Supporting Information

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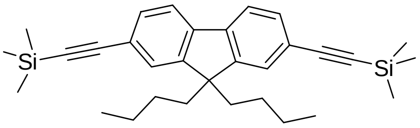
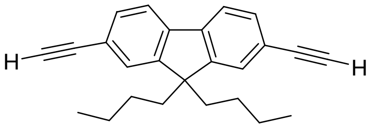
Optical Electron Transfer through 2,7-Diethynylfluorene Spacers in Mixed-Valent Complexes Containing Electron-rich "(η^2-dppe)(η^5-C_5Me_5)Fe" Endgroups

Including:

1. Synthesis of 1 and 1[PF_6]$_2$



Synthesis of 2,7-Bis(trimethylsilylethynyl)-9,9-dibutyl-9*H*-fluorene. Air was removed from a solution of 9,9-dibutyl-2,7-diiodo-9*H*-fluorene (3.0 g, 5.66 mmol) in 30 mL of toluene and 7.5 mL of Et_3N by blowing argon for 20 min. Then CuI (21.6 mg, 0.113 mmol), $Pd(PPh_3)_2Cl_2$ (79.3 mg, 0.113 mmol) and ethynyltrimethylsilane (2.4 mL, 1.67 g, 16.98 mmol) were added, and deaeration was continued for 10 min. Thereafter, the mixture was stirred at 40 °C for 16 h. The solvents were evaporated and the residue was purified by column chromatography (heptane) to yield 2.35 g (88%) of the title compound. Anal. calcd (%) for $C_{31}H_{42}Si_2$ (470.85): C, 79.08, H, 8.99; found: C, 78.88, H, 9.12. HRMS (EI) *m/z* calcd for $C_{31}H_{42}Si_2$ ($M^{+}\cdot$): 470.2825; found: 470.2848. ^1H NMR (200.1 MHz, $CDCl_3$, δ in ppm) 7.64 (d, J = 7.5 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H), 7.46 (s, 2H), 1.98 (m, 4H), 1.08 (m, 4H), 0.69 (t, J = 7.3 Hz, 6H), 0.55 (m, 4H), 0.33 (s, 18H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, δ in ppm) 150.9, 140.9, 131.3, 126.2, 121.8, 119.9, 106.1, 94.3, 55.2, 40.2, 25.8, 23.1, 13.8, 0.1.



Synthesis of 9,9-Dibutyl-2,7-diethynyl-9*H*-fluorene. To a solution of 2,7-bis(trimethylsilylethynyl)-9,9-dibutyl-9*H*-fluorene (1.94 g, 4.12 mmol) in 100 mL of THF/MeOH (3/1) was added 30 mL of aqueous KOH (1 M), and the mixture was stirred at 20 °C for 15 min. Dichloromethane and water were added and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic phases were dried (Na_2SO_4). The residue obtained after removal of the solvents was purified by column chromatography (heptane/ CH_2Cl_2 80:20) to yield 1.26 g (94%) of the title compound. Anal. calcd (%) for $C_{25}H_{26}$ (326.48): C, 91.97; H, 8.03; found: C, 92.17; H, 8.07. HRMS (EI) *m/z* calcd for $C_{25}H_{26}$ ($M^{+}\cdot$): 326.2035; found: 326.2036. ^1H NMR (200.1 MHz, $CDCl_3$, δ in ppm) 7.63 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.46 (s, 2H), 3.15 (s, 2H), 1.94 (m, 4H), 1.07 (m, 4H), 0.67 (t, J = 7.2 Hz, 6H), 0.54 (m, 4H). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, δ in ppm) 151.0, 140.9, 131.2, 126.5, 120.8, 119.9, 84.5, 77.4, 55.1, 40.0, 25.8, 22.9, 13.7.

Synthesis of $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}{\equiv}\text{C}(2,7\text{-C}_{21}\text{H}_{24})\text{C}{\equiv}\text{CFe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})$ (1). In a Schlenk tube 842 mg $\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})\text{Cl}$ (1.3 mmol, 2,0 eq), 220 mg 9,9-dibutyl-2,7-diethynylfluorene (0.83 mmol, 1.0 eq) and 273 mg KPF_6 (1.4 mmol, 2.2 eq) were dissolved in MeOH (30 mL). The solution was stirred and heated to 35 °C overnight. The brown suspension was allowed to settle and was filtrated. The solid was washed with degassed MeOH (2×10 mL) at 0 °C and extracted with CH_2Cl_2. The solvent was removed and the brown solid was dried under vacuum to afford 834 mg of solid which was characterized by NMR as the bis-vinylidene complex $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC=CH}(2,7\text{-C}_{21}\text{H}_{24})\text{HC=CFe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})$. To this solid, 202 mg of ^{t}BuOK (1.6 mmol, 2.5 eq) in THF (30 mL) were added. The solution was stirred for 2 h and the solvent was removed. After extraction with toluene and evaporation of the solvent, the solid was washed with degassed pentane (2×10 mL) and MeOH (10 mL) at 0°C to afford the desired $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}{\equiv}\text{C}(2,7\text{-C}_{21}\text{H}_{24})\text{C}{\equiv}\text{CFe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})$ complex (**1**) as an orange solid (734 mg, 73 %). Anal. Calc for $\text{C}_{97}\text{H}_{102}\text{P}_4\text{Fe}_2$: C, 77.49 H, 6.48; Found: C, 77.51, H 6.86. MS (ESI) m/z calc. for $\text{C}_{97}\text{H}_{102}\text{P}_4\text{Fe}_2$ ($\text{M}^{+\bullet}$): 1502.5631; found: 1502.5641. FT-IR (υ, KBr, cm^{-1}): 2043 (s, C≡C); 1600, (s, Ar). ^{31}P NMR (81 MHz, C_6D_6, δ in ppm): 100.7 (s, P_{dppe}). ^{1}H NMR (200 MHz, C_6D_6, δ in ppm): 8.10 (m, 8H, $H_{\text{o-dppe}}$), 7.53 (d, 2H, $^3J_{\text{H,H}}$ = 7.6 Hz, H_{flu}), 7.30-6.95 (m, 36H, H_{flu} et H_{dppe}), 2.68 (m, 4H, $H_{\text{CH2-dppe}}$), 2.05 (m, 4H, $\text{C}H_{2\text{Bu}}$), 1.82 (m, 4H, $\text{H}_{\text{CH2-dppe}}$), 1.57 (s, 30H, $\text{C}_5(\text{C}H_3)_5$), 1.19 (m, 4H, $\text{C}H_{2\text{Bu}}$), 1.03 (m, 4H, $\text{C}H_{2\text{Bu}}$), 0.70 (t, 6H, $^3J_{\text{H,H}}$ = 6.8 Hz, $\text{C}H_{3\text{Bu}}$). CV (CH_2Cl_2, 0.1 $^n\text{Bu}_4\text{NPF}_6$, 0.1 V.s^{-1}): E° = -0.12, -0.21 V/ECS (ΔE_p = 60 mV, i_{pa}/i_{pc} = 1.0). UV–Vis (CH_2Cl_2, λ_{max}/nm, $\varepsilon/10^3$ $\text{dm}^3.\text{M}^{-1}.\text{cm}^{-1}$): 264 (sh, 35.5), 300 (sh, 26.7), 450 (37.4).

Synthesis of $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}{\equiv}\text{C}(2,7\text{-C}_{21}\text{H}_{24})\text{C}{\equiv}\text{CFe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})][\text{PF}_6]_2$ (1[PF$_6$]$_2$). In a Schlenk tube, $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}{\equiv}\text{C}(2,7\text{-C}_{21}\text{H}_{24})\text{C}{\equiv}\text{CFe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})$ (200 mg, 0.13 mmol) and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}][\text{PF}_6]$ (88 mg ,0.27 mmol, 2 eq) were solubilized in CH_2Cl_2 (15 mL) and the solution was stirred for 2 h. After partial removal of the solvent (to *ca.* 5 mL), pentane (60 mL) was added and the solvents were filtrated. The residue was then washed with thoroughly degassed toluene (2×2 mL) and pentane (2 mL) at 0 °C to obtain the desired $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}{\equiv}\text{C}(2,7\text{-C}_{21}\text{H}_{24})\text{C}{\equiv}\text{CFe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})][\text{PF}_6]_2$ dication (**1**[PF$_6$]$_2$) as a dark green solid (188 mg, 80 %). FT-IR (υ, KBr, cm^{-1}): 1980 (s, C≡C), 1585 (w, Ar), 839 (vs, PF_6^-). UV–Vis–Near-IR (CH_2Cl_2, λ_{max}/nm, $\varepsilon/10^3$ $\text{dm}^3.\text{M}^{-1}.\text{cm}^{-1}$): 270 (sh, 37.4), 344 (27.7), 496 (8.9), 630 (3.0), 772 (13.7), 820 (sh, 10.7), 1844 (0.4).

2. Details about Cyclic Voltammetry Experiments and Simulation Procedure

Cyclic voltammograms were recorded for the oxidation of the dinuclear complex **1**. This compound exhibits two overlapping single-electron reversible waves. It is noticeable that the difference is larger in CH_2Cl_2 than in acetone in agreement with a lower dielectric constant of the solvent in the first case. In a situation where the two electron processes overlap as in the case of **1** in acetone, the determination of the two standard potentials E^0_1 and E^0_2 can be derived from the half-sum between the anodic and cathodic peaks and the peak-to-peak potential difference (ΔE_p). Comparison with tabulated working curves or with numerical simulations provides the corresponding ΔE^0 differences.[1] These simplified treatments require that the kinetics of the electron transfer processes do not affect the cyclic voltammetric response. The measurement also demands an exact compensation of the residual ohmic drop of the working electrode that was obtained using a home-made potentiostat as previously described.[2] We checked that these two conditions were obeyed by examining the variations of ΔE_p as a function of the scan rate and found only negligible variations for scan rates below 1 $V.s^{-1}$.[1,2] ΔE_p tends towards a limit (113-115 mV in CH_2Cl_2 and 90-94 mV in acetone) that corresponds to the thermodynamics of the electron transfer processes which leads to differences of $\Delta E^0 = 111$ mV and 84 mV in CH_2Cl_2 and in acetone, respectively. It is also noticeable that the small variations of ΔE_p with the scan rate ($<$ 1 $V.s^{-1}$) show that the electron transfer kinetics are relatively fast, and thus, that the reorganization energies associated with the change of the redox state are small, as expected from previous work on related compounds.[2,3] The agreement between experimental and simulated curves was then checked by full simulations of the voltammograms in CH_2Cl_2 (Fig. 1) and acetone (Fig. S1), using the DigiElch 4.x software[4] and the E^0 values previously derived. Capacitance background current was added in simulations for easier comparison.

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[1] Hapiot, P.; Kispert, L; Konovalov, VV; Savéant. J.-M. *J.Am.Chem.Soc*. **2001**, *123*, 6669-6677.

[2] Andrieux, C.P.; Hapiot, P.; Savéant, J.-M. *Chem. Rev*. **1990**, *90*, 723-738.

[3] S. Ibn Ghazala, F. Paul, L. Toupet, T. Roisnel, P. Hapiot and C. Lapinte, *J. Am. Chem. Soc.*, 2006, **128**, 2463-2476.

[4] ElchSoft. http://www.elchsoft.com/. (b) Rudolph, M. *J. Comp. Chem.* **2005**, *26*, 633 and references therein.

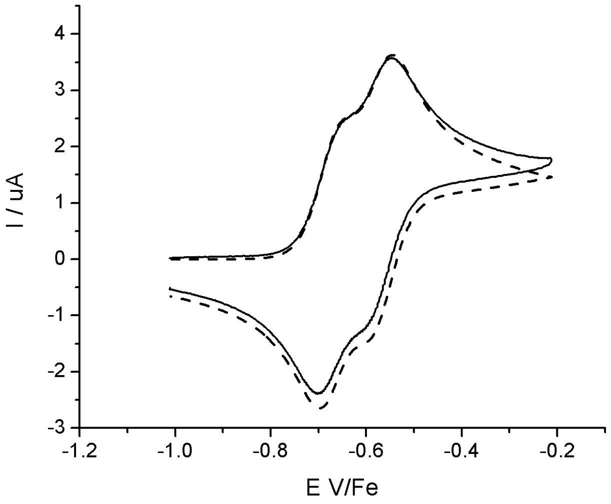

Figure S1a. Voltammograms of **1** in CH_2Cl_2 (TBAH, 0.2 M; 25°C) on a 1 mm-diameter gold disk electrode. Experimental (plain line) and simulated (dotted line) Scan rate 0.2 V.s^{-1}.

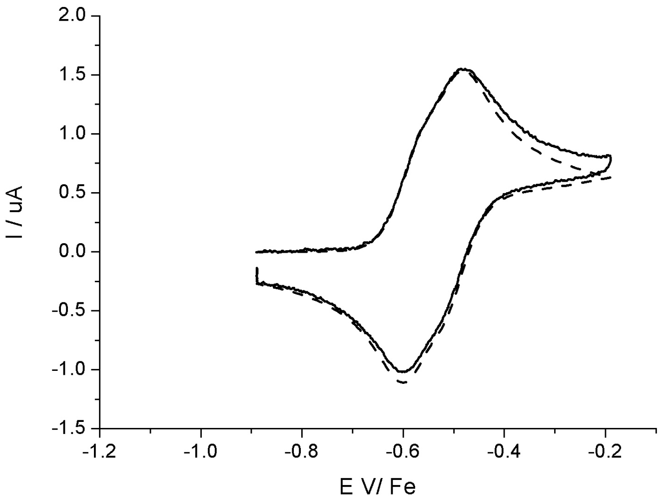

Figure S1b. Voltammograms of **1** in acetone (TBAH, 0.2 M; 25°C) on a 1 mm-diameter gold disk electrode. Experimental (plain line) and simulated (dotted line) Scan rate 0.2 V.s^{-1}.

3. UV, IR and NIR Spectra obtained from Equimolar Mixtures of 1 and 1[PF$_6$]$_2$

***Preparation of the Mixture containing* 1[PF$_6$].** Equimolar amounts of the complexes **1** (33.5 mg) and **1**[PF$_6$]$_2$ (40 mg) were admixed in dichloromethane (50 mL) and stirred for 15 mn at 20° C, the solution was then evaporated to dryness and the resulting solid crushed. This solid was subsequently dissolved in the desired solvent and considered as being "**1**[PF$_6$]".

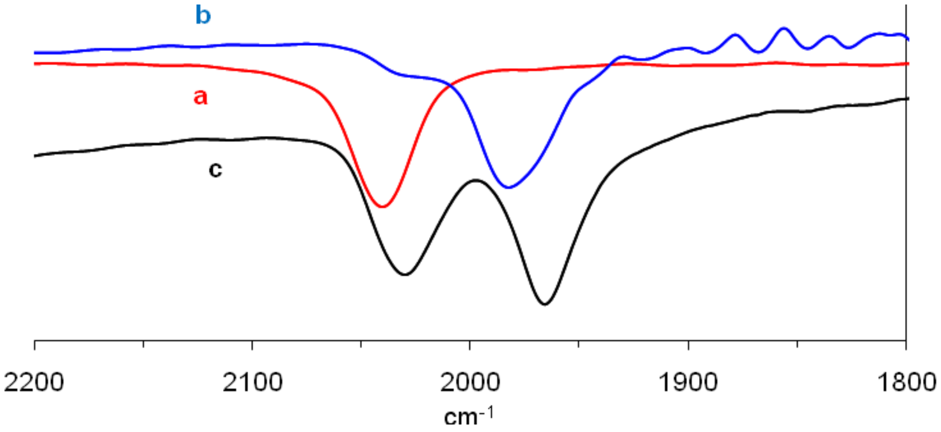

Figure S2. Infrared spectra of **1** (a) and **1**[PF$_6$]$_2$ (b) complexes and of an equimolar mixture of **1** and **1**[PF$_6$]$_2$ (c) in dichloromethane (KBr window).

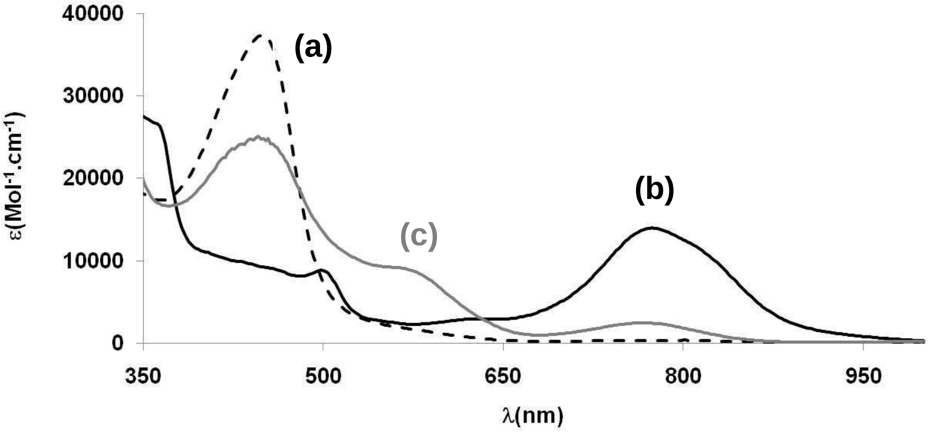

Figure S3. UV-vis spectra of **1** (a) and **1**[PF$_6$]$_2$ (b) complexes and of an equimolar mixture of **1** and **1**[PF$_6$]$_2$ (c) in dichloromethane.

4. Solvatochromy and Deconvolution of the Near-IR Absorption

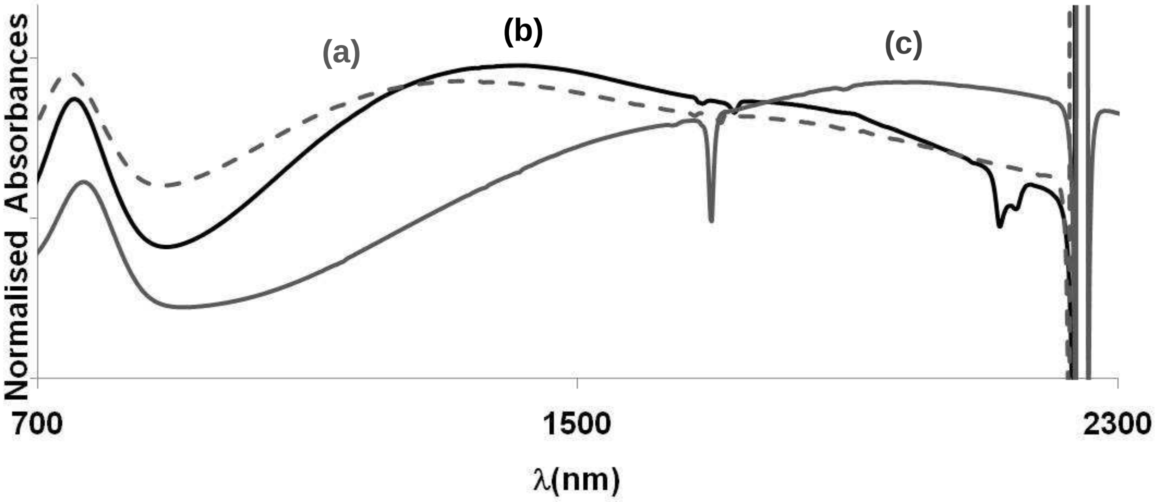

Figure S4. Equimolar Mixture of **1** and **1**[PF_6]$_2$ in Acetonitrile (Dotted Gray Line; a)**,** in Acetone (Plain Dark Line; b) and in Dichloromethane (Plain Grey Line; c).

Table S1. Near-IR Data for **1**[PF$_6$] in Dichloromethane and Acetone (Classical Treatment)

Solvent	Band	$\bar{\nu}_{max}$ in cm^{-1} [a] (ε in M^{-1} cm^{-1}) [b]	$(\bar{\nu}_{1/2})_{exp}$ (cm^{-1}) [a]	d_{ab} (Å) [c]	$(\bar{\nu}_{1/2})_{theo}$ (cm^{-1}), [d]	H_{ab} (cm^{-1}) [a,e]
Dichloromethane	B	5570 (170)	1500	/	3590	/
	C	4670 (6050)	3050	15.9	3280	380
	D	7140 (3770)	3050	/	4060	/
	E	10120 (1490)	3050	/	4830	/

[a] Values ± 25 cm^{-1}. [b] Values ± 10 M^{-1}.cm^{-1}. [c] Evaluated from X-ray structure of **1**. [d] Calculated following equation 2. [e] Calculated following equation 3.

Note that the much higher intensities of the sub-bands C-E preclude an accurate simulation of the "forbidden" LF transition that should be present for **1**[PF$_6$] near 5500 cm^{-1} (B), since it is fully “buried” in the near-IR band. According to previous investigations with mononuclear Fe(III) model complexes these LF transitions should take place near ca. 2500 cm^{-1} and 5000 cm^{-1} and are significantly narrower than IVCT bands ($\nu_{½} \approx$ 1500 cm^{-1}). The present deconvolution was obtained considering this process at 5500 cm^{-1}.