Pergamon

Tetrahedron Letters, Vol. 37, No. 33, pp. 5979-5982, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01235-X

Semiconducting Charge Transfer Complexes from [60]Fullerene-Tetrathiafulvalene (C_{60}-TTF) Systems

Nazario Martín*, Luis Sánchez and Carlos Seoane*

Departamento de Química Orgánica, Facultad. de Química, Universidad Complutense, E-28040 Madrid, Spain

Raquel Andreu, Javier Garín and Jesús Orduna

Departamento de Química Orgánica , ICMA, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain

Abstract: *The first CT-complexes of covalently bound [60]Fullerene-tetrathiafulvalene (TTF) systems with tetrafluorotetracyano-p-quinodimethane ($TCNQF_4$) show a semiconducting behaviour.*

Electron donor fragments such as porphyrine,[1] phthalocyanine,[2] ferrocene,[3] and tetrathiafulvalene[4] have been covalently attached to the C_{60} core by different synthetic procedures and very weak or negligible intramolecular CT-interactions from the donor moiety to the acceptor [60]fullerene was observed.

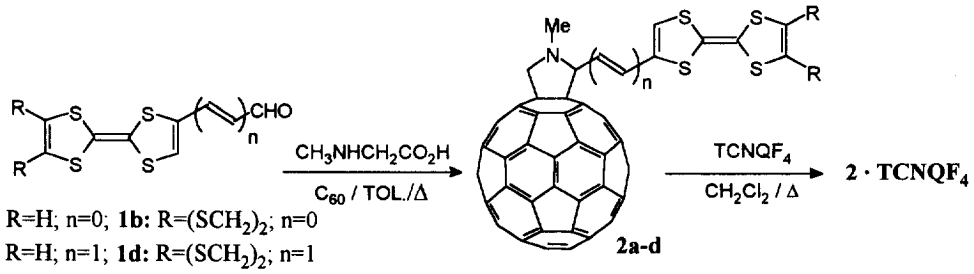
The first direct observation of a definite intramolecular CT interaction from a phenyl ring to C_{60} was recently shown as a very weak band around 470 nm (log ε 3.2) in the electronic spectra, which was shifted toward longer wavelength with increasing solvent polarizability.[5] A photoinduced intramolecular electron transfer process that causes quenching of the fluorescence has also been detected in the organofullerene comprising the donating aniline group attached to the fullerene fragment by a saturated heterocyclic bridge.[6]

Considering the moderate electron donor character of the above donor units, the introduction of stronger electron-donors in close proximity to the C_{60} surface may be expected to lead to self-doping bichromophoric materials useful in the design of novel molecular electronic devices.[7]

In this context, we report herein the preparation of a series of covalently linked [60]fullerene-tetrathiafulvallene (TTF) derivatives (**2**) and their UV-Vis and electrochemical characterization. Furthermore, we have synthesized the first CT-complexes from compounds **2** and strong electron-acceptor molecules. Although it is expected that the C_{60} core should not be engaged in the CT process, to the best of our knowledge the study of these novel complexes has not previously been carried out and will allow to evaluate the effect of the presence of the C_{60} moiety on the conducting properties of the radical-ions.

Among the suitable procedures for the functionalization of [60]fullerene, the 1,3-dipolar cycloadditions of azomethine ylides to C_{60} play a prominent role.[8] We have selected this synthetic approach for the preparation of the target molecules **2** which were obtained in a 32-39 % yield by treating sarcosine, [60]fullerene and the respective formyl-substituted TTFs (**1**) in refluxing toluene for 24-48 h. Products were isolated[9] by flash chromatography (neutral silica gel, cyclohexane and toluene:cyclohexane).

Functionalization of TTF is currently an active research field and the starting formyl-TTF derivatives were prepared by following the previously reported procedures[10] by lithiation of TTF and subsequent formylation (**1a**) and a multistep synthetic procedure for compounds **1b-d** involving a Wittig reaction.



1a: R=H; n=0; **1b:** R=$(SCH_2)_2$; n=0
1c: R=H; n=1; **1d:** R=$(SCH_2)_2$; n=1

Scheme

The structure of compounds **2a-d** was supported on their analytical and spectroscopic data (UV-Vis, FTIR, ^{1}H-NMR, ^{13}C-NMR and FAB mass spectra). In ^{1}H-NMR spectra the signals of the pyrrolidine protons appeared at δ 4.9 and 4.1 as doublets (J=9.5 Hz; geminal hydrogens) and δ 4.8 (CH) in agreement with related derivatives.

It has already been established that the 1,3-dipolar cycloadditions of azomethine ylides occurs at the 6,6-ring juction of the C_{60} framework.[3] The ^{13}C-NMR spectrum for compound **2a**[11] shows, in addition to the N-Me group at δ 40.2, the signals at δ 66.4, 69.5, 77.2 and 79.4 for the sp^3 carbons at the 6,6-ring junction and the remaining pyrrolidine carbons. The UV-Vis spectra shows the typical weak absorption band at 430 nm of dihydrofullerene, and no photoinduced intramoleular CT-band is observed.

The electrochemical properties of compounds **2a-d** have been studied by cyclic voltammetry at room temperature and the data are collected in the Table along with data for TTF and C_{60} as reference compounds.

Table: Redox properties of novel compounds **2a-d**

Compound	R	n	$E^{1/2}_{1\,ox}$	$E^{1/2}_{2\,ox}$	E_1^{red}	E_2^{red}	E_3^{red}	E_4^{red}
2a	H	0	0.41	0.76	-0.67	-1.04	-1.53	-2.05
2b	$(SCH_2)_2$	0	0.50	0.78	-0.71	-1.05	-1.56	-2.10
2c	H	1	0.43	0.76	-0.67	-1.08	-1.58	-2.19
2d	$(SCH_2)_2$	1	0.54	0.78	-0.71	-1.19	-1.61	-2.20
TTF	—	—	0.37	0.70	—	—	—	—
C_{60}	—	—	—	—	-0.60	-1.00	-1.52	-2.04

[a]All potentials in V vs SCE; Tol:MeCN (4:1); scan rate 200 mV/s; 0.1 mol·dm^{-3} $NBu_4^+ClO_4^-$; GCE as working electrode

The cyclic voltammograms of compounds **2a-d** show four one-electron quasireversible reduction waves corresponding to the reduction steps of the fullerene moiety (Figure). The first reduction potential in these compounds (**2a-d**) is shifted to negative values by 70-110 mV compared with [60]fullerene. This observation is in agreement with the saturation of a double bond in the C_{60} core which raises the LUMO energy of the resulting organofullerene.[12]

A comparison of the reduction potential values shows that the first reduction potentials are the same for **2a** and **2c** and for **2b** and **2d**, thus indicating the negligible effect of the double bond on the accepting ability of the C_{60} moiety (Table).

On the oxidation side, compounds **2a-d** show the presence of two reversible one-electron oxidation waves to the radical cation and dication respectively of the TTF moiety. Compared to the oxidation steps of the parent TTF (Table), the first oxidation potentials are shifted to more positive values by about 40-55 mV for compounds **2a** and **2c**.

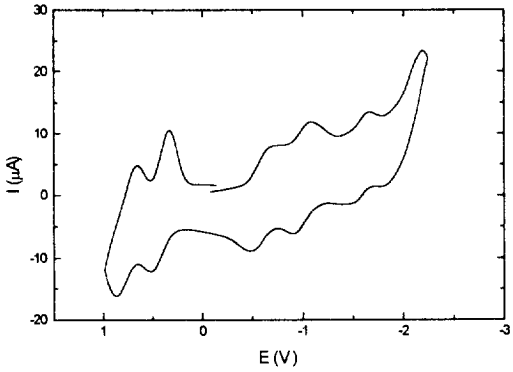


Figure . Cyclic Voltammogram of compound **2c** at 200 mV/s

Substitution on the TTF system by the ethylendithio fragments results in an additional shift to positive values for compounds **2b** and **2d** by about 120-160 mV relative to the first oxidation potential of the unsubstituted TTF (Table).

Compounds **2** containing the C_{60} core covalently linked to the strong donor TTF are very appealing systems for the preparation of charge transfer complexes by combination with strong acceptor molecules. To the best of our knowledge, these complexes have not been previously studied and, in this work, we report our preliminary results on the preparation of the first examples. Thus, compounds **2a** and **2c** did not form CT-complexes with strong acceptors such as tetracyano-*p*-quinodimethane (TCNQ, $E^{1/2}_{red}$=0.21 in CH_2Cl_2) and dicyano-*p*-quinodiimine (DCNQI, $E^{1/2}_{red}$=0.21 in CH_2Cl_2). However, when they were mixed with the stronger acceptor tetrafluorotetracyano-*p*-quinodimethane ($TCNQF_4$, $E^{1/2}_{red}$=0.62 in CH_2Cl_2), a rapid formation of the CT-complex occurs.[13] The black solid thus obtained shows the presence of characteristic charge transfer bands in the visible region of the electronic spectrum, showing a donor-acceptor stoichiometry of 1:1 as resulting from the elemental analyses. Conductivity measurements on a powdered sample for **2a:TCNQF$_4$** and **2c:TCNQF$_4$** as a two-probe compressed pellet at different temperatures showed the material to be semiconductors (σ_r=10^{-7} Scm^{-1}).

In summary, we have established that TTF and its substituted derivatives can be conveniently attached to the C_{60} framework to form C_{60} based D-σ-A systems which show well-defined electrochemical properties. This synthetic approach allows to modify the chain length linking both donor and acceptor moieties. These systems

are suitable precursors for the preparation of intermolecular CT-complexes, by reaction with strong acceptors, exhibiting semiconducting properties. The study of novel intra and intermolecular interactions will be useful for the development of C_{60} based molecular materials with potential applications in molecular electronics and is currently under investigation.

Acknowledgements: Financial support by the CICYT of Spain (Grants: PB 92-0237 and PB 94-0577) is gratefully acknowledged.

REFERENCES AND NOTES

1. Drovestkaya, T.; Reed, Ch.A.; Boyd, P. *Tetrahedron Lett.* **1995**, 36, 7971-7974.
2. Linssen, T.G.; Dürr, K.; Hanack, M.; Hirsch, A. *J. Chem. Soc. Chem. Commun.* **1995**, 103-104.
3. Maggini, M.; Karlsson, A.; Scorrano, G.; Sandonà, G.; Farnia, G.; Prato, M. *J. Chem. Soc. Chem. Commun.* **1994**, 589-590.
4. Maggini, M.; Scorrano, G.; Prato, M.; Sandona, G.; Farnia, G.; Meneghetti, M.; Pecile, C. p 1165 in Proccedings of the symposium on Recent Advances in the Chemistry ans Physics of Fullerenes and Related Materials.
5. Matsubara, Y.; Tada, H.; Nagase, S.; Yoshida, Z. *J. Org. Chem.* **1995**, 60, 5372.
6. Williams, R.M.; Zwier, J.M.; Verhoeven, J. W. *J. Am. Chem Soc.* **1995**, 117, 4093-4099.
7. Taylor, R.; Walton, D.R. *Nature* **1993**, 363, 685-693.
8. Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, 115, 9798-9799.
9. Selected spectroscopic data for compound **2c**: FT-IR (KBr,cm^{-1}): 2776, 1457, 668, 639, 526; ^{1}H-NMR (δ,$CDCl_3$:CS_2, 2:1): 6.83 (d, 1H, J=15.4), 6.37 (s, 1H), 6.28 (m, 2H), 6.01 (dd, 1H, J_1=15.4, J_2=8.8), 4.85 (d, 1H, J=9.5), 4.34 (d, 1H, J=8.8), 4.10 (d, 1H, J=9.5), 2.85 (s, 3H). UV-Vis (log ε) (CH_2Cl_2): 258 (4.9), 322 (4.6), 430 (3.9). FAB^+-MS: 1005 (20%)
10. Andreu, R.; Garín, J.; Orduna, J.; Savirón, M.; Uriel, S. *Tetrahedron Lett.* **1995**, 36, 4319-4322.
11. The spectroscopic data of compound **2a**, together with other different substituted fulleropyrrolidines, have been very recently reported: Prato, M.; Maggini, M.; Giacometti, C.; Scorrano, G.; Sandonà, G.; Farnia, G. *Tetrahedron* **1996**, 52, 5221-5234.
12. Suzuki, T.; Maroyama, Y.; Akasaba, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, 116, 1359-1363.
13. Selected spectroscopic data for complexes: **2a·TCNQF$_4$·0.5 CH_2Cl_2:** FT-IR (KBr, cm^{-1}): 2189, 2169, 575, 526; UV-Vis (CH_2Cl_2): 594, 692, 762. Elem.Anal.: Calc.for $C_{163}H_{20}N_{10}F_8S_8Cl_2$: % C, 75.38, % H, 0.78, % N, 5.39. Found: % C, 75.52, % H, 1.22, % N, 5.53. **2c·TCNQF$_4$·CH_2Cl_2:** FT-IR (KBr, cm^{-1}): 2190, 2169, 575, 526; UV-Vis (CH_2Cl_2): 596, 692, 760. Elem Anal.: Calc.for $C_{84}H_{11}N_5F_4S_4Cl_2$: % C, 73.90, % H, 0.81, % N, 5.13. Found: % C, 74.05, % H, 1.16, % N, 5.28.

(*Received in UK* 31 *May* 1996; *revised* 17 *June* 1996; *accepted* 21 *June* 1996)