A series of host-guest coordination polymers containing viologens: syntheses, crystal structures, thermo/photochromism and influence factors of the thermo/photochromic behaviors

Wei-Qiu Kan,[a] Yuan-Chun He,*[c] Shi-Zheng Wen*[b] and Pu-Su Zhao[a]

[a]*Jiangsu Province Key Laboratory for Chemistry of Low-Dimensional Materials, School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huaian 223300, PR China.*

[b]*Jiangsu Province Key Laboratory of Modern Measurement Technology and Intelligent Systems, School of Physics and Electronic Electrical Engineering, Huaiyin Normal University, Huaian 223300, PR China.*

[c]*College of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, PR China.*

* Corresponding authors

E-mail: szwen@hytc.edu.cn (S.Z. Wen)

Tel : +86 517 83525083

Fax: +86 517 83525083

E-mail: heyc240@nenu.edu.cn (Y.C. He)

Tel : +86-537-84458301

Fax: +86-537-84458301

Experimental section

Materials and methods

The tricarboxylic acid H_3L was synthesized by following the procedures reported in the literature.[1] Other reagents were purchased and used without further purification. The element analyses data were collected on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra data were recorded on a Nicolet AVATAR360 spectrometer from KBr pellets in the range of 4000–400 cm^{-1}. The thermogravimetric analyses measurements were performed on a NETZSCHSTA 449F3 thermal analyzer from room temperature to 800 °C under nitrogen atmosphere. PXRD spectra of the samples were recorded on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 0.154 nm) and 2θ ranging from 5 to 40°. The experimental PXRD patterns are nearly identical with the corresponding simulated ones except the intensities of some peaks (Figure S1). UV-vis absorption spectra data were recorded using a Cary 500 spectrophotometer from 200 to 800 nm. In-situ testing method has been used for the collection of UV-vis absorption spectra of compound **1** at 150 ℃. The electron paramagnetic resonance spectra data were collected on a Bruker ESP 300E electron paramagnetic resonance spectrometer. In-situ testing method has been used for the collection of EPR spectra of compound **1** at 150 ℃ and compounds **3**, **4** and **7** under visible light. The X-ray photoelectron spectroscopy were measured on a ThermoFisher ESCALAB250 X-ray photoelectron spectrometer (powered at 150 W) using Al Kα radiation (λ = 8.357 Å).

Caution! *Viologens, $Co(OAc)_2{\cdot}4H_2O$, $Mn(OAc)_2{\cdot}4H_2O$, $Cd(OAc)_2{\cdot}2H_2O$ and dimethylsulfoxide are all poisonous for human health and experiments should only be handled with proper protocols to avoid accidents.*

Synthesis of $[Co(DMBPY)_{0.5}(L)]{\cdot}H_2O$ (1)

H_3L (39.2 mg, 0.1 mmol), $Co(OAc)_2{\cdot}4H_2O$ (49.8 mg, 0.2 mmol), $DMBPY{\cdot}Cl_2$ (25.7 mg, 0.1 mmol) and 15 mL H_2O was sealed in a 20 mL Teflon reactor and heated at 140 °C for 3 days. After cooling to room temperature, green crystals of compound **1** were obtained in a yield of 58%. Anal. Calcd for $C_{28}H_{22}CoNO_8$ (M_r = 559.4): C, 60.12; H, 3.96; N, 2.50%. Found: C, 60.25; H, 3.89; N, 2.41%. IR (cm^{-1}): 3734 (w), 3441

(m), 3047 (m), 2892 (w), 2557 (w), 1642 (s), 1575 (s), 1509(m), 1451 (m), 1398 (s), 1354 (s), 1269 (s), 1189 (w), 1127 (m), 1057 (s), 955 (w), 893 (w), 832 (w), 777 (s), 720 (m), 666 (w), 467 (w).

Synthesis of $[Mn(DMBPY)_{0.5}(L)]\cdot H_2O$ (2)

H_3L (39.2 mg, 0.1 mmol), $Mn(OAc)_2\cdot 4H_2O$ (24.5 mg, 0.1 mmol), $DMBPY\cdot Cl_2$ (12.85 mg, 0.05 mmol) and 15 mL H_2O was sealed in a 20 mL Teflon reactor and heated at 130 °C for 3 days. After cooling to ambient temperature, yellow crystals of compound **2** were obtained in a yield of 47%. Anal. Calcd for $C_{28}H_{22}MnNO_8$ (M_r = 555.41): C, 60.55; H, 3.99; N, 2.52%. Found: C, 60.41; H, 3.89; N, 2.61%. IR (cm^{-1}): 3730 (w), 3451 (m), 3042 (w), 2896 (w), 1637 (s), 1575 (s), 1513 (w), 1451 (m), 1402 (s), 1349 (s), 1269 (s), 1194 (m), 1124 (s), 1093 (s), 1052 (s), 893 (w), 821 (m), 787 (s), 715 (m), 666 (w), 476 (w), 419 (s).

Synthesis of $[Cd(DEBPY)_{0.5}(L)]\cdot H_2O$ (3)

H_3L (39.2 mg, 0.1 mmol), $Cd(OAc)_2\cdot 2H_2O$ (53.3 mg, 0.2 mmol), $DEBPY\cdot Br_2$ (37.4 mg, 0.1 mmol) and 15 mL H_2O was sealed in a 20 mL Teflon reactor and heated at 130 °C for 3 days. After cooling to room temperature, yellow crystals of compound **3** were obtained in a yield of about 25%. Anal. Calcd for $C_{29}H_{24}CdNO_8$ (M_r = 626.91): C, 55.56; H, 3.86; N, 2.23%. Found: C, 55.44; H, 3.95; N, 2.32%. IR (cm^{-1}): 3725 (w), 3428 (m), 3052 (m), 2859 (w), 1615 (s), 1557 (s), 1447 (s), 1376 (s), 1261 (m), 1176 (w), 1119 (w), 1034 (m), 923 (w), 835 (w), 777 (s), 725 (m), 666 (w), 569 (w), 520 (w), 422 (w).

Synthesis of $[Cd_5(DEBPY)_{0.5}(HL)(L)_3(H_2O)_3]\cdot 2H_2O$ (4)

H_3L (39.2 mg, 0.1 mmol), $Cd(OAc)_2\cdot 2H_2O$ (26.7 mg, 0.1 mmol), $DEBPY\cdot Br_2$ (18.5 mg, 0.05 mmol) and 15 mL H_2O was sealed in a 20 mL Teflon reactor and heated at 140 °C for 3 days. After cooling to room temperature, yellow crystals of compound **4** were obtained in a yield of about 40%. Anal. Calcd for $C_{95}H_{72}Cd_5NO_{33}$ (M_r = 2317.63): C, 49.23; H, 3.13; N, 0.60%. Found: C, 49.34; H, 3.23; N, 0.66%. IR (cm^{-1}): 3730 (w), 3406 (m), 3056 (w), 1722 (w), 1540 (s), 1447 (s), 1371 (s), 1265 (m), 1127 (m), 1039 (m), 933 (w), 821 (w), 769 (m), 733 (w), 671 (w), 614 (w), 471 (w).

Synthesis of $[Cd(DEBPY)_{0.5}(L)(H_2O)]\cdot H_2O$ (5)

H_3L (39.2 mg, 0.1 mmol), $Cd(OAc)_2\cdot 2H_2O$ (53.3 mg, 0.2 mmol), $DEBPY\cdot Br_2$ (37.4 mg, 0.1 mmol), 10 mL H_2O and 5 mL dimethylsulfoxide (DMSO) was sealed in a 20 mL Teflon reactor and heated at 140 °C for 3 days. After cooling to room temperature, yellow crystals of compound **5** were obtained in a yield of about 46%. Anal.Calcd for $C_{29}H_{26}CdNO_9$ (M_r = 644.93): C, 54.01; H, 4.06; N, 2.17%. Found: C, 54.14; H, 3.98; N, 2.28%. Found: C, 55.44; H, 3.95; N, 2.32%. IR (cm^{-1}): 3725 (w), 3414 (m), 3056 (m), 2874 (w), 1611 (s), 1557 (s), 1447 (s), 1376 (s), 1256 (m), 1181 (w), 1119 (m), 1034 (s), 919 (w), 839 (w), 787 (m), 720 (m), 662 (w), 569 (w), 498 (w), 422 (m).

Synthesis of $[Mn(DEBPY)_{0.5}(L)]\cdot H_2O$ (6)

H_3L (39.2 mg, 0.1 mmol), $Mn(OAc)_2\cdot 2H_2O$ (49.0 mg, 0.2 mmol), $DEBPY\cdot Br_2$ (37.4 mg, 0.1 mmol) and 15 mL H_2O was sealed in a 20 mL Teflon reactor and heated at 140 °C for 3 days. After cooling to ambient temperature, yellow crystals of compound **6** were obtained in a yield of 38%. Anal. Calcd for $C_{29}H_{24}MnNO_8$ (M_r = 569.44): C, 61.17; H, 4.25; N, 2.46%. Found: C, 61.07; H, 4.14; N, 2.40%. IR (cm^{-1}): 3725 (w), 3446 (m), 3056 (m), 2861 (w), 1633 (s), 1580 (s), 1447 (m), 1402 (s), 1349 (s), 1261 (m), 1176 (w), 1119 (m), 1048 (m), 888 (w), 853 (w), 787 (s), 711 (m), 662 (w), 574 (w), 419 (m).

Synthesis of $[(DEBPY)_{0.5}(H_2L)]\cdot 1.25H_2O$ (7)

The preparation of compound **7** was similar to that of compound **3**, except that after cooling to room temperature, the mixture was kept undisturbed for two days. Yellow crystals of compound **7** were obtained in a yield of 21%. Anal. Calcd for $C_{29}H_{26.5}NO_{8.25}$ (M_r = 521.02): C, 66.85; H, 5.13; N, 2.69. Found: C, 66.79; H, 5.19; N, 2.58%. IR (cm^{-1}): 3730 (w), 3402 (m), 3060 (m), 2865 (w), 1722 (w), 1540 (s), 1451 (s), 1404 (s), 1367 (s), 1265 (m), 1127 (m), 1034 (m), 933 (w), 870 (w), 826 (w), 769 (s), 733 (m), 666 (w), 471 (w).

X-ray crystallography

Single-crystal X-ray diffraction data of compounds **1**–**7** were recorded on a Bruker SMART APEX II diffractometer with graphite-monochromated Mo Kα radiation (λ =

0.71073 Å) at 293 K. Absorption corrections were applied using a multi-scan technique. Structures of **1-7** were solved by Direct Method of SHELXS-97[2] and refined by full-matrix least-squares techniques using the SHELXL-97 program.[3] Non-hydrogen atoms of the compounds were refined with anisotropic temperature parameters. All hydrogen atoms on carbon atoms were generated geometrically and refined using a riding model with d(C–H) = 0.93 Å, U_{iso} = 1.2U_{eq}(C) for aromatic rings, d(C–H) = 0.97 Å, U_{iso} = 1.2U_{eq}(C) for CH_2 and d(C–H) = 0.96 Å, U_{iso} = 1.5U_{eq}(C) for CH_3. Hydrogen atoms of water molecules for compounds 1-7 were located from difference Fourier maps and refined as riding atoms with d(O–H) = 0.823-0.892 Å and U_{iso} = 1.5U_{eq}(O). Selected bond lengths and angles of compounds **1-7** are listed in Tables S1-S7.

Table S1 Selected bond lengths [Å], angles (º) and hydrogen bonds for compound **1**

Co(1)-O(1)	1.9762(19)	Co(1)-O(4)$^{\#1}$	2.027(2)
Co(1)-O(6)$^{\#2}$	2.052(2)	Co(1)-O(7)$^{\#3}$	2.061(2)
Co(1)-O(3)$^{\#4}$	2.0947(19)		
O(1)-Co(1)-O(4)$^{\#1}$	111.77(8)	O(1)-Co(1)-O(6)$^{\#2}$	101.88(9)
O(4)$^{\#1}$-Co(1)-O(6)$^{\#2}$	92.49(9)	O(1)-Co(1)-O(7)$^{\#3}$	100.18(9)
O(4)$^{\#1}$-Co(1)-O(7)$^{\#3}$	90.24(9)	O(6)$^{\#2}$-Co(1)-O(7)$^{\#3}$	154.95(9)
O(1)-Co(1)-O(3)$^{\#4}$	91.42(8)	O(4)$^{\#1}$-Co(1)-O(3)$^{\#4}$	156.81(8)
O(6)$^{\#2}$-Co(1)-O(3)$^{\#4}$	82.63(9)	O(7)$^{\#3}$-Co(1)-O(3)$^{\#4}$	85.12(9)

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
O(1W)-H(1A)···O(2)	0.838(10)	2.093(15)	2.844(4)	149(3)
O(1W)-H(1B)···O(1W)$^{\#8}$	0.823(9)	2.533(6)	3.061(6)	123.0(6)
C(15)-H(15)···O(5)	0.93	2.35	2.698(4)	101.8
C(19)-H(19)···O(2)$^{\#9}$	0.93	2.52	3.432(4)	166.1
C(23)-H(23)···O(1W)$^{\#6}$	0.93	2.58	3.474(5)	161.3
C(24)-H(24)···O(7)$^{\#10}$	0.93	2.38	3.230(4)	152.4
C(28)-H(28C)···O(3)$^{\#11}$	0.96	2.34	3.234(5)	155.2

Symmetry transformation used to generate equivalent atoms: $^{\#1}$ $x + 1, y, z$; $^{\#2}$ $–x + 1, -y + 1, z + 1$; $^{\#3}$ $x + 1, y - 1, z + 1$; $^{\#4}$ $–x + 1, -y, -z + 2$; $^{\#6}$ $x - 1, y, z$; $^{\#8}$ $–x + 2, -y, -z + 1$; $^{\#9}$ $–x + 1, -y + 1, -z$; $^{\#10}$ $-x, -y + 1, -z$; $^{\#11}$ $x, y, z – 1$.

Table S2 Selected bond lengths [Å], angles (º) and hydrogen bonds for compound **2**

Mn(1)-O(5)$^{\#1}$	2.0468(19)	Mn(1)-O(7)$^{\#2}$	2.119(2)
Mn(1)-O(2)$^{\#3}$	2.1351(19)	Mn(1)-O(1)	2.171(2)
Mn(1)-O(6)$^{\#4}$	2.1728(19)		
O(5)$^{\#1}$-Mn(1)-O(7)$^{\#2}$	111.96(8)	O(5)$^{\#1}$-Mn(1)-O(2)$^{\#3}$	108.35(8)
O(7)$^{\#2}$-Mn(1)-O(2)$^{\#3}$	91.53(8)	O(5)$^{\#1}$-Mn(1)-O(1)	99.29(8)
O(7)$^{\#2}$-Mn(1)-O(1)	89.79(8)	O(2)$^{\#3}$-Mn(1)-O(1)	149.53(8)
O(5)$^{\#1}$-Mn(1)-O(6)$^{\#4}$	95.57(8)	O(7)$^{\#2}$-Mn(1)-O(6)$^{\#4}$	152.42(8)
O(2)$^{\#3}$-Mn(1)-O(6)$^{\#4}$	80.71(8)	O(1)-Mn(1)-O(6)$^{\#4}$	84.15(8)
O(5)$^{\#1}$-Mn(1)-Mn(1)$^{\#3}$	164.65(6)	O(7)$^{\#2}$-Mn(1)-Mn(1)$^{\#3}$	78.56(5)
O(2)$^{\#3}$-Mn(1)-Mn(1)$^{\#3}$	58.88(5)	O(1)-Mn(1)-Mn(1)$^{\#3}$	91.68(5)
O(6)$^{\#4}$-Mn(1)-Mn(1)$^{\#3}$	74.77(5)		

D-H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(1W)-H(1A)···O(7)$^{\#2}$	0.846(10)	2.44(2)	3.238(3)	158(5)
O(1W)-H(1B)···O(1W)$^{\#8}$	0.841(10)	2.478(7)	2.977(6)	118.9(6)
C(4)-H(4)···O(4)$^{\#9}$	0.93	2.48	3.396(3)	166.5
C(10)-H(10)···O(3)	0.93	2.34	2.691(3)	102.1
C(27)-H(27)···O(1)$^{\#6}$	0.93	2.29	3.158(4)	154.7
C(28)-H(28A)···O(6)$^{\#10}$	0.96	2.60	3.231(4)	123.6

Symmetry transformation used to generate equivalent atoms: $^{\#1}$ $x + 1, y - 1, z + 1$; $^{\#2}$ $x, y - 1, z + 1$; $^{\#3}$ $-x + 1, -y + 1, -z$; $^{\#4}$ $-x + 1, -y + 2, -z - 1$; $^{\#6}$ $x - 1, y + 1, z - 1$; $^{\#8}$ $-x + 1, -y + 1, -z + 1$; $^{\#9}$ $-x, -y + 2, -z$; $^{\#10}$ $-x, -y + 3, -z - 2$.

Table S3 Selected bond lengths [Å], angles (º) and hydrogen bonds for compound **3**

Cd(1)-O(11)$^{\#1}$	2.156(3)	Cd(1)-O(12)$^{\#2}$	2.210(3)
Cd(1)-O(7)$^{\#3}$	2.244(3)	Cd(1)-O(6)	2.261(3)
Cd(1)-O(13)$^{\#4}$	2.319(3)	Cd(1)-Cd(1)$^{\#3}$	3.2728(12)
O(11)$^{\#1}$-Cd(1)-O(12)$^{\#2}$	116.33(11)	O(11)$^{\#1}$-Cd(1)-O(7)$^{\#3}$	100.44(11)
O(12)$^{\#2}$-Cd(1)-O(7)$^{\#3}$	92.15(12)	O(11)$^{\#1}$-Cd(1)-O(6)	101.78(11)
O(12)$^{\#2}$-Cd(1)-O(6)	95.32(11)	O(7)$^{\#3}$-Cd(1)-O(6)	150.36(10)
O(11)$^{\#1}$-Cd(1)-O(13)$^{\#4}$	91.01(10)	O(12)$^{\#2}$-Cd(1)-O(13)$^{\#4}$	152.55(10)

O(7)$^{\#3}$-Cd(1)-O(13)$^{\#4}$	79.82(11)	O(6)-Cd(1)-O(13)$^{\#4}$	80.41(11)
O(11)$^{\#1}$-Cd(1)-Cd(1)$^{\#3}$	157.54(8)	O(12)$^{\#2}$-Cd(1)-Cd(1)$^{\#3}$	85.63(8)
O(7)$^{\#3}$-Cd(1)-Cd(1)$^{\#3}$	82.37(7)	O(6)-Cd(1)-Cd(1)$^{\#3}$	69.71(7)
O(13)$^{\#4}$-Cd(1)-Cd(1)$^{\#3}$	67.38(7)		

D-H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(1W)-H(1A)···O(1W)$^{\#7}$	0.844(10)	2.517(7)	3.043(7)	121.3(6)
O(1W)-H(1B)···O(10)$^{\#1}$	0.846(10)	2.19(2)	2.980(5)	155(4)
C(24)-H(24)···O(1W)$^{\#8}$	0.93	2.41	3.288(6)	157.6
C(25)-H(25)···O(7)	0.93	2.53	3.423(5)	160.8
C(26)-H(26)···O(6)$^{\#9}$	0.93	2.46	3.376(5)	168.5

Symmetry transformation used to generate equivalent atoms: $^{\#1}$ -*x*, -*y*, -*z* + 2; $^{\#2}$ –*x* + 1, -*y*, -*z* + 2; $^{\#3}$ –*x* + 1, -*y* + 1, -*z* + 1; $^{\#4}$ *x*, *y* + 1, *z* – 1; $^{\#7}$ –*x* + 1, -*y*, -*z* + 1; $^{\#8}$ *x*, *y* + 1, *z*; $^{\#9}$ *x* + 1, *y*, *z*.

Table S4 Selected bond lengths [Å], angles (º) and hydrogen bonds for compound **4**

Cd(1)-O(7)$^{\#1}$	2.222(4)	Cd(1)-O(5)$^{\#2}$	2.283(4)
Cd(1)-O(2)	2.302(4)	Cd(1)-O(3W)	2.357(4)
Cd(1)-O(4)$^{\#2}$	2.405(6)	Cd(1)-O(10)$^{\#3}$	2.440(4)
Cd(2)-O(6)$^{\#1}$	2.219(4)	Cd(2)-O(11)$^{\#3}$	2.222(4)
Cd(2)-O(1)	2.256(4)	Cd(2)-O(8)	2.260(4)
Cd(2)-O(26)$^{\#4}$	2.383(3)	Cd(2)-O(9)	2.536(3)
Cd(3)-O(15)	2.239(4)	Cd(3)-O(1W)	2.334(3)
Cd(3)-O(18)$^{\#5}$	2.337(4)	Cd(3)-O(26)$^{\#4}$	2.342(3)
Cd(3)-O(9)	2.368(3)	Cd(3)-O(17)$^{\#5}$	2.414(3)
Cd(4)-O(16)	2.246(4)	Cd(4)-O(25)$^{\#4}$	2.250(3)
Cd(4)-O(2W)	2.259(4)	Cd(4)-O(28)$^{\#6}$	2.328(4)
Cd(4)-O(27)$^{\#6}$	2.376(3)	Cd(4)-O(10)$^{\#3}$	2.384(3)
Cd(5)-O(17)	2.243(3)	Cd(5)-O(27)$^{\#6}$	2.271(4)
Cd(5)-O(21)$^{\#7}$	2.297(4)	Cd(5)-O(22)	2.328(4)
Cd(5)-O(20)$^{\#7}$	2.329(4)	Cd(5)-O(23)	2.347(4)
O(7)$^{\#1}$-Cd(1)-O(5)$^{\#2}$	141.62(14)	O(7)$^{\#1}$-Cd(1)-O(2)	90.48(14)

O(5)$^{\#2}$-Cd(1)-O(2)	102.72(14)	O(7)$^{\#1}$-Cd(1)-O(3W)	81.67(15)
O(5)$^{\#2}$-Cd(1)-O(3W)	94.22(15)	O(2)-Cd(1)-O(3W)	160.72(15)
O(7)$^{\#1}$-Cd(1)-O(4)$^{\#2}$	85.68(17)	O(5)$^{\#2}$-Cd(1)-O(4)$^{\#2}$	56.00(17)
O(2)-Cd(1)-O(4)$^{\#2}$	108.1(2)	O(3W)-Cd(1)-O(4)$^{\#2}$	89.0(2)
O(7)$^{\#1}$-Cd(1)-O(10)$^{\#3}$	129.62(13)	O(5)$^{\#2}$-Cd(1)-O(10)$^{\#3}$	88.37(13)
O(2)-Cd(1)-O(10)$^{\#3}$	80.68(12)	O(3W)-Cd(1)-O(10)$^{\#3}$	90.78(13)
O(4)$^{\#2}$-Cd(1)-O(10)$^{\#3}$	144.23(16)	O(6)$^{\#1}$-Cd(2)-O(11)$^{\#3}$	127.56(13)
O(6)$^{\#1}$-Cd(2)-O(1)	88.82(13)	O(11)$^{\#3}$-Cd(2)-O(1)	81.52(13)
O(6)$^{\#1}$-Cd(2)-O(8)	99.48(13)	O(11)$^{\#3}$-Cd(2)-O(8)	132.15(13)
O(1)-Cd(2)-O(8)	92.45(13)	O(6)$^{\#1}$-Cd(2)-O(26)$^{\#4}$	85.09(13)
O(11)$^{\#3}$-Cd(2)-O(26)$^{\#4}$	99.07(12)	O(1)-Cd(2)-O(26)$^{\#4}$	172.73(13)
O(8)-Cd(2)-O(26)$^{\#4}$	92.46(12)	O(6)$^{\#1}$-Cd(2)-O(9)	143.86(12)
O(11)$^{\#3}$-Cd(2)-O(9)	85.00(12)	O(1)-Cd(2)-O(9)	114.07(12)
O(8)-Cd(2)-O(9)	54.32(12)	O(26)$^{\#4}$-Cd(2)-O(9)	73.18(11)
O(15)-Cd(3)-O(1W)	90.03(13)	O(15)-Cd(3)-O(18)$^{\#5}$	84.15(13)
O(1W)-Cd(3)-O(18)$^{\#5}$	103.42(12)	O(15)-Cd(3)-O(26)$^{\#4}$	126.23(12)
O(1W)-Cd(3)-O(26)$^{\#4}$	86.08(13)	O(18)$^{\#5}$-Cd(3)-O(26)$^{\#4}$	148.61(13)
O(15)-Cd(3)-O(9)	112.66(13)	O(1W)-Cd(3)-O(9)	156.89(12)
O(18)$^{\#5}$-Cd(3)-O(9)	84.05(12)	O(26)$^{\#4}$-Cd(3)-O(9)	77.08(12)
O(15)-Cd(3)-O(17)$^{\#5}$	135.34(12)	O(1W)-Cd(3)-O(17)$^{\#5}$	83.76(12)
O(18)$^{\#5}$-Cd(3)-O(17)$^{\#5}$	54.96(12)	O(26)$^{\#4}$-Cd(3)-O(17)$^{\#5}$	97.50(12)
O(9)-Cd(3)-O(17)$^{\#5}$	82.89(12)	O(16)-Cd(4)-O(25)$^{\#4}$	122.12(13)
O(16)-Cd(4)-O(2W)	84.54(13)	O(25)$^{\#4}$-Cd(4)-O(2W)	91.17(13)
O(16)-Cd(4)-O(28)$^{\#6}$	151.88(13)	O(25)$^{\#4}$-Cd(4)-O(28)$^{\#6}$	83.43(12)
O(2W)-Cd(4)-O(28)$^{\#6}$	108.33(14)	O(16)-Cd(4)-O(27)$^{\#6}$	100.34(12)
O(25)$^{\#4}$-Cd(4)-O(27)$^{\#6}$	137.54(12)	O(2W)-Cd(4)-O(27)$^{\#6}$	92.60(13)
O(28)$^{\#6}$-Cd(4)-O(27)$^{\#6}$	55.35(12)	O(16)-Cd(4)-O(10)$^{\#3}$	81.65(13)
O(25)$^{\#4}$-Cd(4)-O(10)$^{\#3}$	96.04(12)	O(2W)-Cd(4)-O(10)$^{\#3}$	166.20(13)
O(28)$^{\#6}$-Cd(4)-O(10)$^{\#3}$	84.25(13)	O(27)$^{\#6}$-Cd(4)-O(10)$^{\#3}$	90.00(12)
O(17)-Cd(5)-O(27)$^{\#6}$	90.62(12)	O(17)-Cd(5)-O(21)$^{\#7}$	144.51(13)

O(27)$^{\#6}$-Cd(5)-O(21)$^{\#7}$	90.88(13)	O(17)-Cd(5)-O(22)	113.28(13)
O(27)$^{\#6}$-Cd(5)-O(22)	95.86(13)	O(21)$^{\#7}$-Cd(5)-O(22)	101.83(13)
O(17)-Cd(5)-O(20)$^{\#7}$	93.49(13)	O(27)$^{\#6}$-Cd(5)-O(20)$^{\#7}$	121.99(13)
O(21)$^{\#7}$-Cd(5)-O(20)$^{\#7}$	56.43(12)	O(22)-Cd(5)-O(20)$^{\#7}$	133.70(13)
O(17)-Cd(5)-O(23)	94.36(13)	O(27)$^{\#6}$-Cd(5)-O(23)	150.73(13)
O(21)$^{\#7}$-Cd(5)-O(23)	101.31(14)	O(22)-Cd(5)-O(23)	55.79(13)
O(20)$^{\#7}$-Cd(5)-O(23)	86.51(13)		

D-H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(13)-H(13A)...O(5W)	0.82	1.88	2.694(7)	172.3
O(1W)-H(1A)...O(4W)	0.85	1.84	2.689(5)	173.9
O(1W)-H(1B)...O(20)$^{\#9}$	0.85	1.82	2.669(5)	173.8
O(2W)-H(2A)...O(22)	0.85	1.86	2.704(5)	172.3
O(2W)-H(2B)...O(1W)	0.85	1.95	2.795(5)	172.4
O(3W)-H(3A)...O(28)$^{\#6}$	0.85	1.91	2.673(6)	149.5
O(3W)-H(3B)...O(25)$^{\#4}$	0.85	2.20	2.965(6)	150.6
O(4W)-H(4A)...O(23)$^{\#5}$	0.86	1.94	2.745(6)	154.2
O(4W)-H(4B)...O(19)$^{\#9}$	0.86	2.03	2.880(6)	171.1
O(5W)-H(5A)...O(4)$^{\#10}$	0.83	2.21	2.982(9)	155.4
O(5W)-H(5B)...O(3)$^{\#11}$	0.86	2.14	2.995(7)	173.3
C(16)-H(16)...O(14)$^{\#11}$	0.93	2.41	3.162(9)	137.8
C(33)-H(33)...O(12)	0.93	2.40	2.744(7)	101.3
C(52)-H(52)...O(27)$^{\#6}$	0.93	2.59	3.455(6)	155.4
C(75)-H(75)...O(22)	0.93	2.47	3.178(6)	133.2
C(78)-H(78)...O(14)$^{\#9}$	0.93	2.41	3.332(8)	174.3
C(90)-H(90B)...O(5)$^{\#1}$	0.97	2.48	3.416(9)	160.9
C(91)-H(91)...O(1)	0.93	2.33	3.179(7)	151.2
C(95)-H(95)...O(2)$^{\#5}$	0.93	2.42	3.249(8)	147.9

Symmetry transformation used to generate equivalent atoms: #1 –*x* + 1, -*y*, -*z*; #2 –*x* + 2, -*y*, -*z*; #3 *x* + 1, *y*, *z*; #4 –*x* + 1, -*y*, -*z* + 1; #5 *x* - 1, *y*, *z*; #6 –*x* + 2, -*y*, -*z* + 1; #7 –*x* + 2, -*y* + 1, -*z* + 1; #9 –*x* + 1, -*y* + 1, -*z* + 1; #10 *x* - 1, *y* + 1, *z*; #11 –*x* + 1, -*y* + 1, -*z*.

Table S5 Selected bond lengths [Å], angles (º) and hydrogen bonds for compound **5**

Cd(1)-O(7)#1	2.2283(19)	Cd(1)-O(1)	2.232(2)
Cd(1)-O(6)#2	2.250(2)	Cd(1)-O(1W)	2.3436(16)
Cd(1)-O(5)#3	2.3964(17)	Cd(1)-O(4)#3	2.4005(17)
O(7)#1-Cd(1)-O(1)	95.63(8)	O(7)#1-Cd(1)-O(6)#2	125.33(7)
O(1)-Cd(1)-O(6)#2	94.73(8)	O(7)#1-Cd(1)-O(1W)	88.60(7)
O(1)-Cd(1)-O(1W)	172.87(6)	O(6)#2-Cd(1)-O(1W)	87.44(7)
O(7)#1-Cd(1)-O(5)#3	145.01(7)	O(1)-Cd(1)-O(5)#3	84.35(7)
O(6)#2-Cd(1)-O(5)#3	89.39(7)	O(1W)-Cd(1)-O(5)#3	88.89(6)
O(7)#1-Cd(1)-O(4)#3	90.20(7)	O(1)-Cd(1)-O(4)#3	90.35(7)
O(6)#2-Cd(1)-O(4)#3	143.21(7)	O(1W)-Cd(1)-O(4)#3	83.89(6)
O(5)#3-Cd(1)-O(4)#3	54.84(6)		

D-H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(1W)-H(1A)···O(2)#7	0.85	1.88	2.714(2)	167.8
O(1W)-H(1B)···O(2W)#3	0.84	2.16	2.919	149.9
O(2W)-H(2A)···O(4)	0.85	1.93	2.744(3)	159.7
C(4)-H(4)···O(7)#8	0.93	2.56	3.437(3)	158.2
C(12)-H(12)···O(2)#9	0.93	2.51	3.405(3)	162.5
C(24)-H(24)···O(2)#9	0.93	2.38	3.135(3)	138.7
C(25)-H(25)···O(1W)#10	0.93	2.37	3.258(3)	159.1
C(26)-H(26)···O(1)#8	0.93	2.35	3.232(3)	158.9
C(28)-H(28A)···O(1)#8	0.97	2.56	3.444(4)	151.9
C(28)-H(28B)···O(5)#11	0.97	2.32	3.242(4)	157.3

Symmetry transformation used to generate equivalent atoms: #1 *x* - 1, *y* - 1, *z* - 1; #2 –*x* + 2, -*y* + 2, -*z* + 3; #3 *x*, *y* - 1, *z* - 1; #7 –*x* + 1, -*y* + 1, -*z* + 2; #8 –*x* + 2, -*y* + 1, -*z* + 3; #9 –*x* + 1, -*y* + 1, -*z* + 3; #10 *x*, *y*, *z* + 1; #11 *x*, *y* - 1, *z*.

Table S6 Selected bond lengths [Å], angles (º) and hydrogen bonds for compound **6**

Mn(1)-O(3)$^{\#1}$	2.0479(17)	Mn(1)-O(1)	2.108(2)
Mn(1)-O(7)$^{\#2}$	2.114(2)	Mn(1)-O(6)$^{\#3}$	2.156(2)
Mn(1)-O(2)$^{\#4}$	2.1664(19)		
O(3)$^{\#1}$-Mn(1)-O(1)	112.22(7)	O(3)$^{\#1}$-Mn(1)-O(7)$^{\#2}$	108.13(8)
O(1)-Mn(1)-O(7)$^{\#2}$	90.46(8)	O(3)$^{\#1}$-Mn(1)-O(6)$^{\#3}$	99.20(8)
O(1)-Mn(1)-O(6)$^{\#3}$	89.12(8)	O(7)$^{\#2}$-Mn(1)-O(6)$^{\#3}$	150.57(7)
O(3)$^{\#1}$-Mn(1)-O(2)$^{\#4}$	95.46(7)	O(1)-Mn(1)-O(2)$^{\#4}$	152.27(7)
O(7)$^{\#2}$-Mn(1)-O(2)$^{\#4}$	81.96(8)	O(6)$^{\#3}$-Mn(1)-O(2)$^{\#4}$	84.85(8)

D-H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(1W)-H(1A)···O(1)$^{\#6}$	0.87	2.44	3.133(3)	136.7
O(1W)-H(1A)···O(6)$^{\#8}$	0.87	2.60	3.321(3)	141.0
O(1W)-H(1B)···O(4)	0.85	2.14	2.942(4)	158.3
C(8)-H(8)···O(2)	0.93	2.42	2.745(3)	100.6
C(8)-H(8)···O(3)	0.93	2.43	2.749(3)	100.1
C(11)-H(11)···O(5)	0.93	2.41	2.748(3)	101.1
C(19)-H(19)···O(4)$^{\#9}$	0.93	2.39	3.272(4)	159.2
C(24)-H(24B)···O(2)$^{\#10}$	0.97	2.40	3.215(3)	141.0
C(28)-H(28)···O(1W)$^{\#1}$	0.93	2.51	3.350(4)	149.6
C(29)-H(29)···O(6)$^{\#11}$	0.93	2.29	3.193(3)	164.5

Symmetry transformation used to generate equivalent atoms: $^{\#1}$ *x* + 1, *y*, *z*; $^{\#2}$ -*x*, -*y*, -*z* + 1; $^{\#3}$ *x*, *y* + 1, *z* – 1; $^{\#4}$ -*x*, -*y* + 1, -*z*; $^{\#6}$ *x* - 1, *y*, *z*; $^{\#8}$ *x* - 1, *y* + 1, *z*-1; $^{\#9}$ –*x* - 1, -*y*, -*z* + 2; $^{\#10}$ *x*, *y*, *z* + 1; $^{\#11}$ -*x*, -*y*, -*z* + 2.

Table S7 Hydrogen bonds for compound **7**

D-H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(4)-H(4A)···O(1W)$^{\#3}$	0.82	1.78	2.581(3)	167.2
O(6)-H(6A)···O(1)$^{\#4}$	0.82	1.76	2.566(4)	168.6
O(1W)-H(1A)···O(2)$^{\#1}$	0.892(10)	1.891(12)	2.777(4)	172(4)
O(1W)-H(1B)···O(1)	0.892(10)	1.933(14)	2.800(4)	163(4)
C(23)-H(23)···O(2W)$^{\#5}$	0.93	2.33	2.993(13)	127.5

C(23)-H(23)···O(2W)$^{\#6}$	0.93	1.77	2.537(13)	138.3
C(28)-H(28A)···O(1W)$^{\#1}$	0.97	2.62	3.461(8)	145.4
C(28)-H(28B)···O(5)$^{\#7}$	0.97	2.56	3.029(8)	110.1
C(30)-H(30)···O(2)	0.93	2.65	3.280(5)	126.0

Symmetry transformation used to generate equivalent atoms: $^{\#1}$ $-x+2, y, -z+1/2$; $^{\#3}$ $-x+2, -y, -z$; $^{\#4}$ $x, y-1, z$; $^{\#5}$ $x-1/2, y-1/2, z$; $^{\#6}$ $-x+3/2, y-1/2, -z+1/2$; $^{\#7}$ $x, -y, z+1/2$.

References

1 P. Du, Y. Yang, J. Yang, B. K. Liu and J. F. Ma, *Dalton Trans*., 2013, **42**, 1567-1580.

2 G. M. Sheldrick, SHELXS-97, Programs for X-ray crystal structure solution. Göttingen, Germany: University of Göttingen; 1997.

3 G. M. Sheldrick, SHELXL-97, Programs for X-ray crystal structure refinement. Göttingen, Germany: University of Göttingen; 1997.

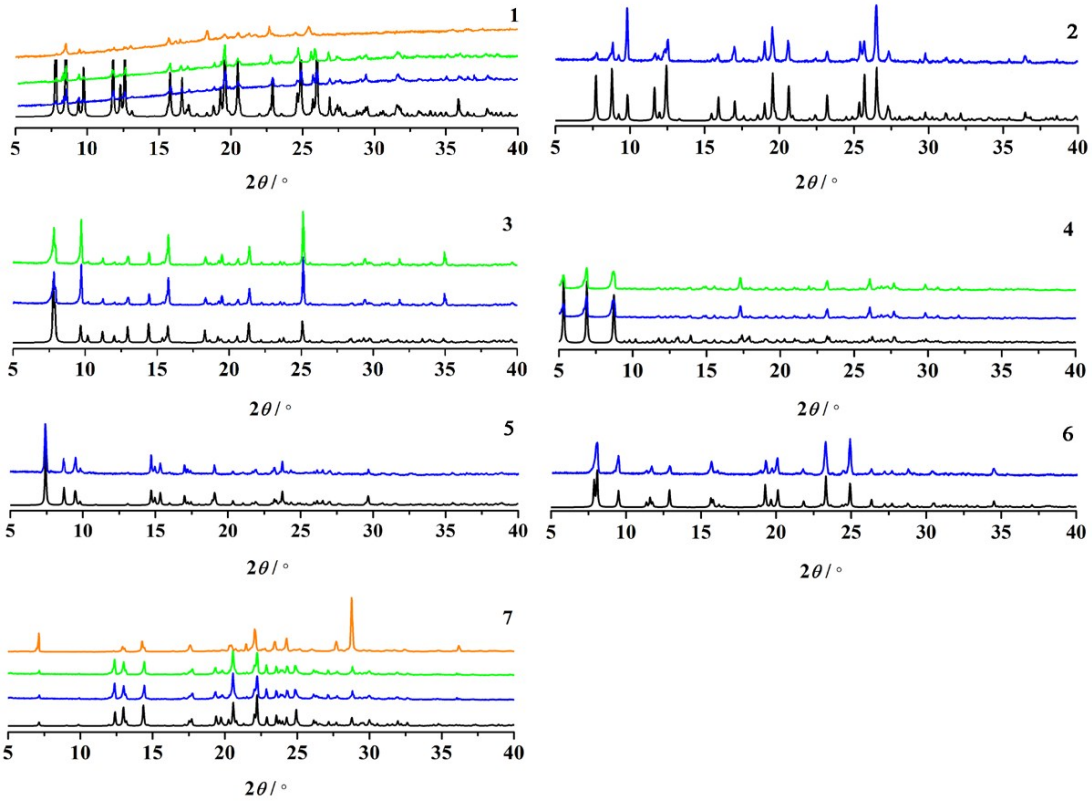
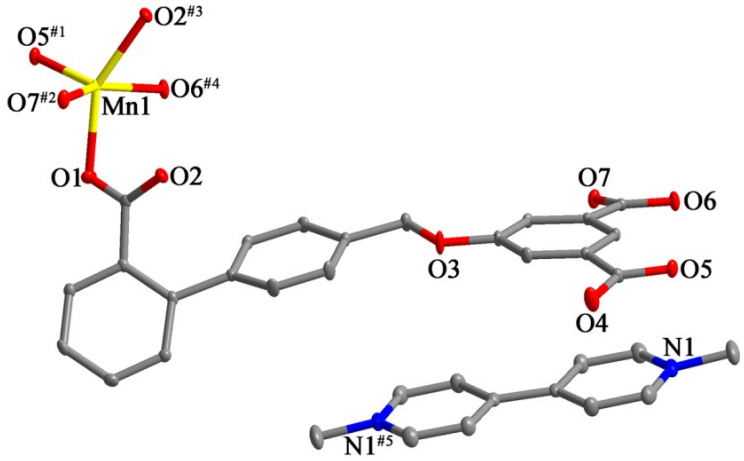
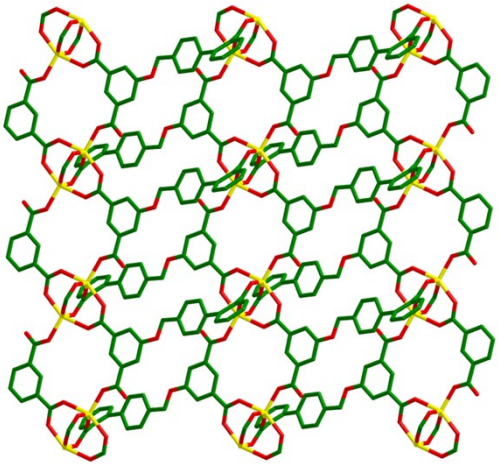


Fig. S1 PXRD patterns of compounds **1-7** (black lines represent the simulated PXRD spectra, blue lines represent the PXRD spectra of the as synthesized compounds,

green lines represent the PXRD spetra of the compounds after thermo/photochromic processes at room temperature, orange lines represent the PXRD spectra at 150 °C for **1** and 130 °C for **7**).



(a)



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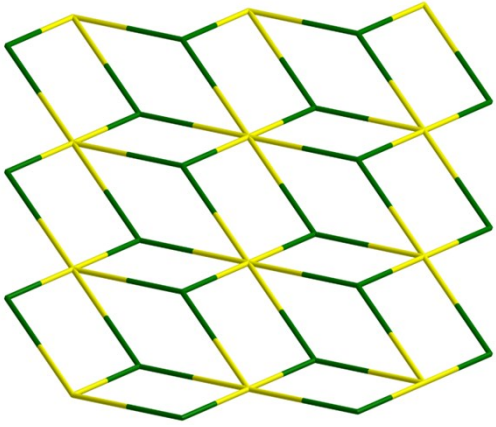
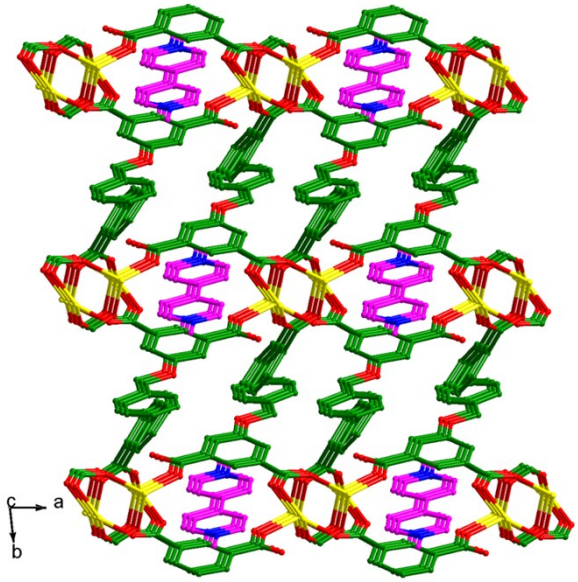
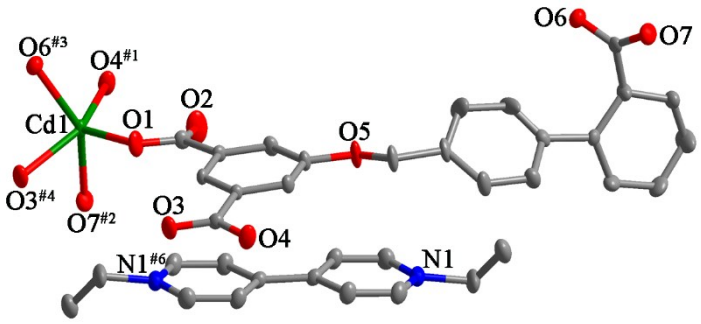


(c)

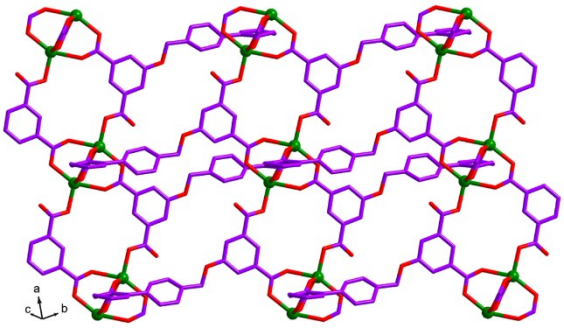


(d)

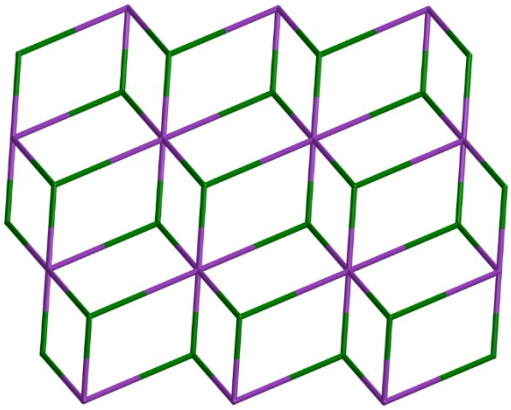
Fig. S2 (a) ORTEP view of compound **2** showing the coordination environment of Mn(II) ion with lattice water molecule and hydrogen atoms omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: $^{\#1}$ $x + 1, y - 1, z + 1$; $^{\#2}$ $x, y - 1, z + 1$; $^{\#3}$ $-x + 1, -y + 1, -z$; $^{\#4}$ $-x + 1, -y + 2, -z - 1$; $^{\#5}$ $-x, -y + 3, -z - 1$. (b) View of the host 2D layer formed by the Mn(II) ions and L^{3-} anions. (c) 2D (3,6)-connected network with the Schläfli symbol of $(4^3)(4^6{\cdot}6^6{\cdot}8^3)$. (d) View of the host-guest 3D supramolecular architecture of compound **2**.



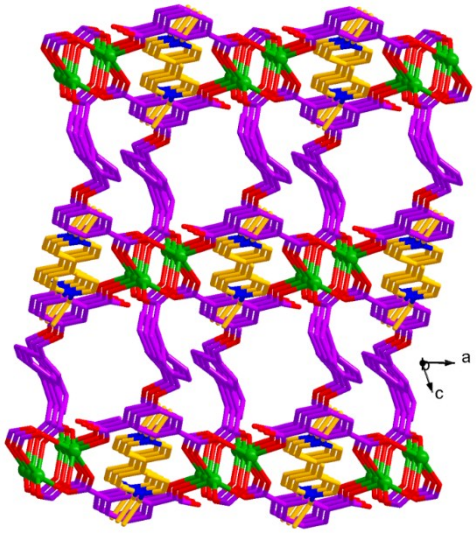
(a)



(b)



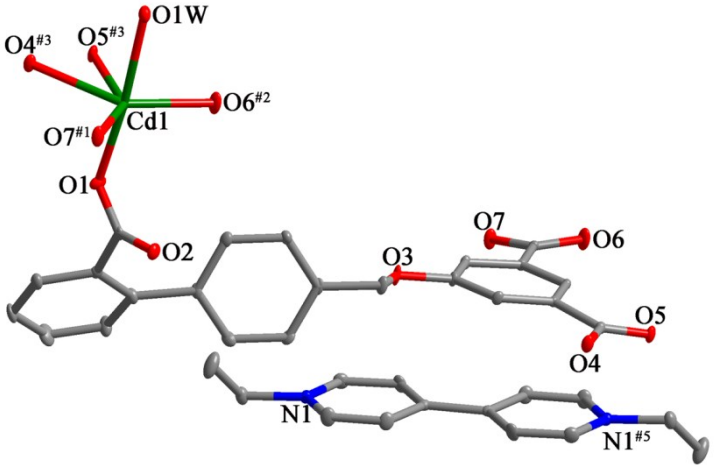
(c)



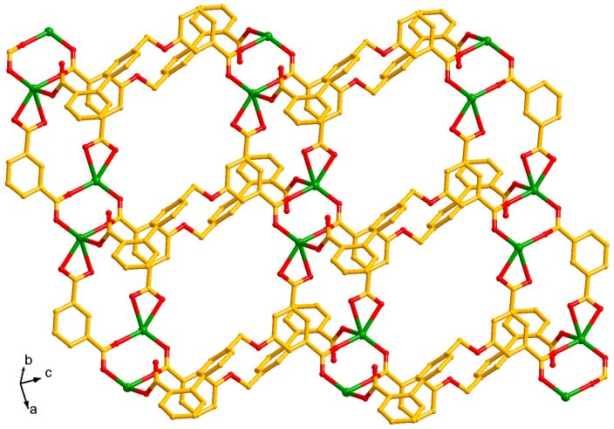
(d)

Fig. S3 (a) ORTEP view of compound **3** showing the coordination environment of Cd(II) ion with lattice water molecule and hydrogen atoms omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: [#1] $x + 1, y, z$; [#2] $x + 1, y + 1, z - 1$; [#3] $-x, -y, -z + 2$; [#4] $-x, -y + 1, -z + 1$; [#5] $–x + 1, -y + 1, -z + 1$; [#6] $-x, -y, -z + 1$. (b) View of the host 2D layer formed by the Cd(II) ions and L^{3-} anions. (c) 2D (3,6)-connected

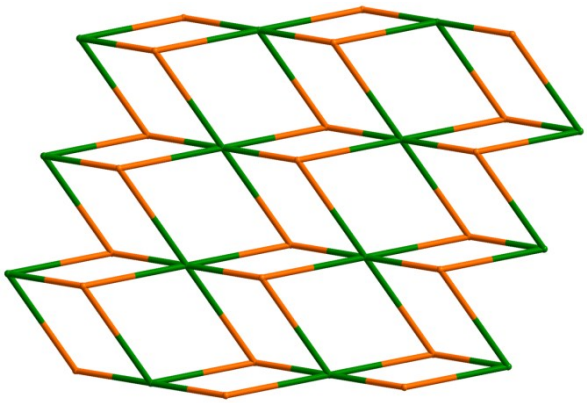
network with the Schläfli symbol of $(4^3)(4^6{\cdot}6^6{\cdot}8^3)$. (d) View of the host-guest 3D supramolecular architecture of compound **3**.



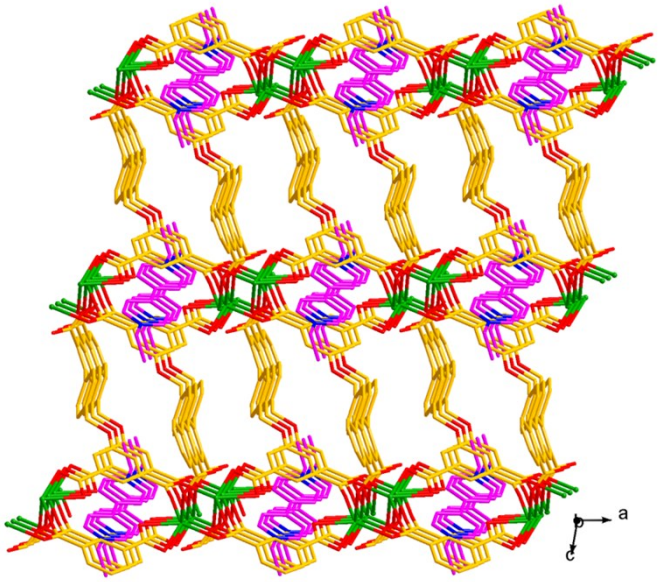
(a)



(b)

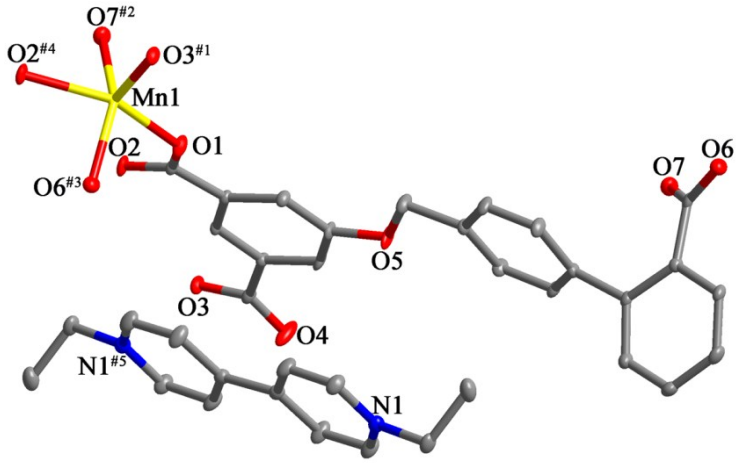


(c)

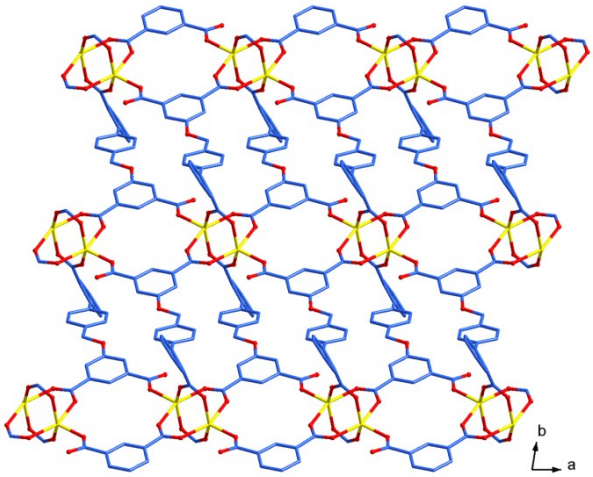


(d)

Fig. S4 (a) ORTEP view of compound **5** showing the coordination environment of Cd(II) ion with lattice water molecule and hydrogen atoms omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: $^{\#1}$ x - 1, y - 1, z – 1; $^{\#2}$ –x + 2, -y + 2, -z + 3; $^{\#3}$ x, y - 1, z – 1; $^{\#5}$ –x + 2, -y + 2, -z + 4. (b) View of the host 2D layer formed by the Cd(II) ions and L^{3-} anions. (c) 2D (3,6)-connected network with the Schläfli symbol of $(4^3)(4^6{\cdot}6^6{\cdot}8^3)$. (d) View of the host-guest 3D supramolecular architecture of compound **5**.



(a)



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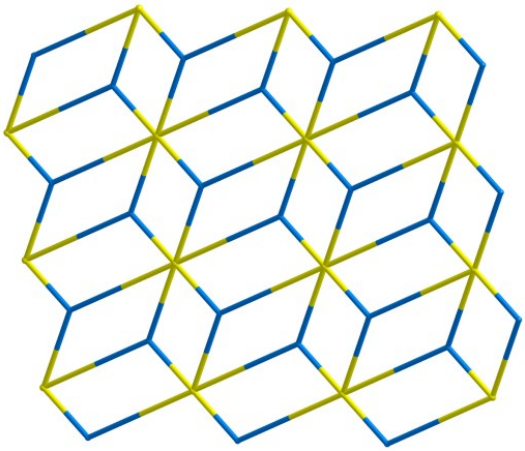

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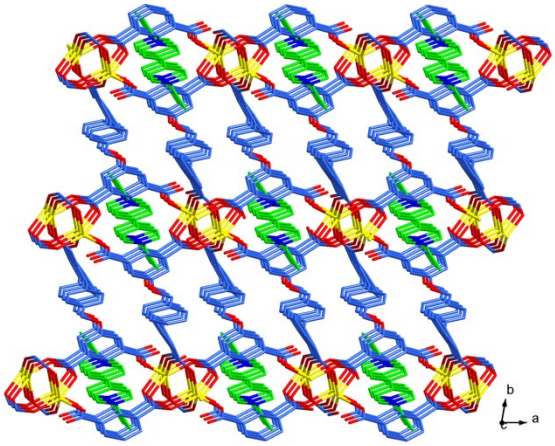
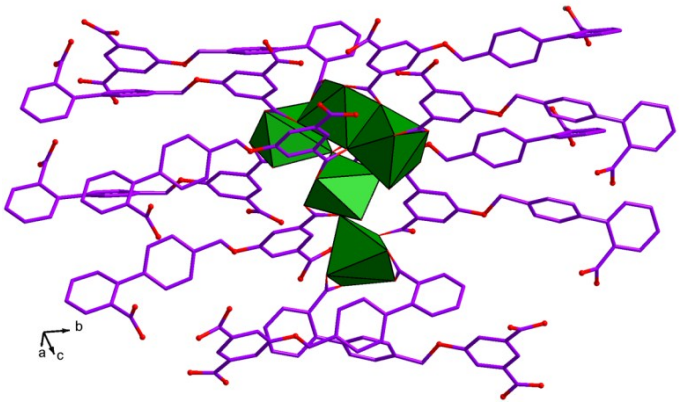


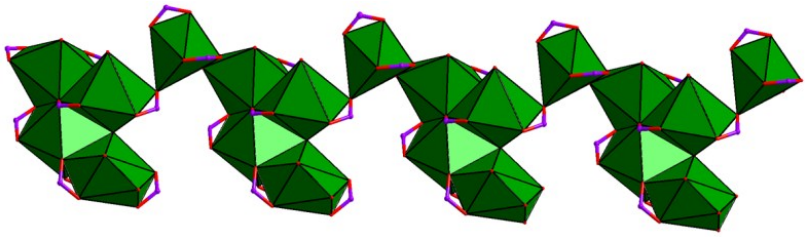
(d)

Fig. S5 (a) ORTEP view of compound **6** showing the coordination environment of Mn(II) ion with lattice water molecule and hydrogen atoms omitted for clarity (30% probability displacement ellipsoids). Symmetry codes: $^{\#1}$ $x + 1$, y, z; $^{\#2}$ $-x$, $-y$, $-z + 1$;

[#3] $x, y + 1, z - 1$; [#4] $-x, -y + 1, -z$; [#5] $-x - 1, -y + 1, -z + 1$. (b) View of the host 2D layer formed by the Cd(II) ions and L^{3-} anions. (c) 2D (3,6)-connected network with the Schläfli symbol of $(4^3)(4^6 \cdot 6^6 \cdot 8^3)$. (d) View of the host-guest 3D supramolecular architecture of compound **6**.



(a)



(b)

Fig. S6 (a) The 11-connected node in compound **4**. (b) 1D chain formed by the pentanuclear units in compound **4**.

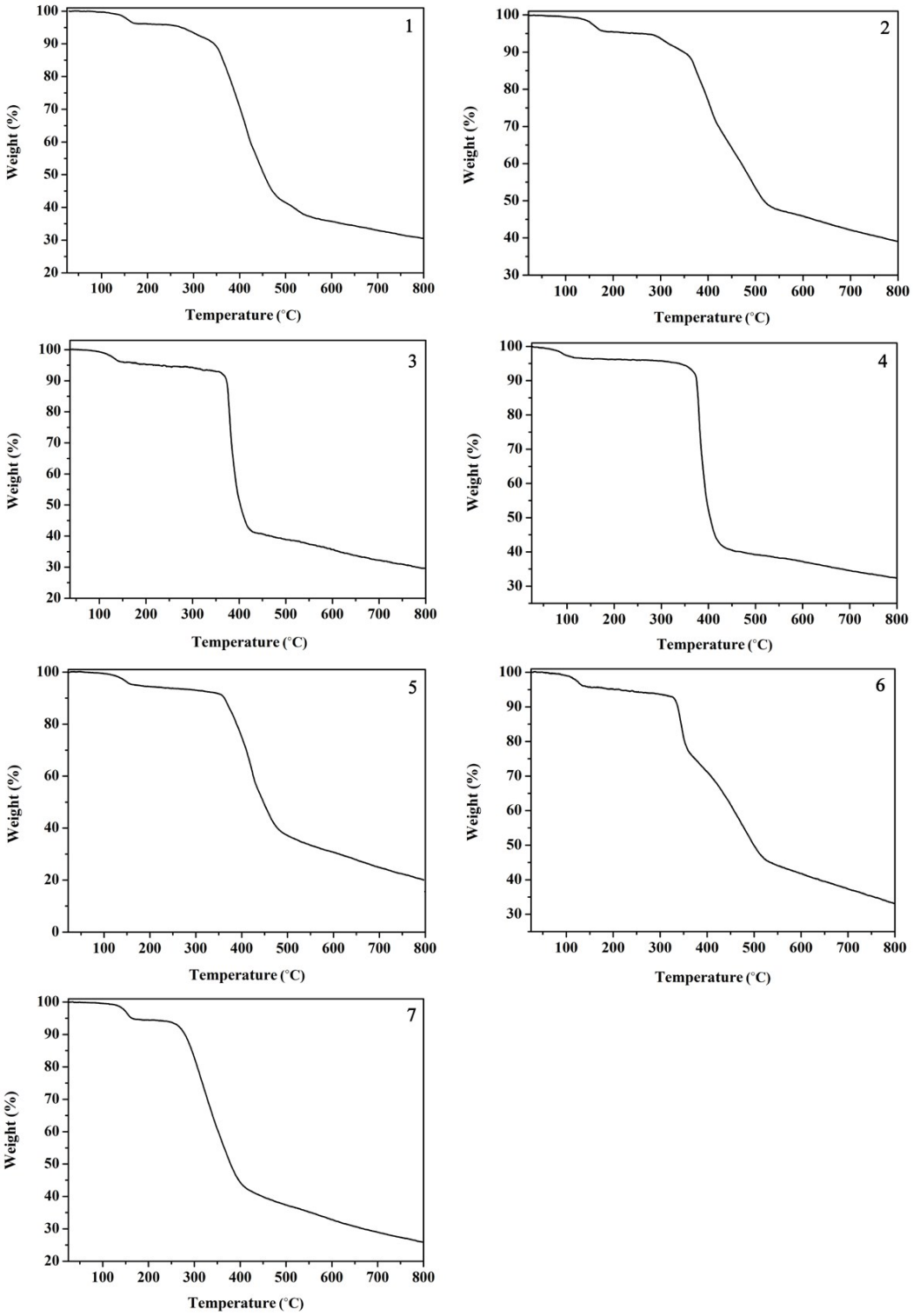


Fig. S7 TGA curves of compounds **1**-**7**.

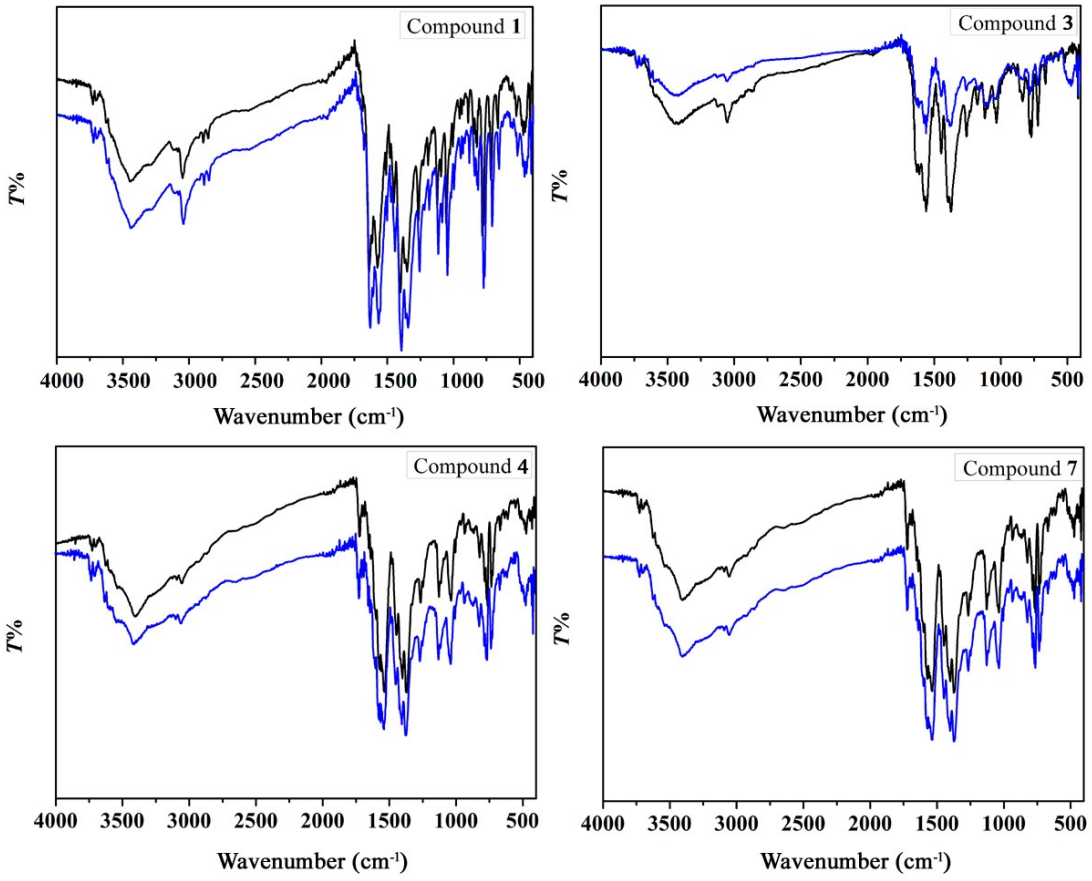


Fig. S8 IR spectra of compounds **1**, **3**, **4** and **7** before and after thermo/photochromism.

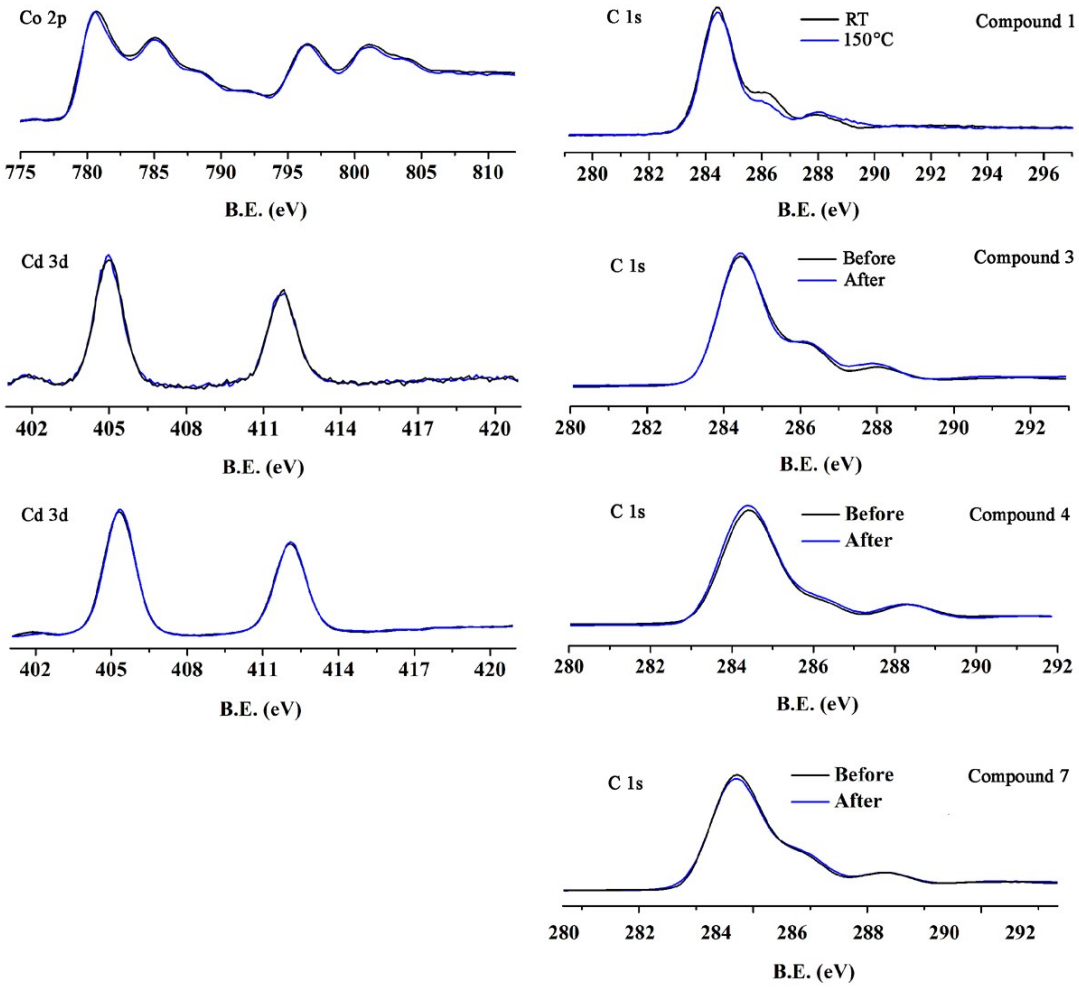


Fig. S9 XPS core-level spectra of Co 2p/Cd 3d and C 1s of compounds **1**, **3**, **4** and **7** before and after thermo/photochromism.

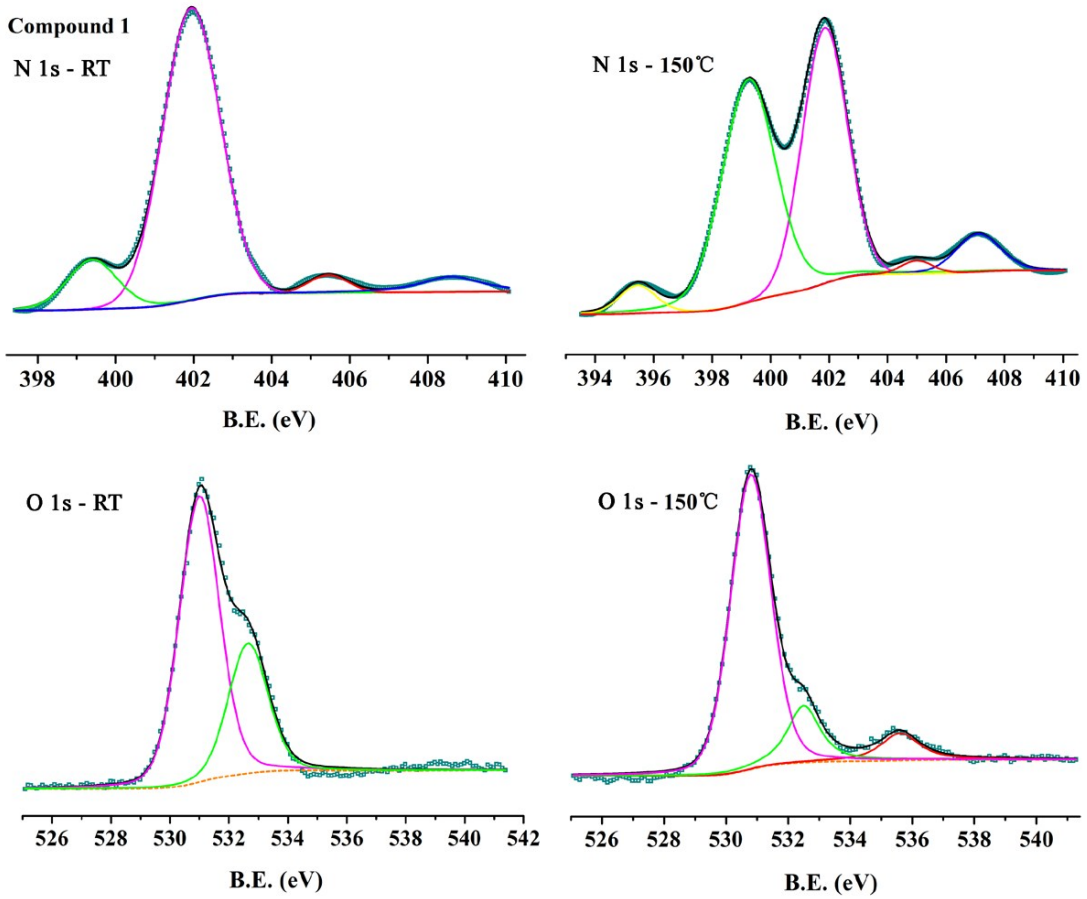


Fig. S10 XPS core-level spectra of N 1s and O 1s of compound **1** at room temperature and 150 °C.

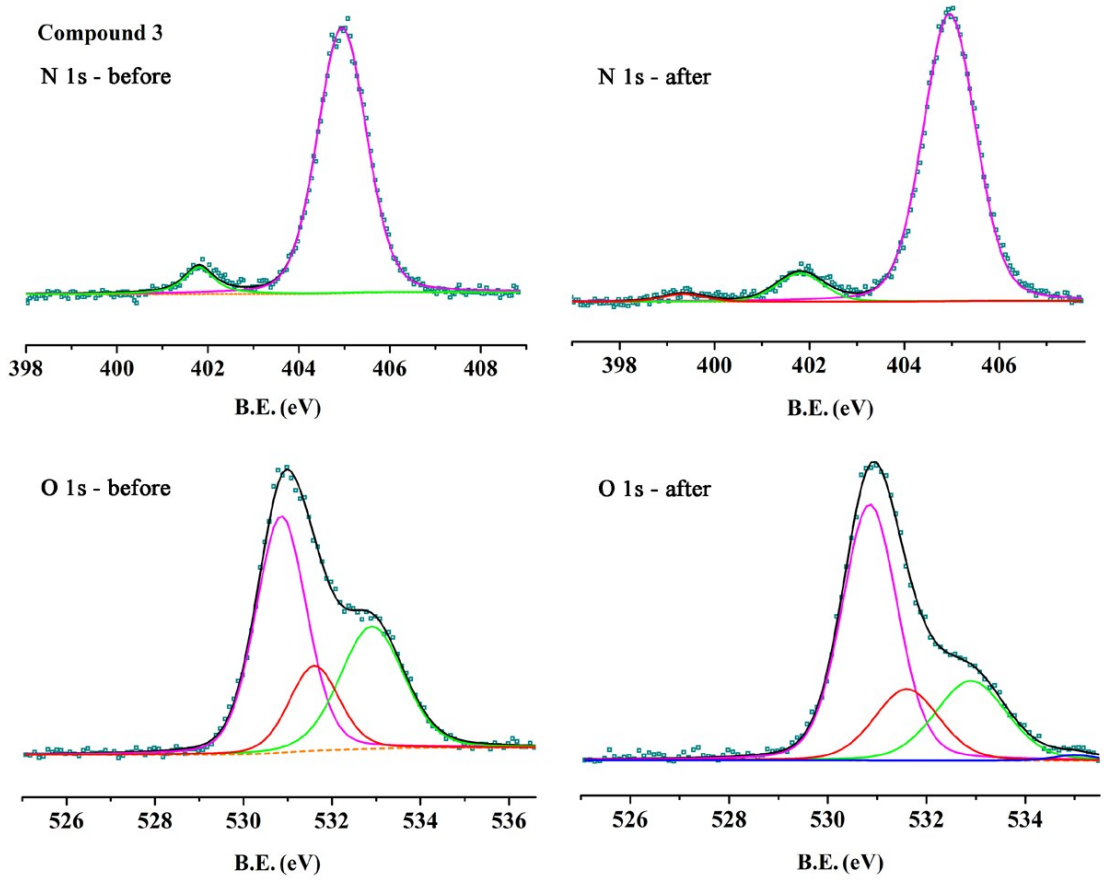


Fig. S11 XPS core-level spectra of N 1s and O 1s of compound **3** before and after photochromism.

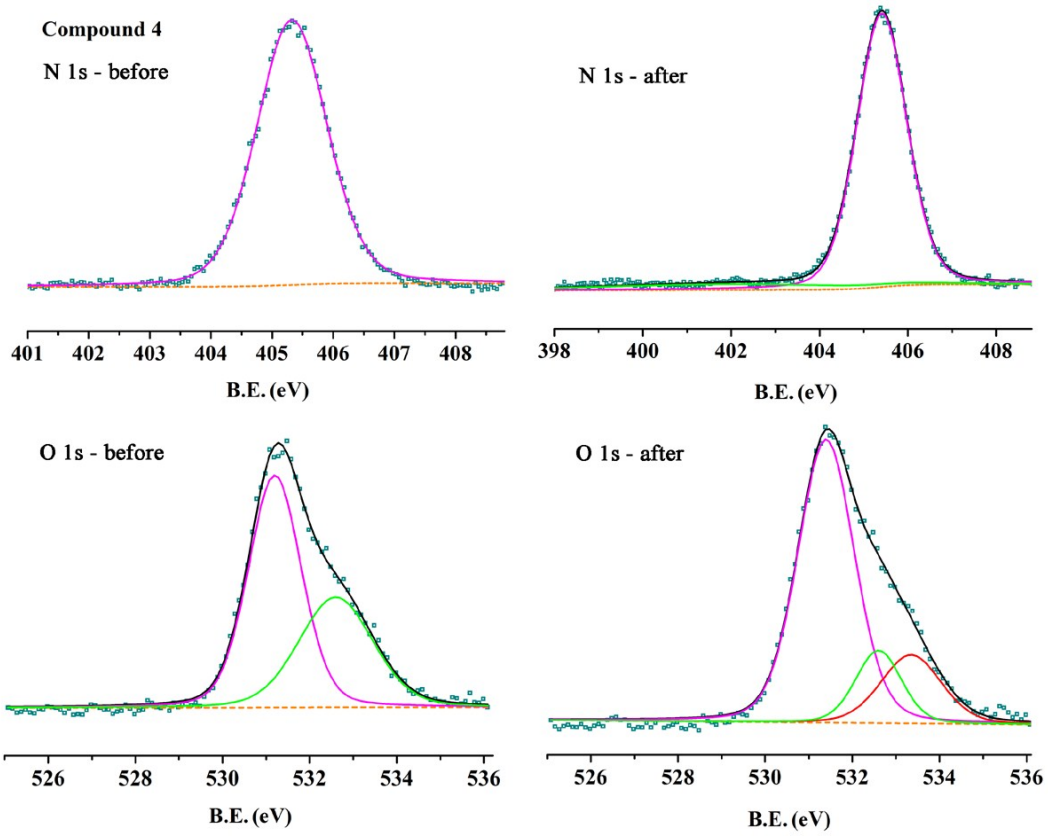


Fig. S12 XPS core-level spectra of N 1s and O 1s of compound **4** before and after photochromism.

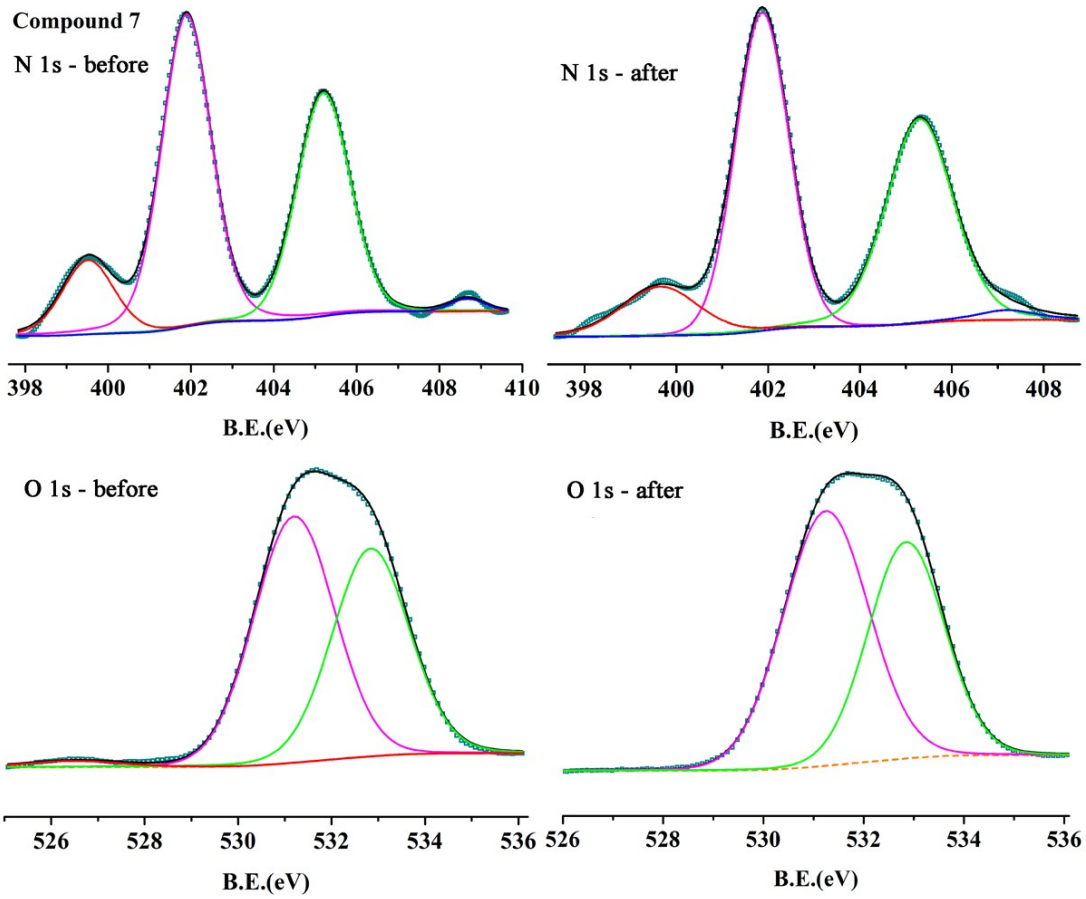


Fig. S13 XPS core-level spectra of N 1s and O 1s of compound **7** before and after photochromism.

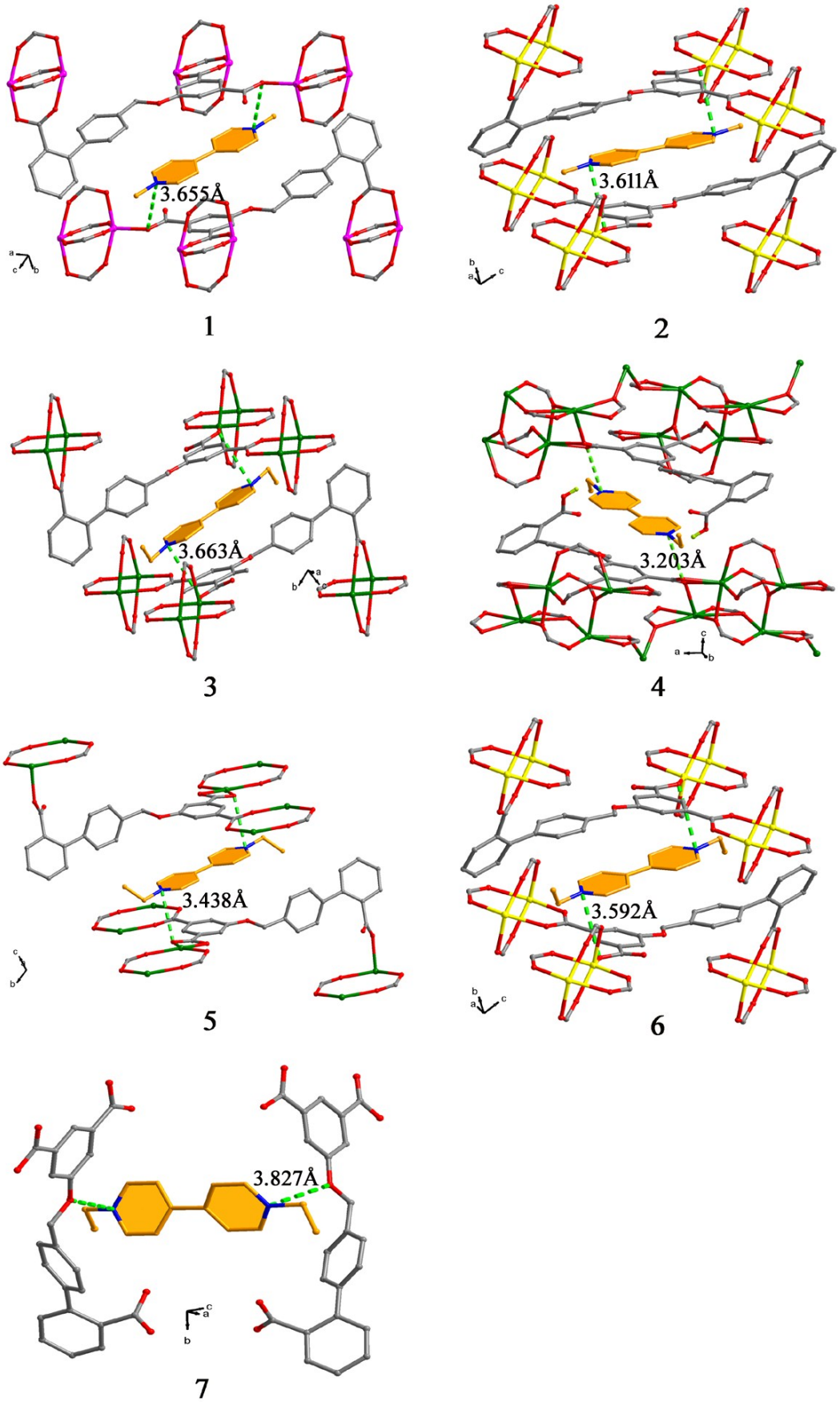


Fig. S14 The nearest N···O paths in compounds **1**-**7**.