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Optical Recognition of *n*-Butylammonium and 1,5-Pentanediammonium Picrates by a Calix[5]arene Monolayer Covalently Assembled on Silica Substrates

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High quality silica substrates were functionalized with a covalent 4-$ClCH_2C_6H_4SiCl_3$ monolayer. To these, a calix[5]arene bearing a 12-aminododecyl moiety at the lower rim was then covalently bonded, producing a new calix[5]arene-based monolayer on silica substrates. The surface chemical characterization of these hybrid materials was carried out by X-ray photoelectron spectroscopy. The optical sensing properties of this monolayer were studied at room temperature by UV−vis measurements. The system is shown to have recognition properties for *n*-butylammonium ions at parts per million levels and for a biologically relevant analyte such as 1,5-pentanediammonium ion (cadaverine$\cdot$2H$^+$). The adopted synthetic procedure has proven to be effective in transferring molecular properties to a solid state device.

Introduction

Syntheses based on covalent assembly of appropriate molecules on suitable inorganic substrates represent one of the most effective approaches toward the construction of functional molecular architectures that can produce hybrid inorganic/organic nanomaterials and supramolecular systems, valuable for the development of devices displaying specific single molecule properties.[1−5]

Despite the increasing interest, our knowledge of molecular properties at the solid state level is still limited, and this remains a challenge for both scientific and technological reasons. In this context, the covalent immobilization of a monolayer of appropriate molecules on solid substrates probably represents the most suited prerequisite to accomplish this task.

Selective detection of chemicals at low concentrations is one of the most promising applications of molecular-based thin films. Various sol−gels, polymers, and other solid-state systems have been shown to be able to detect analytes in trace amounts.[6−13] In particular, monolayers obtained from well-defined organic compounds or metal complexes are known to selectively interact with target compounds.[10−14]

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(1) (a) Shi, F. N.; Cunha-Silva, L.; Sá Ferreira, R. A.; Mafra, L.; Trindade, T.; Carlos, L. D.; Almeida Paz, F. A.; Rocha, J. *J. Am. Chem. Soc.* **2008**, *130*, 150. (b) Massue, J.; Quinn, S. J.; Gunnlaugsson, T. *J. Am. Chem. Soc.* **2008**, *130*, 6900. (c) Yan, B.; Lu, H.-F. *Inorg. Chem.* **2008**, *47*, 5601. (d) Su, Y.; Li, L.; Li, G. *Chem. Commun.* **2008**, 4004. (e) Altman, M.; Zenkina, O.; Evmenenko, G.; Dutta, P.; van der Boom, M. E. *J. Am. Chem. Soc.* **2008**, *130*, 5040.

(2) (a) Crivillers, N.; Mas-Torrent, M.; Perruchas, S.; Roques, N.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C.; Basabe-Desmonts, L.; Ravoo, B. J.; Crego-Calama, M.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **2007**, *46*, 2215. (b) Moloney, M. P.; Gun'ko, Y.; Kelly, J. M. *Chem. Commun.* **2007**, 3900. (c) Ipe, B. I.; Yoosaf, K.; Thomas, K. G. *J. Am. Chem. Soc.* **2006**, *128*, 1907. (d) Wang, L.; Yoon, M.-H.; Lu, G.; Yang, Y.; Facchetti, A.; Marks, T. J. *Nat. Mater.* **2006**, *5*, 893.

(3) (a) Shukla, A. D.; Das, A.; van der Boom, M. E. *Angew. Chem., Int. Ed.* **2005**, *44*, 3237. (b) Yoon, M.-H.; Facchetti, A.; Marks, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 4678.

(4) Liu, Z.; Yasseri, A. A.; Lindsey, J. S.; Bocian, D. F. *Science* **2003**, *302*, 1543.

(5) Hatzor, A.; Weiss, P. S. *Science* **2001**, *291*, 1019.

(6) (a) Aoki, P. H. B.; Volpati, D.; Riul, A.; Caetano, W.; Constantino, C. J. L. *Langmuir* **2009**, *25*, 2331. (b) Acharya, J. R.; Zhang, H.; Li, X.; Nesterov, E. E. *J. Am. Chem. Soc.* **2009**, *131*, 880. (c) Ligler, F. S. *Anal. Chem.* **2009**, *81*, 519. (d) Blaszczyk-Lezak, I.; Aparicio, F. J.; Borras, A.; Barranco, A.; Alvarez-Herrero, A.; Fernandez-Rodriguez, M.; Gonzalez-Elipe, A. R. *J. Phys. Chem. C* **2009**, *113*, 431.

(7) (a) Roberts, M. E.; Mannsfeld, S. C. B.; Tang, M. L.; Bao, Z. *Chem. Mater.* **2008**, *20*, 7332. (b) Allendorf, M. D.; Houk, R. J. T.; Andruszkiewicz, L.; Talin, A. A.; Pikarsky, J.; Choudhury, A.; Gall, K. A.; Hesketh, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 14404. (c) Tao, S.; Yin, J.; Li, G. *J. Mater. Chem.* **2008**, *18*, 4872. (d) Tonezzer, M.; Melegari, M.; Maggioni, G.; Milan, R.; Della Mea, G.; Dalcanale, E. *Chem. Mater.* **2008**, *20*, 6535. (e) Dahlin, A. B.; Jönsson, P.; Jonsson, M. P.; Schmid, E.; Zhou, Y.; Höök, F. *ACS Nano* **2008**, *2*, 2174. (f) Cattani-Scholz, A.; Pedone, D.; Dubey, M.; Neppl, S.; Nickel, B.; Feulner, P.; Schwartz, J.; Abstreiter, G.; Tornow, M. *ACS Nano* **2008**, *2*, 1653. (g) Gordon, R.; Sinton, D.; Kavanagh, K. L.; Brolo, A. G. *Acc. Chem. Res.* **2008**, *41*, 1049. (h) Anker, J. N.; Hall, W. P.; Lyandres, O.; Shah, N. C.; Zhao, J.; Van Duyne, R. P. *Nat. Mater.* **2008**, *7*, 442.

(8) (a) Slowing, I. I.; Trewyn, B. G.; Giri, S.; Lin, V. S. Y. *Adv. Funct. Mater.* **2007**, *17*, 1225. (b) Basabe-Desmonts, L.; Reinhoudt, D. N.; Crego-Calama, M. *Chem. Soc. Rev.* **2007**, *36*, 993. (c) Pirondini, L.; Dalcanale, E. *Chem. Soc. Rev.* **2007**, *36*, 695.

(9) (a) Barbe, J.-M.; Canard, G.; Brandes, S.; Guilard, R. *Chem.−Eur. J.* **2007**, *13*, 2118. (b) Dale, T. J.; Rebek, J., Jr. *J. Am. Chem. Soc.* **2006**, *128*, 4500.

(10) Onclin, S.; Ravoo, B. J.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **2005**, *44*, 6282.

(11) (a) Zhang, S.; Lue, F.; Gao, L.; Ding, L.; Fang, Y. *Langmuir* **2007**, *23*, 1584. (b) Chu, B. W.-K.; Yam, V. W.-W. *Langmuir* **2006**, *22*, 7437. (c) Dubey, M.; Bernasek, S. L.; Schwartz, J. *J. Am. Chem. Soc.* **2007**, *129*, 6980.

In spite of all the progress made during the past decade, the development of efficient molecular-based detection systems for given analytes still remains a challenge. Preservation and possibly enhancement of the molecular recognition properties of the sensing agent at the solid-state interface is often difficult to achieve. Designing device-quality monolayer-based sensors requires not only selectivity and sensitivity toward a specific analyte but also a high degree of stability and a fast, nondestructive read-out process. In addition, sensor regeneration is another key requirement which needs to be taken into account.

It has already been reported that cation−π interactions play an important role in the recognition of positively charged guests by the electron-rich π-systems of natural[15] and synthetic[16] hosts. Calixarenes,[17] when suitably functionalized, can provide three-dimensional, rigid, π-rich cavities for the selective inclusion of organic cations in nonpolar media.[18] Among the different families of calix[*n*]arenes, *p*-*tert*-butylcalix[5]arene crown-6 ethers[19] and *p*-*tert*-butylcalix[5]arenes[20] are particularly effective in discriminating linear from branched alkylammonium ions by means of *endo*-complexation,[21] as long as both *tert*-butyl groups at the wide rim[22,23] and moieties bulkier than the ethoxyethoxy one at the narrow rim are introduced[24] to keep the molecule in a locked *cone* conformation. Calix[5]arenes not only bind linear alkylammonium (RNH_3^+) ions efficiently and selectively but are also excellent candidates for the selective detection in solution of basic α-amino- and ω-aminoacids,[20] as well as aliphatic biogenic di- and polyamines.[25]

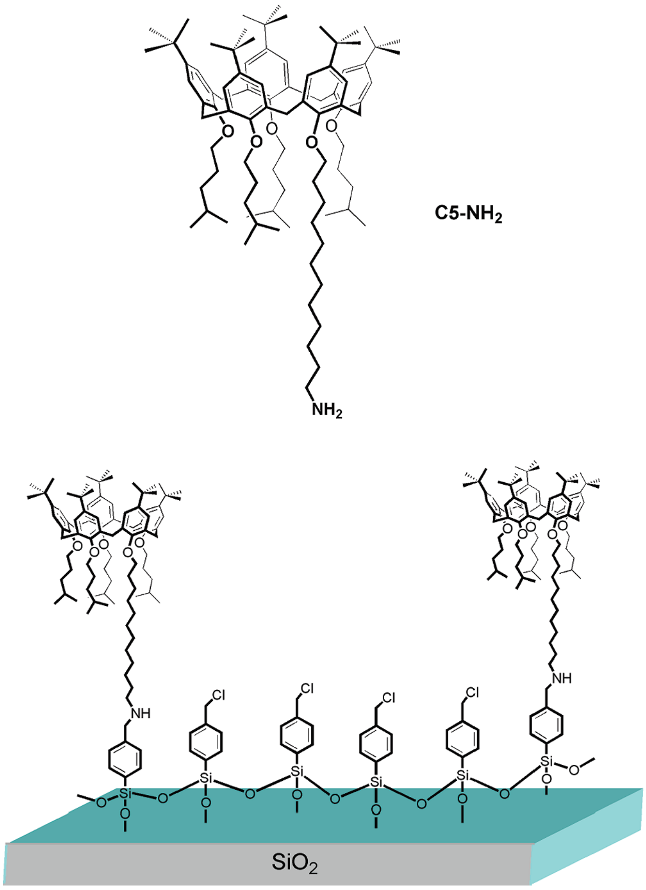

Figure 1. Representation of the calixarene precursor **C5-NH$_2$** and the calix-SAM.

The advantages of calixarene monolayer-based sensors include (i) the need for only a small amount of calixarene to generate a large active surface, (ii) no consumption of sensing material, and (iii) no diffusion limitations because the surface-confined sensing molecules are in direct contact with the target analyte. In light of these potential advantages, we have now developed a prototype calix[5]arene-based monolayer (hereafter designated as calix-SAM), covalently bound to quartz substrates (Figure 1), which is capable of selectively detecting amines and diamines (i.e., butylamine and cadaverine, respectively) in the form of (di)picrate salts. This model study may provide the basis for the development of more sophisticated calix[5]arene-SAMs for the detection of analytes of biological interest incorporating the *n*-butylammonium structural motif (e.g., γ-aminobutyric acid, ε-aminocaproic acid, lysine-containing peptides, etc.), with a view

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(12) (a) Gulino, A.; Gupta, T.; Altman, M.; Lo Schiavo, S.; Mineo, P. G.; Fragalà, I. L.; Evmenenko, G.; Dutta, P.; van der Boom, M. E. *Chem. Commun.* **2008**, 2900. (b) Gulino, A.; Gupta, T.; Mineo, P. G.; van der Boom, M. E. *Chem. Commun.* **2007**, 4878. (c) Gulino, A.; Fragalà, I.; Scamporrino, E.; Vitalini, D. *J. Phys. Chem. C* **2007**, *111*, 14125. (d) Gulino, A.; Giuffrida, S.; Mineo, P.; Purrazzo, M.; Scamporrino, E.; Ventimiglia, G.; van der Boom, M. E.; Fragalà, I. *J. Phys. Chem. B* **2006**, *110*, 16781. (e) Gulino, A.; Mineo, P.; Scamporrino, E.; Vitalini, D.; Fragalà, I. *Chem. Mater.* **2006**, *18*, 2404. (f) Frydman, E.; Cohen, H.; Maoz, R.; Sagiv, J. *Langmuir* **1997**, *13*, 5089. (g) Gulino, A.; Mineo, G. P.; Bazzano, S.; Vitalini, D.; Fragalà, I. *Chem. Mater.* **2005**, *17*, 4043. (h) Gulino, A.; Bazzano, S.; Mineo, P.; Scamporrino, E.; Vitalini, D.; Fragalà, I. *Chem. Mater.* **2005**, *17*, 521. (i) Gulino, A.; Mineo, P.; Scamporrino, E.; Vitalini, D.; Fragalà, I. *Chem. Mater.* **2004**, *16*, 1838.

(13) Schierbaum, K. D.; Weiss, T.; van Veizen, E. U. T.; Engbersen, J. F. J.; Reinhoudt, D. N.; Gopel, W. *Science* **1994**, *265*, 1413.

(14) Biavardi, E.; Favazza, M.; Motta, A.; Fragalà, I. L.; Massera, C.; Prodi, L.; Montalti, M.; Melegari, M.; Condorelli, G. G.; Dalcanale, E. *J. Am. Chem. Soc.* **2009**, *131*, 7447.

(15) (a) Schärer, K.; Morgenthaler, M.; Paulini, R.; Obst-Sander, U.; Banner, D. W.; Schlatter, D.; Benz, J.; Stihle, M.; Diederich, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 4400. (b) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210 and references cited therein.

(16) (a) Sarri, P.; Venturi, F.; Cuda, F.; Roelens, S. *J. Org. Chem.* **2004**, *69*, 3654 and references cited therein. (b) Kearney, P. C.; Mizoue, L. S.; Kumpf, R. A.; Forman, J. E.; McCurdy, A.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 9907.

(17) Gutsche, C. D. *Calixarenes, An Introduction*, 2nd ed.; The Royal Society of Chemistry: Cambridge, 2008.

(18) For recent examples see (a) Le Gac, S.; Jabin, I. *Chem.−Eur. J.* **2008**, *14*, 548. (b) Fehlinger, M.; Abraham, W. *J. Inclusion Phenom.* **2007**, *58*, 263. (c) Rozhenko, A. B.; Schoeller, W. W.; Letzel, M. C.; Decker, B.; Agena, C.; Mattay, J. *Chem.−Eur. J.* **2006**, *12*, 8995.

(19) Pappalardo, S.; Parisi, M. F. *J. Org. Chem.* **1996**, *61*, 8724.

(20) Arnaud-Neu, F.; Fuangswasdi, S.; Notti, A.; Pappalardo, S.; Parisi, M. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 112.

(21) Recently it has been reported that a *p*-methyl-calix[5]arene crown-3 is able to bind arylalkylammonium ions: Gargiulli, C.; Gattuso, G.; Liotta, C.; Notti, A.; Parisi, M. F.; Pisagatti, I.; Pappalardo, S. *J. Org. Chem.* **2009**, *74*, 4350.

(22) Stewart, D. R.; Krawiec, M.; Kashyap, R. P.; Watson, W. H.; Gutsche, C. D. *J. Am. Chem. Soc.* **1995**, *117*, 586.

(23) (a) De Salvo, G.; Gattuso, G.; Notti, A.; Parisi, M. F.; Pappalardo, S. *J. Org. Chem.* **2002**, *67*, 684. (b) Gattuso, M.; Notti, A.; Pappalardo, S.; Parisi, M. F. *Tetrahedron Lett.* **1998**, *39*, 1969.

(24) Ferguson, G.; Notti, A.; Pappalardo, S.; Parisi, M. F.; Spek, A. L. *Tetrahedron Lett.* **1998**, *39*, 1965.

(25) Ballistreri, F. P.; Notti, A.; Pappalardo, S.; Parisi, M. F.; Pisagatti, I. *Org. Lett.* **2003**, *5*, 1071.

to possible applications in the biochemical, environmental, and analytical fields.

Experimental Details

ACS grade reagents and solvents, some of them packed under nitrogen, were used throughout the present syntheses. Calix[5]arene **C5-NH$_2$** was available from previous studies.[26] Fused silica (quartz) substrates were cleaned by immersion into a "piranha" solution (98% H_2SO_4/30% H_2O_2, 70:30 v/v) at 85 °C for 50 min and then left to cool to room temperature. Substrates were then repeatedly rinsed with double distilled water and kept in a H_2O/30% H_2O_2/NH_3 5:1:1 (v/v/v) mixture at room temperature for 1 h.[27−29] A final wash with double distilled water, followed by drying under vacuum was carried out just prior to coupling agent (CA) deposition. All the successive sample manipulations were performed in a glovebox under a N_2 atmosphere. Routinely, freshly cleaned substrates were dipped, at room temperature for 25 min, in a 0.4:100 (v/v) *n*-pentane solution of the chemisorptive reagent, trichloro[4-(chloromethyl)phenyl]silane (siloxane), to afford a CA monolayer.[12,27−29] The siloxane-coated substrates were washed with copious amounts of *n*-pentane, sonicated in acetone for 3 min to remove any physisorbed CA, then immersed into a stirred 1.4×10^{-3} M CH_3CN/toluene (50:50 v/v) solution of **C5-NH$_2$**, and kept at 90 °C for 72 h. The calix-SAM monolayer thus formed was cooled to room temperature and sonicated with CH_3CN, toluene, and THF to remove any residual unreacted **C5-NH$_2$**.

X-ray photoelectron spectra (XPS) were measured at 45°, relative to the surface plane with a PHI 5600 Multi Technique System which gives good control of the electron takeoff angle (base pressure of the main chamber 3×10^{-10} Torr).[30] Spectra were excited with Al Kα radiation. Structures due to $K\alpha_2$ satellite radiation were subtracted from the spectra prior to data processing. XPS peak intensities were obtained after Shirley background removal.[30c] Procedures to account for steady state charging effects have been described elsewhere.[30] Experimental uncertainties in binding energies lie within ±0.45 eV. Deconvolution of a number of these spectra was carried out by fitting the spectral profiles with a series of symmetrical Gaussian envelopes after subtraction of the background. This process involves data refinement, based on the method of the least-squares fitting, carried out until there was the highest possible correlation between the experimental spectrum and the theoretical profile. The *R*-factor (residual or agreement factor), $R = [\sum(F_o - F_c)^2/\sum(F_o)^2]^{1/2}$, after minimization of the function $\sum(F_o - F_c)^2$, converged to R values ≤ 0.035.[30d]

Table 1. XPS Derived Atomic Concentration Analysis for the Calix-SAM

	Si	C	O	N	Cl
as synthesized	16.9	46.3	32.6	0.7	3.5
after basic washing	16.5	44.7	38.2	0.6	0

UV−vis measurements were carried out on a UV−vis V-650 Jasco spectrophotometer, and the spectra shown below were recorded with a ±0.2 nm resolution. The temperature was kept at 25 °C, and measurements were repeated using five different monolayers.

Atomic force microscopy (AFM) measurements were performed with a Solver P47 NTD-MDT instrument in semicontact mode (resonance frequency 150 Hz). The monolayer surface was homogeneous and flat. Root-mean-squared roughness measured for 1000 × 1000 nm scan areas was 0.3 nm.

Results and Discussion

The calix-SAM was synthesized by covalent grafting of calixarene **C5-NH$_2$** to quartz substrates that were previously cleaned and silylated.[12] The silylation reaction was performed under rigorously inert atmosphere with trichloro[4-(chloromethyl)phenyl]silane, a bifunctional coupling agent that binds both the substrate and **C5-NH$_2$**.[12] This calixarene monolayer was found to be insoluble in toluene, MeCN, THF, Et_2O, and EtOH and thermally and temporally robust (vide infra). The monolayer strongly adheres to the substrate, and as a result cannot be removed by the "scotch-tape decohesion" test[3a,28] nor by mechanical abrasion with a task wiper, as evidenced by XPS measurements.

The molecular characterization of the calix-SAM monolayer was carried out by X-ray photoelectron spectroscopy. This technique is ideal as it permits high vertical resolution, gives information on the bonding states of the grafted molecules,[27] and allows estimation of the surface elemental composition, once the relevant atomic sensitivity factors have been taken into account.[30b,31] The reaction between **C5-NH$_2$** and the chlorobenzyl-terminated monolayer is not quantitative owing to its high molecular footprint. The observed ratio (Table 1), Cl/N = 5 ± 0.5, indicates ~16% yield. Figure 2a shows the XPS spectrum of the calix-SAM in the N 1s energy region. The high-resolution N 1s spectrum shows a main peak at 400.0 eV and, in addition, a higher binding energy shoulder at 401.7 eV (calculated intensity after spectrum deconvolution amounted to ca. 30% of the overall spectral profile). The latter accounts for the presence of a species bearing a protonated nitrogen atom,[27,30b] which is most likely formed upon release of HCl during the monolayer formation step. Given that **C5-NH$_2$** undergoes fast self-assembly upon exposure to acids (even in trace amounts),[26] it is reasonable to assume that formation of the **C5-NH$_2$·HCl** species triggers the inclusion process depicted on the right-hand side of Figure 2a.

This observation is also supported by NMR measurements on the calixarene solution, recovered after the

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(26) Pappalardo, S.; Villari, V.; Slovak, S.; Cohen, Y.; Gattuso, G.; Notti, A.; Pappalardo, A.; Pisagatti, I.; Parisi, M. F. *Chem.—Eur. J.* **2007**, *13*, 8164.

(27) Motiei, L.; Altman, M.; Gupta, T.; Lupo, F.; Gulino, A.; Evmenenko, G.; Dutta, P.; van der Boom, M. E. *J. Am. Chem. Soc.* **2008**, *130*, 8913.

(28) Facchetti, A.; Beverina, L.; van der Boom, M. E.; Dutta, P.; Evmenenko, G.; Shukla, A. D.; Stern, C. E.; Pagani, G. A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 2142 and references therein.

(29) Yerushalmi, R.; Scherz, A.; van der Boom, M. E. *J. Am. Chem. Soc.* **2004**, *126*, 2700.

(30) (a) Gulino, A.; Condorelli, G. G.; Mineo, P.; Fragalà, I. *Nanotechnology* **2005**, *16*, 2170. (b) Briggs, D. In *Practical Surfaces Analysis*, 2nd ed.; Briggs, D., Seah, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 1995; Vol. *1*, p 244. (c) Repoux, M. *Surf. Interface Anal.* **1992**, *18*, 567. (d) Young, R. A. In *Introduction to the Rietveld Method in The Rietveld Method*; Young, R. A., Ed.; Oxford University Press: Oxford, U.K., 2002; p 22. (e) Gulino, A.; Lupo, F.; Fragalà, M. E.; Lo Schiavo, S. *J. Phys. Chem. C* **2009**, *19*, 3507.

(31) (a) Cohen, H.; Zenkina, O. V.; Shukla, A. D.; van der Boom, M. E. *J. Phys. Chem. B* **2006**, *110*, 1506. (b) Frydman, E.; Cohen, H.; Maoz, R.; Sagiv, J. *Langmuir* **1997**, *13*, 5089.

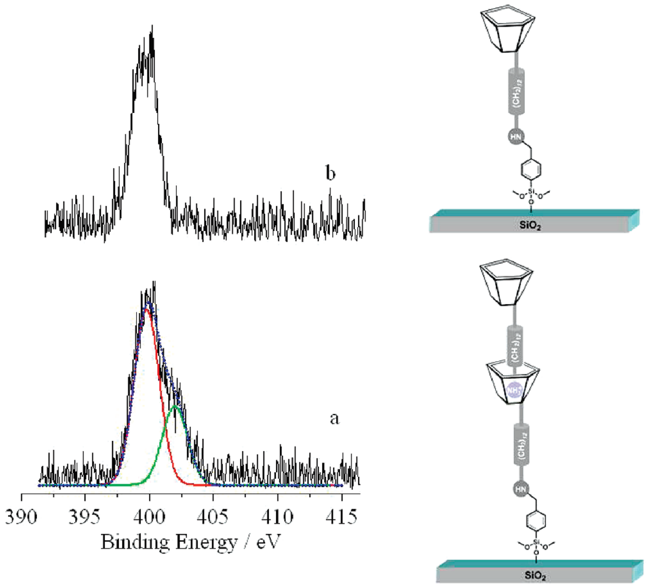

Figure 2. Left-hand side: Al Kα excited XPS in the N 1s energy region for the calix-SAM: (a) as synthesized and (b) after basic washing. Right-hand side: schematic representation of a grafted calixarene molecule with its cavity (a) filled by a **C5-NH$_3^+$** ion, accounting for the higher binding energy shoulder, and (b) empty, accounting for the main peak.

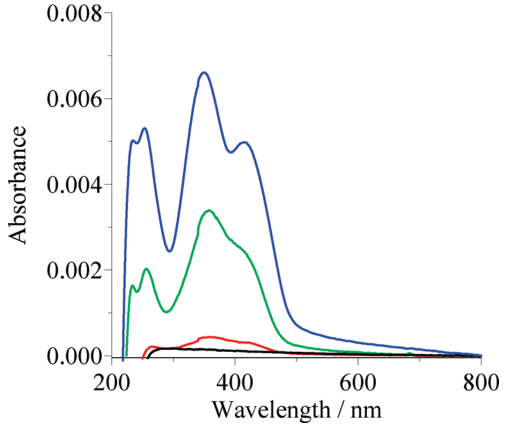

Figure 3. UV−vis spectra of the calix-SAM as such (black trace) and after 1 min of immersion into 1.5 × 10^{-3} M CH_3CN solutions of *n*-$BuNH_3^+Pic^-$ (green trace) or *t*-$BuNH_3^+Pic^-$ (red trace) or cadaverine dipicrate (blue trace) salts followed by rinsing in CH_3CN and drying by a N_2 stream.

preparation of the calix-SAM monolayer. Solvent evaporation from this solution, followed by solubilization of the residue obtained in CD_2Cl_2,[32] showed, in the ^1H NMR spectrum, the presence of peaks (δ = 5.63 and −1.86 to 0.73 ppm)[26] diagnostic[20,24] for an *endo*-cavity inclusion of the terminal $-(CH_2)_5NH_3^+$ moiety of one calixarene unit inside the π-rich cavity of a second one. Direct integration of these resonances against those corresponding to unreacted **C5-NH$_2$** indicated the presence of ~4% of self-assembled species (that is **C5-NH$_3^+$⊂C5-NH$_2$** and/or **C5-NH$_3^+$⊂C5-NH$_3^+$**). Removal of the **C5-NH$_3^+$** ions included on the calix-SAM monolayer surface was accomplished by treatment with a basic THF solution[33] and confirmed by subsequent XPS analysis. Figure 2b shows the absence of the shoulder centered at 401.7 eV and, consequently, confirms that **C5-NH$_3^+$** ions bound to the calix-SAM monolayer can be removed by simple rinsing in basic media. XPS analysis, prior to and after the rinsing procedure in basic media,[33] also indicates that the $-CH_2Cl$ groups of the unreacted siloxane benzyl chloride derivatives present on the functionalized SiO_2 surface were transformed into $-CH_2OH$ ones. This conversion is corroborated by the disappearance of the XPS signal accounting for the chlorine $2p_{3/2,1/2}$ spin−orbit components (doublet at 198.8 and 200.7 eV).[30a,31] Physisorption was excluded by a control experiment carried out on a hydrophilic SiO_2 terminated surface that had previously been exposed to a 1 × 10^{-3} M CH_3CN solution of **C5-NH$_2$** for 24 h and then rinsed. In this case, XPS analysis did not show any nitrogen signal, thus excluding the presence of calixarene molecules on the substrate surface. Using eq 1 where n_N represents the number of N-containing molecules/cm^3 in the monolayer, σ is the photoelectron cross-section, λ is the inelastic mean free path, $T(E)$ is the analyzer transmission function of the XPS instrument, d is the monolayer thickness, and θ is the photoelectron takeoff angle, it was possible to estimate n_N corresponding to the surface coverage of the SAM with **C5-NH$_2$** molecules.[30e] Two different thicknesses were used for these calculations: one equal to 28 Å, as obtained from single-crystal X-ray structural analysis of the analogous 5,11,17,23,29-pentakis(1,1-dimethylethyl)-31,32,33,34,35-penta(4-methylpentyloxy)calix[5]arene,[34] the other equal to 20 Å, by assuming a 45° molecule grafted geometry[35] with respect to the substrate surface. Values of 5.7 × 10^{13} and 6.8 × 10^{13} molecules/cm^2, respectively, were obtained. The resulting molecular footprints were then calculated to be 175 and 147 Å^2, respectively.[12,36]

$$\frac{I_N}{I_{Si}} = \frac{n_{N(atom/cm^3)}\sigma_N\lambda_{N/monolayer}T(E_N)(1-e^{d_{N/monolayer}/(\lambda_{N/monolayer}\cos\theta)})}{n_{Si(atom/cm^3)}\sigma_{Si}\lambda_{Si/Si}T(E_{Si})(1-e^{d_{N/monolayer}/(\lambda_{Si/monolayer}\cos\theta)})} \quad (1)$$

Bearing in mind the known proclivity of calix[5]arenes to selectively recognize and bind linear alkylammonium ions and, at the same time, the ubiquity of amino/ammonium moieties in compounds of biological interest (e.g., basic amino acids, biogenic and trace amines[37]), *n*-butylammonium picrate, *t*-butylammonium picrate, and 1,5-pentanediammonium dipicrate (*n*-$BuNH_3^+$-Pic^-, *t*-$BuNH_3^+Pic^-$ and $Pic^-H_3N^+(CH_2)_5NH_3^+Pic^-$, respectively) were tested as model analytes suitable for optical

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(32) Prior to its use, solvent was percolated through neutral Al_2O_3 to eliminate any traces of HCl.

(33) The treatment involved immersion of the calix-SAM for 2 min into a THF solution saturated with aqueous 0.5 M NaOH, followed by washing with copious amounts of double distilled water and THF and subsequent drying under a N_2 stream.

(34) Gattuso, G.; Notti, A.; Pappalardo, S.; Parisi, M. F.; Pilati, T.; Resnati, G.; Terraneo, G. *CrystEngComm* **2009**, *11*, 1204.

(35) (a) Gulino, A.; Lupo, F.; Condorelli, G. G.; Amato, M. E.; Fragalà, M. E.; Scarlata, G. *J. Mater. Chem.* **2008**, *18*, 5011. (b) Condorelli, G. G.; Motta, A.; Fragalà, I. L.; Giannazzo, F.; Raineri, V.; Caneschi, A.; Gatteschi, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 4081.

(36) (a) Killampalli, A. S.; Ma, P. F.; Engstrom, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 6300. (b) Dube, A.; Chadeayne, A. R.; Sharma, M.; Wolczanski, P. T.; Engstrom, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 14299.

(37) Gerner, E. W.; Meyskens, F. L. *Nat. Rev. Cancer* **2004**, *4*, 781.

sensing by the calix-SAM. Picrate was specifically chosen as the counterion of the target analyte to make sure that binding to the calix-SAM monolayer would result in a UV−vis active species.

Figure 3 shows the UV−vis spectra of the calix-SAM as such (black trace), and after 1 min immersion into 1.5×10^{-3} M CH_3CN solutions of either n-$BuNH_3^+Pic^-$ (green trace), t-$BuNH_3^+Pic^-$ (red trace), or $Pic^-H_3N^+(CH_2)_5NH_3^+Pic^-$ (blue trace), followed by rinsing in CH_3CN and drying by a N_2 stream. According to these spectra, the calix-SAM senses different amounts of alkylammonium ions bound to its π-rich calixarene cavities, by displaying increasing absorbance values in response to the presence of picrate counterions ($\lambda_{max} = 359$ nm) chemisorbed onto the monolayer. This optical behavior is supported by a control experiment carried out, under the same experimental conditions described above, with a solution of tetra-n-butylammonium picrate. In this case, in agreement with the fact that the tetra-n-butylammonium cation is too large to be accommodated inside the calixarene cavity, no UV−vis absorption of the calix-SAM was observed (data not shown). The calix-SAM, on the other hand, is able to detect the dipicrate salt of cadaverine ($Pic^-H_3N^+(CH_2)_5NH_3^+Pic^-$) and, in accordance with the bis-anionic nature of this salt, the absorbance (peak height at 359 nm) was, in this case, found to be twice as intense compared to that for n-$BuNH_3^+Pic^-$.

Spectra in Figure 3 show that in the case of the linear alkylammonium ions (n-$BuNH_3^+$), the absorbance value at 359 nm is almost 1 order of magnitude higher than the one observed for the branched analogue (t-$BuNH_3^+$). Given that n-$BuNH_3^+Pic^-$ and t-$BuNH_3^+Pic^-$ display almost identical ε values in MeCN solution (17 737 ± 18 and 17 591 ± 18 $M^{-1}cm^{-1}$, respectively), it follows that our calix-SAM monolayer possesses a peak selectivity for linear alkylammonium ions. This selectivity is also substantiated by the absorbance displayed (Figure 3, blue trace) by the calix-SAM in the presence of the linear alkyldiammonium dipicrates ($Pic^-H_3N^+(CH_2)_5NH_3^+Pic^-$; $\varepsilon = 34\,436 \pm 34$ $M^{-1}cm^{-1}$ in CH_3CN).

Longer contact periods of the calix-SAM with the solutions of either linear (n-$BuNH_3^+Pic^-$, $Pic^-H_3N^+(CH_2)_5NH_3^+Pic^-$) or branched ($t$-$BuNH_3^+Pic^-$) alkyl(di)ammonium (di)picrates did not significantly change the optical absorbances (Figure S1, Supporting Information). In all instances, rinsing of the samples with a basic THF solution caused reactivation of the optical absorbance (vide supra), as judged by UV−vis spectroscopy. Figure 4 shows that the ability of the monolayer to sense n-$BuNH_3^+Pic^-$ and t-$BuNH_3^+Pic^-$ remains substantially unchanged after several exposure/recovery cycles. Although some variations in the intensities of the absorption minima and maxima are observed (±12%), these modest changes do not affect the overall monolayer performance. They can be ascribed to the "wettability" of the monolayer, which, at the molecular level, is not exactly the same after each immersion cycle in the MeCN solution of n-$BuNH_3^+Pic^-$.[3a] No hysteresis was observed, and shape and peak positions of absorption maxima remained unchanged.

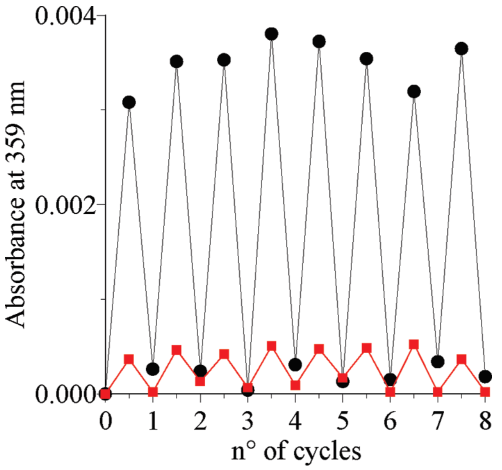

Figure 4. Changes in the absorbance (measured at 359 nm) of the calix-SAM during the cyclic detection/reactivation processes. Black and red circles refer to n-$BuNH_3^+Pic^-$ and t-$BuNH_3^+Pic^-$, respectively.

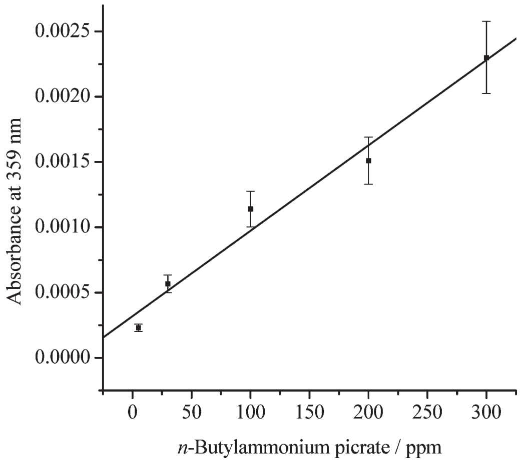

Figure 5. Optical absorbance of the calix-SAM, measured at 359 nm, vs the n-butylammonium picrate ppm level. The R^2 value of the fit is 0.989.

According to previous data in solution (UV−vis,[20] NMR,[38] and potentiometric[39]) and in the solid state,[34] the affinity of calix[5]arenes for linear RNH_3^+ ions results from a number of concurring intermolecular interactions which include (i) tripodal hydrogen bonding of the ammonium moiety to three of the five phenolic oxygen atoms; (ii) cation−π interactions[40] between the positive nitrogen—behaving as a Lewis acid—and the π-rich cavity of the calixarene; and (iii) CH−π interactions,[41] mainly occurring between the α- and β-methylene groups of the n-butylammonium ion and the aromatic rings of the calixarene. In agreement with these studies[20,39] the present results confirm a very moderate affinity of the branched alkylammonium ions for the calix-SAM.

Using the Beer−Lambert law ($A = \varepsilon lc$, where A is the absorbance and ε, l, and c are the extinction coefficient,

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(38) Cafeo, G.; Gattuso, G.; Kohnke, F. H.; Notti, A.; Occhipinti, S.; Pappalardo, S.; Parisi, M. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2122.

(39) Giannetto, M.; Mori, G.; Notti, A.; Pappalardo, S.; Parisi, M. F. *Anal. Chem.* **1998**, *70*, 4631.

(40) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.

(41) Nishio, M.; Hirota, H.; Umezawa, Y. *The CH/π Interaction. Evidence, Nature and Consequences*; Wiley-VCH: New York, 1998.

the thickness of the monolayer, and the concentration of the calixarene molecules in the monolayer, respectively), the surface coverage $d_{\mathrm{surf}} = A\varepsilon^{-1}$ (number of *n*-$BuNH_3^+$ ions/cm^2 on the calix-SAM) can be calculated.[42] Taking into account the ε value of 17 737 ± 18 M^{-1} cm^{-1} in MeCN and all the absorbance values obtained after 1 min of immersion of the calix-SAM in the *n*-$BuNH_3^+Pic^-$ solution, during the cycling processes shown in Figure 4, the calculated picrate density values are in the $5.3-6.4 \times 10^{13}$ molecules/cm^2 range, thus giving values very close to those measured by XPS. These results are consistent with an approximately 1:1 calixarene/*n*-$BuNH_3^+$ interaction of the calix-SAM and stress the fact that all the calixarene molecules present on the monolayer are available for sensing.

Remarkably, heating of the calix-SAM at 100 °C, in the presence of air for 8 days, does not affect its performance (Figure S2, Supporting Information). A similar stability was also detected when the sensor was left at room temperature in contact with air for a period as long as 7 months (Figure S3, Supporting Information). Furthermore, the detection range of the calix-SAM sensor toward *n*-$BuNH_3^+Pic^-$ was found to be linear in the 0.3−500 ppm concentration range (Figure 5).[43] All the results collected in the present studies point to a successful transfer of simple host−guest properties from molecular level to a solid state film.

Conclusion

A new monolayer of calix[5]arene molecules, covalently assembled to a silylated substrate, was synthesized and characterized by UV−vis and XPS measurements. The novel monolayer architecture allows specific recognition functions that can be used for the design of an efficient *n*-alkylammonium solid sensor, and the adopted synthetic procedure has proven to be effective in transferring molecular properties to a solid state architecture. The optical properties of the system can be restored after rinsing for 1 min in a basic THF solution. The optical absorbance of the system is apparently not affected by thermal treatments (up to 100 °C), thus placing the present monolayer in a rare class of functional monolayer-based assemblies that are highly stable.[10,12,44] Finally, these interesting findings provide motivation for further studies involving the syntheses of similar calixarene molecules having appropriate substituents to grant optical bands in the visible region. Such systems, upon guest inclusion, will undergo conformational/geometrical changes and hence electronic structure variations that in turn will generate optical spectra, enabling detection even of analytes that in themselves do not show bands in the visible region.

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Supporting Information Available: Uv−vis spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) Li, D. Q.; Swanson, B. I.; Robinson, J. M.; Hoffbauer, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 6975.

(43) (a) Carturan, S.; Tonezzer, M.; Quaranta, A.; Maggioni, G.; Buffa, M.; Milan, R. *Sens. Actuators, B* **2009**, *137*, 281. (b) Maggioni, G.; Carturan, S.; Tonezzer, M.; Quaranta, A.; Della Mea, G. *Sens. Actuators, B* **2008**, *131*, 496. (c) Tonezzer, M.; Quaranta, A.; Maggioni, G.; Carturan, S.; Della Mea, G. *Sens. Actuators, B* **2007**, *122*, 620. (d) Tonezzer, M.; Maggioni, G.; Quaranta, A.; Carturan, S.; Della Mea, G. *Sens. Actuators, B* **2007**, *122*, 613.

(44) Gupta, T.; van der Boom, M. E. *J. Am. Chem. Soc.* **2006**, *128*, 8400.