Supporting Information

Phenylcarboxyl-decorating Tetraphenylethene with Diverse Molecular RIM-induced Emission from Host-guest Inclusion and Aggregation Formation

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Caption of Content

Fig. S1 ^{1}H NMR spectrum of **1** in DMSO-d_6. The residual solvent signals are marked with asterisks.

Fig. S2 ^{13}C NMR spectrum of **1** in DMSO-d_6. The residual solvent signals are marked with asterisks.

Fig. S3 ^{1}H NMR spectrum of **2** in DMSO-d_6.

Fig. S4 ^{13}C NMR spectrum of **2** in DMSO-d_6. The residual solvent signals are marked with asterisks.

Fig. S5 ^{1}H NMR spectrum of **3** in DMSO-d_6.

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Fig. S7 . ESI-MS spectrum of compound **3**.

Fig. S8 2D COSY spectrum of compound **3** in DMSO-d$_6$.

Fig. S9 ^{1}H NMR spectrum of compound **4** in DMSO-d_6.

Fig. S10 ^{13}C NMR spectrum of **4** in DMSO-d_6.

Fig. S11 2D COSY spectrum of **4** in DMSO-d_6.

Fig. S12 ESI-MS spectrum of compound **4**.

Fig. S13 (A) Fluorescence spectra and (B) plots of the fluorescence intensity at 460 nm of **TPE-COOH** in THF-water mixtures with different water fractions. Concentration: 30 μM; λ_{ex}: 330 nm (10 nm, 10 nm); 283K.

Fig. S14 Change in fluorescence intensity at 455 nm of **TPE-COOH** upon addition of 2 equiv. α-CD in different water fraction THF-water mixtures. Concentration: 30 μM (contain 1.1 equiv. NaOH); λ_{ex}: 330 nm (10 nm, 10nm); 283 K.

Fig. S15 (A) Fluorescence spectra and (B) plots of the fluorescence intensity at 455 nm of **TPE-COOH** in DMSO-water mixtures with different water fractions. Concentration: 30 μM; λ_{ex}: 330 nm (10 nm, 10nm); 283 K.

Fig. S16 Change in fluorescence intensity at 455 nm of **TPE-COOH** upon addition of 2 equiv. α-CD in different water fraction THF-water mixtures. Concentration: 30 μM; λ_{ex}: 330 nm (10 nm, 10nm); 283 K.

Fig. S17 Benesi–Hildebrand plot of 1/(F-F_0) vs. 1/[α-CD].

Fig. S18 Job's plot for the complexation of **TPE-COOH** and α-CD in DMSO-water (f_w = 50%) by monitoring the fluorescence intensity at 455 nm. The total concentration of **TPE-COOH** and α-CD was fixed at 50 μM.

Fig. S19 ESI-MS spectrum of a mixture of **TPE-COOH** and α-CD (20 equiv.) in water.

Fig. S20 Change in UV-Vis spectrum of **TPE-COOH** upon titration with α-CD in DMSO-water mixture (f_w = 50%). Concentration: 30 μM.

Fig. S21 UV-Vis spectra of **TPE-COOH** in DMSO-water mixtures with different water fractions (10%, 50%, 60%, 90%). Concentration: 30 μM.

Fig. S22 (A) Change in fluorescence spectrum of **TPE-COOH**⊂α-CD upon titration with **AD-COOH** in DMSO-water (f_w = 50%) and (B) plots of the fluorescence intensity at 455 nm against [**AD-COOH**]/[**TPE-COOH**⊂α-CD]. Concentration: 30 μM (contain 1.1 equiv. NaOH); λ_{ex}: 330 nm (10 nm, 10 nm); 283 K.

Fig. S23 (A) Change in fluorescence spectrum of **TPE-COOH**⊂α-CD upon titration with *trans*-**BPA**(contain 1.1 equiv. NaOH) in DMSO-water mixture (f_w = 50%) and (B) plots of the fluorescence intensity at 455 nm against [*trans*-**BPA**]/[**TPE-COOH**⊂α-CD]. Concentration: 30 μM (contain 1.1 equiv. NaOH); λ_{ex}: 330 nm(10 nm, 10nm); 283 K.

Fig. S24 Electronic absorption spectra of **PBA** in *cis* and *trans* state (1.8 × 10^{-3} M).

Fig. S25 Change in fluorescence spectrum of **TPE-COOH, PBA** and α-CD(1 : 2 : 1) upon irradiation with 365 nm(10 W) and (B) plots of the fluorescence intensity at 455 nm against time. λ_{ex}: 330 nm (10 nm, 10nm); 283 K.

Fig. S26 Change in fluorescence spectrum of **TPE-COOH, PBA** and α-CD (1 : 2 : 1) upon irradiation with halogen lamp(300W, equipped with a band-pass filter > 435 nm) and (B) plots of the fluorescence intensity at 455 nm against time. λ_{ex}: 330 nm (10 nm, 10nm); 283 K.

Experimental section

General Remarks.

Dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were distilled from anhydrous $MgSO_4$. Tetrahydrofuran (THF) was distilled from sodium wire and benzophenone under nitrogen. Column chromatography was carried out on a silica gel column (Qingdao Haiyang, 200-300 mesh) with the indicated eluents. All the other reagents and solvents such as methyl 4-hydroxybenzoate, diphenylmethane, 4-methylbenzophenone, *n*-butyllithium in hexane (2.5 mol/L), N-bromosuccinimide(NBS), 2,2'-azobis(2-methylpropionitrile) (AIBN), α-CD, β-CD, γ-CD, 1-adamantanecarboxylate, and 4-(phenylazo)benzoic acid were used as received.

NMR spectra were recorded on a Bruker DPX 400 spectrometer (^1H: 400 MHz, ^{13}C: 100 MHz) in DMSO-d_6. Spectra were referenced internally using the residual solvent resonances ($\delta = 2.50$ for ^1H NMR) relative to $SiMe_4$ ($\delta = 0$ ppm). ^{13}C NMR spectra were referenced internally by using the solvent resonances ($\delta = 39.52$ ppm for DMSO-d_6). Electronic absorption spectra were recorded on a Hitachi U-2900 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-7000 spectrophotometer. ESI-MS spectra were taken on a Thermo MSQ Plus mass spectrometer.

*Synthesis of 1-(4-Methylphenyl)-l,2,2-triphenylethylene **1**.*

To a solution of diphenylmethane (2.02 g, 12 mmol) in dry THF (20 mL) was added 4 mL of a 2.5 M solution of *n*-butyllithium in hexane (10 mmol) at 0 °C under nitrogen. The resulting orange-red solution was stirred for 1 h at this temperature. 4-

Methylbenzophenone (1.77 g, 9 mmol) was then added and the reaction mixture was warmed to room temperature and stirred for another 6 h. The reaction was quenched by addition of 10 % aqueous ammonium chloride solution. The organic layer was extracted with dichloromethane (3×50 mL), and the combined organic layers were washed with a saturated brine solution and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the resulting crude alcohol was dissolved in 80 mL of toluene in a 150 mL round-bottom flask fitted with a Dean-Stark trap. A catalytic amount of *p*-toluenesulphonic acid (342 mg, 1.8 mmol) was added, and the mixture was refluxed for 4 h and cooled to room temperature. The toluene layer was washed with 10% aqueous $NaHCO_3$ solution and dried over anhydrous $MgSO_4$. After evaporating the solvent and recrystallization from dichloromethane and methanol, white powder was obtained (2.65 g, 85%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) , δ (TMS, ppm): 7.08-7.17 (m, 9H, ArH), 6.92-6.99 (m, 8H, ArH), 6.84 (d, 2H, J = 8.0 Hz, ArH), 2.20 (s, 3H, -ArCH$_3$). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ: 143.24, 140.41, 140.14, 140.06, 135.54, 130.51, 128.32, 127.23, 127.65, 126.33, 20.59.

Synthesis of 1-[4-(Bromomethyl)phenyl]-1,2,2-diphenylethene ***2***.

1-(4-Methylphenyl)-l,2,2-triphenylethylene (1.73 g, 5.0 mmol), NBS (0.98 g, 5.5 mmol), and AIBN (16 mg, 0.1 mmol) in CCl_4 (70 mL) was heated at 80 °C for 24 h. Then the reaction mixture was cooled to room temperature and filtered. After the solvent was evaporated, the crude product was purified by silica gel column chromatography using petroleum ether as eluent to give white solid in 48% yield (1.02 g). ^{1}H NMR (400 MHz, DMSO-*d*$_6$), δ (TMS, ppm): 7.20 (d, 2H, J = 8.4 Hz, ArH), 7.04-7.18 (m, 9H, ArH), 6.92-7.02 (m, 8H, ArH), 4.61(s, 2H, -ArCH$_2$-). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 143.16, 142.99, 142.96, 142.93, 140.96, 139.94, 135.96, 131.51, 131.12, 13.90, 130.52, 129.72, 127.99, 127.79, 127.70, 126.69, 126.59, 126.50, 34.25.

Synthesis of Methyl 4-((4-(1,2,2-triphenylvinyl)benzyl)oxy)benzoate ***3****.*

A mixture of 1-[4-(bromomethyl)phenyl]-1,2,2-diphenylethene (1.28 g, 3 mmol), 4-methyl hydroxybenzoate (1.26 g, 6 mmol), and potassium carbonate (1.66 g, 12 mmol) in DMF (80 mL) was heated at 80 °C overnight. The reaction mixture was poured into ice water. After filtration, the solid product was dissolved in CH_2Cl_2 and washed with 1 N NaOH (3×50 mL) and dried over anhydrous $MgSO_4$. After the solvent was removed, the crude product was purified by silica-gel chromatography using CH_2Cl_2 and hexane (1:1 v/v) as eluent to give a white solid product (0.61 g , 42%). ^{1}H NMR (400 MHz, DMSO-d$_6$) , δ (TMS, ppm): 7.90 (d, 2H, J = 8.8 Hz, ArH), 7.23 (d, 2H, J = 8.0 Hz, ArH), 7.09-7.16(m, 9H, ArH), 7.08 (d, 2H, J = 8.8 Hz, ArH), 7.00 (d, 2H, J = 8.0 Hz, ArH), 6.95-6.99 (m, 6H, ArH), 5.07 (s, 2H, -ArCH$_2$-), 3.91 (s, 3H, -COOCH$_3$). ^{13}C NMR (DMSO-d$_6$) δ: 143.00, 142.97, 140.75, 140.11, 134.42, 131.10, 130.64, 130.52, 127.76, 127.31, 126.50, 121.98, 114.71, 69.30, 51.74. ESI-MS: Found an isotopic cluster peaking at m/z $[M]^+$ 496.95; Calculated for $C_{35}H_{28}O_3$, 496.20. *Synthesis of 4-((4-(1,2,2-Triphenylvinyl)benzyl)oxy)benzoic acid* ***4****.*

A solution of compound **3** (100 mg) in THF (5 mL) was added slowly to a mixture of water (10 mL) and MeOH (45 mL) which was previously saturated with NaOH. The mixture was stirred at 40 °C for 4 h. The reaction mixture was cooled to room temperature and nutrilized with 1 N HCl until the pH reached about 7. The white precipitate was filtered and washed with water (95 mg, 95 %). ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm):12.62 (s, 1H, -COOH), 7.87 (d, 2H, J = 8.0 Hz, ArH), 7.22 (d, 2H, J = 8 Hz, ArH), 7.06-7.16 (m, 9H, ArH),7.05 (d, 2H, J = 8.0 Hz, ArH), 7.00 (d, 2H, J = 8.0 Hz, ArH), 6.96-6.99 (m, 6H, ArH), 5.07 (s, 2H, -ArCH$_2$-). ^{13}C NMR (DMSO-d_6) δ: 143.08, 142.60, 140.64, 140.19, 135.20, 130.57, 130.52, 130.44, 127.80, 127.74, 127.71, 127.16, 126.44, 113.06, 68.96. ESI-MS: Found an isotopic cluster peaking at m/z [M-H]$^-$ 480.83; Calculated for $C_{34}H_{26}O_3$, 481.19.

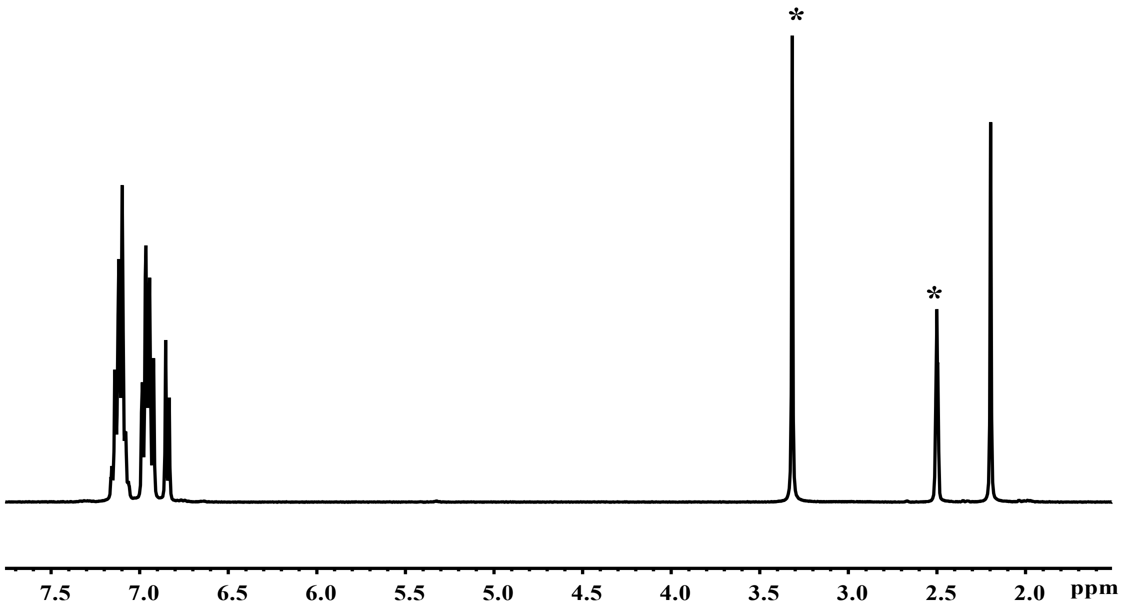


Fig. S1 ^{1}H NMR spectrum of **1** in DMSO-d_6. The residual solvent signals are marked with asterisks.

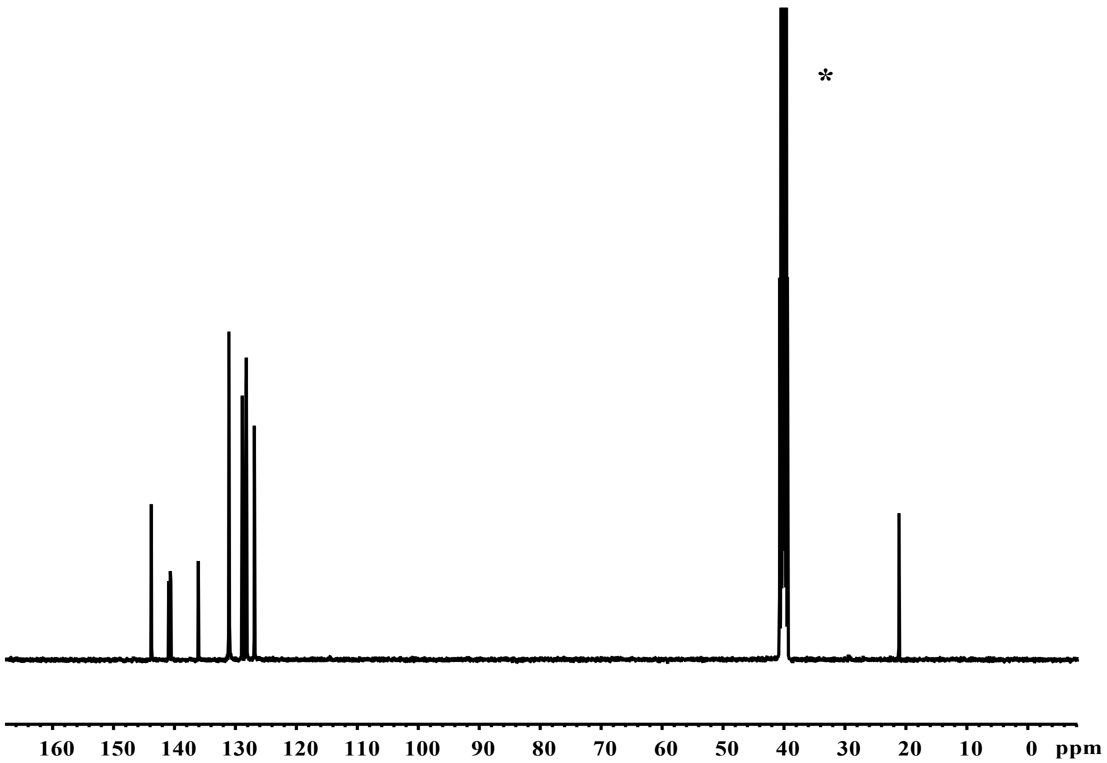


Fig. S2 ^{13}C NMR spectrum of **1** in DMSO-d_6. The residual solvent signals are marked with asterisks.

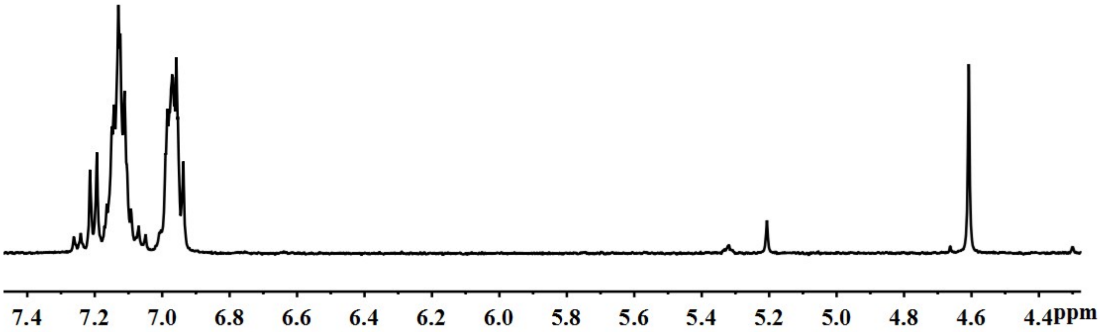


Fig. S3 ^{1}H NMR spectrum of **2** in DMSO-d_6.

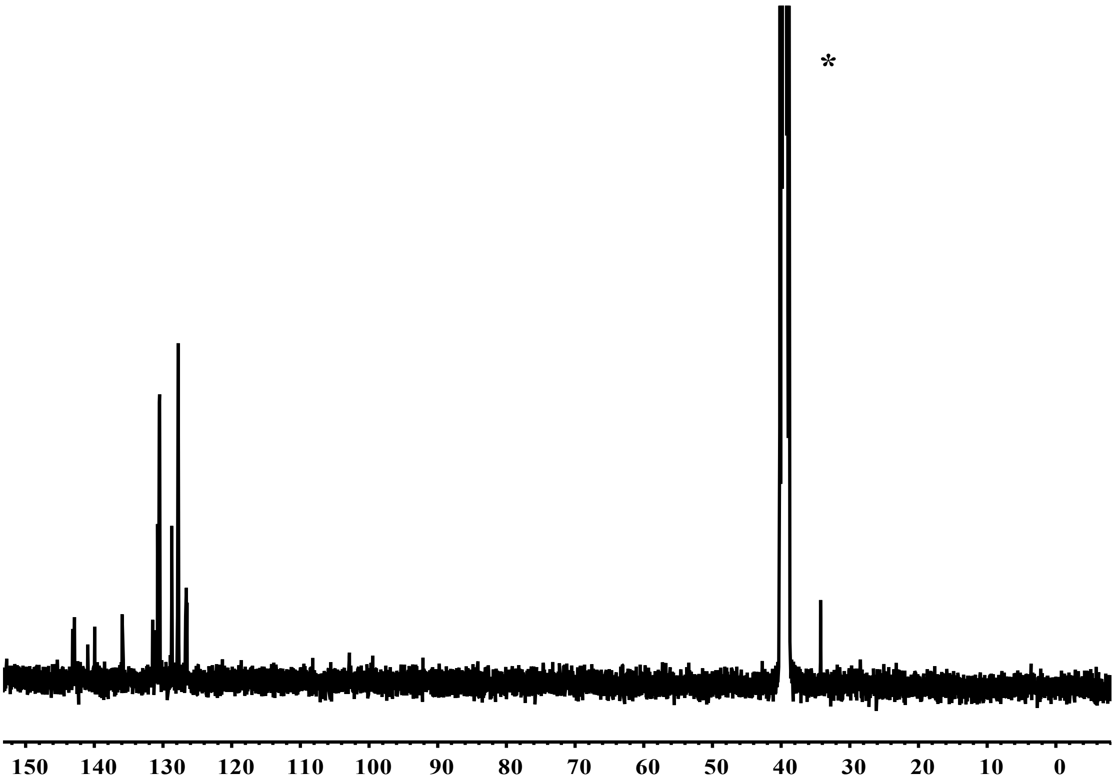


Fig. S4 ^{13}C NMR spectrum of **2** in DMSO-d_6. The residual solvent signals are marked with asterisks.

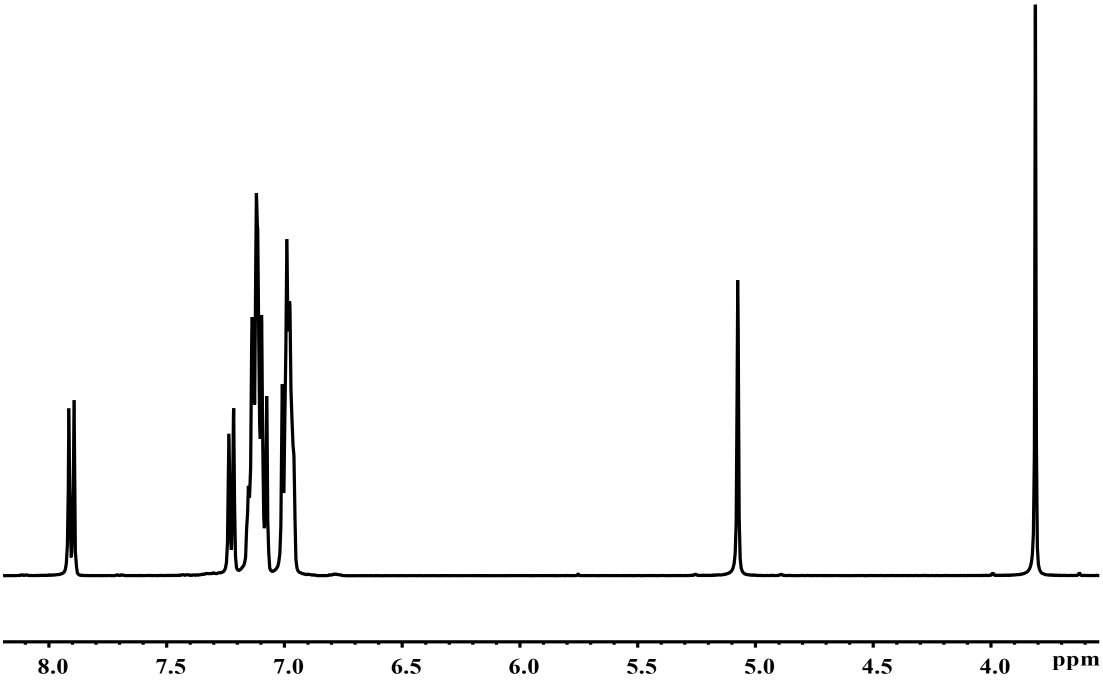


Fig. S5 ^{1}H NMR spectrum of **3** in DMSO-d_6.

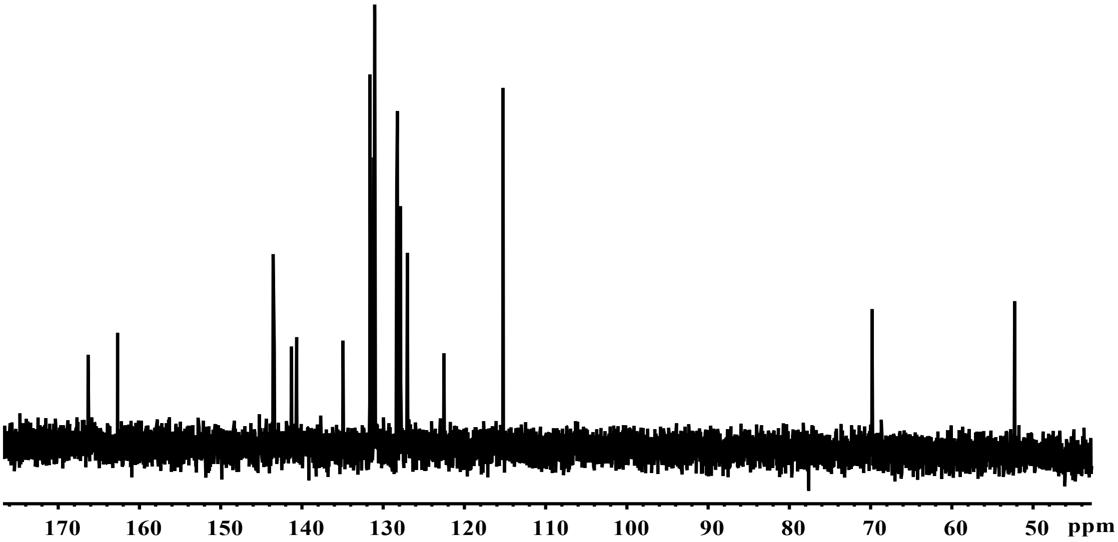


Fig. S6 ^{13}C NMR spectrum of **3** in DMSO-d_6.

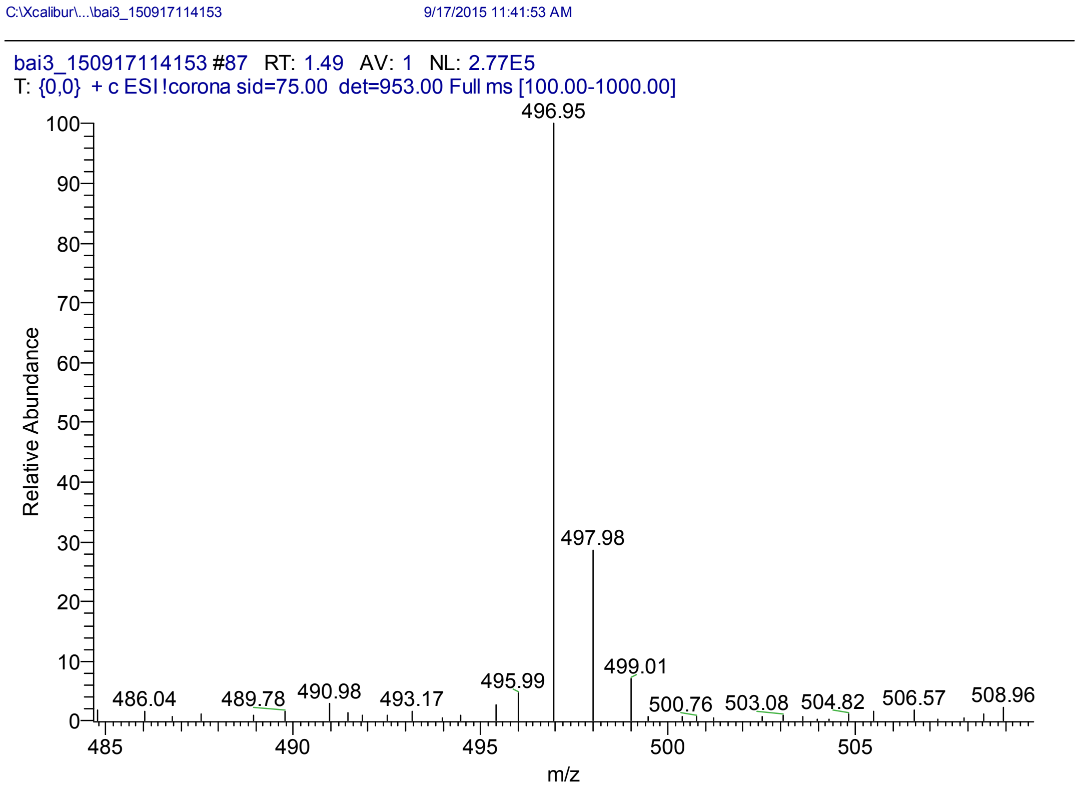


Fig. S7 . ESI-MS spectrum of compound **3**.

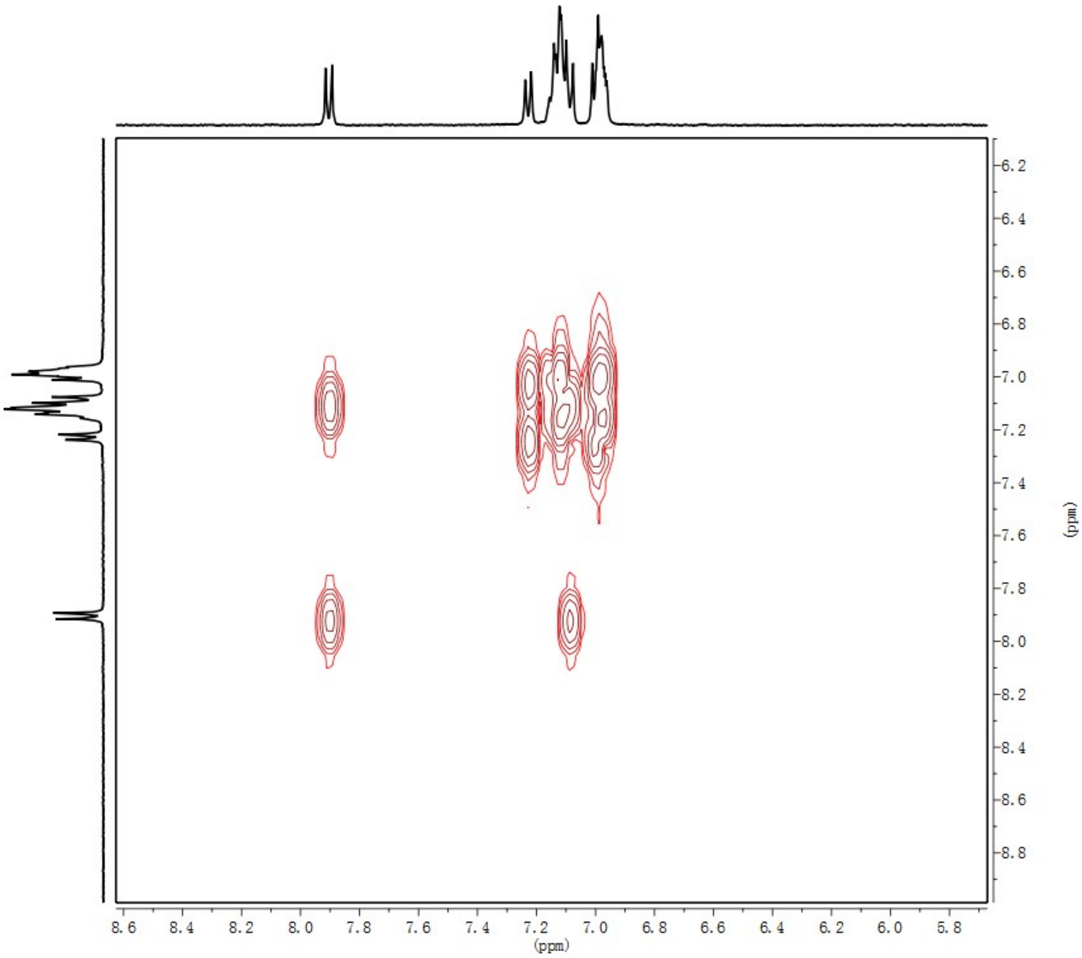


Fig. S8 2D COSY spectrum of compound **3** in DMSO-d_6.

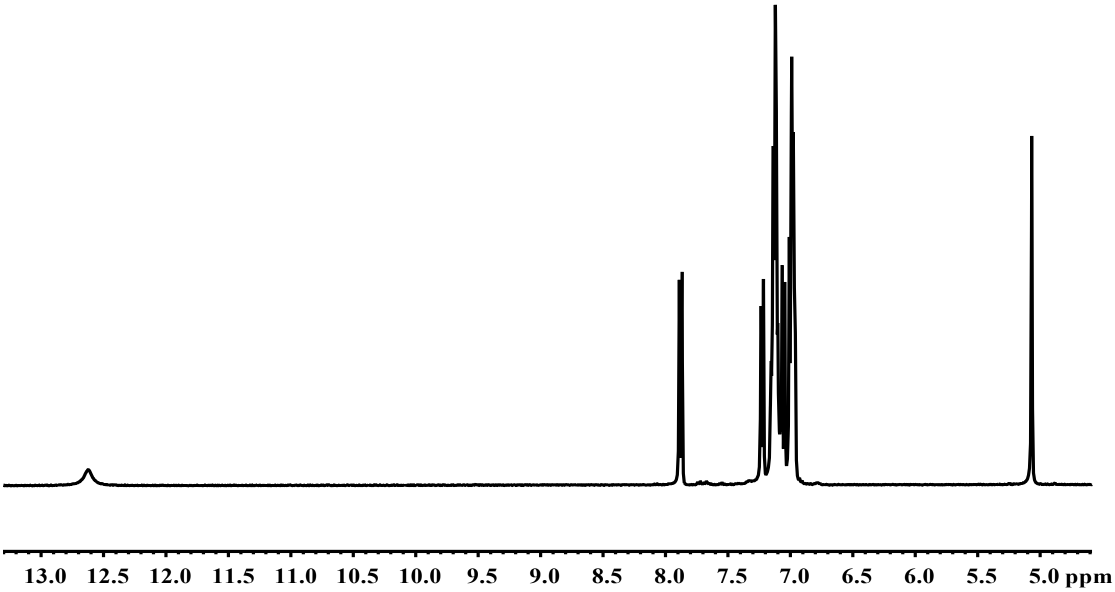


Fig. S9 ^{1}H NMR spectrum of compound **4** in DMSO-d_6.

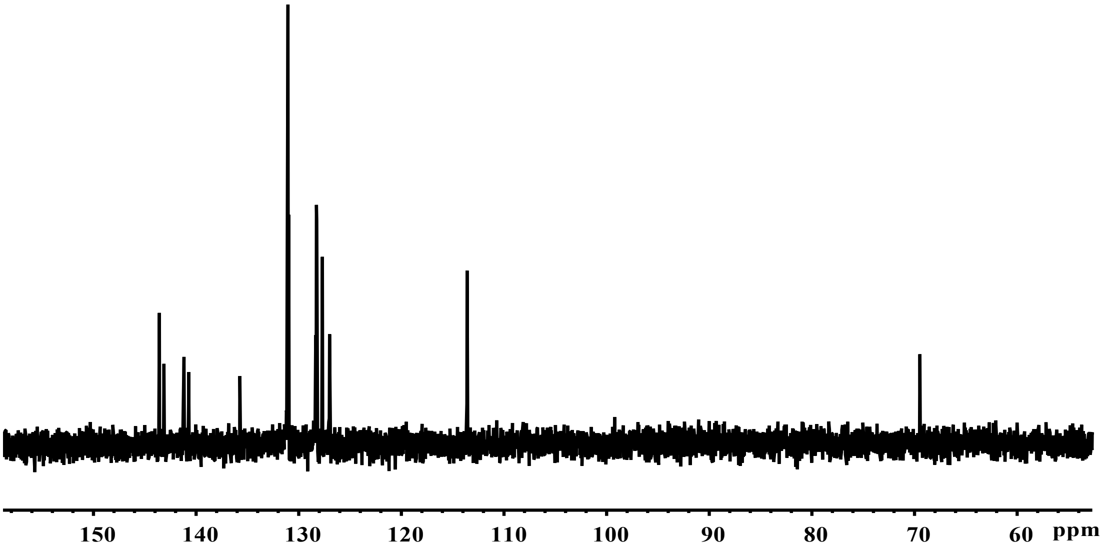


Fig. S10 ^{13}C NMR spectrum of **4** in DMSO-d_6.

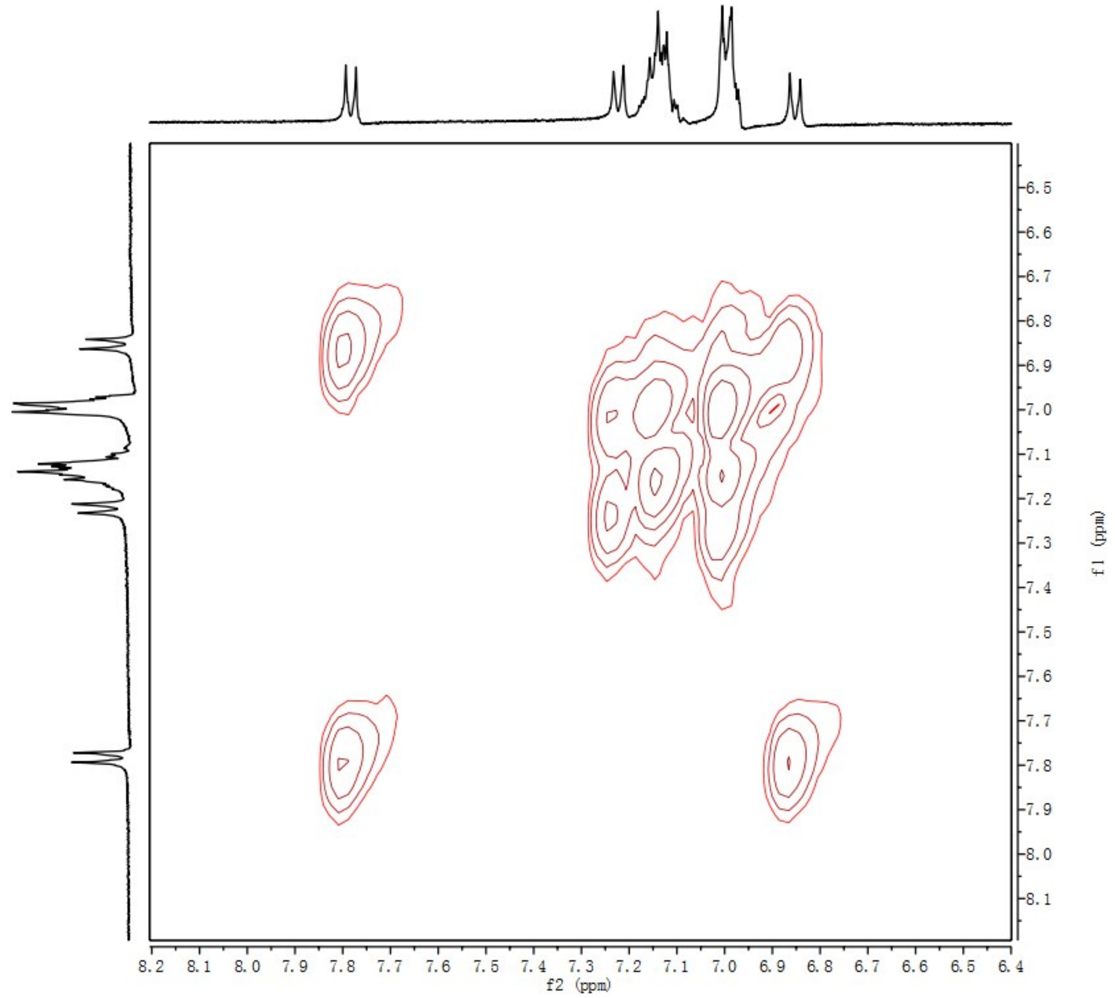


Fig. S11 2D COSY spectrum of **4** in DMSO-d_6.

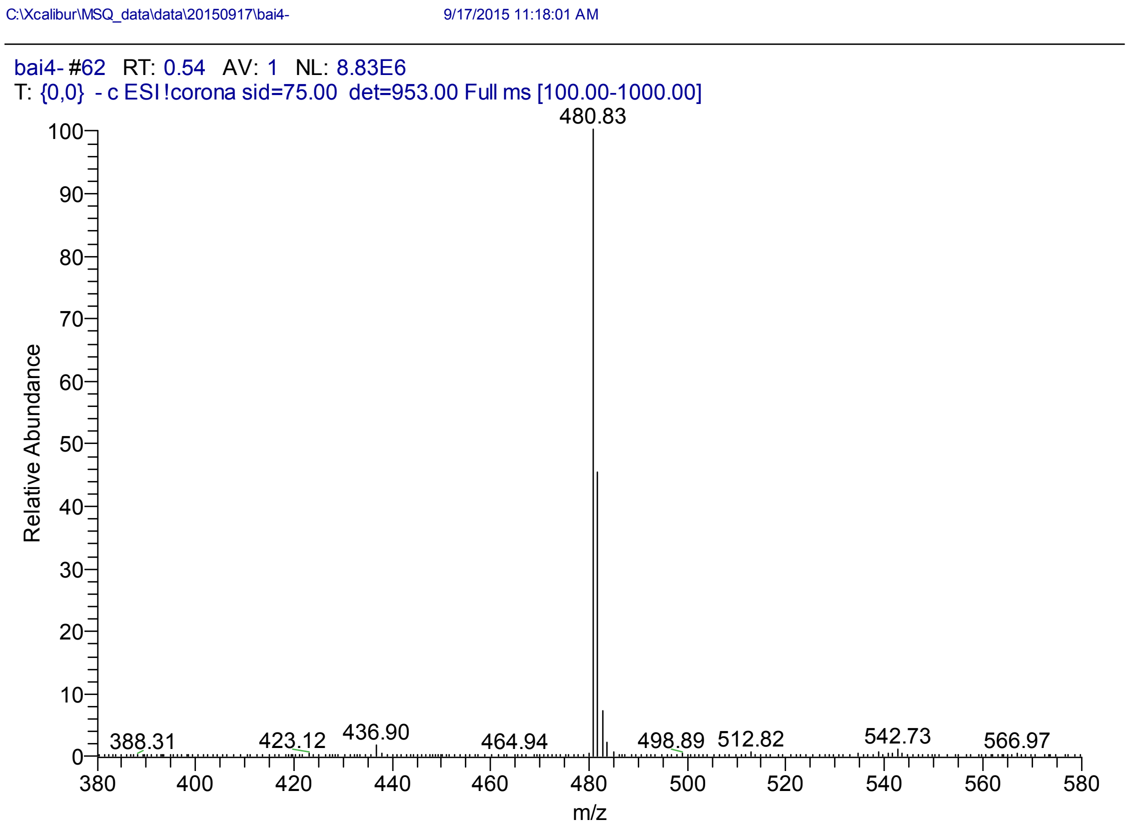
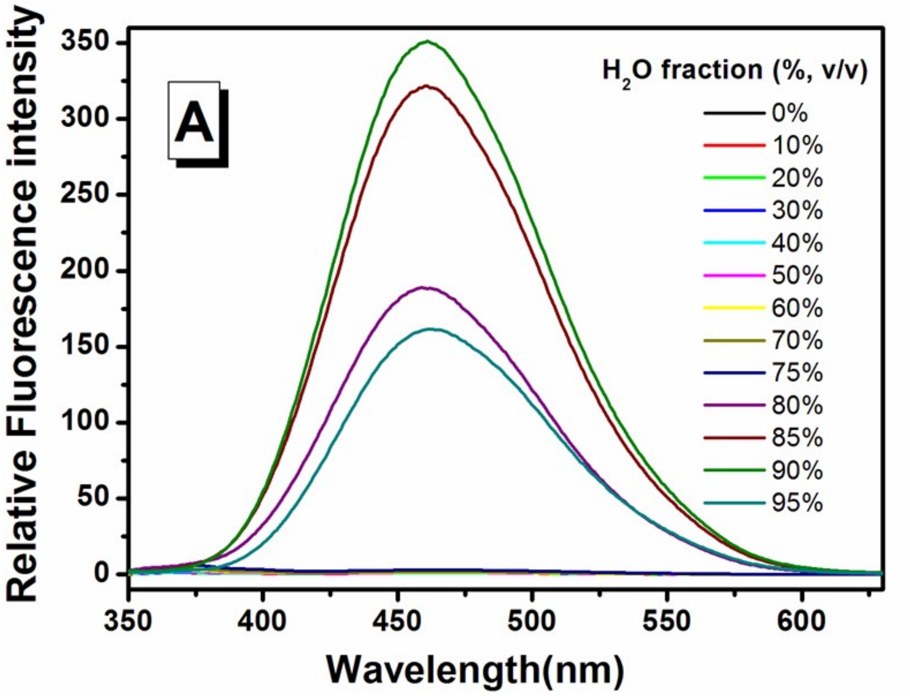


Fig. S12 ESI-MS spectrum of compound **4**.



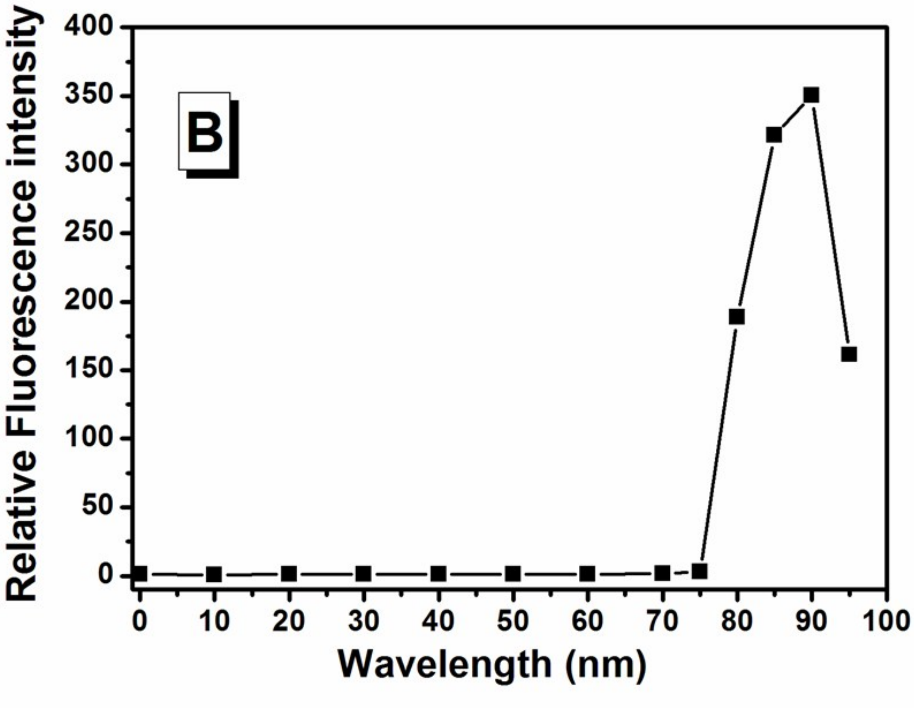


Fig. S13 (A) Fluorescence spectra and (B) plots of the fluorescence intensity at 460 nm of **TPE-COOH** in THF-water mixtures with different water fractions. Concentration: 30 μM; λ_{ex}: 330 nm (10 nm, 10 nm); 283K.

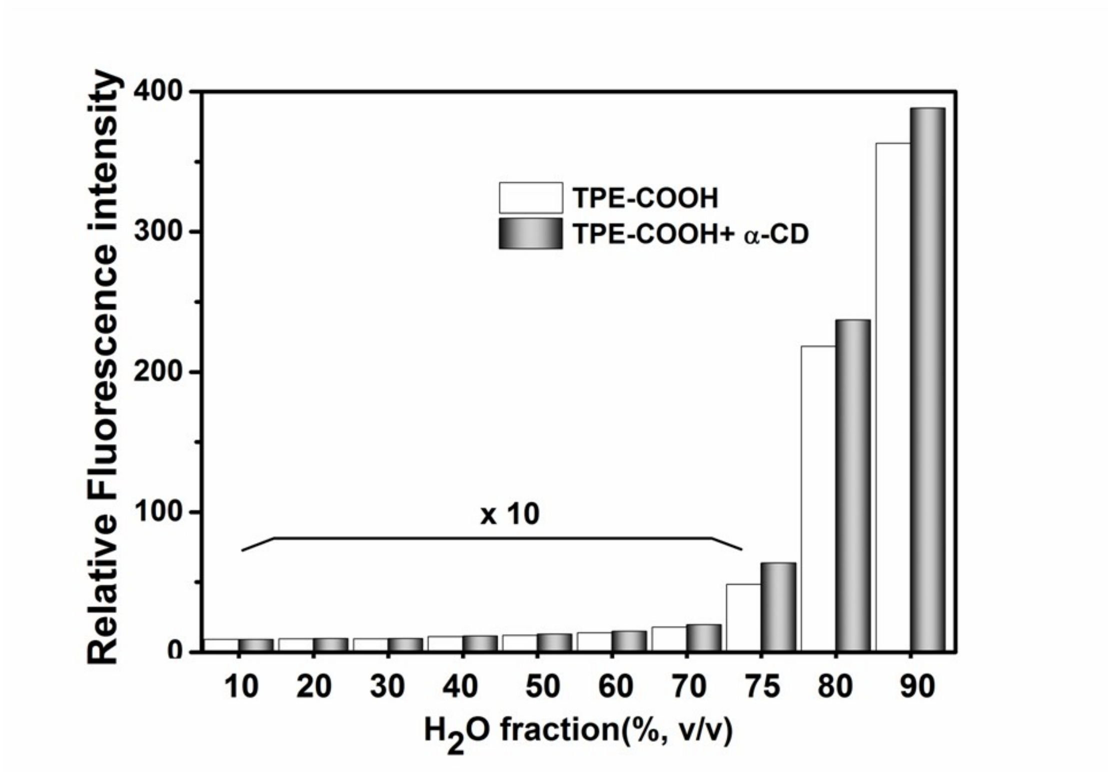


Fig. S14 Change in fluorescence intensity at 455 nm of **TPE-COOH** upon addition of 2 equiv. α-CD in different water fraction THF-water mixtures. Concentration: 30 μM (contain 1.1 equiv. NaOH); λ_{ex}: 330 nm (10 nm, 10nm); 283 K.

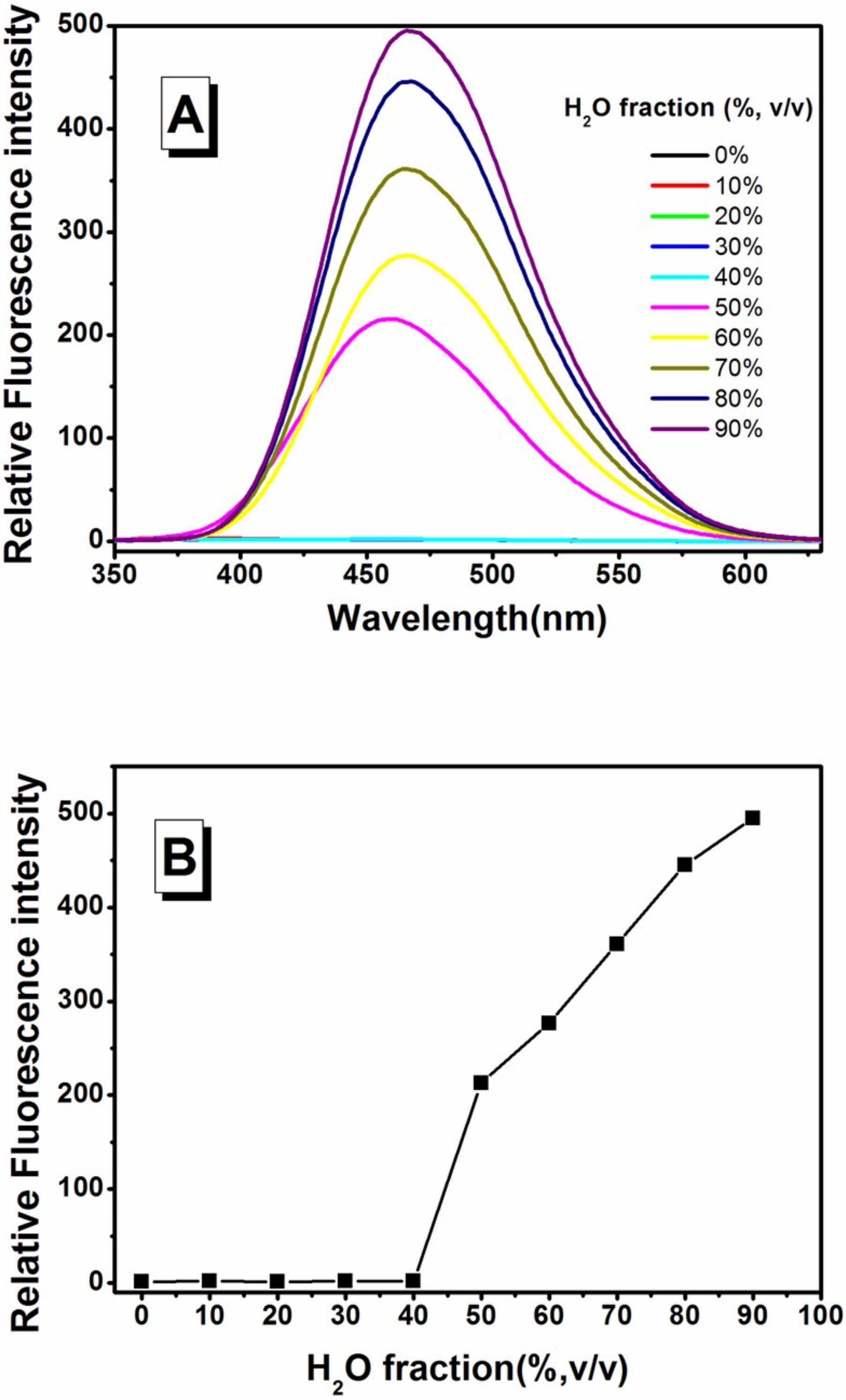


Fig. S15 (A) Fluorescence spectra and (B) plots of the fluorescence intensity at 455 nm of **TPE-COOH** in DMSO-water mixtures with different water fractions. Concentration: 30 μM; λ_{ex}: 330 nm (10 nm, 10nm); 283 K.

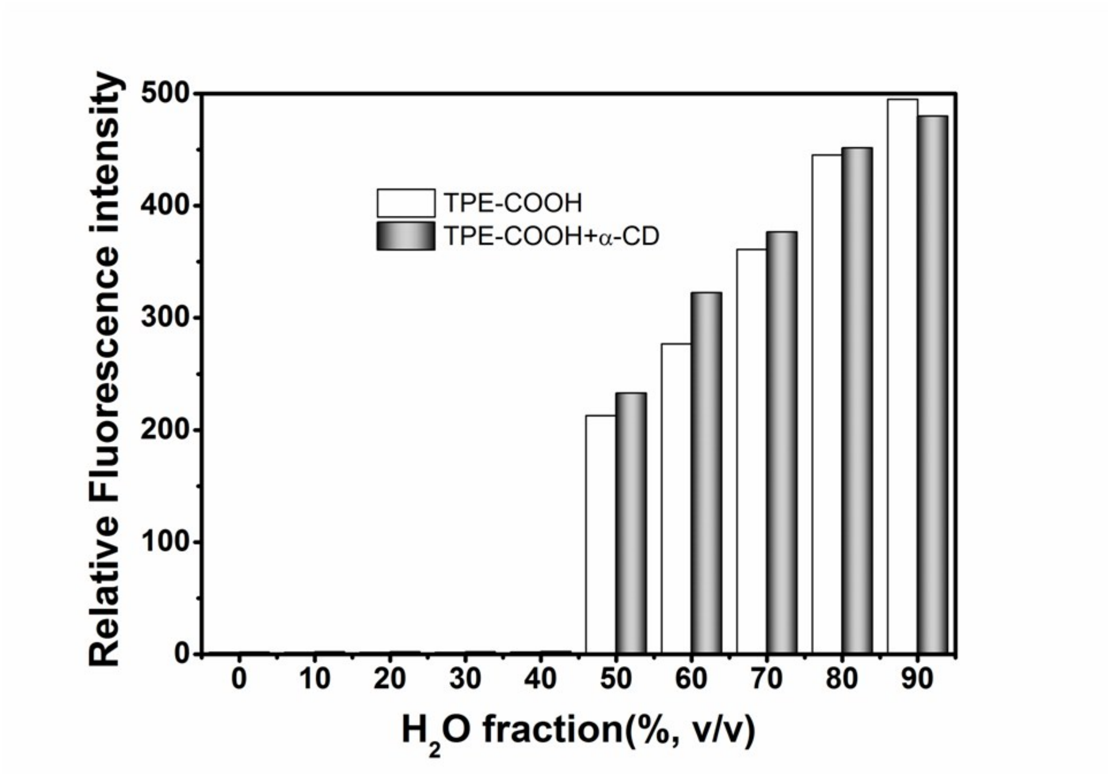


Fig. S16 Change in fluorescence intensity at 455 nm of **TPE-COOH** upon addition of 2 equiv. α-CD in different water fraction THF-water mixtures. Concentration: 30 μM; λ_{ex}: 330 nm (10 nm, 10nm); 283 K.

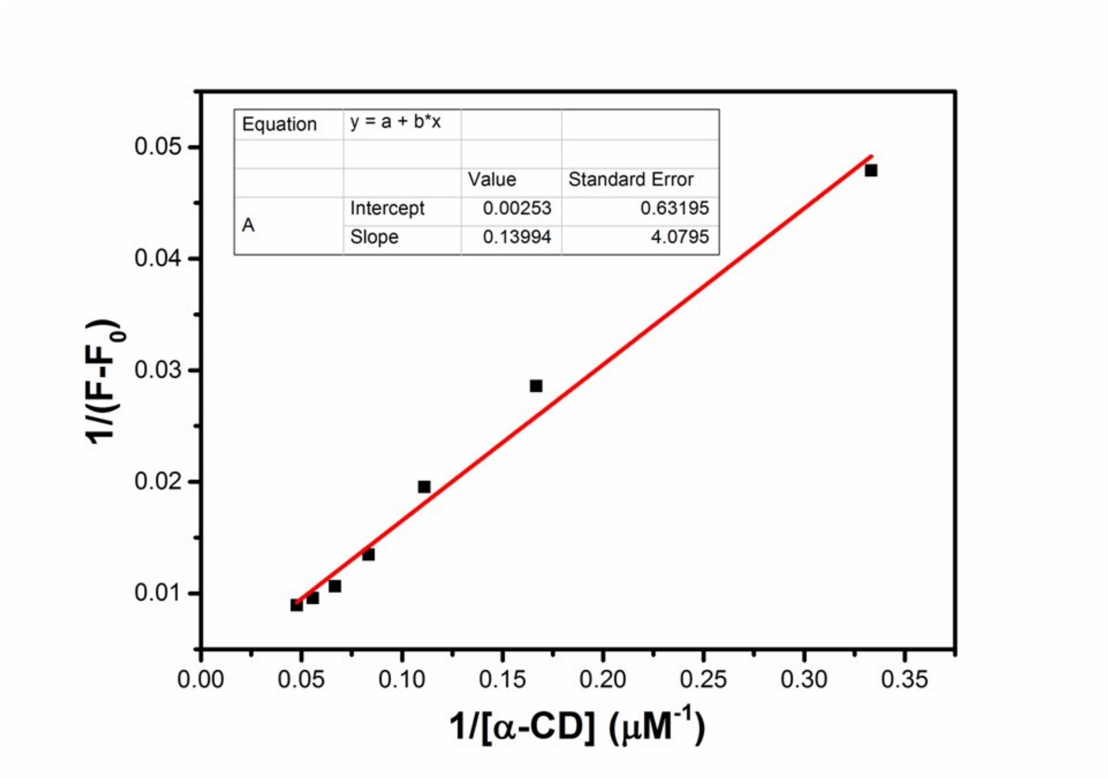


Fig. S17 Benesi–Hildebrand plot of 1/(F-F_0) vs. 1/[α-CD].

Equation: Y = a + b*X

Parameter	Value	Error
a	0.0253	0.63195
b	0.13994	4.0795

K_a = a/b = 0.0253/0.13994 =0. 181 μM^{-1} = 1.81×10^5 M^{-1}

To calculate K_a, the changes in the fluorescence intensity for the **TPE-COOH** in the presence of varying α-CD concentrations were fitted using the Benesi-Hildebrand equation (1:1 stoichiometric interaction):

$$\frac{1}{F-F_0}=\frac{1}{F_\infty-F_0}+\frac{1}{K_a\times(F_\infty-F_0)\times[\alpha-CD]}$$

Where F_0 is the fluorescence intensity at 455 nm in the absence of the α-CD, F is the fluorescence intensity at the corresponding α-CD concentration, and F_∞ corresponds to the maximum fluorescence intensity at 455 nm when all guest molecules are complexed with the α-CDs.

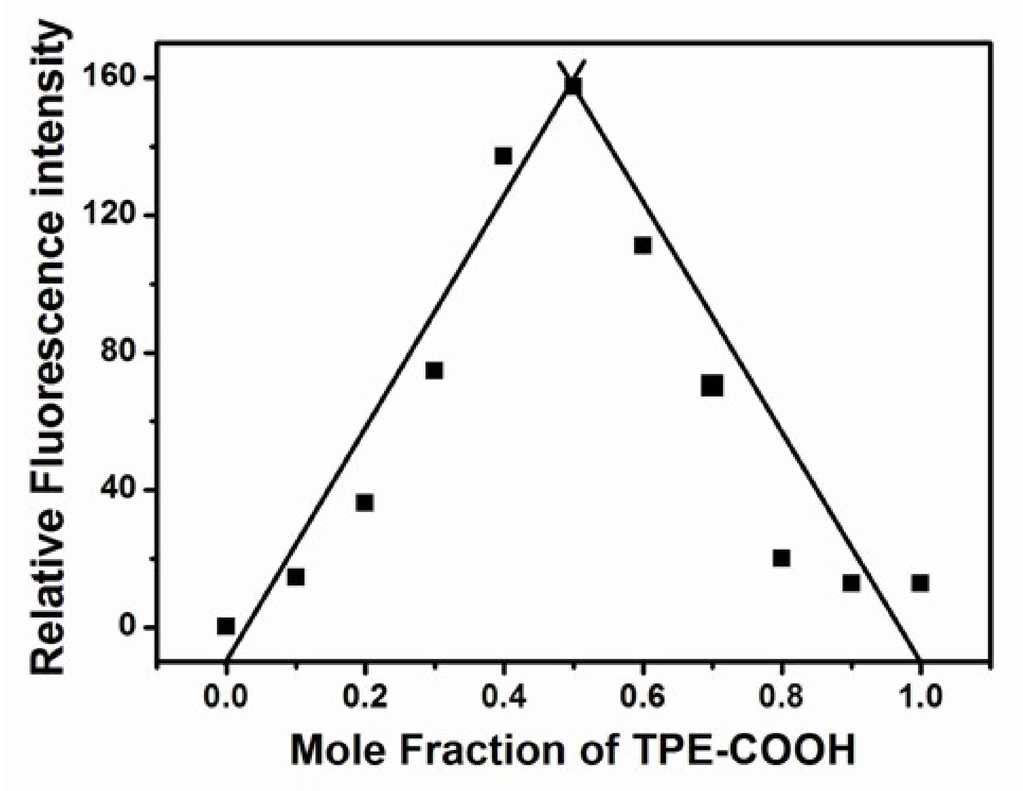


Fig. S18 Job's plot for the complexation of **TPE-COOH** and α-CD in DMSO-water (f_w = 50%) by monitoring the fluorescence intensity at 455 nm. The total concentration of **TPE-COOH** and α-CD was fixed at 50 μM.

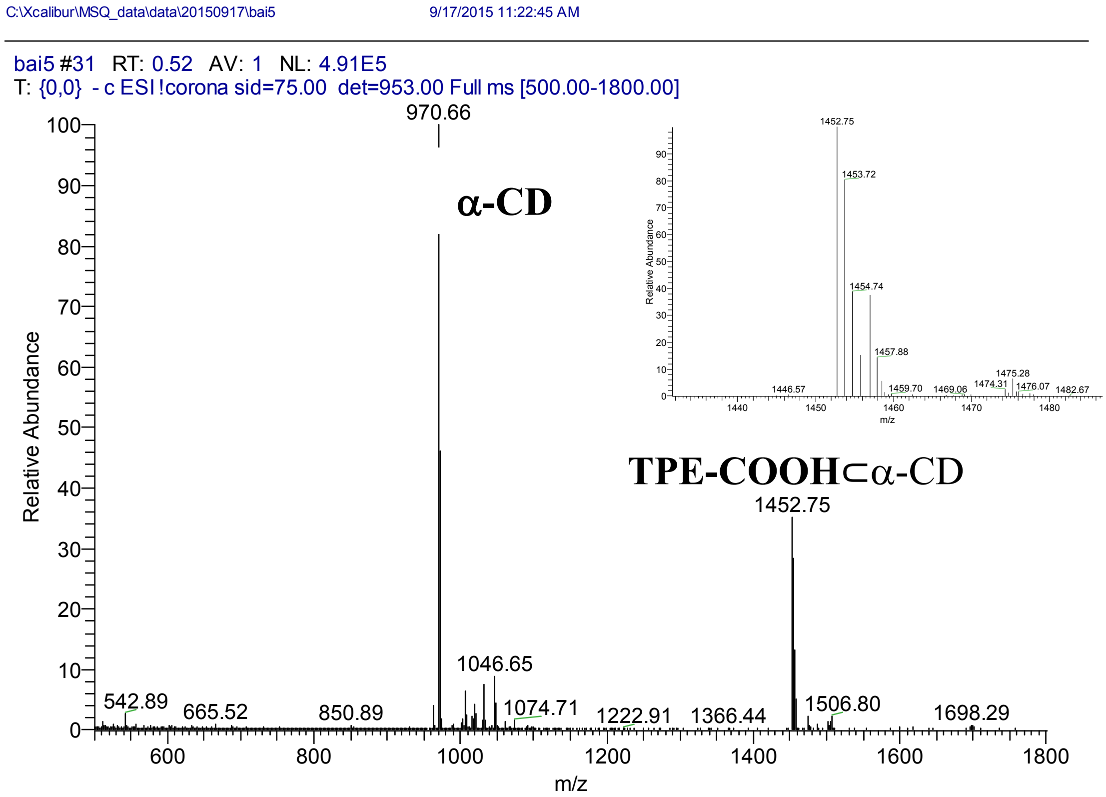


Fig. S19 ESI-MS spectrum of a mixture of **TPE-COOH** and α-CD (20 equiv.) in water.

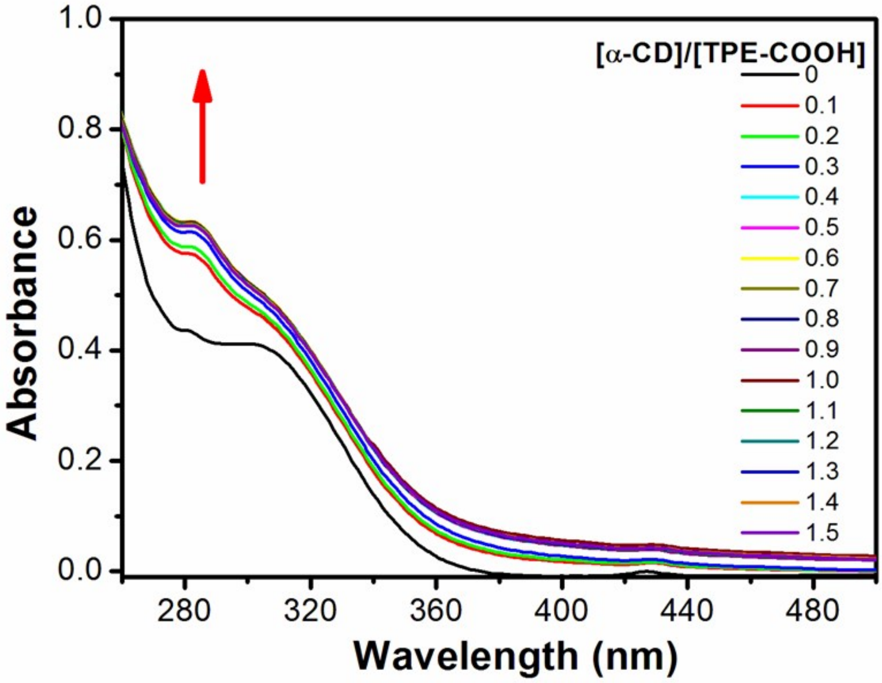


Fig. S20 Change in UV-Vis spectrum of **TPE-COOH** upon titration with α-CD in DMSO-water mixture (f_w = 50%). Concentration: 30 μM.

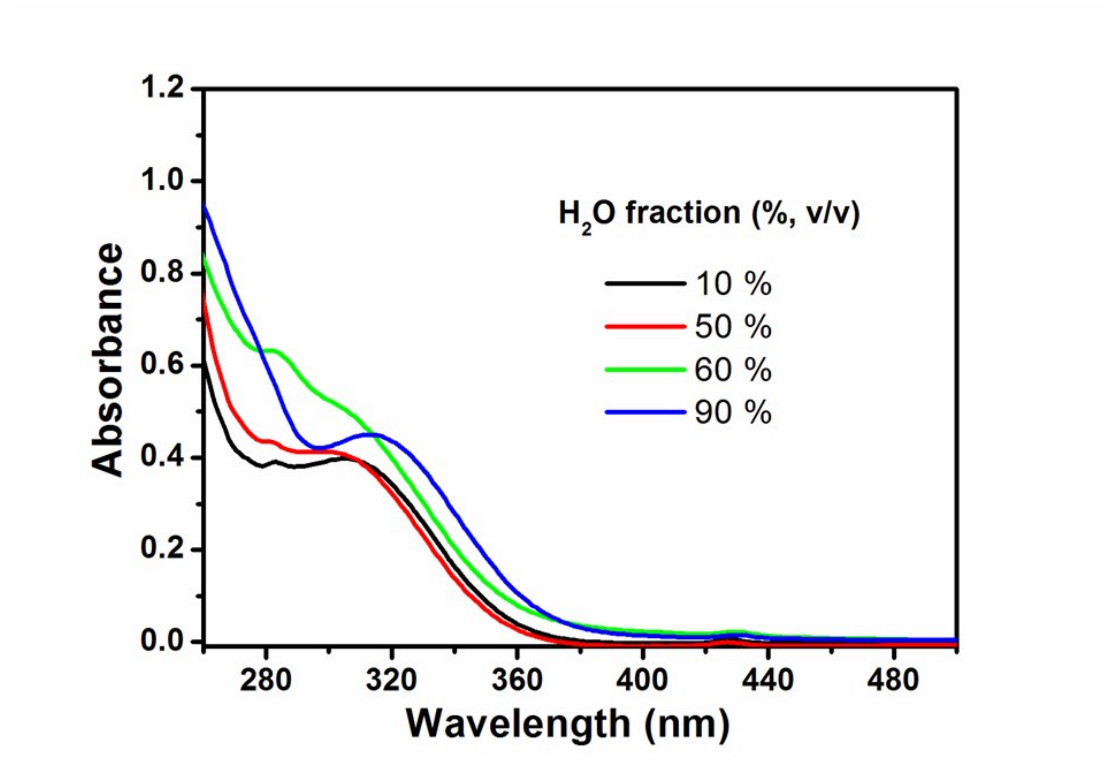


Fig. S21 UV-Vis spectra of **TPE-COOH** in DMSO-water mixtures with different water fractions (10%, 50%, 60%, 90%). Concentration: 30 μM.

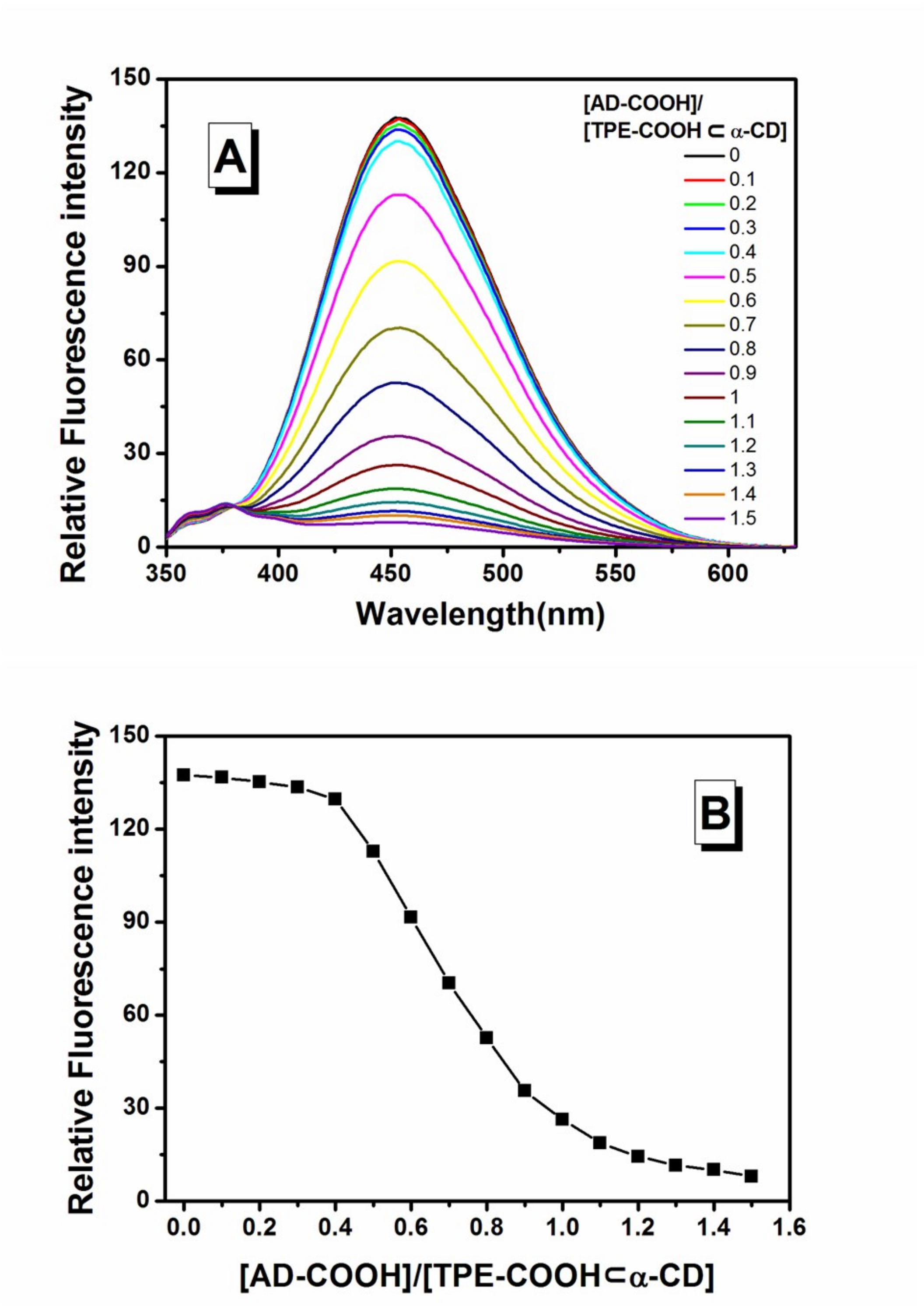


Fig. S22 (A) Change in fluorescence spectrum of **TPE-COOH**⊂α-CD upon titration with **AD-COOH** in DMSO-water (f_w = 50%) and (B) plots of the fluorescence intensity at 455 nm against [**AD-COOH**]/[**TPE-COOH**⊂α-CD]. Concentration: 30 μM (contain 1.1 equiv. NaOH); λ_{ex}: 330 nm (10 nm, 10 nm); 283 K.

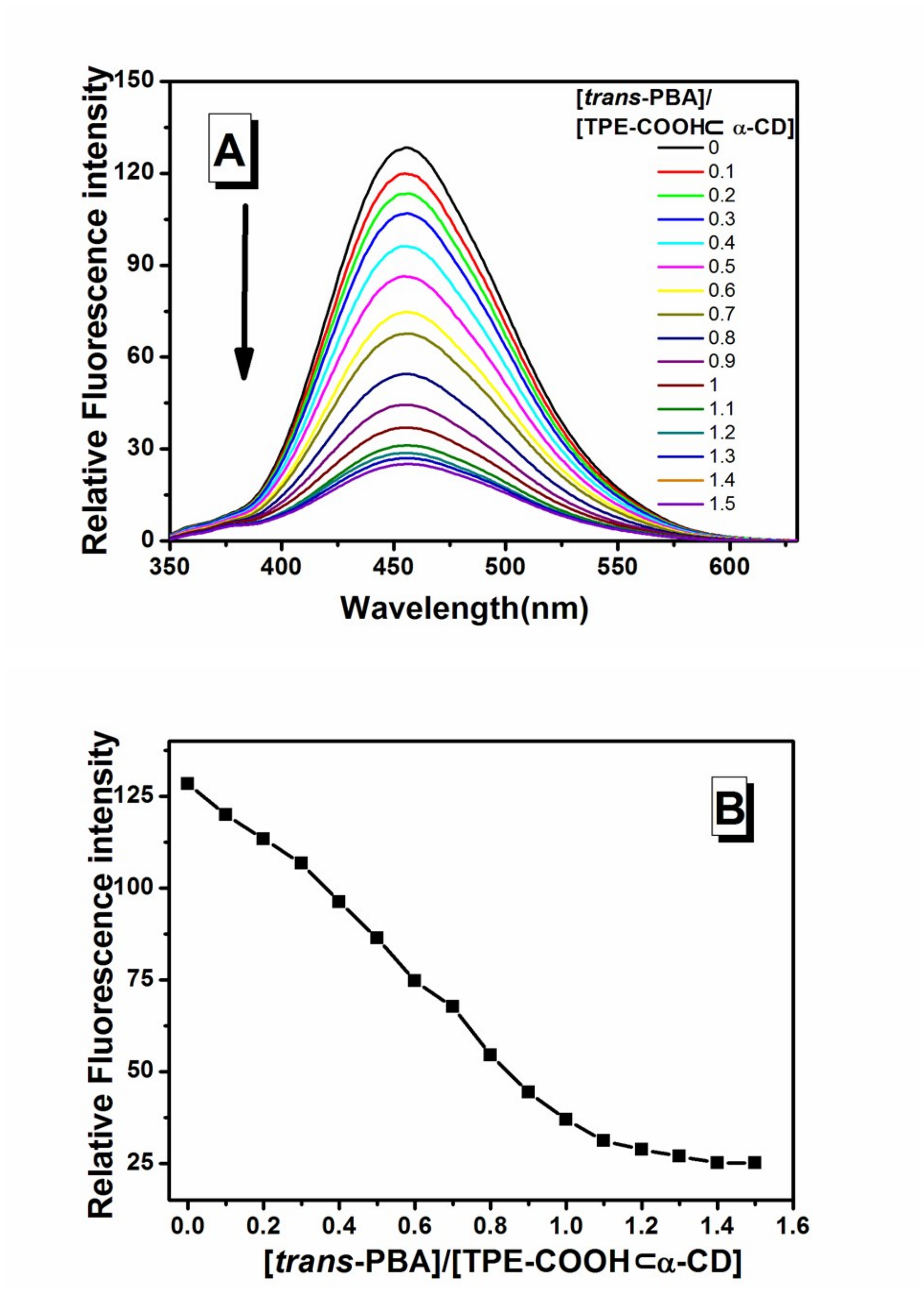


Fig. S23 (A) Change in fluorescence spectrum of **TPE-COOH**⊂α-CD upon titration with *trans*-**BPA**(contain 1.1 equiv. NaOH) in DMSO-water mixture (f_w = 50%) and (B) plots of the fluorescence intensity at 455 nm against [*trans*-**BPA**]/[**TPE-COOH**⊂α-CD]. Concentration: 30 μM (contain 1.1 equiv. NaOH); λ_{ex}: 330 nm (10 nm, 10nm); 283 K.

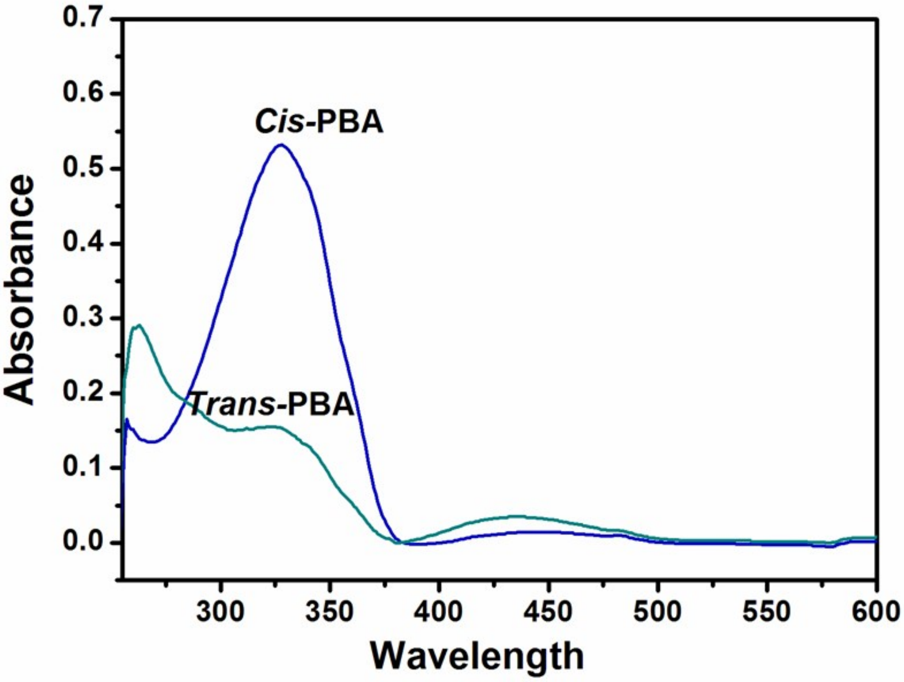


Fig. S24 Electronic absorption spectra of **PBA** in *cis* and *trans* state (1.8×10^{-3} M).

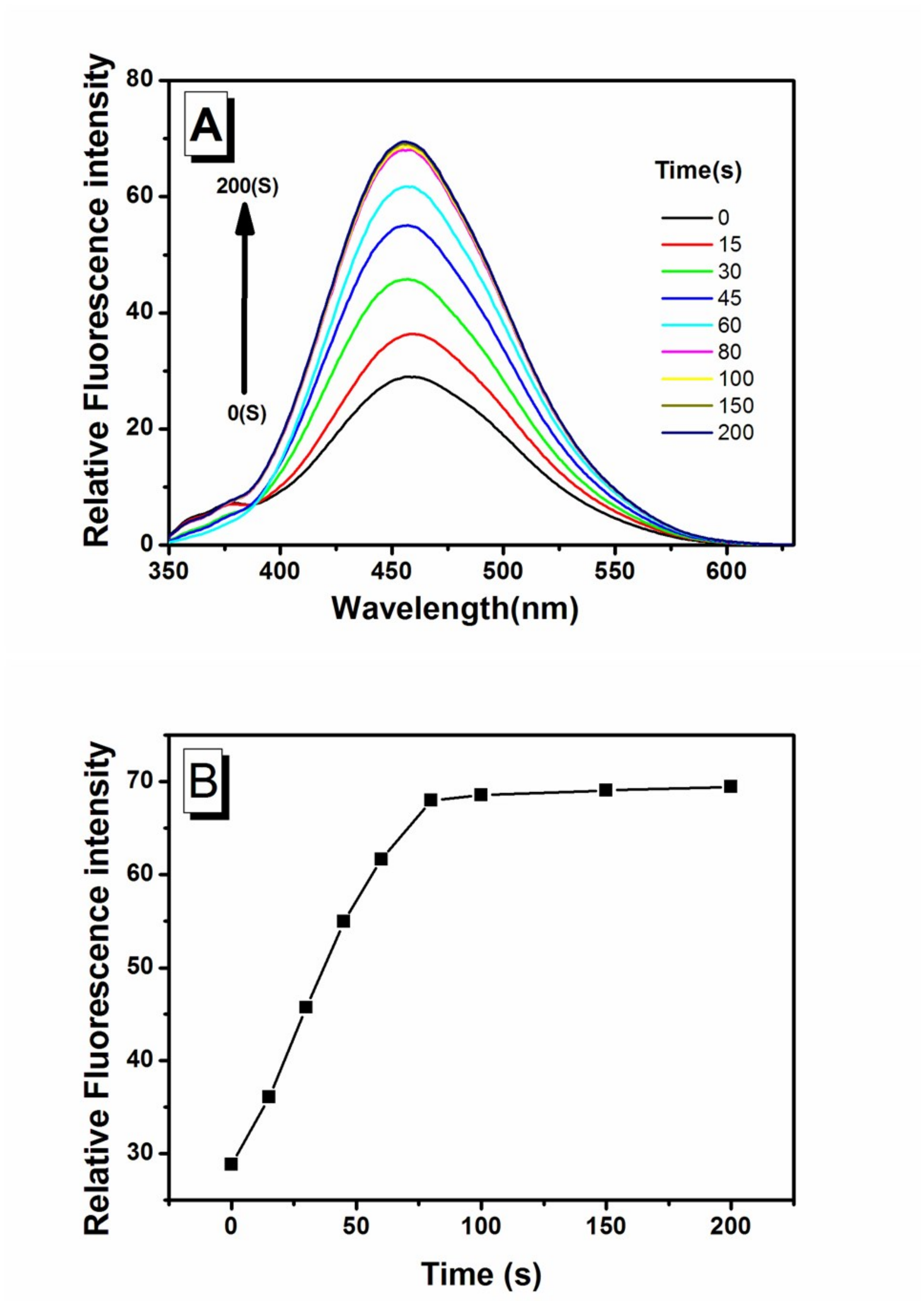
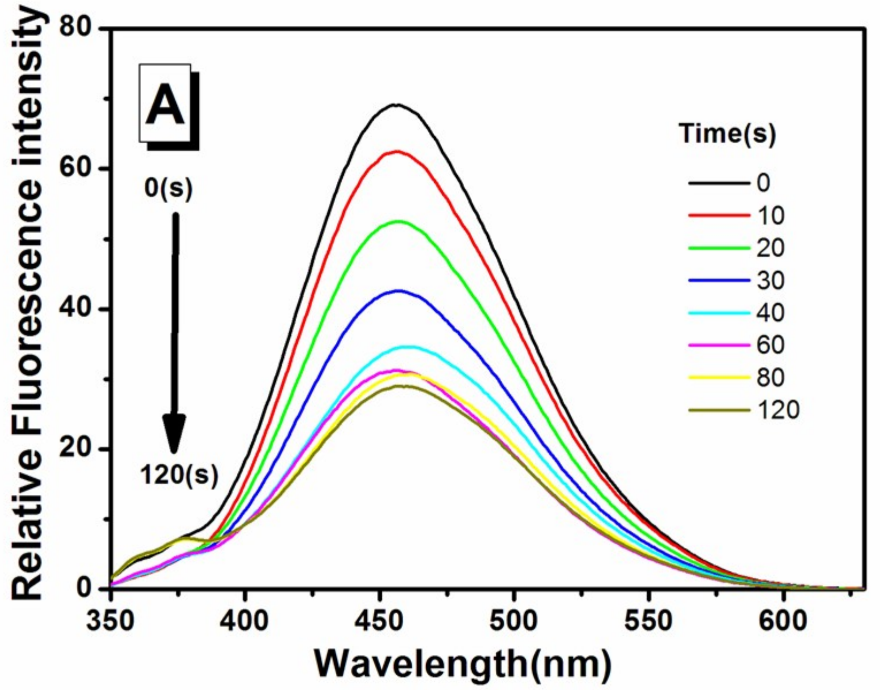


Fig. S25 Change in fluorescence spectrum of **TPE-COOH, PBA** and α-CD (1 : 2 : 1) upon irradiation with 365 nm(10 W) and (B) plots of the fluorescence intensity at 455 nm against time. λ_{ex}: 330 nm (10 nm, 10nm); 283 K.



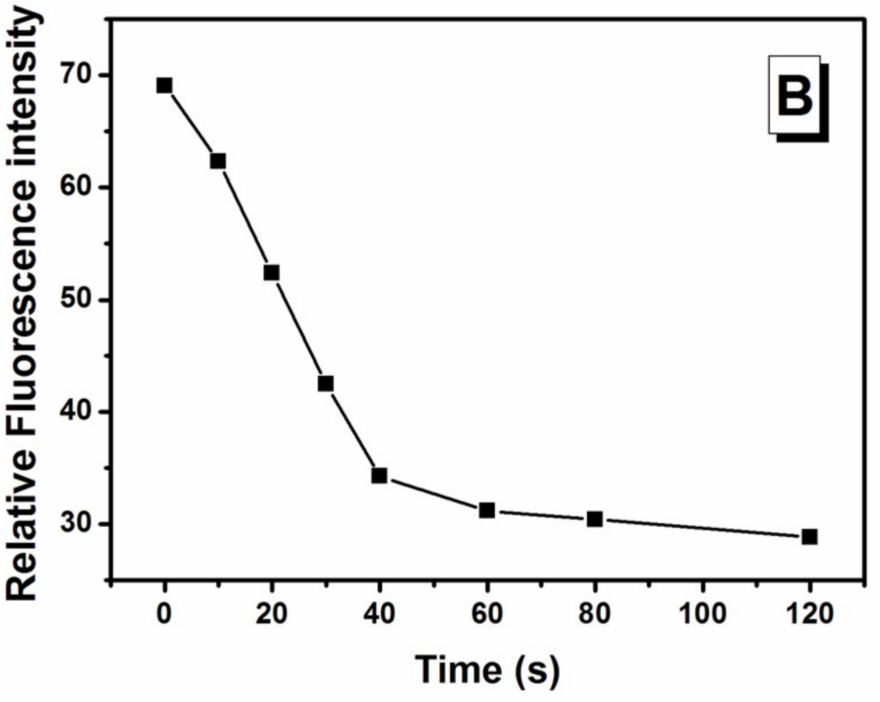


Fig. S26 Change in fluorescence spectrum of **TPE-COOH, PBA** and α-CD (1 : 2 : 1) upon irradiation with halogen lamp (300W, equipped with a band-pass filter > 435 nm) and (B) plots of the fluorescence intensity at 455 nm against time. λ_{ex}: 330 nm (10 nm, 10nm); 283 K.