Electronic Supplementary Information (ESI)

Introducing 2-(2-carboxyphenoxy)terephthalic acid as a new versatile building block for design of diverse coordination polymers: Synthesis, structural features, luminescence sensing, and magnetism

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Synthesis and analytical data for 2–13

Synthesis of $[Mn(\mu\text{-Hcpta})(phen)(H_2O)]_n$ (2). A mixture of $MnCl_2{\cdot}4H_2O$ (59.4 mg, 0.30 mmol), H_3cpta (60.4 mg, 0.20 mmol), phen (60.0 mg, 0.3 mmol), NaOH (16 mg, 0.40 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 65% based on H_3cpta). Anal. Calcd for $C_{27}H_{18}MnN_2O_8$: C, 58.60; H, 3.28; N, 5.06. Found: C, 58.83; H, 3.25; N, 5.01%. IR (KBr, cm^{-1}): 3387 m, 3076 w, 1697 m, 1615 s, 1544 s, 1472 w, 1416 s, 1380 s, 1273 w, 1227 s, 1192 m, 1145 w, 1100 m, 1038 w, 998 w, 951 m, 885 w, 865 w, 844 m, 788 m, 767 m, 726 m, 660 w, 634 w, 542 w.

Synthesis of $\{[Cd_3(\mu_3\text{-HL})(\mu_4\text{-L})(\mu\text{-Cl})(H_2O)_4]\cdot 2H_2O\}_n$ (3). A mixture of $CdCl_2{\cdot}H_2O$ (60.3 mg, 0.3 mmol), H_3cpta (60.4 mg, 0.2 mmol), NaOH (20.0 mg, 0.50 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}. Colourless block-shaped crystals of **3** were isolated manually, washed with distilled water and dried (yield 55% based on $CdCl_2{\cdot}H_2O$). Anal. Calcd for $C_{30}H_{27}Cd_3ClO_{20}$: C, 33.36; H, 2.52. Found: C, 33.62; H, 2.57%. IR (KBr, cm^{-1}): 3438 s, 1707 w, 1594 s, 1554 s, 1493 w, 1446 w, 1401 s, 1268 w, 1216 m, 1156 w, 1094 w, 1038 w, 956 m, 890 w, 859 m, 809 m, 767 m, 726 w, 696 w, 665 w, 593 w, 517 w.

Synthesis of $\{[Cd_3(\mu_6\text{-cpta})_2(py)_2]\cdot 5H_2O\}_n$ (4). A mixture of $CdCl_2{\cdot}H_2O$ (60.3 mg, 0.30 mmol), H_3cpta (60.4 mg, 0.20 mmol), py (0.5 mL, 6.3 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}. Colorless block-shaped crystals of **4** were isolated manually, washed with distilled water and dried (yield 65% based on $CdCl_2{\cdot}H_2O$). Anal. Calcd for $C_{40}H_{34}Cd_3N_2O_{19}$: C, 40.58; H, 2.89; N, 2.37. Found: C, 40.76; H, 2.92; N,

2.35%. IR (KBr, cm^{-1}): 3678 m, 3131 w, 1600 w, 1574 w, 1529 s, 1482 s, 1446 s, 1411 s, 1385 w, 1355 w, 1293 w, 1227 s, 1145 w, 1104 w, 1068 w, 1038 w, 956 w, 915 w, 875 m, 850 m, 823 m, 798 w, 747 s, 696 s, 660 m, 624 w, 594 w, 568 w, 537 w.

Synthesis of $[Mn_3(\mu_5\text{-cpta})_2(2,2'\text{-bipy})_2]_n$ (5). A mixture of $MnCl_2{\cdot}4H_2O$ (59.4 mg, 0.3 mmol), H_3cpta (60.4 mg, 0.2 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 **5** were isolated manually, washed with distilled water and dried (yield 55% based on $MnCl_2{\cdot}4H_2O$). Anal. Calcd for $C_{50}H_{30}Mn_3N_4O_{14}$: C, 55.83; H, 2.81; N, 5.21. Found: C, 55.61; H, 2.83; N, 5.17%. IR (KBr, cm^{-1}): 1595 s, 1554 m, 1533 m, 1493 w, 1477 w, 1441 m, 1396 s, 1355 s, 1299 w, 1242 m, 1156 w, 1094 w, 1054 w, 1038 w, 1018 w, 951 w, 890 w, 865 w, 839 w, 823 w, 793 w, 762 m, 737 w, 711 w, 665 w, 645 w, 630 w, 598 w, 532 m.

Synthesis of $[Mn_3(\mu_4\text{-cpta})_2(phen)_3(H_2O)_2]_n$ (6). Synthesis of **6** was similar to **5** except using phen (60.0 mg, 0.30 mmol) instead of 2,2′-bipy. Yellow block-shaped crystals of **6** were obtained (yield 60% based on $MnCl_2{\cdot}4H_2O$). Anal. Calcd for $C_{66}H_{42}Mn_3N_6O_{16}$: C, 59.16; H, 3.16; N, 6.27. Found: C, 59.34; H, 3.20; N, 6.22. IR (KBr, cm^{-1}): 3218 w, 3060 w, 1605 s, 1554 s, 1513 m, 1477 w, 1446 w, 1421 s, 1396 s, 1349 s, 1227 m, 1145 w, 1100 w, 1048 w, 956 w, 865 w, 843 m, 823 w, 793 w, 767 m, 727 m, 665 w, 640 w, 593 w.

Synthesis of $\{[Zn_3(\mu_3\text{-cpta})_2(phen)_3]{\cdot}3H_2O\}_n$ (7). Synthesis of **7** was similar to **6** except using $ZnCl_2$ (41.0 mg, 0.30 mmol) instead of $MnCl_2{\cdot}4H_2O$. Colourless block-shaped crystals of **7** were obtained (yield 60% based on $ZnCl_2$). Anal. Calcd for $C_{66}H_{46}Zn_3N_6O_{17}$: C, 56.97; H, 3.33; N, 6.04. Found: C, 57.03; H, 3.30; N, 6.09. IR (KBr, cm^{-1}): 3530 m, 3065 w, 1610 s, 1559 s, 1513 m, 1482 w, 1426 s, 1390 s, 1227 m, 1151 w, 1124 w, 1100 w, 1038 w, 951 w, 910 w, 844 m, 787 m, 753 w, 727 m, 666 w, 645 w, 542 w.

Synthesis of {[$Cd_2(\mu_4$-cpta)(μ-Cl)$(phen)_2]_n$ (8). Synthesis of **8** was similar to **6** except using $CdCl_2 \cdot H_2O$ (60.3 mg, 0.30 mmol) instead of $MnCl_2 \cdot 4H_2O$. Colorless block-shaped crystals of **8** were obtained (yield 55% based on $CdCl_2 \cdot H_2O$). Anal. Calcd for $C_{39}H_{23}Cd_2ClN_4O_7$: C, 50.92; H, 2.52; N, 6.09. Found: C, 50.71; H, 2.54; N, 6.11. IR (KBr, cm^{-1}): 3443 w, 3071 w, 1595 s, 1569 s, 1508 m, 1488 w, 1452 w, 1431 s, 1406 s, 1370 s, 1299 w, 1253 w, 1232 s, 1145 w, 1094 m, 1033 w, 962 w, 900 w, 865 m, 839 s, 818 m, 803 m, 767 s, 727 s, 665 m, 640 m, 594 w, 548 w, 517 w.

Synthesis of {[$Cd_3(\mu_5$-cpta)$_2(phen)_2(H_2O)_2]_n$ (9). Synthesis of **9** was similar to **8** except using $Cd(NO_3)_2 \cdot 4H_2O$ (92.5 mg, 0.30 mmol) instead of $CdCl_2 \cdot H_2O$. Colourless block-shaped crystals of **9** were isolated manually, washed with distilled water and dried (yield 60% based on $Cd(NO_3)_2 \cdot 4H_2O$). Anal. Calcd for $C_{54}H_{34}Cd_3N_4O_{16}$: C, 48.69; H, 2.57; N, 4.20. Found: C, 48.47; H, 2.59; N, 4.16%. IR (KBr, cm^{-1}): 3264 w, 3055 w, 1600 s, 1564 s, 1518 m, 1477 m, 1441 m, 1396 s, 1360 s, 1293 w, 1232 s, 1145 m, 1099 m, 1048 w, 997 w, 962 m, 911 m, 850 s, 803 m, 758 m, 727 s, 701 m, 661 m, 640 m, 599 w, 553 w, 517 w.

Synthesis of [$Cd_3(\mu_4$-cpta)$_2(phen)_3(H_2O)_2]_n$ (10). Synthesis of **10** was similar to **8** except using $CdSO_4 \cdot 8/3H_2O$ (76.9 mg, 0.30 mmol) instead of $CdCl_2 \cdot H_2O$. Colourless block-shaped crystals of **11** were obtained (yield 55% based on $CdSO_4 \cdot 8/3H_2O$). Anal. Calcd for $C_{66}H_{42}Cd_3N_6O_{16}$: C, 52.42; H, 2.80; N, 5.56. Found: C, 52.67; H, 2.82; N, 5.50. IR (KBr, cm^{-1}): 3254 w, 3055 w, 1605 s, 1559 s, 1477 m, 1452 w, 1401 s, 1360 s, 1293 w, 1223 s, 1145 m, 1094 m, 1043 w, 992 w, 956 m, 906 m, 843 s, 803 m, 757 s, 727 s, 701 m, 661 m, 634 m, 599 w, 548 w, 517 w.

Synthesis of [$Cd_3(\mu_5$-cpta)$_2(H_2$biim$)_2]_n$ (11). A mixture of $CdCl_2 \cdot 4H_2O$ (60.3 mg, 0.30 mmol), H_3cpta (60.4 mg, 0.20 mmol), H_2biim (40.2 mg, 0.3 mmol), NaOH (16 mg, 0.40 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}. Colourless block-shaped crystals of **11** were isolated manually, washed with distilled water and dried

(yield 65% based on H_3cpta). Anal. Calcd for $C_{42}H_{26}Cd_3N_8O_{14}$: C, 41.90; H, 2.18; N, 9.31. Found: C, 41.26; H, 2.16; N, 9.35%. IR (KBr, cm^{-1}): 1604 w, 1570 s, 1524 m, 1490 m, 1452 w, 1390 s, 1366 w, 1298 w, 1260 w, 1096 m, 1040 w, 994 w, 954 w, 892 w, 870 w, 848 w, 796 w, 774 m, 752 m, 712 m, 690 m, 616 w, 536 w.

Synthesis of $[Zn_2(\mu_6\text{-cpta})(\mu\text{-Hbiim})]_n$ (12). Synthesis of **12** was similar to **11** except using $ZnCl_2$ (41.0 mg, 0.30 mmol) instead of $CdCl_2{\cdot}H_2O$. Colourless block-shaped crystals of **12** were obtained (yield 60% based on $ZnCl_2$). Anal. Calcd for $C_{21}H_{12}Zn_2N_4O_7$: C, 44.79; H, 2.15; N, 9.95. Found: C, 45.08; H, 2.17; N, 9.91. IR (KBr, cm^{-1}): 1634 s, 1557 m, 1510 w, 1497 w, 1407 s, 1355 s, 1299 w, 1237 s, 1201 w, 1164 w, 1133 m, 1097 m, 1035 w, 957 m, 895 w, 854 w, 824 w, 808 w, 751 m, 715 w, 689 m, 591 w, 528 w.

Synthesis of $[Ni_3(\mu_3\text{-cpta})_2(phen)_3(py)_3(H_2O)_3]_n$ (13). A mixture of $NiCl_2{\cdot}6H_2O$ (71.1 mg, 0.30 mmol), H_3cpta (60.4 mg, 0.20 mmol), phen (60.0 mg, 0.30 mmol), py (0.5 mL, 6.3 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}. Green block-shaped crystals of **12** were obtained (yield 55% based on $NiCl_2{\cdot}6H_2O$). Anal. Calcd for $C_{81}H_{58}Ni_3N_9O_{17}$: C, 60.60; H, 3.64; N, 7.85. Found: C, 60.38; H, 3.67; N, 7.81. IR (KBr, cm^{-1}): 3413 w, 3071 m, 1590 s, 1549 s, 1518 m, 1482 w, 1446 m, 1426 m, 1406 s, 1370 s, 1304 w, 1227 m, 1150 w, 1094 m, 1043 m, 1007 w, 951 w, 895 w, 850 s, 793 s, 783 m, 731 m, 701 m, 654 w, 640w, 589 w, 528 w.

Table S1. Selected bond lengths [Å] and angles [°] for the compounds **1**–**13**[a].

1					
Cd(1)-O(1)	2.415(3)	Cd(1)-O(1)#1	2.452(3)	Cd(1)-O(2)#1	2.495(3)
Cd(1)-O(6)	2.335(3)	Cd(1)-O(8)	2.311(3)	Cd(1)-N(1)	2.375(3)
Cd(1)-N(2)	2.421(4)				
O(8)-Cd(1)-O(6)	79.46(10)	O(8)-Cd(1)-N(1)	124.18(11)	O(6)-Cd(1)-N(1)	147.79(11)
O(8)-Cd(1)-O(1)	155.39(10)	O(6)-Cd(1)-O(1)	79.91(10)	N(1)-Cd(1)-O(1)	80.15(11)
O(8)-Cd(1)-N(2)	87.32(11)	O(6)-Cd(1)-N(2)	93.24(11)	N(1)-Cd(1)-N(2)	68.99(12)
O(1)-Cd(1)-N(2)	107.12(11)	O(8)-Cd(1)-O(1)#1	93.95(10)	O(6)-Cd(1)-O(1)#1	86.73(10)
N(1)-Cd(1)-O(1)#1	110.43(11)	O(1)-Cd(1)-O(1)#1	71.58(11)	N(2)-Cd(1)-O(1)#1	178.69(12)
O(8)-Cd(1)-O(2)#1	78.22(10)	O(6)-Cd(1)-O(2)#1	131.30(10)	N(1)-Cd(1)-O(2)#1	78.76(11)
O(1)-Cd(1)-O(2)#1	106.08(10)	N(2)-Cd(1)-O(2)#1	128.03(11)	O(1)#1-Cd(1)-O(2)#1	52.62(10)
Cd(1)-O(1)-Cd(1)#1	108.42(11)				
2					
Mn(1)-O(1)	2.166(2)	Mn(1)-O(2)#1	2.174(2)	Mn(1)-O(7)#1	2.149(2)
Mn(1)-O(8)	2.114(2)	Mn(1)-N(1)	2.323(2)	Mn(1)-N(2)	2.283(3)
O(8)-Mn(1)-O(7)#1	85.79(8)	O(8)-Mn(1)-O(1)	95.87(8)	O(7)#1-Mn(1)-O(1)	103.02(8)
O(8)-Mn(1)-O(2)#1	172.58(8)	O(7)#1-Mn(1)-O(2)#1	86.88(8)	O(1)-Mn(1)-O(2)#1	86.89(7)
O(8)-Mn(1)-N(2)	95.59(9)	O(7)#1-Mn(1)-N(2)	163.56(8)	O(1)-Mn(1)-N(2)	93.16(8)
O(2)#1-Mn(1)-N(2)	91.13(8)	O(8)-Mn(1)-N(1)	84.69(9)	O(7)#1-Mn(1)-N(1)	91.59(8)
O(1)-Mn(1)-N(1)	165.39(8)	O(2)#1-Mn(1)-N(1)	94.39(8)	N(2)-Mn(1)-N(1)	72.27(9)
3					
Cd(1)-O(1)	2.218(8)	Cd(1)-O(3)	2.480(7)	Cd(1)-O(5)#1	2.419(8)
Cd(1)-O(6)	2.243(7)	Cd(1)-O(8)	2.254(8)	Cd(1)-O(10)	2.614(8)
Cd(1)-O(11)	2.206(7)	Cd(2)-O(4)#1	2.257(8)	Cd(2)-O(11)	2.312(7)
Cd(2)-O(12)	2.494(8)	Cd(2)-O(15)	2.286(8)	Cd(2)-O(16)	2.328(8)
Cd(2)-Cl(1)	2.554(3)	Cd(3)-O(6)	2.362(7)	Cd(3)-O(7)	2.429(8)
Cd(3)-O(13)#2	2.610(11)	Cd(3)-O(14)#2	2.271(10)	Cd(3)-O(17)	2.329(9)
Cd(3)-O(18)	2.297(10)	Cd(3)-Cl(1)	2.581(3)		
O(11)-Cd(1)-O(1)	121.6(3)	O(11)-Cd(1)-O(6)	87.4(3)	O(1)-Cd(1)-O(6)	141.0(3)
O(11)-Cd(1)-O(8)	121.5(3)	O(1)-Cd(1)-O(8)	87.9(3)	O(6)-Cd(1)-O(8)	98.8(3)
O(11)-Cd(1)-O(5)#1	74.9(3)	O(1)-Cd(1)-O(5)#1	79.0(3)	O(6)-Cd(1)-O(5)#1	85.2(3)
O(8)-Cd(1)-O(5)#1	163.1(3)	O(11)-Cd(1)-O(3)	148.6(3)	O(1)-Cd(1)-O(3)	72.3(3)
O(6)-Cd(1)-O(3)	70.1(3)	O(8)-Cd(1)-O(3)	84.5(3)	O(5)#1-Cd(1)-O(3)	81.4(3)
O(11)-Cd(1)-O(10)	66.8(2)	O(1)-Cd(1)-O(10)	82.7(3)	O(6)-Cd(1)-O(10)	135.7(3)
O(8)-Cd(1)-O(10)	69.1(3)	O(5)#1-Cd(1)-O(10)	118.9(3)	O(3)-Cd(1)-O(10)	144.3(2)
O(4)#1-Cd(2)-O(15)	101.6(3)	O(4)#1-Cd(2)-O(11)	114.8(3)	O(15)-Cd(2)-O(11)	142.2(3)
O(4)#1-Cd(2)-O(16)	87.5(3)	O(15)-Cd(2)-O(16)	84.9(3)	O(11)-Cd(2)-O(16)	86.9(3)
O(4)#1-Cd(2)-O(12)	167.5(3)	O(15)-Cd(2)-O(12)	88.9(3)	O(11)-Cd(2)-O(12)	53.8(3)
O(16)-Cd(2)-O(12)	86.7(3)	O(4)#1-Cd(2)-Cl(1)	98.2(2)	O(15)-Cd(2)-Cl(1)	91.9(2)
O(11)-Cd(2)-Cl(1)	92.5(2)	O(16)-Cd(2)-Cl(1)	173.9(3)	O(12)-Cd(2)-Cl(1)	88.1(2)
O(14)#2-Cd(3)-O(18)	126.8(4)	O(14)#2-Cd(3)-O(17)	80.6(4)	O(18)-Cd(3)-O(17)	79.8(3)
O(14)#2-Cd(3)-O(6)	79.7(3)	O(18)-Cd(3)-O(6)	148.5(4)	O(17)-Cd(3)-O(6)	89.9(3)
O(14)#2-Cd(3)-O(7)	130.5(3)	O(18)-Cd(3)-O(7)	95.1(4)	O(17)-Cd(3)-O(7)	82.9(4)
O(6)-Cd(3)-O(7)	53.9(2)	O(14)#2-Cd(3)-Cl(1)	116.2(3)	O(18)-Cd(3)-Cl(1)	89.1(3)

O(17)-Cd(3)-Cl(1)	163.2(3)	O(6)-Cd(3)-Cl(1)	93.2(2)	O(7)-Cd(3)-Cl(1)	85.6(2)
O(14)#2-Cd(3)-O(13)#2	52.9(4)	O(18)-Cd(3)-O(13)#2	81.0(4)	O(17)-Cd(3)-O(13)#2	96.3(4)
O(6)-Cd(3)-O(13)#2	129.9(3)	O(7)-Cd(3)-O(13)#2	176.1(3)	Cl(1)-Cd(3)-O(13)#2	94.4(3)
Cd(2)-Cl(1)-Cd(3)	111.68(12)	Cd(1)-O(11)-Cd(2)	116.6(3)		
4					
Cd(1)-O(1)	2.445(3)	Cd(1)-O(2)	2.533(3)	Cd(1)-O(4)#3	2.338(3)
Cd(1)-O(5)#3	2.468(3)	Cd(1)-O(4)#3	2.338(3)	Cd(1)-O(7)#1	2.269(3)
Cd(1)-N(1)	2.290(4)	Cd(2)-O(2)	2.353(3)	Cd(2)-O(2)#3	2.353(3)
Cd(2)-O(4)	2.295(3)	Cd(2)-O(4)#3	2.295(3)	Cd(2)-O(6)#1	2.226(3)
Cd(2)-O(6)#4	2.226(3)				
O(7)#1-Cd(1)-O(1)#2	87.80(11)	O(7)#1-Cd(1)-N(1)	175.30(13)	O(1)#2-Cd(1)-N(1)	96.73(13)
O(7)#1-Cd(1)-O(4)#3	87.98(11)	O(1)#2-Cd(1)-O(4)#3	158.95(10)	N(1)-Cd(1)-O(4)#3	87.35(12)
O(7)#1-Cd(1)-O(1)	83.66(11)	O(1)#2-Cd(1)-O(1)	75.18(11)	N(1)-Cd(1)-O(1)	98.66(12)
O(4)#3-Cd(1)-O(1)	124.76(9)	O(7)#1-Cd(1)-O(5)#3	84.45(11)	O(1)#2-Cd(1)-O(5)#3	104.78(10)
N(1)-Cd(1)-O(5)#3	93.17(12)	O(4)#3-Cd(1)-O(5)#3	54.27(10)	O(1)-Cd(1)-O(5)#3	168.10(10)
O(7)#1-Cd(1)-O(2)	79.35(11)	O(1)#2-Cd(1)-O(2)	126.33(9)	N(1)-Cd(1)-O(2)	98.82(12)
O(4)#3-Cd(1)-O(2)	72.93(9)	O(1)-Cd(1)-O(2)	51.85(9)	O(5)#3-Cd(1)-O(2)	125.09(9)
O(6)#1-Cd(2)-O(6)#4	89.77(15)	O(6)#1-Cd(2)-O(4)#3	87.42(11)	O(6)#1-Cd(2)-O(4)	113.09(10)
O(4)#3-Cd(2)-O(4)	151.64(15)	O(6)#1-Cd(2)-O(2)#3	169.56(10)	O(6)#4-Cd(2)-O(2)#3	92.70(10)
O(4)#3-Cd(2)-O(2)#3	82.27(10)	O(4)-Cd(2)-O(2)#3	77.18(10)	O(2)#3-Cd(2)-O(2)	86.68(14)
Cd(2)-O(2)-Cd(1)	96.36(10)	Cd(2)-O(4)-Cd(1)#3	103.68(10)		
5					
Mn(1)-O(1)#2	2.348(2)	Mn(1)-O(2)#2	2.206(2)	Mn(1)-O(4)	2.162(2)
Mn(1)-O(6)#1	2.102(2)	Mn(1)-N(1)	2.266(2)	Mn(1)-N(2)	2.218(2)
Mn(2)-O(1)	2.237(2)	Mn(2)-O(1)#2	2.237(2)	Mn(2)-O(4)	2.187(2)
Mn(2)-O(4)#2	2.187(2)	Mn(2)-O(7)#1	2.161(2)	Mn(2)-O(7)#3	2.161(2)
O(6)#1-Mn(1)-O(4)	86.60(8)	O(6)#1-Mn(1)-O(2)#2	149.92(8)	O(4)-Mn(1)-O(2)#2	93.46(8)
O(6)#1-Mn(1)-N(2)	93.87(8)	O(4)-Mn(1)-N(2)	120.37(8)	O(2)#2-Mn(1)-N(2)	111.65(8)
O(6)#1-Mn(1)-N(1)	81.51(9)	O(4)-Mn(1)-N(1)	162.68(8)	O(2)#2-Mn(1)-N(1)	90.60(9)
N(2)-Mn(1)-N(1)	73.23(9)	O(6)#1-Mn(1)-O(1)#2	93.16(7)	O(4)-Mn(1)-O(1)#2	77.21(7)
O(2)#2-Mn(1)-O(1)#2	57.78(7)	N(2)-Mn(1)-O(1)#2	161.42(8)	N(1)-Mn(1)-O(1)#2	90.86(8)
O(7)#3-Mn(2)-O(4)#2	87.71(7)	O(7)#1-Mn(2)-O(4)#2	92.29(7)	O(7)#3-Mn(2)-O(1)#2	88.21(7)
O(7)#1-Mn(2)-O(1)#2	91.79(7)	O(4)#2-Mn(2)-O(1)#2	100.89(7)	O(4)-Mn(2)-O(1)#2	79.11(7)
Mn(2)-O(1)-Mn(1)#2	93.78(7)	Mn(1)-O(4)-Mn(2)	100.70(8)		
6					
Mn(1)-O(2)	2.165(2)	Mn(1)-O(4)#1	2.157(2)	Mn(1)-O(7)#2	2.204(3)
Mn(1)-O(8)	2.209(2)	Mn(1)-N(1)	2.297(3)	Mn(1)-N(2)	2.311(3)
Mn(2)-O(1)	2.086(3)	Mn(2)-O(1)#2	2.045(3)	Mn(2)-O(7)#2	2.330(3)
Mn(2)-N(3)	2.091(4)	Mn(2)-N(3)#2	2.473(4)		
O(4)#1-Mn(1)-O(2)	82.44(9)	O(4)#1-Mn(1)-O(7)#2	110.16(10)	O(2)-Mn(1)-O(7)#2	90.10(9)
O(4)#1-Mn(1)-O(8)	84.95(9)	O(2)-Mn(1)-O(8)	166.92(9)	O(7)#2-Mn(1)-O(8)	97.54(9)
O(4)#1-Mn(1)-N(1)	157.72(11)	O(2)-Mn(1)-N(1)	89.97(10)	O(7)#2-Mn(1)-N(1)	90.68(10)
O(8)-Mn(1)-N(1)	100.50(10)	O(4)#1-Mn(1)-N(2)	87.99(10)	O(2)-Mn(1)-N(2)	92.85(10)
O(7)#2-Mn(1)-N(2)	161.84(10)	O(8)-Mn(1)-N(2)	83.20(10)	N(1)-Mn(1)-N(2)	71.42(11)
O(1)#2-Mn(2)-O(1)	101.53(15)	O(1)#2-Mn(2)-N(3)	156.83(13)	O(1)-Mn(2)-N(3)	99.69(12)
O(1)#2-Mn(2)-O(7)#2	94.64(10)	O(1)-Mn(2)-O(7)#2	98.17(10)	N(3)-Mn(2)-O(7)#2	91.46(12)
O(1)#2-Mn(2)-N(3)#2	89.37(12)	O(1)-Mn(2)-N(3)#2	125.20(11)	N(3)-Mn(2)-N(3)#2	70.70(17)

O(7)#2-Mn(2)-N(3)#2	134.68(10)	Mn(1)#2-O(7)-Mn(2)#2	120.55(10)		
7					
Zn(1)-O(1)	1.977(4)	Zn(1)-O(2)	2.522(4)	Zn(1)-O(5)#1	1.956(4)
Zn(1)-N(1)	2.094(4)	Zn(1)-N(2)	2.075(4)	Zn(2)-O(6)	2.194(4)
Zn(2)-O(6)#2	2.194(4)	Zn(2)-O(7)	2.158(4)	Zn(2)-O(7)#2	2.158(4)
Zn(2)-N(3)	2.096(5)	Zn(2)-N(3)#2	2.096(5)		
O(5)#1-Zn(1)-O(1)	116.43(16)	O(5)#1-Zn(1)-N(2)	106.61(18)	O(1)-Zn(1)-N(2)	124.99(16)
O(5)#1-Zn(1)-N(1)	121.75(17)	O(1)-Zn(1)-N(1)	103.12(16)	N(2)-Zn(1)-N(1)	79.70(18)
O(5)#1-Zn(1)-O(2)	91.70(15)	N(1)-Zn(1)-O(2)	146.55(15)	N(2)-Zn(1)-O(2)	90.56(15)
O(1)-Zn(1)-O(2)	57.04(14)				
8					
Cd(1)-O(1)	2.232(4)	Cd(1)-O(3)#1	2.337(4)	Cd(1)-O(4)#1	2.376(5)
Cd(1)-N(1)	2.369(5)	Cd(1)-N(2)	2.369(5)	Cd(1)-Cl(1)	2.575(2)
Cd(2)-O(2)	2.269(4)	Cd(2)-O(6)#2	2.683(6)	Cd(2)-O(7)#2	2.196(4)
Cd(2)-N(3)	2.345(5)	Cd(2)-N(4)	2.353(5)	Cd(2)-Cl(1)	2.540(2)
O(1)-Cd(1)-O(3)#1	99.85(17)	O(1)-Cd(1)-N(1)	85.95(17)	O(3)#1-Cd(1)-N(1)	81.06(17)
O(1)-Cd(1)-N(2)	144.06(18)	O(3)#1-Cd(1)-N(2)	101.98(18)	N(1)-Cd(1)-N(2)	69.80(19)
O(1)-Cd(1)-O(4)#1	108.79(18)	O(3)#1-Cd(1)-O(4)#1	54.72(15)	N(1)-Cd(1)-O(4)#1	134.70(17)
N(2)-Cd(1)-O(4)#1	107.1(2)	O(1)-Cd(1)-Cl(1)	93.90(11)	O(3)#1-Cd(1)-Cl(1)	142.07(12)
N(1)-Cd(1)-Cl(1)	135.41(13)	N(2)-Cd(1)-Cl(1)	86.10(14)	O(4)#1-Cd(1)-Cl(1)	87.41(12)
O(7)#2-Cd(2)-O(2)	92.53(16)	O(7)#2-Cd(2)-N(3)	102.78(18)	O(2)-Cd(2)-N(3)	156.95(18)
O(7)#2-Cd(2)-N(4)	104.55(18)	O(2)-Cd(2)-N(4)	89.10(17)	N(3)-Cd(2)-N(4)	70.56(18)
O(7)#2-Cd(2)-Cl(1)	132.23(14)	O(2)-Cd(2)-Cl(1)	90.43(12)	N(3)-Cd(2)-Cl(1)	91.82(14)
N(4)-Cd(2)-Cl(1)	123.16(12)	O(7)#2-Cd(2)-O(6)#2	52.08(16)	Cl(1)-Cd(2)-O(6)#2	87.11(12)
N(4)-Cd(2)-O(6)#2	137.63(18)	N(3)-Cd(2)-O(6)#2	80.51(18)	O(2)-Cd(2)-O(6)#2	122.51(16)
Cd(2)-Cl(1)-Cd(1)	90.15(5)				
9					
Cd(1)-O(2)#2	2.320(3)	Cd(1)-O(4)	2.356(3)	Cd(1)-O(6)#1	2.292(3)
Cd(1)-O(8)	2.329(3)	Cd(1)-N(1)	2.336(3)	Cd(1)-N(2)	2.371(3)
Cd(2)-O(2)#1	2.392(3)	Cd(2)-O(2)#2	2.392(3)	Cd(2)-O(5)	2.181(3)
Cd(2)-O(5)#3	2.181(3)	Cd(2)-O(6)#1	2.512(3)	Cd(2)-O(6)#2	2.512(3)
O(6)#1-Cd(1)-O(2)#2	73.68(10)	O(6)#1-Cd(1)-O(8)	117.66(11)	O(2)#2-Cd(1)-O(8)	86.30(11)
O(6)#1-Cd(1)-N(1)	128.64(11)	O(2)#2-Cd(1)-N(1)	157.55(11)	O(8)-Cd(1)-N(1)	84.31(12)
O(6)#1-Cd(1)-O(4)	77.19(12)	O(2)#2-Cd(1)-O(4)	98.02(10)	O(8)-Cd(1)-O(4)	165.14(11)
N(1)-Cd(1)-O(4)	86.50(11)	O(6)#1-Cd(1)-N(2)	142.92(12)	O(2)#2-Cd(1)-N(2)	88.55(11)
O(8)-Cd(1)-N(2)	92.63(11)	N(1)-Cd(1)-N(2)	71.60(12)	O(4)-Cd(1)-N(2)	73.36(12)
O(5)#3-Cd(2)-O(2)#1	94.05(10)	O(5)-Cd(2)-O(2)#1	85.95(10)	O(5)#3-Cd(2)-O(6)#2	96.89(11)
O(5)-Cd(2)-O(6)#2	83.11(11)	O(2)#1-Cd(2)-O(6)#2	68.61(10)	O(2)#2-Cd(2)-O(6)#2	111.39(10)
Cd(1)-O(6)#1-Cd(2)	96.39(13)	Cd(1)-O(2)#2-Cd(2)	99.01(12)		
10					
Cd(1)-O(1)	2.452(2)	Cd(1)-O(1)#1	2.452(2)	Cd(1)-O(7)	2.180(3)
Cd(1)-O(7)#1	2.180(3)	Cd(1)-N(3)	2.349(3)	Cd(1)-N(3)#1	2.349(3)
Cd(2)-O(1)	2.302(2)	Cd(2)-O(4)#2	2.273(3)	Cd(2)-O(6)#1	2.344(3)
Cd(2)-O(8)	2.347(3)	Cd(2)-N(1)	2.367(3)	Cd(2)-N(2)	2.373(3)
O(7)-Cd(1)-O(7)#1	110.22(18)	O(7)-Cd(1)-N(3)	146.23(10)	O(7)#1-Cd(1)-N(3)	95.88(12)
N(3)-Cd(1)-N(3)#1	70.61(15)	O(7)-Cd(1)-O(1)	80.86(11)	O(7)#1-Cd(1)-O(1)	88.38(10)
N(3)-Cd(1)-O(1)	78.78(10)	N(3)#1-Cd(1)-O(1)	117.49(9)	N(3)-Cd(1)-O(1)#1	117.49(9)

O(1)-Cd(1)-O(1)#1	161.17(13)	O(4)#2-Cd(2)-O(1)	107.86(10)	O(4)#2-Cd(2)-O(6)#1	77.20(10)
O(1)-Cd(2)-O(6)#1	87.97(9)	O(4)#2-Cd(2)-O(8)	81.33(9)	O(1)-Cd(2)-O(8)	112.06(9)
O(6)#1-Cd(2)-O(8)	154.37(9)	O(4)#2-Cd(2)-N(1)	155.48(11)	O(1)-Cd(2)-N(1)	91.38(11)
O(6)#1-Cd(2)-N(1)	88.77(11)	O(8)-Cd(2)-N(1)	105.85(10)	O(4)#2-Cd(2)-N(2)	88.84(11)
O(1)-Cd(2)-N(2)	159.94(11)	O(6)#1-Cd(2)-N(2)	84.97(11)	O(8)-Cd(2)-N(2)	80.74(11)
N(1)-Cd(2)-N(2)	69.75(12)	Cd(2)-O(1)-Cd(1)	127.70(10)		
11					
Cd(1)-O(1)	2.211(3)	Cd(1)-O(3)#1	2.278(3)	Cd(1)-O(6)#2	2.348(3)
Cd(1)-O(7)#2	2.455(3)	Cd(1)-N(1)	2.304(4)	Cd(1)-N(2)	2.308(4)
Cd(2)-O(2)	2.267(3)	Cd(2)-O(2)#3	2.267(3)	Cd(2)-O(3)#1	2.307(3)
Cd(2)-O(3)#2	2.307(3)	Cd(2)-O(7)#1	2.311(3)	Cd(2)-O(7)#2	2.311(3)
O(1)-Cd(1)-O(3)#1	82.98(12)	O(1)-Cd(1)-N(1)	93.59(14)	O(3)#1-Cd(1)-N(1)	124.94(13)
O(1)-Cd(1)-N(2)	87.44(15)	O(3)#1-Cd(1)-N(2)	158.35(13)	N(1)-Cd(1)-N(2)	74.89(15)
O(1)-Cd(1)-O(6)#2	149.39(13)	O(3)#1-Cd(1)-O(6)#2	86.73(12)	N(1)-Cd(1)-O(6)#2	115.75(13)
N(2)-Cd(1)-O(6)#2	91.83(14)	O(1)-Cd(1)-O(7)#2	94.74(12)	O(3)#1-Cd(1)-O(7)#2	77.63(11)
N(1)-Cd(1)-O(7)#2	156.80(12)	N(2)-Cd(1)-O(7)#2	83.89(13)	O(6)#2-Cd(1)-O(7)#2	54.82(11)
O(2)-Cd(2)-O(3)#2	90.83(11)	O(2)-Cd(2)-O(3)#1	89.17(11)	O(2)-Cd(2)-O(7)#1	86.08(10)
O(2)#3-Cd(2)-O(7)#1	93.92(10)	O(3)#2-Cd(2)-O(7)#1	80.05(11)	O(3)#1-Cd(2)-O(7)#1	99.95(11)
Cd(1)#4-O(3)-Cd(2)#4	98.20(12)	Cd(2)#4-O(7)-Cd(1)#5	93.23(11)		
12					
Zn(1)-O(1)	2.002(4)	Zn(1)-O(3)#2	2.111(4)	Zn(1)-O(7)#1	1.971(4)
Zn(1)-N(1)	2.255(5)	Zn(1)-N(2)	2.005(4)	Zn(2)-O(2)	1.967(4)
Zn(2)-O(4)#2	1.945(4)	Zn(2)-O(6)#1	1.947(4)	Zn(2)-N(4)#3	1.981(4)
O(7)#1-Zn(1)-O(1)	119.73(17)	O(7)#1-Zn(1)-N(2)	120.30(19)	O(1)-Zn(1)-N(2)	119.05(19)
O(7)#1-Zn(1)-O(3)#2	95.72(18)	O(1)-Zn(1)-O(3)#2	95.48(17)	N(2)-Zn(1)-O(3)#2	88.37(17)
O(7)#1-Zn(1)-N(1)	91.01(18)	O(1)-Zn(1)-N(1)	90.63(17)	N(2)-Zn(1)-N(1)	78.78(17)
O(3)#2-Zn(1)-N(1)	167.15(15)	O(4)#2-Zn(2)-O(6)#1	115.50(19)	O(4)#2-Zn(2)-O(2)	106.28(19)
O(6)#1-Zn(2)-O(2)	117.33(19)	O(4)#2-Zn(2)-N(4)#3	107.88(19)	O(6)#1-Zn(2)-N(4)#3	97.8(2)
O(2)-Zn(2)-N(4)#3	111.57(18)				
13					
Ni(1)-O(1)	2.053(3)	Ni(1)-O(6)#1	2.096(3)	Ni(1)-O(8)	2.077(3)
Ni(1)-N(1)	2.097(3)	Ni(1)-N(2)	2.095(3)	Ni(1)-N(3)	2.111(3)
Ni(2)-O(3)	2.084(3)	Ni(2)-O(3)#2	2.084(3)	Ni(2)-N(4)	2.116(3)
Ni(2)-N(4)#2	2.115(3)	Ni(2)-N(5)	2.080(4)	Ni(2)-O(9)	2.090(3)
O(1)-Ni(1)-O(8)	90.36(11)	O(1)-Ni(1)-N(2)	84.26(12)	O(8)-Ni(1)-N(2)	168.97(11)
O(1)-Ni(1)-O(6)#1	92.11(11)	O(8)-Ni(1)-O(6)#1	94.25(10)	N(2)-Ni(1)-O(6)#1	95.57(11)
O(1)-Ni(1)-N(1)	87.14(11)	O(8)-Ni(1)-N(1)	90.57(11)	N(2)-Ni(1)-N(1)	79.57(13)
O(6)#1-Ni(1)-N(1)	175.13(12)	O(1)-Ni(1)-N(3)	177.86(12)	O(8)-Ni(1)-N(3)	91.18(12)
N(2)-Ni(1)-N(3)	93.98(13)	O(6)#1-Ni(1)-N(3)	89.26(12)	N(1)-Ni(1)-N(3)	91.36(12)
N(5)-Ni(2)-O(3)	87.65(11)	O(3)#2-Ni(2)-O(3)	97.17(15)	N(5)-Ni(2)-O(9)	179.26(17)
O(3)-Ni(2)-O(9)	92.83(10)	N(5)-Ni(2)-N(4)#2	91.73(13)	O(3)#2-Ni(2)-N(4)#2	91.94(11)
O(3)-Ni(2)-N(4)#2	170.84(12)	O(9)-Ni(2)-N(4)#2	87.70(12)	N(4)#2-Ni(2)-N(4)	78.94(18)

[a] Symmetry transformations used to generate equivalent atoms: #1 –*x*+1, –*y*+1, –*z* for **1** #1 –*x*+1, *y*+1/2, –*z*+1/2 for **2**; #1 –*x*+2, –*y*+2, –*z*; #2 –*x*+1, –*y*+2, –*z*+1 for **3**; #1 –*x*+2, –*y*, –*z*+1; #2 –*x*+3/2, –*y*+1/2, –*z*+1; #3 –*x*+2, *y*, –*z*+3/2; #4 *x*, –*y*, *z*+1/2 for **4**; #1 –*x*+1, *y*–1/2, –*z*+3/2; #2 –*x*+1, –*y*+1, –*z*+2; #3 *x*, –*y*+3/2, *z*+1/2 for **5**; #1 –*x*+1/2, *y*+1/2, –*z*+1/2; #2 –

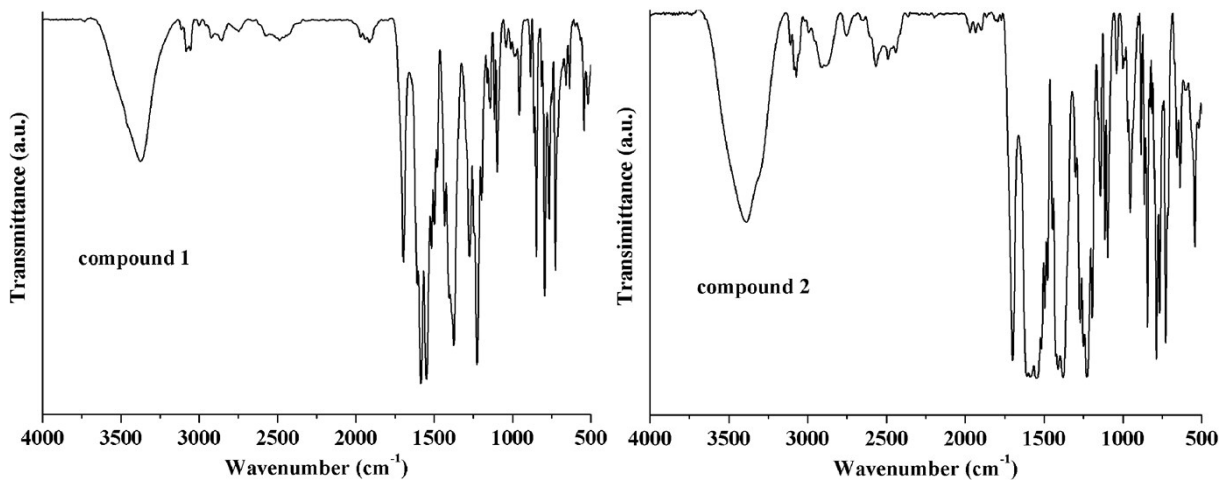
x+1, y, –z+1/2 for **6**; #1 –x, –y+1, –z; #2 –x+1, y, –z+1/2 for **7**; #1 –x+3/2, y+1/2, –z+1/2; #2 –x+1, –y, –z for **8**;. #1 –x, y+1/2, –z+3/2; #2 x, –y+1/2, z+1/2; #3 –x, –y+1, –z+2 for **9**; #1 –x+2, y, –z+1/2; #2 x+1/2, y+1/2, z for **10**;. #1 –x+1/2, y–1/2, –z+1/2; #2 x–1/2, –y+1/2, z–1/2; #3 –x, –y, –z; #4 –x+1/2, y+1/2, –z+1/2; #5 x+1/2, –y+1/2, z+1/2 for **11**; #1 –x+1/2, y–1/2, –z+2; #2 x, –y+1, z+1/2; #3 x–1/2, –y+1/2, z for **12**; #1 x, y, z–1; #2 x, –y+1/2, z for **13**.

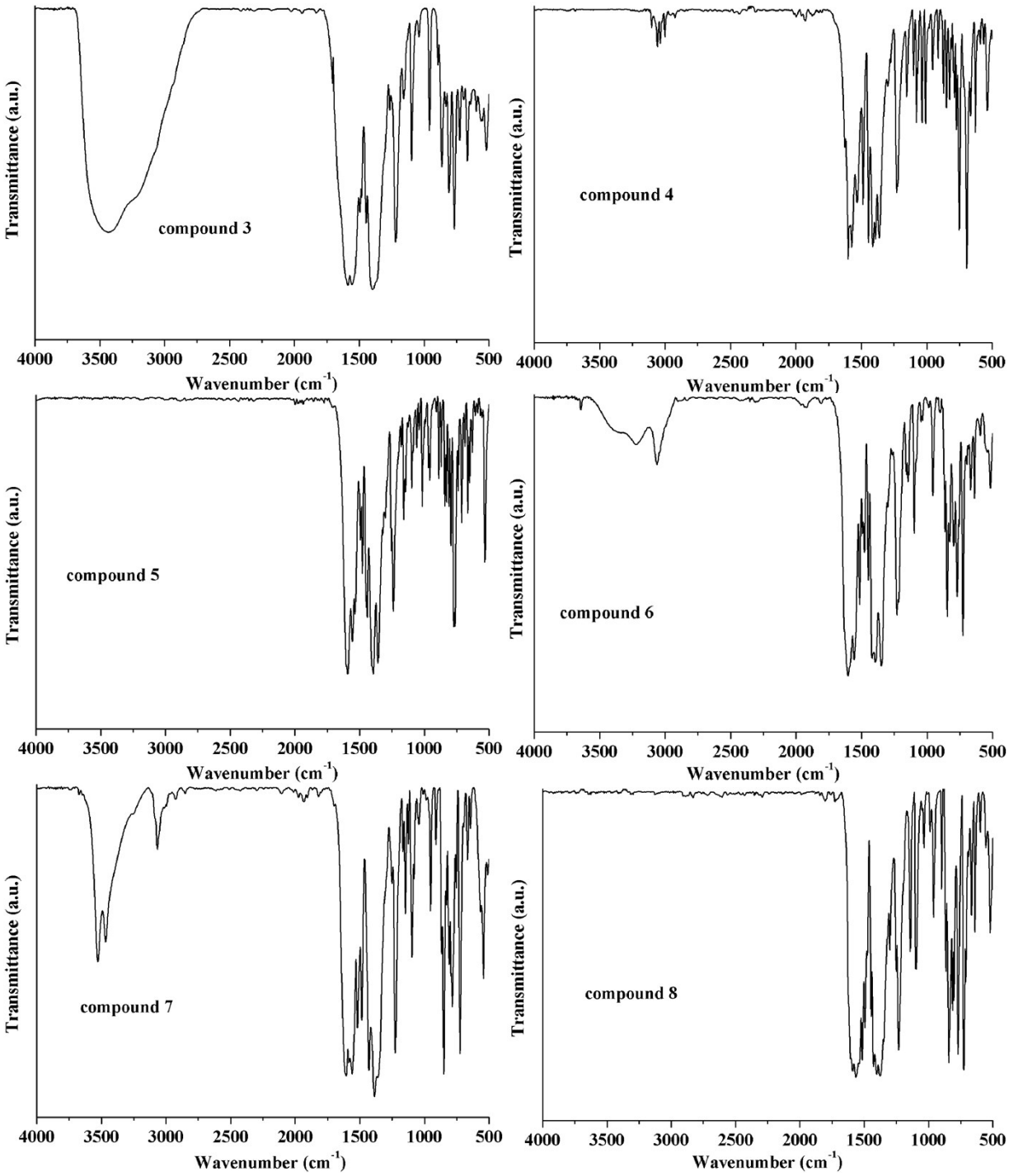
Table S2. Hydrogen bonds in crystal packing [Å, °] of **1–3**, **6**, **7**, and **9–13**.

Complexes	D-H…A	*d*(D-H)	*d*(H…A)	*d*(D…A)	∠DHA	Symmetry code
1	O(3)-H(3)···O(7)	0.82	1.81	2.611	163.5	-*x*+1, -*y*+1, -*z*+1
	O(8)-H(1W)···O(7)	0.86	1.98	2.812	164.0	
	O(8)-H(2W)···O(2)	0.86	1.92	2.743	160.0	*x*-1, *y*, *z*
2	O(4)-H(4)···O(6)	0.82	1.82	2.622	165.4	-*x*+1, -*y*+1, -*z*
	O(8)-H(1W)···O(1)	0.85	1.90	2.726	165.6	-*x*+1, *y*-1/2, -*z*+1/2
	O(8)-H(2W)···O(6)	0.82	2.00	2.763	154.3	-*x*+1, *y*+1/2, -*z*+1/2
3	O(15)-H(1W)···O(2)	0.85	1.85	2.705	179.7	-*x*+1, -*y*+2, -*z*
	O(15)-H(3W) ···Cl(1)	0.85	2.63	3.482	179.9	
	O(16)-H(4W) ···O(5)	0.85	2.10	2.949	179.5	-*x*+2, -*y*+2, -*z*
	O(17)-H(5W) ···O(14)	0.85	2.13	2.975	179.4	-*x*+1, -*y*+2, -*z*+1
	O(17)-H(6W) ···O(8)	0.85	1.80	2.652	179.3	-*x*+2, -*y*+2, -*z*+1
	O(18)-H(7W) ···O(9)	0.84	1.83	2.669	179.0	-*x*+2, -*y*+2, -*z*+1
	O(18)-H(8W) ···Cl(1)	0.85	2.50	3.427	179.9	
	O(19)-H(9W) ···O(4)	0.85	194	2.793	176.6	*x*-1, *y*, *z*+1
6	O(8)-H(1W)···O(3)	0.84	1.94	2.750	160.1	-*x*+1/2, *y*+1/2, -*z*+1/2
	O(8)-H(2W)···O(6)	0.82	2.15	2.826	140.3	-*x*+1, *y*, -*z*+1/2
7	O(8)-H(1W)···O(1)	0.85	2.06	2.908	179.6	*x*, -*y*+1, *z*+1/2
	O(8)-H(2W)···O(4)	0.85	1.97	2.824	179.1	*x*, *y*, *z*+1
9	O(8)-H(1W)···O(7)	0.88	1.86	2.741	171.7	*x*+1, -*y*+1/2, *z*+1/2
	O(8)-H(2W)···O(1)	0.69	2.00	2.664	162.2	*x*, -*y*+1/2, *z*+1/2
10	O(8)-H(1W)···O(5)	0.85	1.88	2.728	179.6	*x*+1/2, *y*+1/2, *z*
	O(8)-H(2W)···O(2)	0.85	2.02	2.875	178.6	-*x*+2, -*y*+1, -*z*
11	N(3)-H(1)···O(4)	0.86	2.11	2.852	144.6	*x*-1, *y*, *z*
	N(4)-H(2)···O(4)	0.86	2.22	2.902	136.1	*x*-1, *y*, *z*
12	N(3)-H(3)···O(2)	0.86	2.06	2.900	163.9	*x*+1/2, -*y*+1/2, *z*
13	O(8)-H(1W)···O(7)	0.85	1.72	2.571	179.8	*x*, *y*, *z*-1
	O(8)-H(2W)···O(2)	0.85	1.80	2.654	179.7	
	O(9)-H(3W)···O(4)	0.85	1.79	2.639	179.6	

Table S3. The C–O_{ether}–C angles and dihedral angles between aromatic rings in $Hcpta^{2-}$/ $cpta^{3-}$ Ligands (º).

Ligand	∠ C–O_{ether}–C	Dihedral Angle	Complex
$Hcpta^{2-}$	116.46	79.48	**1**
$Hcpta^{2-}$	118.94	81.60	**2**
$Hcpta^{2-}$	117.09	81.90	**3**
$cpta^{3-}$	119.27	82.65	**3**
$cpta^{3-}$	118.05	86.34	**4**
$cpta^{3-}$	120.02	86.78	**5**
$cpta^{3-}$	121.12	79.69	**6**
$cpta^{3-}$	115.00	87.69	**7**
$cpta^{3-}$	119.69	76.74	**8**
$cpta^{3-}$	118.52	77.03	**9**
$cpta^{3-}$	119.49	83.76	**10**
$cpta^{3-}$	117.77	86.54	**11**
$cpta^{3-}$	118.30	86.06	**12**
$cpta^{3-}$	115.63	81.28	**13**




Transmittance (a.u.)
compound 3
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)
Transmittance (a.u.)
compound 4
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)
Transmittance (a.u.)
compound 5
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)
Transmittance (a.u.)
compound 6
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)
Transmittance (a.u.)
compound 7
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)
Transmittance (a.u.)
compound 8
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber (cm-1)

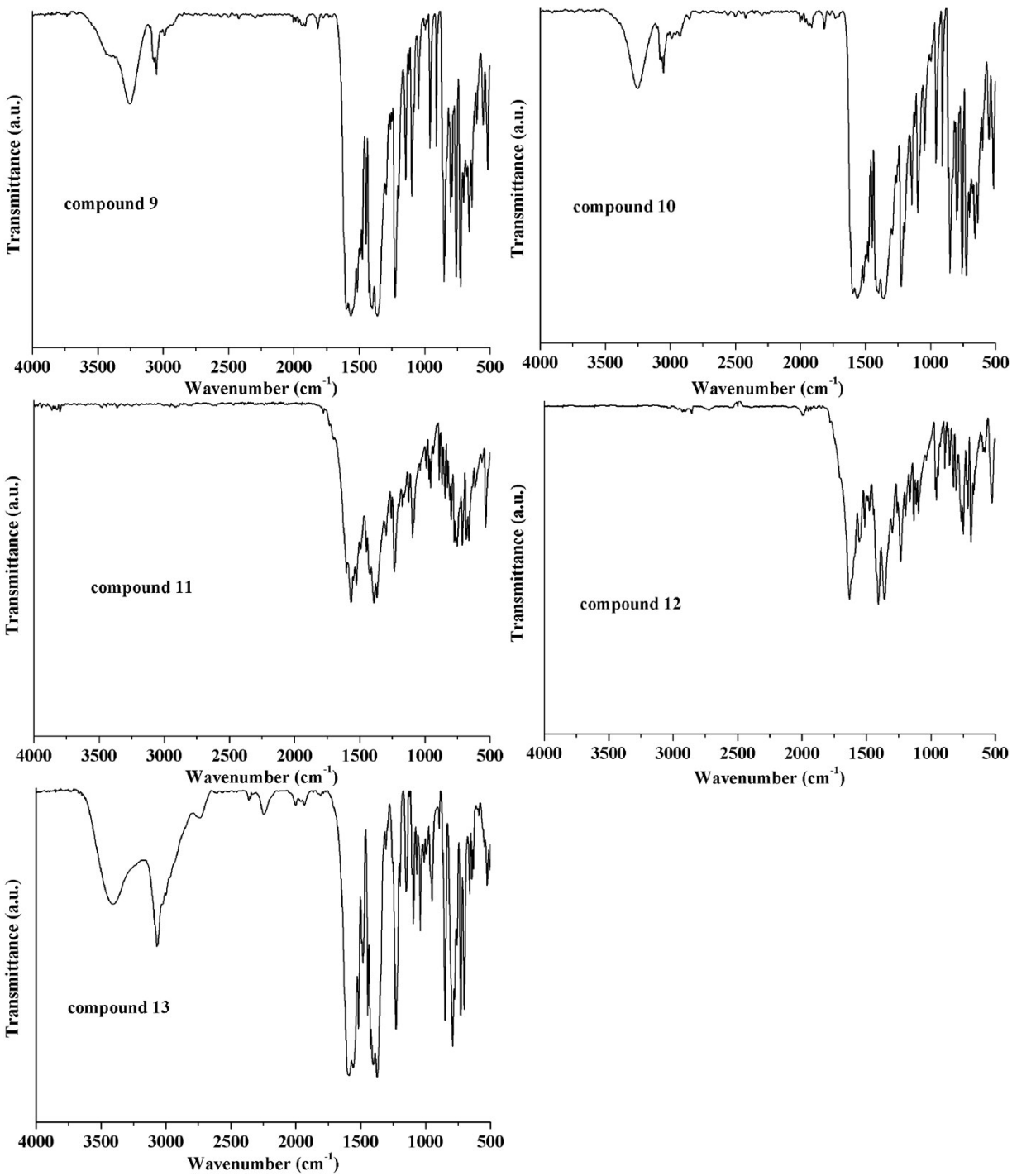


Fig. S1. The FT-IR spectra for compounds **1**–**13**.

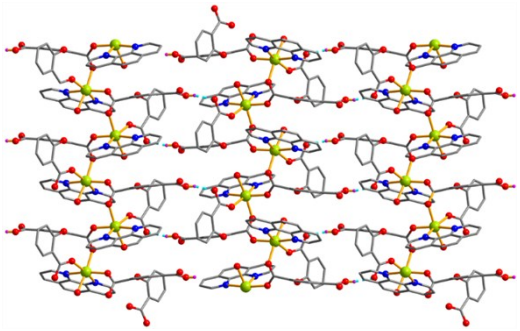


Fig. S2. 2D H-bonded network in **2** seen along the *bc* plane (blue lines represent the H-bonds).

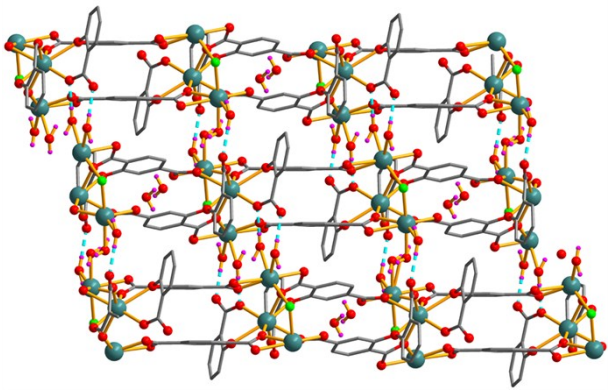


Fig. S3. 2D supramolecular network in **3** viewed along the *bc* plane.

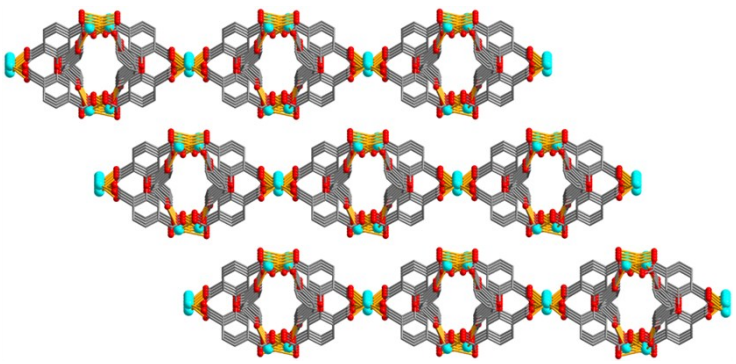


Fig. S4. Packing pattern showing a 3D H-bonded net in **7** along the *c* axis. The H atoms and phen ligands are omitted for clarity.

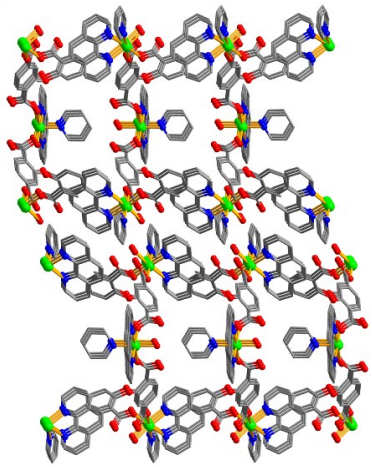
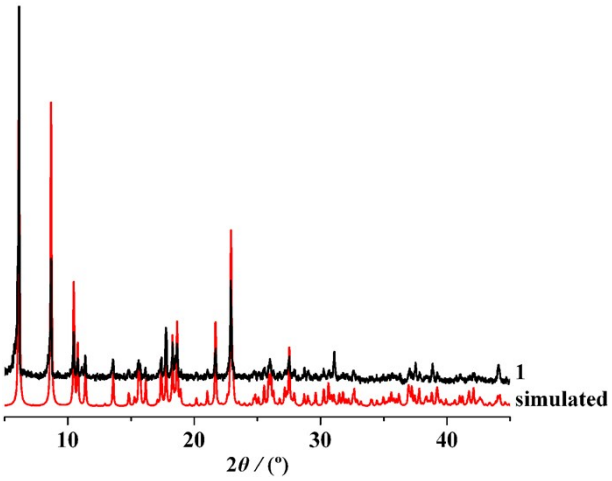
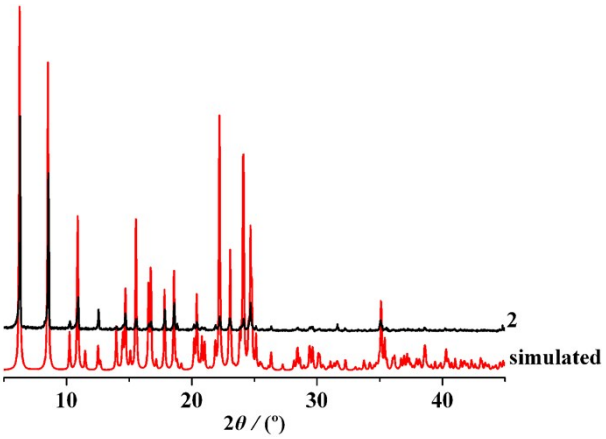
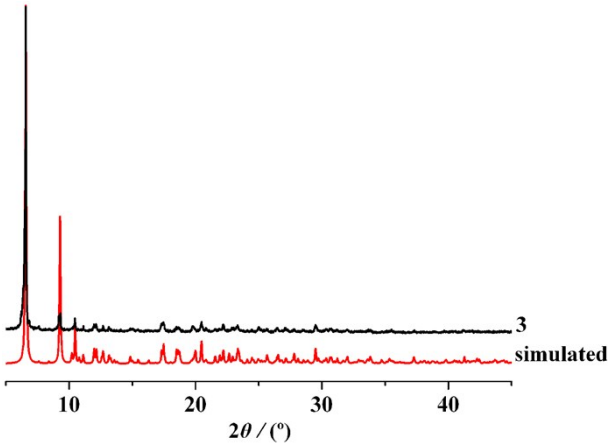
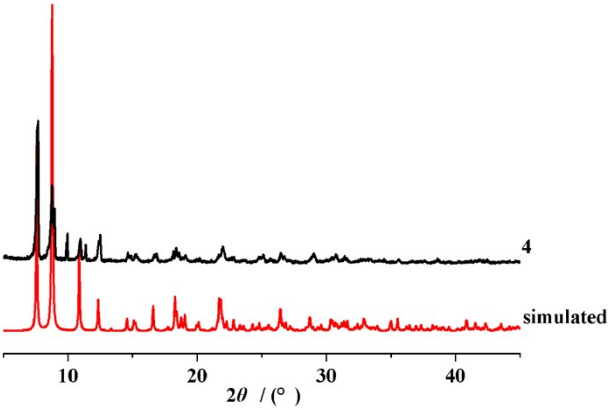


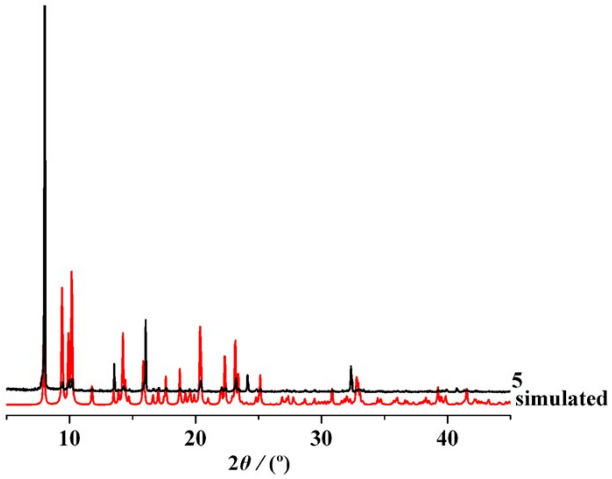
Fig. S5. Packing diagram showing a 3D supramolecular net in **13** along the *ab* plane.

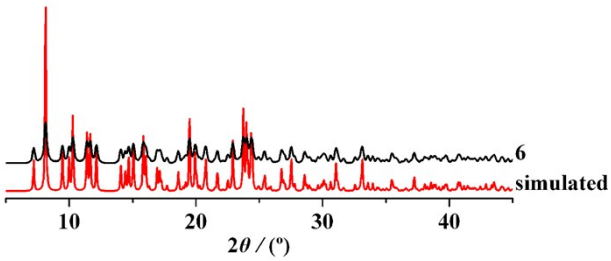

1
simulated
10
20
30
40
2θ / (°)


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 / (°)

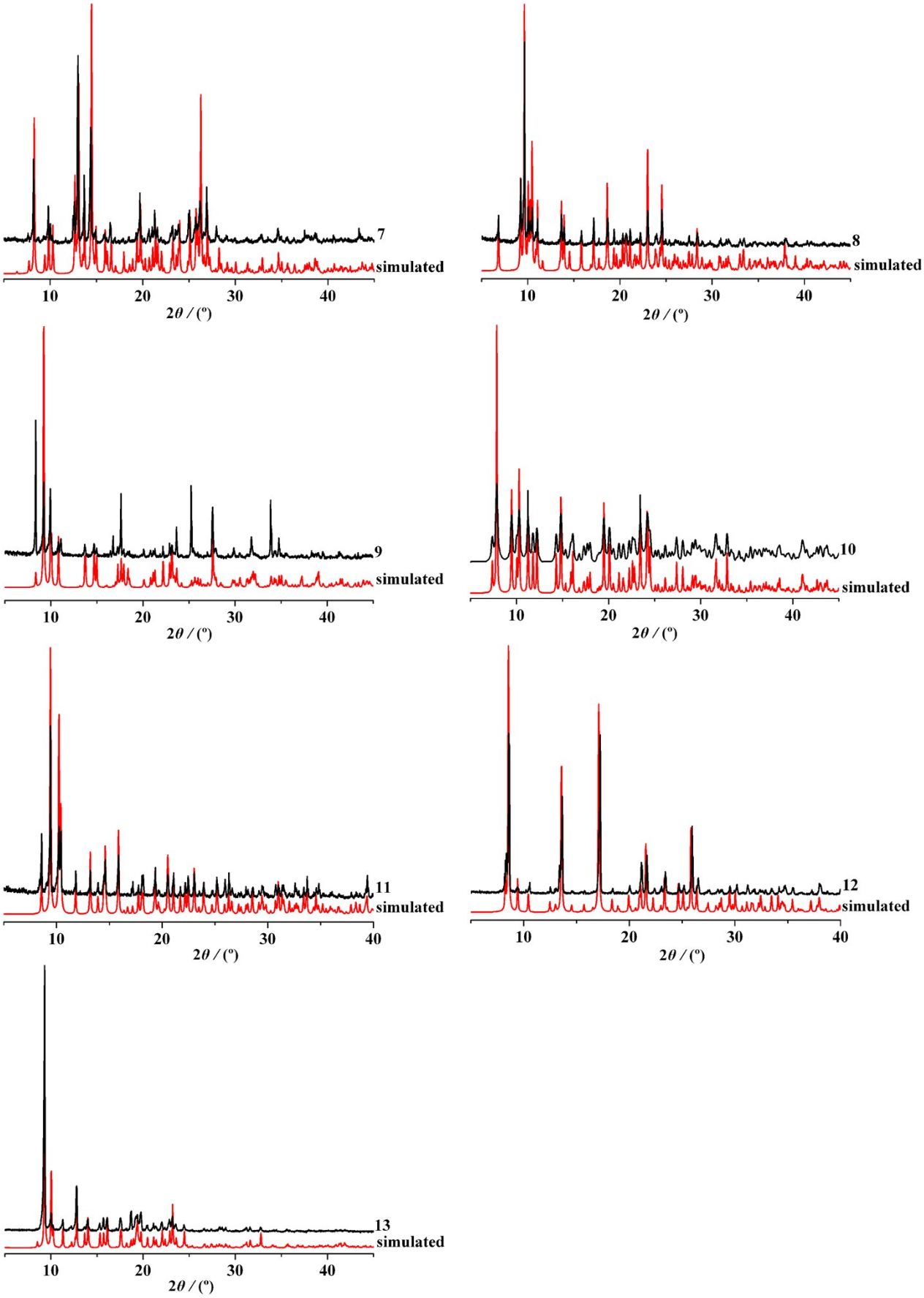


Fig. S6. PXRD patterns of compounds **1**–**13** at room temperature. Black paterns correspnond to the experimental data obtained using the as-synthesized bulk samples. Red patterns were simulated from the single crystal X-ray data.

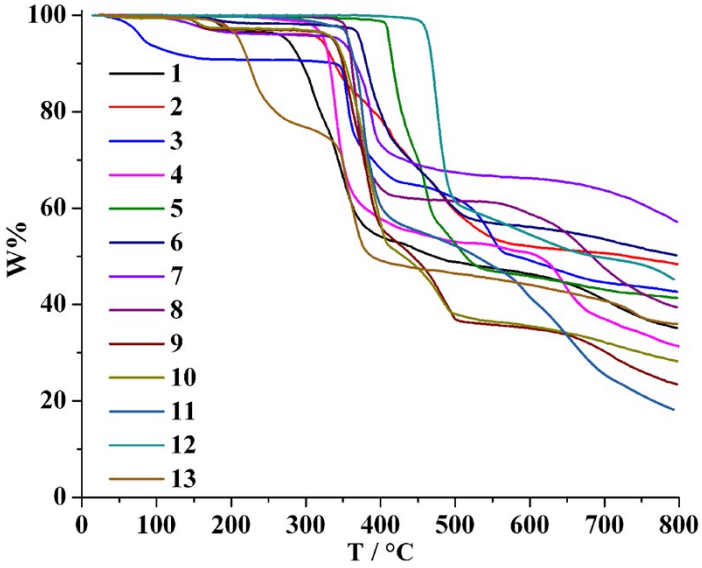


Fig. S7. Thermogravimetric analysis (TGA) curves of compounds **1**–**13**.

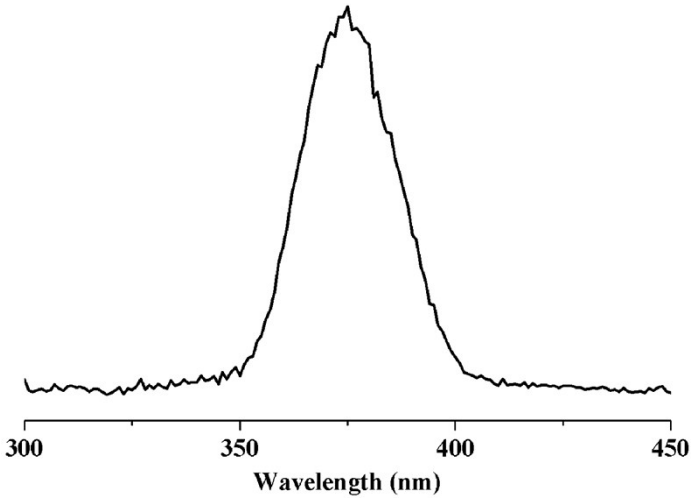


Fig. S8. Solid state excitation spectrum of compound **4**; maximum at 375 nm.

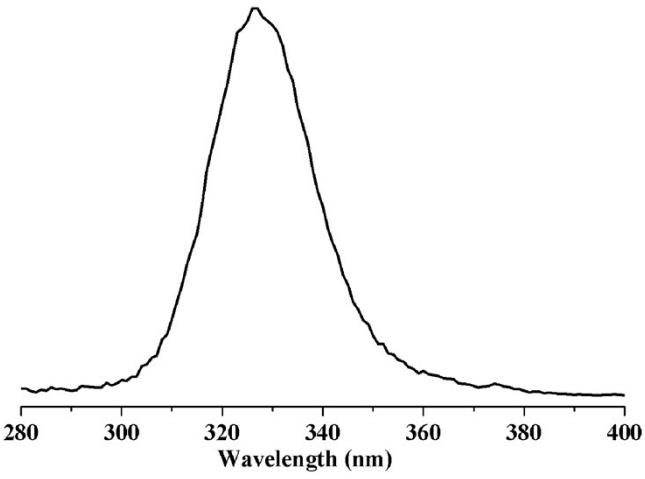


Fig. S9. Excitation spectrum of compound **4** (5 mg) dispersed in water (5 mL); maximum at 325 nm.

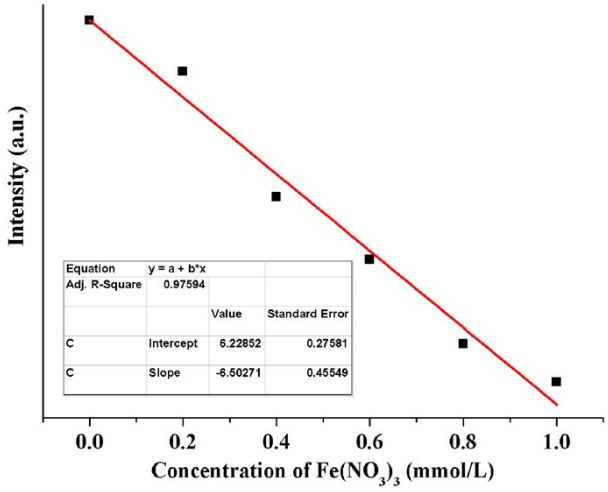


Fig. S10. The relationship between luminescence intensity and Fe^{3+} ion concentration. The red line corresponds to a fit to the linear relationship.

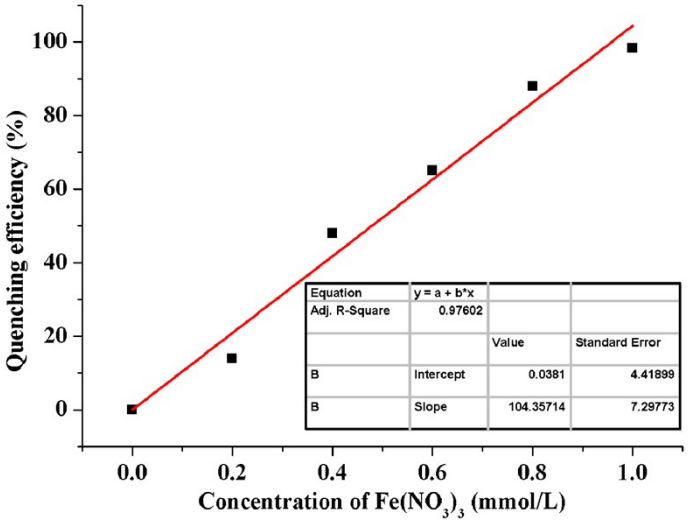


Fig. S11. The fitting plot of the quenching efficiency with the increasing concentration of Fe^{3+}, the red line corresponds to a fit to the linear relationship.

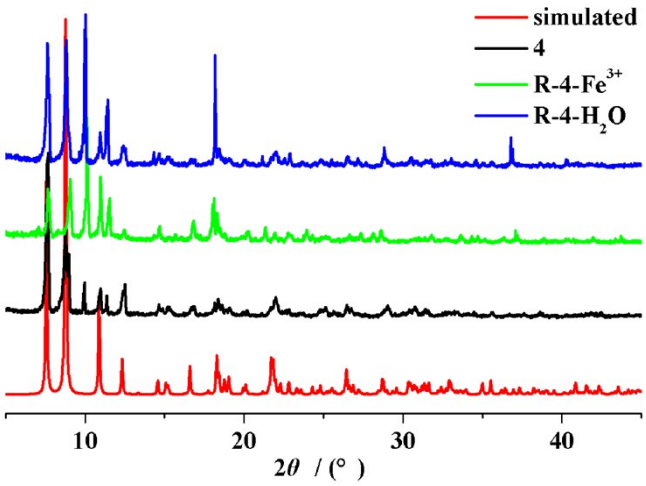


Figure S12. Powder X-ray diffraction patterns of compound **4**: simulated, as-synthesized, after immercion into aqueous solution of $Fe(NO_3)_3$ (R-4-Fe^{3+}), and recovered after sensing tests (R-4-H_2O).