Electronic Supplementary Information

Highly efficient electrochemical recognition and quantification of amine enantiomers based on a guest-free homochiral MOF

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S1. Reagents and materials

Enantiomers R(+)/S(−)-α-methylbenzylamine (99%) were purchased from Aladdin (Aladdin Chemistry Co. Ltd., Shanghai, China). L-leucine, salicylaldehyde and other chemicals were purchased from Sinopharm (Sinopharm Chemical Reagent Co., Ltd, Beijing, China). All chemicals are of analytical reagents grade and used as received without further purification. Ultrapure water (18.2 MΩ cm) was obtained from a Water Pro water purification system (Labconco Corporation, Kansas City, MO) and used throughout the experiments.

S2. Instruments and characterization

Elemental analyses (C, H, N) were achieved on a Perkin-Elmer Model 2400 analyzer. Scanning Electron Microscopy (SEM) images were obtained from an FEI Quanta FEG250 Scanning Electron Microscope (America). Thermogravimetric (TG) analyses were carried out under flowing nitrogen at a heating rate of 10 °C·min−1 on a STA449C integration thermal analyzer. Powder X-ray Diffraction (PXRD) data were collected at room temperature (298 K) on a D8 FOCUS Powder X-ray Diffractometer (Germany, BRUKER AXS GMBH). The solid state CD spectra were obtained using a J-815 spectropolarimeter (Jasco, Japan). The Brunauer-Emmett-Teller (BET) surface area analysis was performed on an ASAP 2020/TriStar 3000 (Micromeritics) using nitrogen adsorption at 77 K. All electrochemical measurements were performed on a CHI760D electrochemical workstation (Shanghai CH Instruments Co., China).

S3. Single crystal X-ray structure determination

Single crystal data collection for $(Cu_4L_4)_n$ was made on an Oxford Diffraction Gemini E (Enhance Cu X-Ray source, Kα, λ = 1.54184 Å) equipped with a graphite monochromator and ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd) at room temperature (298K). The structure was solved with the XSS4 structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Parameters for data collection and refinement are summarized in Table S1. Selected bond lengths and angles are given in Table S2.

Table S1 Phase data for $(Cu_4L_4)_n$

Space-group	*P* 1 (1) - triclinic
Cell	a=8.5213(3) Å b=12.9489(4) Å c=13.3149(5) Å α=68.372(3)° β=82.029(4)° γ=89.978(4)° V=1350.50(9) Å^3 Z=1

Table S2 Atomic parameters for $(Cu_4L_4)_n$

Atom	Ox.	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U [Å^2]
C1		1a	1		1.0297(10)	0.1479(7)	0.5509(7)	
C2		1a	1		1.0674(10)	0.0684(8)	0.5041(7)	
H2		1a	1		1.06800	-0.00650	0.54800	0.0500
C3		1a	1		1.1033(15)	0.1026(10)	0.3929(9)	
H3		1a	1		1.13210	0.05080	0.36130	0.0810
C4		1a	1		1.0973(17)	0.2149(11)	0.3260(9)	
H4		1a	1		1.12230	0.23850	0.25040	0.0910
C5		1a	1		1.0550(14)	0.2862(10)	0.3733(8)	
H5		1a	1		1.04890	0.36030	0.32840	0.0700
C6		1a	1		1.0199(10)	0.2590(7)	0.4830(6)	
C7		1a	1		0.9551(10)	0.3420(7)	0.5286(7)	
H7A		1a	1		0.84330	0.32210	0.55580	0.0460
H7B		1a	1		0.96250	0.41390	0.46920	0.0460
C8		1a	1		1.1736(10)	0.4319(7)	0.5823(6)	
H8		1a	1		1.23290	0.42380	0.51740	0.0430
C9		1a	1		1.1288(11)	0.5530(7)	0.5502(8)	
H9A		1a	1		1.09240	0.56570	0.61680	0.0520
H9B		1a	1		1.03940	0.56230	0.51040	0.0520
C10		1a	1		1.2566(12)	0.6443(8)	0.4811(9)	
H10		1a	1		1.35230	0.62920	0.51620	0.0760
C11		1a	1		1.299(2)	0.6413(13)	0.3645(11)	
H11A		1a	1		1.20330	0.64330	0.33320	0.1690
H11B		1a	1		1.35060	0.57410	0.36930	0.1690
H11C		1a	1		1.36830	0.70440	0.31920	0.1690
C12		1a	1		1.2041(17)	0.7579(9)	0.4765(14)	
H12A		1a	1		1.11210	0.77550	0.44040	0.1440
H12B		1a	1		1.28830	0.81300	0.43680	0.1440
H12C		1a	1		1.17870	0.75680	0.54940	0.1440
C13		1a	1		1.2777(9)	0.3975(6)	0.6708(7)	
C14		1a	1		1.1101(9)	0.0382(7)	0.9470(6)	
C15		1a	1		1.0992(9)	0.1158(7)	0.9959(7)	
H15		1a	1		1.09190	0.19040	0.95340	0.0450
C16		1a	1		1.0990(12)	0.0844(8)	1.1067(7)	
H16		1a	1		1.08530	0.13700	1.13900	0.0640
C17		1a	1		1.1193(15)	-0.0256(9)	1.1698(7)	

H17	1a	1	1.12770	-0.04620	1.24350	0.0780
C18	1a	1	1.1267(13)	-0.1025(8)	1.1235(7)	
H18	1a	1	1.12980	-0.17700	1.16780	0.0630
C19	1a	1	1.130(1)	-0.0741(7)	1.0107(7)	
C20	1a	1	1.1409(11)	-0.1633(7)	0.9654(7)	
H20A	1a	1	1.14230	-0.23540	1.02350	0.0480
H20B	1a	1	1.23740	-0.15150	0.91360	0.0480
C21	1a	1	0.969(1)	-0.2564(6)	0.8769(7)	
H21	1a	1	1.06890	-0.26840	0.83750	0.0430
C22	1a	1	0.9180(11)	-0.3651(7)	0.9730(7)	
H22A	1a	1	0.97640	-0.36800	1.03150	0.0520
H22B	1a	1	0.80650	-0.36230	0.99900	0.0520
C23	1a	1	0.939(2)	-0.4701(9)	0.9543(10)	
C24	1a	1	0.9934(16)	-0.4815(11)	0.8635(11)	
H24A	1a	1	1.02460	-0.41900	0.80070	0.0910
H24B	1a	1	1.00140	-0.55220	0.86110	0.0910
C25	1a	1	0.922(2)	-0.5651(11)	1.0628(13)	
H25A	1a	1	0.88440	-0.63130	1.05500	0.1450
H25B	1a	1	0.84680	-0.54790	1.11460	0.1450
H25C	1a	1	1.02260	-0.57680	1.08830	0.1450
C26	1a	1	0.8528(9)	-0.2121(6)	0.7925(6)	
C27	1a	1	0.4513(10)	0.5389(7)	0.9424(7)	
C28	1a	1	0.4740(11)	0.6208(8)	0.9849(7)	
H28	1a	1	0.49620	0.69440	0.93770	0.0530
C29	1a	1	0.4638(14)	0.5938(10)	1.0953(9)	
H29	1a	1	0.47200	0.65010	1.12230	0.0790
C30	1a	1	0.4416(16)	0.4849(10)	1.1667(8)	
H30	1a	1	0.44460	0.46610	1.24090	0.0840
C31	1a	1	0.4147(13)	0.4045(9)	1.1255(8)	
H31	1a	1	0.39520	0.33120	1.17410	0.0700
C32	1a	1	0.4152(10)	0.4274(7)	1.0135(7)	
C33	1a	1	0.3639(10)	0.3388(7)	0.9744(7)	
H33A	1a	1	0.34750	0.26850	1.03610	0.0480
H33B	1a	1	0.26280	0.35720	0.94850	0.0480
C34	1a	1	0.6039(10)	0.2500(7)	0.9229(8)	
H34	1a	1	0.63460	0.26350	0.98540	0.0590
C35	1a	1	0.5466(12)	0.1279(8)	0.9648(10)	
H35A	1a	1	0.54820	0.10520	0.90300	0.0680
H35B	1a	1	0.43740	0.12040	1.00010	0.0680
C36	1a	1	0.6477(14)	0.0474(10)	1.0475(12)	
H36	1a	1	0.76100	0.06810	1.02210	0.1010
C37	1a	1	0.6070(19)	-0.0738(10)	1.0456(16)	
H37A	1a	1	0.51620	-0.10870	1.09920	0.1840
H37B	1a	1	0.69630	-0.11910	1.06190	0.1840
H37C	1a	1	0.58440	-0.06560	0.97450	0.1840
C38	1a	1	0.598(2)	0.0604(15)	1.1591(11)	
H38A	1a	1	0.54520	0.12840	1.14750	0.1700

H38B	1a	1	0.69110	0.06230	1.19200	0.1700
H38C	1a	1	0.52790	-0.00140	1.20660	0.1700
C39	1a	1	0.7455(8)	0.2848(6)	0.8352(7)	
C40	1a	1	0.6911(9)	0.6321(6)	0.5445(6)	
C41	1a	1	0.6915(10)	0.5537(7)	0.4996(7)	
H41	1a	1	0.66040	0.48060	0.54470	0.0490
C42	1a	1	0.7374(12)	0.5792(8)	0.3867(7)	
H42	1a	1	0.73680	0.52370	0.35800	0.0620
C43	1a	1	0.7836(12)	0.6889(9)	0.3189(7)	
H43	1a	1	0.81510	0.70770	0.24430	0.0670
C44	1a	1	0.7820(11)	0.7677(8)	0.3634(7)	
H44	1a	1	0.81220	0.84070	0.31760	0.0600
C45	1a	1	0.7362(9)	0.7441(6)	0.4770(7)	
C46	1a	1	0.7293(10)	0.8347(7)	0.5211(7)	
H46A	1a	1	0.80500	0.82330	0.57180	0.0460
H46B	1a	1	0.75640	0.90600	0.46190	0.0460
C47	1a	1	0.5285(10)	0.9326(7)	0.6093(7)	
H47	1a	1	0.61350	0.94530	0.64670	0.0470
C48	1a	1	0.5140(11)	1.0418(7)	0.5110(8)	
H48A	1a	1	0.58990	1.04330	0.44900	0.0540
H48B	1a	1	0.40870	1.04190	0.49120	0.0540
C49	1a	1	0.5426(19)	1.1459(8)	0.5338(11)	
C50	1a	1	0.5425(16)	1.1593(10)	0.6291(12)	
H50A	1a	1	0.52250	1.09830	0.69450	0.1000
H50B	1a	1	0.56240	1.22970	0.62960	0.1000
C51	1a	1	0.568(2)	1.2450(11)	0.4226(14)	
H51A	1a	1	0.46910	1.25880	0.39410	0.1640
H51B	1a	1	0.64490	1.22760	0.37230	0.1640
H51C	1a	1	0.60490	1.31010	0.43260	0.1640
C52	1a	1	0.3763(9)	0.8957(7)	0.6929(7)	
Cu1	1a	1	1.07268(9)	0.21347(7)	0.73208(7)	
Cu2	1a	1	1.0169(1)	-0.02538(7)	0.77321(7)	
Cu3	1a	1	0.56479(9)	0.46393(7)	0.76540(7)	
Cu4	1a	1	0.52783(9)	0.70381(7)	0.71490(7)	
N1	1a	1	1.0318(8)	0.3548(5)	0.6181(5)	
H1	1a	1	0.95280	0.38900	0.65510	0.0370
N2	1a	1	1.0000(8)	-0.1588(6)	0.9102(6)	
H2A	1a	1	0.90630	-0.15330	0.95930	0.0400
N3	1a	1	0.4773(8)	0.3237(6)	0.8860(6)	
H3A	1a	1	0.41420	0.28600	0.85210	0.0430
N4	1a	1	0.5689(8)	0.8338(5)	0.5770(6)	
H4A	1a	1	0.49360	0.82810	0.52970	0.0420
O1	1a	1	0.9930(7)	0.1178(4)	0.6605(4)	
O2	1a	1	1.3906(8)	0.4591(6)	0.6616(6)	
O3	1a	1	1.2413(7)	0.3034(4)	0.7518(4)	
O4	1a	1	1.1106(7)	0.0696(4)	0.8380(4)	
O5	1a	1	0.7507(7)	-0.2770(5)	0.7885(5)	

O6	1a	1	0.8745(8)	-0.1102(5)	0.7291(5)
O7	1a	1	0.4578(7)	0.5618(5)	0.8350(4)
O8	1a	1	0.8547(7)	0.2166(5)	0.8388(5)
O9	1a	1	0.7408(7)	0.3715(4)	0.7512(4)
O10	1a	1	0.6474(7)	0.6073(4)	0.6504(4)
O11	1a	1	0.2697(7)	0.9572(5)	0.6939(5)
O12	1a	1	0.3662(7)	0.7907(5)	0.7553(6)

S4. Synthesis of H_2L ligand, N-(2-hydroxybenzyl)-L-leucine

The ligand [N-(2-hydroxybenzyl)-L-leucine], l-H2L)] was synthesized according to the literature,[1] with minor modifications. Typically, salicylaldehyde (1.20 g, 10 mmol) in ethanol (10 mL) was added to a solution of L-leucine (0.1312g, 10 mmol) in water (30 mL) containing KOH (0.56 g, 10 mmol). The yellow solution was stirred for 30 min at room temperature, and then cooled in an ice bath. An excess of sodium borohydride (0.46 g, 12 mmol) in water (5 mL) was added to the mixture formed Schiff base intermediate. The yellow color slowly discharged after 10 min. The solution was acidified with hydrobromic acid to a pH of 3.5-5.0. The resulting solid was filtered off, washed with ethanol, and recrystallized from water/ethanol (1:1) and dried to give the final product (70% yield) as a white powder. Elemental analysis for $C_{13}H_{19}N_2O_3$ Caled: C, 62.13%; H, 7.62%; N, 11.15%. Found: C, 62.05 %; H, 7.70%; N, 11.20%.

S5. Synthesis of homochiral $(Cu_4L_4)_n$

For synthesis of $(Cu_4L_4)_n$ suitable for single crystal X-ray diffraction, ligand H_2L (7.5 mg, 0.0316 mmol) was dissolved in a mixture of LiOH aqueous solution (0.75mL, 0.1mol L^{-1}), EtOH (1mL) and acetonitrile (1mL). $CuCl_2{\cdot}2H_2O$ aqueous solution (0.3mL, 0.1mol L^{-1}) was added into the H_2L solution, then the mixture was sealed in a 10 mL of a vial at room temperature. Flaky crystals of $(Cu_4L_4)_n$ were obtained after 2 days.

For rapid synthesis of $(Cu_4L_4)_n$ nanocrystals, ligand H_2L (11.8mg, 0.05 mmol) was dissolved in LiOH aqueous solution (0.5mL, 0.0126g mL^{-1}), DMF (0.5mL) and DMSO (0.25mL). $Cu(OAc)_2$ (0.0100g) was added into H_2L solution under room temperature. The mixture turned turbid immediately, and after 2 min, the crystals were isolated by centrifugation, washed with water, and dried in a high yield (75%). Elemental analysis for $Cu_4C_{52}H_{68}N_4O_{12}$ (%) Calcd: C, 52.25%; H, 5.73%; N, 4.69%. Found: C, 53.11%; H, 5.68%; N, 4.75%.

The enantiomer of $(Cu_4L_4)_n$, homochiral $(Cu_4L_4)_n$´was synthesized exactly as $(Cu_4L_4)_n$, except *d*-HL was used instead of *l*-HL. The ligand, *d*-HL was synthesized as *l*-HL as above, except D-leucine was used instead of L-leucine. Elemental analysis for $Cu_4C_{52}H_{68}N_4O_{12}$ (%) Calcd: C, 52.25%; H, 5.73%; N, 4.69%. Found: C, 53.49%; H, 5.69%; N, 4.74%.

S6. Fabrication and measurements of chiral sensor

Glassy carbon electrodes (GCE, Φ= 4 mm) was carefully polished with 0.1 μm and 0.05 μm alumina slurry to obtain a mirror-like surface. After this, GCE washed ultrasonically with ultrapure water, nitric acid (1:1, v/v), sodium hydroxide (0.1 mol·cm^{-3}) and ethanol, respectively, and dried in air at room temperature.

A suspension containing 3.0 mg of $(Cu_4L_4)_n$, 250uL of water, 750 μL of ethanol and 30uL of Naifion was sonicated for 15 min at room temperature. Electrode modification was performed by dropping 7 μL of this solution on the surface of glassy-carbon electrode (GCE), which was dried in the air for 12 h at room temperature.

All electrochemical experiments were implemented with three electrode system. The bare or the modified GCE (4 mm in diameter), a platinum wire and a saturated calomel electrode (SCE) were used as working electrode, the counter electrode and the reference electrode, respectively. All measurements were conducted at room temperature (25±2 ^{o}C).

References

1. J. D. Ranford, J. J. Vittal, D. Wu, and X. Yang, *Angew. Chem. Int. Ed.*, 1999, **38**, 3498.