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Functionalized Dibenzo[*g*,*p*]chrysenes: Variable Photophysical and Electronic Properties and Liquid−Crystal Chemistry

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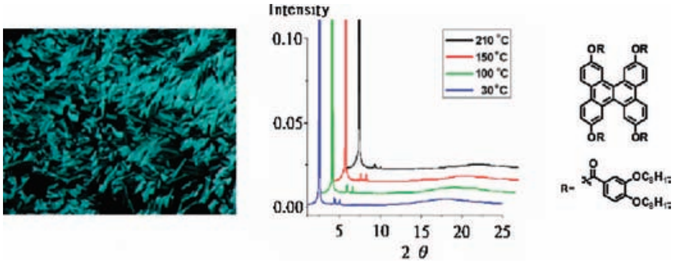
ABSTRACT



The photophysical and electronic properties of dibenzo[*g*,*p*]chrysenes bearing electron-rich and -deficient substituents vary markedly with these substituents. The chemistry of the first liquid−crystalline dibenzo[*g*,*p*]chrysene is also described.

Discotic molecules of benzenoid polycyclic aromatic hydrocarbons (BPAHs) such as triphenylenes, dibenzopyrenes, and hexabenzocorenenes represent organic materials of one important class.[1] These molecules tend to form columnar (liquid)−crystalline because of outstanding hole-transport mobility.[2] Although substantial progress has been achieved in preparing discotic molecules of new BPAHs, little work[3] has targeted their functionalization to alter their photophysical and electronic properties. Synthesis of these discotic molecules relies largely on Scholl oxidation,[4–6] which generally works for reacting benzenes tethered with alkoxy and alkyl substituents rather than electron-deficient substituents.[3]

Dibenzo[*g*,*p*]chrysenes as discotic molecules of BPAHs attract interest because of their notable fluorescent properties such as good quantum yields, small Stoke shifts, and long-

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(1) (a) Iyer, V. S.; Wehmeire, M.; Brand, J. D.; Keegstra, M. A.; Müllen, K. *Angew. Chem., Int. Ed.* **1997**, *36*, 1604. (b) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267. (c) Grimsdale, A. C.; Müllen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5592. (d) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718.

(2) (a) van de Craats, A. M.; Warman, J. M.; Fechtenkötter, A.; Brand, J. D.; Harbison, M. A.; Müllen, K. *Adv. Mater.* **1999**, *11*, 1469. (b) van de Craats, A. M.; Stutzmann, N.; Bunk, O.; Nielsen, M. M.; Watson, M.; Müllen, K.; Chanzy, H. D.; Sirringhaus, H.; Friend, R. H. *Adv. Mater.* **2003**, *15*, 495.

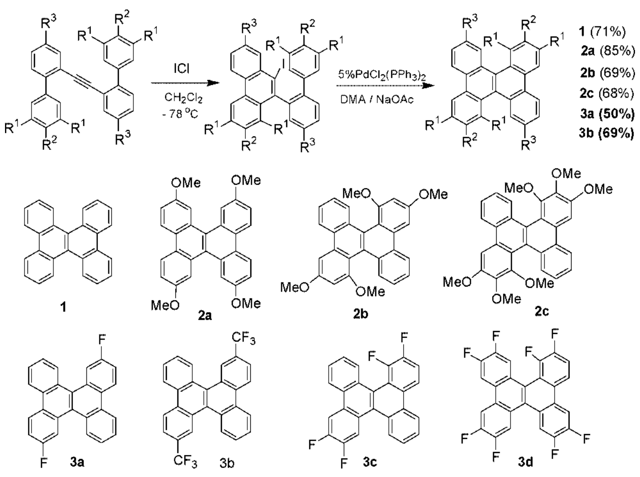
(3) To the best of our knowledge, electron-deficient BPAHs are only known for hexafluorohexabenzocoronenen but remain unknown for small discotic BPAHs including triphenylenes and dibenzopyrenes. For hexafluorohexabenzocoronenen, see: Kikuzawa, Y.; Mori, T.; Takeuchi, H. *Org. Lett.* **2007**, *9*, 4817.

(4) For synthesis of triphenylenes via Scholl oxidation, see the following reviews: (a) Kumar, S. *Liq. Cryst.* **2005**, *32*, 1089. (b) Kumar, S.; Manickam, M. *Chem. Commun.* **1997**, *17*, 1615.

10.1021/ol801029x CCC: $40.75

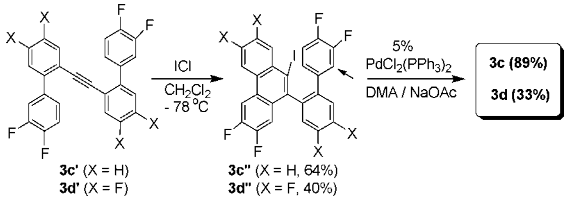
lived excited states.[7] The synthesis of dibenzo[*g*,*p*]chrysenes was generally hampered by long procedures before Swager's SbCl$_5$/MeOH oxidation of bis(biaryl)acetylenes,[7] but the method is limited strictly to electron-rich benzenes. We reported[8a] preliminary success in the synthesis of dibenzo[*g*,*p*]chrysenes **1** and **2a**−**c** containing unsubstituted and electron-rich substituents via sequential ICl-induced cyclization and Mizoroki−Heck coupling,[9] as depicted in Scheme 1. We sought to vary the photophysical and electronic properties of dibenzo[*g*,*p*]chrysenes bearing both electron-rich and -deficient substituents. We here report a notable liquid−crystalline (LC) behavior of one representative dibenzo[*g*,*p*]chrysene **4**.

Scheme 1



We applied this synthesis to dibenzo[*g*,*p*]chrysenes **3a** and **3b** bearing bis(fluoro) and bis(trifluoromethyl) groups respectively, which were obtained in 50% and 69% overall yields in such a reaction sequence. As shown in Scheme 2, this two-step synthesis works also for dibenzo[*g*,*p*]chrysenes **3c** and **3d** bearing four and eight fluoro groups, respectively; these two products resulted from activation of the ortho C(2)−H bond of the 3,5-difluorophenyl group. Minor side products formed with **3c** and **3d** were removed through their crystallization in hot THF.[10]

Scheme 2



With dibenzo[*g*,*p*]chrysenes **1**, **2a**−**c**, and **3a**−**d** bearing electron-rich and -deficient substituents in hand, we examined their UV absorption spectra to study their electronic properties. As shown in Figure 1, the UV absorptions of fluoro- and trifluoromethyl derivatives **3a**−**d** have onsets at 392−402 nm, near 396 nm for parent species **1**; these compounds have similar energy gaps. For methoxy derivatives **2a**−**c**, we observed a significant shift in the UV absorption, ca. 25−30 nm red-shifted from that of compound **1**. Figure 2 shows emission spectra of **1**, **2a**−**c**, and **3a**−**d**, which exhibit small Stoke shifts relative to their UV absorption spectra ($\Delta\nu$ < 20 nm). Compound **1** emits two maxima at 396 and 410 nm, whereas its fluoro derivatives **3a**−**d** have the emissions

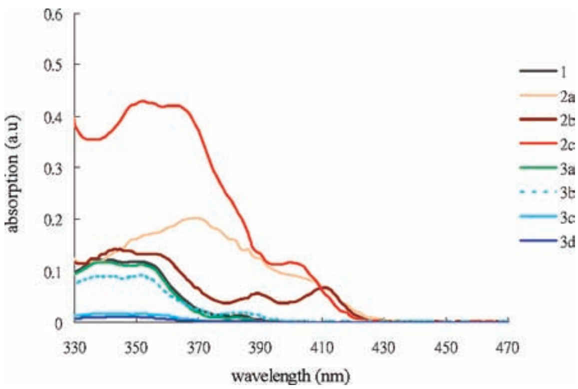


Figure 1. UV absorption spectra of dibenzo[*g*,*p*]chrysenes in CH$_2$Cl$_2$.

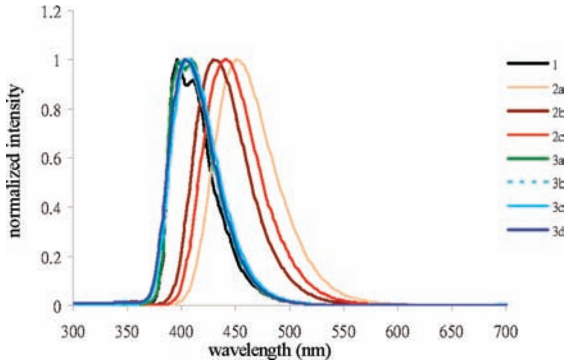


Figure 2. Fluorescent emission spectra of dibenzo[*g*,*p*]chrysenes in CH$_2$Cl$_2$.

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(5) For synthesis of BPAHs via Scholl oxidation, see the following selected examples: (a) Tomovič, Ž.; Watson, M. D.; Müllen, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 755. (b) Iyer, V. S.; Yoshimura, K.; Enkelmann, V.; Epsch, R.; Rabe, J. P.; Müllen, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 2696. (c) Artal, M. C.; Toyne, K. J.; Goodby, J. W.; Barberá, J.; Photinos, D. J. *J. Mater. Chem.* **2001**, *11*, 2801. (d) Liu, W.-J.; Zhou, Y.; Ma, Y.; Cao, Y.; Wang, J.; Pei, J. *Org. Lett.* **2007**, *9*, 4187. (e) Kumar, S.; Varshney, S. *Mol. Cryst. Liq. Cryst.* **2002**, *378*, 59.

(6) For a leading reference for Scholl oxidation, see: King, B. T.; Kroulik, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279.

(7) Yamaguchi, S.; Swager, T. *J. Am. Chem. Soc.* **2001**, *123*, 12087.

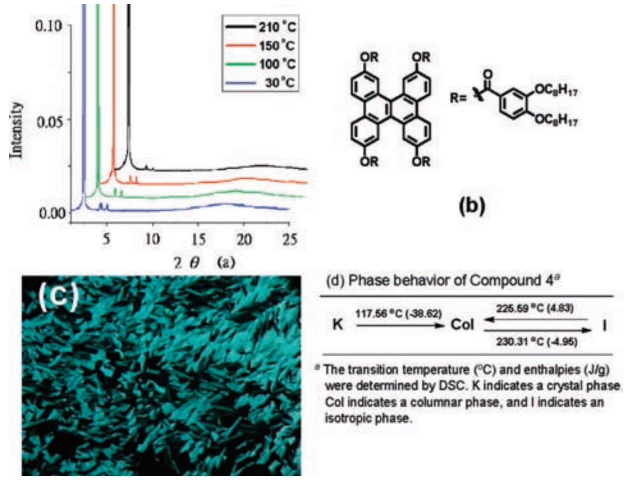
(8) (a) Li, C.-W.; Wang, C.-I.; Liao, H.-Y.; Chaudhuri, R.; Liu, R.-S. *J. Org. Chem.* **2007**, *72*, 9203. (b) Shen, H.-C.; Tang, J.-M.; Chang, H.-K.; Yang, C. W.; Liu, R.-S. *J. Org. Chem.* **2005**, *70*, 10113.

maximum at the same region (407−412 nm); methoxy derivatives **2a**, **2b**, and **2c** exhibited fluorescence spectra at longer wavelengths in blue regions, respectively, with maxima at 426, 452, and 442 nm, respectively. For their fluorescence spectra, as shown in Table 1, compound **1** and its fluoro derivatives **3a−d** have the quantum yields ca. 0.12−0.19, but methoxy derivatives are more fluorescent with $\Phi = 0.26-0.49$,[11] which is presumably enhanced by the steric effects of methoxy groups to reduce intermolecular energy transfer.[11] We estimated the HOMO energy levels from their oxidation potentials ($E_{1/2}^{\mathrm{ox}}$)[12] and obtained the LUMO energy levels from the onset of their UV absorptions; the results appear in Table 1. Although fluoro derivatives **3a−d** have the same energy gaps (3.10−3.18 eV) as their parent species 1 (3.16 eV), both the HOMO and LUMO energy levels of **3a−d** were lowered equally (ca. 0.13−0.6 eV) by fluoro and trifluoromethyl substituents. This phenomenon was observed also for hexafluoro-substituted hexabenzocoronenes.[3] In contrast, we observed a decrease in the energy gaps (2.84−2.91 eV) for compounds **2a−c** because their methoxy groups raise their HOMO orbitals more than their LUMO orbitals.

Table 1. Photophysical Properties of Functionalized Dibenzo[*g*,*p*]chrysenes

compd	Φ (%)	$E_{1/2}^{\mathrm{ox}}$ (V)	HOMO (V)	band gap (V)	LUMO (V)
1	19.3	0.85	5.65	3.16	2.49
2a	35.2	0.55	5.35	2.88	2.47
2b	48.7	0.49	5.29	2.84	2.45
2c	26.0	0.61	5.41	2.91	2.50
3a	12.4	1.12	5.92	3.18	2.74
3b	16.8	1.39	6.19	3.10	3.09
3c	12.4	1.00	5.80	3.18	2.62
3d	13.2	1.18	5.98	3.18	2.80

A columnar liquid crystal structure is an important characteristic for discotic molecules, and such a mesophase is virtually unknown[13] for pure dibenzo[*g*,*p*]chrysens that have a twisted nonplanarity.[14] We prepared dibenzo[*g*-,*p]*chrysene **4** tethered with four benzoate chains using tetra(methoxy)-substituted species **2a** as an initial reagent (see the Supporting Information). The phase behavior of compound **4**, characterized by thermal analysis, polarized optical microscopy, and powder X-ray diffraction, is summarized in Figure 3. The DSC analysis showed typical columnar phase transitions, crystal-to-columnar-to-isotropic (Cr → Col →I). Compound **4** melted into columnar phase at 117.8 °C and cleared at 230.3 °C into an isotropic state. This species is thermally stable above that clearing temperature, but it decomposes above 376 °C. The temperature range of its columnar phase is wide, ca. $\Delta T = 112.5$ °C on heating curve. Furthermore, a large enthalpy ($\Delta H = 9.55$ KJ/mol on heating cycle) was observed for the $\mathrm{Col_h} \rightarrow \mathrm{I}$ transition, indicating a large molecular order in the columnar phase. Under an optical microscopy, upon heating, species **4** melted to a fluid phase with columnar superstructures, and typical pseudo-focal-conic textures with linear birefrigent defects were observed. The dark area implies a homeotropic domain, in which the molecules are all perpendicularly aligned within the two glass slides. The diffraction pattern performed at 150.0 °C showing a strong peak with $d \approx 30.10$ Å and two weaker peaks with $d \approx 17.42$ Å and 15.09 Å was observed. These patterns are characteristic of two-dimensional hexagonal columnar arrangement (Colh) with a *d*-spacing ratio of $1{:}(1/3)^{1/2}{:}(1/4)^{1/2}$, which were assigned to Miller indices 100, 110 and 200.[15] These data imply a lattice constant of $a = 34.76$ Å. A liquid-like correlation, a so-called halo peak, between the rigid core was observed at a wide-angle region for 4.30−4.44 Å. These diffraction data indicate that the hexagonal columnar structural arrangement persisted at 30 °C.[16]



(d) Phase behavior of Compound 4[a]

$$\mathrm{K} \xrightarrow{117.56\,^{\circ}\mathrm{C}\ (-38.62)} \mathrm{Col} \underset{230.31\,^{\circ}\mathrm{C}\ (-4.95)}{\overset{225.59\,^{\circ}\mathrm{C}\ (4.83)}{\rightleftarrows}} \mathrm{I}$$

[a] The transition temperature (°C) and enthalpies (J/g) were determined by DSC. K indicates a crystal phase Col indicates a columnar phase, and I indicates an isotropic phase.

Figure 3. (a) Temperature-dependent XRD diffraction scan from 210 to 30 °C. (b) Structure of compound **4**. (c) Optical texture observed at 210 °C. (d) DSC thermographs.

We measured charge-transport properties of compound **4** using the time-of-flight (TOF) transient photocurrent technique with the device configuration: glass/ITO (120 nm)/

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(9) For the synthesis of new BPAHs via Mizoroki−Heck coupling, see: Wegner, H. A.; Reisch, H.; Rauch, K.; Demeter, A.; Zachariasse, K. A.; de Meijere, A.; Scott, L. T. *J. Org. Chem.* **2006**, *71*, 9080.

(10) Compounds **1**, **2a−c**, and **3a**,**b** have good solubility in THF, CH_2Cl_2, benzene, and toluene, whereas species **3c** and **3d** are less soluble in these solvents.

(11) Swager and co-workers reported[7] $\Phi = 0.24-0.35$ for some alkoxy-substituted dibenzo[*g*,*p*]chrysenes, near values of compounds **2a−c**.

(12) The cyclic voltammograms of compounds **1**, **2a−c**, and **3a−d** are provided in the Supporting Information.

(13) Octaalkoxy-substituted dibenzo[*g*,*p*]chrysenes showed a columnar phase in the presence of charge transfer (C-T) complex trinitrofluorenone in a 2:1 molar ratio. In the absence of that C-T additive, these alkoxy-substituted species only showed melting points at 139−165 °C, respectively. Compound **4** is the first reported dibenzo[*g*,*p*]chrysene having a columnar liquid−crystalline structure. See ref 5e.

(14) The twisted structure of dibenzo[*g*,*p*]chrysene **1** has been reported: Herbstein, F. H. *Acta Crystallogr.* **1979**, *B35*, 1661.

(15) Wang, J. Y.; Song, J. H.; Lin, Y. S.; Lin, C.; Sheu, H. S.; Lee, G. H.; Lai, C. K. *Chem. Commun.* **2006**, 4912.

(16) For fluorescent polycyclic aromatic compounds, see: Boydston, A. J.; Pecinovsky, C. S.; Chao, S. T.; Bielawski, C. W. *J. Am. Chem. Soc.* **2007**, *129*, 14550.

compound **4** (5 μm)/ITO(120 nm)/glass. After capillary injection at its melted state (250 °C), compound **4** was then annealed around 230 °C (40 min) to induce liquid−crystalline molecular arrangements. By rapidly cooling the aligned sample to 30 °C (ca. 60 °C/min), the molecular alignment mediated by the fluidic mesomorphism was preserved to form a rather uniform solid film as monitored by polarized light microscope.[17,18] Conoscopy characterization of the molecular alignment orientation on the ITO surface reveals the homeotropic arrangement of molecules (i.e., the face-on configuration).[17] Compound **4** exhibits bipolar carrier transport; the field-dependence of mobilities in Figure 4 follows the universal Poole−Frenkel relationship: $\mu = \exp(\beta E^{1/2})$, where β is the Poole−Frenkel factor.[19,20] Such a relationship is often observed in noncrystalline organic systems and could be attributed to effects of energetic and positional disorder on the hopping conduction.[16,17] Compound **4** shows a hole mobility up to 9.3 × 10^{-6} cm^2/V•s for fields from 2.4 × 10^5 to 4.0 × 10^5 V/cm and electron mobility up to 3.9 × 10^{-6} cm^2/V•s for fields from 3.2 × 10^5 to 4.4 × 10^5 V/cm.

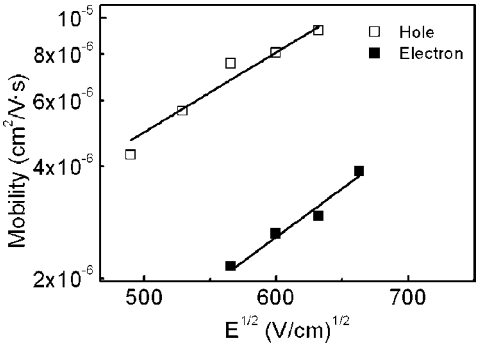

Figure 4. Mobilities vs $E^{1/2}$ for compound **4** at 25 °C.

In summary, we report variations of the photophysical and electronic properties of dibenzo[*g,p*]chrysenes by their electron-rich and -deficient substituents, in particular their HOMO−LUMO energy levels, UV absorptions, and fluorescent emissions. We report also the first liquid−crystalline dibenzo[*g,p*]chrysene **4**,[21] which exhibited an hexagonal columnar structure supercooled at 30 °C; this structural arrangement allows reasonable hole and electron mobility in a thin film prepared on capillary injection.[22,23]

Acknowledgment. We thank the National Science Council, Taiwan, for support of this work.

Supporting Information Available: Experimental procedures including synthesis, cyclic voltammograms, spectral data of key compounds, measurement of charge mobilities, DSC curve, MALDI-TOF mass spectrum, and TOF transients of compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Born, M.; Wolf, E. *Principles of Optics*, 4th ed.; Pergamon, Oxford, 1969.

(18) The details in the measurement of charge mobilities, structural characterization of thin film on ITO, and TOF transients of compound **4** are provided in the Supporting Information.

(19) Wu, C.-C.; Liu, T.-L.; Lin, T.-T.; Hung, W.-Y.; Ke, T.-H.; Wong, K.-T.; Chao, T.-C. *Appl. Phys. Lett.* **2004**, *85*, 1172.

(20) Bässler, H. *Philos. Mag.* **1992**, *B 65*, 795.

(21) Triphenylenes represent small discotic BPAHs, which have been studied much more extensively than other molecules. The liquid−crystal temperature ranges of triphenylenes are highly dependent on their substituents; only few exceptions showed a wide range (>100 °C)[22] with a columnar strcuture that can be supercooled at room temperatures.[23a] Reported triphenylenes only conducted hole transport with outstanding mobility.[23]

(22) Kumar, S. *Liq. Cryst.* **2004**, *31*, 1037.

(23) (a) Adam, D.; Schuhmacher, P.; Simmerer, J.; Haussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141. (b) Boden, N.; Bushby, R. J.; Clements, J.; Movaghar, B. *J. Mater. Chem.* **1999**, *9*, 2081. (c) Arikainen, E. O.; Boden, N.; Bushby, R. J.; Clements, J.; Movaghar, B.; Wood, A. *J. Mater. Chem.* **1995**, *5*, 2161.