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Polycyclic Aromatic Materials

Chiral Teropyrenes: Synthesis, Structure, and Spectroscopic Studies

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In memory of Professor Marilyn M. Olmstead

Abstract: We present the inaugural synthesis of a chiral teropyrene achieved through a four-fold alkyne benzannulation catalyzed by $InCl_3$, resulting in good yields. The product underwent thorough characterization using FT-Raman and FT-IR spectroscopies, demonstrating a close agreement with calculated spectra. X-ray crystallographic analysis unveiled a notable twist in the molecule‘s backbone, with an end-to-end twist angle of 51°, consistent with computational predictions. Experimentally determined enantiomeric inversion barriers revealed a significant energy barrier of 23 kcal/mol, facilitating the isolation of enantiomers for analysis by circular dichroism (CD) and circularly polarized luminescence (CPL) spectroscopies. These findings mark significant strides in the synthesis and characterization of chiral teropyrenes, offering insights into their structural and spectroscopic properties.

In the middle of the 20th century, the chemistry of polycyclic aromatic hydrocarbons (PAHs) was intensely studied by Erich Clar who proposed the idea of sextet theory of PAHs (Clar's rule).[1] Since Clar's seminal work, there has been an exponential increase in research on PAH chemistry. This is primarily driven by the vast potential of PAH systems to be used in next-generation technologies,[2] which in turn has accelerated the development of new synthetic methodologies.[3] The physical and chemical properties of PAHs and nanographenes (large PAHs between 1–100 nm in size)[4] are directly related to their size, shape, topology, and are of great interest to the synthetic community.[5] Pyrene has been widely used as a building block for the construction of π-molecular systems, dyes, molecular sensors, covalent organic frameworks (COF) materials, and other useful PAHs.[6,7] Pyrene derivatives have attracted a lot of attention because of their easy modifiability and predictable chemistry.[7a,8] Larger derivatized pyrenacenes (homologues of pyrene) would be of significant value because their extended conjugation will lead to interesting optical and electronic properties. However, larger pyrenacenes, such as peropyrenes and teropyrenes, are rarely reported, presumably because of their difficult preparation, poor solubility, and the challenges associated with their functionalization.[9] Thus, development of chemical methods to access these and longer pyrenacene molecules would be highly valuable.[10]

The high-energy alkyne functionality can be utilized to make cyclic and polycyclic scaffolds[11] using various synthetic tools such as the Diels–Alder reaction,[12] Friedel–Crafts acylations,[13] and Lewis or Brønsted acid-promoted alkyne benzannulation reactions.[3c,d,14] Our group is first to synthesize a chiral peropyrene by a four-fold alkyne benzannulation reaction promoted by triflic acid.[15] The peropyrene is stable and highly soluble, allowing for its interesting chiroptical and photophysical properties to be

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studied. The molecule displays steric repulsion of the two aryl substituents within the same *bay* region, causing it to adopt a twisted backbone with an end-to-end twist angle of 28°, as determined by X-ray crystallographic analysis. Chiral peropyrenes exhibit circularly polarized luminescence making this material useful in chiroptic applications.[10a,15] The inversion barrier for enantiomerization is determined experimentally to be 29 kcal/mol and is supported by quantum mechanical calculations. This high barrier can be attributed to the bulky substituents within the same *bay* regions, which allows for the resolution of the two enantiomers for study.[15] The approach demonstrates that functionalizing *bay*, *cove*, and *fjord* regions with bulky substituents is an excellent way to arrive at large chiral nanographene structures.

In 1975, Misumi and co-workers reported the first non-functionalized teropyrene from multilayered metacyclophanes by a three-fold transannular cyclodehydrogenation sequence (Figure 1a).[16] The solubility of this compound was poor; therefore, it was only characterized by UV–vis spectroscopy. Over three decades later, Bodwell and co-workers reported the synthesis of a series of bent teropyrenes (teropyrenophanes) utilizing cyclodehydrogenation/oxidation as the key step (Figure 1b).[17] This drastically improved the field as these bent teropyrenophanes were soluble, enabling them to be fully characterized spectroscopically and by X-ray crystallography. Chalifoux and co-workers have recently shown that alkyne benzannulation is a useful and efficient strategy for the synthesis of nanographenes,[14a,15,18] heteronanographenes,[19] and for the synthesis of graphene nanoribbons (GNRs).[3c] Using a four-fold alkyne benzannulation strategy, they were able to synthesize functionalized teropyrene derivatives that show high solubility in various organic solvents (Figure 1c).[18] These teropyrenes were found to be chiral (twisted) in the solid state with end-end twist angles up to 30°. However, racemization was facile under ambient conditions making it difficult to separate their enantiomers. To the best of our knowledge, chiral teropyrenes have never been reported. Herein, we report the first synthesis and characterization of a chiral teropyrene using a four-fold alkyne benzannulation onto a substituted pyrene derivative (Figure 1d).

2,7-Dibromo-4,5,9,10-tetramethoxypyrene **1** was synthesized in three steps starting from commercially available pyrene following a reported procedure (Scheme 1).[20] Dialkynylboronic esters **2a** and **2b** were synthesized following a known procedure.[3c] A double Suzuki cross-coupling reaction of substrates **1** and either **2a** or **2b** provided tetraalkyne intermediates **3a**,**b**, respectively, in good yields. With the precursor **3a** in hand, we subjected it to a four-fold alkyne benzannulation reaction catalyzed by $InCl_3$ to successfully obtain teropyrene **4a** in 52 % isolated yield. More sterically demanding derivative **4b** was synthesized under the same reaction conditions in an excellent 90 % yield. What is remarkable about these chiral teropyrenes is that they are highly soluble in many common organic solvents, including nonpolar solvents, such as hexane. It was found that enantiomeric separation by semi-preparative chiral HPLC was only successful with compound **4b** (see the Supporting Information for details), and this derivative became the focus of further studies (see below).

The structure of teropyrene **4b** was unambiguously confirmed by single crystal X-ray crystallographic analysis of the racemate (Figure 2a). The structure clearly shows that the backbone of the chiral teropyrene is considerably twisted with an end-to-end twist angle of 51°, as determined from the mean planes generated from the terminal benzenoid rings (Figure 2b). The dihedral angle within each *bay* region is 26°. Interestingly, the two terminal benzenoid rings of the teropyrene represented with Clar sextets (Figure 1) have expected bond lengths that range from 1.392–1.415 Å, whereas the centralized benzeneoid rings represented with

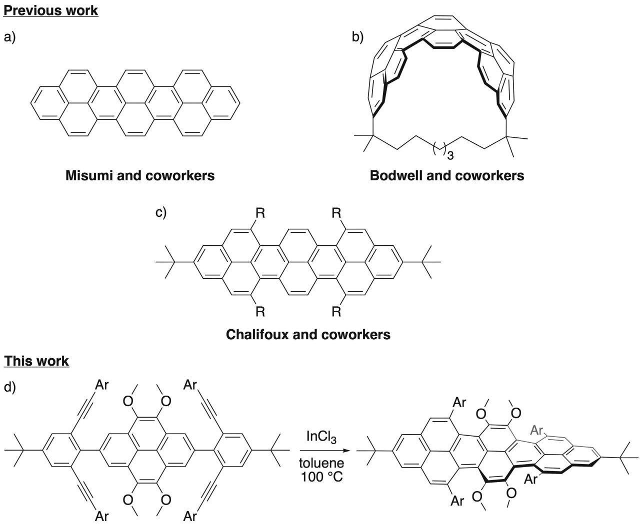
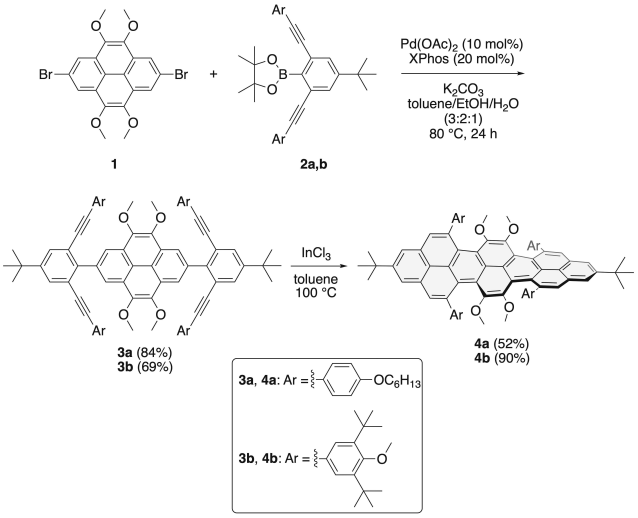


Figure 1. Previous work on teropyrenes, including a) non-functionalized teropyrene,[16] b) 1,1,9,9-tetramethyl[8](2,11)teropyrenophane,[36] and c) functionalized teropyrenes (R = aryl, heteroaryl, and alkyl).[18] d) The synthesis of chiral teropyrenes (this work).



Scheme 1. Synthesis of teropyrenes **4a** and **4b** by double Suzuki cross-coupling followed by four-fold alkyne benzannulation catalyzed by $InCl_3$.

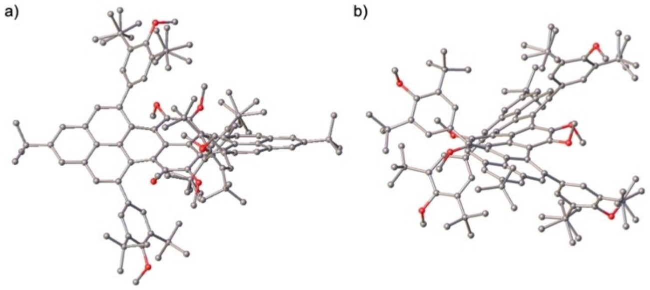


Figure 2. a) X-ray structure (ball and stick) of **4b**, hydrogens are removed for clarity. Carbon atoms are represented by gray spheres and oxygen atoms by red, b) end view of **4b**.

Clar sextets have longer bond lengths of 1.423–1.433 Å. All of the K-edges have bond lengths consistent with double bonds with bond lengths ranging from 1.366–1.377 Å, as is seen with pyrene and similar systems.[15,18a,b,21] The central methoxy groups maintain a fairly planar arrangement with only a slight dihedral of 11° angle between them due to twisting of the backbone. It is clear that the main driver for twisting in the structure is the steric strain imparted by the large 3,5-di-*tert*-butyl-4-methoxyphenyl groups. Of course, other stereoisomers are possible in which each aryl can either be above or below the closest neighboring methoxy group. However, the twisted arrangement of the backbone places the large aryl groups as far apart as possible, which explains why the *M,M,M,M* and *P,P,P,P* enantiomers are the lowest energy stereoisomers. The large aryl groups not only clash with one another but also with the core methoxy groups. Broad aryl signals are observed in the ^{1}H NMR spectrum under ambient conditions due to restricted rotation of the single bond, connecting the aryl group to the backbone, within the newly formed *bay* regions (Figure S9). VT NMR studies show that the two sets of broad peaks in aromatic and aliphatic regions coalesce at 75 °C. This corresponds to a rotational barrier of 15.4 kcal/mol for the aryl groups and is slightly higher than similarly substituted chiral peropyrenes.[22]

FT-Raman and FT-IR spectra were recorded for chiral teropyrene **4b** in the solid state and compared to spectra simulated from DFT calculations (Figures S2 and S3, respectively). The experimental spectra agree very nicely with the calculated spectra with the Raman spectra dominated by G and D bands that are expected for graphene-like molecules (see the Supporting Information for a full discussion of the FT-Raman and FT-IR results).

The enantiomerization barrier of **4b** was experimentally determined to be 23 kcal/mol (see the Supporting Information for details). The stereochemical stability of compound **4b** allowed for its separation using semi-preparative chiral HPLC and analysis of the enantiomers by UV/Vis Circular Dichroism (CD) and Circularly Polarized Luminescence (CPL) spectroscopies (Figure 3). DFT optimization of the *M,M,M,M* enantiomer and calculation of the CD spectrum by TD-DFT correlates well with the signals observed for the second-eluted enantiomer and permits configuration assignment (Figure 3a). The CD spectra of **4b** show strong Cotton effects, with Δε values near 500 at 300 nm. The CD spectra resemble those of similar PAHs, chiral peropyrenes, but the signals are significantly red-shifted by about 120 nm on account of the extended conjugation.[15,22] Interestingly, the lowest energy absorption for **4b** at 630 nm is also redshifted by about 60 nm relative to other reported teropyrenes (Figure 3b).[18b,c] Also of note is that the first absorption feature exhibits vibronic components with a typical band shape seen in peropyrenes and teropyrenes. Here, the dissymmetry factor (g_{abs}; the ratio of Δε/ε) is constant in the range of the first transition features (550–630 nm) with a value of 1.0×10^{-3}. The recorded CPL spectrum is quite noisy and suggests that racemization is taking place during the CPL measurements. Therefore, the dissymmetry factor (g_{lum}) is significantly underestimated (Figure 3c). The renormalized fluorescence spectra were recorded on the same apparatus and superimposed on the noisy CPL signal, thus showing that the shape of fluorescence and CPL features are the same (Figures 3c,d). One may also notice that the CPL sign is the same as the first CD band sign, as expected when ground and excited state structures are very similar. These observations have been evidenced for other chiral PAHs[15] and helicene-based hybrids.[23]

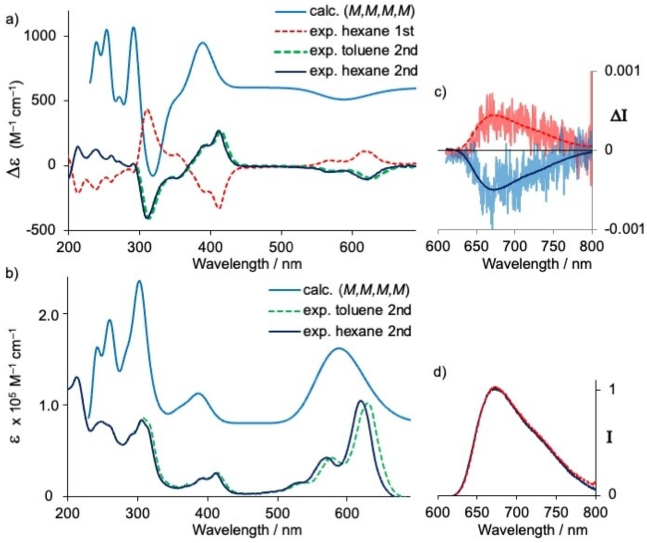


Figure 3. a) Experimental CD spectra for the two eluted fractions of compound **4b**: first eluted enantiomer (red line, solvent = hexane) second eluted enantiomer (black line, solvent = hexane; green hashed line, solvent = toluene), and comparison with calculated CD spectrum on an optimized *M,M,M,M* structure (light blue). b) Experimental and calculated absorption spectra. c) Experimental CPL spectra of the two eluted fractions of compound **4b**. d) Normalized fluorescence spectra.

The optimized geometry of **4b** is strikingly similar to that obtained by X-ray data, with a twist angle of 53° (see Figure S6). The first excited state of compound **4b** has also been optimized, obtaining a very similar structure, with a twist angle of 54°. The orbitals involved in the first absorption transition and in emission are reported in Figure S7, rotational strengths are quite similar and, in both cases, they originate from electric and magnetic dipole transition moments directed along the long axis of the compound.

In conclusion, our study highlights a highly efficient synthetic pathway for the first chiral teropyrenes, which employs a four-fold alkyne benzannulation reaction catalyzed by $InCl_3$. These electron-rich conjugated molecules exhibit good solubility in a variety of common organic solvents, facilitating comprehensive spectroscopic characterization using diverse methods. Through X-ray crystallographic analysis of a single crystal of chiral teropyrene **4b**, we documented substantial steric repulsion among substituents in the bay regions, inducing significant backbone twisting. Notably, the racemization barrier of chiral teropyrene derivative **4b** was determined to be 23 kcal/mol, allowing successful separation of the enantiomers by chiral HPLC. This enabled in-depth exploration of their chiroptical and photophysical properties. The molecule shows strong Cotton effects, particularly in the high energy region of the absorption spectrum. The strong fluorescence properties of teropyrenes,[18b] coupled with the inherent chirality of **4b**, results in CPL properties. These findings underscore the multifaceted potential of chiral teropyrenes in diverse applications, opening avenues for further exploration and utilization in materials science and beyond.

Supporting Information

Data including NMR, IR, Raman, CD, CPL, X-ray, chiral HPLC, polarimetry, and computations can be found in the Supporting Information. The authors have cited additional references within the Supporting Information.[24–30]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: nanographenes · teropyrene · benzannulation · chirality · circularly polarized luminescence

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