Supporting Information

Simple and visual approach for enantioselective recognition through supramolecular gels with specific selectivity

Xuemei Xu, Lang Qu, Jintong Song, Dehua Wu, Xiangge Zhou, and Haifeng Xiang*

College of Chemistry, Sichuan University, Chengdu, 610041, China

Experimental Section

Materials and Instrumentation. All reagents were purchased from commercial suppliers and used without further purification. All the Salen ligands were prepared according to previous reports.14 1HNMR (400MHz) spectra were recorded in DMSOd6 or EtOH-d6. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. UV/vis absorption spectra were recorded using a U5100 (Hitachi) spectrophotometer with quartz cuvettes of 1 cm pathlength. Fluorescence spectra were obtained using F-7000 Fluorescence spectrophotometer (Hitachi) at room temperature. The slit width was 5 nm and 2.5 nm for excitation and emission. The photon multiplier voltage was 400 V. CD spectra were recorded using a Chirascan plus qCD (Applied Photophysics) at room temperature. Samples in solution and powder were contained in 1 cm path length quartz cuvettes (3.5 mL volume) and quartz tube, respectively. C, H, and N element analyses were performed by employing Flash1112 elemental analyzers (Thermo Fisher Scientific). CD spectra were recorded using a Chirascan plus qCD (Applied Photophysics) at room temperature. Samples in solution and powder were contained in 1 cm path length quartz cuvettes (3.5 mL volume) and quartz tube, respectively. Rheological measurements were performed on a HAAKE RS6000 rheometer. TEM experiments were performed on Tecnai G² F20 S-Twin transmission electron microscope with an accelerating voltage of 200 kV. TEM samples were prepared by direct depositing a single submicrometer fiber on the formvar-coated copper grids. The SEM images were taken on JSM-7500F scanning electron microscope operating at 5.0 kV. SEM samples were prepared by depositing submicrometer or micrometer fibers onto silicon wafers. PXRD was measured by Powder X-ray Diffractometer (Shimadzu XRD-6100).

X-ray Crystallographic Analysis. The determination of the unit cell and data collection for four single crystal samples were performed on a Xcalibur E X-ray single crystal diffractometer equipped with graphite monochromator Mo K α (λ =0.71073 Å) radiation. The data collection was executed using CrysAlisPro program. Structures were solved by direct method and successive Fourier difference syntheses (SHELXS-

97), and were refined by full matrix least-squares procedure on F2 with anisotropic thermal parameters for all nonhydrogen atoms (SHELXL-97).

Preparation of gels: The gels were prepared through a heating-cooling process. The mixtures of (S)1 and (R)BINAM were heated at 60 °C in EtOH solution for several minutes and then were cooled to room temperature. Gelation appeared after 5–60 minutes when they were kept at room temperature.

Interference experiments: Different equivalents of amino/chiral compounds, aldehyde compounds, anions, cations $(1.0-0.10 \text{ mol } \text{dm}^{-3} \text{ sodium or potassium salts}$ in water) were added to the EtOH solution of **(S)1** (25 mmol dm^{-3}) and/or **(R)BINAM** (12.5 mmol dm^{-3}) and then the mixture solutions were followed the same procedure of preparation of gels. For the fluorescent titration, the concentration of **(R)BINAM** (10 µmol dm^{-3} , 10 mL) was fixed, and then various **(S)1** were added by a microsyringe. All types of measurements were monitored at about 2 hours after the preparation of mixture solution at room temperature.

(S)/(R)-1,1'-binaphthalene-2,2'-bis(methoxymethyloxy) -3-carbaldehyde ((S)/(R)2)²¹ t-BuLi (1.3 M in pentane 50.4 mL, 38.8 mmol) was added dropwise to a solution of (S)/(R)-2,2'-bis(methoxymethyloxy)-1,1'-binaphthalene (11.08 g, 29.6 mmol) in 360 mL dry THF over 15 min at -78 °C. After stirring for 1 h, DMF (2.96 mL, 38.4 mmol) was added dropwise, and then 1.5 h later, additional DMF (1.1 mL, 14.3 mmol) was added to the reaction mixture. The mixture was allowed to warm to room temperature slowly and stir for 9 h, which was quenched with saturated NH₄Cl and extracted with ethyl acetate for three times. The combined extracts were washed with water and brine, and dried over dry Na₂SO₄. The solvent was removed under reduced pressure at room temperature. Purification by column chromatography (petroleum ether/ethyl acetate = $25:1 \sim 20:1 \sim 10:1$) gave 6.55 g (S)/(R)2 as a light yellow-green solid (yield 55 %). 2.44 g (22 %) of the starting material was also recovered by column chromatography. ¹H NMR (400 MHz, DMSO-d6): δ 10.47 (s, 1H), 8.64 (s, 1H), 8.25 (d, J = 8.1 Hz, 1H), 8.14 (d, J = 9.1 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 9.2 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.42 (dtt, J = 13.4, 6.4, 3.3 Hz, 2H), 7.29 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H),

5.24 (d, J = 6.9 Hz, 1H), 5.14 (d, J = 6.9 Hz, 1H), 4.79 (d, J = 5.9 Hz, 1H), 4.68 (d, J = 5.8 Hz, 1H), 3.09 (s, 3H), 2.88 (s, 3H). ¹³C NMR (101 MHz, DMSO-d6): δ 191.28 (s), 153.40 (s), 152.97 (s), 136.67 (s), 133.65 (s), 131.74 (s), 130.70 (d, J = 12.7 Hz), 130.25 (s), 129.82 (s), 129.48 (d, J = 6.3 Hz), 128.55 (s), 127.24 (d, J = 13.2 Hz), 126.52 (s), 125.71 (s), 125.02 (s), 124.50 (s), 118.61 (s), 116.42 (s), 100.08 (s), 94.41 (s), 56.89 (s), 55.92 (s), 39.99 (s).

(*S*)/(*R*)-1,1'-binaphthalene-2,2'-diol-3-carbaldehyde ((*S*)/(*R*)1): Concentrated HCl (73 mL of a 12 M solution) was added dropwise to a solution of (*S*)/(*R*)2 (6.55 g, 16.28 mmol) in THF (50 mL) at 0 °C. After it was stirred for 6 h at room temperature, the solution was extracted ethyl acetate (three times) and washed with water, saturated NaHCO₃ and brine. After dried over dry Na₂SO₄ and removed of solvent in vacuum. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to give 3.94 g (*S*)/(*R*)1 as a bright yellow powder (yield 77 %). ¹H NMR (400 MHz, DMSO-d6): δ 10.33 (s, 1H), 10.12 (s, 1H), 9.44 (s, 1H), 8.62 (s, 1H), 8.12 (dd, J = 6.3, 3.1 Hz, 1H), 7.90 (dd, J = 13.4, 8.3 Hz, 2H), 7.50 – 7.31 (m, 3H), 7.29 – 7.17 (m, 2H), 7.04 – 6.97 (m, 1H), 6.93 (d, J = 8.3 Hz, 1H). ¹³C NMR (101 MHz, DMSO-d6): δ 197.33 (s), 153.68 (d, J = 13.0 Hz), 137.58 (s), 136.82 (s), 130.59 (s), 130.38 (s), 129.87 (s), 128.55 (d, J = 6.7 Hz), 127.78 (s), 126.75 (s), 125.09 (s), 124.43 (d, J = 11.1 Hz), 123.34 (s), 122.97 (s), 119.01 (s), 113.78 (s), 39.98 (s).

Schiff Base (*R'*,*S*,*R'*)/(*S'*,*R*,*S'*)4:²⁰ A mixture of (*S*)/(*R*)BINAM (0.284 g, 1 mmol) and (*R*)/(*S*)1 (0.628 g, 2 mmol) in absolute ethanol (50 mL) was refluxed for about 10 h to yield a yellow precipitate. The crude product was filtered at room temperature and washed with ice-cold ethanol to afford a yellow solid. (0.83 g, 95 %). ¹H NMR (400 MHz, DMSO-d6): δ 11.70 (dd, J = 9.6, 1.0 Hz, 2H), 9.37 (s, 1H), 9.18 (s, 1H), 8.98 (d, J = 4.2 Hz, 2H), 8.10 – 7.99 (m, 3H), 7.98 – 7.89 (m, 3H), 7.83 (ddd, J = 10.6, 8.1, 4.6 Hz, 5H), 7.74 (dd, J = 11.0, 9.0 Hz, 2H), 7.59 (d, J = 7.8 Hz, 1H), 7.38 (dt, J = 9.2, 7.7 Hz, 2H), 7.33 (d, J = 8.9 Hz, 1H), 7.31 – 7.17 (m, 9H), 7.07 (td, J = 7.6, 0.7 Hz, 2H), 6.96 (t, J = 8.5 Hz, 2H), 6.87 (t, J = 7.9 Hz, 2H), 6.80 (d, J = 8.5 Hz, 1H), 6.71 (d, J = 8.5 Hz, 1H). ¹³C NMR (101 MHz, DMSO-d6): δ 154.22 (d, J = 8.3 Hz), 153.31 (d, J = 8.3 Hz), 144.74 (s), 135.58 (dd, J = 11.3, 5.3 Hz), 134.13 (d, J = 2.1 Hz), 133.02 (d, J = 8.3 Hz), 144.74 (s), 135.58 (dd, J = 11.3, 5.3 Hz), 134.13 (d, J = 2.1 Hz), 133.02 (d, J = 8.3 Hz), 144.74 (s), 135.58 (dd, J = 11.3, 5.3 Hz), 134.13 (d, J = 2.1 Hz), 133.02 (d, J = 8.3 Hz), 144.74 (s), 135.58 (dd, J = 11.3, 5.3 Hz), 134.13 (d, J = 2.1 Hz), 133.02 (d, J = 8.3 Hz), 144.74 (s), 135.58 (dd, J = 11.3, 5.3 Hz), 134.13 (d, J = 2.1 Hz), 133.02 (d, J = 8.3 Hz), 144.74 (s), 135.58 (dd, J = 11.3, 5.3 Hz), 134.13 (d, J = 2.1 Hz), 133.02 (d, J = 8.3 Hz), 144.74 (s), 135.58 (dd, J = 11.3, 5.3 Hz), 134.13 (d, J = 2.1 Hz), 133.02 (d, J = 8.3 Hz), 144.74 (s), 145.74 (s), 145.75 (s), 1

= 11.1 Hz), 132.33 (d, J = 7.3 Hz), 130.52 (d, J = 8.4 Hz), 129.39 (dd, J = 7.7, 4.7 Hz), 129.23 – 128.47 (m), 128.41 (d, J = 3.7 Hz), 127.93 (s), 127.53 (t, J = 6.2 Hz), 126.72 – 125.96 (m), 125.30 – 124.58 (m), 124.54 (s), 124.20 – 123.47 (m), 122.86 (d, J = 3.9 Hz), 121.51 (d, J = 5.9 Hz), 119.04 (d, J = 15.8 Hz), 117.07 (d, J = 5.6 Hz), 114.92 (d, J = 3.0 Hz), 39.99 (s).

(S)/(R)-1,1'-binaphthalene-2,2'-diol-3,3'-carbaldehyde ((S)/(R)3): they were prepared according to previously described procedure (A. M. DeBerardinis, M. Turlington, J. Ko, L. Sole, and L. Pu, J. Org. Chem., 2010, 75, 2836-2850).



¹H NMR and ¹³C NMR spectra of (*S*)2 in DMSO-d6.





¹H NMR and ¹³C NMR spectra of (*S*)1 in DMSO-d6.



¹H NMR and ¹³C NMR spectra of (*R',S,R'*)4 in DMSO-d6.



HRESIMS spectrum (positive ion mode) of (S)2.



LRESIMS spectrum (positive ion mode) of (S)2.



HRESIMS spectrum (positive ion mode) of (S)1.



LRESIMS spectrum (positive ion mode) of (S)1.



HRESIMS spectrum (positive ion mode) of (*R'*,*S*,*R'*)4.



LRESIMS spectrum (positive ion mode) of (*R',S,R'*)4.

Table S1 Gelation ability of (S)1/(R)BINAM ($(S)1 = 25 \text{ mmol dm}^{-3}$, (R)BINAM =

Solvents	Phase ^{a)}
МеОН	Р
EtOH	G
CH ₂ Cl ₂	S
CHCl ₃	S
1,2-dichloroethane	S
DMSO	S
DMF	S
Acetone	S
Ethyl acetate	S
benzene	S
1,4-Dioxane	S
Ether	Ι
THF	S
Toluene	S
n-Hexane	Ι
MeCN	Р
Cyclohexane	Ι

12.5 mmol dm⁻³) in different solvents in air at 25 $^{\circ}$ C

a) G = gel, I = insoluble, S = solution, P = precipitate

Gelation ability of different molar ratio (S)1/(R)BINAM ($(S)1 = 25 \text{ mmol dm}^{-3}$, 1.5wt%) in EtOH in air at 25 °C

molar ratio	Heating temperature	Time
1:0.1	60 °C	38 min
1:0.2	60 °C	29 min
1:0.5	60 °C	6 min

1:1	60 °C	10 min
1:2	60 °C	11 min
1:4	70 °C	58 min

Table S2 Gelation ability of **(S)1** with different amine/chiral compounds (**(S)1** = 25 mmol dm⁻³, amine compounds = 12.5 mmol dm⁻³) in EtOH.

Amine compounds	Color	Phase ^{a)}
(R,R)-1,2-Diaminocyclohexane $((R,R)$ cy)	orange	S
(R,R)-1,2-Diphenylethylenediamine $((R,R)$ DiPh)	orange	S
(<i>R</i>)-(+)-4-Methoxy-alpha-methylbenzylamine ((<i>R</i>)MAM)	orange	S
o-Phenylenediamine (PDA)	yellow	S
n-Butylamine (BA)	orange	S
n-Heptylamine (HA)	orange	S
1,2-ethanediamine (EDA)	orange	S
1,12-Dodecanediamine (DDA)	orange	S
D/L-tartaric acid (D/L -TC)	orange	S
D/L-Ala	yellow	S
D/L Arg	orange	Р
D/L Asp	yellow	Ι
D/L Cys	yellow	S
D/L Glu	yellow	Ι
D/L His	yellow	Р
D/L Ile	yellow	S
D/L Leu	yellow	S
D/L Met	yellow	Р
D/L Pro	yellow	S
D/L Ser	yellow	S
D/L Trp	yellow	S
D/L Val	yellow	Р
D-Asn	yellow	Р
D-Gln	yellow	Р
D-Lys	orange	Р
D-Phe	yellow	S

D-Thr	yellow	Р
D-Tyr	yellow	Ι
D/L Ribose (Rib)	yellow	S

Aldehyde compounds	Colour	Phase ^{a)}
Benzaldehyde (BAH)	yellow	S
Formaldehyde (HCHO)	colorless	Р
Paraformaldehyde (PAH)	colorless	Ι
Salicylaldehyde (SAH)	orange	S
2-Hydroxy-1-naphthaldehyde (NSAH)	yellow	Р
3,5-Dichlorosalicyaldehyde (3,5-Cl)	red	Р
3,5-di-tert-butylsalicylaldehyde (3,5-Bu)	yellow	S
4-(Diethylamino)salicylaldehyde (4-NEt ₂)	orange	S
3-Nitrosalicylaldehyde (3-NO ₂)	orange	Р
3-Methoxysalicylaldehyde (3-MeO)	orange	Р

Table S3 Gelation ability of (*R*)**BINAM** with different aldehyde compounds $((R)BINAM = 12.5 \text{ mmol dm}^{-3}, \text{ aldehyde compounds} = 25 \text{ mmol dm}^{-3})$ in EtOH

Cation	Colour	Phase ^{a)}
Cu ²⁺	brown	G
Zn ²⁺	yellow	G
Al ³⁺	orange	G
Na ⁺	yellow	G
Mg ²⁺	yellow	G
K ⁺	yellow	G
Ag ⁺	yellow	G
Li ⁺	yellow	G
Ca ²⁺	yellow	G
Fe ²⁺	black	G
Fe ³⁺	black	G

Table S4 Gelation ability of **(S)1** and **(R)BINAM** upon adding different $M^{n+}((S)1 = 25$ mmol dm⁻³, **(R)BINAM** = 12.5 mmol dm⁻³ and $M^{n+} = 12.5$ mmol dm⁻³) in EtOH

Anion	Colour	Phase ^{a)}
Br-	yellow	G
CO ₃ ^{2–}	orange	G
NO ₃ -	yellow	G
MeCO ₂ -	yellow	G
F-	yellow	G
S ²⁻	orange	G
P ₂ O ₇ ⁴⁻	yellow	G
HS-	yellow	G
HSO ₃ -	orange	G
SO4 ²⁻	yellow	G
I-	yellow	G
NO ₂ -	yellow	G
Cl-	yellow	G
SO ₃ ²⁻	yellow	G
H ₂ PO ₄ -	yellow	G
PO ₄ ³⁻	orange	G
OH-	orange	G

Table S5 Gelation ability of (*S*)1 and (*R*)**BINAM** upon adding different X^{n-} ((*S*)1 = 25 mmol dm⁻³, (*R*)**BINAM** = 12.5 mmol dm⁻³ and X^{n-} = 12.5 mmol dm⁻³) in EtOH.

Table S6 Gelation ability of **(S)1** and **(R)BINAM** upon adding different amino acids $((S)1=25 \text{ mmol dm}^{-3}, (R)BINAM = 12.5 \text{ mmol dm}^{-3} \text{ and amino} = 12.5 \text{ mmol dm}^{-3})$ in EtOH.

Amino	Colour	Phase ^{a)}	Amino	Colour	Phase ^{a)}
D-Ala	yellow	G	L-Ala	yellow	G
D-Arg	orange	G	<i>L</i> -Arg	orange	G
D-Asp	yellow	G	L-Asp	yellow	G
D-Cys	yellow	G	L-Cys	yellow	G
D-Glu	yellow	G	L-Glu	yellow	G
D-His	yellow	G	<i>L</i> -His	yellow	G
D-Ile	yellow	G	<i>L</i> -Ile	yellow	G
D-Leu	yellow	G	L-Leu	yellow	G
D-Met	yellow	G	L-Met	yellow	G
D-Pro	yellow	G	<i>L</i> -Pro	yellow	G
D-Ser	yellow	G	L-Ser	yellow	G
D-Trp	yellow	G	<i>L</i> -Trp	yellow	G
D-Val	yellow	G	L-Val	yellow	G
D-Asn	yellow	G	L-Asn	yellow	G
D-Gln	yellow	G	L-Gln	yellow	G
D-Lys	orange	G	L-Lys	orange	G
D-Phe	yellow	G	L-Phe	yellow	G
D-Thr	yellow	G	<i>L</i> -Thr	yellow	G
D-Tyr	yellow	G	<i>L</i> -Tyr	yellow	G



Scheme S1 Synthesis of chiral 1,1'-binaphthyls in this work.



Fig. S1 Absorption spectra of of (S)1 (10 μ mol dm⁻³), (R)BINAM (10 μ mol dm⁻³), (S)1:(R)BINAM (10: 5 μ mol dm⁻³), and (S)1/(R)BINAM gels ((S)1 = 25 mmol dm⁻³, (R)BINAM = 12.5 mmol dm⁻³) in EtOH.



Fig. S2 Single-crystal X-ray diffraction structures and arrangements (*R*)**BINOL**. Some H atoms are omitted.



Fig. S3 Single-crystal X-ray diffraction structures and arrangements of (S)1 and (R)BINAM. Some H atoms are omitted.



Fig. S4 Florescent spectra of (*R*)**BINAM** (10 μ mol dm⁻³ in EtOH) upon adding different equivalents of (*S*)1 (excited at 285 nm).





(b)

(c)



(d)



Fig. S5 ¹H NMR spectra of **(S)1/(***R***)BINAM** gels ((**S)1** = 25 mmol dm⁻³) in EtOH-d6 at 25 °C: (a) molar ratio 1:0.5, solution (diphenylmethane as internal standard = 25 mmol dm⁻³); (b) molar ratio 1:0.5, gel (diphenylmethane as internal standard = 25 mmol dm⁻³); (c) molar ratio1:1, solution (diphenylmethane as internal standard = 25 mmol dm⁻³); (d) molar ratio 1:1, gel (diphenylmethane as internal standard = 25 mmol dm⁻³); (e) molar ratio 1:4, solution (diphenylmethane as internal standard = 50 mmol dm⁻³); (f) molar ratio 1:4, gel (diphenylmethane as internal standard = 50 mmol dm⁻³).



Fig. S6 Oscillatory rheological measurements of (S)1/(R)BINAM gels $((S)1 = 25 \text{ mmol} \text{ dm}^{-3} \text{ with different equivalents of } (R)$ BINAM in EtOH).



¹H NMR spectra of (*R*)BINAM in EtOH-d6 (solution, 2 mmol dm⁻³) at 25 °C.



Partial ¹H NMR spectra of **(S)1/(R)BINAM** solution in EtOH-d6 at 25 °C: molar ratio 1:0.5, **(S)1** = 25 mmol dm⁻³, **(R)BINAM** = 12.5 mmol dm⁻³, diphenylmethane as internal standard = 25 mmol dm⁻³.



Partial ¹H NMR spectra of **(S)1/(R)BINAM** gel in EtOH-d6 at 25 °C: molar ratio 1:0.5, **(S)1** = 25 mmol dm⁻³, **(R)BINAM** = 12.5 mmol dm⁻³, diphenylmethane as internal standard = 25 mmol dm⁻³.



Partial ¹H NMR spectra of **(S)1/(R)BINAM** solution in EtOH-d6 at 25 °C: molar ratio 1:1, **(S)1** = 25 mmol dm⁻³, **(R)BINAM** = 25 mmol dm⁻³, diphenylmethane as internal standard = 25 mmol dm⁻³.



Partial ¹H NMR spectra of **(S)1/(R)BINAM** gel in EtOH-d6 at 25 °C: molar ratio 1:1, **(S)1** = 25 mmol dm⁻³, **(R)BINAM** = 25 mmol dm⁻³, diphenylmethane as internal standard = 25 mmol dm⁻³.



Partial ¹H NMR spectra of **(S)1/(R)BINAM** solution in EtOH-d6 at 25 °C: molar ratio 1:4, **(S)1** = 25 mmol dm⁻³, **(R)BINAM** = 100 mmol dm⁻³, diphenylmethane as internal standard = 50 mmol dm⁻³.



Partial ¹H NMR spectra of (*S*)1/(*R*)BINAM gel in EtOH-d6 at 25 °C: molar ratio 1:4, (*S*)1 = 25 mmol dm⁻³, (*R*)BINAM = 100 mmol dm⁻³, diphenylmethane as internal standard = 50 mmol dm⁻³.



Partial ¹H NMR spectra of (S)1/(R)BINAM solutions in EtOH-d6 at 25 °C: Bottom: molar ratio 1:0.5, (S)1 = 25 mmol dm⁻³, (R)BINAM = 12.5 mmol dm⁻³; Middle: molar ratio 1:1, (S)1 = 25 mmol dm⁻³, (R)BINAM = 25 mmol dm⁻³; Top: molar ratio 1:4, (S)1 = 25 mmol dm⁻³, (R)BINAM = 100 mmol dm⁻³. Diphenylmethane as internal standard.



Partial ¹H NMR spectra of (*S*)1/(*R*)BINAM gels in EtOH-d6 at 25 °C: Bottom: molar ratio 1:0.5, (*S*)1 = 25 mmol dm⁻³, (*R*)BINAM = 12.5 mmol dm⁻³; Middle: molar ratio 1:1, (*S*)1 = 25 mmol dm⁻³, (*R*)BINAM = 25 mmol dm⁻³; Top: molar ratio 1:4, (*S*)1 = 25 mmol dm⁻³, (*R*)BINAM = 100 mmol dm⁻³. Diphenylmethane as internal standard.



Partial ¹H NMR spectra of (*S*)1/(*R*)BINAM in EtOH-d6. Bottom: gel, molar ratio 1:0.5, (*S*)1 = 50 mmol dm⁻³, (*R*)BINAM = 25 mmol dm⁻³. Top: solution, molar ratio 1:0.5, (*S*)1 = 5 mmol dm⁻³, (*R*)BINAM = 2.5 mmol dm⁻³.