Supporting Information for

Coordination polymer-templated photoinduced [2 + 2] dimerization of

pyridine-based derivative

Jie Qin, Na Qin, Cui-Hong Geng, Jian-Ping Ma, Qi-Kui Liu, Chao-Wei Zhao, and Yu-Bin Dong*

College of Chemistry, Chemical Engineering and Materials Science, Key Laboratory of Molecular and Nano Probes, Engineering Research Center of Pesticide and Medicine Intermediate Clean Production, Ministry of Education, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University, Jinan 250014, People's Republic of China Email: yubindong@sdnu.edu.cn
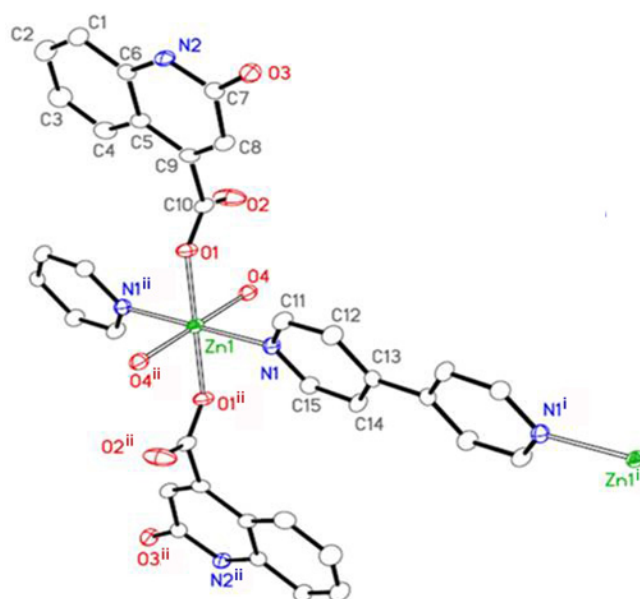
* to whom correspondence should be addressed

Fig. S1 ORTEP figure (displacement ellipsoids drawn at 30% probability level, Symmetry codes: (i) −x, −y−1, −z; (ii) −x, −y, −z+1).
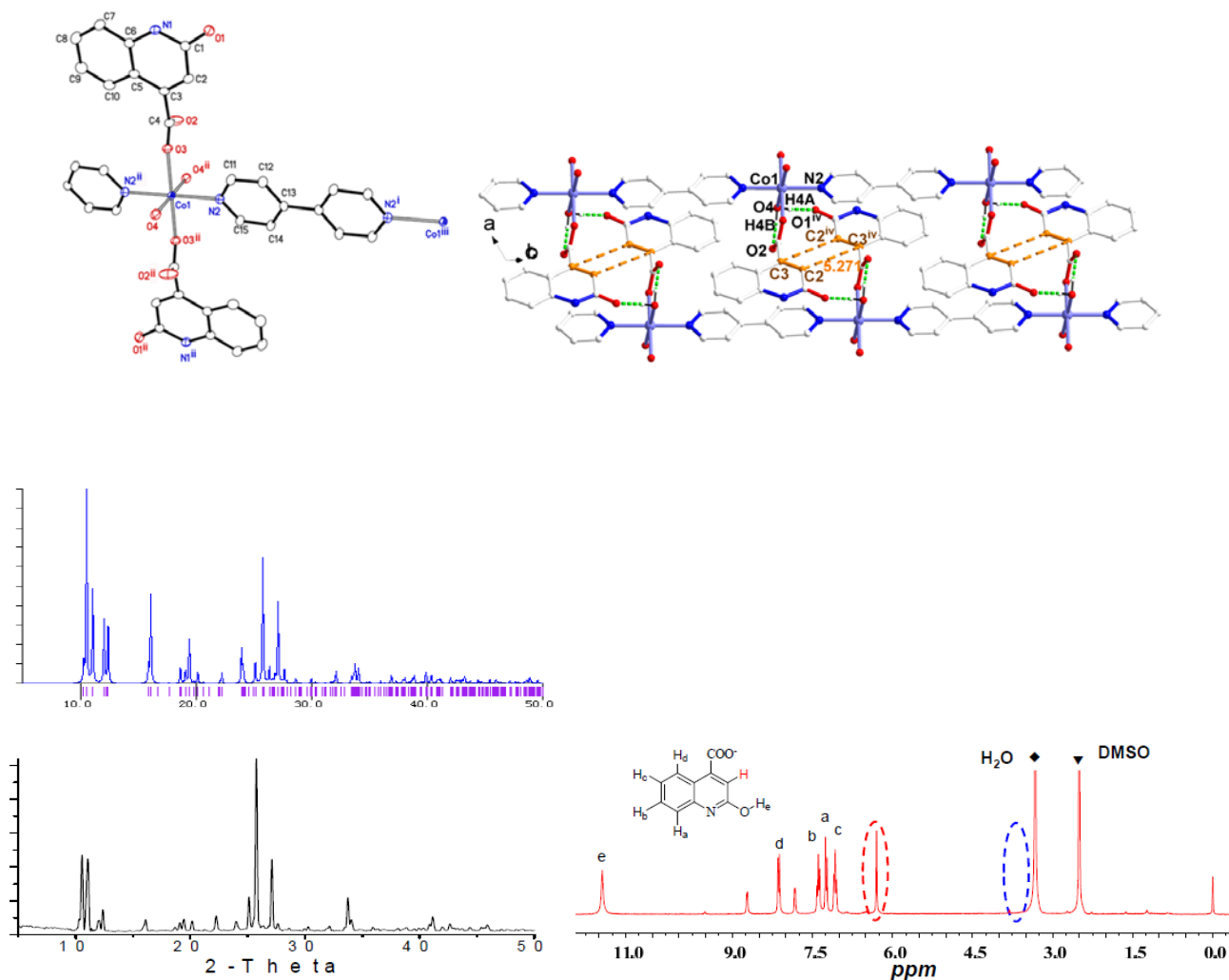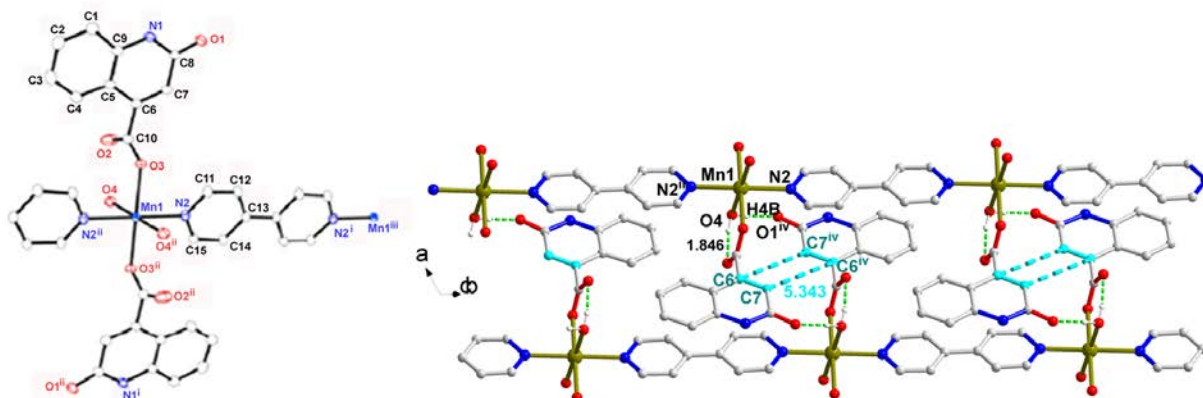
Fig. S2 ORTEP figure (top left, displacement ellipsoids drawn at 30% probability level, Symmetry codes: (i) −x, −y−1, −z−1; (ii) −x, −y, −z; (iii) x, y−1, z−1), crystal structure (top right, Symmetry code: (iv) 1−x, −y, −z), simulated (blue) and experimental (black) XRPD patterns, and ^{1}H NMR (300 MHz, DMSO-d^6, 25°C, TMS) spectrum of **2** (bottom). The diagnostic peak of pyridyl-H (δ = 6.30 ppm) on **L1** is marked in red ellipse for clarity, and no cyclobutane resonance for **L2** in the blue ellipse was found.
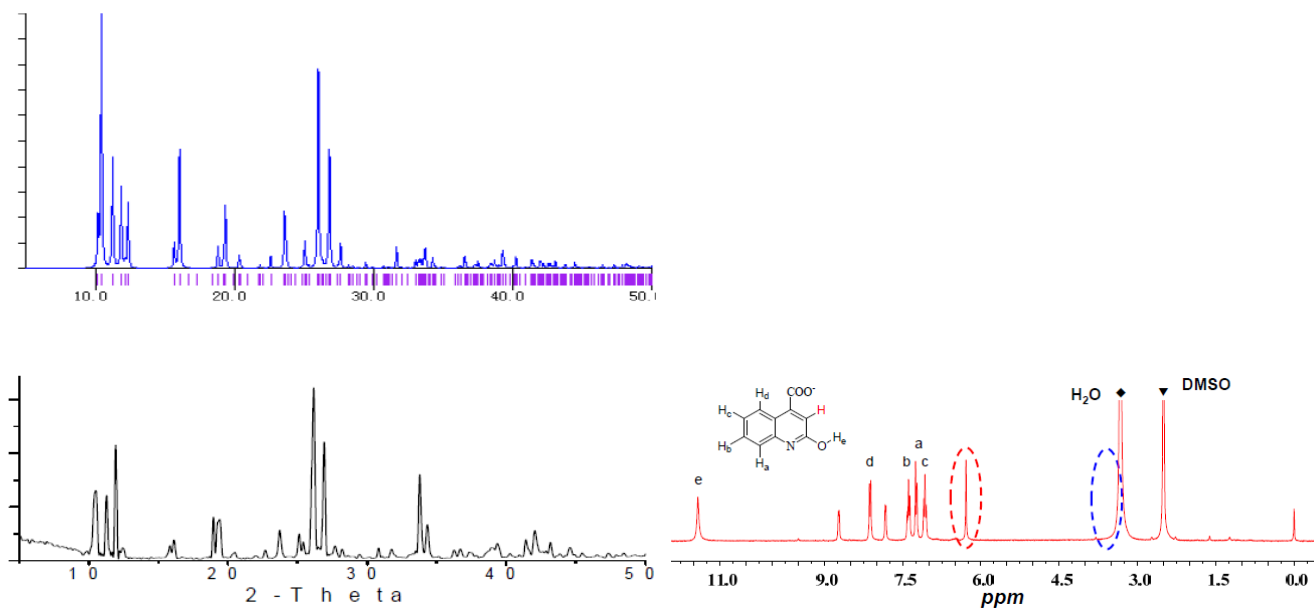
Fig. S3 ORTEP figure (top right, displacement ellipsoids drawn at 30% probability level, Symmetry codes: (i) −x, −y, −z−1; (ii) −x, −y+1, −z; (iii) x, y−1, z−1), crystal structure (top right, Symmetry code: (iv) x, y−1, z−1), simulated (blue) and experimental XRPD patterns (black), and ^{1}H NMR (300 MHz, DMSO-d^6, 25°C, TMS) spectrum of **3** (bottom). The diagnostic peak of pyridyl-H (δ = 6.28 ppm) on **L1** is marked in red for clarity, and no cyclobutane resonance for **L2** in the blue ellipse was found.

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Fig. S4 ORTEP figure (top left, displacement ellipsoids drawn at 50% probability level, Symmetry codes: (i) −x+2, −y+3, −z+3; (ii) −x+2, −y+2, −z+2; (iii) x, y+1, z+1), crystal structure (top right, Symmetry codes: (i) −x+2, −y+3, −z+3; (iv) −x+1, −y+2, −z+2), simulated (blue) and experimental XRPD patterns (black), and ^{1}H NMR (300 MHz, DMSO-d^6, 25°C, TMS) spectrum of **4** (bottom). The diagnostic peak of pyridyl-H (δ = 6.85 ppm) on **L1** is marked in red for clarity, and no cyclobutane resonance for **L2** in the blue ellipse was found.
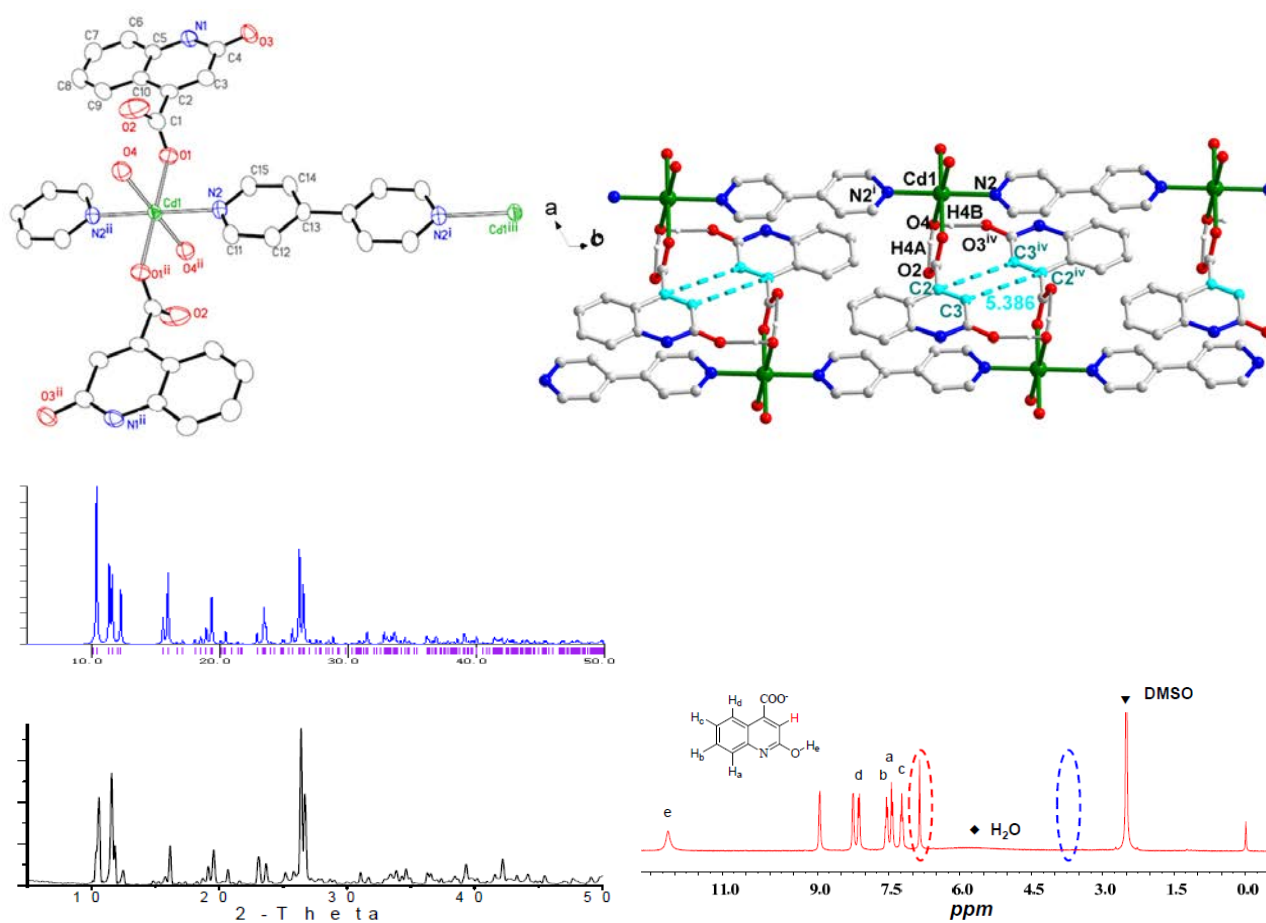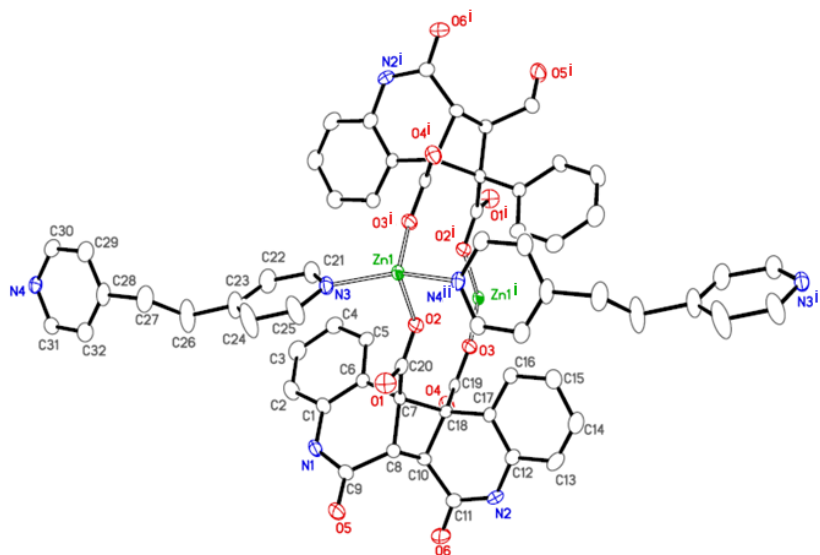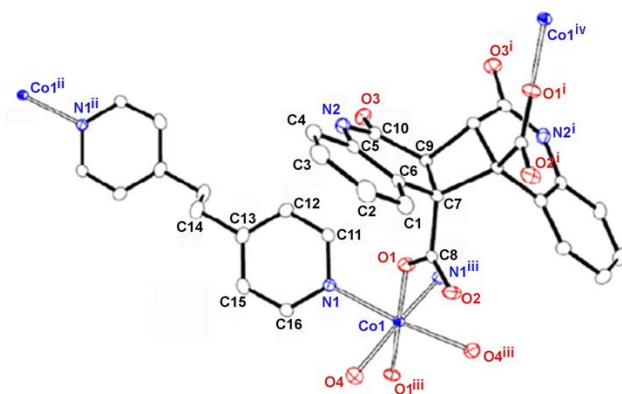

Fig. S5 ORTEP figure of **5** (displacement ellipsoids drawn at 30% probability level, Symmetry codes: (i) −x+1, −y, −z; (ii) x, y−1, z).

Fig. S6 ORTEP figure (top, displacement ellipsoids drawn at 30% probability level) of **6**. Simulated (blue) and experimental XRPD patterns (black), and ^{1}H NMR (300 MHz, CD$_3$OD, 25 °C, TMS) spectrum of **6** are also shown in the figure (bottom left and right). The signal marked in blue ellipse corresponds to the diagnostic peak of substituted cyclobutane protons (δ = 3.78 ppm) for **L2**, meanwhile the diagnostic peak of pyridyl-H for **L1** in red ellipse disappeared. (Symmetry codes: (i) −x, y, −z+1/2; (ii) −x+1, −y+1, −z; (iii) −x+1, y, −z+1/2; (iv) x−1, y, z).
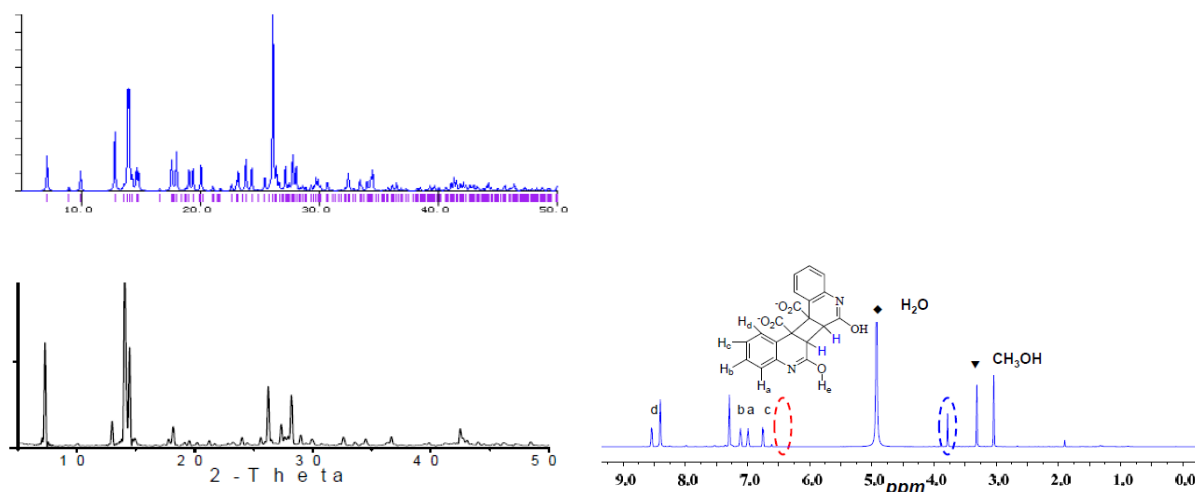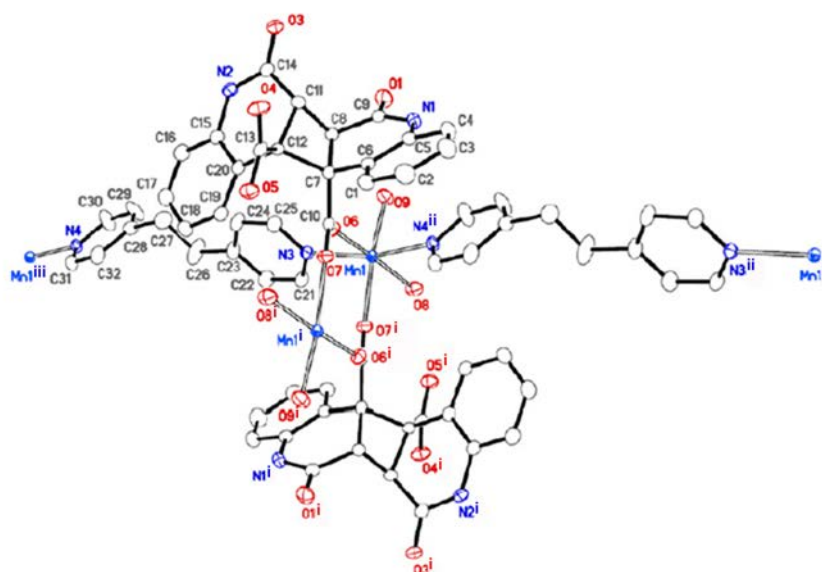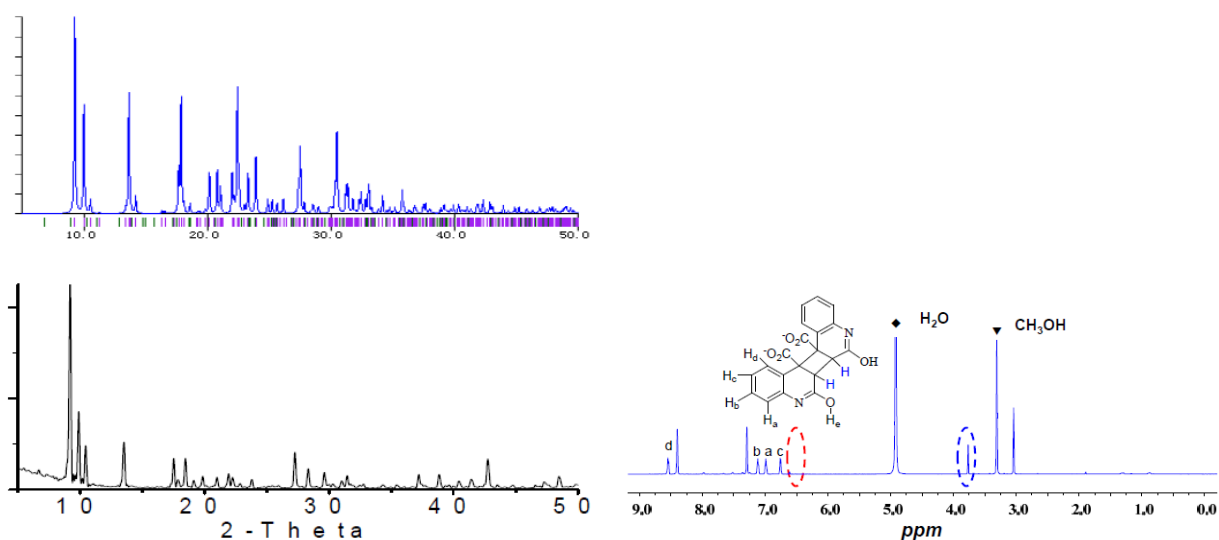
Fig. S7 ORTEP figure (top, displacement ellipsoids drawn at 30% probability level) of **7**. Simulated (blue) and experimental XRPD patterns (black), and ^{1}H NMR (300 MHz, CD$_3$OD, 25 °C, TMS) spectrum of **7** are also shown in the figure (bottom left and right). The signal marked in blue corresponds to the diagnostic peak of substituted cyclobutane protons (δ = 3.77 ppm) for **L2**, meanwhile the diagnostic peak of pyridyl-H for **L1** in red ellipse disappeared. (Symmetry codes: (i) −x+3/2, −y+1/2, −z+2; (ii) x+1/2, y+1/2, z; (iii) x−1/2, y−1/2, z)
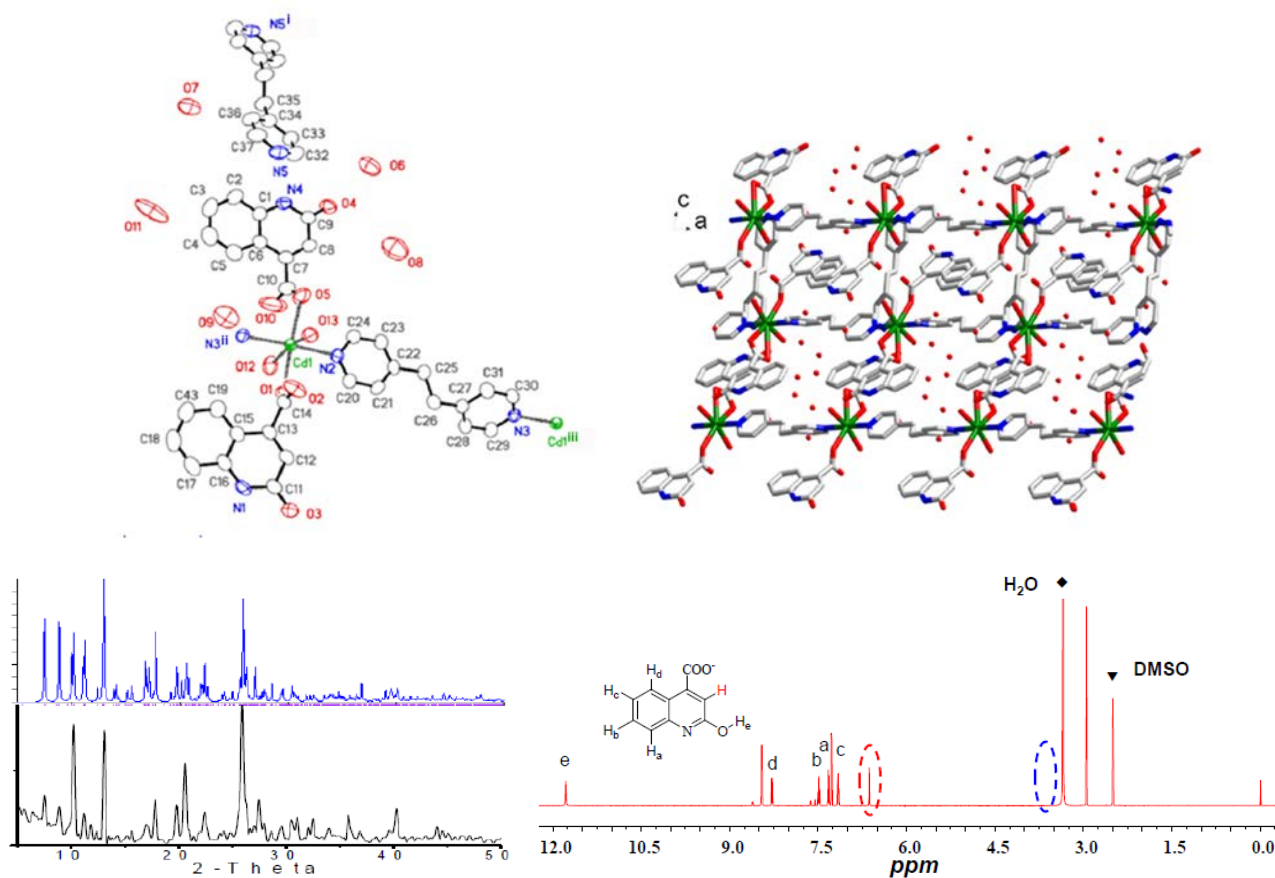

Fig. S8 ORTEP figure (top left, displacement ellipsoids drawn at 50 % probability level) and crystal pattern of **8** (top right; Symmetry codes: (i) −x+1, −y+1, −z; (ii) x+1, y−1, z; (iii) x−1, y+1, z). The

uncoordinated bpa ligands (highlighted in green color) and water molecules are located between the layers. The distances between water oxygen atoms are in the range of 2.786-2.847 Å. The average value is 2.81 Å which is significantly longer than that of **6**. The water guest molecules are hydrogen bonded to the framework. In addition, simulated (blue) and experimental XRPD patterns (black), and ^{1}H NMR (300 MHz, DMSO-d^6, 25°C, TMS) spectrum of **8** are also shown in the figure (bottom left and right). The diagnostic peak of pyridyl-H (δ = 6.63 ppm) for **L1** is marked in red ellipse for clarity, and no cyclobutane proton resonance for **L2** in the blue ellipse was found.
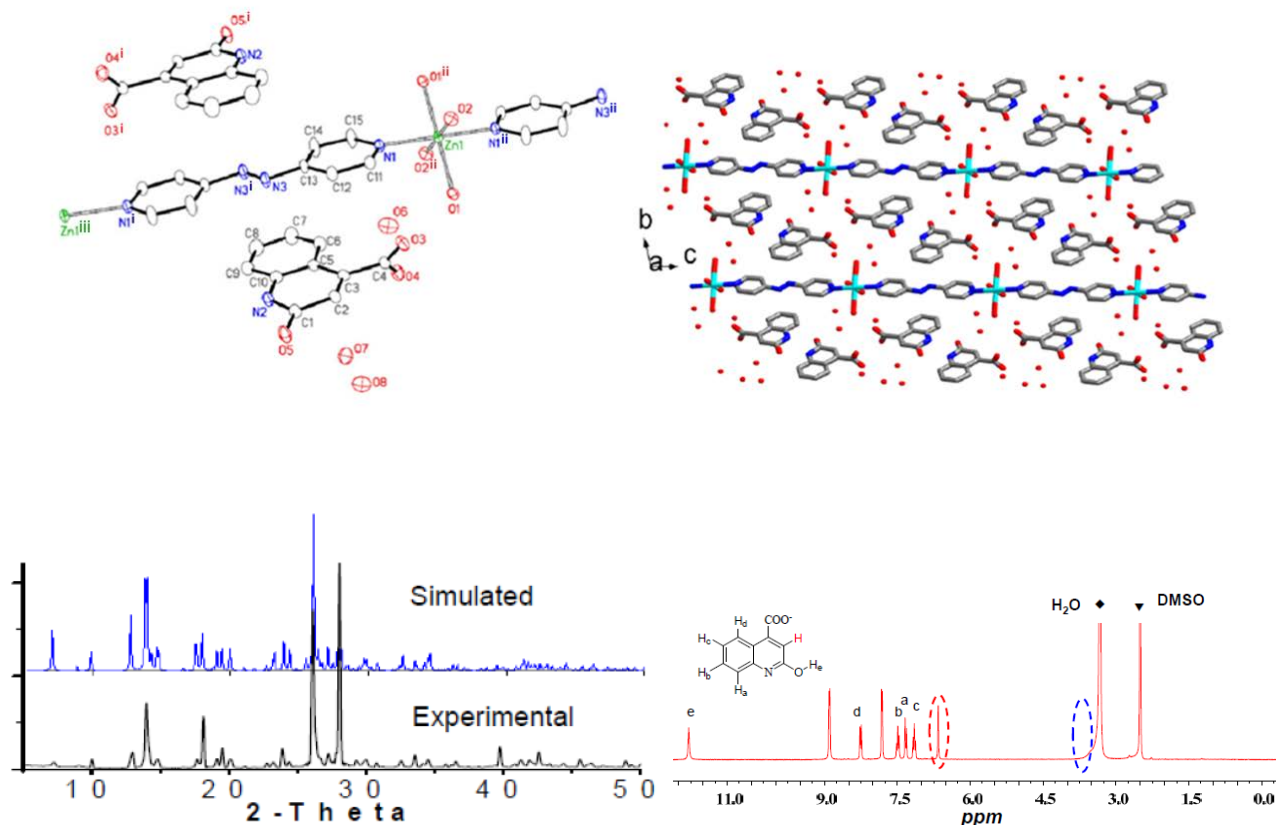

Fig. S9 ORTEP figure (top left, displacement ellipsoids drawn at 30% probability level, Symmetry codes: (i) −x, −y, −z+1; (ii) −x, −y, −z+2; (iii) x, y, z−1) and crystal pattern of **9** (top right). In addition, simulated (blue) and experimental XRPD patterns (black), and ^{1}H NMR (300 MHz, DMSO-d^6, 25°C, TMS) spectrum of **9** are also shown in the figure (bottom left and right). The diagnostic peak of pyridyl-H (δ = 6.66 ppm) for **L1** is marked in red for clarity, and no cyclobutane proton resonance for **L2** in the blue ellipse was found.
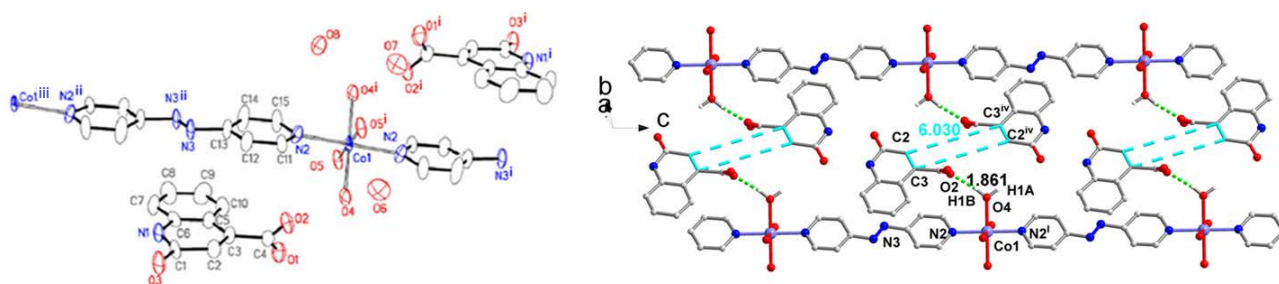
Fig. S10 ORTEP figure (top left, displacement ellipsoids drawn at 30% probability level, Symmetry codes: (i) −x, −y+1, −z+1; (ii) −x, −y+1, −z; (iii) x, y, z−1). The **L1** ligands are located between the chains with a pyridyl C=C distance at 6.030 Å (top right, Symmetry codes: (i) −x, −y+1, −z+1; (iv) −x+1, −y+2, −z+1). In addition, simulated (blue) and experimental XRPD patterns (black), and ^{1}H NMR (300 MHz, DMSO-d^6, 25 $^\circ$C, TMS) spectrum of **10** are also shown in the figure (bottom left and right). The diagnostic peak of pyridyl-H ($\delta = 6.25$ ppm) for **L1** is marked in red for clarity, and no cyclobutane proton resonance for **L2** in the blue ellipse was found.
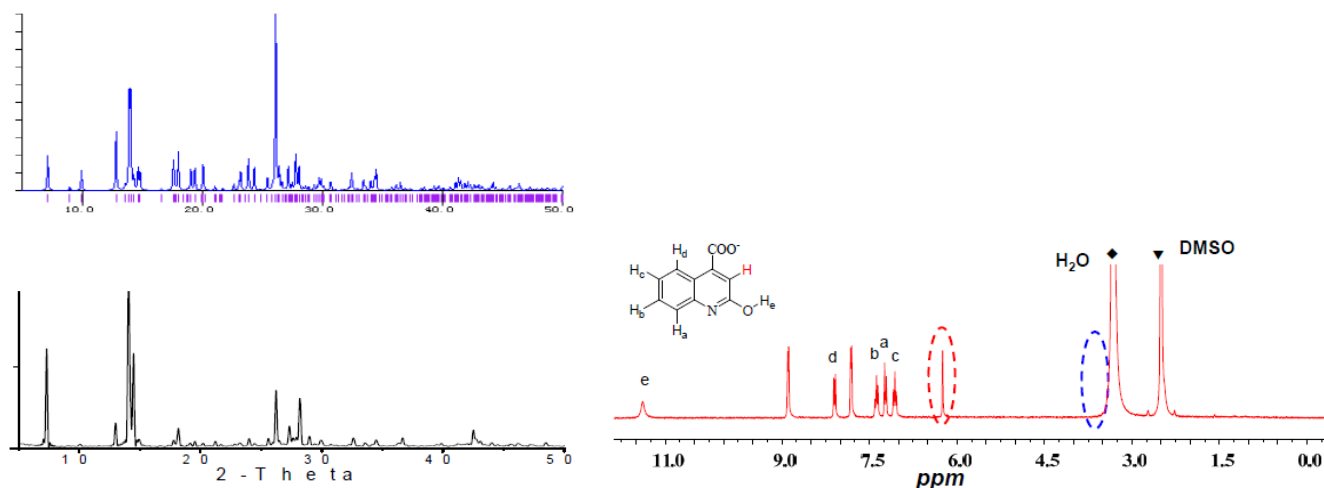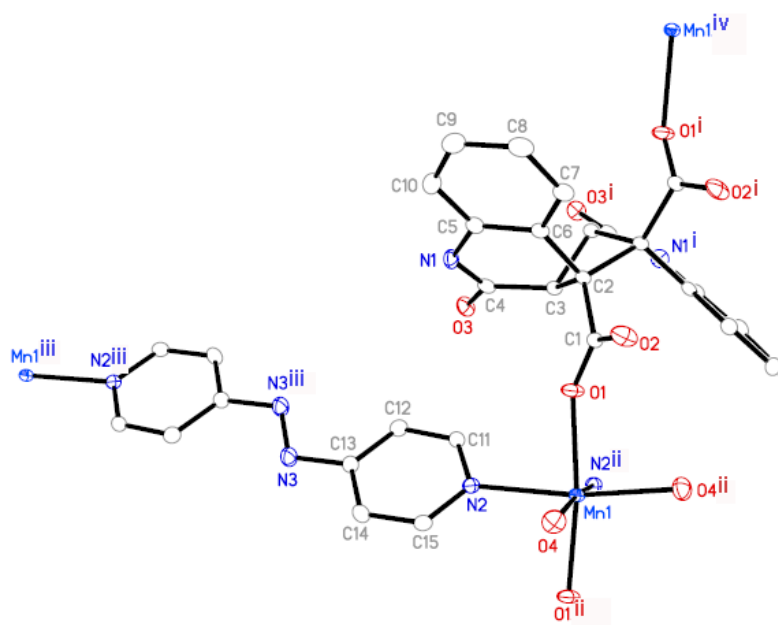

Fig. S11 ORTEP figure of **11** (displacement ellipsoids drawn at 50% probability level, Symmetry codes: (i) −x, y, −z+1/2; (ii) −x+1, y, −z+1/2; (iii) −x+1, −y+1, −z; (iv) x−1, y, z).
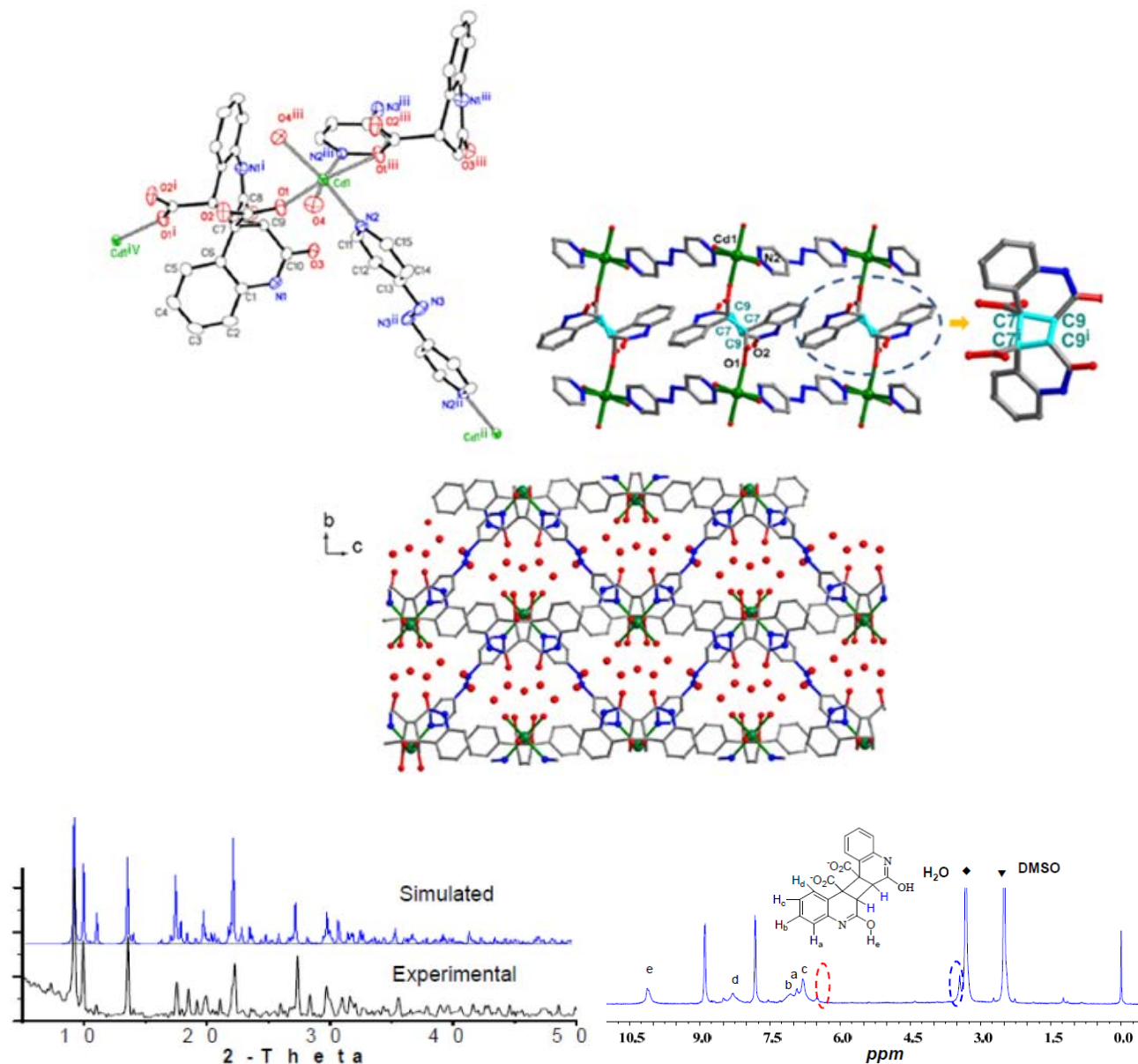
Fig. S12 ORTEP figure (top left, displacement ellipsoids drawn at 30% probability level, Symmetry codes: (i) −x+2, y, −z+1/2; (ii) −x+1, −y, −z; (iii) −x+1, y, −z+1/2; (iv) x+1, y, z). The **L2** ligands bind the {Cd(azpy)}$_n$ chains into an undulating layer (top right, Symmetry code: (i) −x+2, y, −z+1/2). Crystal patterns (middle, view down a axis). Compared to **11**, similar coordination pattern and H-bonded water chain were found in **12**. The average O···O distance is 3.034 Å which is slightly longer than that of **11**. Simulated (blue) and experimental XRPD patterns (black), and ^{1}H NMR (300 MHz, DMSO-d^6, 25 °C, TMS) spectrum of **12** are also shown in the figure (bottom). The signal marked in blue corresponds to the diagnostic peak of substituted cyclobutane protons (δ = 3.45 ppm) in blue ellipse for **L2**, meanwhile the diagnostic peak of pyridyl-H for **L1** in the red ellipse disappeared
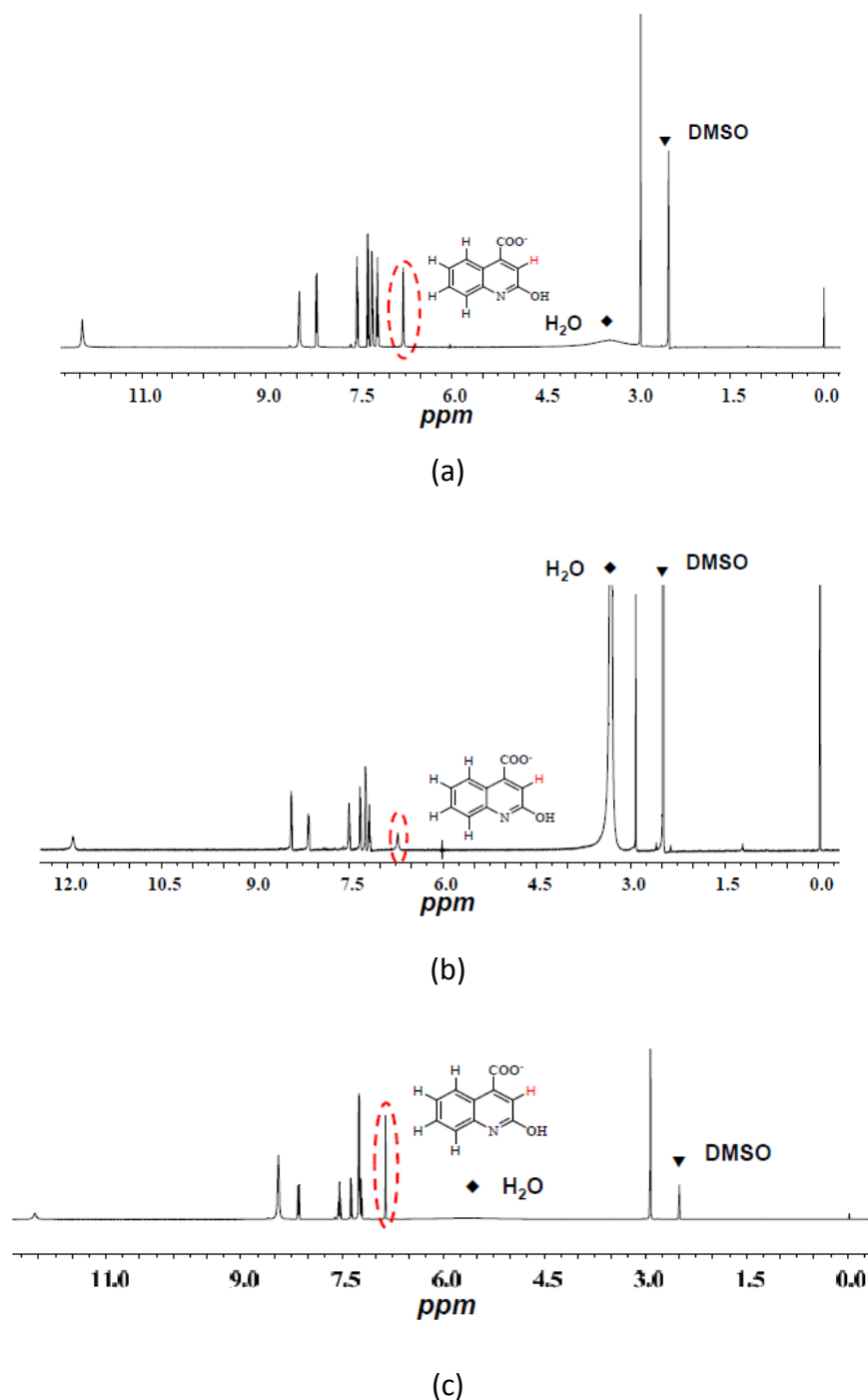
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(a)

(b)

(c)

Fig. S13 The ^{1}H NMR (600 MHz, DMSO-d^6, 25°C, TMS) spectra for parallel experiments. (a) An aqueous solution of **L1** (6 mg, 0.032 mmol), Zn(OAc)$_2$ (7 mg, 0.038 mmol) and bpa (5.8 mg, 0.031 mmol) was sealed in a glass tube and heated at 150°C for 2 days, and then the resulting solution was kept in the dark for 10 days to generate clear solution. (b) The above reaction solution was just exposed to ambient light without hydrothermal process. (c) **L1** and bpa without Zn(II) ion were heated under hydrothermal condition, then kept the resulting solution in ambient light. As shown above, the peaks at ~6.8 ppm (the diagnostic peak for Py-H of **L1**) indicate no dimerization reaction happened in these parallel experiments, which is further supported by the absence of signals at ~3.5 ppm (the diagnostic peak for cyclobut-H on **L2**).

Table S1. The expected chemical shifts of **L1** and **L2** for all the 12 compounds and the corresponding tested conditions.

Entry	Molecular formular	Expected chemical shift	Observed chemical shift	Deuterated solvents
1	Zn(**L1**)$_2$(bipy)	6.60~6.80[1]	6.68	DMSO-d^6
2	Co(**L1**)$_2$(bipy)	6.20~6.30[2]	6.30	DMSO-d^6
3	Mn(**L1**)$_2$(bipy)	6.20~6.30[2]	6.28	DMSO-d^6
4	Cd(**L1**)$_2$(bipy)	6.60~6.80[1]	6.85	DMSO-d^6
5	Zn(**L2**) (bpa)	3.40~3.50[1]	3.50	DMSO-d^6
6	Co(**L2**) (bpa)	3.70~3.80[2]	3.78	CD$_3$OD-d^4
7	Mn(**L2**) (bpa)	3.70~3.80[2]	3.77	CD$_3$OD-d^4
8	Cd(**L1**)$_2$(bpa)	6.60~6.80[1]	6.63	DMSO-d^6
9	Zn(**L1**)$_2$ (azpy)	6.60~6.80[1]	6.66	DMSO-d6
10	Co(**L1**)$_2$ (azpy)	6.20~6.30[2]	6.25	DMSO-d^6
11	Mn(**L2**)(azpy)	3.70~3.80[2]	3.77	CD$_3$OD-d^4
12	Cd(**L2**)(azpy)	3.40~3.50[1]	3.45	DMSO-d^6

[1] Tested with the metal ions in the deuterated solvents. The H at the third position of substituted quinoline in **L1** was expected at 6.60~6.80 and the H of substituted cyclobutane in **L2** was expected at 3.40~3.50.

[2] Tested after the metal ions were removed from the original crystal samples using NaOH. The H at the third position of substituted quinoline in **L1** was expected at 6.20~6.30 and the H of substituted cyclobutane in **L2** was expected at 3.70~3.80.