Electronic Supplementary Information

Acridine based metal-organic framework host-guest featuring efficient photoelectrochemical-type photodetector and white LED

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Experimental section

1. Materials and general methods

5-ethoxyisophthalic acid (EtOIPA), cadmium acetate and acridine (AD) were bought from commercial providers and used without further purification. The Powder X-ray diffraction (PXRD) analyses were recorded on a RigakuDmax2500 diffractometer with Cu-Kα radiation in arrange of 5−50° with a scan speed of 10 °/minute. Thermo gravimetric analyses (TGA) were conducted from room temperature to 800 °C using TG/DTA 6300 simultaneous thermal analyzer under a air atmosphere at a heating rate of 10 °C/min. The UV−vis absorption spectrum were measured on UH4150 spectrophotometer with a slit of 6 nm. Fourier transform infrared spectroscopy (KBr pellets) were measured on a Magna 750 FT-IR spectrophotometer in the 4000-400 cm^{-1} wavelength range. Room temperature photoluminescence spectra, quantum yield and time-resolved lifetime were tested on an Edinburgh FLS1000 fluorescence spectrometer equipped with time-resolved single photon counting-multi-channel scaling (MCS) mode. The morphology of the title MOF coated ITO film was investigated by a field emission scanning electron microscope (SEM Sigma 500). The current–voltage characteristic of the LED device was detected by Keithley 2400 source meter with the increase of voltage from 0 to 9 V. The photoluminescence spectrum of the LED device can be obtained from Edinburgh FLS1000 fluorescence spectrometer with the Keithley 2400 source meter as additional power source.

Photoelectrochemical (PEC)-type photodetector were measured by a CHI 660E

electrochemical workstation in a standard three-electrode system with 0.5 M Na_2SO_4 aqueous solution, MOF coated indiumtin oxide (ITO) glass, platinum wire and Ag/AgCl as electrolyte, working electrode, counter electrode, and reference electrode, respectively. The cyclic voltammograms (CV) was tested in a voltage range of -0.6 to 0.6 V vs Ag/AgCl with scan rate of 50 mV/s. The transient current density–time curves were recorded under the periodically discontinuous 300 W Xe lamp illumination at a bias potential of 0 and -0.5 V. Electrochemical impedance spectroscopy (EIS) Nyquist plots were obtained at the potential of 0 V and -0.5 V potential in three-electrode system. The wavelength-dependent photocurrent was tested by a photoelectrochemical analyzer equipped with a Omni-λ150 monochromator by using above three-electrode system in 0.5 M Na_2SO_4 aqueous solution.

2. Syntheses of [Cd$_3$(EtOIPA)$_4$(HAD)$_2$]H$_2$O (1)

A mixture of 5-ethoxyisophthalic acid (0.2 mmol, 0.0420 g), acridine (0.1 mmol, 0.0179 g), cadmium acetate (0.5 mmol, 0.1332 g) and deionized water (8ml) was sealed in a Teflon-lined stainless steel vessel, heated to 120 °C for 48 h. After cooling to room-temperature naturally, yellow sheet crystals **1** were washed several times with deionized water and dried in air. Yield: 50% (based on Cd). IR (KBr pellet, cm^{-1}): 3468 m, 3087 w, 2985 w, 2904 w, 2380 w, 1661 w, 1579 s, 1448 m, 1382 s, 1318 m, 1266 m, 1116 m, 1056 s, 889 m, 779 s, 723 s, 603 w, 457 m.

3. Preparation of the LED device

A mixture of MOF powders (50 mg) as phosphor and organic silica gel (about 2 mL)

4. X-ray crystal structure

Single-crystal X-ray diffraction data for $[Cd_3(EtOIPA)_4(HAD)_2]H_2O$ (**1**) were collected at normal temperature (293K) on an Oxford Diffraction SuperNova area-detector diffractometer with mirror optics monochromated Mo Kα radiation (λ = 0.71073 Å). The data collection, data reduction and empirical absorption correction were conducted by CrysAlisPro.[1] The crystal structure were solved by direct methods, using SHELXS-2014 and lasted-squares refined with SHELXL-2014, and using anisotropic thermal displacement parameters for all non-hydrogen atoms.[2,3] The crystallographic data and selected bond length/angle for $[Cd_3(EtOIPA)_4(HAD)_2]·H_2O$ (**1**) were listed in Table S1. The CIF file of $[Cd_3(EtOIPA)_4(HAD)_2]·H_2O$ (**1**) (CCDC No. 2174954) can be gained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Table S1. Crystallographic data for **1**.

MOF	**1**
Formula	$C_{65}H_{54}Cd_3N_2O_{21}$
Formula weight	1550.31
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.3911(4)
b (Å)	17.2576(7)
c (Å)	19.1393(7)
α (°)	108.185(3)
β (°)	100.971(3)
γ (°)	107.234(3)
V (Å^3)	2959.3(2)
Z	2
Dc (g cm^{-3})	1.740
μ (mm^{-1})	1.153
R_{int}	0.0267
Goof	1.195
R_1 / wR_2 [I >2σ(I)]	0.0467/0.1096
R_1 / wR_2 (all data)	0.0568/0.1142

Table S2. Selected bond length/angle for **1**.

Atoms	Length/Å	Atoms	Length/Å
Cd1–O1	2.560(4)	Cd1–O2	2.257(3)
Cd1–O6	2.216(4)	Cd1–O8#1	2.402(4)
Cd1–O9#1	2.354(4)	Cd1–O11	2.235(4)
Cd2–O2#2	2.326(3)	Cd2–O2	2.326(3)
Cd2–O7#2	2.273(3)	Cd2–O7	2.273(3)
Cd2–O12	2.220(4)	Cd2–O12#2	2.220(4)
Cd3–O4#2	2.428(4)	Cd3–O4#5	2.428(4)
Cd3–O14	2.234(3)	Cd3–O14#6	2.234(3)
Cd3–O16	2.218(3)	Cd3–O16#6	2.218(3)
Cd4–O4#7	2.269(4)	Cd4–O13#4	2.311(4)
Cd4–O14#4	2.496(3)	Cd4–O17#1	2.240(4)
Cd4–O19	2.233(4)	Cd4–O18	2.491(4)

Atoms	Angle/°	Atoms	Angle/°
O1–Cd1–O18#1	88.51(14)	O2–Cd1–O1	53.55(12)
O2–Cd1–O8#1	99.33(13)	O2–Cd1–O9#1	139.25(13)
O2–Cd1–O18#1	121.14(14)	O6–Cd1–O1	97.20(15)
O6–Cd1–O2	109.81(14)	O6–Cd1–O8#1	146.56(13)
O6–Cd1–O9#1	91.89(13)	O6–Cd1–O11	94.39(15)
O6–Cd1–O18#1	119.12(15)	O8#1–Cd1–O1	86.92(14)
O9#1–Cd1–O1	90.83(14)	O11–Cd1–O2	107.60(14)
O11–Cd1–O1	160.48(14)	O11–Cd1–O9#1	104.46(15)
O11–Cd1–O8#1	92.02(15)	O2#2–Cd2–O2	180.0
O11–Cd1–O18#1	99.50(15)	O7#2–Cd2–O2	92.27(13)
O7–Cd2–O2#2	92.26(13)	O7#2–Cd2–O2#2	87.74(13)
O7–Cd2–O2	87.74(13)	O12–Cd2–O2	82.00(14)
O7–Cd2–O7#2	180.0	O12–Cd2–O2#2	98.00(14)
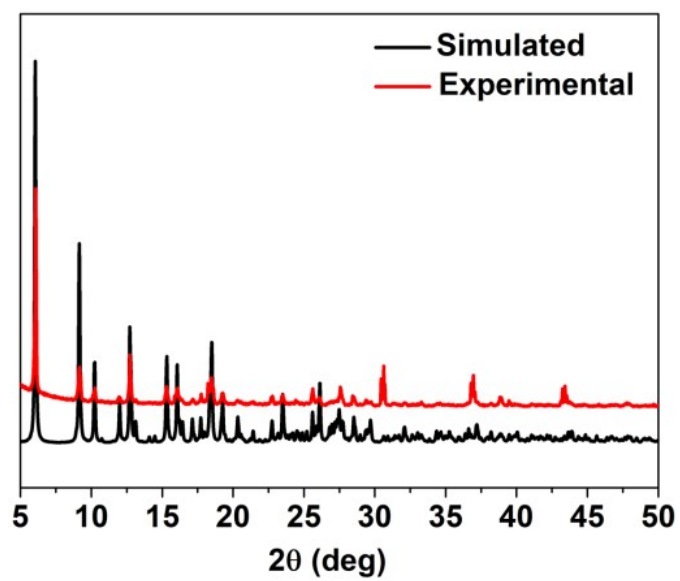
Figure S1. PXRD patterns of $[Cd_3(EtOIPA)_4(HAD)_2] \cdot H_2O$ (**1**).
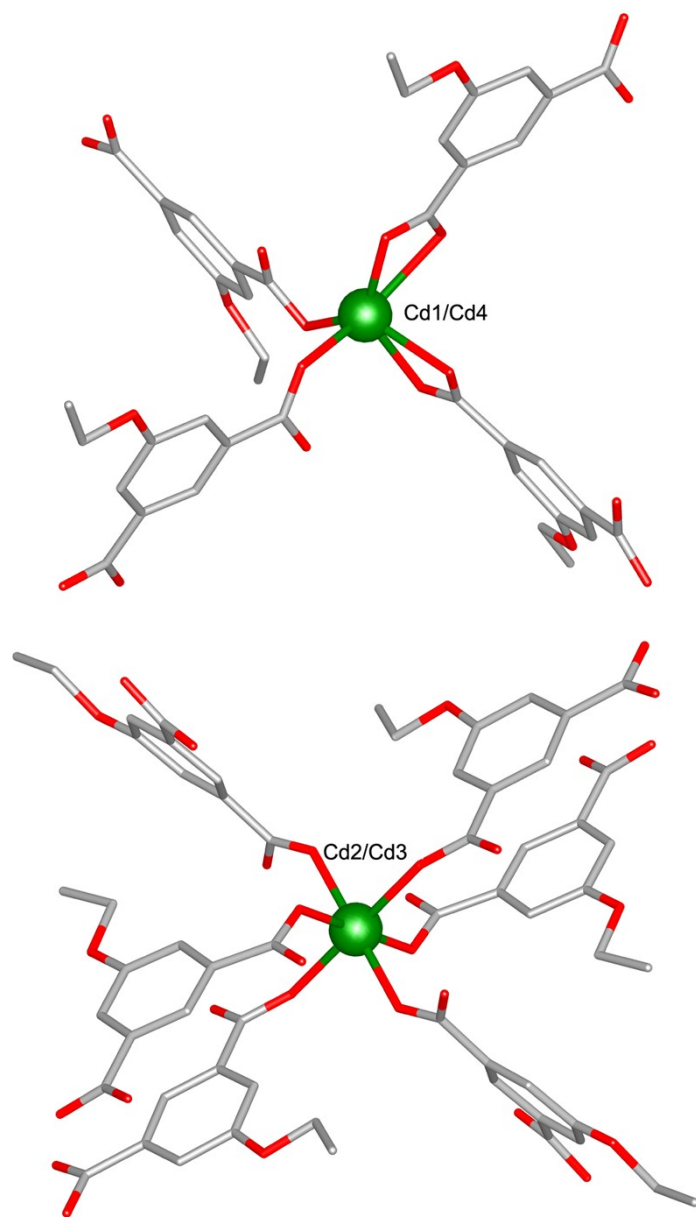
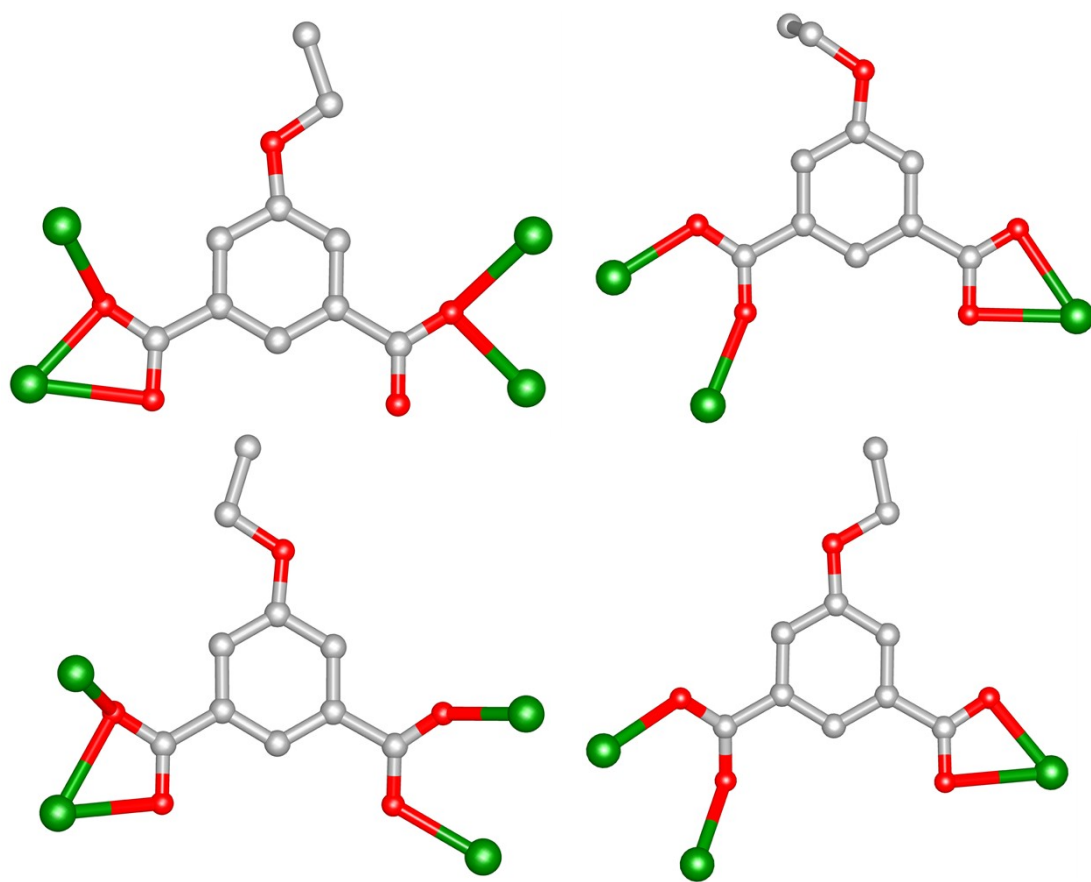**Figure S2.** Coordination environments of four independent Cd(II) ions in **1**.

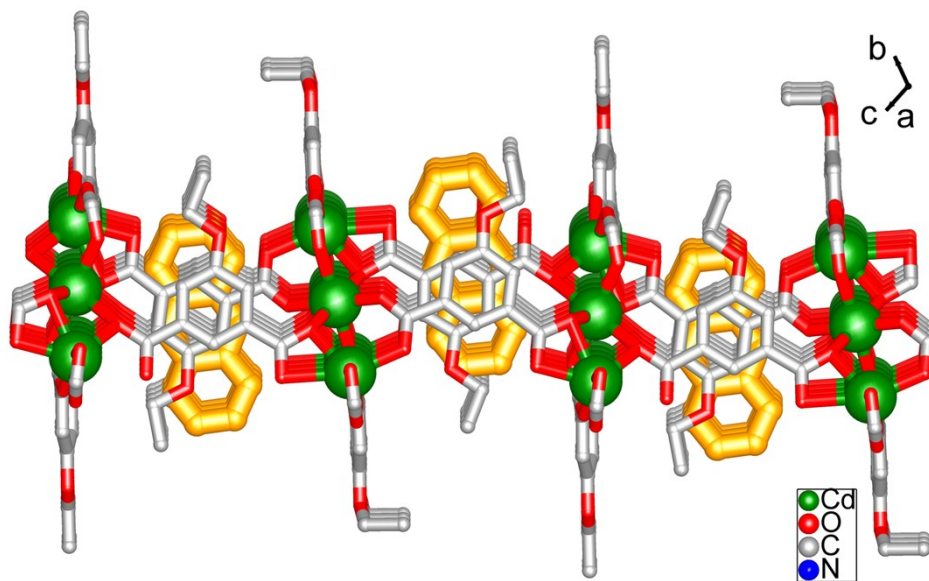**Figure S3.** Coordination modes of EtOIPA ligand in **1**.

Figure S4. View of the 2D network of **1** along a direction with protonated AD guests loaded in each grids in **1**.
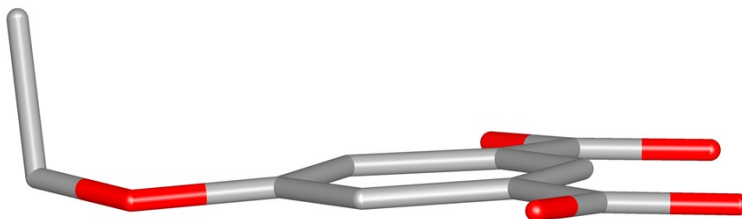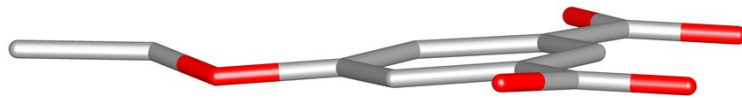
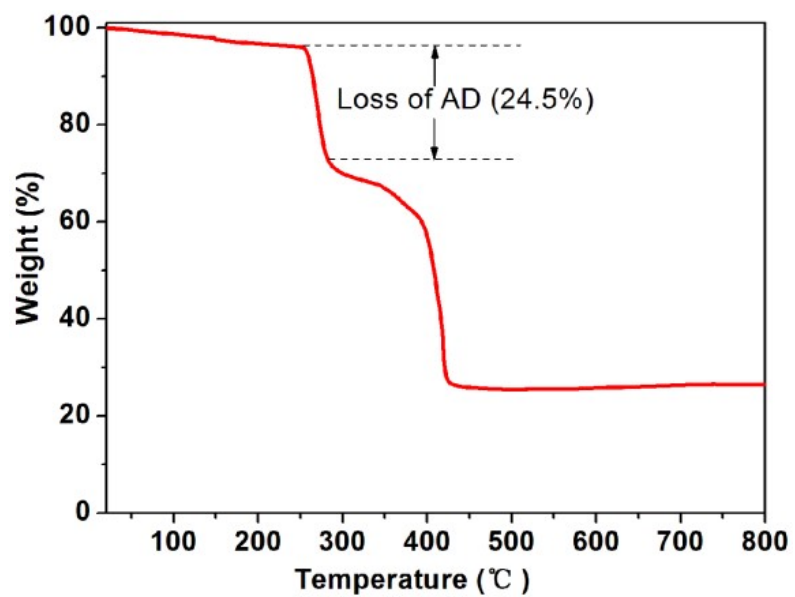**Figure S5.** Steric configuration of EtOIPA ligand in **1**.

Figure S6. Thermo gravimetric analysis curve of $[Cd_3(EtOIPA)_4(HAD)_2]\cdot H_2O$ (**1**).
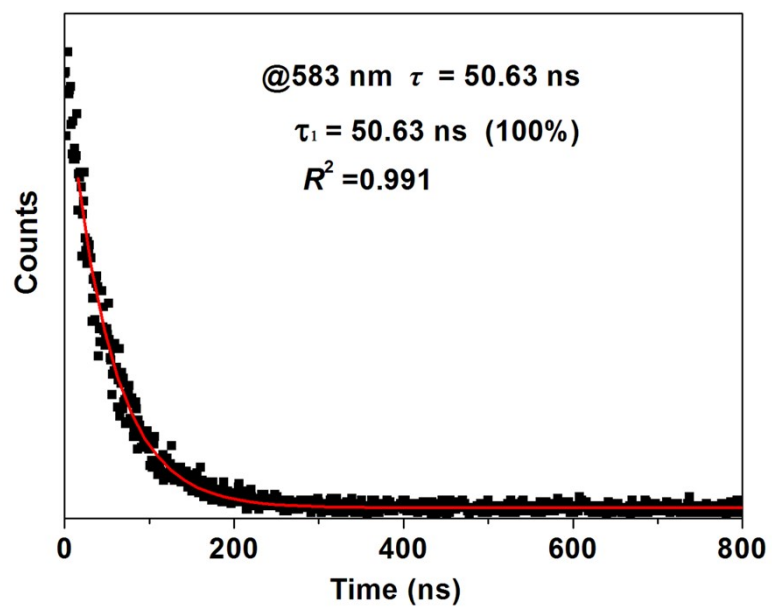
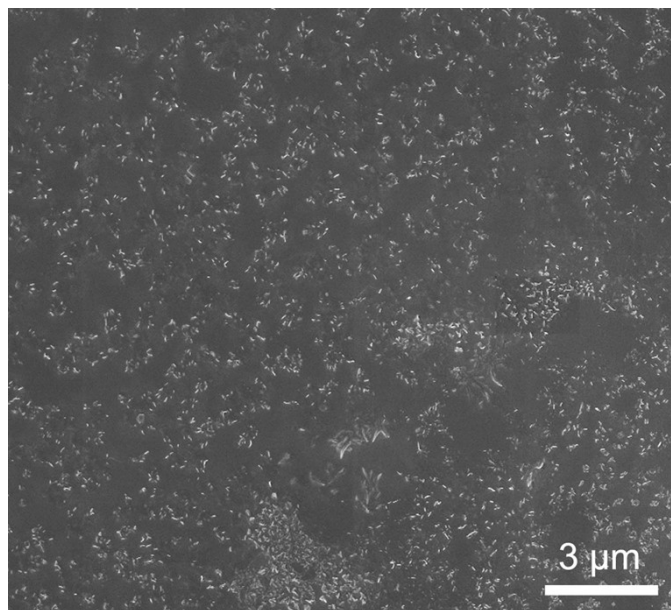**Figure S7.** PL decay curve of **1** measured at room temperature.

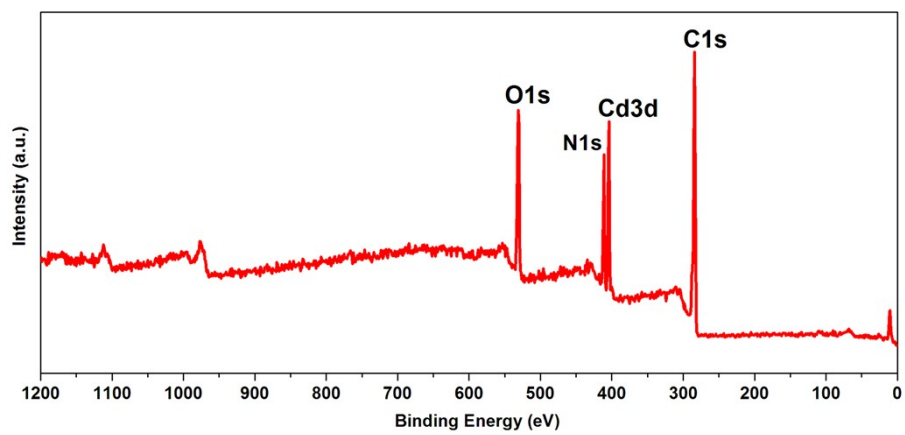**Figure S8.** SEM image of the title MOF coated ITO film.

Figure S9. XPS spectrum of the MOF coated ITO film after PEC measurements.

Supporting References

1. CrysAlisPro, Rigaku Oxford Diffraction, Version 1.171.39.6a.

2. G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64**, 112.

3. (*a*) B. Delley, *J. Chem. Phys*. 1990, **92**, 508; (*b*) B. Delley, *J. Chem. Phys*. 2000, **113**, 7756.