Fullerenes

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Self-Assembly Made Durable: Water-Repellent Materials Formed by Cross-Linking Fullerene Derivatives[**]

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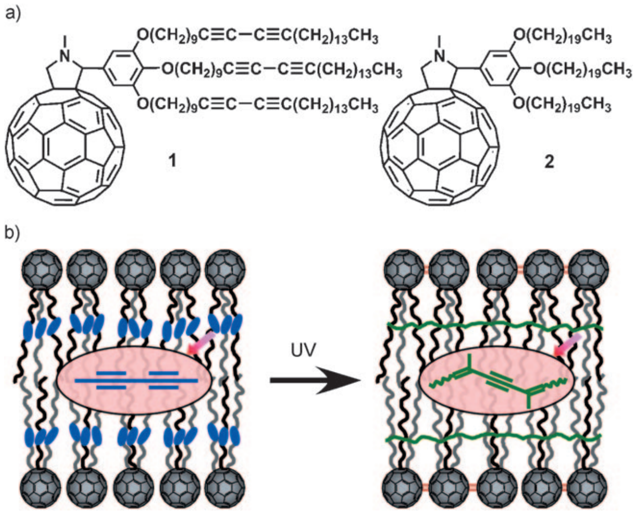
The fine-tuning of the interactions between π-conjugated molecules can enable the development of supramolecular materials that have attractive properties.[1] However, the low strength and stability of these materials, which are organized by weak noncovalent interactions, impose limitations for certain applications. Most self-organized materials suffer from structural changes when exposed to organic solvents, high temperatures, or mechanical stress. Accordingly, it is crucially important to harness the sophisticated functional properties found in noncovalent assemblies while imparting them with the structural durability offered by covalent chemistry. To address this problem, covalent cross-linking of self-organized structures has been developed and has received much attention. For instance, click chemistry,[2] diene metathesis,[3] and disulfide bond formation[4] have been successfully utilized to stabilize various structures such as gel fibers, self-assembled nanotubes, and host frameworks.[5] Subtle control of the reaction conditions is required to maintain the structure and morphology and to simultaneously achieve efficient covalent cross-linking, which are the key factors that determine the final performance of the supramolecular materials in practical applications.

The fullerene C_{60} possesses unique physicochemical properties,[6] and is a promising candidate for the construction of versatile supramolecular architectures.[7–10] We recently demonstrated that fullerene derivatives bearing three saturated aliphatic chains (such as **2**) self-assemble into unique supramolecular nano- or microscopic architectures by π–π and van der Waals interactions. By tuning the boundary conditions of self-assembly, well-defined one-, two-, or three-dimensional objects with various macroscopic morphologies can be observed.[11] This strategy demonstrates the feasibility of constructing supramolecular materials through the combination of appropriate molecular design and self-assembly algorithms. However, these materials are structurally fragile because of the weak intermolecular forces, which is a disadvantage in technologies that require high durability. Herein, we present a new design based on a fullerene derivative (**1**, Scheme 1) that contains diacetylene (DA) functional groups, which are well-known photo-cross-linkers,[12] in long aliphatic chains. This derivative self-assembles into flakelike microparticles with a bilayer structure at the molecular level. Irradiation with ultraviolet light leads to effective cross-linking of both DA and C_{60} moieties, while maintaining their nano- and macroscopic organization. This process gives rise to a material with remarkable resistivity to



Scheme 1. a) Molecular structures of fullerene derivatives modified with diacetylene (**1**) and saturated aliphatic chains (**2**) employed in this study and b) a schematic representation of the photo-cross-linking process in the bilayer structural subunit of **1**.

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solvent, heat, and mechanical stress. Moreover, the surface of the cross-linked flakelike objects combines a water-repellent nature with durability.

The fullerene derivative **1** was obtained in five steps[13,14] starting from 1-hexadecyne (see Scheme S1 in the Supporting Information) and unambiguously characterized by ^{1}H and ^{13}C NMR, FTIR, and UV/Vis spectroscopy, and MALDI-TOF mass spectrometry. Self-organized objects were prepared from **1** as follows: A solution of **1** (2.2 mg, 1 μmol) in a mixture of THF/MeOH (3:2 v/v, 1 mL) at 50 °C was cooled to 20 °C and stored at −14 °C for 24 h to afford a dark-yellow precipitate in quantitative yield. MeOH (3 mL) was added to ensure complete formation of the precipitate, which was stable in solution at room temperature. Flakelike microparticles of compound **2**, which was used as a reference, were prepared according to our previously published procedure[11c] by heating a solution of **2** (1 mM) in 1,4-dioxane to 70 °C followed by cooling to room temperature. The self-assembled particles were removed from the dispersions and spread onto a water surface to form a compact and uniform particle layer at the air–water interface, which was then transferred onto various substrates (Si, quartz, or glass) and dried under vacuum for further studies.[15]

The field-emission scanning electron microscopy (SEM, Figure 1 a) image shows that **1** reproducibly self-assembles into flakelike particles around 1 μm in size with crumpled petal-shaped structures around 100 nm in thickness. High-resolution cryogenic transmission electron microscopy (HR-cryo-TEM) studies at the edge of the particle reveal a multilamellar structure (Figure 1 b). Fast Fourier transform (FFT) analysis (Figure 1 b, inset) indicates a lamellar periodicity of (5.7 ± 0.1) nm. In addition, the appearance of third-order spots in the FFT indicated that the lamellar organization is highly periodic. By taking into account the dimensions of **1** (ca. 4.5 nm), we propose that the molecular arrangement in the assembly is a bilayer structure with interdigitated and/or disordered alkyl chains.

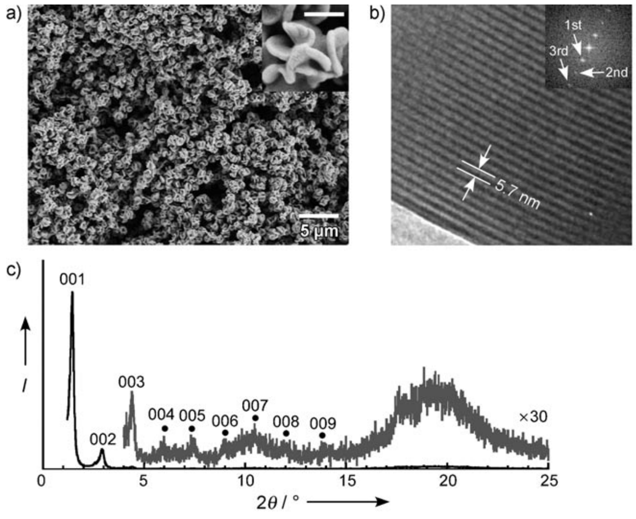

Figure 1. a) SEM image of the self-organized particles of **1** prepared from THF/MeOH solution. The inset shows an enlarged particle image (scale bar = 500 nm). b) HR-cryo-TEM image of the edge of one particle. The inset shows the corresponding FFT analysis showing the 1st, 2nd, and 3rd order spots. The periodicity of the lamellae is 5.7 nm. c) X-ray diffraction pattern of the self-organized particles of **1** at 25 °C. The corresponding *d*-spacing value is 6.0 nm.

The multilamellar arrangement suggested from HR-cryo-TEM studies is consistent with the XRD analysis of **1**. As shown in Figure 1 c, the XRD pattern of the bulk precipitate of **1** measured at 25 °C displays reflections of the (001) to (009) planes, which indicate a long-range ordered lamellar structure. The interlayer distance obtained from the XRD analysis is 6.0 nm, which is slightly larger than that obtained from TEM analysis and may result from different experimental conditions such as temperature or pressure. Moreover, the two broad halos that appear at approximately 10.3° and 19.4° can be attributed to the in-plane average distance between neighboring C_{60} molecules (ca. 8.7 nm) and the average distance between molten alkyl chains (ca. 0.46 nm, see below), respectively. The UV/Vis spectrum of the particles of **1** at 25 °C shows three bands with absorption maxima at 333, 270, and 256 nm. When compared to the absorption maxima of a solution of **1** in *n*-hexane, these bands are red-shifted by 17, 16, and 2 nm, respectively, which indicates π–π interactions between the neighboring C_{60} molecules in the assembled objects (see Figure S2 in the Supporting Information).[11] The FTIR spectrum of the particles of **1** at 25 °C displays asymmetric and symmetric methylene stretching bands at 2924 and 2852 cm^{-1}, respectively, which suggests that the alkyl chains are not in a crystalline state.[16] This result is in agreement with differential scanning calorimetry (DSC) data of the bulk precipitate of **1**. A broad shoulder around 15 °C and a peak centered at 29.1 °C, which correspond to the pretransition and the solid–liquid crystalline transition of the alkyl chain, are observed with ΔH and ΔS values of 55.4 kJ mol^{-1} and 180 J mol^{-1} K^{-1}, respectively, for the later peak (see Figure S9a in the Supporting Information). In addition, because of the orthorhombic subcell structure of the oligomethylene units, the methylene scissoring mode shows a broadly split band at around 1463 cm^{-1} in the FTIR spectrum, which indicates that parts of the alkyl chains could be interdigitated (Figure S3 in the Supporting Information).[17] These results confirm that the assembled particle of **1** is composed of bilayer structural subunits with noncrystalline and partially interdigitated alkyl chains (Scheme 1 b).

Photoinduced cross-linking studies on the flakelike particles with cross-linkable DA and fullerene moieties were carried out. Photoreactions of the DA moieties were studied by FTIR spectroscopy (Figure 2). Upon irradiation at 25 °C with a 150 W low-pressure Hg lamp, the IR absorption bands at 2256 and 2191 cm^{-1}, assigned to the asymmetric vibrational mode of the DA monomer, gradually decreased. This is accompanied by the appearance of a new band centered at 2212 cm^{-1}, which is assigned to the asymmetric vibrational mode of the C≡C bond in the poly(diacetylenes) (PDs).[12a,c] To unambiguously assign the spectral changes, an IR investigation of the precursor molecule of **1** (Scheme S1 in the Supporting Information) containing the DA moieties was carried out. UV irradiation caused a similar trend in the FTIR spectra (Figure S4 in the Supporting Information). The bands at 2256 and 2179 cm^{-1} gradually disappeared, and a new band

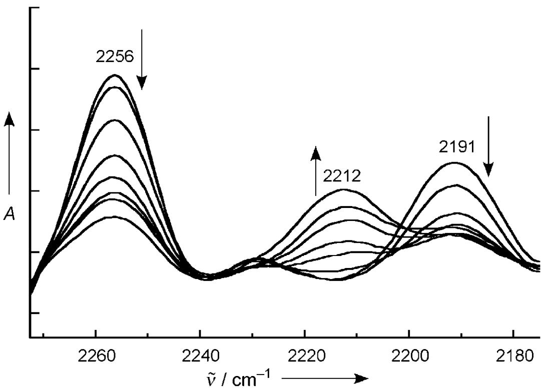

Figure 2. FTIR spectra of the assembled particle of **1** upon UV irradiation from 0 to 11 h under an Ar atmosphere at 25 °C.

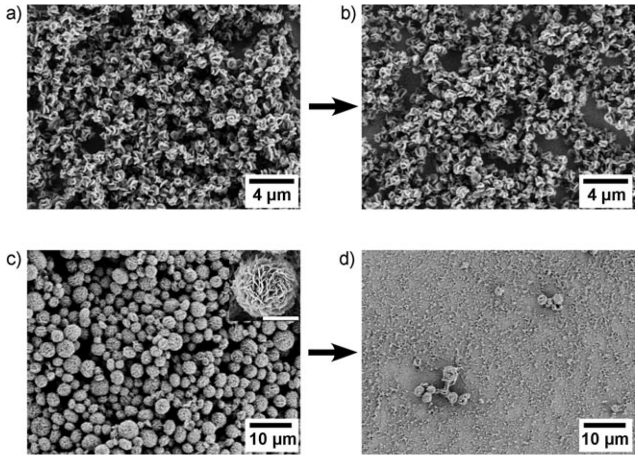

Figure 3. SEM images of the cross-linked particles assembled from **1** a) before and b) after exposure to chloroform for 12 h. The last two images show photoirradiated particles assembled from **2** c) before and d) after rinsing with chloroform for 5 s. The inset in (c) shows an enlarged image of particle **2** (scale bar = 3 µm).

centered at 2215 cm^{-1} appeared. Photopolymerization of DA groups results in an absorption band at around 550 nm if PDs with long conjugation lengths are produced.[12b] This is clearly observed for the precursor DA molecule (Figure S5 in the Supporting Information), but not for the self-assembled species of **1**, which suggests that photo-cross-linking in the latter produces PDs of varying length and conformation.[12e] The moderate conjugation may be caused by imperfect DA alignment in the assembly of **1**, which hinders polymerization to yield PDs with extended conjugation. The absence of an isosbestic point in the IR spectra (Figure 2) indicates that more than two species are involved in the cross-linking reaction. It is noteworthy that UV irradiation results in photoaddition reactions between neighboring C_{60} moieties (Scheme 1 b), which is indicated by the decreased and broadened characteristic absorption of C_{60} (Figure S6 in the Supporting Information) as well as the disappearance of the pentagonal pinch mode of C_{60} at 1467 cm^{-1} in the Raman spectra (see Figure S7 in the Supporting Information).[18] Although the detailed assignments of the dimerized or polymerized C_{60} structures need further careful analysis, the lamellar organizations in the assemblies are maintained even after the photo-cross-linking (see Figure S8 in the Supporting Information).

The cross-linked flakelike particles of **1** display a remarkable resistivity to organic solvents. As observed by SEM (Figure 3 a, b), the cross-linked particles maintain their shape after immersion in chloroform for 12 hours. In sharp contrast, non-cross-linked particles are completely dissolved by the same solvent within seconds. Moreover, a control experiment employing self-organized globular particles prepared from **2** (without the DA group) indicated that cross-linking of DA moieties is indispensible for the achievement of a robust material. As shown in Figure 3 c, d, when exposing the photoirradiated particles of **2** to chloroform for five seconds, most of the particles disassembled and dissolved in the solvent. The sparsely preserved residue might be caused by the photoaddition reaction between the neighboring C_{60} moieties.

In addition to the solvent tolerance, the thermal stability and stiffness of the cross-linked particles of **1** are remarkably enhanced. Before cross-linking, the DSC thermogram (see Figure S9a in the Supporting Information) of the particles displays two endothermic peaks that are attributed to the phase transition from the solid to the mesomorphic phase (29.1 °C) and from the mesomorphic phase to the isotropic phase (140.3 °C). On the other hand, a thermogram of the cross-linked particles (see Figure S9b in the Supporting Information) shows only small endothermic peaks with less than 5 % intensity of the original phase transition temperatures, which correspond to remaining monomer. At the same time, a broad peak around 51 °C appears, which is assigned to the glass transition of the alkyl chains in the cross-linked species. Although the melting point of **1** is 140.3 °C, no visible changes in the organized structures were seen in the SEM images, even when the cross-linked particles were heated at 150 °C for up to 12 h (see Figure S10a in the Supporting Information).

AFM force spectroscopy allows the determination the mechanical properties of a material.[19] Analysis of the data of force versus deformation can provide information about stiffness and adhesion (typical force versus deformation curves (approach and retract) of a sample before and after UV treatment are shown in Figure S11a, b in the Supporting Information). Based on several measurements (see the Supporting Information), UV irradiation of **1** resulted in a remarkable increase of the determined stiffness of about 25-fold (from below $(0.54\pm0.48)\,N\,m^{-1}$ to $(14.5\pm1.7)\,N\,m^{-1}$) and a decrease in the adhesion (from 425 nN to 140 nN). The results clearly reveal that UV irradiation of the flakelike particles of **1** results in a robust assembly and a less adhesive glassy material.

For practical applications, covalent cross-linking of self-organized supramolecular materials opens a path for the development of functional materials with improved durability. In the present study, we demonstrate the potential of using cross-linked particles formed from DA-functionalized fullerene derivatives as a robust water-repellent surface. The nature of water repellency is important in daily life and in industry for self-cleaning coatings and anti-wetting agents,[20] which mimic the surface properties of the Lotus leaf.[21] According to the Cassie model, the microscopic roughness on the particle surface accommodates tiny pockets, which entrap air and enhance the surface hydrophobicity.[22] Contact angle (CA) measurements showed that a surface that was fully covered with the flakelike (fractal-shaped) particles of **1** indeed exhibits high water repellency, with a CA of around 146.2° (Figure 4a). This value is significantly larger than the corresponding CA of 102.1° of a flat surface made by spin-coating with non-assembled **1** (Figure S12a in the Supporting Information). Because the non-cross-linked surface is not durable enough, heating at 150 °C for 5 seconds disrupts the fractal morphology completely because of its low melting point (140.3 °C) and results in a flat surface film with a CA of 100.8° (Figure 4b). In sharp contrast, after UV irradiation of the particles, the cross-linked surface retained its water repellency ($CA \approx 145°$; Figure 4c) even when heated to 200 °C (Figure 4d and Figure S10b in the Supporting Information) or when exposed to aqueous acid (pH 1) or base (pH 12; Figure S12b in the Supporting Information). It was found that immersion of the surface in various organic solvents including solvents in which **1** is soluble, such as chloroform, THF, or toluene does not influence the surface wettability as the CA remains above 144° (see Figure S12b in the Supporting Information). In comparison with other water-repellent surfaces explored so far, the high durability of these surfaces is quite uncommon, as most surfaces are only durable to high-polarity organic solvents such as acetone and alcohols, or temperatures below 100 °C.[11c,20]

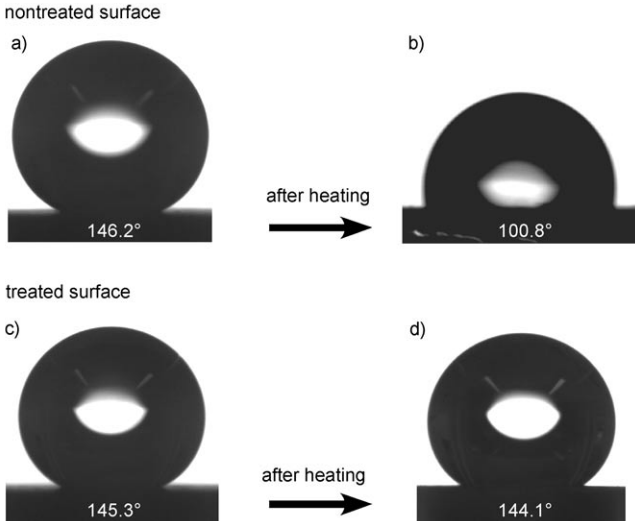

Figure 4. Water contact angles at surfaces of assembled particles of **1** a) before and b) after heating the surface, which was not UV-treated, at 150 °C for 5 s, and c) before and d) after heating the UV-treated sample at 200 °C for 12 h.

In summary, self-organization of the diacetylene-functionalized trialkylated fullerene **1** into microparticles and its photoinduced cross-linking has been investigated. Flakelike microparticles with a highly ordered bilayer structural subunits were prepared reproducibly by precipitation from a THF/methanol mixture. Photoirradiation effectively cross-links both the diacetylene and C_{60} moieties, which leads to supramolecular materials with significantly enhanced stiffness ($>$25-fold) and remarkable resistivity to various organic solvents, acidic or basic aqueous media, as well as to heating up to 200 °C. The potential of this strategy is illustrated by the fabrication of a highly durable water-repellent surface that satisfies some of the requirements for water-repellent materials, such as facile and substrate independent production, high durability to different ambient or harsh conditions, as well as enhanced mechanical stiffness. The design of molecular building blocks that self-assemble into well-defined hierarchical architectures following topochemical cross-linking is expected to be an important research direction in supramolecular materials science, for instance, towards coating technologies in micro- or nano-electromechanical systems (MEMS/NEMS). Further investigations into the photoelectronic performances that originate from the rich π conjugation in these assemblies are underway.

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