Supporting Information

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

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Concepció Rovira and Jean-François Nierengarten**

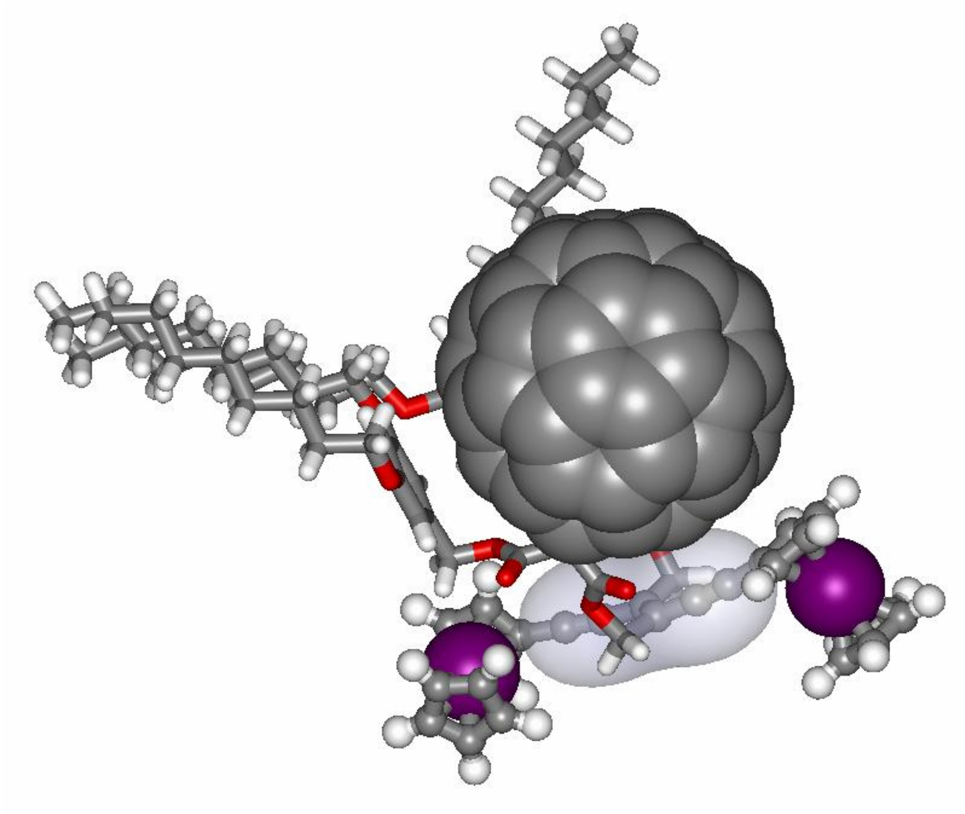


Figure S1A. Calculated structure of compound **1** (molecular modeling performed with Spartan at the PM3 level). The dodecyl chains have been replaced by octyl chains in the calculations.

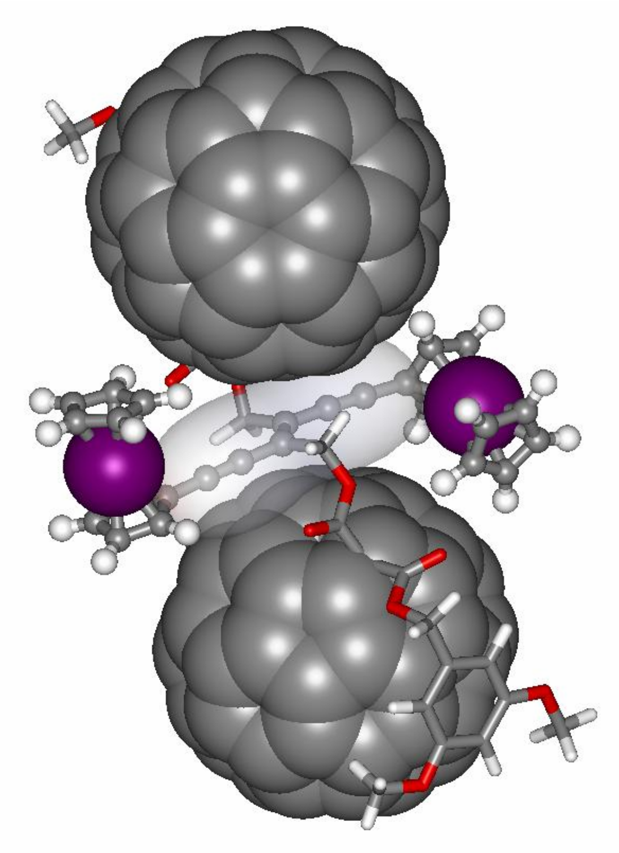


Figure S1B. Calculated structure of compound **2** (molecular modeling performed with Spartan at the PM3 level). The dodecyl chains have been replaced by methyl groups in the calculations.

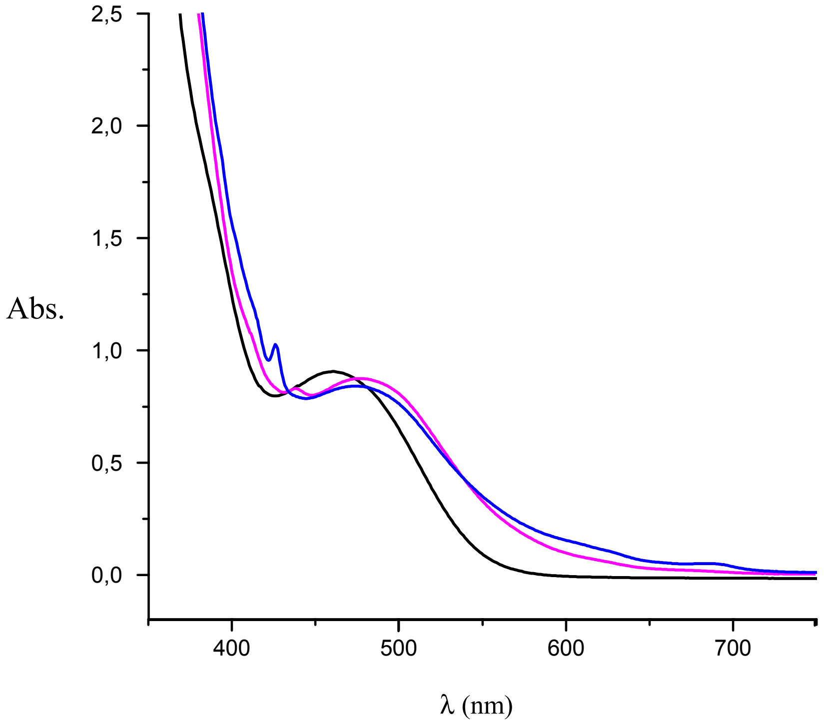


Figure S2. UV/vis spectra of CH_2Cl_2 solutions of compounds **1** (magenta), **2** (blue) and **3** (black).

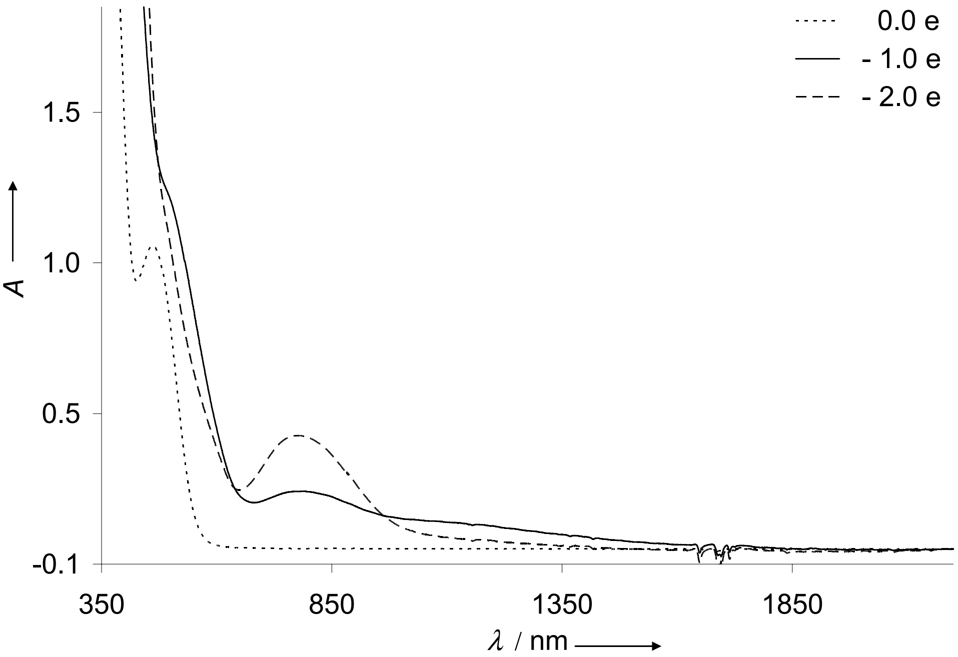


Figure S3. Vis-NIR spectra of compound **3**, $\mathbf{3}^{+}$ and $\mathbf{3}^{2+}$ in dichloromethane with 0.15 M [(*n*-Bu$_4$)N]PF$_6$.

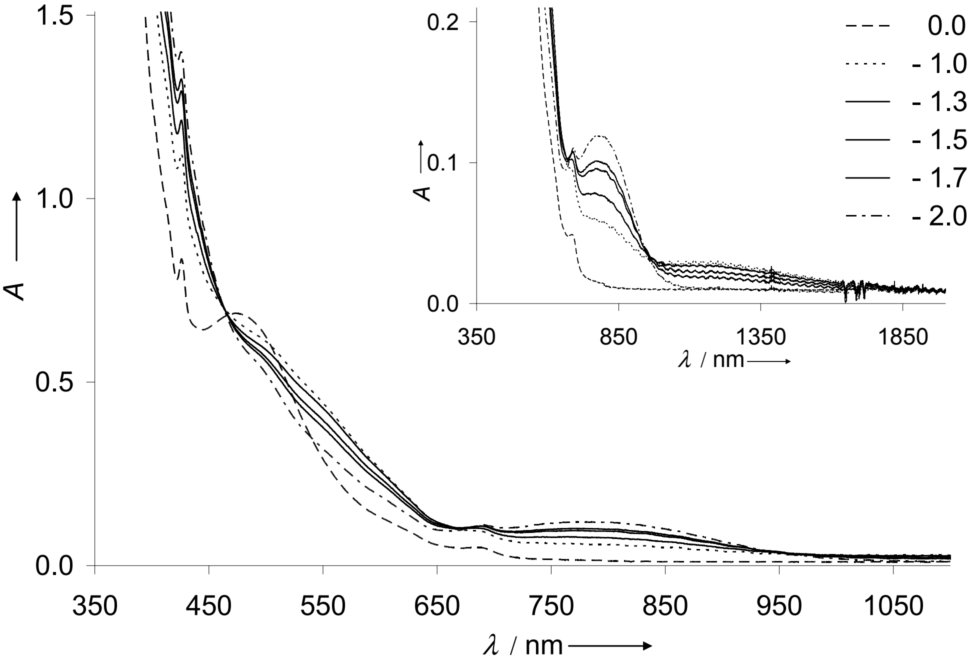


Figure S4. Vis-NIR spectra of compound **2** (dashed line) and the evolution of the spectra during the course of the oxidation process from the mixed valence species $\mathbf{2}^{+}$ (dotted line) to $\mathbf{2}^{2+}$ (dashed-dotted line) in dichloromethane with 0.15 M [(n-Bu$_4$)N]PF$_6$.

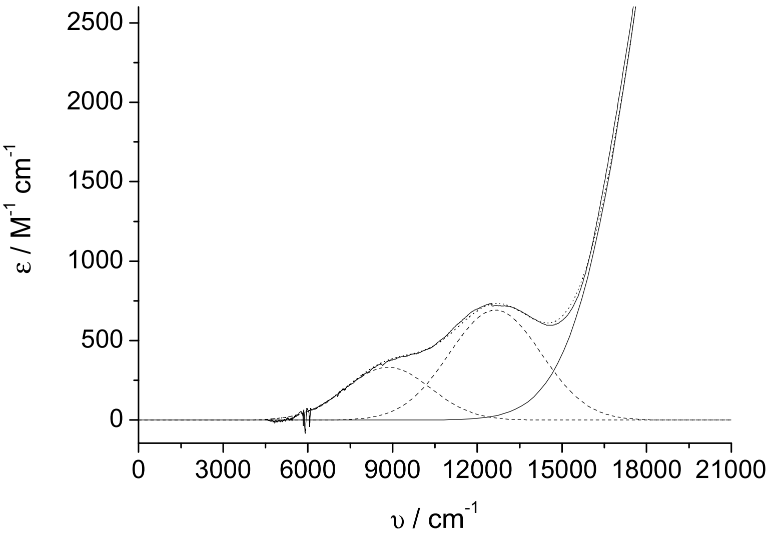


Figure S5. Deconvolution of the NIR spectrum of the mixed valence species derived from **3**$^+$.

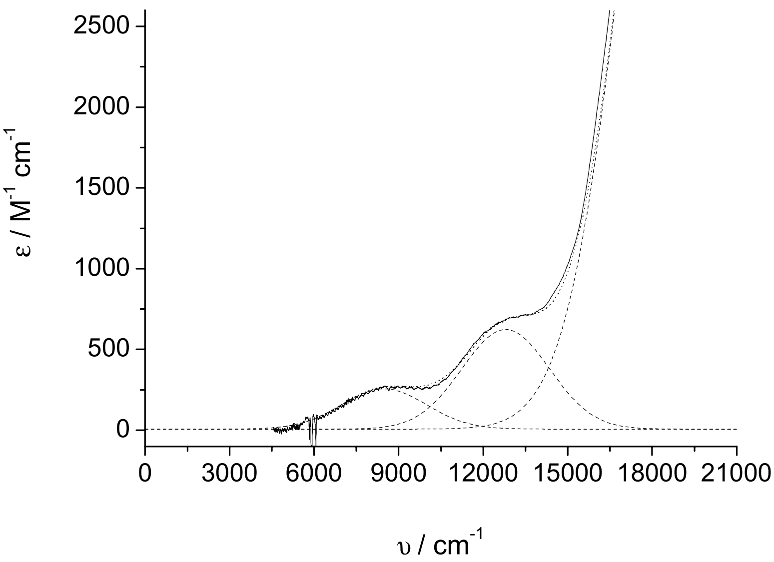


Figure S6. Deconvolution of the NIR spectrum of the mixed valence species derived from $\mathbf{1}^+$.

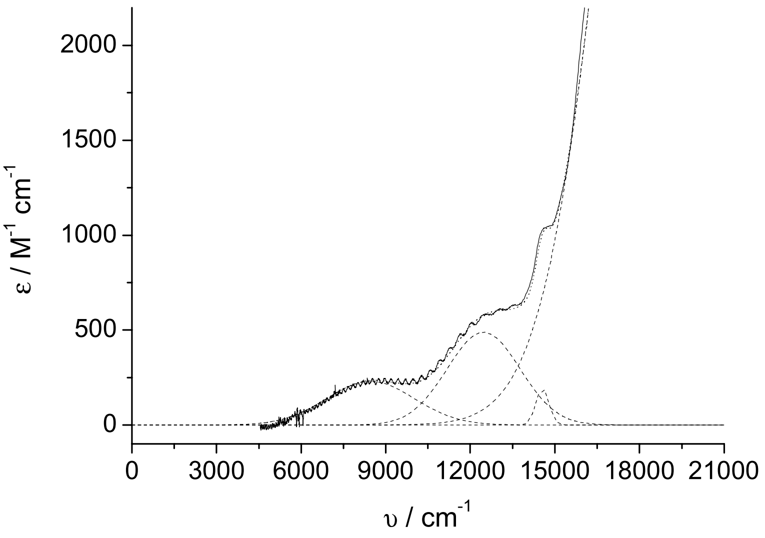


Figure S7. Deconvolution of the NIR spectrum of the mixed valence species derived from **2**$^+$.

Table S1. UV/Vis data of compounds **1-3** in dichloromethane, and $\mathbf{1}^{+}$-$\mathbf{3}^{+}$ and $\mathbf{1}^{2+}$-$\mathbf{3}^{2+}$ in dichloromethane with 0.15 M [(*n*-Bu$_4$)N]PF$_6$.

Compound	λ_{max} / nm (ε/ M^{-1} cm^{-1})
3	382 (sh), 464 (4301)
$\mathbf{3}^{+}$	494 (5050), 791 (820), 1131 (370)
$\mathbf{3}^{2+}$	503 (sh), 785 (1610)
1	323 (11996), 437 (6428), 478 (6802), 614 (sh), 644 (276), 676 (149)
$\mathbf{1}^{+}$	436 (10529), 550 (sh), 686 (992), 781 (670), 1179 (268)
$\mathbf{1}^{2+}$	436 (12890), 555 (sh), 781 (1232)
2	328 (91620), 426 (9541), 476 (7793), 616 (sh), 644 (599), 687 (411)
$\mathbf{2}^{+}$	426 (12952), 501 (6955), 547 (sh), 686 (992), 802 (560), 1182 (215)
$\mathbf{2}^{2+}$	426 (16172), 498 (6044), 559 (sh), 686 (1147), 798 (1255)

Table S2. Calculated V_{ab} values for compounds $\mathbf{1}^+$-$\mathbf{3}^+$ using Hush or Mulliken-Hush equations.

Compound	V_{ab}/cm^{-1}	
	Hush	**Mulliken-Hush**
$\mathbf{1}^+$	209	150
$\mathbf{2}^+$	199	145
$\mathbf{3}^+$	263	177

Hush equation: $V_{ab} = \left[2.05\times10^{-2}\sqrt{\varepsilon_{max}\,\tilde{\nu}_{max}\,\Delta\tilde{\nu}_{1/2}}\right]R^{-1}$

Mulliken-Hush equations:

$$V_{ab} = \frac{\mu_{eg}\cdot\tilde{\nu}_{max}}{\Delta\mu_{ab}} \qquad (1)$$

$$\mu_{eg} = 0.09584\sqrt{\frac{\int\varepsilon(\tilde{\nu})\mathrm{d}\tilde{\nu}}{\tilde{\nu}_{max}}} \qquad (2)$$

$$\Delta\mu_{ab} = \sqrt{\Delta\mu_{eg}{}^2 + 4\mu_{eg}{}^2} \qquad (3)$$

In equation 1 $\tilde{\nu}_{max}$ is the energy of the electronic transition, μ_{eg} is the transition moment of the IV-CT band which can be calculated by eq 2, and $\Delta\mu_{ab}$ is the diabatic dipole moment difference which can be traced back to purely quantities by eq 3 where $\Delta\mu_{eg} = \mu_e$-μ_g is the adiabatic dipole moment difference.

Experimental Section

The cyclic voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100. Experiments were performed at room temperature in an homemade airtight three–electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca 1cm² apparent surface. The working electrode was a Pt microdisk (0.5mm diameter). The supporting electrolyte $[nBu_4N][BF_4]$ (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled over CaH_2 prior to use. The solutions used during the electrochemical studies were typically 10^{-3} M in complex compound and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230). Under these experimental conditions, Fc+/Fc is observed at +0.54 ± 0.01 V *vs*. SCE

Oxidations were performed by electrolysis in a three-electrode cell under argon using dry CH_2Cl_2 as a solvent and 0.15 M $[(n\text{-Bu})_4N]PF_6$ as supporting electrolyte. The progress of the oxidation was followed chronoamperometrycally by 263A of EG&PAR potenciostat-galvanostat. The reference electrode ($Ag/AgNO_3$) and the counter electrode were separately immersed in the solvent containing the supporting electrolyte and isolated from the bulk solution by a glass fit. The working electrode was a platinum grid. UV-vis-near IR absorption spectra were regularly recorded by transferring a small aliquot of the solution contained in the electrochemical cell into a UV quartz cell for different average number of removed electrons. UV-Vis-Near IR spectra were recorded on a Varian Cary 5 E spectrophotometer.

Synthesis

General. All reagents were used as purchased from commercial sources without further purification. Solvents were dried using standard techniques prior to use. All reactions were performed in standard glassware under an inert argon atmosphere. Evaporation was done using water aspirator and drying *in vacuo* at 10^{-2} Torr. Column chromatography: Merck silica gel 60, 40-63 μm (230-400 mesh). TLC: Precoated glass sheets with silica gel 60 F_{254} (Merck), visualization by UV light. Melting points were determined on an Electrothermal Digital Melting Point apparatus and are uncorrected. UV/Vis spectra (λ_{max} in nm (ε)) were measured on a Hitachi U-3000 spectrophotometer. IR spectra (cm^{-1}) were determined on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AM 300 (300 MHz) with solvent signal as reference. FAB-mass spectra (m/z; % relative intensity) were taken on a *ZA HF* instrument with 4-nitrobenzyl alcohol as matrix. MALDI-TOF mass spectra were taken on a Brucker BIFLEX^{TM} matrix-assisted laser desorption time-of-flight mass spectrometer (MALD-TOF) equipped with the SCOUT^{TM} High Resolution Optics with a X-Y multi-sample probe and a gridless reflector, a saturated solution of 1, 8, 9-trihydroxyanthracene (dithranol ALDRICH EC: 214-538-0) in CH_2Cl_2 was used as a matrix.

Compound **3**. DCC (97 mg, 0.48 mmol) was added to a solution of **4** (100 mg, 0.2 mmol), AcOH (0.03 mL, 0.44 mmol), HOBt (12 mg, 0.08 mmol) and DMAP (10 mg, 0.08 mmol) in CH_2Cl_2 (20 mL) at 0 °C under argon. The mixture was stirred for 12 h, filtered through a celite pad and concentrated. Column chromatography (SiO_2, hexane/CH_2Cl_2 1:1) yielded **3** (0.1 g, 83%) as an orange powder. ^1H NMR (300 MHz, $CDCl_3$): 4.99 (s, 4 H), 4.47 (m, 4 H), 4.28 (m, 4 H), 4.23 (s, 10 H), 2.18 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): 170.64, 125.96, 101.84, 81.93, 71.54, 70.11, 69.39, 64.40, 64.10, 20.95. Anal. calcd for $C_{32}H_{28}O_4Fe_2.H_2O$: C 63.4, H 5.0. Found: C 63.9, H 4.7. FAB-MS: 588.1 ($[M]^+$; calcd. for $C_{32}H_{28}O_4Fe_2$ 588.07).

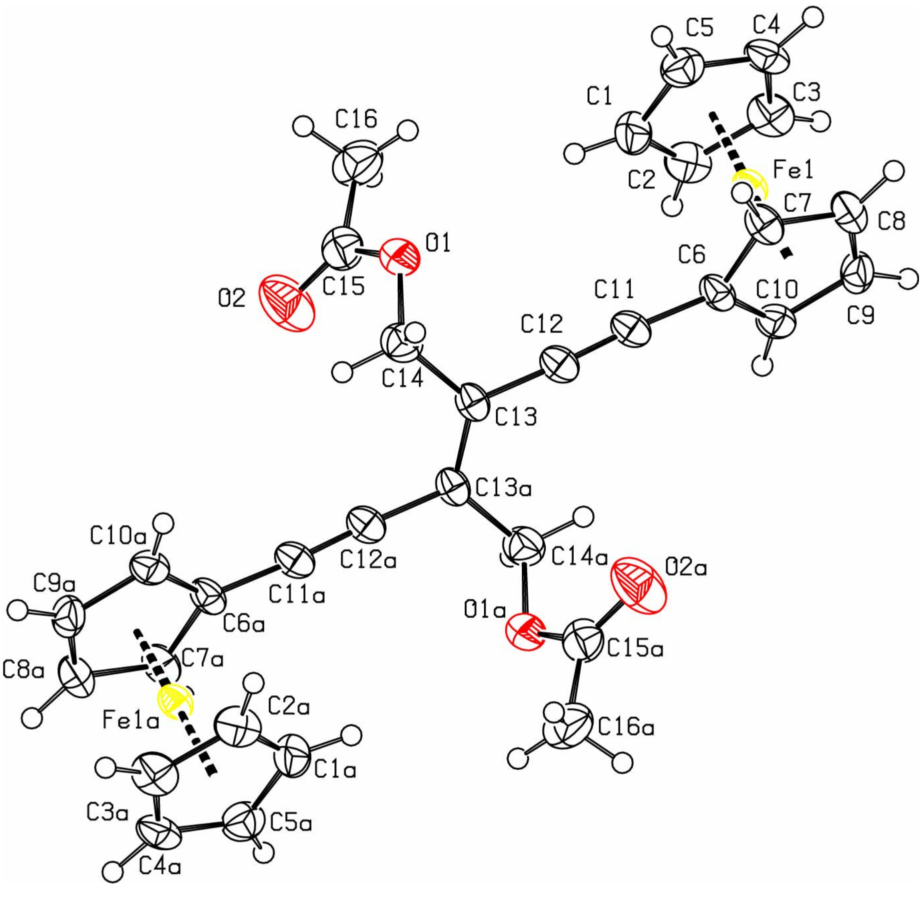
Compound **6**. DCC (0.21 g, 1.06 mmol) was added to a solution of **4** (0.22 g, 0.44 mmol), **5** (0.54 g, 0.96 mmol), and DMAP (21 mg, 0.17 mmol) in CH_2Cl_2 (30 mL) at 0 °C under argon. The mixture was stirred for 12 h, filtered through a celite pad and concentrated. Column chromatography (SiO_2, CH_2Cl_2/hexane 3:2) yielded **6** (0.3 g, 44%) as an orange glassy product. ^{1}H NMR (300 MHz, $CDCl_3$): 6.47 (d, *J* = 2Hz, 4 H), 6.40 (t, *J* = 2Hz, 2 H), 5.10 (s, 4 H), 5.06 (s, 4 H), 4.47 (m, 4 H), 4.26 (m, 4 H), 4.21 (s, 10 H), 3.91 (t, *J* = 6Hz, 8 H), 3.55 (s, 4 H), 1.75 (m, 8 H), 1.43-1.21 (m, 72 H), 0.88 (t, *J* = 7Hz, 12 H).

Compound **1**. DBU (0.1 mL, 0.68 mmol) was added to a solution of C_{60} (0.12 g, 0.17 mmol), I_2 (94 mg, 0.37 mmol) and **6** (0.27 g, 0.17 mmol) in toluene (250 mL) at room temperature under argon. The solution was stirred for 12 h, filtered through a short plug of SiO_2 and concentrated. Column chromatography (SiO_2, CH_2Cl_2/hexane 1:1) yielded **1** (0.12 g, 31%) as a dark orange glassy product. ^{1}H NMR (300 MHz, $CDCl_3$): 6.45 (d, *J* = 2Hz, 2 H), 6.43 (d, *J* = 2Hz, 2 H), 6.34 (t, *J* = 2Hz, 1 H), 6.33 (t, *J* = 2Hz, 1 H), 6.07 (d, *J* = 10Hz, 1 H), 5.41-5.15 (m, 6 H), 4.74 (d, *J* = 10Hz, 1 H), 4.63 (m, 2 H), 4.53 (m, 1 H), 4.49 (m, 1 H), 4.34 (s, 5 H), 4.31 (m, 2 H), 4.25 (s, 5 H), 4.21 (m, 2 H), 3.83 (t, *J* = 6Hz, 8 H), 1.71 (m, 8 H), 1.43-1.27 (m, 72 H), 0.89 (t, *J* = 7Hz, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.59, 162.52, 162.35, 161.97, 160.34, 148.71, 148.26, 147.41, 147.35, 147.23, 146.02, 145.85, 145.79, 145.70, 145.68, 145.63, 145.49, 145.35, 145.11, 144.98, 144.93, 144.50, 144.45, 144.40, 144.15, 144.06, 143.76, 143.60, 143.63, 143.55, 143.50, 143.06, 143.03, 142.77, 142.42, 142.37, 141.04, 140.41, 140.26, 137.83, 136.73, 136.57, 136.00, 135.93, 135.22, 128.22, 127.60, 106.90, 106.82, 103.42, 103.32, 101.49, 101.45, 84.78, 83.52, 83.41, 77.20, 72.03, 71.80, 71.74, 70.42, 70.23, 69.62, 69.56, 69.52, 69.46, 68.44, 68.05, 67.31, 67.19, 67.05, 64.12, 64.06, 31.93, 29.71, 29.64, 29.45, 29.37, 29.26, 26.10, 22.70, 14.14. Anal. calcd for $C_{156}H_{132}O_{12}Fe_2$: C 81.1, H 5.8. Found: C 81.1, H 6.1. MALDI-MS: 2309.81 ($[MH]^+$; calcd. for $C_{156}H_{133}O_{12}Fe_2$ 2309.85).

Compound **2**. DBU (0.1 mL, 0.68 mmol) was added to a solution of C_{60} (0.24 g, 0.34 mmol), I_2 (94 mg, 0.37 mmol) and **6** (0.27 g, 0.17 mmol) in toluene (250 mL) at room temperature under argon. The solution was stirred for 12 h, filtered through a short plug of SiO_2 and concentrated. Column chromatography (SiO_2, CH_2Cl_2/hexane 1:1) and after a GPC column (CH_2Cl_2) yielded **2** (0.25 g, 49%) as a brown glassy product. ^1H NMR (300 MHz, $CDCl_3$): 6.53 (d, J = 2Hz, 4 H), 6.37 (t, J = 2Hz, 2 H), 5.45 (s, 4 H), 5.42 (s, 4 H), 4.61 (m, 4 H), 4.29 (m, 14 H), 3.85 (t, J = 6Hz, 8 H), 1.72 (m, 8 H), 1.43-1.26 (m, 72 H), 0.89 (t, J = 7Hz, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$): 163.29, 163.26, 160.40, 145.41, 145.21, 145.17, 145.13, 145.10, 145.05, 144.96, 144.81, 144.69, 144.57, 144.53, 144.36, 143.80, 143.74, 142.97, 142.92, 142.77, 142.14, 142.10, 141.86, 141.78, 140.78, 140.70, 140.05, 138.17, 136.61, 125.59, 107.23, 103.88, 101.76, 72.15, 71.41, 70.50, 69.86, 69.05, 68.09, 31.92, 29.70, 29.64, 29.47, 29.36, 29.29, 26.15, 22.69, 14.13. Anal. calcd for $C_{216}H_{132}O_{12}Fe_2.CH_2Cl_2$: C 83.6, H 4.3. Found: C 83.6, H 4.6. MALDI-MS: 2311.61 (95, $[M-C_{60}]^+$, calcd. for $C_{156}H_{132}O_{12}Fe_2$ 2311.04), 3031.57 (100, $[M]^+$, calcd for $C_{216}H_{132}O_{12}Fe_2$ 3031.04).

X-ray crystal structure of 3.

Single crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **3**. A crystal was mounted on a Nonius Kappa-CCD area detector diffractometer ($Mo\ K\alpha\ \lambda$ = 0.71073 Å). The complete conditions of data collection (Denzo software) and structure refinements are given below. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structure was solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software.[1] The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereo-chemistry and refined using a riding model in SHELXL97.



Orange-red crystal; crystal dimension : 0.10×0.08×0.07 mm^3; $C_{32}H_{28}Fe_2O_4$, M = 588.24 g.mol^{-1}; triclinic; space groupe 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; $1.71° < \theta < 30.12°$, 7706 independent reflections with 4332 having $I > 2\sigma(I)$; 332 parameters; Final results :

$R_1(F^2)$ = 0.0534; $wR_2(F^2)$ = 0.1594, Goof = 0.99, maximum residual electronic density = 0.778 $e^-.Å^{-3}$.

Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication n° CCDC-624690. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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1) Sheldrick, G.M., SHELXL97, University of Göttingen, Germany, **1997**.