ChemComm

COMMUNICATION
Jaume Veciana, Concepció Rovira,
Jean-François Nierengarten *et al.*
Changes in electronic couplings
of mixed-valence systems due
to through-space intramolecular
interactions

FEATURE ARTICLE
Mary A. Reppy and
Bradford A. Pindzola
Biosensing with polydiacetylene
materials: structures, optical properties
and applications

1359-7345(2007)42;1-1

Changes in electronic couplings of mixed-valence systems due to through-space intramolecular interactions†

Teresa M. Figueira-Duarte,[a] Vega Lloveras,[b] José Vidal-Gancedo,[b] Aline Gégout,[a] Béatrice Delavaux-Nicot,[a] Richard Welter,[c] Jaume Veciana,*[b] Concepció Rovira*[b] and Jean-François Nierengarten*[a]

The strength of the electronic interactions between the two redox moieties in fullerene-substituted mixed-valence bis(ferrocenylethynyl)ethene derivatives is modulated by the through-space intramolecular electronic interactions of C_{60} with the bridging conjugated system.

Mixed-valence compounds, which have two redox sites in different oxidation states linked by a bridge that mediates the transfer of holes (electrons) from one site to the other, are excellent benchmarks for the study of intramolecular electron transfer phenomena.[1] Interestingly, the calculated electronic coupling (V_{ab}) for systems with the same donor–acceptor distances, is sensitive to the bridge electronic structure and shows a significant dependence for the bridge conformations.[2] In principle, intra- and/or inter-molecular interactions of electron rich or electron deficient molecular subunits spatially close to the π-conjugated bridge should also modulate its ability of carrying one electron from one redox unit to the other but this has never been shown to the best of our knowledge. To demonstrate such an effect, we have designed compounds **1** and **2** containing two-ferrocenyl moieties[3] bridged with a *E*-1,2-diethynylethene unit[4,5] and bearing one or two fullerene groups capable of giving rise to intramolecular π–π interactions with the bridging π-conjugated nanowire. Comparison of the electronic coupling parameters of **1** and **2** with the one derived from model compound **3** revealed a significant effect resulting from this through-space intramolecular electronic interactions.

Fullerene bis-adduct **1** was obtained by taking advantage of the versatile regioselective reaction developed in the Diederich group[6] which led to C_{60} bis-adducts by a cyclization reaction at the C sphere with bis-malonates in a double Bingel cyclopropanation. To this end, bis-malonate **6** was prepared by esterification of diol **4**[5] with acid **5**[7] [dicyclohexylcarbodiimide (DCC),

N,N-dimethylaminopyridine (DMAP)] (Fig. 1). Reaction of **6** with C_{60} (1 equiv.), I_2 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene afforded the C_1 symmetric *cis*-2 bis-adduct **1** in 31% yield.
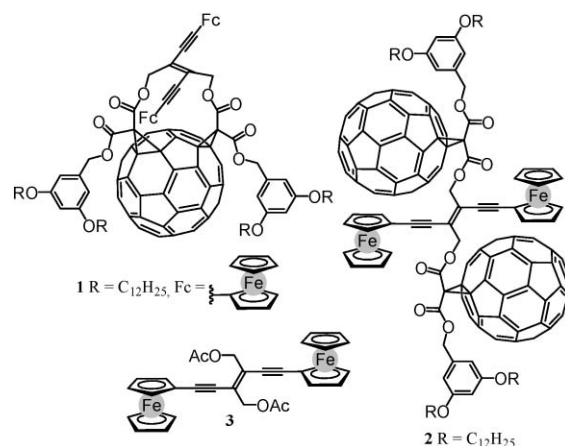
The relative position of the two cyclopropane rings on the C_{60} core in **1** was determined based on the molecular symmetry (C_1) deduced from the ^{1}H- and ^{13}C-NMR spectra. It is also well-established that the 1,2-vinylenebis(methylene)-tethered bis-malonates produce regioselectively the *cis*-2 addition pattern at C_{60}.[6] Compound **2** was also prepared from bis-malonate **6**. In this case, the reaction was performed at a higher concentration with an excess of C_{60} (2.2 equiv.). The bis-fullerene derivative was thus obtained in 49% yield.
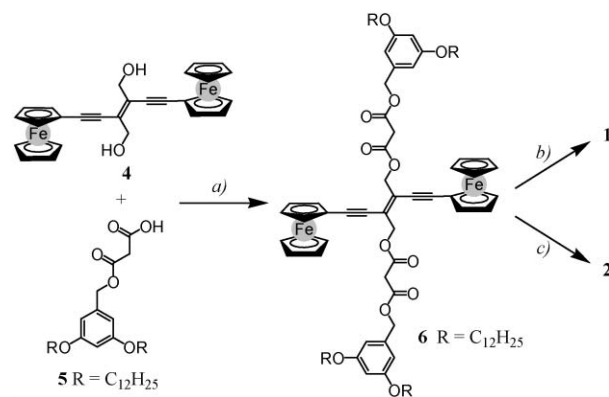
Fig. 1 Preparation of compounds **1** and **2**; Reagents and conditions: (a) **5**, DCC, DMAP, CH_2Cl_2, 0 °C to rt, 12 h (44%); (b) C_{60} (1 equiv.), PhMe, DBU, I_2, rt, 12 h (31%); (c) C_{60} (2.2 equiv.), PhMe, DBU, I_2, rt, 12 h (49%).

[a]*Groupe de Chimie des Fullerènes et des Systèmes Conjugués, Laboratoire de Chimie de Coordination du CNRS (UPR 8241), 205 route de Narbonne, 31077, Toulouse Cedex 4, France. E-mail: jfnierengarten@lcc-toulouse.fr; Fax: +33 (0) 5 61 55 30 03*
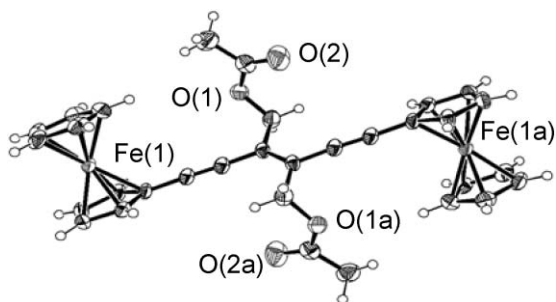[b]*Institut de Ciència de Materials de Barcelona, Campus Universitari de Bellaterra, Cerdanyola, 08193, Spain. E-mail: cun@icmab.es; vecianaj@icmab.es; Fax: +34 9 35 80 57 29*
[c]*Laboratoire DECOMET, Université Louis Pasteur 4, rue Blaise Pascal, 67000, Strasbourg, France. E-mail: welter@chimie.u-strasbg.fr; Fax: +33 (0) 3 90 24 12 11*

Fig. 2 ORTEP view with partial numbering of compound **3** (only one of the conformers is shown), the additional "a" characters in the atom labels indicate that these atoms are at equivalent position ($2 - x, 1 - y, - z$), thermal ellipsoids include 50% of the electron density.

Dicyclohexylcarbodiimide (DCC)-mediated esterification of acetic acid with diol **4** afforded model compound **3** in 83% yield. The *E*-configuration of the alkene fragment in **3** was unambiguously confirmed by X-ray crystallography (Fig. 2).‡ The unit cell of the crystal structure contains four molecules in two slightly different conformations. It can be noted that the both conformers lie about inversion centers. The center to center Fe–Fe distances for the two conformers were found to be 11.7789(8) and 11.9134(8) Å.

The relative potentials of the redox processes in compounds **1–3** were determined by cyclic voltammetry (CV) in CH_2Cl_2 solutions containing 0.1 M [(n-Bu)$_4$N]BF$_4$ as supporting electrolyte (Table 1). All compounds show only one quasi-reversible two-electron process attributed to the simultaneous oxidation of the two ferrocene units.[8] This result suggests the presence of very weak electronic interactions between the two redox centers[9] since in the case of strong or moderate electronic interactions between the two units, two electrochemical waves are anticipated. Comparison of the oxidation potential of the ferrocene moieties in **3** with those obtained for **1** and **2** shows only a very weak effect of the fullerene moieties in good agreement with the calculated structures of **1** and **2** revealing no specific through-space intramolecular π–π interactions between the C_{60} units and the ferrocenyl groups in both cases (Fig. S1†). In the cathodic region, **1** and **2** give rise to two reduction waves in the studied electrochemical window (up to −1.25 V) corresponding to the first and second reductions of the fullerene.

The UV-vis spectra obtained in CH_2Cl_2 for all compounds are characterized by a very strong absorption with a maximum between 320 and 328 nm which are assigned to a localized ligand-centered π–π* electronic transition (L–π*) (Fig. S2†). In addition

to this band another less energetic and weaker absorption is visible between 464 and 478 nm which is assigned to another localized excitation with a lower energy produced either by two nearly degenerate transitions, a Fe^{II} d-d transition[10] or a metal-to-ligand charge transfer (MLCT) process (d_π–π*).[11] These bands are significantly red-shifted (Table S1†) in **1** and **2** with respect to compound **3** suggesting substantial ground state interactions between the fullerene and the π-conjugated bridge. This was confirmed by molecular modelling studies revealing π–π stacking interactions between the C_{60} units and the diethynylethene core (Fig. S1†). In addition, compounds **1** and **2** show bands, which do not appear in compound **3**, at around 325, 430, 644 and 680 nm assigned to the absorption of the fullerene. In compound **2**, with two fullerene moieties, the bands centred at 643 and 687 nm have a molar extinction coefficient practically twice than those at the similar position of compound **1** with only one C_{60} unit.

Oxidized species derived from all the compounds were generated electrochemically and their formation followed by absorption spectroscopy. Thus, a stepwise Coulommetric titration was performed on a *ca*. 1×10^{-3} mol L^{-1} solution of compounds **1**, **2** and **3** in CH_2Cl_2, with [(n-Bu$_4$)N]PF$_6$ (0.15 M) as supporting electrolyte, and absorption spectra were regularly recorded for different average number ($0 \leqslant n \leqslant 2$) of removed electrons. UV-Vis-NIR data for the mixed valence species are collected in Table 2. As a typical example, Fig. 3 shows the evolution of the spectra of compound **1** during its oxidation process.

For all the compounds, the characteristic ferrocenyl bands disappear during the oxidation process, while some shoulders appear between 500 and 555 nm and are attributed to the ferrocenium ions as well as a band at around 800 nm assigned to a ligand to metal charge transfer (LMCT) band of the ferrocenium ion.[12] The latter band doubles more or less its intensity when going from the formation of the first to the second ferrocenium ion. Interestingly, during the oxidation process of compounds **1**, **2**, and **3** a new weak and broad band centered at 1182, 1179, and 1131 nm, respectively, appears and increases continuously until complete formation of their mixed valence compounds. Afterwards, for $1 \leqslant n \leqslant 2$ average number of removed electrons the intensity of this band decreases until it disappears when the dications **1^{2+}**, **2^{2+}** and **3^{2+}** are completely formed (see Fig. 3, inset). This behaviour is typical for an intervalence charge transfer (IV-CT) band due to the presence of an intramolecular electron transfer process in a Class II mixed valence compound.[13] The spectral data of IV-CT bands obtained from the deconvolution (see Fig. S5-7†) of the experimental spectra of **1$^+$–3$^+$** are summarized in Table 2. From the characteristics of the IV-CT band, the effective electronic coupling V_{ab} (in cm^{-1}) between both ferrocene redox centres can be determined, using eqn (1) developed by Hush.[14]

Table 1 Electrochemical properties of **1**, **2**, and **3** determined by CV on a Pt working electrode in CH_2Cl_2 + 0.1 M [(n-Bu$_4$)N]BF$_4$ at room temperature

Compound	Oxidation E_1	Reduction E_1	E_2
1	+0.72^{a,b}	−0.59^a	−0.96^c
2	+0.72^{a,b}	−0.52^{a,b}	−0.94^{b,c}
3	+0.71^{a,b}	—	—

^{a} Values for $(E_{pa} + E_{pc})/2$ in V *vs.* SCE at a scan rate of 0.1 Vs^{-1}. ^{b} Bielectronic process. ^{c} Irreversible process, E_p value measured at 0.1 Vs^{-1}.

Table 2 Spectral data of the IV-CT bands obtained from the deconvolution of the experimental spectra of **1$^+$–3$^+$** and calculated V_{ab} values

Compound	ν_{max}/cm^{-1}	ε_{max}/M^{-1}·cm^{-1}	$\Delta\nu_{1/2}$/cm^{-1}	$R_{M\text{-}M}$/Å	V_{ab}/cm^{-1}
1$^+$	8484	487	3532	11.85	209
2$^+$	8460	430	3650	11.85	199
3$^+$	8842	740	3532	11.85	263
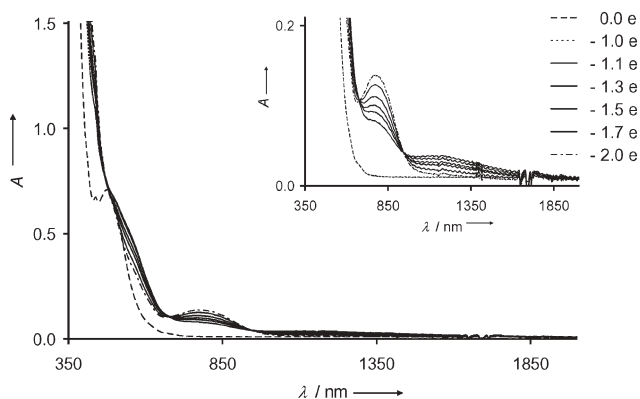
Fig. 3 Vis-NIR spectra of compound **1** (dashed line) and the evolution of the spectra during the course of the oxidation process from the mixed valence species **1⁺** (dotted line) to **1²⁺** (dashed-dotted line) in dichloromethane with 0.15 M [(n-Bu₄)N]PF₆.

$$V_{ab} = \left[2.05 \times 10^{-2} \sqrt{\varepsilon_{max} \overline{v_{max}} \Delta \overline{v_{1/2}}} \right] R^{-1} \qquad (1)$$

In this equation, $\Delta v_{1/2}$ (in cm^{-1}) is the half-height band width of the IV-CT band, R (in Å) the distance between the redox centers (here, the intermetallic distance, as determined by the X-ray crystal structure of **3**), ε_{max} (in M^{-1} cm^{-1}) is the maximum molar extinction coefficient, and v_{max} (in cm^{-1}) the wavenumber at the maximal absorbance. Eqn (1) gives an effective electronic coupling (V_{ab}) for **3⁺**, **1⁺** and **2⁺** of 263, 209 and 199 cm^{-1}, respectively, taking into account the comproportionation constants to recalculate the molar extinction coefficient. A similar trend for V_{ab} values of **1⁺**–**3⁺** were found when Hush-Mulliken model was applied (see Supporting information†).[14] Interestingly, the electronic coupling between the two redox centers is influenced by the through-space intramolecular interactions of the C₆₀ units with the π-conjugated bridge.[15] In other words, the HOMO–LUMO gap of the conjugated nanowire is affected by the electrostatic field generated by the neighbouring electron withdrawing C₆₀ units and, as a result, the electronic interactions among the two redox centres are different. The decreased electronic coupling in **2** with respect to **1** is in good agreement with this interpretation. Indeed, the simultaneous influence of two fullerenes increases the effect on the electronic interaction between the two electroactive units. In conclusion, the C₆₀ electron acceptor behaves like an applied electric field on the molecular wire and modulates its charge mobility. In this way, compounds **1** and **2** can be seen as primitive mimics of a field-effect transistor-like behaviour at the molecular level.

Notes and references

‡ C₃₂H₂₈Fe₂O₄ (M = 588.24 g mol^{-1}), triclinic; space groupe $\bar{P}1$; a = 9.6870(3) Å; b = 11.4770(4) Å; c = 12.5620(5) Å; α = 108.28(5)°; β = 93.06(5)°; γ = 93.80(5)°; Z = 2; Dc = 1.481 g cm^{-3}; μ (Mo Kα) = 1.136 mm^{-1}; F(000) = 608; a total of 11644 reflections collected; 1.71° < θ < 30.12°, 7706 independent reflections with 4332 having $I > 2\sigma(I)$; 332 parameters; Final results : $R_1(F^2)$ = 0.0534; w$R_2(F^2)$ = 0.1594, Goof = 0.99, maximum residual electronic density = 0.778 e⁻Å^{-3}. CCDC 624690. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707522g

1 W. Kaim, A. Klein and M. Glöckle, *Acc. Chem. Res.*, 2000, **33**, 755; J.-P. Launay, *Chem. Soc. Rev.*, 2001, **30**, 386; K. D. Demadis, C. M. Hartshorn and T. J. Meyer, *Chem. Rev.*, 2001, **101**, 2655.
2 A. Kyrychenko and B. Albinsson, *Chem. Phys. Lett.*, 2002, **366**, 291; S. B. Sachs, S. P. Dudek, R. P. Hsung, L. R. Sita, J. F. Smalley, M. D. Newton, S. W. Feldberg and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 1997, **119**, 10563; K. Petterson, A. Kyrychenko, E. Rönnow, T. Ljungdahl, J. Martensson and B. Albinsson, *J. Phys. Chem. A*, 2006, **110**, 310; M. P. Eng, T. Ldungdahl, J. Martensson and B. Albinsson, *J. Phys. Chem. B*, 2006, **110**, 6483.
3 For reviews on biferrocenyl-based mixed valence derivatives, see: D. Astruc, *Acc. Chem. Res.*, 1997, **30**, 383; S. Barlow and D. O'Hare, *Chem. Rev.*, 1997, **97**, 637.
4 For a review on 1,2-diethynylethene derivatives, see: F. Diederich, *Chem. Commun.*, 2001, 219.
5 Changes in the strength of the mixed-valence interaction between the two ferrocene moieties in *E* and *Z*-bis(ferrocenylethynyl)ethene derivatives have been already reported, see: R. Sakamoto, M. Murata and H. Nishihara, *Angew. Chem., Int. Ed.*, 2006, **45**, 4793.
6 J.-F. Nierengarten, V. Gramlich, F. Cardullo and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2101–2103.
7 J.-F. Nierengarten and J.-F. Nicoud, *Tetrahedron Lett.*, 1997, **38**, 7737.
8 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.
9 The comproportionation constants K_c could not be evaluated from the electrochemical data, but their values should be of the statistical factor (4).
10 G. L. Geoffroy and M. S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979; Y. S. Sohn, D. N. Hendrickson and H. B. Gray, *J. Am. Chem. Soc.*, 1971, **93**, 3603.
11 S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry and S. R. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3715.
12 V. Lloveras, A. Caballero, A. Tárraga, M. Desamparados Velasco, A. Espinosa, K. Wurst, D. J. Evans, J. Vidal-Gancedo, C. Rovira, P. Molina and J. Veciana, *Eur. J. Inorg. Chem.*, 2005, 2436.
13 M. Robin and P. Day, *Adv. Inorg. Radiochem.*, 1967, **10**, 247.
14 N. S. Hush, *Coord. Chem. Rev.*, 1985, **64**, 135; R. J. Cave and M. D. Newton, *J. Chem. Phys.*, 1997, **106**, 9213.
15 Molecular modeling studies also reveal that conformations of the π-conjugated bridge as well as the angle of the ferrocene units with respect to the bridge, in **1** and **2** are very similar to that of **3**. This suggests that the most important contributions are the through-space bridge/C₆₀ interactions rather than changes in the bridge's conformation.