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

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Gold particles are modified with surface-attached bis(\(\beta\)-cyclodextrin) 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,\(^1\) superconductive,\(^2\) electrical,\(^3\) and biochemical properties.\(^4\) 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\(^5\) always exist as a mixture of \(C_{60}\), \(C_{70}\) and higher homologues, the separation of fullerenes becomes a challenge for chemists. Generally, several methods are applied to separate \(C_{60}\) from fullerene mixtures,\(^6\) 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),\(^7\) cyclodextrin (CD),\(^8\) or calixarene,\(^9\) 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,\(^10,11\) especially in a wide variety of areas including optoelectronic nanodevices,\(^11,12\) chemical sensors,\(^13\) nanotechnology,\(^14\) and biological sciences.\(^15\) 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 \(C_{60}\). Because \(\beta\)-CD, a cyclic oligosaccharide with seven D-glucose units linked by \(\alpha\)-1,4-glycosidic bonds, can only form a 2 : 1 inclusion complex with \(C_{60}\)\(^16\) but does not interact with \(C_{70}\) and higher fullerene analogues, this T\(\beta\)-CD fragment modified gold nanoparticle can be used as a recycling extractor for \(C_{60}\) (Scheme 2).

Scheme 1

T\(\beta\)-CD fragment modified gold nanoparticle 2 was prepared from HAuCl\(_4\) and bis(\(\beta\)-CD) 1. In the preparation, HAuCl\(_4\) 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.\(^17,18\) 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.\(^19\) Moreover, no S–H stretching band at 2560 \text{ cm}^{-1} \text{ 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 \(^1\)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.\(^19\)
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 C60 to form 2 : 1 inclusion complexes. Therefore, we can use these Tβ-CD fragment modified gold nanoparticles as captors for C60. Commercially available C60 and C70 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 C60 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 C60 with 2 is proved by UV-vis and TEM. The UV spectrum (See ESI†) of 2 (0.1 mg mL⁻¹) 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 C60 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. In addition, besides the shoulder peak at 260 nm, a shoulder at ca. 340 nm, which is assigned to the characteristic absorption band of C60, also appears in the UV spectrum of the C60-2 assembly. Moreover, the toluene extract of the C60-2 assembly gives a UV-vis spectrum that presents the typical bands of C60, indicating the partial solubilization of the C60 sample by Tβ-CD fragment modified gold nanoparticles in aqueous solution arising from the inclusion complexation of attached β-CDs with C60. Further evidence comes from the fluorescence behavior. In a control experiment, the unmodified gold nanoparticles are nonfluorescent but the Tβ-CD fragment modified gold nanoparticles 2 emit fluorescence with the emission maximum at ca. 410 nm in aqueous solution. After reaction with C60, the C60-2 assembly emits stronger fluorescence benefiting from the good photophysical property of C60 linkers (see ESI†). Furthermore, the TEM image also validates the aggregation of 2 in the presence of C60. Fig. 1b gives a rough insight into the size and shape of the C60-2 assembly, which are in sharp contrast to the well-isolated homogeneous nanoparticles of 2 in the absence of C60 (Fig. 1a). Therefore, we deduce a possible structure (see ESI†) of the C60-2 assembly, where C60 molecules actively behave as noncovalent inter-particle linkers to assemble the discrete Tβ-CD fragment modified gold nanoparticles into large supramolecular architectures attributed to the stoichiometric 1 : 2 inclusion complexation between C60 and β-CD cavities.

Similar experiments were performed using C70 instead of C60, 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 C₆₀ can form 1 : 2 inclusion complexes with β-CDs, while C₇₀ is too large to be accommodated in the β-CD cavity.

After validating the effective capturing of the Tβ-CD fragment modified gold nanoparticles 2 towards C₆₀, we subsequently examined the controlled release of C₆₀ from the assembly. 2-Adamantanol is reported to have a very high binding ability towards C₆₀, which is quitesimilar to the image of free 2-adamantanol as a precipitate. 1H NMR demonstrates that the included 2-adamantanol is negligible after treating the filtrate by ethanol. In a typical experiment, 2-adamantanol is added to the system. In a typical experiment, the design of functional hybrid materials based on supramolecular separation techniques of fullerenes, but may also open the door to systems.

These results may not only have important applications in the separation techniques of fullerenes, but may also open the door to functional hybrid materials based on supramolecular systems.

Notes and references


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