Electronic Supplementary Information (ESI)

A thin-layered chromatography plate prepared from naphthalimide-based receptor immobilized SiO_2 nanoparticles as a portable chemosensor and adsorbent for Pb^{2+}

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Experimental Section

General: ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 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. The optical absorption spectra of the samples were obtained at 278-77 K using a UV–vis spectrophotometer (Hitachi U-2900). All fluorescence spectra were recorded in RF-5301PC spectrophotometer.

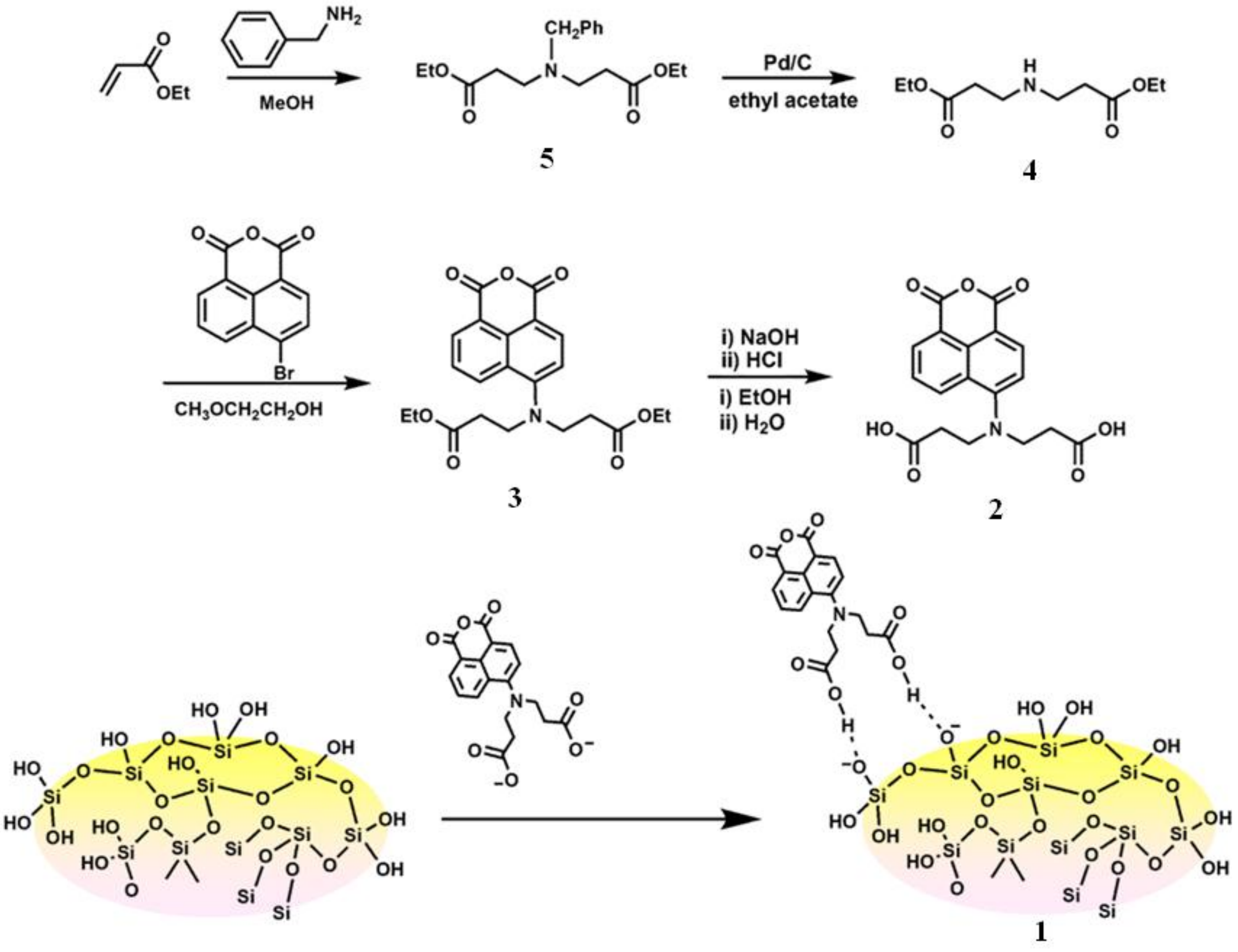
SEM observations: For transmission electron microscopy (TEM), a piece of the gel was placed on a carbon-coated copper grid (400 mesh) and removed after one min, leaving some small patches the sample on the grid. The specimens were examined with a JEOL JEM-2010 transmission electron microscope operating at 200 kV using an accelerating voltage of 100 kV and a 16 mm working distance. Scanning electron micrographs of the samples were taken with a field emission scanning electron microscope (FE-SEM, Philips XL30 S FEG). The accelerating voltage of SEM was 5–15 kV and the emission current was 10 μA.

Photophysical studies: Fluoroscence spectra of **1** (10.o mg) were observed upon addition of various metal ions (0-10.0 equivalents) in aqueous solution at pH 7.

Preparation of compound 3. Under nitrogen, a solution of 4-bromo-1,8-naphthalic anhydride (0.6 g, 2.18 mmol) compound **4** (0.7 g, 3.26 mmol) in 2-methoxyethanol (40 mL) was refluxed for 48 h, the mixture was evaporated by rotary evaporation and dissolved in CH_2Cl_2 (150 mL). The organic layer was washed with water (3 x 100 mL), dried over anhydrous Na_2SO_4, and filtered. After the solution was evaporated under reduced pressure, the crude product was purified by column chromatography (silica, $CHCl_3$/EtOH 99:1) to give 0.52 g of **3** (6.7 % yield). ^{1}H NMR (300 MHz, CDCl3, δ): 1.24 (t, 6H, J = 25 Hz), 2.77 (t, 2H, J = 25 Hz), 2.86 (t, 2H, J = 20 Hz), 4.16 (q, 2H, J = 24 Hz), 6.75 (d, 1H, J = 28), 7.65 (t, 1H, J = 25 Hz), 8.15 (d, 1H, J = 28), 8.50 (d, 1H, J = 28 Hz), 8.62 (d, 2H, J = 24). ESI-MS (*m/z*) Calcd. for $C_{22}H_{23}N_1O_7$: 413.1. Found: 440.1 [Na(**3**)]$^+$. FT-IR: 3004.32, 1712.97, 1362.10, 1420.66, 1221.97, 1092.20 and 901.51 cm^{-1}. Element analysis: calculated for $C_{22}H_{23}N_1O_7$: C 63.92 H 5.61 N 3.39 O 27.09 Found C 64.12 H 5.87 N 3.19

Preparation of compound 2: Compound **3** (0.6 g, 1.4 mmol), was dissolved in ethanol (20 mL). To this was added NaOH (0.87 g, 21.7 mmol) and the resulting solution refluxed for 6 h. Progress of this hydrolysis reaction was periodically monitored by TLC. Upon complete consumption of the ester, the reaction mixture was acidified with conc. H_2O and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered and concentrated to dry ness to afford pure compound **2** (84.2% yield). ^1H NMR (300 MHz, $CDCl_3$, δ): 2.55 (t, 2H, J = 26 Hz), 2.71 (t, 2H, J = 23 Hz), 3.61 (t, 2H, J = 21 Hz), 4.23 (t, 2H, J = 25 Hz), 6.8 (d, 1H, J = 29 Hz), 7.68 (t, 1H, J = 26 Hz), 8.2 (d, 1H, J = 29 Hz), 8.4 (d, 1H, J = 25 Hz), 8.7 (d, 1H, J = 28 Hz), 12.3 (s, 2H). ^{13}C NMR (75.4 MHz, DMSO-d6): δ 173.5 173.2 164.0 163.1 150.8 134.6 130.9 129.7 129.0 124.5 122.0 120.5 108.1 104.1 49.0 35.9 33.5 33.0. FT-IR : 3404, 2924, 2584, 1723, 1682, 1639, 1576, 1549, 1357, 1261, 1233 and 1022 cm^{-1}. ESI-MS (m/z) Calcd. for $C_{18}H_{15}N_1O_7$: 357.0. Found: 356.1 (M^-). Element analysis: calculated for $C_{18}H_{15}N_1O_7$: C 60.51 H 4.23 N 3.92 O 31.34 Found C 60.87 H 4.51 N 4.23.

Preparation of compound 1: Compound **2** (35 mg) was dissolved in anhydrous toluene (20 mL). The silica nanoparticle (27 mg) was added as a solid. The suspension of silica was stirred under reflux condiions for 24 h in toluene. Then, the collected solid was washed copiously with toluene (50 mL) to rinse away any surplus **2** and dried under vacuum. FT-IR : 3404, 2924, 2584, 1723, 1682, 1639, 1576, 1549, 1357, 1261, 1233 and 1022 cm^{-1}



Scheme S1. Preparation Method of 2-immobilized SiO_2 nanoparticle (**1**).

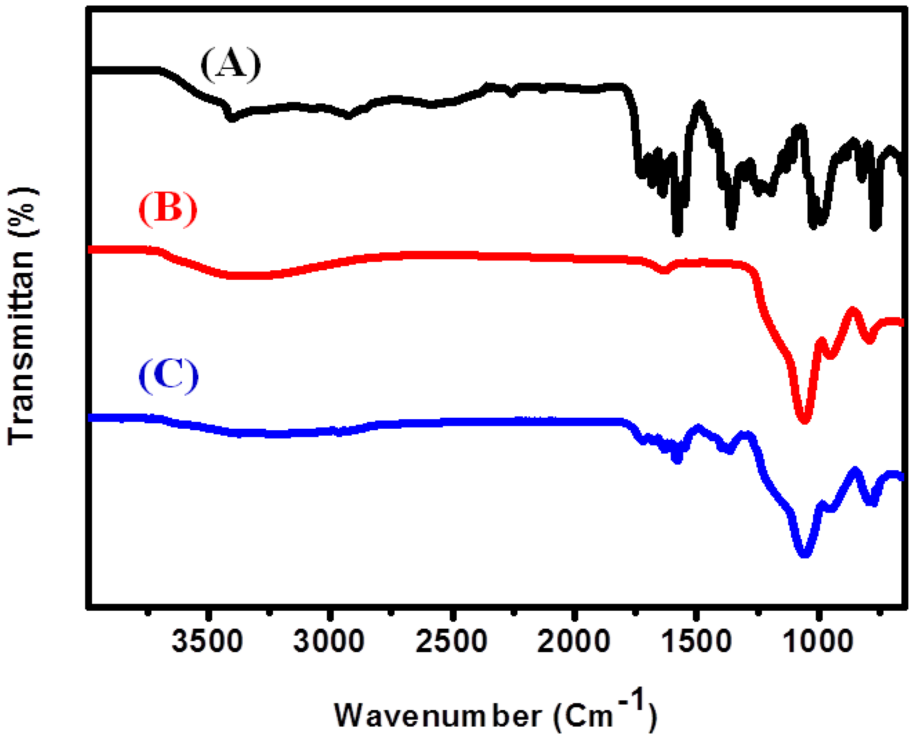


Fig. S1 FT-IR spectra of (a) **2**, (b) mesoporous silica and (c) **1**.

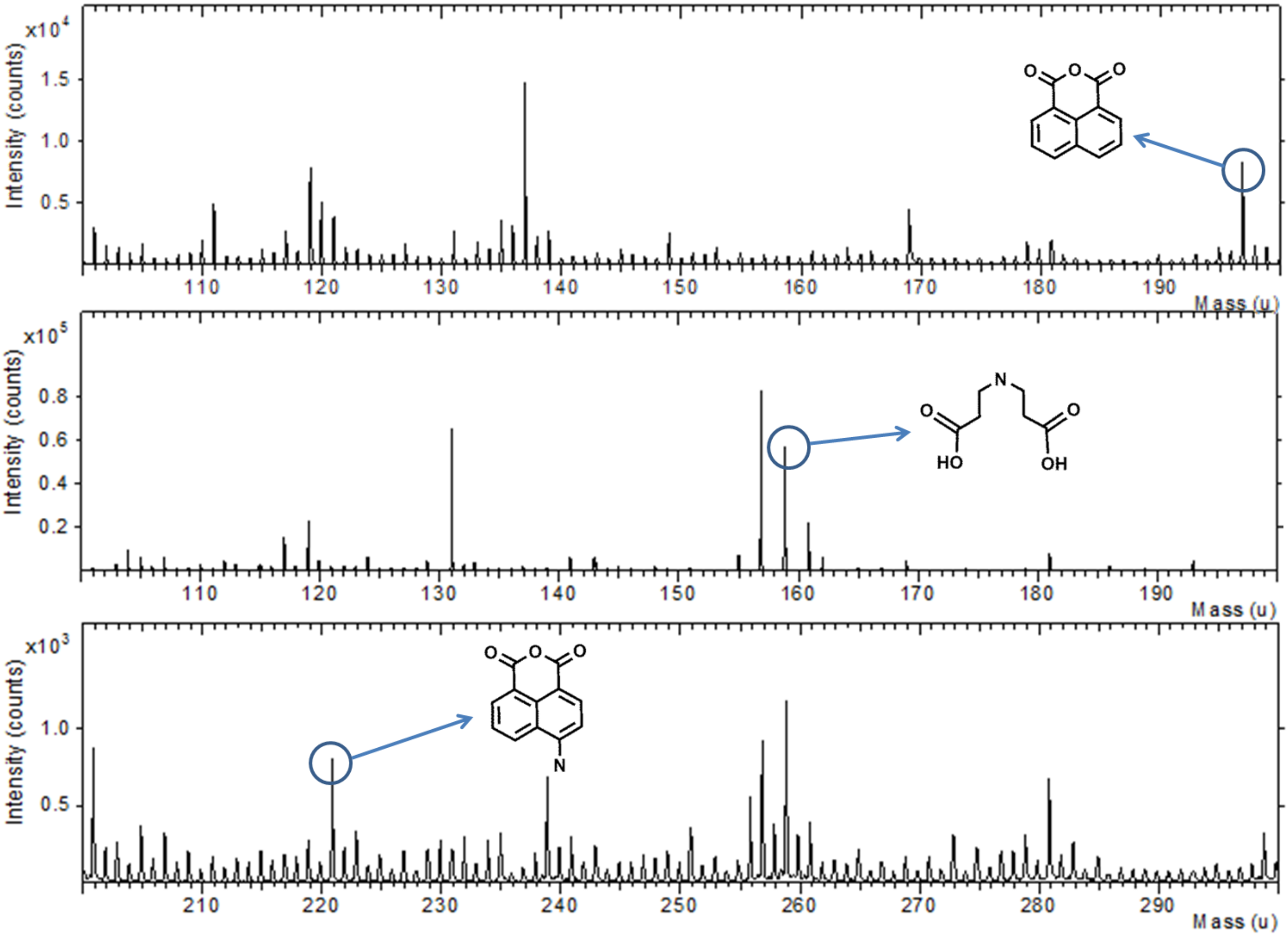


Fig. S2 TOF-SIMS spectrum of **1**.

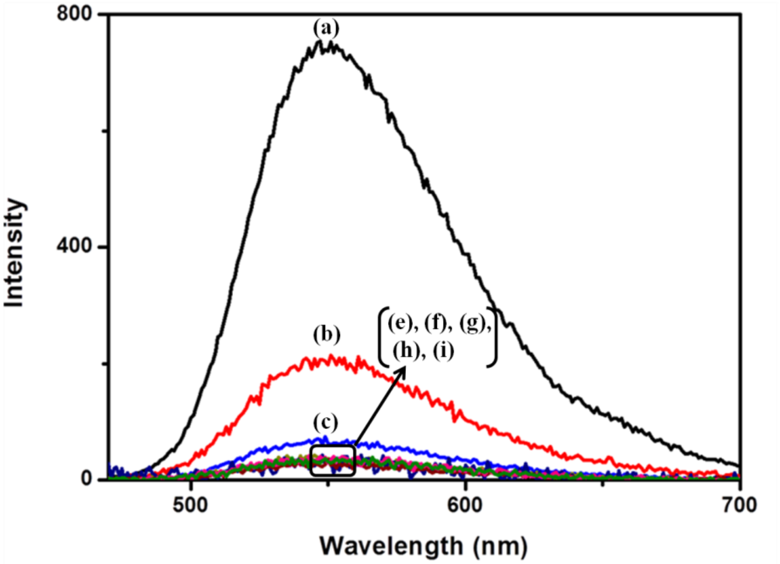


Fig. S3 Time course of the fluorescence intensity of **1** (10.0 mg**)** upon addition of Pb^{2+} (10.0 equiv) in aqueous solution at pH 7; a) 0 min, (b) 0.5 min, (c) 1 min, (d) 2 min, (e) 3 min, (f) 4 min, (g) 5 min, (h) 6 min, (i) 7 min and (j) 8 min

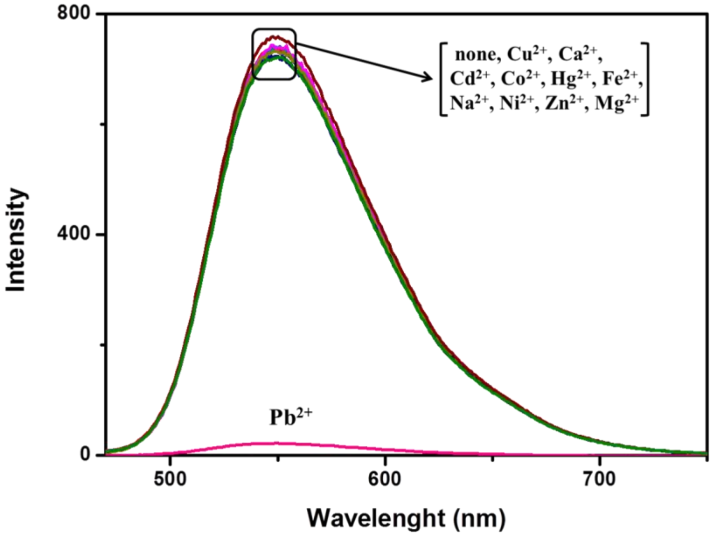


Fig. S4 Fluorescence intensity of **1** (10.0 mg) with Pb^{2+} (10.0 equiv) in the presence of other metal ions such as Cu^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+}, Fe^{2+}, Na^{2+}, Ni^{2+}, Zn^{2+} and Mg^{2+} ions in water at pH 7.

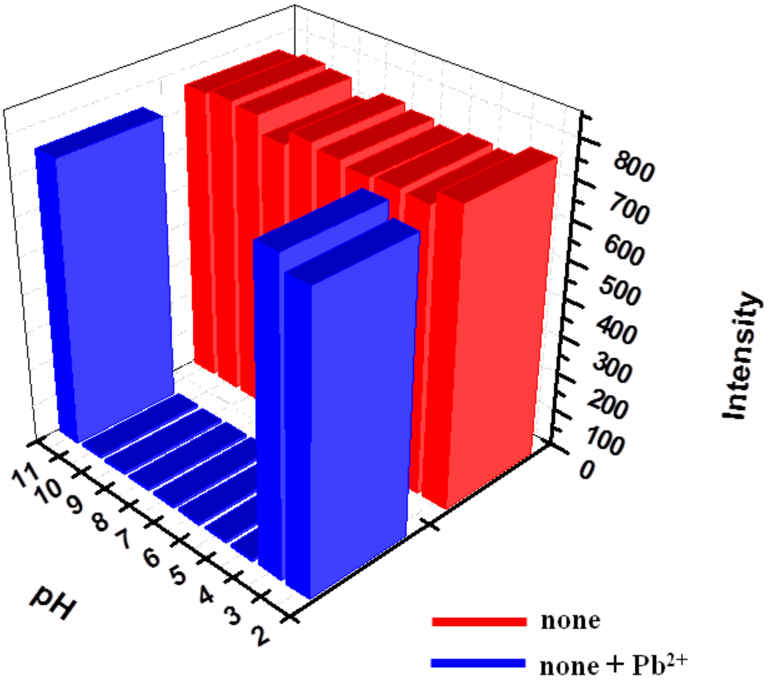


Fig. S5 Fluorescence intensity of **1** (10.0 mg) before and after addition of metal ions (5.0 equivalents) at different pH values.