**Supporting Information**

# Metal(II)-assisted hydrolysis of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (tpymt): synthesis, crystal structure and magnetic properties of $[Co(bpcam)_2]ClO_4 \cdot dmso \cdot H_2O$, $[Co(bpcam)_2]_2[Co(NCS)_4] \cdot dmso \cdot H_2O$ and $[Ni(bpcam)_2] \cdot H_2O$ [Hbpcam = bis(2-pyrimidylcarbonyl)amide]†

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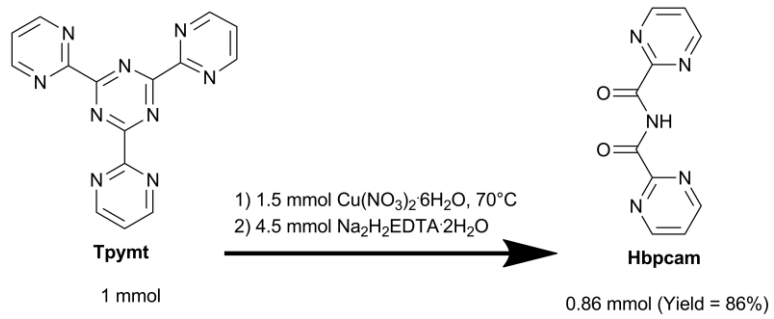
**Details of synthesis and characterization of Hbpcam:** The Hbpcam was obtained with a yield of 86%, by using a similar methodology to isolate the Hbpca ligand.[16b]




$^1$H NMR ($CDCl_3$): δ 7.69 (t, 2H, *J* = 4.9Hz), 9.05 (q, 4H, *J* = 4.9Hz), 12.88 (s, 1H). Anal. Calc. for $C_{10}H_7N_5O_2$: C, 52.40; H, 3.05; N, 30.57; Found: C, 52.37; H, 3.16; N, 30.8%. IR (KBr/$cm^{-1}$): 3330s [ν(N-H)]; 1771s [ν(C=O)].

**IR spectra of Hbpcam and complexes 1-3:**

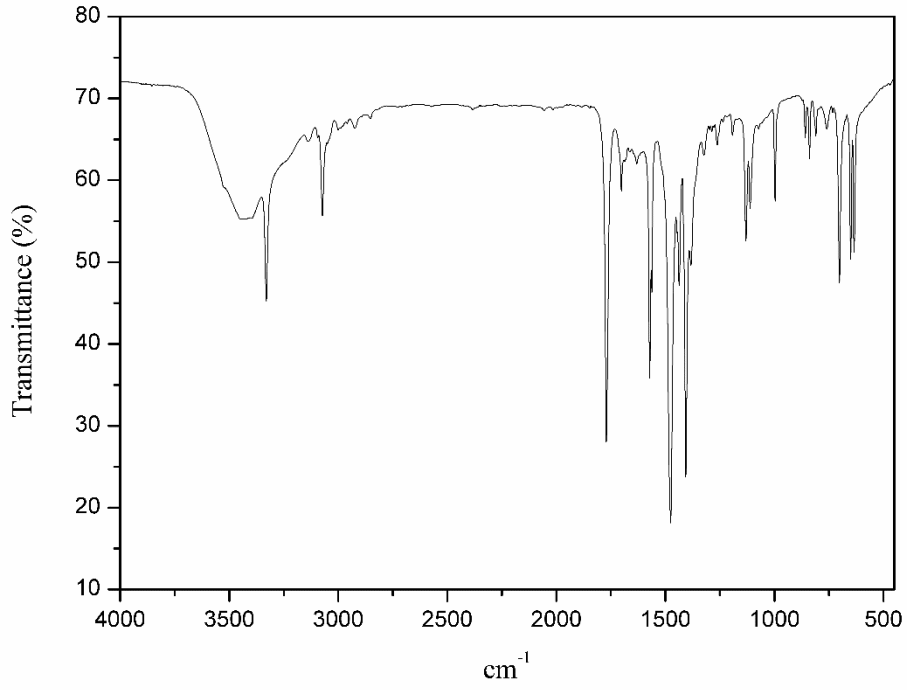



**Fig. S1** FTIR spectra of **Hbpcam.**

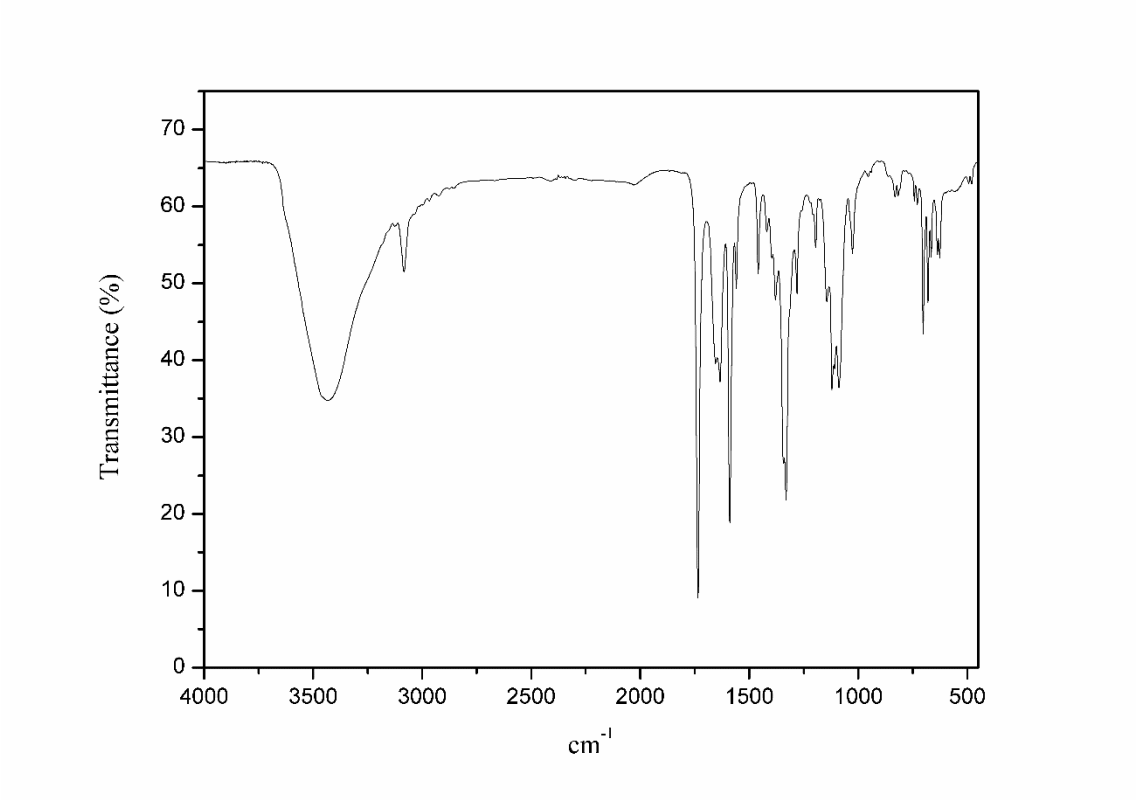



**Fig. S2** FTIR spectra of **1.**

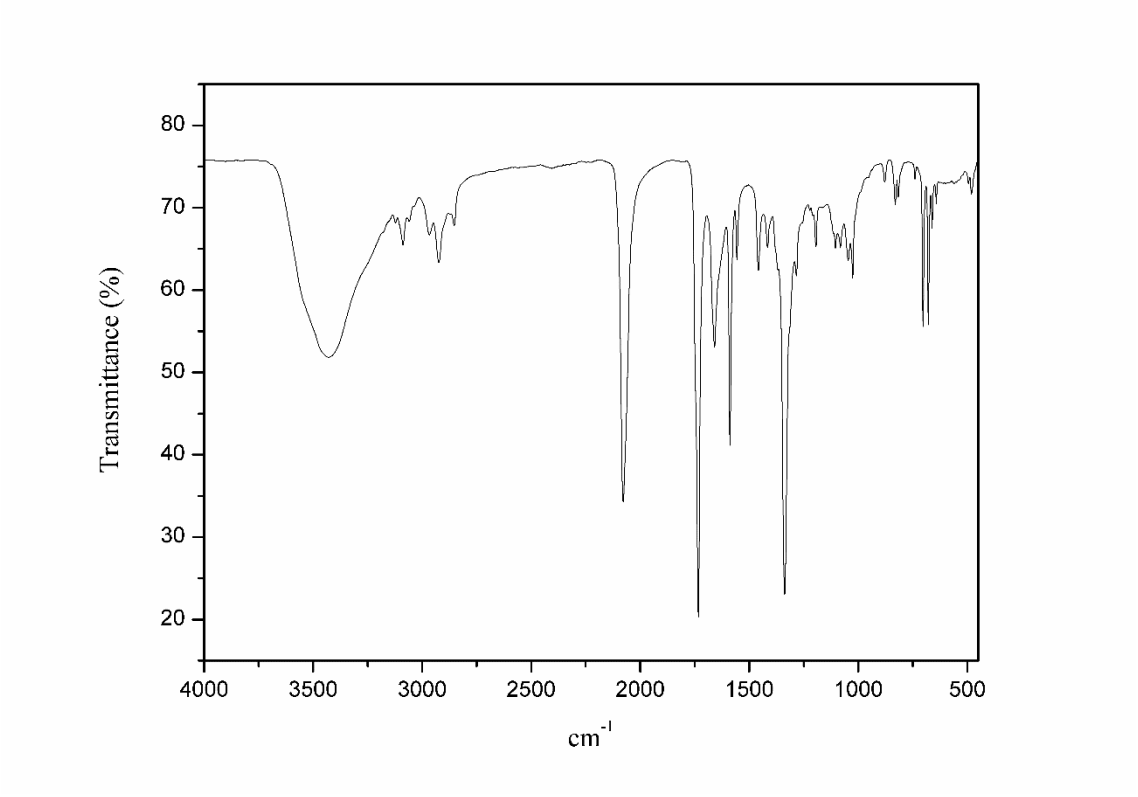



**Fig. S3** FTIR spectra of **2.**

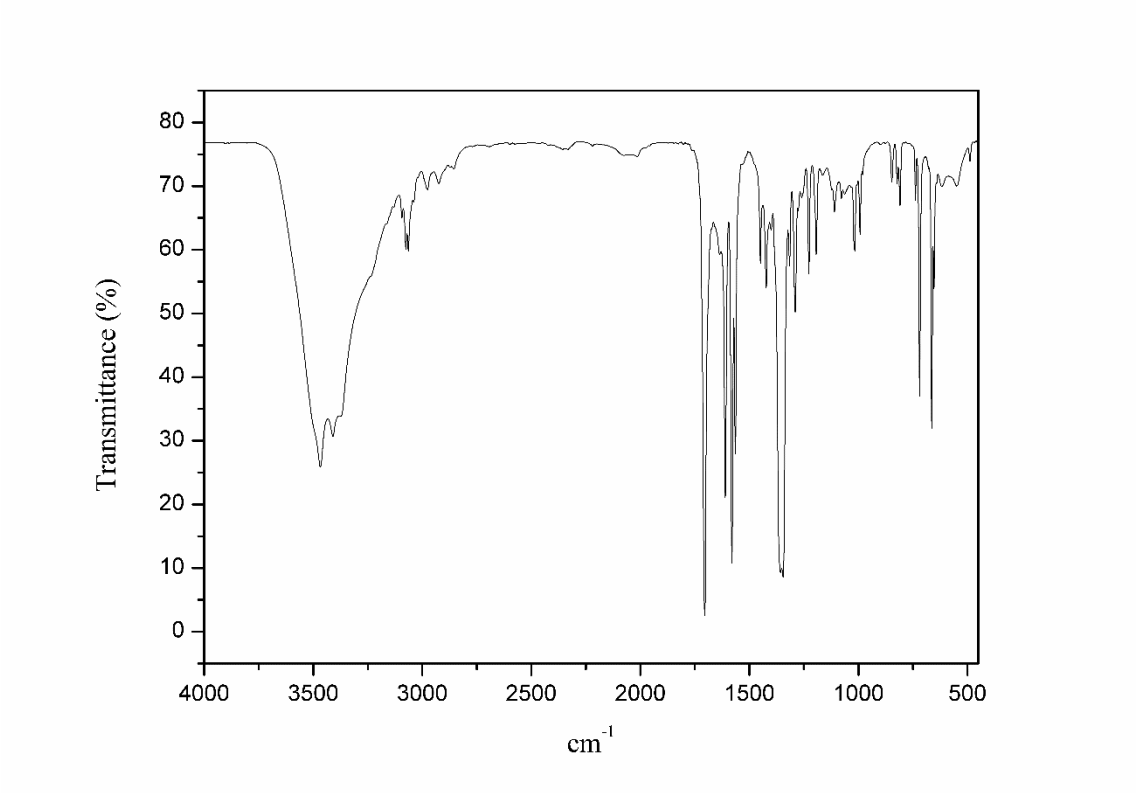



**Fig. S4** FTIR spectra of **3.**

**UV-Vis spectra on solid samples of 1-3:**

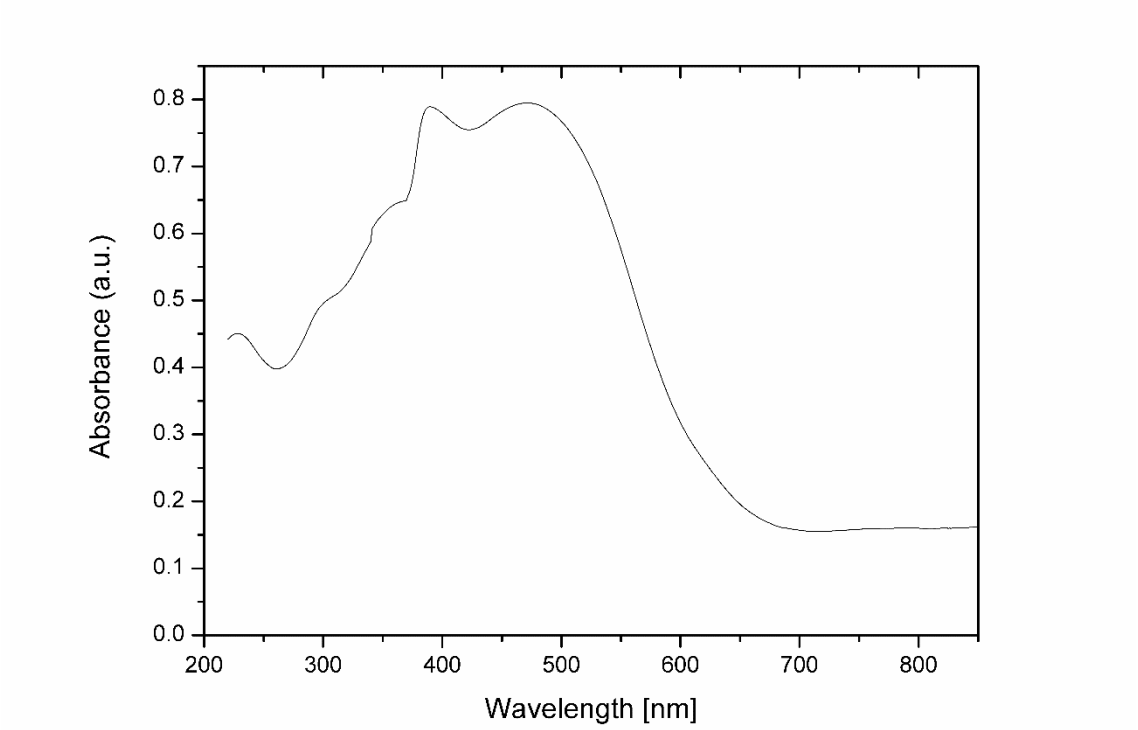



**Fig. S5** UV-Vis spectra on a solid sample of **1.**

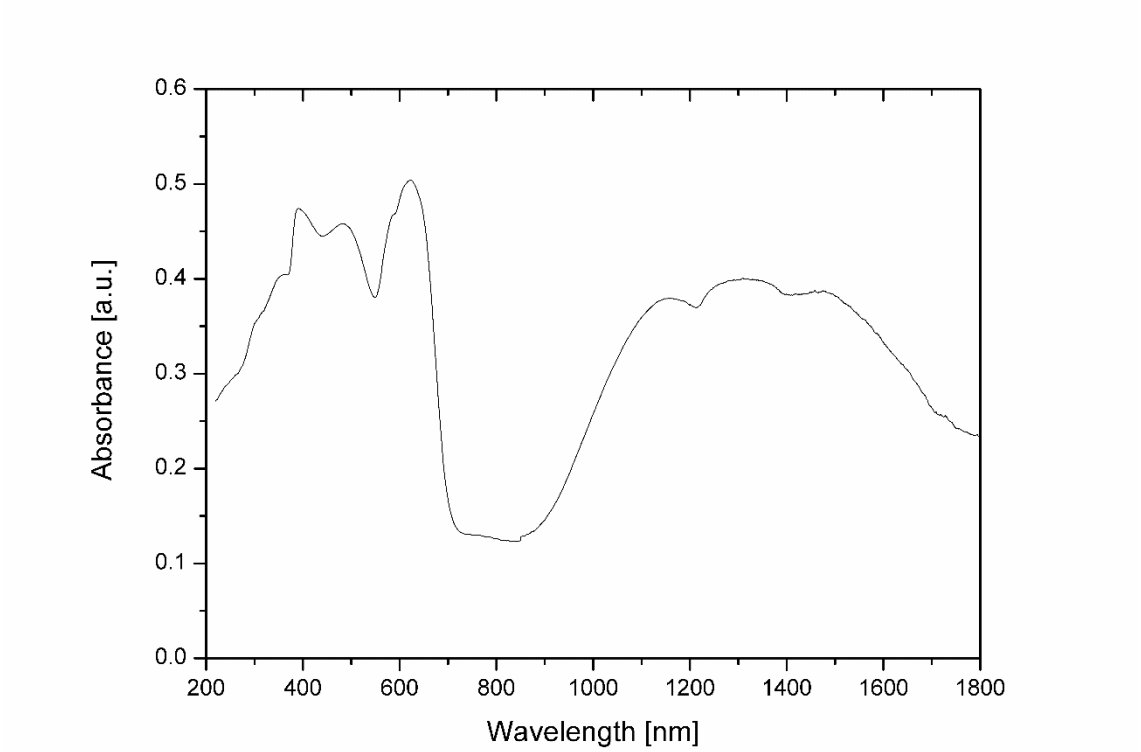



**Fig. S6** UV-Vis spectra on a solid sample of **2.**

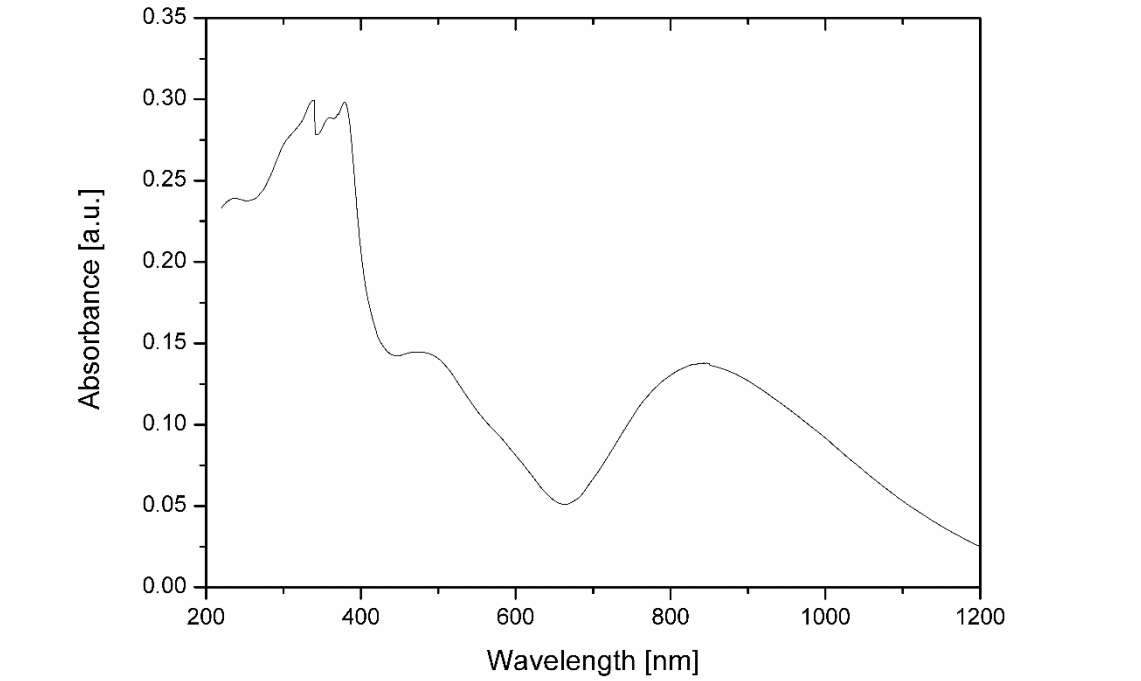



**Fig. S7** UV-Vis spectra on a solid sample of **3.**

**Intermolecular interactions in 2:**

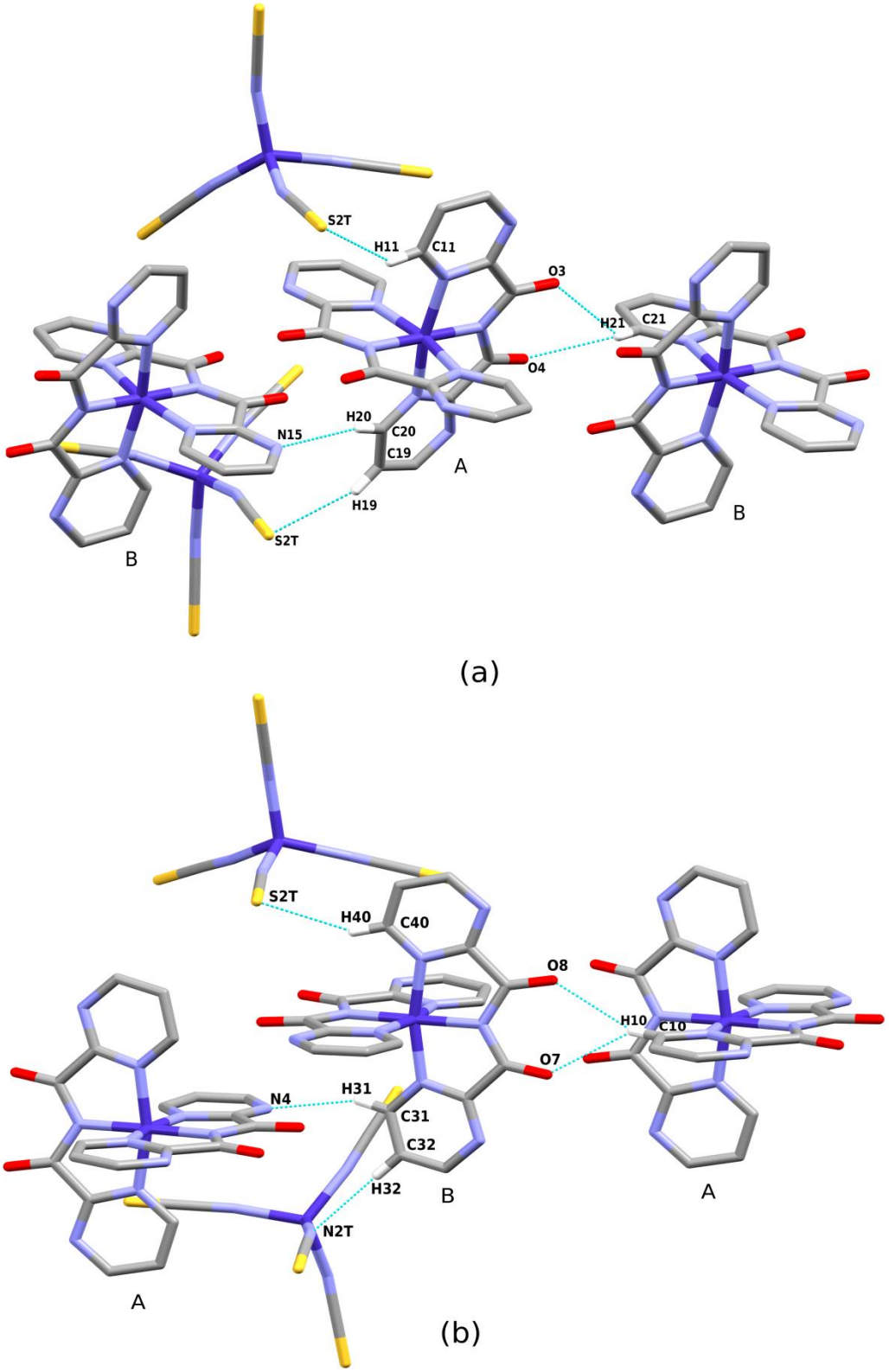



**Figure S8.** A view of the intermolecular interactions in crystal structure **2** responsible for the deviation from planarity of the (a) **A** and (b) **B** complex cations.

**Cyclic voltammogram of 1:**

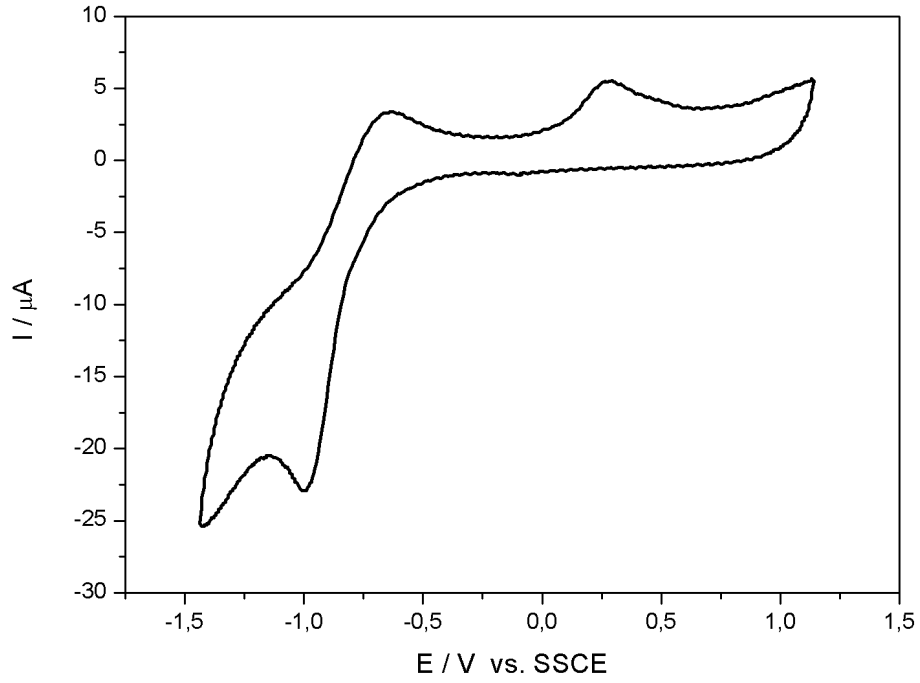



**Fig. S9** Cyclic voltammogram of **1** (0.1 M) in MeCN. Potentials are vs. SSCE, with scan rate 100 mV $s^{-1}$, glassy carbon working electrode, and 0.1 M $n$Bu$_4$NPBu$_6$.

**$\chi_M T$ versus $T$ plots:**

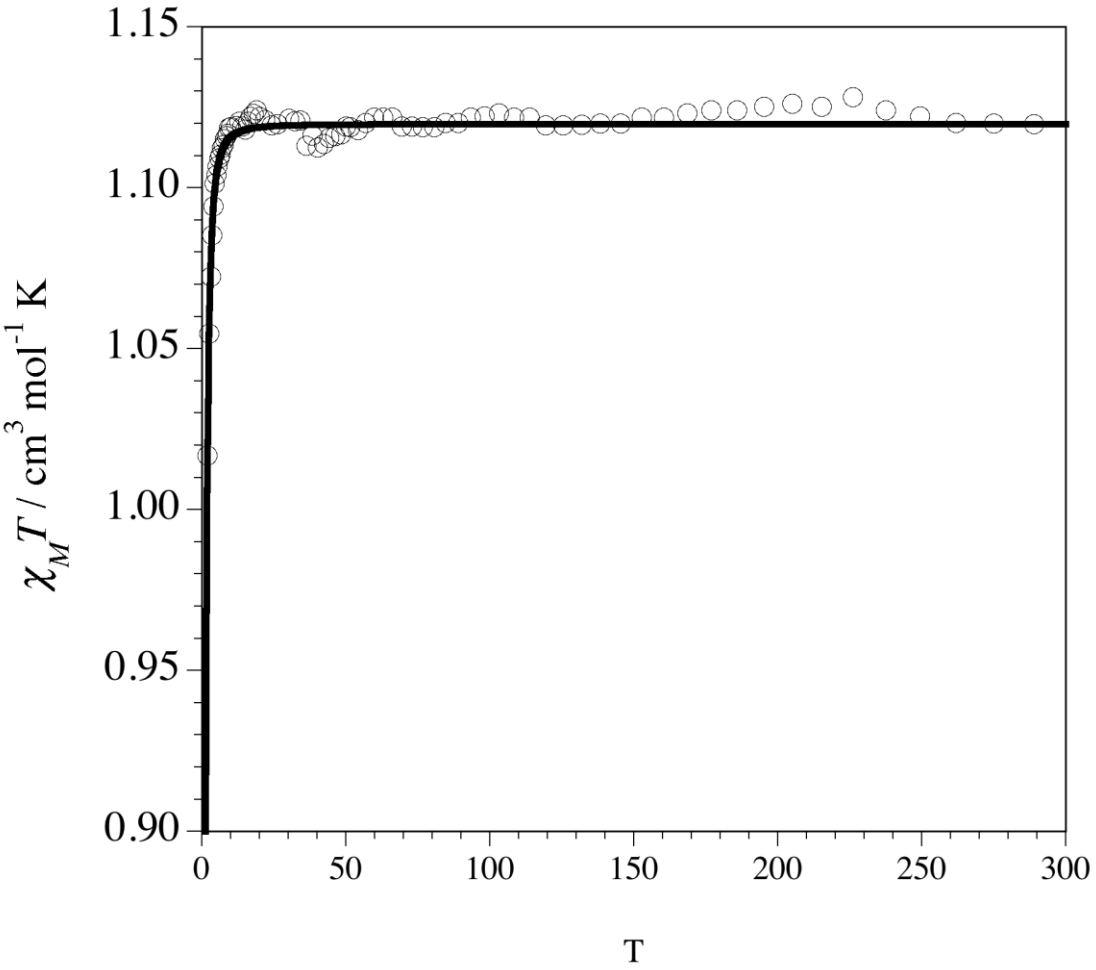



**Figure S10**. Thermal dependence of $\chi_M T$ for **3**: (o) experimental; (—) best-fit curve through eqn (3) (see text).

**Crystallographic data and refinement parameters:**

**Table S1. Crystal data and refinement statistics for the complexes 1-3.**

| | **1** | **2** | **3** |
|---|---|---|---|
| Structural formula | $C_{22}H_{20}N_{10}ClCoO_{10}S$ | $C_{46}H_{32}N_{24}Co_3O_{10}S_5$ | $C_{20}H_{14}N_{10}NiO_5$ |
| Fw (g/mol) | 710.92 | 1416.54 | 533.12 |
| Crystal system | monoclinic | monoclinic | triclinic |

| | | | | |
|---|---|---|---|---|
| Space group | | $P2_1/n$ | $Cc$ | $P(-1)$ |
| $Z$ | | 4 | 4 | 2 |
| $T$ (K) | | 298(2) | 298(2) | 150(2) |
| Unit cell dimensions | $a$ | 10.1227(2) | 19.5807(5) | 8.8015(15) |
| | $b$ | 22.0252(6) | 24.4918(6) | 10.0257(17) |
| | $c$ | 12.4721(3) | 14.4619(4) | 13.876(2) |
| | α | 90 | 90 | 74.233(3) |
| | β | 94.1980(10) | 117.8860(10) | 83.559(3) |
| | γ | 90 | 90 | 64.292(3) |
| $V$ (Å$^3$) | | 2773.25(11) | 6130.1(3) | 1061.7(3) |
| $\rho_{calc}$ (Mg/m$^3$) | | 1.703 | 1.535 | 1.668 |
| Absorption coefficient μ (mm$^{-1}$) | | 0.866 | 1.046 | 0.973 |
| $\theta$ range for data collection (°) | | 1.85 – 27.43 | 1.66 - 26.44 | 1.52 – 27.58 |
| Index ranges | | $-12 \leq h \leq 9$ | $-24 \leq h \leq 23$ | $-11 \leq h \leq 11$ |
| | | $-28 \leq k \leq 23$ | $-30 \leq k \leq 30$ | $-13 \leq k \leq 13$ |
| | | $-16 \leq l \leq 8$ | $-18 \leq l \leq 16$ | $-18 \leq l \leq 17$ |
| Data collected | | 19908 | 22885 | 12287 |
| Unique reflections | | 5927 | 10478 | 4765 |
| Observed reflections [ $I$ | | 4832 | 8975 | 3468 |

| | | | |
|---|---|---|---|
| $> 2\sigma(I)$] | | | |
| Symmetry factor ($R_{int}$) | 0.0329 | 0.0231 | 0.0546 |
| Completeness to $\theta_{max}$ (%) | 98.6 (up to 25°) | 98.3 | 97.1 |
| $F(000)$ | 1448 | 2862 | 544 |
| Refined parameters | 442 | 794 | 328 |
| Goodness-of-fit on $F^2$ ($S$)[a] | 1.037 | 0.677 | 1.015 |
| Final $R_1$[b] factor [$I >$ $2\sigma(I)$] | 0.0415 | 0.0422 | 0.0535 |
| $wR_2$[c] factor (all data) | 0.1117 | 0.1440 | 0.1478 |
| Largest diff. peak / hole ($e$ Å$^{-3}$) | 0.415/-0.497 | 0.562/-0.749 | 1.460/-0.650 |

**Table S2**. Selected bond lengths (Å) and angles (deg) in **1-3**

| $[M1(bpcam)_2]^+$ | **1** | **2** | | **3** |
|---|---|---|---|---|
| | | **A** | **B** | |
| M1[a] -N1 \| N11 | 1.9444(19) | 1.928(6) | 1.921(7) | 2.112(3) |
| M1-N2 \| N12 | 1.8975(18) | 1.887(5) | 1.903(6) | 2.018(3) |
| M1-N3 \| N13 | 1.9433(19) | 1.943(6) | 1.956(6) | 2.096(3) |
| M1-N6 \| N16 | 1.939(2) | 1.948(6) | 1.932(6) | 2.081(3) |
| M1-N7 \| N17 | 1.8934(18) | 1.908(5) | 1.898(6) | 2.014(3) |
| M1-N8 \| N18 | 1.9461(19) | 1.941(6) | 1.927(6) | 2.114(3) |
| N2-M1-N1 \| N12-M1-N11 | 82.90(8) | 82.9(2) | 83.3(2) | 78.58(10) |

| | | | | |
|---|---|---|---|---|
| N3-M1-N1 \| N13-M1-N11 | 166.09(8) | 165.7(2) | 166.0(2) | 158.13(11) |
| N6-M1-N1 \| N16-M1-N11 | 90.84(8) | 91.1(2) | 92.0(2) | 91.68(10) |
| N7-M1-N1 \| N17-M1-N11 | 98.29(8) | 98.4(2) | 94.7(2) | 102.13(11) |
| N1-M1-N8 \| N11-M1-N18 | 90.69(8) | 89.8(2) | 90.5(2) | 91.91(10) |
| N2-M1-N3 \| N12-M1-N13 | 83.19(8) | 82.8(2) | 82.7(2) | 79.56(10) |
| N2-M1-N6 \| N12-M1-N16 | 97.09(8) | 97.1(3) | 97.5(2) | 102.29(11) |
| N7-M1-N2 \| N17-M1-N12 | 178.80(8) | 178.5(2) | 177.9(2) | 178.48(11) |
| N2-M1-N8 \| N12-M1-N18 | 96.96(8) | 97.5(2) | 96.3(2) | 99.13(11) |
| N6-M1-N3 \| N16-M1-N13 | 90.68(8) | 91.3(2) | 89.9(2) | 92.86(11) |
| N7-M1-N3 \| N17-M1-N13 | 95.61(8) | 95.9(2) | 99.3(2) | 100.73(10) |
| N3-M1-N8 \| N13-M1-N18 | 91.18(8) | 91.4(2) | 90.9(2) | 91.60(10) |
| N7-M1-N6 \| N17-M1-N16 | 82.95(8) | 82.3(2) | 82.8(2) | 79.20(10) |
| N6-M1-N8 \| N16-M1-N18 | 165.95(8) | 165.4(2) | 166.2(2) | 158.57(11) |
| N7-M1-N8 \| N17-M1-N18 | 83.01(8) | 83.2(2) | 83.4(2) | 79.38(11) |

| $[M2(NCS)_4]^{2-}$ | **2** |
|---|---|
| M2[b]-N1T | 1.946(8) |
| M2-N2T | 1.928(14) |
| M2-N3T | 1.943(10) |
| M2-N4T | 1.965(8) |
| N1T-M2-N2T | 103.6(5) |
| N1T-M2-N3T | 110.5(4) |
| N1T-M2-N4T | 112.6(4) |
| N2T-M2-N3T | 110.0(4) |
| N2T-M2-N4T | 103.8(4) |
| N3T-M2-N4T | 115.3(4) |

[a] M1 means either Co1, Co2 or Ni1, in which N1-N8 is coordinated to Co1 or Ni1, while N11-N18 coordinates to Co2.

[b] M2 means Co3 in structure **2**.