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Synthesis of Polyaromatic Hydrocarbons from Bis(biaryl)diynes: Large PAHs with Low Clar Sextets

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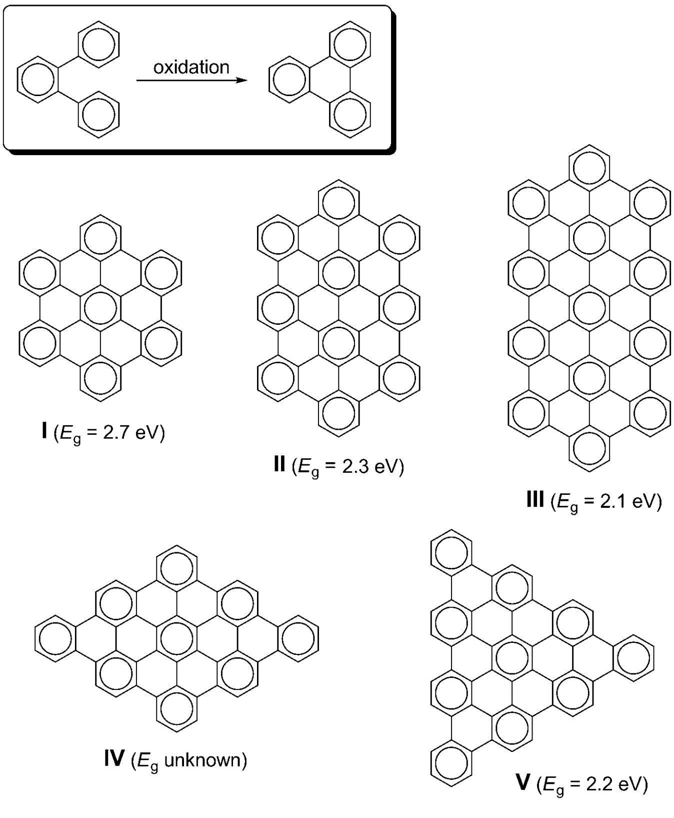
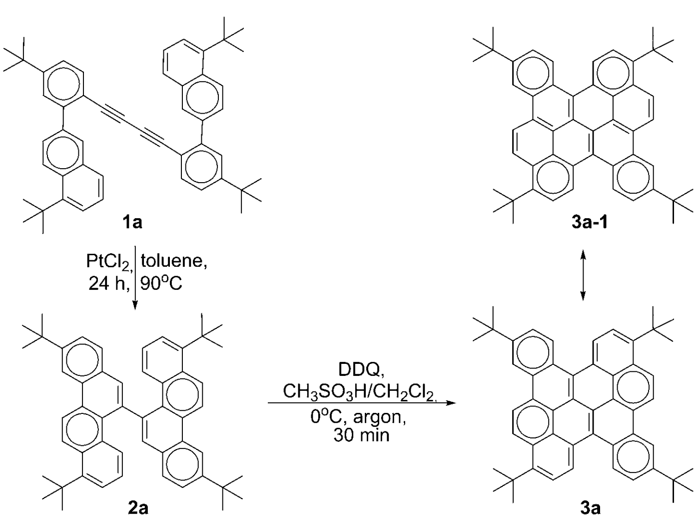
Large polyaromatic hydrocarbons (PAHs) have found various applications in organic opto-electronic devices.[1] The reported large PAHs were generally prepared from the Scholl oxidation of 1,2-diphenylbenzene units; several representatives[2,3] **I**–**V** are depicted in Scheme 1. Due to the fully populated Clar π sextets,[4] the reported large PAHs typically have irreducible highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO–LUMO) energy gaps ($E_g > 2.1$ eV),[2,3] in addition to difficulties of functionalization. Large PAHs with fewer aromatic π sextets would not only facilitate electron delocalization to create small energy gaps,[5] but also generate an open-shell ground state with singlet or triplet biradicals.[6] Few practical methods have been available[5,6] for the preparation of large PAHs with small Clar π sextets. Here, we report a new synthetic approach toward such PAHs using readily prepared bis(biaryl)diynes (see the Supporting Information).



Scheme 1. Large PAHs prepared from Scholl oxidations.



Scheme 2. A short synthesis of PAH **3a**.

Scheme 2 shows the two-step synthesis of novel benzo[*a*]dinaphtho[2,1,8-*cde*:1′,2′,3′,4′-*ghi*]perylene **3a**, of which the Clar formula is represented by two resonance structures comprising four aromatic sextets. The treatment of the starting bis(biaryl)diyne **1a** with PtCl$_2$ (10 mol %) in hot toluene (90 °C, 24 h, 10^{-2} M) enabled a two-fold aromatization[7] to form 5,5′-bichrysene **2a** in 88 % yield. Among various oxidants, we found that the intramolecular oxidative cyclization is performed best with 2,3-dichloro-5,6-dicyano benzoquinone (DDQ)/CH$_3$SO$_3$H[8] in CH$_2$Cl$_2$ (0 °C, 30 min, 10^{-2} M), giving orange solid **3a** in 95 % yield. We also obtained single crystals of **3a** for X-ray diffraction;[9] the ORTEP drawing in Figure 1 reveals the S$_2$-symmetry, resulting from the steric interaction between the two cove regions[10] at the A′- and C-rings (or A- and C′-rings). The central portion of the molecular geometry is highly distorted from planarity

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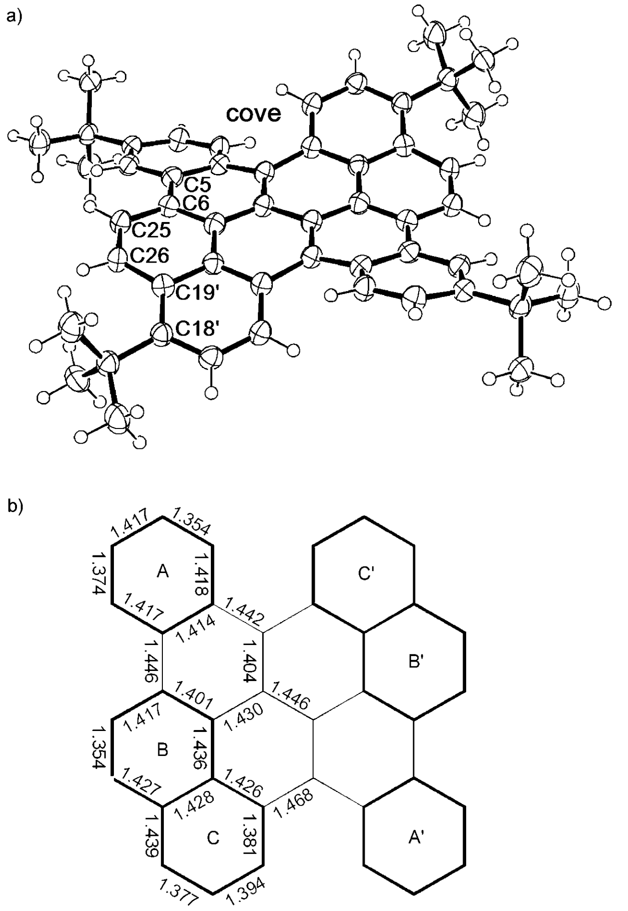
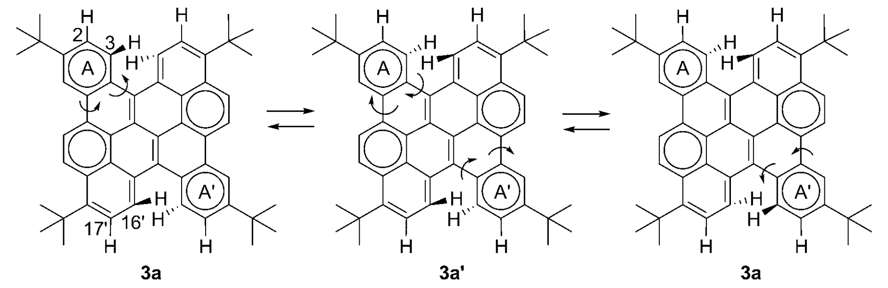


Figure 1. a) ORTEP drawing of **3a** measured at 100 K, b) bond lengths.

with a large dihedral angle (36.6°) between the **A** and **C′** rings. The crystallographic data support our proposed Clar formula **3a** and **3a-1** that the A-ring represents a benzene unit and the **B**–**C** rings resembles a naphthalene moiety. The long C(18′)−C(19′) length (1.439 Å) supports resonance structure **3a**, whereas the short C(25)−C(26) bond (1.354 Å) implies structure **3a-1**.



Scheme 3. Interconversion of the enantiomeric pair **3a**.

In $C_2D_2Cl_4$, we observed seven proton signals for species **3a** in the aromatic regions ($\delta = 7.9$–9.4 ppm) at 253 K. Among them, four doublets nearby the cove and bay regions became broad as temperatures were raised to 293 K with the rest of the signals remaining unchanged. As the temperatures were raised to 353 K, all proton NMR signals became well resolved again without alteration of the pattern (Figure 2). This dynamic behavior suggests the racemization of the enantiomeric pair of **3a** via intermediate **3a′**, which has C_2-symmetry (see Scheme 3). Such a motion is achievable by rotation of the sigma bond around the A-ring.

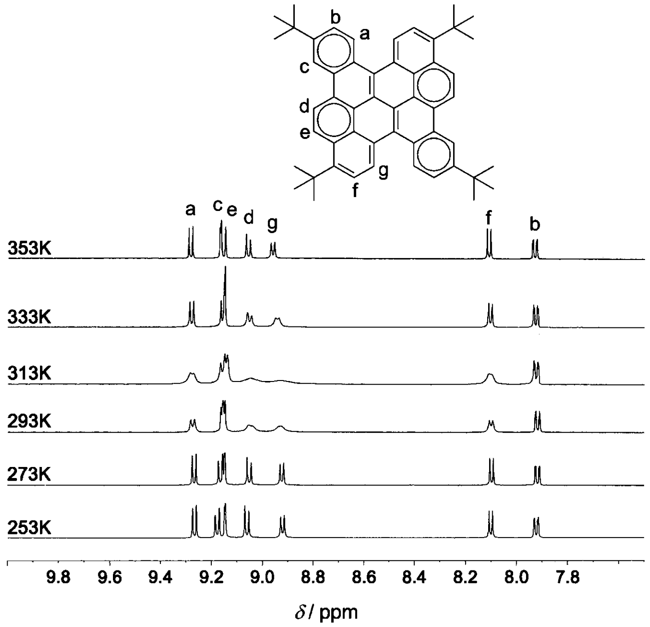


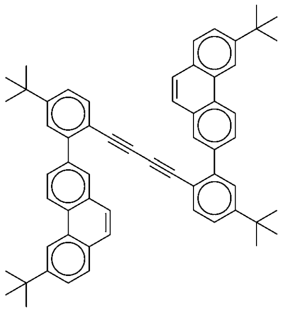
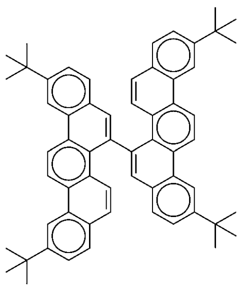
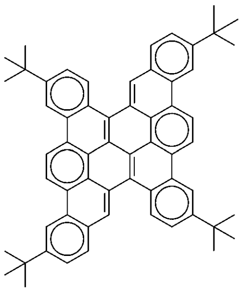
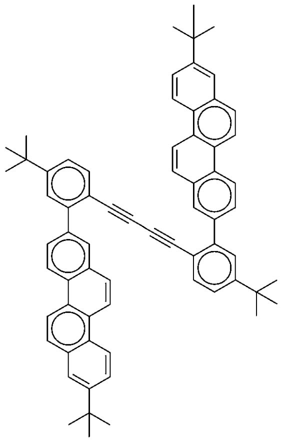
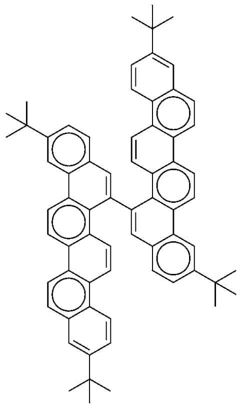
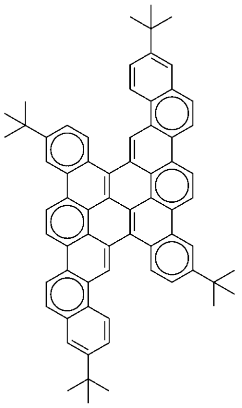
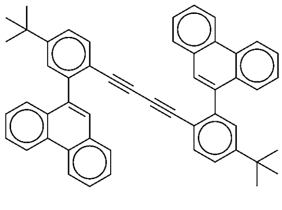
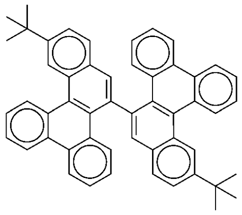
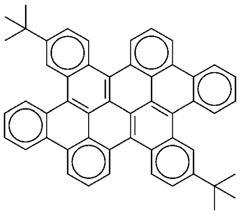
Figure 2. Temperature-dependent proton NMR spectra of compound **3a** in $C_2D_2Cl_4$ (600 MHz).

Table 1 shows the applicability of this new synthesis to bis(biaryl)diynes **1b**–**1d**, which delivered novel PAHs **3b**–**3d** of medium sizes, and of which the hypothetic Clar representations are based on an assumption that the central benzene rings are nonplanar due to the steric congestion of the cove regions. Both steps gave desired compounds **2b**–**2d** and **3b**–**3d** with yields exceeding 71%. Targeted molecules **3b**–**3d** are soluble in common organic solvents including chloroform, dichloromethane, and tetrahydrofuran; purifications were conducted by column chromatograph. The characterization of compounds **3b**–**3d** relies on elemental analysis, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass, high resolution mass spectrometry (HRMS), ^{1}H and ^{13}C NMR spectra; herein, we also observed similar dynamic proton NMR spectroscopy behavior caused by the racemization of the enantiomeric pair **3b**–**3d**.

To our delight, this new synthesis is applicable to a large PAH **4** containing only six Clar-sextets; the modified proto-

Table 1. A short synthesis of PAHs **3b**–**3d**.

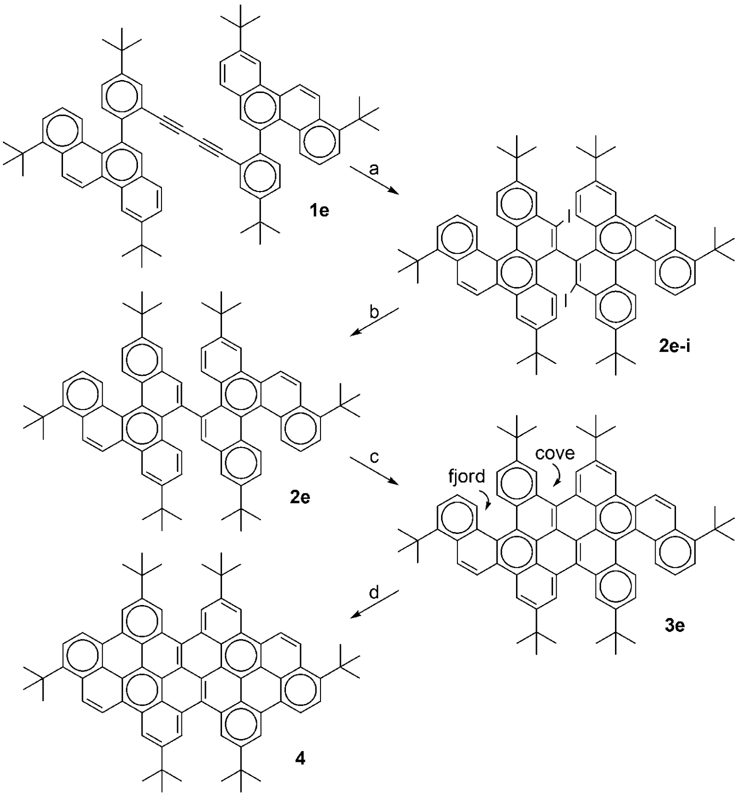
$$\boxed{\textbf{1b-1d}} \xrightarrow[\text{toluene, } 90^{\circ}\text{C}]{PtCl_2,} \boxed{\textbf{2b-2d}} \xrightarrow[CH_3SO_3H/CH_2Cl_2 \;\; 0^{\circ}\text{C, argon}]{\text{DDQ,}} \boxed{\textbf{3b-3d}}$$

Substrate	Reaction 1[a,c]	Reaction 2[b,c]
 **1b**	 **2b** (28 h, 88 %)	 **3b** (30 min, 93 %)
 **1c**	 **2c** (28 h, 71 %)	 **3c** (30 min, 89 %)
 **1d**	 **2d** (24 h, 75 %)	 **3d** (30 min, 90 %)

[a] $PtCl_2$ (10 mol %), toluene (10^{-2} M). [b] DDQ (2.1 equiv), CH_3SO_3H/CH_2Cl_2 (1/10, v/v). [c] Yields are given after purification by column chromatography on silica gel.

col is shown in Scheme 4. The $PtCl_2$-catalyzed aromatization of bis(biaryl)diyne (**1e**) was unsuccessful with protracted heating (90 °C, 72 h), but the use of ICl[11] (2.2 equiv) in cold CH_2Cl_2 (−78 °C, 3 h) effected the aromatization smoothly to give the desired compound **2e**–**2i** in 83 % yield. The treatment of species **2e**–**2i** with *n*-butyl lithium (*n*BuLi) in cold tetrahydrofuran (−78 °C) provided the desired **2e** in 96 % yield. The oxidative cyclization of species **2e** with DDQ/CH_3SO_3H in cold CH_2Cl_2 (0 °C, 30 min) produced the desired product **3e** in 89 % yield. Although compound **3e** possess both cove and fjord chiralty,[10] we observed only one set of well-defined proton NMR signals, which showed no dynamical behavior over the range 223 to 353 K. We envisage that only one diastereomeric product is preferably produced because of its particular stability.[12] The dynamic behavior is impeded by a simultaneous alternation of both cove and fjord chiralty.[12] Further oxidative coupling of compound species **3e** at the fjord region is accomplished by DDQ/CF_3SO_3H in dichloromethane (0 °C, 30 min) to give a large rhombus-shaped PAH **4** (84 %) as an air-stable purple solid, of which the structure is identified by ^1H NMR spectroscopy and its nuclear overhauser effect (NOE).

Table 2 presents the photophysical properties of compounds **3a**–**3e** and **4**. Notably, these six PAHs have the same UV/Vis absorption patterns (Figure 3 a), including two major maxima between 300–400 nm, and three maxima in the region 400–550 nm; this observation indicates that their electronic structures belong to the same family. For the family **3a**–**3c**, we observed bathochromic shifts with increasing benzene arrays in their UV/Vis and photoluminescence (PL) spectra (Figure 3 b). This phenomenon truly reflects an effective delocalization since there is a two-benzene alteration for the **3a**→**3b**→**3c** sequence. As we expected, the large PAH **4** has the largest wavelengths in both absorption (574 nm) and emission spectra (593 nm). The emission maxima of compounds **3a**–**3e** and **4** are highly dependent on their concentrations (Figures S1–S6 in the Supporting Information). The emission maxima of species **3a** appeared at 512 nm at 10^{-6}–10^{-7} M, gradually becoming red-shifted to 514–519 nm at 10^{-5}–10^{-4} M, and further to 548 nm at 10^{-3} M due to increasing molecular aggregation. According to cyclic voltammetry (CV; Figure S8 in the Supporting Information), compounds **3a** and **3b**, **3d** and **3e**, and **4** show two reversible oxidations (0–1.25 V vs. Fc^+/Fc) and one irreversible reduction (−1 to −1.75 V). In addition to these common CV features, species **3c** exhibits an additional oxidation curve at 0.25 V. This information indicates a superior



Scheme 4. Synthesis of PAH **4**: a) ICl (2.2 equiv), CH_2Cl_2, −78 °C 83 %; b) *n*BuLi (2.2 equiv), THF, −78 °C; H_2O, 91 %; c) DDQ (2.1 equiv), CH_3SO_3H/CH_2Cl_2 (1/10, v/v), argon, 0 °C, 89 %; d) DDQ (2.1 equiv), CF_3SO_3H/CH_2Cl_2 (1/10, v/v), argon, 0 °C, 84 %.

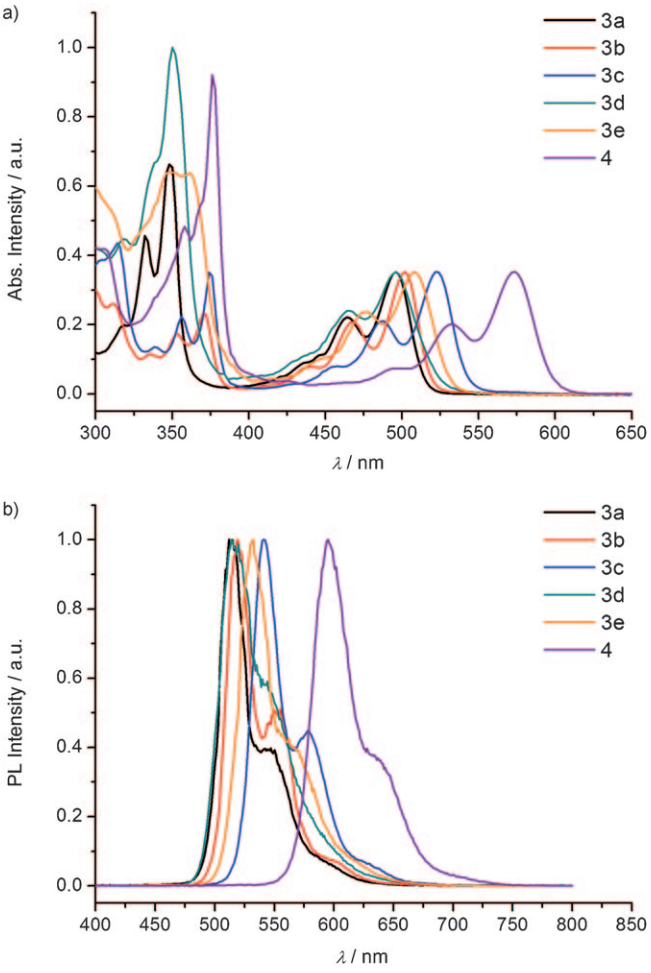


Figure 3. a) UV/Vis absorption spectra of compound **3a** (black), **3b** (red), **3c** (blue), **3d** (dark cyan), **3e** (orange), and **4** (purple) in CH_2Cl_2 (10^{-5} M), b) photoluminescence spectra in CH_2Cl_2 (10^{-6} M).

cation-delocalization for compound **3c**. We speculate that the initially generated cation at one naphthalene affects the same oxidation on the other naphthalene to give two separate oxidation curves.[7b] We estimated the HOMO energy levels from their oxidation potentials, and derived their LUMO energy levels from the energy gaps provided by the UV/Vis spectra. For compounds **3a**–**3c** we observed a gradual decrease in the energy gap (2.41–2.28 eV), reflecting an extensive conjugation. Notably, the large PAH **4** has a small gap (2.07 eV), which is smaller than the gaps reported for the large PAHs **I**–**V**.

In summary, we have developed a new synthesis of medium-sized PAHs with low Clar sextets. This two-step synthesis involves starting bis(biaryl)diynes, which undergo initial $PtCl_2$-catalyzed aromatizations and subsequent DDQ oxidation. The resulting PAH products have aromatic characters on the outer benzenes and polyene properties on the central framework due to the nonplanar cove regions. Photophysical evidence indicates an efficient electron delocalization within the frameworks of these PAHs. This convenient approach is applicable to a large PAH **4** that has small energy gap (2.07 eV) even though the molecule is nonplanar.

Table 2. Optical and electrochemical data.

PAHs	Abs_{max} [nm][a]	PL [nm][b]	HOMO [eV][c]	LUMO [eV][d]	E_g [eV][e]	Φ_{PL}[b,f]
3a	332, 348, 436, 464, 496	512	−5.05	−2.64	2.41	0.34
3b	354, 370, 440, 468, 502	515	−5.04	−2.66	2.38	0.25
3c	356, 374, 454, 489, 522	539	−4.94	−2.66	2.28	0.47
3d	338, 350, 434, 465, 496	512	−5.16	−2.80	2.36	0.31
3e	348, 360, 448, 476, 508	530	−5.10	−2.77	2.33	0.55
4	358, 376, 494, 532, 574	593	−4.93	−2.86	2.07	0.34

[a] 10^{-5} M in CH_2Cl_2. [b] 10^{-6} M in CH_2Cl_2. [c] HOMO was calculated from the oxidation potential of CV. [d] LUMO was calculated by the sum of HOMO and E_g. [e] Calculated from the UV/Vis absorption. [f] Coumarin 1 as the standard.

Experimental Section

Synthesis of compound 1a: Nitrogen was bubbled through a mixing solution of toluene (80 mL), EtOH (20 mL), and water (20 mL) for 30 min. 1,4-Bis(2-bromo-4-*tert*-butylphenyl)buta-1,3-diyne (2.34 g, 4.96 mmol), [Pd(PPh_3)$_4$] (575 mg, 0.5 mmol), K_2CO_3 (4.1 g, 29.76 mmol), and 2-(5-tert-butylnaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.01 g, 9.95 mmol) were added to this solution. The mixture was heated at 80 °C for 24 h. The solution was extracted three times with ethyl acetate. After removal of the solvent in vacuo, the crude material was purified by column chromatography (dichloromethane/hexane = 1:10) to afford compound **1a** (2.1 g, 63 %) as a yellow solid.

Synthesis of compound 2a: A reaction tube containing $PtCl_2$ (20 mg, 0.07 mmol) was dried in vacuo for 1 h, and vacuum was filled with nitrogen with a nitrogen balloon. To this round bottom flask was added compound **1a** (500 mg, 0.74 mmol) and toluene (74 mL), and the mixture was stirred at 25 °C for 5 min before it was heated at 90 °C for 24 h. After removal of the solvent in vacuo, the crude material was purified by column chromatography (dichloromethane/hexane = 1:5) to afford compound **2a** (440 mg, 88 %) as a yellow solid.

Synthesis of compound 3a: Methanesulfonic acid (1 mL) was added, by using a syringe, to a mixture of bichrysene **2a** (65 mg, 0.096 mmol) and DDQ (46 mg, 0.2 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C under argon atmosphere. After 30 min, the mixture was quenched with saturated $NaHCO_3$ solution (10 mL), and then extracted with CH_2Cl_2 twice. The combined extracts were washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, the crude material was purified by column chromatography (dichloromethane/hexane = 1:5) to afford compound **3a** (61 mg, 95 %) as an orange solid.

Acknowledgements

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Keywords: aromaticity · hydrocarbons · oxidation · synthetic methods · UV/Vis spectroscopy

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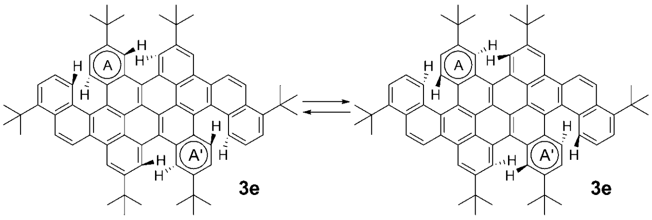
[12] For compound **3e**, we envisage that the two cove regions have the same stereochemistry as that of **3a**; hence, the chirality of fjord region is dependent on the cove stereochemistry because the A-ring should have the three hydrogen atoms coplanar with the benzene ring. Therefore an alteration of the cove chirality is always accompanied by the change of fjord chirality.



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