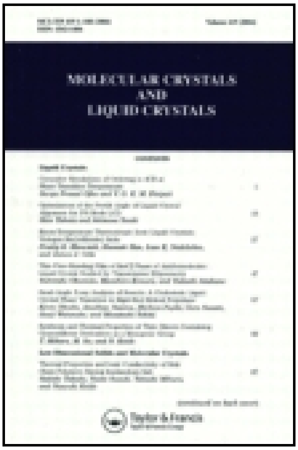

Molecular Crystals and Liquid Crystals

A Surface Plasmon Resonance Investigation of the Selective Interaction of Organic Vapors with Cavitands

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A SURFACE PLASMON RESONANCE INVESTIGATION OF THE SELECTIVE INTERACTION OF ORGANIC VAPORS WITH CAVITANDS

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A class of supramolecules, called cavitands, that have been shown to exhibit discotic phases depending on the structure, are shown to have potential for sensing applications. Certain cavitands (macrocyclic compounds based on resorcinarenes) display selectivity of interactions with organic vapors. We use Surface Plasmon Resonance (SPR) to demonstrate this principle. The two cavitands chosen for this study, had both a different size and shape of the pre-organized cavity and were exposed to a variety of aromatic and chlorinated hydrocarbons. QxCav-1 (cavitand) was found to have a marked preference for the aromatic compounds; with the sequence of selectivity, determined by SPR to

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be nitrobenzene > toluene > benzene. MeCav-2 (cavitand) on the other hand, showed higher selectivity to dichloromethane with respect to aromatic vapors at room temperature. Cavitands therefore represent attractive sensing materials, with potential for application in devices using optical transduction schemes based on a refractive index change.

Keywords: macrocyclic compounds; cavitands; columnar phase; gas sensing; selectivity; surface plasmon resonance

INTRODUCTION

Chemical Vapor Detection continues to be a field of intense activity [1–12]. A variety of sensing materials [7,8,10,11,13,15] have been developed using multiple transduction schemes [7–9,14,16,17]. Examples include polymeric materials [18], which undergo a change in some physical property such as electrical conductivity when chemical vapors are partitioned into the polymer layer and molecular receptors which form host-guest complexes with analytes based on weak intermolecular interactions [19]. Among the several classes of supramolecular structures available, phosphorus-bridged cavitands have shown to exhibit high selectivity for detection of short chain linear alcohols [14]. The selectivity of such systems arise from the presence of synergistic CH-π and H-bonding interactions between cavitand and analyte. The potential of cavitands for sensing simple organic and aromatic hydrocarbon species in the form of vapors has been demonstrated using the quartz crystal microbalance (QCM) by a number of groups [20–25]. Researchers are also increasingly interested in studying these systems using SPR as a transduction mechanism [7,8,15,26–28]. For example self-assembled monolayers of cavitands have been used, in aqueous medium, to detect the presence of steroids [15] and a number of neutral molecules such as benzoic acid and p-nitrophenol [29].

In order to utilize these cavitands (with enforced cavities) as a sensing surface for organic species it was important initially to verify that binding of the target analyte to the sensor surface caused suitable perturbation in the refractive index as to produce a measurable signal change in the SPR. The technique of SPR has received significant attention recently. It has been extensively used in the study of surface interactions of proteins (both specific and non-specific), and in the development of chemical sensors and biosensors for a number of species [30]. SPR is highly adaptable and can be incorporated into a number of sensing formats, including fiber optic sensors. This would allow sensors, for example, to be integrated into fiber optic communication lines (for distributed sensing applications) [7].

In this manuscript, we demonstrate that deeper quinoxaline-bridged cavitand and methylene-bridged cavitand can be used as sensing materials with SPR devices. For this work, two different cavitands were chosen, QxCav-**1** [1] presenting a 8.3 Å deep vase shaped cavity and MeCav-**2** [2] giving a 3.3 Å deep meniscus-like cavity, as illustrated in Figure 1. The molecular recognition properties of QxCav have been extensively studied in the solid state [1,3], in solution [1,3] and in the gas phase [4–6] and exploited as sensitive layers in chemical sensors [17,20–24]. The results presented here demonstrate that cavitands can be used in conjunction with SPR detection as sensing devices for organic aromatic species, in the vapor phase, thereby extending the range of applications for such sensing materials.

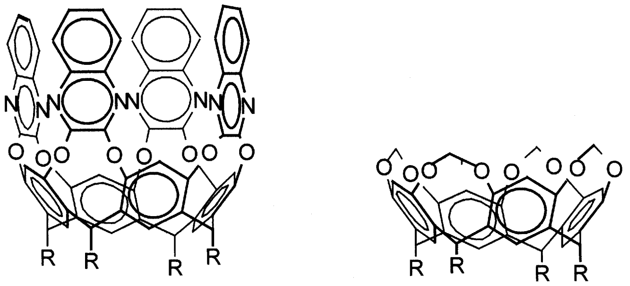
EXPERIMENTAL SECTION

Reagents

QxCav-1 (quinoxaline-bridged cavitand) and **MeCav-2** (methylene-bridged cavitand) were synthesized according to well established methods [2,31]. All chemicals (Aldrich Chemical Co.) were of analytical reagent grade.

Substrate Preparation

A cover glass was cleaned prior to gold deposition with a hot "piranha" solution (30:70 v/v mixture of H_2O_2 and H_2SO_4); (Warning: solution reacts violently with many organic materials and must be used with extreme caution and should not be stored in sealed containers). The gold metal film, required by SPR for generating plasmons was deposited onto the cleaned cover glass (22 mm × 22 mm, THOMAS SCIENTIFIC) using a vacuum



QxCav-**1** MeCav-**2**

FIGURE 1 Molecular structure of **QxCav-1** and **MeCav-2**. For both cavitands, $R = C_{11}H_{23}$.

evaporator (Edwards Auto 306). Evaporation, from a gold coin (Canadian coin, 99.99%), was preformed at a vacuum of 10^{-6} bar and at a rate of 0.02–0.04 nm s^{-1} resulting in a 50 nm gold film on the cover glass, as determined via a crystal oscillator. The sensing layer was produced by spin coating (Model P6700) a solution of **QxCav-1** or **MeCav-2** (0.38 mM in acetone) at 4000 rpm for 60 s at room temperature. Polyepichlorohydrin (PECH) solution (0.1% in chloroform) was spin coated (4000 rpm for 60 s) on gold as a reference sensing layer. The coated surfaces were then ready for analysis with the SPR instrumentation. A least squares fitting procedure was applied for theoretical fitting of the experimental data to the Fresnel's reflection formula and values of 43 ± 3 Å and 1.40 ± 0.01 are obtained for the film thickness and refractive index of cavitands, respectively.

SPR Instrumentation and Measurements

The SPR system was set up here and was based on the Kretschmann configuration [32]. Here, a prism was used to couple the wavevectors of the incoming light beam with that of the plasmons [32]. A schematic of the SPR set up and the flow cell used to generate the organic vapors is shown in Figure 2. The glass prism was made of standard BK7 glass (60 degrees, 17 mm high, 22 mm by 32 mm at the base, refractive index n = 1.5, Howard Jonson Optical Laboratories). Index matching fluid from Cargille Inc. was used to index match the prism to the cover glass (n = 1.51). A semiconductor diode laser (HeNe, 1.0 mW, p polarized at 632.8 nm from Newport Corporation) was used as the light source. The polarized light is incident on the prism and reflected back from the base of the prism onto a photodetector (818 Series, Newport Corporation). Variable angles were selected by means of a stepper motor controlled goniometer with a

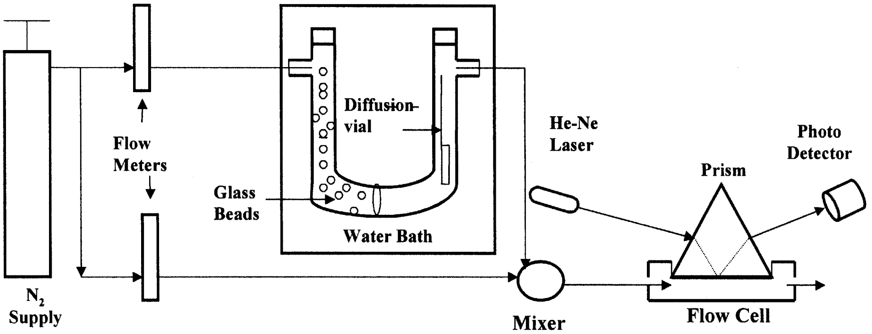


FIGURE 2 Schematic diagram of analyte flow system and surface plasmon resonance (SPR) experimental set up.

resolution of 0.1 degrees. The data acquisition was completely automated through a computer program, with a typical SPR scan angle (40° to 80°) taking 8 minutes.

To expose organic vapors of precisely known concentration to cavitands, a flow cell was constructed from a block of Teflon. The flow cell was designed to provide an inlet and outlet for the analyte vapors and an opening to seat the cavitand coated glass slide and prism. To generate ppm levels of organic vapors, a diffusion vial (D-5.0 mm capillary, VICI Metronics Inc.) was placed in a temperature controlled (to within 0.1 degrees) water bath from PolySciences Inc. The diffusion vial is filled with analyte liquid (toluene, nitrobenzene, benzene, and dichloromethane) using 5 mL syringe needles (VICI Metronics). The vapors of the organic liquid are diluted with a stream of dinitrogen. The flow of both the carrier gas (dinitrogen) and the analyte are precisely controlled (accuracy of 1–2%) using mass flow controllers (DFC26, AALBORG INC.) and mixed in the appropriate proportions before being introduced into the Teflon chamber for exposure to the cavitands. The responses were monitored for 200 s after exposure to the saturated analyte in the nitrogen stream and then the sensors were flushed with dry nitrogen to restore the resistance to baseline. A software program controlled the flow of the carrier gas as well as the organic vapors.

RESULTS AND DISCUSSION

In order to determine the selectivity and sensitivity of cavitands to analytes, the following analytes were chosen: nitrobenzene, toluene, benzene and dichloromethane. The concentrations of these analytes are calculated from the vapor pressure (based on Antoine's law) [33]. Concentrations were varied over a wide range (0–1000 ppm) by altering the flow rate of the diluent gas which was accurately measured to within 1 to 2%. The ppm levels chosen for each analyte were different and dependent on the boiling point and therefore the vapor pressure of the liquid.

Typical SPR curves are shown in Figure 3. Figure 3a illustrates two curves. The curve with open circles (minimum at 45.7°) represents the SPR response for the bare gold film and the second curve (solid circles with minimum at 48.8°) is due to the presence of **QxCav-1** spin coated on the surface. Figure 3b shows the shift in plasmon angle due to exposure of **QxCav-1** to 98 ppm concentration of toluene vapors. Similar plasmon angle curves (although with characteristic plasmon angle shifts) were obtained for all the analyte-cavitand interactions studied.

The plasmon angle shift shows a linear increase with concentration of toluene vapor for **QxCav-1**. A calibration curve was performed and the regression coefficient (from a linear least squares fit) was found to be equal

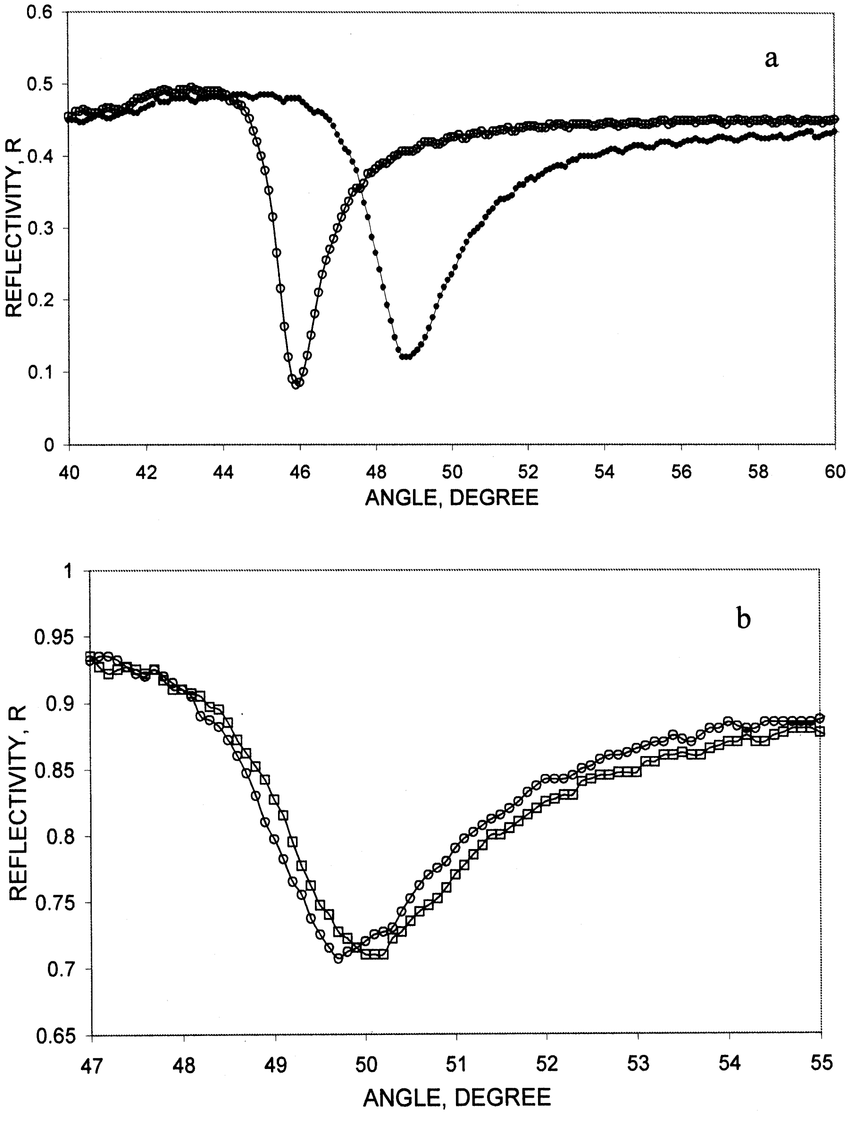


FIGURE 3 (a) SPR curve with bare gold film (open circle), SPR curve after spin coating with **QxCav-1** (solid circle); (b) Plasmon angle shifts due to interaction of 98 ppm of toluene (open box) with **QxCav-1**. The solid lines in each plot are drawn connecting the points to guide the unaided eye and does not represent a theoretical fit.

to 0.99 and the slope of the straight line (wherein the plasmon angle shift is plotted against concentration) yielded a sensitivity of 5.1 ± 0.2 mdeg/ppm. Based on this level of sensitivity and the angular resolution achievable with the SPR instrumentation used, the limit of detection was estimated to be 40 ± 3 ppm for toluene vapors. Similarly, the sensitivity of **QxCav-1** towards benzene and nitrobenzene were 0.8 ± 0.14 mdeg/ppm and 1100 ± 400 mdeg/ppm respectively. For dichloromethane, however, the sensitivity was determined to be much lower for **QxCav-1** (about 0.15 mdeg/ppm). For the aromatic vapors therefore, the selectivity sequence expressed by **QxCav-1** was nitrobenzene > toluene > benzene. Previous studies with quinoxaline-bridged receptors, using SAW (surface acoustic wave) transducers, showed that sensor responses were mainly determined by dispersion interactions between the analyte and the layer, with small differences between PECH and QxCav [34,35]. The underlying host-guest interactions were dominated by the energetically overwhelming dispersion forces. In this case, the different transduction mechanism, highly reduces the detection signal due to the importance of dispersion forces, as shown by the negligible responses of PECH. Clearly then, host-guest interactions between analyte and cavitand contribute significantly to the SPR sensor responses. In this context, the high sensitivity of **QxCav-1** towards nitrobenzene may be rationalized in terms of enhanced CH-π interactions due to the presence of an electron withdrawing group on the analyte [6].

Similar measurements were performed to determine the sensitivity of **MeCav-2** and it was observed that the sensitivity of this cavitand is higher for dichloromethane than aromatic vapors. The slope of the straight line, which refers to the sensitivity observed for **MeCav-2** towards dichloromethane, was 0.9 ± 0.3 mdeg/ppm where the regression coefficient for the line best fit was equal to 0.98. Table 1 shows plasmon angle shift for both

TABLE 1 Plasmon Angle Shifts Due to Interaction of Cavitand and Different Concentration of Organic Vapor Including PECH Polymer

Analyte	Concentration, PPM	QXCav-1 $\Delta\theta_P$	MeCav-2 $\Delta\theta_P$	PECH $\Delta\theta_P$
Nitrobenzene	0.18	0.1	0.1	0.1
	1.5	0.3	0.1	0.1
Toluene	37	0.2	0.1	0.1
	98	0.5	0.1	0.1
Benzene	174	0.1	0.1	0.1
	368	0.3	0.1	0.1
Dichloromethane	336	0.1	0.2	0.1
	636	0.1	0.4	0.1

cavitands and PECH (polymer chosen for comparison) towards nitrobenzene, toluene, benzene, and dichloromethane vapors at different concentrations. The higher selectivity of **MeCav-2** toward dichloromethane, although unexpected, may be rationalized assuming that dichloromethane interacts preferentially with the bottom part of the cavity (the resorcinarene skeleton) and not with the cavity walls (the quinoxaline moieties) [36], which can be accessed more readily in case of **MeCav-2** compared to **QxCav-1**. Inspection of the two cavities with respect to their size and shape helps to explain why the two cavitands behave differently towards the aromatic analytes. The interior of **QxCav-1** offers a much larger contact surface for CH-π interactions than that of **MeCav-2**, since the aromatic analytes are completely engulfed within the cavity as evident from crystallographic studies [3].

It is important to note that the cavitands are deposited on the surface of the substrate using a spin coating process. As such, it is expected that an amorphous film is formed on the surface. It would be interesting to compare the selectivity of cavitands when ordered columnar phases are obtained. For example, if the cavitands are “assembled” on the surface such that all the “cavities” face outward (as opposed to other orientations with respect to the solid surface), perhaps higher selectivity and sensitivity may be obtained. Such experiments are currently in progress.

CONCLUSION

Cavitands are shown to be selective in their interactions with organic vapors. This selectivity arises from a combination of the size and shape of the cavitands. Also important are the synergistic interactions between cavitands and analytes. Surface Plasmon Resonance has been shown to be a suitable transduction platform for transducing the signal arising from the refractive index change (from complexation of analyte with cavitands). **QxCav-1** responds preferentially to aromatic analytes while cavitand **2** demonstrates higher affinity towards dichloromethane. The potential of cavitands for the sensing of organic vapors therefore has been extended from the typical mass sensing transduction platform to include optical transduction schemes based on refractive index changes. For example, one could envisage using SPR sensors based on fiber optics for distributed sensing applications. Also, state of the art instrumentation, capable of milli degree angular resolution, should allow for sensing in the ppb concentration range using this approach.

This article is dedicated to Prof. S. Chandrasekhar, Centre for Liquid Crystal Research, Bangalore, India to mark the 25th anniversary of the discovery of Discotic Liquid Crystals [37].

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