Supporting Information

White-Light Emission from a Single Organic Compound with Unique Self-Folded Conformation and Multistimuli Responsiveness

Dengfeng Li,[#] Wende Hu,[#] Jie Wang, Qiwei Zhang, Xiao-Ming Cao, Xiang Ma*, He Tian

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, Center for Computational Chemistry and Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science & Technology, Shanghai 200237, P. R. China.

[#] These authors contribute equally to this work

Corresponding Author
*maxiang@ecust.edu.cn

Materials, general procedures and synthesis.

Materials. All other reagents were commercially available and used as supplied without further purification. Solvents were purified according to standard laboratory methods. The molecular structures were confirmed using 1H NMR, 13C NMR and high-resolution ESI mass spectroscopy.

General. ^{1}H and ^{13}C NMR spectra were measured on a Brüker AV-400 spectrometer. 2D ROESY, COSY NMR spectra were measured on a Brüker AV-500 spectrometer. The electrospray ionization (ESI) high-resolution mass spectra were tested on a HP 5958 mass spectrometer. The UV-Vis absorption spectra were obtained on a Varian Cary 100 UV-Vis spectrophotometer (1-cm quartz and 1-mm cell were used). The emission and excitation spectra were performed on HORIBA FluoroMax 4 fluorescence spectrometer. Quantum yields were measured by using an integrating sphere on an HORIBA FluoroMax 4 fluorescence spectrometer. Conductivity measurements were taken on a Mettler Toledo-S213 SevenCompact™. The geometry optimizations are performed for the ground states by employing density functional theory (DFT)[1] with B3LYP[2] at the basis set level of 6-311+G(d,p). Vibrational frequency calculations at the same level of theory were carried out to derive the Zero-Point-Energy (ZPE) and entropy corrections at 298.15 K. In addition, SMD model[3] is adopted for consideration of solvent environments which is the recommended for computing solvation energy. In order to characterize the nature of the excited states, the M06-2X functional[4] were employed in the singlet states, due that M06-2X provides reasonable excitation energies for long-range charge transfer excitations and a large set of conjugated molecules.[5] All calculations are performed using the Gaussian package.[6] The WLE gel was prepared using commercial agarose as gelator. 2.5 mL NP4C aqueous solution (c = 0.1 mM) and 50 mg agarose were mixed and then heated to dissolve at 95 ℃. The transparent mixture was allowed to cool down and finally formed the hydrogel (~2 wt%).

1.3 Synthesis

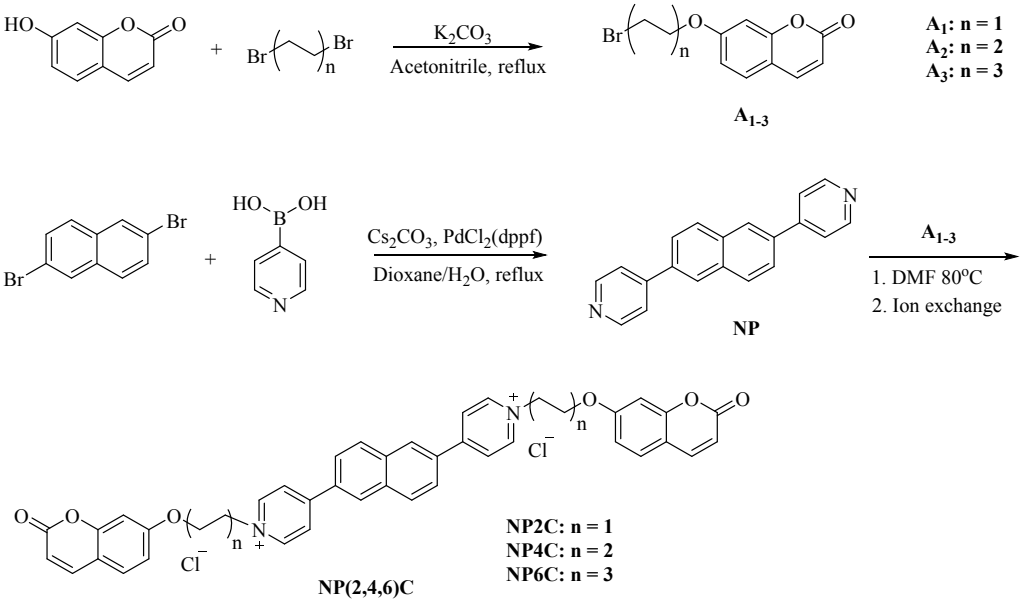

Figure S1. Schematic illustration of the synthesis of **NP(2,4,6)C**.

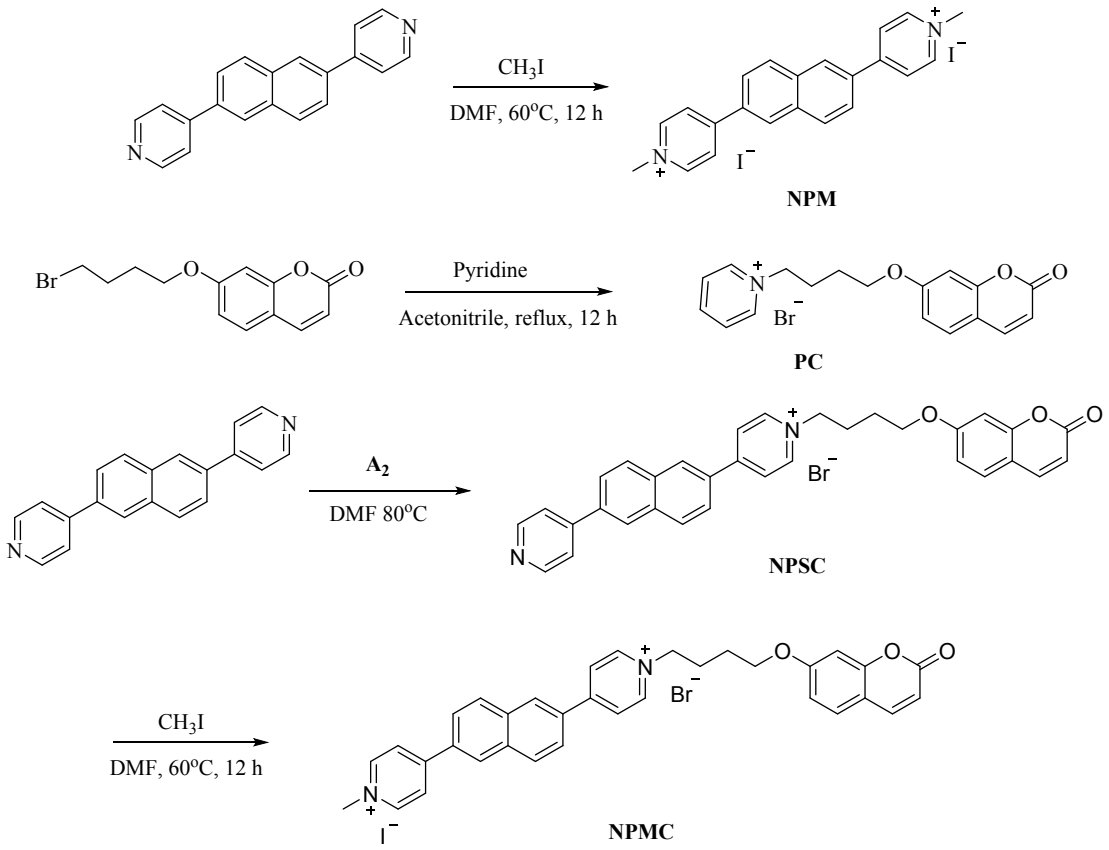

Figure S2. Schematic illustration of the synthesis of NPM, PC and NPMC.

Synthesis of 7-(2-bromoethoxy)-2H-chromen-2-one (A_1).

Compound A_1 was synthesized conveniently in one step from commercial material 7-hydroxyl coumarin and 1,2-dibromoethane according to literature procedure.[7]

Synthesis of 7-(4-bromobutoxy)-2H-chromen-2-one (A_2).

Compound A_2 was synthesized according to literature procedure.[8]

Synthesis of 7-((6-bromohexyl) oxy)-2H-chromen-2-one (A_3).

Compound A_3 was synthesized according to literature procedure.[9]

Synthesis of 2,6-di(pyridin-4-yl) naphthalene (NP).

Pyridin-4-ylboronic acid (0.86 g, 7.0 mmol, 4.0 eq), Cs_2CO_3 (2.28 g, 7.0 mmol, 4.0 eq) and $PdCl_2$(dppf) (25.5mg, 0.035 mmol, 0.02 eq) were added to a solution of 2,6-dibromonaphthalene (0.5 g, 1.75 mmol, 1.0 eq) in 1,4-dioxane/H_2O (90 mL, 5:1, v/v). The reaction mixture was stirred at 100 °C under argon for 24 h and filtered after cooling to room temperature. After the filtrate was concentrated, water (30 mL) was added and the mixture was extracted with ethyl acetate (3×50 mL). The combined organic phase was washed with water (3×50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, and then evaporated to afford a pure brown solid, which was further purified by silica gel column chromatography (dichloromethane/methanol = 30:1 v/v/v) to provide compound 1 (0.41 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.73 (dd, J = 4.5, 1.6 Hz, 2H), 8.17 (d, J = 1.6 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.83 (dd, J = 8.5, 1.6 Hz, 1H), 7.66 (dd, J = 4.5, 1.7 Hz, 2H). ^{13}C

NMR (100 MHz, $CDCl_3$, δ) 150.43, 147.90, 136.38, 133.48, 129.51, 126.23, 125.44, 121.82. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{20}H_{15}N_2]^+$, 283.1235; found, 283.1225.

Synthesis of 4,4'-(naphthalene-2,6-diyl) bis(1-(2-((2-oxo-2H-chromen-7-yl) oxy) ethyl) pyridin-1-ium) chloride (NP2C).

A solution of compound NP (100 mg, 0.35 mmol, 1.0 eq) and A_1 (0.38 g, 1.42 mmol, 4.0 eq) in DMF (3 mL) was stirred for 24 h at 80 °C. The precipitate was collected by filtration and washed with acetonitrile and dichloromethane to provide the pure compound as a yellow solid, the counter anion of which was later exchanged to chloride to get the compound NP2C (0.22 g, 85% yield) with better water-solubility. ^{1}H NMR (400 MHz, DMSO-d_6, δ) 9.26 (d, J = 6.9 Hz, 2H), 8.91 (s, 1H), 8.75 (d, J = 7.0 Hz, 2H), 8.33 (q, J = 8.7 Hz, 2H), 8.00 (d, J = 9.5 Hz, 1H), 7.66 (d, J = 8.7 Hz, 1H), 7.08 (d, J = 2.3 Hz, 1H), 6.98 (dd, J = 8.6, 2.4 Hz, 1H), 6.32 (d, J = 9.5 Hz, 1H), 5.11 (d, J = 4.7 Hz, 2H), 4.72 (d, J = 4.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ) 160.43, 160.10, 155.16, 154.55, 145.61, 144.19, 134.00, 132.96, 130.63, 129.66, 129.01, 125.58, 124.72, 113.01, 112.63, 101.69, 66.74, 58.89. HRMS (ESI) m/z: $[M-2Cl]^{2+}/2$ calcd for $[C_{42}H_{32}N_2O_6]^{2+}/2$, 330.1105; found, 330.1130.

Synthesis of 4,4'-(naphthalene-2,6-diyl) bis (1-(4-((2-oxo-2H-chromen-7-yl) oxy) butyl) pyridin-1-ium) chloride chloride (NP4C).

NP4C was prepared from NP and A_2 by a similar procedure as described for the synthesis of NP2C. Pure NP4C was obtained as a yellow solid (90% yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ) 9.27 (d, J = 6.9 Hz, 2H), 8.90 (s, 1H), 8.73 (d, J = 6.9 Hz, 2H), 8.37 – 8.28 (m, 2H), 7.98 (d, J = 9.5 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.00 (d, J = 2.3 Hz, 1H), 6.95 (dd, J = 8.6, 2.4 Hz, 1H), 6.28 (t, J = 9.8 Hz, 1H), 4.74 (t, J = 7.2 Hz, 2H), 4.16 (t, J = 6.2 Hz, 2H), 2.26 – 2.08 (m, 2H), 1.93 – 1.77 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD, δ) 162.14, 161.84, 155.65, 144.66, 144.26, 134.65, 133.46, 130.84, 129.15, 128.69, 125.20, 112.69, 112.09, 100.97, 67.41, 60.61, 27.77, 25.39. HRMS (ESI) m/z: $[M-2Cl]^{2+}/2$ calcd for $[C_{46}H_{40}N_2O_6]^{2+}/2$, 358.1443; found, 358.1444.

Synthesis of 4,4'-(naphthalene-2,6-diyl) bis(1-(6-((2-oxo-2H-chromen-7-yl) oxy) hexyl) pyridin-1-ium) chloride (NP6C).

NP6C was prepared from NP and A_3 by a similar procedure as described for the synthesis of NP2C. Pure NP6C was obtained as a pale yellow solid (82% yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ) 9.23 (d, J = 6.9 Hz, 2H), 8.89 (s, 1H), 8.71 (d, J = 6.9 Hz, 2H), 8.32 (q, J = 8.7 Hz, 2H), 7.97 (d, J = 9.5 Hz, 1H), 7.61 (d, J = 8.6 Hz, 1H), 6.97 (d, J = 2.3 Hz, 1H), 6.93 (dd, J = 8.6, 2.4 Hz, 1H), 6.27 (d, J = 9.5 Hz, 1H), 4.65 (t, J = 7.2 Hz, 2H), 4.08 (t, J = 6.3 Hz, 2H), 2.02 (dd, J = 14.2, 7.3 Hz, 2H), 1.82 – 1.73 (m, 2H), 1.50 (d, J = 8.0 Hz, 2H), 1.41 (d, J = 6.5 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD, δ) 162.55, 161.91, 155.68, 144.61, 144.30, 134.58, 133.49, 130.81, 129.08, 128.68, 125.21, 125.15, 112.74, 112.52, 111.85, 100.76, 68.05, 60.80, 30.77, 28.28, 25.27, 25.15. HRMS (ESI) m/z: $[M-2Cl]^{2+}/2$ calcd for $[C_{50}H_{48}N_2O_6]^{2+}/2$, 386.1751; found, 386.1756.

Synthesis of 4,4'-(naphthalene-2,6-diyl) bis (1-methylpyridin-1-ium) iodide (NPM).

NP (100 mg, 0.35 mmol, 1.0 eq) and CH_3I (0.5 g, 3.54 mmol, 10.0 eq) were dissolved in DMF (3 mL) and stirred at 60 °C for 12 h. After removal of the excess unreacted CH_3I, the precipitate was collected by filtration and washed with acetonitrile to afford compound NPM as a yellow solid (149 mg, 75% yield). ^{1}H NMR (400

MHz, DMSO-d_6) δ 9.12 (d, J = 6.9 Hz, 2H), 8.90 (s, 1H), 8.69 (d, J = 7.0 Hz, 2H), 8.33 (dd, J = 20.6, 8.7 Hz, 2H), 4.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.09, 146.26, 134.45, 133.45, 131.07, 129.22, 126.03, 124.95, 47.70. HRMS (ESI) m/z: $[M-2I]^{2+}/2$ calcd for $[C_{22}H_{20}N_2]^{2+}/2$, 156.0813; found, 156.0801.

Synthesis of 1-(4-((2-oxo-2H-chromen-7-yl) oxy) butyl) pyridin-1-ium bromide (PC).

A_2 (0.15 g, 0.51 mmol, 1.0 eq) and pyridine (401 mg, 5.07 mmol, 10.0 eq) were dissolved in acetonitrile (5 mL) and refluxed under argon for 12 h. Compound PC was collected as a white solid after filtration when the reaction mixture was cooled to room temperature. ^{1}H NMR (400 MHz, DMSO-d_6, δ) 9.15 (d, J = 5.5 Hz, 2H), 8.63 (t, J = 7.8 Hz, 1H), 8.26 – 8.12 (m, 2H), 8.01 (d, J = 9.5 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.00 (d, J = 2.3 Hz, 1H), 6.94 (dd, J = 8.6, 2.4 Hz, 1H), 6.30 (d, J = 9.5 Hz, 1H), 4.71 (t, J = 7.4 Hz, 2H), 4.13 (t, J = 6.3 Hz, 2H), 2.23 – 1.98 (m, 2H), 1.78 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ) 161.58, 160.26, 155.38, 145.56, 144.81, 144.33, 129.51, 128.15, 112.71, 112.54, 101.21, 60.40, 27.59, 25.00. HRMS (ESI) m/z: $[M-Br]^+$ calcd for $[C_{18}H_{18}NO_3]^+$, 296.1281; found, 296.1280.

Synthesis of 1-(4-((2-oxo-2H-chromen-7-yl) oxy) butyl) pyridin-1-ium bromide (NPSC).

A_2 (82.9 mg, 0.28 mmol, 0.8 eq) was added into the solution of a solution of NP (100.0 mg, 0.35 mmol, 1.0 eq) in 1.5 mL DMF. The reaction mixture was stirred at 80 ^{o}C under argon overnight and then cooled to room temperature. After filtration, the filtrate was dropwise added to ethyl acetate to afford compound NPSC (124.2 mg, 77%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, δ) 8.38 (d, J = 7.0 Hz, 2H), 8.02 (s, 1H), 7.92 – 7.86 (m, 4H), 7.74 (s, 1H), 7.44 (dt, J = 15.4, 7.8 Hz, 3H), 7.29 (dd, J = 8.6, 1.8 Hz, 1H), 7.15 (d, J = 9.5 Hz, 1H), 7.10 (dd, J = 4.5, 1.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 1H), 6.18 (d, J = 2.3 Hz, 1H), 6.12 (dd, J = 8.6, 2.4 Hz, 1H), 5.45 (d, J = 9.5 Hz, 1H), 3.88 (t, J = 7.2 Hz, 2H), 3.33 (t, J = 6.3 Hz, 2H), 1.33 (d, J = 7.1 Hz, 2H), 1.01 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ) 161.63, 160.37, 155.41, 154.35, 150.29, 146.56, 144.92, 144.40, 136.76, 134.45, 132.95, 131.61, 130.29, 130.14, 129.60, 128.93, 126.25, 125.81, 125.00, 124.73, 121.66, 112.80, 112.55, 112.44, 101.25, 67.65, 59.62, 27.56, 25.12. HRMS (ESI) m/z: $[M-Br]^+$ calcd for $[C_{33}H_{27}N_2O_3]^+$, 499.2022; found, 499.2025.

Synthesis of 1-methyl-4-(6-(1-(4-((2-oxo-2H-chromen-7-yl)oxy)butyl)pyridin-1-ium-4-yl)naphthalen-2-yl)pyridin-1-ium bromide iodide (NPMC).

NPSC (80 mg, 0.14mmol, 1.0 eq) and CH_3I (196.4 mg, 1.4 mmol, 10.0 eq)were dissolved in 2.0 mL DMF and stirred at 60 ^{o}C for 12 h. After the removal of the excess unreacted CH_3I, compound NPMC (98 mg, 81.2%) was collected as a yellow solid after precipitation from the reaction mixture when cooled to room temperature. ^{1}H NMR (400 MHz, DMSO-d_6, δ) 9.24 (d, J = 6.9 Hz, 2H), 9.12 (d, J = 6.9 Hz, 2H), 8.89 (s, 2H), 8.70 (dd, J = 12.0, 7.0 Hz, 4H), 8.32 (dd, J = 20.3, 8.7 Hz, 4H), 7.98 (d, J = 9.5 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.95 (dd, J = 8.6, 2.4 Hz, 1H), 6.27 (d, J = 9.5 Hz, 1H), 4.72 (t, J = 7.1 Hz, 2H), 4.38 (s, 3H), 4.16 (t, J = 6.3 Hz, 2H), 2.17 (s, 2H), 1.84 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ) 161.60, 160.34, 155.39, 154.07, 153.63, 145.81, 145.00, 144.37, 134.04, 134.00, 133.02, 132.96, 130.67, 129.58, 128.91, 128.79, 125.60, 124.97, 124.52, 112.78, 112.53, 112.41, 101.24, 67.64, 59.72, 47.29, 27.53, 25.09. HRMS (ESI) m/z: $[M-Br-I]^{2+}/2$ calcd for $[C_{34}H_{30}N_2O_3]^{2+}/2$, 257.1123; found, 257.1123.

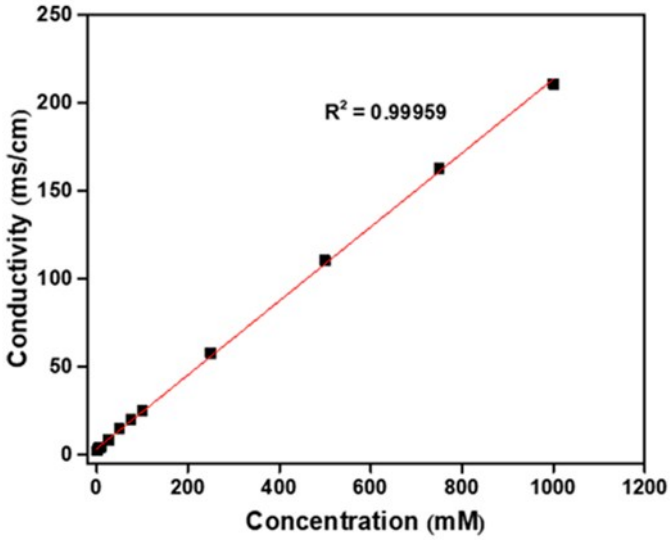

Figure S3. Plot of conductivity versus the concentrations of NP4C aqueous solution at 25 °C. [NP4C]: 1μM ~ 1mM.

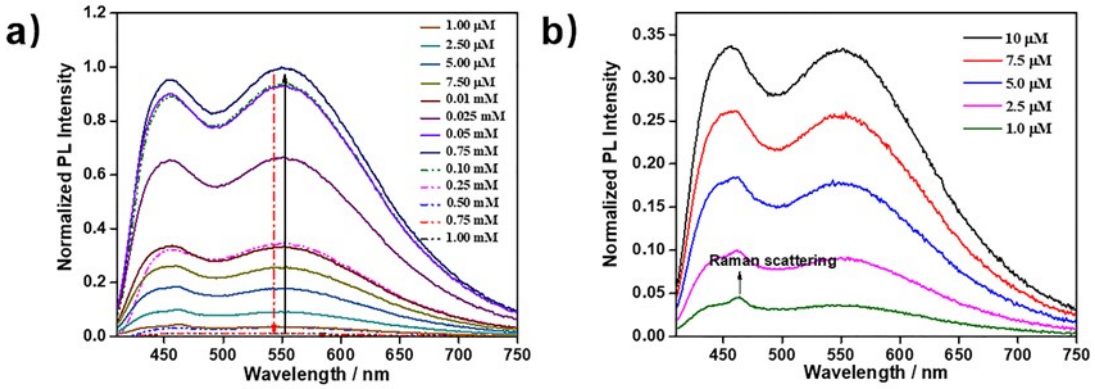

Figure S4. a) Fluorescence spectra of aqueous NP4C solutions at various concentrations (from 1μM~1mM). b) Partial magnification of PL spectra at extremely diluted concentration (from 1~10 μM). Excitation wavelength 400 nm, 25 °C.

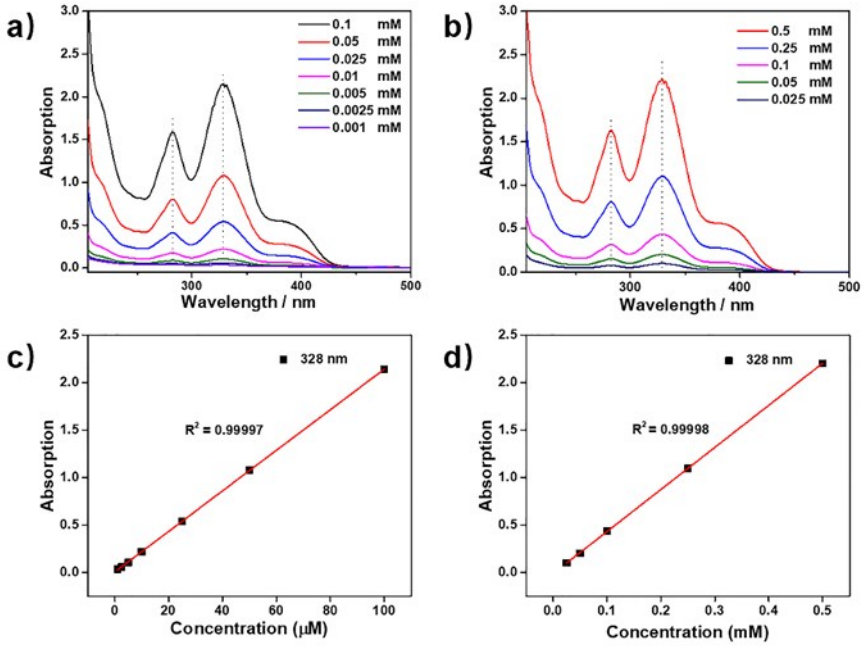

Figure S5. Absorption spectra of NP4C aqueous solutions at various concentration respectively range from a) 1.0 μM to 0.1 mM (1-mm optical length) and b) 0.025 mM to 0.5 mM (1-cm optical length), 25 °C. c), d) absorption intensities at 328 nm wavelength of NP4C aqueous solutions at various concentrations respectively corresponding to a) and b).

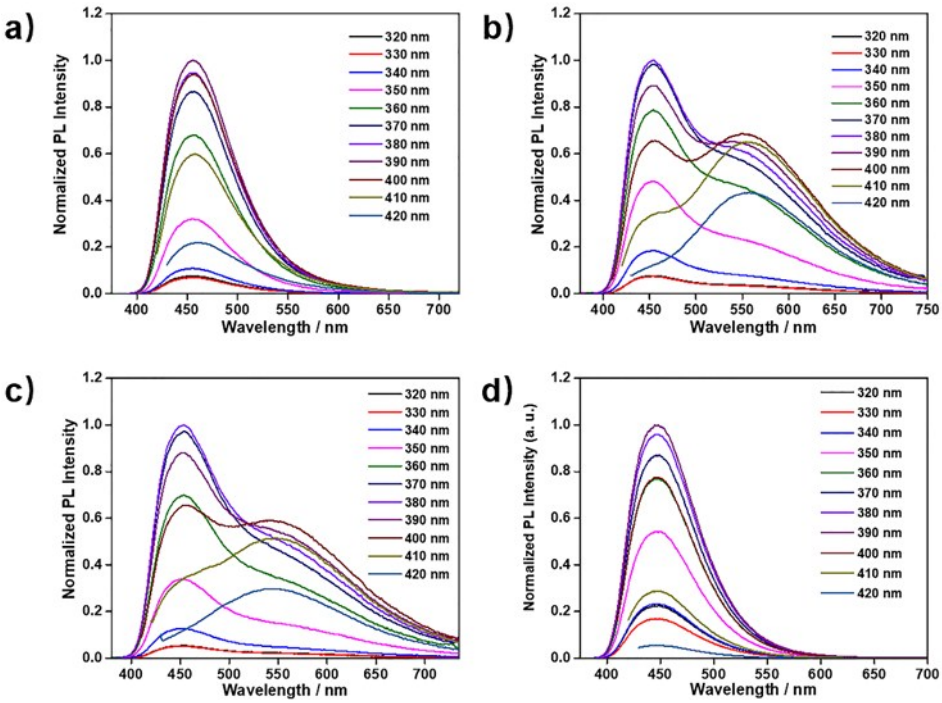

Figure S6. Fluorescence spectra of a) NP2C, b) NP4C, c) NP6C and d) NPM in aqueous solution using various excitation wavelengths, [NP2C] = [NP4C] = [NP6C] = [NPM] = 0.1 mM, 25 °C.

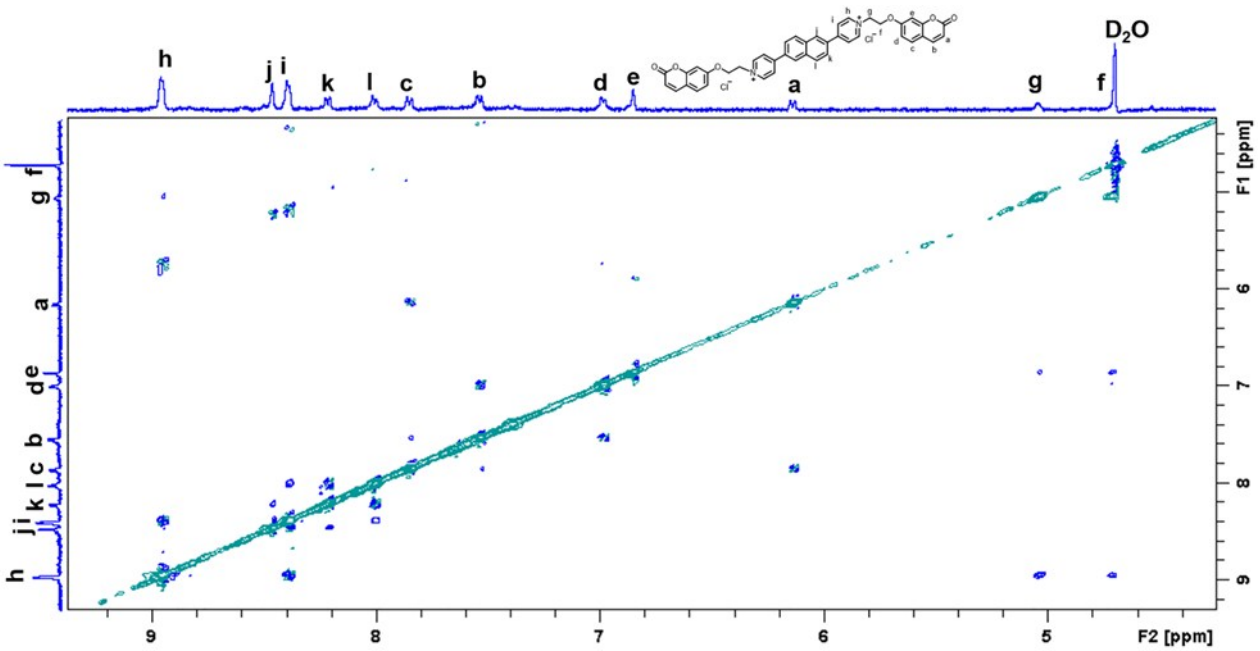

Figure S7. 2D ROESY NMR spectrum of NP2C in D_2O with water suppression, [NP2C] = 1.0 mM, 25 °C.

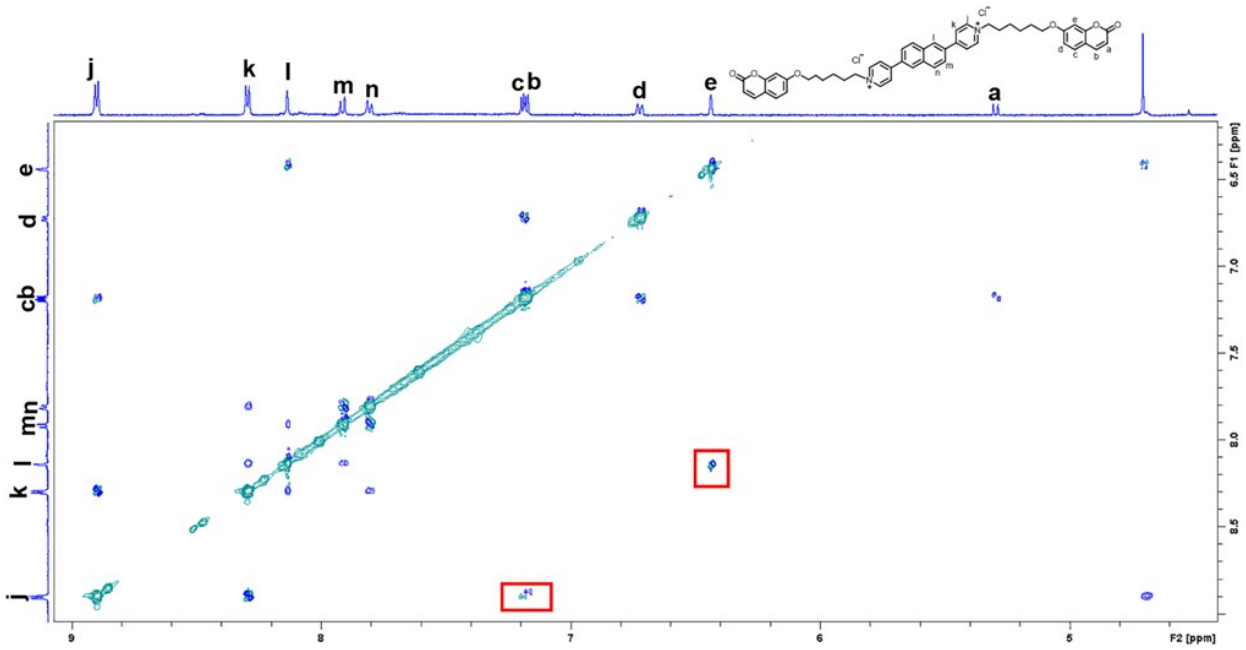

Figure S8. 2D ROESY NMR spectrum of NP6C in D_2O with water suppression, [NP6C] = 1.0 mM, 25 °C.

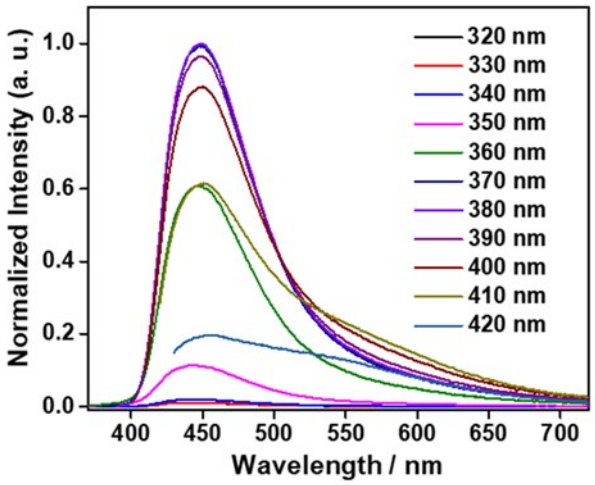

Figure S9. Fluorescence spectra of NPMC aqueous solution using various excitation wavelengths, [NPMC] = 0.1 mM, 25 ^{o}C.

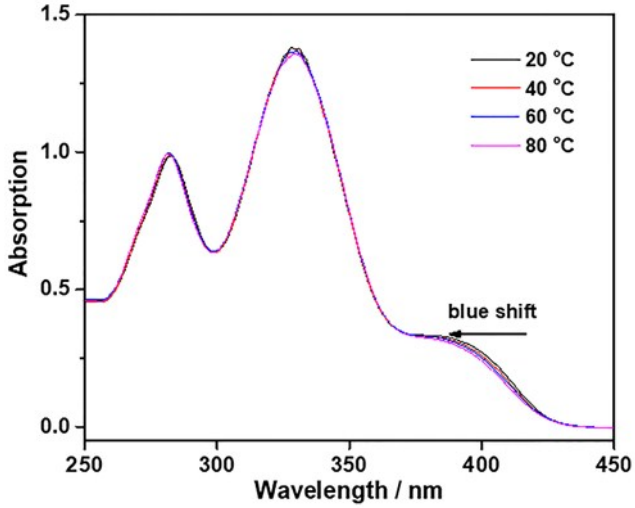

Figure S10. UV-vis absorption spectra of NP4C aqueous solution at various temperatures, [NP4C] = 0.02 mM.

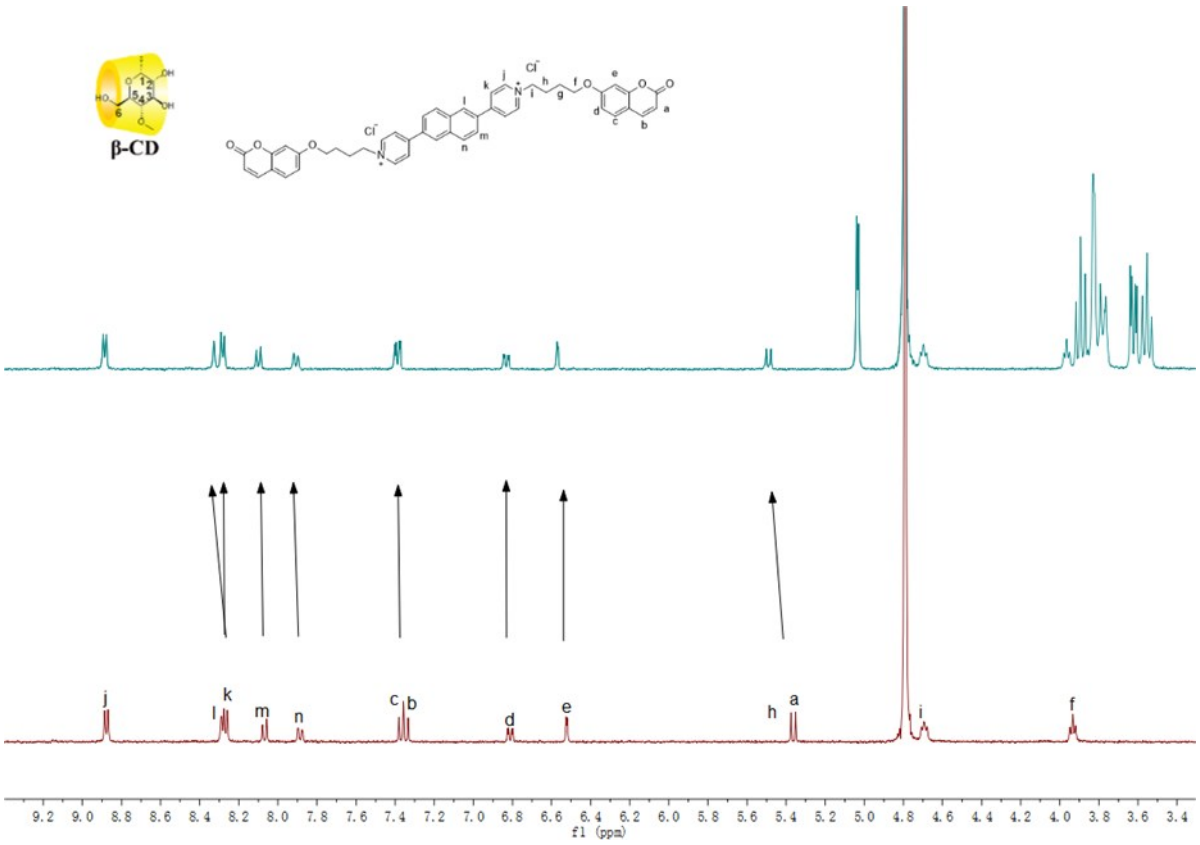

Figure S11. ^{1}H NMR spectrum of a) NP4C, b) NP4C@β-CD (molar ratio 1:2), [β-CD] = 2.0 mM, [NP4C] = 1.0 mM, D_2O, 25 ^{o}C

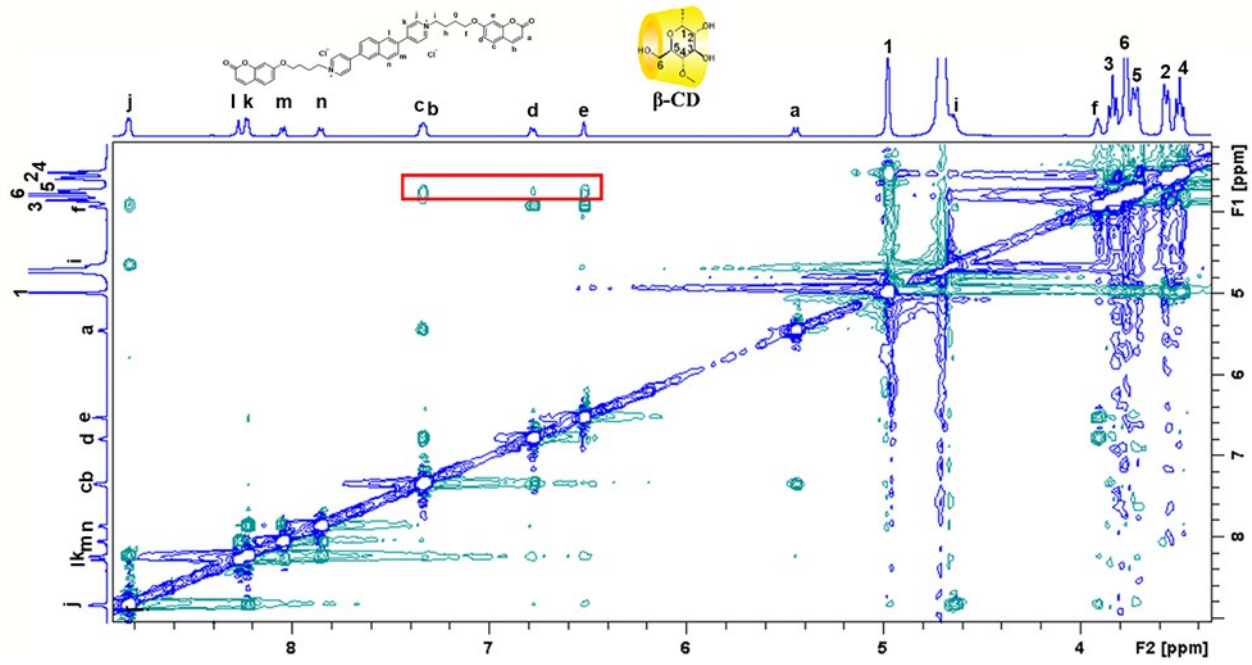

Figure S12. 2D ROESY NMR spectrum of NP4C@β-CD aqueous solution with water suppression ([NP4C] = 1.0 mM, [β-CD] = 2.0 mM, D_2O, 25 ^{o}C).

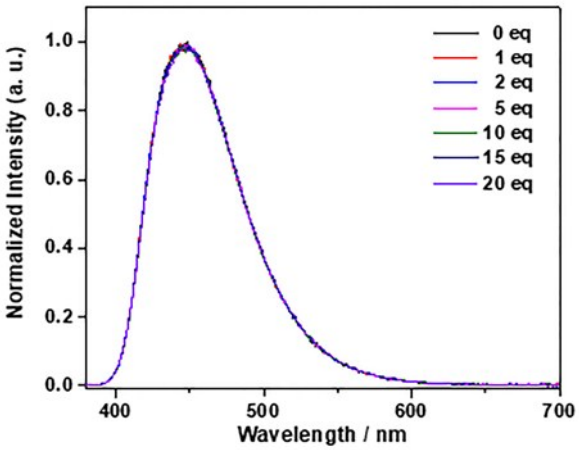

Figure S13. PL emission spectra of NPM aqueous solution titrated with β-CD, [NPM] = 25 μM, 25 °C.

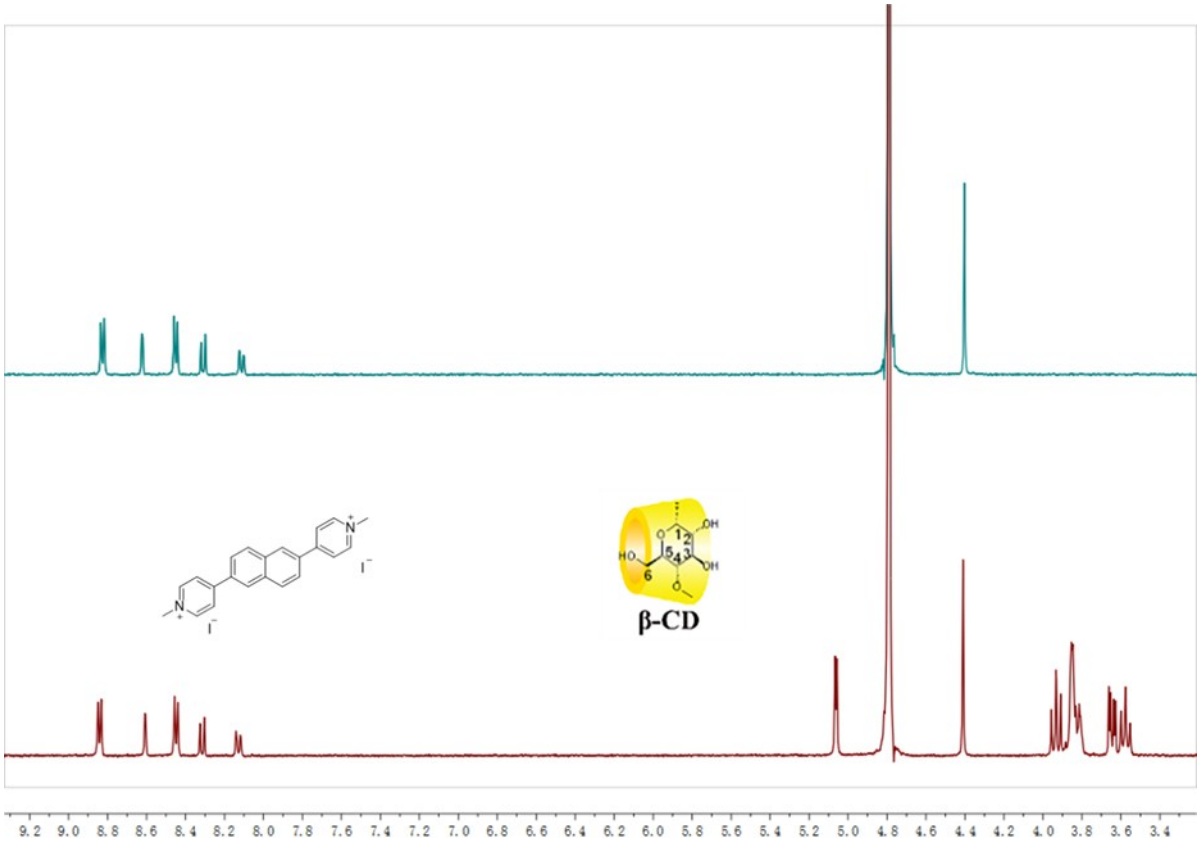

Figure S14. ^{1}H NMR spectrum of a) NPM, b) NPM@β-CD (1:1 molar ratio, [β-CD] = 1.0 mM, [NPM] = 1.0 mM, D_2O, 25 °C).

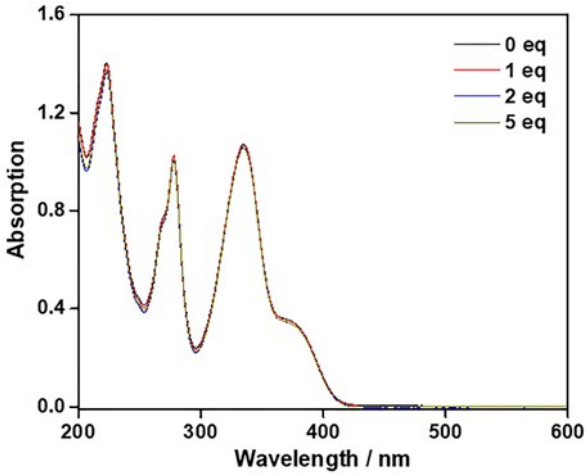

Figure S15. Absorption spectra of NPM aqueous solution titrated with β-CD, [NPM] = 25 μM, 25 °C.

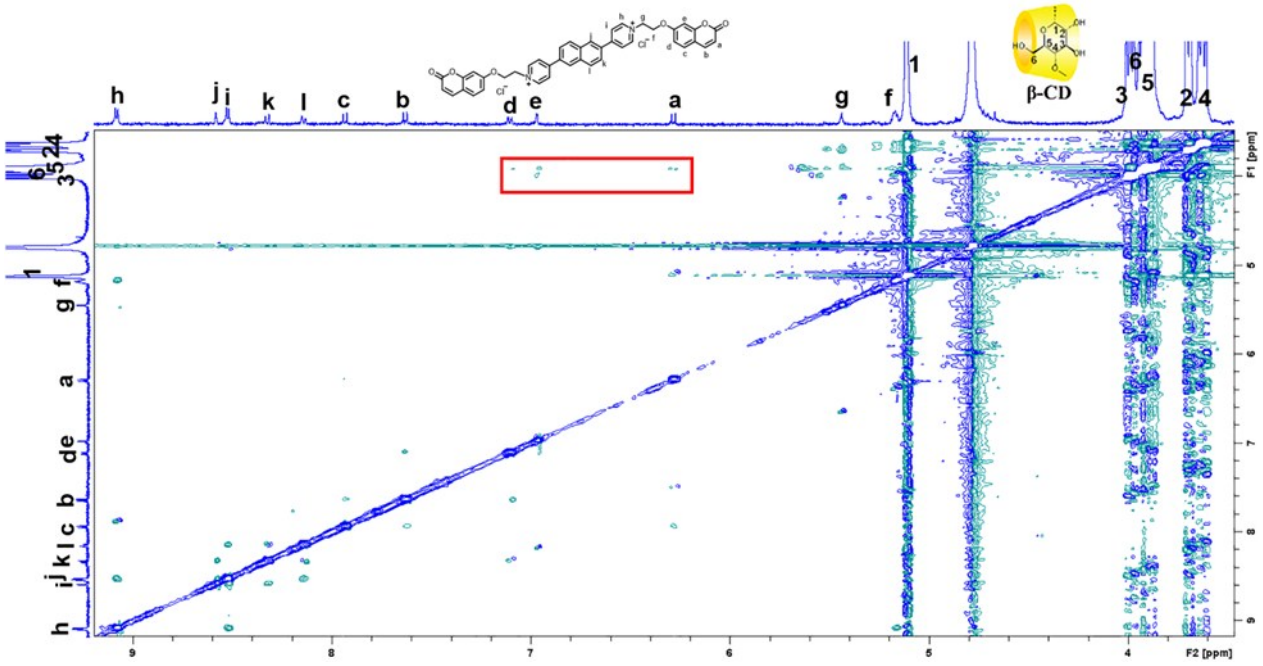

Figure S16. 2D ROESY NMR spectrum of NP2C@β-CD aqueous solution with water suppression ([NP2C] = 1.0 mM, [β-CD] = 2.0 mM, D_2O, 25 °C).

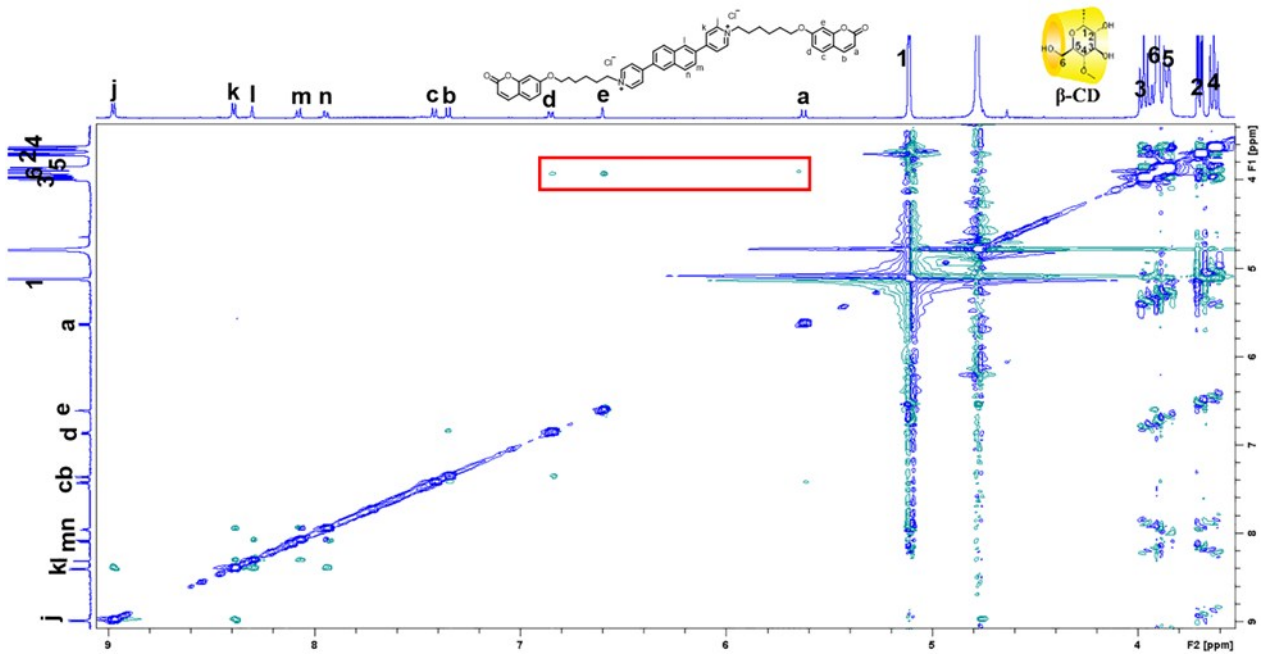

Figure S17. 2D ROESY NMR spectrum of NP6C@β-CD aqueous solution with water suppression ([NP6C] = 1.0 mM, [β-CD] = 2.0 mM, D_2O, 25 °C).

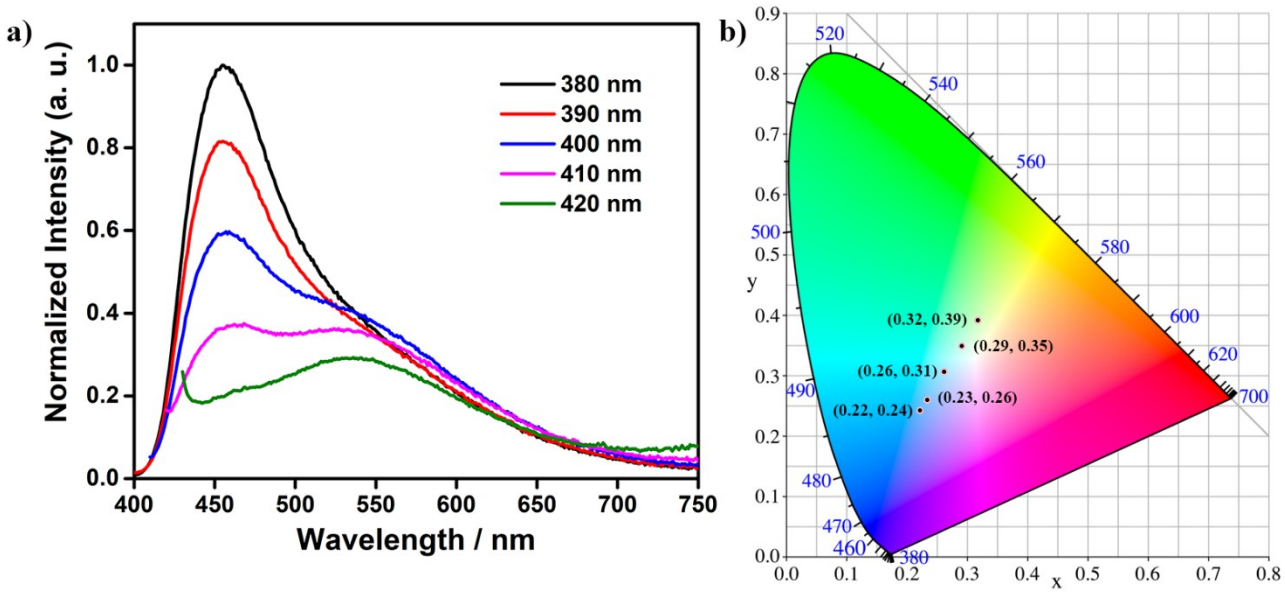

Figure S18. a) PL emission spectra of WLE gel ([NP4C] = 0.1 mM) using different excitation wavelength, 25 °C; b) the calculated CIE coordinates for WLE gel in the 1931 CIE chromaticity diagram according to the fluorescence spectra in a).

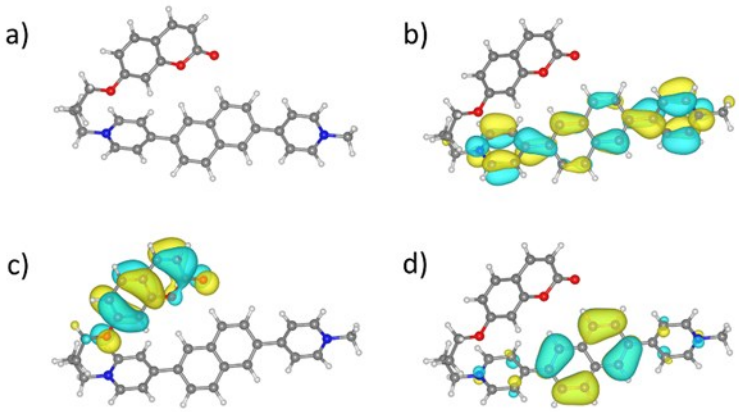

Figure S19. a) The optimized structure of NPMC calculated at B3LYP/6-311+G(d,p) level; b) the LUMO, c) the HOMO and d) HOMO - 1 of NPMC.

Calculations including the frontier molecular orbitals and the optimized structure of NPMC were implemented. Similar to NP4C, the HOMO and LUMO of NPMC distributed in the coumarin groups and the PN unit, respectively, which hinted the possibility of CT process. Besides, the optimized structure obtained from DFT calculations showed the existence of self-folding behaviour, but the stacking only occurred on the edge of the acceptor and donor groups. This imperfect conformation could only slightly influence the ICT efficiency, which reflected on the inconspicuous yellow-green emission of NPMC. TD-DFT calculations also demonstrated the oscillator strength of CT emission was so small (f = 0.008), indicating the weak yellow-green luminescent efficiency (Table 1).

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