Bis-functionalized fullerene-dibenzo[18]crown-6 conjugate: synthesis and cation-complexation dependent redox behavior†

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A one-step synthesis of bis-pyrrolidine functionalized fullerene-dibenzo[18]crown-6 conjugate and its metal cation complexation to the crown ether entity dependent redox behavior is reported.

Fullerenes functionalized to bear cation receptors like crown ether or cryptand are an important class of compounds since the cation binding affects the redox potential of the fullerene sphere, thereby providing an electrochemical signal for cation recognition.[1] However, in most of the covalently linked fullerene-crown ether conjugates this redox behavior was not observed due to the large distances between the ionophore-bound cation and the C_{60} sphere.[2] Only recently, Diederich, Echegoyen, and coworkers synthesized and provided electrochemical evidence for cation-induced redox potential changes in a series of bis- and tetra- functionalized crown-ethers bearing C_{60} and C_{70} *Bingel* adducts.[3] In the present study, we have bis-functionalized C_{60} to bear a dibenzo[18]crown-6 tether by using Prato's fulleropyrrolidine synthetic methodology[4] (Scheme 1) and report metal cation-induced electrochemical redox potential changes.

The synthesis of the C_{60}-crown ether conjugate, **1** was carried out by reacting C_{60}, sarcosine, and octahydrohexaoxadi-benzo[*a,j*]cyclooctadecene-2,13-dicarboxaldehyde (Aldrich) by using the procedure based on 1,3-dipolar cycloaddition of azomethine ylides[4] to C_{60} followed by chromatographic separation of the product on a silica gel column.‡ This technique afforded the product in one step. The ¹H NMR studies revealed the presence of at least three geometric isomers of the product. *Ab initio* calculations at the HF/STO-2G or B3LYP/3-21G(*) levels were performed to visualize the possible geometric isomers. Of the 8 possible 6–6 linked isomers, based on geometric considerations of the crown-entity, the *trans* isomers were found to be more favorable (see Scheme 1 for position notation of the bis-adducts[5]). It may be mentioned here that for each of the geometric isomers, there are several (as many as 16) possible methylene connections for the crown ether, and for each of these connections several energetically closely separated conformers exist depending upon the position of the *N*-

methyl group (axial or equatorial positions) and 2-pyrrolidine ring (up or down) (See ESI† for pictures of the representative calculated molecules). Complexation of K^+ also revealed stable structures and the distance between K^+ and the nearest carbon atom of C_{60} was found to be 2.77, 3.07 and 4.55 Å respectively for the *trans*-1, *trans*-2 and *trans*-4 geometric isomers. The *trans*-1 isomer was found to be very tightly stretched and the present results suggest that its K^+ binding is an energy demanding process (over 60 kcals mol⁻¹ higher than *trans*-2) even though this could be one of the three isomers formed. The potential shifts of the C_{60} redox couples upon cation complexation to the crown ether cavity reported in this paper are the average values of these geometric isomers.

Cyclic voltammetry§ was used to evaluate the redox potentials of the bis-functionalized fullerene-crown ether conjugate and also to probe the effect of metal ion insertion into the crown ether cavity on the redox potentials of the C_{60} entity. Fig. 1 shows cyclic voltammograms of pristine C_{60}, mono-functionalized fulleropyrrolidine, and bis-functionalized C_{60}-crown ether conjugates, **1** while Table 1 lists the half-wave potentials for the first two one-electron reversible C_{60} based redox processes of these compounds. Based on the ΔE_{pp} values and the cathodic-to-anodic current ratio, the first two reductions of **1** were found to be electrochemically and chemically reversible. With increasing numbers of pyrrolidine rings on the C_{60} spheroid, the reductions revealed a cathodic shift, that is, the reductions became more difficult, a trend similar to that reported earlier for bis- and tetra-alkyllated C_{60} adducts.[2,3] The potential shift for a given redox couple between pristine C_{60} and mono-pyrrolidine adduct of C_{60} was ~ 110 mV while this shift
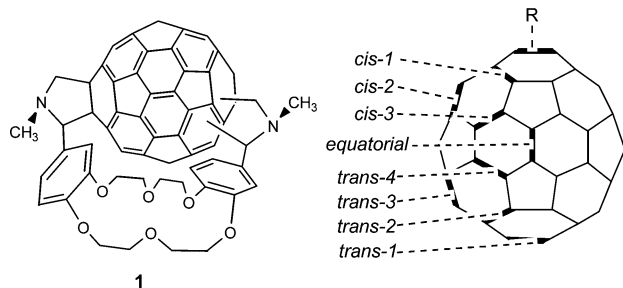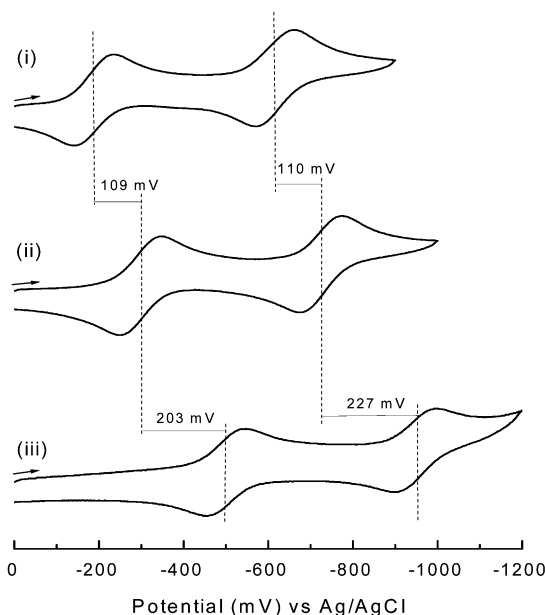

Scheme 1

Fig. 1 Cyclic voltammograms of (i) C_{60}, (ii) 2-phenylfulleropyrrolidine and (iii) **1** in toluene–acetonitrile (4 : 1 v/v). Scan rate = 100 mV s⁻¹.

was almost double between the mono- and bis-fulleropyrroli-dine adducts.[7]

Complexation of metal ions to the crown ether cavity of **1** revealed anodic shifts of the C_{60} redox waves (Table 1). Metal ion binding to the crown ether cavity was independently verified by ESI-mass spectral measurements (see ESI†). Metal ions of higher affinity to 18-crown-6, such as K^+ revealed the highest shift of about 40 mV (Fig. 2) while this shift for other metal ions ranged between 10–35 mV depending upon the redox states of the employed cations (M^+ or M^{2+}) and C_{60}. The cation-induced potential shifts observed in the present study are slightly smaller than that reported in literature for bis-functionalized crown-ether bearing C_{60} and C_{70} *Bingel* adducts.[3] The nature of the potential shift depends upon the charge density of the metal ion, its state of solvation, its interactions with the local crown-ether dipoles, its fit into the crown ether cavity, and the distance between the metal ion and the fullerene surface. For K^+ binding, owing to a better fit into the crown ether cavity as compared to Li^+, NH_4^+ (tripod H-bonding to the crown ether) and Na^+ greater potential shifts are observed. Interestingly, owing to the different sizes, the dicationic Ca^{2+} and Ba^{2+} revealed relatively smaller potential shifts. These dicationic metal ions may not interact with the crown ether

cavity tightly thus increasing the distance between the metal ion and the fullerene surface. However, it is important to note that anodic shifts of the C_{60} redox waves were observed for all of the metal cations employed in the present study providing electro-chemical evidence for cation recognition.

In summary, we have described a one-step procedure to synthesize a bis-functionalized fullerene–crown ether conjugate by 1,3-dipolar cycloaddition of azomethine ylides to C_{60} and demonstrated metal ion induced potential changes of the C_{60} redox processes as electrochemical evidence for cation recognition. Further studies along this line are in progress.

Table 1 Electrochemical half-wave redox potentials (*vs.* Ag/AgCl) in toluene–acetonitrile (4 : 1 v/v) for fullerene compounds and fullerene-crown ether conjugates, **1** in the presence of different metal ions[a]. Scan rate = 100 mV s^{-1}

Compound	$E^1_{1/2}$	Shift/mV[c]	$E^2_{1/2}$	Shift/mV[c]
C_{60}	−189	—	−616	—
2-phenylfulleropyrrolidine	−298	—	−726	—
1[b]	−501	—	−953	—
1 + K^+	−467	34	−915	38
1 + Na^+	−474	27	−923	30
1 + Li^+	−482	19	−945	10
1 + NH_4^+	−481	20	−923	30
1 + Ca^{2+}	−486	15	−929	24
1+ Ba^{2+}	−486	15	−934	19

[a] 10 Equivalents of metal ions (as perchlorate or hexafluorophosphate salts) were used to ensure complete complexation. [b] Addition of 5 equivalents of [2,2,2]cryptand resulted in no significant changes in the redox potentials. [c] The shift in potentials were also confirmed by the addition of ferrocene as internal standard.
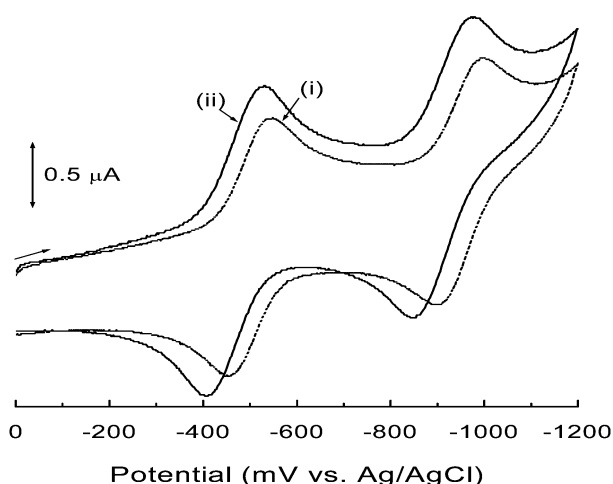

Fig. 2 Cyclic voltammograms of **1** (i) in the absence and (ii) in the presence of KPF_6 in toluene:acetonitrile (4 : 1 v/v). Scan rate = 100 mV s^{-1}.

Notes and references

‡ ^{1}H NMR (400 MHz, CDCl$_3$–CS$_2$), δ ppm, 6.50–7.50 (m, 6H, phenyl H), 3.00–5.00 (m, 22H, pyrrolidine and crown ether H), 2.73, 2.69, 2.63 (s, s, s, 6H, (3 isomers) methyl H); UV-vis in DMF, λ_{max}/nm 299 (sh), 421; ESI mass in CH$_2$Cl$_2$ calcd. 1189.2, found 1190.6 (M) and 1223.5 (M + CH$_3$OH).
§ Cyclic voltammograms were recorded on a EG&G Model 263A potentiostat–galvanostat using a three electrode system. A platinum button or glassy carbon electrode was used as the working electrode. A platinum wire served as the counter electrode and a Ag/AgCl was used as the reference electrode. All the solutions were purged prior to electrochemical and spectral measurements using nitrogen gas. The UV-visible spectral measurements were carried out with a Shimadzu Model 1600 UV-visible spectrophotometer. The computational calculations were performed by *ab initio* HF/STO-2G and B3LYP/3-21G(*) methods with GAUSSIAN 98 software package[6] on various PCs and a SGI ORIGIN 2000 computer.

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