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Copper(II) Coordination to Ligands Immobilized on Photoluminescent Porous Silicon

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Increased preorganization can be achieved by immobilizing ligands on solid supports. Photoluminescent porous silicon, which can undergo facile hydrosilylation, was used as a support for open chain neutral N- and O-donor ligands. The abilities of these ligands to bind the divalent metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} are examined. Immobilized ligands selectively complexed Cu(II) over the other metal ions studied. Ligands immobilized on photoluminescent porous silicon also removed a significant amount, up to 98%, of Cu(II) from copper(II)-spiked, organic-rich, seawater samples.

Introduction

Potentially toxic metal ions in wastewater streams can be introduced into aquatic environments and have harmful effects on people, plants, and animals. Consequently, the removal of these metals to levels below generally accepted water quality criteria is an important issue for industrial, military, or municipal entities that produce such wastewaters. Current methods of metal ion removal from aqueous systems include flocculation, precipitation, evaporative recovery, ion exchange, membrane separation, and reductive electrolysis.[1] These methods are all effective at removing bulk metal ions; however, they are not designed for the *selective* removal of specific target metal ions.

Typical wastewaters contain a mixture of environmentally benign metal ions, essential metal ions, and toxic metal ions. It is desirable to remove only the toxic metal ions, leaving essential and benign metal ions in solution. Moreover, concentrations of benign alkali metal and alkaline earth metal ions may be several orders of magnitude higher than those of potentially toxic transition metal ions. Consequently, a ligand-based system may be easily saturated with benign metal ions prior to toxic metal ion coordination. To use a ligand-based metal ion removal system in complicated aqueous matrixes, it is essential to construct the ligand so it is highly selective toward a particular set of toxic metal ions. In this study we concentrate on copper(II) since it is known to be toxic and water quality criteria for copper(II) are in the range of 2.9−4.8 ppb.[2,3]

In aqueous solutions metal ions are typically found as aquo or aquo/hydroxo ions.[4] Prior to ligand binding, waters of hydration must be removed from the metal, which costs energy. Any conformational change that the ligand must undergo prior to binding to the metal ion also costs energy. To minimize the energy penalty to bring the ligand into the correct conformation for binding to a metal ion, the ligand should be designed so that the number, nature, and three-dimensional orientation of donor atoms are matched as closely as possible to the metal ion. This structural design of ligand is referred to as multijuxtapositional fixedness,[5] preorganization,[6] prestraining,[7] predisposition,[8] and pre-

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(1) Förstner, U.; Wittmann, G. T. W. *Metal Pollution in the Aquatic Environment*; Springer-Verlag: New York, 1979.

(2) U.S. EPA: *Ambient Water Quality Criteria for Copper*; U.S. Environmental Protection Agency: Washington, DC, 1984; EPA-440/5-84-031.

(3) U.S. EPA: *Ambient Water Quality Critera-Saltwater Copper Addendum (Draft)*; U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology: Washington, DC, 1985; EPA-NTRREV-MET.

(4) Martell, A. E.; Hancock, R. D. *Metal Complexes in Aqueous Solutions*; Plenum: New York, 1996.

(5) Busch, D. H.; Farmery, K.; Goedken, V.; Katovic, V.; Melnyk, A. C.; Sperati, C. R.; Tokel, N. *Adv. Chem. Ser.* **1971**, *No. 100*, 44.

(6) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Brown, S. B.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 3645−3657.

(7) McDougall, G. J.; Hancock, R. D.; Boeyens, J. C. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1438−1444.

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orientation.[9] These principles have the central goal of designing a ligand so that the number of donor atoms, nature of donor atoms, and conformation of ligand are as closely matched as possible to the structure that exists when the ligand is bound to the target metal ion.

Immobilized ligands have the major advantage of convenience in wastewater treatment since the separation of the metal−ligand complex is trivial. However, one problem associated with immobilizing a small molecule on a solid support is characterization of the supported species. Chosen wisely, the particular support can be utilized for other functions, such as metal ion sensing.[10−13] Work from the Buriak, Sailor, and Canham laboratories, most notably, has clearly demonstrated that photoluminescent porous silicon is an attractive support for ligands.[14−16]

Photoluminescent porous silicon is a hydride-terminated silicon surface that undergoes facile white light and Lewis acid mediated hydrosilylation under ambient conditions.[12−14,17−25] Moreover, the hydrosilylation reactions are analogous to those of tris(trimethylsilyl)silane, $(SiMe_3)_3$-SiH.[23,26] Buriak characterized the hydrosilylation products, $(SiMe_3)_3SiR$, and found spectroscopic similarities with the same species, R, bound to photoluminescent porous silicon.[14,18] Therefore, $(SiMe_3)_3SiH$ is a good model for the hydride-terminated silicon surface.

Formation of the hydride-terminated, photoluminescent porous silicon surface is relatively straightforward with cell designs found in the literature.[15,25,27] Presence of the surface is confirmed by a bright orange glow under UV radiation and characteristic Si−H stretch at 2100 cm^{-1} and bend at 665 cm^{-1} in attenuated total reflectance (ATR) IR spectra of the surface.[12,20,21,23,28] White light mediated hydrosilylation with terminal alkenes and alkynes is achieved with a 100 W desk lamp and the neat ligand. Hydrosilylation is confirmed by the absence of a C=C or C≡C stretch in the ATR spectrum of the surface.[14]

In this paper, we report the addition of N- and O-donor monodentate and chelating ligands to photoluminescent porous silicon and test their ability to bind the divalent metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} in aqueous solutions.

Methods

Flame atomic absorption spectroscopy (FAAS) was performed on a Perkin-Elmer 3110 instrument using hollow cathode lamps. Absorbances for Cu^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} were monitored at the 216.5, 352.5, 213.9, and 283.3 nm lines, respectively. Slit widths were 0.2 nm for Ni^{2+} and Cu^{2+} analyses and 0.7 for Pb^{2+} and Zn^{2+}. Scanning electron microscopy was performed on a Philips XL 30S FEG SEM instrument operating at 2 keV with a spot size of 1, a working distance of 3 mm, and under 7.7×10^{-6} Torr. ATR IR spectra were recorded on a Nicolet Nexus 670 FTIR with an InspectIR attachment containing a silicon crystal. Standard 1000 ± 1% ppm metal ion solutions in 2% or 5% HNO_3 were obtained from Fisher and diluted to the target concentration of about 10 ppm. Concentrations of the final standard solutions were determined by FAAS using standard curves for each metal.

The overall experimental methodology involved four steps: (i) preparation of photoluminescent porous silicon by electrochemically etching a p-doped silicon (100) surface with a 1:1 solution of 48% aqueous HF in ethanol; (ii) attachment of ligands to the surface by means of white light mediated hydrosilylation; (iii) confirmation of ligand binding with ATR IR spectroscopy; (iv) determination of the amount of metal ion bound to the ligand on the surface by FAAS.

Electrochemical Etching. Silicon wafers (n-type, p-doped silicon (100) surface with a resistivity of 0.0700−0.1500 Ω·cm and a thickness of 525 μm) were obtained from Mitsubishi Silicon America. All ligands were obtained from commercial sources and used without further purification. The Teflon etching cell was constructed according to the designs in the literature, with a 1.5 × 8 × 6.5 cm piece of Teflon screwed to a metal backing with Teflon nuts and washers.[25,27] The silicon wafer was placed on an aluminum cathode in the Teflon etching cell. A platinum anode was placed in the solution above the wafer in the cell and a 1:1 solution of 48% aqueous HF in ethanol added. Current with a density of 82 mA/cm^2 was passed through the wafer for 9.5 min after which the HF was replaced. Once the fresh HF solution was added, the current density was reduced to 9.1 mA/cm^2 for the remaining 8.5 min. The presence of photoluminescence on the surface was confirmed by orange illumination under UV light.

Hydrosilylation. All the ligands utilized in this study are shown in Figure 1.

To achieve hydrosilylation, the neat ligand (100 μL) was placed directly on the silicon wafer and allowed to stand under a 100 W desk lamp for between 1 (for a terminal C≡C ligand) and 12 h (for a terminal C=C ligand).[20,23] After illumination, the surface was washed with chloroform to remove any excess ligand and dried under a stream of argon. An ATR IR spectrum of the final silicon surface was recorded and ligand binding was confirmed by noting the absence of the C=C or C≡C stretch in the ligand.

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(8) Stack, T. D. P.; Hou, Z.; Raymond, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 6466.
(9) Anicini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. J. *J. Chem. Soc., Dalton Trans.* **1978**, 578.
(10) Janshoff, A.; Dancil, K.-P. S.; Steinem, C.; Greinder, D. P.; Lin, V. S.-Y.; Gutner, C.; Motesharei, K.; Sailor, M. J.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 12108−12116.
(11) Lin, V. S.-Y.; Motesharei, K.; Dancil, K.-P. S.; Sailor, M. J.; Ghadiri, M. R. *Science* **1997**, *278*, 840−843.
(12) Buriak, J. M. *Chem. Commun.* **1999**, 1051−1060.
(13) Stewart, M. P.; Buriak, J. M. *Adv. Mater.* **2000**, *12*, 859−869.
(14) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271−1308.
(15) Canham, L. T. *Properties of porous silicon*; Inspec: London, 1997.
(16) Green, W. H.; Letant, S.; Sailor, M. J. In *Electrochemistry of Nanomaterials*; Hodes, G., Ed.; Wiley-VCH Verlag: Weinheim, Germany, 2001; pp 141−167.
(17) Holland, J. M.; Stewart, M. P.; Allen, M. J.; Buriak, J. M. *J. Solid State Chem.* **1999**, *147*, 251−258.
(18) Schmeltzer, J. M.; Porter, L. A., Jr.; Stewart, M. P.; Buriak, J. M. *Langmuir* **2002**, *18*, 2971−2974.
(19) Buriak, J. M. *J. Lumin.* **1999**, *80*, 29−35.
(20) Stewart, M. P.; Buriak, J. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3257−3260.
(21) Buriak, J. M.; Stewart, M. P.; Geders, T. W.; Allen, M. J.; Choi, H. C.; Smith, J.; Raftery, D.; Canham, L. T. *J. Am. Chem. Soc.* **1999**, *121*, 11491−11502.
(22) Buriak, J. M. *Adv. Mater.* **1999**, *11*, 265−267.
(23) Buriak, J. M.; Allen, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 1339−1340.
(24) Stewart, M. P.; Buriak, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 7821−7830.
(25) Sailor, M. J.; Lee, E. J. *Adv. Mater.* **1997**, *9*, 783−793.
(26) Kopping, B.; Chatgilialoglu, C.; Zehnder, M.; Giese, B. *J. Org. Chem.* **1992**, *57*, 3994−4000.
(27) Halimaoui, A. In *Properties of Porous Silicon*; Canham, L., Ed.; INSPEC IEE: Exeter, U.K., 1997; pp 12−22.
(28) Xu, D.; Guo, G.; Gui, L.; Tang, Y.; Zhang, B. R.; Qin, G. G. *J. Phys. Chem. B* **1999**, *103*, 5468−5471.

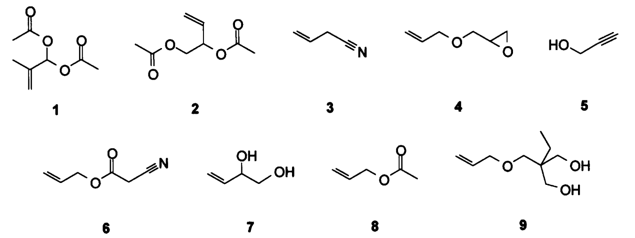

Figure 1. Ligands attached to photoluminescent porous silicon through white light mediated hydrosilylation used in this study. All the ligands are liquids and contain a terminal $C{=}C$ or $C{\equiv}C$ bond, which enables facile hydrosilylation reactions.

Metal Ion Binding to Immobilized Ligands. To determine the amount of metal ion bound to the ligand supported on the photoluminescent porous silicon surface, four solutions were prepared: (i) a blank with 10.0 mL of a 10.0 ppm standard metal ion solution; (ii) a silicon chip *that has not been etched* with 10.0 mL of a 10.0 ppm standard metal ion solution; (iii) a photoluminescent porous silicon chip *without an immobilized ligand* and 10.0 mL of a 10.0 ppm standard metal ion solution; (iv) the immobilized ligand on a photoluminescent silicon support in 10.0 mL of a 10.0 ppm standard metal ion solution.

Solutions were placed on a shaking table in closed, acid-washed, high-density polyethylene (HDPE) containers for various amounts of time (24 h to 10 days). Subsequently, the solutions were analyzed with FAAS. All solutions were unbuffered and had pH values of ca. 6.7.

Results and Discussion

Ligand Immobilization. Buriak demonstrated that small molecules terminating in $C{=}C$ or $C{\equiv}C$ functionalities rapidly undergo hydrosilylation on photoluminescent porous silicon.[14] Even though the mechanism of hydrosilylation is uncertain, Buriak demonstrated that the terminal $C{\equiv}C$ is more active than the terminal $C{=}C$, which results in significantly shorter reaction times with alkynes than alkenes.[18,24]

Buriak further demonstrated that tris(trimethylsilyl)silane, $(SiMe_3)_3Si{-}H$, undergoes analogous hydrosilylation chemistry to the photoluminescent porous silicon surface.[14] The presence of the silicon hydride terminated surface was confirmed by the Si−H bend at 665 cm^{-1} in the ATR spectrum of the surface. The presence of photoluminescence is also confirmed by the bright orange glow of the surface under UV light. The instrumentation available limited us to a spectral range of 3000−1000 cm^{-1}; therefore, we confirmed the presence of the hydride surface by photoluminescence and an Si−H peak at 2085 cm^{-1}. Since many species show a peak centered at 2100 cm^{-1}, this peak alone is not diagnostic for the presence of Si−H when ligands are bonded to the surface. However, in the case of allyl acetate, there are no peaks between 2946 and 1745 cm^{-1} in the FTIR spectrum of the neat ligand, but there is a strong Si−H stretch at 2120 cm^{-1} in the ATR spectrum of the immobilized ligand. In all cases, the FTIR spectra of free ligands and ATR IR spectra of immobilized ligands show evidence of the appropriate functional groups. There is no spectroscopic evidence (very strong peak at 1093 cm^{-1}) for any oxidation of the silicon surface either during etching or during hydrosilylation.

When allyl cyanide, **3**, is bonded to the silicon surface, the $C{\equiv}N$ stretch at 2300−2100 cm^{-1} is noted in the ATR spectrum of the final product but the $C{\equiv}C$ stretch (2200−2100 cm^{-1}) of the free ligand is substantially reduced. It is possible that some free ligand is trapped in the pores of the photoluminescent porous silicon, which would account for the small peak between 2200 and 2100 cm^{-1} in the ATR spectrum of the modified surface. Similarly, the carbonyl containing ligands all show the presence of a $C{=}O$ peak in the ATR spectrum of the immobilized ligand around 1850−1750 cm^{-1} but a severe reduction in the $C{=}C$ peak around 1500−1400 cm^{-1}. As anticipated, the ligands listed in Figure 1 all bind through the terminal $C{\equiv}C$ or $C{=}C$ functionalities rather than $C{\equiv}N$ or $C{=}O$.

Further confirmation of ligand binding to the photoluminescent porous silicon surface was obtained using scanning electron microscopy (SEM). SEM photomicrographs of the silicon (100) surface are shown in Figure 2; the tetrahedral geometry about the silicon atoms is clearly evident at both 100 and 50 μm.

SEM experiments confirmed both ligand binding and the presence of varying pore sizes of the photoluminescent porous silicon. In Figure 3, at 80 000× magnification, the pores of the photoluminescent porous silicon are clearly noted. Pore sizes are estimated to be between 8 and 92 nm, which is in agreement with literature.[29] In addition, there is clearly a morphological difference between the surface without bound ligand and the surface with bound ligand. Since the SEM experiment uses ultrahigh vacuum, 7.7×10^{-6} Torr, any adsorbed free ligand is unlikely to remain on the surface. Also evident in Figure 3 are the small and large pores of the photoluminescent porous silicon. In Figure 4, the presence of the bound organic ligand stacked up on the surface is clearly evident.

To our knowledge, there are no reports in the literature on immobilization of ligands on photoluminescent silicon followed by subsequent binding of metal ions.[14] Depending on ligand loading and morphology of the silicon surface, several possibilities for metal ion chelation are feasible. For example, when propargyl alcohol, **5**, is bound to the surface, it is possible for two (or more) ligands to coordinate the same metal ion (Figure 5).

Metal Ion Binding to Ligands Immobilized on Photoluminescent Porous Silicon. Since such small quantities of materials were used, nondestructive determination of the amount of ligand immobilized on the photoluminescent porous silicon proved intractable. Prior to determining the amount of metal ion bound by the ligand immobilized on the photoluminescent silicon surface, the ability of both silicon wafers and photoluminescent silicon without ligand to bind metal ions needed to be determined. The photoluminescent silicon removed between 0 and 46% of all metal ions from solution. However, it is likely the metal ion is either physisorbed onto the silicon surface or trapped in the pores on the porous photoluminescent silicon. In several

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(29) Hérino, R. In *Properties of Porous Silicon*; Canham, L., Ed.; INSPEC IEE: Exeter, U.K., 1997; pp 89−96.

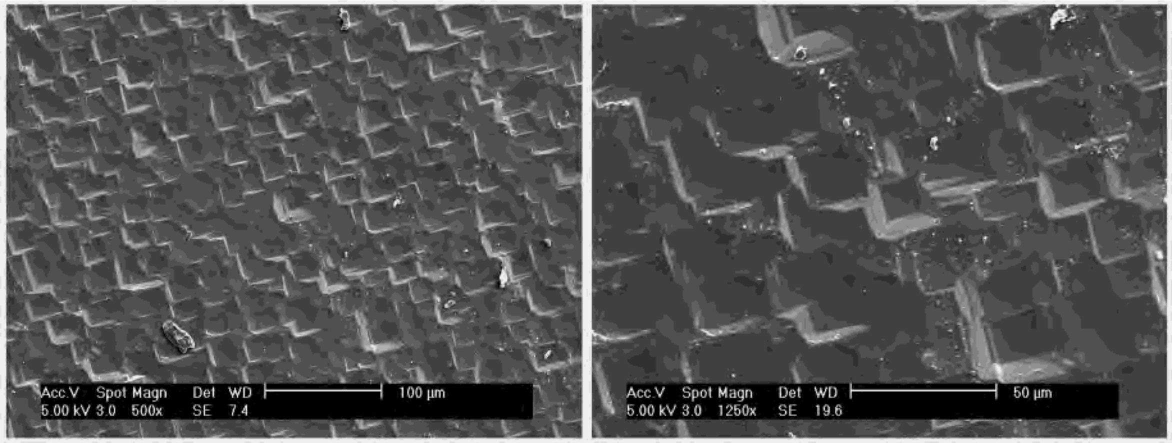

Figure 2. Scanning electron microscopy photomicrographs of the silicon (100) surface used in this study. The micrograph on the left is at 100 μm magnification, and the one on the right, at 50 μm.

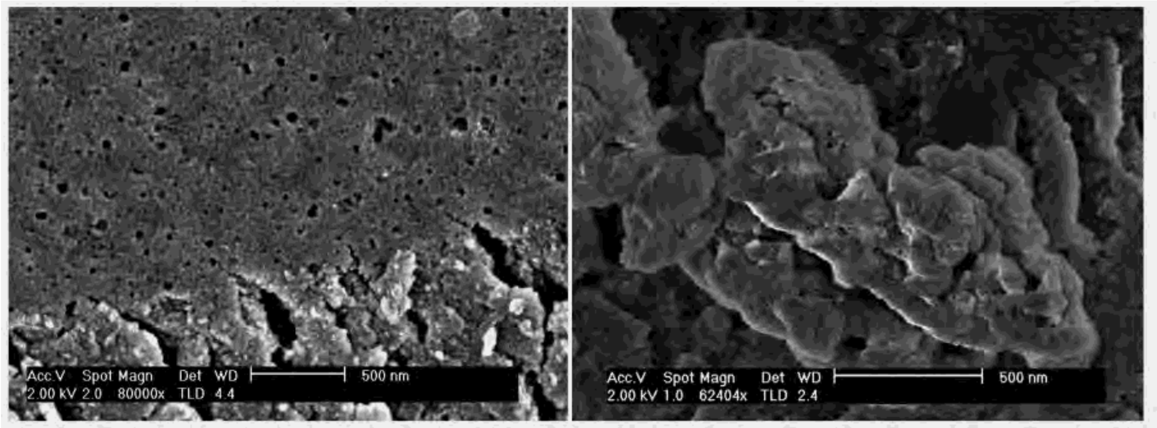

Figure 3. Scanning electron microscopy photomicrographs of the photoluminescent porous silicon surface (left) and trimethylolpropane monoallyl ether immobilized on photoluminescent porous silicon surface (right) at 500 nm magnification.

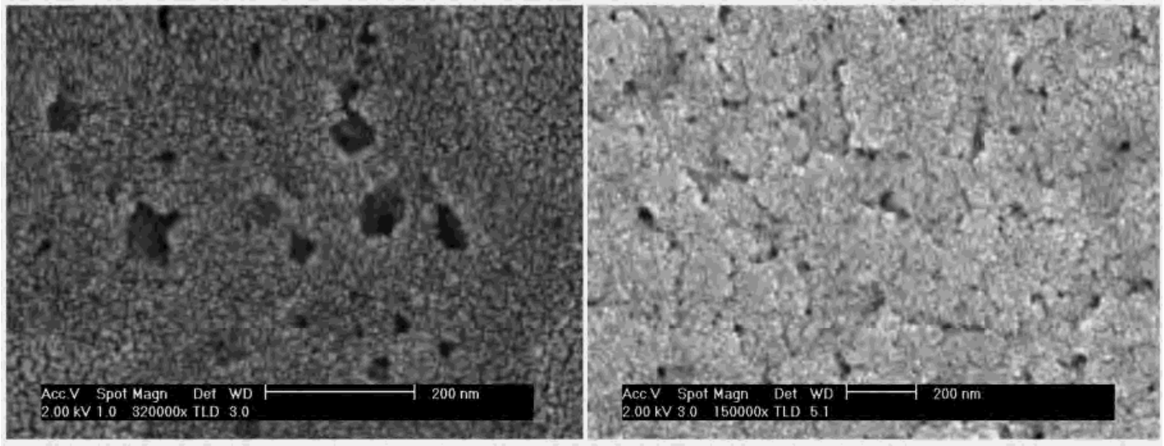

Figure 4. Scanning electron microscopy photomicrographs of the photoluminescent porous silicon surface (left) and trimethylolpropane monoallyl ether immobilized on photoluminescent porous silicon surface (right) at 200 nm magnification.

cases, ligands bound to the surface bind more metal from solution than the photoluminescent porous silicon (Table 1). Since the ATR results indicated that ligands are chemically bound to the surface through Si−C bonds, we conclude that the metal ion is coordinated to the ligand on the surface rather then being physi- or chemisorbed to the modified photoluminescent porous silicon surface.

Single Metal Ion Studies. Since it is impossible to determine directly how much metal ion is bound to the immobilized ligand in the small quantities of material used in this study, FAAS was used to determine the amount of metal ion remaining in solution. In the first set of reactions, we determined the amount of metal ion remaining in solution after a silicon wafer with immobilized ligand was placed in a standard metal ion solution for 24 h. Four individual metal ions were utilized: Pb^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+} (Table 1).

Three of the four metal ions studied, Pb^{2+}, Zn^{2+}, and Ni^{2+}, showed a very modest amount of metal ion binding to the

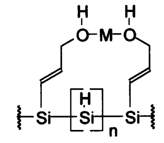

Figure 5. Chelation of one metal ion by two ligands that occupy close positions on the photoluminescent porous silicon surface.

Table 1. Residual Concentrations (in ppm) and Percent Metal Ion Bound to the Immobilized Ligands from 12 ppm Standard Nickel(II), 12 ppm Standard Copper(II), 10 ppm Standard Zinc(II), and 11 ppm Standard Lead(II) Solutions

	residual concn				% metal ion bound			
ligand	Ni^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}
1	12	5.2	10	10	0	57	0	5.0
2	12	6.1	9.9	10	0	49	1.1	5.0
3	12	11	9.9	10	0	8.3	1.1	5.0
4	12	11	9.5	10	0	8.3	4.7	5.0
5	12	5.8	9.5	10	0	52	4.7	5.0
6	12	11	9.5	10	0	8.3	4.7	5.0
7	11	9.7	9.5	9.8	8.0	19	4.7	7.0
8	11	7.7	9.5	10	8.0	35	4.7	5.0
9	11	6.1	9.5	10	8.0	49	4.7	5.0

immobilized ligands (up to 8% across the series of ligands studied; Table 1). It is important to note that the precision of the FAAS instrument is about 5% and there are only two significant figures in absorbance readings. It is possible that a concentration of metal ion remaining in solution appears, within experimental error, to be higher than that added originally. Under these circumstances, we conclude that no metal ion was complexed by the immobilized ligand.

Copper(II) showed a significantly greater amount of ion complexation to the immobilized ligands (8.3−57%; Table 1). From these results, the ligands immobilized on photoluminescent porous silicon in this study show selective copper(II) complexation over the other metal ions considered. This result is important since copper(II) is a known contaminant in natural and wastewaters.

Lead(II) is known to exhibit very slow kinetics, so it is possible that the reaction times were too short for the solution to come to equilibrium (see below).[30−32] Hancock demonstrated that lead(II) has a high affinity for N-donor macrocycles, and most of the ligands reported in this study contain O-donors.[33,34] Therefore, we expect all the ligands in this study to have a low affinity for Pb^{2+}, which was observed.

Hancock proposed a series of ligand design rules that take into account the principles of preorganization.[6] In these rules, Hancock notes that five-membered chelate rings are selective toward *large metal ions* whereas six-membered chelate rings are selective toward *small metal ions*. Since the hard−soft acid−base properties of these ligands are all similar,[35] and the ionic radii are different with lead(II) being much larger than the other two metal ions,[36] we can use Hancock's principles of ligand design to gain some insight into the coordination chemistry on the surface.

Allyl glycidyl ether, **4**, is an epoxide in the free-state, which will open in aqueous solution to form an alcohol. During hydrosilylation the neat ligand was placed directly on the silicon surface and then an ATR IR spectrum was recorded. To determine whether the atmospheric water in the laboratory is sufficient to open the epoxide, 250 μL of the ligand was left in an open container for 24 h and an IR spectrum recorded which shows a clear peak due to OH stretch at 3368 cm^{-1}. Therefore, we conclude that the aqueous metal ion solution will certainly cause the formation of the alcohol. The presence of the alcohol in the immobilized ligand is evidenced by an OH stretch at 3400 cm^{-1} in the ATR IR spectrum. The primary alcohol analogue of **4** has the potential to form a six-membered chelate ring, which should show selectivity toward zinc(II) over lead(II).

Allyl cyanoacetate, **6**, can form a six-membered chelate ring by binding through the carbonyl oxygen and terminal nitrogen atoms. Immobilized allyl cyanoacetate should show moderate selectivity toward zinc(II) over lead(II) and nickel(II) (Table 1). However, the small quantities of nickel(II), zinc(II), and lead(II) do not allow us to definitively confirm these anticipated binding selectivities. However, immobilized ligands **3**, **4**, and **6** show the lowest affinity toward copper(II) (Table 1).

Care must be taken in comparing metal ion complexation by a given immobilized ligand for different sets of experiments because there is no guarantee that the morphology of the silicon surface is the same between runs. Therefore, it is possible that ligand loadings are different between runs.

Copper(II) is known to form very stable complexes with many different ligands,[4] so it is not surprising that Cu^{2+} is bound best by all ligands studied (Table 1). One possible reason for the enhanced stability of the copper(II) complexes on the surface resides in the Jahn−Teller distortion. The Cambridge Crystallographic Database was searched for all high-quality ($R < 10\%$), monomeric complexes with no reported crystallographic disorder and no reported errors, which yielded 129 structures containing six Cu−O bonds.[37] All structures that contained Cu−O bonds outside of three standard deviations of the mean were rejected. The average basal Cu−O distance is 2.01 ± 0.10 Å ($n = 195$) and axial Cu−O distance is 2.36 ± 0.12 Å ($n = 195$). In addition, the Jahn−Teller distortion in Cu^{2+} halides shows axial bond elongation from 0.34 to 0.78 Å,[36] so the Cu^{2+} ion exhibits sufficient bond distance flexibility so that it can potentially bind two donor atoms on adjacent walls of a pore. Also, the axial ligand elongation in copper(II) complexes is known to accelerate Cu^{2+} ligand substitution kinetics.[30−32] Therefore, the extent of copper(II) binding to the ligands on the photoluminescent porous silicon can be attributed to these two phenomena.

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(30) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*, 2nd ed.; Wiley: New York, 1997.

(31) Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanisms*; Longman: Essex, U.K., 1999.

(32) Jordan, R. B. *Reaction Mechanisms of Inorganic and Organometallic Systems*, 2nd ed.; Oxford University Press: New York, 1998.

(33) Carlton, L.; Hancock, R. D.; Maumela, H.; Wainwright, K. P. *J. Chem. Soc., Chem. Commun.* **1994**, 1007−1008.

(34) Maumela, H.; Hancock, R. D.; Carlton, L.; Reibenspies, J.; Wainwright, K. P. *J. Am. Chem. Soc.* **1995**, *117*, 6698−6707.

(35) Martell, A. E.; Hancock, R. D. *Metal complexes in aqueous solutions*; Plenum Press: New York, 1996.

(36) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.

(37) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31−37.

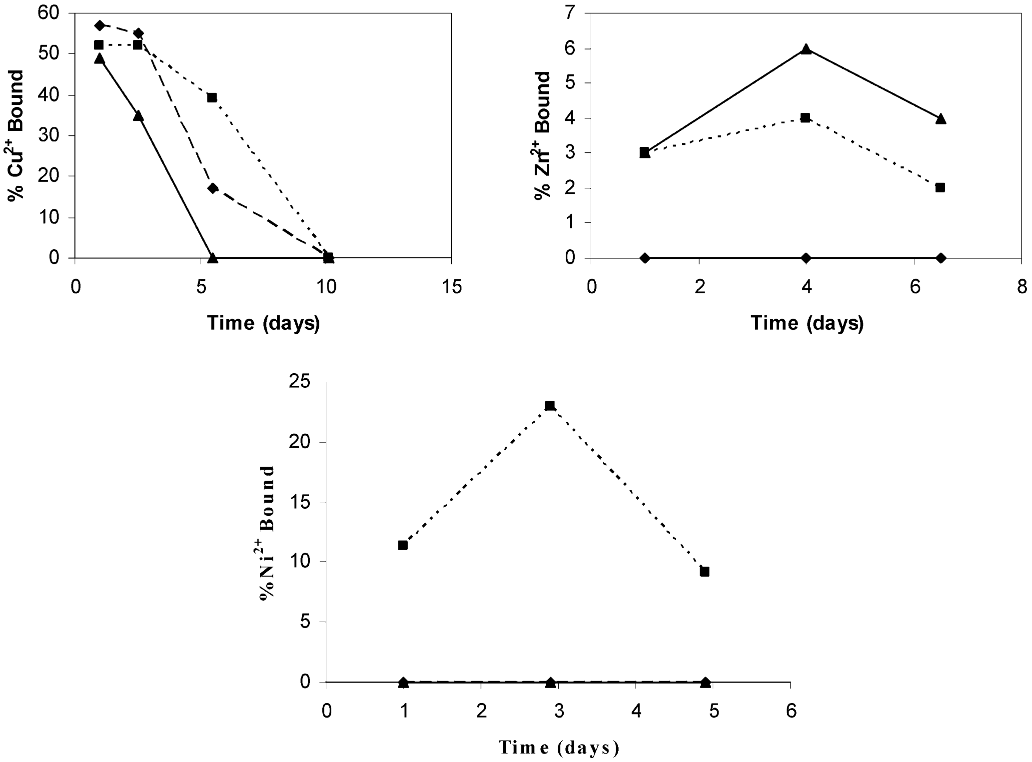

Figure 6. Plot of percent metal ion bound versus time for copper(II), zinc(II), and nickel(II) samples. The diamonds represent the data for **1**, the squares represent data for **5**, and the triangles represent data for **9** immobilized on photoluminescent porous silicon. All solutions initially contained ca. 10.0 ppm metal ion at a pH ca. 6.9.

Ligand Binding as a Function of Time. It is possible that the ability of the immobilized ligands to bind copper(II) is a kinetic phenomenon, since copper(II) is known to have a water exchange rate constant 2 orders of magnitude greater than zinc(II) and 4 orders of magnitude greater than nickel(II).[38] To test this hypothesis, silicon wafers containing immobilized ligands were placed in separate ca. 10 ppm solutions of metal ion (pH ca. 6.7), the solutions were shaken for up to 10 days, and the aqueous layer was analyzed as a function of time.

Results for copper(II) show that metal ion was released from the surface back into solution after 1−3 days, depending on the ligand (Figure 6).

Zinc(II), lead (II), and nickel(II) showed little binding onto the immobilized ligand and insignificant release back into solution (Figure 6; results not shown for lead(II)). Subsequent tests with copper(II) solutions showed that, once released, the immobilized ligand did not rebind metal ion. As expected, the lead(II) ion proved significantly less labile than the other metal ions. The inertness of lead(II), often articulated as the “inert pair effect”, is consistent with these data.

Competitive Ligand Reactions. To gauge how strongly copper(II) binds to ligands on the photoluminescent porous silicon surface, a series of competitive ligand binding experiments were performed. Two ligands were chosen which have large formation constants with copper(II): ethylenediaminetetraacetate (EDTA^{4-}; log $K_1 = 18.7$ [38]); diethylenetriaminepentaacetate (DTPA; log $K_1 = 21.1$ [39]). Solutions containing EDTA^{4-}:copper(II) ratios in the range of 0.1:1 to 10:1 were examined, whereas DTPA was used at 10:1 ligand-to-metal ratio. All solutions were at an initial pH of ca. 6.7.

At nearly all EDTA concentrations, a large fraction (typically > 60%) of copper(II) was bound preferentially to the immobilized ligands (Table 2). There was considerable variability between some ligands and EDTA concentrations, which may be attributable to the affinity of immobilized ligands for copper(II) as well as run-to-run differences in the quality and quantity of ligand immobilization on the photoluminescent silicon surface. There was significantly less copper(II) binding by the immobilized ligands in the presence of DTPA in a 10:1 ligand-to-metal ratio, with some ligands (**3**, **4**, and **6**) showing no ability to out-compete DTPA. However, a few ligands (**1**, **2**, and **9**) were still able to complex 40−50% of the metal even in the presence of the very strong competing ligand.

We also tested the ability of the immobilized ligands to bind copper(II) from natural organic-rich estuarine samples from the lower Cape Fear River estuary (CFE) and Atlantic Intracoastal Waterway (AIW) in southeastern North Carolina. These waters contain ligands with very high conditional stability constants with respect to copper(II) of log $K'_{\mathrm{cond}} > 13$ [40] (corrected for the effects of ionic strength and competing reactions).[40] Unfiltered water samples from both sites were collected off docks in acid-washed HDPE containers.

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(38) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993.

(39) Martell, A. E.; Smith, R. M. *Stability Constants*, *Supplement No. 1*, *Special publication No. 25*; Chemical Society: London, 1971.

Table 2. Concentrations (in ppm) and Percent Copper(II) Bound to the Immobilized Ligands from a Standard Copper(II) Solution with Different Competitive Ligands

	1.6×10^{-5} *M* EDTA (1.7×10^{-4} *M* Cu^{2+} std)		1.6×10^{-4} *M* EDTA (1.7×10^{-4} *M* Cu^{2+} std)		1.6×10^{-3} *M* EDTA (1.4×10^{-4} *M* Cu^{2+} std)		1.6×10^{-3} *M* DTPA (1.7×10^{-4} *M* Cu^{2+} std)	
ligand	resid concn	% bound	resid concn	% bound	resid concn	% bound	resid concn	% bound
1	0.91	92	6.3	43	3.0	66	5.8	47
2	2.7	76	3.3	75	2.6	71	6.5	41
3	0	100	8.3	24	3.0	66	12	0
4	1.8	84	11	0	7.0	23	12	0
5	2.7	75	5.4	51	2.6	71	7.7	30
6	4.5	59	9.2	17	3.5	61	12	0
7	5.5	50	3.3	70	1.7	81	9.8	11
8	0.91	92	3.3	70	0.43	95	7.3	34
9	0.91	92	4.0	64	1.7	81	6.0	45

Table 3. Concentrations (ppm) and Percent Copper(II) Bound from Copper(II)-Spiked Samples from the Cape Fear Estuary and Atlantic Intracoastal Waterway

	Cape Fear River water				Atlantic Intracoastal Waterway water	
	pH < 2.0 (4.3 ppm std Cu^{2+} soln)		pH = 3.8 (15 ppm std Cu^{2+} soln)		pH < 2.0 (11 ppm std Cu^{2+} soln)	
ligand	resid concn	% Cu^{2+} bound	resid concn	% Cu^{2+} bound	resid concn	% Cu^{2+} bound
1	0.27	74	3.2	78	9.7	12
2	0.23	95	0	100	9.1	17
3	0.77	82	8.0	45	9.7	12
4	0.92	79	1.8	88	11	0
5	0.12	97	12	19	11	0
6	0.77	82	9.4	36	11	0
7	0.12	97	0.33	98	11	0
8	0.077	98	0.33	98	11	0
9	0.15	97	2.7	82	11	0

Samples were spiked with ca. 4.3−11 ppm copper(II), and photoluminescent porous silicon wafers containing immobilized ligands were immersed in separate solutions as described previously. No adjustment was made to the pH of the solutions, which were <2 for the AIC and CFE samples. (The stock standard metal ion solutions from Fisher are all prepared in 2% or 5% nitric acid, which accounts for the low pH of the solution.) Preliminary attempts to buffer these solutions to ca. 7−8 with PIPES (piperazine-*N*,*N*′-bis(2-ethanesulfonic acid)) resulted in a clouding of the solutions containing the immobilized ligands, suggesting perhaps some type of interaction between the buffer and ligands. Consequently, we used unbuffered test solutions. Results of these experiments are shown in Table 3.

Samples from the AIC showed the expected low metal ion complexation anticipated from a very acidic environment (between 0 and 17% metal ion bound; Table 3). However, CFE samples showed remarkably high binding affinities (74−98%) even at low pH. To ensure these binding affinities were consistent, a second sample of Cape Fear River water was spiked with copper(II) at pH 3.8, which showed 19−100% binding of copper(II) to the immobilized ligands (Table 3). Moreover, these high binding affinities are observed in the extremely complicated matrix of the saline CFE, which contains many alkali metal, alkaline earth metal, and other metal ions that all compete for donor atoms on the immobilized ligands, as well as relatively strong natural dissolved ligands which compete with the immobilized ligands for copper(II). The immobilized ligands are still capable of removing a significant amount of metal ion from the natural water sample.

Copper(II) Leaching. A leaching experiment was conducted to determine if it is possible to remove copper(II) from selected immobilized ligands (**1**, **5**, and **9**) once the silicon wafers are removed from copper(II)-containing water samples. Immobilized copper(II) complexes of these ligands were placed in 10.0 mL of either HNO_3 solution (pH < 2) or water (pH 6.9−7.2), placed on a shaking table for 24 h and subsequently analyzed by FAAS. The three ligands released most metal ion at acidic pH, as expected (100% metal ion release for **1** and **5** and 62% for **9**). Encouragingly, at neutral pH **1** and **5** did not release a significant amount of copper(II) (33%) but **9** released all the bound copper(II). In a blank study, a piece of photoluminescent porous silicon with physisorbed copper(II) metal ion was placed in 10.0 mL of either HNO_3 (pH < 2) or water (pH 6.9−7.2) and released 100% of the copper(II) at acidic pH and 53% at pH 7.2. At pH < 2, **9** retains more Cu^{2+} than the blank. Similarly, at pH 7.2, **1** and **5** also retained more metal ion than the blank.

Conclusions

A number of ligands were bound to photoluminescent porous silicon by means of hydrosilylation. Ligand binding was confirmed with attenuated total reflectance FTIR spectroscopy and scanning electron microscopy. All immobilized ligands showed selective binding toward copper(II) over nickel(II), zinc(II), and lead(II). The morphology of the surface was proposed to help in metal ion coordination by creating a binding environment that is optimal for copper(II). Metal ions were demonstrated to reversibly bind to ligands immobilized on the surface. In complicated natural water matrixes, the immobilized ligands removed a substantial amount of copper(II) from the solution.

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(40) Shank, G. C.; Skrabal, S. A.; Whitehead, R. F.; Kieber, R. J. *Limnol. Oceanogr.* **2002**, to be submitted.

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