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Luminescent Bow-Tie-Shaped Decaaryl[60]fullerene Mesogens

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Molecular shape is a primary factor in the formation of mesogenic superstructures,[1] yet it is often unclear whether the bulk properties, such as optical properties, can be controlled by the shape of individual molecules. Rod, disk, and bent-core mesogens form a variety of liquid crystals (LCs) that exhibit anisotropic and switching properties that are conducive to numerous applications.[2] Because of its unique isotropic structure and nanometer size, [60]fullerene has provided new opportunities for the development of new classes of mesogens,[3] especially those possessing a large three-dimensional structure, e.g., C_{5v} or *pseudo*-C_{5v} symmetric pentaaryl[60]fullerene ($C_{60}Ar_5X$, X = H, Me, CpFe)[4] and T_h symmetric hexa(organo)fulllerenes[5] that can hardly be developed from small molecules. When a $C_{60}Ar_5X$ molecule bears large Ar groups, the molecule resembles a badminton shuttlecock and forms columnar stacks in the LC mesophase.[4] The deca-aryl fullerenes ($Ar_5MeC_{60}Ar_5Me$) **1**−**4** (Figure 1) contain a *pseudo*-D_{5d} symmetric structure[6] that represents a head/head superposition of two $C_{60}Ar_5Me$ molecules. These molecules are unique for their central hoop-shaped [10]cyclophenacene moiety[6] (colored orange in Figure 1), which exhibits anisotropic luminescence.[7]

Herein we report on the synthesis and properties of a new class of mesogens—bow-tie-shaped mesogens, which form a smectic mesophase that emits light anisotropically.[8] The anisotropic property of the light emission can be changed by the uniaxial shearing of the LC film[7c,d,9] because of the change in the long-range spatial alignment of the emissive [10]cyclophenacene moiety in the bulk.[10] The LCs of **1** exhibit luminescence with a quantum yield of $\Phi = 0.21$, which is the highest reported value for fullerene derivatives.[6,11]

Compounds **1**−**4** were synthesized in two synthetic operations from [60]fullerene (see Supporting Information). Differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD) studies indicated that compounds **1** and **2** exhibit a layered mesomorphism, while compounds **3** and **4** form a crystalline structure.

A DSC analysis of compound **1** (C_{18}) showed only one mesophase over a wide temperature range ($\Delta T = 240$ °C), in which we observed one endothermic transition at 17 °C (79.7 kJ·mol^{-1}, $T_{cr\text{-}lc}$) and another at 257 °C (27.4 kJ·mol^{-1}, $T_{lc\text{-}iso}$). During subsequent heating−cooling cycles at a rate of 10 °C/min, we found a quick and reversible phase transition (Figure 2a) that took place much faster than the transition observed for the corresponding $C_{60}Ar_5X$ molecules.[4d] Upon the second heating to 241 °C, we observed a fan-shaped POM texture (Figure 2b), which persisted for several months at room temperature. The XRD pattern at 195 °C showed a strong (01) reflection at $2\theta = 2.54°$ (d spacing = 3.48 nm), with a (02) reflection ($2\theta = 5.02°$, Figure 2c). In addition, a broad halo centered at $2\theta \approx 19.4°$ indicated molten alkyl chains.

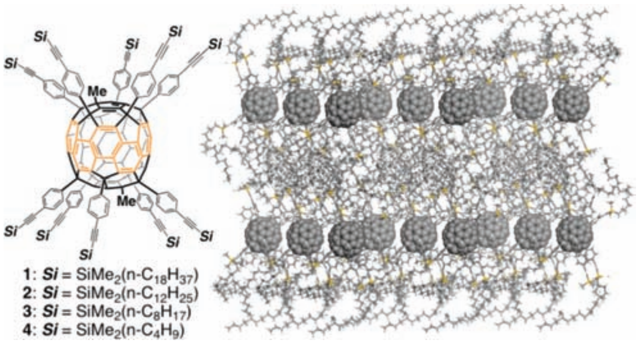

Figure 1. Structure of compounds **1**−**4** (left) and a schematic illustration of the proposed smectic organization of **1** based on XRD data (right).

The XRD data exhibited a 2D smectic periodicity over a wide temperature range.

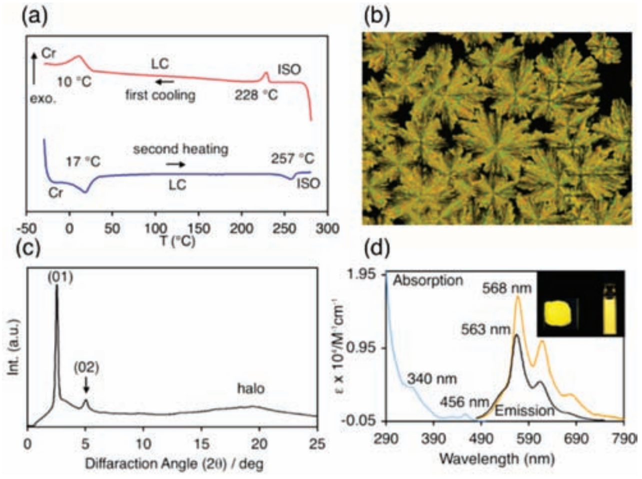

Figure 2. Properties of **1** (C_{18}). (a) DSC trace. (b) POM texture under crossed polarizer (× 20 times) at 241 °C on the second heating process. (c) XRD data at 195 °C. (d) Absorption and emission of a cyclohexane solution (blue and orange curves, respectively), and emission of casted film (black curve). Both samples were excited at 366 nm. Insert: pictures of yellow photoluminescence of solid **1** on the left and **1** in cyclohexane on the right.

Compound **2** (C_{12}) exhibited a 3D smectic mesophase.[12] Unlike the 2D smectic phase where the molecules are ordered to form a layer but disordered within the layer, LCs of **2** exhibited periodicity within the lamella layer as indicated by the reflections of the positional order (d_{010}) and a long-range ordering of lamellas (d_{001} to d_{006}) (Figures S1 and S2). It also showed a higher $T_{lc\text{-}iso}$ of 310 °C (22.6 kJ·mol^{-1}, Figure S5). Compounds **3** (C_8) and **4** (C_4), which bear much shorter alkyl chains, showed only a crystalline phase. XRD indicated that the fullerene moiety is aligned in a plane with

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the longer molecular axis perpendicular to this plane (cf. Figure 1). The interlayer distance in the LCs and crystals of **1**−**4** ((001) reflections at 195 °C) increases linearly as the alkyl chain length increases (from **1** to **4** and 3.48 to 1.80 nm; Figure S3). We therefore conclude that the alkyl chains are sandwiched between the fullerene layers, as illustrated in Figure 1. We ascribe this microphase segregation to the mesogens' bow-tie molecular shape and the incompatibility of the alkyl chains with the fullerene core. Note that the latter contributed to the formation of one-dimensional stacking of the conical $C_{60}Ar_5X$ molecules.[4]

Compounds **1**−**4**, which bear an emissive 40π-electron [10]cyclophenacene system, exhibit photoluminescence (PL).[6] As shown in Figure 2d, compound **1** exhibits intense absorption bands at <400 nm, with a shoulder at 340 nm, and some weak absorption in the visible ranges (maxima at 428 and 456 nm) that are characteristic of the [10]cyclophenacene moiety. Upon excitation of compound **1** at 366 nm in cyclohexane, we observed two intense emission peaks with a maximum at 568 nm and with a PL quantum yield of $\Phi_{sol} = 0.21$ (absolute measurement), which is the highest value thus far reported for fullerene derivatives. For the drop-casted film, we also observed an emission at 563 nm with a comparable quantum yield of $\Phi_{film} = 0.18$, which strongly suggests that the cyclophenacene chromophores are spatially separated from each other in the LCs and do not suffer much from self-quenching in the excited state.

A chromophore emits light polarized along its transition moment;[13a] therefore, if a chromophore is spatially oriented in the bulk, the bulk will emit light anisotropically. This is exemplified by the GFP chromophore, which is oriented along the long crystal axis, yielding a highly polarized emission with a ratio of parallel ($I_{\parallel}$, 0°) to perpendicular ($I_{\perp}$, 90°) emission that is close to $I_{0°}/I_{90°} = 10$.[13b] In the smectic LC of **1**, the emissive cyclophenacene group is rigidly embedded in the lamellar layers, (Figure 1), and hence will cause anisotropic light emission from the bulk LCs if there is any long-range ordering of the lamellar structure in the bulk.

Indeed, after settling a rotatable polarizer between the sample and the detector, a thermally annealed LC film of **1** showed anisotropic light emission with a ratio of 0.79 ($I_{0°}/I_{90°}$), and when it was uniaxially sheared, the ratio changed, *albeit* modestly, to 0.40 (366 nm excitation) (Figure S10). Such anisotropic emission and its change upon the application of a mechanical force must have occurred because of the long-range alignment of the cyclophenacene chromophore in the LC film.

In conclusion, decaaryl[60]fullerene molecules ($Ar_5MeC_{60}Ar_5Me$) **1**−**4** display a unique bow-tie shape, which is found in the central fullerene part forming a layered structure whose longer molecular axis is perpendicular to the plane. This molecular orientation causes the alignment of the emissive [10]cyclophenacene rings in the plane of the layer and allows the bulk LC phase to emit light anisotropically due to the presence of ordered lamellas in the smectic phase. It is apparent that such long-range ordering is far from perfect, and hence, the ratio of anisotropic emission remains low. However, once a way is found to improve the ordering, the macroscopic emissive property of **1**−**4** will generate interesting applications when combined with organic light-emitting diode technology.[14]

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Supporting Information Available: Synthesis, DSC, optical textures, XRD, and anisotropic photoluminescence. This material is available free of charge via the Internet at http://pubs.acs.org

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