Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Non-Covalent Functionalization of High-Surface Area Nanomaterials: A New Class of Sorbent Materials

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Experimental

Preparation of thiol ligands

Commercially available *benzyl mercaptan (BM),* and *1,4- bis(mercaptomethyl)benzene (BMMB*) were used as received.

2-(mercaptomethyl)naphthalene (MN)
2-bromomethylnaphthalene (4.26 g) and thiourea (2.2 g) were dissolved in acetone (180 mL). This solution was refluxed for two hours and the white solid thiouronium salt was filtered, washed three times with acetone (100 mL), dried under vacuum, and used without further purification. The crude thiouronium salt was dissolved in degassed 2 M aqueous NaOH (180 mL). This was heated to 90 °C and this temperature was maintained for 2 hours under argon. After cooling, degassed HCl (4 M) was added slowly via cannula until the pH of the mixture was acidic. The thiol product was extracted into dichloromethane, dried with Na_2SO_4, and evaporated to dryness. White, crystalline product was obtained in 91% yield; characterization data were consistent with prior syntheses of this compound.[1]

3,3-Diphenylbenzo[c]thiophene-1(3H)-thione (DTP)
Was prepared as described in literature, with slight variation. For example when working with 1.9085 grams of lactone precursor, after the reaction was complete the product was mostly concentrated to give the desired product in 20 mL of xylenes. This was then stirred in an ice bath with 40 mL of (1:1) K_2CO_3 (2M)/acetone for 1 hour, the organic layer was removed and allowed to evaporated over several days yielding pure crystals. After 2 days crystals were isolated in 22% yield, which can be greatly increased with multiple crystallizations; characterization data were consistent with the prior report of this compound.[2] The crystal structure for this compound was not previously reported, and is now shown ESI Figure S1. For crystallographic data in CIF or other electronic format see CCDC 1408666.

Ph-SAMMS
In a typical preparation of Ph-SAMMS, MCM-41 (5.1 g) with 3.5 nm pores was stirred in dry toluene (50 mL) for 30 min. H_2O (1.2 ml) was added and this was stirred for an additional hour. Trimethoxyphenysilane (3.95 g) was added and the reaction was heated to reflux. After 18 hours the methanol was removed by evaporation at 120 °C. The reaction was filtered hot through a fritted funnel and subsequently washed three times with methanol (200 mL). The white powdery material was dried at room temperature for 2 hours and then placed under vacuum for 6 hours. This method yielded a material with 1.6 phenyl rings per nm^2.

Non-covalent SH-SAMMS
Typical preparation of the non-covalent materials the desired thiol containing arene ligand and Ph-SAMMS (300 mg) are incubated in dichloromethane (5 mL) overnight, the amount of arene ligand was varied for desired coverage. For example, if 0.50 mmol thiol groups per gram material were desired 0.15 mmol of thiol ligand was added to 300 mg of

Ph-SAMMS. The solvent is then evaporated away overnight. The resulting material was thoroughly washed with methanol (200 mL).

TGA analysis

TGA was performed on a TA Instruments© Q500 using platinum pans, air as the balance gas and N_2 as the purge gas. The heating program was as follows: Ramp 5 °C/min to 110 °C, isothermal for 30 min, ramp 5 °C/min to 1000 °C, isothermal for 10 minutes, end. All TGA experiments were run in triplicate.

Ellman's test for thiols

Ellman's reagent, 5,5'-dithiobis(2-nitrobenzoic Acid), was purchased from TCI America. The tests were performed an aqueous sodium phosphate (0.1 M) buffer containing EDTA (1 mM) adjusted to pH 7.8. The extinction coefficient was determined using cysteine as a thiol standard and was measured at peak absorbance near 412 nm. Before measurement all solutions were filtered through a 0.2 micron filter. The Ellman's test is time-sensitive and all measurements were performed 11-20 minutes after addition of the Ellman's reagent to the material or standard solution. For Ph-SAMMS materials, one microliter of methanol per 2 mg sorbent was added to facilitate surface wetting. All Ellman's tests were performed in triplicate. When the results for the Ellman's tests are compared to TGA measurements of the same material, the tests typically differ by 1-3% if at all. The Ellman's test yields the lower value. This may be due to the kinetic restriction of mass transport through the material during the timeline of the Ellman's experiment. For our surface thiol measurements, standard deviation across four or more measurements was found to be 0.003 mmol SH per g material. This corresponds on a relative standard deviation of about 6% for materials with low thiol density and a deviation of less than 1% for more densely functionalized materials.

DTP leaching test

The lack of a single thiol group made this molecule unfit for Ellman's test, thus the concentration was determined by UV-Vis analysis monitoring the absorbance at 287nm using standard calibration curves. We were unable to detect any leaching into nanopure water.

Metal uptake analysis

Metal uptake studies were carried out using filtered Columbia River water (pH 7.8) from Hanford, Washington, doped with 50 ppb each target metal. Prepared metal solutions (10 mL) were aliquoted into polypropylene tubes and spiked with a small volume of sorbent suspended in deionized water to obtain the liquid-to-solid ratios of 5000 (mL/g). Phenyl-SAMMS sorbents was preconditioned with one microliter of methanol per 2 mg sorbent to enable effective surface wetting. Contact times were 2 hours with agitation at 60 Hz on an orbital shaker. After contact, the water was filtered through a 0.2 micron filter, diluted with 2% HNO_3, and Hg, Cd, Ag, and Pb content were analyzed using ICP-MS (Agilent 7500 ce, Agilent Technologies, CA). Ge and In were used as internal standards or metals of similar mass at 10 ppb. All samples were run in triplicate.

Preparation of lauric acid Fe_3O_4 nanoparticles

These particles were prepared by Cynthia Warner following the method described in reference 2: $Fe(acac)_3$ (6 mmol), 1,2-hexadecanediol (30 mmol), lauric acid (18 mmol), and laurylamine (18 mmol) were dissolved in benzyl ether (80 mL) and heated to 300 °C at a rate of 4 °C min^{-1} under argon. The solution was refluxed for 30 minutes, cooled to room temperature, transferred to conical vials (50 mL), and ethanol (20 mL) was added to each vial. The tubes were centrifuged, the supernatant decanted, and the pelleted nanoparticles suspended in ethanol. This process was repeated until the obtained supernatant was clear. The black solid was suspended in hexanes and centrifuged to remove insoluble particle aggregates. The particles remaining in hexanes following centrifugation were then collected and dried under argon.

Preparation of benzoic acid Fe_3O_4 nanoparticles by ligand exchange

Lauric Acid Fe_3O_4 NPs were suspended in toluene (2 mL) and combined with benzoic acid (15 mg/mL) dissolved in methanol (2 mL). The mixture was stirred for 18 hours at room temperature. The nanoparticles were retrieved by magnetic decantation then washed several times with ethanol, acetone, and water to remove lauric acid and excess benzoic acid. The benzoic acid Fe3O4 NPs were dried under argon.

Application of 2-mercatomethylnaphthalene to benzoic acid Fe_3O_4 nanoparticles

Benzoic acid Fe_3O_4 nanoparticles (60 mg) were suspended in dichloromethane (10 mL) by sonication for 20 min in a scintillation vial. MN (65 mg) was dissolved in dichloromethane (5 mL) and added to the nanoparticle suspension. This mixture was incubated for 24 hours with agitation at 60 Hz. The vial was then uncapped and the solvent allowed to evaporate. Nanoparticles were then suspended in methanol (5 mL) by sonication for 5 minutes. They were then retrieved by magnetic separation. This methanol wash was performed three times followed by a water wash.

Characterization of Nanoparticles

BET and TGA methods were identical to those for silica based materials. STEM and EDX data is included in ESI Figure S2.

References:

1. L. F. Newcomb, T. S. Haque, and S. H. Gellman, *J. Am. Chem. Soc.*, 1995, **117**, 6509–6519.
2. T. J. Dickerson, T. J. Dickerson, N. N. Reed, N. N. Reed, J. J. LaClair, J. J. LaClair,

and K. D. Janda, *J. Am. Chem. Soc.*, 2004, **126**, 16582–16586.

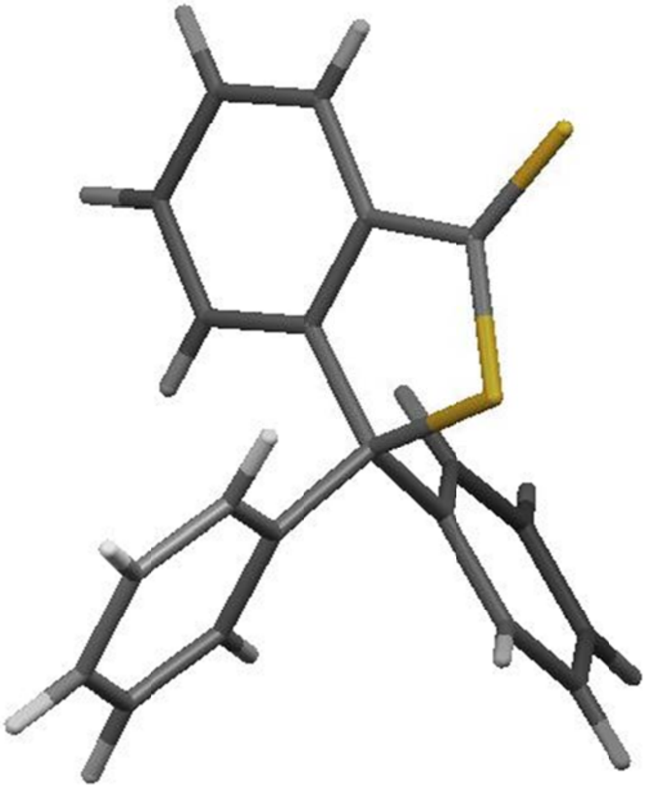

Figure S1. Crystal structure of 3,3-Diphenylbenzo[c]thiophene-1(3H)-thione (DTP).

Table S.1. %RSD values for K_d measurements

	Cd	Hg	Pb	Ag
MCM-41	<1	4	32	52
Ph-SAMMS	10	3	4	4
SH-SAMMS	18	2.2	50	n/a
0.05 SH per g	11	10	18	n/a
0.26 SH per g	1	22	4	n/a
0.55 SH per g	7	6	24	n/a

The relative standard deviation (%RSD) for the Kd values reported in Table 3. Measurements of low final concentration (Cf) often approach the limit of quantification of even the best analytical techniques. These very low Cf measurements have correspondingly high %RSD. Since very low Cf measurements are associated with high Kd, higher Kd values are also associated with high %RSD. n/a indicates that Cf was below the limit of quantification and, thus, could not be measured. In these cases, the limit of quantification was used in place of Cf.

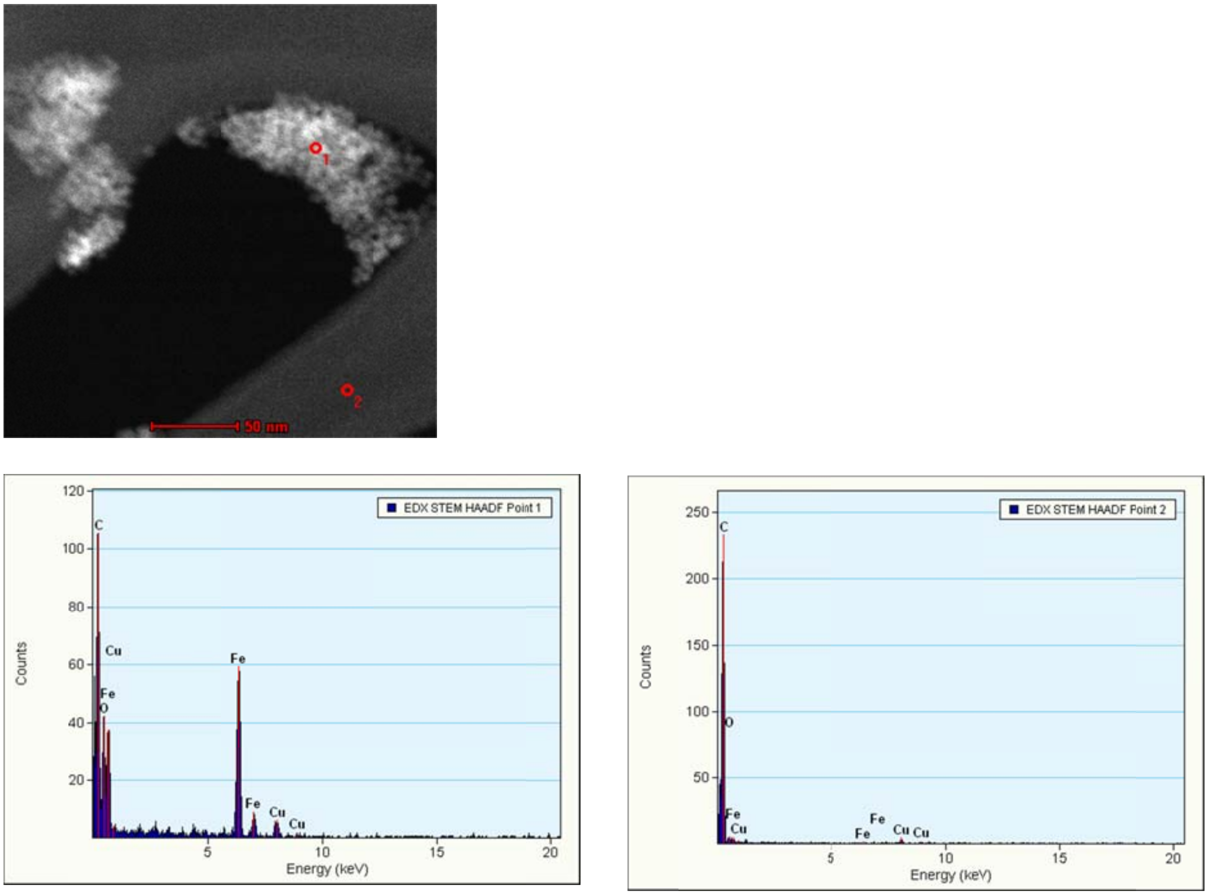

Figure S2: TEM image (top) and EDX analysis of functionalized Fe_3O_4 nanoparticles. EDX analysis does not indicate the presence of sulfur. The left chart indicates EDX counts in region one. As acontrol, the right chart indicates EDX counts of the TEM grid (lacey carbon). This is probably due to relatively low concentration of S compared that of Fe and O. Based on analysis of the TGA data, one would expect the sulfur content of the functionalized Fe_3O_4 NPs to account for less than 1% of the weight of the material. The amount of S relative to Fe, O, and even C, is so small in these materials that detecting it by EDX is not practical. However, observations of their sorption characteristics along with TGA analysis seem sufficient to confirm that the Fe_3O_4 NPs are indeed thiol-bearing materials.