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Optical electron transfer through 2,7-diethynylfluorene spacers in mixed-valent complexes containing electron-rich “(η²-dppe)(η⁵-C₅Me₅)Fe” endgroups†Floriane Malvolti,^a Cedric Rouxel,^b Olivier Mongin,^b Philippe Hapiot,^a Loic Toupet,^c Mireille Blanchard-Desce^b and Frédéric Paul*^a

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We report in this communication the study of the intramolecular electron transfer through a 2,7-diethynylfluorenyl spacer in the Fe(II)/Fe(III) mixed-valent (MV) complex [(η²-dppe)(η⁵-C₅Me₅)FeC≡C(2,7-C₂₁H₂₄)C≡CFe(η⁵-C₅Me₅)(η²-dppe)][PF₆]₂ (**1**[PF₆]₂). The complex is generated *in situ* by comproportionation from its homovalent dinuclear Fe(II) and Fe(III) parents (**1** and **1**[PF₆]₂). It is shown that electronic delocalization is much more effective through a 2,7-fluorenyl than through a 4,4'-biphenyl bridging unit.

In the field of molecular electronics,^{1–6} the understanding of structural features influencing the intramolecular electron transfer has become decisive for optimizing the design of smart molecular-sized devices.^{7,8} While electron-transfer through several (hetero)aromatic units has been thoroughly investigated,⁹ to our knowledge, no electronic coupling through 2,7-diethynylfluorenyl-based bridges has been reported so far. Indeed, among the various such dinuclear transition metal complexes reported,^{10,11} most of them featured electron-poor metal centers and presented no other stable and isolable redox state(s), except perhaps for a few derivatives reported by Raithby and Wong.^{12,13} But even in these cases, the properties of the mixed-valent state of these compounds were not investigated. In the frame of a project aimed at developing redox-switchable multiphotonic absorbers,^{14–17} we recently synthesized the homovalent Fe(II) and Fe(III) compounds **1** and **1**[PF₆]₂ (Chart 1) featuring the electron-rich “(η²-dppe)(η⁵-C₅Me₅)Fe” endgroups.

We thus logically wondered about the intramolecular electron-transfer properties of the Fe(II)/Fe(III) mixed valent (MV)

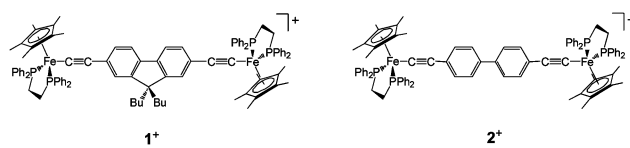
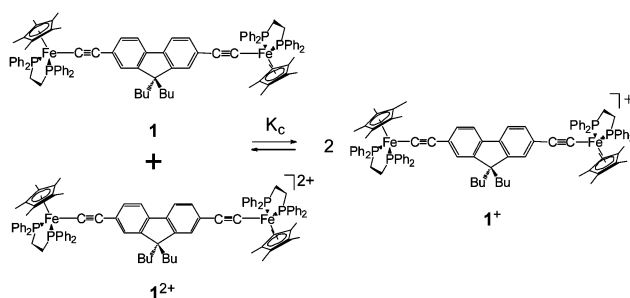


Chart 1

congener of these compounds (**1**[PF₆]₂).^{1,8} Likewise to its 4,4'-biphenyl analogue (**2**[PF₆]₂) previously studied in our group¹⁸ or to other related dinuclear carbon-rich MV derivatives,^{7,19–21} **1**[PF₆]₂ certainly constitutes another example of organometallic molecular wire.^{8,9} In that respect, we have previously shown that a remarkably large electronic coupling ($H_{\text{FeFe}} \cong 145 \text{ cm}^{-1}$) was operative between the redox-active endgroups of **2**[PF₆]₂ in spite of the large intramolecular distance between them (*ca.* 16 Å).¹⁸ The coplanarity of the fluorenyl unit, which should result in a better overlap of its π-manifold, is anticipated to increase the electronic coupling between the redox-active endgroups relative to a 4,4'-biphenyl spacer. However, the loss of axial symmetry with the 2,7-fluorene spacer might simultaneously result in detrimental quantum interferences.^{22,23} Thus, in order to clearly establish how the electronic coupling is modified when progressing from **1**[PF₆]₂ to **2**[PF₆]₂, we have decided to experimentally determine H_{FeFe} for **1**[PF₆]₂.

Given that a MV complex is always in equilibrium with its homovalent parents, we first wondered about the thermodynamic stability of **1**[PF₆]₂ in the comproportionation equilibrium (Scheme 1).²⁴ Based on the well known eqn (1),²⁵ it was immediately apparent from the cyclic voltammogram of **1** (or **1**[PF₆]₂) that



Scheme 1

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† Electronic supplementary information (ESI) available: Synthesis of **1** and **1**[PF₆]₂. CIF file for **1**. Simulation procedure of the voltammogram used for **1**. UV and IR spectra obtained from equimolar mixtures of **1** and **1**[PF₆]₂. Solvatochromy and deconvolution of the near-IR absorption. CCDC reference number 694575. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10231a

the corresponding MV compound has not a sufficient stability to be quantitatively isolated by chemical oxidation of **1**, since the voltammogram exhibits strongly overlapping waves for the two stepwise (and chemically reversible) iron-centred oxidations (see ESI†). Moreover, when coming close together, the apparent potential difference between these redox waves does not match anymore with the real ΔE° value.²⁶ Accurate values of the corresponding redox potentials in dichloromethane were obtained by simulation of this voltammogram (−0.11 and −0.22 V vs. ECS) and a thermodynamic equilibrium constant (K_c) of 76 ± 8 could be derived for this comproportionation reaction at 25 °C from the difference between these redox potentials ($\Delta E^\circ = 111 \pm 3$ mV).

$$(RT/F)\log(K_c) = \Delta E^\circ \quad (1)$$

Notably, this potential separation is significantly larger than that previously determined for $2[\text{PF}_6]$ (62 mV), in line with a larger electronic interaction taking place between the redox endgroups in $1[\text{PF}_6]$, which also translates in a larger stability constant for this MV complex (a K_c value of 11 had been found for $2[\text{PF}_6]$). While ensuring a good solubility of the compound, the two butyl chains on the fluorene spacer possibly contribute to increase ΔE° by limiting any pi-stacking or ion pairing in solution (Fig. 1). Interestingly, when the cyclic voltammetry is repeated in acetone, the separation between the redox waves is hardly discernible, indicating a much smaller comproportionation constant in this solvent possessing a higher dielectric constant. Under these conditions, simulation is needed to derive ΔE° and a K_c value of 28 ± 6 can be found for $1[\text{PF}_6]$ in acetone.

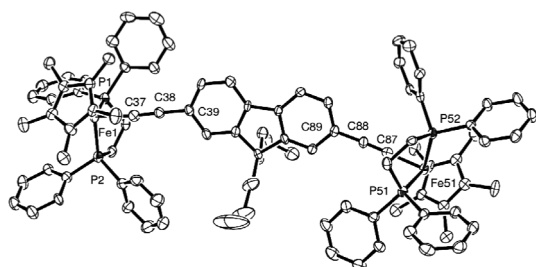


Fig. 1 ORTEP of **1** (50% probability level).

In order to study $1[\text{PF}_6]$ in CH_2Cl_2 , the mixed valent complex was generated after solubilizing equimolar quantities of **1** and $1[\text{PF}_6]_2$ in this solvent.^{27,28} According to the K_c value found, $1[\text{PF}_6]$ will be present in 81% in solution along with 9.5% of **1** and 9.5% of $1[\text{PF}_6]_2$. The infrared spectrum of this medium in the 1900–2000 cm^{-1} range reveals the presence of two new strong $\nu_{\text{Fe}=\text{C}}$'s overlapping the corresponding modes of **1** and $1[\text{PF}_6]_2$ (ESI†). These absorptions, typical of $\text{Fe}(\text{II})-\text{C}\equiv\text{C}$ and a $\text{Fe}(\text{III})-\text{C}\equiv\text{C}$ acetylides, evidence the presence of distinct and localized redox sites in $1[\text{PF}_6]$.²⁹ Also, after thawing an equimolar mixture of **1** and $1[\text{PF}_6]_2$ in $\text{CH}_2\text{Cl}_2/1,2\text{-C}_2\text{H}_4\text{Cl}_2$, a rhombic signal can be detected by ESR at 77 K ($g_1 = 1.983$, $g_2 = 2.035$ and $g_3 = 2.380$). The latter is typical of a low-spin $\text{Fe}(\text{III})$ -centred radical in cationic piano-stool acetylide complexes.³⁰ In accordance with the voltammetric study, these data establish $1[\text{PF}_6]$ as a Class-II MV compound in the classification of Robin and Day.^{31,32}

We next turned our attention to the electronic absorptions of $1[\text{PF}_6]$. In the UV-vis range, the equimolar mixture between **1**

and $1[\text{PF}_6]_2$ reveals a spectrum resembling that of the parent homovalent complexes. However, several among the most intense transitions are shifted relative to these detected for pure **1** and $1[\text{PF}_6]_2$, in line with the presence of $1[\text{PF}_6]$ in the medium. Then, in the near-IR range, an intense and *new* absorption is detected at ca. 5075 cm^{-1} which was absent for pure solutions of **1** and $1[\text{PF}_6]_2$. Actually, **1** is silent in this spectral range, whereas $1[\text{PF}_6]_2$ presents only a very weak absorption at 5423 cm^{-1} ($\epsilon = 410 \text{ M}^{-1} \text{ cm}^{-1}$) corresponding to a forbidden ligand field (LF) transition.^{18,30} The broad absorption at 2000 nm is thus diagnostic of the MV complex $1[\text{PF}_6]$. Considering the energy ($\tilde{\nu}_{\text{max}} = 4995 \text{ cm}^{-1}$) of the maximum, the halfwidth [$(\tilde{\nu}_{1/2})_{\text{exp}} > 6000 \text{ cm}^{-1}$] and also the (non-gaussian) shape of this band (Fig. 2), it cannot correspond to a single intervalence charge transfer (IVCT) band (see eqn (2)) but most likely results from several overlapping sub-bands.

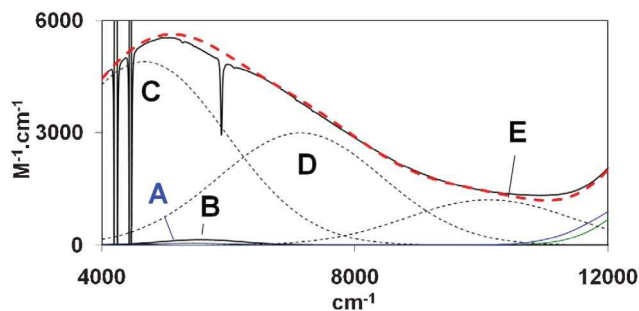


Fig. 2 Near-IR spectra for an equimolar mixture of **1** and $1[\text{PF}_6]_2$ in dichloromethane ($1.3 \times 10^{-4} \text{ M}$ in total) and proposed de-convolution (sub-bands A–E: see text). Apparent extinction coefficients ($0.81 \times \epsilon$) are given in ordinate.

The near-IR band was then deconvoluted into several Gaussian sub-bands (ESI†). One evident contribution (A) corresponds to the weak ligand LF transition of $1[\text{PF}_6]_2$ present in the medium (9.5%), but its impact on the band shape is negligible. Another contribution (B) certainly originates from a similar LF transition taking place on the $\text{Fe}(\text{III})$ site of $1[\text{PF}_6]$.³³ Again this sub-band should not be strongly influencing the band shape of the near-IR transition detected for the MV complex. Actually, (at least) three much more intense contributions need to be considered to properly reproduce the observed band shape (C–E). Notably, three such sub-bands were often considered in near-IR band deconvolutions for related organoiron MV derivatives.^{18,34,35} For MV complexes possessing an unpaired electron on metal d sub-levels lying close in energy to the HOMO-1/HOMO-2 levels, in pseudo-octahedral environments, when a sizable metal–metal interaction is mediated by the bridging ligand, these might be associated with the sought IVCT and two interconfigurational transitions.³⁶ Thus, similarly to what we did with the MV complex $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C}(1,4\text{-C}_6\text{H}_4)\text{C}\equiv\text{CFe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})(3[\text{PF}_6])$,^{18,30} the most intense sub-band at lowest energy (C) was considered to correspond to the IVCT transition. In line with this hypothesis, this sub-band (along with D and E) is hypsochromically shifted when the dichloromethane solvent is changed for a solvent with a higher dielectric constant such as acetone or acetonitrile. This observation allows us to refine further the classification of the $1[\text{PF}_6]$ as a Class-IIA MV complex.

$$(\tilde{\nu}_{1/2})_{\text{theo}} = (2310 \cdot \tilde{\nu}_{\text{max}})^{1/2} \quad (2)$$

$$H_{\text{ab}} = (2.06 \times 10^{-2} / d_{\text{ab}})(\epsilon_{\text{max}} \tilde{\nu}_{\text{max}} \Delta \tilde{\nu}_{1/2})^{1/2} \quad (3)$$

The sub-bands C–E were considered to have similar halfwidths in the deconvolution procedure,³¹ with $\tilde{\nu}_{1/2}$ constrained to remain close to the theoretical value predicted by the Hush theory (eqn (2)).^{37,38} A fair fit can be obtained by this approach (Fig. 2), yielding a sensible reorganisation energy for the IVCT ($\lambda \approx 4670 \text{ cm}^{-1}$; $\tilde{\nu}_{1/2} = 3050 \text{ cm}^{-1}$; $\epsilon = 6050 \text{ M}^{-1} \text{ cm}^{-1}$) and sensible transition energies for the two interconfigurational processes D and E (7140 cm^{-1} and 10100 cm^{-1}).¹⁸

Finally, using the classic Hush equation (eqn (3)), a H_{FeFe} value of ca. 380 cm^{-1} was derived for **1**[PF₆] from the energy, intensity and halfwidth of the sub-band C (IVCT). These electronic couplings are quite important for two metal centres located ca. 16 \AA apart (Fig. 1).^{9,39} This nanoscopic distance outlines further the strong delocalization of the unpaired electron–hole in this organometallic MV compound. In line with established trends,^{25,40} the larger H_{FeFe} value found for **1**[PF₆] relative to **2**[PF₆], confirms our initial belief that the co-planarity of the central aromatic spacer is beneficial to the electronic communication. This rather large H_{FeFe} value found for **1**[PF₆], along with the intensity of its IVCT absorption, is reminiscent of signatures usually observed for more strongly coupled MV complexes (Class-IIB), such as **3**[PF₆] previously mentioned.¹⁸

In conclusion, we have established here that the 2,7-fluorenyl spacer allows us to significantly improve the electronic communication between the $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}]^{n+}$ ($n = 0, 1$) redox-active endgroups compared with the 4,4'-diethynylbiphenyl spacer in the corresponding MV complexes. In dichloromethane, when compared with **2**[PF₆], this translates in a large increase of the comproportionation constant (K_c) of **1**[PF₆] (Scheme 1) and in a smaller improvement (2.6 fold) of the electronic coupling between the redox endgroups. However, according to the H_{FeFe} value(s) found, the end-to-end electron transfer is now clearly adiabatic for **1**[PF₆] ($H_{\text{FeFe}} \geq 200 \text{ cm}^{-1}$),⁴¹ and becomes much faster than in the Class-IIA MV analogue **2**[PF₆].

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