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# Highly Water-soluble [60]Fullerene-ethylenediamino- $\beta$ -cyclodextrin Inclusion Complex: The Synthesis and Self-assembly with Poly (Acrylic Acid)

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A highly water-soluble [60]fullerene inclusion complex bicapped with ethylenediamino- $\beta$ -cyclodextrin was prepared, which was further used to construct uniform cubical microstructure with poly (acrylic acid). The formation of the inclusion complex was confirmed by NMR studies. The analysis of X-ray photoelectron spectroscopy and thermogravimetric analysis data revealed that the fullerene molecule was bicapped with  $\beta$ -cyclodextrin. The self-assembly of [60]fullerene inclusion complex with poly (acrylic acid) was investigated by UV-Vis spectroscopic titrations, supporting a 1:1 monomeric units binding model and yielding a complex stability constant of  $9.8 \times 10^3 \text{ M}^{-1}$ . The cubical microstructure formed was proved to be a crystalline structure by transmission electron spectroscopy measurements.

**Keywords:** Water-soluble; [60] Fullerene;  $\beta$ -cyclodextrin; Inclusion complex; Self-assembly

## INTRODUCTION

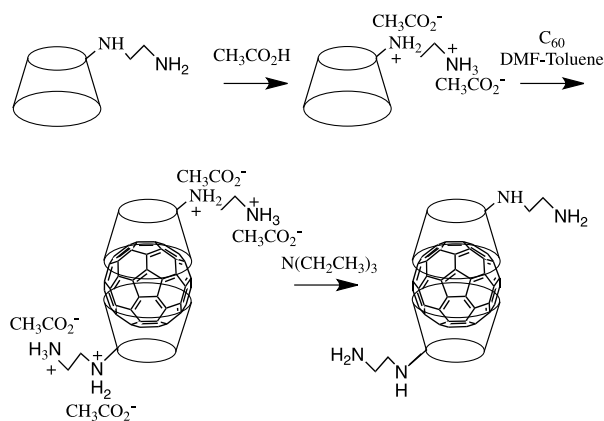
The unique physical and chemical properties of  $\text{C}_{60}$  make it an attractive component to be incorporated in supramolecular assemblies [1–4]. Especially the covalent fullerene functionalisation leading to the development of spectacular supramolecular architectures, including rotaxanes, catenanes, DNA complexes, diads and triads for photoinduced electron and energy transfer and ordered thin films [4–9]. All of these molecular assemblies and supramolecular arrays featured distinct properties as a consequence of the presence of the fullerene components. However, the covalent modification damaged the skeleton of fullerene inevitably, resulting in the deviation of its intrinsic properties. Inclusion complexes of  $\text{C}_{60}$  by macrocyclic hosts have been proved

to be successful in keeping the aromatic structure [10–14]. By this strategy, an attempt to increase the water solubility of fullerene, which can be of great importance for potential biological applications, has been also attracting increasing interest [15,16].  $\gamma$ -Cyclodextrin is well-known for the preparation of water-soluble cyclodextrin-[60]fullerene inclusion complex [16]. Recently  $\beta$ -cyclodextrin, the cheapest cyclodextrin, has been reported for the first time to bicap  $\text{C}_{60}$ , despite the poor solubility of the complex in water [17]. Herein, we present the synthesis of a highly water-soluble [60]fullerene-ethylenediamino- $\beta$ -cyclodextrin inclusion complex. By substituting one of the hydroxyl groups of a  $\beta$ -CD with ethylenediamine [18], water solubility of the inclusion complex is improved remarkably. Also, the amino groups of the complex enable it further self-assembly with relevant groups. By the interactions between amino groups of the inclusion complex and carboxyl groups of poly (acrylic acid), cubical microstructures have been constructed.

## RESULTS AND DISCUSSION

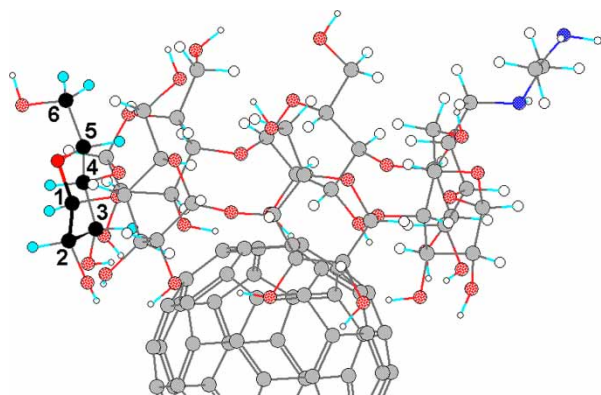
The synthesis of the inclusion complex is sketched in Scheme 1. Mono-6-deoxy-6-ethylenediamino- $\beta$ -cyclodextrin was synthesized according to a previous report [18]. Owing to the existence of the strong interactions between amino groups and  $\text{C}_{60}$ ,  $\beta$ -CDa acetate was used to achieve a bicapped  $\text{C}_{60}$ / $\beta$ -CDa acetate inclusion complex primarily. Then the complex was treated with triethylamine to remove the acetic acid. As expected, this inclusion

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SCHEME 1 Synthesis of the  $C_{60}/\beta$ -CDa complex.

complex obtained was highly water-soluble with a solubility reaching to  $10^{-2}$  M at room temperature.

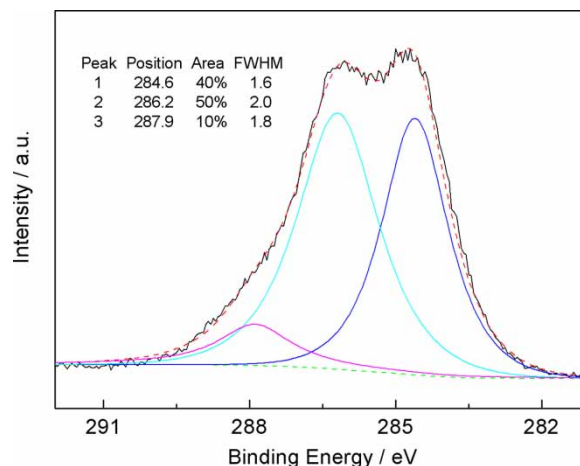
The IR spectrum of  $C_{60}/\beta$ -CDa complex is dominated by bands associated with  $\beta$ -CDa molecule. However, some weak bands are also observed at  $526.22\text{ cm}^{-1}$  and  $582.25\text{ cm}^{-1}$ , consistent with the presence of [60]fullerene. The intermolecular interactions between  $C_{60}$  and  $\beta$ -CDa in the complex were elucidated by  $^{13}\text{C}$ -NMR spectroscopy, in which the carbons undergo substantial chemical shifts. The  $^{13}\text{C}$  chemical shift of  $C_{60}$  in  $C_{60}/\beta$ -CDa complex is  $165.70\text{ ppm}$  in  $\text{D}_2\text{O}$ , while this value for  $C_{60}/\gamma$ -CD complex is  $144.05\text{ ppm}$  in  $\text{D}_2\text{O}$  [19]. Referenced with  $^{13}\text{C}$  chemical shift of  $C_{60}$  in  $[\text{D}_6]$  benzene ( $143.23\text{ ppm}$ ) [19], the distinct  $22.47\text{ ppm}$  downfield shift indicates that small cavity of  $\beta$ -CD affects the electronic environment of fullerene carbons intensively. The results can be interpreted partially with the energy-minimized molecular model at B3LYP/6-31G\* level shown in Fig. 1. All the glucopyranoside building blocks are relatively rigid and exist in a  ${}^4\text{C}_1$  chair conformation. The secondary hydroxyl groups OH(2) and OH(3) are in equatorial positions. Although the torus is stabilized by intramolecular hydrogen bonds, it is still flexible enough to permit

FIGURE 1 Energy-minimized partial molecular model of  $C_{60}/\beta$ -CDa complex at B3LYP/6-31G\* level (side-view).TABLE I  $^{13}\text{C}$ -NMR chemical shifts for the carbons of the glucose units in  $\beta$ -CDa and  $C_{60}/\beta$ -CDa complex in  $\text{D}_2\text{O}$ 

	$\delta$ (ppm)					
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
$\beta$ -CDa	97.9	68.1	69.1	77.2	67.9	56.4
Complex	103.7	72.2	73.3	82.4	72.0	59.2
Difference	5.8	4.1	4.2	5.2	4.1	2.8

considerable deviations from regular toroidal shape [20]. However, the time-averaged glucose building blocks are equivalent by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy [21]. Complete rotation of a glucose unit about the C(1)—O—C(4') bonds is not possible for steric reasons. Thus H(3) and H(5) are always situated within the torus. Since the ether oxygen atoms connecting adjacent glucose units are toward inner cavity of  $\beta$ -CD, the inclusion of [60]fullerene tensions the C(1)—O—C(4') bonds, consequentially. As shown in Table I, chemical shifts of all carbons shift toward down field. Among those, C(1) and C(4) change obviously, which may be attributed to C(1)—O—C(4') bond tension.

The electronic structure of  $C_{60}/\beta$ -CDa complex was analyzed by measuring binding energy spectra of  $\text{C}1\text{s}$  electrons. As shown in Fig. 2, the main line of XPS spectrum displays a broad and asymmetric shape. The Gaussian analyses of XPS data of  $\text{C}1\text{s}$  show the presence of three components (indicated by colored solid lines named with 1, 2 and 3 respectively). The  $\text{C}1\text{s}$  binding energies observed for  $\text{sp}^2$  carbons ( $C_{60}$ ,  $\text{C}=\text{C}$ ) are centered at  $284.6\text{ eV}$  with a narrow FWHM of  $1.6\text{ eV}$ . Compared with pristine  $C_{60}$  ( $284.7\text{ eV}$ ) [22], the small shift toward the lower binding energy side indicates that the skeleton of [60]fullerene is kept well. A small peak at  $287.9\text{ eV}$  is assigned to hemiketal carbon (C-1 of the glucose units, O—C—O). All of the other  $\text{sp}^3$  carbons

FIGURE 2 XPS spectrum of the  $\text{C}1\text{s}$  binding energy of  $C_{60}/\beta$ -CDa complex and the curve-fitting analysis showing the oxidation states of carbon.

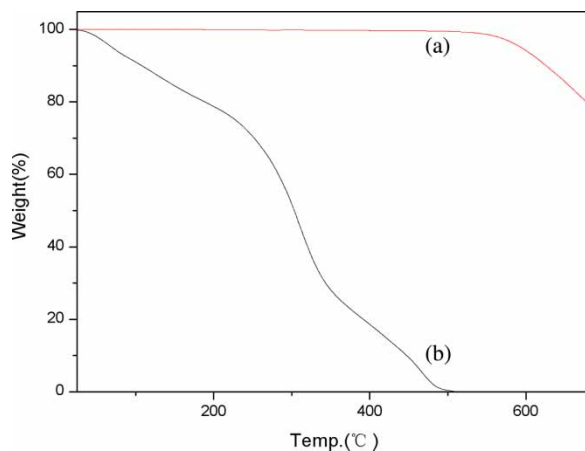


FIGURE 3 TGA curves: (a) pristine [60]fullerene, (b)  $C_{60}/\beta$ -CDa complexes.

covalently connected one oxygen or nitrogen atom, including C(2)–C(6) of glucose units and carbons of ethenediamino groups attached to  $\beta$ -CD, are centered at 286.2 eV. Accordingly, multi-species carbons broaden the FWHM to 2.0 eV. The intensities of  $C_{1s}$  components are estimated from integration of the peak area. The relative intensities for peak 1, 2 and 3 obtained by normalizing them to the total area are 40%, 50% and 10%, respectively. Correspondingly, the molar ratio of  $C_{60}/\beta$ -CDa is 1:2, which is in good agreement with experimental results.

The TGA investigations were achieved at a heating rate of  $2^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. The complex shows obviously two-stage decomposition

$$\Delta A = \frac{\Delta\varepsilon([H]_0 + [G]_0 + 1/K_s) \pm \sqrt{\Delta\varepsilon^2([H]_0 + [G]_0 + 1/K_s)^2 - 4\Delta\varepsilon^2[H]_0[G]_0}}{2} \quad (4)$$

at elevated temperatures (Fig. 3). The first stage of weight loss is attributed to the  $\beta$ -CDa. Therefore, the ca. 25% weight loss of the second stage is mainly caused by the decomposition of [60]fullerene. However, the formation of the complex results in a remarkably early degradation of  $C_{60}$  (beginning from about  $350^\circ\text{C}$ ) compared with the pristine [60]fullerene (beginning from about  $520^\circ\text{C}$ ). Thermogravimetric analysis of the complex suggests a 1:2  $C_{60}/\beta$ -CDa structure, which is in agreement with the aforementioned results.

Apart from host-guest self-assembly in  $\beta$ -CDa/ $C_{60}$ , the complex can further self-assemble with pAA by interactions between amino groups and carboxyl groups. The interactions of  $\beta$ -CDa/ $C_{60}$  complexes with pAA were investigated by UV-Vis spectroscopic titrations carried out in  $\text{H}_2\text{O}$ . In the UV titration studies, the concentration of the  $\beta$ -CDa/ $C_{60}$  complexes was kept constant ( $1.6 \times 10^{-5} \text{ M}$ ) and the change of the absorption was followed as a function of increasing pAA concentration referenced with same concentration of aqueous pAA solution. Thus,

the change of absorption was contributed totally from the influence of pAA. As seen in Fig. 4, absorption spectra of aqueous solution of  $C_{60}/\beta$ -CDa inclusion complex show a wide absorption band from 600 nm to 200 nm. The UV titration experiments reveal a significant decrease of absorption with the increase of pAA concentration. The complexation of a guest (G, pAA) with host (H,  $C_{60}/\beta$ -CDa) is expressed by Eq. (1).



The UV spectral change ( $\Delta A$ ) upon addition of guest, defined as  $\Delta A = A_0$  (without guest) –  $A$  (with guest), is assumed to be proportional to the concentration of inclusion complex produced, i.e.  $\Delta A = \Delta\varepsilon[HG]$ . The extinction coefficient  $\varepsilon$  is taken as a sensitivity factor for the UV change induced by the addition of one molar guest. Then, the complex stability constant ( $K_s$ ) is given by Eq. (2), where  $[H]_0$  and  $[G]_0$  are the initial concentrations of host and guest.

$$K_s = \frac{[HG]}{[H][G]} = \frac{\Delta A/\Delta\varepsilon}{([H]_0 - \Delta A/\Delta\varepsilon)([G]_0 - \Delta A/\Delta\varepsilon)} \quad (2)$$

We obtain (3) from (2) [23]

$$\frac{1}{\Delta A} = \frac{1}{K_s \Delta\varepsilon [H]_0 [G]_0} + \frac{1}{\Delta\varepsilon [H]_0} \quad (3)$$

Equation (3) is solved for  $\Delta A$  to give Eq. (4) and the curve fitting, using a non-linear least squares method, was employed in the determination of  $K_s$  values.

As illustrated in insert Fig. 4, analysis of the decrease of absorption at 200 nm as a function of increasing pAA concentration provided supports for a 1:1 monomeric units binding model and yields a complex stability constant of  $K_s = 9.8 \times 10^3 \text{ M}^{-1}$  [24]. This result indicates that interactions between  $C_{60}/\beta$ -CDa complex and pAA have taken place and these assembly motifs exhibit a significantly high stability. The driving force for  $C_{60}/\beta$ -CDa-pAA assemblies is suggested not to be constrained to electrostatic interactions, hydrogen bonding interaction also existed between the  $-\text{NHR}$  (or  $\text{NH}_2$ ) groups of  $\beta$ -CDa/ $C_{60}$  complexes and the  $-\text{COOH}$  groups of pAA. Owing to the presence of pAA backbone, the assemblies of  $C_{60}/\beta$ -CDa and pAA aggregated together, resulting in a decrease of absorption.

To form novel supramolecular structures, self-assembly of the [60]fullerene inclusion complex with pAA was performed in a very dilute aqueous solution ( $5.8 \times 10^{-5} \text{ M}$ ) with a molar ratio of amino groups/carboxyl groups about 1:2. The transmission electron spectroscopy (TEM) images (Fig. 5a,b) show



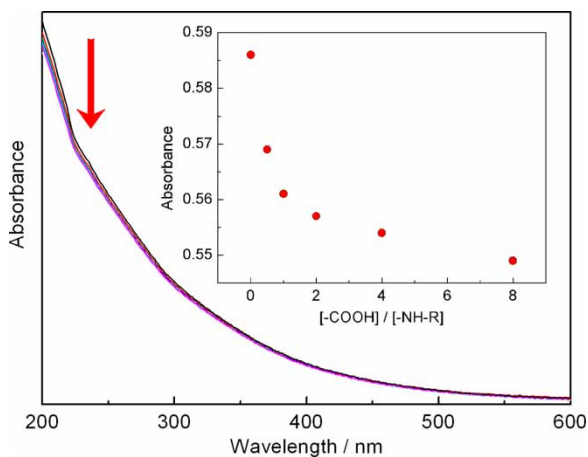


FIGURE 4 Absorption spectra of  $C_{60}/\beta$ -CDa complexes at increased concentration of pAA in  $H_2O$  referenced with same concentration of aqueous pAA solution. Inset: absorption of  $C_{60}/\beta$ -CDa complex ( $1.6 \times 10^{-5}$  M) at 200 nm plotted as a function of the varied amino groups/carboxyl groups molar ratio in  $H_2O$ .

that the complex and pAA can form a large quantity of cubical microstructure with lots of nanowhiskers protruding out of the surface. With side lengths of about 700–800 nm, the microstructures maintained their integrity despite vigorous ultrasonic treatment applied to them prior to the TEM measurement. The electron diffraction pattern of the microstructure with the aid of a TEM (Fig. 5c) proves a crystalline structure. The water-soluble long-chain additive pAA was believed to play a key role in the self-assembly process between  $C_{60}/\beta$ -CDa and pAA and subsequent space-limited growth of supramolecular crystalline structure.

## CONCLUSION

We have succeed in creating the  $NH_2-(CH_2)_2-NH-$  $\beta$ -cyclodextrin-[60]fullerene complex. This capped [60]fullerene inclusion complex modified with amino groups exhibits good solubility in water, and

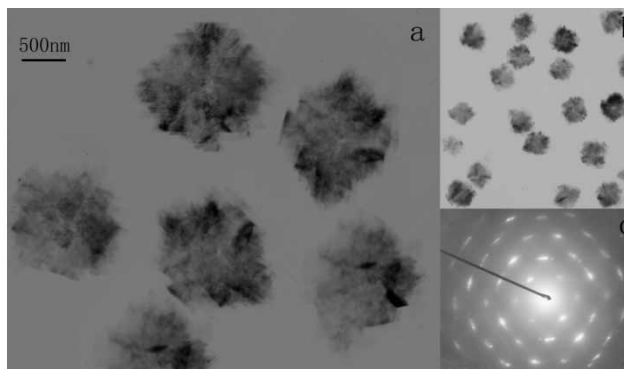


FIGURE 5 TEM image of self-assembled inclusion complex with pAA: (a) center-projecting nanostructure; (b) overall appearance; (c) the electron diffraction pattern.

can further assemble with pAA to form supramolecular structures. The [60]fullerene skeleton is kept undamaged as an intrinsically good electron acceptor in the complex. It is expected to be an ideal self-assembly block to perform the investigation in fields of chemistry and biology.

## MATERIALS AND METHODS

Most of the chemical reagents were received commercially without further purification. Ethylenediamine, DMF, triethylamine, toluene,  $CH_3CN$  and poly (acrylic acid) (pAA) ( $M_v 1.25 \times 10^6$  Da) used in reactions and spectroscopic investigations were analysis grade quality. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlK $\alpha$  radiation. The base pressure was about  $3 \times 10^{-9}$  mbar. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. NMR spectra were recorded on a Bruker AVANCE 300 (300 MHz) spectrometer. Chemical shifts were referred to solvent signals and tetramethylsilane. The UV-Vis absorption spectra were recorded on a TU-1900 spectrometer. Transmission electron microscopy (TEM) measurements were carried out with a Hitachi H-800 instrument with a tungsten filament at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) was recorded using Perkin-Elmer TGA7 and FT-IR spectra were measured on a Bruker Tensor-27.

### Synthesis of $C_{60}/\beta$ -CDa Complex

Mono-6-deoxy-ethylenediamino- $\beta$ -cyclodextrin ( $\beta$ -CDa) was prepared according to previous report [18]. 60 mg  $\beta$ -CDa (0.05 mmol) was dissolved in 15 mL acetic acid and kept stirring for 12 hours. Then excess acetic acid was removed on a rotary evaporator. The resulting  $\beta$ -CDa acetate was dissolved in 43 mL DMF, into which [60]fullerene toluene solution (0.02 mmol in 15 mL toluene) was dropped. The mixture was kept stirring at room temperature for two weeks. Thereafter, the resulting solution was poured into excess triethylamine (120 mL) and kept stirring for 10 min to produce a brown precipitate. Then the filtered precipitate was dissolved in distilled water. An aqueous solution was obtained by centrifuge. After removal of the solvent, the resulting powder was recrystallized by  $H_2O$  and  $CH_3CN$  (v/v, 1:3; yield: 29.3%).

### Self-assembly with pAA

0.72 g poly (acrylic acid) (pAA) was dissolved in 100 mL distilled water. 8 mL  $C_{60}/\beta$ -CDa complex (12.3 mg, 0.004 mmol) aqueous solution and 0.32 mL

former pAA aqueous solution were added to 60 ml distilled water. The mixture was kept stirring for 3 days at room temperature and then left static. Thereafter, the resulting mixture was centrifuged at 4000 rpm for 30 minutes. After the supernatant liquid was discarded, the final product was washed by distilled water for three times.

### Acknowledgement

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