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Hierarchically Imprinted Sorbents for the Separation of Metal Ions

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Molecular imprinting involves arranging monomers of polymerization synthesis around a template molecule so that complexes between the monomer and template molecules are formed.[1−7] Subsequent polymerization of the monomer molecules results in trapping template molecules in a highly cross-linked amorphous polymer matrix. Extraction of the imprint molecules leaves a predetermined arrangement of ligands and a tailored binding pocket. Such imprinted polymers have been used to mimic antibody functions, to resolve racemates, and to separate mixtures of metal cations.[1] Thus far, the 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. Here, we report the first synthesis of imprinted hybrid sorbent materials with precise control of not only adsorption sites but also pore structures. The concepts behind our multilevel imprinting are as follows. Surfactant micelles and metal ions both act as templates in these *hierarchically imprinted* sorbents. The metal ion and the surfactant are removed from the silica matrix via 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, the removal of the metal ion from the 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, the removal of the surfactant micelles results in the formation of relatively large, cylindrical pores (diameter 25−40 Å) that give the gel an overall porosity which includes large surface areas and excellent metal ion transport kinetics.[8−16] This combination of high capacity and selectivity, coupled with fast kinetics,[17] makes these materials ideal candidates for many applications. Because the whole 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*.,[18] and Schacht *et al*.[19] have 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 amphililic triblock copolymers. Holland *et al*.[20] 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 reported here bridges this gap by combining molecular-scale imprinting and mesophase template synthesis with surfactants. These materials should find extensive applications in sensors and separations.

To illustrate the potential of this double-imprinting methodology, Cu^{2+}-selective, ordered mesoporous sorbents were chosen to demonstrate the basic principles. An extensive literature study[21,22] already exists concerning *singly* imprinted polymers for copper separations. The synthetic procedure to produce doubly imprinted sorbents is similar to that of co-assembling synthesis.[11−15] The bifunctional ligand used to complex the Cu^{2+} template is 3-(2-aminoethylamino) propyltrimethoxysilane, $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OMe)_3$ (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 by standard literature procedures.[23] The typical procedure involves mixing cetryltrimethylammonium bromide (CTAB), tetraethylothosilicate (TEOS), Cu(aapts)$_2^{2+}$, water, and base (NaOH) in relative molar ratios of 0.12:1.0:0.15:130:0.7. The mixture is heated and stirred at 100 °C for 24 h. The solid blue product is then recovered by filtration. This is then 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 amounts of 1 N HNO_3 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 Cu^{2+} template. Doubly imprinted sorbents containing the anionic sodium dodecylsulfate (SDS)[24] and the neutral dodecylamine (DDA)[25] surfactants were prepared using a similar protocol. The use of surfactants in the sorbent synthesis is crucial. The sorbents *singly* imprinted with Cu(aapts)$_2^{2+}$ all have very small surface areas (<20 m^2/g), the Cu^{2+}-uptake capacity is one-fifth of those of the doubly imprinted sorbents.

Doubly imprinted and control blank functionalized mesoporous silica samples prepared by means of this procedure have surface areas in range of 200−600 m^2/g.[26] Although the pore-size

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Table 1. Competitive Loading of M_1 (Cu^{2+}) and M_2 (Zn^{2+}) by Copper-imprinted and Control Blank Mesoporous Sorbents Made with the Precursor Silica and Functional Ligand Molar Ratio 1.0:0.15 at pH 5.0 (Acetic Acid/Sodium Acetate Buffer)

type	solution[a] Cu (M)	Zn(M)	% Cu Abs[d]	% Zn Abs[d]	Cu K_d (mL/g)	Zn K_d (mL/g)	*k*	*k*′
nonimp-aapts (CTAB)[b]	0.001	0.001	99.66	99.77	29000	44000	0.66	
imp-aapts (CTAB)[c]	**0.001**	**0.001**	**99.17**	**10.13**	**11000**	**67**	**160**	**240**
nonimp-aapts (CTAB)	0.001	0.01	99.67	55.81	30000	130	240	
imp-aapts (CTAB)	**0.001**	**0.01**	**99.17**	**10.13**	**13000**	**11**	**1100**	**4.6**
nonimp-aapts (SDS)	0.001	0.001	96.07	44.59	2400	71	34	
imp-aapts (SDS)	**0.001**	**0.001**	**99.56**	**13.31**	**23000**	**15**	**1500**	**44**
nonimp-aapts (SDS)	0.001	0.01	93.37	10.64	1400	10	140	
imp-aapts (SDS)	**0.001**	**0.01**	**99.98**	**2.40**	**82000**	**2.5**	**33000**	**240**
nonimp-aapts (DDA)	0.001	0.001	99.70	90.40	32000	940	34	
imp-aapts (DDA)	**0.001**	**0.001**	**99.60**	**40.00**	**25000**	**66**	**370**	**11**
nonimp-aapts (DDA)	0.001	0.01	96.00	18.00	2400	22	109	
imp-aapts (DDA)	**0.001**	**0.01**	**99.50**	**12.20**	**19000**	**14**	**1300**	**12**

[a] Initial solutions. [b] Nonimp-aapts (CTAB) = nonimprinted sorbent synthesized with CTAB surfactant. [c] Imp-aapts (CTAB) = imprinted sorbent synthesized with CTAB surfactant. [d] Percentage metal ion absorbed (± 0.01).

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 10−20%. Small-angle X-ray scatterings show a peak around $Q = \sim 1.2-2.4\ \mathrm{nm}^{-1}$, which agrees with the corresponding pore size determined by nitrogen adsorption experiments.[26] The close match between the UV−vis spectrum of $Cu(aapts)_2^{2+}$ in methanol and that of $Cu(b\text{-}aapts)_2^{2+}$ (b-aapts = aapts ligand covalently 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.[26] The absorption peak position is consistent with the fact that Cu^{2+} is coordinated with 4-amine ligands since both 3- and 2-amine-coordinated copper complexes have absorption peaks in much longer wavelength.[27]

To test the selectivity of our new sorbents, we conducted competitive ion-binding experiments using aqueous Cu^{2+}/Zn^{2+} mixtures and a typical batch procedure.[28] This system constitutes one of the most stringent tests for ion-binding selectivity because both ions have identical charge, are of similar size, and exhibit high affinities for amine ligands. If a sorbent is simultaneously exposed to mixtures of different metal ions, preferential binding of those ions with the highest binding affinity will be observed. The selectivity coefficient, *k*, for the binding of a specific metal ion in the presence of competitor species can be obtained from equilibrium binding data according to methods given previously.[21]

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* values over 10 000 and the largest *k*′ over 200. 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.[29] The new double-imprinting approach offers a significant improvement in selectivity.

In conclusion, a novel design for template-selective recognition sites on mesoporous sorbents through hierarchical double imprinting is described. Unlike the mesoporous sorbents synthesized by surface functionalization,[30,31] precise control of the stereochemical arrangement of ligands on the adsorption sites can be achieved with this new methodology. Surface areas, controllable pore sizes, structural rigidities, and thermal stabilities achieved with the current silica-based imprinted sorbents are superior to those of imprinted organic polymers. This methodology has resulted in a new class of ordered mesoporous sorbents with molecular recognition capabilities. In addition to selective sorbents, the design principles illustrated by these results may lead us to new applications in areas such as chemical sensors and catalysis for these *hierarchically imprinted* materials.

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Supporting Information Available: Schematic representation of the double imprinting process. UV−vis spectra of $Cu(aapts)_2^{2+}$ in methanol and that of $Cu(b\text{-}aapts)_2^{2+}$ (b-aapts = aapts ligand covalently bonded to silica). Adsorption kinetics curve of Cu^{2+} on Cu^{2+} imprinted dodecylamine/aapts sorbent. Small-angle X-ray scatterings of hierarchially imprinted sorbents. Surface areas and porosity data of imprinted and nonimprinted sorbents (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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