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Star-Shaped Hexa-*peri*-hexabenzocoronene "Heptamer": Synthesis and Self-Assembly

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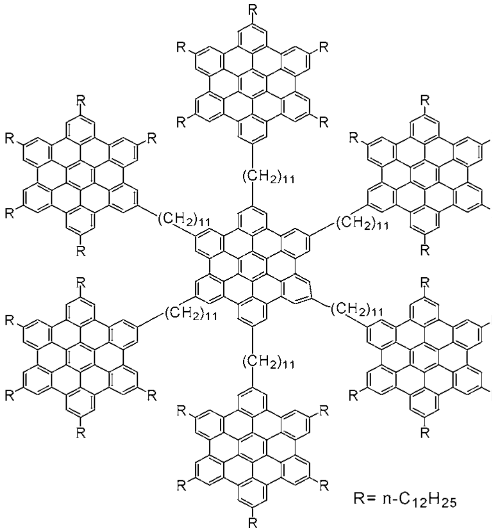
ABSTRACT



A star-shaped hexa-*peri*-hexabenzocoronene "heptamer" was prepared, which showed a strong tendency to aggregate in solution and in the bulk states. Higher order was found in a high-temperature, columnar liquid crystalline phase due to the higher mobility of the molecules in comparison with the low-temperature solid. In addition, physical gel formation was observed due to the presence of covalent intercolumnar interactions.

Columnar liquid crystals based on disc-like mesogens such as triphenylene, porphyrin, phthalocyanine, and hexa-*peri*-hexabenzocoronene (HBC) have attracted attention due to their remarkable self-assembling properties and promising applications as charge transporting materials in organic electronic devices.[1] Incorporation of these discotics into the main chain or side chain of polymers has resulted in a new class of liquid crystalline materials.[2] The large aromatic core of HBC derivatives leads to high order parameters in the mesophase and to high photoconductivities.[3] However, one-dimensional topologically extended *para*- and *ortho*-connected HBC oligomers and polymers showed less ordered columnar structures presumably due to the linker stiffness

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[1] (a) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267−1300. (b) Bushby, R. J.; Lozman, O. R. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 569−578. (c) Simpson, C. D.; Wu, J.; Watson, M. D.; Müllen, K. *J. Mater. Chem.* **2004**, *14*, 494−504. (d) de la Torre, G.; Nicolau, M.; Torres, T. In *Phthalocyanines: Synthesis, Supramolecular Organization and Physical Properties (Supramolecular Photosensitive and Electroactive Materials)*; Nalwa, H. S., Ed.; Academic Press: New York, 2001.

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and large intermolecular torsion angles.[4] On the other hand, an HBC dimer **1** (Figure 1) connected by a flexible, aliphatic alkyl chain displayed an ordered hexagonal columnar LC phase similar to that of hexakis(*n*-dodecyl)-*peri*-hexabenzocoronene (**HBC-C$_{12}$**).[5] Thereby, the dimer **1** suppressed the room-temperature crystalline phase found in **HBC-C$_{12}$** and gelated organic solvents such as toluene, suggesting the existence of intercolumnar physical cross-linking. Gel formation has been widely observed in hydrogen-bonded π-conjugated discotics and oligomers due to the H-bonding, $\pi-\pi$ interactions, and dipole−dipole interactions;[6] however, non-H-bonded aromatic compounds rarely formed gels.[7] To further understand the structure−property relationships, a star-shaped HBC “heptamer” **2** (heptamer of HBC units) in which seven HBC units are connected by flexible aliphatic chains in a hexagonal symmetry was synthesized and self-assembly in solution, bulk-state and gel-state was studied.

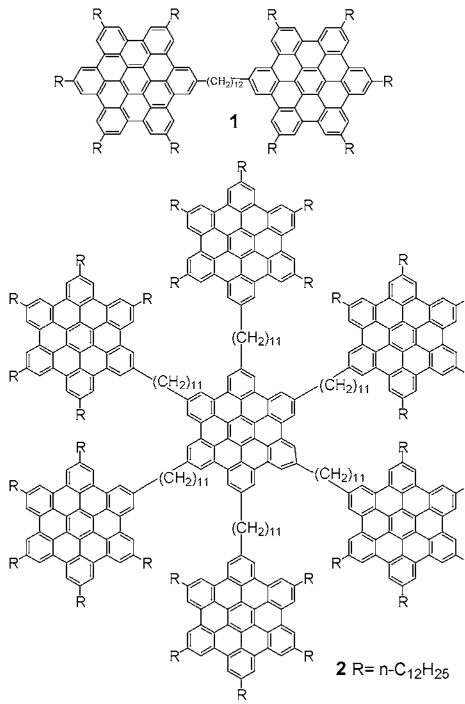
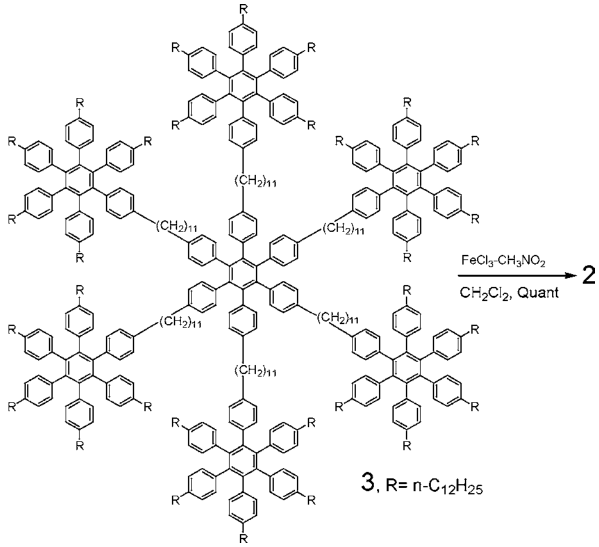


Figure 1. Chemical structures of compounds **1** and **2**.

HBC derivatives have been conventionally synthesized by oxidative cyclodehydrogenation of the corresponding hexaphenylbenzene (HPB) precursors.[8] As such, the key step toward molecule **2** was the synthesis of the star-shaped HPB heptamer **3**, which was then treated with FeCl$_3$, dissolved in CH$_3$NO$_2$, affording compound **2** in quantitative yield (Scheme 1).

Scheme 1. Synthesis of HBC Heptamer **2**



A divergent approach was used to prepare the precursor **3** (Scheme 2). Pd-catalyzed Kumada coupling of the 1-bromo-4-trimethylsilylbenzene (**4**) with freshly prepared 11-magnesium bromoundec-1-ene (**5**) afforded trimethyl-(4-undec-10-enyl-phenyl)-silane (**6**) in 84% yield. Transformation of the olefin in **6** into alkylborane by treating with 9-BBN and subsequent Suzuki coupling[9] reaction with bis(4-bromophenyl)acetylene **7** [10] gave compound **8** in 54% yield. The hexaphenylbenzene derivative **9** carrying six trimethylsilyl (TMS) groups was then synthesized by dicobalt octacarbonyl catalyzed cyclotrimerization of **8** in refluxing dioxane in 81% yield. Attempts at preparing compound **9** by 6-fold Suzuki coupling reactions between hexakis (4-bromophenyl)benzene[11] and the borane compound of **6** failed due to the instability of the TMS groups under basic conditions. The TMS groups in **9** were then converted to iodides by treating with iodine monochloride to obtain molecule **10** in high yield (90%). Six-fold Sonogashira coupling of **10** with 4-*n*-dodecylphenylacetylene afforded **11** in 66% yield. The target compound **3** was then obtained by 6-fold [4 + 2] Diels−Alder cycloaddition between **11** and tetrakis(4-dodecylphenyl)cyclopentadienone (**12**) in 70% yield.

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(6) (a) Tamaru, S.; Nakamura, M.; Takeuchi, M.; Shinkai, S. *Org. Lett.* **2001**, *3*, 3631−3634. (b) Ikeda, M.; Takeuchi, M.; Shinkai, S. *Chem. Commun.* **2003**, 1354−1355.

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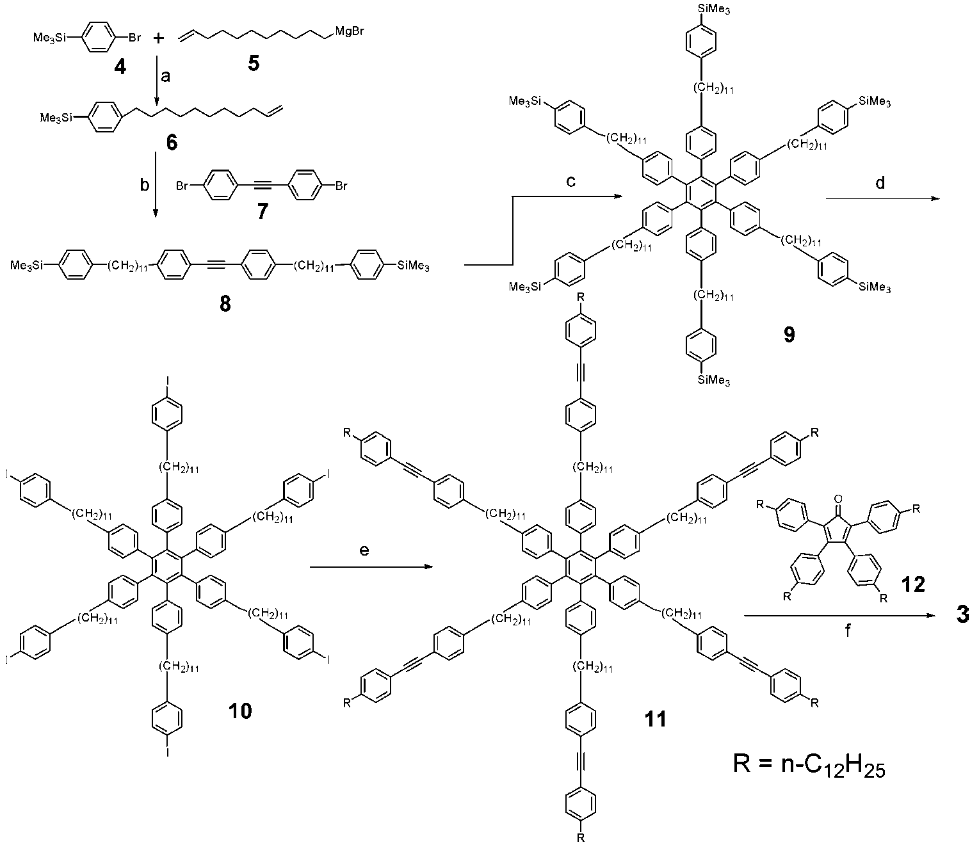
(10) Pisula, W.; Tomovic, Z.; El Hamaoui, B.; Watson, M. D.; Pakula, T.; Müllen, K. *Adv. Funct. Mater.* **2005**, *15*, 893−904.

(11) Wu, J.; Watson, M. D.; Müllen, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 5329−5333.

Scheme 2. Synthesis of Compound **3**[a]



[a] Reaction conditions: (a) Pd(dppf)Cl_2, THF, rt, 84%; (b) 9-BBN, NaOH, Pd(dppf)Cl_2, 54%; (c) $Co_2(CO)_8$, dioxane, reflux, 81%; (d) ICl, $CHCl_3$, 90%; (e) 4-*n*-dodecylphenylacetylene, Pd$(PPh_3)_4$, CuI, piperidine, 55 °C, 66%; (f) diphenyl ether, reflux, 70%

All intermediate compounds were well characterized by mass spectroscopy, microanalysis, and NMR spectroscopy (Supporting Information). The complete cyclodehydrogenation (loss of 84 H) of **3** was confirmed by MALDI-TOF mass spectrum of **2** for which only one sharp molecular ionic peak at 9624 was observed (Supporting Information). Compound **2** is soluble in organic solvents such as THF and toluene. Solution NMR measurements revealed, however, only a weak and broad resonance at the aromatic region even at higher temperatures (130 °C) for long time (2 days) (Supporting Information). This can be explained by aggregation of the HBC molecules induced by strong π-stacking and intercolumnar interactions (vide infra).

In comparison with a hexakis(3,7-dimethyloctyl)-*peri*-hexabenzocoronene[12] (**HBC-C$_{8,2}$**, inset in Figure 2), which has good solubility in normal organic solvents and well-resolved UV−vis and fluorescence spectra, the HBC heptamer **2** in toluene showed broad absorption and emission bands (Figure 2). Hyperchromic shift (ca. 9 nm) in absorption and a large bathochromic shift (more than 40 nm) in the fluorescence spectrum of **2** were observed, suggesting strong face-to-face π-interactions between the HBC units. The long-wavelength band is assigned to excimer emission as found in other π-aggregates.[5] With increasing concentration, the relative intensity of the shoulders at 594−599 nm increased, indicating a larger size of the aggregates at higher concentrations.

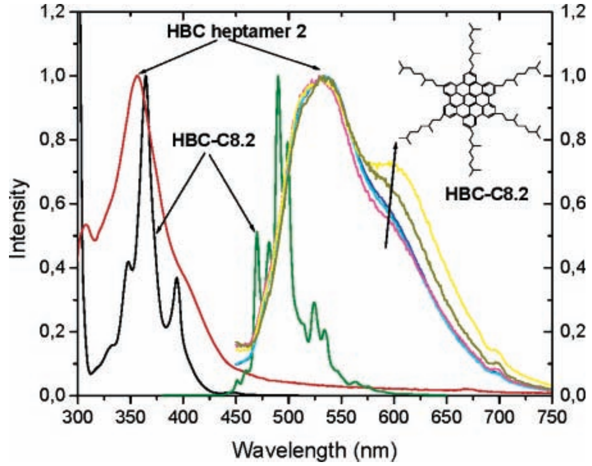


Figure 2. Normalized UV−vis absorption spectra of **HBC-C$_{8,2}$** (black) and **2** (red) in toluene. Fluorescence spectra of **HBC-C$_{8,2}$** (green) and **2** (cyan to yellow). The arrow at 594−599 nm indicates trend with an increase on concentration.

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[12] Fechtenkötter, A.; Tchebotareva, N.; Watson, M. D.; Müllen, K. *Tetrahedron* **2001**, *57*, 3769−3783.

The thermal behavior of the HBC heptamer **2** in the bulk state was investigated by means of differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffractometry (XRD). The second DSC heating scan of **2** revealed a broad endothermal peak at 35 °C that corresponds to the transition from the solid state into the mesophase. After annealing **2** at 400 °C for 1 h under argon, fanlike textures were obtained under POM (Figure 3), suggesting the formation of a hexagonal, ordered, columnar liquid crystalline phase (D_h).

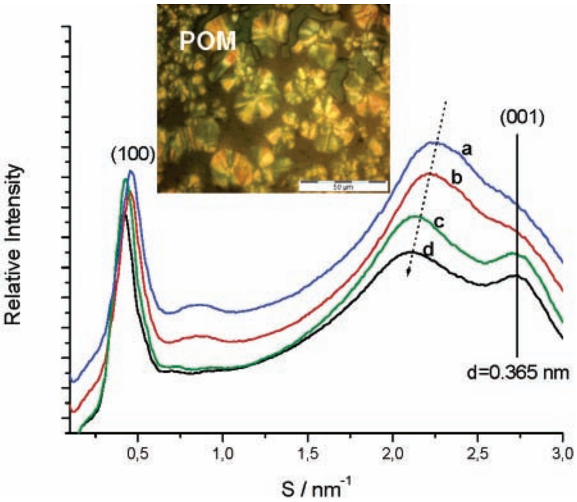

Figure 3. Wide-angleXRD patterns of **2** at (a) room temperature, (b) heating to 100 °C and then cooling to room temperature, (c) 100 °C, (d) 150 °C. Inset is the POM image of **2** after annealing at 400 °C for 1 h, showing fan-shaped textures.

Wide-angle XRD measurements on solid sample **2** were performed at different temperatures (Figure 3). In all cases, a sequence of reflections at small angle region were observed and their reciprocal space distances disclosed a ratio of 1:2:$\sqrt{3}$, indicating a hexagonal two-dimensional lattice of the HBC columns. With increasing temperature, the unit cell parameter also (i.e., the intercolumnar distance) increased from 2.48 nm at room temperature to 2.68 nm at 100 °C and 2.77 nm at 150 °C. This tendency is expected for discotic LCs and can be explained by the higher mobility of both HBC molecules and alkyl chains at higher temperatures. The broad halos found at ca. 4.3−4.8 Å were assigned to the alkyl chain interactions and displayed a similar temperature dependence.

The single alkyl chain substituted HBCs typically show long-range, ordered columnar superstructures at room temperature and less ordered columnar LC phases at high temperatures as indicated by the sharpness and intensity of the (001) reflections in the wide-angle region.[13] In contrast, the HBC heptamer **2** exhibited the reverse behavior. For example, at room temperature, only a weak and broad (001) reflection at ca. 3.65 Å due to the intracolumnar π-stacking distance was observed. Upon heating, this reflection became sharper and the relative intensity increased, suggesting a longer-range columnar order at higher temperatures. When the sample was cooled to room tempearure, the sharp (001) reflection peaks became weak again. In addition, the monomer **HBC-C$_{12}$** has a highly ordered crystalline phase below 60 °C, but the star-shaped HBC heptamer only displayed a less ordered solid phase at room temperature. This is reasonable because the HBC units in **2** are covalently linked by flexible aliphatic chains and an ideal “top-on-top” super seven-HBC-column structure is entropically disfavored; thus, statistical intramolecular stacking and intercolumnar cross-linking by $\pi-\pi$ interactions will each occur in the solid phase at low temperature, leading to a disordered structure. However, at higher temperatures, the HBC units become highly mobile, such self-healing behavior resulting in more ordered columnar structure at higher temperatures. Similar star-shaped triphenylene heptamers have been reported,[14] where covalent connection of triphenylene suppressed the crystallization of triphenylene derivatives; however, a detailed study of the temperature dependence was not made.

Gel formation was observed for HBC heptamer **2** in *n*-heptane and toluene, respectively, with a concentration of 10 g/L. The gel structure formed in toluene was a kind of colloidal, three-dimensional architecture with cross-linked aggregates as the frame of the architecture (Supporting Information), suggesting strong intra- and intermolecule $\pi-\pi$ interactions between HBC units. It should be noted that such gel formation occurred mainly due to $\pi-\pi$ interactions, but without any additional H-bonding or dipole−dipole interactions!

In summary, a novel star-shaped HBC heptamer **2** was synthesized by a facile procedure. Compared to the monomer **HBC-C$_{12}$**, the heptamer **2** showed different self-assemblying motifs, for example, suppression of the crystallization at low temperature and formation of long-range order phase at higher temperatures. Organic solvents could also be gelated by heptamer **2**, from which the gelation was mainly induced by $\pi-\pi$ interactions. Charge transport through the multiply self-assembled HBC columns is currently under investigation.

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Supporting Information Available: Synthetic procedures and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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