Supporting Information

Electrospray Ionization: an efficient approach to deposit polymetallic molecular switches onto gold surfaces

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Table of contents

1. Experimental Procedures

Syntheses. All air sensitive reactions were carried out under argon atmosphere using standard schlenk techniques and solvents dried with a MBraun solvent purification system (MB SPS-800). Commercially available chemicals were used as received. The 4-trimethylsilyl-bromobenzene, the 1,2,3dioxaborolane4,4',5,5'-tetramethyl2-(3thienyl), sodium pyrazolide (NaPz) and $Bu_4N[Fe^{III}(Tp)(CN)_3]$ compounds were prepared as described in literature procedures.[1,2,3,4] Pyrazole was purchased from Alfa Aesar and was sublimed under vacuum before use. All other chemicals were purchased from Aldrich Chemicals or Alfa Aesar and were used as received.

NMR spectra were recorded on Bruker Avance spectrometers at 300 K. ^1H, ^{13}C and ^{133}Cs spectra were recorded at 7.1 or 9.1 T. Chemical shifts, δ, are given in ppm with reference to residual solvent signals.

FT-IR spectra were recorded in the 300-4000 cm^{-1} range. Measurements were carried out on a Vertex 70 Bruker instrument using the attenuated total reflection (ATR) technique on solid samples (with a 4 cm^{-1} resolution).

UV-Visible absorption spectrum was recorded on a JASCO V670 spectrometer at ambient temperature in solvent solution of $\{Cs \subset [Fe^{II}(Tp)(CN)_3]_4[Co^{III}(^{TPh}Tp)]_4\}ClO_4$ (0.1 mM) using a 10 mm quarts cuvette.

Elemental analyses (C, H, N). Analyses were carried out using a vario MICRO cube apparatus from Elementar at the Institut de Chimie des Substances Naturelles (ISCN) at Gif-sur-Yvette (CNRS).

Mass spectrometric analyses were performed at the Institut Parisien de Chimie Moléculaire (IPCM). The ESI-MS experiments were carried out using a LTQ-Orbitrap XL from Thermo Scientific (Thermo

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[1] M. J. Harper, E. J. Emmett, J. F. Bower and C. A. Russell, *Journal of the American Chemical Society*, 2017, **139**, 12386–12389.

[2] J. Han, J. Qi, X. Zheng, Y. Wang, L. Hu, C. Guo, Y. Wang, Y. Li, D. Ma, W. Qiao and Z. Y. Wang, *J. Mater. Chem. C*, 2017, **5**, 159–165.

[3] P. J. Bailey, P. Pinho and S. Parsons, *Inorganic Chemistry*, 2003, **42**, 8872–8877.

[4] R. Lescouëzec, F. Lloret, M. Julve, J. Vaissermann, M. Verdaguer, *Inorg. Chem.*, 2002, ***41***, 5943-5945.

Fisher Scientific, Courtaboeuf, France) and operated in positive ionization mode, with a spray voltage at 3.6 kV. Applied voltages were 40 and 100 V for the ion transfer capillary and the tube lens, respectively. The ion transfer capillary was held at 275°C. Detection was achieved in the Orbitrap with a resolution set to 100,000 (at m/z 400) and a m/z range between 200-4000 in profile mode. Spectrum was analyzed using the acquisition software XCalibur 2.1 (Thermo Fisher Scientific, Courtaboeuf, France). The automatic gain control (AGC) allowed accumulation of up to 2.10^5 ions for FTMS scans, Maximum injection time was set to 300 ms and 1 µscan was acquired. 10 µL was injected using a Thermo Finnigan Surveyor HPLC system (Thermo Fisher Scientific, Courtaboeuf, France) with a continuous infusion of acetonitrile at 100 $\mu L.min^{-1}$.

Cyclic voltammetry measurements were carried out at room temperature in a standard cell equipped with a platinum wire counter electrode, a calomel reference electrode (SCE) and a glassy-carbon working electrode (Ø = 3mm) using an AUTOLAB PGSTAT 100 electrochemical analyzer. The measurements were performed under nitrogen atmosphere in a dried acetonitrile solution of $\{Cs \subset [Fe^{II}(Tp)(CN)_3]_4[Co^{III}(^{TPh}Tp)]_4\}ClO_4$ cube (10^{-4}M) and $[Bu_4N][PF_6]$ (0.1M) as supporting electrolyte.

Electrospray Ionisation (EI) deposition was carried out in the Laboratoire de Réactivité de Surfaces (LRS) using an electrospray deposition system from Molecular Spray Ltd. (U.K.). A solution of $\{Cs \subset [Fe^{II}(Tp)(CN)_3]_4[Co^{III}(^{TPh}Tp)]_4\}ClO_4$ in 1,2-dichloroethane at 5.10^{-4} M was introduced in a syringe under dark conditions at room temperature. The ions of molecules were produced by applying a voltage of 2 kV to a flow of 1µL/min of solution in the needle of the syringe. At the tip of the needle, the produced charge droplets were introduced in a first vacuum chamber through a capillary (250 µm inner diameter). The charged droplets are guided toward the surface via three differential pumping stages where the solvent evaporates leading to the $\{Cs\subset[Fe^{II}(Tp)(CN)_3]_4[Co^{III}(^{TPh}Tp)]_4\}^{+}$~~ClO~~$_4$ ion beam. During the electrospray deposition, the partial pressure in the main chamber was around 10^{-7} Torr.

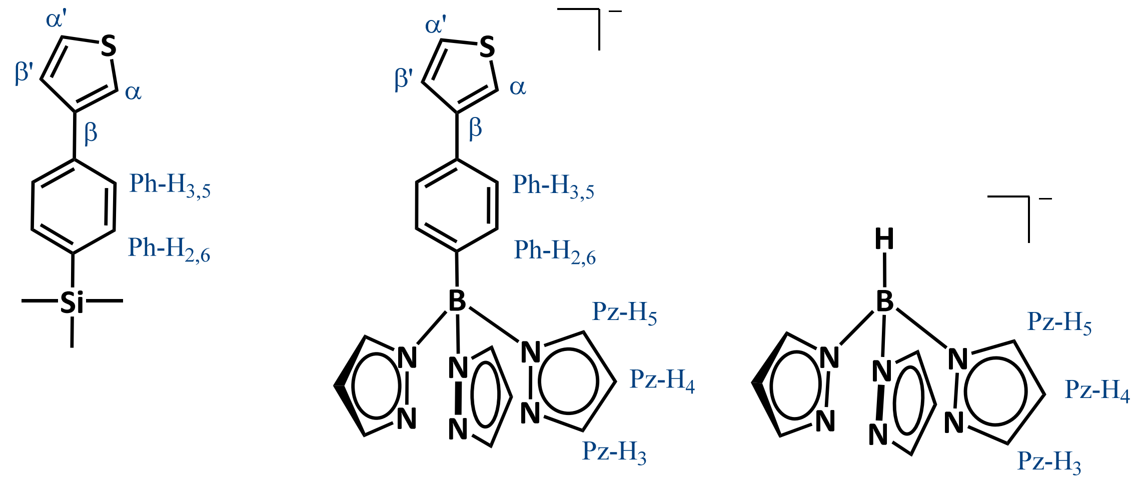
X-ray Spectroscopy (XPS) and **Polarization-Modulation Infra-Red Reflection Absorption Infrared Spectroscopy (PM-IRRAS)** experiments were carried out in situ by using multitechnique UHV chambers. The Au(111) single crystal was routinely cleaned in vacuum (base pressure equal to 10^{-10} Torr) by cycles of Ar^+ ion sputtering ($P_{Ar} = 2 \times 10^{-6}$ Torr, 250 V) and annealing to 850 K. The surface cleanliness and structure were checked by AES and LEED, respectively, prior to the compound adsorption.

PM-IRRAS spectra were recorded using a Nicolet 5700 spectrometer equipped with a nitrogen-cooled

MCT wide-band detector. A ZnS grid polarizer and ZnSe photoelastic modulator to modulate the incident beam between p and s polarization were placed prior to the sample. The spectrometer was interfaced to the UHV chamber via ZnSe windows. The reflected light was focused onto the detector at an optimal incident angle of 85°. All spectra were obtained after 1024 scans at 8 cm^{-1} resolution.

For **XPS analyses**, the sample was transferred to the adjacent UHV XPS chamber immediately after the $\{Cs\subset[Fe^{II}(Tp)(CN)_3]_4[Co^{III}(^{TPh}Tp)]_4\}ClO_4$ cube electrospray ionization. Analyses were performed using a SPECS (PhoibosMCD 100) spectrometer (SPECS, Germany) equipped with a monochromatized aluminum X-ray source (hν = 1486.6 eV) powered at 10 mA and 15 kV, and a Phoibos 150 hemispherical energy analyzer. The resulting analyzed area was about 5 mm of diameter. A pass energy of 20 eV was used for survey scan and 10 eV for narrow scans. In the latter conditions, the full width at half maximum (FWHM) of the Ag 3d5/2 peak of a standard silver sample was about 0.9 eV. The single crystal was fixed on the support, and no charge stabilization device was used on this conducting sample. The pressure in the analysis chamber during measurement was around 10^{-10} Torr. The photoelectron collection angle, θ, between the normal to the sample surface and the analyzer axis was 0°. The following sequence of spectra was recorded: survey spectrum, Au 4f, C 1s, Co 2p, Cs 3d and Fe 2p, N 1s, O 1s, and S 2p. The binding energy scale was set by adjusting the Fermi level to zero. This yields a binding energy position of the Au $4f_{7/2}$ peak at 84.3 eV. The data treatment was performed with the Casa XPS software (Casa Software Ltd., UK). The peaks were decomposed using a linear baseline, and a component shape defined by the product of a Gauss and Lorentz function, in a 70:30 ratio. Molar concentration ratios were calculated using peak areas normalized according to Scofield factors.

2. Syntheses



TPhSiMe$_3$ **^{TPh}Tp** **Tp**

Scheme 1. Precursor and ligands used for the synthesis of the {Cs ⊂ [Fe^{II}(Tp)(CN)$_3$]$_4$[Co^{III}(^{TPh}Tp)]$_4$}ClO$_4$ cube. Thiophene and tris(pyrazolyl)borate nomenclatures are indicated in blue and were used for NMR assignments when possible.

2.1. Synthesis of [4-(3-Thienyl)phenyl](trimethyl)silane (TPhSiMe$_3$)

Under argon atmosphere, 1,3,2-dioxaborolane-4,4’,5,5’-tetramethyl-2-(3-thienyl) (2.5 g; 12 mmol) and 4-trimethylsilyl-bromobenzene (2.3 g; 10 mmol) were added to a degassed mixture of toluene/ethanol (80/8 mL) and 2M solution of aqueous Na_2CO_3 (20mL). $Pd(PPh_4)_3$ (0.231 g, 0.2 mmol) was then added and the reaction was stirred under reflux for 1 day. After cooling down to room temperature, the reaction was poured into a mixture of water and toluene (2:1, 150mL). The organic phase was separated, washed with water, dried over sodium sulfate and concentrated. Then, the desired compound was isolated by column chromatography on silica gel (eluent: toluene) as white solid. Yield: 60% (1,40g).

Elemental analyses calculated for $C_{13}H_{16}SSi \cdot 0.05\ H_2O$: C 66.92, H 6.96; Found C 66.92, H 7.04.

^{1}H NMR (400MHz, CD_2Cl_2): δ = 7.60-7.54 (AA’BB’, 4H), 7.50 (dd, J_1=1.84 Hz, J_2=2.93Hz, 1H, Thio); 7.43-7.39 (m, 2H, Thio); 0.28 (s, 9H, $SiMe_3$) ppm. ^{13}C (100MHz, CD_2Cl_2) : δ = 142.2 (Cq), 139.3 (Cq), 135.3 (Cq), 133.8 (Ph), 126.2 (Thio-CH), 126.1 (Thio-CH), 125.6(Ph), 120.4 (Thio-CH), -1.1(SiMe3) ppm.

2.2. Synthesis of ^{TPh}Tp ligand

BBr_3 (1M in DCM, 5.5 mL) was added dropwise to a stirred solution of [4-(3-Thienyl)phenyl](trimethyl)silane (1.1 g, 5 mmol) in dichloromethane (5 mL) and the solution was stirred at room temperature for 4h, under argon atmosphere. After removal of all the volatile materials a yellow solid was obtained. The resulting solid was dissolved in dichloromethane (10 mL) and Me_3SiNMe_2 (1.8 mL, 10.8 mmol) was added dropwise at 0°C. The mixture was warmed to room temperature over 1h and stirred for 4 additional hours. All the volatiles were removed under reduced pressure and the yellow residue dried under vacuum for 3h. The resulting solid was dissolved in dry toluene (30 mL) and added on a suspension of pyrazole (0.73 g, 10.8 mmol) and NaPz (0.53 g, 5.9 mmol) in toluene (30 mL) at room temperature, under argon atmosphere. The reaction was then heated to reflux for 16h. Eventually the suspension was concentrated under reduced pressure and was filtered hot on a sintered glass filter. The precipitate was washed with toluene (3x20 mL) and hexane (3x20 mL). The resulting solid was dried under vacuum at 50 °C for 30min. The desired compound was obtained as a white solid and used without further purification.

^{1}H NMR (300 MHz, dmso-d_6) : $\delta = 7.67$ (m, 1H, Thio); 7.60-7.55 (overlapped signals, 3H, part AA'BB' & Thio); 7.48-7.46 (m, 1H, Thio); 7.41 (m, 3H, Pz-H_3 or H_5), 7.36 (part AA'BB', 2H); 6.93 (m, 3H, Pz-H_3 or H_5), 6.01 (m, 3H, Pz-H_4) ppm.

2.3. Synthesis of $\{Cs \subset [Fe^{II}(Tp)(CN)_3]_4[Co^{III}(^{TPh}Tp)]_4\}ClO_4$

$Bu_4N[Fe^{III}(Tp)(CN)_3]$ (0.231 g, 0.4 mmol) was dissolved in DMF (5mL) with $Co^{II}(ClO_4)_2.6H_2O$ (0.116 g, 0.4 mmol) and the mixture was stirred at room temperature for 5 min. Then, CsI (0.414 g, 1.6 mmol) was added and the reaction was vigorously stirred for 5 additional minutes, prior to the addition of the ^{TPh}Tp ligand (0.236g, 0.6 mmol). After 2 days, the resulting suspension was centrifuged, the supernatant was recovered and evaporated leading to a dark blue solid. This latter was washed with a mixture of DMF/Et_2O (2:8) and a series of centrifugation-washings (with the same solvent mixture) was carried out until the supernatant was clear. Then, the blue solid was dissolved in CH_2Cl_2 and filtered to remove a red precipitate. The filtrate was evaporated, the obtained solid was dissolved in a mixture of CH_2Cl_2/ Et_2O (7:3) and the suspension was filtered (to remove inorganic salts). This treatment was repeated 2 more times. The desired compound was then isolated as a dark blue powder (260 mg, 78% yield).

Elemental analyses calcd for $C_{124}H_{104}B_8Co_4Fe_4N_{60}S_4CsO_4Cl\cdot 3.15\ C_4H_{10}O\cdot 0.3\ CH_2Cl_2$: C 45.68, H 3.81, N 23.35; Found C 45.72, H 3.74, N 23.27.

^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.60$ (m, 3H, Pz-H_3 or H_5); 8.19 (m, 3H, Pz'-H_3 or H_5); 7.79 (d, J= 8.25 Hz, 2H, Ph-$H_{2,6}$); 7.69 (d, J= 8.25 Hz, 2H, Ph-$H_{3,5}$); 7.58 (m, 3Hz, Pz-H_3); 7.54-7.52 (m, 1H, Thio-

Hα); 7.50 (m, 3Hz, Pz'-H_3); 7.43-7.38 (m, 2H, Thio-($H_{\alpha'}$ & $H_{\beta'}$); 6.35 (m, 3H, Pz-H_4), 6.15 (m, 3H, Pz'-H_4) ppm. **^{13}C NMR (CD_2Cl_2, 100 MHz)**: δ = 179.5 (Ph-C_1); 145.5 (Pz'-C_3 or C_5); 145.1 (Pz-C_3 or C_5); 141.5 (Thio-C_β), 138.2 (Pz- C_3 or C_5), 136.4 (Ph-C_4); 135.6 (Pz'- C_3 or C_5); 134.6 (Ph-$C_{2,6}$); 126.6 (Thio-$C_{\beta'}$or $C_{\alpha'}$); 126.3 (Ph-$C_{3,5}$); 126.0 (Thio- $C_{\beta'}$or $C_{\alpha'}$); 120.9 (Thio-Cα); 106.4 (Pz-C_4); 104.6 (Pz'-C4) ppm[5]. **^{133}Cs (CD_2Cl_2, 52.5 MHz)**: δ = 48.14 ppm.

HRMS (ESI) calculated for $[C_{124}H_{104}B_8Co_4Fe_4N_{60}S_4Cs]^+$: 3241.3454, found 3241.3445

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[5] Pz and Pz' are used to denote protons belonging to the same trispyrazolyl borate moiety, *i.e*. either those of the Tp ligand or the ^{TPh}Tp ligand.

3. HRMS experiments

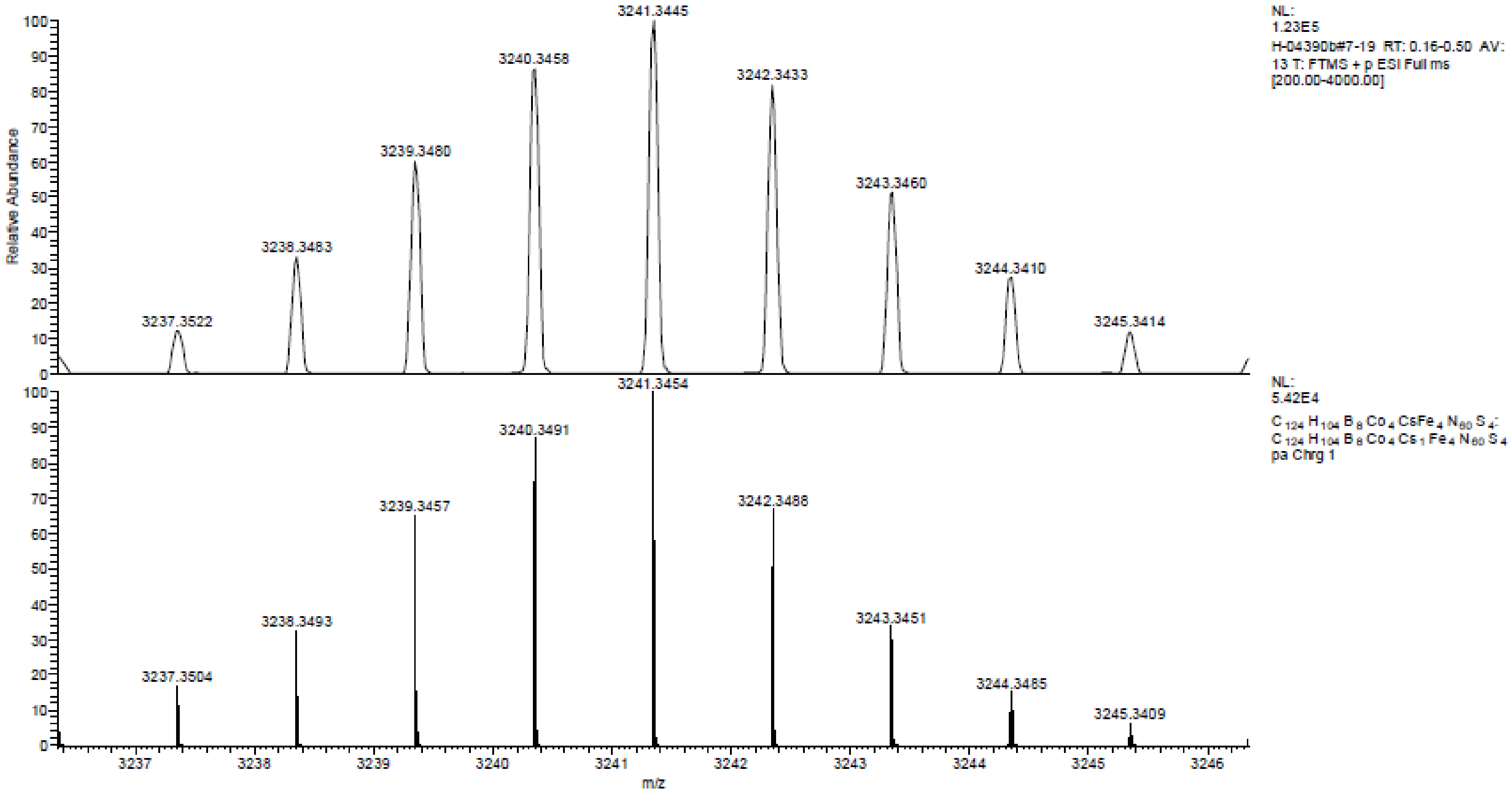

Figure S1. HRMS of **{Cs ⊂ [Fe^{II}(Tp)(CN)$_3$]$_4$[Co^{III}(^{TPh}Tp)]$_4$}ClO$_4$**, experimental (top) and theoretical (bottom) spectra.

4. NMR characterizations

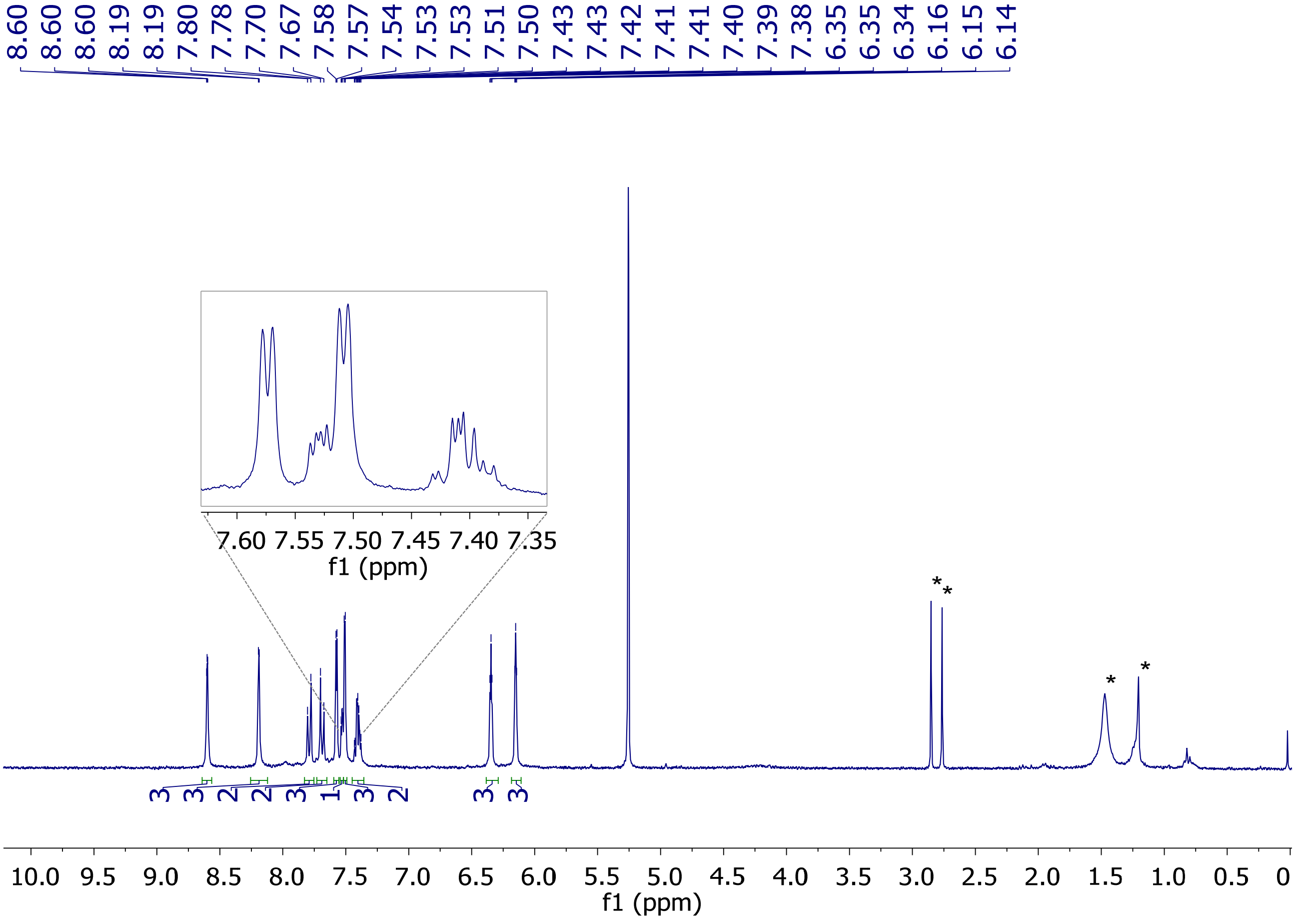

Figure S2. ^{1}H NMR spectrum (CD_2Cl_2, 300 K, 7.1 T) of **{Cs ⊂ [Fe^{II}(Tp)(CN)$_3$]$_4$[Co^{III}(^{TPh}Tp)]$_4$}ClO$_4$.** Stars denote residual solvents.

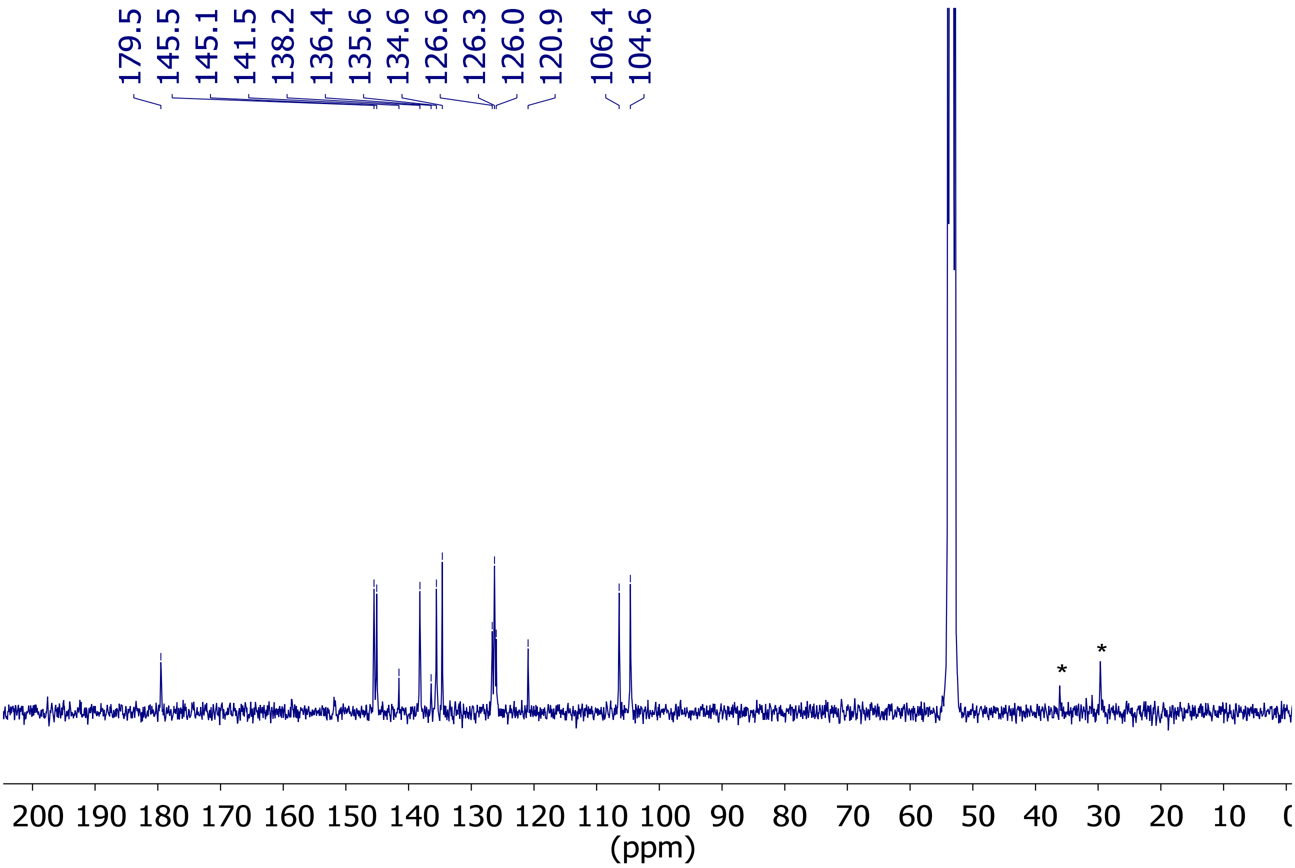

Figure S3. ^{133}Cs NMR spectrum (CD_2Cl_2, 300 K, 9.1 T) of **{Cs ⊂ [Fe^{II}(Tp)(CN)$_3$]$_4$[Co^{III}(^{TPh}Tp)]$_4$}ClO$_4$**. Stars denote residual solvents.

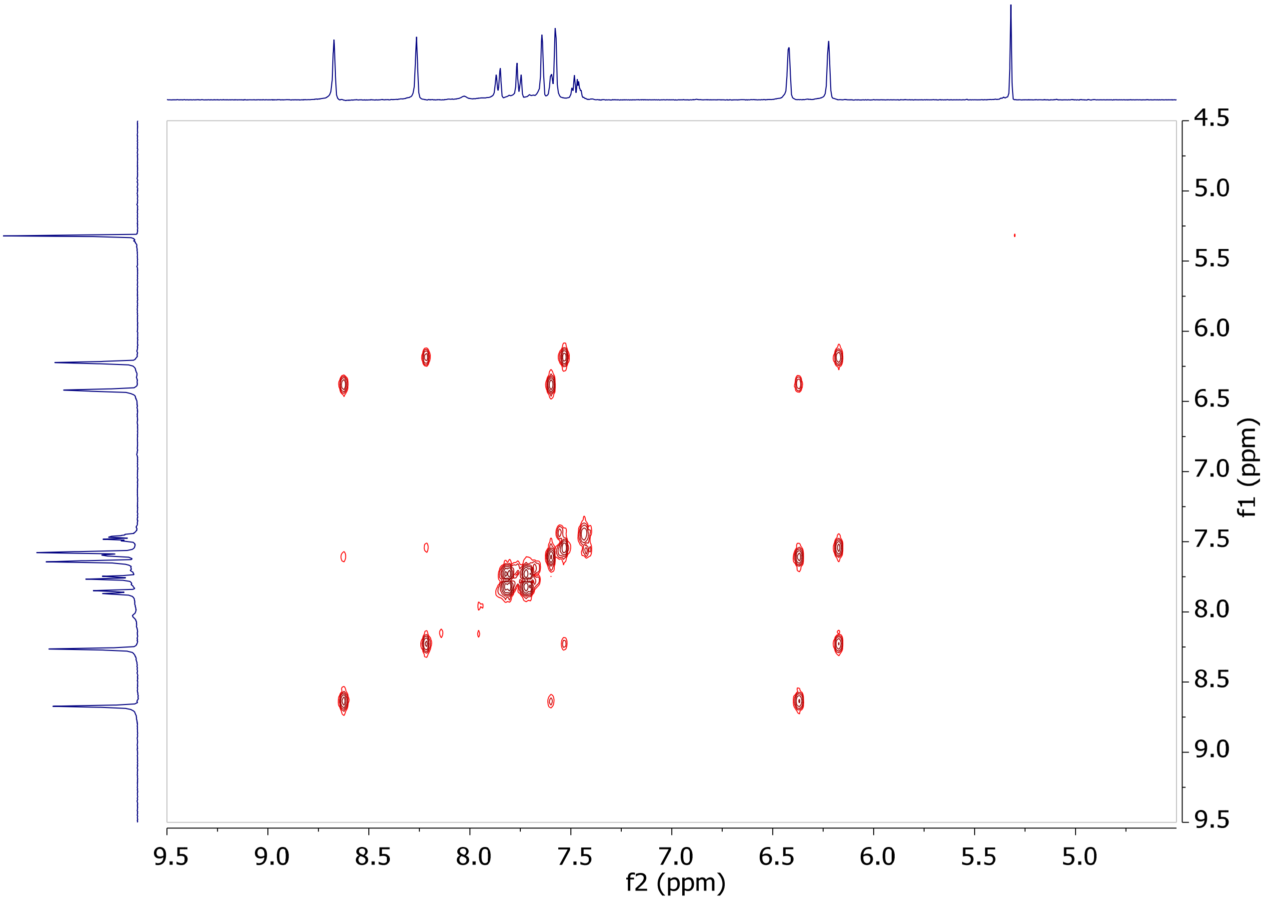

Figure S4. ^1H-^1H COSY spectrum (CD_2Cl_2, 300 K, 9.1 T) of **{Cs ⊂ [Fe^{II}(Tp)(CN)$_3$]$_4$[Co^{III}(^{TPh}Tp)]$_4$}ClO_4.**

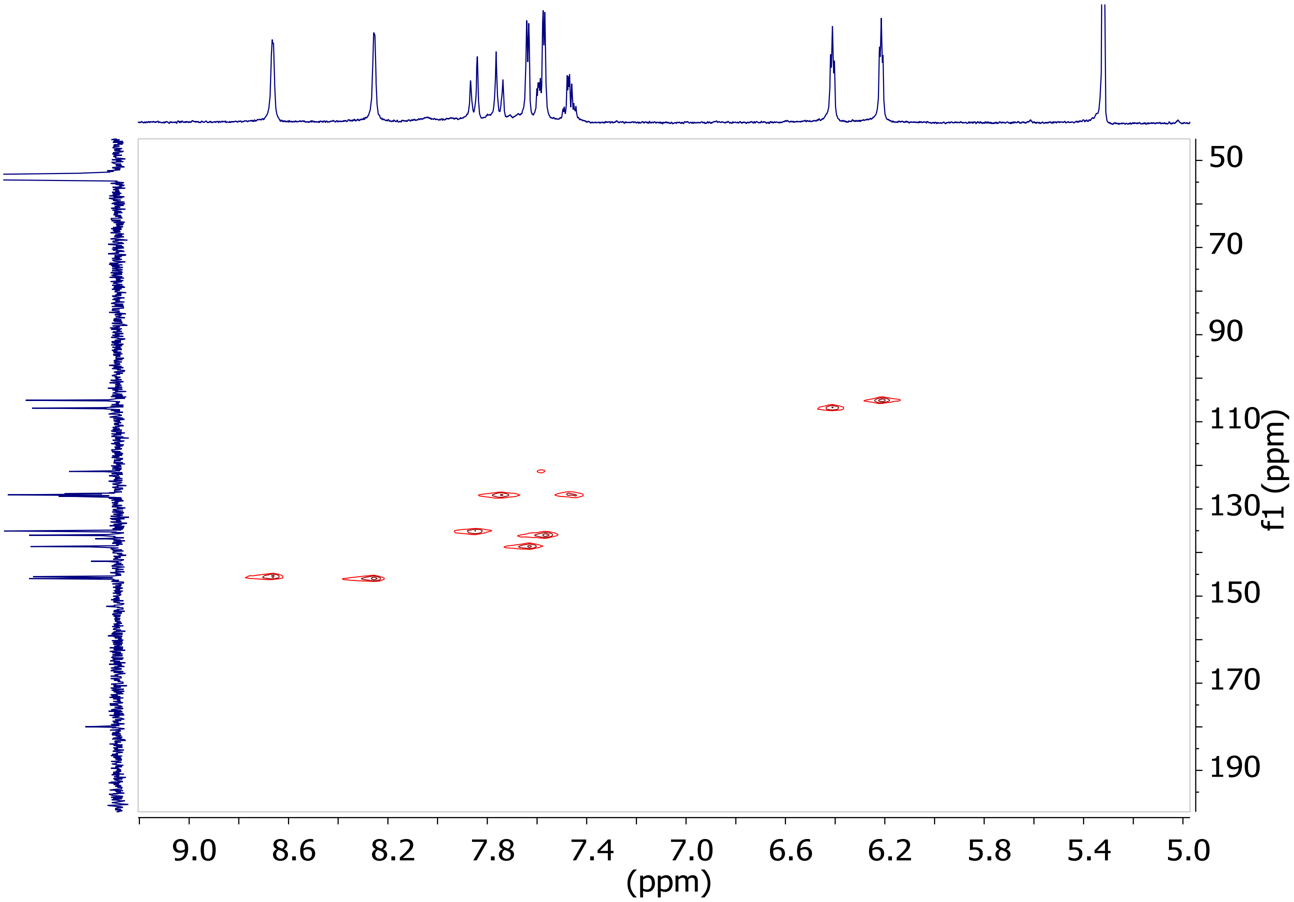

Figure S5. ^{1}H-^{13}C HSQC spectrum (CD_2Cl_2, 300 K, 9.1 T) of **{Cs ⊂ [Fe^{II}(Tp)(CN)$_3$]$_4$[Co^{III}(^{TPh}Tp)]$_4$}ClO$_4$.**

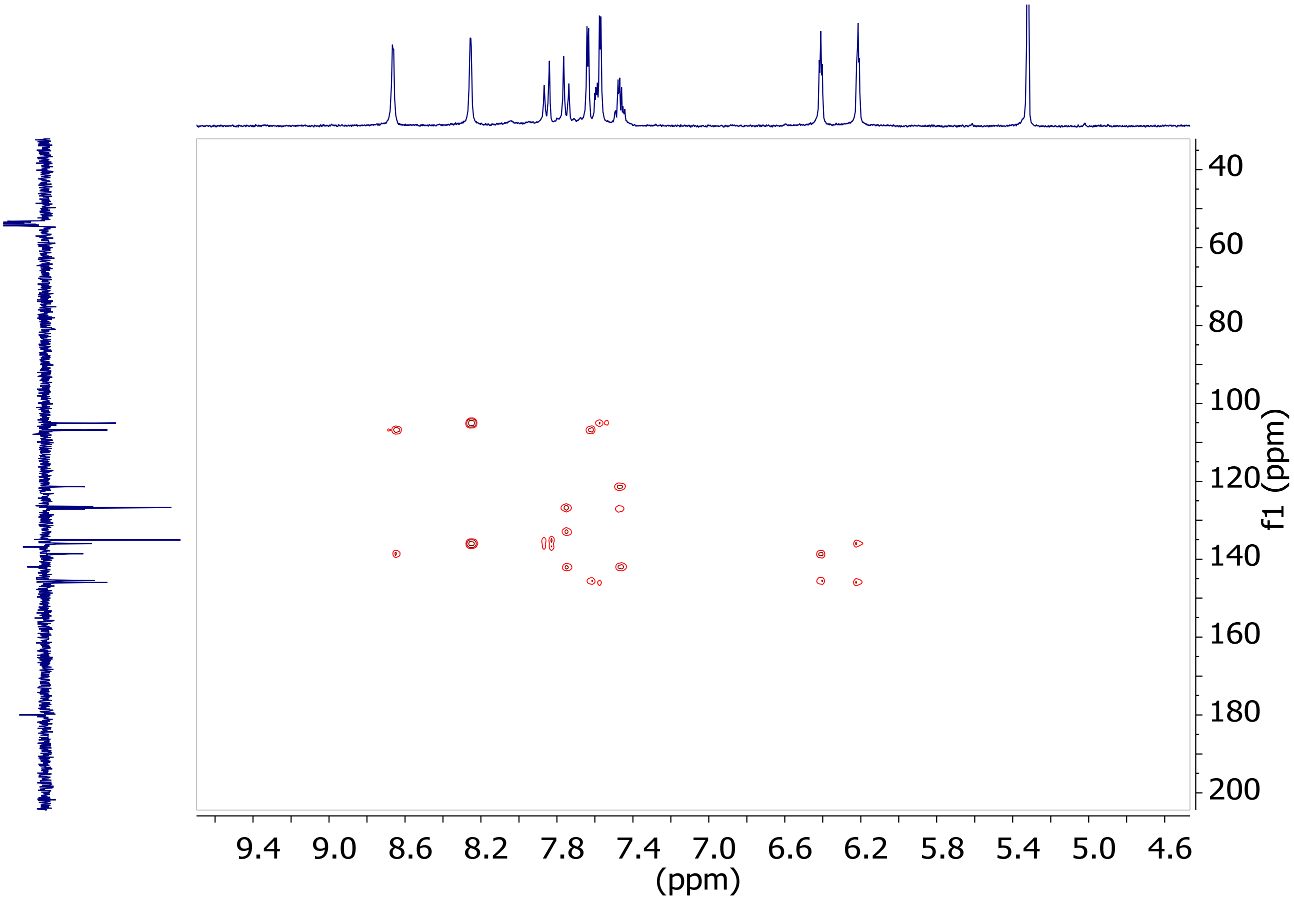

Figure S6. ^{1}H-^{13}C HMBC spectrum (CD_2Cl_2, 300 K, 9.1 T) of **{Cs ⊂ [Fe^{II}(Tp)$(CN)_3$]$_4$[Co^{III}(^{TPh}Tp)]$_4$}ClO_4.**

5. Cyclic voltammetry experiment

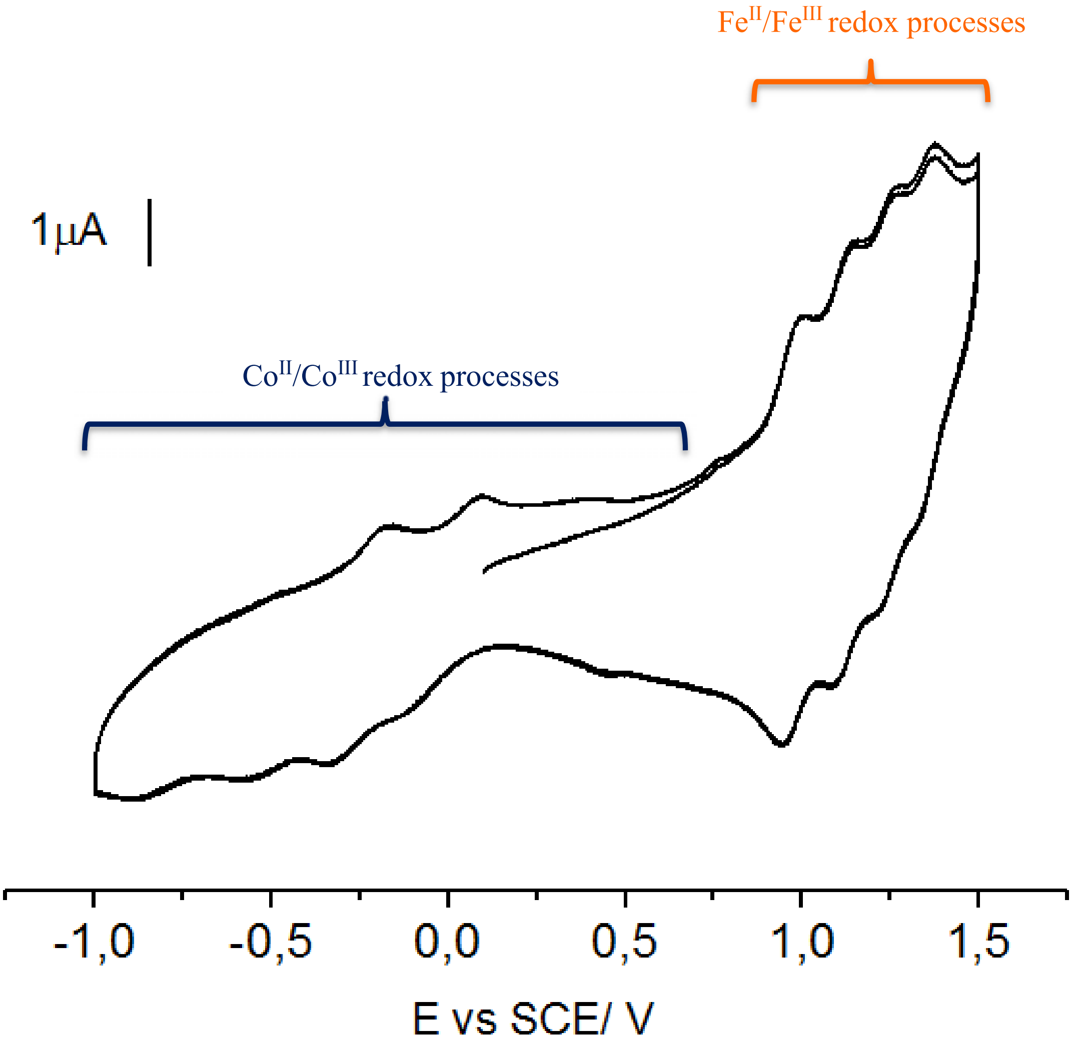

Figure S7. Cyclic voltammogram of **{Cs⊂[Fe^{II}(Tp)(CN)$_3$]$_4$[Co^{III}(^{TPh}Tp)]$_4$}ClO$_4$.**in acetonitrile with TBAPF$_6$ (0.1M), at v = 100 mV.s^{-1}.

6. FT-IR characterization

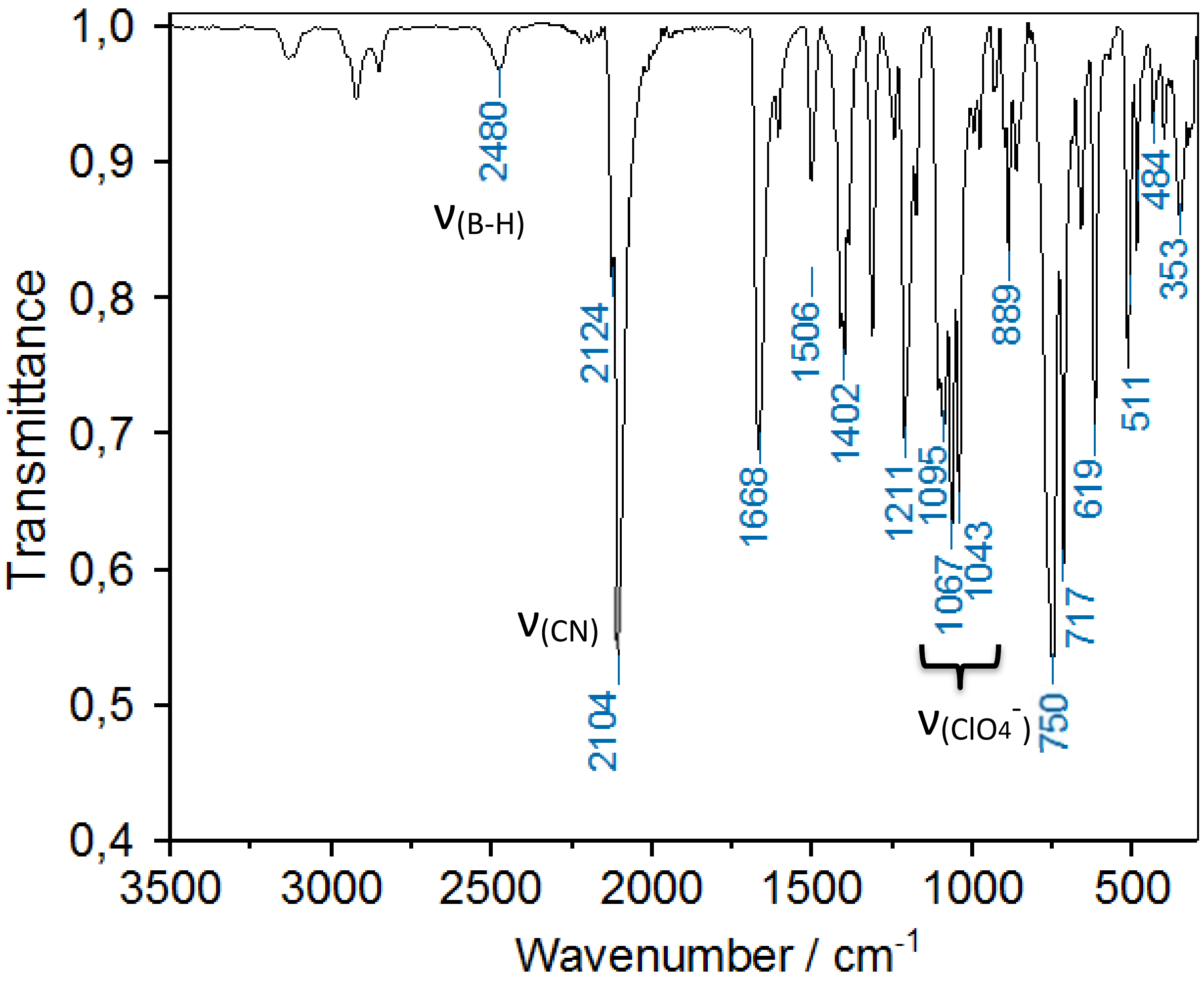

Figure S8. FT-IR spectrum of $\{\mathbf{Cs}\subset[\mathbf{Fe}^{\mathrm{II}}(\mathbf{Tp})(\mathbf{CN})_3]_4[\mathbf{Co}^{\mathrm{III}}({}^{\mathbf{TPh}}\mathbf{Tp})]_4\}\mathbf{ClO}_4$ crystalline powder.

7. UV-vis absorption spectrum

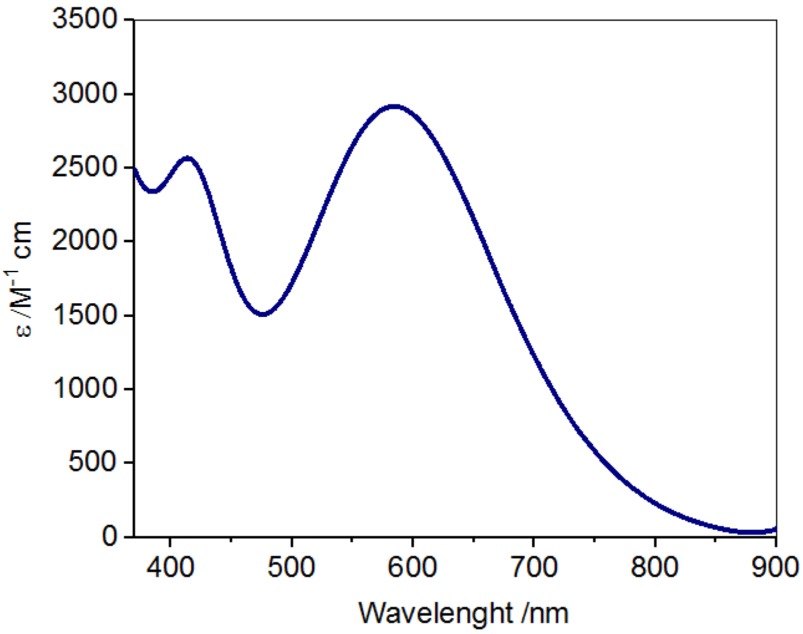

Figure S9. UV-visible spectrum of **$\{Cs\subset[Fe^{II}(Tp)(CN)_3]_4[Co^{III}(^{TPh}Tp)]_4\}ClO_4$** in dichloromethane at 10^{-4} M, 273K.

The broad and asymmetric band observed at ca 585 nm is due to the FeCo charge transfer transition while the band centred at *ca*. 410 nm is due to the LMCT band of the $\{Fe(Tp)(CN)_3\}^{2-}$ subunits.

8. XPS measurements

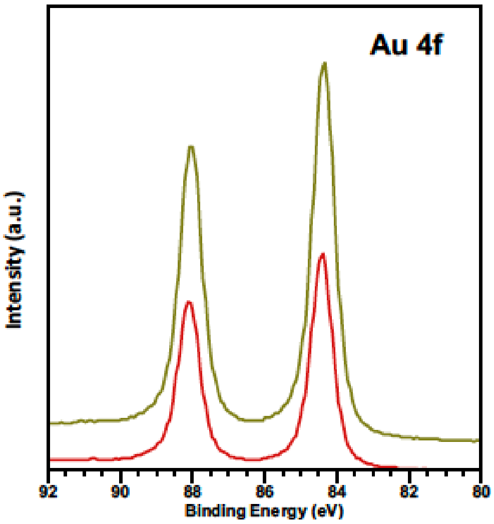

Figure S10. Au 4f peaks recorded prior to (top) and after (bottom) EI deposition of the **Cs⊂{Fe$_4$Co$_4$}** molecule.

If the surface is considered as atomically smooth and the adlayer is continuous with a constant thickness, the apparent intensity ratio of Au 4f signal recorded prior to and after the EI deposition of the Cs⊂{Fe$_4$Co$_4$} molecule may be computed using the following equation:

$$\frac{I_{Au}^{Ad}}{I_{Au}^{S}} = \exp(-\frac{t}{\lambda_{Au}^{Ad} cos\theta})$$

where I_{Au}^{S} andI_{Au}^{Ad} are the intensity of Au 4f peak recorded prior to (S: substrate) and after EI deposition of molecules (Ad: adlayer), θ is the take-off angle (θ = 0°). The electron inelastic mean free paths (IMFP), λ_{Au}^{Ad}, was calculated using the Quases program[6] and the TPP2M formula,[7] considering the adlayer composition deduced from the stoichiometry of the Cs⊂{Fe$_4$Co$_4$} molecule. By taking a density of 1.5 and an energy gap of 2.3 eV, λ_{Au}^{Ad} was equal to 3.5 nm.

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[6] http://www.quases.com

[7] Tanuma, S.; Powell, C. J.; Penn, D. R. Calculations of Electron Inelastic Mean Free Paths (IMFPs)VI. Analysis of the Gries Inelastic Scattering Model and Predictive IMFP Equation. *Surf. Interface Anal.* **1997,** *25*, 25-35.