[1]<Supporting Information>

Systematic Design of Secondary Building Units by an Efficient Cation-Directing Strategy under Regular Vibrations of Ionic Liquids

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Contents:

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1. Supplementary Structural Tables.

Table S1 Crystal data for polymers **1-4**

	1	**2**	**3**	**4**
Formula	$C_{18}H_{17}BrCoN_2O_4$	$C_{86}H_{66}Co_7N_4O_{28}$	$C_{88}H_{68}Co_6N_4O_{26}$	$C_{132}H_{116}BrCo_4N_8Na_5O_{32}$
M_r (g mol^{-1})	464.18	2015.94	1951.04	2756.91
T (K)	296(2)	296(2)	296(2)	296(2)
Space group	$P2_1/n$	$Pbca$	$C2/c$	$P4/n$
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Tetragonal
a (Å)	10.3019(16)	19.719(2)	20.270(4)	24.6698(15)
b (Å)	15.482(3)	15.6642(17)	16.336(3)	
c (Å)	10.9190(16)	27.118(3)	24.664(5)	9.9668(12)
β (deg)	92.482(3)		101.671(4)	
V (Å^3)	1739.9(5)	8376.1(16)	7998(3)	6065.8(9)
Z	4	4	4	2
Dc (g cm^{-3})	1.772	1.599	1.620	1.509
μ (mm^{-1})	3.310	1.437	1.302	0.970
Limiting indices	$-12 \le h \le 11$ $-17 \le k \le 18$ $-12 \le l \le 8$	$-23 \le h \le 23$ $-16 \le k \le 18$ $-29 \le l \le 32$	$-21 \le h \le 24$ $-19 \le k \le 12$ $-27 \le l \le 29$	$-23 \le h \le 29$ $-29 \le k \le 27$ $-9 \le l \le 11$
GOF on F^2	1.020	1.072	1.027	1.058
R_1, wR_2 [$I > 2\sigma(I)$]	0.0317, 0.0807	0.0460，0.1191	0.0530, 0.1243	0.0459, 0.1175
R_1, wR_2 [all data]	0.0430, 0.0842	0.0686，0.1280	0.0737, 0.1333	0.0681, 0.1258

Table S2. Selected bond lengths (Å) and bond angles (°) for polymer **1**.

bond	length	bond	length
Co(1)–O(1A)	2.040(2)	Co(1)–O(2B)	2.051(2)
Co(1)–O(4C)	2.058(2)	Co(1)–O(3)	2.063(2)
Co(1)–Br(1)	2.4622(6)		
bond angle	degree	bond angle	degree
O(1A)–Co(1)–O(2B)	156.89(10)	O(1A)–Co(1)–O(4C)	88.99(11)
O(2B)–Co(1)–O(4C)	88.30(11)	O(1A)–Co(1)–O(3)	86.82(11)
O(2B)–Co(1)–O(3)	86.78(11)	O(4C)–Co(1)–O(3)	157.05(10)
O(1A)–Co(1)–Br(1)	101.55(7)	O(2B)–Co(1)–Br(1)	101.47(8)
O(4C)–Co(1)–Br(1)	101.89(8)	O(3)–Co(1)–Br(1)	101.06(8)

Symmetry codes A: 1/2 + *x*, 1/2 – *y*, –1/2 + *z*; B: 3/2 – *x*, *y* – 1/2, 3/2 – *z;* C: 2 – *x*, –*y*, 1 – *z*

Table S3. Hydrogen bond parameters (Å, º) of polymer **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry transformation for A
C(13)–H(13A)···Br(1)	0.96	2.80	3.727(9)	164	5/2 – x, –1/2 + y, 1/2 – z
C(13)–H(13C)···O(4)	0.96	2.49	3.358(9)	150	3 – x, –y, 1 – z
C(13')–H(13D)··· Br(1)	0.96	2.92	3.819(10)	156	2 – x, –y, 1 – z
C(13')–H(13E)···O(2)	0.96	2.56	3.310(10)	135	5/2 – x, –1/2+y, 3/2 – z

Table S4. Selected bond lengths (Å) and bond angles (°) for polymer **2**.

bond	length	bond	length
Co(1)–O(13)	1.9317(18)	Co(1)–O(10B)	1.942(2)
Co(1)–O(2)	1.945(2)	Co(1)–O(7A)	1.976(2)
Co(2)–O(14)	2.0654(18)	Co(2)–O(11)	2.069(2) 3
Co(2)–O(8A)	2.077(2)	Co(2)–O(6B)	2.089(2)
Co(2)–O(1)	2.143(2)	Co(2)–O(13)	2.1453(19)
Co(3)–O(14)	2.0633(18)	Co(3)–O(5)	2.0747(19)
Co(3)–O(13)	2.0811(18)	Co(4)–O(14)	1.9555(19)
Co(4)–O(3)	1.959(3) 8	Co(4)–O(12)	1.975(2) 3
Co(4)–O(9)	1.979(2)		
bond angle	degree	bond angle	degree
O(13)–Co(1)–O(10B)	131.08(9)	O(13)–Co(1)–O(2)	113.16(9)
O(10B)–Co(1)–O(2)	99.22(10)	O(13)–Co(1)–O(7A)	99.48(9)
O(10B)–Co(1)–O(7A)	106.34(10)	O(2)–Co(1)–O(7A)	105.27(10)
O(14)–Co(2)–O(11C)	94.77(8)	O(14)–Co(2)–O(8A)	172.36(8)
O(11C)–Co(2)–O(8A)	92.15(8)	O(14)–Co(2)–O(6B)	92.62(8)
O(11C)–Co(2)–O(6B)	91.19(8)	O(8A)–Co(2)–O(6B)	90.47(8)
O(14)–Co(2)–O(1)	84.42(8)	O(11C)–Co(2)–O(1)	84.09(8)
O(8A)–Co(2)–O(1)	93.10(8)	O(6B)–Co(2)–O(1)	174.19(8)
O(14)–Co(2)–O(13)	83.40(7)	O(11C)–Co(2)–O(13)	178.13(8)
O(8A)–Co(2)–O(13)	89.70(8)	O(6B)–Co(2)–O(13)	88.53(7)
O(1)–Co(2)–O(13)	96.07(8)	O(14)–Co(3)–O(5B)	92.64(8)
O(14)–Co(3)–O(5)	87.36(8)	O(14)–Co(3)–O(13)	85.06(7)
O(14B)–Co(3)–O(13)	94.94(7)	O(5B)–Co(3)–O(13)	87.45(7)
O(5)–Co(3)–O(13)	92.55(7)	O(14)–Co(4)–O(3D)	110.11(12)
O(14)–Co(4)–O(12C)	106.09(9)	O(3D)–Co(4)–O(12C)	120.18(13)
O(14)–Co(4)–O(9)	119.49(9)	O(3D)–Co(4)–O(9)	93.77(12)
O(12C)–Co(4)–O(9)	107.70(10)		

Symmetry codes : A: 1/2 + *x*, 1/2 – *y*, –1/2 + *z*; B: 1/2 – *x*, –*y*, 3/2 + *z;* C: –*x*, 1/2 + *y*, 1/2 – *z* ; D –1/2 – *x*, –1/2 + *y*, *z*;

Table S5. Hydrogen bond parameters (Å, º) of polymer **2**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry transformation for A
C(5)–H(5A)···O(3)	0.93	2.41	2.731(5)	100	
C(8)–H(8A)···O(4)	0.93	2.38	3.009(9)	125	
C(16)–H(16A)···O(2)	0.93	2.55	3.416(4)	154	
C(23)–H(23A)···O(6)	0.93	2.34	2.953(4)	123	
C(28)–H(28A)···O(10)	0.93	2.38	2.713(4)	101	
C(32)–H(32A)···O(1)	0.93	2.60	3.412(4)	147	–x, –1/2 + y, 1/2 – z
C(35)–H(35A)···O(9)	0.93	2.26	2.857(5)	121	
C(37)–H(37A)···O(8)	0.93	2.27	3.181(6)	167	–1/2 – x, –y, –1/2 + z

Table S6. Selected bond lengths (Å) and bond angles (°) for polymer **3**.

bond	length	bond	length
Co(1)–O(2A)	2.045(4)	Co(1)–O(5)	2.047(4)
Co(1)–O(1)	2.075(3)	Co(1)–O(10)	2.129(4)
Co(1)–O(11)	2.149(4)	Co(1)–O(6B)	2.208(4)
Co(2)–O(4)	2.025(4)	Co(2)–O(12C)	2.031(4)
Co(2)–O(3A)	2.038(4)	Co(2)–O(1)	2.056(3)
Co(2)–O(8)	2.137(3)	Co(2)–O(9)	2.350(4)
Co(3)–O(7B)	1.958(4)	Co(3)–O(13C)	1.966(4)
Co(3)–O(8D)	1.984(3)	Co(3)–O(1)	1.986(3)
bond angle	degree	bond angle	degree
O(2A)–Co(1)–O(5)	94.71(18)	O(2A)–Co(1)–O(1)	99.84(14)
O(5)–Co(1)–O(1)	96.36(15)	O(2A)–Co(1)–O(10)	167.20(17)
O(5)–Co(1)–O(10)	89.36(18)	O(1)–Co(1)–O(10)	91.74(14)
O(2A)–Co(1)–O(11)	106.93(16)	O(5)–Co(1)–O(11)	86.84(16)
O(1)–Co(1)–O(11)	152.70(15)	O(10)–Co(1)–O(11)	61.11(16)
O(2A)–Co(1)–O(6B)	84.64(16)	O(5)–Co(1)–O(6B)	175.61(16)
O(1)–Co(1)–O(6B)	88.03(14)	O(10)–Co(1)–O(6B)	90.37(17)
O(11)–Co(1)–O(6B)	89.20(17)	O(4)–Co(2)–O(12C)	162.13(18)
O(4)–Co(2)–O(3A)	92.2(2)	O(12C)–Co(2)–O(3A)	85.8(2)
O(4)–Co(2)–O(1)	100.13(15)	O(12C)–Co(2)–O(1)	97.74(15)
O(3A)–Co(2)–O(1)	95.13(16)	O(4)–Co(2)–O(8)	86.66(15)
O(12C)–Co(2)–O(8)	91.74(18)	O(3A)–Co(2)–O(8)	168.41(16)
O(1)–Co(2)–O(8)	96.42(12)	O(4)–Co(2)–O(9)	82.18(15)
O(12C)–Co(2)–O(9)	81.93(16)	O(3A)–Co(2)–O(9)	110.72(16)
O(1)–Co(2)–O(9)	154.00(13)	O(8)–Co(2)–O(9)	57.70(12)
O(7B)–Co(3)–O(13C)	103.56(18)	O(7B)–Co(3)–O(8D)	123.05(15)
O(13C)–Co(3)–O(8D)	101.15(15)	O(7B)–Co(3)–O(1)	120.05(15)
O(13C)–Co(3)–O(1)	109.66(15)	O(8D)–Co(3)–O(1)	97.72(13)
Co(3)–O(1)–Co(2)	112.38(14)	Co(3)–O(1)–Co(1)	106.19(14)
Co(2)–O(1)–Co(1)	108.93(14)		

Symmetry codes: A: 1/2 – *x*, 1/2 + *y*, 1/2 – *z*; B: –1/2 + *x*, 1/2 + *y*, *z*; C: 1/2 + *x*, 1/2 + *y*, *z*; D: 1/2 – *x*, 3/2 – *y*, –*z*

Table S7. Hydrogen bond parameters (Å, º) of polymer **3**.

D–H···A	D(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry transformation for A
O(1)–H(1A)···O(13)	0.85	2.54	3.337(4)	157	–x, 1 – y, –z
C(8)–H(8A)···O(5)	0.93	2.50	3.034(13)	117	5/2 – x, –1/2 + y, 1/2 – z
C(11)–H(11B)···O(3)	1.26	2.21	3.171(18)	130	
C(16)–H(16A)···O(7)	0.93	2.37	2.71(3)	101	
C(16)–H(16B)···O(7)	0.96	2.36	2.71(3)	101	
C(20)–H(20A)···O(4)	0.93	2.52	3.45(2)	173	
C(20)–H(20B)···O(8)	0.99	2.51	3.15(2)	122	
C(23)–H(23A)···O(6)	0.93	2.19	2.83(3)	125	
C(23)–H(23A)···O(11)	0.93	2.35	3.19(3)	150	1/2 + x, –1/2 + y, z
C(23)–H(23B)···O(6)	1.05	2.17	2.83(3)	119	
C(23)–H(23B)···O(11)	1.05	2.57	3.19(3)	118	1/2 + x, –1/2 + y, z
C(29)–H(29A)···O(12)	0.93	2.26	2.621(14)	102	
C(32)–H(32A)···O(13)	0.93	2.20	2.854(17)	126	

Table S8. Selected bond lengths (Å) and bond angles (°) for polymer **4**.

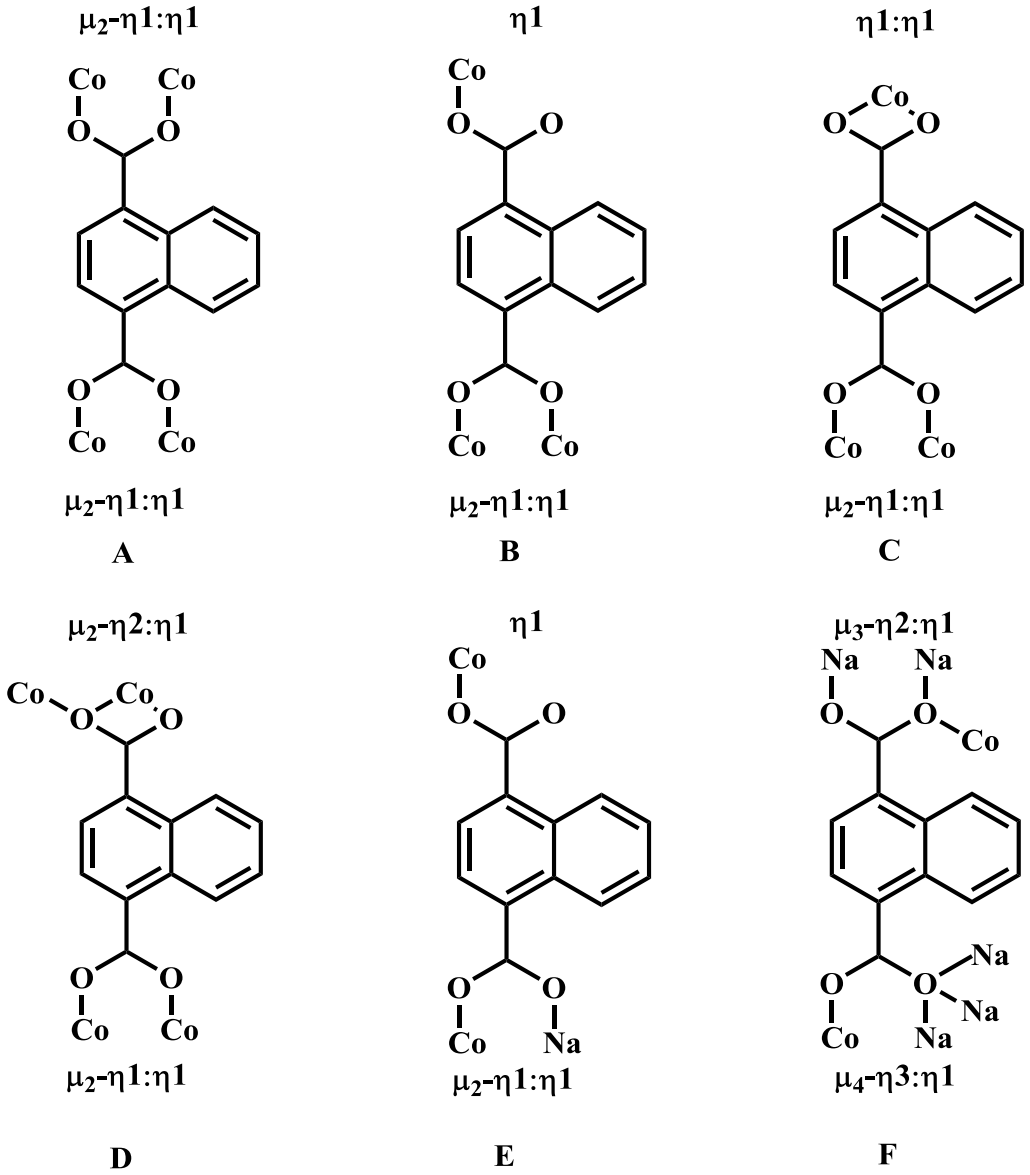
bond	length	bond	length
Co(1)–O(3B)	1.936(2)	Co(1)–O(7)	1.981(3)
Co(1)–O(5C)	1.996(3)	Co(1)–O(2A)	2.006(2)
Co(1)–Na(1)	3.3854(15)	Na(1)–O(8)	2.285(3)
Na(1)–O(1)	2.313(3)	Na(1)–O(4B)	2.496(3)
Na(1)–O(4D)	2.546(3)	Na(1)–O(2A)	2.572(3)
Na(1)–Br(1)	2.9695(14)	Na(1)–Na(2D)	3.305(2)
Na(1)–Na(1E)	3.8436(19)	Na(2)–O(4)	2.330(2)
Na(2)–Br(1F)	3.077(3)	Na(2)–Na(1F)	3.305(2)
bond angle	degree	bond angle	degree
O(3B)–Co(1)–O(7)	112.94(13)	O(3B)–Co(1)–O(5C)	126.90(14)
O(7)–Co(1)–O(5C)	98.68(14)	O(3B)–Co(1)–O(2A)	114.15(11)
O(7)–Co(1)–O(2A)	102.39(12)	O(5C)–Co(1)–O(2A)	98.14(13)
O(8)–Na(1)–O(1)	93.25(11)	O(8)–Na(1)–O(4B)	90.84(10)
O(1)–Na(1)–O(4B)	172.19(11)	O(8)–Na(1)–O(4D)	100.26(11)
O(1)–Na(1)–O(4D)	91.91(10)	O(4B)–Na(1)–O(4D)	80.81(11)
O(8)–Na(1)–O(2A)	86.74(11)	O(1)–Na(1)–O(2A)	99.04(10)
O(4B)–Na(1)–O(2A)	87.82(9)	O(4D)–Na(1)–O(2A)	166.69(10)
O(8)–Na(1)–Br(1)	172.61(9)	O(1)–Na(1)–Br(1)	93.86(8)
O(4B)–Na(1)–Br(1)	82.34(7)	O(4D)–Na(1)–Br(1)	81.53(7)
O(2A)–Na(1)–Br(1)	90.15(7)		

Symmetry codes: A: *y*, 3/2 – *x*, *z*; B: *y*, 3/2 – *x*, –1 + *z*; C: 1 – *y*, 1/2 + *x*, –*z*; D: *x*, *y*, –1 + *z*; –1/2 + *z*; E: 3/2 – *y*, *x*, *z*; F: *x*, *y*, 1 + *z;*

Table S9. Hydrogen bond parameters (Å, º) of polymer **4**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
C(8)–H(8A)···O(3)	0.93	2.37	2.865(4)	113
C(11)–H(11A)···O(1)	0.93	2.49	3.032(5)	117
C(17)–H(17A)···O(1)	0.93	2.58	3.366(5)	143
C(20)–H(20A)···O(7)	0.93	2.36	2.903(5)	117

2. Supplementary Structural Figures.



Scheme S1. The observed coordination modes of the 1,4-ndc^{2-} ligands in **1**-**4**.

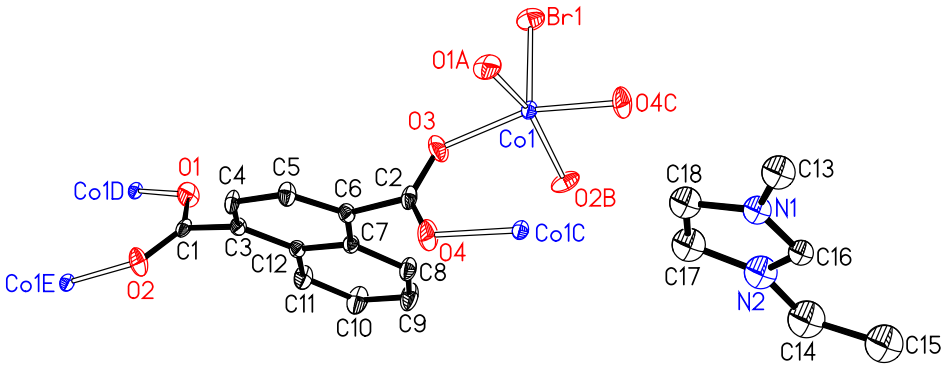


Figure S1. ORTEP view of **1** with the atom numbering scheme. The atoms are represented by 30% probability thermal ellipsoids. All the H atoms are omitted for clarity. Symmetry codes: A 1/2 + *x*, 1/2 – *y*, – 1/2 + *z*; B 3/2 – *x*, –1/2 + *y*, 3/2 – *z*; C 2 – *x*, – *y*, 1 – *z*; D –1/2 + *x*, 1/2 – *y*, 1/2 + *z*; E. 3/2 – *x*, 1/2 + *y*, 3/2 – *z*.

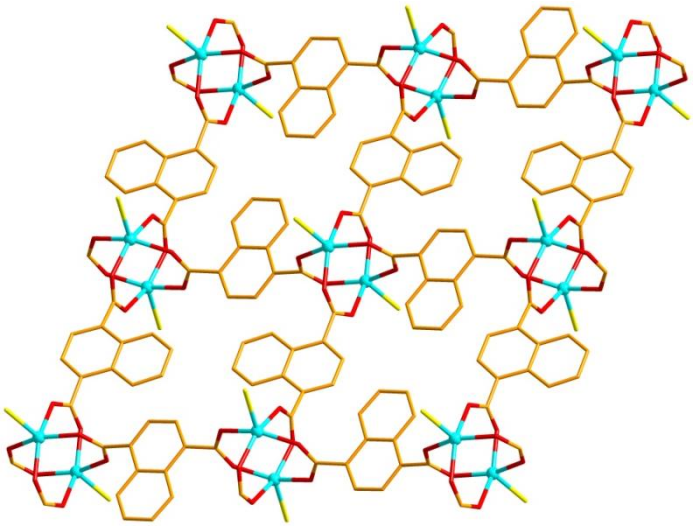


Figure S2. A view of the 2D anionic layer in **1** with hydrogen atoms omitted for clearly.

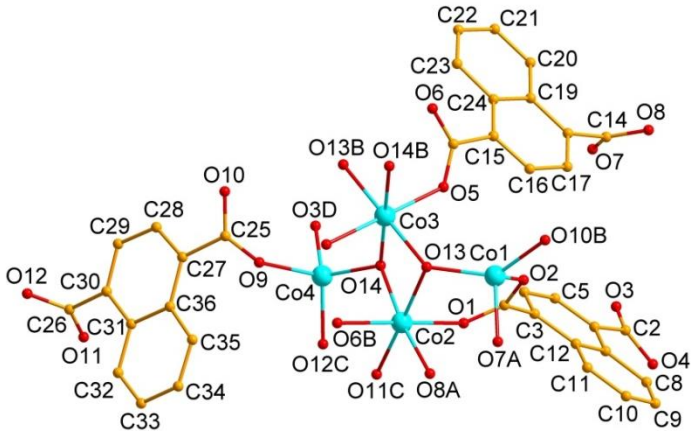


Figure S3. (a) The coordination environments for Co atoms in **2** with H atoms and $[PMIm]^+$ omitted for clarity. Symmetry codes: A 1/2 + *x*, 1/2 – *y*, 1 – *z*; B – *x*, – *y*, 1 – *z*; C – *x*, 1/2 + *y*, 1/2 – *z*; D –1/2 – *x*, –1/2 + *y*, *z*.

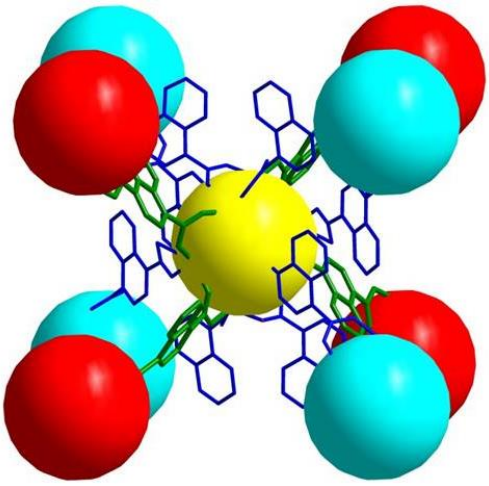


Figure S4. Each SBU (yellow ball) connected to eight others (turquoise and red balls) through twelve 1,4-ndc^{2-} including four “double-bridges” (blue) and four “single-bridge” (green) along multi-direction.

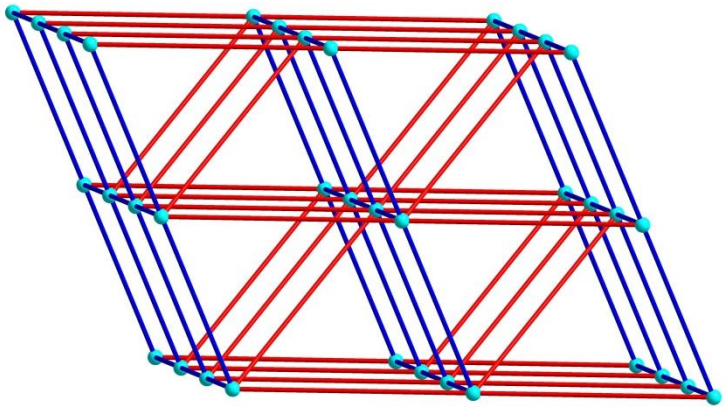


Figure S5. The eight-connected topological framework of **2** in which the nodes represent heptanuclear SBUs, the red bonds represent “single-bridge” and the blue bonds represent “doubly-bridges”.

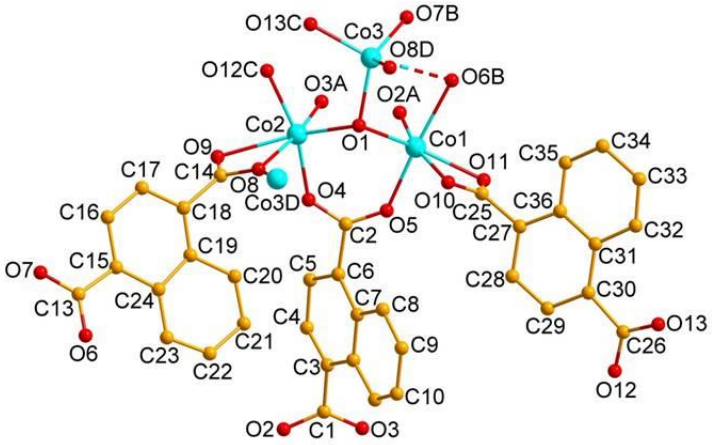


Figure S6. (a) The coordination environments of Co(II) ions in **3** with H atoms and $[BMIm]^+$ omitted for clarity. Symmetry codes: A 1/2 – *x*, 1/2 + *y*, 1/2 – *z*; B –1/2 + *x*, 1/2 + *y*, *z*; C 1/2 + *x*, 1/2 + *y*, *z*; D 1/2 – *x*, 3/2 – *y*, –*z*.

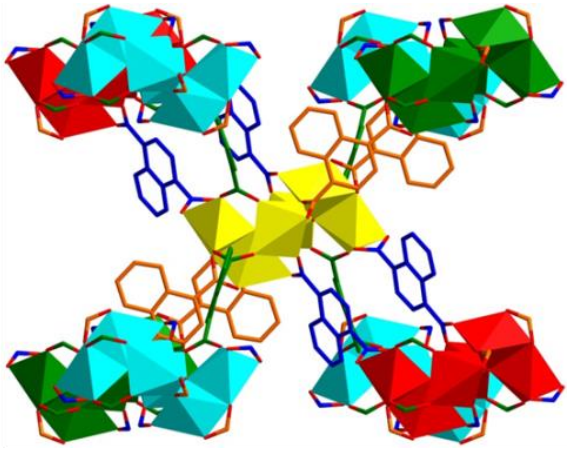


Figure S7. The hexanuclear SBU (yellow polyhedron) with eight adjacent SBUs (four turquoise, two green and two orange polyhedrons) by twelve linkages including four “single-bridge” (green) and four “doubly-bridges” (orange and blue).

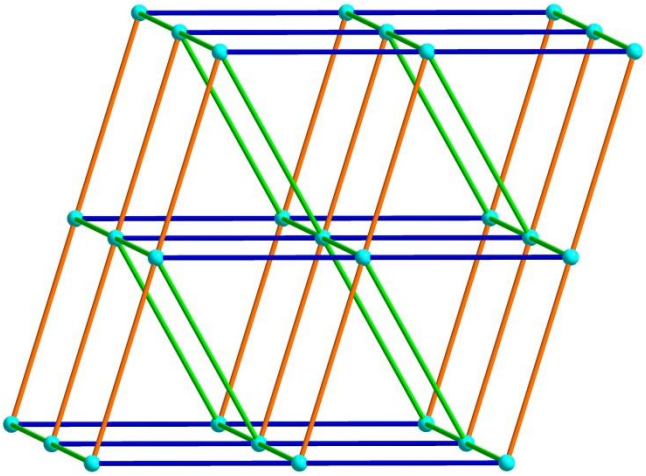


Figure S8. The eight-connected topological framework of **3** in which the nodes represent hexanuclear SBUs, the bright green bond represents “single-bridge”, the blue and orange bonds represent two kinds of coordination modes of “doubly-bridges”.

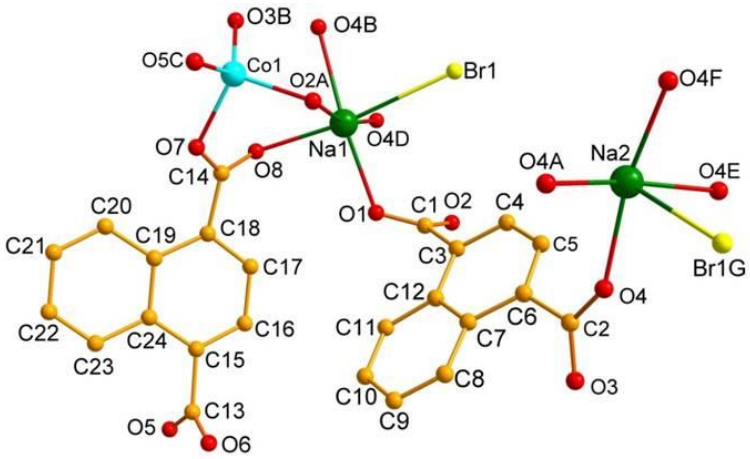


Figure S9. The coordination environments of Co(II) and Na(I) ions in **4** with H atoms and $[AMIm]^+$ omitted for clarity. Symmetry codes: A *y*, 3/2 – *x*, *z*; B *y*, 3/2 – *x*, –1 + *z*; C 1 – *y*, 1/2 + *x*, –*z*; D *x*, *y*, –1 + .*z*; E 3/2 – *y*, *x*, *z*; F 3/2 – *x*, 3/2 – *y*, *z*; G *x*, *y*, 1 + *z*.

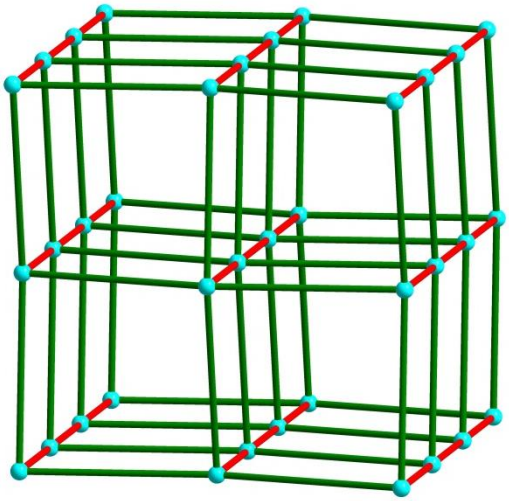


Figure S10. The six-connected topological structure of **4** in which the nodes represent heterometal SBUs, the green bonds represent “doubly-bridges” and the red bonds represent “fourfold-bridges”.

4. Additional Measurements.

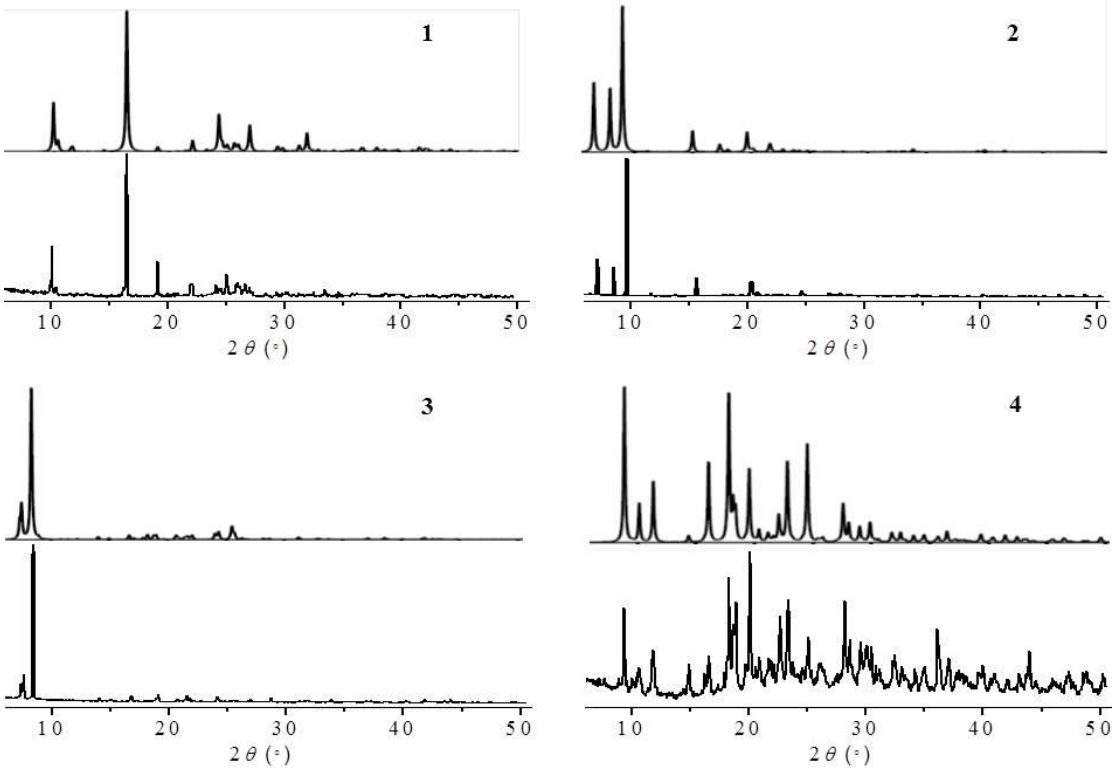


Figure S11. The X-ray powder diffraction (XRPD) patterns that of the bulk samples (down) and those calculated from the single-crystal diffraction data (up) for **1-4** at room temperature.

5. Additional magnetic properties.

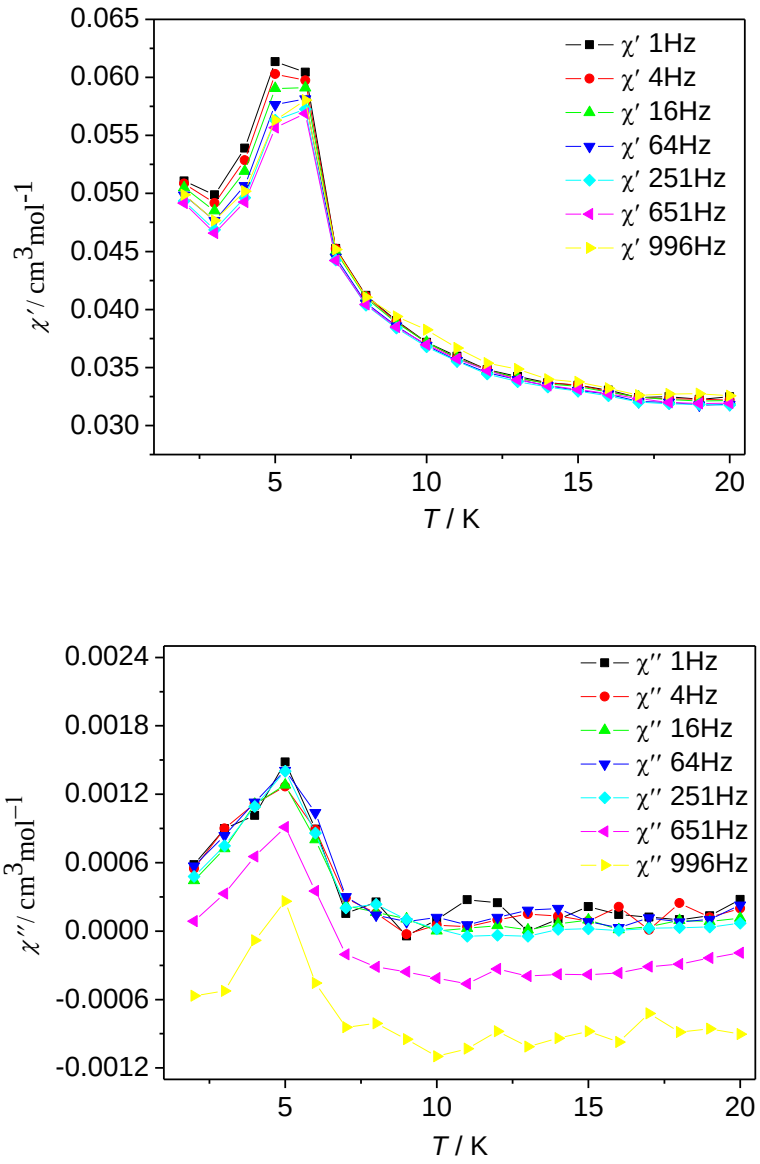


Figure S12. Temperature dependence of the real part (up) and the imaginary part (bottom) of the ac susceptibility of **1** in a 3 Oe ac field at different ac frequency with a zero applied dc field.

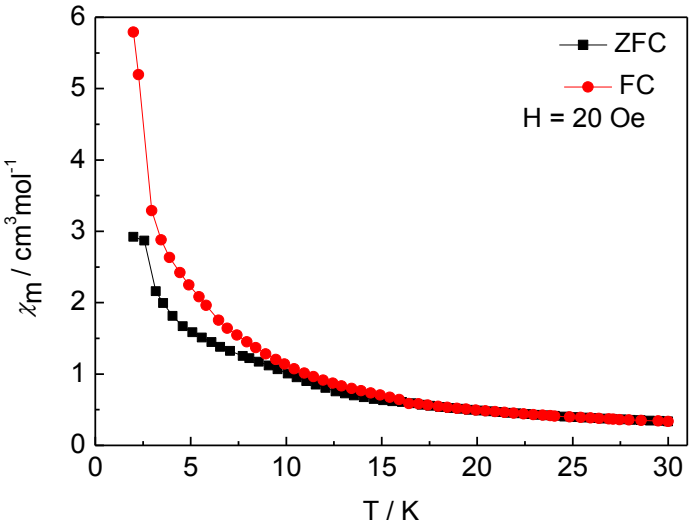


Figure S13. Field cooling and zero-field cooling (FC/ZFC) magnetization curves of **4** at 20 Oe.

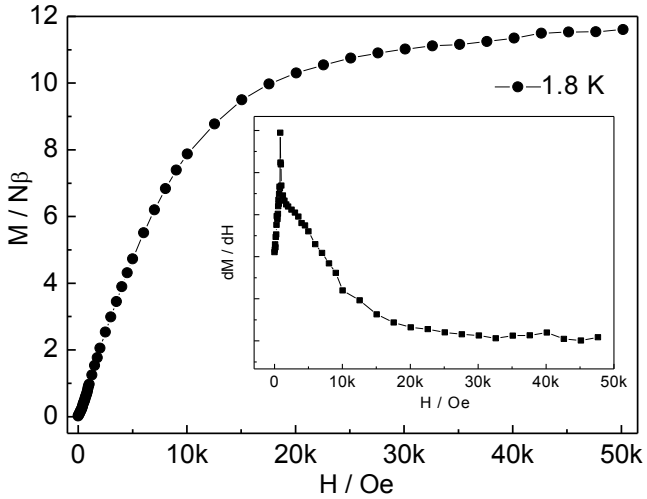


Figure S14. Field dependence of isothermal magnetization curve for **4** at 1.8 K. The inset shows the $\delta M / \delta H$ curve at 1.8 K.

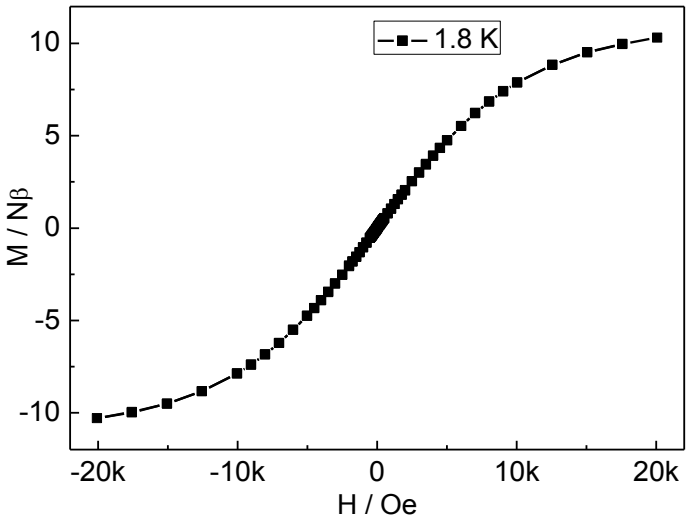


Figure S15. The hysteresis loop at 1.8 K for **4**.

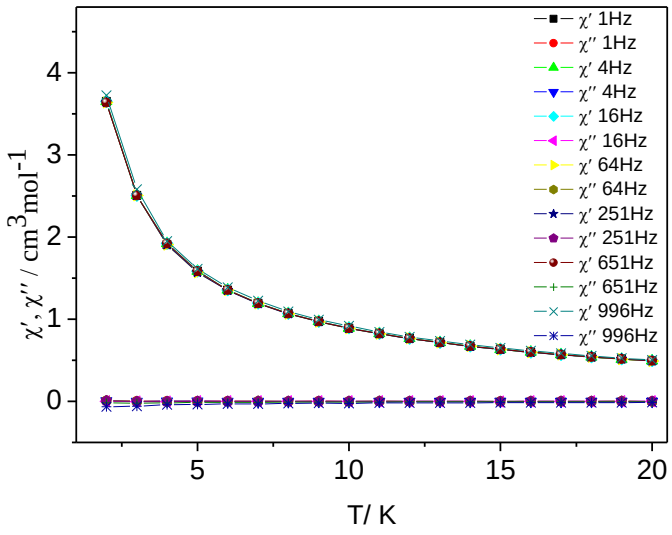


Figure S16. Temperature dependence of the real part (χ′) and the imaginary part (χ″) of the ac susceptibility of **4** in a 3 Oe ac field at different ac frequency with a zero applied dc field.