Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

H-Bond Interaction Traps Vibrating Fluorophore in Polyurethane Matrix for Bifunctional Environmental Monitoring

Wen Li, Mengyuan Qiao, Ziyu Chen, Xin Jin, Yonghao Su, Xuanying Chen, Lifang Guo*, Zhiyun Zhang*, Jianhua Su

Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Centre, Frontiers Science Center for Materiobiology and Dynamic Chemistry, East China University of Science & Technology, Shanghai 200237, China

Contents

1. Materials and General Methods

Synthesis and characterization. All reagents were purchased from commercial sources and used without further purification. The reaction solvents were extra dry solvents. The reverse osmosis water produced by laboratory water purification system (HHitech, SmartQ15). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer and Ascend 600 spectrometer using *d*-chloroform or DMSO-d_6 as solvent and tetramethylsilane (TMS, $\delta = 0$ ppm) as the internal standard. High-resolution mass spectrometry (HRMS) spectra were recorded with a Waters electrospray ionization (ESI) mass spectroscope.

Spectroscopic measurements. Fourier transform infrared (FTIR) spectroscopy was performed with attenuated total reflection (ATR) method using Thermo Scientific Nicolet 6700 FTIR spectrophotometer. A Nicolet CARY 100 spectrophotometer and an Edinburgh Instruments Fluorescence Spectrometer FLS1000 fluorimeter were used to acquire absorption and emission spectra, respectively. All the spectroscopic pure reagents used were obtained through distillation column rectification.

2. Details of the Synthetic Routes

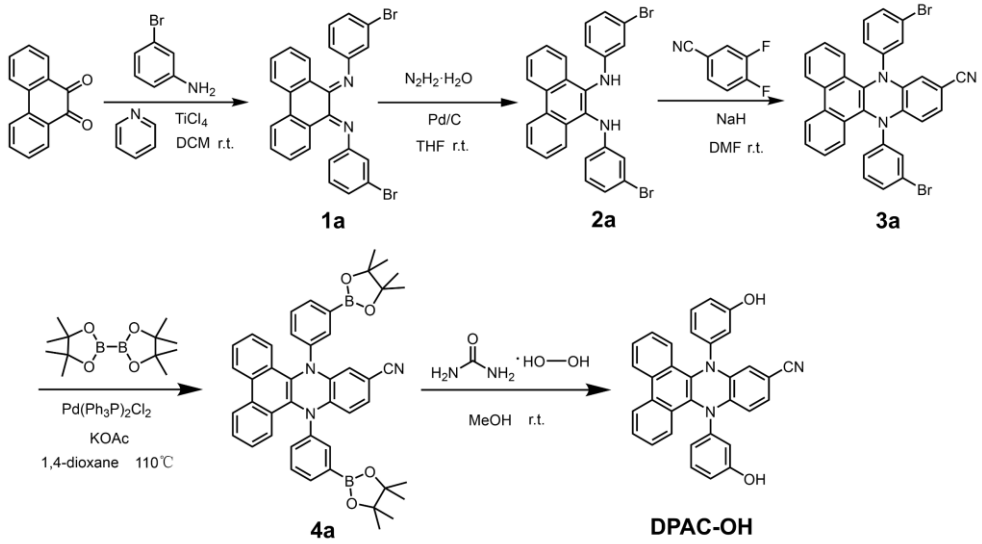

Figure S1. Synthesis routes of **DPAC-OH**.

The synthesis of (9,10)-*N,N*-bis(3-bromophenyl)phenanthrene-9,10- diamine (1a): To a stirred solution of phenanthrene-9,10-dione (1.00 g, 4.81 mmol), 3-bromoaniline (2.46 g, 14.43 mmol) and Pyridine (1.14 g, 14.43 mmol) in anhydrous dichloromethane (40 mL) was added titanium tetrachloride (2.73 g, 14.43 mmol) at room temperature. After stirring for 2 h, the original orange solution gradually became red. After removing the solvent in vacuo, and the residue was washed with ethanol (50 mL) to afford the compound **1a** as a red solid (1.90 g yield 76.6%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.19 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.32 (d, J = 16.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.36, 150.40, 134.46, 134.40, 133.20, 131.35, 129.84, 127.79, 126.95, 124.77, 122.65, 122.53, 118.21, 40.41. HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{26}H_{16}Br_2N_2$, 515.9660, found: 515.9772.

The synthesis of *N,N*-bis(3-bromophenyl)phenanthrene-9,10-diamine(2a)： **1a** (1.00 g, 1.94 mmol) were then mixed with palladium carbon (100 mg) in THF (20 mL), and hydrazine hydrate (0.58 g, 11.64 mmol) was added in batches. This reaction was conducted under a positive pressure of argon. After stirring for 3 h, the resulting mixture was filtered. The filtrate was evaporated in vacuo, and the residue was washed with ethanol (50 mL) to afford the compound **2a** as a red solid (0.91 g yield 90.9%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.69 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.19 (s, 1H), 6.95 – 6.81 (m, 2H), 6.66

(s, 1H), 6.42 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) *δ* 147.75, 130.66, 130.50, 130.20, 129.71, 127.27, 126.90, 124.69, 123.33, 123.12, 122.51, 117.74, 113.60, 77.26. HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{26}H_{18}Br_2N_2$, 517.9816, found: 517.9832.

The synthesis of 9,14-bis(3-bromophenyl)-9,14-dihydrodibenzo[*a,c*] phenazine-11-carbonitrile (3a): To a stirred solution of N-bis (3-bromophenyl) phenanthrene-9,10-diamine (1.00 g, 1.93 mmol) and NaH (0.28 g, 11.58 mmol) in 20 mL DMF was added 3,4-difluorobenzonitrile (0.27 g, 2.9 mmol). This reaction was conducted under a positive pressure of argon at room temperature. After stirring for 3 h, water was added to quench this reaction, a large number of solids precipitated, and the filter was removed to obtain the filter cake. The residue was purified by column chromatography (silica gel, petroleum ether/dichloromethane 1:1) to obtain a white solid (1.03 g yield 86.6%). ^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 8.79 (d, *J* = 10.56Hz, 2H), 8.03 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.73 (s, 2H), 7.62 (dt, *J* = 19.4, 7.8 Hz, 3H), 7.18 (t, *J* = 2.0 Hz, 2H), 7.11 – 7.02 (m, 5H), 7.00 – 6.92 (m, 2H), 6.93 – 6.81 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) *δ* 149.15, 148.23, 148.23, 147.55, 144.88, 136.87, 136.82, 130.87, 130.45, 130.32, 130.21, 128.48, 128.32, 127.64, 127.63, 127.44, 127.41, 127.34, 125.63, 125.33, 124.14, 124.11, 123.39, 123.31, 123.09, 120.23, 119.67, 118.21, 116.25, 109.55, 77.26. HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{33}H_{19}Br_2N_3$, 616.9925, found: 616.9932.

The synthesis of 9,14-bis(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) -9,14-dihydrodibenzo[*a,c*]phenazine-11-carbonitrile (4a)： Compound **3a** (1.00 g, 1.62 mmol) was dissolved in 1, 4-dioxane (10 mL), followed by the addition of 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (2.06 g, 8.1 mmol), $Pd(Ph_3P)_2Cl_2$ (0.03 g,0.162 mmol）and KOAc (0.4 g, 4.86 mmol). The reaction mixture was heated to 110 °C for 2 h. After cooling to room temperature, the reaction mixture was diluted with water (50 mL) and extracted with ethyl acetate (3×50 mL). The combined organic layer was dried over anhydrous $MgSO_4$, filtrated, and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether/dichloromethane 5:1) to give the compound **4a** as a light yellow solid (1.15 g yield 95.0%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.95 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 1.8 Hz, 1H), 8.10 – 7.89 (m, 2H), 7.77 – 7.69 (m, 1H), 7.62 (dt, *J* = 14.6, 7.4 Hz, 1H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.34 – 7.19 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) *δ* 149.31, 146.99, 146.21, 144.55, 136.25, 136.16, 134.76, 131.28, 130.25, 130.11, 129.87, 129.68, 129.53, 129.42, 128.77, 128.72, 128.53, 127.74, 127.18, 126.96, 126.61,

126.54, 125.99, 125.35, 124.49, 124.34, 124.30, 123.33, 123.10, 123.00, 122.34, 118.88, 108.25. HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{45}H_{43}Br_2N_3O_4$, 712.3518, found: 712.3520.

The synthesis of 9,14-bis(3-hydroxyphenyl)-9,14-dihydrodibenzo[*a*,*c*] phenazine-11-carbonitrile (DPAC-OH)： Compound **4a** (1.00 g, 1.41 mmol) was dissolved in MeOH (100 mL), followed by the addition of urea peroxide (0.39 g, 4.23 mmol) at room temperature. After stirring for 7 d, the solution changed from turbidity to clarity. After removed the organic solvent by distillation under reduced pressure, the reaction mixture was diluted with water (50 mL) and extracted with ethyl acetate (3×50 mL). The combined organic layer was dried over anhydrous $MgSO_4$, filtrated, and concentrated. The residue was washed with ethanol (50 mL) to afford the compound **DPAC-OH** as a white solid (0.61 g yield 87.6%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.33 (d, J = 8.4 Hz, 1H), 8.92 (d, J = 8.2 Hz, 1H), 8.34 (d, J = 1.8 Hz, 1H), 8.06 – 7.90 (m, 2H), 7.87 – 7.84 (m, 0H), 7.75 – 7.54 (m, 4H), 6.94 (dt, J = 21.4, 8.2 Hz, 1H), 6.63 – 6.30 (m, 5H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 158.93, 157.41, 157.34, 148.09, 147.75, 146.86, 143.08, 135.32, 134.98, 129.56, 129.33, 129.26, 129.04, 128.88, 128.31, 127.62, 127.29, 126.75, 126.62, 126.40, 125.85, 124.72, 123.27, 123.04, 122.96, 117.99, 109.79, 109.45, 109.01, 108.09, 107.05, 105.91, 104.41. HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{33}H_{21}Br_2N_3O_2$, 491.1634, found: 491.1628.

The preparation of PU$_{DPAC\text{-}OH}$ and PU$_{DPAC}$. The polytetrahydrofuran (Mn = 1000) (3.0 g, 3.0 mmol) and 4, 4-diphenylmethane diisocyanate (MDI) (1.26 g, 5.04 mmol) were placed in a 100 ml beaker, and tetrahydrofuran solution (30 ml) was added and stirred well. Then catalyst dibutyltin dilaurate (EDBTDT) (4 drops) was added dropwise into a beaker and stirred at room temperature for 3 h until the solution was transparent and viscous. Subsequently, chain extenders 1, 4-butanediol (294.00 mg, 3.06 mmol) and **DPAC-OH** (10.00 mg, 0.02 mmol) respectively dissolved in tetrahydrofuran solution (10 ml) were added in sequence and stirred for more than 10 h. Finally, the viscous solution became clear and transparent by centrifugation. Spreading out with a surface dish, a transparent polymer film (**PU$_{DPAC\text{-}OH}$**) could be obtained after the evaporation of the solvent. It is worth noting that the perforated plastic wrap can be used to limit the volatilization rate of tetrahydrofuran to prevent bubbles generation in the film. PU$_{DPAC}$ was prepared by the same method as **PU$_{DPAC\text{-}OH}$**.

3. Structural Characterization

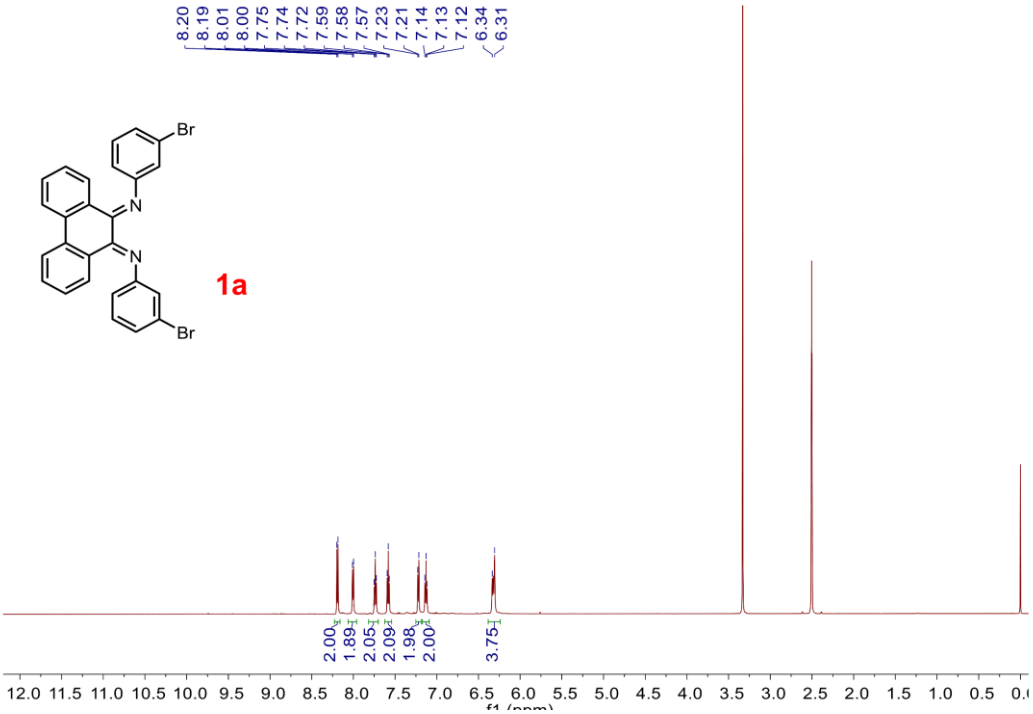

Figure S2. ^{1}H NMR spectrum (600 MHz) of **1a** in DMSO-d_6.

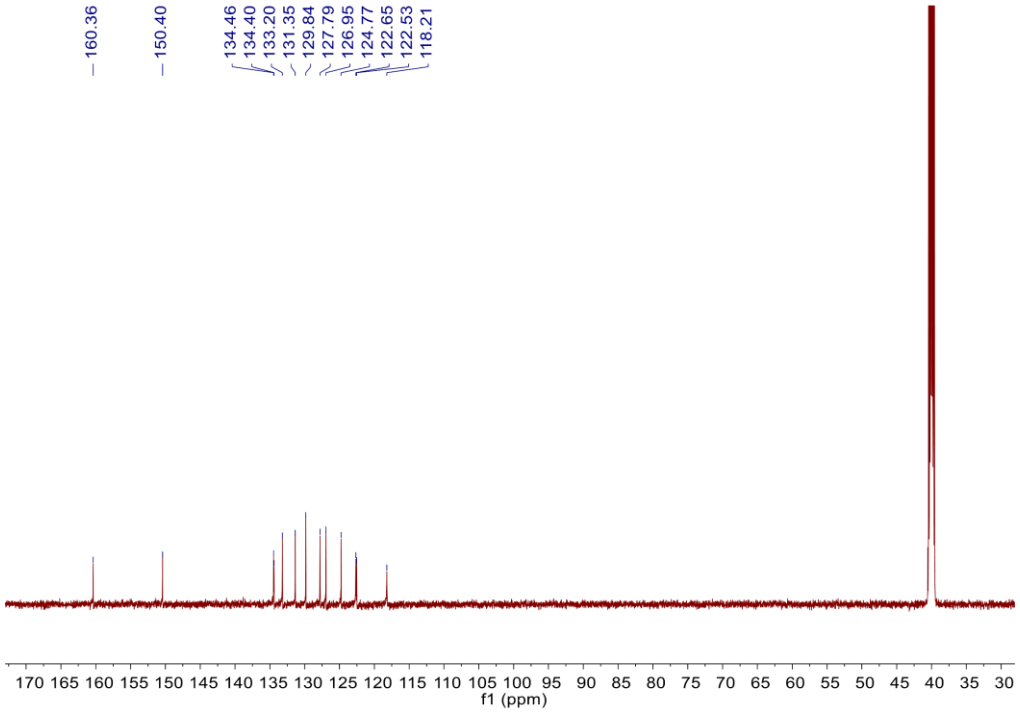

Figure S3. ^{13}C NMR spectrum (151 MHz) of **1a** in DMSO-d_6.

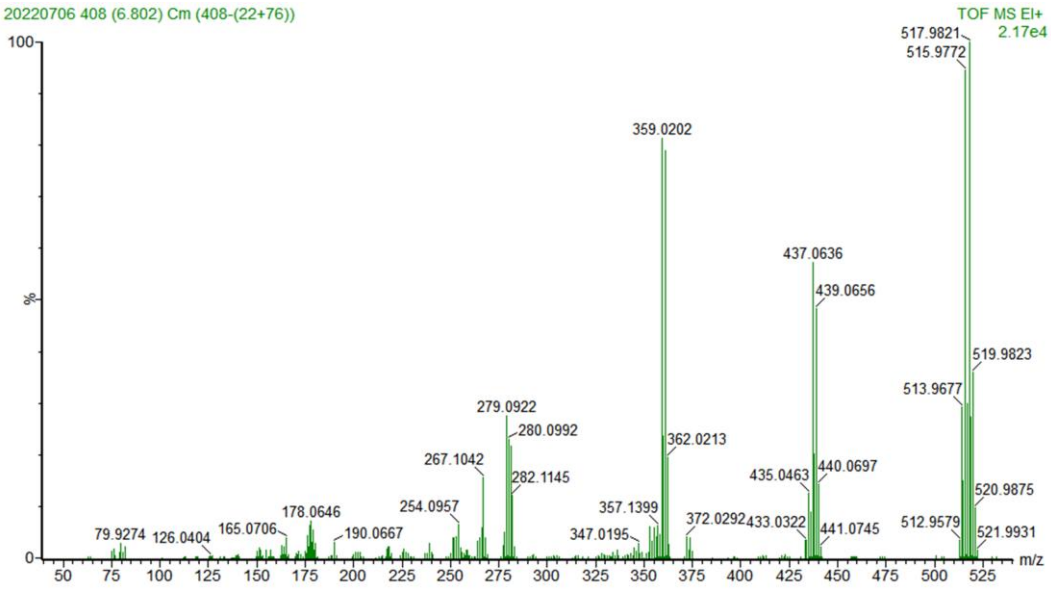

Figure S4. HRMS (ESI) spectrum of **1a**.

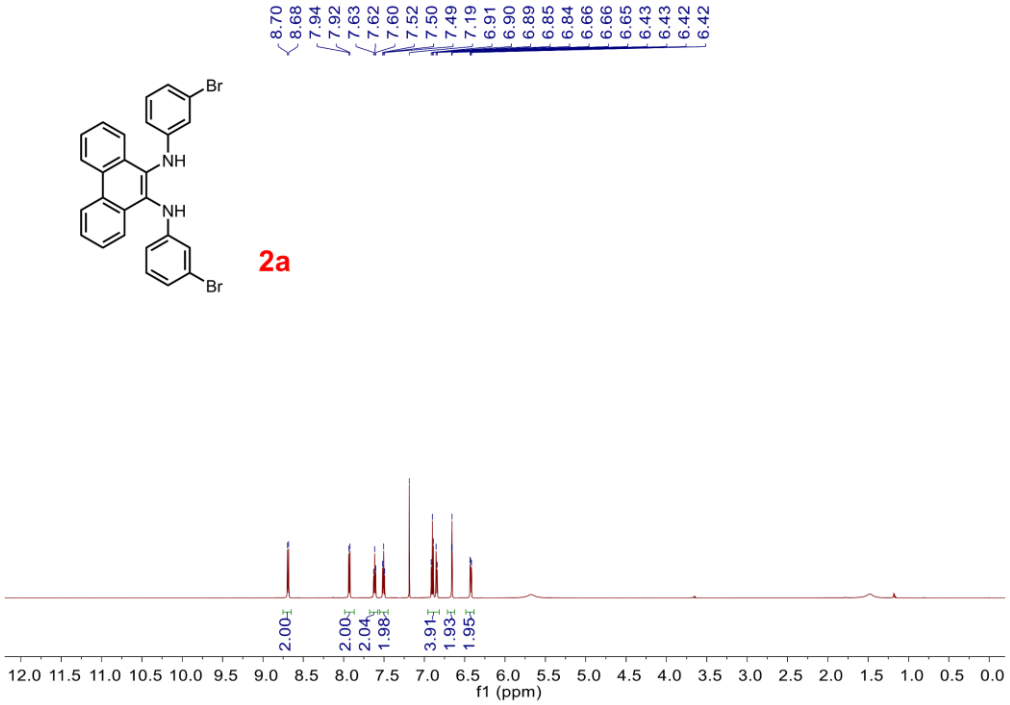

Figure S5. ^{1}H NMR spectrum (600 MHz) of **2a** in Chloroform-*d*.

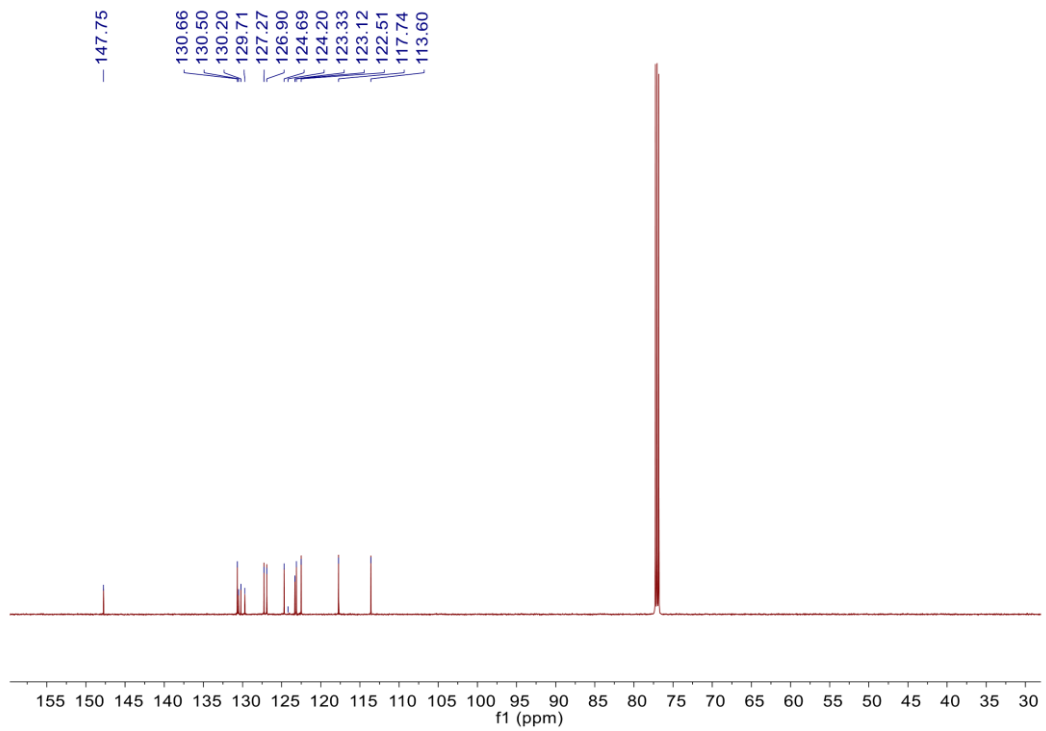

Figure S6. ^{13}C NMR spectrum (151 MHz) of **2a** in Chloroform-*d*.

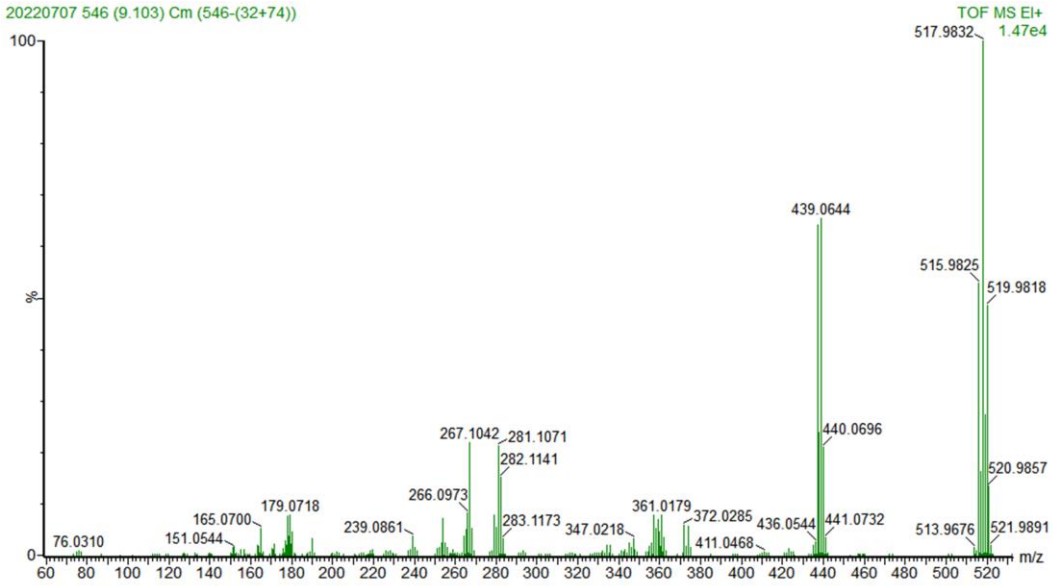

Figure S7. HRMS (ESI) spectrum of **2a**.

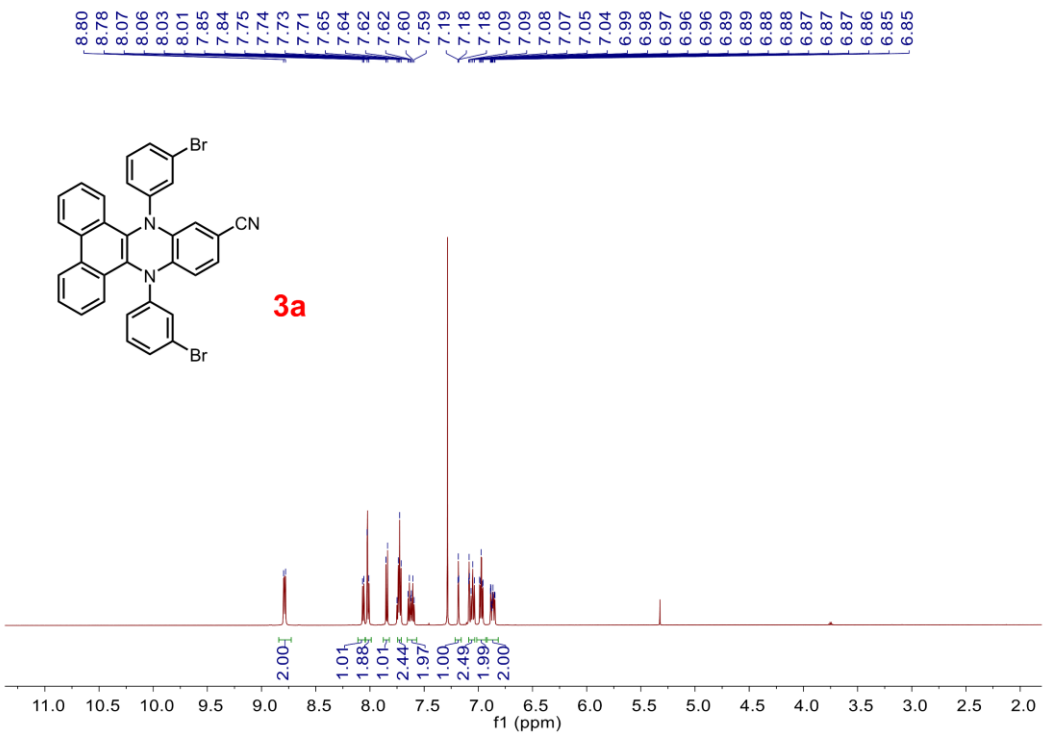

Figure S8. ^{1}H NMR spectrum (600 MHz) of **3a** in Chloroform-*d*.

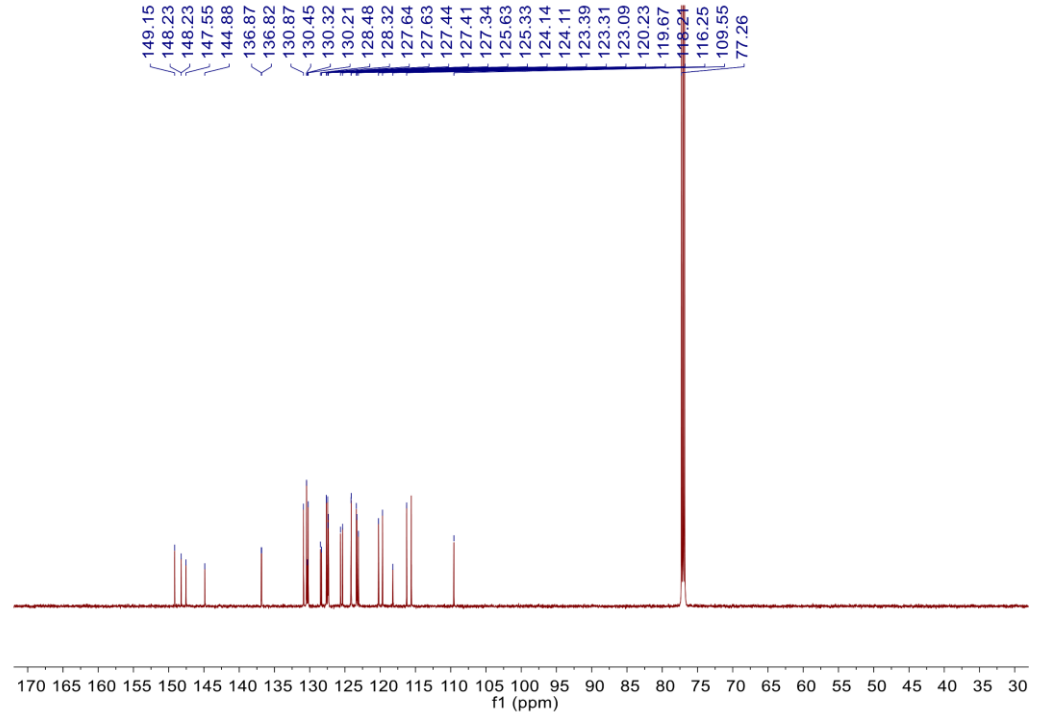

Figure S9. ^{13}C NMR spectrum (151 MHz) of **3a** in Chloroform-*d*.

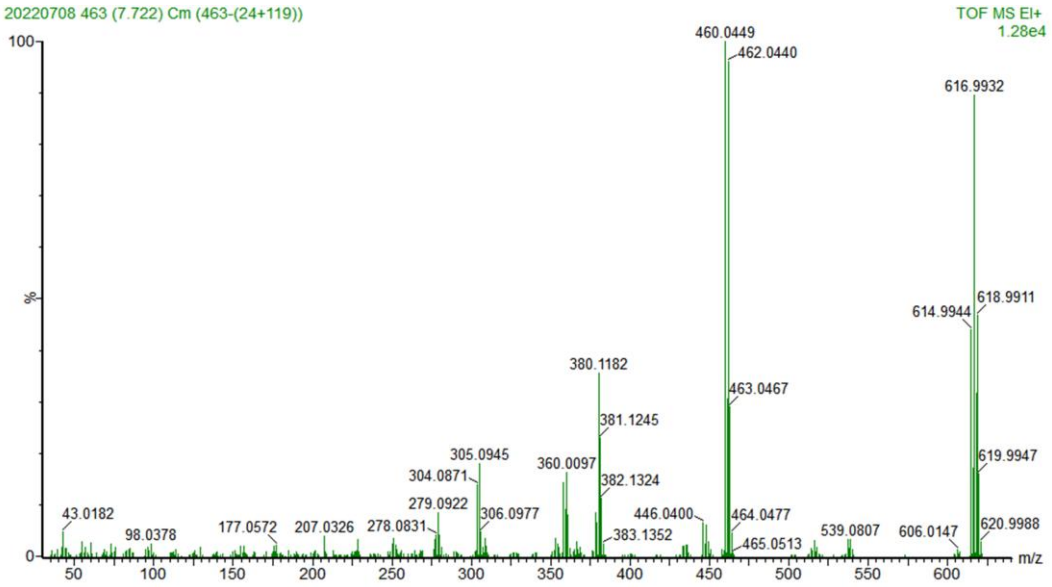

Figure S10. HRMS (ESI) spectrum of **3a**.

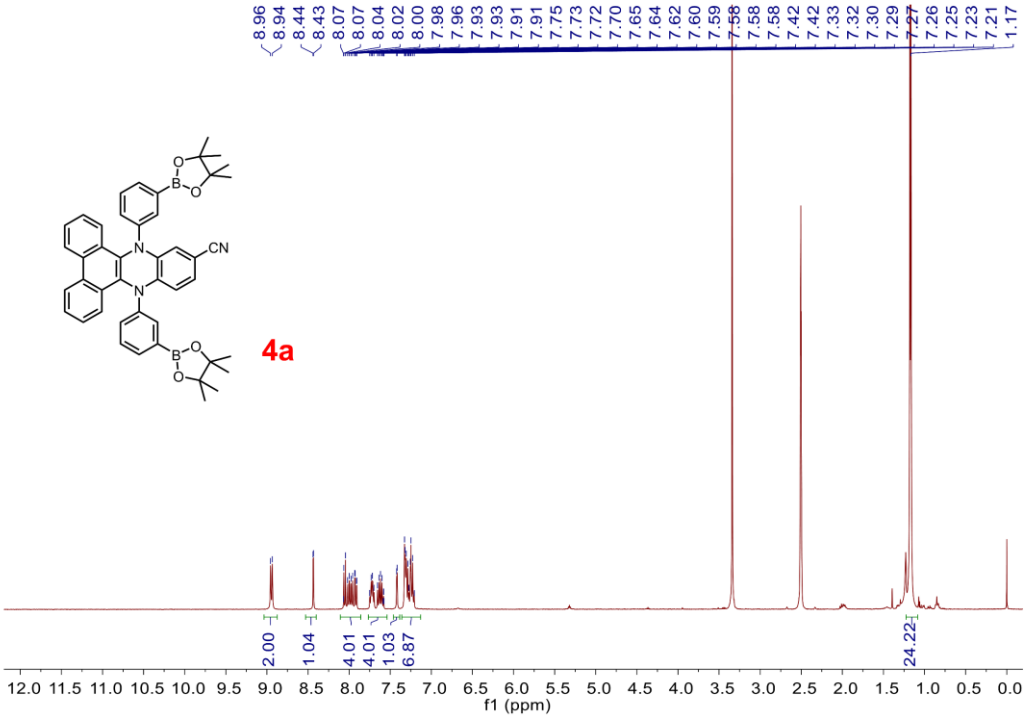

Figure S11. ^{1}H NMR spectrum (600 MHz) of **4a** in DMSO-d_6.

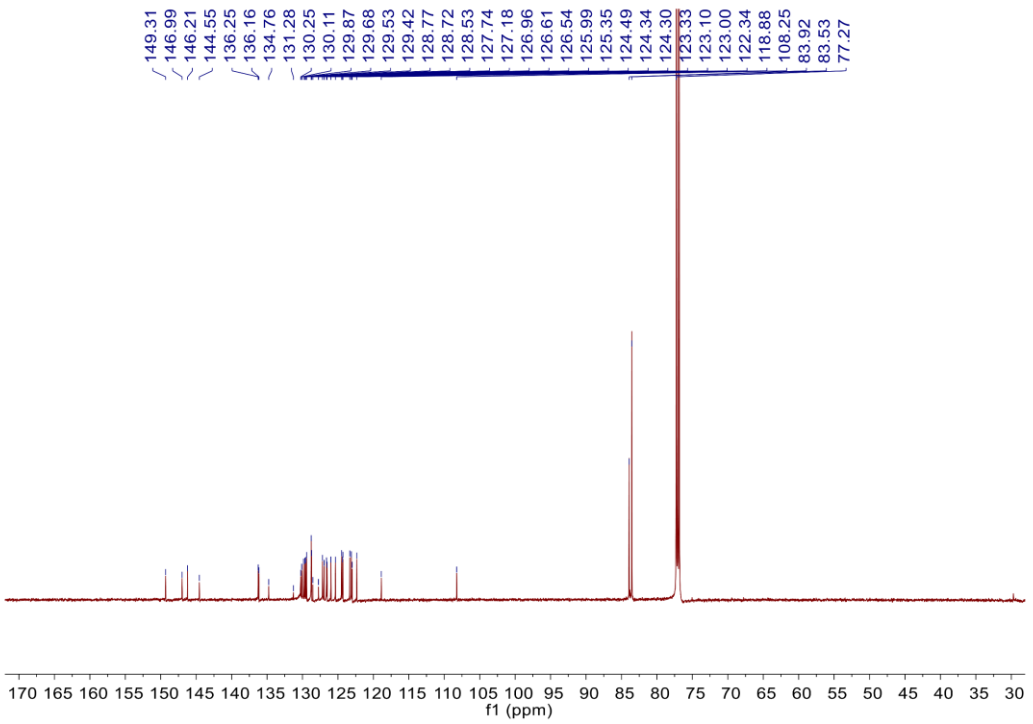

Figure S12. ^{13}C NMR spectrum (151 MHz) of **4a** in Chloroform-*d*.

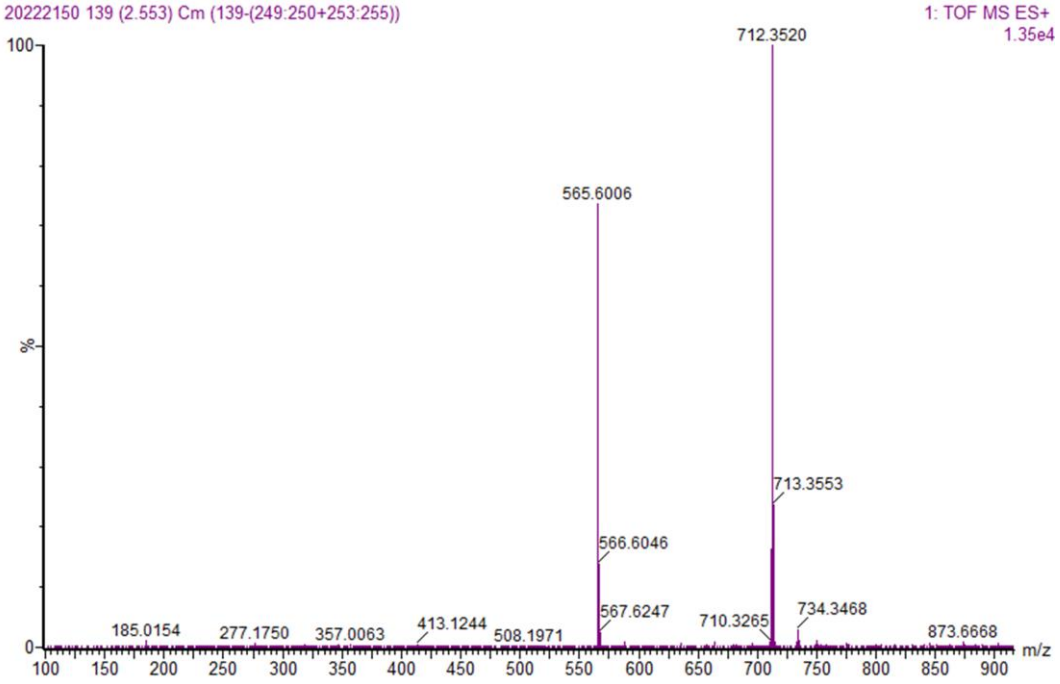

Figure S13. HRMS (ESI) spectrum of **4a**.

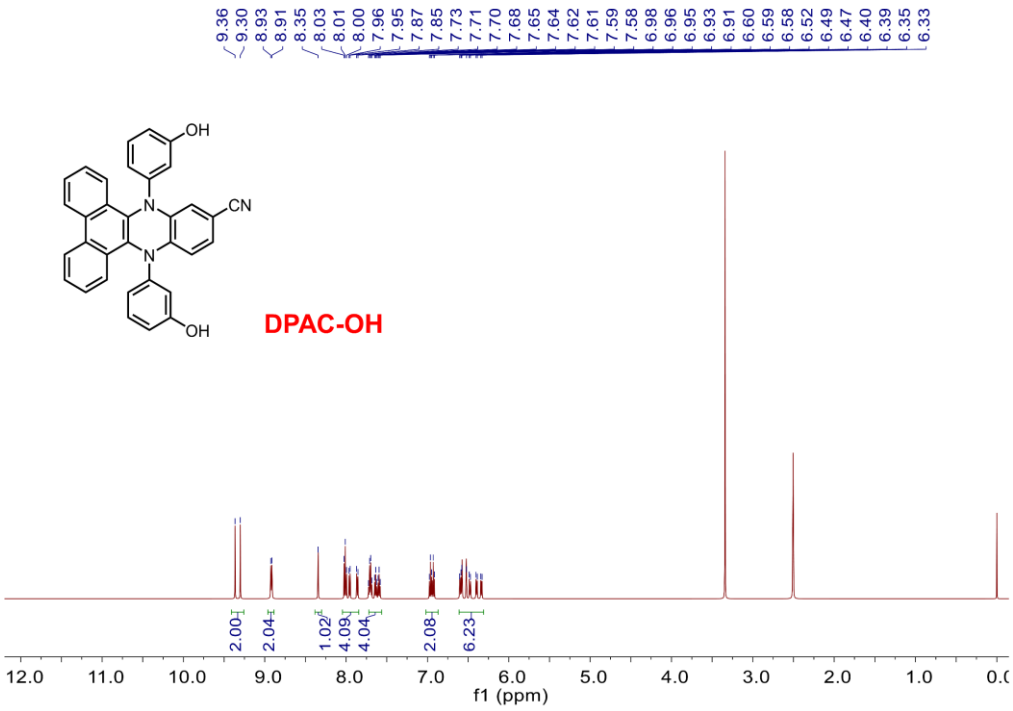

Figure S14. ^{1}H NMR spectrum (600 MHz) of **DPAC-OH** in DMSO-*d*$_6$.

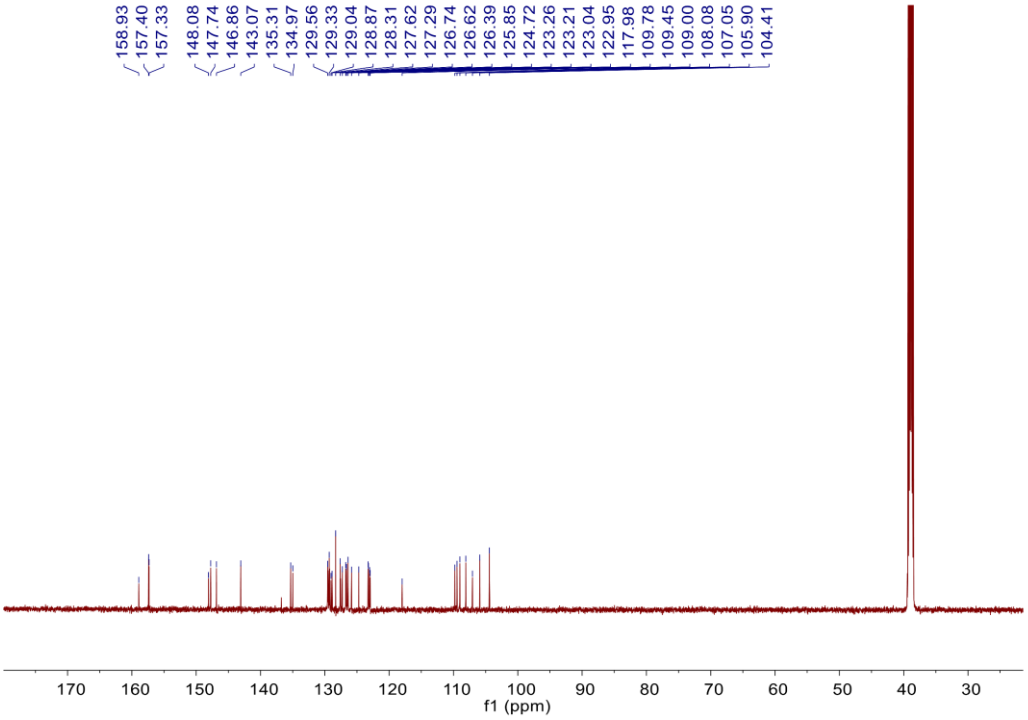

Figure S15. ^{13}C NMR spectrum (151 MHz) of **DPAC-OH** in DMSO-*d*$_6$.

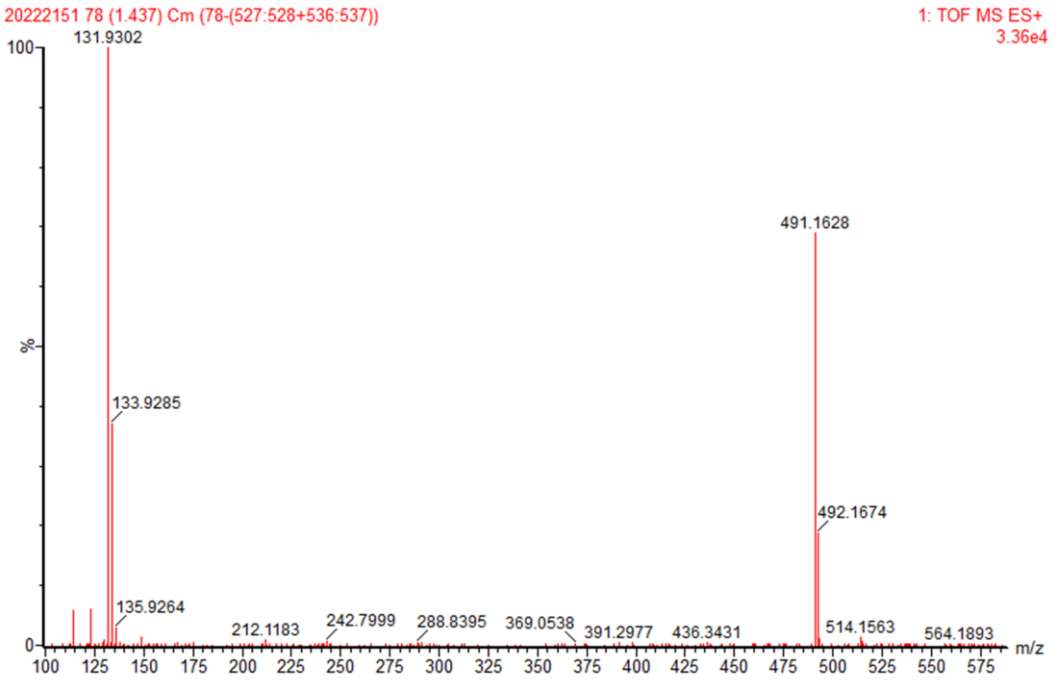

Figure S16. HRMS (ESI) spectrum of **DPAC-OH**.

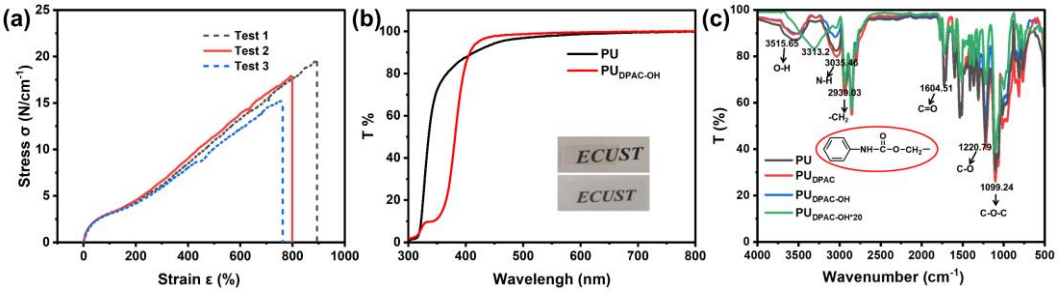

Figure S17. (a) The stress-strain curve of PU three tests. (b) The transmittance of PU and **PU$_{DPAC-OH}$**, and the pictures show that putting a film on the text "ESCUT" will not obscure the view. (c) Fourier transform infrared spectra of PU, PU$_{DPAC}$, **PU$_{DPAC-OH}$** and PU$_{DPAC-OH*20}$ with a twenty-fold **DPAC-OH**.

FTIR spectrum analysis: The reaction between the polytetrahydrofuran and MDI was confirmed by the absence of a characteristic peak at 2275 cm^{-1} - 2250 cm^{-1} and the presence of an N-H stretching vibration characteristic peak at 3035.46 cm^{-1}. The characteristic peaks of 2939.03 cm^{-1}, 1604.51 cm^{-1}, 1220.79 cm^{-1}, and 1099.24 cm^{-1} were derived from the stretching vibration of -CH_2, C=O, C-O, and C-O-C, respectively. Compared with PU and PU$_{DPAC}$, the characteristic peak of -OH at 3515.65 nm is slightly moving towards low wavenumber and tends to become wider. However, the characteristic peak of phenolic hydroxyl group is not seen in **PU$_{DPAC-OH}$**, which is mainly attributed to the added concentration was too low. To verify this hypothesis, we increased the concentration of **DPAC-OH** in PU (PU$_{DPAC-OH*20}$), it can be clearly seen

that the phenolic hydroxyl group moves towards a wide characteristic peak with a lower wavenumber of 3313.2 cm^{-1}, which conforms to the characteristics of intermolecular association hydrogen bonds.

4. Ultraviolet Absorption Spectra

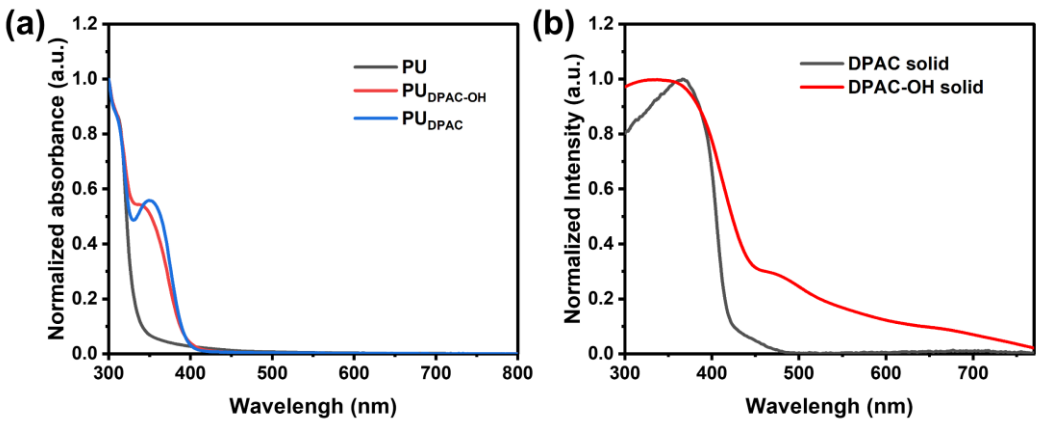

Figure S18. (a) UV absorption spectra of the films. (b) UV absorption spectra of the powders.

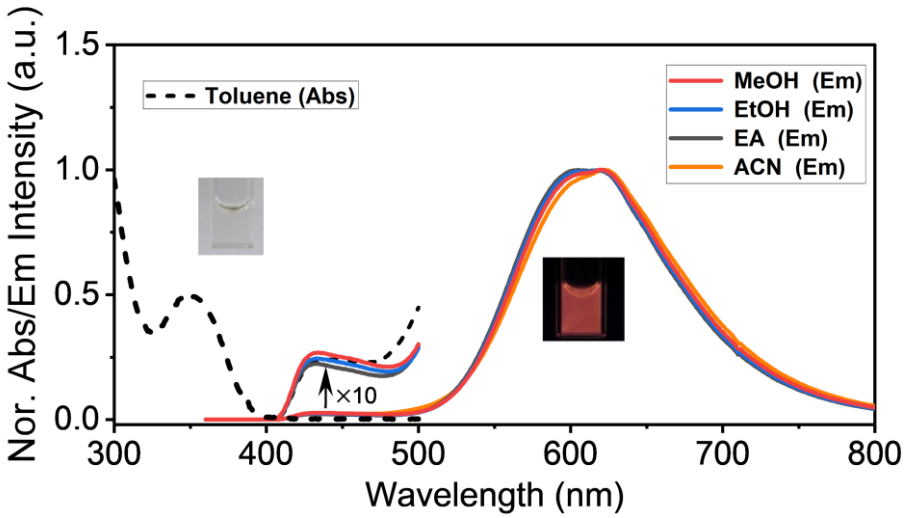

Figure S19. Absorption (Abs) and emission (Em) spectra of DPAC in different solvents (The solution concentration is: 1×10^{-5} mol/L).

5. Photophysical Data Related with the E_T^N

Table S1 The polarity parameters of various solvents and the ratio of fluorescence emission wavelength of **PU$_{DPAC-OH}$**.

Solvent	Relative Polarity (E_T^N)	I_{red} / I_{blue}
Toluene	0.099	1.48025
Diethyl ether	0.117	1.21961
DMSO	0.444	0.80178
ACN	0.46	1.10368
Isopropanol	0.546	0.70749
N-pentanol	0.586	0.66063
N-butanol	0.586	0.8531
N-propanol	0.617	0.84717
EtOH	0.654	0.79824
1，4-butanediol	0.704	0.25441
1，3-propanediol	0.747	0.24903
MeOH	0.762	0.52316
Ethanediol	0.79	0.23334
H_2O	1	0.16242

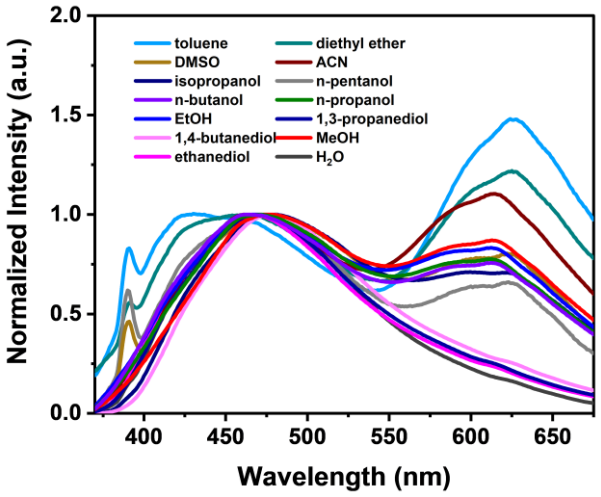

Figure S20. Normalized spectra of **PU$_{DPAC-OH}$** exposed to different solvents under ultraviolet excitation at 360 nm.

6. Rheological Data

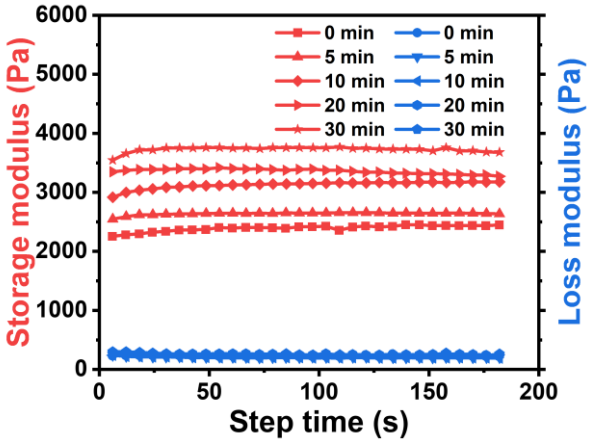

Figure S21. The rheological curve of **PU$_{DPAC-OH}$** film with the process of exposing EtOH solvent vapor.

7. Spectra Data

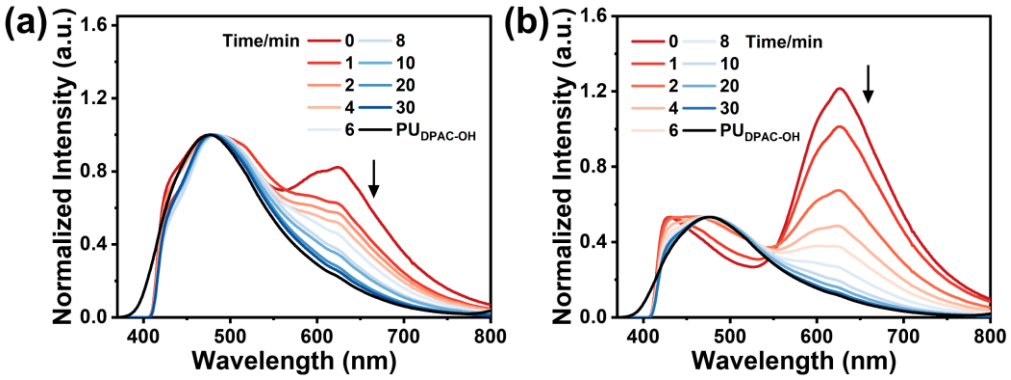

Figure S22. Time-dependent emission spectra of pre-fumigated **PU$_{DPAC-OH}$** with solvent evaporation. (a) MeOH and (b) ethyl acetate (EA).

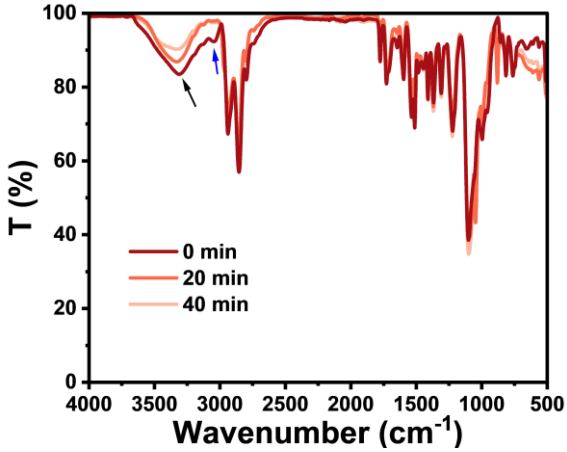

Figure S23. Fourier transform infrared spectra tracking of PU$_{DPAC-OH*20}$ during ethanol fumigation.

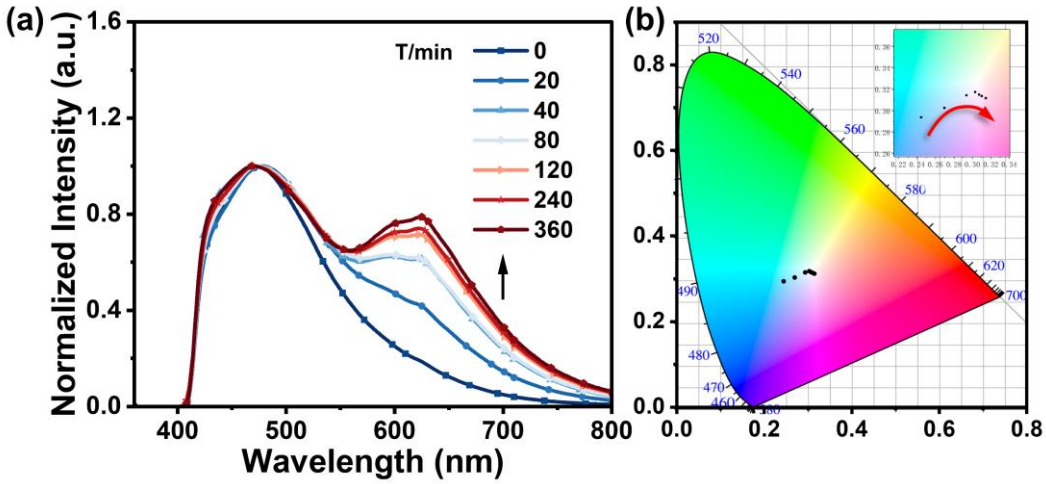

Figure S24. (a) Time-dependent fluorescence spectra of **PU$_{DPAC-OH}$** during EtOH solvent fumigation and (b) the corresponding CIE coordinates.

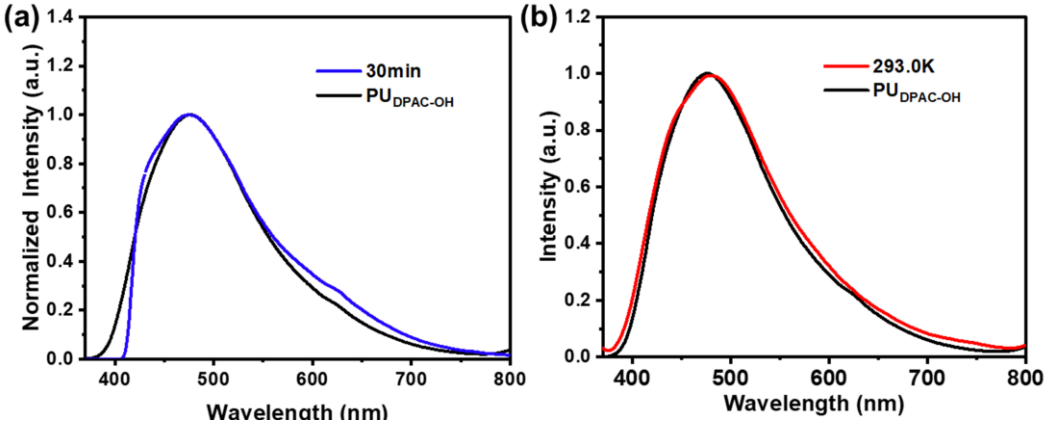

Figure S25. (a) Comparison of fluorescence spectra after fumigation with ethanol: the fluorescence of film (blue line) after evaporating for 30 minutes and the fluorescence of standard sample **PU$_{DPAC-OH}$** (black line). (b) Comparison of fluorescence spectra after temperature change: the fluorescence of film (red line) at 293K and the fluorescence of standard sample **PU$_{DPAC-OH}$** (black line).

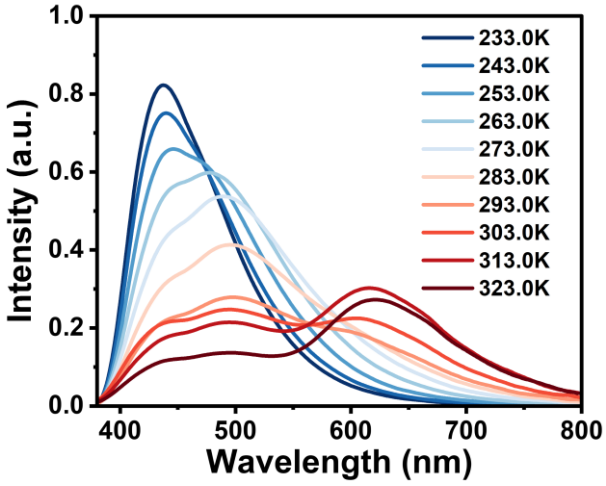

Figure S26. Time-dependent fluorescence spectra of polytetrahydrofuran (Mn = 1000) solution for **DPAC-OH** (The solution concentration is 1×10^{-5} mol/L).