COMMUNICATION

Lamellar organization of discotic dimer enforced by steric manipulation†

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Dibenzo[a,c]phenazine dimer mesophases exhibited a lamellar assembly as demonstrated by XRD diffraction. This is a new successful molecular design to achieve a hierarchical supramolecular assembly for dimeric discotic liquid crystals. All the mesophases are readily frozen into a glassy state at room temperature.

Recent interests have been centred on the synthesis of dimer liquid crystals, which can exhibit interesting properties, similar to those for higher liquid crystal oligomers and polymers, especially in their ability to form highly ordered anisotropic glasses on cooling down to below the glass transition temperature. To date, rod-shaped liquid crystalline dimers are the most well studied, together with the investigation of the driving forces that give rich polymorphism.[1–6] In comparison, the number of discotic liquid crystal (DLC) dimers is relatively small and studies have been restricted to the discussion of the factors controlling their supramolecular assembly. Among the most studied dimeric DLCs are the triphenylene dimers, with a flexible spacer, which have been recently reviewed,[7–10] together with other dimers based on benzene,[11,12] phthalocyanine,[13] cyclotetraveratrylene,[14] and hexabenzocoronenes.[15] In general, the spacer length of the DLCs must be equal to, or longer than the peripheral side chains, to prevent steric crowding within the molecule for the disc to pack into columns. As such, the dimeric discotic family of mesogens showed columnar mesophases, with their discogens packing through both an inter- and an intra-columnar manner.[8] A rigid acetylenic linker has been found to drive a DLC dimer into the nematic phase,[16,17] and the use of a half-fluorinated linker resulted in a mono-phase segregation, to give a lamellar organization.[18] Although there has been an increasing interest in discotic dimers, the chemical and physical behaviours of this

family of mesogens have not yet been thoroughly investigated or fully understood. Our interest is to model the discotic dimer system using dibenzo[a,c]phenazine, which favours an anti-parallel packing of the core, and to determine possible variations of their mesogenic and self-assembly properties.

A discotic dimer with a spacer length shorter than the peripheral side chain has been reported not to form a mesophase. We have recently reported that a DLC dimer containing a dibenzo[a,c]phenazine discogen exhibits a columnar hexagonal mesophase even when the spacer length is shorter than the peripheral side chains. This was attributed to the dibenzo[a,c]phenazine core favouring an anti-parallel packing of the discogen, thereby stabilizing intra-columnar packing.[19] Here, we have designed a new series of dibenzo[a,c]phenazine dimers, having a bulky isopropoxy group at the α-position to the linker (Fig. 1). It is highly likely that the space required by the isopropxy group, in proximity to the spacer, can provide steric crowding within the molecule, preventing intra-molecular packing. Being aware of the fact that the dibenzo[a,c]phenazine favours an anti-parallel stacking interaction to form a column, we anticipated that this

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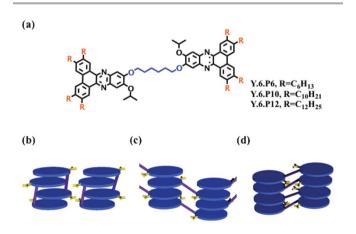
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Fig. 1 (a) Molecular structures of dibenzo[a,c] phenazines (**Y.6.P6**, **Y.6.P10**, and **Y.6.P12**); three possible stacking arrangements of discotic dimers: (b) the intercalated intra-columnar, (c) the intercalated, and (d) the non-intercalated inter-columnar anti-parallel packing.
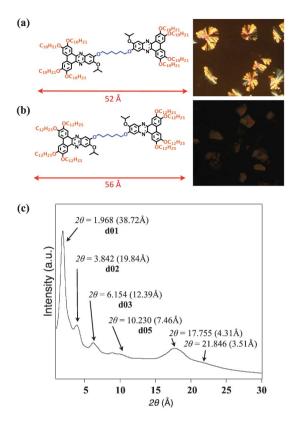
Fig. 2 Molecular lengths and POM micrographs of (a) **Y.6.P10**, (b) **Y.6.P12** at room temperature on cooling from its isotropic melt, and (c) synchrotron radiation XRD pattern of **Y.6.P12** at 60 °C on cooling in a glass capillary.

new model would lead to the discovery of a new hierarchical supramolecular assembly. Here, we report on a new scenario of the lamellar organization of a discotic dimer at the mesophase, manifested by the steric effect in proximity to the linker in **Y.6.P10** and **Y.6.P12** (Fig. 1), from XRD diffraction experimental analysis.

Isopropoxy-substituted dibenzo[*a,c*]phenazine dimers **Y.6.P6**, **Y.6.P10**, and **Y.6.P12** were prepared as shown in Scheme S1 (see ESI†). All compounds were extensively purified and their self-organization studied by differential scanning calorimetry (DSC), polarized light optical microscopy (POM), and variable temperature X-ray diffraction (XRD).

All the synthesized compounds **Y.6.P6**, **Y.6.P10**, and **Y.6.P12** were found to be liquid crystalline under POM (see Fig. 2a and b and ESI†). The DSC of compound **Y.6.P6** (Table 1) with the peripheral side-chain of the same length as that linker, on second heating, has a melting point (Col_h–Iso) at 181.2 °C ($\Delta = 11.3$ kJ mol^{-1}); and on cooling the isotropic liquid to room temperature did not show crystallization, but was frozen into a glass transition liquid crystalline material, as indicated by the exothermic peak ($\Delta = -8.7$ kJ mol^{-1}). The XRD profile for **Y.6.P6** showed at the small angle region, one very sharp strong reflection indexed as (100) and the second weak reflection indexed as a (210) reflection with a reciprocal spacing ratio of 1:($\sqrt{7}$) typical for a Col_h 2-D lattice at the mesophase (see ESI†). On cooling to room temperature, no crystallization was detected by DSC and XRD, revealing the formation of a Col_h glassy phase with good stability, that lasted for

more than six months. The introduction of the isopropoxy group into the dimer has the following consequences: (i) dramatically increases the melting temperature, as well as clearing temperature, (ii) eases the formation of a glassy state for an extended period, and (iii) forms only a hexagonal columnar mesophase, as compared to our previously reported similar straight-chain dimers, which show polymorphism.[19] From the above observations, the introduction of the more sterically demanding isopropoxy group did indeed change the mesogenic properties of the DLC dimer. It is postulated that the steric effect of the isopropoxy group at the α-position to the linker might disfavour intra-columnar packing, as indicated by the inability to undergo polymorphism, and that the dibenzo[*a,c*]phenazine core, with an anti-parallel orientation of adjacent discs, forms intercalated inter-columnar packing.

In terms of the intercalated intra-molecular packing model, the linker must be at least of similar length or longer than the peripheral side chains. Now the question arises as to whether the lateral dipole in dibenzo[*a,c*]phenazine, which enforced the packing of the discogen, can induce a new hierarchical organization when the peripheral chain is longer than the linker of the discotic dimer and also with a bulky isopropyl group at close proximity to the linker? We next synthesized **Y.6.P10** and **Y.6.P12**, whereby the tetraalkoxy peripheral side chain is longer than the linker, and they are both liquid crystalline under POM examination (Fig. 2a and b). Interestingly, the XRD diffraction patterns in the small angle region for **Y.6.P10** (see ESI†) and **Y.6.P12** (Fig. 2c) at 60 °C, show a remarkably different pattern from that of **Y.6.P6**. The XRD patterns for **Y.6.P10** and **Y.6.P12** show (01) and its corresponding higher order reflections. The *d*-spacing estimated from the higher order reflections at $2\theta = 2.00, 4.11, 6.73, 10.53$ for **Y.6.P10**, and $2\theta = 1.97, 3.84, 6.15, 10.23$ for **Y.6.P12**, are in the ratios 1 : 1/2 : 1/3 : 1/5, thus indicating the presence of a well-defined lamellar, or layered structure. The (01) reflection for **Y.6.P10** and **Y.6.P12** corresponds to a distance of 38.11 Å and 38.72 Å respectively. The lamellar structure can be explained by the steric effect attributable to the isopropxy group in proximity to the linker of the dimer, which prohibits intra-molecular and intercalated inter-molecular packing. On the other hand, the interlayer spacing is shorter than the length of a fully extended conformation for **Y.6.P10** (52 Å) and **Y.6.P12** (56 Å) using the MM2

Table 1 Phase transition behaviours of dibenzo[*a,c*]phenazine (**Y.6.P6**, **Y.6.P10**, and **Y.6.P12**)

Compound	Phase transition temperature/°C and enthalpy (kJ mol^{-1})[a]
Y.6.P6	Col_{hg} 39.6, Col_h 181.2 (11.3), **Iso**; Iso 176.5 (−13.8), Col_h 25.4, Col_{hg}
Y.6.P10	D_{Lg} 17.7, D_L 97.7(74.1), **Iso**; Iso 74.8 (−74.6), D_L 24.7, D_{Lg}
Y.6.P12	D_{Lg} 38.6, D_L 101.0(103.7), **X**, 105.0 (80.9), **Iso**; Iso 78.8 (−83.0), D_L 9.0, D_{Lg}

[a] Determined from the DSC profiles in second heating–cooling cycle at a scanning rate of 10 °C min^{-1}. Cr, crystal; Col_h, hexagonal columnar LC phase; Col_{hg}, glassy hexagonal columnar phase; D_L, lamellar phase; D_{Lg}, glassy lamellar phase; X, unknown phase; Iso, isotropic melt.
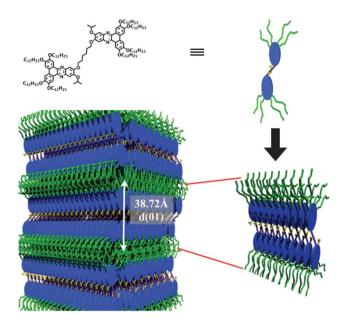
Fig. 3 Schematic representation of the hierarchical self-assembled D_L phase of tilted-**Y.6.P12**.

method, as illustrated in Fig. 2a and b. On the other hand, a similar dimer having a hexyloxy group[19] instead of the isopropoxy group, as in **Y.6.P12**, has been reported to adopt a folded conformation in the hexagonal columnar liquid crystalline state, with an inter-columnar distance of 25.43 Å, which is shorter than that observed in the XRD. The newly observed layer spacing is therefore shorter than the calculated molecular length of the fully extended dimer for an intercalating model, and longer than the previously proposed folded C-shape conformation for intra-molecular packing of the dimer that formed a hexagonal columnar phase.[19] Therefore, it was deduced that the molecular plane of the dimers **Y.6.P10** and **Y.6.P12** is tilted against the normal layer at the lamellar mesophase, and the parameter of the first reflection in the XRD at (01) corresponds to the layer distances of 38.11 Å and 38.72 Å respectively. In this lamellar structure, the π–π interaction between the discotic cores will have to take place in the lamellar layer. The model for the mesophase of compound **Y.6.P12** is shown in Fig. 3, whereby the interlayers are held together through the interdigitation of the flexible peripheral chains. Furthermore, the spaces in-between the linkers are filled by the isopropoxy groups. The lamellar mesophases of **Y.6.P10** and **Y.6.P12** showed lower melting and clearing temperatures, as compared to **Y.6.P6** (Table 1). Importantly, these lamellar mesophases, on cooling to room temperature, readily form glasses that can last for months.

Conclusions

In summary, we have successfully implemented a new molecular design concept, in which a bulky isopropoxy group is introduced to the proximity of the linking chain between the discogens of dimeric discotic liquid crystals, to direct lamellar assembly at the mesophase. Furthermore, the liquid crystal order is preserved in the glassy state at room temperature, a property desirable for many device applications.

Acknowledgements

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