### **Electronic Supplementary Information for**

## Achiral non-fluorescent molecule assisted enhancement of circularly

#### polarized luminescence in naphthalene substituted histidine

#### organogel

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### S1. Synthetic procedures and gelation tests.



Scheme S1. Synthesis of L-α-NapHis

**Materials:** All starting materials and solvents were purchased from Acros, TCI or Beijing Chemicals and used as received unless otherwise stated. Solvents were purified and dried according to standard methods. Milli-Q water (18.2 M $\Omega$  cm<sup>-1</sup>) was used in all cases.

Synthesis of  $\alpha$ -Naphthalene substituted Histidine ( $\alpha$ -NapHis): L- $\alpha$ -histidine methyl ester dihydrochloride (2.5g, 10 mmol) was dissolved in dry dichloromethane (250 mL), and added with triethylamine (2.2 g, 22 mmol). The mixture was stirred at room temperature for 1 h. Then 1-Naphthyl isocyanate (1.7 g, 10 mmol) was added into the mixture dropwise, the mixture was stirred at room temperature for 2 h. The solvent was removed to 30 mL under reduced pressure, the remaining mixture was filtered and washed by Milli-Q water for three times, then dried under vacuum to give 3.3 g of pure L- $\alpha$ -NapHis. The product was white solid, yield 92 %.

<sup>1</sup>H NMR (300 MHz, d6-DMSO, 25 °C, TMS): δ=11.89 (s, 1H), 8.83 (s, 1H), 8.13 – 8.04 (m, 1H), 7.99 – 7.83 (m, 1H), 7.61 – 7.46 (m, 2H), 7.41 (t, J = 7.9 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 6.87 (s, 1H), 4.58 (dd, J = 13.7, 6.1 Hz, 1H), 3.65 (s, 2H), 2.98 (d, J=6.0 Hz, 1H).



**Figure S1.** <sup>1</sup>H-NMR spectra of  $\alpha$ -NapHis.

#### ESI-MS Spectrum







ESI-MS: m/z (%): calcd. for  $C_{18}H_{18}N_4O_3$  M<sup>+</sup>: m/z=339.3; found M<sup>+</sup>: m/z=339.3 and [M+Na]<sup>+</sup>: m/z=361.2



Scheme S2. Synthesis of L-β-NapHis

The synthesis steps of  $\beta$ -NapHis were similar with  $\alpha$ -NapHis.

<sup>1</sup>H NMR (300 MHz, d6-DMSO, 25 °C, TMS):  $\delta$ =11.98 (s, 1H), 9.08 (s, 1H), 8.03 – 7.92 (m, 1H), 7.80 – 7.74 (m, 1H), 7.65 – 7.55 (m, 2H), 7.43 (t, J = 7.9 Hz,

1H), 6.87 (s, 1H), 6.61 (d, J = 7.8 Hz, 1H), 4.55 (dd, J = 13.7, 6.1 Hz, 1H), 3.64 (s, 2H), 2.98 (d, J=6.0 Hz, 1H).

ESI-MS: m/z (%): calcd. for  $C_{18}H_{18}N_4O_3$  M<sup>+</sup>: m/z=339.3; found [M+Na]<sup>+</sup>: m/z=361.2

**Instruments and methods:** <sup>1</sup>H NMR spectra were recorded on a Bruker AV300 (300 MHz) spectrometer. Mass spectral data were measured by LCMS-2010 (ESI-MS) instrument. Scanning electron microscopy (SEM) was carried out on a Hitachi S-4800 FE-SEM microscope. Xerogel on silica plate were prepared for the measurement of Fourier transform infrared (FT-IR) spectra on a JASCO FT/IR-660 plus spectrophotometer with a wave number resolution of 4 cm<sup>-1</sup> at room temperature. X-ray diffraction (XRD) was carried out on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with CuKα radiation (λ=1.5406 Å), which was operated at 45 kV, 100 mA.

**Procedures:** For the SEM measurements, a small amount of gels was placed onto a single-crystal silicon plate (Pt-coated) after being vacuum dried for 12 h. In the case of preparing samples for XRD measurements, gels were cast onto glass plates and dried under vacuum. Pellets made from the mixture of vacuum-dried supramolecular polymers and KBr powders were used for FT-IR spectral measurements.

**Gelation studies:** All the supramolecular gels were prepared in septum-capped test tubes. The  $\alpha$ -Naphthalene substituted Histidine ( $\alpha$ -NapHis) and benzoic acids with equal molar ratio were dispersed in EA/MeCN=1:1 and then heated until transparent. The obtained clear solution was sonicated and the gels formation was confirmed by the tube-inversion method.

Single solvent	Phase <sup>a</sup>	Mixed solvent (1:1)	Phase <sup>b</sup>
Methylbenzene	Insoluble	EA/Methylbenzene	Partial gel
Cyclohexane	Insoluble	EA/Cyclohexane	Partial gel
THF	Solution	EA/THF	Partial gel
Acetone	Solution	EA/ Acetone	Partial gel
DCM	Solution	EA/DCM	Partial gel
MeCN	Partial gel	EA/MeCN	Gel
Ethyl Acetate(EA)	Partial gel	EA	Partial gel
Methanol	Solution	EA/Methanol	Solution
EtOH	Solution	EA/EtOH	Solution
DMSO	Solution	EA/DMSO	Solution
DMF	Solution	EA/DMF	Solution
Chloroform	Solution	EA/CHCl <sub>3</sub>	Solution

Table S1. Solvent selection of  $\alpha$ -NapHis and  $\alpha$ -NapHis/BA system

<sup>a,b</sup> All these cases require ultrasound.

For gelation studies of  $\beta$ -NapHis, all above solvents could not form gels.

# **S2. Supplementary Figures**



Scheme S3. Schematic illustration of the process to obtain the NapHis organogel.



**Figure S3.** SEM images of the self-assembled structure at nanoscale for  $\alpha$ -NapHis and the co-assembly of  $\alpha$ -NapHis and benzoic acid. (A)  $\alpha$ -NapHis precipitate without sonication, (B)  $\alpha$ -NapHis gel formed in ethyl acetate/acetonitrile = 1:1, (C)  $\alpha$ -NapHis/BA = 10:1, (D)  $\alpha$ -NapHis/BA = 2:1. AFM images of  $\alpha$ -NapHis (gel) (E) and  $\alpha$ -NapHis/BA=1:1 co-gel (F).

As shown in Fig. 2E and F (body manuscript), when the molar ratio of  $\alpha$ -NapHis/BA was 10 : 1, the CD and CPL signals were almost unchanged compared with those of the individual  $\alpha$ -NapHis. When increasing the amount of BA in  $\alpha$ -NapHis/BA from 10 : 1 to 2 : 1 and 1 : 1, both the CD and CPL signals increased gradually, and the strongest intensity was obtained for  $\alpha$ -NapHis/BA = 1:1. A further

increase of the  $\alpha$ -NapHis/BA ratio to 1 : 2 revealed the gel could not form under the same conditions.



**Figure S4.** Normalized FL spectra (A) of  $\alpha$ -NapHis in gel state and DMSO solution, FT-IR spectra (B) of  $\alpha$ -NapHis in gel state and precipitate state without sonication.



**Figure S5.** UV-vis (A) and CD(B) spectra of L- $\alpha$ -NapHis (solid line) and D- $\alpha$ -NapHis (dash line) gels with three acids.



**Figure S6.** FT-IR spectra of  $\alpha$ -NapHis/BA (A) and XRD patterns of co-assemblies of  $\alpha$ -NapHis/BA (B).



**Figure S7.** XRD pattern of  $\beta$ -NapHis/BA, which showed crystalline nature.



**Figure S8.** FL spectra of α-NapHis solution (0.03 M in EA/MeCN, 1:1, v/v).

A			В		
[	Acid	G <sub>lum</sub> (×10 <sup>-3</sup> )		Molar ratio	G <sub>lum</sub> (×10 <sup>-3</sup> )
	α-NapHis/BA	3.0		α-NapHis/BA=1:1	3.0
	α-NapHis/PAA	1.4		α-NapHis/BA=2:1	0.9
	α-NapHis/PFA	1.5		α-NapHis/BA=10:1	0.7
	α-NapHis	0.5		α-NapHis	0.5

**Figure S9.**  $G_{lum}$  value of  $\alpha$ -NapHis/Acids=1:1 (A) and  $\alpha$ -NapHis/BA co-gels in different ratios (B). BA is benzoic acid, PAA is p-anisic acid and PFA is p-fluorobenzoic acid.



**Figure S10.** Stacked <sup>1</sup>H-NMR spectra of  $\alpha$ -NapHis,  $\alpha$ -NapHis/BA=1:1,  $\alpha$ -NapHis/BA=2:1 and BA in d<sub>6</sub>-DMSO (the concentration of NapHis is 0.15 M). With the increasing of BA, aromatic proton signals on imidazole moved to downfield, indicating that nitrogen atom in imidazole unit was protonated. Notes: Proton **a** is located at -CH between two nitrogen atoms on imidazole. BA is benzoic acid.