Supporting Information

for

Fast, Sensitive, Selective and Reversible Fluorescent Monitoring of TATP in Vapor Phase

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1. Synthesis and Characterization

Synthesis of compound 2

The compound of dibromoisocyanuric acid (ADBIC, 5.36 g) suspended in 50 mL of oleum ($H_2SO_4 \cdot SO_3$) was slowly added dropwise to a suspension of 1,4,5,8 - naphthalene tetracarboxylic dianhydride (NDA, 5 g) in 50 mL oleum. The temperature of the mixture was heated to 85 °C and maintained at this temperature for 48 h. After cooling to room temperature, the mixture was poured into ice and stirred 1 h. The yellow precipitate was collected by filtered and washed with water, and dried in a vacuum oven. Finally, a pale yellow solid was obtained (6.50 g, 15.30 mmol, yield: 82.2%). This compound can be used for next step without further purification.

Synthesis of compound 3

The compound of **compound 2** (2.3 g) was suspended in acetic acid (40 mL). Then 5-amino-1-pentanol (1.7 mL) was added into the suspension. The reaction mixture was stirred at 120 ºC for 4 h. And then it was cooled to room temperature and filtered by vacuum. The filter cake was washed with water, and then the resulting solid was purified by column chromatography on silica gel with a mixture of $CHCl_2$: acetone (100:1, *v/v*) as eluent, getting a pale yellow solid (734 mg, yield 20%). ^{1}H NMR (δ ppm, 600 MHz, $CDCl_3$): 8.99 (s, 2H, naphthalene), 4.22-4.19 (t, 4H, CH_2), 4.09-4.07 (t, 4H, CH_2), 2.05 (s, 6H, CH_3), 1.81-1.76 (m, 4H, CH_2)，1.75-1.70 (m, 4H, CH_2), 1.53- 1.48 (m, 4H, CH_2); ^{13}C NMR (δ ppm, 151 MHz, $CDCl_3$): δ13C NMR (151 MHz, CDCl3) δ 171.89, 160.74, 139.44, 128.48, 125.17, 123.41, 64.33, 41.00, 28.28, 27.30, 23.71. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ calc. for $C_{28}H_{28}Br_2N_2O_8Na$ 701.0105, found 701.0095.

Synthesis of compound 4

A 100 mL flask was charged with **compound 3** (0.500 g, 0.734mmol), Ruphos (0.045 g, 0.0001 mol)，RuPhos Pd G3 (0.061 g, 0.001 mol) and $CsCO_3$ (0.718 g, 0.003 mol) . The flask was sealed and evacuated/backfilled with nitrogen (3×). A degassed dry 1,4-dioxane (30 mL) was then added, the reaction was flushed again with nitrogen. Following the addition of azetidine (149 µL, 2.2 mmol), the reaction mixture was stirred at 100 °C for 3 h. After cooling to room temperature, the reaction mixture was filtered by diatomite and washed with $CHCl_2$. The filtrate was collected and removed the solvent in vacuum. Finally, a purple powder was obtained (0.325 g, 0.514 mmol, yield: 70%).The residual was title compound without further purification.
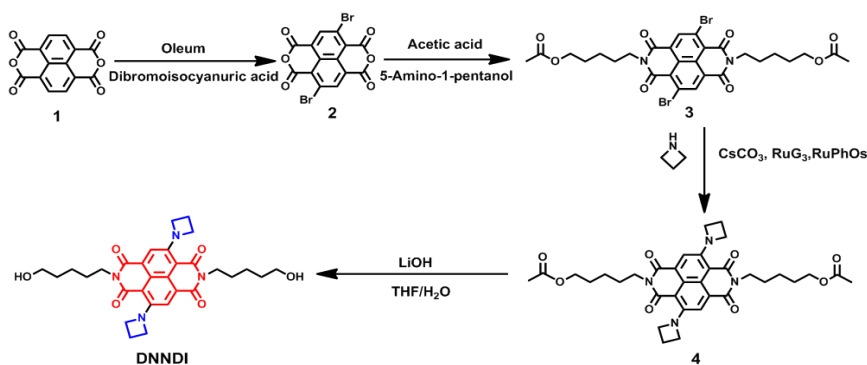
Synthesis of DNNDI

To a solution of residual (compound 4) in previous step in THF (20 mL) was added H_2O (7 mL), LiOH (100 mg) and stirred at room temperature for 30 min. Then the resulting solution was heated to 65 °C and stirred overnight. After cooling to room temperature, the solvent in the reaction mixture was removed in vacuum, and then separated by column chromatography on silica gel with a mixture of $CHCl_2$: MeOH = 20 : 1 as eluent to afford title compound as purple powder (0.254 g, 0.462mmol, yield: 90%). ^{1}H NMR (δ ppm, 600 MHz, $CDCl_3$): 7.95 (s, 2H, naphthalene), 4.29-4.27 (t, 8H, CH_2), 4.18- 4.16 (t, 4H, CH_2), 4.12-4.08 (t, 4H, CH_2), 2.47-2.42 (m, 4H, CH_2), 1.76-1.72 (m, 4H, CH_2), 1.71-1.68 (m, 4H, CH_2), 1.5-1.45 (m, 4H, CH_2); ^{13}C NMR (151 MHz, CDCl3) δ 163.61, 161.87, 150.07, 124.74, 122.22, 120.76, 104.63, 61.92, 54.93, 40.45, 32.05, 27.78, 23.16, 15.94. HRMS (ESI-Orbitrap) m/z: [M+H]$^+$ calc. for $C_{30}H_{36}N_4O_6Na$ 571.2527, found 571.2518.

Synthesis of DNNDI-A

Dimethylamine (130.52 mg, 0.65mmol) was added dropwise to the solution of **compound 3** (200 mg, 0.29 mmol) in 20 mL of 2-methoxyethanol. Then the solution was refluxed for 3 h until the mixture turned to navy blue. After cooling to room temperature, the purple solid was collected by filtering, washed with methanol and dried in a vacuum oven (0.156 g, 0.256 mmol, yield: 87%). ^{1}H NMR (600 MHz, CDCl3) δ 8.45 (s, 1H, naphthalene), 4.21-4.19 (t, 2H, CH_2), 4.08-4.06 (t, 2H, CH_2), 3.18 (s, 6H, CH_3), 2.04 (s, 3H, CH_3), 1.77-1.69 (m, J = 30.4 Hz, 4H, CH_2), 1.52-1.46 (m, 2H, CH_2). HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ calc. for $C_{32}H_{41}N_4O_8H$ 609.2919, found 609.2913.

2. Supplementary Figures

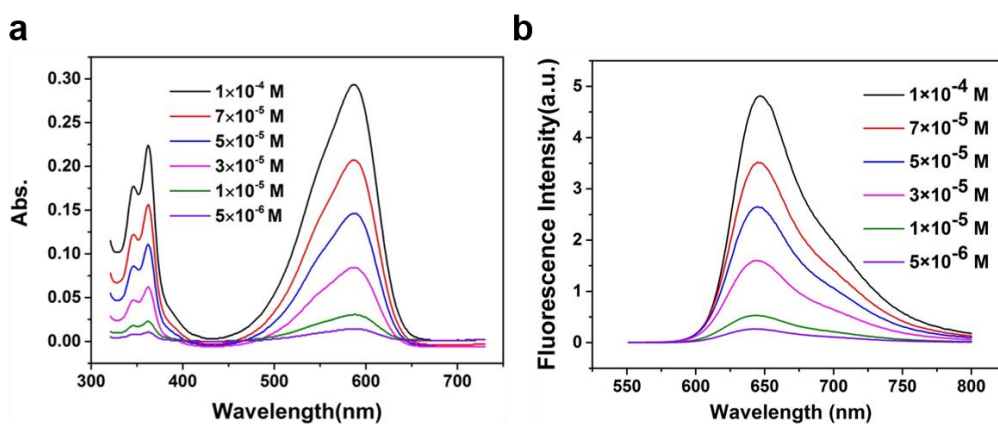**Scheme 1** Schematic illustration for the synthesis route of DNNDI.

Fig. S2 Concentration effection. UV-Vis spectra (a) and fluorescence spectra (b) of DNNDI in $CHCl_3$ at room temperature (λ_{ex} = 360 nm).
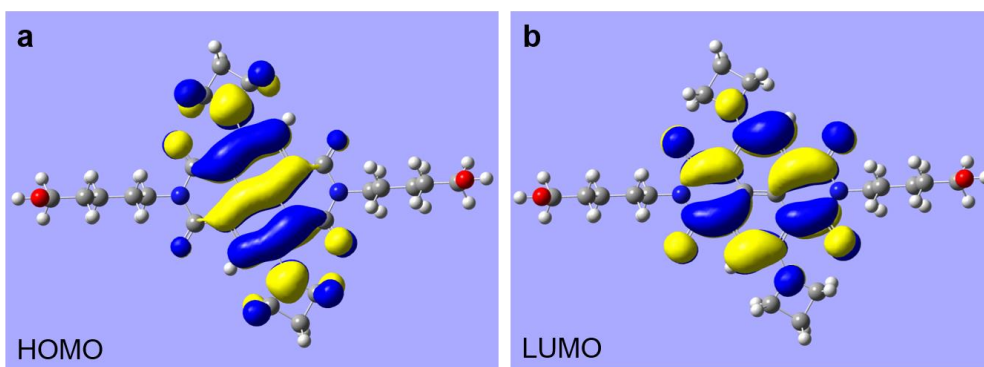

Fig. S2 The calculated electron density distributions of the HOMO (a) and LUMO (b) orbitals for DNNDI in the excited state.

S_6	———————	4.1415 eV	299.37 nm	f = 0.0001
S_5	———————	4.0811 eV	303.80 nm	f = 0.0000
S_4	———————	4.0452 eV	306.49 nm	f = 0.0002
S_3	———————	3.8785 eV	319.67 nm	f = 0.2022
S_2	———————	3.6803 eV	336.89 nm	f = 0.0039
S_1	———————	2.3415 eV	529.51 nm	f = 0.2377
S_o	———————			

Fig. S3 The energy level of structure DNNDI (Note: the density functional theory (DFT) was calculated at vacuum state)
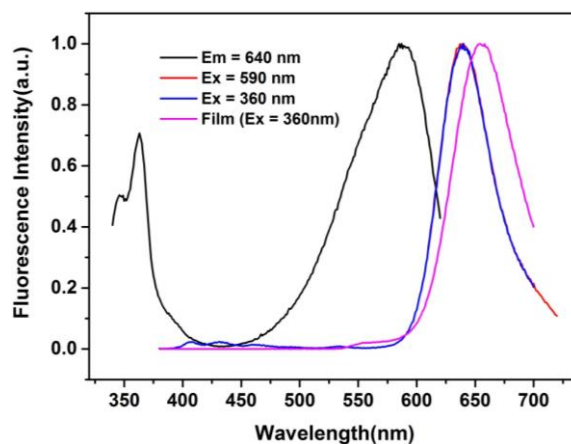
Fig. S4 The normalized excitation (black) and emission (red, blue) spectra of DNNDI in $CHCl_3$ and the emission spectrum (magenta) of DNNDI film with test paper as a substrate.
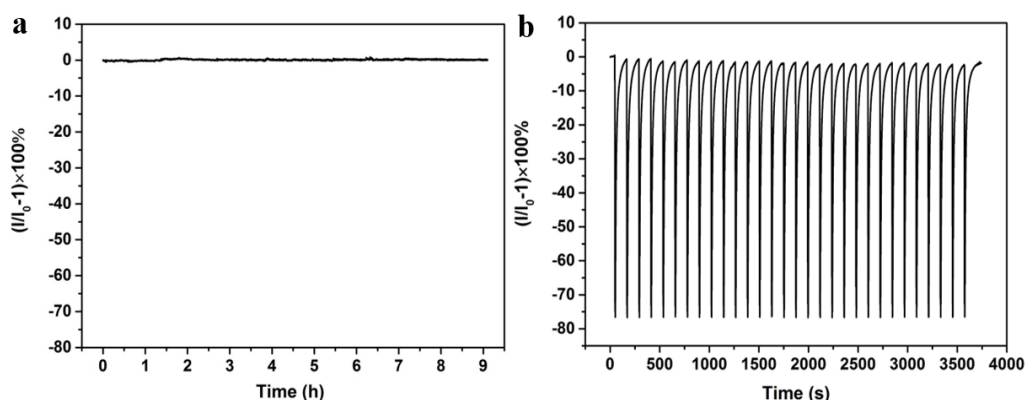
Fig. S5 (a) The photochemical stability of DNNDI-based fluorescent film (λ_{ex} = 360 nm, λ_{em} = 650 nm); (b) Reversibility test of the film response to acetone saturated vapor at room temperature.

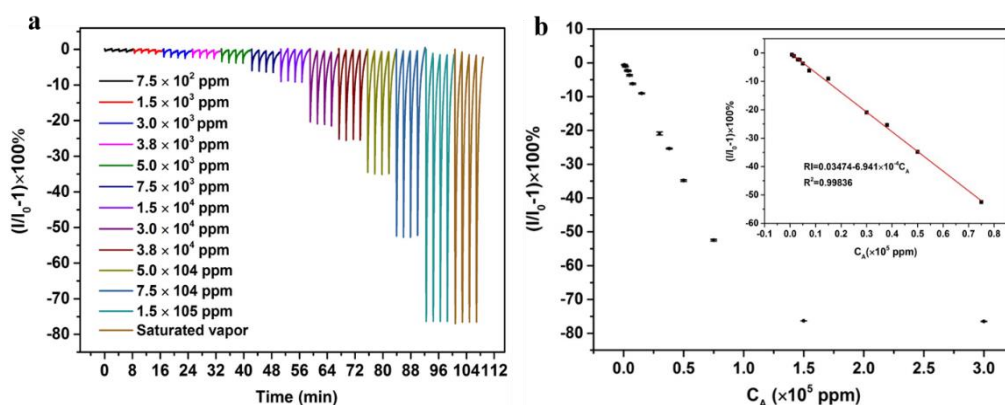**Note:** The measurements were done on a homemade device.

Fig. S6 (a) Fluorescent intensity variation of DNNDI film monitored at 650 nm (λ_{ex} = 360 nm) responding to different concentrations of acetone vapor. (b) Scatter map of the film variation responding to different concentrations of acetone vapor. Inset: a plot of the differences in the response intensities against the concentrations of acetone.

Solvent	TOL	DCM	THF	EA	DIO	Acetone	DMF	Film
Q.Y.(%)	61.05	48.77	32.52	28.42	42.76	21.52	22.03	14.72

Table S1 The fluorescence quantum yields of DNNDI in different solvents.

Note: TOL (toluene), DCM (dichloromethane), THF (tetrahydrofuran), EA (ethyl acetate), DIO (1,4-dioxane), DMF (*N*,*N*-dimethyformamide).

Methods	DL	Response time	Linear range	Reversibility	References
Electrochemistry	<100 ppt (g)	-	-	No	12
QCL-PAS	58 ppb (g)	-	-	No	14
Fluorescence	0.5 ppm (g)	>10 s	30-80ppm	No	20
Fluorescence	0.2 ppb (g)	100 s	10-1000ppt	No	25
Fluorescence	0.1mg (l)	>15 min	-	No	27
Fluorescence	0.1 mg (s)	10 min	0.1-2.0 mg	No	28
Fluorescence	0.5 mg (l)	30 min	0.5-100 mg	No	29
Fluorescence	3 mg (s)	1h	3-25 mg	No	30
Fluorescence	**0.5 μg/mL (g)**	**1s**	**0.5-8 μg/mL**	**Yes**	**This work**

Table S2 Comparison of present work with the reported methods on the detection of TATP.

Note: "g" means the detection target was TATP vapor; "l" means the detection target was TATP solution; "s" means the detection target was TATP powder.

3. The Luminescent Properties of DNNDI and DNNDI-A

To further demonstrate the importance of azetidine substituent, we synthesized a control compound modified by dimethylamine substituent named as DNNDI-A. As shown in Fig. R2, DNNDI shows much stronger fluorescence emission both in solution and film state compared with DNNDI-A.
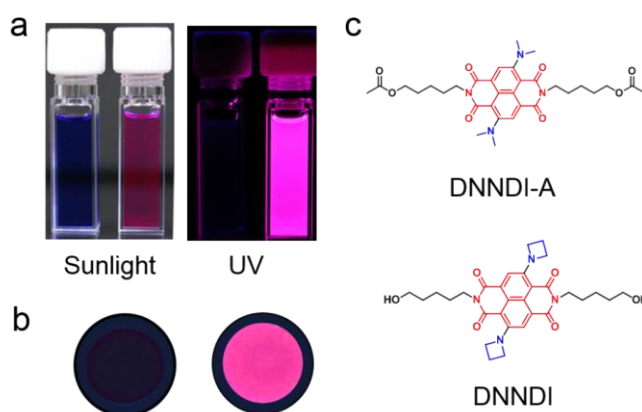

Figure S7 (a) The pictures of control compound DNNDI-A and DNNDI in CHCl$_3$ solutions under sunlight and UV light (365 nm); (b) The pictures of control compound DNNDI-A and DNNDI in film state under UV light (365 nm); (c) The structures of DNNDI and control compound DNNDI-A.

4. The Fabrication Process of the Test Paper

Commercially available filter paper (Whatman®, standard number: No GB/T1914-2007) was employed as the substrate for fabrication of the sensing films. 20 μL of the DNNDI solution (1×10^{-4} mol/L) in the mixed solvents (toluence: MeOH = 2: 1) was dropped onto the filter paper without any special treatment. After 5 minutes for drying in air, the sensor paper was ready to be used in the device.

5. The Stern-Volmer (Ksv) Analysis for TATP Quenching

Quenching of fluorescence can be determined by the Stern-Volmer equation: [1-3]

$$\frac{I_0}{I} = 1 + K_{SV}[Q]$$

Here I_0 and I are the fluorescence intensities in the absence and presence of TATP vapor, respectively, $[Q]$ is the concentration of quencher, and K_{SV} is the Stern-Volmer constant which is related to the quenching efficiency. The standard deviation of the K_{SV} was calculated by 15 determination results. ($K_{SV} = 0.00342$)
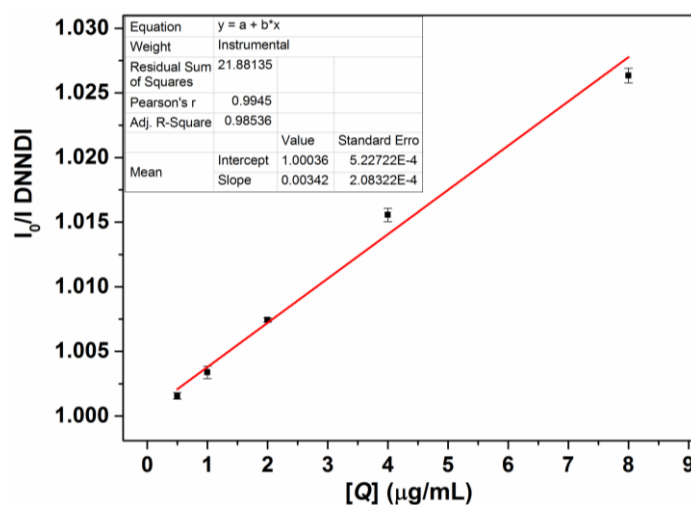

Equation	y = a + b*x	
Weight	Instrumental	
Residual Sum of Squares	21.88135	
Pearson's r	0.9945	
Adj. R-Square	0.98536	
	Value	Standard Erro
Mean Intercept	1.00036	5.22722E-4
Slope	0.00342	2.08322E-4

Fig. S8 Automated plot generation of Stern–Volmer equation.

6. NMR Spectra and MS Spectra of Intermediates and Target Molecule

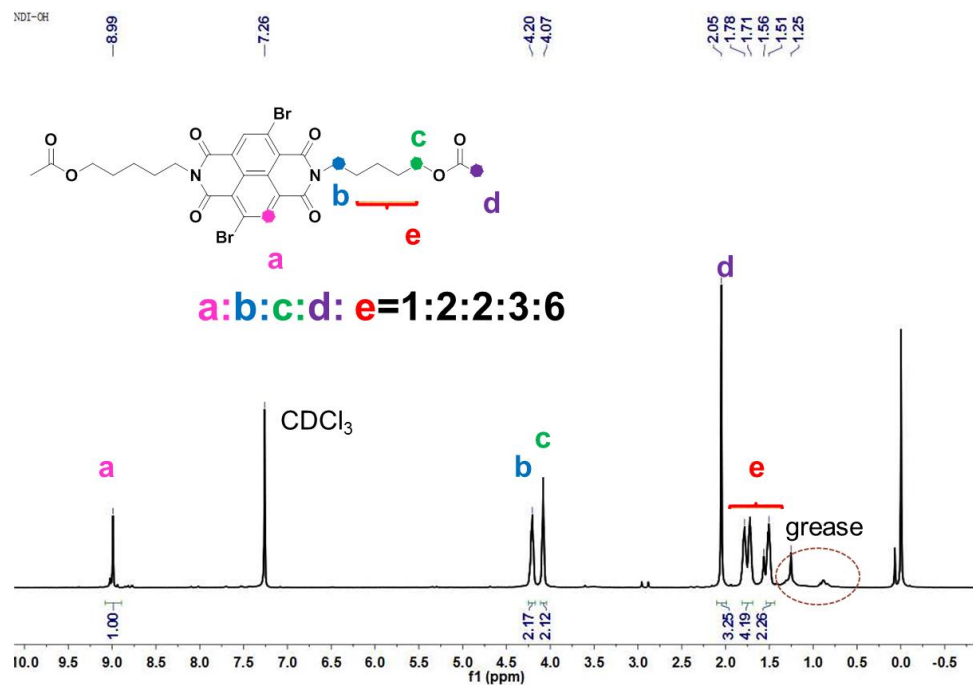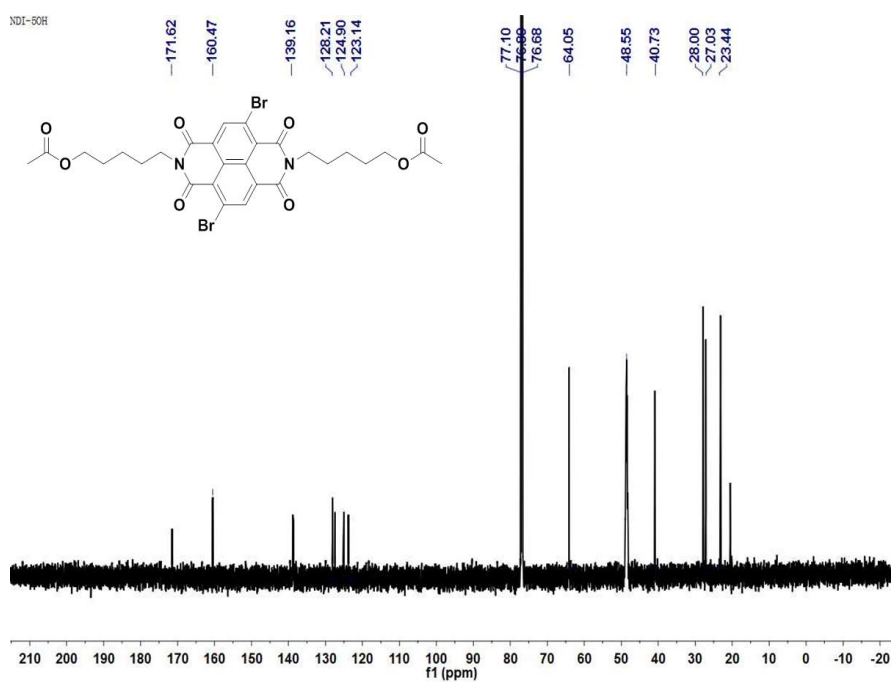**Fig. S9** The ^{1}H NMR spectrum of compound 3

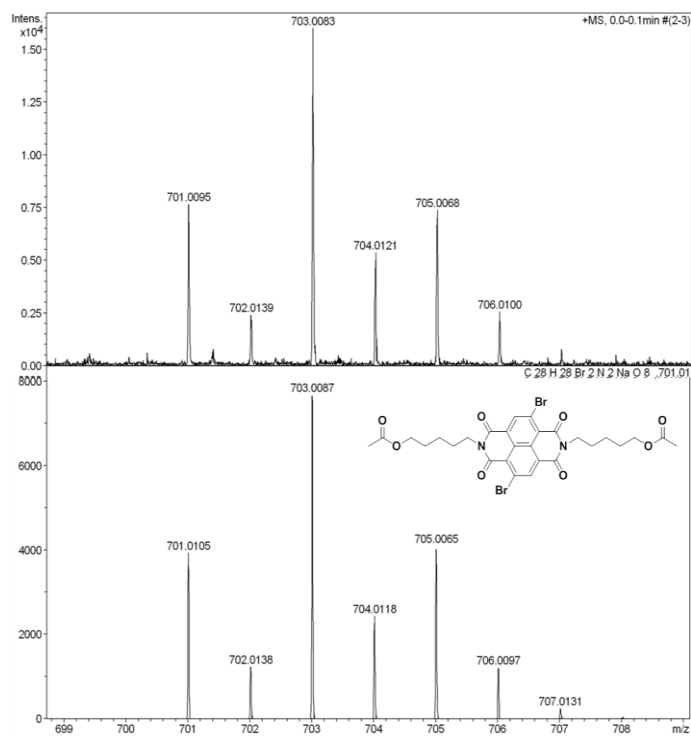
Fig. S10 The ^{13}C NMR spectrum of compound 3

Fig. S11 The MS spectrum of compound 3
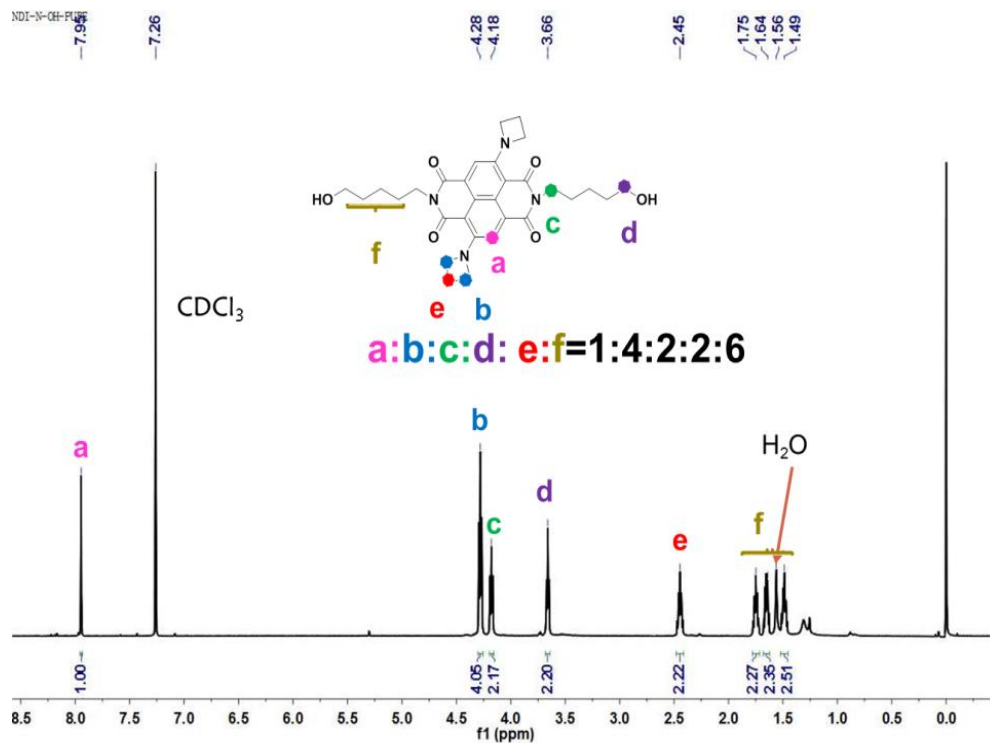

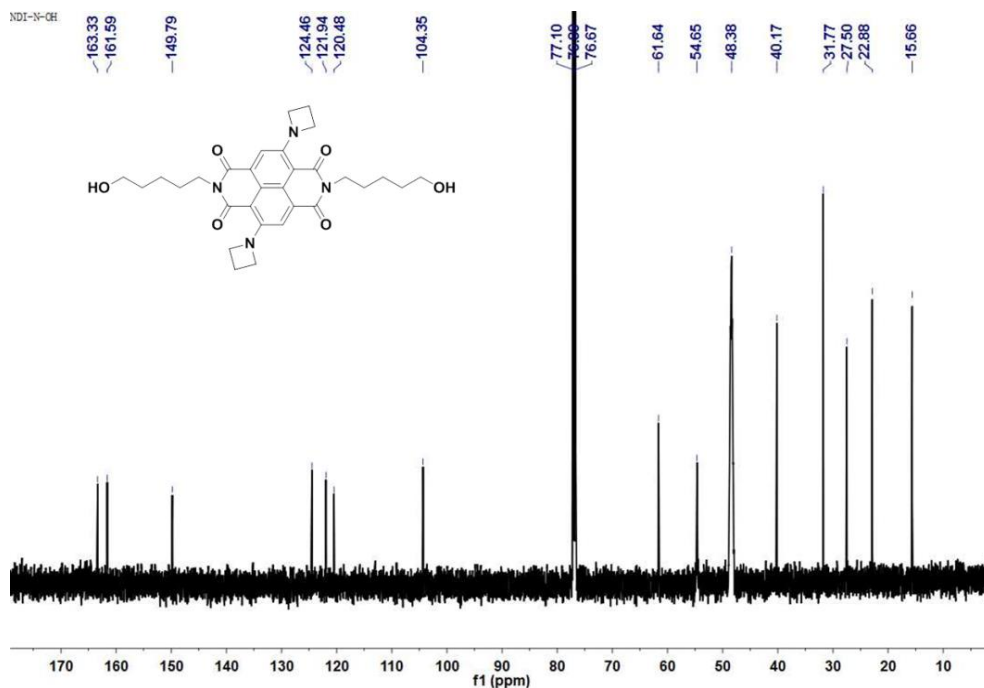**Fig. S12** The ^{1}H NMR spectrum of DNNDI

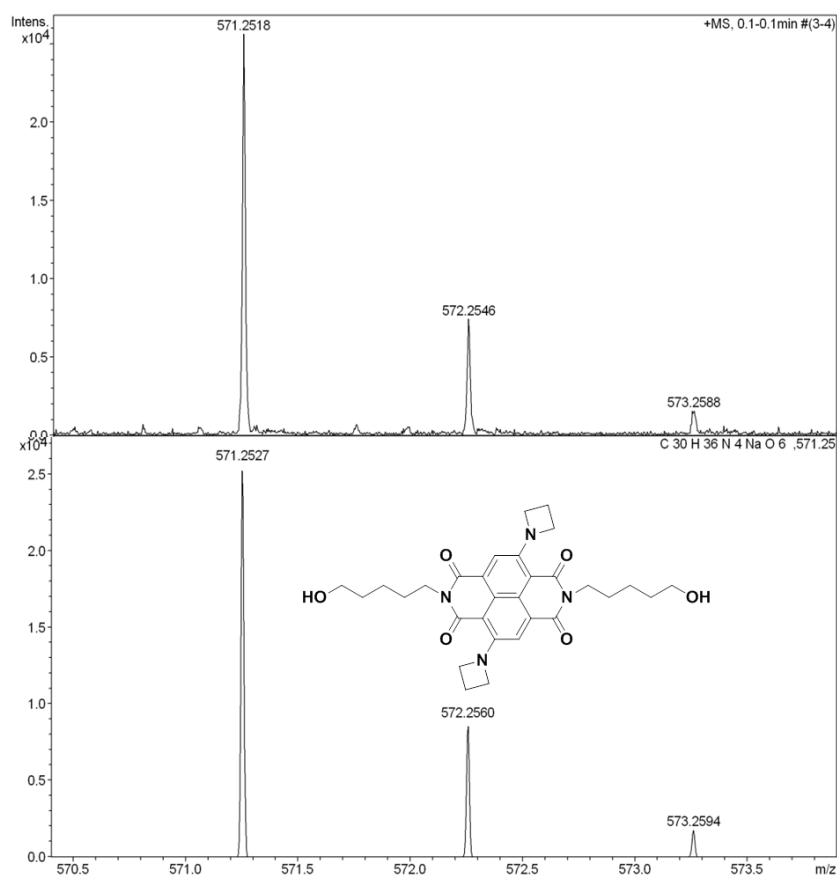**Fig. S13** The ^{13}C NMR spectrum of DNNDI
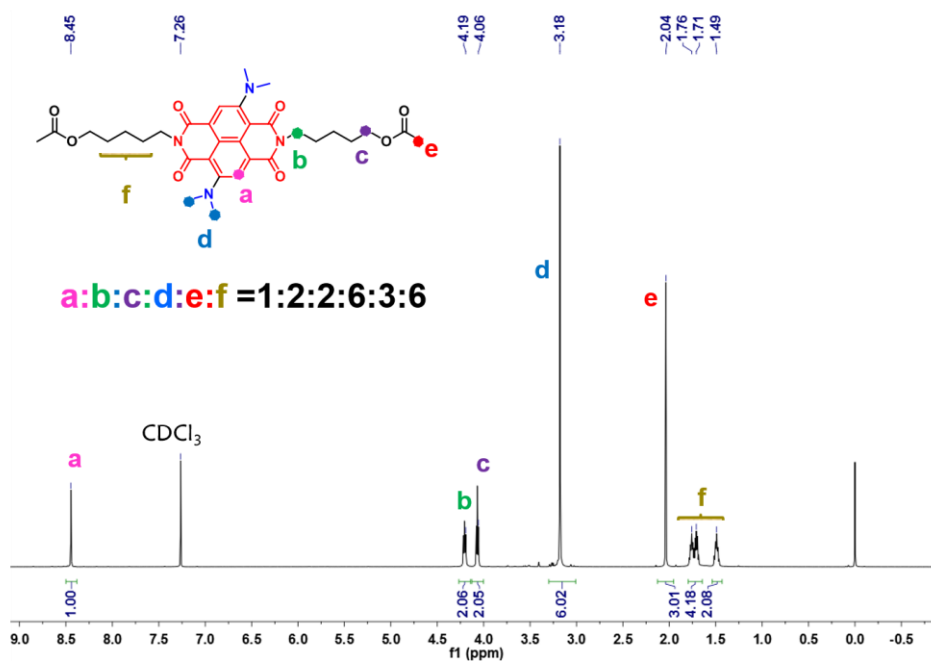

Fig. S14 The MS spectrum of DNNDI

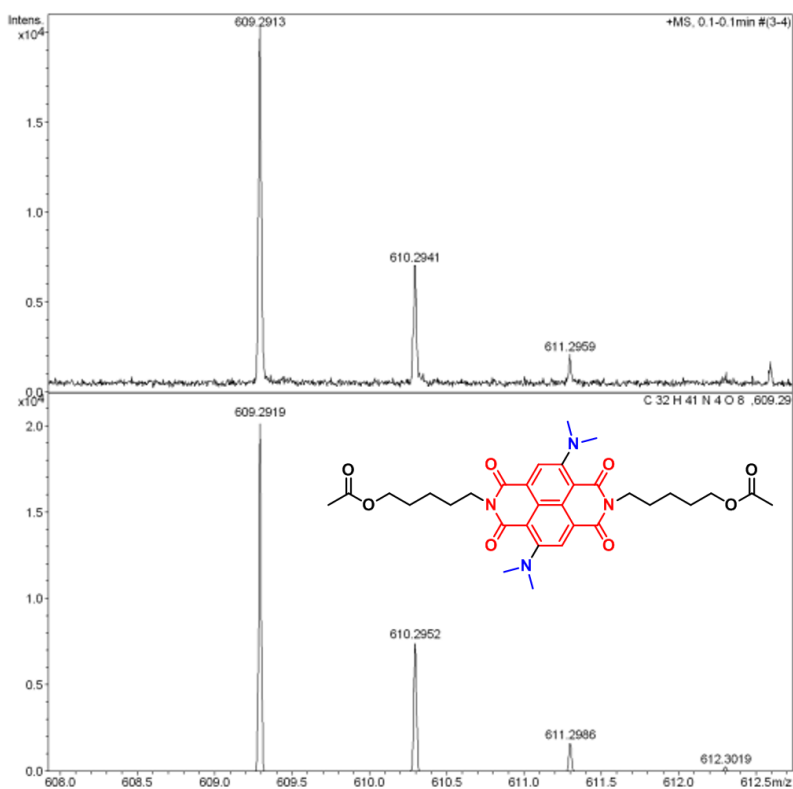**Fig. S15** The ^{1}H NMR spectrum of DNNDI-A

Fig. S16 The MS spectrum of DNNDI-A

References:

[1] J. R. Lakowicz, Principles of Fluorescence Spectroscopy, Kluwer Academic/ Plenum Publishers, New York, 1999, 239.

[2] W. B. Chen, X. Wang, X. J. Tu, D. J. Pei, Y. Zhao, X. Q. Guo, *Small*, 2008, **4**, 759–764.

[3] K. P. L. Kuijpers, C. Bottecchia, D. Cambié, K. Drummen, N. J. König, Timothy Noël, *Angew. Chem. Int. Ed.*, 2018, **57**, 11278 -11282.