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A supramolecular oligophenylenevinylene–C_{60} conjugate

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Abstract—A new methanofullerene derivative with an ammonium subunit has been prepared and its ability to form a supramolecular complex with an oligophenylenevinylene (OPV)–crown ether conjugate evidenced by NMR, electrospray mass spectrometry and luminescence experiments. © 2003 Elsevier Science Ltd. All rights reserved.

In light of their unique electronic properties, fullerene derivatives are suitable building blocks for the preparation of molecular devices displaying photoinduced energy and electron transfer processes.[1] Whereas research focused on the use of C_{60} as the acceptor in covalently bound donor–acceptor pairs has received considerable attention,[1] only a few related examples of fullerene-containing non-covalent assemblies have been described so far.[2,3] As part of our research on compounds combining C_{60} with π-conjugated oligomers,[4] we have decided to develop a non-covalent approach for their preparation. The assembly of the two molecular components by using supramolecular interactions rather than covalent chemistry appears particularly attractive since the range of systems that can be investigated is not severely limited by the synthetic route. In

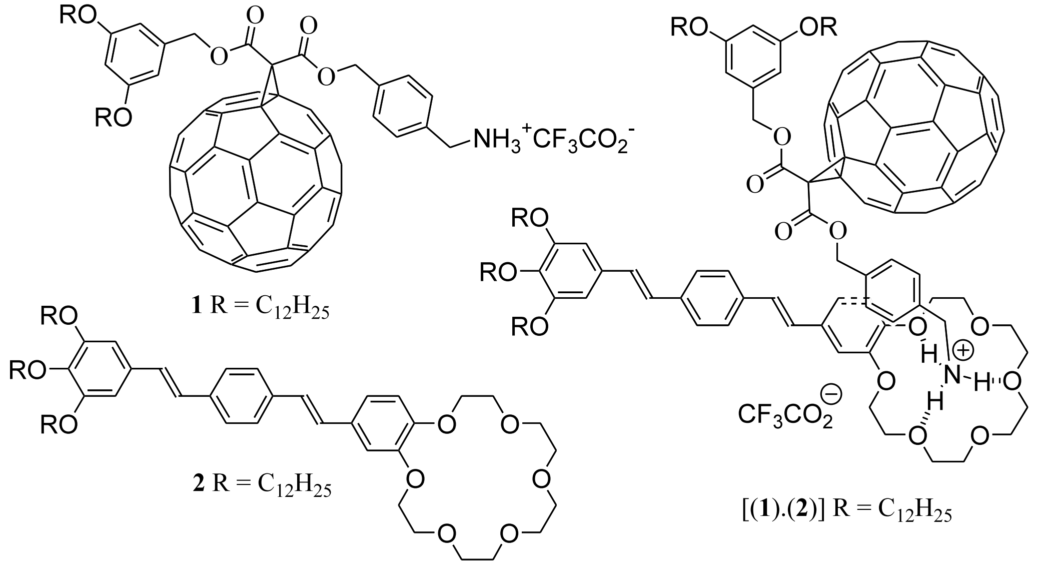

Figure 1. The supramolecular C_{60}–OPV assembly obtained from ammonium **1** and crown ether **2**.

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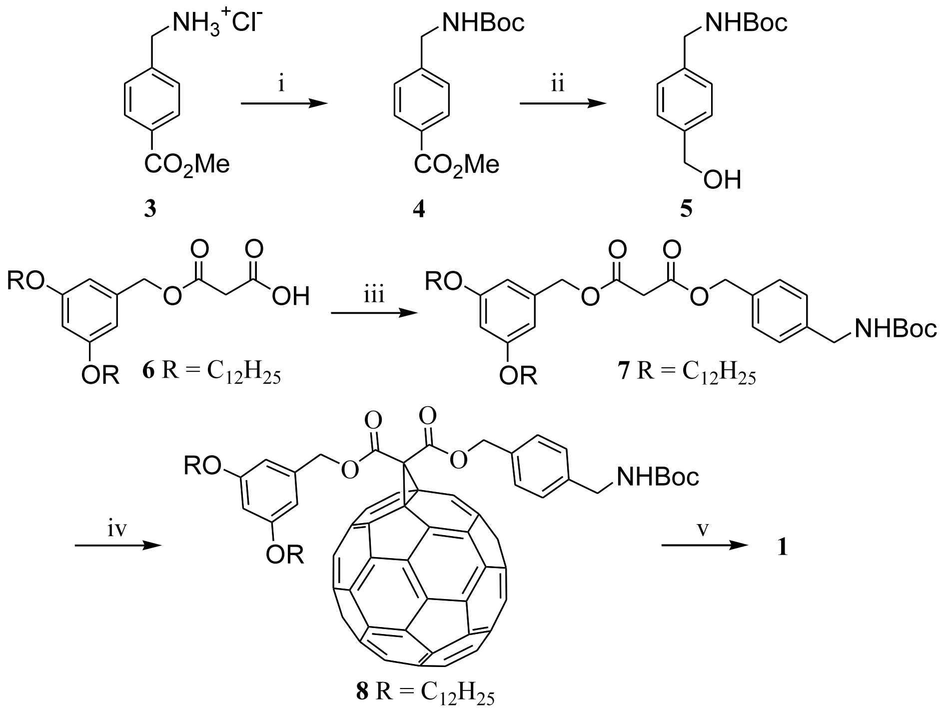

Scheme 1. *Reagents and conditions*: (i) Boc_2O, KOH, THF, H_2O, rt (91%); (ii) $LiAlH_4$, THF, 0°C (93%); (iii) **5**, DCC, DMAP, CH_2Cl_2, 0°C to rt (63%); (iv) C_{60}, I_2, DBU, toluene, rt (61%); (v) CF_3CO_2H, CH_2Cl_2, rt (99%).

this paper, we show that methanofullerene derivative **1** bearing an ammonium unit is able to form a supramolecular complex with the oligophenylenevinylene (OPV)–crown ether conjugate **2**[5] by using the well-known ammonium–crown ether interaction (Fig. 1).[6] Preliminary luminescence studies also reveal the occurrence of an intramolecular photoinduced process in this new supramolecular C_{60}–OPV assembly.

The strategy employed for the preparation of the functionalized methanofullerene derivative **1** is based upon Bingel type chemistry.[7] To this end, malonate **7** was prepared in three steps from methyl 4-(aminomethyl)-benzoate hydrochloride (**3**) (Scheme 1). The commercially available compound **3** was converted to its *t*-butylcarbonyl (Boc) derivative as previously described.[8] LAH reduction of the resulting protected derivative **4** afforded **5** in 93% yield. *N*,*N'*-Dicyclohexylcarbodiimide (DCC)-mediated esterification of benzylic alcohol **5** with carboxylic acid **6**[9] yielded malonate **7**. The reaction of C_{60} with compound **7**, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under Bingel conditions then gave methanofullerene **8** in 61% yield. Finally, removal of the Boc group with CF_3CO_2H afforded the targeted derivative **1** as its trifluoroacetate salt in a quantitative yield. The structure and purity of all new compounds were confirmed by ^1H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

The ability of the fullerene derivative **1** to form a supramolecular complex with the OPV–crown ether conjugate **2** was first evidenced by ^1H NMR studies in $CDCl_3$. The comparison between the ^1H NMR spectra of **1**, **2** and a 1:1 mixture of both compounds (Fig. 2) revealed complexation-induced changes in chemical shifts for some protons, in particular for those of the 4-(aminomethyl)benzyl moiety in **1** and of the benzo-crown ether unit in **2**. The latter observations are in good agreement with the proposed structure of the supramolecular complex obtained from **1** and **2**. The association constant (K_a) and the Gibbs free energy of complexation (ΔG^0) for the binding of **1** to **2** were deduced from the complexation-induced changes in

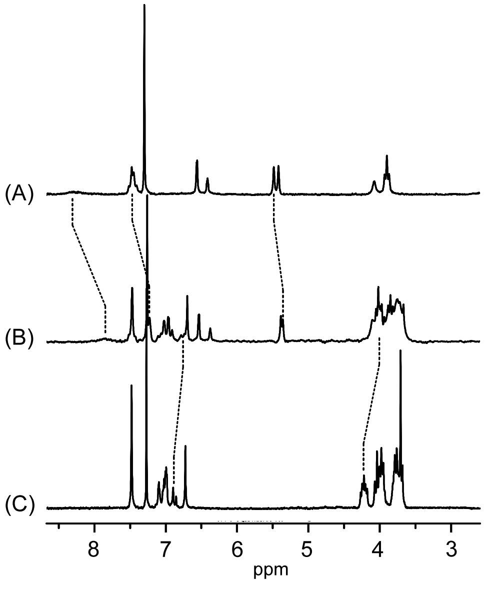

Figure 2. ^1H NMR spectra (200 MHz, $CDCl_3$) of **1** (A), **2** (C) and a 1:1 mixture of both compounds (B).

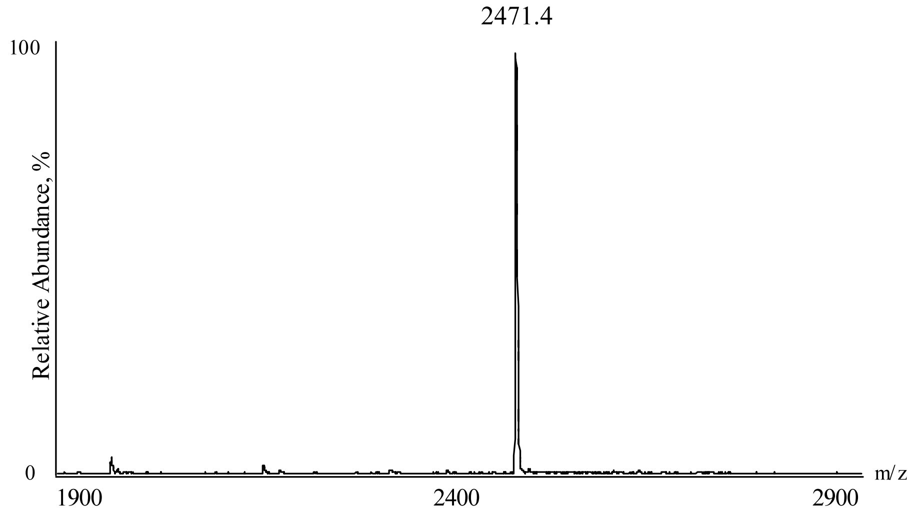

Figure 3. ES mass spectrum (Vc = 40 V) recorded from an equimolar mixture (10^{-4} M) of **1** and **2** in CH_2Cl_2.

chemical shifts of the 4-(aminomethyl)benzyl protons in ^{1}H NMR binding titrations ($CDCl_3$, 298 K).[10] The K_a value for the 1:1 complex was determined to be 3500± 200 M^{-1} corresponding to a ΔG^0 of −4.8 kcal/mol.

The formation of the 1:1 complex [(**1**)·(**2**)] was also evidenced in the gas phase by electrospray mass spectrometry (ES-MS).[3a] Unlike other mass spectrometric methods, ES-MS allows pre-existing ions in solution to be transferred to the gas phase without fragmentation. The soft ionization technique, mainly developed by Fenn and co-workers,[11] is now commonly applied to the study of large non-covalent assemblies[12] and appears as ideally suited to characterize the non-covalent complex formed from **1** and **2**. The positive ES mass spectrum (Fig. 3) recorded from a 1:1 mixture of **1** and **2** displayed only one singly charged ion peak at $m/z = 2471.4$ which can be assigned to the 1:1 complex after loss of the trifluoroacetate counteranion (calculated $m/z = 2471.3$).

The complexation between **1** and **2** was also investigated in CH_2Cl_2 by luminescence studies. A large decrease in intensity of the characteristic OPV emission was observed when the fullerene ammonium salt **1** was added to a CH_2Cl_2 solution of **2**.[13] This decrease can be attributed, at least in part, to the reabsorption of the OPV luminescence by the fullerene derivative **1**. However, experiments carried out in parallel with mixtures of **2** and **8** which are not able to form a supramolecular complex show that the decrease in luminescence intensity mainly originates from an intramolecular photoinduced process in the supramolecular C_{60}–OPV conjugate [(**1**)·(**2**)].[3a] Further evidence for an intramolecular quenching of the OPV excited state by the fullerene moiety in [(**1**)·(**2**)] was obtained from the experiment depicted in Figure 4.

Addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) (1.5 equiv.) to the 1:1 mixture of **1** and **2** in CH_2Cl_2 causes an increase of the OPV emission. Actually, the fluorescence intensity of the resulting solution was found to be similar to that of the reference solution containing **8** and **2**. In other words, the treatment with a base deprotonates the ammonium moiety of **1** and, thereby, disrupts the non-covalent bonding interactions that brought the components together. Addition of trifluoroacetic acid (2 equiv.) to the CH_2Cl_2 solution regenerates the ammonium center, thus allowing the formation of the supramolecular complex, and the luminescence intensity of final solution is the same as that of the starting 1:1 mixture of **1** and **2**. The observed decrease in luminescence intensity originates from either energy or electron transfer from the photoexcited OPV to the C_{60} acceptor in the supramolecular complex [(**1**)·(**2**)]. Steady state measurements are not sufficient to determine the nature of the quenching because the residual OPV emission overlaps the much weaker fullerene emission, thus prohibiting clean excitation spectroscopy. Detailed photophysical studies are currently under investigation and will be reported in due time.

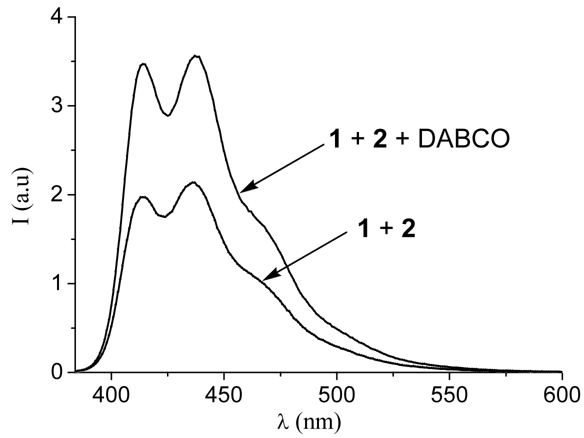

Figure 4. Emission spectra ($\lambda_{exc} = 372$ nm corresponding to the maximum of absorption of **2**) of an equimolar mixture of **1** and **2** in CH_2Cl_2 before and after addition of DABCO (1.5 equiv.).

Acknowledgements

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10. The ^{1}H NMR binding studies were performed at 298 K in $CDCl_3$. The concentration of **1** was kept constant (0.5 mM). Increasing amounts of **2** were added (0.2 to 2 mM; 12 data points) and the chemical shift (δ) of the protons of the 4-(aminomethyl)benzyl moiety in **1** were observed. The complexation-induced variation of the chemical shift ($\Delta\delta$) was plotted against the concentration of **2**. The complexation data (K_a, ΔG^0, $\Delta\delta_{sat}$) were obtained by iteration using a nonlinear regression analysis curve-fitting software developed in the laboratories of Professor François Diederich: Associate V.1.6, Blake Peterson, Ph.D. thesis, University of California at Los Angeles, 1994.
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13. The association constant for the binding of **1** to **2** determined by a fluorescence titration in CH_2Cl_2 was similar to the value deduced from the NMR binding studies. This titration was performed according to the procedure described by Armaroli and co-workers in Ref. 2a.