Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

Supramolecular Spectral/Visual Detection of Urinary Polyamines through Synergetic/Competitive Complexation with γ-CD and CB[7]

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1 General

Chemicals and instruments

All of the chemicals used for synthesis were analytically pure and were used as received. Solvents were dried and distilled before use for synthesis. ^{1}H NMR spectra were recorded at room temperature on a Bruker AMX–400 (400 MHz) in $CDCl_3$ or DMSO-d_6 with TMS as an internal standard. HRMS were measured with a Waters–Q–TOF Premiers (ESI). UV-vis spectra were obtained on JASCO V–650. Fluorescence spectra were acquired using Fluoromax-4 spectrofluorometer. ITC data were acquired using VP-ITC.

2 Synthesis

Py-1 460 mg (2 mmol) of pyrene-1-carboxaldehyde was added to 80 mL of methanol, and then 670 μL (6 mmol) of p-aminobenzylamine was added. The reaction mixture was allowed to react overnight at room temperature. 80 mg (2 mmol) of sodium borohydride was added while the temperature of the flack was kept at 0 °C in an ice bath and then stirred for 3h after the addition at room temperature. The solvent was removed under reduced pressure. The resulting solid was dissolved in dichloromethane and washed with water to remove the inorganic salt. The solvent was removed under reduced pressure again. The resulting solid was purified with silica gel chromatography to give pale yellow solid (yield: 71%).

Py-2 0.5 mL of triethylamine was added to a 250 mL-flask containing 444 mg (2 mmol) of 4-dimethylaminobenzylamine dihydrochloride and 100 mL ethanol. As the solid was dissolved completely, 690 mg (3 mmol) of pyrene-1-carboxaldehyde was added. The reaction mixture was allowed to react overnight at room temperature. 380 mg (10 mmol) of sodium borohydride was added while the temperature of the flack was kept to be 0 °C in an ice bath and then stirred for 3h at room temperature. The solvent was removed under reduced pressure. The resulting solid was dissolved in dichloromethane and washed with water to remove the inorganic salt. The solvent was removed under reduced pressure again. The resulting solid was eluted with silica gel chromatography to give pale yellow solid (yield: 57%).

Py-3 460 mg (2 mmol) of pyrene-1-carboxaldehyde was added to 80 mL of methanol, and then 96 mg (0.7 mmol) of 2-aminonaphthalene was added. The reaction mixture was allowed to react overnight at room temperature.100 mg (2.7 mmol) of sodium borohydride was added while the temperature of the flack was kept to be 0 °C in an ice bath and then stirred for 3h at room temperature. The solvent was removed under reduced pressure. The resulting solid was dissolved in dichloromethane and washed with water to remove the inorganic salt. The solvent was removed under reduced pressure again. The resulting solid was eluted with silica gel chromatography to give pale yellow solid (yield: 65%).

Py-4 115 mg (0.5 mmol) of pyrene-1-carboxaldehyde was added to 80 mL of methanol and then 720 mg (5 mmol) of 1,8-diaminooctane was added. The reaction mixture was allowed to react overnight at room temperature. 190 mg (5 mmol) of sodium borohydride was added while the temperature of the flack was kept to be 0 °C in an ice bath and then stirred for 3h at room temperature. The solvent was removed under reduced pressure. The resulting solid was dissolved in dichloromethane and washed with water to remove the inorganic salt. The solvent was removed under reduced pressure again. The resulting solid was eluted with silica gel chromatography to give pale yellow solid (yield: 81%).

3 NMR and HRMS spectra

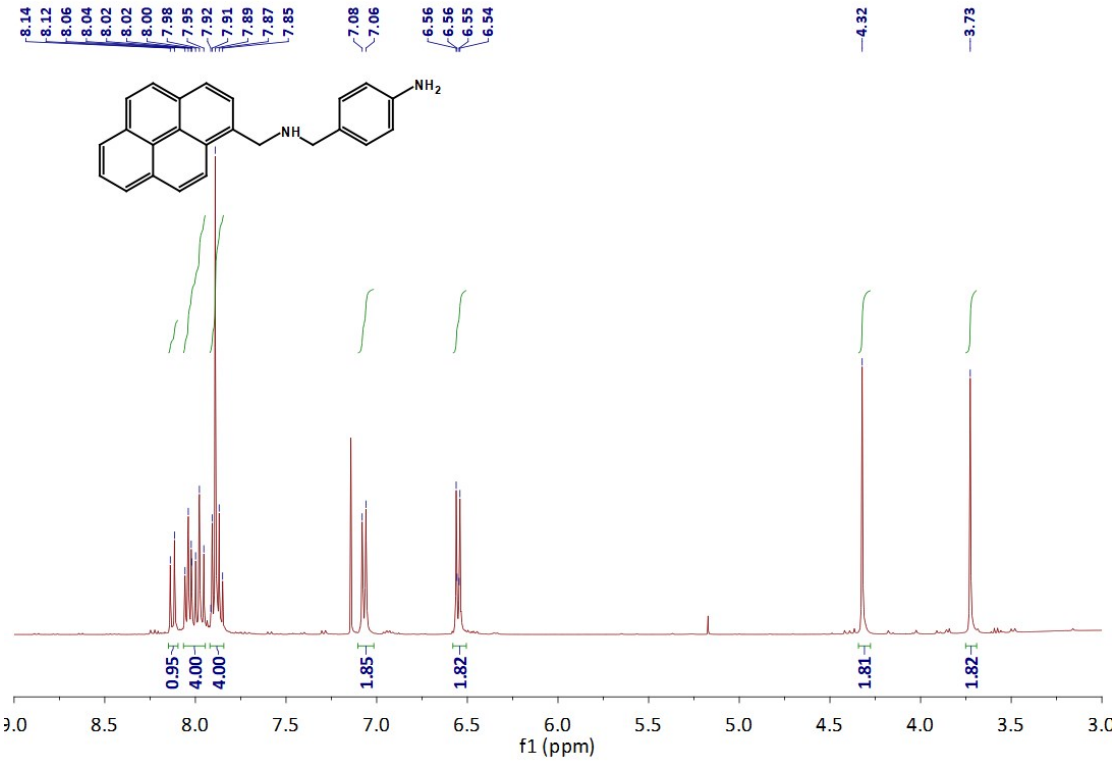


Figure S1 ^{1}H NMR spectrum (400 MHz, chloroform–*d*, room temperature) of **Py-1**.

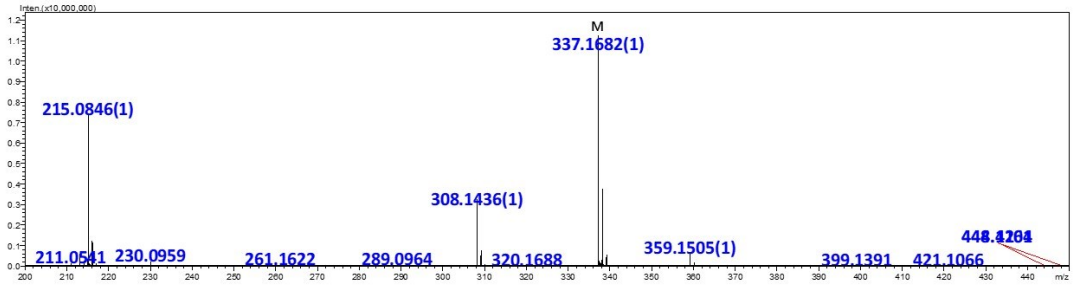


Figure S2 Mass spectrum of **Py-1**. Assignment of main peaks: m/z $[M+H]^{+}$, 337.170, found: 337.1682.

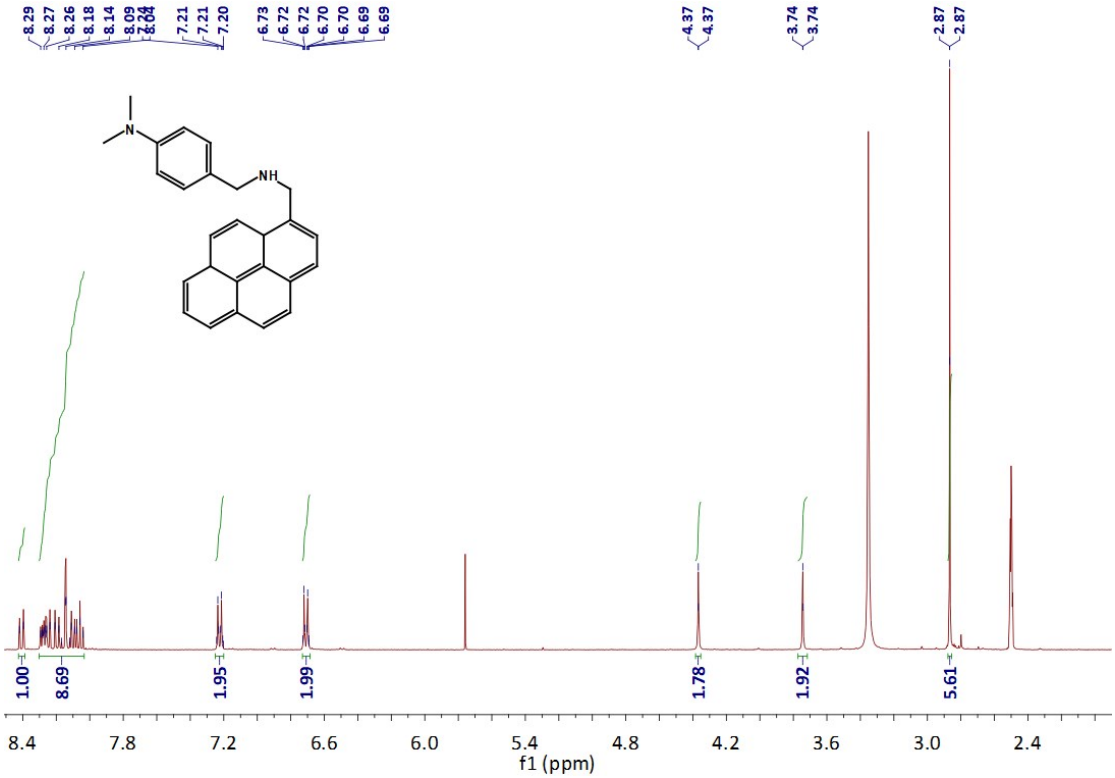


Figure S3 ^{1}H NMR spectrum (400 MHz, dimethyl sulfoxide–d_6, room temperature) of **Py-2**.

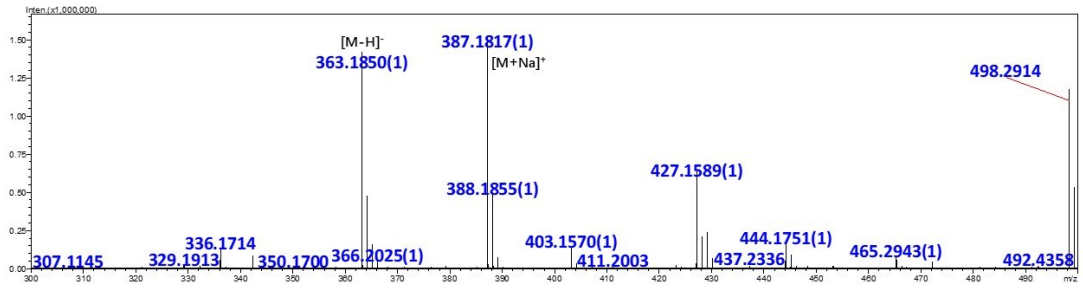


Figure S4 Mass spectrum of **Py-2**. Assignment of main peaks: m/z $[M+H]^+$, 387.184, found: 387.1817.

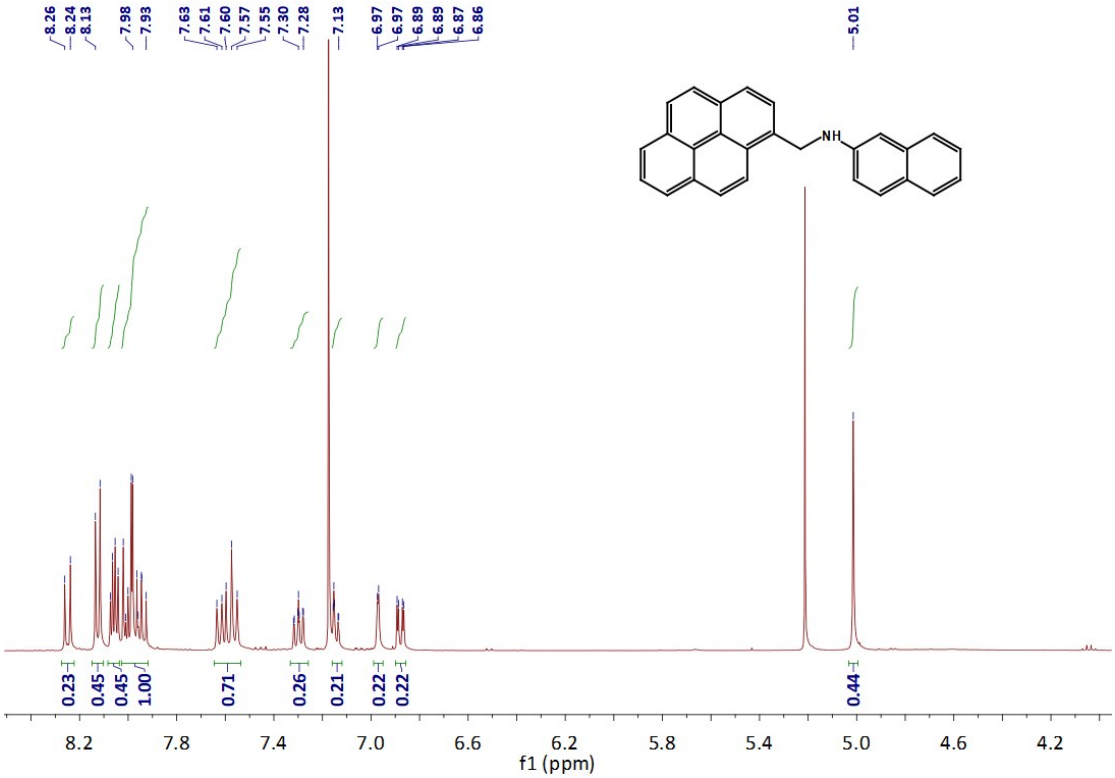


Figure S5 ^{1}H NMR spectrum (400 MHz, chloroform–*d*, room temperature) of **Py-3**.

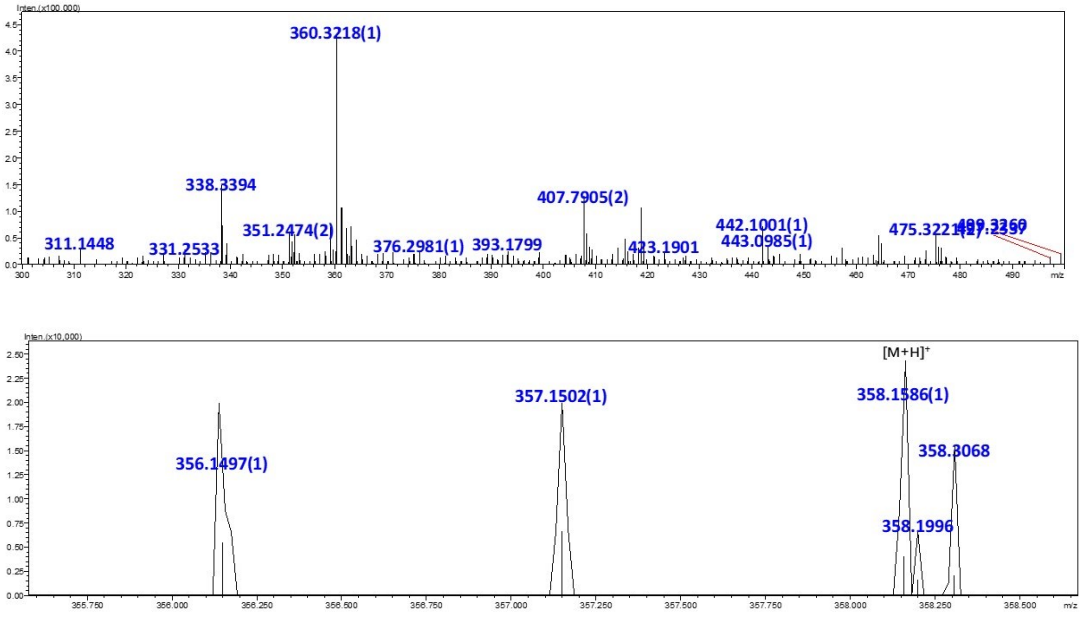


Figure S6 Mass spectrum of **Py-3**. Assignment of main peaks: m/z $[M+H]^{+}$, 358.160, found: 358.1586.

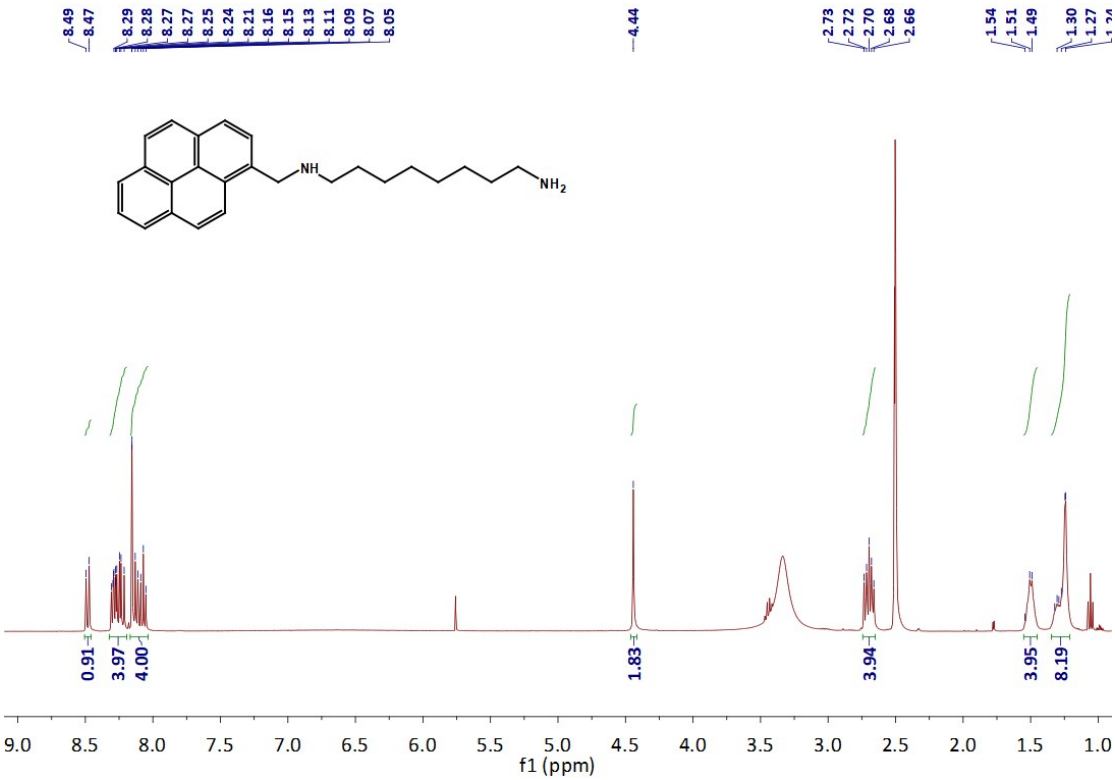


Figure S7 ^{1}H NMR spectrum (400 MHz, dimethyl sulfoxide–d_6, room temperature) of **Py-4**.

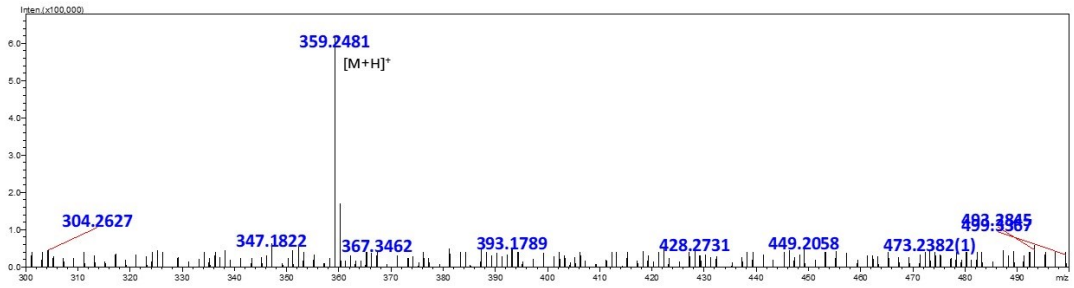


Figure S8 Mass spectrum of **Py-4**. Assignment of main peaks: m/z $[M+H]^+$, 359.249, found: 359.2481.

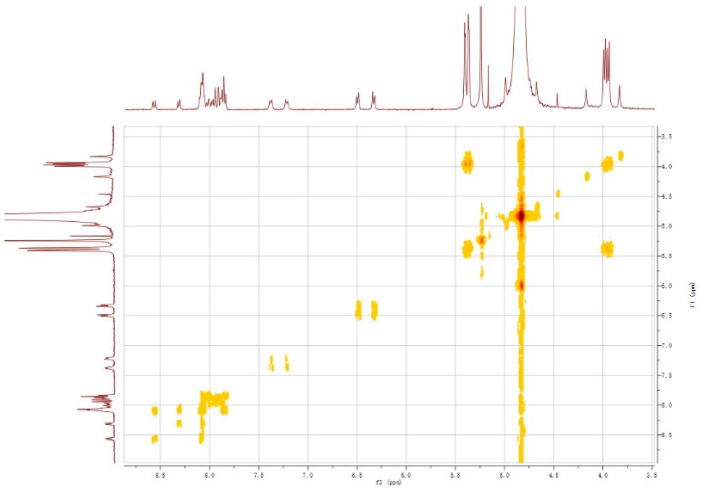


Figure S9 Correlation spectroscopy of inclusion compound composed by **Py-1** (1 mM) and CB[7] (0.5 mM) (5% DCl with 25% DMSO-d_6 in it, 400 MHz).

4 Isothermal Titration Calorimetry

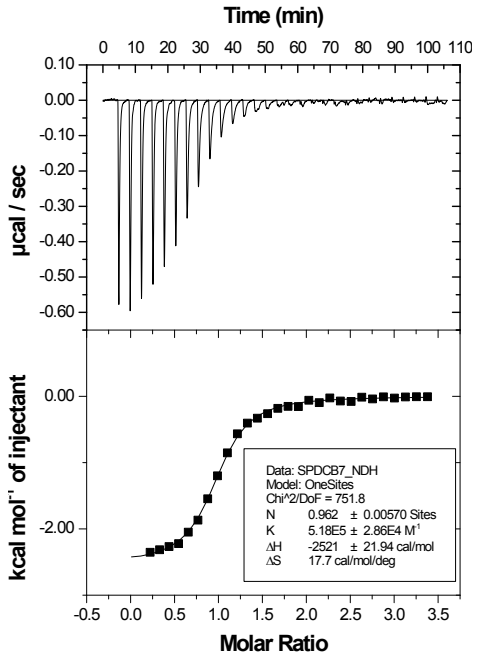


Figure S10 ITC data for the titration of 0.05 mM CB[7] solution by 0.75 mM spermidine solution in a borate buffer (pH 9).

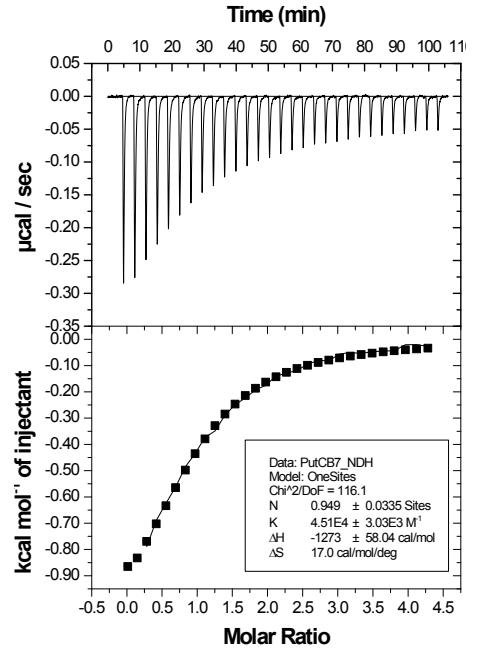


Figure S11 ITC data for the titration of 0.05 mM CB[7] solution by 0.95 mM putrescine solution in a borate buffer (pH 9).

5 Fluorescence spectra of host and guest binding complexes

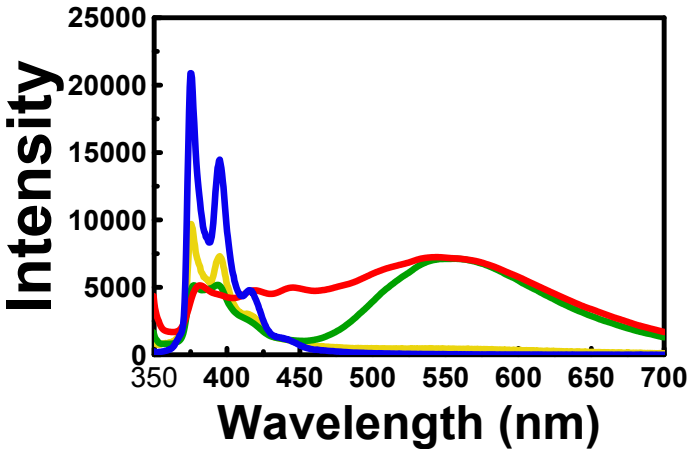


Figure S12 The fluorescence emission spectra of 10 μM **Py-1** (yellow), **Py-2** (green), **Py-3** (red) and **Py-4** (blue) in ethanol solution measured at 25 °C; λ_{ex} = 340 nm.

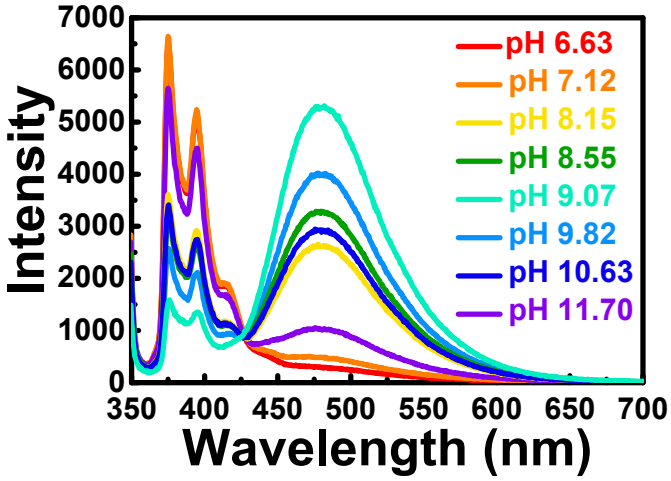
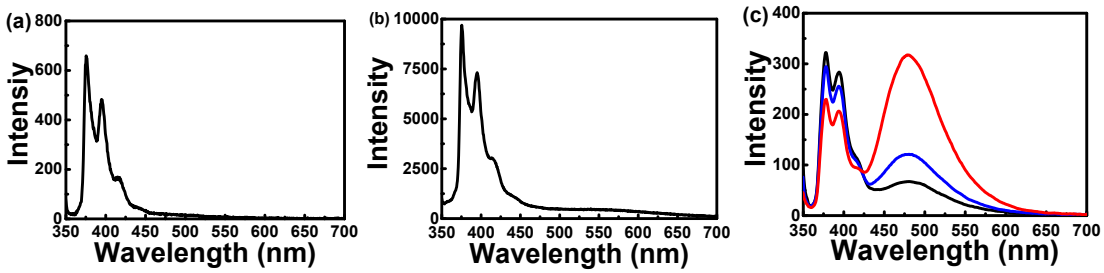


Figure S13 Fluorescence spectra of 10 μM **Py-1** as a function of pH in the presence of 5 mM γ-CD at 25 °C; λ_{ex} = 340 nm.



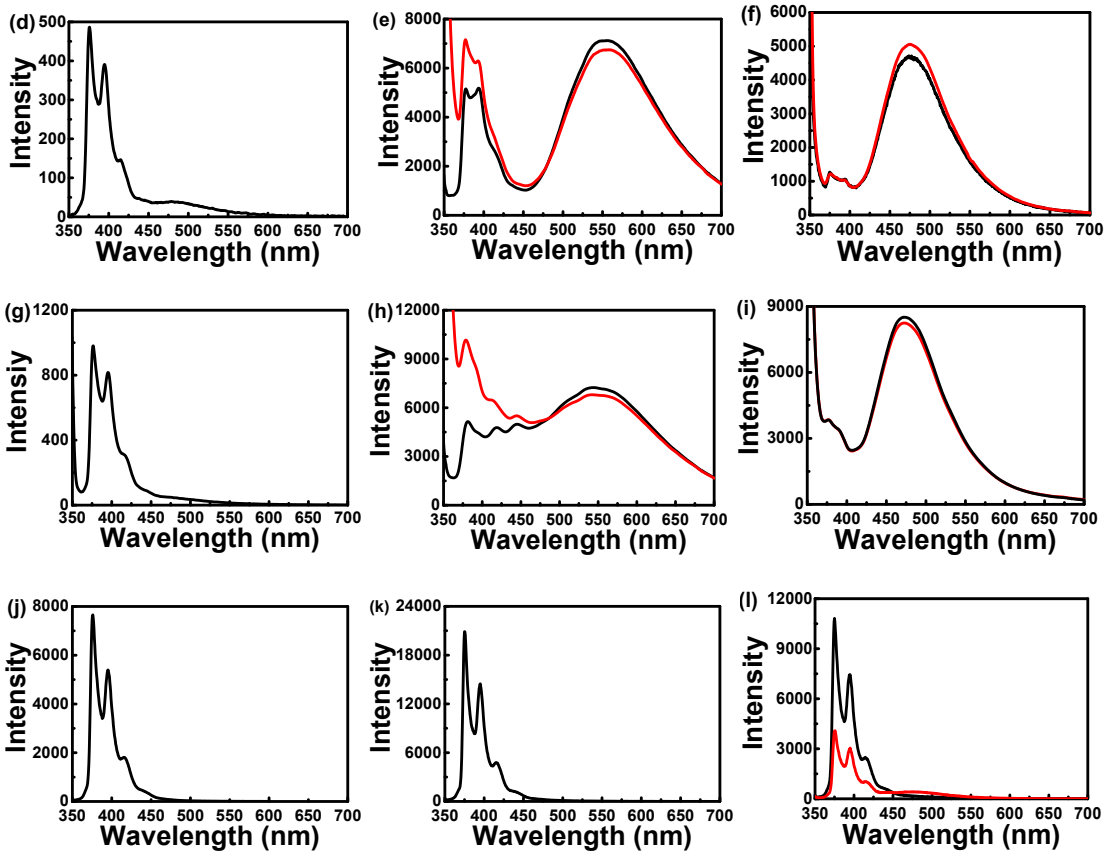


Figure S14. (a) Fluorescence spectra of **Py-1** (10 μM) in ethyl acetate at 25 °C; λ_{ex} = 340 nm. (b) Fluorescence spectra of **Py-1** (10 μM) in methanol at 25 °C; λ_{ex} = 340 nm. (c) Fluorescence spectra of **Py-1** (10 μM) in absence (black) of any host and in the presence (red and then blue) of γ-CD (5 mM) and then γ-CD (5 mM) & CB[7] (10 μM) in ultra pure water at 25 °C; λ_{ex} = 340 nm. (d) Fluorescence spectra of **Py-2** (10 μM) in ethyl acetate at 25 °C; λ_{ex} = 340 nm. (e) Fluorescence spectra of **Py-2** (10 μM) in absence (black) and presence (red) of CB[7] (10 μM) in methanol at 25 °C; λ_{ex} = 340 nm. (f) Fluorescence spectra of **Py-2** (10 μM) in absence (black) and presence (red) of CB[7] (10 μM) in ultra pure water at 25 °C; λ_{ex} = 340 nm. (g) Fluorescence spectra of **Py-3** (10 μM) in ethyl acetate at 25 °C; λ_{ex} = 340 nm. (h) Fluorescence spectra of **Py-3** (10 μM) in absence (black) and presence (red) of CB[7] (10 μM) in methanol at 25 °C; λ_{ex} = 340 nm. (i) Fluorescence spectra of **Py-3** (10 μM) in absence (black) and presence (red) of CB[7] (10 μM) in ultra pure water at 25 °C; λ_{ex} = 340 nm. (j) Fluorescence spectra of **Py-4** (10 μM) in ethyl acetate at 25 °C; λ_{ex} = 340 nm. (k) Fluorescence spectra of **Py-4** (10 μM) in methanol at 25 °C; λ_{ex} = 340 nm. (l) Fluorescence spectra of **Py-4** (10 μM) in absence (black) and presence (red) of γ-CD (5 μM) in ultra pure water at 25 °C; λ_{ex} = 340 nm.

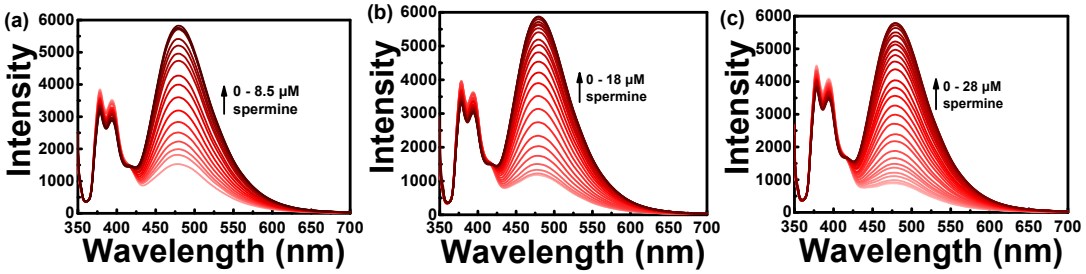


Figure S15. Excimer emission of **Py-1** (10 μM) quenched by CB[7] (10 μM (a); 20 μM (b); 30 μM (c)) and recovered by spermine in in a borate buffer (pH 9) containing 5 mM γ-CD at 25 °C; λ_{ex} = 340 nm.

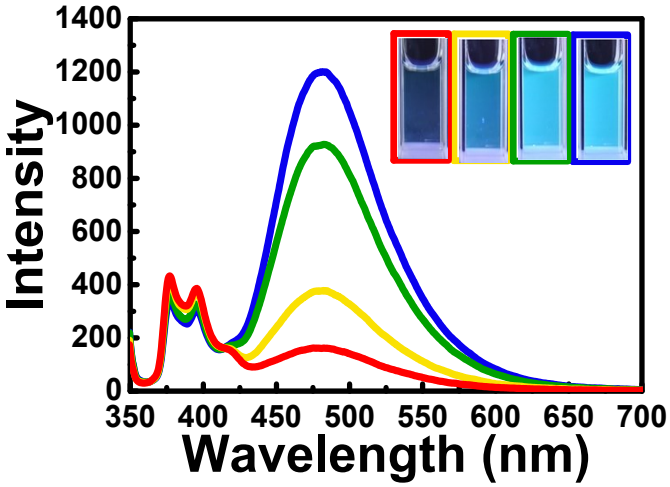


Figure S16 Fluorescence spectra of the solution containing 10 μM **Py-1**, 5 mM γ-CD and 30 μM CB[7] in the absence (red) and presence of urinary polyamines of healthy concentrations (yellow), urinary polyamines of solid tumor concentrations (green) and urinary polyamines of blood tumor concentrations (blue) in a borate buffer (pH 9) at 25 °C; λ_{ex} = 340 nm (urinary polyamines of healthy concentrations, solid tumor concentrations and blood tumor concentrations refer to Table S1).[28] Insets are the photographs of the corresponding samples.

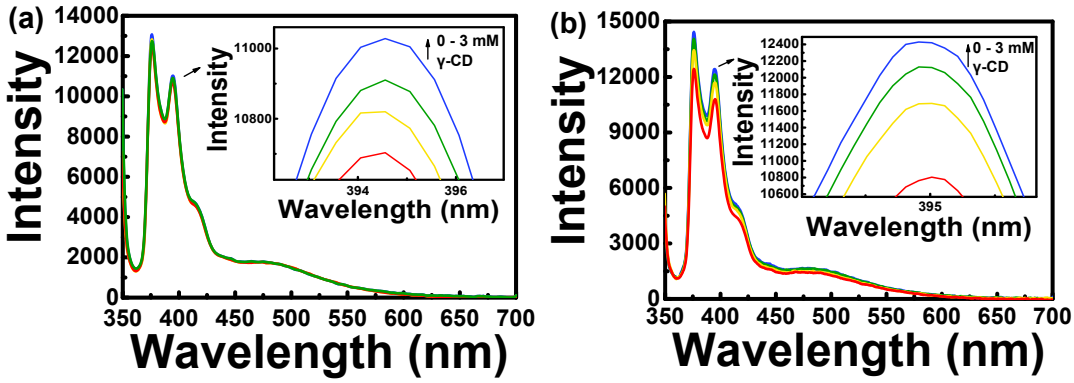


Figure S17 Fluorescence spectra of 10 μM **Py-1** as a function α-CD (a) or β-CD (b) (at pH 9.0 borate buffer solution) at 25 °C; λ_{ex} = 340 nm.

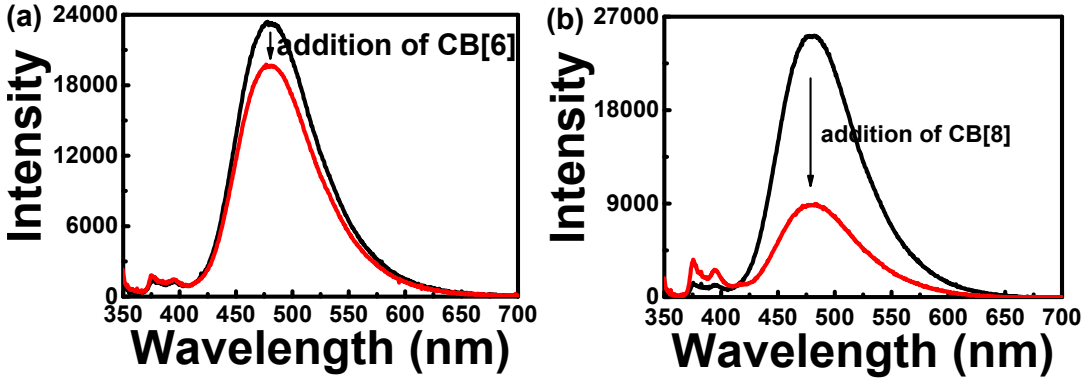


Figure S18 Emission spectral change of 10 μM **Py-1** in the presence of 5 mM γ-CD upon addition of 10 μM CB[6] (a) or 10 μM CB[8] (b) in a borate buffer (pH 9) at 25 °C; λ_{ex} = 340 nm.