124 *Chem. Mater.* **2003,** *15,* 124−130

Room Temperature Discotic Liquid Crystalline Thin Films of Hexa-*peri*-hexabenzocoronene: Synthesis and Optoelectronic Properties

Chong-yang Liu,[†] Andreas Fechtenkötter,[‡] Mark D. Watson,[‡] K. Müllen,[‡] and Allen J. Bard*[,†]

Department of Chemistry and Biochemistry, The University of Texas at Austin,
Austin, Texas 78712, and Max-Planck-Institut für Polymerforschung,
Ackermannweg 10, D-55128 Mainz, Germany

Received July 1, 2002. Revised Manuscript Received October 14, 2002

The compound hexa-(3,7,11,15-tetramethylhexadecanyl)hexa-*peri*-hexabenzocoronene (HBC-$C_{4/16}$), soluble in most organic solvents such as chloroform and THF, was synthesized. This compound shows a stable discotic hexagonal columnar mesophase between −36 and 231 °C. Symmetrical sandwich cells of ITO/HBC-$C_{4/16}$/ITO (~1 μm thick) were prepared by capillary filling by the molten state for the studies of their optical and optoelectronic properties. Two distinct textures, one very bright and the other gray, were clearly seen in thin films of HBC-$C_{4/16}$ between two crossed polarizers in an optical microscope at room temperature. Short-circuit photocurrents (I_{sc}) were obtained with such cells, and the gray areas generated a much higher short circuit photocurrent compared to that of the bright spots. This photocurrent difference was attributed to different orientations of the HBC-$C_{4/16}$ molecular columns relative to the ITO electrode surface. The charge trapping and detrapping effects found earlier with other materials, such as zinc porphyrins (ZnODEP), and of potential use in optoelectronic data storage were also observed with these cells.

Introduction

Discotic liquid crystalline molecules, often synthesized by adding long hydrocarbon tails to a flat core,[1,2,3] are capable of stacking spontaneously into individual molecular columns behaving electronically as one-dimensional molecular "wires".[4,5] These interesting structures show a number of promising applications such as in optoelectronic memory devices[6−9] and solar cells.[10] Here, we report a newly synthesized derivative of hexa-*peri*-hexabenzocoronene which shows an ordered hexagonal columnar (Col_{ho}) liquid crystalline phase over a wide temperature range between −36 and 231 °C with interesting optoelectronic properties.

Recently, we investigated a number of organic thin films sandwiched between two pieces of indium tin oxide (ITO)-coated glass.[11−14] These films were made by capillary action filling of thin layer cells by the molten state (isotropic liquid phase) of the materials. However, this approach did not work initially with a number of derivatives of hexa-*peri*-hexabenzocoronene (HBC). The major problem was that the melting points of the materials were often above 420 °C, which was much higher than the decomposition temperature of the epoxy spacers used in the ITO sandwich cells. Consequently, the mechanical structure of the empty ITO cells collapsed well before the capillary filling took place. In some cases, the isotropic melting point was not observed before the decomposition of the molecule for several of the alkyl or phenyl−alkyl substituted HBC compounds.[15,16,17] A number of research groups have recently demonstrated that when branching points are introduced into the aliphatic side chains of discotic liquid crystals, the temperature range of the mesophase was widened[18,19] and the temperature for forming the

---

[†] The University of Texas at Austin.
[‡] Max-Planck-Institut für Polymerforschung.
(1) Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A. *Pramana* **1977**, *9*, 471.
(2) Herwig, P.; Kayser, C. W.; Müllen, K.; Spiess, H. W. *Adv. Mater.* **1996**, *8*, 510.
(3) Fox, M. A.; Vincent, J. R.; Melamed, D.; Torimoto, T.; Liu, C.-Y.; Bard, A. *J. Chem. Mater.* **1998**, *10*, 1771−1776.
(4) Craats, A. M.; Warman, J. M.; Müllen, K.; Geerts, Y.; Brand, J. *Adv. Mater.* **1998**, *10*, 36.
(5) (a) Liu, C.-Y.; Pan, H.-L.; Tang, H.; Fox, M. A.; Bard, A. J. *J. Phys. Chem.* **1995**, *99*, 7632. (b) Adam, D.; Haarer, D.; Closs, F.; Frey, T.; Funhoff, D.; Siemensmeyer, K.; Schuhmacher, P.; Ringsdorf, H. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 1366−70.
(6) Liu, C.-Y.; Pan, H.-L.; Fox, M. A.; Bard, A. J. *Science* **1993**, *261*, 897.
(7) Liu, C.-Y.; Pan, H.-L.; Fox, M. A.; Bard, A. J. *Chem. Mater.* **1997**, *9*, 1422.
(8) Liu, C.-Y.; Bard, A. J. *Electrochem. and Solid-State Lett.* **2001**, *4*, 1−3.
(9) Liu, C.-Y.; Pan, H.-L.; Bard, A. J.; Fox, M. A. U.S. Patent 5327373.
(10) (a) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Phys. Chem.* **1989**, *93*, 4227. (b) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119.
(11) Liu, C.-Y.; Bard, A. J. *Acc. Chem. Res.* **1999**, *32*, 235−245.
(12) Liu, C.-Y.; Bard, A. J. In *Conjugated Oligomers, Polymers, and Dendrimers: From Polyacetylene to DNA*; Brédas, J.-L., Ed.; De Boeck Université: Paris, 1999; pp 85−116.
(13) Liu, C.-Y.; Bard, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 5575.
(14) Liu, C.-Y.; Lynch, V.; Bard, A. J. *Chem. Mater.* **1997**, *9*, 943.
(15) Brown, S. P.; Schnell, I.; Brand, J. D.; Müllen, K.; Spiess, H. W. *J. Am. Chem. Soc.* **1999**, *121*, 6712.
(16) Fechtenkötter, A.; Saalwächter, K.; Harbison, M. A.; Müllen, K.; Spiess, H. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 3039.
(17) Fechtenkötter, A.; Tchebotareva, N.; Watson, M. D.; Müllen, K. *Tetrahedron* **2001**, *57*, 3769.
(18) Collard, D. M.; Lillya, C. P. *J. Am. Chem. Soc.* **1989**, *111*, 1829.

10.1021/cm020701q CCC: $25.00

isotropic liquid decreased. Schouten and co-workers reported that for discotic phthalocyanines, the temperatures for the transitions from the discotic mesophase to the isotropic liquid were reduced by 175 °C on changing the alkyl substitution from a pentoxy to a branched dodecaoxy chain.[20] This led us to the synthesis of a derivative of hexa-*peri*-hexabenzocoronene with alkyl chains containing sixteen carbon atoms and four branching methyl groups (HBC-$C_{4/16}$), effectively lowering its isotropic melting point to about 231 °C.

Experimental Section

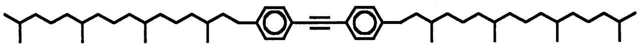
Characterization. The ITO/HBC-$C_{4/16}$/ITO (~1 μm thick) sandwich cells were prepared in the same way as reported earlier.[11-14] Briefly, two pieces of ITO-coated glass (Delta Technologies) were spaced about 1 μm apart and glued together with epoxy cement. The HBC-$C_{4/16}$ was placed at the opening between the ITO pieces and heated to a temperature of 250 °C, where it formed the isotropic liquid phase and filled the cell by capillary action. The thin films were examined with an optical microscope (Olympus model BHTU) with unpolarized or polarized light. The current was measured with a CH Instruments (Austin, Texas) model 660 electrochemical workstation. A halogen lamp (300 W) operated at 80 V was used as a light source. Other photocurrent measurements were made with the optical microscope as described earlier:[21] samples were fixed on the stage and the light beam was focused to a spot of 140 μm on a pre-selected domain on the film. The internal light source of the microscope was strong enough to generate a detectable photocurrent.

^{1}H NMR and ^{13}C NMR spectra were recorded in $C_2D_2Cl_4$ on a Bruker DRX 500 with use of the solvent proton or carbon signal as internal standard. Mass spectra were obtained on a VG Instruments ZAB 2-SE-FPD by using field desorption. Elemental analysis was carried out on a Foss Heraeus Vario EL.

Differential scanning calorimetry (DSC) was carried out with a Mettler DSC 30 with heating and cooling rates of 10 K/min. A Zeiss Axiophot with a nitrogen-flushed Linkam THM 600 hot stage was used to characterize the polarization microscopy textures.

Materials. 3,7,11,15-Tetramethyl-2-hexadecene-1-ol (**1**) was used as received from Aldrich. [$PdCl_2$(dppf)] was used as received from Strem. THF (ACS reagent, Riedel-de Haen) was refluxed over potassium and distilled freshly before use. All other materials were used as received.

Synthesis. *4,4′-Bis(3,7,11,15-tetramethylhexadecenyl)diphenylacetylene (**5**).*



5

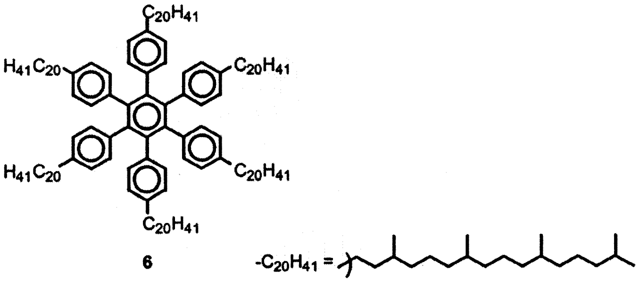
In a 250-mL two-necked round-bottom flask, 60 mL of a 1 M solution of 3,7,11,15-tetramethylhexadecenyl-1-magnesium bromide (prepared immediately prior to use from 1-bromo-3,7,11,15-tetramethylhexadecane and magnesium) was added dropwise to a solution of 5 g (14.9 mmol) of 4,4′-dibromodiphenylacetylene (**4**) dissolved in 150 mL of dry THF and 1 g of [$PdCl_2$(dppf)] catalyst. The resulting mixture was stirred under reflux in an inert atmosphere overnight. The reaction was quenched with methanol, and the solvent was removed under reduced pressure. Purification using column chromatography on silica gel with petrol ether as the eluent afforded 5.5 g of **5** as a colorless oil. Yield: 50%.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 80 °C): $\delta = 7.4$ (d, ^{3}J (H,H) = 8.5 Hz, 4H, CH_2), 7.14 (d, ^{3}J (H,H) = 8.5 Hz, 4H, CH_2), 2.61 (m, 4H, α-CH_2), 1.63 (m, 2H, CH), 1.52 (m, 2H, CH), 1.45 (m, 4H, 2 × CH), 1.26 (m, 24H, 6 × CH_2), 1.15 (m, 8H, 2 × CH_2), 1.09 (m, 8H, 2 × CH_2), 0.92 (m, 6H, CH_3) 0.78 (m, 24H, 4 × CH_3).

^{13}C NMR (125 MHz, $C_2D_2Cl_4$): $\delta = 144.0$, 131.9, 128.8, 120.8, 89.4, 39.7, 39.0, 38.9, 37.8, 37.7, 37.6, 33.8, 33.1, 33.0, 32.8, 28.3, 25.1, 24.82, 24.80, 24.7, 23.1, 23.0, 20.14, 20.11, 20.08, 20.00, 19.9.

MS (FD, 8 kV): m/z (%) = 738.9 (100) [M^+] (calcd for $C_{54}H_{90}$ = 739.29).

Hexa(4-(3,7,11,15-tetramethylhexadecenyl)phen-1-yl)benzene (**6**)



6

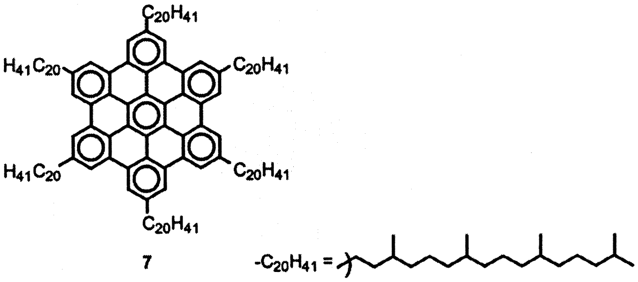
A 100-mL round-bottom flask equipped with a reflux condenser was charged with 1.1 g (1.5 mmol) 4,4′-bis(3,7,11,15-tetramethylhexadecenyl) diphenylacetylene (**5**). Then 115 mg (0.34 mmol) of [$Co_2(CO)_8$] was added under argon to the degassed solution. After refluxing for 5 h, the solvent was evaporated under vacuum, and the residue was purified using column chromatography on silica gel with petrol ether as the eluent, yielding 0.94 g of **6** as a colorless viscous oil. Yield: 85%.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): $\delta = 6.64$ (d, ^{3}J (H,H) = 8.0 Hz, 12H, CH), 6.57 (d, ^{3}J (H,H) = 8.2 Hz, 12H, CH), 2.31 (m, 12H, α-CH_2), 1.52 (m, 6H, CH), 1.37 (m, 18H, 3 × CH), 1.26 (m, 72H,; 6 × CH_2), 1.19 (m, 18H, CH_3), 1.09 (m, 48H, 4 × CH_2), 0.85 (m, 54H, 3 × CH_3), 0.78 (d, ^{3}J (H,H) = 5.8 Hz, 18H, CH_3).

^{13}C NMR (75 MHz, $C_2D_2Cl_4$): $\delta = 140.4$, 139.3, 138.7, 131.8, 126.5, 39.7, 39.0, 38.9, 37.77, 37.73, 37.69, 37.62, 37.53, 33.2, 33.0, 32.4, 28.2, 25.0, 24.7, 24.6, 22.9, 22.8, 20.02, 19.94, 19.89.

MS (FD, 8 kV): m/z (%) = 2218.5 (100) [M^+] (calcd for $C_{162}H_{270}$ = 2217.88).

Hexa-(3,7,11,15-tetramethylhexadecanyl)hexa-peri-hexabenzocoronene (HBC-$C_{4/16}$) or (**7**).



7

A 250-mL two-necked round-bottom flask was charged with 0.5 g (0.23 mmol) of hexakis(4-(3,7,11,15-tetramethylhexadecenyl)phen-1-yl)benzene (**6**) and 80 mL of CH2Cl2. Using a glass capillary, a constant stream of argon was bubbled through the solution. Then 0.7 g (4.3 mmol) of $FeCl_3$ dissolved in 8 mL of CH_3NO_2 was added dropwise using a syringe. After 30 min. the mixture was quenched with methanol and the precipitate was filtered. The resulting yellow solid was

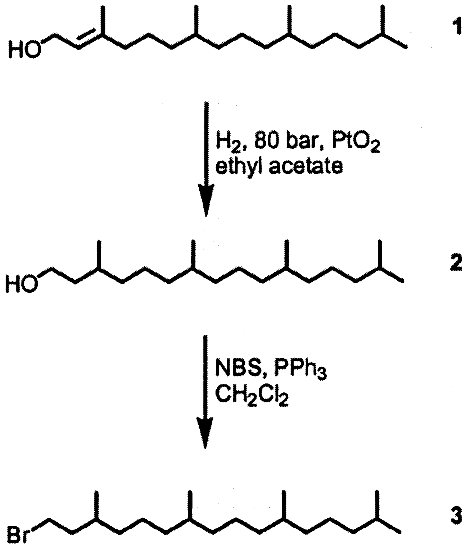
---

(19) Schouten, P. G.; van der Pol, J. F.; Zwikker, J. W.; Drenth, W.; Picken, S. J. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 291.

(20) Schouten, P. G.; Warman, J. H.; de Haas, M. P.; van Nostrum, C. F.; Gelinck, G. G.; Nolte, R. J. M.; Copyn, M. J.; Zwikker, J. W.; Engel, M. K.; Hanack, M.; Chang, Y. H.; Ford, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 6880.

(21) Liu, C.-Y.; Tang, H.; Bard, A. J. *J. Phys. Chem.* **1996**, *100*, 3587.

Scheme 1. Hydrogenation and Bromination of Phytol 1 Resulting in Alkyl Chain 3



reprecipitated from THF with methanol and dried under vacuum. Passage through a short silica gel column with toluene as eluant followed by drying under reduced pressure yielded 0.41 g (81%) of **7**.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): $\delta = 8.92$ (s, 12H. CH), 3.28 (m, 12H. α-CH_2), 2.12 (m, 6H, CH), 1.96 (m, 6H, CH), 1.81 (m, 6H, CH), 1.60 (m, 6H, CH), 1.55−1.47 (m, 24H, CH_2), 1.30−1.26 (m, 60H, CH_2), 1.19 (d, ^{3}J (H,H) = 6.1 Hz, 18H, CH_3), 1.15−1.07 (m, 36H, CH_2), 0.92 (d, ^{3}J (H,H) = 6.1 Hz, 18H, H_3), 0.85 (m, 54H, CH_3).

^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 80 °C): $\delta = 140.7$, 130.1, 123.5, 121.6, 119.7, 40.0, 39.7, 38.00, 37.9, 37.79, 37.77, 37.69, 37.62, 35.0, 33.5, 28.1, 25.0, 24.8, 22.9, 22.8, 20.22, 20.17, 20.13, 20.02, 19.97.

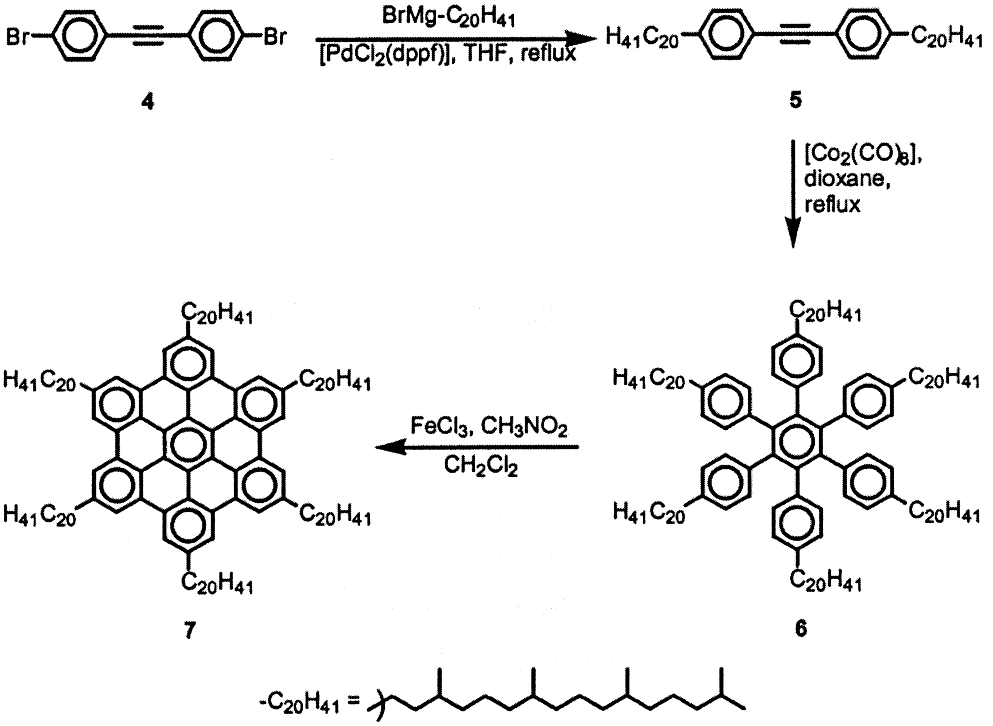
UV/Vis: λ nm (log ϵ) = 229 (5.22), 359 (5.34). mp: 231 °C. MS (FD, 8 kV): m/z (%) = 2206.7 (100) [M^{+}] (calcd for $C_{162}H_{258}$ = 2205.83). EA Calcd. (%) for $C_{162}H_{258}$: C 88.21, H 11.79; found: C 88.56, H 11.91. DSC: K→Col_{ho} T = −36 °C, ΔH = 13.5 kJ/mol

Results and Discussion

Synthesis. These chains are derived from phytol **1** (Scheme 1), which is universally distributed in green plants as a component of the chlorophyll molecule in which it is present in ester combination, and as a component part of phylloquinone (Vitamin K_1) and tocopherols (Vitamin E).[22] Commercially available phytol, 3,7,11,15-tetramethyl-2-hexadecene-1-ol (**1**) was hydrogenated according to a modified procedure of Gramatica[22] to yield compound **2** as demonstrated in Scheme 1.[17] Replacement of the hydroxyl group by a bromine atom was carried out using N-bromosuccinimide and triphenylphosphine in methylene chloride (Scheme 1).[23]

The following steps, leading to the substituted HBC-$C_{4/16}$ (**7**) as depicted in Scheme 2, were carried out according to procedures used previously.[16,17] 3,7,11,15-Tetramethyl-hexadecylmagnesiumbromide was coupled with **4** under Kumada coupling conditions using [PdCl2(dppf)][24] as the catalyst in THF to yield the alkyl substituted diphenylacetylene **5** as a colorless oil in 50% yield. In a subsequent cyclotrimerization reaction under catalytic action of $Co_2(CO)_8$,[25] **5** was transferred to the hexaphenylbenzene derivative **6** with 85% yield. The resulting crude product was easily purified using standard column chromatography. The final step for this reaction sequence was the oxidative planarization of the six pendant phenyl rings in **6**, with concurrent loss of twelve hydrogens. The cyclodehydrogenation[15,16] was carried out by adding a solution of $FeCl_3$ in nitromethane to the hexaphenylbenzene precursor **6** in dichloromethane to afford the alkyl substituted hexabenzocoronene **7**. Isolated yields after purification using column chromatography and slow reprecipitation were on the order of 80%.

Scheme 2. Synthetic Pathway Leading to HBC-$C_{4/16}$ (7)



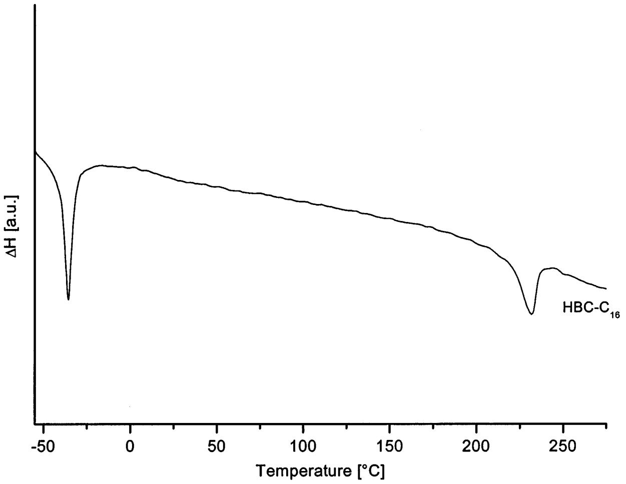


Figure 1. Differential scanning calorimetry traces of HBC-$C_{4/16}$.

Table 1. Phase Transition Temperatures of Peripherally Hexasubstituted Hexabenzocoronenes with Branched and Unbranched Alkyl Chains

	T [°C]	
compound	K→Col	Col→I
HBC-C_{12}[15]	107	417
HBC-C_8*[17]	96	~430
HBC-C_8[17]	81	~420
HBC-$C_{4/16}$	−36	231

The resulting HBC derivative contains six alkyl chains with sixteen carbon atoms and four branching methyl groups and is henceforth referred to as HBC-$C_{4/16}$. The optical appearance is very much like that of a resin. The bulk material has a dark yellow color and is malleable at room temperature.

DSC and Optical Microscopy of HBC-$C_{4/16}$. To detect phase transitions and to determine the corresponding transition temperatures and enthalpies, differential scanning calorimetry (DSC) was performed on HBC-$C_{4/16}$. The heating and cooling rates were 10 K/min.

Figure 1 shows the recorded DSC curve for compound HBC-$C_{4/16}$. The peak onset in the DSC is defined as the transition temperature. During the first heating run, the sample gave rise to two endothermic peaks; subsequent cooling and heating showed both peaks to be reversible. Figure 1 shows only the third heating run, here the peak at −36 °C is related to the crystalline-to-mesophase transition (K→Col). On heating HBC-$C_{4/16}$, the peak at 231 °C corresponds to the mesophase-to-isotropic phase transition (Col→I). The isotropic phase lasts until 300 °C; above this temperature HBC-$C_{4/16}$ starts to decompose as determined by thermogravimetric analysis.

This is the first time that thermally stable isotropic phases have been obtained for mesomorphic hexabenzocoronenes which are peripherally substituted with non-functionalized alkyl chains. Table 1 shows the DSC data, together with data obtained earlier[16,17,26,27] for hexabenzocoronenes substituted with linear unbranched and branched alkyl chains.

The reduction of the melting point by branching and lengthening the attached alkyl chain is thought to be related to additional steric crowding by neighboring chains as a consequence of the latter, and to more conformational disorder in the vicinity of the branches.

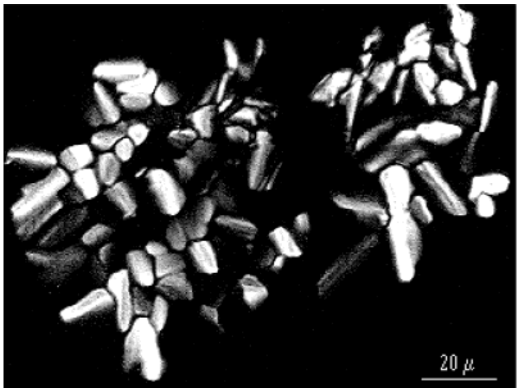


Figure 2. Micrograph of HBC-$C_{4/16}$ thin film (~1 μm thick) sandwiched within two ITO-coated glass slides under an optical microscope between two crossed polarizers at room temperature.

When a sample of HBC-$C_{4/16}$ is placed between two glass slides at room temperature, the dark yellow spreadable substance is found to be birefringent as shown in Figure 2. It seems certain that this HBC derivative exhibits liquid crystalline behavior even below room temperature. Upon heating, a highly fluid isotropic liquid appears above 231 °C. On slow cooling from the melt fan-shaped textures appear at 225 °C. The texture is characteristic of a hexagonal columnar mesophase.[19]

Optoelectronic Properties. The room-temperature discotic liquid crystalline thin film of HBC-$C_{4/16}$ showed clear photoconductive behavior. Current as a function of bias voltage from ITO/HBC-$C_{4/16}$/ITO cell is shown in Figure 3. The dark current was neglible.

When the light was turned off, the photo-current decreased back to the baseline. Moreover, a short-circuit photocurrent (I_{sc}) was observed at zero bias voltage. As reported with other organic thin films, the I_{sc} was produced by a preferential charge injection at the HBC-$C_{4/16}$ and ITO interface. Following the dissociation of the photogenerated excitons, electrons near the interface were injected from the HBC-$C_{4/16}$ molecules into the irradiated ITO electrode, while positive charges moved through the organic thin film and reached the other ITO electrode. This result suggests that the HBC-$C_{4/16}$ molecules were stacked in reasonably ordered columns allowing the charge carriers to move across the cell, as in the case of stacked liquid crystal porphyrin molecules.

Figure 4 shows I_{sc} as a function of time. Unlike the photo response from porphyrin discotic liquid crystalline thin films, where I_{sc} quickly reached its steady state upon irradiation, the I_{sc} shown in Figure 4 first jumped up to a given level and then only slowly increased to the steady state. This suggests that a charge trapping process was involved at the early period of the photo-

---

(22) Gramatica, P.; Manitto, P.; Speranza, G. *Tetrahedron* **1987**, *43*, 4481.

(23) Schweizer, E. E.; Creasy, W. S.; Light, K. K.; Shaffer, E. T. *J. Org. Chem.* **1969**, *34*, 212.

(24) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

(25) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969.

(26) Stabel, A.; Herwig, P.; Müllen, K.; Rabe, J. P. *Angew. Chem.* **1995**, *107*, 1768.

(27) Herwig, P.; Kayser, C. W.; Müllen, K.; Spiess, H. W. *Adv. Mater.* **1996**, *8*, 510.

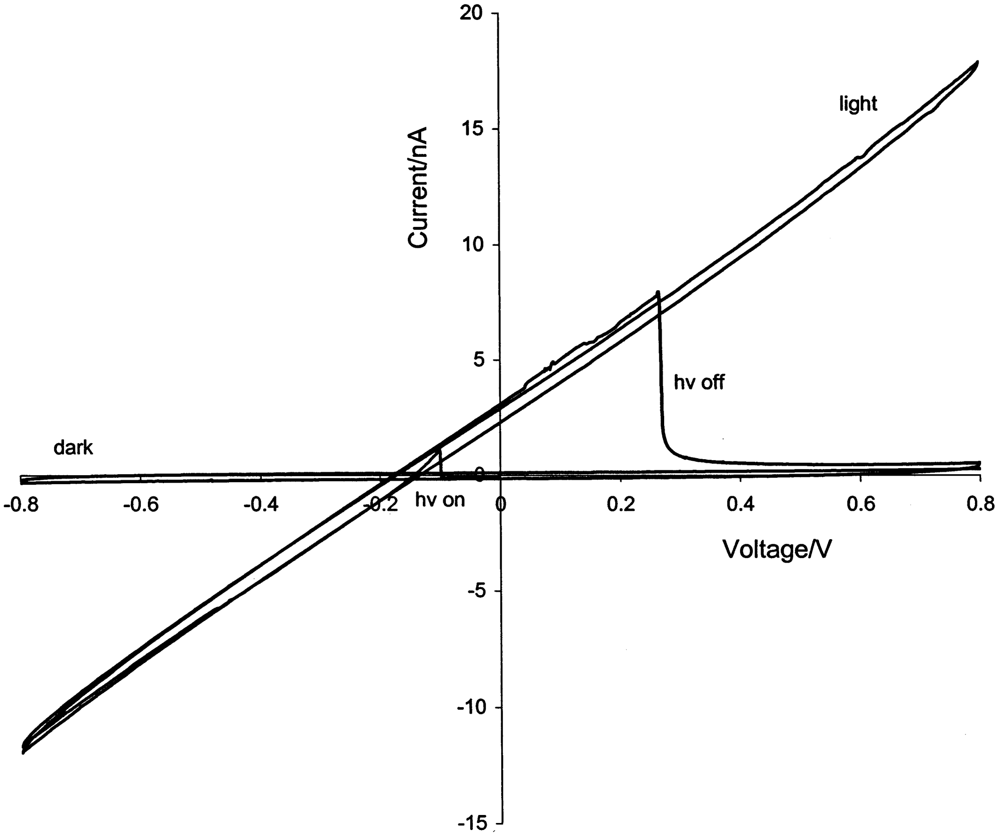


Figure 3. Photo and dark current as a function of bias voltage obtained from an ITO/HBC-$C_{4/16}$**7**/ITO cell. Scan rate, 50 mV/s.

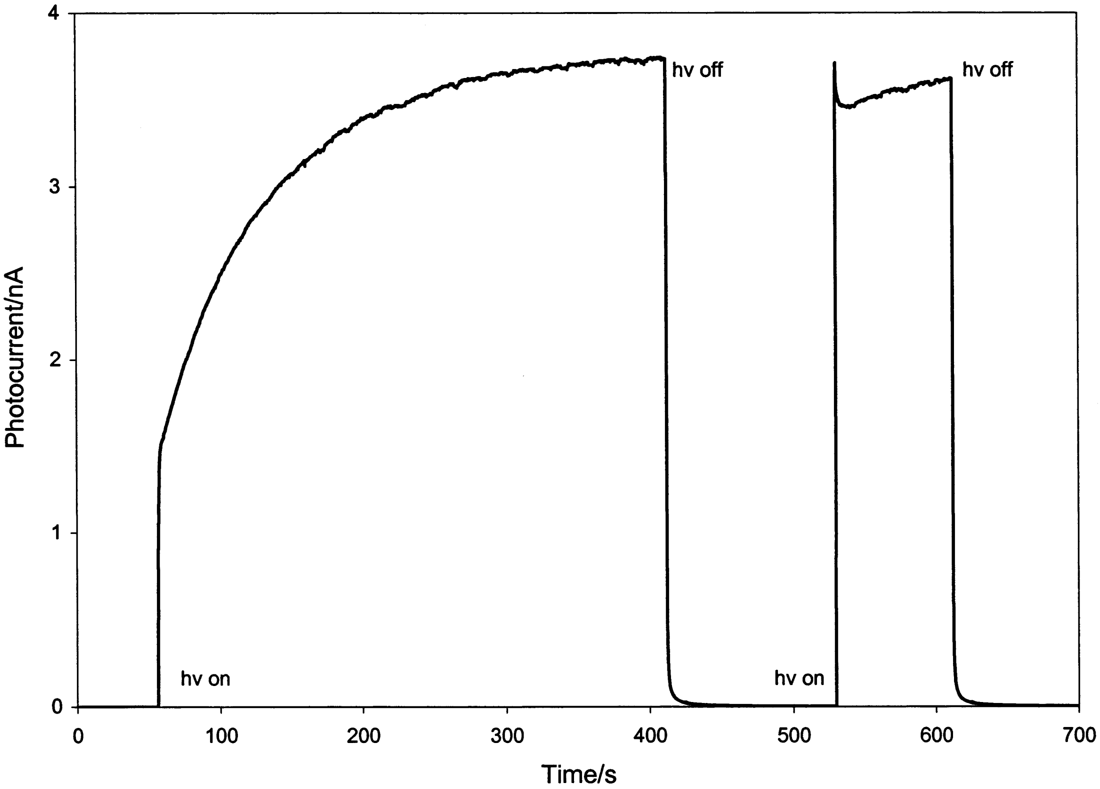


Figure 4. Short-circuit photocurrent as a function of time from an ITO/HBC-$C_{4/16}$/ITO cell.

current production. Because the light intensity was fixed over time, the total number of charge carriers generated should not change with time. However, the charge trapping process consumed a substantial fraction of the total charge carriers at the beginning of irradiation leading to a small I_{sc}. As the traps were gradually filled, I_{sc} increased slowly toward its steady-state value. A stable I_{sc} was seen only when the dynamic trapping and detrapping processes attained the same rates. When the light was turned off for 3 min. and then turned on again,

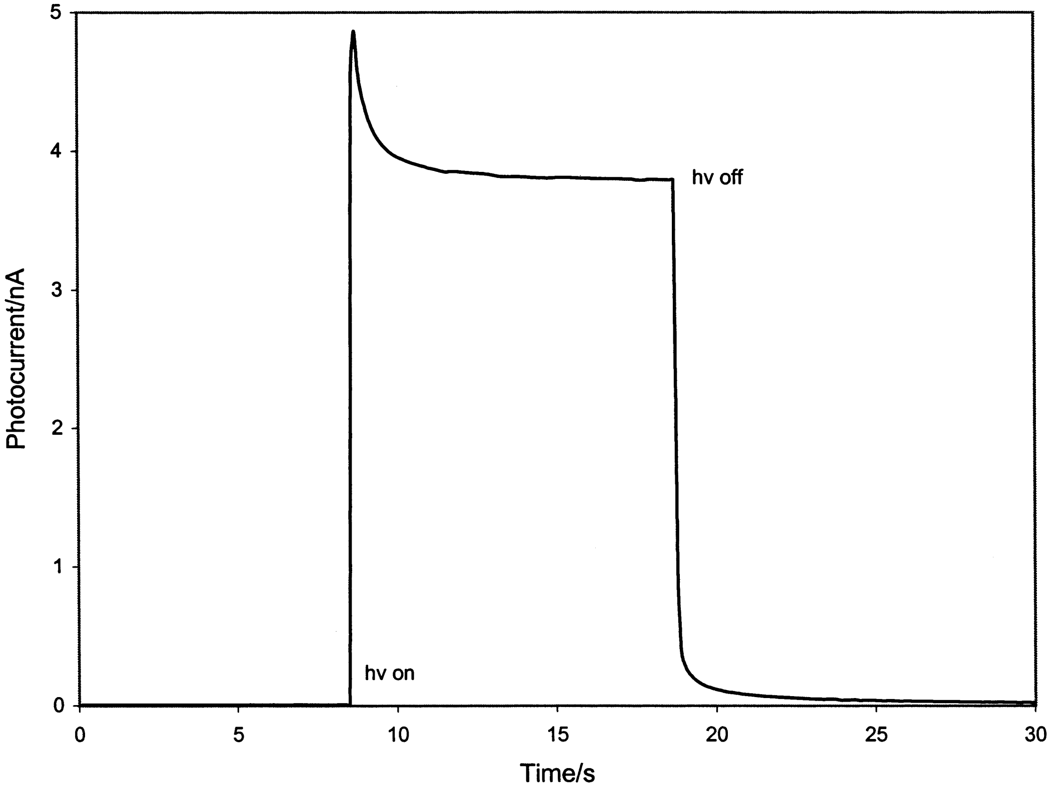


Figure 5. Photodischarge current as a function of time from an ITO/HBC-$C_{4/16}$/ITO cell after the cell had been charged under a bias of −0.75 V with irradiation followed by a period of 60 s under short-circuit conditions in the dark.

the initial I_{sc} was very close to the previous steady state value. Considering the traps were essentially filled during the first irradiation period, only a small number of the traps that were emptied during the dark period had to be refilled.

As reported earlier with the porphyrin and a number of other organic thin films,[5−9] charge trapping and detrapping could be used for optoelectronic data storage. If the empty state of the traps represent an electronic digital “0”, then a filled state of the traps could represent a digital “1”. The writing and reading of information correspond to the charge trapping/detrapping processes and are carried out by the application of suitable electrical excitation under illumination. The ultimate resolution with films of this type is very high because the photoconduction along the stacks is much higher than that from stack to stack, so single-stack trapping should, in principle, be possible. The same procedure worked also with HBC-$C_{4/16}$ thin films. For example, with a bias voltage of −0.75 V applied to the irradiated ITO electrode under irradiation for one minute, charge in the form of electrons was stored within the film. The cell was then held at short-circuit in the dark for another minute to demonstrate no loss of the trapped charge under these conditions. When the cell was irradiated at short-circuit, charge detrapping occurred and an I_{sc} as a function of time was recorded (Figure 5). An anodic discharge current spike was observed as a result of charge detrapping. Similarly, a cathodic discharge current spike was seen after the cell was initially charged under a positive bias voltage with irradiation. The charge trapping and detrapping was reversible. As shown in Figures 4 and 5, both the charge trapping and detrapping under irradiation approached the same steady-state level.

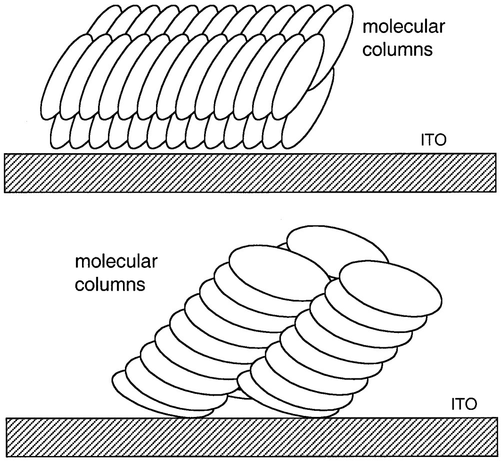


Figure 6. Proposed limiting orientations of HBC-$C_{4/16}$ molecular columns relative to the ITO electrode surface.

Orientation of Molecular Columns vs I_{sc}. As demonstrated with a number of organic single-crystal thin films, the crystal orientation has a significant influence on the optoelectronic properties.[21,28,29] In the case of the discotic liquid crystalline thin film of HBC-$C_{4/16}$, the electronically quasi-one-dimensional structure should show a similar effect, because the conductivity is expected to be highest along the molecular column and lowest perpendicular to it. In an actual measurement, however, such a difference would be difficult to measure because the molecular columns may not extend all the way from one electrode to another without interruption. Moreover, molecular columns with differ-

---

[28] Saito, T.; Liu, C.-Y.; Bard, A. J. *Chem. Mater.* **1997**, *9*, 1318.
[29] Liu, C.-Y.; Bard, A. J. *Chem. Mater.* **2000**, *12*, 2353−2362.

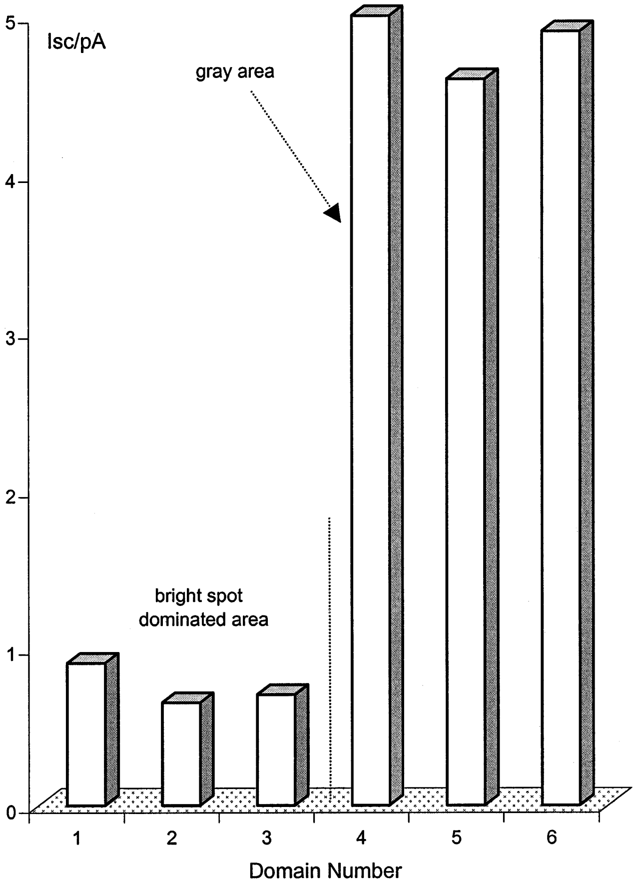


Figure 7. Steady-state short-circuit photocurrents from an ITO/HBC-$C_{4/16}$/ITO cell at six different locations under identical experimental conditions. Irradiated spot size, 140 μm diameter.

ent orientations could stack over one another, leading to a structure similar to a polycrystalline one. We found, however, that when the organic thin films prepared from the molten state became about 1 μm thick, the crystal orientation, and thus the molecular packing, were almost always fixed and extended from one ITO electrode to the other.[28,29,30] This could be verified under an optical microscope with two crossed polarizers. We believe the same thing happened here with the HBC-$C_{4/16}$ film as shown in Figure 2. Note that the area that appears black in this figure was actually gray and its structure was clearly seen. It appeared dark in the figure only because the contrast between the bright and the gray area was so large. Overall, about 80% of the film area was gray.

The planar HBC-$C_{4/16}$ molecule is symmetrical and does not have a directional dipole moment. Therefore, the molecular columns have to be tilted with respect to the ITO electrode surface to show birefringence. Figure 6 shows the proposed two limiting molecular column orientations relative to the ITO surface. When the columns are essentially parallel to the ITO plane (top, Figure 6), the largest birefringence is expected, and such a configuration would produce the brightest spots shown in Figure 2. On the other hand, when the columns are perpendicular to the ITO surface, no birefringence should be observed. We propose the bottom structure in Figure 6, or one close to it, as the one responsible for the gray ("dark") areas in Figure 2. To test this assignment, photocurrent measurements were performed with an optical microscope. In this case, the light beam was adjusted to about 140 μm diameter and the I_{sc} was collected at both bright areas and gray areas in six different locations. Figure 7 shows the results. The photocurrents generated at the different bright areas were about the same, and so were the currents at the dark areas, but I_{sc} was much smaller at bright spots than in gray areas. Considering the experimental conditions were identical for all these measurements, the observed photocurrent difference has to be related to the different molecular column orientations. The structure shown at the top of Figure 6 is obviously an unfavorable one for photocurrent production compared to the other structure at the bottom in Figure 6. These data seem to confirm the correlation between the HBC-$C_{4/16}$ column orientation and their appearance (Figure 2) discussed above.

Conclusion

A soluble derivative of hexa-*peri*-hexabenzocoronene containing six alkyl chains, each of which has sixteen carbon atoms and four branching methyl groups, was synthesized. Such discotic liquid crystal molecules formed ordered molecular columns that acted as one-dimensional molecular wires and showed photoconduction down a stack. The orientation of the columns with respect to the ITO surface had a dramatic influence on photocurrent generation and the optical textures observed under an optical microscope between two crossed polarizers at room temperature. Thin films of HBC-$C_{4/16}$ also showed charge trapping and detrapping properties potentially useful for optoelectronic information storage.[6−9,31]

Acknowledgment. The support of the National Science Foundation (CHE-9876855) and the Robert A. Welch Foundation is gratefully acknowledged. A.F., M.D.W., and K.M. acknowledge financial support from the Zentrum für Multifunktionelle Werkstoffe und Miniaturisierte Funktionseinheiten (BMBF O3N 6500), and the EU project DISCEL (G5RD-CT-2000-00321).

CM020701Q

---

(30) Liu, C.-Y.; Bard, A. J. *Chem. Mater.* **1998**, *10*, 840.

(31) Liu, C.-Y.; Hasty, T.; Bard, A. J. *J. Electrochem. Soc.* **1996**, *143*, 1916.