Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

Imidazole-appended *p*-phenyl-Cu(II) ensemble as a chemoprobe for histidine in biological samples

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Experimental Section

Characterization. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX 300 apparatus. Mass spectra were obtained by a JEOL JMS-700 mass spectrometer. The optical absorption spectra of the samples were obtained at 298K using a UV–Vis spectrophotometer (Thermo Evolution 600). All fluorescence spectra were recorded in RF-5301PC spectrophotometer. Elemental analyses were performed with a Perkin Elmer 2400 series II.

SEM observations. For Scanning electron micrographs of the samples were taken with a field emission scanning electron microscope (FE-SEM, Philips XL30 S FEG). The accelerating voltage of SEM was 5–15 kV and the emission current was 10 μA.

Preparation of aggregated 1. Stock solution of **1** in methanol with a concentration 0.1 μM was prepared. Aliquots (300 μL) of the stock solutions were transferred to 5 mL volumetric flasks. After adding appropriate amounts of methanol, water (2.7 mL) was added dropwise under vigorous stirring to furnish 1 μM solutions with defined fractions of water (fw = 0-100%). Spectral measurements of the resultant solutions or aggregate suspensions were performed immediately.

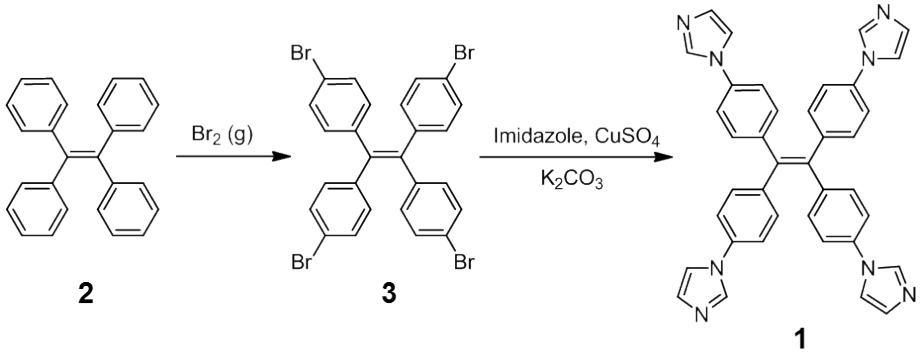
Preparation of aggregated 1 with Cu^{2+}. Stock solution of **1** in methanol was diluted to 1 μM using water (fw = 90 vol%), followed by the addition of an aliquot of copper ion. The final concentration of the copper ion was 0.666 μM unless specified. The solutions were mixed by Vortex and stood for 10 minute prior to spectral measurement.

Test of limit of detection. The limit of detection (LOD) was calculated using the general definition proposed by Harris.[1] The LOD should correspond to the concentration of an element necessary to yield a net signal equal to two times the standard deviation of 10 blank measurements. For the histidine in this study the LOD found was 20 ng/mL. The reproducibility of the **1** signals (in terms of relative standard deviation) was 3.9 %. This was determined by analysing 10 standards containing 1 mg/L of histidine.

Synthesis of compound 3: The compound **3** was prepared according to a literature procedure. In the lower part of a desiccator was placed an open vessel containing bromine (11.58 mL, 217.16 mmol). An evaporating dish containing finely powdered tetraphenylethylene (10.3 g, 31.02 mmol) was placed on the rack above the bromine. The lid of the desiccator was not completely closed thereby leaving a small vent for the escape of hydrogen bromide that is formed in the reaction. After four days, a reddish brown solid was formed which was then allowed to stand until constant weight was obtained. The crude product was recrystallized with dichloromethane/methanol (2:1) to produce white crystals (18.0 g, 90 %); ^{1}H NMR ($CDCl_3$) δ: 6.85 (8H, d, J = 8.56 Hz,), 7.26 (8H, d, J = 8.56 Hz,) .^{13}C NMR ($CDCl_3$) δ : 121.50, 131.52, 132.98, 139.82, 141.69.

Synthesis of compound 1: The compound **1** was prepared according to a literature procedure. Compound **3** (1.193 g, 2.0 mmol), imidazole (1.09 g, 16.0 mmol), K_2CO_3 (1.52 g, 11.0 mmol), and $CuSO_4$ (0.02 g, 0.08 mmol) were mixed in a 50 mL flask and heated under an nitrogen atmosphere for 24 h to 185 C. The reaction mixture was then cooled to ambient temperature and was washed three times with water. The remaining solid residue was extracted with methanol (70 mL). The methanol solution was decolorized with activated charcoal and filtered. The filtrate was brought to dryness to give a colorless solid. Yield: 0.477 g (0.8 mmol, 40%). ^{1}H NMR (300 MHz, CD_3OD): δ 8.113 (4H, s, N-CH-N), 7.543

(4H, s, imidazole-H), 7.421 (8H, d, J = 8.7, Ar-H), 7.292 (8H, d, J = 8.69, Ar-H), 7.118 (4H, s, imidazole-H). ^{13}C NMR (75 MHz, CD_3OD): δ 145.70, 140.08, 137.58, 136.54, 134.10, 130.04, 122.52, 119.58 ppm . ESI-MS. Calcd for $C_{38}H_{28}N_8$: *m/z* 596.24, 597.64 ($[M + H]^+$). FT-IR: 3421 (OH), 1695 (CO) cm^{-1}. Elem anal. Calcd for $C_{38}H_{28}N_8$: C, 76.49; H, 4.73; N, 18.78. Found: C, 75.98; H, 4.72; N, 18.55.



Scheme S1. Synthetic route of **1**.

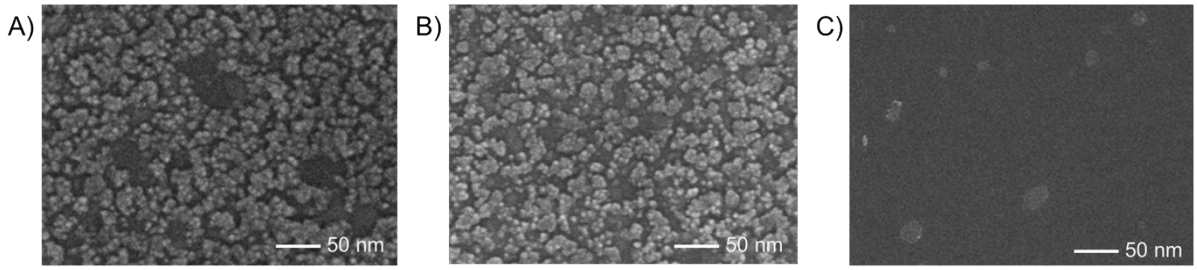


Fig. S1 SEM image of **1** prepared in (A) both pure water and a mixture of water/methanol (B = 90:10 v/v%, C = 40:60 v/v%).

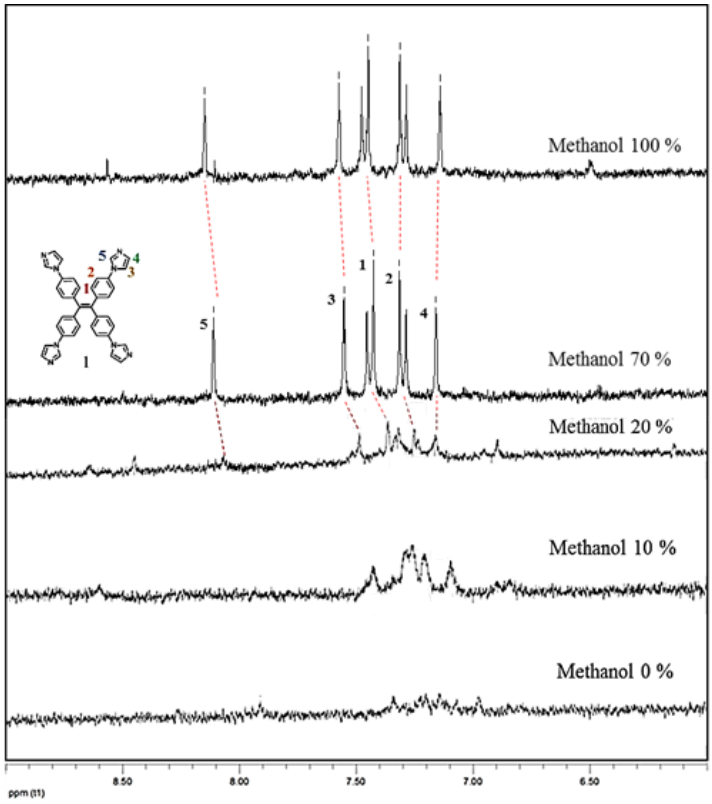


Fig. S2 ^{1}H NMR spectra of **1** (1 μM) at different compositions of solvents in a mixed D_2O and CD_3OD (10:90 v/v%).

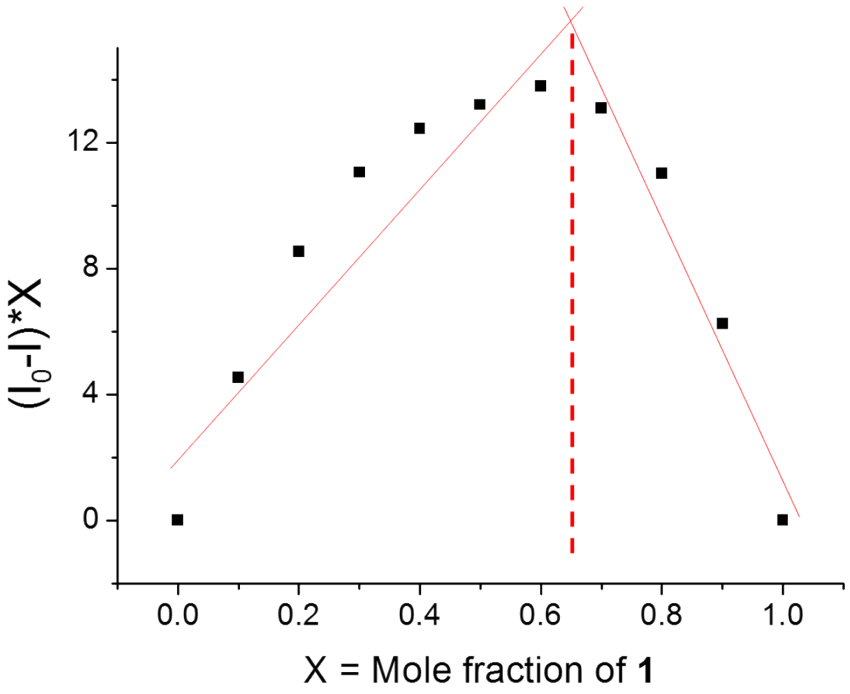


Fig. S3 Job's plot for compound **1** and Cu^{2+} binding (λ_{max} = 345 nm) in a mixed water and methanol (90:10 v/v%).

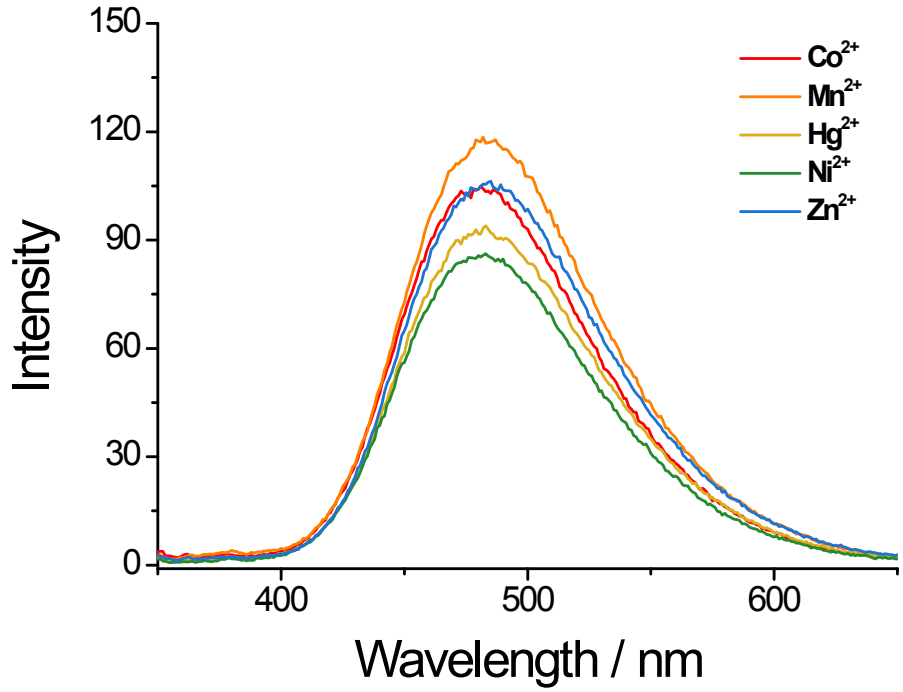


Fig. S4 Photoluminescence spectra of **1** upon addition metal ions in a mixed water and methanol (90:10 v/v%).

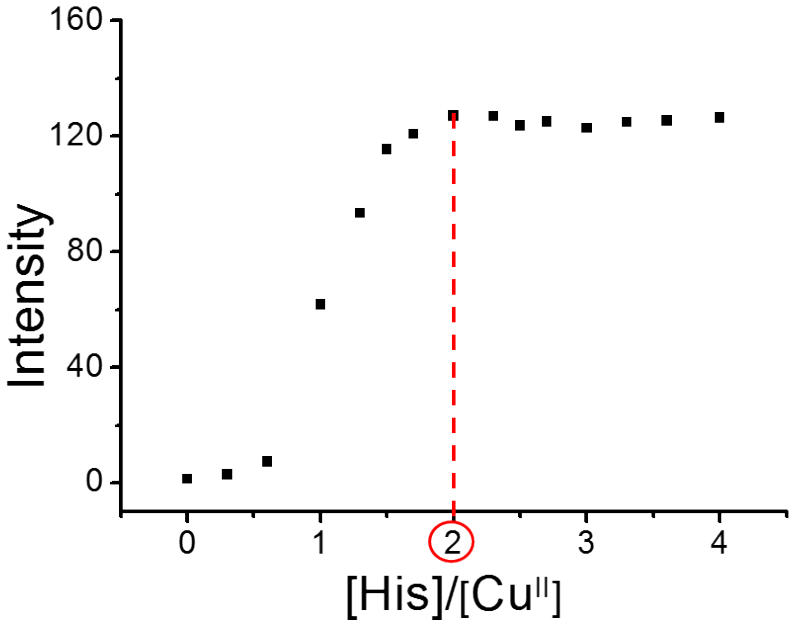


Fig. S5 Plot for fluorescence intensity at 470 nm against the equivalent of His (0~4.0 equivalent) in a mixed water and methanol (90:10 v/v%).

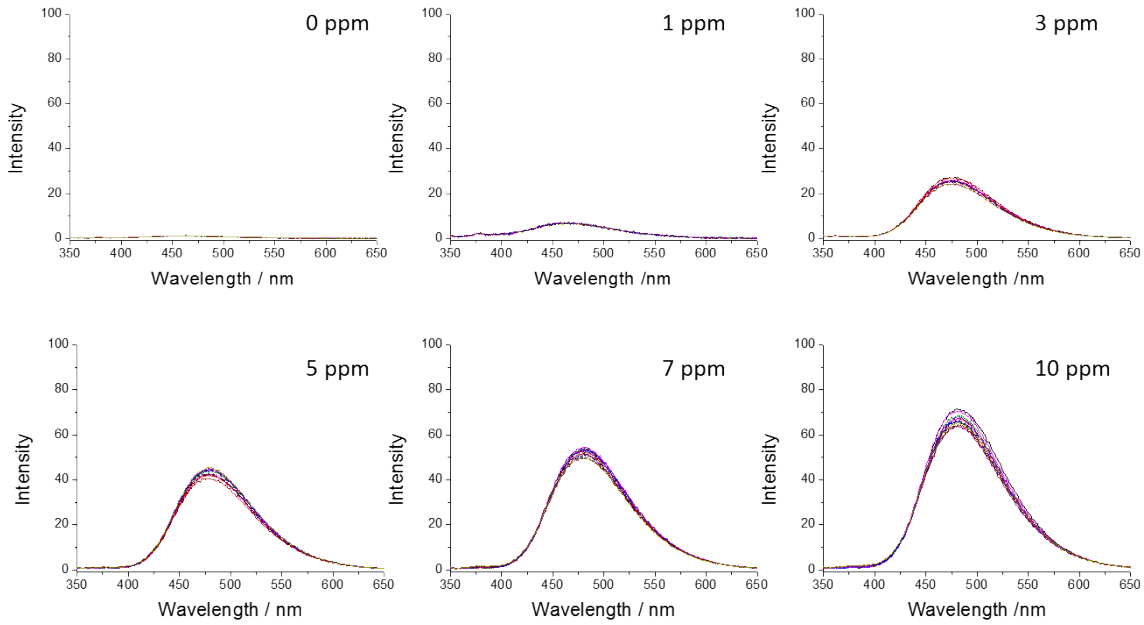


Fig. S6 Photoluminescence spectrum of **1**+Cu^{2+} (1.0 μM) with various concentration of His (0~10 ppm) for limit of detection.

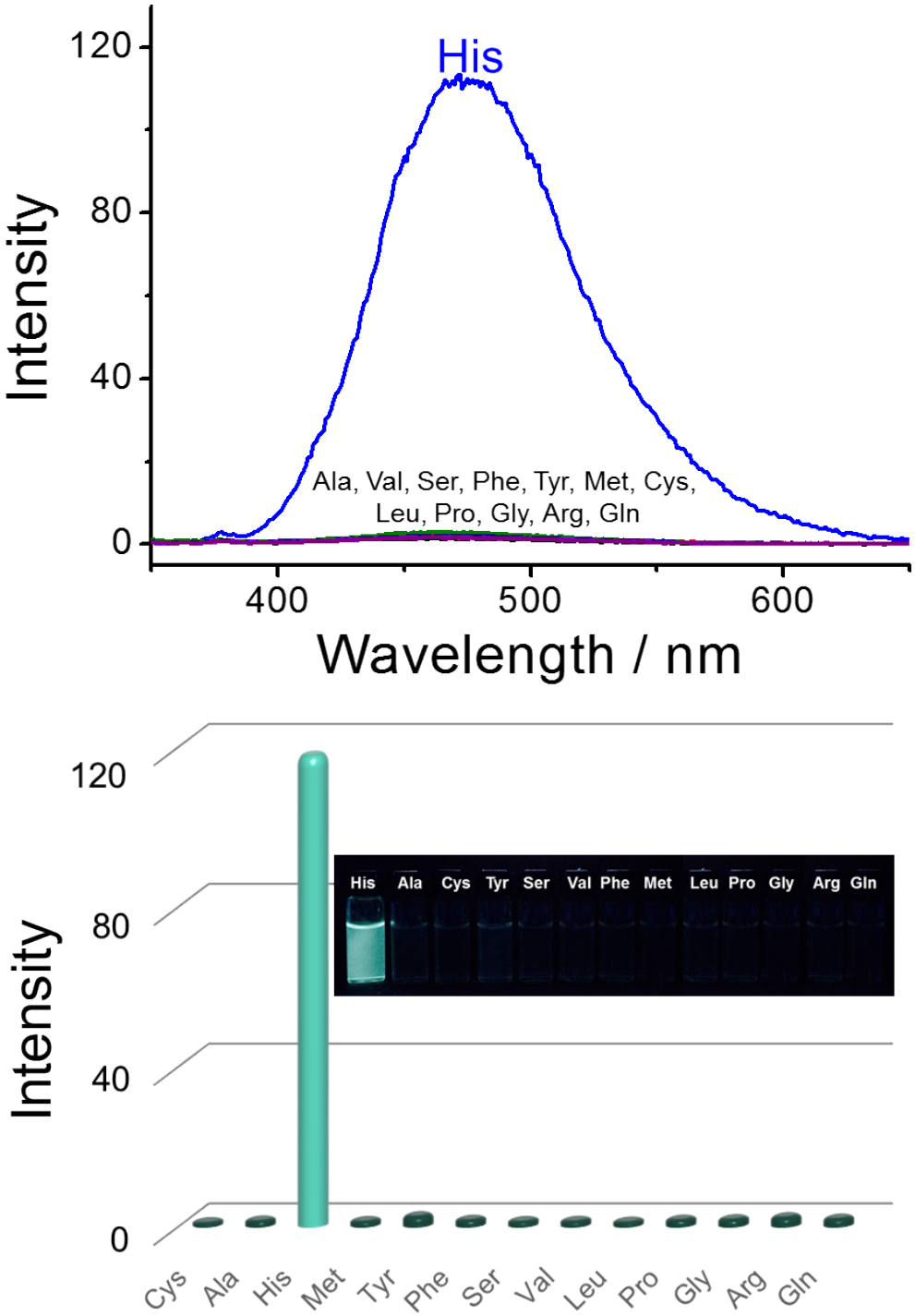


Fig. S7 Photoluminescence spectra of **1** (1.0 μM) with various amino acids (100 equivalent) in a mixed water and methanol (90:10 v/v%).

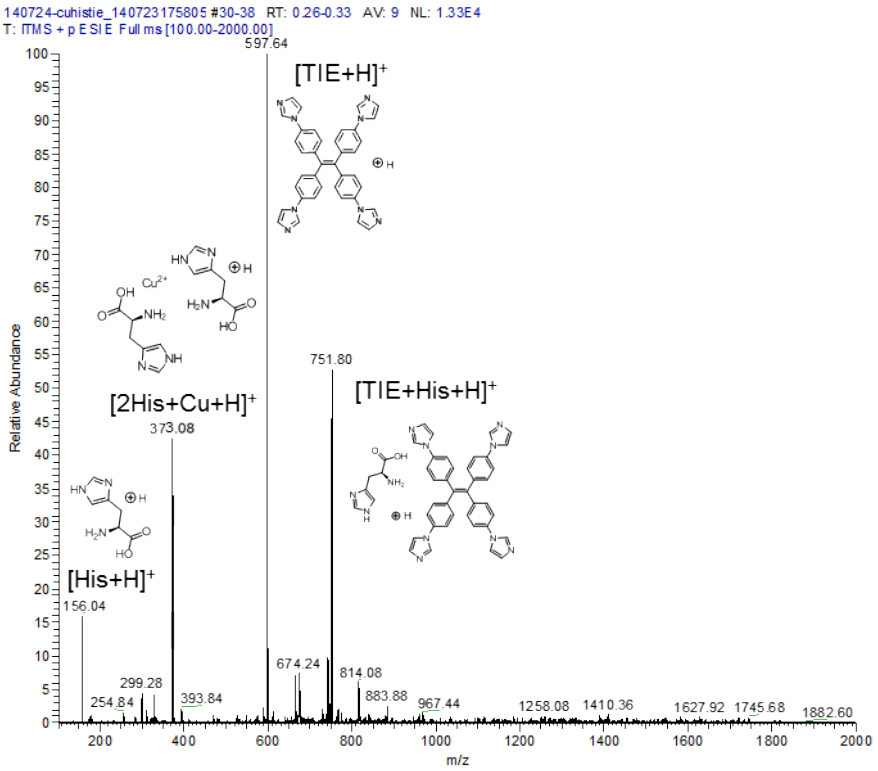


Fig. S8 ESI-MS spectrum of the **1**-Cu^{2+} ensemble upon addition of His.

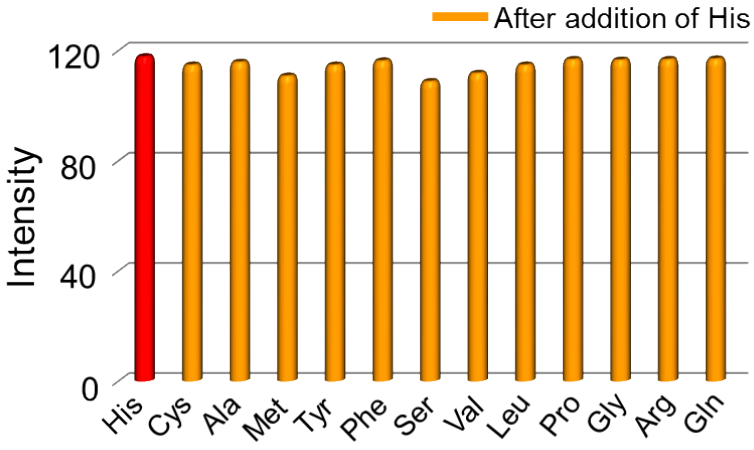


Fig. S9 Fluorescence intensity changes of supramolecular gel **1** upon addition of histidine in competition experiments.

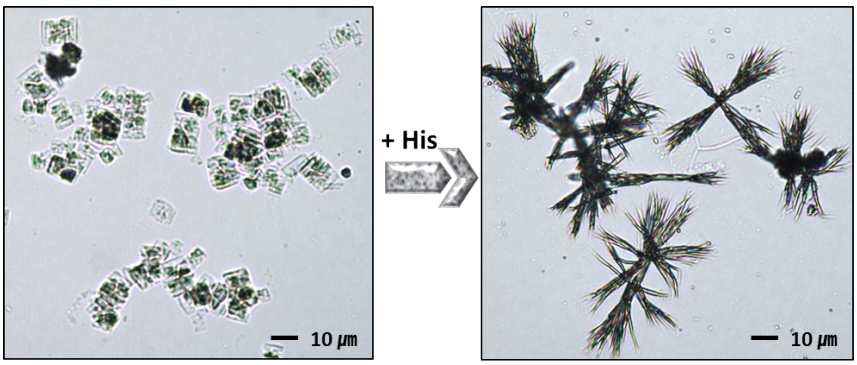


Fig. S10 Microscope image of **1** (1.0 μM) -Cu^{2+} (0.666 equiv.) ensemble in the absence and the presence of His(1.5 equiv.).

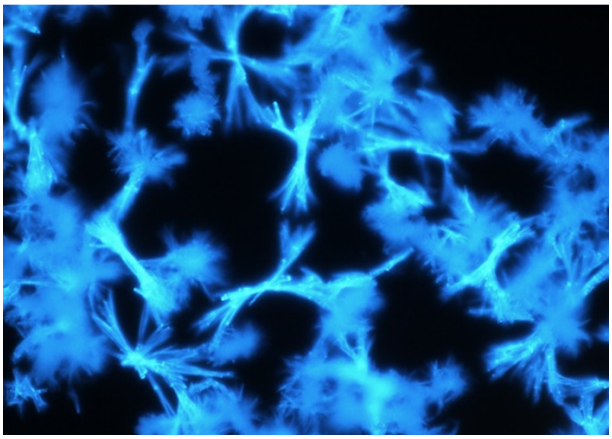


Fig. S11 Fluorescence microscope image of the **1**-Cu^{2+} ensemble with His (1.5 equiv.).

Reference

1 Harris, D.C. (1986), Quantitative Chemical Analysis. W.H. Freeman and Company, USA.