Electronic Supplementary Information for

Solid-State Fluorescent Probe for α, β-Diamine Based on Tetraphenylethylene Skeleton Construction

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Table of Contents

Synthesis of TPE-2OH

4-hydroxybenzophenone (2.0 g, 10 mmol) and zinc powder (2.9 g, 44 mmol) were placed in a 250 mL round-bottomed flask, and 100 mL anhydrous tetrahydrofuran was added under nitrogen protection. The mixture was cooled to -78 ℃, and $TiCl_4$ was added into the reaction system drop by drop. After addition, the mixture was returned to room temperature and reacted for 0.5 h, and then it was heated to 70 °C and refluxed for overnight. After the starting material was completely consumed, it was quenched with 10 % K_2CO_3 aqueous solution. The mixture was extracted with CH_2Cl_2 for three times. The solution was dried with anhydrous magnesium sulfate and filtered. The solvent was evaporated and then the crude product was carried out column chromatography with *n*-hexane/ethyl acetate (V/V, 7:3) as mobile phase to obtain white solid with a yield of 80 %. ^{1}H-NMR (400 MHz, DMSO-d_6), (TMS, ppm): 9.31 (s, 2H, -OH); 7.09 (m, 6H, ArH); 6.95 (dd, 4H, ArH); 6.73 (dd, 4H, ArH); 6.50 (dd, 4H, ArH).

Synthesis of DPEC

TPE-2OH (0.636 g, 1.7 mmol) was dissolved in 80 mL dry toluene in a round bottom flask. Potassium ferricyanide (1.724 g, 5.24 mmol) as the oxidant was dissolved in 80 mL of 5 wt. % potassium hydroxide aqueous solution. The potassium ferricyanide solution was then added dropwise into the TPE-2OH solution within 1 h at room temperature. The reaction was kept at 110 ℃ for 8 h and monitored by TLC. The resulting solution was filtered and evaporated to afford the crude product. Then the crude product was recrystallized using ethanol as solvent to give the red solid in 70% yield, which were characterized by ^{1}H-NMR, ^{13}C-NMR, ESI-MS and 2D-COSY (Figure S1-S6, ESI†). ^{1}H-NMR (400 MHz, $CDCl_3$), (TMS, ppm): 7.49 (dt, 2H, ArH); 7.37 (m, 8H, ArH); 7.20 (q, 4H, =CH); 6.54 (m, 4H, =CH). ^{13}C-NMR (100 MHz, $CDCl_3$), δ: 186.75, 154.66, 137.47, 137.28, 136.44, 132.36, 130.63, 130.41, 130.12, 128.76.

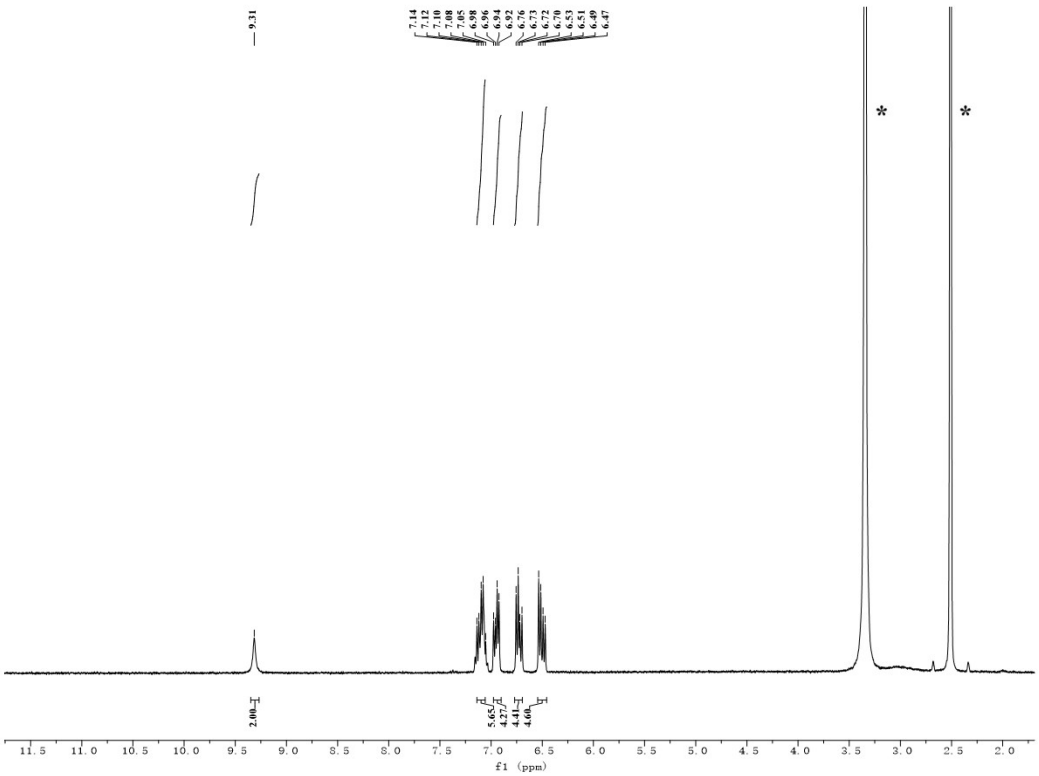


Figure S1. ^{1}H NMR spectrum of TPE-2OH in DMSO-d_6.
The residual solvent signals are marked with asterisks.

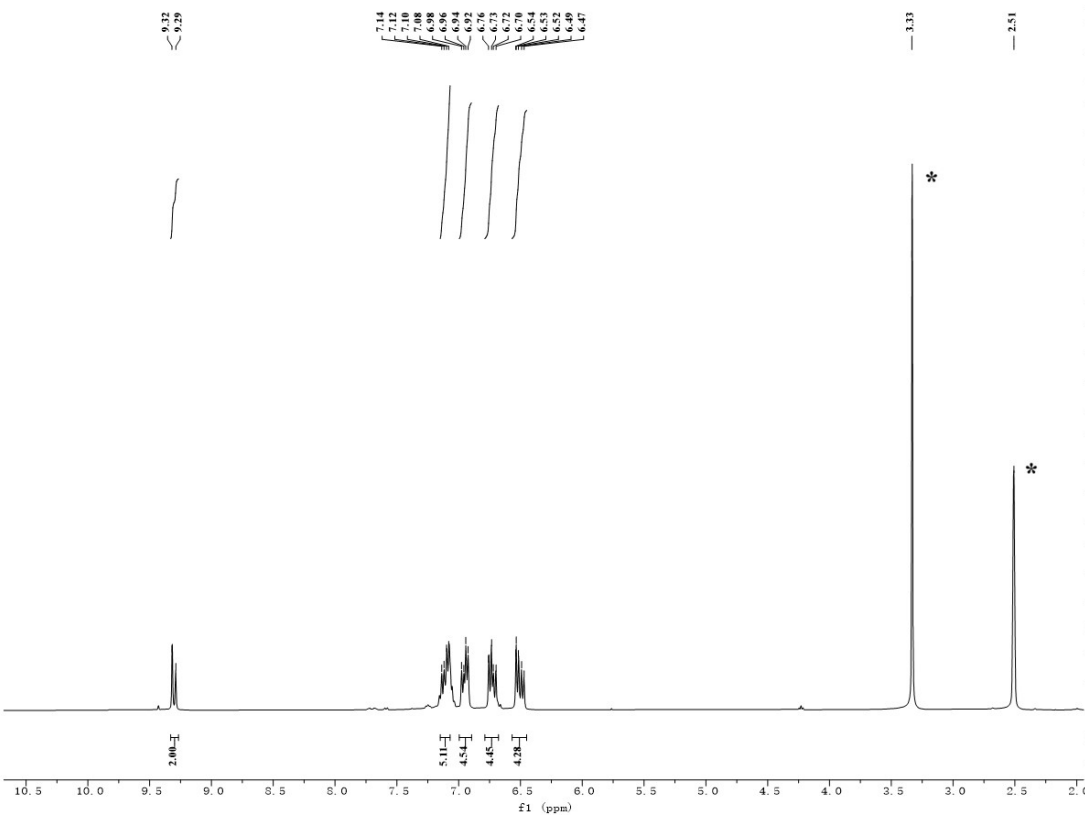


Figure S2. ^{1}H NMR spectrum of product of **DPEC** with EDA in DMSO-d_6.
The residual solvent signals are marked with asterisks.

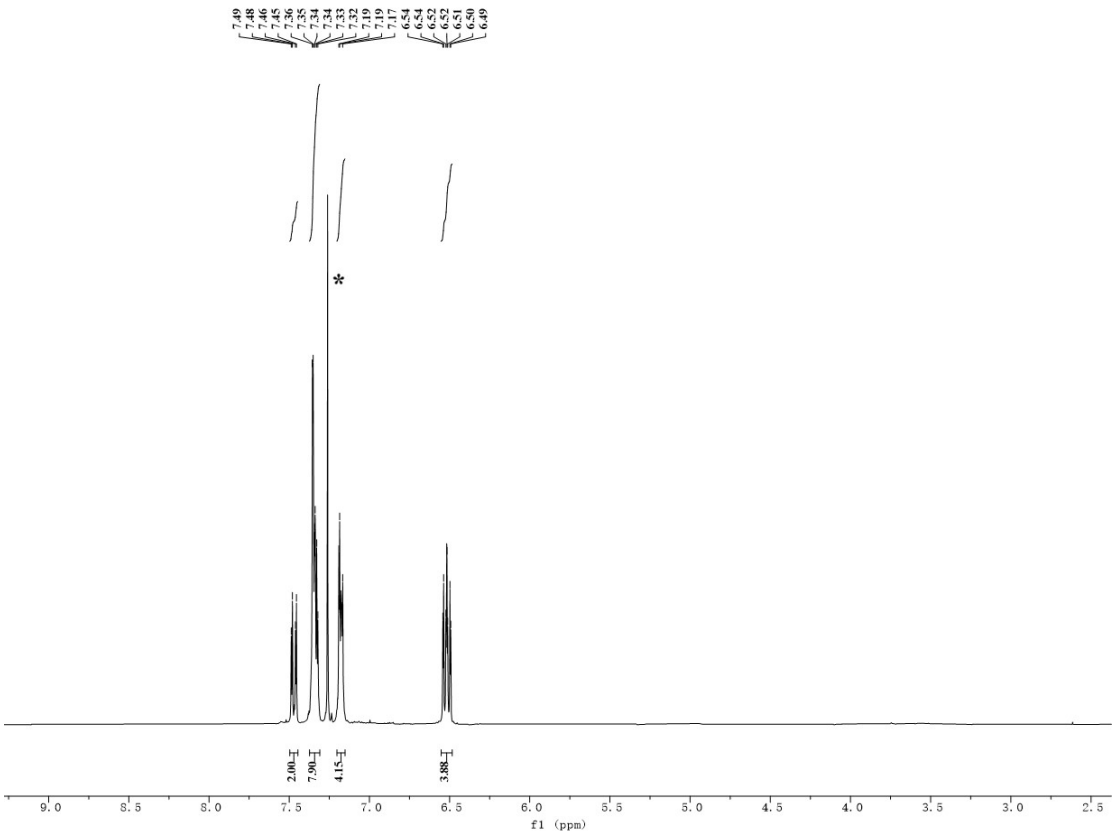


Figure S3. ^{1}H NMR spectrum of **DPEC** in $CDCl_3$.
The residual solvent signals are marked with asterisks.

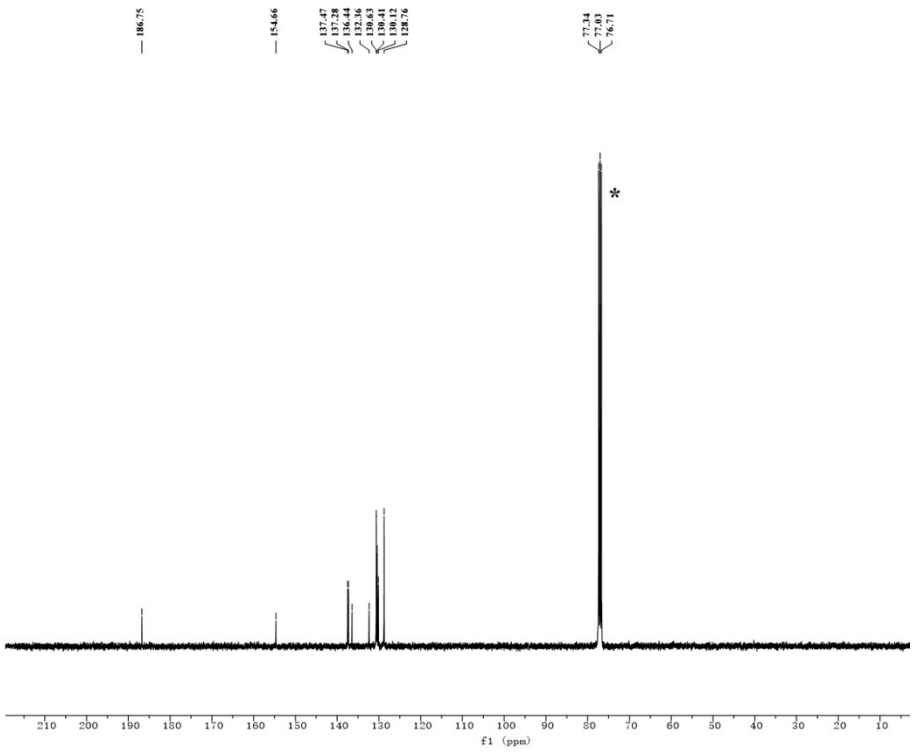


Figure S4. ^{13}C NMR spectrum of **DPEC** in $CDCl_3$.
The residual solvent signals are marked with asterisks.

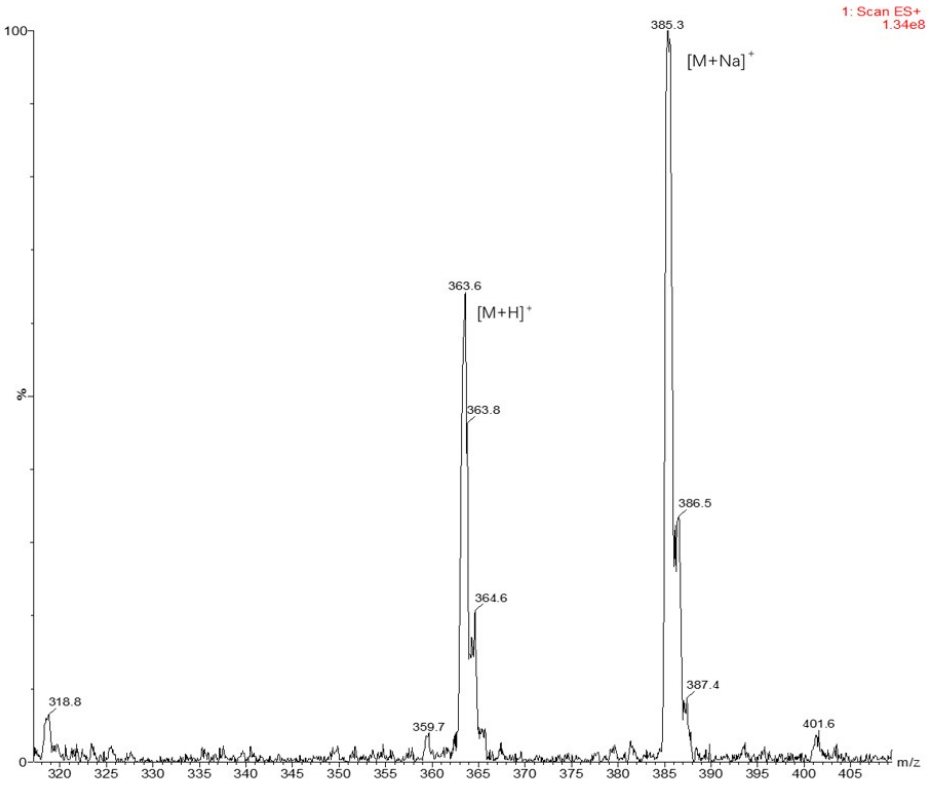


Figure S5. ESI-MS spectrum of **DPEC**.

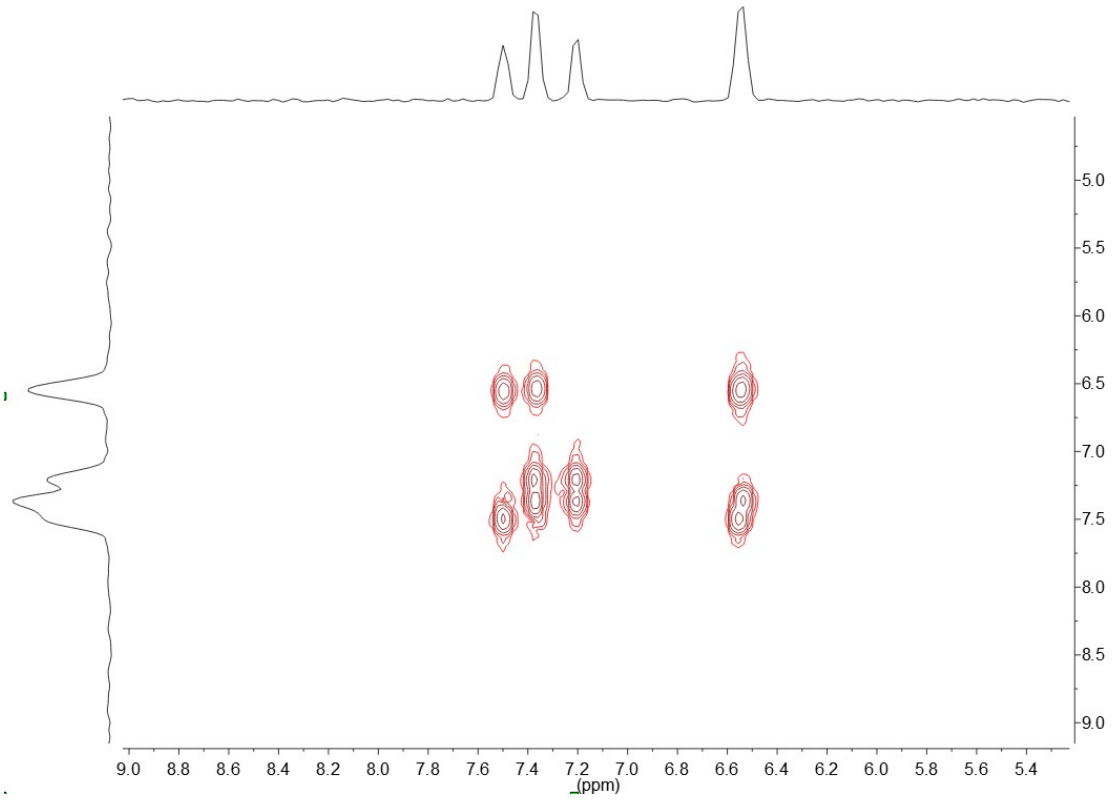


Fig S6. 2D COSY spectrum of **DPEC** in $CDCl_3$.

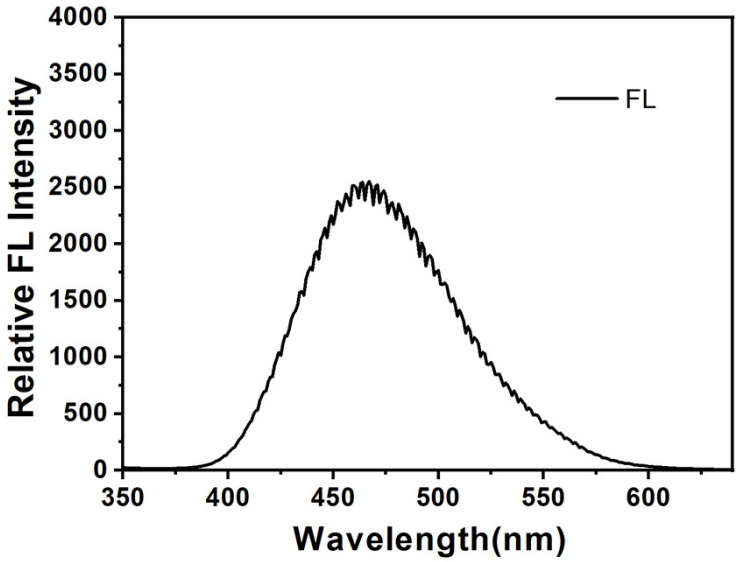


Fig S7. Solid state fluorescence spectra of **TPE-2OH**.

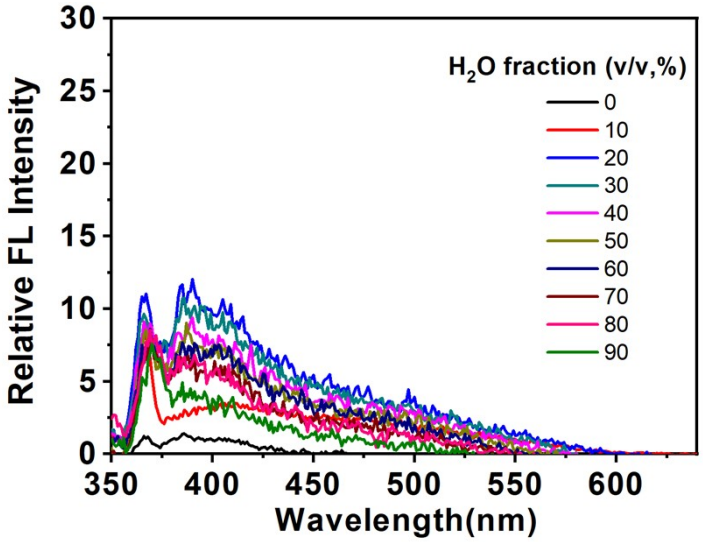


Fig S8. Fluorescence spectra of **DPEC** in DMSO-H_2O mixtures with different water fractions (f_w); Concentration: 30 μM; λ_{ex}: 330 nm (5 nm, 5 nm); 293 K.

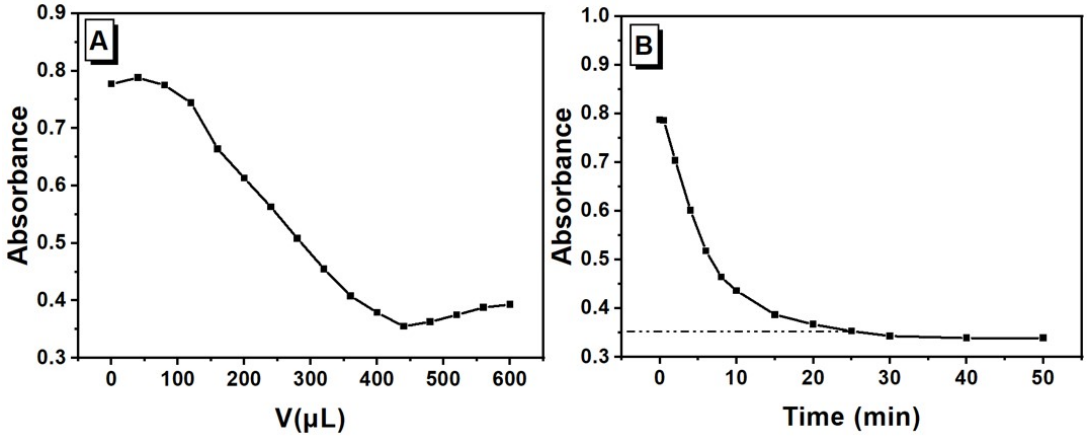
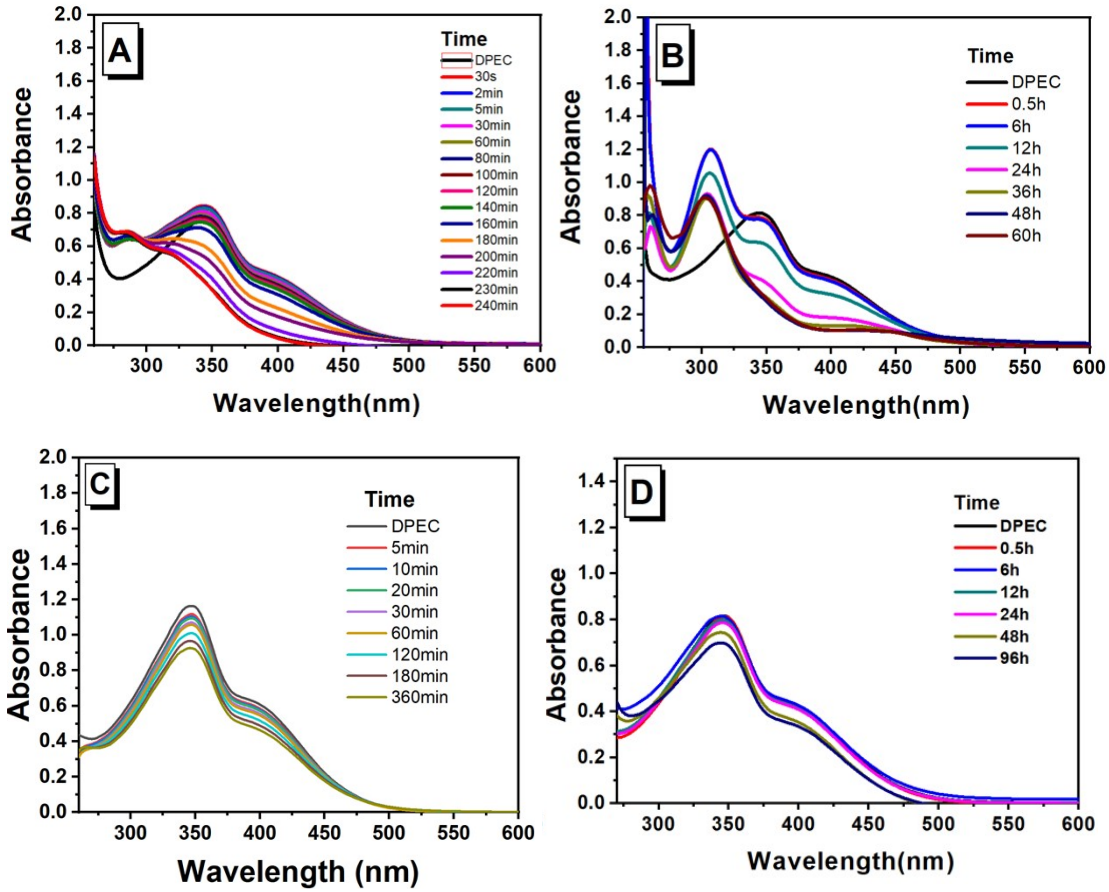


Fig S9. (A) Plot of the changes of absorption at 350 nm of **DPEC** solution in DMSO (30 μM) upon increasing EDA concentrations. (B) Plot of the time changes of absorption peak（350 nm）of **DPEC** solution in DMSO (30 μM) before and after adding 400 μL EDA.



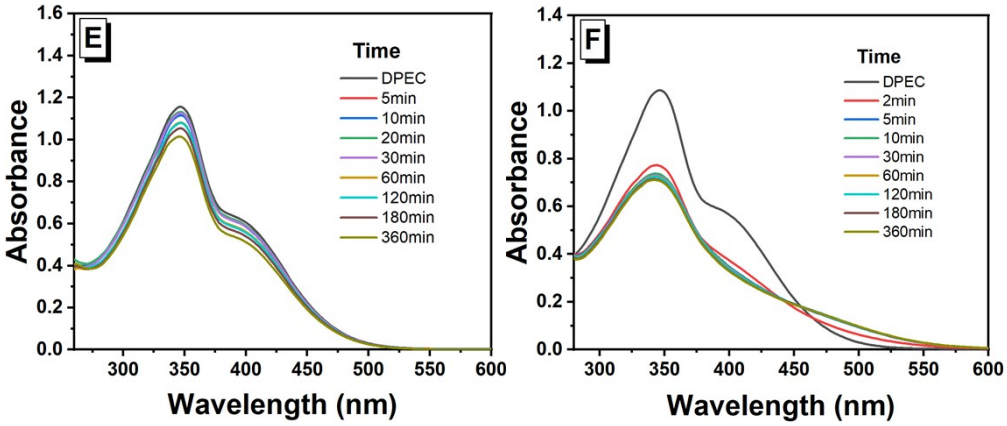


Fig S10. Time-dependent absorption spectra of **DPEC** solution in DMSO (30 μM) before and after adding 400 μL (A) cyclohexanediamine (B) *o*-phenylenediamine (C) ethylamine (D) phenylamine (E) diethylamine (F) propanethiol

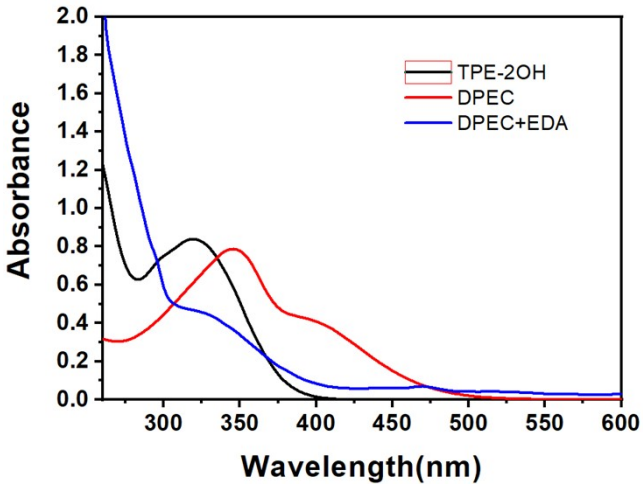


Fig S11. UV−vis absorption spectra in DMSO of **TPE-OH**, **DPEC**, and the reaction product of **DPEC** with EDA; [**DPEC**] = [**TPE-2OH**] = 30 μM.

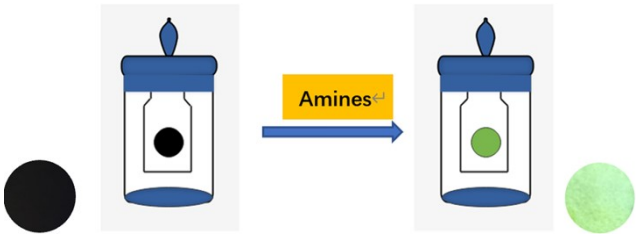
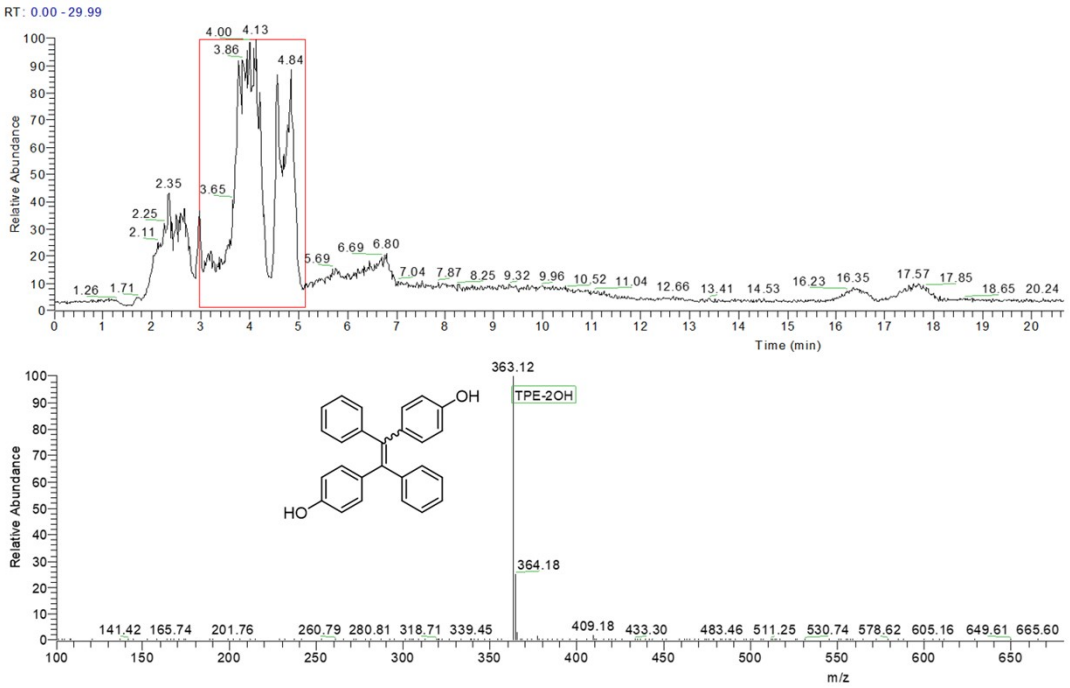


Fig S12. Schematic representation of the subsequent detection of ammonia vapor employing **DPEC** filter paper strips. The real paper-strip photos (outside the chamber) after exposure to amine vapor under a 365 nm UV


RT: 0.00 - 29.99
Relative Abundance
Time (min)
4.00 4.13
3.86
4.84
2.35
3.65
2.25
2.11
5.69
6.69 6.80
1.26 1.71
7.04 7.87 8.25 9.32 9.96 10.52 11.04 12.66 13.41 14.53 16.23 16.35 17.57 17.85 18.65 20.24
363.12
TPE-2OH
OH
HO
364.18
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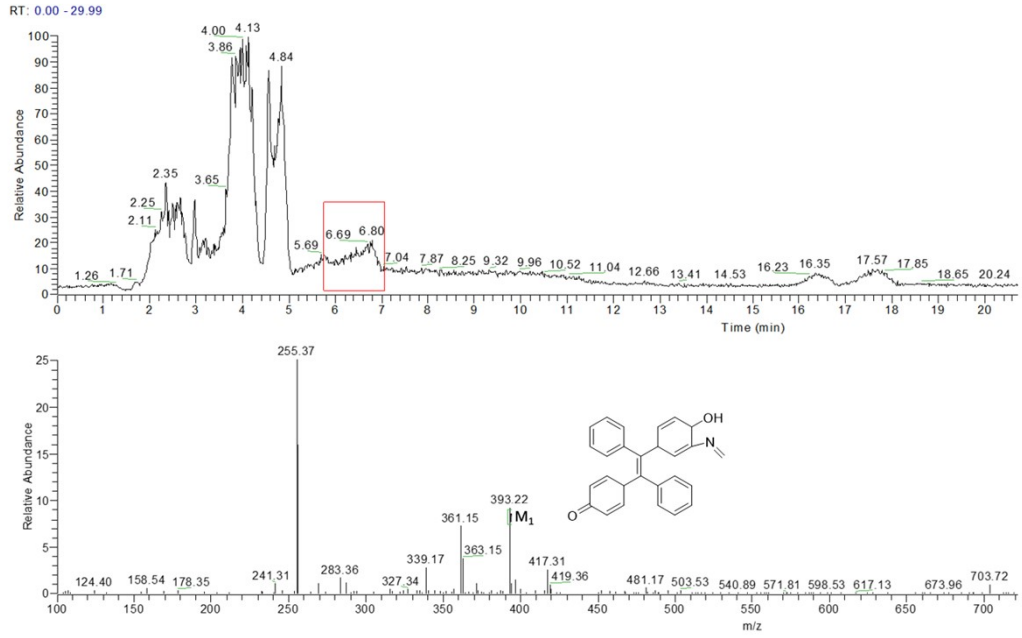
m/z


RT: 0.00 - 29.99
Relative Abundance
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7.04 7.87 8.25 9.32 9.96 10.52 11.04 12.66 13.41 14.53 16.23 16.35 17.57 17.85 18.65 20.24
255.37
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N
O
393.22
M1
361.15
363.15
339.17
417.31
419.36
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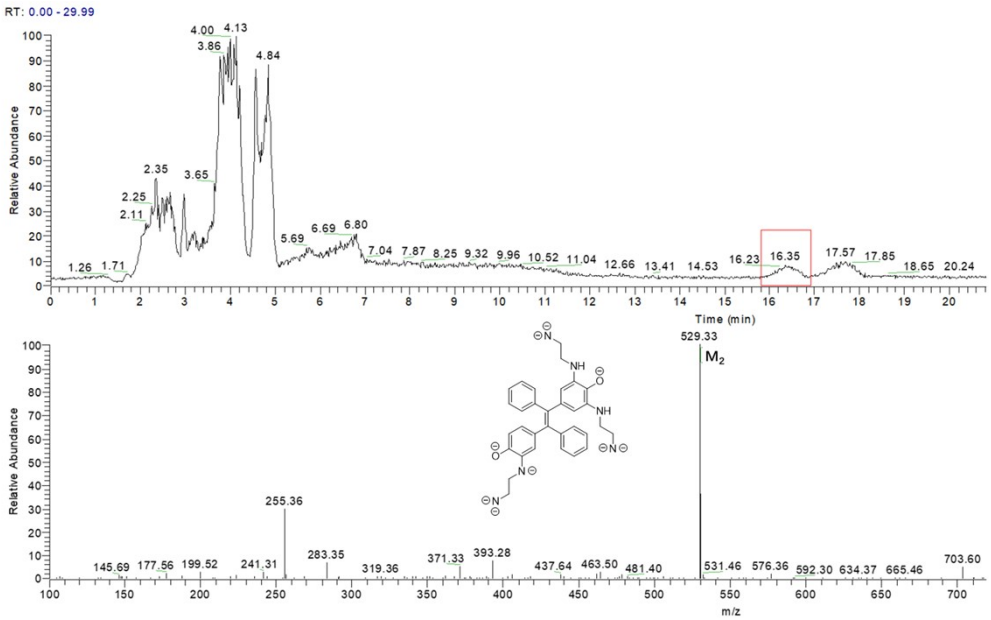

Figure S13. HPLC-MS spectrum of **DPEC** after reacting with EDA. Mobile phase: methyl alcohol /acetonitrile= 4:1.

Table S1 Summary of the HPLC analysis data of DPEC-EDA.

Substances	M (g/mol)	Retention Time (min)
TPE-2OH	**364.44**	**4.13**
M_1	**393.17**	**5.69**
M_2	**529.29**	**16.35**

Determination of limit of detection (LOD)

The calibration curve was first obtained from the respond ratio as a function of the concentration of EDA vapor (Figure S14).

LOD=3δ/S

Where S is the slope of curve equation, and δ represents the standard deviation for FL intensity of test paper in the absence of EDA vapor.

y= 3.2769x+2.2845 (R^2=0.9859)

LOD=3×2.1748/3.2769=1.991 ppm

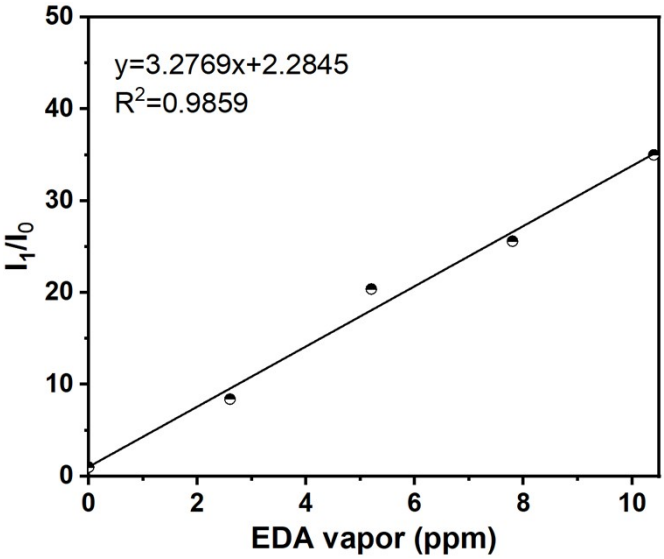

Figure S14. The linear variation of the response ratio (I_1/I_0) under increasing EDA vapor concentrations. Excitation wavelength: 330 nm. The inset shows the linear regression equation.