

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

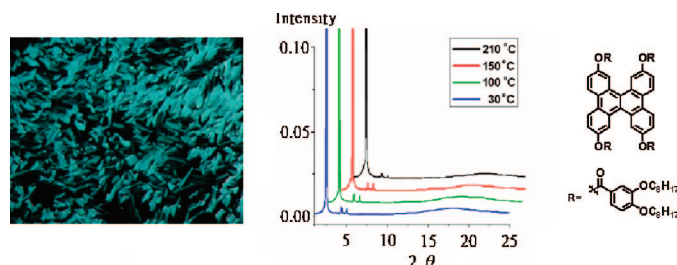
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ABSTRACT



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 hexabenzocoronenes 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 work³ has targeted their functionalization to alter their photophysical and electronic properties. Synthesis of these discotic mol-

ecules 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.

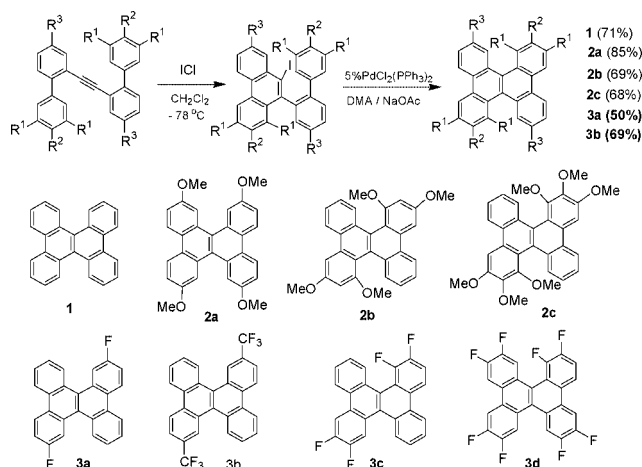
(2) (a) van de Craats, A. M.; Warman, J. M.; Fechtenkötter, A.; Brand, J. D.; Harbison, M. A.; Müllen, K. *Adv. Mater.* **1999**, *11*, 1469. (b) van de Craats, A. M.; Stutzmann, N.; Bunk, O.; Nielsen, M. M.; Watson, M.; Müllen, K.; Chanzy, H. D.; Sirringhaus, H.; Friend, R. H. *Adv. Mater.* **2003**,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

(3) To the best of our knowledge, electron-deficient BPAHs are only known for hexafluorohexabenzocoronenes but remain unknown for small discotic BPAHs including triphenylenes and dibenzopyrenes. For hexafluorohexabenzocoronenes, 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.

lived excited states.⁷ The synthesis of dibenzo[*g,p*]chrysenes was generally hampered by long procedures before Swager's $\text{SbCl}_5/\text{MeOH}$ 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

Scheme 1



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**.

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

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 proper-

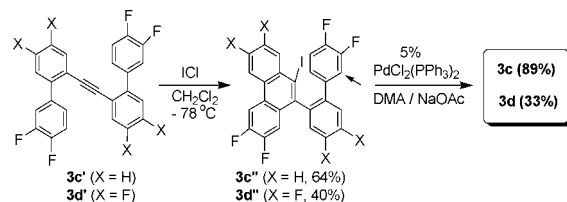
(5) For synthesis of BPAHs via Scholl oxidation, see the following selected examples: (a) Tomović, Ž.; Watson, M. D.; Müllen, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 755. (b) Iyer, V. S.; Yoshimura, K.; Enkelmann, V.; Epsch, R.; Rabe, J. P.; Müllen, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 2696. (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.

Scheme 2



ties. As shown in Figure 1, the UV absorptions of fluoro- and trifluoromethyl derivatives **3a–d** have onsets at 392–402

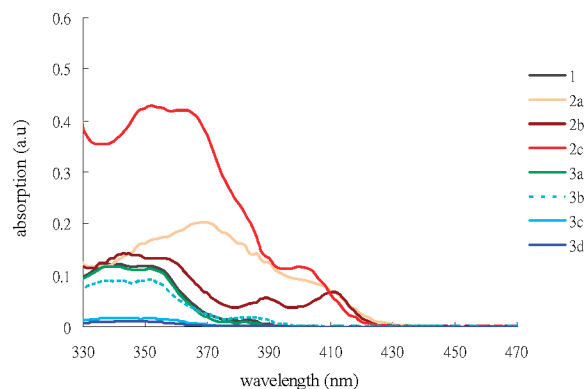


Figure 1. UV absorption spectra of dibenzo[*g,p*]chrysenes in CH_2Cl_2 .

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

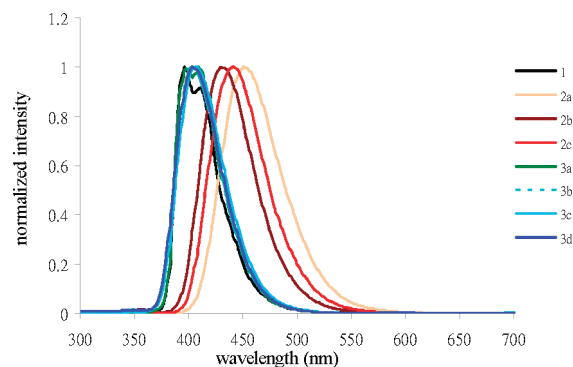


Figure 2. Fluorescent emission spectra of dibenzo[*g,p*]chrysenes in CH_2Cl_2 .

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

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 ($E_{1/2}^{\text{ox}}$)¹² and obtained the LUMO energy levels from the onset of their UV absorptions;

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

compd	Φ (%)	$E_{1/2}^{\text{ox}}$ (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

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.

A columnar liquid crystal structure is an important characteristic for discotic molecules, and such a mesophase is virtually unknown¹³ for pure dibenzo[*g,p*]chrysenes 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

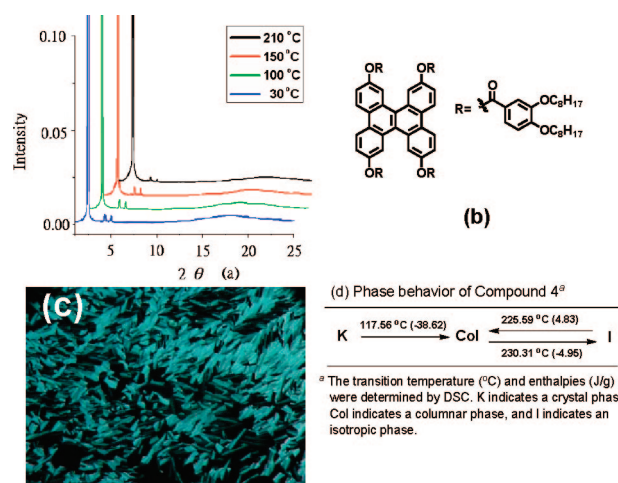


Figure 3. (a) Temperature-dependent XRD diffraction scan from 210 to 30 °C. (b) Structure of compound **4**. (c) Optical texture observed at 210 °C. (d) DSC thermographs.

columnar phase transitions, crystal-to-columnar-to-isotropic (Cr $\rightarrow$ Col $\rightarrow$ 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 Col_h $\rightarrow$ 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 birefringent 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 (Col_h) 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

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)/

(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, CH₂Cl₂, benzene, and toluene, whereas species **3c** and **3d** are less soluble in these solvents.

(11) Swager and co-workers reported⁷ $\Phi = 0.24$ –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: Herstein, 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 $^{\circ}\text{C}$), compound **4** was then annealed around 230 $^{\circ}\text{C}$ (40 min) to induce liquid–crystalline molecular arrangements. By rapidly cooling the aligned sample to 30 $^{\circ}\text{C}$ (ca. 60 $^{\circ}\text{C}/\text{min}$), 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

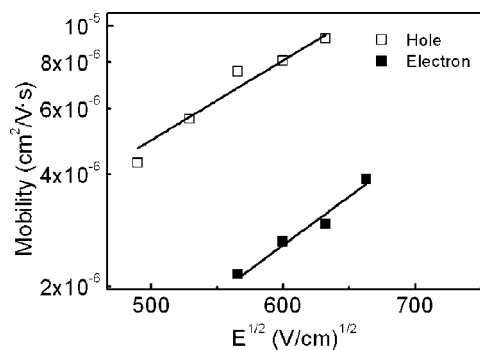


Figure 4. Mobilities vs $E^{1/2}$ for compound **4** at 25 $^{\circ}\text{C}$.

universal Poole–Frenkel relationship: $\mu = \exp(\beta E^{1/2})$, where β is the Poole–Frenkel factor.^{19,20} Such a relationship is

(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.

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 $9.3 \times 10^{-6} \text{ cm}^2/\text{V}\cdot\text{s}$ for fields from 2.4×10^5 to $4.0 \times 10^5 \text{ V}/\text{cm}$ and electron mobility up to $3.9 \times 10^{-6} \text{ cm}^2/\text{V}\cdot\text{s}$ for fields from 3.2×10^5 to $4.4 \times 10^5 \text{ V}/\text{cm}$.

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 $^{\circ}\text{C}$; 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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(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 ($>100 \text{ }^{\circ}\text{C}$)²² with a columnar structure 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.; Eitzbach, 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.