

# Thio[2-(benzoylamino)ethylamino]- $\beta$ -CD fragment modified gold nanoparticles as recycling extractors for [60]fullerene†

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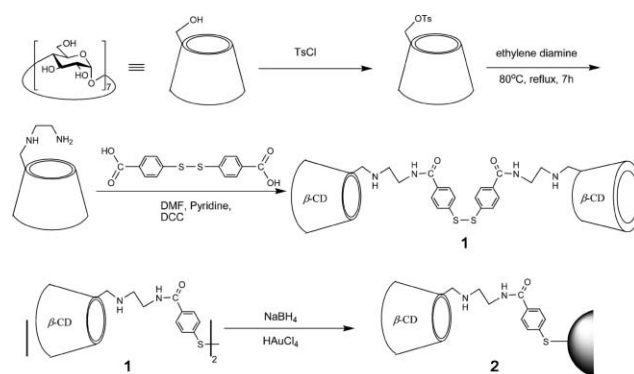
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Gold particles are modified with surface-attached bis( $\beta$ -cyclodextrin)s bearing S–S bridges to give water-soluble cyclodextrin-modified gold nanoparticles, which are successfully used as recycling extractors for [60]fullerene.

Fullerenes, spherical  $\pi$ -electron systems containing tens of unsaturated carbons, show many interesting magnetic,<sup>1</sup> superconductive,<sup>2</sup> electrical,<sup>3</sup> and biochemical properties.<sup>4</sup> Thus, fullerenes and their derivatives have attracted extensive interest in recent years and have been successfully applied in many fields of materials science and biological technology. Because the fullerenes prepared *via* the thermal reactions of appropriate carbon sources under various conditions<sup>5</sup> always exist as a mixture of C<sub>60</sub>, C<sub>70</sub> and higher homologues, the separation of fullerenes becomes a challenge for chemists. Generally, several methods are applied to separate C<sub>60</sub> from fullerene mixtures,<sup>6</sup> such as sublimation, liquid chromatography, column chromatography, capillary electrophoresis and recrystallization. However, these methods usually require a large amount of organic solvents, a long time course or special instruments and do harm to the environment. Recently, some approaches involving the inclusion of unmodified fullerenes into water-soluble polymers and synthetic receptors, such as poly(*N*-vinylpyrrolidone),<sup>7</sup> cyclodextrin (CD),<sup>8</sup> or calixarene,<sup>9</sup> to form host–guest inclusion complexes or supramolecular assemblies have been reported. These approaches provide the possibility to solubilize and separate fullerenes using the supramolecular method. On the other hand, gold nanoparticles modified with synthetic receptors recently represent a very active topic of science and technology,<sup>10,11</sup> due to their extensive application in a wide variety of areas including optoelectronic nanodevices,<sup>11,12</sup> chemical sensors,<sup>13</sup> nanotechnology,<sup>14</sup> and biological sciences.<sup>15</sup> In the present work, we prepared a thio[2-(benzoylamino)ethylamino]- $\beta$ -CD (T $\beta$ -CD) fragment modified gold nanoparticle (Scheme 1), and investigated its selective association and dissociation behavior with C<sub>60</sub>. Because  $\beta$ -CD, a cyclic oligosaccharide with seven D-glucose units linked by  $\alpha$ -1,4-glucose bonds, can only form a 2 : 1 inclusion complex with C<sub>60</sub><sup>16</sup> but does not interact with C<sub>70</sub> and higher fullerene analogues, this T $\beta$ -CD fragment modified gold nanoparticle can be used as a recycling extractor for C<sub>60</sub> (Scheme 2).

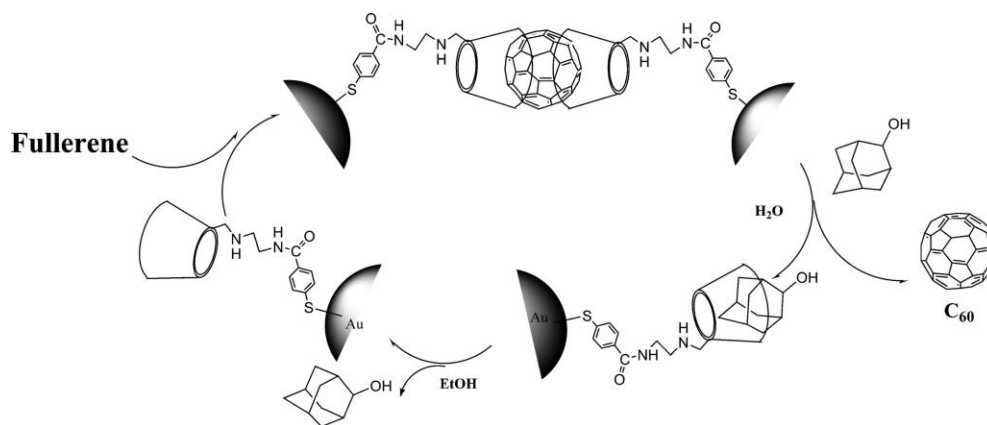


Scheme 1

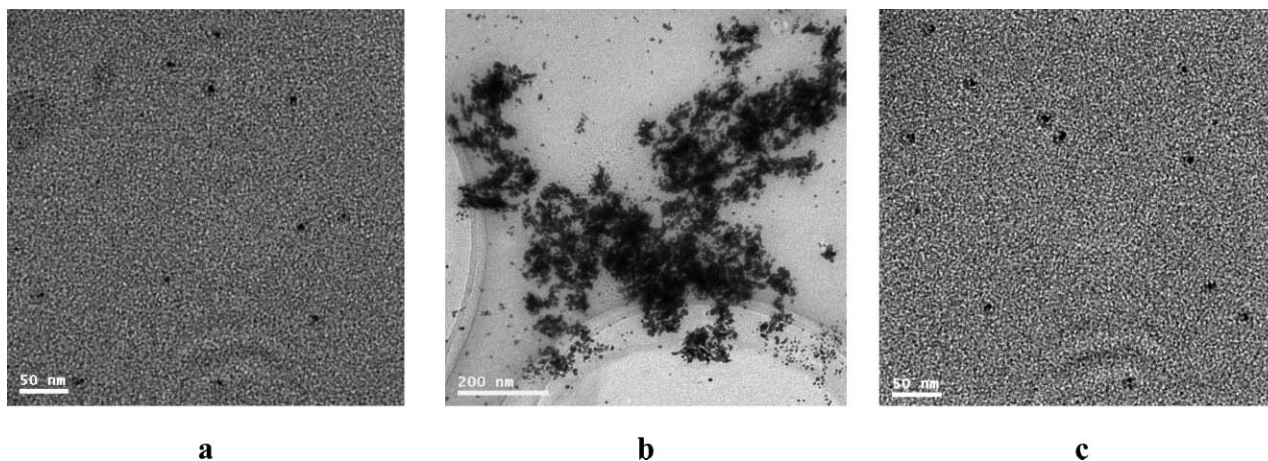
T $\beta$ -CD fragment modified gold nanoparticle **2** was prepared from HAuCl<sub>4</sub> and bis( $\beta$ -CD) **1**. In the preparation, HAuCl<sub>4</sub> was reduced to form metallic gold nuclei. Subsequently, the fast adsorption of disulfides onto the surface of gold nuclei broke the S–S bond in **1** to give thio[2-(benzoylamino)ethylamino]- $\beta$ -CD fragment modified gold nanoparticles through the formation of S–Au bond.<sup>17,18</sup> The particle formation was evidenced by the obvious color changes of the solution from yellow to deep brown. The resulting T $\beta$ -CD fragment modified gold nanoparticles can be isolated as a deep brown solid and show a very good solubility in water, where they can remain dissolved yielding a stable, clear solution without any apparent aggregation or precipitation for several weeks as simply monitored by UV-vis measurements. Some spectral and microscopic data give useful information about the structure of the T $\beta$ -CD fragment modified gold nanoparticle **2**. The FT-IR spectrum (see ESI†) of **2** strongly resembles that of the free bis( $\beta$ -CD) **1**, which is consistent with previous observations in similar systems.<sup>19</sup> Moreover, no S–H stretching band at *ca.* 2560 cm<sup>-1</sup> can be found in the FT-IR spectrum of **2**, indicating the conversion of the S–S bond in bis( $\beta$ -CD) **1** to the S–Au bond when bis( $\beta$ -CD) **1** chemisorbs on the surface of gold nanoparticles. In addition, the <sup>1</sup>H NMR spectrum of **2** also displays the characteristic signals of the corresponding protons in **1**, especially the characteristic signals of aromatic protons and CD's backbone protons (C1–H, C2–H, C3–H, C4–H, C5–H, C6–H). These data jointly afford evidence for the formation of T $\beta$ -CD fragment modified gold nanoparticles. Particle size determinations using transmission electron microscopy (TEM) yield an average particle diameter of 6.6 ± 1.0 nm for gold nanoparticle **2** (Fig. 1a) with a reasonable degree of monodispersity by individual measurements on at least 200 particles (see ESI)†. The surface coverage of CD units on the nanoparticles is estimated as 65% by the elemental analysis.<sup>19b</sup>

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† Electronic supplementary information (ESI) available: measurements; preparation of **1** and **2**; FT-IR spectra of **1** and **2**; size distribution histogram of **2**; UV-vis spectra of **2**, C<sub>60</sub>-**2** assembly and the toluene extract of C<sub>60</sub>-**2** assembly; fluorescence spectra of **2** and C<sub>60</sub>-**2** assembly. See http://dx.doi.org/10.1039/b507650a



Scheme 2



**Fig. 1** (a) A typical high-resolution TEM image of **2**, which displays a representative selection of the nearly spherical nanoparticles. (b) A low-magnification TEM image of  $C_{60}$ -induced assembly of **2**. (c) A representative high-resolution TEM image of  $C_{60}$ -induced assembly of **2** after adding 2-adamantanol.

By examining the structure of **2**, we can find that there are a number of free CD cavities attached on the surface of gold nanoparticles, all of which have the capability to bind  $C_{60}$  to form 2 : 1 inclusion complexes. Therefore, we can use these T $\beta$ -CD fragment modified gold nanoparticles as captors for  $C_{60}$ . Commercially available  $C_{60}$  and  $C_{70}$  are used to test the selective capturing ability of **2** toward fullerenes. In a typical experiment, 50 mg of **2** is dissolved in 80 mL of water, and then 10 mg of  $C_{60}$  is added to the solution under stirring. After 3 days, the unreacted solid is removed by filtration, and the filtrate is evaporated under reduced pressure to dryness. The residue is dried under vacuum at 50 °C to give a deep brown solid (55 mg).

The association of  $C_{60}$  with **2** is proved by UV-vis and TEM. The UV spectrum (See ESI†) of **2** (0.1 mg mL<sup>-1</sup>) shows a characteristic band for the surface plasmon resonance (SPR) absorption of gold at 550 nm. Moreover, a shoulder peak at *ca.* 260 nm, which is assigned to the absorption of the phenyl chromophore, is also observed. After reaction with  $C_{60}$  for about 1 h, the SPR band of **2** red shifts to 594 nm, accompanied with an increase of the scattering envelope. This red shift is attributed to the coupled plasmon absorption of gold nanoparticles in close contact, demonstrating the formation of particle aggregates.<sup>17</sup> In addition, besides the shoulder peak at 260 nm, a shoulder at *ca.* 340 nm, which is assigned to the characteristic absorption band of  $C_{60}$ , also

appears in the UV spectrum of the  $C_{60}$ -**2** assembly. Moreover, the toluene extract of the  $C_{60}$ -**2** assembly gives a UV-vis spectrum that presents the typical bands of  $C_{60}$ , indicating the partial solubilization of the  $C_{60}$  sample by T $\beta$ -CD fragment modified gold nanoparticles in aqueous solution arising from the inclusion complexation of attached  $\beta$ -CDs with  $C_{60}$ . Further evidence comes from the fluorescence behavior. In a control experiment, the unmodified gold nanoparticles are nonfluorescent but the T $\beta$ -CD fragment modified gold nanoparticle **2** emits fluorescence with the emission maximum at *ca.* 410 nm in aqueous solution. After reaction with  $C_{60}$ , the  $C_{60}$ -**2** assembly emits stronger fluorescence benefiting from the good photophysical property of  $C_{60}$  linkers (see ESI†). Furthermore, the TEM image also validates the aggregation of **2** in the presence of  $C_{60}$ . Fig. 1b gives a rough insight into the size and shape of the  $C_{60}$ -**2** assembly, which are in sharp contrast to the well-isolated homogeneous nanoparticles of **2** in the absence of  $C_{60}$  (Fig. 1a). Therefore, we deduce a possible structure (see ESI†) of the  $C_{60}$ -**2** assembly, where  $C_{60}$  molecules actively behave as noncovalent inter-particle linkers to assemble the discrete T $\beta$ -CD fragment modified gold nanoparticles into large supramolecular architectures attributed to the stoichiometric 1 : 2 inclusion complexation between  $C_{60}$  and  $\beta$ -CD cavities.

Similar experiments were performed using  $C_{70}$  instead of  $C_{60}$ , but no inclusion and aggregation phenomena were found even

after a longer time course. This can be explained from the size-fit concept of host-guest complexation. CPK molecular model experiments demonstrate that only  $C_{60}$  can form 1 : 2 inclusion complexes with  $\beta$ -CDs, while  $C_{70}$  is too large to be accommodated in the  $\beta$ -CD cavity.

After validating the effective capturing of the T $\beta$ -CD fragment modified gold nanoparticle **2** towards  $C_{60}$ , we subsequently examined the controlled release of  $C_{60}$  from the assembly. 2-Adamantanol is reported to have a very high binding ability with the CD cavity.<sup>20</sup> Therefore, the guest molecule that is included in the CD cavity should be driven out when 2-adamantanol is added to the system. In a typical experiment, an excess amount of 2-adamantanol was added to an aqueous solution of the  $C_{60}$ -**2** assembly, and the mixture was kept under ultrasonic shake for 10 minutes. Then, the insoluble solid was collected by filtration and washed with ethanol to remove the unreacted 2-adamantanol, and the residue was characterized to be  $C_{60}$ . Moreover, by weighing the residue, we can deduce that 50 mg of **2** could capture *ca.* 5 mg of  $C_{60}$ . In addition, the TEM image also confirms the effective release of  $C_{60}$ . As seen from Fig. 1c, the TEM image of the filtrate shows a number of discrete nanoparticles, which is quite similar to the image of free **2**. This result indicates that 2-adamantanol excludes the  $C_{60}$  from the  $\beta$ -CD cavity. It is noteworthy that, in the present case, the CD cavities around the gold particle surface are still occupied by many 2-adamantanol molecules, which is disadvantageous to the recycling of these T $\beta$ -CD fragment modified nanoparticles as  $C_{60}$  extractors. Generally, CD cavities always bind guest molecules strongly in water due to hydrophobic interactions but weakly in organic phase. Therefore, we can effectively remove the included 2-adamantanol by adding organic solvent. In a typical experiment, the filtrate was evaporated under reduced pressure to remove most of solvent. Then, ethanol was added until no more precipitate deposited. The precipitate was collected by filtration, and dissolved in a small amount of water. Then, ethanol was added again to give free **2** as a precipitate. <sup>1</sup>H NMR demonstrates that the included 2-adamantanol is negligible after treating the filtrate by ethanol.

In another experiment, an equimolar mixture of  $C_{60}$  and  $C_{70}$  was added to a solution of **2**. After stirring the reaction mixture for 3 days, the unreacted solid is removed by filtration, and an excess amount of 2-adamantanol was added to the filtrate. The mixture was kept under ultrasonic shake for 10 minutes. Then, the insoluble solid was collected by filtration and washed with ethanol to remove the unreacted 2-adamantanol, and the residue was characterized to be  $C_{60}$  only. This result demonstrated that the modified gold nanoparticle **2** could selectively capture  $C_{60}$  from a mixed fullerene system.

In conclusion, we succeed in achieving water-soluble T $\beta$ -CD fragment modified gold nanoparticles through the association of bis( $\beta$ -CD)s possessing S-S bonds with gold particles. These nanoparticles can selectively capture  $C_{60}$  to form large supramolecular assemblies, and the captured  $C_{60}$  can be sufficiently released by adding 2-adamantanol. More importantly, this capture-release process can be easily recycled under the appropriate conditions. These results may not only have important applications in the separation techniques of fullerenes, but may also open the door to the design of functional hybrid materials based on supramolecular systems.

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