Porous Silicon Coated with Calixarene Carboxylic Acid Derivatives: Effects on Luminescence Quenching Selectivity

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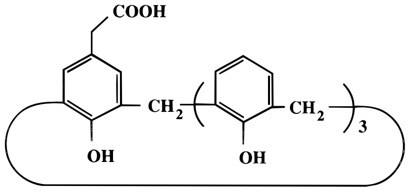
The discovery of visible light emission from porous silicon (PS) in 1990 by Canham[1] has initiated extensive studies designed to understand the fundamental origins of the observed light emission[2] and exploit its potential applications in devices such as light-emitting diodes,[3] biosensors,[4] and antireflection coatings in solar cells.[5] One characteristic property of porous Si warranting concern is the well-documented tendency of the hydride-rich porous silicon surface to oxidize at room temperature, which can impact the photoluminescence (PL) and electroluminescence (EL) of PS.[6,7] To stabilize the surface several groups have pursued approaches to surface derivatization of porous Si with the specific goal of stable, long-term passivation, and generation of a surface with unique chemical stability and selectivity.[8−10] In this paper we demonstrate that carboxylic acid derivatives of macrocyclic cavity-containing molecules known as calixarenes can form thin films on the surface of porous Si. This treatment yields a stable interface demonstrating selectivity with regard to photoluminescence quenching behavior by Cu(II) ions or amines.

Calix[*n*]arenes are methylene-linked phenolic macrocycles available in several cavity sizes ([*n*] specifying the number of phenol moieties in the molecule) and a variety of functional groups at the top and bottom rims of the cavity. The particular derivatives of interest in this study possess carboxyl groups on their upper rim, hydroxyl groups on the lower rim, with *n* varying from four to eight.

Porous Si layers were formed from p-type, ⟨100⟩, CZ-grown, boron-doped Si (6−8 Ω cm) by etching at a constant current density of 50 mA/cm^2 in a solution of a 1:1 mixture of 48% HF:95% ethanol for 20 min. The structures of the calix[*n*]arene carboxylic acid derivatives used in this study are illustrated in Figure 1. Films were formed by exposure of 150 μL of a 0.01 M solution of the relevant carboxylic acid derivative in CH_2Cl_2 on a 1 cm × 1 cm PS substrate for 10 min and allowed to air dry. For the PL quenching experiments freshly prepared 0.01 M solutions of $Cu(NO_3)_2$ in water as well as 0.01 M solutions of amines (*n*-propylamine, *n*-butylamine, *n*-pentylamine) in heptane were used. PL experiments were performed using a Spex Fluorolog-2 instrument in a manner similar to that previously described.[11]



calix[4]arene carboxylic acid

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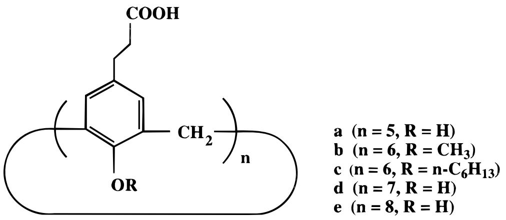

calix[n]arene carboxylic acids, n = 5-8

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Figure 1. Structures of calixarene carboxylic acid derivatives used in this study.

By the method described above, a film of a given calix[*n*]arene carboxylic acid can be deposited onto a freshly-prepared porous silicon surface which appears uniform to the unaided eye after solvent evaporation. In contrast, use of the parent calixarene with *tert*-butyl groups at the upper rim tend to form sub-millimeter-sized aggregates on the PS surface, suggesting that it is the COOH groups that interact with the surface (*vide infra*). From an examination of the infrared spectra of the calix[*n*]arene carboxylic acid-coated porous Si samples one can detect the presence of a C═O stretching mode at 1710 cm^{-1}, a broad OH stretching mode at 3200 cm^{-1}, and several aromatic stretching modes between 1500−900 cm^{-1}. Compared to the IR spectra of these calixarenes in a KBr matrix, a shift of the OH stretch mode (−25 cm^{-1}) and the carbonyl mode (+9 cm^{-1}) is observed upon film formation on PS. The calix[*n*]arene carboxylic acid film(s) can be easily removed with a CH_2Cl_2 wash, with little change observed in the silicon hydride and oxide vibrational modes of the porous Si substrate. When immersed in aqueous or heptane solution(s) for 6 h there is no detectable dissolution of the film as evidenced by IR spectroscopic analysis of the treated substrate before and after solvent immersion. The PL spectra of coated PS samples show only a slight blue-shift of 10−20 nm compared to as-formed PS, with a complete retention of intensity. This is in contrast to the known diminution of PL intensity which occurs when a covalent silyl ester type linkage is formed to the PS surface.[9] Taken in concert, these results are consistent with the presence of Van der Waals forces or hydrogen bonding which are responsible for the interactions between PS and calixarene multilayers.

Given the known sensitivity of porous Si PL to quenching by small molecules,[11−17] the impact of the calixarene carboxylic acids on these types of experiments was then examined. One problem associated with PL quenching experiments at a porous

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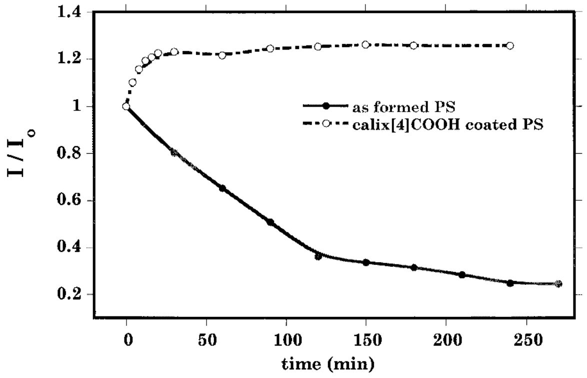

Figure 2. Comparison of the effect of UV (375 nm) irradiation on the normalized PL intensity of (a) as-formed PS and (b) calix[4]arene carboxylic acid coated PS, both immersed in water.

Table 1. PL Quenching Data by Cu(II) on Calixarene-Coated p-Type PS[a]

calixarene	PL quenching % $(I_f - I_o)/I_o \times 100$	calixarene	PL quenching % $(I_f - I_o)/I_o \times 100$
1	−21(7)	**2e**	−76(8)
2a	−44(4)	**2b**	−45(4)
2d	−58(6)	**2c**	−23(8)

[a] I_o = intial PL intensity in the absence of quencher, and I_f = final PL intensity after quenching to saturation. For each type of material, the data were averaged from at least three trials.

Si/water interface is that for freshly-prepared PS, the PL tends to be irreversibly quenched in water under UV irradiation (λ_{ex} ~ 375 nm in our experiments) as a consequence of Si nanocrystallite oxidation. Figure 2 illustrates this degradation behavior for an uncoated PS sample, where the PL is diminished by nearly 80% in 4 h, never truly reaching a useful steady-state intensity. In contrast, comparable experiments with calix[*n*]-arene-COOH-coated PS show an *increase* in integrated PL intensity of ~25% in 20−30 min (Figure 2); this enhancement is observed for calixarene-COOH-coated PS samples immersed in water as well as heptane. Given the previous observation of steady-state enhancement of PS PL upon exposure to the weak organic acid trifluoroacetic acid (TFA), it is likely that it is the COOH terminus that is involved in the enhancement.[11]

In Table 1 the influence of calixarene cavity size comprising the film(s) with regard to Cu(II) ion-induced porous Si PL quenching is noted. The addition of a dilute solution of Cu^{2+} is known to result in a reduction of the visible PL of the porous Si;[15] a gradual increase in Cu(II) ion concentration results in further PL quenching until a steady-state level is reached, with no significant changes in spectral line shape. It is found that at this saturation point the largest percentage of porous Si PL can be quenched from samples coated with calix[8]arene carboxylic acid (76%), followed by porous Si coated with carboxylic acid derivatives of calix[7]arene (58%), calix[5]arene (44%), and calix[4]arene (21%). These differences in PL quenching as a function of calixarene film are mirrored in plots of the reciprocal of normalized PL intensity versus concentration of Cu^{2+} quencher (see Supporting Information). At quencher concentrations of 2×10^{-3} M and below, these data can be fit to a Stern−Volmer equation and binding constants derived from the slope; a 1 order of magnitude difference is observed in the K_{sv} values between calix[8]-COOH-coated PS and calix[4]-COOH-coated PS (1504 versus 128 M^{-1}, respectively). For the case of a calixarene carboxylic acid with six phenol residues (calix[6]arene), only derivatives with alkoxy groups at the lower rim (rather than the usual OH) were available. For PS samples coated with calix[6]arene carboxylic acid with OCH_3 groups at the lower rim, a PL quenching percentage of 45% is observed, quite similar to that of the calix[5]arene carboxylic acids. The introduction of larger alkyl groups (n-C_6H_{13}) at the lower rim of the calix[6]-COOH derivative results in an even further diminution of the percentage of integrated PL that can be quenched by the copper ions, presumably as a result of larger steric hindrance.

From the above data, it is clear that the choice of calixarene size comprising the film does impact the percentage of PS PL that can be quenched by Cu(II) ions. The influence of size and conformation of a given calixarene molecule on packing and resultant film morphology is likely a dominant factor in determining this trend. An examination of calixarene-COOH film morphology on Si by atomic force microscopy (AFM) reveals a stark contrast between the calix[4]arene carboxylic acid derivative and the calix[8]arene analogue (Supporting Information). The coverage provided by the calix[4]arene carboxylic acid derivative gives a far smoother film, while the calix[8]arene acid derivative yields a much rougher surface full of relatively large pores for more efficient Cu transport. In principle, accessible domains exist at the porous Si surface both within an individual calixarene molecule and between adjacent calixarene molecules, depending on the packing.[18] To a first approximation, it seems reasonable that a quencher molecule would choose the least sterically restricted path, given a choice. Given the known cavity sizes of calixarenes,[19] Cu(II) ions are unlikely to diffuse through a single calix[4]arene annulus to the porous Si surface in an endomolecular fashion but rather via an exomolecular process through voids between different calixarene molecules in the film. The possibility of endomolecular diffusion may increase, however, as the cavity size increases along with the conformational flexibility of a given calixarene molecule.

Preliminary experiments for porous Si surfaces coated with calixarene-COOH derivatives and their quenching behavior by amines (in heptane) have also been carried out. Exposure of these modified porous Si surfaces to dilute (micromolar) amounts of either *n*-propyl, butyl, or pentyl amines results in the diminution of steady-state PL intensity, with saturation reached at some point. As expected, uncoated porous Si permits the highest percentage of PS PL to be quenched in these particular substrates, approximately 80% (similar to values for other known PS substrates).[11] It is found that 25% of the integrated PS PL can be quenched for calix[8]COOH-coated PS, while only 6% can be quenched with calix[4]COOH-coated PS. In either case one cannot discriminate between the three amines for a given calixarene coating, but these results do mirror the Cu(II) results in terms of the discriminating behavior between the calixarene molecules of different size. The smaller percentage of PL quenching by amines in these coated PS surfaces likely reflects the importance of Coulombic interactions in the Cu(II) quenching processes, but acid/base interactions between amine and calixarene cannot be excluded at present.

In conclusion, we have coated luminescent porous Si with calixarene carboxylic acid derivatives which show excellent stability in aqueous media and quenching selectivity dependent on the size of the calixarene. Carboxylic acid groups apparently play an important role in the PL enhancement of porous Si.

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Supporting Information Available: AFM images and Stern−Volmer plots (4 pages). See any current masthead page for ordering and Internet access instructions.

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(19) Cavity sizes of calixarenes: the calix[4]arene lower rim diameter is 2 Å; that of calix[6]arene is 3 × 6.2 Å (elliptical); that of calix[8]arene is 3 × 11.7 Å.