#### **Supplementary Information for**

# A T-Shaped Triazatruxene Probe for Naked-Eye Detection of HCl Gas with High Sensitivity and Selectivity

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#### **1. Experimental Procedures**

**General Methods.** All commercially available chemicals were of A.R. grade, and all the reagents used were purchased from Sigma-Aldrich, J&K or Xiya Reagent (China). When necessary, solvents and reagents were purified using standard procedures.

NMR spectra were recorded on a Bruker Ultra Shield Plus 400 MHz NMR (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz). The matrix assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF MS) measurements were carried out with a Shimadzu AXIMA-CFR mass spectrometer. UV-visible absorption spectra were recorded on a PerkinElmer Lambda 35. Photoluminescence (PL) spectra were measured using a PerkinElmer LS55. In order to obtain deep insight into the structure-property relationships, the energy levels of TATNFF and TATNFF-HCl complex were carried out by using density functional theory (DFT) at the B3LYP/6-31Glevel.

For ideal gases, the molar volume is given by the ideal gas equation: this is a good approximation for many common gases at the standard temperature and pressure. The ideal gas equation, which was first stated by Émile Clapeyron in 1834 as a combination of Boyle's law and Charles's law, can be rearranged to give an expression for the molar volume of an ideal gas: <sup>1</sup>

$$V_m = \frac{V}{n} = \frac{RT}{P}$$

Hence, for a given temperature and pressure, the molar volume is the same for all ideal gases and is known to the same precision as the gas constant: R = 0.08206 L atm K<sup>-1</sup> mol<sup>-1</sup>, that is a relative standard uncertainty of  $9.1*10^{-7}$ , according to the 2010 CODATA recommended value.<sup>2</sup> The molar volume of an ideal gas at one atmosphere of pressure is 24.465 L mol<sup>-1</sup> at 25 °C (V<sub>m</sub>). In the present

case, we assume that the mixtures of HCl and air are ideal gases. Under the condition of saturation  $(V=0.8 \ \mu L)$ , we get the molar quantity of HCl gas:

$$n_{HC1} = \frac{V}{V_{m}} = \frac{0.8\mu L}{24.465 \text{ L/mol}} = 3.3 \times 10^{-8} \text{ mol}$$

The volume of **TATNFF** solution is 3 mL in the cuvette. According to the concentration (10  $\mu$ M in THF), we get the molar quantity of **TATNFF** solute:

$$n_{TATNFF} = CV = 10 \mu M * 3mL = 1 * 10^{-5} mol / L * 3 * 10^{-3} L = 3 * 10^{-8} mol$$

So n<sub>HCl</sub>≈n<sub>TATNFF</sub>, and this indicates 1:1 binding stoichiometry between **TATNFF** and HCl.

The unit, ppm (parts per million), is a way of quantifying small concentrations, usually mass. It denotes one part per 1,000,000 parts. According to the discussion above, we get the quality of HCl gas:

$$\mathbf{m}_{HC1} = \mathbf{n}_{HC1} * M_{HCI} = \frac{V_{HC1}}{V_{m}} * M_{HCI} = \frac{V_{HC1}}{24.465 \text{ L/mol}} * 36.45g / mol = V_{HC1} * 1.45g / L$$

The volume of THF solution is about 3 mL in the cuvette. The density of THF is 0.89 mg mL<sup>-1</sup> at 25 °C ( $\rho_{HCl}$ ). According to the concentration (10  $\mu$ M in THF), we get the quality of **TATNFF** solution:

 $m_{\rm S} = m_{\rm THF} + m_{\rm TATNFF} = V_{\rm THF} * \rho_{\rm THF} + n_{\rm TATNFF} * M_{TATNFF} = 3mL * 0.889mg / mL * 10^{-3}g / mg + 3 * 10^{-8}mol * 1440.16g / mol = 2.71 * 10^{-3}g$ 

So we get the ppm of HCl gas:

$$\omega_{\rm HC1} = \frac{\rm m_{\rm HC1}}{\rm m_s} = \frac{V_{\rm HC1} * 1.45g / L}{2.71 * 10^{-3}g} * 10^6 \, ppm = V_{\rm HC1} * 5.35 * 10^8 \, \rm ppm/L$$

1.1 Synthesis of 10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (Triazatruxene, TAT)

Under nitrogen, a solution of indolin-2-one (10.0 g, 75.1 mmol) in POCl<sub>3</sub> (50 mL) was stirred and refluxed at 100 °C for 8 h. After cooling, the mixture was poured into ice water, stirred for 2 h. By adding a 10% aqueous potassium hydroxide solution dropwise, the solution was adjusted to neutral pH. The dark green crude product can be obtained after extraction. Subsequently, the crude product was purified on a silica gel column using EA/PE: 1/10, as eluent to get **TAT** (2.4 g) in 28.0% yield as a white solid. <sup>1</sup>H NMR (400 MHz, DMSO, ppm):  $\delta$  11.85 (s, 3H), 8.65 (d, 3H, J = 7.6 Hz), 7.70 (d, 3H, J = 7.8 Hz), 7.34 (dt, 6H, J = 14.7, 7.0 Hz); <sup>13</sup>C NMR (100 MHz, DMSO, ppm):  $\delta$  138.99, 134.25, 122.90, 122.69, 120.30, 119.54, 111.44, 101.03; MALDI-TOF MS (m/z): Calcd for C<sub>24</sub>H<sub>15</sub>N<sub>3</sub>, Exact Mass: 345.13, Mol. Wt.: 345.41, Found: 344.895 (M<sup>+</sup>); Elemental analysis calcd (%): C 83.46, H 4.38, N 12.17. Found: C 83.42, H 4.30, N 12.18.

1.2 Synthesis of 10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (TATR)

A mixture of triazatruxene core (**TAT**) (1.05 g, 3.04 mmol), TBAB (0.10 g, 0.30 mmol) and KOH (1.02 g, 18.24 mmol) in THF (50 mL) was heated under reflux for 30 min. Then C<sub>6</sub>H<sub>13</sub>Br (2.26 g, 13.68 mmol) was added dropwise, and the mixture was heated under reflux for 10 h. The mixture was diluted with dichloromethane, washed with 10% aqueous HCl and then with brine solution. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and the solvents were evaporated under vacuum. The crude product was purified on a silica gel column using DCM/PE: 1/10, as eluent to get **TATR** (1.59 g) in 87.4% yield as white powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.30 (d, J = 8.0 Hz, 3H), 7.64 (d, J = 8.0 Hz, 3H), 7.46 (t, J = 7.5 Hz, 3H), 7.35 (t, J = 7.5 Hz, 3H), 4.96-4.89 (m, 6H), 2.03-1.95 (m, 6H), 1.34-1.21 (m, 18H), 0.81 (t, J = 7.0 Hz, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  141.06, 138.89,

123.52, 122.70, 121.52, 119.64, 110.53, 77.30, 77.04, 76.72, 47.08, 31.45, 29.78, 26.37, 22.48, 13.93; MALDI-TOF MS (m/z): Calcd for C<sub>42</sub>H<sub>51</sub>N<sub>3</sub>, Exact Mass: 597.41, Mol. Wt.: 597.89, Found: 597.70 (M<sup>+</sup>); Elemental analysis calcd (%): C 84.37, H 8.60, N 7.03. Found: C 84.33, H 8.64, N 7.02.

1.3 Synthesis of 5,10,15-trihexyl-3-nitro-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (TAT-NO<sub>2</sub>)

To a solution of **TATR** (3.68 g, 6.2 mmol) in dichloromethane (DCM) (37 mL) was added 65% nitric acid (0.5 mL, 11.1 mmol) at 0 °C. The resulting mixture was stirred for 4 h and then extracted with DCM (100 mL) for three times. The organic layer was dried with anhydrous magnesium sulfate (MgSO<sub>4</sub>) and evaporated to dryness. The residue was purified on a silica gel column eluted with DCM: Petroleum Ether (PE) (1:1) to afford **TAT-NO<sub>2</sub>** (3.1 g) in 76% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.50 (s, 1H), 8.26 (dd, J = 16.5, 7.8 Hz, 4H), 7.65 (d, J = 8.2 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 4.98-4.89 (m, 4H), 4.87-4.80 (m, 2H), 2.04-1.89 (m, 6H), 1.46-1.04 (m, 24H), 0.81 (m, J = 7.0, 2.9 Hz, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  142.84, 141.63, 141.07, 140.46, 139.43, 138.64, 127.98, 123.17, 121.53, 120.13, 115.32, 110.69, 106.30, 104.06, 102.88, 47.16, 31.34, 29.94, 26.10, 22.49, 13.87; MALDI-TOF MS (m/z): Calcd for C<sub>42</sub>H<sub>50</sub>N<sub>4</sub>O<sub>2</sub>, Exact Mass: 642.39, Mol. Wt.: 642.89, Found: 643.01 (M<sup>+</sup>); Elemental analysis calcd (%): C 78.47, H 7.84, N 8.72. Found: C 78.51, H 7.81, N 8.73.

1.4 Synthesis of 5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazol-3-amine (TAT-NH<sub>2</sub>)

Under nitrogen, **TAT-NO<sub>2</sub>** (1.04 g, 1.60 mmol) and palladium on activated carbon (Pd/C) (0.14 g) were dissolved in N,N-dimethyl formamide (20 mL) and the solution was refluxed. Hydrazine

monohydrate (0.6 mL) was added dropwise, and the mixture was stirred at this temperature for 10 h. Pd/C was removed by filtration through Celite and the filtrate was extracted with DCM. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and the solvents were evaporated under vacuum. The crude product was purified on a silica gel column using DCM/PE: 1/4, as eluent to get **TAT-NH<sub>2</sub>** (0.93 g) in 86% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.27 (dd, *J* = 10.6, 8.2 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.64-7.59 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 2.0 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.0 Hz, 1H), 4.89 (dd, J = 16.1, 9.0 Hz, 4H), 4.83-4.76 (m, 2H), 1.96 (d, *J* = 5.9 Hz, 6H), 1.28 (dd, J = 20.2, 5.6 Hz, 18H), 0.85-0.79 (m, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  142.91, 142.82, 141.18, 141.04, 138.33, 138.30, 138.00, 123.49, 122.58, 122.39, 121.52, 121.50, 119.42, 119.39, 116.48, 110.45, 110.27, 109.24, 103.47, 103.14, 96.77, 47.14, 47.07, 46.79, 31.48, 31.47, 31.45, 29.84, 29.73, 29.53, 26.39, 22.51, 22.50, 22.48, 13.94, 13.93; MALDI-TOF MS (m/z): Calcd for C<sub>42</sub>H<sub>52</sub>N<sub>4</sub>, Exact Mass: 612.42, Mol. Wt.: 612.91, Found: 612.576 (M<sup>+</sup>); Elemental analysis calcd (%): C 82.31, H 8.55, N 9.14. Found: C 82.33, H 8.64, N 9.02.

1.5 Synthesis of 2,7-dibromo-N-(5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c] carbazol3-yl)-9H- fluoren-9-imine (**2BrTATNF**)

A mixture of **TAT-NH**<sub>2</sub> (275 mg, 0.45 mmol) and 2,7-dibromo-9H-fluoren-9-one (152 mg, 0.45 mmol) in ethanol (15 mL) was heated under reflux for 10 min. Then glacial acetic acid (0.3 mL) was added dropwise, and the mixture was heated at 120°C for 10 h. The reaction solution was cooled to room temperature. The precipitate was collected by filtration and purified by recrystallization from ethanol to afford **2BrTATNF** (343 mg) in 82% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.31 (dd, J = 11.4, 5.2 Hz, 3H), 8.17 (d, J = 1.6 Hz, 1H), 7.63 (ddd, J = 9.7, 8.0, 2.3 Hz, 3H), 7.5-7.42 (m, 5H), 7.32 (dd, J = 23.4, 4.5 Hz, 3H), 7.09-6.99 (m, 2H), 4.92 (dt, J = 16.3, 9.0 Hz, 6H), 2.07-1.93 (m, 6H),

1.34-1.15 (m, 18H), 0.86-0.74 (m, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 160.44, 146.03, 142.05, 141.67, 141.12, 141.10, 139.63, 139.33, 139.30, 138.78, 138.56, 134.57, 132.40, 129.98, 126.72, 123.49, 123.38, 122.83, 122.69, 122.19, 121.60, 121.55, 121.20, 121.05, 119.70, 111.28, 110.58, 110.53, 103.49, 103.41, 103.35, 100.79, 47.25, 47.10, 47.03, 31.47, 31.36, 29.83, 29.77, 29.74, 26.44, 26.42, 26.35, 22.52, 22.46, 13.96, 13.92, 1.06; MALDI-TOF MS (m/z): Calcd for C<sub>56</sub>H<sub>56</sub>Br<sub>2</sub>N<sub>4</sub>, Exact Mass: 930.29, Mol. Wt.: 932.89, Found: 934.40 (M<sup>+</sup>); Elemental analysis calcd (%): C 70.81, H 6.05, N 6.01. Found: C 70.83, H 6.02, N 6.05.

1.6 Synthesis of 9,9,9",9"-tetrahexyl-N-(5,10,15-trihexyl-10,15-dihydro-5H-diindolo [3,2-a:3',2'-c]car-bazol -3-yl)-9H,9'H,9"H-[2,2':7',2"-terfluoren]-9'-imine (TATNFF)

Under nitrogen, **2BrTATNF** (100 mg, 0.108 mmol), 9,9-Dihexylfluorene-2-bis (boronic acid pinacol ester) (141 mg, 0.430 mmol), TBAB (3.4 mg, 0.011 mmol) and Pd(pph<sub>3</sub>)<sub>4</sub> (12.4 mg, 0.011 mmol) were dissolved in THF (18 mL) and the solution was refluxed. Then aqueous 2 M K<sub>2</sub>CO<sub>3</sub> (6.0 mL) was added dropwise, and the mixture was stirred at 95°C for 48 h. The mixture was subsequently extracted with dichloromethane-water. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and the solvents were evaporated under vacuum. The crude product was purified on a silica gel column using DCM/PE: 1/4, as eluent to get **TATNFF** (86 mg) in 56% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.42-8.37 (m, 2H), 8.30 (d, *J* = 8.1 Hz, 1H), 7.89-7.63 (m, 11H), 7.50-7.28 (m, 10H), 7.24 -7.19 (m, 3H), 7.12-7.06 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 4.95 (d, *J* = 26.2 Hz, 6H), 2.15-1.91 (m, 12H), 1.46 -1.29 (m, 18H), 1.12 (dd, *J* = 15.6, 9.8 Hz, 18H), 0.89-0.59 (m, 37H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  194.21, 151.67, 151.32, 151.04, 142.97, 142.71, 141.18, 140.93, 140.55, 138.55, 135.27, 133.40, 128.85, 127.28, 126.85, 125.64, 124.84, 123.10, 122.94, 121.03, 120.77, 120.09, 119.86, 83.70, 77.35, 77.23, 77.03, 76.71, 55.28, 40.46, 31.51, 31.47, 31.43, 29.71, 29.67, 24.95, 23.79, 22.58, 22.56, 22.52, 13.99,

13.94; MALDI-TOF MS (*m/z*): Calcd for C<sub>105</sub>H<sub>122</sub>N<sub>4</sub>, Exact Mass: 1438.97, Mol. Wt.: 1440.16, Found: 1442.753 (M<sup>+</sup>); Elemental analysis calcd (%): C 87.57, H 8.54, N 3.89. Found: C 87.53, H 8.56, N 3.88.

#### 2. Experimental Graphics



Fig. S1. Apparatus for HCl gas detection.



Fig. S2. Solutions of TATNFF (1  $\mu$ M in THF) in the presence of saturated HF (gas), HCl (gas), HBr (gas), HI (gas), H<sub>2</sub>SO<sub>4</sub> (dilute solution), HNO<sub>3</sub> (dilute solution), H<sub>3</sub>PO<sub>4</sub> (dilute solution), SO<sub>2</sub> (gas),

NO<sub>2</sub> (gas), SOCl<sub>2</sub> (liquid) and CO<sub>2</sub> (gas) without (Left) and with (Right) a UV-lamp (365 nm).



Fig. S3. Absorption spectra of TATNFF (10  $\mu$ M in Acetone) exposed to HCl gas with the different concentration (Left) and the change of absorption intensity with the HCl gas increase (Right).



Fig. S4. PL spectra of TATNFF (10  $\mu$ M in Acetone) exposed to HCl gas with the different concentration (Left) and the change of PL intensity with the HCl gas increase (Right).



Fig. S5. Absorption spectra of TATNFF (10 µM in DMF) exposed to HCl gas with the

different concentration (Left) and the change of absorption intensity with the HCl gas increase (Right).



Fig. S6. PL spectra of TATNFF (10 µM in DMF) exposed to HCl gas with the different concentration

(Left) and the change of PL intensity with the HCl gas increase (Right).



Fig. S7. Absorption spectra of TATNFF (10  $\mu$ M in Cyclohexane) exposed to HCl gas with the different concentration (Left) and the change of absorption intensity with the HCl gas increase (Right).



**Fig. S8.** PL spectra of **TATNFF** (10  $\mu$ M in Cyclohexane) exposed to HCl gas with the different concentration (Left) and the change of PL intensity with the HCl gas increase (Right).



Fig. S9. Absorption spectra of TATNFF (10  $\mu$ M in DCM) exposed to HCl gas with the different

concentration (Left) and the change of absorption intensity with the HCl gas increase (Right).



**Fig. S10.** PL spectra of **TATNFF** (10  $\mu$ M in DCM) exposed to HCl gas with the different concentration (Left) and the change of PL intensity with the HCl gas increase (Right).



Fig. S11. PL responses of TATNFF (10 µM in THF) to saturated HF, HCl, HBr, HI, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>,





Fig. S12. PL spectral changes of TATNFF (10  $\mu$ M in THF) to saturated HF, HCl, HBr, HI, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, HAc, NO<sub>2</sub>, SO<sub>2</sub>, SOCl<sub>2</sub>, and KCl.



Fig. S13. <sup>1</sup>H NMR of TATNFF in CDCl<sub>3</sub> exposed to HCl gas with different volumes.



**Fig. S14.** <sup>1</sup>H NMR of HCl gas in CDCl<sub>3</sub>.



**Fig. S15.** PL spectra of the sensor exposed to saturated HCl gas with the different concentration of **TATNFF** in THF (Left) and the change of PL intensity with the concentration of **TATNFF** increase (Right).



Fig. S16. Fluorescent lifetime tests of TATNFF (10 µM in THF) with HCl gas.

Compd.	τ, ns [λ <sub>em</sub> =400	<τ>, ns [λ <sub>em</sub> =400	τ, ns [λ <sub>em</sub> =544	<τ>, ns [λ <sub>em</sub> =400 nm]
	nm]	nm]	nm]	
TATNFF-HCl	0.67 (84.35%),	0.90	0.68 (86.97%),	0.97
	2.16 (15.65%)		2.95 (13.03%)	

Table S1. Fluorescent lifetime tests of TATNFF (10 µM in THF) with HCl gas.



**Fig. S17.** Calculated spatial representations of HOMO and LUMO for **TATNFF** and **TATNFF**-HCl complex with the DFT B3LYP/6-31G level.



Fig. S18. PL spectra of TATNFF (10  $\mu$ M in THF) exposed to saturated HCl gas with different exposing time (Left) and the change of PL intensity by increasing the exposing time (Right).



Fig. S19. PL spectra of TATNFF (10  $\mu$ M in THF) exposed to saturated HCl gas with different time

under UV lamp in N<sub>2</sub> and in air.

## 3. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra







Fig. S22. <sup>13</sup>C NMR of TAT.



Fig. S23. MALDI-TOF of TATR.



Fig. S25. <sup>13</sup>C NMR of TATR.



















**Fig. S30.** <sup>1</sup>H NMR of **TAT-NH**<sub>2</sub>.



Fig. S31. <sup>13</sup>C NMR of TAT-NH<sub>2</sub>.



















**Fig. S36.** <sup>1</sup>H NMR of **TATNFF**.



Fig. S37. <sup>13</sup>C NMR of TATNFF.

### Reference

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