7.16–7.45 (m, 10H, ArH), 7.84 (d, 2H, $J = 8.2$ Hz, ArH); IR (CHCl$_3$): $\tilde{\nu}$ = 3200, 1360 cm^{-1}; HR-MS (C$_{26}$H$_{22}$N$_2$): calcd: 362.1770; found: 362.1766.

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Imprint Coating: A Novel Synthesis of Selective Functionalized Ordered Mesoporous Sorbents[**]

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Dedicated to Professor T. F. Williams

Polymerization of metal alkoxides in the presence of molecular assemblies of surfactants or related substances as structure directors has resulted in several novel classes of mesoporous and macroporous inorganic materials with extremely high surface areas and ordered mesostructure.[1–4] These materials have now found extensive applications as catalyst supports and chromatographic resins.[4] Recently, Feng et al.[5] and Mercier and Pinnavaia[6] have developed new, effective mesoporous sorbents based on mesoporous materials as supports for the removal of toxic metal ions. The essence of their methodology is to coat surfaces of hexagonally packed mesoporous silica with organic functional groups to enhance their affinities for the targeted metal ions. High capacities and fast kinetics have been observed for these new sorbents.[5–7] The selectivity of these materials relies solely on the affinity of the surface-coated functional ligand for a specific metal ion, with no consideration of the stereochemical interactions between the ligand and metal ion. However, the stereochemical arrangement of the ligand with respect to the targeted metal ion plays a key role in molecular recognition[8] and dative bond formation between the toxic metal ion and coordinating ligands.[5]

We have been interested in the development of sol–gel sorbent materials based upon the potential superior performance offered by molecular imprinting.[9] Herein, we describe a design strategy for imprint-coated, functionalized ordered mesoporous sorbents through surface molecular imprinting. This coating methodology allows precise control of the stereochemical arrangement of ligands on the surfaces of mesopores, which in turn optimizes the binding of a targeted metal ion.

Imprinting methods based on the template approach have been used in cross-linked polymers, as well as in silica gels, to prepare polymeric supports that possess organized solid-state

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structures.[10–12] Imprinting processes generally involve three steps:

1) selection of a target molecule as a template,
2) incorporation of the template into rigid solid networks through in situ copolymerization, and
3) removal of the template, to leave cavities with a predetermined number and arrangement of ligands that later "recognize" or selectively rebind the template or target molecule.

Imprinted materials thus prepared have been shown to combine the binding ability of specifically chosen functional groups or ligands for target molecules with the shape and size characteristics of cavities imprinted into a rigid polymer matrix by a template. Such imprinted organic polymers have been used to resolve racemates[10] and separate mixtures of metal cations.[10–12] One major drawback associated with this bulk molecular imprinting technique is that the kinetics of the sorption/desorption process are unfavorable, as the template and ligand are totally embedded in the bulk polymer matrices and the mass transfer must take place through nonpolar, microporous channels.[10] Furthermore, molecular imprinting studies have thus far all been conducted in disordered polymers or amorphous sol–gel matrices[10] where the inhomogeneity of the cavities produced by the molecular imprinting reduces the selectivity of the final imprinted materials.

In the present report these issues in molecular imprinting are addressed by development of surface imprinting[12] in ordered mesoporous materials. The functional groups are introduced onto the pore surface of mesoporous silica through imprint coating. The key to the current design is to coat the mesopore surface with complexes of the ligands and target metal ions rather than just the free ligands. After removal of the metal ions, the ligand imprints of the template metal ions are created on the mesopore surfaces. This organization reflects both the size and stereochemical signature of the template ion and ultimately should lead to future ion recognition and selective rebinding of the target ion from ion mixtures. We have found that such functionalized, ordered mesoporous materials exhibit significantly greater binding selectivities of the target ion than sorbents prepared by conventional coating methods. The success of our approach is built upon the unique environments of ordered, hexagonally packed mesopore surfaces for conducting surface imprinting. These beneficial characteristics include:

1) circularly curved, extremely rigid pore surfaces with optimum pore diameters (20–100 Å) that match the stereochemical requirements for surface imprinting of four or six coordinate metal ions, and
2) a very uniform distribution of pore size, which allows the generation of the uniform imprints and limits the possible choices of coordination environments or the number of other possible complexes.[10f]

The mesoporous ordered silica hosts used in this study were prepared by a surfactant-assembly pathway, which involves matching the charge between the surfactant and inorganic silica precursors.[1–3] Calcined, ordered mesoporous silica samples prepared by this procedure have surface areas of over 1000 $m^2 g^{-1}$, mesopore volumes of 0.98 $cm^3 g^{-1}$, and average pore sizes of ≈25 Å. Both powder X-ray diffraction and small-angle X-ray scattering[13] show a peak at $2\theta \approx 2°$, which agrees with the pore size determined by the method of Barrett, Joyner, and Halenda.[14]

To illustrate the potential of this imprinting methodology Cu^{2+}-selective, ordered mesoporous sorbents were chosen to demonstrate both the basic principles of the concept and the ease with which imprinted sorbents may be prepared. Furthermore, extensive literature reviews of imprinted polymers for the separation of copper already exists.[11, 15] A critical comparison of the binding properties of our sorbents with imprinted organic polymeric matrices shows the advantages of our imprint-coated mesoporous sorbents (see below). To test the selectivity of our new sorbents we conducted competitive ion-binding experiments on aqueous Cu^{2+}/Zn^{2+} mixtures. This system constitutes one of the most stringent tests for ion-binding selectivity because both ions have identical charge, similar sizes, and exhibit high affinities for amine ligands.

The two imprinting complex precursors used in this study are $[Cu(apts)_x \cdot S_{6-x}]^{2+}$ and $[Cu(aapts)_2S_2]^{2+}$ ($x = 3–5$; S = H_2O or methanol; apts = $H_2NCH_2CH_2CH_2Si(OMe)_3$; aapts = $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OMe)_3$), which were synthesized by standard literature procedures.[16] Molecular mechanics modeling studies[17] have shown the sizes of the most probable conformations for these two complexes to be in the range of 16–25 Å, which are ideal for fitting into mesoporous substrates with pore diameters of 25 Å. Surface imprinting of the support was conducted by mixing stoichiometric amounts of an imprinting precursor with the mesoporous silica in methanol or aqueous solution.[18] Figure 1 shows the UV/Vis spectra of the two imprinting precursors in methanol and

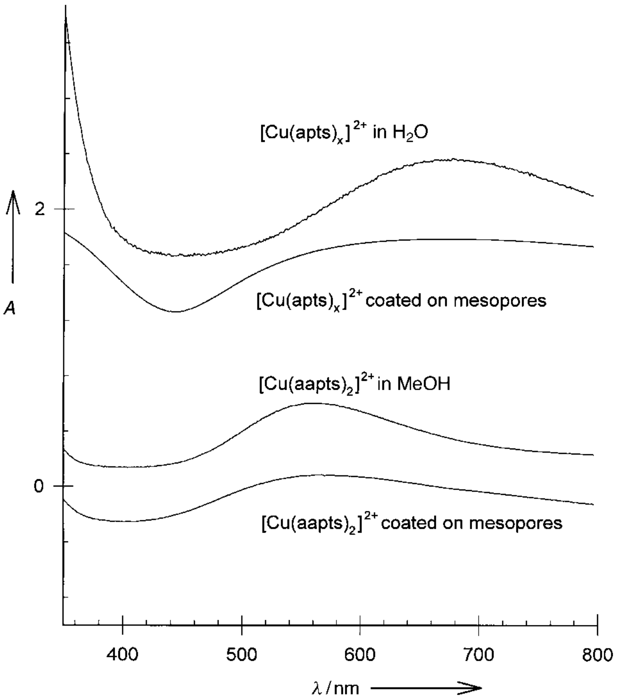

Figure 1. UV/Vis spectra of $[Cu(apts)_x]^{2+}$ and $[Cu(aapts)_2]^{2+}$ in methanol and aqueous solutions, respectively, and of both complexes coated on mesopore surfaces.

aqueous solutions and the corresponding diffuse reflectance spectra of washed and dried imprint-coated mesoporous silica. The close match between the spectra of $[Cu(aapts)_2S_2]^{2+}$ and $[Cu(s\text{-}aapts)_2S_2]^{2+}$ (s-aapts = surface-coated aapts ligand) indicates that the stereochemical environments of the copper ions in the two systems are similar and that the complex is coated on the surfaces of the mesopores.

The absorption band in the UV/Vis spectrum of $[Cu(s\text{-}apts)_xS_{6-x}]^{2+}$ (s-apts = surface-coated apts ligand) is broader than that of the corresponding precursor in solution. On the basis of the average environment rule[19] this indicates that the distribution of distinct copper complexes in the solid phase is broader than that in the solution phase. The locations of the electronic transition bands for all the complexes agree well with those of the model complexes $[Cu(en)_2S_2]^{2+}$ and $[Cu(H_2NR)_xS_{6-x}]^{2+}$ (en = ethylenediamine).[20] Control samples were prepared under identical conditions except that no templating ion (Cu^{2+}) was added to the coating solutions. Amines are protonated below pH = 3 and lose their ability to complex metal cations. This characteristic provides a simple and efficient way to strip the Cu^{2+} template from the imprinted mesoporous sorbents. Thus, template-free imprinted sorbents were easily obtained by soaking the Cu^{2+}-imprinted coatings on mesoporous silica with 1M nitric acid for 20 min. Control mesoporous sorbents were also treated identically to ensure that both types of sorbents had identical treatments of their surfaces. Both imprint-coated and conventionally coated sorbents were then neutralized to pH = 7 and dried in a vacuum oven at 50°C for 6 h before adsorption tests were conducted. A schematic illustration of our imprint-coating process is shown in Figure 2A, while the difference in the final cavity structure between our imprint-coated and conventionally coated mesoporous sorbents is shown in Figure 2B.

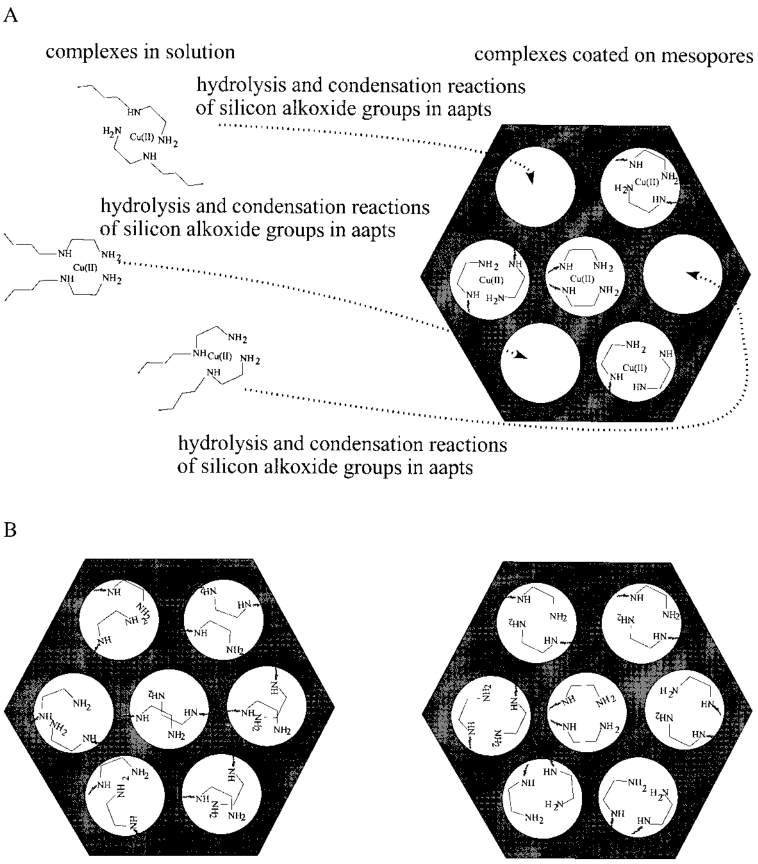

Figure 2. A) Schematic diagram of the imprint-coating process: first the complexes are introduced between target metal ions and bifunctional ligands, then the siloxane groups in the bifunctional ligands are hydrolyzed, and finally covalently coated on the mesopore surfaces. B) Schematic representation of the difference between the cavities generated by conventional coating (left) and imprint coating (right).

The ^{29}Si MAS solid-state NMR spectra of the sorbents produced by imprint coating and that of the corresponding control blank showed two groups of peaks. The peaks around $\delta = -65$ are attributed to silicon atoms tethered to amino groups on surfaces, whereas the peaks around $\delta = -110$ arise from the silicon atoms derived from the original support.[9, 10, 21] The loadings of apts and aapts are estimated from the relative areas of the envelopes for these two groups of peaks to be 0.92 mmol g^{-1} and 0.40 mmol g^{-1}, respectively. This estimation is consistent with the elemental ICP-AE analysis of the solutions after HF digestion of the coated sorbents (ICP = inductively coupled plasma, AE = atomic emission). Both imprint-coated and blank-coated mesoporous sorbents exhibit similar ligand loadings.

Table 1 summarizes the measured adsorption capacities of imprint-coated and conventionally coated (control) mesoporous sorbents for Cu^{2+}. Both imprinted sorbents exhibit distinctly higher effective capacities for Cu^{2+} than their respective control blanks. Furthermore, their capacity does not change after repeated cycles of loading and elution. These properties make them ideal for many separation applications that require recyclable solid phases.

Table 1. Capacity of imprint-coated and conventionally coated mesoporous sorbents with respect to Cu^{2+} uptakes at specific Cu^{2+} concentrations and pH 5.0 (acetic acid/acetate buffer).[a]

Sorbent	Solution	% Cu abs	K_d of Cu[c]	Cu capacity [mmol g^{-1}]
nonimprinted apts[d]	0.001M Cu	98.2	5300	0.098
imprinted apts[e]	0.001M Cu	99.6	26000	0.1
nonimprinted aapts	0.001M Cu	98.5	6800	0.099
imprinted aapts	0.001M Cu	99.7	39000	0.1
nonimprinted aapts	0.0001M Cu	99.2	14000	0.0099
imprinted aapts	0.0001M Cu	100[b]	-	-

[a] In all experiments 0.1 g of each sample was equilibrated with 10 mL of the buffer solution in stoppered plastic vials and these mixtures were stirred for 1 h at room temperature. The uptake of Cu^{2+} by sorbents was measured with a Perkin–Elmer Plasma 400 ICP/AE spectrophotometer. [b] No detectable copper ions were found in the solution after treatment. [c] $K_d = \{(C_i - C_f)/C_f\} \times$ {volume of solution [mL]}/{mass of gel [g]}; where C_i and C_f represent the initial and final solution concentrations, respectively. [d] Nonimprinted apts = sorbent coated by the conventional method. [d] Imprinted apts = sorbent coated by the surface molecular imprinting.

The selectivities of these sorbents were investigated using aqueous solutions of zinc and copper. If a sorbent is simultaneously exposed to mixtures of different metal ions, those ions with the highest binding affinity will be preferential

Table 2. Competitive loading of M_1 (Cu^{2+}) and M_2 (Zn^{2+}) by copper-imprinted and control blank mesoporous sorbents at pH 5.0 (acetic acid/acetate buffer).

Type	Solution concentrations[a]		% Cu abs	% Zn abs	K_d(Cu)	K_d(Zn)	k	k'
	Cu [mol L^{-1}]	Zn [mol L^{-1}]						
nonimprinted apts	0.001	0.01	35.4	63.3	55	170	0.3	–
imprinted apts	0.001	0.01	53.2	68	110	210	0.51	1.7
nonimprinted aapts	0.001	0.001	98.5	96.6	6500	2900	2.3	–
imprinted aapts	0.001	0.001	99.8	82.9	44000	480	91	40
nonimprinted aapts	0.001	0.005	98.5	70	6500	230	28	–
imprinted aapts	0.001	0.005	99.6	52.6	24000	110	220	7.7

[a] Initial concentrations of the solutions.

bound. The selectivity coefficient k for the binding of a specific metal ion in the presence of competitor species [Eq. (1)] can be obtained from equilibrium binding data[11, 22] according to Equation (2), where K_d is the distribution

$$M_1(\text{solution}) + M_2(\text{sorbent}) \rightleftharpoons M_2(\text{solution}) + M_1(\text{sorbent}) \tag{1}$$

$$k = \{[M_2]_{\text{solution}}[M_1]_{\text{sorbent}}\}/\{[M_1]_{\text{solution}}[M_2]_{\text{sorbent}}\} = K_d(\text{Cu})/K_d(\text{Zn}) \tag{2}$$

coefficient. A comparison of the k values of the imprint-coated sorbents with those for blank control samples allows an estimation of the effect of imprinting on selectivity. Following the work by Kuchen and Schram,[11] a relative selectivity coefficient k' [Eq. (3)] can be defined.

$$k' = k_{\text{imprinting-coated}}/k_{\text{control}} \tag{3}$$

Table 2 summarizes K_d and k' values obtained in these selectivity tests for zinc and copper. A comparison of the K_d values for the Cu^{2+}-imprinted samples with the control samples for the aapts-coated sorbent system shows a sixfold increase in K_d for Cu^{2+}, while K_d for Zn^{2+} decreases by the same amount. The value of k' is greater than 1 for all imprint-coated sorbents. A k' value of 40 for the aapts-imprint-coated sorbent is, to the best of our knowledge, the highest value currently reported for the molecular imprinting of metal ions in similar conditions.[11, 15] The value of k' (1.71) for the apts-imprinted sorbent is smaller than that for the aapts ligand. This observation may be attributed to the flexibility of the propyl chain that links the monodentate amine to the support, which allows for an easy redirection of the ligand and a larger range of coordination geometries for these ligands. Accordingly, coordination to a metal ion is less specific and therefore less selective for the target ion. In fact, this also agrees with the UV/Vis spectra (Figure 1) that indicate a broad distribution of the ligand imprints in the apts-imprint-coated sorbent.

In contrast to the results described above, imprint coating on the surfaces of commercial, amorphous silica gel (Aldrich, $\bar{d} = 60$ Å; surface area $= 600\ \text{m}^2\,\text{g}^{-1}$) showed very little evidence of imprinting effects in selectivity experiments.[23] This is consistent with the idea that the shape and curvature of the pore surfaces play pivotal roles in the success of the surface imprinting of inorganic coordination complexes.

In conclusion, surface imprinting has, for the first time, been conducted on ordered, cylindrical surfaces of mesopores, thereby organizing ligand functional groups successfully according to the sizes and stereochemical signatures of template ions. We view these sorbents as solid-state analogues of crown ether-type ligands, which can be tailored for a specific target ion. The simplicity of this technique should lead to a wide variety of new, highly selective sorbents, the properties of which can be optimized for many metal ions with the proviso that they form stable coordination complexes with a suitable bifunctional ligand containing a silane group.[24] Furthermore, this surface imprinting methodology should not be limited to the binding of metal ions. If complexes or molecules can be formed between targeted organic molecules and functional groups that contain a silane group then application of the above methodology should lead to the synthesis of sorbents that exhibit molecular recognition of organic molecules.

Experimental Section

Preparation of ordered mesoporous silica support:[1–3] The typical procedure involves mixing cetyltrimethylammonium bromide (CTAB), water, and base (NaOH). The molar ratio of CTAB:H_2O:NaOH is 0.12:130:0.7. Tetraethylorthosilicate (TEOS) was added to this solution at room temperature and the mixture was then heated at 100 °C for 24 h. The solid product was recovered by filtration.

Preparation of imprint-coated ordered mesoporous sorbent:[18] In a typical preparation $Cu(NO_3)_2 \cdot 3H_2O$ (0.567 g) is added under stirring to MeOH (50 mL). After the $Cu(NO_3)_2 \cdot 3H_2O$ has completely dissolved, aapts is added (1.02 mL). After stiring the mixture for 1 h, mesoporous silica (0.25 g) is added. The solution is stirred and evaporated to dryness. The residue is washed with copious amounts of 1 M HNO_3 to remove all the copper and any excess ligand. The resulting gel is placed in deionized water and titrated with 2 M NaOH to pH 7.5, filtered, washed with deionized water, and placed under vacuum at 80 °C for 4 h. The control blank samples were prepared using an identical procedure but without the addition of $Cu(NO_3)_2 \cdot 3H_2O$. The procedure for coating using water as a solvent is the same as that reported in the literature.[18]

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[23] The highest enhancement of K_d for Cu^{2+} through imprint coating on commercial, amorphous silica is 1.54, which is much less than the best value obtained on the ordered mesopore surfaces.
[24] We have also developed sorbents coated with the imprints of [Zn(aapts)$_2$]$^{2+}$ and [Hg(aapts)$_2$]$^{2+}$ for the selective adsorption of Zn^{2+} and Hg^{2+}. The adsorption capacities of both sorbents were increased by surface imprinting. In the case of the Zn^{2+}-imprinted sorbent a 100% adsorption of Zn^{2+} in 10 mL of a 10^{-3} M solution by 0.1 g of the sorbent was observed. The selectivity of the sorbent imprinted with [Zn(aapts)$_2$]$^{2+}$ was tested using the Zn^{2+}/Cu^{2+} system. The value of k' is 3.3.

Strong N–H···O Hydrogen Bonding in a Model Compound of the Catalytic Triad in Serine Proteases[**]

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The cleavage of peptide bonds is an important reaction in nature that involves the catalytic triad of residues (Ser-His-Asp) in the active site of the serine proteases class of enzymes (Figure 1).[1] A number of studies have suggested that a low-barrier hydrogen bond (LBHB) is involved in the reaction mechanism as a partial proton transfer between His^{57} and Asp^{102}.[2] Formation of a LBHB can account for many of the special physicochemical observations found in some enzymes, but it is still a matter of controversy whether a LBHB contributes significantly toward the catalytic activity of the triad.[3] Much research has been carried out to examine the nature of short, strong hydrogen bonds, and the principal tools of analysis have been ab initio computations on small model systems,[4] crystal structure correlations,[5] and spectroscopic investigations.[6] It is increasingly evident that a number of factors besides the distance between heteroatoms influences the formation of a LBHB. Factors such as matching of pK_a values, involvement in other hydrogen bonds, and steric strain are also of importance. Analysis of charge densities (CDs) in model systems provides an alternative method for studying hydrogen bonds. Charge densities in hydrogen bond systems can be determined experimentally from combined analysis of low-temperature X-ray and neutron diffraction data.[7] Contrary to ab initio theory, experimental CD studies have far fewer restrictions on the size of the model system that can be studied, and the results inherently reflect all interactions in the crystal. Detailed quantitative information about the

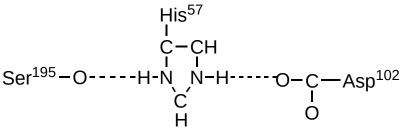

Figure 1. Schematic drawing of the catalytic triad in serine proteases. No formal charges or bond orders have been assumed in the sketch.

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