The functionalised hexa-peri-hexabenzocoronenes by Sonogashira coupling method to modify the columnar mesophase behaviour

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In this paper, we present a series of different thermotropic discotic columnar liquid crystalline forms of mono-substituted functionalised hexabenzocoronene (HBC) carrying five alkyl chains. Using the Sonogashira coupling reaction, 1-ethynyl-4-alkylbenzene, 1-ethynyl-4-alkoxybenzene, and alkyl-4-ethynyl benzoate groups were introduced into mono-bromohexabenzocoronenes to obtain compounds 5–7. These compounds obtained were characterised by 1H and 13C-NMR, UV-Vis, and MALDI-MS spectrometry. The thermotropic liquid crystalline (LC) properties of the compounds were investigated by polarising optical microscopy (POM), differential scanning calorimetry (DSC), and powder X-ray diffractometry (XRD).

Keywords: columnar liquid crystalline; Sonogashira coupling reaction; hexabenzocoronene

1. Introduction

Columnar liquid crystals have achieved considerable prominence in recent years because of their applications in functional materials for nanoscale conductive devices, field-effect transistors, and photovoltaic solar cells.[1–8] The family of discotic liquid crystals is a particularly attractive class of materials because these discotic molecules possess the ability to self-organise into various ordered columnar structures. Additional advantages of columnar discotic liquid crystals include their ease of processing (via solution techniques), the possibility of alignment by shear forces or by the application of electrical or magnetic fields, and their capacity for self-healing.

Alkyl or phenylalkyl six-fold substituted hexabenzocoronenes (HBCs) and their functionalised derivatives are discotic liquid crystalline (LC) materials,[9–12] such as the prominent D6h symmetrically structure (Figure 1), and are partial fragments of graphenes. This class of mesogen has been well recognised for its extremely large mesophase widths (up to 400 °C); a charge carrier mobility along the columnar axis in 1.13 cm2 V−1 s−1 was observed in the crystalline solid phase,[13] and a value as high as 0.5 cm2 V−1 s−1 was found even in their hexagonal columnar LC phase.[14]

The substitution of the aromatic core affects the solubility, thermotropic properties, and their self-assembly ability. Hence, the material’s properties can be adjusted by the architecture of the substituents, for example, the alkyl chain length and the substitution symmetry at the disc corona. The longer and more flexible side chains are expected to decrease the thermal phase transitions – or reducing the number of substituents and maintaining a high substitution symmetry of the disc-shaped building blocks, like the D3 symmetry and C2 symmetry, which are believed to influence significantly their thermal and self-assembly behaviours – are however restricted to their synthetic hitches.[15,16] For the examples given above, by varying the size and geometry of the core of the HBCs, their properties change dramatically. Increasing the size of the core results in enhanced π–π overlap, thus giving rise to larger phase widths and more stable mesophases. Vast differences in the mesoscopic properties can also be observed by changing the periphery. When HBCs are subjected to functionalisation, the influence of the molecular structure on supramolecular ordering in both two-dimensional (2D) and three-dimensional (3D) motives can be investigated. The six-fold hexa-alkyl substituted hexa-peri-hexabenzocoronenes have been thoroughly studied, but C2 symmetry hexa-peri-hexabenzocoronene derivatives are rarely considered because of their multistep synthetic methods.[17] From the synthetic point of view, six-fold hexa-alkyl substituted hexa-peri-hexabenzocoronenes can have only an identical functionalisation of all six phenyl substituents of the hexaphenylbenzene. The synthetic strategy for HBCs with D6h symmetry (Figure 1) was reported by Herwig and co-workers in 1996, in which a four-step synthetic sequence was utilised to prepare alkyl-substituted 4,4’-diphenylacetylenes. The types of substituents are limited, and it is difficult to fine-tune the mesophase properties. To obtain more selectively

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functionalised products, long-term planning for different derivatives with multistep syntheses is necessary.

In this context, a series of \( C_2 \) symmetry HBCs functionalised in the position of \(' \text{para} \) derivatives was synthesised (Scheme 1). The mono-bromo-substituted HBC (1) [10] was used as the starting material then the 1-ethyl-4-alkylbenzene, 1-ethyl-4-alkoxybenzene, and alkyl-4-ethylbenzoate were introduced by the Sonogashira reaction with catalyst Pd (PPh\(_3\))Cl\(_2\) in trimethylamine (TEA) to obtain high yields of compounds 5–7 (80–95%), respectively (The detail experiment methods in Supplemental data).

2. Mesomorphic behaviour

A summary of the thermal behaviour of HBC derivatives derived from differential scanning calorimetry (DSC) and polarising optical microscopy (POM) experiments is shown in Tables 1 and 2. At room temperature, all of the compounds are yellow solids. Upon heating, all compounds enter the columnar discotic mesophase. The columnar hexagonal mesophases were preserved to temperatures over 300 °C. The high isotropisation temperatures are the result of \( \pi-\pi \) stacking in the columnar organisation. Figure 2 (compound 6) reveals textures that are typical columnar hexagonal mesophase, and a well-defined pseudo-focal-conic fan-shaped texture together with homeotropic regions was clearly observed by POM. This mesophase was difficult to identify on the first heating due to the high viscosity of the materials. These textures were observed after annealing the sample for a few minutes at the isotropisation temperature followed by cooling to 200 °C. Theses textures were maintained until the sample temperature was decreased to room temperature, and the compound appeared as a glassy state.

The study of the mesomorphic properties revealed LC behaviour that depended on the chain length and the steric effect of the substituents. The replacement of one peripheral alkyl group in HBC-C\(_{12}\) (Col\(_h\); between 107 °C and \(>420 \degree\)C) [18] with bromo groups means that \(D6h\)-symmetry conformation is converted to the \(C2\)-symmetry conformation. When symmetry of structure was broken to lower symmetry, the melting point was decreased from 107 °C to 74 °C (Table 1) but still own the high clearing point. Based on these results, in our work, the bromo-group of HBC-Br was replaced to 1-ethyl-4-alkylbenzene by Sonogashira reaction, and the average melting point (K to Col\(_{h}\), \(T_m\)) decreased to 53 °C.

The lower melting point of compounds in series 5 is attributed to the resulting lower packing efficiency because of both the lower molecular symmetry and the non-ideal disc-like molecular core with a
Table 1. Optical, thermal, and thermodynamic data of compounds HBC-C12, HBC-Br, and 5 (K = crystal, Colho = ordered hexagonal columnar mesophase, I = isotropic liquid) for the first heating.

| Compounds | Transition | T [°C] | ΔH [Jg⁻¹] |
|-----------|------------|--------|-----------|
| HBC-C12   | K-Colho    | 106.5  | 60.6      |
|           | Colho-I    | 417    | 5.7       |
| HBC-Br    | K-Colho    | 74.1   | 62.5      |
|           | Colho-I    | >420   |           |
| 5a (-C₆H₄)| K-Colho    | 54.6   | 28.9      |
|           | Colho-I    | 325[6] | 11.0      |
| 5b (-C₆H₁₃)| K-Colho   | 52.0   | 106.5     |
|           | Colho-I    | 315[6, 7] |          |
| 5c (-C₇H₃₂)| K-Colho  | 48     | 20.6      |
|           | Colho-I    | 313[6] | 3.5       |
| 5d (-C₁₂H₂₅)| K-Colho | 61.9   | 27.8      |
|           | Colho-I    | 309[6] | 9.2       |

Note: [a]: The mesophase behaviour were reported by reference [10]. [b]: Decomposition noticeable during optical microscopy. [c]: A transition observed by optical microscopy.

Table 2. Optical, thermal, and thermodynamic data of compounds HBC-C12, HBC-Br, and 5d-7 (K = crystal, Colh = hexagonal columnar mesophase, I = isotropic liquid) for the first heating.

| Compounds | Transition | T [°C] | ΔH [Jg⁻¹] |
|-----------|------------|--------|-----------|
| HBC-C12   | K-Colh     | 106.5  | 60.6      |
|           | Colh-I     | 417    | 5.7       |
| HBC-Br    | K-Colh     | 74.1   | 62.5      |
|           | Colh-I     | >420   |           |
| 5d (-C₁₂H₂₅)| K-Colh   | 61.9   | 27.8      |
|           | Colh-I     | 309[6] | 9.2       |
| 6 (-OC₁₂H₂₅)| K-Colh | 54.0   | 11.0      |
|           | Colh-I     | 329[6] | 2.7       |
| 7 (-OC₁₃H₂₅)| K-Colh  | 53.2   | 18.2      |
|           | Colh-I     | 314.8[6] | 2.4      |

Note: [a]: The mesophase behaviour were reported by reference [10]. [b]: Decomposition noticeable during optical microscopy. [c]: A transition observed by optical microscopy.

protruding phenyl substituent. The wider mesophase range is ascribed to the stronger inter-disc attractive interactions provided by the introduced phenyl unit. Compound 5, which changed the chain length of the unique phenyl-containing side arm, gave further manoeuvrability on the transition temperatures. Compound 5c shows the widest mesophase range (265 °C) and the lowest melting point of 48 °C, 59 °C lower than the melting point of HBC-C12. These compounds have a high clearing point (>300 °C) and yield partial decomposition phenomena simultaneously.

Hence, to fine-tune the clearing point is necessary, but it is rigorous work to adjust only the clearing point. We tried to examine the function of the steric effect where 1-ethynyl-4-alkoxybenzene and alkyl-4-ethynyl benzoate groups were used to replace the 1-ethynyl-4-alkylbenzene in compound 5 to afford compounds 6 and 7. The Colh phase of 6 is observed between 54 °C and 329 °C and compound 7 is observed between 53 °C and 315 °C. (Table 2) Both of the clearing points are slightly lower than 420 °C (HBC-C12). These results demonstrate that the symmetry broken in HBC-C12 (D₆h-symmetry) can lead to a significantly descending melting and clearing temperature. However, an attraction-enhancing bulky protrusion is necessary to improve the decomposition phenomenon.

3. X-ray diffraction study

The structure of the different phases of compounds 5–7 were examined by temperature-dependent X-ray diffraction (XRD). At temperatures up to the first highly endothermic phase transition, the diffraction patterns, in combination with the mechanical behaviour, indicated the presence of a crystalline phase. However, the alkyl chains were not well ordered in most cases.

Above the melting point, the XRD patterns of the HBC derivatives 5–7 described in this paper yielded a set of peaks that were characteristic of a hexagonal columnar mesophase (Table 3). Four reflections were observed at low angles, with the first being much more intense than the others. Their reciprocal spacing follows the ratio 1:√3:4, and the reflections can be indexed as (100), (110), (200), and (100) reflections of a quasi-two-dimensional hexagonal lattice with inter-columnar distances of approximately 26 Å to 28 Å. In addition to these reflections, a broad halo with its centre at approximately 4.9 Å was observed and was associated with the liquid-like correlation between...
aliphatic chains. The (001) reflection at approximately 3.5–3.6 Å indicates the periodic stacking of the molecular cores in the columns. With an alkoxy or ester unit in 6 or 7, respectively, the inter-disc distance remained at ~3.5 Å, which indicates that the steric effect adjusts the melting and clearing temperatures but does not change the packing efficiency.

4. Theoretical investigations

We performed theoretical calculations on several HBC model compounds (compounds 5, 6, and 7 with the five C₁₂H₂₅ moieties removed and R = CH₃) to elucidate the substituent effect on the optical properties of the HBCs. Because charge transfer-excited states are expected to play an important role in the electronic spectra, the density functional theory (DFT) with the CAM-B3LYP hybrid functional using the SDD basis set implanted in the GAUSSIAN09 programme was used to optimise the molecular geometries. The stable geometries obtained were verified by all positive vibrational frequencies. Time-dependent DFT (TD-DFT) with the same level of theory was used to calculate the electronic spectra. The results for the electronic spectra of model compounds 5, 6, and 7 are summarised in Table 4. The excitation wavelengths of model compounds 5 and 6 are the same, at 310 nm, but the model compound 7 shows an 8-nm red shift compared to the other two. This red shift is caused by the larger charge transfer character in the excited state induced by the alkyl 4-ethylbenzoate group, demonstrated in Table 4 by the much larger dipole difference (5.13 Debye) between the excited state and the ground state of model compound 7 than model of compounds 5 and 6.

5. Conclusions

The mono-bromo-functionalised HBC, HBC-Br, as a reactive site for coupling reactions leading to a series of new functionalised HBC derivatives (5–7) by
Sonogashira coupling, is found to effectively lower melting points based on the lower molecular symmetry and the non-ideal disc which both result in inefficient molecular packing. When the different protrusion moiety is attraction-enhancing, the mesophase temperature range can be expanded and stabilised. This process can effectively solve the thermal decomposition phenomenon. Applications of this strategy to other columnar systems are worth investigating to develop more thermal stabilisation materials for use in manufacturing applications.

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**Disclosure statement**

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Table 4. The results for electronic excitations from TD-DFT calculations.

| Model compound | Absorption wavelength, $\lambda$ (nm) | Oscillator strength | Coefficients of mono-excitation | State dipole (debye) |
|----------------|----------------------------------------|---------------------|---------------------------------|---------------------|
| 5              | 310                                    | 2.27                | (HOMO)$\rightarrow$(LUMO) 0.39  | Ground 0.66         |
|                |                                        |                     | (HOMO-1)$\rightarrow$(LUMO+1) 0.48 | Excited 0.70        |
| 6              | 310                                    | 2.34                | (HOMO)$\rightarrow$(LUMO) 0.39  | Ground 2.33         |
|                |                                        |                     | (HOMO-1)$\rightarrow$(LUMO+1) 0.48 | Excited 1.50        |
| 7              | 318                                    | 2.40                | (HOMO)$\rightarrow$(LUMO) 0.38  | Ground 2.61         |
|                |                                        |                     | (HOMO-1)$\rightarrow$(LUMO+1) $-0.46$ | Excited 7.75        |

Figure 3. Topologies of compounds 5, 6, and 7 calculated at the CAM-B3LYP level.
Supplemental data

Supplemental data for this article can be accessed here.

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