# The self-assembly of [60]fullerene-substituted 2,2′-bipyridine on the surface of Au(111) and Au nanoparticles

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The cycloaddition reaction of the azide of 4,4′-dimethyl-2,2′-bipyridine to [60]fullerene was used to synthesize a novel [60]fullerene derivative, which was employed to self-assemble on the surface of Au(111) and gold nanoparticles. Scanning tunneling microscopy results show that the [60]fullerene derivative forms a self-assembled monolayer on the Au(111) surface spontaneously. Transmission electron micrographs indicate the presence of spherical particles with an average radius of about 10 nm in the nanoparticle preparations.

The self-assembly of fullerenes and fullerene derivatives onto a variety of substrates such as metals, semiconductors, insulators and cuprate-based high temperature superconductors has been actively investigated.[1–14] For example, thiol derivatives of [60]fullerene spontaneously adsorb on Au(111) surfaces to yield well-ordered monolayers.[12,13] A [60]fullerene derivative covalently linked to 1,10-phenathroline has also been obtained and self-assembled into monolayers on the Au(111) surface.[14] Many reports have pointed out that pyridyl nitrogens can strongly adsorb on Au(111) or Pt(111) surfaces, in much the same way as thiol sulfurs do.[14–18]

Recently, nanostructured materials, especially gold nanoparticles, have attracted considerable attention because of their potential applications in optical and nanoelectronic devices due to their high surface-to-volume ratios and physical properties related to their small size.[19–30] Gold–fullerene structures are promising candidates for novel sensor materials, catalysts, and *bottom-up* fabrication of single-electron transistors.[31] To prepare these gold nanoclusters or colloids with monodispersity, either thiol derivatives or polymers such as poly(vinyl alcohol) and polyacrylonitrile have been generally used as the stabilizers.[21–27] It has been reported recently that [60]fullerene mediates the aggregation of tetraoctylammonium bromide-stabilized gold particles in toluene to form a novel type of nanocomposite with the fullerene relatively weakly bound to the surface of the gold particles.[32] [60]Fullerene derivatives containing a pyridyl group may also act as the stabilizer to spontaneously strongly absorb on the surface of gold nanoparticles by virtue of the strong interaction between the pyridyl nitrogens and the gold surface. In the present paper, a novel [60]fullerene derivative C60BPY containing the 2,2′-bipyridine group has been synthesized to self-assemble on the surface of Au(111) and gold nanoparticles. Scanning tunneling microscopy (STM) images show this molecule can strongly adsorb on the Au(111) surface and transmission electron microscope (TEM) images indicate that gold nanoparticles have formed through the self-assembled technique. The synthetic steps leading to the [60]fullerene derivative and its subsequent self-assembly are presented in Scheme 1.

## Experimental

### General

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker DMX300 spectrometer ($SiMe_4$). Mass spectra were determined with an AEI-MS50 for EI-MS and a BEFLEX III for TOF-MS. FT-IR spectra were measured from KBr pellets on a Perkin-Elmer System 2000 spectrometer. UV-vis absorption spectra were recorded on a Hitachi U-3010 spectrometer. For TEM examination, a drop of the colloidal gold solution was placed on a carbon-coated Cu grid and the chloroform allowed to evaporate. Specimens were examined in a Hitachi 800 transmission electron microscope. For the STM experiment, the gold films that were used as the Au(111) substrate in our experiments were epitaxially grown on freshly cleaved mica sheets in a UHV chamber and briefly flame-annealed before each experiment. The samples were prepared by dipping a Au(111) substrate into a solution of C60BPY in chloroform (concentration less than 1%) for 1 h. All STM experiments were performed with a Nanoscope IIIa SPM (Digital Instruments). STM tips were made of 0.2 mm diameter Pt–Ir (90 : 10) wire and were mechanically cut. All the STM topographic images of C60BPY shown in this paper were acquired at room temperature in constant current mode. No image enhancement was performed, except for background correction.

### Materials

4-(Bromomethyl)-4′-methyl-2,2′-bipyridine was prepared by a method described in the published literature.[33] The azide of 4,4′-dimethyl-2,2′-bipyridine was obtained following methods similar to those previously described and was directly used to react with $C_{60}$.[34]

### Synthesis of C60BPY

The general procedure for the preparation and isolation of C60BPY was as follows. To a solution of $C_{60}$ (36 mg, 0.05 mmol) in chlorobenzene (40 mL), the azide of 4,4′-dimethyl-2,2′-bipyridine (11 mg, 0.05 mmol) was added, and then the

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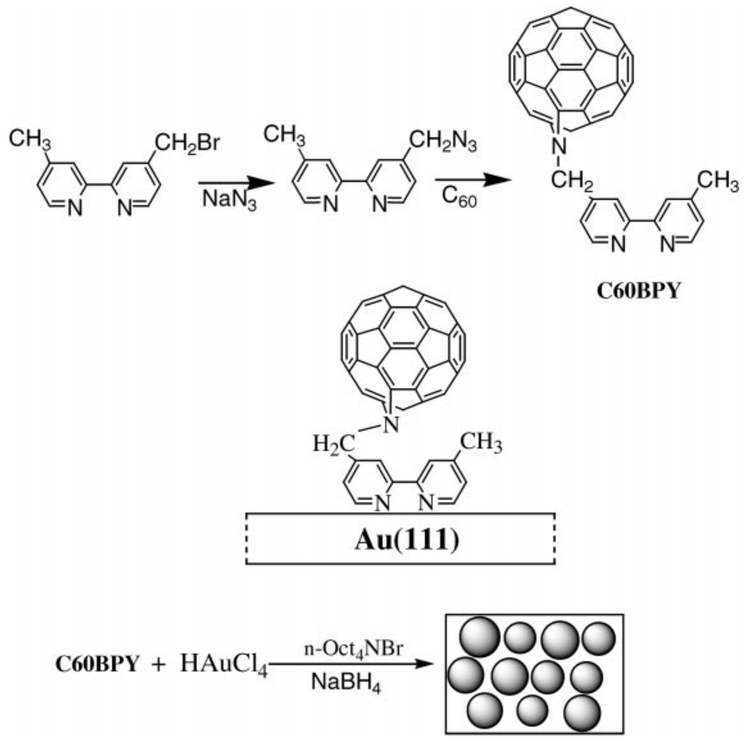

Scheme 1

mixture was stirred and heated to reflux under nitrogen for 24 h. The brown solution was concentrated and the crude solid product was washed with acetone (3 × 20 mL). The resultant solid was then purified by chromatography on silica gel using chloroform–acetone (20 : 1, v/v) as eluent to give C60BPY in a yield of 17%. MS (MALDI-TOF): *m*/*z* 720 $[C_{60}]^+$, 918 $[M + H]^+$, 940 $[M + Na]^+$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 2.48 (s, 3 H), 5.06 (s, 1 H), 5.11 (s, 1 H), 7.92 (s, 1 H), 7.19 (d, 1H, $J = 4.9$ Hz), 8.32 (s, 1 H), 8.59 (d, 1 H, $J = 5.2$ Hz), 8.71 (s, 1 H), 8.86 (m, 1 H); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 29.87, 53.03, 96.139, 108.59, 108.99, 109.69, 120.81, 121.01, 124.01, 125.78, 126.87, 127.04, 128.18, 133.91, 136.53, 136.58, 138.59, 140.99, 141.64, 141.73, 142.19, 142.36, 142.58, 142.73, 142.84, 142.94, 142.98, 143.05, 143.17, 143.26, 143.49, 143.72, 143.86, 144.20, 144.25, 144.36, 144.41, 144.49, 144.67, 144.74, 144.84, 144.92, 145.15, 145.27, 145.34, 145.48, 145.68, 147.82, 148.00, 149.06, 149.59; FTIR (KBr) $\nu$/cm$^{-1}$: 2924.55, 2853.86, 1637.24, 1597.36, 1555.01, 1456.67, 1382.37, 1255.13, 1106.33, 824.63, 665.04, 526.51.

### Preparation of gold nanoparticles

Gold nanoparticles stabilized by C60BPY were prepared following the published method.[21] $HAuCl_4$ (0.01 mmol) in deionized $H_2O$ (5 mL) was added to the phase transfer agent n-$Oct_4NBr$ (0.2 mmol) in $CH_3Cl$ (5 mL) and the resulting mixture was stirred vigorously for 10 min. The organic layer was added to a solution of the stabilizer (C60BPY, 0.05 mmol) in $CHCl_3$ (5 mL), then the reducing agent ($NaBH_4$, 0.1 mmol) in $H_2O$ (5 mL) was dropped into the above solution over a 10 min period. The resulting mixture was stirred overnight at room temperature, filtered and washed with $H_2O$ (3 × 20 mL). The organic layer was separated and evaporated to about 4 mL and EtOH (20 mL) was added to precipitate the gold nanoparticles. The crude gold nanoparticles obtained by centrifugation were re-dissolved in $CHCl_3$ (5 mL) and re-precipitated by addition of EtOH (20 mL). The gold nanoparticles were recovered by centrifugation and dried for 12 h under vacuum.

## Results and discussion

As shown by the $^{13}C$ spectra, C60BPY possesses the 1,6-aza-bridged ring-opened structure.[35,36] The FT-IR spectra (KBr pellet) of C60BPY showed a band consistent with a $C_{60}$ moiety at 527 cm$^{-1}$. C60BPY could be dissolved in chloroform, dichloromethane and 1,2-dichloroethane; however, the solubility of C60BPY was poor in non-polar solvents such as benzene, toluene and ether as well as some polar solvents such as ethanol, methanol, ethyl acetate and acetone.

Fig. 1 shows an STM image of an array of C60BPY molecules self-assembled on a Au(111) surface; the scanning area is 22.5 × 22.5 nm. In the image, it can be seen that there are many bright spots, which are not ordered. The diameter and height of each bright spot are about 1 and 0.4 nm, respectively, which are associated with the geometrical size of isolated $C_{60}$, implying that each bright spot arises from a C60BPY molecule. Previous studies of 2,2′-bipyridine molecules assembled on an Au(111) substrate have shown that 2,2′-bipyridine molecule stand vertically with the nitrogen atoms facing the Au substrate and they stack into polymeric chains like rolls of coins, which is caused by the $\pi$-stacking interactions of the 2,2′-bipyridine molecules.[14–18] In the

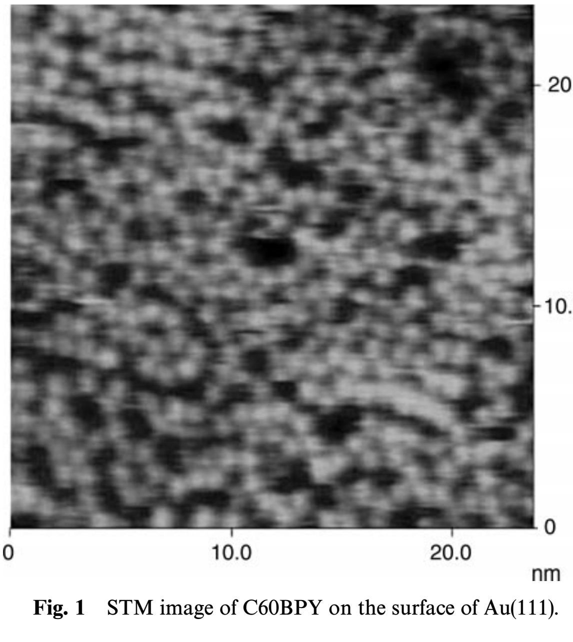

**Fig. 1** STM image of C60BPY on the surface of Au(111).

system of C60BPY assembled on an Au(111) surface, the geometry and size of $C_{60}$ effectively isolates the $\pi$-stacking interactions between the bipyridyl groups in adjacent C60BPY molecules; therefore, the C60BPY molecules form a disordered structure on Au(111). In STM experiments, continuously scanning over this assembled layer has no effect on the image, demonstrating that the interaction of nitrogen atoms with the Au(111) substrate is strong.

The UV-vis absorption spectrum of gold nanoparticles in $CHCl_3$ is shown in Fig. 2. The gold nanoparticle solution displays the specific surface plasmon band of gold clusters with a maximum at about 556 nm, which was ascribed to a collective oscillation of conduction electrons in response to optical excitation.[26,37] In accordance with the UV-vis spectrum, the TEM image in Fig. 3 shows the presence of spherical particles with an average radius of about 10 nm. The size distribution of gold nanoparticles stabilized by C60BPY is shown in Fig. 4. These results demonstrate that gold nanoparticles can be formed using C60BPY as stabilizer, due to the strong interaction of the nitrogen atoms of 2,2′-bipyridine with Au nanoparticle surface.

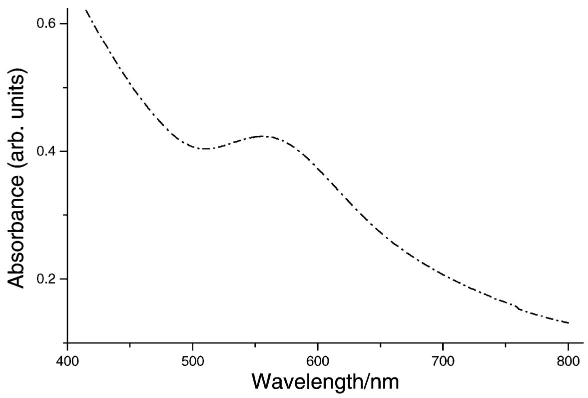

**Fig. 2** UV-vis absorption spectrum of gold nanoparticles stablized by C60BPY in chloroform at room temperature.

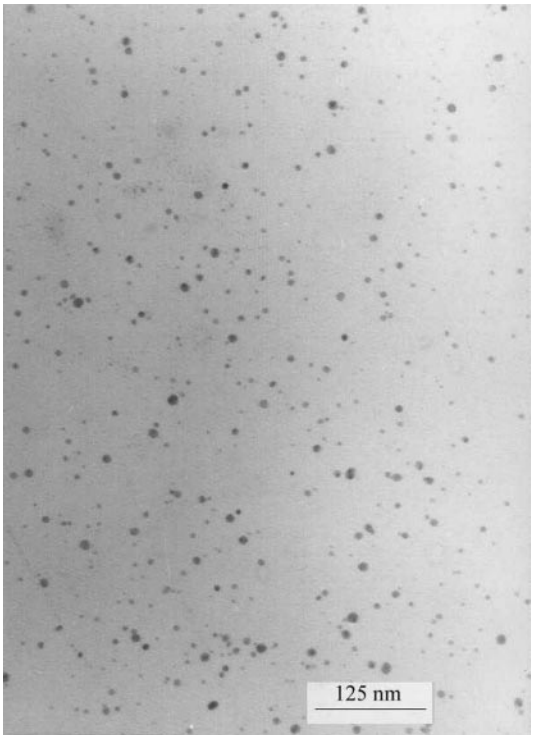

**Fig. 3** TEM image of gold nanoparticles stabilized by C60BPY.

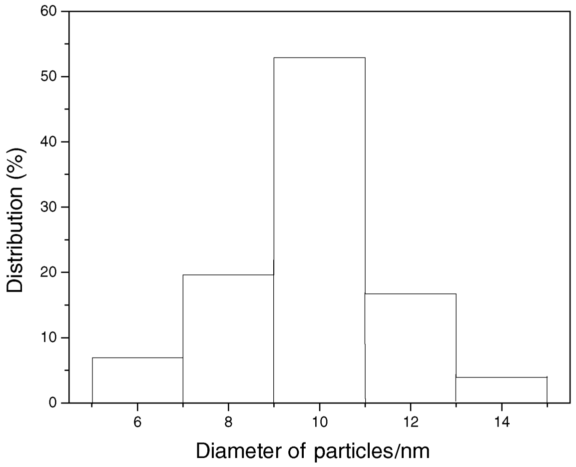

**Fig. 4** Size distribution of gold nanoparticles stabilized by C60BPY.

In conclusion, the novel [60]fullerene derivative C60BPY containing a 2,2′-bipyridyl group was synthesized and was subsequently self-assembled on the surface of Au(111) and onto gold nanoparticles. The STM results show that the [60]fullerene derivative spontaneously forms a good self-assembled monolayer on the Au(111) surface and in the nanoparticle preparation the TEM image indicates the presence of spherical particles with an average radius of about 10 nm.

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