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Fine-tuning supramolecular assemblies of fullerenes bearing long alkyl chains

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Abstract

Fine-tuning of the supramolecularly organized nanometer scale architectures of fullerene derivatives, fulleropyrrolidines substituted with a mono-, di-, or tri(*n*-hexadecyloxy)phenyl group is described. These synthetic fullerene derivatives possess one- (**1**), two- (**2**), or three- (**3**) long alkyl chains. The correlation between the number of alkyl chain multiplicity and the self-organized bilayer structures as the fundamental subunit as well as the superstructures formed in different solvents were investigated using microscopic and spectroscopic techniques. The fullerene derivatives studied formed interdigitated lamellar bilayer structures whose *d* spacing values, estimated by X-ray diffraction patterns, are 2.63 nm for **1**, 3.50 nm for **2**, and 4.28 nm for **3**, respectively. There are the two differing intermolecular forces present due to C_{60} (sp^2-carbons) or alkyl chains (sp^3-carbons). Fullerene moieties always exhibit strong $\pi-\pi$ interactions, while van der Waals interactions between alkyl chains can be altered by variation of their multiplicity. Substitution of three alkyl chains at the fullerene moiety (**3**) was the most effective method for stimulating polymorphism in its derivatives in different solvents.

Keywords: Bilayer structure; Fullerenes; Supramolecular assemblies; Polymorphism

1. Introduction

The morphologies of self-organized structures derived from π-conjugated molecules have recently received considerable attention because the electronic properties of such materials can be enhanced by fine-tuning of intermolecular interactions [1–3]. Manipulation of weak intermolecular forces for construction of new molecular nano- and micro-architectures is a major theme in contemporary chemistry as nanoscience and nanotechnology. For these purposes, π-conjugated functional molecules have been often employed as active components that can serve as molecular nano-electronic devices. Fullerenes and their derivatives are an exemplary class of such molecules being, at the same time highly π-conjugated and nano-sized while possessing fascinating chemical and physical properties. For instance, fullerene films deposited on appropriate substrates and attached to electrodes behave as *n*-type semiconductors [4,5]. Modification of fullerene structures using synthetic methods is a now conventional approach for control of the morphology of fullerenes. Many functional groups have been introduced, often regio- or stereoselectively, for tuning of the physical properties of fullerenes and for construction of supramolecular architectures [6–9]. It has been reported that the amphiphilic fullerene derivatives, which possess hydrophilic moieties substituted at the intrinsically hydrophobic fullerene surface, form spherical vesicles or nano-tubular structures in solution [10–12]. However, the traditional strategy of amphiphilic molecular design does not provide any great insights for the preparation of various dimensional nanoarchitectures due to their limited self-organized nanostructures (spheres or fibers). Recently, we reported supramolecular fullerene nanoarchitectures

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formed under the influence of the two different intermolecular forces due to C_{60} (sp^2-carbons) and alkyl chains (sp^3-carbons). Novel hierarchical supramolecular fullerene architectures with controlled dimensionality were demonstrated in the assemblies obtained using this approach [13,14]. In different solvents, a fullerene derivative (**3**), a fulleropyrrolidine substituted with a 3,4,5-tri(*n*-hexadecyloxy)phenyl group, forms hierarchically ordered assemblies with well-defined 1, 2 and 3D architectures including vesicles (in toluene/2-propanol), fibers (in 1-propanol), disks (in 1,4-dioxane) and cones (in THF/water). In the course of this study, we also discovered serendipitously that fulleropyrrolidines substituted with a 2,4,6-tris(alkyloxy)phenyl group exhibit a fluid phase at room temperature [15]. The key to realization of the room temperature liquid fullerenes was selection of a molecularly-designed substituent, in which each alkyl chain can extend independently to suppress the aggregation of fullerene moieties. These previous reports help us to understand how control of the structure of the supramolecular fullerene assemblies may be achieved by variation of the substitution pattern of the alkyl chains.

Here, we describe a further detailed study regarding the fine-tuning of supramolecularly organized nanoarchitectures of the fulleropyrrolidines substituted with a mono- (**1**), di- (**2**), or tri- (**3**) (*n*-hexadecyloxy)phenyl group and in various solvents. Correlation between the number of alkyl chains and the self-organized bilayer structures as the fundamental subunit, as well as the superstructures formed in various solvents, were investigated by microscopic and spectroscopic techniques. This evaluation indicated that an appropriate hybridization pattern of alkyl chains attached to the fullerene moiety can control the self-organized supramolecular nanoarchitectures, hopefully leading to construction of fullerene-based nanomaterials as components of molecular nanodevices.

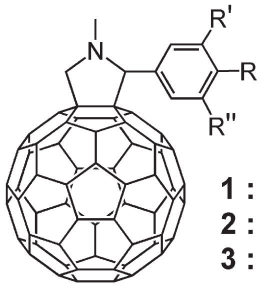
2. Experimental

2.1. Measurements

^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL model AL300 spectrometer at 20 °C. Chemical shifts are reported in ppm downfield from $SiMe_4$, using the solvent's residual signal as an internal reference. Coupling constants (J) are given in Hz. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), and m (multiplet). Infrared spectra (IR) were recorded on a NICOLET NEXUS 670FT-IR spectrometer with HARRICK temperature control cell TFC-M25. UV/Vis spectra were recorded on a Shimadzu U-3600 spectrophotometer with temperature controlled cell holder accessory TCC-240A. The absorption wavelengths are reported in nm with the extinction coefficient in M^{-1} cm^{-1} given in brackets. MALDI-TOF-MS spectra were measured on an Applied Biosystems model Voyager-DE STR in reflector mode with 2-(4-hydroxyphenylazo)benzoic acid (HABA) as matrix. The peak due to the molecular ion is reported in *m*/*z* units. Elemental analyses were performed on a Yanaco model CHN corder MT-6. Differential scanning calorimetry (DSC) measurements were carried out on a Seiko SII DSC 6220 with a Seiko SII EXSTAR 6000 PC Station. XRD powder diffraction patterns were measured at 20 °C using a RIGAKU RINT Ultima III X-ray diffractometer. Scanning electron microscopic (SEM) images were obtained using a HITACHI S-4800 scanning electron microscope at accelerating voltages of 10–15 kV. Silicon (100) was used as a substrate and a platinum coating was performed using a HITACHI E-1030 Ion Sputterer. Transmission electron microscopic (TEM) images were obtained with a JEOL model JEM-100CX transmission electron microscope. One drop of a solution of the supramolecular objects was deposited on a carbon coated copper grid (Ouken Shoji, Elastic Carbon coated Cu 200-A mesh), left to dry under high vacuum, and then observation was performed at room temperature at a voltage of 100 kV (TEM). No staining was used. AFM measurements were carried out using an SII SPA400 with an SPI 4000 Probe Station in dynamic force mode (tapping mode). One drop of a solution of disk objects was spin-coated on a silicon (100) substrate at a spin rate of $r = 1200$ rpm.

2.2. Materials

Fig. 1 shows the chemical structures of the fullerene derivatives employed in this study bearing one- (**1**), two- (**2**), and three- (**3**) hexadecyloxy units at the phenylpyrrolidine moiety. The syntheses of **1** and **3** have been described previously [13,14]. The derivative **2** was synthesized by refluxing the 3,4-bis(*n*-hexadecyloxy)benzaldehyde with *N*-methylglycine and C_{60} in a dry toluene under nitrogen atmosphere for 12 h. After the reaction mixture was cooled to 20 °C and evaporated, the crude product was twice subjected to column chromatography on silica gel eluting with toluene. Removal of the solvent in vacuo followed by preparative GPC (Bio-beads S-X3, THF) afforded **2** (60.0%) as dark brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.86$–0.89 (m, 6H), 1.23–1.81 (m, 56H), 2.81 (s, 3H), 3.96–4.02 (m, 4H), 4.23 (d, $J = 9$ Hz, 1H), 4.85 (s, 1H), 4.98 (d, $J = 9$ Hz, 1H), 6.88 ppm (m, 1H), 6.98 ppm (s, 1H), 7.1–7.5 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.10$, 14.13, 22.67, 22.69, 26.02, 26.05, 29.15, 29.32, 29.34, 29.37, 29.46, 29.62, 29.65, 29.67, 29.70, 29.72, 30.31, 31.91, 31.93, 40.02, 68.95, 69.05, 69.36, 69.96, 77.21, 77.37, 83.38, 125.49, 129.25, 135.78, 135.79, 136.44, 136.56, 139.63, 139.80, 139.96, 140.09, 140.14, 141.53, 141.66, 141.80, 141.89, 142.01, 142.03, 142.08, 142.11, 142.14, 142.22, 142.53, 142.54, 142.57, 142.65, 142.96, 143.13, 144.37, 144.64, 144.67, 145.12, 145.22, 145.25, 145.26, 145.31, 145.45, 145.48, 145.50, 145.53, 145.75, 145.90, 145.92, 146.06, 146.10, 146.13, 146.19, 146.23, 146.28, 146.49, 146.90, 147.27, 147.29, 149.32,



1 : R = $OC_{16}H_{33}$, R' = R'' = H
2 : R = R' = $OC_{16}H_{33}$, R'' = H
3 : R = R' = R'' = $OC_{16}H_{33}$

Fig. 1. Chemical structures of fullerene derivatives (**1**–**3**) employed in this study.