Spacing and Site Isolation of Amine Groups in 3-Aminopropyl-Grafted Silica Materials: The Role of Protecting Groups

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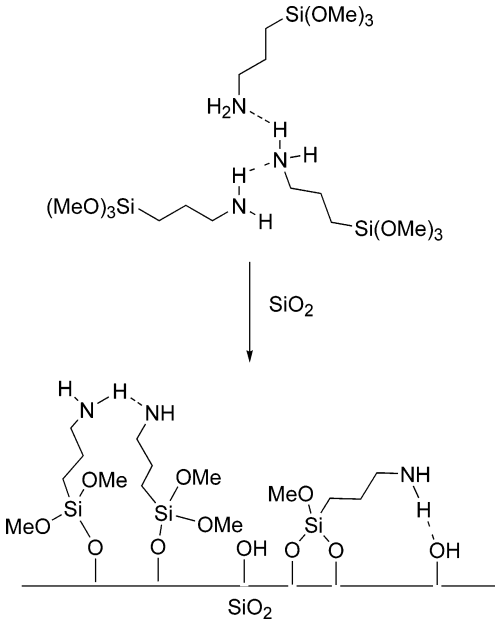
The relative spacing of amines in 3-aminopropylsilyl-grafted silica is studied by solid-state fluorescence spectroscopy of 1-pyrenecarboxylic acid (PCA) and 1-pyrenebutyric acid (PBA) bound to traditionally prepared, deprotected benzyl- or deprotected trityl-spaced aminosilicas. Thermogravimetric analysis and FT-Raman spectroscopy results show evidence that the protected imine can be cleaved to yield the corresponding amine in essentially quantitative yield. The steady-state fluorescence spectroscopic data of either PCA or PBA indicate that the number of amine pairs on the surface separated by a distance of 1 nm or less decreases as the total amine loading decreases. Both the intensity ratio of the excimer band to the monomer band (I_{470}/I_{384} or I_{exc}/I_{mon}) and lifetime decay studies of the fluorophore are useful probes of the amine spacing. Separation of amines on the surface can be achieved by either use of a protected synthesis route or through reduction of the concentration of the unprotected 3-aminopropyltrimethoxysilane used in the grafting solution. However, the two routes lead to materials with significantly different average amine spacings. Due to clustering of unprotected amines in solution before grafting or on the surface during the grafting process, amine−amine distances on the surface of materials prepared by an unprotected synthesis are on average smaller than when a protected synthesis is used. With the protected synthesis, evidence suggests that the amines are more isolated, with larger average amine−amine distances when compared to corresponding materials with a similar amine loading prepared via an unprotected synthesis. This is attributed to both the steric influence of the protecting groups and a reduction in silane clustering in solution due to protection of the amines before grafting. Thus, the mechanism of surface amine spacing when using the protection−deprotection strategy appears to involve both of these factors (especially in the case of trityl-spaced samples).

Introduction

Perhaps no class of organic/inorganic hybrid material has been more widely studied for catalytic and adsorption applications than 3-aminopropylsilyl-modified silicas. Materials in this class are easy to prepare via either the co-condensation[1] of 3-aminopropylsilanes with a silica precursor such as tetraethyl orthosilicate (TEOS) or via the grafting[2] reaction of the aminosilane onto preformed porous or nonporous silica surfaces. Relatively high loadings of amine sites can be achieved via typical synthetic protocols (1.0−1.5 mmol/g solid), with some special synthetic modifications giving loadings of up to 3 mmol/g.[3,4] Higher loadings of nitrogen-bearing groups can also be achieved by building hyperbranched polymers off aminopropyl-functionalized surfaces.[5−7] While these materials are quite useful for a diversity of applications owing to their relatively high loading of amine sites, the development of a molecular level understanding of their surface chemistry is still remarkably

Scheme 1



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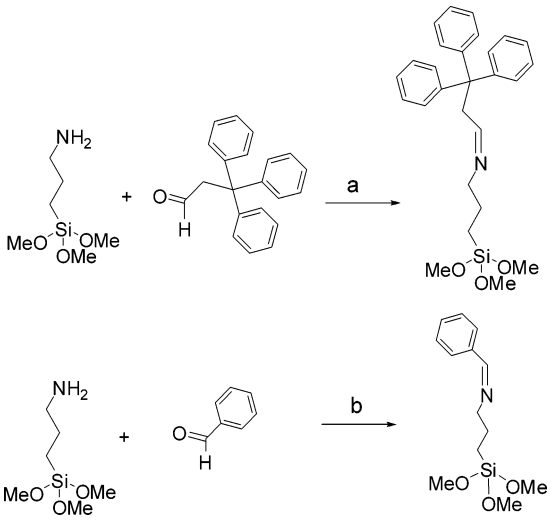
limited, with further development hampered by the variety and complexity of surface amine species that are thought to exist on the surface (Scheme 1). One approach to develop this understanding has been to make "single-site" aminosilica materials with very low amine loading via molecular imprinting.

Imprinting has been successfully used as a tool to create well-defined 3-aminopropylsilyl-modified silicas with good control over the spatial proximity of amine sites.[8] In these cases, protected 3-aminopropylsilyl groups are grafted onto preformed silicas or co-condensed with silica precursors via sol−gel techniques to create 3-aminopropylsilyl sites with controlled spacing.[17−23] A key drawback of this technique is that it has only been applied to create spatially isolated sites at relatively low loadings (from ∼0.09−0.25 mmol/g), whereas for most applications higher loadings are desired (>1 mmol/g). To this end, our group recently utilized a simple method, conceptually related to molecular imprinting,

Scheme 2



to create 3-aminopropylsilyl silica materials with spatially isolated sites in relatively high loadings.[24,25] By protecting the aminopropyl site with a bulky group such as a trityl moiety (Scheme 2a),[25,26] we created 3-aminopropylsilyl-grafted silica materials with relatively isolated, uniformly accessible amine sites at a loading of ∼0.4 mmol/g. These materials proved to be excellent supports for the creation of surface tethered organometallic polymerization catalysts with improved catalytic properties.[27−31]

Our original hypothesis concerning the utility of the trityl-protected 3-aminopropylsilane grafting method was that both the protection of the amine via formation of an imine (Scheme 2a) and the relative bulk of the trityl group (Figure 1) lead to the effective spacing of amines on the surface via both (i) the prevention of the formation of "clusters" of amine groups in hydrophobic grafting solutions (such as toluene) that can react in "packs" on the silica substrate (Scheme 1) and (ii) physical separation of sites on the surface by the bulky trityl group (Scheme 3). Subsequently, we reported a benzyl-protected 3-aminopropyltrimethoxysilane (Scheme 2b),[24] a molecule with very little steric bulk in the protecting group, for the creation of an aminosilica material with a higher amine loading that approached the loading of traditional densely loaded aminopropylsilyl functionalized silicas. Curiously, attempts to probe amine−amine distances on the surface via spectroscopic methods suggested that the amine−amine spacing was different from materials prepared via traditional, unprotected grafting techniques, even though the amine loadings were similar. This suggests that significant steric bulk in the protecting group is not the sole factor that leads to different surface amine site distributions compared to materials made by the traditional method of grafting unprotected 3-aminopropylsilanes onto the silica surface.

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(8) The silica surface contains a disordered array of different species, including isolated silanols, hydrogen-bonded silanols, and areas of condensed siloxane species. For reactions that only or primarily occur with surface silanols (e.g. disilazane reactions[9]) and grafting reactions with organometallic precursors via surface organometallic chemistry,[10] it has been suggested that isolated sites can be created by using dehydroxylated supports treated at temperatures of ≥500 °C. This is suggested to isolate silanols on the surface based on the absence of hydrogen-bonded silanols as observed by FTIR spesctroscopy. However, this approach is not useful for alkoxysilane functionalization, as in the absence of water, grafting can preferentially occur on bare siloxane regions of the silica.[11−13] Thus, although typical reaction schemes such as Scheme 4 show the silanes reacting with surface silanols, it should be noted that silanes also react with bare siloxane regions of the surface. Furthermore, a recent publication by Scott and co-workers shows that dehydroxylation at temperatures of 500 °C still gives a support that contains reactive vicinal silanols, isolated silanols, and siloxane bridges spaced a distance of ∼3 Å from each other.[14] Hence, relying on solely silanol isolation to direct the grafting of unprotected alkoxysilanes will still lead to closely packed, potentially interacting amine sites.[15]
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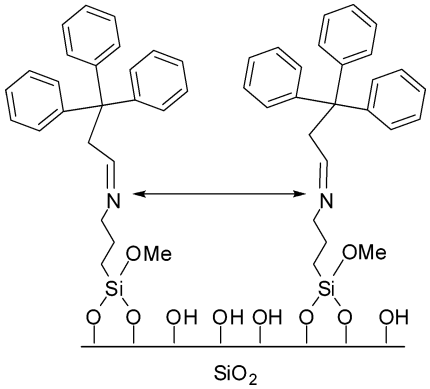
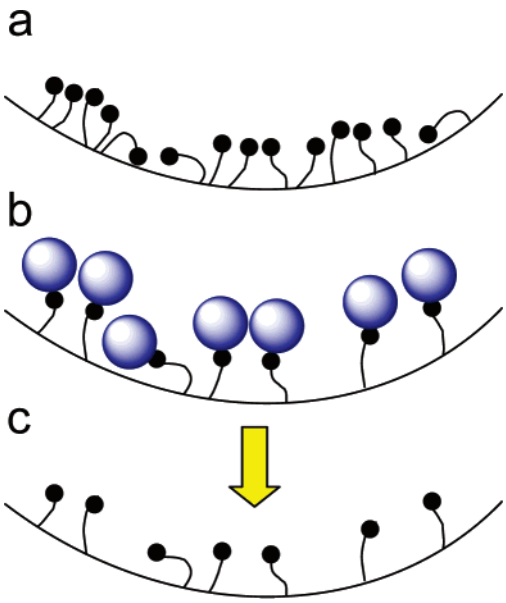


Figure 1. Amine separation due to the bulky trityl protecting group.

Scheme 3. Comparing the Traditional Grafted 3-Aminopropylsilyl Silica (a) with the Protection/ Deprotection (b, c) Strategy[a]



[a] The protection/deprotection method produces separation of the amine sites due to the bulky trityl protecting group.

3-Aminopropylsilyl-modified silica materials prepared by a molecular imprinting approach have been studied on a molecular level in regard to catalytic activity,[17,18,32] adsorption properties,[33,34] site isolation,[18,21,32,35] and organic chain mobility,[35] whereas relatively few reports have focused on the relative spacing and accessibility of amines on the surface of grafted materials with higher loadings.[3,4] In this report, we study the mechanism of spacing using the protected 3-aminopropylsilyl silica grafting approach and employ a fluorescence analytical technique as a sensitive tool to probe the spacing, or degree of site isolation, of these important inorganic−organic hybrid materials. In particular, we use pyrene fluorescence spectroscopic data from a variety of 3-aminopropylsilyl-modified silica materials to assess the degree of site-isolation of surface amines and the role of the protecting group in defining the amine surface density. Furthermore, we show that the amine-protected grafting route is a generally applicable method for the creation of 3-aminopropylsilyl-modified silicas with controllable amine spacings, while dilution of unprotected 3-aminopropyl silanes during grafting results in materials with a relatively higher amount of amine clustering on the surface.

Experimental Section

Materials. The following chemicals were commercially available and used as received: redistilled benzaldehyde (Aldrich), 3,3,3-triphenylpropionic acid (Aldrich), 1.0 M $LiAlH_4$ in tetrahydrofuran (Aldrich), Pluronic 123 (Aldrich), hydrochloric acid (VWR International), anhydrous ether (Aldrich), tetraethyl orthosilicate (Aldrich), 3-aminopropyltrimethoxysilane (Aldrich), 1,1,1,3,3,3-hexamethyldisilazane (Aldrich), anhydrous tetrahydrofuran (Aldrich), anhydrous methanol (Aldrich), 1-pyrenebutyric acid (Aldrich), and 1-pyrenecarboxylic acid (Aldrich). Anhydrous toluene and anhydrous hexanes were further treated by a packed bed solvent purification system utilizing columns of copper oxide catalyst and alumina.[36] All compounds were transferred using standard vacuum line, Schlenk, or cannula techniques under dry, deoxygenated argon or in a drybox under a deoxygenated nitrogen atmosphere in order to reduce/prevent amine−CO_2 interactions.

Synthesis of SBA-15. SBA-15 was synthesized similar to literature methods.[24,37] To 561 g of DI water were added 17.9 g of EO-PO-EO block copolymer and 99.4 g of HCl, and the mixture was stirred overnight. To the micellular solution was added 39.6 g of tetraethyl orthosilicate and the solution was stirred for 5 min. The solution was stirred for 20 h at 35 °C. To swell the pores, a temperature treatment of 80 °C for 24 h was applied. The resulting solid was filtered with copious amounts of DI water and dried overnight at 60 °C. The as-prepared material was calcined using the following temperature program: (1) increasing the temperature (1.2 °C/min) to 200 °C, (2) heating at 200 °C for 1 h, (3) increasing at 1.2 °C/min to 550 °C, and (4) holding at 550 °C for 6 h. Approximately 11.3 g of SBA-15 was collected with this method. Prior to use, the SBA-15 was dried under vacuum at 200 °C for 3 h to remove physisorbed surface water and stored in a nitrogen drybox.[38−40]

Synthesis of Traditional Amine-Functionalized SBA-15 Materials. Excess 3-aminopropyltrimethoxysilane, APTMS, (1.0 g, 5.58 mmol) was added to 1 g of SBA-15 in anhydrous toluene. The mixture was allowed to stir for 24 h at room temperature under argon. The resulting solid was filtered, washed with toluene, dried under vacuum at 50 °C overnight, and then stored in a drybox. TGA showed 1.64 mmol/g SiO_2 of APTMS was immobilized on the SBA-15. Two additional aminosilica materials were synthesized by decreasing the solution concentration of APTMS to produce aminosilicas with lower loadings. For instance, to obtain an amine loading on the SBA-15 of 0.72 mmol/g SiO_2, approximately 0.73 mmol of APTMS in 20 mL of toluene was mixed with 1 g of SBA-15. The same procedure was used to immobilize 1.26 mmol of APTMS on 1 g of SBA-15. Each material was then capped by

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contacting a large excess (2.0 g, 12.4 mmol) of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) with the aminosilica in anhydrous hexanes at room temperature under argon for 24 h. The resulting solid was filtered and washed with toluene and hexanes in a drybox, dried under vacuum at 50 °C overnight, and then stored in a drybox.

Synthesis of Protected Aminoalkoxysilanes. To synthesize the benzyl-protected aminoalkoxysilane, we employed the same procedure as previously reported.[24] Benzaldehyde (0.60 g, 5.65 mmol) was refluxed with 3-aminopropyltrimethoxysilane (APTMS) (1.02, 5.69 mmol) in dry toluene in a 100 mL round-bottom flask equipped with a Dean Stark trap for 24 h. The toluene was removed in vacuo. The excess APTMS was removed under vacuum at 90 °C overnight. NMR data: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.67 (2 H, m), 1.79 (2H, m), 3.57 (9 H, s), 3.60 (2 H, m), 7.40 (3 H, m), 7.72 (2 H, m), 8.27 (1 H, s).

We used a similar procedure to synthesize the trityl-deprotected aminoalkoxysilane.[25,41] First 6.5 g (0.0215 mol) of 3,3,3-triphenylpropionic acid was reduced to the corresponding alcohol by addition of 32.5 mL of 1 M $LiAlH_4$ in anhydrous THF (50 mL) overnight in an ice bath. The solvent was removed from the crude mixture via rotovap (yield $\sim$ 4.6 g). Then, 2 g of the crude mixture containing the synthesized 3,3,3-triphenylpropanol was mixed with 3.64 g of pyridinium dichromate in 100 g of methylene chloride, and the mixture was stirred for 6 h. The solvent was removed by rotovap, and fresh anhydrous ether was added to dissolve the aldehyde. Last, the pyridinium dichromate was removed via two separate filtrations through plugs of silica. NMR data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 (2 H, d), 7.1−7.4 (15 H, m), 9.47 (1 H, s). The aldehyde (1.41 g, 4.92 mmol) was refluxed with APTMS (0.895 g, 4.99 mmol) in dry toluene equipped with a Dean Stark trap for 24 h. The toluene was removed in vacuo. The excess APTMS was removed under vacuum at 90 °C overnight. NMR data: ^{1}H NMR (400 MHz, CD_3OD) δ 0.39 (2 H, t), 1.52 (2 H, m), 3.19 (2 H, t), 3.49 (9 H, s), 3.61 (2 H, m), 7.15−7.36 (15 H, broad), 7.43 (1 H, s).

Synthesis of SBA-15 Functionalized with Benzyl- or Trityl-Protected Aminoalkoxysilanes. The benzylimine spacer (1.0 g, 3.74 mmol) or tritylimine spacer (0.84 g, 1.88 mmol) was added to 2 g of SBA-15 with anhydrous toluene and stirred at room temperature under argon for 24 h. The resulting solid was filtered and washed with toluene in a drybox, dried under vacuum at 50 °C overnight, and then stored in a drybox. The capping step was carried out by contacting a large excess (2.0 g, 12.4 mmol) of HMDS with the protected aminosilica in anhydrous hexanes at room temperature under argon for 24 h. The resulting solid was filtered and washed with toluene and hexanes in a drybox, dried under vacuum at 50 °C overnight, and then stored in a drybox. The capped benzylimine SBA-15 (0.6 g) was added to 60 g of a 1:1:1 solution (by mass) of H_2O/MeOH/HCl(aq). The mixture was stirred in air at room temperature for 6 h. The tritylimine SBA-15 (0.5 g) was hydrolyzed with 50 g of a 2:2:1 solution (by mass) of H_2O/MeOH/HCl(aq) and stirred for 5 h. The deprotected solid was collected via filtration; washed with copious amounts of DI water, anhydrous methanol, and anhydrous THF; and then dried under vacuum at 50 °C overnight. The deprotected SBA-15 (0.5 g), excess HMDS (1.0 g, 6.2 mmol), and anhydrous hexanes were mixed and stirred at room temperature under argon for 24 h. The resulting solid was filtered and washed with toluene and hexanes in a drybox, dried under vacuum at 50 °C overnight, and then stored in a drybox.

Loading of Fluorescent Probe Molecule on Amiopropyl-Functionalized SBA-15 Materials. A 3-fold excess (to amine loading) of 1-pyrenecarboxylic acid or 1-pyrenebutyric acid was added to 500 mg of traditional or deprotected-benzyl or trityl aminosilica in anhydrous toluene.[42] The reaction mixture was refluxed in anhydrous toluene for 24 h under argon. The solid was washed with 6 × 75 mL of both toluene and THF to remove any physisorbed acid. The material was then dried at 60 °C under high vacuum for further removal of solvent.

Material Characterization. FT-Raman spectra were obtained on a Bruker FRA-106. At least 1024 scans were collected for each spectrum, with a resolution of 2−4 cm^{-1}. Thermogravimetic analysis (TGA) was performed on a Netzsch STA409. Samples were heated under a nitrogen and air stream from 30 to 900 °C at a rate of 10 °C/min. The organic loading was measured from the weight loss from 200 to 650 °C. The organic loading was determined by assuming two methoxy linkages to the surface before hydrolysis and three methoxy linkages after. For the traditional amine-functionalized SBA-15, two methoxy linkages were assumed. The loading of the fluorophore was determined by TGA from the weight loss from 200 to 750 °C. Steady-state fluorescence spectra were obtained on a Jobin Yvon Horiba FluoroMax-P spectrometer equipped with single monochromator on both the excitation and emission sides. All emission and excitation spectra were recorded from the front face of the cell containing the solid sample and were corrected for instrumental response using the correction factors provided by the manufacturer. Degassed solid samples for fluorescence and lifetime measurements were prepared in glass tubes equipped with a 0.1 cm quartz cell attachment and were flame-sealed under vacuum ($P \geq 1 \times 10^{-6}$ Torr) to prevent oxygen quenching. Fluorescence lifetimes were measured by time-correlated single photon counting technique on an IBH (Jobin Yvon Horiba) model 5000F instrument equipped with single monochromator on the excitation and emission sides and a picosecond photon detection module (TBX-04). The excitation source was a Nano LED with a pulse width of 800 ps at 336 nm. Data acquisition for all the data reported on solid samples was carried out in a diffuse reflective mode. Degassed samples were subjected to 336 nm excitation pulses, and the emission signals at various wavelengths (i.e. 377 nm, 465 nm) were collected and averaged (i.e. 5000 counts) to obtain the decay profile. Decay analysis and the fitting routine to determine the lifetime(s) for the decay profiles were performed using the DAS6 software provided by IBH.

Results and Discussion

The interaction between amine groups immobilized on silica using a traditional grafting approach has been hypothesized to involve amine−amine hydrogen bonding—although isolated amines and silanol-complexed amines can also be present—due to "clusters" of amine groups in hydrophobic solutions (such as toluene) that can react in "packs" on the silica substrate (Scheme 1).[4] A molecular level understanding of the surface chemistry in these materials requires knowledge about the mechanism of grafting as well as methods to control the amine−amine spacing on the surface. We probe both of these issues here using pyrene fluorescence spectroscopy.

A. Functional Group Spacing by Pyrene Fluorescence Spectroscopy. Fluorescence spectroscopy has been exten-

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sively used as a tool to probe the degree of isolation or location of functional groups in heterogeneous media labeled with fluorescent probes such as pyrene.[43−59] Pyrene molecules form excimers when they can interact at a close distance via stacking.[60,61] In contrast, isolated pyrene molecules fluoresce via a monomeric emission. For example, the distance between two fluorescing pyrene molecules in crystal form yielding an excimer has been calculated to be approximately $3 \leq r \leq 10$ Å, where r is the distance between two pyrene molecules.[61] Thus, it is hypothesized that pyrene molecules must be 1 nm or closer to form excimers, and the presence or lack of excimer formation can be used as a sensitive probe of pyrene separation. Thus, using this as a model for heterogeneous systems, one can infer separation of these pyrene groups via detection of the excimer formation. Antonietti and co-workers reported the effects of changing the silica pore size on the formation of excimers from pyrene molecules confined in the mesopores, which indicated that pore sizes of ∼20−40 Å produce less excimers than mesoporous materials synthesized with >40 Å pores.[62] Wang et al. reported a method by using fluorescence experiments to determine how functional groups on a silica surface migrate when water is present for one month, obtaining a very small migration rate constant of $\sim 10^{-20}$ cm^2/s with a 6 Å distance of separation for excimer formation.[63] By using the excimer formation of pyrene as a test for pyrene−pyrene distances, it is plausible to use fluorescence spectroscopy as a tool to determine the degree of separation between immobilized species on a silica substrate.

Since fluorescence spectroscopy provides an immense amount of information, we characterize various aminopropylsilyl-modified silica surfaces prepared via several techniques, including traditional grafting of unprotected 3-aminopropyltrimethoxysilane as well as grafting of a variety of differently protected 3-aminopropyltrimethoxysilanes, by using either 1-pyrenecarboxylic acid or 1-pyrenebutyric acid as a fluorescent tag. Using these two fluorophores loaded on the different aminosilica materials, we show that the relative separation of these amine groups can be easily determined by fluorescence spectroscopy and that solution "clustering" of these amine functionalities can be reduced by protecting the amines or, to a lesser extent, by dilution of unprotected 3-aminopropyltrimethoxysilane (APTMS) in solution before grafting on the silica surface.

B. Aminosilica Materials Studied. The silica support material used in this study is mesoporous SBA-15.[37] This material was chosen due to its extensively characterized unidimensional hexagonal array of mesopores.[37,65−68] For our studies, the SBA-15 that was synthesized had a BET surface area of 960 m^2/g SiO_2 and a BJH adsorption pore diameter of 65 Å. As indicated by Antonietti et al., using such materials for pyrene confinement studies is ideal due to silica's tailorable pore size as well its stability and inertness.[63]

Our group has studied two types of amine-protecting/spacing protocols using either a trityl- or benzyl-protecting group (Scheme 4).[24,25] First, the protected aminopropylalkoxysilane, in the form of an imine, is reacted to the silica surface under strictly anhydrous conditions to prevent oligomerization. A capping step with HMDS is then used to create a hydrophobic surface and decrease the potential for amine-silanol interactions after deprotection. The hydrolysis of the protecting group is performed in a HCl(aq)/MeOH solution. After deprotection, the surface is capped an additional time in case the aqueous solution formed additional silanols (Scheme 5). The samples prepared via benzyl protection are denoted **2a** and **2b**, and those prepared by trityl protection **3a** and **3b** (Table 1).

As the main comparison material, a traditional grafting approach was used to create aminosilicas without a protecting group. In this study, a 3.5-fold excess of APTMS was reacted with SBA-15, and then the remaining silanols were capped, creating samples **1a** and **1b**. Additional samples with different surface amine loadings were prepared by changing the concentration of APTMS in solution, assuming that all of the added silane ended up grafted on the surface. These materials had amine loadings lower than traditional aminosilica materials made with an excess of alkoxysilane. Samples **1c** and **1d** were synthesized with a loading of 1.26 mmol amine per gram of silica, and samples **1e** and **1f** were synthesized with a loading of 0.72 mmol amine per gram of silica.

Last, all of these aminosilicas were contacted with either 1-pyrenecarboxylic acid (PCA) or 1-pyrenebutyric acid

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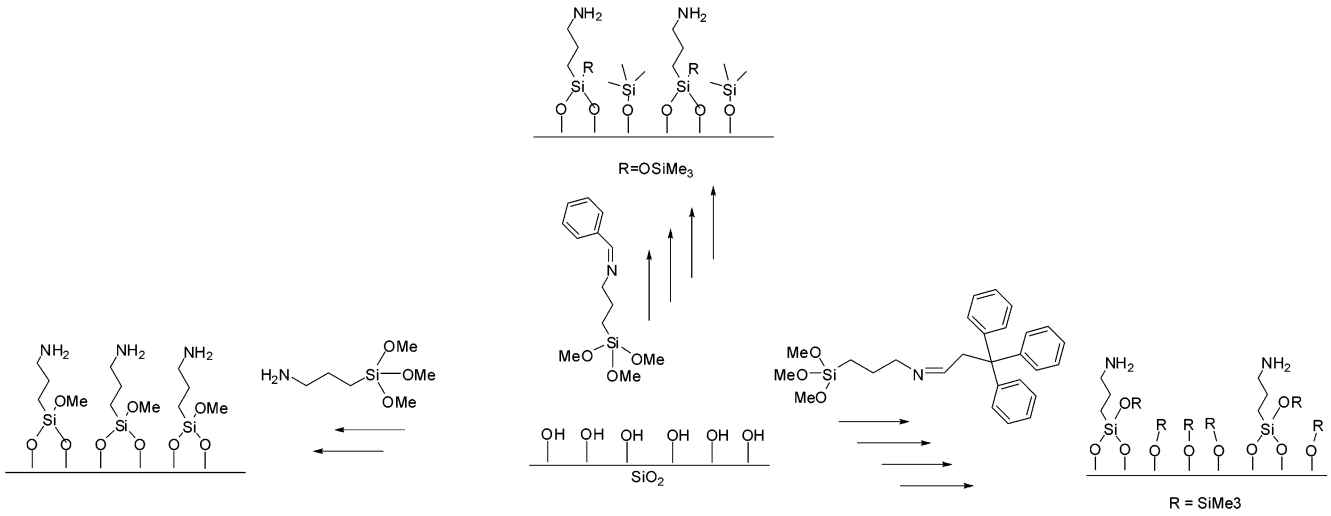
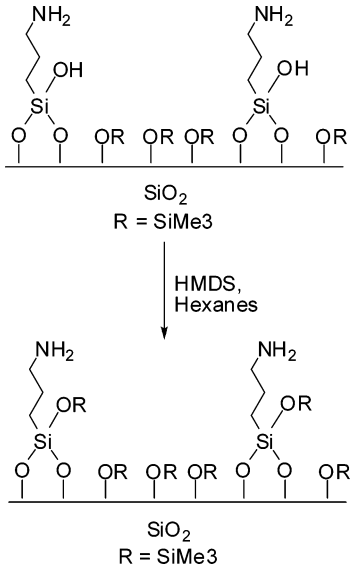
Scheme 4



Scheme 5



(PBA) and studied with both steady-state fluorescence spectroscopy and time-resolved lifetime techniques. Pyrene was the fluorophore chosen due to its well-known ability to form excimers when close enough to another pyrene molecule, as well as the literature precedent of using it in functional group spacing studies.[18,21,61] The carboxylic acid functionalities were used to allow for ionic or hydrogen-bonding interactions between the amines on the surface and the fluorophore (Figure 2),[24] which is discussed in more detail in the next section. Table 1 lists the loadings of the amine groups on the various 3-aminopropylsilyl-functionalized silica materials and the pyrene probe molecules that were loaded on these materials. Similar amine-to-pyrene ratios were obtained on all materials as determined from TGA experiments. Figure 3 shows the FT-Raman spectra of the materials before and after deprotection of the trityl (a and b) or benzyl (c and d) groups compared to traditional aminopropylsilyl functionalized silica (e).

In our previous report on the synthesis of benzyl-deprotected aminopropylsilyl-functionalized silica materials,[24] we noticed that to obtain materials after deprotection that completely lack any residual protecting groups [as determined spectroscopically via the removal of the aromatic C−H transition ($\nu_{\text{C−H aromatic}} = 3100\ \text{cm}^{-1}$) and the C═N transition ($\nu_{\text{C═N}} = 1601\ \text{cm}^{-1}$)], a Dean−Stark trap was needed to prevent oligomerization of the alkoxysilane groups during the synthesis of protected silane via the reaction between the aldehyde and the amine. Initially, we thought that the residual trityl groups within the pore seen in our previous report were there due to the steric bulk of the trityl group and the subsequent difficulty it might have diffusing out of the pore.[25] However, it is now hypothesized that complete removal of all the trityl groups was prevented due to inaccessibility to some sites due to the slight oligomerization of the silane during the synthesis of the protected alkoxysilane. This hypothesis is consistent with the relatively broad ^{1}H NMR resonance observed for the tritylsilane reported previously.[25] In this work, when the tritylimine was synthesized using a Dean−Stark trap to remove the water generated in situ, oligomerization was more likely prevented and the bulky trityl groups were easily removed from the material during deprotection, as shown by the absence of the C−H aromatic transition ($\nu_{\text{C−H aromatic}} = 3100\ \text{cm}^{-1}$) and the C═N transition ($\nu_{\text{C═N}} = 1595\ \text{cm}^{-1}$) (Figure 3b). Thus, in this work, after deprotection of the trityl- (Figure 3b) or benzyl- (Figure 3d) protected aminopropylsilyl-functionalized materials, the main transitions remaining in the FT-Raman

Table 1. Loadings of Organic Groups on SBA-15 and Monomer/Excimer Ratios[a]

sample	protec ting group	loading (mmol NH_2/g SiO_2)	probe molecule	% probe per amine site	I_{exc}/I_{mon}
1a	−	1.64	PCA	34	4.50
1b	−	1.64	PBA	33	110.4
1c	−	1.26	PCA	27	1.10
1d	−	1.26	PBA	35	3.53
1e	−	0.72	PCA	28	0.54
1f	−	0.72	PBA	37	0.89
2a	benzyl	1.35	PCA	37	0.30
2b	benzyl	1.35	PBA	34	1.64
3a	trityl	0.55	PCA	34	0.20
3b	trityl	0.55	PBA	36	0.34

[a] Loadings of protected and deprotected 3-aminopropylsilyl groups as well as loadings of PCA or PBA were determined by thermogravimetric analysis. The excimer-to-monomer ratio (I_{exc}/I_{mon}) was determined for each material based on the probe molecule.

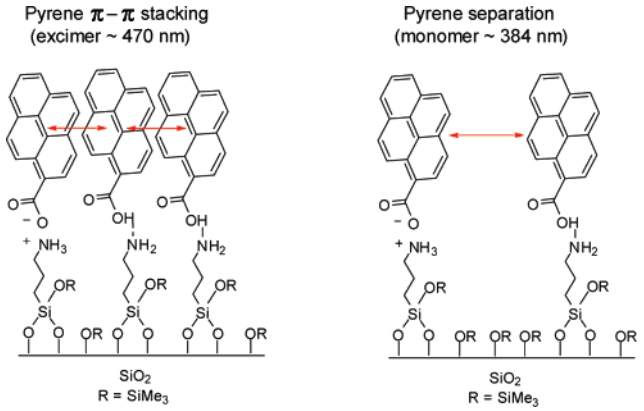


Figure 2. Reaction of PCA on various aminosilicas depicting $\pi-\pi$ stacking (excimer) and monomeric emission.

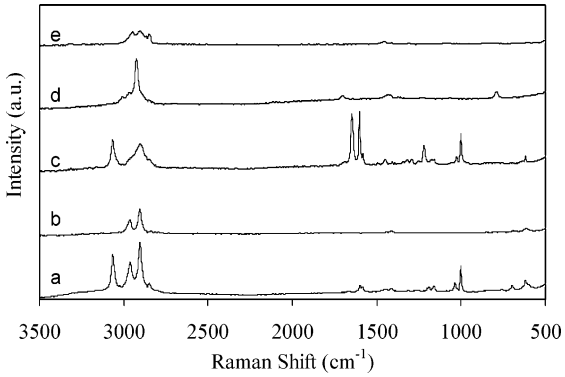


Figure 3. FT-Raman spectra tracking synthesis of the aminosilicas: (a) trityl-protected aminopropylsilyl SBA-15, (b) trityl-deprotected aminopropylsilyl SBA-15, (c) benzyl-protected aminopropylsilyl SBA-15, (d) benzyl-deprotected aminopropylsilyl SBA-15, and (e) traditional (unprotected) aminopropylsilyl SBA-15.

spectra are due solely to the aliphatic C−H bonds in the propyl linker ($\nu_{\text{C-H aliphatic}} = 2840-2990$ cm^{-1}), as is seen in the traditional aminopropylsilyl-functionalized silica material (Figure 3e).

C. Steady-State Emission Experimental Results. Steady-state emission studies were performed to obtain information on the relative separation of amine groups on the surface of the differently prepared aminosilicas. The emission spectra in Figure 4 were obtained by exciting the aminopropylsilyl-functionalized silica materials loaded with 1-pyrenecarboxylic acid (PCA) at 330 nm. From the data, two distinct peaks associated with the pyrene monomer are visible at 384 and 405 nm in all three samples. However, it is obvious that when the traditional grafting approach was used to create the aminosilica, a very broad, intense, structureless peak at 465 nm is also present. This peak corresponds to the pyrene excimers that have formed on this aminosilica material. However, the excimer formation is much less noticeable for the benzyl-deprotected and trityl-deprotected aminosilica. This observation suggests that the amine groups on the surface are distanced enough to prevent the PCA molecules from aggregating and forming excimers. Thus, the amount of excimer (and consequently the pyrene density) tracks well with amine loading. When the ratio of the excimer to monomer (I_{470}/I_{384}) is compared for the various materials, the ratio decreases in the following order: traditional (4.50) > benzyl-deprotected (0.30) > trityl-deprotected (0.20).

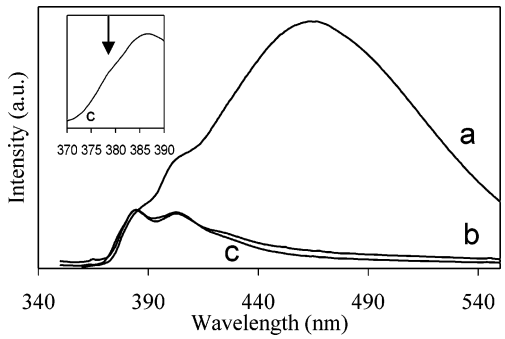


Figure 4. Steady-state fluorescence spectra of PCA loaded on traditional grafted **1a** (a), benzyl-deprotected **2a** (b), and trityl-deprotected **3a** (c) aminosilicas excited at 330 nm.

In our work reporting the benzyl-deprotected aminosilica synthesis, we indicated by FT-IR that the interaction between the PCA and the aminosilica was most likely an acid−base or hydrogen-bonding interaction, due to the lack of amide transitions in the FT-IR spectrum with PCA on an aminosilica.[24] It is good to comment here that work by Milosavljevic and Thomas on pyrene-3-carboxylic acid further supports our studies.[60,68] As indicated in their work, PCA can be present in three different forms: anionic ($PyCOO^-$), neutral (PyCOOH), and protonated ($PyCOOH^+_2$). By changing the pH of the solution, they were able to monitor the excitation and emission of PCA in various environments or media to determine how each species would respond. From their studies, when PCA is anionic, the maxima associated from these two groups were 376, 397, and 416 nm, and when PCA is neutral the maxima were 384, 404, and 425 nm. From our spectra, it is apparent that peaks associated with the neutral forms are present. Upon further analysis, it may be suggested that anionic forms at 377 nm are present as a small shoulder, although these peaks are very difficult to see in the traditional aminosilica, as excimer formation is quite large. This might be expected, as one would assume an equilibrium to be present between the anionic and neutral species. Nevertheless, since the protic, hydrophilic nature of the surface was changed by capping with HMDS, it is expected that the acid fluorophores are most likely interacting with the surface amine groups rather than any surface silanols. This hypothesis was tested by determining the loading of PCA on capped SBA-15. TGA experiments indicate that < 0.01 mmol PCA/g SiO_2 is physically adsorbed on the surface when no amines are present. The hydrophobicity of our sample can be inferred from the observation that the intensity of the 404 nm peak is similar to the 384 nm peak, indicating a more nonpolar environment compared to a silanol-rich, hydrophilic surface environment.[69]

To probe the role of pyrene−amine distance and pyrene flexibility, the various aminosilica materials were also loaded with 1-pyrenebutyric acid (PBA). Here, the aminosilicas were excited at 330 nm (Figure 5). In this case, the excimer formation increases for all of the materials, when compared to the PCA case (Figure 4). It is noteworthy that as the protecting group is changed, when a fluorophore with more

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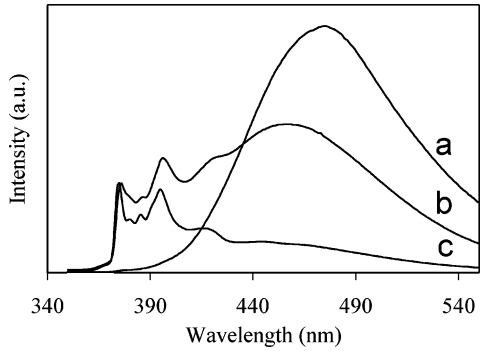

Figure 5. Steady-state fluorescence spectra of PBA loaded on traditional grafted **1b** (a), benzyl-deprotected **2b** (b), and trityl-deprotected **3b** (c) aminosilicas excited at 330 nm.

length is used, the excimer formation appears to be a function of the bulkiness of the protecting group and thus the amine loading. For instance, if the trityl-deprotected aminopropylsilyl-modified silica is compared to the benzyl-deprotected version, the fluorescent data suggest that the amines produced with a bulkier protecting group (such as a trityl functionality) are separated sufficiently to reduce the excimers of the long chain pyrene molecules on the surface, indicating an increase in amine separation. It is also interesting to see how the traditional grafted approach shows essentially no monomeric emission but instead shows strong excimer formation. It is proposed that the amines in this case are so close together the PBA molecules can pack very closely and form virtually all excimers, which can be seen with a red shift to 475 nm. However, when either the trityl- or benzyl-deprotected aminosilicas are examined, the excimer formation is much less compared to the traditional approach. In the case when the amines are separated by a distance of at least a trityl group, the PBA probe molecules are now relatively far away, which prevents formation of as much excimer as was observed in the benzyl-deprotected or traditional grafted aminosilicas. This can be seen when looking at the ratios of excimer (at 475 nm for traditional and 450 nm for benzyl- and trityl-deprotected) to monomer fluorescence (at 375 nm). As the amine groups are separated from closely packed (traditional) to benzyl- and trityl-deprotected aminosilicas, the ratios (I_{exc}/I_{375}) decrease from 110.4 to 1.64 and 0.34, respectively. The ratios for all samples are listed in Table 1.

D. Fluorescent Lifetime Analysis. Steady-state fluorescence gives much information about the separation of probe molecules by tracking the formation of excimers. However, it is also useful to understand more about how the separation of the pyrene molecules attached to the aminosilica surface affects the lifetime of the fluorophore. Shown in Figure 6 is the monomer decay of PCA on the various aminosilicas excited at 336 nm and monitored at 377 nm. For lifetime analyses, the data were fit using the sum of two exponentials with a third exponential component included to fit the scattered light from the instrument (eq 1).[70] When a three-exponential equation was used, the third component had a lifetime value in picoseconds. However, if solely a two-exponential fit was used, a χ^2 value greater than 3.0 was found. To best fit the data and use only a two-exponential fit, eq 1 was used where τ_0 was set to 0.056 ns (eq 2). This fixes the scattered light component and allows for the other two lifetime parameters to be determined (τ_1 and τ_2).

$$I = A + A_0 \exp\left(-\frac{t}{\tau_0}\right) + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

$$\text{where } \tau_0 = 0.056 \text{ ns} \quad (2)$$

(70) HORIBA Jobin Yvon IBH DAS6 Fluorescence Decay Analysis Software User Guide.

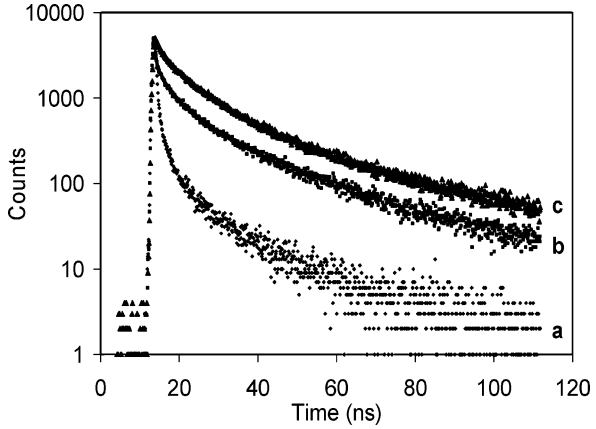

Figure 6. Lifetime decay curves of PCA loaded on traditional grafted **1a** (a), benzyl-deprotected **2a** (b), and trityl-deprotected **3a** (c) aminosilicas excited at 336 nm and monitored at 377 nm.

Table 2. Comparing the Lifetimes of PCA and PBA on Various Aminosilicas Excited at 336 nm and Monitored at 377 nm (PCA) and 375 nm (PBA)

sample	fluorophore	lifetime, τ_1 (ns)	lifetime, τ_2 (ns)	χ^2
1a	PCA	2.0 ± 0.08	14.8 ± 0.31	1.25
1b	PBA	3.0 ± 0.12	24.2 ± 0.58	1.20
2a	PCA	5.5 ± 0.10	27.7 ± 0.22	1.52
2b	PBA	8.3 ± 0.24	54.8 ± 0.24	1.50
3a	PCA	7.3 ± 0.10	32.3 ± 0.22	1.65
3b	PBA	8.6 ± 0.29	114.0 ± 0.80	1.29

When looking at the decay of the PCA in Figure 6, two components are seen: a short lived component and a longer lived component that is more distinct for materials **2a** and **3a**. If the traditional aminosilica was used, the resulting longer lived lifetime of the PCA monomer on the surface is calculated to be 14.8 ± 0.31 ns (**1a**, Table 2). However, if the benzyl- or trityl-deprotected aminosilicas were analyzed, the lifetimes of the longer lived PCA monomer component increase to 27.7 ± 0.22 ns (**2a**) and 32.3 ± 0.22 ns (**3a**), respectively. Considering the longer lived component, the lifetime difference of PCA between the benzyl- and trityl-deprotected aminosilica is roughly 4.6 ns. Thus, the PCA molecules on the surface of either of these materials seem to be very similar. In contrast, when viewing PCA on the traditional aminosilica, the lifetime is reduced by ∼13−17 ns. This indicates that the fluorophores in **1a** are close enough to interact and shorten the lifetime of the monomers by static quenching (excimer formation).

When the lifetimes of PBA are determined on these materials, much larger differences are observed. For instance, on the trityl-deprotected aminosilica, the lifetime of the longer lived PBA molecule is 114.0 ± 0.80 ns (**3b**, Table 2). This lifetime is over four times that of the PBA molecule on traditional aminosilica (**1b**, Table 2). This is expected as

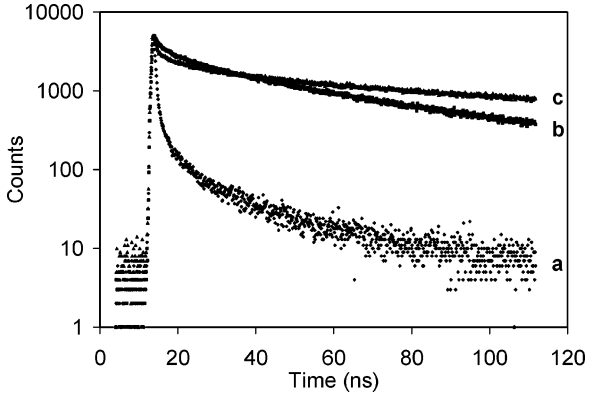

Figure 7. Lifetime decay curves of PBA loaded on traditional grafted **1b** (a), benzyl-deprotected **2b** (b), and trityl-deprotected **3b** (c) aminosilicas excited at 336 nm and monitored at 375 nm.

there is virtually no monomer seen in the steady-state spectrum of the PBA loaded traditional aminosilica (Figure 7), allowing the excimer formation to drastically quench the monomer lifetime. The decay curves of the PBA fluorophore also show two components: a short lived component followed by a longer lived component in the "tail" of the spectrum. It is interesting to compare the "tail" of the benzyl- and trityl-deprotected aminosilicas, as it seems the benzyl-spaced amine groups produce a longer lived PBA molecule early in the decay. However, the amines spaced a distance of the trityl group produce PBA molecules that decay almost in a flatline manner. The fluorescent probes on the trityl-deprotected material are in essence spaced far enough to more than double the lifetime of the PBA probes (**3b**, Table 2) compared to the benzyl-spaced PBA probes (**2b**, Table 2).

E. Changing the Amine Loading in Traditional Grafting. In the above materials, both excimer formation and lifetime track well with amine loading. This suggests the question, is total amine loading the only factor that influences fluorescence properties and hence amine density? To address this issue and to understand how "clustering" of amines in solution affects the proximity of these groups on silica, several samples were made by reducing the concentration of APTMS in toluene to obtain a specific loading on the silica, assuming all the silane was grafted onto the silica surface (materials **1c**−**1f**). This could be an alternative approach to producing isolated sites on a silica surface without the need for amine protection. In this approach, to obtain an amine loading on the SBA-15 of 0.72 mmol/g SiO_2, approximately 0.73 mmol of APTMS in 20 mL of toluene was mixed with 1 g of SBA-15 (**1e** or **1f**). The same procedure was used to immobilize 1.26 mmol of APTMS on 1 g of SBA-15 (**1c** or **1d**). These materials were compared to the material prepared by grafting in the presence of a 3.5-fold excess of 3-aminopropyltrimethoxysilane in solution, our standard or traditional grafting approach (materials **1a** and **1b**, amine loading = 1.64 mmol/g SiO_2). Under the standard conditions the excess silane should cause significant opportunities for amine−amine interactions in solution via "clustering", and these solution-assembled silane clusters may then be transferred onto the surface in "packs" of amino-propyl groups. This clustering might be reduced by both amine protection and reduction in solution amine loading.

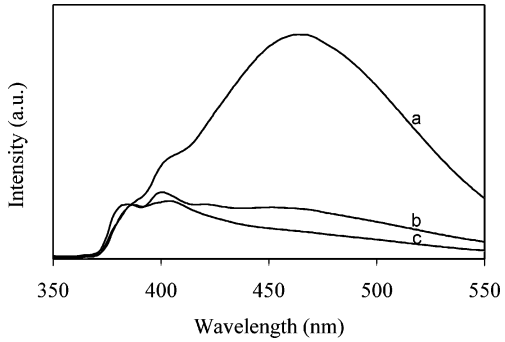

Figure 8. Steady-state fluorescence spectra of PCA loaded on traditional grafted aminosilicas with various amine loadings: 1.64 mmol/g SiO_2 **1a** (a), 1.26 mmol/g SiO_2 **1c** (b), and 0.72 mmol/g SiO_2 **1e** (c) aminosilicas excited at 330 nm.

All the new materials were loaded with PCA or PBA and the fluorescence spectra were obtained.

For the PCA materials (Figure 8), it is obvious that as the amine loading is decreased, the excimer/monomer ratio decreases as well, indicating much more excimer at larger amine loadings. This trend was the same as was observed using the protected synthesis. However, when reducing the amine loading in the unprotected synthesis, it was observed that the degree of excimer formation decreases less rapidly with loading than in the case of materials made via the protected synthesis. Figure 9a illustrates the change in the ratio I_{exc}/I_{mon} as the loading is decreased using either a protected or unprotected synthesis. From these data, it is clear that a protected synthesis results in more evenly spaced amines for a given loading, and amine "packs" on the surface have been limited. Similarly, Figure 9b illustrates how the lifetimes change as the amine loading is decreased using both the protected and unprotected synthesis. Again, it is clear that the two synthetic methods produce materials with different amine spacings at a given total amine loading. An interesting comparison that illustrates this point is between the 0.72 mmol/g SiO_2 traditional aminosilica (**1e**, Figure 8) loaded with PCA and benzyl-deprotected aminosilica (1.35 mmol/g SiO_2) loaded with PCA (**2a**, Figure 4). The ratios of the excimer to monomer (I_{exc}/I_{mon}) for these materials are 0.54 for **1e** and 0.30 for **2a**, indicating that the benzyl-deprotected aminosilica **2a** has roughly one-half the excimer present compared to the unprotected material **1e**, despite the fact that protected material has a 75% greater amine loading. These data strongly suggest that the protected synthesis produces a significantly different material from the diluted, unprotected synthesis. Hence, to prepare isolated amines, it is better to protect the amine groups before immobilization than to attempt amine separation by reducing the amine loading by dilution.

Similar results are seen when PBA was used as the fluorescent probe molecule. As the amine loading was decreased, the excimer/monomer ratio also decreased (Figure 10). When using the PBA probe, the amount of excimer relative to the monomer peak was greater than that of the PCA. This was expected since the PBA probe has a longer linker to the amine, more excimer should be seen since each probe can interact with another probe that is spaced further away.

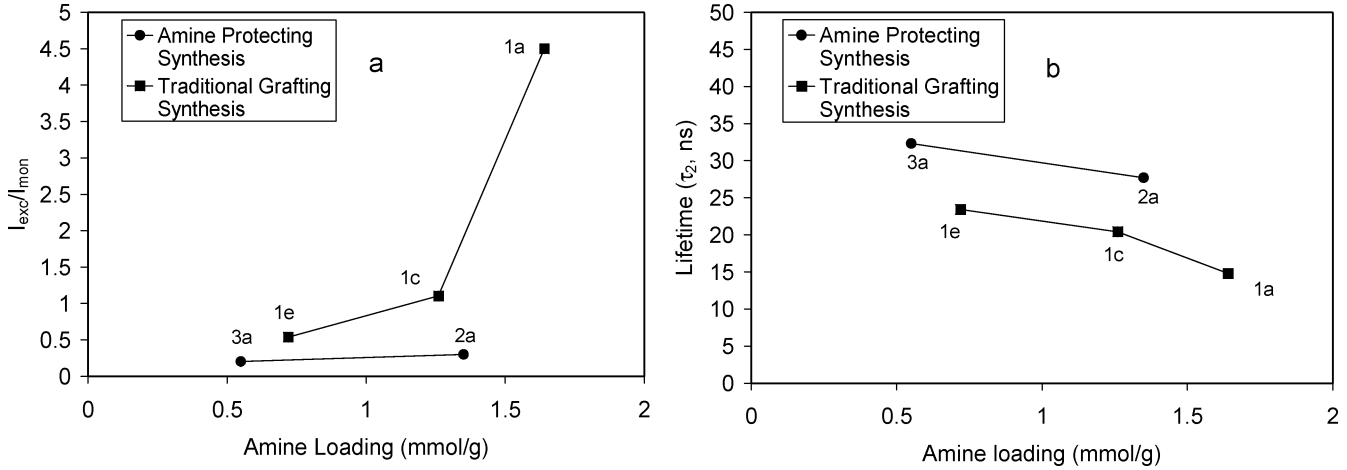

Figure 9. Tracking the intensity of excimer to monomer, I_{exc}/I_{mon}, of PCA (a) and the lifetime, τ_2, of PCA (b) as a function of amine loading for the protection/deprotection aminosilica synthesis versus the traditional grafting synthesis.

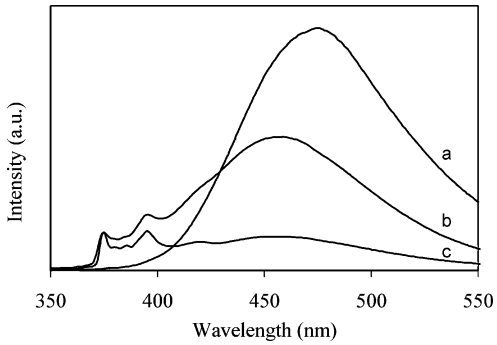

Figure 10. Steady-state fluorescence spectra of PBA loaded on traditional grafted aminosilicas with various amine loadings: 1.64 mmol/g SiO_2 **1b** (a), 1.26 mmol/g SiO_2 **1d** (b), and 0.72 mmol/g SiO_2 **1f** (c) aminosilicas excited at 330 nm.

Table 3. Comparing the Lifetimes of PCA and PBA on Traditionally Grafted Aminosilicas Excited at 336 nm and Monitored at 377 nm (PCA) and 375 nm (PBA)

sample	fluorophore	lifetime, τ_1 (ns)	lifetime, τ_2 (ns)	χ^2
1a	PCA	2.0 ± 0.08	14.8 ± 0.31	1.25
1b	PBA	3.0 ± 0.12	24.2 ± 0.58	1.20
1c	PCA	5.5 ± 0.23	20.4 ± 0.39	1.63
1d	PBA	7.3 ± 0.52	28.7 ± 0.40	2.58
1e	PCA	6.3 ± 0.01	23.4 ± 0.01	1.63
1f	PBA	7.8 ± 0.05	98.5 ± 0.32	1.56

The lifetimes of these materials are shown in Table 3. The results indicate that not only have the aminosilicas produced less excimer when the loading of the amines on the surface is decreased, but the lifetimes of the PCA and PBA monomers are much longer. Therefore, amine density can be reduced to some degree by limiting the concentration of amine sites in solution during the grafting process. However, due to a finite amount of amine clustering that occurs either in solution before grafting or on the surface during the grafting process, the local amine density on the surface is higher at a given overall amine loading when the unprotected grafting approach is used. Thus, this study confirms that amine clustering occurs during the unprotected grafting process. Bass and Katz have also shown that clustering can occur during protected grafting methodologies when using relatively small protecting groups.[71] The data presented here support this finding and show that the use of sterics to control surface site density can be an effective means to control final amine density on the surface, with bulky trityl groups allowing for the synthesis of the most isolated amine sites of the materials studied here.

(71) Bass, J. D.; Katz, A. *Chem. Mater.* **2006**, *18*, 1611.

Conclusions

Recently, we developed a simple methodology for synthesizing aminopropyl-modified silica materials with control over amine spacing.[24,25] Using a protection/deprotection strategy with different sized protecting or "spacing" groups, we created materials with different amine loadings. Probe reaction and spectroscopic tests indicated that these new aminosilica materials were functionally different from traditional aminosilica materials with high amine loadings prepared via grafting. Our hypothesis was that the density of amine sites was controlled by two factors. First, we hypothesized that by preventing aminosilanes from hydrogen bonding or "clustering" in solution, we could prevent these pregrafting amine "clusters" from being transformed into clustered surface species. Thus, we used iminosilanes that could not cluster by hydrogen bonding in solution for grafting. Second, we believed we could use the steric spacing imparted by a bulky protecting group (such as a trityl group) when such species were used as spacers to position the amines on the surface a minimum distance apart. In this work, we probed the average amine−amine surface spacing of a variety of aminosilica materials and used the results to reassess our original amine-spacing hypothesis.

This study addressed the separation of amine groups functionalized on SBA-15 by reacting either PCA or PBA as fluorescent probes to the aminopropylsilyl-modified silica. The data indicate the local surface amine spacing, on a length scale of 1 nm or less, can be manipulated easily by using a protected synthesis route. The combined evidence suggests that local amine−amine distance on the surface is larger on materials prepared by a protected synthesis route than materials with a similar overall amine loading prepared by an unprotected, traditional synthesis. The data suggest that both (i) prevention of amine clustering in solution or during the surface grafting process and (ii) steric spacing of amines on the surface based on the size of the protecting group

influence the excellent average site isolation on functionalized 3-aminopropylsilyl silica surfaces prepared via the protection/deprotection route studied here.

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