Supporting information

Fluorescence Detection of A Broad Class of Explosives with One Zinc (II)-coordination Nanofiber

Wei Xiong,[†,‡,§] Xiaoling Liu,[†,‡,§] Tie Wang,[†,‡] Yifan Zhang,[†,‡] Yanke Che,[*,†,‡] and Jincai Zhao[†,‡]

[†]*Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*.

[‡]*University of Chinese Academy of Sciences, Beijing 100049, China.*

[§]These authors contributed equally.

Corresponding author

*Email: ykche@iccas.ac.cn

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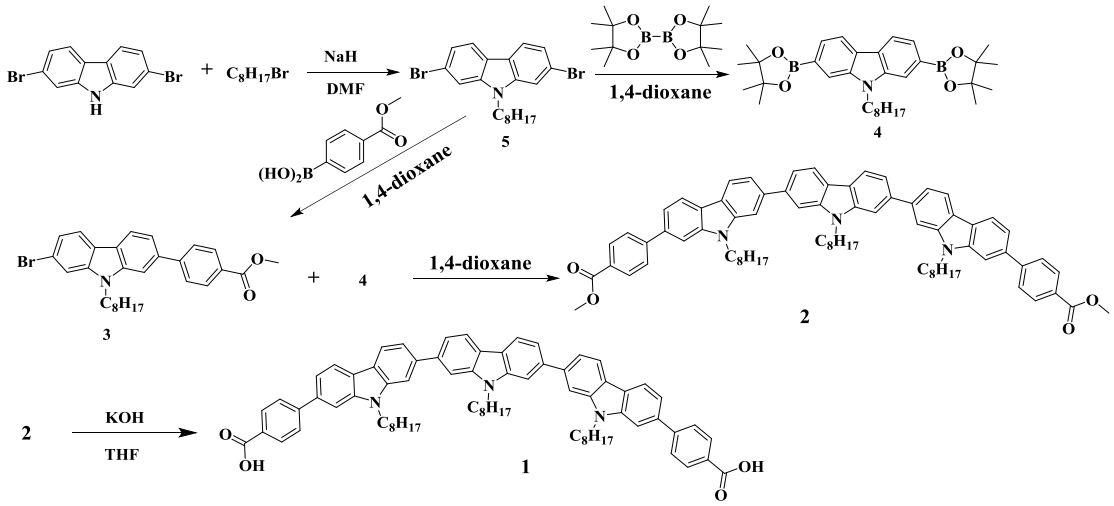
Synthesis

Scheme 1. Synthesis route of molecules 1 and 2.



Synthesis of 2,7-dibromo-9-octyl-9H-carbazole (5)

2,7-Dibromocarbazole (5 g, 15.4 mmol) was dissolved in 40 mL dimethylformamide (DMF) in a 100 ml two-neck round-bottom flask. After the solution was cooled to 0 °C, NaH (444mg, 18.48 mmol) was added into the above solution in small portions. After stirred for 10 minutes, 10 mL DMF solution of 1-bromooctane (3.67 g, 18.48 mmol) was added dropwise. Then the mixture was warm up to room temperature to react and was stirred overnight. After being quenched upon the addition of water (10 mL), the mixture was extracted with ethyl acetate (50 ml * 3) and the resulting organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The residue obtained by filtration and evaporation of the above organic layer was purified by running column chromatography on a silica gel column (petroleum as the eluent), followed by recrystallization in methanol for the target white crystals (6.2 g, 92%). The target compound as obtained was confirmed by ^{1}H NMR as below.

Compound **5:** ^{1}H NMR (Bruker 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).

Synthesis of 9-octyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (4)

2,7-dibromo-9-octyl-9H-carbazole (**5**) (5 g, 11.4 mmol), potassium acetate (15.6 g, 159.6 mmol), 4,4,5,5,-tetramethyl-2-(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2,-dioxaborolane (14.5 g, 57 mmol), and $Pd(dppf)Cl_2$) (835 mg, 1.14 mmol) were dissolved in deoxygenated 1,4-dioxane (80 mL). The mixture was heated to 80 °C under Ar and stirred overnight. After removal of the solvent under reduced pressure, the residue was extracted with ethyl acetate (100 mL * 3) and water (100 mL). The combined organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by running column chromatography on silica gel (Petroleum: Ethyl acetate = 10:1), followed by recrystallization in methanol for the target white crystals (5.4 g, 90%). The target

compound as obtained was confirmed by ^{1}H NMR as below.

Compound **4:** ^{1}H NMR (Bruke 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).

Synthesis of methyl 4-(7-bromo-9-octyl-9H-carbazol-2-yl)benzoate (3)

2,7-dibromo-9-octyl-9H-carbazole (**5**) (2 g, 4.58 mmol), (4(methoxycarbonyl)phenyl)-boronic acid (824 mg, 4.58 mmol), tetra(triphenylphosphine)palladium (544 mg, 0.458 mmol), and potassium carbonate solution (2 M, 10 mL) were dissolved in deoxygenated 1,4-dioxane (50 mL). The reaction mixture was heated to 70 °C and stirred overnight under Ar. After removal of the solvent under reduced pressure, the residue was extracted with ethyl acetate (60 mL * 3) and water (40 mL). The combined organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum: DCM: Ethyl acetate = 8:1:0.1) (1.24 g, 55%). The target compound as obtained was confirmed by ^{1}H NMR as below.

Compound **3** ^{1}H NMR (Bruker 300 MHz, $CDCl_3$): δ 8.15 (m, 3H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.76 (dd, *J* = 6.6 Hz, 1.8 Hz, 2H), 7.58 (dd, *J* = 8.4 Hz, 1.5 Hz, 2H), 7.51 (dd, *J* = 8.1 Hz, 1.5 Hz, 1H), 7.35 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 4.30 (t, *J* = 7.5 Hz, 2H), 3.96 (s, 3H), 1.87 (m, 2H), 1.28-1.23 (m, 10H), 0.88 (t, *J* = 7.2 Hz, 3H).

Synthesis of dimethyl 4,4'-(9,9',9''-trioctyl-9H,9'H,9''H-[2,2',7',2''-tercarbazole]-7,7''-diyl)-dibenzoate 9-octyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (2)

9-octyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**4**) (1 g, 1.88 mmol), methyl4-(7-bromo-9-octyl-9H-carbazol-2-yl)benzoate (**3**) (1.95 g, 3.95 mmol), tetra(triphenyl-phosphine)-palladium (223 mg, 0.188 mmol), and potassium carbonate solution (2 M, 5 mL) were dissolved in deoxygenated 1,4-dioxane (40 mL). The reaction mixture was heated to 85 °C and stirred 8 h under Ar. After removal of the solvent under reduced pressure, the residue was extracted with $CHCl_3$ (60 mL * 3) and water (40 mL). The combined organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (Petroleum: DCM: Ethyl Acetate = 2:1:0.4) (1.04 g, 50%). The target compound as obtained was confirmed by ^{1}H NMR (Figure S11) and MALDI-TOF-MS (Figure S12) as below.

Compound **2** ^{1}H NMR (Bruker 400 MHz, $CDCl_3$): δ 8.32 (m, 10H), 7.8 (d, *J* = 8 Hz, 4H), 7.73 (s, 4H), 7.66 (m, 6H), 7.54 (d, *J* = 8 Hz, 2H), 4.5 (m, 6H), 3.97 (s, 6H), 1.99 (m, 6H), 1.54-1.24 (m, 30H), 0.84 (t, *J* = 4 Hz, 9H). MALDI-TOF-MS: m/z = 1107.7.

Synthesis of 4,4'-(9,9',9''-trioctyl-9H,9'H,9''H-[2,2',7',2''-tercarbazole]-7,7''-diyl)dibenzoic acid (1)

Compound **2** (500 mg, 0.45 mmol) was dissolved in 30 mL THF. Then 10 mL water solution of KOH (4.5 mmol, 265 mg) and Bu_4NBr (0.09 mmol, 29 mg) were added into the above solution. The mixture was refluxed for 6 h and then cooled to room temperature. Dilute HCl (1 M) was added to tune the pH value of the solution to 2-3. The resulting light yellow powder was collected and dried in vacuum (459 mg, 95%). The target compound as obtained was confirmed by ^{1}H NMR (Figure S13) and MALDI-TOF-MS (Figure S14) as below.

Compound **1** ^{1}H NMR (Bruker 300 MHz, DMSO-*d6*): δ 8.31 (d, *J* = 8.1 Hz, 6H), 8.09-7.98 (m, 14H), 7.72 (d, *J* = 8.1 Hz, 4H), 7.62 (d, *J* = 8.7 Hz, 2H), 4.65 (m, 6H), 1.91 (m, 6H), 1.35-1.17 (m, 30H), 0.76 (t, *J* = 6.6 Hz, 9H). MALDI-TOF-MS: m/z =1073.7.

Fabrication of nanofibers from 1 and 2.

Compound **1** (0.047 mmol, 50 mg) was first dissolved in 40 mL DMF and then $Zn(OAc)_2 \cdot 2H_2O$ (0.047 mmol, 10.3 mg) in 10 mL DMF was added dropwise. The mixture was stirred (300 r/min) at room temperature for 2 days to allow the formation of the Zn^{2+}-**1** coordination nanofibers. Before structure and sensing property characterizations, the resulting nanofibers were collected by centrifugation and washed with DMF and ethanol thoroughly.

Compound **2** (0.0009 mmol, 1 mg) dissolved in 1 mL $CHCl_3$ was injected into 10 mL methanol or ethanol and aged for 10 h to allow the self-assembly of the nanofibers. These resulting nanofibers suspended in the solution can be simply transferred onto a substrate for morphology and property characterizations.

Property characterizations

RDX, PETN, TNT, DNT, DMNB, S_8 were purchased from commercial company (J&K), and used without any purification.

The fluorescence quenching of the nanofibers by explosives were measured on a home-built detector (Figure S5). The corresponding solution concentrations of different explosives were obtained by diluting a known concentration of explosive (1 mg/ml, dissolving in acetone, purchasing from commercial company (J&K)) to get a diluted solution (1 ng/μL or 10 ng/μL). The changes of fluorescence spectra were recorded with an Ocean Optics USB4000 fluorometer using a 385 nm LED lamp as the light source. The fluorescence quenching by explosives was carried out by placing a certain amount of corresponding explosive to an entry to the thermal desorber (the temperature was set as 170 °C), where the vaporized explosives would be pumped onto the the Zn^{2+}-**1** coordination nanofibers in a quartz tube by an air pump (200 mL/min). The the Zn^{2+}-**1** coordination nanofibers film deposited inside the quartz tube was prepared by casting 15 μL ethanol solution of the suspending nanofibers (1 mg/mL) into a quartz tube which was dried slowly in air with solvent vaporization.

Other Supporting Figures and Table.

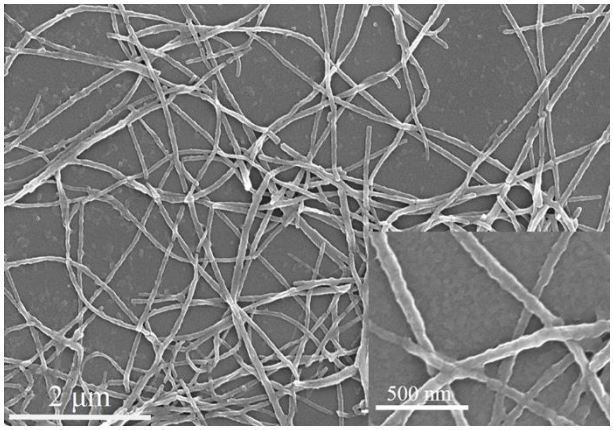


Figure S1. SEM images of **1**-Zn^{2+} coordination nanofibers. Inset: A magnified SEM image of **1**-Zn^{2+} coordination nanofibers.

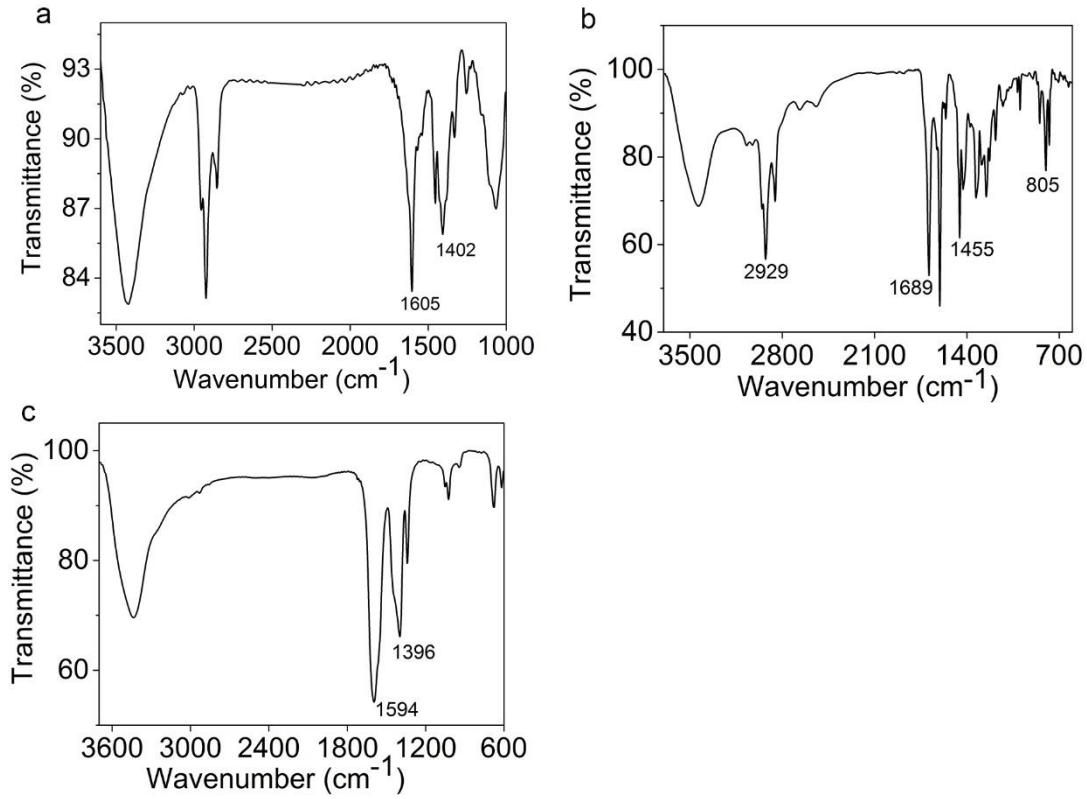


Figure S2. (a) FT-IR spectrum of **1**-Zn^{2+} coordination nanofibers that were casted onto a $1cm^2$ KBr disc from a suspension of nanofibers in ethanol. (b) FT-IR spectrum of molecule **1** on a $1cm^2$ KBr disc. (c) FT-IR spectrum of $Zn(OAc)_2 \cdot 2H_2O$ on a $1cm^2$ KBr disc.

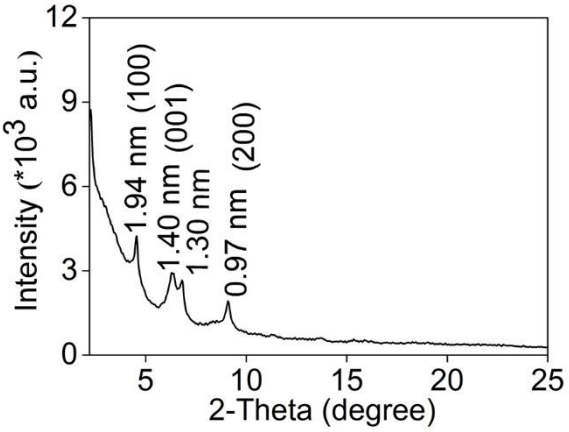


Figure S3. XRD patterns of **1**-Zn^{2+} coordination nanofibers.

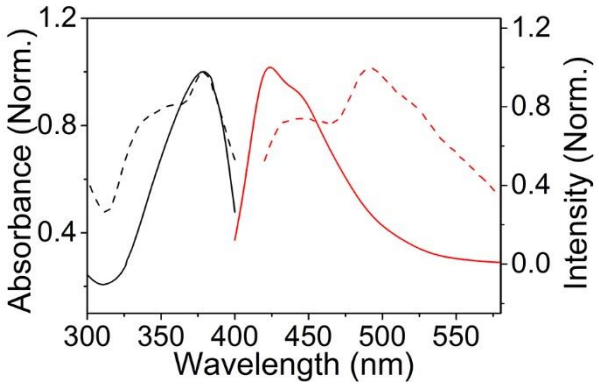


Figure S4. Left: Absorption spectra (black) of molecule **1** in DMF (0.31 μM) (solid)and **1**-Zn^{2+} coordination nanofibers dispersion (dashed). Right: Fluorescence spectra (red) of molecule **1** in DMF (0.31 μM) (solid) and solid fluorescence of **1**-Zn^{2+} coordination nanofibers (dashed).

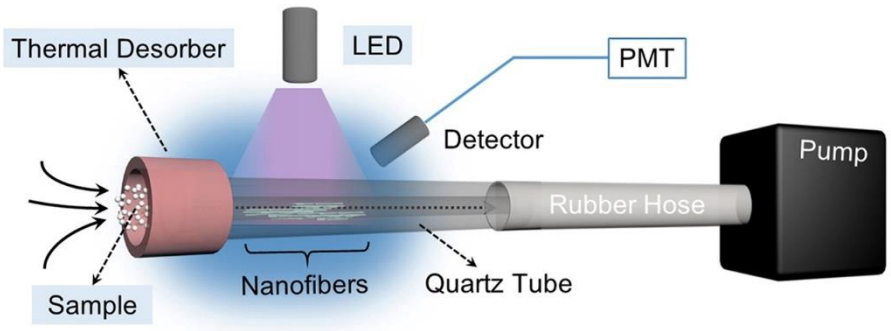


Figure S5. Schematic representation of a home-built optical detector used in this work to detect the explosives.

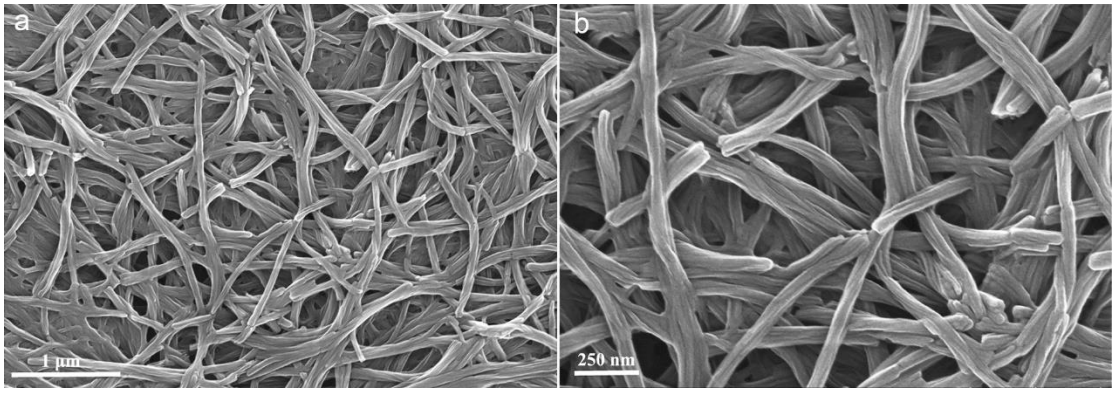


Figure S6. (a, b) SEM images of the nanofibers assembled from **2**.

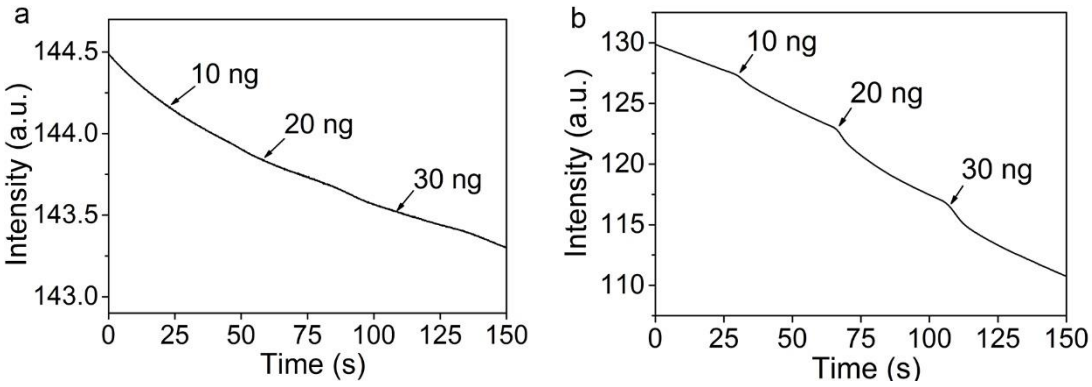


Figure S7. (a) No fluorescence response of the nanofibers from **2** upon exposure to the vapor of various amounts of RDX. Note that the smoothly decreasing fluorescence intensity of nanofibers results from the photobleaching. (b) Fluorescence quenching of the nanofibers from **2** upon exposure to the vapor of various amounts of PETN.

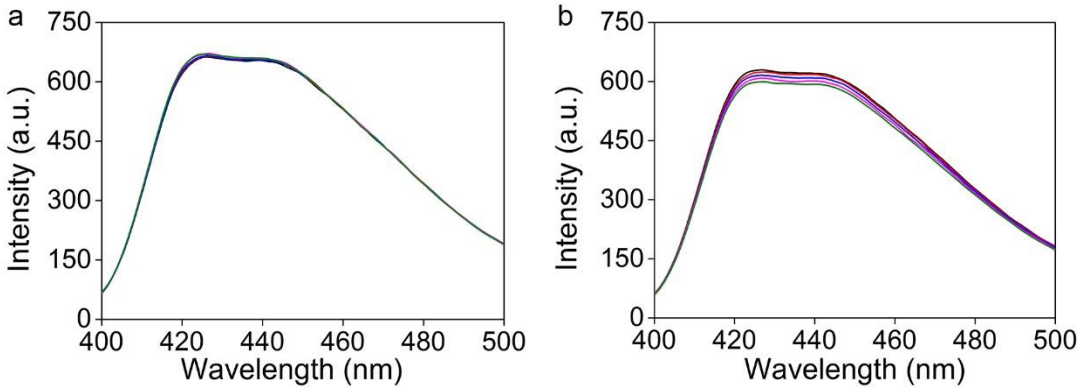


Figure S8. (a) Fluorescence spectra of molecule **2** (0.53 μM) in DMF in the presence of various concentrations of RDX, (0, 0.8, 1.5, 2.3, 3.1, 3.9 mM). (b) Fluorescence spectra of molecule **2** (0.50 μM) in DMF) in the presence of various concentrations of PETN, (0, 0.8, 1.5, 2.3, 3.1, 3.9 mM).

Table S1. HOMO and LUMO energies calculated for explosives and **1**-Zn^{2+} complexes at the B3LYP/6-31G* level of theory carried out by Gaussian 03 suite of programs.[1]

Compound	LUMO (eV)	HOMO (eV)	Band gap (eV)
TNT [a]	-3.483	-8.435	4.952
DNT [a]	-2.966	-8.109	5.143
RDX [a]	-2.531	-8.245	5.714
PETN [a]	-3.075	-8.707	5.633
DMNB	-2.943	-8.308	5.365
1-Zn^{2+}	-2.127	-5.810	3.683

[a] Cited from ref 2.

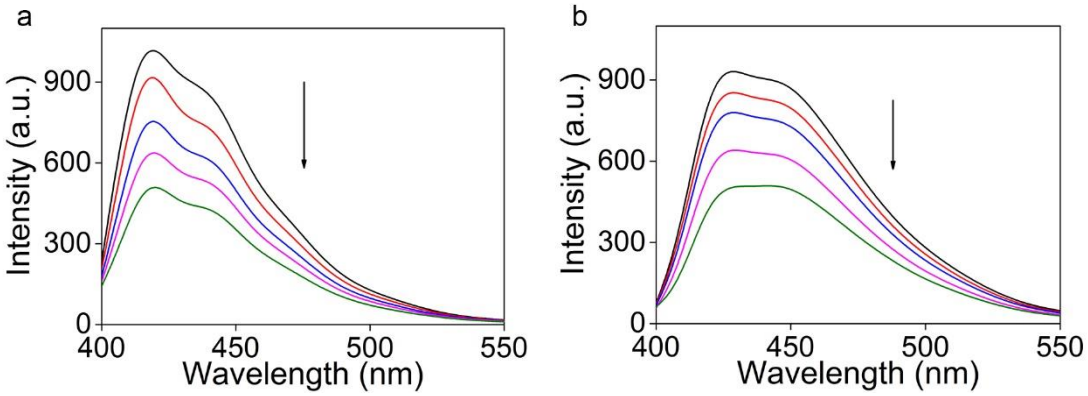


Figure S9. (a) Fluorescence spectra of **1**-Zn^{2+} complex in DMF (0.36 μM) in the presence of various concentrations of sulfur (0, 1.5, 3, 4.5, 5.5 mM). (b) Fluorescence spectra of molecule **2** in DMF (0.70 μM) in the presence of various concentrations of sulfur, (0, 1.5, 3, 4.5, 5.5 mM).

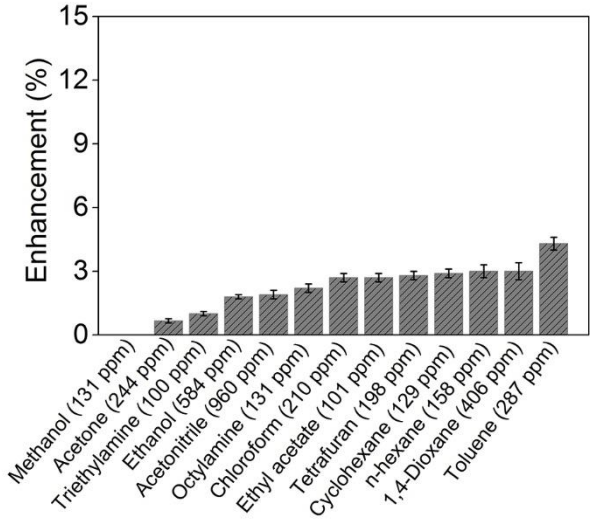


Figure S10. Enhanced fluorescence response of **1**-Zn^{2+} coordination nanofibers when exposed to common solvent vapors.

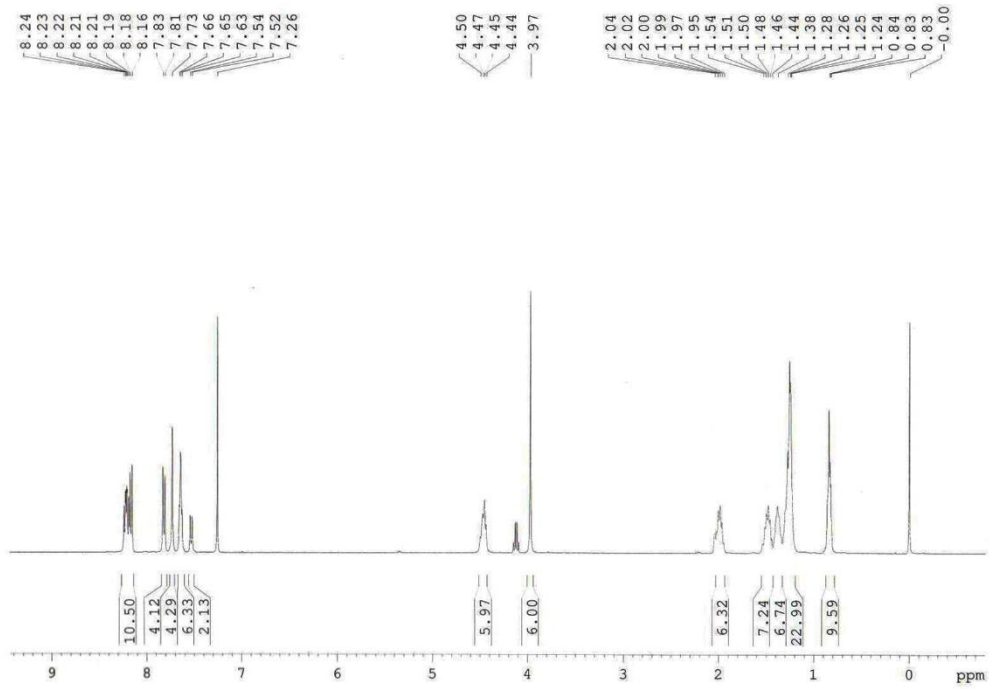


Figure S11. ^{1}H NMR spectrum of molecule **2**.

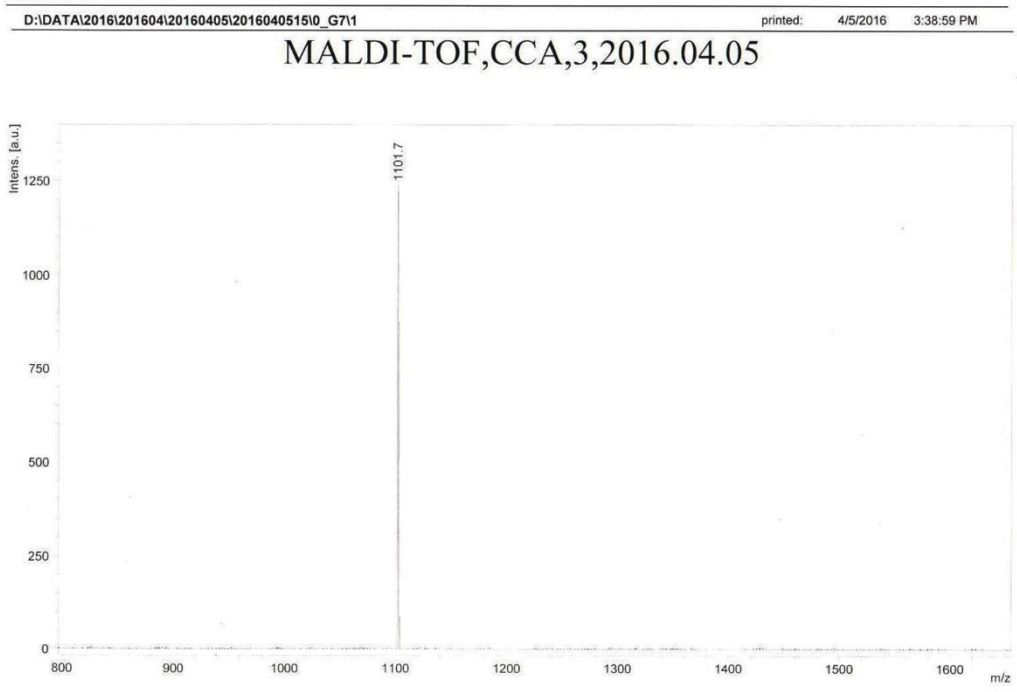


Figure S12. MALDI-TOF-MS spectrum of molecule **2**.

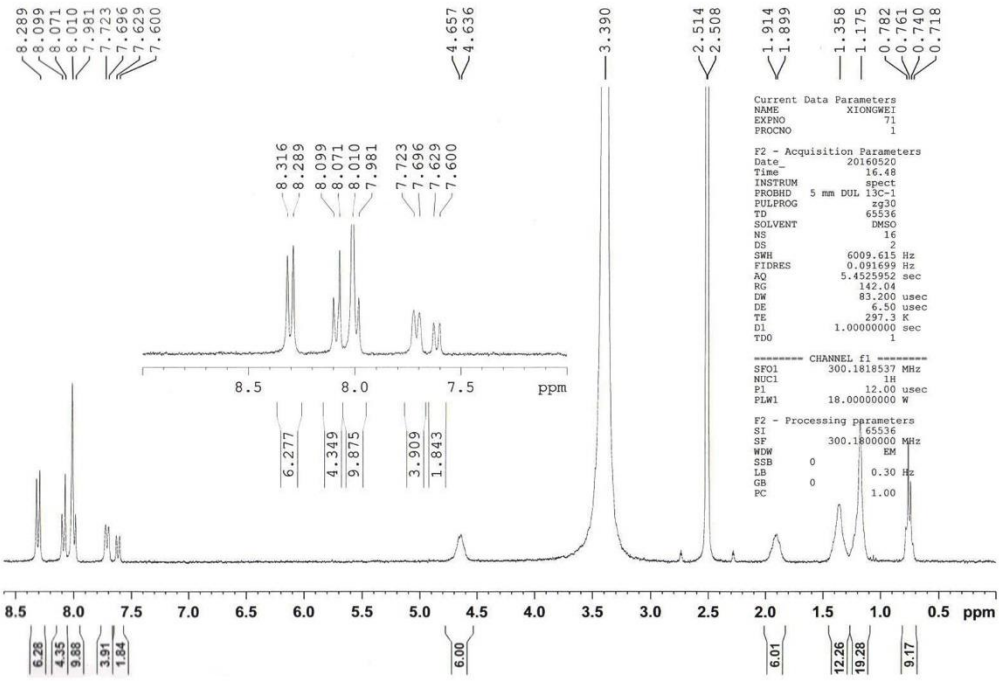


Figure S13.[1]H NMR spectrum of molecule **1**.

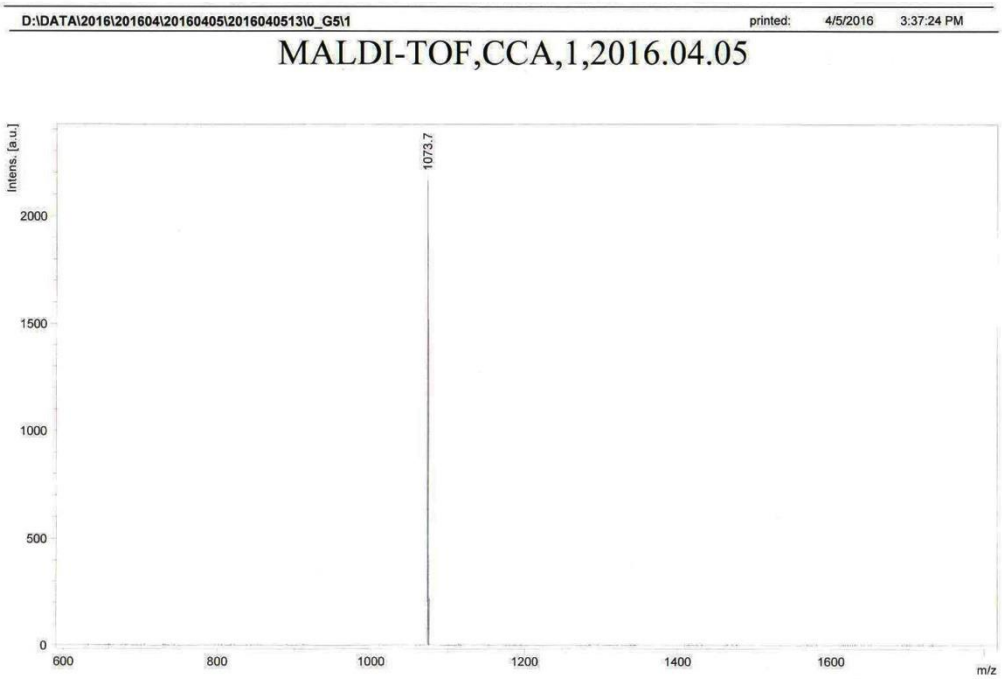


Figure S14. MALDI-TOF-MS spectrum data of molecule **1**.

References

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(2) Sanchez, J. C.; DiPasquale, A. G.; Rheingold, A. L.; Trogler, W. C. *Chem. Mater.* **2007**, *19*, 6459-6470.