ChemComm

Stabilisation of charge-separated states *via* gain of aromaticity and planarity of the donor moiety in C_{60}-based dyads

Nazario Martín,*[a] Luis Sánchez[a] and Dirk M. Guldi*[b]

[a] *Departamento de Química Orgánica I, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain*
[b] *Radiation Laboratory, University of Notre Dame, Indiana, USA. E-mail: nazmar@eucmax.sim.ucm.es*

Received (in Liverpool, UK) 2nd November 1999, Accepted 26th November 1999

The gain of aromaticity and planarity, associated with the oxidation of a π-extended TTF electron donor, is the key feature for obtaining strong stabilisation of photolytically generated radical pairs in novel C_{60}-based dyads.

The remarkable electron-acceptor properties of fullerenes[1] evoked the implementation of fullerenes as an electron acceptor unit in the design of novel artificial light harvesting superstructures.[2] One viable approach to photosynthesis modelling has been the covalent linkage of various redox active chromophores. In this context, light-induced intramolecular charge-separation (CS) has been reported for several C_{60}-based donor–acceptor systems endowed with various electron donors. CS evolves, in most of these systems, from the singlet excited state of the fullerene unit through a series of small distance intramolecular electron transfer events yielding a charge-separated state.[3,4]

The ultimate goal is to design a system that converts sunlight into a usable form of energy with a near unit quantum efficiency. The key to accomplish this is to optimise the stability of the charge-separated state. This requirement led researchers to pursue two important concepts: (i) the increase of the donor–acceptor separation, and (ii) the use of multicomponent systems (donor–acceptor triads, tetrads, *etc.*) either in conjunction or separately.[5]

We reported recently a strategy probing organic donor molecules [*e.g.* tetrathiafulvalenes (TTFs)], linked to the fullerene core, that gain rather than lose aromaticity on CS. In particular, the one-electron oxidised form of TTF forms the 1,3-dithiolium cation, which, in contrast to the ground state, displays an extended aromatic character.[6] In fact, the lifetime of the charge-separated state was increased by a factor of *ca.* 4 relative to comparable systems that do not contain TTF.[6]

Here we present the synthesis of novel fulleroids and methanofullerenes endowed with highly conjugated TTFs having a *p*-quinodimethane structure. Cyclic voltammetry is combined with optical absorption and emission spectroscopy to study the electronic properties and excited-state interactions in dyads **3a**,**b** and **4a**,**b**.

The motivation for the current work stems from the possibility of obtaining a higher degree of stabilisation of the oxidised donor *via* adding aromatic arenes to the heteroaromatic rings of TTF. Addition of the latter is expected to enhance the aromatic stabilisation energy. In the oxidised form, the π-conjugation is extended over the entire anthracene backbone and as a net result, the dicationic species is completely aromatic.[7]

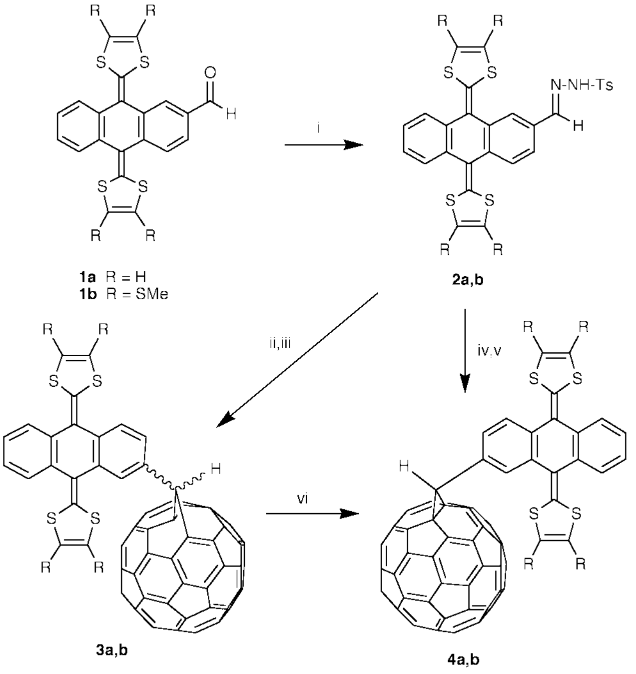
The syntheses of dyads **3a**,**b** and **4a**,**b** were carried out by a cycloaddition reaction of diazo compounds with C_{60}.[8] In the present case, diazo compounds are generated *in situ* from the extended TTF containing *p*-tosylhydrazones (**2a**,**b**) by treatment with base. Compounds **2a**,**b** are in turn prepared in good yields from the respective aldehydes (**1a**,**b**)[9] and toluene-*p*-sulfonohydrazide (Scheme 1).

The reaction of *p*-tosylhydrazones (**2a**,**b**) with C_{60} under basic conditions in toluene at 70 °C afforded the kinetic product **3a**,**b** in 27–31% yield as a mixture of the two possible [5,6] isomers.[10] [6,6]Methanofullerenes (**4a**,**b**) were prepared either under basic conditions from *p*-tosylhydrazones (**2a**,**b**) with C_{60} in refluxing toluene or from the respective [5,6]fulleroid (**3a**,**b**) by refluxing for 30 h in toluene in quantitative yield.

The ^{1}H NMR spectra of fulleroids **3a**,**b** confirm the presence of both [5,6] isomers, showing the combination of two singlets at δ 6.9 ppm (*i.e.* the isomer with the methylene hydrogen atom above a five-membered ring) and 4.1 (*i.e.* the isomer with the methylene hydrogen atom above a six-membered ring).[11] In contrast, [6,6]methanofullerenes (**4a**,**b**) give rise to a typical ^{1}H NMR singlet at $\delta \sim 5.2$ corresponding to the cyclopropane proton.†

All compounds studied show the presence of four one-electron reduction steps of the fullerene core, similar to those found for the parent C_{60}, though the underlying reduction potentials are shifted to more negative values. This shift evolves from the partial loss of conjugation of the C_{60} sphere, which raises the LUMO energy of the resulting modified fullerenes.[12] Although the [5,6]fulleroids do not undergo the loss of conjugation and retain the 60π electron configuration of C_{60}, essentially no difference in the reduction potentials were found between the two isomers (*i.e.* [5-6] *vs.* [6-6], see Table 1).[13] In the anodic region, a single two-electron oxidation wave, to form the dication of the TTF moiety, was noticed for all dyads (**3a**,**b** and **4a**,**b**).[7]

Pico- and nano-second-resolved transient absorption measurements with C_{60}–(π-extended)TTF donor–acceptor dyads (**3a**,**b** and **4a**,**b**) in toluene, CH_2Cl_2 and PhCN reveal the instantaneous formation of the fullerene singlet excited state.



Scheme 1 *Reagents and conditions*: i, $TsNHNH_2$, $CHCl_3$; ii, MeONa, Py; iii, C_{60}, PhMe, 70 °C; iv, MeONa, Py; v, C_{60}, PhMe, reflux; vi, PhMe, reflux.

Table 1 Data for **3a**,**b** and **4a**,**b**

		$\Theta/10^{-4}$	τ/ns				
Compound	Solvent	Fluorescence	Fluorescence	Singlet	Charge separation	E_{red}/V^a	E_{ox}/V^a
3a	PhMe	0.42	0.191	0.124	not measured		
3a	CH_2Cl_2	0.18	0.135	0.104	150	−0.68, −1.12, −1.62, −2.00	0.48
3a	PhCN	0.06	< 0.1	0.051	202		
3b	PhMe	1.86	0.410	0.329	not measured		
3b	CH_2Cl_2	1.04	0.250	0.176	107	−0.65, −1.07, −1.59, −1.95	0.59
3b	PhCN	0.41	< 0.1	0.104	211		
4a	PhMe	0.48	0.230	0.176	not measured		
4a	CH_2Cl_2	0.18	0.190	0.113	110	−0.67, −0.99, −1.59, −1.95	0.45
4a	PhCN	0.06	< 0.1	0.099	220		
4b	PhMe	2.1	0.379	0.400	not measured		
4b	CH_2Cl_2	1.34	0.343	0.316	95	−0.64, −0.98, −1.61, −1.95	0.55
4b	PhCN	0.54	< 0.1	0.140	180		
C_{60}						−0.60, −1.07, −1.64, −1.93	
5[b]							0.45

[a] In V *vs*. SCE; GCE; $Bu_4N^+ClO_4^-$ (0.1 M); PhMe–MeCN (4 : 1); 200 mV s^{-1}; **5**: 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene; in CH_2Cl_2.

Due to the presence of the electron donor [*i.e.* (π-extended)TTF] the singlet excited state absorption (λ_{max} ~ 880 nm) transforms rapidly into a broadly absorbing product. It should be noted that the decay kinetics of the singlet excited state absorption correlates with the grow-in kinetics of the new species.

Spectroscopic evidence suggests that this newly formed transient can be ascribed to the charge-separated radical pair, namely, $C_{60}^{\bullet -}$–(π-extended)$TTF^{\bullet +}$. In particular, maxima at 660 and 680 nm are in excellent agreement with the pulse radiolytically generated (π-extended)TTF π-radical cations at 660 (R = H) and 675 nm (R = SMe), respectively.[14] On the other hand, the two isomeric fullerenes give rise to different π-radical anion absorptions at 1040 ([6-6]-closed)[15] and 1070 nm ([6-5]-open).[16]

Generally, the intramolecular ET rates (see Table 1) depend on (i) the donor strength of the π-extended tetrathiafulvalene derivative (*e.g.* R = H *vs.* R = SMe), (ii) the excited state energy of the fullerene derivative (*e.g.* [6-6]-closed *vs.* [6-5]-open isomer) and (iii) the solvent polarity (*e.g.* toluene *vs.* PhCN).

Independent confirmation for the rapid and, more importantly, solvent-dependent deactivation of the fullerene singlet excited state in dyads **3a**,**b** and **4a**,**b** evolves from complementary fluorescence measurements. The fluorescence quantum yields (Θ) and also the fluorescence lifetimes (τ) showed, beside a marked solvent dependence, a correlation with the donor strength of the TTF moiety. Specifically, Θ and τ values in photoexcited **3a** and **4a** are lower relative to **3b** and **4b**, respectively.

The lifetimes of the charge-separated states in all these C_{60}–(π-extended)TTF dyads (**3a**,**b** and **4a**,**b**) are remarkable. For example, they are in the range of several hundred nanoseconds in deoxygenated PhCN and slightly lower in the less polar CH_2Cl_2. In contrast, the parent TTF dyads (*e.g.* a donor moiety that undergoes simply a gain of aromaticity upon oxidation) or zinc tetraphenylpoprhyrin dyads (*e.g.* an electron donor which lacks both the gain in planarity and in aromaticity upon oxidation) yielded radical pairs with lifetimes of about 2[6] and 0.5 ns,[4] respectively. Therefore, we rationalise the increased stability of the $C_{60}^{\bullet -}$-(π-extended)$TTF^{\bullet +}$ pair with the stabilisation of the donor. The gain of aromaticity and planarity, associated with this oxidation, yields a state of lower energy. Consequently, reduction of the oxidised (π-extended)TTF donor, in a sense of charge recombination, requires a higher activation energy to proceed than the corresponding processes in C_{60}–TTF and C_{60}–ZnTPP dyads.

We are indebted to DGICYT (Project PB98-0818) for financial support. Part of this work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy (contribution No. NDRL-4188 from the Notre Dame Radiation Laboratory).

Notes and references

† *Selected data* for **4b**: 34% yield (100% from **3b**); ν_{max}(KBr)/cm^{-1} 1545, 1450, 1276, 800, 754, 644, 526 cm; δ_H($CDCl_3$–CS_2, 2 : 1, 300 MHz) 8.08 (1H, s), 7.87 (1H, m), 7.69 (1H, m), 7.53 (2H, m), 7.31 (2H, m), 5.41 (1H, s), 2.43 (12H, m); δ_C($CDCl_3$–CS_2, 2:1, 75 MHz) 151.6, 149.4, 145.5, 145.0, 144.9, 144.5, 144.4, 144.2, 143.9, 143.5, 142.8, 140.7, 136.4, 136.3, 135.1, 134.5, 134.3, 134.2, 134.1, 130.8, 130.5, 128.9, 128.6, 127.8, 126.4, 126.3, 125.5, 125.4, 125.3, 125.2, 122.9, 109.8, 107.5, 77.2, 75.1, 43.1, 29.8, 29.7, 29.6, 29.4; λ_{max}(CH_2Cl_2)/nm (log ε) 264 (4.49), 326 (4.18), 364 (4.18), 420 (4.00), 434 (4.03); *m/z* (FAB$^+$) 1296 (M^+, 21%).

1 L. Echegoyen and L. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593.
2 H. Kurreck and M. Hüber, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 849.
3 N. Martín, L. Sánchez, B. Illescas and I. Pérez, *Chem. Rev.*, 1998, **98**, 2527.
4 H. Imahori and Y. Sakata, *Adv. Mater.*, 1997, **9**, 537; H. Imahori and Y. Sakata, *Eur. J. Org. Chem.*, 1999, 2445.
5 K. A. Jolliffe, S. J. Langford, M. G. Ranasinghe, M. J. Shephard and M. N. Paddon-Row, *J. Org. Chem.*, 1999, **64**, 1238.
6 N. Martín, L. Sánchez, M. A. Herranz and D. M. Guldi, submitted for publication.
7 N. Martín, L. Sánchez, C. Seoane, E. Ortí, P. M. Viruela and R. Viruela, *J. Org. Chem.*, 1998, **63**, 1268; M. R. Bryce, A. J. Moore, M. Hasan, G. J. Ashwell, A. T. Fraser, W. Clegg, M. B. Hursthouse and A. I. Karaulov, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1450.
8 T. Suzuki, Q. Li, K. C. Khemani, F. Wudl and Ö. Almarsson, *Science*, 1991, **254**, 1186.
9 N. Martín, I. Pérez, L. Sánchez and C. Seoane, *J. Org. Chem.*, 1997, **62**, 5690.
10 For the first preparation of fulleroids from *p*-tosylhydrazones, see: J. C. Hummelen, B.W. Knight, F. LePeq and F. Wudl, *J. Org. Chem.*, 1995, **60**, 532.
11 M. Prato, V. Luccini, M. Maggini, E. Stimpfl, G. Scorrano, G. Eirmann, T. Suzuki and F. Wudl, *J. Am. Chem. Soc.*, 1993, **115**, 8479.
12 M. Maggini, A. Karlsson, G. Scorrano, G. Sandona, G. Farnia and M. Prato, *J. Chem. Soc., Chem. Commun.*, 1994, 589.
13 M. Eiermann, F. Wudl, M. Prato and M. Maggini, *J. Am. Chem. Soc.*, 1994, **116**, 8364.
14 D. M. Guldi, N. Martín and L. Sánchez, unpublished results.
15 D. M. Guldi, H. Hungerbühler and K.-D. Asmus, *J. Phys. Chem.*, 1995, **99**, 9380.
16 Since this is the first report on the π-radical anion absorption band of a [6-5]-open fulleroid, we conducted complementary pulse radiolytic experiments to reduce the fullerene under experimental conditions described in ref. 15. The recorded spectrum with λ_{max} at 1070 nm is identical to the photolytically generated spectrum and, thus, serves as additional confirmation for the spectral assignment.

Communication a908770b