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# Dissymmetrical Chiral Peropyrenes: Synthesis via Iridium-Catalyzed C−H Activation/Alkyne Benzannulation and Study of Their Properties

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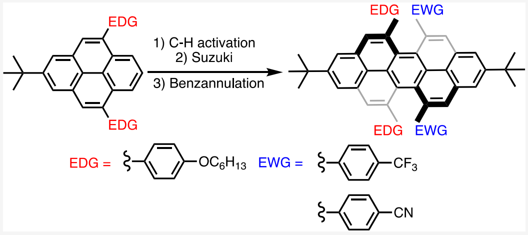
**ABSTRACT:** Dissymmetrical chiral peropyrenes with electron-rich and electron-deficient aryl substituents in the *bay* regions were synthesized via iridium-catalyzed C−H activation and alkyne benzannulation. The electronic properties were studied using cyclic and differential pulse voltammetry. The enantiomers were separated and exhibited high $g_{lum}$ and $g_{abs}$ values in circularly polarized luminescence (CPL) and circular dichroism (CD), respectively. Variable-temperature NMR experiments were conducted on symmetrical and dissymmetrical chiral peropyrenes to compare the barrier to rotation of the aryl groups in the *bay* region.



With the popularity of organic electronic devices on the rise, more effort has been geared toward the creation of a wider range of well-defined polycyclic aromatic hydrocarbons (PAHs) of both planar and contorted geometries with optoelectronic properties suitable for device applications.[1−5] Bottom-up synthetic strategies allow for the synthesis of complex—and just as importantly soluble—π-conjugated materials, the properties of which can be tuned through synthetic design to suit specific applications in organic field-effect transistors (OFETs), organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), and flexible-organic field-effect transistors (FOFETs).[6−8] Pyrene, in particular, has been shown to perform well in these applications due to its innate photophysical properties.[9] As such, derivatives of pyrene and materials bearing pyrenyl groups have been widely studied in this field. Alternatively, one can expand the π-electron system of pyrene through the addition of fused rings to further tune the properties of the material. The one-dimensionally π-extended analogue of pyrene, peropyrene[10,11] (Figure 1), also shows promise as a viable candidate for similar applications in the growing field of nanomaterials science.[12,13]

In 2016, it was shown that the reliable and facile preparation of soluble peropyrene and teropyrene derivatives can be achieved through alkyne benzannulation chemistry using Brønsted acids.[14,15] This methodology was later used to prepare the first axially chiral peropyrene, but the method is limited to alkyne precursors bearing electron-rich aryl groups.[16] In 2017, the Chalifoux group showed that indium(III) chloride ($InCl_3$) can be used to expand the scope of alkyne precursors to include electron-neutral and electron-poor aryl substituents as well as alkynes bearing only alkyl groups.[17] This π-Lewis acid method led to peropyrenes and teropyrenes in greater yield under milder conditions than the previous Brønsted acid method. In the preparation of chiral peropyrene using either the Brønsted or the π-Lewis acid methodology, electron-deficient alkyne aryl precursors gave no fully cyclized desired product. This was presumably due to the aromatic backbone becoming more electron deficient as each alkyne cyclization occurred, thus making the backbone less reactive toward subsequent electrophilic aromatic substitutions. To test this idea, a dissymmetrical teropyrene precursor with electron-rich ethynylaryl groups on one end and electron-poor ethynylaryl groups on the other was synthesized. It was hypothesized that the electron-rich groups cyclize first and then aid in the later benzannulation of the electron-poor groups by enhancing the nucleophilicity of the backbone and allowing for full benzannulation to occur. The reaction worked

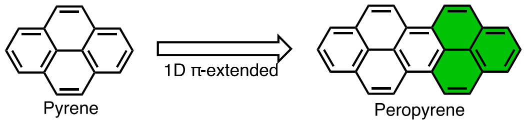


**Figure 1.** Pyrene expansion to peropyrene through the addition of a phenalenyl group (green).

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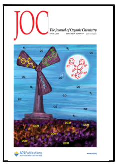

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well to produce a dissymmetrical push−pull teropyrene (Figure 2).[17] In the current work, we hypothesized that an electron-rich pyrene core will aid in an analogous benzannulation process to give dissymmetrical push−pull chiral peropyrenes.

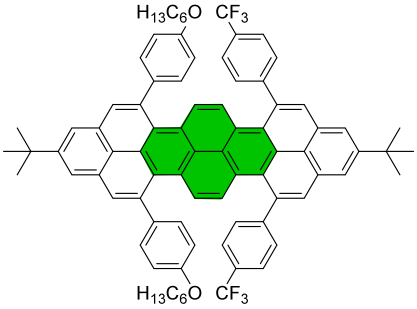


**Figure 2.** Dissymmetrical teropyrene.

Our assumption that the electronics of the aromatic core play a crucial role to ensure the full benzannulation of electron-poor diyne substituents factored into the design of these dissymmetrical chiral peropyrenes. Using the dissymmetrical teropyrene shown in Figure 2 as a model, we envisioned the preparation of similarly constructed chiral peropyrenes with analogous aryl substituents. Not only would this lead to new method development but also a dissymmetrical chiral peropyrene would have two electronically opposing aryl substituents overlapping each other, possibly resulting in a dynamic charge-transfer process, or a "push−pull" system localized in the *bay* region.[18,19] The crystal structures of our symmetrical chiral peropyrene showed a twisted backbone caused by the repulsion between the two aryl groups in the same *bay* region. They also showed that the aryl groups were ∼2.9 Å apart and the molecules, themselves, had a face-to-face interplanar molecular packing distance of 9.0 Å. Given that the space between the aryl groups is already very small in symmetrical chiral peropyrenes, installing electronically opposing aryl substituents in the *bay* region could make new dynamic chiral peropyrenes with smaller HOMO−LUMO gaps and enhanced chiroptical properties.[20]

Herein, we report the synthesis of the first dissymmetrical, axially chiral peropyrene using C−H activation on a complex pyrene system. Two different electron-deficient diyne derivatives were prepared to investigate the difference in the photophysical properties and barrier to rotation of the aryl groups in the *bay* regions relative to a previously reported symmetrical chiral peropyrene.[16] The barriers to enantiomerization are expected to be similarly high (∼29 kcal/mol), as was reported for the symmetrical chiral peropyrene. Both chiral derivatives were studied by cyclic voltammetry (CV), differential pulse voltammetry (DPV), and UV−vis and fluorescence spectroscopy. Due to the high enantiomerization barrier, the enantiomers were easily separated, and the circular dichroism (CD) and circularly polarized luminescence (CPL) properties were examined. A variable-temperature (VT) study was conducted on both dissymmetrical and symmetrical chiral peropyrenes to compare the barrier to rotation of the aryl groups in the *bay* regions.

The challenge of creating a dissymmetrical variant of this molecule stems from the inability to reliably couple two different diyne precursors to a smaller aromatic core. Suzuki cross-coupling attempts following analogous literature procedures resulted in a single coupling accompanied by protodehalogenation of the aromatic halide and an inseparable mixture of side products (Figure 3).[16,17]

However, inspired by these byproducts, we decided to intentionally make compound **S4** (Supporting Information) through Suzuki cross-coupling with iodobenzene (Scheme 1). We then used **S4** to make pyrene **1** in good yield through alkyne benzannulation with $InCl_3$ and silver bis(trifluoromethanesulfonyl)imide ($AgNTf_2$). The design of this pyrene, with a *tert*-butyl group at the 2 position and a hydrogen on the 7 position of the pyrene core, allowed us to

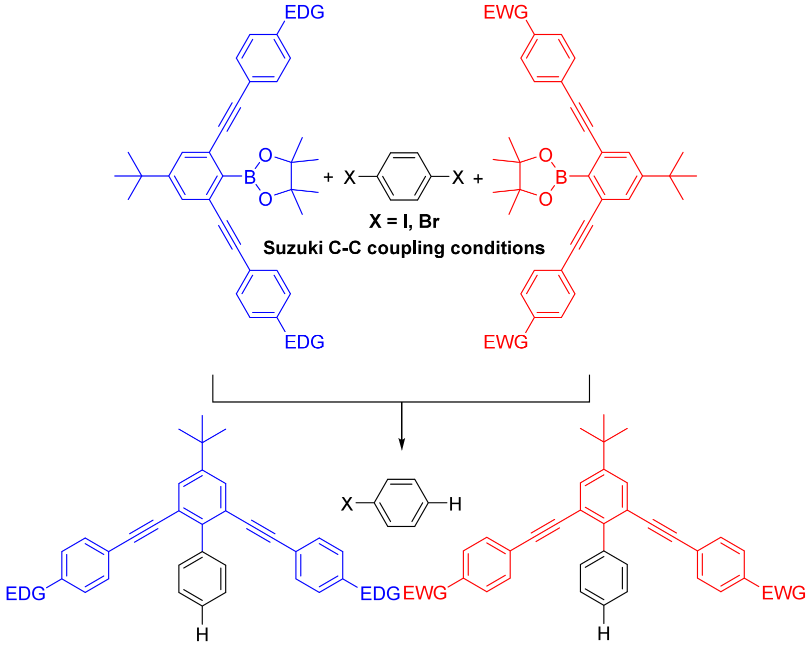
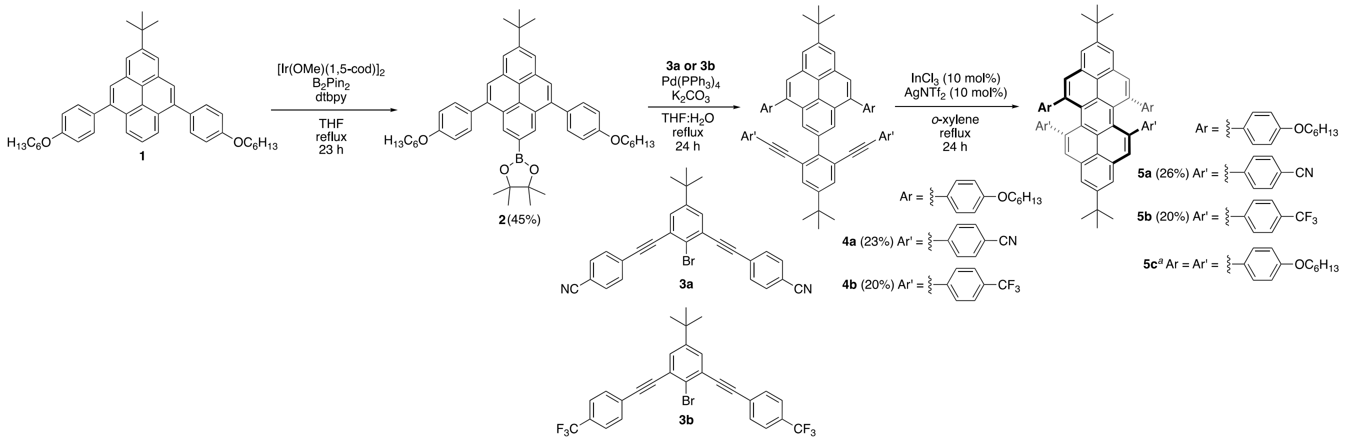


**Figure 3.** Results using previous literature methods for preparation of chiral peropyrenes.

**Scheme 1. Synthesis of Dissymmetrical Chiral Peropyrene**[b]



[a]Peropyrene **5c** was synthesized following a literature procedure.[17]. [b]Intermediates **S2**, **S3**, and **3b** were synthesized following literature procedures and are provided in the Supporting Information.

use iridium-catalyzed C−H activation to borylate the unfunctionalized end of the pyrene to obtain compound **2** in moderate yield.[21] Compounds **3a** and **3b** were coupled to **2** via Suzuki cross-coupling to produce compounds **4a** and **4b** in adequate yields. Two-fold alkyne benzannulation was achieved by using $InCl_3$ and $AgNTf_2$ in *o*-xylene to produce chiral peropyrenes **5a** and **5b**. The electron-rich, symmetrical chiral peropyrene **5c** was prepared following the literature procedure.[16]

The NMR spectra of compounds **5a** and **5b** show broad peaks for the aryl substituents at room temperature due to a high degree of restricted rotation arising from their proximity to one another in the *bay* region. Variable-temperature (VT) NMR experiments were conducted to determine rotational barriers for both aryl substrates. We wondered if the electrostatic interactions between the electron-deficient and the electron-rich aryl groups in the *bay* region would influence the rotational barrier. We found that both the symmetrical compound **5c** and the dissymmetrical compound **5b** chiral peropyrenes had the same rotational barrier of 14.4 kcal/mol. The corresponding calculations for the rotational barriers are in the Supporting Information.

Cyclic voltammetry and differential pulse voltammetry (see Supporting Information) experiments were conducted and are summarized in Table 1. Both compounds exhibited two reversible oxidations and two reductions, one of which was reversible. The electrochemical HOMO−LUMO gaps of **5a** and **5b** were calculated to be 2.37 and 2.35 eV, respectively, slightly smaller than the previously reported value of 2.42 eV for **5c**.[17] These values are slightly lower than the calculated value of 2.50 eV for **5a** and **5c** (Table SI-2). The HOMO and LUMO orbitals for **5a** and **5c** primarily reside on the core with small contributions to the HOMO from the electron-rich aryl substituents (Figure SI-11).

**Table 1. Photochemical and Electrochemical Properties for Compounds 5a and 5b**[a]

| compound | $E_{red}$ (V) | $E_{ox1}$ (V) | $E_{ox2}$ (V) | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | $E_g$ (eV) |
|---|---|---|---|---|---|---|
| **5a** | −2.01 | 0.36 | 0.85 | −4.76 | −2.39 | 2.37 |
| **5b** | −2.05 | 0.30 | 0.77 | −4.70 | −2.35 | 2.35 |
| **5c** | −1.66 | 0.76 | | −5.16 | −2.74 | 2.42 |

[a]Electrochemical data were obtained by DPV vs the Fc/Fc$^+$ redox couple as an internal standard. Voltammograms were recorded at 298 K in dry, degassed methylene chloride ($c \approx 2.5 \times 10^{-4}$ M) with 0.1 M $(n\text{-Bu})_4NPF_6$ under an argon atmosphere. The HOMO and LUMO energies were calculated using reported literature methods.[17] Data for **5c** was obtained from previous literature.[17]

Both dissymmetrical compounds exhibit similar absorption and emission patterns as well as fluorescence lifetimes (Figure 4, Table 2). This data was consistent with the previously

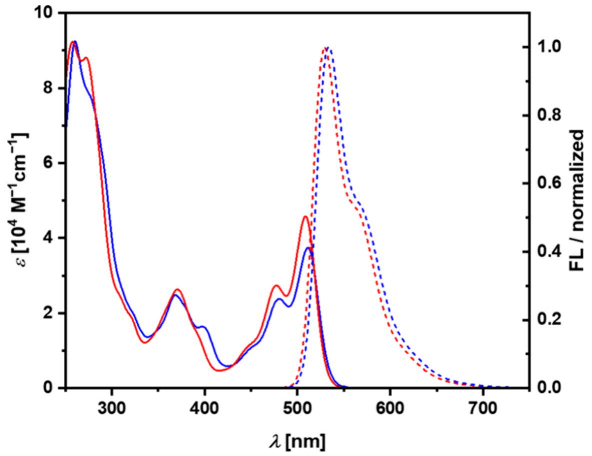


**Figure 4.** UV−vis ($c \approx 2 \times 10^{-5}$ M) (solid line) and normalized fluorescence (dotted line) spectra of **5a** (blue) and **5b** (red) measured in $CH_2Cl_2$ at 293 K.

**Table 2. Photophysical Properties of Compounds 5a and 5b**[a]

| compound | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | τ (ns) | Φ |
|---|---|---|---|---|
| **5a** | 511 | 533 | 3.40 | 44% |
| **5b** | 508 | 529 | 3.14 | 48% |
| **5c** | 512 | 531 | | 23% |

[a]Maxima of the absorbance and emission spectra and emission lifetimes for both chiral compounds **5a** and **5b** were determined. Both absorption and emission spectra were measured in $CH_2Cl_2$ at 293 K. The data for **5c** were obtained from previous literature.[16]

reported spectra of **5c**.[17] The fluorescence quantum yields for **5a** and **5b** were 44% and 48%, respectively. Interestingly, this is approximately double that reported for compound **5c** ($\phi$ = 22%). This suggests that small changes in the structure and electronics of the chiral peropyrene, even on the peripheral aryl groups, can have a significant effect on the optical properties.

The enantiomers of **5a** and **5b** were separated by HPLC on a chiral semipreparative column, and their CD and CPL properties were studied (Figure 5). Compound **5a** shows a strong Cotton effect toward the higher energy absorbance ($g_{abs}$ = 5.1 × $10^{-3}$; 320 nm). Similarly, compound **5b** also exhibits a strong Cotton effect in the higher energy absorbance ($g_{abs}$ = 4.9 × $10^{-3}$; 340 nm). Both compounds showed an average $g_{lum}$ of ~1.1 × $10^{-3}$ from 500 to 625 nm (Figures SI-5 and SI-6). These values are slightly higher than those reported for compound **5c**, which had reported values for $g_{abs}$ and $g_{lum}$ of ~1.2 × $10^{-3}$ and ~7.7 × $10^{-4}$, respectively.[16]

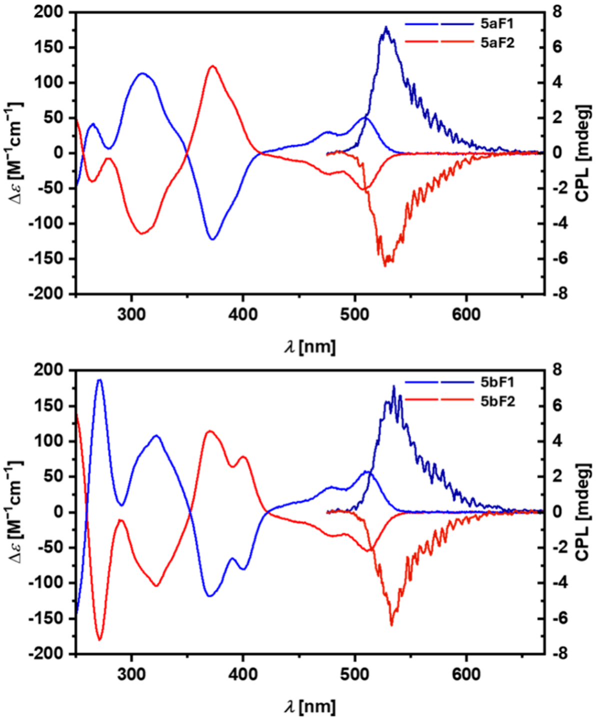


**Figure 5.** CD (light red and blue lines) and CPL (dark red and blue lines) of **5a** (a) and **5b** (b) in $CH_2Cl_2$ at 293 K.

In summary, the first dissymmetrical, axially chiral peropyrene was successfully prepared through the iridium-catalyzed C−H activation of a complex pyrene system. The C−H activation/alkyne benzannulation methodology is an efficient way to synthesize more complex PAHs that would otherwise be extremely difficult to obtain using other methods. The close proximity of the appended aryl groups in the chiral peropyrenes led to smaller HOMO and LUMO energy gaps and improved CD and CPL properties relative to a previously reported symmetrical chiral peropyrene. Using VT-NMR experiments, we were able to calculate the barriers of rotation of both symmetrical and dissymmetrical chiral peropyrenes. Interestingly, no observable difference could be detected as the electrostatic effects were not strong enough to significantly slow down aryl group rotation. Nonetheless, this new methodology allows us to greatly expand the size and complexity of PAHs, including desymmetrization of the backbone, and improve our understanding of how functionalization affects the optoelectronic properties of the molecules.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.3c02985.

> Additional experimental details, materials, methods, HPLC, absorption, emission, CD, CPL, and NMR spectra (PDF)

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### Author Contributions

S.P.G. synthesized and characterized (NMR, IR, MS) most of the intermediates and all of the final compounds and wrote most of the manuscript. J.S. separated enantiomers by preparative chiral HPLC, conducted absorption, emission/lifetime, CD, CPL, and CV experiments, and wrote those sections of the manuscript. R.J.M. calculated the rotational barriers from VT-NMR experiments and helped edit and write the manuscript. J.K. synthesized intermediates **1** and **2**. F.W. supervised J.S. and oversaw experiments conducted at the CNC and hosted W.A.C. as a Humboldt Fellow. W.A.C. conceived the project, analyzed data, and edited and helped write the manuscript.

### Notes

The authors declare no competing financial interest.

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