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## Optical electron transfer through 2,7-diethynylfluorene spacers in mixed-valent complexes containing electron-rich $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}$ endgroups.

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Optical electron transfer through 2,7-diethynylfluorene spacers in mixed-valent complexes containing electron-rich “ $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}^{\text{II}}$ ” endgroups†Floriane Malvolti,<sup>a</sup> Cedric Rouxel,<sup>b</sup> Olivier Mongin,<sup>b</sup> Philippe Hapiot,<sup>a</sup> Loic Toupet,<sup>c</sup> Mireille Blanchard-Desce<sup>b</sup> and Frédéric Paul<sup>\*a</sup>

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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  $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C}(2,7\text{-C}_{21}\text{H}_{24})\text{C}\equiv\text{CFe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})][\text{PF}_6]$  ( $1[\text{PF}_6]$ ). The complex is generated *in situ* by comproportionation from its homovalent dinuclear Fe(II) and Fe(III) parents ( $1$  and  $1[\text{PF}_6]_2$ ). 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,<sup>1–6</sup> the understanding of structural features influencing the intramolecular electron transfer has become decisive for optimizing the design of smart molecular-sized devices.<sup>7,8</sup> While electron-transfer through several (hetero)aromatic units has been thoroughly investigated,<sup>9</sup> 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,<sup>10,11</sup> 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.<sup>12,13</sup> 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,<sup>14–17</sup> we recently synthesized the homovalent Fe(II) and Fe(III) compounds  $1$  and  $1[\text{PF}_6]_2$  (Chart 1) featuring the electron-rich “ $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}^{\text{II}}$ ” endgroups.

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

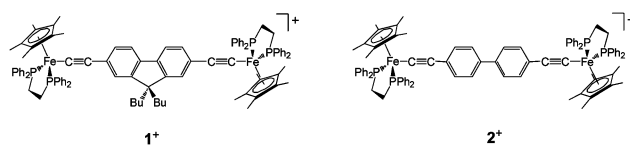
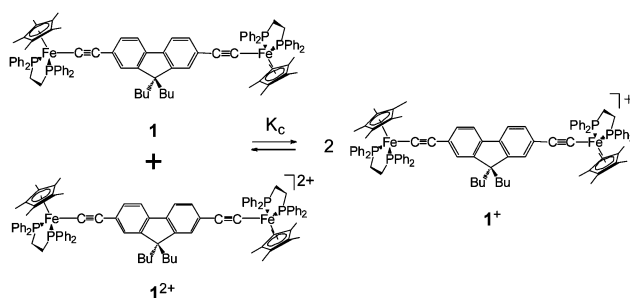


Chart 1

congener of these compounds ( $1[\text{PF}_6]$ ).<sup>1,8</sup> Likewise to its 4,4'-biphenyl analogue ( $2[\text{PF}_6]$ ) previously studied in our group<sup>18</sup> or to other related dinuclear carbon-rich MV derivatives,<sup>7,19–21</sup>  $1[\text{PF}_6]$  certainly constitutes another example of organometallic molecular wire.<sup>8,9</sup> 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  $2[\text{PF}_6]$  in spite of the large intramolecular distance between them (*ca.* 16 Å).<sup>18</sup> The coplanarity of the fluorenyl unit, which should result in a better overlap of its  $\pi$ -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.<sup>22,23</sup> Thus, in order to clearly establish how the electronic coupling is modified when progressing from  $1[\text{PF}_6]$  to  $2[\text{PF}_6]$ , we have decided to experimentally determine  $H_{\text{FeFe}}$  for  $1[\text{PF}_6]$ .

Given that a MV complex is always in equilibrium with its homovalent parents, we first wondered about the thermodynamic stability of  $1[\text{PF}_6]$  in the comproportionation equilibrium (Scheme 1).<sup>24</sup> Based on the well known eqn (1),<sup>25</sup> it was immediately apparent from the cyclic voltammogram of  $1$  (or  $1[\text{PF}_6]_2$ ) that



Scheme 1

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† Electronic supplementary information (ESI) available: Synthesis of  $1$  and  $1[\text{PF}_6]_2$ . CIF file for  $1$ . Simulation procedure of the voltammogram used for  $1$ . UV and IR spectra obtained from equimolar mixtures of  $1$  and  $1[\text{PF}_6]_2$ . 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  $\Delta E^\circ$  value.<sup>26</sup> 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  $76 \pm 8$  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**[PF<sub>6</sub>] (62 mV), in line with a larger electronic interaction taking place between the redox endgroups in **1**[PF<sub>6</sub>], which also translates in a larger stability constant for this MV complex (a  $K_c$  value of 11 had been found for **2**[PF<sub>6</sub>]). While ensuring a good solubility of the compound, the two butyl chains on the fluorene spacer possibly contribute to increase  $\Delta E^\circ$  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  $\Delta E^\circ$  and a  $K_c$  value of  $28 \pm 6$  can be found for **1**[PF<sub>6</sub>] in acetone.

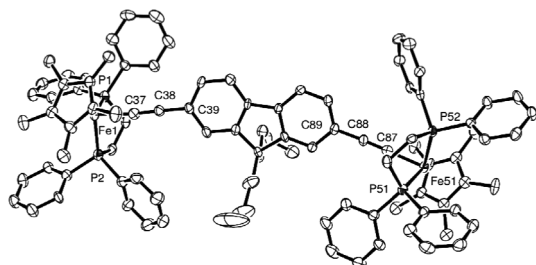


Fig. 1 ORTEP of **1** (50% probability level).

In order to study **1**[PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub>, the mixed valent complex was generated after solubilizing equimolar quantities of **1** and **1**[PF<sub>6</sub>]<sub>2</sub> in this solvent.<sup>27,28</sup> According to the  $K_c$  value found, **1**[PF<sub>6</sub>] will be present in 81% in solution along with 9.5% of **1** and 9.5% of **1**[PF<sub>6</sub>]<sub>2</sub>. The infrared spectrum of this medium in the 1900–2000 cm<sup>−1</sup> range reveals the presence of two new strong  $\nu_{\text{Fe}=\text{C}}$ 's overlapping the corresponding modes of **1** and **1**[PF<sub>6</sub>]<sub>2</sub> (ESI†). These absorptions, typical of Fe(II)–C≡C and a Fe(III)–C≡C acetylides, evidence the presence of distinct and localized redox sites in **1**[PF<sub>6</sub>].<sup>29</sup> Also, after thawing an equimolar mixture of **1** and **1**[PF<sub>6</sub>]<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>/1,2-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>, 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 Fe(III)-centred radical in cationic piano-stool acetylide complexes.<sup>30</sup> In accordance with the voltammetric study, these data establish **1**[PF<sub>6</sub>] as a Class-II MV compound in the classification of Robin and Day.<sup>31,32</sup>

We next turned our attention to the electronic absorptions of **1**[PF<sub>6</sub>]. In the UV-vis range, the equimolar mixture between **1**

and **1**[PF<sub>6</sub>]<sub>2</sub> 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**[PF<sub>6</sub>]<sub>2</sub>, in line with the presence of **1**[PF<sub>6</sub>] in the medium. Then, in the near-IR range, an intense and *new* absorption is detected at ca. 5075 cm<sup>−1</sup> which was absent for pure solutions of **1** and **1**[PF<sub>6</sub>]<sub>2</sub>. Actually, **1** is silent in this spectral range, whereas **1**[PF<sub>6</sub>]<sub>2</sub> presents only a very weak absorption at 5423 cm<sup>−1</sup> ( $\epsilon = 410 \text{ M}^{-1} \text{ cm}^{-1}$ ) corresponding to a forbidden ligand field (LF) transition.<sup>18,30</sup> The broad absorption at 2000 nm is thus diagnostic of the MV complex **1**[PF<sub>6</sub>]. 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.

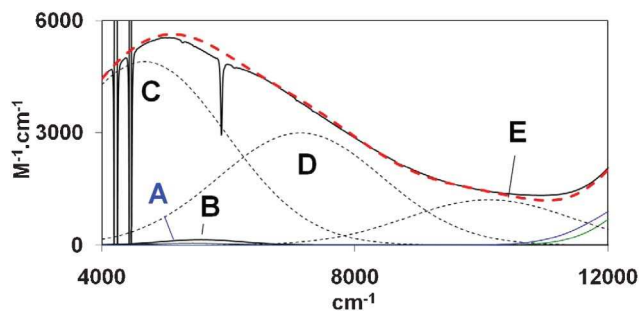


Fig. 2 Near-IR spectra for an equimolar mixture of **1** and **1**[PF<sub>6</sub>]<sub>2</sub> in dichloromethane ( $1.3 \times 10^{-4} \text{ M}$  in total) and proposed de-convolution (sub-bands A–E; see text). Apparent extinction coefficients ( $0.81 \times \epsilon$ ) are given in ordinate.

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**[PF<sub>6</sub>]<sub>2</sub> 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 Fe(III) site of **1**[PF<sub>6</sub>].<sup>33</sup> 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.<sup>18,34,35</sup> 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.<sup>36</sup> Thus, similarly to what we did with the MV complex  $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C}(1,4\text{-C}_6\text{H}_4)\text{C}\equiv\text{CFe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})(\text{3[PF}_6\text{)}]$ ,<sup>18,30</sup> 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**[PF<sub>6</sub>] 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,<sup>31</sup> with  $\tilde{\nu}_{1/2}$  constrained to remain close to the theoretical value predicted by the Hush theory (eqn (2)).<sup>37,38</sup> 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 ( $7140 \text{ cm}^{-1}$  and  $10100 \text{ cm}^{-1}$ ).<sup>18</sup>

Finally, using the classic Hush equation (eqn (3)), a  $H_{\text{FeFe}}$  value of ca.  $380 \text{ cm}^{-1}$  was derived for **1**[PF<sub>6</sub>] from the energy, intensity and halfwidth of the sub-band C (IVCT). These electronic couplings are quite important for two metal centres located ca.  $16 \text{ \AA}$  apart (Fig. 1).<sup>9,39</sup> This nanoscopic distance outlines further the strong delocalization of the unpaired electron–hole in this organometallic MV compound. In line with established trends,<sup>25,40</sup> the larger  $H_{\text{FeFe}}$  value found for **1**[PF<sub>6</sub>] relative to **2**[PF<sub>6</sub>], confirms our initial belief that the co-planarity of the central aromatic spacer is beneficial to the electronic communication. This rather large  $H_{\text{FeFe}}$  value found for **1**[PF<sub>6</sub>], 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**[PF<sub>6</sub>] previously mentioned.<sup>18</sup>

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**[PF<sub>6</sub>], this translates in a large increase of the comproportionation constant ( $K_c$ ) of **1**[PF<sub>6</sub>] (Scheme 1) and in a smaller improvement (2.6 fold) of the electronic coupling between the redox endgroups. However, according to the  $H_{\text{FeFe}}$  value(s) found, the end-to-end electron transfer is now clearly adiabatic for **1**[PF<sub>6</sub>] ( $H_{\text{FeFe}} \geq 200 \text{ cm}^{-1}$ ),<sup>41</sup> and becomes much faster than in the Class-IIA MV analogue **2**[PF<sub>6</sub>].

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