Synthesis of a [{Mono-*N*-(4-vinylbenzyl)-1,4,7-triazacyclononane}$_2$Hg](OTf)$_2$ Sandwich Complex, Polymerization of this Monomer with Divinylbenzene, and Hg^{2+} Ion Selectivity Studies with the Demetallated Resin[‡]

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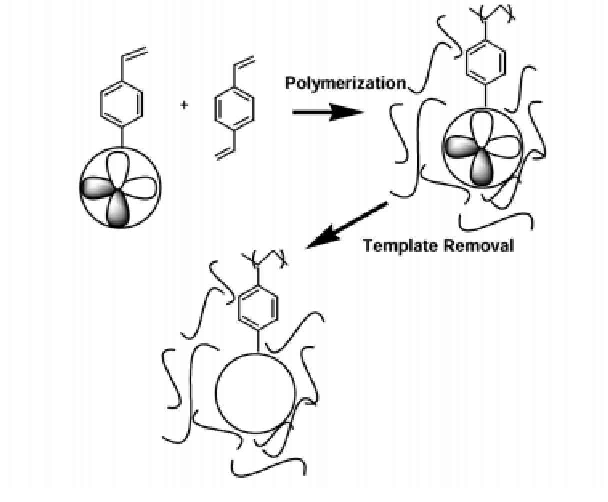
We have synthesized a novel, 1,4,7-triazacyclononane (TACN)-Hg^{2+} sandwich monomer, [{mono-*N*-(4-vinylbenzyl)-1,4,7-TACN}$_2$Hg](OTf)$_2$, which was co-polymerized with the cross-linking agent divinylbenzene to form a Hg^{2+}-ion templated polymer that was demetallated (>96%) with 6 N HCl, and subsequently found to be highly selective to reintroduced Hg^{2+} ions in competition with Cd^{2+}, Ag^{+}, Pb^{2+}, Cu^{2+}, and Fe^{3+} ions at pH 2, the ionic radius and the thermodynamic parameter being more critical than imprinting.

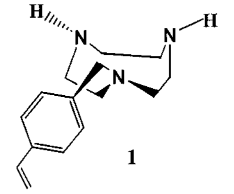
Introduction

The elegant concept of templated polymers was introduced by Wulff and Mosbach, and further developed by Shea, among others,[1] and initially involves formation of a vinyl monomer host and a bound guest acting as a template. This vinyl monomer host-guest template complex is then polymerized with a cross-linking agent, which provides spatially regulated sites in the polymer matrix and, if possible, the continual recognition of the removable guest template in subsequent reintroduction steps (Scheme 1).



Scheme 1. The templated polymer concept

More importantly, the area of metal-ion templated polymers has received much less attention than the corresponding organic compound templated polymers.[2] Recently, we extended the metal-ion templated polymer field to a novel system that utilized the mono-*N*-(4-vinylbenzyl)TACN ligand (**1**) and found that the monomeric Zn^{2+} sandwich complex of **1**, [{mono-*N*-(4-vinylbenzyl)TACN}$_2$Zn](OTf)$_2$, could be polymerized to provide the same spatial sandwich arrangement in the polymer matrix (2:1 ratio of TACN:Zn).[3,4] Subsequent demetallation of the Zn^{2+}-templated polymer with 6 N HCl, followed by reintroduction of the Zn^{2+} ions in competition with Ni^{2+}, Co^{2+}, and Mn^{2+} at pH 4.5, maintained the ≈2:1 TACN:Zn ratio, and there-



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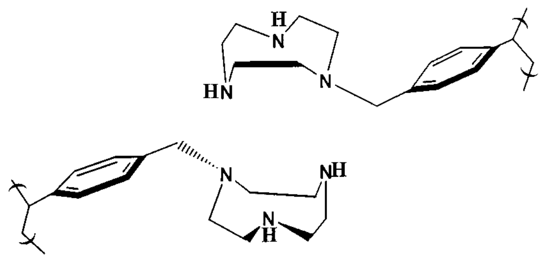

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[‡] Metal-ion-templated Polymers, 3. − Part 2: Ref.[4]

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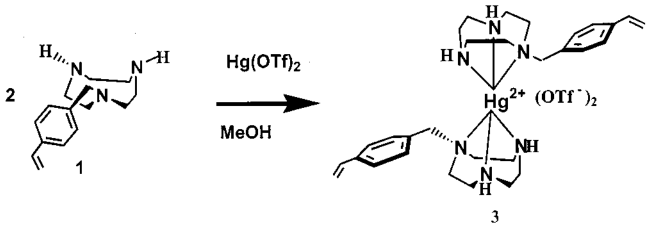
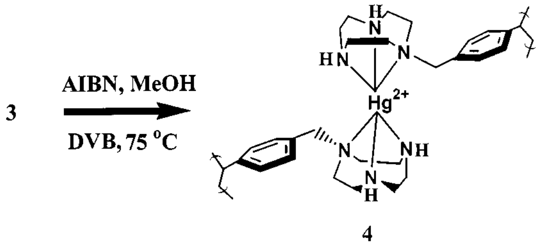
fore *allowed us to speculate that the demetallated polymer also had a sandwich arrangement of TACN ligands, polymer* **2**, *with the distance between the polymeric TACN ligands possibly a consequence of the ionic radius of Zn (0.69 Å).*

Results and Discussion

To further determine whether this interesting result was a consequence of the ionic radius of the template metal-ion used in the original polymerization reaction, which would possibly allow selective metal-ion removal from aqueous acidic solution, we prepared the Hg^{2+} (with a larger ionic radius of 1.10 Å) templated sandwich monomer of ligand **1**, [{mono-*N*-(4-vinylbenzyl)-1,4,7-TACN}$_2$Hg](OTf)$_2$ (**3**),[3,4] [Equation (1)] in 70% yield, and polymerized it with the cross-linking agent 80% divinylbenzene (DVB) using AIBN in methanol at 75 °C (overnight in a Schlenk tube covered with aluminum foil) to provide the Hg^{2+}-templated polymer **4** [Equation (2)].



(1)



(2)

62 % Crosslinked; 8% Hg; TACN, 0.84 mmol/g
2:1 TACN: Hg ratio

After the total removal of the template Hg^{2+} ion from **4** with 6 N HCl, a demetallated bulk polymer resulted (0.35% Hg, > 96% removed), which had very high selectivity for reintroduced Hg^{2+} ions in competition with a mixture of Cd^{2+} (0.97 Å; 518:1), Pb^{2+} (1.21 Å; 259:1), Ag^{+} (1.26 Å; 1111:1), Cu^{2+} (0.72 Å; 165:1), and Fe^{3+} ions (0.53 Å; 24:1), at pH 2.0, with very high equilibrium selectivity coefficients, $K_{Hg^{2+}/M^{n+}}$, in favor of the Hg^{2+} ion (Table).[5]

Initial observations indicate that the template Hg^{2+} ion is able to compete extremely effectively with metal ions of similar or larger ionic radii, as well as with those that are smaller. However, to our total surprise, we found that the reintroduced Hg^{2+}-ion content in the bulk demetallated polymer was now *15.6% Hg*, and this provided a ratio of TACN:Hg of ~1:1, dramatically different from the Zn^{2+} demetallated polymer, which gave a ~2:1 TACN:Zn/Cu ratio upon reintroduction of Zn^{2+} or Cu^{2+} ions.[3] More importantly, we had previously verified, in a control experiment,[3] that we were *not able* to synthesize a polymer of the vinyl monomer **1** *without the metal ion template*, in order to show that this non-templated polymer lacked selectivity, in comparison to the templated polymer, for the metal ions studied. We observed soluble oligomers by FAB-MS analysis, but no insoluble polymer. We therefore concluded that the metal ions are critical for the dramatic increase in polymerization rates for the templated metal-ion complexes of vinyl monomer **1**, presumably due to an electronic effect.

Clearly, it appears that as you go to metal ions with higher ionic radii, such as Hg^{2+}, the larger distances between the TACN ligands may cause them to operate independently, as suggested in the demetallated Hg^{2+}-selective polymer formed from **4** (Table 1). It is also important to note that in the *absence* of the competing Hg^{2+} ion very small amounts of the other competitor metal ions were removed from solution with demetallated **4**. This is especially dramatic for Cu^{2+} ions (0.83%; ionic radius, 0.72 Å), which were found to be highly selective when reintroduced into the *sandwich arrangement* of polymer **2** (initially Zn templated), where it was observed that ~2% Cu^{2+} ions were removed from acidic solution (pH 2, Cu:Fe = 240:1 vs. 4:1 in Table 1; 5−8% at pH 4.5).[3] This latter result may add some

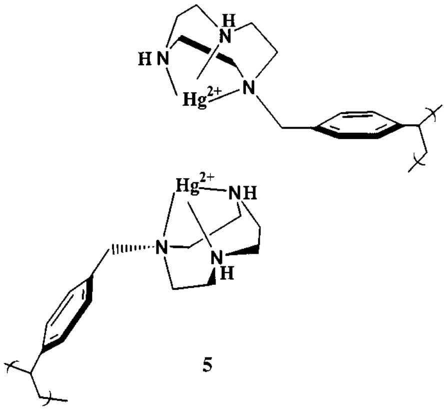
Table 1. Competitive metal-ion selectivity studies with the demetallated Hg^{2+} polymer

Metal ion[c]	In the presence of Hg^{2+} ions [$K_{Hg^{2+}/M^{n+}}$]	In the absence of Hg^{2+} ions
Hg^{2+}	15.6% (777.7 μmol/g)	–
Cd^{2+}	0.017% (1.5 μmol/g) [2.2×10^{8}]	not determined
Ag^{+}	0.008% (0.7 μmol/g) [9.8×10^{9}]	0.26% (24.1 μmol/g)
Pb^{2+}	0.063% (3.0 μmol/g) [1.6×10^{8}]	0.018% (0.87 μmol/g)
Cu^{2+}	0.030% (4.7 μmol/g) [6.7×10^{8}]	0.83% (130.6 μmol/g)
Fe^{3+}	0.18% (32.2 μmol/g) [1.9×10^{7}]	0.23% (41.2 μmol/g)

[a] Demetallated Hg^{2+} polymer (6 mg) and a mixture of metal ions (0.04 M each) were suspended in a stirring H$_2$O solution (10 mL) at room temperature for 18 h (pH = 2). The resulting polymer was washed thoroughly with H$_2$O and MeOH, and then dried in vacuo over P$_2$O$_5$ for 24 h. Inductive Coupled Plasma (ICP) was used for all the metal analyses. − [b] The reported numbers represent % metal ion by weight, and μmol/g of polymer (in parentheses) indicates the mol of each metal ion on the final collected polymer (per gram). − [c] The counter ion used for the selectivity studies was NO$_3^{-}$; therefore, Hg analysis for the sandwich Hg^{2+} polymer from polymerization of **3** (prior to demetallation) was back-calculated to be 8.3% instead of 7.66%, where the counter ion was OTf.

credence to the concept that the ionic radius of the template metal-ion has an effect on both the selectivity of reintroduced metal ions and on the ability of the polymeric TACN ligands to either maintain the sandwich arrangement (Zn^{2+}, Cu^{2+}) or to operate independently (Hg^{2+}).

Thus, our results suggest that the high selectivity for reintroduced Hg^{2+} ions might be better predicated on the basis of the thermodynamic stability of the complex between Hg^{2+} and the proposed polymeric arrangement of the demetallated TACN ligands, as shown in polymer **5**, as well as, to some extent, on the larger ionic radius.



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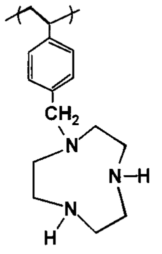
More importantly, as discussed, we were never able to synthesize a non-templated polymer of vinyl monomer **1** to compare to the templated polymer **2**. However, in order to overcome this dilemma, we found that simply anchoring a TACN ligand on a 6% crosslinked chloromethylated **PS-DVB** bead gave **PS-TACN** (0.7 mmol/g) with a statistical distribution of TACN ligands rather than a sandwich arrangement, which demonstrated a dramatically lower selectivity for Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Mn^{2+} ions, as well as a greatly diminished capacity (a ratio of 0.014!; ratio of Cu/Zn = 41:1 vs. 240:1 in polymer **2**).[4]



PS-TACN

In contrast, similar preliminary studies with **PS-TACN** and Hg^{2+} ions show high selectivity, as do all the polymer pendant ligands we have studied with Hg^{2+}.[5] Accordingly, the **PS-TACN** results further strengthen the concept of the spatial sandwich arrangement of TACN ligands in a templated polymer matrix being a novel method for the selectivity of metal ions of smaller ionic radius, as well as for the removal of higher capacities of those metal ions from aqueous solution, while also implicating the ionic radius in the apparent loss of the sandwich arrangement for a higher-than-expected Hg^{2+}-ion capacity. Additionally, other parameters could include the softness of the Hg^{2+} ion and its affinity for the relatively soft nitrogen atom (a thermodynamic effect with an equilibrium selectivity coefficient of $K > 10^7$), as well as the preorganized geometry of the TACN ligands in the surrounding coordination sphere.

It is interesting to note that the $[(TACN)_2Cd]^{2+}$ sandwich complex has been characterized by X-ray analysis[6] and shows Cd−N bond lengths of ~2.3 Å and a distance between the two TACN ligands of ~3.3 Å. This type of X-ray data may, in the future, provide more definitive information on the relationship between the ionic radius of the template metal-ion and the TACN:metal ratio of the reintroduced metal ions. Moreover, tying the two *N*-(4-vinylbenzyl)TACN ligands together with an appropriate sized tether might prevent the TACN ligands from operating independently with larger sized metal ions. Finally, the application of these TACN-templated polymers in environmental remediation studies, especially for highly selective Hg^{2+} ion removal from acidic waste streams containing benign metal ions such as Fe^{3+}, as well as for Hg^{2+}-ion sensor applications, will be pursued in the future.[7]

Experimental Section

***N*-(4-vinylbenzyl)-1,4,7-triazacyclononane, 1:**[8] A 50-mL 2-necked Schlenk flask equipped with a J-coiled condenser was charged with TACN (500.0 mg, 3.87 mmol), followed by the addition of EtOH (12 mL, deoxygenated), and the second neck was capped with a septum. $LiOH\cdot H_2O$ (35.8 mg, 0.85 mmol) in 5 mL of deoxygenated H_2O was then added in one portion to this stirring mixture through the septum. The resulting solution was slightly cloudy and was allowed to stir at 50 °C in an oil bath for 2 h, after which time the septum was replaced with an addition funnel, and 4-vinylbenzyl chloride (115.0 mg, 0.75 mmol) in 5 mL of EtOH was added dropwise to the reaction flask through this funnel under N_2. The reaction mixture was refluxed under N_2 and the course of the reaction was followed by TLC (EtOAc/MeOH = 2:3 with a drop of Et_3N). After 3 h, the reaction mixture was concentrated on a rotary evaporator to ~5 mL. About 15 mL of H_2O was added to the residue and CH_2Cl_2 (25 mL × 3) was used to extract the product. The combined CH_2Cl_2 extracts were then washed with brine (20 mL) and dried with Na_2SO_4, filtered, and the collected filtrate was concentrated on a rotary evaporator to ~10 mL. The impurity was removed by adding a small amount of pentane to the resulting CH_2Cl_2 solution until a cloudy suspension was observed. The mixture was then allowed to sit at room temperature for 15 min., and any precipitate or suspension was filtered off. The process was repeated three times until no appreciable cloudiness was observed upon the addition of pentane. The solution was then concentrated to ~ 1 mL and pentane was used to solidify the desired compound upon removing the solvent on a high vacuum line. The obtained solid was further dried in vacuo over P_2O_5 to give the title compound as a pale-yellow, foamy solid (144.2 mg, 78%). If the product did not solidify after the removal of solvent, more pentane was added to the resulting residue along with a small amount of CH_2Cl_2 and the solvent was removed on a high vacuum line. Another alternative to solidify the product was by using Et_2O instead of pentane. The title compound (mp 58−60 °C) was hygroscopic and was kept in the freezer, and in the dark.

[{*N*-(4-vinylbenzyl)-1,4,7-triazacyclononane}$_2$Hg](OTf)$_2$, 3: Compound **1** (169.6 mg, 691.2×10^{-3} mmol) was placed in a 100-mL round flask, followed by the addition of MeOH (25 mL, deoxygenated). An addition funnel was then connected to the top of the flask and Hg(OTf)$_2$ (172.0 mg, 344.8×10^{-3} mmol) in 10 mL of MeOH (deoxygenated) was added dropwise to the reaction flask through the addition funnel over 30 min. in the dark. The flask was then covered with aluminum foil. Upon the addition of Hg(OTf)$_2$ solution, some cloudiness was observed. The reaction was allowed to stir at room temperature for 48 h, and any insoluble species were filtered off. The solvent was removed from the filtrate on a high vacuum line to give a foamy, pale-yellow solid. This solid was transferred into a N$_2$-filled glove box, and ~3 mL of MeOH was added to make a solution. The resulting solution was slightly cloudy, and some insoluble species were observable. A small amount of Et$_2$O was then added until the solution turned cloudy. The resulting mixture was allowed to sit at room temperature for 2 min., and precipitate was filtered off over a Celite bed. This process was repeated three times, and the solvent of the final filtrate was removed on a high vacuum line to yield an off-white foamy solid, which was further dried in vacuo over P$_2$O$_5$ to give the title complex in 70% (238.1 mg) yield. The title complex was found to be light sensitive, and demercuriation occured upon exposing a solution of the title complex to light and air for a long time.

^{1}H NMR (400 NMR,CD$_3$OD) $\delta = 7.47-7.30$ (m, 8 H), 6.73 (dd, *J* = 10.9, 17.5, 2 H), 5.77 (d, *J* = 17.5, 2 H), 5.23 (d, *J* = 10.9, 2 H), 3.84 (s, 4 H), 3.10−2.74 (m, 24 H). − FAB/MS (*m*-nitrobenzyl alcohol) *m*/*z* (%) = 990 (1) [M$^+$]. − $C_{32}H_{46}F_6HgN_6S_2O_6 \cdot 9H_2O \cdot 2CH_3OH$: calcd. C 33.6, H 5.98, N 6.91; found C 34.3, H 6.20, N 6.26.

Table 2. Polymerization[3] of monomer **3**

Monomer **3** (M)	Cross-linker[b]	Conv. (%)[c]	Polymer **4**[d]
0.045	DVB/EVB 0.180	40	Monomer/ Cross-linker 1:1.6

[a] Polymerization in MeOH with 0.006 M AIBN at 78 °C overnight. − [b] Contained 80% divinylbenzene (DVB) and 20% ethylvinylbenzene (EVB). − [c] Based on DVB/EVB. − [d] C 72.57, H 7.22, N 3.52, Hg 7.76; TACN:Hg ratio is 2.1:1, 7.66% Hg (ICP). TACN capacity is 0.84 mmol/g of resin.

Acknowledgments

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[1] [1a] G. Wulff, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1812. − [1b] G. Wulff, in *Biomimetic Polymers* (Ed.: C. G. Gebelein), Plenum Press: New York. **1990**, p. 1. − [1c] G. Wulff, in *Polymeric Reagents and Catalysts* (Ed.: W. T. Ford), ACS Symposium Series 308, American Chemical Society, Washington, **1986**, p. 186. − [1d] K. Mosbach, *Trends Biochem. Sci.* **1994**, *19*, 19 and references therein. − [1e] K. Shea, *Trends Polym. Sci.* **1994**, *2*, 166 and references therein. − [1f] *Molecular and Ionic Recognition with Imprinted Polymers* (Eds.: R. A. Bartsch and M. Maeda), ACS Symposium Series 703, American Chemical Society, Washington, DC, **1998**, and chapters and references therein.

[2] [2a] A. D. Pomgailo, V. S. Savost′yanov, *Synthesis and Polymerization of Metal- Containing Monomers*, CRC Press: Boca Raton, **1994**, p. 134 and references therein. − [2b] P. K. Dahl, F. H. Arnold, *Macromolecules* **1992**, *25*, 7051. − [2c] T. Rosatzin, L. I. Andersson, W. Simon, K. Mosbach, *J. Chem. Soc., Perkin Trans. 2* **1991**, 1261. − [2d] S. N. Gupta, D. Neckers, *J. Poly. Sci. Polym. Chem. Ed.* **1982**, *20*, 1609. − [2e] W. Kuchen, J. Schram, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1695. − [2f] H. Nishide, J. Deguchi, E. Tsuchida, *Chem. Lett.* **1976**, 169. − [2g] H. Nishide, E. Tsuchida, *Makromol. Chem.* **1976**, *177*, 2295. − [2h] M. Kato, H. Nishide, E. Tsuchida, T. Sasaki, *J. Polym. Sci. Polym. Chem. Ed.* **1981**, *19*, 1803. − [2i]M. Biswas, A. Mukherjee, in *Advances in Polymer Science*, Springer Verlag, Berlin Heidelberg, **1994**, vol. 115, p. 89 and references therein. − [2j] X. Zeng, G. M. Murray, *Sep. Sci. Technol.* **1996**, *31*, 2403.

[3] H. Chen, M. M. Olmstead, R. L.Albright, J. Devenyi, R. H. Fish, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 642.

[4] R. H. Fish in ref.[1f], chapter 16, p. 238.

[5] S.-P. Huang, K.J. Franz, E. H. Arnold, J. Devenyi, R. H. Fish, *Polyhedron* **1996**, *15*, 4241.

[6] H. Strasdeit, A.-M. Duhme, M. Weber, S. Pohl, *Acta Crystallogr., Sect. C* **1992**, *48*, 437.

[7] T. F. Baumann, J. G. Reynolds, G. A. Fox, *Chem. Commun.* **1998**, 1637 and references therein.

[8] Revised synthetic procedure for **1** (see reference 3 for all analytical data for **1**, and the polymerization procedure used for the preparation of polymer **4**).

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