C_{60} based nanoparticles: self-assembly of a novel fullerene derivative

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A novel salt-derivatized [60]fullerene pyrrolidine nitroxide has been synthesized which readily forms ball-like nanoparticles through self-assembly. Transmission electron microscopy images indicate the formation of spherical particles with a diameter of 80–130 nm, and an LB film of the compound was obtained; the nanoparticles and the LB film were also examined by tapping mode atomic force microscopy.

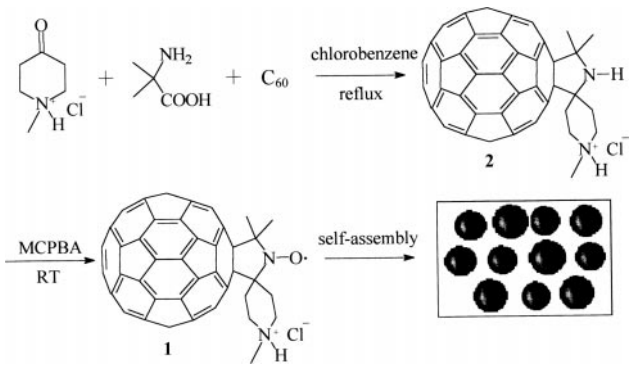
The aggregated states of [60]fullerene have aroused much interest. Gelators with a chiral center can be self-assembled into long strands with a helical structure,[1,2] and previously reported gelators feature in most cases a fibrous structure.[3–7] Recently, nanorods were also obtained by the self-assembly technique.[8] We have been interested in the synthesis of C_{60} and C_{70}-based stable nitroxides, focusing on the preparation of novel magnetic materials.[9–11] The main strategy of our research is to obtain C_{60}-based magnetic materials with multiple spins, in which the magnetic properties may be improved through multiple spin–spin interactions. The usual method of multiaddition to obtain multiple spin units is difficult.[12] However, the self-assembly technique is a powerful method for the preparation of highly ordered arrangements of molecules in the solid state *via* the formation of clusters. Self-assembled nanostructures with nitroxides in each unit may produce novel magnetic properties due to the ordered arrangement of the spin magnetic moments. We describe here the preparation and the supramolecular assembly of a C_{60}-pyrrolidine nitroxide ammonium chloride (**1**) that can form novel nanoparticles.

C_{60}-pyrrolidine ammonium chloride (**2**) was prepared from C_{60}, 2-aminoisobutyric acid and *N*-methylpiperidone hydrochloride in 27% yield through a 1,3-dipolar cycloaddition reaction.†[13–15] A mixture of C_{60} (72 mg, 0.1 mmol), 2-aminoisobutyric acid (20.6, 0.2 mmol) and *N*-methylpiperidone hydrochloride (30 mg, 0.2 mmol) in dry chlorobenzene (70 ml) was refluxed for 4 days under a nitrogen atmosphere. The resulting mixture was isolated by chromatography on silica gel with 10 : 1 toluene–methanol as eluent.

1 was obtained in 91% yield by oxidization of **2** (Scheme 1) as follows.‡ A dry chlorobenzene solution of *m*-chloroperbenzonic acid (45 mg, 0.26 mmol) was added dropwise to compound **2** (24 mg, 0.026 mmol) in dry chlorobenzene (30 ml), the mixture was stirred at room temperature for 2 days. Afterwards the mixture was washed three times with a cold 5% solution of Na_2CO_3 and a saturated aqueous solution of NaCl and the solvent removed under reduced pressure.

To our knowledge, this is a new method for the synthesis of a stable nitroxide from an ammonium salt. The nanoparticles were prepared by leaving the 10 : 1 chlorobenzene–methanol solution at room temperature for a few days and then dried *in vacuo*.

The self-assembled nanoparticles can be observed by electron microscopy. A transmission electron microscopy (TEM) image of the self-assembled nanoparticles is shown in Fig. 1. The figure reveals the ball-like nanoparticles whose diameters are in the 80–130 nm range. The ball-like structures are proposed to be formed from numerous molecules of **1** by intermolecular juxtaposition. Atomic force microscopy (AFM) investigation of the nanoparticles deposited on mica was expected to yield additional information about the structure of the nanoparticles. All AFM measurements were carried out in tapping mode. The surface image shows more regular and homogeneous particle shapes with diameters of 75–95 nm (Fig. 2). Compared to the TEM image, the sizes of particles revealed by AFM are smaller. It is possible that the different particle sizes result from the different substrates. Considering that compound **1** dissolves better in a aprotic–protic solvent mixture such as chlorobenzene–methanol, due to the presence of an ionic group, amphipathy presumably plays a major role in forming the fullerene-based nanoparticles. The stable free radical **1** exhibits characteristic triplet ESR signals (Fig. 3) due to nitrogen splitting in the nitroxide radical (α_N = 14.3 G); the *g* value is 2.0077.



Scheme 1

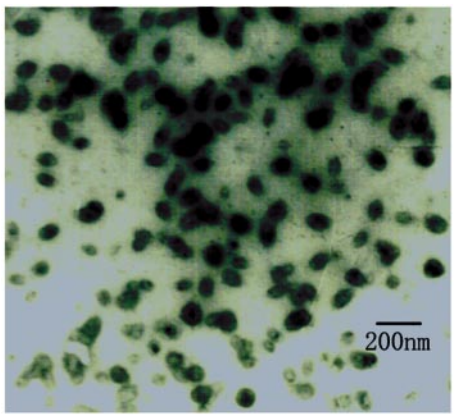


Fig. 1 TEM image of compound **1** in 10 : 1 chlorobenzene–methanol.

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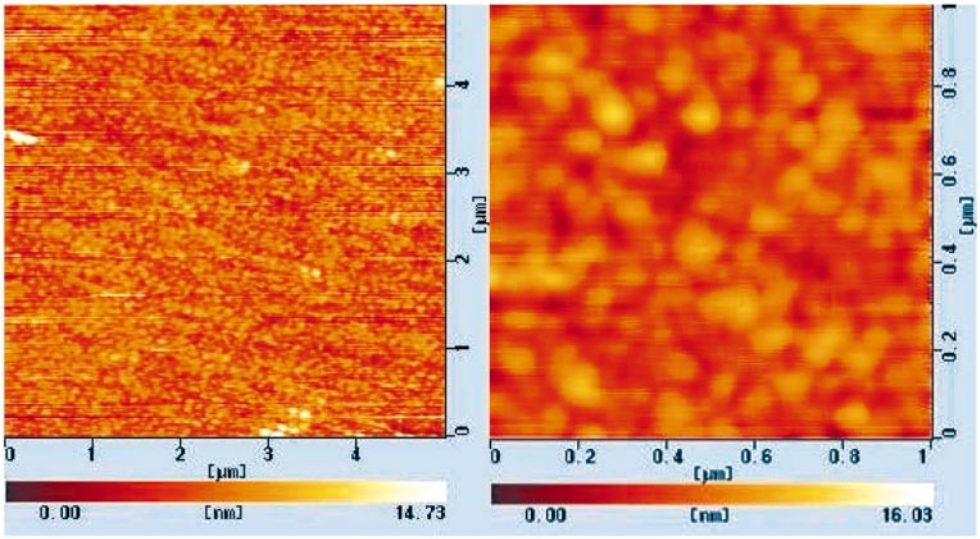

Fig. 2 AFM photographs of the nanoparticles of compound **1** on different scales: 5 μm (left); 1 μm (right). Elevations and depressions are represented by the light and dark areas, respectively.

To further investigate the formation of the nanoparticles, the monolayer film of the salt-derivatized C_{60} was prepared by the Langmuir–Blodgett (LB) technique. The π–A curve shows that the surface pressure increases rapidly at 75 Å^2 per molecule until the film collapses at 37 Å^2 per molecule with a collapse pressure of 48 N m^{-1}. These results indicate that an amphiphile salt-derivatized C_{60} film should readily form on a water subphase. However, the area per molecule is an unexpected 72 Å^2, which is smaller than the calculated value of about 100 Å^2. This can be interpreted in terms of aggregate formation. Fig. 4 shows a typical surface image of the LB film on mica obtained by AFM of a randomly selected area. The image shows that many unhomogeneous aggregates, ranging from 70 to 100 nm, are deposited as a relatively flat film. These aggregates are formed by self-assembly owing to the methanol evaporating far faster than the chlorobenzene. The formation of the aggregates results in a decrease in the area per molecule.

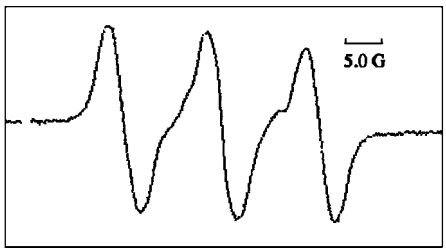

Fig. 3 ESR spectrum of compound **1** in 10 : 1 chlorobenzene–methanol.

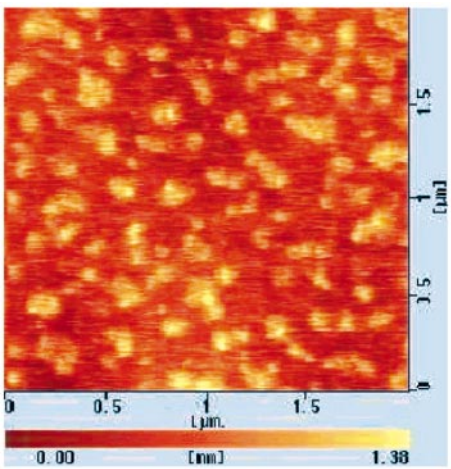

Fig. 4 AFM photographs of the LB film of compound **1** on mica. Elevations and depressions are represented by the light and dark areas, respectively.

In summary, the first C_{60} pyrrolidine nitroxide ammonium chloride has been synthesized. This compound can be used to construct nanoparticles using a facile method. The fullerene nanoparticles provide a route capable of forming supramolecular structures that may provide novel photoelectric properties.

Acknowledgements

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Notes and references

† Selected data for **2**: δ_H (300 MHz, *o*-$C_6D_4Cl_2$): 3.43–3.32 (m, 4H), 3.16–2.82 (m, 4H), 2.92 (s, 3H), 2.52 (s, 6H), 2.08 (br s, 1H). δ_C (75 MHz, *o*-$C_6D_4Cl_2$): 153.7 (1C), 153.5 (1C), 153.4 (2C), 148.6 (1C), 147.5 (1C), 145.2 (1C), 144.4 (1C), 144.2 (4C), 144.1 (2C), 144.0 (4C), 143.9 (1C), 143.8 (1C), 143.7 (1C), 143.3 (2C), 143.1 (4C), 142.9 (1C), 142.7 (1C), 142.5 (4C), 141.4 (1C), 140.9 (1C), 140.8 (4C), 140.6 (2C), 140.4 (2C), 140.3 (2C), 139.8 (4C), 138.1 (1C), 137.9 (1C), 133.4 (2C), 133.3 (1C), 133.2 (2C), 132.5 (1C), 131.8 (1C), 82.6 (1C), 82.1 (1C), 78.4, 73.9, 71.2, 69.4, 38.6, 30.6. MALDI-TOF-MS: calc. for $C_{69}H_{19}N_2$: 875; found: 873. FT-IR (KBr): ν 3306, 2925, 1462, 1429, 1381, 1147, 1065, 783, 562, 528 cm^{-1}.

‡ Selected data for **1**: MALDI-TOF-MS: calc. for $C_{69}H_{18}N_2O$: 890; found: 891. FT-IR(KBr): ν 2963, 2924, 1736, 1427, 1376, 1261, 1088, 1023, 804, 527 cm^{-1}.

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