

## Lamellar Assembly of Conical Molecules Possessing a Fullerene Apex in Crystals and Liquid Crystals

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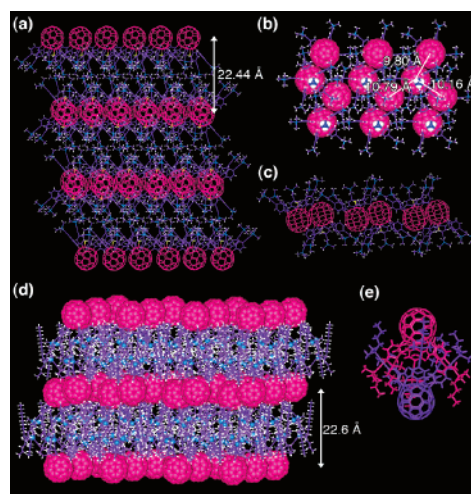
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The supramolecular arrangement of molecules through noncovalent interactions into ordered structures is among the central issues of nanoscience and nanotechnology.<sup>1,2</sup> Fullerene-containing mesogens thus attracted the interest of our group and others since they raise the hope that one can draw new properties out of such molecules and the resulting mesophases.<sup>3,4</sup> However, covalent attachment of fullerene molecules to a mesomorphic promoter molecule such as cholesterols and dendrimers did not result in the desired properties in some cases, because the grafted fullerene groups tend to disturb the organization of the original mesogenic molecules. Sometime ago we used the [60]fullerene molecule itself as the central element of mesomorphism<sup>5</sup> and reported that shuttlecock-shaped molecules, C<sub>60</sub>R<sub>5</sub>H [R = C<sub>6</sub>H<sub>4</sub>-Ph-4 or C<sub>6</sub>H<sub>4</sub>-{OCO-C<sub>6</sub>H<sub>3</sub>-(OC<sub>12</sub>H<sub>25</sub>)<sub>2</sub>-3,4}-4], stack together to form a polar columnar structure<sup>6</sup> and that this new strategy can be expanded to the creation of silicon-<sup>6b</sup> and metal-containing redox-active liquid crystalline phases.<sup>6c</sup> We report herein that suitable modification of the C<sub>60</sub>R<sub>5</sub> structure leads to the formation of layered lamellar structures in crystals and liquid crystals (Figure 1a,d).

To achieve the columnar stacking of the shuttlecock molecules, we previously used large aromatic R groups such as a biphenyl group so that the five R groups embrace the second fullerene molecule to form the one-dimensional stack. To achieve the layer formation, we need to prevent such stacking. Being aware of the fact that fullerene and hydrocarbon do not mix together well, we synthesized a series of amphiphilic compounds **1–7**, in which a fullerene core is connected to many hydrocarbon groups by silyl acetylene tethers. The silicon atom facilitates installation of the hydrocarbon substituents through a simple Grignard operation. We also installed a methyl group to the center of the molecular cavity to prevent the head-to-tail stacking.<sup>7</sup>

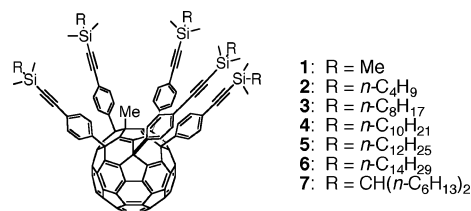
The prototype molecule, C<sub>60</sub>(C<sub>6</sub>H<sub>4</sub>C≡CSiMe<sub>3</sub>)<sub>5</sub>Me (**1**), was synthesized in one step by the reaction of [60]fullerene with Mg(Br)C<sub>6</sub>H<sub>4</sub>C≡CSiMe<sub>3</sub> in the presence of CuBr·SMe<sub>2</sub>,<sup>8</sup> followed by trapping of a cyclopentadienide copper intermediate with iodomethane (see Supporting Information). Similarly, a homologous series of compounds **2–6** bearing linear alkyl chains and **7** bearing branched chains were obtained (Chart 1). These products were obtained in an isolated yield of better than 85%.

Single crystals of **1**·(toluene)<sub>2</sub> and **2** suitable for X-ray crystallographic studies were obtained by slow diffusion of ethanol into a toluene (for **1**) or chlorobenzene (for **2**) solution. Figure 1a shows the lamellar structure of **1** where the distance between the fullerene layers is 22.44 Å and toluene molecules exist between the layers. The top and the side views of a single layer indicate that the molecules are arranged alternately with the R groups and the methyl group attached to the fullerene core (blue carbon and white hydrogen atoms) upward and downward (Figure 1b, c). The short distances (9.80 and 10.16 Å) between neighboring fullerene cores suggest a strong fullerene/fullerene interaction within the same layer.



**Figure 1.** Layered structure in the crystal of **1** and the liquid crystal of **4**. (a) Crystal packing of **1**·(toluene)<sub>2</sub> (view is along the (010) axis; solvent molecules located between the layers are omitted for clarity); (b) top view of a single layer; (c) side view of a single layer; (d) a model of the smectic liquid crystal of **4**, based on the XRD data described in the text; (e) an interdigitated dimer in the crystal packing of **2**.

### Chart 1



The crystal packing of **2** can be described as a pseudolamellar system (Supporting Information), in which two molecules are interdigitated (Figure 1e) and there resulted a shorter interlayer distance of 16.22 Å. In this way, the crystal can gain stabilization through the van der Waals interaction between the five side chains. As the alkyl chains on the mesogen molecule become longer, the volume between the neighboring fullerene layers becomes larger and the interlayer distance increases accordingly (vide infra).

We then investigated the liquid crystalline properties of the molecules **3–6** possessing longer alkyl chains. They are studied by a combination of polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). Their mesophases were characterized by the birefringence and fluidity as observed by POM. Typically, batonnet textures characteristic of a smectic phase were observed after cooling from the isotropic liquid phase (see Supporting Information).

The results of DSC analysis are summarized in Table 1. Molecule **3** showed a mesophase over a relatively narrow temperature range

**Table 1.** Phase Transition Behavior of the Liquid Crystalline Molecules **3–6** on the Second Heating<sup>a</sup>

compound		phase transition temperature (°C)				
<b>3</b>	G	140	Sm	223	Iso	
<b>4</b>	G	48	Sm	178	Iso	
<b>5</b>	G	19	Sm	147	Iso	
<b>6</b>	G	11	Sm	126	Iso	

<sup>a</sup> Abbreviations: G, glassy; Sm, smectic phase; Iso, isotropic liquid. Transition temperatures were determined by DSC at the rate of 10 °C min<sup>-1</sup> and were taken at the top of each transition peak or at the mid temperature (for glassy/liquid crystal transition).

above 140 °C. As the alkyl chains become longer in **4–6**, the liquid crystal phase appears over a wider temperature range, and **6** was found to be liquid crystalline even at room temperature. Expectedly, the phase-to-phase transition temperatures become progressively lower as the side chains become longer from **3** to **6**.

The X-ray diffraction pattern for **4** at 130 °C (Supporting Information) showed an intense diffraction at  $2\theta = 3.92^\circ$  ( $d = 22.6$  Å) accompanied by a small peak at  $2\theta = 7.83^\circ$ , which corresponds to the smectic layering of the molecules. In addition, there appeared small peaks with  $d$ -spacing values of 17.2, 14.7, 12.9, and 10.1 Å and several small peaks over a broad halo owing to the molten aliphatic chains centered at 4.5 Å. These small peaks must be due to the regularity of the positions of C<sub>60</sub> core within the layer,<sup>9</sup> as we have seen in the case of the crystalline molecule shown in Figure 1b. We consider this as an indication of a smectic phase more structurally ordered than the conventional SmA and SmC phases, which is an interesting issue worthy of further studies. The pattern was compared with simulations based on the single-crystal diffractions of **1** and **2** (Supporting Information). The pattern for **4** resembled that of **1** much better than that of **2** particularly for the intense 22.6 Å peak (21.8 Å by simulation of **1**·(toluene)<sub>2</sub> as opposed to 16.2 Å for **2**), suggesting that **4** does not form the interdigitated dimer structure but instead forms the true layered structure. The dimer formation is not any more favored perhaps because the hydrocarbon chains are too bulky and too flexible in the liquid crystalline state to achieve tight interdigitation of two molecules. A model of such supramolecular organization of **4** is shown in Figure 1d.

The XRD analyses of **3**, **5**, and **6** also showed similar patterns from which we concluded that their interlayer distances are 20.5, 23.9, and 25.8 Å, respectively. The side-chain lengths and the interlayer distances determined for **3–6** show good linear correlation (Supporting Information). Molecule **7** however did not show any mesophase as analyzed by POM and DSC. It is probable that the bulky tails disturb suitable molecular arrangement.

Notable was the very slow time scale of the mesophase formation. A well-resolved XRD data of **4** could be obtained only after heating at 130 °C for 7 h after warming from room temperature and only after heating at 130 °C for 10 h after cooling from the isotropic liquid state. We can ascribe this slow kinetics to the large molecular size and to the multiplicity of the molecular interactions that need time for adjustment of the supramolecular ordering.<sup>10</sup> Similar observations were made for **3**, **5**, and **6**.

The shuttlecock molecules that have previously shown to form columnar structures can now be made self-assembled into layered, lamellar structures in crystals and liquid crystals. By suitable choice

of the substituents, the smectic mesophase can be made stable over a wide temperature range. The structure ordering is primarily the result of tight fullerene/fullerene packing within the layer and secondarily due to hydrocarbon/hydrocarbon interactions in the space between the neighboring fullerene layers. We expect that the observations shed light on the mechanism of the formation of bilayer vesicles from C<sub>60</sub>Ph<sub>5</sub><sup>-</sup> molecules dissolved in water.<sup>11</sup> The close packing of fullerene molecules within the layer suggests the use of such ordering for the achievement of high performance in organic electronics applications.<sup>12</sup>

**Supporting Information Available:** Procedures for the synthesis of new compounds, crystallographic data of **1** and **2** (CIFs), optical textures of **4**, DSC data and XRD data of **3–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA068780K