Electronic Supplementary Information (ESI)

Colorimetric and fluorescent nanofibrous film as a chemosensor for Hg^{2+} in aqueous solution prepared by electrospinning technique and host-guest interaction

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1. Materials

Rhodamine B (RhB) and β-cyclodextrin (β-CD) were purchased from Sigma-Aldrich. 1-Adamantanemethanol (AD-CH_2OH), 4-toluene sulfonyl chloride (TSO-Cl), acrylic acid, methyl methacrylate, triethylamine and carbon disulfide were obtained from Alfa. All the reagents and inorganic metal salts with analytical grade (Shanghai Chemical Reagents Co. China) were used without further purification. The solutions of metal ions were prepared from NaCl, KCl, $CaCl_2$, $MgSO_4$, $FeCl_3$, $Mn(NO_3)_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $Zn(NO_3)_2$, $C_4H_6CdO_4 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$, $Hg(NO_3)_2$, $AgNO_3$, $Pb(NO_3)_2$, respectively, and were dissolved in deionized water. KH_2P0_4-NaOH buffer solutions with different pH values were prepared from proper amounts of KH_2P0_4 and NaOH (analytical grade) under adjustment by a pH meter.

2. Characterization

^1H NMR spectra were measured on a Bruker AV-400 spectrometer with chemical shifts reported as parts per million (in $CDCl_3$, TMS as internal standard). IR spectra were recorded on a Bruker Vector-22 spectrometer. The pH values of the test solutions were measured with a glass electrode connected to a Mettler-Toledo Instruments DELTA 320 pH meter (Shanghai, China) and adjusted if necessary. Fluorescence spectra were determined on a Hitachi F-4500. UV-Vis spectra were recorded on a Hitachi U-3010 UV-Vis spectrophotometer. High Voltage Power (0-50 kV) DW-P503-1AC (Tianjin, China), Scanning electron microscope (SEM) and SII: SPI3800N (Japan) were also used.

Procedures for metal-ion sensing: Stock solutions of the mercury ions (2.0×10^{-4} mol L^{-1}) were prepared in deionized water, and was then diluted to (2.0×10^{-4} molL^{-1}-1.0×10^{-4} mol L^{-1}) with DMF-H_2O (50 μM, KH_2P0_4-NaOH buffer at pH 7.2, 1:10, v/v) solution. Titration experiments were performed by placing 4.0 mL of a solution of Hg^{2+} (2.0×10^{-4} molL^{-1}-1.0×10^{-4} mol L^{-1}) in a quartz standard fluorlmeter cells of 1 cm optical path length, and then the inclusion complex nanofibrous film (size: 1.4 cm × 4.0 cm, weight: 0.0215±0.0005 g) was added to the standard fluorlmeter cells of Hg^{2+} solution for fluorescence spectra measurement. All test solutions were slowly stirred for 1 min and then allowed to stand at room temperature for 30 min. For fluorescence measurements, excitation wavelength was provided at 525 nm, and emission spectra was collected from 530 to 700 nm. Both excitation and emission slit widths were set to be either 1.5 or 5 nm.

2.1. Synthesis of Thiocarbamido-SRhB-β-CD (fluorophore moiety 3)

Thiocarbamido-SRhB-β-CD was prepared via the established literature procedure [G. Fang, M. Xu, F. Zeng and S. Wu, Langmuir 2010, 26(22), 17764-17771].

Rhodamine B (5g, 10.46mmol) was dissolved in 180mL of anhydrous ethanol, then ethylenediamine (12.56g, 209mmol) was added to it as soon as possible at 40□, and the temperature was raised to 85□ slowly. After 24 h, the solvent was evaporated under reduced pressure, then CH_2Cl_2 (100 mL) and water (200mL) were added to the residue, and the organic layer was separated, washed five times with water, and dried over anhydrous Mg_2SO_4. After filtration of Mg_2SO_4, the solvent was removed under reduced pressure to give an orange powder. The crude material was purified by flash

col- umn chromatography to give white product SRhB. (CH_2Cl_2/EtOH/ Et_3N, 5:1:0.1) Yield: 92%. ^{1}H NMR(ESI) (400MHz, $CDCl_3$): 1.519-1.565 (m, 6H), 1.632-1.757 (m, 6H), 3.726-3.764 (d, 2H), 4.426-4,468(t, 2H), 5.798-5.851(m, 1H), 6.061-6.184(m, 1H), 6.373-6.436(d, 1H). IR (KBr, cm^{-1}): 2900, 2849, 1723, 1633, 1452, 1402, 1292, 1266, 1196, 1179, 1055, 981 and 804. HRMS calcd for $C_{30}H_{38}N_4O$. [MH^+]: 485.3.

Thiocarbamido-SRhB-β-CD (fluorophore moiety **3**) was synthesized as follows: The reaction vessel was wrapped with aluminum foil to ensure the reaction took place in the dark. Under the protection of nitrogen, SRhB (0.05g, 0.10 mmol) was dissolved in 15 mL of anhydrous THF, the solution was cooled down to -15□, triethylamine (0.7 mL) was added to it, then CS_2 (0.95g, 12.4mmol) was added dropwise to the above solution, and the mixture was stirred for 24 h. KOH solution was used to absorb any gas resulting from the reaction. Afterward, TSO-Cl (0.25g, 1.4 mmol) was added to the solution; the reaction mixture was gradually heated to room temperature and kept at this temperature for 1 h. The reaction mixture was filtered, solvent was evaporated under vacuum, and the obtained powder was purified by silica gel column chromatography (petroleum ether : ethyl acetate was 3:1) to give the light-yellow crystalline SRhBNCS. Then SRhB-NCS was dissolved in 10 mL of anhydrous DMF, 6-NH_2-β-CD (0.359 mmol) was added to the solution, and the solution was kept at room temperature for 24 h. Afterward, acetone was added to the solution, forming a precipitate. Upon filtration, the precipitate was recrystallized from an acetone-water mixture. The white crystal product was obtained. Yield: 62 %. ^{1}HNMR (ESI) (400 MHz, DMSO-d6) δ: 7.81 (d, 1H), 7.49 (m, 2H), 7.02-6.99 (t, 1H), 6.35-6.27 (m, 6H),

5.86-5.62 (m, 14H), 4.89-4.73 (m, 6H), 4.43 (m, 6H), 4.2 (m, 1H), 3.63-3.13 (m, 21 H), 1.15-1.07 (t, 12H). HRMS calcd for $C_{75}H_{110}N_6O_{36}S$. [MH^+]: 1703.7.

2.2. Synthesis of 1-Adamantylmethyl acrylate (ADMA)

The solution of 1-adamantane methanol (5 g, 30.1 mmol) in 10 mL of dry dichloromethane and dry triethylamine (1.5 g, 15 mmol) was cooled below 5□ and acryloyl chloride (2.72 g, 30.1 mmol) was added dropwise to the solution under nitrogen atmosphere. The reaction was continued at 5□ for 5 h, then was brought to room temperature, and was stirred for another 12 h. The reaction mixture was then poured into water and extracted with dichloromethane. The organic layer was respectively washed with 0.1 mol/L HCl, 0.1 mol/L $NaHCO_3$ and brine solution and was finally dried over anhydrous Mg_2SO_4. The organic layer was filtered and the pure product was obtained as a viscous liquid via vacuum distillation. Yield=5.8 g (77%). ^{1}H NMR (400MHz, $CDCl_3$): 1.519-1.565 (m, 6H), 1.632-1.757 (m, 6H), 3.726-3.764 (d, 2H), 4.426-4,468(t, 2H), 5.798-5.851(m, 1H), 6.061-6.184(m, 1H), 6.373-6.436(d, 1H). IR(KBr, cm^{-1}): 2900, 2849, 1723, 1633, 1452, 1402, 1292, 1266, 1196, 1179, 1055, 981 and 804. HRMS(ESI) calcd for $C_{14}H_{20}O_2$. [MH^+]: 220.1.

2.3. Synthesis of Poly (MMA-co-ADMA)

The synthetic route is shown in Scheme 1. Poly (MMA-co-ADMA) was prepared by the copolymerization of ADMA and MMA with AIBN as a thermal initiator. Briefly, ADMA (1.00 g, 4.85 mmol), MMA (2.0 g, 20mmol) of, and AIBN (0.03 g. 18.27mmol) in 10 mL DMF were mixed and stirred at 70℃ for 24 h under a nitrogen atmosphere. The obtained Poly (MMA-co-ADMA) was transparent and achromatous.

It was dissolved in $CHCl_3$ (20 mL) and precipitated with methanol (200 mL). After successive dissolution and precipitation several times (4 times), Poly (MMA-co-ADMA) was filtrated on a glass filter and dried under vacuum at 50℃ to a constant weight. Yield=1.87 g (62.33%). The degree of the substitution of the adamantane group determined by ^1H NMR was found to be 7.54%. (400MHz, $CDCl_3$): 3.59 (s, $-CH_3$), 1.99-1.54 (m, CH_2-CH-COO and adamantane), 0.84-1.02 (m, adamantane). IR(KBr, cm-1): 2990, 2954, 2909, 2850, 1734, 1675, 1485, 1449, 1386, 1273, 1239, 1192, 1146, 986, 963, 842 and 747.

2.4. Preparation of electrospinning solution and poly (MMA-co-ADMA) nanofibrous film (nanofibrous film 2)

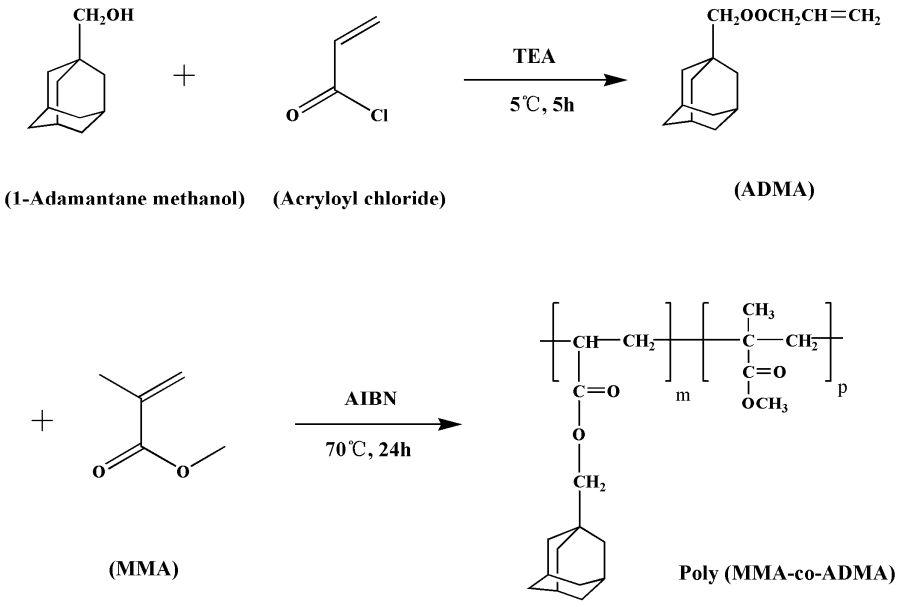
Nanofibrous film **2** was synthesized via copolymerization and electrospinning according to our previously reported method [W. Wang, Q. Yang, L. Sun, H. Wang, C. Zhang, X. Fei, M. Sun and Y. Li, *J. Hazard. Mater*., 2011, **194**, 185-192].

Poly (MMA-co-ADMA) of 0.8 g was added to the 2.7 g solution of DMF to prepare precursor solution with a concentration of 23 wt%. The solution was rapidly stirred for 24 h at room temperature. The resulting clear homogenous solution was used for electrospinning the film.

A burette with an inserted Cu rod to connect the high-voltage supply was filled with the precursor solution. An aluminum foil served as the counter electrode. The distance between the burette tip and the receiver was fixed at 17 cm. The high-voltage supply was fixed at 15 kV. The spinning rate was controlled at about 4 ml/h by adjusting the angle of inclination of the burette. The electrospinning was performed at 25℃.

2.5. Preparation of Thiocarbamido-SRhB-β-CD/Poly (MMA-co-ADMA) inclusion complex nanofibrous film (nanofibrous film 1).

Thiocarbamido-SRhB-β-CD (2×10^{-3} mol) in 100 mL of DMF-water (1:10, v/v) solution was stirred at 50℃ until the solution was clear. Then, the nanofibrous film (size: 1.4 cm×3.5 cm, weight: 0.0215±0.0005g) was added to the above solution. The solution was slowly stirred at 50℃ for at least 24 h. The reaction mixture was cooled to room temperature and deionized water was added to it. The resulting white inclusion complex film was washed with deionized water (2 × 15 mL) at 50℃ twice then with methanol (2 × 20 mL) at room temperature. After vacuum desiccation, the Thiocarbamido-SRhB-β-CD/Poly (MMA-co-ADMA) inclusion complex nanofibrous film (nanofibrous film 1) was obtained. Yield: 70-80%.



Scheme S1. Synthetic route of **ADMA** and **Poly (MMA-co-ADMA)**.

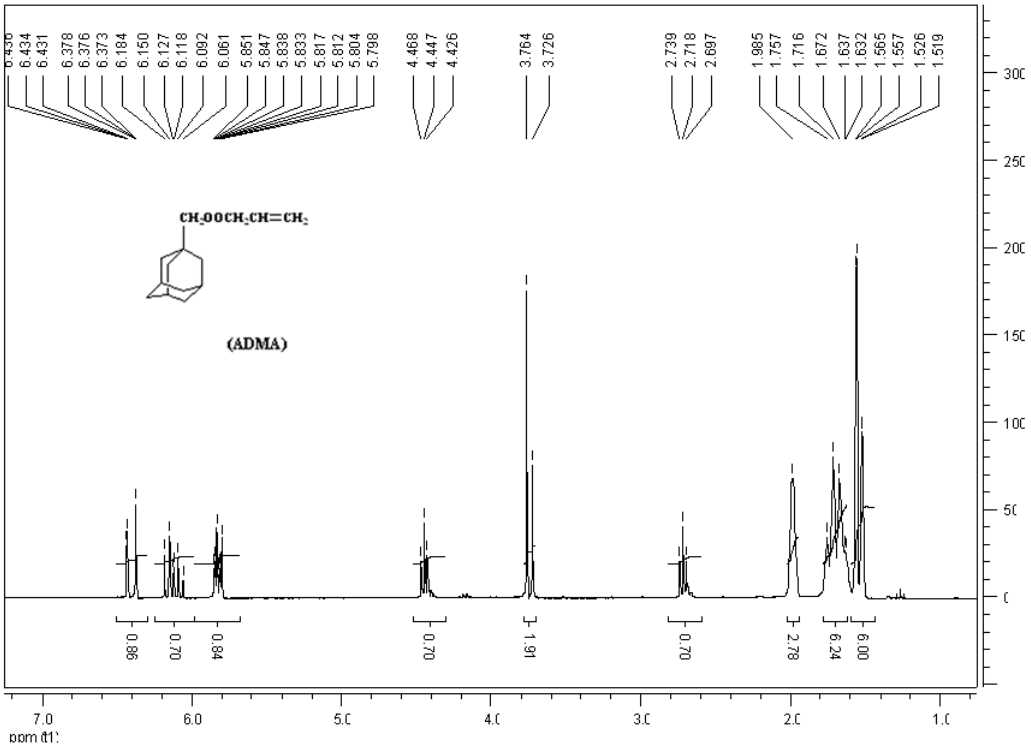


Fig. S1 ^{1}H NMR spectrum of **ADMA** in $CDCl_3$.

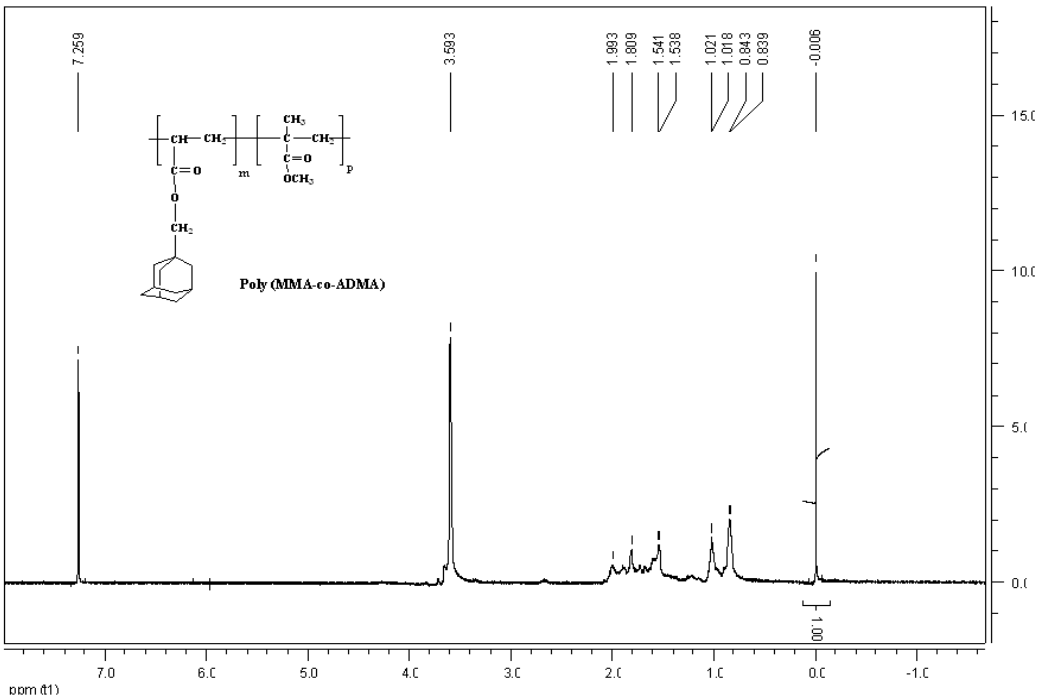


Fig. S2 ^{1}H NMR spectrum of **Poly (MMA-co-ADMA)** in $CDCl_3$.

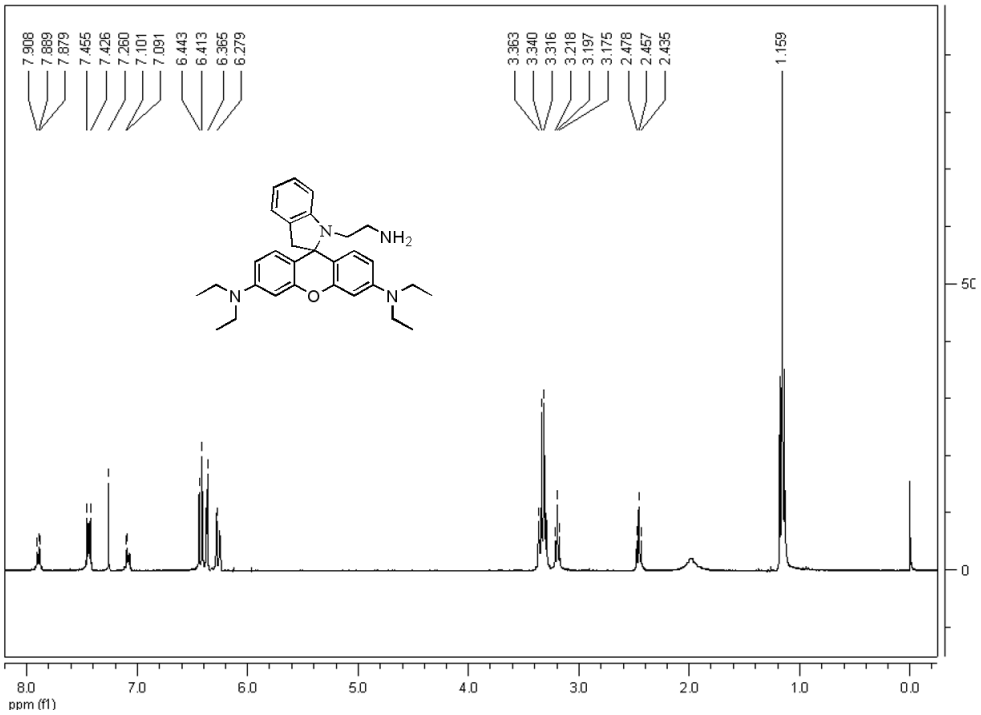


Fig. S3 ^{1}H NMR spectrum of **SRhB** in $CDCl_3$.

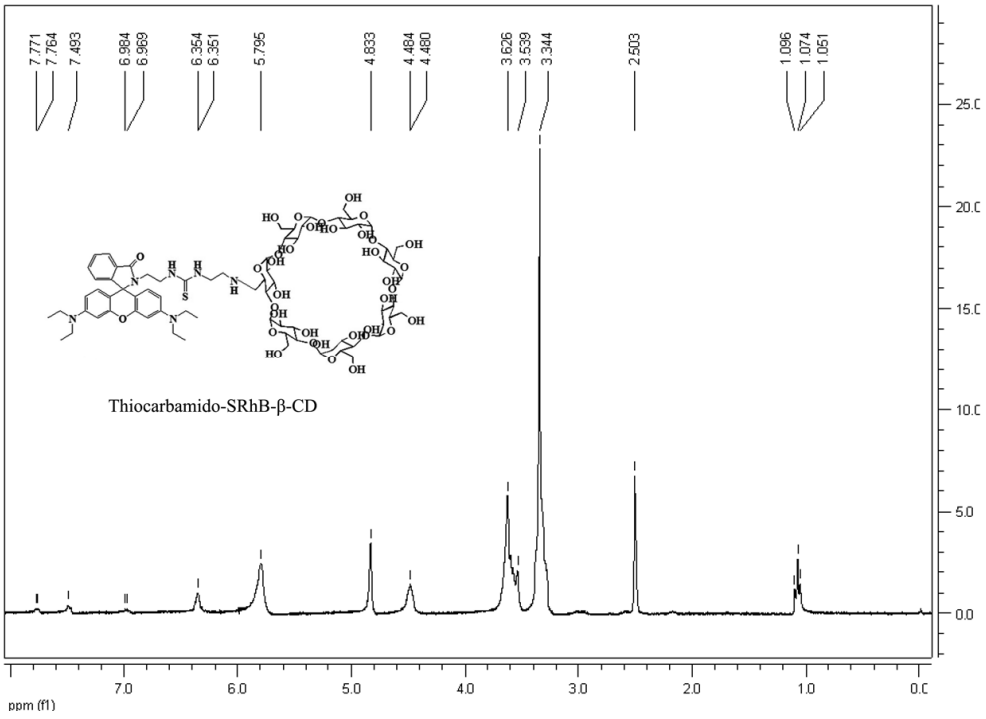


Fig. S4 ^{1}H NMR spectrum of **Thiocarbamido-SRhB-β-CD** in $CDCl_3$.

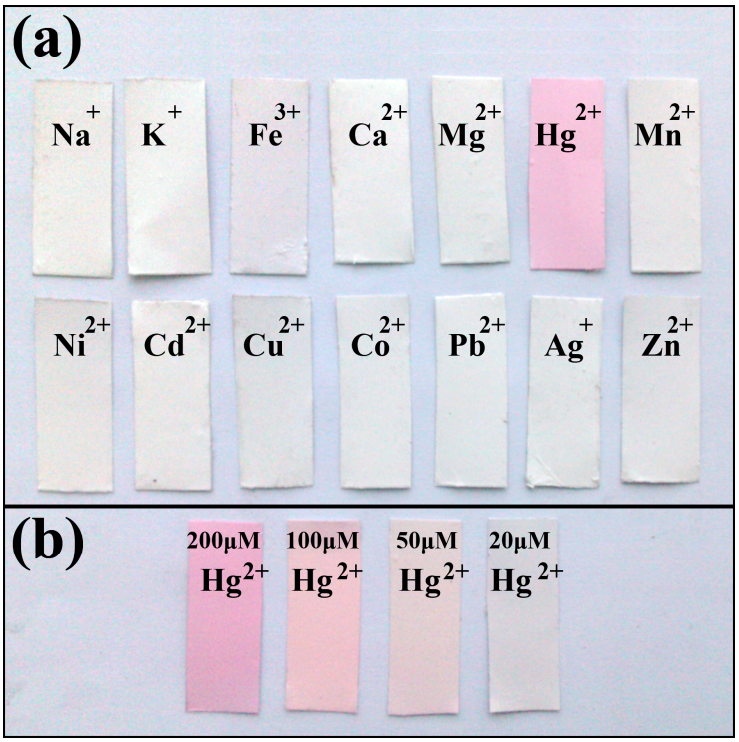


Fig. S5 (a) Photograph of nanofibrous film in the presence of various metal ions (1.0×10^{-3} M except Hg^{2+} that is 2.0×10^{-4} M) in DMF-H_2O (1:10, v/v, pH=7.20) solution . (b) From left to right was nanofibrous film after 200μM, 100μM, 50μM and 20μM Hg^{2+} involvement.

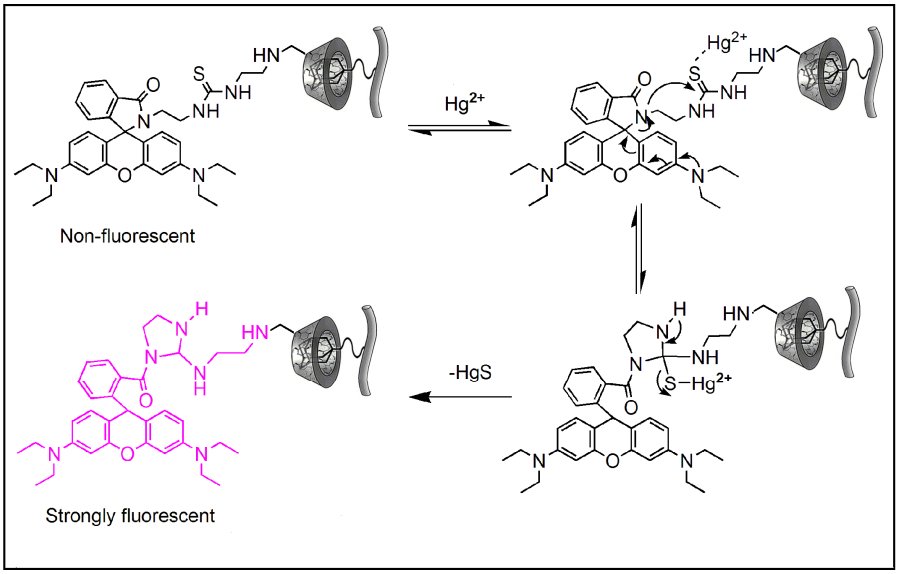


Fig. S6 The fluorescence enhancement mechanism of nanofibrous film **1** in the presence of Hg^{2+}.

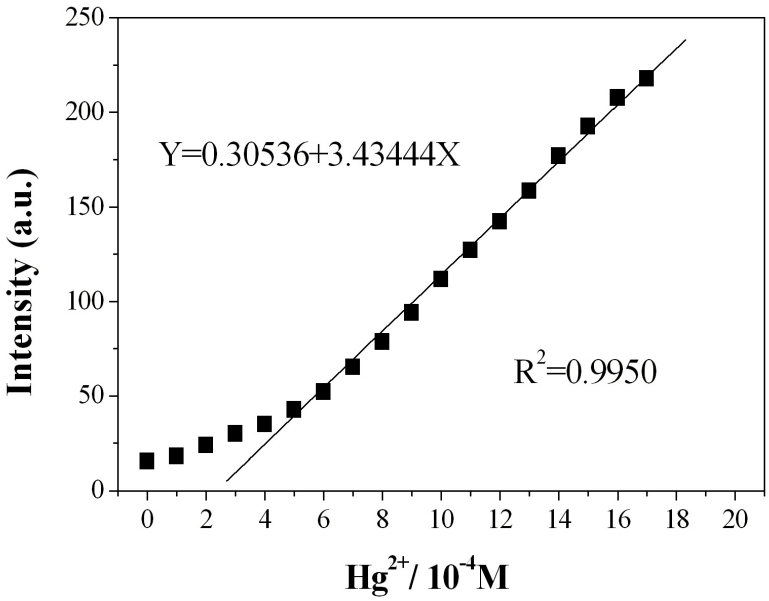


Fig. S7 Curve of fluorescence intensity of nanofibrous film **1** at 584 nm versus increasing concentration of Hg^{2+}.

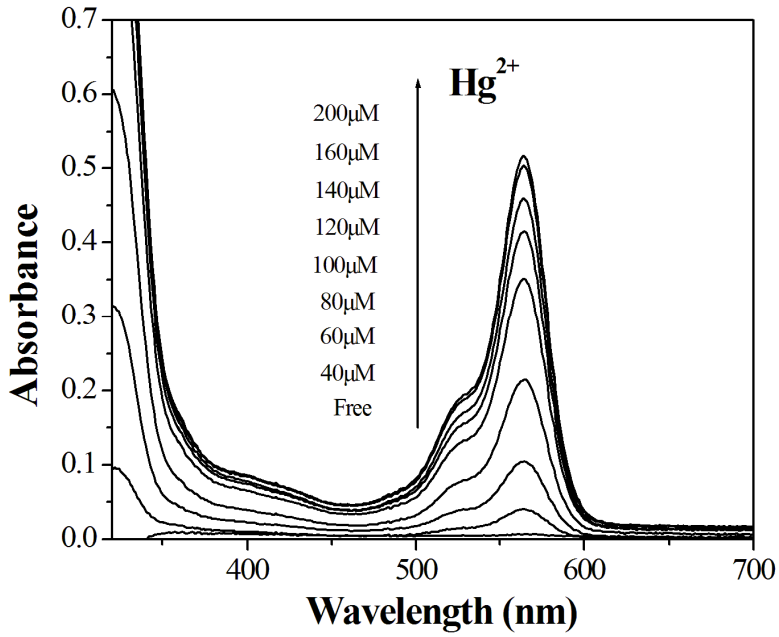


Fig. S8 Solid UV-vis absorbance spectra of the inclusion complex nanofibrous film **1** upon addition of Hg^{2+} (From down to up: 4.0×10^{-5} mol L^{-1}, 6.0×10^{-5} mol L^{-1}, 8.0×10^{-5} mol L^{-1}, 1.0×10^{-4} mol L^{-1}, 1.2×10^{-4} mol L^{-1}, 1.4×10^{-4} mol L^{-1}, 1.6×10^{-4} mol L^{-1} and 2.0×10^{-4} mol L^{-1}).

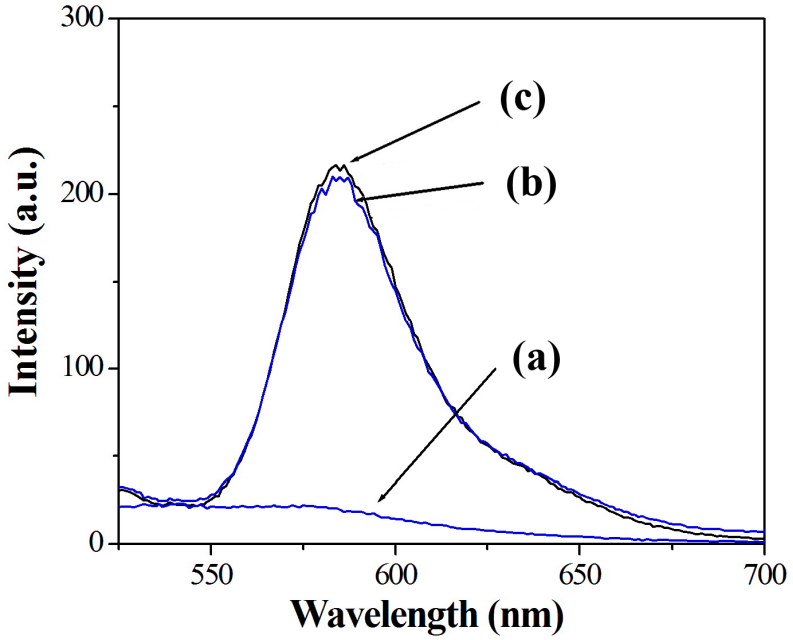


Fig. S9 (a) Curve of fluorescence intensity of nanofibrous film **1** at 584 nm after soaking for 24 h. (b) fluorescence intensity of nanofibrous film upon exposure to aqueous solutions of Hg^{2+} (2.0×10^{-4} mol L^{-1} DMF-H_2O = 1:10, v/v, pH=7.20) after soaking for 24 h. (c) fluorescence intensity of nanofibrous film **1** in the presence of Hg^{2+} (2.0×10^{-4} mol L^{-1}) before soaking.