

Hierarchically Imprinted Sorbents

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Abstract: A double imprinting methodology was developed to synthesize novel materials with hierarchical structures. On the microporous level (1–3 Å), metal ions served as template. On the mesoporous level (diameters of 25–40 Å), micellar structures produced by self-assembly of surfactant molecules were used as templates. Removal of both metal ions and surfactant micelles resulted in the formation of imprints with different sizes within the silica matrix, each with a specific function. This research opens vast opportunities for the applications of ordered mesoporous materials in the area of molecular recognition such as separations, chemical sensors, and catalysts.

Keywords: hierarchical structures • mesoporosity • molecular imprinting • molecular recognition • sorbents

inorganic interfaces. Thirdly, patterned organic compartments (vesicles) are used to shape biomaterials through “organized reaction fields”.

We have recently introduced a facile approach to the production of hierarchical microstructure and mesostructures.^[7] The essence of our new methodology is the combination of two powerful imprinting techniques at different scales: 1) molecular imprinting^[8–15] and 2) micelle templating synthesis.^[16–24] These hierarchical materials may find important applications as smart sorbents for environmental clean-up. The motivation for the synthesis of hierarchical materials with microscopic and mesoscopic form centers around the synergistic importance of stereochemistry, pore size, and surface area in determining such properties as flow and transport phenomena, capacity, and selectivity in separation efficiency. The general concept provides a rational way to synthesize hierarchical materials for separation applications.

Introduction

Hierarchical structures can be found in nature from the macroscopic level to the microscopic level. Biomaterials are selectively self-organized from molecular- to macro-length scales, with organized units of subassemblies that are generated to serve biological purposes. They are chosen smartly from a multitude of options. Recently, research has been initiated to mimic biomineralization processes and chemically produce hierarchical structures.^[1–6] Notably, the research groups of Ozin and Mann have established a morphosynthesis approach to inorganic and hybrid materials with complex forms.^[1–3] Three methodologies are predominantly used in their material synthesis. First, complex macroscopic morphological forms can be produced by fluctuating chemical processes involving local perturbations in the fluid–solid interface during mineralization. Secondly, organic assemblies such as micelles are used as scaffold-like templates to direct mineralization along, around, and between the organic–

Concept

Imprinting methods based on the template approach^[7–14, 25] have been used in cross-linked polymers as well as in silica gels to prepare polymeric supports possessing solid-state organized structures (Figure 1). Imprinting processes generally involve three steps: a) selection of a target molecule as a template; b) incorporation of the template into rigid solid networks through in situ copolymerization; c) removal of the template, leaving cavities with a predetermined number and arrangement of ligands that later “recognize” or selectively

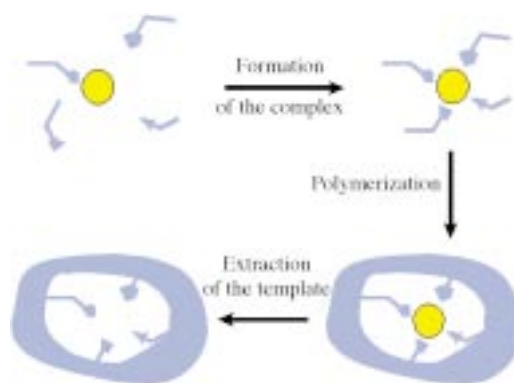


Figure 1. Schematic diagram of molecular imprinting.

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rebind the template or target molecule. The imprint cavity is produced by the template that is present during the formation of the solid matrix. After the templating species is removed from the polymer, a predetermined arrangement of ligands and a tailored binding pocket is left. 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 materials have been used to resolve racemates^[8] and separate mixtures of metal cations.^[8, 10, 25, 26]

From a combinatorial chemistry perspective,^[27] the imprinting synthesis of a polymeric system can be regarded as a screening process to select a specific target polymer configuration from a dynamic combinatorial library of polymer precursor solutions. In conventional polymerization, there is no “selection” process using a guest molecule and, accordingly, the polymer configuration finally obtained results from a random quenching of the polymer precursor solution. A comparison of these two polymerization processes is provided in Figure 2. One major drawback associated with the current bulk molecular imprinting technique is that organization of precursor monomers has been achieved mainly in *inhomogeneous* organic polymer matrices, with little control over structural parameters, such as pore sizes and surface areas. The kinetics of the sorption–desorption process is unfavorable, as the template and ligand are embedded in the bulk polymer matrices and mass transfer must take place through nonpolar, microporous channels.

Recently, molecular scale imprinting was expanded by the scientists from Mobil to the mesoscale level.^[16] This breakthrough in catalyst synthesis has resulted in a novel methodology for preparing mesoporous inorganic materials with extremely high surface areas and ordered mesostructures. Mesoporous silicon, aluminum, and transition metal oxides have been prepared. The essence of this new methodology is the use of molecular assemblies of surfactants or related substances as templates during the formation of oxides. The mechanism for the organization of such meso-

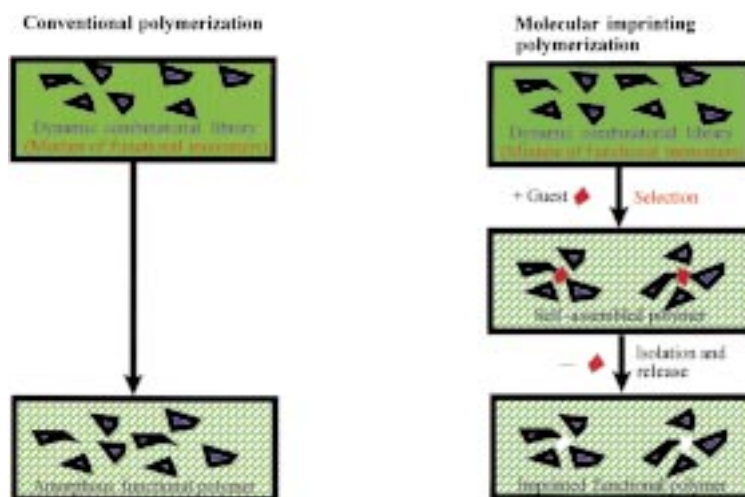


Figure 2. Combinatorial chemistry view of molecular imprinting and conventional polymerization processes.

structure involves electrostatic interactions and charge matching between micellar assemblies of quaternary ammonium cations and anionic silicate oligomer species. Stucky and co-workers^[17b] have developed a model that makes use of the cooperative organization of inorganic and organic molecular species in three-dimensional arrays. They divided the global surfactant-directed ordered porous material synthetic process into three reaction steps: multidentate binding of the silicate oligomers to the cationic surfactant and the silicate, preferential silicate polymerization in the interface region, and charge density matching between the surfactant and the silicate. This micelle-based template synthesis can be viewed as a mesoscale imprinting process.

Our approach to the synthesis of hierarchical materials is based on the combination of the above two-scale imprinting syntheses. Figure 3 gives a schematic illustration of our hierarchical imprinting methodology for synthesis of sorbents. The concepts behind our multilevel imprinting are as follows.

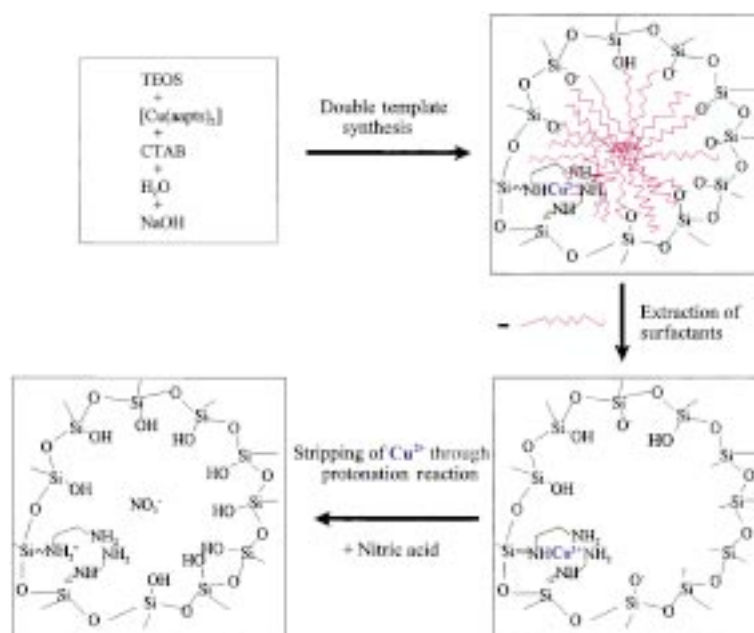


Figure 3. Schematic diagram showing the synthesis of a hierarchically imprinted sorbent using Cu^{2+} and CTAB simultaneously as templates.

Surfactant micelles and metal ions both act as templates in these *hierarchically* imprinted sorbents, simultaneously. The metal ion and the surfactant are removed from the silica matrix through acid leaching and ethanol extraction, respectively. This results in the formation of different-sized imprints within the silica matrix, each with a specific function. On the microporous level, removal of the metal ion from the corresponding complex leaves cavities (1–3 Å) that exhibit ionic recognition. These pores give the sorbent enhanced selectivity for the given ion. On the mesoporous level, removal of the surfactant micelles results in the formation of relatively large, cylindrical pores (diameters of 25–40 Å) that give the gel an overall porosity, including large surface areas and excellent metal-ion transport kinetics.^[28–30] Pore sizes can be easily controlled by the chain length of the surfactant molecules. This combination of high capacity and selectivity, coupled with fast kinetics, makes these materials ideal candidates for many applications. Because the entire process utilizes template or imprinting synthesis twice and on different length scales, it can be viewed as a hierarchical double-imprinting process. Recently, Yang et al.,^[5a] Schacht et al.,^[5b] and Fan et al.^[6] demonstrated the hierarchical organization of three-dimensional structures patterned over multiple-length scales (10 nm to several micrometers) through the combination of micromolding and cooperative assembly of inorganic sol–gel species with amphiphilic triblock copolymers. Holland et al.^[4] reported the synthesis of porous materials with simultaneous microscale and macroscale orders. To our knowledge, structures on the mesoscale and microscale with a hierarchical organization have yet to be synthesized. Our work bridges this gap by combining molecular scale imprinting and mesoscale template synthesis with surfactants. These materials should find extensive applications in sensors and separations.

The use of surfactant assembly to create pore sizes and surface areas is fundamentally different from the standard procedure for synthesizing molecularly imprinted polymers using a porogenic solvent.^[31, 32] In the latter case, porosities normally collapse when solvents are removed. The dependence of the imprinting effect on solvents is not due to the porosity created by solvent molecules; rather the observed dependence arises because the imprinted organic polymers swell to different extents in different solvents. This swelling effect determines the so-called porogenic effect. The best swelling effect is achieved using the same solvent in the selectivity or capacity test as was used in synthesizing the imprinted polymer. Therefore, the use of different solvents in synthesizing imprinted polymers is *fundamentally* not a molecular imprinting process, while the surfactant template synthesis in our hierarchical imprinting process is. In an imprinting process, the template molecules need to interact strongly with the precursor monomers so that the stereochemistry of the templates can be “memorized” in the polymers. However, one of the criteria in choosing a good solvent for molecular imprinting is to optimize the interaction between target molecules and precursor monomers, but not solvent molecules and precursor monomers. If the latter interaction is too strong, the entire imprinting process for the target molecule will be undermined. In our double-imprinting

system, both the ion and the cylindrical micelle templates interact with the different parts of the sol–gel precursors. The ion templates coordinate with diamine functional ligands, while the cylindrical micelle templates interact with Si-OH or Si-O⁻. This double-template synthesis results in the reported hierarchically structure in our mesoporous materials. The pore structures and surface areas remain after the removal of the surfactant templates and do not swell upon contact with organic solvents.

Synthesis and Characterization

In order to illustrate the potential of this double-imprinting methodology, Cu²⁺-selective, ordered mesoporous sorbents were chosen to demonstrate the basic principles. An extensive literature study^[8, 11, 26, 33] already exists concerning *singly* imprinted polymers for copper separations. The synthetic procedure used to produce doubly imprinted sorbents is similar to that of coassembling synthesis.^[34–39] The bifunctional ligand used to complex the Cu²⁺ template is 3-(2-aminoethylamino) propyltrimethoxysilane, H₂NCH₂CH₂NH-CH₂CH₂CH₂-Si(OMe)₃ (aapts). The ethylenediamine group in this ligand is known to form strong bidentate dative bonding with many metal ions. The imprinting complex precursor used in this study is [Cu(aapts)₂]²⁺, which was synthesized using standard literature procedures.^[40] The typical procedure involves mixing cetyltrimethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS), [Cu(aapts)₂]²⁺, water, and base (NaOH). The mixture is heated, and the solid blue product is later recovered by filtration. It is well known that amines are protonated below a pH of 3 and lose their ability to complex metal cations. This characteristic provides a simple and efficient way to strip the Cu²⁺ template from the imprinted mesoporous sorbents. The surfactant is also known to be extractable with ethanol/HCl. Accordingly, the blue filtrate is refluxed in ethanol/HCl to extract the surfactant templates with ethanol and to strip the copper-ion templates by protonation of the diamine functional groups. The final material is washed with copious volumes of 1N HNO₃ to ensure the complete removal of the copper-ion templates. The control blank samples are prepared using an identical procedure without the addition of the Cu²⁺ template. Both hierarchically imprinted and control blank sorbents are neutralized to a pH of 7 and dried using a vacuum oven at 50 °C for 6 h before adsorption tests are conducted. Doubly imprinted sorbents containing the anionic sodium dodecylsulfate (SDS)^[41] and the neutral dodecylamine (DDA)^[42] surfactants were prepared using a similar protocol. The use of surfactants in the sorbent synthesis is crucial. All the sorbents *singly* imprinted with [Cu(aapts)₂]²⁺ have very small surface areas (< 50 m² per g); the Cu²⁺-uptake capacity is one-fifth of those of the doubly imprinted sorbents. On the contrary, doubly imprinted and control-blank functionalized mesoporous silica samples prepared by means of this procedure have surface areas in range of 200 to 600 m²g⁻¹. Although the pore-size distributions of the imprinted and control blank samples are very similar, the surface areas of the imprinted samples are less than those of the control blanks by 10 to 20%.

Figure 4 shows the UV/Vis spectrum of $[\text{Cu}(\text{aapts})_2]^{2+}$ in a methanol solution and the corresponding diffuse reflectance spectrum of a washed- and dried- as-synthesized mesoporous silica. The close match between the spectrum of $[\text{Cu}(\text{aapts})_2]^{2+}$ and that of $[\text{Cu}(\text{b-aapts})_2]^{2+}$ (b-aapts = aapts ligand covalently

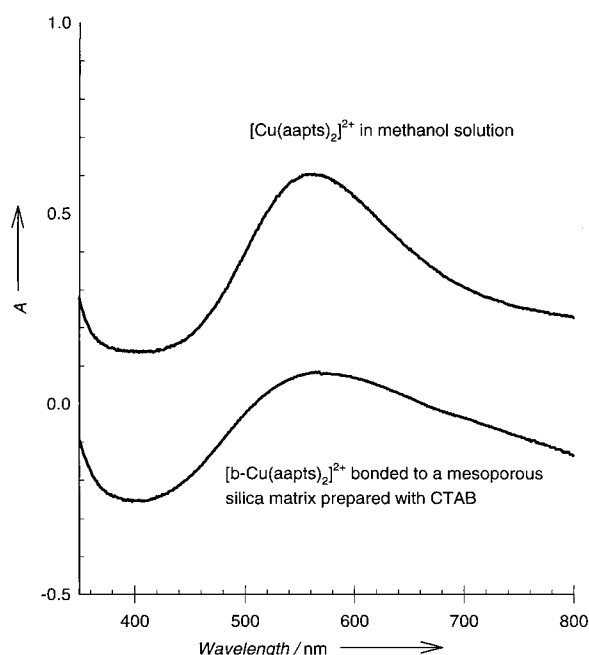


Figure 4. UV/Vis spectra of $[\text{Cu}(\text{aapts})_2]^{2+}$ in methanol and immobilized in a mesoporous sorbent prepared by CTAB as a structure directing reagent.

bonded to silica) indicates that the stereochemical environments of the copper ion in the two systems are similar and that the complex is doped into the bulk silica matrix. The absorption position of the peak is consistent with the fact that Cu^{2+} is coordinated with four amine ligands since both three and two amine-coordinated copper complexes have absorption peaks at much longer wavelengths.^[43] Therefore, the imprint of Cu^{2+} is successfully formed in the mesoscopic composite materials.

Small-angle X-ray scatterings (Figure 5) of the surfactant-free hybrid mesoporous sorbents show a peak around $Q = 1.2 - 2.4 \text{ nm}^{-1}$, which agrees with the corresponding pore size determined by nitrogen adsorption experiments. This indicates that the long-range order or worm-type structure organized by the surfactant templates is retained for the surfactant-extracted imprinted sorbents.^[5] Therefore, control over the mesoscopic level is successful.

Sorption Test

Competitive ion-binding studies were conducted with Cu^{II} and Zn^{II} ions in order to measure the selectivity of the imprinted material. The Zn^{II} ion was chosen as the competitor species since it has the same charge and nearly identical size and also binds well with the diamine ligand. In addition, zinc is also usually present in industrial effluents containing copper, such as electroplating waste and acid mine drainage.^[44] The

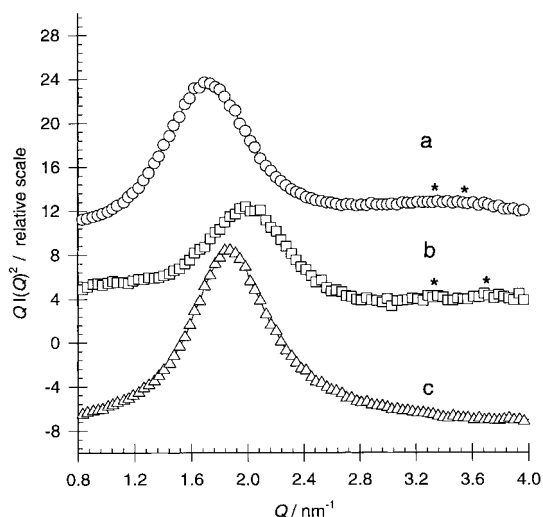


Figure 5. Small-angle scatterings of hierarchically imprinted sorbents using a) CTAB, b) SDS, and c) DDA, where $Q = (4\pi/\lambda)\sin(\theta/2)$, $\lambda = \text{X-ray wavelength (0.154 nm)}$, and $\theta = \text{scattering angle}$. The asterisks in a) and b) indicate the other diffraction peaks from the hexagonally packed mesoporous materials. No additional diffraction peaks in c) are consistent with the fact that the neutral surfactant template DDA gives rise to the worm-structured mesoporous materials.

selectivity coefficient, k , for the binding of a specific ion in the presence of competitor species can be obtained from equilibrium binding data^[26] according to Equation (2):

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

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

where K_d is the distribution coefficient, expressed as:

$$K_d = \{(C_i - C_f)/C_f\} \times \{\text{volume solution (mL)}\} / \{\text{mass gel (g)}\} \quad (3)$$

Here, C_i is the initial solution concentration and C_f is the final solution concentration. Comparison of the k values for the imprinted and control blank gels can show the effect that imprinting has on the metal-ion selectivity for a given material. A measure of the increase in selectivity due to molecular imprinting can be defined by the ratio of the selectivity coefficients of the imprinted and nonimprinted materials:

$$k' = k_{\text{imprinted}}/k_{\text{non-imprinted}} \quad (4)$$

Table 1 summarizes values for the distribution constant (K_d), selectivity coefficient of the sorbent toward Cu^{2+} (k), and the relative selectivity coefficient (k') obtained in these competitive ion-binding experiments between zinc and copper ions. A comparison of the k values for the Cu^{2+} -imprinted sorbents with the corresponding control samples shows a significant increase in k for Cu^{2+} through imprinting, with the largest $k = 33000$ and the largest $k' = 240$. We have recently reported a synthesis of imprint-coated sorbents with the largest k value around 90 and the largest k' value around 40, which are, to our knowledge, the highest k and k' values currently achieved for molecular imprinting of metal ions.^[25c] Our current double-

Table 1. Competitive loading of $M_1(\text{Cu}^{2+})$ and $M_2(\text{Zn}^{2+})$ by copper-imprinted and control blank mesoporous sorbents made with the precursor silica and functional ligand of molar ratio 1.0:0.15 at pH 5.0 (acetic acid/sodium acetate buffer).

Type	Solution ^[a]		% Cu abs. ^[b]	% Zn abs. ^[b]	K_{d} [mL g ⁻¹]	Zn_{Kd} [mL g ⁻¹]	k	k'
	Cu [M]	Zn [M]						
nonimp-aapts (CTAB) ^[c]	0.001	0.001	99.66	99.77	29 000	43 000	0.67	–
imp-aapts (CTAB) ^[d]	0.001	0.001	99.17	40.12	12 000	67	180	270
nonimp-aapts (CTAB)	0.001	0.01	99.67	55.81	30 000	130	230	–
imp-aapts (CTAB)	0.001	0.01	99.24	10.13	13 000	11	1200	4.6
nonimp-aapts (SDS)	0.001	0.001	96.07	44.59	2 400	80	30	–
imp-aapts (SDS)	0.001	0.001	99.56	13.31	23 000	15	1500	50
nonimp-aapts (SDS)	0.001	0.01	93.37	10.64	1 400	12	120	–
imp-aapts (SDS)	0.001	0.01	99.98	2.40	82 000	2.5	33 000	280
nonimp-aapts (DDA)	0.001	0.001	99.70	90.40	32 000	940	34	–
imp-aapts (DDA)	0.001	0.001	99.60	40.00	25 000	66	370	11
nonimp-aapts (DDA)	0.001	0.01	96.00	18.00	2 400	22	109	–
imp-aapts (DDA)	0.001	0.01	99.50	12.20	19 000	14	1 300	12
nonimp-aapts (no surf.) ^[e]	0.001	0.001	72.40	11.20	260	13	20	–
imp-aapts (no surf.) ^[f]	0.001	0.001	71.80	8.77	250	9.6	36	1.3

[a] Initial solutions. [b] Percentage metal ion absorbed (± 0.01). [c] Nonimp-aapts (CTAB) = non-imprinted sorbent synthesized with CTAB surfactant. [d] Imp-aapts (CTAB) = imprinted sorbent synthesized with CTAB surfactant. [e] Nonimp-aapts (no surf.) = non-imprinted sorbent synthesized without surfactant templates (other conditions were kept identical). [f] Imp-aapts (no surf.) = imprinted sorbent synthesized without surfactant templates (other conditions were kept identical).

imprinting approach gives rise to a significant improvement in selectivity. In Table 1, the batch-test results for the sorbents prepared without the use of surfactant templates are also listed. The $K_{\text{d}}(\text{Cu})$ and k values of the imprinted sorbent are 250 and 26, respectively. Both values are significantly less than those of the doubly imprinted sorbents. The low $K_{\text{d}}(\text{Cu})$ value for the *singly* imprinted sorbent can be attributed to its small surface area (26 m² per g; see Table 2). This further demonstrates the importance of using surfactant templates to generate large surface areas in our *doubly* imprinted sorbents.

Table 2. Surface areas and total pore volumes.

Sorbent	B.E.T. Surface area [m ² per g]	Total pore volume [cm ³ per g]
imp-aapts (DDA)	240	0.16
nonimp-aapts (DDA)	260	0.15
imp-aapts (SDS)	260	0.45
nonimp-aapts (SDS)	330	0.46
imp-aapts (CTAB)	520	0.69
nonimp-aapts (CTAB)	570	0.65
imp-aapts (no surf.)	26	0.04
nonimp-aapts (no surf.)	24	0.04

Conclusion

A new molecular imprinting methodology has been developed to synthesize hierarchical materials. This new methodology makes use of the recent advances in the controlled synthesis of mesoporous materials and combines them with molecular level imprinting techniques. This procedure produces imprinted mesoporous hybrid sorbent materials that exhibit not only fast binding kinetics and high capacities but also molecular recognition capabilities. We view these new sorbents as solid-state analogues to crown ether-type ligands that are tailored for a specific target ion. The simplicity of this technique should lead to a wide variety of 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. Furthermore, this hierarchical imprinting methodology should not be limited to the synthesis of sorbents for the binding of metal ions. If complexes or molecules can be formed between targeted organic molecules and functional groups containing a silane group, application of the above methodology should lead to the synthesis of sorbents which exhibit molecular recognition of organic molecules. The general design principles illustrated by these results highlight opportunities in areas such as selective sorbents, chemical sensors, and catalysts offered by the imprinted mesoporous materials as molecular recognition devices.

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