Electronic Supplementary Material (ESI) for Analyst.

Electronic Supplementary Information (ESI)

Fluorometric/colorimetric logic gates based on BODIPY-functionalized mesoporous silica

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Experimental Section

Characterization. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX 300 apparatus. IR spectra were obtained for KBr pellets, in the range 400 - 4000cm^{-1}, with a shimadzu FT-IR 8400S instrument, and Mass spectra were obtained by a JEOL JMS-700 mass spectrometer. All fluorescence spectra were recorded in RF-5301PC spectrophotometer. Time-of-flight Second Ion Mass Spectrometer (TOF-SIMS) was analyzed on Model PHI 7200 equipped with Cs and Ga ion guns for positive and negative ion mass detection.

TEM observations. For transmission electron microscopy (TEM), a sample of mesoporous silica particles was placed on a carbon-coated copper grid (400 mesh) and removed after one min, leaving some small patches the sample on the grid. The specimens were examined with a TF30ST transmission electron microscope operating at 300 kV using an accelerating voltage of 300 kV and a 16 mm working distance.

Preparation of mesoporous silica. 2.5 g of n-hexadecyltrimethylammonium bromide (C_{16}TMABr, 0.007 mol) was dissolved in 50 g of deionized water, and 13.2 g of aqueous ammonia (32 wt%, 0.25 mol) and 60.0 g of absolute ethanol (EtOH, 1.3 mol) were added to the surfactant solution. The solution was stirred for 15 min (250 rpm) and 4.7 g TEOS (0.022 mol, freshly distilled) was added at one time resulting in a gel with the following molar composition : 1TEOS: 0.3 C_{16}TMABr : 11NH_3 :144H_2O, 58EtOH. After drying overnight at 363 K, the sample was heated to 823 K (rate: 1K min) in air and kept at that temperature for 5 h.

Immoblization of 3-MPTMS onto mesoporous silica (SiO_2-SH). (3-Mercaptopropyl)triethoxysilane (0.5 mL) was dissolved in mesoporous silica nanoparticles suspension of anhydrous toluene (10 mL) and it was stirred under reflux in N_2 for 24 h. The collected solid was washed several times with ethanol to rinse away excess. The solid product was dried by vacuum. ^{13}C CP-MAS: 8.6, 26.8, 49.4 ppm. FT IR: 3500-3000, 2960, 2927, 2852, 2002, 1870, 1634 cm^{-1}.

Preparation of BODIPY-functionalized silica nanoparticle (1). Compound **2** (0.38 mmol, 0.2 g) and SiO_2-SH (500 mg) were dissolved in dry acetonitrile (40 mL). Potassium carbonate (1.8 g, 13 mmol) was then added, and the mixture was heated at reflux for 24 h. The reaction mixture was filtered off in order to remove the excess of potassium carbonate, and the collected solid was washed several times with methylene dichloride, ethanol to rinse away excess. The solid product was dired by vacuum.

AND logic gate system: An aqueous solution (3 mL) dispersed of nanomaterial **1** (5.0 mg) was added to a well, followed by addition of 30μL of $Hg(NO_3)_2$ (11.6 and 23.2 μM) and 30μL of $Zn(NO_3)_2$ (11.6 and 23.2 μM). The UV absorbance was measured immediately. the UV was recorded on addition the five possible input combinations: i) 30μL of $Hg(NO_3)_2$,; ii) 30μL of $Zn(NO_3)_2$ (11.6 and 23.2 μM); and iii) 30μL of $Hg(NO_3)_2$ (11.6 μM) and 30μL of $Zn(NO_3)_2$ (11.6 μM).

NAND logic gate: An aqueous solution (3 mL) dispersed of nanomaterial **1** (5.0 mg) was added to addition of 30μL of $Hg(NO_3)_2$ (11.6 and 23.2 μM) and 30μL of $Zn(NO_3)_2$ (11.6 and 23.2 μM). The light emission was measured immediately. The emission spectra were observed on addition of the five possible input combinations: i) 30μL of $Hg(NO_3)_2$,; ii) 30μL of $Zn(NO_3)_2$ (11.6 and 23.2 μM); and iii) 30μL of $Hg(NO_3)_2$ (11.6 μM) and 30μL of $Zn(NO_3)_2$ (11.6 μM).

NOR logic gate: An aqueous solution (3 mL) dispersed of nanomaterial **1** (5.0 mg) was added to 30μL of $Ni(NO_3)_2$ (11.6 and 23.2 μM) and 30μL of $Cu(NO_3)_2$ (11.6 and 23.2 μM) solution. The emission changes were observed immediately. The fluorescence changes were recorded on addition the five possible input combinations: 30μL of Ni $(NO_3)_2$; ii) 30μL of $Cu(NO_3)_2$ (11.6 μM); and iii) 30μL of $Ni(NO_3)_2$ (11.6 μM) and 30μL of $Cu(NO_3)_2$ (11.6 μM).

Preparation of compound 7. To a solution of N-phenyldiethanolamine (17.36 g, 95.8 mmol) in DMF (33 mL) was added a cooled solution of phosphorus oxychloride (40 mL, 4.5 equiv.) in DMF (67 mL, 9 equiv.) and the resulting mixture was stirred at 90°C for 4 hours. After cooling to room temperature, the mixture was poured over crushed and stirred for 1 hour at 0°C. The precipitated product was then collected by filtration and recrystallized from ethanol to give 4-(bis(2-chloroethyl)amino)benzaldehyde as tan needles. Yield 97%. Mp 88-89°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.68 (t, J = 6.9 Hz, 4H), 3.84 (t, J = 6.9 Hz, 4H), 6.75 (d, J = 9.0 Hz, 2H), 7.77 (d, J = 9.0 Hz, 2H), 9.78 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz) : δ 40.0, 53.3, 111.3, 126.7, 132.3, 150.9, 190.1. FT-IR : 2964, 2746, 1668, 1592, 1560, 1521, 1405, 1361, 1285, 1167, 1140, 962, 819, 750, 715, 605 cm^{-1}. ESI-MS (*m/z*) Calcd. for $C_{11}H_{13}Cl_2NO$: 245.04. Found: 246.20 $[M+1]^+$. Element analysis: calculated for $C_{11}H_{13}Cl_2NO$: C 53.68 H 5.32 N 5.69; Found C 53.42 H 5.21 N 5.45.

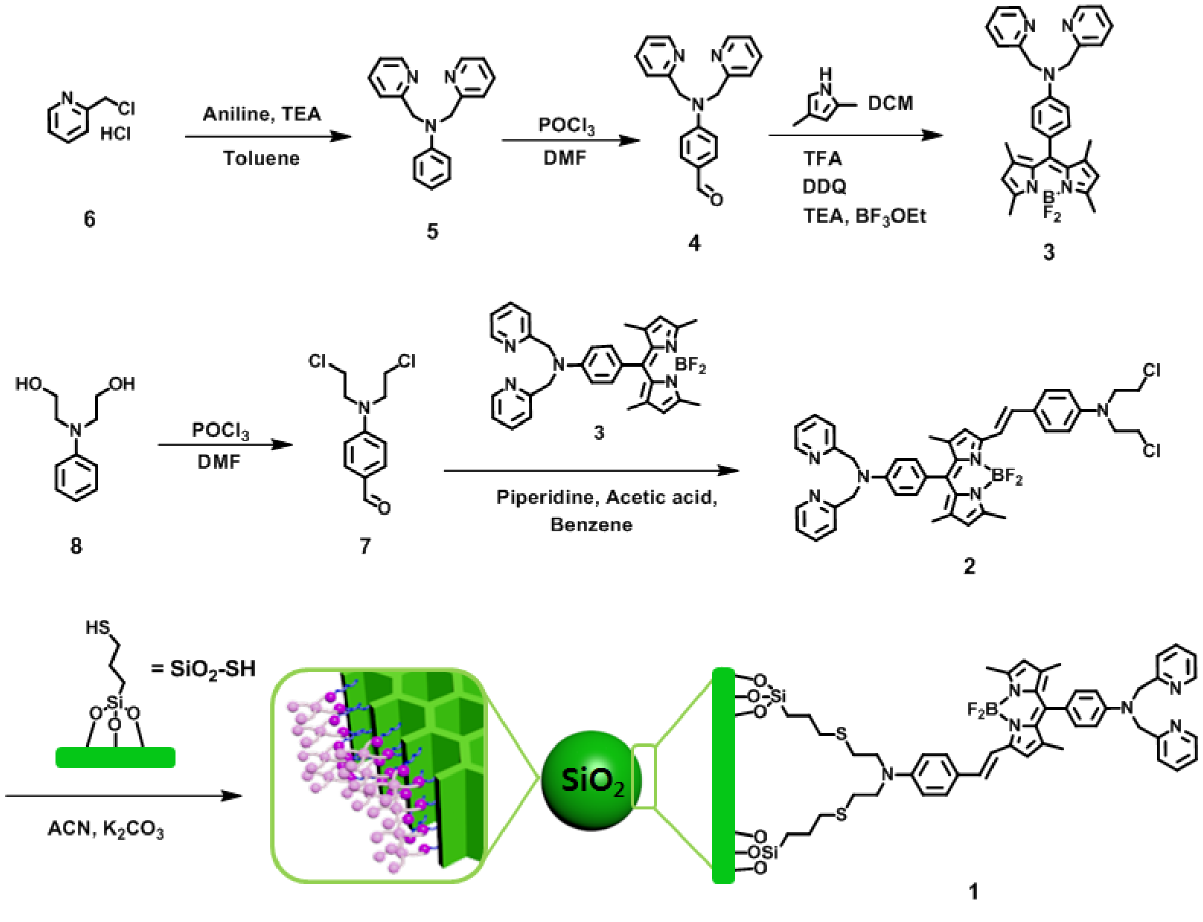
Preparation of compound 5. To a solution of 2-chloromethylprydine (6 g, 35 mmol) in toluene (10 mL), aniline (1.5 mL, 16 mmol), and triethylamine (9 mL, 64 mmol) were added under N_2 protection. The mixture was stirred vigorously for 12 h at 120 °C. The mixture was extracted with CH_2Cl_2, and the extract was washed with H_2O and dried with $MgSO_4$. After evaporation of the solvent, the desired product (1.87 g) was obtained as beige solid in 42% yield via column chromatography (silica, CH_2C1_2/AcOEt, 3/1, v/v). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.83(s, 4H), 6.71(m, *J* = 20 Hz, 3H), 7.17(m, *J* = 12 Hz, 4H), 7.27(d, *J* = 8 Hz, 2H), 7.62(t, *J* = 16 Hz, 2H), 8.60(d, *J* = 4 Hz, 2H). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 57.37, 112.55, 117.29, 120.86, 122.12, 129.39, 136.93, 148.24, 149.81, 158.91. ESI-MS (*m/z*) Calcd. for $C_{18}H_{17}N_3$: 275.13. Found: 276.15 $[M+1]^+$. Element analysis: calculated for $C_{18}H_{17}N_3$: C 78.52 H 6.22 N 15.26; Found C 78.27 H 6.32 N 15.38.

Preparation of compound 4. $POCl_3$ (1 mL, 17 mmol) was added into the solution of DMF (2 mL, 26 mmol) in 2 portions in 0.5 h, and cooled in an ice bath. Then the solution was stirred for 0.5 h. Compound **5** (0.600 g, 2.18 mmol) in DMF (1 mL) was added in portions in 20 min. The mixture was heated for 6 h at 80 °C and poured into H_2O (5 mL), and then neutralized to pH 6-8 with Na_2CO_3 along with stirring. The mixture was extracted with CH_2Cl_2, and dried with $MgSO_4$. Via column chromatography (silica, CH_2C1_2/AcOEt, 2/1, v/v), the desired product (0.263 g) was obtained as yellow oil in 40% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.92 (s, 4H), 6.80 (d, *J* = 8 Hz, 2H), 7.21(m, *J* = 16 Hz, 4H), 7.66 (m, *J* = 24 Hz, 4H), 8.61(d, *J* = 4 Hz, 2H), 9.71(s, 1H). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 57.08, 112.00, 120.68, 122.46, 126.38, 132.04, 137.00, 149.94, 153.11, 157.20, 190.21. ESI-MS (*m/z*) Calcd. for $C_{19}H_{17}N_3O$: 303.14. Found: 304.14 $[M+1]^+$. Element analysis: calculated for $C_{19}H_{17}N_3O$: C 75.23 H 5.65 N 13.85; Found C 75.02 H 5.82 N 13.53.

Preparation of compound 3. To a 250 mL round-bottomed flask containing 100 mL argon-degassed CH_2Cl_2 were added 2,4-dimethyl pyrrole (0.4 g, 4 mmol), compound **4** (0.6 g, 1.98 mmol) and one drop of trifluoroacetic acid. The solution was stirred under N_2 at room temperature for 1d. After addition of a solution of DDQ (0.45 g, 1.98 mmol) in 10 mL of CH_2Cl_2 to the reaction mixture, stirring was continued for 30 min. 6 mL of Et_3N and 5 mL of $BF_3.OEt_2$ were successively added and after 30 min, the reaction mixture was washed with water (3 x 300 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography using $CHCl_3$: Methanol (100:3 v/v) as the eluant. Orange solid (0.25 g, 23%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.60 (2H, d, *J* = 6.48Hz, ArH), 7.62 (2H, t, *J* = 7.71 Hz, ArH), 7.22 (2H, d, *J* = 7.84 Hz, ArH), 7.18 (2H, t, *J* =6.58 Hz, ArH), 6.98 (2H, d, *J* = 8.80, ArH), 6.80 (2H, d, *J* = 8.80, ArH), 5.95 (2H, s, ArH), 4.87 (4H, s, C*H2*), 2.52 (6H, s, C*H*3), 1.45 (6H, s, C*H*3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 158.3, 154.8, 149.8, 149.7, 148.8, 143.1, 136.7, 128.9, 123.3, 122.2, 120.9, 113.2, 57.4, 14.5. ESI-MS (*m/z*) Calcd. for $C_{31}H_{30}BF_2N5$: 521.26. Found: 522.41 $[M+1]^+$. Element analysis: calculated for $C_{31}H_{30}BF_2N_5$: C 71.41 H 5.80 N 13.4; Found C 71.33, H 5.89, N 13.12.

Preparation of compound 2. Compound **3** (0.38 mmol, 0.2 g) was dissolved in Benzene (10 mL) and **7** (0.57 mmol, 0.14 g) was added to the solution. After stirring for 30 min, acetic acid (0.33 mL, 5.7 mmol) and piperidine (0.57 mL, 5.7 mmol) were added to the solution and then the reaction mixture was stirred for 6h over the Dean Stark apparatus at 110 °C and removed solvent. Via column chromatography (silica, CH_2C1_2/MeOH, 100/3, v/v), the desired product (0.043 g) was obtained as purple solid in 15% yield. ^{1}H NMR (300 MHz,

$CDCl_3$): δ 8.65 (m, 1H), 7.72 (s, 1H), 7.51 (m, 1H), 7.32 (d, 1H), 7.26 (d, 1H), 7.05 (d, 1H), 6.81 (d, 1H), 6.68 (d, 1H), 6.58 (s, 1H), 5.97 (s, 1H), 4.95 (s, 1H), 3.80 (t, 1H), 3.67 (t, 1H), 2.58 (s, 1H), 1.48 (d, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 158.30, 153, 149.78, 148, 142.69, 136.79, 135.98, 129.41, 129.22, 126.32, 123.57, 122.21, 120.94, 120.54, 117, 115, 113.14, 111.89, 57.42, 53.38, 40.36, 14.86, 14.63. Anal. Calcd. for $C_{42}H_{41}BCl_2F_2N_6$: C, 67.3 H, 5.51 N, 11.21 %. Found: C, 67.1 H, 5.45 N, 11.38 %. ESI-MS (*m/z*) Calcd. for $C_{42}H_{41}BCl_2F_2N_6$: 748.30. Found: 749.48 $[M+1]^+$. Element analysis: calculated for $C_{42}H_{41}BCl_2F_2N_6$: C 67.30 H 5.51 N 11.21; Found C 67.52 H 5.19 N 11.28.



Scheme S1. Preparation method of functionalized mesoporous SiO_2 nanoparticle **1**.

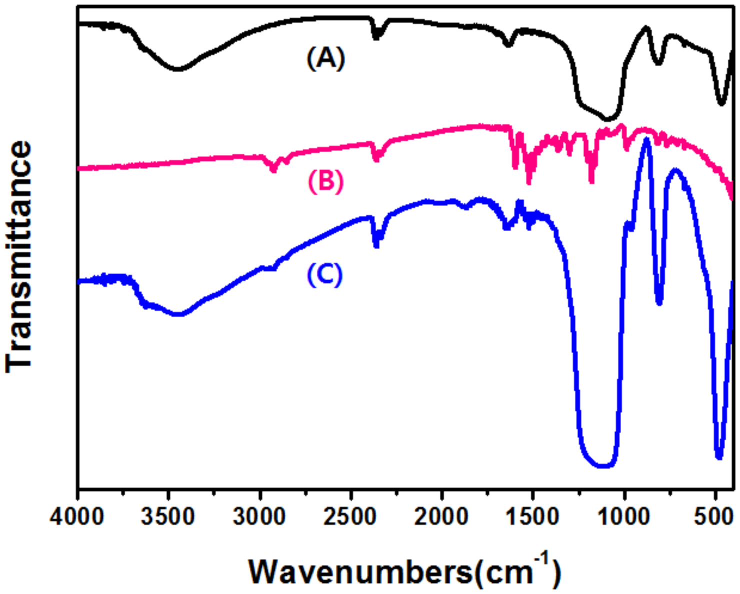


Fig. S1 FT-IR spectra of (A) mesoporous SiO_2 nanoparticle, (B) **2** and (C) functionalized mesoporous SiO_2 **1**.

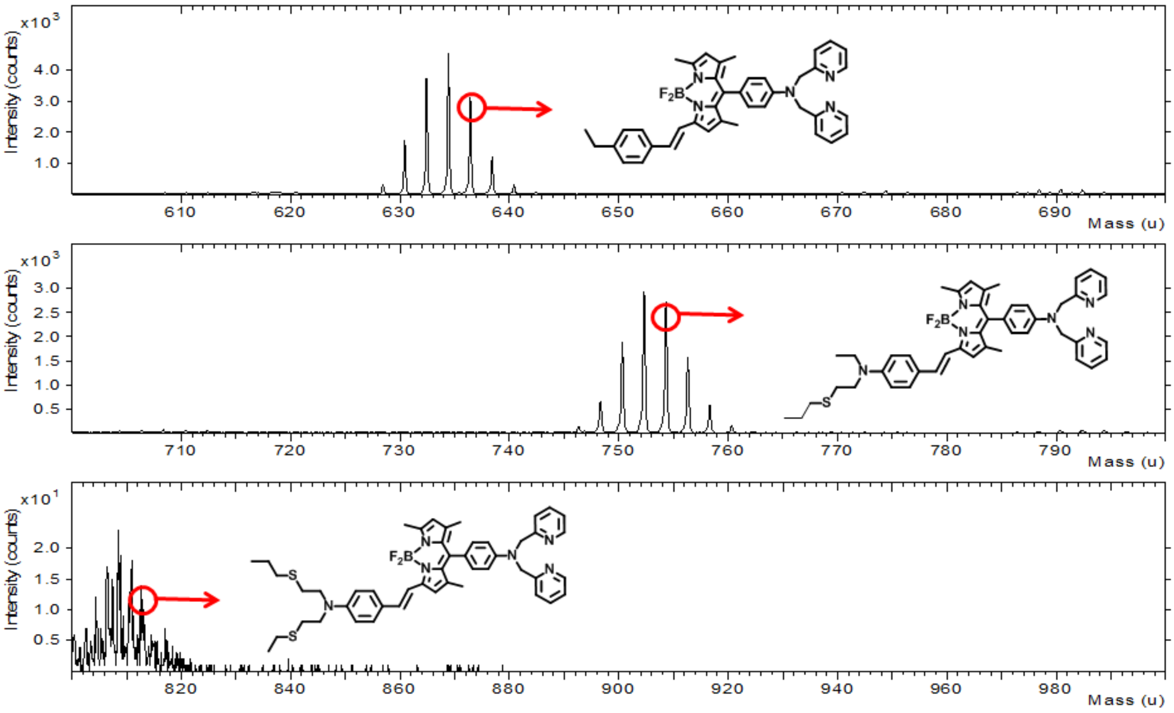


Fig. S2 TOF-SIMS spectrum of functionalized mesoporous SiO2 **1**.

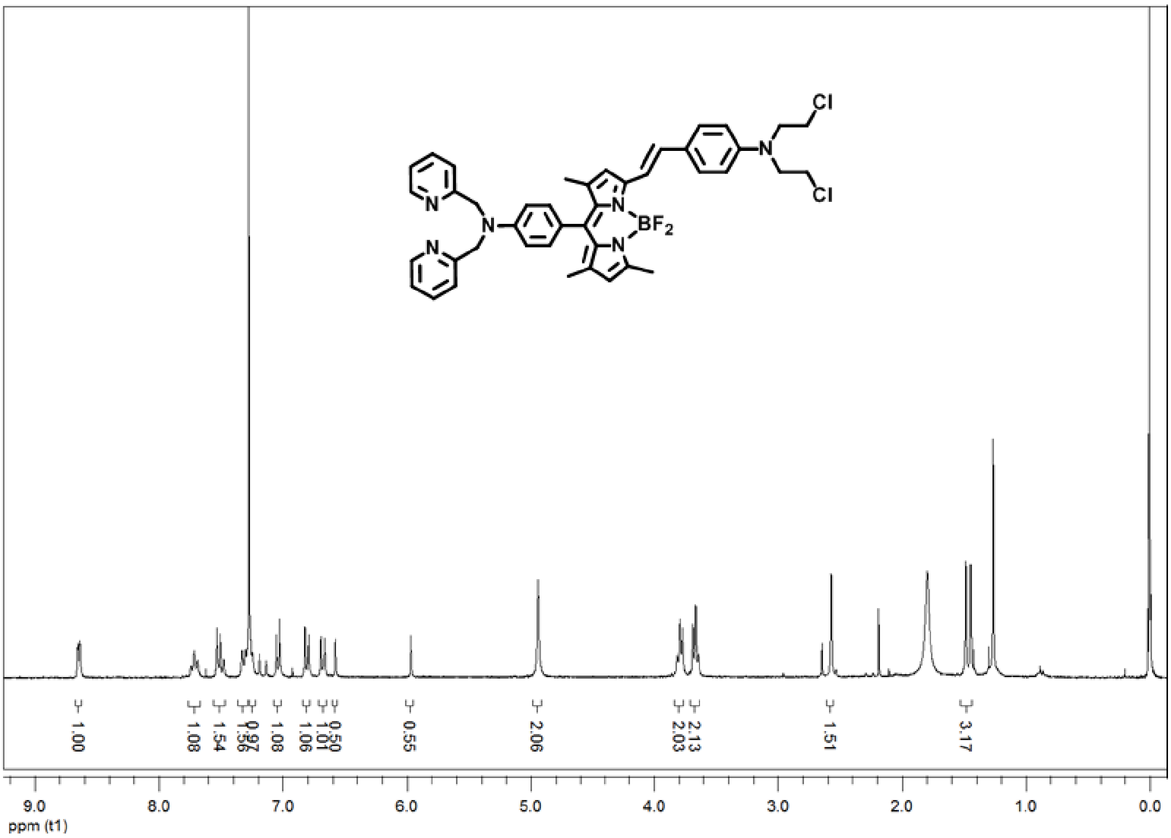


Fig. S3 ^{1}H NMR spectrum of **2** recorded in DMSO-d_6.

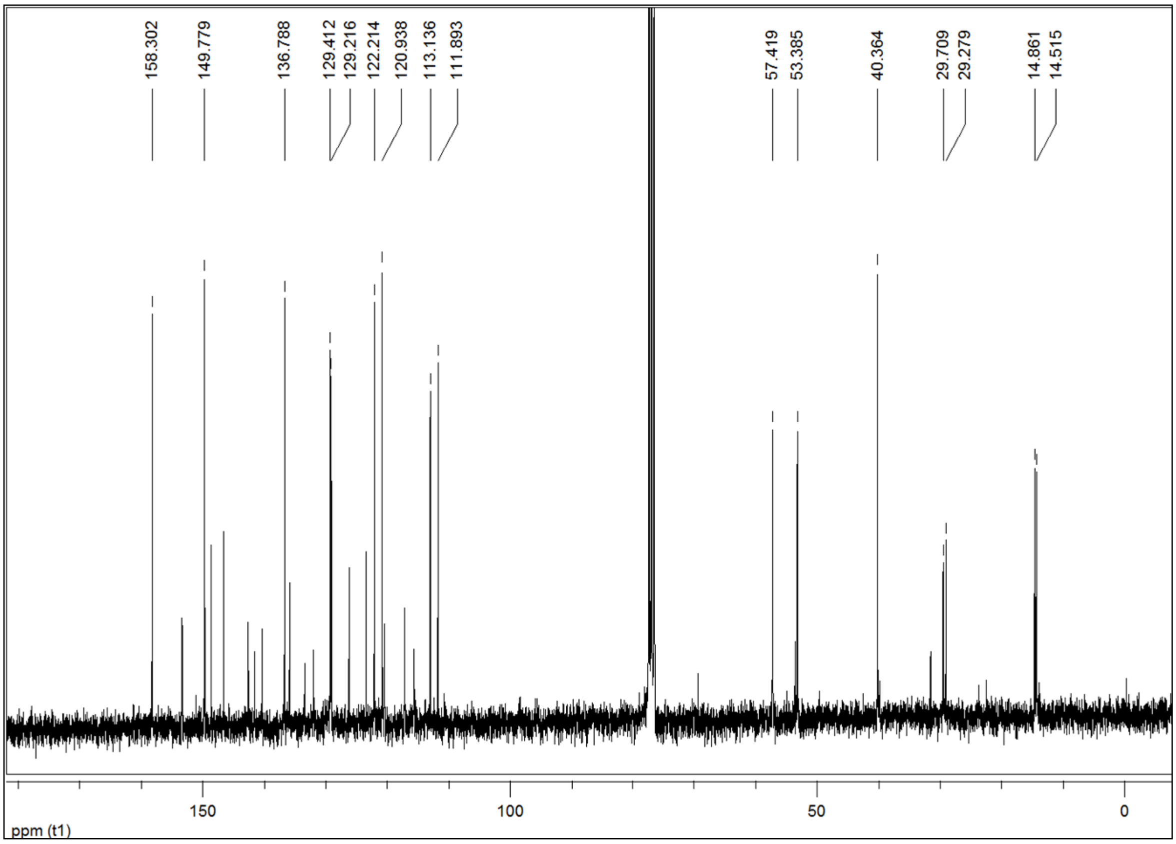


Fig. S4 ^{13}C NMR spectrum of **2** recorded in DMSO-d$_6$.

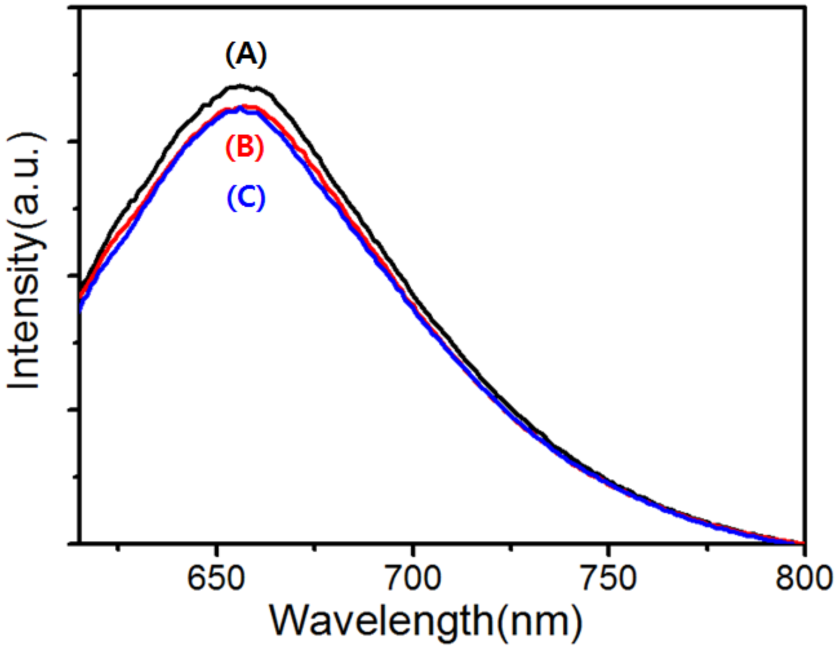


Fig. S5 Emission spectra of functionalized mesoporous SiO$_2$ (**1**) (5.0 mg) without (A; black line) and with (B) Hg(II) (23.2 μM; red line) and (C) Zn(II) (23.2 μM; blue line) in aqueous solution.

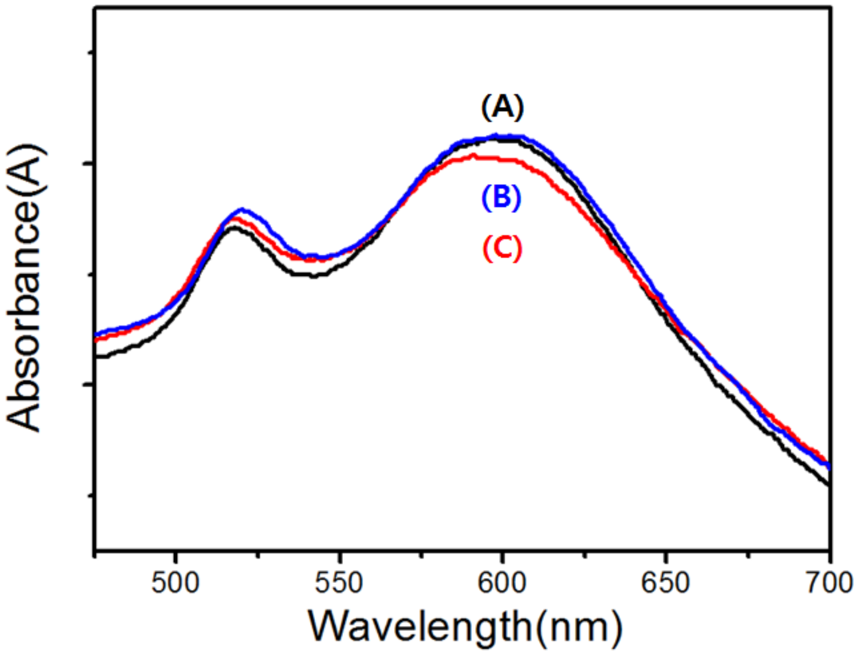


Fig. S6 Absorption spectra of functionalized mesoporous SiO_2 (**1**) (5.0 mg) without (A; black line) and with (B) Hg(II) (23.2 μM; red line), (C) Zn(II) (23.2 μM; blue line) in aqueous solution.

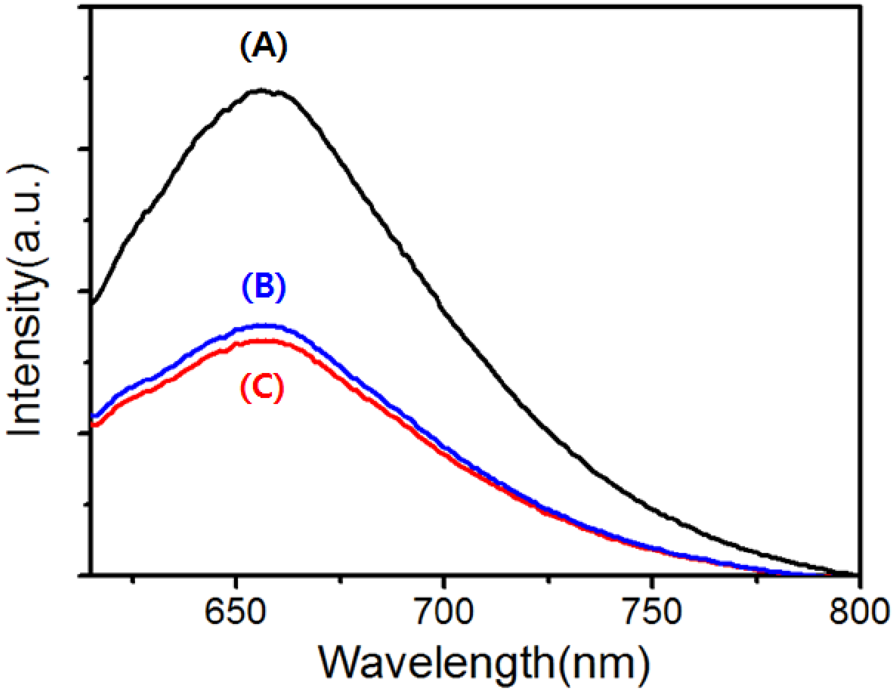


Fig. S7 Emission spectra of functionalized mesoporous SiO_2 (**1**) (5.0 mg) without (A) and with (B) Ni(II) (23.2 μM), (C) Cu(II) (23.2 μM) in aqueous solution.