Durable Modification of Silica Aerogel Monoliths with Fluorescent 2,7-Diazapyrenium Moieties. Sensing Oxygen near the Speed of Open-Air Diffusion

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Received April 7, 1999. Revised Manuscript Received May 24, 1999

Silica sol−gels were covalently modified with *N*-(3-trimethoxysilylpropyl)-2,7-diazapyrenium bromide (DAP). Luminescent aerogels are created in which none of the fluorophore leaches from the gels during either the washing or supercritical drying necessary to prepare DAP-modified aerogels. The bulk density (0.17 g/cm^3), N_2-adsorption surface area (870 m^2/g), and thermogravimetric and scanning electron micrographic characteristics of the dye-modified aerogels remain identical to those of the unmodified silica aerogels. The bulk concentration of the dye in the aerogels was ≤6.6 mM; at these loadings the aerogels demonstrate bulk photoluminescence. As based on the mesoporous surface area, the surface coverage of the dye is 7−8% of a monolayer. The absorption, emission, and O_2-quenching characteristics of the diazapyrenium dye in the aerogels parallel those obtained in alcoholic (rather than aqueous) solution, which further indicates that the dopant molecules are isolated from each other and that they see an environment with a ∼OH polarity. Time-resolved emission studies indicate that all DAP moieties reside in a single type of microenvironment. Emission quenching of ∼1-cm-diameter monoliths of DAP−silica aerogel is complete in <15 s, which compares very favorably with the best response times for pyrene guests in micrometer-thick xerogel films. The apparent diffusion coefficient of O_2 or Ar in the DAP−aerogel monoliths was estimated at ≥0.01−0.02 cm^2/s, which is only 10× less than the unimpeded diffusion coefficient of Ar in air.

Introduction

Porous, optically clear silica materials with composition identical to glass can be prepared by low-temperature sol−gel chemistry, which involves hydrolysis and polycondensation of Si-based precursors (often silicon alkoxides) followed by drying.[1,2] Drying under ambient conditions typically affords xerogels that are less dense than bulk amorphous silica (∼1 g/cm^3 versus ∼2.2 g/cm^3, respectively). Supercritical drying of the wet gel yields silica aerogels with ultralow densities that can approach 0.004 g/cm^3.[1,3−5] Because organic and biological molecules are temperature sensitive, and therefore incompatible with the high temperatures required in regular glass processing, sol−gel syntheses have created a variety of novel advanced materials by incorporating carefully selected functional molecules in sol−gel-derived glasses.[6,7]

Because sol−gel-derived materials are underdense solids, and therefore porous, leaching of small-molecule dopants (or guests) from the solid is a common problem.[8,9] Leaching is particularly acute when gels are processed to aerogels since multiple washing steps occur to replace the pore liquid (typically an alcohol solvent and a small amount of water for silicate gels) with a pure solvent prior to supercritical fluid (SCF) drying.[1−3] A further opportunity to extract any guests or modifiers incorporated within the silica network occurs when SCF CO_2 is used to dry the wet gels. Efficient solvent exchange of the pore liquid requires solvents miscible with CO_2(l), so the pore liquid is first exchanged by acetone or amyl acetate washes before exchange with CO_2(l), followed by supercritical processing.

Leaching of molecular guests can be eliminated by covalently binding the modifier or guest to the gel

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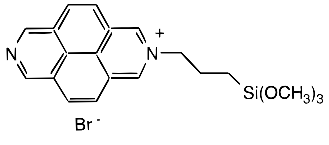
framework.[9] Covalent attachment requires a significant synthetic effort, and we are aware of only a limited number of cases where alkoxysilyl-modified chromophores have been bonded to silicate xerogels.[10-20]

In this paper we describe the preparation and characterization of luminescent silica aerogels derived from cogelation of tetramethoxysilane with *N*-(3-trimethoxysilylpropyl)-2,7-diazapyrenium bromide (DAP). DAP is a luminescent molecule able to covalently bond via its $-Si(OCH_3)_3$ functionality with silanols (Si−OH) on the silica sol or gel framework. The chromophoric core of DAP is analogous to pyrene, which has been used extensively as a photophysical probe of the local pore environment during sol−gel processes and of the resulting materials,[12,21,22] and therefore offers a convenient reference to explore luminescence in silica aerogels. DAP is also a base which leaves open possibilities for further studies not available to pyrene, and ultimately it can be diquaternized to create a dopant fluorophore with two points of attachment to the silica framework.



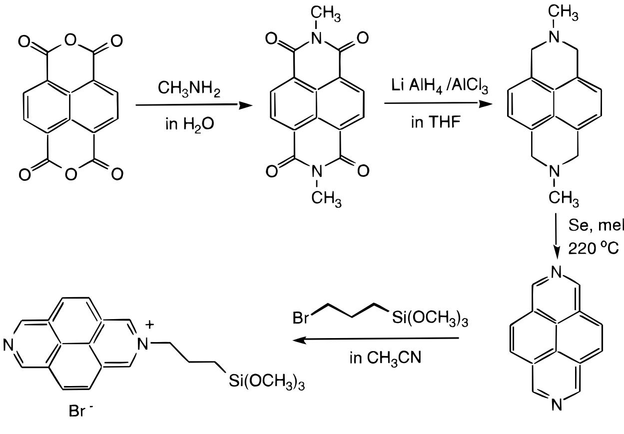
DAP

The relevant materials properties that have been questioned in this study are (a) aerogel structure at levels of doping adequate for functional behavior (e.g., as an oxygen sensor), (b) leaching of the dopant, and (c) spatial and temporal accessibility of DAP in the aerogel network. Experimental evidence shows that aerogel monoliths doped with DAP equilibrate with oxygen and argon in the gas phase in less than 15 s, as contrasted with the much longer response time of chemically related xerogel thin films.

Experimental Procedures

Synthesis of 2,7-Diazapyrene. 2,7-Diazapyrene was prepared from naphthalene tetracarboxylic dianhydride (Aldrich) in a three-step process (see Scheme 1) following standard literature procedures.[23] The overall yield of the sublimed product was 37%: mp (sealed tube) 277.7−279 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.4 (s, 4H), 8.0 (s, 4H); UV−vis (THF) $\lambda_{max}(\epsilon)$ [nm (M^{-1} cm^{-1})] 305 (sh), 319 (21 750), 333 (25 260), 362 (5550), 383 (8370); emission (THF) λ_{max} (relative intensity/%) 385 (100), 407 (68), 430 (20); high-resolution FAB (*m*/*z*) calculated for $(C_{14}H_9N_2)^+$ 205.0687, found 205.0765.

Scheme 1. Synthesis of *N*-(3-Trimethoxysilylpropyl)-2,7-diazapyrenium Bromide (DAP)



DAP

Synthesis of *N*-(3-Trimethoxysilylpropyl)-2,7-diazapyrenium Bromide (DAP). A CH_3CN solution (300 mL) containing 2,7-diazapyrene (0.868 g, 0.004 25 mol) and 3-trimethoxysilylpropyl bromide (12.509 g, 0.051 44 mol) was refluxed under argon for 41 h. The yellow precipitate was collected, washed with warm acetonitrile, and dried under vacuum at 40 °C for 3 days to give 1.270 g of DAP (74% yield): mp >260 °C dec; ^{1}H NMR (D_2O, 500 MHz; hydrolyzed) δ 9.78 (s, 2 H), 9.69 (s, 2 H), 8.65 (d, J = 9.0 Hz, 2 H), 8.51 (d, J = 9.0 Hz, 2 H), 5.12 (t, J = 7.1 Hz, 2 H), 2.40 (br quin, J = 8 Hz, 2 H), 0.78 (br t, J = 8 Hz, 2 H); high-resolution FAB (*m*/*z*) calculated for the cation $(C_{17}H_{17}N_2O_3Si)^+$ 325.4184, found 325.1013.

Aerogel Preparation. A base-catalyzed sol−gel procedure was carried out by mixing two solutions: one (solution A) containing 3.839 mL of tetramethoxysilane (TMOS, Alfa/Aesar) and 4.5139 mL of methanol (Mallinckrodt), and another (solution B) containing 4.5139 mL of methanol, 1.5139 mL of 18 MΩ cm water (Barnstead NANOpure) and 20 μL of NH_4OH (30% in water, Aldrich). Solution B was added to solution A with stirring, and the resulting solution was poured into 1-cm-diameter polyethylene vials, covered with Parafilm to prevent solvent evaporation, and left to gel (~15 min) and subsequently to age for 24 h. To prepare DAP−silica gels, DAP was dissolved in water, and that solution was used as a stock solution for the preparation of solution B. The concentration of DAP in the gels was varied by using different volumes of the stock solution.

At the end of the aging period, all gels were removed from their molds and placed in 20-mL vials filled with ethanol. Ethanol was changed five times, once every 2 h, and then replaced by acetone. Samples were soaked in acetone overnight, followed by washing in acetone (five times, once every 2 h). After a second overnight residence in acetone, the samples were transferred fully submerged in acetone into a cooled (10−13 °C) autoclave (Fisons Bio-Rad E3000) where acetone was extracted and replaced by liquid CO_2. The pore liquid was taken supercritical by increasing the temperature and pressure inside the autoclave above the critical point of CO_2 (31 °C, 7.4 MPa). The passage over the critical point is confirmed by the disappearance of the meniscus at the surface of the liquid CO_2. The samples were kept under supercritical CO_2 for ~30 min to ensure that CO_2 in the micropores went into the gas phase, after which gaseous CO_2 was vented slowly over 45 min.

Aged and ethanol-washed silica gels were post-doped with DAP by soaking them for 24 h in a solution of either 14.3 mL of DAP (6.6 mM) in methanol/water (12.8:1.5 v/v) containing

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10 μL of NH_4OH (30% in water, Aldrich) or 14.5 mL of DAP (6.6 mM) in methanol/water (4.9:9.6 v/v) containing 0.117 g of HNO_3 (J.T. Baker Ultrex). At the end of the soaking period the base-catalyzed solution was depleted of DAP, while the emission intensity of the acid-catalyzed solution was visibly diminished, but not depleted. The post-doped gels were washed with ethanol again and then acetone and dried supercritically as described above.

Aerogel Characterization. Aerogels were characterized by SEM (Hitachi S-4700 field emission scanning electron microscope), thermogravimetric analysis (TGA) under flowing argon (Rheometric Scientific model STA 1500 analyzer), nitrogen physisorption (Micromeritics ASAP 2010 accelerated surface area and porosimetry system), absorption spectroscopy (Hitachi U3000 spectrophotometer), and emission spectroscopy (SPEX Fluorolog 1681 0.22-m double spectrometer). Photographs were taken using Kodak 400-ASA film and a Nikon AF N6006 camera with a Micro-Nikkor 55-mm lens (Figure 1; *f*-stop 2.8; shutter speed 1/15 s under ambient illumination and 2 s under UV illumination using two 4-W long-wavelength UVP Blak-Ray UV lamps) or an AF Nikkor 28-70 mm zoom lens set at 70 mm (Figure 2; *f*-stop 3.6; shutter speed 3 s).

Because of the high optical transparency of the aerogels, UV−vis absorption studies were made on aerogel monoliths placed directly in the light path of the spectrophotometer, while for emission studies, the photoluminescence was monitored at 90° to the excitation beam. Time-resolved emission data were obtained with a system composed of an ORIEL pulsed N_2 laser model 79111 (5 ns), a Spectrograph model 77480, and an InstaSpecV image intensifier/CCD detector using a Stanford Research Systems, Inc. four-channel delay/pulse generator model DG535. Excited-state lifetimes were determined by curve fitting using the Cricket Graph 1.3.2 software package on a Macintosh computer.

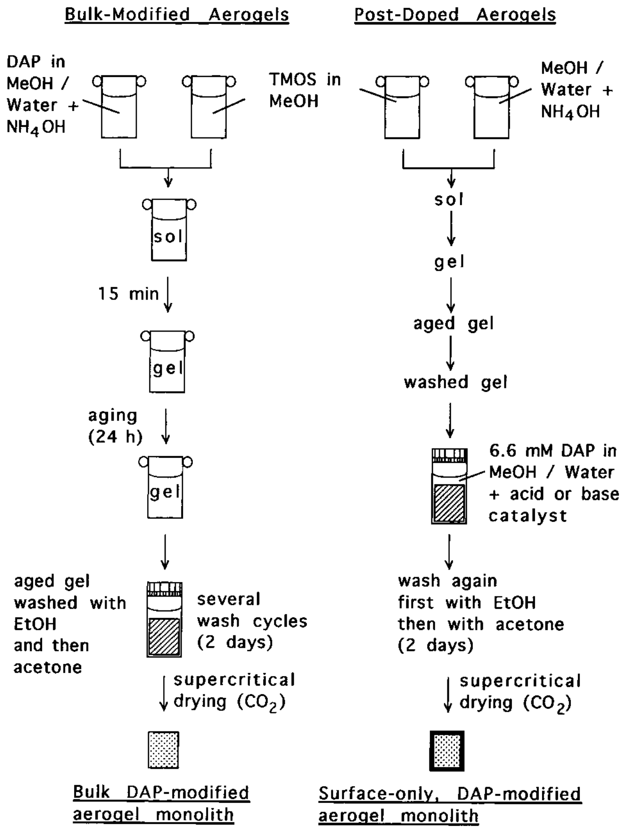
Solutions of DAP were degassed for emission studies by bubbling argon for 5 min, and were saturated with oxygen similarly. Aerogel monoliths were deaerated under a flowing stream of argon for 15 min or saturated with oxygen similarly. To vacuum degas aerogels for emission and lifetime studies, aerogel monoliths were placed in Pyrex culture tubes (13 × 100 mm), which were then elongated above the aerogel samples (∼35 mm long) with an oxygen flame. The elongated tubes were degassed under vacuum (50 mTorr) for 24 h. At the end of that period and while still under vacuum, the glass at the elongated part of the tubes was melted with an oxygen flame to seal the aerogels under vacuum. Solutions of DAP for emission studies were degassed with three freeze−pump−thaw cycles and flame-sealed.

Results and Discussion

Preparation and General Materials Characterization of Aerogels Incorporating DAP. 2,7-Diazapyrene was synthesized following Hunig's procedure,[23] and quaternized with 3-trimethoxysilylpropyl bromide by refluxing in CH_3CN or CH_2Cl_2,[24,25] Scheme 1. The monoquaternized product is insoluble in these solvents and precipitates out, but it is soluble in ethanol and more soluble in water, in which the trimethoxysilyl groups are completely hydrolyzed, as indicated by both NMR spectroscopy and FAB spectrometry.

Bulk-modified DAP−silica aerogels were synthesized according to standard procedures for base-catalyzed hydrolysis and condensation of TMOS (Scheme 2).[26,27] Figure 1 shows photographs of typical native (left) and DAP bulk-modified (right) silica aerogel monoliths under ambient (top) and 365-nm UV light (bottom) illumination. Only DAP-doped aerogels are photoluminescent, emitting a blue light.

Scheme 2. Flowchart of Preparative Procedures for DAP-Doped Silica Aerogels



It is absolutely essential for the scope of this study that the aged gels be first washed with ethanol; direct washing with acetone produces gels with a light brown tint, which persists after supercritical drying. These DAP-free silica aerogels are photoluminescent with a broad featureless band between 500 and 600 nm. The brown tint deepens the longer the aged silica gels stay in contact with acetone during the first washing cycle, and disappears if the dried gels are sintered in air at 500 °C for 0.5 h, at which point the aerogels no longer photoluminesce. These phenomena are attributed to base-catalyzed aldol condensation products derived from acetone. Washing the residual base catalyst from the gels with ethanol before introducing acetone prevents the side reactions, and the resulting silica aerogels remain colorless (even without calcination) and nonphotoluminescent, unless modified with DAP. Although DAP is soluble in ethanol, leaching of DAP from the dye-modified silica gels is not observed; no ethanol mother liquor from any ethanol washing photoluminesces. The absence of photoluminescence in the washes indicates that, after 24 h of aging, all the dye molecules introduced into the sol have covalently attached to the silicate framework.

In an alternative procedure, aged and ethanol-washed base-catalyzed silica gels were post-doped with DAP as described in the Experimental Section and summarized in Scheme 2. Diffusion of dopants into sol−gel-derived

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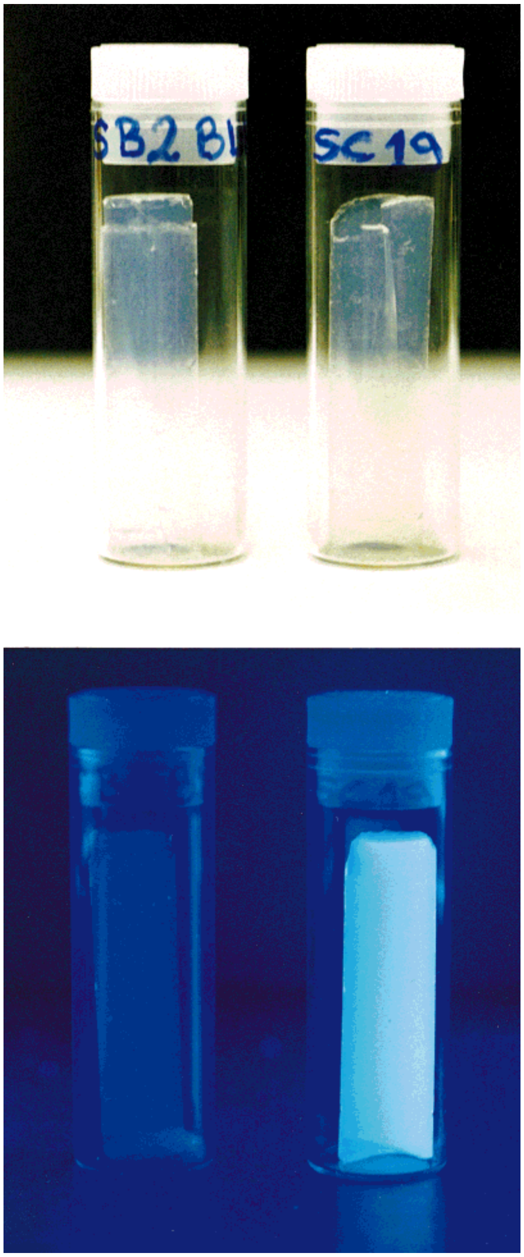

Figure 1. Photographs of a native silica aerogel monolith (left) and of a DAP-doped silica aerogel monolith (right) under ambient illumination (top) and under 365-nm UV light (bottom).

materials has been described before;[28] however, postdoping silica gels with DAP by either acid- or base-catalyzed hydrolysis visibly leads to gels (and ultimately to aerogel monoliths) that are luminescent only at their exterior (Figure 2). Unlike the apparently uniform distribution of the dye during copolymerization with TMOS, DAP-introduced postgelation localizes within a thin layer at the geometric boundary of the gels. These phenomena are not difficult to reconcile: as DAP diffuses from solution into the gel, it reacts with the Si–OH groups on the near-boundary surfaces of the silica gel framework. Because of the very large surface area of the silica gel (see Table 1 below) and the low concentration of DAP in the bathing solution, almost all DAP ends up chemisorbed near the outer surface of the monolith.

Useful photoluminescent properties for bulk-modified DAP–silica aerogels have been obtained with amounts of DAP (apparent bulk concentrations <7 mM) which are inadequate to register a difference in either the IR spectrum or the TGA traces of the silicate framework relative to the unmodified silica aerogel. TGA of monomer DAP demonstrates a high thermal stability with degradation starting above 260 °C in argon. Thermogravimetric analyses of native and DAP–silica aerogels are identical and show an initial loss of mass, presumably water, at <50 °C, with another loss of mass (~6.5%) between 300 and 500 °C. The origin of the second mass loss is not due to the presence of DAP, as it appears for both native and DAP–silica aerogels. The second mass loss may be due to residual nonphotoluminescent organic condensation side products originating from the wash cycles. Support for this argument comes from the fact that the second mass loss disappears after samples are sintered in air at 500 °C.

The microstructure of a bulk-modified DAP–silica aerogel monolith (shown in Figure 3) is indistinguishable from that characteristic of a base-catalyzed silica aerogel.[29] The mesopores are defined by the surfaces of the beadlike colloidal particles that are linked together to form the silica framework. Microscopically this material must have a very high surface area, which is confirmed by nitrogen physisorption, as summarized in Table 1. The BET surface areas[29,30] for native silica aerogel and a bulk-modified DAP–silica aerogel are identical within experimental error (~870 m^2/g). The N_2 adsorption–desorption isotherms exhibit the slight hysteresis customary of mesoporous materials,[31] such as base-catalyzed silica aerogels.[32] Both materials exhibit a broad range of pore sizes with average pore diameters (APD) also typical of mesoporous materials. Copolymerization of DAP and TMOS creates organically modified aerogels that are physically very similar to pure silica aerogels.

Photophysical Studies. DAP was chosen as the dopant because its optical, primarily photoluminescent, properties not only provide a probe of structure and environment in covalently doped aerogels, but also may lead to useful applications. The spectroscopic characterization of a typical bulk-modified DAP–silica aerogel is shown in Figure 4. The absorption and excitation spectra of DAP–silica aerogels coincide precisely. The two absorption/excitation vibronic bands at 300–350 nm and 360–440 nm are attributed to the $S^0 \rightarrow S^1$ and $S^0 \rightarrow S^2$ transitions, respectively. The inset of Figure 4 shows that the absorption of bulk-doped DAP–silica aerogel monoliths follows a Beer–Lambert linear relationship with concentration.

Emission studies with our silica aerogels were carried out with both vacuum-degassed monoliths and samples deaerated under a flowing stream of argon. Because the

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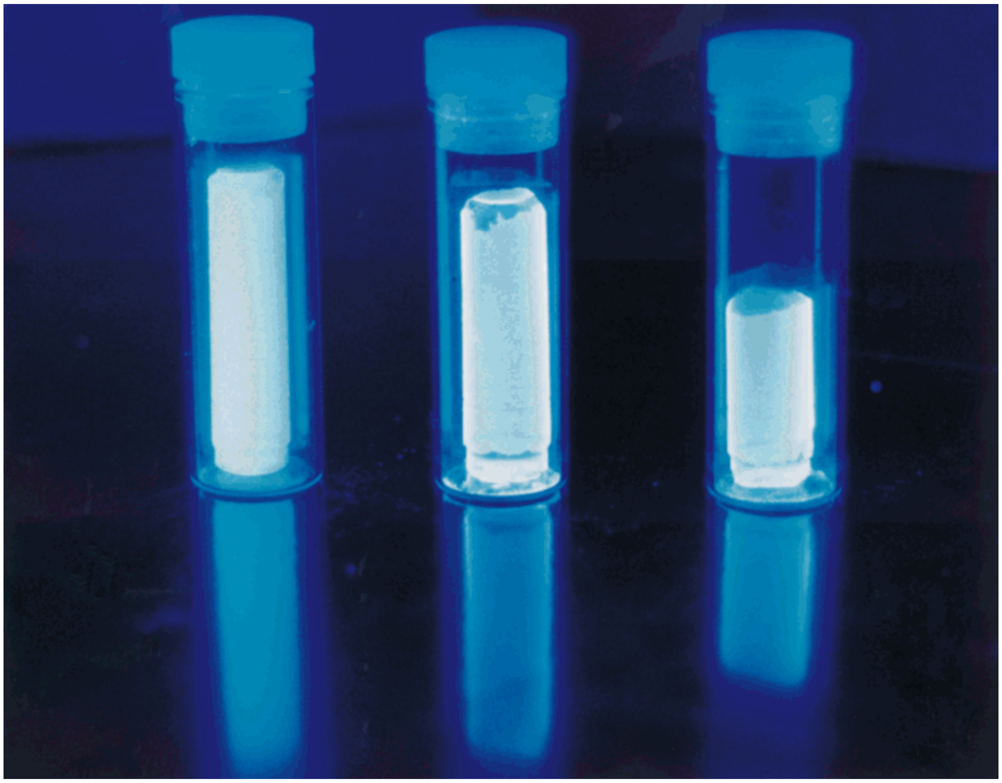

Figure 2. Photographs of DAP–silica aerogel monoliths under UV (365 nm) light: (left) bulk-modified; (middle) base-catalyzed post-doped; (right) acid-catalyzed post-doped. Post-doping leads to confinement of DAP only within a thin skin close to the geometrical boundary of the monolith.

Table 1. Results from N_2-Adsorption Studies

aerogel	BET surface area/(m^2/g) [mesoporous surface area/(m^2/g)]	APD/ nm	bulk density/ (g/cm^3)
native	870 [581]	7.7	0.16_5
DAP-modified	873 [518]	10.2	0.17_0

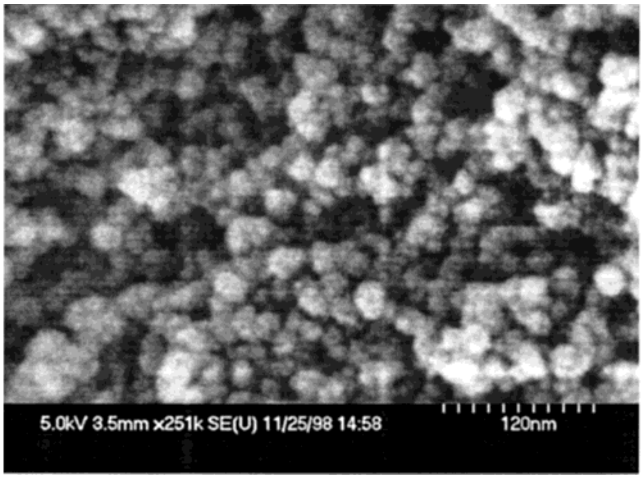

Figure 3. SEM image of a DAP-doped aerogel. $[DAP]_{app}$ = 6.64 mM.

TGA data indicate that DAP–silica aerogels lose water near ambient temperature, prolonged vacuum degassing (>24 h) was used to eliminate possible solvation effects of water on the emission spectra of DAP immobilized in the silica network.

Although it is known that certain types of native silica xerogels can be photoluminescent,[33] our native silica aerogels do not photoluminesce above background, unless base-catalyzed condensation of acetone is allowed to occur, as described above. Emission that was recently reported for undoped silica aerogels was due to defects in the silica framework introduced purposefully via treatment with microwaves (600 W at 2.45 GHz) in the presence of H_2 or NH_3.[34]

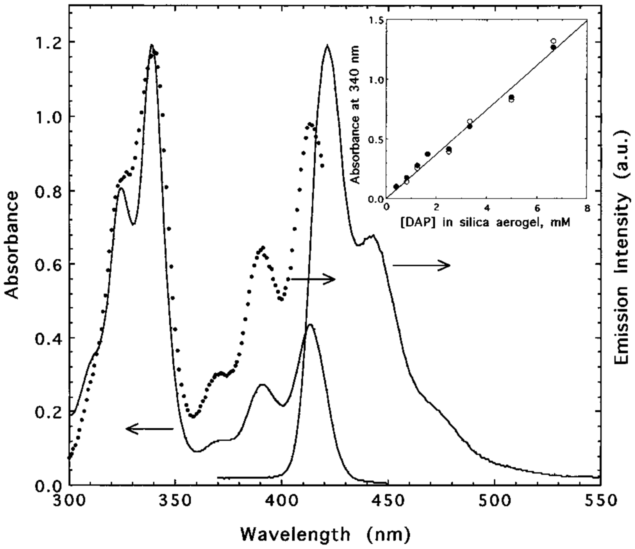

Figure 4. Absorption, emission, and excitation spectra of a DAP–silica aerogel monolith. $[DAP]_{app}$ = 6.64 mM. Inset: Absorbance of DAP-modified silica aerogels as a function of the apparent bulk concentration of DAP (filled circles and open circles represent data from two separate sets of concentration-varied, bulk-modified DAP–silica aerogel monoliths).

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Solid samples of DAP are not photoluminescent either, while solutions of DAP emit with a λ_{max} of 420 nm in methanol (or ethanol) and a λ_{max} of 416 nm in water. Silica aerogels covalently modified with DAP are strongly luminescent, as shown in Figure 1. The position and intensity of the emission spectrum of DAP−silica aerogels (Figure 4) are identical to those of the emission spectra of solutions of DAP in alcohol and remain unchanged whether the aerogels are deaerated with argon or the same samples are sealed in ampules under vacuum. A small (7 nm) Stokes shift occurs between the 0−0 absorption and emission maxima, so the emission with λ_{max} at 420 nm is attributed to $S^1 \rightarrow S^0$ fluorescence. The emission characteristics indicate that DAP moieties are isolated from one another and are located in an environment with a polarity similar to that of an alcoholic solution. We attribute the ~OH nature of that environment to silanols rather than to residual MeOH/EtOH, as will be discussed further below.

We are aware of only a few other publications reporting luminescence of doped aerogels, including doping with Al^{3+},[35] fullerenes,[36] and perhaps most relevant to this study, the fluorescent dye 1,4-bis[5-phenyl-2-oxazolyl]benzene (POPOP) to enhance the efficiency of Cerenkov threshold detectors by spectrally matching the near-UV part of the Cerenkov emission to the light-collection system.[37] As would be expected for a non-covalently linked dopant, a significant loss of POPOP occurred during the washing cycles.

Unlike the linear absorbance−concentration correlation shown in the inset of Figure 4, the emission intensity of the same aerogel samples does not vary linearly with concentration, at least for the most concentrated samples (Figure 5). As the same deviations from linearity are observed with both Ar-degassed solutions of DAP and DAP−silica aerogels under vacuum (compare parts A and B of Figure 5), these deviations cannot be due to an aerogel matrix effect. These deviations plausibly arise from fluorescence self-absorption in the more concentrated samples because of the strong overlap of the 0−0 absorption and emission bands (Figure 4). The variability seen in Figure 5A probably arises from random imperfections in the optical quality of aerogels that promote undesirable reflections and light scattering. Figure 5 demonstrates that the behavior of DAP in silica aerogels parallels its behavior in solution in one other important aspect: oxygen quenches the emission intensity of DAP in both the bulk-modified silica aerogel samples and solution.

Probing the Accessibility of DAP in Aerogel Monoliths by Oxygen Emission Quenching. Oxygen is the model quencher that has been used to evaluate the accessibility of photoluminescent dopants in sol−gel-derived materials.[38−40] The steady-state emission intensity, *I*, at 420 nm of any of the DAP-doped aerogel samples under 1 atm of oxygen drops to about 2/3 of its corresponding value under vacuum, *I*° (Figure 6). Over the concentration range shown in Figure 5, $I°/I = 1.5 \pm 0.2$ for DAP−silica aerogels and 1.3 ± 0.2 for DAP in

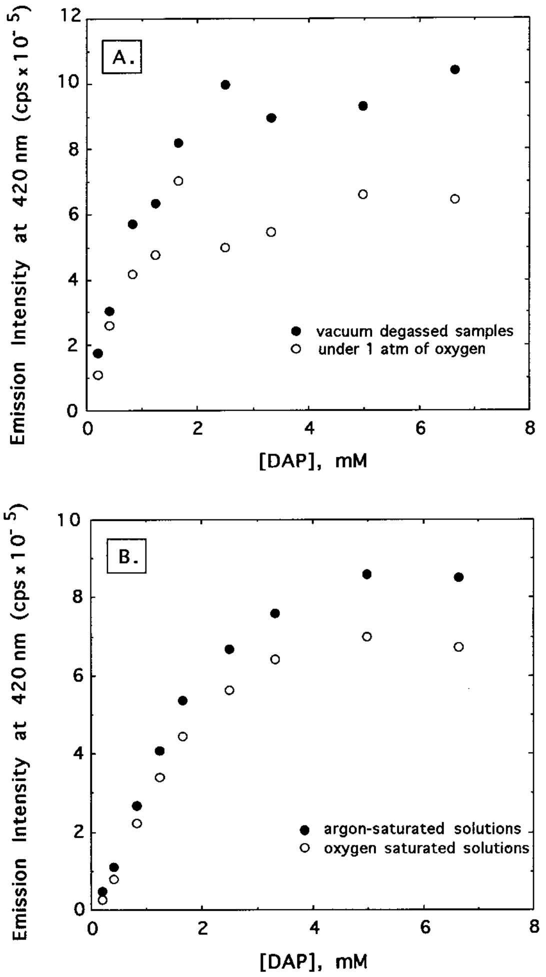

Figure 5. (A) Emission intensity at λ_{max} (420 nm) of bulk-modified DAP−silica aerogels as a function of the apparent bulk concentration of DAP. (B) Emission intensity at λ_{max} (420 nm) of ethanol/H_2O solutions (12.8:1.5 v/v) with variable concentrations of DAP.

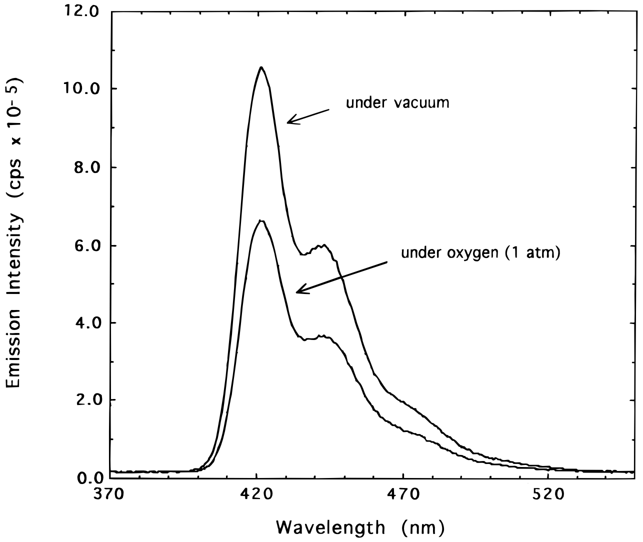

Figure 6. Emission spectra of a DAP−silica aerogel monolith under Ar and under O_2. $[DAP]_{app} = 4.98$ mM.

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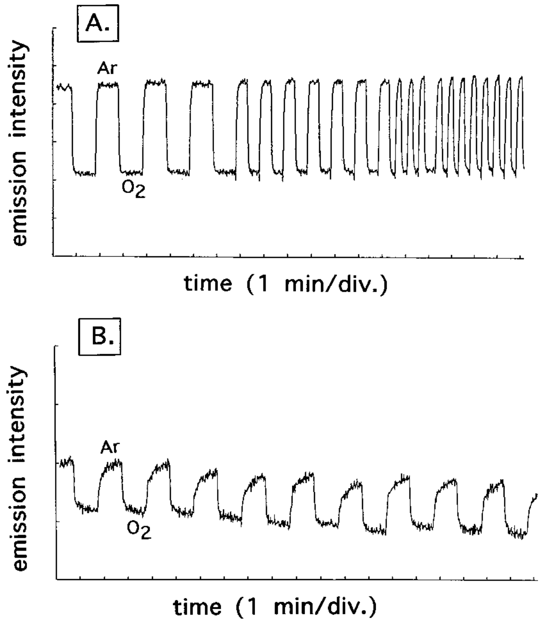

Figure 7. (A) Response of a bulk-modified DAP−silica aerogel monolith to an alternating stream of Ar and O_2. $[DAP]_{app}$ = 6.64 mM. The fastest switching rate was every 15 s; emission was monitored at 420 nm. (B) Response of a bulk-modified DAP−silica xerogel monolith to an alternating stream of Ar and O_2. $[DAP]_{app} \approx 55$ mM. Emission was monitored at 440 nm.

ethanol/water (12.8:1.5 v/v). These values are used below in conjunction with the Stern−Volmer equation to assess the facility of approach of individual oxygen molecules to DAP bound to silica, relative to DAP dissolved in solution.

Oxygen emission quenching offers a convenient means to investigate the temporal accessibility of DAP in bulk-modified silica aerogel monoliths: samples were placed in the light path of an emission spectrophotometer, and the surrounding environment was alternated between argon and oxygen. DAP-modified silica aerogel monoliths respond fully within 15 s, which is about as fast as the flow could be switched reproducibly between the two gases (Figure 7A). The response time to O_2/Ar of 1-cm-diameter DAP−silica aerogel monoliths is estimated at <8 s[41] and is among the fastest of all sol−gel-derived materials, including thin (~0.5 μm thick) pyrene-doped silica xerogel films.[39] Since the monolith radius (r) is 0.5 cm, an estimate of the lower limit of the diffusion coefficient, D, of oxygen or argon in the aerogels prepared according to our procedure can be obtained using the random walk equation ($r^2 = 2Dt$) and is calculated as (1.0−2.0) × 10^{-2} cm^2/s. For comparison, the diffusion coefficient of argon in air under standard conditions is 0.148 cm^2/s,[42] while the diffusion coefficient of oxygen in water is ~2 × 10^{-5} cm^2/s.[43] These results are not surprising given the low density of silica aerogels (Table 1) and their mostly empty, highly porous microstructure (Figure 3).

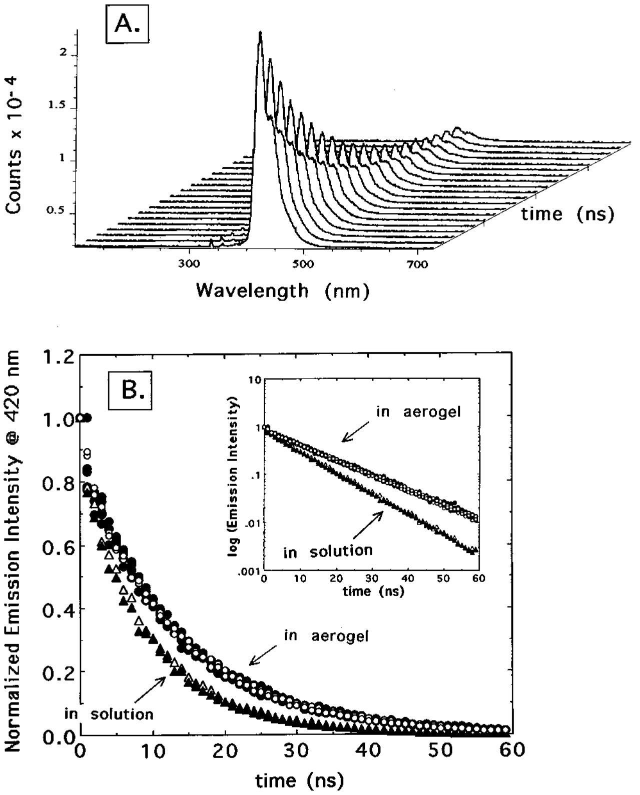

Figure 8. (A) Time-resolved emission from a DAP-doped aerogel monolith ($[DAP]_{app}$ = 0.88 mM). Successive spectra were obtained every 2 ns; each spectrum is the average of 10 spectra. The decaying spike at 337.1 nm is the edge of the N_2 laser excitation pulse (duration 5 ns). (B) Comparison of the emission decay from the bulk-modified DAP−silica aerogel samples of Figure 5A (dark circles), with the emission decay of DAP in solution (triangles; two samples, both at ~7.0 mM in methanol/water, 12.8:1.5 v/v) and with the emission decay of DAP post-doped silica aerogels (open circles; two samples). Inset: Logarithmic plots of emission intensity vs time. The linearity proves that DAP emits with a single lifetime.

The response time of bulk-modified DAP−silica aerogel monoliths is contrasted with that of bulk-modified DAP−silica xerogel monoliths (0.5 × 0.5 × 1.0 cm^3, with an average pore diameter of 3 nm), which were synthesized with the same ratios of reagents used to prepare the DAP−silica aerogels, and left to dry slowly in air over 5 weeks. The emission intensity of the xerogel DAP−silica monolith in response to alternating streams of oxygen and argon is shown in Figure 7B. The DAP−silica xerogels shrink to ~1/8 of their original volume, so their final DAP concentration is higher than in the corresponding aerogels. This increase resulted in significant self-absorption of the emitted light at 420 nm, so the weaker emission at 440 nm was monitored for the xerogels. As shown in Figure 7B, the response time of the xerogels is so slow that, even after 1 min of flowing gas, neither O_2 nor Ar reaches equilibrium within the xerogel monoliths.

Probing the Location and Accessibility of DAP in Aerogels via Emission Lifetime Studies. Typical time-resolved emission data for both bulk-modified and post-doped DAP−silica aerogel monoliths (Figure 8A) confirm that the emission spectra shown in Figures 4 and 6 are due to a single emitting species, as opposed

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[41] Rotating the stopcock between gas streams took ~3 s. The volume of the tubing between the stopcock and the cuvette was 12 cm^3, and the empty volume in the 5-cm^3 cuvette around the aerogel monolith was 2.3 cm^3; the flow rate of Ar and O_2 was ~200 cm^3/min; thus, it is calculated that the actual steady-state response time of the monolith to either gas was $t \leq 8$ s.

[42] *CRC Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1995; pp 6−255.

[43] Ikeuchi, H.; Hayafuji, M.; Aketagawa, Y.; Taki, J.; Sato, G. P. *J. Electroanal. Chem.* **1995**, *396*, 553.

to overlapping spectra of different species (i.e., from DAP and some impurity). The decay of the emission intensity at 420 nm for the various aerogel samples of Figure 5A is compared in Figure 8B with the data from the emission decay of (a) DAP in solution and (b) post-doped aerogel samples. All emission decay data are fit by single-exponential functions (correlation ≥0.998). The lifetime, $\tau°$, of the photoluminescent state (S^1) of DAP is 13.8 ± 0.2 ns in the aerogel samples and 10.08 ± 0.01 ns in solution. The emission lifetime of DAP in post-doped aerogel monoliths is 13.8 ± 0.3 ns, which is equal to its lifetime in the bulk-modified aerogel samples.

Dunn and Zink have identified four types of microenvironments where dopants can be located in sol–gel matrixes.[21] Emission lifetimes of xerogel dopants are used to probe these different possible microenvironments in sol–gel materials, and if multiple exponential decays are observed, they are usually thought of as arising from dopant molecules residing at different sites of the sol–gel network.[44] Since only a single emission lifetime is observed for DAP in the aerogel matrix, whether copolymerized with TMOS or post-doped, we conclude that all DAP moieties are located in a similar microenvironment. In general, rigid environments (or molecules) lead to longer exited-state lifetimes relative to more flexible ones.[45] Therefore, it is not surprising that DAP has a longer lifetime when anchored to the silica framework than it has in solution.

Logically, post-doping silica gels with DAP preferentially anchors the dye onto the surface of the preformed colloidal silica domains that comprise the mesoporous network of the aerogel. Because the emission lifetime of DAP in bulk-modified and post-doped silica aerogels is the same, it is reasonable to conclude that, in both cases, the DAP moieties are located on the surface of the rough silica colloids rather than statistically represented within them. Because $R'Si(OR)_3$ hydrolyzes more slowly than $Si(OR)_4$,[2,9] it is also logical that DAP only modifies the surfaces of silica colloids even when copolymerized with TMOS. The environmental similarity indicates that the silica colloids are surface-terminated with silanols with which DAP can react and any unreacted surface silanols provide an environment similar to that of an alcohol solution. On the basis of the BET surface area (i.e., the surface area of the mesopores only), and the concentration of DAP in the most concentrated sample of Figure 5 (6.64 mM), the surface coverage of the mesoporous area is 0.076×10^{-10} mol/cm^2, which corresponds to 7–8% of a monolayer.

Finally, it is known that the quenching mechanism of singlet excited states by oxygen, a triplet ground-state molecule, involves formation of triplet exiplexes via a bimolecular process.[46] The bimolecular quenching rate constant, k_q, of the luminescent excited state (S^1) of DAP by O_2 can be calculated by applying the Stern–Volmer relationship, $I°/I = 1 + k_q\tau°[O_2]$,[47] where $I°/I$ is known for both aerogels and solution from the data of Figure 5, $\tau°$ is the lifetime of the luminescent excited state in the absence of quencher (derived for both aerogels and solution from the data of Figure 8B), and $[O_2]$ is the corresponding concentration of oxygen.[48] The bimolecular quenching constant of the S^1 excited state of DAP by oxygen is $(8 \pm 3) \times 10^8$ M^{-1} s^{-1} in the aerogel and $(5 \pm 3) \times 10^9$ M^{-1} s^{-1} in solution. The diffusion-controlled bimolecular rate constant for the reaction of DAP* with O_2, as calculated via the Smoluchowski equation,[49,50] is 4.5×10^{12} M^{-1} s^{-1} in the aerogel and 6×10^9 M^{-1} s^{-1} in solution. Clearly, the bimolecular quenching constant of DAP* by oxygen in solution is diffusion controlled, while the same constant in the aerogel is lower than both the corresponding diffusion-controlled limit and the k_q value in solution. This finding is consistent with the proposed location of DAP on the surface of the networked silica particles that comprise the mesopores because surface-bound DAP is configurationally less accessible to oxygen than it is in solution. This physical constraint leads to a higher activation barrier toward exiplex formation and consequently a lower bimolecular quenching rate constant for DAP in the aerogel than in solution.

Summary and Outlook

As expected, a guest that covalently bonds to the silicate framework of sol–gel-derived materials does not leach out of the nanostructure during liquid-phase processing and supercritical drying. This quantitative modification permits doping at a precisely prescribed level for a desired function. Aerogel-associated guests experience ready access to probe molecules diffusing in from the surrounding gas- or liquid-phase environment because the low-density, open-structured morphology of aerogels serves as a molecular autobahn. Aerogels offer ideal platforms for chemical sensors because a single architecture combines fluent mass transport, optical transparency, enormous surface-to-volume ratios, and controlled modification with molecular and particulate guests.[51] The fact that post-doped silica gels are modified with only a thin boundary skin of DAP implies that the best response times ultimately obtainable with any sol–gel type of material will come from post-doped aerogel films. Recent work shows that pyrene post-doped tips (20 μm in diameter) of sol–gel-derived optical fibers respond to O_2/N_2 faster than mid-doped tips.[38b]

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(44) See, for example: (a) Innocenzi, P.; Kozuka, H.; Yoko, T. *J. Phys. Chem.* **1997**, *101*, 2285. (b) Castellano, F. N.; Heimer, T. A.; Tandhasetti, M. T.; Meyer, G. J. *Chem. Mater.* **1994**, *6*, 1041. (c) Narang, U.; Wang, R.; Prasad, P. N.; Bright, F. V. *J. Phys. Chem.* **1994**, *98*, 17. (d) MacCraith, B. D.; McDonagh, C.; O'Keeffe, G.; McEvoy, A. K.; Butler, T.; Sheridan, F. R. *SPIE Sol–Gel Opt. III* **1994**, *2288*, 518.

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(46) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; CRC Press: Boston, MA, 1991; p 168.

(47) The Stern–Volmer expression has been used in conjunction with sol–gel-derived materials before,[39,43d] and it has been pointed out that the linear relationship between $I°/I$ and $[O_2]$ is valid only when there is a single emissive species or excited state in a single type of an environment. According to the dynamic photoluminescence data of Figure 8, DAP in bulk-modified and post-doped aerogels emits with a single lifetime; therefore, direct application of the Stern–Volmer expression is appropriate.

(48) The concentration of oxygen in the gas phase (at standard conditions of temperature and pressure) is 44.6 mM, and in a methanol/water solution (12.8:1.5 v/v) it is ca. 6 mM.

(49) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; p 169.

(50) In applying the Smoluchowski equation, it was assumed that (1) for O_2 to quench DAP* the two molecules should approach each other at a distance of 4 Å and (2) the diffusion coefficient of O_2 in the aerogel monolith is at least 1.5×10^{-2} cm^2/s (as estimated in this study in conjunction with the data of Figure 7) and 2×10^{-5} cm^2/s in water.[43]

(51) Morris, C. A.; Anderson, M. L.; Stroud, R. M.; Merzbacher, C. I.; Rolison, D. R. *Science* **1999**, *284*, 622.

Finally, it has been proposed that molecules that offer more than one point of attachment to the silicate network will better preserve, postgelation, any alignment imposed by an externally applied force field during gelation.[17−19,52] Such a molecule could be obtained for instance by diquaternization of 2,7-diazapyrene with groups bearing the trimethoxysilyl functionality. From our perspective, however, orientation under field is a necessary, but not a sufficient, requirement to synthesize an aligned composite: preservation of alignment also requires that the nanoscale network does not collapse during drying. With this additional criterion, base-catalyzed optically clear aerogels are, among sol−gel-derived materials, ideal platforms to design and explore applications that require aligned anisotropic materials.

Acknowledgment. This work was supported by the Defense Advanced Research Projects Agency (DARPA), the Office of Naval Research, the Air Force Office of Scientific Research (Grant F496-20-94-1-0449), and the Petroleum Research Fund, administered by the ACS (Grant No. 30396-G7). M.L.A. acknowledges an American Society for Engineering Education−ONR Postdoctoral Fellowship. We acknowledge the Washington University NIH Mass Spectrometry Resource for the FAB mass spectra and C. Vierrether (UMR Materials Research Center) for her assistance with SEM.

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