Electronic supplementary information (ESI)

Unique (3,9)-connected porous coordination polymers constructed by tripodal ligands with bent arms†

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Table S1. Crystallographic Data and Structural Refinements.

Complex	**1**	**2**	**3**
Formula	$C_{72}H_{43}Co_3N_6O_{13}$	$C_{72}H_{43}Co_3N_6O_{13}$	$C_{72}H_{43}Co_3N_{30}O$
Formula weight	1376.91	1376.91	1521.15
Temperature (K)	150(2)	150(2)	150(2)
Crystal system	Trigonal	Trigonal	Trigonal
Space group	*R*32	*R*3	*R*-3*c*
a/Å	24.811(1)	20.186(1)	27.3444(8)
c/Å	21.455(2)	20.2891(8)	71.115(2)
V/Å^3	11438(1)	7159.7(8)	46050(3)
Z	6	3	12
D_c/g cm^{-3}	1.199	0.958	0.658
reflns coll.	22971	16498	59766
unique reflns	5787	6431	6840
R_{int}	0.0761	0.0667	0.0926
R_1 [$I > 2\sigma(I)$][a]	0.0380	0.0502	0.0727
wR_2 [$I > 2\sigma(I)$][b]	0.0826	0.1258	0.2478
R_1 (all data)	0.0571	0.0535	0.1062
wR_2 (all data)	0.0914	0.1282	0.2902
GOF	1.052	1.059	1.031
Flack	0.018(9)	0.037(12)	/

[a] $R_1=\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 =[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Analysis of the topological features of the three related (3,9)-connected nets.[a]

Topo.	vertex	cs_1	cs_2	cs_3	cs_4	cs_5	cs_6	cs_7	cs_8	cs_9	cs_{10}	cum_{10}	td10
wys (new)	ligand	3	22	23	116	65	272	129	494	215	782	2122	2068
	cluster	9	12	69	44	195	98	387	174	645	272	1906	
eee	ligand	3	22	23	113	65	271	129	491	215	781	2114	2062
	cluster	9	12	69	44	195	98	387	174	645	272	1906	
xmz	ligand	3	22	23	114	65	270	129	492	215	780	2114	2062
	cluster	9	12	69	44	195	98	387	174	645	272	1906	
nia-d	ligand	3	18	53	110	179	272	377	506	647	812	2978	3152
	cluster	9	32	75	134	213	308	423	554	705	872	3326	

[a] Calculated by the TOPOS package [(a) Blatov, V. A. TOPOS, A Multipurpose Crystallochemical Analysis with the Program Package; Samara State University, Russia, 2004. (b) Blatov, V. A. IUCr Comp. Comm. Newsletter 2006, 7, 4 (freely available at http://iucrcomputing.ccp14.ac.uk/iucrtop/comm/ccom/newsletters/2006nov].

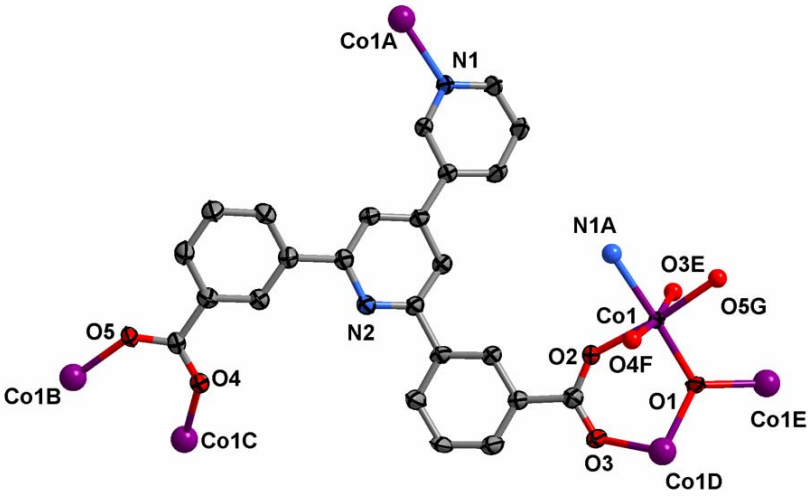

Figure S1. Perspective view of the coordination environment in **1** (at 50% probability; hydrogen atoms are omitted for clarity.). Symmetry codes: A = *y, x*, 1-*z*; B = -2/3+*x*, -1/3+*y*, -1/3+*z*; C = 1/3-*x*+*y*, 2/3-*x*, -1/3+*z*; D = 1-*y*, *x*-*y*, *z*; E =1-*x*+*y*, 1-*x*, *z*; F = 2/3-*y*, 1/3+*x*-*y*, 1/3+*z*; G = 2/3+*x*, 1/3+*y*, 1/3+*z*.

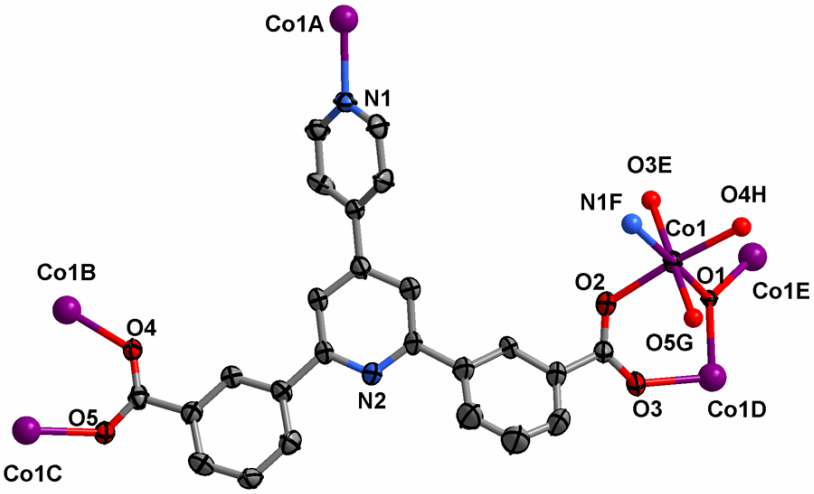

Figure S2. Perspective view of the coordination environment in **2** (at 50% probability; hydrogen atoms are omitted for clarity.). Symmetry codes: A = 2/3-*x*+*y*, 4/3-*x*, 1/3+*z*; B = 4/3-*y*, 2/3+*x*-*y*, 2/3+*z*; C = 1/3-*x*+*y*, 2/3-*x*, 2/3+*z*; D = -*x*+*y*, 1-*x*, *z*; E = 1-*y*, 1+*x*-*y*, z; F = 4/3-*y*, 2/3+*x*-*y*, -1/3+*z*; G = 2/3-*y*, 1/3+*x*-*y*, -2/3+*z*; H = 2/3-*x*+*y*, 4/3-*x*, -2/3+*z*.

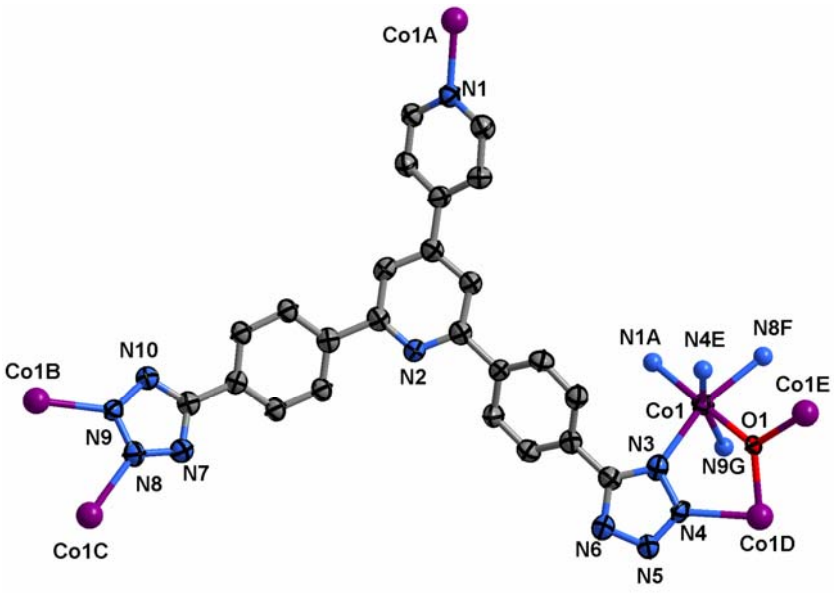

Figure S3. Perspective view of the coordination environment in **3** (at 50% probability; hydrogen atoms are omitted for clarity.). Symmetry codes: A = 1/3+*x*-*y*, 2/3-*y*, 7/6-*z*; B = 1/3-*x*+*y*, -1/3+*y*, 1/6+*z*; C = 1/3+*x*, 2/3+*x*-*y*, 1/6+*z*; 1/3+*x*, 2/3+*x*-*y*, 1/6+*z*; D = 1-*y*, 1+*x*-*y*, z; E = -*x*+*y*, 1-*x*, *z*; F = -1/3+*x*, 1/3+*x*-*y*, -1/6+*z*; G = 2/3-*x*+*y*, 1/3+*y*, -1/6+*z*.

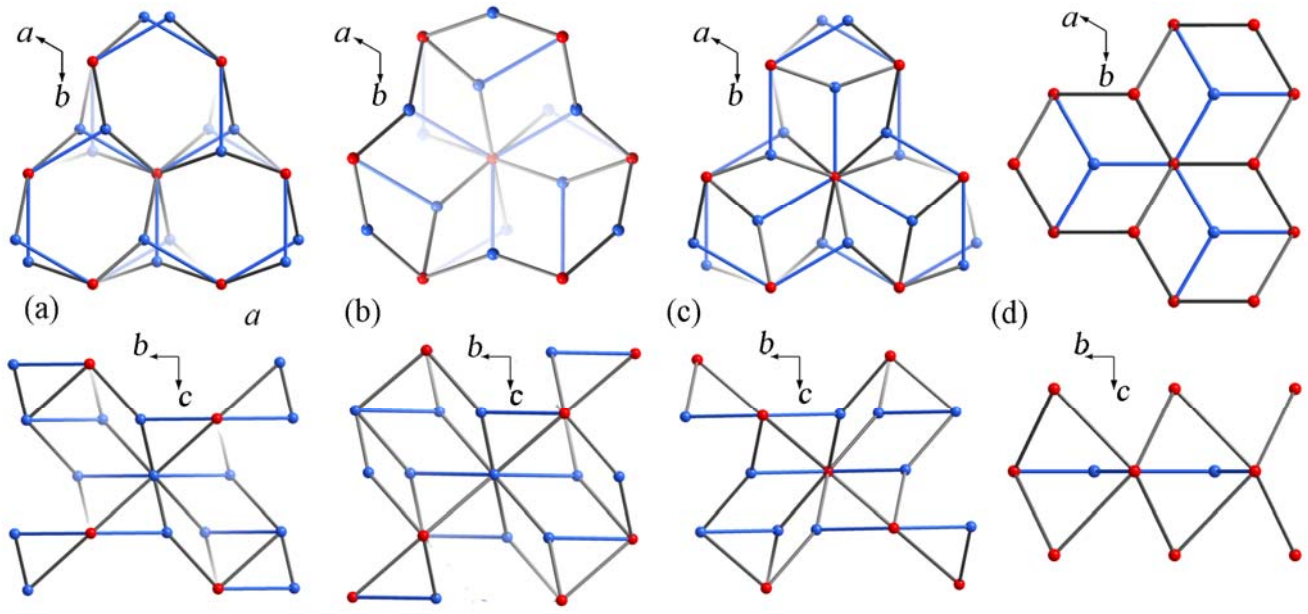

Fig. S4 Parallel projections of the regular (a) **wys**, (b) **eee**, (c) **xmz** and (d) **nia-d** topologies (in their maximum symmetries) along their *c*-axes (top) and *a*-axes (bottom). Blue and red spheres represent the cores of tripodal ligands and center of trinuclear clusters, respectively.

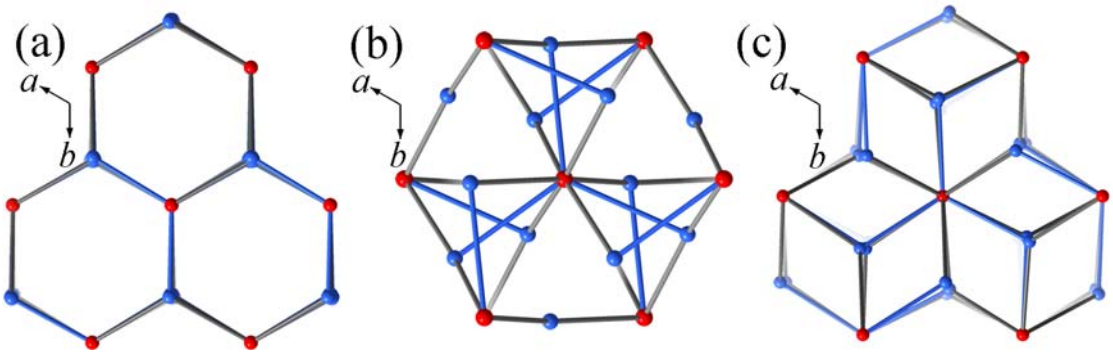

Fig. S5 Parallel projections of the simplified coordination networks of (a) **1** (**wys**), (b) **2** (**wys**), and (c) **3** (**eee**) along their *c*-axes. Blue and red spheres represent the cores of tripodal ligands and center of trinuclear clusters, respectively.

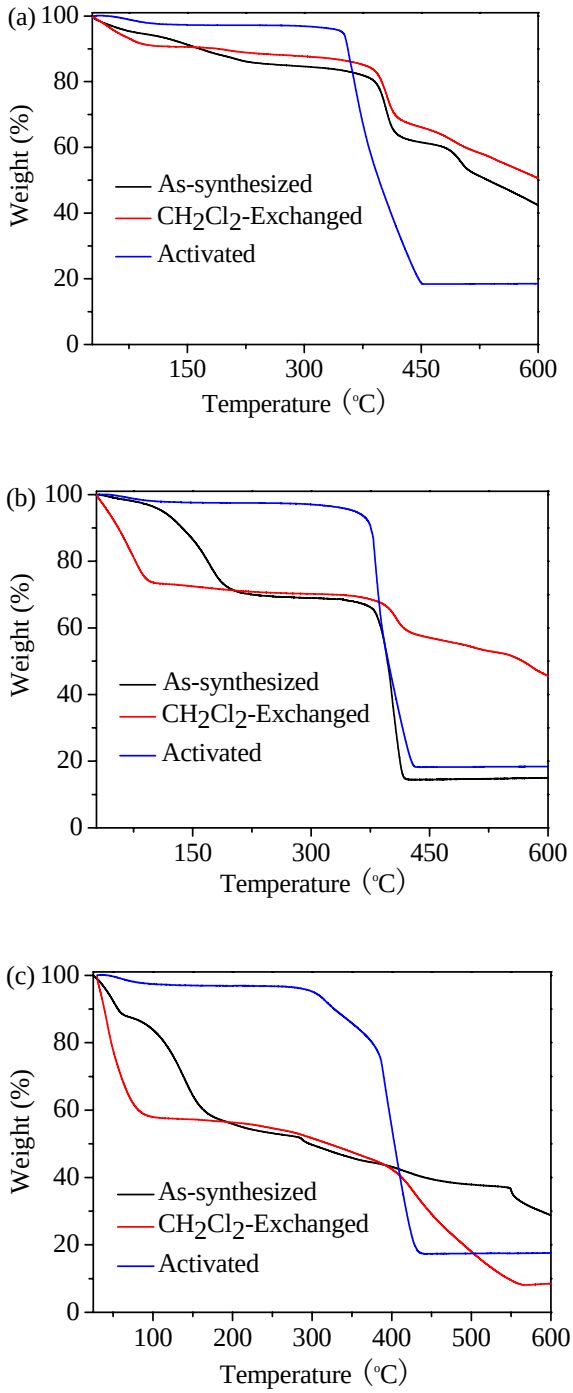

Fig. S6. TG curves of (a) **1**, (b) **2** and (c) **3**. The small weight losses below 100 ^{o}C of the activated samples can be attributed to the adsorbed moisture.

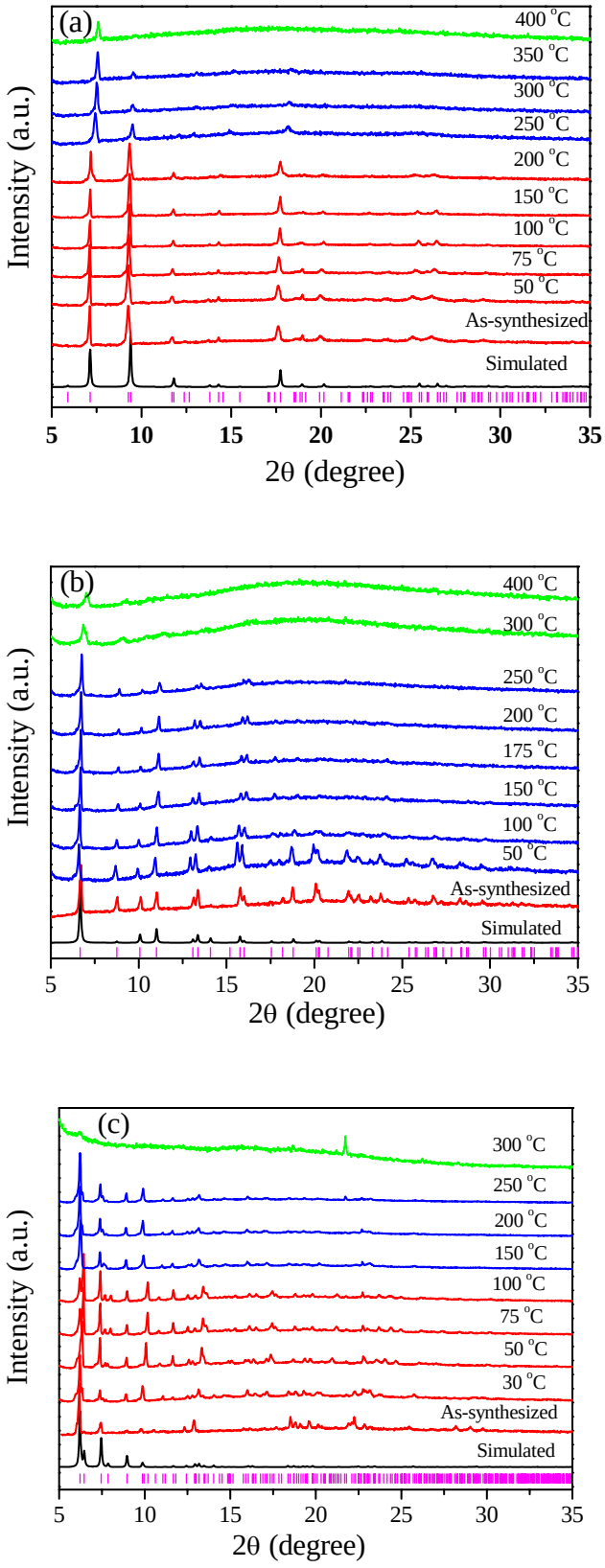

Fig. S7. PXRD patterns of (a) **1**, (b) **2** and (c) **3** after heated at different temperatures under N_2 for 30 min.