Functionalization of fullerene with 4-benzo-9-crown-3 ether

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Functionalization of fullerene *via* covalent addition of substituted 4-benzo-9-crown-3 ether diazonium salt has been described. This procedure is used for the preparation of new derivative fullerenes which is described as a phase transfer catalyst. The covalent grafting has led to a considerable increment in the solubility of fullerene in organic solvents such as, CH_2Cl_2, acetone and ethanol. The covalent grafting of crown ether (4-(benzo-9-crown-3)) to fullerene (Fullerene-CE) has been identified and confirmed by IR, H-NMR, ^{7}Li-NMR and thermogravimetric analysis (TGA) methods. Fullerene-CE in solvents has been used as a phase transfer catalyst for organic reactions. The Fullerene-CE is capable to become the Li^+ host.

Keywords. Covalent grafting, Crown ether, Fullerene, Functionalization, Phase transfer catalyst

Crown ethers are very interesting because of their hydrophobic and Hydrophilic properties of the molecules. They are suitable for binding to a large and spherical organic molecule. This can facilitate dissolution in solvents of different polarities as a Phase transfer catalyst in dehydrohalogenation, Addition, substitution and other organic reactions[1] or in the separation of some metal cations. (Lithium, copper and cadmium)[2]. On the other hand, the small dimension and remarkable physical properties of fullerenes render them unique materials with a wide range of potential applications. Derivatives fullerenes used for nanobiocatalytic systems[3,4], biomedical[5-9], hybrid films with electronic and biomedical properties[10,11] and organic solar cells and transistors[12,13]. In our previous works, we studied functionalization of nanotubes With4-benzo-9-crown-3 ether [14,15]. In this contribution we report functionalization of fullerene with 4-benzo-9-crown-3 ether. Therefore, it is significant to develop a high efficiency for functionalization nanomaterial. This can facilitate the dissolution of nanomaterial in solvents with different polarities that are used as a phase transfer catalyst for organic reactions and separation of some metal cations that the major advantages of the fullerene-CE as a phase transfer catalyst support are: (i) ease of separation from reaction mixture by a simple filtration and (ii) recycling the catalyst.

Experimental Section

The synthesis of benzo-9-crown-3 (3), 4- nitro-benzo9-crown-3 (4) and 4-amino benzo-9-crown-3 (5) are schematically shown[16] in Scheme 1.

Synthesis of benzo-9-crown-3 (3)

Catechol (1) (1.1 g, 0.01 mol), LiOH (0.84 g, 0.02 mol) and distilled water (58 mL) were placed in a 150 mL round bottom flask. To this mixture, the bis 2-choloro ethyl ether (2) (1.43 g, 0.01 mol) was added dropwise and followed by stirring for 30 min. The mixture was then refluxed for 86 h at 100°C. Addition of 5 mL of water and steam distillation produced white crystals of benzo-9-crown-3 ether (3) in yield of 33% (0.60 g).

Synthesis of 4-nitro-benzo-9-crown-3 (4)

Benzo-9-crown-3 ether (3) (1.8 g, 0.01 mol), dichloromethane (40 mL), glacial HOAc (28 mL) and few drops of H_2SO_4 were placed in a 200 mL round bottom flask. Then, HNO_3 (conc.) 5 mL was added drop-wise to this mixture and refluxed for 3 h. The resulting yellow reaction mixture was poured onto 35 g of crushed ice, and then sufficient amount of concentrated aqueous NaOH was added to naturalize the mixture (*p*H control). This material was extracted by dichloromethane (4×25 mL), and the combined organic extracts were dried over anhydrous Na_2SO_4 (5 g). After filtration and solvent removal in vacuum, yellow crystalline 4-nitro-benzo9-crown-3 ether was afforded to yield 71% (1.6 g, m.p. 92–94 °C).
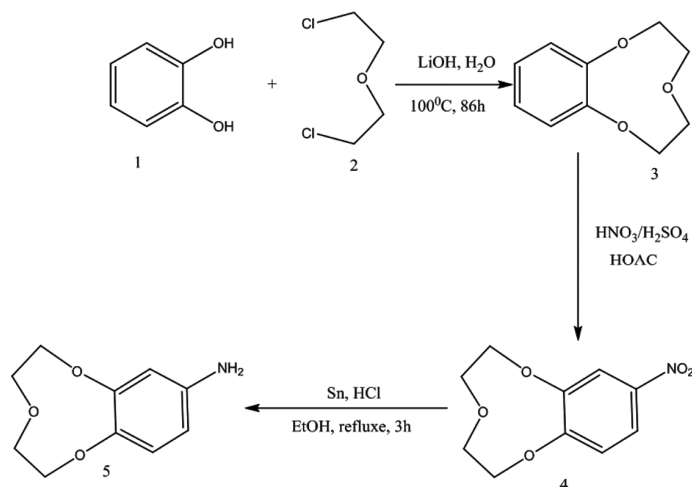
Scheme 1 — Synthesis of 4-amino benzo-9-crown-3 ether (5).

Synthesis of 4-amino benzo-9-crown-3 (5)

To a mixture of 4-nitro-benzo-9-crown-3 ether (4), (0.23 g, 0.01 mol) and tin (0.46 g, 0.004 mol), the solution of HCl (3 mL) in absolute ethanol (5 mL) was added drop-wise and the mixture was refluxed for 3 h. When TLC monitoring indicated no further progress of the reaction, then enough aqueous KOH (conc.) was added to make the solution basic. The reaction mixture was then stirred for 30 min. The white precipitate was washed with $CHCl_3$ (4×5 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4 (1.2 g). Filtration was followed by the solvent removal in vacuum and yielded some light brown oil (1.95 g, 85%). Synthesis of crown ether is shown in Scheme 1.

Covalent grafting of 4-benzo-9-crown-3 ether to Fullerene using 4-amino benzo-9-crown-3 ether (Fullerene –CE)

The Fullerene used for this work were purchased from *Neutrino Co* in its pure form. First, for further purification, fullerene (6 mg, 0.5 mmol of carbon), hydrochloric acid (5 mL) were added, and the mixture was irradiated for 15 min with ultrasound to seprateof metal. The fullerene was separated with centrifuge.

Next, fullerene (6 mg, 0.5 mmol of carbon), 4-aminobenzo-9-crown -3 ether (CE) (4 equiv/mol of carbon) (5), sodium nitrite (4.0 equiv/mol of carbon) and sulfuric acid (4.8 eq /mol of carbon) were added and stirred with a magnetic stirrer for 5 min and then refluxed for 1 hour at 60°C for the production compound 7. The adhesive precipitate was diluted with dichloromethane and filtered through a PTFE (0.45 μm) membrane.The black solid was washed with dichloromethane until the filtrate became colorless[17]. The precipitate was then kept in an oven at 65°C for 24 h overnight and characterized. The functionalization of Fullerene with 4-Benzo-9-crown-3 is shown in Scheme 2.

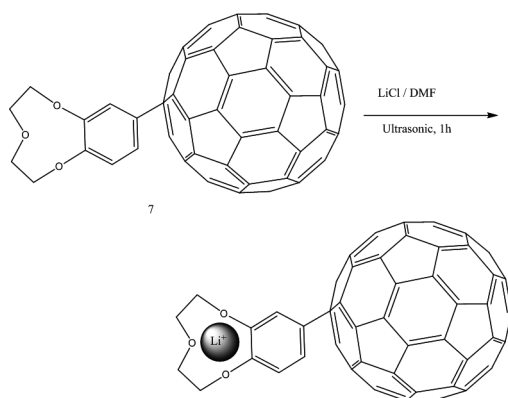**Complexation of Fullerene-4-benzo-9-crown-3 ether with Li^+**

The 4-benzo-9-crown-3 ether which has been grafted on Fullerene is capable of forming metal-complex. Thus, we decided to carry out the complexation experiment, to investigate whether the Fullerene-CE is capable to become the metal ions host. With regard to the fact that the cavity size in 9-crown-3 ethers analogues is naturally proper for Li^+ ion. Therefore, we chose Li^+ ion as a host metal for the complexation.

For this purpose, a suspension of the corresponding grafted Fullerene with 4-benzo-9-crown-3 ether in DMF was prepared and added a solution of the metal salt (LiCl) was added. After a sonication for period of time, the excess of metal salt was removed by filtration through a 0.45 μm polytetrafluoroethylene filter (PTFE—millipore) to separate a Fullerene filter cake, which was washed with distilled water. The filtered cake was then dried in vacuum oven at 50°C for a day. The complexation of covalent grafted Fullerene-4-benzo-9-crown-3 ether with Li^+ is shown in Scheme 3.

Characterization Fullerene-CE and Fullerene-CE-Li^+: The Fullerene-CE (7) was identified by FT-IR, NMR and thermogravimetric analysis (TGA). The hosted Li^+ by 7 and formation of Fullerene-CE-Li^+ (8) was also identified by ^{7}Li-NMR.
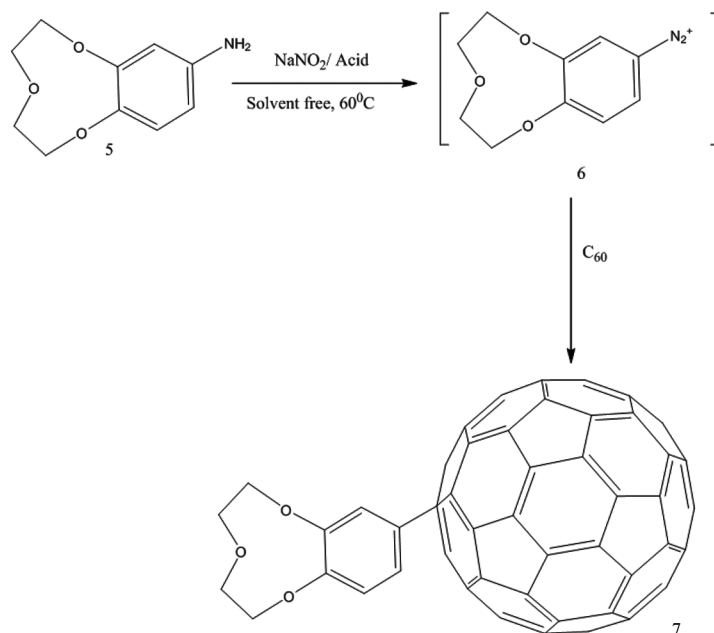
Scheme 2 — Covalent grafting of 4-benzo-9-crown-3 ether to fullerene (7).

Scheme 3 — Incorporation of Li$^+$ in fullerene-CE.

Characterization of fullerene-CE (7)

The functionalized fullerene with 4-amino benzo-9-crown-3 ether (5) on can be indicated by IR spectroscopy method. Figure 1(a), is the IR spectrum of 4-amino benzo-9-crown-3 ether and as it is shown, there is amine functional group on crown ether (ν_{N-H} =3358, 3449 cm^{-1}). Figure 1(b) indicates the IR spectrum of fullerene-CE (7). By comparing both spectrums to each other, in spectrum 1B the presence of a sharp peak at 1050 cm^{-1} in the mid-IR range is attributed to C-O-C ether bonds. The IR spectrum of Fig. 1(b) indicated the formation of the fullerene – CE. Absence of N-H peaks (ν_{N-H} =3358, 3449 cm−1) in this spectrum (1b) is a sign of crown ether binding to fullerene. The sharp peak below 3000cm^{-1},

which is present in both spectrum [Fig.1(a & b)], is the reason for the existence of aliphatic C-H groups of the crown ether.

Also ^{1}H NMR spectrum fullerene-CE(7)in CDCl$_3$ shown in Fig. 2. The solubility of fullerene is usually low (in chloroform and dichloromethane is 250mg L^{-1})[18] but the solubility of fullerene-CE is high (in chloroform and dichloromethane is 186000 mg L^{-1}). The ^{1}H NMR (CDCl$_3$) of the obtained fullerene-CE is in: δ (ppm) = 3.94-4.39 (d, 8H) and 6.98-7.29 (m, 3H). Our observations showed that the solution-state of ^{1}H NMR of fullerene-CE created two big peaks, in the intensity ratio of 8:3. One of the peaks which is double (δ (ppm) = 3.94-4.39) displayed two types of carbon-hydrogen bonds of crown ether. In addition, the presence of one multiplicity peak (δ (ppm) = 6.98-7.29) showed three different types of C–H bonds in aromatic ring.

It is well demonstrated that heating the fullerene-CE in an inert atmosphere (N$_2$) removes the organic moieties and restores the pristine fullerene structure. Therefore, TGA could be a good criterion of the degree of functionalization. Figure 3 indicates the TGA of pristine fullerene and as it is shown there is weight loss at different temperatures. It was observed that weight lost from TGA of fullerene -CE (7) (35°C/min to 600°C in N$_2$) was ≈11%. These results suggest a degree (11%) of functionalization in fullerene-CE (7).
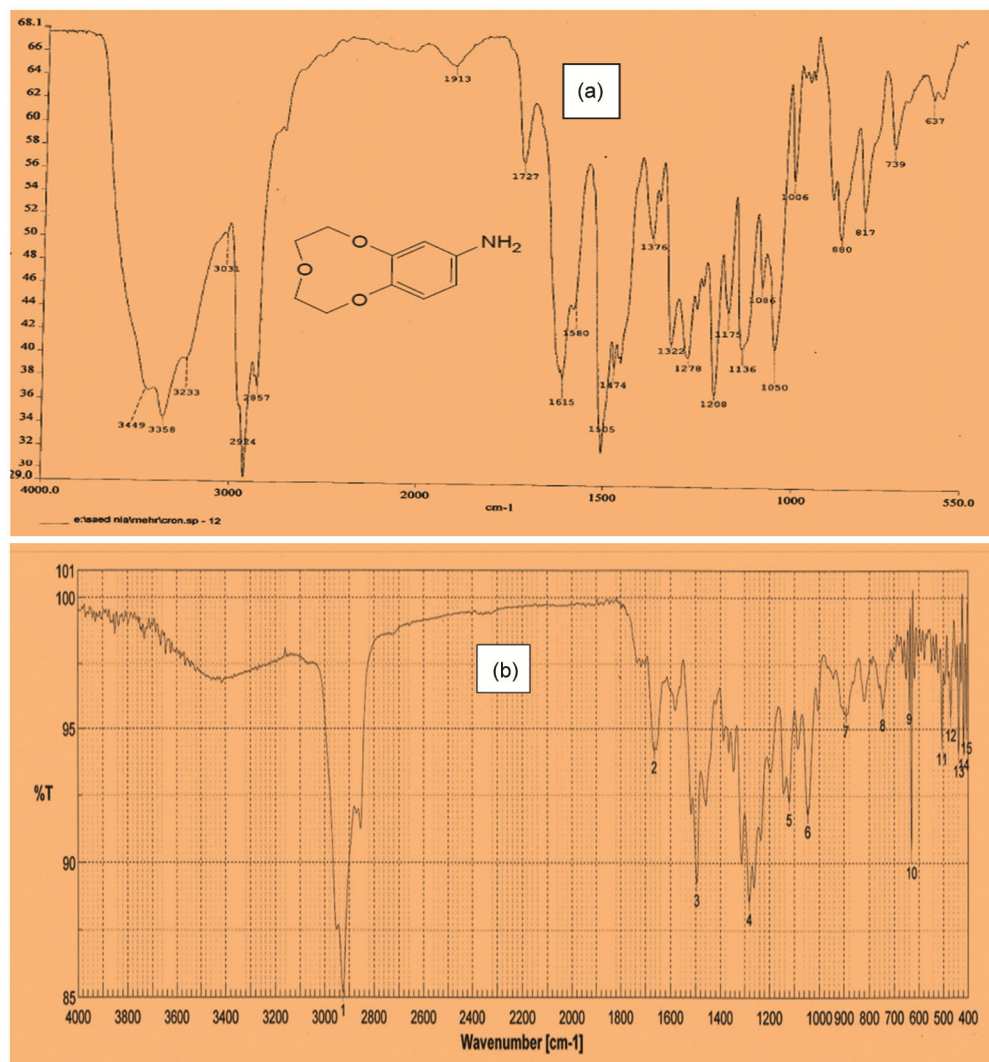
Fig. 1— IR spectra of (a) 4-amino benzo-9-crown-3 ether (6) and (b) Fullerene-CE (7).
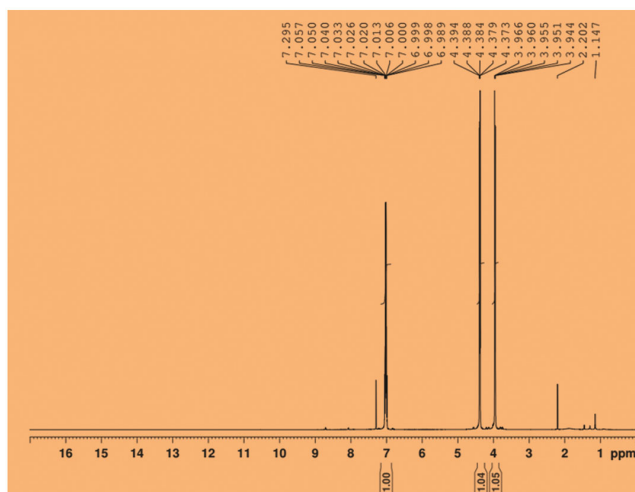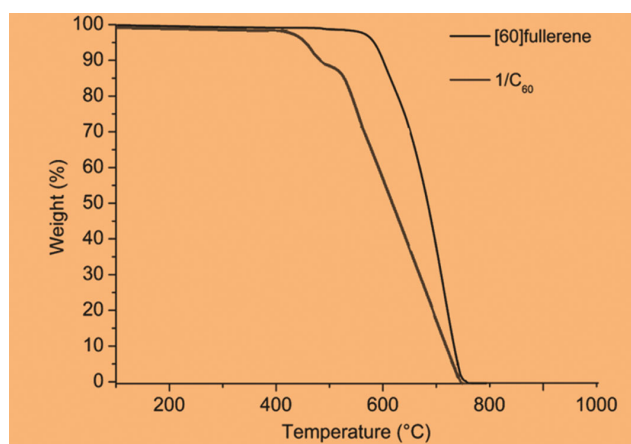

Fig. 2 — NMR spectra of fullerene-CE (7) in CDCl₃.

Fig. 3 — TGA curve of fullerene, Fullerene-CE (7)[Ramp, from 35°C to 800°C at 10°C/min].

Characterization of the fullerene-CE -Li^{+} by ^{7}Li-NMR

To further ascertain the ability of fullerene -CE (7) to host Li^{+}; therefore, fullerene -CE was immersed in a solution of lithium chloride to host the Li^{+} in fullerene-CE. Thus, for this purpose, the ^{7}Li-NMR has been applied for indicating Li^{+} exchange (Fig. 4). In a solution of pure crown ether, because of the fast exchange[19] between the complexed Li^{+} and the
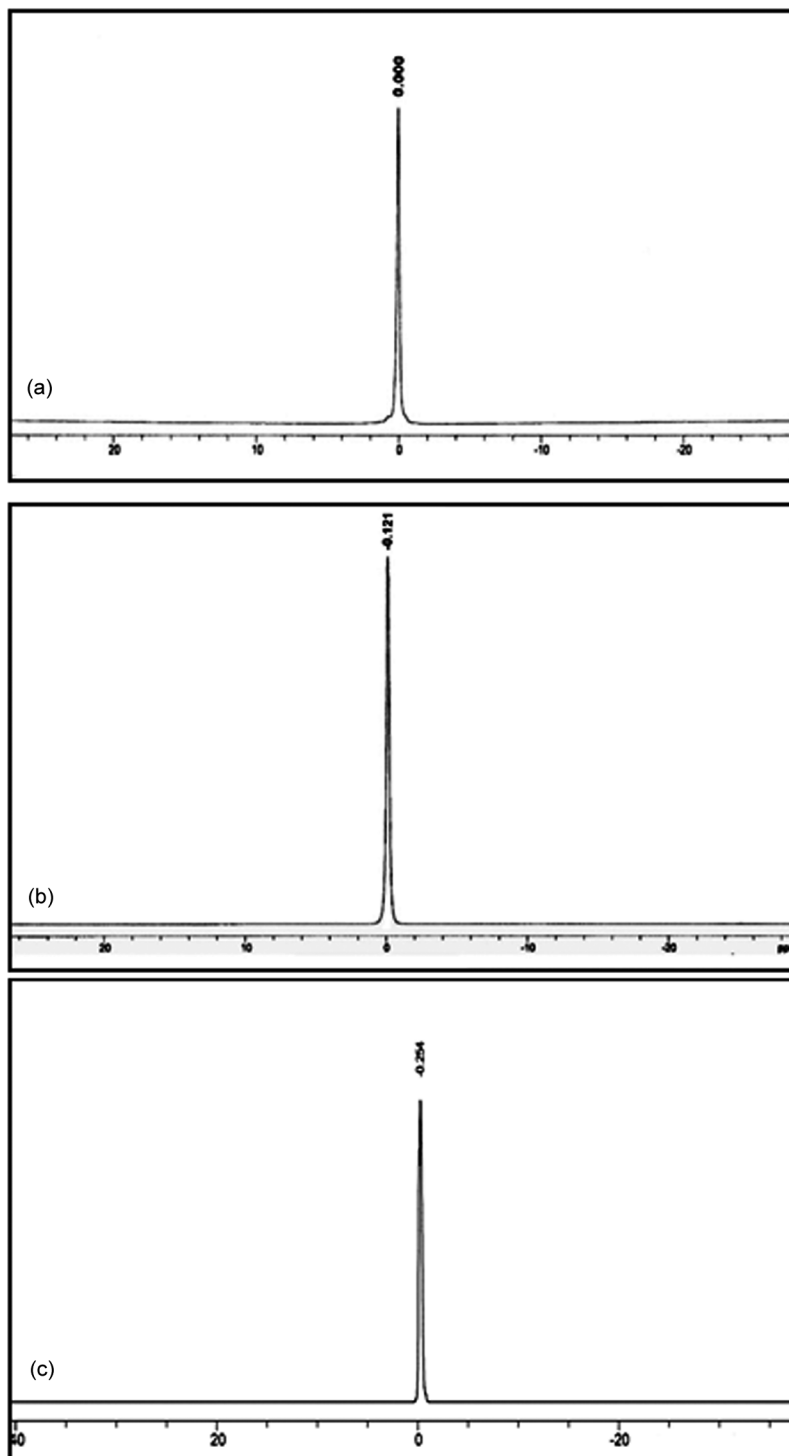

Fig. 4 — ^{7}Li-NMR data. (a) LiCl standard (4M) in H_2O, (δ= 0 ppm); (b) CE- Li^{+} Complex in H_2O, (δ= -0.121 ppm) and (c) SWCNT-CE-Li^{+} Complex in H_2O, (δ= -0.254 ppm).

Table 1 — Solubility of SWCNT- CE in different Solvents [a]

Solvent	Solubility (mg L^{-1})[b]
Dichloromethane	186000
Acetone	15000
Ethanol	6000
Diethyl ether	few
H_2O	c
n-Hexane	c

[a] Values were obtained within range of 10%
[b] Values were obtained at 25 °C
[c] Insoluble

free cation, only single ^7Li peak was observed. In a same circumstance, the solution of fullerene-CE, showed a single narrow ^7Li peak which is implication of fast exchange between hosted Li^+ by the crown ether adducted to fullerene and those of free Li^+ in solution. As the exchange of Li^+ between bonded CE on fullerene and those of free in solution is readily observed and also with regard to the fact that only one ^7Li peak is assigned; therefore, this can be a good witness for our hypothesis, that crown ether is tethered to the fullerene *via* ionic bond. Fullerene-CE (7) can make a complex with the Li^+ through its CE residue. To ensure the ionic bond of crown ether to fullerene, excess unreacted CE could be removed from the adduct by washing with diethyl ether.

The solubility test for fullerene-CE was also conducted (Table 1). For this purpose, the remaining residue after work-up (a black powder) was used. This solid was soluble in CH_2Cl_2, less soluble in EtOH and acetone and insoluble in H_2O and hexane (Table 1).

Conclusion

In conclusion, the adduct of 4-amino benzo-9-crown-3 ether on to fullerene has been explained. The functionalization has been achieved by adding and 4-amino benzo-9-crown-3 to fullerene. Fullerene -CE can host the Li^+ through the crown ether residue bonded on its surface. The major advantages of fullerene-CE as a phase transfer catalyst are: (i) ease of separation from reaction mixture through the simple filtration; (ii) proper carrier of Li^+ and useful source of Li^+ for catalyzing the organic reactions and (iii) ease of reusability and recycling the catalyst.

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