

Synthesis, Characterization, and Chemical Sensitivity of Self-Assembled Bilayers Composed of Polydiacetylenes and Calix[4]arenes Chemically Modified on the Upper Rim

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We report the synthesis, characterization, and sensor-related chemistry of self-assembled polydiacetylene (PDA)/calix[4]arene-X (CA[4]-X; X = -H, -phenylazo, and -dibenzylamino) bilayers on Au surfaces. Surface infrared spectroscopy indicates that acid chloride-terminated PDA self-assembled monolayers (SAMs) react with hydroxyl groups present on the lower rim of the calixarenes to yield ester-linked bilayers. Nanogravimetric titrations of unreacted PDA acid groups with *n*-butylamine indicate that the three CA[4]-X derivatives cover an average of 69% of the PDA surface. The mass titration serves a secondary purpose by passivating voids between calixarenes with *n*-butylamine. The response of the bilayers to four aromatic analytes: anisole, benzene, chlorobenzene, and toluene, was determined using surface acoustic wave (SAW) mass balances. The results indicate that the upper-rim functional groups of CA[4]-X have a significant effect on the sensitivity and selectivity of the bilayer toward the vapor-phase analytes. Increased sensitivity and selectivity are observed for the CA[4]-phenylazo and CA[4]-dibenzylamino bilayers relative to CA[4]-H or a simple methyl-terminated *n*-alkylthiol SAM. We interpret these results in terms of the large -phenylazo and -dibenzylamino functional groups, which enlarge the calixarene cavities and enhance their ability to interact with aromatic analytes by π - π stacking interactions.

Introduction

Here, we report the chemical modification of the upper rims of calix[4]arenes (CA[4]-X, where X = -H, -phenylazo, and -dibenzylamino), the attachment of CA[4]-X to self-assembled monolayers (SAMs) of acid-terminated polydiacetylenes (PDA), and the role the upper-rim modifications play in providing differential responses for a series of aromatic volatile organic compounds (VOCs). The intrinsic size-selectivity of the CA[4] cavities, coupled with their upper rim-adjustable chemical properties, makes them excellent candidates for vapor-phase sensing applications.^{1–9} Additionally, these bilayer materials are highly ordered and, thus, they are easy to characterize and are good model systems for studying the type of weak intermolecular interactions that are relevant to a variety of chemical sensor applications.

Organic thin films have been studied extensively as chemically sensitive interfaces for acoustic wave-based

chemical sensors,^{10–12} and many such materials have been demonstrated to have high selectivities toward particular chemical classes of vapor-phase analytes.^{12–18} More recently, receptor molecules capable of participating in host–guest interactions with VOCs, such as cyclodextrins¹⁹ and calixarenes,^{20,21} have been incorporated into polymer,^{8,22–27} monolayer,^{6,28,29} and Langmuir–Blodgett^{30,31}

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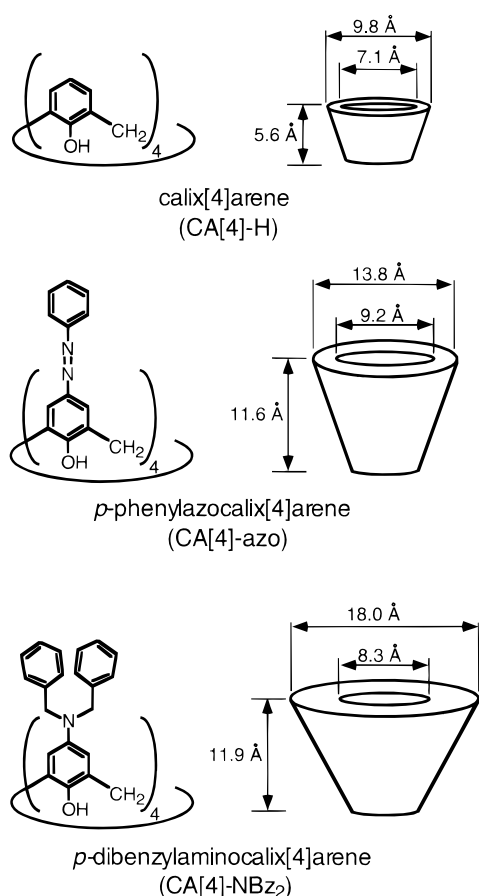
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Scheme 1



films. The receptor molecules are thought to enhance the selectivity and sensitivity of the films toward analytes through specific, yet reversible, host–guest interactions. However, the precise molecular nature of these interactions is not well established at the present time.^{6,29,32,33}

The modified calix[4]arenes used in this study belong to a class of bucket-shaped molecules consisting of 4–11 phenyl subunits.²⁰ CPK estimates of the dimensions of the cone conformations of CA[4]-H, CA[4]-phenylazo, and CA[4]-dibenzylamino are provided in Scheme 1. The host–guest interactions associated with hydrophobic CA[*n*] cavities are usually weak, principally involving van der Waals, induced-dipole, and π – π stacking interactions. The strength and type of intermolecular interactions between analytes and CA[*n*]-X can be tuned by varying the size of the CA[*n*] cavity and the upper- and lower-rim functional groups.³⁴ For example, in a previous report, we discussed the synthesis, characterization, and sensor-related chemistry of polydiacetylene/4-*tert*-butylcalix[*n*]arene (*n* = 4,6) bilayers.²⁹ By comparing the extent of adsorption of six volatile organic compounds (VOCs) onto the calixarene-modified bilayer surfaces with three chemically similar phenyl-functionalized bilayer surfaces lacking defined cavities, we were able to demonstrate that the CA[*n*] cavities play a key role in defining the interfacial chemical affinity of these materials.

In the work described here, the large phenylazo- and dibenzylamino-endgroups are intended to enlarge the

effective cavity size of the calixarenes and enhance π – π stacking interactions between the calixarene hosts and the aromatic guests. After passivating void spaces between the calixarene receptors with relatively inert *n*-butylamine,²⁹ the films were dosed with a series of benzene derivatives having roughly similar structures. The results are compared to a PDA/CA[4]-X bilayer lacking upper functional groups (X = -H) and a hexadecanethiol (C₁₆SH) SAM lacking macrocyclic structure. The films and their interactions with the VOCs were characterized using surface acoustic wave (SAW) mass balances and Fourier transform infrared-external reflectance spectroscopy (FT-IR-ERS).

Experimental Section

Chemicals. 4-*tert*-Butylcalix[4]arene (Aldrich, 95%), anhydrous dimethylformamide (DMF) (Aldrich, 99%), triethylamine (Aldrich, 98%), *n*-hexadecanethiol (Aldrich, 99.5%), anisole (Aldrich, 99.7%), benzene (Aldrich, 99.5%), *n*-butylamine (Aldrich, 99.4%), chlorobenzene (Aldrich, 99.5%), and toluene (EM Science, 99.5%) were used as received. Most chemicals required for synthesizing the diacetylenic alkylthiols were of reagent-grade quality, purchased from Aldrich Chemical Co., and used without further purification.³⁵ Anhydrous sodium hydrogen sulfide was obtained from Alfa/Aesar Chemicals and used as received. Gaseous N₂ obtained from liquid N₂ boil-off was used as a carrier gas for all SAW-device and FTIR-ERS experiments.

Calixarene Modification. Calix[4]arene (CA[4]-H) was prepared from 4-*tert*-butylcalix[4]arene (CA[4]-*t*Bu) following the procedure of Gutsche et al.^{36,37} *p*-Phenylazocalix[4]arene (CA[4]-azo) was prepared following the procedure of Tokuhisa et al.³⁸ Dibenzylaminocalix[4]arene (CA[4]-NBz₂) was prepared directly from *p*-aminocalixarene and benzylbromide. Detailed synthetic procedures will be published elsewhere.³⁹

Substrate Preparation. Au-coated substrates were prepared by electron-beam deposition of 10 nm of Ti followed by 200 nm of Au onto Si(100) wafers.⁴⁰ Au-coated SAW devices were prepared in the same manner on polished ST-cut quartz. Before each experiment, all wafers and devices were cleaned in a low-energy Ar plasma cleaner at medium power for 1 min (Harrick Scientific, NY, model PDC-32G).

Bilayer Preparation. The preparation of PDA/CA[*n*]-*t*Bu bilayers has been discussed in detail previously, and the bilayers discussed here were prepared following a similar procedure.²⁹ Briefly, monolayers were prepared by soaking a Au substrate in a solution of the acid-terminated diacetylene, HS(CH₂)₁₀C≡CC≡C(CH₂)₁₀COOH (DA-COOH).³⁵ The DA-COOH SAMs were polymerized by irradiation with a UV light (λ = 254 nm) for 45 min under flowing N₂ to yield a polymerized monolayer (PDA-COOH). Following polymerization, the substrates were exposed to SOCl₂ vapor to convert the acid functional groups to the more reactive acid chlorides (PDA-COCl).^{35,41} The CA[4] derivatives were covalently bound to the PDA-COCl-modified substrate by soaking overnight in an anhydrous DMF solution containing CA[4]-X and triethylamine. The hydroxyl groups on the lower rim of the calixarenes react with the SAM to yield an ester-linked PDA/CA[4]-X bilayer.^{29,42} *n*-Hexadecanethiol (C₁₆SH) SAMs were formed by soaking a plasma-cleaned Au substrate in a 1 mM ethanolic solution of C₁₆SH overnight. All substrate were rinsed repeatedly with deionized water, acetone, and ethanol before the dosing experiments.

Fourier Transform Infrared-External Reflectance Spectroscopy (FTIR-ERS) and Surface Acoustic Wave (SAW)

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Device-Based Mass Measurements. FTIR-ERS measurements were made using a Bio-Rad FTS-40 spectrometer (Cambridge, MA) equipped with a Harrick Scientific Seagull reflection accessory (Ossining, NY) and a liquid-N₂-cooled MCT detector. All spectra were the sum of 256 individual scans using *p*-polarized light at an 84° angle of incidence with respect to the Au substrate.⁴³

Gravimetric experiments were performed at 25 ± 0.2 °C using 2 (97 MHz) ST-cut quartz oscillators housed in a custom-built flow system.⁴³ Adsorption isotherms were obtained on freshly prepared bilayer films exposed to anisole, benzene, chlorobenzene, and toluene ranging continuously from 0 to 80% *P*/*P*_{sat} and then back to 0% in a N₂ carrier-gas stream. Each analyte dosing experiment was performed over the course of 2 h. The N₂ flow system was computer controlled using Labview programming software (National Instruments, Austin, TX). The saturation vapor pressures of the 4 VOCs are 3.3, 12.3, 28.4, and 95.2 (mmHg at *T* = 25 °C) for anisole, chlorobenzene, toluene, and benzene, respectively.⁴⁴

The change in SAW device frequency (Δf) resulting from VOC adsorption is related to the mass loading per unit area (m_a) through the equation $\Delta f/f_0 = -\kappa c_m f_0 m_a$. Here, f_0 is the SAW resonance frequency (97 MHz), κ is the fractional distance between the centers of the transducers coated by the Au film (0.70 in these experiments), and c_m is the mass sensitivity coefficient for ST-cut quartz (1.33 cm²/(g·MHz)).^{45,46} The frequency shift (Δf) of the SAW device should arise only from mass loading since the PDA/CA[4]-X bilayers are thin, rigid, nonconducting films.⁴⁷

The *n*-butylamine mass calculations assume a surface coverage of 0.78 nmol/cm² for hexagonal close-packed PDA adsorbing at the 3-fold hollow sites of a defect-free Au(111) surface. Additionally, in calculating the surface coverage of *n*-butylamine we assume a 1:1 reaction stoichiometry between *n*-butylamine and the PDA SAMs. Monolayer-equivalent calculations were based on liquid-phase densities of the analytes using the relationship: $\Gamma = [\rho^2 \times \text{MW}] / 6 \times 10^{23}]^{2/3}$, where ρ and MW are the liquid density and molecular weight of the analyte, respectively, and Γ is the surface concentration of the analyte equivalent to one monolayer. Measured CA[4]-X surface coverages assume maximum coverages of 0.19 nmol/cm², 0.10 nmol/cm², and 0.06 nmol/cm² for hexagonal close-packed CA[4]-H, CA[4]-azo, and CA[4]-NBz₂, respectively. All surface-coverage calculations incorporate a measured surface roughness factor of 1.2 ± 0.2.^{40,43}

Results and Discussion

Figure 1 shows FTIR-ERS spectra of a C₁₆SH SAM, a PDA-COOH SAM, and a PDA/CA[4]-H bilayer. The most prominent bands in the C₁₆SH spectrum correspond to the asymmetric and symmetric methyl stretches at 2965 and 2878 cm⁻¹ and the asymmetric and symmetric methylene stretches at 2919 and 2851 cm⁻¹, respectively (Figure 1a). The smaller bands at 1467 and 1381 cm⁻¹ correspond to -CH₃ asymmetric and symmetric bending modes, respectively.⁴⁸

The spectrum of PDA-COOH exhibits characteristic asymmetric and symmetric methylene stretches (2926 and 2854 cm⁻¹, respectively) and a carboxylic acid C=O band at 1717 cm⁻¹ (Figure 1b).^{35,49-51} The small feature at 1464

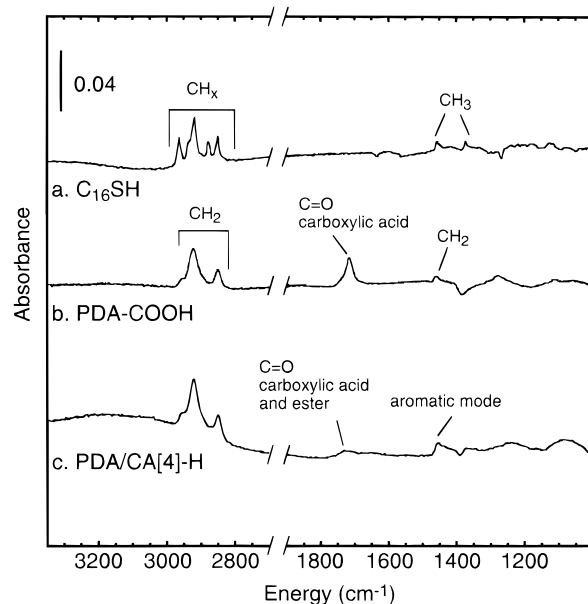


Figure 1. FTIR-ERS spectra of (a) a C₁₆SH monolayer, (b) a PDA-COOH monolayer, and (c) a PDA/CA[4]-H bilayer.

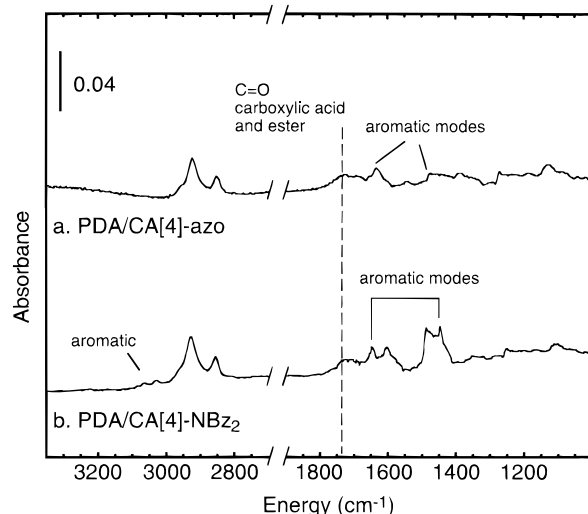


Figure 2. FTIR-ERS spectra of (a) PDA/CA[4]-azo bilayer and (b) a PDA/CA[4]-NBz₂ bilayer.

cm⁻¹ probably arises from the α -CH₂ bending mode.⁵¹ The small shoulder at 2960 cm⁻¹ is an asymmetric methyl stretch originating from hydrocarbons physisorbed to the high-energy acid surface.

Grafting of CA[4]-H to a PDA-COOH film results in a shift and broadening of the C=O band from 1717 to 1735 cm⁻¹ (Figure 1c). This is a consequence of the convolution of two C=O bands: one arising from the new ester linkages and one from unreacted COOH groups. We also observe the appearance of a band at 1467 cm⁻¹, which we attribute to an aromatic stretching mode of the calixarenes.⁵²

Figure 2 shows the FTIR-ERS spectra of PDA/CA[4]-azo and PDA/CA[4]-NBz₂ bilayers. Covalent binding of CA[4]-azo to the PDA surface results in the appearance of an aromatic quadrant stretching mode at 1617 cm⁻¹, due to the phenylazo functional groups, an aromatic stretching mode centered at 1465 cm⁻¹, and a broad C=O band at 1734 cm⁻¹ from the ester linkages between CA[4]-azo and PDA-COOH (Figure 2a). After modification of a

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Table 1. Surface Coverages of CA[4]-X on PDA SAMs

bilayer surface	surface concentration of <i>n</i> -butylamine (nmol/cm ²) ^a	surface coverage of CA[4]-X (%) ^b
PDA/CA[4]-H	0.27	71
PDA/CA[4]-azo	0.29	69
PDA/CA[4]-NBz ₂	0.31	67
PDA/CA[4]- <i>t</i> Bu ^c	0.41	56

^a The surface concentration does not include a surface-roughness factor. ^b The CA[4]-X coverages are referenced to an ideal PDA monolayer present on a flat, defect-free Au(111) substrate (0.78 nmol/cm²) but incorporate a surface-roughness factor of 1.2. ^c The PDA/CA[4]-*tert*-Bu(PDA/*tert*-butylcalix[4]arene) surface coverage was reported previously (ref 29) and is included here for comparison to the other bilayers.

PDA-COOH film with CA[4]-NBz₂, several new bands appear, which are attributable to the monosubstituted benzene rings associated with the dibenzylamino groups. These include a quadrant stretch at 1617 cm⁻¹ and semicircle stretching modes at 1497 and 1451 cm⁻¹. The C=O carboxylic acid/ester mode is evident at 1735 cm⁻¹, and there is an aromatic summation band at 1650 cm⁻¹ and aryl-H modes at 3064 and 3028 cm⁻¹, respectively (Figure 2b). The intensity of these aromatic bands are stronger relative to the other bilayers because of the eight additional benzene groups per calixarene as well as their favorable orientation.³⁹ To verify covalent attachment of all CA[4]-X substituents to the PDA SAMs, we sonicated all of the substrates four times for 5 s each in 1:1 H₂O/acetone. This treatment should remove physisorbed CA[4]-X from the surface, but we observed no change in the FTIR-ERS spectra before and after sonication.

Using a previously described nanogravimetric titration procedure, we dosed the films with *n*-butylamine vapor to determine CA[4]-X surface coverages.²⁹ *n*-Butylamine interacts weakly and reversibly with calix[4]arene cavities but irreversibly with the unreacted acid terminal groups of PDA-COOH. Dosing with *n*-butylamine serves the secondary purpose of filling spaces between CA[4]-X receptors, thereby minimizing their effect on VOC adsorption. The fractional coverage of CA[4]-X on the bilayer surfaces is estimated by subtracting the average *n*-butylamine coverage on the PDA/CA[4]-X bilayers from the *n*-butylamine surface coverage on a PDA-COOH-only SAM and dividing the difference by the latter value. The reaction stoichiometry between *n*-butylamine and free PDA-COOH is 1:1.²⁹

The results of the nanogravimetric titration for the three bilayer surfaces are shown in Table 1. These average mass loadings are based on the results of two experiments performed on independently prepared SAW devices, with the error margin being less than $\pm 10\%$ of a monolayer in all cases. We calculate that CA[4]-H, CA[4]-azo, and CA[4]-NBz₂ cover 71%, 69%, and 67% of the PDA-COOH surface, respectively. On the basis of the sizes of the different calixarenes, these values correspond to CA[4]-X surface concentrations of 0.17, 0.08, and 0.05 nmol/cm², respectively.

After dosing the bilayer-coated SAW devices with *n*-butylamine, the same SAW devices were dosed with anisole, benzene, chlorobenzene, and toluene to test the chemical selectivity of the different upper rim modifications. Each experiment was performed twice in an isothermal chamber on independently prepared SAW devices to ensure reproducibility. The analyte partial pressures ranged from 0 to 80% P/P_{sat} , and the devices were dosed in both directions within this range to test for hysteresis. No hysteresis was observed and therefore, for

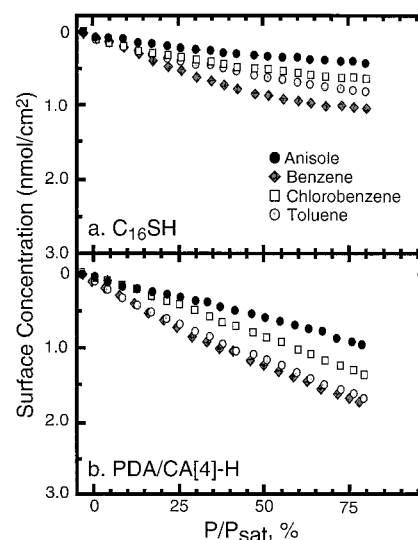


Figure 3. Adsorption isotherms for (a) a C₁₆SH monolayer and (b) a PDA/CA[4]-H bilayer coated onto SAW devices and exposed to anisole, benzene, chlorobenzene, and toluene vapors ranging from 0 to 80% P/P_{sat} in a N₂ carrier gas stream.

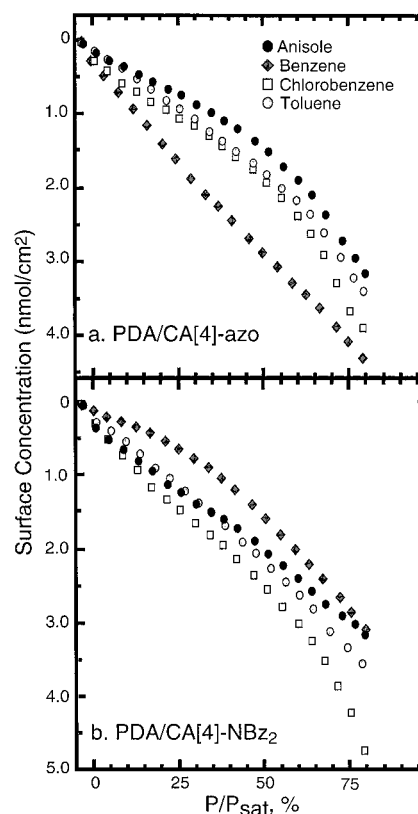


Figure 4. Adsorption isotherms for (a) a PDA/CA[4]-azo and (b) a PDA/CA[4]-NBz₂ bilayer coated onto SAW devices and exposed to anisole, benzene, chlorobenzene, and toluene vapors ranging from 0 to 80% P/P_{sat} in a N₂ carrier gas stream.

increased clarity, only the forward half of the adsorption isotherms are shown in Figures 3 and 4. Additionally, the frequency responses of the SAW devices are normalized for differences in the molecular weights of the analytes by presenting the data in terms of surface concentrations.

Figure 3a shows a series of dosing experiments performed on a C₁₆SH-coated SAW device. The C₁₆SH SAM is used as a control surface because it lacks any macrocyclic structure. The overall magnitude of mass loading for all of the analytes on this surface is quite small: 0.7–1.6

monolayer-equivalents of analyte coverage at $P/P_{\text{sat}} = 80\%$. The tightly packed C_{16}SH surface shows little selectivity toward any particular analyte, which is what we expected given the nonspecific, methyl-terminated interface.¹⁷

Figure 3b shows isotherms for the four analytes on a PDA/CA[4]-H-coated SAW device. The PDA/CA[4]-H bilayer is characterized by shallow cavities, and it lacks upper-rim functionalization that might enhance analyte adsorption. The isotherms follow essentially the same pattern as the C_{16}SH surface, but there is a definite increase in the magnitude of mass loading for all of the analytes. This reflects a more active surface, which we ascribe to the presence of the well-defined calixarene cavities.

An interesting aspect of the phenylazo endgroups is that they are structurally quite rigid.³⁸ This increases the height of the calixarene (Scheme 1), which effectively deepens the cavity and allows for a greater degree of π - π stacking interactions between the calixarene host and the analyte guest. As shown in Figure 4a, the increase in cavity depth of the phenylazo-calixarenes on the PDA/CA[4]-azo bilayer has a significant effect on analyte adsorption. At higher P/P_{sat} values, the magnitude of adsorption of probe molecules is approximately 3–6 times larger than on the C_{16}SH control surface and 2–3 times larger than on the PDA/CA[4]-H surface. The PDA/CA[4]-azo surface demonstrates a particularly strong preference for benzene: approximately 7 monolayer-equivalents adsorb at $P/P_{\text{sat}} = 80\%$. We speculate this enhancement derives from the preferential fit of benzene into the extended phenylazo cavity relative to the other analytes, whose bulkier substituents hinder π - π stacking interactions. Strong evidence for this contention comes from the relative magnitudes of the benzene and toluene data on the PDA/CA[4]-H and PDA/CA[4]-azo surfaces. PDA/CA[4]-H does not distinguish between these two analytes, but the deeper cavity of PDA/CA[4]-azo strongly favors benzene adsorption. Presumably, the methyl group on toluene hinders π - π stacking interactions with the PDA/CA[4]-azo phenyl groups.

As was observed for the phenylazo groups on the PDA/CA[4]-azo surface, the dibenzylamino groups enlarge the effective cavity size of the calixarene, thereby enhancing the degree of π - π stacking interactions for all but one of the aromatic analytes. In contrast to the phenylazo groups, however, the dibenzylamino groups are not rigid. Nevertheless, they have a distinct effect on analyte adsorption: the magnitude of analyte adsorption is roughly 2–5 times larger than on the C_{16}SH and PDA/CA[4]-H surfaces. This enhancement is especially dramatic for chlorobenzene, which adsorbs approximately 9 monolayer-equivalents at $P/P_{\text{sat}} = 80\%$.

Figure 5 shows the surface concentrations of anisole, benzene, chlorobenzene, and toluene, measured at $P/P_{\text{sat}} = 25\%$, for the four different organic interfaces. The highest mass loading responses are generally observed for the PDA/CA[4]-azo and PDA/CA[4]-NBz₂ bilayers. Additionally, the PDA/CA[4]-azo and the PDA/CA[4]-NBz₂ bilayers exhibit enhanced affinities for benzene and chlorobenzene, respectively. As mentioned earlier, the PDA/CA[4]-azo bilayer shows a surprisingly high affinity for benzene relative to all of the other interfaces, including the structurally related PDA/CA[4]-NBz₂ bilayer. Note also that, in contrast to PDA/CA[4]-azo, benzene is the least strongly adsorbed of the four analytes on the PDA/CA[4]-NBz₂ bilayer, which indicates that the importance of π - π stacking interactions is reduced on the PDA/CA[4]-NBz₂ surface.

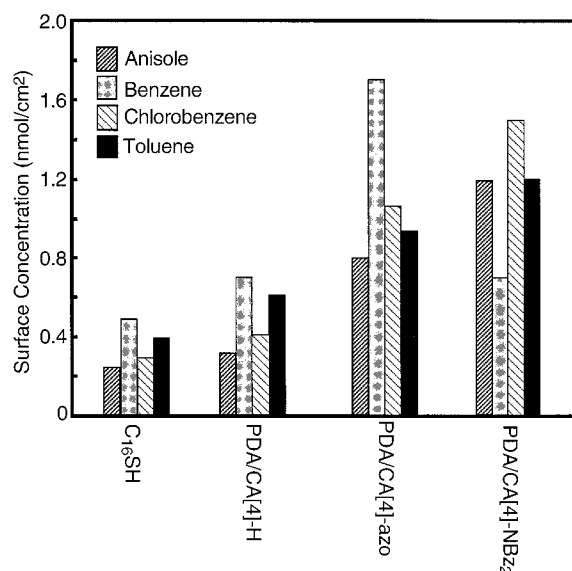


Figure 5. Surface concentrations of anisole, benzene, chlorobenzene, and toluene on a C_{16}SH monolayer and PDA/CA[4]-H, PDA/CA[4]-azo, and PDA/CA[4]-NBz₂ bilayers coated onto SAW devices. Data are for analytes present at $P/P_{\text{sat}} = 25\%$ in a N_2 carrier gas.

It is interesting to compare the VOC surface concentrations relative to the CA[4]-X surface coverages. As discussed earlier, CA[4]-H, CA[4]-azo, and CA[4]-NBz₂ are present on the surface at concentrations of 0.17, 0.08, and 0.05 nmol/cm², respectively. Dosing the three bilayer surfaces with 25%-of-saturation benzene yields surface concentrations of 0.7, 1.7, and 0.7 nmol/cm². The ratio of these values leads to the number of benzene guests per calixarene host: 4:1, 22:1, and 12:1 for the CA[4]-H, CA[4]-azo, and CA[4]-NBz₂ bilayer surfaces, respectively. The host/guest ratios for chlorobenzene are 2:1, 14:1, and 30:1 for the same three bilayers, respectively. These results clearly demonstrate that the host/guest relationship is not based on simple inclusion phenomena. Rather, as we have previously suggested, the calixarene must act as a nucleation site that directs the growth of a low-volatility, multilayer phase of the VOCs on the surface.^{17,29,53} Clearly, the phenylazo- and dibenzylamino- upper-rim modifications greatly enhance this effect relative to the unmodified CA[4]-H bilayer.

Summary and Conclusions

We have reported the preparation and sensor-related chemistry of a series of self-assembled bilayers composed of PDA and upper-rim modified calix[4]arenes. FTIR-ERS measurements indicate that the calixarenes are covalently linked to the PDA-COOH surface through their lower-rim hydroxyl functionalities, and gravimetric experiments show that calixarene surface coverages vary from 67 to 71% of the PDA surface. The analyte dosing data show that the magnitude of analyte/interface interactions is greatly enhanced on the PDA/CA[4]-azo and PDA/CA[4]-NBz₂ bilayers relative to the C_{16}SH and PDA/CA[4]-H control surfaces. Indeed, in most cases there are multiple analyte molecules per calixarene receptor. Thus, we conclude that the calixarenes act to nucleate a low-vapor-pressure phase of the analytes and that the deeper aromatic cavities are particularly effective templates for aromatic VOCs.^{17,29,53} Note that a simple calculation

(53) Crooks, R. M.; Yang, H. C.; McEllistrem, L. J.; Thomas, R. C.; Ricco, A. J. *Faraday Discuss.* **1997**, 107, 285.

indicates that the different surface areas of the organic films, which arise from the differences in the size and shape of the calixarenes, cannot alone account for the differences in measured mass loading. Our results demonstrate the potential of surface-bound calixarenes for chemical sensing applications and represent an important step in the logical design of sensor coatings that are class-specific, selective, durable, and easily synthesized. Presumably, other upper-rim modifications that change the size or electronic characteristics of calixarene cavities would yield chemically independent sensing materials suitable for incorporation into array-based sensing devices.^{18,54}

(54) Ricco, A. J.; Crooks, R. M.; Osbourn, G. C. *Acc. Chem. Res.* **1998**, *31*, 289.

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