COMMUNICATION

ChemComm
www.rsc.org/chemcomm

A light-harvesting fluorinated fullerene donor-acceptor ensemble; long-lived charge separation†

Glenn A. Burley,[a] Anthony G. Avent,[a] Olga V. Boltalina,[b] Ilya V. Gol'dt,[b] Dirk M. Guldi,[c] Massimo Marcaccio,[d] Francesco Paolucci,[d] Demis Paolucci[d] and Roger Taylor[a]

[a] *School of Chemistry, Physics and Environmental Sciences, University of Sussex, Brighton, UK BN1 9QJ. E-mail: G.Burley@sussex.ac.uk; R.Taylor@sussex.ac.uk*
[b] *Chemistry Department, Moscow State University, Moscow 119899, Russia. E-mail: ovb@thermo.chem.msu.ru*
[c] *Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA. E-mail: guldi.1@nd.edu*
[d] *Dipartimento di Chimica, Università di Bologna, 40126 Bologna, Italy. E-mail: paolucci@ciam.unibo.it*

Received (in Cambridge, UK) 3rd October 2002, Accepted 18th November 2002
First published as an Advance Article on the web 4th December 2002

In a first example of a trannulene-based donor–acceptor dyad visible light photoexcitation generates a long-lived (870 ns) charge-separated state.

One of the most intensively investigated areas of fullerene chemistry concerns the photophysical properties of fullerene derivatives covalently tethered to one or more photoactive chromophores.[1] The combination of the ability of [60]fullerene to accept up to six electrons[2] with only small reorganisation energy upon reduction,[1a] renders it an attractive candidate for energy conversion and energy storage. A significant problem with the use of fullerenes as electron-acceptor units is the reduced electron affinity resulting from most derivatisations. However, fluorination of [60]fullerene *enhances* its electron affinity (*e.g.* values for $C_{60}F_{18}$[3] and $C_{60}F_{36}$[4] are *ca.* 3.1 and 3.48 eV compared with 2.67 eV for C_{60}[5]) thus overcoming the deficiencies of conventional derivatisation.

$C_{60}F_{18}$ is a unique member of the fluorofullerene family,[6] possessing a flattened hemisphere comprising an aromatic face surrounded by a fluorinated crown; and a curved "normal" hemisphere akin to its all-carbon parent.[7] Its high electron deficiency and strong visible light absorption (*e.g.* ε_{608} = 13,265 M^{-1} cm^{-1}; ε_{667} = 20,580 M^{-1} cm^{-1} for **1**) renders $C_{60}F_{18}$ a potential synthon for the construction of novel donor–acceptor arrays.

Recently, the first all-*trans* 18π annulenic fluorofullerene (named trannulene) *via* Bingel addition chemistry to $C_{60}F_{18}$ was reported.[8] This simple one-step reaction has the potential for the attachment of a plethora of functionalities in three precise locations on the trannulene surface. As an initial investigation of the utility of these trannulenes for light-harvesting applications, we describe here the formation and photophysical properties of a novel multi-component donor–acceptor array **1** (Fig. 1).

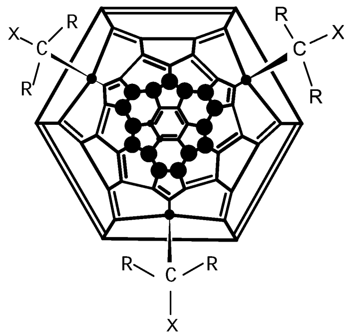


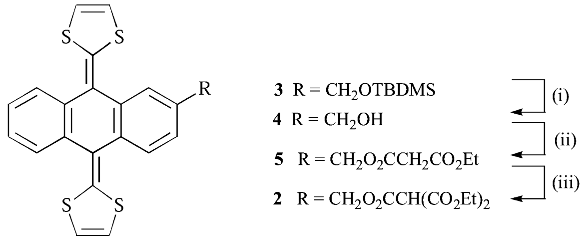
Fig. 1 Structure of **1**; R = CO_2Et, X = CO_2CH_2AnthTTF, ● = F.

Tetrathiafulvalene (TTF) moieties have been shown to be effective electron-transfer partners with [60]fullerene owing to their increase in aromaticity upon oxidation to form 1,3-dithiolium cations.[9] However, toluene solutions of TTF react with $C_{60}F_{18}$ upon concentration of solvent *in vacuo*.[10] The extended analogue of TTF (**2**) was used for this study to circumvent the reaction of the TTF nucleus with the fluorofullerene.

Acid deprotection of **3** (TBDMS = *tert*-butyldimethylsilyl) followed by malonylation of the alcohol **4** gave **5** as a yellow solid (Scheme 1). Due to the low acidity of the malonate protons of **5**, it was converted to the corresponding methanetricarboxylate **2**. Treatment of a toluene solution of $C_{60}F_{18}$ [from fluorination of [60]fullerene with MnF_3–K_2NiF_6 (1:5.5:2.25 weight ratio) at 480 °C, 5.5%] and **2** with DBU afforded the emerald-green trannulene **1** (Scheme 2). The ethyl ester **6** was prepared as a reference.

Electrochemical studies of **1** display a CV curve (Fig. 2) in which the redox processes of the models **2** and **6** are superimposed. This superimposition suggests no interaction between the electron donating and accepting moieties in the ground state. The redox couples at 0.62 and 0.15 V reveal slow heterogeneous electron-transfer kinetics. This corresponds to a three-electron oxidation attributed to the AnthTTF moiety, with approximate $E_{1/2}$ = 0.53 V, and accords with previously reported studies on similar TTF compounds,[11] confirmed by comparison with the CV of **2**.

The reversible one-electron reduction peak ($E_{1/2}$ = −0.005 V) in Fig. 2 is due to the reduction of the trannulene moiety, and is therefore also observed for **6** (Fig. 2). Note that these fullerene derivatives are much more easily reduced than C_{60}. With respect to ferrocene, **6** is reduced at −0.54 V, while, under the



Scheme 1 *Reagents and conditions*: (i) H^+, THF, 94%; (ii) EtO_2CCH_2COCl, pyridine, DCM 0 °C, 71%; (iii) 1. NaH, 2. EtO_2CCl, DMF, 0 °C, 42%.

$$\mathbf{2}\text{ or }C(CO_2Et)_3 \xrightarrow{\text{(i)}} C_{60}F_{15}[C(CO_2Et)_2CO_2R]_3$$

2.0 equiv.

1 R = CH_2AnthTTF 26 %
6 R = Et 29 %

Scheme 2 *Reagents and conditions*: (i) $C_{60}F_{18}$ (1.0 equiv.), DBU (1.9 equiv.), toluene.

---

† Electronic supplementary information (ESI) available: fluorescence spectra of **1** and **6** and UV-vis absorption spectra of **1**, **2** and **6**. See http://www.rsc.org/suppdata/cc/b2/b209724a/

DOI: 10.1039/b209724a

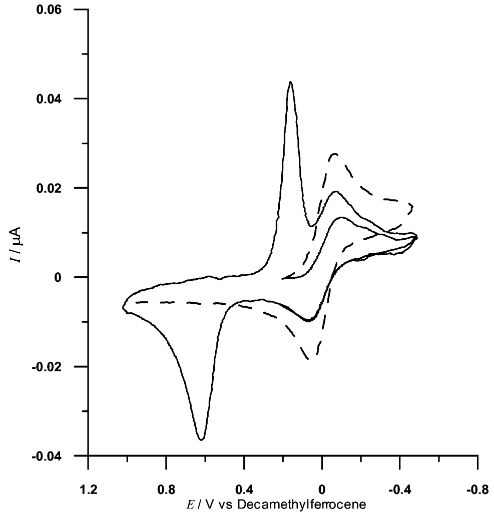


Fig. 2 CV curves of 0.5 mM **1** (full line) and 0.5 mM **6** (dashed line) in 0.05 M $NBu_4^+PF_6^-$, tetrachloroethane solutions. Scan rate: 0.5 V s^{-1}. T = 298 K. Working electrode: Pt. Potential measured with respect to a silver quasi-reference electrode and decamethylferrocene (internal standard).

same conditions, the first reduction of C_{60} is at −1.06 V, *i.e. ca.* 0.5 V more negative. Thus dyad **1** can be both easily oxidised and reduced, the approximate energy of the charge-separated state, AnthTTF$^{\cdot+}$-$C_{60}F_{15}^{\cdot-}$, being 0.54 eV.

Steady-state fluorescence experiments with **6** gave low quantum yields (Φ = 1.1 × 10^{-4}). Matching the absorption of donor–acceptor system **1** at the 665 nm maximum (Fig. S2, see ESI†), where AnthTTF lacks any appreciable absorption, allowed us to probe the impact of the electron donor on the photoexcited fullerene. In fact, in dichloromethane the fluorescence quantum yield of **1** is reduced to 0.55 × 10^{-4} – Fig. S1, see ESI.† Despite their overall low quantum yields, fluorescence lifetimes were successfully determined for **6** and **1**. In particular, a lifetime of 1.61 ns was derived for **6** from fitting the radiative decay around the 695 nm maximum to a mono-exponential fitting procedure. On the other hand, **1** gives rise to a lifetime of 0.68 ns, which corresponds to a moderate electron-transfer quenching efficiency of 43%, due to the semi-flexible nature of the linker.

From the difference between the 665 nm absorption and the 696 nm emission, we estimate a singlet excited state energy of 1.82 eV. This is sufficiently energetic to power in **1** a thermodynamically driven electron transfer to yield AnthTTF$^{\cdot+}$-$C_{60}F_{15}^{\cdot-}$ (*vide infra*).

Transient absorption measurements shed light onto the electron transfer mechanism. Fig. 3 compares the differential absorption changes recorded with a 50 ns delay upon photo-exciting solutions of **6** with those of **1** (2.0 × 10^{-5} M). In the case of **6**, the features correspond to the long-lived (τ = 15 μs) and oxygen-sensitive (k_q = 1.2 × 10^9 M^{-1} s^{-1}) triplet excited state. The observed minima (~400 and 665 nm) and shoulders (450 and 615 nm) match quite well the ground state absorption. Consequently, the bleaching relates to the depletion of the ground state. Also, new and particularly broad triplet–triplet transitions are noted in the near-IR region.

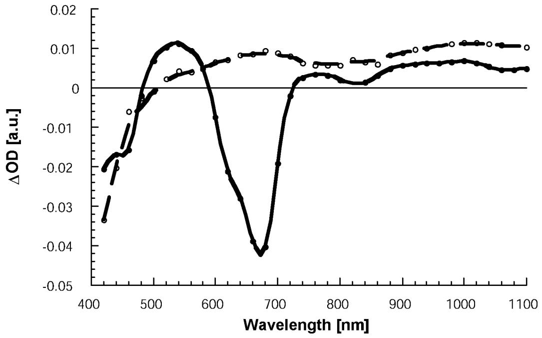


Fig. 3 Transient absorption changes recorded 50 ns upon 337 nm laser excitation of **6** (full line) and **1** (dashed line) in oxygen-free dichloromethane (2.0 × 10^{-5} M).

Quite different is the spectrum seen for **1**, which bears no similarity to the triplet excited state of reference **6**. Around 680 nm, instead of the strong ground-state bleaching, a transient maximum was recorded, which resembles the characteristic fingerprint of the one-electron oxidised AnthTTF$^{\cdot+}$. The near-IR transition was ascribed, by analogy to C_{60} and several of its derivatives, to the one-electron reduced fullerene species, $C_{60}F_{15}^{\cdot-}$. This confirms that the product of the intramolecular singlet excited state deactivation is AnthTTF$^{\cdot+}$-$C_{60}F_{15}^{\cdot-}$.

The charge-separated state is metastable and decays quantitatively to the singlet ground state. A mono-exponential rate law fits best the decay of both fingerprint absorptions, that is, $C_{60}F_{15}^{\cdot-}$ and AnthTTF$^{\cdot+}$. From the corresponding fits we derived a radical pair lifetime of 870 ns.

In conclusion, a novel donor–acceptor ensemble was devised incorporating an all-*trans* 18π annulenic fluorofullerene (trannulene), and extended TTF. Relative to C_{60}, one of the fundamental advantages of trannulenes lies in their improved chromophoric features. Strong visible light absorption, with a maximum at 665 nm (20,580 M^{-1} cm^{-1}), renders them good light-harvesting building blocks. Once photoexcited with visible light, an energetically low lying (0.54 eV) and long-lived (870 ns) charge-separated state is generated *via* a rapid intramolecular electron transfer process.

EPSRC (UK), the University of Bologna, MIUR, C.N.R., Volkswagen Stiftung, and Basic Energy Sciences Office of the US Department of Energy (NDRL-4423) supported this work. We thank Prof. Nazario Martin for helpful discussion.

Notes and references

1 (*a*) D. M. Guldi, *Chem. Soc. Rev.*, 2002, **31**, 22; (*b*) D. M. Guldi and N. Martin, *J. Mater. Chem.*, 2002, **12**, 1978; (*c*) D. M. Guldi and M. Prato, *Acc. Chem. Res.*, 2000, **33**, 695.
2 L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593.
3 K. Ohkubo, R. Taylor, O. V. Boltalina, S. Ogo and S. Fukuzumi, *Chem. Commun.*, 2002, 1952.
4 N. Liu, Y. Morio, F. Okino, H. Touhara, O. V. Boltalina and V. K. Pavlovich, *Synth. Met.*, 1997, **86**, 2289.
5 C. Brink, L. H. Andersen, P. Hvelplund, D. Mathur and J. D. Volstad, *Chem. Phys. Lett.*, 1995, **233**, 52.
6 R. Taylor, *Chem. Eur. J.*, 2001, **7**, 4074.
7 I. S. Neretin, K. A. Lyssenko, M. Y. Antipin, Y. L. Slovokhotov, O. V. Boltalina, P. A. Troshin, A. Y. Lukonin, L. N. Sidorov and R. Taylor, *Angew. Chem., Int. Ed.*, 2000, **39**, 3273.
8 (*a*) X. W. Wei, A. D. Darwish, O. V. Boltalina, P. B. Hitchcock, J. M. Street and R. Taylor, *Angew. Chem., Int. Ed.*, 2001, **40**, 2989; (*b*) X. W. Wei, A. G. Avent, O. V. Boltalina, A. D. Darwish, P. W. Fowler, J. P. B. Sandall, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 2002, 41; (*c*) A. D. Darwish, I. V. Kuvytchko, X. W. Wei, O. V. Boltalina, I. V. Gol′dt, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1118.
9 J. L. Segura and N. Martin, *Angew. Chem., Int. Ed.*, 2001, **40**, 1372.
10 A. D. Darwish, A. G. Avent, O. V. Boltalina, I. Gol'dt, I. Kuvytchko, T. da Ros and R. Taylor, unpublished work.
11 (*a*) S. G. Liu, I. Perez, N. Martin and L. Echegoyen, *J. Org. Chem.*, 2000, **65**, 9092; (*b*) M. A. Herranz, S. Gonzalez, I. Perez and N. Martin, *Tetrahedron*, 2001, **57**, 725; (*c*) G. Kodis, P. A. Liddell, L. de la Garza, A. L. Moore, T. A. Moore and D. Gust, *J. Mater. Chem.*, 2002, **12**, 2100; (*d*) A. J. Moore and M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, 1991, 157.