Novel Benzo-15-crown-5/C_{60} Dyads with Different Chains: Synthesis and Complexation Properties

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Abstract: Using benzo-15-crown-5 derivatives as starting materials, two novel benzo-15-crown-5/C_{60} dyads with different linking chains were designed and synthesized in good yields by 1,3-dipolar cycloaddition of azomethine ylide generated in situ from aldehyde and sarcosine tied to C_{60}. It was found that their UV-Vis absorption spectra could be regulated hypsochromically by metal ions complexation. The long and soft linking chain was favorable for cooperate interaction of crown ether unit and C_{60} unit.

Keywords: C_{60}, benzo-15-crown-5, chain, synthesis, complexation.

1. INTRODUCTION

Fullerene has received considerable attention and much research interest due to its remarkable photophysical, electrochemical and chemical properties [1-3]. Many functional groups or functional units have been introduced for tuning the physical properties of C_{60} and for constructing supramolecular architectures [4-7]. Among all kinds of C_{60} derivatives, [60]fullerene/crown ether conjugates represent the most widely studied example of fullerenes integrating an ether moiety. The covalent linkage of a crown ether moiety on the fullerene core is a unique approach to the construction of functional supramolecular fullerene assemblies [8], such as fullerene crown ether with π-extended TTF derivative [9], [60]fullerene/crown ether with photochemical addition [10], C_{60}/crown ether with Bingel reaction of malonates [11-13]. These target molecules have potential application to form supramolecular complexes and assemblies by metal ion recognition. It was expected that cation binding would affect the redox potential of the fullerene sphere, thereby providing an electrochemically detectable sensoric signal for the recognition event, etc.

Based on the above literatures of fullerene/crown ether dyads, it could be concluded the properties of fullerene/crown ether were decided on not only the structures of crown ether ring but also the structures of linking chains between fullerene and crown ether. 1,3-dipolar cycloaddition of azomethine ylide was widely used to prepare fullerene derivatives effectively, but it was seldom applied to synthesize fullerene/crown ether [14]. Moreover, the influences of the different linking chains between C_{60} and crown ether on properties were not studied up to now. In this paper, we wish to report the design and synthesis of novel benzo-15-crown-5/C_{60} dyads with different linking chains by 1,3-dipolar cycloaddition. Also, it was found that the different linking chain of benzo-15-crown-5/C_{60} dyads made different influences on their properties.

2. RESULTS AND DISCUSSION

The synthetic route was shown in (Scheme **1**). 1, 3-dipolar cycloaddition was a typical reaction for preparing C_{60} derivatives [5]. In order to accomplish 1, 3-dipolar cycloaddition, the formylphenyl Benzo-15-crown-5 derivatives **2** and **6** with different linking chains were prepared preliminarily in ideal yields. By reacting 2,3-dihydroxybenzaldehyde with tetraethylene glycol disulfonate **1** using Na^+ as template cation, formylphenyl benzo-15-crown-5 derivative **2** was obtained in 70% yield in "1+1" condensation mode. On the other hand, the formylphenyl benzo-15-crown-5 derivative **6** was prepared by using benzo-15-crown-5 as starting material, followed by nitration, reduction, acylation, and etherification with 4-hydroxy benzaldehyde. Although, in the *muti*-step synthetic procedures for compound **6**, the purification was simple with recrystallization and the yield was ideal in each step. Subsequently, by treating compounds **2** or **6** with sarcosine and C_{60} in refluxing toluene, the novel benzo-15-crown-5/C_{60} dyads 7 and **8** were obtained *via* 1,3-dipolar cycloaddition of azomethine ylides tied to C_{60}. The isolated yields were 33% and 38% after column chromatography, respectively. Due to the crown ether/C_{60} dyads **7** and **8** with different linking chains, it is expected they showed not only the cooperation complexation action of C_{60} unit and crown ether unit for guest, but also the influence of different linking chains on the complexation ability, which was not discussed in the literatures before.

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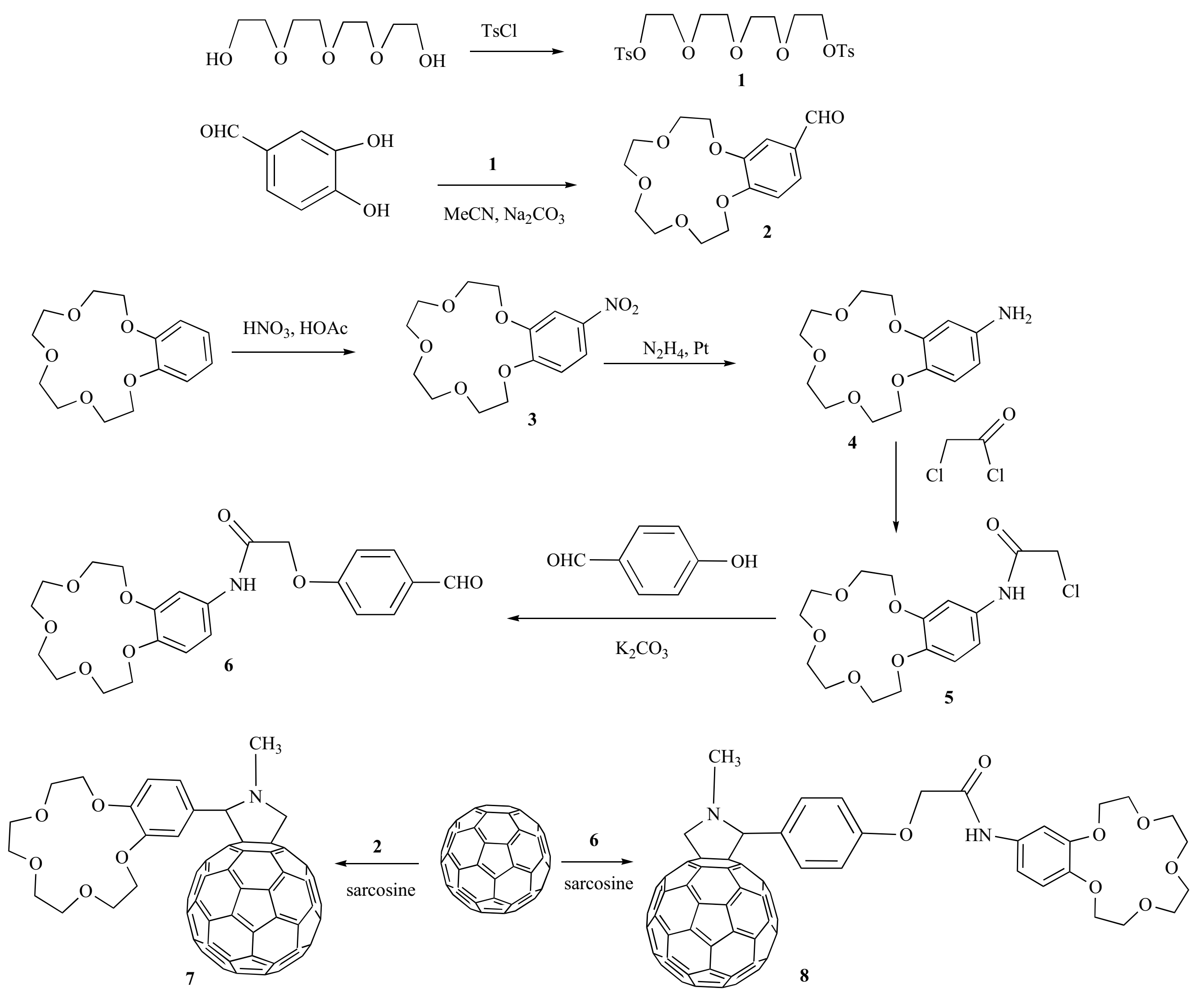

Scheme 1.

The structures of new compounds **7** and **8** were characterized by elemental analyses, UV, IR, ESI-MS, ^1H NMR spectra, *etc*. The UV spectra of compounds **7** and **8** were shown in (Figs. **1** and **2**). The typical absorption features of mono-fulleropyrrolidine at 432 nm could be seen. Their ESI-MS spectra showed corresponding molecular ion peaks at 1043.66 and 1193.68. Also, all the protons of their ^1H NMR spectra were assigned well. Especially, the typical split of NCH_2 (a and a') on pyrrole rings were observed clearly. All these typical characterizations of spectra were similar to the structures of mono-fulleropyrrolidine in the literature [15].

In order to test the influence of different linking chains on their property, UV-Vis absorption spectra of compounds **7** and **8** in $CHCl_3$-MeCN (1:1, v/v) with addition of Na^+ were measured at room temperature as shown in (Figs. **3** and **4**). It could be seen that the absorption of compounds **7** and **8** was hypsochromically shifted by metal ions complexation. When Na^+ was added, the peaks of absorption of compounds **7** and **8** shifted from 328 nm and 276 nm to 325 nm and 270 nm, respectively. The hypsochromic effect was attributed to the complexation with a cation reducing the donor character of the oxygen atoms of crown ether moieties, which could regulate the absorption spectra of crowned [60]fullerpyrrolidine. Moreover, the absorbance of compound **8** after complexation increased obviously comparing with the change of compound **7**. These results indicated that compound **8** with long and soft linking chain produced stronger cooperation complexation than that of compound **7** with short and rigid linking chain. These phenomena were not reported before, which might be attributed to the soft chain of compound **8** which was favorable for the crown ether unit closing to fullerene and then producing stronger interaction between them.

In a word, two novel benzo-15-crown-5/C_{60} dyads with different linking chains were designed and synthesized in good yields by 1,3-dipolar cycloaddition. Their UV-Vis absorption spectra could be regulated hypsochromically by metal ion complexation. The long and soft linking chain was favorable for cooperate interaction between crown ether unit and C_{60} unit. The in-depth studies on syntheses and properties of these kinds of dyads with other linking chains will be investigated in the following work.

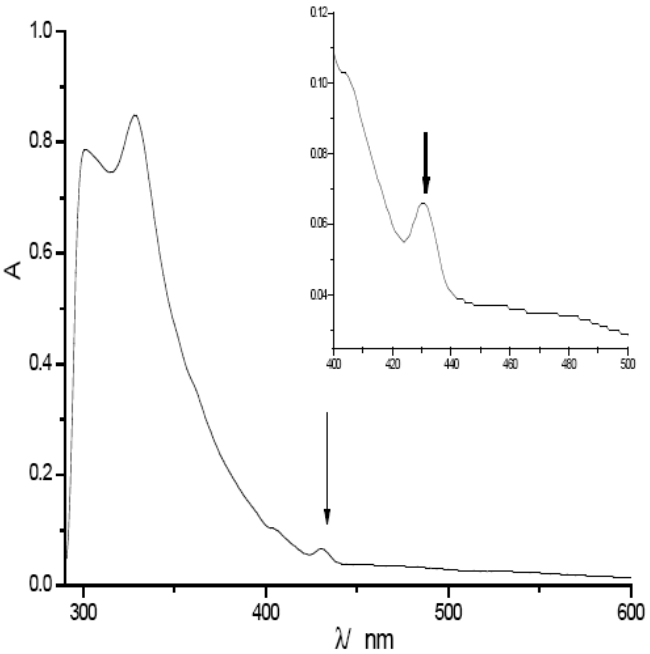

Fig. (1). UV-vis absorption spectrum of compound **7**.

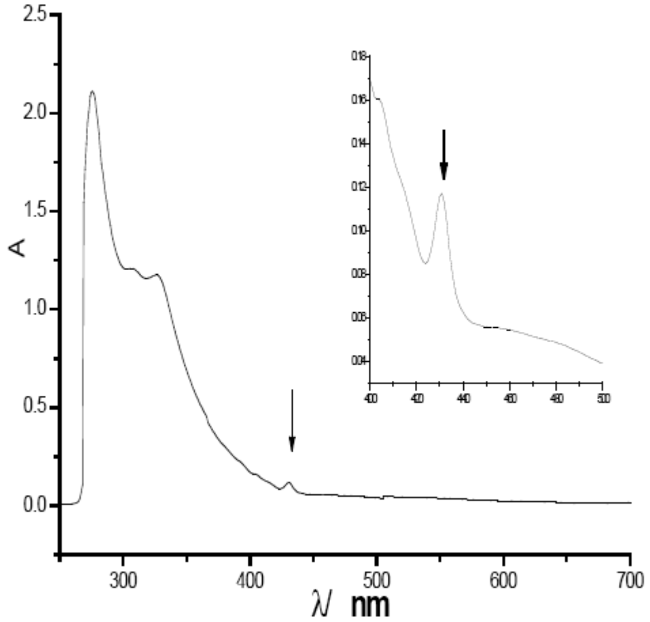

Fig. (2). UV-vis absorption spectrum of compound **8**.

3. EXPERIMENTAL

3.1. Apparatus and Materials

All reagents were purchased from commercial suppliers and used without further purification. All the solvents were purified according to the standard methods before use. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 400 instrument at 30°C. IR spectra were recorded on a Thermo Nicollet AVATAR 5700 FTIR spectrometer using KBr pellet. The UV-vis absorption spectra were measured on a computer-controlled Shimadzu UV2501-PC spectrophotometer. ESI-MS spectra were obtained from DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed at Vario EL III Elemental Analyzer. Compounds **2** and **4** were prepared according to the literature [16].

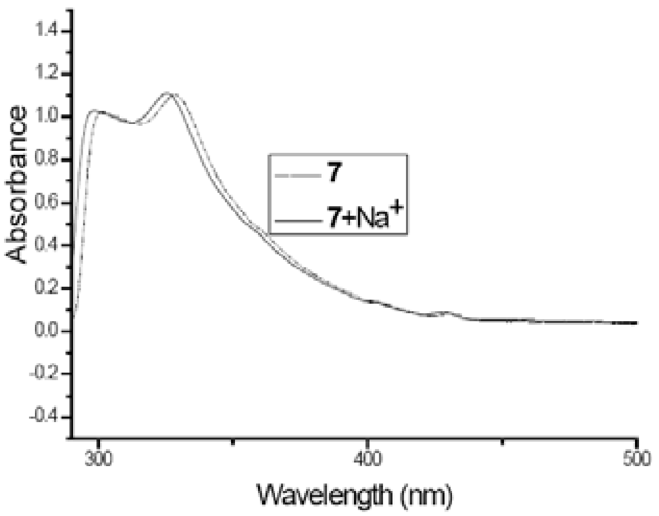

Fig. (3). UV-Vis absorption spectra of compound **7** with addition of anhydrous sodium perchlorate, ratio of **7**/salt = 1:20, concentration of **7**: in 2.0×10^{-5}M, solvent: $CHCl_3$-MeCN (1:1, v/v).

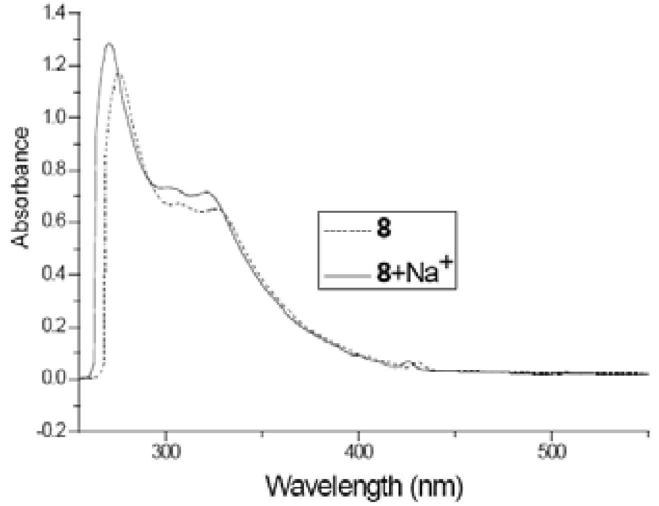

Fig. (4). UV-Vis absorption spectra of compound **8** with addition of anhydrous sodium perchlorate, ratio of **8**/salt = 1:20, concentration of **8**: 2.0×10^{-5}M, solvent: $CHCl_3$-MeCN (1:1, v/v).

3.2. The Procedure for Synthesis of Compound 6

Compound **4** (1.0 g, 3.5 mmol) and 2-chloroacetyl chloride (0.4 g, 3.6 mmol) were stirred in 20 mL dry CH_2Cl_2 at room temperature for overnight purged with N_2. After reaction, the solvent was evaporated to dryness and the light yellow solid was afforded. Then 4-hydroxybenzaldehyde (0.44 g, 3.6 mmol), K_2CO_3 (0.69 g, 5 mmol) and 50 mL of MeCN were added and refluxed for 12 h. TLC detection showed the disappearance of materials. After cooling, the solution was filtered and the solvent was evaporated to dryness. Then 20 mL of methanol was added and precipitation was formed. After dryness, compound **6** was obtained as gray white solid in yield of 80%. Compound **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: (ppm) 3.82~4.15(m, 16H, O**C**H_2**C**H_2O), 4.96 (s, 2H,

OCH_2CO), 6.72~7.45 (m, 7H, ArH), 7.96 (s, 1H, CH), 8.89 (s, 1H, NH).

3.3. The Procedure for Synthesis of Compound 7

A mixture of compound **2** (0.15 g, 0.5 mmol), C_{60} (0.36 g, 0.5 mol), and sarcosine (0.45 g, 5 mmol) in dry toluene (200 mL) was refluxed for 48 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure and the residue was further purified by column chromatography (SiO_2 100-200 mesh, petroleum ether / CH_2Cl_2 (2:1, *V*/*V*) as eluant). The compound **7** was obtained as brown solid in yield of 33%. Compound **7**: m.p. 167~169°C; ^1H NMR (400 MHz, $CDCl_3$) δ: (ppm) 2.80 (s, 3H, CH_3), 3.74~4.14 (m, 16H, OCH_2CH_2O), 4.24 (d, *J*=9.6Hz, 1H, NCH_2), 4.85 (s, 1H,ArCH), 4.96 (d, 1H, *J*=9.6 Hz, NCH_2), 6.81 (s, 1H, ArH), 6.88 (d, *J*=8.0Hz, 1H, ArH), 7.12 (d, *J*=8.0Hz, 1H, ArH); FT-IR (KBr) v / cm^{-1}: 3433, 2920, 2853, 1633, 1508, 1457, 1265, 1132, 1050, 934, 769; MS *m*/*z* (%): 1043.66 (M^+, 40). Anal. calcd for $C_{77}H_{25}NO_5$: C 88.58 H 2.41, N 1.34; found: C 88.53, H 2.47, N 1.31.

3.4. The Procedure for Synthesis of Compound 8

A mixture of compound **6** (0.22 g, 0.5 mmol), C_{60} (0.36 g, 0.5 mol), and sarcosine (0.45 g, 5 mmol) in dry toluene (200 mL) was refluxed for 48 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure and the residue was further purified by column chromatography (SiO_2 100-200 mesh, petroleum ether / CH_2Cl_2 (1:2, *V*/*V*) as eluant). The compound **8** was obtained as brown solid in yield of 38%. Compound **8**: m.p. 182~187°C; ^1H NMR (400 MHz, $CDCl_3$) δ: (ppm) 2.80 (s, 3H, N-CH_3), 3.66~4.14 (m, 16H, OCH_2CH_2O), 4.26 (d, *J*=8.0Hz, 1H, CH_2), 4.86(d, *J*=8.0Hz, 1H, CH_2), 4.90 (s, 1H, CH), 5.34 (s, 2H, OCH_2CO), 6.90~6.99 (bs, 7H, ArH), 7.69 (s, 1H, NH); FT-IR (KBr) v / cm^{-1}: 3426, 2918, 2867, 1675, 1592, 1508, 1451, 1226, 1126, 1050, 942, 828; MS *m*/*z* (%): 1193.68 (M^+, 30). Anal. calcd for $C_{85}H_{32}N_2O_7$: C 85.56 H 2.70, N 2.35; found: C 85.51, H 2.77, N 2.31.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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