

Supporting Information

Photo-induced free radical production in a tetraphenylethylene ligand-based metal-organic frameworks

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1. Reagents

All the materials of analytical grade were used without further purification from commercial suppliers. Bromotriphenylethylene, 1,3-diethylisophthalate-5-boronic acid, tetrakis(triphenylphosphine)palladium(0) and tetrabutylammonium bromide (TBAB) were purchased from Energy Chemical Co., Shanghai, China. All the other materials such as acid, alkali, metal salt and organic solvents were purchased from Sinopharm Chemical Reagent Beijing Co., Beijing, China.

2. Apparatus

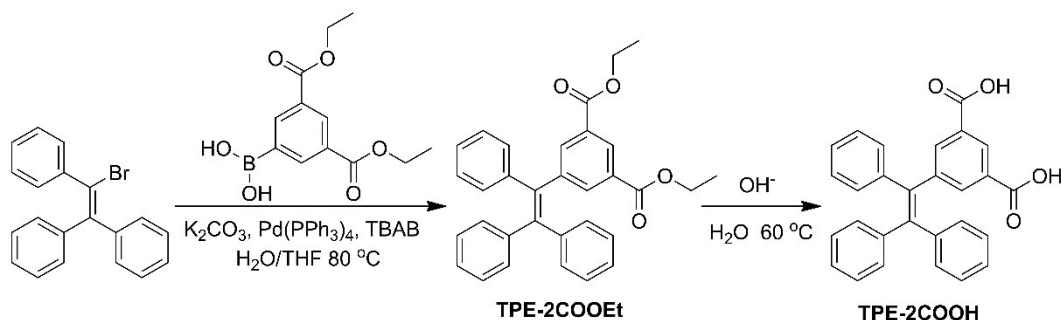
^1H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker 400 Avance NMR spectrometer operated at 400 MHz. ESI-MS spectra were collected using an Agilent Technologies 6420 triple quadrupole LC/MS without using the LC part. Powder X-ray diffraction (PXRD) patterns were collected on a PANalytical X'Pert PRO diffractometer with Cu $\text{K}\alpha_1$ radiation in a 2θ range of $4\text{--}50^\circ$ at room temperature. The Fourier transform infrared (FT-IR) spectra were obtained on a Bruker-ALPHA spectrophotometer with potassium bromide pellets in the scale of $400\text{--}4000\text{ cm}^{-1}$. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C thermal analyzer at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under the air atmosphere. Elemental analyses were performed using a FLASH EA 1112 elemental analyzer. Absorption spectra were recorded on a JASCO-750 UV-vis spectrophotometer. Fluorescence spectra were recorded on a JASCO-FP-8300 fluorescence spectrophotometer. The temperatures in fluorescence measurements were controlled by an ETC-815 peltier thermostatted single cell holder, which offered a temperature control accuracy of $\pm 0.1\text{ }^\circ\text{C}$. For the measurement of fluorescence spectra at 77 K , PPH-150 powder sample holding stick was used. Fluorescence quantum yields were recorded on an Edinburgh FIS-980 fluorescence spectrometer. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker A300-10/12 EPR spectrometer at 77 K in nearly dark environment under the protection of N_2 . Photographs and videos were taken by a Nikon D5500 camera. The UV light used in the spectroscopic experiments were produced using a CEL-HXF300/CEL-HXUV300 xenon light source with 365 nm cut-off optical filters. After irradiating for 20 s , the spectroscopic data was collected immediately. Unless

otherwise noted, all the measurement experiments were performed at room temperature.

3. Crystal structure determination

The crystallographic data of **1** were collected on a Rigaku Saturn 724 CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 150 K. The absorption corrections were used with the Multi-scan program. The data corrections were executed by Lorentz and polarization effects. The structure of **1** was handled by direct methods and refined with a full-matrix least-squares technique based on F^2 with the SHELXL-97 crystallographic software package [Ref: G. M. Sheldrick, *Acta Cryst. A* **2015**, *71*, 3-8]. All of the non-hydrogen atoms were refined by means of anisotropy. The hydrogen atoms were included in the calculated positions and refined isotropically using a riding model.

4. Synthesis of the ligand



Scheme S1. Synthetic routes for **TPE-2COOEt** and **TPE-2COOH**.

Synthesis of 3,5-diethyl-(1,2,2-triphenylvinyl)benzoate (TPE-2COOEt)

Bromotriphenylethylene (1.34 g, 4 mmol), 1,3-diethylisophthalate-5-boronic acid (1.27 g, 4.8 mmol), K_2CO_3 (1.38 g, 10.0 mmol), TBAB (0.01 g, 0.03 mmol) and Tetrakis(triphenylphosphine)palladium(0) (115.6 mg, 0.1 mmol) were placed in an 150 mL round-bottom flask. Then THF (40 mL) and water (5 mL) were added. The resulting mixture was stirred at 80°C for 24 h under nitrogen atmosphere. After cooling to room temperature, the mixture was extracted with dichloromethane and evaporated. The crude product was purified on a silica-column using PE/EA (20/1 v/v) as eluent. After that, **TPE-2COOEt** (1.54 g, 3.30 mmol) was obtained as a white solid with a yield of 82.6 %. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 1.35 (t, 6H, $J = 6.8 \text{ Hz}$), 4.33 (q, 4H, J

= 7.2 Hz), 7.03-7.16 (m, 15H), 7.92 (d, 2H, $J = 1.6$ Hz), 8.43 (t, 1H, $J = 1.6$ Hz). ^{13}C -NMR (100.6 MHz, CDCl_3) δ (ppm): 14.28, 61.20, 126.82, 126.90, 126.94, 127.77, 127.97, 127.99, 128.56, 130.47, 131.14, 131.24, 136.45, 139.03, 142.41, 142.88, 142.92, 143.00, 144.56, 165.76. ESI-MS spectrometry: m/z calculated for $[\text{M} + \text{Na}]^+$: 499.2; found: 499.6.

Synthesis of 5-(1,2,2-triphenylvinyl)isophthalic acid (TPE-2COOH)

TPE-2COOEt (0.476 g 1.0 mmol) and NaOH (0.800 g, 20 mmol) were dissolved in a mixture of THF (40 mL), MeOH (40 mL) and water (40 mL). The mixture solution was stirred at 60 °C for 10 h. After cooling to room temperature, the organic solvent was evaporated by vacuum. White precipitate was obtained by adjusting the pH value of the mixture to 6 using 2 mol/L HCl solution. The precipitate was collected and dried under reduced pressure. **TPE-2COOH** (0.41 g 0.976 mmol) was obtained as a white solid with a yield of 97.6 %. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 6.09-7.03 (m, 5H), 7.11-7.19 (m, 10H), 7.76 (s, 2H), 8.21 (s, 1H), 13.15 (s, 2H). ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm): 127.2, 127.4, 128.3, 128.5, 128.6, 131.0, 131.1, 131.2, 131.4, 135.9, 139.3, 142.8, 142.9, 143.1, 144.5, 166.8. APCI-MS spectrometry: m/z calculated for $[\text{M} - \text{H}]^-$: 419.1; found: 419.2.

5. Synthesis of the MOFs

Synthesis of $[\text{Cd}_2(\text{TPE-2COO})_2(\text{DMF})_2]_n$ (**1**)

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.0154 g, 0.05 mmol) and **TPE-2COOH** (0.0210 g, 0.05 mmol) were dissolved in a mixture of DMF (3 mL) and H_2O (1 mL). The solution was sealed in a 10 mL hydrothermal synthesis reactor and heated at 100 °C for 24 h, followed by slow cooling to room temperature. Colorless claviform crystals of **1** were obtained in a yield of 82.0% based on **TPE-2COOH**. Elemental analysis calculated for $\text{C}_{68}\text{H}_{64}\text{Cd}_2\text{N}_4\text{O}_{12}$ (%): C 60.26, H 4.76, N 4.13. Found: C 59.95, H 4.61, N 4.22. IR (KBr, cm^{-1}): 3444 (s), 3056 (s), 2926 (w), 1652 (m), 1610 (m), 1558 (m), 1491 (m), 1434 (m), 1368 (s), 1125 (s), 1029 (m), 920 (m), 783 (w), 732 (s), 698 (m), 575 (m).

6. Selected spectra and data referred in the paper

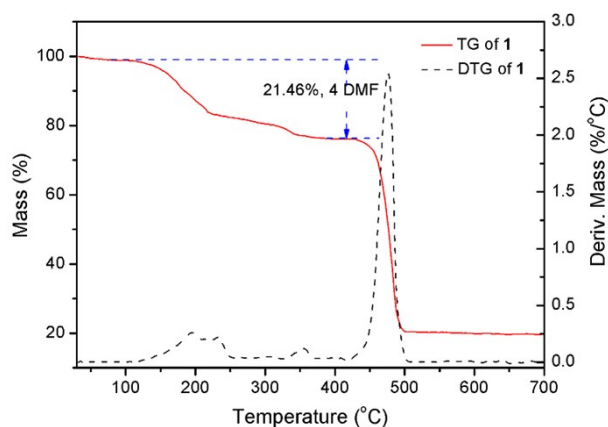


Figure S1. TGA result of **1**.

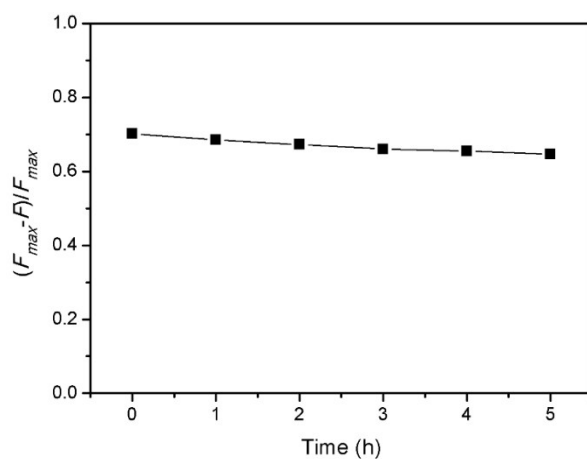


Figure S2. The thermal fading kinetics of **1** at 77K.

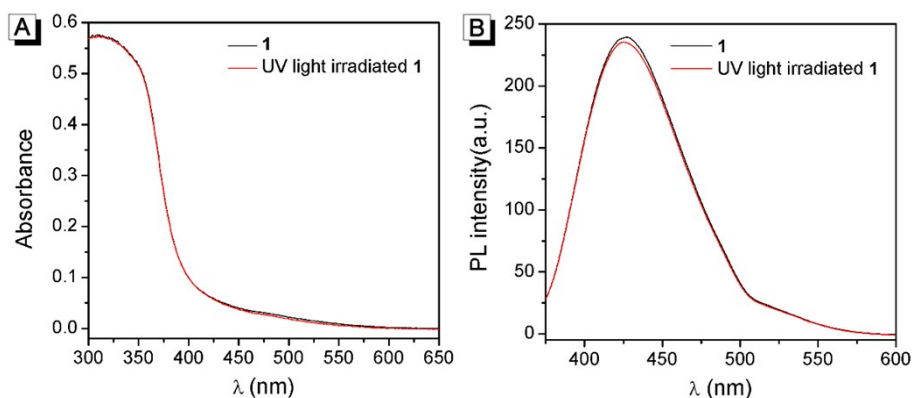


Figure S3. A comparison of A) UV-vis reflectance spectra and B) fluorescence spectra between **1** and UV light irradiated **1**. The UV light irradiated **1** was obtained by continuous irradiating with 365nm UV light (6.2 mW/cm^2) for 3 h, then removed the UV light and kept in dark for 1 min.

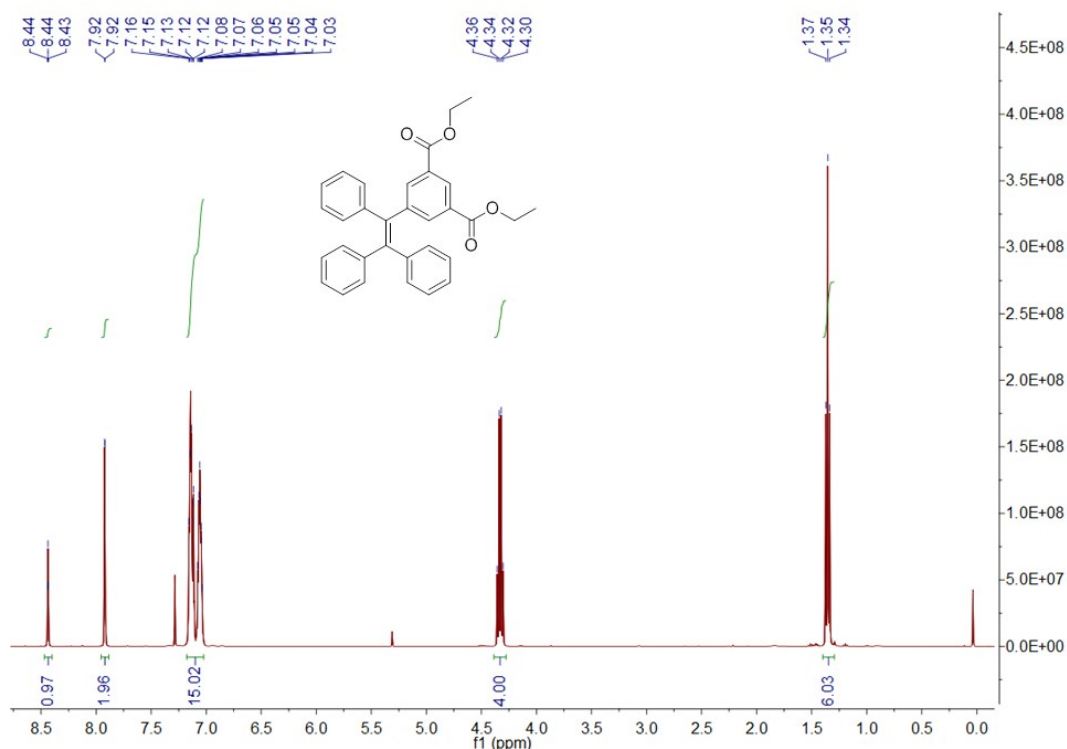


Figure S4. $^1\text{H-NMR}$ spectrum of TPE-2COOEt.

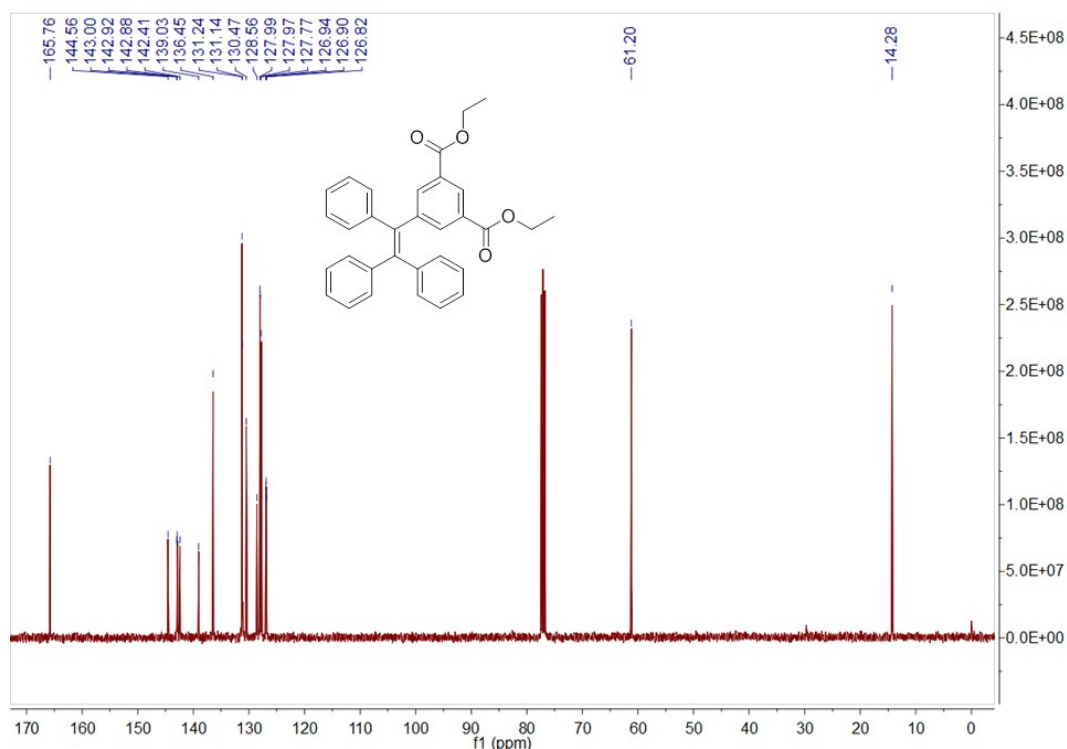


Figure S5. $^{13}\text{C-NMR}$ spectrum of TPE-2COOEt.

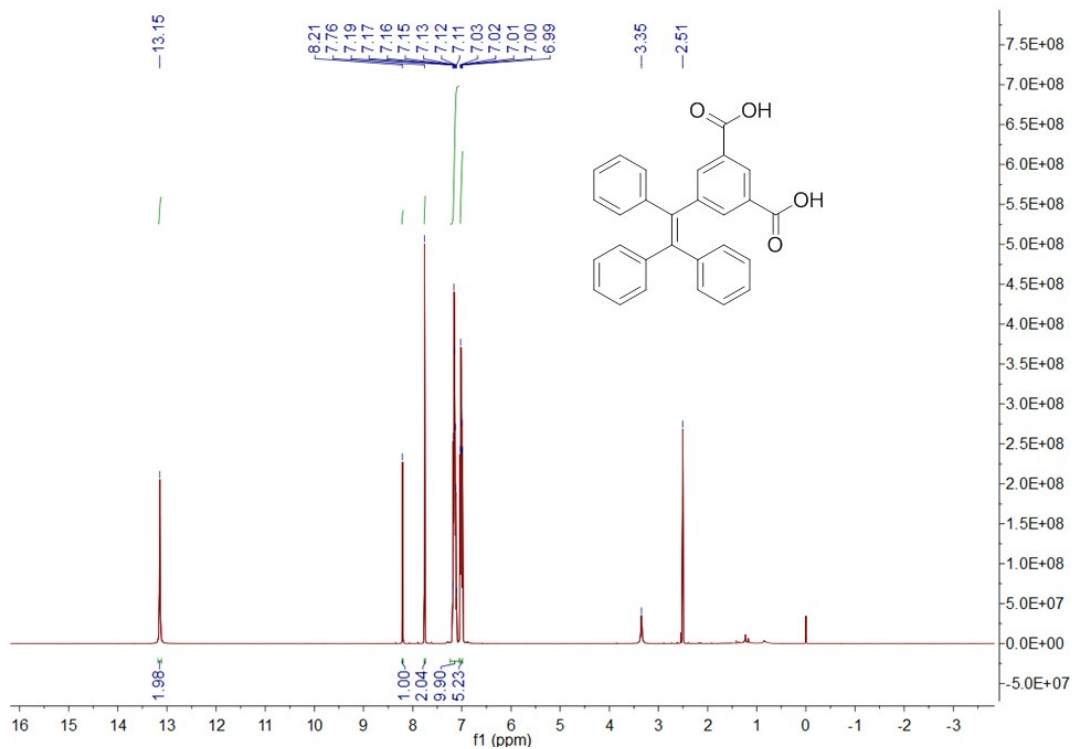


Figure S6. $^1\text{H-NMR}$ spectrum of TPE-2COOH.

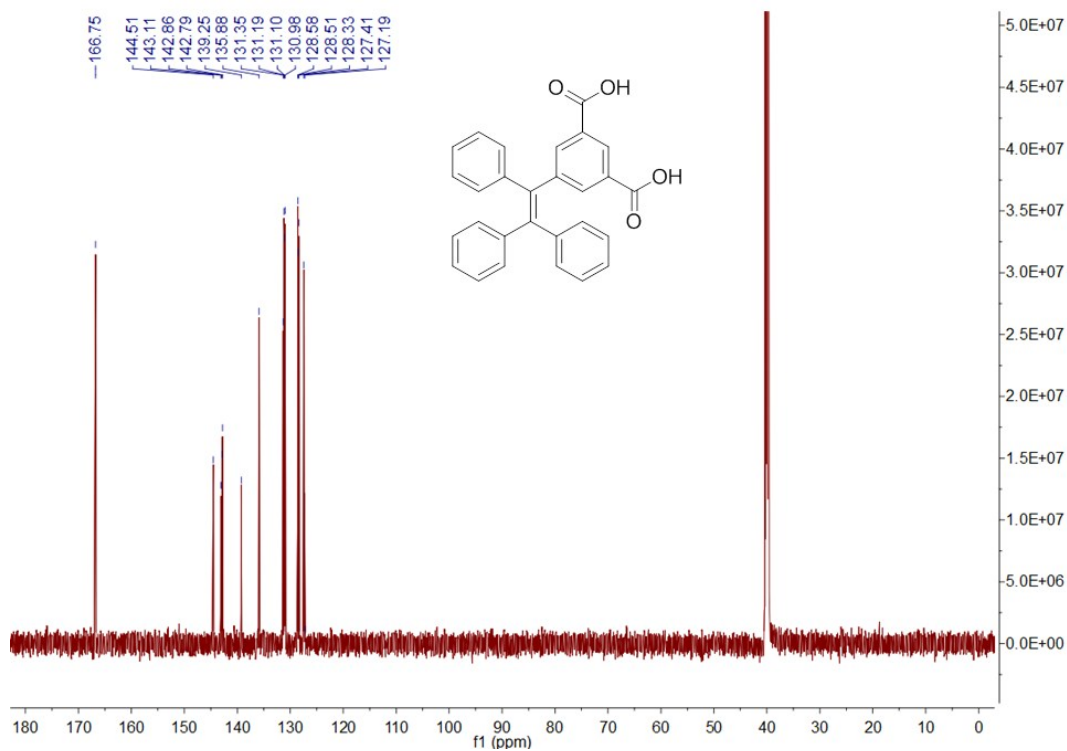


Figure S7. $^{13}\text{C-NMR}$ spectrum of TPE-2COOH.

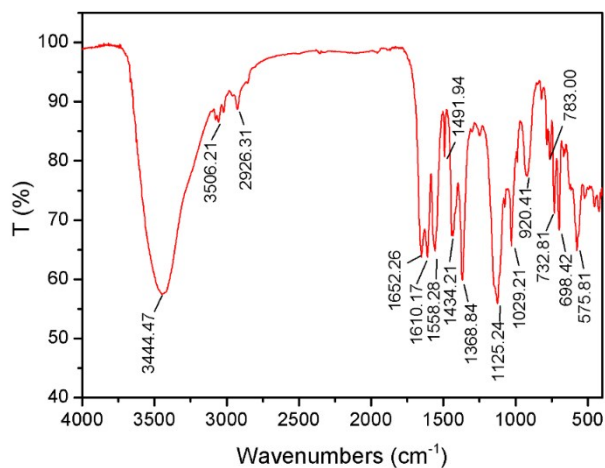


Figure S8. Infrared spectra of **1**

Table S1. The fitting data obtained from Figure 3A and calculated rate constants used in Figure 3B.

Equation	$y = a + b \cdot x$		
Temperature (°C)		Value	Standard Error
5	Intercept	2.45383	0.03016
	Slope (k)	0.09010	0.00104
	Adj. R-Square	0.99339	-
10	Intercept	2.35399	0.06546
	Slope (k)	0.13468	0.00226
	Adj. R-Square	0.98616	-
15	Intercept	1.92260	0.08912
	Slope (k)	0.18207	0.00307
	Adj. R-Square	0.98596	-
20	Intercept	1.48601	0.22619
	Slope (k)	0.31565	0.00780
	Adj. R-Square	0.97038	-
25	Intercept	1.40119	0.30627
	Slope (k)	0.45984	0.01056
	Adj. R-Square	0.97431	-
30	Intercept	0.93508	0.55060
	Slope (k)	0.66900	0.01898
	Adj. R-Square	0.96129	-

Table S2. Crystallographic data and structure refinement details for 1

Complex	1
Formula	C ₆₈ H ₆₄ Cd ₂ N ₄ O ₁₂
CCDC	1857992
F_w	1354.03
Temp.(K)	150(2)
Wavelength(Å)	0.71073
Crystal system	monoclinic
Space group	P2 ₁ /n
a(Å)	17.222(8)
b(Å)	10.281(4)
c(Å)	36.345(18)
α (°)	90
β (°)	102.86(2)
γ (°)	90
V (Å ³)	6274(5)
Z	4
D_c (g·cm ⁻³)	1.433
μ (mm ⁻¹)	0.743
$F(0000)$	2768.0
GOF on F^2	1.145
$R_1^a(I>2\sigma(I))$	0.0857
$wR_2^b(I>2\sigma(I))$	0.1939

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

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

Complex 1			
Cd(1)-O(3)	2.301(6)	Cd(2)-O(1)	2.314(6)
Cd(1)-O(4)	2.389(5)	Cd(2)-O(2)	2.384(6)
Cd(1)-O(6)	2.217(5)	Cd(2)-O(5)	2.216(5)
Cd(1)-O(7)	2.198(4)	Cd(2)-O(8)	2.216(5)
Cd(1)-O(11)#1	2.282(4)	Cd(2)-O(9)#2	2.314(5)
Cd(1)-O(12)#1	2.394(4)	Cd(2)-O(10)#2	2.359(5)
O(3)-Cd(1)-O(4)	178.0(2)	O(1)-Cd(2)-O(2)	176.3(2)
O(3)-Cd(1)-O(12)#1	92.2	O(1)-Cd(2)-O(9)#2	87.4(2)
O(4)-Cd(1)-O(12)#1	89.9(2)	O(1)-Cd(2)-O(10)#2	94.3(2)
O(6)-Cd(1)-O(3)	91.6(2)	O(5)-Cd(2)-O(1)	98.1(2)
O(6)-Cd(1)-O(4)	87.2(2)	O(5)-Cd(2)-O(2)	83.9(2)
O(6)-Cd(1)-O(11)#1	96.28(17)	O(5)-Cd(2)-O(8)	120.05(18)
O(6)-Cd(1)-O(12)#1	151.82(17)	O(5)-Cd(2)-O(9)#2	144.91(17)
O(7)-Cd(1)-O(3)	97.2(2)	O(5)-Cd(2)-O(10)#2	89.12(17)
O(7)-Cd(1)-O(4)	81.9(2)	O(8)-Cd(2)-O(1)	92.0(2)
O(7)-Cd(1)-O(6)	117.43(18)	O(8)-Cd(2)-O(2)	84.3(2)
O(7)-Cd(1)-O(11)#1	145.62(17)	O(8)-Cd(2)-O(9)#2	94.17(17)
O(7)-Cd(1)-O(12)#1	89.72(16)	O(8)-Cd(2)-O(10)#2	148.90(17)
O(11)#1-Cd(1)-O(3)	87.8(2)	O(9)#2-Cd(2)-O(2)	92.7(2)
O(11)#1-Cd(1)-O(4)	93.9(2)	O(9)#2-Cd(2)-O(10)#2	55.83(16)
O(11)#1-Cd(1)-O(12)#1	56.02(15)	O(10)#2-Cd(2)-O(2)	88.8(2)

#1 +x, 1+y, +z; #2 +x, -1+y, +z.