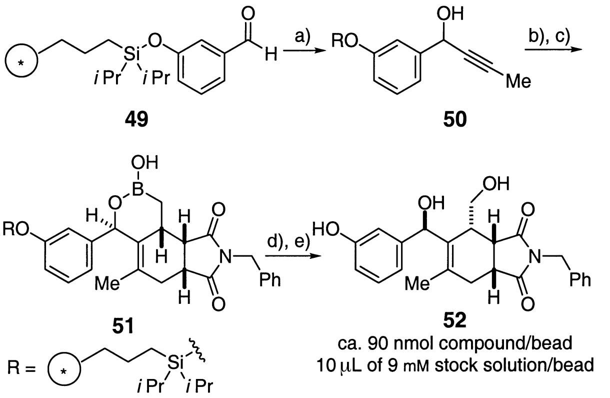

Scheme 4. Boronic ester annulation/Diels–Alder cycloaddition sequence performed on the high capacity bead-linker reagent used in a one-bead, one-stock solution platform for chemical genetics. a) 1-propynylmagnesium bromide, THF, 0 °C → RT; b) **4** (10 equiv), **5** (15 mol %), CH_2Cl_2, 40 °C; c) *N*-benzylmeleimide (8 equiv), PhMe, 80 °C; d) H_2O_2, NaOH, THF; e) HF · pyr/pyr, THF. pyr = pyridine.

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

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[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 ^1H NMR data (see Supporting Information).

Microporous Supramolecular Coordination Compounds as Chemosensory 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/binding event into an externally observable signal.[1] Coordination-based supramolecular chemistry, with its ability to generate an enormous

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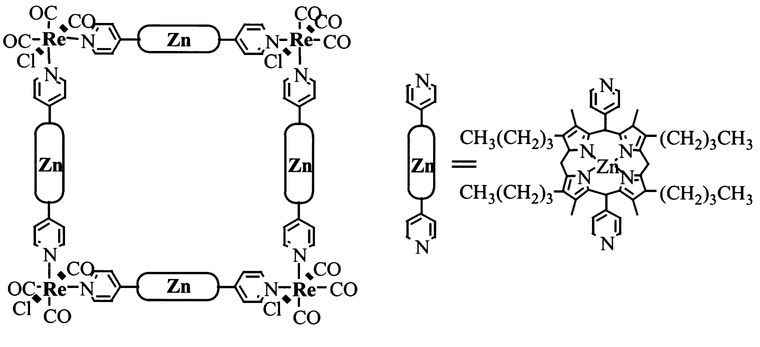
variety of rigid framework assemblies featuring well-defined nanoscale cavities,[2, 3] holds considerable promise for the recognition/binding phase of small-molecule sensing. With these and other chemosensory assemblies or materials, transduction is typically achieved by altering the color, luminescence 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 nanoscale box with a cavity of approximate dimensions 18 × 18 × 18 Å. 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.[4b] 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.



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Periodic lattice structures—the basis for optical sensing—were obtained by micromolding in capillaries, a soft lithography method developed by Whitesides et al.[6] 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.

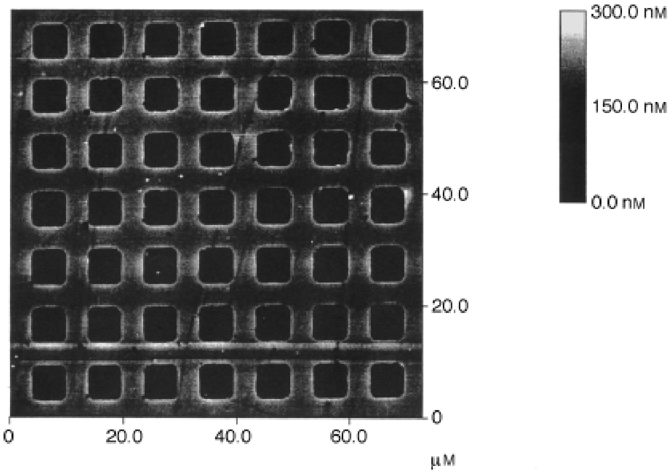


Figure 1. AFM image of a portion of a micropatterned thin film of **1** on glass. The image was obtained in tapping mode.

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 $\lambda \approx 680$ 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[7]—in this case either air (essentially vacuum, $n_1 = 1$), or water ($n_1 = 1.33$). 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 ($\varepsilon_{max} = 1.1 \times 10^6\,\text{M}^{-1}\,\text{cm}^{-1}$).

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_2 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

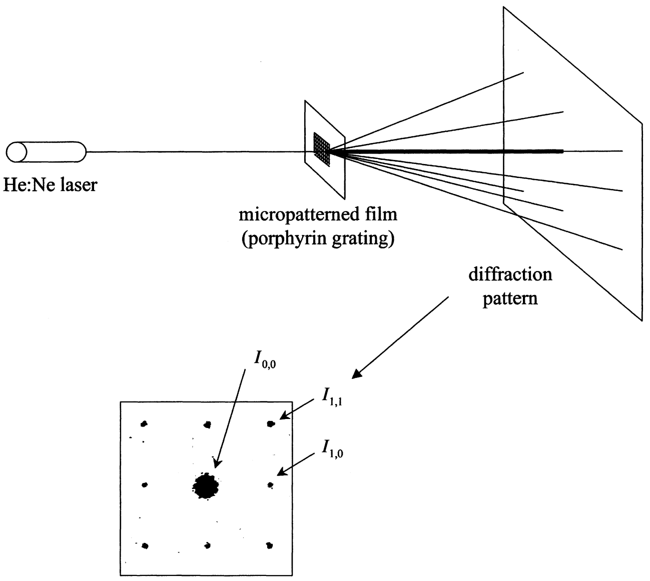


Figure 2. Schematic representation of lattice diffraction. The image shown is of a diffraction measurement made on a micropatterned thin film of **1** with a 633-nm source. The center spot, labeled $I_{0,0}$, corresponds to undiffracted light, whereas the points labeled $I_{1,0}$ and $I_{1,1}$ are one- and two-dimensional first-order diffraction spots. An expanded image (not shown) readily reveals multiple higher-order diffraction spots.

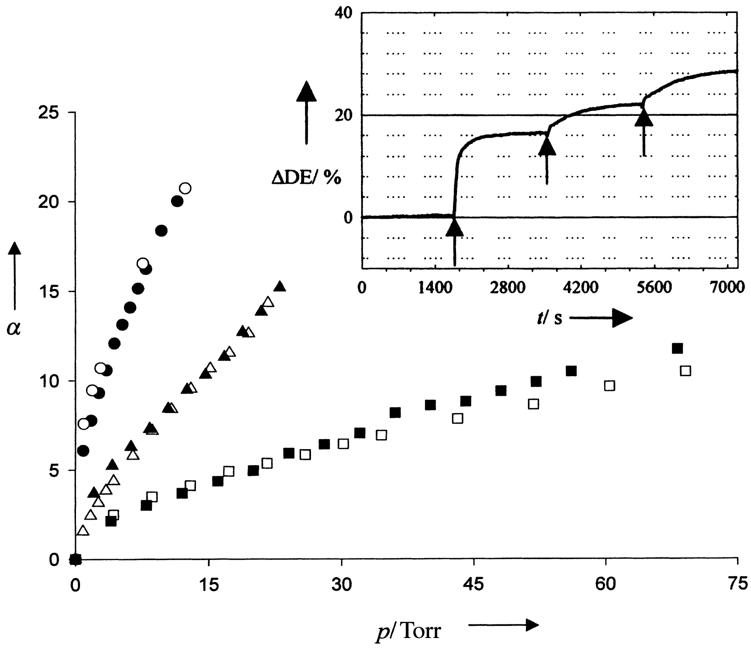
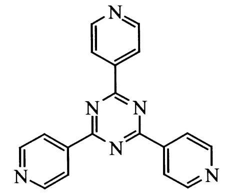


Figure 3. Thin-film sensor response expressed as number of guest molecules α taken up per molecular square **1**. Filled symbols correspond to photonic lattice diffraction measurements; empty symbols correspond to QCM measurements. Key to analytes: ■ = benzene, ▲ = dioxane, ● = pyridine. Inset: Time response of thin-film sensor expressed as percentage change in initial diffraction efficiency. Arrows correspond to consecutive 7-Torr increases in the vapor pressure of pyridine.

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[8] 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.[9, 10] 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^{II} 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_2, increase Δn $(=n_2-n_1)$, 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^{II}/pyridine Lewis acid/Lewis base interactions (formation of weak coordinative bonds).



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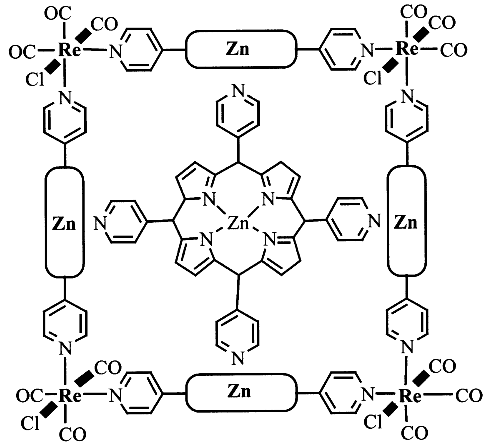
Modification of **1** by incorporation of 5,10,15,20-tetrapyridylporphyrin[4a] to create assembly **3** eliminates the sensitivity of the lattice to the aqueous analyte, both by blocking zinc binding sites and by sterically limiting access to cavities and channels. However, the vapor-phase sensitivity to small organic compounds that can negotiate the smaller cavity entry ports is retained.



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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,[11] several of which are chiral.[12] For example, cavity functionalization with tris(2-aminoethyl)amine renders lattices of **1** responsive to aqueous Zn^{II} ions, whereas functionalization with 1,6-hexanedithiol 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 cavity tailoring 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.[13]

Experimental Section

Compound **1** and assembly **3** were prepared as described previously.[4a,c] Compound **2** was prepared according to the literature method.[14] Micropatterned 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** in chloroform through a 0.45 μm polytetrafluoroethylene membrane (Osmonics) and then adding the solution by syringe to the gold-coated "keyhole" section of a quartz crystal (5 MHz resonator; AT-cut). Both sides of the crystal were coated. Samples were similarly desiccated prior to use. Average QCM film thicknesses (typically 100–400 nm) were determined by assuming close packing within films, redissolving films of known area in dichloromethane, and determining the total number of moles present by electronic absorption measurements. QCM measurements were performed in a sealed glass cell resistant to adsorption and absorption of volatile organic chemicals by using a home-built instrument that has been described previously.[15] Samples were introduced by syringe through a tight-fitting screw cap with a Teflon-lined septum. Diffraction measurements were performed by using the output of a He:Ne laser and recording and then ratioing the intensity of one of the first-order diffraction beams to that of the undiffracted beam. Ratioing diminishes the effects of noise and source-power variations, as well as variations in optical loss due, for example, to subtle changes in sample scattering upon analyte uptake. Intensities were recorded with photodiodes and then digitized and processed by using a module written in-house with Labview software (National Instruments, Austin, Texas). The typical resolution for Δn in these measurements was 5×10^{-4}, a value that could be significantly improved by using a mode-stabilized (power-stabilized) source and by thermostatic control of the detectors. AFM measurements were recorded with a Digital Instruments Bioscope operating in tapping mode.

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[10] Control experiments with lattices composed of a "corner" complex lacking large square cavities ([ReCl(CO)$_3$] ligated to a pair of pyridylporphyrins) revealed strongly diminished capacities for guest uptake.

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