Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Reaction-based fluorescence probes for “turn on” sensing fluoride ions

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Content

1. Instruments and Materials

1.1. Instruments

Fluorescence spectra were recorded with a FS5 Fluorescence spectrophotometer (Edinburgh, England) or a F7000 Fluorescence spectrophotometer (Hitachi, Japan). UV-vis absorption spectra were done with a UV-2600 PC spectrophotometer (Shimadzu, Japan). Nuclear magnetic resonance (NMR) experiments were conducted with a 500 MHz/AVANCE III (Bruker, Switzerland). The experiments of electrospray ionization mass spectrometry (ESI-MS) were performed by using an ABI-3600Q ESI-MS system (Agilent, USA). The experiments of EI-MS were performed by using an GCMS-QP2010 (Shimadzu, Japan) system.

1. 2. Materials

4-Methoxybenzophenone (98%, AR), Diphenylmethane (99%, AR), n-Butyllithium solution with 2.5 M solution in Hexanes, Ammonium chloride(99.8%, GR), Magnesium sulfate anhydrous (AR), Tetrabutylammonium bromide (99%, AR), Tetrabutylammonium chloride (99%, HPLC), Tetrabutylammonium iodide (99%, AR), Tetrabutylammonium phosphate monobasic (98%, AR), Tetrabutylammonium perchlorate (98%, AR), Tetrabutylammonium hydrogen sulfate (98%, AR), Etrabutylammonium acetate (98%, AR), Tetrabutylammonium nitrate (98%,AR), Tetrabutylammonium fluoride (98%, AR), Hydrobromic acid (48%, ACS), and 2,4-Dinitrobenzenesulfonylchloride (98%, AR) were obtained from Energy Chemical (Shanghai, China). 4-Nitrobenzenesulfonylchloride (98%, AR) were obtained from Macklin (Shanghai, China). Tetrahydrofuran (99.5%, Extra Dry, with molecular sieves, Water $\leq$ 50 ppm) and tetrabutylammonium fluoride (TBAF, 1.0 M solution in THF) were purchased from Energy Chemical (Shanghai, China). *p*-Toluenesulfonic acid monohydrate (98.5%, ACS) was obtained from Aladdin (Shanghai, China). d_6-DMSO was obtained from Macklin (Shanghai, China). All other reagents and chemicals were from commercial sources of analytical-reagent grade. Distilled-water was obtained from a Milli-Q system.

2. The synthesis procedures of TPEONO$_2$ and TPEO(NO$_2$)$_2$

Probes TPEONO$_2$ and TPEO(NO$_2$)$_2$ were prepared according to the synthetic route shown in Fig. S1.

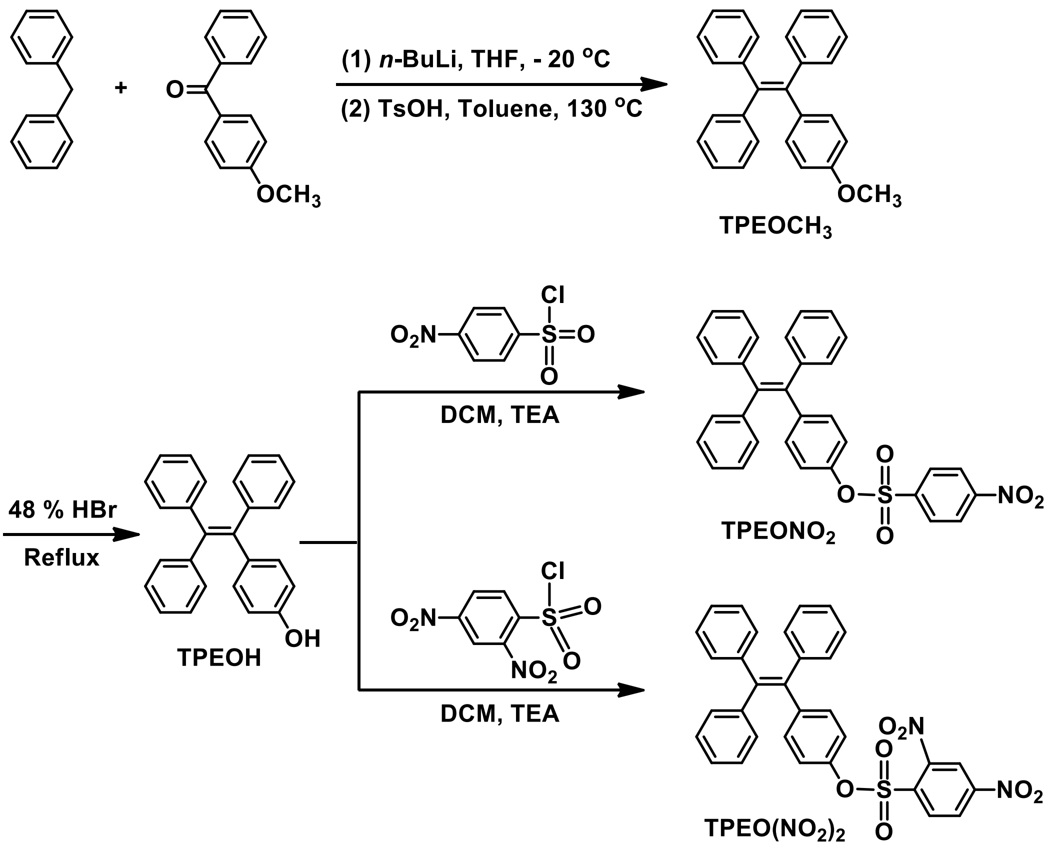


Fig. S1 The synthesis route of *$TPEONO_2$ and $TPEO(NO_2)_2$* [S1-S2]

References:

S1. J. Nie, N. Li, Z. Ni, Y. Zhao and L. Zhang, *Tetrahedron Lett.*, 2017, **58**,1980.

S2. S. R. Bandatmakuru, S. R. Amasa, V. R. Arava and M. C. S. Subha, *Der Pharma Chemica*, 2014, **6**, 299. (http://derpharmachemica.com/archive.html)

2.1. The synthesis procedure of $TPEOCH_3$

The detailed synthesis procedure of $TPEOCH_3$ as follows: first, diphenylmethane (2.02 g, 12 mmol) was dissolved in 20 mL anhydrous tetrahydrofuran, and then 4 mL *n*-butyllithium solution (2.5 M, dissolved in *n*-hexane) was added in above solution at -40 ℃ under the protection of N_2 gas. The resulting orange-red solution was stirred for *ca.*30 min and the temperature was kept at -40 ℃ under the protection of N_2 gas. Next, 4-methoxybenzophenone (2.54 g, 12 mmol) was dissolved in 10 mL anhydrous tetrahydrofuran, and this solution was added to the above mixed solution to be stirred for 30 min at -40 ℃ under the protection of the N_2 gas and the color of the solution was gradually changed to pale green. Then, this mixed solution was allowed to warm to room temperature and stirring was continued for 3 h. The reaction solution was quenched with 10 mL 1 M ammonium chloride. Then, the organic phase was extracted by adding dichloromethane, and washed several times with ultrapure water. The washed organic phase was dried by adding anhydrous magnesium sulfate and allowed to stand overnight. Then, the solvent was separated and evaporated to afford a crude product containing -OH group. After that, the obtained crude product containing -OH group was dissolved in 50 mL toluene, and transferred to a distillation apparatus with a water separator. *p*-toluenesulfonic acid (342 mg, 1.8 mmol) was added into this apparatus and this mixed solution was refluxed for *ca.* 3 h, and then cooled to room temperature. The toluene layer was washed several times with saturated Na_2CO_3 solution, and dried by anhydrous magnesium sulfate for overnight. The product was obtained by a silica-gel column chromatography method using petroleum ether/ethyl acetate of 18/1 (v/v) as eluent. White solid of compound $TPEOCH_3$ was obtained with the yield of 35%.

^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.18-7.07 (m, 9H), 6.99–6.94 (m, 6H), 6.87 (d, J = 8.7 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 3.77(s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 158.09, 144.04, 144.00, 143.99, 140.53, 140.10, 136.12, 132.53, 131.39, 131.36, 131.33, 127.72, 127.60, 126.35, 126.24, 126.23, 113.05, 55.09.

(EI-MS) m/z: [M] calcd for $C_{27}H_{22}O$, 362.16; found m/z, 362.

2.2. The synthesis procedure of TPEOH

The synthesis procedure of TPEOH as follows: first, the pure $TPEOCH_3$ (1.72 g, 4.4 mmol) was dissolved in 100 mL glacial acetic acid solution, and 50 mL 48% HBr solution was added to the above solution. The mixed solution was stirred for 12 h under refluxing and then cooled to room temperature. The solvent was evaporated by a rotatory evaporator. The obtained product was dissolved in ethyl acetate, and successively washed for several times with saturated Na_2CO_3 solution and saturated NaCl solution, respectively. The solid of pure compound TPEOH was obtained by a silica-gel column chromatography method using petroleum ether/ethyl acetate of 12/1 (v/v) as the eluent, with the yield of 75%.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.36 (s, 1H), 7.18-7.03 (m, 9H), 7.00-6.90 (m, 6H), 6.74 (d, J = 8.6 Hz, 2H), 6.51 (d, J = 6.7 Hz, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ: 156.41, 144.18, 144.04, 141.03, 139.58, 134.16, 132.38, 131.20, 131.17, 131.13, 128.27, 128.20, 128.15, 126.84, 126.70, 115.12.

HRMS (ESI-TOF) m/z: $[M-H]^-$ calcd for $C_{26}H_{19}O$, 347.1436; found, 347.1440.

2.3. The synthesis procedure of TPEONO$_2$

The synthesized TPEOH (34.8 mg, 0.1 mmol) was dissolved in 20 mL dichloromethane, and 5 mL 0.05 mM TEA was added by using a syringe into the TPEOH solution. This mixed solution was stirred at 0 ^{o}C in a low temperature magnetic stirrer. Then, 10 mL *p*-nitrobenzenesulfonyl chloride dichloromethanene solution (44.2 mg, 0.2 mmol) was slowly added and stirred at 0 ^{o}C for 1 h. This reaction was monitored by TLC. After the reaction was finished, 20 mL ultrapure water was added into the reaction solution and the mixed solution was stirred for 30 min at room temperature. The organic phase was separated and the aqueous phase was extracted by using dichloromethane. The combined organic phase was washed for several times with saturated Na_2CO_3 solution and saturated NaCl solution, respectively. The separated organic phase was dried by anhydrous magnesium sulfate overnight. The pure TPEONO$_2$ was obtained by a silica-gel column chromatography method using petroleum ether/ethyl acetate of 18/1 (v/v) as the eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.85 (d, J = 2.8 Hz, 1H), 8.35 (dd, J_1 = 9.3 Hz, J_2 =2.7 Hz, 1H), 7.26 - 7.14 (m, 9H), 7.14 -7.12 (m, 2H), 7.11 - 7.03 (m, 6H), 6.96 (d, J = 9.2 Hz, 1H), 6.89 (d, J = 6.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 150.88, 147.40, 143.62, 143.35, 142.96, 142.78, 142.25, 140.65, 139.26, 132.77, 131.28, 131.16, 131.14, 129.93, 127.89, 127.80, 127.75, 126.85, 126.80, 126.70, 124.21, 121.45.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{32}H_{23}NSO_5$, 556.1189; found, 556.1196.

2.4. The synthesis procedure of TPEO(NO$_2$)$_2$

Similar to the synthesis procedure of TPEONO$_2$, the synthesized TPEOH (34.8 mg, 0.1 mmol) was dissolved in 20 mL dichloromethane, and 5 mL 0.05 mM TEA was added by using a syringe into the TPEOH solution. This mixed solution was stirred at 0 ^{o}C in a low temperature magnetic stirrer. Then, 10 mL 2,4-dinitrobenzenesulfonyl chloride dichloromethanene solution (53.3 mg, 0.2 mM) was slowly added and stirred at 0 ^{o}C for 1 h. This reaction was monitored by TLC. After the reaction was finished, 20 mL ultrapure water was added into the reaction solution and the mixed solution was stirred for 30 min at room temperature. The organic phase was separated and the aqueous phase was extracted by using dichloromethane. The combined organic phase was washed for several times with saturated $NaHCO_3$ solution and saturated NaCl solution, respectively. The separated organic phase was dried by anhydrous magnesium sulfate overnight. The pure $TPEO(NO_2)_2$ was obtained by a silica-gel column chromatography method using petroleum ether/ethyl acetate of 18/1 (v/v) as the eluent.

^1H NMR (500 MHz, $CDCl_3$) δ: 8.85 (d, J = 2.8 Hz, 1H), 8.35 (dd, J_1 = 9.3 Hz, J_2 =2.7 Hz, 1H), 7.26 - 7.14 (m, 9H), 7.14 -7.12 (m, 2H), 7.11 - 7.03 (m, 6H), 6.96 (d, J = 9.2 Hz, 1H), 6.89 (d, J = 6.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.16, 151.69, 143.36, 143.05, 142.50, 142.16, 141.37, 139.43, 139.40, 133.51, 131.28, 131.20, 131.17, 128.68, 127.89, 127.83, 127.74, 126.81, 126.74, 122.05, 119.82, 118.22.

3. The procedures of spectral experiments, ^1H NMR titration experiments and MS experiments of probe cleaved by F^- ions

3.1. The water content effect on the fluorescence of mixed solution of probes and F^- ions

A certain amount of $TPEONO_2$ or $TPEO(NO_2)_2$ DMF solution was mixed with a certain amount of 10 mM F^- ions stock solution. The mixed solutions were heated for 40 min under 80 °C water bath. Then, 10 mM HEPES buffer solution of pH 7.4 and DMF solvent were added to the above mixed solution to afford different water contents, from 0% to 99% (by volume). The total volume was 3 mL, and the final probe concentration was 10 μM, and F^- ions concentration was 80 μM.

3.2. Fluorescence sensing

3.2.1 Fluorescence sensing of F^- ions for a series of concentration

Various volumes of 10 mM F^- ions stock solution was added into a certain volume of probe $TPEONO_2$ or $TPEO(NO_2)_2$ DMF solution. The total volume of the mixed solution was fixed as 150 μL before it was heated up to 80 °C for 40 min. 10 mM HEPES buffer solution of pH 7.4 was added to the above mixed solution for affording a total volume of 3 mL (equal to water content of 95%). The final concentration of probe was 10 μM.

3.2.2 Fluorescence sensing of F^- ions spiked in drinking water sample

100 mL drinking water sample (taken from the tape at lab) was added to a 50 mL flask. Then, certain amounts of F^- ions were spiked in the water sample and the water in the flask was removed by using a rotatory under vacuum. Then, 0.2 mL DMF was introduced into the flask to dissolve added F^- ions to obtain the sample for further fluorescence measurement. The procedure of fluorescence measurement refers to 3.2.1, by using the resulting sample solution to replace the F^- ions standard solution.

3.3. ^1H NMR titration experiments of probe $TPEONO_2$ towards F^- ions

5.3 mg probe $TPEONO_2$ and 130.8 mg tetrabutylammonium fluoride were dissolved in 0.5 mL d_6-DMSO, respectively. Then, $TPEONO_2$ solution was transferred into the NMR tube, and various amounts of F^- ions solution were added into the NMR tube containing $TPEONO_2$ solution to afford the molar ratios of 0:1, 0.2:1, 0.4:1, 0.8:1, 1.0:1, and 1.2:1, respectively. The mixed solution was heated up to 80 ^oC for 40 min. ^1H NMR spectra were measured by using a 500 MHz nuclear magnetic resonance spectrometer.

3.4. MS experiments of probe $TPEONO_2$ cleaved by F^- ions

26.5 mg probe $TPEONO_2$ was dissolved in 0.5 mL DMF (0.1 M). 250.5 mg tetrabutylammonium fluoride was dissolved in another 0.5 mL DMF (1.0 M). Then, 150 μL 0.1 M $TPEONO_2$ solution and 150 μL 1.0 M F^- ions solution were mixed and heated up to 80 ℃ for 40 min. The reaction solution was separated by TLC method, and the biggest spot were carefully scraped off and soaked into ethanol solvent. The supernatant was used to conduct the experiment of ESI-MS.

3.5. ^1H NMR titration experiments of probe $TPEO(NO_2)_2$ towards F^- ions

The procedure was similar to that of $TPEONO_2$.

3.6. MS experiments of probe $TPEO(NO_2)_2$ cleaved by F^- ions

The procedure was similar to that of $TPEONO_2$.

4. ^1H NMR, and ^{13}C NMR results of $TPEONO_2$ and $TPEO(NO_2)_2$

4.1. ^1H NMR, ^{13}C NMR, and MS of $TPEOCH_3$

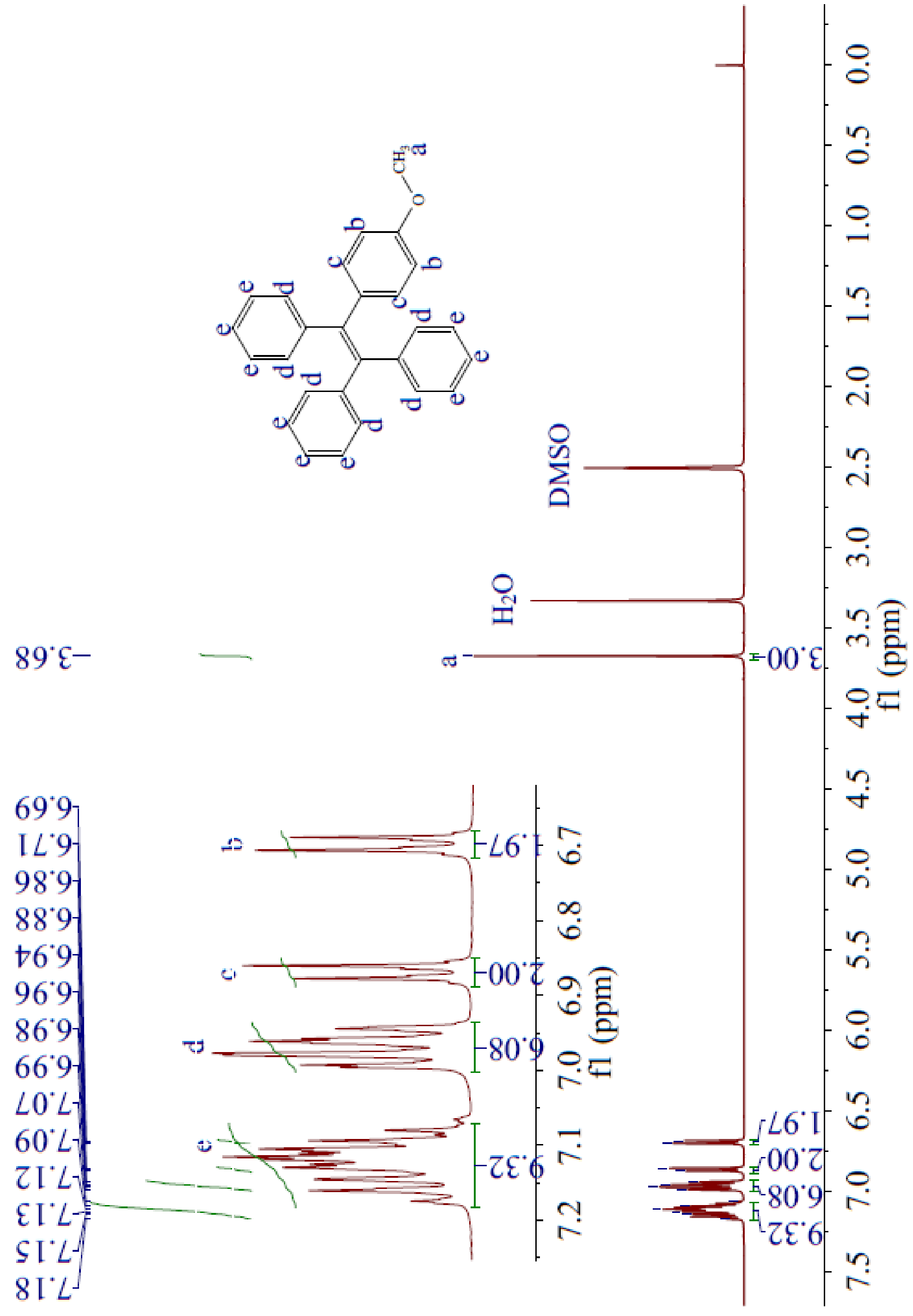


Fig. S2 ^{1}H NMR of TPEOCH$_3$

^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.18 - 7.07 (m, 9H), 6.99 - 6.94 (m, 6H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 3.68 (s, 3H).

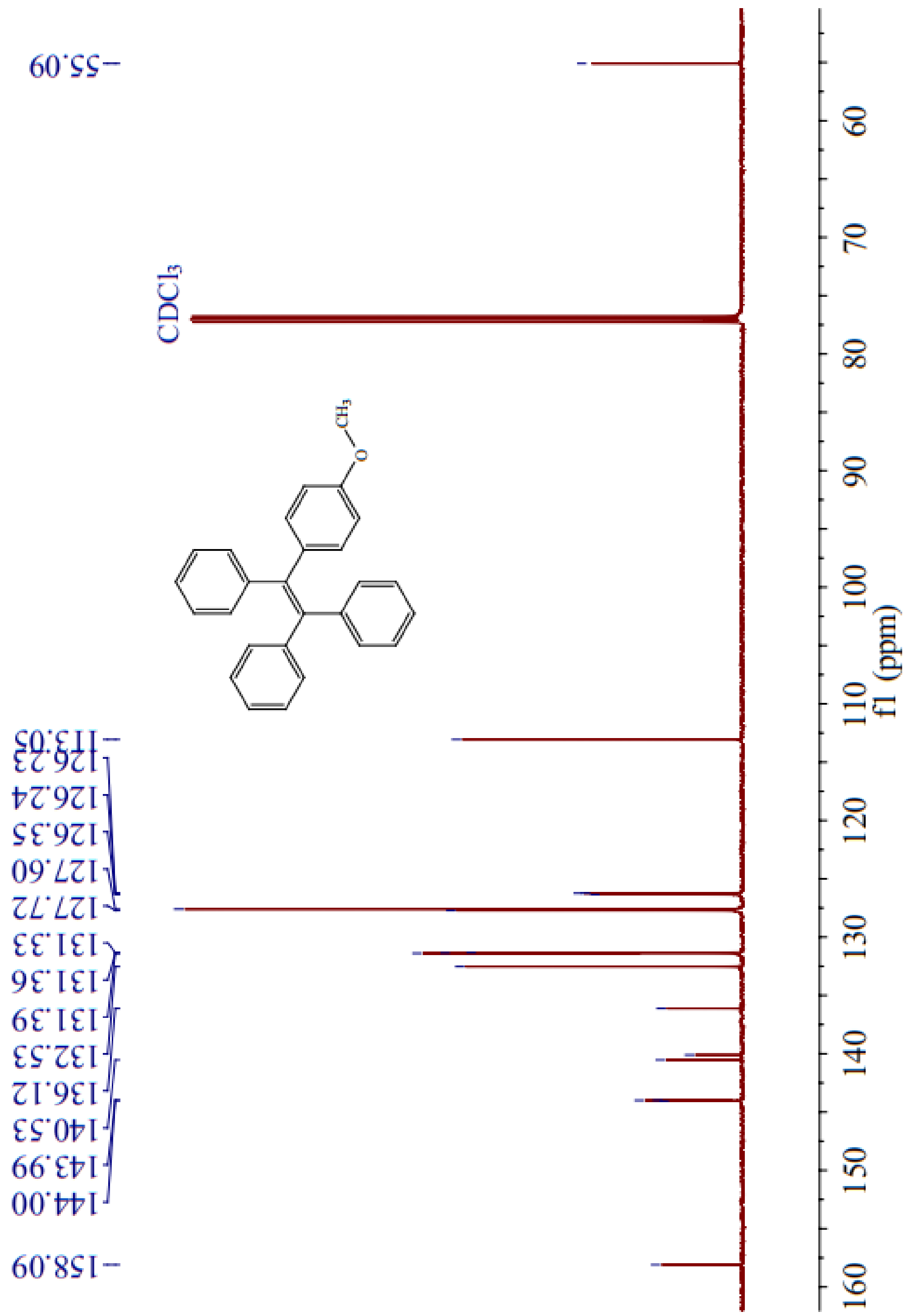


Fig. S3 ^{13}C NMR of TPEOCH$_3$

^{13}C NMR (126 MHz, CDCl$_3$) δ: 158.09, 144.04, 144.00, 143.99, 140.53, 140.10, 136.12, 132.53, 131.39, 131.36, 131.33, 127.72, 127.60, 126.35, 126.24, 126.23, 113.05, 55.09.

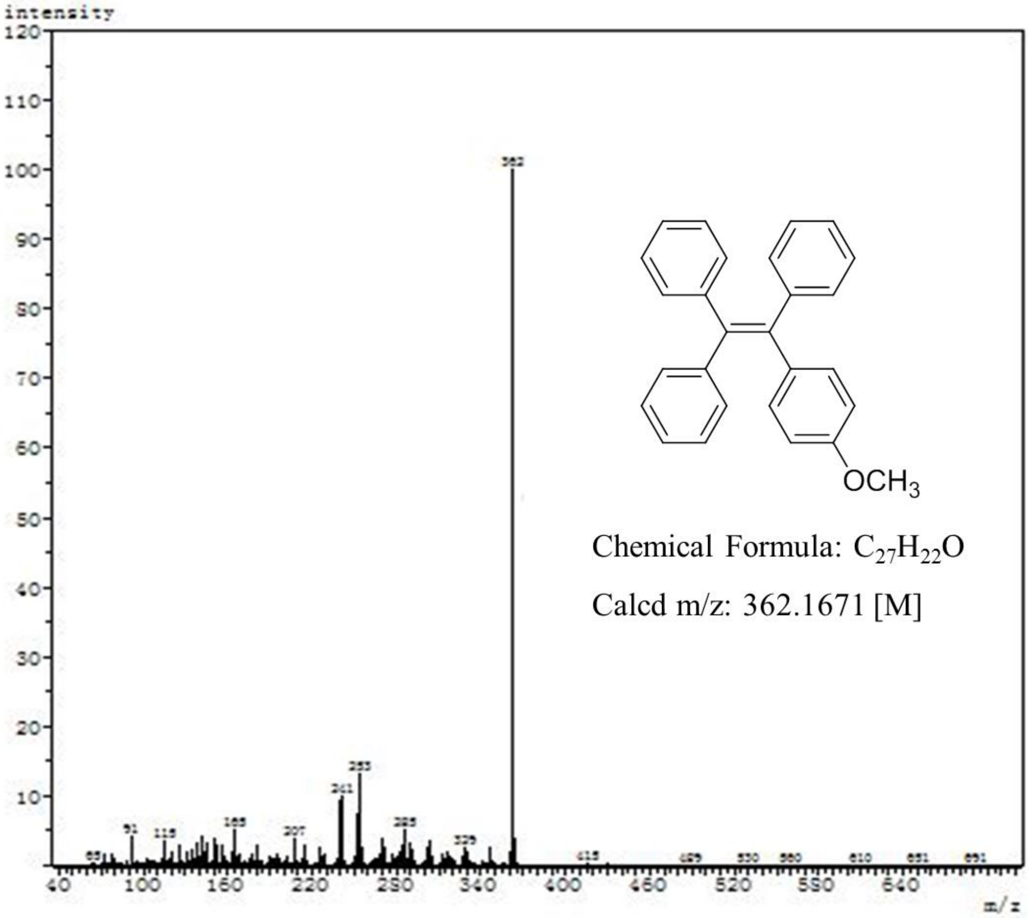


Fig. S4 EI-MS of TPEOCH$_3$

4.2. ^{1}H NMR, ^{13}C NMR, and MS of TPEOH

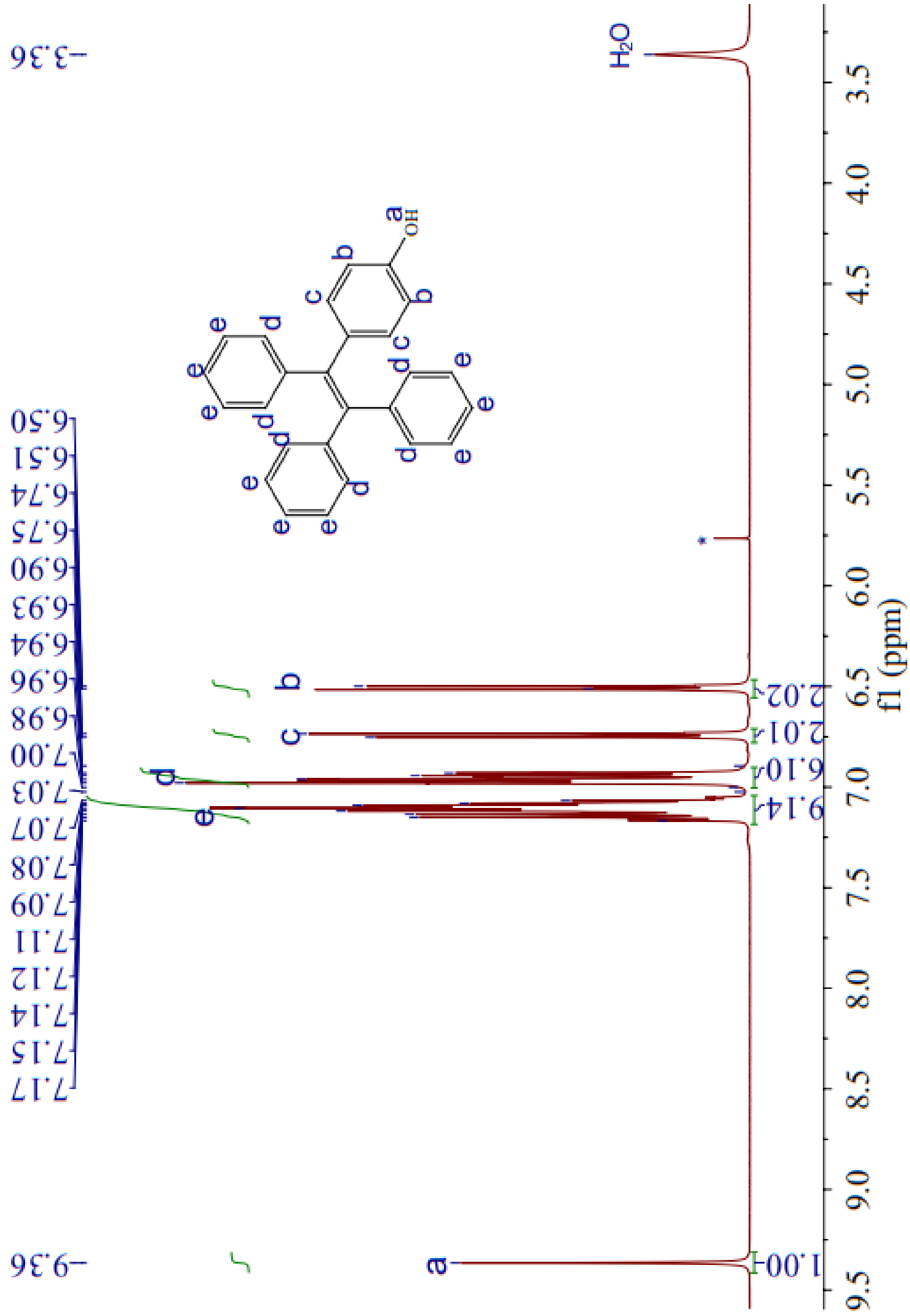


Fig. S5 ^{1}H NMR of TPEOH

^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.36 (s, 1H), 7.18 - 7.03 (m, 9H), 7.00 - 6.90 (m, 6H), 6.74 (d, J = 8.6 Hz, 2H), 6.51 (d, J = 6.7 Hz, 2H).

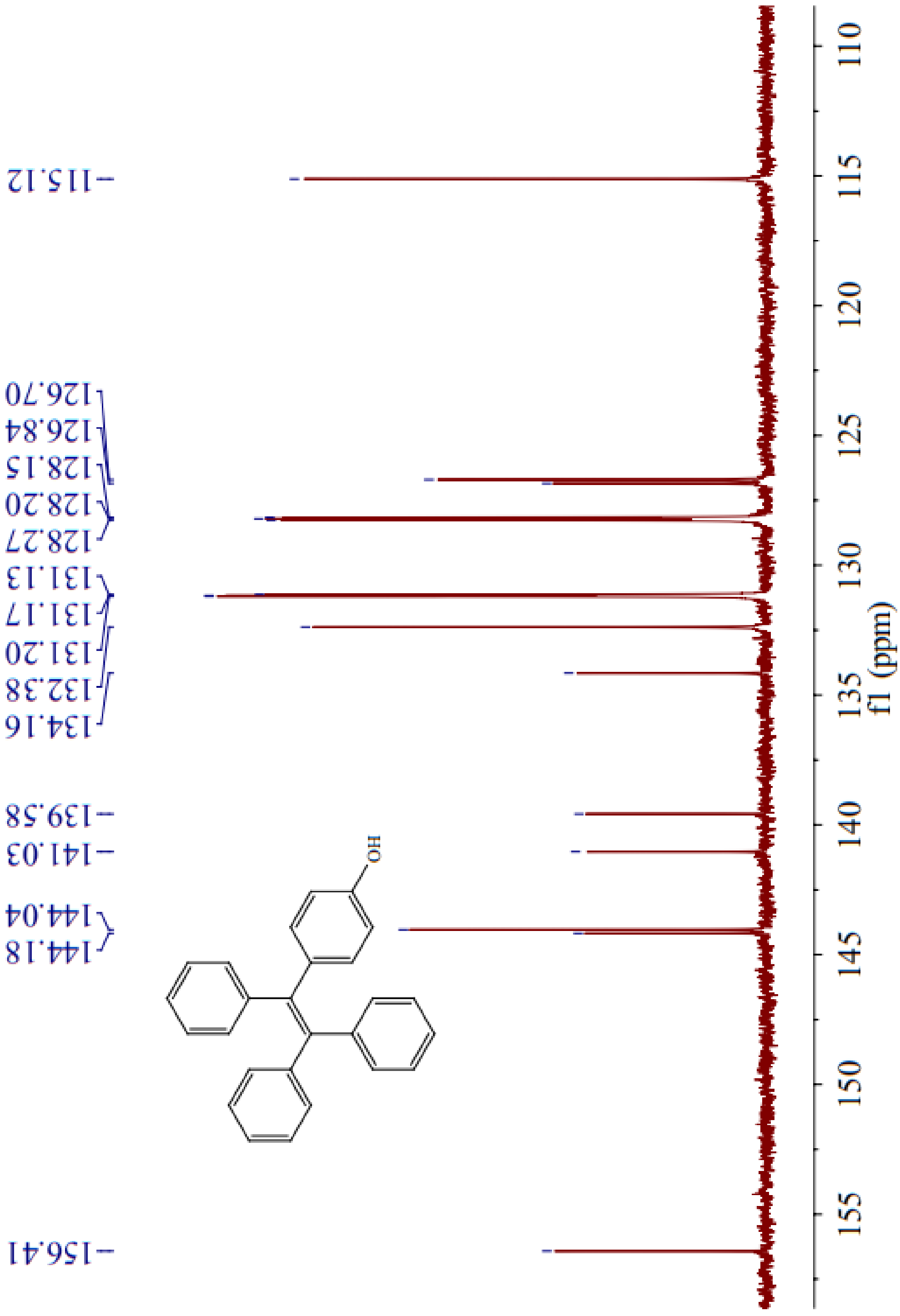
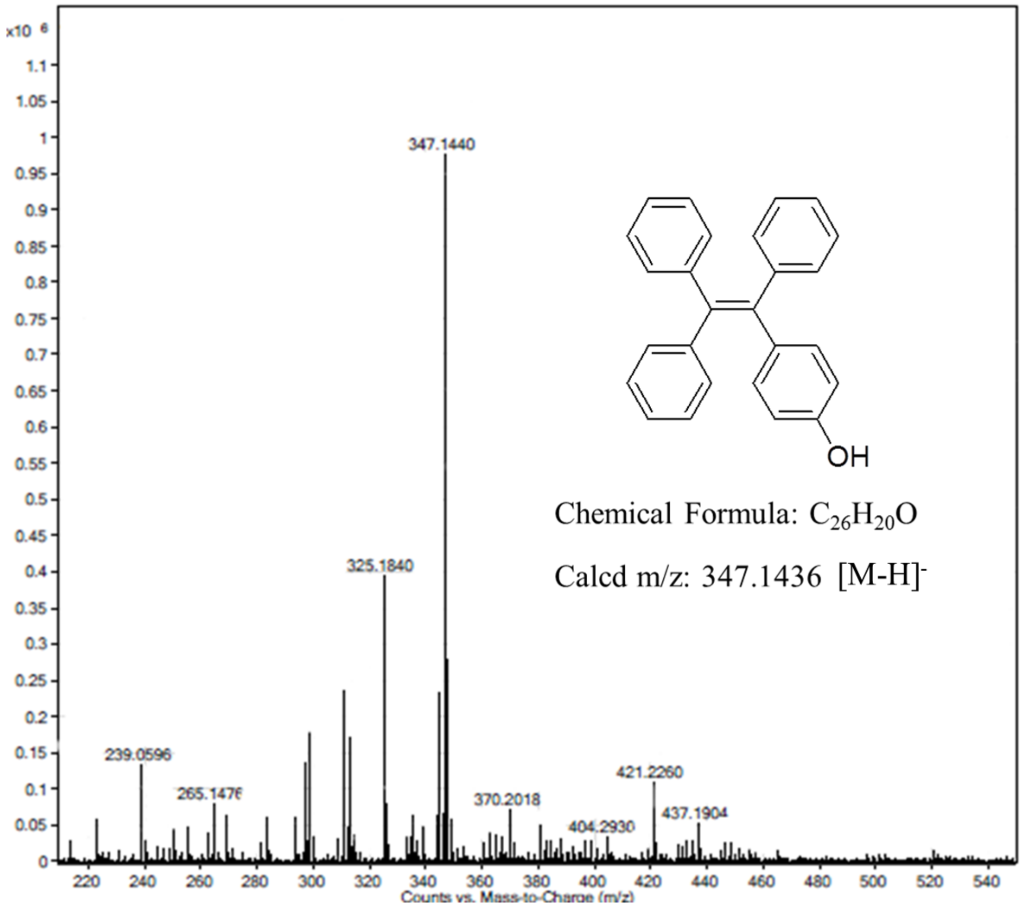


Fig. S6 ^{13}C NMR of TPEOH

^{13}C NMR (126 MHz, DMSO-d_6) δ: 156.41, 144.18, 144.04, 141.03, 139.58, 134.16, 132.38, 131.20, 131.17, 131.13, 128.27, 128.20, 128.15, 126.84, 126.70, 115.12.



Chemical Formula: $C_{26}H_{20}O$

Calcd m/z: 347.1436 $[M\text{-}H]^-$

Fig. S7 ESI-MS of TPEOH (negative ion mode)

4.3. ^{1}H NMR, ^{13}C NMR, and MS of TPEONO$_2$

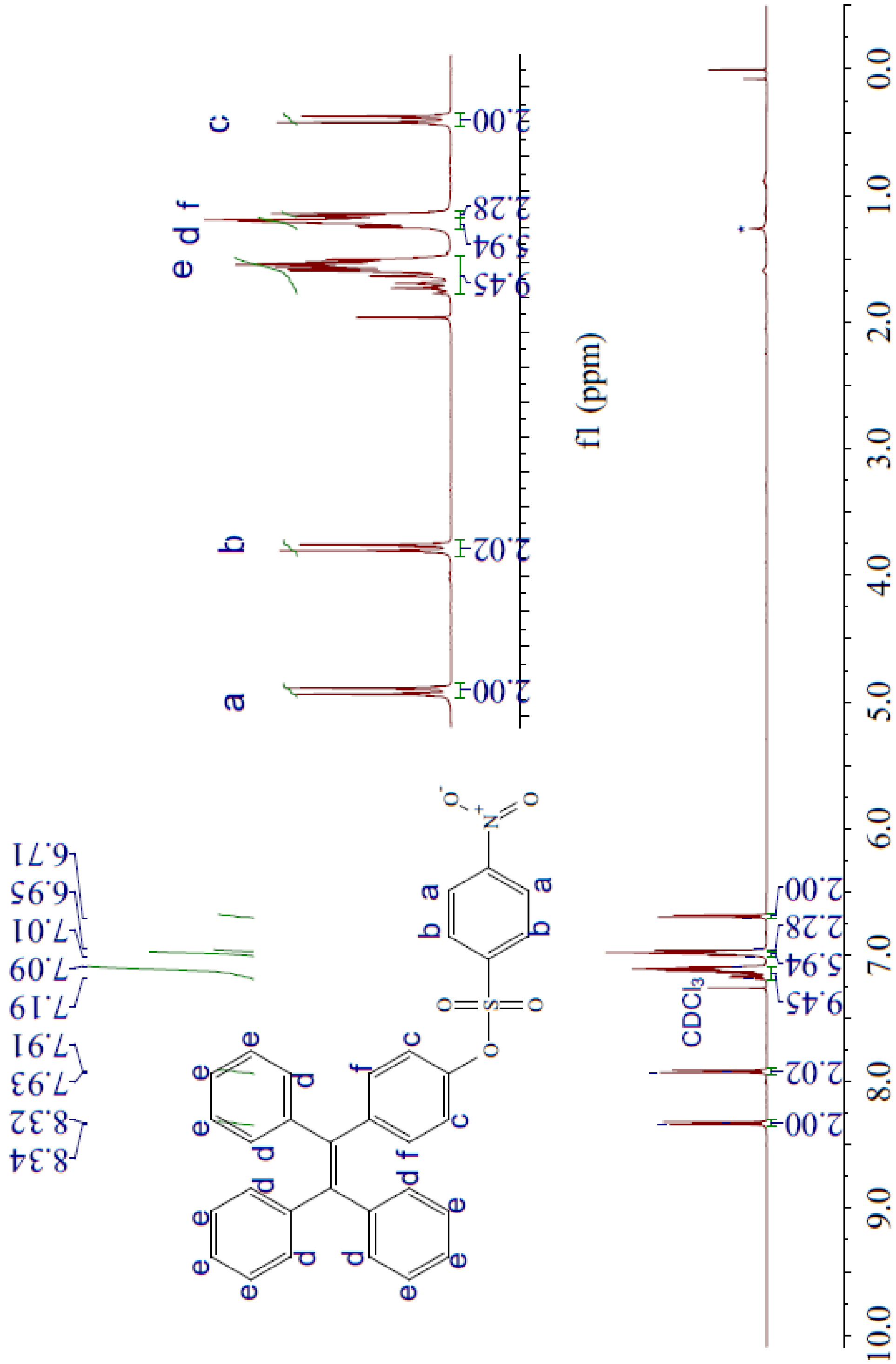


Fig. S8 ^{1}H NMR of TPEONO$_2$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.33 (d, *J* = 9.2 Hz, 2H), 7.92 (d, *J* = 7.0 Hz, 2H), 7.19 - 7.09 (m, 9H), 7.01 - 6.97 (m, 6H), 6.97 - 6.95 (m, 2H), 6.70 (d, *J* = 11.5 Hz, 2H).

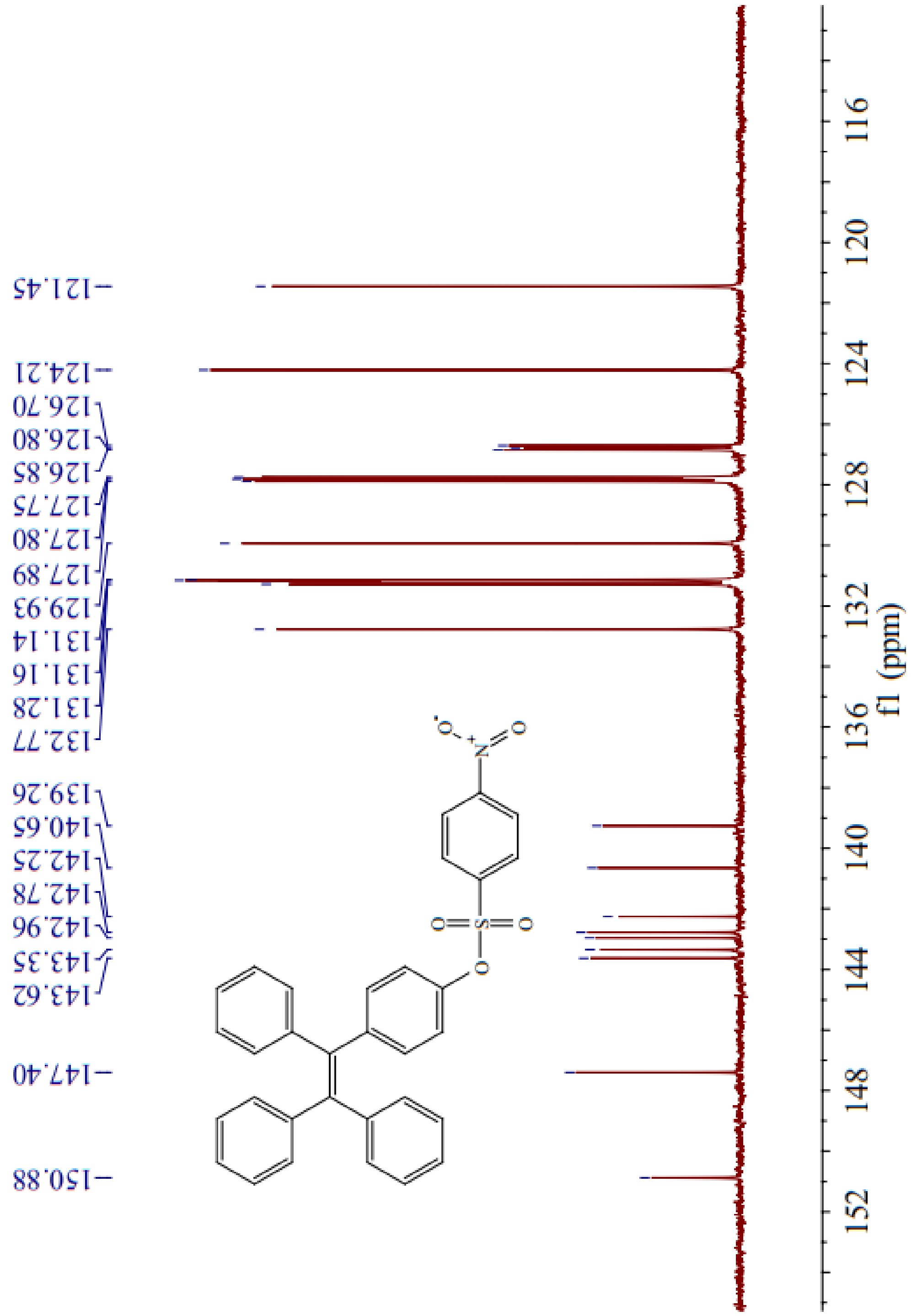


Fig. S9 ^{13}C NMR of TPEONO$_2$

^{13}C NMR (126 MHz, CDCl$_3$) δ: 150.88, 147.40, 143.62, 143.35, 142.96, 142.78, 142.25, 140.65, 139.26, 132.77, 131.28, 131.16, 131.14, 129.93, 127.89, 127.80, 127.75, 126.85, 126.80, 126.70, 124.21, 121.45.

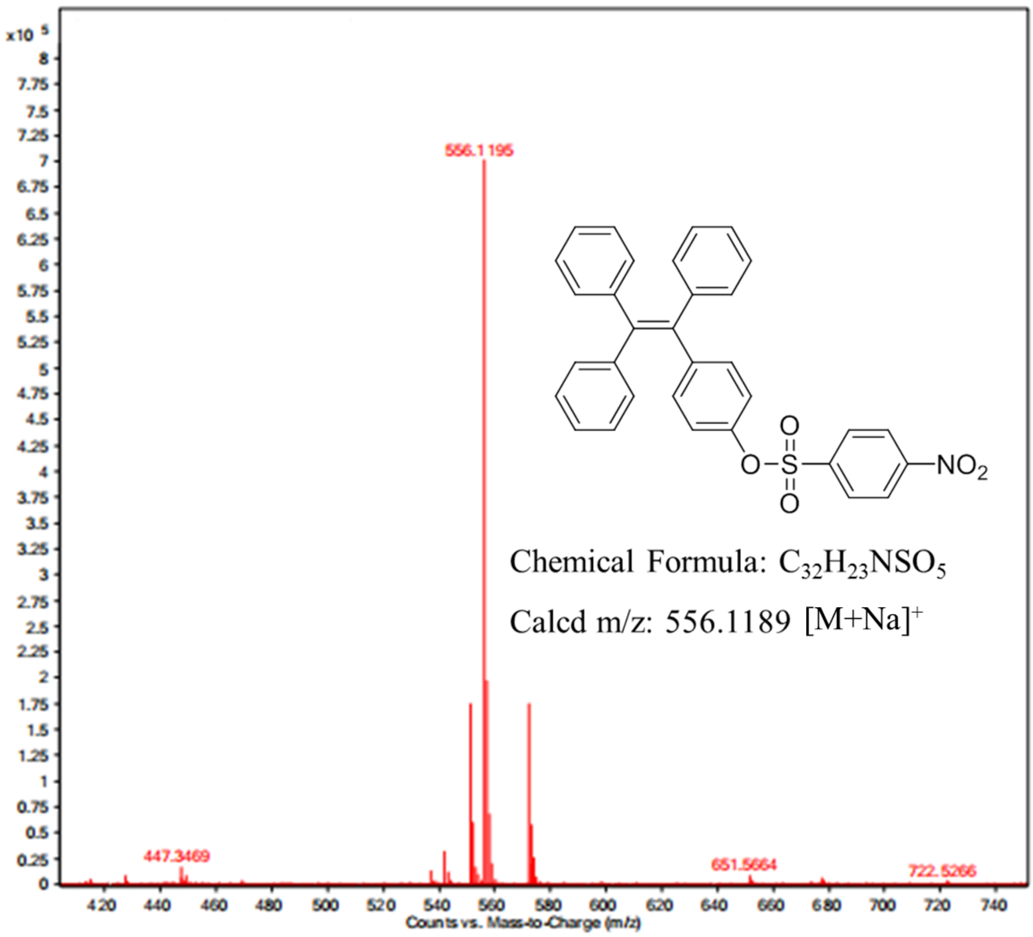


Fig. S10 ESI-MS of TPEONO$_2$ (positive ion mode)

4.4. ^{1}H NMR, ^{13}C NMR of TPEO(NO$_2$)$_2$

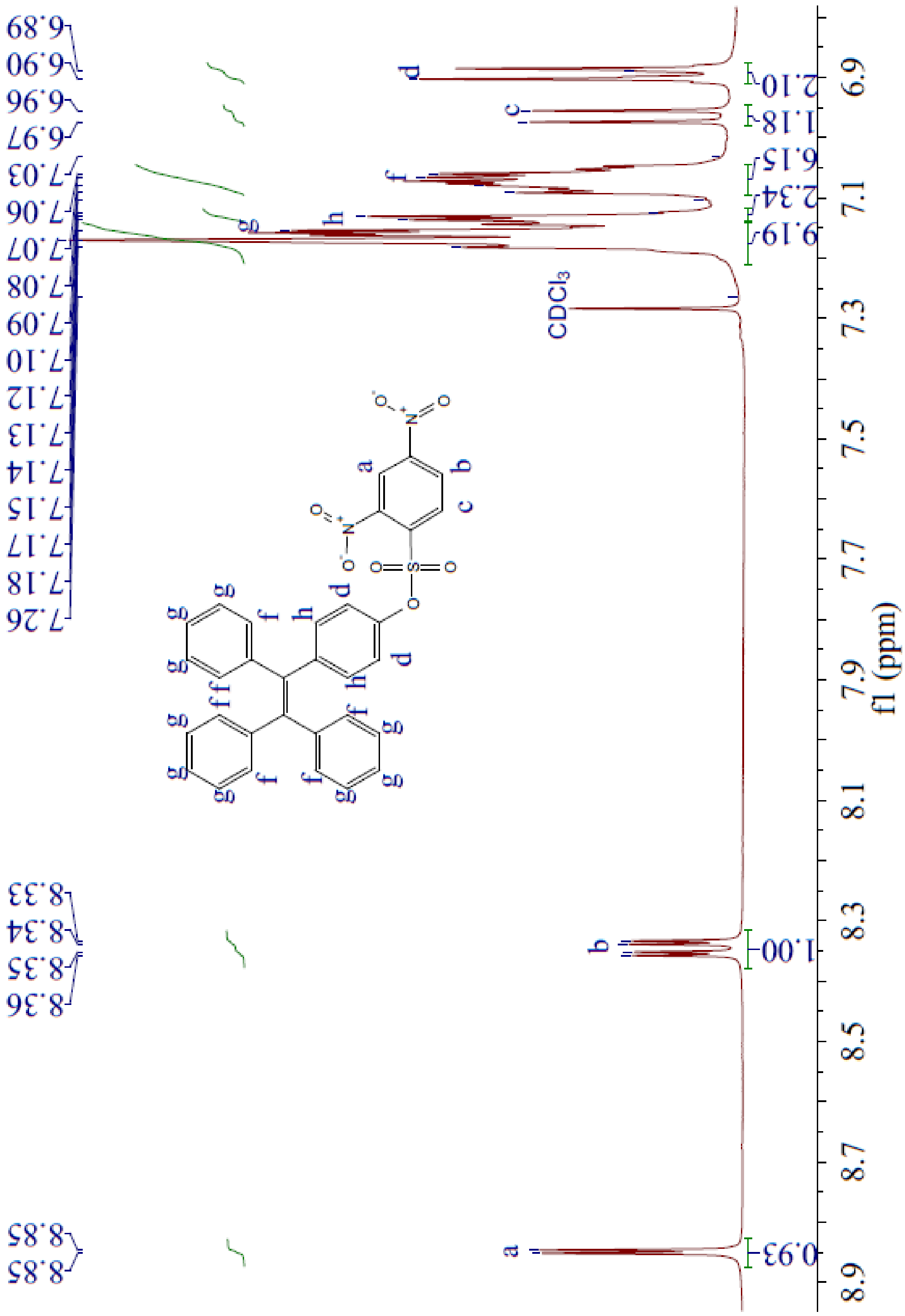


Fig. S11 ^{1}H NMR of TPEO(NO$_2$)$_2$

^{1}H NMR (500 MHz, CDCl$_3$) δ: 8.85 (d, J = 2.8 Hz, 1H), 8.35 (dd, J_1 = 9.3 Hz, J_2 =2.7 Hz, 1H), 7.26 - 7.14 (m, 9H), 7.14 -7.12 (m, 2H), 7.11 - 7.03 (m, 6H), 6.96 (d, J = 9.2 Hz, 1H), 6.89 (d, J = 6.8 Hz, 2H).

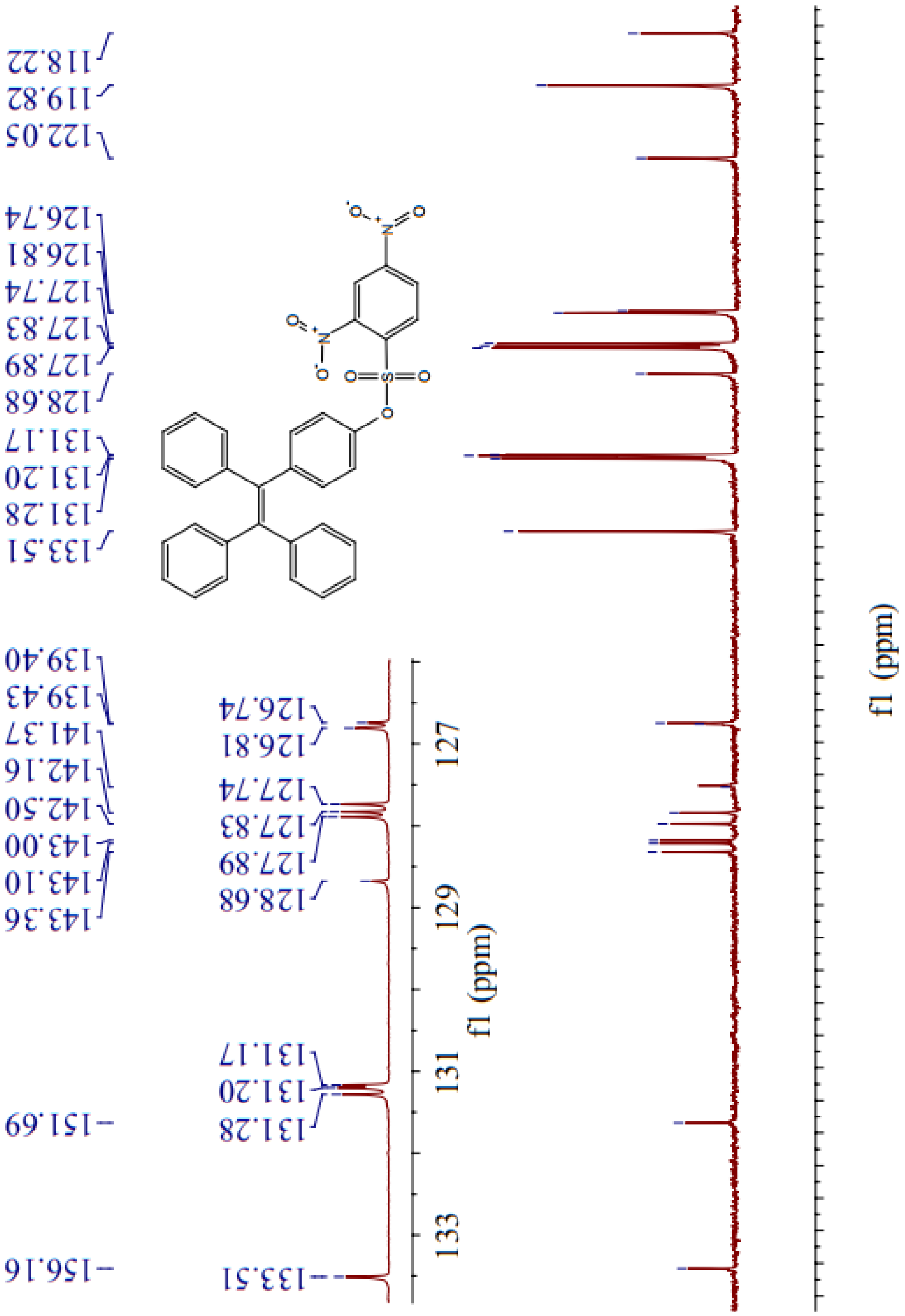


Fig. S12 ^{13}C NMR of TPEO$(NO_2)_2$

^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.16, 151.69, 143.36, 143.05, 142.50, 142.16, 141.37, 139.43, 139.40, 133.51, 131.28, 131.20, 131.17, 128.68, 127.89, 127.83, 127.74, 126.81, 126.74, 122.05, 119.82, 118.22.

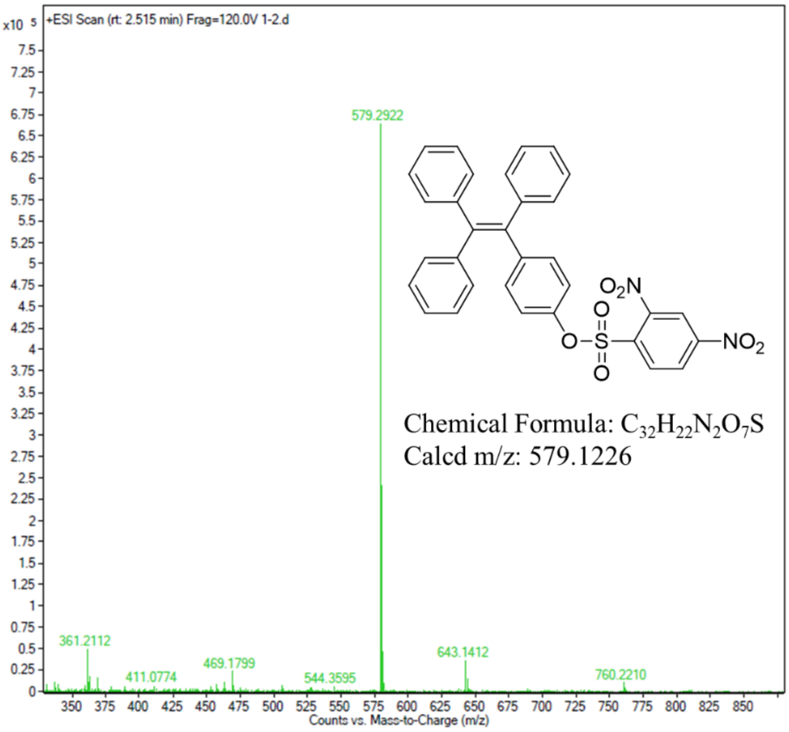


Fig. S13 ESI-MS of TPEO$(NO_2)_2$ (positive ion mode)

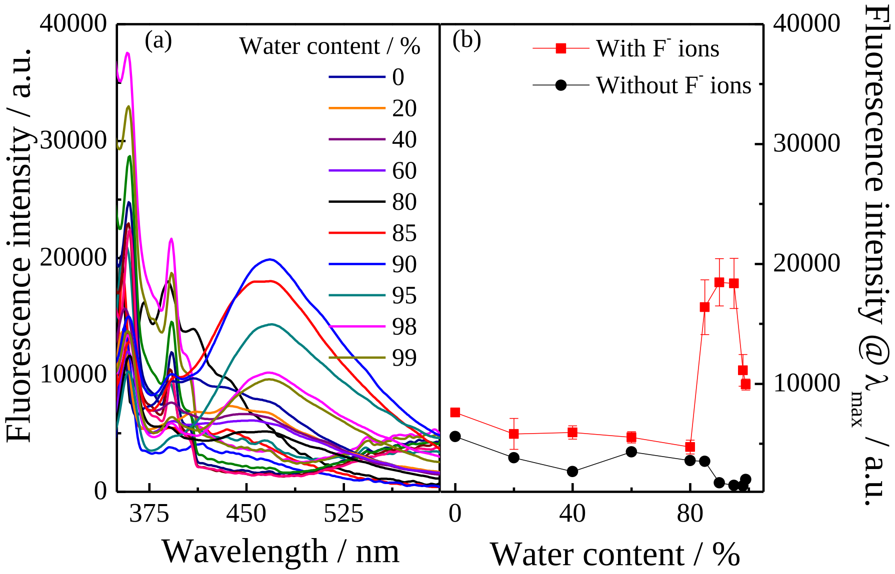
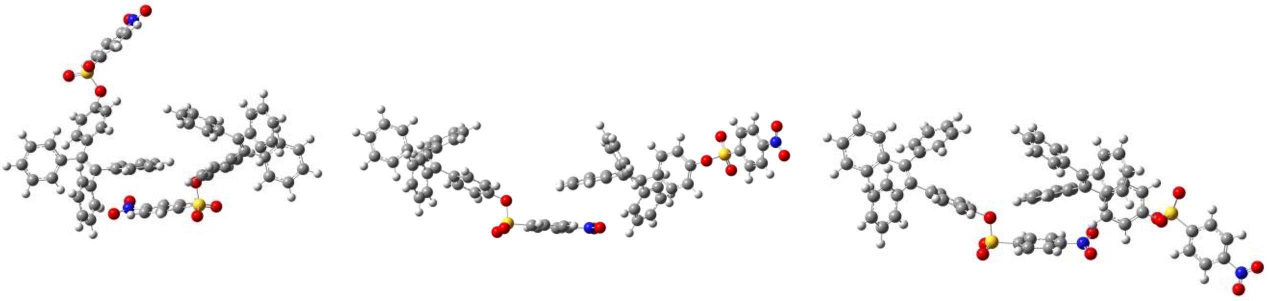
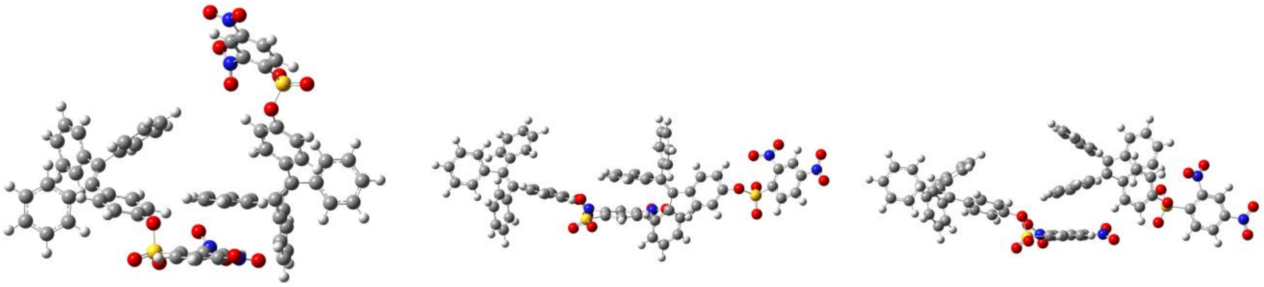


Fig. S14 (a) The fluorescence change of TPEO$(NO_2)_2$ (10 μM) in the presence of 80 μM F^- ions under different water content (by volume) and the relationships between the fluorescence intensity at maximum emission wavelength and water content in the presence of (black dots) and absence of (red dots) F^- ions. Error bars were obtained by measuring three parallel solutions.



-17.4 kcal/mol -12.4 kcal/mol -15.8 kcal/mol

Fig. S15 The comparison of the other optimized configuration of TPEONO$_2$ dimer. Note, red, yellow, and blue balls represent O, S, and N atoms, respectively.



-22.3 kcal/mol -20.3 kcal/mol -17.4 kcal/mol

Fig. S16 The comparison of the other optimized configuration of TPEO(NO$_2$)$_2$ dimer. Note, red, yellow, and blue balls represent O, S, and N atoms, respectively.

The geometries and frequencies of the TPEONO$_2$/TPEO(NO$_2$)$_2$ monomers and dimers were optimized by using the Gaussian 09 program.[S3] The most stable structures were confirmed with no negative frequencies of the harmonic vibrational frequencies. The basis set superposition error (BSSE) was corrected by the counterpoise (CP) method.[S4] All of the calculations were performed using the M062X method and the 6-311G** basis set. The solvation effects were taken into account in the calculations by using the SMD solvation model.

S3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A.

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S4. S. F. Boys and F. Bernardi, *Mol. Phys*., 1970, **19**, 553.

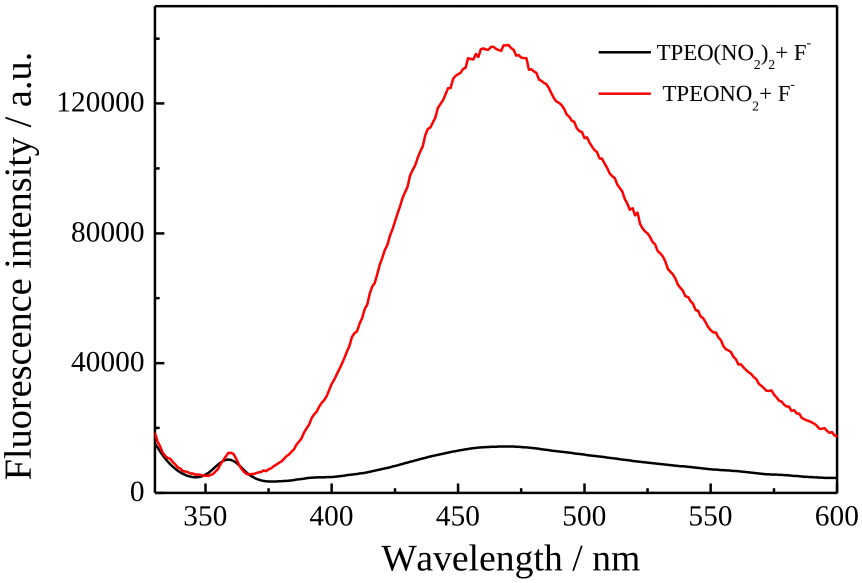

Fig. S17 The fluorescence spectra of TPEONO$_2$ (red line) and TPEO(NO$_2$)$_2$ (black line) in the presence of F$^-$ ions. [probe] = 10 μM; [F$^-$] = 80 μM; 10 mM HEPES buffer solution of pH 7.4 containing 5% DMF (by volume); reaction time of 40 min.

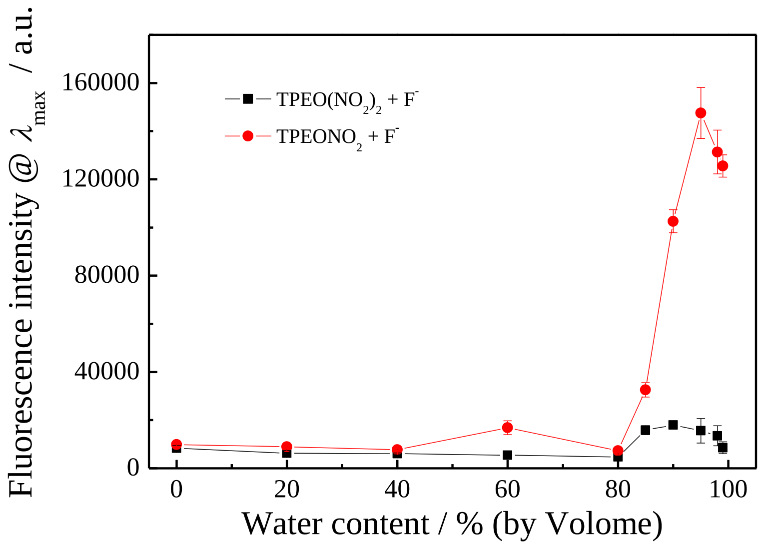

Fig. S18 The relationship between the fluorescence intensity at maximum emission wavelength of TPEONO_2 (red dots) and TPEO(NO_2)$_2$ (black dots) in the presence of F^- ions and water content (%, by volume). [probe] = 10 μM; [F^-] = 80 μM; 10 mM HEPES buffer solution of pH 7.4 containing various volumes of DMF (by volume); reaction time of 40 min. Error bars were obtained by measuring three parallel solutions.

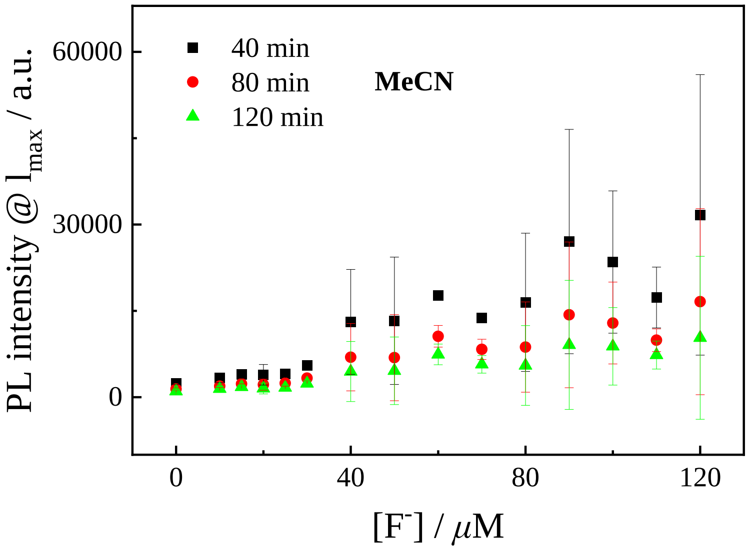

Fig. S19 The relationship between the fluorescence intensity and F^- concentration (0-120 μM) with different reaction times (40, 80, and 120 min). Experimental conditions: [TPEONO_2] = 10 μM; volume ratio of HEPES buffer solution to MeCN is 95 / 5 ([HEPES] = 50 mM, pH = 7.02); slit width: 2.5 nm / 5 nm; λ_{ex} = 320 nm; λ_{em}(max) = 470 nm. Error bars were obtained by measuring three parallel solutions.

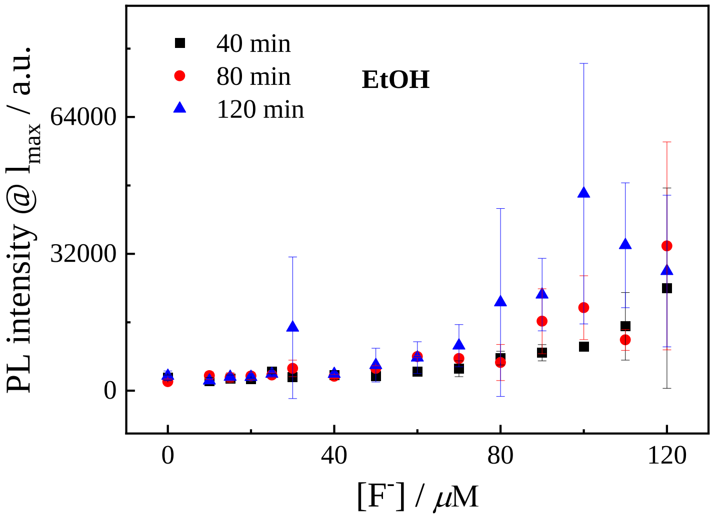

Fig. S20 The relationship between the fluorescence intensity and F^- concentrations (0-120 μM) with different reaction times (40, 80, and 120 min). Experimental conditions: [TPEONO$_2$] = 10 μM; volume ratio of HEPES buffer solution to EtOH is 95 / 5 ([HEPES] = 50 mM, pH = 7.02); slit width: 2.5 nm / 5 nm; λ_{ex} = 320 nm; λ_{em}(max) = 470 nm. Error bars were obtained by measuring three parallel solutions.

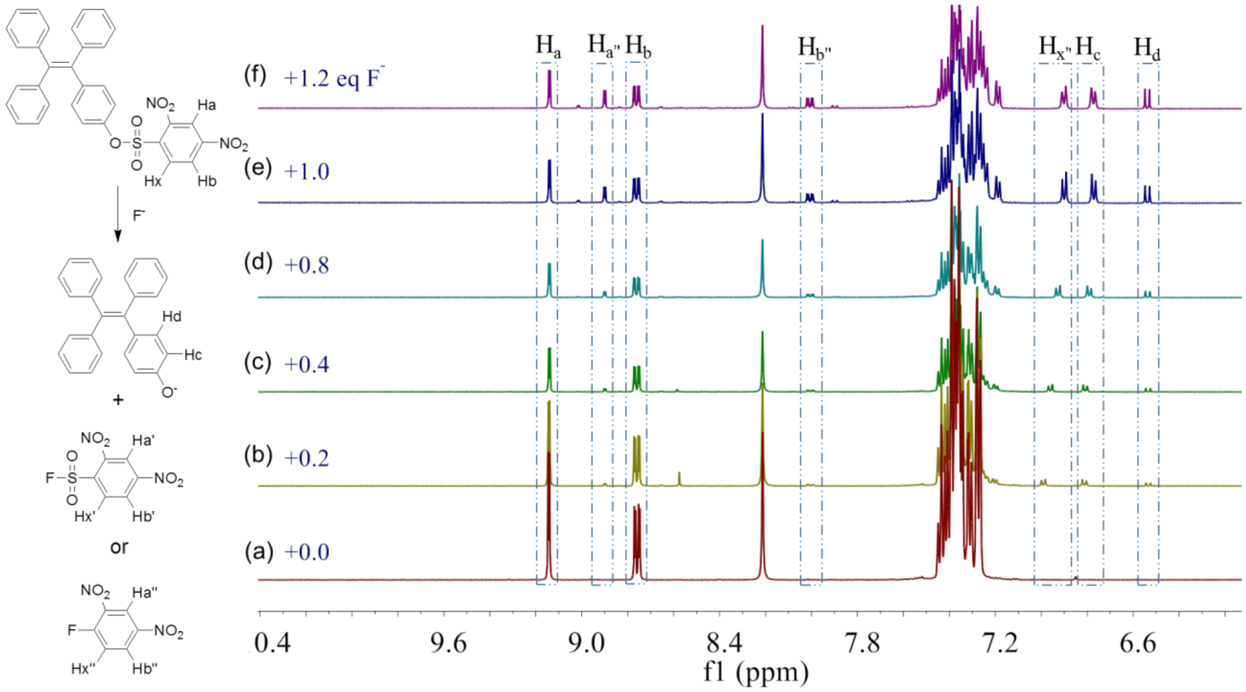

Fig. S21 ^{1}H NMR titration spectra of probe TPEO(NO$_2$)$_2$ (50 mM) towards F^- ions in DMF-d_7 solvent. (a) only TPEO(NO$_2$)$_2$, (b) TPEO(NO$_2$)$_2$ + 0.2 eq. F^- ions, (c) TPEO(NO$_2$)$_2$ + 0.4 eq. F^- ions, (d) TPEO(NO$_2$)$_2$ + 0.8 eq. F^- ions, (e) TPEO(NO$_2$)$_2$ + 1.0 eq. F^- ions, and (f) TPEO(NO$_2$)$_2$ + 1.2 eq. F^- ions.

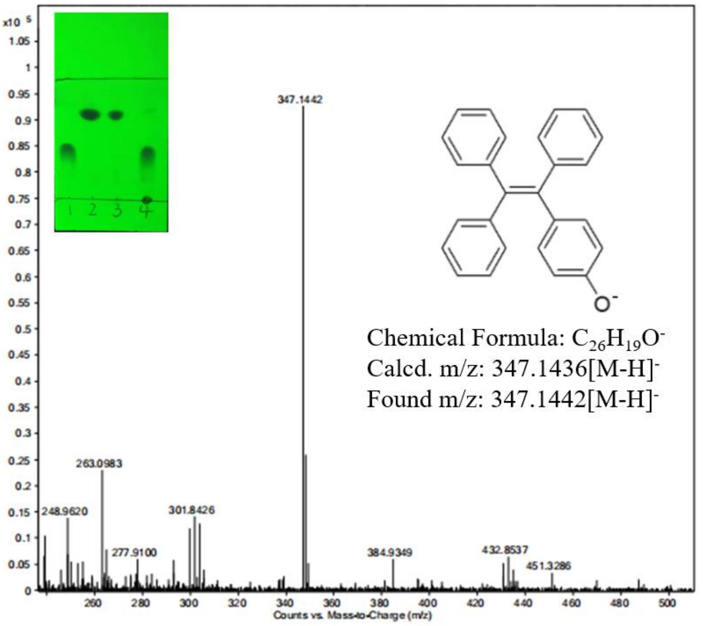

Fig. S22 ESI-MS of the product of $TPEO(NO_2)_2$ cleaved by F^- ions. The inset is the TLC image of TPEOH (1), of $TPEO(NO_2)_2$ (2), of mixing $TPEO(NO_2)_2$ and F^- ions immediately taken for TLC (3), and of mixing $TPEO(NO_2)_2$ and F^- ions under 80 °C for 1 h, taken for TLC (4). The biggest spot in (4) was carefully scraped off and collected to soak into methanol solvent, and the supernatant was used for the experiment of ESI-MS.

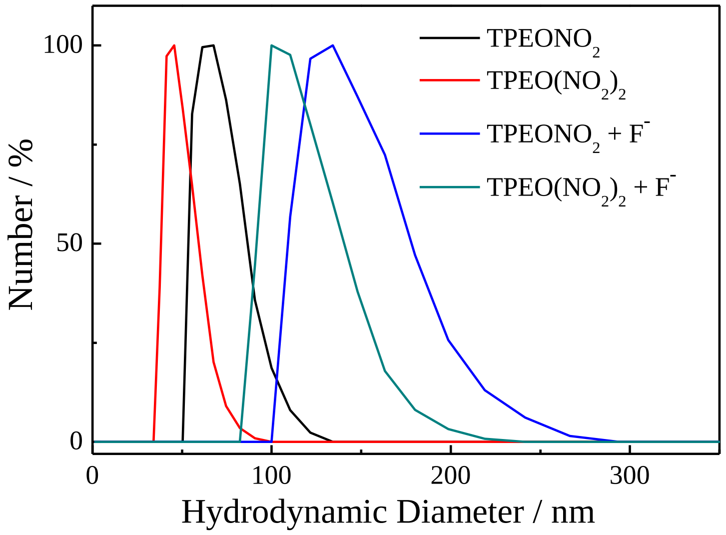

Fig. S23 The DLS test of $TPEONO_2$ (black line), $TPEO(NO_2)_2$ (red line), and $TPEONO_2 + F^-$ ions (green line), $TPEO(NO_2)_2 + F^-$ ions (blue line). $[TPEONO_2] = 10\ \mu M$; $[TPEO(NO_2)_2] = 10\ \mu M$; $[F^-] = 80\ \mu M$; 10 mM HEPES of pH 7.4 ($V_{water}/V_{DMF}=9/1$); temperature of 80 °C; reaction time of 40 min.

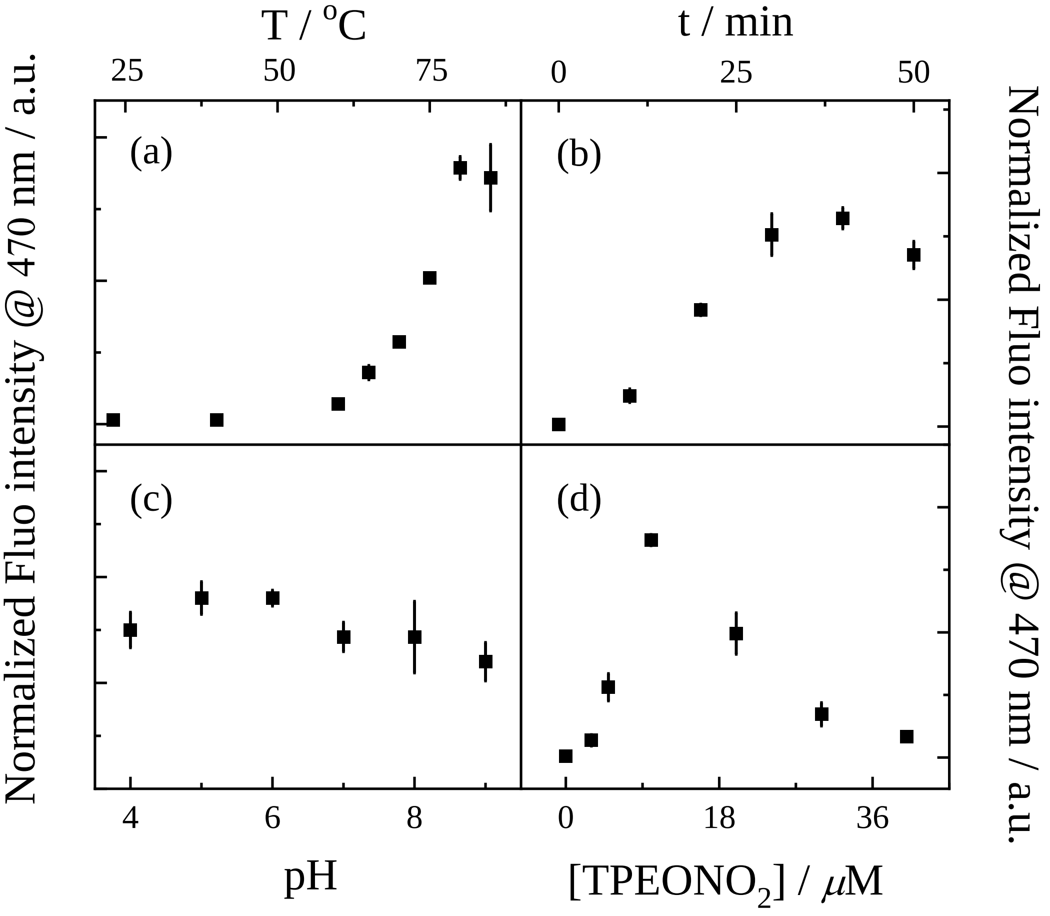

Fig. S24 Temperature (a), reaction time (b), pH (c) and $TPEONO_2$ concentration (d)-dependent the fluorescent intensity changes of the mixed solution of $TPEONO_2$ and F^- ions. Experiment conditions: [$TPEONO_2$] = 10 μM (a, b and c); [TBAF] = 80 μM (a, b, c and d); the reaction temperature was 80 °C (b, c and d); the reaction time was 40 min (a, c and d); pH 7.4 (a, b and d) was controlled by using 10 mM HEPES buffer solution and the content of buffer solution was 95% (a, b, c and d, by volume). Error bars were obtained by measuring three parallel solutions.

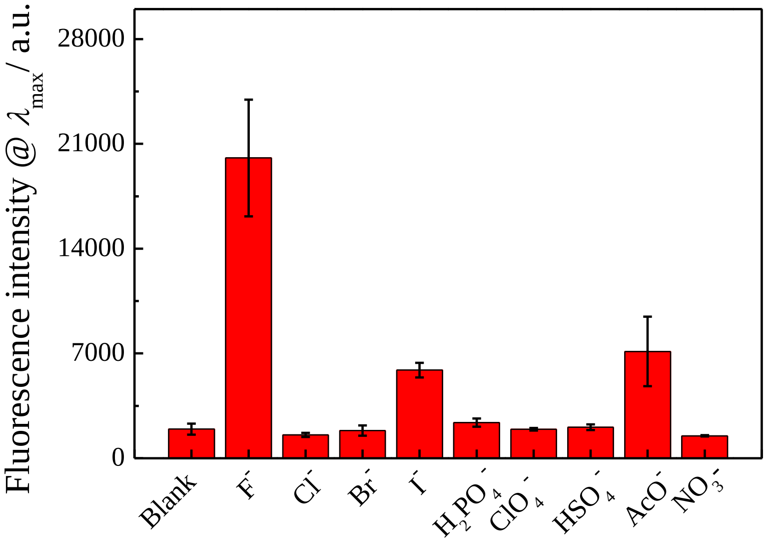

Fig. S25 The fluorescence response of 10 μM $TPEO(NO_2)_2$ towards various anions (80 μM) in 10 mM HEPES buffer solution of pH 7.4 containing 5% DMF (by volume). The reaction was conducted under 80 ℃ for 1 h. Error bars were obtained by measuring three parallel solutions.

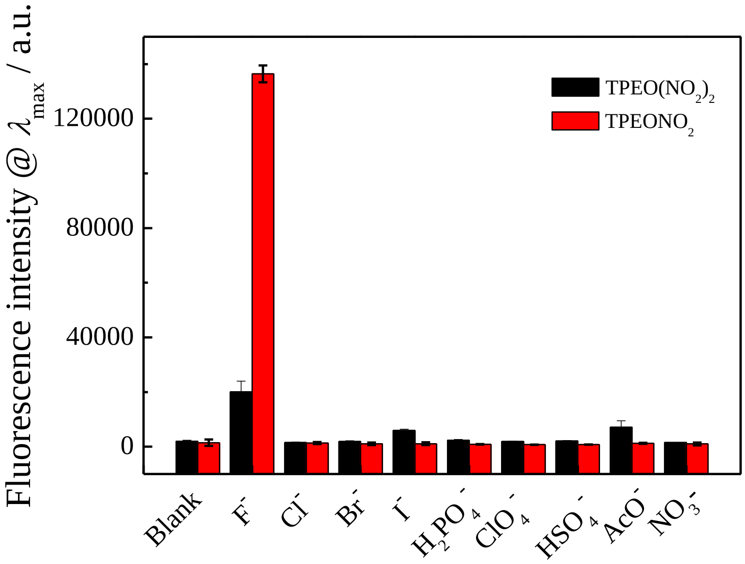

Fig. S26 The comparison of the fluorescence response of 10 μM $TPEONO_2$ and 10 μM $TPEO(NO_2)_2$ towards various anions (80 μM) in 10 mM HEPES buffer solution of pH 7.4 containing 5% DMF (by volume). The reaction was conducted under 80 ℃ for 1 h. Error bars were obtained by measuring three parallel solutions.

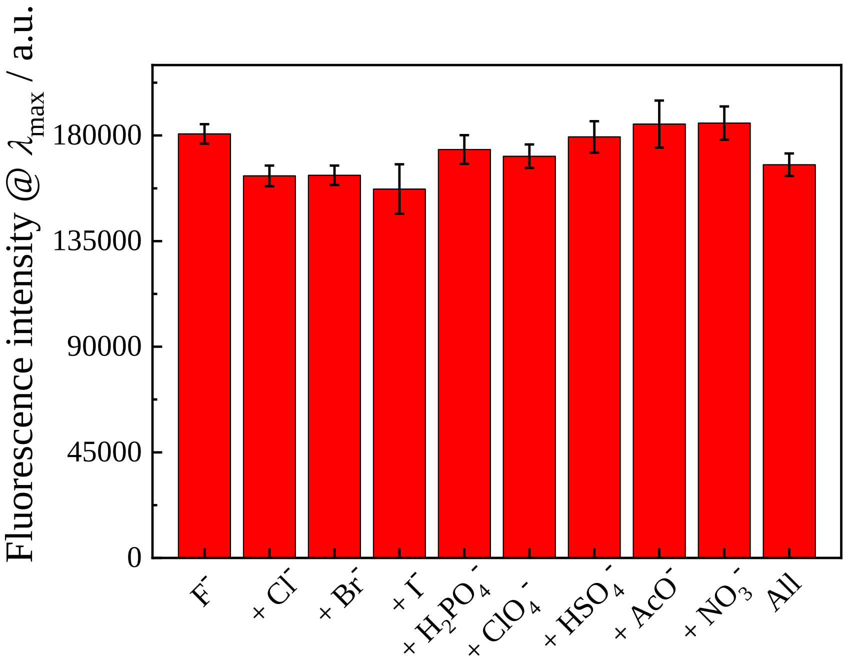

Fig. S27 The fluorescence response of 10 μM $TPEONO_2$ towards F^- ions of 80 μM plus co-existing anions of concentration of 400 μM. 'All' means all the tested interference anions were presented with a concentration of 30 μM of each anion. [$TPEONO_2$] = 10 μM. Error bars were obtained by measuring three parallel solutions.

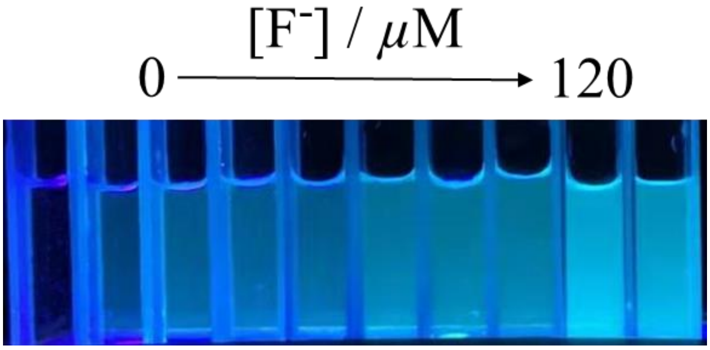

Fig. S28 The image of probe $TPEONO_2$ in the presence of various F^- ions concentration from 0 to 120 μM under the illumination of 365 nm wavelength UV lamp.

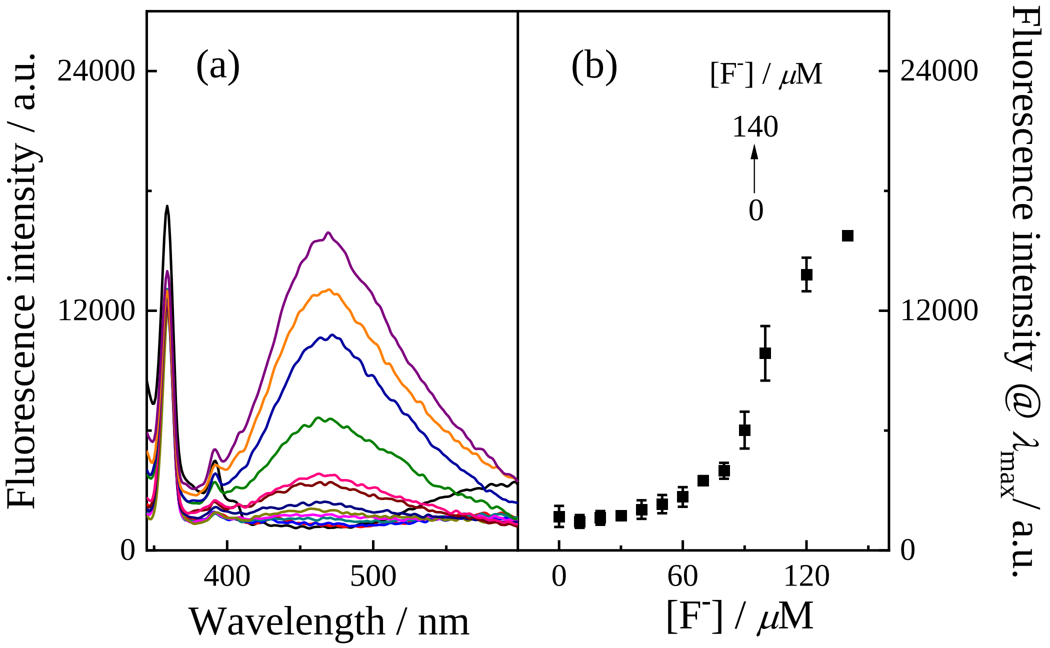

Fig. S29 The fluorescence response of 10 μM TPEO$(NO_2)_2$ towards F^- ions concentration ranged from 0 to 140 μM (a). The relationship curve between fluorescence intensity at 470 nm wavelength and F^- ions concentration (b). Error bars were obtained by measuring three parallel solutions.

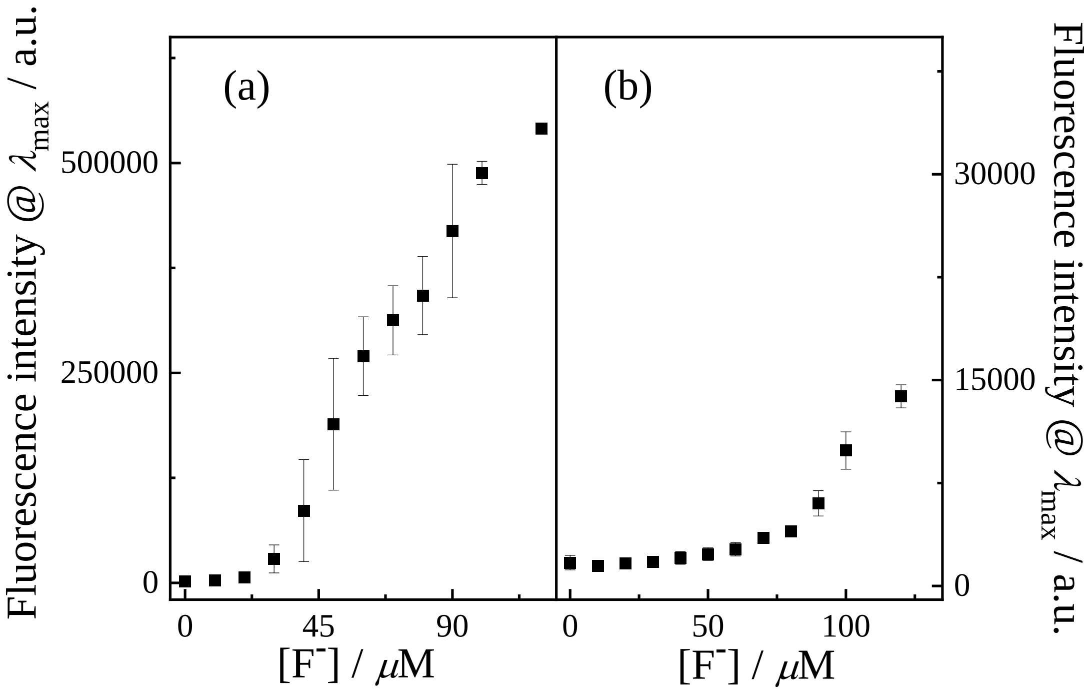

Fig. S30 The relationship curve between the fluorescence intensity at 470 nm wavelength and F^- ions concentration in 10 μM TPEONO$_2$ (a) and 10 μM TPEO$(NO_2)_2$ (b). Error bars were obtained by measuring three parallel solutions.

Table S1: Comparison of interaction type, LOD, and medium in this work and other reported references.

No.	Probe	Interaction between probe and analyte	LOD (μM)	Medium	Ref.
1	Derivative N-(3-(benzo[d]thiazol-2-yl)-4-(tert-butyldiphenylsilyloxy)phenyl)-benzamide	Cleaving Si-O bond	100 ppb (5.2 μM)	2 mM CTAB aqueous solution	S5
2	Trihexylsilylacetylene-containing BODIPY dye	Cleaving Si-C bond	0.0674	Acetone	S6
3	PEG-FITC-Si	Cleaving Si-O bond	19 ppb (1.0 μM)	CTAB-HEPES	S7
4	2-(Cyanomethyl) pyridine derivative	Deprotonation of C-H group	6.73	CH_3CN	S8
5	BODIPY-benzimidazole	Hydrogen bonding	0.093	CH_3CN	S9
6	Tert-butyldiphenylsilyl (TBDPS) substituted 8-hydroxyquinoline derivative	Cleaving Si-O bond	3.8	Dioxane/ HEPES (1:1)	S10
7	4-Amino-1,8-naphthalimide derivative containing a tert-butyldimethylsilyl group	Cleaving Si-O bond	0.067 ppm (3.52 μM)	DMSO/HEPES (1:1)	S11
8	2-Hydroxy-1-naphthalene formaldehyde bis-schiff	Hydrogen bonding and deprotonation	0.014	DMSO	S12
9	Tri-benzimidazolyl star-shape FC molecules	Hydrogen bonding and deprotonation	0.284	DMSO	S13
10	Thiocarbohydrazide-conjugated coumarin derivative	Hydrogen bonding	9.2	CH_3CN (0.25% DMSO)	S14
11	$TPEONO_2$	Cleaving S-O bond	0.10	HEPES (5% DMF)	This work

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