

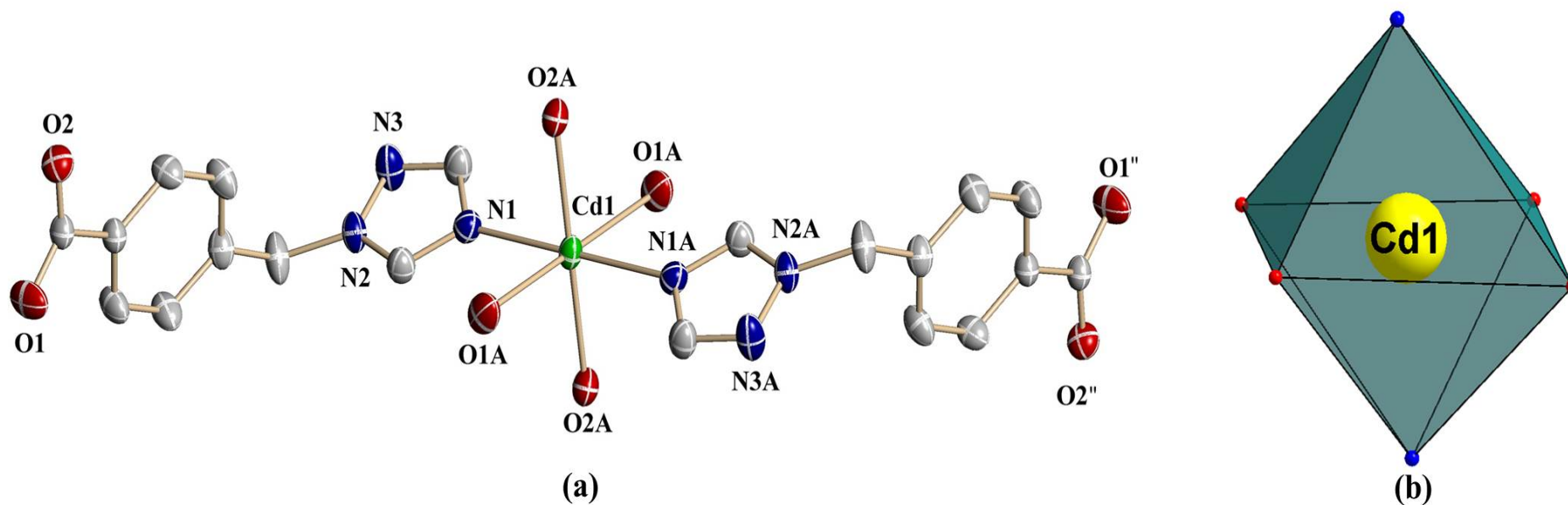
## Supporting Information

**An insight into the controllable synthesis of Cd(II) complexes with a new multifunctional ligand and its application in dye-sensitized solar cells and luminescence properties**

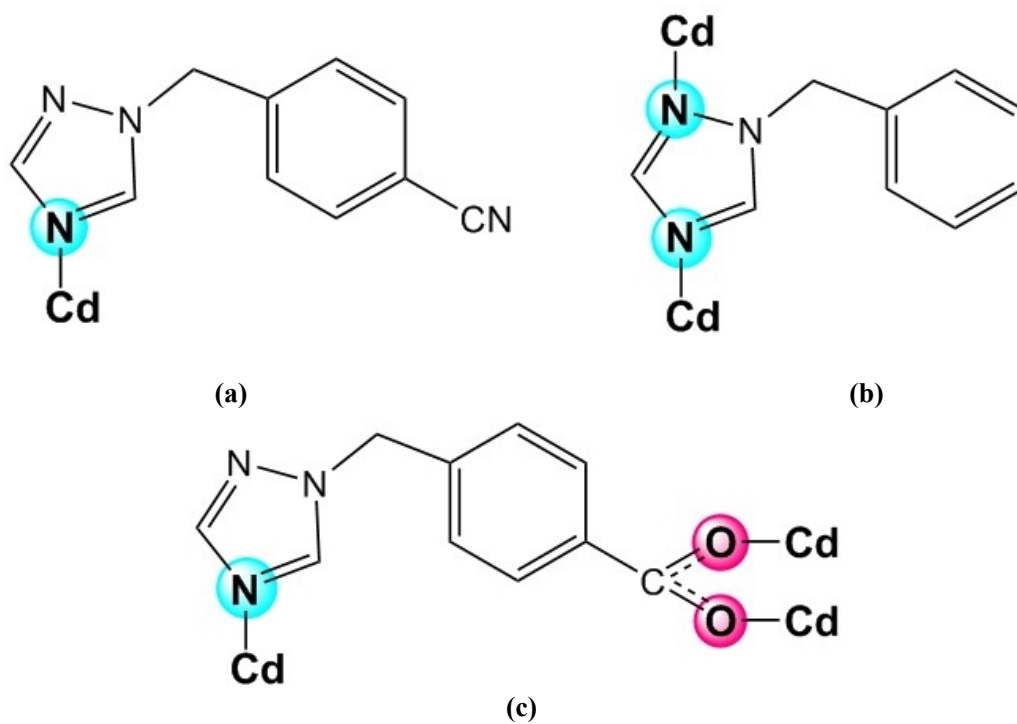
**Song Gao,<sup>a</sup> Rui Qing Fan,<sup>\*,a</sup> Xin Ming Wang,<sup>a</sup> Liang Sheng Qiang,<sup>a</sup> Li Guo Wei,<sup>a</sup> Ping Wang,<sup>a</sup> Hui Jie Zhang,<sup>a</sup> Yu Lin Yang<sup>\*,a</sup>, Yu Lei Wang<sup>b</sup>**

*<sup>a</sup> Department of Chemistry, Harbin Institute of Technology, Harbin 150001, P. R. of China*

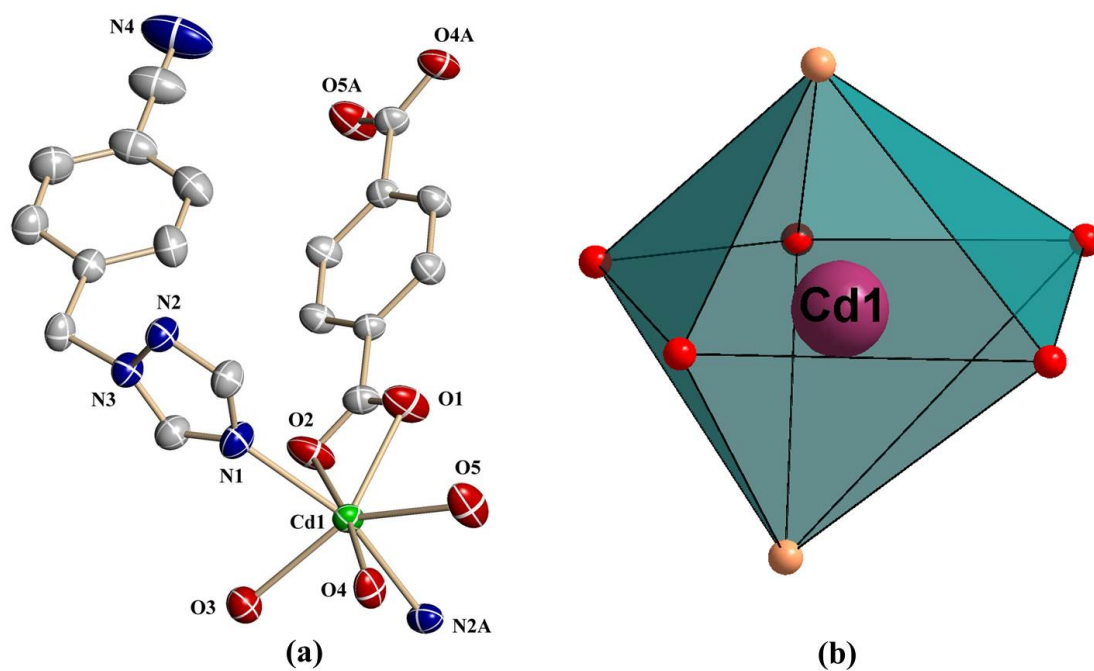
*<sup>b</sup> National Key Laboratory of Science and Technology on Tunable Laser, Harbin Institute of Technology, Harbin 150080, P. R. of China*



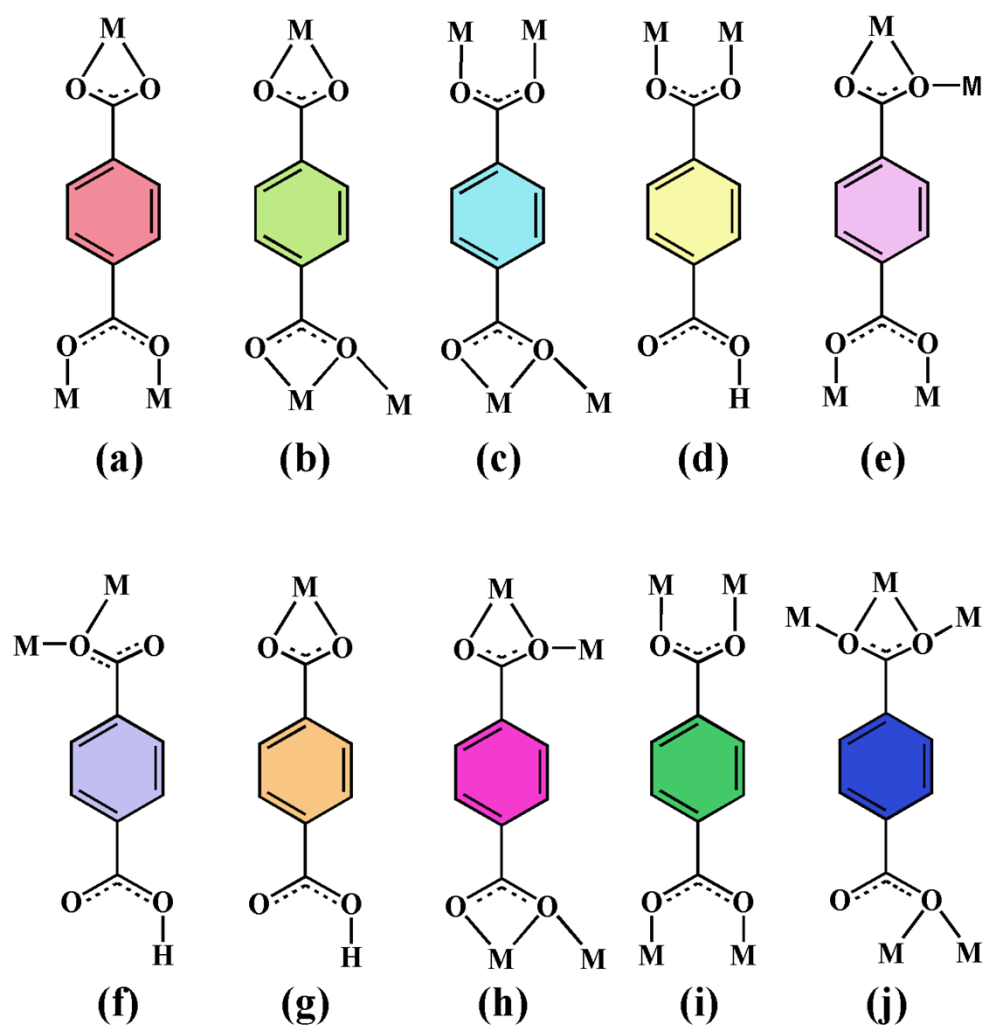
**Fig. S1** (a) The structural unit of **1** with labeling scheme and 50% thermal ellipsoids (water molecules and hydrogen atoms are omitted for clarity). (b) Polyhedral representation of the coordination sphere of the Cd<sup>2+</sup> centre, with display octahedron geometry arrangement in **1**.



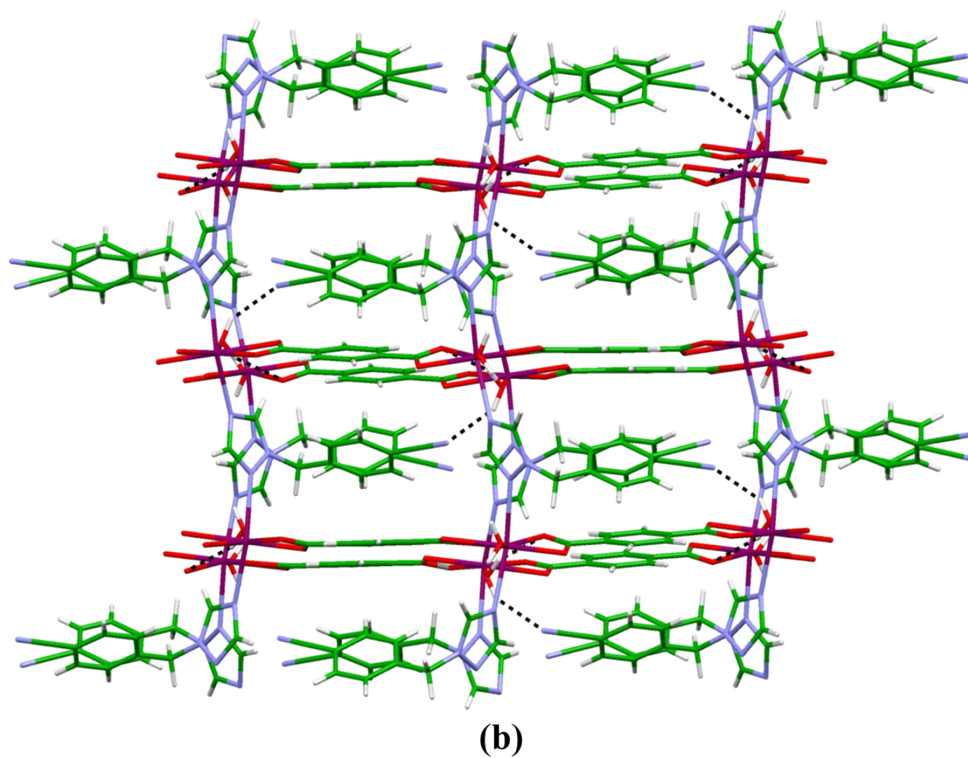
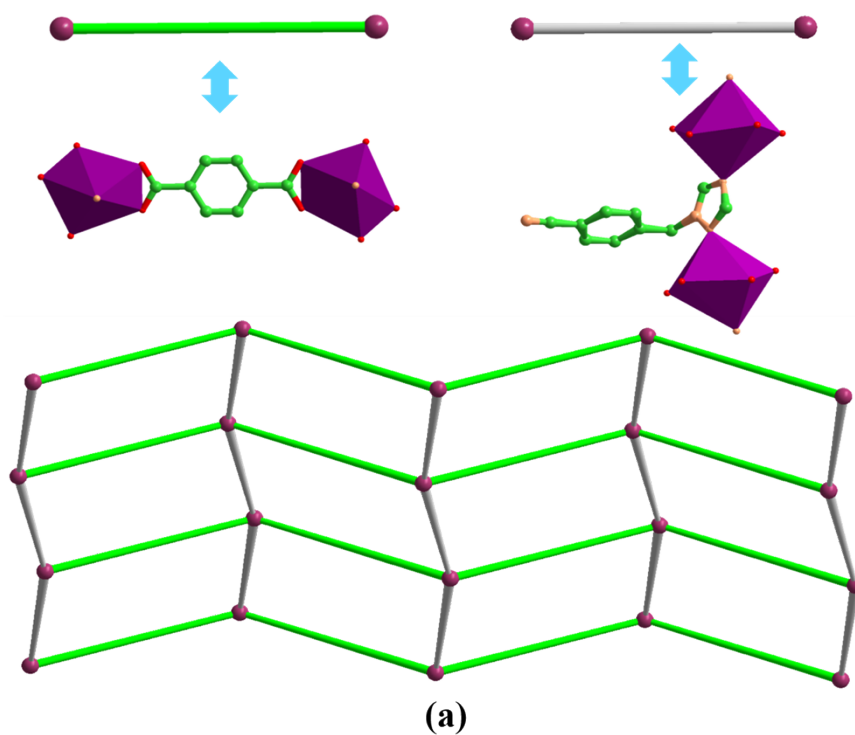
**Scheme S1** The coordination modes of TMCB and TMCBA ligands.



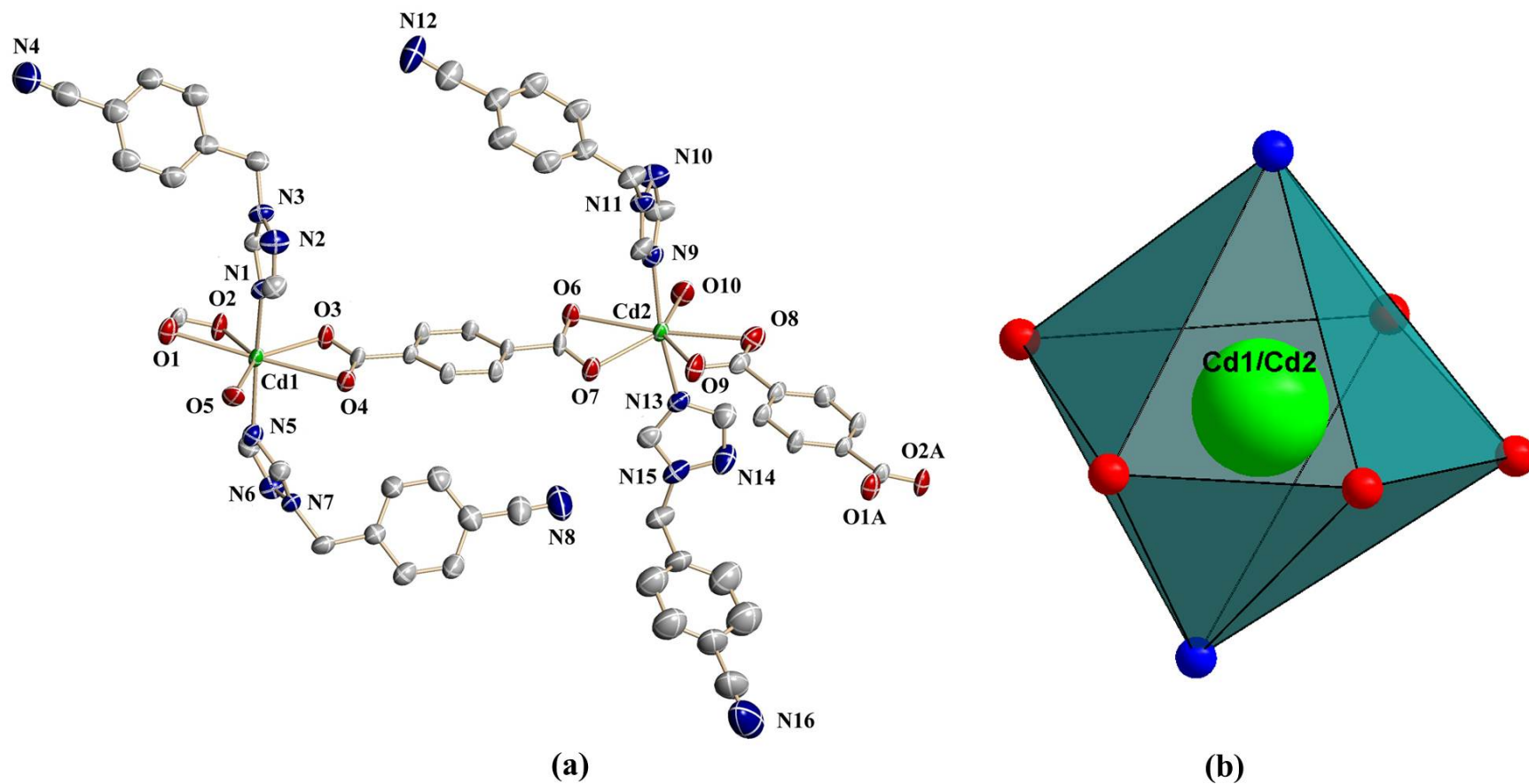
**Fig. S2** (a) The structural unit of **2** with labeling scheme and 50% thermal ellipsoids (hydrogen atoms are omitted for clarity). (b) Polyhedral representation of the coordination sphere of the Cd<sup>2+</sup> centre, with display distorted pentagonal bipyramid arrangement in **2**.



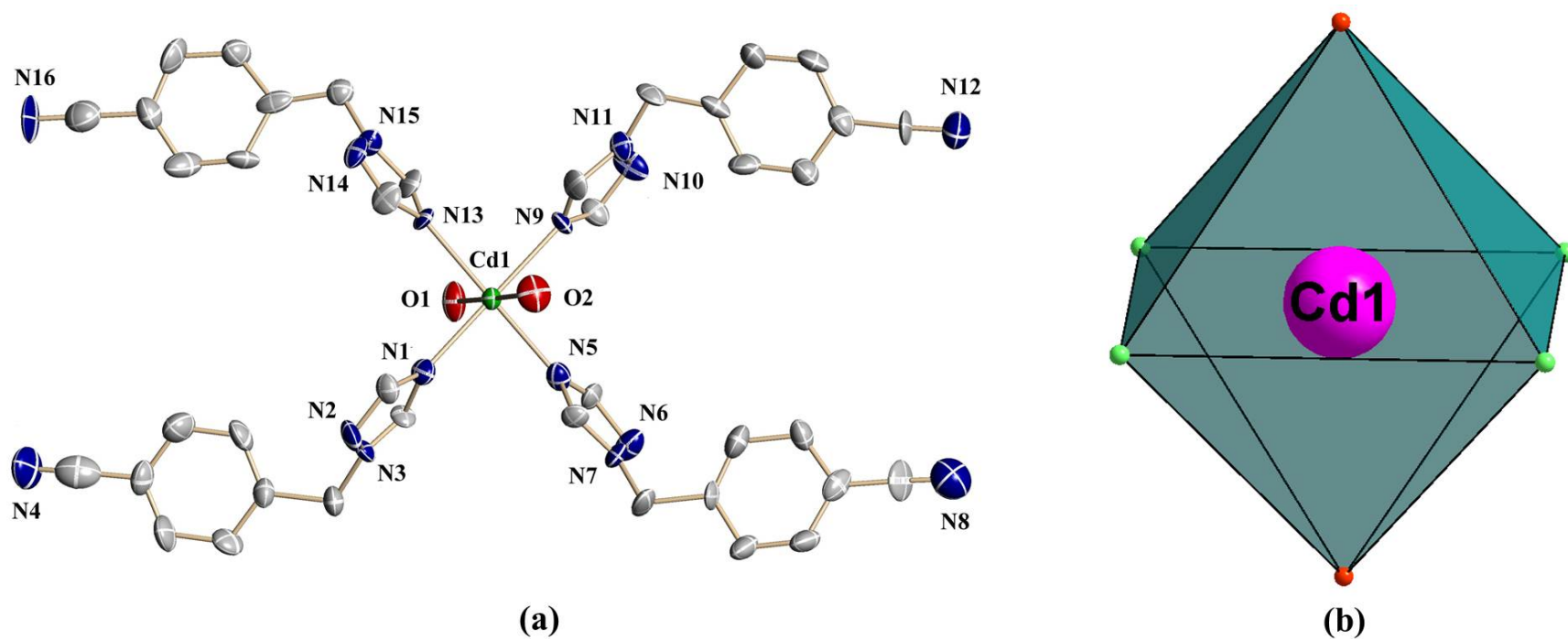
**Scheme S2** The coordination modes of 1,4- $H_2bda$  ligand.



**Fig. S3** (a) The 2D 4-connected  $4^4$  topology in its most symmetrical form distinguished by different colors ( $\text{Cd}^{2+}$ , eggplant ball; TMCB, gray linkers; 1,4- $\text{H}_2\text{bda}$ , green linkers) (b) A 3D supramolecular structure of **2** (hydrogen bonding black dashed line).

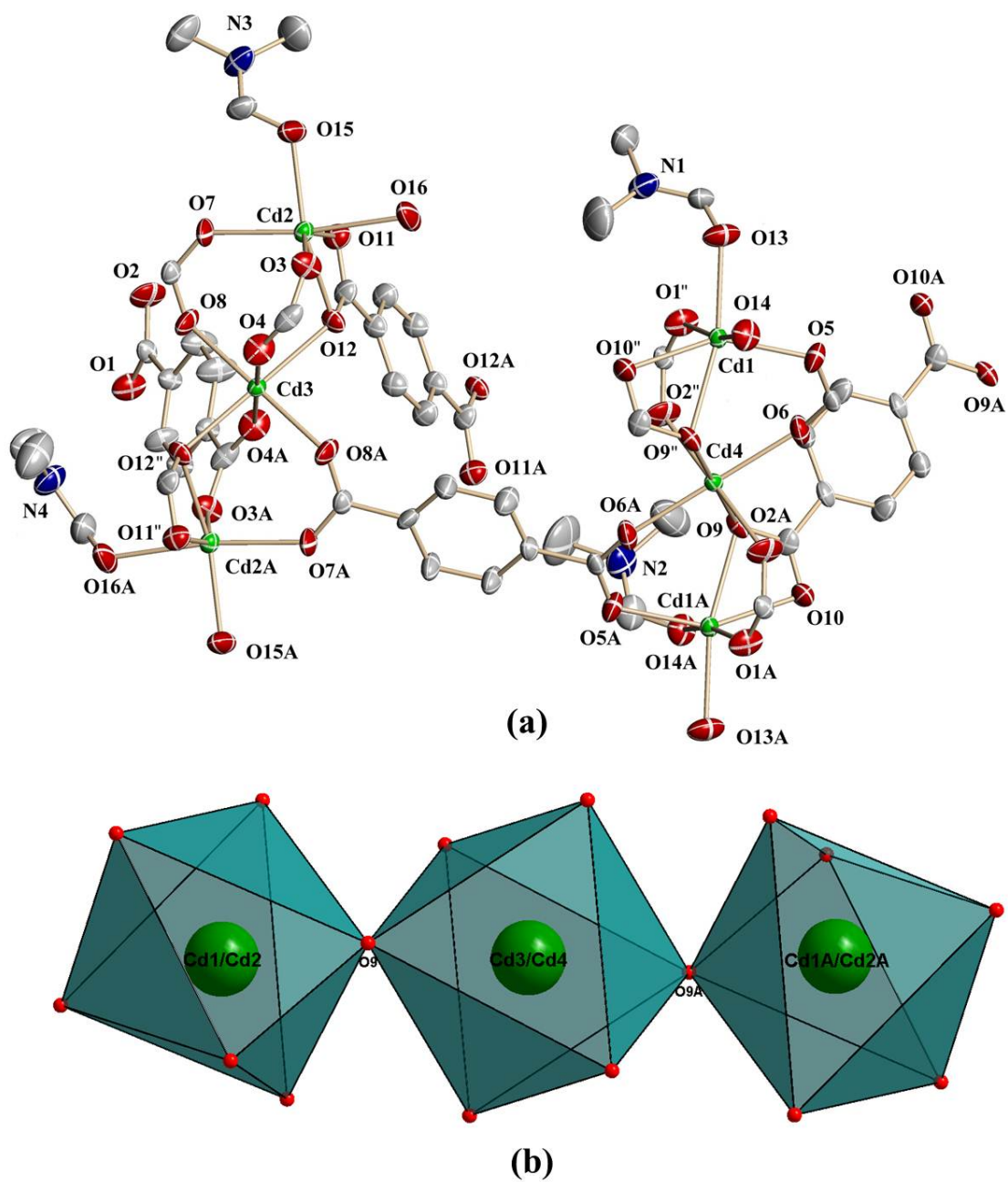


**Fig. S4** (a) The structural unit of **3** with labeling scheme and 50% thermal ellipsoids (water molecules and hydrogen atoms are omitted for clarity). (b) Polyhedral representation of the coordination sphere of the Cd<sup>2+</sup> centre in **3**.

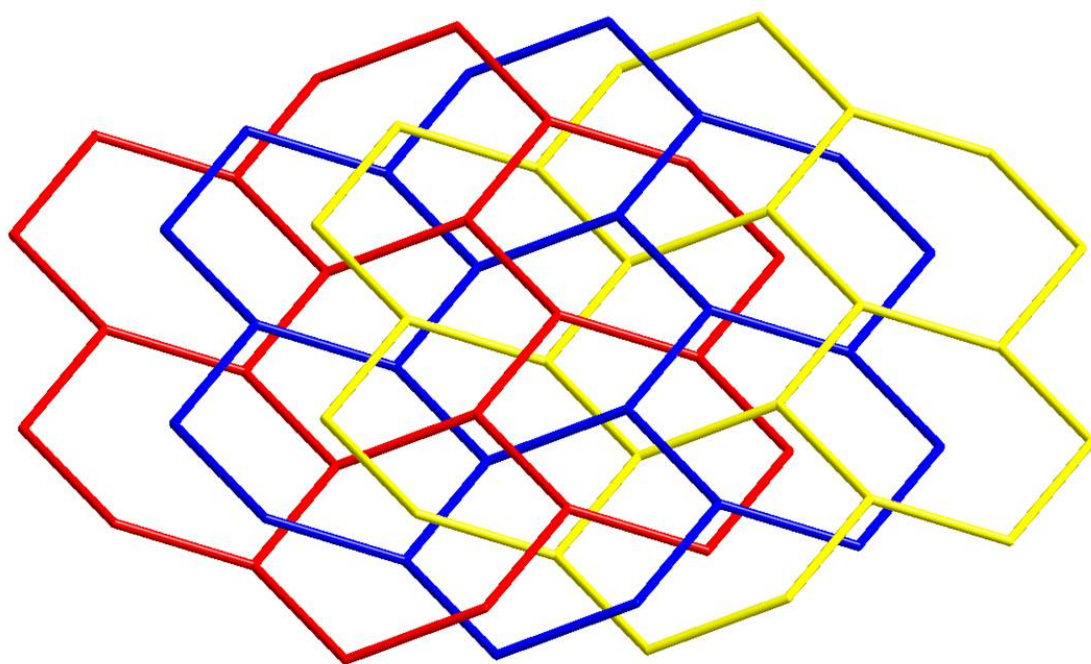


**Fig. S5** (a) The structural unit of **4** with labeling scheme and 50% thermal ellipsoids (water molecules and hydrogen atoms are omitted for clarity). (b) Polyhedral representation of the coordination sphere of the Cd<sup>2+</sup> centre in **4**.

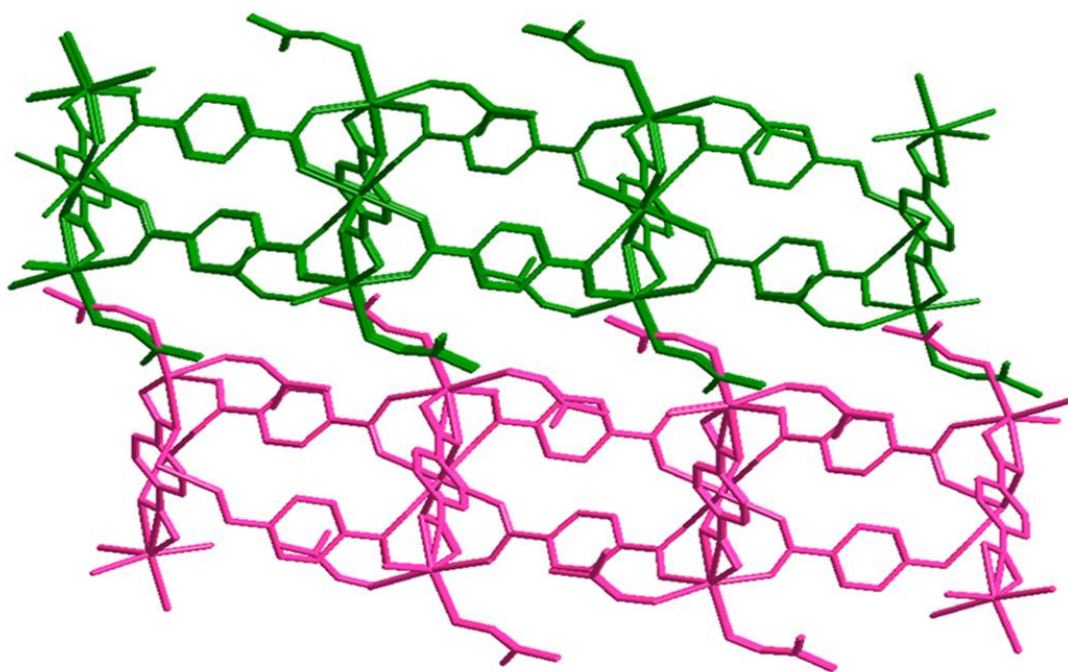




**Fig. S6** (a) The structural unit of **5** with labeling scheme and 50% thermal ellipsoids (water molecules and hydrogen atoms are omitted for clarity). (b) Polyhedral representation of the coordination sphere of the  $\text{Cd}^{2+}$  centre in **5**.

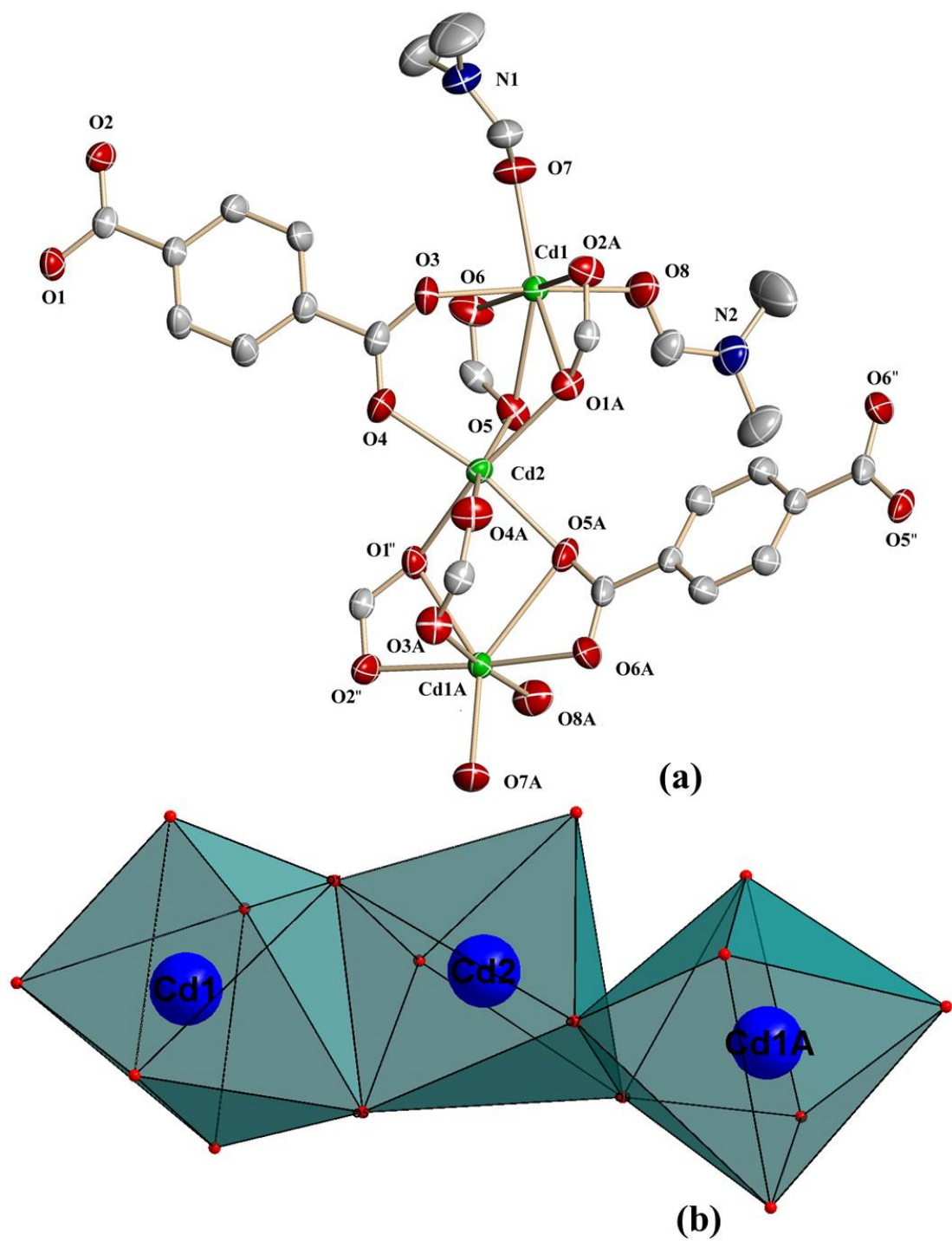


(a)

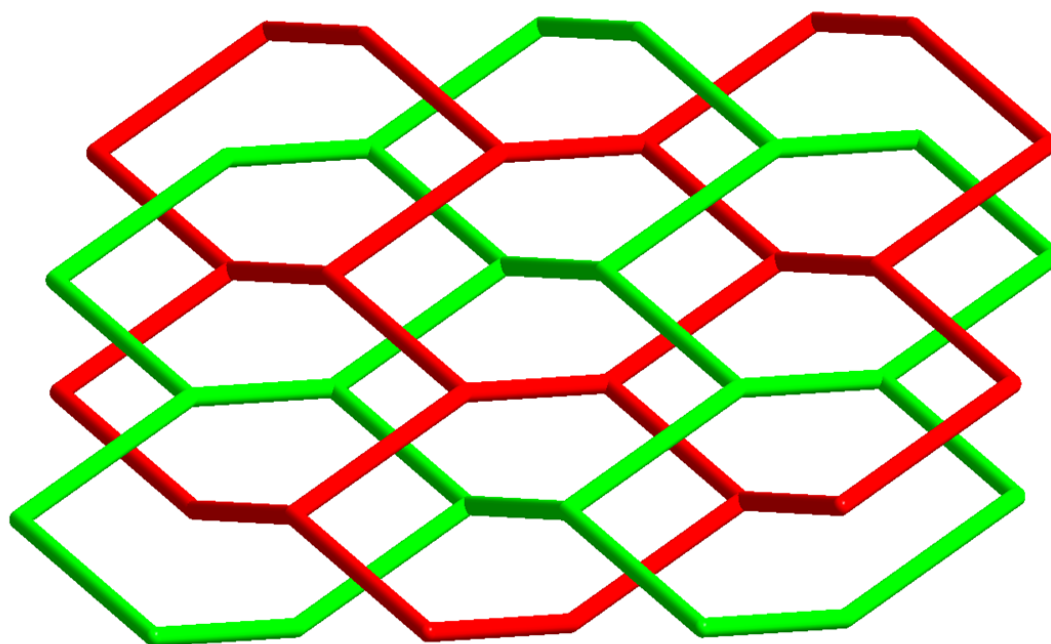


(b)

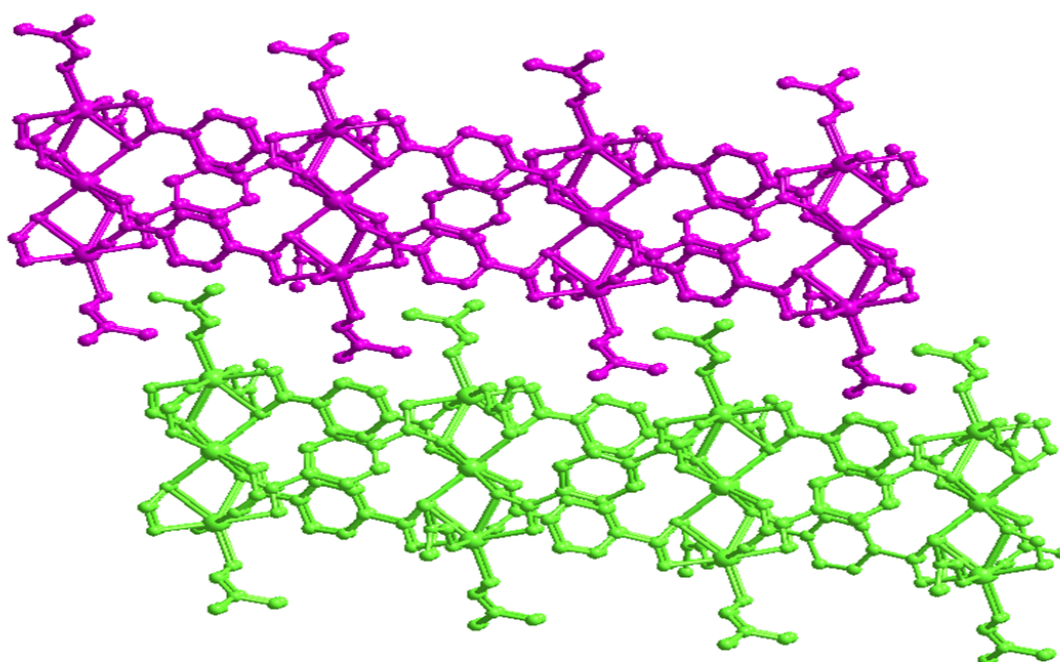
**Fig. S7** (a) The topological representation of threefold interpenetrating network of **5**. (b) A 3D supramolecular structure of **5** (intermolecular forces between the molecules).



**Fig. S8** (a) The structural unit of **5'** with labeling scheme and 50% thermal ellipsoids (water molecules and hydrogen atoms are omitted for clarity). (b) Polyhedral representation of the coordination sphere of the  $\text{Cd}^{2+}$  centre in **5'**.

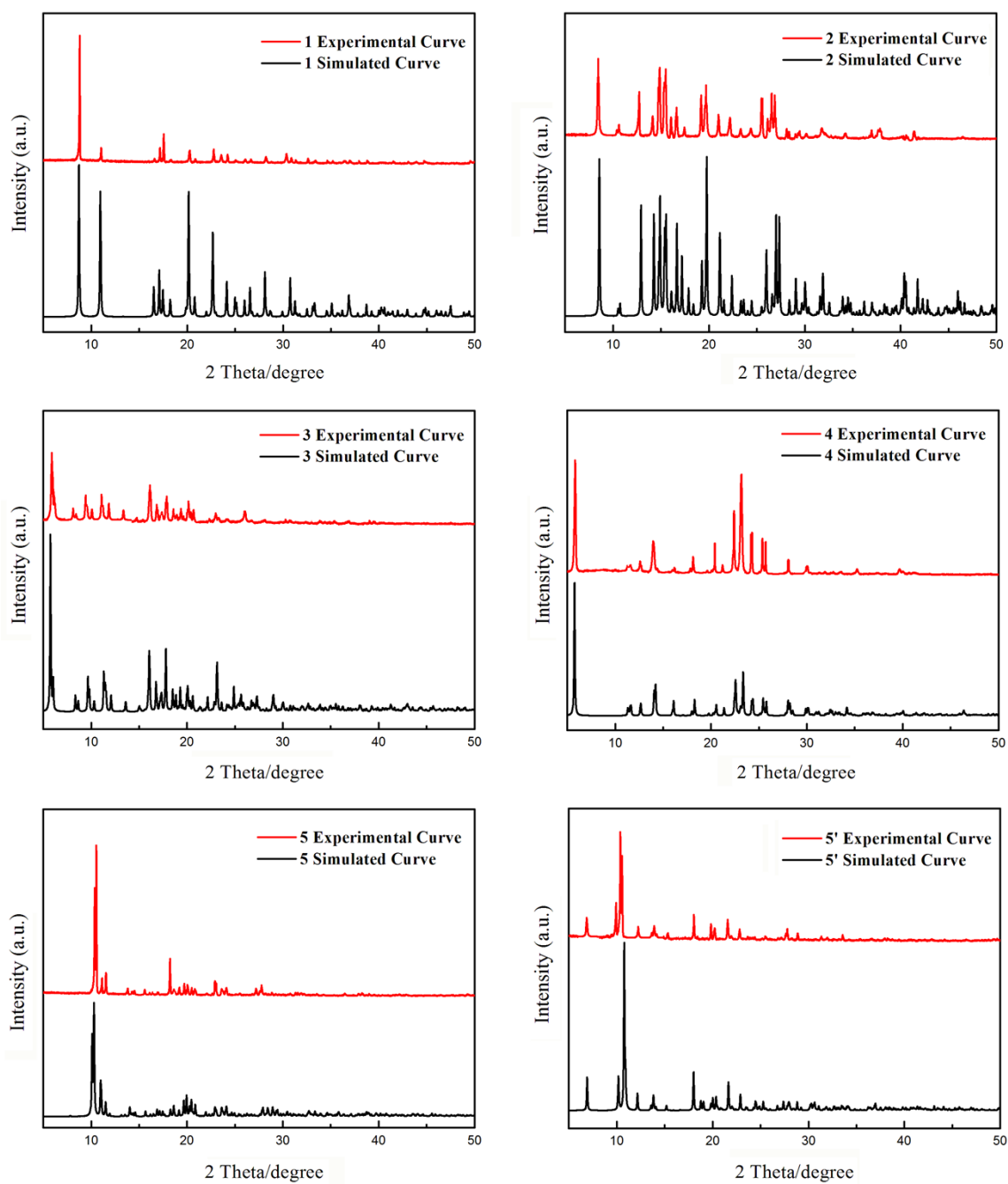


(a)



(b)

**Fig. S9** (a) The topological representation of twofold interpenetrating network of **5'**. (b) A 3D supramolecular structure of **5'** (intermolecular forces between the molecules).



**Fig. S10** The PXRD contrast curves of complexes 1–5'.

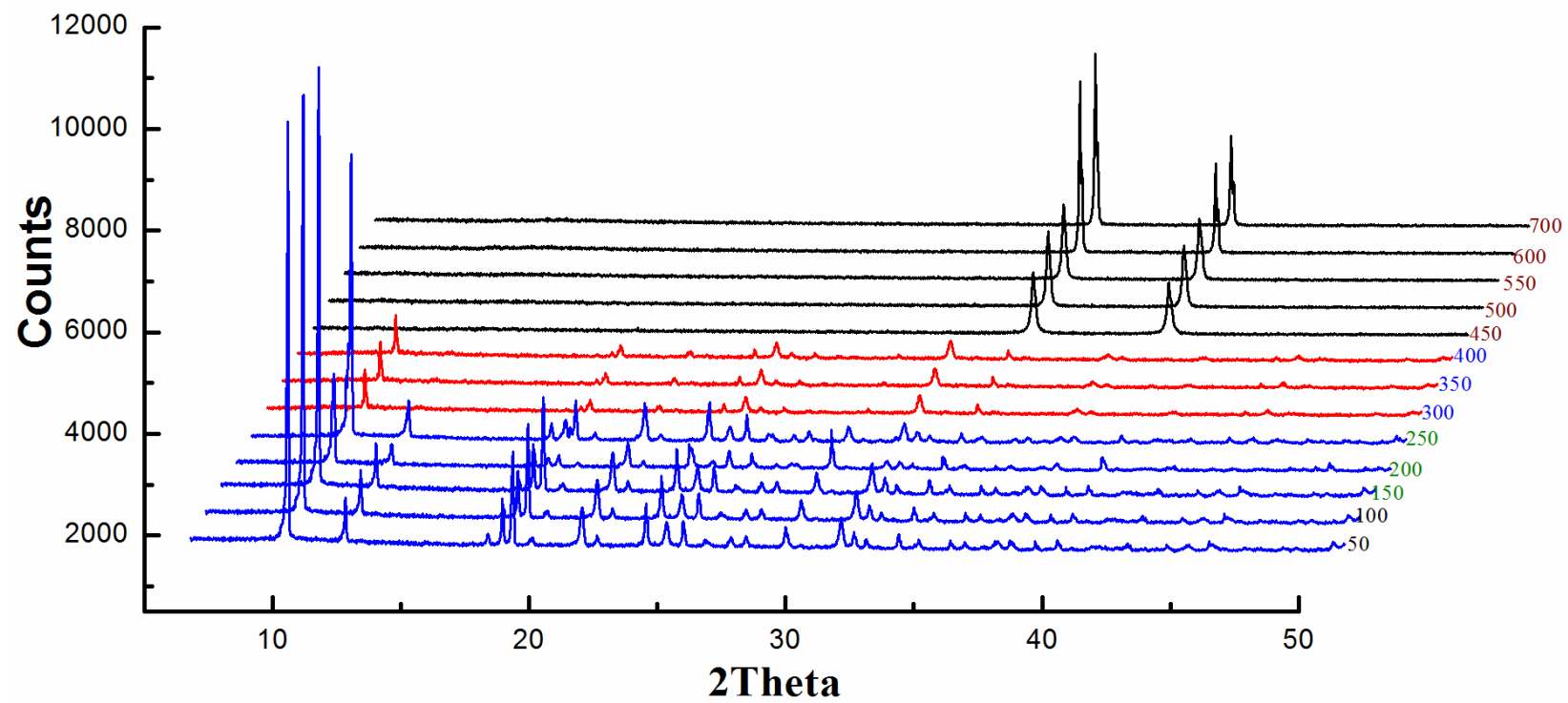
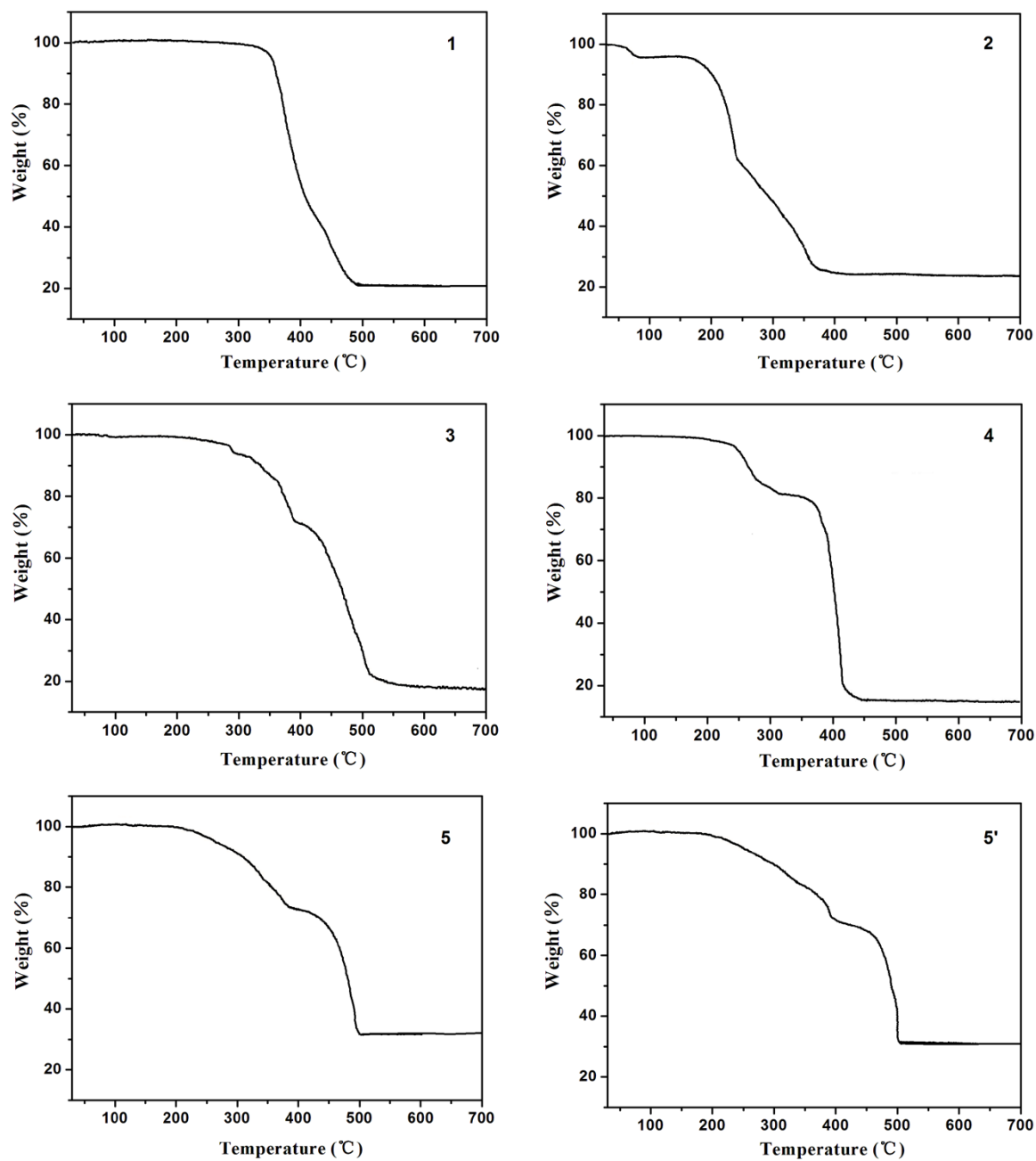
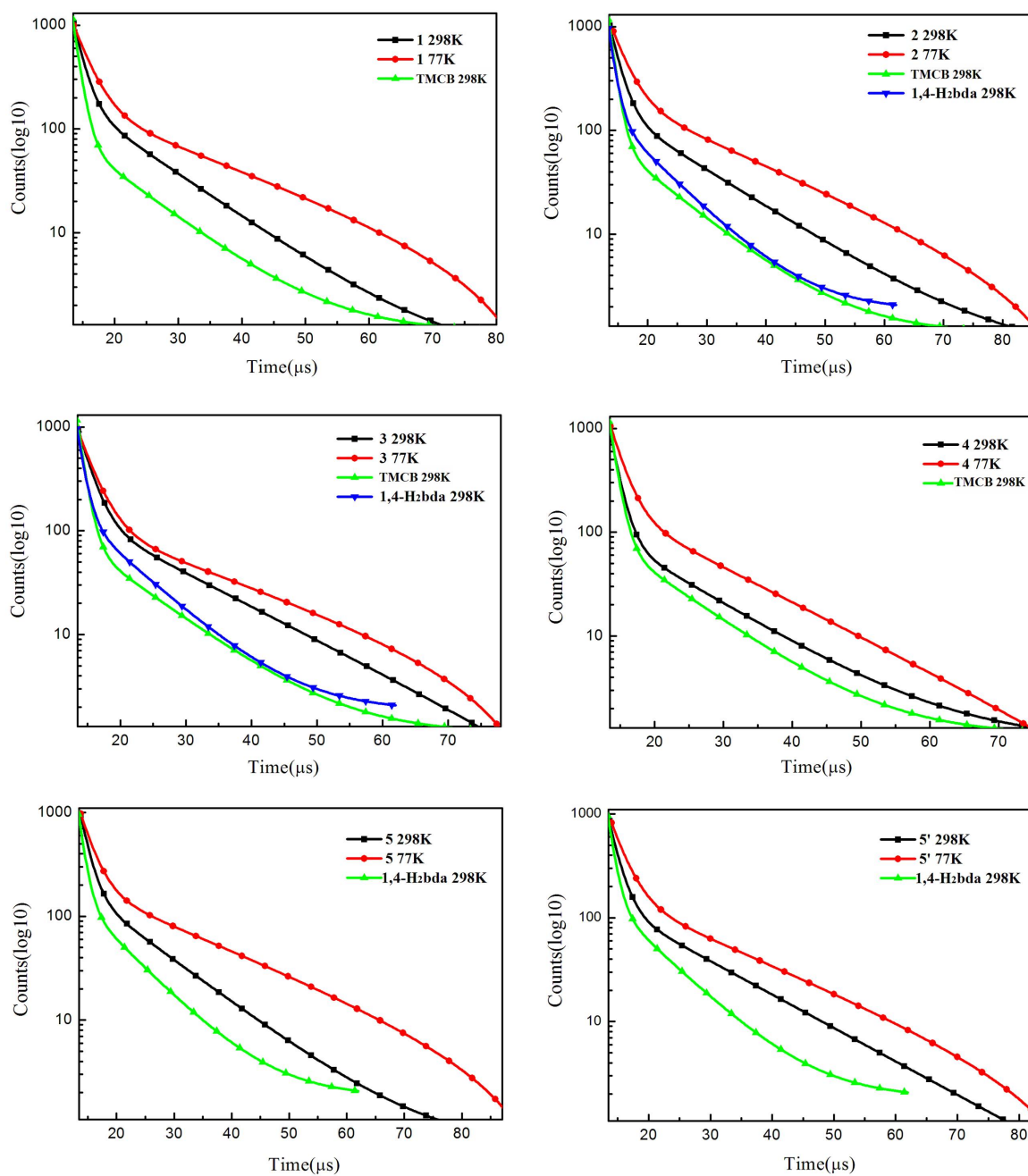


Fig. S11 X-ray thermodiffractograms of 1.



**Fig. S12** The TGA curves of complexes 1–5'.



**Fig. S13** The decay curves of complexes 1–5' at 298 K, 77 K and TMCB, 1,4-H<sub>2</sub>bda at 298 K in solid state.



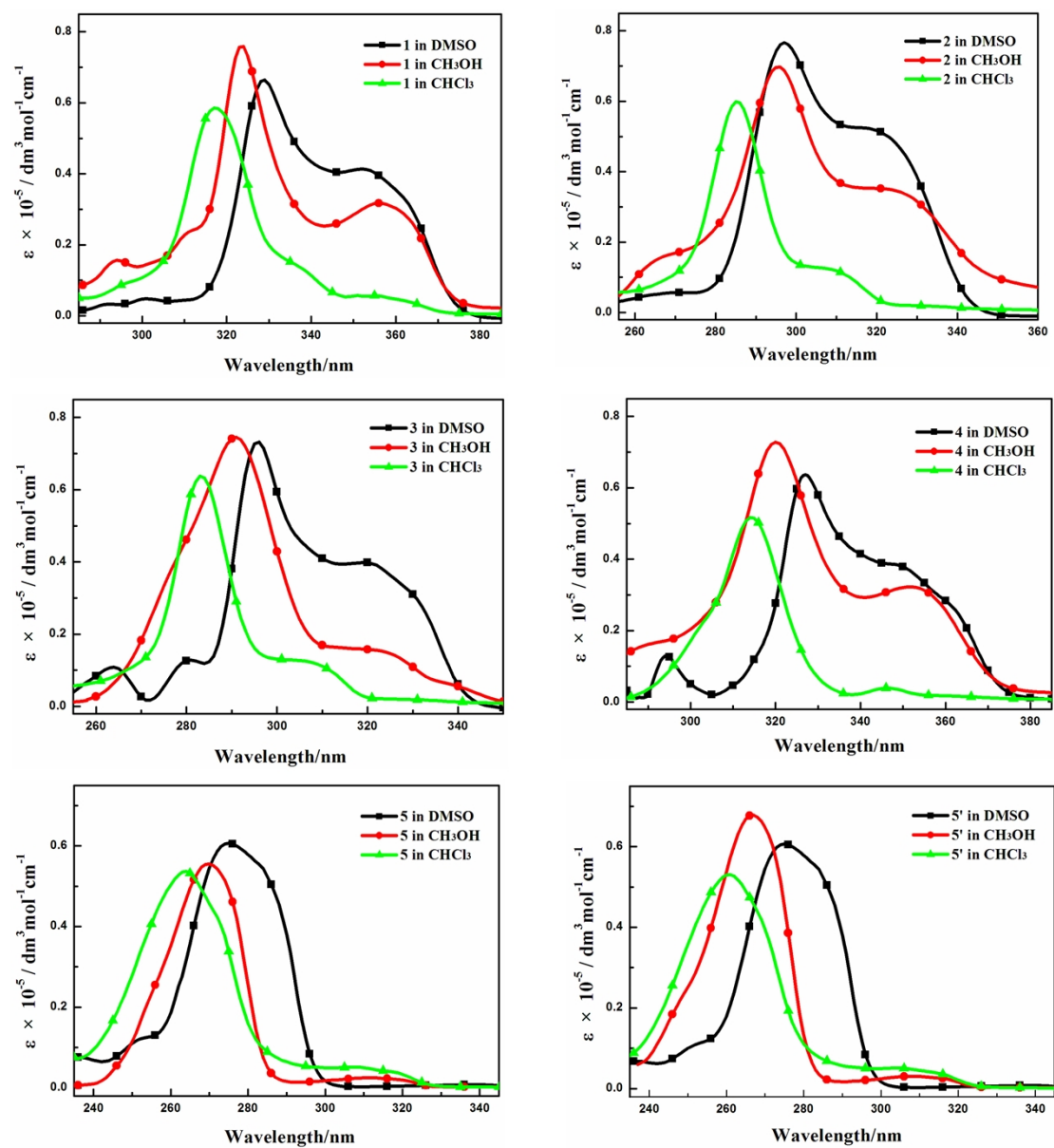
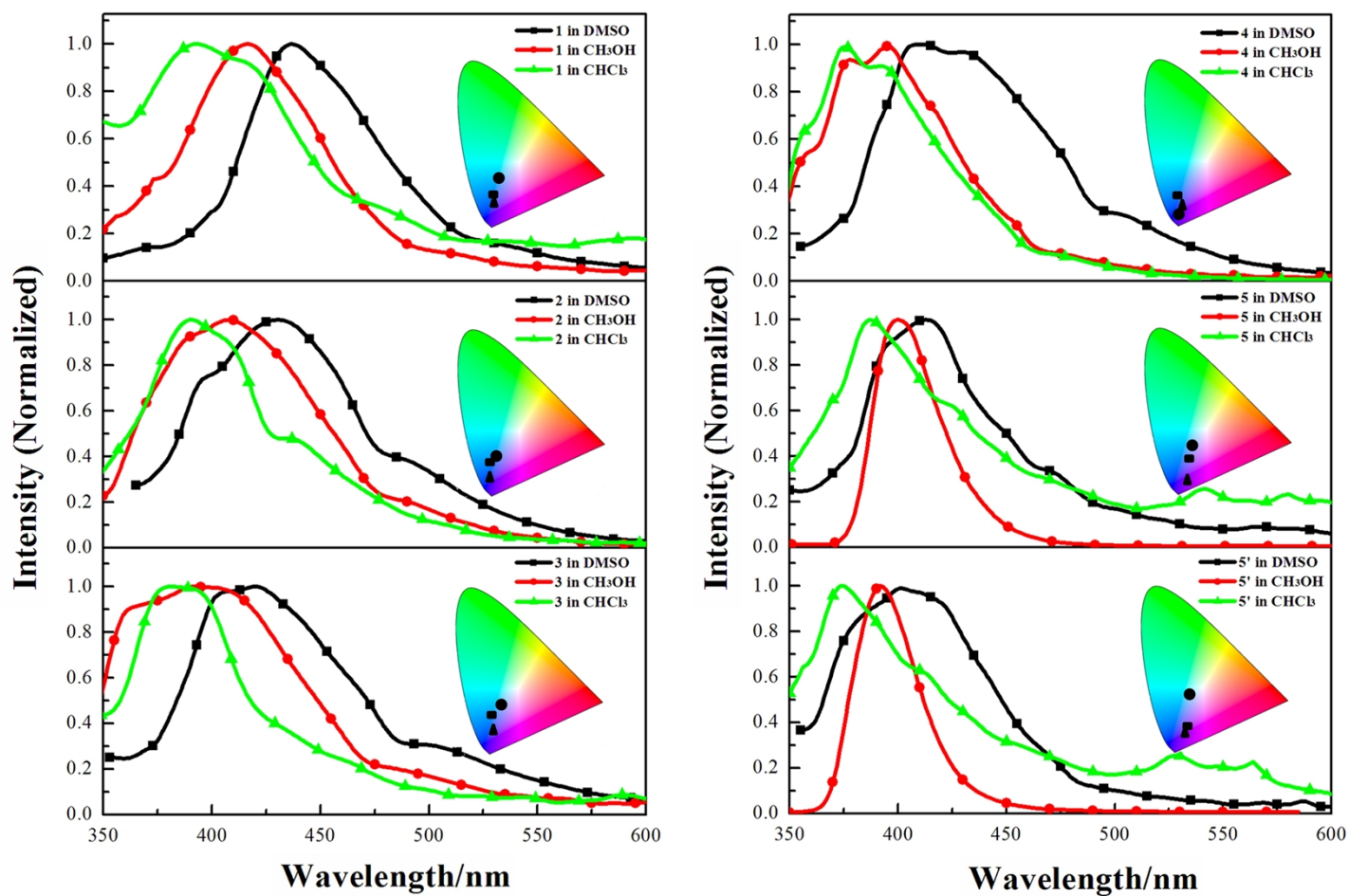
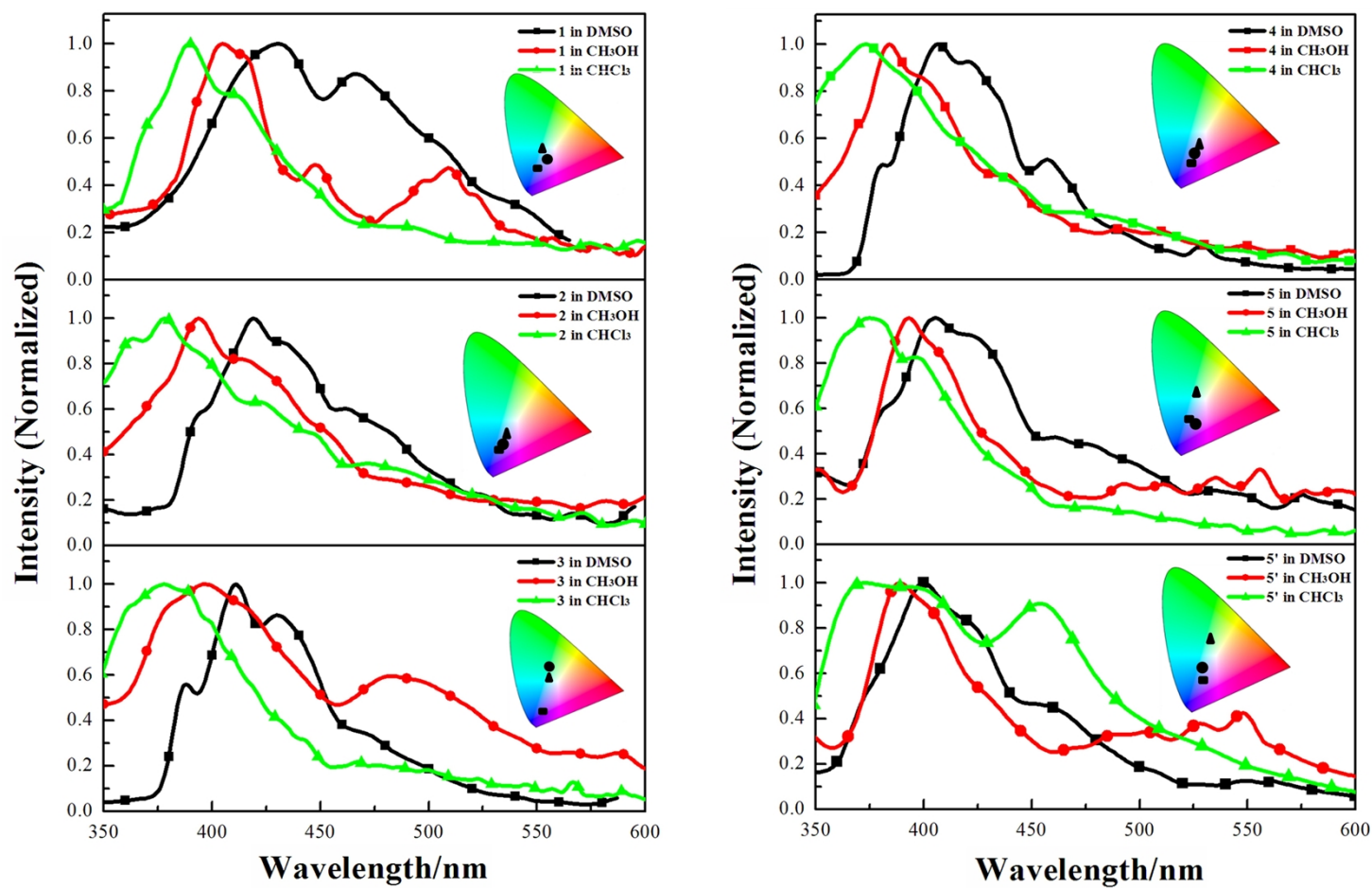


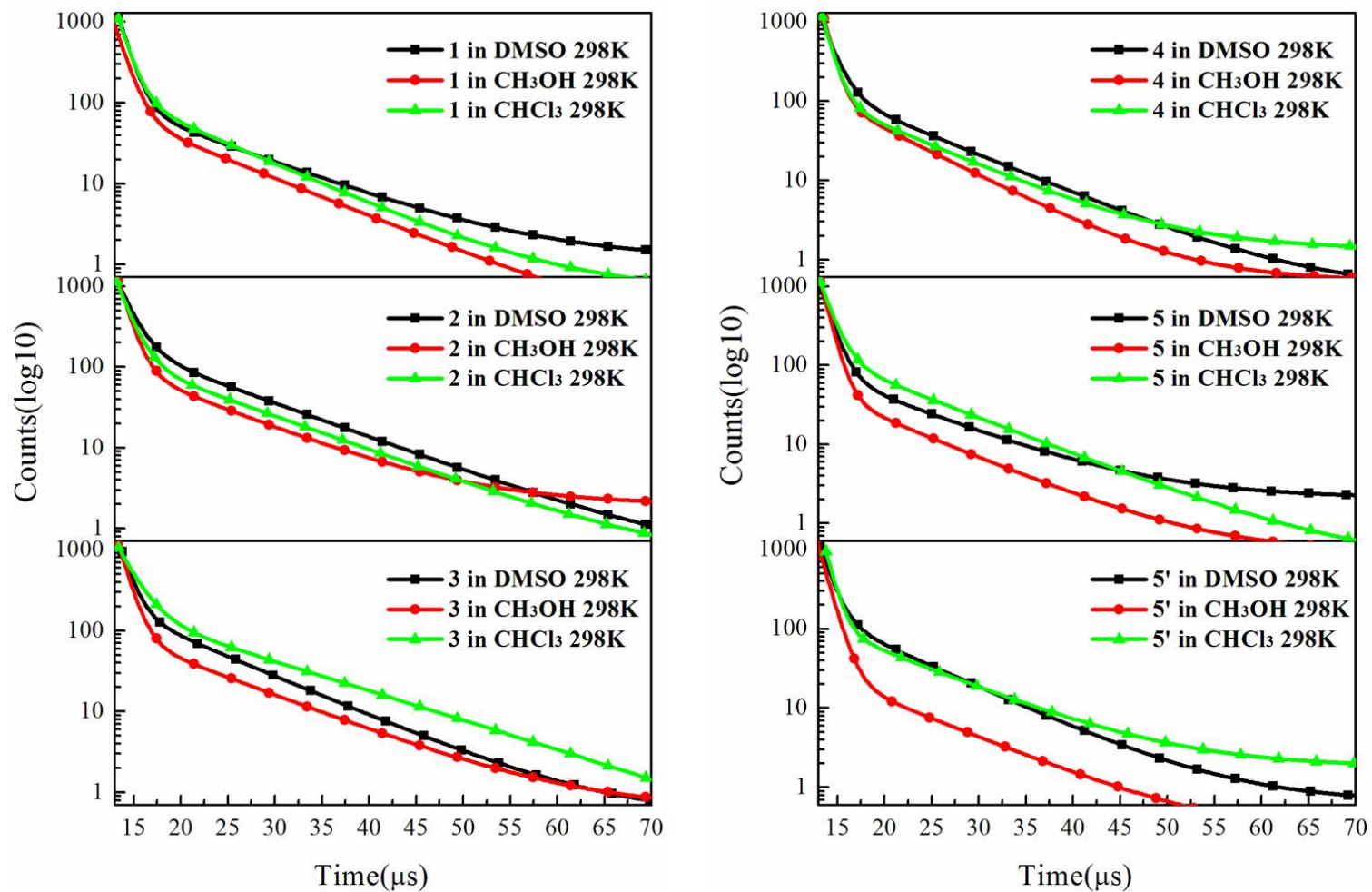
Fig. S14 UV absorption spectra of complexes 1–5'



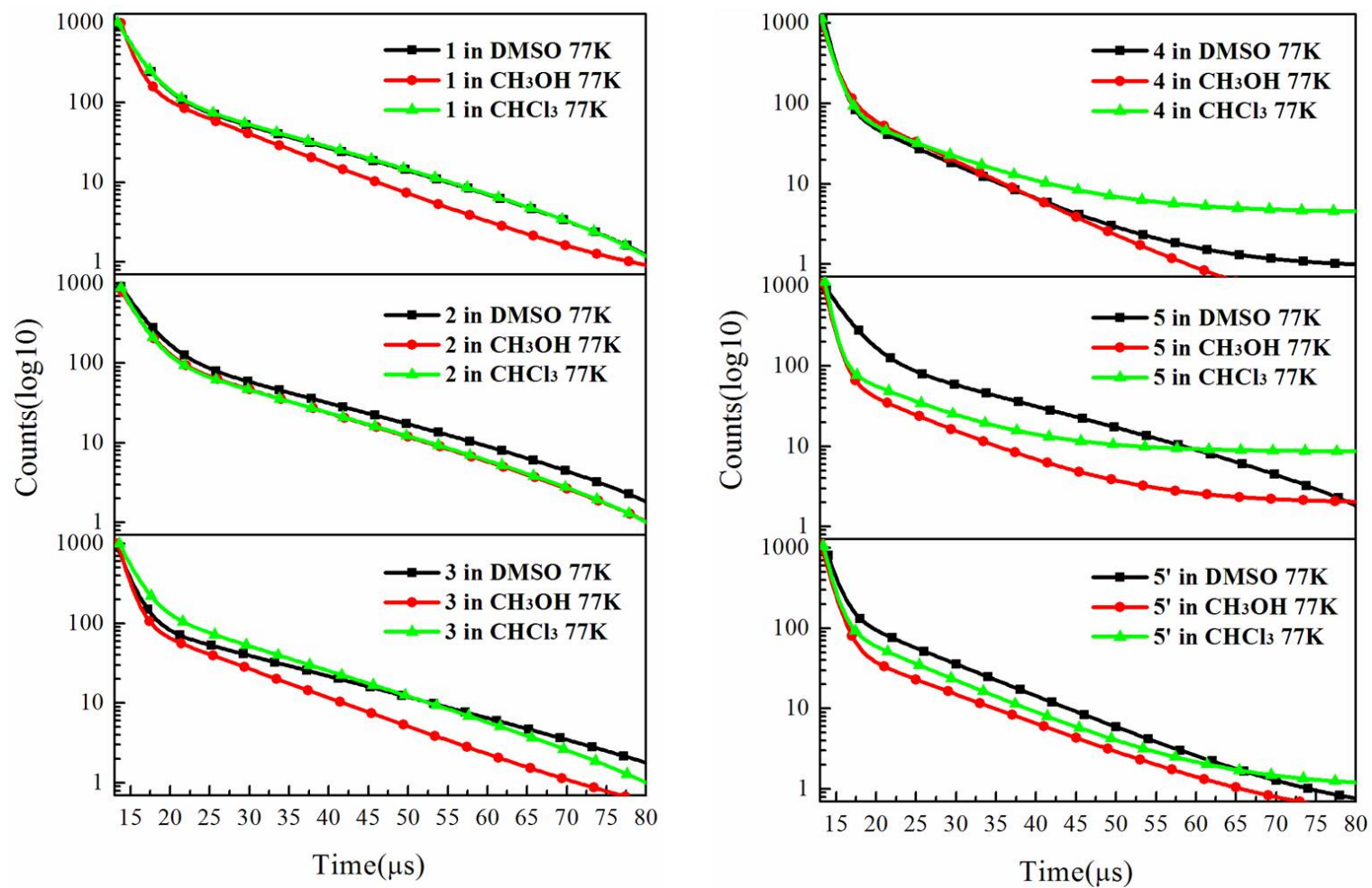
**Fig. S15** Normalized emission spectra of complexes 1–5' in DMSO, CH<sub>3</sub>OH and CHCl<sub>3</sub> solutions (concentration: (M)  $\approx 10^{-5}$  M) at 298 K and the corresponding color coordinate diagram of emission.



**Fig. S16** Normalized emission spectra of complexes **1–5'** in DMSO, CH<sub>3</sub>OH and CHCl<sub>3</sub> solutions (concentration: (M)  $\approx 10^{-5}$  M) at 77 K and the corresponding color coordinate diagram of emission.



**Fig. S17** The decay curves of complexes 1–5' measured in DMSO, CH<sub>3</sub>OH and CHCl<sub>3</sub> solutions at 298 K.



**Fig. S18** The decay curves of complexes 1–5' measured in DMSO, CH<sub>3</sub>OH and CHCl<sub>3</sub> solutions at 77 K.

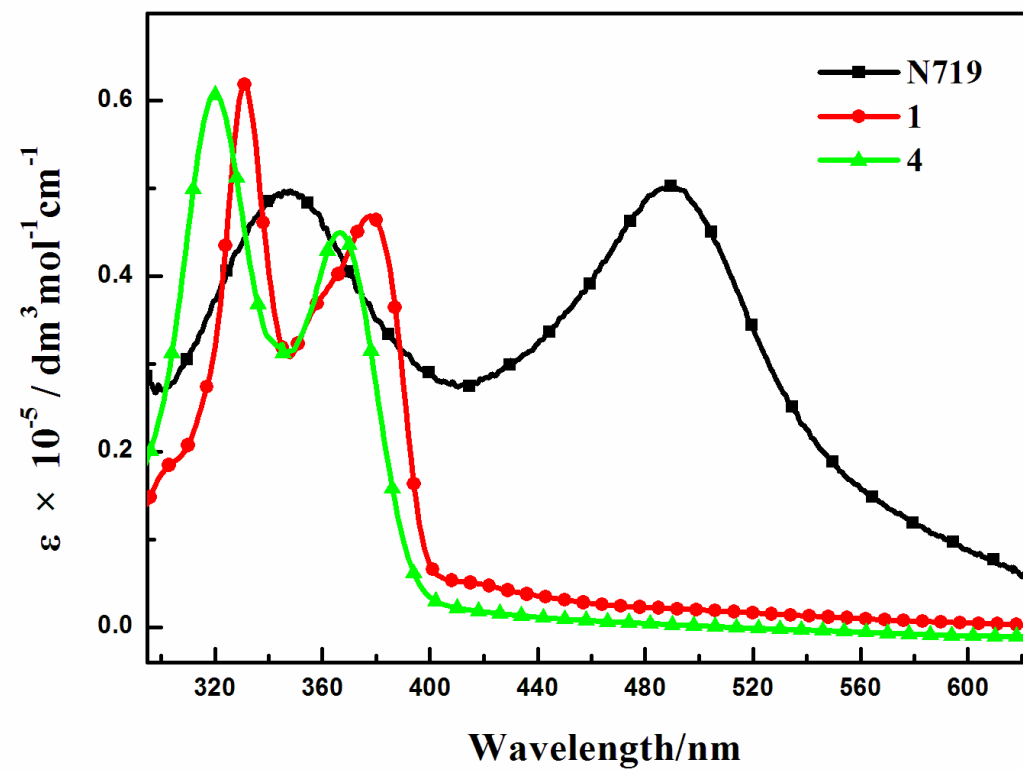
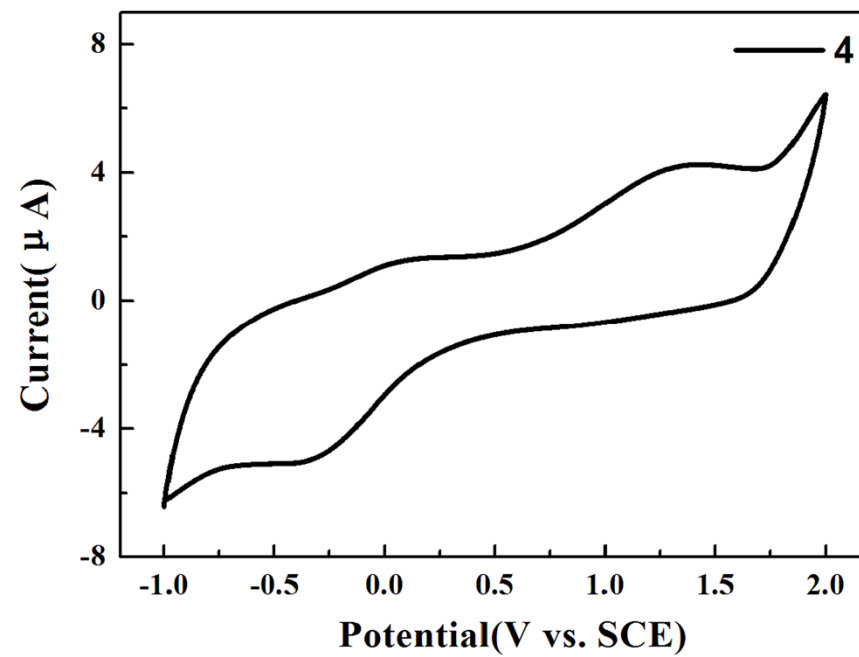
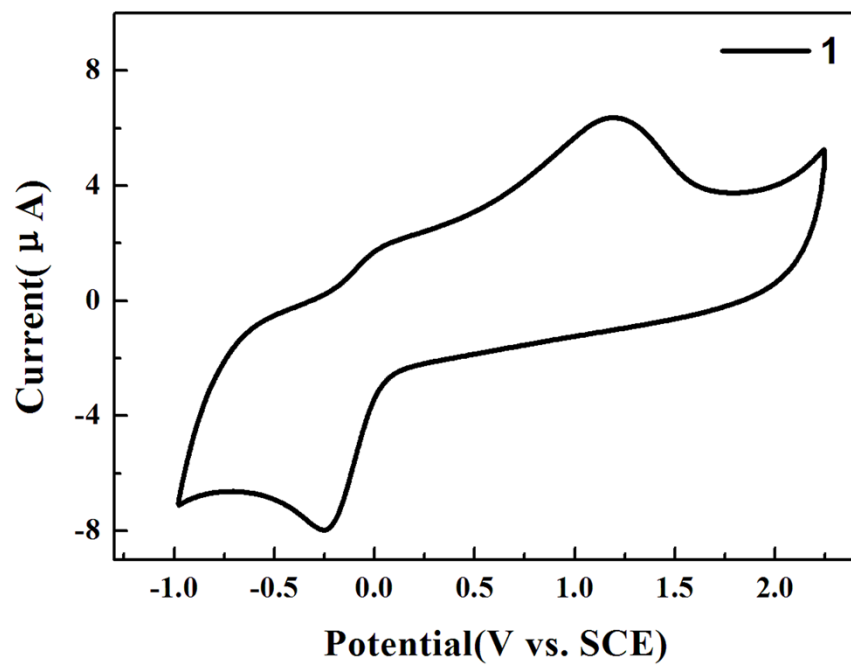


Fig. S19 UV absorption spectra of 1, 4 and N719 in ethanol.



**Fig. S20.** Cyclic voltammograms of complexes **1** and **4** in ethanol solution containing 0.1 M TBAPF<sub>6</sub> solution.

**Table S1** Luminescence data for complexes **1–5'**, TMCB and 1,4-H<sub>2</sub>bda ligands.

Complexes	Absorption (nm) $\epsilon/\text{dm}^3\text{cm}^{-1}\text{mol}^{-1}$	Excitation ( $\lambda$ , nm)	Emission ( $\lambda_{\text{max}}$ , nm)	CIE (x, y)	Lifetime ( $\mu\text{s}$ )			Quantum yields( $\Phi$ ) <sup>b</sup>	Conditions <sup>a</sup>		
					$\tau_1$ ( $\mu\text{s}$ )	$A_1\%$	$\tau_2$ ( $\mu\text{s}$ )				
<b>1</b>	301 (4822), 329 (66432), 352 (41390)	326	437	0.18, 0.12	1.07	59.50%	10.10	40.50%	8.88	0.160	DMSO, 298K
	294 (24132), 324 (75801), 356 (31733)	326	416	0.18, 0.10	1.07	54.73%	8.60	45.27%	7.62	0.087	CH <sub>3</sub> OH, 298K
	317 (58520), 350 (5509)	326	393, 417 <sup>sh</sup>	0.21, 0.18	1.14	66.14%	9.26	33.86%	7.69	0.123	CHCl <sub>3</sub> , 298K
	—	326	461, 479 <sup>sh</sup>	0.23, 0.29	1.43	42.97%	10.37	57.03%	9.53	—	Solid State, 298K
	—	326	430, 466 <sup>sh</sup>	0.15, 0.17	2.25	45.46%	16.33	54.54%	14.88	—	DMSO, 77K
	—	326	405, 448 <sup>sh</sup> , 509 <sup>sh</sup>	0.19, 0.24	1.33	39.59%	11.36	60.41%	10.65	—	CH <sub>3</sub> OH, 77K
	—	326	390, 410 <sup>sh</sup>	0.22, 0.21	2.23	45.90%	16.20	54.10	14.74	—	CHCl <sub>3</sub> , 77K
	—	326	509, 531 <sup>sh</sup>	0.30, 0.58	2.38	39.88%	19.32	60.12%	18.04	—	Solid State, 77K
<b>2</b>	272 (5678), 297 (76647), 321 (5124)	326	395 <sup>sh</sup> , 430, 489 <sup>sh</sup>	0.16, 0.12	1.43	44.65%	10.25	55.35%	9.36	0.086	DMSO, 298K
	269 (16587), 296 (69675), 324 (34547)	326	408	0.16, 0.08	1.06	59.20%	9.30	40.80%	8.13	0.066	CH <sub>3</sub> OH, 298K
	285 (59861), 309 (12182)	326	391, 438 <sup>sh</sup>	0.17, 0.10	1.32	54.30%	10.31	45.70%	9.12	0.087	CHCl <sub>3</sub> , 298K
	—	326	455, 481 <sup>sh</sup>	0.21, 0.26	1.56	43.96%	12.14	56.04%	11.17	—	Solid State, 298K
	—	326	394 <sup>sh</sup> , 419, 433 <sup>sh</sup> , 463 <sup>sh</sup>	0.17, 0.15	2.58	44.99%	17.58	55.01%	15.97	—	DMSO, 77K
	—	326	399, 420 <sup>sh</sup>	0.23, 0.21	2.16	42.48%	15.19	57.52%	13.95	—	CH <sub>3</sub> OH, 77K
	—	326	363 <sup>sh</sup> , 378, 422 <sup>sh</sup> , 472 <sup>sh</sup>	0.21, 0.20	2.08	45.41%	15.72	54.59%	14.37	—	CHCl <sub>3</sub> , 77K
	—	326	501, 520 <sup>sh</sup> , 600 <sup>sh</sup> , 672 <sup>sh</sup>	0.28, 0.55	2.41	33.33%	17.60	66.67%	16.63	—	Solid State, 77K
<b>3</b>	280 (12648), 296 (73199), 320 (39546)	326	420, 500 <sup>sh</sup>	0.18, 0.15	1.03	61.41%	9.72	38.59%	8.47	0.104	DMSO, 298K
	291 (74570), 321 (15690)	326	362 <sup>sh</sup> , 400	0.19, 0.12	1.08	39.74%	8.81	60.26%	8.23	0.076	CH <sub>3</sub> OH, 298K
	283 (63731), 307 (12346)	326	381	0.22, 0.16	1.77	46.72%	12.01	53.28%	10.84	0.093	CHCl <sub>3</sub> , 298K
	—	326	449	0.19, 0.23	1.79	47.29%	13.50	52.71%	12.26	—	Solid State, 298K
	—	326	388 <sup>sh</sup> , 411, 430 <sup>sh</sup>	0.17, 0.09	1.54	45.37%	16.96	54.63%	15.88	—	DMSO, 77K
	—	326	397, 482 <sup>sh</sup>	0.24, 0.26	1.17	48.58%	11.85	51.42%	10.94	—	CH <sub>3</sub> OH, 77K
	—	326	378, 390 <sup>sh</sup>	0.24, 0.21	1.85	41.54%	14.15	58.46%	13.10	—	CHCl <sub>3</sub> , 77K
	—	326	496, 516 <sup>sh</sup> , 542 <sup>sh</sup>	0.22, 0.38	2.27	47.15%	19.85	52.85%	18.22	—	Solid State, 77K
<b>4</b>	295 (13309), 327 (64180), 350 (37686)	326	411, 431 <sup>sh</sup>	0.17, 0.12	1.23	54.28%	8.87	45.72%	7.79	0.089	DMSO, 298K
	291 (16434), 320 (72809), 352 (32256)	326	376 <sup>sh</sup> , 395	0.18, 0.08	0.85	56.80%	7.21	43.20%	6.36	0.055	CH <sub>3</sub> OH, 298K
	314 (51673), 347 (3884)	326	376, 393 <sup>sh</sup>	0.16, 0.06	0.93	57.52%	8.40	42.48%	7.43	0.067	CHCl <sub>3</sub> , 298K
	—	326	436, 458 <sup>sh</sup>	0.17, 0.12	1.19	59.94%	11.03	40.06%	9.66	—	Solid State, 298K
	—	326	381 <sup>sh</sup> , 407, 420 <sup>sh</sup> , 457 <sup>sh</sup>	0.19, 0.12	1.03	60.11%	9.60	39.89%	8.41	—	DMSO, 77K



	—	326	384, 399 <sup>sh</sup> , 438 <sup>sh</sup>	0.25, 0.22	1.20	56.58%	9.11	43.42%	7.95	—	CH <sub>3</sub> OH, 77K
	—	326	373	0.22, 0.20	1.12	59.94%	10.35	40.06%	9.06	—	CHCl <sub>3</sub> , 77K
	—	326	472, 493 <sup>sh</sup> , 528 <sup>sh</sup> , 639 <sup>sh</sup>	0.23, 0.31	1.78	45.04%	13.00	54.96%	11.87	—	Solid State, 77K
5	252 (12066), 275 (60679)	326	413	0.17, 0.12	1.10	65.13%	9.33	34.87%	7.84	0.091	DMSO, 298K
	270 (55529)	326	400	0.18, 0.08	0.89	75.57%	8.62	24.43%	6.75	0.027	CH <sub>3</sub> OH, 298K
	264 (53660)	326	387	0.16, 0.06	1.18	52.98%	9.38	47.02%	8.36	0.070	CHCl <sub>3</sub> , 298K
	—	326	438, 461 <sup>sh</sup>	0.27, 0.21	1.42	40.09%	10.59	59.91%	9.83	—	Solid State, 298K
	—	326	382 <sup>sh</sup> , 405, 422 <sup>sh</sup> , 460 <sup>sh</sup>	0.19, 0.12	0.98	64.67%	10.48	35.33%	9.09	—	DMSO, 77K
	—	326	393, 494 <sup>sh</sup>	0.25, 0.22	0.81	53.80%	9.26	46.20%	8.48	—	CH <sub>3</sub> OH, 77K
	—	326	375, 397 <sup>sh</sup>	0.22, 0.20	0.97	61.33%	9.86	38.67%	8.66	—	CHCl <sub>3</sub> , 77K
	—	326	481, 531 <sup>sh</sup>	0.20, 0.28	2.12	33.03%	19.11	66.97%	18.23	—	Solid State, 77K
5'	250 (9982), 276 (60500)	326	401	0.19, 0.09	1.06	51.26%	8.11	48.74%	7.26	0.088	DMSO, 298K
	267 (67850)	326	392	0.19, 0.06	1.00	86.04%	8.92	13.96%	5.68	0.037	CH <sub>3</sub> OH, 298K
	260 (52956)	326	374	0.26, 0.28	0.87	49.89%	9.05	50.11%	8.34	0.090	CHCl <sub>3</sub> , 298K
	—	326	433, 480 <sup>sh</sup>	0.20, 0.16	1.53	44.50%	13.48	55.50%	12.48	—	Solid State, 298K
	—	326	400, 420 <sup>sh</sup> , 459 <sup>sh</sup>	0.18, 0.14	1.21	35.02%	10.75	64.98%	10.20	—	DMSO, 77K
	—	326	389, 485 <sup>sh</sup>	0.25, 0.33	1.01	50.56%	10.18	49.44%	9.34	—	CH <sub>3</sub> OH, 77K
	—	326	373, 396 <sup>sh</sup> , 454 <sup>sh</sup>	0.18, 0.17	1.14	67.40%	11.49	32.60%	9.73	—	CHCl <sub>3</sub> , 77K
	—	326	478, 515 <sup>sh</sup>	0.20, 0.25	2.26	36.53%	17.21	63.47%	16.16	—	Solid State, 77K
TMCB	—	—	—	—	—	—	—	—	—	0.027	DMSO, 298K
	—	—	—	—	—	—	—	—	—	0.007	CH <sub>3</sub> OH, 298K
	—	—	—	—	—	—	—	—	—	0.011	CHCl <sub>3</sub> , 298K
	—	326	408	0.20, 0.19	0.97	63.33%	9.33	36.67%	8.06	—	Solid State, 298K
1,4-H <sub>2</sub> bda	—	—	—	—	—	—	—	—	—	0.012	DMSO, 298K
	—	—	—	—	—	—	—	—	—	0.005	CH <sub>3</sub> OH, 298K
	—	—	—	—	—	—	—	—	—	0.004	CHCl <sub>3</sub> , 298K
	—	326	405	0.19, 0.12	0.99	48.10%	7.67	51.90%	6.96	—	Solid State, 298K

a Concentration in DMSO, CH<sub>3</sub>OH and CHCl<sub>3</sub> solutions: (M) =  $1 \times 10^{-5}$  M.

b Determined using quinine sulfate in 0.1 M sulphuric acid ((M) =  $1 \times 10^{-5}$  M,  $\Phi_s = 0.546$ )

## Experimental Section

### Materials and Methods

All reactants are reagent grade and used as purchased commercially without further purification. Infrared spectra were obtained from KBr pellets using a Nicolet Avatar-360 Infrared spectrometer in the 4000–400  $\text{cm}^{-1}$  region.  $^1\text{H}$  NMR (400 MHz) spectra were recorded on a Bruker ACF 400 MHz at room temperature. ESI-MS spectra were recorded with Finnigan MATLCQ<sup>TM</sup> mass spectrometer (USA) with a dual electrospray-ionization source. Powder X-ray diffraction (PXRD) patterns were recorded in the  $2\theta$  range of 5–50° using Cu  $K\alpha$  radiation by Shimadzu XRD-6000 X-ray Diffractometer. Elemental analyses were performed on a Perkin-Elmer 240c element analyzer. The thermal analysis was performed on a ZRY-2P thermogravimetric analyzer from 30 °C to 700 °C with heating rate of 10 °C  $\text{min}^{-1}$  under a flow of air. UV spectra were obtained on a Perkin-Elmer Lambda 20 spectrometer. Luminescence analysis and luminescence decay curves were recorded on Edinburgh FLS920 luminescence spectrometer at 298 K and 77 K. Lifetime studies were performed using photon-counting system with a microsecond pulse lamp as the excitation source. The emission decays were analyzed by the sum of exponential functions. The decay curve is well fitted into a double exponential function:  $I = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ , where  $I$  and  $I_0$  are the luminescent intensities at time  $t = t$  and  $t = 0$ , respectively, whereas  $\tau_1$  and  $\tau_2$  are defined as the luminescent lifetimes. The average lifetime was calculated according to the following equation (1):

$$\frac{\tau_1^2 A_1 \% + \tau_2^2 A_2 \%}{\tau_1 A_1 \% + \tau_2 A_2 \%}$$
 (1). The luminescence quantum yields of complexes were measured

in DMSO,  $\text{CH}_3\text{OH}$ ,  $\text{CHCl}_3$  at room temperature and cited relative to a reference solution of quinine sulfate ( $\Phi = 0.546$  in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ ) as a standard, and they

were calculated according to the well-known equation (2): 
$$\frac{\varphi_{\text{overall}}}{\varphi_{\text{ref}}} = \left( \frac{n}{n_{\text{ref}}} \right)^2 \frac{A_{\text{ref}}}{A} \frac{I}{I_{\text{ref}}}$$

(2) In equation (2),  $n$ ,  $A$ , and  $I$  denote the refractive index of solvent, the area of the emission spectrum, and the absorbance at the excitation wavelength, respectively, and  $\varphi_{\text{ref}}$  represents the quantum yield of the standard quinine sulfate solution. The subscript *ref* denotes the reference, and the absence of a subscript implies an unknown sample. For the determination of the quantum yield, the excitation wavelength was chosen so that  $A < 0.05$ . The cyclic voltammetry (CV) were measured with a

electrochemical workstation (CHI660D, Chenhua, Shanghai) using a three-electrode cell with a Pt working electrode, a Pt wire auxiliary electrode, and a saturated calomel reference electrode in saturated KCl solution. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, Fluka, electrochemical grade) in ethanol as the solvent. Photocurrent-photovoltage (*I-V*) curves were recorded by Keithley model 2400 digital source meter using a mask with an aperture area of 0.16 cm<sup>2</sup>. The irradiance of AM1.5 global sunlight from a filtered 500 W xenon lamp light source was set at 100 mW cm<sup>-2</sup> and was calibrated by a standard silicon solar cell. Based on *I-V* curve, the fill factor (*FF*) is defined as:  $FF = (J_{\max} \times V_{\max}) / (J_{\text{sc}} \times V_{\text{oc}})$ , where  $J_{\max}$  and  $V_{\max}$  are the photocurrent density and photovoltage for maximum power output;  $J_{\text{sc}}$  and  $V_{\text{oc}}$  are the short-circuit photocurrent density and open-circuit photovoltage, respectively. The overall energy conversion efficiency  $\eta$  is defined as:  $\eta = (FF \times J_{\text{sc}} \times V_{\text{oc}}) / P_{\text{in}}$  where  $P_{\text{in}}$  is the power of the incident light. IPCE spectra were recorded with Monochromatic incident photon-to-electron conversion efficiency (IPCE) were measured on an EQE/IPCE spectral response system (Newport). EIS were recorded by CHI660D Electrochemical Analyzer (Chenhua, China), and the measurements were taken over a frequency range of 0.1-100 kHz under standard global AM1.5 solar irradiation or in the dark by applying a forward bias equivalent to  $V_{\text{oc}}$ . The fit and simulation processes are achieved using ZSimpWin software.

### Assembly of DSSCs

The FTO conducting glass (Fluorine-doped SnO<sub>2</sub>, sheet resistance 15  $\Omega$  per square, transmission 90% in the visible) was purchased from NSG, Japan, and cleaned by a standard procedure. N719 [cis-bis(isothiocyanato)bis (2,2-bipyridyl-4,4-dicarboxylato)-ruthenium(II)bis-tetrabutylammonium] was purchased from Solaronix Company, Switzerland. Dye-sensitized solar cells were fabricated using the following procedure. The TiO<sub>2</sub> paste was cast onto the FTO substrate by the screen-printing method, followed by drying at 100 °C for 5 min and this process was repeated for six times, then followed by sintering at 500 °C for 15 min in air to obtain a transparent TiO<sub>2</sub> photoelectrode with the thickness of ca. 10  $\mu\text{m}$ . The co-adsorbent electrodes were prepared by immersing the obtained mesoporous TiO<sub>2</sub> photoelectrode into 0.3 mM **1** or **4** solution in absolute ethanol for 2 h and washed with ethanol and dried with blower, then further immersing the electrodes in 0.3 mM N719 solution in absolute ethanol for 12 h, and then washed with ethanol and dried with blower again. The single N719 sensitized electrodes were prepared by only immersing TiO<sub>2</sub>

photoelectrode into 0.3 mM N719 solution in absolute ethanol for 14 h. The electrolyte used in this work was 0.5 M LiI + 0.05 M I<sub>2</sub> + 0.1 M tert-butyl pyridine in a 1:1 (volume ratio) of acetonitrile-propylene carbonate. The platinum counter electrode was prepared by depositing H<sub>2</sub>PtCl<sub>6</sub> paste onto the FTO glass substrates and then sintered at 450 °C for 30 min. The cells were assembled by sandwiching the electrolyte between the dye sensitized photoanode and the counter electrode and assembly was held together using mini-binder clips.

#### **Synthesis of 4-(1,2,4-triazolylmethyl) cyanobenzene (TMCB).**

A solution containing 1,2,4-triazole, (3453.5 mg, 50.0 mmol), 4-cyanobenzyl chloride (7579.5 mg, 50.0 mmol) and NaOH (2000.0 mg, 50.0 mol) in DMF (40 mL) was heated at 160 °C for 18 h. After wipe out the organic solvent, the mixture was precipitated with 100 mL of distilled water. And then filtrated, the filtering was recrystallization by dichloromethane to give a amount of yellow products. Yiled: 73%. TMCB ligand was characterized by elemental analyses, IR and <sup>1</sup>H NMR (Fig. S21 and Fig. S22). Elemental analysis (%): Calc. for C<sub>10</sub>H<sub>8</sub>N<sub>4</sub> (Mr: 184.20): C, 65.21; N, 30.42; H, 4.38%. Found: C, 65.17; N, 30.47; H, 4.40%. IR (KBr, cm<sup>-1</sup>): 3430 (br, s), 3105(m), 2239(s), 1616(m), 1504 (s), 1435 (m), 1367 (m), 1335 (m), 1280 (s), 1211 (w), 1142 (s), 1068 (w), 1011 (s), 962 (s), 881 (m), 812 (s), 762 (s), 687 (s), 638 (m), 550 (s). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 8.71 (s, 1 H, Tri-*H*<sub>5</sub>), 8.03 (s, 1 H, Tri-*H*<sub>3</sub>), 7.86 (d, 2 H, o-Ph), 7.44 (d, 2 H, m-Ph), 5.55 (s, 2 H, -CH<sub>2</sub>-) ppm.

#### **[Cd(TMCBA)<sub>2</sub>]<sub>n</sub> (1)**

A mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (61.6 mg, 0.2 mmol), TMCB (18.4 mg, 0.1 mmol) and 1,4-H<sub>2</sub>bda (16.6 mg, 0.1 mmol) with a molar ration of 1:1:1 was dissolved in distilled water (5.0 mL). NaOH was added to adjust the final pH to 7.82~7.85. After stirring for 30 minutes in air, it was transferred into a 15 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 5 days. After slow cooling to room temperature, colorless block crystals of **1** were obtained (yield, 42%, based on Cd). Elemental analysis (%): Calc. for C<sub>20</sub>H<sub>16</sub>N<sub>6</sub>O<sub>4</sub>Cd (Mr: 516.80): C, 46.48; N, 16.26; H, 3.12%. Found: C, 46.51; N, 16.22; H, 3.11%. IR (KBr pellet, cm<sup>-1</sup>) for **1** (Fig. S21): 3475 (br, s), 3105(w), 1604 (s), 1548 (s), 1386 (s), 1247 (m), 1130 (m), 1018 (m), 999 (m), 856 (w), 799 (m), 750 (s), 681 (m), 538 (w). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, Fig. S23): δ = 8.70 (s, 1 H, Tri-*H*<sub>5</sub>), 8.03 (s, 1 H, Tri-*H*<sub>3</sub>), 7.85 (d, 2 H, o-Ph), 7.43 (d, 2 H, m-Ph), 5.55 (s, 2 H, -CH<sub>2</sub>-) ppm. ESI-MS for **1** (Fig. S24): *m/z* = 471.7847 [M -

COOH]<sup>-</sup>, 314.6081 [M – TMCBA]<sup>-</sup>.

**[Cd(TMCB)(1,4-bda)(H<sub>2</sub>O)]<sub>n</sub> (2)**

The procedure of complex **2** was similar to that of **1** without using sodium hydroxide adjusted pH value. Then colorless quadrate crystals of **2** were obtained (yield, 51%, based on Cd). Elemental analysis (%): Calc. for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>5</sub>Cd (Mr: 478.74): C, 45.16; N, 11.70; H, 2.95%. Found: C, 45.11; N, 11.71; H, 2.94%. IR (KBr pellet, cm<sup>-1</sup>) for **2** (Fig. S21): 3542 (br, s), 3124(w), 2245 (m), 1635 (m), 1517 (m), 1380 (s), 1280 (m), 1217 (w), 1136 (m), 1018 (m), 981 (m), 893 (w), 831 (m), 775 (w), 675 (m), 550 (w). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, Fig. S23): δ = 8.71 (s, 1 H, Tri-*H*<sub>5</sub>), 8.07 (s, 1 H, Tri-*H*<sub>3</sub>), 7.95 (s, 4 H, 1,4-bda<sup>2-</sup>-*H*<sub>2,3,5,6</sub>), 7.85 (d, 2 H, *o*-Ph), 7.38 (d, 2 H, *m*-Ph), 5.33 (s, 2 H, -CH<sub>2</sub>-) ppm. ESI-MS for **2** (Fig. S24): *m/z* = 478.0075 [M – H]<sup>-</sup>, 410.7135 [M – Triazole]<sup>-</sup>, 370.7326 [M – 2COOH – 2H<sub>2</sub>O]<sup>-</sup>.

**{[Cd<sub>2</sub>(TMCB)<sub>4</sub>(1,4-bda)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>·3H<sub>2</sub>O }<sub>n</sub> (3)**

The procedure of complex **3** was similar to that of **2** except using molar ratio of 1:1:1 instead of 2:1:1. Then colorless quadrate crystals of **3** were obtained (yield, 45%, based on Cd). Elemental analysis (%): Calc. for C<sub>56</sub>H<sub>50</sub>N<sub>16</sub>O<sub>13</sub>Cd<sub>2</sub> (Mr: 1379.92): C, 48.74; N, 16.24; H, 3.65%. Found: C, 48.70; N, 16.22; H, 3.63%. IR (KBr pellet, cm<sup>-1</sup>) for **3** (Fig. S21): 3456 (br, s), 3062(w), 1693 (w), 1589 (s), 1417 (s), 1298 (w), 1147 (w), 1104 (w), 864 (s), 745 (s), 533 (s). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, Fig. S23): δ = 8.70 (s, 1 H, Tri-*H*<sub>5</sub>), 8.03 (s, 1 H, Tri-*H*<sub>3</sub>), 7.95 (s, 4 H, 1,4-bda<sup>2-</sup>-*H*<sub>2,3,5,6</sub>), 7.83 (d, 2 H, *o*-Ph), 7.41 (d, 2 H, *m*-Ph), δ = 5.33 (s, 2 H, -CH<sub>2</sub>-) ppm. ESI-MS for **3** (Fig. S24): *m/z* = 1163.8258 [M – 2H<sub>2</sub>O – 4COOH]<sup>-</sup>, 321.5613 [0.5M – 2TMCB]<sup>-</sup>.

**{[Cd(TMCB)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·(NO<sub>3</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> (4)**

The procedure of complex **4** was similar to that of **3** without using auxiliary ligand 1,4-*H*<sub>2</sub>bda. Then colorless block crystals of **4** were obtained (yield, 57%, based on Cd). Elemental analysis (%): Calc. for C<sub>40</sub>H<sub>40</sub>N<sub>18</sub>O<sub>10</sub>Cd (Mr: 1045.30): C, 45.96; N, 24.12; H, 3.86%. Found: C, 45.92; N, 24.14; H, 3.84%. IR (KBr pellet, cm<sup>-1</sup>) for **4** (Fig. S21): 3418 (br, s), 3132(w), 2234 (m), 1612 (w), 1524 (m), 1387 (s), 1324 (w), 1281 (m), 1212 (w), 1131 (m), 1013 (m), 982 (m), 826 (m), 770 (w), 676 (m), 546 (m). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, Fig. S23): δ = 8.68 (s, 1 H, Tri-*H*<sub>5</sub>), 8.00 (s, 1 H, Tri-*H*<sub>3</sub>), 7.94 (d, 2 H, *o*-Ph), 7.30 (d, 2 H, *m*-Ph), 5.48 (s, 2 H, -CH<sub>2</sub>-) ppm. ESI-MS for **4** (Fig. S24): *m/z* = 308.5023 [M – 2H<sub>2</sub>O – 2NO<sub>3</sub>]<sup>-</sup>, 885.2684 [M – 4TMCB]<sup>-</sup>.

### **[Cd<sub>1.5</sub>(1,4-bda)<sub>1.5</sub>(DMF)<sub>2</sub>]<sub>2n</sub> (**5**)**

The procedure of complex **5** was similar to that of **2** except using DMF instead of H<sub>2</sub>O. Then colorless block crystals of **5** were obtained (yield, 68%, based on Cd). Elemental analysis (%): Calc. for C<sub>36</sub>H<sub>40</sub>N<sub>4</sub>O<sub>16</sub>Cd<sub>3</sub> (Mr: 1121.95): C, 38.54; N, 4.99; H, 3.59%. Found: C, 38.56; N, 5.01; H, 3.61%. IR (KBr pellet, cm<sup>-1</sup>) for **5** (Fig. S21): 3424 (br, s), 1574 (s), 1499 (m), 1393 (s), 1294 (w), 1150 (w), 1100 (w), 1007 (m), 845 (s), 739 (s), 521 (m). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, Fig. S23): 9.75 (s, 1 H, -CHO), 8.05 (s, 4 H, 1,4-bda<sup>2-</sup>-H<sub>2,3,5,6</sub>), 2.51 (s, 6 H, -N(CH<sub>3</sub>)<sub>2</sub>) ppm. ESI-MS for **5** (Fig. S24): *m/z* = 559.5127 [M - 4DMF - 6COOH]<sup>-</sup>, 425.9328 [0.5M - 3COOH]<sup>-</sup>.

### **[Cd<sub>1.5</sub>(1,4-bda)<sub>1.5</sub>(DMF)<sub>2</sub>]<sub>2n</sub> (**5'**)**

The procedure of complex **5'** was similar to that of **5** except that an additive agent TMCB. Then colorless block crystals of **5'** were obtained (yield, 65%, based on Cd). Elemental analysis (%): Calc. for C<sub>36</sub>H<sub>40</sub>N<sub>4</sub>O<sub>16</sub>Cd<sub>3</sub> (Mr: 1121.95): C, 38.54; N, 4.99; H, 3.59%. Found: C, 38.57; N, 5.00; H, 3.62%. IR (KBr pellet, cm<sup>-1</sup>) for **5'** (Fig. S21): 3430 (br, s), 1567 (s), 1493 (m), 1387 (s), 1300 (w), 1157 (w), 1100 (w), 1013 (m), 845 (s), 745 (s), 527 (m). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, Fig. S23): 9.78 (s, 1 H, -CHO), 8.05 (s, 4 H, 1,4-bda<sup>2-</sup>-H<sub>2,3,5,6</sub>), 2.51 (s, 6 H, -N(CH<sub>3</sub>)<sub>2</sub>) ppm. ESI-MS for **5'** (Fig. S24): *m/z* = 279.7563 [0.5M - 2DMF - 3 COOH]<sup>-</sup>.

### **X-Ray crystal structure determination**

The X-ray diffraction data taken at room temperature for complexes **1-5'** were collected on a Rigaku R-Axis RAPID IP diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures of **1-5'** were solved by direct methods and refined on F<sup>2</sup> by the full-matrix least squares using the SHELXTL-97 crystallographic software.<sup>1,2</sup> Anisotropic thermal parameters are refined to all of the non-hydrogen atoms. The hydrogen atoms were held in calculated positions on carbon atoms and nitrogen atoms and that were directly included in the molecular formula on water molecules. The CCDC 1028900, 1028901, 1028902, 1028903, 1028904 and 1028905 contain the crystallographic data **1-5'** of this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/](http://www.ccdc.cam.ac.uk/) deposit. Crystal structure data and details of the data collection and the structure refinement are listed as Table S2, selected hydrogen bonding data, bond lengths and bond angles of complexes **1-5'** are listed as Table S3-S4.

Reference:

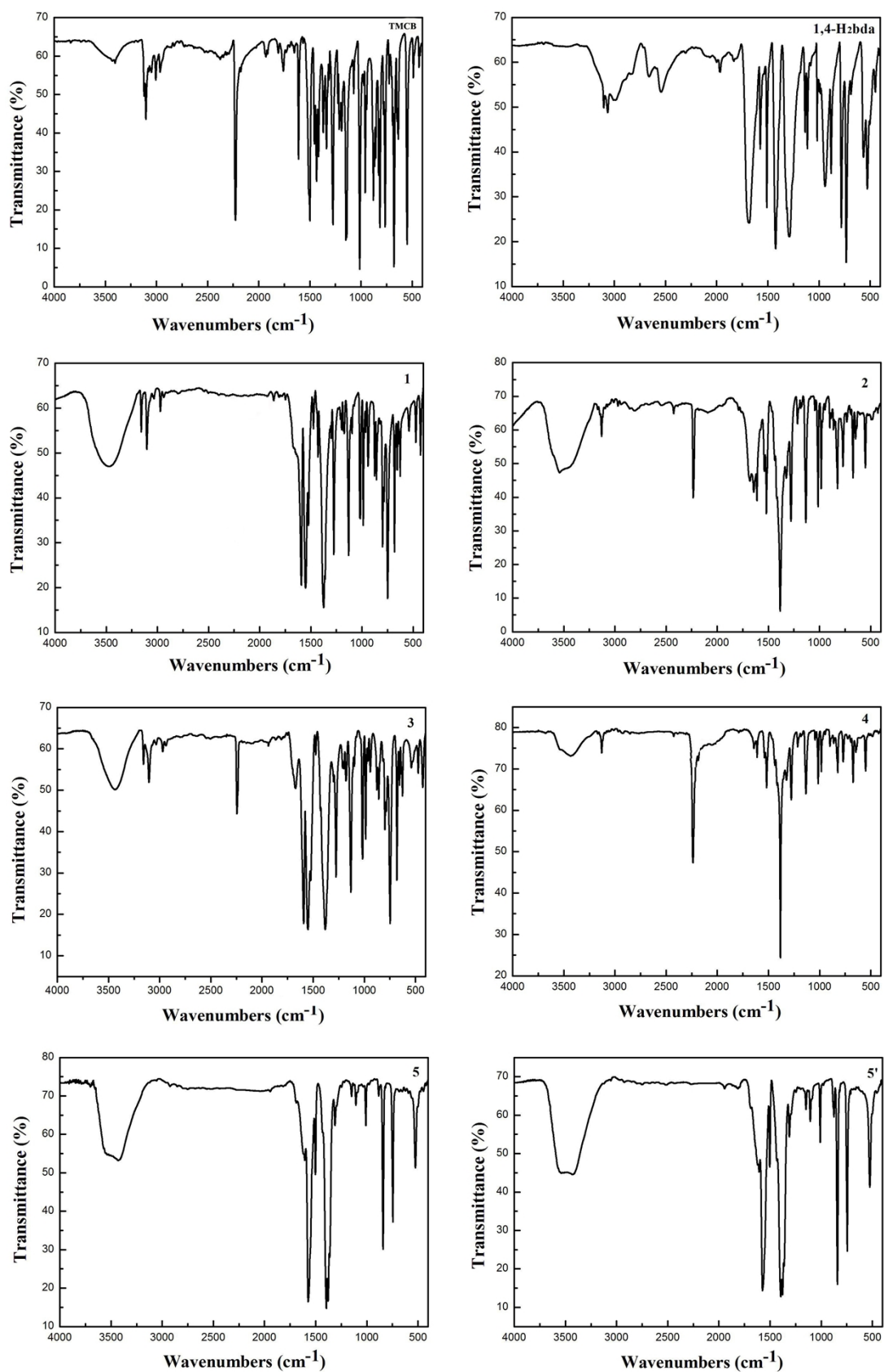
- 1 G. M. Sheldrick, S<sub>HELXL</sub> 97 Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.
- 2 G. M. Sheldrick, S<sub>HELXL</sub> 97 Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1997.

**Table S2** Crystal data and structure refinement parameters of complexes **1–5'**

Identification code	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>5'</b>
Empirical formula	C <sub>20</sub> H <sub>16</sub> N <sub>6</sub> O <sub>4</sub> Cd	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> O <sub>5</sub> Cd	C <sub>56</sub> H <sub>50</sub> N <sub>16</sub> O <sub>13</sub> Cd <sub>2</sub>	C <sub>40</sub> H <sub>40</sub> N <sub>18</sub> O <sub>10</sub> Cd	C <sub>36</sub> H <sub>40</sub> N <sub>4</sub> O <sub>16</sub> Cd <sub>3</sub>	C <sub>36</sub> H <sub>40</sub> N <sub>4</sub> O <sub>16</sub> Cd <sub>3</sub>
Formula mass	516.80	478.74	1379.92	1045.30	1121.95	1121.95
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>Pbca</i>	<b>PError!</b>	<i>P1</i>	<b>PError!</b>	<i>C 2/c</i>
<i>a</i> (Å)	5.224(10)	13.696(3)	11.066(2)	9.101(18)	10.161(2)	28.167(6)
<i>b</i> (Å)	8.802(18)	12.414(3)	17.157(3)	9.116(18)	12.773(3)	9.307(19)
<i>c</i> (Å)	20.434(4)	20.618(4)	17.935(4)	16.216(3)	16.673(3)	17.840(4)
$\alpha$ (°)	90.00	90.00	63.73(3)	97.35(3)	75.01(3)	90.00
$\beta$ (°)	96.91(3)	90.00	73.87(3)	98.03(3)	89.27(3)	114.74(3)
$\gamma$ (°)	90.00	90.00	88.05(3)	119.78(3)	87.55(3)	90.00
<i>V</i> (Å <sup>3</sup> )	932.8(3)	3505.7(12)	2917.7(10)	1125.4(4)	2088.4(7)	4247.7(16)
<i>Z</i>	2	8	2	1	2	4
<i>D<sub>c</sub></i> /(g · cm <sup>-3</sup> )	1.840	1.814	1.571	1.542	1.784	1.754
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	1.215	1.286	0.807	0.564	1.588	1.561
<i>F</i> (000)	516	1904	1396	534	1112	2224
$2\theta$ range (°)	3.06 – 27.48	3.28 – 27.48	2.99 – 27.47	3.21 – 27.48	3.03 – 25.00	3.09 – 27.48
Limiting indices	$-6 \leq h \leq 6$ $-11 \leq k \leq 11$ $-26 \leq l \leq 26$	$-17 \leq h \leq 17$ $-16 \leq k \leq 16$ $-26 \leq l \leq 25$	$-14 \leq h \leq 14$ $-22 \leq k \leq 22$ $-20 \leq l \leq 23$	$-11 \leq h \leq 11$ $-11 \leq k \leq 11$ $-21 \leq l \leq 21$	$-12 \leq h \leq 12$ $-15 \leq k \leq 15$ $-19 \leq l \leq 19$	$-36 \leq h \leq 36$ $-11 \leq k \leq 12$ $-23 \leq l \leq 22$
Data/Restraints/Parameters	2140 / 0 / 142	3989 / 0 / 253	13177 / 2166 / 784	8443 / 3 / 622	7201 / 0 / 535	4859 / 0 / 271
GOF on <i>F</i> <sup>2</sup>	1.234	1.083	1.081	1.113	1.132	0.800
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]						
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0540	0.0292	0.0630	0.0345	0.0303	0.0232
<i>wR</i> <sub>2</sub> <sup>b</sup>	0.1545	0.0670	0.1574	0.0914	0.0974	0.0603
<i>R</i> indices (alldata)						
<i>R</i> <sub>1</sub>	0.0582	0.0393	0.1066	0.0365	0.0369	0.0258
<i>wR</i> <sub>2</sub>	0.1558	0.0701	0.1847	0.0936	0.1110	0.0622
CCDC	1028900	1028901	1028902	1028903	1028904	1028905

$$^a R_1 = \frac{\sum |F_o|}{\sum |F_c|}; \quad ^b wR_2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]]^{1/2}}{\sum [w(F_o^2)]^{1/2}}$$





**Fig. S21** Infrared spectra of complexes 1–5', TMCB and 1,4-H<sub>2</sub>bda recorded from a KBr pellet.

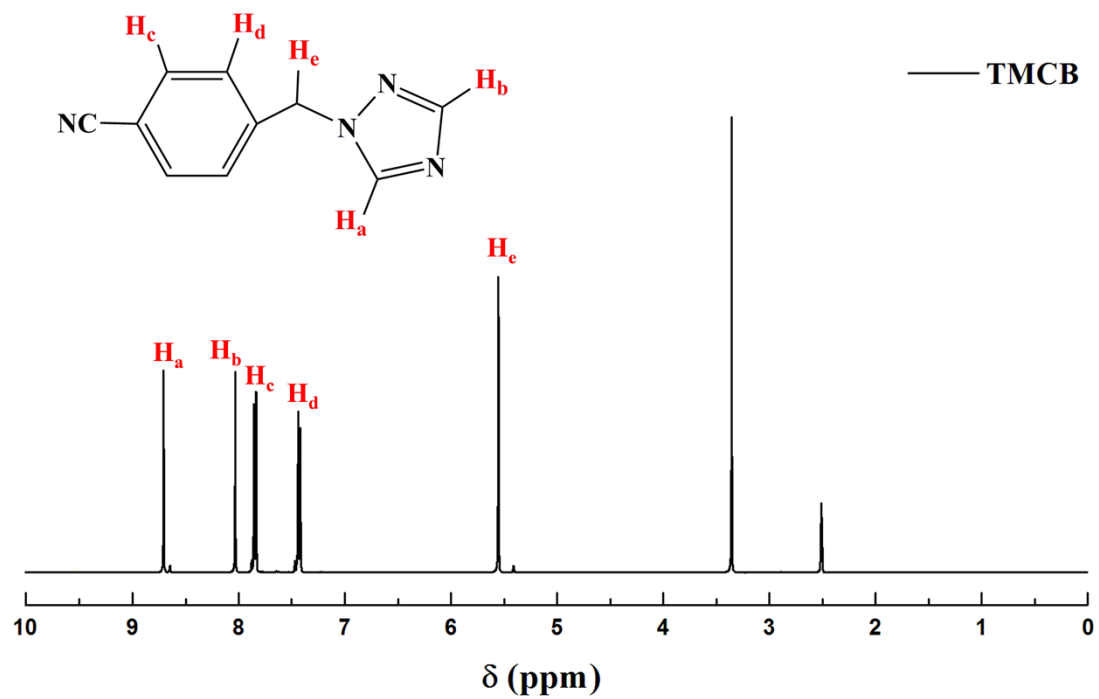
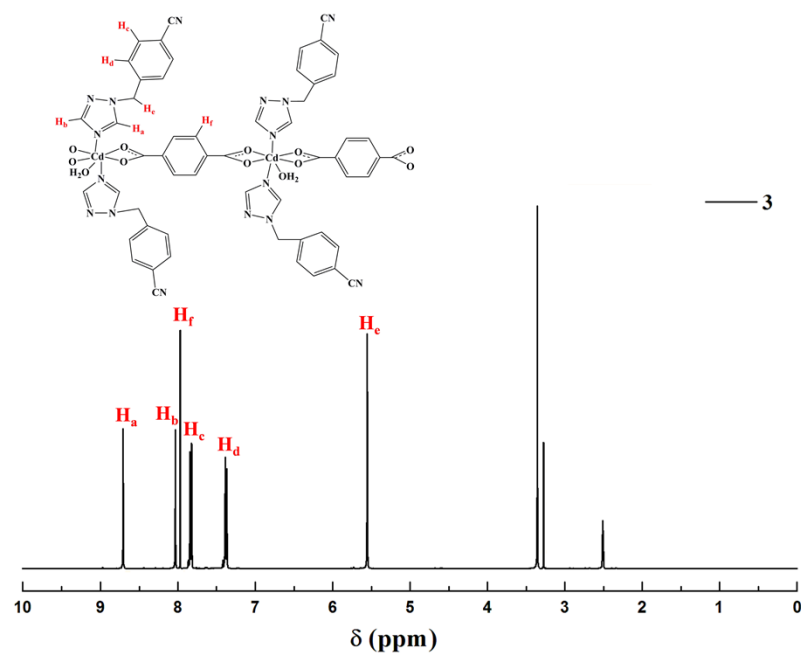
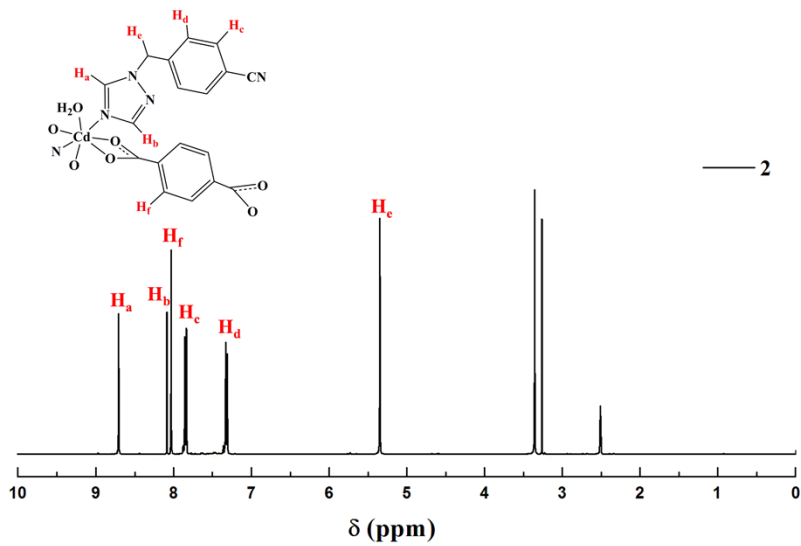
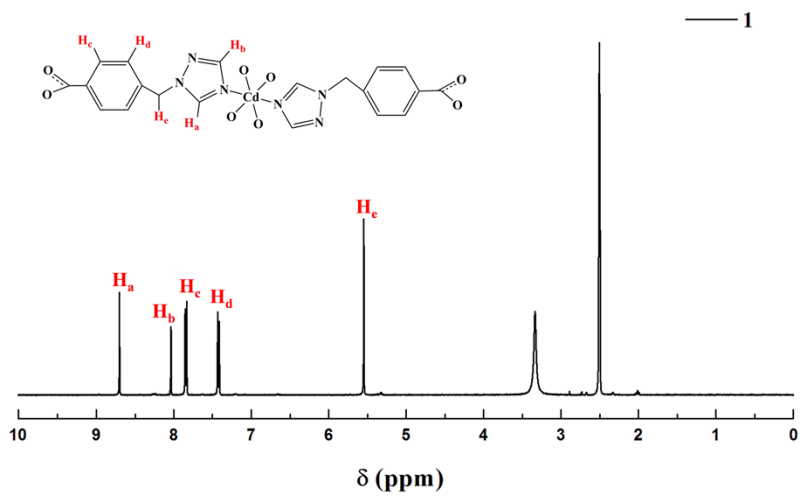


Fig. S22  $^1\text{H}$  NMR spectrum of TMCB ligand in  $\text{DMSO-}d_6$ .



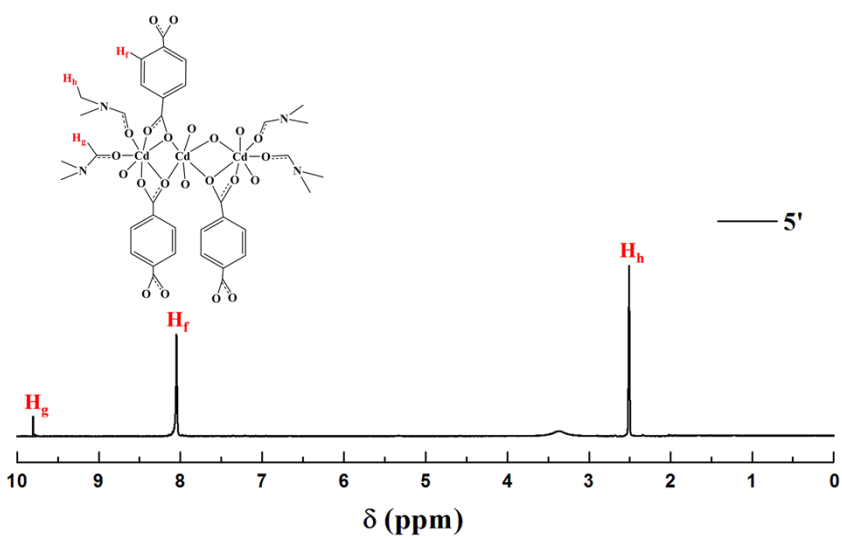
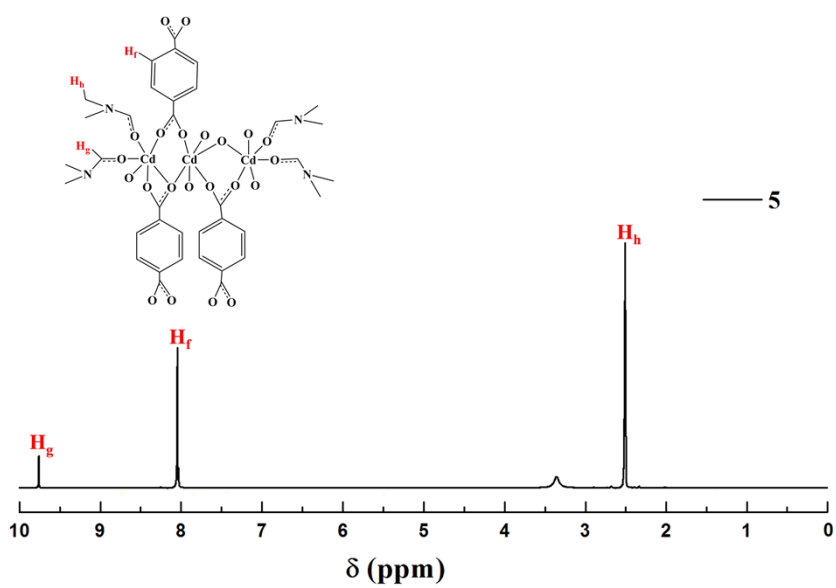
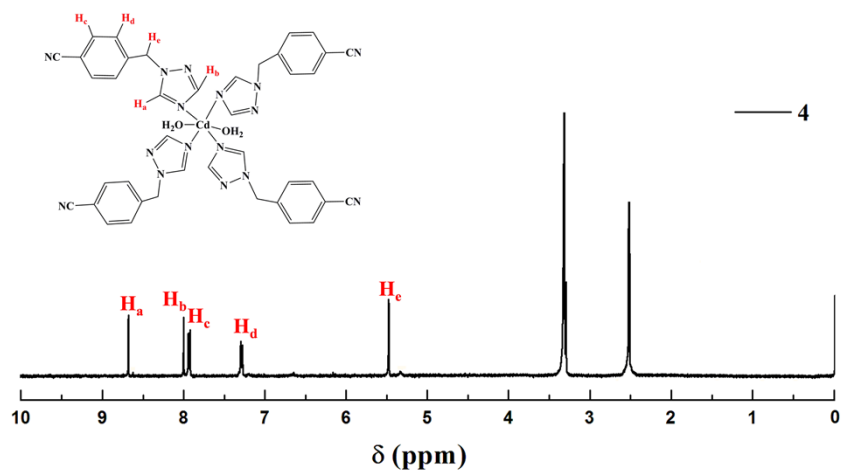
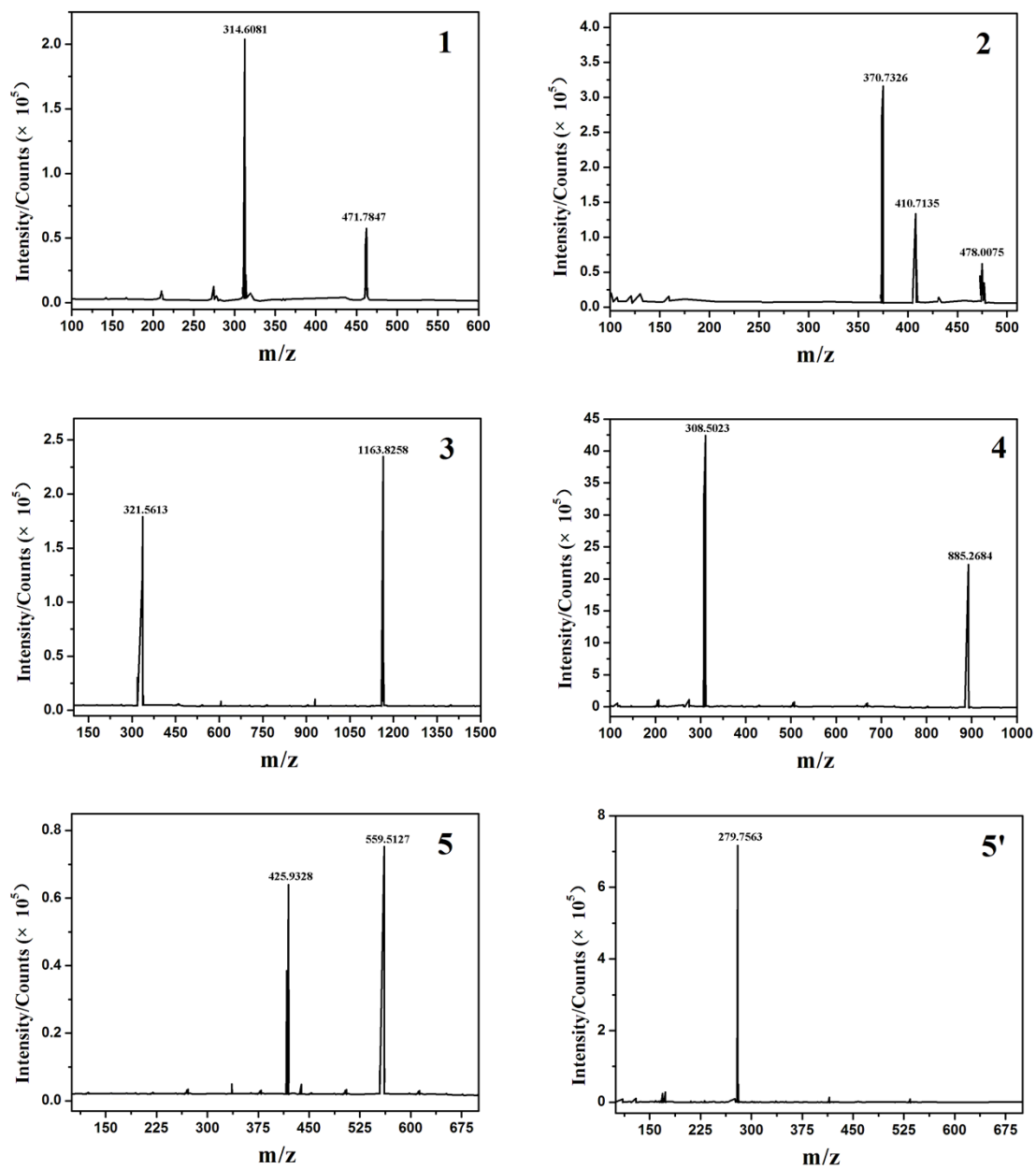


Fig. S23  $^1\text{H}$  NMR spectrum of 1–5' in  $\text{DMSO-}d_6$ .



**Fig. S24** The ESI-MS spectrum of complexes 1–5'.

**Table S3** Hydrogen-bond ( $\text{\AA}$ , deg) for complexes **2–4**.

D-H...A	d(H..A)	<DHA	d(D..A)
<b>2</b>			
O3-H3B...N4 [ -x+2, -y, -z+1 ]	2.291	147.70	3.043
O3-H3C...O5 [ -x+2, y-1/2, -z+1/2 ]	2.602	154.20	3.388
<b>3</b>			
O1W-H1WC...O8 [ x-1, y, z ]	1.870	163.53	2.696
O2W-H2WB...O10 [ x-1, y, z ]	2.135	129.99	2.760
O2W-H2WC...N16 [ -x+1, -y, -z ]	2.657	136.05	3.321
O3W-H3WB...O1 [ -x, -y+1, -z+1 ]	2.046	163.80	2.872
O3W-H3WC...O1 [ x+1, y, z ]	1.980	167.44	2.816
O5-H5A...O3W [ x-1, y, z ]	1.986	157.52	2.790
<b>4</b>			
O1-H1C...O7 [ x, y+1, z-1 ]	2.082	130.35	2.711
O2-H2A...O3 [ -x, -y, -z+1 ]	2.407	121.42	2.941
O2W-H10B...O1 [ x, y, z+1 ]	1.951	160.86	2.768

**Table S4**

Selected bond distance (Å) and angles (°) in complex 1.

1					
Cd(1)-O(1)	2.293(5)	Cd(1)-O(2)#4	2.370(5)	Cd(1)-N(1)#1	2.269(6)
O(1)-Cd(1)-O(2)#4	88.3 (19)	O(1)#3-Cd(1)-O(2)#4	91.6 (19)	N(1)#1-Cd(1)-O(1)#3	95.8(2)
N(1)#1-Cd(1)-N(1)#2	180.0(1)	N(1)#1-Cd(1)-O(1)	84.2(2)	C(10)-O(1)-Cd(1)	144.0(5)
N(1)#2-Cd(1)-O(1)#3	84.2(2)	N(1)#1-Cd(1)-O(2)#4	89.9 (19)	N(1)#1-Cd(1)-O(2)#5	90.1(19)
Symmetry transformations used to generate equivalent atoms:					
#1 -x+2,y+1/2,-z+1/2	#2 x+1,-y+1/2,z+1/2	#3 -x+3,-y+1,-z+1	#4 -x+2,-y+1,-z+1		
#5 x+1,y,z					

Selected bond distance (Å) and angles (°) in complex 2.

2					
Cd(1)-O(1)	2.296(2)	Cd(1)-O(2)	2.508(2)	Cd(1)-O(3)	2.365(2)
Cd(1)-O(4)	2.304(19)	Cd(1)-O(5)	2.438(2)	Cd(1)-N(1)	2.396(3)
Cd(1)-N(2)	2.477(2)				
O(1)-Cd(1)-O(4)	132.9 (7)	O(1)-Cd(1)-O(3)	132.1(7)	O(4)-Cd(1)-O(3)	95.0(7)
O(1)-Cd(1)-N(1)	90.7(9)	O(4)-Cd(1)-N(1)	95.4(8)	O(3)-Cd(1)-N(1)	83.3(8)
O(1)-Cd(1)-O(5)	79.4(7)	O(4)-Cd(1)-O(5)	55.1(7)	O(3)-Cd(1)-O(5)	146.2(7)
N(1)-Cd(1)-O(5)	112.0(8)	O(1)-Cd(1)-N(2)#1	97.3(8)	O(4)-Cd(1)-N(2)#1	92.5(8)
O(3)-Cd(1)-N(2)#1	77.7(7)	N(1)-Cd(1)-N(2)#1	160.0(8)	O(5)-Cd(1)-N(2)#1	87.5(8)
O(1)-Cd(1)-O(2)	53.9(7)	O(4)-Cd(1)-O(2)	173.1(7)	O(3)-Cd(1)-O(2)	78.2(6)
Symmetry transformations used to generate equivalent atoms:					
#1 x+1/2,y,-z+1/2					

Selected bond distance (Å) and angles (°) in complex 3.

3					
Cd(1)-O(1)	2.550(4)	Cd(1)-O(2)	2.347(4)	Cd(1)-O(3)	2.329(4)
Cd(1)-O(4)	2.618(4)	Cd(1)-O(5)	2.365(4)	Cd(2)-O(6)	2.620(4)
Cd(2)-O(7)	2.312(4)	Cd(2)-O(8)#1	2.618(5)	Cd(2)-O(9)	2.318(4)
Cd(2)-O(10)	2.307(4)	Cd(1)-N(1)	2.296(5)	Cd(1)-N(5)	2.312(6)
Cd(2)-N(9)	2.294(5)	Cd(2)-N(13)	2.344(6)		
O(3)-Cd(1)-O(2)	80.8(15)	O(3)-Cd(1)-O(5)	139.5 (15)	O(2)-Cd(1)-O(5)	139.2(16)
O(3)-Cd(1)-O(1)	131.7(13)	O(2)-Cd(1)-O(1)	53.3(13)	O(5)-Cd(1)-O(1)	88.2(14)
O(3)-Cd(1)-O(4)	52.5(13)	O(2)-Cd(1)-O(4)	132.3(13)	O(5)-Cd(1)-O(4)	87.1(14)
O(1)-Cd(1)-O(4)	173.4(13)	O(8)-Cd(2)-O(6)	172.4(13)	O(9)-Cd(2)-O(6)	133.9(15)
O(7)-Cd(2)-O(6)	52.9(13)	O(10)-Cd(2)-O(6)	86.1(15)	O(9)-Cd(2)-O(8)	52.9 (16)
O(7)-Cd(2)-O(8)	134.6(14)	O(10)-Cd(2)-O(8)	86.9(17)	O(7)-Cd(2)-O(9)	82.8(17)
O(10)-Cd(2)-O(9)	139.9(18)	O(10)-Cd(2)-O(7)	135.8(18)	N(1)-Cd(1)-N(5)	168.8(16)
N(1)-Cd(1)-O(3)	92.2(18)	N(5)-Cd(1)-O(3)	92.6(18)	N(1)-Cd(1)-O(2)	101.6(18)
N(5)-Cd(1)-O(2)	89.0(18)	N(1)-Cd(1)-O(5)	84.7(16)	N(5)-Cd(1)-O(5)	84.9(16)
N(5)-Cd(1)-O(4)	84.16(17)	N(1)-Cd(1)-O(4)	90.91(17)	N(5)-Cd(1)-O(1)	100.06(18)
N(1)-Cd(1)-O(1)	84.0(18)	N(13)-Cd(2)-O(6)	100.4(18)	N(9)-Cd(2)-O(6)	83.4(18)
N(13)-Cd(2)-O(8)	81.5(19)	N(9)-Cd(2)-O(8)	93.4(19)	O(9)-Cd(2)-N(13)	90.5(19)
O(7)-Cd(2)-N(13)	90.2(19)	O(10)-Cd(2)-N(13)	81.2(18)	N(9)-Cd(2)-N(13)	169.7(19)
N(9)-Cd(2)-O(9)	93.5(19)	N(9)-Cd(2)-O(10)	89.6(18)	N(9)-Cd(2)-O(7)	99.6(18)
Symmetry transformations used to generate equivalent atoms:					
#1 x+1,y-1,z					

## Selected bond distance (Å) and angles (°) in complex 4.

4					
Cd(1)-O(1)	2.290(6)	Cd(1)-O(2)	2.374(6)	Cd(1)-N(1)	2.276(8)
Cd(1)-N(5)	2.304(8)	Cd(1)-N(9)	2.360(7)	Cd(1)-N(13)	2.344(7)
O(1)-Cd(1)-O(2)	177.6(3)	N(5)-Cd(1)-O(2)	87.4(3)	N(13)-Cd(1)-O(2)	93.2(3)
N(9)-Cd(1)-O(2)	86.8(3)	N(1)-Cd(1)-O(2)	93.6(3)	N(13)-Cd(1)-N(9)	86.4(3)
N(5)-Cd(1)-N(9)	93.1(3)	O(1)-Cd(1)-N(9)	90.9(3)	N(1)-Cd(1)-N(9)	179.5(4)
N(5)-Cd(1)-N(13)	179.2(4)	O(1)-Cd(1)-N(13)	87.4(3)	N(1)-Cd(1)-N(13)	93.7(3)
O(1)-Cd(1)-N(5)	92.0(3)	N(1)-Cd(1)-N(5)	86.8(3)	N(1)-Cd(1)-O(1)	88.7(3)

Symmetry transformations used to generate equivalent atoms:

## Selected bond distance (Å) and angles (°) in complex 5.

5					
Cd(1)-O(1)	2.206(3)	Cd(1)-O(5)	2.210(3)	Cd(1)-O(9)	2.358(3)
Cd(1)-O(10)	2.381(3)	Cd(1)-O(13)	2.283(4)	Cd(2)-O(14)	2.357(4)
Cd(2)-O(3)	2.198(3)	Cd(2)-O(7)#1	2.231(3)	Cd(2)-O(11)	2.369(3)
Cd(2)-O(12)	2.365(3)	Cd(2)-O(15)	2.248(4)	Cd(2)-O(16)	2.411(4)
Cd(3)-O(8)#2	2.233(4)	Cd(3)-O(4)#3	2.236(3)	Cd(3)-O(12)#3	2.324(3)
Cd(4)-O(2)	2.215(4)	Cd(4)-O(6)#4	2.250(3)	Cd(4)-O(9)#4	2.335(3)
O(1)-Cd(1)-O(5)	108.0(14)	O(1)-Cd(1)-O(13)	81.1(14)	O(5)-Cd(1)-O(13)	99.3(16)
O(1)-Cd(1)-O(14)	167.6(14)	O(5)-Cd(1)-O(1)	80.6(14)	O(13)-Cd(1)-O(14)	88.7(14)
O(1)-Cd(1)-O(9)	99.7(13)	O(5)-Cd(1)-O(9)	94.7(14)	O(13)-Cd(1)-O(9)	164.8(14)
O(14)-Cd(1)-O(9)	88.1(13)	O(1)-Cd(1)-O(10)	94.1(14)	O(5)-Cd(1)-O(10)	146.0(14)
O(13)-Cd(1)-O(1)	109.4(15)	O(14)-Cd(1)-O(10)	82.3(14)	O(9)-Cd(1)-O(10)	55.4(12)
O(3)-Cd(2)-O(7)#1	99.5(15)	O(3)-Cd(2)-O(15)	109.3(16)	O(7)#1-Cd(2)-O(15)	83.8(15)
O(3)-Cd(2)-O(12)	98.3(13)	O(7)#1-Cd(2)-O(12)	101.2(13)	O(15)-Cd(2)-O(12)	150.7(14)
O(3)-Cd(2)-O(11)	150.4(14)	O(7)#1-Cd(2)-O(11)	99.2(14)	O(15)-Cd(2)-O(11)	95.3(15)
O(12)-Cd(2)-O(11)	55.5(12)	O(3)-Cd(2)-O(16)	80.4(15)	O(7)#1-Cd(2)-O(16)	171.8(15)
O(15)-Cd(2)-O(16)	88.5(15)	O(12)-Cd(2)-O(16)	86.7(14)	O(11)-Cd(2)-O(16)	84.2(15)
O(8)#2-Cd(3)-O(8)	180.0(1)	O(8)#2-Cd(3)-O(4)	93.1(14)	O(8)#1-Cd(3)-O(4)	86.9(14)
O(8)#2-Cd(3)-O(12)	88.3(14)	O(8)#1-Cd(3)-O(12)	91.7(14)	O(4)#3-Cd(3)-O(12)	92.1(13)
O(4)-Cd(3)-O(12)	87.8(13)	O(12)-Cd(3)-O(12)	180.0(1)	O(2)-Cd(4)-O(2)#4	180.0(1)
O(2)-Cd(4)-O(6)	94.9(16)	O(2)#4-Cd(4)-O(6)	85.0(16)	O(2)-Cd(4)-O(9)#4	87.4(14)
O(2)#4-Cd(4)-O(9)	92.5(14)	O(6)-Cd(4)-O(9)#4	91.5(12)	O(6)#4-Cd(4)-O(9)	88.5(12)

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z+1 #2 -x+1,-y,-z+1 #3 -x+1,-y-1,-z+2 #4 -x,-y,-z+1

## Selected bond distance (Å) and angles (°) in complex 5'.

5'					
Cd(1)-O(1)	2.473(16)	Cd(1)-O(2)	2.297(16)	Cd(1)-O(3)#1	2.293(16)
Cd(1)-O(6)	2.278(17)	Cd(1)-O(7)	2.262(17)	Cd(2)-O(8)	2.294(17)
Cd(1)-O(5)	2.619(2)	Cd(2)-O(4)#2	2.211(16)	Cd(2)-O(4)#1	2.211(16)
Cd(2)-O(5)#3	2.290(15)	Cd(2)-O(1)#3	2.457(19)		
O(7)-Cd(1)-O(6)	89.4(7)	O(7)-Cd(1)-O(3)#1	87.6(7)	O(6)-Cd(1)-O(3)#1	84.2(7)
O(7)-Cd(1)-O(8)	95.7(7)	O(6)-Cd(1)-O(8)	92.9(8)	O(3)#1-Cd(1)-O(8)	175.5(7)
O(7)-Cd(1)-O(2)	91.9(7)	O(6)-Cd(1)-O(2)	172.3(7)	O(3)#1-Cd(1)-O(2)	88.3(6)
O(8)-Cd(1)-O(2)	94.4(7)	O(7)-Cd(1)-O(1)	145.6(6)	O(6)-Cd(1)-O(1)	122.3(6)
O(3)#1-Cd(1)-O(1)	83.3(6)	O(8)-Cd(1)-O(1)	95.4(6)	O(2)-Cd(1)-O(1)	54.8(6)
O(7)-Cd(1)-O(5)	142.5(6)	O(6)-Cd(1)-O(5)	53.1(6)	O(3)#1-Cd(1)-O(5)	90.3(6)
O(8)-Cd(1)-O(5)	85.3(6)	O(2)-Cd(1)-O(5)	125.4(6)	O(1)-Cd(1)-O(5)	70.8(5)
O(4)#2-Cd(2)-O(4)	97.8(10)	O(4)#2-Cd(2)-O(5)	88.4(7)	O(4)#1-Cd(2)-O(5)	165.3(6)
O(4)#2-Cd(2)-O(5)	165.3(6)	O(4)#1-Cd(2)-O(5)	88.4(7)	O(5)#3-Cd(2)-O(5)	88.7(9)
O(4)#2-Cd(2)-O(1)	100.9(6)	O(5)#3-Cd(2)-O(1)	76.9(5)	O(5)-Cd(2)-O(1)#3	92.4(6)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1,z-1/2 #2 -x,-y+1,-z+1 #3 -x,y,-z+1/2