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The First Dumbbell-type C_{60} Dimer Connected by a Double Donor Spacer

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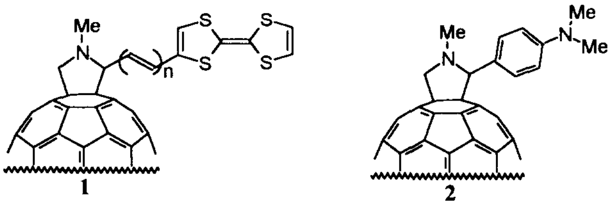
Abstract: *A dumbbell-type [60]fullerene dimer in which both C_{60} units are covalently attached to a double donor spacer has been prepared by a double cycloaddition of azomethine ylide to C_{60}. The CV data indicate that the dimer behaves electrochemically as two independent donor-acceptor units.*

The synthesis and characterization of dimers and oligomers containing two or more [60]fullerene units has received, comparatively to the [60]fullerene chemistry, much less attention in spite of the interesting properties they could exhibit.[1] Only a quite limited number of organofullerenes with more than one cage have been so far reported and most of the synthetic procedures involve an oxidation coupling reaction of terminal alkynes[2] or bifunctional cycloaddition reactions described for diazo compounds,[3] dienes[4] or cyanogen di-*N*-oxide as a double 1,3-dipole.[5] Oxo- and methylene-bridged [60]fullerene dimers containing fullerene-fullerene bonds have also been recently reported by thermal treatment of $C_{60}O$.[6]

[60]Fullerene behaves as a powerful electron acceptor[7] which shows interesting electronic and electrochemical properties. Thus, several donor-acceptor (D-A) systems in which the C_{60} core is covalently attached to the donor moiety have been described.[8] We have recently reported the first semiconducting intermolecular charge transfer complexes from C_{60}-TTF systems (**1**) (TTF: tetrathiafulvalene) by reaction with strong acceptor molecules.[9] Only in a few cases an intramolecular photoinduced charge separation has been observed in these D-A systems the lifetime of the charge separated state being in the subnanosecond range.[10] Compound **2**, comprising the donating aniline group linked to the C_{60} cage by a saturated heterocyclic bridge, has been recently reported to show an intramolecular photoinduced charge separation in polar solvents which causes quenching of the fluorescence.[11]

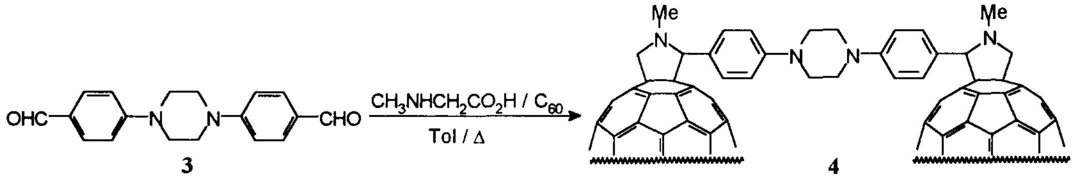


1 **2**

Chart 1

In this communication we report the preparation of a dumbbell-type [60]fullerene dimer (**4**) in which both C_{60} cages are connected through a pyrrolidine ring to the donor fragments. Formally, compound **4** could be considered as the dimer of fulleropyrrolidine **2** in which both monomeric units are attached by the two methyl radicals of the *N,N*-dimethylaniline moiety. The structure of the novel "buckydumbbell" (**4**) was supported on its spectroscopic and electrochemical characterization. Compound **4** represents the first example in which two C_{60} cages are covalently attached to an organic addend acting as electron-donor unit and, consequently, the electronic interaction between the electroactive moieties is of particular interest.

1,3-Dipolar cycloadditions of azomethine ylides to C_{60} is a suitable procedure for the functionalization of [60]fullerene[12] which, however, has not been previously used for the preparation of dimeric [60]fullerenes. Compound **4** was obtained by following this synthetic approach in a 34 % yield by reacting sarcosine, [60]fullerene and dialdehyde (**3**) in refluxing toluene for 24 h. (Scheme). Compound **4** was obtained as a black precipitate in the reaction medium which was collected by filtration. Dimer **4** showed an extremely low solubility in most of the common organic solvents, which prevented its purification by chromatography. Further purification was accomplished by washing exhaustively by centrifuging in toluene, methanol and ether.



3

4

Scheme

The precursor dialdehyde **3** was synthesised by reaction of *p*-fluorobenzaldehyde and piperazine by following the method previously reported.[13] Although the low solubility of **4** prevented the recording of the ^{13}C NMR spectrum, the cycloaddition of azomethine ylides has been previously established to occur at the [6,6]ring junction of the fullerene,[12] as it occurs for compound **2**.[11]

The UV-Vis spectrum show the presence of a band at around 410 nm, in addition to the typical weak absorption band at 430 nm of dihydrofullerenes, thus confirming the [6,6]-closed character of the dimer. The FTIR spectrum show the presence of both donor and acceptor fragments. Thus, a very strong C_{60} band was observed at 527 cm^{-1} and the C-H stretching bands at 2850 cm^{-1} and the aromatic vibrations at 1600 and 1500 cm^{-1}. In ^1H NMR spectrum the signals of the pyrrolidine protons are shown at δ 4.95 and 4.2 as doublets (J = 9.68 Hz; geminal hydrogens) and δ 4.85 (CH) in agreement with related derivatives. The N-Me groups appear as a singlet at δ 3.35 and the piperazine hydrogens at 3.56. Finally, the aromatic protons appear as two multiplets at δ 7.0 and 7.6. No mass spectral molecular ion was observed using FAB technique in both positive and negative ion modes. It has been previously reported that some dumbbell compounds resist all mass spectrometric attempts, including MALDI and electrospray techniques.[4a, 4c, 8]

The electrochemical properties of compound **4** have been studied by cyclic voltammetry in *o*-dichlorobenzene (ODCB) as solvent at room temperature and the data are collected in the Table along with those of C_{60} and dialdehyde **3** as reference compounds. We have also prepared the monomer **2** in order to determine its electrochemical data, which had not been previously reported, for comparison purposes.

Table: Redox properties of dumbell-type C_{60} dimer and reference molecules (in Volts).

Compound	E_1^{ox}	E_1^{red}	E_2^{red}	E_3^{red}	E_4^{red}
4	0.57	-0.67	-1.07	-1.54	-1.98
2	0.44	-0.71	-1.09	-1.67	-2.04
3	0.61	—	—	—	—
C_{60}	—	-0.65	-1.06	-1.52	-1.79

SCE *vs* Pt; $Bu_4N^+ClO_4^-$; GCE as working electrode; scan rate: 200 mV/s

The cyclic voltammogram of compound **4** (Figure) shows, in addition to the presence of four quasi reversible reduction waves, similarly to that found for the parent [60]fullerene, the presence of an oxidation wave corresponding to the oxidation of the *N,N*-dialkylaniline donor fragments. This assignement was confirmed by comparison with the CV of **3** which shows the oxidation wave slightly anodically shifted due, probably, to the presence of the two formyl groups and their electron-withdrawing character. The reduction potentials of **4** appear at more negative potentials than C_{60} as it is observed for 1,2-dihydrofullerenes.[9, 14] The presence of these redox waves clearly indicates that compound **4** behaves electrochemically as the monomer **2** with no interaction between both monomeric units. The *N,N*-dimethylaniline donor moiety shows a slightly better donor ability than the donor unit in **4** and, consequently, the reduction potentials values in compound **2** appear cathodically shifted, related to dimer **4**. To the best of our knowledge, only two papers describing dumbbell-shape molecules have reported their CV data[2b, 3] and no electronic interaction was observed between both C_{60} cages. In our case, the CV data have an additional analytical and structural character since both donor and acceptor moieties are clearly observed in the voltammogram of compound **4**, thus confirming its structure.

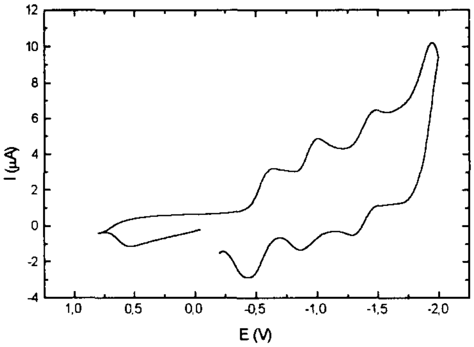


Figure: Voltammogram of dumbbell-type dimer **4**.

In summary, we have carried out the synthesis and electrochemical characterization of the first dumbbell-type C_{60} dimer connected by two electron-donor fragments. The CV data indicate that this molecule behaves as two independent monomers, similarly to that found for the previously reported molecule **2**. Work is in progress to determine by photophysical studies whether intramolecular energy transfer and electron transfer process take place in this novel dumbbell-type A-D-D-A molecule.

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