Electronic Supplementary Information (ESI)

Detection and adsorption of Hg^{2+} by new mesoporous silica and membrane material grafted with chemodosimeter

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[1] These authors have the same contribution to this work.

Synthesis of compound 1

Under a dry atmosphere of nitrogen, 5-(aminoethylene) amino-2,1,3-benzothiadiazole (1.26 g, 6.5 mmol) was dissolved in anhydrous tetrahydrofuran (THF, 30 mL). The solution was cooled to 0 °C and then a solution of n-butylisothiocyanate (1.26 g, 11.0 mmol) in THF (10 mL) was added dropwise under stirring. After 0.5 h at this temperature, the resultant yellow reaction mixture was allowed to warm gently to room temperature and stirred overnight. The solvent was then evaporated under reduced pressure. The residue was purified by column chromatography on silica using CH_2Cl_2 as eluent to yield 1.18 g (59%) of **1** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.90 (t, 3H, J = 7.4 Hz, CH_3), 1.34 (m, 2H, CH_2CH_3), 1.54 (m, 2H, $CH_2CH_2CH_3$), 3.28 (m, 2H, NCH_2), 3.46 (m, 2H, NCH_2), 4.03 (m, 2H, NCH_2), 5.36 (s, 1H, NH), 5.93 (m, 2H, NH, NH), 6.71 (s, 1H, benzene-H), 7.04 (d, 1H, J = 9.4 Hz, benzene-H), 7.70 (d, 1H, J = 9.6 Hz, benzene-H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 13.66, 19.55, 30.74, 42.12, 91.74, 120.81, 126.17, 149.65, 149.78, 157.06. HRMS (EI+, *m/z*): $[M]^+$ calcd for $C_{13}H_{19}N_5S_2$, 309.1082; found, 309.1088.

Synthesis of compound 3

Under a dry atmosphere of nitrogen, 5-(aminoethylene) amino-2,1,3-benzothiadiazole (1.36 g, 7.0 mmol) was dissolved in anhydrous tetrahydrofuran (THF, 30 mL). The solution was cooled to 0 °C and then a solution of 3-(triethoxysilyl) propylisothiocyanate (2.21 g, 8.4 mmol) in THF (10 mL) was added dropwise under

stirring. After 1 h at this temperature, the resultant yellow reaction mixture was allowed to warm gently to room temperature and stirred overnight. The solvent was then evaporated under reduced pressure. The residue was purified by column chromatography on silica using 15:1 CH_2Cl_2-EtOAc as eluent to yield 1.54 g (48%) of **3** as yellowish green liquid. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 0.64 (t, 2H, *J* = 7.6 Hz, $SiCH_2$), 1.21 (t, 9H, *J* = 7.0 Hz, $(OCH_2CH_3)_3$), 1.42 (m, 2H, CH_2CH_3), 1.72 (m, 2H, CH_2CH_2Si), 3.33 (m, 2H, NCH_2), 3.44 (m, 2H, NCH_2), 3.81 (q, 6H, *J* = 7.2 Hz, $(OCH_2CH_3)_3$), 4.04 (m, 2H, NCH_2), 5.54 (s, 1H, NH), 6.29 (m, 2H, NH, NH), 6.69 (s, 1H, benzene-H), 7.06 (d, 1H, *J* = 9.4 Hz, benzene-H), 7.69 (d, 1H, *J* = 9.2 Hz, benzene-H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 7.43, 14.16, 18.27, 21.06, 22.47, 44.55, 58.61, 60.45, 93.05, 121.34, 125.50, 148.96, 150.29, 156.98. HRMS (EI+, *m/z*): $[M]^+$ calcd for $C_{18}H_{31}N_5O_3S_2Si$, 457.1638; found, 457.1637.

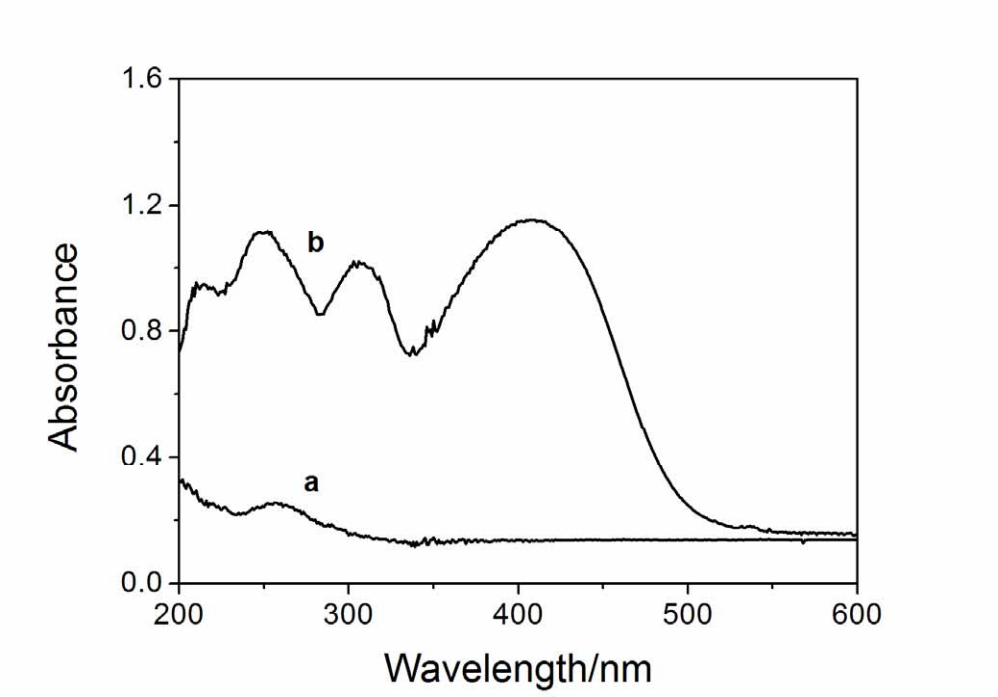

Fig. S1 UV–vis diffuse reflectance spectra of (a) mesoporous silica and (b) **MCM-3T**.

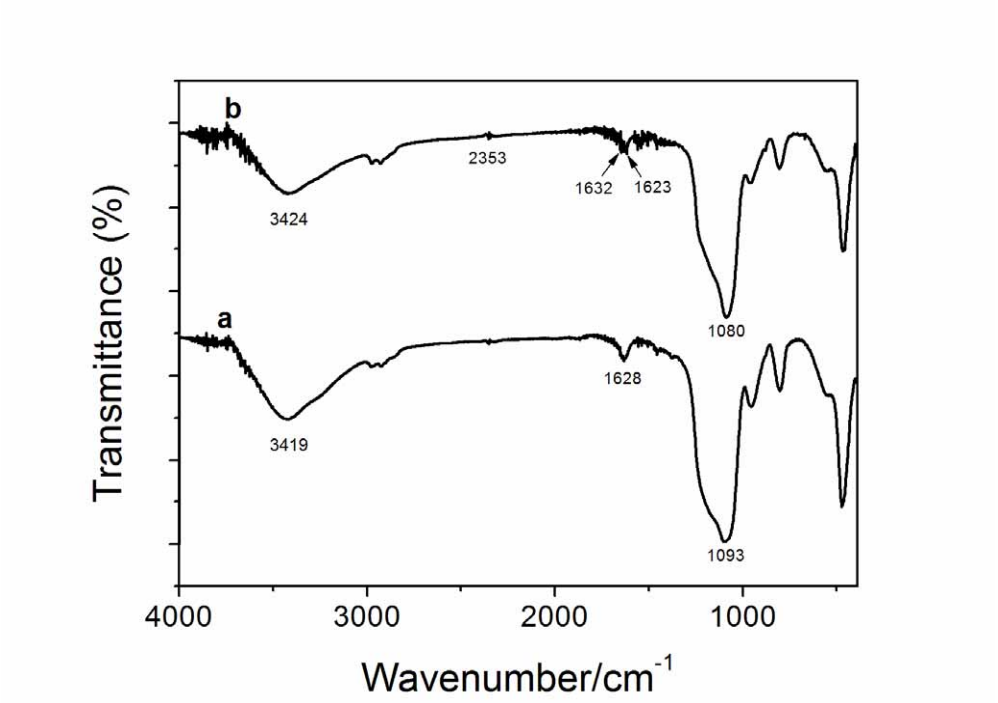

Fig. S2 IR spectra of (a) mesoporous silica and (b) **MCM-3T**.

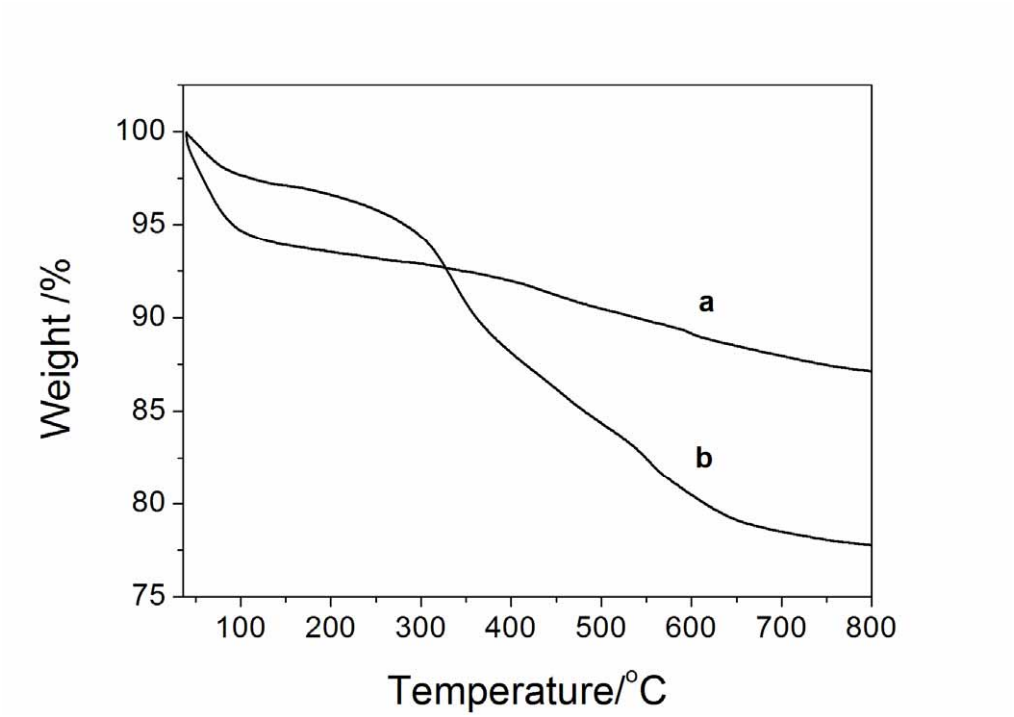

Fig. S3 Thermogravimetric analysis data of (a) mesoporous silica and (b) **MCM-3T**.

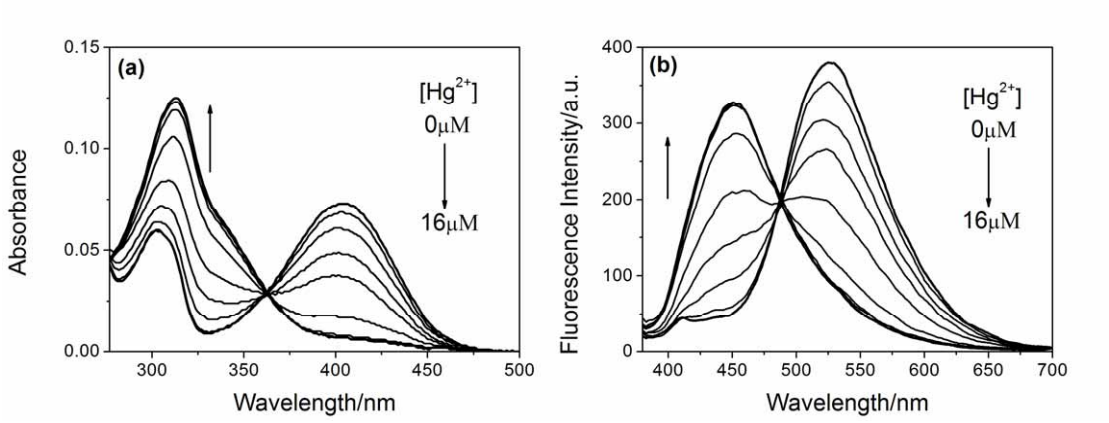

Fig. S4 (a) UV–vis spectra of **1** (1.0×10^{-5} M) and Hg^{2+} (0-1.6×10^{-5} M) in CH_3CN–H_2O (1:1, v/v) at 25 °C; (b) Fluorescence titration of **1** (1.0×10^{-5} M) with Hg^{2+} (0-1.6×10^{-5} M) in CH_3CN–H_2O (1:1, v/v) at 25 °C, λ_{ex}= 361 nm.

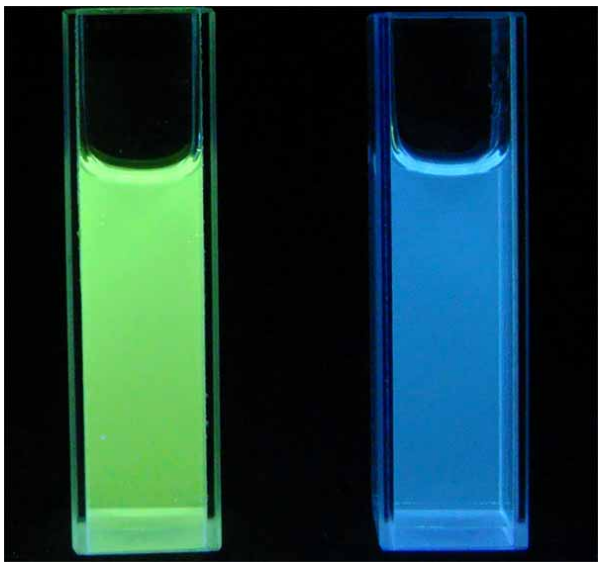

Fig. S5 The fluorescence emission response of **1** (10 μM) upon addition of 2 equiv. of Hg^{2+} in $CH_3CN–H_2O$ (1:1, v/v) solution. Left to right: the emission of **1**, the emission of **1** with Hg^{2+} (irradiated at 365 nm using UV lamp)

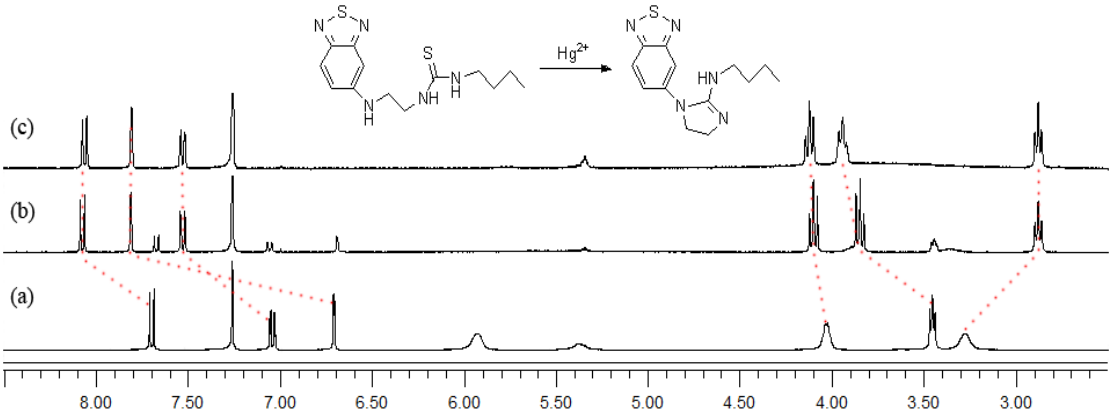

Fig. S6 Partial ^1H NMR (400 MHz) titrations of **1** (5×10^{-3} M) in $CDCl_3$ at 25 °C with Hg^{2+} (a) none; (b) 0.7 equiv.; (c) 3 equiv..

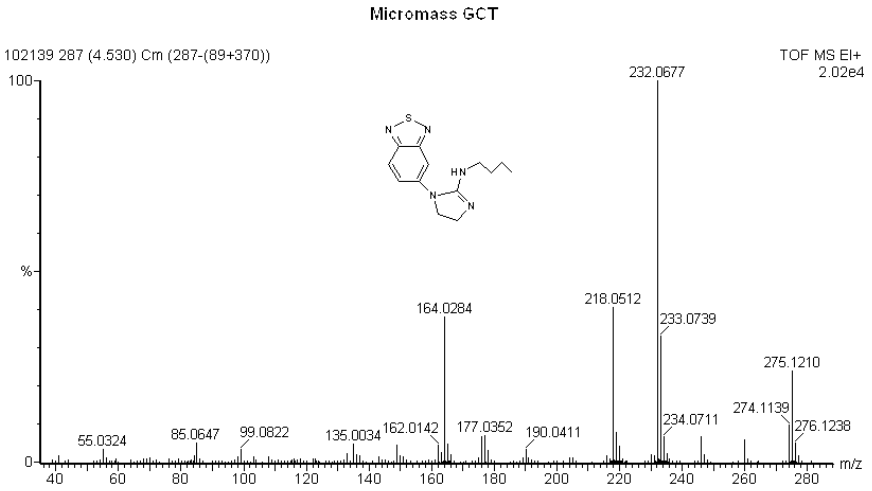

Fig. S7 HRMS (EI+) spectrum of compound **1** (10μM) with Hg^{2+} (30μM) in $CH_3CN–H_2O$ (1:1, v/v) solution.

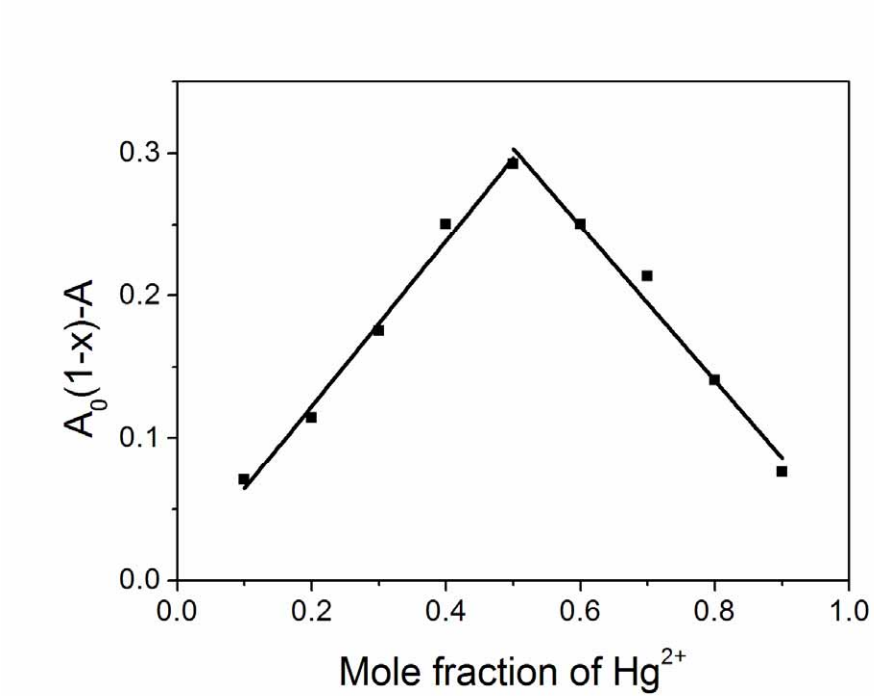

Fig. S8 Job's plot of **1** and Hg^{2+}, A and A_0 are the absorbance value at 405 nm of **1** in the presence and absence of Hg^{2+}, respectively; the total concentration of **1** and Hg^{2+} is 1.0×10^{-4} M in $CH_3CN–H_2O$ (1:1, v/v) solution at 25 °C.

Fig. S9 Fluorescence images of **1** (1.0×10^{-5} M) on addition of different metal ions in CH_3CN–H_2O (1:1, v/v) solution. Left to right: free metal ions, Ni^{2+} (1.0×10^{-4} M), Zn^{2+} (1.0×10^{-4} M), Cd^{2+} (1.0×10^{-4} M), Co^{2+} (1.0×10^{-4} M), Hg^{2+} (2.0×10^{-5} M), Cu^{2+} (1.0×10^{-4} M), Ag^{+} (1.0×10^{-4} M), Pb^{2+} (1.0×10^{-4} M).

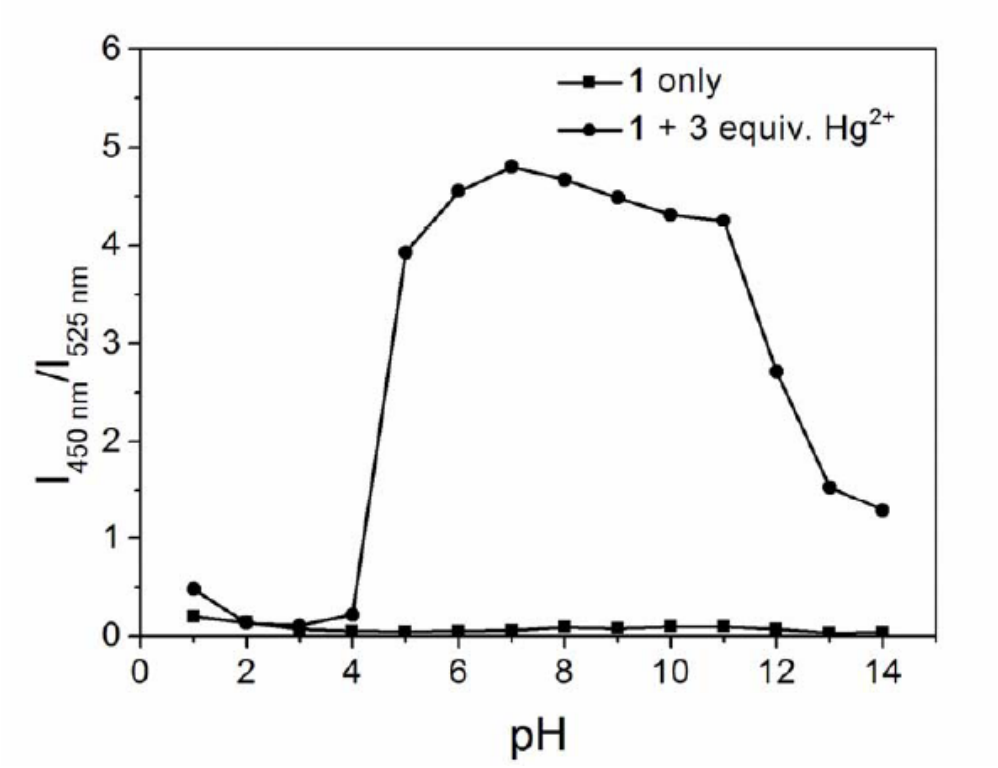

Fig. S10 Fluorescence ratios ($I_{450\ nm}/I_{525\ nm}$) of free **1** (10 μM) and **1** + 3 equiv. of Hg^{2+} in CH_3CN–H_2O (1:1, v/v) with different pH conditions at 25 °C. λ_{ex} = 361 nm.

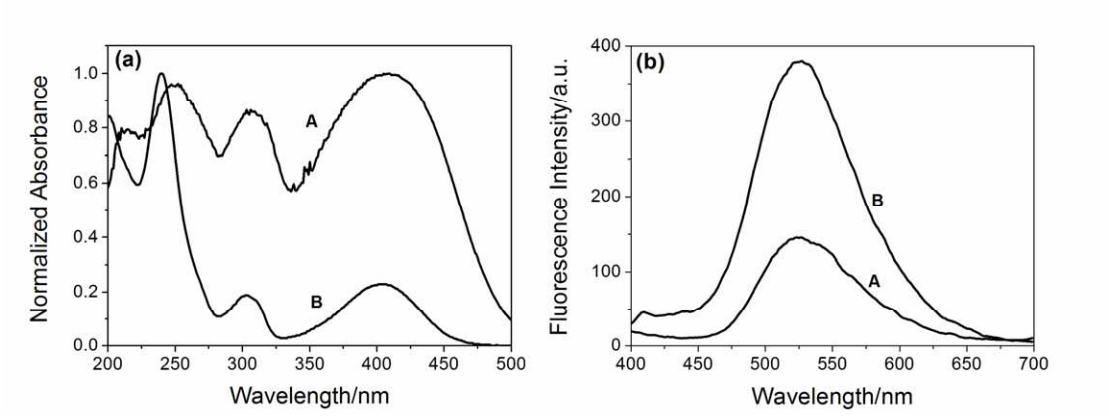

Fig. S11 (a) Absorption and (b) fluorescence spectra of (A) **MCM-3T** and (B) chemodosimeter **1** in $CH_3CN–H_2O$ (1:1, v/v) solution.

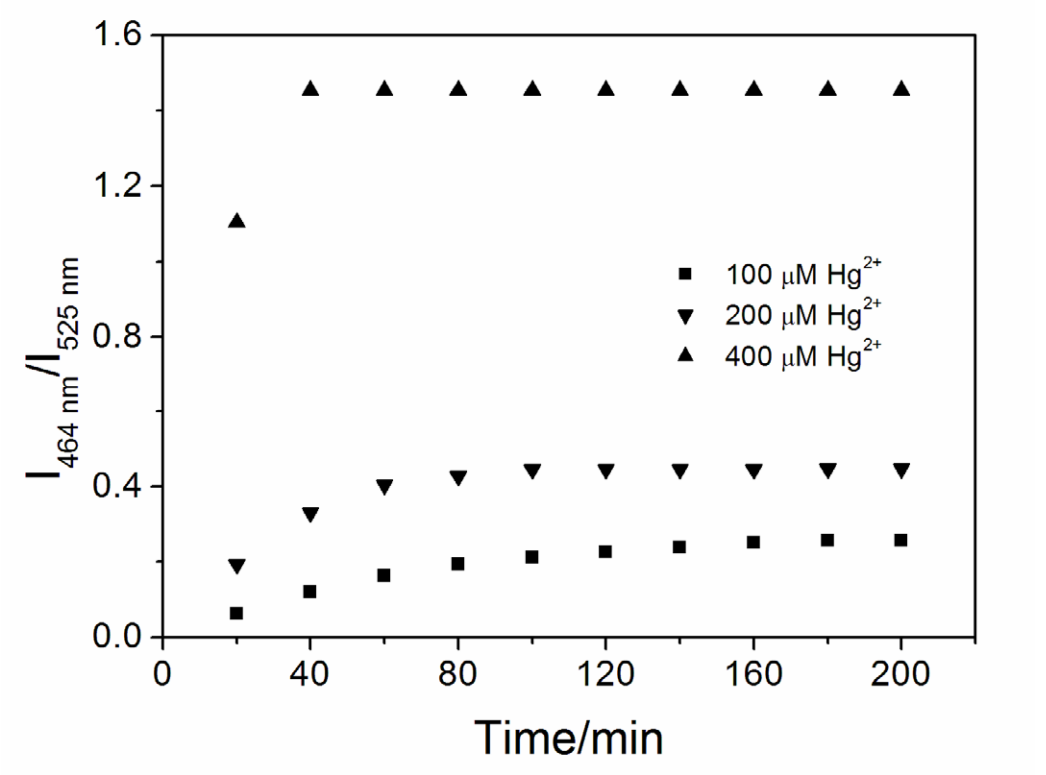

Fig. S12 Fluorescence ratios ($I_{464\ nm}/I_{525\ nm}$) of **MCM-3T** (0.5 mg mL^{-1}) over time with the addition of Hg^{2+} (100, 200, 400 μM) in $CH_3CN–H_2O$ (1:9, v/v) solution at 25 °C. λ_{ex} = 361 nm.

Fig. S13 Photographs of emission colors of **MCM-3T** (0.5 mg ml^{-1}) towards different concentrations of Hg^{2+} (0-4.0×10^{-4} M) in $CH_3CN–H_2O$ (1:9, v/v) solution under the radiation of (a) room light and (b) a UV lamp.

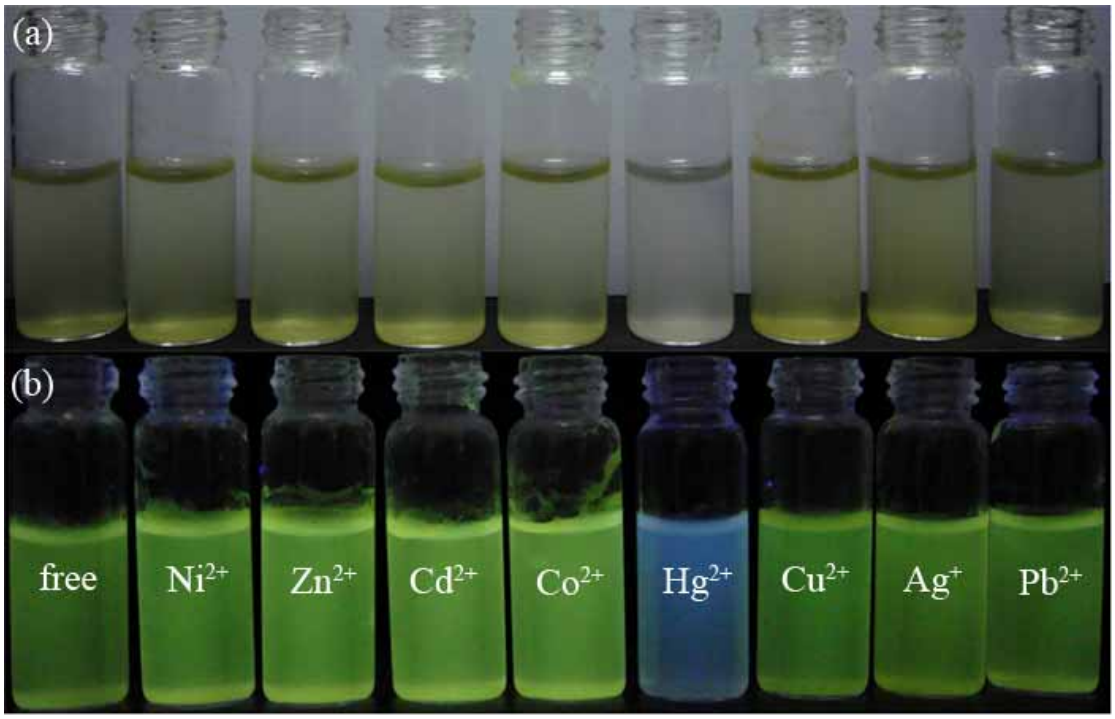

Fig. S14 (a) Color images and (b) fluorescence images of CH_3CN–H_2O (1:9, v/v) suspensions of **MCM-3T** (0.5 mg ml^{-1}) on addition of different metal ions. Left to right: free metal ions, Ni^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+}, Cu^{2+}, Ag^{+}, Pb^{2+}.

Table S1 Adsorption isotherm parameters for Hg^{2+} on **MCM-3T** (temperature 25 °C, pH at 6.0).

Adsorption isotherm	Parameter	**MCM-3T** Value of parameter	R^2
Langmuir	K_L (L $mmol^{-1}$)	41.2653	0.6833
	q_L (mmol g^{-1})	0.9894	
Freundlich	K_F (L g^{-1})	0.9174	0.9412
	n	5.8688	
Redlish-Peterson	K_R (L g^{-1})	1424.7496	0.9399
	α_R (L $mmol^{-1}$)	1532.8991	
	β	0.8591	

Langmuir Isotherm: $$q_e = \frac{K_L \times q_L \times C_e}{1 + K_L \times C_e} \quad (1)$$

Freundlich Isotherm: $$q_e = K_F \times C_e^{\frac{1}{n}} \quad (2)$$

Redlish-Peterson Isotherm: $$q_e = \frac{K_R \times C_e}{1 + \alpha_R \times C_e^{\beta}} \quad (3)$$

where q_e is the amount of sorbate per unit of adsorbent (mmol g^{-1}), C_e is the

equilibrium concentration (mmol L^{-1}), q_L is the saturation capacity of the adsorbent (mmol g^{-1}), K_L is the Langmuir isotherm constant (L $mmol^{-1}$). K_F and 1/n in the Freundlich model are the Freundlich constant and the heterogeneity factor, respectively. K_R is the Redlish-Peterson isotherm constant (L g^{-1}), α_R is the Redlich-Peterson isotherm constant (L $mmol^{-1}$), and β is the exponent, which lies between 0 and 1. If β=1, the Redlich-Peterson equation becomes a Langmuir type form.[1]

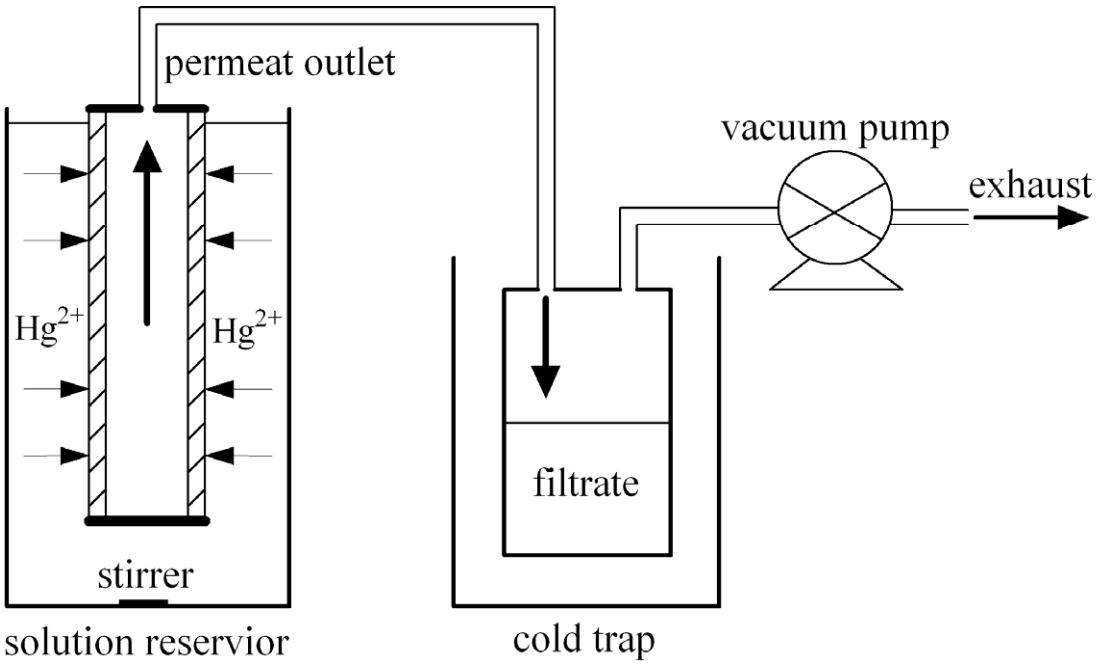

Fig. S15 Illustration of the membrane system.

References

1 X. M. Xue and F. T. Li, *Micropor. Mesopor. Mater.*, 2008, **116**, 116.

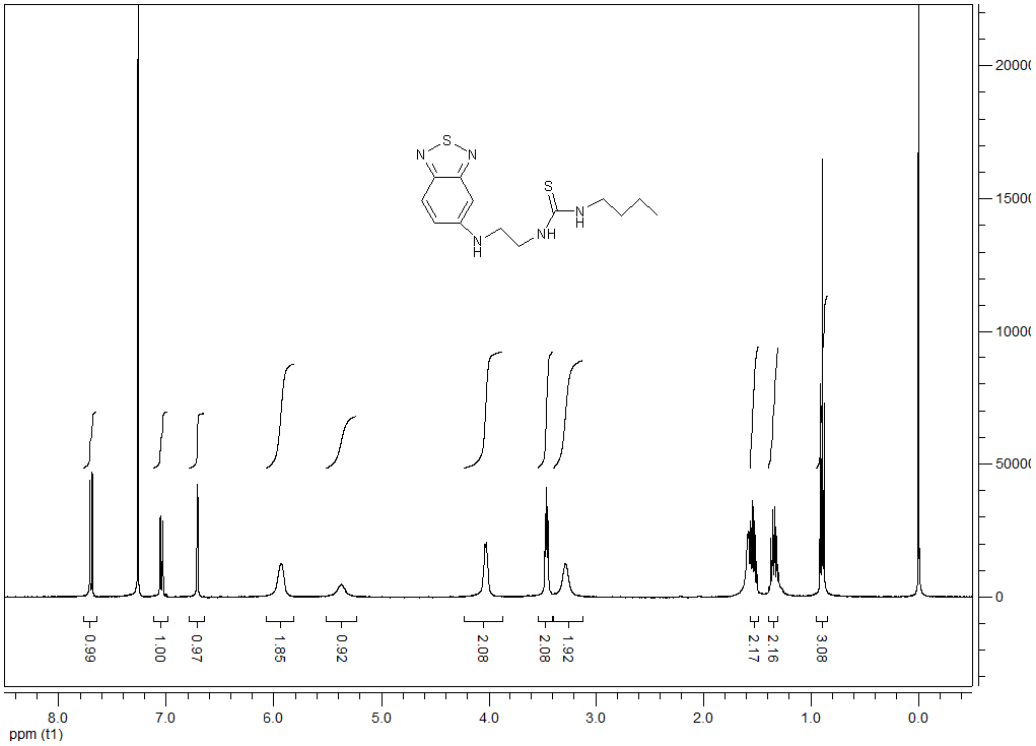

Fig. S16 ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1**.

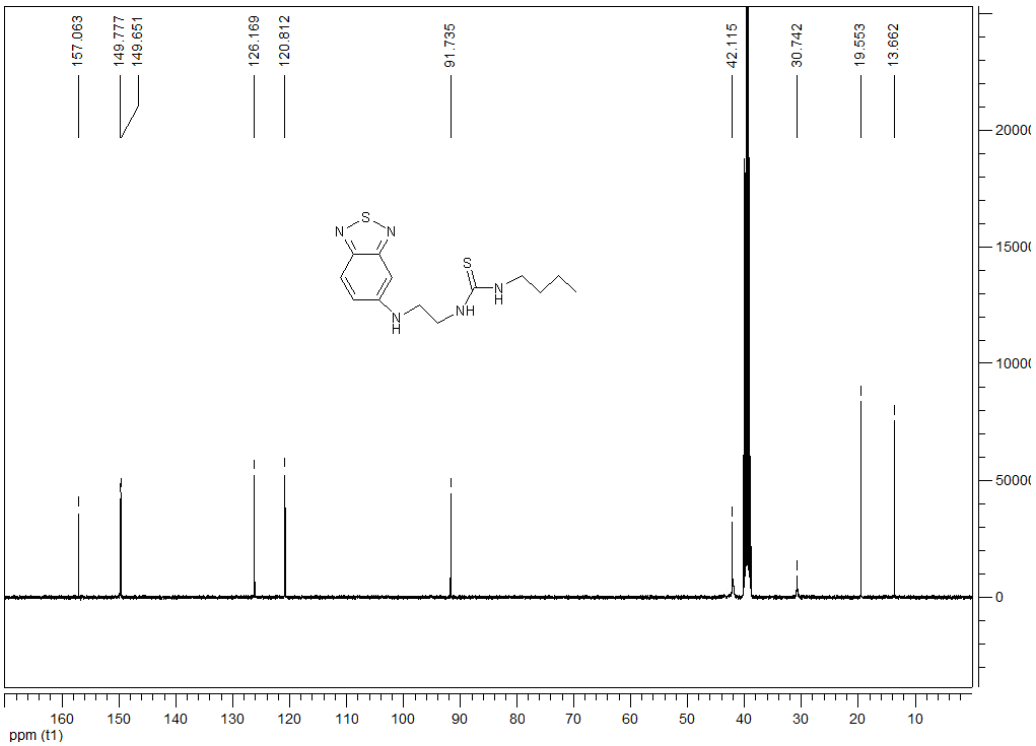

Fig. S17 ^{13}C NMR (DMSO-d_6, 100 MHz) spectrum of compound **1**.

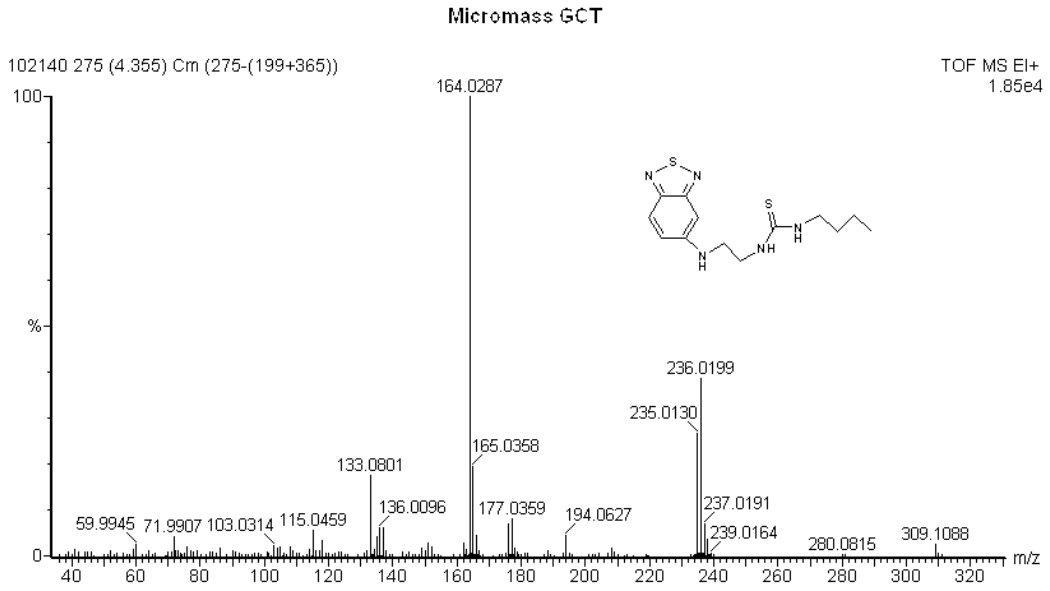

Fig. S18 HRMS (EI+) spectrum of compound **1**.

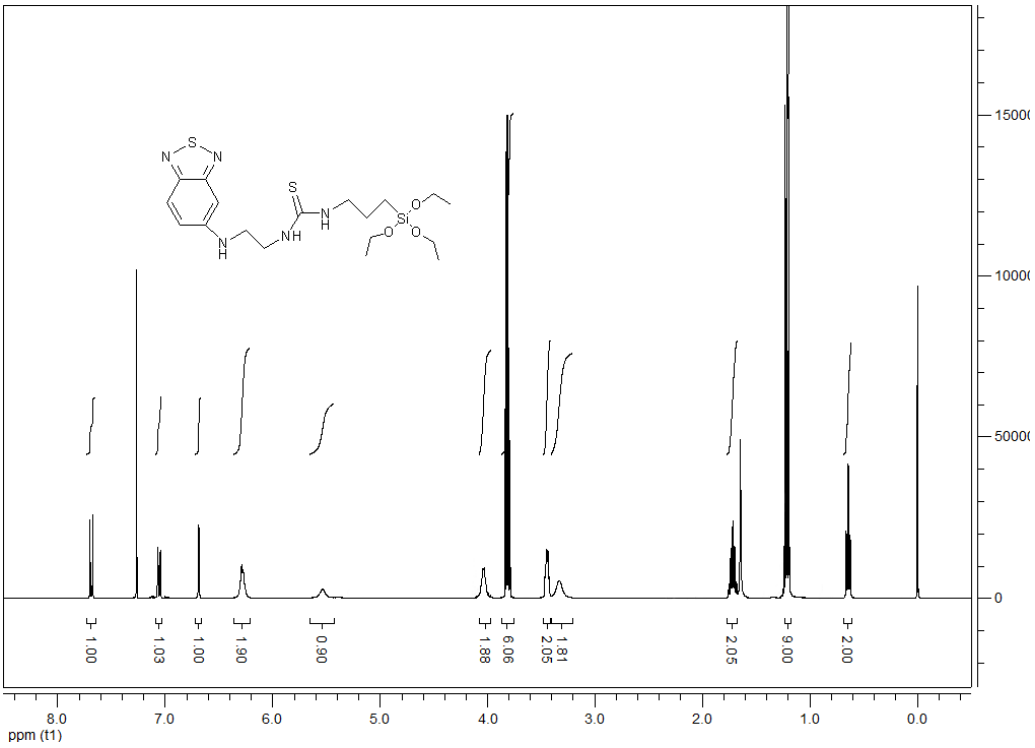

Fig. S19 ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3**.

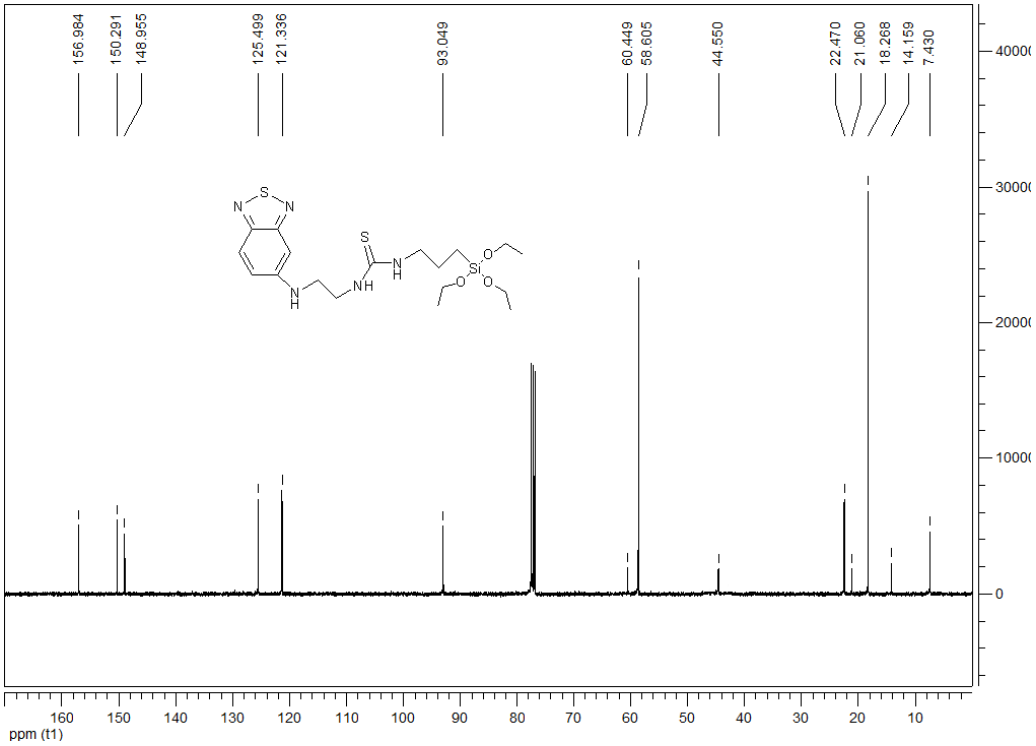

Fig. S20 ^{13}C NMR (DMSO-d_6, 100 MHz) spectrum of compound **3**.

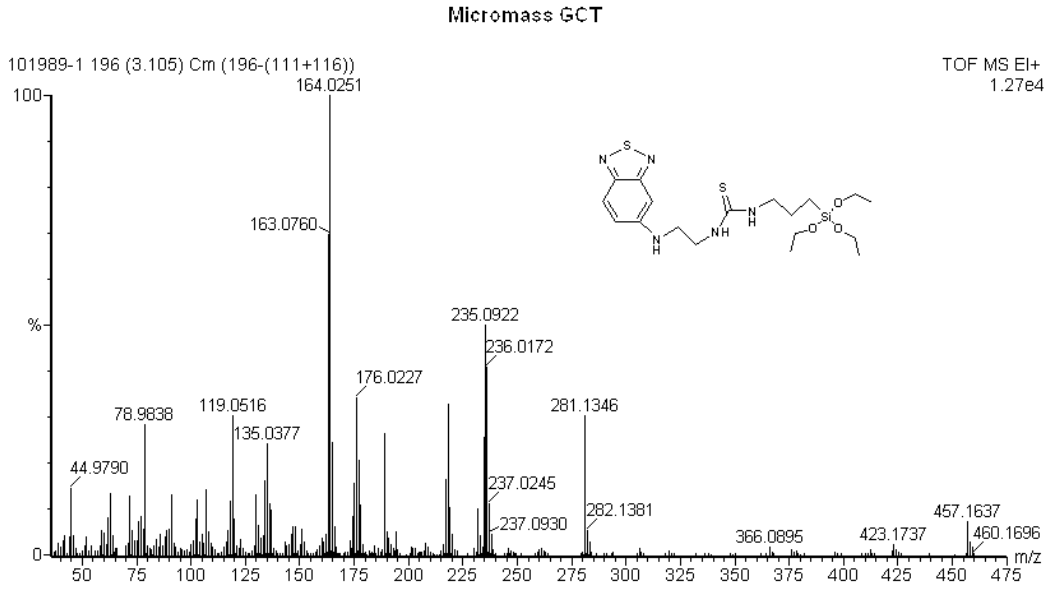

Fig. S21 HRMS (EI+) spectrum of compound **3**.