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Columnar liquid crystalline bis-N-annulated quaterrylenes†

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Columnar liquid crystalline bis-*N*-annulated quaterrylenes have been prepared from readily available *N*-annulated perylenes by DDQ/Sc(OTf)₃ oxidative coupling and ring-fusion.

Liquid crystalline π -conjugated materials,¹ which possess both order and mobility at molecular, supramolecular and macroscopic levels, are typically designed in such a way that flexible chains are attached to a rigid π -delocalised core. These materials offer the possibility for high degree of order and extensive π -orbital overlap leading to high charge-carrier mobilities, and potentially being more easily processed from solution or from an isotropic melt than π -stacked crystalline materials. Molecular shape, micro-segregation of incompatible parts, and specific molecular interactions are important factors that drive the formation of various LC phases. Rod-shaped molecules prefer an arrangement in layer structures whereas molecules with disc-like geometry preferably organize into columnar mesophases. Among them, one-dimensional (1D) functional materials constructed by thermotropic and lyotropic columnar liquid crystals, e.g., triphenylene,² hexabenzocoronene³ and perylene diimide derivatives,⁴ have attracted special attention, whereby the control of their molecular packing and long-range organization through the design of the building block represents a prime concern for the performance.⁵

In search of high performance organic semiconductors for molecular devices, oligo(peri-naphthalene) (oligo-PN, Fig. 1) is recognized as one of the most promising molecular scaffolds because of its intriguing structural and electro-optical properties. Whereas the physical properties of perylene (1, n = 0), the first member in the series of the oligo-PNs, have been



Fig. 1 Oligo-PNs and bis-*N*-annulated quaterrylenes.

extensively studied,⁶ some important intermediates with large rylene units have also been reported.⁷ To date, the higher homologues have been still rarely explored due to the lack of selective synthesis of these compounds as well as their improcessability caused by their poor solubility and high melting points.

We are particularly interested in the bottom-up synthesis of graphene nano-ribbons-type π -conjugated molecules based on perylene bisimides and heteroatom-annulated perylenes. Recently we reported the facile synthesis of bis-*N*-annulated quaterrylenes and tri-*N*-annulated hexarylenes from easily available *N*-annulated perylene derivatives (NPs), which is conducted by DDQ/Sc(OTf)₃ oxidative coupling and ring-fusion.⁸ Herein, we present our initial studies which promise the establishment of a new type of highly ordered columnar liquid crystalline materials based on bis-*N*-annulated quaterrylenes. Accordingly, we elucidate their structures by fiber wide-angle X-ray scattering (WAXS) experiments performed at different temperatures.

The synthesis of liquid crystalline bis-*N*-annulated quaterrylenes is outlined in Scheme 1. The key starting material were



Scheme 1 Synthesis of liquid crystalline 8: (i) NBS, DMF, 25 °C, 2 h, 82%; (ii) 4-(methoxycarbonyl)benzeneboronic acid, Pd(PPh₃)₄, THF, K₂CO₃, 66 °C, 12 h, 87%; (iii) Sc(OTf)₃, DDQ, dichloromethane, 25 °C, 10 min, 98%; (iv) KOH, THF, 66 °C, 24 h, 98%; (v) 2-decyl-1-tetradecanol, EDAC, DMAP, CH₂Cl₂, 25 °C, 12 h, 63%; (vi) Sc(OTf)₃, DDQ, toluene, 110 °C, 8 h, 62% for **8a**; 60% for **8b**.

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NPs (3) with dove-tailed alkyl chain and dodecyl chain, which were obtained in 96% yield by deprotonation of N-annulated perylene with NaH and subsequently alkylation with branched alkyl bromide and *n*-dodecyl bromide, respectively. Subsequent regioselective NBS bromination provided the key building blocks, named mono-brominated NPs (4). Suzuki-Miyaura coupling of 4 and arylboronic acid affords mono-end-taped NPs (5). The controllable oxidative homo-coupling of 5 allowed the preparation of the key precursor 6 due to the block of one active peri-position by less reactive phenyl ester groups. When 7 was treated with five equivalents of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and scandium trifluoromethanesulfonate [Sc(OTf)₃]⁹ in toluene at 110 °C for 8 hours, bis-N-annulated quaterrylenes with dove-tailed and linear alkyl chains were successfully achieved in 60% yield. It is remarkable that under this simple condition, the expansion of π -system with flexible chains was successfully and highly effectively achieved along the long molecular axis, which opens a new avenue towards liquid crystalline graphene ribbon-type molecules.

The absorption and fluorescence spectra of 8a and 8b in THF are shown in Fig. 2. In comparison with *tert*-butyl substituted quaterrylene, compounds 8 display a bathochromic shift (18 nm) absorption band probably due to the electron-donating effect of nitrogen bridges, with maxima at 678, 622, 576, 528 nm. It is interesting to emphasize that although the absorption and emission maxima of 8a and 8b are almost the same, the introduction of a sterically bulky end group at the lateral position of the core has a strong influence on the absorption coefficient as a reflection of the strong aggregation of 8a.

It should be also noted that although the emission quantum yields of perylene and terrylene are high, those of quaterrylene and longer rylenes are very weak. However, compounds **8a** and **8b** exhibit very strong fluorescence. Theoretical calculations reveal that the optically active $1B_u$ state lies below the dark B_{3g} or $2A_g$ state for perylene and terrylene, which results in strong fluorescence, while a crossover to $S_1 = 2A_g$ occurs and leads to much weaker fluorescence for quaterrylene. When heteroatom bridges are introduced at the lateral position of the core, the charge distribution at the frontier orbitals is significantly modified and the lowest-lying state is stabilized from even-parity to odd-parity, thus allowing light-emission.¹⁰ The fluorescence efficiencies of **8a** and **8b** were estimated by measuring the fluorescence quantum



Fig. 2 UV/vis absorption (solid line) and fluorescence emission spectra (dotted line) of **8a** (red line) and **8b** (blue line) in THF $(1 \times 10^{-5} \text{ M})$.

yields ($\Phi_{\rm F}$) (see ESI[†]) of 0.40 for **8a** and 0.30 for **8b** in THF using cresyl violet as the standard. Time profiles of fluorescence intensities of both compounds are shown in Fig. S1 (ESI[†]), revealing a relatively long fluorescence lifetime ($\tau_1 = 2.77$ ns), which indicates that these two compounds are rare liquid crystal-line materials with strong fluorescence in the near-infrared region.

The phase behaviour of compounds 8 was investigated with differential scanning calorimetry (DSC, Fig. S3, ESI[†]) and polarized optical microscopy (POM). The DSC thermograms of 8a show two phase transitions in the second heating cycle. The first appears at 126 °C (enthalpy 12.6 J g^{-1}) and is attributed to a crystal-liquid crystal phase change. The below discussed structure study reveals the molecular packing for each solid phase. The second peak at 276 °C (enthalpy 7.4 J g⁻¹) was verified by POM as the isotropization point. Two phase transitions were also observed for **8b** at 15 $^{\circ}$ C (15.3 J g⁻¹) and 174 $^{\circ}$ C (1.4 J g^{-1}) . The latter peak is related to the isotropic melting, while despite the relatively high enthalpy the low temperature transition does not induce any structural modification. This is in accordance with the optical textures for 8b which display in POM identical birefringent fan-shaped domains, as also 8a, over the whole temperature range for the solid phases (Fig. 3).

The structural analysis was performed on two-dimensional wide-angle X-ray scattering (2D WAXS) results obtained for different temperatures. Both compounds **8a** and **8b** assemble in all determined phases into quasi one-dimensional lamellate stacks.

The small-angle equatorial reflections in the pattern in Fig. 4a indicate that the 1D stacks of **8a** are arranged in an orthorhombic lattice to each other with a = 3.90 nm and b = 2.76 nm as the parameters (top view Fig. 5). The parameter a is in agreement with the length of the long molecular axis, while the relatively large b is assigned to a herringbone arrangement of the molecules (side view Fig. 5). The meridional reflection in the wide-angle region corresponds to an intracolumnar period of 0.47 nm of tilted, π -stacked molecules (Fig. 4a). Such molecular tilting towards the columnar axis is characteristic for crystalline phases



Fig. 3 POM images for (a) 8a and (b) 8b both recorded with crosspolarisers at 30 °C. The cooling rate was 1 °C min⁻¹. The scale bar corresponds to 100 µm.



Fig. 4 Two-dimensional wide-angle X-ray scattering (2D WAXS) patterns of **8a** at (a) 30 °C (crystalline phase), (b) 140 °C (liquid crystalline phase), (c) **8b** at -60 °C.



Fig. 5 Schematic illustration of the arrangement of 8a at 30 °C.

of alkyl substituted disc-shaped molecules.¹¹ Heating to the liquid crystalline state changes the orthorhombic parameters slightly to a = 3.52 nm and b = 3.19 nm, but the intracolumnar order decreases significantly as indicated by the blurred meridional reflections which are related to an average molecular distance of 0.44 nm. The formation of the columnar disordered phase is due to the high steric hindrance of the branched alkyl chains at higher temperatures as also observed for other types of discotics.¹² The pronounced amorphous halo and a low number of reflections in the pattern due to the reduced order are typical indications for a liquid crystalline state (Fig. 4b).

In the crystalline phase, compound **8b** forms also stacks with tilted molecules. The off-meridional reflections indicate that the tilting angle varied slightly from 40° at temperature of 30 °C to 30° at temperature of -60 °C (Fig. 4c), while the 1D structures are arranged in a monoclinic unit cell with a = 4.11 nm, b = 2.48 nm and $\gamma = 110^{\circ}$ at 30 °C (Fig. S2, ESI†) and in an orthorhombic fashion with a = 4.13 nm and b = 2.77 nm at -60 °C. The larger tilting angle of **8b** in comparison to **8a** is attributed to the additional branched alkyl chains attached at the lateral position of the core.

In conclusion, a new efficient synthetic method towards liquid crystalline bis-N-annulated quaterrylenes from easily available N-annulated perylene derivatives by DDQ/Sc(OTf)₃ oxidative coupling and ring fusion is presented. Theoretical calculation reveals that due to the introduction of the heteroatom bridges at the lateral position of the core, the charge distribution at the frontier orbitals is significantly modified, which leads to the tremendous changes from weak fluorescence of quaterrylene to strong fluorescence of bis-N-annulated quaterrylene. The structural analysis in the solid-state demonstrated that the combination of the intermolecular π - π interaction of bis-Nannulated quaterrylene moieties and the nano-segregation of the building blocks guided the formation of one-dimensional supramolecular lamellar assemblies, which are expected to be attractive candidates for charge-transporting materials in organic optoelectronic devices.

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