

Selective functionalisation of Re_6 Cluster Anionic Units ($\text{Q} = \text{S}, \text{Se}$): From Hexa-Hydroxo $[\text{Re}_6\text{Q}_8(\text{OH})_6]^{2-}$ to neutral *Trans*- $[\text{Re}_6\text{Q}_8\text{L}_4\text{L}'_2]$ Hybrid Building Blocks.

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Experimental section

Cyclic voltammetry measurements were carried out with a Potentiostat eDAQ instrument. A single-compartment voltammetric cell was equipped with a platinum working electrode, a platinum wire auxiliary electrode and a SCE reference. The experiments were performed using (n-Bu₄N)PF₆ (0.2M or 0.1M) as supporting electrolyte in dry and deoxygenated CH₂Cl₂ under argon atmosphere at room temperature at 100 mV.s⁻¹. IR spectra were recorded on KBr pellets with a Bruker Equinox 55 FTIR spectrometer. UV–Vis absorption measurements were performed on a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Luminescence spectra were recorded on a Fluorolog-3™ fluorescence spectrometer (FL3-22, Horiba Jobin Yvon). Elemental Analysis were performed in the CRMPO with a Microanalyser Flash EA1112 CHNS/O Thermo Electron. NMR spectra were recorded on a Bruker Avance 300P. All peaks were referenced to the methyl signals of TMS at $\delta = 0$ ppm. Single crystals suitable for X-Ray analysis were obtained for compounds **1**_{a,b} by slow evaporation of a concentrated solution of **1**_{a,b} dissolved in dichloromethane. In the case of compounds **2**_{a,b}, single crystals were obtained by gas diffusion of ether in a solution of **2**_{a,b} dissolved in dichloromethane.

KER determination

MS analyses were performed on a JMS-700 (JEOL LTD, Akishima, Tokyo, Japan) double focusing mass spectrometer with reversed geometry. Fast atom bombardment (FAB) was used as ionization method in positive ion mode with 3-nitrobenzylalcohol (Sigma-Aldrich) as matrix. A 2 μ L matrix of the matrix solution containing the functionalized cluster was directly deposited onto the FAB target maintained on direct insertion probe. The sample was introduced into the ion source of the mass spectrometer and irradiated with a xenon gun at a 5 keV energy and a emission current of 10.6 mA. The source pressure was kept at $2 \cdot 10^{-5}$ Torr with a 32°C source temperature. A 10 kV acceleration voltage was applied. The high-resolution mass spectra (typically $R = 6000$ at 10% valley definition) were measured by electric-field scan. Cesium Iodide (CSI) was used for the calibration of the different scan modes. To obtain good signal-to-

noise ratio, were determined averaging a large number of scans (in 2-5 min overall acquisition time) in a narrow energy-window.

Refine_special_details on structure 1a: $\text{Re}_6\text{S}_8(\text{TBP})_4(\text{OH})_2$

CCDC695751; formula: C36 H54 N4 O2 Re6 S8

The structure contains large accessible voids. Contrary to the Se homologous, the SQUEEZE procedure was not used owing to satisfactory low remaining density peaks after refinements. However, some solvent molecules must be highly disordered in the voids since single crystals collapse when they are removed from the solvent and left on air. Thus the data collection was carried out at low temperature (100K). H from hydroxyl group of the asymmetric unit was not generated owing to the sp^3 hybridization of O that implies a random distribution of H atoms on several positions. These positions are located on the circle that can be generated according to a rotation of a OH group around the Re-O bonds. The methyl carbon atoms of tert-butyl groups were each splitted over two positions (50%-50%) and were refined isotropically with a same atomic displacement parameter.

Refine_special_details on structure 1b: $\text{Re}_6\text{Se}_8(\text{TBP})_4(\text{OH})_2$

CCDC695751; formula C36 H54 N4 O2 Re6 Se8

The structure contains large accessible voids. Indeed, a squeeze procedure has been used in order to remove electronic density peaks from solvent molecules. H atoms from tert-butyl pyridine moieties were located using idealized geometry and were refined using riding model. H from hydroxyl group of the asymmetric unit was not generated owing to the sp^3 hybridization of O that implies a random distribution of H atoms on several positions. These positions are located on the circle that can be generated by rotation of OH group around the Re-O bonds.

Ueq of C6 is low compared to C7 C8 C9 leading to an alarm of type A. False alarms may occur for terminal groups such as the t-butyl moiety (<http://journals.iucr.org/services/cif/checking/PLAT242.html>). Owing to the random distribution of carbon C7, C8, C9 and rather high Uiso, the corresponding hydrogen atoms were not generated.

Synthetic procedures

[Re₆S₈(TBP)₄(OH)₂] compound 1a

K₄[Re₆S₈(OH)₆] (2.5 g, 1.53 mmol), *tert*-butylpyridine (TBP) (20.69 g, 153 mmol) were dissolved into 100 cm³ of H₂O and heated under reflux for 2 days. When cooled to room temperature, the mixture was extracted with CH₂Cl₂ (3 x 50 cm³). The resulting organic phase was washed with H₂O (3 x 50 cm³), dried over MgSO₄ and solvent was removed under reduced pressure. The product was purified by two successive recrystallisations in CH₂Cl₂/diethyl ether to give [Re₆S₈(TBP)₄(OH)₂] as yellow solid (yield:71 %, 2.12 g). (Found : C, 22.31 ; H, 2.92 ; N, 2.83 ; S, 13.20 % Re₆S₈C₃₆H₅₄N₄O₂. requires C, 22.19 ; H, 2.79 ; N, 2.88 ; S, 13.16 %).

m/z (ESI) 1951.93 (M : 1952.02)

δ_H(500 MHz, CDCl₃, TMS): 9.36 (8H, d, J = 6.8 Hz, 4 x H^{ortho} pyridine), 7.21 (8H, d, J = 6.8 Hz, 4 x H^{meta} pyridine), 1.29 (36H, s, 12 x -CH₃)

δ_C (75.46 MHz, CDCl₃, TMS): 30.19, 35.32, 122.22, 158.31, 164.77

[Re₆Se₈(TBP)₄(OH)₂] compound 1b

The same procedure was used with K₄[Re₆Se₈(OH)₆] (1.5 g, 0.75 mmol), *tert*-butylpyridine (TBP) (10.07 g, 75 mmol) into 50 cm³ of H₂O to obtain [Re₆Se₈(TBP)₄(OH)₂] as orange solid (yield:74 %, 1.29 g). (Found : C, 18.16; H, 2.37; N, 2.35 %. Re₆Se₈C₃₆H₅₄N₄O₂. 3 H₂O requires: C, 18.18; H, 2.54; N, 2.37 %)

FAB/HRMS 2308.2 [Re₆Se₈(TBP)₄(OH)]⁺

δ_H(500 MHz, CDCl₃, TMS): 9.66 (8H, d, J = 6.7 Hz, 4 x H^{ortho} pyridine), 7.09 (8H, d, J = 6.7 Hz, 4 x H^{meta} pyridine), 1.29 (36H, s, 12 x -CH₃)

δ_C(75.46 MHz, CDCl₃, TMS): 30.19, 35.29, 121.66, 160.53, 164.32

[Re₆S₈(TBP)₄(L¹)₂] compound 2a

[Re₆S₈(TBP)₄(OH)₂] (0.2 g, 0.098 mmol) and 3,4,5-trimethoxybenzoic acid (L¹) (Alfa Aesar, 0.416 g, 1.96 mmol) were placed in a flask filled with chlorobenzene (30 cm³) and heated under

reflux in an Ar atmosphere for 2 days. When cooled to room temperature, the solvent was removed under reduced pressure and the obtained solid was washed with diethyl ether (5 x 20 cm³) to give **[Re₆S₈(TBP)₄(L¹)₂]** (57 %, 0.133 g) as brown-orange solid (yield:78 %, 0.185 g).

(Found : C, 28.11; H, 3.13; N, 2.33 %. Re₆S₈C₅₆H₇₄N₄O₁₀. 2 H₂O requires: C, 28.18; H, 3.26; N, 2.37 %)

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1614 (C=O)

δ_{H} (300 MHz, CDCl₃, TMS): 9.40 (8H, d, J = 6.8 Hz, 4 x H^{ortho} pyridine), 7.49 (4H, s, 2 x H-Ar), 7.25 (8H, d, J = 6.8 Hz, 4 x H^{meta} pyridine), 3.95 (12H, s, 2 x meta-OCH₃), 3.89 (6H, s, 2 x para-OCH₃), 1.30 (36H, s, 12 x -CH₃)

δ_{C} (75.46 MHz, CDCl₃, TMS): 30.21, 35.67, 56.34, 60.89, 107.62, 122.37, 131.13, 140.32, 152.30, 158.53, 164.92, 172.67

[Re₆Se₈(TBP)₄(L¹)₂] compound 2b

The same procedure was used with [Re₆Se₈(TBP)₄(OH)₂] (0.2 g, 0.086 mmol) and 3,4,5-trimethoxybenzoic acid (L¹) (Alfa Aesar, 0.365 g, 1.72 mmol) into 30 cm³ of chlorobenzene to obtain **[Re₆Se₈(TBP)₄(L¹)₂]** as a brown solid (yield:78 %, 0.185 g).

(Found : C, 24.52; H, 2.73; N, 1.98 %. Re₆Se₈C₅₆H₇₄N₄O₁₀ requires: C, 24.78; H, 2.82; N, 2.06 %)

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1614 (C=O)

δ_{H} (300 MHz, CDCl₃, TMS): 9.66 (8H, d, J = 6.8 Hz, 4 x H^{ortho} pyridine), 7.46 (4H, s, 2 x H-Ar), 7.11 (8H, d, J = 6.8 Hz, 4 x H^{meta} pyridine), 3.93 (12H, s, 2 x meta-OCH₃), 3.89 (6H, s, 2 x para-OCH₃), 1.28 (36H, s, 12 x -CH₃)

δ_{C} (75.46 MHz, CDCl₃, TMS): 30.17, 35.31, 56.33, 60.86, 107.40, 121.79, 140.34, 152.30, 160.75, 164.45, 172.86

3,4,5-tris(octyloxy)benzoic acid: compound HL²

Methyl-3,4,5-trishydroxybenzoate (2.5 g, 13.6 mmol), K₂CO₃ (9.4 g, 68 mmol) and 1-bromooctane (7.9 g, 40.7 mmol) were placed in a flask filled with butan-2-one (100 cm³). The reaction mixture was heated under reflux during 2 days under Ar atmosphere and cooled to room

temperature. After addition of H₂O (150 cm³), the mixture was extracted with CH₂Cl₂ (4 x 50 cm³). The resulting organic phase was washed with H₂O (4 x 50 cm³), dried over MgSO₄ and solvent was removed under reduced pressure. The obtained solid was dissolved in ethanol (50 cm³), a solution of KOH (1.91 g, 34 mmol) in H₂O (10 cm³) was added and the mixture was heated under reflux for 2h and then allowed to cool to room temperature. The solvent was removed under reduced pressure, the obtained solid was placed in H₂O (150 cm³), HCl_{conc} (5 cm³) was added and the solution was stirred for 5h. The product was filtered and purified by recrystallisation in ethanol to give the desired compound (yield:77 %, 5.3 g) as a white solid.

(Found: C, 72.97; H, 10.74 %. C₃₁H₅₄O₅. 0.18 H₂O requires: C, 73.00; H, 10.74 %);
 $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1688 (C=O)

δ_{H} (300 MHz, CDCl₃, TMS): 11.7 (1H, s, -OH), 7.36 (2H, s, H-Ar), 4.06 (6H, m, 3 x -O-CH₂-), 1.73 (6H, m, 3 x -O-CH₂-CH₂-), 1.50 (6H, m, 3 x -O-CH₂-CH₂-CH₂-), 1.33 (24H, m, 3 x -O-CH₂-CH₂-CH₂-(CH₂)₄-), 0.91 (9H, m, 3 x -CH₃)

δ_{C} (75.46 MHz, CDCl₃): 14.12, 22.70, 26.7, 29.35, 30.35, 31.9, 69.20, 73.58, 108.56, 123.63, 143.19, 152.97, 171.97

[Re₆S₈(TBP)₄(L²)₂] compound 3a

[Re₆S₈(TBP)₄(OH)₂] (0.150 g, 0.073 mmol) and 3,4,5-tris(octyloxy)benzoic acid (HL²) (0.820 g, 1.46 mmol) were placed in a flask filled with chlorobenzene (40 cm³) and heated under reflux in an Ar atmosphere for 2 days. When cooled to room temperature, the solvent was removed under reduced pressure and the obtained solid was washed with n-pentane (5 x 20 cm³) to give [Re₆S₈(TBP)₄(L²)₂] as an orange solid (yield:80 %, 0.171 g).

(Found : C, 39.61 ; H, 5.62 ; N, 1.81 ;S, 8.47%. Re₆S₈C₉₈H₁₅₈N₄O₁₀. 3H₂O requires C, 39.50 ; H, 5.55 ; N, 1.88 ; S, 8.61%))

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1616 (C=O)

δ_{H} (300 MHz, CDCl₃, TMS): 9.40 (8H, d, J = 6.7 Hz, 4 x H^{ortho} pyridine), 7.44 (4H, s, 2 x H-Ar), 7.22 (8H, d, J = 6.7 Hz, 4 x H^{meta} pyridine), 4.03 (12H, m, 6 x -O-CH₂-), 1.78 (12H, m, 6 x -O-CH₂-CH₂-), 1.49 (12H, m, 6 x -O-CH₂-CH₂-CH₂-), 1.28 (84H, m, 6 x -O-CH₂-CH₂-CH₂-(CH₂)₄- + 12 x -CH₃), 0.90 (18H, m, 6 x -CH₃)

δ_C (75.46 MHz, CDCl₃, TMS) 14.10, 22.67, 26.15, 29.31, 30.17, 31.85, 35.30, 69.22, 73.35, 109.25, 122.29, 130.65, 140.71, 152.19, 158.56, 164.80, 173.16

[Re₆Se₈(TBP)₄(L²)₂] compound 3b

[Re₆Se₈(TBP)₄(OH)₂] (0.150 g, 0.065 mmol) and 3,4,5-tris(octyloxy)benzoic acid (HL²) (0.330 g, 0.65 mmol) were placed in a flask filled with chlorobenzene (25 cm³) and heated under reflux in an Ar atmosphere for 2 days. When cooled to room temperature, the solvent was removed under reduced pressure and the obtained solid was washed with n-pentane (5 x 20 cm³) to give [Re₆Se₈(TBP)₄(L²)₂] as orange solid (yield:71 %, 0.179 g). (Found : C, 35.86 ; H, 4.81 ; N, 1.71. Re₆Se₈C₉₈H₁₅₈N₄O₁₀ requires C, 35.66 ; H, 4.82 ; N, 1.69)

FAB/HRMS: 3302 [Re₆Se₈(TBP)₄(L²)₂]

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1616 (C=O)

δ_H (300 MHz, CDCl₃, TMS): 9.66 (8H, d, J = 6.7 Hz, 4 x H^{ortho} pyridine), 7.41 (4H, s, 2 x H-Ar), 7.11 (8H, d, J = 6.7 Hz, 4 x H^{meta} pyridine), 4.04 (12H, m, 6 x -O-CH₂-), 1.80 (12H, m, 6 x -O-CH₂-CH₂-), 1.49 (12H, m, 6 x -O-CH₂-CH₂-CH₂-), 1.28 (84H, m, 6 x -O-CH₂-CH₂-CH₂-(CH₂)₄- + 12 x -CH₃), 0.90 (18H, m, 6 x -CH₃)

δ_C (75.46 MHz, CDCl₃, TMS): 14.62, 23.04, 26.36, 29.72, 30.29, 32.13, 35.46, 68.82, 73.43, 107.86, 122.05, 130.34, 139.60, 152.13, 160.60, 164.44, 173.71

Supplementary Figures

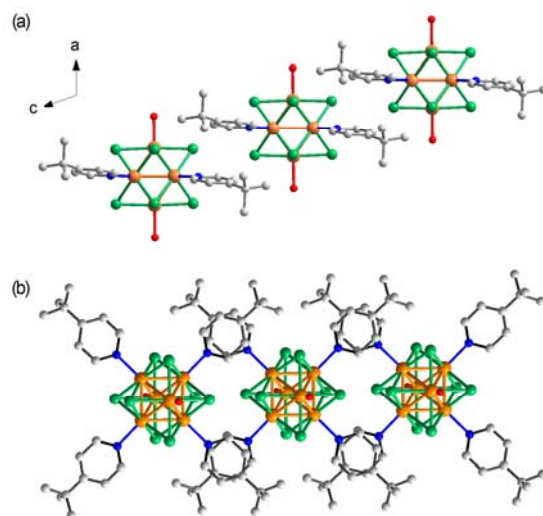


Fig S1: Representation of a) the chain of cluster units along the c-axis in the crystal structure of **1**, b) projection of a cluster chain

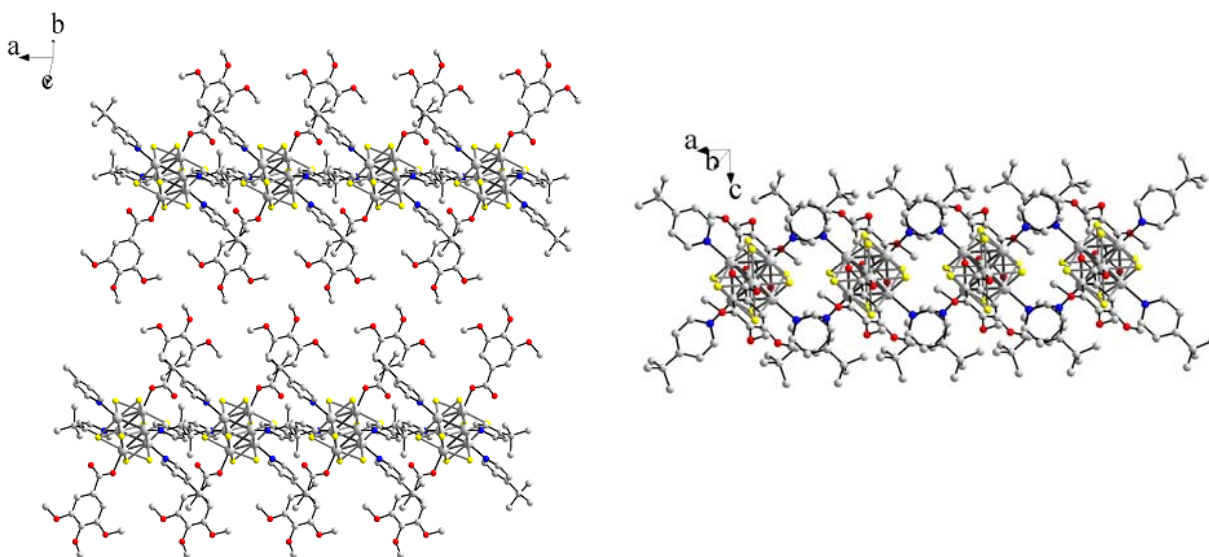


Fig S2: Representation of a) the chain of cluster units along the a-axis in the crystal structure of **2a**; CH_2Cl_2 molecules are omitted for clarity b) projection of a cluster chain

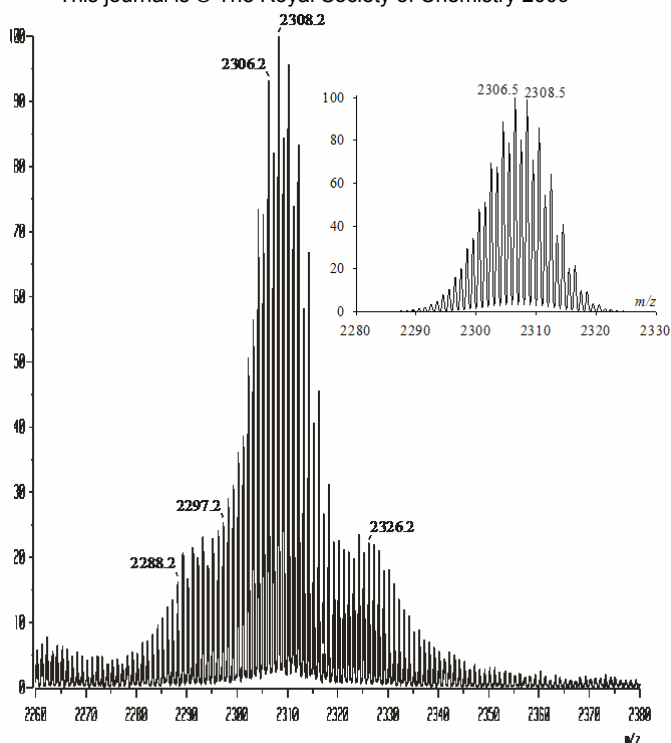


Fig S3. High-resolution ($R = 6000$) FAB mass spectrum of **1b** and theoretical isotopic distribution for an elementary composition corresponding to $C_{36}H_{53}N_4OR_6Se_8$ (see the insert).

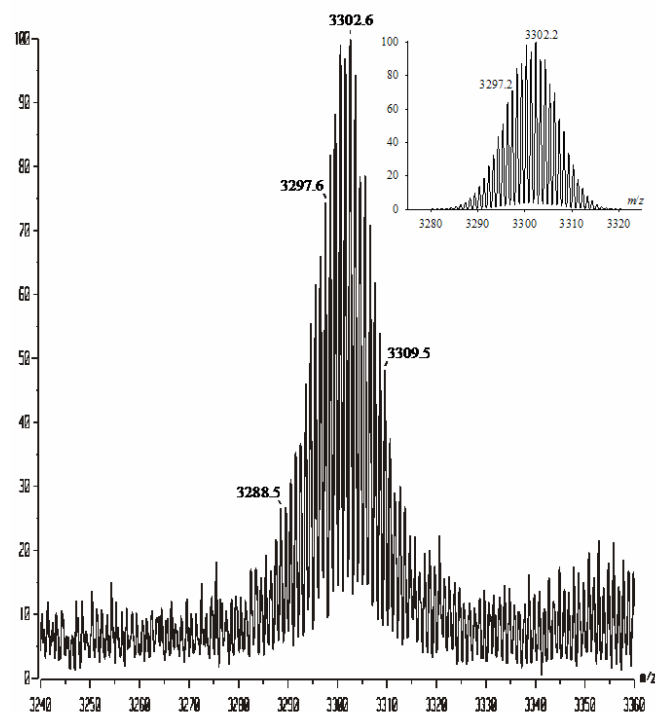


Fig S4. High-resolution ($R = 6000$) FAB mass spectrum of **3b** and theoretical isotopic distribution for an elementary composition corresponding to $C_{98}H_{158}N_4O_{10}Re_6Se_8$ (see the insert).

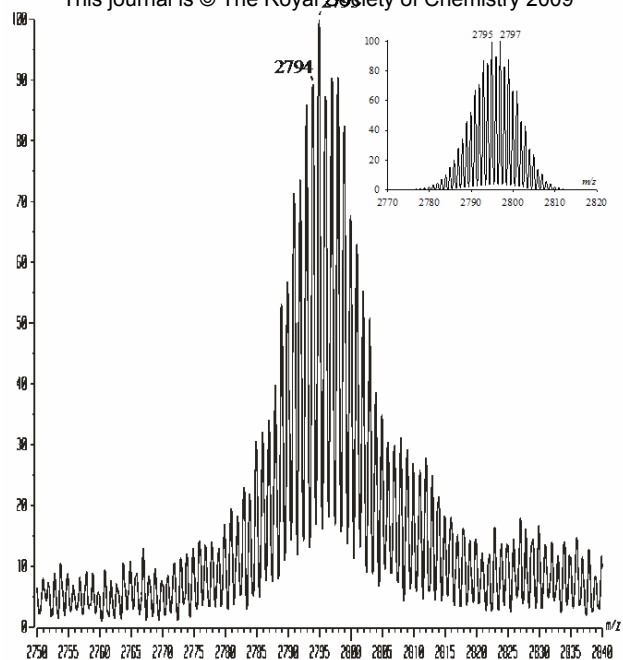


Fig S5. High-resolution ($R = 6000$) FAB mass spectrum of **3b** and theoretical isotopic distribution for an elementary composition corresponding to the loss of one carboxylate: $C_{67}H_{105}N_4O_5Re_6Se_8$ (see the insert).

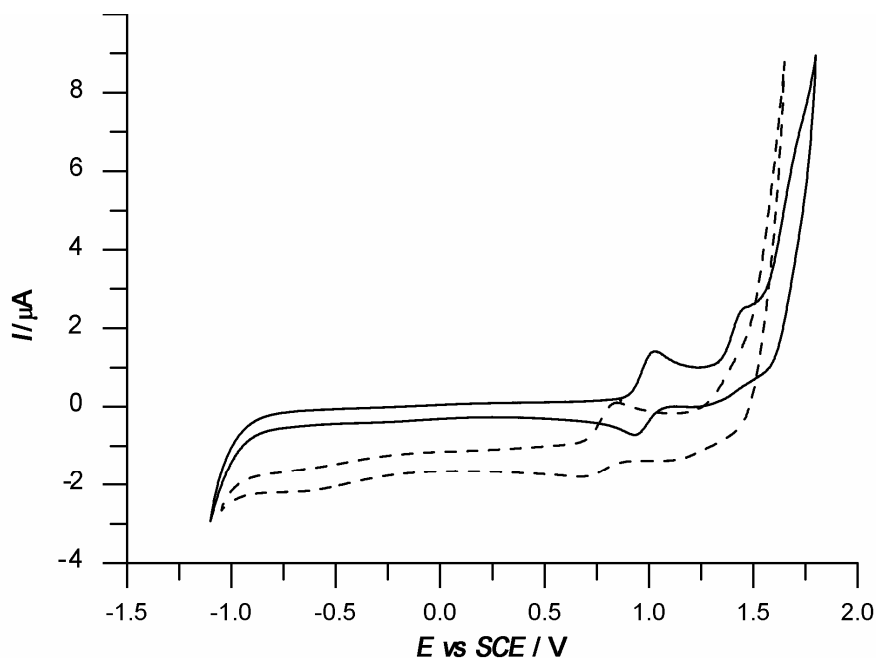


Fig S6: Cyclic voltammograms obtained for **2a** (plain line) and **2b** (dashed line) in a 0.1 M $[Bu_4N]PF_6/CH_2Cl_2$ solution.

The irreversible oxidation signal observed around 1.5 V is a multielectronic process due to the decomposition of the compound.

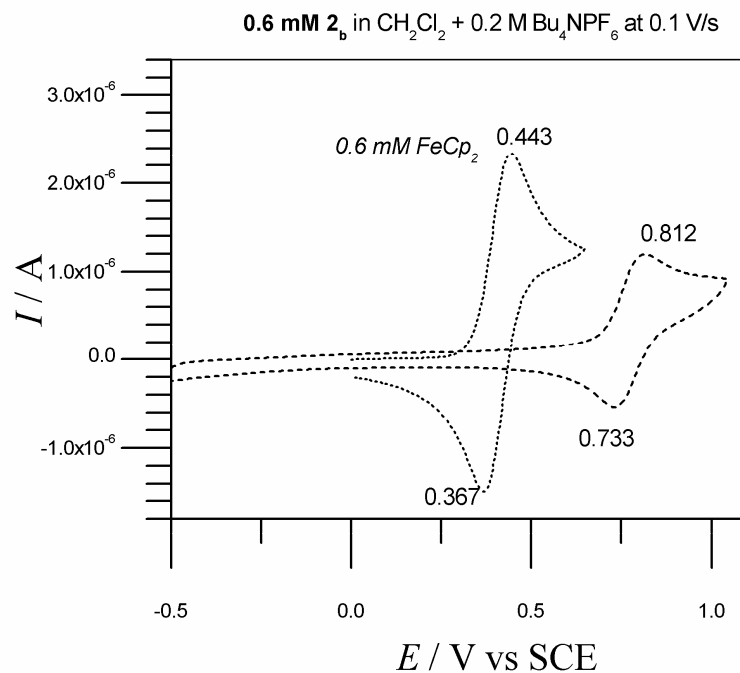


Fig S7: Cyclic voltammograms obtained for **2_b** (dashed line) and FeCp₂ (dotted line) at $c=0.6 \times 10^{-3} \text{ mol.l}^{-1}$ in a 0.2 M [Bu₄N]PF₆/CH₂Cl₂ solution.

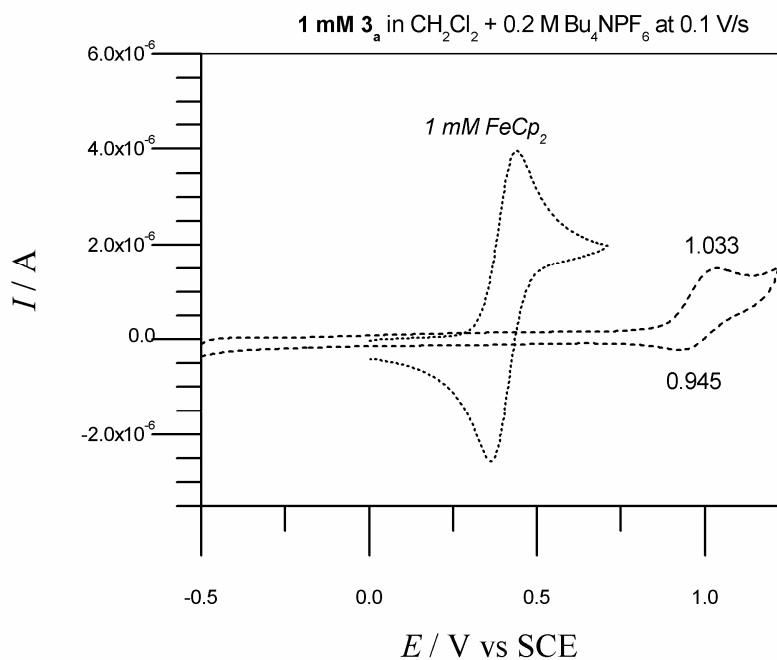


Fig S8: Cyclic voltammograms obtained for **3_a** (dashed line) and FeCp₂ (dotted line) at $c=1 \times 10^{-3} \text{ mol.l}^{-1}$ in a 0.2 M [Bu₄N]PF₆/CH₂Cl₂ solution.

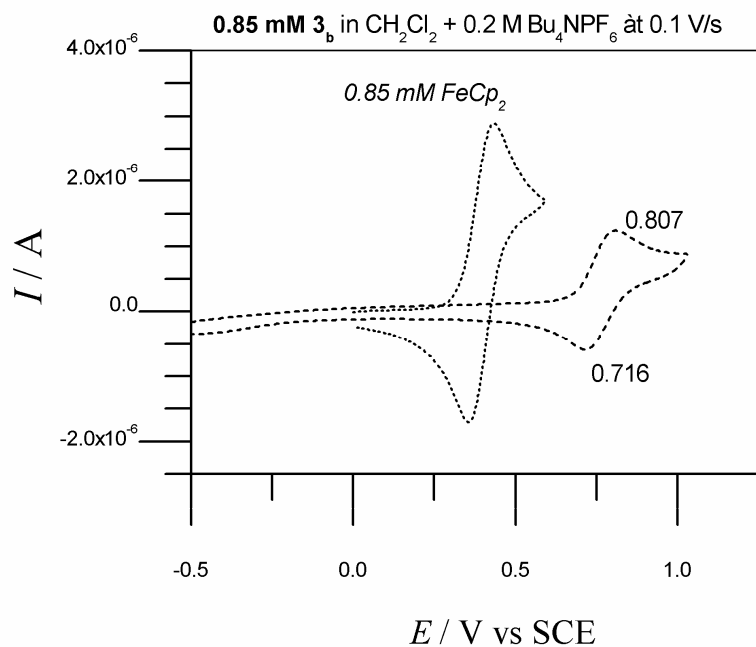


Fig S9: Cyclic voltammograms obtained for **3b** (dashed line) and FeCp₂ (dotted line) at $c=0.85 \cdot 10^{-3} \text{ mol.l}^{-1}$ in a 0.2 M [Bu₄N]PF₆/CH₂Cl₂ solution.

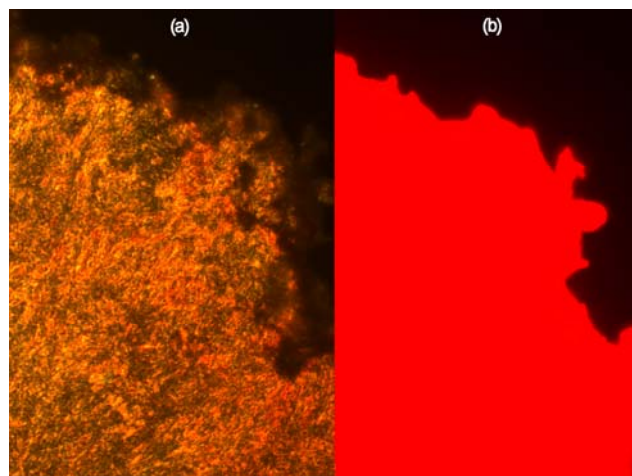


Fig. S10: Optical microscope pictures under (a) polarized light, (b) laser irradiation at $\lambda_{\text{exc}} = 405 \text{ nm}$ of compound **3a**.

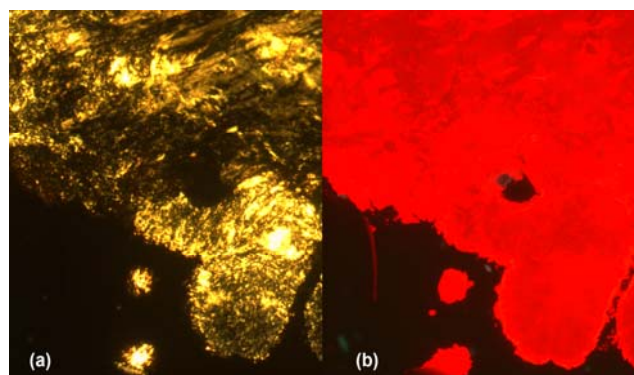


Fig. S11: Optical microscope pictures under (a) polarized light, (b) laser irradiation at $\lambda_{\text{exc}} = 405$ nm of compound **3b**.