Functionalized Hexa-*peri*-hexabenzocoronenes: Stable Supramolecular Order by Polymerization in the Discotic Mesophase

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The synthesis and mesomorphic properties of hexa-*peri*-hexabenzocoronene (HBC) substituted with terminally functionalized *n*-alkyl chains are reported. Mono- and bisfunctionalized derivatives are accessible via Hagihara−Sonogashira coupling of bromosubstituted HBC derivatives and functionalized alkynes. Hexasubstituted hexa-*peri*-hexabenzocoronene derivatives are obtained using a cobalt octacarbonyl catalyzed cyclotrimerization of suitably substituted diphenylacetylenes, followed by an oxidative cyclodehydrogenation with iron(III) chloride dissolved in nitromethane. Thermal polymerization of HBC derivatives containing acryloyl or methacryloyl functions at the terminal position of the alkyl chains has been achieved in the liquid crystalline phase. Thereby, a network is obtained in which the Col_{ho} superstructure of the liquid crystalline phase is preserved and appears to be stable between −100 °C and 300 °C.

Introduction

In the past two decades discotic liquid crystalline materials have attracted great research interest. Currently, more than 1500 different discotic mesogenes are known[1] and are typically composed of flat, rigid aromatic cores substituted with long alkyl chains. In view of applications the formation of polymers containing discotic mesogens with a well-defined supramolecular structure organized in large homogeneous domains is often required. However, polymeric discotic liquid crystals have been relatively little explored due to difficulties in synthesizing monodisperse polymerizable monomers containing the mesogenic moiety, although, the synthesis of polymers, consisting of triphenylene-based discotic mesogens as side groups and in the main chain, have been reported.[2−6] A significant problem is that the alignment of polymeric discotics is difficult to achieve due to enhanced viscosity. Attempts to overcome this problem include mechanical shearing during the synthesis of the polymer or the utilization of the Langmuir−Blodgett technique.[7−9] As an alternative approach, the in-situ polymerization of discotic monomers aligned by surface forces in the mesophase provides a means to fix the discotic mesophase structure in a polymer network and thereby maintain the mesophase order over a broader temperature range.[10−13] A prerequisite for this method is the synthesis of monomers exhibiting a stable mesophase. For the established triphenylene derivatives, the stability of the Col_h phase is known to be highly sensitive to structural constraints such as the modification of the alkyl chains or the presence of cross-linkers with the result that supramolecular order decreases or vanishes during the polymerization process.[4,5,7,8] In contrast, monomers of liquid crystalline phthalocyanines which form a stable hexagonally ordered mesophase over a broad temperature range can be in-situ polymerized in the mesophase leading to a network in which the mesomorphic order of the monomer has been shown to be preserved.[13]

Recently, we reported the synthesis and liquid crystalline behavior of *n*-alkyl substituted hexa-*peri*-hexabenzcororonenes (HBC) **1a**−**c** (Figure 1).[14,15] In the liquid crystalline state, these disklike molecules arrange in a hexagonally ordered superstructure which is stable over a very broad temperature range. High charge carrier mobility along the columnar axis was observed in the mesophase.[16] Furthermore, we achieved a regiospecific synthesis of bromine substituted HBC derivatives (see Scheme 1; **2a** and **2b**), which had then

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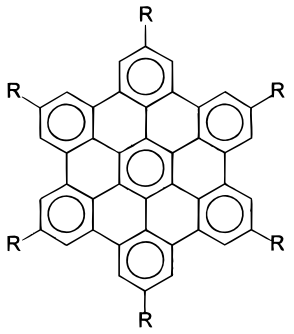

1a-c

Figure 1. Hexaalkyl-substituted hexa-*peri*-hexabenzocoronenes **1a**−**c**.

been transformed into various donor and acceptor substituted HBC derivatives.[17]

On the basis of these results we describe in this paper a regiospecific synthesis of various HBC derivatives with functional groups at the end of the aliphatic chain, such as carboxylic esters, carboxylic acids, and alcohols. Having these compounds available, it is possible to introduce polymerizable end groups. Acrylate and methacrylate monomers were chosen to make use of in-situ polymerization routes with the aim of preserving the mesogenic hexagonal superstructure over a very broad temperature range in a polymeric network. In addition, HBC derivatives with such terminal polar substituents are suitable for obtaining ordered mono- and multilayers by LB techniques.[18,19] The results of these investigations will be presented elsewhere.

Experimental Section

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$, $CDCl_3/CS_2$ (1:1), and $C_2D_2Cl_4$ on a Bruker DPX 250 and Bruker 500 DRX using the solvent proton or carbon signal as internal standard. Melting points were determined on a Büchi hot stage apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet FT-IR 320 spectrophotometer. Mass spectra were either obtained on VG Instruments ZAB 2-SE-FPD by using FD, VG trio 2000 by using EI, or Bruker Reflex-TOF. MALDI TOF mass spectra were measured using 1,8,9-trihydroxyanthracene as matrix. Elemental analysis were carried out on a Foss Heraeus Vario EL.

Differential scanning calorimetry (DSC) was measured on a Mettler DSC 30 with heating and cooling rates of 5−10 °C min^{-1}. First-order transition temperatures were reported as the minima of their endothermic peaks during heating. A Zeiss Axiophot with a nitrogen flushed Linkam THM 600 hot stage was used to characterize the polarization microscopy textures and to estimate clearing temperatures. Heating and cooling rates varied between 5 and 20 °C min^{-1}.

X-ray diffraction experiments were performed using a Siemens D 500 Kristalloflex with a graphite-monochromatized Cu Kα X-ray beam, emitted from a rotating Rigaku RV-300 anode. The temperature of the samples, which were directly on a copper sample holder or in glass capillaries, was measured by a bimetal sensor and calibrated by reference measurements.

Materials. The starting materials and catalysts for the chemical reactions were purchased from Fluka, Strem, and Aldrich and used as received. Arcyloyl chloride and methacryloyl chloride were distilled freshly before use. All other chemicals were reagent grade and purchased from commercial sources.

*Methyl 10-Undecynoate (**3**).* To a solution of 10-undecynoic acid (8.83 g, 48.43 mmol) in methanol (200 mL) was added concentrated sulfuric acid (2.0 mL). After refluxing for 2 h, the mixture was poured into a saturated sodium hydrogen carbonate solution and extracted with dichloromethane. The organic layer was washed with water and dried with magnesium sulfate. After removal of the solvent, the residue was purified by column chromatography on silica gel with dichloromethane to yield **3** (9.1 g, 96%) as a colorless oil. MS (EI): *m*/*z* (%) = 197.0 [M$^+$]. IR (neat): 3298, 2933, 2857, 2117, 1738, 1458, 1436, 1362, 1326, 1300, 1241, 1196, 1173, 1133, 1101, 1016, 994, 880, 849, 724, 634, and 559 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.62 (s, 3H), 2.26 (t, J = 7.3, 2H), 2.13 (dt, J = 7.3, 2.6, 2H), 1.89 (t, J = 2.6, 1H), 1.57 (m, 2H), 1.47 (m, 2H), and 1.38−1.23 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.16, 84.60, 68.04, 51.33, 34.01, 29.02, 29.01, 28.82, 28.59, 28.38, 24.86, and 18.31.

*2-(10-Methoxycarbonyldec-1-ynyl)-5,8,11,14,17-pentadodecyl-hexa-peri-hexabenzocoronene (**4a**).* To a solution of 2-bromo-5,8,11,14,17-pentadodecyl-hexa-*peri*-hexabenzocoronene (**2a**) (1.0 g, 0.69 mmol), copper iodide (57 mg, 0.3 mmol), and tetrakis(triphenylphosphine)palladium(0) (182 mg, 0.17 mmol) in piperidine (200 mL) was added methyl 10-undecynoate (358 mg, 1.82 mmol). The resulting mixture was stirred at 80 °C for 24 h under an argon atmosphere. The reaction mixture was poured into saturated aqueous ammonium chloride and extracted with hot toluene. The organic layer was washed with a saturated ammonium chloride solution and water and then dried with magnesium sulfate. After removal of the solvent the residue was purified by column chromatography on silica gel with hot dichloromethane/toluene (1:1). After recrystallization in *n*-heptane, **4a** (865.9 mg, 80%) was obtained as yellow crystals. MS (FD, 8 kV): *m*/*z* (%) = 1558.2 (100) [M$^+$]. IR (KBr disk): 3062, 2951, 2919, 2850, 1743, 1611, 1581, 1466, 1434, 1420, 1371, 1347, 1306, 1270, 1233, 1193, 1166, 1135, 1100, 1085, 1024, 983, 861, 742, 720, 679, and 611 cm^{-1}. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 330 (4.45), 346 (4.86), 363 (5.22), 374 (4.80), 394 (4.73), and 407 (4.27). ^{1}H NMR (500 MHz, 50% $CDCl_3/CS_2$): δ 8.40 (s, 2H), 8.13 (s, 2H), 8.02 (s, 4H), 7.99 (s, 2H), 7.98 (s, 2H), 3.67 (s, 3H), 2.89 (t, J = 7.9, 2H), 2.87 (t, J = 7.9, 4H), 2.83 (t, J = 8.1, 4H), 2.78 (t, J = 7.3, 2H), 2.38 (t, J = 7.5, 2H), 2.03−1.80 (m, 12H), 1.80−1.72 (m, 4H), 1.67−1.25 (m, 96H), and 0.90 (t, J = 9.6, 15H). ^{13}C NMR (125 MHz, 50% $CDCl_3/CS_2$): δ 173.44, 139.29, 139.13, 139.10, 129.83, 129.02, 128.96, 128.81, 128.45, 123.60, 123.21, 122.48, 122.29, 120.92, 120.65, 120.53, 120.45, 119.08, 118.94, 118.68, 118.17, 89.82, 82.48, 51.06, 37.29, 37.20, 34.02, 32.45, 32.39, 32.05, 31.98, 30.31, 30.27, 30.10, 30.04, 29.96, 29.88, 29.54, 29.45, 29.41, 25.09, 22.88, 20.15, and 14.19. Anal. Calcd for $C_{114}H_{156}O_2$: C, 87.86; H, 10.09. Found: C, 87.78; H, 10.14.

*2,5-Bis(10-methoxycarbonyldec-1-ynyl)-8,11,14,17-tetradodecyl-hexa-peri-hexabenzocoronene (**4b**)* was synthesized from 2,5-dibromo-8,11,14,17-tetradodecyl-hexa-*peri*-hexabenzocoronene (**2b**) as described for **4a**. Yield: 80%. MS (FD, 8 kV): *m*/*z* (%) = 1585.0 (100) [M$^+$]. IR (KBr disk): 2921, 2850, 1742, 1611, 1466, 1433, 1373, 1169, and 866 cm^{-1}. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 333 (4.55), 350 (4.94), 366 (5.26), 397 (4.77), 408 (4.46), 446 (3.64),454 (3.66), 462 (3.52), and 473 (3.46). ^{1}H NMR (500 MHz, 50% $CDCl_3/CS_2$): δ 8.36 (s, 2H), 8.33 (s, 2H), 8.13 (s, 2H), 8.10 (s, 6H), 3.66 (s, 6H), 2.97 (t, J = 6.6, 8H), 2.78 (t, J = 7.3, 4H), 2.37 (t, J = 7.5, 4H), 2.03−1.95 (m, 12H), 1.67−1.25 (m, 98H), and 0.88 (t, J = 6.7, 12H). ^{13}C NMR (125 MHz, 50% $CDCl_3/CS_2$): δ 173.76, 139.57, 129.12, 129.02, 128.97, 128.38, 126.22, 123.95, 123.88, 123.44, 122.31, 122.18, 121.22, 121.20, 120.84, 120.75, 119.51, 119.41, 119.09, 118.97, 118.41, 90.11, 82.29, 51.19, 37.36, 37.33, 34.09, 32.46, 32.41, 32.03, 30.32, 30.29, 30.10, 30.02, 29.94, 29.86, 29.77, 29.57, 29.55, 29.52, 29.43, 29.40, 25.09, 22.82, 20.12, and 14.14. Anal. Calcd for $C_{114}H_{150}O_4$: C, 86.42; H, 9.54. Found: C, 86.44; H, 9.53.

*2-(10-Methoxycarbonyldec-1-yl)-5,8,11,14,17-pentadodecyl-hexa-peri-hexabenzocoronene (**5a**).* A mixture of 2-(10-meth-

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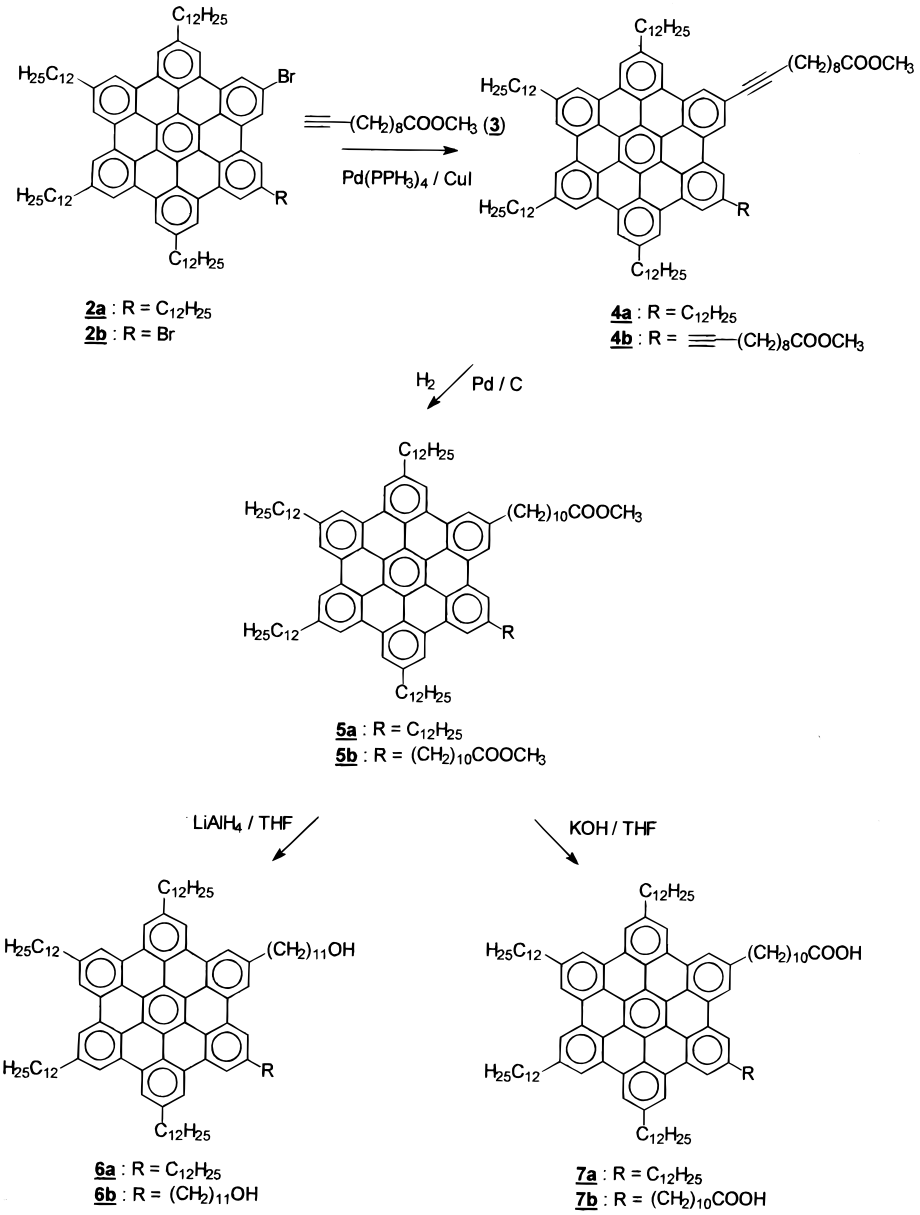
Scheme 1. Synthesis of Mono- and Bis-ω-Functionalized HBCs



oxycarbonyldec-1-ynyl)-5,8,11,14,17-pentadodecyl-hexa-*peri*-hexabenzocoronene (4**a**) (830 mg, 0.53 mmol) and palladium (10%) on activated carbon (285 mg) in tetrahydrofuran (200 mL) was stirred at room temperature for 16 h under a hydrogen atmosphere. After removal of the catalyst by filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane/toluene (1:1) to yield **5a** (785.6 mg, 94%) as yellow crystals. MS (FD, 8 kV): *m*/*z* (%) = 1561.6 (100) [M^+]. IR (KBr disk): 3062, 2951, 2919, 2850, 1744, 1611, 1583, 1467, 1435, 1421, 1372, 1349, 1296, 1200, 1191, 1167, 1136, 1024, 986, 877, 860, 749, 742, 720, 679, and 617 cm^{-1}. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 315 (4.28), 327 (4.50), 344 (4.94), 360 (5.30), 371 (4.91), 391 (4.83), and 404 (4.29). ^1H NMR (500 MHz, 50% $CDCl_3/CS_2$): δ 8.26−8.20 (br, 12H), 3.62 (s, 3H), 2.93 (br, 12H), 2.28 (t, J = 7.5, 2H), 1.92 (br, 12H), 1.66−1.23 (m, 104H), and 0.89 (t, J = 6.9, 15H). ^{13}C NMR (125 MHz, 50% $CDCl_3/CS_2$): δ 173.53, 139.42, 129.36, 122.91, 120.78, 119.15, 51.05, 37.29, 33.99, 32.51, 32.37, 32.04, 30.21, 30.05, 30.01, 29.93, 29.85, 29.76, 29.53, 29.48, 29.31, 25.02, 22.86, and 14.18. Anal. Calcd for $C_{114}H_{160}O_2$: C, 87.63; H, 10.32. Found: C, 87.65; H, 10.35.

*2,5-Bis(10-methoxycarbonyldec-1-yl)-8,11,14,17-tetradodecyl-hexa-peri-hexabenzocoronene (**5b**)* was synthesized from 2,5-bis(10-methoxycarbonyldec-1-ynyl)-8,11,14,17-tetradodecyl-hexa-*peri*-hexabenzocoronene (**4b**) as described for **5a**. Yield: 95%. MS (FD, 8 kV): *m*/*z* (%) = 1592.4 (100) [M^+]. IR (KBr disk): 3060, 2920, 2852, 1741, 1610, 1583, 1468, 1435, 1234, 1169, and 860 cm^{-1}. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 328 (4.45), 344 (4.90), 360 (5.28), and 391 (4.79). ^1H NMR (250 MHz, 50% $CDCl_3/CS_2$): δ 8.14 (br, 12H), 3.63 (s, 6H), 2.87 (br, 12H), 2.28 (t, J = 7.5, 4H), 1.90 (br, 12H), 1.66−1.20 (m, 100H), and 0.87 (t, J = 6.4, 12H). ^{13}C NMR (125 MHz, 50% $CDCl_3/CS_2$): δ 173.19, 139.56, 129.52, 123.06, 120.95, 119.32, 50.86, 37.31, 33.91, 32.43, 32.03, 30.15, 30.02, 29.98, 29.91, 29.84, 29.73, 29.51, 29.47, 29.29, 25.01, 22.87, and 14.16. Anal. Calcd for $C_{114}H_{158}O_4$: C, 85.98; H, 10.00. Found: C, 86.24; H, 10.17.

*2-(11-Hydroxyundecyl)-5,8,11,14,17-pentadodecyl-hexa-peri-hexabenzocoronene (**6a**).* To a solution of 2-(10-methoxycarbonyldecyl)-5,8,11,14,17-pentadodecyl-hexa-*peri*-hexabenzocoronene (**5a**) (302 mg, 0.19 mmol) in tetrahydrofuran (90 mL) was added lithium aluminum hydride (76 mg, 1.99 mmol). After stirring at room temperature for 10 min, the reaction mixture was poured into water and extracted with hot toluene. The organic layer was washed with water, dried with magnesium sulfate, and concentrated under reduced pressure. The residue was purified by recrystallization from *n*-heptane to yield **6a** (288.3 mg, 97%) as yellow crystals. (*n*-heptane). MS (FD, 8 kV): *m*/*z* (%) = 1533.8 (100) [M^+]. UV/vis ($CHCl_3$) λ_{max},

nm (log ϵ): 326 (4.50), 344 (4.92), 360 (5.28), 371 (4.93), 391 (4.83), 403 (4.34), and 415 (4.02). ^{1}H NMR (500 MHz, 50% $CDCl_3/CS_2$): δ 8.17 (s, 12H), 3.59 (t, J = 6.6, 2H), 2.90 (t, J = 7.8, 12H), 1.92 (m, 12H), 1.63−1.24 (m, 106H), and 0.89 (t, J = 7.0, 15H). ^{13}C NMR (125 MHz, 50% $CDCl_3/CS_2$): δ 139.28, 129.26, 122.81, 120.67, 119.03, 62.94, 37.27, 32.94, 32.52, 30.24, 30.06, 30.02, 29.94, 29.86, 29.63, 29.53, 25.89, 22.86, and 14.18. Anal. Calcd for $C_{113}H_{160}O$: C, 88.45; H, 10.51. Found: C, 88.35; H, 10.60.

*2,5-Bis(11-hydroxyundecyl)-8,11,14,17-tetradodecyl-hexa-peri-hexabenzocoronene (**6b**)* was synthesized from 2,5-bis(10-methoxycarbonyldec-1-yl)-8,11,14,17-tetradodecyl-hexa-*peri*-hexabenzocoronene **(5b)** as described for **6a**. Yield: 86%. MS (FD, 8 kV): m/z (%) = 1562.68 (100) [M$^+$]. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 330 (4.52), 344 (4.91), 361 (5.27), 391 (4.81), 435 (3.52), 440 (3.56), and 447 (3.52). ^{1}H NMR (500 MHz, pyridine-d_5): δ 8.90−8.87 (br, 12H), 4.75 (br, 2H), 3.85 (t, J = 6.6, 4H), 3.31 (br, 12H), 2.23 (br, 12H), 1.85−1.24 (m, 106H), and 0.96 (br, 12H). ^{13}C NMR (125 MHz, pyridine-d_5): δ 140.46, 140.43, 130.13, 119.75, 109.56, 61.95, 37.15, 33.36, 32.15, 32.09, 31.76, 30.01, 29.97, 29.83, 29.72, 29.59, 29.20, 26.17, 22.44, and 13.64. Anal. Calcd for $C_{112}H_{158}O_2$: C, 87.55; H, 10.36. Found: C, 87.49; H, 10.46.

*2-(10-Carboxidecyl)-5,8,11,14,17-pentadodecyl-hexa-peri-hexabenzocoronene (**7a**)*. A solution of 2-(10-methoxycarbonyldecyl)-5,8,11,14,17-pentadodecyl-hexa-*peri*-hexabenzocoronene (**5a**) (396 mg, 0.25 mmol) and lithium iodide (3.77 g, 28.16 mmol) in pyridine (40 mL) was heated at reflux for 12 h under an argon atmosphere. After removal of the solvent, water (300 mL) was added to the mixture, which was then acidified with a 10% hydrochloric acid solution and extracted with hot toluene. After removal of the solvent, the residue was recrystallized from *n*-heptane to yield **7a** (313 mg, 80%) as yellow crystals. MS (FD, 8 kV): m/z (%) = 1548.9 (100) [M$^+$]. IR (KBr disk): 3062, 2951, 2920, 2850, 1709, 1611, 1583, 1488, 1466, 1435, 1422, 1373, 1349, 1226, 877, 860, 743, 720, and 615 cm^{-1}. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 327 (4.27), 344 (4.68), 360 (5.03), 371 (4.69), 383 (4.53), 391 (4.60), 403 (4.13), and 415 (3.87). ^{1}H NMR (500 MHz, 50% $CDCl_3/CS_2$): δ 8.01 (br, 12H), 2.79 (br, 10H), 2.39 (br, 2H), 1.86 (br, 10H), 1.74−1.23 (m, 108H), and 0.89 (t, J = 6.0, 15H). ^{13}C NMR (125 MHz, 50% $CDCl_3/CS_2$): δ 139.01, 129.06, 122.62, 120.44, 118.81, 37.21, 32.52, 32.05, 30.27, 30.08, 30.03, 29.95, 29.87, 29.53, 22.86, and 14.17. Anal. Calcd for $C_{113}H_{158}O_2$: C, 87.65; H, 10.28. Found: C, 85.49; H, 10.44.

*2,5-Bis(10-carboxidecyl)-8,11,14,17-tetradodecyl-hexa-peri-hexabenzocoronene (**7b**)*. A total of 400 mg (0.25 mmol) of 2,5-bis(10-methoxycarbonyl-decyl)-8,11,14,17-tetradodecyl-hexa-*peri*-hexabenzocoronene (**5b**) was dissolved in 200 mL of tetrahydrofuran under an argon atmosphere and a solution of 400 mg of potassium hydroxide in 2 mL of water/8 mL of methanol was added. The resulting mixture was heated at reflux for 24 h. The mixture was acidified with 10% hydrochloric acid, and a small amount of toluene was added to obtain a phase separation. The organic layer was separated and dried with sodium sulfate, and the solvent was removed under reduced pressure. The residue was recrystallized from *n*-heptane to yield **7b** (325 mg 89%) as yellow crystals. MALDI-TOF: m/z = 1562.68 [M$^+$]. IR (KBr disk): 3062, 2920, 2850, 2673, 1709, 1610, 1583, 1531, 1468, 1371, 1284, 1240, 1136, 939, 860, 748, and 719 cm^{-1}. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 329 (4.17), 344 (4.70), 360 (5.09), 391 (4.55), and 405 (3.79). ^{1}H NMR (500 MHz, 50% $CDCl_3/CS_2$): δ 8.10 (br, 12H), 2.84 (br, 12H), 2.38 (br, 4H), 1.88 (br, 12H), 1.70−1.23 (m, 102H), and 0.88 (t, J = 6.0, 12H). Anal. Calcd for $C_{113}H_{158}O_2$: C, 85.99; H, 9.92. Found: C, 84.75; H, 9.59.

*Methyl 11-(4-bromophenyl)-10-undecynoate (**9**)*. To a solution of 4-bromoiodobenzene (20.08 g, 70.97 mmol), copper iodide (672 mg, 3.53 mmol), and tetrakis(triphenylphosphine)-palladium(0) (1.26 g, 1.80 mmol) in piperidine (280 mL) was added methyl 10-undecynoate (9.71 g, 35.91 mmol). The resulting mixture was stirred at room temperature for 3 h under an argon atmosphere. The reaction mixture was poured into a saturated ammonium chloride solution and extracted with dichloromethane. The organic layer was washed with a saturated ammonium chloride solution and water and dried with magnesium sulfate. After removal of the solvent, the residue was purified by column chromatography on silica gel with petroleum ether to yield **9** (22.19 g, 89%) as a colorless oil. MS (FD, 8 kV): m/z (%) = 350.5 (100) [M$^+$]. IR (neat): 2932, 2855, 2773, 2232, 1900, 1738, 1486, 1464, 1435, 1394, 1367, 1349, 1328, 1295, 1259, 1236, 1196, 1171, 1132, 1096, 1071, 1039, 1010, 882, 865, 824, 783, 725, 704, 636, 571, and 522 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 8.5, 2H), 7.21 (d, J = 8.5, 2H), 3.63 (s, 3H), 2.34 (t, J = 7.0, 2H), 2.27 (t, J = 7.5, 2H), 1.63−1.52 (m, 4H), 1.43−1.37 (m, 2H), and 1.32−1.27 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.12, 132.94, 131.32, 123.04, 121.45, 91.62, 79.58, 51.33, 34.00, 29.05, 29.02, 28.86, 28.76, 28.51, 24.85, and 19.34.

*Methyl 11-(4-bromophenyl)undecanoate (**10**)*. A mixture of methyl 11-(4-bromophenyl)-10-undecynoate (**9**) (22.2 g, 63.16 mmol) and palladium (10%) on activated carbon (6.5 g) in tetrahydrofuran (600 mL) was stirred at room temperature for 5 days under hydrogen atmosphere. After removal of the catalyst by filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane/petroleum ether (1:1) to yield **10** (18.2 g, 81%) as colorless needles. Mp: 35.0−35.8 °C. MS (FD, 8 kV): m/z (%) = 354.3 (100) [M$^+$]. IR (KBr disk): 3025, 2995, 2940, 2922, 2851, 1733, 1694, 1488, 1473, 1453, 1449, 1434, 1416, 1405, 1382, 1363, 1350, 1314, 1304, 1282, 1249, 1233, 1216, 1206, 1188, 1178, 1166, 1113, 1105, 1089, 1068, 1048, 1021, 1011, 993, 979, 969, 944, 884, 862, 832, 827, 803, 783, 762, 739, 718, 709, 698, 601, 536, 506, and 461 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 8.2, 2H), 7.02 (d, J = 8.2, 2H), 3.64 (s, 3H), 2.53 (t, J = 7.6, 2H), 2.28 (t, J = 7.5, 2H), 1.63−1.52 (m, 4H), and 1.32−1.21 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.27, 141.81, 131.24, 130.15, 119.24, 51.38, 35.33, 34.10, 31.27, 29.44, 29.38, 29.20, 29.12, and 24.93. Anal. Calcd for $C_{18}H_{27}O_2Br$: C, 61.00; H, 7.68. Found: C, 61.09; H, 7.55.

*Methyl 11-[4-(trimethylsilylethynyl)phenyl]undecanoate (**11**)*. To a warm (50 °C) solution of methyl 11-(4-bromophenyl)-undecanoate (**10**) (14.91 g, 41.96 mmol), triphenylphosphine (1.22 g, 4.67 mmol), copper iodide (838 mg, 4.40 mmol), and *trans*-dichlorobis(triphenylphosphine)palladium(II) (1.66 g, 2.37 mmol) in triethylamine (200 mL) was added trimethylsilylacetylene (11.9 mL, 8.27 g, 84.20 mmol). The resulting mixture was stirred at 80 °C for 24 h under an argon atmosphere. The reaction mixture was poured into a saturated ammonium chloride solution and extracted with dichloromethane. The organic layer was washed with a saturated ammonium chloride solution and water and then dried with magnesium sulfate. After removal of the solvent, the residue was purified by column chromatography on silica gel with dichloromethane/petroleum ether (1:1) to yield **11** (13.05 g, 83%) as a colorless oil. MS (FD, 8 kV): m/z (%) = 372.5 (100) [M$^+$]. IR (neat): 3078, 3027, 2992, 2928, 2855, 2157, 1946, 1909, 1741, 1608, 1506, 1463, 1436, 1419, 1410, 1362, 1249, 1222, 1198, 1172, 1125, 1111, 1020, 865, 843, 760, 739, 700, 637, 577, and 541 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, J = 8.2, 2H), 7.07 (d, J = 8.2, 2H), 3.64 (s, 3H), 2.56 (t, J = 7.8, 2H), 2.28 (t, J = 7.6, 2H), 1.63−1.52 (m, 4H), 1.31−1.21 (m, 12H), and 0.22 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.27, 143.59, 131.85, 128.27, 120.23, 105.40, 93.21, 51.37, 35.84, 34.07, 31.14, 29.43, 29.38, 29.36, 29.19, 29.12, 29.10, 24.92, and 0.01.

*Methyl 11-(4-ethynylphenyl)undecanoate (**12**)*. To a solution of methyl 11-[4-(trimethylsilylethynyl)phenyl]undecanoate (**11**) (6.23 g 16.72 mmol) in DMF (100 mL) was added a solution of potassium fluoride (1.94 g, 33.43 mmol) in water (10 mL). After stirring at room temperature for 3 h, the reaction mixture was poured into water and extracted with toluene. The organic layer was washed with water, dried with magnesium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane/petroleum ether (1:1) to yield **12** (4.10 g, 82%) as a colorless oil. MS (FD, 8 kV): m/z (%) = 300.4 (100) [M$^+$]. IR (neat): 3291, 3081, 3027, 2995, 2929, 2853, 2108, 1910, 1733, 1608, 1508, 1464, 1436, 1413, 1362, 1250, 1197, 1172, 1125,

1112, 1020, 842, 821, 723, 700, 652, 644, 609, 555, and 515 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, $J = 8.2$, 2H), 7.20 (d, $J = 8.2$, 2H), 3.74 (s, 3H), 3.11 (s, 1H), 2.67 (t, $J = 7.8$, 2H), 2.38 (t, $J = 7.6$, 2H), 1.75−1.61 (m, 4H), and 1.44−1.31 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.25, 143.91, 132.02, 128.38, 119.24, 83.86, 76.38, 51.36, 35.85, 34.09, 31.14, 29.43, 29.38, 29.36, 29.18, 29.16, 29.10, and 24.93.

*Bis[4-(10-methoxycarbonyldecyl)phenyl]acetylene (**13**).* To a solution of methyl 11-(4-bromophenyl)undecanoate (**10**) (13.50 g, 36.73 mmol), copper iodide (1.33 g, 6.99 mmol), and tetrakis-(triphenylphosphine)palladium(0) (4.04 g, 3.50 mmol) in triethylamine (400 mL) was added methyl 11-(4-ethynylphenyl)-undecanoate (**12**) (10.51 g, 34.98 mmol). The resulting mixture was stirred at 80 °C for 24 h under an argon atmosphere. The reaction mixture was poured into a saturated ammonium chloride solution and extracted with dichloromethane. The organic layer was washed with a saturated ammonium chloride solution and water and then dried with magnesium sulfate. After removal of the solvent the residue was purified by column chromatography on silica gel with dichloromethane/petroleum ether (1:1). After recrystallization in methanol **13** was obtained (10.17 g, 50%) as colorless plates. Mp: 68.3−69.9 °C. MS (FD, 8 kV): m/z (%) = 574.7 (100) [M^+]. IR (KBr disk): 3030, 3002, 2919, 2849, 1733, 1609, 1557, 1520, 1470, 1456, 1438, 1415, 1379, 1351, 1329, 1296, 1280, 1263, 1233, 1203, 1170, 1117, 1094, 1054, 1020, 994, 971, 899, 882, 846, 818, 783, 754, 737, 719, 704, 551, and 519 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.41 (d, $J = 8.0$, 4H), 7.12 (d, $J = 8.0$, 4H), 3.64 (s, 6H), 2.58 (t, $J = 7.6$, 4H), 2.28 (t, $J = 7.4$, 4H), 1.65 (m, 8H), and 1.33−1.21 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.29, 143.18, 131.45, 128.42, 120.64, 88.93, 51.39, 35.89, 34.11, 31.21, 29.46, 29.43, 29.38, 29.21, 29.12, and 24.95. Anal. Calcd for $C_{38}H_{54}O_4$: C, 79.39; H, 9.47. Found: C, 79.26; H, 9.58.

*1,2,3,4,5,6-Hexa[4-(10-methoxycarbonyldecyl)phenyl]benzene (**14**).* A solution of bis[4-(10-methoxycarbonyldecyl)-phenyl]acetylene (**13**) (10.03 g, 17.44 mmol) and dicobalt octacarbonyl (663 mg, 1.94 mmol) in 1,4-dioxane (600 mL) was heated at reflux for 10 h under an argon atmosphere. After removal of the solvent, the residue was purified by column chromatography on silica gel with dichloromethane/ethyl acetate (5:1) to yield **14** (9.30 g, 92%) as pale yellow crystals. Mp: 46.8−47.2 °C. MS (FD, 8 kV): m/z (%) = 1725.7 (100) [M^+]. IR (neat): 3083, 3047, 3023, 2995, 2924, 2853, 1900, 1733, 1607, 1564, 1516, 1467, 1435, 1418, 1363, 1252, 1198, 1170, 1114, 1020, 943, 882, 836, 759, 745, 722, 692,671, 645, 590, and 550 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.64 (d, $J = 8.2$, 12H), 6.58 (d, $J = 8.2$, 12H), 3.64 (s, 18H), 2.30 (t, $J = 7.1$, 12H), 2.28 (t, $J = 7.4$, 12H), 1.66−1.66 (m, 24H), and 1.43−1.02 (m, 72H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.25, 140.27, 138.98, 138.29, 131.40, 126.42, 51.38, 35.34, 34.12, 31.19, 29.58, 29.52, 29.47, 29.29, 29.18, 28.85, and 24.98. Anal. Calcd for $C_{114}H_{162}O_{12}$: C, 79.39; H, 9.47. Found: C, 79.33; H, 9.51.

*2,5,8,11,14,17-Hexa(10-methoxycarbonyldecyl)hexa-peri-hexabenzocoronene (**15**).* To a stirred solution of 1,2,3,4,5,6-hexa-[4-(10-methoxycarbonyldecyl)phenyl]benzene (**14**) (5.00 g, 2.90 mmol) in dichloromethane (500 mL) was added dropwise a solution of anhydrous iron(III) chloride (8.57 g, 52.85 mmol) in nitromethane (30 mL). An argon stream was bubbled through the reaction mixture during the reaction. After stirring for another 10 min, the reaction was quenched with methanol (1 L). The precipitated solid was collected by filtration, washed with methanol, and dried under vacuum. The residue was purified by column chromatography on silica gel with hot ethyl acetate/dichloromethane (1:1). After recrystallization from a mixture of dichloromethane/*n*-heptane (3:1) **15** was obtained (1.92 g, 39%) as yellow crystals MS (FD, 8 kV): m/z (%) = 1711.2 (100) [M^+]. IR (KBr disk): 3060, 2994, 2923, 2851, 1737, 1610, 1582, 1467, 1435, 1417, 1364, 1314, 1295, 1280, 1265, 1250, 1233, 1216, 1201, 1168, 1118, 1104, 1064, 1023, 993, 976, 876, 869, 844, 745, 721, 674, and 610 cm^{-1}. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 327 (4.51), 344 (4.93), 360 (5.30), 371 (4.87), 391 (4.82), and 403 (4.27). ^1H NMR (300 MHz, 50% $CDCl_3/CS_2$): δ 8.32 (s, 12H), 3.62 (s, 18H), 2.97 (t, $J = 7.8$, 12H), 2.28 (t, $J = 7.4$, 12H), 1.94 (m, 12H), and 1.68−1.29 (m, 84H). ^{13}C NMR (75 MHz, 50% $CDCl_3/CS_2$): δ 173.71, 139.63, 129.53, 123.06, 120.96, 119.32, 51.11, 37.34, 33.99, 32.53, 30.15, 29.98, 29.92, 29.72, 29.46, 29.28, and 25.00. Anal. Calcd for $C_{114}H_{150}O_{12}$: C, 79.95; H, 8.83. Found: C, 80.00; H, 8.70.

*2,5,8,11,14,17-Hexa(10-hydroxyundecyl)hexa-peri-hexabenzocoronene (**16**).* Lithium aluminum hydride (1.33 g, 35.1 mmol)) was suspended in dry tetrahydrofuran (250 mL). A solution of 2,5,8,11,14,17-hexa(10-methoxycarbonyldecyl)hexa-*peri*-hexabenzocoronene (**15**) (2.0 g, 1.16 mmol) in dry tetrahydrofuran (250 mL) was added dropwise. After stirring at room temperature for 4 h, the reaction mixture was quenched with a mixture of tetrahydrofuran/ethanol (10:1). The inorganic precipitate was filtered and extracted several times with hot tetrahydrofuran. A total of 100 mL of water was added to the organic solution followed by a small amount of toluene to obtain a phase separation. After separation of the organic solution this procedure was repeated twice. The organic solution was dried with sodium sulfate, again under addition of a small amount of toluene. The solvent was removed under reduced pressure until the product started to precipitate. After crystallization overnight the precipitate was collected and dried under vacuum. Yield: 1.6 g, 89%. MS (FD, 8 kV): m/z (%) = 1533.8 (100) [M^+]. ^1H NMR (500 MHz, pyridine-d_5): δ 8.98 (s, 12H), 3.88 (t, $J = 6.4$, 12H), 3.29 (t, $J = 7.8$, 12H), 2.18 (m, 12H), and 1.83−1.50 (m, 106H). ^{13}C NMR (125 MHz, pyridine-d_5): δ 140.44, 130.10, 123.45, 121.58, 119.72, 61.92, 37.22, 33.40, 32.29, 30.08, 29.89, 29.85, 29.83, 29.77, 29.73, 29.62, and 26.22.

*2,5,8,11,14,17-Hexa(10-carboxidecyl)hexa-peri-hexabenzocoronene (**17**).* A total of 500 mg (0.307 mmol) of 2,5,8,11,14,-17-hexa(10-methoxycarbonyl-undecen-1-yl)hexa-*peri*-hexabenzocoronene (**15**) was dissolved in 500 mL of tetrahydrofuran under an argon atmosphere and a solution of 500 mg of potassium hydroxide in 5 mL of water/10 mL of methanol was added. The resulting mixture was heated at reflux for 3 days. The mixture was acidified with 10% acid chloride, and a small amount of toluene was added to obtain a phase separation. The organic layer was dried with sodium sulfate and concentrated until incipient cloudiness, and heptane was added to favor complete precipitation. The solid was collected by filtration and dried under vacuum to yield **17** (4.75 g 95%) as yellow crystals. MALDI-TOF: m/z = 1627.38 [M^+]. IR (KBr disk): 2919, 2848, 1697, 1610, 1432, and 860 cm^{-1}. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 329 (4.17), 344 (4.70), 360 (5.09), 391 (4.55), and 405 (3.79). ^1H NMR (300 MHz, DMSO-d_6): δ 11.83 (br, 6H), 7.39 (br, 12H), 3.21 (br, 12H), 2.56 (br, 12H), 2.25 (t, $J = 7.5$, 12H), 1.78 (br, 12H), and 1.65−1.39 (m, 72H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 174.23, 137.46, 127.55, 120.88, 119.40, 116.84, 36.23, 33.78, 31.48, 29.50, 29.46, 29.36, 29.07, 28.87, and 24.67.

*2-(11-Acryloyloxyundecyl)-5,8,11,14,17-pentadodecyl-hexa-peri-hexabenzocoronene (**18a**).* To a solution of 2-(11-hydroxyundecyl)-5,8,11,14,17-pentadodecyl-hexa-*peri*-hexabenzocoronene (**16**) (100 mg, 0.065 mmol), *N*,*N*-dimethylaniline (3.3 mL, 3.16 g, 26.0 mmol), and 2,6-di-*tert*-butyl-*p*-cresol (45.2 mg, 0.21 mmol) in tetrahydrofuran (30 mL) was added freshly distilled acryloyl chloride (0.53 mL, 590 mg, 6.52 mmol). After stirring at 50 °C for 5 h under an argon atmosphere, the mixture was poured into water (300 mL). The precipitate was collected by filtration, washed with ethanol and purified by recrystallization from dichloromethane/methanol to yield **18a** (81 mg, 79%) as yellow crystals. (CH_2Cl_2/methanol). IR (KBr disk): 3062, 2952, 2920, 2850, 1728, 1611, 1583, 1467, 1421, 1406, 1372, 1349, 1294, 1267, 1188, 1057, 983, 962, 876, 859, 809, 743, 720, and 614 cm^{-1}. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 327 (4.42), 344 (4.85), 360 (5.21), 371 (4.83), 391 (4.75), and 405 (4.20). ^1H NMR (500 MHz, 50% $CDCl_3/CS_2$): δ 8.21 (br, 12H), 6.35 (dd, $J = 17.3$, 1.7, 1H), 6.08 (dd, $J = 17.3$, 10.4, 1H), 5.76 (dd, $J = 10.4$, 1.7, 1H), 4.12 (t, $J = 6.9$, 2H), 2.92 (br, 12H), 1.92 (br, 12H), 1.69−1.23 (m, 106H), and 0.89 (t, $J = 6.9$, 15H). ^{13}C NMR (125 MHz, 50% $CDCl_3/CS_2$): δ 165.72, 139.35, 129.82, 129.31, 128.50, 122.86, 120.73, 119.10, 64.45, 37.28, 32.51, 32.04, 30.22, 30.05, 30.01, 29.94, 29.90, 29.85, 29.77, 29.53, 29.47, 28.75, 26.08, 22.86, and 14.18. Anal. Calcd for

$C_{116}H_{162}O_2$: C, 87.71; H, 10.28. Found: C, 87.14; H, 10.41.

*2,5,8,11,14,17-Hexa(11-acryloyloxyundecyl)hexa-peri-hexabenzocoronene (**19a**)* was synthesized from 2,5,8,11,14,17-hexa(10-hydroxyundecyl)hexa-*peri*-hexabenzocoronene (**16**) as described for **18a**. IR (KBr disk): 3062, 2924, 2852, 1724, 1637, 1610, 1583, 1468, 1406, 1371, 1298, 1267, 1201, 1055, 984, 862, 810, and 721 cm^{-1}. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 344 (4.84), 360 (5.23), 372 (4.81), 391 (4.76), and 405 (4.20). ^1H NMR (500 MHz, 50% $CDCl_3/CS_2$): δ 8.54 (br, 12H), 6.35 (dd, J = 17.2, 1.5, 6H), 6.08 (dd, J = 17.2, 10.7, 6H,), 5.76 (dd, J = 10.7, 1.5, 6H,), 4.08 (t, J = 6.7, 12H), 3.08 (t, J = 7.8, 12H), 2.04−1.98 (m, 12H), and 1.66−1.23 (m, 96H). ^{13}C NMR (125 MHz, 50% $CDCl_3/CS_2$): δ 165.26, 139.98, 129.83, 129.47, 128.43, 123.38, 121.34, 119.71, 64.24, 37.35, 32.43, 30.05, 29.95, 29.91, 29.81, 29.71, 29.42, 28.76, and 26.05. Anal. Calcd for $C_{126}H_{162}O_{12}$: C, 80.99; H, 8.74. Found: C, 80.25; H, 8.79.

*2,5,8,11,14,17-Hexa(11-methacryloyloxyundecyl)hexa-peri-hexabenzocoronene (**19b**)* was synthesized from 2,5,8,11,14,-17-hexa(10-hydroxyundecyl)hexa-*peri*-hexabenzocoronene (**16**) and methacryloyl chloride as described for **18a**. IR (KBr disk): 3062, 2920, 2850, 1720, 1637, 1612, 1583, 1468, 1402, 1373, 1323, 1296, 1259, 1167, 1074, 1012, 935, 860, 814, and 721 cm^{-1}. UV/vis ($CHCl_3$) λ_{max}, nm (log ϵ): 345 (4.84), 360 (5.23), 371 (4.80), 392 (4.74), and 403 (4.20). ^1H NMR (500 MHz, 50% $CDCl_3/CS_2$): δ 8.39 (s, 12H), 6.05 (m, 6H), 5.49 (m, 6H), 4.10 (t, J = 6.7, 12H), 3.02 (t, J = 7.95, 12H), 2.03−1.93 (m, 12H), 1.91 (s, 18H), and 1.68−1.24 (m, 96H). ^{13}C NMR (125 MHz, 50% $CDCl_3/CS_2$): δ 139.80, 136.53, 129.67, 124.84, 123.21, 121.10, 119.46, 64.66, 37.36, 32.50, 30.13, 29.98, 29.96, 29.84, 29.77, 29.71, 29.41, 28.73, 26.09, and 18.22. Anal. Calcd for $C_{132}H_{174}O_{12}$: C, 81.19; H, 8.98. Found: C, 81.26; H, 8.83.

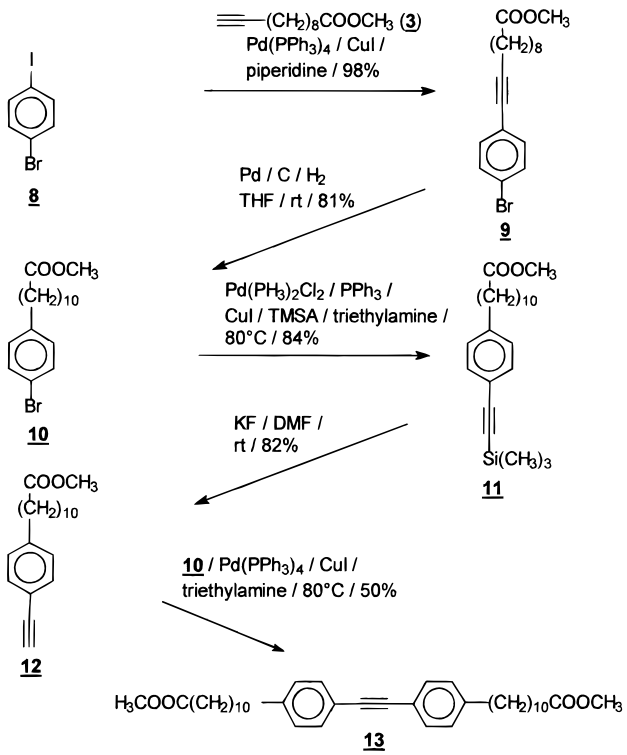
Results

Synthesis. The Hagihara−Sonogashiracoupling offers the possibility of introducing ω-functionalized alkanes via their corresponding alkynes through reaction with the bromo-functionalized HBCs **2a** and **2b** as shown for methyl 10-undecynoate (**3**, Scheme 1).[20] After a palladium-catalyzed hydrogenation of the triple bond, the esters **5a** and **5b** were obtained in high yields from which reduction by lithium aluminum hydride or demethylation by lithium iodine in pyridine as well as with potassium hydroxide in THF yielded the mono- and bis-alcohol **6a** and **6b** or the acids **7a** and **7b**, respectively.

To obtain HBC derivatives with a functional group at the terminal position of all six alkyl chains we fall back on a cyclotrimerization of a suitably substituted diphenylacetylene,[21] a method which we have previously reported for the synthesis of the precursor of hexa-*n*-alkyl-substituted HBC.[14] The diphenylacetylene **13** was obtained in a reaction sequence essentially based on Hagihara−Sonogashira coupling reactions (see Scheme 2): First, methyl 10-undecynoate (**3**) and 4-bromoiodobenzene (**8**) were coupled to yield **9**, followed by the hydrogenation of the triple bond. Reacting the resulting bromide **10** with trimethylsilylacetylene gave **11.** After removal of the trimethylsilyl group with potassium fluoride in DMF, the so-obtained phenylacetylene derivative **12** was coupled with the bromide **10**, yielding the desired ω-functionalized diphenylacetylene **13**.

Cyclotrimerization of the diphenylacetylene **13** in 1,4-dioxane then afforded the hexasubstituted hexaphenylbenzene **14** (Scheme 3). The oxidative cyclodehydrogenation using iron(III) chloride/nitromethane as reagent

Scheme 2. Synthesis of ω-Functionalized Diphenylacetylene



gave the hexa-*peri*-hexabenzocoronene derivative **15**.[15,17] Reduction of the six ester groups with lithium aluminum hydride resulted quantitatively in the hexa-ω-hydroxyundecyl-substituted HBC **16**, while the hydrolysis of the hexaester **15** with potassium hydroxide in THF yielded the hexaacid **17**.

Finally, to obtain the acrylates **18**/**19a** and the methacrylate **19b** (Figure 2), the ω-hydroxyundecyl-substituted HBC derivatives **6a** or **16** were reacted with a large excess of acryloyl chloride or methacryloyl chloride. The presence of a radical inhibitor like 2,6-di-*tert*-butyl-*p*-cresol is required to prevent spontaneous polymerization of the monomers during the esterification.

In general, the HBC derivatives presented in this paper were found to be soluble in most organic solvents, in particular in carbon disulfide. Compounds **16** and **17** were exceptions in that although they were soluble in THF or pyridine they exhibited a solubility rather low in less polar solvents such as chloroform or toluene.

All HBC derivatives have been characterized by solution-state NMR spectroscopy. It is important to note that chemical shifts and line widths of the resonances of aromatic as well as the α- and β-methylene protons were observed to be concentration dependent. The broadening and the concentration dependence of the signals are believed to be a consequence of aggregation phenomena, with the effect being most pronounced in the case of the resonance signals of the aromatic protons. In this respect, we note that in solid-state ^1H NMR investigations of hexaalkyl-substituted HBC derivatives, very marked shifts of both aromatic and aliphatic resonances are observed as a consequence of shielding due to the nearby aromatic cores.[15,22] System-

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(22) Brown, S. P.; Schnell, I.; Brand, J. D.; Müllen, K.; Spiess, H. W. *J. Mol. Structure* **2000**, *521*, 179.

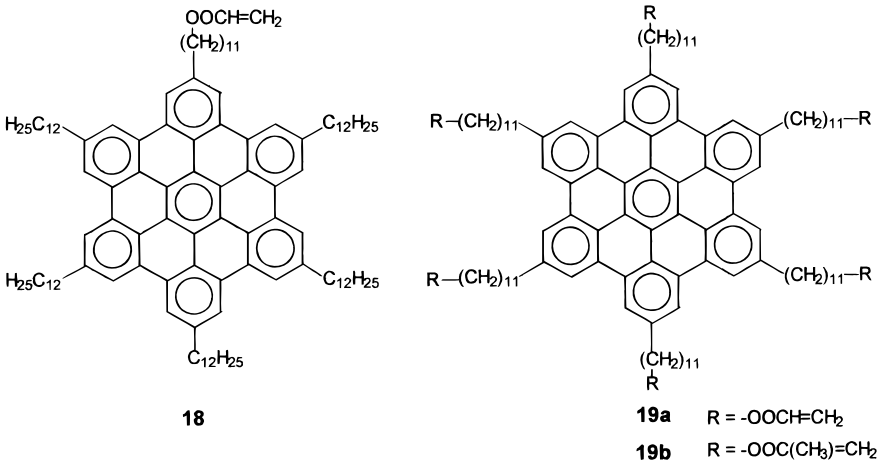
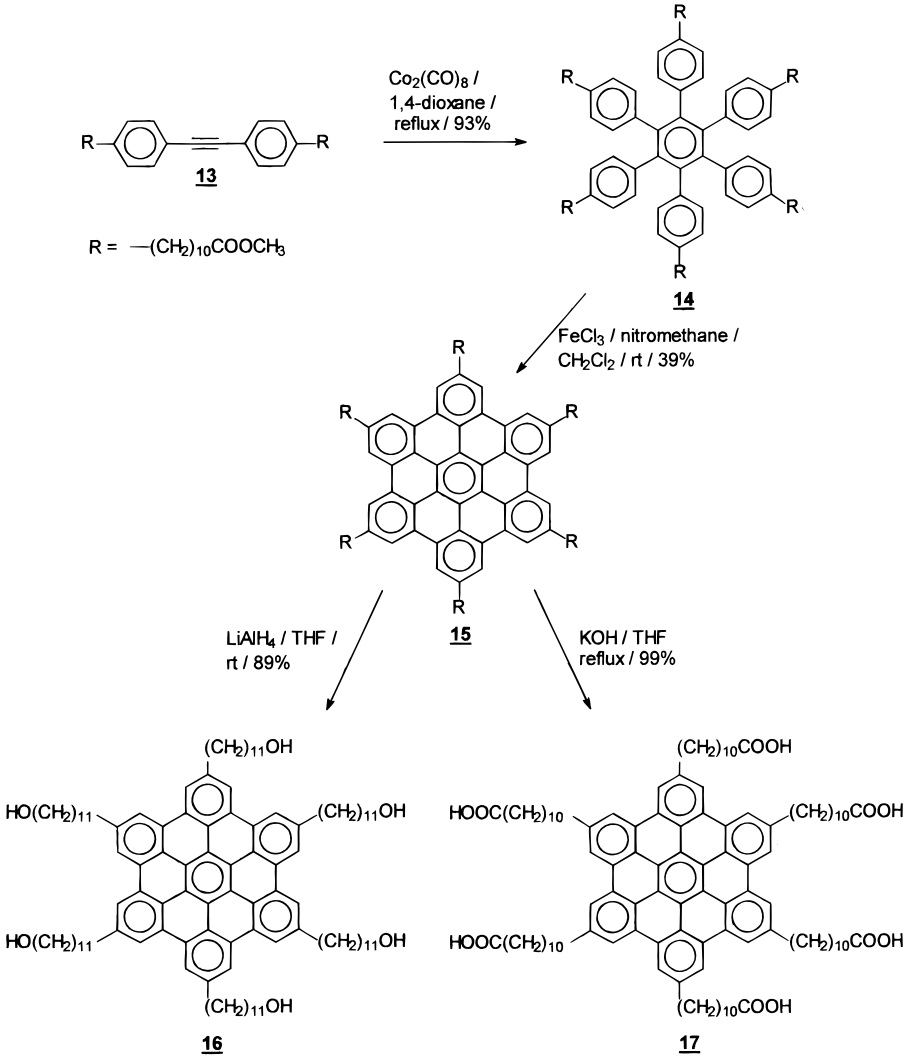


Figure 2. Acrylates and methacrylates of HBC.

Scheme 3. Synthesis of Hexa-ω-Functionalized HBCs



atic studies of the aggregation phenomena of HBC derivatives in solution are under way and will be presented elsewhere.

Phase Behavior and Supramolecular Structure. The mesophase behavior of the above-described hexa-*peri*-hexabenzocoronenes **4**−**7** and **15**−**17** was examined by X-ray diffraction, differential scanning calorimetry (DSC), and polarization microscopy (Table 1). In the DSC, typically, one strongly endothermic phase transition was observed during heating at about 70−100 °C, which is attributed to a crystalline−liquid crystalline transition. Once in the mesophase, no other phase transition was observed at temperatures below 350 °C, where decomposition starts. The observed phase transitions were reversible, even though some pronounced supercooling (up to 60 °C) was observed, which led to

Table 1. Optical, Thermal, and Thermodynamic Data of HBC Derivatives (C = crystal, Col_{Ho} = (Ordered Hexagonal) Columnar Mesophase, I = Optically Isotropic Liquid)

compound	transition	T (°C)	ΔH (J g^{-1})
4a	C−Col_{ho}	69[a]	59
	Col_{ho}−I	390[b]	
4b	C−Col	56[a]	46
5a	C−Col_{ho}	100[a]	48
	Col_{ho}−I	413[b]	
5b	C−Col	73[a]	48
6a	C−Col	106[a]	49
	Col−I	410−415[b]	
6b	C−Col	115[a]	48
7a	C−Col_{ho}	108[a]	43
7b	C−Col	108	41
15	C−Col	79[a]	66
	Col−I	370−410[b]	
16	C−Col	158[a]	39
17	C−Col	100−140[a]	13
18	C−Col	75−100[c]	32
	polymerization	140−180[c]	3
19a	C−Col_{ho}	80−97[c]	76
	polymerization	100−210[c]	147
19b	C−Col_{ho}	40−80[c]	66
	polymerization	98−200	105

[a] Phase transition observed by DSC during second heating. [b] Phase transition observed by polarization microscopy. [c] Phase transition observed by DSC during first heating.

only a partial recrystallization in some cases.

This interpretation of the DSC measurements was confirmed by optical microscopy, which was performed using a drop cast film (dichloromethane) of the hexabenzocoronenes **4**−**7** and **15**−**17**. The initially obtained film was only partially crystalline due to fast evaporation of the solvent, thus resulting in a sample of low birefringence at room temperature. The transition into the mesophase was indicated by increased birefringence on heating, but below 200 °C only uncharacteristic textures were observed. Above 200 °C, mostly fanlike textures emerged, indicating the existence of a columnar mesophase, as observed for many other HBC derivatives (Figure 3).[17] At temperatures of about 400 °C, a transition into an optically isotropic phase was observed. Fast cooling of the liquid induced—sometimes after pronounced supercooling—a transition back into the mesophase without noticeable decomposition resulting in large fanlike domains.

Temperature-dependent X-ray diffraction of the HBC derivatives **4**−**7** and **15**−**17** indicates that they are best described as crystalline at room temperature even though the alkyl chains are not well-ordered in most cases. At temperatures above the strongly endothermic transition observed in the DSC, the diffraction pattern changes and the typical diffraction pattern of an ordered hexagonal columnar structure are detected. The reciprocal spacing of the first three or four reflexes follows the ratio 1:$\sqrt{3}$:$\sqrt{4}$:$\sqrt{7}$ and they can be indexed as 10, 11, 20, and 21 reflexes of a two-dimensional hexagonal lattice (see for example the pattern due to **4a** in Figure 4, Table 2). At about 1/4.7 Å^{-1} a broad halo is observed, which is due to the liquidlike correlation of the alkyl chains. The 001 reflex at about 1/3.5−1/3.6 Å^{-1} indicates the periodic stacking of the molecules within the columns.

Polymerization Experiments. As mentioned in the Introduction, the aim of this work is to fix the supramolecular order of the mesophase by polymerization. In principle, photopolymerization has the advantage that the polymerization can be initiated at any temperature. For instance, the system can be macroscopically ordered in the mesophase and subsequently photopolymerized.[10,11] However, in the case of monomers based on e.g. phthalocyanines or porphyrins which show an absorption band in the same range as the photoinitiator, photopolymerization is not successful.[13,23] In addition,

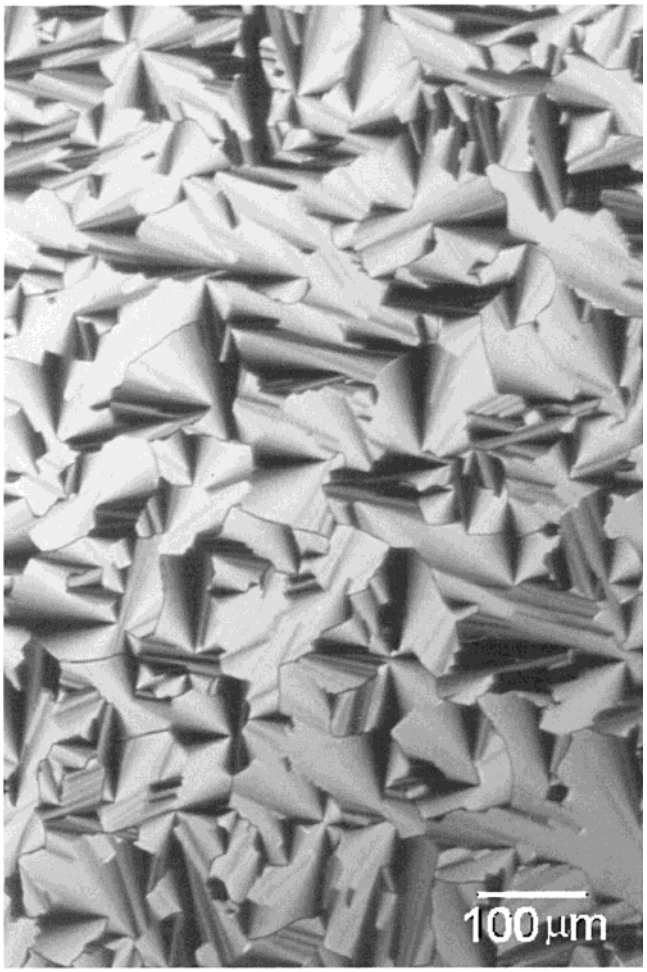


Figure 3. Typical optical textures of the hexagonal discotic mesophase observed for **6a** under polarized light (crossed polarizers) at 366 °C (cooling).

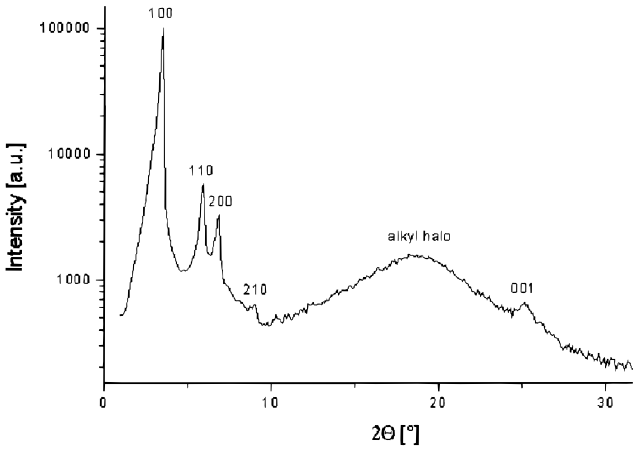


Figure 4. X-ray powder diffraction pattern for the HBC derivative **4a** at 160 °C (cooling).

Table 2. Lattice Spacings Obtained by X-ray Diffraction

compound	*h*	*k*	*l*	*d* (Å)	lattice constant (Å)		*T* (°C)
4a	1	0	0	25.3	$a = 29.2$	Col_{ho}	160
	1	1	0	14.7			
	2	0	0	12.8			
	2	1	0	9.7			
	0	0	1	3.53	3.53		
5a	1	0	0	25.2	$a = 29.1$	Col_{ho}	170
	1	1	0	14.5			
	2	0	0	12.4			
	0	0	1	3.56	$c = 3.56$		
5b	1	0	0	24.7	$a = 28.5$	Col_{ho}	170
	1	1	0	14.3			
	2	0	0	12.4			
	0	0	1	3.56	$c = 3.56$		
17	1	0	0	26.4		Col_o[a]	170
	1	1	0	16.3			
	2	0	0	14.8			
	0	0	1	3.53			
poly19a	1	0	0	27.3	$a = 31.5$	Col_{ho}	30
	1	1	0	15.8			
	0	0	1	3.61	$c = 3.61$		
poly19b	1	0	0	28.3	$a \approx 32.3$	Col_{ho}[b]	30
	1	1	0	15.9			
	0	0	1	3.52	$c = 3.52$		

[a] Slight distortion from the hexagonal structure. [b] The 110-reflex is unusually broad indicating a slight distortion from the hexagonal structure.

during our attempts at photopolymerization of the HBC derivative **19a**, we observed that the original, light yellow material turned brownish, indicating some decomposition of the material, presumably due to absorption by HBC at the wavelength of the UV lamp.

Therefore, we concentrated on the thermally initiated polymerization of the monomers. The polymerization experiments were carried out in the DSC apparatus under an inert nitrogen atmosphere. The conversion of the acrylates/methacrylates to the corresponding polymer was calculated from the heat of polymerization using the literature known values for acrylates (78 kJ mol^{-1}) and methacrylates (60 kJ mol^{-1}), respectively (integration of the DSC exotherms).[11,24] DSC control of the thermal polymerization of the monoacrylate **18** was already shown to succeed without an initiator. However, the observed polymerization enthalpies (3 J/g) were rather low and the degree of conversion amounted to only 5% of the double bonds. Nevertheless, even this relatively low conversion has a strong influence on the phase behavior of the material. In the first heating cycle of **18**, the transition from the crystalline into the liquid crystalline phase occurs at 89 °C with a transition enthalpy of 32 J/g which is typical for most of the HBC derivatives we have investigated to date.[17] After polymerization the transition temperature is reduced to 56 °C and the transition enthalpy is 37 J/g. Because of the low solubility of **poly18**, GPC analysis gave no reliable result, but MALDI-TOF MS analysis of **poly18** proved the existence of oligomers up to tetramers (here, the notation **poly18**, **poly19a**, and **poly19a** refers to polymers produced from the respective monomer**)**.

DSC control of the thermal polymerization of **19a** and **19b** showed that no initiator is needed to achieve a high conversion (Figure 5), with a polymerization degree

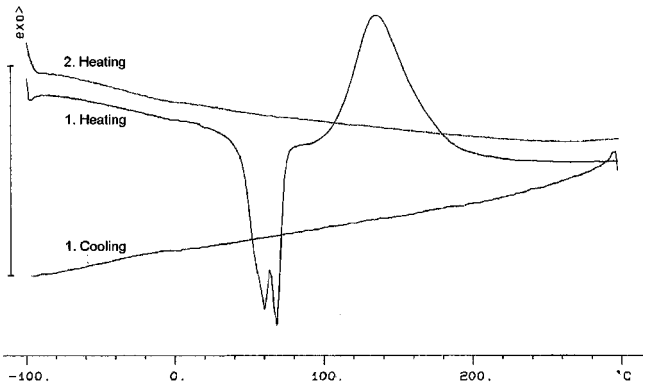


Figure 5. DSC control of the thermal polymerization of the **19b** indicating a conversion rate of about 57%.

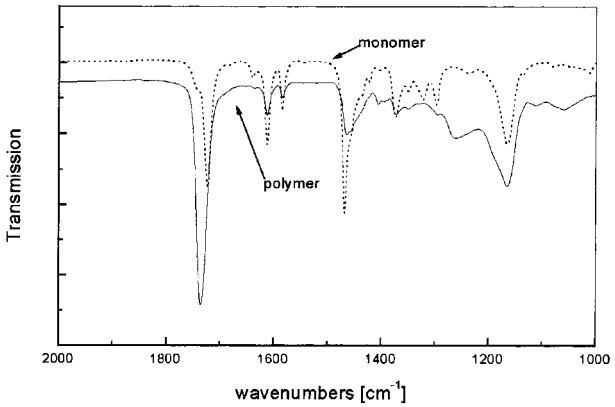


Figure 6. IR-spectra of **19a** and after polymerization of **19a**.

being found to equal 60% and 57% of double bonds, respectively, corresponding to 3−4 polymerized groups per molecule. Such a high degree of polymerization prevents any further phase transitions after the formation of the network, as evidenced that no glass transition was observed even down to temperatures as low as −50 °C. In addition, the brittle 3D network obtained did not show any solubility even at high temperature, prohibiting further characterization of the product by GPC or MALDI-TOF MS.

The high yield of polymerization of **19a**/**b** was further confirmed by IR spectroscopy (Figure 6) which showed that the intensity of the characteristic band due the acrylate double bond at 1639 cm^{-1} was significantly reduced, while the absorption of the carbonyl group was shifted from 1724 to 1736 cm^{-1}.

X-ray diffraction at room temperature of **poly19a** and **poly19b** showed that both compounds form highly ordered hexagonal columnar structures as indicated by the clearly detectable 100, 110, and 001 reflexes (see for example Figure 7), even though the aromatic cores are strongly interconnected in the three-dimensional network. Moreover, this structure exists at least between −50 °C and about 300 °C, the latter corresponds to the onset of the thermal decomposition of the material and, in addition, even after several weeks no change in the X-ray pattern could be observed.

Discussion

The HBC derivatives **4**−**7** and **15**−**17** described in this paper all form very stable Col_{ho} phases independent of the nature and number of functional groups. In the

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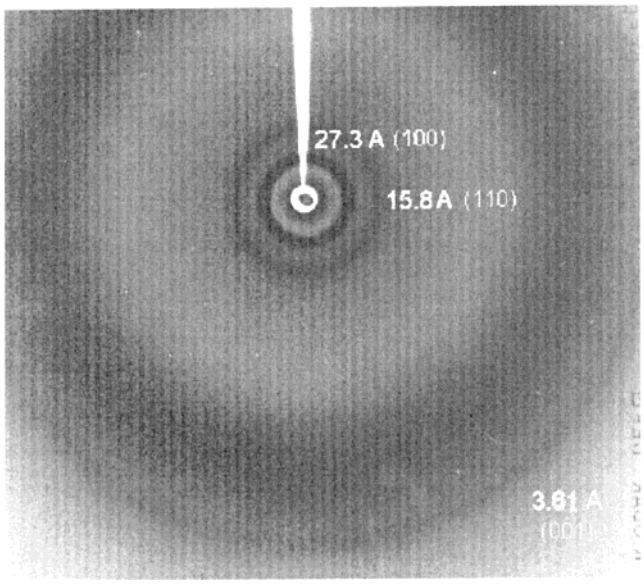

Figure 7. X-ray powder diffraction pattern for **poly19a** at 30 °C.

case of the acrylate derivatives **18a**/**19a** and methacrylate derivative **19b**, respectively, spontaneous thermal polymerization occurs in the mesophase. The low degree of conversion of **18a** is probably due to the high viscosity of the monomer and the relatively low concentration of polymerizable groups. In the case of **19a** and **19b** the relative concentration of polymerizable groups is strongly increased. We expect this effect to lead to higher conversion and thereby the formation of a highly cross-linked 3D network. X-ray analysis of **poly19a** and **poly19b** unambiguously shows that the ordered hexagonal columnar structure of the mesophase is maintained in the polymer (Figure 7), indicating that the strong $\pi-\pi$ interaction of the aromatic core dominates the packing behavior. The cross-linked alkyl chains are on one hand flexible enough to enable a well-ordered hexagonal packing, but on the other hand they are short and stiff enough to prohibit any phase transitions. In contrast, cross-linking of polymers consisting of acrylate/methacrylate based triphenylene monomers results in loss of supramolecular order.[5,8] We believe that the stability of the mesophase, due to the strong $\pi-\pi$ interaction of the extended aromatic cores of HBC derivatives, prevents the destruction of supramolecular order during the polymerization process due to, for instance, volume shrinkage during the polymerization.[24]

Conclusion

In this paper, we have described the regiospecific synthesis of mesomorphic alkyl-substituted HBC derivatives with up to six alkyl groups terminally functionalized with carboxylic ester, carboxylic acid, and hydroxy groups. Furthermore, introducing acrylic and methacrylic groups gives access to networks, whereby the hexagonal ordered columnar superstructure of the mesophase is preserved. We have previously shown that low molecular mass derivatives of liquid crystalline HBCs can be aligned by mechanical shearing, e.g. by extrusion to a fiber. The diffraction pattern of these fibers proved that the orientation of the columns is along the fiber axis.[17] Having at hand polymerizable mesogenic HBC derivatives such as **19a** and **19b,** it should now be possible to align them mechanically to combine the fixed microscopic order within a uniform macroscopic orientation. This may provide thermally and mechanical stable systems for one-dimensional charge transport.

Acknowledgment. Financial support by the European Commission (TMR-Program Sisitomas) and by the Volkswagen Stiftung is gratefully acknowledged.

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