<Electronic Supporting Information>

A water-stable homochiral luminescent MOF constructed from achiral acylamide-containing dicarboxylate ligand for enantioselective sensing of penicillamine

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Section S1. Materials and Physical Measurements

All chemicals were of analytical grade and used without further purification. The elemental analyses for C H and N were carried out on a Perkin-Elmer 2400 II analyzer. Infrared spectra were recorded on a Nicolet-5700 FT-IR spectrophotometer with KBr pellets in the 4000-400 cm⁻¹ region. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere with a heating rate of 10 °C min⁻¹ using a Netzsch STA 449C thermal analyzer. The powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) at room temperature. The measurements of SHG were carried out on the sieved powder samples by using the Kurtz and Perry method with a 1064 nm Q-switch laser.^{S1} The N₂ adsorption/desorption isotherms were measured volumetrically using a Micromeritics ASAP 2020 surface area. The contact angle toward water was recorded with an Attension TL101 (Biolin Scientific). The photoluminescence spectra were measured on a Hitachi F-4600 fluorescence Spectrometer. The lifetime measurements were measured on an Edinburgh Instruments FSL980 Fluorescence Spectrometer. The liquid-state CD spectra were conducted on a Jasco J-810 spectropolarimeter.

Section S2. Experimental Section

Synthesis of {[Cd(L)(4,4'-bipy)] DMA 5H₂O}_{*n*} (1). A mixture of H₂L (45.4 mg, 0.1 mmol), Cd(NO₃)₂ 4H₂O (30.8 mg, 0.1 mmol) and 4,4'-bipyridine (15.6 mg, 0.1 mmol) in 7 ml of DMA/H₂O (2:5, v/v) was placed in a Teflon-lined stainless steel vessel and heated at 120 °C for 3 days, and then cooled to room temperature at a rate of 5 °C/h. Colorless block-shaped crystals were obtained. Anal. Calcd for C₄₀H₄₃N₅O₁₂Cd: C, 53.49; H, 4.83; N, 7.80%. Found: C, 53.42; H, 4.89; N, 7.84%. IR (KBr, cm⁻¹): 3270, 3051, 1651, 1602, 1519, 1397, 1321, 1256, 1179, 1148, 1106, 1074, 1017,909, 881,859, 808, 789, 699, 631, 500, 446.

Activation of 1a. The as-synthesized sample of 1 was immersed into anhydrous methanol for 3 days, methanol was refreshed three times during the exchange. Then similar immersion was utilized to treat the sample with dichloromethane to remove methanol molecules. After the removal of dichloromethane by centrifuging, the wet sample was dried under vacuum at 80 °C for 12 h to yield activated 1 (denoted as 1a). Solid samples of activated 1a were ground into powder and used for sensing experiments. The framework of 1a retains its integrality after removal of guest molecules confirmed by TGA and powder X-ray diffraction (PXRD) (Fig. S10)

Section S3. X-ray Crystallography

Single-crystal X-ray diffraction data were collected on a Bruker SMART-1000 CCD diffractometer with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation at room temperature. The structures were solved by direct methods and refined with full-matrix least-squares on F^2 using the SHELX-2017/1 program package.⁸² All non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms on ligands were placed in idealized positions with isotropic thermal parameters. The hydrogen atoms on amide groups, isolated water molecules and isolated DMA molecules were found from the different Fourier maps, while the hydrogen atoms attached to carbon atoms were generated geometrically and refined by using a riding mode. Crystal and refinement data are summarized in Table S1, the selected bond lengths and bond angles are listed in Table S2. CCDC 1821252 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

	1
Empirical formula	$C_{40}H_{43}N_5O_{12}Cd$
Formula weight	898.19
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2
Flack	0.04(2)
<i>a</i> (Å)	13.8223(11)
<i>b</i> (Å)	25.3271(17)
<i>c</i> (Å)	11.6674(9)
$V(\text{\AA}^3)$	4084.5(5)
Ζ	4
$ \rho_{\text{calcd}} (\text{g cm}^{-3}) $	1.461
$\mu (\mathrm{mm}^{-1})$	0.603
<i>F</i> (000)	1848
heta range ()	2.284 to 28.493
Index ranges	$-15 \le h \le 18, -31 \le k \le 33, 15 \le l \le 15$
Data/restraints/parameters	9943/0/522
GOF on F^2	1.034
$R_1^{a}, w R_2^{b} [I > 2\sigma(I)]$	0.0582, 0.1126

Table S1. Crystal data and structure refinement parameters for 1.

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|; {}^{b}wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}.$

Bond lengths						
Cd1-O1	2.306(6)	Cd1-O2	2.806(6)			
Cd1-O2A	2.283(6)	Cd1-O5C	2.437(6)			
Cd1-O6C	2.340(6)	Cd1-N3	2.301(6)			
Cd1-N4B	2.324(7)					
Bond angles						
O1-Cd1-O2	49.5(2)	O1-Cd1-O2A	129.2(2)			
O1-Cd1-O5C	137.8(2)	O1-Cd1-O6C	83.5(2)			
O1-Cd1-N3	89.6 (3)	O1-Cd1-N4B	91.3(3)			
O2-Cd1-O2A	79.8(2)	O2-Cd1-O5C	171.1(2)			
O2-Cd1-O6C	132.7(2)	O2-Cd1-N3	88.4(3)			
O2-Cd1-N4B	88.1(3)	O2A-Cd1-O5	92.9 (2)			
O2A-Cd1-O6C	147.1(2)	O2A-Cd1-N3	86.7(3)			
O2A-Cd1-N4B	88.5(3)	O5C-Cd1-O6C	54.3(2)			
O5C-Cd1-N3	96.2(3)	O5C-Cd1-N4B	86.7(3)			
O6C-Cd1-N3	98.1(3)	O6C-Cd1-N4B	87.4(3)			
N3-Cd1-N4B	174.5(3)					

Table S2. Selected bond lengths (Å) and angles ($\ref{schedule}$ for 1.

Symmetry codes, A: -x, 2-y, z; B: x, y, -1+z; C: -1.5+x, 1.5-y, -z.

Table S3. Hydrogen bonds for 1.

D-H ···A	D-H (Å)	$\mathrm{H}\cdot\cdot\mathrm{A}(\mathrm{\AA})$	$D \cdots A (Å)$	D-H ···A ()
N1-H1A ··· O12	0.93	1.82	2.755 (11)	175.0
N2-H2A ··· O8	0.91	1.91	2.822 (11)	178.0
O8-H8A ··· O7	0.85	1.93	2.666 (16)	145.0
O8-H8B ··· O12F	0.85	2.21	3.021 (13)	159.0
O9D-H9A ·· O10D	0.85	2.02	2.769 (13)	146.0
O9E-H9B ··· O3	0.85	2.17	2.944 (12)	152.0
O10D-H10B ··· O4	0.85	2.18	3.002 (12)	161.0
O11H-H11A ·· O5C	0.85	2.11	2.912 (12)	157.0
O11D-H11B ··· O9D	0.85	1.93	2.775 (14)	173.0
012G-H12A ··· O6C	0.85	1.87	2.647 (11)	152.0
O12G-H12B ··· O1	0.85	1.95	2.743 (10)	156.0

Symmetry codes, C: -1.5+x, 1.5-y, -z; D: 2-x, 1-y, z; E: 3/2-x, 1/2+y, 1-z; F: 1/2+x, 3/2-y, -z; G: -1/2+x, 3/2-y, -z; H: -1/2+x, 3/2-y, 1-z.

	a	b	С	R_1	wR_2	Flack	Goodness-of-
						parameter	fit on F^2
1	13.8223(11)	25.3271(17)	11.6674(9)	0.0582	0.1126	0.04(2)	1.034
2	13.8555(12)	25.388(2)	11.6912(11)	0.0745	0.1749	0.04(4)	1.034
3	13.910(5)	25.472(9)	11.761(4)	0.0882	0.1981	0.06(6)	1.112
4	13.8254(12)	25.361(2)	11.6938(11)	0.0450	0.0944	0.014(17)	1.040
5	13.8582(11)	25.401(2)	11.6894(9)	0.0752	0.1812	-0.04(5)	1.195
6	13.8374(13)	25.351(2)	11.6808(12)	0.0728	0.1814	0.04(4)	1.224
7	13.8058(11)	25.298(2)	11.6522(9)	0.0871	0.2061	0.03(5)	1.046
8	13.8402(11)	25.391(2)	11.6657(8)	0.0946	0.2294	0.08(7)	1.087
9	13.8673(11)	25.422(2)	11.7259(9)	0.0937	0.1827	0.07(6)	1.083

Table S4. A summary of structure determinations of 9 randomly selected crystals in the products of **1** from the same crystallization: the R factors and Flack absolute structure parameters for each refinement.



Fig. S1 Coordination environment of Cd²⁺ in **1**, the isolated water molecules, isolated DMA molecule and H atoms are omitted for clarity. (Symmetry codes, A: -x, 2-y, z; B: x, y, -1+z; C: -1.5+x, 1.5-y, -z).



Fig. S2 Coordiation modes of carboxylate groups in L^{2-} ligand in 1.



Fig. S3 3D framework of 1 along the *c* axis.



Fig. S4 View of the H-bonding interactions between water and the NH group of the acylamide groups. The X-ray crystallographic results clearly demonstrate that guest water molecules could easily interact with the -NH and -C=O moieties of the acylamide groups *via* N-H \cdots O and O-H \cdots O hydrogen bonds (O[water] \cdots N[acylamide] = ca. 2.8 Å, O[water] \cdots O[acylamide] = ca. 3.0 Å).



Fig. S5 Solid-state CD spectra of bulk sample of 1 from seven batches (curves 1–7).



Fig. S6 Solid-state CD spectra of 12 randomly selected crystals of 1.



Fig. S7 Oscilloscope traces of the SHG signals for the powders of 1.



Fig. S8 The dihedral angles of the aromatic rings in L^{2-} ligand.

Section S4. General characterizations

Contact angles of water



Fig. S9 Contact angles of water in 1a.

Thermal Analysis (TGA) and Powder X-ray Diffraction (PXRD) Properties. TGA was carried out under N₂ atmosphere. The TGA curve shows an obvious weight loss of 19.73% in the temperature range of 110–235 °C, corresponding to the loss of five water molecules and one DMA molecule (calculated: 19.68%). No further weight loss was observed below 360 °C (Fig. S10a). The phase purity of the as-synthesiaed sample was confirmed by comparing its experimental PXRD patterns to that simulated based on the single crystal structure (Fig. S10b).



Fig. S10 (a) The TGA curves for 1 and 1a. (b) PXRD of 1, 1a and the sample of 1a treated by D-Pen and L-Pen.

Section S5. Fluorescent Sensing of D/L-Pen

The fine grinding sample **1a** (2 mg) was dispersed in 5 mL water by ultrasonication, which was subsequently placed in a quartz cell of 1 cm width for fluorescence measurements. For all measurements, the fluorescence spectra of **1a** were recorded at 298 K with maximum emission wavelength at 460 nm ($\lambda_{ex} = 340$ nm). 200 μ L solution of each analyte (1 mM) was added to 1 mL the dispersion of **1a** in water, and then the fluorescence efficiency was calculated by $[(I_0-I)/I_0] \times 100\%$, where I_0 and I are the initial fluorescence intensity and the fluorescence intensity in the presence of analyte, respectively. All the titrations were carried out by gradually adding analytes (1 mM) solution in an incremental fashion. Each titration was repeated at least three times to get concordant value.



Fig. S11 Liner relation between fluorescence intensity of 1a and the concertration of D-Pen.



Fig. S12 Liner relation between fluorescence intensity of 1a and the concertration of L-Pen.

 Analyte
 S (μM⁻¹)
 Standard Deviation (σ)
 Detection limit^a (μM)

 D-Pen
 23.72
 6.8
 0.9

 L-Pen
 10.13
 7.0
 2.1

Table S5. The values of *S*, Standard deviation and detection limit of 1a toward D-Pen and L-Pen at room temperature.

^{*a*}Detection limit is calculated according to the formula: LOD = $3\sigma/S$, σ : standard deviation, S: slope.

Table S6. The comparison of different analytic methods for recognition of Pen.

Method	Linear range	Sensitivity of Pen	LOD of Pen	Ref.	
EC ^{<i>a</i>}	$606000~\mu\text{M}$	μM 0.0497 $\mu A \mu M^{-1}$ (D-Pen)		[S3a]	
EC ^{<i>a</i>}	0.06-7.5 and 7.5-140 $\mu\mathrm{M}$	$0.3060 \mu A \mu M^{-1}$	$0.01\mu\mathrm{M}$	[S3b]	
EC ^a	0.05-300 μM	$0.5155 \mu A \mu M^{-1}$	0.21 μM	[S3c]	
ECL ^b	100 5000 M		31 µM (D-Pen)	[S4]	
	100–3000 μΝι		33 µM (L-Pen)		
CE ^c	57 11477M	1770.00 $\mu A \mu M^{-1}$ (D-Pen)	17.3 µM (D-Pen)	[S5]	
	<i>37</i> -11477 μW	1386.67 µA µM ⁻¹ (L-Pen)	17.3 µM (L-Pen)		
Luminescent	20.167.14	23.72 μM ⁻¹ (D-Pen)	0.9 µM (D-Pen)		
method with MOF	20-107 μivi	10.13 µM ⁻¹ (L-Pen)	2.1 µM (L-Pen)	1 nis work	

^aElectrochemistry, ^belectrochemiluminescence, ^ccapillary electrophoresis.



Fig. S13 (a) Time-resolved fluorescence decay of **1a** before and after addition of D-Pen (IRF = Instrument Response Function). (b) Temperature dependent SV plots generated by the addition of D-Pen. (c) FTIR spectra of **1a**, D-Pen and **1a**+D-Pen complex. (d) Benesi–Hildebrand plots of **1a** with D-Pen and L-Pen.



Fig. S14 Adsorption isotherms of D-Pen and L-Pen in 1a at room temperature in aqueous solutions.

References

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