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## COMMUNICATION

## Discotic hexa-*peri*-hexabenzocoronenes with strong dipole: synthesis, self-assembly and dynamic studies<sup>†</sup>

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Strong dipole moments have been built into two hexa-*peri*hexabenzocoronene (HBC) derivatives (1 and 2) originating from the push-pull structure of the molecules with one electrondonating and one electron-withdrawing substituent. The influence of dipole moment on the self-assembly of HBCs in solution and in bulk has been investigated.

Discotic liquid crystalline (LC) molecules, which are generally composed of a rigid flat core and a periphery of flexible alkyl substituents, can self-assemble into well-ordered columnar superstructures under the influence of  $\pi$ -interactions.<sup>1</sup> Typical examples are triphenylene and hexa-peri-hexabenzocoronene (HBC) derivatives. Tremendous efforts have been devoted to achieve highly ordered columnar superstructures of discotic molecules in bulk.<sup>2</sup> To this end, additional intermolecular forces, such as hydrogen bonds,<sup>3</sup> amphiphilic<sup>4</sup> and dipole–dipole interactions,<sup>5</sup> are often utilized to improve their supramolecular organization. It has been demonstrated that dipole-dipole forces can effectively stabilize the columnar mesophase of triphenylene and dibenzophenazine derivatives.<sup>5,6</sup> Moreover, stronger dipole-dipole interplay can even assist half-disc shaped mesogens to arrange into well-defined hexagonal columnar LC phases.7

Our previous results encouraged us to introduce even stronger dipole moments at the HBC core (Scheme 1, 1 and 2) with the aim to further improve the stability of the liquid crystalline phase, but simultaneously to ensure pronounced molecular interactions in solution. In this work, we present HBCs 1 and 2 with dipole moments of 8.25 D and 8.64 D, respectively, which are significantly higher than those of the earlier studied HBC derivatives.

The synthesis of 1 and 2 was accomplished through a stepwise substitution of 3 (Scheme S1, ESI<sup>†</sup>) as illustrated in Scheme 1. Based on the different reactivity of iodo- and bromo- groups, compound 3 was mono-cyanated with cuprous

cyanide at 65 °C resulting in 4. The remaining bromo group was then converted into an amino substituent *via* a Buchwald cross-coupling reaction with a diphenyl amine leading to the target compound (1 or 2). The strong aggregation in solution does not allow one to measure the dipole moments of 1 and 2. Therefore, these values were calculated as  $\mu = 8.25$  D for 1 and  $\mu = 8.64$  D for 2 using the Becke three-parameter Lee–Yang–Parr (B3LYP) functional and 6-31G(d,p) basis set in the Gaussian 03 package.<sup>8</sup>

The <sup>1</sup>H-NMR chemical shifts were monitored in  $d_2$ -1,1,2,2tetrachloroethane at different temperatures and concentrations (see Fig. 1). It has been well established that an upfield shift of aromatic proton signals is a signature of intermolecular association involving  $\pi$ -stacking interaction.<sup>9</sup> Interestingly, below 60 °C the peaks for 1 and 2 are broad in sharp contrast to other hexaalkyl-substituted HBC derivatives, suggesting strong intermolecular forces of these HBCs at low temperature.<sup>10</sup> The six different aromatic protons only appear as six sharp singlets above 90 °C indicating the existence of monomeric species at high temperature (Fig. 1a).<sup>11</sup> The signals of the aromatic protons, which are located next to the cyano group in 1 (Ha) and 2 (Hb), are shifted up-field by 0.20 and 0.11 ppm, respectively, when the temperature drops from 140 °C to 30 °C. For comparison, a 0.26 ppm upfield shift of the aromatic proton resonance was observed for the non-polar hexa-dodecyl substituted HBC



**Scheme 1** Synthesis of the dipole functionalized HBCs (1 and 2): (i) CuCN, THF, Pd(PPh<sub>3</sub>)<sub>4</sub>, reflux, 15 h, 81%, (ii) di-tolyl amine, Pd<sub>2</sub>(dba)<sub>3</sub>, *t*-Bu<sub>3</sub>P, sodium butoxide, toluene, 80 °C, 16 h, 79%, (iii) di-4-methoxylphenyl amine, Pd<sub>2</sub>(dba)<sub>3</sub>, *t*-Bu<sub>3</sub>P, sodium butoxide, toluene, 80 °C, 16 h, 74%.

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Fig. 1 Aromatic region of (a) <sup>1</sup>H-NMR spectra recorded at different temperatures of 1 (left) and 2 (right), measured for  $2.05 \times 10^{-2}$  M CDCl<sub>2</sub>CDCl<sub>2</sub> solutions; (b) <sup>1</sup>H-NMR spectra of 1 (left) and 2 (right) recorded at various concentrations, measured for CDCl<sub>2</sub>CDCl<sub>2</sub> solutions at 60 °C, 500 MHz.

(HBC-C12) during cooling from 120 °C to 60 °C.<sup>12</sup> Through the comparison of the temperature dependent <sup>1</sup>H-NMR signals recorded for 1, 2 and HBC-C12, the smaller upfield shifts of 1 (0.20 ppm) and 2 (0.11 ppm) from 140 °C to 30 °C than that of HBC-C12 (0.26 ppm, from 120 °C to 60 °C) over a narrower temperature range indicate a remarkable thermal stability of aggregates formed by 1 and 2. This result undoubtedly validates the improved intermolecular attractive interplay based on additional dipole–dipole interactions.

Upon increasing the concentration from  $1.00 \times 10^{-5}$  to  $2.05 \times 10^{-2}$  M at 60 °C, the resonance of Ha in **1** (Fig. 1b left) is upfield shifted by 0.38 ppm (from 8.89 to 8.51 ppm); and a comparable upfield shift of 0.39 ppm (from 8.93 to 8.54 ppm) is recorded for Hb in **2** (Fig. 1b right), however, within a much narrower concentration range (from  $3.00 \times 10^{-5}$  to  $1.20 \times 10^{-2}$  M). The upfield shifts of the aromatic proton resonances at lower temperatures or in concentrated solutions reflect a typical co-facial molecular stacking of aromatic cores.<sup>12</sup> Obviously, the weaker temperature and stronger concentration dependence observed for **2** reflects an increased stability of the aggregates caused by the larger molecular dipole in comparison to **1**.

The self-association constant  $K_A$  of 1 was calculated as a typical example according to the nearest neighbour attenuated K (AK) model<sup>13</sup> using a non-linear least-squares curve fitting method with the <sup>1</sup>H-NMR experimental data of Ha collected at different concentrations (Tables S1 and S2, ESI†). For comparison, the values for the  $C_3$ -symmetric substituted HBC with three methoxy groups (HBC-OMe) and HBC-C12<sup>14</sup> (Scheme S2, ESI†) are also listed in Table S2.† Both compounds HBC-OMe and HBC-C12 carry less bulky alkyl side chains and are therefore expected to show strong aggregation in solution. Although the calculated chemical shifts for the monomers ( $P_{\alpha}$ ) of all three compounds are identical, the self-association constant ( $K_A$ ) of 1 is more than twice that of HBC-OMe and about three times that of HBC-C12.

values  $(P_{\alpha})$  for all three compounds indicate that the aromatic protons in these monomers are situated in a nearly identical chemical environment. However, the larger  $K_A$  values for 1 and HBC-OMe clearly demonstrate a tendency for molecular aggregation caused by the additional intermolecular dipole-dipole forces. Especially, in the case of 1, the calculated chemical shift of the molecule within a molecular stack  $(P_{\varepsilon})$  is upfield shifted by nearly 1 ppm as compared to either HBC-OMe or HBC-C12. In a face-to-face aggregate of HBCs, the aromatic protons of one molecule are localized in the secondary magnetic field of the neighbouring aromatics which results in a shielding effect. The strength of this effect depends on the size of aggregates.<sup>15</sup> Thus, the  $P_{\varepsilon}$  value of 1 further proves the existence of larger molecular aggregates as compared to HBC-OMe and HBC-C12. Additionally, the parameter  $\varphi$ , which describes the ability of a molecule to form a dimer in the AK model,<sup>13</sup> is 7-times larger for 1 in comparison to HBC-OMe and HBC-C12. Thereby, the large  $K_{\rm A}$ ,  $\varphi$  and  $P_{\xi}$  values of 1 unambiguously reveal the effect of a strong in-plane molecular dipole (8.25 D) on the formation of larger aggregates.

Differential scanning calorimetry (DSC) reveals the absence of any phase transition in the temperature range from -100 °C to 250 °C for both compounds 1 and 2 (Fig. S5, ESI<sup>†</sup>). Two-dimensional wide-angle X-ray scattering (2D WAXS) experiments on oriented fibers point towards an identical organization for both compounds that does not change over the whole investigated temperature range.<sup>16</sup> In both cases, the 2D patterns indicate a characteristic hexagonal columnar liquid crystalline packing (Fig. S6 and S7<sup>†</sup>). The assignment of the hexagonal columnar structure is based on the ratio of  $1:\sqrt{3}:2$  for the positions of the strong equatorial reflections. The distinct meridional wide-angle reflections are attributed to the  $\pi$ -stacking distance of 0.35 nm of the aromatic cores along the columnar axis. The weak reflections at intermediate distances suggest dipole-dipole correlations with an angle of about  $90^{\circ}$  as revealed by the azimuthal intensity distribution. In fact, most dipole functionalized HBCs show such a pattern reflecting the enhanced dipoledipole correlations within the columnar mesophase.<sup>17</sup> These static correlations improve with decreasing temperature (Fig. S6b<sup>†</sup>) for reasons that will become clear below through the dynamic investigation.

The molecular dynamics, that completely relax the dipole moment within the liquid crystal mesophase, was explored by Dielectric Spectroscopy (DS). In fact, it has been recently shown that some molecular dynamics can be activated by the dielectric stimulus even in unsubstituted HBCs.<sup>18</sup> Fig. 2 gives representative dielectric loss curves for the three compounds (4, 2 and 1) at 313 K. The curves display asymmetric broadening towards lower frequencies that can best be described by a summation of two Havriliak–Negami functions (ESI†).<sup>19</sup> The characteristic frequencies at maximum loss for the two main processes are indicated by arrows in Fig. 2. The increase at lower frequencies is due to the ionic conductivity whereas an additional local process ( $\beta$ -process) is evident at higher frequencies.

The relaxation times at maximum loss for the main  $\alpha$  and  $\alpha'$  processes are plotted in Fig. 3 in the usual Arrhenius representation. Both processes exhibit a strong temperature



Fig. 2 Dielectric loss curves as a function of frequency for 1 (triangles), 2 (squares) and 4 (circles) at 313 K. The arrows indicate the approximate positions of the  $\alpha$ - and  $\alpha'$ -processes associated with the disc axial motion.

dependence that is distinctly different from an Arrhenius law and can best be fitted by the Vogel-Fulcher-Tammann (VFT) equation (ESI<sup>†</sup>). Interestingly, there exist two glass temperatures for each compound. Both processes are associated with a dipolar relaxation within the liquid crystalline phase. The  $\alpha$ process reflects the fast axial motion that leaves an uncompensated residual dipole moment.<sup>17</sup> Responsible for this residual dipole moment and the presence of the slower process are the dipolar correlations within the columns as determined by WAXS. Subsequently, this residual dipole moment relaxes completely through the  $\alpha'$ -process at a longer time scale. The distribution of relaxation times reveals that both processes are of collective nature (they involve several discs) but the slower process, that completely randomizes the dipole, is more collective. Thus, the two glass temperatures in these dipole functionalized HBCs reflect the freezing of the partial  $(\alpha)$ and complete  $(\alpha')$  dipole randomization. Earlier DS studies



Fig. 3 Arrhenius relaxation map for compounds 4 (circles), 2 (squares) and 1 (triangles). The processes correspond to the  $\alpha$ -process (fast axial motion) (filled symbols) and the slower  $\alpha'$  process (collective slow motion) (open symbols). Lines are fits to the VFT equation.

on functionalized HBCs with weaker dipoles showed that the disc axial dynamics are dictated largely by the phase state.<sup>18</sup> The present series indicates a strong  $\tau(T)$  dependence of the disc axial motions within the mesophase. As expected, the dynamics of **4** are the fastest and give rise to the lower freezing temperatures in Table S3 (ESI<sup>†</sup>). The disc axial motion in **1** and **2** is substantially slower giving rise to higher freezing temperatures for the disc rotational dynamics.

In summary, two novel dipole functionalized HBC derivatives 1 and 2 were synthesized based on the  $C_{2v}$ -symmetric building block 3. The strong molecular dipole moment in both HBCs 1 and 2 provides additional intermolecular dipole–dipole interactions. The strong dipole was revealed to exert significant effect on the self-association of 1 and 2 in solution as well as the dynamic processes within the liquid crystalline mesophase.

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