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Hierarchically Organized Soft-Materials Based on Fullerenes

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Abstract. Simple chemical modifications of fullerene (C60) with long aliphatic chains provide
novel type amphiphilic molecules playing in organic solvents due to the two different
intermolecular interactions, namely π–π on C60 and van der Waals interactions on aliphatic
chain moiety, respectively, and open a door developing supramolecular soft-materials having
hierarchically organized architectures, various morphologies and functions based on fullerenes.
By tuning the length and number of aliphatic chains on the derivatives as well as experimental
conditions such as solvents, temperature, substrates for preparation of the assemblies, the
assembled fullerenes showed various faces such as creating of many unique-shaped objects
with controlled their dimensionality. For instance, nanowires and thin disks with single bilayer
thickness in nanometer size, globular, fibrous, conical objects in mesoscopic (sub-micrometer)
scale and flower-shaped and direction-controlled spiral objects in micrometer scale are
obtained. As bulk states, thermotropic liquid crystals and room temperature (isotropic) liquid
fullerenes are interestingly prepared from this molecular designs and showed not only their
fluid natures and comparably high carrier mobility as fullerene-based organic-semiconductor
phenomena. In addition, nano-carbon superhydrophobic surface with fractal morphology of the
two-tier roughness on a nano- and microscopic scale was created from one of the
supramolecular objects. The all of hierarchical supramolecular assemblies describing in this
review is derived from fine-tuning intermolecular interactions of fullerene derivatives bearing
long aliphatic chains.

1. Introduction
The motivation in this study is how to bridge “supramolecular chemistry” and “material sciences”.
The former is more related to organic chemistry, colloids and interfaces chemistry based on molecular
organizations, while the latter one is required intrinsic functionalities, processability and stability of
materials. In fact, nowadays there are many researches towards to development of field emission
transistors (FET), organic light emitting diodes (OLED) and so forth containing organic substances [1,
2]. In most cases, conductive or semiconductive organic molecules or polymers are applied in these
purposes. However, there are rarely considered that prepared (designed and synthesized) molecules
can be hierarchically assembled into desired morphologies using a strategy of the supramolecular
chemistry and became multi-tasked materials with opto-/electric-properties [3]. The selected candidate for the requirements in this study is fullerene (C_{60}). The C_{60} and the derivatives are one kind of promising organic materials because of the electron-transport property (n-type organic semiconductor), rich electrochemistry, photo-responsibility (light synthetic model materials), bio-activity and so on [4, 5]. Although there have been many researches studied on supramolecular chemistry of C_{60}, for instance, formation of the self-organized structures, liquid crystalline materials and molecular recognitions, there are only few reports concerning the properties and applications of supramolecular assemblies of fullerenes [6, 7]. With a view to regulation of their assembled superstructures, conventional amphiphilic approaches, which are based on the substitution of hydrophilic moieties at the intrinsically hydrophobic C_{60}, has been applied in many cases [8-11]. However, controlling the shape of the assemblies is not well-established so far, and only spherical vesicles or tubular assemblies are obtained in this strategy.

Herein, in this review, the author’s recent studies related development of novel type soft-materials based on supramolecular chemistry using unique fullerene derivatives bearing long aliphatic chains as the molecular constituent are described. Fulleropyrrolidines functionalized with a multi(alkyloxy)phenyl group (Figure 1) satisfy some of requirements to be better soft-materials such as a high C_{60} content in the molecule, a predictable compact packing, a highly ordered mesophase and controllable the dimensionality of the self-organized structures. Moreover, fulleropyrrolidines form stable species under electrochemical reduction of the C_{60} cage and thus as redox-active soft-materials. The developed supramolecular fullerene nano- and micro-architectures are utilizing the intermolecular forces introduced by C_{60} (π-π) and aliphatic chain interaction (van der Waals). A delicate balance between the π-π and van der Waals interactions in the assemblies leads to a wide variety of supramolecular architectures.

**Figure 1.** Chemical structures of fullerene derivatives employing in this study.

2. **Dimension Controllable Supramolecular Fullerene Assemblies**

Fullerene derivatives bearing three alkyloxy aliphatic chains (Figure 1, 1-7) were prepared by refluxing the corresponding alkyloxybenzaldehyde with N-methylglycine and C_{60} in dry chlorobenzene, and unambiguously characterized by ¹H and ¹³C NMR, FT-IR and UV-visible spectroscopy, as well as MALDI-TOF mass spectroscopy [12-16]. Fullerene derivative (4), a
fulleropyrrolidines functionalized with a 3,4,5-(hexadecyloxy)phenyl group showed polymorphism [12, 17, 18], different well-defined architectures, on the supramolecular assemblies in various solvent systems (Figure 2). The sample preparation is quite simple as follows. Self-assembled supramolecular objects were prepared by evaporation to dryness of a 1 mL chloroform solution of 4 ([4] = 1.0 mM) followed by addition of 1 mL of the respective solvents. Subsequent heating 60-70 °C for 2 hours resulted in light brown mixtures, which were aged at 20 °C for 24 hours, prior to microscopy examination. Solvents of variable polarity used in these experiments included 2-propanol/toluene mixtures, 1-propanol, H2O/THF mixture, 1-butanol, 1,4-dioxane and enantiopure 2- (S)- or (R)-butanol. Mixtures in a 2-propanol/toluene solution were subsequently cooled to 5 °C for at least 12 hours and ultrasonication was performed at 5 °C for 1 hour. 1,4-Dioxane solution of 4 was also subsequently cooled to 5 °C for 12 hours, resulting in formation of dark brown colored precipitates. As shown field emission scanning electron microscopic (SEM) images in Figure 2, fullerene derivative 4 self-assembles into hierarchically ordered nano- and micro-architectures, such as vesicles with an average diameter of 250 nm in 1:1 2-propanol/toluene mixture at room temperature (Figure 2a), fibers with partially twisted tapes in 1-propanol (Figure 2b), conical objects with diameter of 60 nm perforated at the cone apex in 1:1 H2O/THF mixture (Figure 2c), microspheres with diameters of 1-2 μm (Figure 2d) and maracas-like (Figure 2e) under ultrasonication at 5 °C for 60 min and 30 min, respectively. Windmill-like sheets architectures were obtained in a 1:2 2-propanol/toluene mixture at 20 °C as brown precipitates (Figure 2f). Uncommon self-organized architectures of 4, jellyfish-like, are seen from objects prepared in 1-butanol at 20 °C (Figure 2g). Furthermore the left-handed spiral microstructures were obtained from 2-(R)-butanol (Figure 2h), whereas 2-(S)-butanol provided right-handed spiral objects (Figure 2i) of 3-6 μm in diameters.

Figure 2. SEM images of spherical (a), fibrous (b), conical (c), microspherical (d), maracas-like (e), windmill-like (f), jellyfish-like (g), left-handed (h) and right-handed (i) spiral objects of 4 obtained various solvent conditions. Detail conditions are described in the main text. Reprinted with permission from [12], Nakanishi T et al, 2005 Chem. Commun. 5982. © 2005, Royal Society of Chemistry. [17], Nakanishi T et al, 2007 Small 3, 2019. © 2007, WILEY-VCH.
Even flat disk-shape objects are one of the attractive morphologies in surfactant assemblies [19], normally, two-dimensional planar sheet assemblies turn into tubular assemblies with cigar-like scrolls via rolling up of the sheet in order to minimize the total elastic energy [20]. In this current study, however, planar windmill-like sheet assemblies overlie each other without scrolling the sheets and also the spiral objects are originating from disk-shaped precursor assemblies. Further studies for understanding the formation mechanism, including theory, of the 2-dimensional assemblies and the reasons of the tetra-clefts formation, the anisotropic growth as well as of the influence of the chiral solvent at the molecular level on the microscopic spiral morphogenesis are still required. Slight differences of the aliphatic chain length and numbers of the derivatives cause great morphology changes in their supramolecular assemblies. Remarkably, these reference derivatives 5-7 [14, 18] never showed polymorphs in various organic solvents as seen in 4 [12, 17, 18].

Interestingly C_{60} itself also forms various shaped assemblies under different sample preparation procedures such as liquid-liquid interfacial precipitation [21] and solvent-induced reprecipitation process [22]. These researches proved three dimensional π-π interactions on the C_{60} cores offer them assembling into different single crystalline arrangements and resulting in various shaped C_{60} microcrystalline structures. Research examples described here open a new path how to prepare supramolecular soft-materials based on fullerenes together with desired morphologies.

3. Supramolecular Shape-Shifter from Nano-Disk to Micro-Flower Architectures

To further diversify the library of supramolecular fullerene objects, for instance, with fractal shape, the understanding of the formation mechanism of self-assembled microscopic objects was become more interested in. In 1,4-dioxane solution of 4 at 20 °C, disks with diameters of 0.2–1.5 μm (Figure 3a) and a 4.4 nm thickness (Figure 3b), confirmed by atomic force microscopy, were obtained [12]. The thickness is good agreement with the thickness of aliphatic chain-interdigitated single bilayer (see schematic model in Figure 3c). In fact, structural analyses of the assembled objects or cast thin films of 4 by cryo-TEM, DSC, FT-IR, UV-Vis spectroscopies and XRD indicated multi-bilayer organized structures with the layer distance around 4.4 nm are contributing into the supramolecular assemblies of 4. In other words, the hierarchical organization of 4 consists of interdigitated bilayer-based nanostructures, which further assemble into microscopic architectures such as flowerlike objects [17] (Figure 3f). The flowerlike assemblies obtained as precipitates after cooling down to 5 °C the 1,4-dioxane solution from at 20 °C and several micrometers in size (3-10 μm) with crumpled sheet- or flakelike nanostructures several tens of nanometers in thickness.

Direct observation of the intermediate structure forming from nano objects to microscopic objects helps to deep understanding of the formation mechanism [17]. Rapid cooling of the homogeneous 1,4-dioxane solution of 4 from 60 °C to 5 °C yields intermediate assembled structures of the flowerlike objects. The pre-formed disk objects seen at 20 °C loosely roll up at the edges (Figure 3d). The rolling distortions take place in every quarter of the disk, resulting in square-shaped objects having four corners with conical shapes developed by the encounters of the rolled or folded edges on the disks. Such bending of a thin sheet is, in general, energetically more favourable than stretching it. When the rolling-up proceeds continuously, spatial congestions occur at the four corners, resulting in crumpling, bending, stretching, and fracture of the disks (Figure 3e). After these transformations are complete, the bilayer growth at the edges continues, fixing the spatial conformation of the crumpled sheets, and this transformation leads to the final form of the flower-shaped objects (Figure 3f). These results indicate the transformation (shape-shift) mechanism from molecular assembled bilayer disks into microscopic flower-shaped objects based of fullerene derivative 4. Importantly, the ability to self-organize well-defined, discrete microscopic objects with complex morphologies may stimulate further advances in component design and self-assembly theory that go beyond simple morphologies, such as micelles, vesicles and tubes.
Figure 3. SEM (a) and AFM (b) images of disk-shaped assemblies formed in of 4 as a precursor for the flower formation. The proposed structural model of bilayer assembly (c). SEM images of square-shaped objects loosely rolled up in every corner (d), the further rolled-up objects of crumpled structures at the four corners (e), and the final flower-shaped objects (f). Reprinted with permission from [17], Nakanishi T et al, 2007 *Small* 3, 2019. © 2007, WILEY-VCH.

4. Superhydrophobic Objects Based on Supramolecular Assembles of Fullerenes
Molecular self-organization of a fullerene derivative (1), a fulleropyrrolidines functionalized with a 3,4,5-(eicosyloxy)phenyl group, leaded to macroscopic globular objects with a two-tier roughness on the micro- and nanoscopic length scale (Figure 4a) precipitated from 1,4-dioxane solution after heating and subsequently cooling to room temperature [23]. Surface resulting from simple casting of these objects are superhydrophobic with a water contact angle of 152° (Figure 4b) and surprisingly durable towards polar organic solvents, and acidic/basic aqueous media, as well as heating [23]. The durability of the fabricated structures is related to the apolar nature of the constituents in combination with strong π-π and van der Waals interactions of C_{60} moieties and aliphatic chains.

Figure 4. SEM image (a) of globular objects of 1 precipitated from 1,4-dioxane. A photograph of water droplet (b) on the surface (contact angle of 152°). Reprinted with permission from [23], Nakanishi T et al, 2008 *Adv. Mater.* 20, 443. © 2008, WILEY-VCH.
It is also the fractal morphology and two-tier roughness of the globular objects of 1 on both the nano- and microscopic length scale, originating from the hierarchical self-organization starting from bilayer formations, which adds to the superhydrophobicity of the resulting surfaces. In contrast to most other methods used for the preparation of superhydrophobic surfaces [24], the prepared thin films described here are readily re-used or recovered by simply dissolving them in chloroform. This is an advantage for superhydrophobic surfaces created from hierarchical supramolecular assemblies.

5. Thermotropic Liquid Crystals of Fullerenes

Fullerene $C_{60}$ is one kind of promising electron-transport materials as an $n$-type organic semiconductor [25]. Although various morphologies of $C_{60}$-containing liquid crystals (LC) have been studied in the past decade [26], there is only an example the carrier mobility of fullerenes in the LC state has been evaluated very recently [27]. However, the conducted value, $\sim 10^{-4}$ cm$^2$/Vs, was not large enough for charge transporting materials, probably due to the moderate ordered structure and the low $C_{60}$ content in the mesophase. Our fullerene derivatives satisfy the requirements for a high carrier mobility in the $C_{60}$-containing mesomorphic materials: a high $C_{60}$ content up to 50\% (in the case of 2) and a highly ordered mesophase. Moreover, fulleropyrrolidines form stable species under electrochemical reduction of the $C_{60}$ cage and thus act as redox-active mesomorphic materials [28].

Thermal properties of 1 have been examined by a combination of DSC, POM and XRD. Thermotropic mesophase of 1 is seen in temperature range between 62 to 193 °C, and shows optical texture under polarized optical microscope (Figure 5a), which exhibit birefringence and confirmed the fluid nature. The XRD pattern for 1 at 185 °C shows a strong peak at $2\theta = 1.58^\circ$ assigned $(0 \ 0 \ 1)$, and spacing $= 5.59$ nm, accompanied by higher ordered peaks up to $(0 \ 0 \ 14)$ (Figure 5b). In addition, a broad halo centred at $2\theta \approx 19^\circ$ is assigned to the molten alkyl chains. These higher-degree peaks in the XRD pattern reveal a long-range ordered lamellar mesophase comparable to ordered smectic phase. Derivatives 2 and 4 also showed similar LC characteristics having long-range ordered lamellar mesophase. In other cases of derivatives 3, 5, 6, 7 were found to be non-mesomorphic. The mesomorphic fullerenes feature reversible electrochemistry ($E_{\text{red,1}} = -0.70$ and $E_{\text{red,2}} = -0.87$ V) and a comparably high electron carrier mobility, $\sim 3 \times 10^{-3}$ cm$^2$/Vs for 1 at 120 °C evaluated by a conventional time-of-flights setup (ToF), making them attractive components for fullerene-based soft materials [28].

Figure 5. POM texture of mesophase of 1 at 190 °C (a) and XRD patterns of 1 at 185 °C (b). Reprinted with permission from [28], Nakanishi T et al, 2008 J. Am. Chem. Soc. 130, 9236. © 2008, American Chemical Society.
6. Room Temperature Liquid Fullerenes

In the course of above studies, it was discovered serendipitously that fulleropyrrolidines substituted with a 2,4,6-tris(alkyloxy)phenyl group (8-10) exhibit a fluid phase at room temperature (Figure 6a) [16]. The key point is to select, as the substituent group, a structure which is molecularly-designed in such a way that the alkyl chains spread independently, and cohesion of the fullerene moiety is skillfully suppressed. For derivatives 8-10 studied and over the measured frequency range of the rheological behavior, the loss modules $G''$ is higher than the storage modules $G'$ and suggests liquid-like behavior. As a result of a systematic investigation of the fluid behavior of liquid fullerenes and their functions, the viscosity of the liquid can be controlled by changing the length of the introduced alkyl chain has been discovered (Figure 6b). Interestingly, the longer alkyl chain length is reducing efficiently the viscosity, which is completely opposite trend of a phenomenon of viscosity in normal alkane molecules.

Moreover, because the liquid fullerenes retain the characteristic properties of fullerenes, the liquid is electrochemically active. Cast films of the liquid fullerenes showed two-reductive events of C$_{60}$. As a further advantage of the liquid, this material also has relatively high hole mobility estimated from transient photocurrent measurements, $-3 \times 10^{-2}$ cm$^2$/Vs for 8 at 20 °C [16]. These features make it an extremely attractive novel carbon material for future applications.

Figure 6. Photographs (a) of room temperature liquid fullerenes (8-10) and (b) results of rheology (complex viscosity) experiments of 8-10 at a strain amplitude of 0.01. Reprinted with permission from [28], Nakanishi T et al, 2006 J. Am. Chem. Soc. 128, 10384. © 2006, American Chemical Society.

7. Conclusion

By simple molecular design, combination of C$_{60}$ ($\pi-\pi$) and aliphatic chains (van der Waals), dimensionally regulated supramolecular objects were successfully prepared and enabled us to construct various organic soft-materials (superhydrophobic surfaces, thermotropic liquid crystals, room temperature liquid fullerenes, etc.) based on fullerenes with unique morphologies and the electric functions. Additional parameter to control the self-organization of molecules, such as interaction between molecules and substrate, can be also applied in the present fullerene derivatives, resulting in perfectly straight fullerene nanowires on graphite [13, 15]. The systems described here open the door for novel methodologies developing supramolecular fullerene soft-materials with controlled dimensionality and the desired fullerene functionalities.

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