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 dibromoisoocyanuric acid (ADBIC, 5.36 g) suspended in 50 mL of oleum (H₂SO₄·SO₃) 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 °C 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 CHCl₃:acetone (100:1, v/v) as eluent, getting a pale yellow solid (734 mg, yield 20%). ¹H NMR (δ ppm, 600 MHz, CDCl₃): 8.99 (s, 2H, naphthalene), 4.22-4.19 (t, 4H, CH₂), 4.09-4.07 (t, 4H, CH₂), 2.05 (s, 6H, CH₃), 1.81-1.76 (m, 4H, CH₂), 1.75-1.70 (m, 4H, CH₂), 1.53-1.48 (m, 4H, CH₂); ¹³C NMR (δ ppm, 151 MHz, CDCl₃): 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 C₂₈H₂₈Br₂N₂O₈Na 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 (3x). 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$_2$O (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$_3$ : 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, CDCl$_3$) 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$_4$O$_6$Na 571.2527, found 571.2518.
Synthesis of DNNDI-A

Dimethylamine (130.52 mg, 0.65 mmol) 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) $\delta$ 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$_4$O$_8$H 609.2919, found 609.2913.
2. Supplementary Figures

Scheme 1 Schematic illustration for the synthesis route of DNNDI.

Fig. S2 Concentration effect. UV-Vis spectra (a) and fluorescence spectra (b) of DNNDI in CHCl$_3$ at room temperature ($\lambda_{ex}$ = 360 nm).

Fig. S2 The calculated electron density distributions of the HOMO (a) and LUMO (b) orbitals for DNNDI in the excited state.
Fig. S3 The energy level of structure DNNDI (Note: the density functional theory (DFT) was calculated at vacuum state)

<table>
<thead>
<tr>
<th>State</th>
<th>Energy (eV)</th>
<th>Wavelength (nm)</th>
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<tr>
<td>So</td>
<td>4.1415</td>
<td>299.37</td>
<td>0.0001</td>
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<tr>
<td>S0</td>
<td>4.0811</td>
<td>303.80</td>
<td>0.0000</td>
</tr>
<tr>
<td>S0e</td>
<td>4.0452</td>
<td>306.49</td>
<td>0.0002</td>
</tr>
<tr>
<td>S3</td>
<td>3.8785</td>
<td>319.67</td>
<td>0.2022</td>
</tr>
<tr>
<td>S2</td>
<td>3.6803</td>
<td>336.89</td>
<td>0.0039</td>
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<tr>
<td>S1</td>
<td>2.3415</td>
<td>529.51</td>
<td>0.2377</td>
</tr>
</tbody>
</table>

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 ($\lambda_{ex} = 360$ nm, $\lambda_{em} = 650$ 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 ($\lambda_{ex} = 360$ 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.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>TOL</th>
<th>DCM</th>
<th>THF</th>
<th>EA</th>
<th>DIO</th>
<th>Acetone</th>
<th>DMF</th>
<th>Film</th>
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<tr>
<td>Q.Y. (%)</td>
<td>61.05</td>
<td>48.77</td>
<td>32.52</td>
<td>28.42</td>
<td>42.76</td>
<td>21.52</td>
<td>22.03</td>
<td>14.72</td>
</tr>
</tbody>
</table>

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 ($N,N$-dimethylformamide).
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.

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

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

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 CHCl₃ 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 \((K_{SV})\) Analysis for TATP Quenching

Quenching of fluorescence can be determined by the Stern-Volmer equation: \[ \frac{I_0}{I} = 1 + K_{SV}[Q] \]

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. \((K_{SV} = 0.00342)\)

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:

