potential to provide access to complex and diverse small molecules efficiently.

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[15] The stereochemistry of the acetoxides (43 and 44) was established by analysis of NOE data (see Supporting Information).
[16] Cleavage of 100 beads containing the diol derived from oxidation of 51 provided 5.5 mg of crude 52 which was estimated to be >70% pure on inspection of the 'H NMR data (see Supporting Information).

Microporous Supramolecular Coordination Compounds as Chemosensoric Photonic Lattices**

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Chemical sensing—whether for human health assessment, environmental quality monitoring, or myriad other purposes—generally entails: a) recognition and binding, adsorption, or other interaction with the molecule or ion to be sensed, and b) transduction of the recognition/bindng event into an externally observable signal. Coordination-based supramolecular chemistry, with its ability to generate an enormous

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variety of rigid framework assemblies featuring well-defined nanoscale cavities[2–3] holds considerable promise for the recognition/binding phase of small-molecule sensing. With these and other chemosensory assemblies or materials, transduction is typically achieved by altering the color, luminescence intensity, redox potential, or other observable property unique to the assembly or analyte. This venerable strategy is indeed effective, but it imposes an additional sensor-design criterion that may or may not be easy to incorporate. Furthermore, the chosen transduction strategy may be difficult to generalize. We report here proof-of-concept sensing of both volatile and condensed-phase analyte molecules by using recently developed microporous supramolecular coordination compounds, in which signal transduction is achieved by a chemically universal technique based on modulated diffraction of visible light by a photonic lattice composed of the chemosensory material.

The supramolecular assembly 1 was used as a building block for the fabrication of microporous thin films.[4] The compound was obtained in a single step in quantitative yield from [ReCl(CO)5] and the difunctional porphyrin ligand by a process best described as directed assembly. Ignoring, for the moment, torsional motion around the rhenium/bridging ligand/rhenium axes, the assembly defines an open-ended moment, torsional motion around the rhenium/bridging ligand axis, the assembly defines an open-ended moment, torsional motion around the rhenium/bridging ligand axis.

X-ray crystal structures of related compounds show that they generally pack with cavities aligned to form semi-infinite one-dimensional channels.[2a,b,5] We have shown that thin films of 1 are excellent condensed-phase molecular sieves that completely exclude a 24 Å-diameter probe molecule but allow 15 Å-diameter and smaller probe molecules to permeate rapidly.[6] Important here is the absence of potentially channel blocking counterions (1 is electrically neutral). The cavities or channels instead contain only solvent. Notably, the coordination chemistry is sufficiently robust that removal of the weakly bound solvent molecules does not collapse the cavities; instead they can be repeatedly emptied and refilled without loss of nanoscale porosity. The absence of counterions also renders the compounds completely insoluble in water, a useful property for many sensing applications.

Periodic lattice structures—the basis for optical sensing—were obtained by micromolding in capillaries, a soft lithography method developed by Whitesides et al.[8] Briefly, a micropatterned elastomeric stamp was prepared by spreading a polymer precursor over a lithographic master (an atomic force microscopy (AFM) calibration grid) and allowing the polymer to cure. The stamp was then placed on a puddle consisting of a dilute (ca. 0.5 mM) solution of 1 in chloroform, typically on a glass platform. Slow solvent evaporation in a chloroform-rich atmosphere yielded a square-perforated grid composed of 1, which covered a few square millimeters and contained several thousand perforations. From AFM images (Figure 1), each perforation measures 9.8 × 9.8 μm with an average depth of 155 nm.

![AFM image of a portion of a micropatterned thin film of 1 on glass. The image was obtained in tapping mode.](image)

The observed lattice periodicity is appropriate for diffraction of visible light, as shown schematically in Figure 2 for coherent light of wavelength 633 nm from a He:Ne laser. The characteristic diffraction pattern is also easily observable by the naked eye on illumination with a simple laser pointer (diode laser with λ ≈ 680 nm). In the thin-film limit, the diffraction efficiency (DE) depends quadratically on the degree of refractive index contrast Δn between the photonic lattice and the surrounding medium—in this case either air (essentially vacuum, n1 = 1), or water (n2 = 1.33). Index-matching experiments indicate a refractive index of about 1.7 for the lattice material itself, whereby the high value is due in part to an off-resonance enhancement effect associated with the extraordinarily high extinction coefficient of the molecular square (ε_max = 1.1 × 10^9 M⁻¹ cm⁻¹).

Given an estimated void volume of greater than 50%, the lattice is best viewed as a composite of coordination compound and vacuum, with an effective refractive index n_eff that is a volume-weighted average of the indices of the two components. Uptake of a molecular guest fills some of the vacuum and creates a ternary lattice/vacuum/guest composite with a refractive index that differs from the index of the simple lattice/vacuum composite. The guest-induced change in refractive index for the composite will change the degree of contrast and change DE. Figure 3 illustrates the response of a
lattice of 1 to each of three volatile organic guest molecules in a nitrogen atmosphere. Also shown are data from a series of quartz-crystal microgravimetry measurements designed to assess the quantitative validity of the photonic lattice-diffraction technique. The comparison reveals nearly quantitative agreement, and also illustrates the sensitivity of the diffraction method. A more detailed consideration reveals that, for each of the guests, the first four guest molecules are bound more strongly than the rest. For pyridine as a guest, the first four molecules are bound about 100 times more strongly, and electronic absorption measurements indicate, as expected, that the preferential binding entails axial ligation of the four available Zn sites in the walls of the square. With the exception of that from the four strongly bound imine groups, the diffraction response is rapidly reversed upon removal of the analyte.

Since all molecules have refractive indices greater than unity, that is, higher than that of vacuum, any molecule that can be bound or absorbed by a vacancy-containing lattice will increase $n$, increase $\Delta n (= n_2 - n_1)$, and increase DE. In principle, therefore, the photonic lattice-diffraction technique is a chemically universal sensing technique. Most molecules also have refractive indices that exceed that of water, and this suggests sensing in aqueous phases by means of displacement of water by guests having an affinity for the nanoscale cavities. We found, for example, that the model compound, 2,4,6-tris(4-pyridyl)-1,3,5-triazine (2) when present in water at submillimolar concentrations, can be readily sensed in this way, where the driving forces for guest uptake by the supramolecular lattice material are diminution of hydrophobic interactions and, as noted above for vapor-phase sensing, creation of Zn/pyridine Lewis acid/Lewis base interactions (formation of weak coordinative bonds).

Modification of 1 by incorporation of 5,10,15,20-tetrapyridylporphyrin to create assembly 3 eliminates the sensitivity of the lattice to the aqueous analyte, both by blocking zinc binding sites and by sterically limiting access to cavities and channels. However, the vapor-phase sensitivity to small organic compounds that can negotiate the smaller cavity entry ports is retained.

Finally, chemical tailoring of the nanoscale cavities, for example, by incorporation of receptor groups with high affinities for specific ions or molecules, opens up tremendous...
possibilities for constructing highly specific photonic lattice based sensors or arrays of sensors. Using porphyrinic zinc(ii) as an anchoring site, we have prepared more than 100 cavity variants,[13] several of which are chiral.[12] For example, cavity functionalization with tris(2-aminoethyl)amine renders lattices of 1 responsive to aqueous Zn\textsuperscript{II} ions, whereas functionalization with 1,6-hexanediol enhanced the lattice response to molecular iodine by a mechanism involving formation of a charge-transfer complex. As we will show elsewhere, photonic lattice sensitivity and selectivity can also be enhanced, in many cases, by making diffraction measurements under resonance conditions, that is, at optical wavelengths coincident with lattice-based electronic transitions.

In summary, microporous molecular materials, obtained by directed coordinative assembly methods, have been used to construct chemoresponsive photonic lattices capable of functioning as chemical sensors. The photonic lattice method is, in principle, a chemically general method that requires only that the target molecule or ion contain polarizable electrons. We are currently exploring in a more general way the utility of the target molecule or ion contain polarizable electrons. We are currently exploring in a more general way the utility of the method for imparting enhanced sensitivity and selectivity to microporous molecular materials. We also are evaluating the applicability of the photonic lattice methodology to problems involving other kinds of lattice materials.[14]

Experimental Section

Compound 1 and assembly 3 were prepared as described previously.[16,14] Compound 2 was prepared according to the literature method.[14] Micro-patterned films, prepared as described above, were stored in a vacuum desiccator overnight prior to use in sensing experiments. Films for QCM studies were prepared by passing a saturated solution of 1,6-hexanediol enhanced the lattice response to molecular iodine by a mechanism involving formation of a charge-transfer complex. As we will show elsewhere, photonic lattice sensitivity and selectivity can also be enhanced, in many cases, by making diffraction measurements under resonance conditions.

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[9] The diffraction experiment was calibrated by normalizing versus the QCM response for one of the analytes at one concentration, and then employing the same normalization factor for other concentrations and other analytes. Thus, we ignore differences in refractive indices for the various analytes. In principle, the expected absolute chemo-response in the diffraction experiment can be calculated on the basis of knowledge of the absolute diffraction efficiency, the fractional void volume of the microporous material, the lattice thickness, the refractive index of the analyte, and the potentially wavelength dependent refractive indices of the empty and analyte-filled lattice material. By using a combination of measurements and best guesses for these quantities, we find that the absolute diffraction responses in Figure 3 are about two times smaller than anticipated. The basis for the discrepancy is unclear, but it may simply reflect errors in estimates for some of the required input parameters.

[10] Control experiments with lattices composed of a “corner” complex lacking large square cavities ([ReCl(CO)\textsubscript{3}] ligated to a pair of pyridylporphyrins) revealed strongly diminished capacities for guest uptake.


