Supporting Information

Tunable Fluorescence Behaviors of Supramolecular System Based on a Fluorene Derivative and Cucurbit[8]uril and Its Application for ATP Sensing

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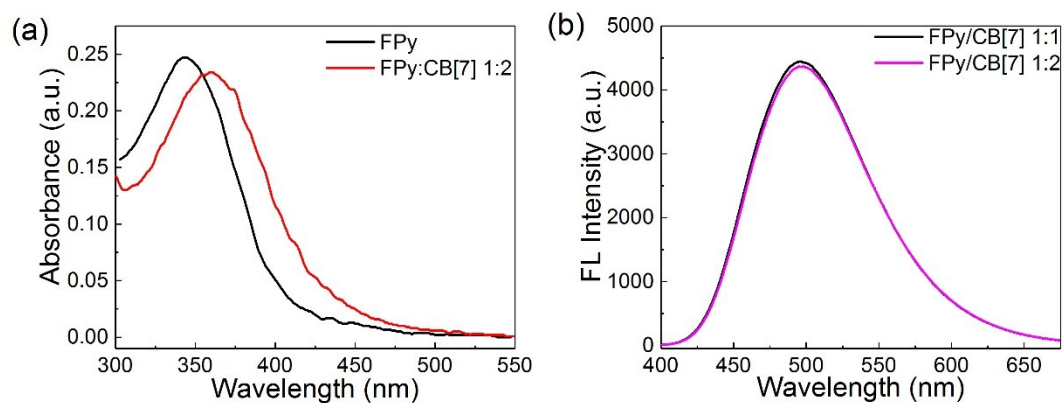Email: lidong@mater.ustb.edu.cn; cuiqianling@ustb.edu.cn

Figure S1. (a) The UV-vis absorption and (b) fluorescence emission spectra of FPy/CB[7] in water. The excitation wavelength is 345 nm and the concentration of FPy is 10 μM.
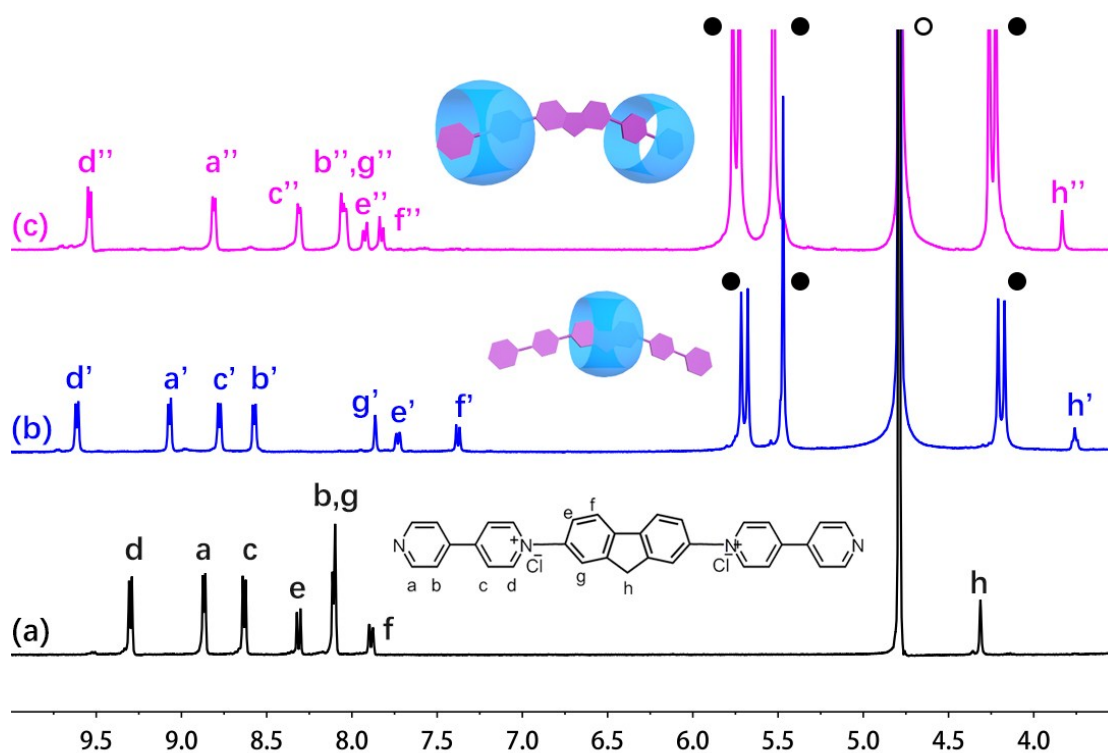

Figure S2. ^{1}H NMR spectra (400 MHz, 298K): (a) FPy (5.0 mM) in D$_2$O, (b) FPy/CB[7](1:1), (c) FPy/CB[7](1:2). The CB[7] and solvent are denoted as symbol ● and ○, respectively.
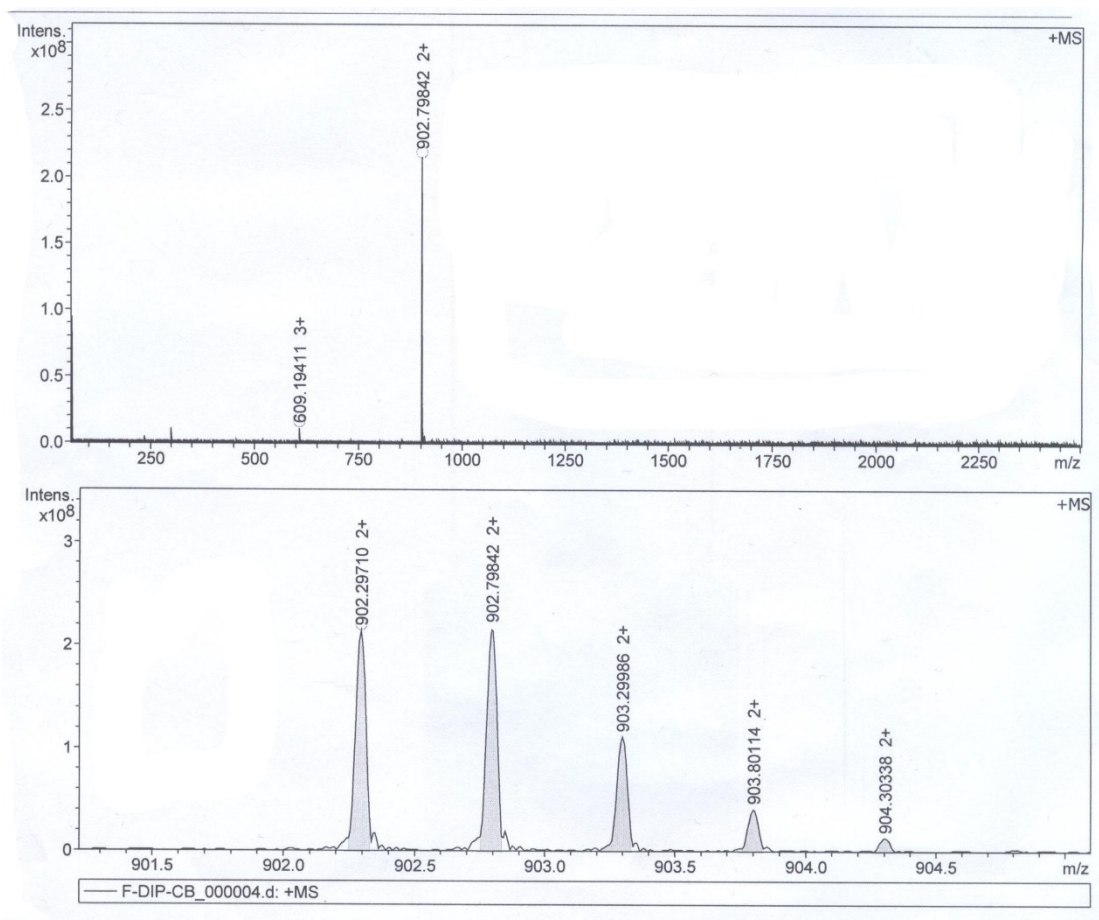
Figure S3. High-resolution ESI-MS spectra for FPy/CB[8] (1:1) complexes.
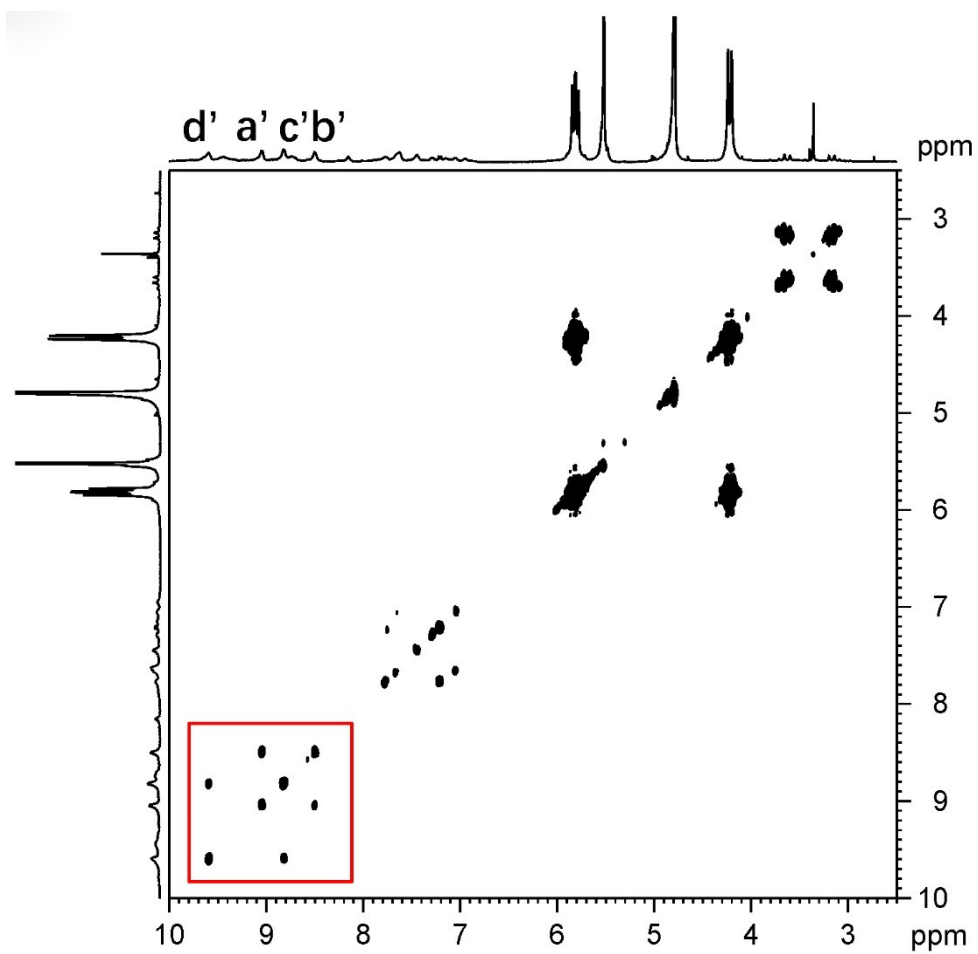
Figure S4. COSY ^{1}H NMR spectrum (400 MHz, 298 K) of the 1:1 solution of FPy and CB[8] (5 mM) in D_2O

Calculation of the stability constant of FPy/CB[7] (1:1) and FPy/CB[8] (1:1) by ^{1}H NMR integration
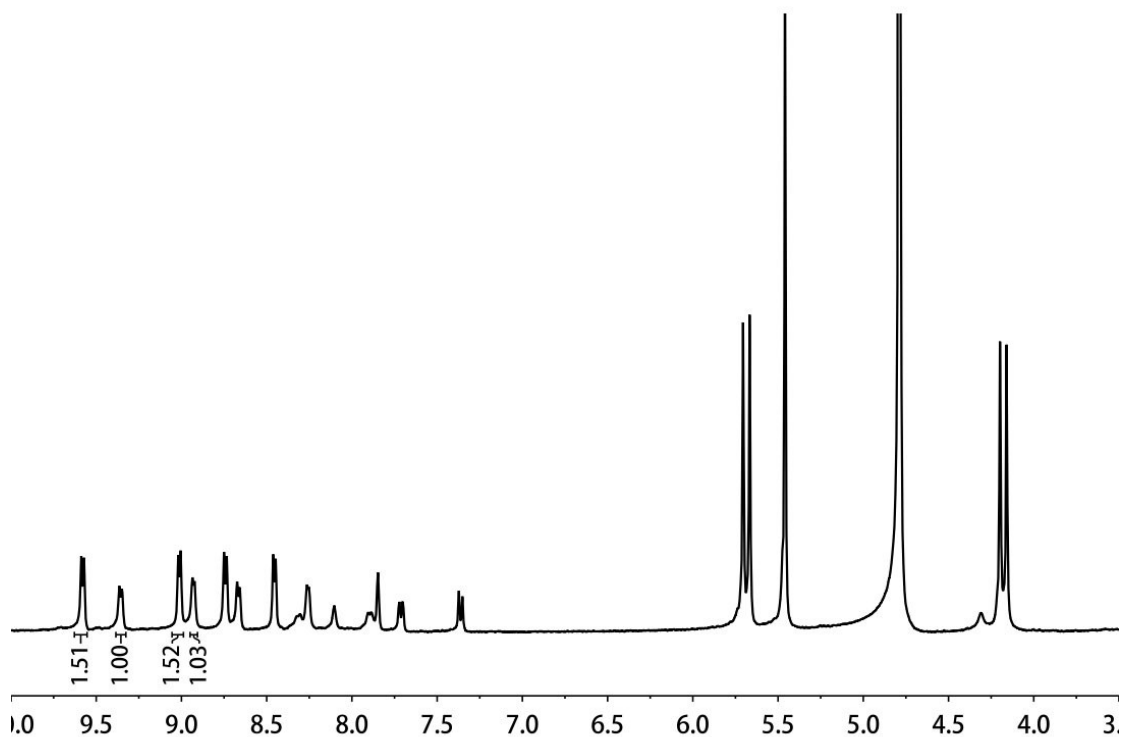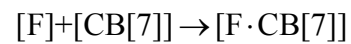

Figure S5. ^{1}H NMR spectrum of FPy in the presence of 0.6 equiv of CB[7] (D$_2$O, 400 MHz, 298 K, [FPy] = 10 mM).

With addition of different portions of CB[7], the binding process contains only one equilibrium, so it can be explained as one equation. From the ^{1}H NMR spectra, it can be found that the equilibrium exhibits slow exchange on the NMR timescale in which both "free" and "bound" guests can be distinguished in the spectra. The binding constant of FPy and CB[7] can be calculated by single-point method from the integral ratio of complexed and uncomplexed protons of FPy. Taking H$_d$ as example, we can use 1.51/1.00 as the ratio of "bound" and "free" guest. We assume the minimum free CB[7] concentration is 0.01 mM, which is reported as the maximal saturated concentration for CB[7] in water without the assistance of any guest. Thus, the lower

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limit for the stability constant K_S could be calculated[1-2] as 1.47×10^5 M^{-1}.

$$[F]+[CB[7]] \rightarrow [F \cdot CB[7]]$$

$$K_s = \frac{[F \cdot CB[7]]}{[CB[7]]_{free} \times [F]_{free}} = \frac{[F_{bound}]}{[CB[7]]_{free} \times [F]_{free}}$$

$$[CB[7]_{free}] < 10^{-5} M$$

$$K_s = \frac{1.51/2.51}{(1.00/2.51) \times 10^{-5}} = 1.51 \times 10^5 M^{-1}$$

For proton H_d,

$$K_s = \frac{1.52/2.55}{(1.03/2.55) \times 10^{-5}} = 1.48 \times 10^5 M^{-1}$$

For proton H_c.

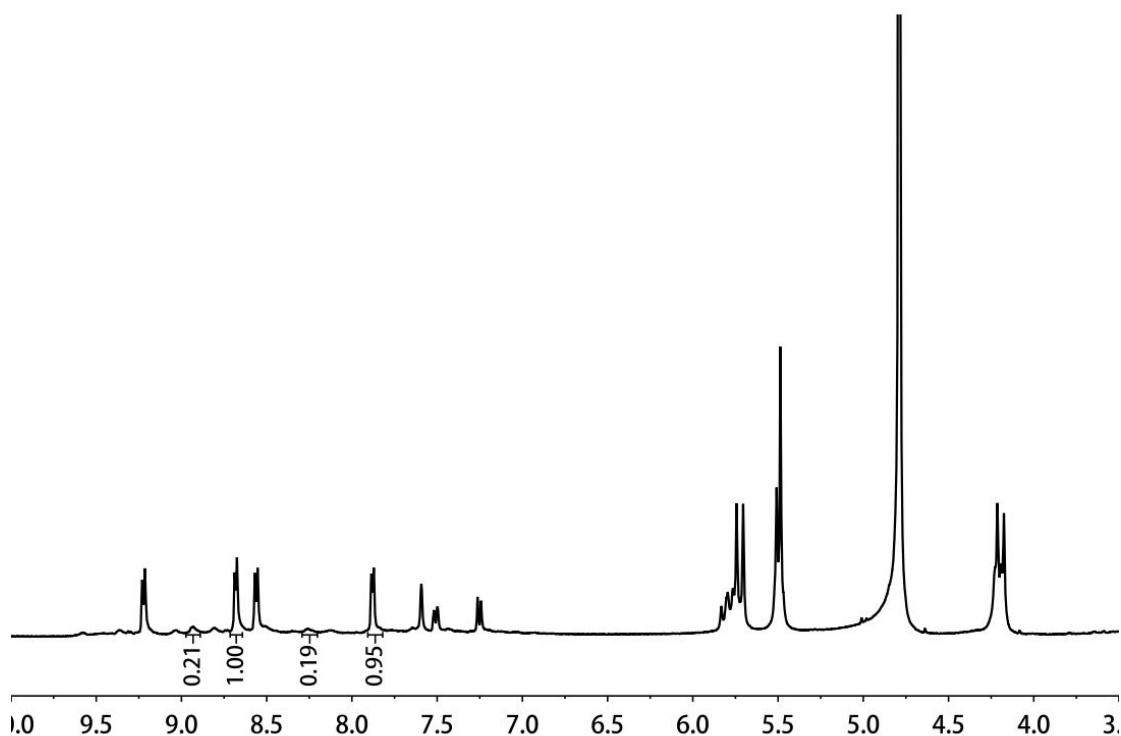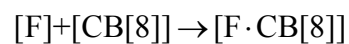Thus, $K_s = \frac{1.51 + 1.48}{2} \times 10^5 = 1.49 \times 10^5 M^{-1}$

Figure S6. ^{1}H NMR spectrum of FPy in the presence of 0.6 equiv of CB[8] (D$_2$O, 400 MHz, 298 K, [FPy] = 10 mM).

For FPy /CB[8] (1:1),

$$[F] + [CB[8]] \rightarrow [F \cdot CB[8]]$$

$$K_s = \frac{[F \cdot CB[8]]}{[CB[8]]_{free} \times [F]_{free}} = \frac{[F_{bound}]}{[F]_{free} \times [CB[8]]_{free}}$$

$$[CB[8]]_{free} < 10^{-5} M$$

$$K_s = \frac{0.21/1.21}{(1.00/1.21) \times 10^{-5}} = 2.1 \times 10^4 M^{-1}$$

For proton H$_a$,

$$K_s = \frac{0.19/1.94}{(0.95/1.94) \times 10^{-5}} = 2.0 \times 10^4 M^{-1}$$

For proton H$_b$.

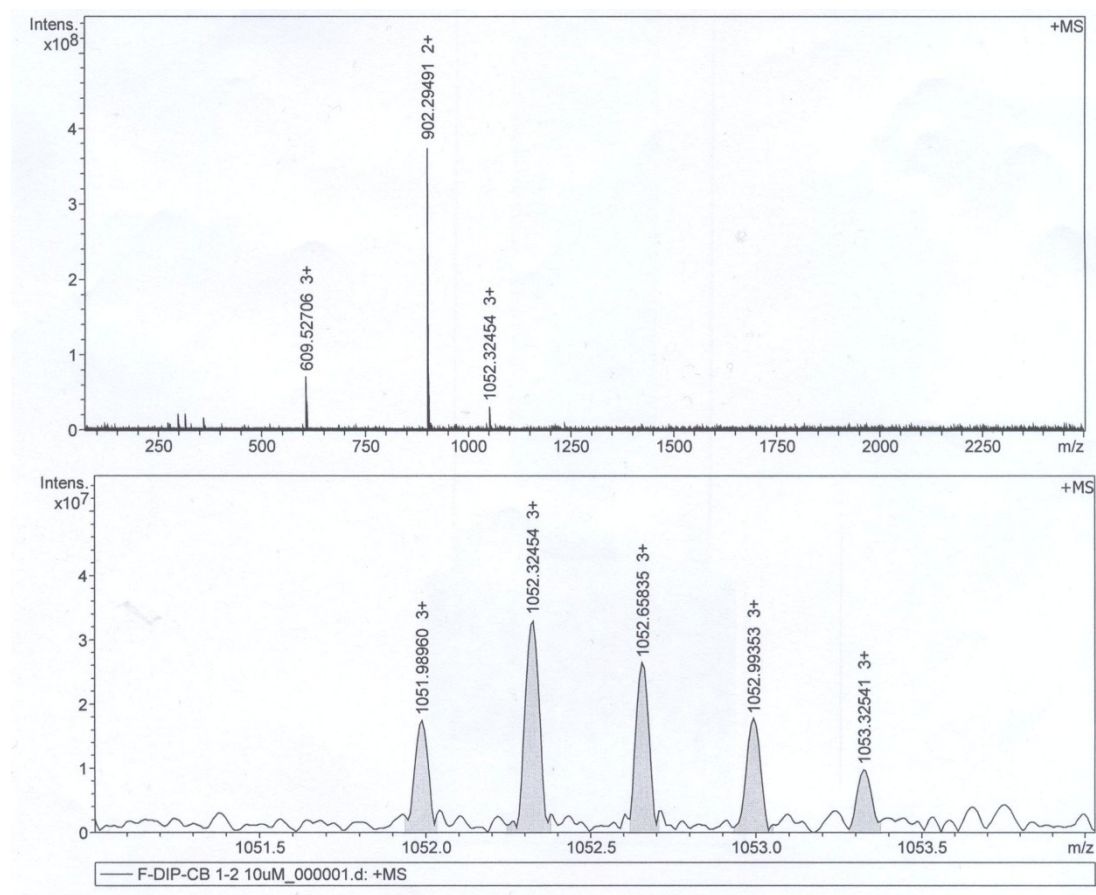Thus, $K_s = \frac{2.1 + 2.0}{2} \times 10^4 = 2.05 \times 10^4 M^{-1}$

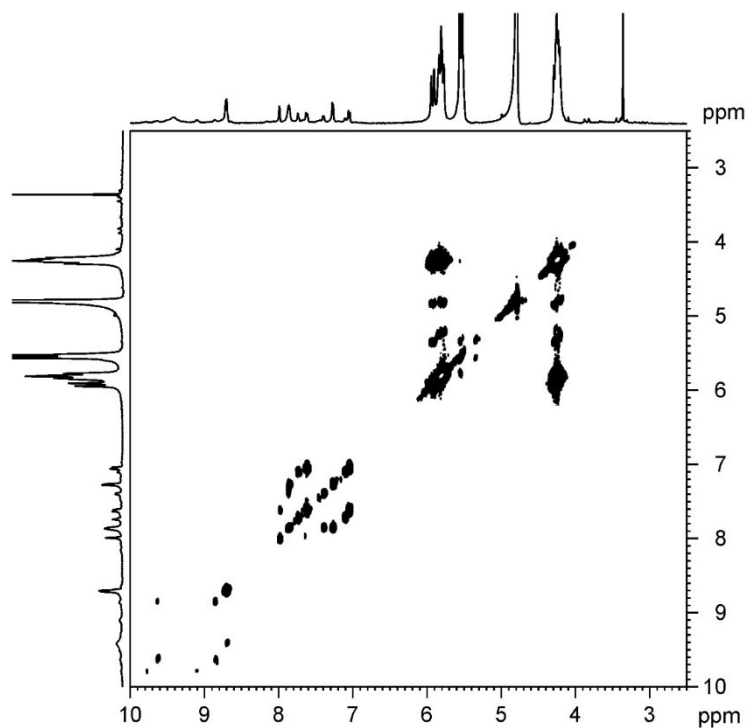**Figure S7.** High-resolution ESI-MS spectra for FPy/CB[8] (1:2) complexes.

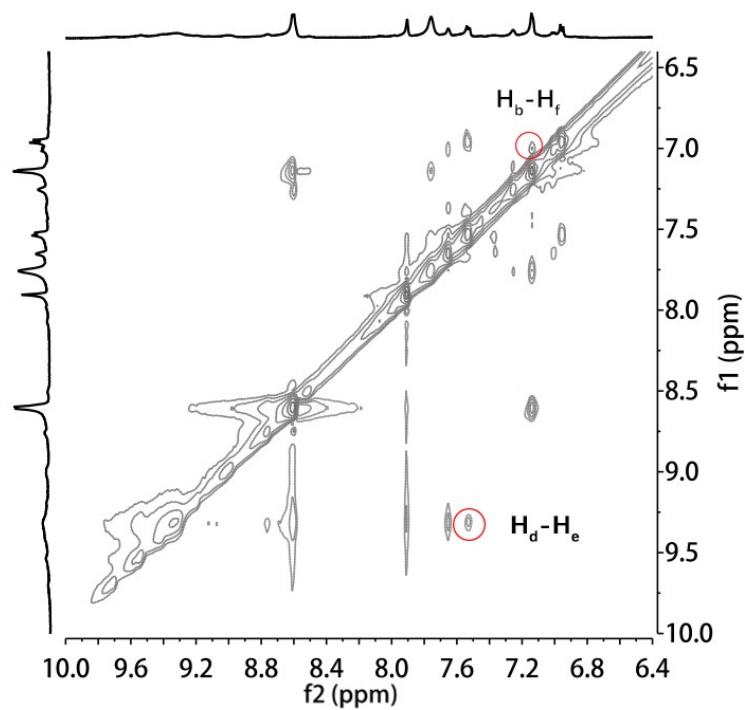**Figure S8.** COSY ^{1}H NMR spectrum (400 MHz, 298 K) of the 1:2 solution of FPy and CB[8] (5 mM) in D$_2$O.

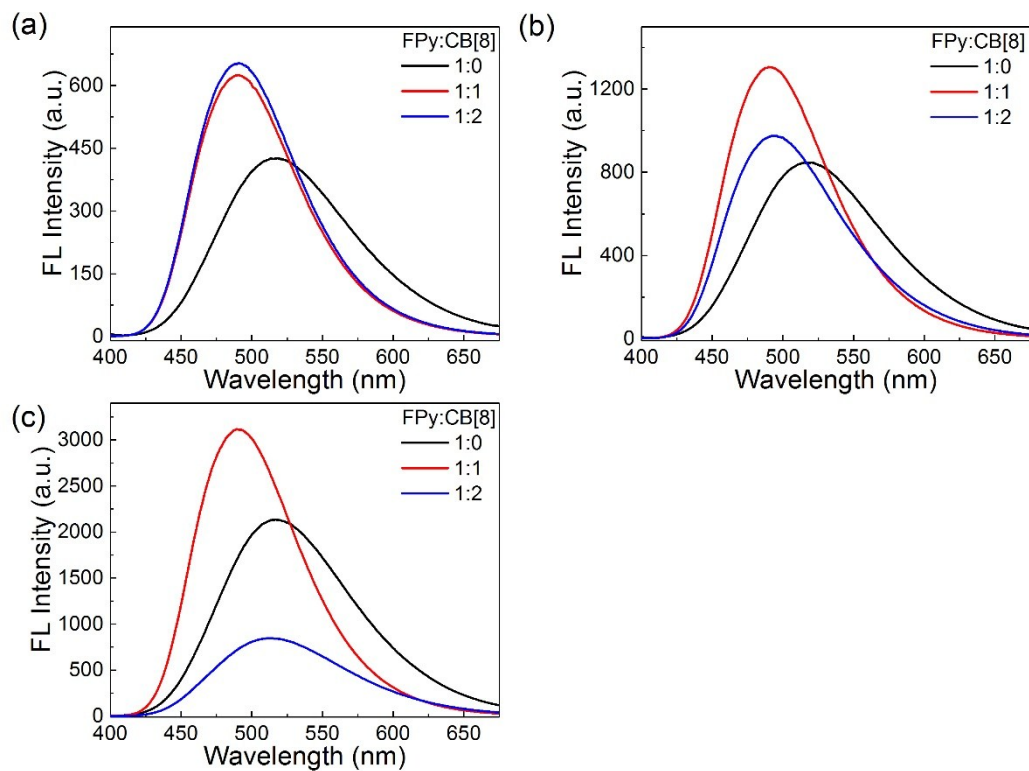**Figure S9.** ^{1}H-^{1}H ROESY spectrum (500 MHz, 298 K) of the 1:2 solution of FPy and CB[8] (5 mM) in D$_2$O.

Figure S10. The fluorescence emission spectra of FPy, FPy/CB[8] (1:1), FPy/CB[8] (1:2), (a) c(FPy) = 1 μM, (b) c(FPy) = 2 μM, and (c) c(FPy) = 5 μM.
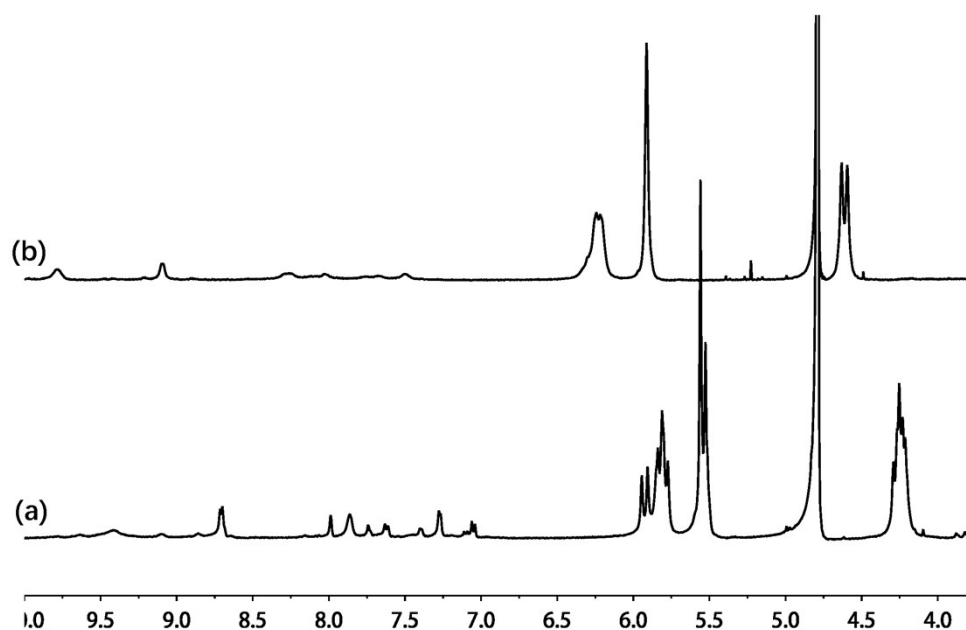
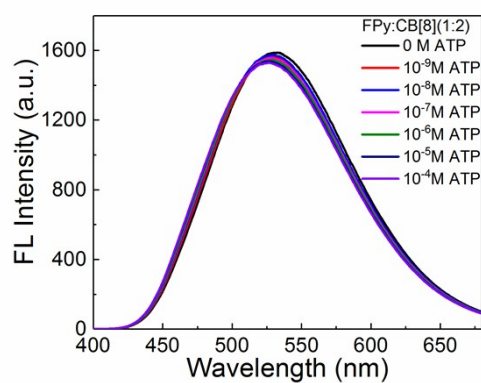**Figure S11.** ^{1}H NMR spectra of FPy/CB[8] (1:2) in D_2O at (a) 298K and (b) 333K.

Figure S12. Fluorescence spectra of FPy/CB[8] (1:2) complex upon continuous addition of ATP with concentration from 1 nM to 0.1 mM.
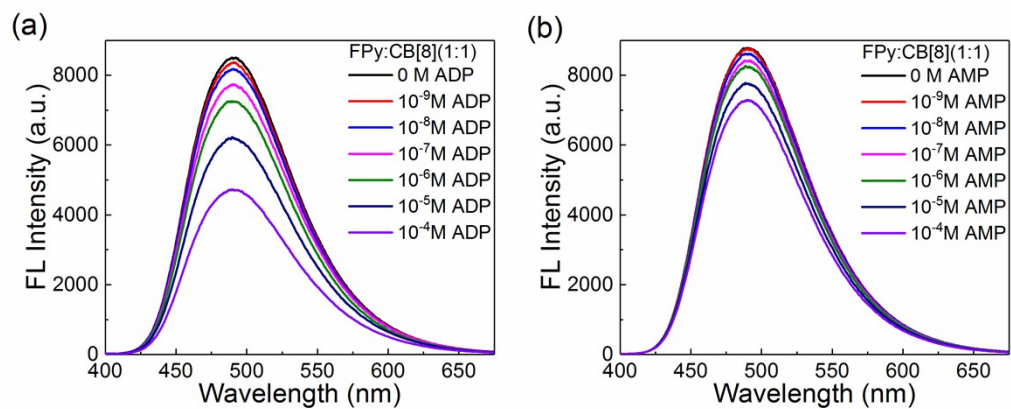
Figure S13. (a) Fluorescence spectra of FPy/CB[8] (1:1) upon continuous addition of ADP with concentration from 1 nM to 0.1 mM. (b) Fluorescence spectra of FPy/CB[8] (1:1) upon continuous addition of AMP with concentration from 1 nM to 0.1 mM.
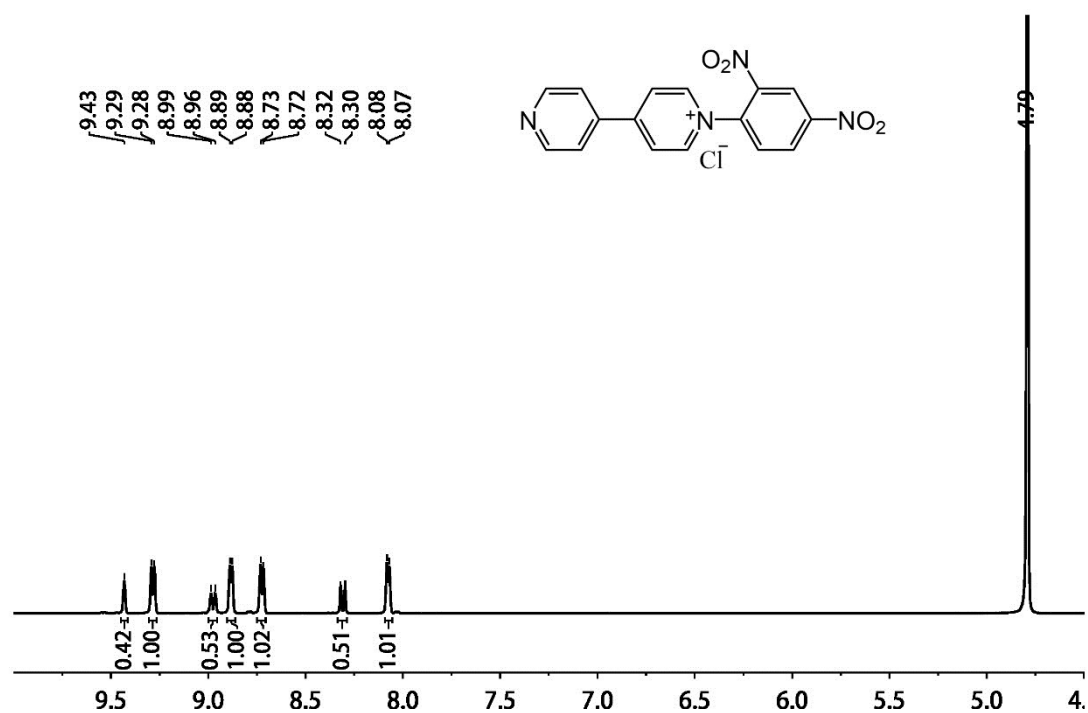
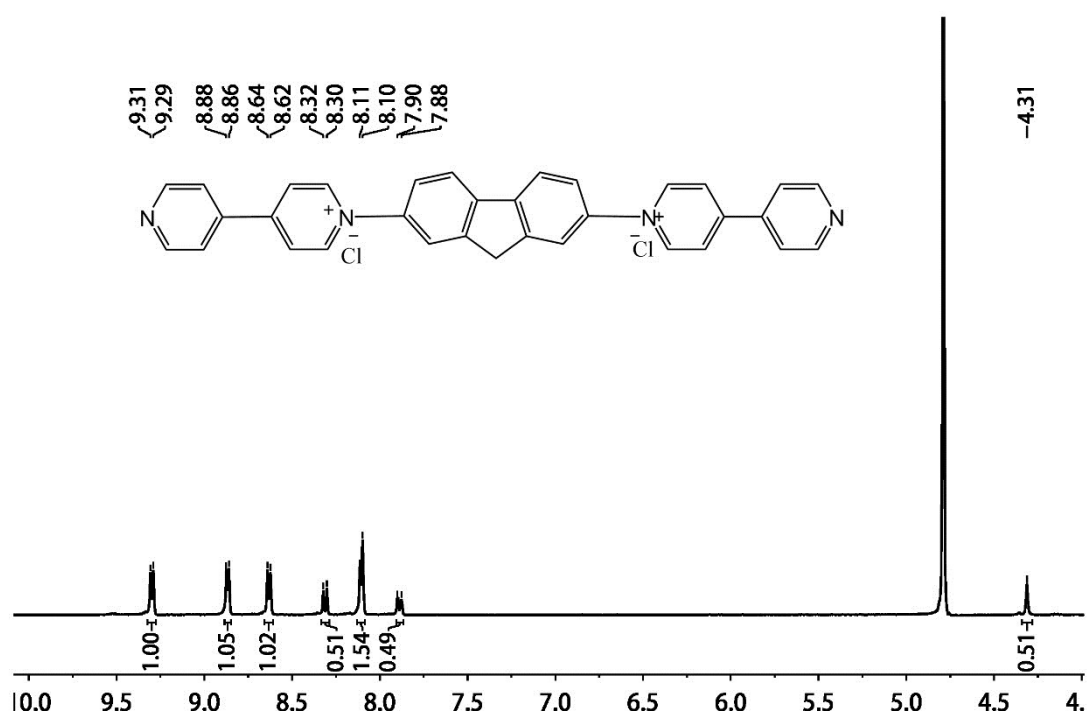**Figure S14.** ^{1}H NMR spectrum of compound 1 (D$_2$O, 400 MHz, 298K).

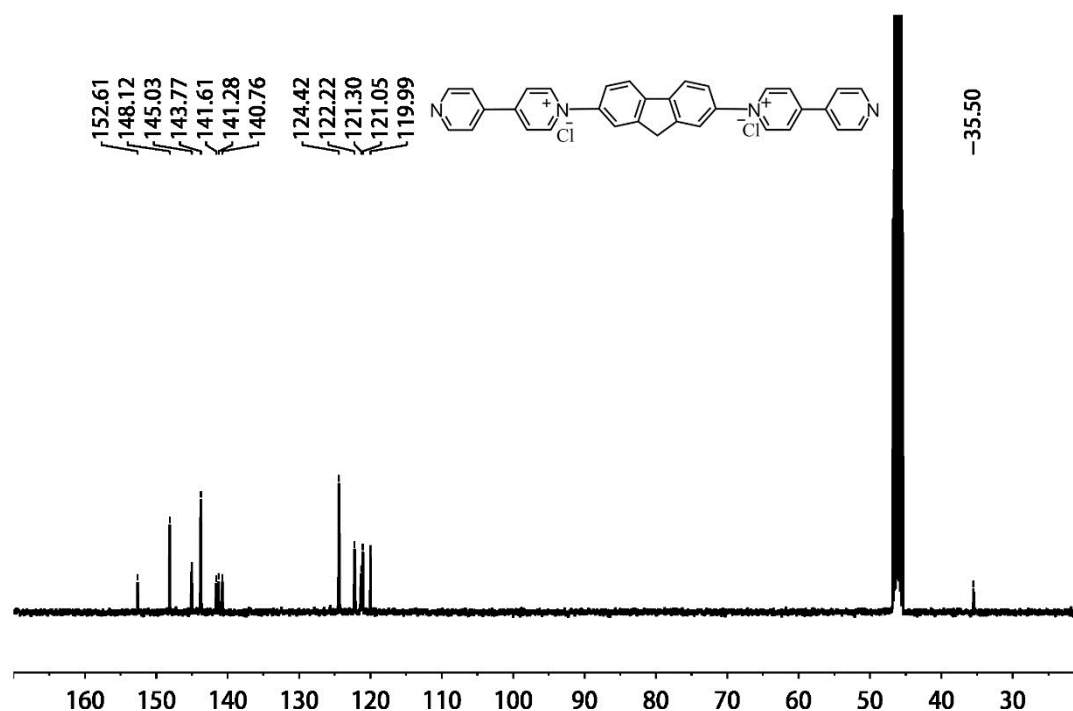**Figure S15.** ^{1}H NMR spectrum of FPy (D$_2$O, 400 MHz, 298K).

Figure S16. ^{13}C NMR spectrum of FPy (D$_2$O, 100 MHz, 298K).

REFERENCES

(1) Zhang, Z. J.; Zhang, Y. M.; Liu, Y., Controlled molecular self-assembly behaviors between cucurbituril and bispyridinium derivatives. *J. Org. Chem.* **2011,** *76*, 4682-4685.

(2) Liu, L.; Zhao, N.; Scherman, O. A., Ionic liquids as novel guests for cucurbit[6]uril in neutral water. *Chem. Commun.* **2008**, 1070-1072.