

Electronic Supplementary Information (ESI)

Reversible optical solid sensor based on acyclic-type receptor immobilized SBA-15 for the high selective detection of Hg (II) ion in aqueous media

*Eunjeong Kim, Hee Eun Kim, Soo Jin Lee, Shim Sung Lee, Moo Lyong Seo and Jong Hwa Jung**

Department of Chemistry and Research Institute of Natural Sciences, Gyeongsang National University,
Jinju, 660-701, S. Korea

Experimental section

Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 apparatus. IR spectra of silica powder pellets were obtained using a Shimadzu FT-IR 8400S and the MS spectrum was obtained with a JEOL JMS-700 mass spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Siemens D8 Advance diffractometer using Cu K_α radiation and a secondary monochromator. Transmission electron microscopy (TEM) images were captured with a JEOL JEM-2100 F microscope. EDX analysis was conducted with a JEOL ultra-thin window (UTW)-type EDX detector capable of detecting boron and an OXFORD EDS system for signal processing in a 180-s live time. Nitrogen-adsorption isotherms were measured at 78 K on a Micromeritics ASAP 2010 analyzer. Thermal gravimetry analysis (TGA) was conducted on a TA SDT Q600 with a heating rate of 10 °C/min using a Pt pan in air. Heating temperature was scanned from 25 °C to 900 °C.

Preparation of mesoporous silica. Mesoporous silica was synthesized starting from the preparation of a hydrochloric acid solution of P-123. Tetraethyl orthosilicate (TEOS) was then added and the mixture was stirred at 40 °C for 20 h. The molar composition was 1:5.9:193:0.017 TEOS:HCl:H₂O:P-123. The aging was performed at 65 °C for 1 day and the solid was filtered, washed and dried at 90 °C. For cleaving the template to generate the mesopores, 1.0 g of as-synthesized SBA-15 was mixed with 100 mL of 60 wt % H₂SO₄ solution and refluxed at 95 °C for 1 day. The product was recovered by washing with water and dried at 90 °C. To generate micropores, the acid-treated sample was heated to 200 °C in air. To remove cationic surfactants, dried fiber-like flocculates and particles were calcined in a box furnace in air at 500 °C for 5 h, with a ramp rate of 1 °C/min.

Measurements of UV-Vis spectrum: UV-vis spectroscopy analysis was carried out on a Shimadzu UV-2401 PC UV-Vis spectrophotometer. Studies were carried out on fast scan mode with slit widths of 1.0 nm, using matched quartz cell. Studies were carried out in H₂O and/or buffered conditions. When buffered conditions were used the solutions contained 135 mM NaCl and 20 mM HEPES Buffer, at pH 7.4.

Immobilization of receptor 5 onto mesoporous silica. Compound **5** (100 mg) was dissolved in toluene (10 mL). The mesoporous silica (100 mg) or a commercial silica particle (100 mg) was added as a solid. The suspension of mesoporous silica was stirred in a reflux condition for 24 h in toluene. Then, the collected solid was washed copiously with toluene (50 mL) to rinse away any surplus **5** and dried under vacuum.

Hydrolysis of mesoporous silica immobilized with 5. To obtain acid form receptor (**1**) attached to mesoporous silica, the mesoporous silica immobilized with receptor **5** was dispersed in methanol (2 mL). The suspension of silica was maintained for 10 h at room temperature. After filtration, the solid product was washed with Na₂CO₃ solution and water and dried.

Coloration and extraction of metal ions by ARMS. The ARMS (10 mg) was added to the metal ions solution (all as chloride, 5.0 equiv with respect to **1** anchored to the ARMS). The mixture was stirred for 10 min. After filtration, the concentration of metal ions was analyzed by ICP (DX-500, DIONEX). Also,

UV-vis spectrum of metal-loaded **ARMS** was measured by Shimadzu UV-2401 PC UV-Vis spectrophotometer.

Photophysical studies of ARMS. UV-vis spectroscopy analysis was performed in water suspension of 5×10^{-4} M **ARMS**. Studies were carried out in H₂O and/or buffered conditions. When buffered conditions were used the solutions contained 135 mM NaCl and 20 mM HEPES Buffer, at pH 7.4. Test solutions were 20 mL for metal titrations and 20 or 25 mL for pH studies. In addition, to reversibility, UV-VIS spectrum was measured. EDTA (10 mmol, 2 mL) was added to **ARMS** suspension (at pH 7.4) to remove Hg²⁺ ion bound **ARMS**. Then, the absorption change of H₂O suspension of **ARMS** was observed by UV-vis spectroscopy.

Compound 3: To a 50 mL round bottom flask, *o*-anisidine (**2**) was added ethylbromoacetate in the potassium dihydrogen phosphate in CH₃CN (10mL). The reaction mixture was maintained for 10 h at 60 °C. After cooled to room temperature, the reaction mixture was reduced down, dissolved into CHCl₃ (50 mL) and washed with water (2 x 30 mL). The organic phase was dried over MgSO₄ and reduced to oil. The crude product was purified on a silica column using 70:30 Hex:EtOAc, to produce **3** as a white solid. m.p. 78-80 °C; ¹H NMR (300 MHz, CDCl₃, TMS) δ = 6.87 (d, ²J (H,H) = 12.3 Hz, 1H; Ar-H), 4.20 (d, ²J (H,H) = 7.2 Hz, 1H; Ar-H), 3.80 (s, 3H; CH₃) 1.26 (t, ³J(H,H) = 7.2Hz, 6H; CH₃) ¹³C NMR (300 MHz, CDCl₃, TMS) δ =171, 151, 122, 120, 119, 111, 77, 77, 77, 76, 60, 55, 53, 30, 14, ; IR (KBr): ν = 3393, 3090, 2931, 2853, 1740, 1653, 1373, 1032, 751 cm⁻¹ HRMS (FAB⁺) m/z 295.14 [(M+H)⁺ calcd for C₁₅H₂₁NO₅:295.16]. Anal. Cald for C₁₅H₂₂NO₅: C, 61.00; H, 7.17; N, 4.74. found: C, 60.68; H, 7.23; N, 4.69.

Compound 4: To a 50 mL round bottom flask, *o*-amino benzoic acid (1.047 g, 7.5 mmol) was added which contained a solution of 1:1, THF : H₂O (20 mL) and NaNO₂ (0.5261 g, 7.6 mmol). To the solution, which was, being stirred at 0 °C, HCl (1.0 mL, 12 M) was slowly added. This solution was added drop

wise to a 100 mL single neck round bottom flask which contained the appropriate ester (**3**) (6.8 mmol) in a solution of 1:1 THF : H₂O (40 mL). This solution was at 0 °C for approximately 2 hours. This solution was left stirring overnight at room temperature. The resulting dark red solution was reduced down, dissolved into CHCl₃ (60 mL) and washed with water (2 x 30 mL). The organic phase was dried over MgSO₄ and reduced to oil. The crude product was purified on a silica column using 70:30 Hex:EtOAc, to produce **4** as a bright red solid. m.p. 101-103 °C; ¹H NMR (300 MHz, CDCl₃, TMS) δ = 8.10 (d, ²J (H,H) = 7.75 Hz, 1H; Ar-H), 7.59 (d, ²J (H,H) = 7.2 Hz, 1H; Ar-H), 7.48 (t, ³J(H,H) = 7.8Hz, 1H; Ar-H), 6.9 (d, ²J (H,H) = 4.5 Hz, 1H; Ar-H), 4.18 (m, 8H), 3.8 (s, 3H; CH₃), 1.26(t, ³J (H,H) = 7.2 Hz, 6H; CH₃) ¹³C NMR (300 MHz, CDCl₃, TMS) δ =187, 182, 154, 144, 135, 134, 134, 133, 133, 127, 127, 125, 120, 116, 58, 43, 42, 23, 18, ; IR (KBr): ν = 3414, 3270, 2940, 2856, 1870, 1735, 1637, 968, 804 cm⁻¹; HRMS (FAB⁺) m/z 443.17 [(M+H)⁺ calcd for C₂₂H₂₅N₃O₇: 443.20]. Anal. Cald for C₂₂H₂₅N₃O₇: C, 59.59; H, 5.68; N, 9.48. found: C, 60.11; H, 5.80; N, 9.35.

Compound 5: 4 (250 mg, 0.42 mmol) was suspended in ethyl acetate (10 mL). The mixture was stirred under nitrogen for two minutes and then cooled to 0 °C. 1-Hydroxybenzotriazole (HOBt, 68 mg, 0.5 mmol) and dicyclohexyl carbodiimide (DCC, 1.870 g, 9.07 mmol) were added simultaneously as a mixture of solids. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The precipitate was removed by filtration. The filtrate was then washed with NaHCO₃ aq. (satd.) and NaHSO₄ aq. (satd.). The solution was dried with MgSO₄ and the solvent was removed by rotary evaporation to produce a reddish crude. This crude product was purified by column chromatography (silica-gel, n-hexane: ethyl acetate, 1:1, R_f= 0.45) to give the product (1.24 g, 65%). m.p. 115-117 °C; ¹H NMR (300 MHz, DMSO) δ = 7.5, 7.5, 7.4(m, 3H) 6.9, 6.8, 6.8, 6.7 (m, 4H), 4.17(t, ³J(H,H) = 6.9Hz, 1H; Ar-H), 3.79 (s, 3H), 1.73(t, ³J(H,H) = 2.4Hz, 1H; Ar-H) 1.24 (m, 15H); IR (KBr): ν = 3414, 3270, 2940, 2856, 1870, 1735, 1637, 1121, 968, 804 cm⁻¹; HRMS (FAB⁺) m/z 646.30 [(M+H)⁺ calcd for

$C_{31}H_{46}N_4O_9Si:646.34$]. Anal. Cald for $C_{31}H_{46}N_4O_9Si$: C, 57.56; H, 7.17; N, 8.66. found: C, 57.71; H, 7.02; N, 8.33.

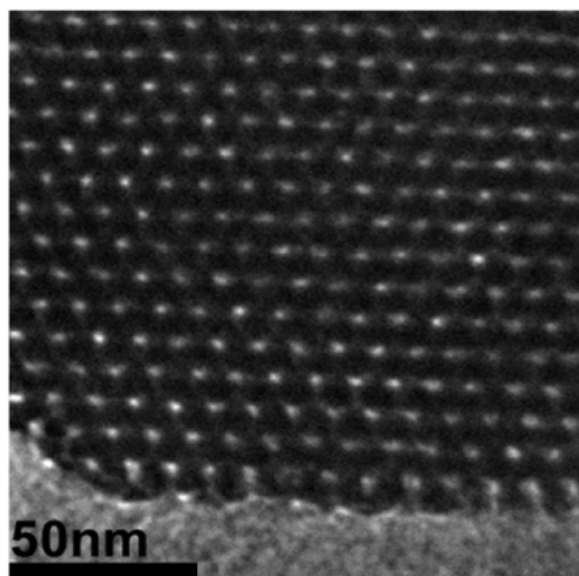


Fig. S1 TEM image of mesoporous silica.

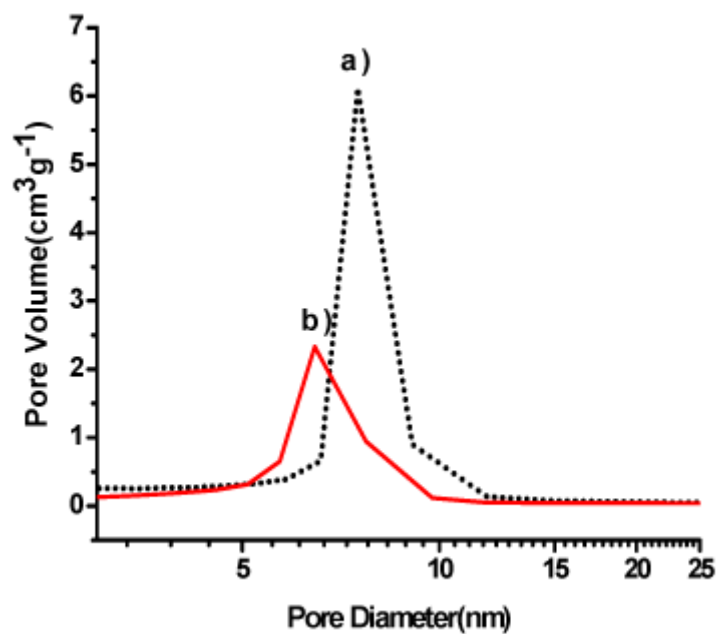


Fig. S2 Barrett-Joyner-Halenda(BJH) pore diameters of (a) mesoporous silica and (b) ARMS.

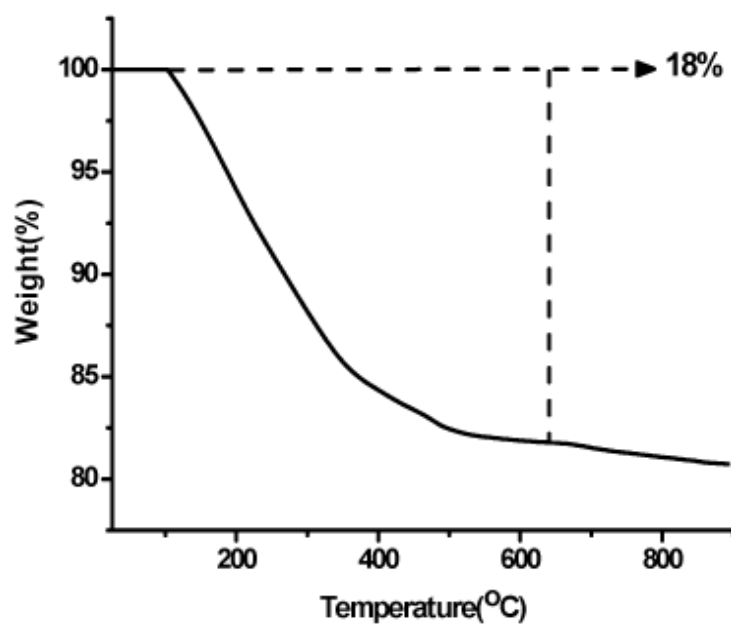


Fig. S3 Thermogravimetric analysis data of ARMS.

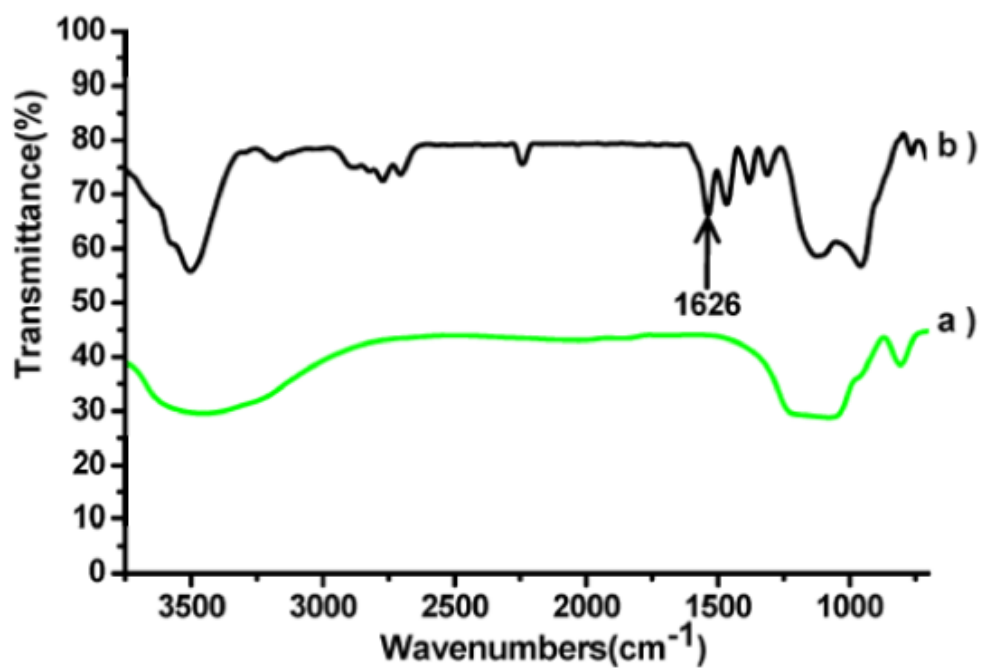


Fig. S4 FT-IR spectra of (a) mesoporous silica (SBA-15), and (b) ARMS.

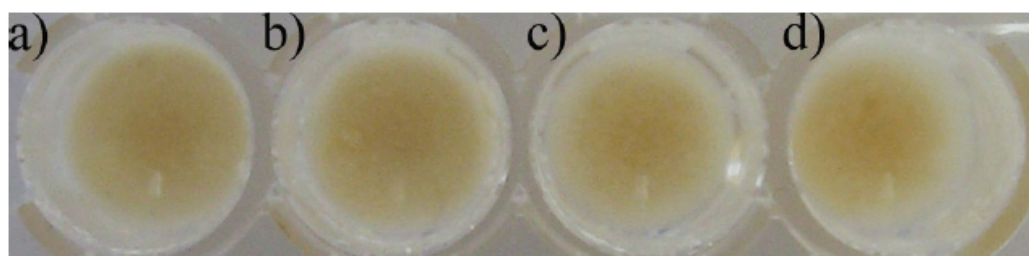


Fig. S5 The colorimetric response of H₂O suspension samples of **ARMS** (5.0 mg) in the (a) absence and the presence of (b) KCl, (c) CaCl₂ and (d) SrCl₂.

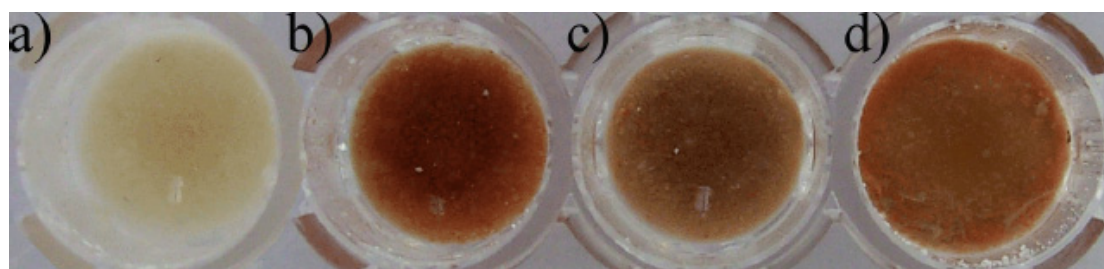


Fig. S6 Color changes of **ARMS** (5.0 mg) in the (a) absence and the presence of (b) HgCl_2 , (c) $\text{Hg}(\text{NO}_3)_2$, and (d) $\text{Hg}(\text{ClO}_4)_2$.

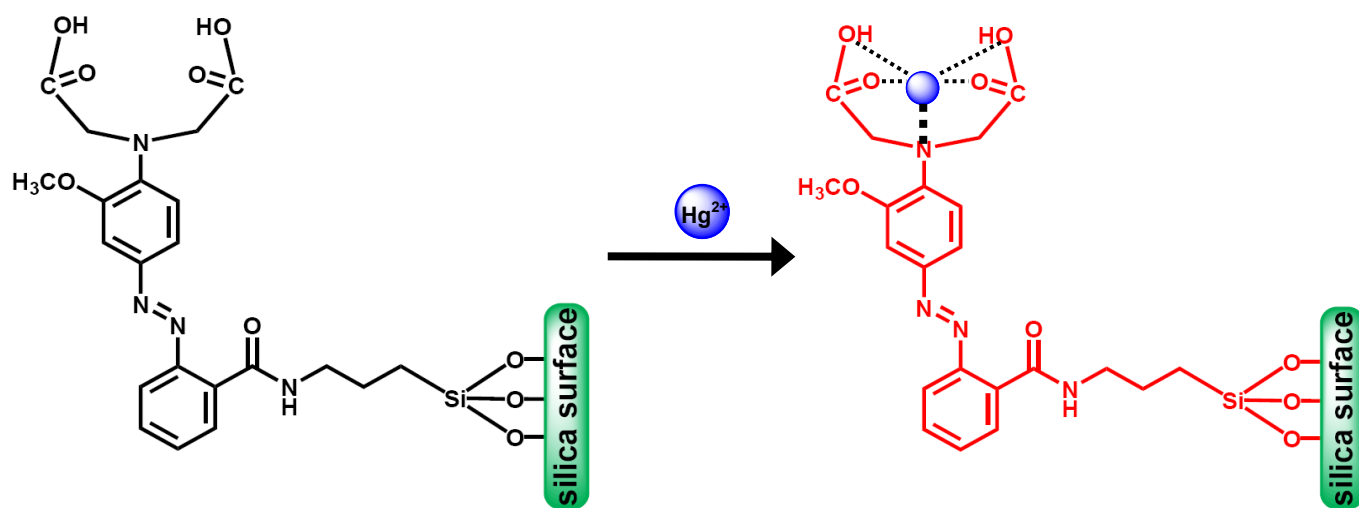


Fig. S7 Proposed structure for receptor 1 complex attached on ARMS with Hg^{2+} ion.

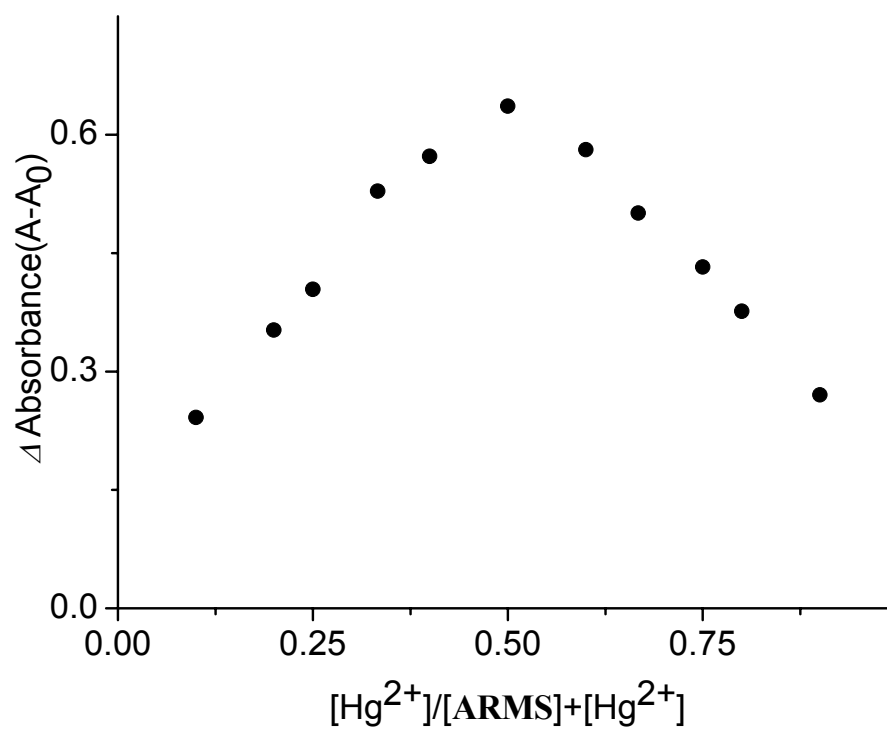


Fig. S8 Job's plot for ARMS with Hg²⁺.

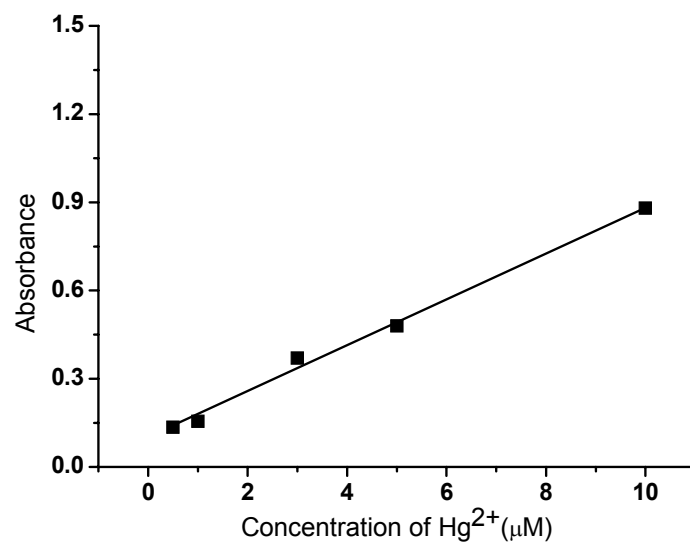


Fig. S9 Calibration curve of concentration of Hg²⁺ ion against absorption intensity of AFMS (at 510 nm).

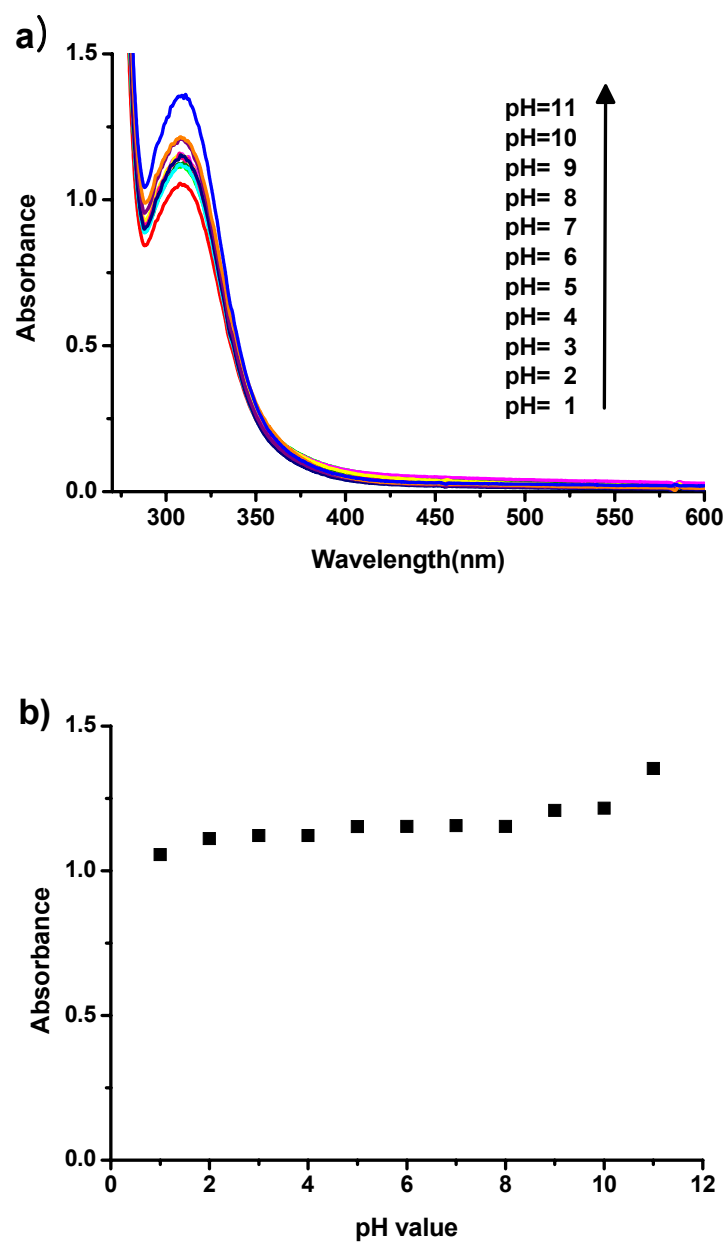


Fig. S10 (a) UV-vis spectra of ARMS at different pH values and (b) plot of pH values against absorption intensity of ARMS.