Electronic Supplementary Material for CrystEngComm

<Supporting information>

pH-Controlled Change of the Coordination Modes of the Highly Symmetrical Multitopic Ligand and Metal-Oxygen Arrays to Construct Coordination Assemblies

Bo Zheng, Junfeng Bai*, Zhuxiu Zhang

State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing
210093, P. R. China
E-mail: bjunfeng@nju.edu.cn

Materials

High-purity (98%) 3,4-dihydroxy-3-cyxlobutene-1,2-dione (squaric acid) were purchased from the Aldrich Chemical Co. Inc. All other chemicals were of **AR** grade.

Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a PE-2400CHN analyzer. Powder X-ray diffraction (XRD) patterns were collected in a Shimadzu XRD-6000 (operating at 40 kV and 30 mA) with graphite-monochromatized Cu Kα radiation (wavelength = 1.5147Å). Thermogravimetric (TG) analysis was displayed on PerKinElmer Pyris 1 TGA under atmospheric pressure with N_2 as the carrier gas.

Synthesis

Complex 1: A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (197mg, 0.64 mmol), squaric acid (100 mg, 0.88 mmol), KOH (100 mg, 1.78 mmol) and H_2O (5 ml) was stirred for ca. 10 min in air (pH=3), then transferred and sealed in a 23 ml Teflon-lined autoclave, which was heated at 190 °C for 48 h. After cooling to the room temperature, the colorless block crystals were obtained. After filtration, the crystals were washed with little water and dried in a vacuum desiccator to give 0.0517 g (31 % based on $Cd(NO_3)_2{\cdot}4H_2O$). The powder X-ray diffraction pattern of the bulk product was in agreement with the simulated pattern from single-crystal analysis, demonstrating the phase purity of the product (Figure S9). Anal. Calcd. for $CdC_4H_4O_6$: C, 18.44; H, 1.55%. Found: C, 18.48; H, 1.52%. IR(KBr, pellet): 3251 (s, br), 2889 (sh), 1508 (s), 1099 (m), 654 (m) cm^{-1}.

Complex 2: A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (197mg, 0.64 mmol), squaric acid (100 mg, 0.88 mmol), KOH (125 mg, 2.23 mmol) and H_2O (5 ml) was stirred for ca. 10 min in air (pH=4), then transferred and sealed in a 23 ml Teflon-lined autoclave, which was heated at 190 °C for 48 h. After cooling to the room temperature, the colorless block crystals were obtained. After filtration, the crystals were washed with little water and dried in a vacuum desiccator to give 0.0622 g (49 % based on $Cd(NO_3)_2{\cdot}4H_2O$). The powder X-ray diffraction pattern of the bulk product was in agreement with the simulated pattern from single-crystal analysis, demonstrating the phase purity of the product (Figure S10). Anal. Calcd. for $Cd_3C_8H_2O_{10}$: C, 16.14; H, 0.34%. Found: C, 16.21; H, 0.31%. IR(KBr, pellet): 3485 (s, br), 3426 (sh), 1527 (s), 1464 (sh), 1088 (m), 839 (m), 767 (m), 729 (m), 671 (w), 635 (m) cm^{-1}.

Complex 3: A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (197mg, 0.64 mmol), squaric acid (100 mg, 0.88 mmol), KOH (133 mg, 2.38 mmol) and H_2O (5 ml) was stirred for ca. 10 min in air (pH=4.5), then transferred and sealed in a 23 ml Teflon-lined autoclave, which was heated at 190 °C for 48 h. After cooling to the room temperature, the colorless block crystals were obtained. After filtration, the crystals were washed with little water and dried in a vacuum desiccator to give 0.0653 g (55 % based on $Cd(NO_3)_2{\cdot}4H_2O$). The powder X-ray diffraction pattern of the bulk product was in agreement with the simulated pattern from single-crystal analysis, demonstrating the phase purity of the product (Figure S11). Anal. Calcd. for CdC_2HO_3: C, 12.95; H, 0.54%. Found: C, 12.31; H, 0.52%. IR(KBr, pellet): 3421 (s, br), 2874 (w), 2575 (w), 2212 (w), 1750 (w, sh), 1475 (s, br), 1431(sh), 1086 (m), 899 (w), 879 (w, sh), 761(m) cm^{-1}.

Complex 4: A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (197mg, 0.64 mmol), squaric acid (100 mg, 0.88 mmol), KOH (159 mg, 2.83 mmol) and H_2O (5 ml) was stirred for ca. 10 min in air (pH=6), then transferred and sealed in a 23 ml Teflon-lined autoclave, which was heated at 190 °C for 48 h. After cooling to the room temperature, the colorless block crystals were obtained. After filtration, the crystals were washed with little water and dried in a vacuum desiccator to give 0.0676 (57 % based on $Cd(NO_3)_2{\cdot}4H_2O$). The powder X-ray diffraction pattern of the bulk product was in agreement with the simulated pattern from single-crystal analysis, demonstrating the phase purity of the product (Figure S12). Anal. Calcd. for CdC_2HO_3: C, 12.95; H, 0.54%. Found: C, 12.89; H, 0.51%. IR(KBr, pellet): 3467 (s), 2872 (w), 1743 (w), 1505 (s, br), 1088 (m), 857 (w), 795 (m), 715 (m) cm^{-1}.

Crystallographic Analyses

Data were measured on a Bruker Smart Apex II CCD diffractometer at 291 K using graphite monochromated Mo/Kα radiation (λ = 0.71073 Å), respectively. Data reduction was made with the Bruker Saint program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package. The coordinates of the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were put in calculated positions or located from the Fourier maps and refined isotropically with the isotropic vibration parameters related to the non-hydrogen atom to which they are bonded. CCDC 732255 and 732257 for complexes **2**-**4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

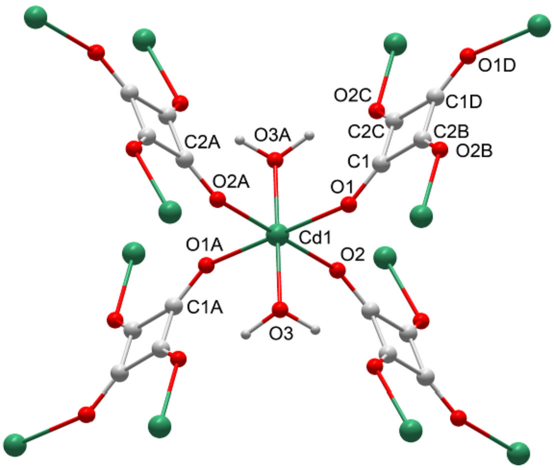
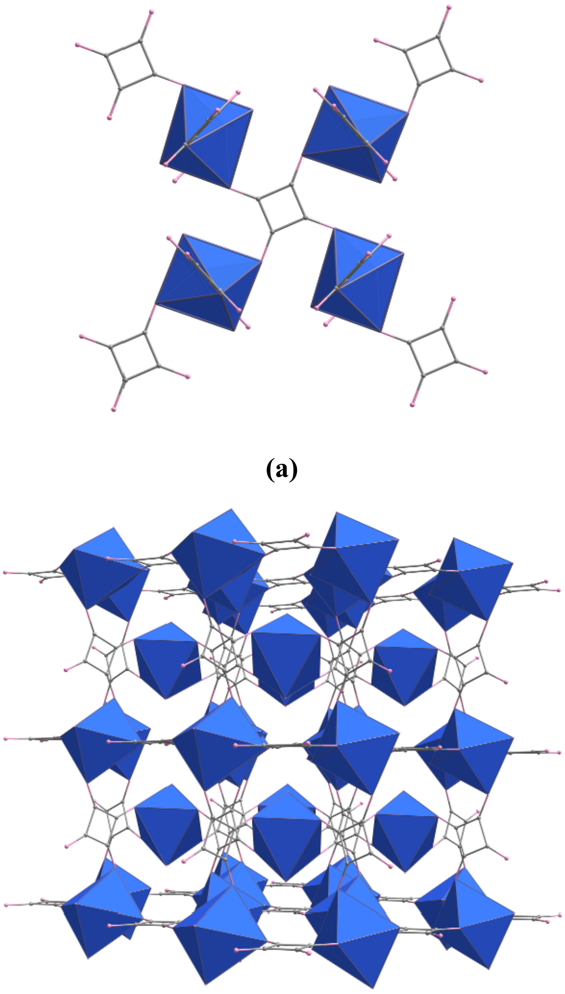


Fig. S1. Coordination environment of the Cd(II) ion in **1**. Symmetry codes：A: 2/3 - x, 1/3 - y, 1/3 - z; B: 1 - x + y, 1 - x, z; C: 1 - x, 1 - y, - z; D: x - y, x, - z。



(a)

(b)

Fig. S2. (a) Tetradentate coordination mode of the squarate ligand in **1**, (b) 3-D network of **1** along the b axis.

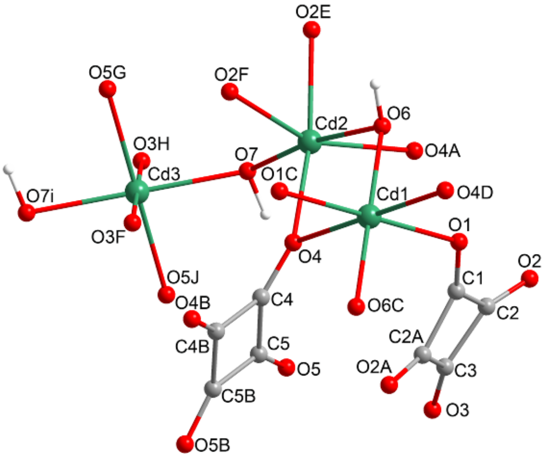
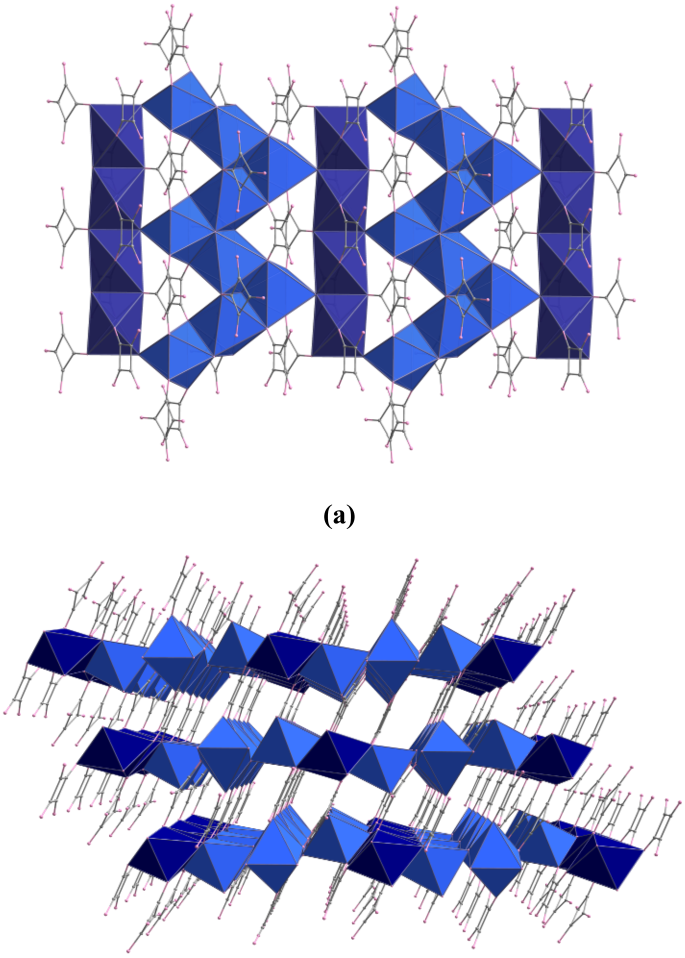


Fig. S3. Coordination environment of the Cd(II) ion in **2**. Symmetry codes： A, x, -y, z; B, x, 1-y, z; C, 0.5-x, 0.5+y, -z; D, 0.5-x, 0.5-y, -z; E, -0.5+x, -0.5-y, z; F, -0.5+x, 0.5+y, z; G, -0.5+x, 0.5-y, z; 0.5-x, 0.5-y, -z; H, 1-x, y, 1-z; I, 0.5-x, 0.5+y, 1-z.



(a)

(b)

Fig. S4. (a) Infinite Cd-O-Cd layers in **2** parallel with *bc* plane consisting of zigzag chains (light blue) and straight linear chains (dark blue); (b) the 3D network of **2** along the b axis.

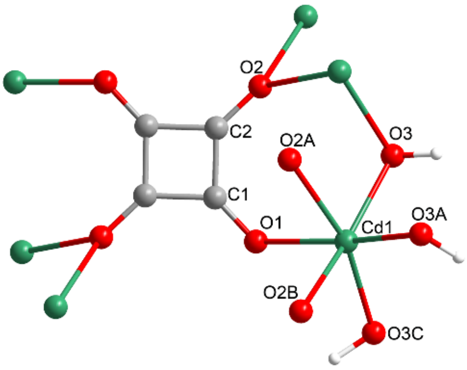
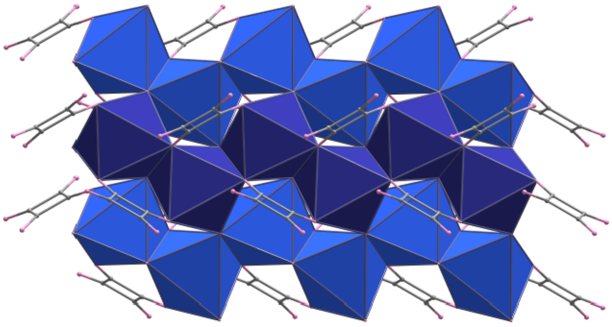
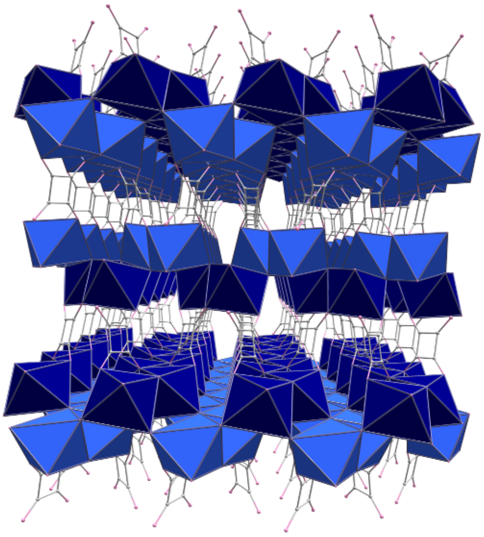


Fig. S5. Coordination environment of the Cd(II) ion in **3**. Symmetry codes：A, 0.5- x, 0.5+y, z; B, x, 1+y, z; C, 1-x, 0.5+y, 0.5-z.



(a)



(b)

Fig. S6 (a) Infinite Cd-O-Cd layers in **3** parallel with *ab* plane consisting of zigzag chains (light blue and dark blue); (b) the 3D network of **3** along the *b* axis.

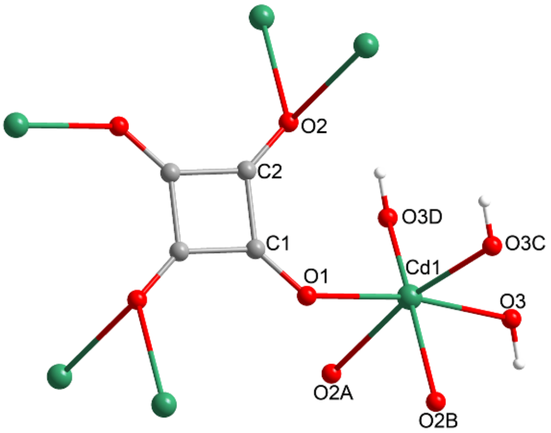
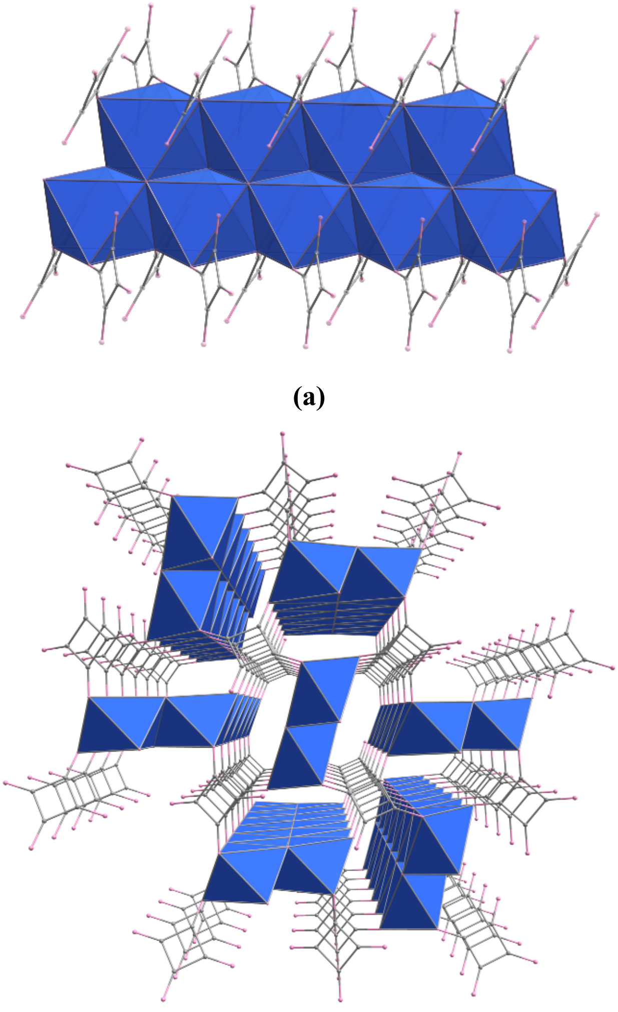


Fig. S7. Coordination environment of the Cd(II) ion in **4**. Symmetry codes: A, x, 1.5-y, -0.5+z; B, -1+x, 1.5-y, -0.5+ z; C, 2-x, 1-y, -z; D, 3-x, 1-y, -z.



(a)

(b)

Fig. S8. (a) 1D Cd-O-Cd double chains in **4** along *a* axis; (b) View of the 3D network of **4** along the *a* axis.

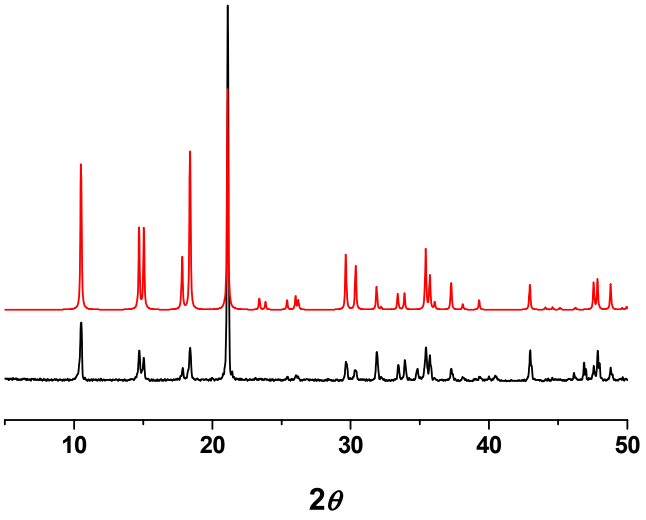


Fig. S9 XRPD patterns for **1**: (red) calculated, and (black) as-synthesized.

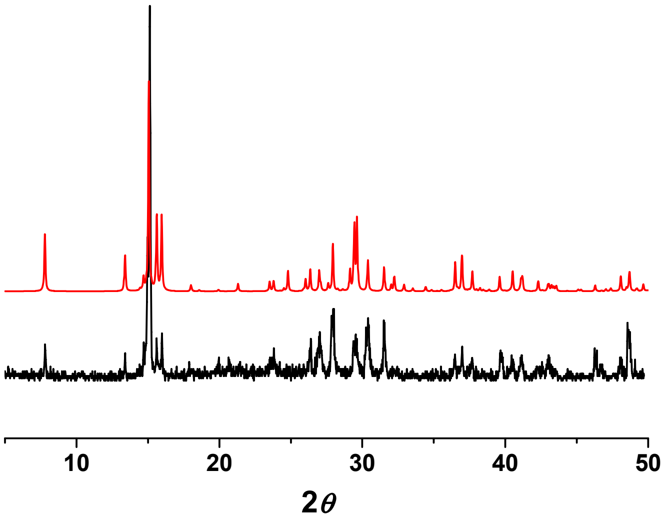


Fig. S10 XRPD patterns for **2**: (red) calculated, and (black) as-synthesized.

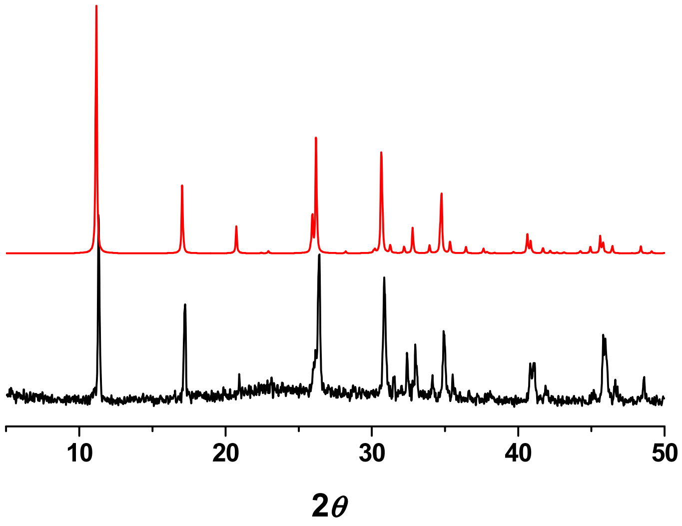


Fig. S11 XRPD patterns for **3**: (red) calculated, and (black) as-synthesized.

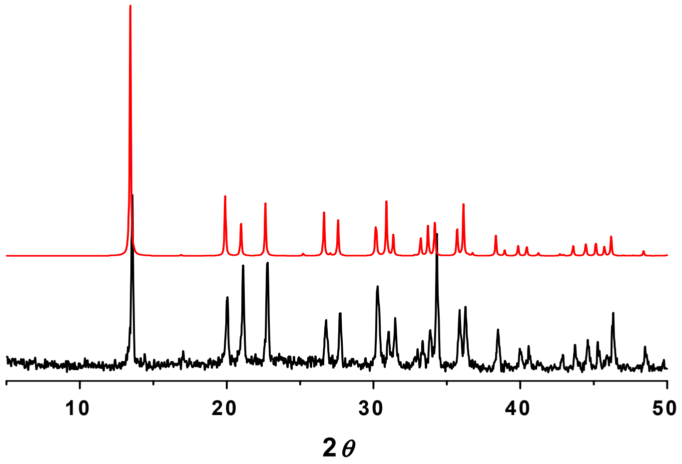


Fig. S12 XRPD patterns for **4**: (red) calculated, and (black) as-synthesized.

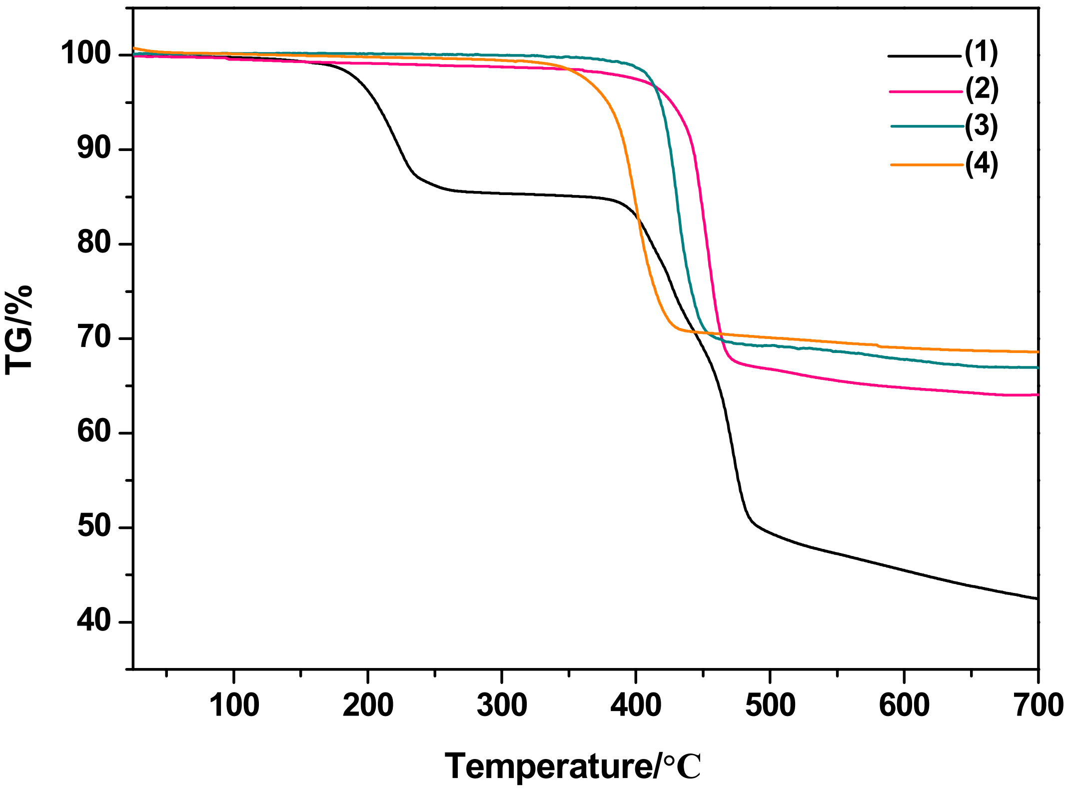


Fig. S13 Thermal gravimetric analysis (TGA) curves of complexes **1**, **2**, **3**, and **4**.