Electronic Supplementary Information for

Construction of an artificial light-harvesting system with two-step sequential energy transfer based on supramolecular polymers

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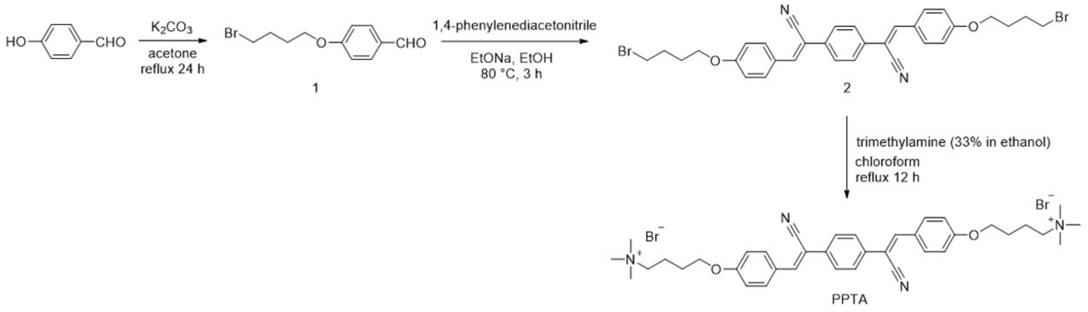
Experimental

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 the carbon-coated copper grid (300 mesh) and drying by slow evaporation.



Scheme S1. Synthetic route of **PPTA**.

Synthesis of 1: A mixture of phydroxybenzaldehyde (2.44 g, 20 mmol), 1,3-dibromopropane (6.12 mL, 60 mmol), K_2CO_3 (2.76 g, 20 mmol), and tetrabutyl ammonium bromide (0.1 g) in acetone (50 mL) was refluxed in a double-necked round bottom flask (100 mL) equipped with a condenser for 10 h. After this time, the reaction mixture was cooled and the solvent was evaporated under reduced pressure and the resulting residue was redissolved in chloroform (150 mL) and washed with water. The organic layer was then dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product thus obtained was purified by silica gel column chromatography (petroleum ether and ethyl acetate, 5:1) to give 1 as a pale yellow oil in 70% yield (3.41 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.86 (s, 1H), 7.92 – 7.76 (m, 2H), 7.11 (d, J = 8.6 Hz, 2H), 4.12 (s, 2H), 3.60 (t, J = 6.6 Hz, 2H), 1.91 (dt, J = 43.1, 7.1 Hz, 4H) ppm.

Synthesis of 2: To a mixture of 4-(3-bromopropoxy)benzaldehyde (3.97 g, 12.8 mmol), 1,4-phenylenediacetonitrile (1.00 g, 6.42 mmol), and EtOH (50 mL) was added equivalent amount of sodium ethoxide. The resulting solution was then stirred at room temperature for 3 h. The resulting yellow precipitate was collected by filtration, and washed with EtOH successively to give 2 as a yellow solid (4.23 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 4H), 7.71 (d, J = 1.9 Hz, 4H), 7.52 (s, 2H), 7.02 – 6.91 (m, 4H), 4.07 (t, J = 6.0 Hz, 4H), 3.55 – 3.46 (m, 4H), 2.12 – 1.95 (m, 8H) ppm.

Synthesis of PPTA: Compound 2 was synthesized according to the literature report[S1]. Compound 2 (0.606 g, 1 mmol) and trimethylamine (33% in ethanol, 1 mL) were dissolved in chloroform (8 mL) and refluxed overnight. The mixture was concentrated under reduced pressure and washed by anhydrous ether to give PPTA as a yellow solid (0.699 g, 0.93 mmol, 93%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (s, 2H), 7.99 (d, J = 8.4 Hz, 4H), 7.86 (s, 4H), 7.15 (d, J = 8.5 Hz, 4H), 4.13 (s, 4H), 3.07 (s, 18H), 3.03 (s, 4H), 1.88 – 1.75 (m, 8H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.03, 143.37, 134.83, 131.84, 126.77, 126.61, 118.69, 115.54, 106.78, 67.58, 65.45, 52.71, 52.66, 25.97, 19.68 ppm; ESI-MS: m/z $[M - 2Br]^{2+}$ calcd for $[C_{38}H_{48}N_4O_2]^{2+}$ 296.1884.

Synthesis BSC4: Bis-p-sulfonatocalix[4]arene (BSC4) was synthesized according to the previous literature[S2]. ^{1}H NMR (400 MHz, D_2O) δ 7.76 (s, 4H), 7.63 (s, 4H), 7.47 (s, 4H), 7.27 (s, 4H), 4.53 (s, 4H), 4.33 (d, *J* = 14.3 Hz, 4H), 3.89 (d, *J* = 14.3 Hz, 4H), 3.50 – 3.21 (m, 8H) ppm; ^{13}C NMR (101 MHz, D_2O): δ 154.38, 154.16, 134.83, 134.02, 133.75, 133.69, 128.79, 128.58, 127.95, 127.19, 126.71, 126.46, 74.78, 31.63 ppm.

Energy-transfer efficiency calculation: The first step 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 PPTA-BSC4+EY assembly (donor and acceptor) and PPTA-BSC4 assembly (donor) respectively when excited at 360 nm. The energy-transfer efficiency (Φ_{ET}) was calculated as 36.6% in aqueous environment, measured under the condition of [PPTA] = 7.66×10^{-5} M, [BSC4] = 3.83×10^{-5} M, [EY] = 7.66×10^{-7} M.

The second step 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 PPTA-BSC4+EY+SR101 assembly (donor and acceptor) and PPTA-BSC4+EY assembly (donor) respectively when excited at 360 nm. The energy-transfer efficiency (Φ_{ET}) was calculated as 40.8% in aqueous environment, measured under the condition of [PPTA] = 7.66×10^{-5} M, [BSC4] = 3.83× 10-5 M, [EY] = 7.66×10^{-7} M, [SR101] = 3.83×10^{-7} M.

Antenna effect calculation: The first step antenna effect was calculated based on the excitation spectra using **equation S2**: Antenna effect = $(I_{DA,360} - I_{D,360})/I_{DA,515}$. Where $I_{D,360}$ and $I_{DA,515}$ are the fluorescence intensities at 555 nm with the excitation of the donor at 360 nm and the direct excitation of the acceptor at 515 nm, respectively. $I_{DA,365}$ is the fluorescence intensities at 555 nm of the PPTA-BSC4 assembly, which was normalized with the PPTA-BSC4+EY assembly at 532 nm. The antenna effect value was calculated as 15.4 in water, measured under the condition of [PPTA] = 7.66×10^{-5} M, [BSC4] = 3.83×10^{-5} M, [EY] = 7.66×10^{-7} M.

The second step antenna effect was calculated based on the excitation spectra using **equation S2**: Antenna effect = $(I_{DA,360} - I_{D,360})/I_{DA,580}$. Where $I_{D,360}$ and $I_{DA,580}$ are the fluorescence intensities at 620 nm with the excitation of the donor at 360 nm and the direct excitation of the acceptor at 580 nm, respectively. $I_{DA,360}$ is the fluorescence intensities at 620 nm of the PPTA-BSC4 +EY assembly, which was normalized with the PPTA-BSC4+EY+SR101 assembly at 592 nm. The antenna effect value was calculated as 20.3 in water, measured under the condition of [PPTA] = 7.66×10^{-5} M, [BSC4] = 3.83×10^{-5} M, [EY] = 7.66×10^{-7} M, [SR101] = 3.83×10^{-7} M.

General procedure for the photodehalogenation reaction of α-

bromoacetopheonederivatives: α-Bromoacetophenone (40 mg, 0.20 mmol, 1.0 equiv.), diethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Hantzsch ester) (56 mg, 0.22 mmol, 1.1 equiv.), and N, N-diisopropylethylamine (DIPEA) (52 mg, 0.40 mmol, 2.0 equiv.) were dissolved in the freshly prepared PPTA-BSC4+EY+SR101 assembly solution (0.4 mol%, 10 mL). The mixture was degassed with nitrogen for 30 minutes, and was subsequently irradiated by white LEDs (10 W/cm^2) at room temperature for 8 h. After that, it was extracted with dichloromethane, and the combined organic layer was dried with anhydrous Na_2SO_4. Then the organic solvent was concentrated in vacuo and purified by flash column chromatography with petroleum ether/ethyl acetate to afford the corresponding products.

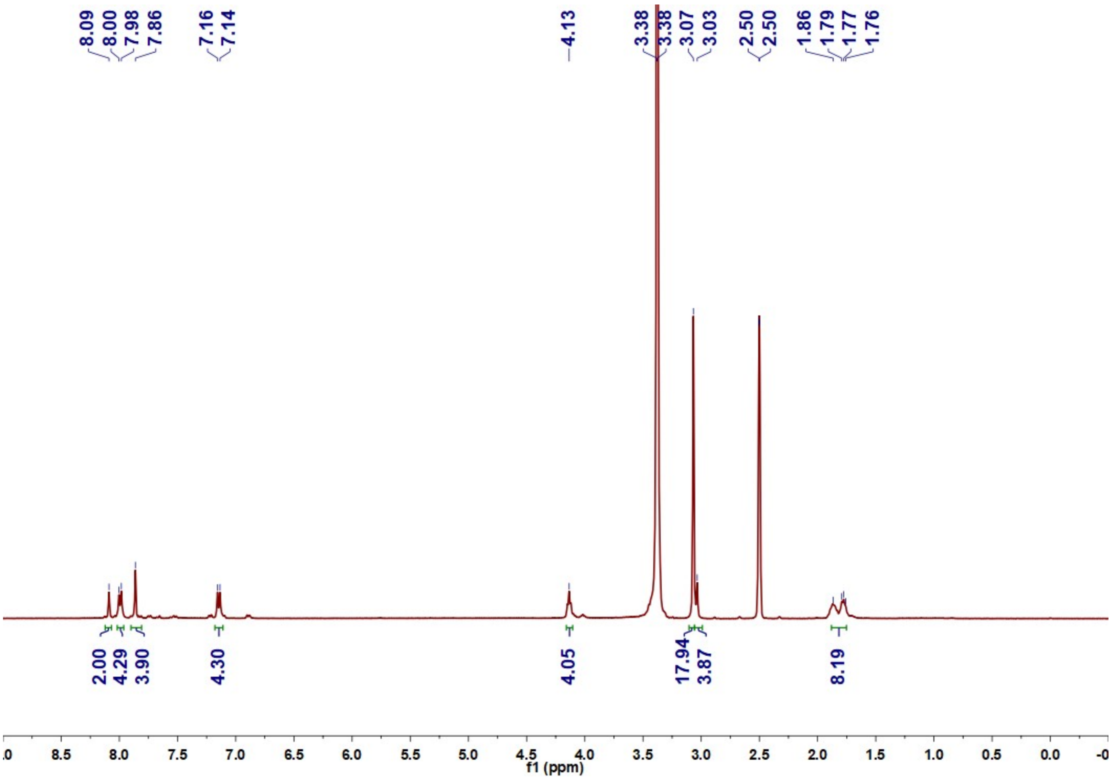


Fig. S1 ^{1}H NMR spectrum of **PPTA** in DMSO-d_6.

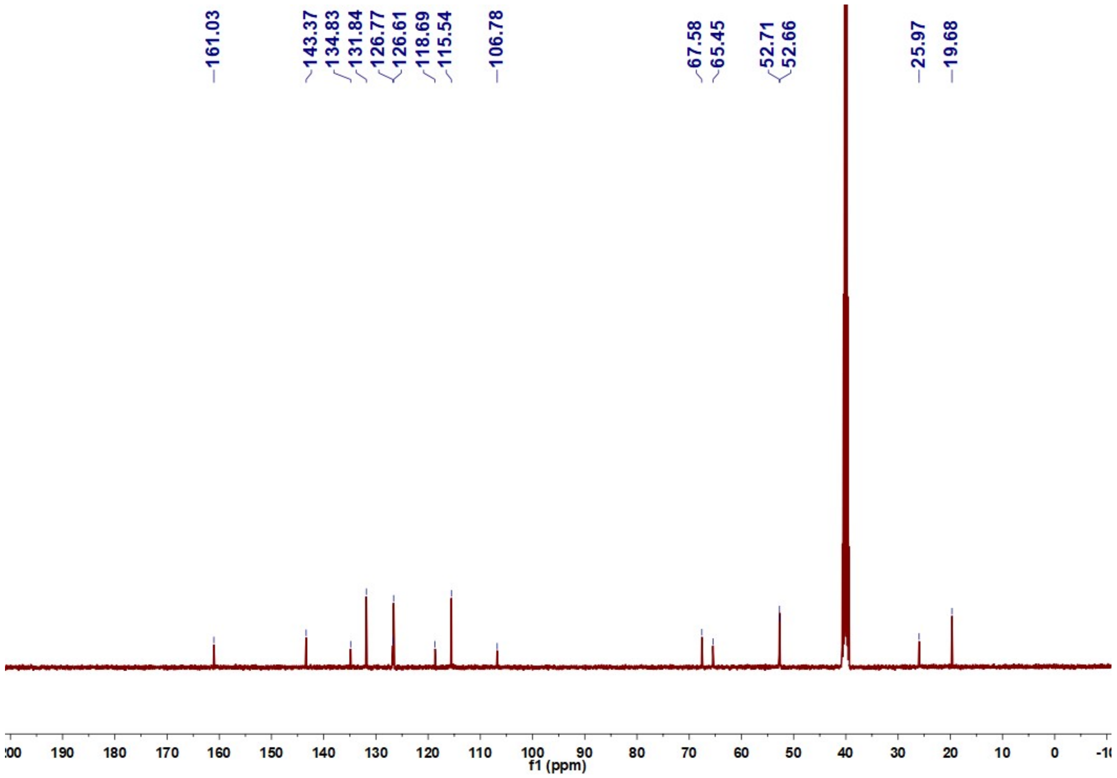


Fig. S2 ^{13}C NMR spectrum of **PPTA** in DMSO-d_6.

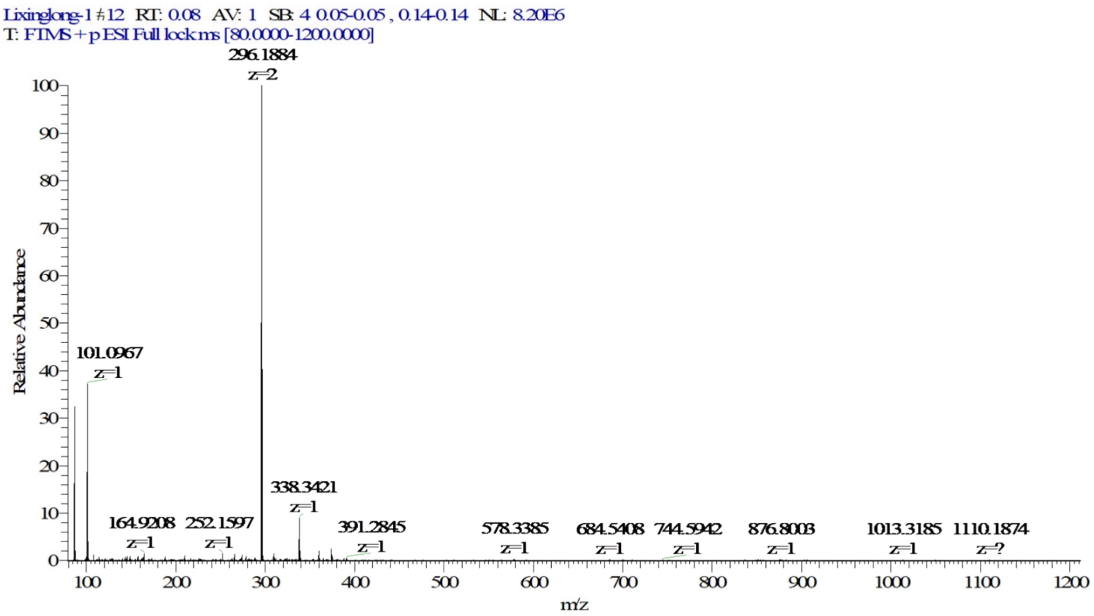


Fig. S3 ESI-MS spectrum of **PPTA**.

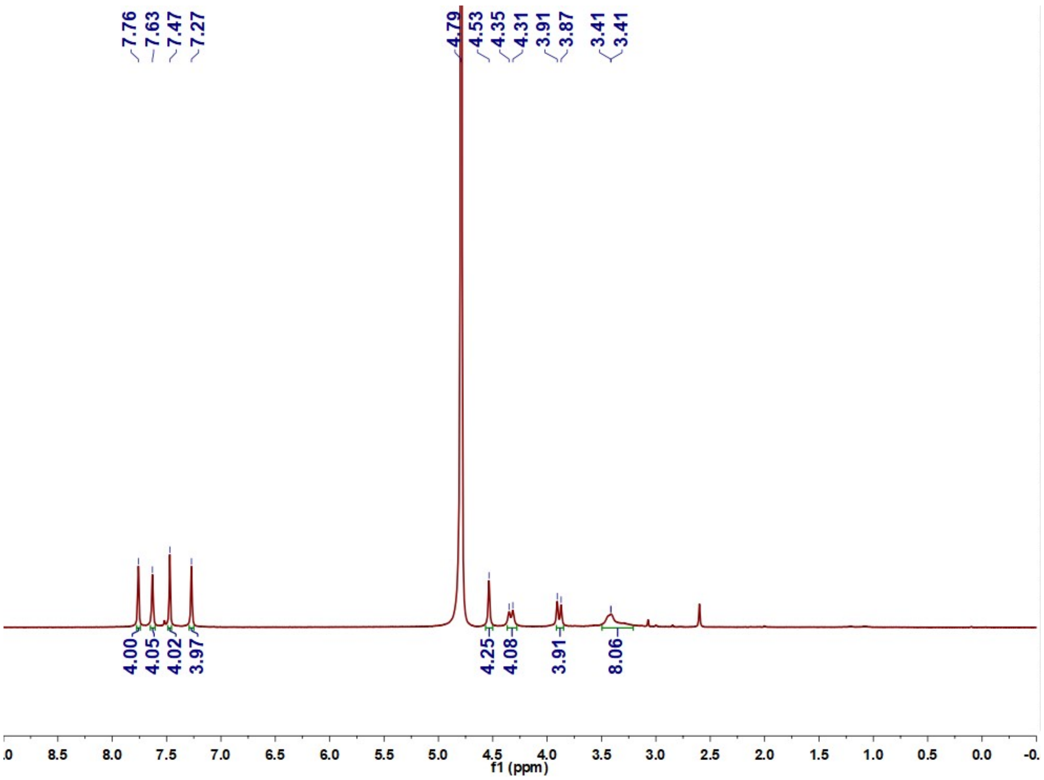


Fig. S4 ^{1}H NMR spectrum of **BSC4** in D_2O.

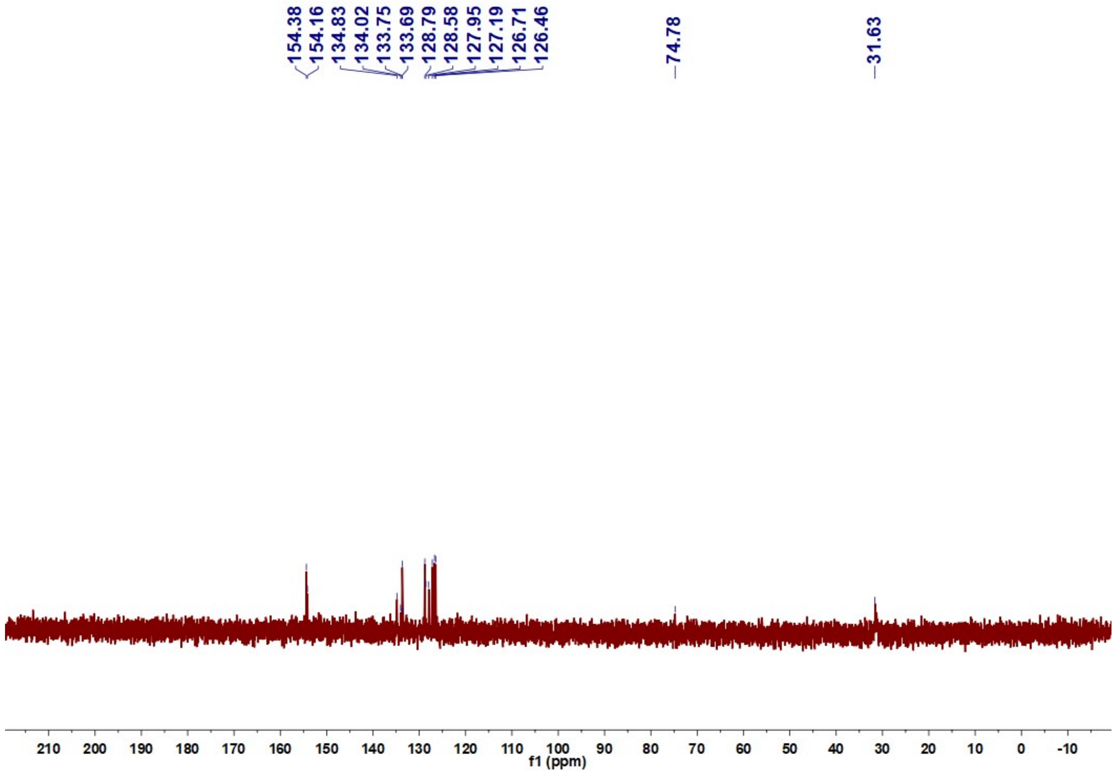


Fig. S5 ^{13}C NMR spectrum of **BSC4** in D_2O.

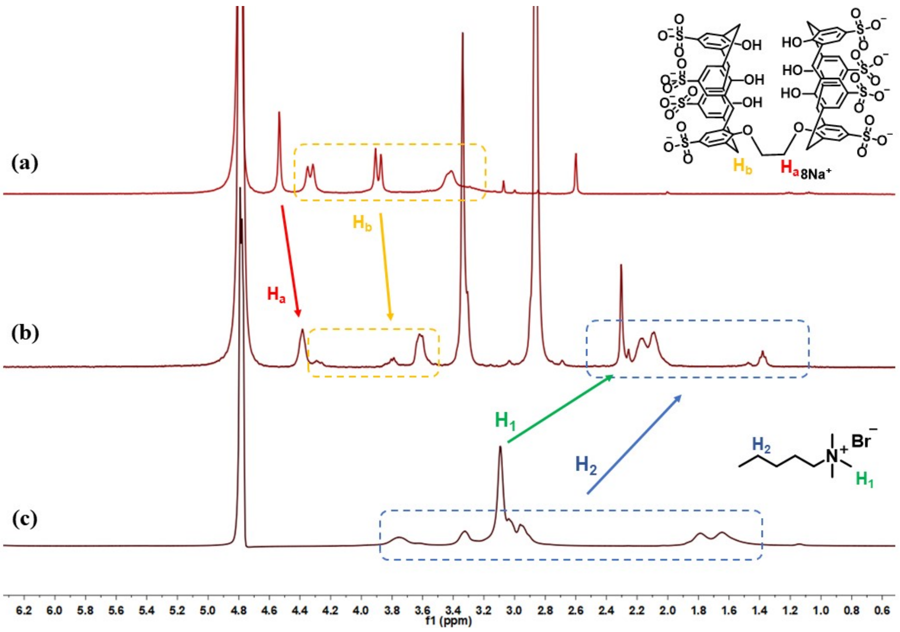


Fig. S6 ^{1}H NMR spectra: (a) BSC4 (4×10^{-4}M), (b) BSC4 (4×10^{-4}M), PPTA (2×10^{-4}M) and (c) PPTA (2×10^{-4}M).

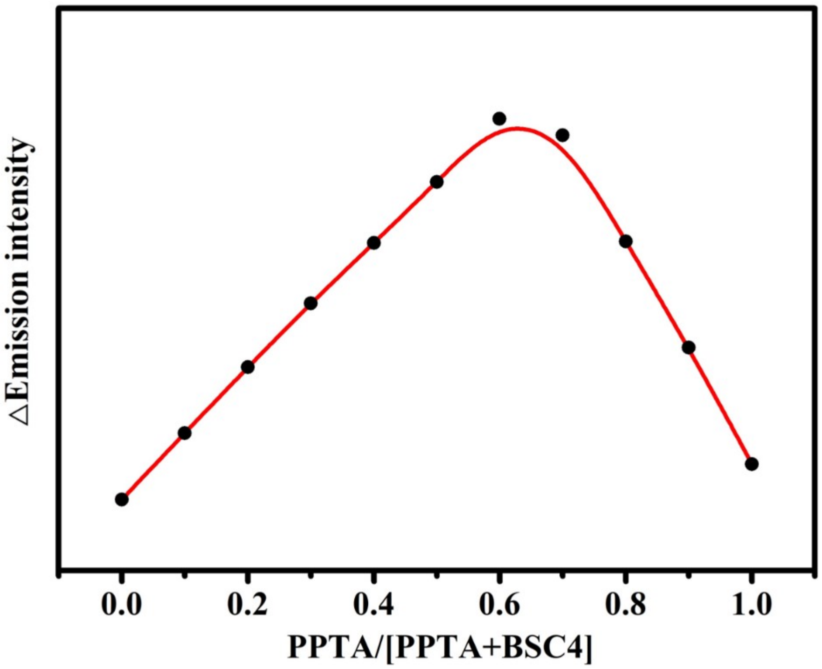


Fig. S7 Job's plot of the changes in emission spectra at 475 nm; excitation wavelength was 360 nm; the total concentration of **PPTA** and BSC4 was fixed at 7.66×10^{-5} M.

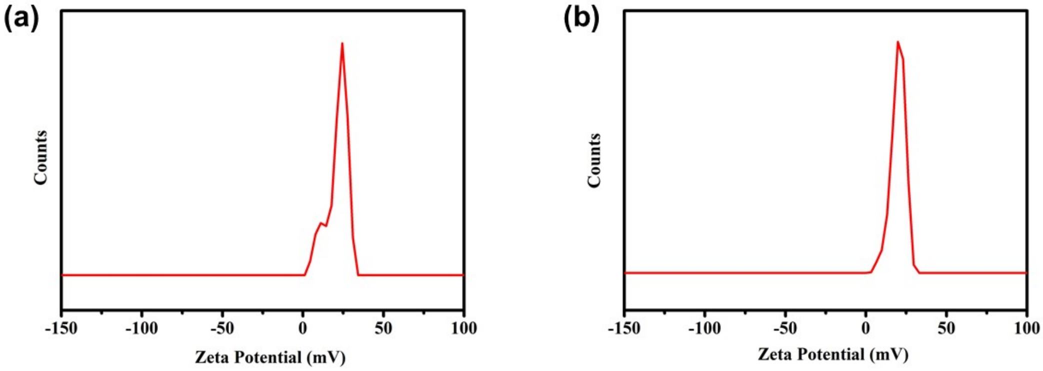


Fig. S8 Zeta potential of **PPTA** before and after addition of BSC4.

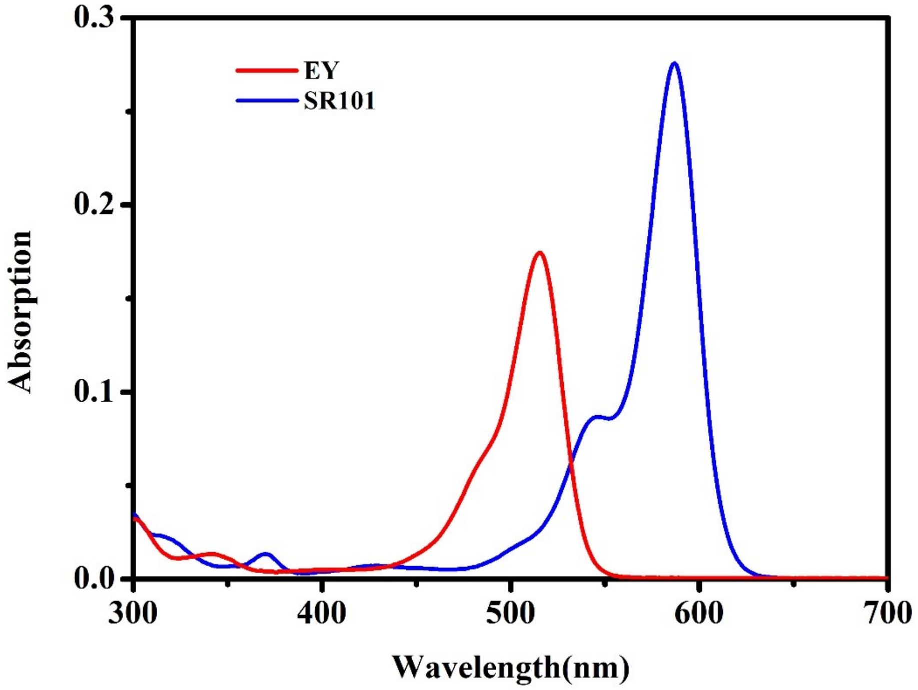


Fig. S9 UV-Vis spectra of EY and SR101.

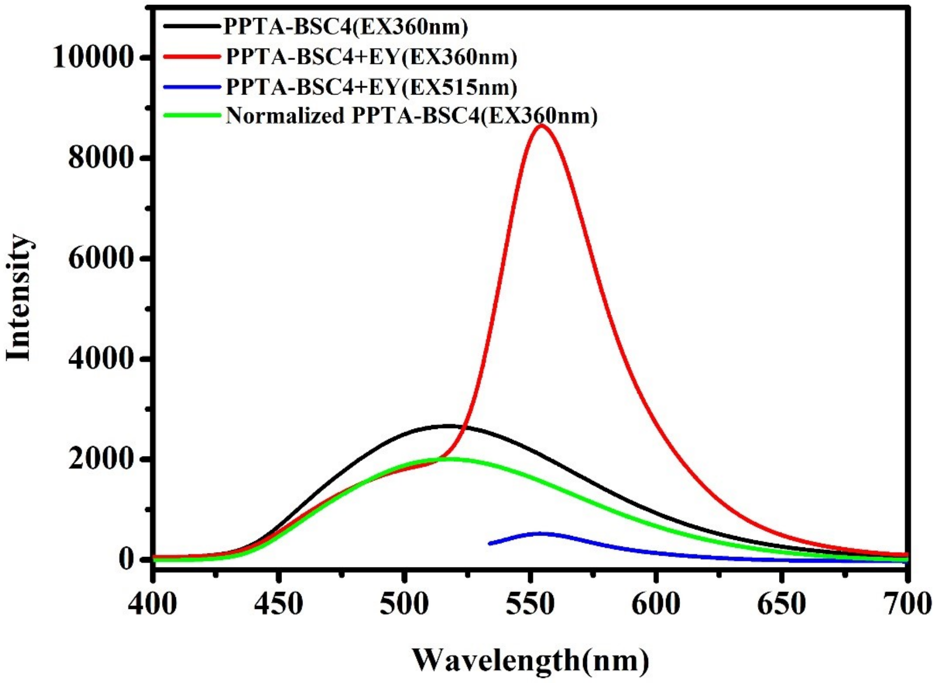


Fig. S10 Fluorescence spectra of **PPTA**-BSC4+EY in aqueous solution, blue line (acceptor emission, λ_{ex} = 515 nm). The green trace represents the fluorescence spectrum (λex = 360 nm) of **PPTA-**BSC4, which was normalized according to the fluorescence intensity at 515 nm of the red trace ([**PPTA**] = 7.66×10^{-5} M, [BSC4] = 3.83×10^{-5} M, [EY] = 7.66×10^{-6} M.

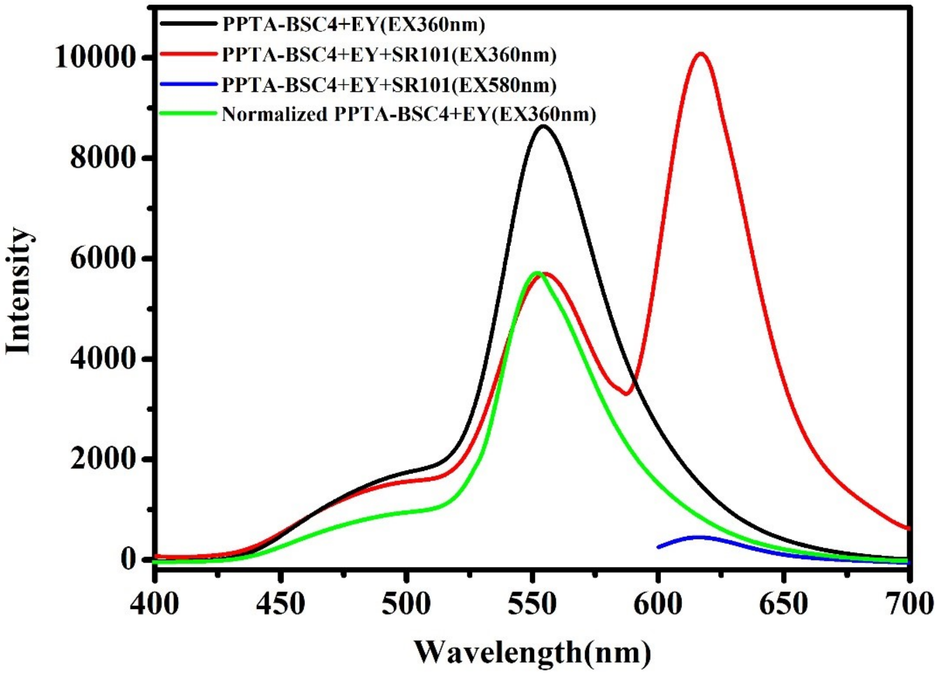


Fig. S11 Fluorescence spectra of **PPTA**-BSC4+EY+SR101 in aqueous solution, blue line (acceptor emission, λ_{ex} = 580 nm). The green trace represents the fluorescence spectrum (λex = 360 nm) of **PPTA-**BSC4+EY, which was normalized according to the fluorescence intensity at 555 nm of the red trace ([**PPTA**] = 7.66×10^{-5} M, [BSC4] = 3.83×10^{-5} M, [EY] = 7.66×10^{-6} M, [SR101] = 3.56×10^{-6} M.

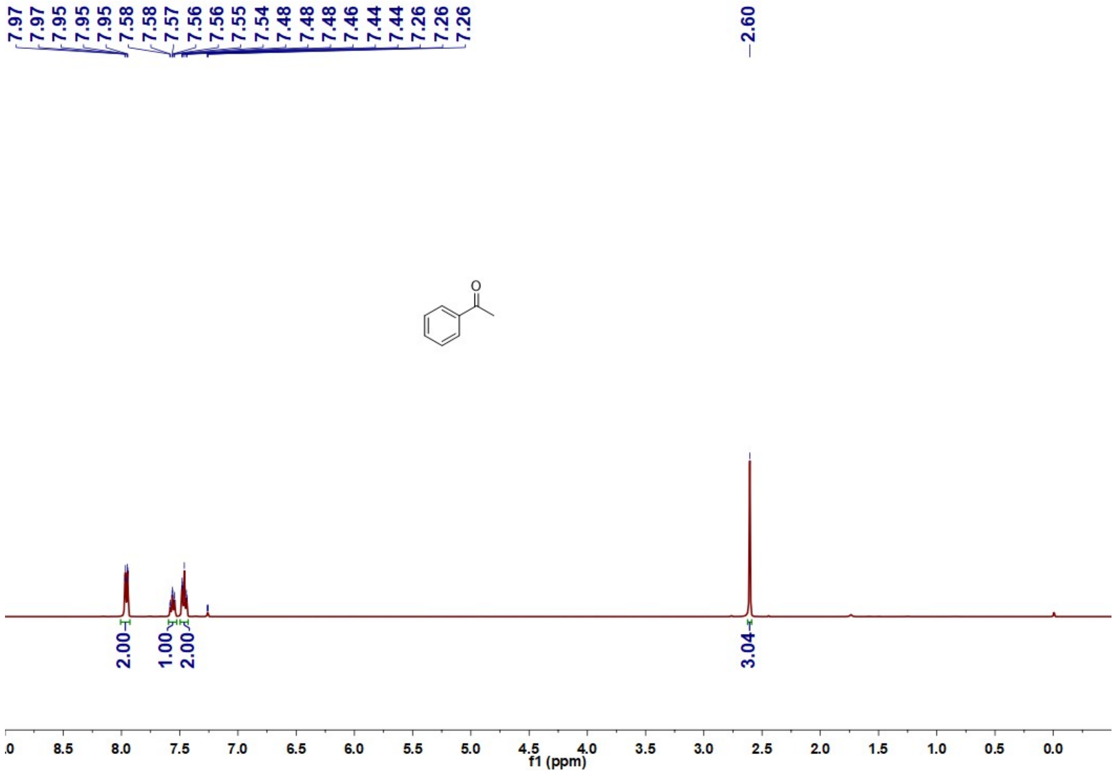


Fig. S12 ^{1}H NMR of acetophenone in $CDCl_3$.

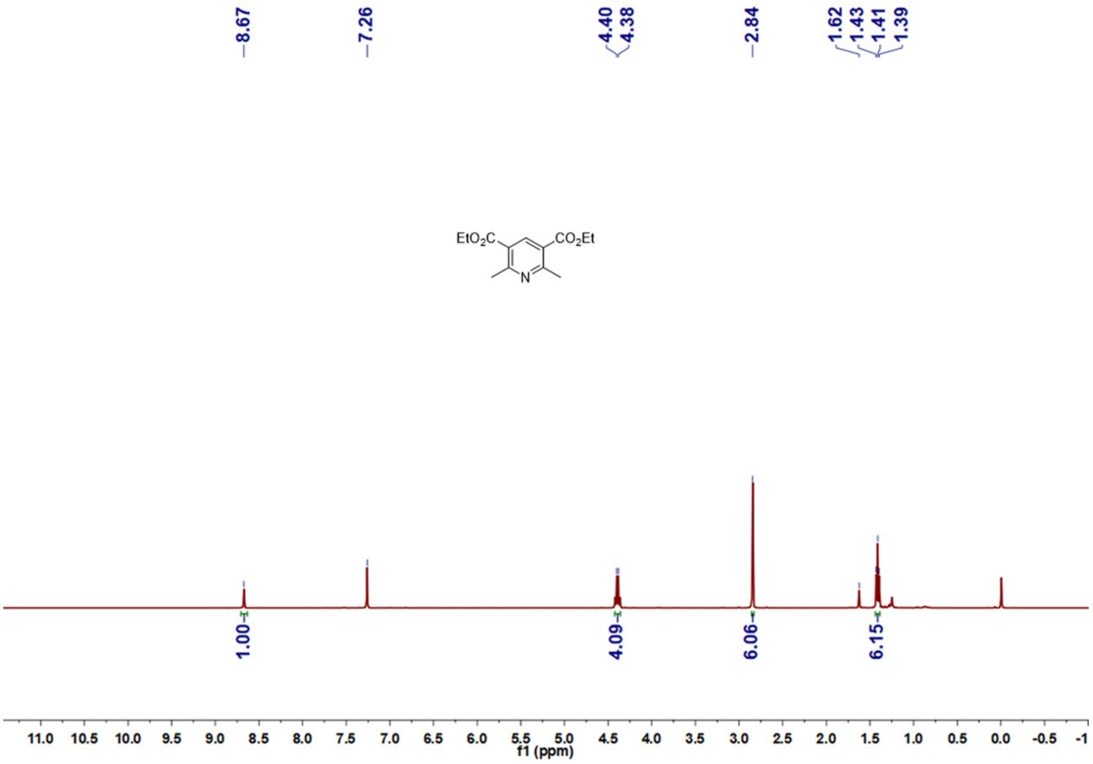


Fig. S13 ^{1}H NMR of by-products in $CDCl_3$.

[S1] R. K. Mishra, S. Vijayakumar, A. Mal, V. Karunakaran, J. C. Janardhanan, K. K. Maiti, V. K. Praveen and A. Ajayaghosh, *Chem. Commun.,* 2019, **55**, 6046-6049.

[S2] D. S. Guo, S. Chen, H. Qian, H. Q. Zhang and Y. Liu, *Chem. Commun.,* 2010, **46**, 2620-2622.