolved emission by a rapid conformational equilibration in the excited state, which gives rise to the dominant contribution from the lowest energy, fully planar rotamer. When the rotation of the arylenethynlenes is restricted and the co-planar rotamer is dominant, as it occurs in stretched poly(ethylene) films, the excitation and absorption spectra become narrow and red-shifted. By contrast, when aggregation is present, the red shift is more pronounced and an additional low energy band is sometimes observed. A single molecule study of a related poly(9,10-anthracenediyl-ethynylene-1,4-phenylene-ethynylene) has further highlighted the importance of conformation in phenyleneethynylene systems. In addition, density functional theory calculations of 2,5-dimethoxy-p-phenyleneethynylene oligomers support the conclusion that twisting about the triple bond leads to a shortening of conjugation length and a widening of the HOMO-LUMO gap. A number of studies
Figure 1.2.4.1. (a) Simplified structure used to calculate the ground and vertical excited state energies as a function of one and two phenylene torsion angles. (b) Calculated ground state and excited state energy surfaces at the TD-DFT B3LYP 6-31G(d) level of theory plotted against one (dashed line) or two (dotted line) phenylene torsion angles. Blue, purple, and violet arrows correspond to the excitation energies of the corresponding BEPEB, BEPE and DEB-like chromophores proposed in Figure 1.1.1.

have been performed on phenyleneethynylenes with pentiptycene units. These studies have indicated that the incorporation of pentiptycene units into the phenyleneethynylene backbone generally decreases fluorophore aggregation and prevents the corresponding broadening of the emission.\textsuperscript{15,28}

In order to correlate qualitatively the phenylene twist geometries with absorption and emission data, we performed TD-DFT calculations at the B3LYP 6-31G(d) level of theory. The results obtained using a simplified model system consisting of the unadorned BEPEB chromophore are
shown in Figure 1.2.4.1.a and plotted in Figure 1.2.4.1.b. The model considers a frame of reference given by the plane of the central phenylene and explores variations in energy as a function of rotation of one or both aromatic end groups. As shown in Figure 1.2.4.1.b, changes in energy for rotation about the alkyne bonds in the ground state are less than 1.0 kcal/mol between the fully co-planar chromophore (Figure 5b, 0° torsion) and that with the two outer phenylenes at a 90° (or -90°) torsion angle. The corresponding energy difference in the excited state is significantly larger, i.e., 9.9 kcal/mol. However, the energy difference is much smaller, 2.7 kcal/mol, when only one of the two outer phenylene rings is rotated by 90° while the other two remain coplanar. The vertical excitation energies calculated in this manner are in good qualitative agreement with experimental data for analogous compounds.\textsuperscript{31} We set out to qualitatively validate this trend by comparing the spectra of the BEPEB chromophore containing dirotor 1 with those of model compounds containing BEPE and DEB chromophores in their structures: compounds 8 and 10, and 4 respectively.

\textbf{Figure 1.2.4.2.} Fluorescence excitation and emission of dirotor BEPEB 1 and model chromophores BEPE 8, BEPE 10, and DEB 4 in deoxygenated methylcyclohexane solutions at room temperature.
Table 1.2.4.1. Photophysical properties of the BEPEB, BEPE and DEB chromophores in dirotor 1, and model compounds 8, 10, and 4 in dilute methylcyclohexane solutions at room temperature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{0-0 \text{ fl}}$ (nm)</th>
<th>$\lambda_{0-0 \text{ abs}}$ (nm)</th>
<th>$\varepsilon_{0-0 \text{ abs}}$ ($M^{-1} cm^{-1}$)</th>
<th>$\varepsilon_{303}$ ($M^{-1} cm^{-1}$)</th>
<th>$\Phi_{\text{fl}}$</th>
<th>$\tau_{\text{fl}}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEPEB 1</td>
<td>376</td>
<td>369</td>
<td>39,437</td>
<td>25,866</td>
<td>0.85</td>
<td>$\leq 0.6^a$</td>
</tr>
<tr>
<td>BEPE 8</td>
<td>351</td>
<td>346</td>
<td>20,099</td>
<td>18,329</td>
<td>0.29</td>
<td>1.4</td>
</tr>
<tr>
<td>BEPE 10</td>
<td>345</td>
<td>342</td>
<td>63,732</td>
<td>59,046</td>
<td>0.84</td>
<td>$\leq 0.6$</td>
</tr>
<tr>
<td>DEB 4</td>
<td>342</td>
<td>333</td>
<td>7,033</td>
<td>2,178</td>
<td>0.70</td>
<td>5.5</td>
</tr>
</tbody>
</table>

$^a$ Fluorescence lifetimes were shorter than the time resolution of our current instrument.

The photophysical properties of the three fluorophores 1, 4, 8, and 10 are summarized in Table 1.2.4.1 and their fluorescence excitation and emission spectra are shown in Figure 1.2.4.2. Included in the table are the position of the $\lambda_{0-0}$ bands for absorbance and fluorescent emission, the molar extinction coefficient ($\varepsilon_{0-0}$), and the extinction coefficient at $\lambda=303$ ($\varepsilon_{303}$, the wavelength used to measure fluorescence lifetimes), the quantum yield of fluorescence ($\Phi_{\text{fl}}$), and the fluorescence lifetime ($\tau_{\text{fl}}$). As expected, both the excitation and emission spectra are red-shifted as the number of conjugated aromatic groups and alkyne linkages increases. A red-shift in fluorescence emission of 9 nm was determined from DEB 4 to BEPE 8, and a shift of 25 nm when comparing BEPE 8 to the full BEPEB chromophore of 1. This result is in qualitative agreement with the quantum mechanical calculations. The excited state lifetimes of the three chromophores decrease with increasing conjugation length; however, BEPE 10 has a significantly shorter lifetime than BEPE 8. The molar extinction coefficient at $\lambda_{0-0\text{ abs}}$ increases linearly with conjugation length for all chromophores except BEPE 10, which has a much higher extinction coefficient than the others. The fluorescence quantum yields appear to be independent of conjugation length, with BEPE 8 having the lowest quantum yield while BEPEB 1, DEB 4,
and BEPE 10 have significantly higher yields. It should be noted that two BEPE model chromophores are listed, one which contains a pentiptycene moiety but lacks symmetry (BEPE 8), and one which does not contain a pentiptycene moiety but preserves symmetry (BEPE 10). In this case, the pentiptycene moiety proved an essential component of a model chromophore; while the three pentiptycene containing compounds follow clear trends in their photophysical properties, BEPE 10 is an outlier. This discrepancy lead us to examine the excitation and emission spectra of the pentiptycene-free analogue of diethynyl pentiptycene 4: 1,4-diethynyl benzene. As can be seen in figure 1.2.4.3, the two compounds have quite different spectra: the λ₀₀ bands for absorbance and emission in diethynyl benzene are at 285 and 291 nm respectively, about 50 nm lower than in diethynyl pentiptycene 4. Attempts to elucidate the role of the pentiptycene moiety using ZINDO/S calculations proved unsuccessful.

![Fluorescence excitation and emission spectra of diethynylbenzene and diethynylpentiptycene (4).](image)

Figure 1.2.4.3. Fluorescence excitation and emission spectra of diethynylbenzene and diethynylpentiptycene (4).

In order to experimentally determine whether changes in fluorophore planarization result in substantial changes in the emission spectra one needs conditions where the distribution of twist angles and phenylene rotation is restricted. Considering the relatively flat ground state rotational energy surface of 1, one should expect a statistical distribution of all possible phenylene torsion
angles to exist in solution, from perfectly planar to perfectly orthogonal. Thus, by flash freezing these solutions it should be possible to capture a “snapshot” of the torsion angle population. To document this, a dilute solution (1.49 μM) of molecular dirotor 1 was prepared in toluene and its fluorescence spectra measured both at 298 K and at 77 K (Figure 8). The fluorescence emission spectrum of trimer 1 measured at 298 K does not vary as a function of excitation energies and consists of a strong 0-0 band followed by four vibrationally resolved maxima with decreasing intensities. This observation is consistent with a distribution of phenylene angles in the ground state, which are able to equilibrate to the lowest energy coplanar conformation during their excited state lifetime. Thus, mainly the emission of the lower energy coplanar fluorophore is observed, as illustrated by the spectrum shown in cyan color in the bottom part of Figure 1.2.4.4. The spectra corresponding to **BEPE 8** and the **DEB 4** are increasingly blue-shifted, as shown by the spectra labeled in violet and purple. The fluorescence emission spectrum of **BEPEB 1** measured in toluene glasses at 77 K showed the postulated heterogeneity. As phenylene rotation is prevented by the frozen matrix, it is possible to detect a broad range of rotamers by varying the excitation energy. As illustrated in the top frame of Figure 1.2.4.4, excitation at higher energy wavelengths (*i.e.*, 295 nm) preferentially addresses fluorophores that give higher energy emission assigned to the doubly twisted structures that approach the spectral properties of the model **DEB 4**. Also shown in the top of Figure 1.2.4.4: a systematic shift in the excitation wavelength from 295 to 350 nm results in a similar shift in the onset of emission. While the spectra are highly heterogeneous and it would be difficult to excite any given species selectively, as the spectrum evolves, it acquires a qualitative resemblance to the spectrum of model **BEPE 8**, and eventually the one of **BEPEB** dirotor 1.
Figure 1.2.4.4. (Top) Fluorescence emission of BEPEB molecular diror 1 in frozen toluene at 77K excited at wavelengths that range from 295 to 350 nm, compared to (Bottom) the emission spectra of model DEB 4 (violet), model BEPE 8 (purple) and BEPEB dirotor 1 (blue) in toluene at room temperature. 

While the fluorescence results from diror 1 in solution and in glassy matrix support a strong effect of aromatic torsion angles in the absorption and emission spectra, it was also important to confirm that the BEPEB diror 1 remains emissive in the crystalline state. With that in mind, we carried out fluorescence excitation and emission experiments by front-face excitation and detection at 77 K and at 298 K with finely powdered samples of 1 grown from toluene. As illustrated in Figure 1.2.4.5, the solid state excitation and emission spectra measured at 77 K (blue spectra) were red-shifted by ca. 10 nm when compared to those measured in solution (black spectra). The solid state excitation spectrum shows a strong 0-0 transition by ca. 385 nm and an interesting new band at ca. 405 nm. The emission spectrum obtained upon excitation at 405 nm is red shifted verses the one obtained with a 385 nm excitation wavelength (Figure 1.5.26). Notably, an increase in temperature to 298 K resulted in a substantial increase of the 405 nm band and a remarkable change in the shape of the emission envelop where the band of the 0-0
transition by ca. 385 nm disappears, suggesting that emission (red spectrum) occurs from the lower energy emitter after efficient energy transfer.\textsuperscript{32}

![Fluorescence spectra](image)

**Figure 1.2.4.5.** Fluorescence excitation (top) and emission (bottom) spectra of phenyleneethynylene molecular dirotor 1 in solution (black), in the crystalline state at 77 K (blue) and in crystalline state at 298 K (red). The arrow shown in the excitation spectra indicates the thermal population of a red-shifted emissive species in the solid state, which we assign to the fully coplanar conformation.

In order to account for the solid state fluorescence observations we propose a model based on two distinct absorbing species with equilibrium concentrations that change as function of temperature. It is reasonable to assume that the major component is the one documented by single crystal X-ray diffraction, with the external phenylene rotators adopting angles of 34.2° with respect to the plane of phenyl ring in the central pentiptycene. The second and minor
component shows the characteristics of a chromophore that is more coplanar and has a lower fluorescence excitation energy. The relative intensities of the band at 420 nm suggest that the population of the minor component increases as a function of temperature, as expected by an increase in mobility within the crystal lattice. In addition, changes in the emission spectrum as function of temperature require that energy transfer from the twisted component to the coplanar species is significantly more favorable at higher temperature. These observations can also be understood as arising from reabsorption of all higher energy emission by neighboring chromophores resulting in an observed emission band which is red-shifted. Given the high density of chromophores within the crystal lattice, it is not surprising that at temperatures where phenylene motion is facile (295 K) only the lowest energy emission is able to reach the detector.

1.3. Conclusions

We have presented the synthesis, crystal structure, solid-state dynamics, and photophysical properties of a phenyleneethynylene molecular dirotor 1 and its deuterated isotopologue, 1-\textsuperscript{d}_8, embedded in the structure of a pentiptycene stator. The role of the bulky pentiptycene is to provide both a central shielding stator and a fixed phenylene, so that the two flanking but linearly conjugated phenylene rotators can explore a variety of torsion angles to affect their excitation energies and photophysical properties in the solid state. X-Ray diffraction studies have shown that molecular dirotor 1 packs in such a manner that all the phenyleneethynylene chromophores are arranged in parallel, so that they all share the same internal rotational axis, as required for the development of functional materials. Variable temperature quadrupolar echo \textsuperscript{2}H-NMR studies have shown that phenylene rotator two-fold flipping is facile at room temperature, with an activation energy of 9.0 kcal/mol and a Brownian rotational frequency of approximately 2.6 MHz. This energy barrier is lower than those previously shown to help align phenylene flipping
with external AC fields, indicating that externally influencing phenylene rotation with an electric field should be feasible in this system.⁴ We have also shown that the phenyleneethynylene chromophore displays a remarkable spectral heterogeneity in rigid glasses, as expected for a chromophore that is capable of displaying significant fluorescence changes as a function of its inter-phenylene torsion angles. These results provide a very promising platform for the development of molecular dirorors whose amphidynamic nature allows for the rapid shifting of solid-state fluorescence emission and optical properties with the application of an electric field.

1.4. Experimental Section.

1.4.1. General Methods

Commercial reagents were used without additional purification.

²H NMR spectra were simulated using the program Express 1.0.²² A 180° jump model with quadrupole coupling constant of 180 kHz and an asymmetry parameter of 0.02 was used. A log-Gaussian distribution of 19 phenylene jump rates (σ = 1.5) centered around each nominal phenylene jump rate was generated. A weighted average of the simulated spectra were superimposed to generate the final simulated spectra.

1.4.2. Synthesis and Characterization

1.4.2.1 Synthesis of (3-(4-iophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene

3: A three neck flask containing 150 mL THF and 75 mL diisoproplyamine was purged with argon for 1 hour. 2 (1.3 g, 4.4 mmol), 1,4-diiodobenzene (7.18 g, 21.8 mmol), bis(triphenylphosphine)palladium dichloride (185 mg, 0.264 mmol), and copper iodide (50 mg, 0.528 mmol) were added to the flask and the reaction mixture was brought to reflux. The reaction mixture was refluxed 12 h then cooled to room temperature and quenched with saturated aqueous ammonium chloride. The aqueous layer was extracted 2 x with DCM. The organic
fractions were combined, dried over magnesium sulfate and evaporated under vacuum. The product was purified by flash chromatography, first using hexanes to elute excess diiodobenzene and switching to 2:1 hexanes:DCM to elute. 1.34 g (61%) of the colorless solid product were recovered. Anal.: m.p.: 120.6 – 121.4 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 8.1$, 2H), 7.27 – 7.15 (m, 13H), 6.86 – 6.81 (m, 2H), 6.76 (d, $J = 8.1$, 1H), 3.69 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 159.3, 146.6, 144.9, 137.4, 133.1, 129.1, 128.9, 128.0, 126.9, 123.0, 121.7, 115.5, 111.9, 97.0, 93.7, 84.2, 56.1, 55.1; IR (DRIFT cm$^{-1}$) 3058, 3026, 2997, 2965, 2937, 2834, 1604, 1579, 1482, 1445, 1433, 1289, 1241, 1049, 816, 747, 695; MS (ESI/APCI m/z) calculated for C$_{28}$H$_{21}$IO+H 501.0715, found 501.0710.

1.4.2.2. (3-($d_4$-4-bromophenyl)-1-(3-methoxyphenyl)prop-2-yn-1,1-diyl)dibenzene 3-$d_4$:

A three-neck flask containing 100 mL tetrahydrofuran and 50 mL diisopropylamine was purged with argon for 2 hours. 2 (995 mg, 3.3 mmol), $d_4$-1,4-dibromobenzene (3225 mg, 13.5 mmol), bis(triphenylphosphine)palladium dichloride (121 mg, 0.17 mmol), and copper iodide (157 mg, 0.82 mmol) were added to the flask, and the flask was purged for another 10 minutes. The reaction mixture was heated to reflux for 18 hours, it was then cooled and quenched with saturated ammonium chloride. The crude product was extracted into dichloromethane and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure and the residue was re-dissolved in dichloromethane and loaded onto a silica gel column. The product was eluted with hexanes/dichloromethane, with a gradient from 80:20 to 50:50. The solvent was evaporated, to give a colorless solid (1.01 g, 60%). Excess $d_4$-1,4-dibromobenzene (2.11 g) was recovered with high purity. Anal.: m.p.: 118.3 – 119.6 °C; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.32-7.24 (m, 10H), 7.22 (t, $J = 8.0$ Hz, 1H), 6.90 (m, 2H), 6.81 (ddd, $J = 8.1$, 2.4, 0.9 Hz, 1H), 3.73 (s, 3H); $^{13}$C (CDCl$_3$, 75 MHz) $\delta$ 159.4, 146.7, 145.0, 129.1, 129.0, 128.1, 127.0, 122.3, 122.0,
121.8, 115.6, 111.9, 96.8, 84.0, 56.2, 55.2; IR (DRIFT cm\(^{-1}\)) 3085, 3065, 3045, 3026, 3015, 2955, 2932, 2903, 2835, 1598, 1578, 1482, 1446, 1432, 1287, 1255, 1050, 756, 736, 697; mass (MALDI m/z) calculated for C\(_{28}\)H\(_{17}\)D\(_4\)BrO 456.10, found 456.32.

1.4.2.3. \textit{6,13-bis((4-(3-(methoxyphenyl))-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis(1,2]benzeno)pentacene 1:} Diethynyl pentiptycene 4 (159 mg, 0.33 mmol) was dispersed in 75 mL tetrahydrofuran, and purged with argon in an addition funnel for 1 hour. 3 (500 mg, 1.0 mmol), bis(triphenylphospnene) palladium dichloride (23.4 mg, 0.033 mmol), and copper iodide (3.2 mg, 0.017 mmol) were dissolved in 75 mL tetrahydrofuran and 75 mL diisopropylamine in a three-neck flask, purged with argon for 1 hour, and heated to reflux. Diethynyl pentiptycene 4 dispersion is added over 6 hours, a 10 mL portion of THF was used to rinse residual pentiptycene into the reaction flask. Reaction was allowed to continue at reflux for another hour at which point all 4 has been consumed by TLC; it was then quenched with saturated ammonium chloride and extracted into dichloromethane, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography with a 70:30 to 60:40 hexanes:DCM eluent. The solvent was evaporated under reduced pressure to yield 1 as a white powder with strong violet fluorescence (134 mg, 33%).

Crystallization of 1 by slow evaporation of a 4:1 DCM:toluene mixture afforded small square crystals. Anal.: m.p.: decomposes; \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta 7.74\) (d, \(J = 8.1\), 4H), 7.65 (d, \(J = 8.1\), 4H), 7.4 – 7.26 (m, 30H), 6.98 – 6.93 (m, 12H), 6.87 – 6.85 (dd, \(J = 8.1, 1.7\) Hz, 2H), 5.87 (s, 4H), 3.79 (s, 6H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta 159.3, 146.6, 144.9, 144.7, 144.0, 131.7, 131.5, 129.1, 128.9, 128.0, 126.9, 125.2, 123.9, 123.7, 122.8, 121.7, 115.5, 114.6, 111.9, 97.9, 96.5, 86.5, 84.7, 56.2, 55.1, 52.2; IR (DRIFT cm\(^{-1}\)) 3062, 3020, 2968, 2930, 1598, 1488, 1458,
1290, 1248, 1181, 1035, 836, 751, 697; MS (ESI/APCI m/z) calculated for C_{94}H_{62}O_{2}+NH_{4} 1240.5093, found 1240.5088.

1.4.2.4. 1-d_{8}: Diethynyl pentiptycene 4 (207 mg, 0.43 mmol) was dispersed in 75 mL tetrahydrofuran, and purged with argon in an addition funnel for 1 hour. 3-d_{4} (596 mg, 1.3 mmol), bis(triphenylphosphine) palladium dichloride (30.2 mg, 0.043 mmol), and copper iodide (4.1 mg, 0.0215 mmol) were dissolved in 75 mL tetrahydrofuran and 75 mL diisopropylamine in a three-neck flask, purged with argon for 1 hour, and heated to reflux. Diethynyl pentiptycene 4 dispersion was added over 24 hours, a 10 mL portion of THF was used to rinse residual pentiptycene into the reaction flask. Reaction was allowed to continue at reflux for another 24 hours, it was then quenched with saturated ammonium chloride and extracted into dichloromethane, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography with a 60:40 hexanes:DCM eluent. The solvent was evaporated under reduced pressure to yield 1-d_{8} as a white powder with strong violet fluorescence (288 mg, 54%). Crystallization of 1-d_{8} by slow evaporation of a 4:1 DCM:toluene mixture afforded small square crystals. Anal.: m.p.: decomposes; \textsuperscript{1}H NMR (CDCl_{3}, 500 MHz) \(\delta\) 7.39-7.33 (m, 24H), 7.32-7.30 (m, 4H), 7.28 (t, \(J = 8.0\) Hz, 2H), 6.99-6.93 (m, 12H), 6.87 (dd, \(J = 8.5, 2.5, 2H\), 5.87 (s, 4H), 3.79 (s, 6H); \textsuperscript{13}C (CDCl_{3}, 125 MHz) \(\delta\) 159.7, 146.9, 145.2, 144.9, 144.2, 129.4, 129.2, 128.3, 127.2, 125.5, 124.0, 122.9, 122.0 115.8, 115.0, 112.2, 98.2, 96.7, 86.8, 84.9, 56.5, 55.4, 53.6, 52.5; IR (DRIFT cm\(^{-1}\)) 2955, 2922, 2853, 1599, 1457, 1251, 1051; MS (MALDI) calculated for C_{94}H_{54}D_{8}O_{2} 1230.53, found 1230.53.

1.4.2.5. 6-ethynyl-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene 7: Pentiptycene quinone 3 (50 mg, 0.11 mmol) is dissolved in dry THF in a flame dried flask under argon. To generate 1-octynyllithium solution 1-octyne (103 mg,
0.93 mmol) is dissolved in 8 mL dry THF in a flame dried flask under argon and the solution is cooled to -78°C, n-butyllithium (0.5 mL, 1.6 M in hexane, 0.80 mmol) is added. 1-octynyllithium solution is titrated into the pentaptycene quinone 3 solution at -78°C until TLC shows that pentaptycene quinone 3 has been completely consumed. A solution of trimethylsilylethynyllithium is prepared by adding n-butyllithium (0.5 mL, 1.6 M in hexane, 0.80 mmol) to a solution of ethynyltrimethylsilane (88 mg, 0.90 mmol) in 8 mL dry THF at -78°C. Trimethylsilylethynyllithium solution is titrated into the mono-reacted pentaptycene quinone until it is consumed by TLC. The reaction mixture is warmed to room temperature and acidified with 1M HCl and extracted into DCM and washed with water. The organic layer is dried over magnesium sulfate and evaporated to yield the crude asymmetric diol. This product dissolved in acetone and stirred overnight at room temperature with a solution of tin(II) chloride hydrate (69 mg, 0.27 mmol) in 50% acetic acid to give the rearomatized asymmetrical diyne. The reaction mixture was extracted into DCM and the organic layer was washed with a saturated solution of sodium bicarbonate, the organic layer was dried over magnesium sulfate and evaporated. The product mixture was purified by preparatory TLC (80:20 hexane/DCM) and found to contain a 1 to 2 mixture of TMS protected diyne 6 and deprotected terminal diyne 7. Both products were redissolved in THF and stirred overnight at room temperature with an excess of potassium hydroxide in water. The reaction mixture was washed with brine and the brine layer was re-extracted with DCM, the combined organic layers were washed with brine then dried over magnesium sulfate and evaporated to give 7 as a waxy yellow solid (29 mg, 48%). Anal.: m.p.: 109.6 – 112.3 °C; ^1H NMR (500 MHz, CDCl₃) δ 7.36 – 7.32 (m, 8H), 6.94 – 6.93 (m, 8H), 5.81 (s, 2H), 5.79 (s, 2H), 3.66 (s, 1H), 2.75 (t, J = 6.7 Hz, 2H), 1.87 (pent., J = 7.2 Hz, 2H), 1.76 (pent., J = 7.2 Hz, 2H), 1.53 – 1.48 (m, 4H), 1.01 (t, J = 7.0 Hz, 3H); ^13C (CDCl₃, 125 MHz) δ
144.9, 144.8, 144.2, 143.6, 125.2, 125.1, 123.7, 123.6, 116.1, 112.6, 98.15, 83.9, 79.2, 75.9, 52.0, 51.9, 31.4, 29.0, 28.7, 22.7, 19.8, 14.1; IR (DRIFT cm\(^{-1}\)) 3297, 3069, 3043, 3022, 2960, 2927, 2855, 2150, 1680, 1458, 1260, 1088, 1017; mass (ESI/APCI m/z) calculated for C\(_{44}\)H\(_{34}\)NH\(_4^+\) 580.3004, found 580.3023.

1.4.2.6. 6-((4-(3-(methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene 8: A solution of 8 mL diisopropyl amine in 16 mL THF is purged with argon in a 3 neck flask. After 1 hour, asymmetrical pentiptycene 7 (29 mg, 0.5 mmol), half-rotor 3 (31 mg, 0.06 mmol), bis(triphenylphospnene) palladium dichloride (3.5 mg, 0.005 mmol), and copper iodide (0.6 mg, 0.003 mmol) were added quickly to the purged solvents and the mixture was purged with argon for an additional half hour. The reaction mixture stirred at reflux for 12 hours under argon. The cooled reaction mixture was washed with saturated ammonium chloride, the ammonium chloride was extracted with DCM, the combined organic layers were washed with brine and dried over magnesium sulfate and evaporated under reduced pressure. The product was purified by preparatory TLC by 3 subsequent elutions with 80:20 hexane/DCM. The product 8 was isolated as an off-white solid (13 mg, 27%).

Anal.: m.p.: decomposes; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.1\) Hz, 2H), 7.64 (d, \(J = 8.1\) Hz, 2H), 7.40 – 7.26 (m, 19H), 6.98 (t, \(J = 2.0\) Hz, 1H), 6.96 – 6.93 (m, 9H), 6.85 (dd, \(J = 8.0, 2.5\) Hz, 1H), 5.83 (s, 2H), 5.82 (s, 2H), 3.79 (s, 3H), 2.76 (t, \(J = 6.7\) Hz, 2H), 1.88 (pent., \(J = 7.3\) Hz, 2H), 1.77 (pent., \(J = 7.3\) Hz, 2H), 1.56 – 1.50 (m, 4H), 1.01 (t, \(J = 7.0\) Hz, 3H); \(^{13}\)C (CDCl\(_3\), 125 MHz) \(\delta\) 159.4, 146.8, 145.1, 145.0, 144.9, 143.8, 143.7, 131.8, 131.6, 129.2, 129.0, 128.1, 127.0, 125.2 (2 carbons with coincident chemical shifts), 123.8, 123.8, 123.7, 123.1, 121.8, 115.9, 115.6, 113.7, 112.0, 98.3, 97.8, 96.0, 86.8, 84.8, 76.2, 56.3, 55.2, 52.3, 52.1, 31.6,
29.7, 28.8, 22.8, 20.0, 14.2; IR (DRIFT cm\(^{-1}\)) 3063, 6022, 2960, 2851, 1723, 1598, 1584, 1458, 1258, 1084, 1023; mass (ESI/APCI m/z) calculated for C\(_{72}H_{54}O^+\)NH\(_4^+\) 952.4518, found 952.4542.

1.4.2.7. 1,2-bis(4-(3-(methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethyne 10: A three neck flask containing 10 mL THF and 5 mL diisopropylamine was purged with argon for 1 hour. (1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene 3 (106 mg, 0.357 mmol), 1,2-bis(4-bromophenylethyne 9 (50 mg, 0.149 mmol), bis(triphenylphosphine)palladium dichloride (10.5 mg, 0.015 mmol), and copper iodide (1.5 mg, 0.008 mmol) were added to the flask and the reaction mixture was brought to reflux. The reaction mixture was refluxed for 1.5 hours then cooled to room temperature and quenched with saturated aqueous ammonium chloride. The aqueous layer was extracted 2 x with DCM. The organic fractions were combined, dried over magnesium sulfate and evaporated under vacuum. The product was purified by prep-TLC with a 70:30 hexanes/DCM eluent. The band containing 10 was extracted with copious DCM and dried under vacuum. 85 mg (74%) of the colorless solid product were recovered. Anal.: m.p. 205.1 – 206.7 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.43-7.4.39 (m, 8H), 7.28-7.19 (m, 22H), 7.17 (t, \(J = 8.0\) Hz, 2H), 6.86 (t, \(J = 2.1\) Hz, 2H), 6.83 (ddd, \(J = 0.8, 1.5, 7.8\) Hz, 2H), 6.74 (ddd, \(J = 0.7, 2.5, 8.2\) Hz, 2H), 3.68 (s, 1H); \(^{13}\)C (CDCl\(_3\), 500 MHz) \(\delta\) 159.5, 146.9, 145.2, 131.7, 131.6, 129.3, 129.1, 128.2, 127.1, 123.7, 122.8, 121.9, 115.7, 112.1, 97.8, 90.9, 85.0, 56.4, 55.3; IR (DRIFT cm\(^{-1}\)) 3053, 2958, 2835, 1598, 1579, 1484, 1446, 1433, 1292, 1245, 1053, 838, 698; mass (MALDI m/z) calculated for C\(_{58}H_{42}O_2\) 770.32, found 770.01.

1.4.3. Quantum Yield Determination

Quantum yields of compounds 1, 8, 10, and 4 were determined using anthracene, naphthalene and p-terphenyl as standards. At least six solutions of each analyte in methylecyclohexane were
prepared in a range of optical densities from 0 to 0.1 and degassed for 10 minutes with argon to remove oxygen. UV absorbance and fluorescence spectra were recorded for each solution and plots of integrated fluorescence intensity verses absorbance at the excitation wavelength were prepared for each analyte. The plots were fitted to a linear equation; the slope of each line is proportional to the fluorescence quantum yield of that compound, the absolute quantum yield is calculated from the slopes of the analyte and the standard and the known absolute quantum yield of the standard.  

$$\Phi_X = \Phi_{std.} \left( \frac{slope_X}{slopestd.} \right)$$  

Because each analyte absorbs and emits in a slightly different window, the three standards were picked to cover the entire range and their spectra and were checked against each other to confirm the robustness of the measurement; in the quantum yields reported have an error of ± 0.05 units.
### 1.5. Supplementary figures

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Figure 1.5.1. $^1$H-NMR (300 MHz, CDCl$_3$) spectrum of (3-(4-iodophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (3)
Figure 1.5.2. $^{13}$C-NMR (75 MHz, CDCl$_3$) spectrum of (3-(4-iodophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (3)
Figure 1.5.3. ATR-FTIR spectrum of (3-(4-iodophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (3)
Figure 1.5.4. $^1$H-NMR (300 MHz, CDCl$_3$) spectrum of (3-$(d_4$-4-bromophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene ($3-d_4$)
Figure 1.5.5. $^{13}$C-NMR (75 MHz, CDCl$_3$) spectrum of (3-$(d_4$-4-bromophenyl)-1-(3-methoxyphenyl)prop-2-yn-1,1-diyl)dibenzene (3-$d_4$)
Figure 1.5.6. ATR-FTIR spectrum of \(3-(d4-4\text{-bromophenyl})-1-(3\text{-methoxyphenyl})\text{prop-2-ynyl-1,1-diyl)dibenzene (3-}d_d\))
Figure 1.5.7. $^1$H-NMR (500 MHz, CDCl$_3$) spectrum of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (1)
Figure 1.5.8. $^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (1)
Figure 1.5.9. ATR-FTIR spectrum of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (1)
Figure 1.5.10. $^1$H-NMR (500 MHz, CDCl3) spectrum of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (1-$d_8$)
Figure 1.5.11. $^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (1-$d_8$)
Figure 1.5.12. ATR-FTIR spectrum of 6,13-bis(4,3-methoxyphenyl)-3,3-diphenylprop-1-
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Figure 1.5.13. $^1$H-NMR (500 MHz, CDCl$_3$) spectrum of 6-ethynyl-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (7)
Figure 1.5.14. $^{13}$C-NMR (125 MHz, CDCl3) spectrum of 6-ethynyl-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (7)
Figure 1.5.15. ATR-FTIR spectrum of 6-ethynyl-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (7)
Figure 1.5.16. $^1$H-NMR (500 MHz, CDCl$_3$) spectrum of 6-((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (8)
Figure 1.5.17. $^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of 6-((4-((3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis[[1,2]benzeno]pentacene (8)
Figure 1.5.18. ATR-FTIR spectrum of 6-((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (8)
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**Figure 1.5.22.** Arrhenius plot of phenylene flipping rate verses temperature, as determined by line-shape analysis.

**Figure 1.5.23.** Powder x-ray diffraction pattern of 6,13-bis((4-(3-(methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzono)pentacene (1), 6,13-bis((4-(3-(methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzono)pentacene (1-d8), and simulated powder x-ray diffraction pattern from single crystal structure of 1-d8.
Figure 1.5.24. TGA of crystals of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynl)-5,7,12,14-tetrahydro-5,14:7,12-bis[1,2]benzeno)pentacene (1). Loss of 23% of mass prior to decomposition is attributed to the loss of toluene from the crystal structure.

Figure 1.5.25. DSC of crystals of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynl)-5,7,12,14-tetrahydro-5,14:7,12-bis[1,2]benzeno)pentacene (1).
Figure 1.5.26. Emission spectra of solid samples of 1 obtained upon excitation at 380 nm and 405 nm.

1.6. Computation details:

Computations of the ground and excited state energies of the model chromophore (see Figure 5) were performed on the commercially available Spartan '02 program at the B3LYP/6-31G(d) level of theory. The ground and excited state energies are computed for the planar chromophore, for conformations with the central phenylene at torsion angles of 30°, 60°, and 90°, and for a conformation with a terminal phenylene at a 90° torsion angle.

**Planar chromophore:**

SCF total energy:  -998.9218750 hartrees

TDFT Energy:  -998.8071096 hartrees First Excited State

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Central phenylene at 30° torsion angle:

SCF total energy: -998.9215750 hartrees

TDFT Energy: -998.8036165 hartrees First Excited State

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2  C  0.199236  -1.183818  7.721628
Central phenylene at 60° torsion angle:

SCF total energy: -998.9209969 hartrees

TDFT Energy: -998.7948989 hartrees First Excited State

1  H   0.556366   -2.076383   8.269629
Central phenylene at 90° torsion angle:

SCF total energy: -998.9206070 hartrees

TDFT Energy: -998.7887699 hartrees First Excited State
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1.7. References


16. Crystallographic parameters of 1: Empirical formula at 100(2) K: C$_{94}$H$_{62}$O$_2$•4(C$_7$H$_8$)$_4$, formula weight: 1591.97, space group: P-1, $Z = 1$, $a = 10.562(2)$ Å, $b = 12.190(2)$ Å, $c = 18.671(4)$ Å, $\alpha = 95.819(2)^\circ$, $\beta = 105.130(2)^\circ$, $\gamma = 103.746(3)^\circ$, $V=2219.6(7)$ Å$^3$, $R = 7.26\%$, $wR = 17.22\%$.


23 The program Express 1.0 from the Vold lab is also available on the web. Vold, R. L.; Hoatson, G. L. *J. Magn. Reson.* **2009**, *198*, 57.


Chapter 2

Synthesis, photophysical characterization, and preliminary electro-optic studies of a Crystalline Phenyleneethynylene Molecular Compass
2.1 Introduction

One of the long-term goals of the molecular gyroscopes project is the development of crystalline materials with electro-optic properties that are made possible by the freely rotating dipoles that are in-turn made possible by the molecular gyroscope architecture.\(^1\) To this end, a number of molecular gyroscopes with dipolar rotators have been synthesized. These molecules mimic the functionality of macroscopic compasses in that their dipolar rotators, like a compass’s needle, are addressable by magnetic or electric fields. Therefore, this class of molecules has been termed “molecular compasses”. Molecular compasses have primarily used the reliable trityl-stator architecture (see in figure 3.1.1, left),\(^2\) however compasses taking advantage of the newly developed steroidal-stator have also been developed (figure 3.1.1, right).\(^3\) Molecular compasses often crystalize isomorphically with their non-polar analogues, which posses simple phenylene rotators. this is the case for A-E, H-J; however sometimes the perturbations caused by the additional polar substituents prevent crystallization (F and G), or result in polymorphism (K and L). As with nonpolar rotators, the solid state rotation of molecular compasses can be characterized by variable temperature solid state \(^2\)H NMR if the rotator is deuterated and/or by \(^1\)C CP-MAS NMR if the rotator carbons’ chemical shifts are well separated from other non-rotating carbon shifts in the molecule. Unique to molecular compasses and other dipolar rotor molecules is rotational characterization by dielectric spectroscopy, in which alternating current of different frequencies is applied to the material, when the current frequency is equal to the rotation frequency, a loss peak is detected; by performing this experiment over a range of frequencies and temperatures the barrier to rotation can be calculated.\(^4\)
Figure 2.1.1. Examples of molecular compasses: molecules that possess bulky stators (blue) and a dipolar rotator (red) that has freedom of rotation within the crystal lattice.

In the search for molecular compasses with electro-optic properties, architectures that incorporate an extended chromophore are intriguing candidates. Chapter 1 describes the rotational dynamics and photophysical properties of a molecular gyroscope in which two phenylene rotators make up part of a phenyleneethynylene chromophore. This system has the advantage of a visible wavelength fluorescence emission and a barrier to phenylene rotation (9.0 kcal/mol), which compares favorably with the rotation barriers seen in previous gyroscopes and compasses (14-15 kcal/mol for D in figure 3.1.1). A striking ~ 35 nm blue shift in fluorescence emission was demonstrated when the phenylene rotation is restricted in frozen solutions. By incorporating a dipolar rotator into this system we hope to take advantage of its already established favorable properties while adding the additional functionality of rotators that are addressable by an electric or magnetic field. Figure 2.1.2 shows the target molecular compass with bis-2,3-difluorophenylene rotators 1-f; the variability of the conjugation length of the phenyleneethynylene core with phenylene rotation is highlighted.
2.2. Results and Discussion

2.2.1. Synthesis and Spectroscopic Characterization

Synthesis of the fluorinated molecular compasses was analogous to the synthesis of non-fluorinated parent compound that was recently reported by our group (Figure 2.2.1.1). (1-(3-methoxyphenyl)prop-2-yn-1,1-diyl)dibenzene 2 was prepared as described by Commins and Garcia-Garibay; diethynlpentiptycene 4 was prepared as described by Yang and Swager. 2, 3-Difluoro-1,4-diiodobenzene was prepared from 1,2-difluorobenzene as described by Rausis and Schlosser. Trityl alkyne 2 is coupled with the appropriate aryl halide to give the half rotor 3-f_1 or 3-f_2; 4 equivalents of aryl halide are used to minimize the formation of the symmetrical doubly coupled product. After the reaction is complete, the excess aryl halide is easily recovered in high yields and purity. The half rotor 3-f_1 or 3-f_2 is then subjected to a second Sonogashira reaction with diethynlpentiptycene 4 to give the full rotator 1-f_2 or 1-f_4. This time, 3 equivalents of half

**Figure 2.1.2.** Target molecular compass “1-f_4” with the variable conjugation length of the phenyleneethynylene chromophore highlighted.
rotor $3\text{-f}_1$ or $3\text{-f}_2$ are used to ensure that the reaction goes to completeness; the excess half rotor can also be recovered in high yields and purity.

![Chemical structure](image)

Figure 2.2.1.1. The synthesis of fluorinated molecular compasses $1\text{-f}_2$ and $1\text{-f}_4$. The fluorine atom occupies position 27 or 28 or both.

The synthesis of $1\text{-f}_4$ proceeded smoothly in moderate yields, however the synthesis of full rotator $1\text{-f}_2$ presented more challenges, since three regioisomers are possible arising from the combination of the two possible regioisomers of the half rotator $3\text{-f}_1$. Our initial Sonogashira coupling yielded a 3 to 1 mixture of the 4-bromo-3-fluorophenyl and 4-bromo-2-fluorophenyl isomers of the half rotator $3\text{-f}_1$. This selectivity is similar to what was found by Reimann and
Langer in their study of site-selective Sonogashira reactions of 1,4-dibromo-2-fluorobenzenes: the less sterically hindered and more electron deficient position \textit{meta} to the fluorine substituent is preferred. These two isomers are not separable by column chromatography and are taken forward to the next step. Analogous selectivity is observed in the full rotator forming reaction, that is, the minor 4-bromo-2-fluorophenyl product is significantly more reactive than the major 4-bromo-3-fluorophenyl product; the product ratios for this reaction are shown in figure 2.2.1.2. This difference in reactivity meant that the excess \textbf{3-i}, which can be recovered from the coupling reaction is enriched in the less reactive 4-bromo-3-fluorophenyl isomer; the recovered ratio is 90 to 10. This recovered material was subjected to Sonogashira coupling conditions once more and as expected gave a different product ratio for \textbf{1-f} as shown in figure 2.2.1.2. It should be possible to achieve high regiopurity by continuing the process iteratively however in this work no subsequent iterations were attempted. It was possible to deduce the ratios of the product isomers by examining the \textsuperscript{1}H and \textsuperscript{19}F NMR spectra; the values from the NMR studies were corroborated by the crystal structure.
Figure 2.2.1.2. Starting material and product regioisomer distributions of two subsequent batches of 1-f₂.

The \(^1\)H and \(^{13}\)C NMR spectra of 1-f₂, 1-f₁, 3-f₂, and 3-f₁ are generally analogous to their non-fluorinated analogues, which were discussed in chapter 1. As expected the main differences occur on or near the fluorinated rotator. In the half rotors 3-f₂ and 3-f₁ the phenylene rotator protons H₁₆ and H₁₇ are shifted upfield from their positions in the non-fluorinated analogue; in 3-f₂ both signals appear as doublet of doublet of doublets being coupled to each other as well as both fluorine atoms, in 3-f₁ only H₁₆ is a doublet of doublet of doublets being coupled to H₁₇, F₂₇, and H₂₈, while H₁₇ is a doublet of doublets and does not couple with H₂₈. In full rotors 1-
f4 and 1-f2 only one rotator proton is distinct from the multitude of other aromatic signals: H17. It appears as a doublet of doublet of doublets, being coupled to H16, F27, and F28 in 1-f4; in 1-f2 it is only coupled to H16 and F27. Outside of the phenylene rotators, the fluorine atoms appear to exert a through-space effect on two other sets of protons: the bridgehead protons of the pentiptycene moiety H23 are shifted downfield relative to their position in 1 when a fluorine atom is present in position 27, and H7 is shifted downfield when a fluorine atom is present in position 28. In 1-f4 both of these shifts occur. In 1-f2 these shifts were used for the identification and quantification of the regioisomers present. The 13C NMR for these molecules is distinguished by distinctive C-F coupling for up to 4 bonds away. The chemical shifts and C-F coupling constants for the phenylene rotators and adjacent alkyne carbons of both fluorinated and non-fluorinated molecular gyroscopes are shown in table 2.2.1.1. The C-F coupling constants were in reasonably good accord with those reported for other fluorinated aromatic compounds.10 The long range coupling constants were effected by whether an alkyne substituent was present between the coupled carbon and fluorine or not; if a substituent was present the coupling constant was lower than if only hydrogen was present; a similar phenomenon was previously reported for substituted fluorobenzene derivatives.11

Table 2.2.1.1. 13C-NMR chemical shifts and splitting for the phenylene rotator carbons in fluorinated and non-fluorinated molecular gyroscopes. See figures 2.2.1.1. and 2.2.1.2 for structures and numbering of fluorinated structures. For non-fluorinated structures, R from figure 3.2.1.1 = H.

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<td>J = 3.3</td>
<td></td>
</tr>
<tr>
<td>C17</td>
<td>137.4</td>
<td>133.1</td>
<td>128.45</td>
<td>134.03</td>
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<td>127.</td>
<td>132.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J = 4.4</td>
<td>J = 3.5</td>
<td>J = 1.8</td>
<td>J = 4.0</td>
<td>J = 1.6</td>
<td></td>
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</tbody>
</table>
2.2.2. Crystal Structure

Our initially targeted molecular compass 1-f₄ proved impossible to crystalize. Due to low solubility, the solvent choices were limited to chlorinated and aromatic solvents; combinations of dichloromethane or chloroform or carbon tetrachloride with benzene, toluene, or p-xylene in various proportions were tried. In all solvent systems, the solids recovered were amorphous by PXRD. This result was perplexing because the non-fluorinated analogue of 1-f₄ is highly crystalline and it is counterintuitive that such a small structural change would make such a large difference to crystallinity. To explore the origins of this difference and in an attempt to produce a fluorinated molecular rotor that could be crystalized, the bismonofluor analogue 1-f₂ was synthesized. Diffraction quality crystals of 1-f₂ were readily obtained by the slow evaporation of a saturated solution in 1:4 toluene/dichloromethane. The resulting crystal structure was isomorphous with the non-fluorinated analogue 1; the crystallographic parameters of both compounds are displayed in Table 2.2.2.1 and Figure 2.2.2.1 shows an overlay of both structures. This packing arrangement is ideal for solid-state functionality because the molecular long axes are packed in a parallel manner (see chapter 1), meaning that the rotor dipoles are also parallel.
Table 2.2.2.1. Crystallographic parameters of 1 and 1-f₂

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nonfluorinated 1</th>
<th>Bismonofluoro 1-f₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₉₄H₆₂O₂•4(C₇H₈)</td>
<td>C₉₄H₆₀F₂O₂•4(C₇H₈)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1591.97</td>
<td>1627.95</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P1</td>
<td>P1</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Dimensions, mm</td>
<td>0.2 x 0.1 x 0.05</td>
<td>0.2 x 0.1 x 0.05</td>
</tr>
<tr>
<td>Color, morphology</td>
<td>colorless platelets</td>
<td>colorless platelets</td>
</tr>
<tr>
<td>Temperature, K</td>
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<td>100(2)</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
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<td></td>
</tr>
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<td>10.6744(3)</td>
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<tr>
<td>b, Å</td>
<td>12.190(2)</td>
<td>12.1480(4)</td>
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<tr>
<td>c, Å</td>
<td>18.671(4)</td>
<td>18.5822(6)</td>
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<tr>
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<tr>
<td>β, deg</td>
<td>105.130(2)</td>
<td>105.435(2)</td>
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<td>2221.74(12)</td>
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<tr>
<td>R</td>
<td>7.26%</td>
<td>6.24%</td>
</tr>
<tr>
<td>w2R</td>
<td>17.22%</td>
<td>17.38%</td>
</tr>
<tr>
<td>Packing coefficient</td>
<td>0.709</td>
<td>0.712</td>
</tr>
</tbody>
</table>
Figure 2.2.2.1. An overlay of structures 1 (purple) and 1-f₂ (green) at 100 K, showing the isomorphous packing of these two compounds.

As we had hoped examination of the structure of the bismonofluoro compound 1-f₂ provided insight into the reasons for the non-crystallinity of 1-f₄, figure 2.2.2.2 shows 1-f₂ with close contacts highlighted as red lines. As can be seen, each phenylene rotator has two close contacts with neighboring molecules (shown in red), one on each side of the rotator. These close contacts range between 2.687 Å and 2.825 Å, approximately the sum of the van der Waals radii of hydrogen and carbon. If one of these hydrogen atoms were replaced with fluorine atom, the contact would be about 0.8 Å: shorter than the sum of the van der Waals radii. Thus, while one fluorine atom per rotator can be accommodated within the crystal lattice, a second fluorine atom ortho to the first will not fit. Of course, it is theoretically possible for the bisdifluoro compound 1-f₄ to crystallize as some other polymorph, however we were unable to achieve this. It should also be noted that the fluorine occupancy from the crystal structure is in excellent accord with the occupancy deduced from NMR studies: the site closer to the pentiptycene (on C27) has 83.3% fluorine occupancy, the site closer to the trityl group (on C28) has 16.2% fluorine occupancy, the numbers from the NMR studies are 84.3% and 15.7% respectively. Due to the symmetry within
the crystal lattice each phenylene rotator is equivalent and therefore it was only possible to get a F27 to F28 occupancy ratio rather than explicit data about each of the three isomers present.

Figure 2.2.2.1-f2 within the crystal lattice, showing close contacts in red.

The packing coefficient (see table 2.2.2.1) is a measure of free volume within a crystal; it is defined as the van der Waals volume of the molecules in the unit cell divided by the total volume in the unit cell.\textsuperscript{12} Our group has previously shown that rotational dynamics in molecular gyroscopes increase as packing coefficients decrease.\textsuperscript{13} It was calculated here as described previously by our group using van der Waals volumes from Bondi\textsuperscript{14} and Gavezzotti\textsuperscript{15}. The packing coefficient for 1-f2 is slightly higher than for 1; this is to be expected since the unit cells are nearly identical except for the inclusion of two additional fluorine atoms. Nonetheless, it is still lower than the values for some other molecular gyroscopes that have been shown to rotate at room temperature.

2.2.3. Photophysical studies

The photophysics of the non-fluorinated molecular gyroscope 1 have been discussed extensively in chapter 1. In short, the excitation and emission spectra of 1 are dependent on phenylene torsion angle, when the phenylene groups are planar, the emission spectrum is red-
shifted relative to its value when phenylene groups are twisted. Based on those studies, we concluded that the majority of emission in room temperature solutions is from the planar rotamer, however in frozen solutions emission from the twisted rotamer can be observed because planarization during the excited state lifetime is prevented. The fluorinated molecular compasses are expected to have very similar properties. At room temperature, the fluorinated compasses do behave very much like their non-fluorinated analogue, the fluorescence excitation and emission spectra of all three compounds are shown in figure 2.2.3.1, and their photophysical data are presented in table 2.2.3.1. There is a very small red shift in fluorescence emission as additional fluorine atoms are added to the structure, and the 0-0 absorbance band at ~370 nm becomes stronger relative to the absorbance band at ~350 nm. The quantum yield of fluorescence is smaller for 1-f rotor than for the non-fluorinated rotor, while the fluorescence lifetime increases with increasing fluorine content. While the relationship between fluorination and the photophysical properties of fluorophores is complex, a red shift upon fluorination is frequently observed. Fluorination generally decreases the quantum yield of fluorescence, though an increase in quantum yields was observed in fluorinated meso phenyl borondipyrromethene derivatives. The effect of fluorination on fluorescence lifetime is similarly variable, depending on the degree and location of fluorination. Interestingly, in a study of the photophysics of the most analogous set of fluorinated and non-fluorinated phenyleneethynlenes we were able to find, the effect of fluorination was the opposite of what we observe here, with a blue shift in fluorescence emission and an increase in quantum yield upon fluorination.
Table 2.2.3.1. Fluorescence emission, absorbance, quantum yield, and lifetimes of fluorinated and non-fluorinated molecular gyroscopes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{0,0,fl} (nm))</th>
<th>(\lambda_{0,0,abs} (nm))</th>
<th>(\Phi_{fl})</th>
<th>(\tau_{fl} (ns))</th>
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<tbody>
<tr>
<td>1-f(_4)</td>
<td>382</td>
<td>373</td>
<td>0.56</td>
<td>1.03</td>
</tr>
<tr>
<td>1-f(_2)</td>
<td>381</td>
<td>371</td>
<td>--</td>
<td>0.65</td>
</tr>
<tr>
<td>1</td>
<td>376</td>
<td>369</td>
<td>0.85</td>
<td>0.56</td>
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</table>

Figure 2.2.3.1. Fluorescence excitation and emission (solid), and UV-Vis absorbance (dashed) spectra of fluorinated and non-fluorinated molecular gyroscopes.

Perhaps the most interesting aspect of the photophysical behavior of non-fluorinated molecular gyroscope 1 is its variable emission in frozen solution, discussed in chapter 1. This phenomenon is observed as a blue shift in fluorescence emission in frozen solutions when shorter excitation
wavelengths are used. We were curious about whether this phenomenon would be conserved upon fluorination. We found that while this property is still present, it decreases with increasing fluorine content (figure 2.2.3.2). In the non-fluorinated molecular gyroscope 1, the onset of emission at short excitation wavelengths is 334 nm and the peak emission is at 355 nm. In 1-f₂, the onset of emission occurs at 349 nm, in 1-f₄ it occurs at 358 nm. In both fluorinated compasses the peak emission in frozen solutions is never shifted from the room temperature value. This loss of fluorescence variability in frozen solution upon fluorination of the phenylene rotator would seem to indicate that the twisted rotamer is less prevalent in fluorinated compasses than in non-fluorinated gyroscopes. It is difficult to imagine a steric justification for this change in rotamer distribution; if anything the added bulk of a fluorine atom on the phenylene rotator ought to increase the prevalence of the twisted rotamer. From an electronic standpoint, the presence of fluorine atoms arguably increases the conjugation of the phenyleneethynylene chromophore and would therefore increase the preference for planarity. To explore these intuitions, calculations were performed using density functional theory at the B3LYP 6-13G(d) level of theory on a simplified fluorinated chromophore analogous to the simplified chromophore used for calculations in chapter 1. The distribution of rotamers in frozen solutions should be based on the ground state energy differences between the rotamers. We found that in the non-fluorinated chromophore the planar rotamer is 0.8 kcal/mol lower in energy than the twisted rotamer (in which each phenylene is at a 90° torsion angle to its neighbors). In the bis-difluorinated chromophore of 1-f₄, the energy difference is 1.0 kcal/mol. These values would lead to a nearly 4-fold difference in the populations of the twisted chromophores at 77K; in 1 they should make up 0.53% of the population and in 1-f₄ they are 0.14% of the population. These calculations provide support to the notion that the twisted chromophore is less prevalent in frozen solutions of
fluorinated molecular compasses than in frozen solutions of the non-fluorinated molecular gyroscopes. Nonetheless it seems unlikely that the low percentage of twisted chromophore calculated for 1 at 77K could completely obscure the longer wavelength emission of the more prevalent planar rotamer in that system, therefore these numbers are best viewed as qualitative support only.

![Figure 2.2.3.2.](image)

**Figure 2.2.3.2.** Molecular compass solutions (1-f4 top, 1-f2 bottom) in toluene, at 77K (colored lines) and at room temperature (black line). Fluorescence emission wavelength varies with excitation wavelength at 77K but is constant at room temperature.

### 2.2.4. Optical Kerr effect

Molecular compasses 1-f2 and 1-f4 are expected to have electro-optical properties in the solid state as a result of their freely rotating dipolar fluorophenylene groups. In the absence of an
electric field, the rotating dipoles are expected to have a random orientation with no net dipole moment, however in the presence of a strong field some degree of alignment should occur. This field induced net dipolar alignment will transform these materials from centrosymmetric to non-centrosymmetric allowing for switchable second harmonic generation.\textsuperscript{22} As an investigation of this possibility, 1-f\textsubscript{2} and 1-f\textsubscript{4} were tested as optical Kerr gate materials. In the optical Kerr experiment, a strong laser pulse (800 nm in this case) generates an electric field within the sample and temporarily induces birefringence as the dipolar rotators align with the field.\textsuperscript{23} In our preliminary tests, 11 mg/mL solutions of 1-f\textsubscript{2} and 1-f\textsubscript{4} in chloroform were drop cast onto a glass substrate and their induction of birefringence on white light was assessed. As of this writing, the induced birefringence signal from the molecular compass films has been indistinguishable from the birefringence induced in the glass substrate itself.\textsuperscript{24} It is plausible that optical Kerr birefringence signals might be generated in single crystals of 1-f\textsubscript{2} however so far small crystal sizes have made these experiments impractical.

2.3. Conclusion

Molecular compasses 1-f\textsubscript{2} and 1-f\textsubscript{4} have been synthesized. These are the first examples of molecular gyroscopes that incorporate both the phenyleneethynylene chromophore and dipolar rotators. Synthesis of 1-f\textsubscript{4} was straightforward, however it was not possible to obtain a crystalline sample of this material under any of the conditions we attempted. 1-f\textsubscript{2} was a more challenging synthetic goal because three chromatographically inseparable regioisomers are possible. Ultimately, a 70\% to 28\% to 2\% mixture of these isomers was characterized and taken on to further experiments. 1-f\textsubscript{2} was successfully crystalized and is isomorphous with its nonpolar parent compound 1 (chapter 1); this packing arrangement of parallel molecular long axes makes 1-f\textsubscript{2} an ideal candidate for solid-state electro-optic effect studies. Frozen solutions of 1-f\textsubscript{2} and 1-f\textsubscript{4}
were tested for variable fluorescence; they were found to experience a smaller range of fluorescence emission wavelengths than their nonpolar parent compound 1; in-fact, the range of possible fluorescence emission wavelengths went down as the fluorine content went up, this may be due to differences in the ground state rotamer distribution of the fluorinated compounds. Despite apparently possessing ideal qualities for switchable electro-optic materials, attempts to observe the optical Kerr effect in thin films of 1-f$_2$ and 1-f$_4$ have been unsuccessful so far.

2.4. Experimental

2.4.1. Synthesis and Characterization

2.4.1.1. Synthesis of (3-(2,3-difluoro-4-iodophenyl)-1-(3-methoxyphenyl)prop-2-yn-1,1-diyl)dibenzene (3-f$_2$).

Trityl alkyne 2 (1.00 g, 3350 μmol), 2,3-difluoro-1,4-diiodobenzene (4.90 g, 13.41 mmol), 100 mL tetrahydrofuran, and 50 mL diisopropylamine were placed in a three-neck flask equipped with a magnetic stir bar and a condenser; argon was bubbled through the solution for one hour. Bis(triphenylphosphine)palladium dichloride (222 mg, 335 μmol), copper iodide (32 mg, 167 μmol) were added and the argon purging was continued for an additional 30 minutes. The mixture was stirred overnight at reflux. The reaction was quenched with saturated ammonium chloride, the aqueous layer was extracted with dichloromethane and the combined organic layer was dried over magnesium sulfate. The crude product was purified by column chromatography with an eluent gradient from 80:20 to 60:40 hexanes/DCM; the excess 2,3-difluoro-1,4-diiodobenzene (3.52 g) was recovered in high purity and 3 was isolated as a colorless solid (1.29 g, 72%): mp 147.3-149.7; $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.44 (ddd, J = 8.3, 5.6, 1.9 Hz, 1H), 7.32-7.28 (m, 10H), 7.22 (t, J = 8.0 Hz, 1H), 7.01 (ddd, J = 8.3, 6.3, 1.9 Hz, 1H), 6.93 (t, J = 2.1 Hz, 1H), 6.85 – 6.80 (m, 2H), 3.75 (s, 3H); $^{19}$F NMR (CDCl$_3$, 282 MHz) δ -116.3 (ddd, J = 22.2,
5.5, 1.8 Hz, 1F), -130.8 (ddd, J = 22.2, 6.2, 1.9 Hz, 1F); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 159.4, 150.7 (dd, J = 257.5, 15.8 Hz), 150.6 (dd, J = 246.6, 13.4 Hz), 146.1, 144.4, 133.1 (d, J = 4.4 Hz), 129.3, (d, J = 18.6 Hz), 129.1, 129.0, 128.2 (d, J = 4.2 Hz), 128.1, 127.5, 127.1, 121.7, 115.3, 112.3, 103.4 (d, J = 4.0 Hz), 82.1 (d, J = 22.5 Hz), 56.4, 55.2; IR (DRIFT cm$^{-1}$) 3058, 3026, 2942, 2834, 1599, 1580, 1485, 1474, 1447, 1287, 1244, 1216, 1065, 1043, 868, 810, 778, 753, 695; mass (DART m/z) positive mode: 537.05214 calculated for C$_{28}$H$_{19}$F$_2$IO+H, 537.0506 found, negative mode: 536.0454 calculated for C$_{28}$H$_{19}$F$_2$IO, 536.0433 found.

2.4.1.2. Synthesis of 6,13-bis((2,3-difluoro-4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (1-f$_4$).

Difluoro half-rotator 3-2f (1.01 g, 1880 μmol), bis(triphenylphosphine)palladium dichloride (75 mg, 107 μmol), copper iodide (6 mg, 31 μmol), 100 mL tetrahydrofuran, and 100 mL diisopropylamine were placed in a three-neck flask equipped with a magnetic stir bar, a condenser and an addition funnel; argon was bubbled through the solution for 1 hour to purge oxygen. Diethynylpentptycene 4 (300 mg, 627 μmol) was suspended in 100 mL tetrahydrofuran in the addition funnel and purged with argon for 1 hour. The half-rotator and catalyst solution was brought to a gentle reflux and the diethynylpentptycene suspension was slowly added, dropwise over 3 hours; the reaction mixture was allowed to reflux overnight. The reaction was quenched with saturated ammonium chloride, the aqueous layer was extracted with dichloromethane and the combined organic layer was dried over magnesium sulfate. The crude product was purified by column chromatography, with an 80:20 to 60:40 hexanes:dichloromethane eluent, giving 1 as a colorless solid with strong violet fluorescence (389 mg, 300 μmol, 48%). Mp: decomposes; $^1$H-NMR (CDCl$_3$, 300 MHz) δ 7.48 (ddd, J = 8.2, 5.9, 1.4 Hz, 2H), 7.42-7.28 (m, 32H) 7.03 (t, J = 2.0 Hz, 2H), 6.98 (dd, J = 5.3, 3.1 Hz, 8H), 6.93
- 6.86 (m, 4H), 5.91 (s, 4H), 3.81 (s, 6H); $^{19}$F NMR (CDCl$_3$, 282 MHz) δ -133.8 (ddd, $J = 21.0, 6.0, 1.3$ Hz, 2F), -134.1 (ddd, $J = 21.0, 6.2, 1.2$ Hz, 2F); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 159.5, 151.6 (dd, $J = 258.2, 17.9$ Hz, 2C), 151.3 (dd, $J = 249.4, 11.7$ Hz, 2C), 146.1, 144.6, 144.5, 144.4, 129.2, 129.0, 128.2, 127.8 (d, $J = 4.0$ Hz, 2C), 127.1, 127.0 (d, $J = 4.0$ Hz, 2C), 125.4, 123.9, 121.8, 115.3, 114.8 (d, $J = 13.8$ Hz, 2C), 114.6, 113.8 (d, $J = 12.6$ Hz, 2C), 112.4, 104.3 (d, $J = 3.8$ Hz, 2C), 92.8 (d, $J = 3.6$ Hz, 2C), 89.2 (d, $J = 4.1$ Hz, 2C), 77.6 (d, $J = 4.3$ Hz, 2C), 56.6, 55.2, 52.2; IR (DRIFT cm$^{-1}$) 3062, 3022, 2964, 2932, 2834, 1603, 1579, 1486, 1471, 1459, 1448, 1433, 1380, 1308, 1288, 1249, 1234, 1178, 1049, 822, 752, 697, 674; mass (DART m/z) positive mode: 1295.4446 calculated for C$_{94}$H$_{58}$F$_4$O$_2$+H, 1295.4412 found, negative mode: 1294.4317 calculated for C$_{94}$H$_{58}$F$_4$O$_2$, 1294.4378 found.

2.4.1.3. Synthesis of (3-(4-bromo-3-fluorophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene + (3-(4-bromo-2-fluorophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (3-f$_1$).

Trityl alkyne 2 (400 mg, 1.34 mmol), 1,4-dibromo-2-fluorobenzene (1.36 g, 5.36 mmol), 40 mL tetrahydrofuran, and 20 mL diisopropylamine were placed in a three-neck flask equipped with a magnetic stir bar and a condenser; argon was bubbled through the solution for one hour. Bis(triphenylphosphine)palladium dichloride (94 mg, 134 μmol), copper iodide (13 mg, 67 μmol) were added and the argon purging was continued for an additional 30 minutes. The mixture was stirred overnight at reflux. The reaction was quenched with saturated ammonium chloride, the aqueous layer was extracted with dichloromethane and the combined organic layer was dried over magnesium sulfate. The crude product was purified by column chromatography with an eluent gradient from 80:20 to 70:30 hexanes/DCM; 3-f$_1$ was isolated as a colorless solid (277 mg, 43%). The product is an inseparable 3 to 1 mixture of both regioisomers; 4-bromo-3-
fluorophenyl is the major product. Anal: mp 99.8 – 100.2 °C; (3-(4-bromo-3-fluorophenyl)-1-(3-methoxyphenyl)prop-2-yn-1,1-diyl)dibenzene: 1H NMR (CDCl3, 300 MHz) δ 7.49 (dd, J = 8.2, 7.2 Hz, 1H), 7.32-7.21 (m, 12H), 7.16 (ddd, J = 8.2, 1.8, 0.7 Hz, 1H), 6.87 (t, J = 1.6 Hz, 1H), 6.86-6.80 (m, 2H), 3.73 (s, 3H); 19F NMR (CDCl3, 282 MHz) δ -106.9 (ddd J = 9.0, 7.2, 0.6 Hz, 1F); 13C NMR (CDCl3, 125 MHz) δ 159.3, 158.6 (d, J = 248.0 Hz, 1C), 146.3, 144.7, 133.3, 129.0, 128.9, 128.5 (d, J = 3.5 Hz, 1C), 128.1, 127.0, 124.5 (d, J = 8.7 Hz, 1C), 121.7, 119.3 (d, J = 21.3 Hz, 1C), 115.5, 111.9, 109.1 (d, J = 21.0 Hz, 1C), 97.6, 83.1 (d, J = 2.5 Hz, 1C), 56.1, 55.1; (3-(4-bromo-2-fluorophenyl)-1-(3-methoxyphenyl)prop-2-yn-1,1-diyl)dibenzene 1H NMR δ (CDCl3, 300 MHz) 7.34-7.21 (m, 14H), 6.96 (t, J = 2.1 Hz, 1H), 6.88 – 6.80 (m, 2H), 3.75 (s, 3H); 19F NMR (CDCl3, 282 MHz) δ –107.08 (dd J = 8.5, 7.6 Hz, 1F); 13C NMR (CDCl3, 125 MHz) 162.7 (d, J = 255.8 Hz, 1C), 159.3, 146.3, 144.6, 134.0 (d, J = 1.8, 1C), 129.1, 128.9, 128.0, 127.2 (d, J = 3.6 Hz, 1C), 127.0, 122.2 (d, J = 8.9 Hz, 1C), 121.7, 119.1 (d, J = 21.5 Hz, 1C), 115.3, 112.2, 111.3 (d, J = 16.0 Hz, 1C), 102.0 (d, J = 3.1 Hz, 1C), 77.8, 56.4, 55.1; IR (DRIFT cm−1) 3083, 3058, 3024, 2928, 2851, 2836, 1597, 1582, 1555, 1484, 1476, 1446, 1433, 1403, 1312, 1290, 1242, 1184, 1154, 1137, 1047, 1024, 868, 819, 780, 753, 722, 695; mass (DART m/z) positive mode: 471.07543 calculated for C28H20BrFO+H, 471.07590 found.

2.4.1.4. Synthesis of 6,13-bis((2-fluoro-4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (1-f2).

Fluorinated half-rotator 3-f1 (502 mg, 1070 µmol), bis(triphenylphosphine)palladium dichloride (25 mg, 35 µmol), copper iodide (3 mg, 18 µmol), 100 mL tetrahydrofuran, and 100 mL diisopropylamine were placed in a three-neck flask equipped with a magnetic stir bar, a condenser and an addition funnel; argon was bubbled through the solution for 1 hour to purge oxygen. Diethynylpentopycine 4 (170 mg, 355 µmol) was suspended in 100 mL tetrahydrofuran
in the addition funnel and purged with argon for 1 hour. The half-rotator and catalyst solution was brought to a gentle reflux and the diethynylpentiptycene suspension was slowly added, dropwise over 3 hours; the reaction mixture was allowed to reflux overnight. The reaction was quenched with saturated ammonium chloride, the aqueous layer was extracted with dichloromethane and the combined organic layer was dried over magnesium sulfate. The crude product was purified by column chromatography, with an 80:20 to 60:40 hexanes:dichloromethane eluent, giving 1-f₂ as a colorless solid with strong violet fluorescence (245 mg, 55%). Anal.: mp: decomposes; ¹H NMR (CDCl₃, 300 MHz) 7.71 (dd, J = 7.8, 7.5 Hz, 2H), 7.45 – 7.29 (m, 34H), 6.98 – 6.85 (m, 14H), 5.93 (s, 4H), 3.79 (s, 6H); ¹³F NMR (CDCl₃, 282 MHz) -109.59 (dd, J = 9.6, 7.3 Hz, 2F); ¹³C NMR (CDCl₃, 125 MHz) 162.6 (d, J = 252.0 Hz), 159.4, 146.5, 144.8, 144.7, 144.2, 132.8 (d, J = 1.6), 129.1, 129.0, 128.2, 127.6 (d, J = 3.3), 127.1, 125.3, 123.9, 123.9 (d, J = 14.8), 121.8, 118.7 (d, J = 22.4), 115.6, 114.7, 112.0 (d, J = 16.0), 112.0, 98.9, 91.9 (d, J = 3.3), 90.2, 83.8 (d, J = 2.8), 56.3, 55.2, 52.2; IR (DRIFT cm⁻¹) 3061, 3022, 2968, 1598, 1580, 1548, 1488, 1458, 1447, 1413, 1381, 1290, 1248, 1182, 1041, 879, 824, 753, 696; mass (MALDI m/z) 1258.456136 calculated for C₉₁H₆₀F₂O₂, 1258.0971 found.
2.5. Supplementary Figures

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<th>CONTENT</th>
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</tbody>
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\[(3-\text{(4-bromo-3-fluorophenyl)-1-}(3\text{-methoxyphenyl})\text{prop-2-ynyl-1,1-diyl})\text{dibenzene} + \]

\[(3-\text{(4-bromo-2-fluorophenyl)-1-}(3\text{-methoxyphenyl})\text{prop-2-ynyl-1,1-diyl})\text{dibenzene (3-f)}\]
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(3-(4-bromo-3-fluorophenyl)-1-(3-methoxyphenyl)prop-2-yn-1,1-diyl)dibenzene +

(3-(4-bromo-2-fluorophenyl)-1-(3-methoxyphenyl)prop-2-yn-1,1-diyl)dibenzene (3-f$_1$)
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Figure 2.5.12. ATR-FTIR spectrum of 6,13-bis((2-fluoro-4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (1-f₂)
2.6. References


21 The Boltzmann distribution: \( N_1/N_2 = e^{-(E_1-E_2)/RT} \) is used to calculate the ratios.


24 Optical Kerr experiments were performed by Jagannada Challa, working under Professor Benjamin Schwartz.
Chapter 3

Identification and measurement of chemical and microstructural changes in bird feathers as markers of light induced degradation
3.1 Introduction

Artists and collectors have long admired bird feathers for their striking colors and patterns, and for the intricacy of their structure. Bird feathers have been incorporated into art objects by many cultures and have also been preserved in taxidermy specimens for both decorative and scientific proposes, therefore, feathered objects are present in many museum and private collections. However, the very intricate structure and vivid colors which make feathers appealing can present preservation challenges. While fugitive pigments found in conventional artworks can be protected to some extent by varnishes that filter UV light, featherwork would be destroyed by varnishing. It is therefore important that museums and collectors store feathered objects in conditions which will maximize their lifespan. To this end, museums have adopted a standard for the amount of light exposure feathered objects should be subjected to: up to 3 million lux hours if ultraviolet light is not filtered or 100 million lux hours if UV light is filtered. However, given the wide variation of feather types, it is to be expected that there will be considerable variation in feather light sensitivity. Up to this point, reports on feather light sensitivity have focused on visible changes, i.e. fading, and have included little direct investigation of the chemical changes occurring within feathers. Here we intend to provide a more complete picture of what light aging does to feathers by monitoring changes in their infrared and x-ray photoelectronic spectra as well as changes in their amino-acid content, by observing color changes under both visible and ultraviolet illumination, and by quantifying their pigment content.

When studying light induced feather degradation, it is important to consider both their protein structure and their pigmentation. Feathers are made up primarily of β-keratin, a structural amino acid which is common to bird feathers and scales as well as reptile scales. β-keratin is about 100 residues long, it contains a 32 residue 3 turn twisted β-sheet; these sheets form pairs with
sheets from adjacent β-keratin molecules; the sheet pairs form helical stacks which are supported and surrounded by a matrix formed from the disordered region of the proteins.\textsuperscript{5} The disulfide bonds, which are of great structural importance, form within the disordered region of the protein rather than between the β-sheets themselves. The amino acid content of bird feathers is similar across species: feathers contain about 7.6-15.9\% cystine and are also rich in glutamic acid, glycine, proline and serine. From a photochemical perspective, it is worthwhile noting the concentrations of the aromatic amino acids, which will be the major chromophores in the 250-310 nm range: 0.2-0.9\% histidine, 0.6\% tryptophan, 2.2-5.0\% phenylalanine, and 1.6-2.3\% tyrosine.\textsuperscript{6,7,8}

Bird feathers can contain a highly complex mixture of pigments as well as refractive structural color features. For this study, we have limited our feather selection to two types of birds: the scarlet ibis (\textit{Eudocimus ruber}) and the broad breasted domestic turkey (\textit{Meleagris gallopavo}). The scarlet ibis has brilliant red feathers whose color comes primarily from β-carotene derivatives canthaxanthin and guaraxanthin.\textsuperscript{9} This relatively simple pigment system was chosen for our preliminary study for ease of analysis, however we hope to perform additional studies with more complexly pigmented feathers in the future. Broad breasted turkey feathers possess no pigment and were selected so that changes in the β-keratin protein could be observed without pigment interference.

Four aging conditions were selected in order to provide a worst case to best case range of conditions for feather storage: UV light (340 nm lamps), window light (26\% transmission of 300-365 nm, 75\% transmission of 400-700 nm), MR16 museum light bulbs (400-700 nm light), and darkness. A feather aging period of 100 days was selected to emulate the length of a typical museum exhibition, timepoints of 3 days, 10 days, and 29 days were also taken.
While the photochemical degradation of feathers has not been widely studied up to this point, we can rely to some extent on the extensive research about the photodegradation of wool for guidance. Wool, like other animal hair, is composed of $\alpha$-keratin rather than $\beta$-keratin, however despite their structural differences; these proteins have similar amino acid contents. Wool experiences photodegradation when exposed to UV light, but also when exposed only to visible (>320 nm) light, however the character of the degradation is not the same across wavelengths: UV aged wool yellows, while blue light aged wool bleaches. Given that the amino acid chromophores present do not absorb visible light, other unidentified chromophores are presumably involved in the visible light aging of wool. We have confirmed that feather aging is similar in many respects to wool aging. Feathers aged in UV containing light show increasing levels of oxidized amino acids, particularly the cystine oxidation product cysteic acid. Feathers aged in UV-free light show much less severe damage: the only detectable changes are in the pigment rather than the structural protein. We have also shown that examination of feathers under UV light can reveal photo-induced damage long before it becomes detectable by other methods.

### 3.2. Results and Discussion

#### 3.2.1. Examination under visible and UV light

<table>
<thead>
<tr>
<th>Condition</th>
<th>Visible Light</th>
<th>365 nm Illumination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (darkness)</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>Museum Light</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>Window Light</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>UV Light</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Figure 3.2.1.1. Photographs of light-aged and control feathers under visible (left) and UV (right) light; the tips of the feathers were exposed to light, whereas the bases were covered. The dramatic effects of UV aging can clearly be seen in the UV aged scarlet ibis feather (top panel, bottom row) which retains a vibrant red color at the base but has been entirely photobleached at the tip.

Aged feathers were photographed under ordinary visible illumination and with a UV light source that allowed for the observation of UV induced visible fluorescence (UVIVF). Recently it has been found that UVIVF may play an important role in the mating displays of birds, however the chromophores responsible for fluorescence in bird plumage have not been fully elucidated. Nonetheless, it is clear that examination of feathers and other natural materials under UV light can reveal chemical properties that may not be apparent under ordinary illumination. Figure 3.2.1.1 shows scarlet ibis and turkey feathers that have been aged for 100 days. Feathers that have undergone UV aging exhibit very severe damage including yellowing and extensive loss of feather barbules and some loss of feather barbs. In the scarlet ibis feathers, an almost total loss of color is also observed. Under UV light, an increase in fluorescence is observed, giving both feather tips a greenish white appearance. Indeed, UV induced changes are already apparent after only 3 days of aging: yellowing of the turkey feathers is observed. After 10 days UV aging, fading of scarlet ibis feathers detectible under visible illumination and an increase in the UVIVF of the exposed regions of the feathers is also apparent. These results are qualitatively consistent with what has been observed in wool fibers aged under UV light: both a
reduction in mechanical strength and yellowing are observed. Under a fluorescent microscope, the 3-5 mm of wool fibers closest to the tip have a bright fluorescence at wavelengths longer than 450 nm when excited at 350-400 nm. While still on the sheep, the tip of the wool fiber receives the highest dose of UV radiation from sunlight, the lower portions of the fiber being shaded by the tips. Wool fiber tips are also yellower than the rest of the fiber; in wool fibers yellowing and increase in UVIVF are concomitant.

The window aged feathers and the feathers that were subjected to accelerated museum aging for 100 days appear unchanged under visible light, however examination under UV light reveals that light exposure has in fact caused some changes in the feathers. The exposed regions have less UVIVF and therefore appear darker than the unexposed regions. This darkening occurs after 29 days of aging in the window aged feathers and after 100 days aging in the museum light aged samples. It is worth pointing out that the direction of change is opposite in the UV aged feathers and the museum and window aged feathers, that is: aging feathers under UV causes an increase in their UVIVF, whereas aging them in primarily visible light leads to a decrease in their UVIVF. This may indicate that different photochemical processes are brought about by light of different energy. While photobleaching of wool caused by exposure to visible light has been reported, to the best of our knowledge, no loss of UVIVF has been reported. The loss of UVIVF may be the result of the formation of new emission quenching species or the destruction of fluorescence emitting species.

3.2.2. Fluorescence Spectroscopy

In an attempt to corroborate the photographed changes in UV induced visible fluorescence (Figure 3.2.1.1), fluorescence spectra of the feather samples were gathered. Interestingly the fluorescence changes, which are quite noticeable in photographs, produce only subtle spectral
changes. Figure 3.2.2.1 shows the emission spectrum of a turkey feather that has been UV aged for 0-29 days; the excitation wavelength is 365 nm. There is a slight spectral red-shift, and an increase in emission centered at 505 nm. This corresponds to a greenish emission which is observable in the UV induced fluorescence photographs. It was not possible to gather spectral data for the feather that had been aged 100 days due to extensive feather deterioration.

Light scattering caused by feather structure and leading to spectral artifacts was quite problematic. A number of attempts were made to reduce scattering by grinding and pressing feather material however this did not remove the spectral artifacts. Further attempts were made to suppress scattering by saturating feathers in cresol which has an identical refractive index to feather keratin (RI = 1.54)\textsuperscript{20}, however these also proved unsuccessful. In the end, an adequate suppression of scattering was achieved by widening the excitation slit to 4 nm and narrowing the emission slit to 0.5 nm.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fluorescence_spectra.png}
\caption{Fluorescence spectra of turkey feathers aged from zero to 29 days. A very slight increase in the fluorescence shoulder seen at ~500 nm is observable.}
\end{figure}
3.2.3. Analysis of pigments in scarlet ibis feathers

![Change in feather pigment vs. log(time)](image)

**Figure 3.2.3.1.** The change in scarlet ibis feather pigment over time under three aging conditions.

Scarlet ibis feather pigment was extracted and analyzed by UV-Vis spectrometry as described by McGraw and the total carotenoid pigment content was quantified; separation of the individual pigments was beyond the scope of this study.\textsuperscript{21} Absorbance maxima values ranged from 460-475 nm, which is consistent with the presence of ketocarotenoid (specifically canthaxanthin).\textsuperscript{22,23} The formula described by McGraw et al.\textsuperscript{24} was used to determine the total carotenoid concentration, using the extinction coefficient of 2200 for canthaxanthin.\textsuperscript{25} There is quite a large variation in the pigment content both from feather to feather as well as in different parts of an individual feather. In unexposed feathers, the pigment content varied from 47 to 938 μg pigment per gram of feather. The largest intra feather variation was a difference of 417 μg/g between the feather tip and the lower portion, with the tip having the most pigment and appearing most saturated. This inconsistency in unaged feathers makes the interpretation of data somewhat more difficult. It is not possible to simply record the loss of pigment in aged feathers, since feathers at each timepoint may possess drastically different amounts of pigment. Instead, the pigment content of the tip was subtracted from the pigment content in the covered portion of the feather for each timepoint to give a “pigment change parameter” (Figure 3.2.3.1). For control
The pigment change parameter is always negative because the tips have more pigment. The window, museum, and UV aged feathers exhibit a clear trend of increasing pigment change parameters, indicating that while the feather tips may still contain more pigment than the bases, they tend to have a smaller pigment advantage over time. Only in UV aged feathers do the feather tips eventually become less pigmented than the bases. These results are consistent with the feather photographs, however pigment extraction appears to be somewhat more sensitive to small changes in pigment content as changes in window and museum aged feathers could not be observed visually.

### 3.2.4. Infrared Spectroscopy

Figure 3.2.4.1. Difference IR spectra for UV aged turkey and scarlet ibis feathers

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy detects the vibration of chemical bonds; it is a particularly useful technique for museum samples as it is non-destructive. We have found that our unaged feather spectra were quite similar to previously reported feather ATR-IR spectra of feathers. Significant changes were not observed in the FTIR spectra of feather samples aged in window or museum light, however UV aged feathers changed

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dramatically. The majority of the spectral changes occur below 1700 cm$^{-1}$ and are consistent with an increasing concentration of keratin oxidation products. Figure 3.2.4.1 shows the difference spectra of UV aged scarlet ibis and turkey feathers verses control feathers; a feather sample which has been chemically oxidized by soaking for 5 days in 30% hydrogen peroxide is also included for reference. The chemically oxidized feather spectra have two clearly defined peaks at 1175 and 1040 cm$^{-1}$, which can be attributed to the symmetric and asymmetric S=O stretching of cysteic acid.$^{27}$ Interestingly, the feather spectra of the unaged scarlet ibis and the turkey were nearly identical with the exception of a peak at 1040 cm$^{-1}$ which is present in the turkey feathers but absent in the ibis feathers, this is presumably the result of the turkey feather vendor’s disinfecting peroxide wash causing a small amount of feather oxidation. The changes seen in chemically oxidized feather samples are quite similar to changes seen in chemically oxidized wool and human hair samples.$^{28,29,30}$ In the UV aged feathers, the cysteic acid bands are also prominent however an additional, more difficult to assign band is also seen at 1090 cm$^{-1}$. This peak may be attributable to cystine S-monoxide, which typically absorbs at 1070-1080 cm$^{-1}$. A peak at 1090 cm$^{-1}$ would also be consistent with alanine sulfinic acid which typically absorbs at 1093 cm$^{-1}$. In previous studies of UV oxidized wool, both of these species have been detected. An increase in the absorbance at 1720 cm$^{-1}$ is also observed, appearing as a subtle increase in the shoulder of the prominent carbonyl stretch in IR spectrum, but much more prominent in the difference spectrum. To the best of our knowledge, such a change has not been reported in the IR spectra of oxidized wool or hair, however a close examination of the published spectra of oxidized wool does reveal an increase in the shoulder of the carbonyl peak.$^{33}$ Due to the density of possible functional groups in this region, this peak is extremely difficult to assign with any certainty. It would be consistent with a carboxylic acid or a ketone, which could be
produced by the oxidation of amino acid side chains or the hydrolysis of the peptide backbone. Alternately, the increase may be due to changes in the keratin secondary structure; studies of the denaturation and recrystallization of feather keratin have shown an increase in this shoulder as well.26

3.2.5. X-ray Photoelectron Spectroscopy

![Figure 3.2.5.1. XPS spectra of the S 2p peak of aged and unaged turkey and scarlet ibis feathers.](image)

X-ray photoelectron spectroscopy (XPS) monitors electron energy levels and can give information about a sample’s elemental content and bonding. The broadband XPS spectrum of feathers is quite similar to the spectrum of wool: photoelectron peaks are observed for O 1s, N 1s, C 1s, S 2s, and S 2p at 533, 400, 285, 230, and 165 eV respectively. In wool, the sulfur 2p region of the XPS spectrum has been extensively studied.36,37 In untreated wool, the S 2p peak occurs at 164 eV,39,40 corresponding to cystine; wool which has been oxidized by plasma, corona discharge, or chlorine water has a S 2p peak at 168 eV which has been identified as cysteic acid.37 Wool that has been treated with performic acid or hydrogen peroxide has peaks at 165.5 and 167 eV which correspond to cystine monoxide and alanine sulfinic acid respectively.41 For
unaged feathers, the scarlet ibis and turkey spectra already show significant differences in their S 2p peak: ibis feathers have a fairly clean cystine peak centered at 163 eV while turkey feathers have two additional peaks at 165.5 and 168 eV which can be identified as cystine monoxide and alanine sulfinic acid based on the wool studies. As noted above, this difference is almost certainly due to the vendor’s pre-treatment of the turkey feathers with hydrogen peroxide.

As with the FTIR analysis, only the samples that were aged under UV light showed significant XPS spectral changes. Figure 3.2.5.1 shows the sulfur 2p region in both turkey and scarlet ibis feathers which have been UV aged. After only 3 days UV exposure, significant changes were already observed: in turkey feathers the cystine monoxide peak at 165.5 is lost, in the ibis feathers a new peak at 168 eV begins to grow while the reduced sulfur peak at 163 eV decreases in size. After 10 days of UV aging, the cysteic acid peak becomes more prominent for both types of feather. By 29 days, the reduced sulfur peak is gone in the turkey feathers, while it takes the full hundred days before this peak is eliminated from the scarlet ibis feather spectrum. Intriguingly, the total area of the sulfur 2p peak increases as the feathers become more oxidized.

We have also investigated the carbon 1s region and have found that oxidized carbon peaks grow as the feathers are aged in UV light. In unaged feathers, the carbon 1s region is dominated by the peak at 285 eV which corresponds to carbon bonded to carbon or hydrogen however there is a small shoulder at 286 eV from carbon bonded to oxygen or nitrogen, and a small peak at 288 eV from carbonyl carbons. As feathers are aged both of these oxidized carbon peaks become more prominent. Table 3.2.5.1 summarizes the changes observed in the carbon 1s region; for both types of feathers, the oxidized carbon peaks go from being about 8% of the total carbon peak height each to being about 22% of the total carbon peak height.
Table 3.2.5.1. Carbon bonding distributions in UV aged and unaged turkey and scarlet ibis feathers.

<table>
<thead>
<tr>
<th>Peak (eV)</th>
<th>Unaged Turkey</th>
<th>Unaged Scarlet Ibis</th>
<th>100 day UV Turkey</th>
<th>100 day UV Scarlet Ibis</th>
</tr>
</thead>
<tbody>
<tr>
<td>285: CC/CH</td>
<td>83%</td>
<td>90%</td>
<td>61%</td>
<td>58%</td>
</tr>
<tr>
<td>286: CO/CN</td>
<td>9%</td>
<td>10%</td>
<td>21%</td>
<td>25%</td>
</tr>
<tr>
<td>288: C=O</td>
<td>7%</td>
<td>6%</td>
<td>18%</td>
<td>24%</td>
</tr>
</tbody>
</table>

3.2.6. GCMS analysis of cysteine and cysteic acid

In an attempt to chemically corroborate the changes which were readily apparent under UV light but were undetectable by XPS or FTIR in the window and MR16 light aged feathers, an amino acid analysis by GCMS was undertaken. Based on the XPS and FTIR results, we focused our analysis on cystine and its photooxidation product cysteic acid. The amino acids were hydrolyzed by heating in hydrochloric acid under nitrogen and subsequently functionalized with trimethylsilyl groups prior to injecting into the GCMS, as reported by Gehrke. Figure 6 shows the change in the cysteic acid/cystine ratio over time. As also shown by XPS and FTIR, the cysteic acid content of UV aged feathers increases dramatically with time. It is also intriguing that the cysteic acid/cystine ratio of turkey feathers is almost two orders of magnitude higher than for scarlet ibis feathers over most of the samples; again, this may be the legacy of the peroxide wash given to the turkey feathers by the vendor. A trend of an increasing cysteic acid to cystine ratio over time was observed for both UV and window aged feathers. After 100 days of window aging, the cysteic acid to cystine ratio is 4.9 times higher than the average among unaged scarlet ibis feathers and 7.2 times higher than the average among unaged turkey feathers. For UV aged feathers, the results were of course more dramatic, due to extensive feather
disintegration, the 100 day aged sample could not be analyzed, but after only 29 days the cysteic acid to cystine ratio was 25.9 times higher than unaged ibis feathers and 35.6 times higher than unaged turkey feathers.

![Figure 3.2.6.1](image)

**Figure 3.2.6.1.** Cysteic acid to cystine ratio verses time in turkey and scarlet ibis feathers aged in all conditions.

### 3.3. Conclusion

We have found that examination of feathers under UV light reveals photo-induced changes in feathers long before they are detectable by other means; changes that are undetectable under visible light can be clearly seen under UV light, particularly in unpigmented feathers. Light damage caused by UV exposure leads to an increase in UVIVF while visible light aging leads to a decrease in UVIVF. Apparently the photochemical reactions responsible for light damage to feathers are wavelength dependent and different pathways are in effect under visible and UV excitation; these results are similar to those seen in wool.

In UV chamber aged feathers, the oxidation of cystine residues is the predominant change observed. Cystine oxidation results in the breaking of disulfide bonds and eventually in feather disintegration after long exposure. The FTIR and XPS spectral changes observed in UV aged
feathers are quite similar to those which have been reported in UV aged wool: they show evidence of increasing concentrations of cysteic acid, cystine monooxide and alanine sulfinic acid. Amino acid analysis corroborates these results: in UV aged feathers the cysteic acid to cystine ratio increases dramatically with aging time. UV aged scarlet ibis feathers also showed the most dramatic loss of pigmentation over time.

Window aged feathers, which receive a small dose of both visible and UV light, showed much more subtle changes than the UV chamber aged samples. These feathers were indistinguishable from the control group by XPS and FTIR, however amino acid analysis revealed that the cysteic acid to cystine ratio does increase over time. Presumably, with longer aging periods these changes would become detectable by FTIR and XPS as well. Interestingly, while color changes could not be observed by examination under visible light, significant pigment loss was apparent in window aged scarlet ibis feathers after only 10 days.

UV-free museum light aged feathers suffered the least damage over time. By XPS, FTIR, and GCMS analysis of cysteic acid to cystine ratio they were indistinguishable from control group feathers after 100 days aging. As with the window-aged feathers, pigment loss was detectable by pigment extraction before any visible fading could be observed. It is of course unsurprising that pigment loss is caused by visible light aging.

3.4. Experimental section

*Feather Provenance*

Scarlet Ibis (*Eudocimus ruber*) wing and tail feathers were donated by Judy St. Leger, SeaWorld Parks and Entertainment, San Diego, California; Dr. Stephanie Allard, Palm Beach Zoo, Palm Beach, Florida; and Busch Gardens Tampa Bay, Tampa, Florida; they were not washed or processed in any way prior to the start of the study. Domestic Broad Breasted White
Turkey (*Meleagris gallopavo*) wing feathers were purchased from SmileyMe, Arapahoe, North Carolina; they were washed with Wool Wash and sterilized with peroxide by the vendor prior to the commencement of this study.

**Feather Aging**

Ultraviolet aged feathers were held in a chamber with F-40T12TR50 Westinghouse 5000K lamps bulbs with peak UV emission at 340 nm; the radiant energy was 71,750 mW/m³, the average UV content was 68,250 µw/lm. Window aged feathers were placed by a south facing window with 26% transmission between 300 and 380 nm, and 76% transmission between 400 and 700 nm; the average illuminance was 5,000 lux. Museum aged feathers were held in a homemade stainless steel ventilated chamber with GE Precise MR 16 bulbs ACG141CI which emit primarily in the 400 to 700 nm range; the average illuminance was 20,700 lux with a UV content of 6.0 µw/lm on average. In all cases, the top half of the feathers was fully exposed to light whereas the bottom half was protected from most of illumination by acid free cardstock. Unfortunately, the cardstock did not completely shield the bottom half of feathers from light, therefore a small amount of light aging even for the covered portions of the feathers is expected. Future studies will employ a more lightfast shielding material. Control samples were stored in darkness for the entire aging period.

**Chemical oxidation of feathers**

Feathers were incubated in an aqueous solution of 30% hydrogen peroxide at room temperature for 5 days. Prior to analysis, they were either allowed to air dry or were washed with water, then acetone and allowed to dry; sample drying conditions did not affect results.

**Photographic observations of feathers under visible and ultraviolet light**

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Ultraviolet induced fluorescence feather images were taken using a Mini Crimescope Alternate Light Source and 365 nm filter, SPEX Forensics, Edison New Jersey and a Nikon D90 camera with a 2e filter.

Pigment extraction

Exposed and unexposed ibis feather portions were trimmed and weighed with an electronic balance to the nearest 0.01 mg, with a target mass of 10.00 mg. To each tube of feathers, 2 ml acidified pyridine was added and the capped tubes were held at 95°C for 2 hrs. The tubes were cooled to room temperature, 2 ml deionized water was added, and the tubes were inverted twice to mix. 1.5 mL hexane: 2-methoxy-2-methylpropane (1:1, v/v) was added and the tubes were shaken vigorously for 30 seconds, and then centrifuged for 5 minutes at 3000 rpm. The organic (top) layer which contains the feather pigments was transferred to a fresh labeled 1.5 mL screw-cap Eppendorf tube and evaporated to dryness under a stream of nitrogen. The residue was redisolved in 1 mL ethanol and the absorbance was measured with a Beckman-Coulter DU 520 UV/Vis spectrophotometer.

GCMS analysis of feather protein

One to two mg of each feather sample was weighed out and placed in a glass ampule with 1 mL 6 N hydrochloric acid for each 1 mg of feather. The ampule was evacuated and flame sealed to exclude oxygen and was subsequently heated for 4 hours at 145°C to hydrolyze the amide bonds. The solution was transferred to high recovery autosampler vials and was evaporated with a nitrogen stream at 50°C. To remove hydrochloric acid, the residue was suspended in 40 μL water then evaporated under nitrogen, then suspended in 40 μL ethanol and evaporated under nitrogen. A derivatization solution was prepared by mixing 0.5 mL dry pyridine with 1 mL N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 60 μL of this solution was added to each vial.
Vials were capped and heated for 15 minutes at 75° C, they were then immediately injected into the GC/MS.

GC/MS Conditions: A ZB-1 (30 m x 0.25 mm x 0.25 µm) capillary column was used for the separation. Helium carrier gas was set to a linear velocity of 50 cm/sec. Split injection was used 20:1 and was set to 270°C. The MS transfer line was set to 280°C. The GC oven temperature program was: 105°C; 40°C/min to 280°C; isothermal for 1 min. Total run time is 5.38 min. Single ion monitoring conditions were used (m/z 268); the retention time of cysteic acid was 3.74 min., the retention time of cystine was 5.22 min.

**FTIR of feathers**

Feather spectra were obtained with a Perkin Elmer Spectrum 100 FTIR spectrometer equipped with a Universal Attenuated Total Reflectance (ATR) sampling accessory. Feathers were placed face down on the ATR crystal of the FTIR and force was applied using the pressure arm until acceptable signal to noise ratio was achieved; four scans were averaged for each spectrum.

**XPS of feathers**

XPS spectra were collected using an AXIS Ultra DLD spectrometer from Kratos Analytical. Feathers were affixed face up to the sample holder using copper tape. The spectra were measured using a monochromatic Ar⁺ ion source; charge neutralization was employed due to the insulating nature of feather samples. Binding energy was calibrated using the C 1s peaks (BE = 285 eV). Broad band spectra as well as high resolution spectra for the C 1s, N 1s, O 1s, and S 2p regions were collected. It was necessary to average 3 scans for the S 2p region in order to obtain an adequate signal to noise ratio.

**Fluorescence of feathers**
Fluorescence spectra were collected using an FLS920 spectrometer from Edinburgh Instruments. In order to minimize scattering caused by feather structure, the monochromatic slits were set at 4 nm.

3.5. References


Chapter 4

The observation of transients in microcrystalline suspensions of 1,1,3,3-tetraphenylacetone
4.1. Introduction

The photodecarbonylation reaction of dibenzyl ketone derivatives has been extensively investigated both mechanistically and in terms of its synthetic utility. Figure 4.1.1 shows the basic form of the reaction: two subsequent α-cleavage steps yield a pair of stabilized benzylic radicals, in crystals these combine to give the geminate recombination product (shown), in solution a variety of termination steps are possible. Indeed, this forced geminate recombination in the solid-state has been shown to have significant synthetic utility: providing a route to adjacent quaternary stereogenic centers which are otherwise difficult to access.¹

![Figure 4.1.1](image)

**Figure 4.1.1.** The photodecarbonylation of a dibenzyl ketone derivative in the solid state; the crystal lattice is represented by the dotted line.

Despite the synthetic importance of the crystalline solid-state versions of these reactions, most investigations of the transient species involved have focused on reactions in solution,² in micelles,³ and in zeolites.⁴ This gap is understandable given the experimental difficulty inherent in applying traditional transmission based spectroscopic methods to solids, which have very high optical densities. This difficulty can be overcome by employing microcrystalline suspensions, which have solid-like relativities but solution-like optical densities.⁵ A number of recent studies have shown that the observation of solid-state transient species is possible in microcrystalline suspensions.⁶ And indeed, a spin-polarized radical pair triplet state (corresponding to the radical pair in Figure 4.1.1) was recently observed in a time resolved electron paramagnetic resonance (TREPR) study of the photodecarbonylation of a dibenzyl ketone derivative (2,4-bis(4-
methoxyphenyl)-2,4-dimethylpentan-3-one). However, the popular laser flash photolysis technique has not yet been employed to observe transient absorbance signals for this class of reaction in the solid-state, it is the goal of this work to address that deficiency.

Initially, we had hoped to corroborate the TREPR study mentioned above, however the transient absorbance signals for the benzylic radicals involved proved too weak *vide infra*. We therefore turned to 1,1,3,3-tetraphenylacetone (TPA) as our reactant, in order to take advantage of the stronger transient absorbance of the diphenylmethyl radical. The mechanism of the photodecarbonylation of TPA is detailed in Figure 4.1.2. In solution the initial intersystem crossing (ISC) and α-cleavage steps which give RP1 occur very rapidly ( > 3 ns), the decarbonylation step which gives RP2 is somewhat slower (~ 8 ns). RP2 is by far the longest-lived transient species in this reaction, having lifetimes in the microsecond regime under most conditions. In solution, the fate or RP2 is dependent on the presence of oxygen, in oxygen-free environments tetraphenylethane (TPE) is the major product; when oxygen is present benzophenone dominates. In the solid-state TPE is invariably the major product.

![Mechanism of photodecarbonylation of TPA](image)

**Figure 4.1.2.** The mechanism of the photodecarbonylation of tetraphenylacetone.
In order to observe TPA transients in microcrystalline suspensions by laser flash photolysis we have employed a flow-cell to maximize the signal to noise ratio for this irreversible reaction. We have also screened a variety of conditions for the formation of microcrystalline suspensions with the goal of minimizing scattering. We have confirmed by PXRD that the crystal packing for the microcrystalline suspensions is the same as for the bulk solid. We performed product analysis by GCMS and NMR to confirm the product distributions for the reaction in the bulk solid, in microcrystalline suspensions, and in solution. Finally, we have obtained a transient absorbance spectrum and kinetic data for RP2 in microcrystalline suspensions.

4.2. Results and Discussion

4.2.1. Development of Laser Flash Photolysis flow cell protocol

Initial attempts to observe dicumyl ketone (DCK) transients in acetonitrile, ethanol, and methylcyclohexane solutions were unsuccessful. Only at high optical densities (~ 0.9 A.U. at 266 nm) could any transient signal be observed, however attempts to improve the signal to noise ratio by accumulating data proved unsuccessful. Examination of the UV spectra of samples before and after exposure to the laser revealed significant sample change after only three laser shots. Due to the irreversibility of the decarbonylation reaction and the high power of the laser (90 mJ at 266 nm), in a conventional cuvette the starting material is completely consumed before adequate signal to noise can be achieved by accumulating data from multiple laser pulses. A quartz flow cell system was installed in place of the conventional sample chamber to provide a fresh supply of unreacted ketone. Flow rates from 17 mL/min to 0.75 mL/min were tried and even at very low flow rates (0.75 mL/min) it was possible to accumulate data; adequate signal to noise was achieved by averaging 100 scans. In the case of TPA, strong transient absorbance signals can be observed even without the flow cell system, however use of the flow cell does improve the signal.
to noise for this compound as well, therefore it was employed in all subsequent studies at a flow rate of 1.2 mL/min.

4.2.2. Microcrystalline suspension optimization

Since its introduction by Kasai et al. in 1992, the reprecipitation method of preparing organic microcrystalline suspensions has been widely adopted, however it has only rarely been used in transient absorbance studies. Microcrystalline suspensions are potentially ideal for the study of solid-state photochemical reactions and their reactive intermediates because they allow for variable sample loading and the use of transmission based methods, unlike bulk solid and single crystal techniques.

The preparation of microcrystalline suspensions with adequate optical properties for transient absorbance spectroscopy can be challenging. For successful observation of transients, it is essential that light scattering by the microcrystalline suspension be kept to a minimum as any scattering drastically reduces the signal to noise ratio. Light scattering by small particles is dependent on particle composition, geometry, size, and on the wavelength of light. All other factors being equal, larger particles cause more scattering and shorter wavelengths of light are scattered more efficiently than longer wavelengths. It is therefore extremely important to maintain small particle sizes when working with shorter excitation wavelengths. This may account for the fact that the majority of examples of TA spectroscopy of microcrystalline suspensions have involved both excitation and transient absorbance at fairly long wavelengths (≥ 355 nm and ≥ 400 nm respectively). Even in cases where excitation wavelengths have been shorter (~250 nm), transient absorbance has been detected at longer wavelengths (> 450 nm). However, the n to π* transition which is necessary to excite the aliphatic ketones of both DCK and TPA occurs at ~300 nm and the benzylic and diphenylmethyl radicals which are generated
absorb at 315 nm and 330 nm respectively. To the best of our knowledge, this will be the first report of the transient absorbance of microcrystalline suspensions with both excitation and transient absorbance at wavelengths shorter than 350 nm.

The literature on microcrystalline suspensions contains a wide variety of methods for their preparation. In general, a small amount of analyte solution in a water miscible solvent is injected into vigorously stirred, vortexed or sonicated water with or without surfactant. In some cases, the resulting suspensions are post-processed with incubation, additional sonication, or the addition of surfactants to prevent microcrystal aggregation. In this work, we strove to find the optimum microcrystalline suspension protocol to minimize scattering. We evaluated scattering qualitatively by comparing the UV-Vis spectra of the microcrystalline suspensions with the spectrum of the analyte in solution; a reduction in the transmission of light at wavelengths longer than the solution absorbance can be attributed to scattering, indeed this phenomenon is present in many of the published spectra of microcrystalline suspensions.6d,13

In our attempt to minimize scattering we varied organic solvent, surfactant type and concentration, and analyte concentration. In our initial studies with DCK, we found that scattering is extensive when no surfactant is used and that the addition of sodium dodecyl sulfate (SDS) reduces this scattering. This reduction of scattering with the addition of surfactant is dependent on the concentration of surfactant and we found that scattering can be almost completely eliminated with SDS concentrations higher than 20 mM, unfortunately this is significantly higher than the critical micelle concentration for SDS which is 1 mM. While this surfactant concentration is only a tenth of concentrations used in studies of DCK in micelles,14 it is still high enough that some micellar DCK could potentially be present which could complicate data analysis. Whether or not micellar DCK was present in these microcrystalline suspensions,
no DCK transients were observable in these suspensions so they were not investigated further. We also looked into using cetyltrimethylammonium bromide (CTAB) for the preparation of microcrystalline suspensions, however we achieved similar results as with SDS, that is CTAB was able to reduce scattering however it did not enable the observation of DCK transients.

To test the effect of organic solvent on microcrystalline suspension formation we prepared suspensions using tetrahydrofuran, acetonitrile, ethanol, and acetone. Ethanol proved unsuitable because of limited DCK solubility. Tetrahydrofuran had good DCK solubility however its suspensions were highly scattering. Both acetonitrile and acetone gave suspensions with fairly low scattering however acetone has a strong absorbance peak at 260 nm, which was expected to interfere with DCK or TPA absorbance in that region and complicate results. Therefore, acetonitrile was settled on as the solvent of choice for further experiments.

All other factors being equal, we found that as expected increasing analyte concentration increases scattering. Interestingly, not only is absolute scattering increased at higher analyte concentrations, but scattering relative to absorbance also increases. This may be explained by higher chances of particle aggregation when concentrations are higher.

Despite learning a fair amount about microcrystalline suspension preparation from our studies on DCK, it never became possible to observe DCK transients in any microcrystalline suspension we attempted. This is likely due to the relatively low molar absorptivity of the benzylic radicals produced by DCK: 9000 M$^{-1}$cm$^{-1}$.15 We decided to shift our focus to TPA which produces diphenylmethyl (DPM) radicals whose molar absorptivity is between five and ten times as high: it has been reported at 80,000 M$^{-1}$cm$^{-1}$16 and 40,000 M$^{-1}$cm$^{-1}$.17 Figure 4.2.2.1 shows the UV-Vis spectra of TPA in both solution and in microcrystalline suspension with and without surfactant. As with DCK, the addition of surfactant greatly reduces scattering in TPA microcrystalline
suspensions, indeed scattering decreases as surfactant concentration increases, however in order to avoid the possibility of micellar TPA we kept the surfactant concentration below the critical micelle concentration. We found that CTAB is much more potent than SDS at reducing scattering in TPA and DCK suspensions, indeed it is necessary to use more than 40 times the concentration of SDS to achieve an equivalent reduction in scattering. It is possible that favorable electrostatic interactions between the positively charged cetyltrimethylammonium ion and the electronegative carbonyl group of TPA and DCK may allow for better microcrystal stabilization, no such favorable interaction is possible with the negatively charged dodecyl sulfate ion. We found that a TPA concentration of 40 μM and a CTAB concentration of 0.45 mM gave an adequate transient signal to noise ratio for our laser flash photolysis studies. This CTAB concentration is below the critical micelle concentration (0.92 mM) and well below CTAB concentrations that have previously been used for the preparation of micellar TPA (50 mM). 15

Figure 4.2.2.1. UV-Vis spectra of 40 μM TPA in solution (blue), and microcrystalline suspension (orange) with CTAB concentrations from zero to 0.9 mM. Scattering is reduced in microcrystalline suspensions as surfactant concentration increases.
After finding a suitable protocol for the formation of minimally scattering microcrystalline suspensions we wished to confirm that the crystal packing of TPA in suspension was similar to its packing in the bulk solid. Figure 4.2.2.2 displays the powder X-ray diffraction (PXRD) spectra of bulk TPA and TPA microcrystalline suspensions both with and without surfactant. Microcrystalline suspensions display characteristic peak broadening that indicates small particle size, however both spectra also suffer from a loss of peaks and an underlying broadness, which indicates a significant amorphous character. Nonetheless, the overall spectral similarity indicates that the crystal packing within the microcrystalline suspension is similar to the packing in the bulk solid. It is also apparent that the presence of surfactant does not drastically alter the crystal packing. We also looked at the PXRD spectrum after 47 hours of photolysis in the bulk, at this point only 26% conversion to TPE has been achieved (vide infra) so it is unsurprising that the spectrum is largely similar to that of the bulk solid before photolysis.

**Figure 4.2.2.2.** PXRD spectra of TPA bulk powder (A), CTAB stabilized microcrystalline suspension of TPA in water (B), surfactant-free microcrystalline suspension of TPA in water (C), TPA bulk powder after 47 hours photolysis (26% conversion to TPE) (D).
4.2.3. Product analysis

The product analysis for the photolysis of DCK both in the solid state and in solution has been previously reported: in solution the major product is dicumane (60%) with isopropyl benzene (10%), α-methylstyrene (10%), and assorted unidentified side-products making up the remaining mass; in the solid state the reaction goes cleanly to dicumane (99%). However, to the best of our knowledge, a complete product analysis for the photolysis of TPA has not been reported. An early report of the photochemistry of TPA and related compounds indicates that tetraphenylethane (TPE) is the major photoproduct, but does not identify the side products. A study of TPA photolysis in Na-X zeolite highlighted the critical importance of oxygen to the final product distribution: in an oxygen-free environment TPE was the major product and diphenyl methane (10-20%) made up the remaining mass; when oxygen was present, benzophenone and five unidentified products in addition to TPE were detected.

The results of TPA product analysis are summarized in Table 4.2.3.1, product distributions were assessed by both GCMS and NMR, in general the two techniques were in good accord, however when benzophenone was present its concentration appeared to be many times higher by NMR than by GCMS, this is presumably due to the different ionization efficiencies of the various photoproducts. In the bulk solid, the reaction proceeds cleanly giving only tetraphenylethane (TPE) as photoproduct, however after 47 hours, 73.6% of the sample is still TPA starting material. This is a common feature of the photolysis of bulk solids and is attributable to the reaction only taking place near the surface of crystals because photons are unable to reach the interior. The reaction is far more efficient in microcrystalline suspensions however after 24 hours it still isn’t complete and it isn’t as clean: in addition to TPE (70.9%), benzophenone and two unknown side products make up 2.8 and 13.2 percent of the sample.
respectively. The reaction proceeds much more quickly when CTAB is used in the formation of the microcrystalline suspension, after 3 hours only 9.7% of the starting material remains, it is likely that this is due to a smaller crystal size allowing for greater photonic access to the starting material. Unfortunately, the discrepancy between the NMR and GCMS results is quite pronounced when looking at the product distribution of the microcrystalline suspension that was prepared with CTAB: by NMR benzophenone is much more prevalent in this sample, making up 25.9% of the product, by GCMS it makes up only 3.1%. In any case, since previous reports have indicated that oxygen is essential for benzophenone formation, this side-product could be eliminated by running the reaction in an oxygen free environment. In acetonitrile solutions the reaction proceeds much more quickly with less than 1% of the starting material remaining after 4 hours; benzophenone is the major product, making up 74.8% and of the sample with TPE making up the remaining mass.

Table 4.2.3.1. Photolysis product distributions (%) of TPA in various conditions by GCMS and (NMR).

<table>
<thead>
<tr>
<th>Product (retention time)</th>
<th>TPA (10.9 min)</th>
<th>TPE (9.5 min)</th>
<th>Benzophenone (6.6 min)</th>
<th>Unk. (6.1 min)</th>
<th>Unk. (6.0 min)</th>
<th>Unk. (5.7 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Solid, 47 h</td>
<td>73.6 (70.4)</td>
<td>26.4 (29.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microcrystalline suspension, 4 h</td>
<td>56.4 (56.2)</td>
<td>41.9 (40.4)</td>
<td></td>
<td>1.7 (3.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microcrystalline suspension, 24 h</td>
<td>13.0 (13.4)</td>
<td>70.9 (74.6)</td>
<td>2.8 (4.3)</td>
<td>1.4 (11.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microcrystalline suspension with CTAB, 3 h</td>
<td>9.7 (10.0)</td>
<td>83.7 (58.8)</td>
<td>3.1 (25.9)</td>
<td></td>
<td>4.1 (5.3)</td>
<td></td>
</tr>
<tr>
<td>Solution (ACN), 4h</td>
<td>0.9 (n.d.)</td>
<td>23.5 (8.9)</td>
<td>74.8 (91.1)</td>
<td></td>
<td></td>
<td>0.7</td>
</tr>
</tbody>
</table>
The striking change in photoproduct distribution between the solid-state and solution phase samples of TPA is reminiscent of other photodecarbonylation reactions. While solution phase photodecarbonylation reactions can produce a wide variety of products that are the result of non-geminate recombination, disproportionation, and sometimes reaction with the solvent or other reagents, in the solid-state geminate recombination is favored above other pathways. It is noteworthy that while benzophenone is the dominant photoproduct in solution, it is not detected at all in the bulk solid, even though the reaction was carried out in the presence of oxygen. This outcome may be explained in two ways: either geminate recombination is rendered much more favorable than oxidation by the topochromatic constraints within the crystal lattice, or it may be that oxygen penetration into the crystal was too low for oxidation to occur, or both. Microcrystalline suspensions appear to be an intermediate case: low quantities of benzophenone are produced, presumably surface reactivity is much more important in microcrystals than in bulk crystals. Interestingly, benzophenone is a more significant product when surfactant is present. Again, this is likely due to smaller microcrystal sizes in surfactant containing suspensions. The possibility of greater oxygen solubility in surfactant containing water was considered, however below the critical micelle concentration, oxygen solubility does not increase much with CTAB concentration.

4.2.4. Laser flash photolysis of tetraphenylacetone

4.2.4.1. Transient absorbance spectrum

The absorbance spectrum of the diphenylmethyl radical (DPM) has been reported in solution in acetonitrile, methanol, and cyclohexane, as well as in micelles and in zeolites. The absorbance spectrum is independent of radical source (spectra have been reported for TPA and diphenylmethyl chloride parented radicals). There is negligible solvatochromic shift across the
solvents studied and indeed, even in micelles and zeolites the $\lambda_{\text{max}}$ appeared within the same narrow range: from 330 to 332 nm. Our solution transient absorbance spectrum of TPA (Figure 4.2.4.1.1.) is in good accord with those reported by other sources having a $\lambda_{\text{max}}$ at 330 nm, however we observe an additional weak absorbance band at 520 nm that has not been noted by other sources. It is tempting to attribute this band to benzophenone ($\lambda_{\text{max}} = 530$ nm) produced during the course of the experiment however product analysis showed no benzophenone after photolysis and the relative intensity of the band was not effected by the presence of oxygen in the sample. More likely it was simply not noted in earlier studies because it was not within the wavelength range they examined.

Figure 4.2.4.1.1. Transient absorbance spectra of TPA in 40 uM solution (blue circles) and 40 uM microcrystalline suspension in water stabilized by 0.45 mM CTAB (red squares). Insert: normalized plots.
Figure 4.2.4.1.1 also shows the transient absorbance spectrum of a TPA microcrystalline suspension; to the best of our knowledge this is the first reported spectrum of the DPM radical in the solid state. The peak absorbance is red-shifted by 10 nm versus the solution spectrum to 340 nm and is less featured; the absorbance seen at 520 nm in solution is not observed here. The red shift in solid-state transient absorbance is unsurprising, a similar red shift in the solid-state spectra of ground state compounds is commonplace. It should also be noted that the signal intensity in the microcrystalline suspension is only about one fifth of what is seen in solutions with identical concentrations of TPA (Δ O.D.: 1.02 × 10⁻² and 5.27 × 10⁻² respectively), there are a number of possible explanations for this. Possibly the absorptivity of the DPM radical is lower when it is held close to its geminate partner within the crystal lattice rather than escaping into solution. Time-resolved EPR studies on a related system suggest that after decarbonylation in microcrystalline suspensions the free electrons of the two DPM radicals produced by decarbonylation are only separated by 5 Å. This may indeed be an extreme version of the effect observed by Arita and coworkers where the absorbance signal of the DPM radical is lower in a more viscous solvent than in a less viscous solvent, the crystal lattice acting like a superlatively viscous solvent. Alternately, it may be that the relatively poor optical quality of the microcrystalline suspension leads to a much lower efficiency in generation of DPM radicals, or that DPM radicals are only generated near the surface of microcrystals leading to a lower effective concentration of TPA molecules actually capable of undergoing alpha-cleavage and decarbonylation to produce DPM radicals.

4.2.4.2. Transient Kinetics

The initial steps of the photodecarbonylation of TPA, excitation to the singlet state and intersystem crossing to the triplet state followed by alpha cleavage, occur within the ~5 ns of the
laser pulse and are not individually observable in this experimental set up. In solution, after the rapid growth of DPM transient absorbance that occurs during the laser pulse, a second slower growth in signal is observed, shown in Figure 4.2.4.2.1. This second growth step is attributed to the relatively slow decarbonylation of the phenacetyl radicals yielding an additional equivalent of DPM radicals. In previous work, it has not been possible to observe this growth at room temperature in isooctane. That it can be seen here is likely due to the longer lifetime of phenacetyl radicals in acetonitrile relative to nonpolar solvents. However, the slow growth region was so small in comparison to the fast growth and decay regions that it was not possible to reliably establish the decarbonylation rate. In microcrystalline suspensions, no such slow growth region was observed. This may be because the decarbonylation step is intrinsically faster in the solid or it may be that the increased noise in the microcrystalline suspension traces obscure this relatively subtle feature.

**Figure 4.2.4.2.1.** A representative transient absorption trace of TPA in oxygen-free solution showing the fast growth, slow growth, and decay regions.
After alpha cleavage and decarbonylation the DPM radical signal slowly decays as the DPM radicals combine to give tetraphenylethane, react with oxygen if it is present to form benzophenone, or terminate by some other route. The rate of recombination of DPM radicals in solution has been well fit by a second order rate law in a number of studies and is diffusion controlled. Two early studies found the second order rate constant for DPM radical disappearance to be $2.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; the recombination rate was the same for DPM generated from TPA or from diphenylmethyl chloride. In the presence of oxygen, the decay rate is significantly faster with a second order decay constant of $3.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. A more recent study used the recombination of the DPM radical as a model system for verifying the Smoluchowski theory for diffusion controlled reactions and reported a slightly lower rate of $1.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. Intriguingly, the transient absorbance decay for the DPM radical in solution was not well fit by a second-order rate law in our experiment; instead a first-order rate law gave a better fit. Figure 4.2.4.2.2 shows the relevant plots for the decay of DPM in oxygen-free acetonitrile solution, the results were qualitatively similar when oxygen was present. An examination of the experimental conditions of the previous studies does not provide a clear culprit for this discrepancy, however a few important differences may be noted. Two out of the three studies used diphenylmethyl chloride as their DPM radical source and the only study which used TPA as the source monitored the decay by excited state emission of the DPM\* radical rather than by direct DPM radical absorbance detection. It is also the case that the 90 mJ at 266 nm laser used in this work for the generation of DPM radicals was significantly more powerful than the lasers used in other studies. It may be that geminate recombination processes lead to a pseudo first order decay under these conditions.
Table 4.2.4.2.1 summarizes the first order decay constants and lifetimes of the DPM radicals in acetonitrile solution and in microcrystalline suspensions both with and without oxygen. Figure 4.2.4.2.3 displays the decay curves for the DPM radicals under the same conditions. It is clear that while oxygen has a profound effect on the decay rate in solution, it has virtually no effect in microcrystalline suspensions. This is additional evidence that oxygen is not able to penetrate DPM microcrystals and provide the quenching effect that is so prominent in solution. The DPM decay rate is significantly slower in microcrystalline suspension than in solution. This is explained by two additional barriers to recombination which a geminate pair of DPM radicals held within the rigid crystal lattice face relative to DPM radicals in solution: the DPM radical pair is generated in the triplet state and must undergo an intersystem crossing step before it can recombine, and the radical pair is not as free to move into optimum recombination geometry as it would be in solution. It is worthwhile to compare the DPM lifetime in microcrystalline suspension with its lifetime in zeolites (44,000 ns)\textsuperscript{28} and in micelles (840 ns)\textsuperscript{14} as these values bracket the microcrystalline suspension lifetime (5000 ns) and the conditions are comparable in

![Figure 4.2.4.2.](image-url)
different respects. The long lifetime in zeolites represents the boundary case of DPM radicals at low concentrations and in a rigid media, DPM radicals in microcrystalline suspension can be seen as an example of the high concentration in a rigid media case. Micelles on the other hand represent a small and concentrated packet of DPM radicals that are still relatively mobile and therefore have faster recombination lifetimes verses both microcrystalline suspensions and solutions. The decay rate of the unidentified transient absorbance at 520 nm is also reported, it is slightly shorter than the decay of the main transient absorbance at 330 nm suggesting that it is not absorbance from the DPM radical itself but from some other transient species.

**Table 4.2.4.2.1.** Rate constants and lifetimes for the decay of the DPM radical under various conditions.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>( \lambda ) (nm)</th>
<th>( k ) (s(^{-1}))</th>
<th>( \tau ) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution in ACN, argon purged</td>
<td>330</td>
<td>6.9 \times 10^5</td>
<td>1440 ± 25</td>
</tr>
<tr>
<td></td>
<td>520</td>
<td>9.5 \times 10^6</td>
<td>1050 ± 65</td>
</tr>
<tr>
<td>Solution in ACN, oxygen purged</td>
<td>330</td>
<td>3.9 \times 10^5</td>
<td>260 ± 15</td>
</tr>
<tr>
<td>Microcrystalline suspension, argon</td>
<td>340</td>
<td>2.1 \times 10^5</td>
<td>4800 ± 125</td>
</tr>
<tr>
<td>purged</td>
<td>340</td>
<td>2.0 \times 10^5</td>
<td>5000 ± 165</td>
</tr>
</tbody>
</table>
4.3. Conclusion

This has been the first report of transient absorbance spectra and kinetics for the photodecarbonylation of a dibenzyl ketone derivative in a microcrystalline suspension. While this class of reaction has been extensively studied under other conditions (solutions, micelles, and in zeolites) the synthetic utility of the solid-state version makes it worthy of additional scrutiny. We have developed a protocol for the preparation of minimally scattering microcrystalline suspensions of TPA and have confirmed that the crystal packing is similar in microcrystals and the bulk powder. Our product analysis has shown that while these reactions go cleanly to TPE in the solid state, benzophenone is the major product in solution. The transient absorbance signal for TPA in microcrystalline suspension is slightly (10 nm) red shifted verses the solution spectrum, and the transient lifetimes are significantly longer.
4.4. Experimental

4.4.1. Sample Preparation

Solutions for laser flash photolysis were prepared in acetonitrile at a 40 μM concentration and were purged with argon to remove dissolved oxygen or purged with air to oxygenate the sample. Microcrystalline suspensions were prepared by injecting 800 μL of 10 mM solution of TPA in ACN into 200 mL of rapidly stirred 450 μM CTAB solution in water to give a final TPA concentration of 40 μM. Microcrystalline suspensions were photolyzed immediately as they were found to lose optical quality over time.

4.4.2. Laser Flash Photolysis

Transient absorbance data was collected using an LP920 Laser Flash Photolysis Spectrometer from Edinburgh Instruments, equipped with a Tektronix TDS3032C oscilloscope. The fourth harmonic (266 nm; 6 ns pulse duration, 90 mJ) from a Brilliant B 850 mJ Nd:YAG laser from Quantel was used for sample excitation. The sample compartment was modified to accommodate a quartz flowcell; analyte solutions and suspensions were pumped into the cell using a Masterflex tubing pump from Cole-Parmer equipped with polytetrafluoroethylene tubing at a rate of 1.2 mL/min. Between 5 and 50 scans were averaged for each decay to obtain an adequate signal to noise ratio. In general, more scans were necessary for microcrystalline suspensions than for solutions due to the lower transient absorbance signal strength. In cases where oxygen was being excluded, argon was bubbled through the analyte during the course of the experiment.

4.4.3. Product Analysis

Solutions of TPA in acetonitrile, solid TPA, and microcrystalline suspensions of TPA both with and without surfactant were photolyzed in a Rayonet photo reactor equipped with 253 nm lamps. For microcrystalline suspensions: 500 μL of 100 mM TPA in ACN was quickly pipetted
into 200 mL of water or 450 μM aqueous CTAB solution to give a cloudy suspension with TPA concentration of 250 μM. Solutions and microcrystalline suspensions were stirred with a magnetic stir bar during photolysis, the solid was crushed into a thin layer on a microscope slide. After photolysis, the products were isolated from the microcrystalline suspensions by extraction into three portions of diethyl ether, drying the combined organic layer with brine followed by magnesium sulfate and evaporating. Photolyzed ACN solutions were simply evaporated under reduced pressure.

Photolyzed samples were analyzed using an Agilent 6890-5975 GC-MS and by solution NMR (CDCl₃). Ion fragmentation was fairly extensive in the mass spectrum of all of the identified compounds, however use of the NIST Mass Spectral Library aided in photoproduct identification. Spectral features used to identify TPA and its photoproducts are described below.

*Tetrapheyl Acetone (TPA):* ¹H NMR (CDCl₃, 300 MHz) δ 7.38-7.27 (m, 12 H), 7.21-7.18 (m, 8H), 5.30 (s, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 205.5, 138.0, 129.1, 128.7, 127.3, 63.5; GCMS: retention time 10.9 min, base peak 167 m/z. The NMR spectra of TPA matched previously reported spectra. While the molecular ion peak (362 m/z) was not observed by GCMS, 167 m/z is a plausible fragment for this compound. The α-proton peak at 5.3 ppm was typically used for quantification.

*Tetraphenylethane (TPE):* ¹H NMR (CDCl₃, 500 MHz) δ 7.17-7.16 (m, 8 H), 7.12-7.09 (m, 8H), 7.03-6.98 (m, 4H), 4.77 (s, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 143.3, 128.4, 128.0, 125.7, 56.2; GCMS: retention time 9.5 min, base peak 167 m/z. While pure TPE was never generated in these experiments, the NMR spectra could be determined from the 70.9% TPE sample, which was generated after a 24 hour photolysis of a surfactant-free microcrystalline suspension of TPA. Once again, the molecular ion (334 m/z) is not seen, however the combination of NMR evidence,
the different retention time from TPA, and the mass spectrum’s excellent agreement with the TPE spectrum from the NIST database gives strong support to the assignment. Once again, the α-proton peak at 4.77 ppm provided the most convenient handle for NMR quantification.

Benzophenone: $^1$H NMR (CDCl$_3$, 500 MHz) δ 7.82-7.80 (m, 4H), 7.61-7.58 (m, 2H), 7.50-7.48 (m, 4H); GCMS: retention time 6.5-6.8 min, base peak 105 m/z, molecular ion 182 m/z. The aromatic protons of benzophenone are downfield of the aromatic signals of all other products of TPA photolysis and were therefore used for NMR quantification.

Unknown at 6.0 retention time: While it was not possible to determine the structure of this compound, when a GCMS signal at 6.0 minutes having base peak 205 m/z is observed, an $^1$H NMR signal at 5.01 ppm is also observed, this signal accounts for a similar proportion of the photoproducts if it is assumed to be a 2H signal.
4.5. Supplementary Figures

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<td>160-162</td>
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Figure 4.5.1. $^1$H NMR (CDCl$_3$, 500 MHz) spectrum of 1,1,3,3-tetraphenylacetone (TPA)
Figure 4.5.2. $^{13}$C NMR (CDCl$_3$, 125 MHz) spectrum of 1,1,3,3-tetraphenylacetone (TPA)
Figure 4.5.3. $^1$H NMR (CDCl$_3$, 300 MHz) spectrum of TPA after 47 hours photolysis in the bulk solid.
Figure 4.5.4. $^1$H NMR (CDCl$_3$, 500 MHz) spectrum of TPA after 4 hours photolysis in ACN solution.
Figure 4.5.5. $^1$H NMR (CDCl$_3$, 500 MHz) spectrum of TPA after 24 hours photolysis in surfactant-free microcrystalline suspension.
Figure 4.5.6. $^1$H NMR (CDCl$_3$, 500 MHz) spectrum of TPA after 3 hours photolysis in CTAB stabilized microcrystalline suspension.
Figure 4.5.7. $^1$H NMR (CDCl$_3$, 500 MHz) spectrum of TPA after photolysis in the LFP, only trace photoproducts are observed.
Table 4.5.8. GCMS retention times and peak areas for the photolysis of **TPA** under various conditions.

<table>
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<tr>
<th>Retention Time (min)</th>
<th>5.7</th>
<th>6</th>
<th>6.1</th>
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<th>9.5</th>
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<tr>
<td>TPA</td>
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<td>----</td>
<td>----</td>
<td>----</td>
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<td>----</td>
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Figure 4.5.9. Mass spectrum of GCMS peak at 10.9 min (TPA).

Figure 4.5.10. Mass spectrum of GCMS peak at 9.5 min (TPE).
**Figure 4.5.11.** Mass spectrum of GCMS peak at 6.5-6.8 min (**Benzophenone**).

**Figure 4.5.12.** Mass spectrum of GCMS peak at 6.1 min (unknown).
Figure 4.5.13. Mass spectrum of GCMS peak at 6.0 min (unknown).

Figure 4.5.14. Mass spectrum of GCMS peak at 5.7 min (unknown).
4.6. References


