

Supporting Information

Ferrocene-based Porous Organic Polymer: Synthesis, Characterization and Electrochemical Study

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1. General Information

1.1 Materials

1,2-dichloroethane was dried over calcium hydride and distilled. All other commercially available reagents and solvents were used without further purification. Commercially available starting materials were bought from Sigma-Aldrich, depending upon their availability.

1.2 General Instrumentations and Methods

1.2.1. Powder X-Ray Diffraction (PXRD)

Powder X-ray diffraction patterns were recorded in a Shimadzu XRD7000 diffractometer, using Cu-K α radiation with a $\Delta 2\theta = 0.02^\circ$ in the 2° to 90° 2θ range.

1.2.2. Fourier Transform Infrared (FT-IR)

The infrared spectra in the $400\text{--}4000\text{ cm}^{-1}$ region was recorded. The samples were prepared as diluted KBr pellets using a FTLA-2000 spectrometer.

1.2.3. Solid State NMR Spectra

^{13}C CP MAS NMR spectra were collected on a 9.4 T WB Bruker Avance III spectrometer operating at Larmor frequencies of 100.3 MHz (for ^{13}C) and 3.2 mm double-resonance MAS probe was employed. Samples were spun in ZrO_2 rotors and registered at room temperature. High resolution spectra were recorded using CP-MAS method (cross-polarization - magic angle spinning) at 10 KHz. Samples were referenced to glycine (C=O, 176.03 ppm vs. TMS). Acquisitions were performed using CP. ramp. 100 pulse sequence using 4.5 μs proton 90° degree pulse and recycle delay of 4 s. All spectra were recorded 3ms for contact time.

1.2.4. Textural Properties

Pretreatment

FPOP was left under vacuum (0.015 mmHg) and heating ($T_f = 80^\circ\text{C}$) for 18h. After this time, it was taken immediately to analysis.

Analysis

The surface areas and pore size distribution were found by N_2 adsorption/desorption, in the Quantachrome Nova 2200e. The isotherms were measured using a liquid nitrogen bath (77 K). The P/P_0 relative pressure values for the BET area were chosen from 5×10^{-3} to 0.3 (Multi-BET). The pore size was determined using the NLFDT (Non-local Density Functional Theory) method, slit/cylindrical pore, whose calculation model was based on carbon adsorbate. The total pore volume V_p was calculated from the nitrogen adsorption data at relative pressure $P/P_0 \approx 0.98 - 0.99$ and the pore size distribution was calculated from the desorption curve.

N_2 adsorption and desorption curves for FPOP (Strategy A)

The product prepared by Strategy A showed a much lower BET specific surface area ($5\text{ m}^2\text{ g}^{-1}$), indicating that there was no formation of a porous material (Figure S1).

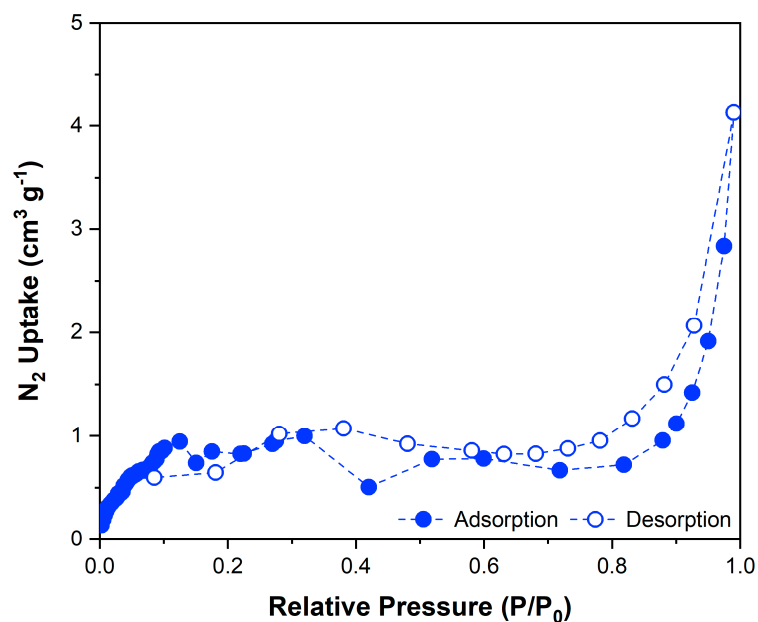


Figure S1. N₂ adsorption/desorption isotherm for FPOP (Strategy A), typical of non-porous materials.

1.2.5. Elemental Analysis

Elemental analysis (C, H, N) was carried out on in a CHNS series on Thermo Finnigan-CE Instruments Flash EA 1112 under standard conditions (T combustion reactor 900 °C, T GC column furnace 65 °C, multi-separation SS GC column, He flow 130 mL/min, O₂ flow 250 mL/min).

1.2.6. ICP-AES

ICP-AES - Inductively Coupled Plasma - Atomic Emission Spectroscopy of Fe, B and Na was carried out on ICP-AES Horiba Jobin-Yvon, France, Ultima, model equipped with a 40,68 MHz RF generator, Czerny-Turner monochromator with 1,00 m (sequential) and autosampler AS500.

1.2.7. Thermal Analyses

Differential scanning calorimetry (DSC) analysis were tested by TA Instruments Q-series TM Q2000 DSC with a refrigerated cooling system. The sample is continuously purged with 50 mL/min of nitrogen. About 2 mg of compound was crimped in hermetic aluminium sample pans with lid. Thermogravimetric analysis (TGA) was carried out using Setaram Labsys EVO by the Laboratório de Análises at LAQV/UCIBIO – REQUIMTE. The sample (~12 mg) was continuously purged with argon from 30 °C to 600 °C at 10 °C/min.

1.2.8. Electrochemical Methods

Analyses were performed in a standard three electrode set up: a modified working, an Ag/AgCl reference, and a coiled Pt wire counter electrode. Before analyses, the electrolyte (1 M H₂SO₄ in deionized water or ACN + 0.1 M TBAP) was purged with nitrogen for 15 minutes. The working electrodes were modified with FPOP or monomer (ferrocene) slurries that were prepared by grinding active material (35 wt.%), PVDF (5 wt.%), and carbon black (60 wt.%) with 0.3 mL of DMF or acetone) for 20 minutes in an agate mortar and pestle. The paste was subsequently transferred to a vial with additional 0.7 mL of solvent and sonicated for 10 minutes. A portion of this (3 μ L) was pipetted onto the tip of the electrode which was dried under high vacuum overnight before use.²

1.2.9. Cyclic Voltammetry

Cyclic voltammetry (CV) measurements were performed on an Autolab PGSTAT 12 potentiostat/galvanostat, controlled with GPES software version 4.9 (Eco-Chemie), using a cylindrical three-electrode configuration cell of 5 mL. A glassy carbon electrode (GC) (MF-2013, ϕ = 1.6 mm, BAS inc.) was used as the working electrode and a Pt wire was used as an auxiliary (counter) electrode. All potentials refer to an SCE (3 M KCl) reference electrode (Metrohm). Prior to use, the working electrode was polished in aqueous suspensions of 1.0 and 0.3 μ m alumina (Beuhler) over 2–7/8" micro-cloth (Beuhler) polishing pads, then rinsed with water and methanol. Different scan rates were used to characterize the electrochemical responses in the suitable electrochemical window.

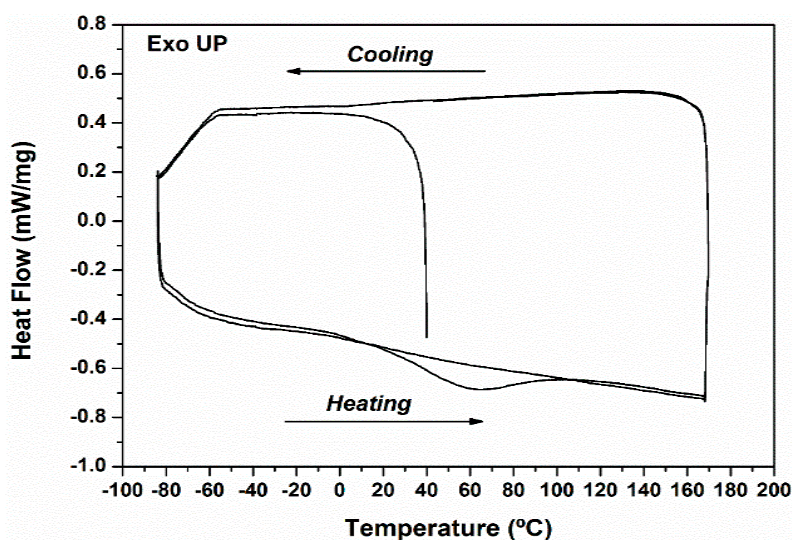


Figure S2. Heat flow thermogram for FPOP obtained upon heating and cooling rate of $10\text{ }^{\circ}\text{C min}^{-1}$, exhibiting no thermal events besides the evaporation of the adsorbed water in the first heating run.

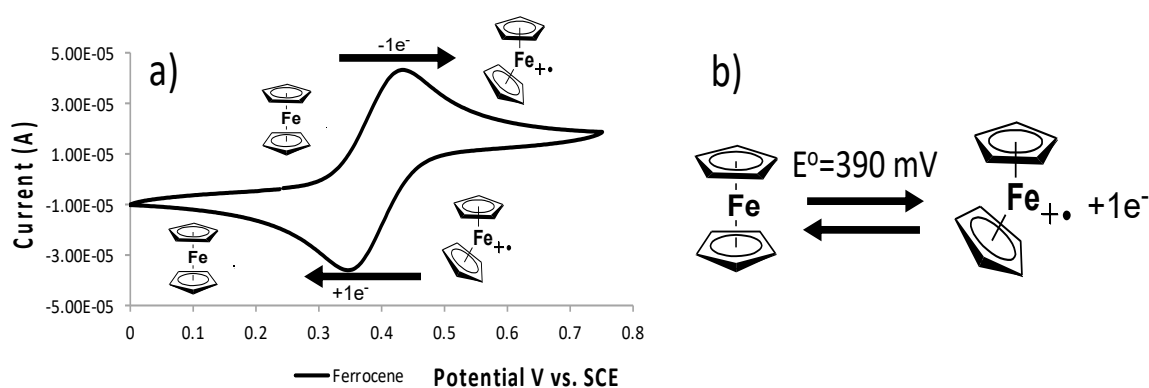
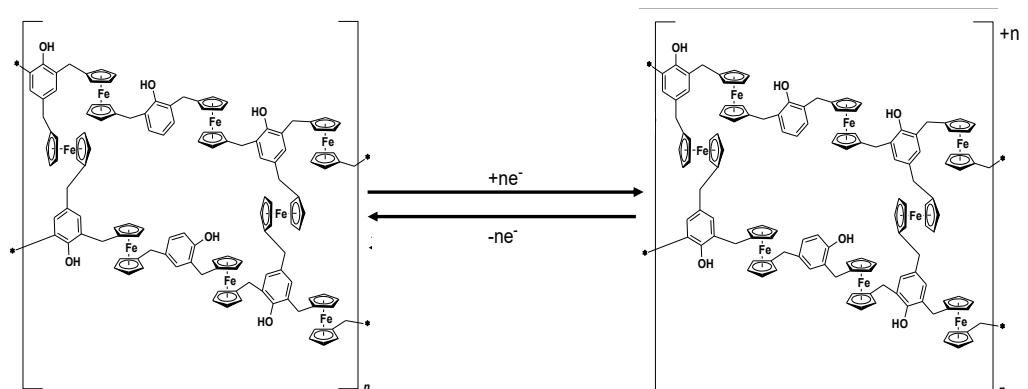


Figure S3. Cyclic voltammogram of 1 mM of Fc in ACN + 0.1 M TBAP at a scan rate of 100 mV/s and b) oxidation and reduction reaction of ferrocene (Fc) to ferrocenium (Fc^+) and vice-versa.

CV experiments in solution of Ferrocene, presents a well-known and fully reversible mono electronic electron transfer (ET) Fc/Fc^+ redox couple. The electron radical is fully stable in this media as illustrated in Figure S3 and Table S1. The Fc/Fc^+ redox couple is illustrated by the oxidation of ferrocene to ferrocenium and at the back scan is also clear the reduction of the ferrocenium to ferrocene with a standard potential (E^0) of 390 mV *vs.* SCE (an anodic peak, $E_{\text{pa}} = 430\text{ mV vs. SCE}$ and $\Delta E = 80\text{ mV}$). It is important to note that ΔE that corresponds to the peak-to-peak separation ($\Delta E = E_{\text{pa}} - E_{\text{pc}}$) is greater than 58 mV. A possible explanation for the difference in ΔE could be due to a combination: a) of a slower ET kinetics and b) non-compensated coulombic solution resistance. The oxidation potential shifts in the case of the substitution to the cyclopentadienyl. The potential is higher in substituted than in unsubstituted ferrocene due to the introduction of the electron withdrawing group that make the oxidation process more difficult (shifting the potentials to higher values) but is lower with electron donating groups. The electrode materials were firstly evaluated by CV studies in 3-

electrode configuration cell, firstly in ACN + 0.1 M TBAP at several scan rates and at adequate electrochemical windows (EW).



Scheme S1. Schematic of the possible oxidation and reduction of the FPOP materials

For a comparison the results of analysis for the FPOP modified electrode material were compared to the results obtained in the solution of ferrocene in ACN + 0.1 M TBAP that shows one reversible electron transfer at 390 mV (see Figure S3 and entry 1 of Table S1). All the results are calculated by an average value of the scan rates. It can be observed also for this modification that occurred a shift in the potentials in particular for anodic peak potential (E_{pa} = 395 mV *vs.* SCE), standard potential (E^0 = 353 mV *vs.* SCE) and peak to peak separation (ΔE = 85 mV) to lower values. Possibly, an easier oxidation ferrocene units of the adsorbed material occur then when ferrocene is in solution (E_{pa} = 35 mV and E^0 = 37 mV).

Table S1. Standard potential, anodic peak potential (in mV *vs.* SCE) and ΔE_p for ferrocene and FPOP modified electrodes in different solvents at 20 °C.

| Entry | Electrolyte | Compound | E^0 mV ^{a)} | E_{pa} mV ^{b)} | ΔE mV ^{c)} | WE |
|-------|-----------------------------|---|---------------------------|------------------------------|-----------------------------|--------------|
| 1 | ACN+TBAP | Fc | 390 | 430 | 80 | GC |
| 2 | ACN+TBAP | $\text{Fc}(\text{CH}_2)_9\text{N}^+(\text{CH}_3)_3$ | 613 | 678 | 131 | GC |
| 3 | ACN+TBAP | FPOP | 353 | 395 | 85 | GCE/CBP/FPOP |
| 4 | ACN+TBAP | FPOP | 351 | 415.5 | 129 | AuE/CBP/FPOP |
| 5 | 1 M H_2SO_4 | FPOP | 254.7 | 306.7 | 110 | AuE/CBP/FPOP |
| 6 | 1 M H_2SO_4 | FPOP | 202 | 277 | 75 | AuE/CBP/FPOP |

^{a)} Standard potential, calculated as $E^0 = (E_{pc} + E_{pa})/2$ measured *vs.* SCE, ^{b)} anodic peak potential E_{pa} in mV (*vs.* SCE) All the results are calculated by an average value of the several scan rates (E_p +/- 10mV) and ^{c)} $\Delta E = (|E_{pc}| - |E_{pa}|)$ in mV.

In the case of the gold disk modified electrode AuE/CBP/FPOP, the CV was performed in the matching experimental conditions (see Figure S4). A similar behavior was observed to the GCE/CBP/FPOP electrode: here is an n electron ET reversible process that presents $E_{pa} = 415.5$ mV *vs.* SCE, $E^0 = 351$ mV *vs.* SCE and $\Delta E = 129$ mV. In this media, the FPOP modification presents a higher anodic peak potential for 21.5 mV in respect to GCE/CBP/FPOP and peak-to-peak separation of 44 mV. A possible explanation for this difference is that the modification is slower in terms of reaction redox kinetic.

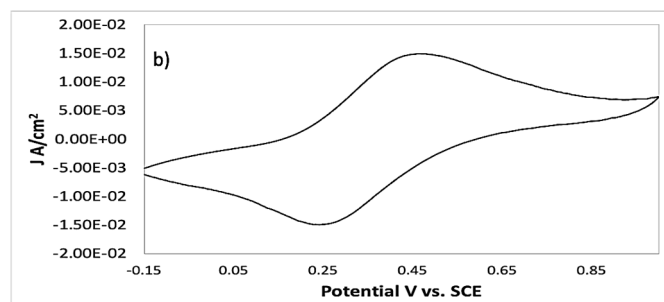
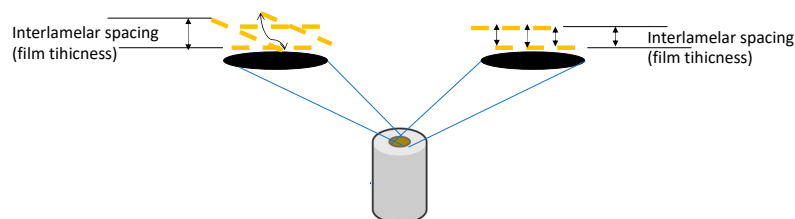


Figure S4. Cyclic voltammogram in ACN + 0.1M TBAP of the AuE/CBP/FPOP electrode at scan rates of 50mV/s



Scheme S2. Schematic of the possible film thickness and intercalation spacing for the diffusion of the electrolyte in to the FPOP materials upon oxidation and reduction process.

The modified AuE/CBP/FPOP (see Figure S5a) and PtE/CBP/FPOP (see Figure S5b) electrodes were also studied in 1M H_2SO_4 and a similar behaviour is observed for both modified electrodes: there is a typical fully reversible n-electron ET electrochemical behaviour. In the case of the AuE/CBP/FPOP, the anodic peak potential, standard and peak-to-peak separation were: $E_{pa} = 306.7$ mV *vs.* SCE, $E^0 = 254.7$ mV *vs.* SCE and $\Delta E = 110$ mV, respectively. In the case of aqueous solution, the peak potential is 96.3 mV lower, its standard potential shifts 108.8 mV also to lower potentials and the peak-to-peak separation also decrease in the 1 M H_2SO_4 indicating a faster electron transfer in this material in the presence of the strong acid.

Figure S5b presents the CV study performed on PtE/CBP/FPOP modified electrode in 1 M H_2SO_4 . It shows a reversible electron transfer with anodic peak potential (E_{pa}) at 277 mV *vs.* SCE, cathodic peak potential (E_{pc}) 202 mV *vs.* SCE and a standard potential (E^0) of 240 mV *vs.* SCE. The $\Delta E = 75$ mV is indicative about the easiest oxidation and reduction processes.

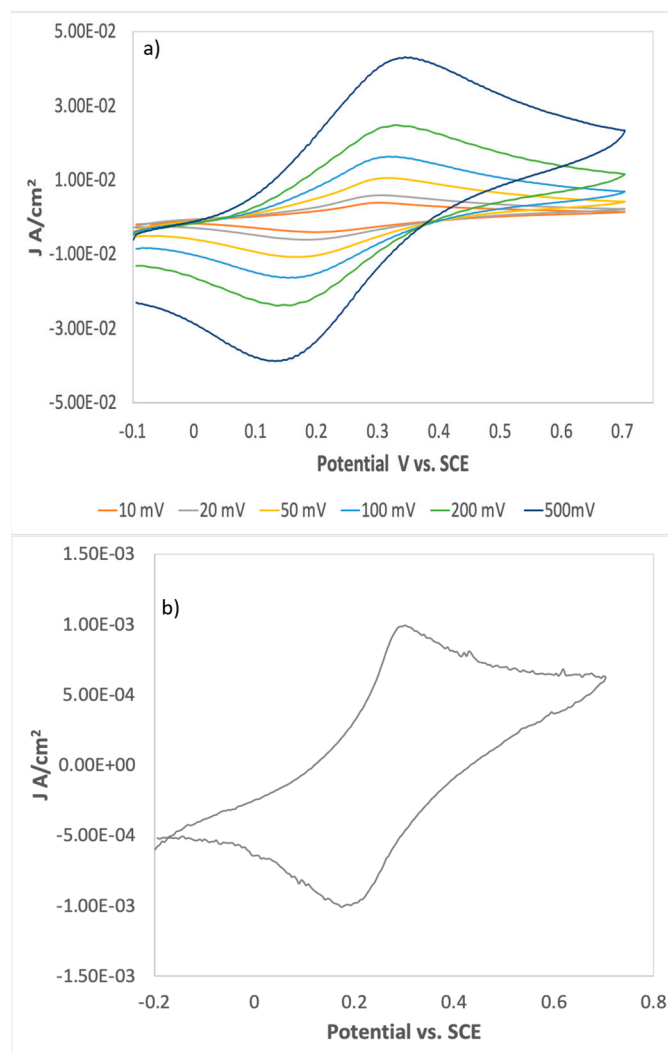


Figure S5. a) Cyclic voltammograms of the AuE/ CBP/FPOP electrode in 1M H₂SO₄ at different scan rates of 10, 20, 50, 100, 200 and 500 mV/s and b) Cyclic voltammograms of the PtE/CBP/FPOP in 1 M H₂SO₄, at scan rates of 100 mV/s.

In summary, the preliminary results for the voltammetric analysis using a modified electrode in both aqueous and organic solutions indicate that the redox reaction is diffused controlled. On AuE/CBP/FPOP modified electrode the E^0 is approximately the same as the GCE/CBP/FPOP but the E_{pa} is higher for the AuE/CBP/FPOP than for the GCE/CBP/FPOP. When the PtE/CBP/FPOP and Au/CBP/FPOP are tested in acidic conditions, both presented electrochemical response and the potentials are lower. Additionally, it could be observed that ΔE for the modified AuE/CBP/FPOP electrode in ACN + 0.1 M TBAP is 19 mV higher than the ones observed for the 1 M H₂SO₄. The lowest ΔE was obtained on the modified PtE/CBP/FPOP electrode possessing 75 mV lower than all the values obtained for the ACN + 0.1 M TBAP. In the case of aqueous solution 1 M H₂SO₄ it is also important to consider that H⁺ and SO₄²⁻ have lower diffusion coefficients is possible to understand that the same electrode showed a higher E_p and E^0 in organic solvent media than in aqueous media.

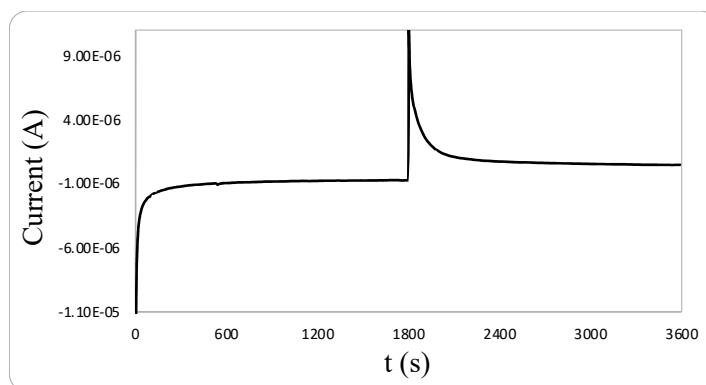


Figure S6. The chart represents current vs time for the Electrolysis of the FPOP oxidation coloration and reduction bleaching reaction of ferrocene (Fc) to ferrocenium (Fc^+) core materials in the FPOP in the ECD using as electrolyte the LiOTf:4EG.

2. Synthesis of Ferrocene-based Porous Organic Polymer

2.1. Synthesis from phenol (*Strategy A*)

The mixture of phenol (2.65 mmol; 250 mg), ferrocene (7.95 mmol; 1479 mg; 2.25 equiv.) and paraformaldehyde (15.9 mmol; 477 mg; 2.25 equiv.) under argon, was dissolved in dry 1,2-dichloroethane (10 mL). The solution was cooled to 0 °C for 5 minutes, $\text{BF}_3\cdot\text{Et}_2\text{O}$ (17.49 mmol; 2.16 mL; 2.5 equiv.) was added drop wisely and reaction mixture was left to stir for 24 h slowly reaching room temperature. After that time, a dark brown suspension was formed. The reaction mixture was then diluted with dichloromethane (10 mL) and quenched with saturated ammonium bicarbonate solution. At this point it had an appearance of a black emulsion. Excess sodium thiosulfate (2.0 g) was added and the reaction was left to stir in inert atmosphere for 3 days until it changed to a stable light brown colour. Since it was still an inseparable suspension, all the volatiles were evaporated to dryness with addition of some ethanol in order to prevent solvent bubbling. The solid residue was washed with water, ethanol and dichloromethane, filtered off and extracted with dichloromethane in Soxhlet extractor for 24 h. The remaining solid was dried in vacuum to provide dark brown powder (98%).

CP-MAS ^{13}C solid-state NMR: 155.06, 131.36, 116.55, 88.46, 69.86, 2938.

FTIR (KBr, cm^{-1}): 3435, 3082, 2913, 2839, 1797, 1631, 1511, 1428, 1354, 1225, 1169, 1102, 1029, 920, 813, 754, 477.

2.2. Synthesis from Bakelite (*Strategy B*)

To the mixture of solid Bakelite (0.328 mmol; 217 mg), excess of ferrocene (5.38 mmol; 1000 mg; 2.05 equiv.) and paraformaldehyde (5.38 mmol; 161.5 mg; 2.05 equiv.) was added, under argon, dry 1,2-dichloroethane (10 mL). The mixture was cooled to 0°C for 5 minutes and it

was added drop wisely $\text{BF}_3\cdot\text{Et}_2\text{O}$ (5.38 mmol; 664 μL ; 2.05 eq.) and the reaction mixture was left to stir for 24 h slowly reaching room temperature. After that time a brownish suspension was formed, as well as black precipitate in the form of a ring on the walls of the flask. The reaction mixture was diluted with dichloromethane (10 mL) and quenched with saturated ammonium carbonate solution. The brownish suspension was carefully removed from the black precipitate (decanted into another flask) and carefully evaporated with addition of some ethanol in order to prevent solvent jumping. After evaporation the brownish residue was washed on filter with ammonium carbonate solution, distilled water, ethanol and diethyl ether until the washings were colourless and then extracted in Soxhlet extractor for 24h with dichloromethane. The remaining solid was dried under vacuum and 473 mg of yellow-brown powder was isolated (60%).

Although slightly different in colour, the characterization of compounds prepared by two methods was nearly completely identical.

For compounds prepared by *Strategy B*:

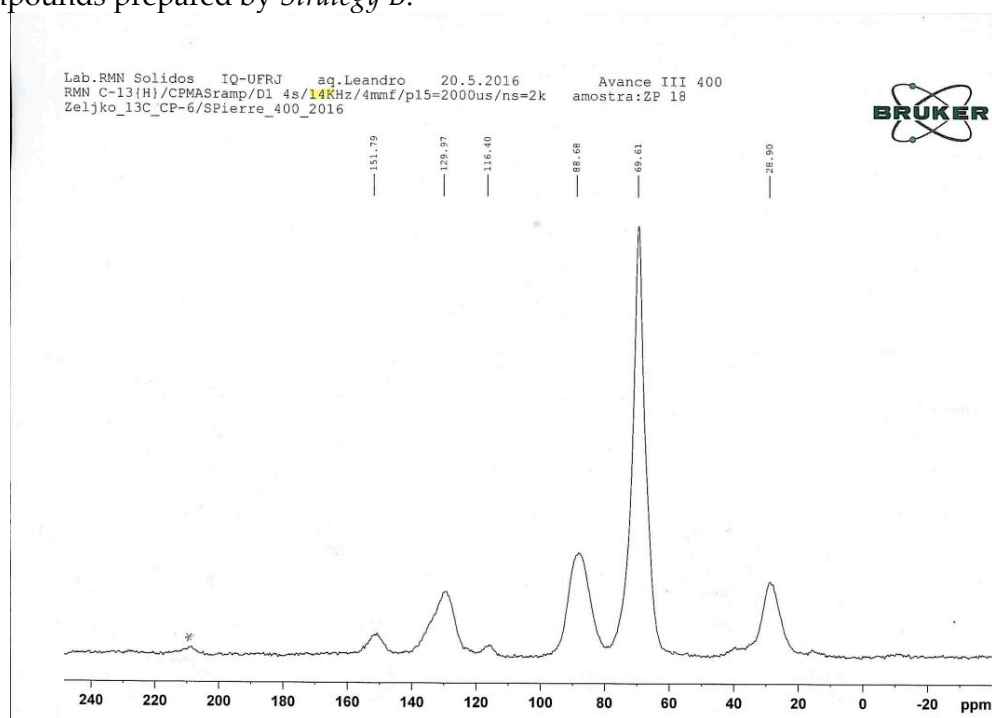


Figure S7. CP-MAS ^{13}C solid-state NMR spectrum *Strategy B*

CP-MAS ^{13}C solid-state NMR: 151.79, 129.97, 116.40, 88.68, 69.61 and 28.90 ppm.

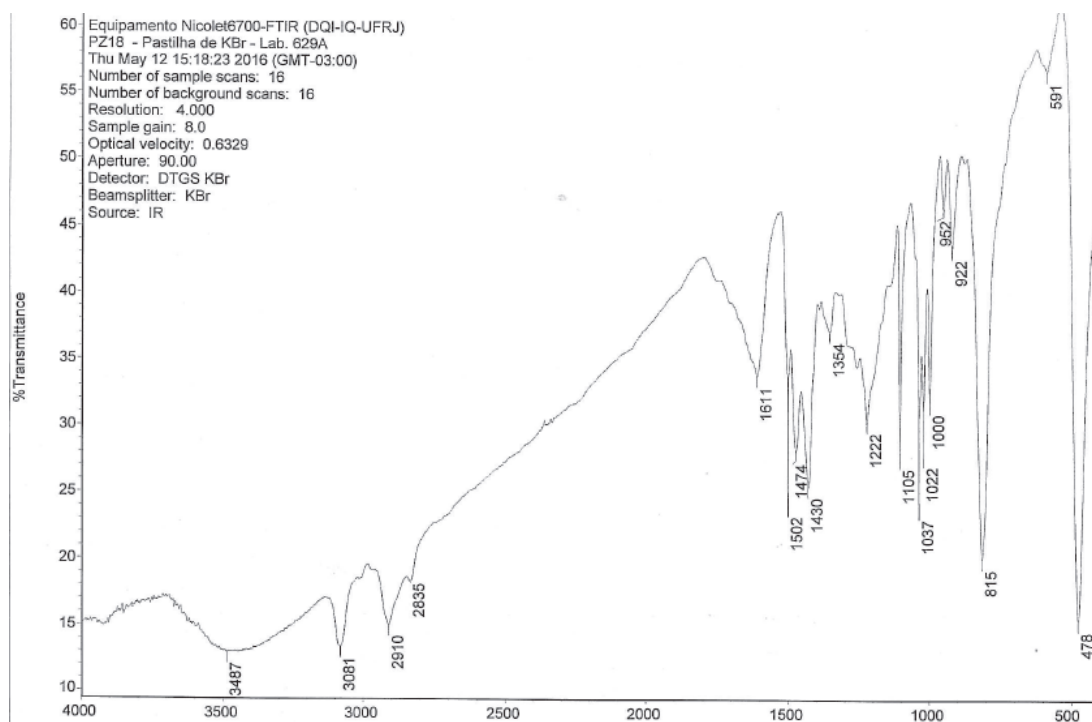


Figure S8. FTIR (KBr, cm^{-1}) spectrum of *Strategy B*

FTIR (KBr, cm^{-1}): 3487, 3081, 2910, 2835, 1611, 1502, 1474, 1430, 1354, 1222, 1105, 1037, 1022, 1000, 952, 922, 815, 591, 478.

$\text{C}_{132}\text{H}_{116}\text{O}_6\text{Fe}_8\text{Fe}(\text{OH})_2 \cdot 3.5\text{H}_2\text{O}$, found: C, 65.95 (elemental analysis); H, 4.94 (elemental analysis); Fe 21.16 (ICP); B 0.06 (ICP) and Na 0.17 % (ICP). $\text{C}_{132}\text{H}_{116}\text{O}_6\text{Fe}_8\text{Fe}(\text{OH})_2 \cdot 3.5\text{H}_2\text{O}$ requires per unit: C 66.11; H 5.25 and Fe 20.96 %. Extraction and titration of inorganic Fe(II)/Fe(III) was also achieved using adapted method of *Lucchesi and Hirn*¹ finding approximately 0.6:8 ratio Fe(II)/Fe(III) to ferrocene unit.

Obs.: Small quantity of Na and B found was slightly reduced in repeated analysis by aqueous washing and probably is due to precipitation of some less soluble sodium borate inside the cavity (less than $0.1\text{Na}_2\text{B}_4\text{O}_7$ per unit/cavity).

References

- (1) Lucchesi, C. A.; Hirn, C. F. EDTA Titration of Total Iron in Iron(II) and Iron(III) Mixtures. Application to Iron Driers. *Anal. Chem.* **1960**, 32 (9), 1191–1193. <https://doi.org/10.1021/ac60165a044>.
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