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Supporting Information

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Supporting Information for

Chiral Octupolar Metal-Organoboronic NLO Frameworks with the Exceptional (14, 3) Topology

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Table of Content

1**. Materials and General Procedures.**

All of the chemicals are commercial available, and used without further purification. Elemental analyses of C, H and N were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectrum was recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. The solid state CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). ^{1}H and ^{13}C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at resonance frequencies of 100.63 MHz. Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10 ^{o}C min^{-1} on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu Kα radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. Electrospray ionization mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as mobile phase.

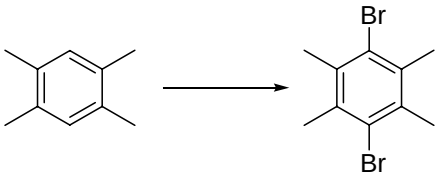
Second Harmonic Generation Measurement: Kurtz powder SHG measurements were performed on ground samples. Particle sizes were graded using standard sieves; sizes from 90-120 μm were studied. The fundamental wavelength of 1064 nm from a Nd:YAG laser was used. The powder second harmonic signals were compared to that of α-quartz to determine the relative SHG efficiencies of the samples. For comparison, sieved KDP (KH_2PO_4) powder (90-120 μm) was also measured and used as an additional reference. For each sample, three measurements were taken and the average value was reported. In the following table, α-quartz is the SHG of α-quartz.

Particle size (μm)	SHG /α-quartz							
	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1B** (apohost)	**1C** (apohost)
90-120	15	25	35	11	20	17	26	35

X-ray Crystallography. Single-crystal XRD data for the compounds was collected on on a Bruker Smart 1000 CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at room temperature. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996). The structure was solved using direct method, and refined by full-matrix least-squares on *F*2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997). All non-H atoms were refined anisotropically. Crystal data and details of the data collection are given in **Table S1**. The selected bond distances and angles are presented in **Tables S2-S5**. Compounds **1a, 1d-1f** are isostructural to **1b**, **2** and **3**, as evidenced by powder XRD and cell parameter determinations (see experimental section for details). Preliminary single-crystal X-ray diffraction further confirmed that **1d** is isostructural to **1b**, but the nitrate anions could not be located during to serious disorder and weak data collection.

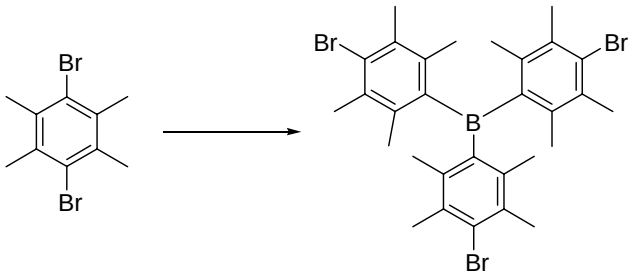
2. Synthesis of H_3**L**

1,4-dibromo-2,3,5,6-tetramethylbenzene:



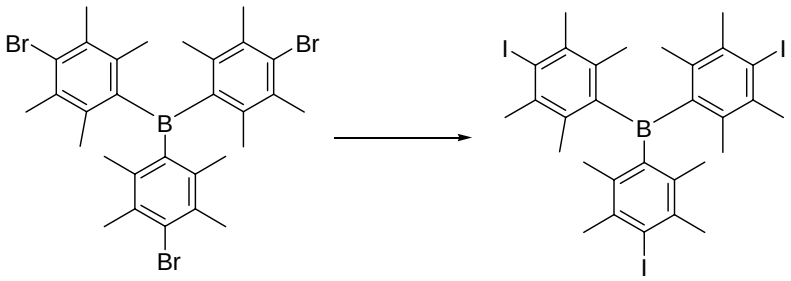
1,2,4,5-tetramethylbenzene (10g, 74.6mmol) and iodine (0.394g, 1.56mmol) were dissolved in 380ml dichloromethane, and then Br_2 (9ml, 175.6mmol) in 40ml dichloromethane was added dropwise under a dry N_2 atmosphere over 30min while being careful to exclude all light. The reaction mixture was refluxed for 1h. Excess Br_2 was quenched by the addition of 20ml of 5M aqueous sodium hydroxide. The organic fraction was washed several times with water and dried over $MgSO_4$. The solution was concentrated under reduced pressure, and the product was recrystallized from dichloromethane to afford 1,4-dibromo-2,3,5,6-tetramethylbenzene (16.76g, 77%) as a colorless needle-shaped solid. ^{1}HNMR ($CDCl_3$) δ：2.48 (s, 12H).

Tris(bromoduryl)borane:



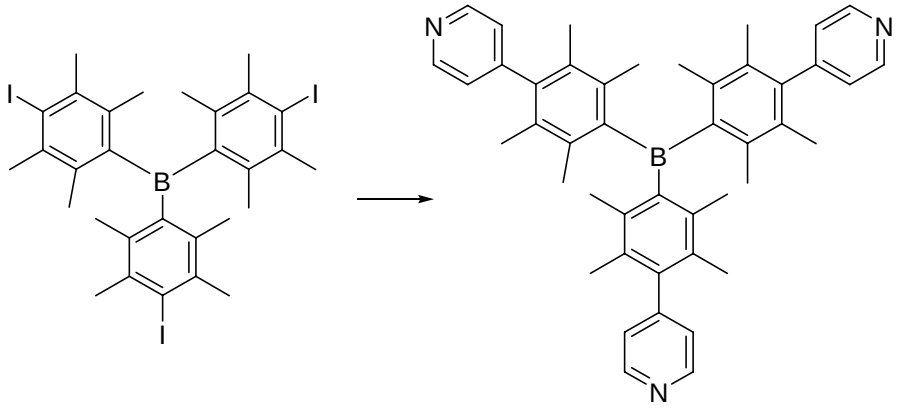
To a solution of 1,4-dibromo-2,3,5,6-tetramethylbenzene (10g, 34.3mmol) in dry Et_2O (300ml) was added dropwise a pentane solution of n-BuLi (2.5M, 13.6ml, 34mmol) at -78℃. The reaction mixture was allowed to warm to 0℃ and stirred for 20min, and then $BF_3{\cdot}OEt_2$ (1.4ml, 11.2mmol) was added to the mixture at -78℃. The reaction mixture was warmed up to room temperature over 1h and stirred for 16h. After addition of water, a part of white product can be obtained by filter, and the left mixture was extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by washing with diether ether and methanol to afford tris(bromoduryl)borane (5.5g, 75%) as a colorless solid. ^{1}HNMR ($CDCl_3$) δ：2.34 (s, 18H) , 1.99 (s, 18H).

Tris(iododuryl)borane:



To a solution of tris(bromoduryl)borane (5.23g, 8.1mmol) in dry THF (200ml) was added dropwise a pentane solution of *t*-BuLi (1.5M, 33ml, 49.3mmol) at -78℃. The reaction mixture was stirred for 50min. To the reaction mixture was added a THF (80ml) solution of iodine (9.4g, 37.0mmol) at-78℃. The reaction mixture was warmed up to room temperature over 1h and stirred for 11h. The reaction mixture was concentrated under reduced pressure. After addition of water, the mixture was extracted with Et_2O. The extract was washed with aqueous solution of $Na_2S_2O_3$ and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by washing with diether ether and methanol to afford tris(iododuryl)borane (4.9g, 77%) as a colorless solid. ^{1}HNMR ($CDCl_3$) δ：2.43 (s, 18H), 2.03 (s, 18H).

Tris(4-(4-pyridyl)duryl)borane (L):



Tris(iododuryl)borane (4.73g, 6mmol), 4-pyridylboronic acid (4.43g, 36mmol), K_2CO_3 (8.28g, 60mmol) and Pd $(PPh_3)_4$ (0.69g, 0.6mmol) were weighted into a 500mL Schlenk flask which was then pump-purged with N_2 three times. Toluene (160mL) and EtOH/H_2O (80mL, 3:5) were added under a dry N_2 atmosphere. The mixture was heated to reflux with stirring and maintained at this temperature for 24h. The reaction mixture was cooled to room temperature and extracted with CH_2Cl_2. The combined organic layers were washed several times with brine, dried over $MgSO_4$ and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (2:1 hexane-EtOAc) to afford tris(4-(4-pyridyl)duryl)borane (2.69g, 70%) as a white solid. ^{1}H NMR ($CDCl_3$) δ: 1.84(s, 18H), 2.06 (s, 18H), 7.10 (d, 6H), 8.65 (d, 6H); ^{13}C NMR ($CDCl_3$) δ：151.9, 150.0, 149.5, 140.8, 136.2, 130.7, 125.2, 20.4, 18.1. ESI-MS: m/z 642.7 (Calcd *m/z* 642.4 for $[L+H]^+$) (see Figure **S12**).

3**.** Synthesis of compounds **1-3**

A mixture of $CdBr_2 \cdot 4H_2O$ (0.005 mmol), **L** (0.005 mmol), DMSO (1 mL), CH_3OH (2 mL) and toluene (0. 5 mL) was sealed in a 10 mL vial with a screw cap and heated at 80 ºC for two days. The mix ture was then cooled to room temperature and colorless crystals of **1b** suitable for X-ray diffraction were collected, washed with ether and dried in air. The other seven compounds were synthesized in a similar procedure by using their corresponding salts. The products can be best formulated as $[MX_2\mathbf{L}]\cdot G$ (MX_2 = $CdCl_2/Br_2/I_2/(NO_3)_2/(OAc)_2/(ClO_4)_2$ **1a-1f**, $CuCl_2$ **2**, $CoCl_2$ **3;**G = $2H_2O$ for **1**and **2** and $3/2CH_3OH \cdot H_2O$ for **3)**] on the basis of microanalysis, IR and TGA. All Cd crystals of **1** are colorless, the copper crystals are bule and the cobalt crystals are purple. The solid-state CD measurements indicated that all compounds are CD silent and so the bulky samples are racemic. Yield: **1a**, 3.0 mg, 70 %; **1b**, 3.8 mg, 81 %; **1c**, 3.8 mg, 72 %; **1d**, 3.1 mg, 68 %; **1e**, 3.5 mg, 71 %; **1f**, 3.5 mg, 78 %; **2**, 3.5 mg, 86 %; **3**, 3.3 mg, 80 %.

Elemental Analysis data of **1a**:
Anal (%). Calcd for C45H52BCdCl2N3O2: C, 62.77; H, 6.09; N, 4.88. Found: C, 61.94; H, 6.00; N, 4.83. IR (KBr, cm^{-1}): 3430(m), 2910(w), 1608(s), 1538(w), 1422(w), 396(s), 1300(m), 1264(m), 1220(m), 1068(m), 954(m), 860(m), 818(w), 802(s), 706(w), 650(s), 616(w)**.** Cell parameters: a = 17.884(2), b = 17.884(2), c = 47.9927(10) Å, alpha = 90, beta = 90, gamma = 120º, V = 13293(4) $Å^3$.

Elemental Analysis data of **1b**: Anal (%). Calcd for C45H52BBr2CdN3O: C, 56.90; H, 5.52; N, 4.42. Found: C, 56.11; H, 5.48; N, 4.39. IR (KBr, cm^{-1}): 3432 (m), 2986 (w), 1610 (s), 1558 (w), 1420(m), 1394(s)**,** 1300(w), 1260(m), 1218(m), 1068(s), 954(m), 862(m), 820 (m), 802(m), 652(m), 614(w).

Elemental Analysis data of **1c**:
Anal (%). Calcd for C45H52BCdI2N3O2: C, 51.77; H, 5.02; N, 4.03. Found: C, 51.12; H, 4.97; N, 4.00. IR (KBr, cm^{-1}): 3422 (m), 2914(w), 1608(s), 1540 (w), 1418(w), 1394(m), 1260(m), 1216(m), 1170(w), 1066(m), 952(m), 862(m), 802(m), 704(w), 650(m), 612(w).

Elemental Analysis data of **1d**:
Anal (%). Calcd for C45H52BCdN5O8: C, 59.12; H, 5.73; N, 7.66. Found: C, 58.92; H, 5.73; N, 7.64. IR (KBr, cm^{-1}): 3398(m), 2912(w), 1610(s), 1540(w), 1384(m), 1282(w), 1266(m), 1220(m), 1068(s), 1022(w), 954(s), 862(s), 818(w), 802(m), 652(w), 616(w). Cell parameters: a = 17.934(3), b = 17.934(3), c = 47.893(3) Å, alpha = 90, beta = 90, gamma = 120º, V = 13339(4) $Å^3$.

Elemental Analysis data of **1e**:

Anal (%).C45H52BCdCl2N3O10: C, 54.65; H, 5.30; N, 4.25. Found: C, 54.12; H, 5.27; N, 4.20. IR (KBr, cm^{-1}): 3422(w), 2910(w), 1592(s), 1558(w), 1538(w), 1396(s), 1298(m), 1260(s), 1168(m), 1070(m), 954(s), 860(s), 818(w), 800(s), 640(w), 612(w) Cell parameters: a = 18.0336(14), b = 18.0336(14), c = 48.013(2) Å, alpha = 90, beta = 90, gamma = 120º, V = 13522.3(16) $Å^3$.

Elemental Analysis data of **1f**:
Anal(%).C49H58BCdN3O6: C, 64.80; H, 6.44; N, 4.63. Found: C, 64.06; H, 6.37; N, 4.60. IR (KBr, cm^{-1}): 3432(m), 2934(w), 1592(m), 1452(w), 1394(m), 1298(w), 1260(m), 1214(w), 1168(m), 1070(w), 954(m), 860(s), 818(w), 798(s), 700(w), 640(m), 612(w). Cell parameters: a = 17.9136(11), b = 17.9136(11), c = 47.8913(11) Å, alpha = 90, beta = 90, gamma = 120º, V = 13309.2(12) $Å^3$.

Elemental Analysis data of **2**:
Anal (%). Calcd for C45H52BCl2CuN3O2: C, 66.55; H, 6.45; N, 5.17. Found: C, 66.12; H, 6.40; N, 5.21. IR (KBr, cm^{-1}): 3422 (m), 2904(w),1608 (s), 1538 (w), 1454(w), 1416(m), 1394(s), 1300(m), 1262(s), 1214(s), 1170(m), 1078(w), 1066(m), 954(m), 862(m), 820 (w)**,** 804(m).

Elemental Analysis data of **3**:
Anal (%). Calcd for C46.5H56BCl2CoN3O2.5: C, 66.68; H, 6.74; N, 5.02. Found: C, 66.02; H, 6.67; N, 5.01. IR (KBr, cm^{-1}): 3422 (m), 2910(w), 1612 (s), 1538 (w), 1456(m), 1418(m), 1394(s), 1302(m), 1262(s), 1216(s), 1170(m), 1090(w), 1066(m), 954(m), 862(m), 820 (w)**,** 804(m).

4**. Table S1**. Crystal data and structure refinement for **1b, 1c**, **2** and **3**.

Identification code	**1b**	**1c**	**2**	**3**
Empirical formula	C45H52BBr2CdN3O2	C45H52BCdI2N3O2	C45H52BCuN3O2	C46.5H56BCl2CoN3O2.5
Formula weight	949.93	1043.91	812.15	837.58
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal
Space group	R32	R32	R32	R32
Unit cell dimensions	a = 18.169(3) Å c = 47.599(10) Å	18.343(3) 48.214(10)	17.830(3) 47.730(10)	17.674(3) 48.066(10)
Volume ($Å^3$), Z	13607(4), 12	14049(4), 12	13140(4), 12	13002(4), 12
Density (calculated) (mg/m^3)	1.391	1.481	1.232	1.284
Absorption coefficient (mm^{-1})	2.281	1.821	0.659	0.561
F(000)	5784	6216	5124	5304
Theta range for data collection (º)	3.10 to 25.00	3.22 to 25.00	3.14 to 25	3.16 to 25
Limiting indices	-21<h< 21, -21<k<20, -56<l< 56	-21<h< 21, -21<k<21, -57<l< 50	-21<h< 21, -21<k<20, -56<l< 56	-21<h<21, -21<k<21, --57<l<57
Reflections collected	35530	21869	31213	34054
Independent reflections	5316 (Rint = 0.1018)	5504 (Rint = 0.0316)	5152 (Rint=0.047)	5075(Rint=0.065)
Completeness to theta	25.00º, 99.2 %	25.00º, 99.4 %	25.00º, 99.4 %	25.00º, 99.4 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5316/ 0 / 321	5504 / 0 / 321	5152 / 0 / 325	5075 / 1 / 331
Goodness-of-fit on F^2	1.089	1.022	1.048	1.079
Final R indices [I>2sigma(I)]	R1=0.0542, wR2=0.1458	R1=0.0437, wR2=0.1151	R1=0.0576,wR2=0.1582	R1 = 0.0664,wR2 = 0.1815
R indices (all data)	R1=0.0653, wR2=0.1623	R1=0.0488, wR2=0.1188	R1=0.0637, wR2=0.1582	R1=0.07888, wR2=0.1956
Absolute structure parameter	0.025(16)	0.00(3)	0.019(18)	0.00(3)
Largest diff. peak and hole ($e.Å^{-3}$)	0.811 and -0.994	0.835 and -0.847	0.521 and -0.361	0.839 and -0.605

5**. Table S2**. Selected bond lengths [Å] and angles [º] for **1b**

Cd(1)-N(1)	2.295(5)
Cd(1)-N(2)	2.257(7)
Cd(1)-N(1)#1	2.296(5)
Cd(1)-Br(1)#1	2.6706(10)
Cd(1)-Br(1)	2.6707(10)
Cd(2)-N(3)#2	2.280(7)
Cd(2)-N(3)#3	2.280(7)
Cd(2)-N(3)	2.280(7)
Cd(2)-Br(2)#4	2.6824(12)
Cd(2)-Br(2)	2.6824(12)
B(1)-C(9)	1.579(8)
B(1)-C(9)#5	1.579(8)
B(1)-C(22)	1.581(13)
B(2)-C(31)	1.593(8)
B(2)-C(31)#6	1.593(8)
B(2)-C(31)#7	1.593(8)

N(2)-Cd(1)-N(1)	116.02(14)
N(2)-Cd(1)-N(1)#1	116.02(14)
N(1)-Cd(1)-N(1)#1	128.0(3)
N(2)-Cd(1)-Br(1)#1	97.05(2)
N(1)-Cd(1)-Br(1)#1	87.43(15)
N(1)#1-Cd(1)-Br(1)#1	86.40(15)
N(2)-Cd(1)-Br(1)	97.05(2)
N(1)-Cd(1)-Br(1)	86.40(15)
N(1)#1-Cd(1)-Br(1)	87.42(15)
Br(1)#1-Cd(1)-Br(1)	165.89(5)
N(3)#2-Cd(2)-N(3)#3	120.0
N(3)#2-Cd(2)-N(3)	120.0
N(3)#3-Cd(2)-N(3)	120.0
N(3)#2-Cd(2)-Br(2)#4	90.0
N(3)#3-Cd(2)-Br(2)#4	90.0
N(3)-Cd(2)-Br(2)#4	90.0
N(3)#2-Cd(2)-Br(2)	90.0
N(3)#3-Cd(2)-Br(2)	90.0
N(3)-Cd(2)-Br(2)	90.0
Br(2)#4-Cd(2)-Br(2)	180.0
C(9)-B(1)-C(9)#5	119.7(8)
C(9)-B(1)-C(22)	120.2(4)
C(9)#5-B(1)-C(22)	120.2(4)
C(31)-B(2)-C(31)#6	120.000(1)
C(31)-B(2)-C(31)#7	120.000(1)
C(31)#6-B(2)-C(31)#7	120.000(2)

Symmetry transformations used to generate equivalent atoms: N
#1 -x-2/3,-x+y-1/3,-z-1/3 #2 -y,x-y,z #3 -x+y,-x,z
#4 y,x,-z #5 -x,-x+y,-z #6 -y+1,x-y+3,z #7 -x+y-2,-x+1,z

6. **Table S3**. Selected bond lengths [Å] and angles [º] for **1c**

Cd(1)-N(2)	2.318(7)
Cd(1)-N(1)	2.373(5)
Cd(1)-N(1)#1	2.374(5)
Cd(1)-I(1)#1	2.8273(7)
Cd(1)-I(1)	2.8274(7)
Cd(2)-N(3)#2	2.342(6)
Cd(2)-N(3)	2.342(6)
Cd(2)-N(3)#3	2.342(6)
Cd(2)-I(2)	2.8405(10)
Cd(2)-I(2)#4	2.8405(10)
B(1)-C(9)#5	1.603(7)
B(1)-C(9)	1.603(7)
B(1)-C(22)	1.606(12)
B(2)-C(31)	1.613(8)
B(2)-C(31)#6	1.613(8)
B(2)-C(31)#7	1.613(8)

N(2)-Cd(1)-N(1)	116.21(13)
N(2)-Cd(1)-N(1)#1	116.21(13)
N(1)-Cd(1)-N(1)#1	127.6(3)
N(2)-Cd(1)-I(1)#1	95.822(17)
N(1)-Cd(1)-I(1)#1	87.05(14)
N(1)#1-Cd(1)-I(1)#1	87.81(14)
N(2)-Cd(1)-I(1)	95.820(17)
N(1)-Cd(1)-I(1)	87.81(14)
N(1)#1-Cd(1)-I(1)	87.05(14)
I(1)#1-Cd(1)-I(1)	168.36(3)
N(3)#2-Cd(2)-N(3)	120.000(1)
N(3)#2-Cd(2)-N(3)#3	120.0
N(3)-Cd(2)-N(3)#3	120.000(2)
N(3)#2-Cd(2)-I(2)	90.0
N(3)-Cd(2)-I(2)	90.0
N(3)#3-Cd(2)-I(2)	90.0
N(3)#2-Cd(2)-I(2)#4	90.0
N(3)-Cd(2)-I(2)#4	90.0
N(3)#3-Cd(2)-I(2)#4	90.0
I(2)-Cd(2)-I(2)#4	180.0
C(9)#5-B(1)-C(9)	120.2(7)
C(9)#5-B(1)-C(22)	119.9(3)
C(9)-B(1)-C(22)	119.9(3)
C(31)-B(2)-C(31)#6	120.0
C(31)-B(2)-C(31)#7	120.000(1)
C(31)#6-B(2)-C(31)#7	120.000(1)

Symmetry transformations used to generate equivalent atoms: N
#1 -x+2/3,-x+y+1/3,-z+1/3 #2 -y+1,x-y+2,z #3 -x+y-1,-x+1,z
#4 y-1,x+1,-z #5 -x,-x+y,-z #6 -y,x-y-1,z
#7 -x+y+1,-x,z

7. **Table S4**. Selected bond lengths [Å] and angles [º] for **2**

Cu(1)-N(1)	2.049(4)
Cu(1)-N(1)#1	2.049(4)
Cu(1)-N(2)	2.190(5)
Cu(1)-Cl(1)	2.2896(14)
Cu(1)-Cl(1)#1	2.2897(14)
Cu(2)-N(3)#2	2.104(5)
Cu(2)-N(3)#3	2.104(5)
Cu(2)-N(3)	2.104(5)
Cu(2)-Cl(2)	2.287(2)
Cu(2)-Cl(2)#4	2.287(2)
B(1)-C(9)#5	1.593(5)
B(1)-C(9)	1.593(5)
B(1)-C(16)	1.596(8)
B(2)-C(33)	1.604(5)
B(2)-C(33)#6	1.604(5)
B(2)-C(33)#7	1.604(5)
N(1)-Cu(1)-N(1)#1	136.53(19)
N(1)-Cu(1)-N(2)	111.73(10)
N(1)#1-Cu(1)-N(2)	111.74(10)
N(1)-Cu(1)-Cl(1)	88.25(12)
N(1)#1-Cu(1)-Cl(1)	88.88(12)
N(2)-Cu(1)-Cl(1)	93.88(4)
N(1)-Cu(1)-Cl(1)#1	88.88(12)
N(1)#1-Cu(1)-Cl(1)#1	88.24(12)
N(2)-Cu(1)-Cl(1)#1	93.88(4)
Cl(1)-Cu(1)-Cl(1)#1	172.24(8)
N(3)#2-Cu(2)-N(3)#3	120.0
N(3)#2-Cu(2)-N(3)	120.000(1)
N(3)#3-Cu(2)-N(3)	120.000(1)
N(3)#2-Cu(2)-Cl(2)	90.0
N(3)#3-Cu(2)-Cl(2)	90.0
N(3)-Cu(2)-Cl(2)	90.0
N(3)#2-Cu(2)-Cl(2)#4	90.0
N(3)#3-Cu(2)-Cl(2)#4	90.0
N(3)-Cu(2)-Cl(2)#4	90.0
Cl(2)-Cu(2)-Cl(2)#4	180.0
C(9)#5-B(1)-C(9)	120.4(5)
C(9)#5-B(1)-C(16)	119.8(3)
C(9)-B(1)-C(16)	119.8(3)
C(33)-B(2)-C(33)#6	120.000(1)
C(33)-B(2)-C(33)#7	120.000(1)
C(33)#6-B(2)-C(33)#7	120.000(1)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2/3,-x+y+1/3,-z+1/3 #2 -x+y-1,-x+1,z #3 -y+1,x-y+2,z
#4 y-1,x+1,-z #5 -x,-x+y,-z #6 -y,x-y-1,z
#7 -x+y+1,-x,z .

8. **Table S5**. Bond lengths [Å] and angles [º] for **3**

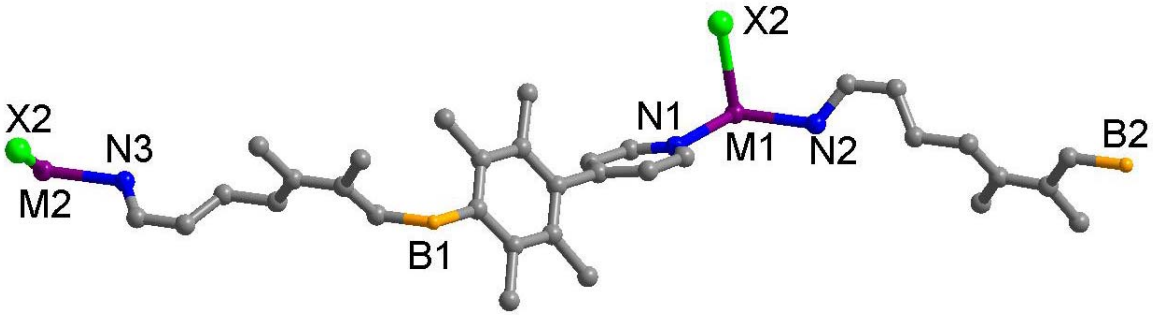
Co(1)-N(2)	2.049(6)
Co(1)-N(1)	2.057(5)
Co(1)-N(1)#1	2.057(5)
Co(1)-Cl(1)	2.3996(18)
Co(1)-Cl(1)#1	2.3997(18)
Co(2)-N(3)#2	2.029(6)
Co(2)-N(3)#3	2.029(6)
Co(2)-N(3)	2.029(6)
Co(2)-Cl(2)#4	2.467(3)
Co(2)-Cl(2)	2.467(3)
B(1)-C(16)	1.578(11)
B(1)-C(9)#5	1.588(7)
B(1)-C(9)	1.588(7)
B(2)-C(33)	1.594(6)
B(2)-C(33)#6	1.594(6)
B(2)-C(33)#7	1.594(6)

N(2)-Co(1)-N(1)	112.25(13)
N(2)-Co(1)-N(1)#1	112.25(13)
N(1)-Co(1)-N(1)#1	135.5(3)
N(2)-Co(1)-Cl(1)	97.00(5)
N(1)-Co(1)-Cl(1)	87.37(16)
N(1)#1-Co(1)-Cl(1)	87.34(15)
N(2)-Co(1)-Cl(1)#1	97.00(5)
N(1)-Co(1)-Cl(1)#1	87.34(15)
N(1)#1-Co(1)-Cl(1)#1	87.36(16)
Cl(1)-Co(1)-Cl(1)#1	165.99(9)
N(3)#2-Co(2)-N(3)#3	120.0
N(3)#2-Co(2)-N(3)	120.000(1)
N(3)#3-Co(2)-N(3)	120.000(1)
N(3)#2-Co(2)-Cl(2)#4	90.0
N(3)#3-Co(2)-Cl(2)#4	90.0
N(3)-Co(2)-Cl(2)#4	90.0
N(3)#2-Co(2)-Cl(2)	90.0
N(3)#3-Co(2)-Cl(2)	90.0
N(3)-Co(2)-Cl(2)	90.0
Cl(2)#4-Co(2)-Cl(2)	180.0
C(16)-B(1)-C(9)#5	119.8(3)
C(16)-B(1)-C(9)	119.8(3)
C(9)#5-B(1)-C(9)	120.5(7)
C(33)-B(2)-C(33)#6	120.000(1)
C(33)-B(2)-C(33)#7	120.0
C(33)#6-B(2)-C(33)#7	120.0

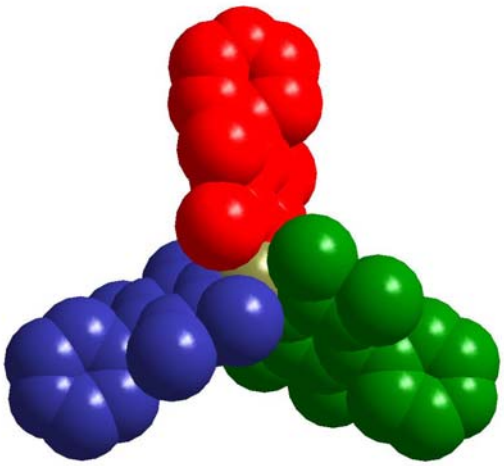
Symmetry transformations used to generate equivalent atoms: N
#1 -x+2/3,-x+y+1/3,-z+1/3 #2 -y+1,x-y+2,z #3 -x+y-1,-x+1,z
#4 y-1,x+1,-z #5 -x,-x+y,-z #6 -y,x-y-1,z
#7 -x+y+1,-x,z

9**. Figure S1**. (a) The asymmetric unit, (b) Space filling modes of the Δ-**L** ligand and (b) the Λ-**L** ligands in **1b, 1c**, **2** and **3**.

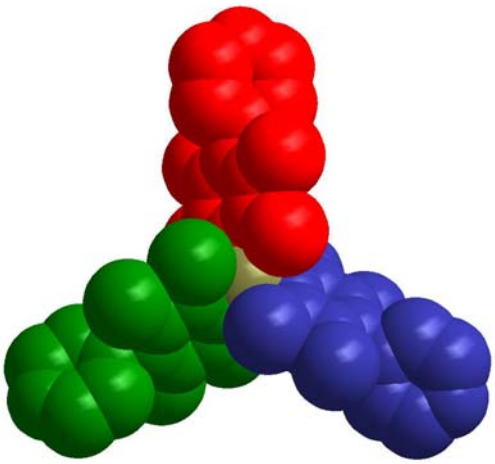
(a)



(b)

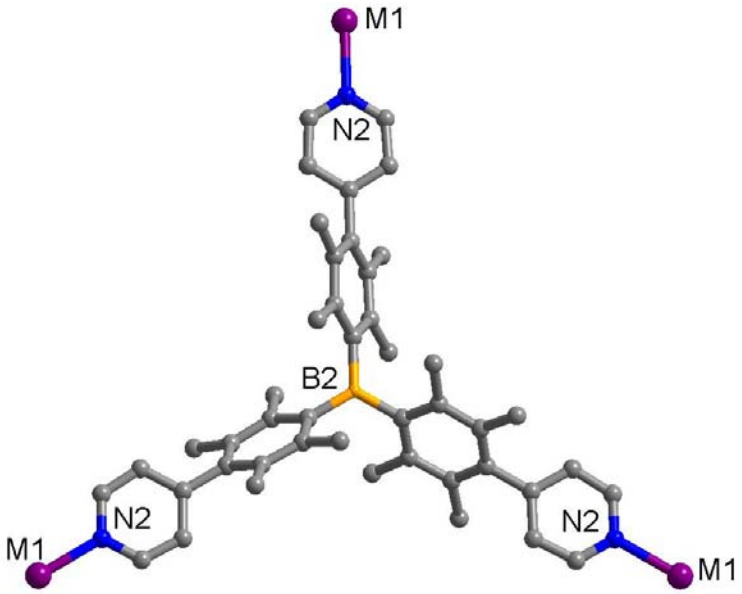


(c)

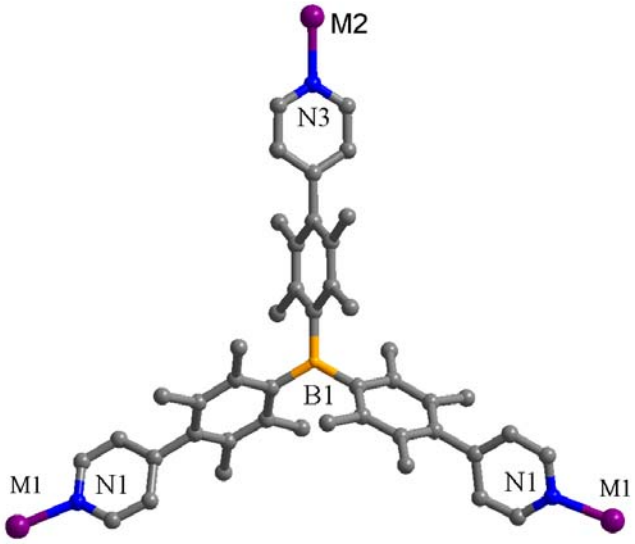


10**. Figure S2**. (a) Coordination environments of the Δ-**L** ligand and (b) the Λ-**L** ligands in **1b** (M = Cd)**, 1c** (M = Cd) , **2** (M = Cu) and **3** (M = Co).

(a)

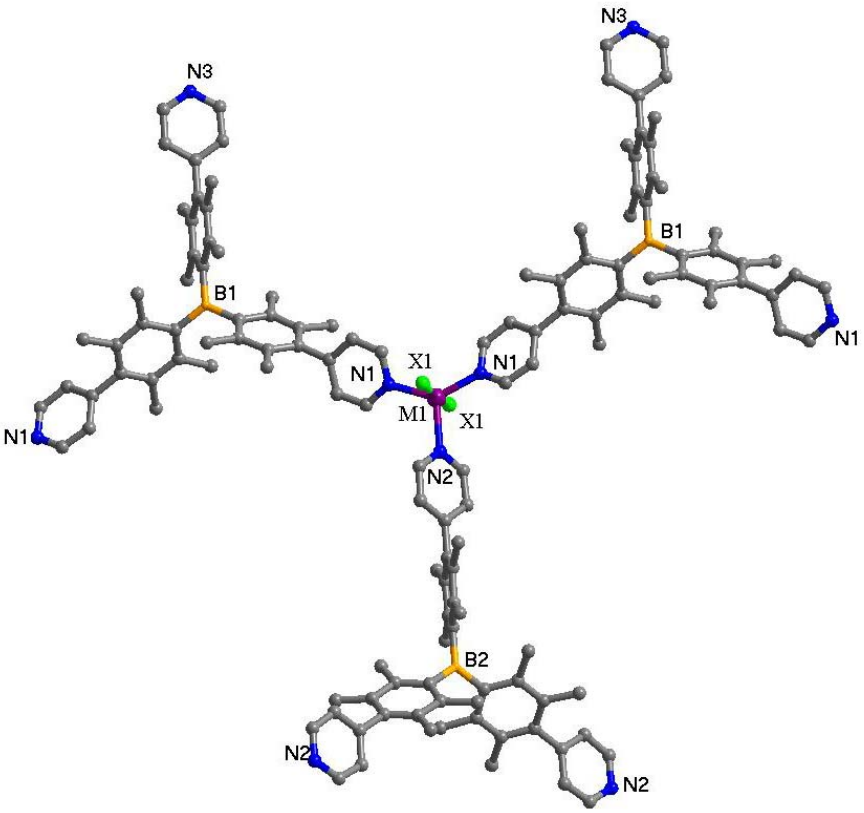


(b)

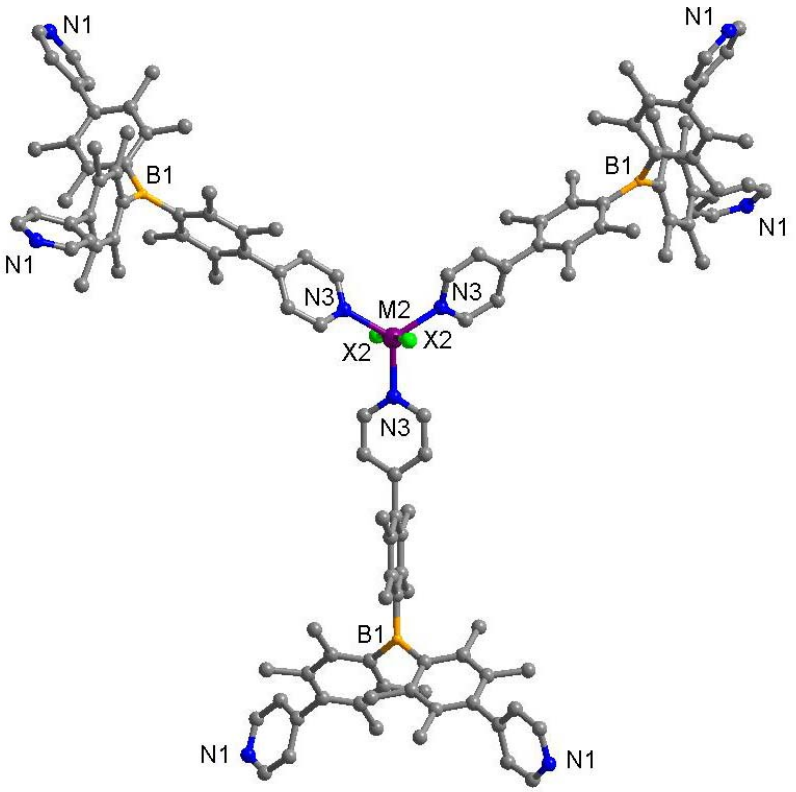


11**. Figure S3**. (a) Coordination environments of the Δ-**L** ligand and (b) the Λ-**L** ligands in **1b** (M = Cd)**, 1c** (M = Cd) , **2** (M = Cu) and **3** (M = Co).

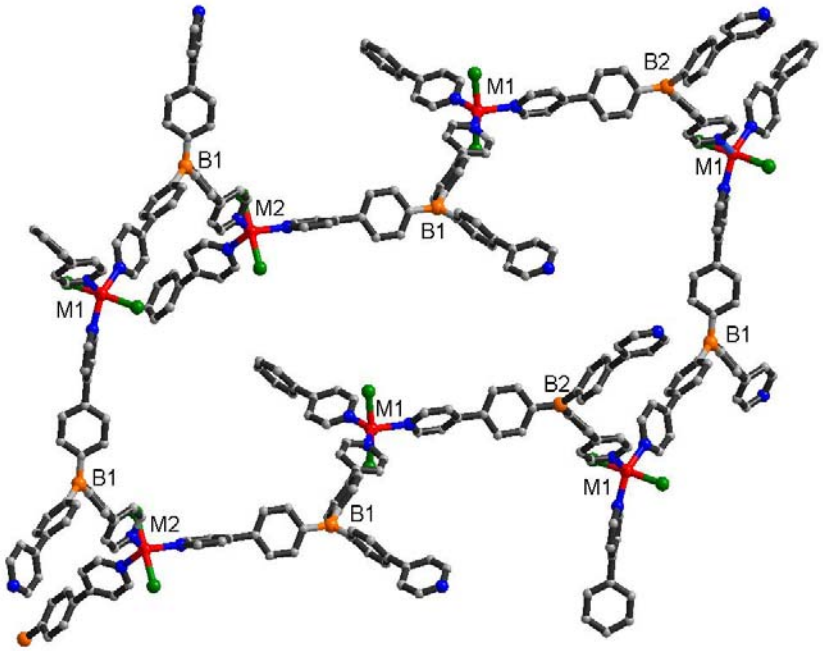
(a)



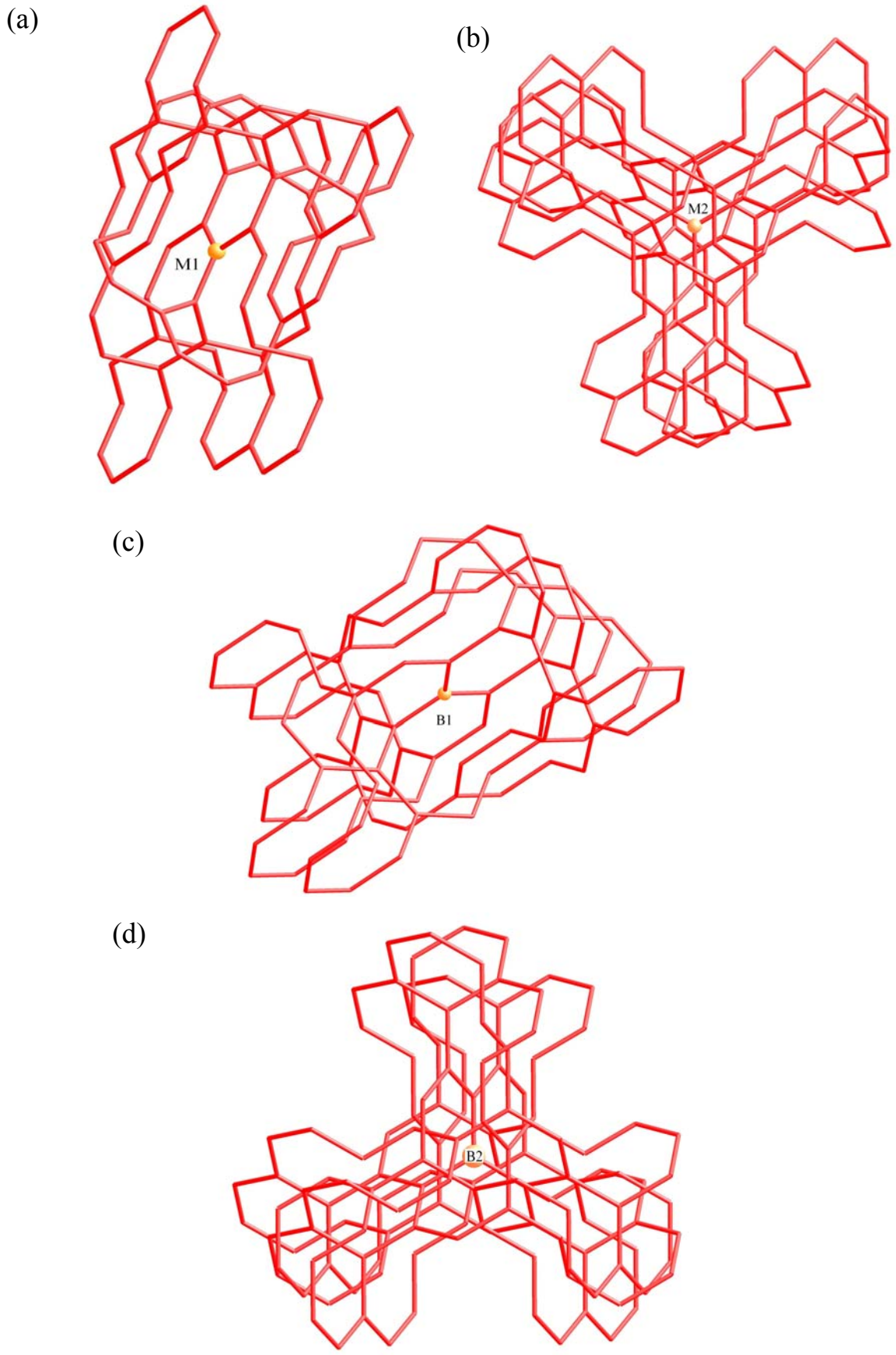
(b)



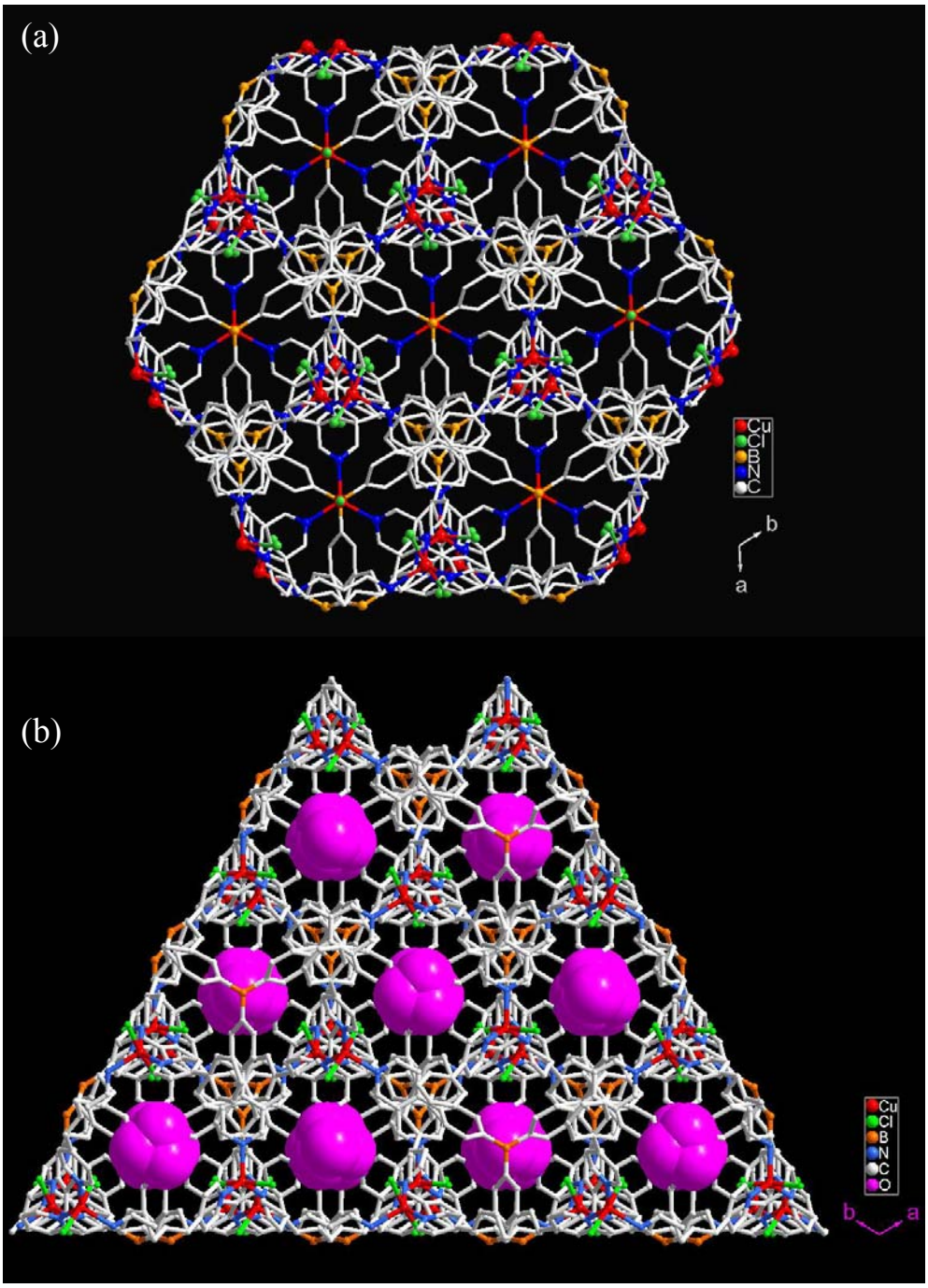
12. **Figure S4**. A view of one 14-membered ring containing seven metal and seven boron atoms in **1b, 1c, 2 and 3** (M = Cd, Cu or Co).



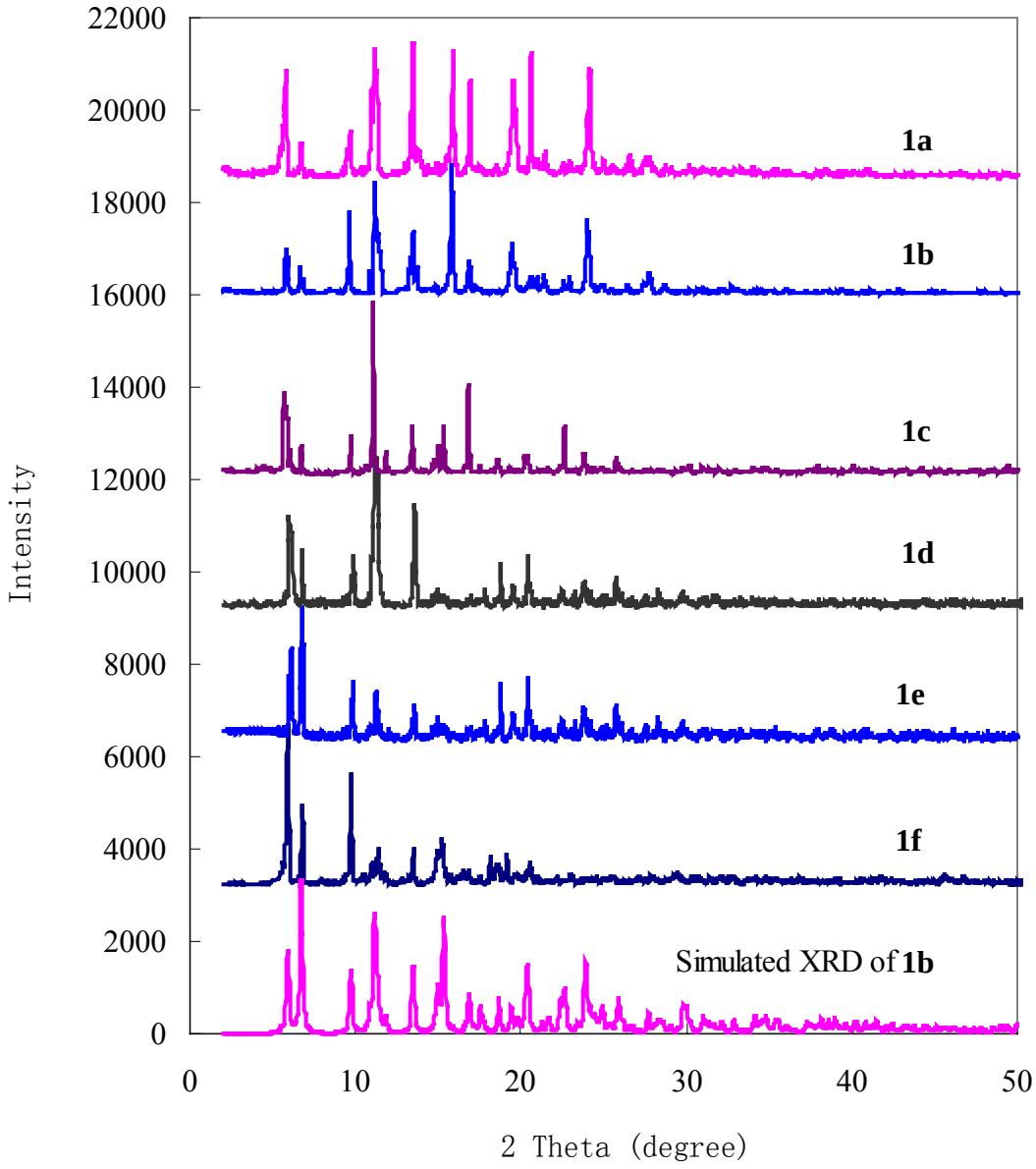
13. **Figure S5**. Schemes showing the (14, 3) network topologies around different nodes: M1 (a), M2 (a), B1 (c) and B2 (d) in **1b, 1c, 2 and 3**.

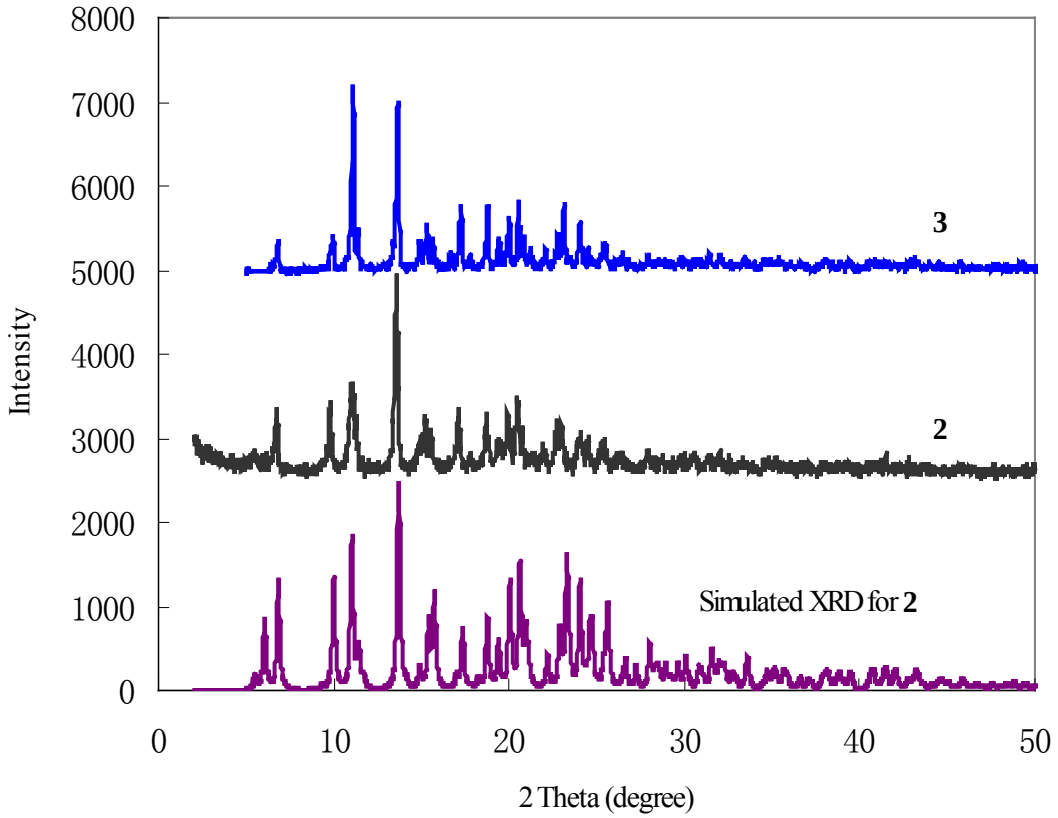


14**. Figure S6**. (a) A view of the 3D structure of **2** (the guest molecule has been omitted) and (b) A view of the 3D structure of **2** showing the guest molecules in space filling model.

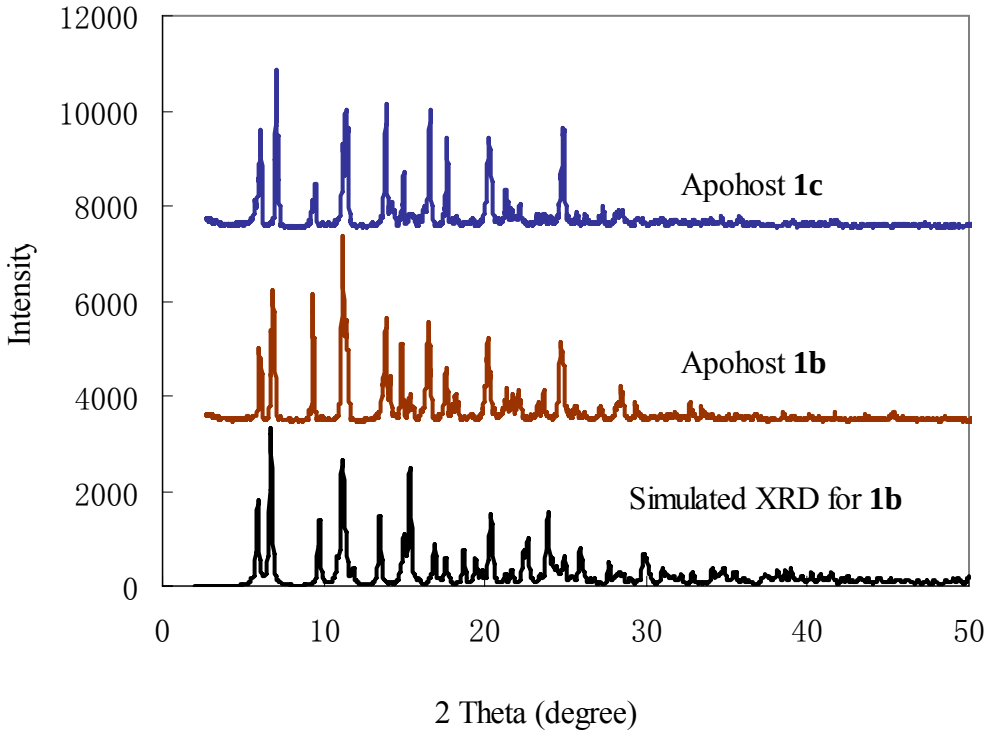


15**. Figure S7**. The PXRD patterns of **1a-1f** and the simulated PXRD pattern of **1b**.

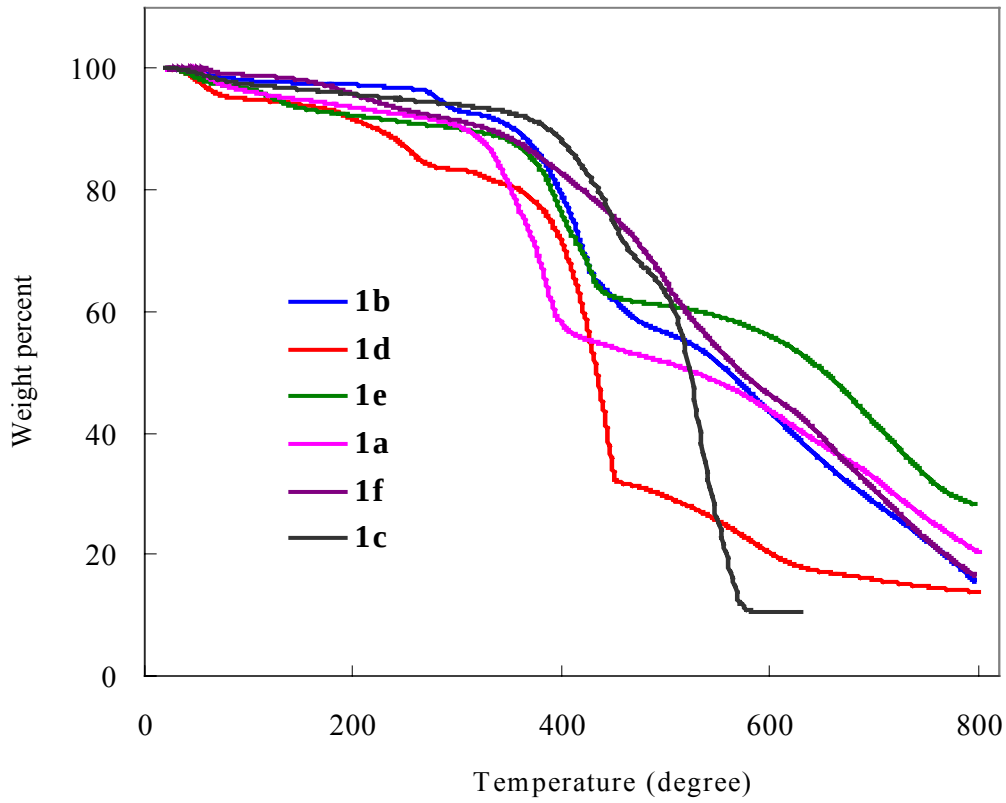




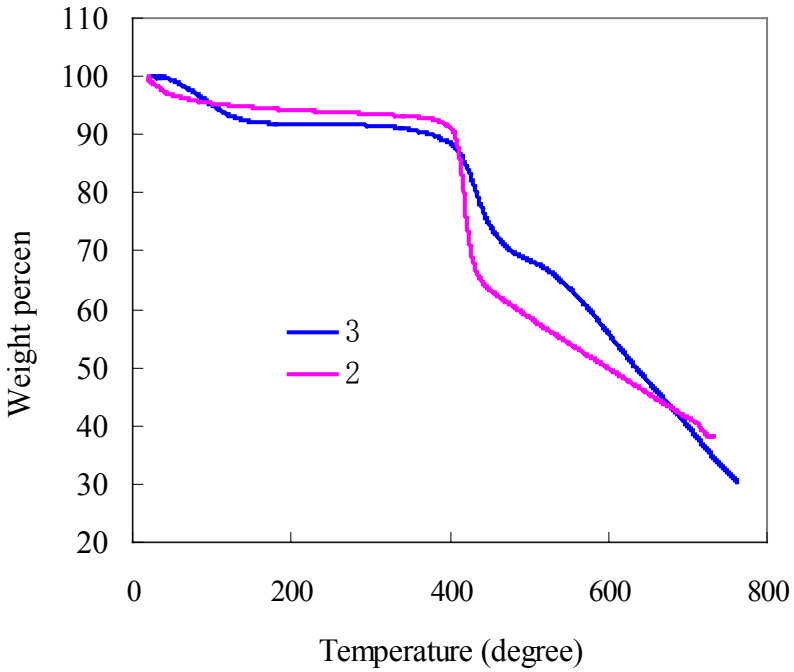
17**. Figure S9**. The PXRD patterns of apohosts **1b** and **1c** and the simulated XRD of **2**.



18. **Figure S10.** TGA curves of **1a-1f**.



19**. Figure S11.** TGA curves of **2** and **3**.



20. Figure S12. ESI-MS of Ligand **L**.