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Haresh Thakellapalli

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Syntheses and Properties of Thiophene-Containing Cycloparaphenylenes and Related Macrocycles and a Strained Cyclophane

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Dissertation submitted to the Eberly College of Arts and Sciences
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in
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ABSTRACT

Syntheses and Properties of Thiophene-Containing Cycloparaphenylenes and Related Macrocycles and a Strained Cyclophane

Haresh Thakellapalli

Thiophene-containing cycloparaphenylenes (CPPs) bearing 8, 10 and 16 aromatic and heteroaromatic units in the macrocyclic structure were constructed. Specifically, two and four units of thiophene-2,5-diyl moiety were incorporated into functionalized [6]- and [12]CPP macro-cyclic carbon frameworks, respectively. Insertion of two 2,2'-bithiophene-5,5'-yl units into a functionalized [6]CPP carbon framework led to the formation of the 10-membered macrocycle. In addition, optical and electrochemical properties of these macrocycles were investigated.

The synthetic pathways for thiophene- and 9-fluorenone-containing donor-acceptor macrocycles were also developed. Synthetic pathways to conjugated macrocycles containing one, two, or three 2,7-bis(2-thienyl)-9H-fluoren-9-one (TFOT) units in the macrocyclic frameworks bearing 10, 16, or 24 aromatic units were developed. The Diels–Alder reaction between (*E,E*)-1-(5-bromo-2-thienyl)-4-(5-iodo-2-thienyl)-1,3-butadiene and dimethyl acetylenedicarboxylate produced the key Diels–Alder adduct for the subsequent macrocyclic ring formation. Oxidative aromatization of the macrocyclic precursors and an acyclic analog with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) under mild conditions led to the formation of fully aromatized macrocycles and a corresponding acyclic analog. In addition, optical properties of the TFOT-containing molecules were recorded, and their electrochemical properties were investigated by cyclic and differential pulse voltammetry. Solvatofluorochromic properties were observed for the TFOT-containing molecules.

Finally, a benz[*a*]anthracene- and naphthalene-containing strained cyclophane was synthesized. The Lewis acid-catalyzed electrocyclization reaction of the (*E,E*)-1,4-bis(4-bromonaphthyl)-(2,3-cyclohexane)-1,3-butadiene produced the key intermediate for the subsequent macrocyclic ring formation. The Ni(cod)₂-mediated heterocoupling reaction of the electrocyclization product followed by an oxidative aromatization with DDQ, produced a benz[*a*]anthracene- and naphthalene-containing strained cyclophane. The structure of this cyclophane was established by X-ray structure analysis. Photophysical and electrochemical properties of this strained cyclophane was also investigated.

Dedicated to
Farmers in India
My wife Sruthi Rangineni
&
My family

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Chapter I

Chapter I

Syntheses and Structures of Thiophene-Containing Cycloparaphenylenes and Related Carbon Nanohoops

Introduction:

Cycloparaphenylenes (CPPs) are the cyclic structures where the benzene units are connected at para positions to each other. CPPs are the single segment of armchair carbon nanotubes, and they can be utilized as templates for the synthesis of armchair carbon nanotubes (Figure I-1) with a uniform diameter.¹ In recent years, synthesis of the cycloparaphenylenes is attracting interest² because of their applications in a variety of nanotechnologies³ due to their unique structural and photophysical and electrochemical properties.⁴

Figure I-1. The Structure of [6]Cycloparaphenylene and (6,6)Armchair Carbon Nanotube.

Bertozi and Jasti's Approach for the First Cycloparaphenylenes Synthesis:

The first cycloparaphenylene synthesis was reported by Bertozi and Jasti (Scheme I-1).^{2a} They designed the L-shaped precursor unit for the synthesis of cycloparaphenylenes. The dimethoxy-protected L-shaped unit **I-1** was synthesized by the addition reaction between 4-iodophenyllithium, derived from 1,4-diiodobenzene **I-2**, and 1,4-benzoquinone followed by

protection of the resulting diiodo-diol compound with methyl iodide at 0 °C. In the L-shaped unit **I-1**, both the phenyl groups are on the same side, which is very crucial for the macrocycle ring formation.⁵ Borylation of **I-1** produced diborylated L-shaped unit **I-3**. The Suzuki-Miyaura coupling reaction between the L-shaped diiodo unit **I-1** and the L-shaped diborylated unit **I-3** produced a mixture of CPP precursors, i.e. [9]CPP precursor **I-4** (2%), [12]CPP precursor **I-5** (10%) and [18]CPP precursor **I-6** (10%), with an overall combined yield of 22%.

Scheme I-1. Synthetic Route for the Preparation of [9], [12], and [18] CPP Precursors I-4, I-5, and I-6

The CPP precursors **I-4**, **I-5**, and **I-6** upon aromatization in the presence of lithium naphthanelide⁶ produced [9]CPP **I-7** (43%), [12]CPP **I-8** (52%), and [18]CPP **I-9** (36%) (Scheme I-2).

Scheme I-2. Aromatization Reaction and Proposed Mechanism

Wang's Approach for the Functionalized Cycloparaphenylene Synthesis:

Earlier, our group utilized the Diels-Alder reaction strategy for the synthesis of a functionalized [9]CPP and two hydrogenated [6]CPP derivatives.⁷ The Diels-Alder reaction between diene **I-10**⁸ and 1,4-benzoquinone in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ produced the Diels-Alder adduct **I-11** (Scheme I-3). Methylation of **I-11** yielded the L-shaped precursor **I-12**. The two bromoaryl groups in the L-shaped precursor **I-12** are *cis* to each other exclusively, which is crucial for the construction of macrocycle ring structure.

Scheme I-3. Synthetic Strategy for the Preparation of L-shaped unit I-12

The L-shaped precursor **I-12** was treated with $\text{Ni}(\text{cod})_2$ to produce the homocoupling products as a mixture of isomers of dimer **I-13** and trimer **I-14**.⁹ Both the dimer **I-13** and trimer

I-14 have two isomers their structures were differentiated by X-ray structure analysis and ^1H NMR spectroscopy (Scheme I-4).

Scheme I-4. Synthetic Strategy for the Preparation of Functionalized CPP Precursors Dimer I-13 and Trimer I-14

Oxidative aromatization of the isomeric mixture of the trimer (*syn*-**I-14a** and *anti*-**I-14b**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)¹⁰ was successfully achieved under the mild condition to produce [9]CPP **I-15** in yield of 88% (Scheme I-5). Due to the strain present in the molecule, dimer **I-13** was not aromatized even under harsh reaction conditions.

Scheme I-5. Synthetic Route for the Functionalized [9]CPP I-15

Itami's Approach for the Heteroaromatic-Incorporated Cycloparaphenylenes:

Heteroaromatic-incorporated cycloparaphenylenes were synthesized and their photophysical and electrochemical properties were investigated. Itami group first synthesized the heteroaromatic incorporated cycloparaphenylenes. They developed synthetic pathways for the pyridine-containing CPPs. Their approach for the pyridine-containing CPP involved the preparation of L-shaped intermediate **I-19** by the addition reaction between 1,4-dibromo benzene **I-16** and 1,4-cyclohexadione **I-17** to produce diol **I-18**, followed by protection with methoxymethyl chloride to produce a 2:1 ratio of *syn:anti* mixture of L-shaped intermediate **I-19**. This L-shaped intermediate **I-19** was then treated with 1,4-phenylboronic acid **I-20** to produce U-shaped dibromide intermediate **I-21** (Scheme I-6).¹¹

Scheme I-6. Synthetic Route for the Preparation of U-shaped unit I-21

This U-shaped dibromide **I-21** was then borylated to produce bisboronic acid **I-22**, which was then treated with an excess amount of bipyridyl-dibromide **I-23** to yield bipyridine-containing U-shaped dibromide unit **I-24**. This bipyridine-containing U-shaped unit **I-24** was coupled with U-shaped bis-boronic acid unit **I-22** to produce [14,4]CPPy precursor **I-25** (Scheme I-7).

Scheme I-7. Synthetic Route for the Pyridine-containing CPP precursor I-25

Finally, the bipyridyl (bpy) containing macrocyclic precursor **I-25** was subjected to aromatization with $NaHSO_4$, *o*-chloranil to produce macrocycle [14,4]CPPy **I-26** (Scheme I-8). Itami and co-workers also investigated the UV-vis and fluorescence properties of [14,4]CPPy **I-26**, which were found to be similar to the parent [18]CPP showing blue fluorescence. Interestingly, the hydrochloric salt of the macrocycle [14,4]CPPy **I-26** in dichloromethane shows a red shift and broadening of the peaks of the UV-vis and fluorescence spectra from blue to greenish yellow fluorescence. It is also worth noting that, fluorescence changes back from greenish yellow to blue after the addition of triethylamine to the acidic solution of [14,4]CPPy **I-26**. This phenomenon was demonstrated as halochromism which was observed first time in CPPs.

Scheme I-8. Preparation of Pyridine-containing Cycloparaphenylene I-26

Itami's Approach for Synthesis of Cyclo-1,4-phenylene-2',5'-thienylenes (CPT):

Itami and coworkers reported the synthesis of the thiophene-containing cyclo-1,4-phenylene-2',5'-thienylenes (CPT). They also investigated the photophysical and electrochemical properties of the radially conjugated CPT's. Because of unique properties of these CPTs, they have potential applications towards material science and photovoltaic cells.

Itami and coworkers synthesized the *cis*-L-shaped unit **I-27** by addition of trimethylsilylacetylene to cyclohexane-1,4-dione followed by protection of the hydroxyl groups in **I-28** with methoxymethyl chloride and deprotection of acetylene groups. That *cis*-L-shaped unit, when subjected to the Glaser coupling reactions, produced cyclic dimer **I-29** (32%), trimer **I-30** (31%), tetramer **I-31** (15%), and pentamer **I-32** (6%) in 84% combined yield (Scheme I-9). Cyclic hexamer **I-33** was obtained in 3% yield at higher concentration. Those mixtures of compounds were separated by using the method reported by Collins.¹² The resultant intermediates were subjected to microwave irradiation in the presence of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ to produce a mixture of cyclo-1,4-cyclohexylene-2',5'-thienylenes (CCyT), i.e. **I-34** (86%), **I-35** (50%), **I-36** (46%), and **I-37** (50%).

Scheme I-9. Synthetic Route for the Preparation of Cyclo-1,4-cyclohexylene-2',5'-Thienylenes I-34, I-35, I-36 and I-37

The cyclo-1,4-cyclohexylene-2',5'-thienylene (CCyT) **I-34**, **I-35**, **I-36**, and **I-37** upon aromatization with $\text{NaHSO}_4 \cdot 4\text{H}_2\text{O}$ under higher temperature (150 °C) for 2 days produced cyclo-1,4-phenylene-2',5'-thienylenes (CPT) macrocycles [4]CPT **I-38** (13%), [5]CPT **I-39** (24%), and [6]CPT **I-40** (3%) (Scheme I-10).¹³

Scheme I-10. Preparation of Cyclo-1,4-Phenylene-2',5'-Thienylenes I-38, I-39, and I-40

Photophysical properties of these cyclo-1,4-phenylene-2',5'-thienylenes (CPTs) were interesting. Absorption maxima of these CPTs were showing a red shift with the increase of the ring size, which was similar to the phenomena among π -conjugated compounds. It was also

reported that increase in ring size from [4]CPT **I-38** to [6]CPT **I-40** caused fluorescence maxima to show a considerable blue shift.

Yamago's Approach for the Synthesis of [4]Cyclo-3,7-dibenzo[*b,d*]thiophene and its *S,S*-dioxide:

Yamago and coworkers reported the synthesis of dibenzo[*b,d*]thiophene- and its *S,S*-dioxide-containing macrocycles (Figure 2). They also investigated the properties of these macrocycles. In their synthetic strategy towards these macrocycles, they prepared bis-stannyl compound **I-44** from the commercially available 3,7-dibromodibenzo[*b,d*]thiophene, the *S,S*-oxide **I-45** and these bis-stannyl compounds were treated (Scheme I-11) with Pt(cod)₂ (cod = 1,5-cyclooctadiene), and the resulting crude was treated with triphenylphosphine to produce the desired macrocycles¹⁴ (Figure I-2).

Figure I-2. The Structures of [4]Cyclo-3,7-dibenzo[*b,d*]thiophene and its *S,S*-dioxide Containing Macrocycles

Scheme I-11. Synthetic Route for the Preparation of [4]cyclo-3,7-dibenzo[*b,d*]thiophene and its *S,S*-dioxide Containing Macrocycles

Reagents and conditions:

(a) (1) BuLi (2.1 equiv.), tetrahydrofuran (THF), $-70\text{ }^{\circ}\text{C}$, 1 h. (2) Me₃SnCl (2.3 equiv.), THF, $-70\text{ }^{\circ}\text{C}$ to rt, 4 h, 92%

or

(1) *i*-PrMgCl-LiCl (2.5 equiv.), THF -20 to $0\text{ }^{\circ}\text{C}$, 2 h. (2) Me₃SnCl (3.0 equiv.), THF, $-20\text{ }^{\circ}\text{C}$ to rt, 4 h, 79%.

(b) Pt(cod)Cl₂ (1.0 equiv.), C₂H₄Cl₂, $60\text{ }^{\circ}\text{C}$, 12 h. (c) PPh₃ (8.0 equiv.), toluene, $90\text{ }^{\circ}\text{C}$, 18 h, [4]CBDT, **I-41**, 2.7%; [4]CBDTO, **I-42**, 5.1%.

UV-vis spectrum of [4]CBDT **I-41** shows 3 absorptions at 337, 370 and a shoulder peak around 400-450 nm. In contrast to this, [4]CBDTO **I-42** shows a single absorption peak at 337 nm. Overall, [4]CBDT **I-41** and [4]CBDTO **I-42** show absorption similar to the parent [8]CPP **I-43**. Fluorescence maxima of [4]CBDT **I-41** occurs at 510 nm and [4]CBDTO **I-42** occurs at 429 and 529 nm. [4]CBDT **I-43** and [4]CBDTO **I-44** show the quantum yields (0.21 and 0.41) higher than that of [8]CPP **I-43** (0.081).¹⁵ This phenomenon was due to the presence of the sulfur atom in DBT and DBTO units. The structure becomes more rigid compared to the biphenyl case in [8]CPP **I-43**. As a result, they reduce the loss of excitation energies as vibrational energies.

The oxidation potential of [4]CBDT **I-41** shows two reversible events at 0.74 and 0.96 V, which was higher than that of [8]CPP **I-45** (0.59 V). There was no oxidation wave observed for [4]CBDTO **I-42**. Macrocycles [4]CBDT **I-41** and [4]CBDTO **I-42** show one quasi-reversible reduction at -2.07 V and -1.57 V , respectively, which were much lower than that of [8]CPP **I-43** (-2.33 V). Moderate and strong inductive effects of sulfur and sulfone were consistent with those experimental results.

Syntheses and Structures of Thiophene-Containing Cycloparaphenylenes and Related Carbon Nanohoops

My research involved the development of synthetic pathways for thiophene-containing macrocycles **I-46** and **I-47** (Figure I-3) with two and four units of thiophene-2,5-diyl moiety, respectively.¹⁶ In addition, macrocycle **I-48** bearing two units of 2,2'-bithiophene-5,5'-diyl moiety was also synthesized.

Figure I-3. The Structures of Thiophene-Containing Cycloparaphenylenes **I-46**, **I-47**, and **I-48**

Results and discussion:

Scheme I-12. Synthetic Route for the Preparation of L-shaped Diiodo Intermediate **I-52**

The synthetic approach used the dibromide intermediate **I-12** as a key precursor. Bisboronic ester **I-49** was prepared by the borylation¹⁷ of dibromide **I-12**, the subsequent Suzuki-Miyaura coupling with 2-iodothiophene **I-50**¹⁸ produced **I-51**. Iodination¹⁹ of **I-51** with *N*-iodosuccinimide (NIS) produced L-shaped diiodide **I-52** (Scheme I-12). The structure of **I-52** was determined by X-ray crystal structure analysis (Figure I-4).

Figure I-4. ORTEP Drawing of the Crystal Structure of **I-52**

The Suzuki-Miyaura coupling reaction between **I-49** and **I-52** produced an isomeric mixture of 8 and 16-membered macrocycles. Two thiophene units are incorporated in the 8-membered macrocycle, which has two isomers, i.e. *syn* isomer (*syn*-**I-53**) which has the two 1,4-dimethoxybenzene groups on the same side of the macrocyclic ring and *anti* isomer (*anti*-**I-53**) which has the two 1,4-dimethoxybenzene groups on the opposite side (Scheme I-13). Four thiophene units were incorporated in the 16-membered macrocycle **I-54**, which comprised of a mixture of 4 different stereoisomers. Because we were unable to separate *syn*-**I-53** and *anti*-**I-53** from **I-54** for structural elucidation, the crude mixture of isomers of **I-53** and **I-54** was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for oxidative aromatization at 60 °C to produce thiophene-containing cycloparaphenylene **I-47** and an isomeric mixture of **I-53**. It was possible to separate **I-53** and **I-47** at this stage. The isomeric mixture of **I-53** containing *syn*-**I-53** and *anti*-**I-53** was again subjected to oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at 150 °C to produce **I-46**. The higher temperature was necessary for the reaction because of higher ring strain²⁰ involved in the formation of macrocycle **I-46**.

Scheme I-13. Synthesis of Thiophene-containing Cycloparaphenylenes **I-46** and **I-47**

Macrocycle **I-46** exhibits several distinct conformational isomers because of the presence of two thiophene-2,5-diyl units and two 5,8-dimethoxynaphth-1,4-diyl units. The ^1H NMR spectrum of **I-46** at 25 °C, exhibited only six signals, ^{13}C NMR spectrum exhibited only 12 signals. This phenomenon of one set of signal observation is due to rapid equilibration among various conformational isomers. However at –60 °C, the ^1H NMR spectrum of **46**, exhibited four doublets appearing at δ 7.73, 7.32, 7.15, and 6.69, which were appeared from the four protons on the benzene rings (Figure I-5). It is also observed that three singlets from the protons on the thienyl and naphthyl rings remained as singlets. This observation is due to the fact of a slow rate of rotation on the NMR time scale, around the carbon-carbon connecting the benzene rings to the 5,8-dimethoxynaphth-1,4-diyl units. The protons at *ortho* position on the benzene rings with respect to the 5,8-dimethoxynaphth-1,4-diyl units become nonequivalent, as are the protons at *meta* position. The activation energy ($\Delta G^\ddagger$) of the rotation is estimated to be 11 kcal/mol at the coalescence temperature of –41 °C. Then again, the rate of rotation of the thienyl groups likely stays faster than the NMR timescale.

Figure I-5. The Temperature Dependent ^1H NMR Spectra of *syn-I-46*

The DFT-optimized structure of *syn-I-46* was depicted in figure I-6. In the DFT-optimized conformation of the all *syn* conformer, *syn-I-46*, the two thienyl groups, and the two 5,8-dimethoxynaphth-1,4-diyl units all pointed toward the same direction. The thienyl groups tilt toward the inner plane of the CPP circle at a 38° angle from the inner plane. This observation is similar to that of what was noticed in the crystal structure of a thiophene-containing CPP.¹³ However, the two 5,8-dimethoxynaphth-1,4-diyl units cant away from the inner plane at a 126° angle.

Figure I-6. The DFT-optimized structure of *syn*-**I-46** with ^1H NMR spectral assignments on the perspective view

The ^1H NMR signal assignments of protons H8 at δ 7.15 and H7 at δ 6.69 were assigned using the NOE studies by selective excitation of methoxy groups and other signals at -80°C . This assignment of signals allowed us to demonstrate that both the H8 and H7 existed on the same side of the macrocyclic ring with the methoxy groups. The signals at δ 7.73 and δ 7.32 were assigned to H7' and H8' respectively. The structure of *syn*-**I-46** showed that H7 and H8 tilt toward the inner plane with H7 being bent toward a magnetically shielded region of the 5,8-dimethoxynaphth-1,4-diyl units, which contributed to shifting the signal upfield. The conformer *anti*-**I-46** with one 5,8-dimethoxynaphth-1,4-diyl unit pointing toward one direction and the other unit pointing toward the opposite direction was found to be higher in energy than *syn*-**I-46** by 1.7 kcal/mol according to the DFT calculations. In addition, the conformer with the two thienyl groups pointing toward the same direction but with the two 5,8-dimethoxynaphth-1,4-diyl units pointing toward the opposite direction is higher still in energy than *syn*-**I-46** by 2.3 kcal/mol.

The DFT-optimized structure of **I-47**, depicted in Figure I-7, and showed that the thienyl groups of the all-*syn* conformer, *syn*-**I-47**, tilt toward the inner plane at a 33° angle from the

inner plane while the 5,8-dimethoxynaphth-1,4-diyl units cant away from the inner plane at a 122° angle.

Figure I-7. The DFT-optimized structures of *syn*-**I-47** (aerial view and perspective view)

The homocoupling reactions of **I-52** in the presence of $\text{Ni}(\text{cod})_2^{21}$ (cod: 1,5-cyclooctadiene) and 2,2'-bipyridyl (bpy) produced dimer **I-55** containing two units of 2,2'-bithiophene-5,5'-diyl moiety as an isomeric mixture, i.e. *syn*-**I-55**, and *anti*-**I-55** isomers. Oxidative aromatization of **I-55** (*syn*-**I-55** and *anti*-**I-55**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at 75 °C produced **I-48** (Scheme I-14). Compared to **I-53**, oxidative aromatization of **I-55** occurred under milder reaction conditions because of larger ring size in the macrocycle **I-48**, and the presence of 2,5-disubstituted thiophene units with the angled orientation of the substituents further decrease the ring strain.

Scheme I-14. Synthetic Route for the Preparation of Bithiophene-Containing Cycloparaphenylene I-48

The DFT-optimized structure of *anti*-**I-48**, depicted in Figure I-8. For the macrocycle **I-48**, the *anti* conformer was found to be most stable conformer with all four thiophene units pointing toward the same direction while the two 5,8-dimethoxynaphth-1,4-diyl units pointing toward the opposite direction. The dihedral angle between the two thiophene groups of the 2,2'-bithiophene-5,5'-diyl units is 23.9° .

Figure I-8. The DFT-optimized structures of *anti*-**I-48** (aerial view and perspective view)

The absorption maxima (λ_{abs}) of **I-46**, **I-47**, and **I-48** occur at 363, 350, and 376 nm, respectively (Table I-1 and Figure I-9). The macrocyclic precursors **I-53** and **I-55** show the absorption maxima at 328 and 372 nm, respectively. It is worth noting that there is a blue shift from **I-46** to **I-47** in the absorption maxima as the ring size increases. This phenomenon is

contradictory to the ring size effect of the thiophene-containing CPPs reported previously.¹³ However, the previously reported thiophene-containing macrocycles¹³ and the macrocycles we synthesized have very different molecular skeletons. The reason for the effect of the ring size on the absorption maxima of the macrocycles we synthesized was not clear at this time and needs to be further investigated. It is also worth noting that, there is a red shift from **I-53** to the fully aromatized **I-46**, whereas **I-55** shows slight red-shift from **I-48**.

Figure I-9. UV-vis (dotted line) & fluorescence (solid line) spectra of **I-46**, **I-47**, and **I-48**

Fully aromatized macrocycles **I-46**, **I-47**, and **I-48** show the fluorescence maxima (λ_{em}) at 512, 481, and 511, respectively. It is also interesting to note that there is a blue shift of λ_{em} from **I-46** to **I-47**. This blue shift is because of increase in the ring size which is similar to what was observed previously.^{13, 22} There is a significant red shift from macrocyclic precursors **I-53** and **I-55** to the aromatized macrocycles **I-46** and **I-48**.

	λ_{abs} (nm)	λ_{em} (nm)	E' vs Fc/Fc ⁺ (V) ^a
I-46	363	512	0.41, 0.79 ^b
I-53	328	412	0.69, 1.01
I-47	350	481	0.53, 0.84, 0.98
I-55	372	471	0.46, 0.65, 0.79
I-48	376	511	0.49, 0.93

Table I-1. Optical and Electrochemical Properties of **I-46**, **I-47**, **I-48**, **I-53**, and **I-55** (^aQuasi-reversible waves with redox potentials (E') identified from differential pulse voltammograms. ^bIrreversible redox event)

Figure I-10. Differential pulse (left) and cyclic (right) voltammograms of **I-46**, **I-47**, and **I-48**

With the assistance of Trevor Butcher and Professor Brian Popp of West Virginia University, the electrochemical properties of these thiophene-containing CPPs and their corresponding reduced precursors (**I-53** and **I-55**) were measured and investigated by cyclic and differential pulse voltammetry using dichloromethane as the solvent. It was reported that the oxidation potentials of 1,4-dimethoxynaphthalene,²³ 2,5-diphenylthiophene,²⁴ and 2,2'-bithiophene-5,5'-diyl²⁴ occurred at 0.42 V, 0.96 V, and 0.68 V, respectively. The initial oxidation behavior of compounds **I-46**, **I-47**, and **I-48** appears at 0.41 V, 0.53 V, and 0.49 V, respectively (Table I-1 and Figure I-10). These data suggest that the initial oxidation events of compounds **I-46**, **I-47**, and **I-48** can be attributed to the 1,4-dimethoxynaphthalene unit. The second oxidation events of **I-46** and **I-47**, occurring at 0.79 V and 0.84 V, respectively, can be attributed to 2,5-

diphenylthiophene unit. The second oxidation potential of **I-46** (0.79 V) was less than that of 2,5-diphenylthiophene (0.96 V) by 0.17 V, which can be attributed to the effect of the ring strain on the oxidation potential. The first oxidation potential ($\Delta E_{1/2}$) decreases significantly from **I-53** to **I-46** by 0.28 V, whereas the first oxidation potential of **I-48** increases slightly from **I-55** by 0.03 V. Increasing peak-to-peak separations with higher scan rates indicates all redox events are quasi-reversible.

I-Conclusion:

By utilizing the Diels-Alder reaction as a key reaction, we have developed the synthesis of the L-shaped unit with *cis* geometry which is crucial for the macrocycle ring formation. Iodination of **I-51** to form **I-52** provides the opportunity for using the Suzuki-Miyaura cross coupling and Ni(cod)₂ mediated homocoupling reactions to produce the macrocyclic precursors. These precursors upon oxidative aromatization with DDQ then lead to the thiophene-containing CPPs. In addition to the synthesis of these macrocycles, photophysical and electrochemical properties were also measured. The consolidation of thiophene-2,5-diyl or 2,2'-bithiophene-5,5'-diyl units into the CPP structures presents open doors for the examination of the photophysical and electrochemical properties of these radially π -conjugated systems.

General Experimental Methods:

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Chemicals, including Ni(cod)₂, 2,2'-bipyridyl, Pd(PPh₃)₄, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl₂), (Bpin)₂, 2-iodothiophene, *N*-iodosuccinimide and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), were purchased

from chemical suppliers and were used as received. The UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer with a 1-nm resolution, and the baseline was corrected with a solvent filled square quartz cell. The fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer with a 2-nm resolution.

Experimental Procedure for I-49. To a degassed solution of **I-12** (8.70 g, 17.39 mmol) in 200 mL of dioxane were added bis(pinacolato)diboron (11.04 g, 43.47 mmol), Pd(dppf)Cl₂ (1.27 g, 1.74 mmol), and potassium acetate (8.53 g, 86.95 mmol), and the mixture was stirred at 100 °C for 8 h. After the solution was allowed to cool to room temperature, 1,4-dioxane was removed in vacuo, and then CH₂Cl₂ (400 mL) and water (200 mL) were added. The resulting mixture was extracted with CH₂Cl₂ (2 × 100 mL), and the combined organic layers were washed with water and brine, dried over Na₂SO₄, and concentrated in vacuo to yield a dark-brown solid. The crude product was purified by silica gel column chromatography using CH₂Cl₂/hexanes (3:7) as eluent to obtain **I-49** (9.25 g, 15.56 mmol, 89% yield) as an off-white solid: mp 255–257 °C; IR 1476, 1256, 1093, 793 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.66 (4 H, d, J = 7.8 Hz), 7.23 (4 H, d, J = 8.2 Hz), 6.71 (2 H, s), 5.94 (2 H, d, J = 3.1 Hz), 4.88 (2 H, d, J = 2.7 Hz), 3.57 (6 H, s), 1.333 (12 H, s), 1.329 (12 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 151.4, 148.1, 134.6, 127.60, 127.58, 127.4, 109.1, 83.5, 55.7, 41.5, 24.9, 24.8; HRMS (ESI) calcd for C₃₆H₄₄B₂O₆ [M]⁺ 594.3319, found 594.3437.

Experimental Procedure for I-51. To a two-neck 1000 mL-flask containing 5.20 g of **I-49** (8.75 mmol), 5.51 g of 2-iodothiophene (**I-50**, 26.24 mmol), and 8.35 g of sodium carbonate (78.77 mmol) and fitted with a condenser and a rubber septum were added toluene (350 mL), ethanol (120 mL), and water (40 mL). The solution was flushed with nitrogen for 10 min, and then 0.506 g of $\text{Pd}(\text{PPh}_3)_4$ (0.438 mmol) was added. The solution was again flushed with nitrogen for 20 min and then heated at 90 °C for 8 h before it was allowed to cool to room temperature. The solvent was removed in vacuo, and 400 mL of CH_2Cl_2 and 200 mL of water were added. The organic layer was separated, and the aqueous layer was extracted with 100 mL of CH_2Cl_2 . The combined organic layers were concentrated, and the residue was purified by flash column chromatography (silica gel/ CH_2Cl_2 :hexanes = 1:5 to 2:5) to produce 4.10 g of **I-51** (8.07 mmol, 92% yield) as a pale yellow solid: mp 181–183 °C; IR 1477, 1256, 1084, 697 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.48 (4 H, d, J = 8.6 Hz), 7.27–7.22 (8 H, m), 7.05 (2 H, dd, J = 5.0, 3.4 Hz), 6.75 (2 H, s), 6.01 (2 H, d, J = 2.7 Hz), 4.91 (2 H, d, J = 2.7 Hz), 3.63 (6 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 151.4, 144.6, 144.2, 131.9, 128.6, 127.9, 127.7, 127.4, 125.6, 124.2, 122.6, 109.2, 55.8, 40.9; HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{26}\text{O}_2\text{S}_2$ $[\text{M}]^+$ 506.1369, found 506.1373.

Experimental Procedure for I-52. To a 1000 mL-flask were added 4.10 g of **I-51** (8.07 mmol) and 4.54 g of *N*-iodosuccinimide (20.18 mmol). The flask was flushed with nitrogen, and then 400 mL of CHCl₃ and 32 mL of acetic acid were added. The reaction mixture was stirred at room temperature for 8 h. The reaction mixture was washed with 150 mL of a saturated sodium thiosulfate solution, 150 mL of a saturated sodium bicarbonate solution, and 150 mL of water. The organic layer was separated, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel/CH₂Cl₂:hexanes = 1:1) to produce 5.90 g of **I-52** (7.76 mmol, 96% yield) as a white solid: mp 133–135 °C; IR 1475, 1256, 1084, 788 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.37 (4 H, d, *J* = 8.2 Hz), 7.21 (4 H, d, *J* = 8.2 Hz), 7.18 (2 H, d, *J* = 3.9 Hz), 6.92 (2 H, d, *J* = 3.5 Hz), 6.75 (2 H, s), 6.01 (2 H, d, *J* = 2.7 Hz), 4.90 (2 H, d, *J* = 2.7 Hz), 3.63 (6 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 151.3, 150.6, 144.7, 137.8, 131.1, 128.7, 127.8, 127.3, 125.4, 124.1, 109.2, 71.7, 55.8, 40.8; HRMS (ESI) calcd for C₃₂H₂₄I₂O₂S₂ [M]⁺ 757.9302, found 757.9301.

Experimental Procedures for **I-53** and **I-54** and Oxidative Aromatization of **I-54** to Form **I-**

47. To a two-neck 1000 mL-flask containing 1.000 g of **I-52** (1.32 mmol), 0.782 g of **I-49** (1.32 mmol), and 0.837 g of sodium carbonate (7.90 mmol) and fitted with a condenser and a rubber septum were added toluene (500 mL), ethanol (200 mL), and water (80 mL). The solution was flushed with nitrogen for 10 min before 0.076 g of Pd(PPh₃)₄ (0.061 mmol) was introduced. The solution was again flushed with nitrogen for 20 min and then was heated at 90 °C for 8 h before it was allowed to cool to room temperature. The solvent was removed in vacuo, and then 300 mL of CH₂Cl₂ and 100 mL of water were added. The organic layer was separated, and the aqueous layer was extracted with 100 mL of CH₂Cl₂. The combined organic layers were concentrated, and the crude residue containing **I-53** and **I-54** was used in the next step without further purification.

To the flask containing the crude mixture of **I-53** and **I-54** was added 1.70 g of DDQ (7.49 mmol). The flask was flushed with nitrogen, and 100 mL of chlorobenzene was added via cannula. The reaction mixture was heated at 60 °C for 2 h before it was allowed to cool to room

temperature. Chlorobenzene was removed in vacuo, and the residue was taken up in 300 mL of CH₂Cl₂. Then 200 mL of a saturated sodium thiosulfate solution was added, and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (2 × 100 mL), and the combined organic layers were washed with 150 mL of a saturated sodium bicarbonate solution and 100 mL of water and then concentrated in vacuo. The residue was purified by silica gel column chromatography using CH₂Cl₂/hexanes (2:3 to 4:1) as eluent to obtain 0.100 g of **I-53** (0.12 mmol, 9% yield) as a white solid and 0.185 g of **I-47** (0.11 mmol, 17% yield) as a yellow solid.

I-53 (major isomer in the sample): mp > 311 °C; IR 1478, 1252, 1093, 789 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 7.24 (8 H, d, *J* = 8.5 Hz), 7.18 (4 H, s), 6.89 (8 H, d, *J* = 8.2 Hz), 6.79 (4 H, s), 6.40 (4 H, dd, *J* = 3.8, 1.8 Hz), 5.15 (4 H, dd, *J* = 3.7, 1.6 Hz), 3.79 (12 H, s); ¹H NMR signals from the minor isomer of **I-53** in the sample: ¹H NMR (CDCl₃, 600 MHz, partial) δ 6.81 (4 H, s), 6.39 (4 H, dd, *J* = 3.7, 1.6 Hz), 3.81 (12 H, s); ¹³C NMR (CDCl₃, 150 MHz) δ 150.8, 143.6, 141.8, 132.0, 130.3, 128.8, 125.0, 122.8, 108.7, 55.8, 39.0; HRMS (ESI) calcd for C₅₆H₄₄O₄S₂ (M⁺) 844.2676, found 844.2677. **I-47**: mp > 376 °C; IR 1610, 1457, 1252, 795 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.58 (16 H, d, *J* = 8.2 Hz), 7.34 (8 H, s), 7.32 (16 H, d, *J* = 8.2 Hz), 7.18 (8 H, s), 6.90 (8 H, s), 3.62 (24 H, s); ¹³C NMR (CDCl₃, 150 MHz) δ 151.1, 144.8, 144.6, 137.3, 131.7, 130.2, 128.4, 125.1, 124.7, 122.7, 107.3, 56.0; HRMS (ESI) calcd for C₁₁₂H₈₀O₈S₄ [M]⁺ 1680.4731, found 1680.4487.

Experimental Procedure for I-46. A 20 mL-pressure tube containing 0.020 g of **I-53** (0.024 mmol) and 0.022 g of DDQ (0.097 mmol) in 4 mL of chlorobenzene was tightly capped with a teflon screw cap. The pressure tube was heated at 150 °C for 3 h before it was allowed to cool to room temperature. Dichloromethane (50 mL) was introduced, and the reaction mixture was passed through a basic alumina column (10 cm). The column was eluted with an additional 100 mL of CH₂Cl₂. The combined eluents were concentrated in vacuo, and the residue was purified by column chromatography (neutral alumina, 50–200 μm, CH₂Cl₂:hexanes = 2:5) to produce 0.008 g of **I-46** (9.5×10^{-3} mmol, 40% yield) as a yellow solid: IR 1733, 1669, 1599, 1255, 802 cm⁻¹; ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.28 (8 H, d, *J* = 8.6 Hz), 7.20 (8 H, d, *J* = 8.2 Hz), 7.12 (4 H, s), 7.02 (4 H, s), 7.00 (4 H, s), 3.82 (12 H, s); ¹³C NMR (CD₂Cl₂, 150 MHz) δ 151.0, 149.0, 144.2, 136.0, 133.04, 132.97, 128.0, 126.9, 125.0, 122.0, 107.6, 56.2; HRMS (ESI) calcd for C₅₆H₄₀O₄S₂ [M]⁺ 840.2363, found 840.2366.

Experimental Procedure for I-55. A 200 mL-flask containing 1.000 g of **I-52** (1.32 mmol) and 0.500 g of 2,2'-bipyridyl (3.20 mmol) was flushed with nitrogen. The flask was then placed in a glove box under a nitrogen atmosphere before 0.872 g of Ni(cod)₂ (3.17 mmol) was added. The

flask was fitted with a condenser and a rubber septum and then removed from the glovebox. Tetrahydrofuran (66 mL) was introduced via cannula, and the reaction mixture was heated under reflux for 48 h before it was allowed to cool to room temperature. The reaction mixture was passed through a short silica gel column (10 cm), and the column was further eluted with ethyl acetate (200 mL) and CH₂Cl₂ (200 mL). The combined eluents were concentrated, and the residue was purified by flash column chromatography (silica gel/CH₂Cl₂: hexanes = 1:5 to 1:1) to produce 0.210 g of **I-55** (0.208 mmol, 16% yield) as a yellow solid. One of the samples containing only one isomer of **I-55**: mp > 342 °C; IR 1477, 1253, 1082, 785 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 7.51 (8 H, d, *J* = 8.2 Hz), 7.26 (8 H, d, *J* = 8.2 Hz), 7.25 (4 H, d, *J* = 3.8 Hz), 7.20 (4 H, d, *J* = 3.8 Hz), 6.75 (4 H, s), 5.95 (4 H, d, *J* = 2.6 Hz), 4.90 (4 H, d, *J* = 2.3 Hz), 3.64 (12 H, s); One of the samples containing both isomers of **I-55** with the ¹H NMR signals of the other isomer occurring at: ¹H NMR (CDCl₃, 400 MHz, partial) δ 7.30 (8 H, d, *J* = 8.2 Hz), 7.195 (4 H, d, *J* = 3.9 Hz), 6.72 (4 H, s), 5.99 (4 H, d, *J* = 3.1 Hz), 3.63 (12 H, s); ¹³C NMR (CDCl₃, 150 MHz) δ 151.4, 144.3, 143.2, 136.3, 131.6, 128.7, 127.7, 127.3, 125.2, 123.2, 123.1, 109.2, 55.8, 41.0; HRMS (ESI) calcd for C₆₄H₄₈O₄S₄ [M]⁺ 1008.2430, found 1008.2374.

Experimental Procedure for I-48. A 200 mL-flask containing 0.200 g (0.198 mmol) of **I-55** and 0.450 g (1.20 mmol) of DDQ was flushed with nitrogen, and then 100 mL of chlorobenzene was introduced by using a syringe. The reaction mixture was heated at 75 °C for 2 h before it

was allowed to cool to room temperature. Dichloromethane (200 mL) was added, and the solution was immediately passed through a neutral alumina column (7 cm high, 2.5 cm in diameter), and the column was further eluted with 300 mL of CH₂Cl₂. The combined eluents were concentrated in vacuo immediately to afford 0.170 g of **I-48** (0.169 mmol, 85% yield) as a yellow solid: mp > 376 °C; IR 1609, 1458, 1251, 794 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 7.37 (8 H, d, *J* = 8.2 Hz), 7.26 (8 H, d, *J* = 8 Hz), 7.11 (4 H, d, *J* = 3.5 Hz), 7.09 (4 H, s), 7.08 (4 H, d, *J* = 3.5 Hz), 6.98 (4 H, s), 3.75 (12 H, s); ¹H NMR (THF-*d*₈, 600 MHz) δ 7.36 (8 H, d, *J* = 8.5 Hz), 7.22 (8 H, d, *J* = 8.4 Hz), 7.16 (8 H, s), 7.05 (4 H, s), 7.03 (4 H, s), 3.71 (12 H, s); ¹³C NMR (THF-*d*₈, 150 MHz) δ 150.6, 144.8, 144.1, 138.7, 136.6, 131.6, 131.1, 127.4, 126.3, 124.7, 122.2, 121.8, 106.8, 54.7; HRMS (ESI) calcd for C₆₄H₄₄O₄S₄ [M]⁺ 1004.2117, found 1004.2049.

I-References:

1. (a) Jasti, R.; Bertozzi, C. R. *Chem. Phys. Lett.* **2010**, *494*, 1-7. (b) Fort, E. H.; Donovan, P. M.; Scott, L. T. *J. Am. Chem. Soc.* **2009**, *131*, 16006-16007. (c) Bodwell, G. J. *Nature Nanotech.* **2010**, *5*, 103-104. (d) Fort, E. H.; Scott, L. T. *Angew. Chem., Int. Ed.* **2010**, *49*, 6626-6628. (e) Omachi, H.; Nakayama, T.; Takahashi, E.; Segawa, Y.; Itami, K. *Nat. Chem.* **2013**, *5*, 572-576. (f) Sanchez-Valencia, J. R.; Dienel, T.; Gröning, O.; Shorubalko, I.; Mueller, A.; Jansen, M.; Amsharov, K.; Ruffieux, P.; Fasel, R. *Nature* **2014**, *512*, 61-64. (g) Liu, B.; Liu, J.; Li, H.-B.; Bhola, R.; Jackson, E. A.; Scott, L. T.; Page, A.; Irle, S.; Morokuma, K.; Zhou, C. *Nano Lett.* **2015**, *15*, 586-595. (h) Sisto, T. J.; Zakharov, L. N.; White, B. M.; Jasti, R. *Chem. Sci.* **2016**, *7*, 3681-3688.
2. (a) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 17646-17647. (b) Takaba, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 6112-6116. (c) Yamago, S.; Watanabe, Y.; Iwamoto, T. *Angew.*

- Chem., Int. Ed.* **2010**, *49*, 757-759. (d) Liu, Y.-Y.; Lin, J.-Y.; Bo, Y.-F.; Xie, L.-H.; Yi, M.-D.; Zhang, X.-W.; Zhang, H.-M.; Loh, T.-P.; Huang, W. *Org. Lett.* **2016**, *18*, 172-175. (e) Li, S.; Huang, C.; Thakellapalli, H.; Farajidizaji, B.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2016**, *18*, 2268-2271. (f) Golder, M. R.; Colwell, C. E.; Wong, B. M.; Zakharov, L. N.; Zhen, J.; Jasti, R. *J. Am. Chem. Soc.* **2016**, *138*, 6577-6582. (g) Kuroda, Y.; Sakamoto, Y.; Suzuki, T.; Kayahara, E.; Yamago, S. *J. Org. Chem.* **2016**, *81*, 3356-3363. (h) Sun, Z.; Miyamoto, N.; Sato, S.; Tokuyama, H.; Isobe, H. *Chem. - Asian J.* **2017**, *12*, 271-275.
3. Sanchez-Valencia, J. R.; Dienel, T.; Gröning, O.; Shorubalko, I.; Mueller, A.; Jansen, M.; Amsharov, K.; Ruffieux, P.; Fasel, R. *Nature*. **2014**, *512*, 61-64.
4. (a) Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S. *J. Am. Chem. Soc.* **2011**, *133*, 8354-8361. (b) Segawa, Y.; Fukazawa, A.; Matsuura, S.; Omachi, H.; Yamaguchi, S.; Irle, S.; Itami, K. *Org. Biomol. Chem.* **2012**, *10*, 5979-5984. (c) Matsui, K.; Segawa, Y.; Itami, K. *Org. Lett.* **2012**, *14*, 1888-1891. (d) Fujitsuka, M.; Cho, D. W.; Iwamoto, T.; Yamago, S.; Majima, T. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14585-14588. (e) Camacho, C.; Niehaus, T. A.; Itami, K.; Irle, S. *Chem. Sci.* **2013**, *4*, 187-195. (f) Kuwabara, T.; Orii, J.; Segawa, Y.; Itami, K. *Angew. Chem., Int. Ed.* **2015**, *54*, 9646-9649. (g) Darzi, E. R.; Hirst, E. S.; Weber, C. D.; Zakharov, L. N.; Lonergan, M. C.; Jasti, R. *ACS Cent. Sci.* **2015**, *1*, 335-342. (h) Van Raden, J. M.; Darzi, E. R.; Zakharov, L. N.; Jasti, R. *Org. Biomol. Chem.* **2016**, *14*, 5721-5727.
5. Alonso, F.; Yus, M. *Tetrahedron*. **1991**, *47*, 7471.
6. Liu, H.-J.; Yip, J.; Shia, K.-S. *Tetrahedron Lett.* 1997, *38*, 2253.

7. Huang, C.; Huang, Y.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2014**, *16*, 2672-2675.
8. Davis, M. C.; Groshens, T. J. *Synth. Commun.* **2011**, *41*, 206–218.
9. (a) Batson, J. M.; Swager, T. M. *Synlett.* **2013**, *24*, 2545–2549. (b) Kayahara, E.; Patel, V. K.; Yamago, S. *J. Am. Chem. Soc.* **2014**, *136*, 2284–2287.
10. Carreño, M. C.; García-Cerrada, S.; Urbano, A. *Chem. Eur. J.* **2003**, *9*, 4118–4131
11. Omachi, H.; Matsuura, S.; Segawa, Y.; Itami, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 10202.
12. A.-C. Bdard, S. K. Collins, *J. Am. Chem. Soc.* **2011**, *133*, 19976.
13. Ito, H.; Mitamura, Y.; Segawa, Y.; Itami, K. *Angew. Chem., Int. Ed.* **2015**, *54*, 159-163.
14. (a) Dias, F. B.; King, S.; Monkman, A. P.; Perepichka, I. I.; Kryuchkov, M. A.; Perepichka, I. F.; Bryce, M. R. J. *Phys. Chem. B.* **2008**, *112*, 6557. (b) Perepichka, I. I.; Perepichka, I. F.; Bryce, M. R.; Pålsson, L.-O. *Chem. Commun.* **2005**, 3397.
15. Fujitsuka, M.; Cho, D. W.; Iwamoto, T.; Yamago, S.; Majima, T. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14585.
16. Thakellapalli, H.; Farajidizaji, B.; Butcher, T. W.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2015**, *17*, 3470-3473.
17. (a) Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508-7510. (b) Meng, H.; Sun, F.; Goldfinger, M. B.; Jaycox, G. D.; Li, Z.; Marshall, W. J.; Blackman, G. S. *J. Am. Chem. Soc.* **2005**, *127*, 2406-2407.
18. Takahashi, K.; Tarutani, S. *Heterocycles.* **1996**, *43*, 1927-1935.

19. (a) Guthrie, D. A.; Tovar, J. D. *Org. Lett.* **2008**, *10*, 4323-4326. (b) Wang, J.-L.; Luo, J.; Liu, L.-H.; Zhou, Q.-F.; Ma, Y.; Pei, J. *Org. Lett.* **2006**, *8*, 2281-2284. (c) Melucci, M.; Barbarella, G.; Zambianchi, M.; Di Pietro, P.; Bongini, A. *J. Org. Chem.* **2004**, *69*, 4821-4828. (d) Zhao, C.; Chen, X.; Gao, C.; Ng, M.-K.; Ding, H.; Park, K.; Gao, Y. *Synth. Met.* **2009**, *159*, 995-1001.
20. (a) Segawa, Y.; Omachi, H.; Itami, K. *Org. Lett.* **2010**, *12*, 2262-2265. (b) Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S. *J. Am. Chem. Soc.* **2011**, *133*, 8354-8361.
21. (a) Huang, C.; Huang, Y.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2014**, *16*, 2672-2675. (b) Segawa, Y.; Miyamoto, S.; Omachi, H.; Matsuura, S.; Šenel, P.; Sasamori, T.; Tokitoh, N.; Itami, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3244-3248. (c) Segawa, Y.; Šenel, P.; Matsuura, S.; Omachi, H.; Itami, K. *Chem. Lett.* **2011**, *40*, 423-425. (d) Sibbel, F.; Matsui, K.; Segawa, Y.; Studer, A.; Itami, K. *Chem. Commun.* **2014**, *50*, 954-956.
22. Camacho, C.; Niehaus, T. A.; Itami, K.; Irle, S. *Chem. Sci.* **2013**, *4*, 187-195.
23. Wartini, A. R.; Staab, H. A.; Neugebauer, F. A. *Eur. J. Org. Chem.* **1998**, 1161-1170.
24. (a) van Haare, J. A. E. H.; van Boxtel, M.; Janssen, R. A. J. *Chem. Mater.* **1998**, *10*, 1166-1175. (b) Apperloo, J. J.; Groenendaal, L. B.; Verheyen, H.; Jayakannan, M.; Janssen, R. A. J.; Dkhissi, A.; Beljonne, D.; Lazzaroni, R.; Brédas, J.-L. *Chem.-Eur. J.* **2002**, *8*, 2384-2396. (c) Salhi, F.; Lee, B.; Metz, C.; Bottomley, L. A.; Collard, D. M. *Org. Lett.* **2002**, *4*, 3195-3198. (d) Nakao, K.; Nishiuchi, T.; Iyoda, M. *Heterocycles.* **2008**, *76*, 727-745. (e)

Kuroda, M.; Nakayama, J.; Hoshino, M.; Furusho, N.; Ohba, S. *Tetrahedron Lett.* **1994**, 35, 3957-3960.

Chapter II

Chapter II

Synthesis and Properties of Macrocycles Containing 2,7-Bis(2-thienyl)-9*H*-fluoren-9-one Units

Introduction:

The optical and electronic properties of 2,7-bis(2-thienyl)-9*H*-fluoren-9-one (**1**, TFOT, Figure II-1) and related compounds have been the subjects of intense current interest.¹ A variety of oligomers and polymers containing thiophene as a donor and 9-fluorenone as an acceptor were prepared for the examination of their optoelectronic properties and the assessment of their potential application in electronic devices.^{1,2} Light-emitting copolymers derived from 9,9-dioctylfluorene and TFOT were prepared and their optical and electroluminescence properties were studied.³ Only acyclic TFOTs and mainly linear oligomers/polymers were synthesized. Incorporating donors and acceptors in a conjugated, macrocyclic structure is being recognized to hold possibilities for tuning electronic properties and for the design of functional materials.⁴ Synthetic pathways to thiophene-containing cycloparaphenylenes (CPPs)⁵ and [4]cyclofluorene⁶ were reported recently. Our interest in the development of macrocyclic structures drove us to create synthetic pathways for TFOT-containing macrocycles. The UV-vis and fluorescence spectra and cyclic voltammetry of these new macrocycles were explored.

Figure II-1. Molecular Structure of 2,7-Bis(2-thienyl)-9*H*-fluoren-9-one (**II-1**, TFOT).

Itami's Approach for the Synthesis of Donor-Acceptor Macrocycles:

Itami group synthesized two acceptor-inserted CPPs, which were reported to display solvatofluorochromic properties due to their donor–acceptor characteristics.^{4a} In this approach, they constructed the macrocycles by using 9,10-anthraquinone as the acceptor and phenyl groups as the donor groups.

In the synthetic approach, they synthesized the U-shaped intermediate **II-2** as a key intermediate (Scheme II-1). Treatment of 1,4-dibromobenzene **II-3** with *t*-BuLi followed by the 1,4-cyclohexanedione monoethyleneacetal **II-4** produced **II-5**, after acidic workup. Protection of intermediate **II-5** with MOMCl produced intermediate **II-6**. The methoxymethyl protected U-shaped intermediate **II-2**⁷ was synthesized by the addition reaction between 1,4-dibromobenzene **II-3** and intermediate **II-6** followed by protection with MOMCl.

Scheme II-1. Synthesis of U-shaped intermediate II-2

The Suzuki-Miyaura coupling reaction between the U-shaped intermediate **II-2** and 2,6-diborylanthraquinone (**II-7**) produced the C-shaped unit **II-8** (Scheme II-2). The Ni(cod)₂-

mediated intramolecular homocoupling reaction of the C-shaped intermediate **II-8** provided **II-9** the precursor of a donor-acceptor macrocycle.

Scheme II-2. Synthesis of Macrocyclic Precursor II-9

The aromatization reaction of the macrocyclic precursor **II-9** with $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ and *o*-chloranil produced functionalized 9,10-anthraquinone inserted donor-acceptor macrocycle **II-10** (Scheme II-3). Macrocycle **II-10** was converted to tetracyano-inserted macrocycle **II-11** by treatment with malononitrile in the presence of TiCl_4 as a Lewis acid to increase the strength of electron affinity of the acceptor.⁸

Scheme II-3. Synthesis of Donor-Acceptor Macrocycles II-10 and II-11

In addition to the synthesis, they also investigated the photophysical properties of these macrocycles with respect to [12]CPP. It was found that absorption maxima of these macrocycles were very similar to [12]CPP with **II-10**, **II-11**, and [12]CPP show absorption maximum at 332, 335, and 338 nm, respectively.

They also measured the fluorescence properties of these macrocycles in CCl₄ against [12]CPP and interesting properties were observed. In the fluorescence spectra, macrocycle **II-10** shows green, macrocycle **II-11** shows red, and [12]CPP shows blue emission. It was also found that macrocycle **II-10** shows very different fluorescence properties in various solvents from green in CCl₄ to orange in chlorobenzene. This solvent dependent phenomenon was explained by the solvatofluorochromic properties of the donor-acceptor molecules, which are capable of intramolecular charge transfer.⁹

Itami group also measured the cyclic voltammetry of the macrocycles along with their corresponding macrocyclic precursors and it was found that only slight differences in the reduction potentials were observed. This observation indicates negligible ring effect on electron-accepting properties.

Jasti's Approach for the Synthesis of Donor-Acceptor Macrocycles:

Jasti and coworkers also reported the synthesis of donor-acceptor macrocycles.¹⁰ Their strategy involves the synthesis of pyridine-containing cycloparaphenylenes followed by the formation of pyridinium units to produce donor-acceptor cycloparaphenylenes. Their synthetic strategy includes the formation of pyridine-containing intermediate **II-12** by using a strategy similar to their earlier synthesis of cycloparaphenylenes (Scheme II-4).¹¹

Scheme II-4. Synthesis of Pyridine-Containing Intermediate II-12

The Suzuki-Miyaura coupling between diborylated intermediate **II-12** and dibromide **II-13** produced the pyridine-containing cycloparaphenylene precursor **II-14**. These precursors upon aromatization with sodium naphthalene produced pyridine-containing cycloparaphenylenes **II-15**, **II-16**, and **II-17** (Scheme II-5).

Scheme II-5. Synthesis of Pyridine-Containing Cycloparaphenylenes II-15, II-16, and II-17.

Another strategy involved the synthesis of dichloride intermediate **II-18** by the Suzuki-Miyaura reaction between **II-19** and 4-chlorophenyl boronic acid (Scheme II-6). Borylation of the dichloride intermediate **II-18** produced **II-20**. The palladium-catalyzed intramolecular coupling reaction of intermediate **II-20** produced six-membered pyridine-containing

cycloparaphenylene precursor **II-21**, which on treatment with sodium naphthalenide and iodine led to the formation of pyridine-containing cycloparaphenylene **II-22**.

Scheme II-6. Synthesis of Pyridine-Containing Cycloparaphenylene II-22.

The synthesis of donor-acceptor cycloparaphenylenes involved the methylation of pyridine-containing macrocycles **II-15**, **II-16** and **II-22** (Scheme II-7) with methyl triflate and methyl iodide in dichloromethane to produce the corresponding pyridinium-containing donor-acceptor cycloparaphenylenes **II-23**, **II-24**, and **II-25**.

Scheme II-7. Synthesis of Donor-Acceptor Macrocycles II-23, II-24 and II-25.

Jasti group also investigated the photophysical and electrochemical properties of these donor-acceptor macrocycles with respect to their corresponding CPPs and pyridine-containing cycloparaphenylenes. Pyridine-containing cycloparaphenylenes **II-15**, **II-16**, and **II-17** and [8]CPP show their absorption maxima at 345, 349, 353, and 341 nm respectively. A slight difference was observed in the absorption maxima of donor-acceptor macrocycles **II-23** and **II-24** at 345 and 350 nm, respectively. The fluorescence spectra of the donor-acceptor macrocycles **II-23** and **II-24** occur at 598 and 630 nm which are red-shifted when compared to their corresponded pyridine-containing cycloparaphenylenes **II-15**, **II-16**, **II-17**, and [8]CPP¹² at 541, 544, 542, and 533 nm, respectively. Pyridine-containing cycloparaphenylenes **II-15**, **II-16**, **II-17**, and [8]CPP shows the reduction waves at −2.39 V, −2.32 V, −2.39 V, and −2.44 V respectively whereas, donor-acceptor containing cycloparaphenylenes **II-23** and **II-24** show a significant difference in reduction potentials at −1.49 V and −1.36 V, respectively.

The UV-vis spectra of [6]CPP, aza[6]CPP **II-22** and *N*-methylaza[6]CPP **II-25** show λ_{max} at 338, 342, and 343 nm, respectively. All of these macrocycles show a minor absorption peak between 350 and 600 nm. Similar to [6]CPP, there is no fluorescence observed for aza[6]CPP **II-22** and *N*-methylaza[6]CPP **II-25**. Electrochemical measurements were done for [6]CPP, aza[6]CPP **II-22** and *N*-methylaza[6]CPP **II-25**, which show a reduction potential at −2.13 V, −2.19 V and −1.42 V and an oxidation potential at 0.440 V, 0.670 V, and 0.660 V, respectively. From all of the electrochemical measurements, it clearly revealed that LUMO was lowered in the donor-acceptor cycloparaphenylenes.

Nuckolls's Approach for the Synthesis of Donor-Acceptor Macrocycles:

Colin Nuckoll's group also developed synthetic strategies for the donor-acceptor macrocycles.¹³ They used bithiophene as the donor and perylene diimide as the acceptor to

construct the donor-acceptor macrocycles. The synthetic strategy involves the double Stille coupling¹⁴ of 1,7-dibromo-PDI **II-26** with 1,4-bis(tributylstannyl)benzene followed by transmetalation of **II-26'** with dichloro(1,5-cyclooctadiene)platinum(II) produced **II-27** (Scheme II-8).¹⁵

Scheme II-8. Synthesis of Platinum-Containing Intermediate II-27

The intermediate **II-27** on treatment with 5,5'-bis(trimethylstannyl)-2,2'-bithiophene produced intermediate **II-28**, which was not isolated but was treated with an excess of triphenylphosphine to produce donor-acceptor macrocycle **II-29** (Scheme II-9).¹⁶ The structure of **II-29** was confirmed by X-ray structure analysis.

Scheme II-9. Synthesis of Donor-Acceptor Macrocycle 29

Macrocycle **II-29** shows absorption at 300-400 nm attributable to bithiophene, 450-550 nm attributable to perylene diimide, and a new strong absorption band at 550-700 nm. This

longer wavelength band is due to the charge transfer between donor bithiophene to the acceptor perylene diimide unit of the macrocycle. In the cyclic voltammetry, the first oxidation and reduction potentials of **29** occur at 0.58 V and −1.07 V, respectively. It is also noteworthy that optical band gap was measured to be 1.6 eV (theoretical 1.8 eV).

Synthesis and Properties of Macrocycles Containing 2,7-Bis(2-thienyl)-9H-fluoren-9-one

Units

Results and discussion:

My research in developing synthetic pathways to TFOT-containing macrocycles with thiophene as the donor and fluorenone as an acceptor involved an initial synthesis of diene **II-30** from the Horner–Wadsworth–Emmons reaction between **II-31**¹⁷ and **II-32** (Scheme II-10).¹⁸ The resulting diene on selective iodination with *N*-iodosuccinimide (NIS)¹⁹ gave 1,3-butadiene **II-33** (Scheme II-10). A [4 + 2] cycloaddition between diene **II-33** and dienophile dimethyl acetylenedicarboxylate (DMAD, **II-34**) at 140 °C produced the Diels–Alder adduct **II-35** in 72% isolated yield. Both the iodothienyl and bromothienyl groups in **35** are *cis* to each other exclusively, which is essential for the subsequent macrocyclic ring formation.

Scheme II-10. Synthesis of Diels-Alder Adduct II-35

The Diels–Alder adduct **II-35** on reduction with diisobutylaluminium hydride (DIBAL-H) produced diol **II-36**, which was then protected with *tert*-butyldimethylsilyl chloride

(TBSCl)/imidazole to produce **II-37** (Scheme II-11). The higher reactivity of iodothienyl unit toward the Suzuki-Miyaura coupling reaction with bis-boronic ester **II-38**²⁰ allowed the selective formation of **II-39a** and **II-39b** containing one TFOT unit as a 1:1 mixture of two isomers. Attempts to install the second TFOT unit into **II-39a** and **II-39b** by coupling with **II-38** to produce a macrocyclic system bearing two TFOT units were unsuccessful.

Scheme II-11. Synthesis of Dibromide Intermediate II-39

However, the cross-coupling reaction of **II-39a** and **II-39b** with boronic ester **II-40**²¹ was successful in producing **41a** and **41b**, which upon treatment with methyl iodide at 120 °C²² yielded diiodide **II-42a** and **II-42b** (Scheme II-12).

Scheme II-12. Synthesis of Diiodo Intermediate II-42

The intramolecular homocoupling reaction²³ of **II-42a/II-42b** in the presence of Ni(cod)₂ (cod being 1,5-cyclooctadiene) and 2,2'-bipyridyl (bpy) then produced an isomeric mixture of

syn-**II-43** and *anti*-**II-43** (1:1) with *syn*-**II-43** having the two sets of the TBSOCH₂ groups on the same side of the macrocyclic ring and *anti*-**II-43** having the two sets on the opposite sides (Scheme II-13). Macrocyclic **II-44** was synthesized by oxidative aromatization of *syn*-**II-43** and *anti*-**II-43** (1:1) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)¹⁹ at 100 °C for 2 h.

Scheme II-13. Synthesis of TFOT-Containing Macrocycles II-43 and II-44

The dibromo intermediate **II-39a/II-39b** upon the Suzuki–Miyaura coupling reactions with phenylboronic acid (**II-45**) produced **II-46a/II-46b**, which on treatment with DDQ for oxidative aromatization produced **II-47** as an acyclic analog of **II-44** (Scheme II-14).

Scheme II-14. Synthesis of Acyclic TFOT-Containing **II-46** and **II-47**

The Ni(cod)_2 -mediated homocoupling reactions of **II-39a/II-39b** produced an isomeric mixture of precursors of dimer and trimer which were not isolated. Instead, oxidative aromatization was carried out with DDQ to furnish dimer **48** and trimer **49** in 7% and 14% isolated yields, respectively, over two steps (Scheme II-15). Dimer **II-48** contains two TFOT units in a macrocyclic system bearing 16 aromatic units, and trimer **II-49** contain three TFOT units in a 24-membered macrocyclic system.

Scheme II-15. Synthesis of TFOT-Containing Macrocycles **II-48** and **II-49**

In addition to synthesis, we investigated the photophysical and electrochemical properties of these donor-acceptor macrocycles. In the UV-vis spectra of TFOT (**II-1**), the absorption band at 348 nm can be attributed to the π - π^* movement of the thiophene units.^{1a,d} The weaker band at around 464 nm can be attributed to an internal charge-transfer (ICT) from a donor thiophene unit to an acceptor 9-fluorenone^{1a,d} unit. This band may also be attributed to the n - π^* transition of the carbonyl group of the 9-fluorenone unit. The n - π^* /ICT transitions of the TFOT-containing molecules in Table 1 are red-shifted from that of **II-1**. In addition, **II-44**, which is fully aromatized with a cyclic structure, was blue-shifted by 30 nm from acyclic analog **II-47**. This shift may be caused by the higher ring strain in the fully aromatized and cyclized **II-44**, which affects the planarity of the aromatic units and the dihedral angles between adjacent aromatic units. Interestingly, the π - π^* transition of fully aromatized and cyclic **II-44** showed a blue shift from that of the partially hydrogenated **II-43**. On the other hand, the π - π^* transition of acyclic but fully aromatized **II-47** is red-shifted from that of **II-46**.

The fluorescence spectrum of **II-1** in dichloromethane showed an emission maximum (λ_{em}) at 571 nm,^{1a,b} whereas **II-44** exhibited two peaks of nearly equal intensity at 454 nm and 573 nm. The longer λ_{em} of all other TFOT-containing molecules are red-shifted from that of **II-1** (Table II-1 & Figure II-2).

Figure II-2. UV-vis (solid line) and fluorescence (dashed lines) spectra of **II-43**, **II-44**, **II-46**, **II-47**, **II-48**, and **II-49**.

	λ_{abs} (nm)		λ_{em} (nm)	$E_{1/2}$ (V vs. Fc/Fc ⁺) ^a
	$\pi-\pi^*$	n- π^*/ICT		
II-1	348	464	419, 571	-1.64, 0.76, ^b 0.99 ^b
II-43	348	482	425, 591	-1.67, 0.74
II-44	340	470	454, 573	-1.65, 0.82, ^b 0.92 ^b
II-46	362	475	429, 595	-1.67
II-47	370	470	453, 594	-1.60
II-48	372	473	596	-1.64, 0.67
II-49	368	476	597	-1.66, 0.76

Table II-1. UV-vis Absorption Maxima, Fluorescence Emission Maxima, and Voltammetric Data

Figure II-3. UV-vis (solid line) spectrum of **II-44** in dichloromethane and fluorescence (dashed lines) spectra of **II-44** in various solvents upon excitation at 365 nm.

With the assistance of Notashia Baughman and Professor Brian Popp of West Virginia University, the electrochemical properties of **II-1**^{1a,b} and TFOT-containing atoms were examined in dichloromethane via cyclic voltammetry (CV) and differential pulse voltammetry (DPV) (Table 1). A single quasi-reversible cathodic event was observed in all compounds. Small variations in $E_{1/2}$ (<50 mV relative to **II-1**) suggest that the LUMO is centered around the 9-fluorenone moiety. Linear and cyclic single donor-acceptor molecules exhibited ill-defined and largely irreversible oxidation behavior except for the hydrogenated precursor **II-43**, which showed a single quasi-reversible anodic event ($E_{1/2} = 0.74$ V). This is attributable to the 4,4'-bis(2-thienyl)biphenyl moiety.²⁴ It is noteworthy that, after aromatization of the hydrogenated precursors **II-43** and **II-46** to form **II-44** and **II-47**, respectively, DPV revealed several irreversible anodic events (>1.0 V). These can be attributed to newly formed 2,5-diphenylthiophene^{19a} and/or 1,4-bis(2-thienyl)benzene groups.²⁵ Larger macrocycles (**II-48** and **II-49**) each exhibit a single quasi-reversible anodic event at a potential consistent with a 5,5'-diphenyl-2,2'-bithiophene unit.^{19a} Anodic events consistent with 2,5-diphenylthiophene and/or 1,4-bis(2-thienyl)benzene units were also observed.

λ_{em} (nm) ^a					
	C ₆ H ₁₄	Et ₂ O	C ₆ H ₆	CH ₂ Cl ₂	CHCl ₃
II-1	554	553	554	571	577
II-44	545	560	569	573	597
II-47	534	555	562	594	580

Table II-2. Solvatofluorochromic Properties of **II-1**, **II-44**, and **II-47**

A modest solvatofluorochromic property was observed for **II-1**, whereas those of **II-44** and **II-47** were more noteworthy (Table 2). The fluorescence color of **II-44** changes from yellowish green in hexanes to reddish orange in chloroform. The ground and excited state electronic configurations of the macrocycles were shown below (Figure II-3). The excited state configuration of the TFOT unit has the radical cation on the thiophene moiety with thiophene as the donor and radical anion on the 9-fluorenone unit as the acceptor. Compound **II-44** shows a positive solvatofluorochromic property going from solvents with lower to higher polarity. This observation can be attributed to the higher dipole moment of **II-44** in the excited state (Figure II-3), which is further stabilized by the more polar solvents. As a result, the energy gaps between HOMO and LUMO became smaller and the emission maxima were red shifted to longer wavelengths.

Figure II-3. Ground state and excited state electronic configurations of **II-44**.

Conclusion: In summary, synthetic pathways leading to conjugated macrocycles **II-44**, **II-48**, or **II-49** containing one, two, or three TFOT units have been developed. Cycloaddition between 1,3-butadiene **II-33** and dimethyl acetylenedicarboxylate (DMAD, **II-34**) produces the Diels–Alder adduct **II-35** with the two thienyl groups *cis* to each other, which is necessary for the subsequent macrocyclic ring formation. Oxidative aromatization of the partially hydrogenated aromatic precursors with DDQ provides easy access to the fully aromatized macrocycles bearing TFOT units. The effects of cyclic and conjugated aromatic structures on UV-vis and fluorescence spectra of these TFOT-containing molecules were investigated, and their electrochemical properties were studied by cyclic and differential pulse voltammetry. Because of the interesting solvatochromic, photophysical and electrochemical properties of these donor-acceptor macrocycles show various potential applications towards the development of OLEDs, dye-sensitized solar cells, and chemosensors and tuning their properties. Development of the theoretical calculations and results illustrating different excitations were on due course.

General Experimental Methods

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Chemicals, including *N*-iodosuccinimide (NIS), dimethyl acetylenedicarboxylate (DMAD, **6**), diisobutylaluminum hydride (DIBAL-H, 1.0 M solution in hexanes), *tert*-butyldimethylsilyl chloride (TBSCl), imidazole, tetrakis(triphenylphosphine)palladium [Pd(PPh₃)₄], [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium [Pd(dppf)Cl₂], bis(pinacolato)diboron [(Bpin)₂], iodomethane, bis(1,5-cyclooctadiene)nickel [Ni(cod)₂], 2,2'-bipyridyl (bpy), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and phenylboronic acid (**II-17**), were purchased from chemical suppliers and were used as received. 2,7-Bis(2-thienyl)-9*H*-

fluoren-9-one (**II-1**),^{1c} diethyl [(5-bromothiophene-2-yl)methyl]phosphonate (**II-2**),⁷ (*E*)-3-(thiophen-2-yl)acrylaldehyde (**3**),⁸ 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluoren-9-one (**II-10**),¹² 3,3-diethyl-1-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]triaz-1-ene (**II-12**)¹³ were synthesized according to the reported procedures. UV-vis absorption spectra were recorded on a spectrophotometer with a 1 nm resolution, and the baseline was corrected with a solvent filled square quartz cell. Fluorescence spectra were recorded on a spectrofluorophotometer with a 2-nm resolution. Infrared (IR) spectra of liquid and solid samples were recorded on a Fourier transform infrared system equipped with a diamond crystal attenuated total reflectance sampling interface. HRMS spectra were obtained on an FT-ICR mass analyzer coupled with electrospray ionization (ESI).

Experimental Procedure for II-30. To a 500-mL flask were added **II-31** (18.71 g, 59.75 mmol), **II-32** (7.50 g, 54.3 mmol), and potassium *tert*-butoxide (7.91 g, 70.5 mmol). The flask was flushed with nitrogen, and then 200 mL of tetrahydrofuran was added. The reaction mixture was stirred at reflux for 2 h before it was cooled to rt. The solvent was evaporated in vacuo, and 100 mL of water was added. The mixture was extracted with 300 mL of dichloromethane. The organic layer was separated and concentrated in vacuo, and the residue was purified by flash column chromatography (silica gel/hexanes) to produce **II-30** (11.80 g, 39.70 mmol, 73% yield) as a pale yellow solid: IR 1601, 1422, 973, 789, 650 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.18 (1 H, d, *J* = 4.7 Hz), 7.01–6.97 (2 H, m), 6.92 (1 H, d, *J* = 3.9 Hz), 6.78 (1 H, d, *J* = 15.7 Hz), 6.72 (1 H, d, *J* = 3.9 Hz), 6.68–6.58 (3 H, m); ¹³C NMR (CDCl₃, 150 MHz) δ 144.5, 142.7, 130.5,

128.9, 128.1, 127.7, 126.2, 126.06, 125.98, 124.7, 124.6, 111.1; HRMS (ESI/FT-ICR) m/z $[M]^+$ calcd for $C_{12}H_9BrS_2$ 295.9324, 297.9303; found 295.9326, 297.9306.

Experimental Procedure for II-33. A 50-mL flask was charged with **II-30** (3.25 g, 10.9 mmol) and NIS (2.72 g, 12.2 mmol). The flask was flushed with nitrogen, and then 10 mL of *N,N*-dimethylformamide was added. The reaction mixture was stirred at rt for 8 h. Ethyl acetate (100 mL) was added, and the reaction mixture was washed with 150 mL of a saturated sodium thiosulfate solution, 150 mL of a saturated sodium bicarbonate solution, and 150 mL of water. The organic layer was separated, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel/hexanes) to produce **II-33** (3.10 g, 7.33 mmol, 67% yield) as a pale yellow solid: IR 1603, 1414, 968, 778 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 7.12 (1 H, d, $J = 3.9$ Hz), 6.92 (1 H, d, $J = 3.5$ Hz), 6.72 (1 H, d, $J = 3.9$ Hz), 6.715–6.60 (3 H, m), 6.58–6.50 (2 H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.7, 144.3, 137.6, 130.6, 128.8, 128.4, 127.4, 126.3, 125.3, 124.9, 111.5, 72.7; HRMS (ESI/FT-ICR) m/z $[M]^+$ calcd for $C_{12}H_8BrIS_2$ 421.8290, 423.8270; found 421.8293, 423.8274.

Experimental Procedure for II-35. A 25-mL pressure vessel containing **II-33** (3.10 g, 7.33 mmol) and dimethyl acetylenedicarboxylate **II-34** (1.41 g, 9.92 mmol) was charged with toluene (5 mL). The solution was flushed with nitrogen for 1 min and then heated at 140 $^{\circ}C$ for 24 h before it was cooled to rt. The solvent was removed in vacuo, and the residue was purified by

flash column chromatography (silica gel, 1:9 EtOAc/hexanes) to produce **II-35** (3.00 g, 5.31 mmol, 72% yield) as a viscous brown liquid: IR 1722, 1433, 1251, 1063, 794 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.10 (1 H, d, $J = 3.9$ Hz), 6.90 (1 H, d, $J = 3.9$ Hz), 6.69 (1 H, d, $J = 3.9$ Hz), 6.62 (1 H, d, $J = 3.5$ Hz), 5.901 (1 H, d, $J = 9.4$ Hz), 5.877 (1 H, d, $J = 9.4$ Hz), 4.70 (1 H, dd, $J = 6.8, 2.0$ Hz), 4.64 (1 H, dd, $J = 6.8, 2.0$ Hz), 3.679 (3 H, s), 3.674 (3 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.05, 167.00, 149.4, 145.0, 136.8, 134.7, 134.6, 129.7, 127.6, 126.3, 125.8, 125.6, 111.6, 72.7, 52.3, 38.9, 38.7; HRMS (ESI/FT-ICR) m/z $[\text{MH}]^+$ calcd for $\text{C}_{18}\text{H}_{15}\text{BrIO}_4\text{S}_2$ 564.8634, 566.8614; found 564.8639, 566.8617.

Experimental Procedure for II-36. To a solution of **II-35** (5.60 g, 9.91 mmol) in 250 mL of dry toluene at -78 $^{\circ}\text{C}$ was added 49.65 mL of a 1.0 M solution of diisobutylaluminum hydride in hexanes (50 mmol). The solution was then warmed to rt and stirred for an additional 10 h. A saturated aqueous solution of ammonium chloride (200 mL) was added, and the resulting solution was filtered through celite. The aqueous layer was extracted with EtOAc (2×200 mL), and the combined organic layers were washed with water and brine, dried over Na_2SO_4 , and concentrated in vacuo to yield a viscous brown liquid. The residue was purified by silica gel column chromatography using EtOAc/hexanes (1:1) as eluent to produce **II-36** (4.11 g, 8.07 mmol, 81% yield) as a viscous brown liquid: IR 3339, 1435, 1001, 795 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.12 (1 H, d, $J = 3.5$ Hz), 6.92 (1 H, d, $J = 3.5$ Hz), 6.75 (1 H, d, $J = 3.9$ Hz), 6.68 (1 H, d, $J = 3.5$ Hz), 5.808 (1 H, d, $J = 10.2$ Hz), 5.798 (1 H, d, $J = 9.8$ Hz), 4.51 (1 H, d, $J = 7.3$ Hz), 4.45 (1 H, d, $J = 6.9$ Hz), 4.36 (2 H, d, $J = 12.6$ Hz), 4.01 (2 H, d, $J = 11.4$ Hz), 2.30 (2 H,

br); ^{13}C NMR (CDCl_3 , 100 MHz) δ 152.3, 148.0, 136.8, 135.59, 135.53, 129.7, 127.4, 126.8, 126.7, 126.0, 111.2, 72.2, 60.33, 60.31, 40.4, 40.3; HRMS (ESI/FT-ICR) m/z $[\text{MH}]^+$ calcd for $\text{C}_{16}\text{H}_{15}\text{BrIO}_2\text{S}_2$ 508.8736, 510.8716; found 508.8740, 510.8720.

Experimental Procedure for II-37. To a solution of **II-36** (4.10 g, 8.05 mmol) in 25 mL of *N,N*-dimethylformamide at 0 °C were added imidazole (2.19 g, 32.2 mmol) and *tert*-butyldimethylsilyl chloride (3.63 g, 24.1 mmol). The solution was then warmed to rt and stirred for an additional 8 h. Ethyl acetate (200 mL) was added, and the resulting solution was washed with water and brine, dried over Na_2SO_4 , and concentrated in vacuo to yield a viscous brown liquid. The residue was purified by silica gel column chromatography using EtOAc/hexanes (1:9) as eluent to produce **II-37** (5.30 g, 7.18 mmol, 89% yield) as a viscous brown liquid: IR 1251, 1064, 833, 773 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.09 (1 H, d, $J = 3.9$ Hz), 6.89 (1 H, d, $J = 3.5$ Hz), 6.71 (1 H, d, $J = 3.5$ Hz), 6.64 (1 H, d, $J = 3.5$ Hz), 5.818 (1 H, d, $J = 9.4$ Hz), 5.806 (1 H, d, $J = 9.8$ Hz), 4.59 (1 H, d, $J = 6.5$ Hz), 4.54 (1 H, d, $J = 6.7$ Hz), 4.378 (1 H, d, $J = 12.2$ Hz), 4.365 (1 H, d, $J = 12.0$ Hz), 3.94 (2 H, d, $J = 12.1$ Hz), 0.891 (9 H, s), 0.888 (9 H, s), 0.013 (3 H, s), 0.007 (3 H, s), -0.007 (3 H, s), -0.015 (3 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.0, 148.5, 136.5, 132.84, 132.80, 129.3, 127.1, 126.9, 126.8, 125.7, 110.4, 71.5, 59.54, 59.52, 38.4, 38.3, 25.9, 18.2, -5.5 ; HRMS (ESI/FT-ICR) m/z $[\text{MH}]^+$ calcd for $\text{C}_{28}\text{H}_{43}\text{BrIO}_2\text{S}_2\text{Si}_2$ 737.0466, 739.0445; found 737.0473, 739.0449.

Experimental Procedure for II-39a and II-39b. To a two-neck 1 L-flask containing **II-37** (5.20 g, 7.05 mmol), bisboronic ester **II-38** (1.02 g, 2.36 mmol), and potassium carbonate (1.95 g, 14.1 mmol) were added *N,N*-dimethylformamide (312 mL) and water (35 mL). The flask was then fitted with a condenser and a rubber septum. The reaction mixture was flushed with nitrogen for 20 min, and then Pd(PPh₃)₄ (0.110 g, 0.095 mmol) was added. The reaction mixture was again flushed with nitrogen for 20 min and then heated at 70 °C for 1.5 h before it was cooled to rt. The solvent was removed in vacuo, and 300 mL of diethyl ether and 200 mL of water were added. The organic layer was separated, and the aqueous layer was extracted with 100 mL of diethyl ether. The combined organic layers were concentrated, and the residue was purified by flash column chromatography (silica gel, 1:9 EtOAc:hexanes) to recover **II-37** (1.20 g, 1.63 mmol) and produce a 1:1 mixture of **II-39a** and **II-39b** (1.70 g, 1.21 mmol, 45% yield) as an orange solid: IR 1723, 1632, 1252, 1070, 841 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.88 (2 H, s), 7.66 (2 H, d, *J* = 7.6 Hz), 7.49 (2 H, d, *J* = 7.8 Hz), 7.24 (2 H, d, *J* = 3.9 Hz), 6.95 (2 H, d, *J* = 3.9 Hz), 6.92 (2 H, d, *J* = 3.9 Hz), 6.77 (2 H, d, *J* = 3.5 Hz), 5.894 (2 H, dd, *J* = 10.5, 3.1 Hz), 5.852 (2 H, dd, *J* = 10.2, 3.1 Hz), 4.60 (4 H, m), 4.43 (2 H, d, *J* = 12.1 Hz), 4.42 (2 H, d, *J* = 12.1 Hz), 4.02 (2 H, d, *J* = 12.1 Hz), 4.00 (2 H, d, *J* = 12.1 Hz), 0.915 (18 H, s), 0.909 (18 H, s), 0.038 (6 H, s), 0.031 (6 H, s), 0.020 (6 H, s), 0.005 (6 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 193.4, 148.7, 147.4, 142.5, 141.7, 135.6, 135.1, 133.0, 132.9, 131.4, 129.3, 127.2, 126.7, 126.6, 125.8, 123.4, 121.2, 120.7, 110.4, 59.7, 59.6, 38.44, 38.35, 25.9, 18.2, -5.4, -5.6; HRMS (ESI/FT-ICR) *m/z* [M]⁺ calcd for C₆₉H₉₀Br₂O₅S₄Si₄ 1396.3109, 1398.3089, 1400.3069; found 1396.3148, 1398.3094, 1400.3096.

Experimental Procedure for II-41a and II-41b. A 25-mL pressure tube containing a 1:1 mixture of **II-39a** and **II-39b** (0.082 g, 0.059 mmol), boronic ester **II-40** (0.041 g, 0.14 mmol), and potassium carbonate (0.049 g, 0.35 mmol) was fitted with a rubber septum and charged with toluene (2 mL), ethanol (0.66 mL), and water (0.22 mL). The solution was flushed with nitrogen for 20 min, and then Pd(PPh₃)₄ (0.0034 g, 0.0029 mmol) was added. The solution was again flushed with nitrogen for 20 min and then heated at 80 °C for 10 h before it was cooled to rt. The solvent was removed in vacuo, and 25 mL of dichloromethane and 20 mL of water were added. The organic layer was separated, and the aqueous layer was extracted with 10 mL of dichloromethane. The combined organic layers were passed through a short silica gel column and concentrated in vacuo to produce a 1:1 mixture of **II-41a** and **II-41b** (0.080 g, 0.050 mmol, 86% yield) as an orange solid: IR 1721, 1276, 836, 765, 750 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.90 (2 H, d, J = 2.0 Hz), 7.67 (2 H, dd, J = 7.8, 2.0 Hz), 7.55 (4 H, d, J = 8.6 Hz), 7.49 (2 H, d, J = 7.8 Hz), 7.42 (4 H, d, J = 8.6 Hz), 7.26 (2 H, d, J = 3.6 Hz), 7.15 (2 H, d, J = 3.5 Hz), 7.00 (2 H, d, J = 3.5 Hz), 6.94 (2 H, d, J = 3.6 Hz), 5.94–5.87 (4 H, m), 4.65–4.60 (4 H, m), 4.455 (2 H, d, J = 12.1 Hz), 4.441 (2 H, d, J = 11.7 Hz), 4.044 (2 H, d, J = 11.7 Hz), 4.037 (2 H, d, J = 11.8 Hz), 3.77 (8 H, q, J = 7.0 Hz), 1.27 (12 H, t, J = 7.4 Hz), 0.90 (36 H, s), 0.028 (6 H, s), 0.025 (6 H, s), 0.001 (12 H, s); ¹³C NMR (CDCl₃, 150 MHz, 25 °C) δ 193.5, 150.3, 147.7, 145.9, 143.2, 142.6, 141.6, 135.7, 135.1, 133.4, 132.9, 131.6, 131.4, 127.3, 126.8, 126.7, 126.4, 126.0, 123.4, 122.0, 121.1, 120.8, 120.7, 59.8, 59.7, 38.4, 26.0, 18.3, -5.44, -5.48; ¹³C NMR (CDCl₃, 150

MHz, $-40\text{ }^{\circ}\text{C}$) Additional signals appeared at δ 48.9, 40.7, 14.6, and 11.1.; HRMS (ESI/FT-ICR) m/z $[\text{MH}]^+$ calcd for $\text{C}_{89}\text{H}_{119}\text{N}_6\text{O}_5\text{S}_4\text{Si}_4$ 1591.7196; found 1591.7267.

Experimental Procedure for II-42a and II-42b. To a 25-mL oven dried pressure tube were added a 1:1 mixture of **II-41a** and **II-41b** (0.080 g, 0.050 mmol) and 1 mL of iodomethane. The reaction mixture was flushed with nitrogen and sealed with a teflon cap before it was heated at $120\text{ }^{\circ}\text{C}$ for 10 h. The reaction mixture was then cooled to rt and concentrated in vacuo. The residue was purified by preparative thin layer chromatography to yield a 1:1 mixture of **II-42a** and **II-42b** (0.040 g, 0.024 mmol, 48% yield) as a viscous orange oil: IR 1720, 1276, 1260, 765, 750 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.89 (2 H, d, $J = 2.0\text{ Hz}$), 7.70 (4 H, d, $J = 8.2\text{ Hz}$), 7.67 (2 H, dd, $J = 7.8, 2.0\text{ Hz}$), 7.49 (2 H, d, $J = 7.8\text{ Hz}$), 7.33 (2 H, d, $J = 8.6\text{ Hz}$), 7.26 (2 H, d, $J = 3.6\text{ Hz}$), 7.19 (2 H, d, $J = 3.5\text{ Hz}$), 6.99 (2 H, d, $J = 3.5\text{ Hz}$), 6.97 (2 H, d, $J = 3.5\text{ Hz}$), 5.916 (2 H, d, $J = 10.2\text{ Hz}$), 5.902 (2 H, d, $J = 10.2\text{ Hz}$), 4.66–4.61 (4 H, m), 4.45 (4 H, d, $J = 12.1\text{ Hz}$), 4.05 (4 H, d, $J = 11.8\text{ Hz}$), 0.910 (18 H, s), 0.907 (18 H, s), 0.035 (6 H, s), 0.030 (6 H, s), 0.009 (6 H, s), 0.007 (6 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 193.4, 147.6, 147.3, 142.6, 141.6, 137.8, 135.7, 135.1, 134.3, 133.2, 133.0, 131.3, 127.2, 127.1, 127.0, 126.7, 126.6, 123.4, 123.1, 121.2, 120.7, 92.1, 59.72, 59.69, 38.41, 38.34, 25.9, 18.3, -5.47 , -5.49 ; HRMS (ESI/FT-ICR) m/z $[\text{M}]^+$ calcd for $\text{C}_{81}\text{H}_{98}\text{I}_2\text{O}_5\text{S}_4\text{Si}_4$ 1644.3458; found 1644.3498.

Experimental Procedure for *syn*-II-43 and *anti*-II-43. A 20 mL-flask containing a 1:1 mixture of **II-42a** and **II-42b** (0.030 g, 0.018 mmol) and 2,2'-bipyridyl (0.0069 g, 0.044 mmol) was flushed with nitrogen. The flask was then placed in a glovebox before Ni(cod)₂ (0.012 g, 0.044 mmol) was added. The flask was then fitted with a condenser and a rubber septum and then removed from the glovebox. Tetrahydrofuran (18 mL) was introduced via cannula, and the reaction mixture was heated at reflux for 24 h before it was cooled to rt. The reaction mixture was passed through a short silica gel column (10 cm), and the column was further eluted with ethyl acetate (20 mL) and dichloromethane (200 mL). The combined eluates were concentrated, and the residue was purified by preparative thin layer chromatography to yield a 1:1 mixture of *syn*-**II-43** and *anti*-**II-43** (0.020 g, 0.014 mmol, 79% yield) as an orange solid: IR 1721, 1276, 1260, 1071, 765, 750 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 8.05 (8 H, d, J = 8.0 Hz), 7.87 (2 H, d, J = 1.8 Hz), 7.86 (2 H, dd, J = 7.6, 1.9 Hz), 7.84–7.82 (4 H, m), 7.78 (8 H, d, J = 8.5 Hz), 7.52 (2 H, d, J = 8.4 Hz), 7.50 (2 H, d, J = 8.0 Hz), 7.25 (2 H, d, J = 3.5 Hz) 7.24 (2 H, d, J = 3.5 Hz), 7.18 (4 H, d, J = 3.4 Hz), 7.03 (2 H, d, J = 3.5 Hz), 7.02 (2 H, d, J = 3.7 Hz), 6.96 (4 H, d, J = 3.4 Hz), 5.95–5.86 (8 H, m), 4.81–4.77 (4 H, m), 4.68–4.65 (4 H, m), 4.48–4.42 (8 H, m), 3.97–3.93 (8 H, m), 0.92 (36 H, s), 0.907 (18 H, s), 0.904 (18 H, s), 0.049 (12 H, s), 0.029 (12 H, s), 0.026 (6 H, s), 0.018 (6 H, s), 0.010 (6 H, s), 0.004 (6 H, s); ¹³C NMR (CDCl₃, 150 MHz) δ 192.6, 148.7, 148.3, 143.79, 143.77, 142.8, 142.6, 138.98, 138.96, 135.8, 135.3, 134.13, 134.08, 133.3, 132.21, 132.18, 130.9, 127.95, 127.92, 127.70, 127.68, 127.4, 126.58, 126.55, 125.8, 125.6,

122.7, 120.99, 120.8, 120.5, 59.59, 59.57, 59.45, 59.41, 39.43, 39.39, 38.5, 25.97, 25.94, 18.31, 18.28, -5.42, -5.44; HRMS (ESI/FT-ICR) m/z $[M]^+$ calcd for $C_{81}H_{98}O_5S_4Si_4$ 1390.5369; found 1390.5382.

Experimental Procedures for II-44. To a 5-mL flask containing a 1:1 mixture of *syn*-**II-43** and *anti*-**II-43** (0.015 g, 0.011 mmol) was added DDQ (0.0073 g, 0.032 mmol). The flask was flushed with nitrogen for 2 min before 2 mL of chlorobenzene was added. The flask was heated at 100 °C for 3 h before it was cooled to rt. The reaction mixture was passed through a 1 cm basic alumina column, and the column was eluted with 50 mL of dichloromethane. The combined eluates were concentrated in vacuo to yield **II-44** (0.013 g, 0.0094 mmol, 86% yield) as an orange solid: IR 1721, 1553, 1466, 1260, 1064 cm^{-1} ; 1H NMR ($CDCl_3$, 600 MHz) δ 7.72 (2 H, d, J = 1.9 Hz), 7.51 (2 H, dd, J = 7.9, 1.8 Hz), 7.50 (4 H, d, J = 8.5 Hz), 7.44 (4 H, d, J = 8.5 Hz), 7.42 (2 H, d, J = 7.9 Hz), 7.28 (2 H, d, J = 4.0 Hz), 7.27 (4 H, s), 7.24 (2 H, d, J = 3.7 Hz), 7.192 (2 H, d, J = 3.7 Hz), 7.190 (2 H, d, J = 3.7 Hz), 4.89 (4 H, s), 4.85 (4 H, s), 0.88 (18 H, s), 0.86 (18 H, s), 0.04 (12 H, s), -0.02 (12 H, s); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 192.7, 147.5, 146.1, 145.9, 145.7, 143.1, 139.8, 138.6, 137.8, 136.2, 136.0, 135.5, 135.0, 133.8, 131.9, 130.3, 127.9, 127.6, 125.23, 125.15, 123.2, 121.7, 121.5, 121.3, 59.8, 59.5, 25.93, 25.89, 18.2, -5.20, -5.26; 1H NMR (C_6D_6 , 600 MHz) δ 7.97 (2 H, dd, J = 1.8, 0.5 Hz), 7.40 (4 H, d, J = 8.5 Hz), 7.31 (2 H, d, J = 3.6 Hz), 7.27 (4 H, d, J = 8.5 Hz), 7.26 (2 H, d, J = 8.0 Hz), 7.23 (2 H, d, J = 3.6 Hz),

7.20 (2 H, d, $J = 8.2$ Hz), 7.17 (2 H, dd, $J = 7.8, 1.9$ Hz), 7.10 (2 H, d, $J = 3.5$ Hz), 6.99 (2 H, d, $J = 3.7$ Hz), 6.88 (2 H, d, $J = 7.8$ Hz), 5.22 (4 H, s), 5.13 (4 H, s), 0.978 (18 H, s), 0.977 (18 H, s), 0.12 (12 H, s), 0.08 (12 H, s); ^{13}C NMR (C_6D_6 , 150 MHz) δ 191.9, 148.4, 146.7, 146.6, 146.0, 143.4, 140.3, 139.2, 138.5, 136.7, 136.5, 135.7, 135.6, 134.1, 131.6, 130.8, 125.51, 125.47, 123.4, 121.95, 121.90, 121.4, 60.4, 60.2, 26.09, 26.07, 18.47, 18.44, -5.00 , -5.07 ; HRMS (ESI/FT-ICR) m/z $[\text{M}]^+$ calcd for $\text{C}_{81}\text{H}_{94}\text{O}_5\text{S}_4\text{Si}_4$ 1386.5056; found 1386.5088.

Experimental Procedure for II-46a and II-46b. A 25-mL pressure tube containing a 1:1 mixture of **II-39a** and **II-39b** (0.025 g, 0.018 mmol), boronic acid **II-45** (0.0048 g, 0.039 mmol), and potassium carbonate (0.015 g, 0.11 mmol) was fitted with a rubber septum and charged with toluene (2 mL), ethanol (0.66 mL), and water (0.22 mL). The reaction mixture was flushed with nitrogen for 20 min, and then $\text{Pd}(\text{PPh}_3)_4$ (0.0010 g, 0.00087 mmol) was added. The reaction mixture was again flushed with nitrogen for 20 min and then heated at 80 °C for 10 h before it was cooled to rt. The solvent was removed in vacuo, and 25 mL of dichloromethane and 20 mL of water were added. The organic layer was separated, and the aqueous layer was extracted with 10 mL of dichloromethane. The combined organic layers were passed through a short silica gel column and concentrated in vacuo to obtain, without further purification, a 1:1 mixture of **II-46a** and **II-46b** (0.023 g, 0.017 mmol, 92% yield) as a viscous orange oil: IR 1721, 1276, 1260, 1069, 751 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.91 (2 H, d, $J = 0.8$ Hz), 7.68 (2 H, dd, $J = 8.0, 1.6$ Hz), 7.60 (4 H, d, $J = 7.2$ Hz), 7.49 (2 H, d, $J = 8.0$ Hz), 7.47–7.35 (4 H, m), 7.28–7.24 (4 H, m), 7.20 (2 H, d, $J = 3.6$ Hz), 7.00 (2 H, d, $J = 3.6$ Hz), 6.97 (2 H, d, $J = 3.6$ Hz), 5.95–5.89 (4 H,

m), 4.66–4.62 (4 H, m), 4.46 (4 H, d, $J = 11.6$ Hz), 4.05 (4 H, d, $J = 12.0$ Hz), 0.91 (36 H, s), 0.036 (12 H, s), 0.011 (12 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 193.4, 147.8, 146.6, 142.9, 142.5, 141.6, 135.7, 135.1, 134.8, 133.3, 132.9, 131.3, 128.8, 128.7, 127.27, 127.22, 127.14, 127.11, 126.8, 126.7, 126.5, 125.5, 123.4, 122.6, 121.2, 120.7, 59.74, 59.68, 38.40, 38.34, 25.9, 18.3, –5.46, –5.49; HRMS (ESI/FT-ICR) m/z $[\text{MH}]^+$ calcd for $\text{C}_{81}\text{H}_{101}\text{O}_5\text{S}_4\text{Si}_4$ 1393.5603; found 1393.5633.

Experimental Procedure for II-47. To a 5-mL flask containing a 1:1 mixture of **II-46a** and **II-46b** (0.015 g, 0.011 mmol) was added DDQ (0.0061 g, 0.027 mmol). The flask was flushed with nitrogen for 2 min before 2 mL of chlorobenzene was added. The flask was heated at 75 °C for 2 h before it was cooled to rt. The reaction mixture was passed through a 1 cm basic alumina column, and the column was eluted with 50 mL of dichloromethane. The combined eluates were concentrated in vacuo to yield **II-47** (0.014 g, 0.010 mmol, 94% yield) as a viscous orange solid: IR 1721, 1472, 1257, 1048, 835 cm^{-1} ; ^1H NMR (CDCl_3 , 600 MHz) δ 7.97 (2 H, d, $J = 1.8$ Hz), 7.76 (2 H, dd, $J = 7.9, 1.8$ Hz), 7.65 (4 H, d, $J = 8.2$ Hz), 7.56 (2 H, d, $J = 7.6$ Hz), 7.463 (2 H, d, $J = 7.6$ Hz), 7.449 (2 H, d, $J = 7.6$ Hz), 7.42–7.39 (6 H, m), 7.32–7.28 (4 H, m), 7.24 (2 H, d, $J = 3.5$ Hz), 7.20 (2 H, d, $J = 4.1$ Hz), 4.94 (8 H, s), 0.910 (18 H, s), 0.904 (18 H, s), 0.071 (12 H, s), 0.062 (12 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 193.4, 144.7, 143.3, 142.8, 142.4, 141.4, 138.81, 138.78, 135.9, 135.42, 135.40, 135.2, 134.4, 131.6, 130.7, 130.5, 129.0, 128.9, 128.8, 127.5,

125.7, 123.8, 123.1, 121.4, 120.9, 59.5, 25.9, 18.3, -5.12, -5.15; HRMS (ESI/FT-ICR) m/z $[M]^+$ calcd for $C_{81}H_{96}O_5S_4Si_4$ 1388.5212; found 1388.5279.

Experimental Procedure for 48 and 49. A 1 L-flask containing a 1:1 mixture of **39a** and **39b** (0.400 g, 0.286 mmol) and 2,2'-bipyridyl (0.108 g, 0.692 mmol) was flushed with nitrogen. The flask was then placed in a glovebox before $Ni(cod)_2$ (0.189 g, 0.687 mmol) was added. The flask was fitted with a condenser and a rubber septum and then removed from the glovebox. Tetrahydrofuran (286 mL) was introduced via cannula, and the reaction mixture was heated at reflux for 24 h before it was cooled to rt. The reaction mixture was passed through a short silica gel column (10 cm), and the column was further eluted with ethyl acetate (200 mL) and dichloromethane (200 mL). The combined eluates were concentrated, and the residue was used in the next step without further purification.

To the flask containing the residue was added DDQ (0.329 g, 1.45 mmol). The flask was flushed with nitrogen, and 5 mL of chlorobenzene was added via a syringe. The reaction mixture was heated at 75 °C for 2 h before it was cooled to rt. Dichloromethane (100 mL) was added, and the solution was immediately passed through a basic alumina column (7 cm high, 2.5 cm in diameter), and the column was further eluted with 150 mL of dichloromethane. The combined eluates were concentrated, and the residue was purified by flash column chromatography (silica

gel, 1:9 EtOAc/hexanes) to produce **II-48** (0.023 g, 0.0093 mmol, 7% yield) as an orange solid and **II-49** (0.050 g, 0.014 mmol, 14% yield) as an orange solid. **II-48**: IR 1722, 1461, 1252, 1054, 831, 772 cm^{-1} ; ^1H NMR (CDCl_3 , 600 MHz) δ 7.93 (4 H, d, $J = 1.3$ Hz), 7.81 (4 H, dd, $J = 7.8, 1.8$ Hz), 7.57 (4 H, d, $J = 7.7$ Hz), 7.469 (4 H, d, $J = 8.0$ Hz), 7.463 (4 H, d, $J = 8.2$ Hz), 7.37 (4 H, d, $J = 3.5$ Hz), 7.26 (4 H, d, $J = 4.0$ Hz), 7.23 (4 H, d, $J = 3.5$ Hz), 7.20 (4 H, d, $J = 3.5$ Hz), 4.964 (8 H, s), 4.956 (8 H, s), 0.916 (36 H, s), 0.911 (36 H, s), 0.08 (24 H, s), 0.07 (24 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) 193.2, 143.4, 142.9, 142.5, 141.3, 138.7, 138.6, 137.7, 135.5, 135.35, 135.33, 135.26, 131.1, 130.8, 130.7, 128.7, 128.4, 123.5, 123.1, 121.8, 120.8, 59.4, 25.94, 25.92, 18.3, -5.1 , -5.2 ; HRMS (ESI/FT-ICR) m/z $[\text{M}]^+$ calcd for $\text{C}_{138}\text{H}_{172}\text{O}_{10}\text{S}_8\text{Si}_8$ 2468.8865, 2469.8898 (with one ^{13}C), 2470.8932 (with two ^{13}Cs); found 2468.8861, 2469.8663, 2470.8653; **II-49**: IR 1722, 1461, 1276, 1260, 1052, 765, 750 cm^{-1} ; ^1H NMR (CDCl_3 , 600 MHz) δ 7.94 (6 H, d, $J = 1.7$ Hz), 7.82 (6 H, dd, $J = 7.8, 1.7$ Hz), 7.54 (6 H, d, $J = 7.7$ Hz), 7.475 (6 H, d, $J = 8.0$ Hz), 7.469 (6 H, d, $J = 8.0$ Hz), 7.35 (6 H, d, $J = 3.7$ Hz), 7.253 (6 H, d, $J = 3.7$ Hz), 7.247 (6 H, d, $J = 3.7$ Hz), 7.21 (6 H, d, $J = 3.5$ Hz), 5.02 (12 H, s), 5.01 (12 H, s), 0.891 (54 H, s), 0.888 (54 H, s), 0.032 (36 H, s), 0.026 (36 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 192.9, 143.6, 142.80, 142.79, 141.5, 138.6, 138.5, 138.0, 135.4, 135.14, 135.06, 131.0, 130.9, 129.9, 127.7, 127.5, 122.9, 122.4, 122.0, 120.8, 59.15, 59.11, 25.91, 25.90, 18.3, -5.2 , -5.3 ; MS (ESI/FT-ICR) m/z $[\text{M}]^+$ calcd for $\text{C}_{207}\text{H}_{258}\text{O}_{15}\text{S}_{12}\text{Si}_{12}$ 3704.3 (with one ^{13}C), 3705.3 (with two ^{13}Cs), 3706.3 (with three ^{13}Cs), 3707.3 (with four ^{13}Cs); found 3704.9, 3705.9, 3706.9, 3707.9.

II-References:

1. (a) Porzio, W.; Destri, S.; Pasini, M.; Giovanella, U.; Ragazzi, M.; Scavia, G.; Kotowski, D.; Zotti, G.; Vercelli, B. *New J. Chem.* **2010**, *34*, 1961-1973. (b) Pasini, M.; Giovanella, U.; Betti, P.; Bolognesi, A.; Botta, C.; Destri, S.; Porzio, W.; Vercelli, B.; Zotti, G.

- ChemPhysChem*. **2009**, *10*, 2143-2149. (c) Loganathan, K.; Pickup, P. G. *Electrochim Acta* **2007**, *52*, 4685-4690. (d) Demadrille, R.; Rannou, P.; Bleuse, J.; Oddou, J.-L.; Pron, A. *Macromolecules* **2003**, *36*, 7045-7054. (e) Çarbaş, B. B.; Kivrak, A.; Önal, A. M. *Electrochim Acta* **2011**, *58*, 223-230. (f) Lincker, F.; Delbosc, N.; Bailly, S.; De Bettignies, R.; Billon, M.; Pron, A.; Demadrille, R. *Adv. Funct. Mater.* **2008**, *18*, 3444-3453. (g) Wang, T.-L.; Shieh, Y.-T.; Yang, C.-H.; Chen, Y.-Y.; Ho, T.-H.; Chen, C.-H. *J. Polym Res.* **2013**, *20*, 213.
2. (a) Linares, M.; Scifo, L.; Demadrille, R.; Brocorens, P.; Beljonne, D.; Lazzaroni, R.; Grevin, B. *J. Phys. Chem. C* **2008**, *112*, 6850-6859. (b) Hayton, J.; Lincker, F.; Demadrille, R.; Linares, M.; Brun, M.; Grevin, B. *Appl. Phys. Express* **2009**, *2*, 091501. (c) Liu, Z.-D.; Chang, Y.-Z.; Ou, C.-J.; Lin, J.-Y.; Xie, L.-H.; Yin, C.-R.; Yi, M.-D.; Qian, Y.; Shi, N.-E.; Huang, W. *Polym. Chem.* **2011**, *2*, 2179-2182.
3. (a) Xu, Y.; Wang, H.; Liu, X.; Wu, Y.; Gao, Z.; Wang, S.; Miao, Y.; Chen, M.; Xu, B. *J. Lumin.* **2013**, *134*, 858-862. (b) Wang, H.; Yang, J.; Sun, J.; Xu, Y.; Wu, Y.; Dong, Q.; Wong, W.-Y.; Hao, Y.; Zhang, X.; Li, H. *Macromol. Chem. Phys.* **2014**, *215*, 1060-1067.
4. (a) Kuwabara, T.; Orii, J.; Segawa, Y.; Itami, K. *Angew. Chem., Int. Ed.* **2015**, *54*, 9646-9649. (b) Darzi, E. R.; Hirst, E. S.; Weber, C. D.; Zakharov, L. N.; Lonergan, M. C.; Jasti, R. *ACS. Cent. Sci.* **2015**, *1*, 335-342. (c) Van Raden, J. M.; Darzi, E. R.; Zakharov, L. N.; Jasti, R. *Org. Biomol. Chem.* **2016**, *14*, 5721-5727. (d) Ball, M.; Nuckolls, C. *ACS. Cent. Sci.* **2015**, *1*, 416-417. (e) Ball, M.; Fowler, B.; Li, P.; Joyce, L. A.; Li, F.; Liu, T.; Paley, D.; Zhong, Y.; Li, H.; Xiao, S.; Ng, F.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2015**, *137*, 9982-9987. (f) Ball, M.; Zhong, Y.; Fowler, B.; Zhang, B.; Li, P.; Etkin, G.; Paley, D. W.; Decatur, J.; Dalsania, A. K.; Li, H.; Xiao, S.; Ng, F.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2016**, *138*, 12861-12867.

5. (a) Ito, H.; Mitamura, Y.; Segawa, Y.; Itami, K. *Angew. Chem., Int. Ed.* **2015**, *54*, 159-163. (b) Thakellapalli, H.; Farajidizaji, B.; Butcher, T. W.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2015**, *17*, 3470-3473. (c) Kayahara, E.; Zhai, X.; Yamago, S. *Can. J. Chem.* DOI:10.1139/cjc-2016-0474.
6. (a) Kayahara, E.; Qu, R.; Kojima, M.; Iwamoto, T.; Suzuki, T.; Yamago, S. *Chem. - Eur. J.* **2015**, *21*, 18939-18943. (b) Liu, Y.-Y.; Lin, J.-Y.; Bo, Y.-F.; Xie, L.-H.; Yi, M.-D.; Zhang, X.-W.; Zhang, H.-M.; Loh, T.-P.; Huang, W. *Org. Lett.* **2016**, *18*, 172-175.
7. Y. Segawa, T. Kuwabara, K. Matsui, S. Kawai, K. Itami. *Tetrahedron*. **2015**, *71*, 4500–4503.
8. F. Bures[~], W. B. Schweizer, C. Boudon, J. P. Gisselbrecht, M. Gross, F. Diederich. *Eur. J. Org. Chem.* **2008**, *6*, 994 –1004.
9. (a) E. M. Kosower. *Acc. Chem. Res.* **1982**, *15*, 259–266; (b) Z. R. Grabowski, K. Rotkiewicz. *Chem. Rev.* **2003**, *103*, 3899–4032.
10. (a) Darzi, E.; Hirst, E.; Weber, C.; Zakharov, L.; Lonergan, M.; Jasti, R. *ACS Cent. Sci.* **2015**, *1*, 335. (b) Van Raden, J. M.; Darzi, E. R.; Zakharov, L. N.; Jasti, R. *Org. Biomol. Chem.* **2016**, *14*, 5721-5727.
11. (a) Evans, P. J.; Darzi, E. R.; Jasti, R. *Nat. Chem.* **2014**, *6*, 404. (b) Xia, J.; Bacon, J. W.; Jasti, R. *Chem. Sci.* **2012**, *3*, 3018–3021. (c) Darzi, E. R.; Sisto, T. J.; Jasti, R. *J. Org. Chem.* **2012**, *77*, 6624–6628. (d) Sisto, T. J.; Golder, M. R.; Hirst, E. S.; Jasti, R. *J. Am. Chem. Soc.* **2011**, *133*, 15800–15802. (e) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 17646–17647.
12. Yamago, S.; Watanabe, Y.; Iwamoto, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 757–759.
13. (a) Ball, M.; Fowler, B.; Li, P.; Joyce, L. A.; Li, F.; Liu, T.; Paley, D.; Zhong, Y.; Li, H.; Xiao, S.; Ng, F.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2015**, *137*, 9982-9987. (b)

- Ball, M.; Zhong, Y.; Fowler, B.; Zhang, B.; Li, P.; Etkin, G.; Paley, D. W.; Decatur, J.; Dalsania, A. K.; Li, H.; Xiao, S.; Ng, F.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2016**, *138*, 12861-12867.
14. (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Zhang, J. X.; Singh, S.; Hwang, D. K.; Barlow, S.; Kippelen, B.; Marder, S. R. *J. Mater. Chem. C* **2013**, *1*, 5093.
15. Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S. *J. Am. Chem. Soc.* **2011**, *133*, 8354.
16. Iwamoto, T.; Watanabe, Y.; Sadahiro, T.; Haino, T.; Yamago, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 8342.
17. Abboto, A.; Beverina, L.; Bradamante, S.; Facchetti, A.; Klein, C.; Pagani, G. A.; Redi-Abshiro, M.; Wortmann, R. *Chem. - Eur. J.* **2003**, *9*, 1991-2007.
18. Steen, R. O.; Nurkkala, L. J.; Angus-Dunne, S. J.; Schmitt, C. X.; Constable, E. C.; Riley, M. J.; Bernhardt, P. V.; Dunne, S. J. *Eur. J. Inorg. Chem.* **2008**, 1784-1794.
19. (a) Thakellapalli, H.; Farajidizaji, B.; Butcher, T. W.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2015**, *17*, 3470-3473. (b) Melucci, M.; Barbarella, G.; Zambianchi, M.; Di Pietro, P.; Bongini, A. *J. Org. Chem.* **2004**, *69*, 4821-4828.
20. Lee, T.; Landis, C. A.; Dhar, B. M.; Jung, B. J.; Sun, J.; Sarjeant, A.; Lee, J.-H.; Katz, H. E. *J. Am. Chem. Soc.* **2009**, *131*, 1692-1705.
21. Korich, A. L.; McBee, I. A.; Bennion, J. C.; Gifford, J. I.; Hughes, T. S. *J. Org. Chem.* **2014**, *79*, 1594-1610.
22. Moore, J. S.; Weinstein, E. J.; Wu, Z. *Tetrahedron Lett.* **1991**, *32*, 2465-2466.

23. (a) Segawa, Y.; Miyamoto, S.; Omachi, H.; Matsuura, S.; Šenel, P.; Sasamori, T.; Tokitoh, N.; Itami, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3244-3248. (b) Segawa, Y.; Šenel, P.; Matsuura, S.; Omachi, H.; Itami, K. *Chem. Lett.* **2011**, *40*, 423-425.
24. Duan, Z.; Hu, D.; Ohuchi, H.; Zhao, M.; Zhao, G.; Nishioka, Y. *Synth. Met.* **2012**, *162*, 1292-1298.
25. Fraind, A. M.; Tovar, J. D. *J. Phys. Chem. B.* **2010**, *114*, 3104-3116.

Chapter III

Chapter III

Synthesis and Properties of a Benz[*a*]anthracene- and Naphthalene-Containing Strained Cyclophane

III-Introduction:

Polyaromatic hydrocarbons (PAHs) are of special interest in organic chemistry due to their unique planarity, stability, and fluorescent properties. Cyclophanes are systems of aromatic groups linked together to form a “ring of rings”. This linkage often forces the aromatic groups to bend out of planarity, resulting in unusual optical and electrochemical properties. Because of their unique properties, cyclophanes have potential applications in material science, host-guest systems, and nanodevices.¹ Even though several cyclophanes have been synthesized in the literature,² synthetic pathways to strained cyclophanes and related aromatic macrocycles are still challenging and need to be further investigated. In this work, we establish a synthetic route for the construction of a strained cyclophane containing benz[*a*]anthracene and naphthalene units.

Matsuyama’s Approach for the Synthesis of a Strained Cyclophane:

Matsuyama and coworkers synthesized 1,8-[1,8-naphthalenediylbis(4',4'-biphenyldiyl)]naphthalene **III-1**, a very stable strained cyclophane,^{2b} by utilizing the copper-catalyzed coupling reaction of 1,8-bis(4-(tributylstannyl)phenyl)naphthalene **III-2**.

Scheme III-1. Synthesis of Strained Cyclophane **III-1**

The synthetic strategy involved the reaction of **III-3** with *n*-butyllithium and zinc chloride to form arylzinc intermediate **III-4**. The Pd(PPh₃)₄-catalyzed coupling reaction of **III-4** (4 equiv) with 1,8-diiodonaphthalene (**III-5**) produced **III-6** in 60% yield. Treatment of intermediate **III-6** with ICl from –20 °C to 50 °C produced diiodo **III-7** in 74% yield. Because metal-catalyzed coupling reactions of **III-7** were unsuccessful, **III-7** was converted to bisstannylated intermediate **III-2** by treatment with *n*-BuLi and *n*-Bu₃SnCl.

The copper-catalyzed homocoupling reaction of **III-2** produced strained cyclophane **III-1** in 41% yield and hydrolyzed products **III-8** and **III-9**. Treatment of **III-5** with biarylzinc chloride **III-10** produced acyclic analog **III-11** in 50% yield (Scheme III-2).³ The acyclic analog **III-11** was used to compare with the face-to-face arrangement of the benzene units in **III-1**.

Scheme III-2. Synthesis of Acyclic Analog **III-11**

Cyclophane **III-1** shows an absorption maximum at 313 nm and an emission maximum at 427 nm. The absorption maxima of **III-8**, **III-9**, and **III-11** are at 302, 315, and 304 nm, respectively. The emission maxima of **III-8**, **III-9**, and **III-11** are at 377, 393, and 389 nm, respectively.

Matsuyama's group also measured the oxidation potentials of cyclophane **III-1** and related acyclic analogs **III-8**, **III-9**, and **III-11** versus F_c/F_c^+ . It is interesting to note that cyclophane **III-1** shows a lower oxidation potential at 0.85 V, while no oxidation peak was observed for **III-8**, **III-9**, and **III-11**.

Pei's Approach for the Synthesis of Cyclophanes:

Jian Pei and co-workers constructed dibenz[*a,j*]anthracene-containing unsaturated cyclophanes by utilizing an intramolecular McMurry olefination reaction (Scheme III-3).^{2f} The synthetic strategy involved alkylation of 3,4-dihydroxy-benzaldehyde **III-12** followed by the Corey-Fuchs reaction of **III-13** to produce alkyne **III-14**. Dialkyne intermediate **III-17** was prepared via Sonagashira coupling between alkyne **III-14** and 1,5-dibromo-2,4-diiodobenzene (**III-15**) followed by Suzuki coupling reactions with phenylboronic acid **III-16**. Intramolecular cyclization of compound **III-17** in the presence of ICl produced dibenz[*a,j*]anthracene iodide **III-18** in almost quantitative yield.⁴

Scheme III-3 Synthesis of Dibenz[*a,j*]anthracene Iodide III-18

A Suzuki coupling reaction between dibenz[*a,j*]anthracene iodide **III-18** and 4-formylphenylboronic acid (**III-19**) produced dibenz[*a,j*]anthracene dicarbonyl **III-20** in about 88% yield (Scheme III-4). The intramolecular McMurry coupling reaction of **III-20** in the presence of TiCl₄ and Zn powder gave strained cyclophane **III-21** in about 63% yield. It is interesting to note that intermolecular coupling products were not observed in this reaction.

Scheme III-4. Synthesis of Dibenz[*a,j*]anthracene-Containing Cyclophane **III-21**

In addition to the synthesis of cyclophane **III-21**, Jian Pei's group extended their synthetic strategy to the synthesis of cyclophanes **III-24**, **III-28**, and **III-29** (Scheme III-5). The strategy involved the Suzuki coupling reaction between **III-18** and 4-acetylphenylboronic acid **III-22** to produce dibenz[*a,j*]anthracene diacetyl intermediate **III-23**, followed by an intramolecular McMurry coupling to produce cyclophane **III-24**. Another synthetic strategy involved the formation of dibenz[*a,j*]anthracene diformyl and dibenz[*a,j*]anthracene diacetyl intermediates **III-26** and **III-27** by the Suzuki coupling reaction between **III-18** and boronic esters **III-25a** ($\text{R} = \text{H}$) and **III-25b** ($\text{R} = \text{CH}_3$), respectively. The resulting intermediates **III-26** and **III-27**, upon treatment with TiCl_4 and Zn powder, produced cyclophanes **III-28** ($\text{R} = \text{H}$) and **III-29** ($\text{R} = \text{CH}_3$) in 67% and 71% yield, respectively.

Scheme III-5. Synthesis of Dibenz[*a,j*]anthracene-Containing Cyclophanes **III-24, **III-28**, and **III-29****

In the ^1H NMR characterization of **III-18**, **III-20**, and **III-21**, the chemical shift of H_b shifted from δ 9.85 ppm in **III-18** to δ 7.25 ppm in **III-20** due to the shielding effect of the benzene rings connected to the dibenz[*a,j*]anthracene unit (Figure III-1). The chemical shift of H_b was further shifted to δ 5.91 ppm in **III-21** after the intramolecular McMurry coupling and because of the additional shielding effects from the $\text{C}=\text{C}$ double bond in **III-21**.

Figure III-1. ^1H NMR Chemical Shifts of III-18, III-20, and III-21

In the UV-vis absorption spectra, all cyclophanes **III-21**, **III-24**, **III-28**, and **III-29** showed an absorption peak at 312 nm, which was assigned to dibenz[*a,j*]anthracene.⁵ The extended cyclophanes **III-28** and **III-29** showed another absorption peak around 270 nm due to the absorption band of the 1,4-diphenylbenzene unit.⁶ In addition, **III-28** and **III-29** showed absorption bands around 400 and 390 nm, respectively, due to the increase in effective conjugation length.

Synthesis and Properties of a Benz[*a*]anthracene- and Naphthalene-Containing Strained Cyclophane

Results & Discussions:

Earlier, our group reported the synthesis of functionalized [9]cycloparaphenylenes ([9]CPPs) bearing nine aromatic units in the macrocyclic structures.⁷ The synthetic approach involved the Diels–Alder reaction of (*E,E*)-1,4-bis(4-bromophenyl)-1,3-butadiene or a related diene with dimethyl acetylenedicarboxylate, followed by nickel-mediated homocoupling reactions and oxidative aromatization to produce functionalized [9]CPPs (Scheme III-6).

Scheme III-6. Synthesis of the Functionalized [9]CPP Bearing Six Carbomethoxy Groups

Our initial idea involved the synthesis of naphthalene-containing cycloparaphenylenes by utilizing a synthetic pathway similar to the synthesis of functionalized [9]CPPs. The synthetic pathway started with the synthesis of 1-bromo-4-iodonaphthalene (**III-30**), which was produced from 1,4-dibromonaphthalene by the treatment with *n*-BuLi followed by I₂ as reported in the literature (Scheme III-7).⁸ The Sonagashira coupling reaction between **III-30** and 1,7-octadiyne **III-31** produced the diyne intermediate **III-32** in 86% isolated yield.⁹ The diyne intermediate **III-32**, on treatment with a mixture of Cp₂ZrCl₂ and *n*-BuLi, gave diene **III-33** in 96% yield.⁹ The Diels-Alder reaction between diene **III-33** and commercially-available dimethylacetylene dicarboxylate (DMAD) was unsuccessful and led to the formation of undesired products.

Scheme III-7. Our Attempt Toward the Synthesis of Naphthalene-Containing Cycloparaphenylene

After careful investigation of the undesired products formed in the Diels-Alder reaction, it was confirmed that an electrocyclization reaction of diene **III-33** occurred upon treatment with a catalytic amount of BF₃·OEt₂, which produced an isomeric dibromide **III-37** in 83% isolated yield. The mechanistic investigation for the formation of **III-37** indicated an initial BF₃·OEt₂-catalyzed isomerization of diene **III-33** to **III-34**, which was isolated and confirmed by NMR

structure analysis. This isomerized diene **III-34** was then heated at 150 °C in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ also leading to **III-37**. The formation of **III-37** from **III-34** suggested that the *cis/trans* isomerization from **III-33** to **III-35** occurred through the formation of intermediate **III-34**. The mechanism for the formation of **III-37** from **III-35** involved electrocyclization to form **III-36** as a key step, followed by a nonconcerted [1,3]-hydrogen shift to form **III-37** bearing a benz[*a*]anthracene unit (Scheme III-8). The $\text{Ni}(\text{cod})_2$ -mediated (cod being 1,5-cyclooctadiene) heterocoupling reactions of **III-37** in the presence of 2,2'-bipyridyl (bpy),¹⁰ followed by oxidative aromatization with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at 150 °C for 4 h, then gave benz[*a*]anthracene- and naphthalene-containing cyclophane **III-38** in 5% isolated yield.

Scheme III-8. Synthesis of Strained Benz[*a*]anthracene- and Naphthalene-Containing Cyclophane **III-38**

The structure of cyclophane **III-38** was confirmed by X-ray structure analysis (Figure III-2). In the crystal structure of **III-38**, the bonds connecting them to the C5 and C7 carbons of the benz[*a*]anthracene units are bent toward each other with bond angles of 114.5° and 115.1° , respectively, as indicated. It was also confirmed that the two naphthyl groups are *anti* to each other.

Figure III-2. X-ray Crystal Structure of Cyclophane III-38

In the ^1H NMR spectrum of cyclophane **III-38**, proton H_1 is magnetically shielded by the two naphthalene aromatic units and is found to shift upfield to δ 4.87 ppm (Figure III-3). Due to deshielding effects, the chemical shift of proton H_{10} appears in the downfield region at δ 9.38 ppm.

Figure III-3. ^1H NMR of Cyclophane III-38

For comparison of optical and electrochemical properties, the monomer unit of cyclophane **III-38** was also synthesized. The synthetic strategy for the synthesis of the monomer involved the treatment of diene **III-33** with 1.0 eq of $\text{BF}_3 \cdot \text{OEt}_2$ at 150 °C for 8 h producing aromatized dibromide **III-39** in 82% yield (Scheme III-9). Oxidative aromatization of **III-39**

with DDQ at 150 °C for 4 h produced **III-40** which, upon treatment with *n*-BuLi and quenching with aqueous HCl, gave the monomer analog **III-41**¹¹ in 86% yield. The ¹H NMR spectrum of **III-41** confirmed the identity of the monomer by comparison with literature data.

Scheme III-9. Synthesis of the Monomer Unit III-41

In addition to synthesis, UV-vis and fluorescence data of **III-38** and **III-41** were measured using degassed dichloromethane as the solvent. Cyclophane **III-38** showed absorption maxima at 290 and 300 nm, with another broad absorption band between 320 and 410 nm. This is a red shift from monomer **III-41**, which shows absorption maxima at 283 and 294 nm (Figure III-4). The fluorescence maxima of cyclophane **III-38** are also red-shifted from 396 and 417 nm in monomer **III-41** to 402 and 429 nm in cyclophane **III-38**.

Figure III-4. UV-vis and Fluorescence Spectra of Cyclophane **III-38 and Monomer **III-41****

With the assistance of Yu Zhang and Professor Carsten Milsmann of West Virginia University, electrochemical properties of cyclophane **III-38** and related monomer **III-41** were measured in tetrahydrofuran. Cyclophane **III-38** shows an irreversible redox potential at -2.58 V and monomer **III-41** shows a reversible redox potential at -2.59 V (Figure III-5).

Figure III-5. Cyclic Voltammetry of Cyclophane **III-38 and Monomer **III-41****

III-Conclusion:

In summary, by utilizing electrocyclization, Ni(cod)₂-catalyzed homocoupling, and oxidative aromatization reactions as key steps, a synthetic route to a strained cyclophane containing benz[*a*]anthracene and naphthalene units was established. A mechanistic pathway involving BF₃·OEt₂-catalyzed isomerization, *cis/trans* isomerization, electrocyclization reaction and a nonconcerted [1,3]-hydrogen shift was proposed. Photophysical and electrochemical properties of the strained cyclophane were investigated.

III-General Experimental Methods

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Chemicals, including bis(1,5-cyclooctadiene)nickel [Ni(cod)₂], 2,2'-bipyridyl (bpy), tetrakis(triphenylphosphine)palladium [Pd(PPh₃)₄], 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 1,7-octadiyne were purchased from chemical suppliers and were used as received. UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer with a 1 nm resolution, and the baseline was corrected with a solvent filled square quartz cell. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer with a 2 nm resolution.

Experimental Procedure for III-31. To a degassed solution of 1-bromo-4-iodonaphthalene (**1**, 6.20 g, 18.6 mmol), Pd(PPh₃)₄ (1.30 g, 1.12 mmol), and CuI (0.213 g, 1.12 mmol) in 200 mL of triethylamine was added 1,7-octadiyne **III-31** (0.970 g, 9.15 mmol), and the mixture was stirred at 70 °C for 8 h. After the solution was cooled to rt, triethylamine was removed in vacuo, and then CH₂Cl₂ (400 mL) and water (200 mL) were added. The resulting mixture was extracted with CH₂Cl₂ (2 × 100 mL), and the combined organic layers were washed with water and brine, dried over Na₂SO₄, and concentrated in vacuo to yield a pale-yellow solid. The pale yellow solid was purified by silica gel column chromatography using ethyl acetate/hexanes (1:9) as eluent to obtain **III-32** (4.05 g, 7.84 mmol, 86% yield) as a pale yellow solid: IR 1381, 834, 762 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.36 (2 H, dd, *J* = 8.0, 1.6 Hz), 8.24 (2 H, dd, *J* = 8.0, 2.0 Hz), 7.70 (2 H, d, *J* = 7.8 Hz), 7.63–7.53 (4 H, m), 7.46 (2 H, d, *J* = 7.8 Hz), 2.68 (4 H, m), 1.98 (4 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 134.5, 131.7, 130.1, 129.4, 127.6, 127.4, 127.3, 126.8, 122.7, 121.7, 95.9, 78.5, 28.0, 19.4; HRMS (ESI/FT-ICR) *m/z* [M+H]⁺ calcd for C₂₈H₂₁Br₂ 515.0005, 516.9984, 518.9964; found 515.0010, 516.9989, 518.9969.

Experimental Procedure for diene III-33. To a solution of Cp₂ZrCl₂ (2.68 g, 9.17 mmol) in THF (70 mL) at −78 °C under an argon atmosphere was added *n*-butyllithium (7.0 mL of a 2.5 M solution in hexanes, 17.5 mmol). After 1 h at −78 °C, **III-32** (3.75 g, 7.26 mmol) in 30 mL of THF under

argon was added slowly via cannula. The reaction mixture was then warmed to rt. After 12 h, the reaction mixture was poured into 300 mL of a 3 M aqueous HCl solution. After 30 min of stirring, the reaction mixture was extracted with dichloromethane (2×100 mL). The combined organic layers were washed with a saturated Na₂CO₃ solution and dried over MgSO₄. After passing through a silica gel column (9.0 cm high, 2.5 cm in diameter), the solvent was evaporated in vacuo, and the residue was washed with cold ethanol to give **III-33** (3.60 g, 6.98 mmol, 96% yield) as a white solid: IR 1503, 1377, 760 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.30 (2 H, dd, $J = 7.8, 1.6$ Hz), 8.14 (2 H, dd, $J = 7.4, 1.6$ Hz), 7.80 (2 H, d, $J = 7.4$ Hz), 7.66–7.57 (4 H, m), 7.26 (2 H, d, $J = 7$ Hz), 7.07 (2 H, s), 2.45 (4 H, m), 1.63 (4 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 146.5, 135.1, 133.6, 132.0, 129.4, 127.6, 127.3, 127.2, 126.6, 125.7, 121.8, 120.9, 30.8, 26.7; HRMS (ESI/Orbitrap) m/z [M]⁺ calcd for C₂₈H₂₂Br₂ 516.0083, 518.0062, 520.0042; found 516.0091, 518.0068, 520.0040.

NMR Data of Isomerized Diene III-34: From the reaction mixture for the preparation of **III-37**, an aliquot of 0.1 mL was removed within 2 h and concentrated in vacuo. The resulting product without further purification was identified as **III-34**: IR 1377, 1261, 755 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 8.33 (1 H, dd, $J = 8.8, 1.5$ Hz), 8.22 (1 H, d, $J = 8.4$ Hz), 8.09 (1 H, d, $J = 8.2$ Hz), 7.79 (1 H, d, $J = 7.6$ Hz), 7.73 (1 H, d, $J = 7.6$ Hz), 7.63–7.52 (4 H, m), 7.40 (1 H, ddd, $J = 8.2, 6.8, 1.2$ Hz), 7.33 (1 H, d, $J = 7.6$ Hz), 7.16 (1 H, dd, $J = 7.6, 0.9$ Hz), 6.76 (1 H, s), 5.68 (1 H, t, $J = 4.2$ Hz), 4.17 (2 H, s), 2.46 (2 H, m), 2.20 (2 H, m), 1.69 (2 H, quintet, $J = 6.2$ Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 139.0, 136.6, 135.3, 135.1, 133.6, 133.4, 132.0, 131.8, 129.6, 129.2, 127.9, 127.5, 127.09, 127.07, 127.0, 126.9, 126.8, 126.5, 125.6, 124.4, 121.4, 121.3, 120.5, 36.3, 27.8, 26.4, 23.0; HRMS (ESI/Orbitrap) m/z [M]⁺ calcd for C₂₈H₂₂Br₂ 516.0083, 518.0062, 520.0042; found 516.0090, 518.0069, 520.0033.

Compound **5** was taken up in dry toluene and heated in the presence of a catalytic amount of $\text{BF}_3 \cdot \text{OEt}_2$ at 150 °C for 24 h to produce **III-37**.

III-37

Experimental Procedure for III-37. To a 25 mL pressure vessel, were added **III-33** (0.700 g, 1.36 mmol), 0.03 mL of $\text{BF}_3 \cdot \text{OEt}_2$ and 1 mL of dry toluene under an argon atmosphere. The reaction mixture was stirred at 150 °C for 24 h before it was allowed to cool to rt. Toluene was evaporated in vacuo, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 5:95) to afford **III-37** (0.585 g, 1.13 mmol, 83% yield) as a white solid: IR 2931, 1738, 1378, 750 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3 , 25 °C) δ 8.31 (1 H, d, J = 8.2 Hz), 8.17 (1 H, d, J = 8.2 Hz), 8.09 (1 H, d, J = 8.8 Hz), 7.71–7.66 (1 H, br), 7.63–7.55 (4 H, m), 7.28 (1 H, s), 7.15 (1 H, br), 5.22 (1 H, br), 3.86 (1 H, d, J = 22.6 Hz), 3.78 (1 H, d, J = 21.7 Hz), 2.26 (2 H, m), 1.90 (1 H, m), 1.74 (1 H, m), 1.62–1.48 (4 H, m); ^1H NMR (600 MHz, CDCl_3 , 60 °C) δ 8.32 (1 H, d, J = 8.6 Hz), 8.31–8.23 (1 H, br), 8.18 (1 H, d, J = 8.2 Hz), 8.09 (1 H, d, J = 8.2 Hz), 7.69 (1 H, d, J = 7.8 Hz), 7.61 (1 H, t, J = 7.6 Hz), 7.57 (1 H, t, J = 7.9 Hz), 7.56 (1 H, t, J = 7.5 Hz), 7.53–7.46 (1 H, br), 7.31 (1 H, s), 7.16 (1 H, d, J = 7.6 Hz), 5.25 (1 H, s), 3.88 (1 H, d, J = 21.2 Hz), 3.79 (1 H, d, J = 21.5 Hz), 2.29 (2 H, m), 1.93 (1 H, m), 1.76 (1 H, m), 1.62–1.50 (3 H, m), 1.43 (1 H, br); ^{13}C NMR (CDCl_3 , 150 MHz, 25 °C) δ 132.7, 130.6, 130.5, 129.9, 129.87, 128.1, 128.0, 127.7, 126.9, 126.5, 125.6, 124.1, 123.6, 121.2, 32.6, 30.3, 28.1, 23.1, 22.7; ^{13}C NMR (CDCl_3 , 150 MHz, –40 °C) δ 142.8, 142.6, 138.6, 136.6, 135.2, 133.3, 132.3, 132.2, 132.1, 131.3, 130.6, 130.2, 130.1, 129.93, 129.88, 129.3, 129.0, 128.0, 127.9, 127.6, 127.4, 127.2, 127.0, 126.8, 126.7, 126.4, 126.3, 52.1, 43.6, 32.3, 32.2, 31.6,

29.96, 29.89, 28.1, 27.6, 22.8, 22.7, 22.5; HRMS (ESI/Orbitrap) m/z $[M]^+$ calcd for $C_{28}H_{22}Br_2$ 516.0083, 518.0062, 520.0042; found 516.0097, 518.0087, 520.0030.

Alternatively, compound **III-33** (0.100 g, 0.193 mmol) was taken up in 2 mL of toluene and heated at 150 °C for 24 h in the presence of a catalytic amount of acetic acid (4 drops) to produce **III-37** (0.092 g, 0.18 mmol, 92% yield) as a white solid.

III-39

Experimental Procedure for III-39. To a 25 mL pressure vessel was added a solution of **III-33** (2.44 g, 4.71 mmol) and $BF_3 \cdot OEt_2$ (1.0 mL, 8.1 mmol) in 2 mL of dry toluene under an argon atmosphere. The reaction mixture was stirred at 150 °C for 24 h before it was cooled to rt. Toluene was evaporated in vacuo, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 5:95) to afford **III-39** (2.00 g, 3.87 mmol, 82% yield) as a brown solid: IR 1727, 1444, 1252, 756 cm^{-1} ; 1H NMR (600 MHz, $CDCl_3$) δ 8.75 (1 H, dd, $J = 8.6, 0.7$ Hz), 8.53 (1 H, s), 8.39 (1 H, dd, $J = 8.0, 1.9$ Hz), 8.27 (1 H, dd, $J = 7.4, 1.3$ Hz), 7.95 (1 H, d, $J = 7.5$ Hz), 7.71 (1 H, ddd, $J = 8.3, 7.0, 1.5$ Hz), 7.66 (1 H, ddd, $J = 8.2, 7.0, 1.3$ Hz), 7.61 (1 H, ddd, $J = 8.1, 6.8, 1.2$ Hz), 7.36 (1 H, s), 7.34 (1 H, ddd, $J = 8.3, 6.7, 1.1$ Hz), 7.23–7.20 (2 H, m), 3.16 (2 H, t, $J = 6.5$ Hz), 2.48 (1 H, dt, $J = 17.3, 6.5$ Hz), 2.21 (1 H, dt, $J = 17.3, 6.2$ Hz), 1.87 (2 H, quintet, $J = 6.2$ Hz), 1.76–1.64 (2 H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 137.1, 137.0, 136.3, 135.5, 133.7, 132.3, 131.0, 129.99, 129.93, 129.90, 128.3, 128.2, 128.0, 127.9, 127.7, 127.5, 127.3, 127.23, 127.22, 126.2, 122.8, 122.7, 121.2, 30.9, 28.0, 23.2, 22.9; HRMS (ESI/FT-

ICR) m/z $[M]^+$ calcd for $C_{28}H_{20}Br_2$ 513.9926, 515.9906, 517.9885; found 513.9934, 515.9914, 517.9891.

III-40

Experimental Procedure for III-40. To a 25 mL flask containing **III-39** (0.100 g, 0.194 mmol) in chlorobenzene (2 mL) was added DDQ (0.265 g, 1.17 mmol). The reaction mixture was heated at 150 °C for 4 h before it was cooled to rt. Dichloromethane (100 mL) was added, and the solution was immediately passed through a basic alumina column (7.0 cm high, 2.5 cm in diameter), and the column was further eluted with 100 mL of dichloromethane. The combined eluates were concentrated, and the residue was purified by flash column chromatography (silica gel/ethyl ace-tate:hexanes = 1:9) to produce **III-40** (0.085 g, 0.17 mmol, 88% yield) as a yellow solid: IR 1503, 1374, 743 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 9.33 (1 H, s), 8.95 (1 H, d, J = 8.2 Hz), 8.44 (1 H, d, J = 8.7 Hz), 8.31 (1 H, d, J = 7.8 Hz), 8.20 (1 H, d, J = 8.2 Hz), 8.03 (1 H, d, J = 7.8 Hz), 7.79 (1 H, t, J = 7.8 Hz), 7.72 (1 H, t, J = 7.6 Hz), 7.64–7.54 (3 H, m), 7.39 (1 H, d, J = 7.8 Hz), 7.36–7.24 (3 H, m), 7.09 (1 H, d, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.9, 134.5, 133.8, 132.2, 131.7, 131.6, 131.4, 130.1, 129.7, 129.6, 129.4, 128.79, 128.76, 128.4, 128.0, 127.9, 127.62, 127.58, 127.3, 126.9, 126.58, 126.56, 126.1, 123.3, 123.1, 122.9, 122.5; HRMS (ESI/Orbitrap) m/z $[M]^+$ calcd for $C_{28}H_{16}Br_2$ 509.9613, 511.9593, 513.9572; found 509.9629, 511.9600, 513.9565.

Recrystallization of **III-40** from a mixture of chloroform and hexanes produced a single crystal suitable for X-ray structure analysis.

Experimental Procedure for Monomer III-41. To a 25 mL flask containing 0.070 g of **III-40** (0.14 mmol) in tetrahydrofuran was added 0.131 mL of n-butyllithium (0.33 mmol) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was for 1 h and quenched with 1.0 N HCl before it was allowed to cool to rt. The reaction mixture was extracted with ethyl acetate ($2 \times 25\text{ mL}$). The combined organic layers were washed with a saturated Na_2CO_3 solution and dried over MgSO_4 . After passing through a short silica gel column, the solvent was evaporated in vacuo, and the residue was purified by flash column chromatography (silica gel/EtOAc:hexanes = 0.5:9.5) to produce 0.043 g of **III-41** (0.12 mmol, 86% yield) as a pale yellow solid: IR 1734, 1505, 748 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 9.36 (1 H, s), 8.95 (1 H, d, $J = 8.2\text{ Hz}$), 8.22 (1 H, d, $J = 8.4\text{ Hz}$), 8.07 (1 H, d, $J = 8.2\text{ Hz}$), 8.01 (1 H, d, $J = 8.3\text{ Hz}$), 7.79 (1 H, d, $J = 7.6\text{ Hz}$), 7.75–7.69 (2 H, m), 7.64–7.60 (1 H, m), 7.34–7.30 (1 H, m), 7.57–7.53 (2 H, m), 7.50–7.46 (1 H, m), 7.42–7.39 (2 H, m), 7.23–7.19 (2 H, m); ^{13}C NMR (CDCl_3 , 100 MHz) δ 136.6, 135.4, 133.7, 133.5, 131.60, 131.56, 131.5, 129.6, 129.1, 128.6, 128.58, 128.5, 128.2, 128.1, 127.2, 127.1, 127.0, 126.7, 126.5, 126.3, 126.0, 125.9, 125.6, 125.58, 125.56, 123.1, 121.9; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{18} [\text{M}]^+$ 354.1403 found 354.1413.

III-38

Experimental Procedure for Cyclophane III-38. A 500 mL flask containing **III-37** (0.575 g, 1.11 mmol) and 2,2'-bipyridyl (0.423 g, 2.71 mmol) was flushed with nitrogen. The flask was then placed in a glovebox before Ni(cod)₂ (0.739 g, 2.69 mmol) was added. The flask was fitted with a condenser and a rubber septum and then removed from the glovebox. THF (110 mL) was introduced via cannula, and the reaction mixture was heated at reflux for 24 h before it was cooled to rt. The reaction mixture was passed through a silica gel column (10 cm high, 1.5 cm in diameter), and the column was further eluted with ethyl acetate (150 mL) and dichloromethane (150 mL). The combined eluates were concentrated, and the residue was used in the next step without further purification. To the flask containing the residue was added DDQ (0.500 g, 2.20 mmol). The flask was flushed with nitrogen, and chlorobenzene (3 mL) was added by using a syringe. The reaction mixture was heated at 130 °C for 4 h before it was cooled to rt. Dichloromethane (100 mL) was added, and the solution was immediately passed through a basic alumina column (7.0 cm high, 2.5 cm in diameter), and the column was further eluted with dichloromethane (100 mL). The combined eluates were concentrated, and the residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 1:9) to produce **III-38** (0.020 g, 0.028 mmol, 5% yield) as a white solid: mp >230 °C; IR 1725, 1459, 1263, 762 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.38 (2 H, s), 9.08 (2 H, dd, *J* = 8.3, 1.0 Hz), 8.42 (2 H, dd, *J* =

8.5, 1.3 Hz), 8.34 (2 H, dd, $J = 8.4, 1.3$ Hz), 8.21 (2 H, dd, $J = 7.8, 1.3$ Hz), 7.82 (2 H, ddd, $J = 8.3, 7.0, 1.3$ Hz), 7.72 (2 H, ddd, $J = 7.8, 7.0, 1.0$ Hz), 7.70 (2 H, ddd, $J = 8.4, 6.6, 1.3$ Hz), 7.66 (2 H, ddd, $J = 8.5, 6.6, 1.3$ Hz), 7.42 (2 H, dd, $J = 8.6, 1.3$ Hz), 7.31 (2 H, d, $J = 7.2$ Hz), 7.27 (2 H, dd, $J = 8.3, 1.4$ Hz), 7.15 (2 H, ddd, $J = 8.3, 6.8, 1.4$ Hz), 7.14 (2 H, d, $J = 7.2$ Hz), 7.10 (2 H, ddd, $J = 8.3, 6.8, 1.3$ Hz), 4.87 (2 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 140.9, 138.1, 137.3, 136.3, 135.44, 135.39, 131.7, 131.3, 130.7, 130.5, 130.4, 130.3, 129.7, 129.1, 128.8, 127.74, 127.69, 127.3, 127.1, 126.9, 126.50, 126.45, 126.1, 125.90, 125.83, 125.81, 123.6, 121.7; HRMS (ESI/FT-ICR) m/z $[\text{M}]^+$ calcd for $\text{C}_{56}\text{H}_{32}$ 704.2499; found 704.2504.

Recrystallization of **12** from a mixture of chloroform and hexanes produced a single crystal suitable for X-ray structure analysis.

References:

- (a) Dvornikovs, V.; House, B. E.; Kaetzel, M.; Dedman, J. R.; Smithrud, D. B. *J. Am. Chem. Soc.* **2003**, *125*, 8290–8301. (b) Wang, W.; Xu, J.; Lai, Y. H. *Org. Lett.* **2003**, *5*, 2765–2768. (c) Jeppesen, J. O.; Nielsen, M. B.; Becher, J. *Chem. Rev.* **2004**, *104*, 5115–5131. (d) Camacho, D. H.; Salo, E. V.; Guan, Z. *Org. Lett.* **2004**, *6*, 865–868. (e) Katz, E.; Lioubashevsky, O.; Willner, I. *J. Am. Chem. Soc.* **2004**, *126*, 15520–15532. (f) Bogdan, N.; Grosu, I.; Benoit, G.; Toupet, L.; Ramondenc, Y.; Condamine, E.; Dumitrescu, I. S.; Ple', G. *Org. Lett.* **2006**, *8*, 2619–2622. (g) Cooke, G.; Woisel, P.; Bria, M.; Delattre, F.; Garety, J. F.; Hewage, S. G.; Rabani, G.; Rosair, G. M. *Org. Lett.* **2006**, *8*, 1423–1426. (h) Tanaka, K.; Hori, T.; Osaka, T.; Noguchi, K.; Hirano, M. *Org. Lett.* **2007**, *9*, 4881–4884. (i) Aprahamian, I.; Dichtel, W. R.; Ikeda, T.; Heath, J. R.; Stoddart, J. F. *Org. Lett.* **2007**, *9*, 1287–1290.
 - (a) Hinrichs, H.; Fischer, A. K.; Jones, P. G.; Hopf, H.; Haley, M. M. *Org. Lett.* **2000**, *2*, 969–972. (b) Iyoda, M.; Kondo, T.; Nakao, K.; Hara, K.; Kuwatani, Y.; Yoshida, M.; Matsuyama, H. *Org. Lett.* **2000**, *2*, 2081–2083. (c) Nitschke, J. R.; Zülcher, S.; Tilley, T. D. *J. Am. Chem.*

- Soc.* **2000**, *122*, 10345–10352. (d) Collins, S. K.; Yap, G. P. A.; Fallis, A. G. *Org. Lett.* **2002**, *4*, 11–14. (e) Dobrowolski, M. A.; Cyran'ski, M. K.; Merner, B. L.; Bodwell, G. J.; Wu, J. I.; Schleyer, P. v. R. *J. Org. Chem.* **2008**, *73*, 8001. (f) Chen, H.-B.; Yin, J.; Wang, Y.; Pei, J. *Org. Lett.* **2008**, *10*, 3113–3116. (g) Chan, J. M. W.; Tischler, J. R.; Kooi, S. E.; Bulovic, V.; Swager, T. M. *J. Am. Chem. Soc.* **2009**, *131*, 5659–5666. (h) Venkataramana, G.; Dongare, P.; Dawe, L. N.; Thompson, D. W.; Zhao, Y.; Bodwell, G. J. *Org. Lett.* **2011**, *13*, 2240.
3. Ibuki, E.; Ozasa, S.; Fujioka, Y.; Mizutani, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 845.
4. Yao, T.; Campo, M. A.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 1423–1437.
5. Bayrakceken, F. *Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc.* **2004**, *60*, 3033–3036.
6. Svetlichnyi, V. A.; Kopylova, T. N.; Mayer, G. V.; Lapin, I. N. *Russ. Phys. J.* **2005**, *48*, 901–906.
7. Li, S.; Huang, C.; Thakellapalli, H.; Farajidizaji, B.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2016**, *18*, 2268–2271.
8. Nesterov, E. E.; Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 10083–10088.
9. (a) Takahashi, T.; Tsai, F.-Y.; Li, Y. *Chem. Lett.* 1999, 1173–1174 (b) Morisaki, Y.; Aiki, Y.; Chujo, Y. *Macromolecules* **2003**, *36*, 2594–2597.
10. Segawa, Y.; Miyamoto, S.; Omachi, H.; Matsuura, S.; Šenel, P.; Sasamori, T.; Tokitoh, N.; Itami, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3244–3248.
11. Li, G.; Zhou, S.; Su, G.; Liu, Y.; Wang, P. G. *J. Org. Chem.* **2007**, *72*, 9830.

Appendix Chapter-I

Syn-I-53
or *anti-I-53*

DPFGSENOE spectra (b-c);

Control ^1H NMR spectrum (a)

One bond ($^1J_{\text{H-C}}$)

gHSQCAD correlations

Two ($^2J_{H-C}$) and three ($^3J_{H-C}$)
bond **gHMBCAD** correlations

Expanded Portions of the **gHMBCAD** spectrum (a-b)

Two ($^2J_{\text{H-C}}$) and three ($^3J_{\text{H-C}}$) bond **gHMBCAD** correlations

One bond ($^1J_{\text{HC}}$) correlations

gHSQCAD

gHMBCAD

^{13}C NMR spectrum in CD_2Cl_2 (+25°C)

Temperature dent ^1H NMR spectra (400
MHz NMR, solvent: CD_2Cl_2)

The Free Energy of Activation of Rotation Around the C1–C6 Bond

$$k_c = \frac{\pi}{\sqrt{2}} \sqrt{\Delta v_{AB}^2 + 6J_{AB}^2}$$

$$k_c = 2.22 \sqrt{\Delta v_{AB}^2 + 6J_{AB}^2}$$

The equation to estimate $\Delta G^\ddagger$ using the coalescence temperature is:

$$\Delta G^\ddagger = aT_c \left[10.319 + \log \left(\frac{T_c}{k_c} \right) \right]$$

where $a = 4.575 \times 10^{-3}$ for units of kcal/mol

k_c = rate constant in s^{-1} at the coalescence temperature

Exchanging nuclei are H7 and H7' ; also H8 and H8'

The separation in Hz between H8 and H8' is 96 Hz (Δv) at -80 °C

$$T_c = T (^{\circ}\text{C}) + 273.15 = -41 + 273.15 = 232.15 \text{ K}$$

$$k_c = 2.22 \sqrt{\Delta v_{AB}^2 + 6J_{AB}^2}$$

$$k_c = 2.22 \sqrt{96^2 + 6 \times 2^2} = 213.4 \text{ s}^{-1}$$

$$\Delta G^\ddagger = 4.575 \times 10^{-3} \times 232.15 [10.319 + \log (T_c/k_c)] = 10.99 \text{ kcal mol}^{-1}$$

Free energy of activation: $\sim 11 \text{ kcal mol}^{-1}$

DPFGSENOE spectra (-80°C)

DPFGSENOE (-80°C)

syn-1-46, perspective view

NMR parameters (chemical shifts and coupling constants)

syn-I-55

or

anti-I-55

one of the two isomers

Proton	δ/ppm	J/Hz	Carbon	δ/ppm
H1/H1'	4.90	$^3J_{1,2} = ^3J_{1',2'} = 4.8$	C1/C1'	40.99
H2/H2'	5.95	$^4J_{1,2'} = ^4J_{1',2} = 1.5$	C2/C2'	127.67
4/4'-OCH ₃	3.64	$^5J_{1,1'} = 3.4$	C3/C3'	127.34
H5/H5'	6.75	$^3J_{2,2'} = 9.3$	C4/C4'	151.37
H7/H7'	7.26	$^3J_{7,8} = ^3J_{7',8'} = 8.2$	4/4'-OCH ₃	55.80
H8/H8'	7.51	$^4J_{7,7'} = 2.1$	C5/C5'	109.18
H11	7.25	$^4J_{8,8''} = 1.9$	C6	144.35
H12	7.20	$^5J_{7,8'} = ^5J_{8,7'} = 0.5$	C7/C7'	128.74
		$^3J_{11,12} = 3.8$	C8/C8'	125.17
			C9	131.61
			C10	143.20
			C11	123.17
			C12	123.09
			C13	136.30

DPFGSENOE spectrum (b)
Control ^1H NMR spectrum (a)

DPFGSENOE spectrum (b)
Control ^1H NMR spectrum (a)

^1H - ^1H gCOSY spectrum

$^2J_{H-C}$ and $^3J_{H-C}$ gHMBCAD correlations

Chemical shift assignment of C3/C3' and C4/C4'

based on $^2J_{H-C}$ and $^3J_{H-C}$
gHMBCAD correlations

^1H NMR spectrum in CDCl_3

gHSQCAD

One-bond correlations ($^1J_{\text{HC}}$)

gHMBCAD

Two ($^2J_{\text{HC}}$) and three ($^3J_{\text{HC}}$)
bond correlations

gHMBCAD

Three bond ($^3J_{\text{HC}}$) correlation

ROESYAD

Through space correlations

Expanded portions of the ROESY spectrum (a-b)

a)

b)

Spectrum a): UV-vis absorption spectrum of **I-53** at the concentration of 5.9×10^{-7} M in degassed CH_2Cl_2 . At the absorption maximum $\lambda_{\text{abs}} = 328$ nm, $\varepsilon = 5.2 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$.

Spectrum b): UV-vis absorption spectrum of **I-46** at the concentration of 5.9×10^{-7} M in degassed CH_2Cl_2 . At the absorption maximum $\lambda_{\text{abs}} = 363$ nm, $\varepsilon = 5.7 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$.

c)

d)

Spectrum c): Fluorescence spectrum of **I-53** at the concentration of 3.0×10^{-8} M in degassed CH_2Cl_2 upon excitation at 328 nm. Fluorescence maximum $\lambda_{\text{em}} = 412$ nm.

Spectrum d): Fluorescence spectrum of **I-46** at the concentration of 5.9×10^{-7} M in degassed CH_2Cl_2 upon excitation at 363 nm. Fluorescence maximum $\lambda_{\text{em}} = 512$ nm.

e)

f)

Spectrum e): UV-vis absorption spectrum of **I-55** at the concentration of 6.4×10^{-7} M in degassed CH_2Cl_2 . At the absorption maximum $\lambda_{\text{abs}} = 372$ nm, $\varepsilon = 6.3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$.

Spectrum f): UV-vis absorption spectrum of **I-48** at the concentration of 6.5×10^{-7} M in degassed CH_2Cl_2 . At the absorption maximum $\lambda_{\text{abs}} = 376$ nm, $\varepsilon = 4.3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$.

g)

h)

Spectrum g): Fluorescence spectrum of **I-55** at the concentration of 6.4×10^{-7} M in degassed CH_2Cl_2 upon excitation at 372 nm. Fluorescence maximum $\lambda_{\text{em}} = 471$ nm and $\lambda_{\text{em}} = 444$ nm.

Spectrum h): Fluorescence spectrum of **I-48** at the concentration of 6.5×10^{-7} M in degassed CH_2Cl_2 upon excitation at 376 nm. Fluorescence maximum $\lambda_{\text{em}} = 511$ nm.

i)

j)

Spectrum i): UV-vis absorption spectrum of **I-47** at the concentration of 3.9×10^{-7} M in degassed CH_2Cl_2 . At the absorption maximum $\lambda_{\text{abs}} = 350$ nm, $\epsilon = 1.2 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$.

Spectrum j): Fluorescence spectrum of **I-47** at the concentration of 3.9×10^{-7} M in degassed CH_2Cl_2 upon excitation at 350 nm. Fluorescence maximum $\lambda_{\text{em}} = 481$ nm.

Electrochemical Characterization Methods.

Experiments were recorded using the Pine WaveNow USB potentiostat and BAS electrodes in anhydrous dichloromethane under an argon atmosphere with 100 mM tetrabutylammonium hexafluorophosphate as supporting electrolyte. All samples were analyzed between 0.2-0.5 mM depending on their inherent solubility in dichloromethane. Cyclic voltammograms were collected with a glassy carbon working electrode, platinum wire counter electrode, and Ag/10 mM AgNO₃ (acetonitrile) reference electrode. Differential pulse voltammetry measurements were recorded under the same conditions with the exceptions that a gold working electrode was used. All recorded data are presented versus ferrocene/ferrocenium (Fc/Fc⁺) couple measured under identical conditions.

Compound I-46 – [8⁵]CPP: CV scan-rate dependence (0.30 mM) (A), i_{pa} vs. (scan rate)^{1/2} dependence for the first redox couple (B), and DPV scan (C).

A

B

C

Compound I-47 – [16^S] CPP: CV scan-rate dependence (0.22 mM) (A), i_{pa} vs. (scan rate)^{1/2} dependence for the first redox couple (B), and DPV scan (C).

A

B

C

Compound I-48 – [10^{di-S}] CPP: CV scan-rate dependence (0.50 mM) (A), i_{pa} vs. (scan rate)^{1/2} dependence for the first redox couple (B), and DPV scan (C).

A

B

C

Compound I-53 – reduced-[8^S]: CV scan-rate dependence (0.50 mM) (A), DPV scan (B), i_{pa} vs. (scan rate)^{1/2} dependence for the first and second redox couple (C-D), respectively.

A

B

C

D

Compound I-55 – reduced-[10^{di-S}]: CV scan-rate dependence (0.50 mM) (A), DPV scan (B), i_{pa} vs. (scan rate)^{1/2} dependence for the first and second redox couple (C-D), respectively.

A **B** **C** **D**

Computational Details.

Spin-restricted density functional theory (RDFT) calculations were performed with the Gaussian 09 (G09) program.^{S1} Geometry optimization and normal mode analyses were performed using the M06 functional and the 6-31G(d) basis set to identify all ground state and transition state geometries.^{S2} The identified stationary points met or exceeded all default G09 convergence criteria. Using the same functional-basis set, normal-modes were calculated for each optimized structure to confirm the absence of negative eigenvalues and determine thermochemical corrections. Strain energies were estimated using homodesmotic reactions.^{1a,S3}

References:

(S1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; K. Toyota; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui,

Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Wallingford CT, 2004.

(S2) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(S3) Takaba, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 6112–6116.

Evaluation of Strain Energies for CPP Species.

Computational Coordinates and Energetic Details.

syn-[1-CPP]

Calculation results at DFT-optimized geometry:

Total Energy: -3253.32185081 AU

SCF Convergence: 7.20 E -09

Enthalpy Correction: 0.853418 AU

Free Energy Correction: 0.719672 AU

Three lowest frequencies (cm-1): 21.8,23.0,25.8

C	5.398000	-1.422700	0.784800
C	5.398000	1.423000	0.784600
C	4.992300	-0.698900	1.890900
C	6.121400	-0.717000	-0.232100
C	6.121500	0.717000	-0.232300
C	4.992400	0.699400	1.890800
H	4.452900	-1.210000	2.686900
H	4.453000	1.210700	2.686700
C	4.734900	-2.736600	0.614400
C	2.608600	-4.601400	0.526400
C	4.474000	-3.585200	1.697500
C	4.035900	-2.979300	-0.576400
C	2.998100	-3.892200	-0.620100
C	3.426800	-4.498300	1.659000

H	5.038600	-3.461400	2.621900
H	4.244200	-2.362100	-1.449000
H	2.417400	-3.997300	-1.536900
H	3.167300	-5.056000	2.558900
C	4.735000	2.736800	0.613900
C	2.608500	4.601500	0.526000
C	4.474200	3.585700	1.696900
C	4.035600	2.979200	-0.576800
C	2.997700	3.892100	-0.620400
C	3.427000	4.498700	1.658400
H	5.039100	3.462100	2.621200
H	2.416800	3.996900	-1.537100
H	3.167700	5.056600	2.558300
C	6.866900	-1.404600	-1.240100
C	7.526400	-0.704000	-2.221200
H	8.093300	-1.222500	-2.989400
C	7.526600	0.703500	-2.221300
H	8.093700	1.221700	-2.989500
C	6.867200	1.404300	-1.240200
O	6.908000	2.756200	-1.124300
O	6.907200	-2.756500	-1.124000
C	7.628800	3.479100	-2.085400
H	7.223600	3.325300	-3.097800
H	8.695000	3.203700	-2.084100
H	7.528500	4.533600	-1.815900
C	7.627600	-3.479700	-2.085000
H	7.222400	-3.326000	-3.097500
H	7.527000	-4.534200	-1.815500

H	8.694000	-3.204700	-2.083900	C	-2.997900	-3.892100	-0.620300
C	1.262000	-5.170800	0.615800	C	-3.427000	-4.498700	1.658500
				H	-5.039100	-3.462000	2.621300
				H	-4.243900	-2.361900	-1.449200
S	0.000000	-4.229400	-0.129900	H	-2.417000	-3.997000	-1.537100
C	-1.261900	-5.170800	0.615600	H	-3.167700	-5.056500	2.558400
C	-0.710900	-6.166400	1.385400	C	-4.735000	2.736600	0.614500
C	0.710900	-6.166300	1.385500	C	-2.608600	4.601400	0.526400
H	-1.312800	-6.872000	1.955300	C	-4.474000	3.585300	1.697600
H	1.312700	-6.871900	1.955600	C	-4.036000	2.979400	-0.576400
C	1.261900	5.170800	0.615600	C	-2.998200	3.892300	-0.620000
S	-0.000100	4.229400	-0.129900	C	-3.426800	4.498300	1.659000
C	-1.262000	5.170800	0.615800	H	-5.038700	3.461400	2.622000
C	-0.710900	6.166300	1.385500	H	-4.244300	2.362200	-1.449000
C	0.710900	6.166400	1.385400	H	-2.417500	3.997300	-1.536900
H	-1.312800	6.871900	1.955600	H	-3.167400	5.056000	2.559000
H	1.312800	6.872000	1.955300	C	-6.867100	-1.404300	-1.240300
C	-5.398100	-1.422900	0.784600	C	-7.526400	-0.703500	-2.221400
C	-5.398000	1.422700	0.784900	H	-8.093400	-1.221700	-2.989700
C	-4.992500	-0.699400	1.890800	C	-7.526200	0.704000	-2.221300
C	-6.121500	-0.717000	-0.232300	H	-8.093100	1.222400	-2.989600
C	-6.121400	0.717000	-0.232200	C	-6.866800	1.404500	-1.240200
C	-4.992400	0.699000	1.890900	O	-6.907100	2.756500	-1.124100
H	-4.453100	-1.210700	2.686800	O	-6.907800	-2.756200	-1.124400
H	-4.453000	1.210100	2.687000	C	-7.627400	3.479700	-2.085200
C	-4.735000	-2.736800	0.614000	H	-7.222200	3.325900	-3.097600
C	-2.608600	-4.601500	0.526000	H	-7.526800	4.534200	-1.815600
C	-4.474300	-3.585700	1.697000	H	-8.693800	3.204700	-2.084100
C	-4.035700	-2.979300	-0.576700	C	-7.628400	-3.479100	-2.085500

H	-8.694700	-3.203800	-2.084300
H	-7.528100	-4.533700	-1.816100
H	-7.223200	-3.325400	-3.098000
H	4.243700	2.361800	-1.449300

anti-[1-CPP]

Calculation results at DFT-optimized geometry:

Total Energy: -3253.31733405 AU

SCF Convergence: 4.90 E -09

Enthalpy Correction: 0.853294 AU

Free Energy Correction: 0.717856 AU

Three lowest frequencies (cm-1): 20.1,22.6,23.5

C	5.290500	-1.423600	-1.089600
C	5.290400	1.423800	-1.089500
C	4.747900	-0.698800	-2.134200
C	6.134500	-0.717300	-0.170100
C	6.134500	0.717500	-0.170000
C	4.747800	0.699100	-2.134200
H	4.114600	-1.209300	-2.857900

H	4.114600	1.209500	-2.857900
C	4.665500	-2.745500	-0.851800
C	2.571600	-4.625800	-0.535900
C	4.119400	-3.014500	0.411100
C	4.276300	-3.578700	-1.908500
C	3.244300	-4.495700	-1.758100
C	3.101200	-3.938000	0.566500
H	4.425300	-2.408700	1.262900
H	4.724100	-3.437700	-2.892600
H	2.879300	-5.036800	-2.630900
H	2.643300	-4.062900	1.548600
C	4.665300	2.745700	-0.851700
C	2.571300	4.625900	-0.535800
C	4.119100	3.014500	0.411200
C	4.276200	3.579000	-1.908300
C	3.244100	4.495800	-1.758000
C	3.100800	3.938000	0.566600
H	4.424900	2.408700	1.263000
H	2.879200	5.037100	-2.630700
H	2.642800	4.062700	1.548600
C	7.008000	-1.404800	0.729400
C	7.800600	-0.703600	1.606300
H	8.471400	-1.221900	2.286300
C	7.800500	0.703800	1.606400
H	8.471200	1.222100	2.286400
C	7.007800	1.405000	0.729600
O	7.027300	2.757300	0.614700
O	7.027700	-2.757100	0.614300
C	7.878700	3.481000	1.461400

H	8.934700	3.216100	1.295600	H	-3.540200	-1.206000	2.633800
H	7.633800	3.316600	2.522300	H	-3.540300	1.206200	2.633700
H	7.728300	4.536200	1.219100	C	-4.535600	-2.770400	0.852500
C	7.878400	-3.480900	1.461500	C	-2.580100	-4.704200	0.200000
H	8.934600	-3.216400	1.296200	C	-3.934400	-3.553500	1.846600
H	7.727700	-4.536100	1.219400	C	-4.280900	-3.117000	-0.482200
H	7.633000	-3.316200	2.522300	C	-3.322100	-4.064900	-0.803100
C	1.230900	-5.210900	-0.480300	C	-2.963500	-4.493700	1.529300
S	0.083800	-4.457900	0.595800	H	-4.167500	-3.358700	2.893500
				H	-4.749800	-2.542100	-1.279400
				H	-3.044000	-4.219900	-1.845500
C	-1.269000	-5.272400	-0.140900	H	-2.437200	-5.019800	2.326200
C	-0.832800	-6.098400	-1.144600	C	-4.535900	2.770400	0.852400
C	0.576600	-6.070600	-1.330100	C	-2.580500	4.704300	0.199900
H	-1.511100	-6.690000	-1.756500	C	-3.934800	3.553700	1.846500
H	1.090700	-6.644700	-2.099000	C	-4.281100	3.116900	-0.482400
C	1.230600	5.210900	-0.480300	C	-3.322400	4.064800	-0.803200
S	0.083400	4.458000	0.595800	C	-2.963900	4.493800	1.529100
C	-1.269400	5.272500	-0.141000	H	-4.168000	3.358900	2.893300
C	-0.833100	6.098400	-1.144700	H	-4.749900	2.541900	-1.279500
C	0.576400	6.070600	-1.330200	H	-3.044200	4.219800	-1.845600
H	-1.511300	6.690000	-1.756700	H	-2.437700	5.020100	2.326100
H	1.090400	6.644700	-2.099000	C	-7.133300	-1.404400	-0.256300
C	-5.078400	-1.427200	1.170100	C	-8.081400	-0.703900	-0.961900
C	-5.078500	1.427200	1.170000	H	-8.874400	-1.221900	-1.494000
C	-4.315000	-0.697800	2.062700	C	-8.081400	0.703300	-0.962000
C	-6.091200	-0.718600	0.443400	H	-8.874500	1.221200	-1.494100
C	-6.091200	0.718400	0.443300	C	-7.133400	1.404000	-0.256500
C	-4.315100	0.697900	2.062600	O	-7.139600	2.755400	-0.128300

O	-7.139300	-2.755800	-0.127900
C	-8.148300	3.476700	-0.782400
H	-8.109300	3.332900	-1.873600
H	-7.969300	4.530600	-0.554100
H	-9.149100	3.191300	-0.422300
C	-8.147400	-3.477400	-0.782700
H	-9.148500	-3.192500	-0.423000
H	-7.968000	-4.531200	-0.554600
H	-8.107900	-3.333200	-1.873800
H	4.724000	3.438000	-2.892400

C	4.580600	-0.698400	1.893600
C	6.142100	-0.717900	0.065900
C	6.142100	0.717900	0.065800
C	4.580700	0.698600	1.893500
H	3.883300	-1.207700	2.556500
H	3.883400	1.207900	2.556400
C	4.630200	-2.756700	0.634400
C	2.595200	-4.664400	0.168400
C	4.145700	-3.564100	1.671600
C	4.212100	-3.063100	-0.668800

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C	3.213400	-3.994500	-0.897200
C	3.141700	-4.496600	1.446500
H	4.504700	-3.399400	2.687700
H	4.582500	-2.464900	-1.499800
H	2.805400	-4.110700	-1.901100
H	2.721400	-5.050400	2.286500
C	4.630200	2.756800	0.634200
C	2.595200	4.664500	0.168300
C	4.145900	3.564300	1.671400
C	4.212100	3.063100	-0.668900

Calculation results at DFT-optimized geometry:

Total Energy: -3253.31588064 AU

SCF Convergence: 6.20 E -09

Enthalpy Correction: 0.853212

Free Energy Correction: 0.717428 AU

Three lowest frequencies (cm-1): 18.5,22.3,25.1

C	5.221900	-1.425400	0.907700
C	5.222000	1.425500	0.907600

C	3.213300	3.994500	-0.897300
C	3.141900	4.496700	1.446300
H	4.504900	3.399600	2.687500
H	2.805300	4.110600	-1.901200
H	2.721600	5.050600	2.286400
C	7.089500	-1.404500	-0.757000
C	7.946700	-0.703800	-1.570700
H	8.669700	-1.222200	-2.194700
C	7.946700	0.703600	-1.570800

H	8.669700	1.221900	-2.194900	C	-5.222000	1.425400	0.907800
C	7.089500	1.404400	-0.757100	C	-4.580800	-0.698500	1.893700
O	7.105400	2.756200	-0.636000	C	-6.142200	-0.717900	0.066000
O	7.105400	-2.756300	-0.635400	C	-6.142200	0.718000	0.066000
C	8.013300	3.480500	-1.420900	C	-4.580700	0.698500	1.893700
H	7.839600	3.320100	-2.496500	H	-3.883500	-1.207800	2.556500
H	9.055600	3.213500	-1.186000	H	-3.883500	1.207800	2.556600
H	7.848900	4.535200	-1.185500	C	-4.630300	-2.756700	0.634400
C	8.012200	-3.481000	-1.421300	C	-2.595300	-4.664400	0.168400
H	7.837700	-3.320100	-2.496700	C	-4.145900	-3.564200	1.671600
H	7.847200	-4.535700	-1.186300	C	-4.212200	-3.063100	-0.668800
H	9.054900	-3.214800	-1.187200	C	-3.213500	-3.994500	-0.897200
C	1.260700	-5.235700	-0.042500	C	-3.141900	-4.496700	1.446500
S	-0.000100	-4.642300	1.006500	H	-4.504900	-3.399500	2.687700
C	-1.260900	-5.235700	-0.042500	H	-4.582600	-2.464900	-1.499800
				H	-2.805500	-4.110700	-1.901100
				H	-2.721500	-5.050500	2.286500
C	-0.710500	-5.888300	-1.117100	C	-4.630300	2.756700	0.634500
C	0.710400	-5.888300	-1.117100	C	-2.595300	4.664400	0.168400
H	-1.315100	-6.323300	-1.910900	C	-4.145800	3.564200	1.671600
H	1.315000	-6.323400	-1.910900	C	-4.212200	3.063100	-0.668700
C	1.260800	5.235700	-0.042500	C	-3.213500	3.994500	-0.897100
S	0.000000	4.642300	1.006400	C	-3.141800	4.496600	1.446500
C	-1.260800	5.235700	-0.042500	H	-4.504800	3.399500	2.687700
C	-0.710500	5.888300	-1.117100	H	-4.582600	2.464900	-1.499800
C	0.710400	5.888300	-1.117100	H	-2.805500	4.110700	-1.901000
H	-1.315200	6.323400	-1.910900	H	-2.721500	5.050500	2.286500
H	1.315000	6.323400	-1.911000	C	-7.089600	-1.404400	-0.757000
C	-5.222000	-1.425400	0.907800	C	-7.946700	-0.703700	-1.570700

H	-8.669700	-1.222000	-2.194800
C	-7.946700	0.703800	-1.570700
H	-8.669700	1.222100	-2.194800
C	-7.089600	1.404500	-0.756900
O	-7.105500	2.756300	-0.635400
O	-7.105500	-2.756200	-0.635600
C	-8.011900	3.480900	-1.421800
H	-7.837100	3.319700	-2.497100
H	-7.846700	4.535700	-1.186900
H	-9.054700	3.215100	-1.187900
C	-8.012000	-3.480800	-1.421800
H	-9.054800	-3.214900	-1.187800
H	-7.846800	-4.535600	-1.187000
H	-7.837400	-3.319600	-2.497200
H	4.582500	2.464900	-1.500000

Enthalpy Correction: 1.047228 AU

Free Energy Correction: 0.875288 AU

Three lowest frequencies (cm-1): 3.4,5.3,9.9

C	11.167400	-0.466000	-0.430900
C	8.388900	-0.483200	-1.049200
C	10.624300	0.408400	-1.350800
C	10.326300	-1.477300	0.134200
C	8.920900	-1.481800	-0.172100
C	9.261300	0.397200	-1.657000
H	11.267800	1.170200	-1.789900
H	8.856900	1.147100	-2.336300
C	12.586000	-0.215200	-0.067300
C	15.261300	0.459900	0.558600
C	13.576500	-0.219100	-1.049800
C	12.950000	0.150500	1.233100
C	14.259900	0.478500	1.540100
C	14.892200	0.106500	-0.742000
H	13.308900	-0.488100	-2.071900
H	12.188500	0.161500	2.013000
H	14.522200	0.734500	2.566700
H	15.642200	0.113600	-1.532800
C	6.948900	-0.257500	-1.336200
C	4.253800	0.354000	-1.939700
C	6.058400	0.135200	-0.331600
C	6.473500	-0.320500	-2.647200
C	5.147700	-0.035800	-2.944000
C	4.740400	0.437500	-0.625600
H	6.416400	0.203300	0.695500

[10-paraphenylene]

Calculation results at DFT-optimized geometry:

Total Energy: -3716.31432402 AU

SCF Convergence: 4.40 E -09

H	4.791400	-0.140400	-3.968100	C	2.329700	1.033000	-3.475800
H	4.076800	0.768900	0.173900	H	0.342500	1.505400	-4.315500
C	10.851800	-2.532400	0.954400	H	2.935900	1.180700	-4.366700
C	10.022500	-3.484600	1.490000	C	-7.962100	0.894400	-0.236500
H	10.420300	-4.279000	2.115300	C	-5.201600	1.353000	-0.748000
C	8.646600	-3.484000	1.198500	C	-7.393400	0.596000	-1.458300
H	8.028800	-4.275700	1.613000	C	-7.167200	1.569300	0.744300
C	8.106700	-2.534700	0.368300	C	-5.772600	1.801400	0.485700
O	6.808200	-2.545200	-0.018500	C	-6.037200	0.821300	-1.709600
O	12.195800	-2.543500	1.124400	H	-8.002500	0.094000	-2.209500
C	5.971500	-3.563000	0.457700	H	-5.604500	0.492500	-2.654100
H	5.891400	-3.544700	1.555900	C	-9.346900	0.399500	-0.032000
H	6.324500	-4.557700	0.143500	C	-11.939900	-0.702300	0.213700
H	4.985400	-3.375500	0.022900	C	-9.627300	-0.573500	0.934700
C	12.763400	-3.530000	1.941200	C	-10.380200	0.799900	-0.879400
H	12.357000	-3.494700	2.964000	C	-11.655700	0.262400	-0.758300
H	13.835800	-3.317000	1.972900	C	-10.896400	-1.107400	1.061900
H	12.604400	-4.539300	1.529900	H	-8.831000	-0.899800	1.603500
C	-15.740600	-1.766600	0.319300	H	-10.179700	1.550900	-1.643500
S	-14.700100	-0.463200	-0.195200	H	-12.438400	0.583700	-1.446200
C	-13.267100	-1.294400	0.353200	H	-11.094000	-1.843600	1.840400
C	-13.605700	-2.508200	0.899200	C	-3.752400	1.329600	-1.069200
C	-14.994000	-2.773000	0.880300	C	-1.030100	1.120200	-1.809400
H	-12.866800	-3.206100	1.286400	C	-2.860900	0.553900	-0.320600
H	-15.438500	-3.677200	1.290300	C	-3.262600	1.986600	-2.199000
C	2.864500	0.658400	-2.267600	C	-1.923900	1.897100	-2.556200
S	1.605300	0.553300	-1.063200	C	-1.530000	0.448000	-0.683300
C	0.369700	1.012000	-2.207900	H	-3.229000	0.023000	0.557200
C	0.930100	1.229800	-3.442600	H	-3.940700	2.600400	-2.792100

H	-1.560400	2.455900	-3.417800
H	-0.866100	-0.188900	-0.097600
C	-7.733500	2.082000	1.960000
C	-6.948700	2.727100	2.881500
H	-7.376300	3.110400	3.803700
C	-5.584300	2.956000	2.627800
H	-5.005300	3.507400	3.363300
C	-5.009800	2.537100	1.454600
O	-3.727500	2.816800	1.117700
O	-9.070900	1.923800	2.108600
C	-2.949100	3.573700	2.003500
H	-3.382000	4.572600	2.169800
H	-1.967100	3.677800	1.533300
H	-2.831700	3.071000	2.976300
C	-9.677400	2.386300	3.283900
H	-9.255700	1.900000	4.177500
H	-10.737000	2.128400	3.201100
H	-9.574600	3.477500	3.391500
H	7.152400	-0.629100	-3.442400
C	-17.188300	-1.708100	0.133800
C	-19.979000	-1.641300	-0.187000
C	-17.931300	-2.893800	0.045100
C	-17.873300	-0.488600	0.049600
C	-19.252100	-0.457100	-0.113400
C	-19.310400	-2.860000	-0.106000
H	-17.412900	-3.851400	0.073400
H	-17.319700	0.446900	0.133900
H	-19.763200	0.502500	-0.174400
H	-19.866500	-3.793900	-0.173300

H	-21.060100	-1.614900	-0.311000
C	16.657600	0.807300	0.887900
C	19.316700	1.469200	1.512300
C	17.727300	0.149400	0.268800
C	16.949700	1.803300	1.827800
C	18.264000	2.130300	2.137900
C	19.042100	0.477300	0.575700
H	17.521300	-0.648700	-0.444100
H	16.131200	2.345900	2.300600
H	18.466500	2.913800	2.866800
H	19.858200	-0.052100	0.085900
H	20.347000	1.725500	1.753800

syn-[2-CPP]

Calculation results at DFT-optimized geometry:

Total Energy: -6506.77650525 AU

SCF Convergence: 5.20 E -09

Enthalpy Correction: 1.710897 AU

Free Energy Correction: 1.45664 AU

Three lowest frequencies (cm-1): 5.5, 7.2, 8.3

C	1.216700	10.779900	0.611400	H	0.968100	13.217600	-3.331900
C	-1.628100	10.730000	0.616200	C	-0.948100	12.666200	-2.527500
C	0.502700	10.331300	1.705200	H	-1.477400	13.176500	-3.327400
C	0.499100	11.403800	-0.458700	C	-1.636200	12.058300	-1.507300
C	-0.936800	11.379600	-0.455500	O	-2.987200	12.092300	-1.397100
C	-0.894800	10.306400	1.707400	O	2.520900	12.184200	-1.409600
H	1.042900	9.864800	2.528300	C	-3.721000	12.752100	-2.392000
H	-1.414900	9.821100	2.532500	H	-3.561900	12.299700	-3.383300
C	2.652100	10.406500	0.589500	H	-3.462800	13.821500	-2.443900
C	5.236700	9.267800	0.757100	H	-4.773600	12.646800	-2.115500
C	3.494600	10.689500	1.667200	C	3.228500	12.855800	-2.415800
C	3.142000	9.576900	-0.426200	H	3.073600	12.391300	-3.402200
C	4.406200	9.021700	-0.346900	H	4.285600	12.782000	-2.146800
C	4.764500	10.132700	1.751100	H	2.941100	13.917400	-2.474500
H	3.134300	11.336800	2.467000	C	-6.516500	-8.580900	0.914600
H	2.501700	9.346000	-1.277200	S	-6.727500	-6.978900	0.259200
H	4.757000	8.371500	-1.148700	C	-8.333500	-6.838000	0.924200
H	5.383100	10.327500	2.626800	C	-8.660300	-7.977800	1.617000
C	-3.049000	10.303900	0.598100	C	-7.638000	-8.958400	1.611500
C	-5.586900	9.066200	0.771200	H	-9.625800	-8.114200	2.100200
C	-3.513400	9.465100	-0.422200	H	-7.731600	-9.931300	2.090300
C	-3.895300	10.546700	1.682500	C	-6.837600	8.329400	0.928200
C	-5.142500	9.940900	1.769500	S	-6.984000	6.723200	0.264800
C	-4.755000	8.861500	-0.340000	C	-8.582000	6.513600	0.930700
H	-2.869700	9.265600	-1.278600	C	-8.954000	7.635800	1.629600
H	-5.762800	10.104000	2.650300	C	-7.972500	8.657300	1.628300
H	-5.085900	8.203800	-1.144300	H	-9.923300	7.730300	2.115200
C	1.171200	12.105000	-1.513400	H	-8.104800	9.622800	2.112600
C	0.458900	12.689600	-2.530600	C	-10.739900	-1.629400	0.642700

C	-10.786900	1.215600	0.640800	H	-13.207100	-1.473800	-3.287400
C	-10.313600	-0.897700	1.733800	C	-12.709700	0.461800	-2.494600
C	-11.393200	-0.935800	-0.425700	H	-13.240200	0.972100	-3.293600
C	-11.414800	0.500000	-0.428200	C	-12.118700	1.173200	-1.480400
C	-10.337800	0.499900	1.733200	O	-12.194500	2.523100	-1.377100
H	-9.825200	-1.418600	2.556700	O	-12.118600	-2.984800	-1.359800
H	-9.869800	1.038600	2.556500	C	-12.877800	3.230900	-2.375400
C	-10.312400	-3.049200	0.618000	H	-13.940100	2.943900	-2.421100
C	-9.071500	-5.587000	0.775700	H	-12.425400	3.075600	-3.367400
C	-9.479100	-3.509900	-0.408600	H	-12.799900	4.288000	-2.107700
C	-10.547900	-3.899400	1.701100	C	-12.780600	-3.718800	-2.353100
C	-9.940900	-5.146400	1.780400	H	-12.681400	-4.770900	-2.072700
C	-8.873800	-4.751200	-0.333700	H	-12.326400	-3.565300	-3.344400
H	-9.284300	-2.863600	-1.264100	H	-13.848600	-3.455000	-2.407500
H	-11.198000	-3.563000	2.508900	H	-3.555300	11.200800	2.485600
H	-10.098700	-5.769800	2.660100	C	-1.215700	-10.776600	0.609100
H	-8.220900	-5.079100	-1.143200	C	1.628900	-10.729200	0.614200
C	-10.410400	2.650100	0.618600	C	-0.501600	-10.327900	1.702900
C	-9.268400	5.233800	0.779500	C	-0.498900	-11.400900	-0.460800
C	-9.586000	3.139200	-0.401900	C	0.937100	-11.378900	-0.457000
C	-10.686000	3.492700	1.698000	C	0.895800	-10.303700	1.704900
C	-10.127600	4.762100	1.778700	H	-1.041700	-9.861200	2.525900
C	-9.029300	4.402900	-0.325800	H	1.416500	-9.818300	2.529700
H	-9.360500	2.498700	-1.254100	C	-2.651400	-10.403300	0.588300
H	-11.328800	3.133000	2.501800	C	-5.235900	-9.265000	0.758000
H	-10.316900	5.380700	2.655500	C	-3.493100	-10.687000	1.666300
H	-8.383200	4.753000	-1.131300	C	-3.141800	-9.573000	-0.426700
C	-12.079600	-1.634200	-1.473100	C	-4.406000	-9.018100	-0.346300
C	-12.690500	-0.945300	-2.491000	C	-4.763000	-10.130300	1.751300

H	-3.132300	-11.334900	2.465500	C	6.516900	8.582800	0.912900
H	-2.502000	-9.342000	-1.278000	S	6.726600	6.980600	0.257700
H	-4.757400	-8.367200	-1.147400	C	8.332800	6.838700	0.921900
H	-5.381300	-10.326000	2.627000	C	8.660700	7.978400	1.614300
C	3.050100	-10.304200	0.596300	C	7.639100	8.959800	1.609100
C	5.588500	-9.067700	0.771100	H	9.626400	8.114300	2.097200
C	3.896000	-10.548100	1.680700	H	7.733600	9.932600	2.087600
C	3.515100	-9.464700	-0.423300	C	6.839300	-8.331000	0.928700
C	4.757100	-8.861900	-0.340300	S	6.985700	-6.724600	0.265900
C	5.143500	-9.942800	1.768600	C	8.583600	-6.515200	0.932100
H	3.555500	-11.202700	2.483300	C	8.955500	-7.637600	1.630700
H	5.088700	-8.203700	-1.144000	C	7.974200	-8.659300	1.628800
H	5.763500	-10.106600	2.649500	H	9.924800	-7.732300	2.116400
C	-1.171500	-12.100800	-1.516300	H	8.106400	-9.625000	2.112600
C	-0.459400	-12.687600	-2.532200	C	10.736500	1.628700	0.641000
H	-0.968900	-13.215100	-3.333700	C	10.785800	-1.216200	0.641600
C	0.947700	-12.667400	-2.527800	C	10.308700	0.897700	1.731900
H	1.476500	-13.179800	-3.326700	C	11.391600	0.934900	-0.426000
C	1.636100	-12.060100	-1.507500	C	11.414900	-0.500900	-0.427000
O	2.986800	-12.097900	-1.395600	C	10.333700	-0.499900	1.732400
O	-2.521600	-12.176000	-1.414600	H	9.818900	1.419100	2.553700
C	3.719800	-12.761800	-2.388400	H	9.864600	-1.038400	2.555200
H	3.456300	-13.829900	-2.440400	C	10.309200	3.048700	0.615400
H	4.772200	-12.661600	-2.109600	C	9.069900	5.587100	0.773100
H	3.565100	-12.309200	-3.380300	C	10.548400	3.900400	1.696500
C	-3.228900	-12.852200	-2.417900	C	9.472800	3.507900	-0.409200
H	-2.943600	-13.914700	-2.469500	C	8.868300	4.749600	-0.334400
H	-3.071600	-12.394200	-3.406900	C	9.942200	5.147700	1.775900
H	-4.286300	-12.774400	-2.151100	H	11.200800	3.564700	2.502800

H	9.275000	2.860300	-1.263000	H	2.871800	-9.264000	-1.279600
H	8.213000	5.076400	-1.142300				
H	10.102900	5.772300	2.654100				
C	10.410700	-2.651100	0.619800				
C	9.269900	-5.235200	0.781000				
C	10.685000	-3.492600	1.700500				
C	9.588600	-3.141600	-0.401800				
C	9.032300	-4.405500	-0.325400				
C	10.127100	-4.762200	1.781200				
H	11.326000	-3.131700	2.505100				
H	9.364400	-2.502100	-1.255100				
H	8.388000	-4.756700	-1.131800				
H	10.315500	-5.380100	2.658800				
C	12.077500	1.633000	-1.473800				
C	12.690900	0.943900	-2.490100				
H	13.207800	1.472300	-3.286300				
C	12.712300	-0.463100	-2.491900				
H	13.244500	-0.973700	-3.289600				
C	12.121200	-1.174300	-1.477500				
O	12.199000	-2.523900	-1.372700				
O	12.113300	2.984000	-1.362900				
C	12.884600	-3.231400	-2.369600				
H	12.432400	-3.078400	-3.362000				
H	12.809100	-4.288300	-2.100500				
H	13.946300	-2.942000	-2.415000				
C	12.773300	3.717300	-2.358100				
H	12.321600	3.556800	-3.349500				
H	13.842800	3.459400	-2.409200				
H	12.667200	4.770100	-2.082800				

anti-[2-CPP] **Calculation results at DFT-optimized geometry:**

Total Energy: -6506.76842218 AU

SCF Convergence: 1.40 E -09

Enthalpy Correction: 1.70897 AU

Free Energy Correction: 1.453177 AU

Three lowest frequencies (cm-1): -8.9,5.6,6.8

C	0.594200	10.047700	-0.094700
C	-2.248000	9.831100	0.005400
C	-0.041100	8.822700	-0.032500
C	-0.205600	11.231400	-0.084600
C	-1.640300	11.121700	-0.078800
C	-1.430000	8.718000	0.029800
H	0.564400	7.917300	-0.050800
H	-1.888600	7.733600	0.114000
C	2.071500	9.956600	-0.246100
C	4.767400	9.243300	-0.725000
C	2.818400	9.277000	0.717800
C	2.714800	10.329100	-1.432100
C	4.032500	9.974600	-1.671600
C	4.144900	8.939800	0.490700
H	2.340300	8.991900	1.654800

H	2.149000	10.859400	-2.198000
H	4.485700	10.205400	-2.635400
H	4.700800	8.407500	1.263100
C	-3.695300	9.515000	0.144800
C	-6.248900	8.395000	0.629000
C	-4.294900	8.659400	-0.781400
C	-4.423600	9.853800	1.291000
C	-5.670600	9.300600	1.532800
C	-5.552800	8.121000	-0.553400
H	-3.750700	8.396400	-1.688300
H	-6.181600	9.519000	2.470200
H	-5.990500	7.452700	-1.295700
C	0.377600	12.542200	-0.043100
C	-0.409900	13.663700	-0.095000
H	0.033800	14.655100	-0.062500
C	-1.810600	13.553700	-0.195000
H	-2.401500	14.462700	-0.269900
C	-2.416600	12.323400	-0.190200
O	-3.755900	12.151000	-0.308600
O	1.727300	12.584000	0.075100
C	-4.569400	13.287300	-0.408300
H	-4.332400	13.877700	-1.307300
H	-4.474700	13.935200	0.477100
H	-5.597300	12.920600	-0.477600
C	2.355700	13.836200	0.100600
H	2.146300	14.414800	-0.812800
H	3.429200	13.638100	0.163200
H	2.044100	14.429000	0.974900
C	-5.912500	-8.578800	-0.748300

S	-6.617100	-7.471100	0.399400	H	-8.902800	-6.383900	1.752600
C	-7.898000	-7.033500	-0.701200	H	-8.945200	-5.234000	-2.385300
C	-7.766900	-7.725500	-1.879900	C	-10.927700	1.961600	1.039900
C	-6.650200	-8.595400	-1.906100	C	-9.916700	4.598500	1.129700
H	-8.468200	-7.613800	-2.704600	C	-10.513600	2.612900	-0.127800
H	-6.395300	-9.228000	-2.754100	C	-10.888900	2.675600	2.239700
C	-7.477500	7.681000	0.964900	C	-10.397100	3.974600	2.286100
S	-7.792100	6.124400	0.244300	C	-10.015600	3.902800	-0.084700
C	-9.222600	5.882000	1.209900	H	-10.549500	2.074300	-1.074500
C	-9.423500	6.957500	2.038600	H	-11.213400	2.187100	3.158800
C	-8.443100	7.971300	1.897800	H	-10.318100	4.491000	3.242600
H	-10.266800	7.019100	2.723700	H	-9.671400	4.380500	-1.002500
H	-8.450600	8.898500	2.467500	C	-12.914200	-2.322700	-0.773200
C	-10.856800	-2.313500	0.657900	C	-13.920100	-1.636700	-1.406800
C	-11.155400	0.495200	1.020000	H	-14.664300	-2.163500	-1.997400
C	-10.117000	-1.619100	1.595600	C	-14.041400	-0.242500	-1.261200
C	-11.931300	-1.627000	0.004700	H	-14.870300	0.260300	-1.751200
C	-12.069800	-0.206700	0.172700	C	-13.162800	0.458600	-0.473900
C	-10.270000	-0.242700	1.780500	O	-13.284800	1.785400	-0.221300
H	-9.301500	-2.129600	2.106200	O	-12.807900	-3.674700	-0.793600
H	-9.579600	0.283300	2.438900	C	-14.354800	2.477200	-0.806200
C	-10.330900	-3.651400	0.295300	H	-15.325500	2.083700	-0.465800
C	-8.816700	-5.952100	-0.357500	H	-14.317500	2.429500	-1.905600
C	-9.999100	-3.945600	-1.034000	H	-14.255900	3.518500	-0.488600
C	-9.940500	-4.562500	1.281000	C	-13.752800	-4.405600	-1.526200
C	-9.200800	-5.693700	0.962700	H	-13.470600	-5.457000	-1.425200
C	-9.257000	-5.068100	-1.354500	H	-13.744000	-4.130500	-2.592500
H	-10.278600	-3.243900	-1.819100	H	-14.770700	-4.262000	-1.130900
H	-10.210200	-4.370200	2.319500	H	-3.975700	10.522700	2.025900

C	-0.600200	-10.416600	0.417400	H	0.217000	-14.210600	-2.134000
C	2.218000	-10.214400	0.788800	C	1.997900	-13.259300	-1.396000
C	-0.046900	-9.518800	1.309800	H	2.638600	-14.008400	-1.853100
C	0.264900	-11.372300	-0.206000	C	2.531900	-12.253500	-0.630600
C	1.687500	-11.263500	-0.027300	O	3.856200	-12.148200	-0.361100
C	1.333400	-9.423800	1.496200	O	-1.596700	-12.599600	-1.001100
H	-0.697300	-8.790900	1.792900	C	4.731100	-13.086000	-0.925500
H	1.730600	-8.629900	2.127700	H	4.520100	-14.105600	-0.567000
C	-2.029700	-10.181200	0.096300	H	5.736200	-12.792400	-0.610800
C	-4.633700	-9.220200	-0.455900	H	4.680800	-13.078700	-2.025500
C	-2.968600	-10.013400	1.117100	C	-2.150400	-13.669900	-1.716200
C	-2.434700	-9.907300	-1.216500	H	-1.840900	-14.640300	-1.297400
C	-3.706400	-9.434200	-1.487500	H	-1.868400	-13.637300	-2.780300
C	-4.249200	-9.548100	0.848300	H	-3.235300	-13.566900	-1.628700
H	-2.683300	-10.242400	2.144000	C	6.091900	8.718800	-1.047100
H	-1.714800	-10.017600	-2.027000	S	6.630200	7.240800	-0.293100
H	-3.973600	-9.157200	-2.506900	C	8.087300	7.196300	-1.247100
H	-4.961400	-9.424400	1.664800	C	8.130800	8.271700	-2.098100
C	3.636100	-9.781000	0.864100	C	7.008900	9.130800	-1.983500
C	6.127200	-8.452500	1.069300	H	8.960300	8.445200	-2.781000
C	4.258200	-9.603100	2.102200	H	6.884100	10.039000	-2.569800
C	4.308600	-9.329100	-0.277400	C	7.326400	-7.631800	1.212100
C	5.528300	-8.682000	-0.178600	S	7.672200	-6.369600	0.056600
C	5.479900	-8.953000	2.205300	C	9.024700	-5.786300	0.990100
H	3.754300	-9.951600	3.003900	C	9.181800	-6.543400	2.123300
H	6.018800	-8.325600	-1.085100	C	8.229700	-7.584200	2.245800
H	5.912700	-8.776600	3.189500	H	9.974300	-6.358000	2.845700
C	-0.246700	-12.479200	-0.961500	H	8.210200	-8.288500	3.074900
C	0.605000	-13.374200	-1.559100	C	10.833600	2.178600	-0.949900

C	11.023700	-0.634200	-0.550900
C	10.041600	1.292600	-1.653200
C	11.888700	1.652100	-0.140900
C	12.001800	0.231000	0.038100
C	10.125200	-0.086400	-1.446300
H	9.245800	1.688500	-2.283300
H	9.378500	-0.733300	-1.904800
C	10.377900	3.591500	-0.995500
C	8.969000	6.035800	-1.139000
C	9.861500	4.191900	0.158300
C	10.231600	4.264800	-2.210000
C	9.544100	5.470300	-2.282300
C	9.169200	5.388000	0.089000
H	9.977600	3.685600	1.116500
H	10.629600	3.813000	-3.118800
H	9.389100	5.949000	-3.249200
H	8.752800	5.823400	0.997800
C	10.753400	-2.037900	-0.156800
C	9.708900	-4.559700	0.587900
C	10.566700	-2.373900	1.191000
C	10.458600	-3.009500	-1.117800
C	9.946000	-4.248000	-0.754700
C	10.056900	-3.606700	1.557300
H	10.769700	-1.627200	1.958000
H	10.623200	-2.782000	-2.171100
H	9.718200	-4.986100	-1.524300
H	9.851900	-3.819700	2.606200
C	12.876100	2.501200	0.458600
C	13.896900	1.969300	1.205800

H	14.646100	2.612300	1.659500
C	14.027400	0.575700	1.352500
H	14.878800	0.189900	1.906600
C	13.128200	-0.278700	0.764300
O	13.262800	-1.628100	0.782900
O	12.750600	3.827100	0.205100
C	14.341000	-2.179500	1.487900
H	15.307000	-1.860100	1.066200
H	14.246100	-3.264500	1.393200
H	14.312000	-1.905200	2.554100
C	13.695100	4.704100	0.755300
H	14.708500	4.498400	0.376600
H	13.708700	4.649700	1.855000
H	13.391900	5.709100	0.450000
H	3.844300	-9.463400	-1.254200

[18-paraphenylene]

Calculation results at DFT-optimized geometry:

Total Energy: -6969.71115511 AU

SCF Convergence: 3.90 E -09

Enthalpy Correction: 1.903209 AU

Free Energy Correction: 1.607744 AU

Three lowest frequencies (cm-1): 2.4,3.1,3.6

				C	5.792900	7.068400	0.560500
C	5.215500	3.418300	1.248300	H	5.252900	8.010600	0.533200
C	8.012500	3.440000	0.720600	C	7.177500	7.079800	0.314500
C	5.994500	2.291000	1.416900	H	7.660300	8.031000	0.108500
C	5.857900	4.652900	0.910700	C	7.910500	5.923100	0.387700
C	7.272500	4.663800	0.650900	O	9.259200	5.895100	0.261200
C	7.366800	2.300100	1.154900	O	3.837000	5.852000	1.219600
H	5.505800	1.354900	1.685600	C	9.931200	7.085700	-0.044100
H	7.932500	1.371000	1.218300	H	9.812100	7.837000	0.752300
C	3.751200	3.208500	1.382600	H	9.579500	7.517000	-0.994500
C	0.995500	2.614100	1.607800	H	10.989100	6.823600	-0.136900
C	2.885500	3.388400	0.298600	C	3.083400	7.032300	1.178400
C	3.219300	2.704300	2.571000	H	3.451400	7.775400	1.903100
C	1.867000	2.411900	2.684300	H	2.059800	6.748000	1.439300
C	1.535600	3.104000	0.408600	H	3.088400	7.482700	0.173500
H	3.284500	3.773900	-0.639600	C	31.324700	-3.461500	1.981200
H	3.881500	2.542500	3.421600	S	30.097500	-2.229400	1.850400
H	1.479600	1.999800	3.615600	C	28.975500	-3.327300	1.088900
H	0.880100	3.278400	-0.445100	C	29.539300	-4.574800	0.974300
C	9.424400	3.261400	0.296900	C	30.858500	-4.650500	1.477400
C	12.079600	2.754500	-0.533900	H	29.027400	-5.409200	0.500000
C	10.373100	2.761000	1.188900	H	31.471500	-5.548300	1.434800
C	9.817600	3.479600	-1.029000	C	13.449400	2.525300	-0.981600
C	11.114500	3.228400	-1.437900	S	14.488600	1.371700	-0.185900
C	11.681000	2.521200	0.786300	C	15.819000	1.720100	-1.261100
H	10.085500	2.583200	2.225200	C	15.444400	2.665500	-2.184400
H	11.388800	3.373600	-2.482400	C	14.114100	3.117400	-2.027600
H	12.409200	2.169100	1.517300	H	16.128600	3.057500	-2.933700
C	5.147900	5.901100	0.881600	H	13.664300	3.892400	-2.644400

C	23.687000	-1.636700	-0.482800	C	22.629700	-3.667300	-3.460200
C	20.963900	-0.844700	-0.760000	H	23.054000	-4.310000	-4.227500
C	23.113100	-0.704600	0.358800	C	21.233600	-3.497600	-3.406300
C	22.891400	-2.187600	-1.537300	H	20.605000	-4.067800	-4.085700
C	21.494100	-1.872600	-1.603800	C	20.672400	-2.630500	-2.502200
C	21.789000	-0.284800	0.195000	O	19.334700	-2.470800	-2.361500
H	23.709800	-0.299100	1.175400	O	24.797100	-3.098400	-2.604300
H	21.395000	0.511800	0.825400	C	18.501200	-2.838000	-3.428000
C	25.061800	-2.077800	-0.143900	H	18.863200	-2.416500	-4.379400
C	27.646000	-2.887800	0.678200	H	17.512800	-2.426200	-3.201800
C	25.345000	-3.422900	0.127200	H	18.420600	-3.931400	-3.530200
C	26.088500	-1.147300	0.021800	C	25.389500	-4.172100	-3.283600
C	27.360000	-1.544200	0.414600	H	24.962500	-5.134200	-2.957800
C	26.605100	-3.820500	0.534000	H	26.453800	-4.144900	-3.030600
H	24.550700	-4.163400	0.024500	H	25.276200	-4.082100	-4.375200
H	25.892200	-0.096500	-0.190800	H	9.083700	3.848700	-1.745600
H	28.149700	-0.796800	0.496200	C	-26.915300	-1.436400	0.097000
H	26.788200	-4.867100	0.775400	C	-24.397600	-0.330000	-0.633500
C	19.614600	-0.246300	-0.904800	C	-26.174200	-1.950300	-0.948000
C	17.105000	1.044100	-1.125200	C	-26.454800	-0.245300	0.744200
C	18.766100	-0.129300	0.197000	C	-25.181400	0.311700	0.378100
C	19.191900	0.307500	-2.120400	C	-24.938600	-1.405600	-1.308000
C	17.962700	0.930700	-2.232400	H	-26.531700	-2.849700	-1.448400
C	17.533300	0.501700	0.090700	H	-24.347100	-1.884700	-2.087700
H	19.075900	-0.552200	1.152600	C	-28.105500	-2.230900	0.495600
H	19.841800	0.230700	-2.993100	C	-30.289900	-3.892700	1.177600
H	17.645500	1.327700	-3.196300	C	-29.125000	-2.488200	-0.421400
H	16.900700	0.587800	0.974500	C	-28.182400	-2.836700	1.754300
C	23.444500	-3.027300	-2.559900	C	-29.252700	-3.648900	2.089000

C	-30.203000	-3.298200	-0.084000	H	-29.546300	1.596300	2.641700
H	-29.073100	-2.037200	-1.412600	C	-0.426700	2.319700	1.749200
H	-27.393100	-2.648000	2.482100	S	-1.407100	1.880300	0.373800
H	-29.303900	-4.088600	3.085100	C	-2.841600	1.723200	1.355700
H	-30.978800	-3.494800	-0.824000	C	-2.544000	1.983400	2.671100
C	-22.999300	0.019200	-0.992000	C	-1.188400	2.318400	2.892000
C	-20.318000	0.521300	-1.736500	H	-3.297200	1.972700	3.455900
C	-21.958600	-0.120000	-0.068200	H	-0.786000	2.594000	3.864400
C	-22.673600	0.387300	-2.298600	C	-18.941100	0.801900	-2.130000
C	-21.358000	0.635700	-2.666300	S	-17.594500	0.079700	-1.287700
C	-20.646500	0.131600	-0.428700	C	-16.429100	0.893200	-2.301200
H	-22.194400	-0.413700	0.954600	C	-17.075400	1.658700	-3.240700
H	-21.126300	0.902200	-3.697100	C	-18.485500	1.607300	-3.144800
H	-19.859400	0.039100	0.320400	H	-16.544300	2.277300	-3.960600
C	-27.252900	0.453600	1.711900	H	-19.153600	2.183100	-3.781700
C	-26.782600	1.587100	2.324900	C	-7.992400	0.357900	-0.855800
H	-27.386600	2.107300	3.063000	C	-10.749300	0.210000	-1.541900
C	-25.534800	2.130600	1.968500	C	-8.680400	1.457200	-1.329000
H	-25.210600	3.052800	2.443100	C	-8.655400	-0.911300	-0.838600
C	-24.765300	1.537100	1.000300	C	-10.051400	-0.984200	-1.172100
O	-23.606800	2.073300	0.546400	C	-10.033100	1.383000	-1.671900
O	-28.489800	-0.049700	1.939900	H	-8.173100	2.421300	-1.352100
C	-23.158200	3.277700	1.103900	H	-10.563300	2.287600	-1.968300
H	-22.972800	3.182100	2.185200	C	-6.637200	0.629000	-0.314200
H	-23.878600	4.094100	0.937900	C	-4.126200	1.352300	0.771600
H	-22.218000	3.514900	0.597800	C	-6.339700	0.394200	1.033700
C	-29.297800	0.557300	2.909800	C	-5.662900	1.241900	-1.102600
H	-28.817600	0.551200	3.900800	C	-4.428500	1.595500	-0.572400
H	-30.216800	-0.034600	2.952200	C	-5.110400	0.739100	1.564300

H	-7.089800	-0.080700	1.665900	H	-5.922200	-3.920200	-0.846500
H	-5.877000	1.439600	-2.153100	H	-23.469900	0.485900	-3.036600
H	-3.694800	2.087800	-1.211300	C	-31.434500	-4.750700	1.540500
H	-4.894300	0.519800	2.609500	C	-33.615900	-6.377900	2.239900
C	-12.216300	0.323900	-1.745000	C	-32.729100	-4.444300	1.104400
C	-14.995700	0.703800	-2.102700	C	-31.256100	-5.891000	2.333600
C	-13.113100	0.101300	-0.695000	C	-32.334400	-6.695800	2.679900
C	-12.729800	0.762400	-2.966400	C	-33.808200	-5.248600	1.449400
C	-14.095400	0.935700	-3.149100	H	-32.891300	-3.545900	0.509000
C	-14.472900	0.288400	-0.867900	H	-30.251600	-6.161800	2.658300
H	-12.727100	-0.227500	0.269800	H	-32.170700	-7.582700	3.290300
H	-12.045300	0.939100	-3.796200	H	-34.808100	-4.986100	1.106600
H	-14.473600	1.232900	-4.126700	H	-34.461600	-7.007400	2.511800
H	-15.145800	0.132500	-0.024200	C	32.630500	-3.174900	2.568900
C	-7.953700	-2.131000	-0.553800	C	35.156200	-2.668700	3.686000
C	-8.617700	-3.330900	-0.519100	C	33.193400	-1.892900	2.518800
H	-8.086300	-4.251400	-0.293700	C	33.356400	-4.197100	3.196100
C	-9.988000	-3.400900	-0.828000	C	34.608000	-3.947300	3.742200
H	-10.470800	-4.374000	-0.828700	C	34.441200	-1.643100	3.075300
C	-10.686200	-2.272600	-1.177200	H	32.655700	-1.088700	2.016100
O	-11.980700	-2.299400	-1.575000	H	32.916800	-5.190800	3.274000
O	-6.616000	-2.020900	-0.369600	H	35.153400	-4.754900	4.228200
C	-12.675700	-3.515400	-1.540300	H	34.862500	-0.640400	3.021600
H	-12.256200	-4.245500	-2.250100	H	36.135300	-2.472900	4.119600
H	-13.705800	-3.283400	-1.826500				
H	-12.671300	-3.956600	-0.531500				
C	-5.884200	-3.169800	-0.041400				
H	-6.247500	-3.629300	0.891000				
H	-4.850300	-2.841700	0.098200				

anti-[3-CPP]

Calculation results at DFT-optimized geometry:

Total Energy: – 4356.67018692 AU

SCF Convergence: 4.40 E –09

Enthalpy Correction: 0.956296 AU

Free Energy Correction: 0.797561 AU

Three lowest frequencies (cm⁻¹): 14.0,15.8,17.2

C	6.669900	1.421000	0.783600
C	6.670100	-1.420600	0.783600
C	6.262500	0.700000	1.889600
C	7.358800	0.717100	-0.256100
C	7.358900	-0.716600	-0.256100
C	6.262600	-0.699600	1.889600
H	5.748400	1.219400	2.697500
H	5.748600	-1.219100	2.697500
C	6.082500	2.774900	0.650900
C	4.265900	4.942800	0.629200
C	6.030200	3.681200	1.714700
C	5.295800	3.046600	-0.476300
C	4.406300	4.104400	-0.486900
C	5.138500	4.748100	1.706400
H	6.653600	3.509100	2.592400
H	5.329600	2.364300	-1.324800
H	3.766800	4.260800	-1.355800

H	5.055000	5.388700	2.584300
C	6.082900	-2.774600	0.650800
C	4.266600	-4.942700	0.629000
C	6.030700	-3.681000	1.714600
C	5.296200	-3.046300	-0.476400
C	4.406800	-4.104200	-0.487000
C	5.139100	-4.747900	1.706200
H	6.654100	-3.508800	2.592300
H	3.767400	-4.260600	-1.356000
H	5.055700	-5.388600	2.584000
C	8.079300	1.405300	-1.283400
C	8.712000	0.704200	-2.280900
H	9.258500	1.222300	-3.064000
C	8.712100	-0.703400	-2.280900
H	9.258700	-1.221500	-3.063900
C	8.079500	-1.404600	-1.283400
O	8.125900	-2.756000	-1.169500
O	8.125400	2.756700	-1.169600
C	8.830700	-3.477000	-2.143900
H	9.895700	-3.197700	-2.163100
H	8.405500	-3.326000	-3.148400
H	8.739200	-4.531600	-1.871500
C	8.830500	3.477900	-2.143600
H	9.895500	3.198400	-2.162600
H	8.739000	4.532400	-1.871000
H	8.405500	3.327000	-3.148300
C	-0.712900	6.649300	0.686600
S	-1.535200	5.643600	-0.476900
C	-3.086500	5.920700	0.271800

C	-2.955600	6.789400	1.325800	C	-5.791500	-2.820900	-0.822700
C	-1.619900	7.204200	1.559600	C	-4.186400	-5.044400	-0.133800
H	-3.800000	7.092600	1.941700	C	-5.182000	-3.605200	-1.808800
H	-1.318100	7.835400	2.392700	C	-5.703900	-3.263400	0.504200
C	-0.712100	-6.649400	0.686600	C	-4.914700	-4.350700	0.843300
S	-1.534600	-5.643700	-0.476900	C	-4.391600	-4.695400	-1.473400
C	-3.085800	-5.920800	0.271900	H	-5.281400	-3.316700	-2.855200
C	-2.954800	-6.789500	1.325900	H	-6.178800	-2.680700	1.292300
C	-1.619100	-7.204300	1.559700	H	-4.765500	-4.602300	1.893200
H	-3.799200	-7.092800	1.941900	H	-3.882000	-5.254100	-2.258900
H	-1.317200	-7.835500	2.392700	C	-8.478900	1.403900	-0.082400
C	-6.203100	1.426700	-1.122000	C	-9.543300	0.703400	0.429900
C	-6.203000	-1.427200	-1.121900	H	-10.421200	1.221400	0.806000
C	-5.262600	0.697200	-1.824500	C	-9.543200	-0.704000	0.430000
C	-7.323700	0.718500	-0.579100	H	-10.421000	-1.222100	0.806200
C	-7.323700	-0.719000	-0.579000	C	-8.478700	-1.404500	-0.082200
C	-5.262600	-0.697700	-1.824400	O	-8.460400	-2.756400	-0.199800
H	-4.404900	1.215100	-2.250100	O	-8.460700	2.755800	-0.200200
H	-4.404800	-1.215500	-2.250000	C	-9.596500	-3.471900	0.203900
C	-5.791800	2.820500	-0.822900	H	-9.801000	-3.340800	1.278000
C	-4.187000	5.044200	-0.134000	H	-9.382000	-4.525500	0.006600
C	-5.182300	3.604800	-1.809000	H	-10.488200	-3.169700	-0.367100
C	-5.704400	3.263200	0.503900	C	-9.596900	3.471300	0.203400
C	-4.915500	4.350500	0.843100	H	-10.488600	3.168900	-0.367600
C	-4.392000	4.695100	-1.473600	H	-9.382500	4.524900	0.005900
H	-5.281500	3.316200	-2.855400	H	-9.801400	3.340400	1.277500
H	-6.179500	2.680500	1.292000	H	5.329900	-2.364000	-1.324900
H	-4.766400	4.602300	1.892900	C	3.122000	-5.847800	0.732600
H	-3.882300	5.253800	-2.259100	S	1.591800	-5.250100	0.151800

C	0.734600	-6.646400	0.747400
C	1.608700	-7.515100	1.358600
C	2.951800	-7.058200	1.358500
H	1.288600	-8.457800	1.797500
H	3.777800	-7.611400	1.801200
C	3.121300	5.847800	0.732800
S	1.591200	5.250500	0.151300
C	0.733800	6.646400	0.747500
C	1.607800	7.514800	1.359400
C	2.951000	7.057900	1.359300
H	1.287600	8.457300	1.798800
H	3.776800	7.610900	1.802500

syn-[3-CPP]

Calculation results at DFT-optimized geometry:

Total Energy: -4356.66461796 AU

SCF Convergence: 4.50 E -09

Enthalpy Correction: 0.956412 AU

Free Energy Correction: 0.796278 AU

Three lowest frequencies (cm-1): 11.8,14.1,17.0

C	6.242800	-1.426600	0.866700
C	6.242600	1.429900	0.863900
C	5.321100	-0.694800	1.591300

C	7.342100	-0.718100	0.282200
C	7.341800	0.720400	0.280500
C	5.321100	0.699400	1.590100
H	4.478800	-1.212000	2.047200
H	4.479000	1.217500	2.045300
C	5.833300	-2.830300	0.612400
C	4.223900	-5.085900	0.050800
C	5.274400	-3.594100	1.643700
C	5.694100	-3.308600	-0.697500
C	4.903400	-4.412500	-0.974300
C	4.480900	-4.699200	1.371000
H	5.415000	-3.275900	2.676700
H	6.130100	-2.743300	-1.520100
H	4.713200	-4.694500	-2.009800
H	4.006700	-5.240600	2.190200

C	5.832800	2.833100	0.607300
C	4.222100	5.087300	0.043900
C	5.276600	3.599500	1.638000
C	5.690600	3.308100	-0.703500
C	4.899200	4.411200	-0.981200
C	4.482600	4.704100	1.364400
H	5.419700	3.284000	2.671400
H	4.706300	4.690300	-2.017000
H	4.010500	5.247700	2.183400
C	8.480700	-1.403300	-0.251900
C	9.528200	-0.703300	-0.798300
H	10.393100	-1.221900	-1.202800
C	9.527700	0.703900	-0.800400
H	10.392100	1.221900	-1.206600

C	8.479800	1.404800	-0.255900	C	-7.342600	0.718000	0.283400
O	8.464400	2.757100	-0.142800	C	-5.323600	0.694800	1.595600
O	8.466200	-2.755200	-0.134700	H	-4.482000	-1.217600	2.050600
C	9.592400	3.470800	-0.571900	H	-4.481900	1.212100	2.052600
H	9.771200	3.341900	-1.650800	C	-5.833000	-2.832500	0.608400
H	10.496400	3.164700	-0.022700	C	-4.221500	-5.085500	0.042600
H	9.385000	4.524500	-0.367300	C	-5.277600	-3.600500	1.638300
C	9.594400	-3.469500	-0.562200	C	-5.689300	-3.305000	-0.703100
H	9.772800	-3.343100	-1.641500	C	-4.897500	-4.407600	-0.982000
H	9.387600	-4.522800	-0.355000	C	-4.483300	-4.704600	1.363500
H	10.498400	-3.161700	-0.014000	H	-5.421800	-3.287000	2.672100
C	-0.722500	-6.732900	-0.567200	H	-6.122500	-2.736000	-1.524700
S	-1.589300	-5.664000	0.502700	H	-4.703500	-4.684600	-2.018100
C	-3.110100	-5.978700	-0.290200	H	-4.012200	-5.249700	2.182100
C	-2.936700	-6.889800	-1.301400	C	-5.833500	2.829700	0.613500
C	-1.595700	-7.323500	-1.453400	C	-4.223300	5.084200	0.049600
H	-3.755400	-7.221700	-1.937000	C	-5.275500	3.595100	1.644100
H	-1.271900	-8.016100	-2.227300	C	-5.692900	3.305700	-0.697100
C	-0.725700	6.733100	-0.564900	C	-4.901800	4.409000	-0.975100
S	-1.588800	5.657000	0.500900	C	-4.481700	4.699800	1.370200
C	-3.112600	5.978300	-0.283400	H	-5.417200	3.278900	2.677400
C	-2.942700	6.895500	-1.289600	H	-6.128100	2.738900	-1.519100
C	-1.602000	7.329700	-1.443900	H	-4.710400	4.688900	-2.010900
H	-3.763700	7.232000	-1.919700	H	-4.008500	5.242700	2.188900
H	-1.281100	8.028300	-2.213600	C	-8.479600	-1.404800	-0.256000
C	-6.243600	-1.429800	0.866300	C	-9.526900	-0.704000	-0.801800
C	-6.243900	1.426500	0.869100	H	-10.390700	-1.222000	-1.209100
C	-5.323500	-0.699400	1.594300	C	-9.527400	0.703300	-0.799700
C	-7.342200	-0.720300	0.281700	H	-10.391700	1.221800	-1.205300

C	-8.480500	1.403200	-0.252100
O	-8.466200	2.755200	-0.134800
O	-8.464200	-2.757100	-0.142800
C	-9.594100	3.469400	-0.563400
H	-9.771300	3.343400	-1.642900
H	-9.387700	4.522600	-0.355500
H	-10.498700	3.161100	-0.016300
C	-9.591800	-3.470800	-0.573000
H	-10.496400	-3.164500	-0.024900
H	-9.384800	-4.524500	-0.367900
H	-9.769400	-3.342200	-1.652100
H	6.124600	2.740500	-1.525700
C	3.110400	5.980600	-0.287900
S	1.587800	5.657400	0.498000
C	0.722600	6.733600	-0.566000
C	1.597300	7.331600	-1.445600
C	2.938500	6.898300	-1.293400
H	1.274800	8.030500	-2.214300
H	3.758500	7.235900	-1.924200
C	3.112900	-5.980200	-0.281100
S	1.587300	-5.650300	0.496000
C	0.725800	-6.733800	-0.563600
C	1.603600	-7.337900	-1.435900
C	2.944500	-6.904100	-1.281400
H	1.284000	-8.042900	-2.200300
H	3.766800	-7.246400	-1.906700

syn-anti-[3-CPP]

Calculation results at DFT-optimized geometry:

Total Energy: -4356.66507479 AU

SCF Convergence: 5.50 E -09

Enthalpy Correction: 0.957363 AU

Free Energy Correction: 0.799449 AU

Three lowest frequencies (cm-1): 15.8,17.6,18.5

C	-6.602068	-1.418950	0.779657
C	-6.602015	1.418910	0.779734
C	-6.145710	-0.700567	1.867350
C	-7.339080	-0.716319	-0.226874
C	-7.339042	0.716362	-0.226837
C	-6.145681	0.700453	1.867387
H	-5.597879	-1.223238	2.650909
H	-5.597832	1.223061	2.650976
C	-6.016904	-2.769809	0.604983
C	-4.237681	-4.959841	0.452485
C	-5.257820	-3.003265	-0.549164
C	-5.947218	-3.711775	1.635186
C	-5.074857	-4.794150	1.560587
C	-4.382735	-4.069957	-0.621494
H	-5.305772	-2.287520	-1.369047
H	-6.545244	-3.562818	2.534591

H	-4.981534	-5.477190	2.404943	C	3.090042	-6.041467	0.110095
H	-3.761177	-4.200606	-1.507271	C	2.854569	-7.175532	-0.621966
C	-6.016836	2.769771	0.605129	C	1.500194	-7.609344	-0.577322
C	-4.237623	4.959807	0.452643	H	3.632415	-7.675365	-1.195663
C	-5.257841	3.003300	-0.549060	H	1.115638	-8.463787	-1.129955
C	-5.947085	3.711675	1.635385	C	0.691473	6.797848	0.178243
C	-5.074728	4.794055	1.560791	S	1.625614	5.503877	0.882938
C	-4.382753	4.069990	-0.621381	C	3.090079	6.041489	0.109952
H	-5.305871	2.287616	-1.368992	C	2.854551	7.175523	-0.622139
H	-4.981351	5.477046	2.405180	C	1.500179	7.609335	-0.577416
H	-3.761263	4.200697	-1.507197	H	3.632359	7.675341	-1.195903
C	-8.101955	-1.405162	-1.222696	H	1.115585	8.463758	-1.130053
C	-8.776255	-0.703829	-2.192268	C	6.313581	-1.428952	0.614332
H	-9.355120	-1.221833	-2.951836	C	6.313647	1.429005	0.614256
C	-8.776194	0.704065	-2.192245	C	5.523717	-0.696836	1.480760
H	-9.355010	1.222142	-2.951800	C	7.294190	-0.719746	-0.151461
C	-8.101843	1.405306	-1.222642	C	7.294238	0.719714	-0.151491
O	-8.141558	2.756547	-1.106733	C	5.523752	0.696968	1.480724
O	-8.141824	-2.756401	-1.106829	H	4.770436	-1.214465	2.071868
C	-8.876131	3.479500	-2.057254	H	4.770490	1.214661	2.071800
H	-9.942490	3.204947	-2.040109	C	5.876949	-2.838810	0.451034
H	-8.485799	3.324881	-3.075261	C	4.234688	-5.124797	0.216647
H	-8.770688	4.534005	-1.789676	C	5.514997	-3.338972	-0.806993
C	-8.876506	-3.479228	-2.057362	C	5.518555	-3.588650	1.576963
H	-9.942831	-3.204545	-2.040182	C	4.701789	-4.705090	1.465602
H	-8.771185	-4.533756	-1.789829	C	4.709637	-4.462163	-0.922880
H	-8.486178	-3.324614	-3.075372	H	5.788800	-2.780583	-1.701214
C	0.691438	-6.797847	0.178275	H	5.832428	-3.248136	2.563555
S	1.625527	-5.503840	0.882976	H	4.375241	-5.232042	2.362270

H	4.351367	-4.776326	-1.903177
C	5.877027	2.838859	0.450872
C	4.234736	5.124828	0.216466
C	5.514939	3.338918	-0.807158
C	5.518731	3.588783	1.576776
C	4.701950	4.705212	1.465408
C	4.709577	4.462107	-0.923055
H	5.788631	2.780450	-1.701362
H	5.832693	3.248343	2.563365
H	4.375484	5.232229	2.362067
H	4.351206	4.776189	-1.903341
C	8.319379	-1.404242	-0.881196
C	9.247822	-0.703747	-1.610151
H	10.024841	-1.221636	-2.165240
C	9.247893	0.703499	-1.610156
H	10.024968	1.221303	-2.165246
C	8.319512	1.404099	-0.881220
O	8.329299	2.755692	-0.761163
O	8.328998	-2.755838	-0.761137
C	9.339615	3.471733	-1.418635
H	10.340062	3.174564	-1.067396
H	9.171259	4.525776	-1.182769
H	9.291545	3.334932	-2.510251
C	9.339210	-3.472007	-1.418629
H	9.291129	-3.335211	-2.510245
H	9.170735	-4.526028	-1.182748
H	10.339701	-3.174953	-1.067417
H	-6.545055	3.562667	2.534817
C	-3.113347	5.901407	0.461241

S	-1.558816	5.253794	0.023724
C	-0.753165	6.765865	0.351978
C	-1.661488	7.708512	0.763614
C	-2.994406	7.216561	0.833356
H	-1.370887	8.721029	1.034965
H	-3.847016	7.817535	1.143727
C	-3.113401	-5.901437	0.461107
S	-1.558855	-5.253807	0.023666
C	-0.753209	-6.765877	0.351936
C	-1.661544	-7.708534	0.763522
C	-2.994471	-7.216599	0.833194
H	-1.370947	-8.721051	1.034877
H	-3.847092	-7.817584	1.143512

[12-paraphenylene]

Calculation results at DFT-optimized geometry:

Total Energy: -4819.64149352 AU

SCF Convergence: 3.10 E -09

Enthalpy Correction: 1.150756 AU

Free Energy Correction: 0.956319 AU

Three lowest frequencies (cm-1): 3.5,6.8,7.8

C	-8.849500	0.766600	-1.169900
C	-11.638400	0.342000	-0.793000

C	-9.397700	-0.500400	-1.181800	H	-12.154800	4.957300	-0.944500
C	-9.728000	1.893700	-1.084700	C	-12.004800	2.822700	-0.870400
C	-11.136400	1.679100	-0.893700	O	-13.331400	2.561700	-0.787900
C	-10.766800	-0.709000	-0.996800	O	-7.936800	3.380800	-1.520500
H	-8.730000	-1.358100	-1.256800	C	-14.227000	3.634600	-0.693100
H	-11.151300	-1.726400	-0.931500	H	-14.215300	4.257800	-1.601100
C	-7.365500	0.821600	-1.176000	H	-14.006100	4.271200	0.178000
C	-4.540800	0.718300	-1.105700	H	-15.219500	3.190400	-0.572600
C	-6.641700	0.238400	-2.217500	C	-7.409300	4.672200	-1.651200
C	-6.653800	1.336900	-0.087100	H	-7.856000	5.209400	-2.502400
C	-5.271300	1.291900	-0.053300	H	-6.336800	4.545500	-1.824700
C	-5.254800	0.187400	-2.186400	H	-7.560100	5.266600	-0.736600
H	-7.180100	-0.182400	-3.066800	C	0.573000	0.542000	0.329400
H	-7.202900	1.791800	0.737100	S	2.110000	0.607100	-0.497300
H	-4.743000	1.722300	0.797900	C	2.995700	0.512300	1.005600
H	-4.714300	-0.294900	-3.000100	C	2.126000	0.431500	2.065400
C	-13.024800	-0.035400	-0.417500	C	0.764800	0.448200	1.687900
C	-15.596800	-0.920800	0.357500	H	2.463300	0.388300	3.098500
C	-13.556300	0.302000	0.833200	H	-0.059600	0.394500	2.396400
C	-13.789700	-0.843600	-1.258700	C	19.175500	-2.468700	-1.159300
C	-15.057800	-1.270100	-0.885000	S	18.022000	-2.187500	0.120000
C	-14.811700	-0.133200	1.215800	C	16.805000	-1.632600	-1.000200
H	-12.961800	0.912900	1.512500	C	17.292300	-1.671400	-2.283600
H	-15.647900	-1.866600	-1.581500	C	18.623000	-2.140400	-2.372600
H	-15.188100	0.113300	2.208100	H	16.695800	-1.388300	-3.148100
C	-9.255600	3.240200	-1.243800	H	19.170800	-2.217400	-3.309300
C	-10.118600	4.302700	-1.154500	C	8.762500	0.442300	1.098700
H	-9.756600	5.320500	-1.269700	C	11.546400	0.008200	0.713000
C	-11.496800	4.093300	-0.966700	C	9.289400	-0.829800	1.002800

C	9.658800	1.558100	1.125000	H	12.137500	4.576200	1.322100
C	11.065600	1.338500	0.932600	C	11.954000	2.462500	1.033900
C	10.657300	-1.043100	0.812000	O	13.277300	2.186300	0.943300
H	8.607100	-1.679400	0.998200	O	7.883000	3.029100	1.664200
H	11.027900	-2.056300	0.659500	C	14.196200	3.237200	1.062000
C	7.279500	0.527000	1.101200	H	14.051700	3.997000	0.277900
C	4.454300	0.515000	1.023200	H	15.186900	2.788100	0.946800
C	6.536600	-0.095600	2.105300	H	14.128400	3.725200	2.046900
C	6.587400	1.124200	0.042200	C	7.371400	4.310300	1.907300
C	5.204200	1.123700	0.005000	H	7.802700	4.754100	2.818300
C	5.148700	-0.101400	2.070600	H	6.293000	4.185500	2.041100
H	7.060600	-0.581600	2.928500	H	7.554500	4.988900	1.059700
H	7.152200	1.609700	-0.753400	H	-13.392000	-1.120000	-2.235200
H	4.690300	1.618200	-0.820100	C	-16.931300	-1.346400	0.766600
H	4.591200	-0.612600	2.854700	S	-17.680200	-2.768200	0.086600
C	12.929400	-0.352900	0.310400	C	-19.129500	-2.544200	1.031300
C	15.488200	-1.202800	-0.540100	C	-19.005500	-1.436400	1.832900
C	13.691700	-1.223100	1.089400	C	-17.771100	-0.763500	1.684000
C	13.459900	0.075100	-0.912200	H	-19.804400	-1.090700	2.485100
C	14.714500	-0.333500	-1.326200	H	-17.519000	0.153900	2.211400
C	14.950400	-1.639500	0.675300	C	-3.083100	0.665900	-1.089300
H	13.290700	-1.574600	2.040200	S	-2.196600	0.655100	0.416400
H	12.875400	0.753500	-1.533600	C	-0.661700	0.581100	-0.413100
H	15.116300	0.037600	-2.268400	C	-0.854600	0.562100	-1.774400
H	15.517100	-2.331400	1.299000	C	-2.215000	0.609500	-2.152000
C	9.204900	2.891800	1.402000	H	-0.031000	0.516700	-2.484400
C	10.087300	3.941500	1.432900	H	-2.551700	0.629200	-3.186000
H	9.740800	4.950000	1.640800	C	-20.256800	-3.466100	0.922200
C	11.465300	3.726000	1.249800	C	-22.444800	-5.218800	0.742600

C	-21.140000	-3.626900	1.999200
C	-20.491100	-4.205900	-0.244400
C	-21.570100	-5.075600	-0.330200
C	-22.224500	-4.487900	1.907100
H	-20.953800	-3.085000	2.925800
H	-19.828400	-4.081400	-1.101100
H	-21.734300	-5.638600	-1.247600
H	-22.896900	-4.598400	2.756400
H	-23.292000	-5.898700	0.673300
C	20.510500	-2.991000	-0.878400
C	23.085300	-3.999900	-0.379500
C	21.231600	-3.653000	-1.882400
C	21.106500	-2.850100	0.381800
C	22.377100	-3.353400	0.628600
C	22.505900	-4.144800	-1.637100
H	20.773700	-3.802100	-2.859500
H	20.575400	-2.322900	1.174600
H	22.820700	-3.231000	1.615500
H	23.045600	-4.657500	-2.431900
H	24.082100	-4.392300	-0.186100

biphenyl

Calculation results at DFT-optimized geometry:

Total Energy: -462.918783367 AU

SCF Convergence: 6.20 E -09

Enthalpy Correction: 0.191326 AU

Free Energy Correction: 0.147316 AU

Three lowest frequencies (cm-1):

89.8,97.8,144.2

C	0.135062	0.000050	-0.162527
C	0.019712	-0.078898	1.230275
C	1.148052	-0.079383	2.040845
C	2.416985	-0.000112	1.474902
C	2.546798	0.079240	0.091564
C	1.417595	0.078914	-0.717800
H	-0.971717	-0.113189	1.681749
H	1.035443	-0.133933	3.122678
H	3.301475	-0.000175	2.109580
H	3.535612	0.133728	-0.361533
H	1.527823	0.113269	-1.801592
C	-1.064798	0.000135	-1.023507
C	-2.175151	-0.791804	-0.708254
C	-3.304394	-0.791962	-1.517565
C	-3.346719	0.000295	-2.660940
C	-2.249922	0.792472	-2.986918
C	-1.121624	0.792155	-2.176291
H	-2.138204	-1.435689	0.170371
H	-4.154390	-1.421361	-1.257981

H	-4.231206	0.000357	-3.295620
H	-2.276131	1.421932	-3.875239
H	-0.277372	1.435978	-2.422597

Appendix Chapter-II

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II-39a

II-39b

II-39a

and

II-39b

and

One-bond correlations
(gHSQCAD)

-40°C

S200

Expanded portions of the
gCOSY spectrum (a-d)

long-range couplings

$${}^5J_{25,5}$$

$${}^5J_{26,6}$$

(d)

Expanded portions of the
NOESY spectrum (a-c)

gHMBCAD

S205

$^2J_{\text{HC}}$ and $^3J_{\text{HC}}$
gHMBCAD correlations

gHSQCAD

One-bond correlations

II-47

^1H - ^1H homonuclear correlations

gCOSY

Through space correlations

ROESYAD

One-bond correlations

gHSQCAD

DPFGSENOE subspectrum

Selective excitation of
OCH₂

DPFGSENOE subspectra

One-bond correlations

gHSQCAD

DEPT90

only CH's →

total 9 CH's

APT

→ Cq + CH₂

→ CH + CH₃

a)

Spectrum a): UV-vis absorption spectrum of **II-1** at the concentration of 5.8×10^{-5} M in degassed CH_2Cl_2 . At the absorption maxima $\lambda_{\text{abs}} = 306, 348$, and 464 nm, $\varepsilon = 3.5 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, $2.3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, and $1.9 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$, respectively.

b)

Spectrum b): Fluorescence spectrum of **II-1** at the concentration of 5.8×10^{-5} M in degassed CH_2Cl_2 upon excitation at 348 nm. Fluorescence maxima $\lambda_{\text{em}} = 419$ and 571 nm. Excitation at 306 nm resulted in similar fluorescence maxima.

c)

Spectrum c): UV-vis absorption spectrum of *syn*-**II-43** and *anti*-**II-43** mixture at the concentration of 1.0×10^{-5} M in degassed CH_2Cl_2 . At the absorption maxima $\lambda_{\text{abs}} = 311, 348$, and 482 nm, $\epsilon = 6.2 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, $7.1 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, and $2.2 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$, respectively.

d)

Spectrum d): UV-vis absorption spectrum of **II-46a** and **II-46b** mixture at the concentration of 1.4×10^{-5} M in degassed CH_2Cl_2 . At the absorption maxima $\lambda_{\text{abs}} = 301, 362$, and 475 nm, $\epsilon = 7.9 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, $5.1 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, and $4.7 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$, respectively.

e)

Spectrum e): UV-vis absorption spectrum of **II-44** at the concentration of 1.4×10^{-5} M in degassed CH_2Cl_2 . At the absorption maxima $\lambda_{\text{abs}} = 311, 340$, and 470 nm, $\varepsilon = 2.7 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, $2.3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, and $8.0 \times 10^2 \text{ cm}^{-1} \text{ M}^{-1}$, respectively.

f)

Spectrum f): UV-vis absorption spectrum of **II-47** at the concentration of 1.9×10^{-5} M in degassed CH_2Cl_2 . At the absorption maxima $\lambda_{\text{abs}} = 315, 370$, and 470 nm, $\varepsilon = 4.8 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, $5.1 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, and $4.9 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$, respectively.

g)

Spectrum g): UV-vis absorption spectrum of **II-48** at the concentration of 4.5×10^{-6} M in degassed CH_2Cl_2 . At the absorption maxima $\lambda_{\text{abs}} = 315, 372$, and 473 nm, $\epsilon = 7.2 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, $1.4 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$, and $9.2 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$, respectively.

h)

Spectrum h): UV-vis absorption spectrum of **II-49** at the concentration of 6.7×10^{-6} M in degassed CH_2Cl_2 . At the absorption maxima $\lambda_{\text{abs}} = 316, 368$, and 476 nm, $\epsilon = 1.2 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$, $2.2 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$, and $1.3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, respectively.

i)

Spectrum i): Fluorescence spectrum of *syn*-**II-43** and *anti*-**II-43** mixture at the concentration of 1.0×10^{-5} M in degassed CH_2Cl_2 upon excitation at 348 nm. Fluorescence maxima $\lambda_{\text{em}} = 402$, 425, and 591 nm. Excitation at 311 nm resulted in similar fluorescence maxima.

j)

Spectrum j): Fluorescence spectrum of **II-46a** and **II-46b** at the concentration of 1.4×10^{-5} M in degassed CH_2Cl_2 upon excitation at 362 nm. Fluorescence maxima $\lambda_{\text{em}} = 405$, 429, and 595 nm. Excitation at 300 nm gave similar fluorescence maxima.

k)

Spectrum k): Fluorescence spectrum of **II-44** at the concentration of 1.4×10^{-5} M in degassed CH_2Cl_2 upon excitation at 340 nm. Fluorescence maxima $\lambda_{\text{em}} = 454$ and 573 nm. Excitation at 311 nm gave similar fluorescence maxima.

l)

Spectrum l): Fluorescence spectrum of **II-47** at the concentration of 1.9×10^{-5} M in degassed CH_2Cl_2 upon excitation at 370 nm. Fluorescence maxima $\lambda_{\text{em}} = 453$ and 594 nm. Excitation at 315 nm gave similar fluorescence maxima.

m)

Spectrum m): Fluorescence spectrum of **II-48** at the concentration of 4.5×10^{-6} M in degassed CH_2Cl_2 upon excitation at 372 nm. Fluorescence maximum $\lambda_{\text{em}} = 596$ nm.

n)

Spectrum n): Fluorescence spectrum of **II-49** at the concentration of 6.7×10^{-6} M in degassed CH_2Cl_2 upon excitation at 368 nm. Fluorescence maximum $\lambda_{\text{em}} = 597$ nm.

Figure S1. The fluorescence colors of **II-44** in hexanes, diethyl ether, benzene, dichloromethane, and chloroform upon excitation at 365 nm.

Electrochemical Characterization Methods

Electrochemical experiments were recorded using the Pine WaveNow USB potentiostat and BAS electrodes in anhydrous dichloromethane under an argon atmosphere with 100 mM tetrabutylammonium hexafluorophosphate as supporting electrolyte. All samples were analyzed between 0.25-1.5 mM depending on their solubility in dichloromethane. Cyclic voltammograms were recorded with a glassy carbon working electrode, platinum wire counter electrode, and a silver coil wire quasi-reference electrode. Differential pulse voltammetry measurements were recorded under the same conditions with the exception that a gold working electrode was used. All recorded data are presented versus the ferrocene/ferrocenium (Fc/Fc^+) redox couple. A red triangle within each voltammogram denotes a redox event that is attributed to non-specific analyte deposition on the electrode surface.

2,7-Bis(2-thienyl)-9H-fluoren-9-one (II-1, TFOT): CV at 0.10 V/s (1.5 mM) (A), DPV scan (B), CV at 0.10 V/s of reversible redox event (C).

Compounds II-46a and II-46b: CV at 0.10 V/s (A), CV scan-dependence (0.60 mM) (B), i_{pa} vs. (scan rate)^{1/2} dependence for the first redox couple (C), and DPV scan (D).

Compound II-47: CV at 0.10 V/s (A), CV scan-dependence (0.25 mM) (B), i_{pa} vs. (scan rate)^{1/2} dependence for the first redox couple (C), and DPV scan (D).

A

B

C

D

Compounds *syn-II-43* and *anti-II-43*: CV at 0.10 V/s (A), CV scan-dependence (0.60 mM) (B), i_{pa} vs. (scan rate)^{1/2} dependence for the first redox couple (C), and DPV scan (D).

Compound II-44: CV at 0.10 V/s (A), CV scan-dependence (0.50 mM) (B), i_{pa} vs. (scan rate)^{1/2} dependence for the first redox couple (C), and DPV scan (D).

A

B

C

D

Compound II-48: CV at 0.10 V/s (A), CV scan-dependence (0.25 mM) (B), i_{pa} vs. (scan rate)^{1/2} dependence for the first redox couple (C), and DPV scan (D).

Compound II-49: CV at 0.10 V/s (A), CV scan-dependence (0.30 mM) (B), i_{pa} vs. (scan rate)^{1/2} dependence for the first redox couple (C), and DPV scan (D).

Table S1. Tabulated Voltammetric Data in Dichloromethane: (a) the Differential Pulse Data, (b) the Cyclic Voltammetry Data

	(a)	(b)
Compound	E' (V vs. Fc/Fc⁺)	$E_{1/2}$ (V vs. Fc/Fc⁺)
II-1	−1.69, 0.62, 0.88	−1.64, 0.76, ^a 0.99 ^a
II-46	−1.76, −1.27, −0.82, −0.48, −0.07, 0.38, 0.88	−1.67
II-47	−1.65, 0.43, 0.86, 0.99, 1.16	−1.60
II-43	−1.73, −0.10, 0.72, 0.93	−1.67, 0.74
II-44	−1.70, 0.74, 0.84, 1.20	−1.65, 0.82, ^a 0.92 ^a
II-48	−1.68, 0.68, 0.85, 1.04, 1.30	−1.64, 0.67
II-49	−1.63, 0.71, 0.88, 0.97, 1.29	−1.66, 0.76

^aIrreversible event.

Appendix Chapter-III

III-33

III-40

III-41

77.3186
77.0000
76.6838

Resolution enhancement functions like Gaussian **GB = 0.25** and Lorentzian **LB = -1** has been applied; splitting patterns-a; b-with window functions

Selective decoupling of H10 at 9.38 ppm

simplification of splitting patterns for H12 and H15 (spectral region-c)

DFT B3LYP/6-31G(d)
optimized structure

upfield shift

located in the shielding cone of the
aromatic ring

1D ^1H PSYCHE Pure Shift NMR Spectrum

The PSYCHE (Pure Shift Yielded by Chirp Excitation) NMR experiment largely removes J-Coupling from the Proton NMR signal

Spin system identifications 1D TOCSY spectra (b-e)

(mixing time = 50 ms)

Experimental (a) and calculated splitting patterns of H20, H21, H24, H25, H26, and H27

Experimental (a) and calculated splitting patterns of H4, H5, H6, H7, H12, H13, H14, and H15

1D NOESY spectrum (b-c)

DPFGSENOE pulse sequence

DPFGESONE experimental sub spectrum -(b)

Control ^1H NMR-(a)

DPFGESONE experimental subspectrum (b)

Control ^1H NMR-(a)

DPFGESONE experimental subspectra (b-c)

Control ^1H NMR-(a)

Homonuclear (^1H - ^1H) correlations

gCOSY

Expanded portion of the gCOSY spectrum

NOESY spectrum (a)

Expanded portions (b-c)

gHMBCAD

($^2J_{\text{HC}}$ and $^3J_{\text{HC}}$)

gHSQCAD ($^1J_{\text{HC}}$)

Expanded portion of the
gHSQCAD spectrum