# Supporting Information

## Fast and Ultrasensitive Detection of a Nerve Agent Simulant Using Carbazole-based Nanofibers with Amplified Ratiometric Fluorescence Responses

Chunyan Sun,[†] Wei Xiong,[‡,#] Weidong Ye,[†] Yingxuan Zheng,[‡,#] Ran Duan,[‡] Yanke Che,*[,‡,#] and Jincai Zhao[‡,#]

[†] Department of Chemistry, Shaoxing University, Zhejiang 312000, China
[‡]Key Laboratory of Photochemistry, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[#]University of Chinese Academy of Sciences, Beijing 100049, China

Corresponding author:
*Email: ykche@iccas.ac.cn

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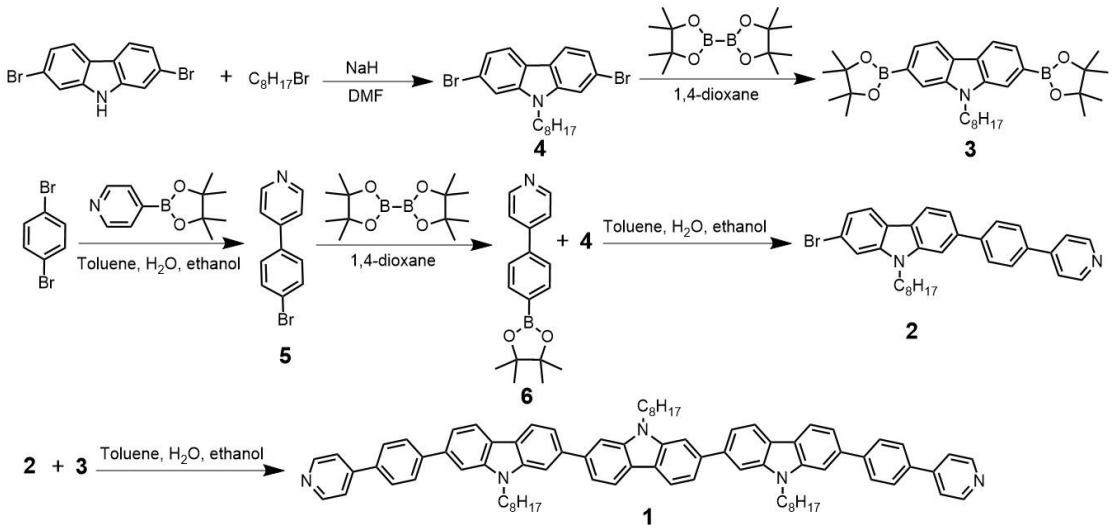
## Synthesis




**Scheme S1.** Synthesis route of molecule **1**.

Molecules **3** and **4** were synthesized by following the previously reported method.[1,2]
Molecule **4**: $^1$H NMR (300 MHz, $CDCl_3$): δ 7.9 (d, *J* = 8.1 Hz, 2H), 7.55 (s, 2H), 7.35 (dd, *J* = 8.4 Hz, 1.2 Hz, 2H), 4.3 (t, *J* = 7.5 Hz, 2H), 1.89 (m, 2H), 1.4-1.25 (m, 10H), 0.91 (t, *J* = 6.9 Hz, 3H).
Molecule **3**: $^1$H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.8 Hz, 2H), 7.88 (s, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 4.37 (t, *J* = 7.2 Hz, 2H), 1.88 (m, 2H), 1.40 (s, 24H), 1.31-1.26 (m, 10H), 0.86 (t, *J* = 6.9 Hz, 3H).

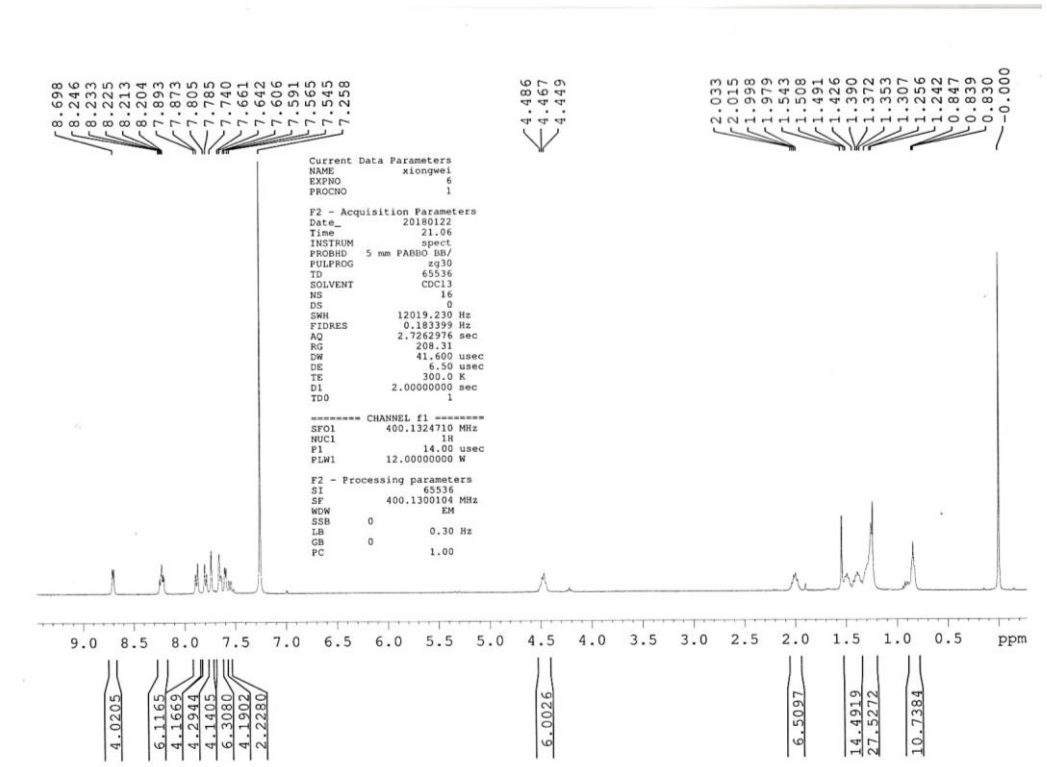
**4-(4-bromophenyl)pyridine (5).** Aqueous solution of potassium carbonate (2 M, 10 mL) was added to a stirred solution of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1.9 g, 8.51 mmol), 1,4-dibromobenzene (2 g, 8.51 mmol), and tetrakis(triphenylphosphine)palladium (510 mg, 0.43 mmol) in a deoxygenated mixed solution of toluene (40 mL) and ethanol (6 mL). Then the mixture was refluxed overnight under Ar. After removal of the solvent under vacuum, the residue was extracted with dichloromethane (3 * 30 mL) and water (40 mL). The combined organic layers were dried over $Na_2SO_4$ and concentrated under vacuum. The residue was purified by column chromatography (silica, dichloromethane: acetone = 100:1) to afford **5** (1.2 g) in 60% yield.
Molecule **5**. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.67 (dd, *J*= 4.4 Hz, 1.6Hz 2H), 7.63 (d, *J*= 8.0 Hz, 2H), 7.51 (d, *J*= 8.0 Hz, 2H), 7.47 (dd, *J*= 4.4 Hz, 1.6Hz, 2H).

**4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine (6).** A mixture of **5** (0.80 g, 3.4 mmol), potassium acetate (1.33 g, 13.6 mmol), bis(pinacolato)diboron (1 g, 4.1 mmol), and $Pd(dppf)Cl_2$ (130 mg, 0.17 mmol) in deoxygenated 1,4-dioxane (30 mL) was stirred overnight at 80 °C under Ar. After removal of the solvent under vacuum, the residue was extracted with ethyl acetate (3 * 30 mL) and water (30 mL). The combined organic layers were washed with saturated NaCl solution, dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by column

chromatography (silica, dichloromethane: acetone = 100:1) to afford **6** (880 mg) in 90% yield.
Molecule **6**. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, *J*= 5.6 Hz, 2H), 7.93 (d, *J*= 8.0 Hz, 2H), 7.65 (d, *J*= 8.0 Hz, 2H), 7.53 (d, *J*= 5.6 Hz, 2H), 1.37 (s, 12H).

**2-bromo-9-octyl-7-(4-(pyridin-4-yl)phenyl)-9H-carbazole (2).** Aqueous solution of potassium carbonate (2 M, 4 mL) was added to a stirred solution of **4** (1.53 g, 3.5 mmol), **6** (990 mg, 3.5 mmol), and tetrakis(triphenylphosphine)palladium (208 mg, 0.175 mmol) in deoxygenated mixed solution of toluene (20 mL) and ethanol (3 mL). Then the mixture was refluxed overnight under Ar. After removal of the solvent under vacuum, the residue was extracted with dichloromethane (3 * 30 mL) and water (40 mL). The combined organic layers were dried over $Na_2SO_4$ and concentrated under vacuum. The residue was purified by column chromatography (silica, dichloromethane: acetone = 30:1) to afford **2** (800 mg) in 45% yield.
Molecule **2**. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J*= 5.6 Hz, 2H), 8.14 (d, *J*= 8.0 Hz, 1H), 7.97 (d, *J*= 8.0 Hz, 1H), 7.85 (d, *J*= 8.0 Hz, 1H), 7.79 (d, *J*= 8.0 Hz, 1H), 7.60 (m, 4H), 7.53 (d, *J*= 8.0 Hz, 1H), 7.36 (d, *J*= 8.0 Hz, 1H), 4.33 (t, *J*= 7.2 Hz, 2H), 1.92 (m, 2H), 1.42-1.24 (m, 10H), 0.87 (t, *J*= 6.4 Hz, 3H).

**9,9',9''-trioctyl-7,7''-bis(4-(pyridin-4-yl)phenyl)-9H,9'H,9''H-2,2':7',2''-tercarbazole (1).** Aqueous solution of potassium carbonate (1 M, 3 mL) was added to a stirred solution of **3** (170 mg, 0.32 mmol), **2** (350 mg, 0.68 mmol), and tetrakis(triphenylphosphine)palladium (38 mg, 0.032 mmol) in deoxygenated mixed solution of toluene (10 mL) and ethanol (1 mL). Then the mixture was refluxed overnight under Ar. After removal of the solvent under vacuum, the residue was extracted with dichloromethane (3 * 60 mL) and water (50 mL). The combined organic layers were dried over $Na_2SO_4$ and concentrated under vacuum. The residue was purified by column chromatography (silica, dichloromethane: acetone = 10:1) to afford **1** (200 mg) in 55% yield. The resulting target compound was confirmed by $^1$H NMR and MALDI-MS as below.
Molecule **1**. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J*= 6.0 Hz, 4H), 8.24-8.20 (m, 6H), 7.89 (d, *J*= 8.0 Hz, 4H), 7.80 (d, *J*= 8.0 Hz, 4H), 7.74 (s, 4H), 7.66 (m, 6H), 7.60 (d, *J*= 6.0 Hz, 4H), 7.56 (d, *J*= 8.0 Hz, 2H), 4.48 (t, *J*= 7.6 Hz, 6H), 2.03 (m, 6H), 1.50-1.24 (m, 30H), 0.84 (t, *J*= 7.2 Hz 9H). MALDI-MS: (m/z) = 1140.8.

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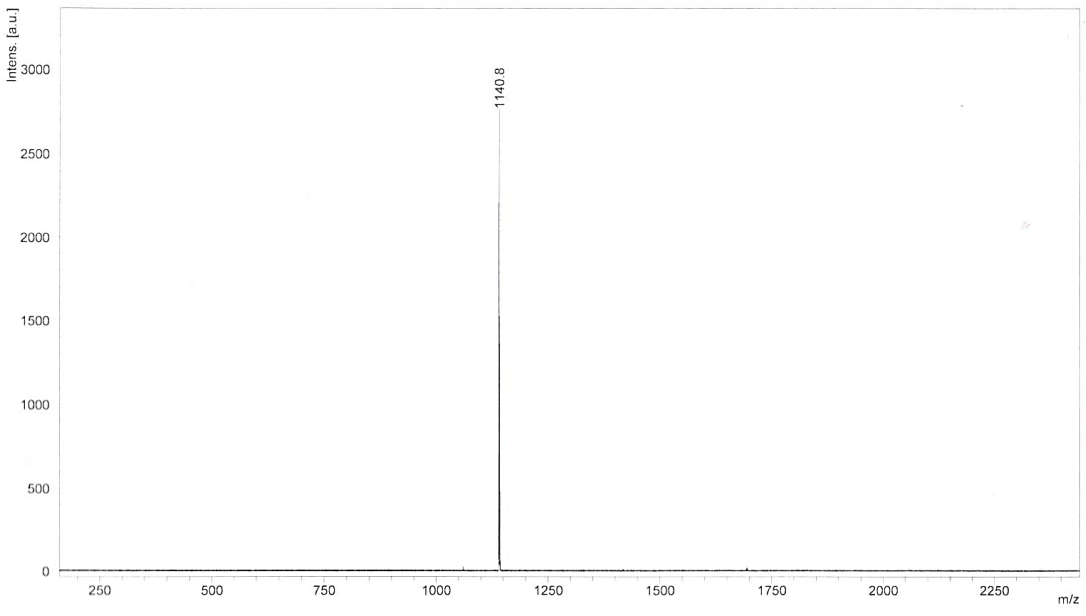


## Fabrication and property characterizations of 1 nanofibers

**1** nanofibers were prepared by injecting 0.1 mL dichloromethane solution of molecule **1** (2 mg/mL) into 0.5 mL hexane in a vial followed by aging for1 day at room temperature. UV-Vis and fluorescence spectra of **1** nanofibers suspended in ethanol were obtained on a PerkinElmer Lambda 35 spectrometer and a F-7000 fluorescence

spectrometer (excited at 375 nm), respectively. Solid-state fluorescence spectra of **1** nanofibers casted onto a quartz slide before and after exposure to DCP vapor were obtained on a F-7000 fluorescence spectrometer (excited at 375 nm). Optical microscopic images of the corresponding nanofibers drop-casted onto a glass slide were recorded on an Olympus FV1000 inverted confocal laser scanning microscopy (CLSM) coupled with a 405 nm laser. XRD pattern of **1** nanofibers was measured using a PAN alytical X'Pert PRO instrument (40 kV, 200 mA). SEM measurement of **1** nanofibers was performed on a Hitachi S-8010 field-emission scanning electron microscopy. The Pt sputtering was performed on a Leica EM SCD 500 instrument where the current and time were set as 15 mA and 120 s, respectively. The fluorescence quantum yields of the **1** nanofibers deposited on a quartz slide before and after exposure to DCP vapor were measured on a Hamamatsu Absolute PL Quantum Yield spectrometer C11247.

## Sensing characterizations

A jar (40 mL) containing 2 ml of DCP was sealed for overnight to obtain the saturated DCP vapor. The diluted vapor concentrations of DCP was obtained by injecting a small volume of the saturated vapor of DCP into a sealed vial (40 mL). For example, injection of 0.5 ml of saturated DCP vapor (132 ppm) into a 40 mL vial will produce the vapor concentration of 1.65 ppm. **1** nanofibers deposited inside the quartz tube were prepared by casting 10 μL hexane solution of the suspending nanofibers (4 μg) into a quartz tube. The solvent in the quartz tube was removed with a capillary and then the resulting quartz tube with nanofibers inside was dried by a blower. Casting nanofibers into the optical tube in our work is a simple and convenient way for the fabrication of sensors. Because of the high porosity of the piled nanofibers, the thickness of the resulting nanofibril film has negligible effect on the sensing performance. The fluorescence responses of **1** nanofibers towards DCP vapor were performed by blowing 10 mL of certain concentrations of DCP vapors into a quartz tube. The vapor was pumped onto **1** nanofibers in the quartz tube by an air pump (the air pump rate, 150 mL/min). The time-dependent fluorescence profiles were recorded with an Ocean Optics USB4000 fluorometer using a 385 nm LED lamp as the light source. The fluorescence responses of **1** nanofibers on a glass slide to various DCP vapors in a sealed cuvette (3 mL) were performed by adding 1 μL DCP in hexane (3.5 μM) into the sealed cuvette containing a little of cotton in the bottom kept at 35 ℃. Fluorescence spectra were obtained using a F-7000 fluorescence spectrometer.

## Other supporting figures

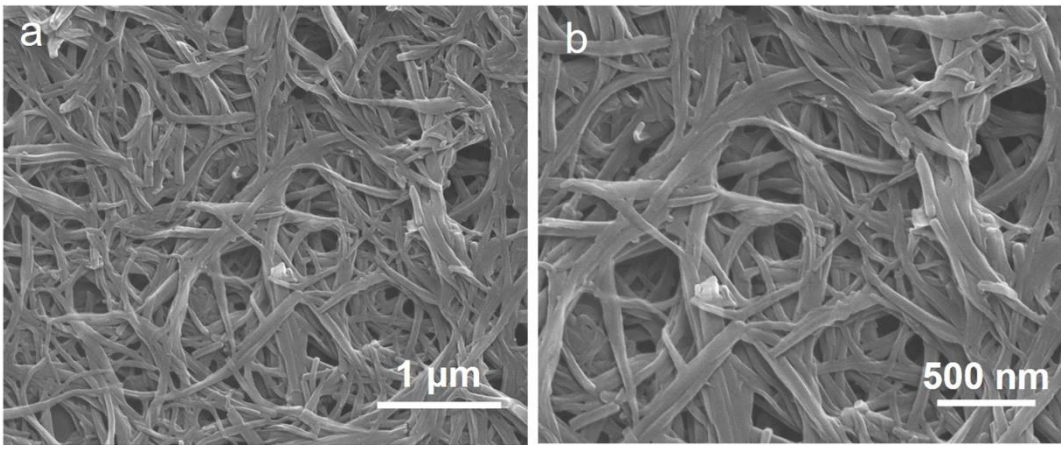


**Figure S1.** (a, b) SEM images of **1** nanofibers.

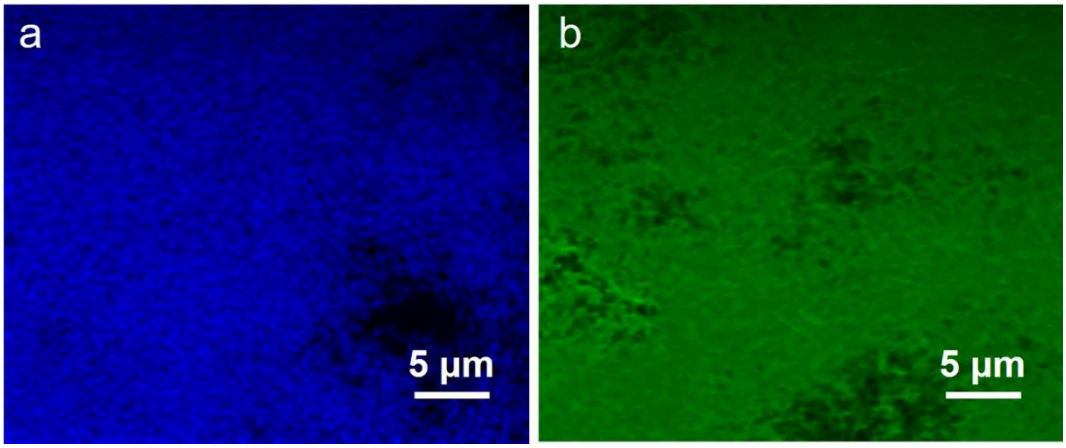


**Figure S2.** Fluorescence-mode optical microscopic images of **1** nanofibers before (a) and after (b) exposure to DCP vapor.

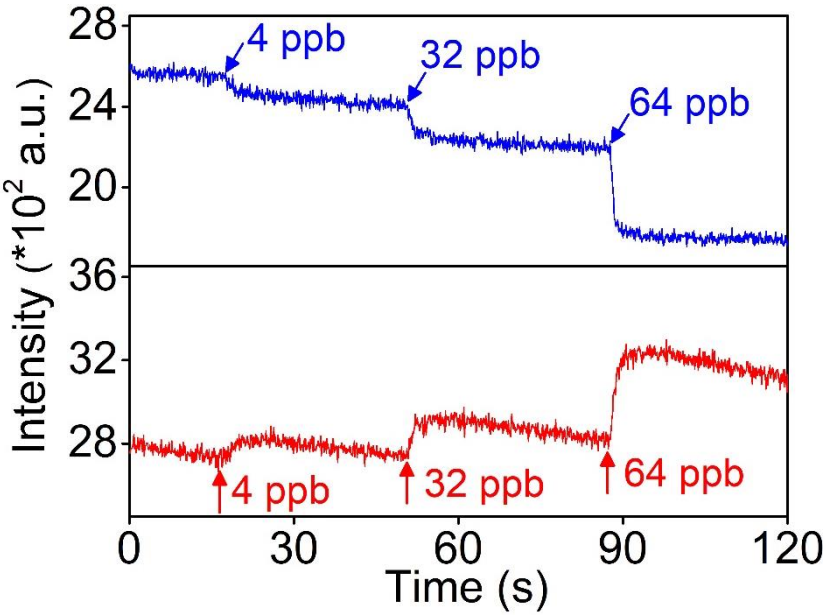


**Figure S3.** Fluorescence responses of **1** nanofibers monitored at 466 nm (blue) and 560 nm (red) upon exposure to DCP vapors at different concentrations.

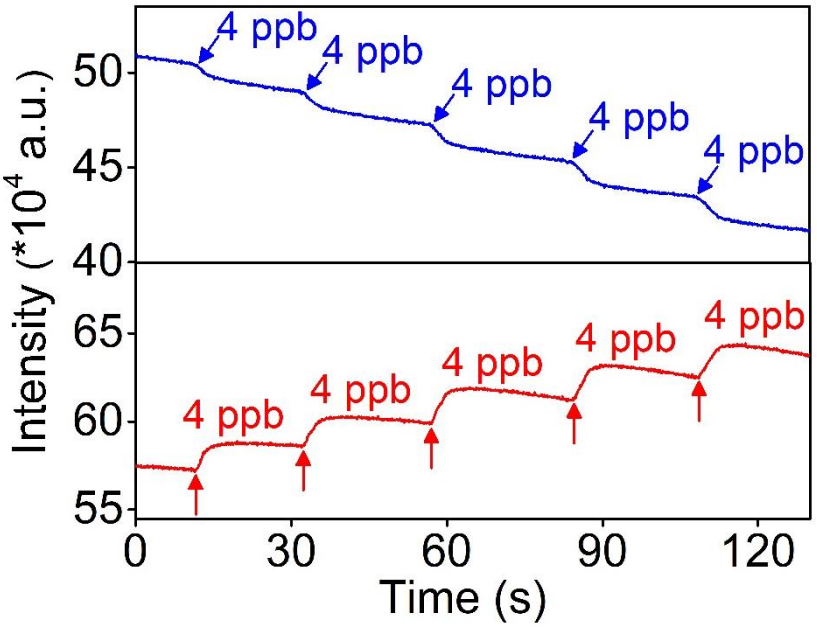


**Figure S4.** Fluorescence responses of **1** nanofibers monitored at a range of 446-486 nm (blue) and 540-580 nm (red) upon exposure to trace DCP vapor (4 ppb).

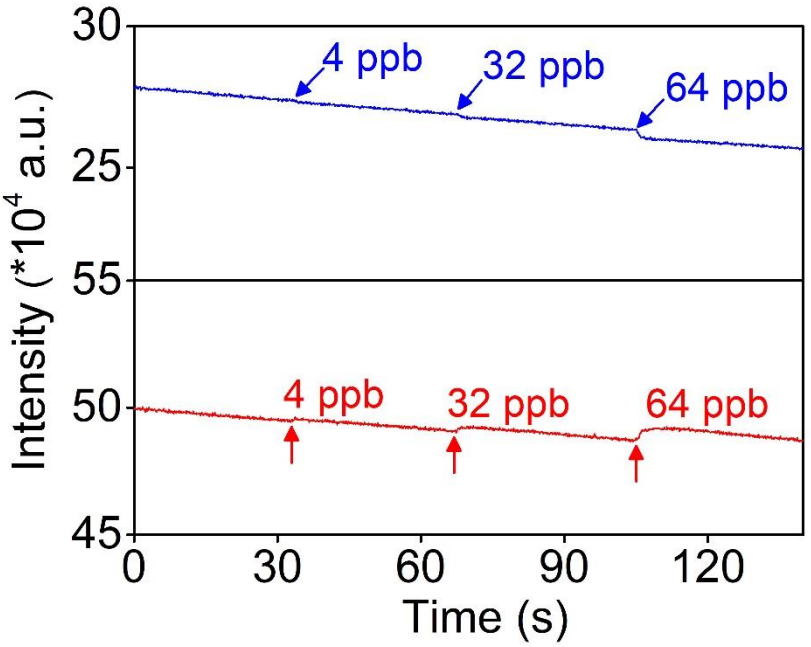


**Figure S5.** Fluorescence responses of the film formed by rapidly casting the dichloromethane solution of **1** (5 mg/mL) into a quartz tube upon exposure to different concentrations of DCP vapors at range of 446-486 nm (blue) and 540-580 nm (red).

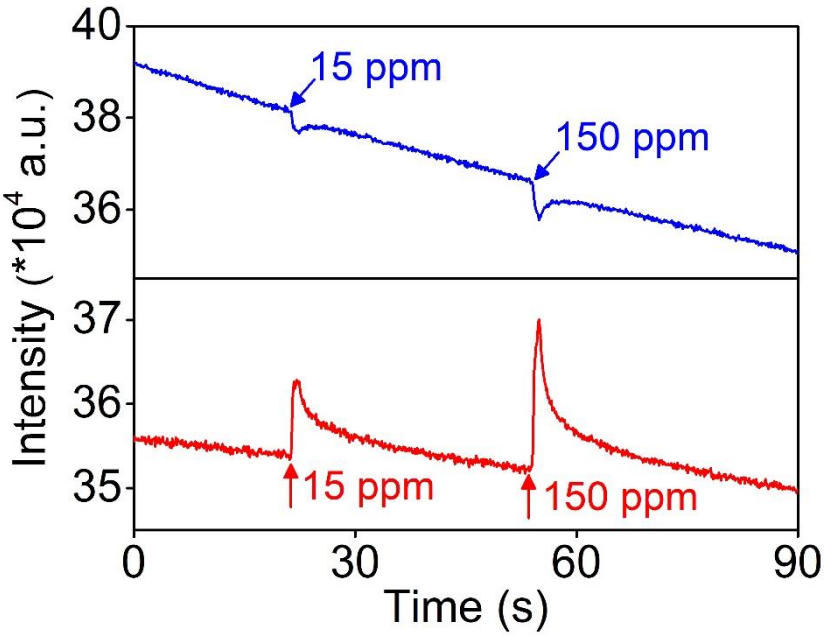


**Figure S6.** Fluorescence responses of **1** nanofibers monitored at range of 446-486 nm (blue) and 540-580 nm (red) upon exposure to acetic acid vapors at different concentrations.

## References

(1) Xiong, W.; Liu, X.; Wang, T.; Zhang, Y.; Che, Y.; Zhao, J. *Anal. Chem.* **2016**, *88*, 10826-10830.
(2) Zhu, Q.; Xiong; W.; Gong, Y.; Zheng, Y.; Che, Y.; Zhao, J. *Anal. Chem.* **2017**, *89*, 11908-11912.