Hydrogen-Bonding Mediated Supramolecular Assembly of Fluorescent Meso-Aryl Porphyrins for Creatinine Monitoring in Biological Samples

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EXPERIMENTAL SECTION

General: All chemicals (solvents, reagents, and chemicals) were purchased from the best-known local chemical suppliers and used without further purification. Solvents were distilled and dried before use.

Spectroscopic studies: The UV−vis spectroscopic studies were recorded on a Shimadzu model 2100 spectrometer. The slit width for the experiment was kept at 5 nm. The stock solution for creatinine was (10mM). On the other hand, fluorescence experiments were performed in an Eclipse spectrofluorometer. The slit-width for the fluorescence experiment was kept at 5 nm (excitation) and 5 nm (emission), and the excitation wavelength was set at 430 nm.

Scanning Electron Microscopy: Solution of probe-**1** &probe-**2** (concentration 10 μM) in PBS buffer medium, then, consecutively, creatinine was added with probes-**1** & 2. All three samples were drop-cast over double-sided tapes attached to the brass stubs and air-dried for 48 h. The samples were then coated with gold vapour and analysed on a Quanta 200 SEM operated at 15 kV.

Dynamic Light Scattering Studies (DLS): DLS measurements were done using a Malvern Zetasizer NanoZS particle sizer (Malvern Instruments Inc., MA) instrument. Samples (probe-**1,** probe-**2,** probe-**1** + creatinine, probe-**2** + creatinine) were prepared in PBS buffer medium and examined under dust-free conditions. Reported mean hydrodynamic diameters were obtained from Gaussian analysis of the intensity-weighted particle size distributions.

Design and Synthesis

P-Cyanobenzaldehyde (292 mg, 2.00 mmol), dipyrromethane (277 mg, 2.00 mmol), and $BF_3{\cdot}Et_2O$ (0.378 mL, 3.00 mmol) were dissolved in dry $CHCl_3$ (300 mL). After stirring for 2 h at room temperature, 1,2,4,5-tetrachlorobenzoquinone (618 mg, 2.46 mmol) was added. The mixture was stirred for 24 h, filtered through silica gel, concentrated, and purified by column chromatography ($CHCl_3$) to afford a purple powder (156 mg, 0.30 mmol, 15% yield).

The probes were synthesised according to the reported literature methods below.

References:

1. Liu, X., Li, H., Zhang, Y., Xu, B., Xia, H., & Mu, Y. Enhanced carbon dioxide uptake by metalloporphyrin-based microporous covalent triazine framework. Polymer Chemistry, 2013, 4(**8**), 2445-2448.

2. H. Lee, H. Park, D. Y. Ryu, W. D. Jang, Chem. Soc. Rev. 2023, **52**, 1947.

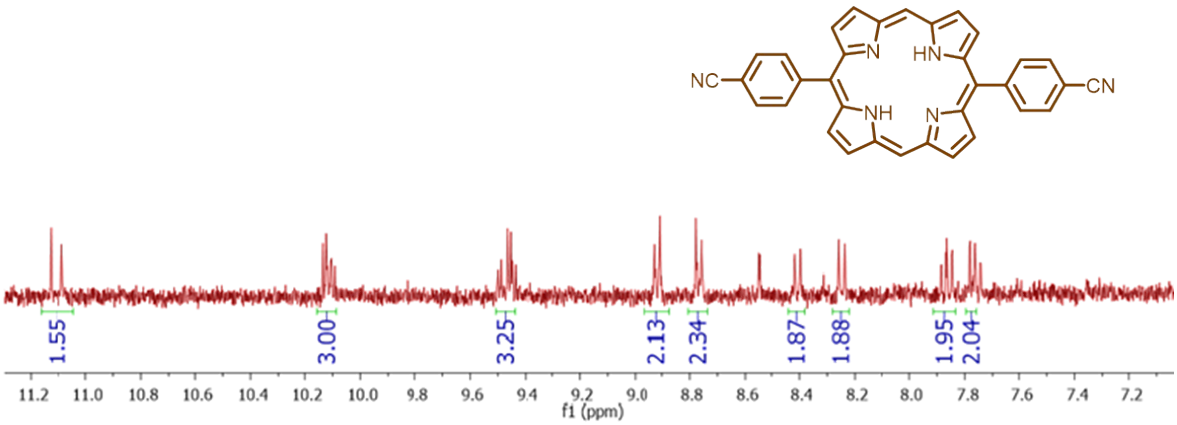

Figure S1: ^{1}H NMR data of probe **1** in DMSO-d6 medium.

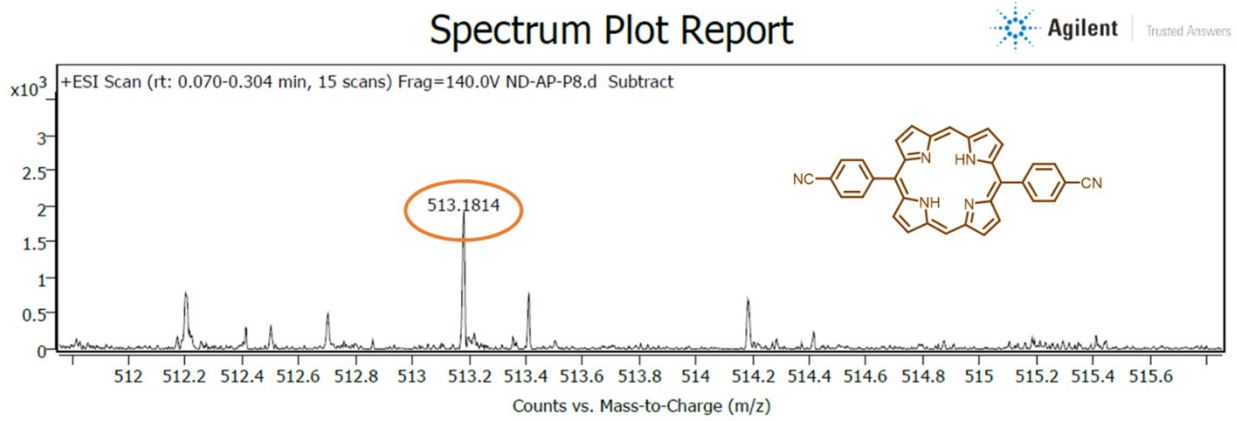

Figure S2: HRMS spectra of probe **1**.

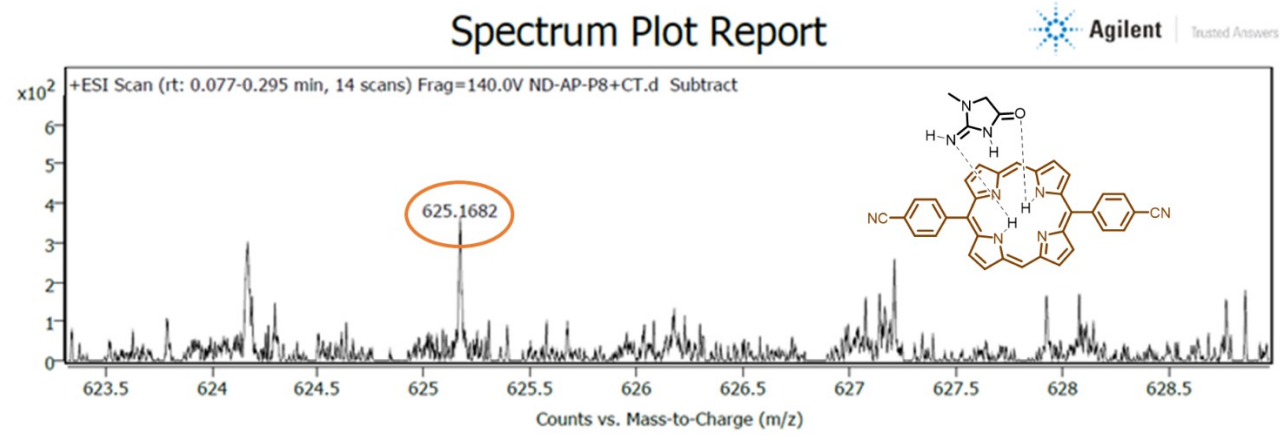

Figure S3: HRMS spectra of probe **1** with creatinine.

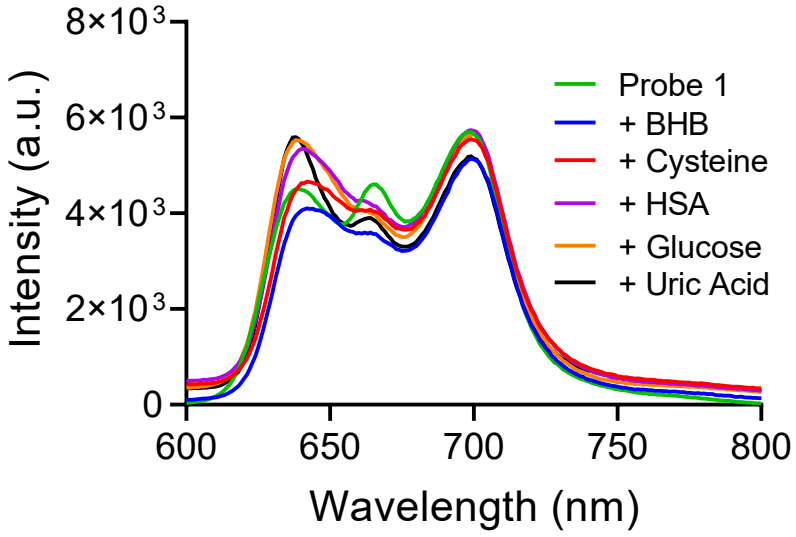

Figure S4: Fluorescence spectra of **1** (10 µM, λex = 440 nm) with bioanalytes (50 µM) in in pH 7 buffered medium.

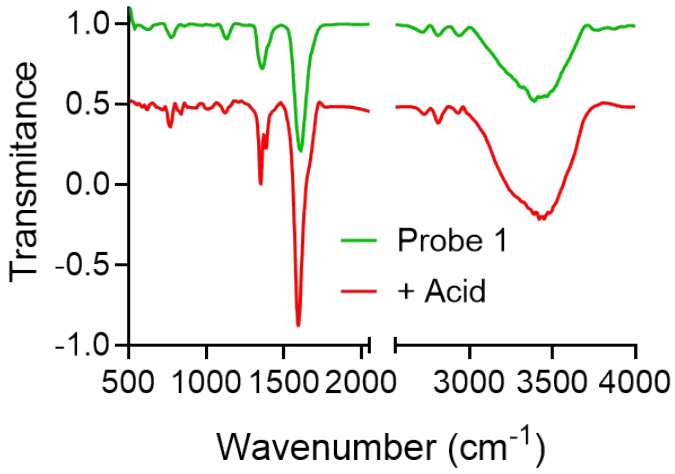

Figure S5: FT-IR spectra of Probe 1 with acid (HCl).

Name	Size (d. nm.)
Probe -1 in water at 40 ˚C	150 ± 8
at 50 ˚C	101 ± 10
at 60 ˚C	89 ± 7

Table T1: Temperature-dependent DLS spectra of probe **1** in water medium.

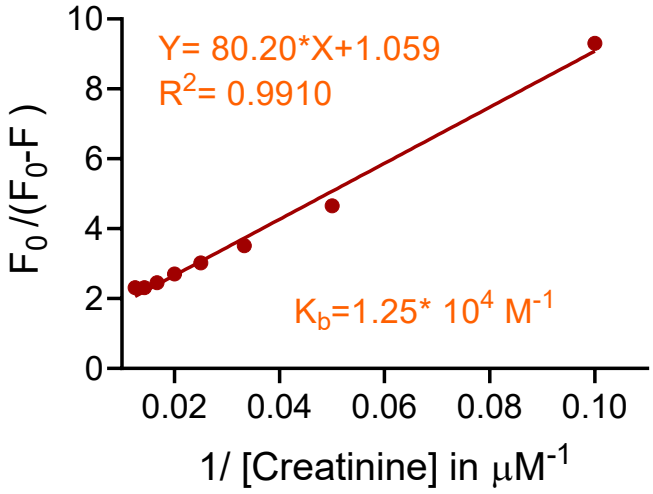

Figure S6: Linear Benesi–Hildebrand plot for the determination of the binding constant of probe **1** with creatinine.

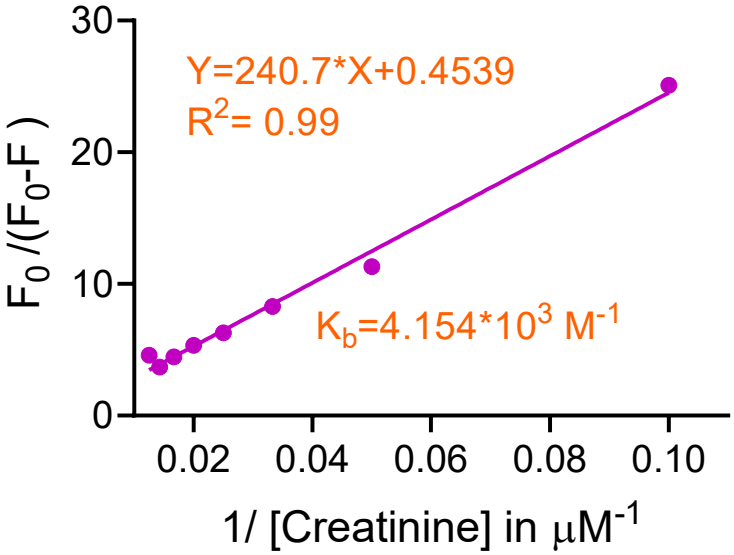

Figure S7: Linear Benesi–Hildebrand plot for the determination of the binding constant of probe **2** with creatinine.