Self-assembly of amphiphilic imidazolium-based hexa-*peri*-hexabenzocoronenes into fibreous aggregates†

Bassem El Hamaoui,[a] Linjie Zhi,[a] Wojciech Pisula,‡[a] Ute Kolb,[b] Jishan Wu*[a] and Klaus Müllen*[a]

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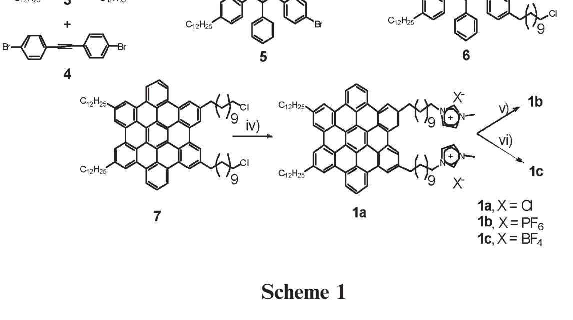
Imidazolium-based amphiphilic hexa-*peri*-hexabenzocoronenes were synthesized and shown to undergo ordered columnar self-assembly in solid-state as well as in solution to yield defined nanofibers upon solution drop casting onto solid substrate.

Self-assembled π-conjugated systems have attracted interest because of their potential applications in "supramolecular electronics", *e.g.* field-effect transistors, photovoltaics, and light-emitting diodes.[1] The self-assembly of such systems is a consequence of combined forces including π-stacking, hydrogen bonding and hydrophobic–hydrophilic interactions. This leads to the formation of defined objects on the nanoscale, which are commonly referred to as "nanostructures". Various π-conjugated polymers and oligomers self-assemble into "one-dimensional" architectures known as nanofibers.[1b] However, the control of their shape and size remains still a challenge.[2,3]

Discotic liquid crystals based on disc-like polycyclic aromatic hydrocarbons such as triphenylenes and hexa-*peri*-hexabenzocoronenes (HBC) give rise to ordered columnar structures in the solid-state due to strong π-interactions between the aromatic cores.[4] Along the columnar axis, high charge carrier mobilities have been determined.[5] Amphiphilic HBCs, in which the HBC core is hexasubstituted by hydrophilic branched ethylene oxide chains, show an enhanced phase separation that induces strong aggregation of the discs either in the solid-state or in polar solvents.[6] An amphiphilic HBC molecule with C_{2v} symmetry has been reported to self-assemble into uniform nanotubes, which, after doping, show conductivities comparable to inorganic semiconducting nanotubes.[7] Hexaalkyltriphenylenes exhibited long-range liquid-crystalline phases after attaching the imidazolium units at the periphery of the discs.[8] Additionally, the presence of both hydrophilic and hydrophobic groups in amphiphilic molecules and polymers resulted in the formation of ordered smectic and nematic phases.[9]

In this communication, novel amphiphilic HBC molecules (**1a**, **1b** and **1c**) carrying two hydrophobic dodecyl chains on one side and two hydrophilic groups, which consist of alkyl chains terminated with ionic imidazolium salts, on the opposite side of the HBC core have been synthesized (Scheme 1). Compared to the triphenylene imidazolium salts, compounds **1a**, **1b** and **1c** consist of a larger aromatic disc with lower symmetry. The amphiphilicity of the HBCs **1a–c** is introduced by the alkyl side chains, on the one side, and the imidazolium salts on the other. The solid-state packing was investigated by 2D-wide-angle X-ray scattering techniques. In such systems, combined secondary forces such as π-stacking of the HBC cores and ion–ion interactions (between imidazolium salts) are important factors to establish organization and stability of the system during the self-assembly process. In addition to the charge transport through the HBC columns, the imidazolium salts may also exhibit ionic channels.[10] It was found that instead of forming nanotubes, these molecules self-assembled into nanofibers, whereby their size and shape were influenced by the evaporation of the solvents.

1a was synthesized according to Scheme 1. The tetrasubstituted tetraphenylcyclopentadienone **3** was obtained according to literature procedures.[11] Diels–Alder cycloaddition of 3,4-bis(4-dodecylphenyl)-2,5-diphenylcyclopentadienone **3**[12] and bis(4-bromophenyl)acetylene **4**[13] afforded 1,2-bis(4-bromophenyl)-4,5-bis(4-dodecylphenyl)-3,6-diphenylbenzene (**5**) in 68% yield. 1,2-Bis(4-(11-chloroundecyl)phenyl)-4,5-bis(4-dodecylphenyl)-3,6-diphenylbenzene (**6**) was synthesized in 60% yield by Pd-catalyzed Suzuki cross-coupling reaction[14] between **5** and freshly prepared organoboranes, which were obtained from the reaction of 11-chloroundecene with 9-borabicyclo[3.3.1]nonane (9-BBN). Oxidative cyclodehydrogenation of precursor (**6**) afforded the corresponding hexa-*peri*-hexabenzocoronene (**7**) in 55% yield. Bis(imidazolium)HBC (**1a**) was then prepared in good yield by heating compound **7** in *N*-methylimidazole overnight followed by precipitation in hexane and washing with dichloromethane. For the preparation of other salts, **1a** was reacted with aqueous solutions of NH_4PF_6 or NH_4BF_4 to afford **1b** and **1c**, respectively.



Scheme 1

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[a] *Max Planck Institute for Polymer Research, Ackermannweg 10, 55128, Mainz, Germany. E-mail: muellen@mpip-mainz.mpg.de; jishan@mpip-mainz.mpg.de; Fax: (+49) 6131 379 351; Tel: (+49) 6131 379 150*

[b] *Institute of Physical Chemistry, Johannes Gutenberg University, Welderweg 11, 55099, Mainz, Germany*

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‡ Present address: Degussa AG, Process Technology & Engineering, Process Technology – New Processes, Rodenbacher Chaussee 4, D- 63457 Hanau-Wolfgang, Germany.

The supramolecular organization of **1a**, **1b** and **1c** was studied by two-dimensional wide-angle X-ray scattering (2D-WAXS).[15] For structural investigations, filaments were prepared by mechanical extrusion.[16] Determined by differential scanning microscopy (DSC), the HBC-imidazolium species **1a** did not show any phase transitions up to the isotropization temperature at 260 °C, which demonstrates a stable solid-state structure. The polarized optical microscopy showed no phase transition up to 270 °C.

The 2D-WAXS pattern of **1a** displayed a series of strong reflections indicating a well-defined supramolecular order with a pronounced alignment of the columnar structures in the extrusion direction (Fig. 1a). The positions of the equatorial reflections were correlated to a 2D rectangular ordered lattice with parameters a = 4.18 nm and b = 2.87 nm (Fig. 1b), describing the intercolumnar arrangement. The meridional reflections suggested an orthogonal packing of the discs with respect to the columnar axis with a disc-to-disc period of 0.36 nm. Presumably, the phase segregation induced by the hydrophilic imidazolium salts and hydrophobic alkyl chains caused these C_{2v} symmetric molecules to form layer-like structures (schematic illustration in Fig. 1c). The packing parameter a describes the distance between layers, whereas b is the period between every HBC disc along such a layer.

In contrast to **1a**, precursor **7**, which bears no imidazolium groups, exhibited temperature dependent bulk properties (Fig. S1†). Above 190 °C, the material showed a liquid crystalline phase with hexagonally arranged columns (a' = 4.39 nm). A 2D rectangular ordered lattice (a = 3.84 nm, b = 2.22 nm) was observed below this temperature, but the packing parameters differed from those of **1a**. The marked difference in the intracolumnar arrangement between **1a** and its precursor **7** illustrates again the significant influence of the two imidazolium groups on the self-assembly and supports the proposed supramolecular order.

The equatorial reflections of HBCs **1b** and **1c** correlate to an orthorhombic lattice, which is virtually identical to **1a** (Fig. S2†). Evidently, the replacement of the chloride anions by BF_4^- and PF_6^- did not influence the intracolumnar packing of the HBCs. Upon increasing the temperature, no structural change appeared. This was not surprising since the counter ion is not connected directly to the HBC core, but only to the imidazolium cation through ionic interactions.

1a showed poor solubility in solvents like CH_2Cl_2 and THF even at elevated temperature, whereas it was slightly soluble in DMF. However, the compound was soluble in both DMSO and water after heating. The UV-vis spectroscopic measurements of compound **1a** in DMSO and water revealed different aggregation behavior in these two solvents (see below).

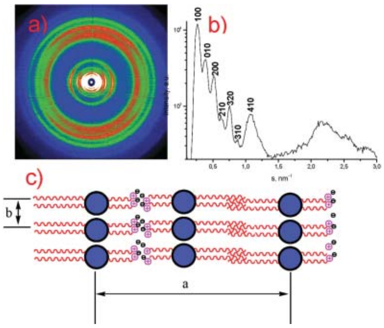

Fig. 1 (a) 2D-WAXS pattern and (b) equatorial intensity distribution from an extruded fiber of compound **1a** at room temperature; (c) suggested packing model of molecules in the solid sate (top view).

^{1}H NMR spectroscopy of **1a**, **1b** and **1c** showed that the signal of the hydrogen atom corresponding to C2 of the imidazolium ring in **1a** was shifted to lower field ($\Delta\delta$ = 0.07 ppm) than the analogous signals in **1b** and **1c** (Fig. S3†). This is presumably a consequence of weak hydrogen bonding between Cl^- and C(2)–H, which is absent for BF_4^- and PF_6^-.[17,18] The weak band at 3055 cm^{-1} in the infrared spectrum of **1a** supports this conclusion (Fig. S4†).[18,19] The latter band was not observed in the spectra of **1b** and **1c** probably because PF_6^- and BF_4^- are only weakly coordinating anions as observed in the literature.[20]

The morphology of **1a** under different preparation conditions was then studied. Slow solvent evaporation of a solution of **1a** in DMSO (1 mg mL^{-1}) on a silicon wafer resulted in tree-like fiber structures (Fig. S5a†), whereby their size was irregular. When ethanol was added slowly to a solution of **1a** in DMSO, and it was allowed to stand for several days, a cloudy precipitate appeared. After complete evaporation of the solvent, scanning electron microscopy (SEM) measurements showed fiber-like nanostructures (Fig. S5b†) that were characterized by transmission electron microscopy (TEM) (Fig. 2a). Uniform individual nanofibers with diameters of about 6 nm were observed. This is about two times the lateral size of molecule **1a**, indicating an assembly of two or three HBC columns. This arrangement would allow the formation of fibers, in which the hydrophobic units lie in the inner part and the hydrophilic polar heads (the imidazolium salts) remain outside (in the hydrophilic medium).[21]

Interestingly, when water was used instead of DMSO, solution drop casting on a SiO_2 substrate and slow evaporation of the solvent provided regular fibers with diameters ranging between 200 and 300 nm (Fig. 2b). Although these fibers are highly sensitive to the electron beam, an electron diffraction pattern with distinct reflections could be obtained rapidly on a single fiber (Fig. 2c) indicating high supramolecular order. Further characterization is in progress. Slow diffusion of hexane (vapor into a saturated chamber) into a solution of **1a** in water led to a precipitate composed of uniform fibers with diameters of around 10–15 nm and lengths of up to several micrometers (Fig. 2d). Additionally, **1a** DMSO–water

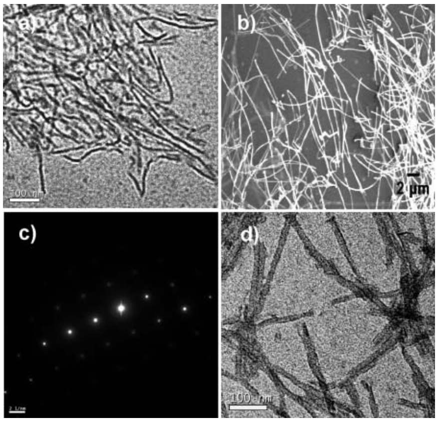

Fig. 2 SEM (b), TEM (a, c) and electron diffraction (c) images after drop-casting of **1a** on SiO_2 (followed by evaporation of solvent): (a) from DMSO–ethanol solution; (b) from water solution; (c) electron diffraction pattern of a single fiber displayed in (b); (d) from water solution in a hexane saturated chamber.

solution afforded nanofibers after solvent evaporation (Fig. S5c†). These results suggested that the diameters of the nanofibers consisting of **1a** can be influenced by the nature of the solvent from which they precipitate. The phase separation induced by the presence of imidazolium halide ions in the corona of the HBC core favored different self-assembly behavior compared to HBCs having ethylene glycol chains (EGC) together with isothiouronium. This is because the self-assembly of the latter HBCs themselves is due to the presence of (EGC) and not due to the ions around as described by Aida *et al.*. This makes imidazolium halide HBCs unique in their properties compared to other amphiphilic ones.

The self-assembly of **1a** into defined nanofibers as shown in Fig. 2 was presumably due to a combination of interactions between the HBC-imidazolium molecules in solution. Since the nature of the solvent influences the nanofiber morphology, the effect of solvent on the aggregation behavior of **1a** in solution was studied by UV-vis and fluorescence spectroscopy. In DMSO (10^{-6} M), typical HBC absorption was found with $\lambda_{\max} = 360$ nm for **1a**, **1b** and **1c**. Upon increasing the proportion of water, the intensities of the bands at 342, 360 and 389 nm all decreased, and a broadening at about 418 nm emerged. This was suggestive of the formation of aggregates in solution (Fig. 6a†).

An isobestic point around 407 nm was observed, indicating a linear dependence of the two bands at 390 and 418 nm. Moreover, the concentration dependent measurement of **1a** in 9 : 1 water–DMSO mixture showed a decrease of the band intensities at high concentration, suggesting a strong aggregation tendency in solution (Fig. S7†). The fluorescence spectra of **1a** in a mixture of DMSO and water with different volume ratios are shown in Fig. 6b.† In pure DMSO, a well-resolved fluorescence spectrum was observed between 470 nm and 600 nm. Upon addition of water, the fluorescence intensity decreased and the emission maximum shifted to longer wavelength. When the DMSO–water ratio reached 4 : 6, an unresolved band centered at 515 nm was observed. The longer wavelength band typically arises from excimer emission,[6b] thus gradual addition of water enhances the hydrophobic interactions and leads to an increase of the size of aggregates.[22,23] Both the UV-vis and fluorescence measurements point toward increasing aggregation with an increasing proportion of water. Therefore, it would seem likely that solvent-related differences in aggregation are responsible for the changes in nanofiber morphology. This behavior correlates well with the reported self-assembly of a hexa-dodecyl substituted HBC derivative.[24] The solubilizing alkyl chains possessed a small steric demand in the periphery of the aromatic disc, which allowed the molecules to approach easily, resulting in a higher aggregation state in a chloroform–methanol mixture.

In conclusion, new amphiphilic HBC molecules have been synthesized. In the solid-state, the molecules packed into layer-like columnar arrangement; while in solution, multiple weak interactions such as π-stacking, hydrophobic and hydrophilic interactions resulted in the self-assembly of HBC discs into defined nanofibers. The corresponding electron diffraction pattern with sharp and strong reflections showed a high supramolecular order and thus indicated the importance of the assistance of water for a slow aggregation procedure. The diameter of the nanofibers was influenced by changing the mixture ratio and the nature of the solvents used for precipitation. Since a high order within the nanofibers has been found due to pronounced aromatic π-stacking and ionic interactions, a high charge carrier mobility and ion conductivity might be expected.

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