

## Supporting Information for

# Dual-State Efficient Chromophore with pH-Responsive and Solvatofluorochromic Properties Based on an Asymmetric Single Benzene Framework

Huijing Liu,<sup>a,b</sup> Sisi Zhang,<sup>b</sup> Liping Ding,<sup>\*,b</sup> and Yu Fang<sup>\*,b</sup>

<sup>a</sup> School of Textile Science and Engineering, Xi'an Polytechnic University, Xi'an 710048, P. R. China

<sup>b</sup> Key Laboratory of Applied Surface and Colloid Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, P. R. China

E-mail: dinglp33@snnu.edu.cn; yfang@snnu.edu.cn

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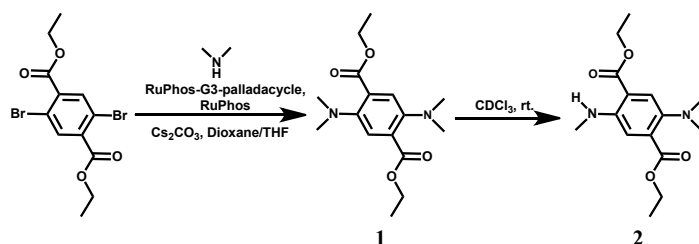
S4.  $^1\text{H}$  and  $^{13}\text{C}$  NMR and HRMS spectra for **1** and **2**.

## **S1. Reagents and instruments**

**Reagents.** Reagents and organic solvents were analytical grade and purchased from commercial suppliers. All the organic solvents for spectroscopic measurements were distilled prior to use. Column chromatographic purification was implemented with silica gel (300-400 mesh). Deuterated solvents of CDCl<sub>3</sub>, d<sub>6</sub>-DMSO and CD<sub>2</sub>Cl<sub>2</sub> were obtained from Cambridge Isotope Laboratories.

**Instruments.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the synthesized compounds were recorded on a Bruker 600 MHz spectrometer and their high-resolution mass spectra were performed by a Bruker maxis UHR-TOF mass spectrometer. UV-vis absorption spectra were measured on a Hitachi U-3900 spectrophotometer. Fluorescence measurements were performed on a time correlated single photon counting Edinburgh Instruments FLS 920 fluorescence spectrometer. Absolute fluorescence quantum yields were measured on the Hamamatsu C9920-02G Quantum Efficiency Measurement. Single-crystal structures were determined using a Bruker D8 Quest Single-crystal X-ray Diffraction spectrometer.

## S2. Synthetic procedures and characterization



Scheme S1 The synthesis routes of **1** and **2**.

### S2.1 Synthesis of diethyl 2,5-bis(dimethylamino) terephthalate (**1**)

To the solids of diethyl 2,5-dibromoterephthalate (1.0 g, 2.63 mmol), RuPhos-G3-palladacycle (0.22g, 0.26 mmol), RuPhos (0.13 g, 0.26 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (2.57g, 7.89 mmol) were added dry 1,4-dioxane (30 mL) and dimethylamine (5.0 mL, 2 M in THF) under N<sub>2</sub> atmosphere. The reaction mixture was stirred at 100 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>. After concentration of the filtrate under reduced pressure, the residue was further purified by column chromatography (PE/EA = 3:1) to afford **1** (0.61g, 75%) as pale-yellow solids. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 7.25 (s, 2H), 4.38 (q, *J* = 7.2 Hz, 4H), 2.78 (s, 12H), 1.41 (t, *J* = 7.2 Hz, 6H). <sup>13</sup>C NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 168.02, 145.26, 127.06, 119.97, 61.05, 44.03, 14.02. ESI-HRMS *m/z*: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub>, 309.1814, found 309.1815.

### S2.2 Synthesis of diethyl 2-methylamino-5-dimethylamino terephthalate (**2**)

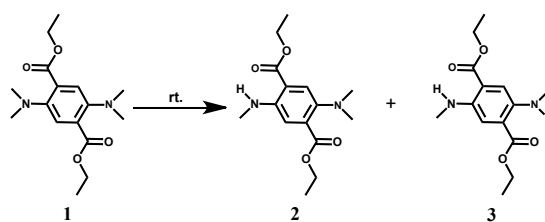
Diethyl 2,5-bis(dimethylamino)terephthalate (**1**) (0.1 g, 0.32 mmol) was dissolved in 1 mL CDCl<sub>3</sub> under room temperature. The yellowish green solution turned into orange red overnight. After removal of the solvent, the dried residue was purified by column chromatography (PE/EA = 1:1) to afford **2** (0.041 g, 45%) as orange red solids. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 7.67 (s, 1H), 7.34 (s, 1H), 6.79 (s, 1H), 4.33 (m, 4H), 2.88 (d, *J* = 4.8 Hz, 3H), 2.66 (s, 6H), 1.37 (t, *J* = 7.2 Hz, 6H). <sup>13</sup>C NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 168.40, 167.81, 147.49, 140.10, 134.18, 122.21, 112.08, 111.61, 61.14, 60.51, 45.03, 29.61, 14.10, 13.98. ESI-HRMS *m/z*: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>23</sub>N<sub>2</sub>O<sub>4</sub>, 295.1658, found 295.1658.

### S2.3 Synthesis of diethyl 2,5-bis(methylamino) terephthalate (**3**)

To the solids of diethyl 2,5-bis(dimethylamino)terephthalate (**1**) (0.05 g, 0.16 mmol)

was added 3 mL CHCl<sub>3</sub> and AcOH (5 μL, 0.087 mmol) under room temperature. The yellowish green solution turned into orange after 48 h. Then the solvent was removed and the residue was further purified by column chromatography (PE/EA = 5:1) to afford **3** (0.015 g, 23%) and **2** (0.002g, 5%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 7.32 (s, 2H), 6.76 (s, 2H), 4.37 (q, *J* = 7.2 Hz, 4H), 2.92 (s, 6H), 1.42 (t, *J* = 7.2 Hz, 6H). <sup>13</sup>C NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm) 167.90, 142.02, 116.82, 113.21, 60.69, 30.04, 14.09. ESI-HRMS *m/z*: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub>, 281.1496, found 281.1493.

**Table S1** Control reaction conditions



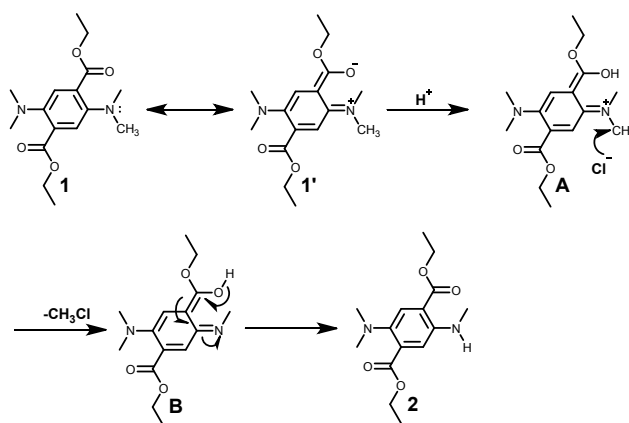
entry	solvent	additive	time (h)	yield (%)
1	CDCl <sub>3</sub>	--	18	<b>2</b> : 45%, <b>3</b> : <1%
2	CDCl <sub>3</sub>	--	48	<b>2</b> : 47%, <b>3</b> : <1%
3	CHCl <sub>3</sub>	--	72	N.R.
4	DMF	--	72	N.R.
5 <sup>a</sup>	CDCl <sub>3</sub>	--	72	N.R.
6 <sup>b</sup>	CHCl <sub>3</sub>	AcOH	48	<b>2</b> : 5%, <b>3</b> : 23%
7	CHCl <sub>3</sub>	HCl	24	<b>2</b> : 19%, <b>3</b> : 3%
8 <sup>c</sup>	CHCl <sub>3</sub>	AcOH	72	<b>2</b> : <1%, <b>3</b> : <5%

a) CDCl<sub>3</sub> was distilled under nitrogen after treated with K<sub>2</sub>CO<sub>3</sub>. b) AcOH, 0.5 eq. c) AcOH, 1.4 eq. N.R., no reaction.

**Note:** In order to investigate the mechanism for the *N*-demethylation of compound **1**, a series of control experiments were designed and examined. When the reaction time was extended, the yields of compound **2** and **3** hardly improved (entry 2). The same reaction in non-deuterated solvents such as CHCl<sub>3</sub> and DMF were also carried out, but gave no product (entry 3 and 4). A reasonable explanation for this is that there is some reagent in CDCl<sub>3</sub> to promote the occurrence of this reaction. In fact, it is known that CDCl<sub>3</sub> is generally easy to decompose to produce some acidic substances such as phosgene and HCl. However, for the analytical grade CHCl<sub>3</sub> as used, because of containing 0.3% ~ 1% ethanol as a stabilizer, it is difficult to decompose under ambient temperature. Thus, when used purified CDCl<sub>3</sub>, no desired product was formed (entry 5). In comparison, when an appropriate amount of HCl and AcOH was applied to the reaction, the *N*-demethylation products were also observed (entry 6 and 7). Furthermore, increasing the amount of AcOH lead to a lower yield due to protonation of **1** (entry 8). These results indicate

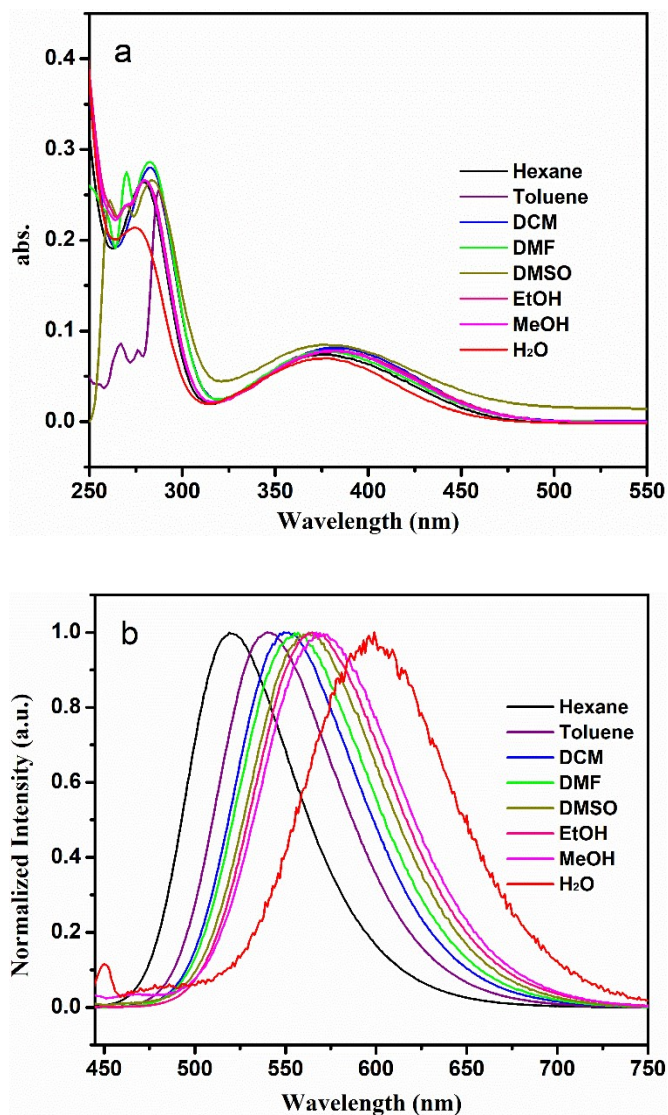
that a trace amount of acidic substance of HCl in CDCl<sub>3</sub> may be a valid reagent to the *N*-demethylation of compound **1**.

On the basis of the above results of the control experiments, a possible mechanism for this *N*-demethylation reaction is proposed. Substrate **1** possesses a resonance structure **1'**. In the presence of acidic substance, the species **1'** interact with H<sup>+</sup> to generate intermediate **A**. Then the resulting intermediate **A** undergoes the reaction of S<sub>N</sub>2 with the anion Cl<sup>-</sup> to form intermediate **B**. Finally, the species **B** undergo intramolecular electron and proton transfer to give desired compound **2**.

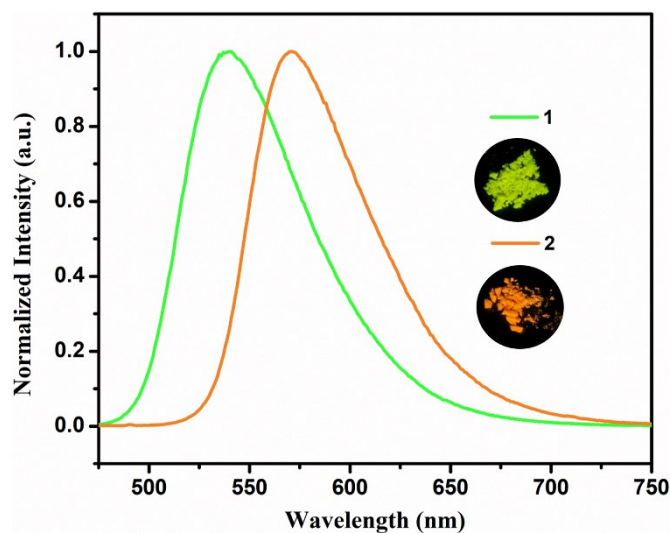


**Scheme S2** Proposed mechanism for the *N*-demethylation of compound **1**.

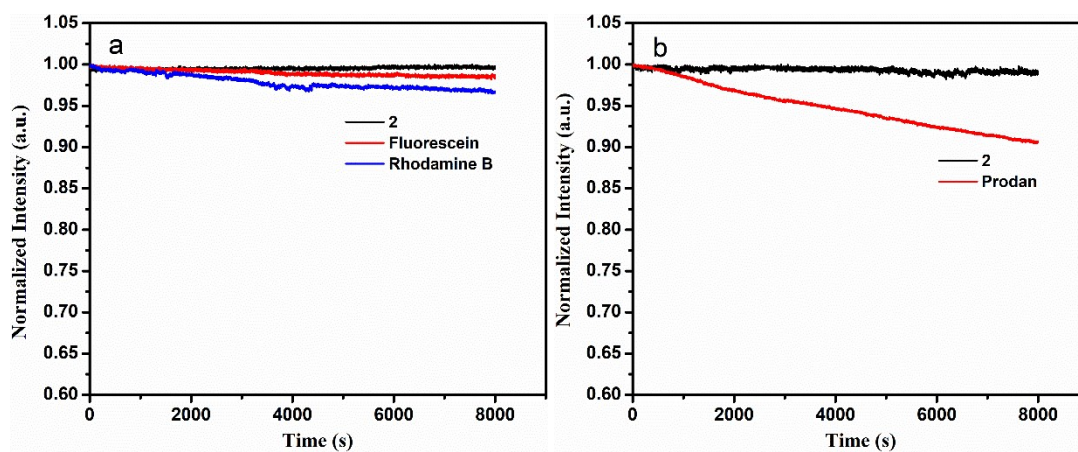
### S3. Supplementary Figures and Tables



**Figure S1** (a) UV-vis absorption and (b) normalized emission spectra of **1** in various solvents (10  $\mu$ M,  $\lambda_{\text{ex}}$  = 400 nm). DCM = dichloromethane, DMF = *N,N*-dimethylformamide.

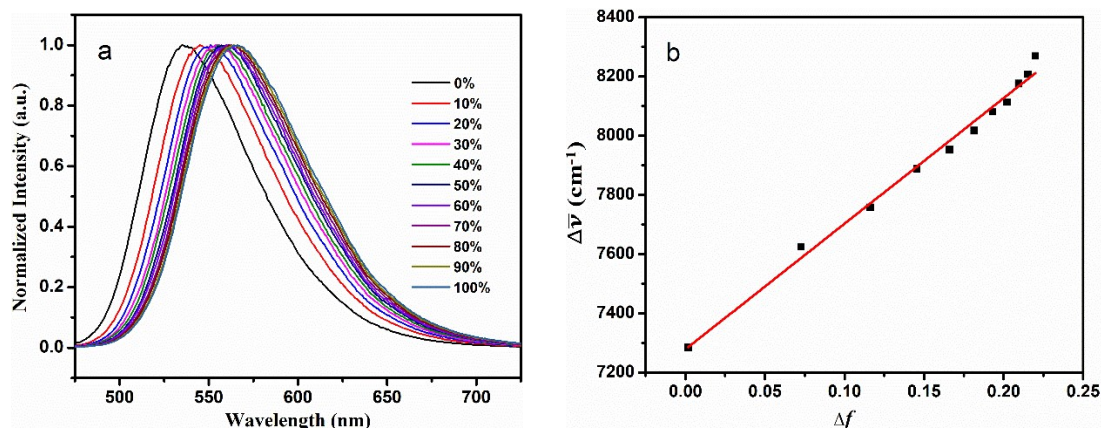


**Figure S2** Normalized emission spectra of **1** and **2** in the solid state. Inset: Fluorescent images of solid **1** and **2** under UV light (365 nm).



**Figure S3** (a) The photochemical stabilities of **2**, fluorescein and rhodamine B in ethanol monitored at their maximum emission wavelengths at a concentration of  $1.0 \times 10^{-5}$  mol/L, respectively. (b) The photochemical stabilities of **2** and Prodan in toluene at the same condition.

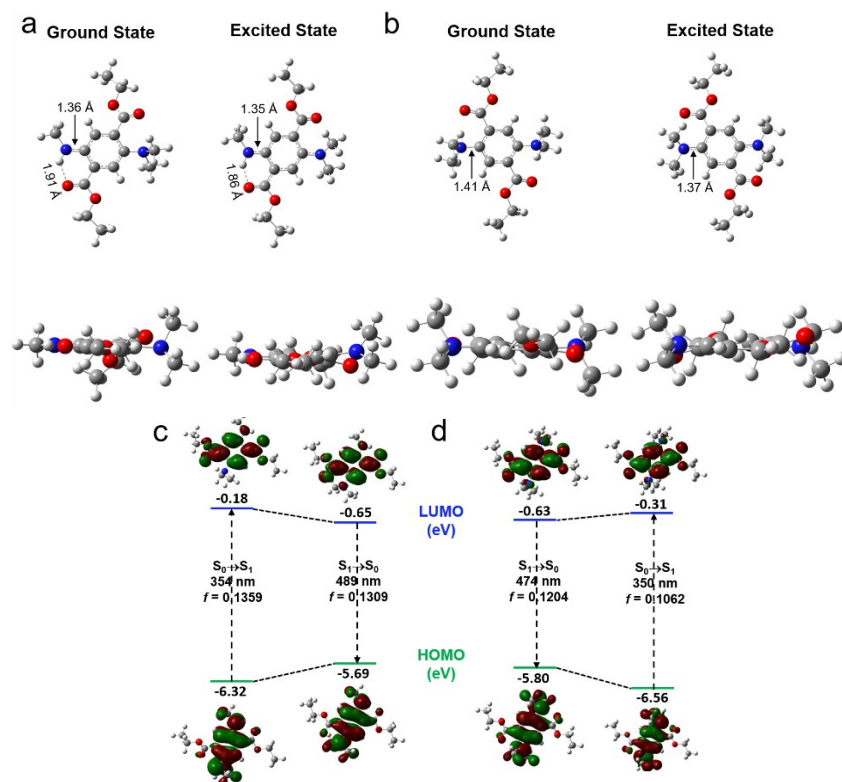




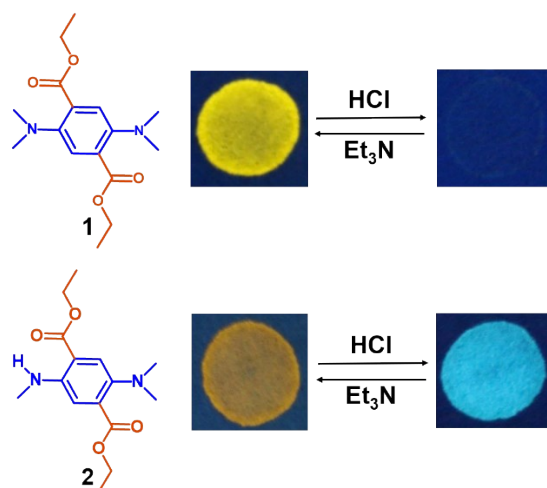
**Figure S4** (a) Fluorescence emission spectra of **2** in *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> of different ratios at a concentration of 10 μM; the excitation wavelength is 400 nm. (b) Trend of the Stokes shift with solvent orientation polarizability ( $\Delta f$ ) for **2** in the mixture of solvents.

**Note:** Through regular variation of the compositions of solvent mixtures of *n*-hexane and CH<sub>2</sub>Cl<sub>2</sub>, high degree linearity of the plot of  $\Delta\nu$  versus  $\Delta f$  is obtained. Using the Lippert-Mataga equation, we estimated the dipole moment change for **2** between the excited and ground states to be 7.3 D.<sup>1</sup>

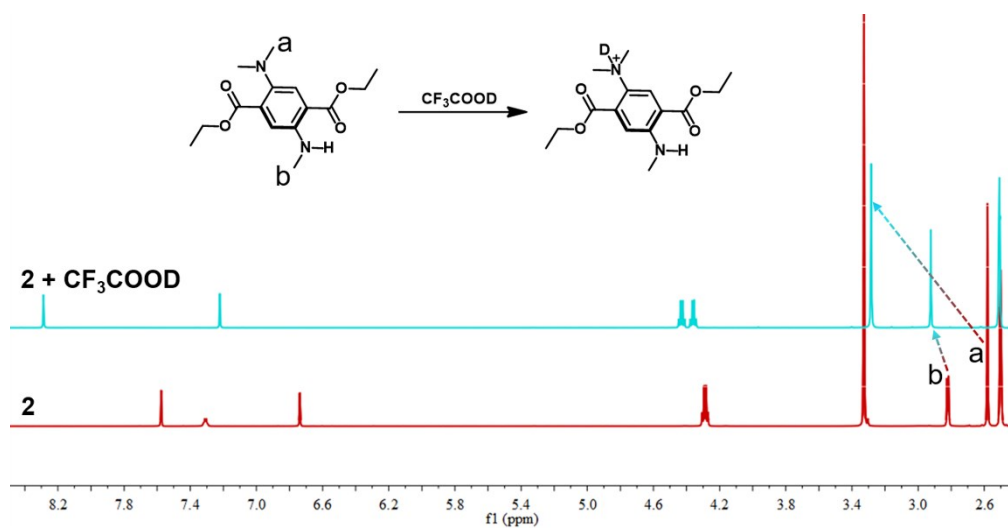
1. J. R. Lakowicz, Principles of Fluorescence Spectroscopy. 3rd ed. Springer: New York, 2006.



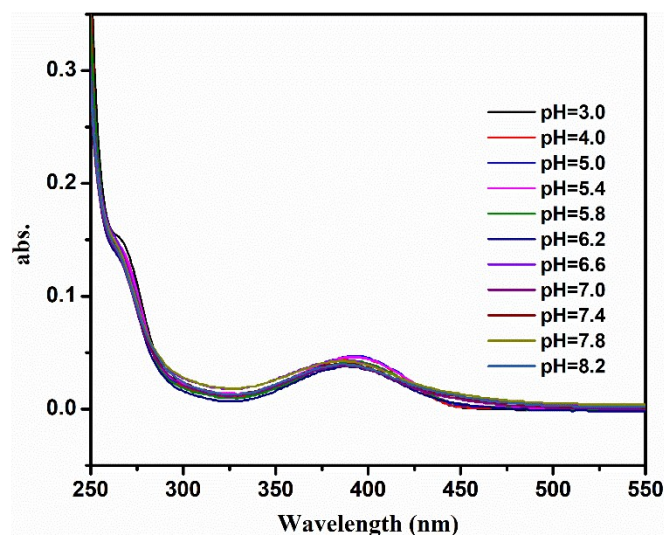
**Figure S5.** (a) Optimized structures of **2** and **1** (b) in the ground and excited states. (c) TD-DFT calculated results of **2** and **1** (d): molecular orbital distributions of HOMO and LUMO in the vertical excitation and emission, rationalization of UV-vis absorption and emission wavelengths and oscillator strengths.



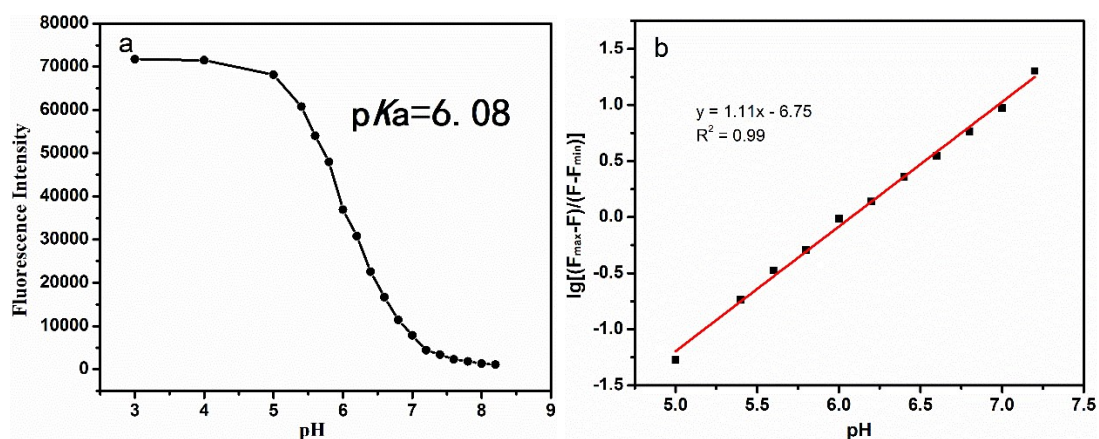
**Figure S6** Photographs of filter papers dipped with **1** and **2** under stimulation of HCl and Et<sub>3</sub>N vapors.



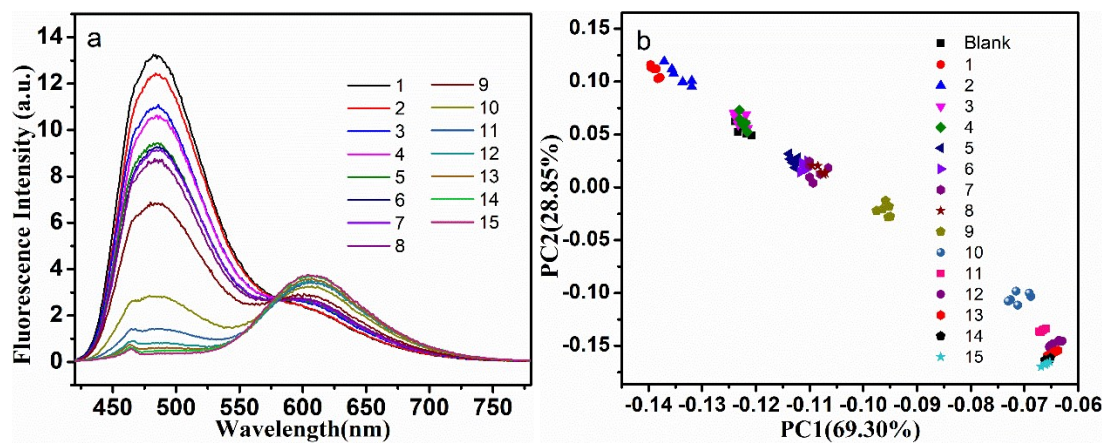
**Figure S7** Partial <sup>1</sup>H NMR spectra of **2** in [D<sub>6</sub>]DMSO and [D<sub>6</sub>]DMSO containing excessive CF<sub>3</sub>COOD.



**Figure S8** UV-vis absorption spectra of 10  $\mu\text{M}$  **2** in (B-R) buffer (10% DMSO) at various pH values.



**Figure S9** (a) The changes of the fluorescence intensity of **2** at 485 nm as a function of pH values of the buffer solution (10% DMSO); (b) linear relationship between  $\lg[(F_{\text{max}} - F)/(F - F_{\text{min}})]$  and pH values in the range of 5.0-7.2.



**Figure S10** (a) Fluorescence spectra of 10  $\mu\text{M}$  **2** in different brands of drinking water (10% DMSO); (b) two dimensional PCA plot for the aqueous solution of 10  $\mu\text{M}$  **2** (10% DMSO) to discriminate 15 different brands of drinking water.

**Table S2** Photophysical data of **2** in solid and selected solvents: solvent polarity parameter  $E_T(30)$ , molar absorption coefficient ( $\epsilon$ ), maximum absorption ( $\lambda_{\text{abs}}$ ) and emission wavelengths ( $\lambda_{\text{em}}$ ), Stokes shifts ( $\Delta\nu$ ), fluorescence quantum yield ( $\Phi_f$ ), lifetimes ( $\tau_f$ ), and radiative ( $k_r$ ) and non-radiative decay rate constants ( $k_{\text{nr}}$ ).

Solvent or solid	$E_T(30)$	$\epsilon(\text{M}^{-1} \text{cm}^{-1})$	$\lambda_{\text{abs}}(\text{nm})$	$\lambda_{\text{em}}(\text{nm})$	$\Delta\nu(\text{cm}^{-1})$	$\Phi_f^a$	$\tau_f(\text{ns})$	$k_r(10^7\text{s}^{-1})$	$k_{\text{nr}}(10^7\text{s}^{-1})$
Hexane	31.0	3885	382	536	7521 (154)	0.36	8.75	4.1	7.3
Toluene	33.9	3901	387	559	7951 (172)	0.48	11.07	4.3	4.7
CH <sub>2</sub> Cl <sub>2</sub>	40.7	3975	390	566	7973 (176)	0.54	13.98	3.9	3.3
DMF	43.2	3747	388	572	8291 (184)	0.27	8.70	3.1	8.4
DMSO	45.1	3977	390	579	8370 (189)	0.21	7.34	2.9	10.8
EtOH	51.9	4301	388	576	8412 (188)	0.25	7.91	3.2	9.5
MeOH	55.4	3586	387	580	8598 (193)	0.18	6.02	3.0	13.6
H <sub>2</sub> O	63.1	4158	389	485/608	5173/9040	0.05	1.45	3.4	65.5
Solid	--	--	--	570	--	0.65	12.59	5.2	2.8

a) Absolute fluorescence quantum yields determined with a calibrated integrating sphere system (errors < 3%).

**Table S3** Photophysical data of **1** in solid and selected solvents: solvent polarity parameter  $E_T(30)$ , molar absorption coefficient ( $\epsilon$ ), maximum absorption ( $\lambda_{\text{abs}}$ ) and emission wavelengths ( $\lambda_{\text{em}}$ ), Stokes shifts ( $\Delta\nu$ ), fluorescence quantum yield ( $\Phi_f$ ), lifetimes ( $\tau_f$ ), and radiative ( $k_r$ ) and non-radiative decay rate constants ( $k_{\text{nr}}$ ).

Solvent or solid	$E_T(30)$	$\epsilon(\text{M}^{-1} \text{cm}^{-1})$	$\lambda_{\text{abs}}(\text{nm})$	$\lambda_{\text{em}}(\text{nm})$	$\Delta\nu(\text{cm}^{-1})$	$\Phi_f^a$	$\tau_f(\text{ns})$	$k_r(10^7\text{s}^{-1})$	$k_{\text{nr}}(10^7\text{s}^{-1})$
Hexane	31.0	3360	375	520	7436	0.36	8.84	4.1	7.2
Toluene	33.9	3441	378	540	7937	0.46	11.32	4.1	4.8
CH <sub>2</sub> Cl <sub>2</sub>	40.7	3350	385	551	7961	0.55	14.27	3.9	3.2
DMF	43.2	3606	377	556	8540	0.12	5.00	2.4	17.6
DMSO	45.1	3481	379	563	8623	0.07	3.08	2.3	30.2
EtOH	51.9	3893	379	565	8686	0.13	4.85	2.7	17.9
MeOH	55.4	3324	381	571	8734	0.06	2.73	2.2	34.4
H <sub>2</sub> O	63.1	--	376	597	9845	<0.01	--	--	--
Solid	--	--	--	540	--	0.95	22.14	4.3	0.23

a) Absolute fluorescence quantum yields determined with a calibrated integrating sphere system (errors < 3%).

**Table S4** Data of X-ray crystallographic analysis of compound **2**.

Empirical formula	C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub>
Molecular weight	294.35
Temperature/K	210
Space group	P21/C
Hall group	-P 2ybc
Unit cell dimensions	a = 18.4663(5) Å, b = 7.8880(2) Å, c = 10.6546(3) Å $\alpha = 90(10)^\circ$ , $\beta = 93.091(10)^\circ$ , $\gamma = 90^\circ$
Volume	1549.71(7) Å <sup>3</sup>
Z	4
Density (calculated)	1.262 g/cm <sup>3</sup>
Absorption coefficient	0.481 mm <sup>-1</sup>
F(000)	632.0
Theta (max)	53.860
Final R indexes (all data)	R <sub>1</sub> = 0.0356, wR <sub>2</sub> = 0.0929
CCDC	2061389

**Table S5** List of the 15 drinking water samples used in this study.

No.	Brand	No.	Brand
1	Wahaha	9	Baisuishan
2	Jinmailang	10	Hanyangquan
3	Youyue	11	Aikua
4	Masterkong	12	Nongfu Spring
5	Chunyue	13	Hengda Spring
6	Jingtian	14	VOSS
7	C'estbon	15	Soda
8	Chunshuiyue		

## S4. $^1\text{H}$ and $^{13}\text{C}$ NMR and HRMS spectra for 1 and 2

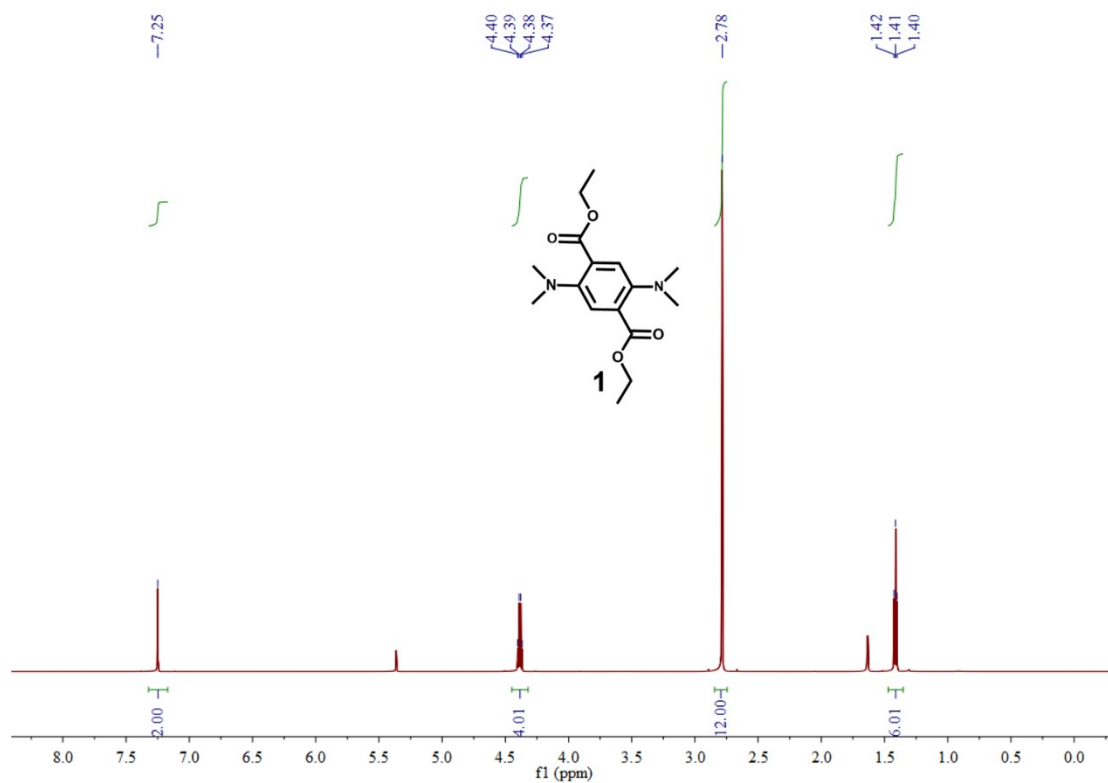


Figure S11  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2$ .

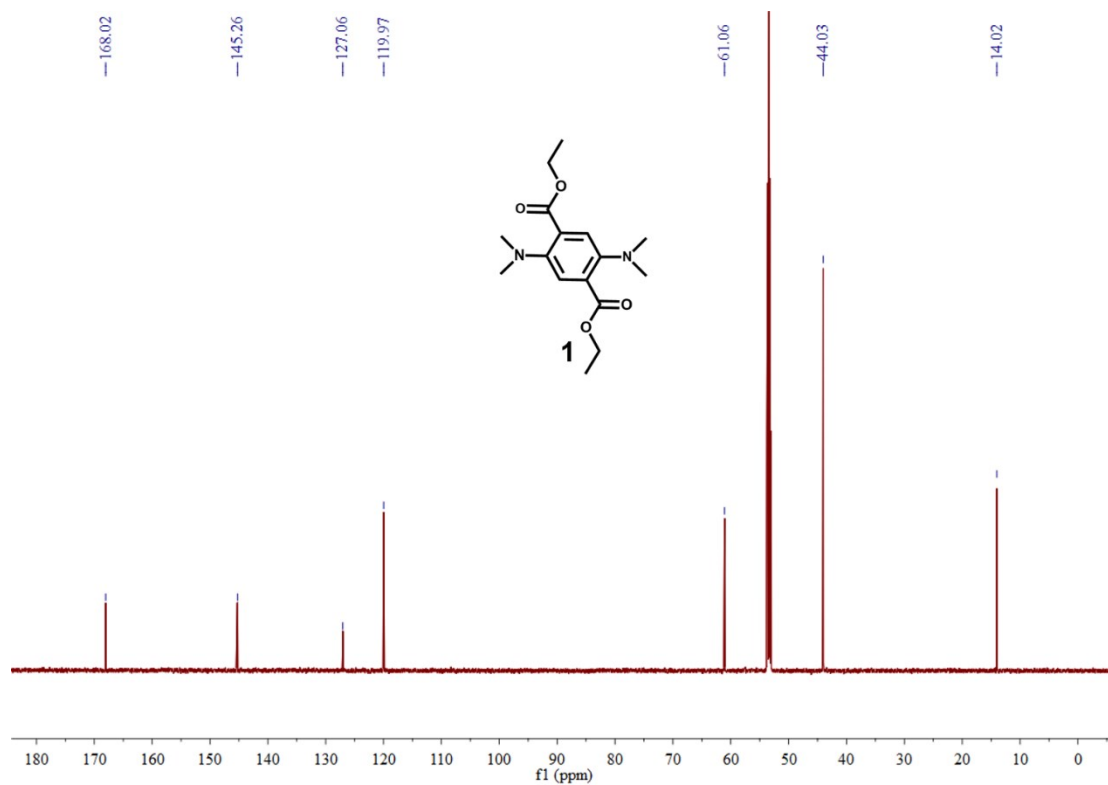
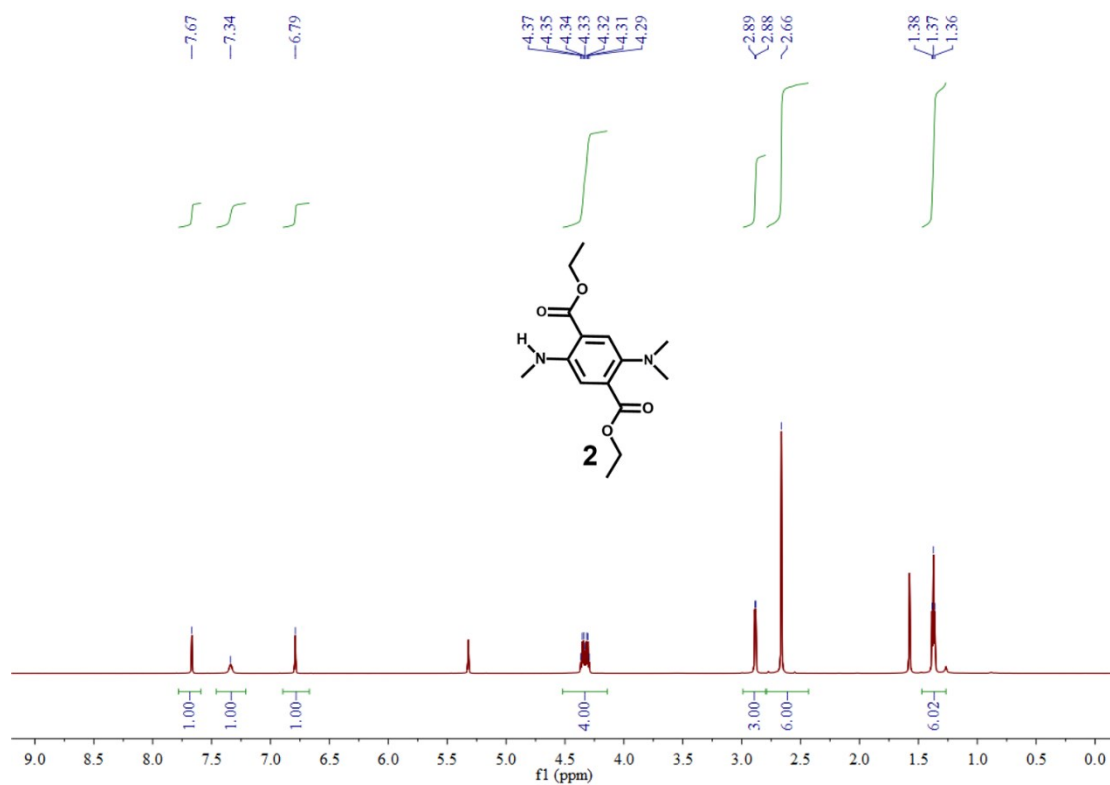
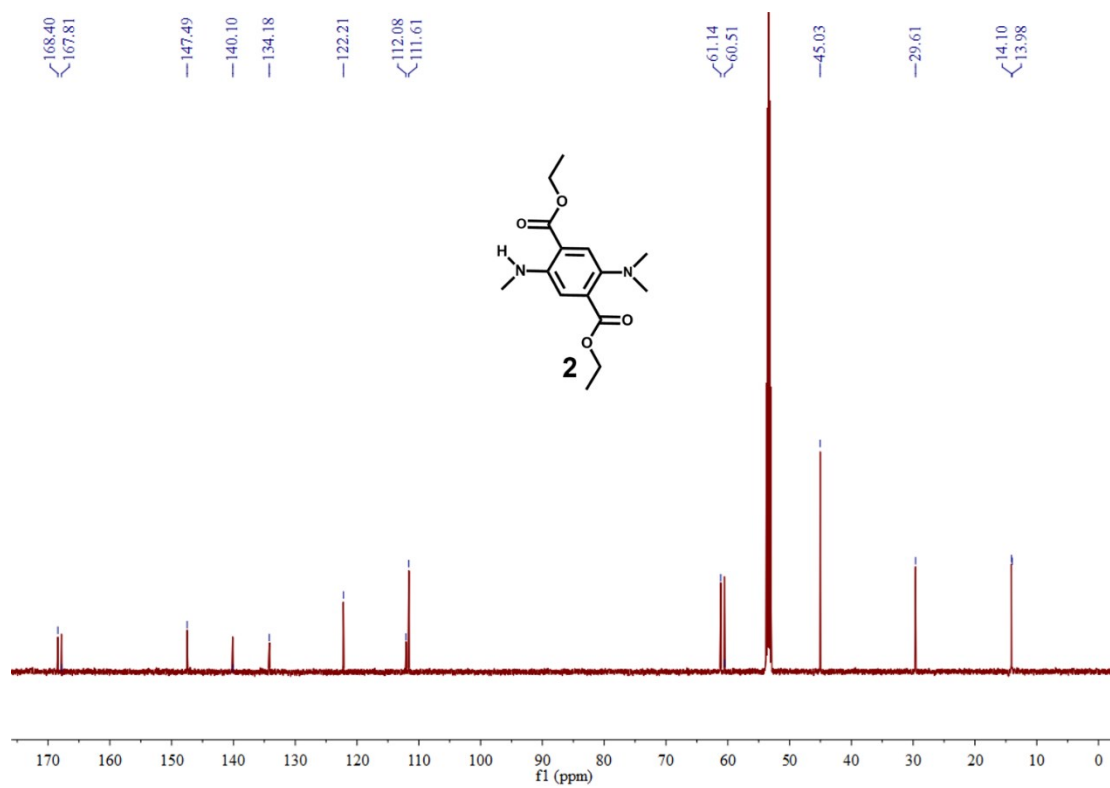


Figure S12  $^{13}\text{C}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2$ .

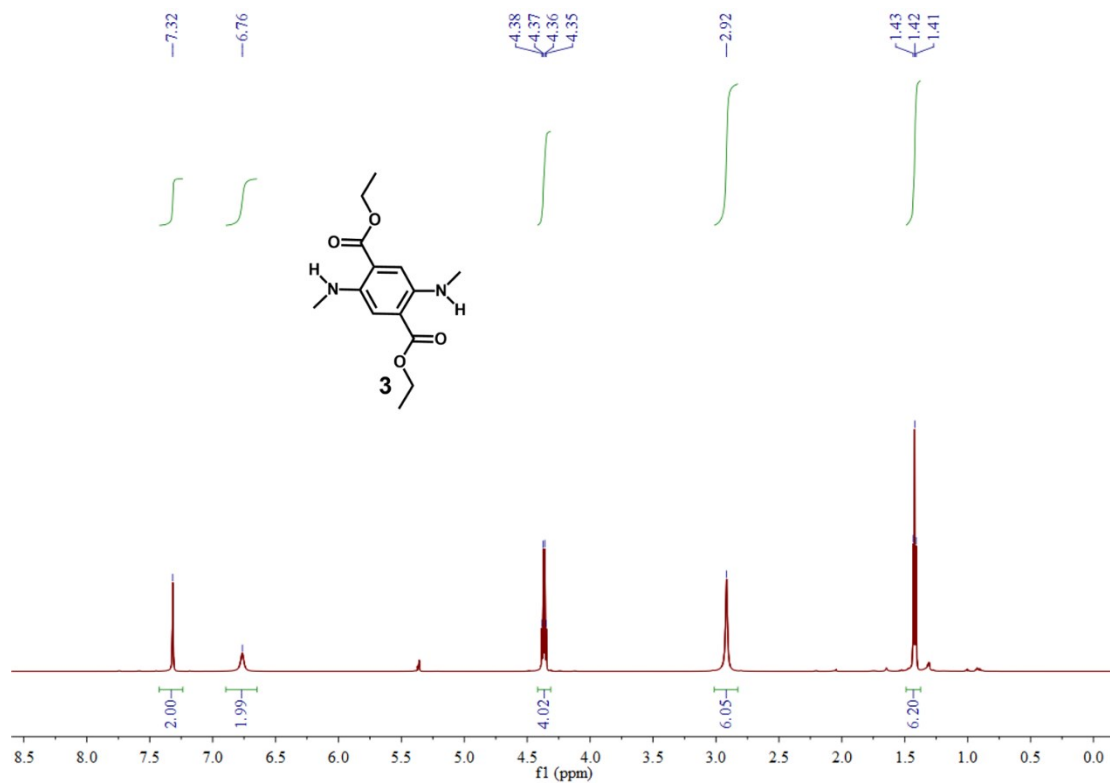


**Figure S13** <sup>1</sup>H NMR spectrum of **2** in CD<sub>2</sub>Cl<sub>2</sub>.

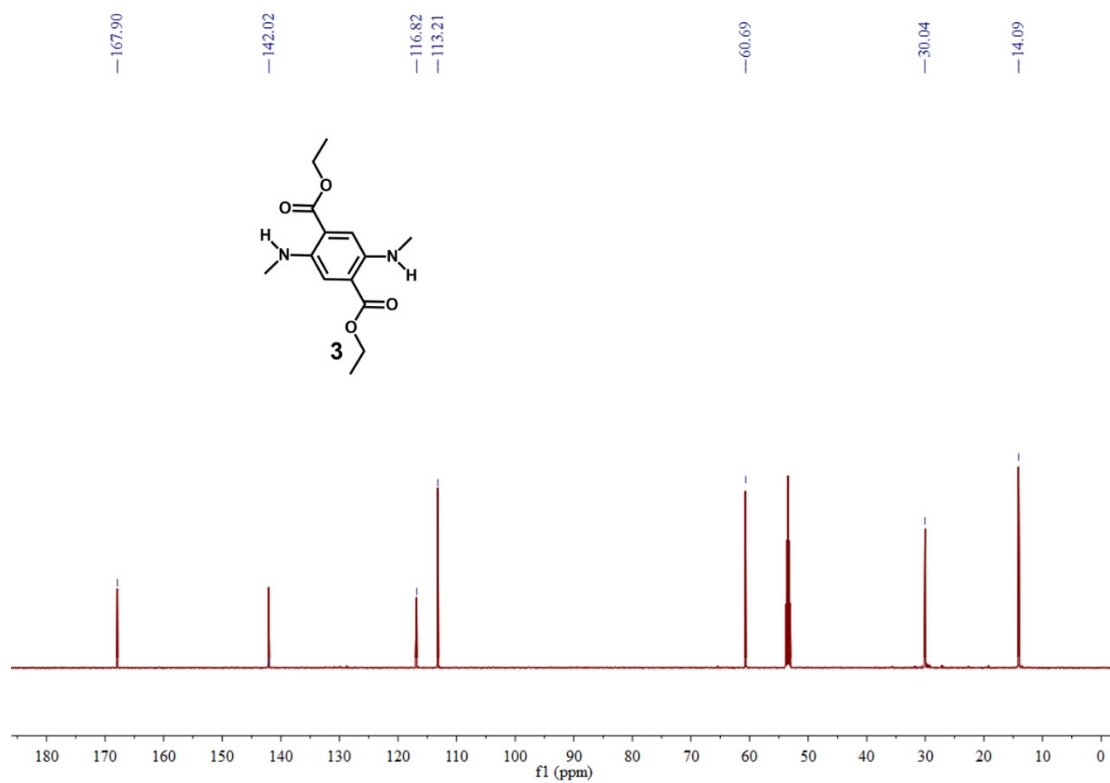


**Figure S14** <sup>13</sup>C NMR spectrum of **2** in CD<sub>2</sub>Cl<sub>2</sub>.

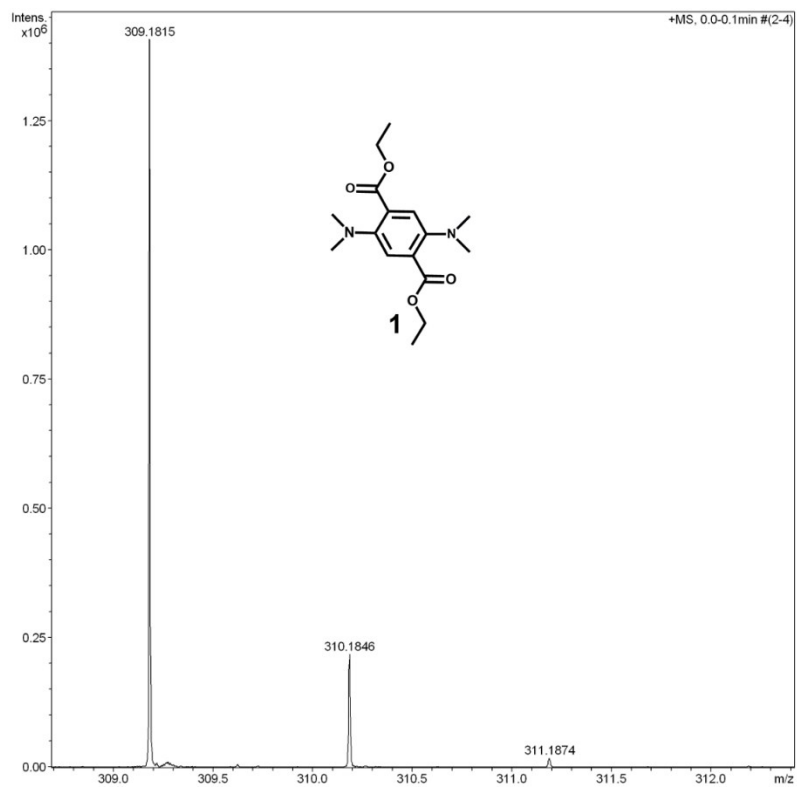




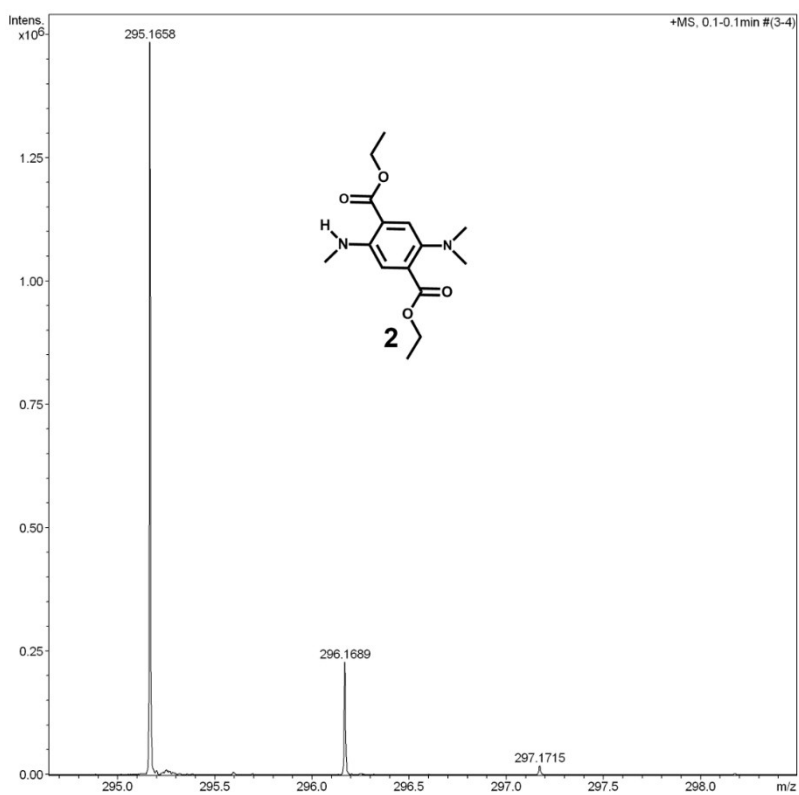
**Figure S15**  $^1\text{H}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$ .



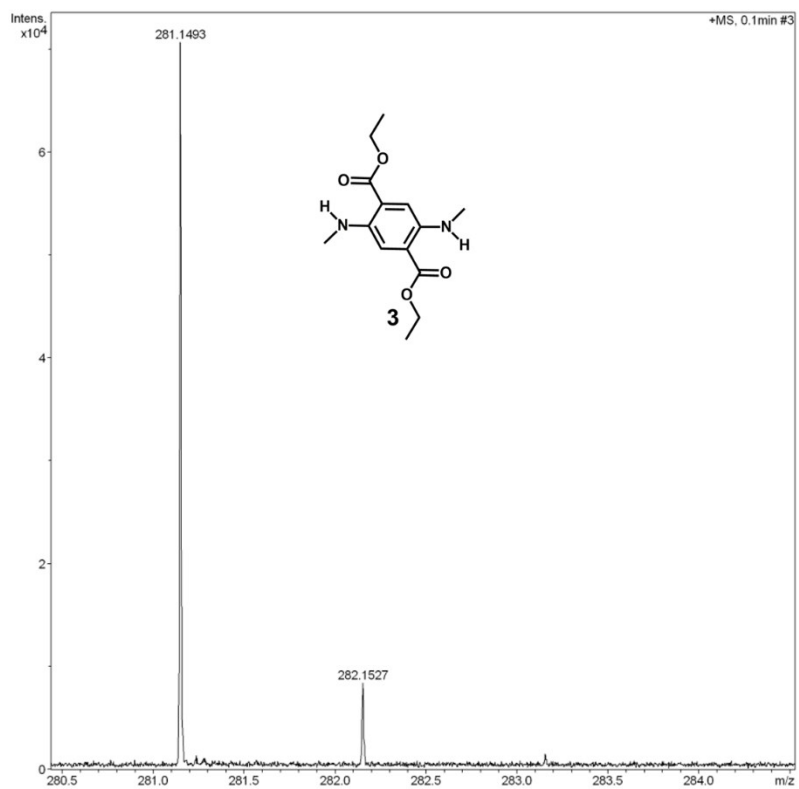
**Figure S16**  $^{13}\text{C}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$ .



**Figure S17** ESI-HRMS spectrum for **1**.



**Figure S18** ESI-HRMS spectrum for **2**.



**Figure S19** ESI-HRMS spectrum for **3**.