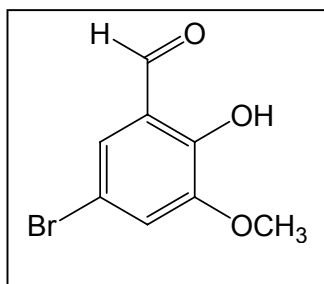


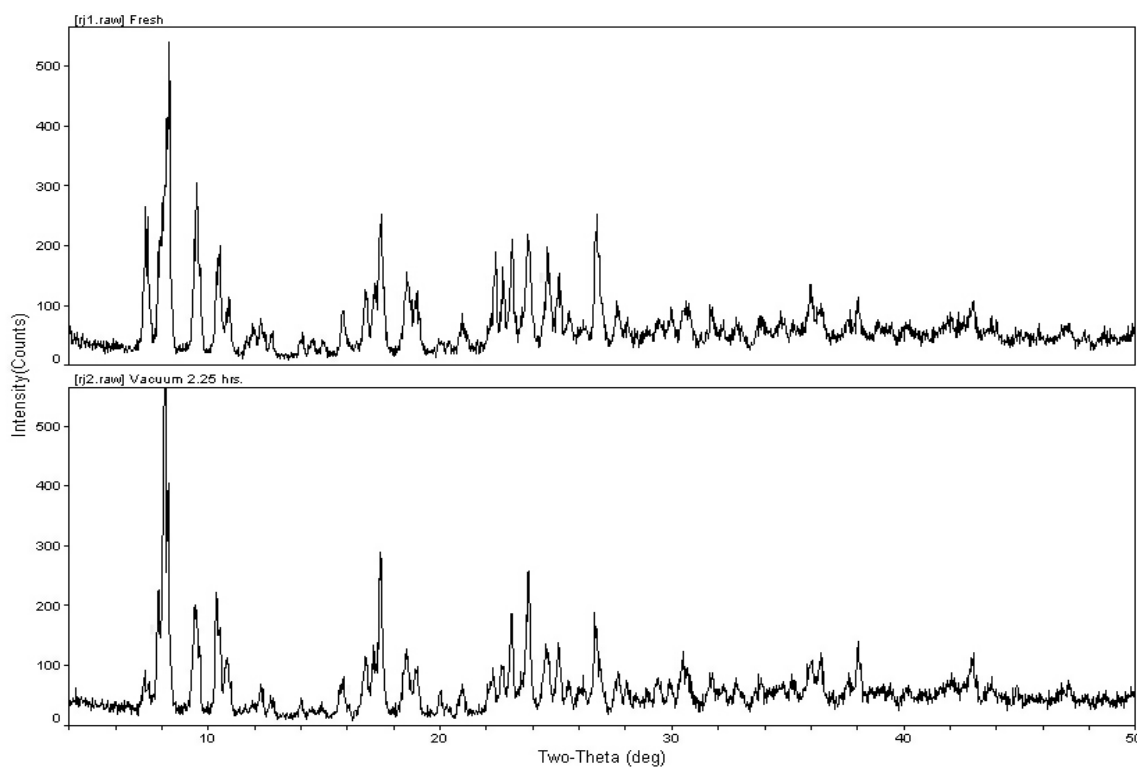
**Reversible Guest Molecule Encapsulation in the 3-D Framework of a
Heteropolynuclear Luminescent Zn_4Eu_2 Cage Complex**

Xiaoping Yang, Benjamin P. Hahn, Richard A. Jones,*
Keith J. Stevenson,* J. Steven Swinnea and Qiaoyin Wu

Supplementary Material



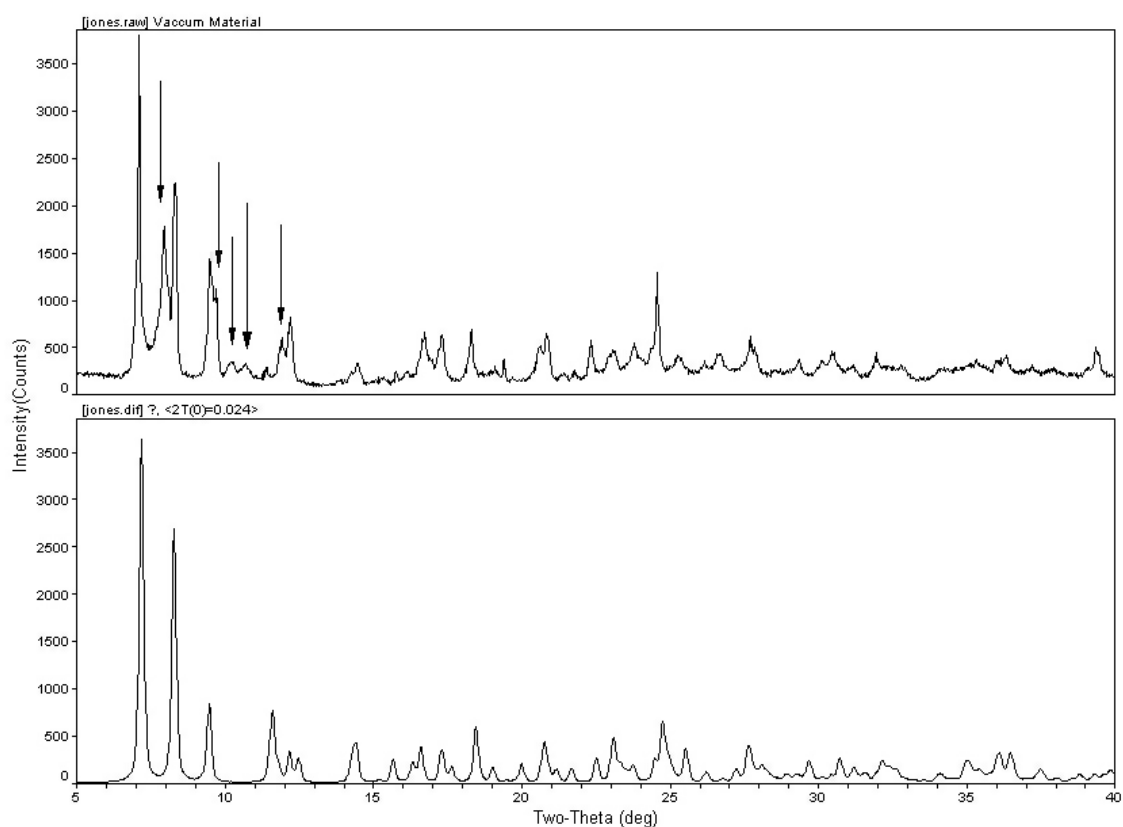
Scheme: HL = 5-bromo-3-methoxysalicylaldehyde



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Figure S1. Powder XRD patterns of 1: Freshly ground (bottom) and after exposure to vacuum (10^{-2} torr) for 2.5 hours (top). Data were collected on a Scintag theta/theta diffractometer fitted with a Cu radiation source and a solid-state detector set to count only Cu K-alpha radiation.



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Figure S2. Powder XRD patterns of 1: Pattern generated from single crystal X-ray data (bottom) and after exposure to vacuum (10^{-2} torr) for 2.5 hours (top). Arrows in the top pattern indicate lines not present in the simulated pattern. The simulated pattern was generated using Jade version 7.0 (Materials Data Inc).

QCM Studies

Experimental Procedure

For QCM measurements, a small quantity of the Zn_4Eu_2 cage complex (**1**), (1.2×10^{-8} mol), was drop-cast onto a gold-titanium 9.995 MHz AT-cut quartz crystal (International Crystal Manufacturing Co., Inc., Oklahoma). Acetonitrile solvent was removed from the host material by placing the crystal under vacuum (2 h). All QCM measurements were conducted inside a home-built gas delivery cell connected to a CH 440 Time-Resolved Electrochemical Quartz Crystal Microbalance (CH Instruments, Texas). Briefly, the crystal sat on an adjustable platform that was sandwiched between two Teflon pieces that could be screwed into place. A glass chamber with a septum was connected to one of the Teflon pieces via an o-ring. All QCM coated crystals were equilibrated in the evacuated gas delivery cell for several hours prior to VOC injections. During each VOC injection trial, the crystal was allowed to oscillate freely, with no VOC injections occurring, for the first 100 seconds of the experiment; this time region was used as a baseline, and a baseline correction was conducted on all QCM measurements. VOCs were introduced in 1 μ l increments through the septum using a 10 μ l gastight syringe (Hamilton Co., Nevada).

Results/Discussion

The quartz crystal microbalance (QCM) is a proven nanogravimetric method for detecting the mass of guest vapor that distributes into a mesoporous host material¹. The Sauerbrey equation 1 relates a change in frequency of the quartz crystal to a change in

mass, where f_0 is the resonant frequency, Δm is the change in mass, A is the working area of the electrode, μ_q is the quartz shear modulus, ρ_q is the density of quartz, and Δf is the change in frequency².

$$[1] \quad \Delta f = \frac{-2f_0^2 \Delta m}{A(\mu_q \rho_q)^{0.5}}$$

This relationship can be reduced to equation 2, where C_f is the proportionality constant relating the change in frequency to a change in mass.

$$[2] \quad \Delta f = -C_f \Delta m$$

For these experiments, the theoretical sensitivity for a 9.995 MHz AT-cut quartz crystal with a 0.2047 cm² electrode area (1.105 Hz/ng) was used as the proportionality constant.

Preliminary studies suggest that diethyl ether and methanol both interact with the mesoporous Zn₄Eu₂ framework upon exposure to the material (Figures 1 and 2). In contrast to weak, non-specific binding (i.e. van der Waals forces), the presence of true host-guest interactions can be confirmed by saturating the host, as there are only a finite number of available sites with which the guest can fill or bind to. Using the frequency shift (Δf_v) determined by the QCM, experimental, or apparent partition coefficients, (K_{exp}), can be calculated from eq. 3 where ρ is the density of the host, C_v is the vapor phase VOC concentration, and Δf_s is the frequency shift of the QCM crystal due to the application of the host complex³.

$$[3] \quad K_{\text{exp}} = \frac{\Delta f_v \rho}{\Delta f_s C_v}$$

Sorption isotherms plotted as a function of the experimental partition coefficient times the guest molecular weight, $K_{\text{exp}} * \text{MW}$, versus normalized partial pressure (P/P_0) of VOC are shown in Figs. 3 and 4⁴. QCM frequency responses extracted from our experiments are consistent with typically observed values for other permeable host materials⁵. It should be noted that acoustic wave devices, such as the QCM and surface acoustic wave (SAW) sensor, have in many cases, been observed to report experimental K values several times higher than K values determined by other methods^{3,6}. Nevertheless, experimental partition coefficients determined using nanogravimetry can be used successfully to plot isotherms demonstrating sorption with a host complex. In this report, we have found that both ether and methanol show a decrease in slope of $K_{\text{exp}} * \text{MW}$ vs. P/P_0 as more of each respective VOC is injected into the QCM chamber, promoting our thesis that a selective host-guest interaction exists between the VOC's ether and methanol with the Zn_4Eu_2 cage complex.

References

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Supplementary Material (ESI) for Chemical Communications
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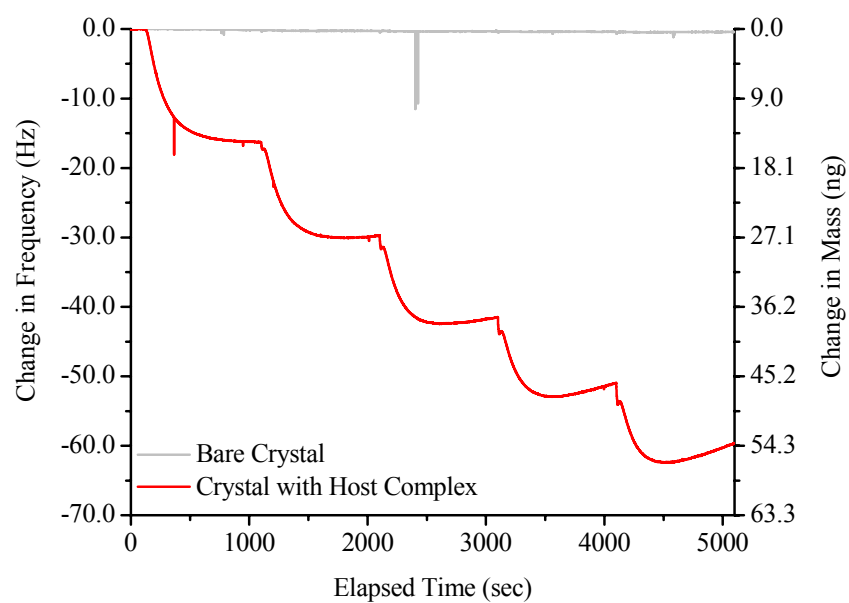


Figure S3. QCM response of the host complex, $[\text{Eu}_2\text{Zn}_4\text{L}_4(\text{OAc})_6(\text{NO}_3)_2(\text{OH})_2]$, to $1 \mu\text{l}$ injections of the guest VOC diethyl ether. The frequency dampening of a crystal coated with the host material (red) is compared to the response of a bare QCM crystal to Et_2O injections at the same time interval (gray).

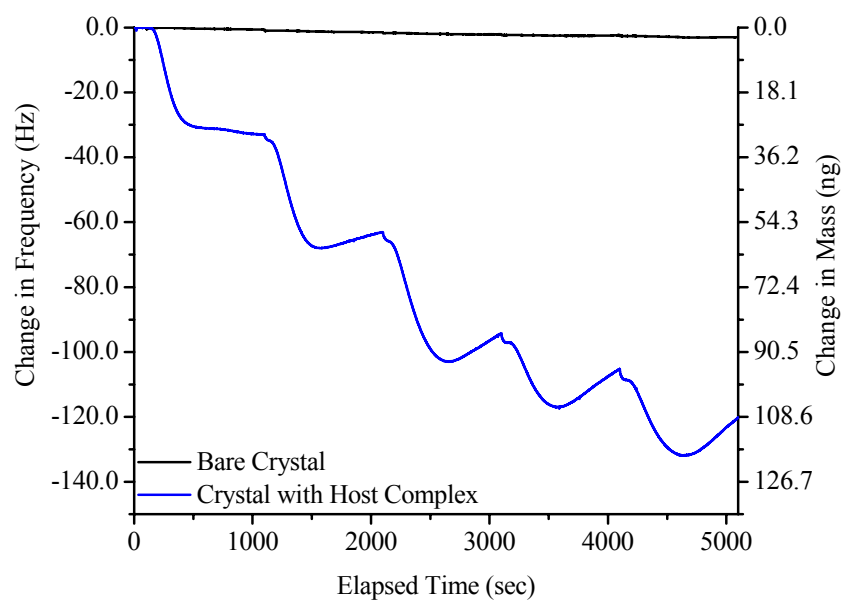


Figure S4. QCM response of the host complex, $[\text{Eu}_2\text{Zn}_4\text{L}_4(\text{OAc})_6(\text{NO}_3)_2(\text{OH})_2]$, to $1 \mu\text{l}$ injections of the guest VOC methanol. The frequency dampening of a crystal coated with the host material (blue) is compared to the response of a bare QCM crystal to Et_2O injections at the same time interval (gray).

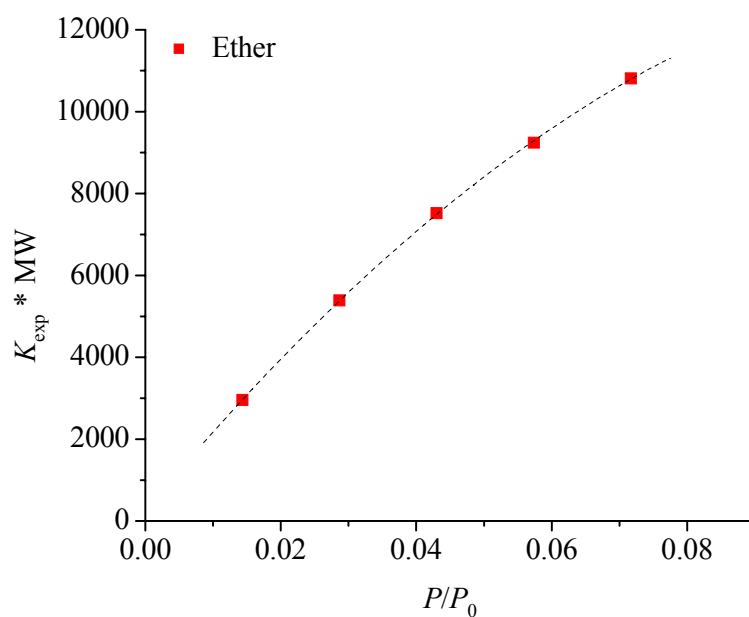


Figure S5. Isotherm of $K_{\text{exp}} * \text{MW}$ vs. P/P_0 for diethyl ether, where K_{exp} is the experimentally determined partition coefficient from eq. 3, MW is the molecular weight (g/mol) of the respective VOC, P is the partial pressure of the guest in the QCM chamber, and P_0 is the saturation pressure.

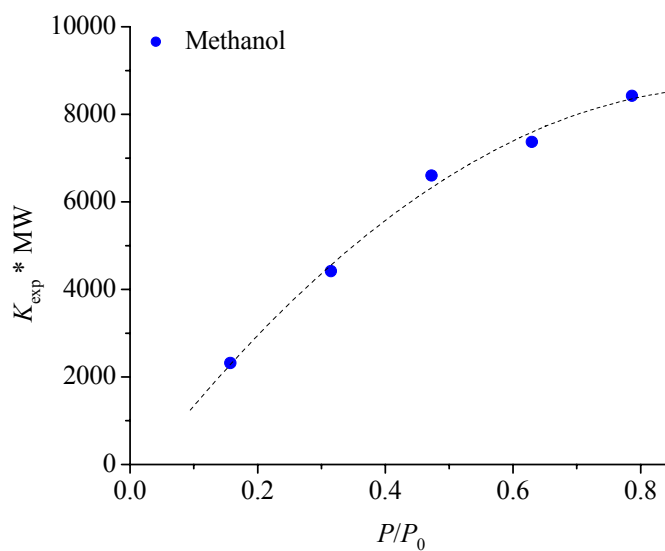


Figure S6. Isotherm of $K_{\text{exp}} * \text{MW}$ vs. P/P_0 for methanol, where K_{exp} is the experimentally determined partition coefficient from eq. 3, MW is the molecular weight (g/mol) of the respective VOC, P is the partial pressure of the guest in the QCM chamber, and P_0 is the saturation pressure.

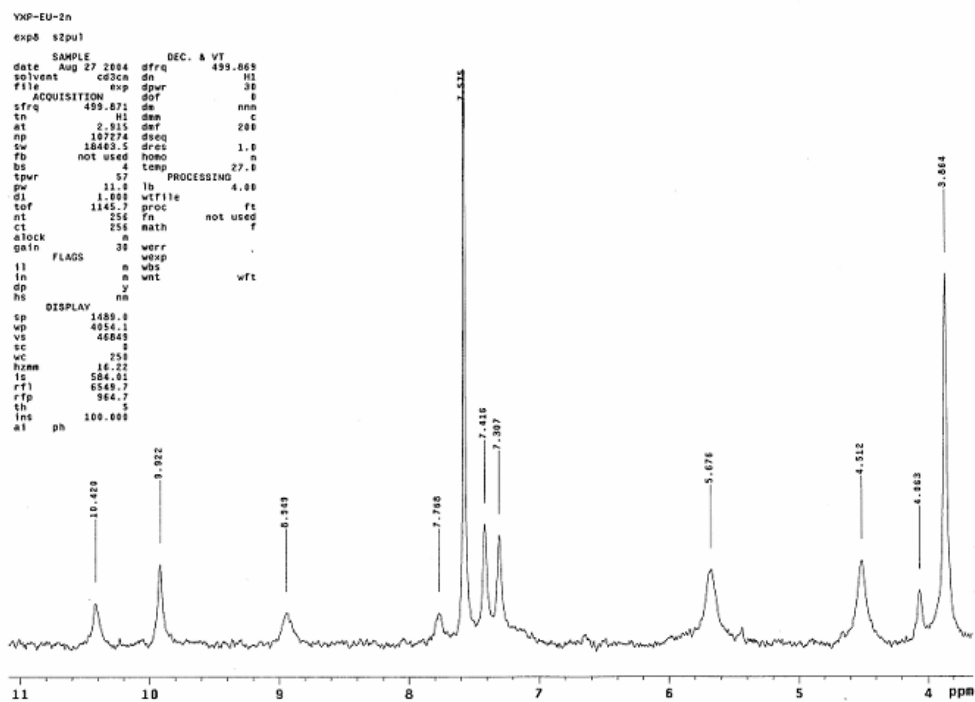


Figure S7. ^1H NMR spectrum of **1** in CD_3CN . (The peaks of solvent and Et_2O , together with a signal at 1.801 ppm, have been omitted for clarity)

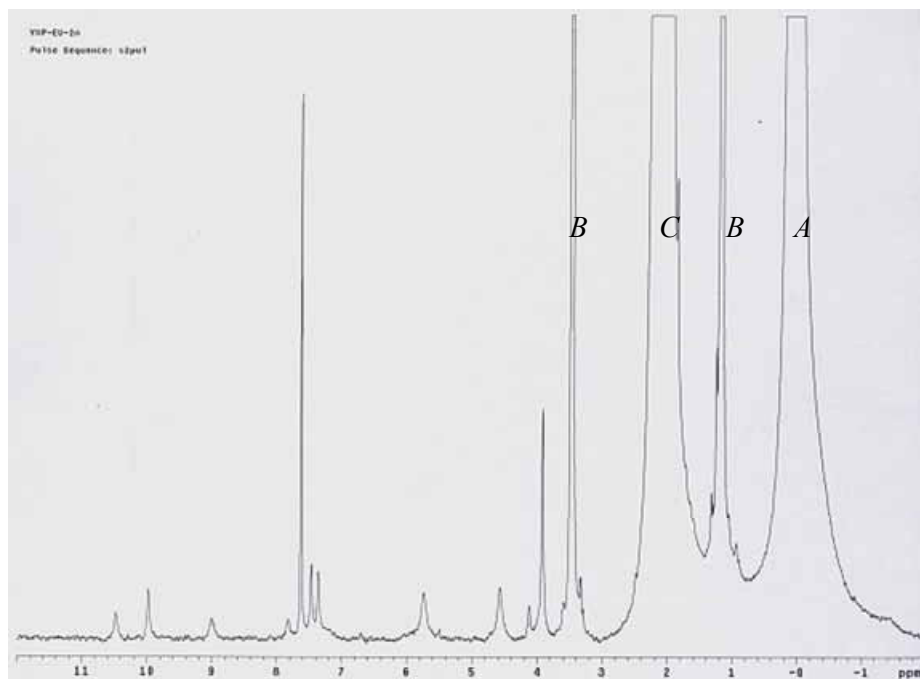


Figure S8. ^1H NMR spectrum of **1** in CD_3CN . (*A*: grease; *B*: Et_2O ; *C*: H_2O and CH_3CN .)
The compound is not very soluble in CD_3CN and this solvent appears to leach Et_2O from the pores of insoluble material since Et_2O peaks are relatively more intense than those of the ligand.