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Fullerene Derivatives That Bear Aliphatic Chains as Unusual Surfactants: Hierarchical Self-Organization, Diverse Morphologies, and Functions

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Abstract: Conventionally, amphiphiles are composed of hydrophobic and hydrophilic units. They are able to exhibit a wide variety of structures depending on the environment. Such features have been applied in supramolecular chemistry, by which apolar and polar groups are implemented in the molecular design. Here we present an attractive approach to introduce unique amphiphilicity. Relatively simple fullerene (C_{60}) derivatives that bear long aliphatic chains behave as uncommon surfactants in organic media. Although two hydrophobic units are used to assemble the derivatives, slight differences in their polarity and chemical nature may make them incompatible and thus arrange them in microphase-separated mesostructures as lamellar ones. These assemblies are maintained by relatively weak forces, π–π interactions among C_{60} moieties and van der Waals forces between alkyl chains. Therefore, the derivatives can undergo "supramolecular polymorphism" by which different supramolecular assemblies arise by changing the conditions of assembly. A simple modification in their substituent motif of derivatives influences the intermolecular interactions and provides a wide variety of supramolecular materials.

Keywords: amphiphiles • fullerenes • polymorphism • supramolecular chemistry • surfactants

Introduction

Amphiphiles are commonly composed of hydrophilic and lipophilic groups. They are one of the most important structural units and are widely studied in chemistry, biochemistry, biophysics, and colloid science;[1–4] the architectures of soaps, fats, and oils have been investigated for more than one hundred years.[2] In an aqueous environment, aggregation of the apolar tails occurs, in which the hydrophobic interior is protected from water by polar heads. The long-range ordering allows amphiphiles to form different types of micelles, vesicles, lamellar phases,[5,6] tubular arrangements, as well as various cubic phases depending on the chemical structure of the amphiphile and the experimental conditions, that is, concentration, temperature, and pressure.[7–11] They are also capable of assembling at the air–water interface as a Langmuir layer or as a self-assembled monolayer on various solid substrates.[12–14]

The approach of amphiphilicity, which is often described by the Israelachvili rule (structural relation to the ratio between the hydrophilic and hydrophobic components in the amphiphile),[15] has been applied to the design of numerous types of building blocks for hierarchical supramolecular assemblies. For example, gluconamides containing imidazole can self-assemble into vesicles, fibers, hollow tubes, and helices depending on the pH and the presence of Cu ions.[7,16] Peptide–amphiphile derivatives can form nanofibers and patterned membranes.[1,17–21] Chirality was introduced to the membrane system by a hydrogen-bonded network composed of glutamate-derived melamine and ammonium-functionalized azobenzene cyanuric acid amphiphiles.[22] In other cases, systems with π-conjugated amphiphiles as a nonpolar tail group were self-assembled to study their potential use for organic electronics.[23–26] Newer types of the compounds are macromolecular, in which dendrimers and block copolymers display amphiphilicity. The unusual supramolecular assemblies composed of giant amphiphiles exhibit unique geometries such as hollow nanospheres, pores, and single and double helices.[2,27]

Another widely studied amphiphilic system is that of fullerene (C_{60}) derivatives. Owing to their intrinsic hydrophobicity and unique electronic and optical properties, the introduction of C_{60} to the amphiphilic system and mimicking of lipid polymorphism will allow the formation of an interesting hybrid system. In this article, we will focus on an atypical surfactant, C_{60} derivatives that bear aliphatic chains; both the head and tail group are hydrophobic. This is not an ordinary class of amphiphiles because, conventionally, surfactants possess hydrophobic and hydrophilic subunits.

Concept

Conventional approach: Advances in C_{60} chemistry have allowed the introduction of new functionalities and the tuning of their properties.[28–31] Mostly the focus has been to derivatize C_{60} with hydrophilic moieties, that is, polar or charged groups.[32–35] Such conventional amphiphiles composed of hydrophobic and hydrophilic units are water soluble and have great potential for biological applications. For example, C_{60} bearing a mono- and dicarboxylic acid group has the ability to cleave DNA, inhibit enzymes, and act as a cytotoxic compound.[32] In addition, this type of amphiphile is a promising candidate for the formation of a Langmuir–Blodgett (LB) layer because it can spread on water.[33]

Akin to the polymorphism of lipids, C_{60} functionalized with hydrophilic groups can self-assemble into various structures in a polar solvent.[36–39] Cassell, Asplund, and Tour

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have reported one of the earliest examples: The cationic species C_{60}–*N*,*N*-dimethylpyrrolidinium iodide (**1**), dissolved in dimethylsulfoxide (DMSO)/water, forms nanorods upon the addition of benzene or vesicles when ultrasonication is applied (Scheme 1). The supramolecular structures were proposed to have a nonpolar C_{60} group associate in the interior of the assembly in a polar environment, whereas the ionic units face outward.[36] A similar approach was applied to anionic species, in which potassium pentaphenyl C_{60} assembled into a bilayer vesicle in water.[40,41]

C_{60} amphiphile composed of hydrophobic units: The molecular assembly of amphiphile units fabricated by the above approach proceeds only in a polar medium. If stable assemblies are possible in a nonpolar environment, a new type of supramolecular structures may be discovered.[42] An obvious approach is to eliminate the hydrophilic units from the C_{60} derivatives. This will increase their solubility in an aprotic solvent. However, amphiphilicity is only preserved if there is sufficient solvophobic or solvophilic difference between the head and tail group. There are reports on assemblies comprising C_{60}-based nonpolar/polar/nonpolar ternary motifs.[43–45] Upon assembly, the hydrophobic tail group protrudes into the environment. In these examples, in addition to the hydrophobic effect, both the presence of the diphenylester group[43] or the potassium counterion[44] introduced other driving forces for the assemblies.

Nakashima and co-workers have reported C_{60} derivatives that bear three alkyl chains with an amide and three ester connectors (**2**–**4**, Figure 1a).[46–49] These molecules lack the high hydrophilic nature of the above-mentioned conventional C_{60} amphiphiles and are thus not water soluble; rather, they are soluble in various organic solvents (i.e., DMF, DMSO, chloroform, benzene, and *n*-hexane). More interestingly, although the molecules are mainly composed of hydrophobic C_{60} and aliphatic chains, they were capable of forming Langmuir films on water.[47,48] The phase transition from crystalline to liquid crystalline was observed, thereby confirming that these systems behave similarly to lipid biomembranes (Figure 1b).[46,49]

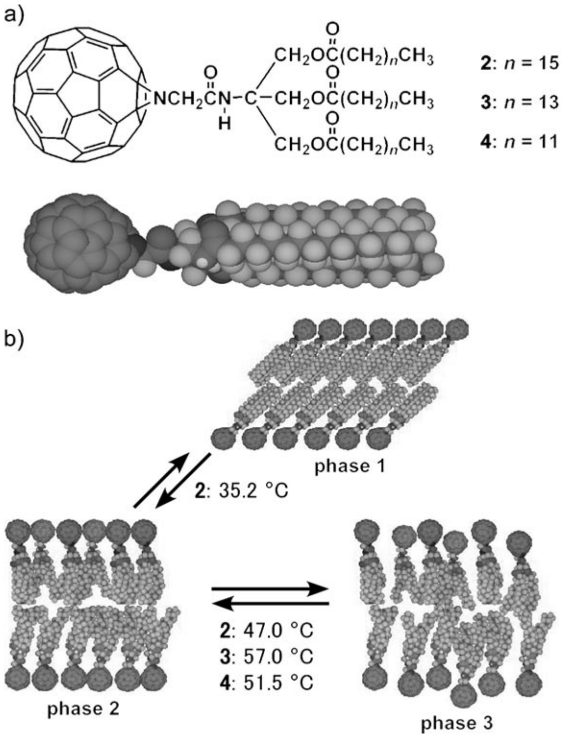
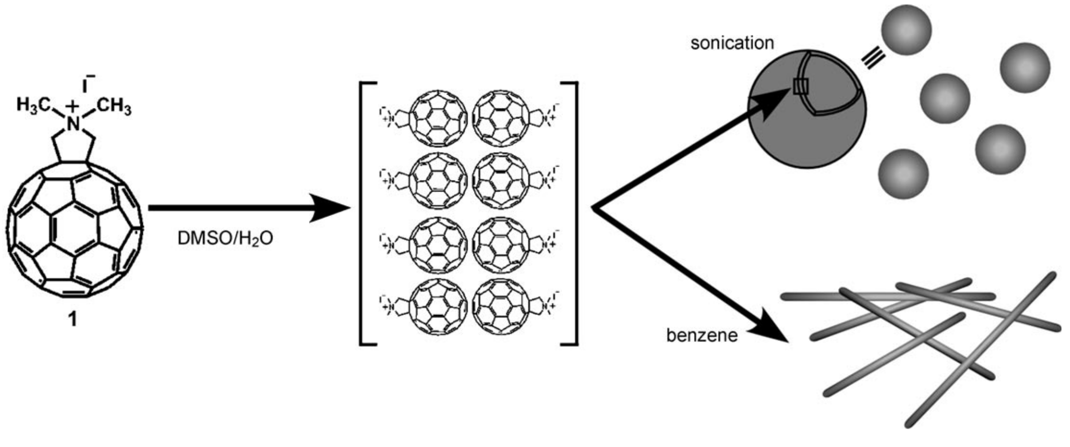


Figure 1. a) Chemical structure (**2**–**4**) and Corey–Pauling–Koltun (CPK) space-filling model of the C_{60} lipid (**2**), with alkyl chains connected to the C_{60} with one amide and three ester moieties. b) Schematic representation of the bilayer system undergoing phase transitions.[46,49]

Although both C_{60} and saturated hydrocarbon chains are hydrophobic, their chemical natures essentially differ. A buckyball (C_{60}) is composed of carbon atoms with three sp^2 hybrid orbitals with one delocalized π orbital such as benzene. As a result, it has a high affinity toward aromatic solvents (i.e., benzene, toluene, xylenes). On the other hand, the saturated hydrocarbon group consists of an sp^3 hybrid and thus has a higher affinity toward alkanes than the aromatic compounds. Such a difference can be the basis of the unusual amphiphilicity and is one of the driving forces for the molecular assemblies in C_{60} derivatives that bear aliphat-



Scheme 1. Vesicles and nanorods formed from a lamellar organization of the C_{60}–*N*,*N*-dimethylpyrrolidinium iodide amphiphile (**1**).[36]

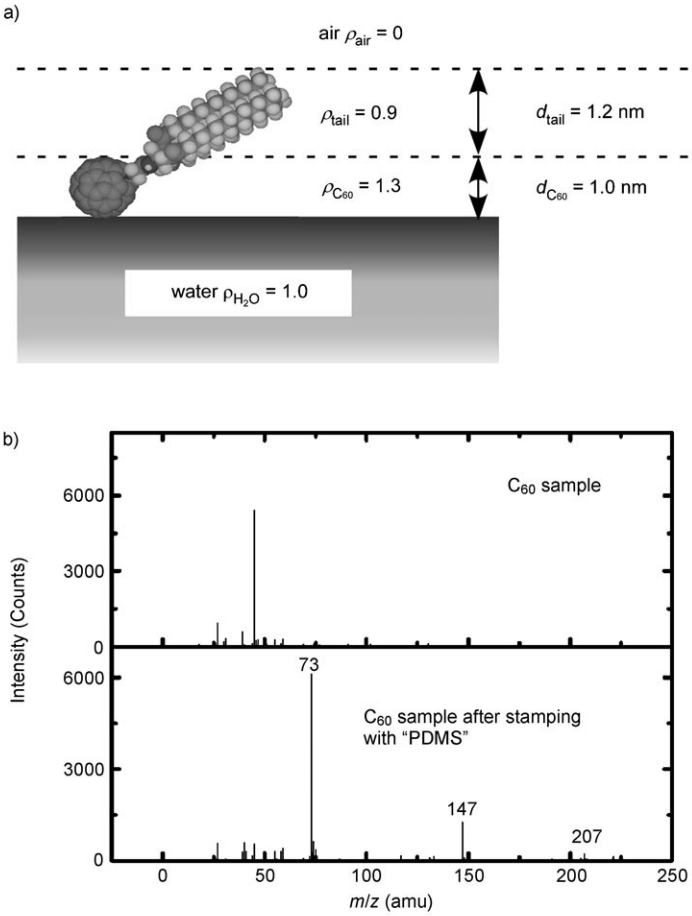


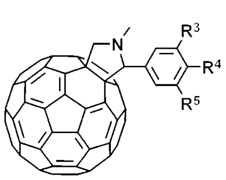
Figure 2. a) Schematic illustration of the Langmuir monolayer assembled from the C_{60} lipid (**2**; Figure 1a), which was based on the results from in situ X-ray reflectivity studies at the air–water interface.[47,48] b) TOF-SIMS spectra before (top) and after (bottom) PDMS was stamped onto a C_{60} film.[57] (Reproduced with permission from the American Chemical Society).

ic chains. In addition, C_{60} is less hydrophobic than the hydrocarbon group; the C_{60} film has lower water contact angles than the alkane monolayer (75–100° for C_{60} and 110° for alkane film),[50–56] and in situ X-ray reflectivity of the Langmuir monolayer of **2** indicated that the C_{60} moieties are located adjacent to the water (Figure 2a).[48] Accordingly, in a relatively polar environment, unlike that of ionic C_{60} amphiphile (Scheme 1), the C_{60} group form the surface of the assembly. In fact, the variation of polarities between these two hydrophobic units is significant enough that the hydrophilic polydimethylsiloxane (PDMS) can adsorb onto C_{60} and not onto other hydrocarbons.[57] This was shown by time-of-flight secondary ion mass spectroscopy (TOF-SIMS), in which peaks of PDMS fragments were only observed after the stamping on a C_{60} film (Figure 2b).

Unlike conventional amphiphiles, for which the molecular assemblies rely mostly on the hydrophobic effect, the unusual surfactants composed of hydrophobic components are sensitive to both the type and polarity of solvents. Conceptually, they should be more versatile in forming various types of self- and supramolecular assemblies.

Assemblies of C_{60} That Bear Aliphatic Chains

We have proposed a series of simple fulleropyrrolidine derivatives with a phenyl ring functionalized with alkyloxy chains (**5**–**10**, Scheme 2)[58,59] The basis of such a design is to keep the cross-sectional width of the C_{60} and the alkoxylated phenyl group comparable; geometrically, the derivatives that are cylindrical in shape (with comparable cross-sectional size between head and tail group) have a propensity to self-assemble into a bilayer.[56,60,61] This will ensure that the curvature is introduced upon an unequal degree of solvation at the two ends of the molecule. The novelty of the design is that the substitution patterns, number, and the type of alkyl chains can be altered by the phenyl substituents, therefore enabling a systematic study. As elaborated in the following sections, such minor variations will have a drastic effect on the morphologies and functions of the resulting supramolecular fullerene structures.



5: $R^3 = R^4 = R^5 = \text{-O-}(CH_2)_{19}CH_3$
6: $R^3 = R^4 = \text{-O-}(CH_2)_{19}CH_3$, $R^5 = H$
7: $R^4 = \text{-O-}(CH_2)_{19}CH_3$, $R^3 = R^5 = H$
8: $R^3 = R^4 = R^5 = \text{-O-}(CH_2)_{15}CH_3$
9: $R^3 = R^4 = R^5 = \text{-O-}(CH_2)_3(CF_2)_7CF_3$
10: $R^3 = R^4 = R^5 = \text{-O-}(CH_2)_9C{\equiv}C\text{-}C{\equiv}C(CH_2)_{13}CH_3$

Scheme 2. Fulleropyrrolidine derivatives (**5**–**10**): the C_{60} with a phenyl ring functionalized with alkyloxy chains with varying chain lengths, substituent position, and type.

Supramolecular polymorphism: There are numbers of C_{60} derivatives that are capable of forming supramolecular assemblies, but only a few that undergo "supramolecular polymorphism." This is because when strong intermolecular forces are introduced into the system, a specific structure dominates and structural transformation will no longer occur. This is seen, for example, in the case in which a hydrogen-bonding moiety is introduced into the molecular design. For instance, the presence of two amides in the C_{60} derivative causes gelation and can form nanowires (by means of the LB method) but it does not lead to other structures.[62] Therefore our system (**5**–**10**) in Scheme 2, in which the self-assembly relies on weak van der Waals forces of alkly chains and π–π interactions of C_{60} moieties, exhibits the unique ability to supramolecularly polymorph.

Hierarchical supramolecular assemblies: A fulleropyrrolidine with 3,4,5-(hexadecyloxy)phenyl (**8**, Scheme 2) assembles various supramolecular structures depending on the solvent (Figure 3). A vesicular aggregate with an average diameter of 250 nm is assembled in the solvent of a 2-propanol/toluene mixture (Figure 3a).[58] High-resolution transmission electron microscopy (HRTEM) reveals an empty core and a wall thickness of 8–9 nm, which corresponds to the two bilayer arrangement. With 1-propanol, 1D fibrous structures resulted with a length greater then 20 μm (Figure 3b).[58]

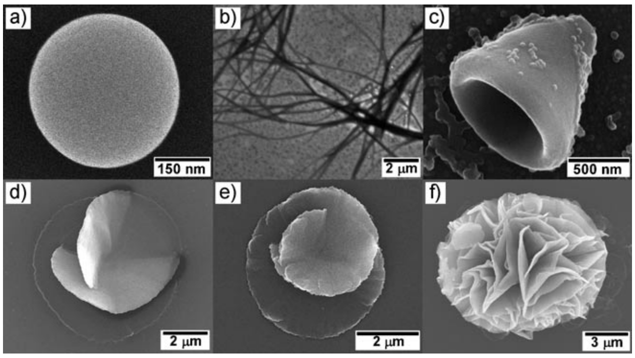


Figure 3. SEM images of **8** assembled into a) vesicular, b) fibrous, c) cone-shaped, d) left-handed spiral, e) right-handed spiral, and f) flowerlike assemblies.[58,61] (Reproduced with permission from the Royal Society of Chemistry).

Cone-shaped objects, with hole diameter of approximately 60 nm and shell thickness of approximately 150 nm, were assembled in an equimolar mixture of water/THF (Figure 3c).[58] Chirality can be introduced into the supramolecular structures, in which left- and right-handed structures result under the presence of 2-(*R*)-butanol and 2-(*S*)-butanol, respectively (Figure 3d and e).[61] A flowerlike object was observed by heating it in 1,4-dioxane at 60 °C for 2 h followed by aging (at around 20 °C for 24 h and subsequently in cooler conditions, around 10 °C, for at least 12 h; Figure 3f).[61]

A supramolecular polymorphism was also observed for the 3,4,5-(eicosyloxy)phenyl derivative (**5**, Scheme 2).[56,60] After solubilization by heating (around 70 °C) in an appropriate solvent, a dark brown precipitate resulted upon cooling as a nonequilibrium product. These precipitates possess three-dimensional architectures in which micrometer-sized globular particles exhibit flaked outer surfaces with submicron features (similar to that of Figure 3f). The size, morphology, and particle dispersity of supramolecular assemblies depended on the solvent and cooling conditions. The particle prepared from 1,4-dioxane (heated and then cooled to around 20 °C) resembled those prepared from derivative **8** (as shown in Figure 3f), albeit with smaller diameter with flakes that are less extended (Figure 4a). With *n*-decane cooled to 5 °C after solubilization of **5**, particles with smaller and denser flakes were formed (Figure 4c). A shaggy particle with pointy flakes is obtained in *n*-dodecane by cooling to around 20 °C (Figure 4d). High-resolution cryogenic-TEM (HR-cryo-TEM) on the edges of these flake structures revealed multilayer nanostructures (Figure 4b) with a lamellar periodicity (estimated from XRD) of a bilayer arrangement; units with alkyl chains interdigitated.[56,59,60] FTIR (methylene asymmetric stretches with a lower wavenumber, 2918 cm^{-1}) and differential scanning calorimetry (DSC) thermograms (crystalline-to-liquid-crystalline phase transition) indicated that the molecules are well-packed and in a crystalline state.[56,59,60]

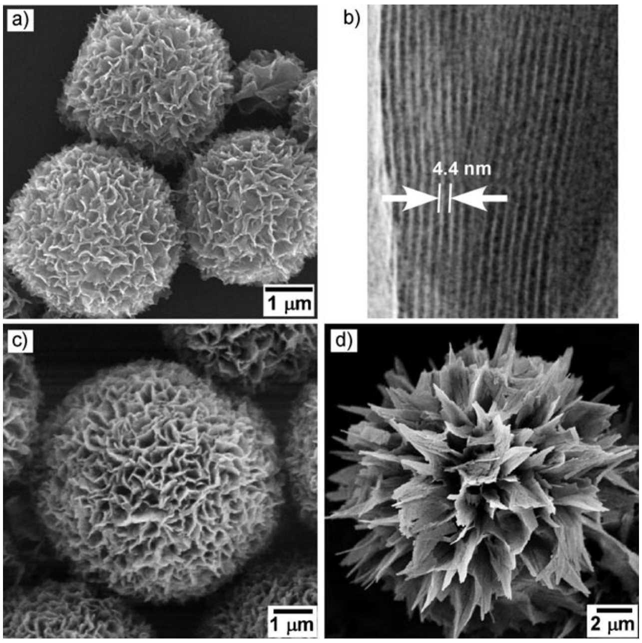


Figure 4. SEM images of **5** assembled in a) 1,4-dioxane, c) *n*-decane, and d) *n*-dodecane.[56,60] b) High-resolution cryogenic TEM image of a flake edge of the microparticle shown in (a). (Reproduced with permission from the Royal Society of Chemistry).

A globular particle was observed with dieicosyloxy-substituted C$_{60}$ as well (**6**, Scheme 2).[56] Compound **6** in 1,4-dioxane (cooled to around 20 °C after solubilization) assembled into large particles with a diameter of a few tens of micrometers (Figure 5a); they are made up of a plating structure with a thickness of around 100 nm (Figure 5b). HR-cryo-TEM, FTIR, XRD, and DSC studies confirmed that the assembled structures are similar to those prepared from **5** and **8**. On the other hand, although the monoeicosyloxy-substituted derivative (**7**, Scheme 2) self-assembled into hierarchically organized objects (Figure 5c and d; from heated 1,4-dioxane solution, vesicle particles or micron sheets were formed upon cooling at around 5 °C and around 20 °C, re-

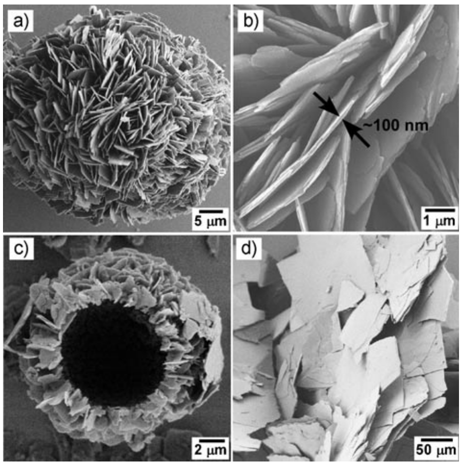


Figure 5. a, b) SEM images of **6** prepared in 1,4-dioxane at 20 °C. SEM images of **7** assembled in 1,4-dioxane at c) 5 and d) 20 °C.[56] (Reproduced with permission from the Royal Society of Chemistry).

spectively), their molecular arrangement was different from that of the above examples. It is multilamellar yet the alkyl tails are in a noncrystalline state (based on the relatively high wavenumber of the IR peak of the methylene asymmetric stretches). A substantial difference in the cross-sectional width of the alkyl group and C_{60} seems to limit the packing of the alkyl chains; therefore they do not form an all-*trans* oligomethylene configuration. It is noteworthy that the crystallinity of C_{60} became higher as the number of alkyl substituents was reduced. The "delicate balance" between the van der Waals and π–π interactions in the assemblies can lead to versatile supramolecular objects.

These hierarchical assemblies are primarily, if not exclusively, multilamellar structures. There are two possible arrangements for a lamellar structure: the configuration in which either the C_{60} or the alkyl group is exposed to the solvent. As described, C_{60} is relatively less hydrophobic than the alkyl tails (Figure 2). Accordingly, we can presume that in nonpolar solvents (i.e., *n*-decane, *n*-dodecane), alkyl tails, and with more polar solvents (i.e., 1,4-dioxane), C_{60} will be situated at the outer layer of the assemblies. This was indeed proven by the microparticles prepared from the C_{60} derivative with 3,4,5-(semiperfluoroalkyloxy)phenyl group (**9**, Scheme 2 and Figure 6d).[56] Due to the small surface free energy of fluorinated compounds, it should even be nonwetting towards oil droplets. However, the microparticles prepared from these molecules in relatively polar solvent (diethoxyethane) did not repel *n*-hexadecane (oil contact angle of 22°); this is an indication that C_{60} is exposed to the outer surface. The dewetting nature of these assemblies toward water will be discussed below.

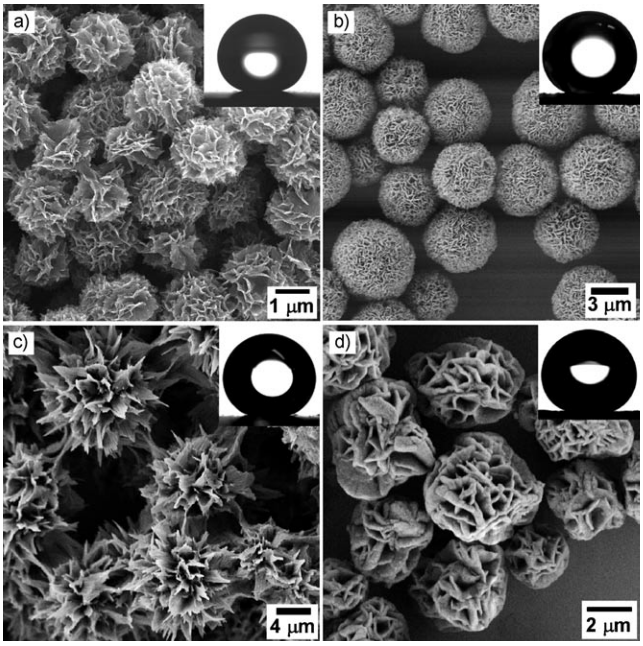


Figure 6. Films prepared from **5** in a) 1,4-dioxane, b) *n*-decane, and c) *n*-dodecane, as well as from d) **9** in diethoxyethane. The insets show water droplets with static water contact angles: a) 152, b) 163, c) 164, and d) 148°, respectively.[56,60] (Reproduced with permission from the Royal Society of Chemistry).

Plasticization and metallization: The major drawback of supramolecular objects is that they are assembled by weak noncovalent interactions. A change in environment (i.e., acidity, solvent, temperature, and mechanical stress) will induce structural changes or disintegration of the assemblies. This limits the potential utilization of these organic/supramolecular materials for certain applications. To tackle such an issue, a photo-crosslinker (diacetylene) was implemented in the long alkyl chains (**10**, Scheme 2). After flaked microparticles were assembled from the derivative, they, both the diacetylene and C_{60} moieties, were polymerized by UV light.[63] This not only retained the surface morphologies, it also became chemically and mechanically robust. The polymerized assembly resists acidic or basic aqueous media, most organic solvents (even in high-solubility solvents for **10**), heat (up to 200 °C), and improved its stiffness by about 25-fold (judged by colloidal probe atomic-force studies).

Another alternative is to transcribe the morphologies of the supramolecular assemblies into more robust matter. A transcription of C_{60}-based microparticles (e.g., the flaked microparticles of **5** in Figure 4a) into various metals was demonstrated. The procedure involved sputtering of the desired metal (Au, Pt, Ti, and Ni) directly onto a thin film of the supramolecular assemblies. This was followed by the removal of the C_{60} template (by means of dissolving in organic solvents). The recovered template can in principle be reused, thereby making the entire process sustainable. Even though the intrinsic properties of C_{60} are lost during transcription, their nano-/micrometric features can greatly enhance certain properties of metal. Nanostructured metal surfaces exhibit plasmonic enhancement, and therefore surface-enhanced Raman scattering (SERS) of the resulting metal nanoflake was demonstrated. The enhancement factor of the Au nanoflake was on an order of magnitude of 10^5.[64]

Morphology-Dependent Functions

Superhydrophobic film: Nano-/microstructured fractal surfaces often display superhydrophobicity, a property that is seen in nature (e.g., Lotus leaf) and is defined as a surface that exhibits water contact angles greater than 150° (an extreme case of dewetting). This phenomenon is caused by air trapped within the rough surface. A water droplet is essentially sitting on top of the film of air (with minimum contact with the surface).[65] Intrinsically, hydrophobic C_{60}-based microparticles with rough nanoflake microstructure (Figure 6) fit all the criteria to be an excellent superhydrophobic material.

To investigate their hydrophobicity, thin films of these particles on a flat substrate (i.e., glass and silicon wafer) were prepared by slow evaporation of the solvent.[56,60] As shown in Figure 6, well-defined 3D fractal architectures demonstrated superhydrophobicity (145–164°: Table 1). In

Table 1. Static water contact angles of films prepared from the assemblies of C_{60} derivatives.

Compound	Solvent	T[a] [°C]	Angle[b] [°]
5	1,4-dioxane	20	152
5	*n*-decane	5	163
5	*n*-dodecane	20	164
6	1,4-dioxane	20	151
7	1,4-dioxane	5	148
9	diethoxyethane	−13	148
10	THF/MeOH	−14	145[c]

[a] Aging temperature. [b] Static water contact angle. [c] The contact angle value was evaluated at the sample after UV treatment.

comparison, spin-casted films had a water contact angle of around 103°. The fractal pattern of the assemblies and therefore the roughness induced a tremendous enhancement of hydrophobicity as predicted by the Cassie–Baxter law.[66]

One of the advantages of these C_{60}-based superhydrophobic surfaces is that they are prepared by self-assembly. Since they dissolve in certain organic solvents (i.e., chloroform and toluene), molecules can be recovered, recycled, and reapplied to a surface. They can be a promising material as they withstand acidic/basic aqueous media, polar organic solvents and heat (stable under 100 °C).[60] Furthermore, by introducing photo-cross-linkers into the alkyl chains of the derivatives and photo-polymerizing, even more robust materials can be fabricated (as discussed in the previous sections). Even after polymerization, the dewetting nature of the surface is preserved.

Liquid crystal: C_{60} is an n-type organic semiconductor. Therefore the amphiphilic nature of the C_{60} derivatives can be applied to the construction of bicontinuous networks of electron-donor and -acceptor phases. Numerous C_{60}-based liquid crystals have been reported.[67–70] Their carrier mobility in the organized C_{60} phase is appealing for their use as charge-transporting materials.[71] If practical C_{60}-based photoconductive liquid-crystalline materials are to be achieved, two factors must be considered: a suitable and dense C_{60} arrangement and a high C_{60} content of the system. In these regards, our fullerenes with aliphatic chains (e.g., **5**, **6**, and **8**) can be good candidates. They act as amphiphiles in solvents (mentioned above) and, furthermore, can behave as good molecular building blocks for liquid-crystalline organizations in solvent-free conditions with C_{60} microphases separated in layers. In addition, a relatively compact molecular design allows for higher C_{60} content (up to around 50 %).[72,73]

The insets of Figure 7a, c, and e display polarized optical microscopy (POM) images of alkylated C_{60} derivatives (**5**, **6**, and **8**) in the mesophase. The thermotropic mesophase was observed in the temperature range of 62–193, 33–223, and 44–226 °C, respectively. They were fluid and yet retained a long-range ordered lamellar mesophase (confirmed by XRD study, Figure 7a, c, and e); they also show birefringence. More importantly, they exhibit high electron carrier mobility (around $3\times10^{-3}\,cm^2V^{-1}s^{-1}$), as investigated by a time-of-flight setup.[72] X-ray diffraction patterns of high-order and systematic intensity variation can be observed. This proves the perfectly lamellar structure and allows detailed studies of the density profile (Figure 7a, c, and e).[73,74] These patterns were well-fit by a three-box electronic density model (Figure 7b, d, and f) with three distinct regions of electron density. The three sections correspond to the C_{60}, alkyl chains, and their connection segment. Judged from XRD, the molecules are arranged in bilayers in which their long axis is arranged perpendicular to the plane of the layers. Unlike the lamellar structures of microparticles introduced in the previous section, in the mesophase, C_{60} derivatives are arranged without interdigitation of alkyl tails. It is apparent that the liquid crystal arises from the balance between the disordering of the alkyl chains (entropic effect) and the attractive C_{60} π–π interactions.[72,73] Our molecular design allows a systematic study of such intermolecular interactions by varying the number, position, and type of alkyl chains. These findings are promising for C_{60}-based soft materials with electrochemical and optoelectronic properties implemented into a device.

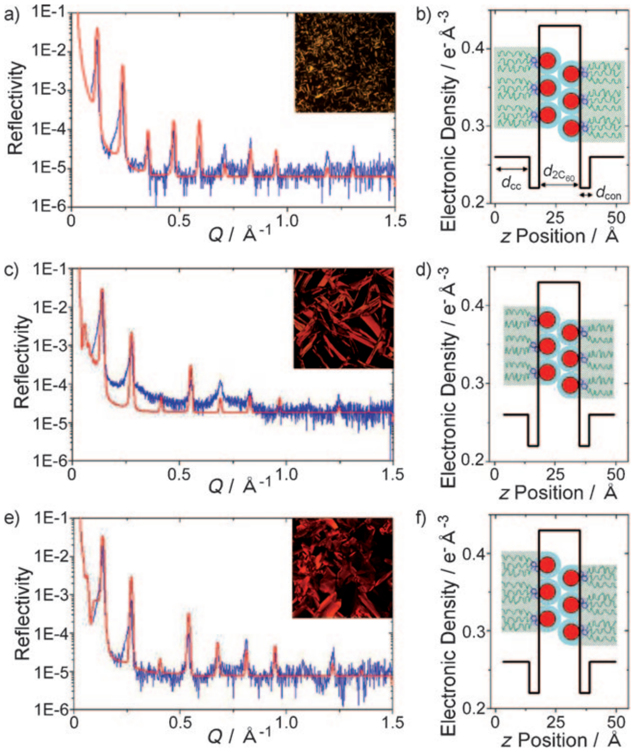


Figure 7. Three-box electronic density profiles and illustration of corresponding molecular arrangements (b, d, and f) derived from the fits (red line) of X-ray diffraction data (a, c, and e, experimental original data in blue line) of **5**, **6**, and **8**, respectively (in the mesophase).[72,73] The insets in a), c), and e) are polarized optical microscopy images. (Reproduced with permission from the American Chemical Society).

Nanocarbon fluid: The position of the alkyl chains on the phenyl group can influence the intermolecular interactions between the C_{60} derivatives and greatly impact the resulting structure. Some of the intriguing examples are the C_{60} deriv-

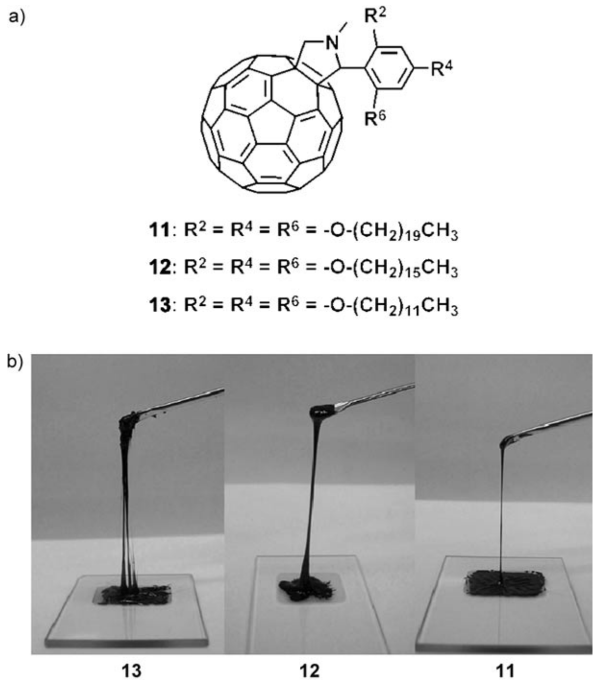


Figure 8. The molecular structure and photo images of room-temperature C_{60} liquids (**11**–**13**).[75] (Reproduced with permission from the American Chemical Society).

atives with alkyl chains tethered at 2,4,6-positions of the phenyl substitution (**11**–**13**, Figure 8a). Such a substitution pattern prevents aggregation of the C_{60} moieties, and they are liquid at room temperature (Figure 8b).[75] Rheology studies of these fluids revealed that the viscosity increases as the length of alkyl chains decreases (approximately 1.2×10^5, 1.3×10^4, and 1.1×10^3 Pa for **13**, **12**, and **11**, respectively). This phenomenon is opposite to that of common alkane molecules. The exact reason for the reversed trend is not certain. Perhaps longer alkyl chains further isolate C_{60} and increase their fluidity. Nevertheless, the redox properties of C_{60} as well as their relatively high hole mobility (around $3\times10^{-2}\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$) in these fluid nanocarbons make them an attractive electronic material.

Summary and Outlook

C_{60} derivatives that bear aliphatic chains act as uncommon amphiphiles. Even though both C_{60} and the alkyl tails are hydrophobic, there is sufficient lipophilic difference among the two moieties to drive long-range ordered structures. In addition, C_{60} is relatively less hydrophobic than alkyl chains and therefore contributes to the unique amphiphilic nature. These derivatives are able to assemble various supramolecular architectures depending on the preparation conditions ("supramolecular polymorphism"). One of the unique features of alkyl-conjugated C_{60} derivatives is their ability to polymorph depending on the environment or on their molecular design. A wide variety of materials (microparticles, thermotropic liquid crystals, and room-temperature liquids) can be prepared by changing the substitution patterns, number, and the type of alkyl chains on the phenyl group of the C_{60} derivative. Their self-assembly relies mainly on relatively weak interactions, the van der Waals interaction of alkyl tails, and π–π interactions among C_{60}. The absence of strong intermolecular forces, such as hydrogen bonding, and the delicate balance between the van der Waals and π–π interactions allows these molecules to exhibit a wide variety of morphologies and functions. Perhaps such phenomena may be also observed with other π-conjugated molecules.[76–78] The next milestone will be to develop a method to implement these novel C_{60} materials into a device. Precise control over their morphology and the direction of their organization at the desired position (i.e., between electrodes) will be critical for further development of supramolecular technology.

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