# Tuning electron transfer through *p*-phenyleneethynylene molecular wires†

**Carmen Atienza,[ab] Nazario Martín,*[a] Mateusz Wielopolski,[b] Naomi Haworth,[c] Timothy Clark[c] and Dirk M. Guldi[b]**

***Received (in Cambridge, UK) 2nd March 2006, Accepted 30th May 2006***
***First published as an Advance Article on the web 23rd June 2006***
**DOI: 10.1039/b603149h**

**Weak wire-like behavior—with a damping factor (*β*) of 0.2 ± 0.05 Å$^{-1}$—has been found in a series of C$_{60}$–wire–*ex*TTF systems (*i.e.*, *p*-phenyleneethynylene): these results contrast with previous observations involving *p*-phenylenevinylene systems.**

Testing electronic conduction through molecular wires constitutes a major challenge in physics, chemistry and engineering. Despite this general interest, only a handful of molecules have been thoroughly studied and their electron transfer dynamics and transport properties evaluated.[1]

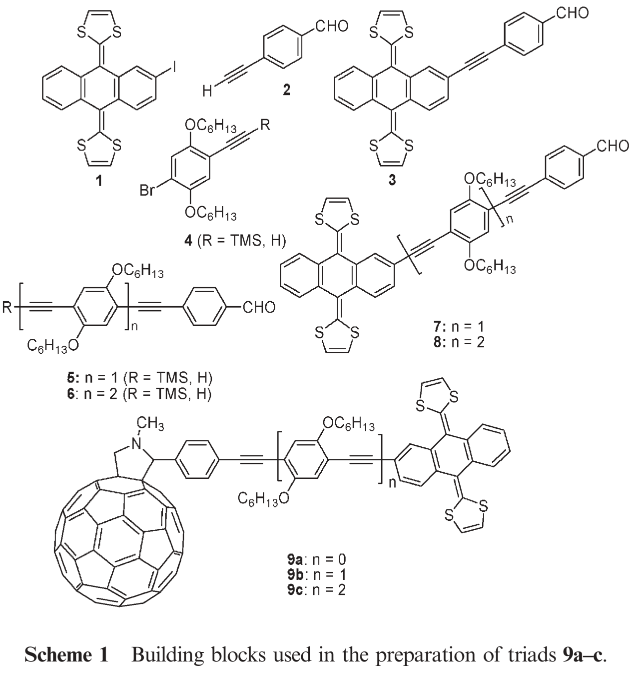
Conceptually, an ideal molecular nanowire should resemble the features of a monodisperse π-conjugated oligomer.[2] Hereby, π-conjugation emerges as a particularly crucial factor to realize (i) small attenuation factors (*i.e.*, electron conduction over large distances), (ii) good contacts with the termini (*i.e.*, electron donors and electron acceptors) and (iii) good orbital mixing (*i.e.*, with donor and acceptor states). Synthetic methodologies—mostly involving cross-coupling reactions—are powerful tools for fine-tuning most of the aforementioned criteria. Notably, we have recently succeeded in demonstrating wire-like behavior in a series of oligo-*p*-phenylenevinylenes (*o*PPV). The different *o*PPV bridges connect an electron accepting [60]fullerene with an extended tetrathiafulvalene (*ex*TTF), that serves as an electron donor. When analyzing variable electron conduction distances, that is, of up to 40 Å, exceptionally low attenuation factors ($\beta = 0.01 \pm 0.005$ Å$^{-1}$) were established.[3] In follow-up work, where the *ex*TTF moieties were replaced by metalloporphryins, these general findings were further corroborated.[4]

In this communication we wish to report on the rational design of a series of novel donor–bridge–acceptor systems using oligo-*p*-phenyleneethynylenes (*o*PPE) bridges,[5] which have been systematically increased from the monomer to the trimer. Our current study sheds light for *the first time* onto the difference between the behavior of *o*PPV and that of *o*PPE in comparable ensembles (*i.e.*, C$_{60}$–*o*PPV–*ex*TTF *versus* C$_{60}$–*o*PPE–*ex*TTF (**9a–c**)).

The oligo-*p*-phenyleneethynylene building blocks **2**, **5** and **6** were designed—see Schemes 1 and S1 (ESI†)—to be sufficiently soluble (*i.e.*, introducing long alkoxy chains) and to bear two functional termini (*i.e.*, linking *ex*TTF and C$_{60}$). *En route* towards target molecules **9a–c** a stepwise approach involving tail functionalization was followed. The syntheses of **3**, **7** and **8** were carried out starting from 2-iodo-*ex*TTF (**1**)[6] by Hagihara–Sonogashira palladium catalyzed cross-couplings with *o*PPE (**2**, **5**, **6**). The *o*PPE were prepared from *p*-ethynylbenzaldehyde (**2**) by reacting them with **4**—palladium(II), copper(I) iodide and PPh$_3$ in piperidine or other secondary amine—to afford **5**.‡ **5** was further reacted with **4** to obtain **6**. The final step of synthesizing **9a–c** involved treating *ex*TTF-containing aldehydes (**3**, **7**, **8**) with C$_{60}$ and sarcosine (*N*-methylglycine) in refluxing chlorobenzene for 3–6 h. The reaction takes place by 1,3-dipolar cycloaddition of the "*in situ*" generated azomethine ylides to C$_{60}$,[7] affording **9a–c** as stable and highly soluble brown solids in moderate yields (33–63%)—see ESI for details on the characterization.

Importantly, in **9a–c** the LUMOs (*i.e.*, −2.7 ± 0.05 eV) are nearly identical to that of the C$_{60}$ reference, while the HOMOs basically resemble that of *ex*TTF (*i.e.*, −7.4 ± 0.05 eV). A summary is given in Fig. S1 and Table S1.†

Compounds **9a–c** were probed in fluorescence and transient absorption studies. For our photophysical assays we added the properties previously determined for the 0-mer, that is, the electron donor acceptor system, in which the anthracenoid core of *ex*TTF



**Scheme 1** Building blocks used in the preparation of triads **9a–c**.

---

[a] *Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, E-28040, Madrid, Spain. E-mail: nazmar@quim.ucm.es; Fax: (+34)913-944-103*
[b] *Institute for Physical and Theoretical Chemistry, University of Erlangen, 91058, Erlangen, Germany. E-mail: dirk.guldi@chemie.uni-erlangen.de; Fax: (+49)9131-852-8307*
[c] *Friedrich-Alexander-Universität Erlangen-Nürnberg, Computer-Chemie-Centrum, Naegelsbachstrasse 25, 91052, Erlangen, Germany*

† Electronic supplementary information (ESI) available: Spectroscopic and MO data. See DOI: 10.1039/b603149h

is linked directly to the carbon of the pyrrolidine skeleton.[3a] 355 nm excitation was chosen, although it populates the singlet excited states of $C_{60}$ (1.76 eV) and that of the *o*PPE (2.6 eV), due to overlapping absorptions. We know, however, from past experiments with $C_{60}$–*o*PPE that when the *o*PPEs are excited, a rapid intramolecular transduction of energy funnels the excited state energy to the fullerene core, generating $^{1*}C_{60}$ quantitatively.[8] Excitation of $C_{60}$, on the other hand, leads directly to $^{1*}C_{60}$. Overall the quantum yield of $C_{60}$ fluorescence amounts to $6.0 \times 10^{-4}$—identical to that of a $C_{60}$-reference that lacks the *o*PPE bridge—ruling out any endothermic electron transfer ($-\Delta G_{CS} > -0.24$ eV) between $C_{60}$ ($E_{red}$: 0.61 ± 0.02 V *versus* Ag/Ag$^{+}$)[8] and *o*PPE ($E_{ox}$: 1-mer: 2.09 V, 2-mer: 2.04 V; 3-mer: 1.96 V *versus* Ag/Ag$^{+}$).[8]

In stark contrast to $C_{60}$–*o*PPE and the $C_{60}$ reference, the fullerene fluorescence is appreciably quenched in **9a–c** (*i.e.*, as low as $0.55 \times 10^{-4}$ in THF)—Fig. S2.† Moreover, the fluorescence quantum yields depend strongly on the length of the *o*PPE bridge: 0-mer: $0.18 \times 10^{-4}$; 1-mer: $0.55 \times 10^{-4}$; 2-mer: $1.8 \times 10^{-4}$.§ Setting these quantum yields in context to the $C_{60}$-reference and its lifetime, the $C_{60}$ fluorescence deactivation rates in the 0-mer, 1-mer, and 2-mer were determined as $2.1 \times 10^{10}$ s$^{-1}$, $6.6 \times 10^{9}$ s$^{-1}$ and $1.3 \times 10^{9}$ s$^{-1}$, respectively. Additionally, we followed the fluorescence at 710 nm, but found only measurable decay rates for the $C_{60}$ reference ($6.6 \times 10^{8}$ s$^{-1}$) and the 2-mer ($2.6 \times 10^{9}$ s$^{-1}$). We must conclude at this point of the investigation that $^{1*}C_{60}$, populated either directly or indirectly, powers an exothermic electron transfer ($-\Delta G_{CS} \approx 0.7$ eV) to yield the radical ion pair state, $C_{60}^{\bullet -}$–*o*PPE–*ex*TTF$^{\bullet +}$.

The aforementioned hypothesis, namely, formation of the radical ion pair state, was corroborated through transient absorption spectroscopy. Importantly, Fig. 1 corroborates the spectral signatures of the one-electron oxidized *ex*TTF$^{\bullet +}$ and the one-electron reduced $C_{60}^{\bullet -}$, which were detected as new transient maxima at 660 and 1000 nm, respectively.[3,9] The spectral identification holds for the 0-mer, 1-mer, and 2-mer, while for the 3-mer only a very broad transient, whose identity remains unknown to us at this stage, dominates the region of interest. It is, however, clear that no radical ion pair is formed for the 3-mer—*vide infra*. Both radical ion pair features, that is, $C_{60}^{\bullet -}$ and *ex*TTF$^{\bullet +}$, decay in the 0-mer ($4.9 \times 10^{6}$ s$^{-1}$), 1-mer ($1.1 \times 10^{6}$ s$^{-1}$), and 2-mer ($3.8 \times 10^{5}$ s$^{-1}$) with similar rates ($-\Delta G_{CR} \approx 1.0$ eV) to reinstate the singlet ground states.

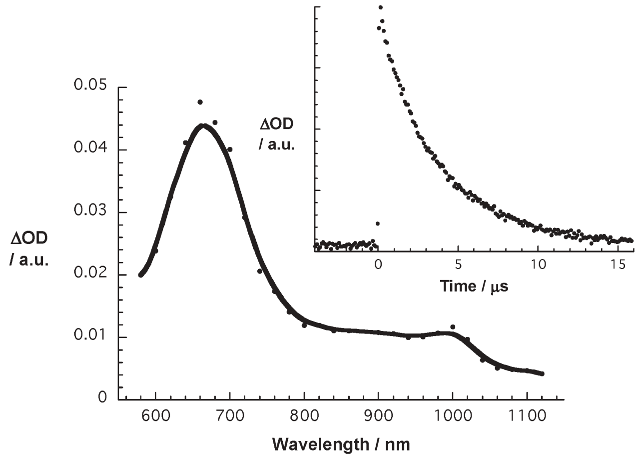


**Fig. 1** Differential absorption spectrum (visible and near-infrared) obtained upon nanosecond flash photolysis (355 nm) of ~$1.0 \times 10^{-5}$ M solutions of $C_{60}$–*o*PPV–*ex*TTF (2-mer) in nitrogen saturated THF with a time delay of 200 ns at room temperature. Insert shows charge recombination dynamics at 660 nm.

Relating the charge separation and charge recombination dynamics in THF to the electron donor acceptor separation (*i.e.*, center-to-center—$R_{CC}$) enabled us to evaluate the damping factor of the *o*PPE bridges—see Fig. 2.[10] Both relationships reveal linear dependences and provided damping factors ($\beta$) that are in perfect agreement with each other: 0.21 ± 0.05 Å$^{-1}$ for charge separation *versus* 0.2 ± 0.05 Å$^{-1}$ for charge recombination. Please note that these values are more than an order of magnitude higher than what we have established earlier for *o*PPV bridges (*i.e.*, 0.01 ± 0.005 Å$^{-1}$).[3]

Extrapolating the relationships to $R_{CC}$ of 28.46 Å, which corresponds to the center-to-center distance in the 3-mer, helps to explain the lack of electron transfer activation in the latter: The rate of electron transfer would be with $3.9 \times 10^{8}$ s$^{-1}$, notably slower than the intrinsic deactivation of the $C_{60}$ singlet excited state ($6.6 \times 10^{8}$ s$^{-1}$)—see marked data point (*i.e*, large square) in Fig. 2.

To shed light on this observation we conducted calculations on the topological and electronic structure of $C_{60}$–*o*PPE–*ex*TTF. Theoretical calculations at DFT and semiempirical AM1 levels revealed that the dihedral angle formed by the phenyl ring adjacent to the pyrolidine and the benzene moiety of the *ex*TTF connected to the oligomer is not planar, and this deviation from planarity increased significantly when semiempirical PM3 was used (Fig. S3†). This lack of planarity could break the electronic coupling between the donor and acceptor units in **9c**, thus accounting for the photophysical outcome.

The investigation of the electronic structure revealed significant differences between the *o*PPE and *o*PPV systems. The HOMO in both systems is strongly localized on the *ex*TTF and the LUMO on the $C_{60}$. According to the common, but oversimplified, one-electron concept, the HOMO–LUMO transition would represent a complete charge-transfer excitation with a very low extinction coefficient. In addition, the HOMO in the $C_{60}$–*o*PPV–*ex*TTF triad reaches into the *o*PPE bridge, whereas the HOMO in the $C_{60}$–*o*PPE–*ex*TTF triad is completely localized on the *ex*TTF. This

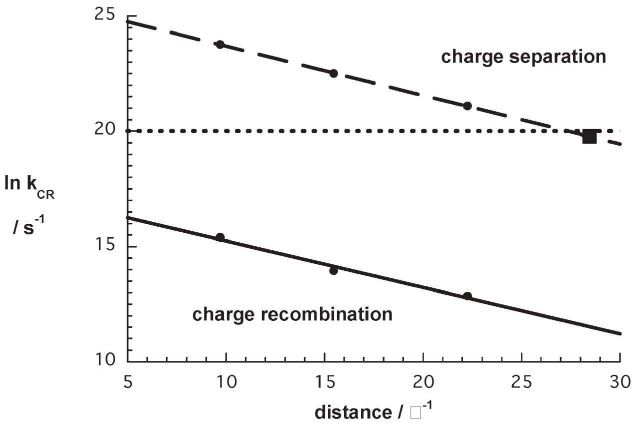


**Fig. 2** Center-to-center distances ($R_{CC}$) dependence of electron transfer rate constants (ln $k_{CR}$) in $C_{60}$–*o*PPV–*ex*TTF in nitrogen saturated THF at room temperature. The dotted line represents the singlet lifetime of $C_{60}$.

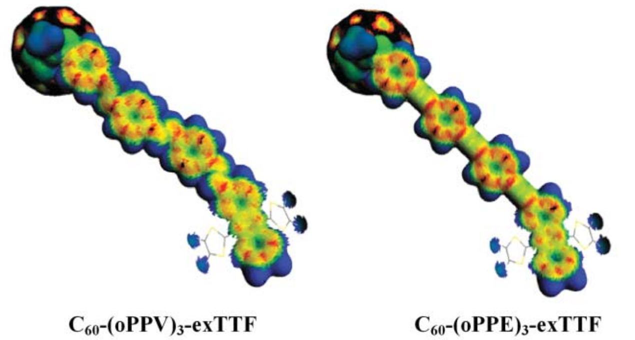


**Fig. 3** Electron affinity maps of C$_{60}$–*o*PPV–*ex*TTF and C$_{60}$–*o*PPE–*ex*TTF was calculated with *Parasuf* and the surfaces were viewed with *Trampl.1d.*

might have a strong influence on the charge-separation process because in the C$_{60}$–*o*PPV–*ex*TTF triad the injection of an electron into the bridge is facilitated through better orbital overlap between the *ex*TTF and the oligomer in comparison to the *o*PPE system (Fig. S4†). This fact was also observed from electron affinity maps (Fig. 3).[11]

In conclusion, we have demonstrated that through a simple exchange of C–C double bonds (*o*PPV) for C–C triplet bonds (*o*PPE) the long-range electron transfer (*i.e.*, charge separation and charge recombination) in electron donor–acceptor conjugates can be considerably altered. Notably, the HOMOs of *o*PPE (*i.e.*, between −8.9 and −8.4 eV) are slightly below those in *o*PPV (*i.e.*, between −8.4 and −7.9 eV), which might diminish possible interactions with C$_{60}$. It is important, however, to consider the temporal limits of the precursor state (*i.e.*, singlet excited state of C$_{60}$). Very similar damping factors (*i.e.*, 0.29 Å$^{-1}$) have recently been reported by Albinsson *et al.*[12]

This work has been supported by the MEC of Spain and Comunidad de Madrid (Projects CTQ2005-02609/BQU and P-PPQ-000225-0505), the Deutsche Forschungsgemeinschaft (SFB 583).

## Notes and references

‡ Compound **5** was obtained together with the dialdehyde homocoupling compound of **2**. However, when the reaction is carried out in refluxing toluene for 17 h, only **5** is obtained in 65% yield.

§ For the 3-mer no appreciable interactions were noted.

1 (*a*) Special issue on Organic Electronics, *Chem. Mater.*, 2004, **16**, 4381; (*b*) R. L. Carrol and C. B. Gorman, *Angew. Chem., Int. Ed.*, 2002, **41**, 4378; (*c*) Special issue on Molecular Wires and Electronics, *Top. Curr. Chem.*, 2005, **257**, 1.
2 (*a*) K. Müllen and G. Wegner, *Electronic Materials: The Oligomer Approach*, Wiley-VCH, Weinheim, Germany, 1998; (*b*) J. L. Segura, N. Martín and D. M. Guldi, *Chem. Soc. Rev.*, 2005, **34**, 31.
3 (*a*) F. Giacalone, J. L. Segura, N. Martín and D. M. Guldi, *J. Am. Chem. Soc.*, 2004, **126**, 5340; (*b*) F. Giacalone, J. L. Segura, N. Martín, J. Ramey and D. M. Guldi, *Chem.–Eur. J.*, 2005, **11**, 4819.
4 G. De La Torre, F. Giacalone, J. L. Segura, N. Martín and D. M. Guldi, *Chem.–Eur. J.*, 2005, **11**, 1267.
5 For representative recent examples of aryleneethynylene molecular wires, see: (*a*) J.-F. Nierengarten, T. Gu, G. Hadziioannou and V. Krasnikov, *Helv. Chim. Acta*, 2004, **87**, 2948; (*b*) Y. Shirai, Y. Zhao, L. Cheng and J. M. Tour, *Org. Lett.*, 2004, **6**, 2129; (*c*) Ch. Wang, A. S. Batsanov, M. R. Bryce and I. Sage, *Org. Lett.*, 2004, **6**, 2181; (*d*) W. Hu, H. Nakashima, K. Furukawa, Y. Kashimura, K. Ajito, Y. Liu, D. Zhu and K. Torimitsu, *J. Am. Chem. Soc.*, 2005, **127**, 2804.
6 M. C. Díaz, B. Illescas, C. Seoane and N. Martín, *J. Org. Chem.*, 2004, **69**, 4492.
7 M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519.
8 C. Atienza, B. Insuasty, C. Seoane, N. Martín, J. Ramey and D. M. Guldi, *J. Mater. Chem.*, 2005, **15**, 124.
9 D. M. Guldi and M. Prato, *Acc. Chem. Res.*, 2000, **33**, 695.
10 R. Marcus, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1111.
11 B. Ehresmann, B. Martin, A. M. H. C. Horn and T. Clark, *J. Mol. Model.*, 2003, **9**, 342.
12 (*a*) K. Pettersson, J. Wiberg, T. Ljungdahl, J. Martensson and B. Albinsson, *J. Phys. Chem. A*, 2006, **110**, 319; (*b*) K. Pettersson, A. Kyrychenko, E. Ronnow, T. Ljungdahl, J. Martensson and B. Albinsson, *J. Phys. Chem. A*, 2006, **110**, 310.