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New functional materials for heavy metal sorption: “Supramolecular” attachment of thiols to mesoporous silica substrates

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Abstract

A new class of sorbent material, which exhibits exceptional metal capture from contaminated natural water, features aromatic thiol ligands reversibly bound to functionalized mesoporous silica through non-covalent interactions and have the potential of being regenerable.

Access to sustainable, clean drinking water is an increasing concern as the Earth's human population continues its steady growth.¹ Degrading water quality in both industrialized and non-industrialized nations has the potential to cause great economic strain on the world's governing bodies.² At the same time, this offers a challenge to researchers to discover new, functional, designer materials that have high uptake capacities and selectivity for environmental contaminants.³ The need to develop inexpensive and efficient water purification media is a high priority.

Current filter media typically consist of granular activated carbon (GAC) or a hybrid material that combines an inorganic oxide such as gamma alumina to achieve satisfactory water purification. This type of filter medium, although common and inexpensive, offers limited uptake potential. Additionally, spent media must be disposed of properly to prevent it from conceivably becoming a source of contamination due to leaching over time. An alternative to “one-shot” filters is the implementation of renewable media capable of many purification cycles before fouling.^{4,5} One such approach is described here with the technique of non-covalent absorption of organothiol ligands onto self-assembled monolayers on mesoporous supports (SAMMSTM).^{6,7} Functionalized mesoporous supports have been found to be excellent sorbent materials, capable of being chemically modified with reactive head groups for toxic metal, metalloid and oxyanion uptake as well as radioactive species.^{8,9} One particular silica-based support, MCM-41, has garnered much attention due to its controllable honeycomb-like porosity, structural integrity, chemical resistivity and high surface area, approaching 1000 m² g⁻¹.¹⁰ A variety of commercially available and synthetically accessible functionalized organosilanes can be affixed inside the pores of the silica support as self-assembled monolayers. The result is a dense population of chelating sites which can achieve exceptionally high uptake levels of target species. It was recognized that phenyl monolayers, in which the aromatic rings were rigidly held upright and perpendicular to the surface, were well suited, both sterically and electronically, to serve as hosts to other functionalized arenes. This approach was envisioned not only to be a very versatile and easy functionalization strategy, but also one that would readily provide for “refreshable” functionalization without the need for acid

stripping.⁵ Herein we describe the functionalization of MCM-41 with phenyl monolayers at various densities to provide a hydrophobic scaffolding for non-covalently bound benzylmercaptan (BM), 1,3- and 1,4-bis(mercaptomethyl)-benzenes (1,3- and 1,4-BMMB, respectively) for use in heavy metal uptake from native waters (Fig. 1).

Thiol-SAMMS derived from covalent attachment of (tris(methoxy)mercaptopropylsilane) to MCM-41 yielding high chelation site densities, have shown excellent uptake levels of soft and moderately soft metal ions such as Hg^{2+} , Pb^{2+} , Cd^{2+} , and Ag^+ .⁹ We have extended the breadth of thiol-SAMMS style sorbent materials with this research to include non-covalently bound mono- and dithiol aryl ligands attached by relatively weak, reversible π -stacking interactions. Remarkably, these materials exhibit comparable metal ion uptake levels to the covalently bound thiol-SAMMS. MCM-41 was functionalized at different surface loading levels by first hydrating the silica surface with a toluene–water mixture (equal to two monolayers of water based on total surface area) followed by addition of trichlorophenylsilane and an overnight stir at room temperature.^{11, 12} Phenyl coverage was determined by gravimetric analysis, taking the change in mass and dividing by the total surface area to give an average distribution of ligand which ranged from 0.01 molecules nm^{-2} (sparsely covered surface) to 3.1 molecules nm^{-2} (near maximum achievable loading accessible by this technique).¹³ Sparsely covered substrates presumably contain island domains rather than complete surface coverage due to the limited chlorosilane present in the reaction mixture.

A comparison of 1,4-BMMB physisorbed onto native MCM-41 *versus* the phenyl modified support (phenyl-SAMMS) containing chemisorbed 1,4-BMMB at two different ligand loading levels revealed a significantly different burn off rate by TGA after the initial water desorption.¹⁴ The result is a relatively rapid weight loss starting around 235 °C and ending near 255 °C (Fig. 2, dashed lines) for the physisorbed ligand. 1,4-BMMB ligand desorption from the phenyl monolayer stabilized silica occurs at a slightly elevated temperature compared to the non-stabilized silica and continues over roughly 200 °C to around 350 °C, verified by the continued detection of SO^+ (47.9 m/z) and SO_2^+ (63.8 m/z) by mass spectrometry.¹⁵ The loss of the phenyl monolayer was observed above 350 °C and continued to 600 °C, also monitored by EI-MS with ions detected at 49.9, 50.8, 51.8 and 78.2 m/z which correspond to C_6H_6^+ fragmentation typical of this type of mass analyzer. The extended burn off range of 1,4-BMMB can be accounted for by an increase in stabilization of the chemisorbed arylthiol ligands afforded by the weak, reversible interactions between phenyl monolayer and adsorbed ligand. Benzylmercaptan (BM) was also found to be stabilized by the phenyl monolayer as indicated by TGA (data not shown) however, a strong, thiol odor emanated from this material making it unsuitable for use in filtration applications. Additionally, uptake levels for BM were less than that of 1,3- and 1,4-BMMB as expected due to the presence of a single thiol group. FT-IR provided useful analysis of the surface makeup by comparing relative intensities of prominent peaks between samples. The thiol S–H and C–S stretching, 2545 and 669 cm^{-1} , respectively, was normalized to the aryl C–H (2926 and 698) and C=C (1595, 1512 and 1431 cm^{-1}) stretching to verify loading of both monolayer and adsorbed ligand. Chemisorbed 1,4-BMMB sorbent material with bound Pb^{2+} or Hg^{2+} lacked any S–H stretching as expected. In addition, powder XRD revealed a dominant (100) peak at 2.11° but lacked higher angle peaks for all substrates. It has been reported that a decrease in peak intensity is directly related to the extent of modification of the pore with organics. We observed a similar decrease in the (100) peak intensity consistent with the chemisorption of 1,4-BMMB on to phenyl-SAMMS.¹⁶ A plot of $\log K_d$ values for phenyl-SAMMS loaded at 3.1 molecules nm^{-2} containing chemisorbed 1,4-BMMB loaded at either 2 : 1 (low) or 1 : 1 (high) shows similar capture levels with the covalently attached thiol-SAMMS in Hanford well water matrix spiked with 500 ppb Hg^{2+} , Pb^{2+} , Cd^{2+} , and Ag^+ ions (Fig. 3, top).¹⁷ 1,3- and 1,4-BMMB exhibited similar uptake levels at near equivalent loadings (Fig. 3, bottom), an unexpected result due to the assumed herringbone arrangement between the phenyl monolayer and the chemisorbed ligands, which

would result in at least one thiol group of 1,4-BMMB being buried in the monolayer to maximize edge to edge contacts (Fig. 4, right).¹⁹ This appears not to be the case due to the similar uptake levels between 1,3- and 1,4-BMMB with lower levels for BM containing only one reactive thiol under similar loadings. A possible explanation is that the BMMB ligands are only partially intercalated into the phenyl monolayer in an offset stacking²⁰ resulting in sufficient accessibility by the metal ions to the bulk of the thiol head groups (Fig. 4, left and middle) or that the covalently attached phenyl monolayer exists in a disordered herringbone configuration which can accommodate further π -stacking from chemisorbed arylthiol ligands.²¹ One interesting observation is that as 1,4-BMMB loading increases, uptake decreases for Hg^{2+} , Cd^{2+} , and Ag^{+} but not for Pb^{2+} . This may be due to the thiol sites becoming buried in the monolayer as loading densities increase, forcing rearrangement of the rings to maximize contacts. It is known from previous studies in our group that densely packed thiol head groups of thiol-SAMMS material are shared by the same metal ion resulting in ML_n species where $n > 1$.⁷ This desire to maximize metal–thiol contacts may manipulate the weakly bound chemisorbed ligands to adopt a more ideal geometry for binding at the various loadings investigated. In either case, the metal affinity levels of the chemisorbed BMMB phenyl-SAMMS is near equal to that of the covalently bound thiol-SAMMS, which has been shown to have affinity levels for heavy metal ions one to three orders of magnitude greater than commercially available thiol-based resins such as GT-73.²²

The effects of density of the covalently bound phenyl layer were also probed by varying the loading from 0.01 phenyl molecules nm^{-2} to as high as 3.1 molecules nm^{-2} while maintaining 1,3- and 1,4-BMMB loading levels equal to previous tests. Surprisingly, the sparsely populated phenyl-SAMMS with chemisorbed BMMB performed equal to that of material of higher phenyl monolayer density. The exact nature of the interaction between the covalently attached phenyl ring and that of chemisorbed BMMB is not well understood at this time, but the bound phenyl ring of the monolayer appears to be capable of acting as a nucleation site resulting in BMMB anchoring to the surface in a stacked or offset manner to provide a surface rich in chelation sites capable of metal ion uptake—a feature lacking with the native silica and phenyl modified support.

In conclusion, the above described materials utilize weak interactions to reversibly bind aromatic molecules containing reactive head groups capable of selective capture of toxic metal ions from aqueous matrices at levels equal to covalently bound analogs. Numerous common organic solvents were screened for use as a means to rinse the captured metal from the sorbent. Both chloroform and pentane (to a lesser extent) were capable of removing Hg complexes resulting in regeneration of pristine phenyl-SAMMS. The ability to refresh or replace the surfaces of highly engineered sorbent support structures, such as mesoporous silica, could significantly increase the range of viable applications for these materials. These studies are ongoing with the potential outcome of producing regenerable filter media.

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Notes and references

1. Shannon MA, Bohn PW, Elimelech M, Georgiadis JG, Marinas BJ, Mayes AM. *Nature* 2008;452:301–310. [PubMed: 18354474]
2. Hightower M, Pierce SA. *Nature* 2008;452:285–286. [PubMed: 18354460]

3. Dermont G, Bergeron M, Mercier G, Richer-Lafleche M. J. Hazard. Mater 2008;152:1–31. [PubMed: 18036735]
4. For representative examples of a variety of regenerable materials, see: a Kantipuly C, Katragadda S, Chow A, Gesser HD. Talanta 1990;37:491–517. [PubMed: 18964972]; b Yordanov AT, Roundhill DM. Coord. Chem. Rev 1998;170:93–124.; c Baumann TF, Reynolds JG, Fox GA. React. Funct. Polym 2000;44:111–120.; d Xu ZY, Zhang QX, Fang HHP. Crit. Rev. Environ. Sci. Technol 2003;33:363–389.
5. Walcarius A, Delacote C. Anal. Chim. Acta 2005;547:3–13.
6. a Pitt MA, Johnson DW. Chem. Soc. Rev 2007;36:1441–1453. [PubMed: 17660877] b Carter TG, Vickaryous WJ, Cangelosi VM, Johnson DW. Comments Inorg. Chem 2007;28:97–122. c Yantasee W, Hongsirakarn K, Warner CL, Choi D, Sangvanich T, Toloczko MB, Warner MG, Fryxell GE, Addleman RS, Timchalk C. Analyst 2008;133:348–355. [PubMed: 18299749] d Yantasee W, Warner CL, Sangvanich T, Addleman RS, Carter TG, Wiacek RJ, Fryxell GE, Timchalk C, Warner MG. Environ. Sci. Technol 2007;41:5114–5119. [PubMed: 17711232]
7. Fryxell GE, Mattigod SV, Lin YH, Wu H, Fiskum S, Parker K, Zheng F, Yantasee W, Zemanian TS, Addleman RS, Liu J, Kemner K, Kelly S, Feng XD. J. Mater. Chem 2007;17:2863–2874.
8. a Fryxell GE, Liu J, Hauser TA, Nie Z, Ferris KF, Mattigod S, Gong M, Hallen RT. Chem. Mater 1999;11:2148–2154. b Fryxell GE, Lin Y, Fiskum S, Birnbaum JC, Wu H. Environ. Sci. Technol 2005;39:1324–1331. [PubMed: 15787373]
9. Feng X, Fryxell GE, Wang L-Q, Kim AY, Liu J, Kemner KM. Science 1997;276:923–926.
10. a Kresge CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS. Nature 1992;359:710–712. b Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CT-W, Olson DH, Sheppard EW, McCullen SB, Higgins JB, Schlenker JL. J. Am. Chem. Soc 1992;114:10834–10842.
11. MCM-41 was first dispersed in toluene by stirring. Water was added, resulting in immediate flocculation of the silica followed by dispersal over 2–3 h of stirring. Trichlorophenylsilane was then added and stirred overnight. The resulting solution was translucent in appearance. Isopropyl alcohol (IPA) was added and the solid filtered, washed with IPA and vacuum dried in an oven at 40 °C.
12. Wasserman SR, Whitesides GM, Tidswell IM, Ocko BM, Pershan PS, Axe JD. J. Am. Chem. Soc 1989;111:5852–5861.
13. Gravimetric analysis was determined by simple mass subtraction of the silanated silica versus the starting mass and by use of a TA Instruments 2950 TGA coupled to an electron impact (EI) Balzers ThermoStar mass spectrometer at a ramp rate of 2° min⁻¹ up to 600 °C and capillary temperature of 100 °C.
14. Phenyl-SAMMS was added to a solution of BM, 1,3-BMMB or 1,4-BMMB dissolved in dichloromethane in a sealed vessel, placed on an orbital shaker and mixed overnight. After mixing, the vessel was uncapped and the solvent was evaporated followed by overnight vacuum drying at 40 °C. Chemisorbed ligand loadings are equal to either 2 : 1 or 1 : 1 phenyl moieties of the functionalized silica to BMMB molecules and are designated as low or high loading, respectively.
15. Degradation and oxidation of 1,4-BMMB occurred due to trace levels of oxygen contamination present in the TGA purge gas resulting in the observation of a large carbon dioxide peak.
16. Yoshitake H, Yokoi T, Tatsumi T. Chem. Mater 2002;14:4603–4610.
17. Metal uptake studies were carried out using filtered groundwater from Hanford, Washington, doped with 500 ppb target metal. pH was adjusted with HNO₃ and contact times were 2 h. The sorbent was preconditioned with a few microlitres of alcohol to enable effective surface wetting. Uptake values are reported as the distribution coefficient (K_d), which is the mass-weighted partition coefficient between the sorbent material and matrix. Under trace level analysis such as this work, K_d is a more relevant value to gauge ion capture rather than mg g⁻¹ (metal ion to sorbent), which is typically used under saturation conditions.
18. All analyses performed in either duplicate or triplicate with variances greater than 10% discarded.
19. Chang S-C, Chao I, Tao Y-T. J. Am. Chem. Soc 1994;116:6792–6805.
20. Hunter CA, Sanders JKM. J. Am. Chem. Soc 1990;112:5525–5534.
21. a Jung HH, Do Won Y, Shin S, Kim K. Langmuir 1999;15:1147–1154. b Sabatani E, Cohenboulakia J, Bruening M, Rubinstein I. Langmuir 1993;9:2974–2981.
22. Chen XB, Feng XD, Liu J, Fryxell GE, Gong ML. Sep. Sci. Technol 1999;34:1121–1132.

Fig. 1.
(top) Graphical representation of organothiol ligands benzylmercaptan (BM), 1,3-bis(mercaptomethyl)benzene (1,3-BMMB), and 1,4-bis(mercaptomethyl)benzene (1,4-BMMB),
(bottom) cartoon representation of functionalized mesoporous silica monolayer (blue disks) and chemisorbed ligands (red disk) in idealized herringbone (left) and offset (right) orientations.

Fig. 2. TGA comparison of various chemisorbed loading densities of 1,4-BMMB on phenyl functionalized MCM-41 (solid lines) *versus* physisorbed 1,4-BMMB on native MCM-41 silica (dashed lines).

Fig. 3.
 $\log K_d$ values of thiol-SAMMS *versus* 1–4-BMMB at two different loading levels (top).
Comparison of 1,3- and 1,4-BMMB at similar loading levels (bottom) in Hanford well water.
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Fig. 4. An idealized model showing possible orientations of the chemisorbed ligands onto the phenyl monolayer with both thiols accessible (left and middle) and 1,4-BMMB with one thiol buried (right).