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Properties Formed by A Fullerene C₆₀-POM Hybrid

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Robust Onionlike Structures with Magnetic and Photodynamic

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We report for the first time the synthesis of a covalently-linked fullerene C_{60} -Dawson POM hybrid, which can form onionlike structures with rich magnetic, electrochemical and photodynamic properties.

Self-assembly plays a vital role in supramolecular chemistry, which can result in multifunctional systems with broad applications.¹ The self-assembly of amphiphilic molecules which bear nanometer-sized building blocks with defined shapes, such as fullerene C_{60} (refers to C_{60} hereafter),² polyoxometalates (POMs)³ and polyhedral oligomeric silsesquioxane (POSS),⁴ is important as the interplay of the forces at this length scale may be quite different compared to small and/or linear molecules, leading to the occurrence of new self-assembly algorithms. Besides amphiphile which consists of only one nanometer-sized building block, in recent years great interest has also been devoted to the hybrids where two such building blocks are covalently connected, which have been termed molecular Janus particles, Janus co-clusters or shape amphiphiles.⁵

As C_{60} has rich optical, electrochemical and photodynamic activities while POMs are well-known for their magnetic and catalytic properties, the idea of covalently linking them to create a new class of amphiphiles becomes quite attractive. However, although hybrids of C_{60} - C_{60} , ^{5a-c} C_{60} -POSS, ^{5c,5d} POM-POSS^{5c,5e,5f} and POSS-POSS^{5c,5g} have been reported, that with a structural model of C_{60} -POM is quite rare. In an earlier work, Bonchio et al. prepared a C_{60} -POM hybrid by directly attaching organosilylfulleropyrrolidines to a lacunary Keggin-type POM (γ -SiW₁₀O₃₆).⁶ However, only the catalytic properties of the hybrid were reported while no self-assembly behavior was addressed. In addition, this synthetic

method carried out on lacunary POM through silylanization can not be generalized to other types of POMs.

Herein, we report the synthesis and aggregation behavior of a fullerene C₆₀-Dawson POM hybrid (1) for the first time. Our strategy (Fig. 1A) to create 1 includes amide coupling between a monosubstituted C₆₀ carboxylic acid (1a) and a Tris-modified, Dawson trivanadium substituted heteropolytungstate (1b) in THF/CH₃CN mixture (for more details, see ESI). The successful synthesis of 1 and its structure features have been fully characterized by a variety of techniques (Fig. S1-S7, Table S1). From FTIR spectra (Fig. S1), signals at 1648 cm⁻¹ (C=O stretching), 1561 cm⁻¹ (N-H bending) and 1220 cm⁻¹ (C-N stretching) indicate the formation of the amide bond, while those at 1086, 951, 907, and 817 cm⁻¹ (from backbone of POM) as well as those in between 3050-2800 cm⁻¹ (from the alkyl chain of the counterions) show that the POM moiety remains intact during the synthesis. From XPS (Fig. S2), signals from V_{2p} , W_{4d} and W_{4f} are evidenced in **1** and the peak intensity of the C_{1s} is much stronger compared to **1b**, which is indicative of the succesful attachment of C_{60} . This conclusion is further proved by elemental analysis and EDX where the content of carbon increases obviously from 1b to 1 (Table S1, Fig. S3). In addition, the EDX results could also confirm the existence of heavy metal elements. Further deconvolution on C_{1s} of 1 from XPS reveals the appearance of new signals from C=C (284.8 eV) and C=O (287.5 eV), which is a further proof for amide bond formation. From ³¹P NMR (Fig. S4, in d_6 -DMSO), it was found that signals of the two phosphorus heteroatoms (P_1, P_2) in the unmodified POM (1b') locates at -7.36 and -13.82 ppm, creating a gap (Δ_{δ}) of 6.46 ppm. Upon Tris modification, Δ_{δ} decreases to 6.05 ppm, which is consistent with the literature report.⁷ Further attachment of the C₆₀ unit does not induce significant changes and Δ_{δ} only slightly increases to 6.11 ppm. In ¹³C NMR (Fig. S5), it can be seen that the signals from the benzene and carbonyl groups of the ester precursor of 1a (1a") move to the high field while others from the linker goes in the opposite direction, which may be caused by diamagnetic/paramagnetic ring currents on the surface of the cage, by the paramagnetism effect of 1b (see below), or by a

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synergistic effect of the two.⁸ From thermogravimetric analysis (TGA, Fig. S6), a two-step weight loss was noticed. The first one around 200 °C is due to the decomposition of the counterions while the second one above 600 °C can be ascribed to the loss of the C₆₀ unit. XRD and DSC measurements (Fig. S7, S8) reveal that **1** is an amorphous solid with high melting points (>200 °C).



Fig. 1 A) Synthetic route of 1. B) Self-assembly of 1 in DMSO. TEM (a, b), HRTEM (c) and SEM (d) images. The concentration of 1 is 5.0 (a, d) and 20.0 (b, c) mg·mL⁻¹, respectively. The scale bar for the magnified image inside image b is 20 nm.

The Dawson POM is soluble in polar solvents including DMSO, DMF and CH₃CN while C_{60} is not. After covalently attached, 1 shows quite similar solubility with the POM moiety, presumably due to the larger size of Dawson POM compared to C₆₀. The unique molecular structure of 1 makes it a unique amphiphile in these POM-friendly solvents with the C_{60} unit as the solvophobic part. We first checked the aggregation behavior of 1 in DMSO and typical results are summarized in Fig. 1B. Observations on two typical samples containing 5.0 mg·mL⁻¹ (~0.78 mmol·L⁻¹) and 20.0 mg·mL⁻¹ (~3.12 $mmol \cdot L^{-1}$) **1** showed the formation of vesicles with diameters of 30-110 nm (image a, b). Sample with a lower concentration (0.6 mg·mL⁻¹) has also been checked and the ability of vesicle formation remains. Further analysis by high-resolution TEM (HRTEM, image c, Fig. S9) gives a thickness of ~3.5 nm for an individual layer (between the arrow heads) and a distance of ~5.0 nm between two adjacent layers (averaged from four repeating units indicated between the two arrows). In scanning electron microscopy (SEM) observations (image d, Fig. S10), contrast variations have also been noticed at the edges of the onionlike aggregates, which further confirms a coreshell structure.

The formation of the onionlike structures demonstrated here should be driven by multiple intermolecular forces including solvent-phobic interaction, van der Waals attraction and π - π stacking among C₆₀ spheres as well as electrostatic interaction and the like-charge attraction⁹ among POM units. As the onionlike structures form in POM-friendly solvent, a structural model of molecular bilayers can be envisaged with POM units stay outside and C₆₀ moleties hide inside. This assumption gains further proof from ¹³C NMR where signals of the carbon atoms from C₆₀ appear as a bulge between 140-150 ppm, which is in sharp contrast with those of C₆₀ monoadducts in a good solvent which exist as a variety of sharp peaks in the same region (Fig. S5). This indicates that upon aggregate formation, the C₆₀ spheres have been internally encapsulated in a quasi-solid state with obvious inter-sphere interactions. In addition, the aggregate formation also leads to peak broadening and baseline roughening in ¹H NMR (Fig. S5), which is consistent with similar phenomenon observed for alkyl chains embedded in molecular aggregates in water, such as vesicles.¹⁰ Fig. 2 gives the illustration of a vesicle which contains four molecular bilayers. The length of **1** in optimized conformation is calculated to be ~2.5 nm, which is more than one half of the thickness of an individual molecular bilayer (~3.5 nm). This indicates that **1** self-organizes in an interdigitated way within the molecular bilayers, which is reasonable from a steric viewpoint considering the relatively small space occupied by the linker.



Fig. 2 Illustration of the formation of onionlike structures. A) Overview of an onionlike aggregate with four bilayers. B) Magnification of the indicated part in the vesicle. C) Structural model of **1** with the sizes of each part indicated. For better clarity, the counterions of the Dawson POM are omitted.

When DMSO was replaced by solvents with similar polarities, such as CH₃CN and DMF, onionlike structures with similar sizes and number of layers have been detected by TEM observations (Fig. 3, a-d, Fig. S11). Dynamic light scattering (DLS) measurements in CH₃CN denote the existence of both unimers and aggregates (Fig. 3b). Next, we checked the robustness of the onionlike structures towards the addition of solvents with much lower or higher polarities. When toluene was added to the series of samples with 5.0 mg·mL⁻¹ 1 in DMSO, the solution remains stable up to the addition of 60% (v/v) toluene, above which precipitation occurs (Fig. S12a). TEM observations showed that the onionlike structures are still present (Fig. 3e, Fig. S13). However, they become highly asymmetric with inhomogenous layer thicknesses. For example, the thickness of the three layers for the half-baked onionlike structure obtained for the sample containing 40% toluene by volume (Fig. 3e1) is measured to be 3.82, 5.07 and 7.24 nm from inside to outside. It could be possible that the penetration of toluene into the C_{60} layer leads to partial disassembly of 1 from the onion, accounting for the appearance of the asymmetric layers. When the volume percentage of toluene increases to 60%, the aggregates are even more difficult to be found. (Fig. 3e2, Fig. S13c). Interestingly, the onionlike structures exhibit high resistance towards the addition of water. For the two series of samples with 5.0 and 0.6 mg·mL⁻¹ 1 in DMSO, the solutions remain stable up to the addition of 99% (v/v) water (Fig. S12b, S12c). TEM observations revealed that the vesicles remain intact within all the solvent compositions. Some typical results are given in Fig. 3f and Fig. S13. Note that 1 is totally insoluble in water. If we change the order of solvent addition, that is, adding water first followed by the addition of

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DMSO, **1** also remains as solid (Fig. S12b). It turns out that **1** can be facilely introduced to water with the help of only a small amount of DMSO, and the robustness of the onionlike structures towards the addition of water should originate from the relatively strong interactions among the C_{60} units in water¹¹ as well as the decreased water solubility of the POM moieties. As both C_{60} and POMs have shown encouraging biological activities,^{12,13} this phenomenon opens the door for the potential applications of **1** in biomedicine.



Fig. 3 a-c) TEM images (a,c) of 20 mg·mL⁻¹ **1** and DLS result (b) of 0.1 mg·mL⁻¹ **1** in CH₃CN. d1,d2) TEM images of 20 mg·mL⁻¹ **1** in DMF. e1,e2) TEM images of 5.0 mg·mL⁻¹ **1** in toluene/DMSO mixtures with the volume percentage of toluene to be 40% and 60%, respectively. f1-f4) TEM images of 5.0 mg·mL⁻¹ **1** in H₂O/DMSO mixtures with the volume percentage of H₂O to be 40%, 60%, 80% and 95%, respectively.

Besides imaging studies, the aggregate formation of **1** in various solvents and binary solvent mixtures can be also monitored by UV-vis measurements. It is known that C_{60} monoadduct in a good solvent exhibits rich absorptions in the UV and visible region. Specifically, the weak sharp peak around 430 nm is very sensitive to the π - π interaction among the C_{60} moieties, and thus can be selected as an indicator of the aggregation of C_{60} derivatives in solutions.¹⁴ For **1a** in THF, the peak around 430 nm can be clearly recorded, indicating that **1a** exhibits as individuals. For **1** in the three selected solvents, (i.e., DMSO, CH₃CN and DMF) as well as in various solvent mixtures, however, this peak vanished totally due to the aggregation of **1** (Fig. S15), which is consistent with the imaging studies mentioned above.

The onionlike structures formed by **1** have rich physicochemical properties originating from both C_{60} and POM moieties, which makes them thoroughly different from their counterparts formed by surfactant mixtures.¹⁵ The magnetic properties of **1** both in solid state and bulk solutions were investigated by superconducting quantum interference device (SQUID) and electron spin resonance (ESR) measurements. The M-H curves of **1** in solid state reveal weak ferrimagnetism both at 300 K and 5 K (Fig. S16). The temperature-dependent ESR spectra of the onionlike structures have been recorded using CH₃CN as a model solvent. As shown in Fig. 4A, unsplitting single line was noticed within the whole investigated temperature range, which can be ascribed to the faster spin-lattice interaction in bulk solution due to the formation of aggregates

compared to that in solid state as evidenced by the well-defined anisotropic eight-line splittings of the ²³V(IV) nuclei derived from the POM unit (Fig. 4B).¹⁶ Notably, the ESR peak intensity decreased dramatically below the freezing point of CH₃CN (~227 K), which was caused by the slower motion of the vesicles at low temperatures. Besides, compared to **1b**, the splittings in **1** become more obvious, indicating that the spin of the hybrid has been slowed down due to the attachment of the C₆₀ unit. The electrochemical properties of **1** together with the two precursor molecules **1a** and **1b** have been investigated by cyclic voltammetry (CV, Fig. 4C, Fig. S17). Originating from the rich redox activities of both **1a** and **1b**, a variety of peaks have been recorded for **1**, albeit most of the peaks become blurry due to the high tendency of **1** to form aggregates.



Fig. 4 A) Temperature-dependent ESR spectra of 5.0 mg·mL⁻¹ **1** in CH₃CN. B) ESR spectra of **1b** and **1** in solid state at room temperature. C) Cyclic voltammetry of **1a** (in dichlorobenzene), **1b** (in DMF) and **1** (in DMF) with 0.1 mol·L⁻¹ tertbutylammonium hexafluorophosphate as supporting electrolyte. D) Generation of ¹O₂ for **1** in aqueous solutions containing 1% (by volume) DMSO under 532 nm green light with a power density of 0.1 W·cm⁻². For comparison, the activity in dark is also given.

 C_{60} and their derivatives are well-known for their capability of production of singlet oxygen $({}^{1}O_{2})$ under light, which forms the basis of their applications in photodynamic therapy (PDT).^{12a} The facile dissolution of 1 in water at the presence of trace DMSO enables us to check the capability of ${}^{1}O_{2}$ production of the onionlike structures, and a dose-dependent manner has been revealed under the irradiation of green light (Fig. 4D). As the precursor 1b only produces quite limited amount of ¹O₂ under the same experimental conditions (Fig. S18), the capability of ${}^{1}O_{2}$ production observed in the onionlike structures can be unambiguously ascribed to the presence of the $C_{\!60}$ unit. In control experiments, the onionlike structures thoroughly lost this capability in the dark. The photodynamic properties of the onionlike structures indicate that the C_{60} moieties well preserve the capability of ${}^{1}O_{2}$ production even trapped in the molecular bilayers. This is exciting considering the great potential of the biological activities exhibited by both $C_{60}^{\ \ 12}$ and POM¹³ as well as the popular applications of vesicles (liposomes)¹⁷ in biomedicine.

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In summary, we have successfully synthesized a fullerene C₆₀-Dawson POM hybrid for the first time and investigated in detail its aggregation behavior in bulk solutions. Driven by the unique self-assembly algorithms exhibited by both C₆₀ and POMs, the C₆₀-POM hybrid can exhibit peculiar aggregation behavior, which has been demonstrated by the formation of onionlike structures. The structural persistance of these aggregates towards the change of solvents reveals the strong intermolecular interactions, which is in contrast to their fragile counterparts formed by traditional surfactants. The rich magnetic, electrochemical and photoresponsive properties of the onionlike structures imply their potential applications in material and life sciences. Current work also implies that traditional amidation can be a facile and clean strategy to covalently link C60 and POMs, which opens the door for the upcoming of a thoroughly new family of amphiphiles. We suppose these initial findings could initiate an enthusiasm on further explorations of new C60-POM hybrid, which can not only add more interesting building blocks for supramolecular chemistry, but also provide new opportunities in other related fields.

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A fullerene C_{60} -Dawson POM hybrid was prepared for the first time, which can aggregate into onionlike structures with magnetic and photodynamic properties.

