

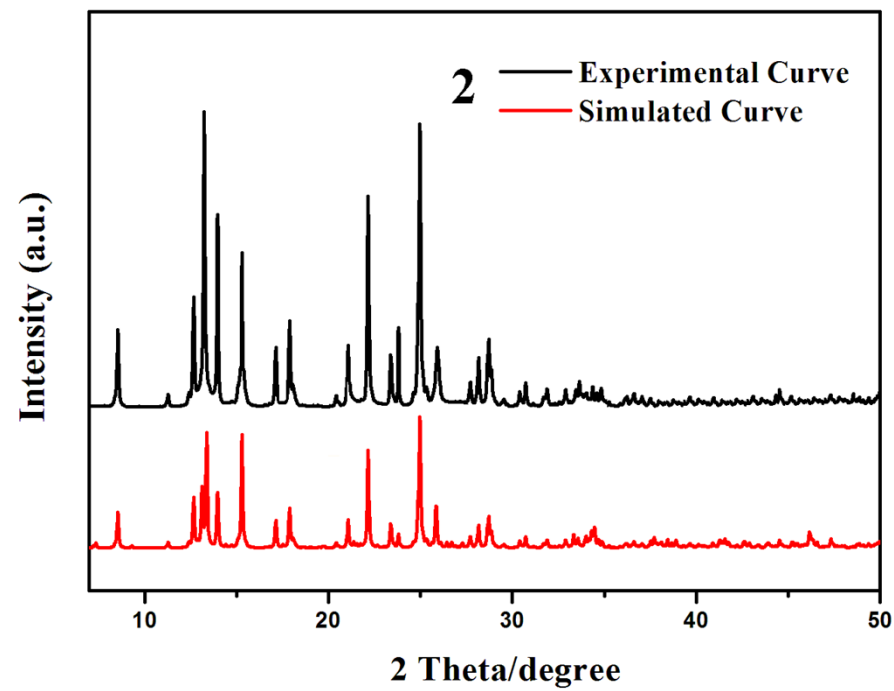
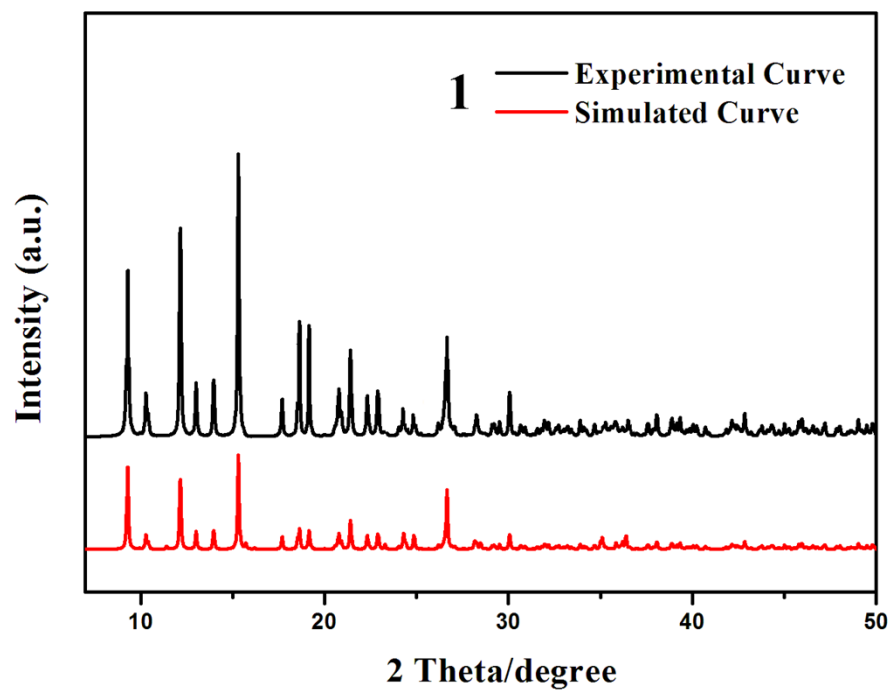
## Supporting Information

### **Advanced Cd<sup>II</sup> Complexes as High Efficiency Co-Sensitizers for Enhanced Dye-Sensitized Solar Cells Performance**

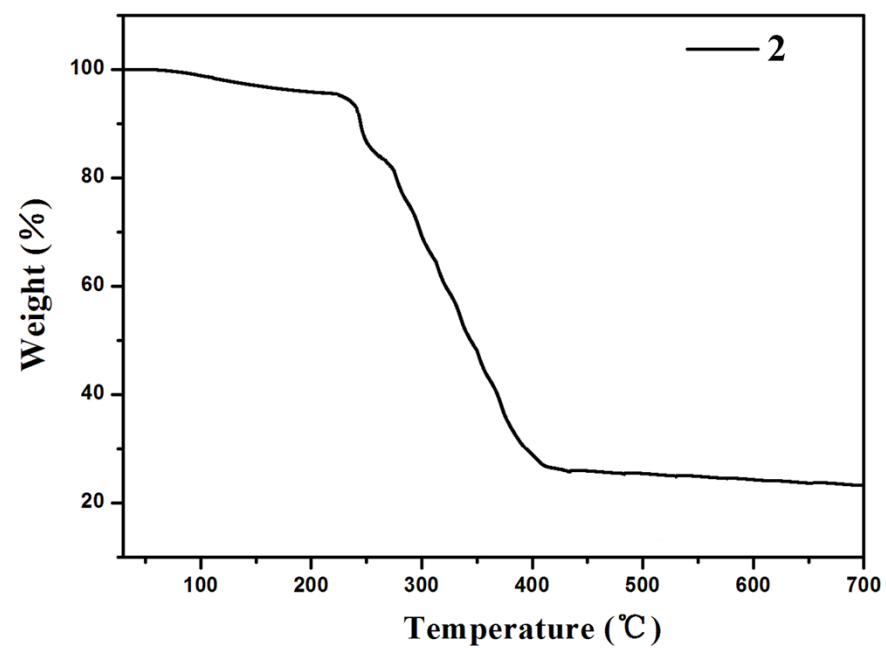
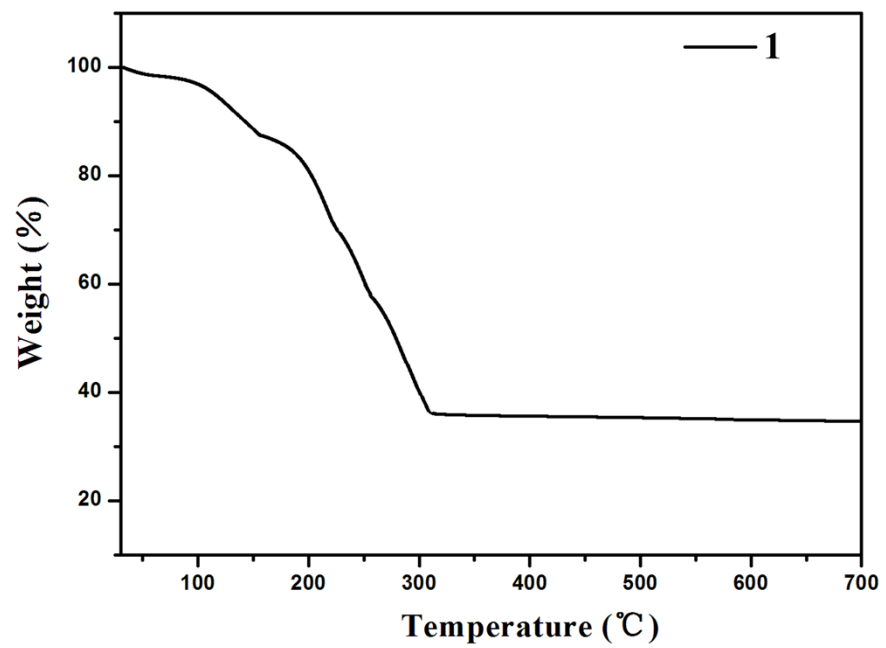
Song Gao,<sup>a</sup> Rui Qing Fan,<sup>\*,a</sup> Xin Ming Wang,<sup>a</sup> Liang Sheng Qiang,<sup>a</sup> Li Guo Wei,<sup>a</sup>  
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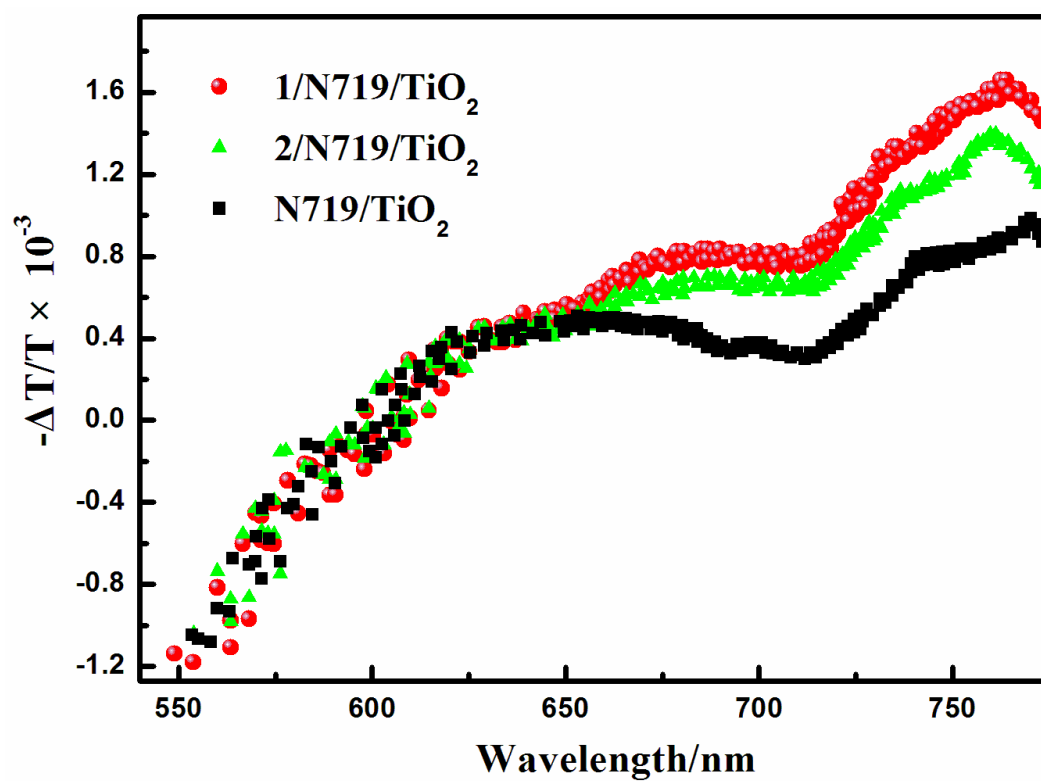
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**Fig. S1** The PXR D contrast curves of complexes **1** and **2**.



**Fig. S2** The TGA curves of complexes **1** and **2**.



**Fig. S3** Transient absorption spectrum (500 ps delay time) of DSSCs based on co-sensitized photoelectrodes and N719 sensitized photoelectrode.

## Experimental Section

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. 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-visible absorption spectra were recorded on SPECORD S600 spectrophotometer (Jena, Germany) for samples in ethanol solution and UV-2250 spectrophotometer (Shimadzu, Japan) for sensitized  $\text{TiO}_2$  films, respectively. 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  $\text{cm}^2$ . The irradiance of AM1.5 global sunlight from a filtered 500 W xenon lamp light source was set at 100  $\text{mW cm}^{-2}$  and was calibrated by a standard silicon solar cell. Based on  $I$ - $V$  curve, the fill factor ( $FF$ ) is defined as:  $FF = (J_{\text{max}} \times V_{\text{max}})/(J_{\text{sc}} \times V_{\text{oc}})$ , where  $J_{\text{max}}$  and  $V_{\text{max}}$  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-current conversion efficiency (IPCE) were measured on an EQE/IPCE spectral response system (Newport). Transient absorption (TA) system based on an amplified Ti:sapphire laser combined with an optical parametric amplifier to obtain excitation light at 532 nm and white-light continuum generation optics to obtain probe light. The light beams were focused on the DSSC under open-circuit conditions from the transparent conductive glass side, and diffusely reflected light was collected by an achromatic lens (80 mm focal length, 50 mm diameter) to relay the probe light to an InGaAs photodetector (Thorlabs, PDA10CS)

through a monochromator (Acton Research, SpectraPro-150). Electrochemical impedance spectroscopy (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  $V_{oc}$ . Absorbed photon-to-current conversion (APCE) efficiency spectra were calculated as IPCE/LHE, where LHE is the light-harvesting efficiency of the dye-sensitized films.

### **Assembly of DSSCs**

The FTO conducting glass (Fluorine-doped SnO<sub>2</sub>, sheet resistance 15 Ω 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. Before screen-printing method, FTO substrate was first treated by 20 mM TiCl<sub>4</sub> aqueous solution in order to reduce the recombination between FTO and electrolyte. The TiO<sub>2</sub> paste was cast onto the FTO substrate by the screen-printing method, and the FTO substrate was treated by 20 mM TiCl<sub>4</sub> aqueous solution again to optimize the TiO<sub>2</sub> thin film, 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 μm. The co-adsorbent electrodes were prepared by immersing the obtained mesoporous TiO<sub>2</sub> photoelectrode into 0.3 mM **1** or **2** 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 [Cd<sub>3</sub>(IBA)<sub>3</sub>(Cl)<sub>2</sub>(HCOO)(H<sub>2</sub>O)]<sub>n</sub> (**1**)**

A mixture of CdCl<sub>2</sub>·2.5H<sub>2</sub>O (45.7 mg, 0.2 mmol), 4-HIBA (18.8 mg, 0.1 mmol) were dissolved in N,N-dimethylformamide (DMF)–H<sub>2</sub>O (1:5, v/v, 6 mL), pH ≈ 5.5. 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 6 days. Then slow cooling to room temperature, colorless block crystals of **1** were obtained in 58% yield (based on 4-HIBA). Anal. Calcd for C<sub>31</sub>H<sub>24</sub>N<sub>6</sub>O<sub>9</sub>Cl<sub>2</sub>Cd<sub>3</sub> (*Mr*: 1032.69): C, 36.06; H, 2.34; N, 8.14%. Found: C, 36.09; H, 2.35; N, 8.16%. IR (KBr pellet, cm<sup>-1</sup>, Fig. S4) for **1**: 3442 (br, s), 1675(s), 1609 (s), 1519(s), 1481(m), 1397(s), 1304(s), 1243(w), 1176(w), 1119(m), 1059(s), 959(m), 849(s), 778(s), 693(w), 647(m), 514(m).

### Synthesis of {[Cd<sub>1.5</sub>(IBA)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]·3.5H<sub>2</sub>O}<sub>n</sub> (**2**)

Reaction mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (61.6 mg, 0.2 mmol), 4-HIBA (18.8 mg, 0.1 mmol), H<sub>2</sub>O (6 mL) were sealed in a 15 mL Teflon lined stainless steel container and heated at 160 °C for 6 days. NaOH solution (0.05 mol L<sup>-1</sup>) was added to adjust the final pH to 8.05~8.10. After the mixture was cooled to room temperature, the colorless platelate crystals of **2** were obtained in 43% yield (based on 4-HIBA). Anal. Calcd for C<sub>30</sub>H<sub>40</sub>N<sub>6</sub>O<sub>15.5</sub>Cd<sub>1.5</sub> (*Mr*: 901.28): C, 39.98; H, 4.47; N, 9.32%. Found: C, 40.23; H, 4.45; N, 9.40%. IR (KBr pellet, cm<sup>-1</sup>, Fig. S4) for **2**: 3467(br, s), 1687(vs), 1604(s), 1520(s), 1484(m), 1431(m), 1379(w), 1301(s), 1243(m), 1186(w), 1123(m), 1061(s), 962(s), 920(m), 852(m), 769(s), 690(m), 643(s), 513(m).

### X-ray Crystallography

The X–ray diffraction data taken at room temperature for complexes **1** and **2** 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** and **2** were solved by direct methods and refined on F<sup>2</sup> by the full–matrix least squares using the SHELXTL–2014 crystallographic software. 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 1041927 and 1041928 contain the crystallographic data **1** and **2** 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 S1, selected hydrogen bonding data, bond lengths and bond angles of **1** and **2** are listed as Table S2–S3.

**Table S1** Crystal data and structure refinement parameters of complexes **1** and **2**.

| Identification code  | <b>1</b>  | <b>2</b>   |
|--|---|--|
| Empirical formula  | C <sub>31</sub> H <sub>24</sub> N <sub>6</sub> O <sub>9</sub> Cl <sub>2</sub> Cd <sub>3</sub> | C <sub>30</sub> H <sub>40</sub> N <sub>6</sub> O <sub>15.5</sub> Cd <sub>1.5</sub> |
| Formula mass   | 1032.69   | 901.28   |
| Crystal system   | Monoclinic  | Orthorhombic   |
| Space group  | <i>P</i> 2(1)/ <i>c</i>   | <i>P</i> bcn   |
| <i>a</i> (Å)   | 8.683(2)  | 24.030(5)  |
| <i>b</i> (Å)   | 19.023(4)   | 14.256(3)  |
| <i>c</i> (Å)   | 20.511(4)   | 20.680(4)  |
| $\alpha$ (°)   | 90.00   | 90.00  |
| $\beta$ (°)  | 102.13(3)   | 90.00  |
| $\gamma$ (°)   | 90.00   | 90.00  |
| <i>V</i> (Å <sup>3</sup> )                                   | 3312.3(1)   | 7084.0(2)  |
| <i>Z</i>   | 4   | 8  |
| <i>D</i> <sub>c</sub> /(g · cm <sup>-3</sup> )               | 2.071   | 1.690  |
| $\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>                      | 2.135   | 0.989  |
| <i>F</i> (000)   | 2008  | 3664   |
| $\theta$ range (°)   | 2.99 – 27.48  | 3.02 – 27.47   |
|  | -10 ≤ <i>h</i> ≤ 11   | -31 ≤ <i>h</i> ≤ 30  |
| Limiting indices   | -23 ≤ <i>k</i> ≤ 24   | -18 ≤ <i>k</i> ≤ 16  |
|  | -26 ≤ <i>l</i> ≤ 26   | -26 ≤ <i>l</i> ≤ 26  |
| Data/Restraints/Parameters                                   | 7587 / 0 / 460  | 8129 / 27 / 537  |
| GOF on <i>F</i> <sup>2</sup>                                 | 1.046   | 1.031  |
| Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] |   |  |
| <i>R</i> <sub>1</sub> <sup>a</sup>                           | 0.0465  | 0.0413   |
| <i>wR</i> <sub>2</sub> <sup>b</sup>                          | 0.1021  | 0.0847   |
| <i>R</i> indices (alldata)                                   |   |  |
| <i>R</i> <sub>1</sub>  | 0.0650  | 0.0689   |
| <i>wR</i> <sub>2</sub>                                       | 0.1077  | 0.0943   |
| CCDC   | 1041927   | 1041928  |

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



**Table S2** Hydrogen-bond ( $\text{\AA}$ , deg) for complexes **1** and **2**.

| D-H...A                                  | d(H..A) | <DHA   | d(D..A) |
|--|---------|--------|---------|
| <b>1</b>                                 |         |        |         |
| O3-H3A...O7 [ -x+1, -y, -z ]             | 1.824   | 178.01 | 2.674   |
| O3-H3C...Cl2 [ x, -y+1/2, z-1/2 ]        | 2.570   | 142.98 | 3.288   |
| <b>2</b>                                 |         |        |         |
| O1W-H1WB...O4 [ x+1/2, -y+3/2, -z ]      | 1.861   | 154.71 | 2.663   |
| O2W-H2WA...O2 [ x, y, z+1 ]              | 1.931   | 166.34 | 2.724   |
| O3W-H3WA...O1 [ -x+1, -y+1, -z+1 ]       | 1.924   | 167.84 | 2.742   |
| O3W-H3WB...O3 [ x, -y+1, z+1/2 ]         | 1.868   | 169.83 | 2.691   |
| O5W-H5WA...O2W [ x-1/2, -y+3/2, -z+1 ]   | 2.022   | 154.39 | 2.834   |
| O6W-H6WA...O3 [ x+1, -y+1, z+1/2 ]       | 2.034   | 170.54 | 2.830   |
| O7W-H7WB...O5 [ -x+1, -y+1, -z+1 ]       | 1.893   | 177.24 | 2.714   |
| O8W-H8WA...O3W [ x+1, y, z ]             | 1.860   | 171.24 | 2.697   |
| O8W-H8WB...O2W [ x+1/2, -y+3/2, -z+1 ]   | 1.880   | 167.16 | 2.702   |
| O9W-H9WA...O1 [ -x+1, -y+1, -z ]         | 1.981   | 162.06 | 2.781   |
| O9W-H9WB...O6 [ -x+1, -y+1, -z+1 ]       | 1.989   | 172.44 | 2.799   |
| O10W-H10A...O1 [ x-1/2, -y+3/2, -z ]     | 1.965   | 159.69 | 2.759   |
| O10W-H10B...O3 [ -x+1/2, -y+3/2, z+1/2 ] | 1.950   | 161.91 | 2.732   |
| O11W-H11W...O5 [ x+1/2, -y+3/2, -z+1 ]   | 1.899   | 169.91 | 2.698   |

**Table S3** Selected bond lengths (Å) and bond angles (°) for complexes **1** and **2**.

| <b>1</b>            |           |                      |          |
|---------------------|-----------|----------------------|----------|
| Cd(1)-N(6)          | 2.234(4)  | Cd(2)-N(4)           | 2.272(4) |
| Cd(1)-O(4)          | 2.236(4)  | Cd(2)-O(6)           | 2.328(4) |
| Cd(1)-O(2)          | 2.307(3)  | Cd(2)-O(5)           | 2.336(3) |
| Cd(1)-O(3)          | 2.374(4)  | Cd(2)-O(1)           | 2.463(4) |
| Cd(1)-O(1)          | 2.456(4)  | Cd(2)-Cl(1)          | 2.522(2) |
| Cd(1)-Cl(1)         | 2.606(2)  | Cd(2)-Cl(2)          | 2.692(2) |
| Cd(3)-N(2)          | 2.251(4)  | Cd(3)-O(9)#2         | 2.283(5) |
| Cd(3)-O(7)#1        | 2.254(4)  | Cd(3)-O(8)#1         | 2.488(4) |
| Cd(3)-Cl(2)#3       | 2.528(2)  | N(4)-Cd(2)-O(6)      | 94.4(1)  |
| N(6)-Cd(1)-O(4)     | 96.0(2)   | N(4)-Cd(2)-O(5)      | 147.9(1) |
| N(6)-Cd(1)-O(2)     | 140.4(2)  | O(6)-Cd(2)-O(5)      | 56.5(1)  |
| O(4)-Cd(1)-O(2)     | 118.4(1)  | N(4)-Cd(2)-O(1)      | 86.2(1)  |
| N(6)-Cd(1)-O(3)     | 89.0(2)   | O(6)-Cd(2)-O(1)      | 91.6(2)  |
| O(4)-Cd(1)-O(3)     | 79.6(1)   | O(5)-Cd(2)-O(1)      | 82.0(1)  |
| O(2)-Cd(1)-O(3)     | 79.3(1)   | N(4)-Cd(2)-Cl(1)     | 96.9(1)  |
| N(6)-Cd(1)-O(1)     | 90.6(1)   | O(6)-Cd(2)-Cl(1)     | 168.1(1) |
| O(4)-Cd(1)-O(1)     | 173.5(1)  | O(5)-Cd(2)-Cl(1)     | 111.6(9) |
| O(2)-Cd(1)-O(1)     | 55.4(1)   | O(1)-Cd(2)-Cl(1)     | 85.6(1)  |
| O(3)-Cd(1)-O(1)     | 100.2(1)  | N(4)-Cd(2)-Cl(2)     | 104.7(1) |
| N(6)-Cd(1)-Cl(1)    | 106.0 (1) | O(6)-Cd(2)-Cl(2)     | 85.6(1)  |
| O(4)-Cd(1)-Cl(1)    | 94.6(1)   | O(5)-Cd(2)-Cl(2)     | 87.6(1)  |
| O(2)-Cd(1)-Cl(1)    | 91.1(1)   | O(1)-Cd(2)-Cl(2)     | 169.0(8) |
| O(3)-Cd(1)-Cl(1)    | 164.5(1)  | O(9)#2-Cd(3)-O(8)#1  | 88.8(2)  |
| N(2)-Cd(3)-O(7)#1   | 101.7(1)  | N(2)-Cd(3)-Cl(2)#3   | 94.2(1)  |
| N(2)-Cd(3)-O(9)#2   | 105.0(2)  | O(7)#1-Cd(3)-Cl(2)#3 | 140.7(1) |
| O(7)#1-Cd(3)-O(9)#2 | 111.1(2)  | O(9)#2-Cd(3)-Cl(2)#3 | 98.9(1)  |
| N(2)-Cd(3)-O(8)#1   | 156.2(2)  | O(8)#1-Cd(3)-Cl(2)#3 | 102.8(1) |
| O(7)#1-Cd(3)-O(8)#1 | 54.8(1)   | O(8)#1-Cd(3)-O(4)#2  | 96.4(1)  |
| N(2)-Cd(3)-O(4)#2   | 78.7(1)   | Cl(2)#3-Cd(3)-O(4)#2 | 143.6(9) |
| O(7)#1-Cd(3)-O(4)#2 | 75.4(1)   | O(9)#2-Cd(3)-O(4)#2  | 50.5(1)  |
| <b>2</b>            |           |                      |          |
| Cd(1)-O(9W)         | 2.320(2)  | Cd(1)-O(7W)          | 2.328(2) |
| Cd(1)-O(10W)        | 2.348(2)  | Cd(1)-O(5W)          | 2.388(2) |
| Cd(2)-O(11W)        | 2.265(3)  | Cd(2)-O(6W)          | 2.276(3) |
| Cd(2)-O(8W)#1       | 2.343(2)  | Cd(1)-N(1)           | 2.269(2) |
| Cd(1)-N(3)          | 2.269(2)  | Cd(2)-N(5)           | 2.293(2) |
| O(9W)-Cd(1)-O(7W)   | 89.7(7)   | O(9W)-Cd(1)-O(10W)   | 175.5(6) |
| O(7W)-Cd(1)-O(10W)  | 92.8(7)   | O(9W)-Cd(1)-O(5W)    | 81.2(6)  |

|                      |          |                      |          |
|----------------------|----------|----------------------|----------|
| O(7W)-Cd(1)-O(5W)    | 170.7(7) | O(10W)-Cd(1)-O(5W)   | 96.4(7)  |
| O(11W)-Cd(2)-O(6W)   | 180.0(1) | O(11W)-Cd(2)-O(8W)#1 | 87.8(4)  |
| O(6W)-Cd(2)-O(8W)#1  | 92.2(4)  | O(11W)-Cd(2)-O(8W)   | 87.8(4)  |
| O(6W)-Cd(2)-O(8W)    | 92.2(4)  | O(8W)#1-Cd(2)-O(8W)  | 175.6(9) |
| N(3)-Cd(1)-O(9W)     | 99.7(7)  | N(1)-Cd(1)-O(9W)     | 85.7(7)  |
| N(3)-Cd(1)-O(7W)     | 87.6(7)  | N(1)-Cd(1)-O(7W)     | 90.2(7)  |
| N(3)-Cd(1)-O(10W)    | 84.1(7)  | N(1)-Cd(1)-O(10W)    | 90.6(7)  |
| N(3)-Cd(1)-O(5W)     | 91.5(7)  | N(1)-Cd(1)-O(5W)     | 91.4(7)  |
| O(11W)-Cd(2)-N(5)#1  | 89.5(6)  | O(6W)-Cd(2)-N(5)#1   | 90.5(6)  |
| O(11W)-Cd(2)-N(5)    | 89.5(6)  | O(6W)-Cd(2)-N(5)     | 90.5(6)  |
| N(5)#1-Cd(2)-O(8W)#1 | 87.8(7)  | N(5)-Cd(2)-O(8W)#1   | 92.2(7)  |
| N(5)#1-Cd(2)-O(8W)   | 92.2(7)  | N(5)-Cd(2)-O(8W)     | 87.8(7)  |
| N(3)-Cd(1)-N(1)      | 174.2(7) | N(5)#1-Cd(2)-N(5)    | 179.0(1) |

Symmetry transformations used to generate equivalent atoms: #1  $x, y+1, z$ ; #2  $-x+1, -y+1, -z$ ; #3  $-x+2, y+1/2, -z+1/2$  for **1**. #1  $-x+2, y, -z+1/2$  for **2**.

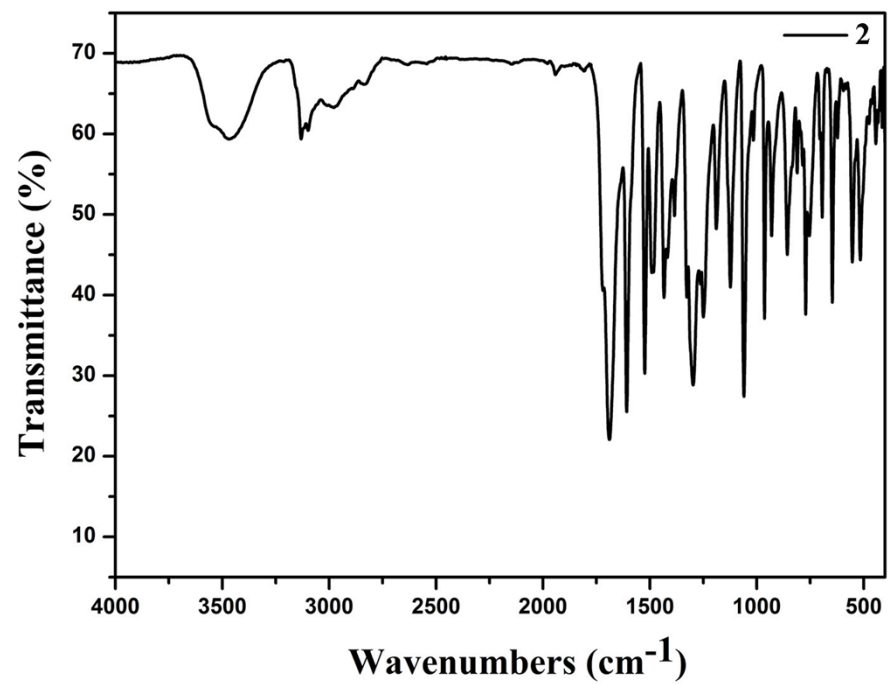
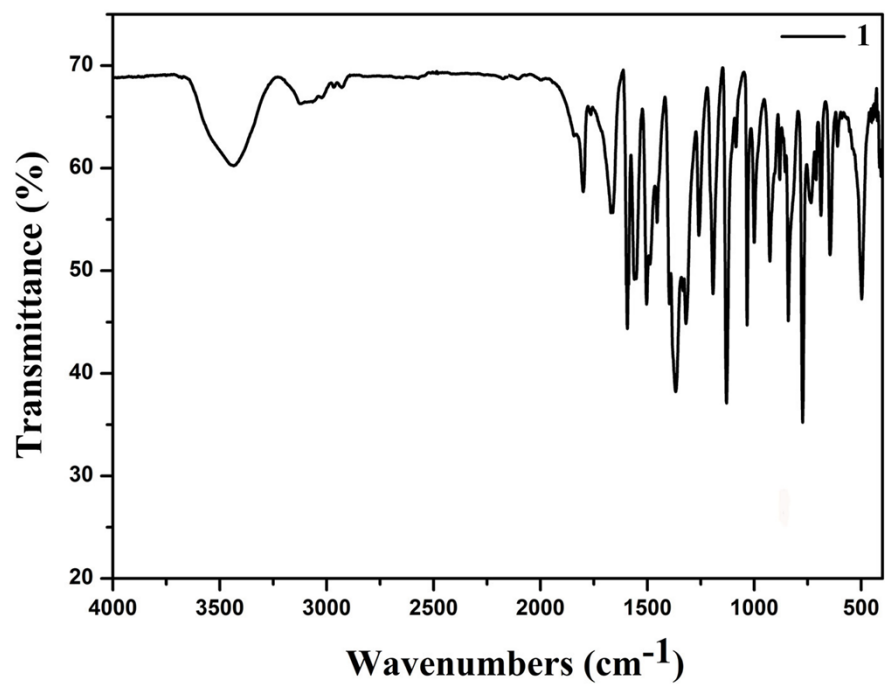


Fig. S4 Infrared spectra of complexes **1** and **2** recorded from a KBr pellet.