Electronic Supplementary Information for

Artificial supramolecular light-harvesting systems based on a pyrene derivative for photochemical catalysis

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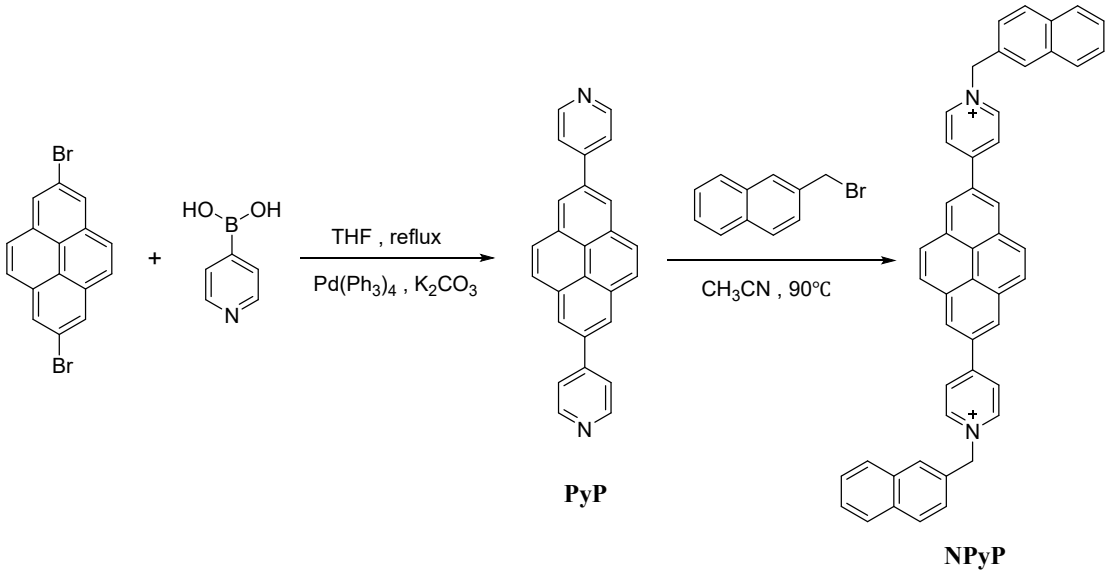
Experimental

Materials: Unless specifically mentioned, all chemicals are commercially available and were used as received.

Characterizations: ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) at 298 K, and the chemical shifts (δ) were expressed in ppm, and J values were given in Hz. UV-vis spectra were obtained on a Shimadzu UV-1601PC spectrophotometer in a quartz cell (light path 10 mm) at 298 K. Steady-state fluorescence measurements were carried out using a Hitachi 4500 spectrophotometer. Dynamic light scattering (DLS) and zeta potential are measured on Malvern Zetasizer Nano ZS90. Transmission electron microscopy (TEM) images were obtained on a JEM 2100 operating at 120 kV. Samples for TEM measurement were prepared by dropping the mixed aqueous solution on a carbon-coated copper grid (300 mesh) and drying by slow evaporation.



Scheme S1. Synthetic route of NPyP.

Synthesis of PyP: 2,7-dibromopyrene (0.50 g, 1.39 mmol), 4-pyridinyl boronic acid (0.51 g, 4.2 mmol), tetrakis(triphenylphosphine)palladium (0.092 g, 0.08 mmol) were added into the mixed solution of tetrahydrofuran (7 mL), toluene (1 mL) and 3 mL of 2 mol/L aqueous potassium carbonate. The mixture was refluxed under nitrogen for 3 days, filtered, and the precipitate was collected and washed with H_2O and methanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 5.1 Hz, 4H), 8.47 (s, 4H), 8.22 (s, 4H), 7.83 (d, J = 5.1 Hz, 4H).

Synthesis of NPyP: NPyP was obtained through the reaction between 2-(bromomethyl)naphthalene and PyP at 85 °C for 3 days in acetonitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.45 (d, J = 6.4 Hz, 4H), 9.09 (s, 4H), 8.89 (d, J = 6.4 Hz, 4H), 8.43 (s, 4H), 8.17 (s, 2H), 8.05 (d, J = 8.6 Hz, 2H), 7.98 (d, J = 7.5 Hz, 4H), 7.71 (d, J = 8.6 Hz, 2H), 7.62 – 7.59 (m, 4H), 6.09 (s, 4H).

Energy-transfer efficiency calculation: The energy-transfer efficiency (Φ_{ET}) was calculated from excitation fluorescence spectra through the equation S1: $\Phi_{ET} = 1 - I_{DA}/I_{D.}$ Where I_{DA} and I_D are the fluorescence intensities of the emission of NPyP-CB[8]+RhB or NPyP-CB[8]+SR101 assembly (donor and acceptor) and NPyP-CB[8] assembly (donor) respectively when excited at 324 nm. The energy-transfer efficiency (Φ_{ET}) was calculated as 50% and 49% in an aqueous environment, measured under the condition of [NPyP] = 1.0×10^{-5} M, [CB[8]] = 1.0×10^{-5} M, [RhB] = 2.5×10^{-6} M, [SR101] = 2.5×10^{-6} M.

Antenna effect calculation: The antenna effect of NPyP-CB[8]-RhB system was calculated based on the excitation spectra using equation S2: Antenna effect = $(I_{DA,324} - I_{D,324}) / I_{DA,550}$. Where $I_{D,324}$ and $I_{DA,550}$ are the fluorescence intensities at 580 nm with the excitation of the donor at 324 nm and the direct excitation of the acceptor at 550nm, respectively. $I_{DA,324}$ is the fluorescence intensities of the NPyP-CB[8] assembly, which was normalized with the NPyP-CB[8]-RhB assembly at 540 nm. The antenna effect value was calculated as 0.92 in water, measured under the condition of [NPyP] = 1.0×10^{-5} M, [CB[8]] = 1.0×10^{-5} M, [RhB] = 2.5×10^{-6} M.

The antenna effect of NPyP-CB[8]-SR101 system was calculated based on the excitation spectra using equation S3: Antenna effect = $(I_{DA,324} - I_{D,324}) / I_{DA,580}$. Where $I_{D,324}$ and $I_{DA,580}$ are the fluorescence intensities at 610 nm with the excitation of the donor at 324 nm and the direct excitation of the acceptor at 580nm, respectively. $I_{DA,324}$ is the fluorescence intensities of the NPyP-CB[8] assembly, which was normalized with the NPyP-CB[8]-SR101 assembly at 540 nm. The antenna effect value was calculated

as 0.81 in water, measured under the condition of [NPyP] = 1.0×10^{-5} M, [CB[8]] = 1.0×10^{-5} M, [SR101] = 2.5×10^{-6} M.

General procedure for the photo-dehalogenation reaction of α-bromoacetopheone and its derivatives: α-Bromoacetophenone or its derivatives (0.20 mmol), diethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Hantzsch ester) (56 mg, 0.22 mmol), and N,N-diisopropylethylamine (DIPEA) (70 μl, 0.40 mmol) were dissolved in the newly prepared NPyP-CB[8]+RhB or NPyP-CB[8]+SR101 solution (0.25 mol%, [NPyP]= 5.0×10^{-5} M, [CB[8]]= 5.0×10^{-5} M, [RhB]=1.25×10^{-5} M, [SR101]=1.25×10^{-5} M, 10 mL). The mixture was degassed with nitrogen and then irradiated with white LED (10 W) at room temperature for 8 hours. Then, the mixture was extracted with dichloromethane and dried with anhydrous Na_2SO_4. Then the organic solution was concentrated in a vacuum and purified by rapid column chromatography to obtain the corresponding product.

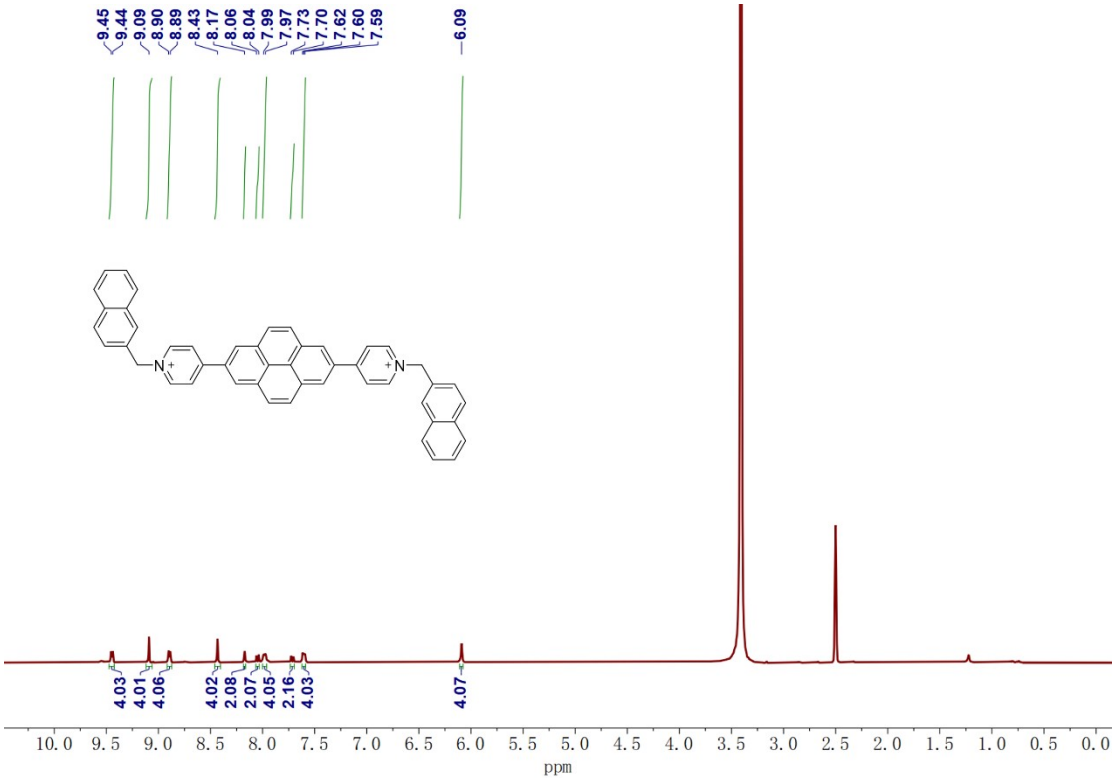


Fig. S1 ^{1}H NMR spectrum of **NPyP** in DMSO-d_6.

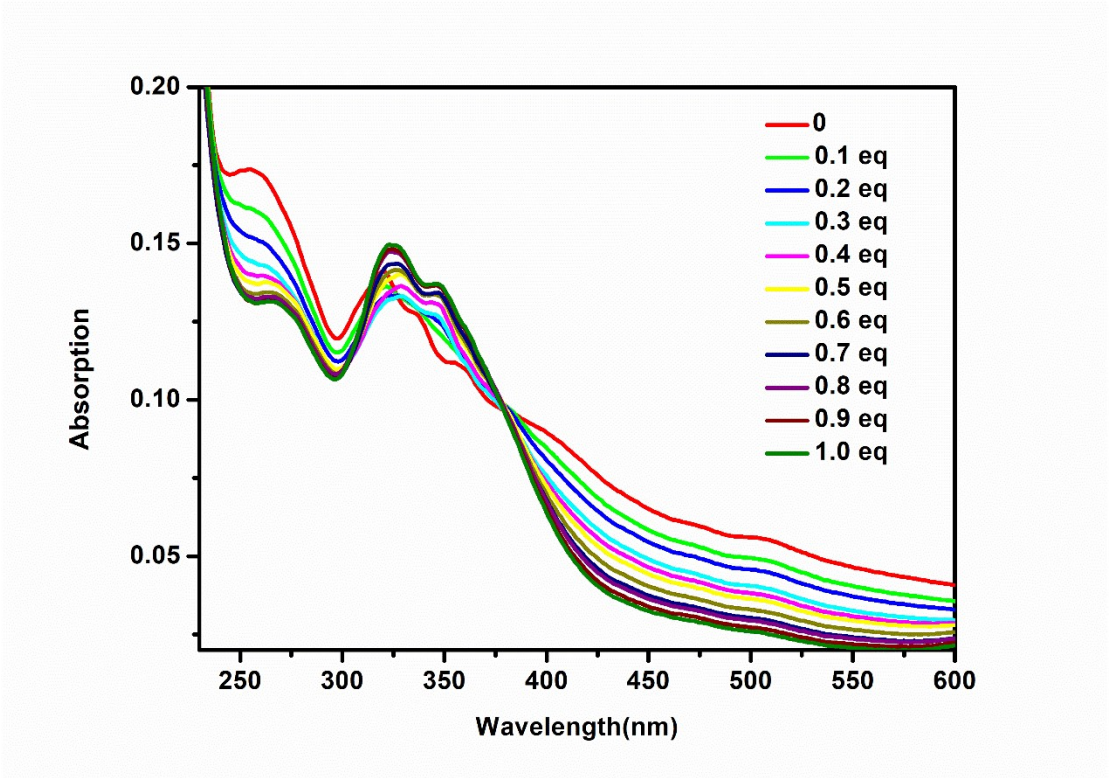


Fig. S2 UV-vis absorption spectra of NPyP with the gradual addition of CB[8] in aqueous solution.

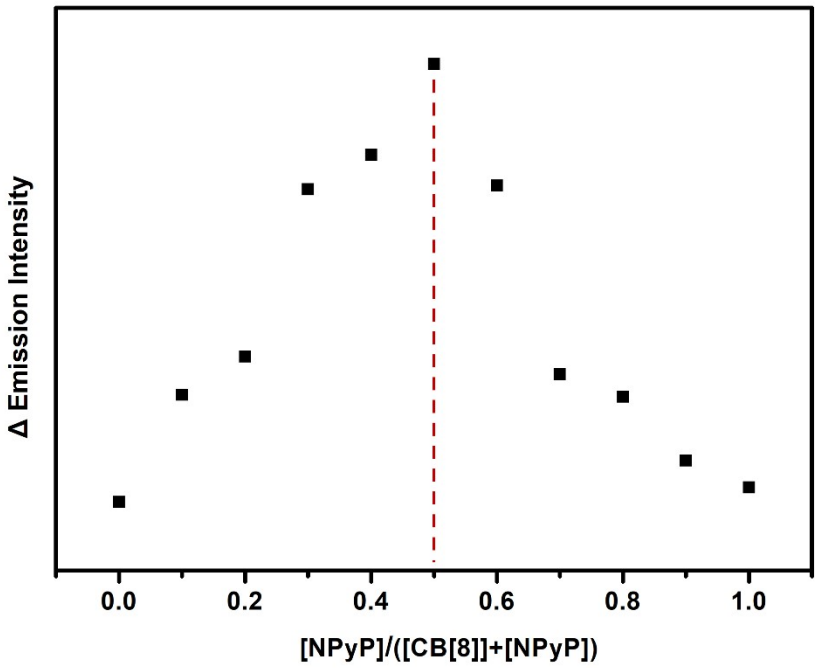


Fig. S3 Job's plot of NPyP-CB[8] system.

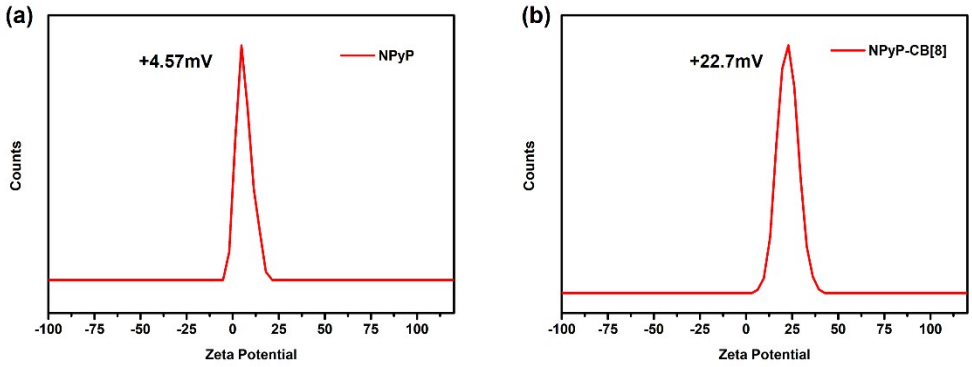


Fig. S4 Zeta potential of NPyP before and after the addition of 1.0 equiv. CB[8].

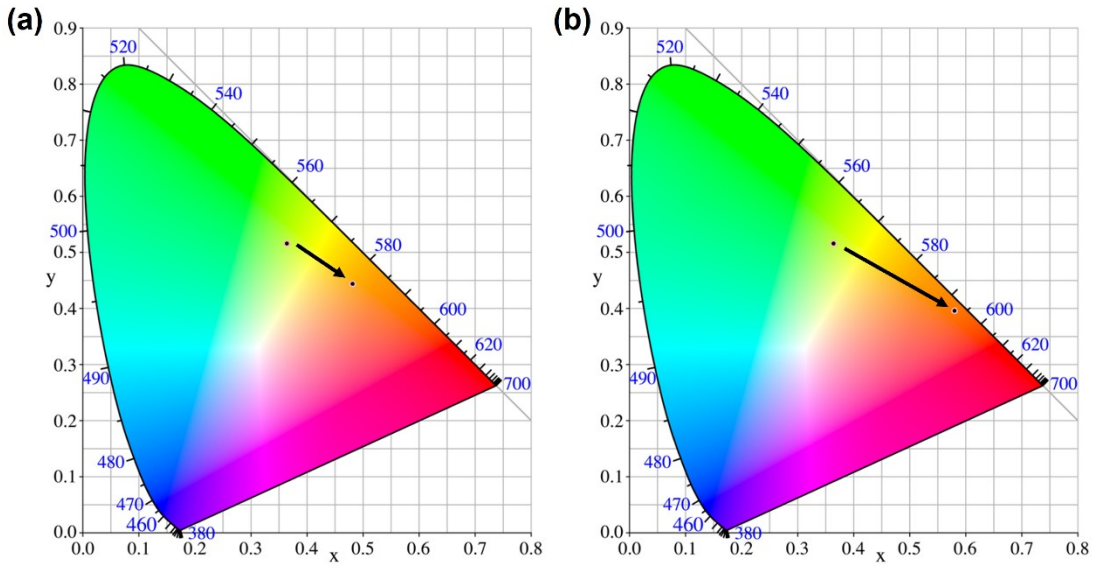


Fig. S5 (a) CIE chromaticity coordinates of NPyP-CB[8]+RhB system. (b) CIE chromaticity coordinates of NPyP-CB[8]+SR101 system.

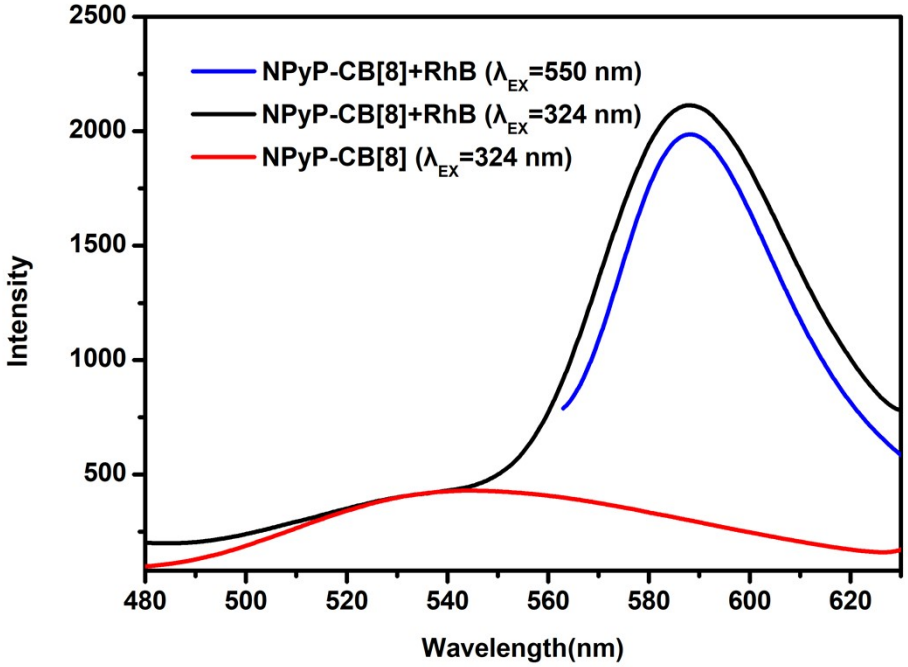


Fig. S6 Red line represents the fluorescence emission spectra of NPyP-CB[8] in an aqueous solution, which was normalized according to the fluorescence intensity at 540 nm of the black line (donor emission, λ_{ex} = 324 nm), the black line represents the fluorescence spectrum of NPyP-CB[8]+RhB, (acceptor emission, λ_{ex} = 324 nm), the blue line represents the fluorescence spectrum of NPyP-CB[8]+RhB with the direct excitation at 550 nm.

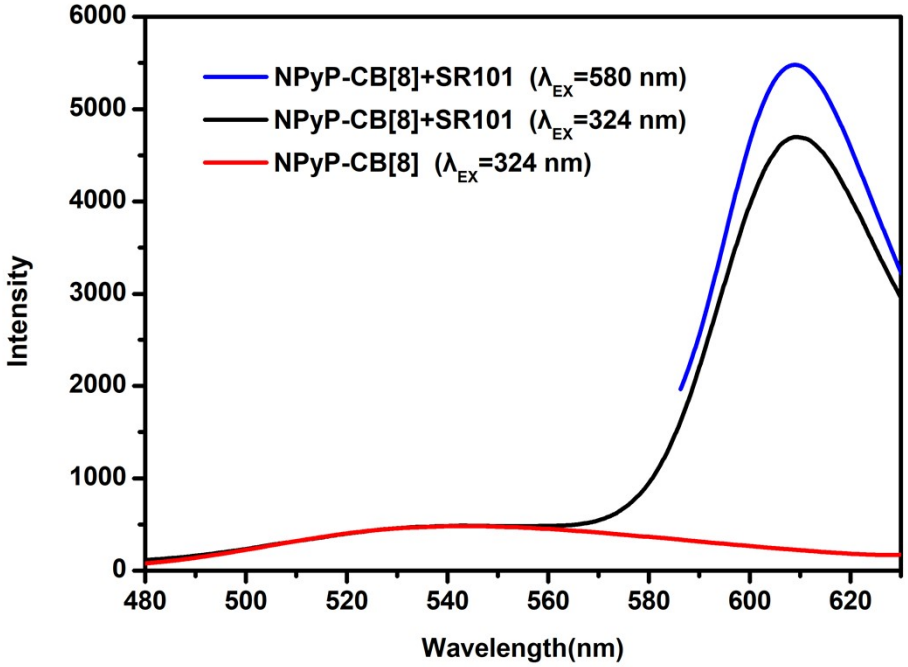
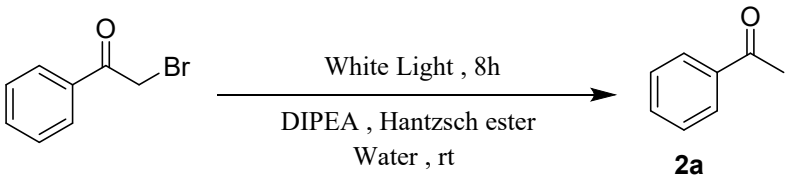


Fig. S7 Red line represents the fluorescence emission spectra of NPyP-CB[8] in an aqueous solution, which was normalized according to the fluorescence intensity at 540 nm of the black line (donor emission, λ_{ex} = 324 nm), the black line represents the fluorescence spectrum of NPyP-CB[8]+SR101, (acceptor emission, λ_{ex} = 324 nm), the blue line represents the fluorescence spectrum of NPyP-CB[8]+SR101 with the direct excitation at 580 nm.

Table S1. Comparative data on catalyst dosage for the dehalogenation reaction of α-bromoacetophenone [a].



2a

Entry	Catalyst	Conditions	Yield[b]/%
1	NPyP-CB[8]+SR101	0.05 mol%	64%
2	NPyP-CB[8]+RhB	0.05 mol%	51%
3	NPyP-CB[8]+SR101	0.15 mol%	86%
4	NPyP-CB[8]+RhB	0.15 mol%	84%
5	NPyP-CB[8]+SR101	0.25 mol%	98%
6	NPyP-CB[8]+RhB	0.25 mol%	89%

[a] Reaction conditions: α-bromoacetophenone (40 mg, 0.20 mmol), Hantzsch ester (56 mg, 0.22 mmol), N,N-diisopropylethylamine (DIPEA) (52 mg, 0.40 mmol), NPyP-CB[8]+RhB or NPyP-CB[8]+SR101 aqueous solution (10 mL),10 W white LEDs, room temperature, N_2, 8 h. [b] Isolated yields.

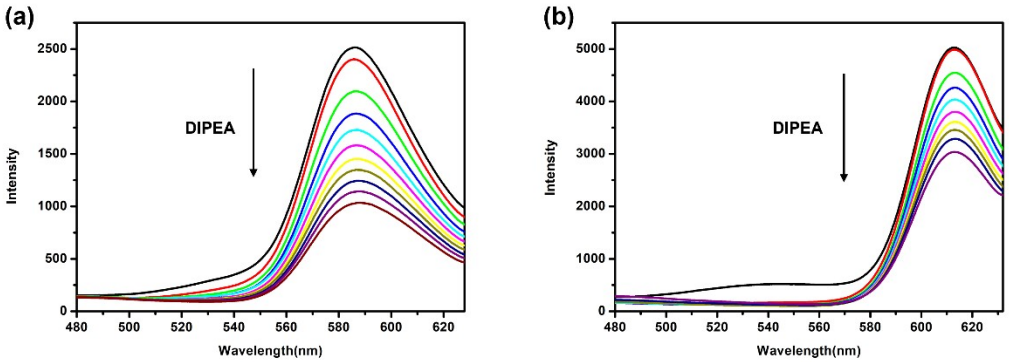
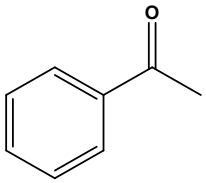


Fig. S8 (a) Fluorescence emission spectra of NPyP-CB[8]+RhB system in water with the addition of DIPEA. (b) Fluorescence emission spectra of NPyP-CB[8]+SR101 system in water with the addition of DIPEA.

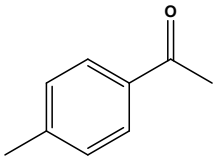
^{1}H NMR data of 2a-2e

2a. **acetophenone**



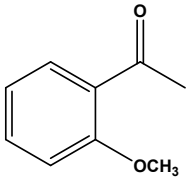
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.91 (m, 2H), 7.61 – 7.52 (m, 1H), 7.51 – 7.41 (m, 2H), 2.61 (s, 3H).

2b. **4-methyl acetophenone**



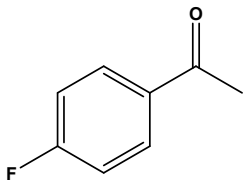
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 6.4 Hz, 1H), 7.26 (d, J = 5.3 Hz, 2H), 2.59 (s, 2H).

2c. **2-methoxy acetophenone**



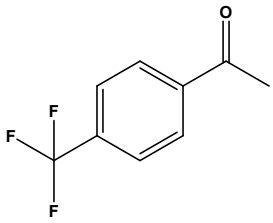
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 6.99 (q, *J* = 7.8 Hz, 2H), 3.92 (s, 3H), 2.62 (s, 3H).

2d. **4-fluoroacetophenone**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 2.55 (s, 3H).

2e. **4-(trifluoromethyl)acetophenone**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 2.62 (s, 3H).

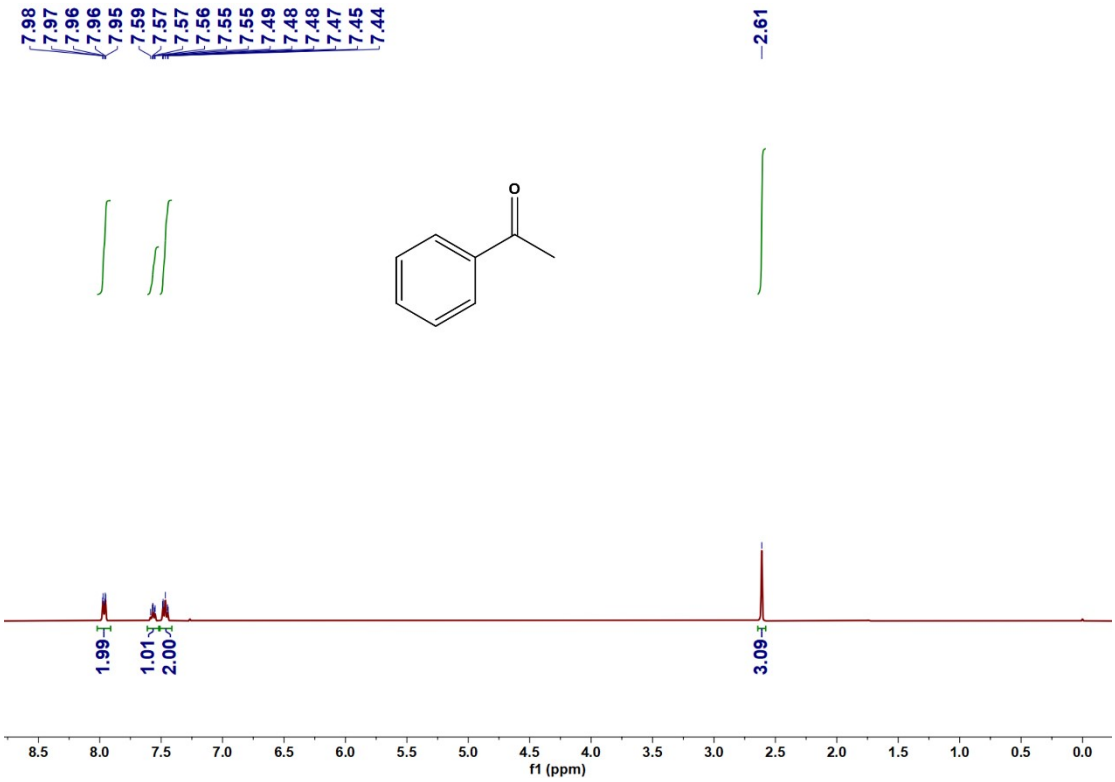


Fig. S9 ^{1}H NMR spectra of **2a** in $CDCl_3$.

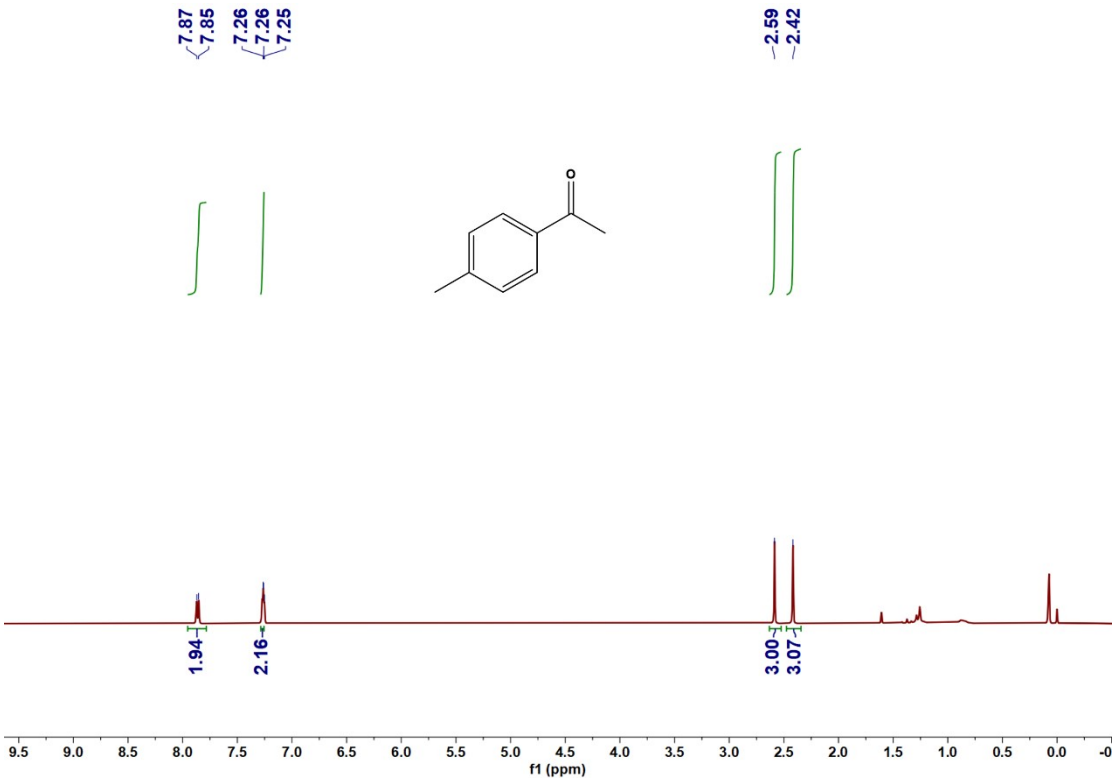


Fig. S10 ^{1}H NMR spectra of **2b** in $CDCl_3$.

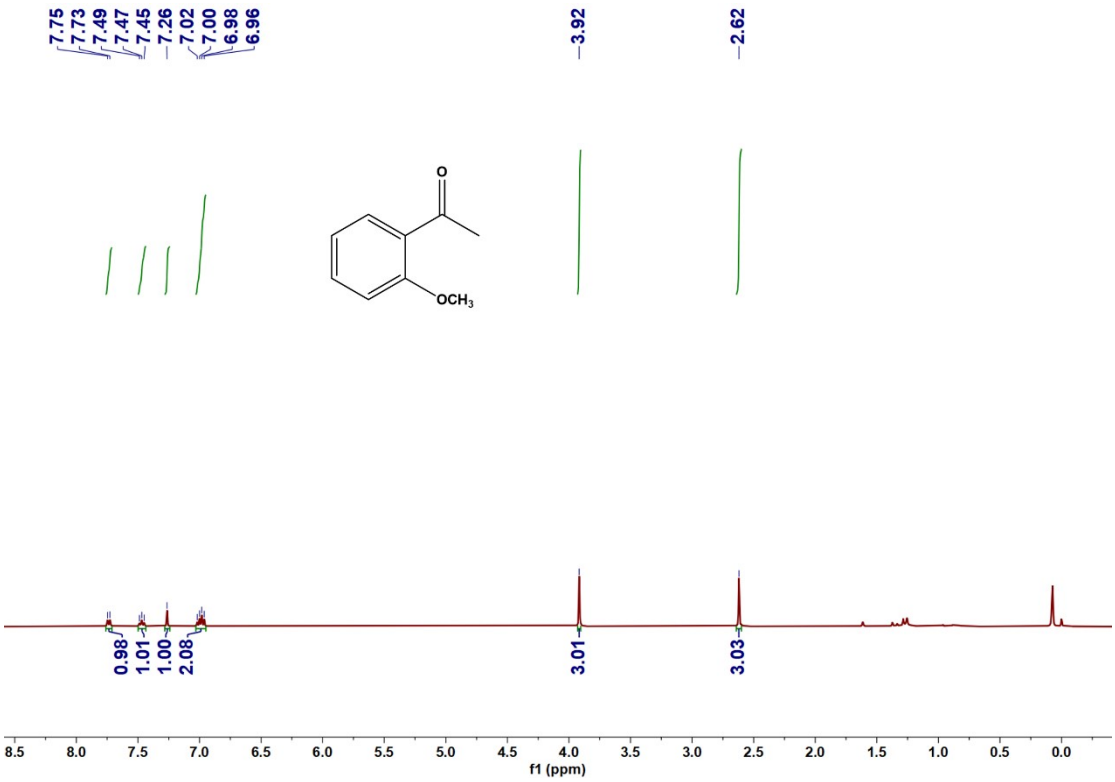


Fig. S11 ^{1}H NMR spectra of **2c** in $CDCl_3$.

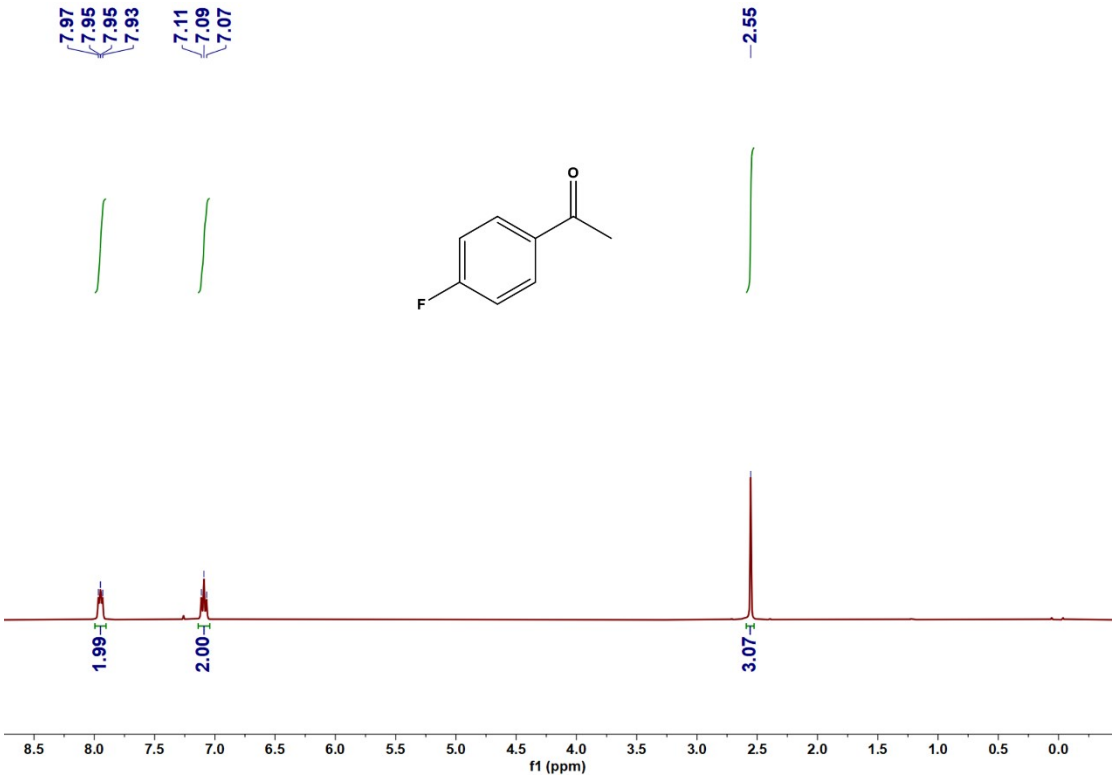


Fig. S12 ^{1}H NMR spectra of **2d** in $CDCl_3$.

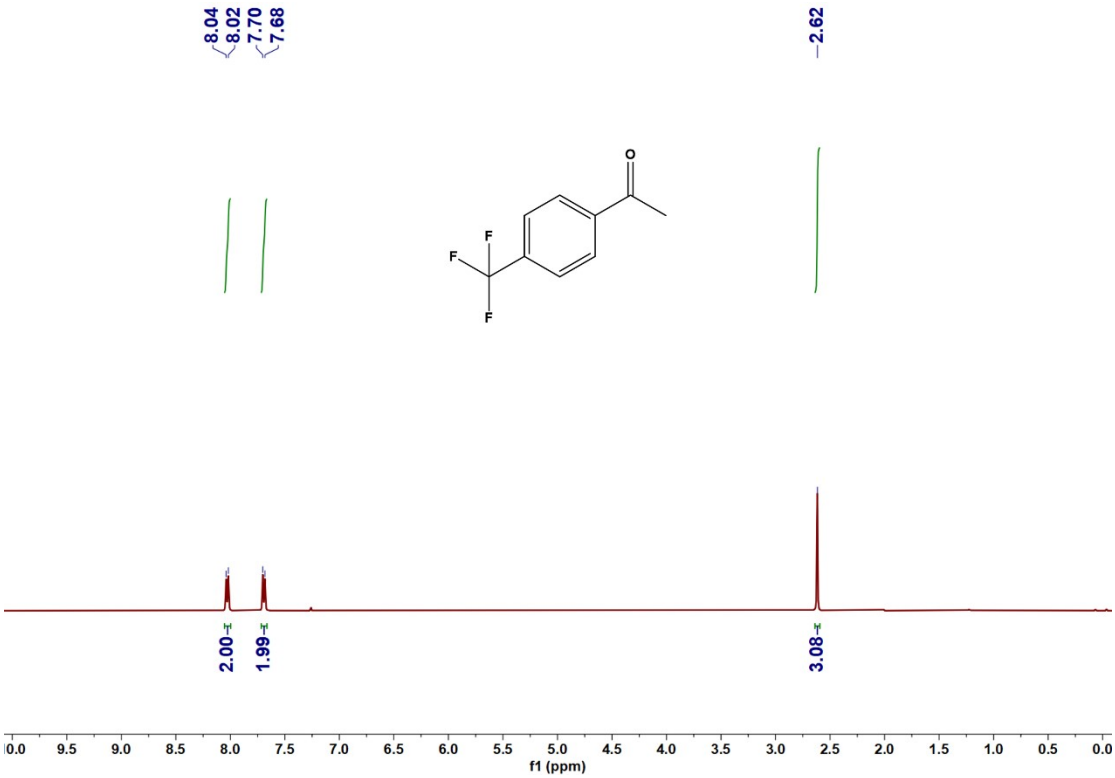


Fig. S13 ^{1}H NMR spectra of **2e** in $CDCl_3$.