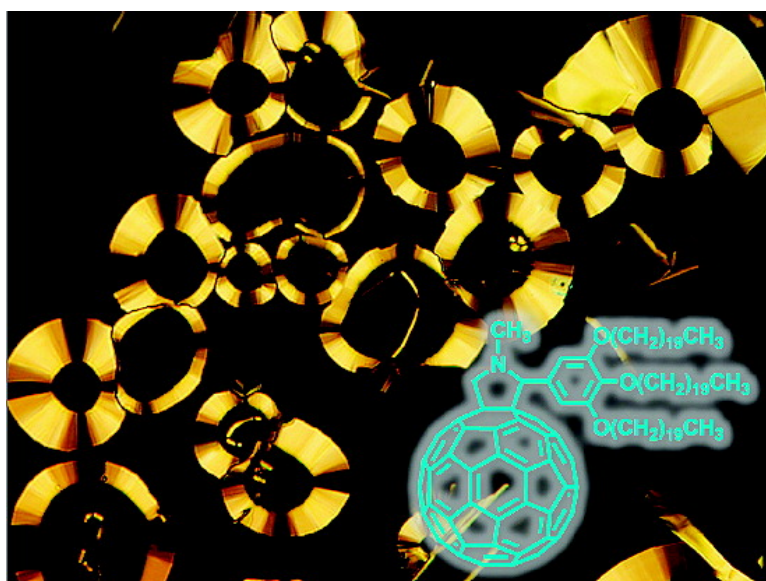


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Electron Transport and Electrochemistry of Mesomorphic Fullerenes with Long-Range Ordered Lamellae

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One of the great challenges in organic-based materials science is the creation of soft materials such as supramolecular materials¹ and mesomorphic materials² with tunable morphologies of the molecular organization and properties. Wet-chemical approaches for thin-film (TFT) and field-effect transistors (FET) using mesomorphic materials like liquid crystalline organic semiconductors are examples for practical devices, since organic single crystals are usually impractical.³ The basic requirements to achieve high carrier mobilities in liquid crystals involve close molecular packing, highly ordered structures, and extended π -conjugation leading to semiconductor features.^{3b} Fullerene C₆₀ is one kind of promising electron-transport material as an *n*-type semiconductor exhibiting relatively high carrier mobility of approximately 1.0 cm² V⁻¹ s⁻¹ in the single crystal and polycrystalline thin films.⁴ Although various morphologies of C₆₀-containing liquid crystals such as nematic, smectic, and columnar phases have been studied in the past decade,⁵ to the best of our knowledge, the carrier mobility of fullerenes in the liquid crystalline state has not been evaluated so far. Typically the C₆₀ content (based on molecular weight) in liquid crystals is only a few percent because of their bulky appendage and is up to 42% at maximum.⁵ Herein, we utilize fulleropyrrolidines functionalized with a multi(alkyloxy)phenyl group (Figure 1a) to satisfy the requirements for a high carrier mobility in the C₆₀-containing mesomorphic materials: a high C₆₀ content (up to 50%), a compact packing, and a highly ordered mesophase. Moreover, fulleropyrrolidines form stable species under electrochemical reduction of the C₆₀ cage⁶ and thus act as redox-active mesomorphic materials. We earlier reported supramolecular fullerene nano- and micro-architectures utilizing the intermolecular forces introduced by C₆₀ (π - π) and alkyl chain interactions (van der Waals).⁷ In this Communication, the formation of a highly ordered lamellar mesophase from simple fullerene derivatives bearing long alkyl chains providing high C₆₀ content and a comparably high electron mobility of $\sim 3 \times 10^{-3}$ cm² V⁻¹ s⁻¹ as well as electrochemical properties is reported.

Fullerenes **1–6** were synthesized following our same strategy as reported previously and unambiguously characterized.⁷ The motivation here is to study the interplay of alkyl chain and fullerene packing on structure formation. Fullerene derivatives **1**, **2**, and **4** exhibit thermotropic polymorphism. In the other cases of derivatives **3**, **5**, and **6** as well as all of the corresponding benzaldehydes as precursors of the derivatives were found to be nonmesomorphic.⁸ The thermal properties of **1**, **2**, and **4** have been examined by a

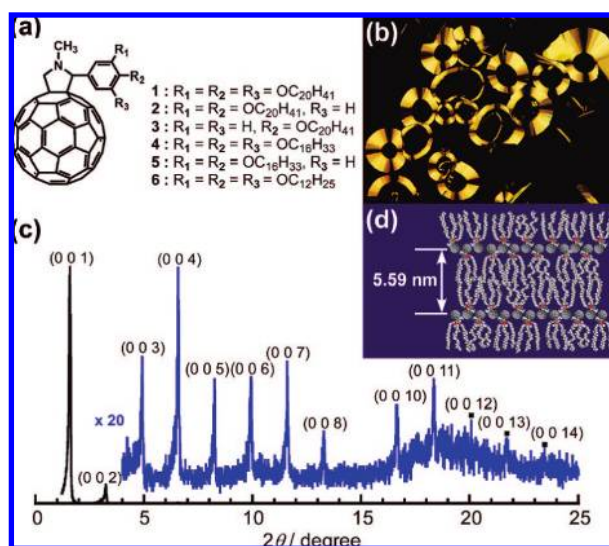


Figure 1. (a) Structure of C₆₀ derivatives (**1–6**); (b) polarizing optical micrographic texture of mesophase of **1** at 190 °C on cooling from the isotropic phase at a rate of 0.1 °C min⁻¹; (c) XRD patterns of **1** at 185 °C; and (d) illustration for the proposed lamellar organization of **1**.

Table 1. Phase Transition Behavior of **1**, **2**, and **4**

derivatives		phase transition temperature (°C) ^a			
1	Cr	62 (72.9)	M _L	193 (31.3)	Iso
2	Cr	44 (37.5) ^b	M _L	226 (12.8)	Iso
4	Cr	33 (31.4)	M _L	223 (10.7)	Iso

^a Transition temperature (°C) and enthalpies (kJ mol⁻¹, in parentheses) determined by DSC on the second heating; 10 °C min⁻¹; cr, crystalline; M_L, mesomorphic lamella; iso, isotropic. ^b Determined by DSC on the first cooling.

combination of differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD). The results of DSC analysis are summarized in Table 1. Upon heating, mainly two endothermic peaks corresponding to the crystalline-to-mesomorphic and mesomorphic-to-isotropic phase transitions were observed in **1**, **2**, and **4**. As the alkyl chains become longer and the number of alkyl chains becomes greater in these derivatives, the crystalline-to-mesomorphic transition temperature becomes higher, while the mesomorphic-to-isotropic transition temperatures become lower. The optical texture of **1** observed with a polarized optical microscope indicates ordered mesomorphic domains (Figure 1b), which exhibit birefringence and confirmed the fluid nature of the material. The optical textures of **2** and **4** also indicate ordered mesomorphic domains (Supporting Information, Figure S2).

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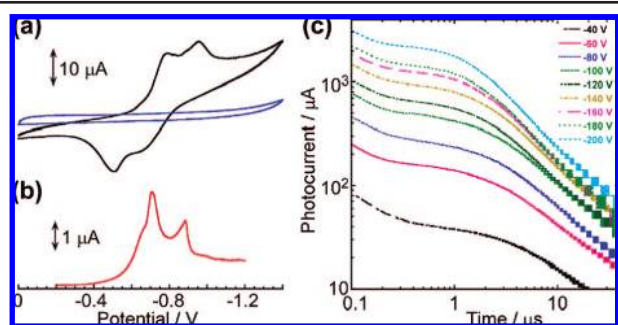


Figure 2. (a) Cyclic (scan rate 0.1 V s^{-1}) and (b) differential pulse (pulse amplitude 25 mV) voltammograms of a cast film of **4** on a glassy carbon electrode (0.1 M aqueous $n\text{-Bu}_4\text{NCl}$ solution, at $60 \text{ }^\circ\text{C}$ (black and red) and at $15 \text{ }^\circ\text{C}$ (blue)). (c) Transient photocurrent curves as a double logarithmic plot for a negative carrier of **1** in the mesophase at $120 \text{ }^\circ\text{C}$.

The XRD pattern for **1** at $185 \text{ }^\circ\text{C}$ shows a strong peak at $2\theta = 1.58^\circ$ assigned (0 0 1) (d spacing = 5.59 nm) accompanied by higher order peaks up to (0 0 14) at $2\theta = 23.44^\circ$ (Figure 1c). In addition, a broad halo centered at $2\theta \approx 19^\circ$ is assigned to the molten alkyl chains. The XRD analyses of **2** and **4** in the mesophase also showed similar patterns with the peaks assigned from (0 0 1) to (0 0 12), from which their interlayer distances are calculated as 4.75 and 4.80 nm , respectively (Figure S3). These higher-degree peaks in the XRD patterns, together with the fluid and birefringent mesophase in the POM, reveal a long-range ordered lamellar mesophase comparable to an ordered smectic phase. A schematic model of the supramolecular organization of **1** is depicted in Figure 1d.

It is advantageous if the electrochemical⁹ and optoelectronic¹⁰ properties of fullerenes in the mesomorphic state are maintained when practical applications are considered. The derivatives display electrochemical activity when measured as cast films on a glassy carbon electrode above the solid/mesomorphic phase transition temperatures. A cast film of **4** (or **1**; see Figure S4) in 0.1 M aqueous $n\text{-Bu}_4\text{NCl}$ solution at $60 \text{ }^\circ\text{C}$ showed the first and second redox events corresponding to the generation of C_{60} monoanion and dianion at potentials of $E_{\text{red},1} = -0.70$ and $E_{\text{red},2} = -0.87 \text{ V}$, respectively (Figure 2a, black, and 2b, red lines). In contrast, no redox response was observed for a cast film of **4** at $15 \text{ }^\circ\text{C}$ in the crystalline state (Figure 2a blue line). The fluid-mesophase evidently facilitates the diffusion of molecules in this system such as supporting electrolyte, solvent, and the fullerene derivative itself.^{2c} We also found that the materials possess a relatively large charge carrier mobility. Figure 2c shows the transient photocurrent curves (log–log plots) of **1** for a negative carrier at $120 \text{ }^\circ\text{C}$ measured using a conventional time-of-flight setup ($\lambda_{\text{ex}} = 356 \text{ nm}$). From the kink points in the log–log plots, which correspond to the transit time, the electron mobility was estimated to be $\sim 3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at an electric field of $2 \times 10^5 \text{ V cm}^{-1}$. This value is comparable to those of smectic liquid crystalline phases of organic semiconductor oligomers^{11a,b} or supramolecular columnar liquid crystals.^{11c} This value is considered a lower limit because the sample is composed of random domains and consequently one expects a higher mobility for a uniformly oriented sample.^{11d} To better understand the charge transport mechanism further detailed temperature dependent experiments are required. The systems are well suited for such studies because the mesophase exists over a broad temperature range. The occurrence of charge carrier mobility and electrochemical activity reveal the advantages of mesomorphic fullerenes.

In summary, long-range ordered lamellar mesophases of fullerene derivatives bearing long alkyl chains were presented and the carrier

mobility of C_{60} in the fluid-mesomorphic state was investigated for the first time. The simple modification of C_{60} by two- (**2**) or three-long alkyl chains (**1** and **4**) permits a high C_{60} content in the mesomorphic materials. The materials are electrochemically active and possess a comparably high electron carrier mobility. Our findings are of interest for the design of fullerene containing soft materials with electrochemical and optoelectronic functions. Moreover, the long-range ordered lamellae described here can be employed as “soft template” materials¹² for the synthesis of two-dimensional polymers or layered material with conductive or optical properties.

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Supporting Information Available: Thermal analyses, electrochemical data as well as TOF analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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