Enantioselective Sol–Gel Materials Obtained by Either Doping or Imprinting with a Chiral Surfactant**

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The formation of chiral porous materials is an on-going quest because of the numerous applications of such materials in separation science, chiral catalysis, and in pharmaceuticals and so forth. Here, we describe two new methods for preparing bulk chiral silica materials, based on the use of a chiral surfactant. By one method the surfactant is used for the imprinting of chiral porosity, and by the second method we use the entrapped surfactant molecules as chiral centers within the silica. The chiral entity in the two types of matrices is different and therefore the enantioselective preferences before and after surfactant removal are not necessarily the same; indeed it was found that chiral discrimination changes before and after surfactant removal. Notably, these adsorbents are capable of recognizing chirality in molecules that have no structural similarity to the imprinting molecule. An additional attractive feature of these materials is their ability to enantioselect in both aqueous media and organic solvents. Specifically, phenylated silica sol–gel (PSG) matrices were doped with the chiral cationic surfactant, (–)-N-dodecyl-N-methylephedrinium bromide (DMB, 1, Scheme 1), and then the DMB was extracted with methanol. The powdered silica matrix was thus rendered chiral both before and after surfactant removal: before, by virtue of the entrapped chiral surfactant within the matrix; and after surfactant removal by forming chiral cavities. Both types of matrices showed general enantioselectivity by preferential adsorption of one enantiomer over several other molecules which are different from the surfactant. The pairs of enantiomers included (R)- and (S)-propranolol (2), (R)- and (S)-binaphthyl-2,2-diy hydrogenphosphate (BINAP) (3), and (R)- and (S)-naproxen (4). In all cases good enantioselectivities were observed, both for the chiralily imprinted powdered monoliths and for the chirally doped ones, with discrimination ratios in the range of 1.22–1.34. The chiral entity in the two types of matrices is different and therefore the enantioselective preferences before and after surfactant removal are not necessarily the same, as indeed was found to be the case. The fact that the discrimination changes before and after surfactant removal attests to the authenticity of the observed enantioselectivity in the two types of chiral materials.

It is in order to cite some relevant background references now: Enantioselectivity towards the enantiomers of the imprinting molecule is more common** than enantioselectivity towards molecules different than the imprinting one, but which are still related to it. Thus, enantioselectivity towards morphine derivatives different than the imprinting derivative was demonstrated by Becket et al.* and by Bartels et al.* for silica prepared from sodium silicate. Enantioselective recognition of structurally related enantiomers is also known for organic polymers. We reiterate here that the enantioselectivity shown in this report is towards unrelated molecules. In another type of study Izutsu et al.* impregnated the pores of silica with l-tartaric acid, and they were able to separate chiral Co complexes on it. As for the entrapment of surfactants in sol–gel materials, this was extensively researched by Levy et al.*, Rottman et al., Frenkel-Muller and Avnir,* Brinker and co-workers, and Stucky and co-workers.* One of the more interesting findings has been that the surfactant can significantly modify the cage properties, and therefore also the co-dopant properties and specific functionalities.* In this work it was reported that the transition between the surfactant monomer and aggregated forms develops continuously within the matrix without an abrupt phase transition (e.g., into micelles, as found in solution), an observation we use below. Another highly important research area in which surfactants have played a key role in sol–gel materials is the preparation of periodically ordered mesoporous structures.* Surfactants have been extensively used in these template-directed syntheses, due to their ability to organize in typical structures such as micelles, rods, vesicles, and lamellae. The technological potential of employing surfactants as structure-directing agents has been implemented in many applications such as in adsorptions and separations, catalysis, sensing, and for ion-exchange. To conclude this background we mention that chiral surfactants are of course widely used in chemistry and some of the many examples include chiral catalysis by micellar electrokinetic chromatography and synthesis of helical materials. As for our own lab, we have shown that chirally imprinted sol–gel-derived thin films exhibit enantioselectivity and, for instance, reported recently surfactant-imprinted films that enantioselect between enantiomer pairs not used for the imprinting. Two important potential applications—chiral chromatography and chiral catalysis of the thin films require the conversion of the thin-films imprint-