Determination of the attenuation factor in fluorene-based molecular wires†

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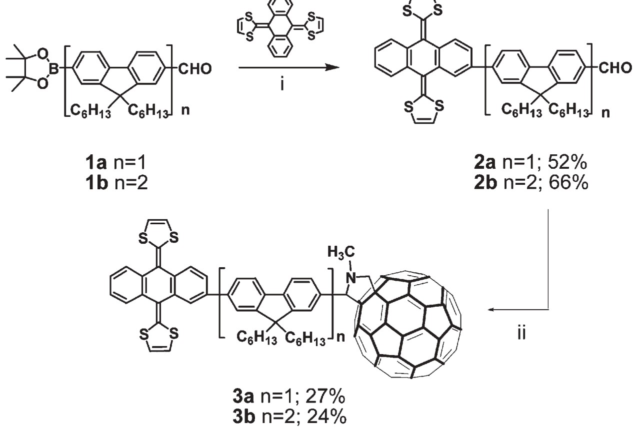
Fluorene-based bridges exhibit a molecular wire-like behaviour in C_{60}–wire–*ex*TTF systems with a very low attenuation factor (β = 0.09 Å^{-1}).

One of the main challenges in *molecular electronics* is the design of appropriate single molecules able to mediate the electron transfer between two reservoirs of electrons.[1] A variety of methods are currently available to determine the conductivity of such molecular wires. Among them, photo-induced electron transfer experiments use Donor–Bridge–Acceptor (DBA) systems in which irradiation can cause the transport of an electron from the donor to the acceptor. Both charge-separation and charge-recombination processes occur with kinetics defined by the electron transfer rate constant: $k_{\mathrm{ET}} = k_0 e^{-\beta r_{\mathrm{DA}}}$, where k_0 is a kinetic prefactor, r_{DA} represents the donor–acceptor distance, and the factor β, which depends primarily on the nature of the bridge, is a key parameter often used as a benchmark to evaluate the wire-like behaviour of the bridge connecting the donor and acceptor units. The smaller this factor β, the longer is the distance over which charge can be conducted efficiently. Typical values for β range between 1.0 and 1.4 Å^{-1} for proteins, and between 0.01 and 0.04 Å^{-1} for highly efficient π-conjugated bridges.[2] Other factors such as the matching of energy levels of the bridge and the donor influence the molecular wire's behaviour strongly and it is therefore important to refer to the same donor and acceptor moieties in order to obtain a reliable comparison between the different π-conjugated oligomers.[2] Extended tetrathiafulvalene (*ex*TTF) and [60]fullerene have recently been used for this purpose and unusually low β values of 0.01 Å^{-1} and 0.20 Å^{-1} have been reported for oligo-*p*-phenylenevinylene[3] and oligo-*p*-phenylenethynylene[4] bridges, respectively.

Fluorene-based oligomers have emerged as a most unusual class of π-conjugated systems showing wire-like behaviour; their energy levels change only slightly when the length of the bridge is increased.[5]

For this reason, we have synthesized a new DBA system constituted by *ex*TTF–(oligofluorene)$_n$–C_{60} (**3a**,**b**) and studied the electronic communication through the oligofluorene by irradiating with light. Interestingly, kinetic experiments displayed a weak distance dependence on the electron transfer process.

Fluorene monomer and dimer **1a**,**b**,[6] featuring solubilising hexyl chains, a formyl group as a link to the C_{60} and a boronic ester, undergo a palladium-catalyzed Suzuki cross-coupling reaction with 2-iodo-*ex*TTF (I-*ex*TTF), affording compounds **2a**,**b** in good yields (Scheme 1). The presence of a formyl group allows the further *in situ* generation of the corresponding azomethine ylides by reaction with sarcosine in refluxing chlorobenzene, to afford the cycloadducts **3a**,**b**[7] by cycloaddition to C_{60} following Prato's protocol.[8]



Scheme 1 (i) Pd(PPh$_3$)$_2$Cl$_2$–toluene, K$_2$CO$_3$–H$_2$O, reflux; (ii) C_{60}, sarcosine, chlorobenzene, reflux.

We first turn to the ground state features of **3a**,**b**. Absorption spectra in toluene, THF and benzonitrile are best described as the linear sums of the three individual constituents: *ex*TTF, oligofluorenes, and C_{60} with the most dominant absorptions at 430 nm (*i.e.*, *ex*TTF), at 345 nm (*i.e.*, oligofluorene) and 300 nm (*i.e.*, C_{60}). This suggests that there is little, if any, electronic communication between *ex*TTF, oligofluorenes and C_{60} in **3a**,**b**. DFT calculations (B3LYP/6-31G*) on the HOMO and LUMO energies of *ex*TTF, *N*-methylpyrrolidinofullerene, the pristine *o*FL oligomers and the C_{60}–*o*FL dyads reveal that the HOMO and LUMO energies *in vacuo* of *ex*TTF (−4.7 eV and −1.2 eV) perfectly match the

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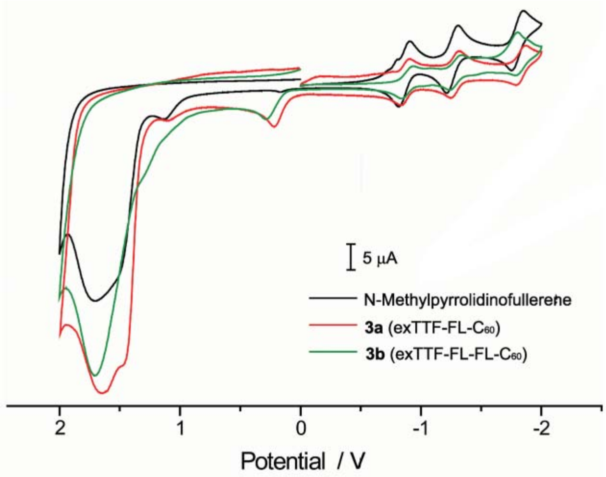

Fig. 1 Cyclic voltammograms of **3a**,**b** and *N*-methylpyrrolidinofullerene as reference measured at 100 mV s^{-1} in a 0.1 M solution of Bu_4NClO_4 in *o*-DCB–MeCN (4 : 1); glassy carbon working electrode, Ag/$AgNO_3$ reference electrode, Pt counter electrode; T = 25 °C.

energies of the oligomer building blocks (−5.1 eV and −1.1 eV), providing good orbital overlap between the donor and the bridge, which is essential for electron transfer between the two units. Interestingly, in the C_{60}–*o*FL dyads the LUMO is lowered to one energy level (−3.0 eV) which is equal to the energy of the LUMO of *N*-methylpyrrolidinofullerene and the HOMO (−5.1 eV) remains energetically unchanged in comparison to pristine fluorenes. Hence, this proves the electron-accepting features of C_{60} and neglects electronic communication between the donor, bridge and acceptor in the ground state. Electrochemical measurements support the absence of significant electronic interactions since the redox potentials determined by cyclic voltammetry for compounds **3a** (E^1_{ox} = 215 mV; E^1_{red} = −874 mV) and **3b** (E^1_{ox} = 281 mV; E^1_{red} = −889 mV) are comparable to those measured for precursor I-*ex*TTF (E^1_{ox} = 232 mV) and *N*-methylpyrrolidinofullerene (E^1_{red} = −863 mV) (Fig. 1).[11]

Furthermore, electron affinity calculations confirm the electron-transfer pathway from the donor over the bridge to the fullerene acceptor. Fig. 2 represents the local electron affinity map of the DBA system **3b**. A homogenous distribution of the electron density (surface) throughout the whole molecule followed by a channel of high electron affinity through the bifluorene bridge resulting in a maximum at C_{60} proves the charge-transfer features of these systems.

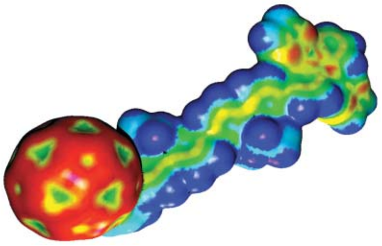

Fig. 2 Electron affinity map of C_{60}–*o*FL_2–*ex*TTF (**3b**) as computed with Parasurf A07[9] and viewed with Tramp 1.1d;[10] from blue to red: low to high.

To determine the rates of charge separation and charge recombination and eventually the corresponding β factor, **3a**,**b** were tested in a series of photophysical assays (*i.e.*, steady-state/time-resolved fluorescence and time-resolved transient absorption measurements).

The first insight into electron-transfer interactions came from fluorescence experiments. Here, in line with our earlier investigations of C_{60}–*o*FL conjugates, we see a nearly quantitative fluorescence quenching of the oligofluorene units. This is a result of an efficient transduction of singlet excited state energies to C_{60}. In stark contrast to the behaviour seen for *o*FL–C_{60} and C_{60}–*o*FL–C_{60},[6] **3a**,**b** give rise to a number of interesting trends. Firstly, the C_{60} fluorescence is not quantitative with quantum yields that are typically only of the order of 0.07×10^{-4} for the monomer and 0.90×10^{-4} for the dimer (note that the quantum yield is 6.0×10^{-4} for comparable C_{60} references). Secondly, a strong solvent dependence emerges, that is, the C_{60} fluorescence quenching intensifies gradually with increasing solvent polarity from, for example, toluene to benzonitrile. Finally, a marked distance dependence is seen. In particular, the C_{60} fluorescence quenching tends to be stronger in **3a** than in **3b**. Summarising the above observations, we postulate charge transfer between the transiently formed C_{60} singlet excited state and the electron donor *ex*TTF.

Conclusive evidence in support of the electron-transfer hypothesis was found in transient absorption measurements. **3a**,**b** were photoexcited with short 387 nm (150 fs) and long 355 nm (5 ns) laser pulses. The short laser pulses, at a wavelength that is absorbed by both oligofluorenes and C_{60}, result in a discernable transient absorption spectrum (*i.e.*, 880 nm maximum) that is attributed to the C_{60} singlet excited state. Again, this results from a rapid singlet excited state transfer. This transient species intersystem crosses in the corresponding *o*FL–C_{60} and C_{60}–*o*FL–C_{60} to form the triplet manifold on a timescale that is typically *ca.* 1.5 ns. In **3a**,**b**, however, the C_{60} singlet excited state features decay much faster. Interestingly, the decay behaviour is an exact reflection of the fluorescence experiments, that is, a notable dependence on the solvent polarity and the distance is observed. More important is the spectroscopic characterization of the transient that develops synchronously with the C_{60} singlet excited decay. Two features, a maximum in the visible region (*i.e.*, 680 nm) and another maximum in the near infrared region (*i.e.*, 1000 nm), confirm the intramolecular formation of the one-electron oxidized *ex*TTF radical cation (*i.e.*, *ex*$TTF^{\bullet+}$) and the one-electron reduced C_{60} radical anion (*i.e.*, $C_{60}^{\bullet-}$), respectively. Fitting the singlet excited state decay and the radical ion pair formation kinetics enabled us to derive the charge-separation rates, which are summarised in Table 1.

Notably, the radical ion pair states are stable on the timescale of our femtosecond experiments and only exhibit a detectable decay in the complementary nanosecond experiments. The decays of the *ex*$TTF^{\bullet+}$ and the $C_{60}^{\bullet-}$ features are strictly first order when

Table 1 Charge-separation and charge-recombination dynamics as determined by femtosecond and nanosecond time-resolved spectroscopic measurements for **3a** and **3b** in THF

	R_{DA}/Å	$k_{\text{charge separation}}$/$s^{-1}$	$k_{\text{charge recombination}}$/$s^{-1}$
3a	16.7	8.9×10^9	7.2×10^5
3b	24.9	4.0×10^9	4.4×10^5

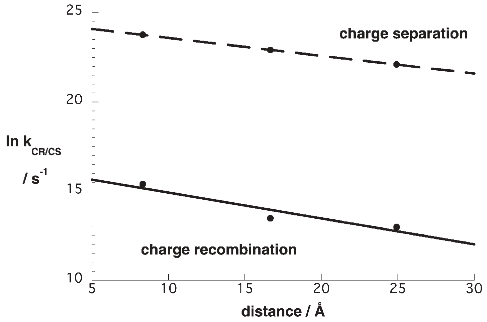

Fig. 3 Centre-to-centre distances (R_{CC}) dependence of charge-separation (ln k_{CS}) and charge-recombination (ln k_{CR}) rate constants in C_{60}–*o*FL–*ex*TTF in nitrogen saturated THF at room temperature. The slope represents β.

plotted, for example, as ln ΔOD *versus* time, and lead to the quantitative reconstitution of the singlet ground state without any appreciable triplet features. The corresponding rate constants are listed in Table 1.

Finally, we determined the β factor by analysing the rate constants (*i.e.*, charge-separation and charge-recombination) as a function of donor–acceptor distance.[12] Common to both relationships is a linear dependence from which a β factor of 0.09 Å^{-1} emerged. In other words, the ability of oligofluorenes to conduct charges lies between that of oligo-*p*-phenylenevinylenes[3] and that of oligo-*p*-phenylenethynylenes.[4] Fig. 3 represents the charge-separation and charge-recombination dynamics as a function of donor–acceptor distance.

In summary, we have demonstrated that fluorene-based oligomers are able to act as efficient cables in C_{60}–*ex*TTF donor–acceptor systems, showing a remarkably low β value (0.09 Å^{-1}).

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Notes and references

1 R. L. Carroll and C. B. Gorman, *Angew. Chem., Int. Ed.*, 2002, **41**, 4378.
2 E. A. Weiss, M. R. Wasielewski and M. A. Ratner, *Top. Curr. Chem.*, 2005, **257**, 103.
3 F. Giacalone, J. L. Segura, N. Martín and D. M. Guldi, *J. Am. Chem. Soc.*, 2004, **126**, 5340.
4 C. Atienza, N. Martín, M. Wielopolski, N. Haworth, T. Clark and D. M. Guldi, *Chem. Commun.*, 2006, 3202.
5 R. H. Goldsmith, L. E. Sinks, R. F. Kelley, L. J. Betzen, W. Liu, E. A. Weiss, M. A. Ratner and M. R. Wasielewski, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 3540.
6 C. van der Pol, M. R. Bryce, M. Wielopolski, C. Atienza-Castellanos, D. M. Guldi, S. Filippone and N. Martín, *J. Org. Chem.*, 2007, **72**, 6662.
7 Triads **3a**,**b** were fully characterized by spectroscopic (UV–Vis, ^{1}H-NMR, ^{13}C-NMR, ESI-MS) and HPLC analyses. However, they decompose during work-up by exposure to air and light. For this reason, these compounds were obtained by purification in the absence of light, being perfectly stable in the solid state (see supplementary information).
8 M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519.
9 *Parasurf A07*, T. Clark, Jr, H. Lin and A. H. C. Horn, 2007, ©CEPOS InSilico Ltd.
10 *Tramp 1.1d*, H. Lanig, R. Koenig and T. Clark, 2005.
11 These values were employed to calculate the energy of the radical ion pair as 1.095 eV, while that of the C_{60} singlet excited state is 1.76 eV.
12 We also included the value determined for directly linked *ex*TTF–C_{60}. See: M. C. Díaz, M. A. Herranz, B. M. Illescas, N. Martín, N. Godbert, M. R. Bryce, C. Luo, A. Swartz, G. Anderson and D. M. Guldi, *J. Org. Chem.*, 2003, **68**, 7711.