Electronic Supplementary Information (ESI)

Hydrothermal assembly, structures, topologies, luminescence, and magnetism of a novel series of coordination polymers driven by a trifunctional nicotinic acid building block

Jin-Zhong Gu [a,*], Xiao-Xiao Liang [a], Yan Cai [a], Jiang Wu [a], Zi-Fa Shi [a], Alexander M. Kirillov [b,*]

[a]Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000 (P. R. China)

[b]Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisbon, Portugal

Fax: (+86) 931-891-5196
E-mail: gujzh@lzu.edu.cn; kirillov@ist.utl.pt

Synthesis and analytical data for 2–13

Synthesis of [Mn(μ$_4$-cpna)(H$_2$O)]$_n$ (2). A mixture of $MnCl_2 \cdot 4H_2O$ (59.4 mg, 0.30 mmol), H_2cpna (77.7 mg, 0.30 mmol), NaOH (24 mg, 0.60 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Yellow block-shaped crystals of **2** were isolated manually, washed with distilled water, and dried (yield 62% based on H_2cpna). Anal. Calcd for $C_{13}H_9MnNO_6$: C, 47.29; H, 2.75; N, 4.24. Found: C, 47.13; H, 2.76; N, 4.21%. IR (KBr, cm^{-1}): 3595 w, 3067 w, 1605 s, 1534 s, 1502 w, 1457 w, 1400 s, 1335 s, 1296 m, 1252 w, 1206 m, 1155 m, 1097 w, 1033 w, 1007 w, 956 w, 917 w, 859 w, 775 m, 698 w, 652 w, 613 w, 543 w.

Synthesis of [Mn(μ$_4$-cpna)(H$_2$O)$_2$]$_n$ (3). A mixture of $MnCl_2 \cdot 4H_2O$ (59.4 mg, 0.3 mmol), H_2cpna (77.7 mg, 0.3 mmol), bpa (51.3 mg, 0.30 mmol), NaOH (24.0 mg, 0.60 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Yellow block-shaped crystals of **3** were isolated manually, washed with distilled water, and dried (yield 54% based on H_2cpna). Anal. Calcd for $C_{13}H_{11}MnNO_7$: C, 44.85; H, 3.18; N, 4.02. Found: C, 44.99; H, 3.16; N, 4.05%. IR (KBr, cm^{-1}): 3595 w, 3067 w, 1599 m, 1541 s, 1502 w, 1457 w, 1406 s, 1335 s, 1303 m, 1252 w, 1206 w, 1162 w, 1097 w, 1014 w, 956 w, 917 w, 859 w, 775 m, 698 w, 652 w, 613 w, 543 w.

Synthesis of [Mn(μ-cpna)(2,2′-bipy)(H$_2$O)$_2$]$_n$ (4). A mixture of $MnCl_2 \cdot 4H_2O$ (59.4 mg, 0.30 mmol), H_2cpna (77.7 mg, 0.30 mmol), 2,2′-bipy (46.8 mg, 0.30 mmol), NaOH (24.0 mg, 0.60 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Yellow block-shaped crystals of **4** were isolated manually, washed with distilled water, and dried (yield 60% based on H_2cpna). Anal. Calcd for $C_{23}H_{19}MnN_3O_7$: C, 54.77; H, 3.80; N, 8.33. Found: C, 54.56; H, 3.82; N, 8.29%. IR (KBr, cm^{-1}): 3343 w, 3118 w, 1605 s, 1554 m, 1496 w, 1438 w, 1380 s, 1309 m, 1264 w, 1245 w, 1199 w, 1155 w, 1097 w, 1058 w, 1019 w, 961 w, 897 w, 852 w,788 w, 769 m, 730 w,

698 w, 620 w, 499 w.

Synthesis of {[Ni(μ$_3$-cpna)(2,2′-bipy)(H$_2$O)]$_2$·H$_2$O}$_n$ (5). The preparation of **5** was similar to that of **4** except $NiCl_2·6H_2O$ (71.3 mg, 0.3 mmol) was used instead of $MnCl_2·4H_2O$. After cooling the reaction mixture to room temperature, green block-shaped crystals of **5** were isolated manually, washed with distilled water, and dried (yield 57% based on H_2cpna). Anal. Calcd for $C_{46}H_{36}Ni_2N_6O_{13}$: C, 55.35; H, 3.64; N, 8.42. Found: C, 55.58; H, 3.67; N, 8.39%. IR (KBr, cm^{-1}): 3543 w, 3060 w, 1599 s, 1561 s, 1444 m, 1393 s, 1367 w, 1284 w, 1245 m, 1206 w, 1162 w, 1090 w, 1058 w, 1007 w, 961 w, 884 w, 846 w, 795 w, 756 m, 737 w, 704 w, 647 w, 562 w, 517 w.

Synthesis of {[Cd(μ$_3$-cpna)(2,2′-bipy)]·2H$_2$O}$_n$ (6). Synthesis of **6** was similar to **4** except using $CdCl_2·H_2O$ (60.3 mg, 0.30 mmol) instead of $MnCl_2·4H_2O$. Colourless block-shaped crystals of **6** were obtained (yield 60% based on $CdCl_2·H_2O$). Anal. Calcd for $C_{23}H_{19}CdN_3O_7$: C, 49.17; H, 3.41; N, 7.48. Found: C, 48.93; H, 3.40; N, 7.52. IR (KBr, cm^{-1}): 3505 w, 3060 w, 1618 s, 1573 s, 1534 w, 1471 w, 1438 m, 1412 s, 1381 s, 1303 w, 1252 m, 1206 m, 1155 w, 1097 w, 1058 w, 1014 w, 961 w, 917 w, 859 w, 820 w, 769 m, 737 w, 698 w, 647 w, 518 w.

Synthesis of [Zn$_2$(μ-cpna)$_2$(2,2′-bipy)$_2$] (7). Synthesis of **7** was similar to **4** except using $ZnCl_2$ (40.9 mg, 0.30 mmol) instead of $MnCl_2·4H_2O$. Colorless block-shaped crystals of **7** were obtained (yield 53% based on H_2cpna). Anal. Calcd for $C_{46}H_{30}Zn_2N_6O_{10}$: C, 57.70; H, 3.16; N, 8.78. Found: C, 57.43; H, 3.18; N, 8.89. IR (KBr, cm^{-1}): 1629 s, 1596 s, 1557 m, 1440 s, 1404 s, 1372 s, 1303 m, 1249 m, 1212 w, 1158 w, 1097 w, 1061 w, 1028 w, 956 w, 908 w, 865 w, 829 w, 804 w, 785 w, 771 m, 735 w, 709 w, 698 w, 651 w, 637 w, 514 w.

Synthesis of [Cu(μ-cpna)(2,2′-bipy)(H$_2$O)]$_n$ (8). Synthesis of **8** was similar to **4** except using $CuCl_2·H_2O$ (45.7 mg, 0.30 mmol) instead of $MnCl_2·4H_2O$. Blue block-shaped crystals of **8** were obtained (yield 55% based on H_2cpna). Anal. Calcd for $C_{23}H_{17}CuN_3O_6$: C, 55.81; H, 3.46; N, 8.49. Found: C, 56.07; H, 3.49; N, 8.41. IR (KBr, cm^{-1}): 3444 w, 3059 w, 1607 m, 1564 m, 1497 w, 1450 w, 1390 s, 1377 m, 1306 w, 1260 w,1209 w, 1148 w, 1057 w, 1012 w, 961 w, 901 w, 855 w, 784 m, 733 w, 698 w, 662 w, 576 w.

Synthesis of {[Mn(μ-cpna)(phen)$_2$]·6H$_2$O}$_n$ (9). Synthesis of **9** was similar to **4** except using phen (20.0 mg, 0.30 mmol) instead of 2,2′-bipy. Yellow block-shaped crystals of **9** were obtained (yield 30% based on H$_2$cpna). Anal. Calcd for $C_{37}H_{35}MnN_5O_{11}$: C, 56.93; H, 4.52; N, 8.97. Found: C, 57.03; H, 4.53; N, 9.02. IR (KBr, cm^{-1}): 3537 w, 3369 w, 3131 w, 1599 m, 1561 s, 1496 w, 1432 m, 1400 w, 1361 s, 1264 m, 1162 w, 1104 w, 1033 w, 994 w, 924 w, 878 w, 795 m, 756 w, 691 m, 647 w, 557 w.

Synthesis of {[Ni(μ$_3$-cpna)(phen)(H$_2$O)]·H$_2$O}$_n$ (10). Synthesis of **10** was similar to **9** except using NiCl$_2$·6H$_2$O (71.3 mg, 0.30 mmol) instead of MnCl$_2$·4H$_2$O. Green block-shaped crystals of **10** were obtained (yield 57% based on H$_2$cpna). Anal. Calcd for $C_{25}H_{19}NiN_3O_7$: C, 56.43; H, 3.60; N, 7.90. Found: C, 56.28; H, 3.62; N, 7.94. IR (KBr, cm^{-1}): 3685 w, 3305 w, 3067 w, 1605 s, 1566 s, 1509 w, 1444 w, 1425 m, 1393 s, 1290 w,1245 w, 1200 m, 1162 w, 1103 w, 1046 w, 1007 w, 961 w, 897 w, 852 m, 788 m, 730 w, 685 w, 633 w, 550 w.

Synthesis of [Zn$_2$(μ-cpna)$_2$(phen)$_2$] (11). Synthesis of **11** was similar to **9** except using ZnCl$_2$ (40.9 mg, 0.30 mmol) instead of MnCl$_2$·4H$_2$O. Colourless block-shaped crystals of **11** were obtained (yield 65% based on H$_2$cpna). Anal. Calcd for $C_{25}H_{15}ZnN_3O_5$: C, 59.72; H, 3.01; N, 8.36. Found: C, 59.91; H, 2.99; N, 8.41. IR (KBr, cm^{-1}): 1618 m, 1599 s, 1560 s, 1509 w, 1451 w, 1419 s, 1380 s, 1303 w, 1245 w, 1206 w, 1155 w, 1096 w, 1013 w, 956 w, 904 w, 852 m, 788 m, 730 m, 646 w, 504 w.

Synthesis of {[Pb(μ$_3$-cpna)(phen)]·H$_2$O}$_n$ (12). Synthesis of **12** was similar to **9** except using PbCl$_2$ (83.4 mg, 0.30 mmol) instead of MnCl$_2$·4H$_2$O. Colourless block-shaped crystals of **12** were isolated manually, washed with distilled water and dried (yield 65% based on H$_2$cpna). Anal. Calcd for $C_{25}H_{17}PbN_3O_6$: C, 45.32; H, 2.58; N, 6.34. Found: C, 45.17; H, 2.55; N, 6.33%. IR (KBr, cm^{-1}): 3459 w, 3048 w, 1593 s, 1547 s, 1457 w, 1425 w, 1381 s, 1309 w, 1258 m, 1206 w, 1162 w, 1090 w, 1007 w, 956 w, 891 w, 859 m, 832 w, 781 m, 723 w, 685 w, 633 w, 608 w, 537 w.

Synthesis of [Ni(μ$_3$-cpna)(4,4′-bipy)$_{0.5}$(H$_2$O)]$_n$ (13). Synthesis of **13** was similar to **5** except using 4,4′-bipy (46.8 mg, 0.30 mmol) instead of 2,2′-bipy. Green block-shaped crystals of **13** were isolated manually, washed with distilled water and dried (yield 55% based on H$_2$cpna). Anal. Calcd for $C_{18}H_{13}NiN_2O_6$: C, 52.47; H, 3.18; N, 6.80. Found: C, 52.31; H, 3.21; N, 6.84%. IR (KBr, cm^{-1}): 3258

w, 3062 w, 1609 s, 1544 s, 1467 m, 1401 s, 1297 w, 1264 m, 1206 w, 1160 w, 1075 w, 1010 w, 971 w, 906 w, 847 m, 821 w, 769 m, 704 w, 625 w, 554 w.

Table S1. Summary of attempted reactions.

Reaction	Reaction mixture composition (molar ratio)	Results[a]
1	$NiCl_2 \cdot 6H_2O$, H_2cpna, NaOH (1:2:2)	no crystals
2	$CdCl_2 \cdot H_2O$, H_2cpna, NaOH (1:2:2)	no crystals
3	$ZnCl_2$, H_2cpna, NaOH (1:2:2)	no crystals
4	$CuCl_2 \cdot H_2O$, H_2cpna, NaOH (1:2:2)	no crystals
5	$PbCl_2$, H_2cpna, NaOH (1:2:2)	no crystals
6	$NiCl_2 \cdot 6H_2O$, H_2cpna, NaOH (1:1:2)	no crystals
7	$CdCl_2 \cdot H_2O$, H_2cpna, NaOH (1:1:2)	no crystals
8	$ZnCl_2$, H_2cpna, NaOH (1:1:2)	no crystals
9	$CuCl_2 \cdot H_2O$, H_2cpna, NaOH (1:1:2)	no crystals
10	$PbCl_2$, H_2cpna, NaOH (1:1:2)	no crystals
11	$CoCl_2 \cdot 6H_2O$, H_2cpna, bpa, NaOH (1:1:1:2)	no crystals
12	$NiCl_2 \cdot 6H_2O$, H_2cpna, bpa, NaOH (1:1:1:2)	no crystals
13	$CdCl_2 \cdot H_2O$, H_2cpna, bpa, NaOH (1:1:1:2)	no crystals
14	$ZnCl_2$, H_2cpna, bpa, NaOH (1:1:1:2)	no crystals
15	$CuCl_2 \cdot H_2O$, H_2cpna, bpa, NaOH (1:1:1:2)	no crystals
16	$PbCl_2$, H_2cpna, bpa, NaOH (1:1:1:2)	no crystals
17	$CoCl_2 \cdot 6H_2O$, H_2cpna, 2,2'-bipy, NaOH (1:1:1:2)	no crystals
18	$PbCl_2$, H_2cpna, 2,2'-bipy, NaOH (1:1:1:2)	no crystals
19	$CoCl_2 \cdot 6H_2O$, H_2cpna, phen, NaOH (1:1:1:2)	no crystals
20	$CdCl_2 \cdot H_2O$, H_2cpna, phen, NaOH (1:1:1:2)	no crystals
21	$CuCl_2 \cdot H_2O$, H_2cpna, phen, NaOH (1:1:1:2)	no crystals
22	$CoCl_2 \cdot 6H_2O$, H_2cpna, 4,4'-bipy, NaOH (1:1:1:2)	no crystals
23	$MnCl_2 \cdot 4H_2O$, H_2cpna, 4,4'-bipy, NaOH (1:1:1:2)	no crystals
24	$CdCl_2 \cdot H_2O$, H_2cpna, 4,4'-bipy, NaOH (1:1:1:2)	no crystals
25	$ZnCl_2$, H_2cpna, 4,4'-bipy, NaOH (1:1:1:2)	no crystals
26	$CuCl_2 \cdot H_2O$, H_2cpna, 4,4'-bipy, NaOH (1:1:1:2)	no crystals
27	$PbCl_2$, H_2cpna, 4,4'-bipy, NaOH (1:1:1:2)	no crystals

[a]No crystals means that the crystallization did not occur or no crystals of sufficient quality were obtained to perform structural determination by single-crystal X-ray diffraction.

Table S2. Selected bond lengths [Å] and angles [°] for the compounds **1**–**13**[a].

1					
Co(1)-O(1)	2.0852(17)	Co(1)-O(1)#1	2.0852(17)	Co(1)-O(4)#2	2.1267(18)
Co(1)-O(4)#3	2.1267(18)	Co(1)-N(1)#4	2.1111(19)	Co(1)-N(1)#5	2.1111(19)
O(1)-Co(1)-O(4)#2	94.55(7)	O(1)-Co(1)-N(1)#4	90.06(7)	O(1)-Co(1)-O(4)#3	85.45(7)
O(1)-Co(1)-N(1)#5	89.94(7)	O(4)#2-Co(1)-N(1)#4	86.49(7)	O(4)#2-Co(1)-N(1)#5	93.51(7)
O(4)#3-Co(1)-N(1)#4	93.51(7)				
2					
Mn(1)-O(1)	2.2711(14)	Mn(1)-O(2)	2.2152(15)	Mn(1)-O(5)#1	2.2359(15)
Mn(1)-O(5)#2	2.0917(15)	Mn(1)-N(1)#3	2.2149(17)	Mn(1)-O(6)	2.1381(17)
O(1)-Mn(1)-O(2)	58.75(5)	O(1)-Mn(1)-O(6)	89.38(6))	O(1)-Mn(1)-O(5)#1	90.14(6)
O(1)-Mn(1)-O(5)#2	103.03(6)	O(1)-Mn(1)-N(1)#3	149.93(6)	O(2)-Mn(1)-O(6)	102.03(7)
O(2)-Mn(1)-O(5)#1	84.84(6)	O(2)-Mn(1)-O(5)#2	154.40(6)	O(2)-Mn(1)-N(1)#3	91.98(6)
O(5)#1-Mn(1)-O(6)	171.62(7)	O(5)#2-Mn(1)-O(6)	95.07(7)	O(6)-Mn(1)-N(1)#3	90.46(6)
O(5)#1-Mn(1)-O(5)#2	76.89(6)	O(5)#1-Mn(1)-N(1)#3	94.14(6)	O(5)#2-Mn(1)-N(1)#3	106.93(6)
Mn(1)-O(5)#2-Mn(1)#4	103.11(6)				
3					
Mn(1)-O(1)	2.130(4)	Mn(1)-O(5)#1	2.259(4)	Mn(1)-O(5)#2	2.205(4)
Mn(1)-O(6)	2.189(6)	Mn(1)-O(7)	2.178(5)	Mn(1)-N(1)#3	2.278(5)
O(1)-Mn(1)-O(6)	94.06(18)	O(1)-Mn(1)-O(7)	95.04(16)	O(1)-Mn(1)-N(1)#3	86.27(16)
O(1)-Mn(1)-O(5)#1	95.22(15)	O(1)-Cd(1)-O(5)#2	171.82(16)	O(6)-Mn(1)-O(7)	86.4(2)
O(6)-Mn(1)-N(1)#3	91.6(2)	O(5)#1-Mn(1)-O(6)	170.29(18)	O(5)#2-Mn(1)-O(6)	93.49(18)
O(7)-Mn(1)-N(1)#3	177.68(17)	O(5)#1-Mn(1)-O(7)	95.62(16)	O(5)#2-Mn(1)-O(7)	88.55(16)
O(5)#1-Mn(1)-N(1)#3	86.16(16)	O(5)#2-Mn(1)-N(1)#3	90.39(16)	O(5)#2-Mn(1)-O(5)#1	77.10(14)
Mn(1)-O(5)#1-Mn(1)#4	102.90(16)				
4					
Mn(1)-O(1)	2.124(2)	Mn(1)-O(4)#1	2.099(2)	Mn(1)-O(6)	2.289(2)
Mn(1)-O(7)	2.198(2)	Mn(1)-N(2)	2.289(3)	Mn(1)-N(3)	2.244(2)
O(1)-Mn(1)-O(6)	172.86(8)	O(1)-Mn(1)-O(7)	93.22(8)	O(1)-Mn(1)-N(2)	87.65(8)
O(1)-Mn(1)-N(3)	96.83(9)	O(1)-Mn(1)-O(4)#1	88.97(8)	O(6)-Mn(1)-O(7)	84.14(8)
O(6)-Mn(1)-N(2)	98.94(8)	O(6)-Mn(1)-N(3)	87.89(9)	O(4)#1-Mn(1)-O(6)	85.35(8)
O(7)-Mn(1)-N(2)	89.43(8)	O(7)-Mn(1)-N(3)	158.43(9)	O(4)#1-Mn(1)-O(7)	105.42(8)
N(3)-Mn(1)-N(2)	72.02(10)	O(4)#1-Mn(1)-N(2)	164.94(9)	O(4)#1-Mn(1)-N(3)	93.84(10)
5					
Ni(1)-O(1)#1	2.067(2)	Ni(1)-O(5)#2	2.047(2)	Ni(1)-O(6)	2.146(2)
Mn(1)-N(1)	2.109(2)	Ni(1)-N(2)	2.063(2)	Ni(1)-N(3)	2.067(2)
O(6)-Ni(1)-N(1)	175.20(7)	O(6)-Ni(1)-N(2)	90.27(8)	O(6)-Ni(1)-N(3)	90.00(8)
O(5)#2-Ni(1)-O(6)	89.59(7)	O(1)#1-Ni(1)-O(6)	88.81(7)	N(1)-Ni(1)-N(2)	94.32(8)
N(1)-Ni(1)-N(3)	92.28(8)	O(5)#2-Ni(1)-N(1)	88.56(8)	O(1)#1-Ni(1)-N(1)	86.77(7)
N(2)-Ni(1)-N(3)	78.65(9)	O(5)#2-Ni(1)-N(2)	95.70(8)	O(1)#1-Ni(1)-N(2)	174.26(8)
O(5)#2-Ni(1)-N(3)	174.34(8)	O(1)#1-Ni(1)-N(3)	95.68(8)	O(1)#1-Ni(1)-O(5)#2	89.96(7)
6					
Cd(1)-O(2)#1	2.237(3)	Cd(1)-O(4)#2	2.441(3)	Cd(1)-O(5)#2	2.294(2)
Cd(1)-N(1)	2.298(3)	Cd(1)-N(2)	2.452(3)	Cd(1)-N(3)	2.355(3)
N(1)-Cd(1)-N(2)	88.86(11)	N(1)-Cd(1)-N(3)	105.43(11)	O(2)#1-Cd(1)-N(1)	90.95(11)
O(4)#2-Cd(1)-N(1)	87.57(11)	O(5)#2-Cd(1)-N(1)	142.64(9)	N(2)-Cd(1)-N(3	68.14(10)
O(2)#1-Cd(1)-N(2)	152.33(11)	O(4)#2-Cd(1)-N(2)	81.30(10)	O(5)#2-Cd(1)-N(2)	89.24(9)
O(2)#1-Cd(1)-N(3)	85.31(11)	O(4)#2-Cd(1)-N(3)	146.14(10)	O(5)#2-Cd(1)-N(3)	108.37(9)
O(2)#1-Cd(1)-O(4)#2	126.35(11)	O(2)#1-Cd(1)-O(5)#2	107.11(10)	O(4)#2-Cd(1)-O(5)#2	55.29(9)
7					

Zn(1)-O(1)	2.0058(1)	Zn(1)-O(2)	2.3803(1)	Zn(1)-N(2)	2.0681(1)
Zn(1)-N(3)	2.0864(1)	Zn(1)-O(5)#1	1.9504(1)		
O(1)-Zn(1)-O(2)	59.49(1)	O(1)-Zn(1)-N(2)	120.80(1)	O(1)-Zn(1)-N(3)	103.18(1)
O(1)-Zn(1)-O(5)#1	131.58(1)	O(2)-Zn(1)-N(2)	93.42(1)	O(2)-Zn(1)-N(3)	154.33(1)
O(2)-Zn(1)-O(5)#1	103.37(1)	N(2)-Zn(1)-N(3)	79.22(1)	O(5)#1-Zn(1)-N(2)	104.00(1)
O(5)#1-Zn(1)-N(3)	102.27(1)				

8

Cu(1)-O(1)	1.9516(2)	Cu(1)-O(2)	2.9096(3)	Cu(1)-O(5)#1	1.9273(2)
Cu(1)-O(6)	2.2504(2)	Cu(1)-N(2)	2.0170(2)	Cu(1)-N(3)	1.9923(2)
O(1)-Cu(1)-O(2)	50.01(1)	O(1)-Cu(1)-O(6)	98.90(1)	O(1)-Cu(1)-N(2)	164.16(1)
O(1)-Cu(1)-N(3)	94.11(1)	O(1)-Cu(1)-O(5)#1	90.03(1)	O(2)-Cu(1)-O(6)	148.36(1)
O(2)-Cu(1)-N(2)	114.40(1)	O(2)-Cu(1)-N(3)	87.13(1)	O(2)-Cu(1)-O(5)#1	90.35(1)
O(6)-Cu(1)-N(2)	96.21(1)	O(6)-Cu(1)-N(3)	90.03(1)	O(5)#1-Cu(1)-O(6)	96.05(1)
N(2)-Cu(1)-N(3)	81.12(1)	O(5)#1-Cu(1)-N(2)	93.09(1)	O(5)#1-Cu(1)-N(3)	172.04(1)

9

Mn(1)-O(1)	2.1049(2)	Mn(1)-O(1)#1	2.1049(2)	Mn(1)-N(2)	2.3284(2)
Mn(1)-N(3)	2.2403(2)	Mn(1)-N(2)#1	2.3284(2)	Mn(1)-N(3)#1	2.2403(2)
O(1)-Mn(1)-N(2)	168.05	O(1)-Mn(1)-N(3)	95.90	O(1)-Mn(1)-O(1)#1	89.73
O(1)-Mn(1)-N(2)#1	88.69	O(1)-Mn(1)-N(3)#1	102.72	N(2)-Mn(1)-N(3)	72.93
N(2)-Mn(1)-N(2)#1	95.24	N(2)-Mn(1)-N(3)#1	89.23	N(3)-Mn(1)-N(3)#1	153.67

10

Ni(1)-O(2)	2.055(3)	Ni(1)-O(4)#1	2.044(3)	Ni(1)-O(6)	2.133(3)
Ni(1)-N(1)#2	2.101(3)	Ni(1)-N(2)	2.078(3)	Ni(1)-N(3)	2.082(4)
O(2)-Ni(1)-O(6)	88.52(11)	O(2)-Ni(1)-N(2)	174.27(14)	O(2)-Ni(1)-N(3)	94.50(12)
O(2)-Ni(1)-N(1)#2	87.36(10)	O(2)-Ni(1)-O(4)#1	90.93(11)	O(6)-Ni(1)-N(2)	91.16(12)
O(6)-Ni(1)-N(3)	89.55(13)	O(6)-Ni(1)-N(1)#2	175.50(11)	O(6)-Ni(1)-O(4)#1	89.91(12)
N(2)-Ni(1)-N(3)	79.78(14)	N(1)#2-Ni(1)-N(2)	93.12(11)	O(4)#1-Ni(1)-N(2)	94.78(13)
N(1)#2-Ni(1)-N(3)	92.57(13)	O(4)#1-Ni(1)-N(3)	174.53(12)	N(1)#2-Ni(1)-O(4)#1	88.36(12)

11

Zn(1)-O(1)	1.952(4)	Zn(1)-O(2)	2.614(4)	Zn(1)-O(4)#1	2.008(5)
Zn(1)-O(5)#1	2.561(5)	Zn(1)-N(2)	2.074(4)	Zn(1)-N(3)	2.077(5)
O(1)-Zn(1)-O(2)	55.36(13)	O(1)-Zn(1)-N(2)	117.30(16)	O(1)-Zn(1)-N(3)	111.54(15)
O(1)-Zn(1)-O(4)#1	134.94(16)	O(1)-Zn(1)-O(5)#1	85.66(14)	O(2)-Zn(1)-N(2)	88.59(16)
O(2)-Zn(1)-N(3)	156.17(17)	O(2)-Zn(1)-O(4)#1	103.47(16)	O(1)-Zn(1)-O(5)#1	96.25(15)
N(2)-Zn(1)-N(3)	80.54(17)	O(4)#1-Zn(1)-N(2)	99.17(17)	O(5)#1-Zn(1)-N(2)	154.22(15)
O(4)#1-Zn(1)-N(3)	99.19(18)	O(5)#1-Zn(1)-N(3)	102.77(16)	O(4)#1-Zn(1)-O(1)#1	55.07(15)

12

Pb(1)-O(1)	2.710(4)	Pb(1)-O(2)	2.328(4)	Pb(1)-O(4)#1	2.647(4)
Pb(1)-O(5)#1	2.498(3)	Pb(1)-N(2)	2.567(4)	Pb(1)-N(3)	2.674(5)
Pb(1)-O(4)#2	3.074(3)				
O(1)-Pb(1)-O(2)	51.30(11)	O(1)-Pb(1)-N(2)	119.39(12)	O(1)-Pb(1)-N(3)	79.14(12)
O(1)-Pb(1)-O(4)#1	72.13(11)	O(1)-Pb(1)-O(5)#1	114.21(13)	O(2)-Pb(1)-N(2)	76.04(12)
O(2)-Pb(1)-N(3)	80.63(12)	O(2)-Pb(1)-O(4)#1	75.45(12)	O(2)-Pb(1)-O(5)#1	82.09(14)
N(3)-Pb(1)-N(2)	63.04(14)	N(2)-Pb(1)-O(4)#1	125.89(14)	N(2)-Pb(1)-O(5)#1	80.54(15)
O(4)#2-Pb(1)-O(1)	74.94(10)	O(4)#2-Pb(1)-O(2)	125.61(11)	O(4)#2-Pb(1)-O(4)#1	97.60(10)
O(4)#2-Pb(1)-O(5)#1	134.44(10)	O(4)#2-Pb(1)-N(2)	136.23(12)	O(4)#2-Pb(1)-N(3)	82.05(12)
N(3)-Pb(1)-O(4)#1	150.21(12)	N(3)-Pb(1)-O(5)#1	142.45(14)	O(4)#1-Pb(1)-O(5)#1	50.72(13)

13

Ni(1)-O(1)#1	2.150(2)	Ni(1)-O(2)#1	2.153(2)	Ni(1)-O(5)#2	2.062(2)
Ni(1)-O(6)	2.039(2)	Ni(1)-N(1)	2.050(2)	Ni(1)-N(2)	2.104(2)

O(6)-Ni(1)-N(1)	94.97(9)	O(6)-Ni(1)-N(2)	90.02(9)	O(1)#1-Ni(1)-O(6)	106.40(8)
O(2)#1-Ni(1)-O(6)	165.89(8)	O(5)#2-Ni(1)-O(6)	90.10(9)	N(1)-Ni(1)-N(2)	95.74(9)
O(1)#1-Ni(1)-N(1)	157.46(8)	O(2)#1-Ni(1)-N(1)	96.52(8)	O(5)#2-Ni(1)-N(1)	88.75(9)
O(1)#1-Ni(1)-N(2)	91.42(9)	O(2)#1-Ni(1)-N(2)	96.92(8)	O(5)#2-Ni(1)-N(2)	175.49(9)
O(1)#1-Ni(1)-O(2)#1	61.33(7)	O(1)#1-Ni(1)-O(5)#2	84.21(9)	O(2)#1-Ni(1)-O(5)#2	82.02(8)

[a] Symmetry transformations used to generate equivalent atoms: #1 –*x*+1, –*y*, –*z*; #2 *x*, *y*, *z*–1; #3 –*x*+1, –*y*, –*z*+1; #4 –*x*+3/2, *y*–1/2, –*z*+1/2; #5 *x*–1/2, –*y*+1/2, *z*–1/2 for **1**; #1 –*x*, *y*, –*z*+1/2; #2 *x*, –*y*+2, *z*+1/2; #3 *x*–1/2, *y*+1/2, *z*; #4 –*x*, –*y*+2, –*z*+1 for **2**; #1 –*x*+1/2, *y*+1/2, –*z*+3/2; #2 *x*–3/2, –*y*+3/2, *z*–1/2; #3 –*x*–1/2, *y*+1/2, –*z*+3/2; #4 –*x*–1, –*y*+2, –*z*+1 for **3**; #1 *x*, *y*+1, *z* for **4**; #1 –*x*+1/2, –*y*+5/2, –*z*+1; #2 *x*, –*y*+2, *z*+1/2 for **5**; #1 –*x*, *y*–1/2, –*z*+1/2; #2 –*x*+1, *y*–1/2, *z*–1 for **6**; #1 –*x*+1, –*y*+1, –*z* for **7**; #1 –*x*+2, *y*+1/2, –*z*+1/2 for **8**; #1 –*x*+3/2, –*y*+1/2, –*z* for **9**; #1 –*x*+3/2, *y*–1/2, –*z*+1; #2 –*x*+1, –*y*+1, –*z*+1 for **10**; #1 –*x*+2, –*y*+1, –*z*+1 for **11**; #1 –*x*+1/2, *y*–1/2, –*z*+1/2; #2 *x*+1/2, –*y*+1/2, *z*+1/2 for **12**; #1 *x*–1, *y*, *z*; #2 –*x*+1, –*y*+2, –*z*+1 for **13**.

Table S3. Hydrogen bonds in crystal packing [Å, °] of **1–6**, **8–10**, **12**, and **13**.

Complexes	D-H…A	*d*(D-H)	*d*(H…A)	*d*(D…A)	∠DHA	Symmetry code
1	O(2)-H(2)···O(5)	0.82	1.67	2.449(4)	159.0	*x*, *y*, *z*-1
2	O(6)-H(1W)···O(1)	0.87	1.88	2.733(2)	168	-*x*+1/2, -*y*+5/2, -*z*+1
	O(6)-H(2W)···O(4)	0.86	1.81	2.668(2)	170	-*x*, *y*+1, -*z*+1/2
3	O(6)-H(1W)···O(2)	0.87	1.85	2.716(7)	169	*x*-1, *y*, *z*
	O(6)-H(2W)···O(3)	0.77	2.57	3.046(7)	122	-*x*-1/2, *y*-1/2, -*z*+3/2
	O(7)-H(3W) ···O(4)	0.87	2.25	2.957(6)	139.0	*x*-3/2, -*y*+3/2, *z*-1/2
	O(7)-H(4W) ···O(4)	0.87	2.06	2.722(6)	132.0	
4	O(6)-H(1W)···O(5)	0.87	1.84	2.695(3)	169	*x*, *y*+1, *z*
	O(6)-H(2W)···O(2)	0.87	1.88	2.710(3)	158	*x*+1, *y*, *z*
	O(7)-H(3W)···N(1)	0.87	1.95	2.820(3)	176.0	-*x*, -*y*+1, -*z*
	O(7)-H(4W)···O(2)	0.871	1.80	2.667(3)	170	*x*+1, *y*, *z*
5	O(6)-H(1W)···O(2)	0.85	1.88	2.724(2)	180.0	-*x*+1/2, -*y*+5/2, -*z*+1
	O(6)-H(2W)···O(4)	0.87	1.89	2.674(3)	148.0	*x*, -*y*+2, *z*+1/2
	O(7)-H(1W)···O(4)	0.85	1.89	2.740(3)	179.0	-*x*+1, -*y*+1, -*z*+1
	O(7)-H(2W)···O(4)	0.85	1.89	2.740(3)	179.0	*x*, -*y*+1, *z*+1/2
6	O(6)-H(1W)···O(4)	0.85	2.05	2.898(7)	180.0	-*x*+1, *y*+1/2, -*z*+1/2
	O(6)-H(2W)···O(7)	0.62	2.38	2.816(10)	130.0	
	O(7)-H(3W)···O(1)	0.62	2.35	2.770(7)	127.0	-*x*, *y*+1/2, -*z*+1/2
	O(7)-H(4W)···O(1)	0.86	1.91	2.770(7)	177.0	-*x*, *y*+1/2, -*z*+1/2
8	O(6)-H(1W)···O(2)	0.88	2.27	2.8039(3)	119.0	*x*-1, *y*, *z*
	O(6)-H(2W)···O(4)	0.87	1.93	2.6479(3)	138.0	-*x*+2, *y*+1/2, -*z*+1/2
9	N(1B)-H(5A)···O(5)	0.97	2.29	3.163(2)	14900	-*x*+1/2, -*y*+1/2, *z*
10	O(6)-H(1W)···O(1)	0.81	1.93	2.703(4)	161	
	O(6)-H(2W)···O(5)	0.92	1.87	2.736(5)	158	-*x*-3/2, *y*-1/2, -*z*+1
	O(7)-H(3W)···O(5)	0.82	1.97	2.779(5)	172.0	*x*-1/2, *y*-1/2, *z*-1/2
	O(8)-H(5W)···O(5)	0.81	2.01	2.811(8)	171.0	-*x*-3/2, *y*-1/2, -*z*+1
12	O(6)-H(2W)···O(1)	0.85	2.08	2.874(11)	155.0	
13	O(6)-H(1W)···O(1)	0.80	1.90	2.690(3)	177	-*x*+2, -*y*+1, -*z*+2
	O(6)-H(2W)···O(4)	0.90	1.66	2.551(3)	167	-*x*+1, -*y*+2, -*z*+1

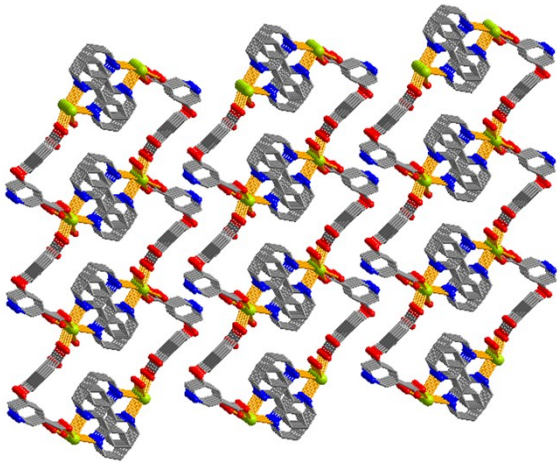


Fig. S1. 3D supramolecular arrangement in the crystal packing of **4** seen along the *a* axis.

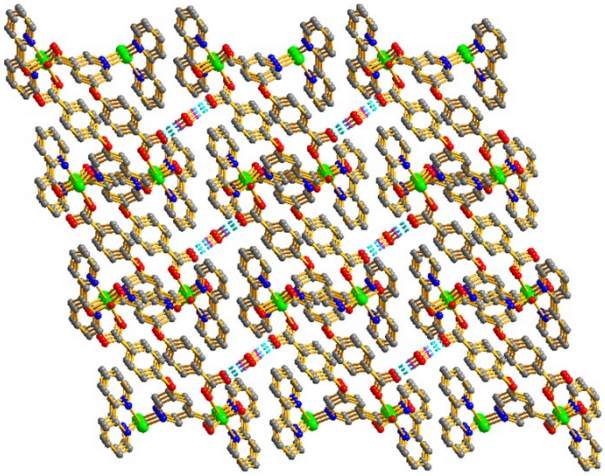


Fig. S2. 3D supramolecular net in **5** seen along the *b* axis (blue lines present the H-bonds).

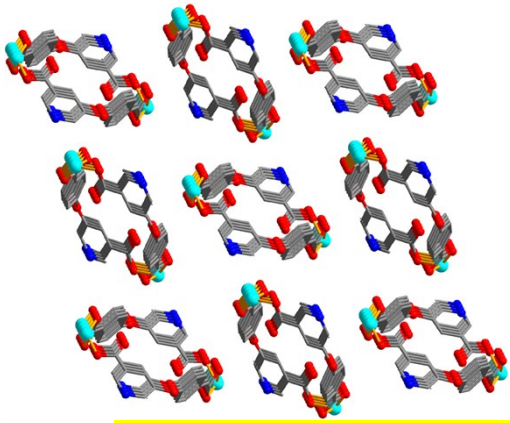


Fig. S3. 3D supramolecular architecture viewed along the *ac* plane in **7**.

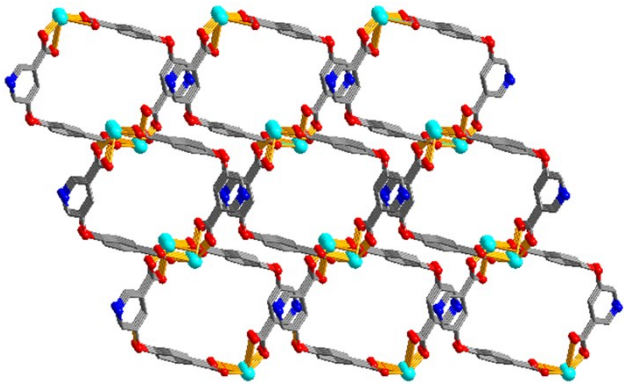
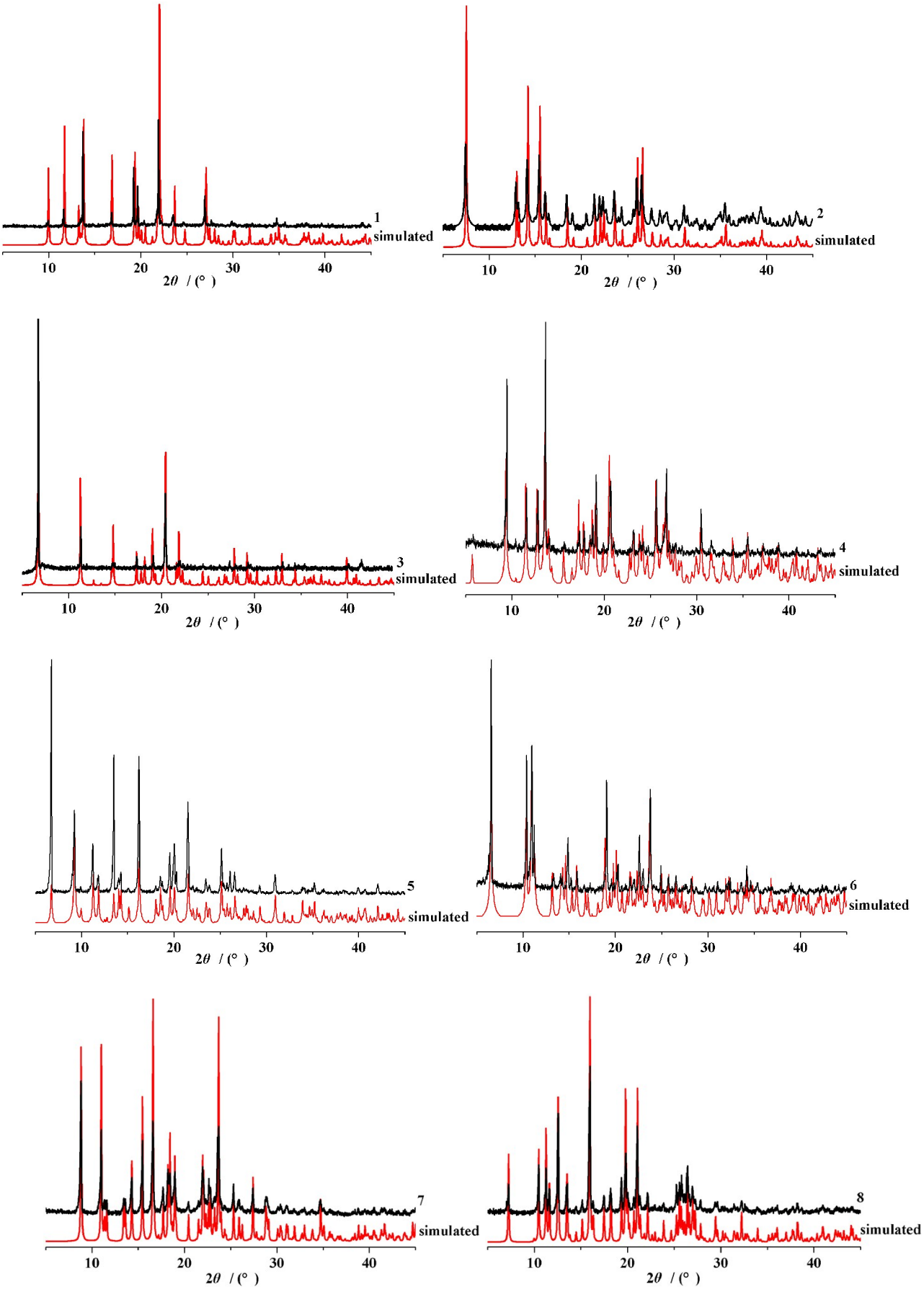


Fig. S4. 3D supramolecular architecture viewed along the *ac* plane in **11**.


1
simulated
10
20
30
40
2θ / (°)
2
simulated
10
20
30
40
2θ / (°)
3
simulated
10
20
30
40
2θ / (°)
4
simulated
10
20
30
40
2θ / (°)
5
simulated
10
20
30
40
2θ / (°)
6
simulated
10
20
30
40
2θ / (°)
7
simulated
10
20
30
40
2θ / (°)
8
simulated
10
20
30
40
2θ / (°)

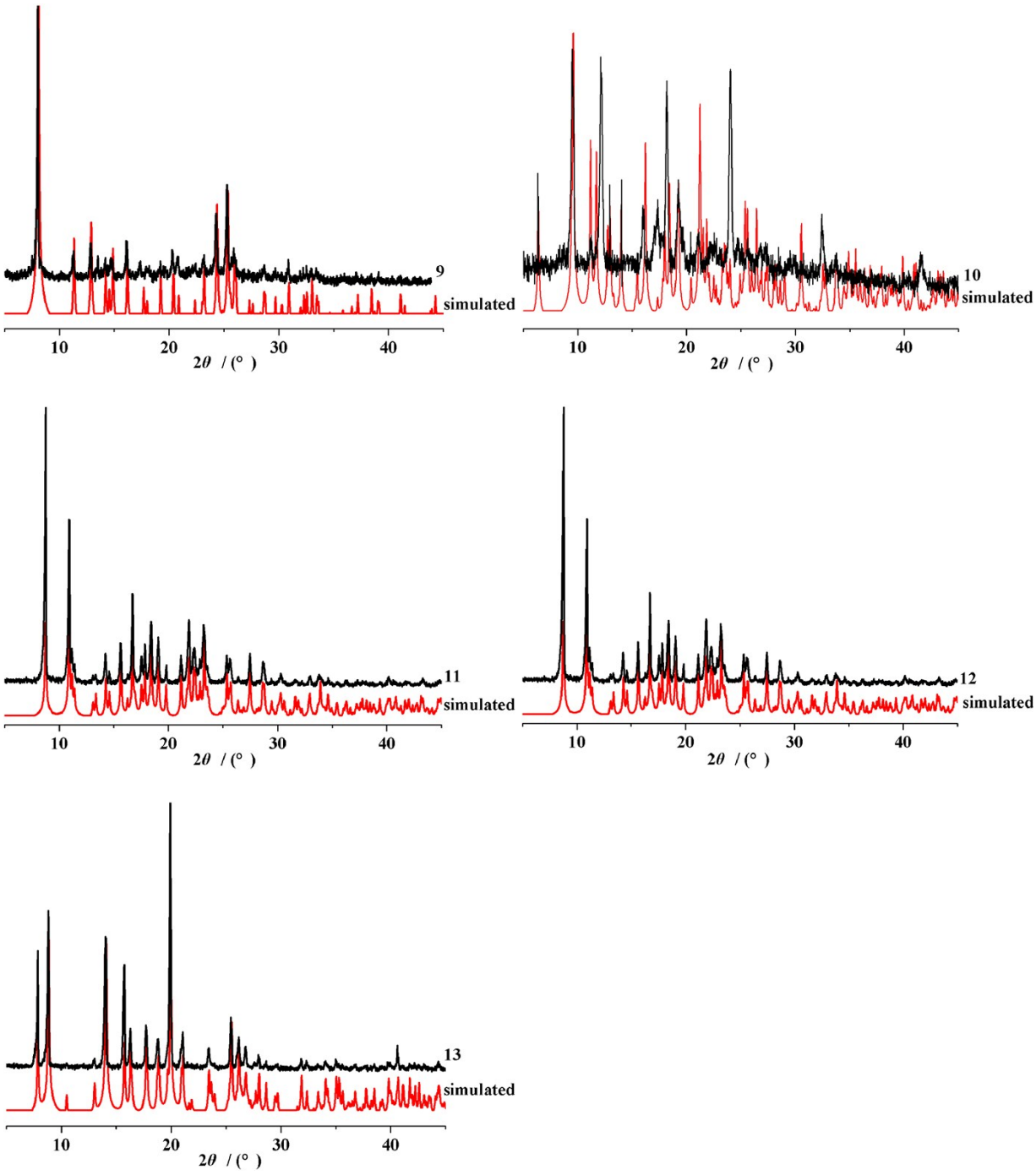


Fig. S5. PXRD patterns of compounds **1**–**13** at room temperature. Black paterns correspnond to the experimental data obtained using the as-synthesized bulk samples. Red patterns were simulated from the single crystal X-ray data.

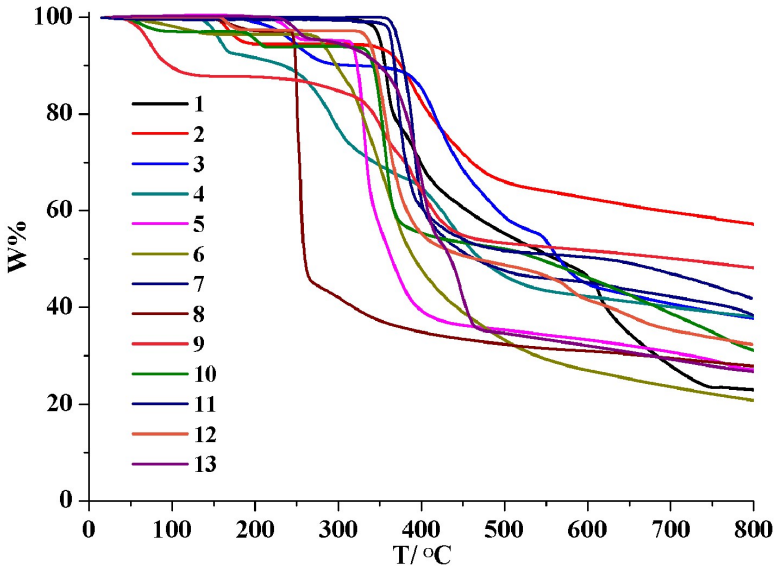


Fig. S6. Thermogravimetric analysis (TGA) curves of compounds **1**–**13**.