Electronic Supplementary Information for

Dimensionality trends in metal-organic frameworks containing perfluorinated or non-fluorinated benzenedicarboxylates

Zeric Hulvey, Joshua D. Furman, Sara A. Turner, Min Tang, and Anthony K. Cheetham

Contents:

Synthesis of 1-20

The ligands used in this study are abbreviated in the text as follows: bpe = 1,2-bis(4-pyridyl)ethane; bpp = 1,3-bis(4-pyridyl)propane; tpa = terephthalate; ipa = isophthalate; tftpa = tetrafluoroterephthalate; tfipa = tetrafluoroisophthalate. The chemicals used in the synthesis of **1**-**20** were all used as received from Aldrich. All syntheses were carried out in Teflon-lined stainless steel autoclaves, isolated by filtration and washed with water and acetone. Specific details for the synthesis of **1**-**20** are given below, along with elemental analysis data for compounds obtained as pure phases. Elemental analysis (C, H, N) was carried out by the Marine Sciences Institute Analytical Laboratory at UCSB.

Co(bpp)(ipa), 1. 0.05 mmol $Co(CH_3CO_2)_2 \cdot 4H_2O$, 0.05 mmol bpp, and 0.05 mmol H_2ipa were added to 3 mL water and heated at 100 °C for 24 h to give small blue-purple block-shaped crystals. Anal. found (wt %): C, 59.6; H, 4.32; N, 6.64. Calcd.: C, 59.9; H, 4.31; N, 6.65.

Co(bpe)(ipa), 2. 0.05 mmol $Co(CH_3CO_2)_2 \cdot 4H_2O$, 0.05 mmol bpe, and 0.05 mmol H_2ipa were added to 3 mL water and heated at 100 °C for 24 h to give small purple block-shaped crystals. Anal. found (wt %): C, 59.0; H, 4.08; N, 6.96. Calcd.: C, 59.0; H, 3.96; N, 6.88.

Co(bpp)(tpa), 3. 0.1 mmol $Co(CH_3CO_2)_2 \cdot 4H_2O$, 0.1 mmol bpp, and 0.1 mmol H_2tpa were added to 5 mL water and heated at 100°C for 18 h to give small purple block-shaped crystals of **3** along with an impurity powder phase.

Ni(bpe)(ipa)(H_2O) • 1.67H_2O, 4. 0.05 mmol $Ni(CH_3CO_2)_2 \cdot 4H_2O$, 0.05 mmol bpe, and 0.05 mmol H_2ipa were added to a mixture of 4 mL water and 1 mL DMF and heated at

100 °C for 18 h to give green block-shaped crystals. Anal. found (wt %): C, 50.7; H, 4.47; N 5.92,. Calcd.: C, 52.8; H, 4.73; N, 6.16.

Ni(bpp)(ipa)(H_2O), 5. 0.2 mmol $Ni(CH_3CO_2)_2 \cdot 4H_2O$, 0.2 mmol bpp, 0.1 mmol H_2ipa and 0.2 mL 1M KOH were added to 5 mL water and heated at 100 °C for 24 h to give green block-shaped crystals. Anal. found (wt %): C, 57.3; H, 4.73; N 6.46,. Calcd.: C, 57.4; H, 4.59; N, 6.38.

Ni(bpp)(tpa)(H_2O)$_2$, 6. 0.2 mmol $Ni(CH_3CO_2)_2 \cdot 4H_2O$, 0.2 mmol bpp, and 0.2 mmol H_2tpa were added to 5 mL water and heated at 100 °C for 24 h to give green block-shaped crystals. Anal. found (wt %): C, 55.2; H, 4.95; N 6.14,. Calcd.: C, 55.2; H, 4.85; N, 6.13.

Zn_2(bpe)(tpa)Cl, 7. 0.1mmol $ZnCl_2$, 0.1 mmol bpe, and 0.1 mmol H_2tpa were added to 5 mL water and heated at 100 °C for 18 h to give colorless block-shaped crystals of **7** along with an impurity powder phase.

Zn(bpe)(ipa), 8. 0.05 mmol $Zn(CH_3CO_2)_2 \cdot 4H_2O$, 0.05 mmol bpe, and 0.05 mmol H_2ipa were added to 3 mL water and heated at 100 °C for 18 h to give colorless block-shaped crystals. Anal. found (wt %): C, 57.3; H, 3.97; N 6.64,. Calcd.: C, 58.0; H, 3.90; N, 6.77.

Cu_4(bpe)$_3$(ipa)$_4$(H_2O)$_2$, 9. 0.1 mmol $Cu(CH_3CO_2)_2 \cdot 4H_2O$, 0.1 mmol bpe, 0.1 mmol H_2ipa and 0.3 mL 1M KOH were added to 5 mL water and heated at 100 °C for 18 h to give blue plate-shaped crystals. Anal. found (wt %): C, 56.6; H, 4.02; N 6.97,. Calcd.: C, 55.1; H, 3.67; N, 5.67.

Zn(bpp)(ipa), 10. 0.05 mmol $Zn(CH_3CO_2)_2 \cdot 4H_2O$, 0.05 mmol bpp, and 0.05 mmol H_2ipa were added to 5 mL water and heated at 100 °C for 18 h to give colorless block-shaped crystals of **10** along with an impurity powder phase.

Co(bpp)(tftpa)(H_2O)$_2$, 11. 0.2 mmol $Co(CH_3CO_2)_2 \cdot 4H_2O$, 0.1 mmol bpp, and 0.2 mmol H_2tftpa were added to 3 mL water and heated at 125 °C for 18 h to give small bright pink square-shaped crystals. Anal. found (wt %): C, 42.7; H, 2.07; N, 3.52. Calcd.: C, 42.7; H, 1.98; N, 3.44.

Cu$_2$(bpe)(tfipa)$_2$(H_2O), 12. 0.1 mmol $Cu(CH_3CO_2)_2 \cdot H_2O$, 0.1 mmol bpe, and 0.1 mmol H_2tfipa were added to 3 mL water and heated at 100 °C for 18 h to give a mixture of small blue crystals of **12** and an unknown blue powder.

Cu(bpp)(tfipa)(H_2O), 13. 0.1 mmol $Cu(CH_3CO_2)_2 \cdot H_2O$, 0.1 mmol bpp, 0.1 mmol H_2tfipa, and 0.2 mL 1 M KOH were added to 3 mL water and heated at 90 °C for 18 h to give a mixture of blue powder, green solids, and small turquoise crystals of **13**.

Cu(bpp)(tftpa), 14. 0.1 mmol $Cu(CH_3CO_2)_2 \cdot H_2O$, 0.1 mmol bpp, and 0.1 mmol H_2tftpa were added to 3 mL water and heated at 90 °C for 20 h to give large dark blue block-shaped crystals. Anal. found (wt %): C, 50.6; H, 2.95; N, 5.69. Calcd.: C, 50.7; H, 2.83; N, 5.63.

Co$_2$(bpe)$_3$(tfipa)$_2$, 15. 0.1 mmol $Co(CH_3CO_2)_2 \cdot 4H_2O$, 0.1 mmol bpe, and 0.1 mmol H_2tfipa were added to 3 mL water and heated at 100 °C for 18 h to give magenta crystals. Anal. found (wt %): C, 54.6; H, 3.23; N, 7.34. Calcd.: C, 54.7; H, 3.18; N, 7.35.

Co(bpe)(tftpa), 16. 0.1 mmol $Co(CH_3CO_2)_2 \cdot 4H_2O$, 0.1 mmol bpe, 0.1 mmol H_2tftpa, and 0.2 mL 1 M KOH were added to 3 mL water and heated at 100 °C for 18 h to give pink crystals. Anal. found (wt %): C, 50.1; H, 2.58; N, 5.88. Calcd.: C, 50.1; H, 2.52; N, 5.85.

$Cu_2(bpp)(tftpa)_2(H_2O)$, 17. 0.1 mmol $Cu(NO_3)_2 \cdot 6H_2O$, 0.1 mmol bpp, and 0.1 mmol H_2tftpa were added to 2 mL water and heated at 90 °C for 6 d to give dark green crystals. Anal. found (wt %): C, 42.7; H, 2.07; N, 3.52. Calcd.: C, 42.7; H, 1.98; N, 3.44.

$Ni_2(bpe)_3(tfipa)_2$, 18. 0.1 mmol $Ni(CH_3CO_2)_2 \cdot 4H_2O$, 0.1 mmol bpe, and 0.1 mmol H_2tfipa were added to 3 mL water and heated at 100 °C for 18 h to give green block-shaped crystals. Anal. found (wt %): C, 54.5; H, 3.21; N, 7.28. Calcd.: C, 54.7; H, 3.18; N, 7.36.

$Zn_2(bpe)_3(tfipa)_2$, 19. 0.1 mmol $Zn(CH_3CO_2)_2 \cdot 2H_2O$, 0.1 mmol bpe, and 0.1 mmol H_2tfipa were added to 3 mL water and heated at 100 °C for 18 h to give a mixture of colorless crystals of **19** and a whitish-yellow solid.

Zn(bpe)(tftpa), 20. 0.1 mmol $Zn(CH_3CO_2)_2 \cdot 2H_2O$, 0.1 mmol bpe, and 0.1 mmol H_2tftpa were added to 3 mL water and heated at 100 °C for 18 h to give colorless needle-shaped crystals. Anal. found (wt %): C, 49.2; H, 2.57; N, 5.79. Calcd.: C, 49.5; H, 2.49; N, 5.77.

Structure determination

All structures were determined using single crystal X-ray diffraction. Measurements for **7** were performed at the Advanced Light Source synchrotron at Lawrence Berkeley Laboratory. Crystals were mounted Kaptan loop using paratone-N oil and placed in a N_2 cryostream at 100 K. Data were then collected at room temperature using a Bruker D8 goniometer and Platinum 200 detector. The high flux synchrotron source of 1 × 1011 photons/s/0.01% BW at 10 keV allowed for very small crystals to be used for diffraction. Data integration was performed using the Bruker SAINT version 7.06 and corrected for Lorentz and polarization effects using SADABS.[1] Measurements for all other compounds were performed on a Siemens SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation, λ = 0.71073 Å) operating at 45 kV and 30 mA. Suitable single crystals were selected under a polarizing microscope and glued to a glass fiber. A hemisphere of intensity data was collected at room temperature. Absorption corrections were made using SADABS.[1]

All of the structures were then solved by direct methods and difference Fourier synthesis and were refined against $|F|^2$ using the SHELXTL software package.[2] The relevant details of structure determination are shown in Table S1. All extinction coefficients refined to within three esd's of zero and were therefore removed from the refinement. Non-hydrogen atoms were refined anisotropically. Riding hydrogens were assigned to the carbon atoms on the bpe, bpp, tpa, and ipa ligands. Hydrogen atoms on water molecules were found in the Fourier difference map and constrained to chemically reasonable positions.

---

[1] Sheldrick, G. M. *SADABS User Guide*; University of Göttingen: Göttingen, **1995**.
[2] Sheldrick, G. M. *SHELXTL-97, A Program for Crystal Structure Determination*, version 5.1; University of Göttingen: Göttingen, **1995**.

CCDC 771582-771601 contains the supplementary crystallographic data for structures **1**-**20**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal Data and Refinement Parameters for 1-20.

compound	**1**	**2**	**3**
formula	$CoC_{21}H_{18}N_2O_4$	$CoC_{20}H_{16}N_2O_4$	$CoC_{21}H_{18}N_2O_4$
molecular weight	421.30	407.29	421.32
crystal system	triclinic	triclinic	orthorhombic
space group	*P*-1	*P*-1	*Pbca*
a (Å)	8.682(2)	10.0719(14)	11.73(3)
b (Å)	10.082(3)	10.0962(16)	16.68(3)
c (Å)	11.810(3)	10.0938(14)	19.55(7)
α	68.382(4)°	78.760(4)°	90
β	82.919(4)°	69.287(4)°	90
γ	78.430(4)°	85.352(4)°	90
V (Å^3)	940.2(4)	941.6(2)	3825(19)
Z	2	2	8
ρ (g cm^{-3})	1.488	1.437	1.463
μ (mm^{-1})	0.943	0.939	0.927
2*θ* range collected	3.72-50.70°	4.12-52.74°	4.16-52.74°
data/restraints/parameters	3413 / 0 / 274	3739 / 120 / 245	3887 / 0 / 253
R_{int}	0.0565	0.2509	0.0534
R_1, wR_2 [$I > 2\sigma(I)$]	0.0533, 0.1160	0.0773, 0.1829	0.0661, 0.1410
R (all data)	0.0888, 0.1281	0.1509, 0.2431	0.0945, 0.1566

compound	**4**	**5**	**6**
formula	$Ni_3C_{60}H_{64}N_6O_{20}$	$NiC_{21}H_{20}N_2O_5$	$NiC_{21}H_{22}N_2O_6$
molecular weight	1365.27	439.09	457.12
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/m$	*P*-1	*C*2/*c*
a (Å)	10.1103(9)	9.4552(17)	16.771(2)
b (Å)	26.854(3)	10.0780(18)	15.488(2)
c (Å)	13.3316(12)	11.923(2)	16.598(2)
α	90	81.037(3)°	90
β	107.234(2)°	71.100(3)°	113.853(3)°
γ	90	65.366(3)°	90
V (Å^3)	3457.1(5)	976.8(3)	3943.0(9)
Z	2	2	8
ρ (g cm^{-3})	1.312	1.493	1.540
μ (mm^{-1})	0.880	1.029	1.027
2*θ* range collected	3.20-46.62°	4.44-46-66°	3.74-52.04°
data/restraints/parameters	5102 / 19 / 429	2824 / 0 / 268	3877 / 0 / 283
R_{int}	0.0845	0.0566	0.0915
R_1, wR_2 [$I > 2\sigma(I)$]	0.0848, 0.2414	0.0411, 0.0860	0.0770, 0.1407
R (all data)	0.1379, 0.2767	0.0640, 0.0927	0.1181, 0.1555

compound	**7**	**8**	**9**
formula	$ZnC_{10}H_8ClNO_2$	$ZnC_{20}H_{16}N_2O_4$	$Cu_4C_{68}H_{54}N_6O_{17}$
molecular weight	275.01	413.72	1481.33
crystal system	triclinic	triclinic	trigonal
space group	*P*-1	*P*-1	$P3_1$
a (Å)	7.165(2)	8.5191(17)	11.109(16)
b (Å)	7.332(2)	9.6341(19)	11.109(16)
c (Å)	10.218(3)	11.562(2)	46.95(9)
α	74.640(4)°	66.500(3)°	90
β	75.171(4)°	76.143(3)°	90
γ	85.179(4)°	89.152(3)°	120
V (Å^3)	500.3(2)	841.4(3)	5018(14)
Z	2	2	3
ρ (g cm^{-3})	1.826	1.633	1.471
μ (mm^{-1})	0.000	1.490	1.328
2*θ* range collected	6.42-57.94°	3.98-50.70°	4.32-50.68°
data/restraints/parameters	1993 / 0 / 136	3061 / 0 / 244	11163 / 4 / 846
R_{int}	0.0246	0.0712	0.1251
R_1, wR_2 [$I > 2\sigma(I)$]	0.0858, 0.2737	0.0508, 0.1112	0.1033, 0.2149
R (all data)	0.0895, 0.2753	0.0688, 0.1184	0.1674, 0.2467

compound	**10**	**11**	**12**
formula	$ZnC_{21}H_{18}N_2O_4$	$CoC_{21}H_{18}F_4N_2O_6$	$CuC_{14}H_8F_4NO_5$
molecular weight	427.74	529.30	409.75
crystal system	monoclinic	triclinic	Triclinic
space group	$P2_1/n$	*P*-1	*P*-1
a (Å)	11.021(14)	11.286(6)	7.509(5)
b (Å)	11.193(16)	11.300(5)	8.497(6)
c (Å)	15.739(13)	17.338(8)	11.853(8)
α	90	79.946(8)°	98.693(10)°
β	104.01(9)°	74.484(8)°	102.646(10)°
γ	90	89.864(8)°	106.529(11)°
V (Å^3)	1884(4)	2095.6(18)	688.8(8)
Z	4	4	2
ρ (g cm^{-3})	1.508	1.678	1.976
μ (mm^{-1})	1.334	0.898	1.665
2*θ* range collected	4.08-52.04°	2.48-48.22°	3.62-49.42°
data/restraints/parameters	3691 / 0 / 253	6584 / 20 / 657	2168 / 3 / 240
R_{int}	0.0731	0.1128	0.0220
R_1, wR_2 [$I > 2\sigma(I)$]	0.0559, 0.1374	0.1023, 0.2182	0.0475, 0.1109
R (all data)	0.0802, 0.1487	0.1898, 0.2671	0.0615, 0.1203

compound	**13**	**14**	**15**
formula	$CuC_{21}H_{16}F_4N_2O_5$	$CuC_{21}H_{14}F_4N_2O_4$	$CoC_{26}H_{18}F_4N_3O_4$
molecular weight	515.90	497.88	571.36
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$C2/c$
a (Å)	10.665(2)	9.4448(9)	30.967(3)
b (Å)	8.0467(16)	15.7681(16)	10.4282(10)
c (Å)	23.644(4)	13.5606(13)	17.1624(15)
α	90	90	90
β	92.984(5)°	107.067(2)°	119.526(2)°
γ	90	90	90
V (Å^3)	2026.4(7)	1930.6(3)	4822.5(8)
Z	4	4	8
ρ (g cm^{-3})	1.691	1.713	1.574
μ (mm^{-1})	1.153	1.203	0.782
2θ range collected	3.44-48.80°	4.06-52.74°	3.02-51.36°
data/restraints/parameters	3337 / 4 / 320	3902 / 0 / 311	4572 / 0 / 361
R_{int}	0.1700	0.0613	0.0723
R_1, wR_2 [$I > 2\sigma(I)$]	0.0943, 0.1635	0.0541, 0.1110	0.0680, 0.1273
R (all data)	0.1614, 0.1900	0.0896, 0.1241	0.1143, 0.1482

compound	**16**	**17**	**18**
formula	$CoC_{20}H_{12}F_4N_2O_4$	$Cu_2C_{29}H_{16}F_8N_2O_9$	$NiC_{26}H_{18}F_4N_3O_4$
molecular weight	479.25	815.52	571.14
crystal system	triclinic	triclinic	monoclinic
space group	P-1	P-1	$P2_1/n$
a (Å)	9.760(4)	9.558(3)	9.9546(13)
b (Å)	10.076(4)	10.492(4)	17.648(2)
c (Å)	11.054(5)	15.180(5)	13.5573(16)
α	67.415(6)°	105.058(5)°	90
β	81.259(7)°	97.070(6)°	99.334(3)°
γ	77.594(6)°	91.781(6)°	90
V (Å^3)	977.4(7)	1455.7(9)	2350.1(5)
Z	2	2	4
ρ (g cm^{-3})	1.628	1.860	1.614
μ (mm^{-1})	0.946	1.573	0.898
2θ range collected	4.00-50.70°	2.80-50.70°	3.82-51.36°
data/restraints/parameters	3543 / 0 / 292	5285 / 4 / 472	4463 / 0 / 343
R_{int}	0.0392	0.0738	0.1102
R_1, wR_2 [$I > 2\sigma(I)$]	0.0579, 0.1307	0.0747, 0.1458	0.0772, 0.1396
R (all data)	0.0837, 0.1443	0.1389, 0.1788	0.1323, 0.1600

compound	**19**	**20**
formula	$ZnC_{26}H_{18}F_4N_3O_4$	$Zn_3C_{60}H_{36}F_{12}N_6O_{12}$
molecular weight	577.80	1457.12
crystal system	monoclinic	triclinic
space group	*C*2/*c*	*P*-1
a (Å)	30.939(7)	10.395(3)
b (Å)	10.454(2)	11.790(3)
c (Å)	17.214(4)	13.331(3)
α	90	102.902(4)°
β	119.258(3)°	110.679(4)°
γ	90	107.159(4)°
V (Å^3)	4857.4(18)	1359.0(6)
Z	8	1
ρ (g cm^{-3})	1.580	1.780
μ (mm^{-1})	1.081	1.429
2*θ* range collected	3.02-52.74°	3.50-52.74°
data/restraints/parameters	4907 / 0 / 361	5332 / 0 / 439
R_{int}	0.0525	0.0538
R_1, wR_2 [$I > 2\sigma(I)$]	0.0564, 0.1139	0.0698, 0.1473
R (all data)	0.0870, 0.1275	0.1290, 0.1768

Structure descriptions of 1-20

Structure of Co(bpp)(ipa), 1. The asymmetric unit of **1** contains a single unique cobalt atom with one ipa ligand and one bpp ligand. The cobalt atom is in a distorted CoO_4N_2 octahedron, coordinated by one bidentate carboxylic acid group (Co-O distances 2.137(4) Å and 2.196(3) Å), two bridging carboxylate groups (Co-O distances 2.027(3) Å and 2.027(3) Å) and two *trans* bpp nitrogen atoms (Co-N distances 2.163(3) Å and 2.143(3) Å). The cobalt-ipa connectivity forms a 1-D ribbon which is decorated with bpp ligands looped back 180° with their aromatic rings in a π-stacked arrangement with a inter-plane angle of 17.8°. The Co atom separation alternates between 4.208(1) Å and 7.393(2) Å. The aliphatic propane chain linking the pyridine rings of the bpp ligand is disordered over two positions. The occupancy of these two positions was constrained to 0.5 for the structure refinement. Compound **1** is anhydrous and the spaces between the decorating pyridine chains are filled by staggered neighboring chains.

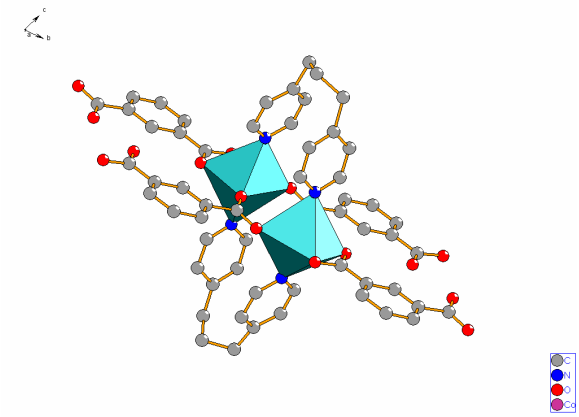


Figure S1. Coordination around CoO_4N_2 octahedra in **1**.

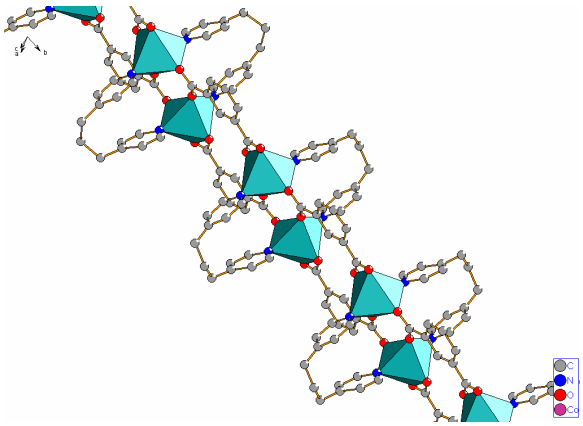


Figure S2. View of one-dimensional chain of **1**.

Structure of Co(bpe)(ipa), 2. Structure **2** contains isolated distorted CoO_4N_2 octahedra linked by two ipa ligands (Co-O distances 2.205(5) Å, 2.144(4) Å, 2.036(4) Å, and 2.011(5) Å) to form a ribbon-like chain with Co-Co distances of 4.466(2) Å and 6.933(4) Å. These chains are then linked to form a two-dimensional sheet by *trans* bpe ligands (Co-N distances 2.174(5) Å and 2.177(5) Å). The sheets are stacked such that the Co-ipa chains lie above and perpendicular to bpe ligands.

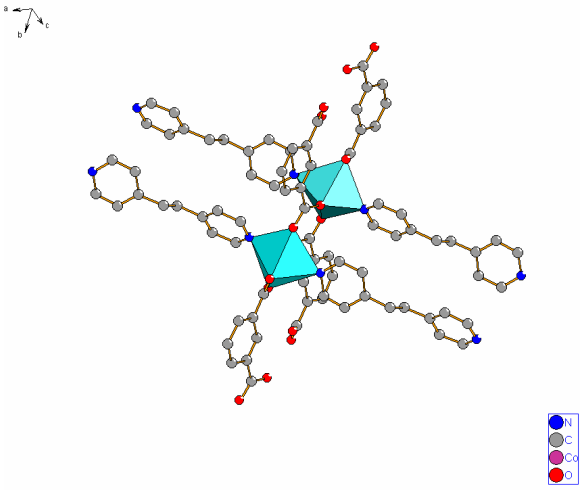


Figure S3. Coordination around CoO_4N_2 octahedra in **2**.

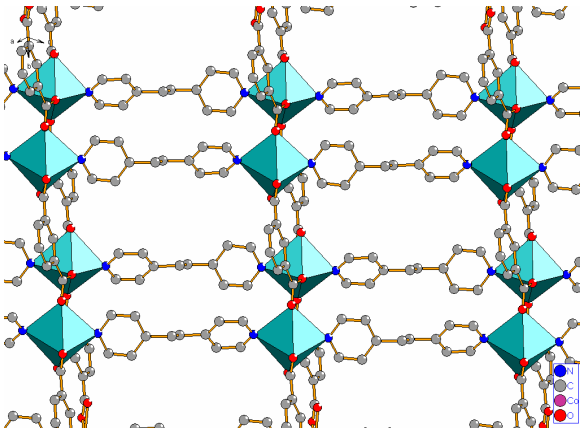


Figure S4. One sheet of **2** viewed from above.

Structure of Co(bpp)(tpa), 3. Structure **3** contains a single crystallographically unique cobalt atom in a distorted CoO_4N_2 octahedron. The asymmetric unit is formed the cobalt atom along with one tpa ligand along the *a* direction and one bpp ligand along the *c* direction. Two bidentate carboxylate groups are coordinated to the cobalt (Co-O bond distances 2.012(6) Å, 2.477(5) Å and 2.071(5) Å, 2.255(8) Å). Two *cis*-bpe ligands complete the coordination (Co-N distances 2.084(5) Å and 2.083(5) Å). The extended network forms a corrugated 2-D sheet where the Co-tpa network is a zig-zag chain connected with bpp ligands alternately extending up or down from the sheet. The structure is anhydrous and the pore space is filled by a second identical interpenetrating network.

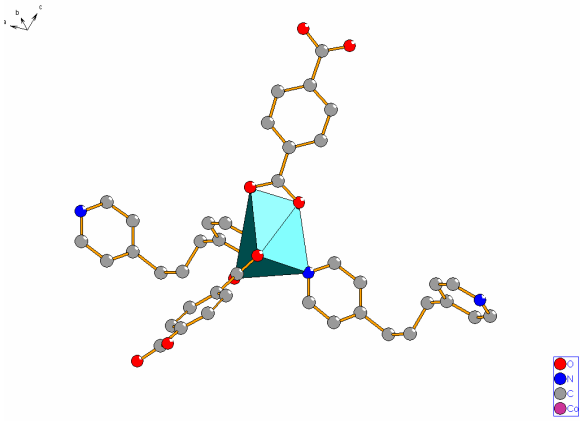


Figure S5. Coordination around CoO_4N_2 octahedron in **3**.

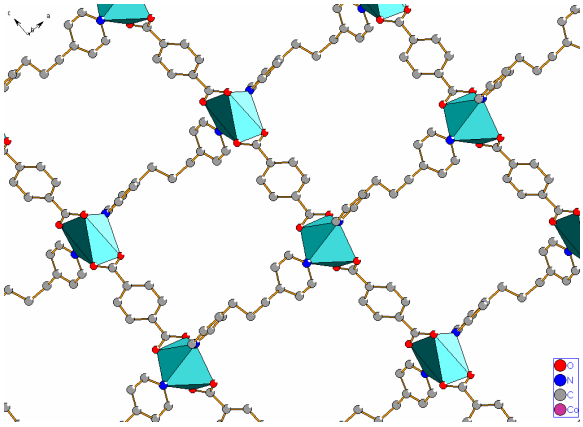


Figure S6. Single sheet of **3** viewed from above.

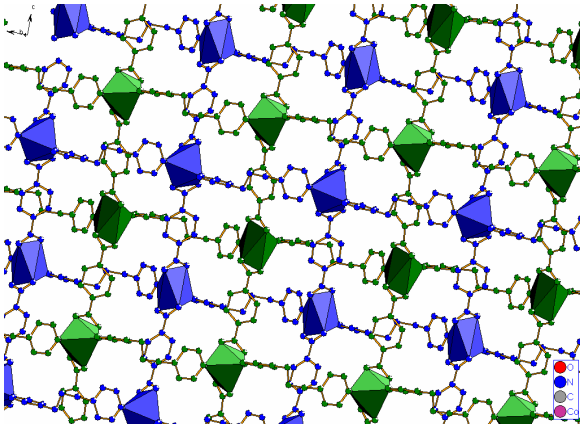


Figure S7. Structure of **3**. with the two interpenetrated sublattices are shaded in blue and green.

Structure of Ni(bpe)(ipa)(H_2O)· 1.67H_2O, 4. The structure of **4** contains two similar but crystallographically unique interpenetrating 2-D sheets. Each sheet contains a distorted NiO_4N_2 octahedron coordinated by one bidentate carboxylic acid group (Ni-O distances 2.112(1) Å, 2.129(1) Å, 2.130(1) Å, and 2.134(1) Å) and a monodentate carboxylic acid group (Ni-O distances 1.993(1) Å and 2.0273(2) Å) from ipa ligands. Two *trans* bpe ligands (Ni-N distances 1.940(1) Å, 2.074(1) Å, 2.089(1) Å, and 2.093(1) Å) are also bound to the metal, and the octahedron is completed by a water molecule (Ni-O distance 2.0579(2)). The ipa ligands lie along the *a* axis forming a metal-ligand-metal chain with alternating monodentate/bidentate bonding. These chains are bridged along the *c* direction by bpe ligands. The bpe ligand is disordered over two positions with the stagger in the chain section taking alternating positions on one of the sheets. The remaining pore space is filled with water molecules.

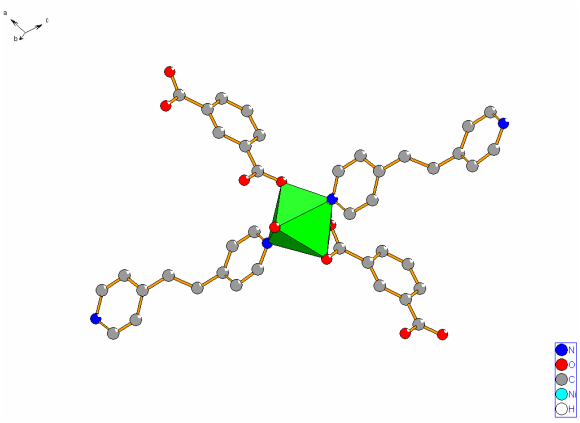


Figure S8. Coordination around NiO_4N_2 octahedron in **4**.

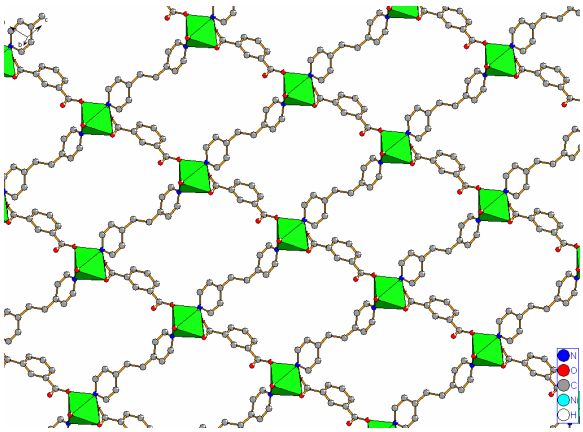


Figure S9. Single layer of **4** viewed from above.

Structure of Ni(bpp)(ipa)(H_2O), 5. The asymmetric unit of **5** contains a single nickel atom coordinated by one bpp ligand, one ipa ligand, and a bound water molecule. The nickel atom is in a distorted NiO_4N_2 octahedron coordinated by a bidentate carboxylic acid group (Ni-O distances 2.084(2) Å and 2.176(3) Å) and a monodentate carboxylic acid (Ni-O distance 2.004(3) Å). Two *cis* bpp ligands (Ni-N distances 2.072(4) Å and 2.059(3) Å) and a water molecule (Ni-O distance 2.128(4) Å) complete the octahedral coordination. Ni-ipa chains form along the *b* direction and are linked by bpp to form a two-dimensional sheet. The sheets stack to fill all pore space but do not interpenetrate.

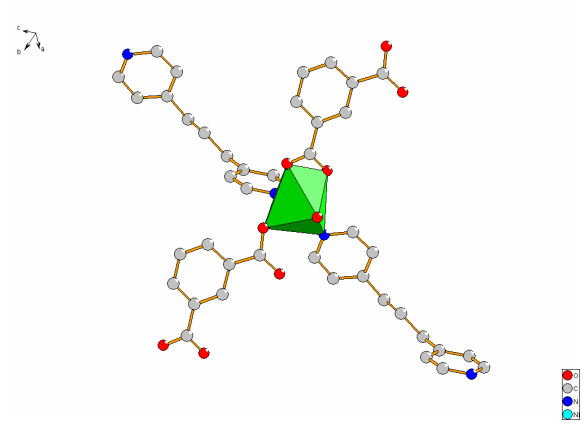


Figure S10. Coordination around NiO_4N_2 octahedron in **5**.

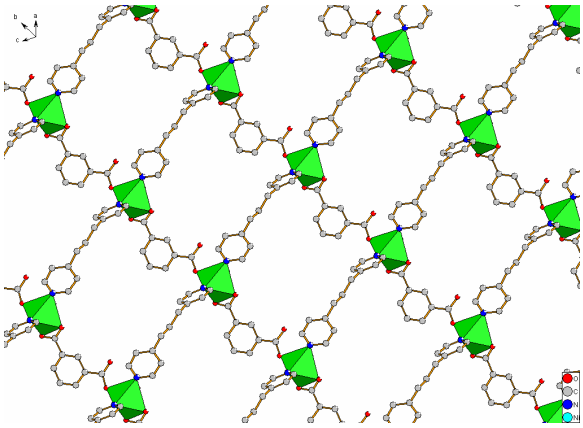


Figure S11. Single sheet of **5** viewed from above.

Structure of Ni(bpp)(tpa)(H_2O)$_2$, 6. The asymmetric unit of structure **6** contains a single nickel atom with one bpp ligand, one tpa ligand, and two bound water molecules. The nickel is octahedrally coordinated by two *trans* monodentate carboxylic acid groups (Ni-O distances 2.106(3) Å and 2.088(4) Å), two *cis* bpp nitrogen atoms (Ni-N distances 2.088(5) Å and 2.083(4) Å) and two bound water molecules (Ni-O distances 2.072(4) Å and 2.090(5) Å). A two-dimensional grid is formed between nickel atoms by tpa ligands in one direction and bpp ligands in another. The open space is filled by a second interpenetrating network of the same arrangement, rotated by 90°. These double layers stack to fill the extended structure.

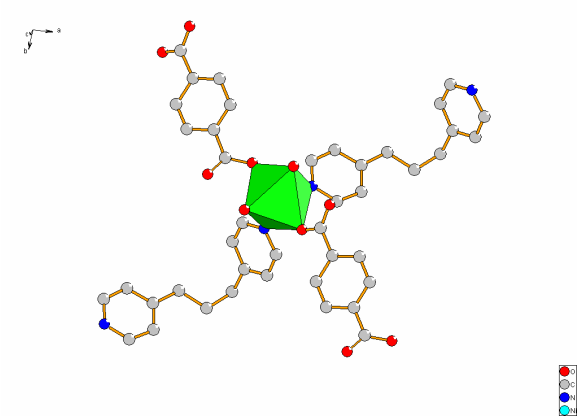


Figure S12. Coordination around NiO_4N_2 octahedron in **6**.

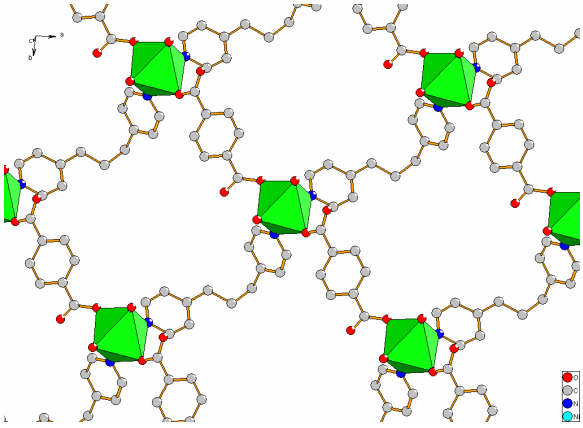


Figure S13. Single sheet of **6** viewed from above.

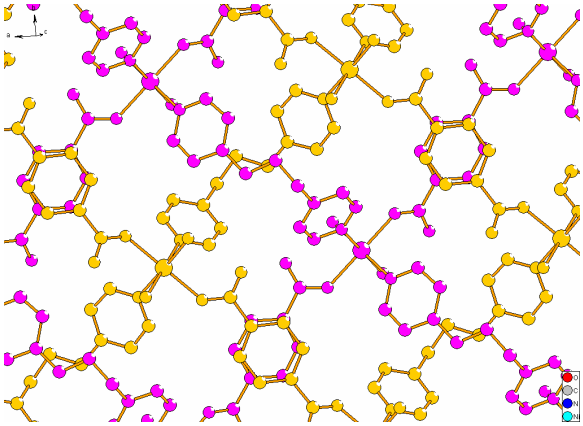


Figure S14. Two-fold interpenetration of the sheet in **6**, with the two sublattices shown in pink and yellow.

Structure of Zn_2(bpe)(tpa)Cl, 7. The asymmetric unit of structure **7** contains one crystallographically unique zinc atom, half of a bpe ligand, half of a tpa ligand, and one chlorine atom. The zinc is tetrahedrally coordinated to two carboxylic acid groups (Zn-O distances 1.992(9) Å and 1.953(8) Å), a bpe nitrogen atom (Zn-N distance 2.025(9) Å), and a chlorine atom (Zn-Cl distance 2.214(4) Å). The ZnO_2NCl tetrahedra form a dimer-like unit due to the two bridging carboxylate groups (Zn-Zn distance 3.689(2) Å). A chain of Zn-tpa chain with the chlorine atoms alternating above and below is linked by the bpe ligands to form an extended two-dimensional sheet. The sheets are stacked such that the chlorine atoms from neighboring sheets fill the pore space formed between the bpe ligands.

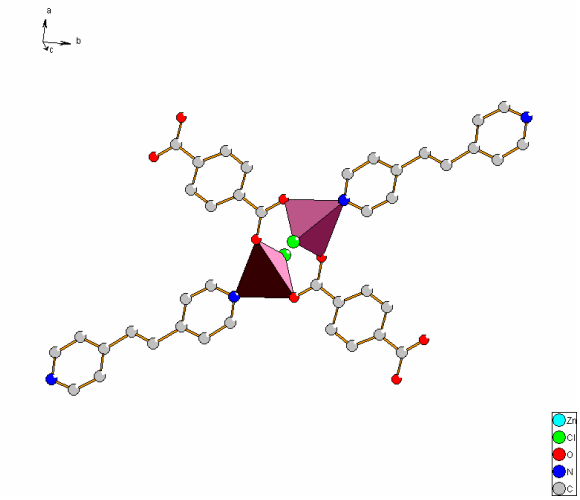


Figure S15. Coordination around ZnO_2NCl tetrahedra in **7**.

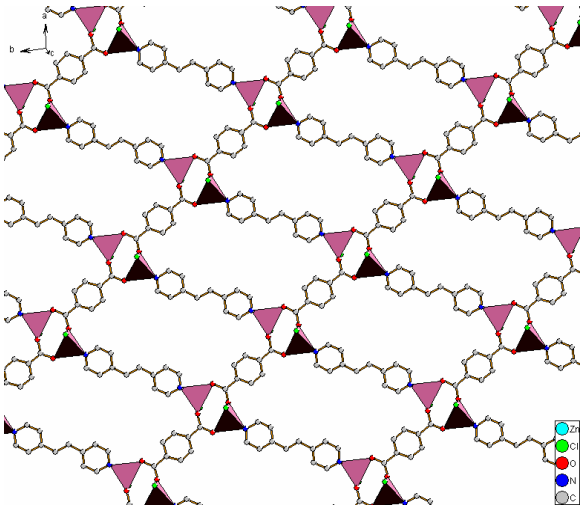


Figure S16. Single sheet of **7** viewed from above.

Structure of Zn(bpe)(ipa), 8. The structure of **8** contains a single unique zinc atom in a distorted ZnO_2N_2 tetrahedron. There are two monodentate carboxylic acid groups (Zn-O distances 1.962(4) Å and 1.943(3) Å) and two bpe ligands (Zn-N distances 2.075(3) Å and 2.067(3) Å). Zn-ipa chains along the *b* direction are linked by bpe ligands in a zig-zag manner to form a corrugated sheet. These sheets are 3 times interpenetrated by staggered other sheets to fill the void space.

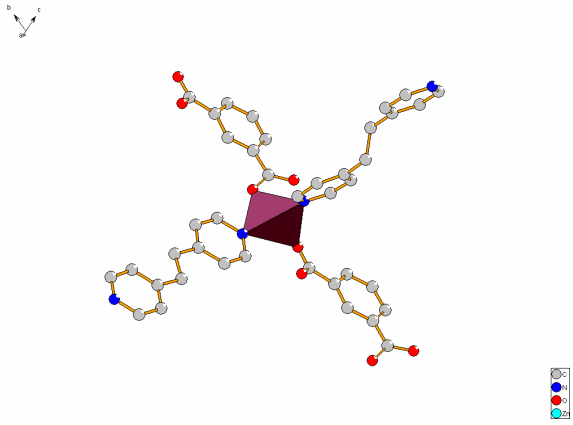


Figure S17. Coordination around ZnO_2N_2 tetrahedron in **8**.

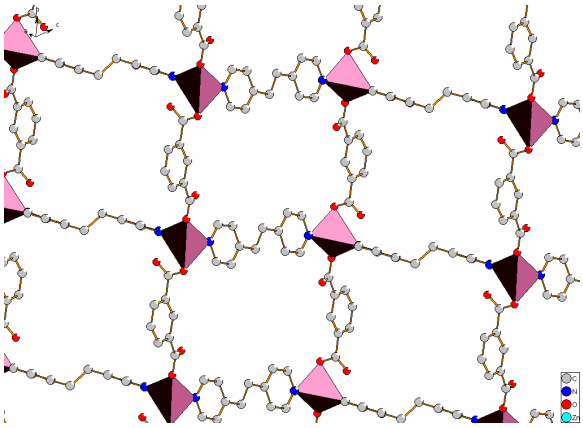


Figure S18. Single layer of **8** viewed from above.

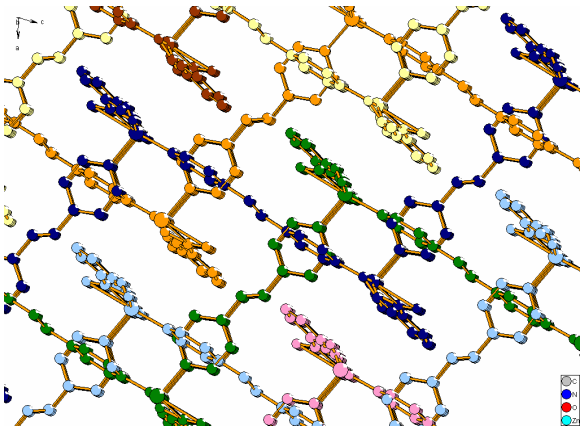


Figure S19. Interpenetration in **8** with different unique sublattices shaded different colors.

Structure of $Cu_4(bpe)_3(ipa)_4(H_2O)$, 9. Structure **9** contains four crystallographically unique Cu atoms. Two of them form a paddlewheel-like dimer (Cu-Cu distance 2.737(4) Å) of CuO_4N square pyramids (Cu-O distances 1.988(14) Å, 1.951(13) Å, 2.096(16) Å, 1.954(14) Å, 2.101(13) Å, 1.942(15) Å, 1.945(14) Å and 1.998(14) Å, Cu-N distances 2.081(11) Å and 2.087(11) Å) with the base of the polyhedra bridged by carboxylic acid groups of the ipa. The nitrogen coordination on these two copper atoms is from *anti*-bpp ligands which arch to the axial position of a neighboring, third copper square pyramid.

This base of this third CuO_2N_3 square pyramid contains *trans* pairs of ipa ligands and bpp ligands (Cu-O distances 1.930(12) Å and 1.946(11) Å, Cu-N distances 2.001(16) Å, 2.24(2) Å and 2.29(2) Å). The ipa ligands from the dimer bridge to a fourth copper atom which occupies a CuO_3N square planar environment bound to two *trans* ipa ligands (Cu-O distances 1.937(12) Å and 1.940(11) Å), a bpe ligand (Cu-N distance 1.955(15) Å) and a water molecule (Cu-O distance 1.964(11) Å). These ligands extend to form a dense, non-interpenetrated 3-dimensional extended network with a 3_1 screw axis along the long 46.95 Å *c* axis of the unit cell forming helical chains of Cu atoms.

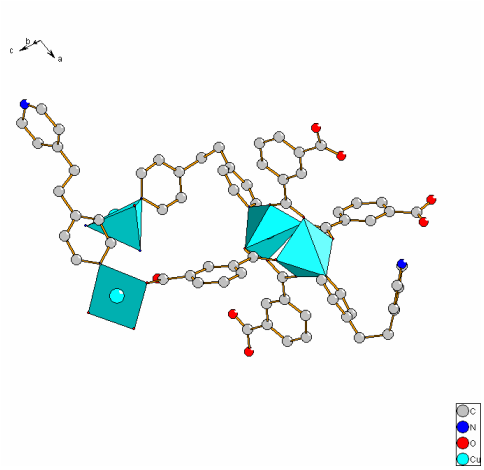


Figure S20. Coordination around copper atoms in **9**.

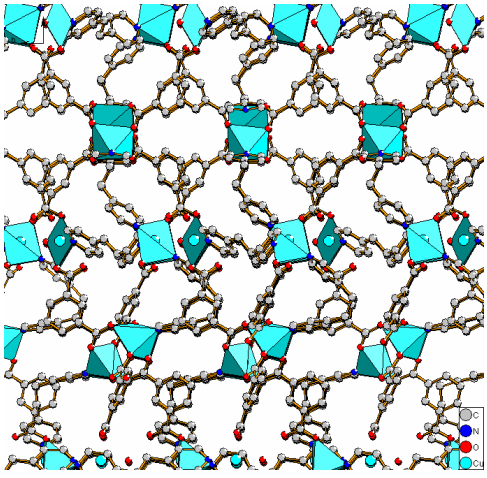


Figure S21. Extended connectivity in **9**.

Structure of Zn(bpp)(ipa), 10. The structure of **10** contains a single unique zinc atom in a distorted ZnO_2N_2 tetrahedron bound to two monodentate ipa ligands (Zn-O distances 1.961(3) Å and 1.952(4) Å) and two bpp ligands (Zn-N distances 2.050(4) Å and 2.039(4) Å). A one-dimensional Zn-isophthalate chain is connected by bpe ligands in two dimensions to form an extended three-dimensional structure. The large pore in the sublattice is large enough to accommodate four-fold interpenetration of other sublattices.

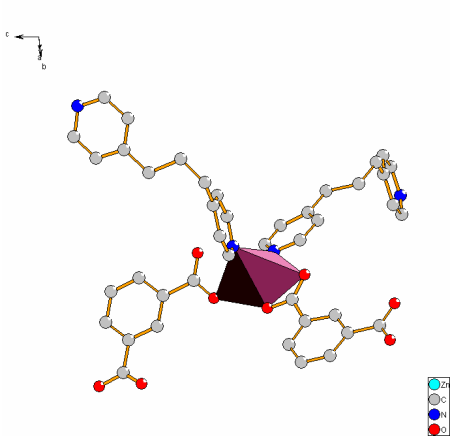


Figure S22. Coordination around ZnO_2N_2 tetahedron in **10**.

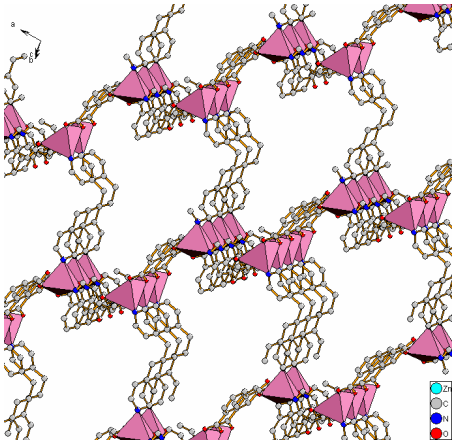


Figure S23. Extended connectivity in **10**.

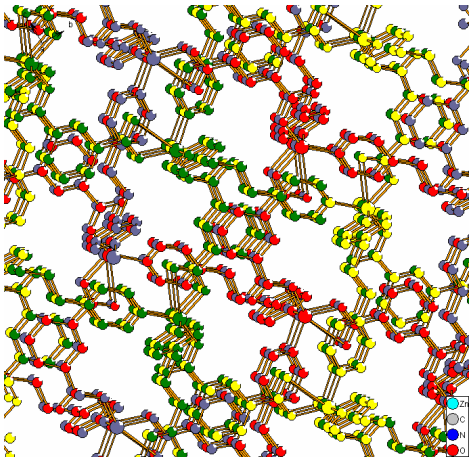


Figure S24. Four-fold interpenetrated structure of **10**.

Structure of Co(bpp)(tftpa)(H_2O)$_2$, 11. Structure **11** contains two crystallographically unique yet extremely similar interpenetrated two-dimensional sheets. Each sheet contains CoO_4N_2 octahedra that bind two *trans* tftpa ligands (Co-O distances 2.084(9) Å, 2.095(8) Å, 2.098(8) Å, and 2.106(7) Å), two *cis*-bpp ligands (Co-N distances 2.087(8) Å, 2.106(9) Å, 2.107(11) Å, and 2.118(11) Å), and two *cis*-water molecules (Co-O distances 2.106(10) Å, 2.111(7) Å, 2.157(9) Å, and 2.177(10) Å). On each of the two unique sheets, the bpp ligands bend in an arch-like shape and connect the octahedra in one direction, and the tftpa ligands connect in a perpendicular direction. The two lattices are rotated approximately 90° with respect to each other and flipped over, such that the bpp ligands on one arch over the rotated bpp ligands on the other.

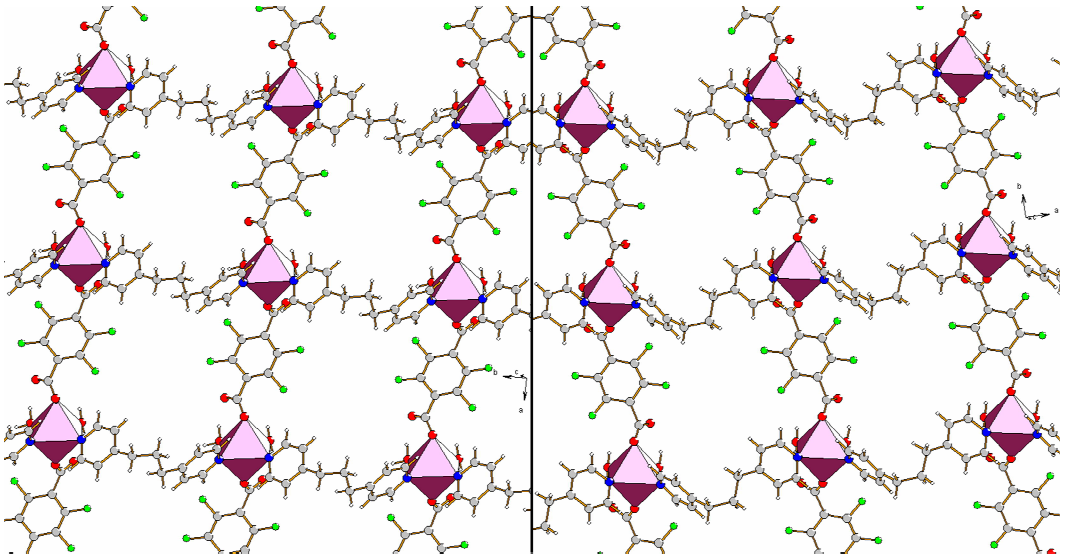


Figure S25. View of the two sheets of **11**; Co(1) sheet on left, Co(2) sheet on right.

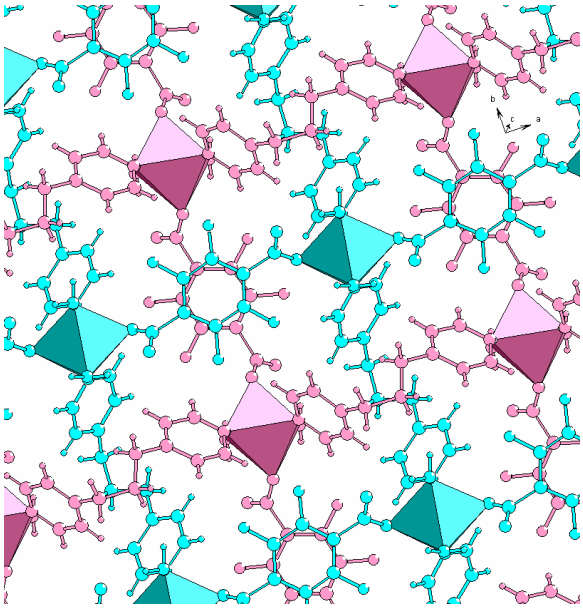


Figure S26. Structure of **11** with the two interpenetrated sheets shaded in pink and blue.

Structure of $Cu_2(bpe)(tfipa)_2(H_2O)_2$, 12. Compound **12** is a two-dimensional coordination polymer built up from edge-sharing dimers of CuO_4N square pyramids (Cu-Cu distance 3.435(2) Å). These dimers are connected in one direction by tfipa ligands and in another direction by a bridging bpe ligand. There are four tfipa ligands bound to the

dimer, each through one of its carboxylate oxygen atoms. The two of these tfipa ligands on the same side of the dimer bridge to the same next dimer down the *b*-axis (Cu-O distances 1.929(3) Å, 1.978(4) Å, 2.428(4) Å). The bpe ligand connects dimers in a second direction, forming the overall layered structure (Cu-N distance 1.991(4) Å). There is also a water molecule bound to each copper atom of the dimer which prevents connectivity in the third direction (Cu-O_w distance 1.974(4) Å).

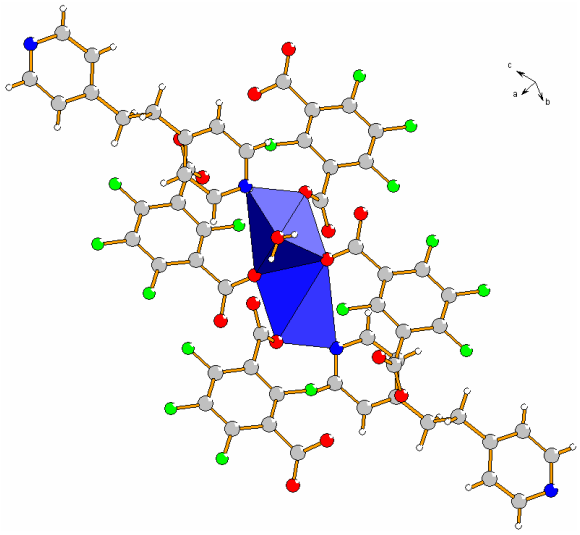


Figure S27. Coordination around dimer in **12**.

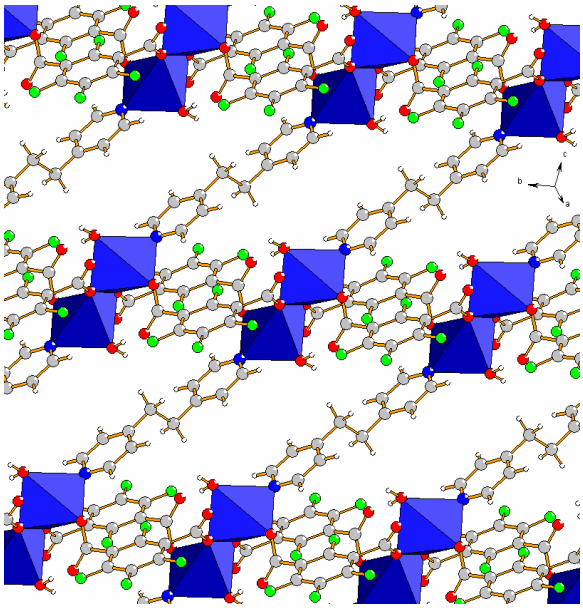


Figure S28. One layer of **12** viewed from above.

Structure of Cu(bpp)(tfipa)(H_2O), 13. The structure of **13** contains isolated CuO_3N_2 square pyramids that bind two bpp ligands (Cu-N distances 1.990(7) Å and 2.003(8) Å), two tfipa ligands (Cu-O distances 1.957(6) Å and 1.982(5) Å), and a water molecule (Cu-O distance 2.266(7) Å). The bpp ligands bridge to other polyhedra along one direction, forming a one-dimensional chain. The tfipa ligands connect to other polyhedra along a zig-zag chain that connects these bpp chains. The resulting structure can be described as a double layer with two layers of bpp chains that are connected by the interweaving tfipa chains.

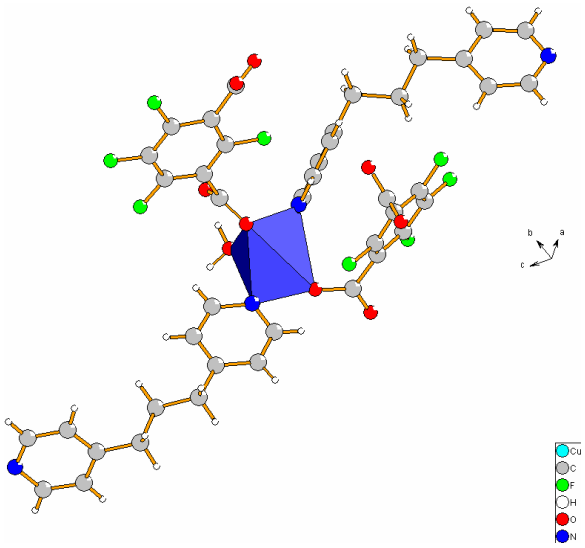


Figure S29. Coordination around CuO_3N_2 square pyramidal polyhedra in **13**.

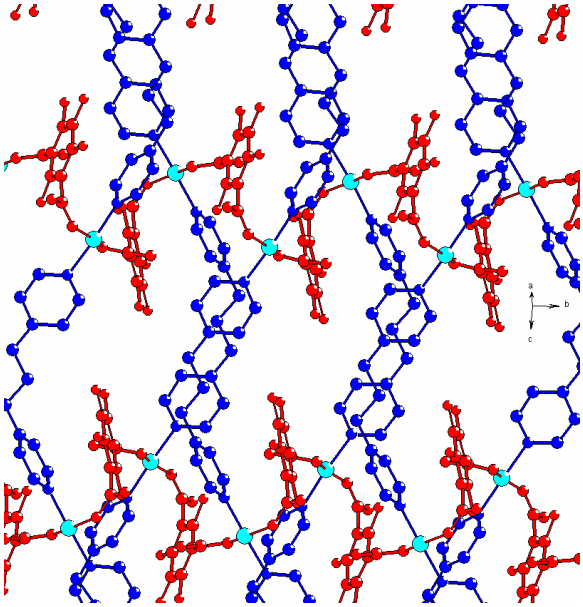


Figure S30. View of single layer of **13** from above. Bpp ligands are shaded in dark blue, and tfipa ligands are shaded in red. The coordinated water molecule on the copper atoms is omitted for clarity.

Structure of Cu(bpp)(tftpa), 14. Compound **14** contains a dimer-like building unit composed of two CuO_3N_2 distorted square pyramids which connect to each other through tftpa ligands to form a two-dimensional coordination polymer. Four tftpa carboxylate groups surround each dimer in a roughly square manner, two of them bridging the two copper atoms (Cu-O distances 1.968(3) Å and 2.348(3) Å), and two of them capping the dimer in the other direction (Cu-O distance 1.985(3) Å). These four tftpa ligands connect the dimer to four others in two directions. Two bpp ligands fold in a U-shaped manner from one of the copper atoms in the dimer to the other, preventing connectivity in a third-dimension (Cu-N distances 2.012(4) Å and 2.017(3) Å). The layers nestle on top of each other such that there is no space in between them.

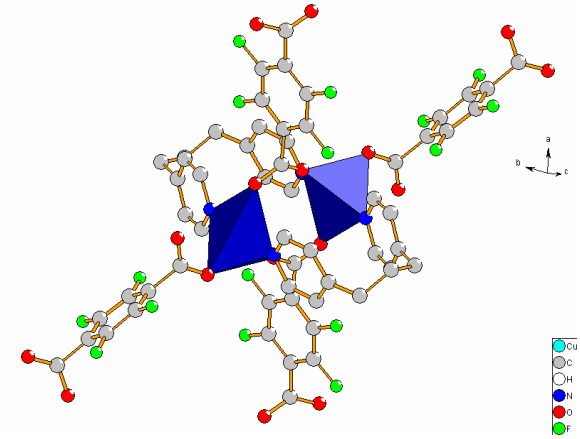


Figure S31. Connectivity around dimer-like unit in **14**.

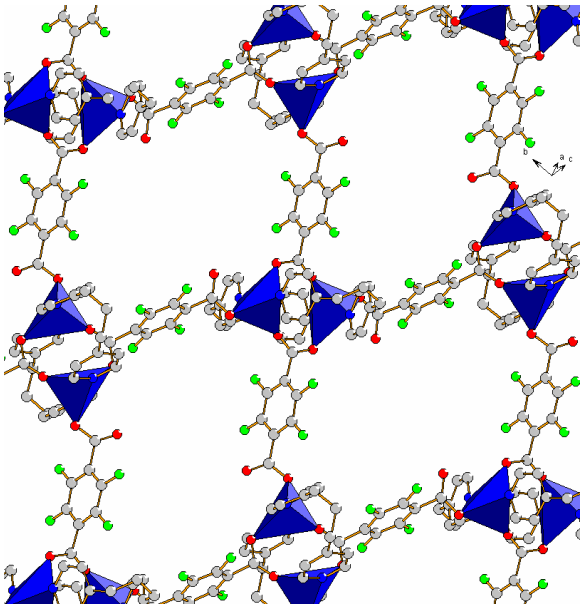


Figure S32. Single layer of **14** viewed from above.

Structure of $Co_2(bpe)_3(tfipa)_2$, 15, and $Zn_2(bpe)_3(tfipa)_2$, 19. Compounds **15** and **19** are roughly isostructural, with only slight differences in metal-ligand bond distances. The metal atoms occupy a MO_2N_3 trigonal bipyramid binding two tfipa ligands and three bpe ligands. There are two unique bpe ligands, one in the *anti* conformation, and the other in the *gauche* conformation. The *anti* bpe ligand occupies the two axial coordination sites on the metal polyhedron (Co-N distances 2.136(3) Å and 2.182(3) Å; Zn-N distances

2.164(3) Å and 2.205(3) Å), and forms an infinite M-*anti*-bpe-M chain. The *gauche* bpe ligand occupies an equatorial position on the metal polyhedron (Co-N distance 2.128(5) Å, Zn-N distance 2.115(4) Å), and forms a bridge between two of these M-*anti*-bpe-M chains. The other two equatorial sites on the metal polyhedron are occupied by the tfipa ligands (Co-O distances 2.009(4) Å and 2.076(4) Å; Zn-O distances 1.985(3) Å and 2.030(3) Å), which form a zig-zag chain linking together the M-*anti*-bpe-M chains completing the three-dimensional connectivity.

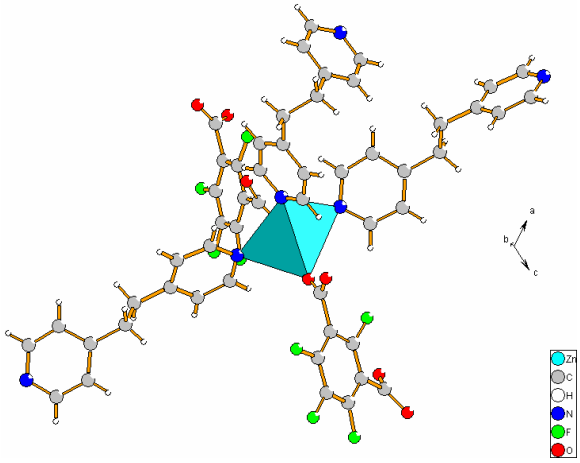


Figure S33. Coordination around metal centers in **15** and **19**.

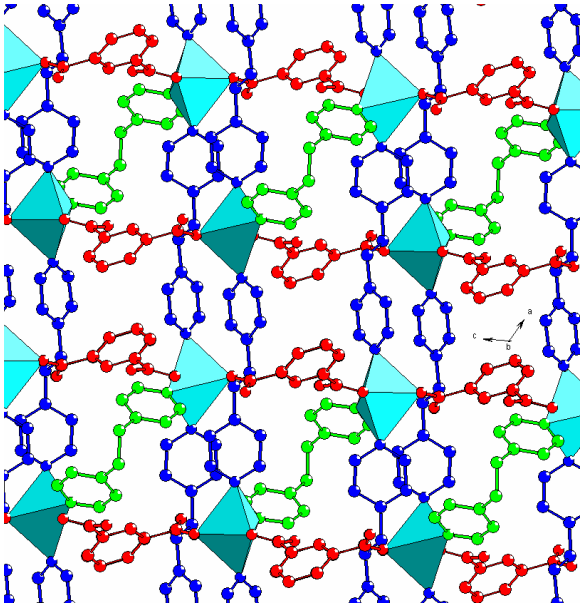


Figure S34. View of connectivity in **15** and **19**. The *anti*-bpe ligands are shown in blue, *gauche*-bpe ligands in green, tfipa ligands in red, and metal polyhedra in turquoise.

Structure of Co(bpe)(tftpa), 16. Compound **16** is a three-dimensional coordination polymer which contains two interpenetrating sublattices. The structure contains a dimer-like building block of two distorted CoO_4N_2 octahedra joined through two bridging carboxylate groups from two tftpa ligands. These two tftpa ligands are bound to both cobalt atoms of the dimer and bridge dimers along the *b*-axis (Co-O distances 2.018(4) Å and 2.042(3) Å). Two other tftpa ligands connect dimers in a nearly perpendicular direction to the other two and bind to one cobalt atom of the dimer through both of its carboxylate oxygen atoms (Co-O distances 2.178(3) Å and 2.219(4) Å), causing the severe distortion of the octahedra. The dimers are connected in the third dimension by a double chain of bpe ligands, bound at the axial positions of each octahedron of the dimer (Co-N distances 2.132(3) Å and 2.154(4) Å). While this sublattice itself contains a large pore, that space is filled with an identical second sublattice such that no porosity exists .

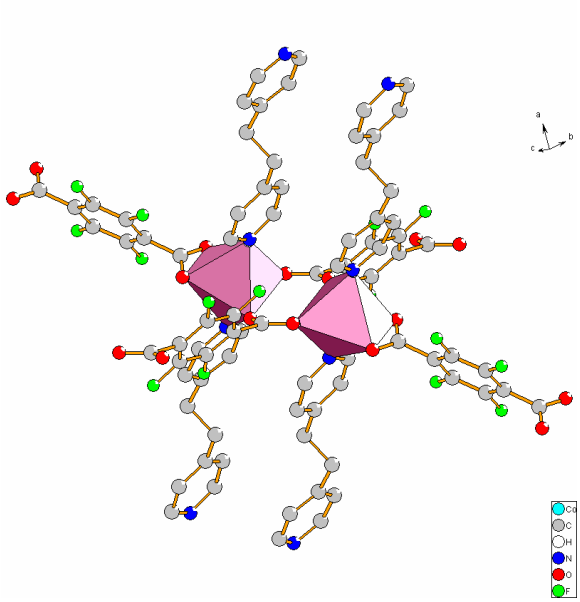


Figure S35. View of dimer-like unit in **16**.

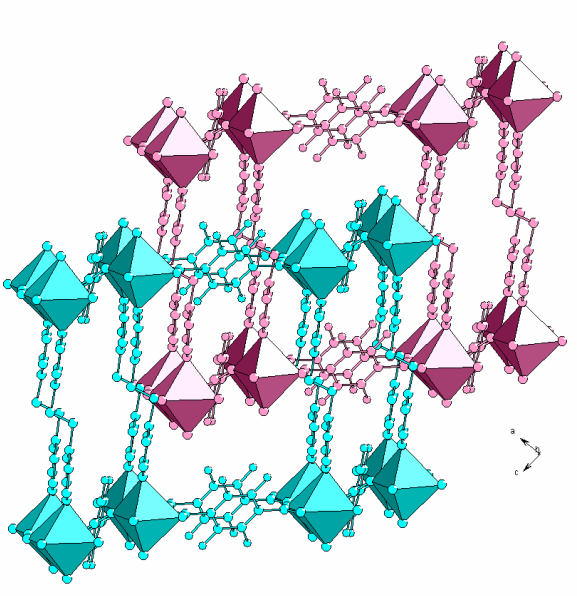


Figure S36. Two-fold interpenetrated structure of **16** viewed roughly down the *b*-axis, with the two sublattices shaded in pink and blue.

Structure of $Cu_2(bpp)(tftpa)_2(H_2O)$, 17. The structure of **17** contains corner-sharing dimers of square pyramidal CuO_4N polyhedra (Cu-Cu distance 3.322(2) Å). Each copper

atom in the dimer is coordinated to one bpp ligand (Cu-N distances 1.980(6) Å and 1.998(7) Å). There are five tftpa ligands surrounding the dimer; one of them bridges both copper atoms through both its carboxylate oxygen atoms (Cu-O distances 1.942(4) Å and 2.021(5) Å), one of them accounts for the shared corner and is bound to both copper atoms through only one of its carboxylate oxygen atoms (Cu-O distances 1.965(5) Å and 2.226(5) Å), and the other three are bound to one copper atom through one of its carboxylate oxygen atoms (Cu-O distances 1.963(5) Å, 1.994(5) Å, and 2.010(5) Å). There is also a water molecule bound to one of the copper atoms on the dimer (Cu-O distance 2.291(7) Å. The dimers are then bound to another dimer through two carboxylate bridges to form a tetramer-like building unit. The Cu-Cu distance (3.041(1) Å) between the two dimers is actually shorter than the intra-dimer Cu-Cu distance. Each tetramer is connected to eight other tetramers in a roughly square-antiprismatic arrangement that results in the three-dimensional structure of **17**. One tetramer connects to six other tetramers through tftpa ligands and two others through bpp ligands.

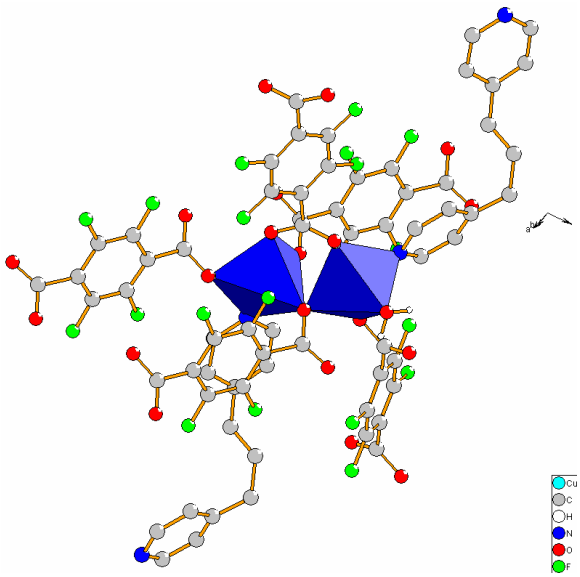


Figure S37. Connectivity around single dimer in **17**.

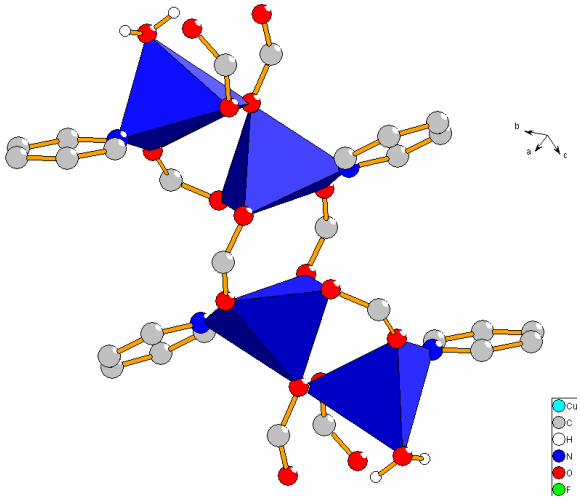


Figure S38. View of carboxylate linkage between two dimers in **17**. Only the coordinating carboxylate group of the tftpa ligands and one pyridine ring of the bpp ligands are shown for clarity.

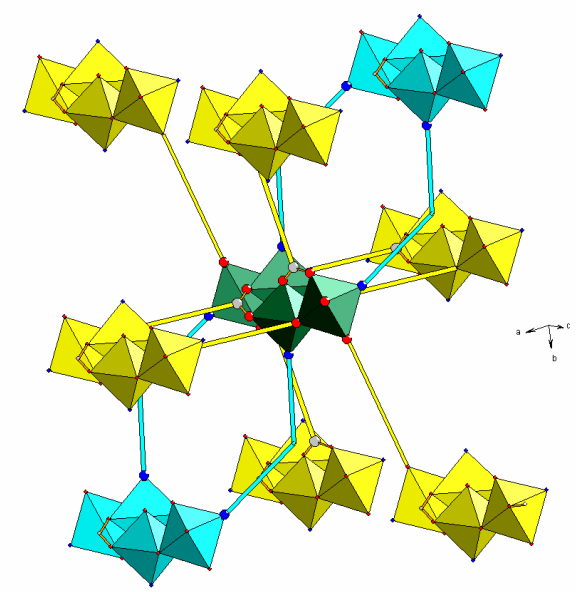


Figure S39. Simplified view of tetramer linkages in **17**. Central tetramer (green) is connected to six other tetramers through tftpa linkages (yellow bonds and polyhedra) and two additional tetramers through bpp linkages (aqua bonds and polyhedra).

Structure of $Ni_2(bpe)_3(tfipa)_2$, 18. Structure **18** has the same formula as **15** and **19** and has many similar structure characteristics. The metal polyhedron, in this case a NiO_3N_3 octahedron, is surrounded by two tfipa ligands and three bpe ligands. In **18**, the three oxygen atoms bound to the metal belong to two tfipa ligands (Ni-O distances 2.025(4) Å, 2.122(4) Å, and 2.201(4) Å). In contrast to **15** and **19**, both bpe ligands display the *anti* conformation. The ligands bridge to the next polyhedron in all three directions to form a 3-D lattice with large open space which allows for three-fold interpenetration of identical sublattices. One of the sublattices is rotated at approximately 90° to the other two.

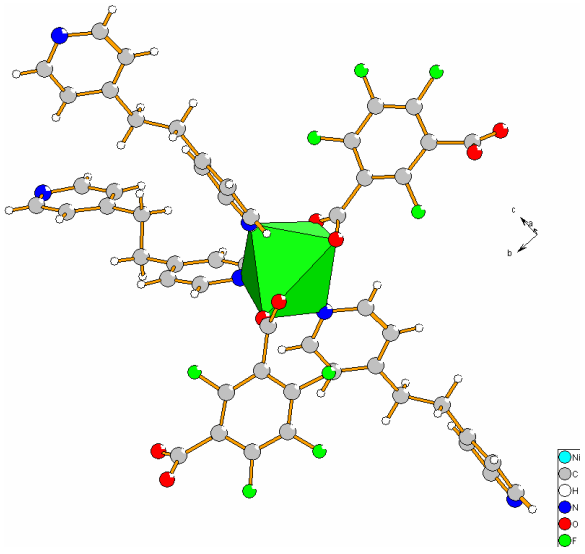


Figure S40. Coordination around metal center in **18**.

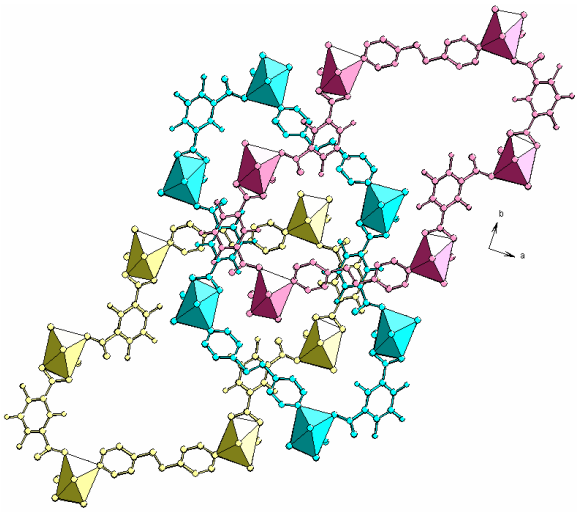


Figure S41. Structure of **18** viewed down the *c*-axis with the three sublattices shaded in pink, blue, and yellow.

Structure of Zn(bpe)(tftpa), 20. Compound **20**, like **16**, is a three-dimensional coordination polymer with two interpenetrating sublattices, however in **20** the polyhedral building block is composed of three metal centers instead of two. This trimer-like unit contains one ZnO_4N_2 octahedron and two identical ZnO_3N_2 trigonal bipyramids which are connected through four bridging carboxylate groups from tftpa ligands. The octahedron lies on the inversion center at the center of the trimer-like unit and is bound to four tftpa ligands around its equatorial positions (Zn-O distances 2.099(6) Å and 2.129(6) Å) and two bpe ligands at its axial positions (Zn-N distance 2.106(4) Å). The two trigonal bipyramids on either side of the octahedron are related through the inversion center; this zinc cation is bound to three tftpa ligands around its equatorial positions (Zn-O distances 2.006(6) Å, 2.043(5) Å and 2.048(6) Å) and two bpe ligands at its axial positions (Zn-N distances 2.142(4) Å and 2.168(4) Å). The connectivity between the trimer-like building blocks is also similar to that seen in **16**, in one direction through the bpe ligands and in

the other two directions through the tftpa ligands. Also as in **16**, the sublattice contains enough empty space to accommodate a second sublattice, which effectively blocks any porosity.

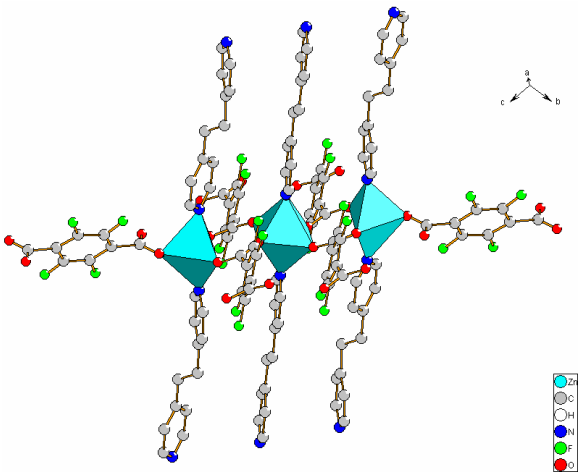


Figure S42. View of trimer-like unit in **20**.

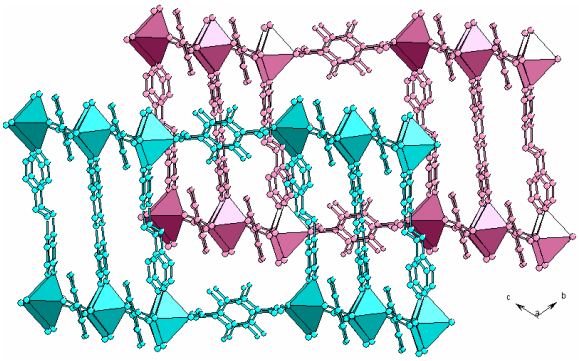
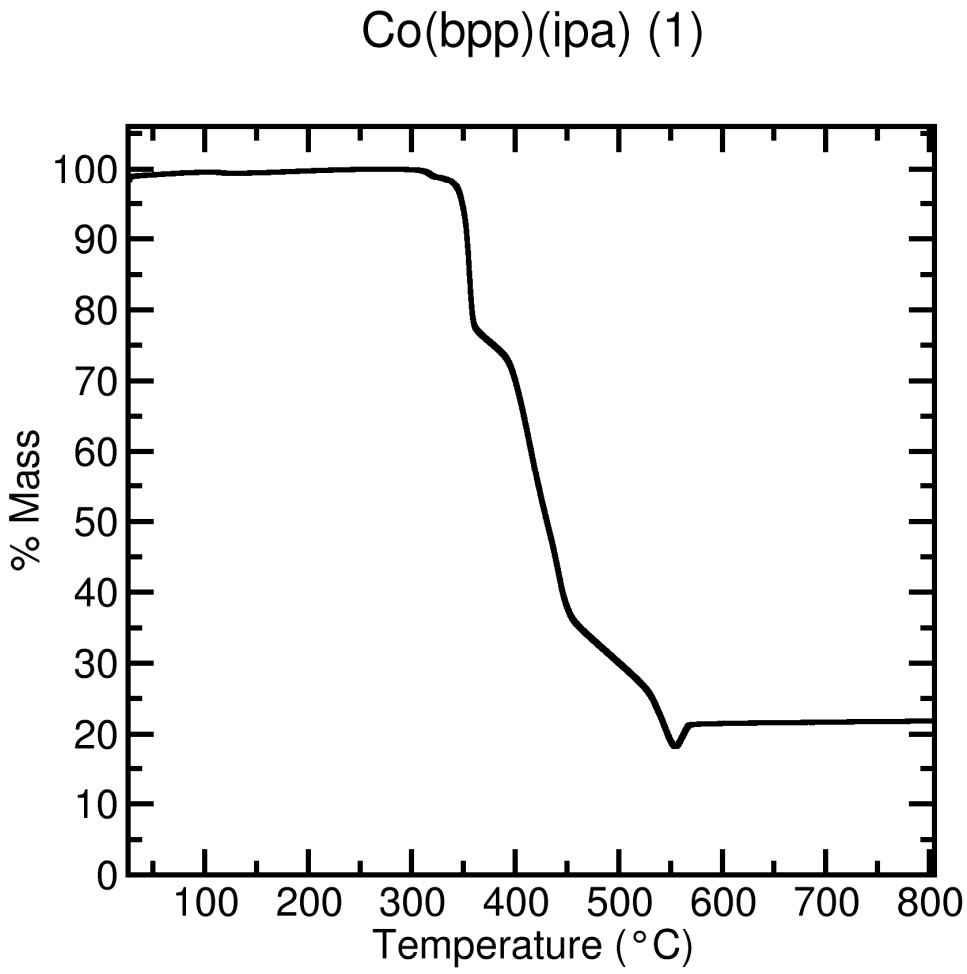
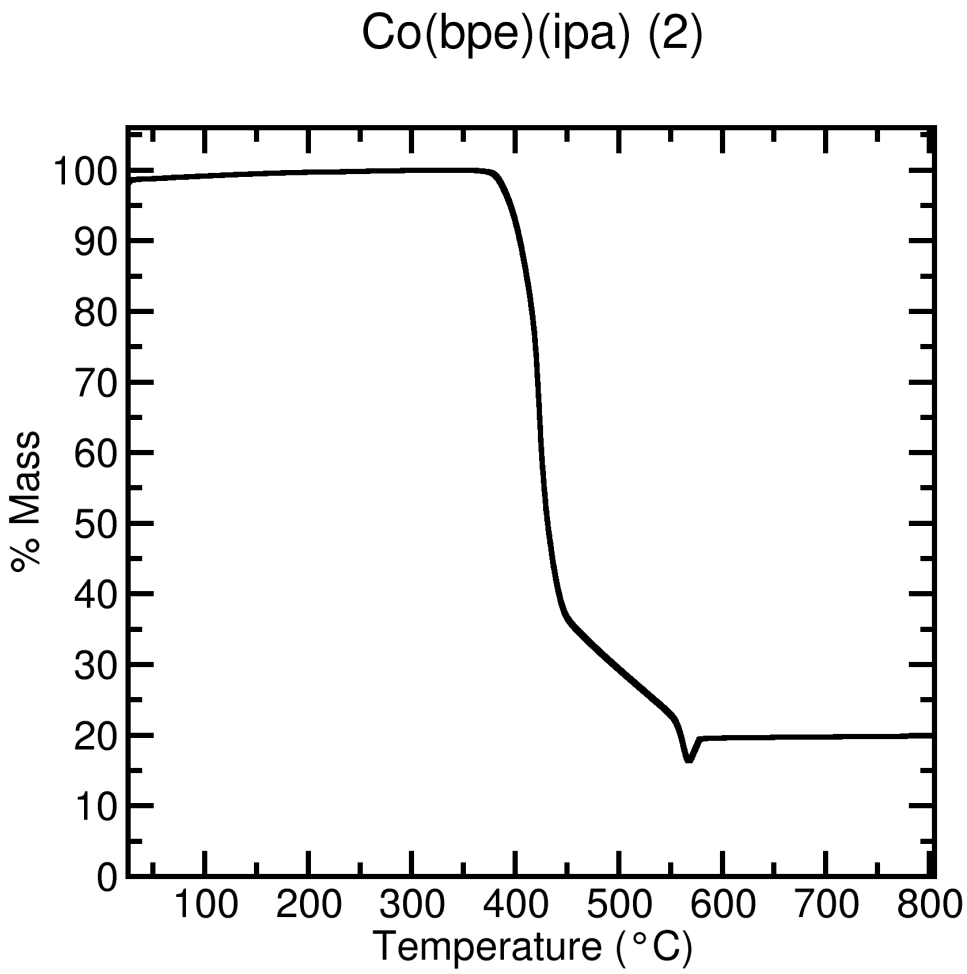


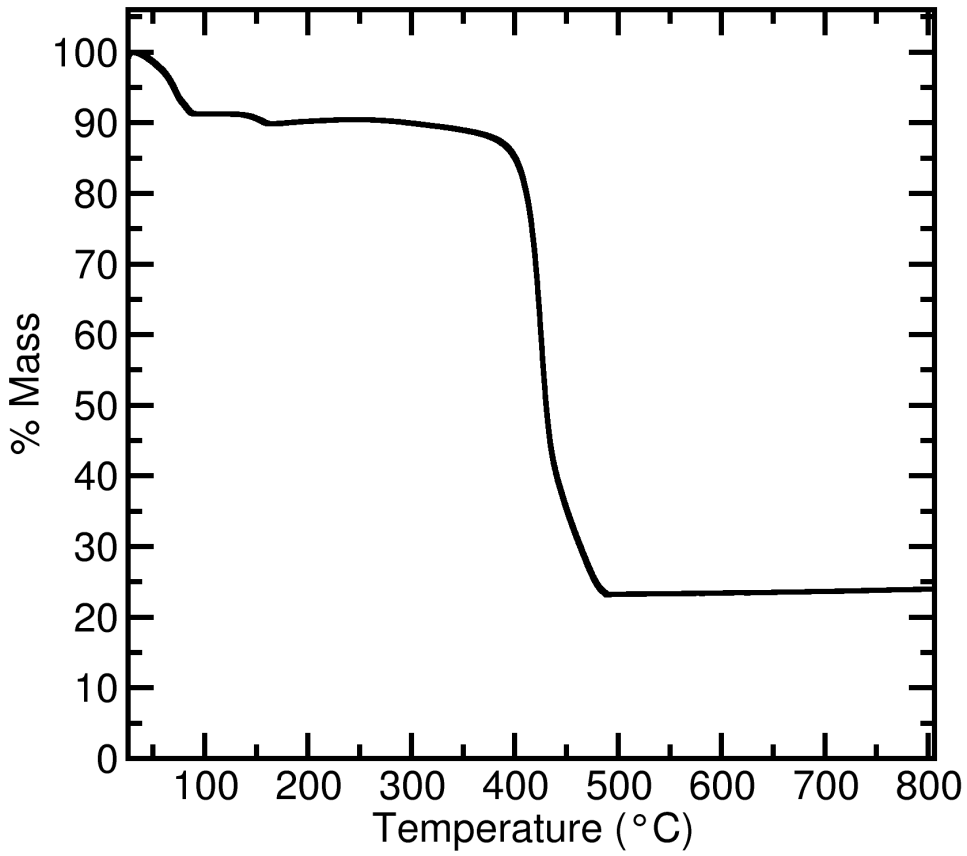
Figure S43. Two-fold interpenetrated structure of **20** viewed roughly down the *a*-axis, with the two sublattices shaded in pink and blue.

Thermogravimetric analysis data for selected compounds

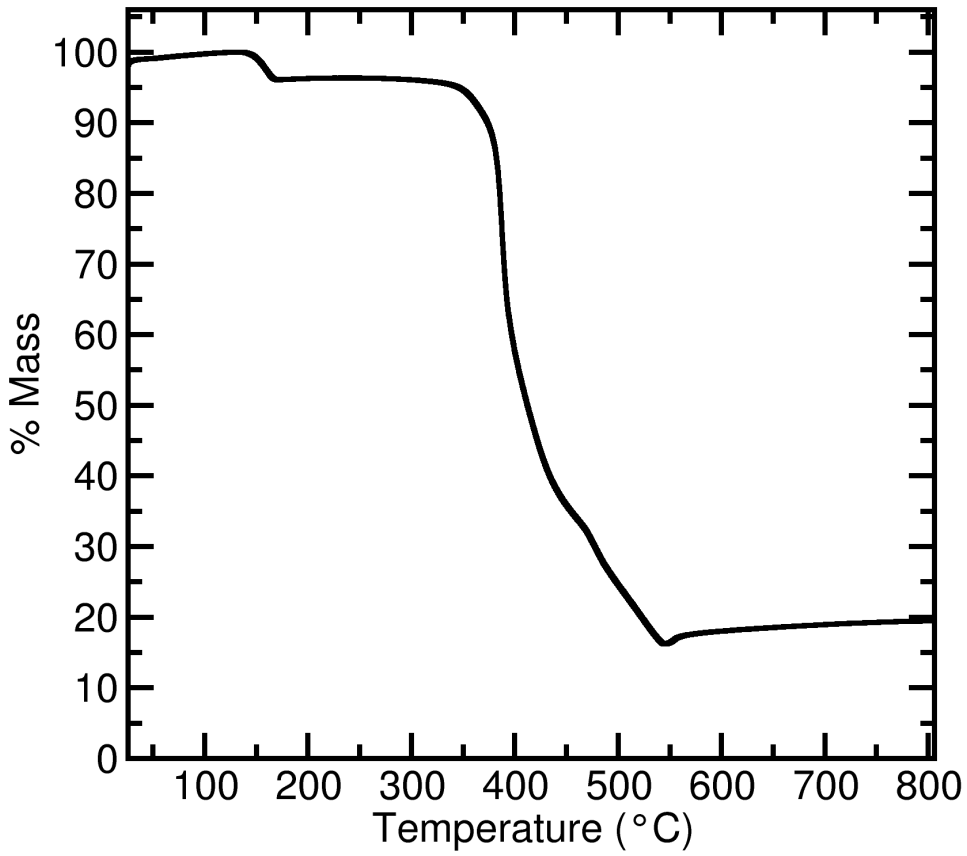



Co(bpe)(ipa) (2)
% Mass
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
500
600
700
800
Temperature (°C)

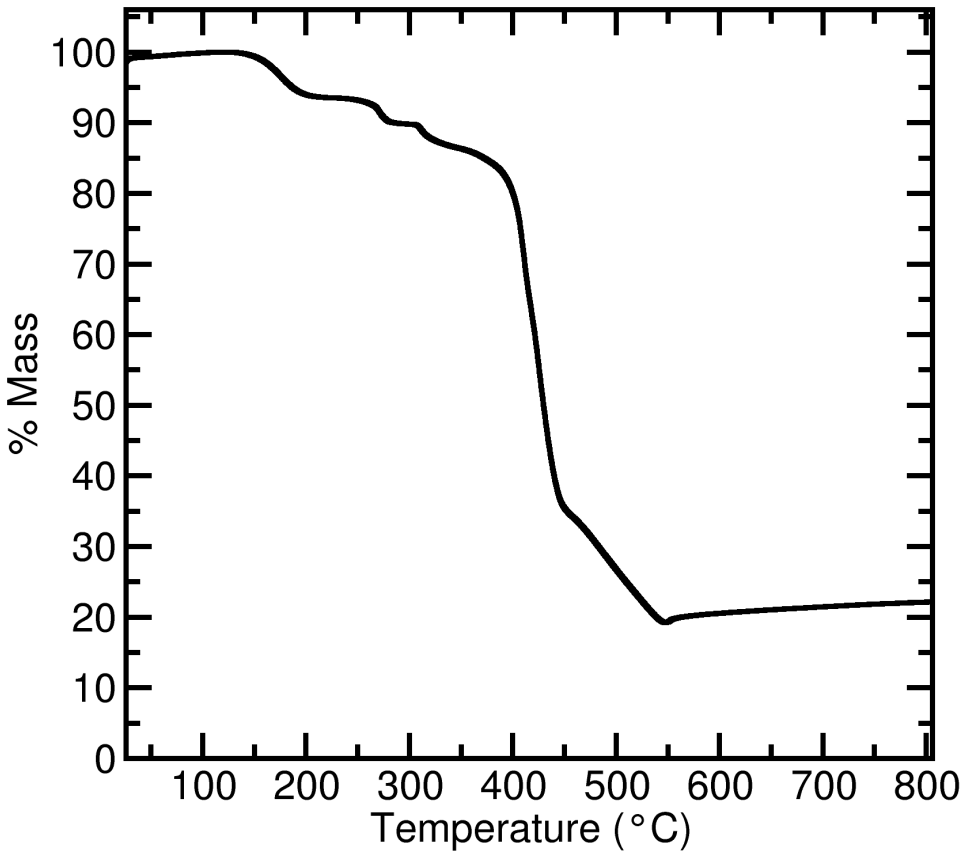
Ni(bpe)(ipa)(H_2O)-1.67H_2O (4)



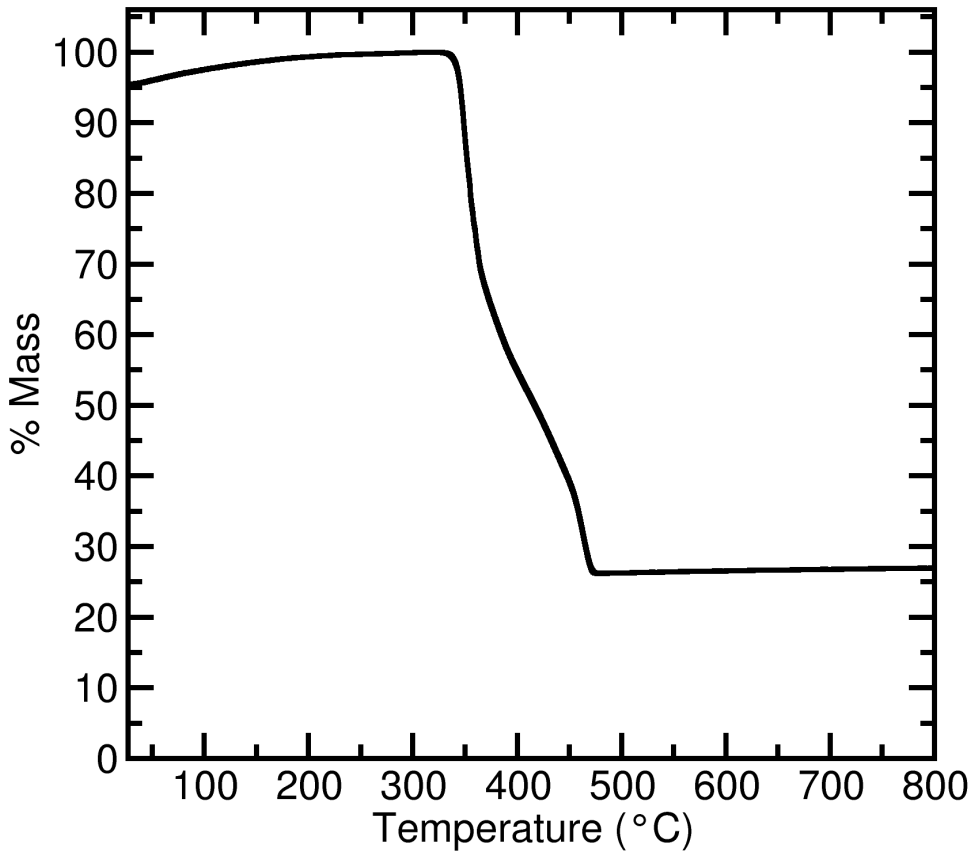
Ni(bpp)(ipa)(H_2O) (5)



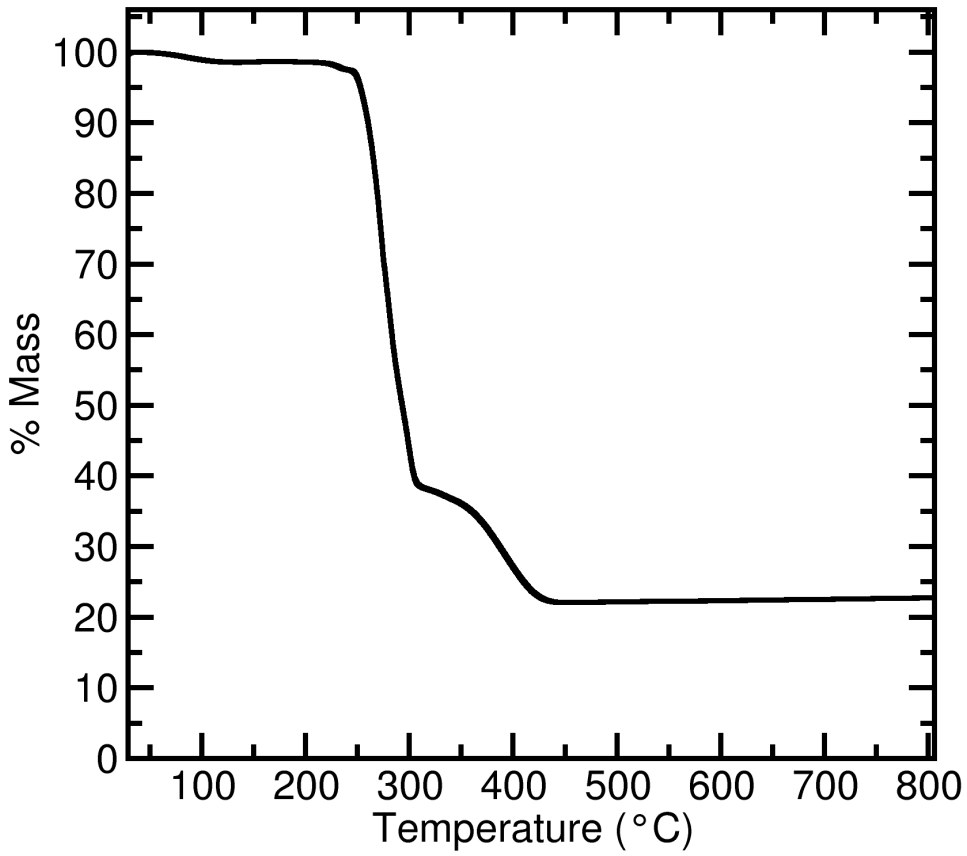
Ni(bpp)(tpa)(H_2O)$_2$ (6)



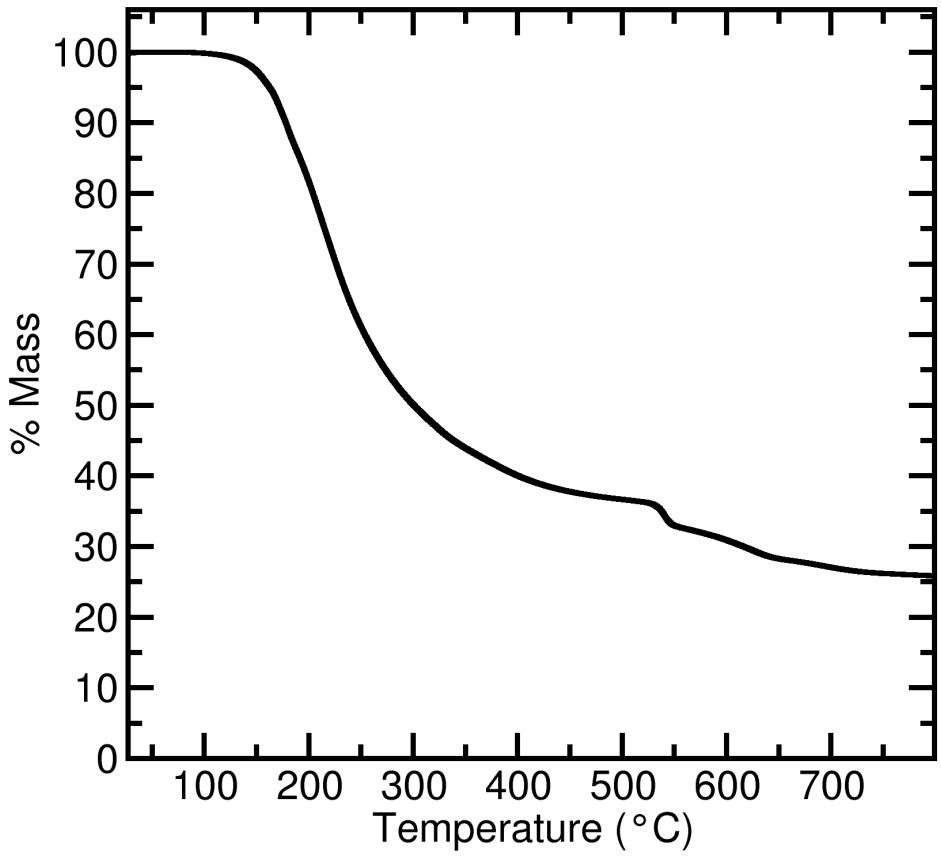
Zn(bpe)(ipa) (8)


% Mass
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
500
600
700
800
Temperature (°C)

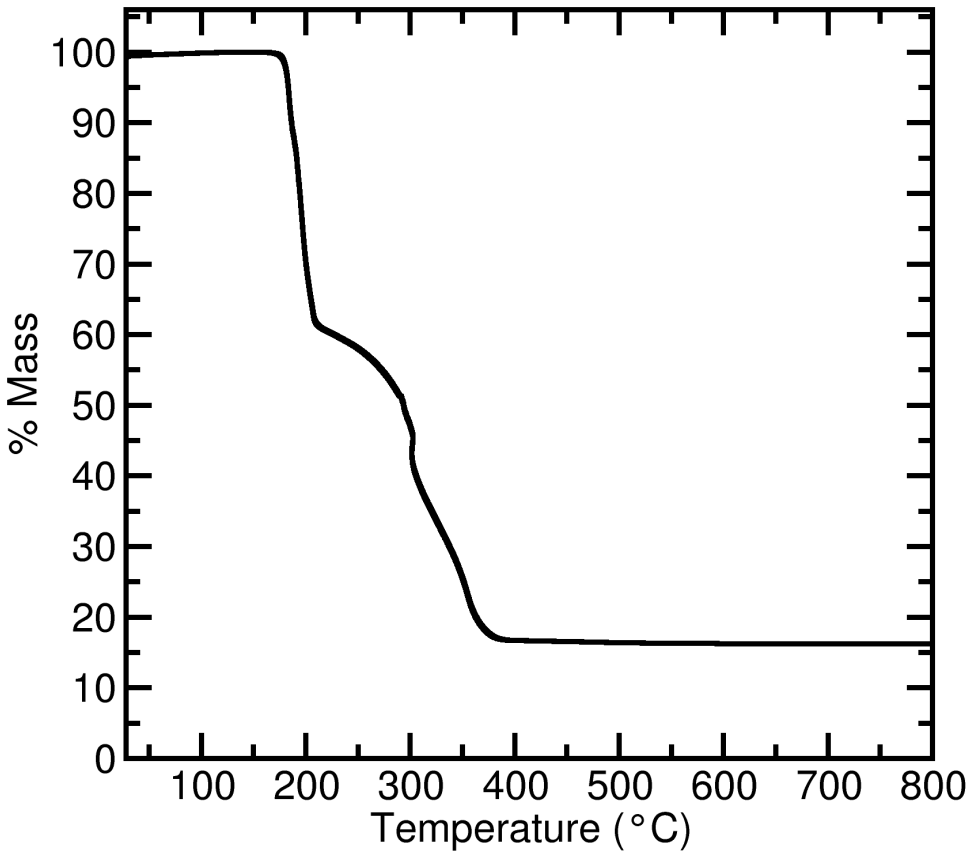
$Cu_4(bpe)_3(ipa)_4(H_2O)_2$ (9)



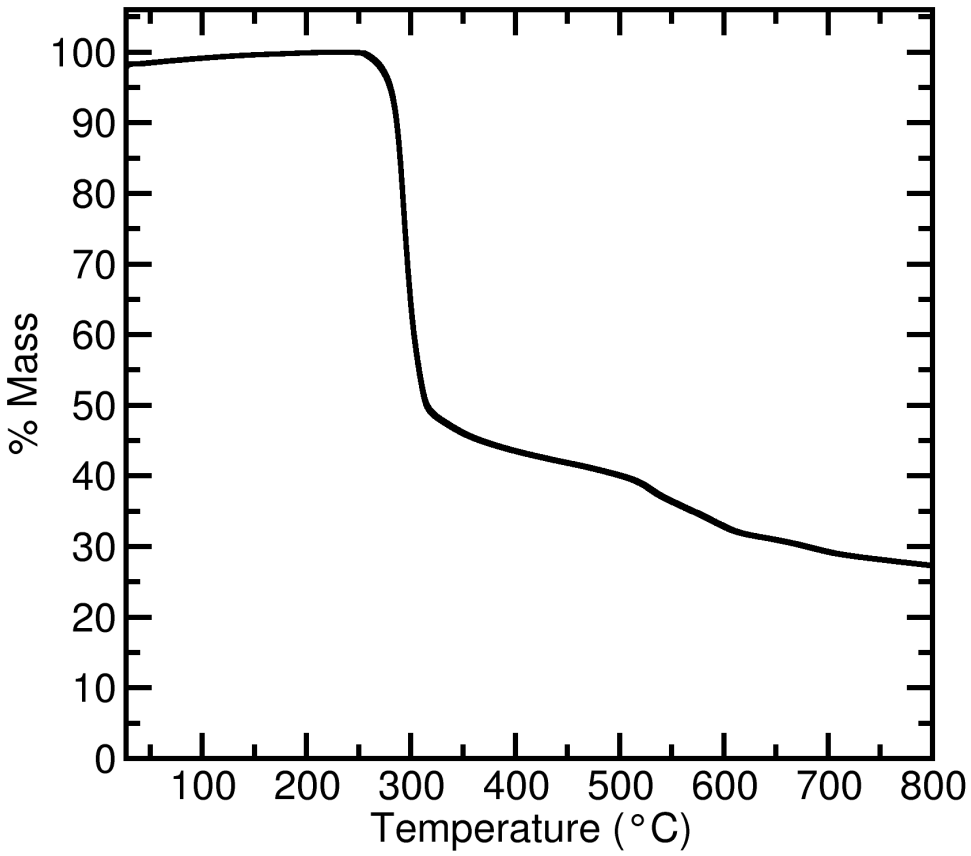
Co(bpp)(tftpa)(H_2O)$_2$ (11)

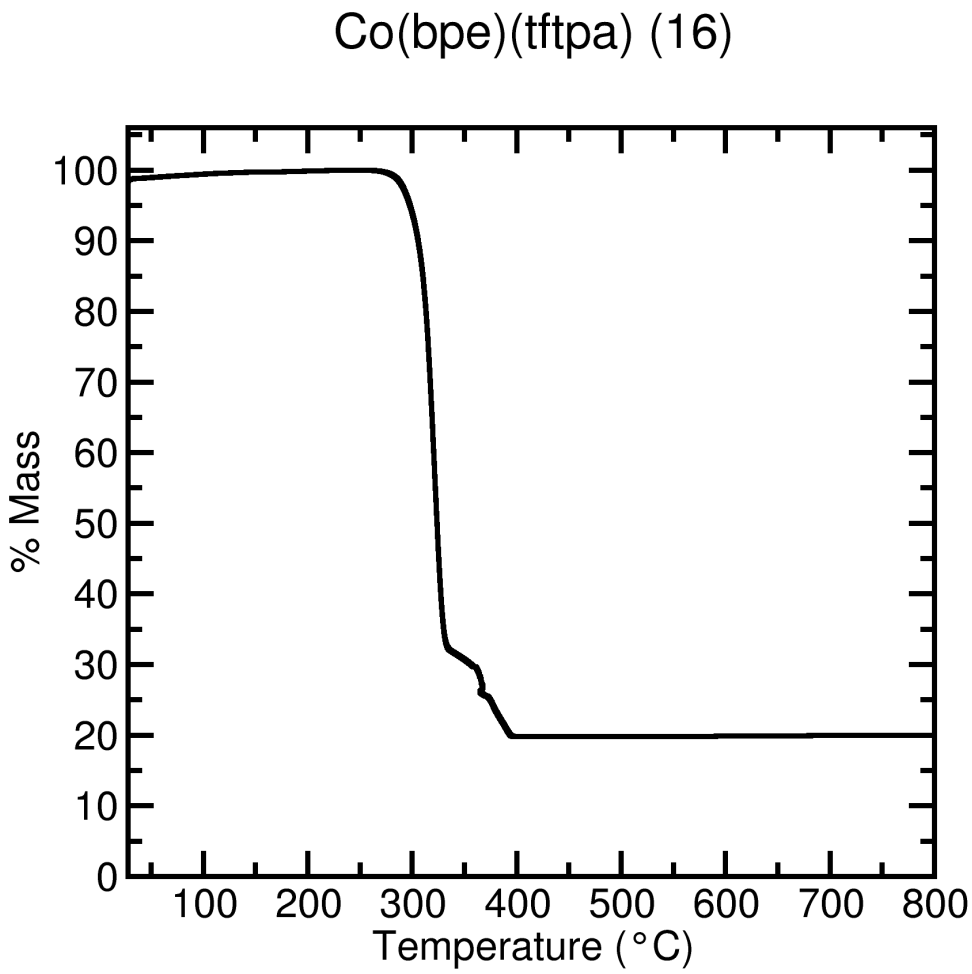


Cu(bpp)(tftpa) (14)

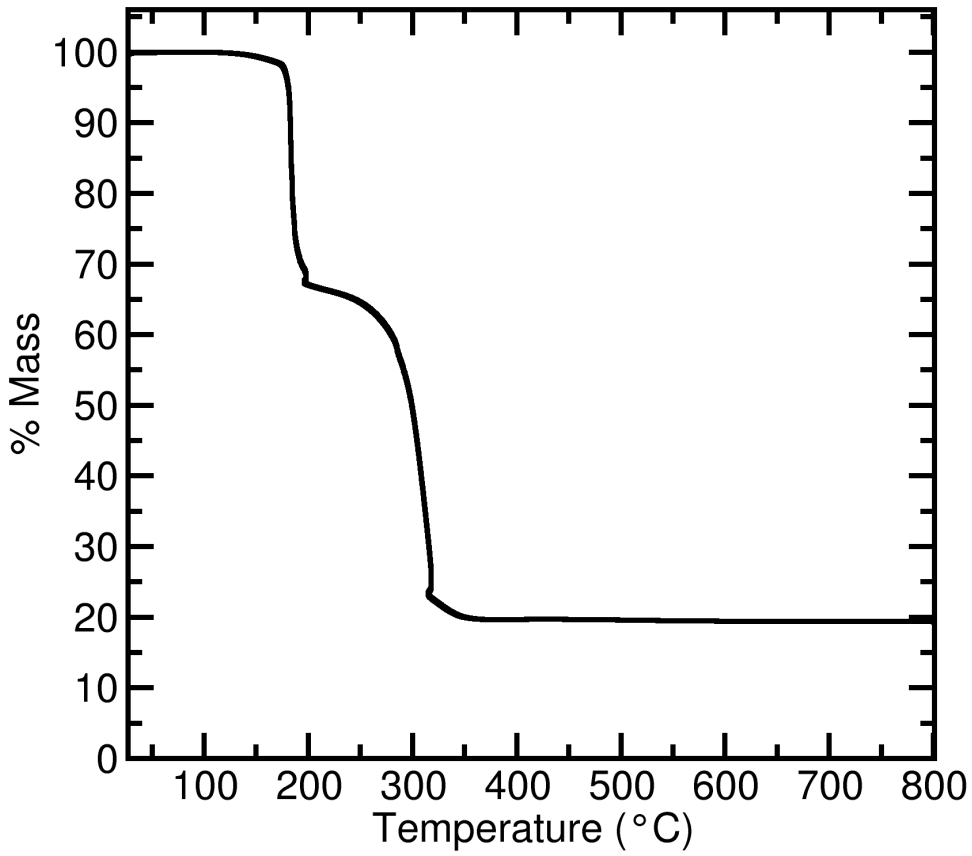


$Co_2(bpe)_3(tfipa)_2$ (15)

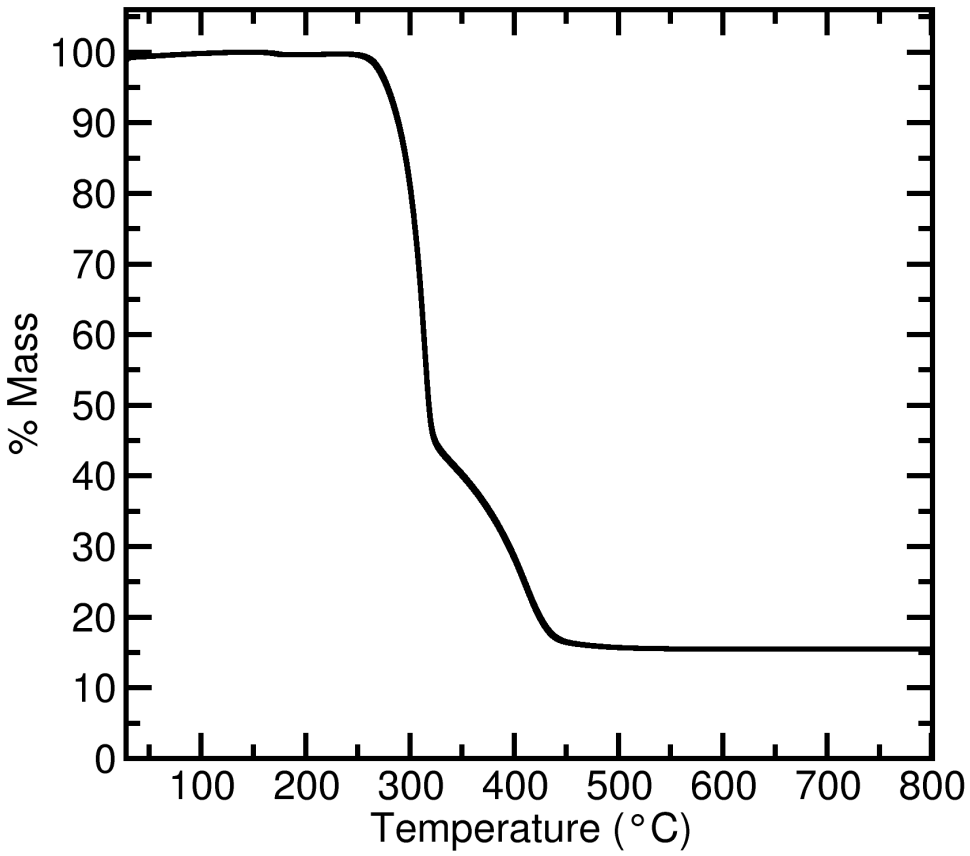


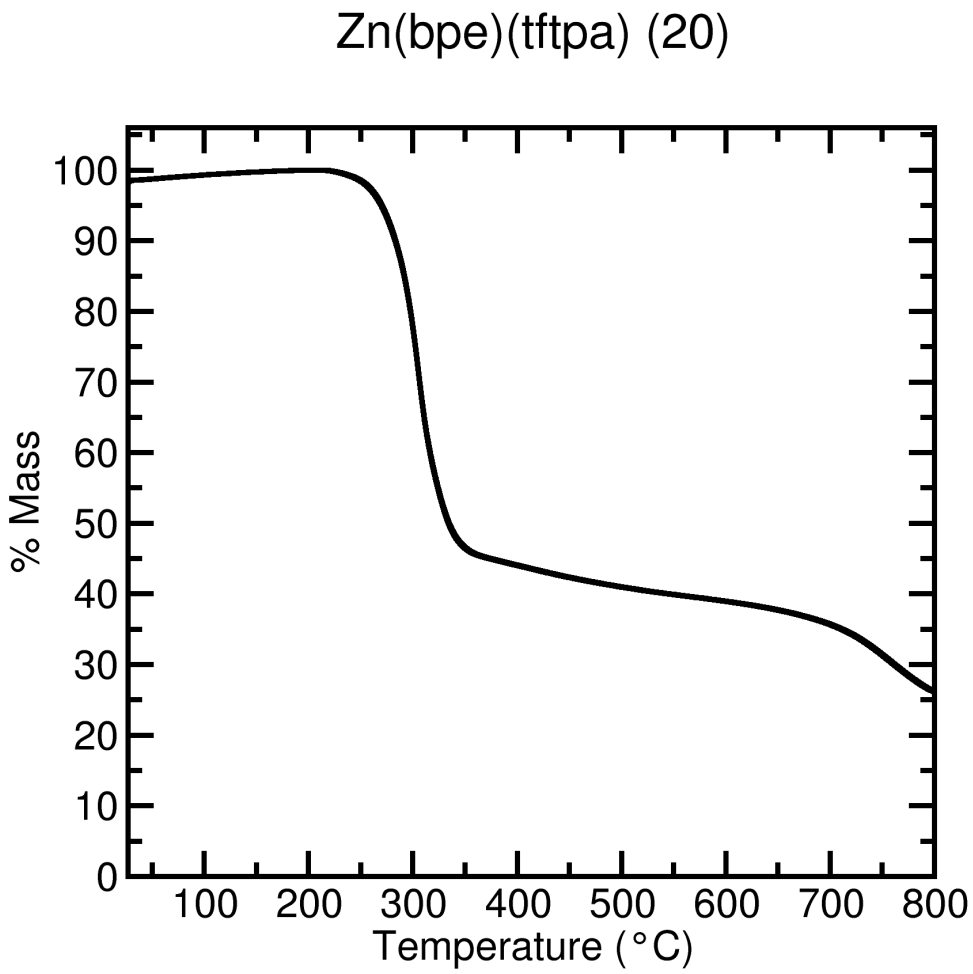

Co(bpe)(tftpa) (16)
% Mass
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
500
600
700
800
Temperature (°C)

$Cu_2(bpp)(tftpa)_2(H_2O)$ (17)



$Ni_2(bpe)_3(tfipa)_2$ (18)




Zn(bpe)(tftpa) (20)
% Mass
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
500
600
700
800
Temperature (°C)