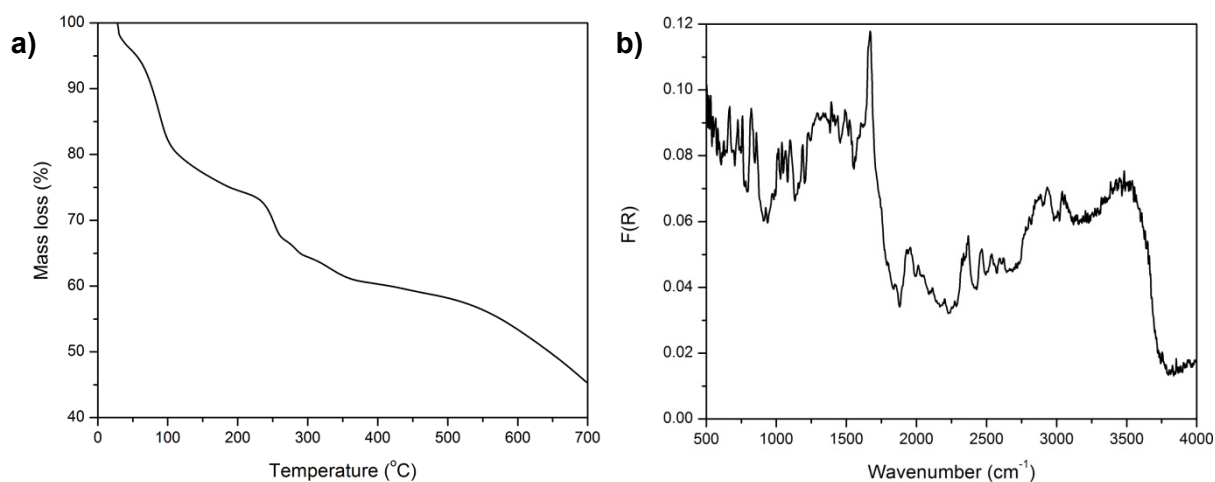*Supplementary Information*

Facile redox state manipulation in Cu(I) frameworks by utilisation of the redox-active tris(4-(pyridin-4-yl)phenyl)amine ligand

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Figure 1. a) Thermal Gravimetric Analysis (TGA) over the range 25-700 °C and b) IR over the range 500-2000 cm^{-1} of the [CuNPy$_3$NO$_3$.solvent]$_n$ framework.
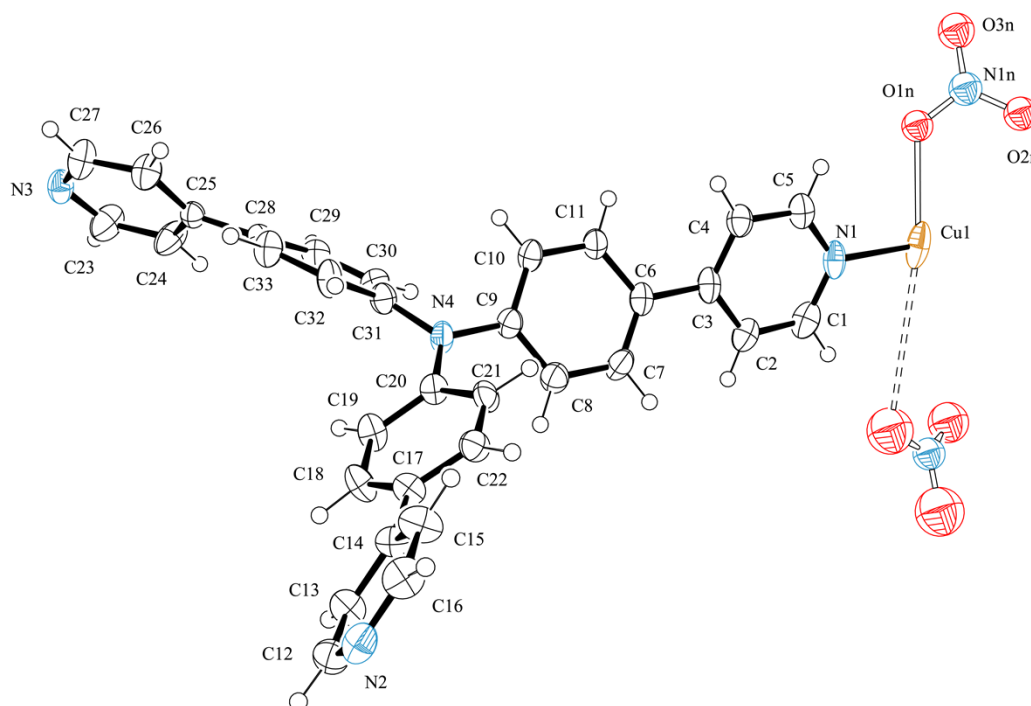
[CuNPy$_3$NO$_3$.solvent]$_n$ Framework

Table 1. Crystal data and structure refinement details for [CuNPy$_3$NO$_3$.solvent]$_n$

Parameter	
Model Formula	C$_{33}$H$_{24}$CuN$_5$O$_3$
M/g mol^{-1}	602.11
Temperature (K)	100(2)
Crystal system	orthorhombic
Space Group	$P222_1$(#17)
Crystal size (mm^3)	0.149 × 0.098 × 0.051
Crystal Colour	yellow
Crystal Habit	balde
a (Å)	9.0770(16)
b (Å)	13.831(2) Å
c (Å)	32.773(6) Å
V (Å^3)	4114.4(12)
Z	4
ρ_{calc} (mg/mm^3)	0.972
λ(MoKα)	0.71073 Å
μ(MoKα)	0.561 mm^{-1}
T(SADABS)$_{min,max}$	0.767, 0.862
$2\theta_{max}$	56.73º
hkl range	-12 12, -18 18, -43 43
Reflections collected	69365/10282[R$_{merge}$ = 0.0754]
Data/ parameters	8019/364
Final R indexes [all data]	R$_1$ = 0.0540, wR$_2$ = 0.1383
Goodness-of-fit on F^2	1.104
Residual Extrema	-0.569, 0.751 e$^-$ Å^{-3}

[*]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections. w=1/[$\sigma^2(F_o^2)$+(0.06P)^2+1.50P] where P=(F_o^2+2F_c^2)/3
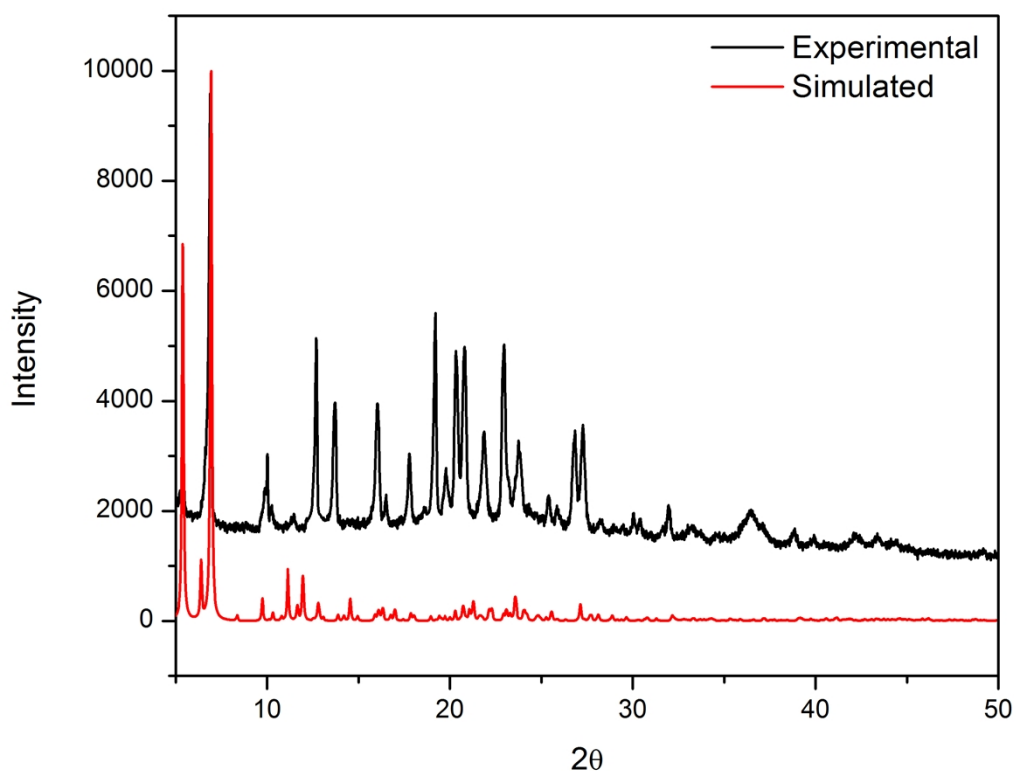
Figure 2. Predicted and as synthesised Powder XRD Pattern for the $[CuNPy_3NO_3.solvent]_n$ framework.

Figure 3. An ORTEP description of the asymmetric unit of the model obtained with SQUEEZE for $[CuNPy_3NO_3.solvent]_n$ with 50% displacement ellipsoids.

[CuNPy$_3$Cl.solvent]$_n$ Framework

**Table 2.** Crystal data and structure refinement details for the [CuNPy$_3$Cl.solvent]$_n$ framework

Parameter	
Model Formula	C$_{33}$H$_{24}$ClCuN$_4$
M/g mol^{-1}	575.55
Temperature (K)	150.0(2)
Crystal system	monoclinic
Crystal size (mm^3)	0.201 × 0.108 × 0.056
Crystal Colour	yellow
Crystal Habit	block
a (Å)	10.05130(10)
b (Å)	28.1929(2)
c (Å)	12.21890(10)
β (°)	112.2430(10)
V (Å^3)	3204.88(5)
Z	4
ρ_{calc} (mg/mm^3)	1.193
λ(CuKα)	1.5418 Å
μ(CuKα)	1.992 mm^{-1}
T(CRYSALISPRO)$_{min,max}$	0.818, 1.00
$2\theta_{max}$	153.19°
hkl range	-12 12, -35 35, -15 14
Reflections collected	62752/6714[R$_{merge}$ = 0.0263]
Data/ parameters	6371/352
Final R indexes [all data]	R$_1$ = 0.0592, wR$_2$ = 0.1787
Goodness-of-fit on F^2	1.047
Residual Extrema	-0.821, 1.859 e$^-$ Å^{-3}

$^*R1 = \Sigma||F_O| - |F_C||/\Sigma|F_O|$ for $F_O > 2\sigma(F_O)$; $wR2 = (\Sigma w(F_O^2 - F_C^2)^2/\Sigma(wF_C^2)^2)^{1/2}$
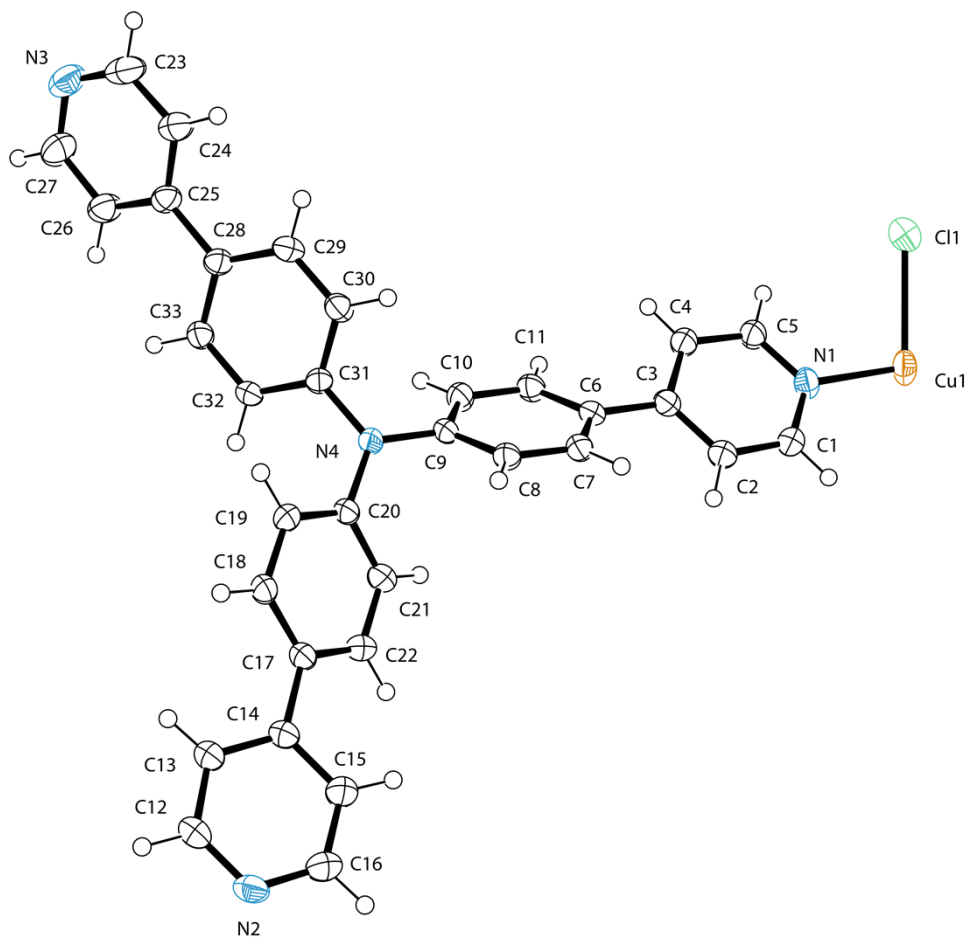
all reflections. w=1/[$\sigma^2(F_O^2)$+(0.06P)^2+1.50P] where P=(F_O^2+2F_C^2)/3
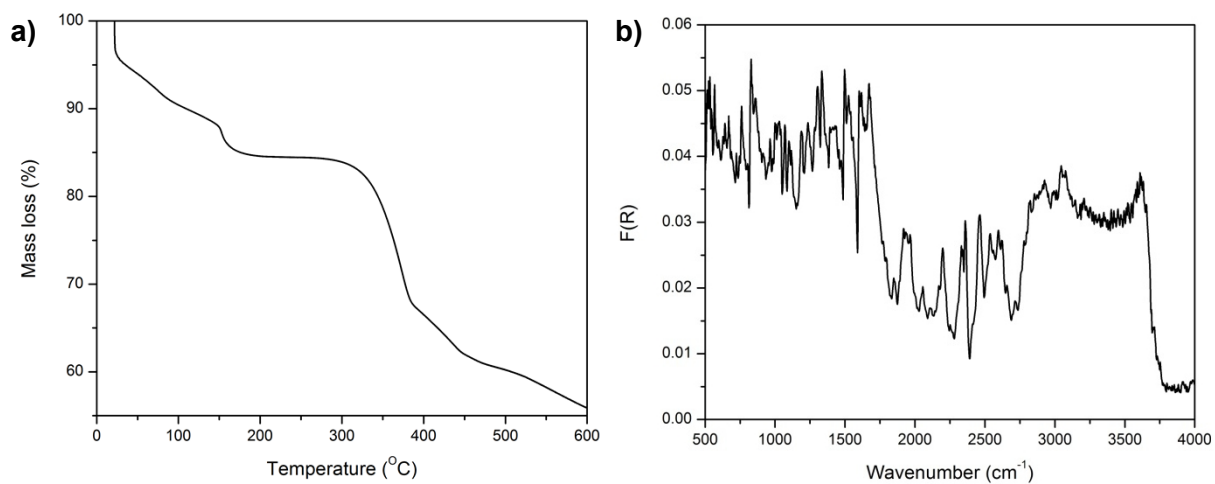
Figure 4. a) TGA over the range 25-600 °C and b) IR spectrum over the range 500-4000 cm^{-1} of the $[CuNPy_3Cl.solvent]_n$ framework.
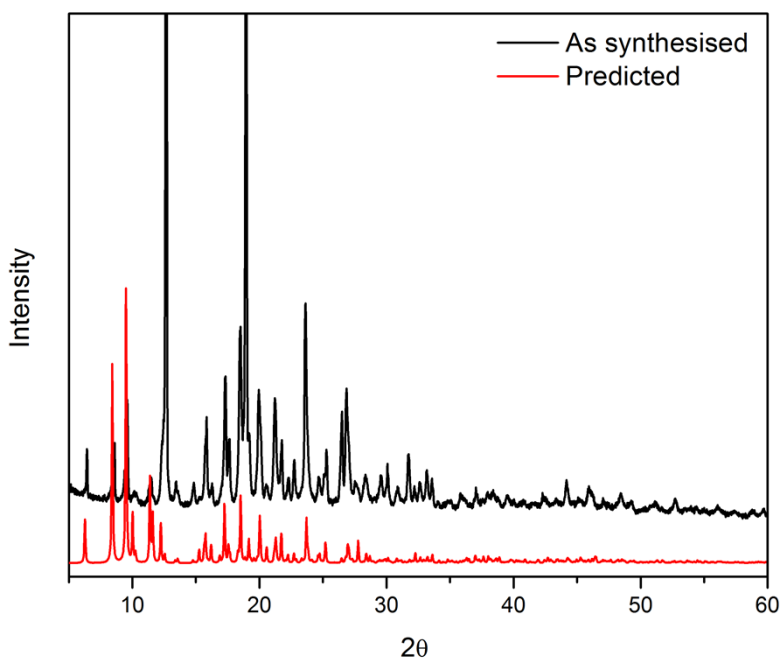
Figure 5. PXRD of the as synthesised $[CuNPy_3Cl.solvent]_n$ framework in comparison with the predicted pattern from the structure determination.

Figure 6. An ORTEP description of the asymmetric unit of the model obtained with SQUEEZE for $[CuNPy_3Cl.solvent]_n$ with 50% displacement ellipsoids.