Electronic Supplementary Information for:

Mixed valency in a neutral 1D Fe-chloranilate coordination polymer

Katelyn M. Clutterbuck,[a] Brendan F. Abrahams,*[a] Timothy A. Hudson[a] and Martin P. van Koeverden[a,b]

[a]School of Chemistry, University of Melbourne, Parkville, Victoria 3010, Australia.

[b]Present Address: School of Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia.

*Email: bfa@unimelb.edu.au

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Experimental

General procedures

All reagents and solvents, other than those specified below, were obtained from commercial sources and used without further purification. Attenuated total internal reflectance (ATR) Fourier-transform infrared (FT-IR) spectra were measured under ambient conditions using a Bruker Alpha II spectrometer fitted with a diamond ATR accessory or a Perkin Elmer Spotlight 100 spectrometer fitted with a ZnSe Universal ATR accessory. FT-IR spectra as KBr discs were measured using a Bruker Tensor 27 FTIR spectrometer. For single crystal X-ray diffraction (SC-XRD) studies, crystals were transferred directly from the mother liquor into a protective oil and placed in a stream of nitrogen at a selected temperature. Data were collected on an Rigaku XtaLAB Synergy-S diffractometer equipped with a Cu-Kα microfocus source or on the MX2[1] beamline at the Australian Synchrotron. Crystal structures were solved using the program SHELXT using intrinsic phasing[2] and refined using the least-squares minimisation on F^2 within SHELXL[3] using the Olex2 GUI[4] program. Unless otherwise noted, the thermal and positional parameters for non-hydrogen atoms in the asymmetric unit were refined anisotropically. Hydrogen atoms were placed at calculated positions using suitable riding models and refined using isotropic displacement parameters derived from their parent atoms.

3,6-Difluoro-2,5-dihydroxy-1,4-benzoquinone (Fluoranilic acid, H_2Fan)

H_2Fan was synthesised using a modified literature procedure[5] in two steps from commercially available 2,3,5,6-tetrafluorohydroquinone, via the intermediate 2,3,5,6-tetrafluoro-1,4-benzoquinone (F_4BQ), also obtained using a modified literature procedure.[6] In brief, $(NH_4)_2Ce^{IV}(NO_3)_6$ (145.1 g, 220 mmol) was dissolved with stirring in H_2O (700 mL). 2,3,5,6-tetrafluorohydroquinone (18.21 g, 100 mmol) was added portion-wise to the stirring Ce^{IV} solution, causing an immediate colour change from a transparent orange solution to a pale-yellow suspension. The reaction was stirred 1 hr at room temperature, then extracted with Et_2O (3 × 200 mL) until the organic extract was colourless. The combined organic phase was washed with H_2O acidified with 2 drops concentrated HCl (2 × 150 mL), brine acidified with 1 drop conc. HCl (150 mL), dried over $MgSO_4$ then concentrated to dryness at reduced pressure, yielding F_4BQ as a pale yellow scaly solid (15.63 g, 86.8%), which was used without further purification. FT-IR (KBr): $\tilde{\nu}$ = 3442 (br s), 1702 (s), 1690 (s), 1677 (s), 1384 (m), 1335 (m), 1266 (w), 1004 (m), 542 (br w) cm^{-1}.

NaOH (9.5582 g, 734 mmol) was dissolved in H_2O (190 mL) and cooled in an ice-water bath to <10 °C. F_4BQ (9.5582 g, 53.1 mmol) dissolved in 1,4-dioxane (75 mL) was added dropwise over 30 min to the vigorously stirring NaOH solution. The reaction was then stirred 30 min at 10 °C, then warmed to 60 °C and stirred 1 hr. The chocolate brown suspension was cooled to room temperature, then the solids were isolated by suction filtration (Por. 3 frit). The product was washed on the frit with 10% w/w NaOH solution (2 × 75 mL), 1:1 v/v EtOH/H_2O (100 mL) then EtOH (100 mL). The chocolate brown solid was then dried 24 hrs at 100 °C yielding olive-green crude Na_2Fan (10.51 g). The crude Na_2Fan (10.51 g) was suspended in H_2O (300 mL) and heated to 60 °C with stirring. Conc. HCl (100 mL) was added dropwise to the stirring suspension, causing precipitation of a dark red crystalline product. The reaction was cooled to room temperature, then the precipitated solids isolated by suction filtration (Por. 3 frit), then

dried by suction yielding an orange-red solid (6.4468 g). The crude orange-red solid was dissolved in the minimum of boiling AcOH (120 mL), hot filtered to remove trace brown residue, then concentrated by boiling the solution down to ca. 80 mL. The intense cherry-red solution was then cooled slowly to rt. The crystallised orange-red rods were isolated by suction filtration (Por. 3 frit), dried by suction then washed with *n*-hexane (2 × 100 mL), before being dried *in vacuo* (0.3 mbar, 80 °C) over KOH. This yielded fluoranilic acid as a bright orange powder (4.88 g, 52.2% from F_4BQ).

3,6-Dichloro-1,2,4,5-tetrahydroxybenzene (H_4Clan)

H_4Clan was synthesised using a modified literature procedure.[7] A suspension of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone (H_2Clan, 6.053 g, 28 mmol) in conc. HCl (120 mL) was heated to 100 °C with stirring. Granulated tin (4.716 g, 40 mg-atom) was added portion-wise and the solution was heated until the orange suspension lightened to a pale–yellow solution. Excess Sn was removed by hot filtration and the filtrate was cooled to room temperature then at 4°C for 36 hours. The product crystallised as off-white needles which were collected by vacuum filtration then washed with cold conc. HCl (20 mL) and chloroform (3 × 25 mL). The product was dried *in vacuo* over KOH, then P_2O_5 to give H_4Clan (3.09 g, 52%). The product is stable for several months when stored under N_2 at 4 °C.

Fe(Fan)(4,4'-bipy)$_2$

An aqueous solution (10 mL) of $FeCl_2{\cdot}4H_2O$ (10.0 mg, 0.05 mmol), $LiOAc{\cdot}2H_2O$ (20.3 mg, 0.04 mmol) and 4,4'-bipy (16.3 mg, 0.10 mmol) was layered below a solution of H_2Fan (8.8 mg, 0.05 mmol) in MeOH (10 mL), separated by a buffer layer of 1:1 v/v MeOH-H_2O (1 mL). Black needles suitable for SC-XRD formed after a week and were collected to give Fe(Fan)(4,4'-bipy)$_2$ (3.96 mg, 15%). The P-XRD pattern on the bulk sample matched the calculated powder pattern obtained from the single crystal structure determination (Figure S1). Anal. Calcd for $Fe(C_6O_4F_2)(C_{10}N_2H_8)_2$: C, 57.59%; N, 10.33%; H, 2.97% Found: C, 57.57%; N, 10.17%; H, 3.18%. FT-IR (ATR): $\tilde{\nu}$ = 1594, 1541, 1498, 1405, 1356, 1005, 804, 617, 500, 432 cm^{-1}.

Fe(Clan)(OPPh$_3$)$_2$

Crystals for single crystal X-ray diffraction

An aqueous solution (15 mL) of $FeSO_4{\cdot}7H_2O$ (28.6 mg, 0.10 mmol) was layered below a solution of H_4Clan (21.2 mg, 0.10 mmol) and triphenylphosphine oxide ($OPPh_3$, 56.1 mg, 0.20 mmol) in acetone (15 mL). After a week, two distinct bands of black crystals had appeared on the wall of the reaction vial above and below the interface of the two layers. The plate-like crystals in the band above the interface were suitable for SC-XRD analysis.

Bulk product

An aqueous solution (10 mL) of $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ (86 mg, 0.22 mmol) and $NaHSO_3$ (23 mg, 0.22 mmol) was placed at the bottom of a 39 mL vial. A 'buffer' layer containing 2.5 mL of acetone and 7.5 mL of water was then carefully layered on top. A solution of H_2Clan (41.8 mg, 0.20 mmol) and triphenylphosphine oxide ($OPPh_3$, 122.4 mg, 0.44 mmol) in acetone (10 mL) was then carefully layered on top of the buffer layer. After a week, a band of black crystals

appeared on the wall of the reaction vial, near the original location of the buffer layer whilst a dark precipitate occupied the base of the vial. Using a Pasteur pipette the precipitate at the bottom of the vial was carefully removed without disturbing the crystals adhering to the vial wall. After all the precipitate from the base was removed the crystals on the vial wall were dislodged and filtered from the solution. The P-XRD pattern on the bulk sample matched the calculated powder pattern obtained from the single crystal structure determination (Figure S3). Yield 12.3 mg. Anal. Calcd for $Fe(C_6O_4Cl_2)(POC_{18}H_{15})_2$: C, 61.57%; H, 3.69%; Found: C, 61.44%; H, 3.72%. FT-IR (ATR): $\tilde{\nu}$ = 1589, 1467, 1435, 1388, 1118, 1068, 1025, 996, 851, 721, 688, 533 cm^{-1}.

Electrical Conductivity Measurements

Ambient temperature electrical conductivity measurements on pressed pellets of $Fe(Clan)(OPPh_3)_2$ were obtained using 2-electrode screw cells similar to those described in literature.[8-10] In air, the screw cells were fabricated by placing two copper dies (D = 3.0 mm) polished to a mirror finish, into a snugly fitting borosilicate tube (ID = 3.0 mm). The tube containing the copper dies was held in a 3D printed PLA cell holder, and the copper dies compressed against each other by two brass screws inserted through the sides of the cell holder. The blank cell length was determined using a calliper. The screw cells were then disassembled and a sample of $Fe(Clan)(OPPh_3)_2$ placed into the glass tube. The pressed pellets were formed *in situ* by compressing the compound between the polished copper dies by tightening the brass screws in the PLA sample holder. The pellet thickness was measured using a calliper. Current-voltage (*I-V*) curves were measured using an Ossila X100 (Sheffield, UK) source-measure unit (SMU) interfaced using locally produced software. The conductivity cells were connected to the SMU via alligator-clip equipped copper cables and BNC cables. The *I-V* curves were measured over the potential window ±0.3 V in 0.01 V steps, and the resulting linear curves (confirming Ohmic behaviour) were fitted with Ohm's Law,

$$J = \sigma E$$

Where J (A cm^{-2}) is the current density, E (V cm^{-1}) is the electrical field strength, and σ (S cm^{-1}) is the electrical conductivity.

Table S1 Crystallographic data

Compound	**Fe(Fan)-(4,4'-bipy)$_2$**	**Zn(Fan)-(4,4'-bipy)$_2$**	**Fe(Clan)(OPPh$_3$)$_2$**	**Fe(Clan)(OPPh$_3$)$_2$**
Formula	$C_{26}H_{16}F_2FeN_4O_4$	$C_{26}H_{16}F_2N_4O_4Zn$	$C_{42}H_{30}Cl_2FeO_6P_2$	$C_{42}H_{30}Cl_2FeO_6P_2$
Formula Weight	542.28	551.80	819.35	819.35
***T* (K)**	100	100	100	300
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	*I2/a*	*I2/a*	*P2/c*	*P2/c*
***a* (Å)**	13.84790(10)	16.3388(4)	12.463(3)	12.662(3)
***b* (Å)**	9.60960(10)	9.7015(2)	13.273(3)	13.378(3)
***c* (Å)**	16.33170(10)	13.8237(3)	12.782(3)	12.892(3)
***α* (°)**	90	90	90	90
***β* (°)**	97.4780(10)	97.072(2)	118.94(3)	119.05(3)
***γ* (°)**	90	90	90	90
***V* (Å^3)**	2154.82(3)	2174.54(8)	1850.3(8)	1909.1(8)
Z	4	4	2	2
Independent Reflections	8666	5086	5500	4054
Reflections Collected	11214	7724	32816	26283
***R*$_1$ (*I*>σ(*I*))**	0.0271	0.0421	0.0630	0.0594
***wR*$_2$**	0.0741	0.1251	0.1960	0.1903

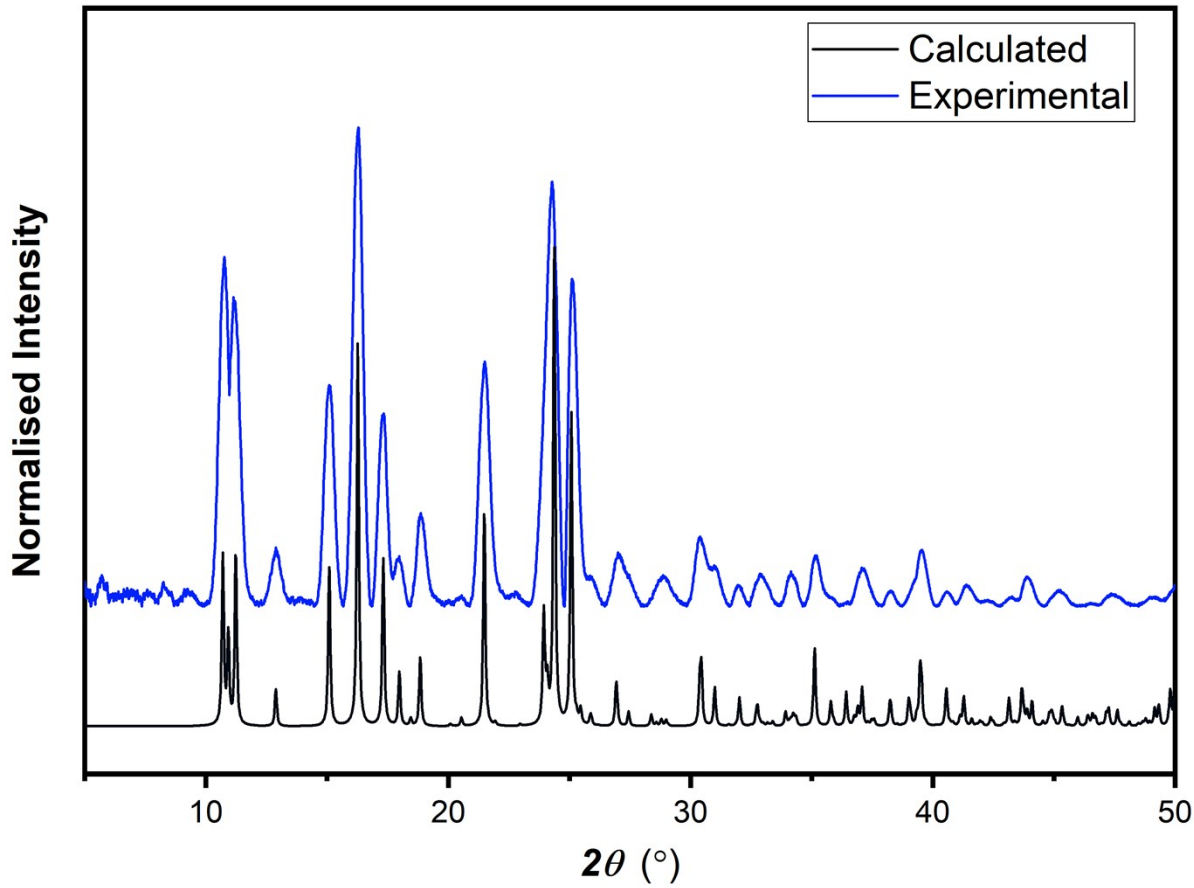


Figure S1 P-XRD (λ = 1.54184 Å) pattern of bulk Fe(Fan)(4,4'-bipy)$_2$ (blue, T = 100 K) and calculated pattern (black, T = 100 K) from SC-XRD of Fe(Fan)(4,4'-bipy)$_2$.

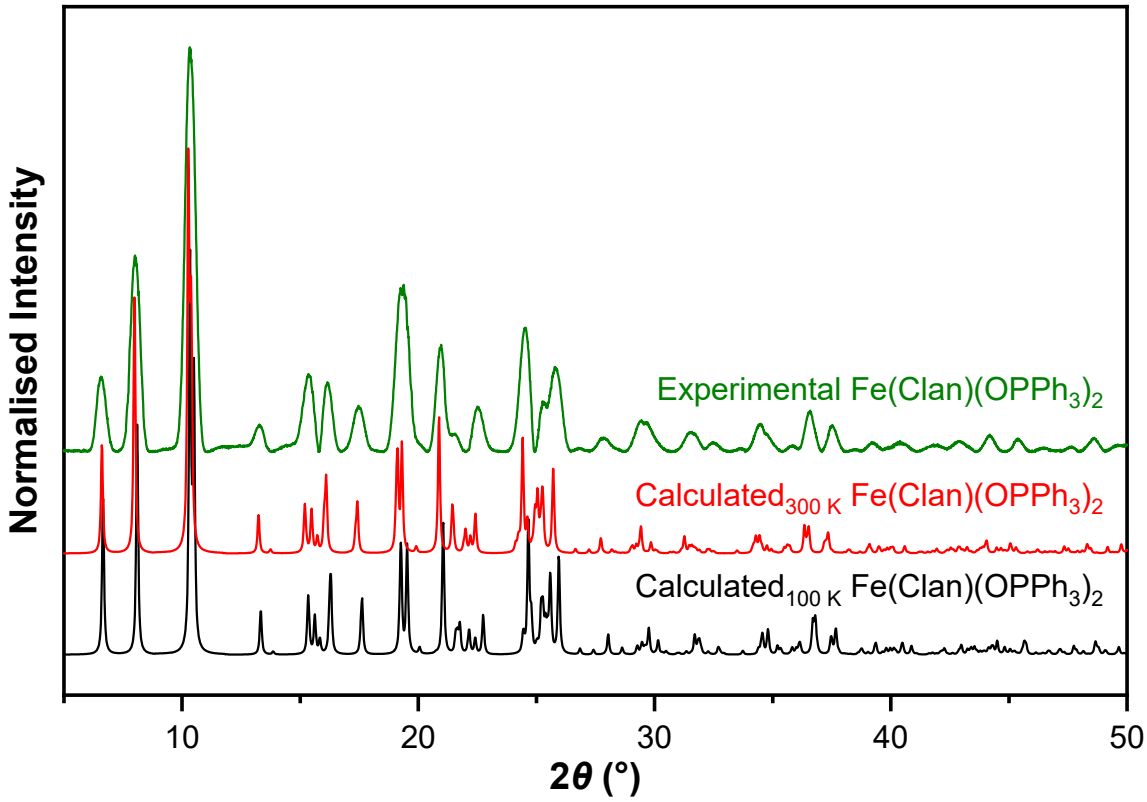


Figure S2 P-XRD (λ = 1.54184 Å) pattern of bulk Fe(Clan)$(OPPh_3)_2$ (green, T = 260 K) and calculated patterns (black, T = 100 K and red, T = 300 K) from SC-XRD of Fe(Clan)$(OPPh_3)_2$.

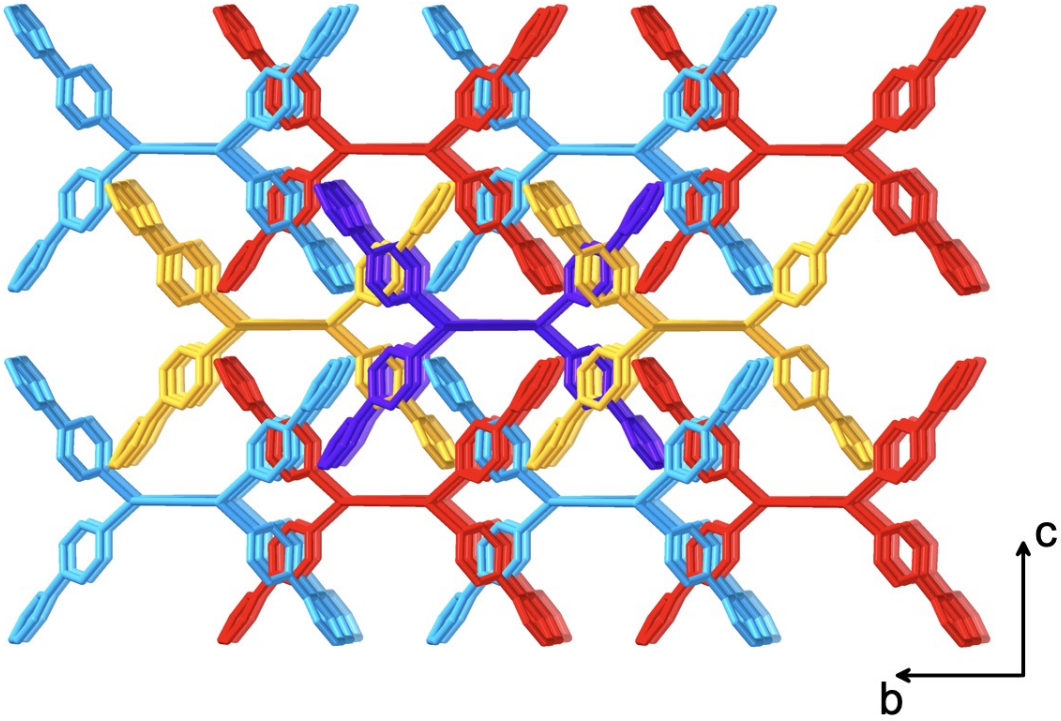


Figure S3 A view of the extended packing of chains in Fe(Fan)(4,4'-bipy)$_2$. Fluoranilate ligands are represented as single rods for clarity. 'A' layers within the ABAB… stacking sequence are represented by pale blue and red chains; a B layer is represented by purple and gold chains. A similar packing arrangement is adopted by the Zn analogue.

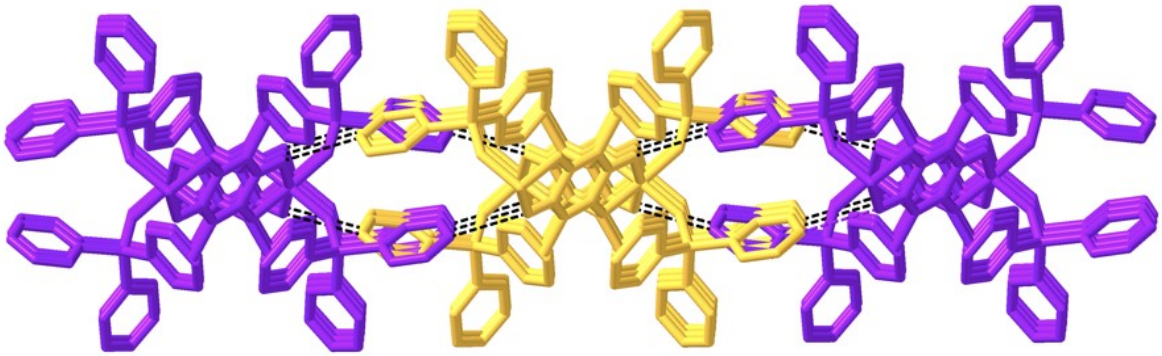


Figure S4 Representation of the packing interactions between chains of Fe(Clan)(OPPh$_3$)$_2$.

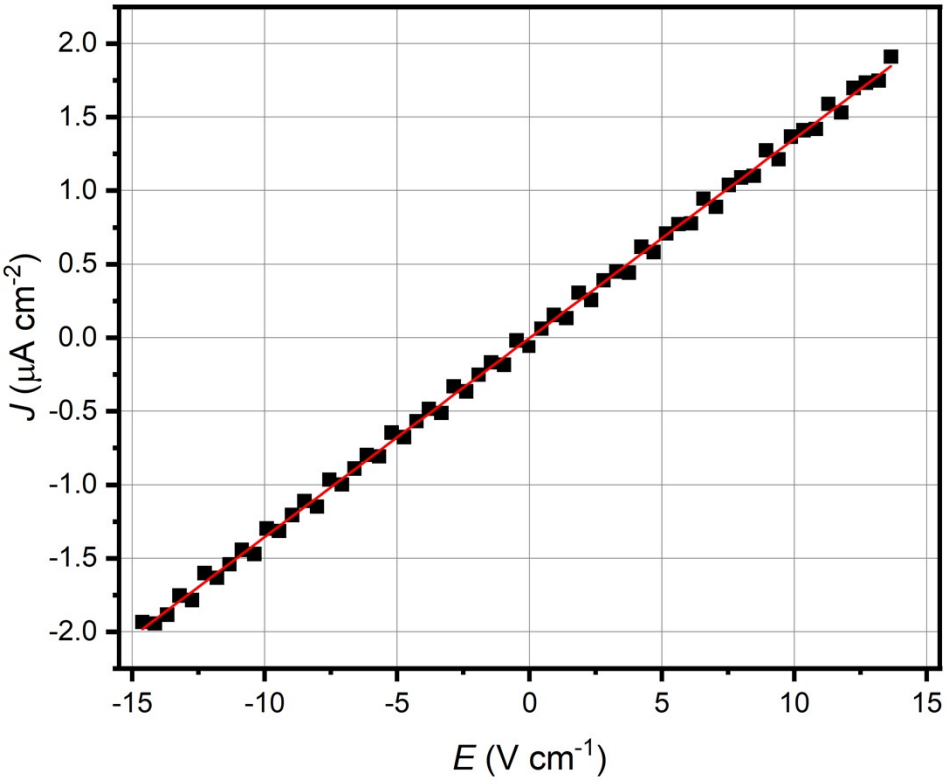
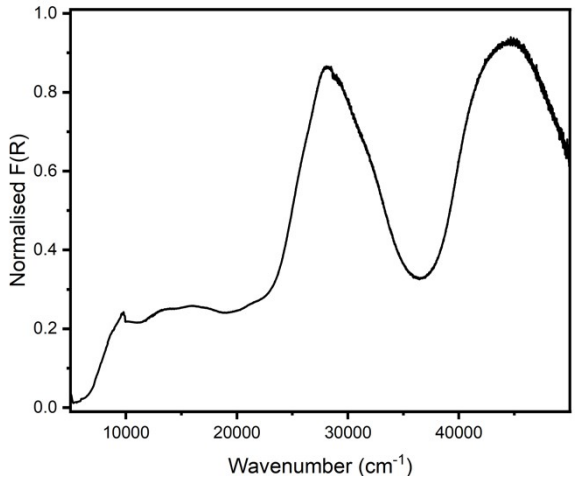


Figure S5 Current density (*J*) vs. electric field strength (*E*) curve for ambient temperature conductivity measurement of $Fe(Clan)(OPPh_3)_2$. Data were measured over the range −0.3 to 0.3 V in 0.01 V steps.

a)



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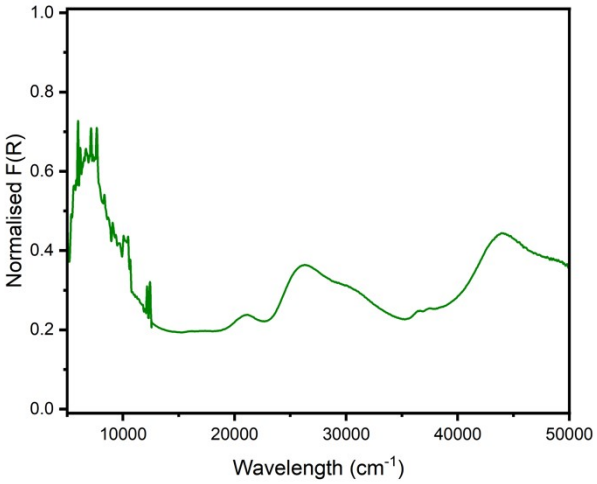


c)

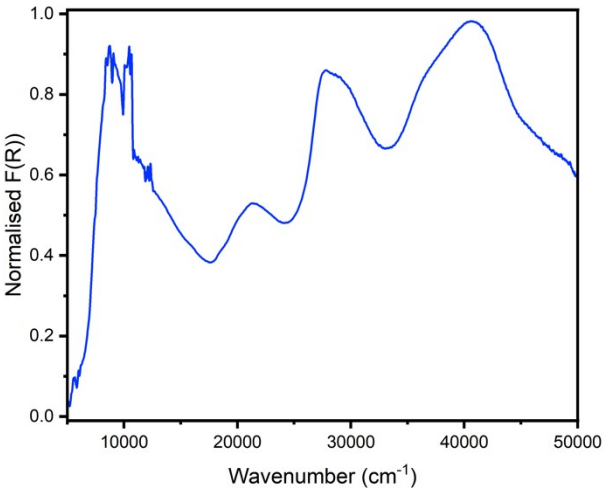
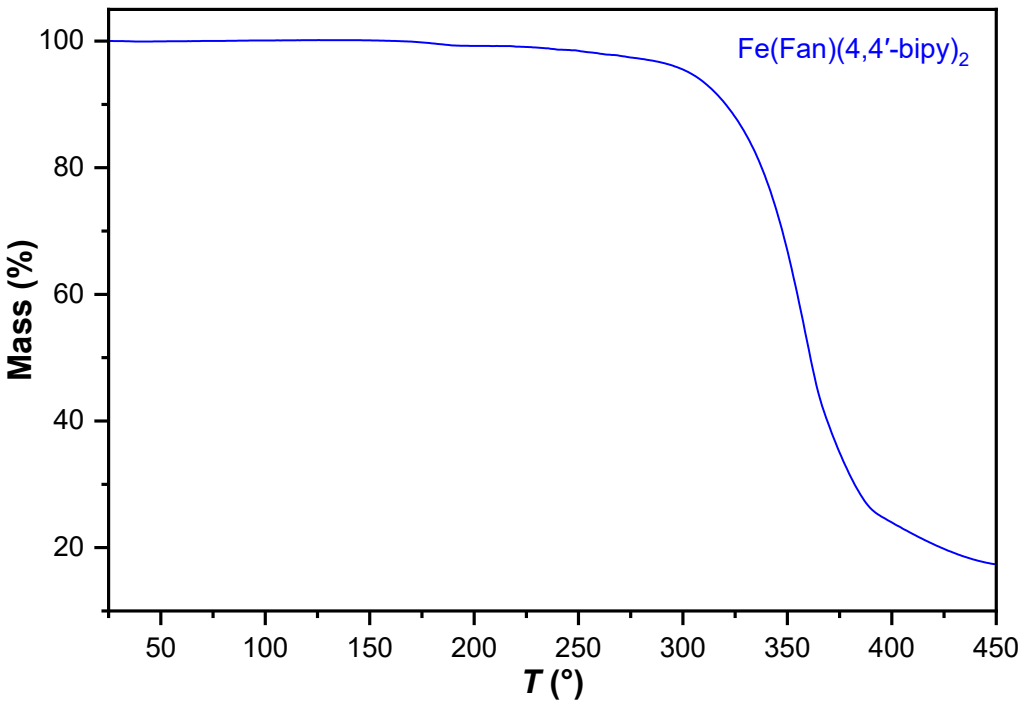


Figure S6 Solid-state UV-Vis-NIR absorption spectra of a) $Fe(Clan)(H_2O)_2$ b) $Fe(Clan)(OPPh_3)_2$ and c) $Fe(Fan)(4,4'\text{-bipy})_2$.

a)



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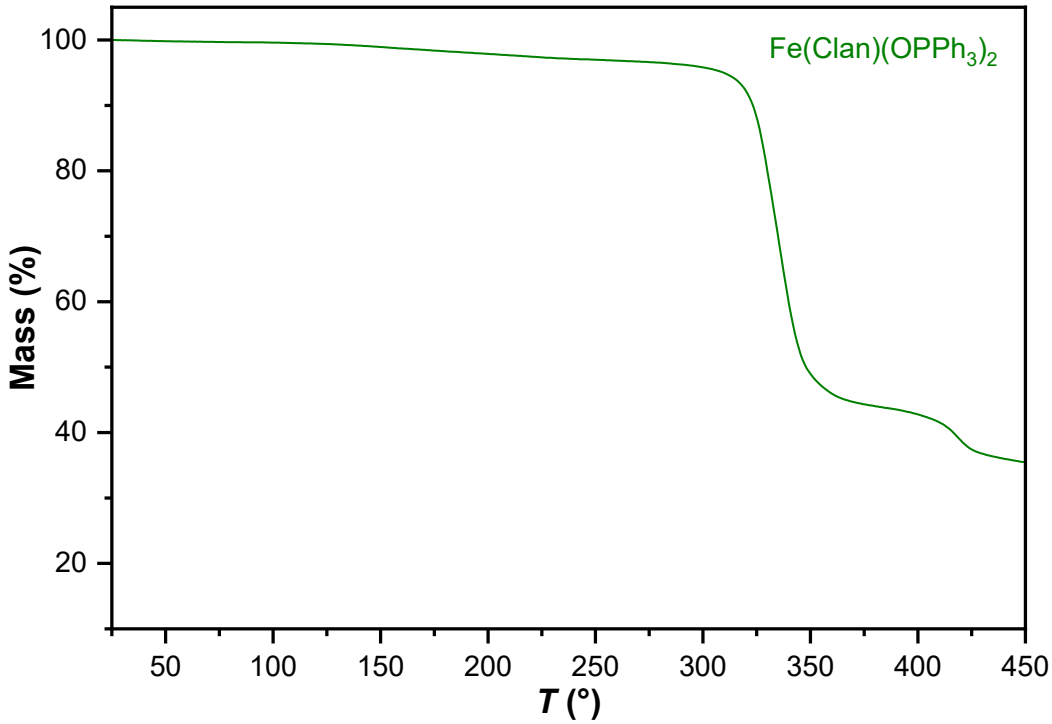

Figure S7 TGA traces for a) Fe(Fan)(4,4'-bipy)$_2$, and b) Fe(Clan)(OPPh$_3$)$_2$.

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