Supplementary Information for

Electrochemical and optical properties of a redox-active Cu(II) coordination framework incorporating the tris(4-(pyridin-4-yl)phenyl)amine ligand

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EXPERIMENTAL DETAILS

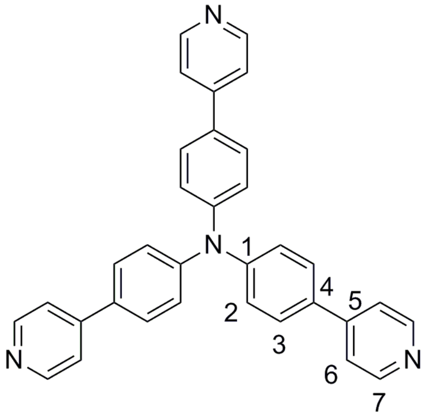
All chemicals and solvents used were used as obtained and used without further purification. Tris(4-bromophenyl)amine[1] and $Pd(PPh_3)_4$[2] were synthesised according to literature procedures. Distilled and degrassed acetonitrile (dried over CaH_2) was used for all experiments requiring acetonitrile. DMF was dried over activated $CaSO_4$.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DMX500 spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C respectively. ^{1}H and ^{13}C NMR chemical shifts were referenced internally to residual solvent resonances. Spectra were recorded at 298K and chemical shifts (δ), with uncertainties of ± 0.01 Hz for 1H and ± 0.05 Hz for ^{13}C are quoted in ppm. Coupling constants (*J*) are quoted in Hz and have uncertainties of ± 0.05 Hz for ^{1}H-^{1}H. Deuterated solvents were obtained from Cambridge Stable Isotopes and used as received.

Microanalyses were carried out at the Chemical Analysis Facility – Elemental Analysis Service in the Department of Chemistry and Biomolecular Science at Macquarie University, Australia. Melting points were carried on a Stuart Melting point SMP11 apparatus from Barloworld Scientific Limited.

Synthesis

Synthesis of Tris(4-(pyridin-4-yl)phenyl)amine (Npy$_3$)



Potassium carbonate (2.29 g, 16.6 mmol) was suspended in a degassed solution of 1,4-dioxane (47.5 mL) and water (2.5 mL). Tris(4-bromophenyl)amine (1.00 g, 2.07 mmol), 4-pyridyl boronic acid (1.63 g, 11.6 mmol) and $Pd(PPh_3)_4$ (122 mg, 0.106 mmol, 5.1 mol%) were then added and the reaction mixture heated at 90 °C under nitrogen for 26 hours. The solvent was removed under vacuum and the bright yellow residue redissolved in dichloromethane. The organic layer was washed three times with water and the combined water layers back extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and the solvent evaporated to yield a bright yellow crude product. The crude product was then purified by column chromatography on silica gel (gradient EtOAc to acetone) to yield the pure product as a pale yellow solid (650 mg, 66%). m.p. >210 °C.

Elemental Analysis: Found C, 83.30; H, 5.21 and N, 11.45; Calculated for $C_{33}H_{24}N_4$: C, 83.17; H, 5.08 and N, 11.76%.

ESI-MS (ESI$^+$, MeOH): 953.33 (Calculated $[2M+1]^+$ = 953.30, 100%) amu.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.63 (d, $^3J_{H6\text{-}H7}$ = 4.5 Hz, 4H, **H**7 pyridyl), 7.59 (d, $^3J_{H2\text{-}H3}$ = 8.5 Hz, 4H, **H**3 phenyl), 7.49 (d, $^3J_{H6\text{-}H7}$ = 4.5 Hz, 4H, **H**6 pyridyl), 7.25 (d, $^3J_{H2\text{-}H3}$ = 8.5 Hz, 4H, **H**2 phenyl) ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 150.5 (**C**7), 150.0 (**C**1), 147.5 (**C**4), 133.1 (**C**5), 128.2 (**C**3), 124.8 (**C**2), 121.2 (**C**6) ppm.

Synthesis of the [Cu(Npy$_3$)Cl$_2$]·DMF framework

Tris(4-(pyridin-4-yl)phenyl)amine (22.4 mg, 4.69 x 10^{-5} mol) and $CuCl_2.2H_2O$ (19.2 mg, 1.12 x 10^{-4} mol) were dissolved in dry and distilled DMF (2.0 mL) in a 20 mL vial and heated in a heating block at 100 °C for 3 days, upon which the fluffy green solid initially observed formed dark yellow block crystals. The crystals were then washed several times with DMF. Yield: 26.5 mg (83%).

UV/Vis/NIR (solid state): 10000, 22500, 29000, 41000 cm^{-1}.

Found C, 63.68; H, 4.79 and N, 10.18; Calculated for $C_{33}H_{24}Cl_2CuN_4$·DMF: C, 63.20; H, 4.57 and N, 10.24%

X-ray single crystal structure of [Cu(Npy$_3$)Cl$_2$].DMF: A single crystal of [Cu(Npy$_3$)Cl$_2$].DMF was mounted on a thin piece of copper wire inserted into a copper mounting pin. The crystal was quenched in a cold nitrogen gas stream from an Oxford Cryosystems Cryostream. An APEXII-FR591 diffractometer employing mirror monochromated MoKα radiation generated from a rotating anode was used for the data collection. Cell constants were obtained from a least squares refinement against 1677 reflections located between 4 and 66° 2θ. Data were collected at 150(2) Kelvin with ω+ϕ scans to 61° 2θ. The data integration and reduction were undertaken with SAINT and XPREP[3], and subsequent computations were carried out with the WinGX[4] and ShelXle[5] graphical user interfaces. A multi-scan absorption correction determined with SADABS[6] was applied to the data.

The structure was solved in the space group *C*1c1(#9) by direct methods with SIR97[7] and extended and refined with SHELXL-97.[8] The asymmetric unit contains the unique unit of the framework and a dimethylformamide solvate molecule. The non-hydrogen atoms in the asymmetric unit were modelled with anisotropic displacement parameters and a riding atom model with group displacement parameters was used for the hydrogen atoms. The absolute structure was established with the Flack parameter[9] refining to 0.00(5).

Table S1. Crystal data and structure refinement details for [Cu(Npy$_3$)Cl$_2$].DMF

Parameter	
Formula	$C_{36}H_{31}Cl_2CuN_5O$
M/g mol^{-1}	684.1
Temperature (K)	150(2)
Crystal system	monoclinic
Crystal size (mm^3)	0.265 × 0.131 × 0.123
a (Å)	14.2786(6)
b (Å)	18.6712(7)
c (Å)	11.8323(4)
β (°)	92.933(2)
V (Å^3)	3150.3(2)
Z	4
ρ_{calc} (mg/mm^3)	1.442
μ (mm$^{-1)}$	0.901
F(000)	1412
Reflections collected	55714/9605[R(int) = 0.0279]
Data/restraints/parameters	9605/2/408
Final R indexes [I>=2σ (I)]	$R_1 = 0.0344$, $wR_2 = 0.0976$
Final R indexes [all data]	$R_1 = 0.0372$, $wR_2 = 0.1100$
Goodness-of-fit on F^2	1.608

$R1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$

Chemical oxidation of the [Cu(Npy$_3$)Cl$_2$]·DMF framework

The Cu^{II} framework (20 mg, 3.26 x 10^{-6} mol) was suspended in acetonitrile (1 mL) and a solution of NOBF$_4$ (3.8 mg, 3.26 x 10^{-6} mol) in acetonitrile (2.5 mL) was added slowly dropwise with vigorous bubbling of nitrogen through the solution (to prevent the liberated NO from undergoing any nitration reaction with the framework) to yield the formation of a yellow/red solid. This was left to stir at room temperature with bubbling of nitrogen for 30 minutes before the reaction mixture was filtered and washed with acetonitrile.

UV/Vis/NIR (solid state): 11000, 20000, 27500, 33000, 41000 cm^{-1}.

Physical Characterisation

General details: Thermal gravimetric analysis was performed under a flow of nitrogen (0.1 L/min) on a TA Instruments Hi-Res Thermogravimetric Analyser from 25-600 °C at 1 °C/min. Powder X-ray diffraction (PXRD) data were obtained on a PANalytical X'Pert PRO Diffractometer producing Cu (1.5406 Å) radiation.

UV/Vis/NIR: UV/Vis/NIR spectroscopy was performed on a Cary 5E Spectrophotometer equipped with a Harrick Praying Mantis accessory, where dried KBr was used for the baseline. Spectra are reported as the Kubelka-Munk transform, where $F(R) = (1-R)^2/2R$ (R is the diffuse reflectance of the sample as compared to KBr). Spectral deconvolution was performed using the curve-fitting subroutine implemented within the Thermo GRAMS AI commercial software package. The following procedure was employed for the analysis of all spectral data. The positions of the underlying components were estimated by examining the first- and second-order derivatives of the bands as a guide to the energies of the major components. While the band parameters for these components varied slightly over repeat iterations, their relative energies, intensities and bandwidths remained constant. Based on the reproducibility of the parameters obtained from the deconvolutions, the uncertainties in the energies (F(R)), intensities and bandwidths ($\Delta F(R)_{1/2}$) were estimated as ± 10 cm^{-1}, 0.001 x 10^3 and ± 10 cm^{-1}, respectively. In all cases, the correlation coefficient (R^2) for the fits reported was >0.995. While the spectra were also adequately fitted using Lorentzian bands, results from the deconvolution procedure using purely Gaussian-shaped bands were adequate.

Electrochemistry: Solid state electrochemical measurements were performed using a Bioanalytical Systems BAS 100A Electrochemical Analyser. Argon was bubbled through solutions of 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ dissolved in distilled CH_3CN. The cyclic voltammograms (CVs) were recorded using a glassy carbon working electrode (1.5 mm diameter), a platinum wire auxiliary electrode and an Ag/Ag+ wire quasi reference electrode. Solid state samples were mounted on the glassy carbon working electrode by dipping the electrode into a paste made of the powder sample in acetonitrile. Ferrocene was added as an internal standard upon completion of each experiment. All potentials are quoted in mV versus Fc^+/Fc^0.

Fluorescence: Fluorescence spectra were performed on a Varian Cary Eclipse Fluorescence spectrophotometer in both solution and solid state. The scan rate used for all measurements was 120 nm/min with a 1 nm data interval. The fluorescence spectrum of the ligand was performed as a solution in acetone in a quartz cuvette (1cm x 1cm x 1cm) with excitation at 380 nm, the emission spectrum obtained from 400-750 nm and slit widths of 2.5 mm used for both excitation and emission. The fluorescence spectrum of the ligand and framework in the solid state was performed by gently pressing a thin film of the dry powder using a spatula onto a quartz plate cut to rest diagonally inside the quartz cuvette used for solution state measurements. The excitation beam was aligned with each measurement to ensure that the solid sample was being irradiated. The sample was excited at 380 nm, the emission spectrum obtained from 400-750 nm and 1.5 mm slit widths used for both excitation and emission. The cuvette and quartz slide were washed with concentrated nitric acid, water and acetone prior to use.

FIGURES

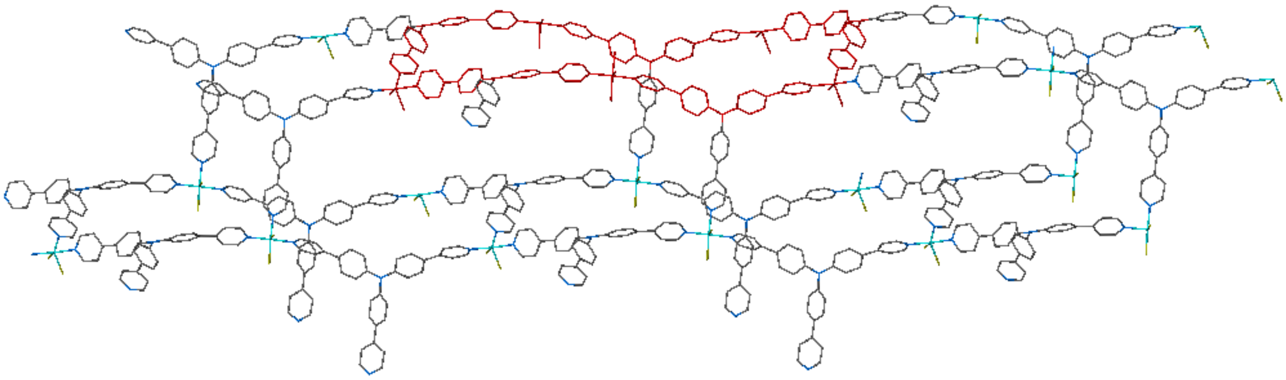


Fig. S1 Crystal structure of the [Cu(Npy$_3$)Cl$_2$].DMF framework showing the series of linked metallocycles and their extended structure (a single metallocycle is highlighted in red). Hydrogen atoms have been omitted for clarity (C = grey, N = blue, Cl = yellow, Cu = cyan).

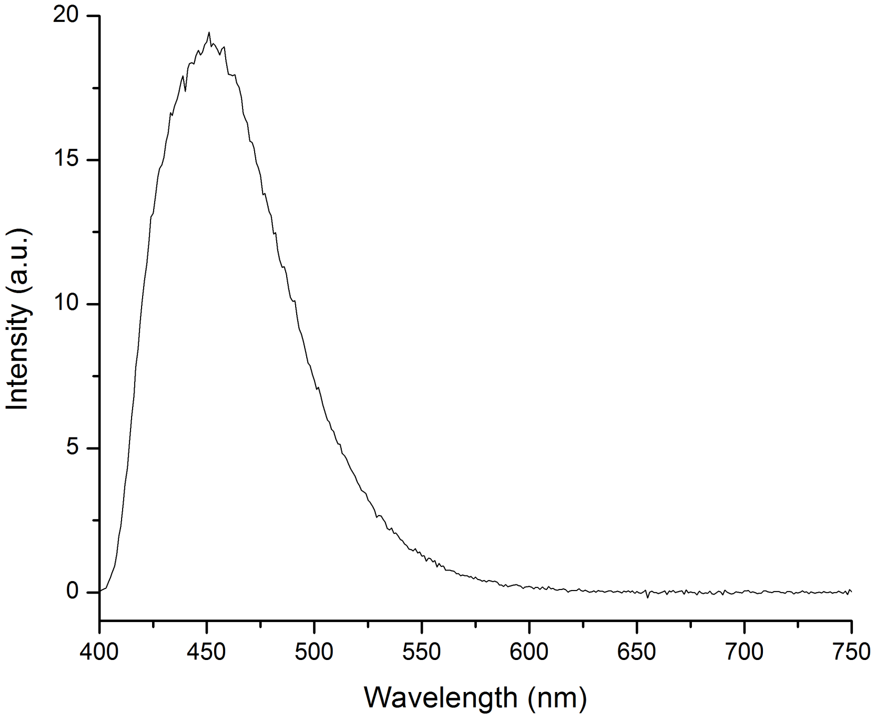


Fig. S2 Solution state fluorescence spectrum of the Npy$_3$ ligand as a solution in acetone

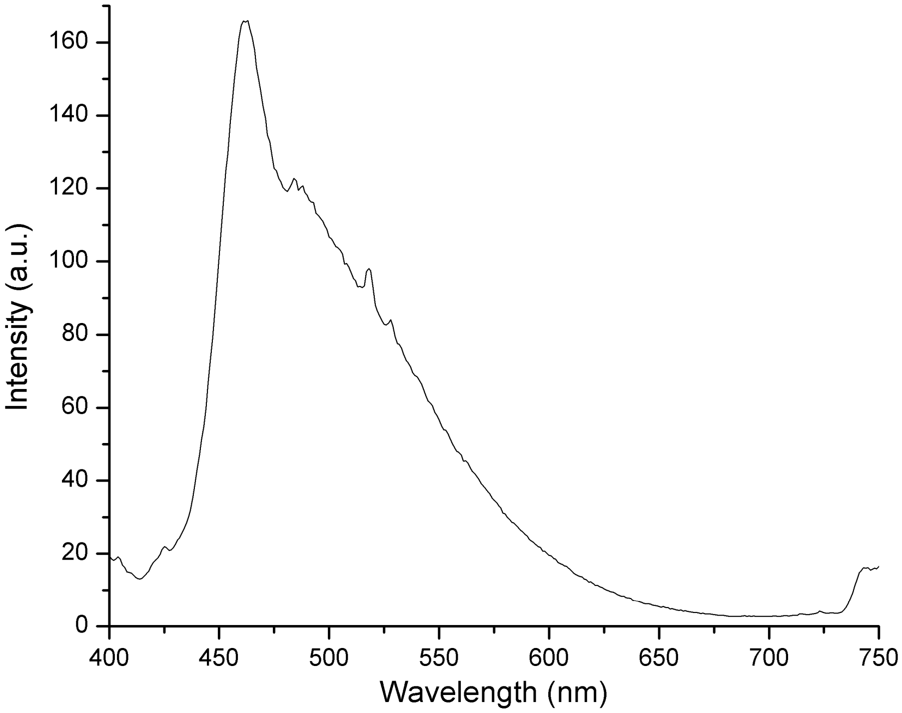


Fig. S3 Solid state fluorescence spectrum of the Npy$_3$ ligand as a thin film on a quartz plate

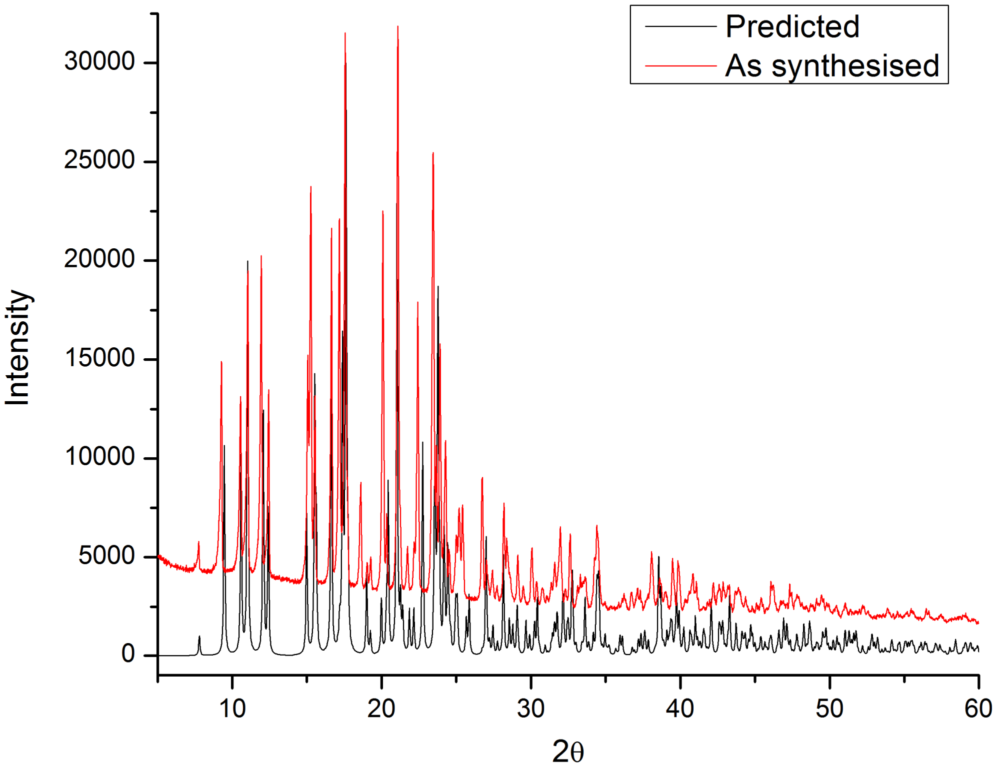


Fig. S4 Predicted and as synthesised Powder XRD Pattern for the [Cu(Npy$_3$)Cl$_2$].DMF framework.

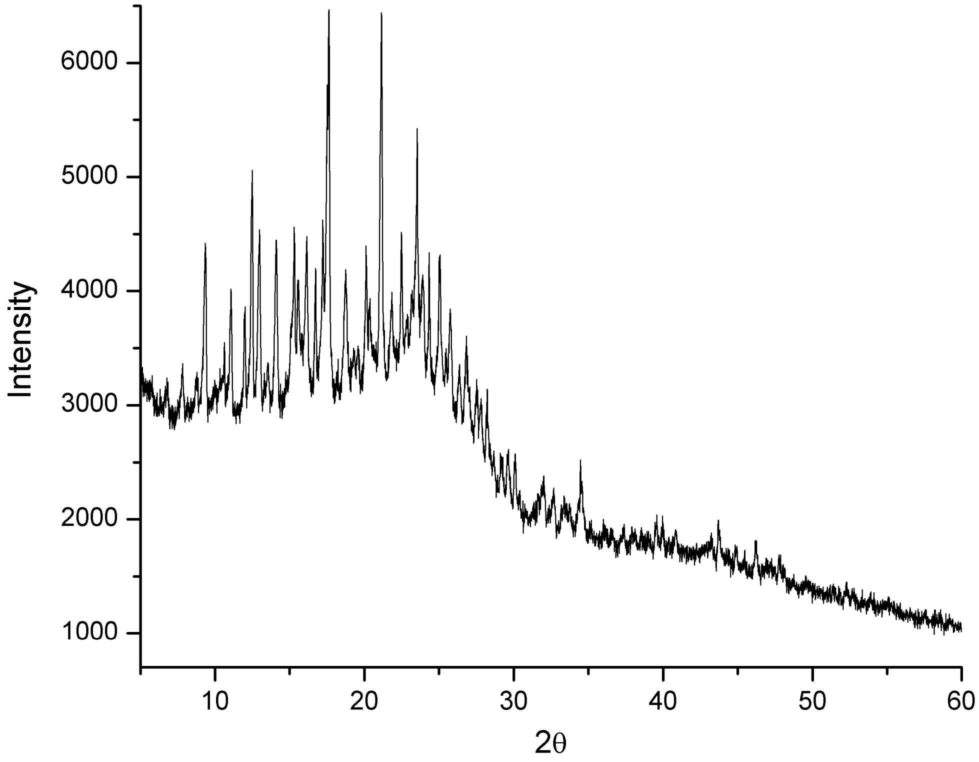


Fig. S5 PXRD Pattern obtained for the oxidised [Cu(Npy$_3$)Cl$_2$].DMF framework.

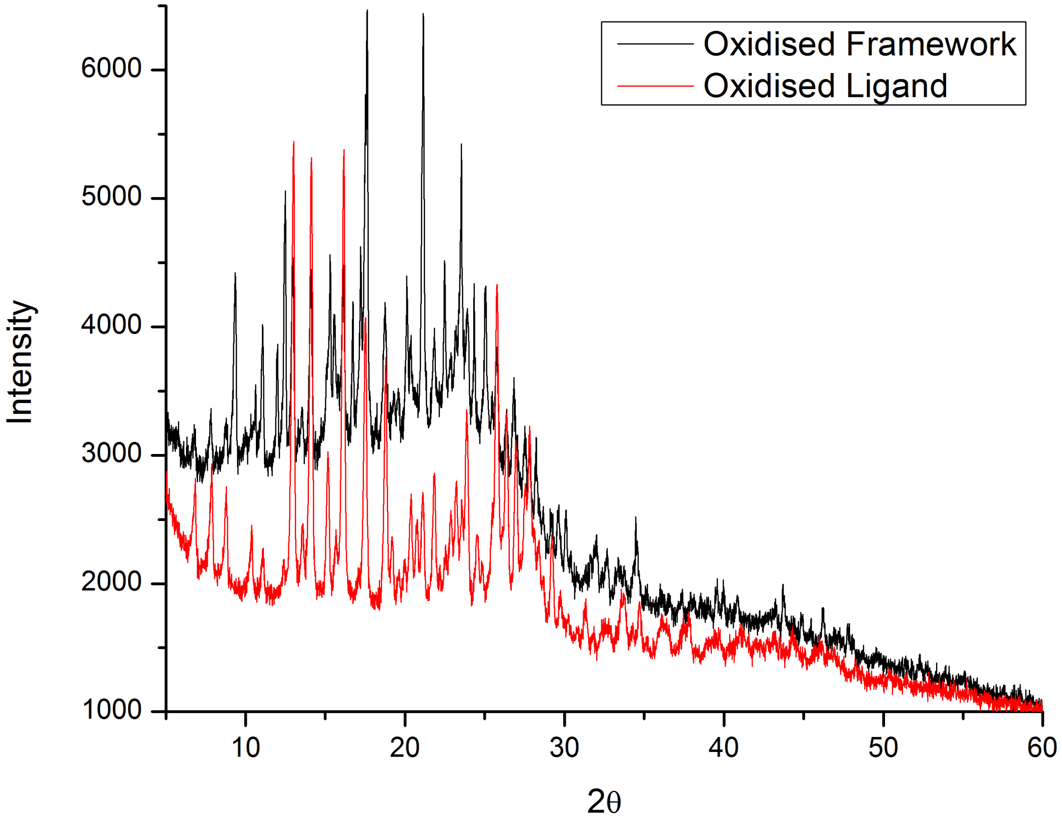


Fig. S6 PXRD Pattern obtained for the oxidised [Cu(Npy$_3$)Cl$_2$].DMF framework overlayed with the PXRD Pattern for the oxidised ligand

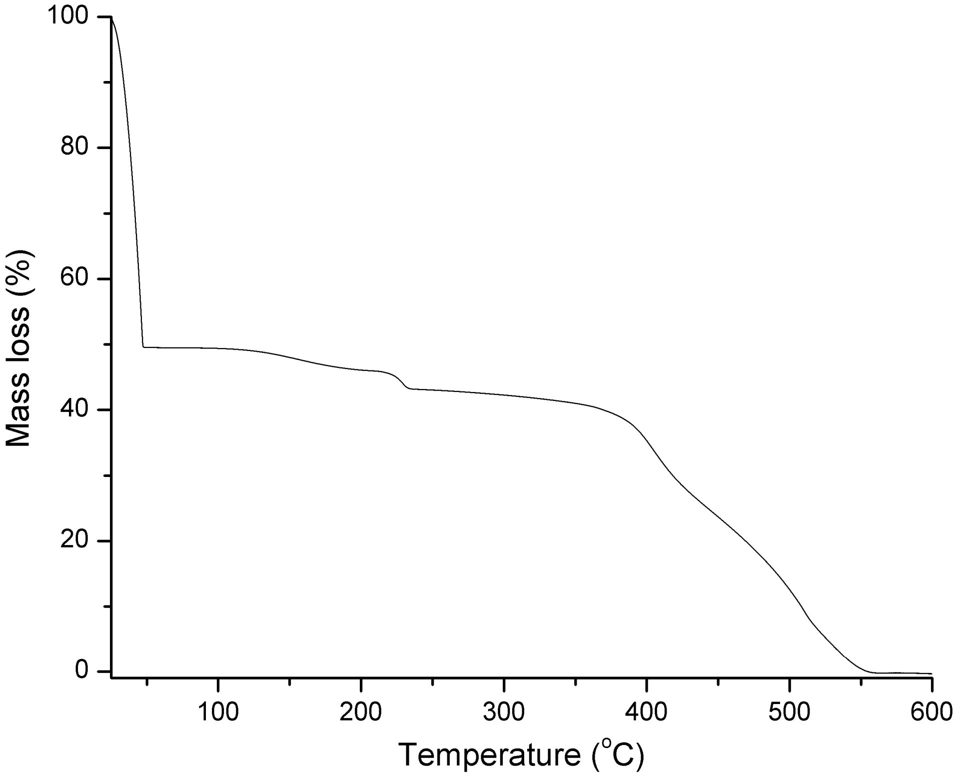
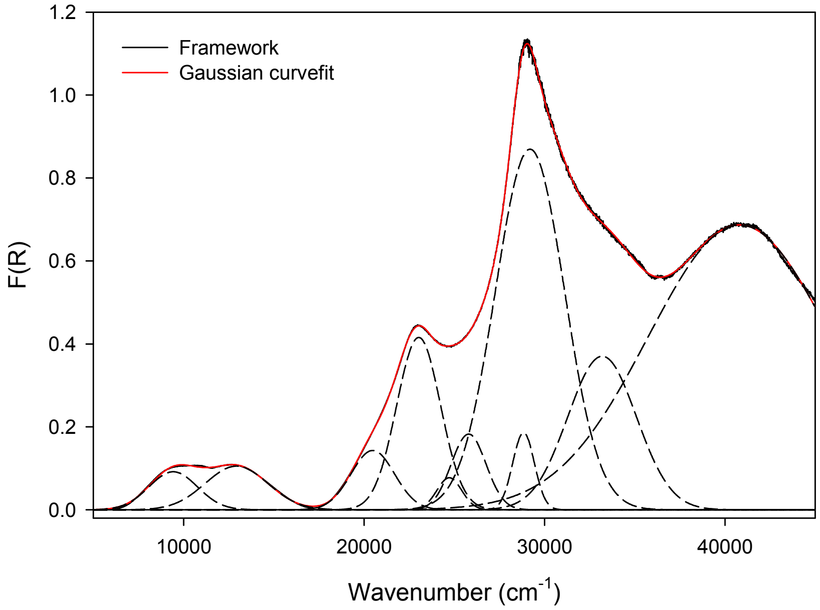
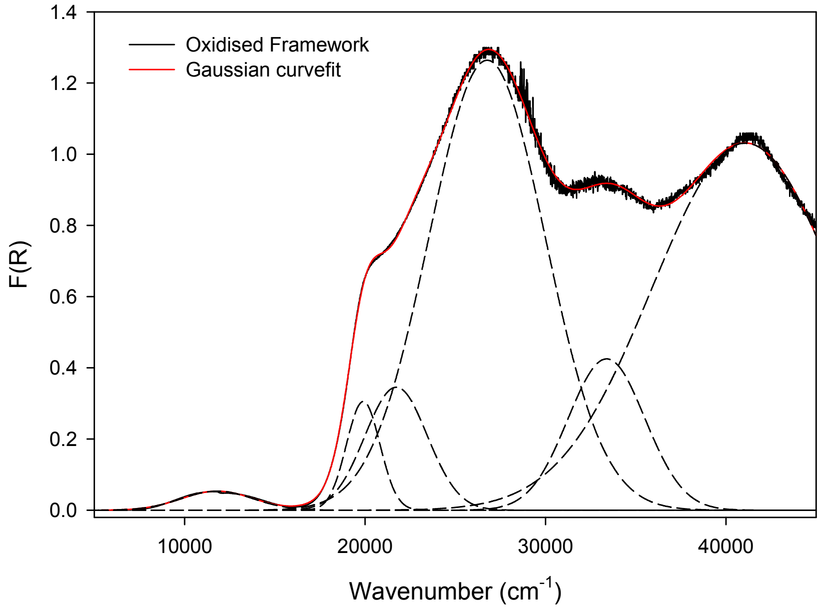


Fig. S7 Thermal Gravimetric Analysis (TGA) of [Cu(Npy$_3$)Cl$_2$].DMF where the sample was loaded wet (mass loss at <50 °C is due to solvent loss from the surface of the solid)



(a)



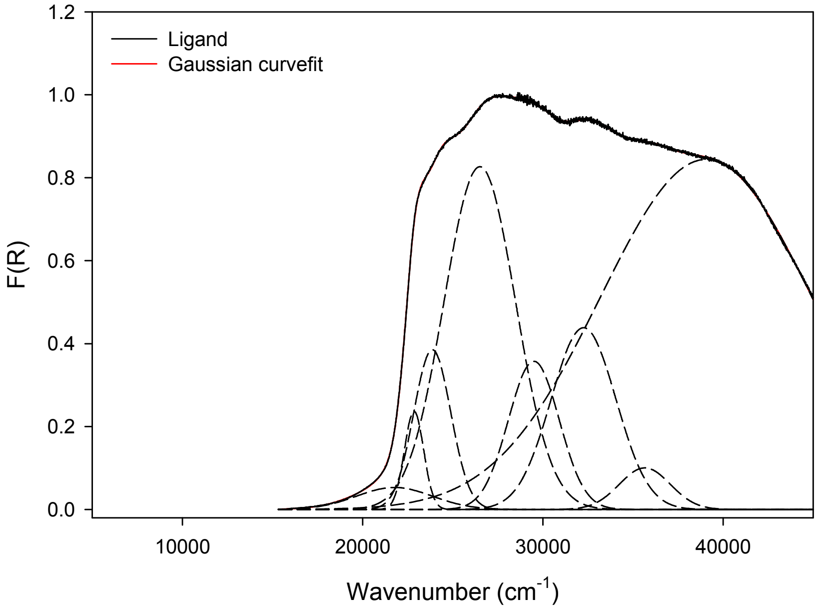
(b)

Fig. S8 Overlay of the UV/Vis/NIR diffuse reflectance spectra for the [Cu(Npy$_3$)Cl$_2$].DMF framework **(a)** and its oxidised analogue **(b)**. The dotted curves represent the best fit Gaussian deconvolution to the overall band manifold.

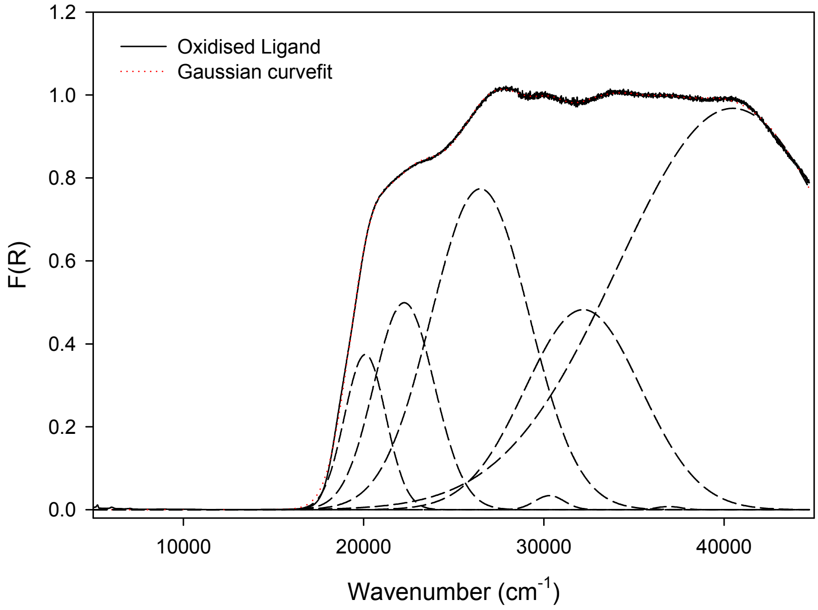
Table S2. Peak parameters[a] from the UV/Vis/NIR diffuse reflectance spectra of the [Cu(Npy$_3$)Cl$_2$].DMF framework and its oxidised analogue. The parameters in bold relate to the overall band manifold (sh = shoulder band).

	F(R) (cm^{-1})	Reflectance (arb. Units)	ΔF(R)$_{1/2}$ (cm^{-1})	Area (cm^{-2})
Framework	**9970**	**0.101**		
	12720	**0.105**		
	23010	**0.444**		
	29010	**1.123**		
	40800	**0.687**		
	9427	0.09158	3153	307.2
	12934	0.1052	4068	455.7
	20484	0.1431	2832	431.5
	23032	0.4155	2865	1267
	24724	0.07715	1621	133.2
	25801	0.1825	2264	440.0
	28845	0.1860	1414	280.1
	29198	0.8696	4518	4182
	33197	0.3702	4477	1764
	40811	0.6868	11943	6936
Oxidised Framework	**11800**	**0.0543**		
	sh 20510	**0.71**		
	26840	**1.289**		
	33135	**0.926**		
	41215	**1.047**		
	11814	0.05378	4668	267.1
	19906	0.3056	2186	711.2
	21733	0.3455	4064	1495
	26774	1.264	7596	10223
	33391	0.4251	5012	2268
	41073	1.031	12128	10346

[a] F(R) represents the energy at the band maximum and ΔF(R)$_{1/2}$ is the bandwidth at half-height.



(a)



(b)

Fig. S9 Overlay of the UV/Vis/NIR diffuse reflectance spectra for the Npy$_3$ ligand **(a)** and its oxidised analogue **(b)**. The dotted curves represent the best fit Gaussian deconvolution to the overall band manifold.

Table S3. Peak parameters[a] from the UV/Vis/NIR diffuse reflectance spectra of the Npy$_3$ ligand and its oxidised analogue. The parameters in bold relate to the overall band manifold.

	F(R) (cm^{-1})	Reflectance (arb. Units)	ΔF(R)$_{1/2}$ (cm^{-1})	Area (cm^{-2})
Ligand	**sh 23385**	**0.785**		
	sh 24590	**0.881**		
	27590	**0.993**		
	32345	**0.945**		
	21767	0.05301	4958	279.4
	22859	0.2364	1261	317.6
	23874	0.3851	2424	993.8
	26508	0.8267	4675	4114
	29502	0.3574	3313	1260
	32261	0.4383	4236	1976
	35657	0.1003	3324	355.1
	39064	0.8442	13822	10510
Oxidised ligand	**sh 21850**	**0.789**		
	27680	**1.017**		
	33770	**1.009**		
	20100	0.3742	2693	1073
	22258	0.4991	3943	2095
	26483	0.7739	6394	5267
	30317	0.03391	1929	69.65
	32188	0.4824	7567	3885
	36930	0.007721	1605	13.19
	40483	0.9678	15000	11560

[a] F(R) represents the energy at the band maximum and ΔF(R)$_{1/2}$ is the bandwidth at half-height.

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