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Energy Transfer Quenching of Porous Si Photoluminescence by Aromatic Molecules

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The ease with which luminescent porous Si can be incorporated into conventional Si microfabrication techniques makes it an attractive material for electroluminescent display,[1–6] detector,[7] and chemical sensor technologies.[8–10] For these applications and to gain a more fundamental understanding of the photophysics of porous Si, we have been attempting to quantify the interfacial electron, hole, and energy transfer pathways accessible to porous Si. These studies should ultimately provide a complete picture of the relationship of luminescent energy states in porous Si to the conduction and valence band edges of the parent bulk crystalline Si, help elucidate the mechanism(s) of radiative and nonradiative decay, and allow the design of efficient electroluminescent or sensor devices with porous Si.

We have previously observed hole transfer quenching of photoluminescence from porous Si by ferrocene,[11] and other workers have observed quenching of porous Si photoluminescence by organic dye molecules.[12,13] In particular, Meyer and co-workers have observed reversible dynamic quenching of porous Si photoluminescence by anthracene and 10-methylphenothiazine, although no specific quenching mechanism could be identified. In this work, we have measured the photoluminescence quenching rates of a series of aromatic organic molecules. The molecules were chosen to try to minimize other potential quenching effects; for example, molecules containing amine groups were avoided because it is known that amines can quench emission from porous Si via a Lewis acid–base interaction.[10,14] The molecules were also chosen to discriminate between electron, hole, or energy transfer mechanisms and have allowed us to conclude that these molecules quench porous silicon photoluminescence predominantly via an energy transfer mechanism. A preliminary report of this work has been presented.[15]

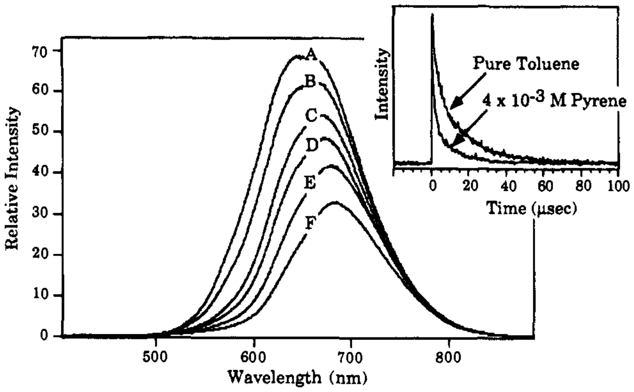

Figure 1. Emission spectra of luminescent porous Si sample upon addition of successive aliquots of pyrene: (A) 6 mL of pure toluene; (B) 1.7 × 10^{-4} M pyrene; (C) 1.1 × 10^{-3} M pyrene; (D) 1.7 × 10^{-3} M pyrene; (E) 2.3 × 10^{-3} M pyrene; and (F) 3.9 × 10^{-3} M pyrene. Excitation source was the 435 nm line of a Hg arc lamp. Inset shows the time-resolved luminescence decay curve measured at 660 nm, with 438 nm pulsed laser excitation.

Luminescent porous Si samples were prepared by a galvanostatic photoetch[8] of n-Si (0.56 Ω-cm resistivity, (100) orientation) in a 50:50 ethanol/HF solution at 5 mA/cm^2 for 30 min. The samples were rinsed with ethanol, dried under a stream of N_2, and then dried *in vacuo* for 30 min prior to use. From this point on, standard Schlenk techniques were used to avoid introduction of air or water.[16] The samples were immersed in 6 mL of pure toluene (Aldrich chemicals HPLC grade, freeze–pump–thaw degassed three times prior to use). Aliquots of a toluene solution of the molecule of interest (Aldrich chemicals) were then introduced via microliter syringe under a nitrogen atmosphere, the solution was stirred for 10 min, and then photoluminescence measurements were made *in situ*. Steady-state photoluminescence measurements were made using a Princeton Instruments liquid nitrogen-cooled CCD detector and an Acton Corp. 0.275 m monochromator, using the 442 nm line from a defocused (~0.5 mW/cm^2) He/Cd laser or 435 nm line from a Hg arc lamp as excitation source. At the end of each titration, an aliquot of several milliliters of pure toluene was added to dilute the solution and check the reversibility of quenching. Quenching was reversible for all molecules reported in this work. Time-resolved photoluminescence data were obtained using an N_2-pumped dye laser (438 nm excitation wavelength), a 0.125 m monochromator, a photomultiplier, and a digital oscilloscope with an instrument-limited time resolution of 200 ns.

Figure 1 shows a series of PL spectra taken from a porous Si sample during the course of a titration with pyrene. There is a systematic loss of PL intensity with increasing pyrene concentration. The time-resolved photoluminescence decay (Figure 1 inset) also shows a distinct decrease in lifetime with added pyrene. Steady-state Stern–Volmer plots for the series of molecules studied yield straight lines (Figure 2). The slope of the Stern–Volmer plot is related to the efficiency of the quenching process via eq 1, where I_0 is the photoluminescence

$$I_0/I = (k_q/(k_r + k_{nr}))[Q] + 1 \qquad (1)$$

intensity in the presence of pure toluene, I is the photoluminescence intensity in the presence of a concentration of quencher [Q] (in moles per liter), k_r is the radiative rate constant, k_{nr} is the intrinsic nonradiative rate constant not dependent on quencher, and k_q represents the rate constant for quenching by the molecular species. The constant k_q can also represent an equilibrium binding constant or a product of binding constant and kinetic rate constant instead of a purely kinetic rate

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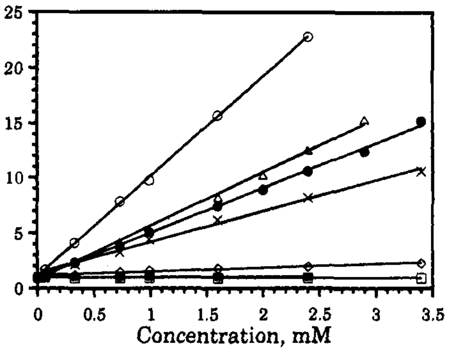

Figure 2. Steady-state Stern–Volmer plots for the series of molecules studied: benzophenone (■), naphthalene (□), pyrene (◇), anthracene (×), 9-bromoanthracene (●), 9-methylanthracene (△,), and 9,10-dimethylanthracene (○). I_0 is the photoluminescence intensity at 660 nm (442 nm excitation) in pure toluene, and I is the corresponding intensity measured in the presence of a given concentration of quencher.

constant.[17] Due to the structural similarity of the aromatic hydrocarbons used in this study, the difference in binding constants with porous Si should not be large enough to account for the large observed difference in Stern–Volmer slopes. For example, the binding constants of naphthalene and pyrene to graphite differ by less than a factor of 2.[18] In addition, time-resolved Stern–Volmer quenching data support a kinetic (dynamic) interpretation of the steady-state Stern–Volmer data, although a direct comparison is complicated by the nonexponential PL decay rates associated with porous Si.[13] Concentration dependencies of the PL decays were analyzed by measuring an "effective τ" as the time at which half the integrated intensity of the PL signal had decayed. It was found that a Stern–Volmer analysis of these lifetime data yielded values of k_q within a factor of 2 of the steady-state measurements.

The quenching mechanism is interpreted as energy transfer from porous Si to the T_1 triplet states of the polycyclic molecular quenchers on the basis of the correlation of the Stern–Volmer-derived quenching rate constants to the published triplet energies of the molecules (Figure 3).[19,20] The plot of $\log(k_q)$ vs triplet energy shows a monotonic increase in quenching rate with decreasing triplet energy. The experiments rule out an electron transfer quenching mechanism on the basis of the lack of detectable quenching by benzophenone. The electrode potential of benzophenone ($E°(BP^{0/-}) = -1.88$ V vs SCE) is only slightly positive of that of anthracene ($E°(An^{0/-}) = -1.92$ V vs SCE),[21] while the difference in observed quenching rates of these two molecules is >2 orders of magnitude (the quenching rate constants reported for benzophenone and naphthalene are probably upper limits due to our inability to accurately measure the very small slopes of the Stern–Volmer plots for these molecules). Similarly, significant contribution from a hole transfer mechanism can be ruled out because the ionization potentials of pyrene and anthracene are essentially the same (7.41 vs 7.45 eV, respectively[22]), while the measured quenching rate for anthracene is an order of magnitude faster than that for pyrene. We cannot completely rule out the possibility of a contribution to quenching via an electron or hole transfer mechanism, although the data do not support either mechanism as the dominant quenching pathway for these aromatic molecules.[23]

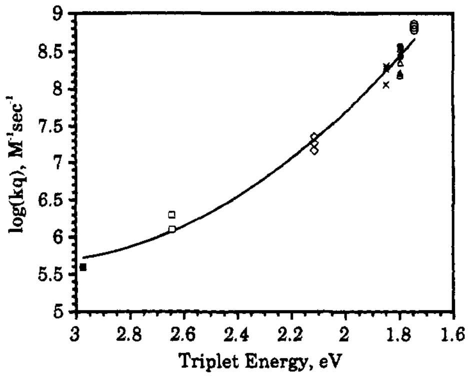

Figure 3. Correlation of the logarithm of k_q to triplet energy of the quencher molecules studied: benzophenone (■), naphthalene (□), pyrene (◇), anthracene (×), 9-bromoanthracene (●), 9-methylanthracene (△), and 9,10-dimethylanthracene (○). Multiple data points represent duplicate runs on different samples. The value of k_q was determined by multiplying the slope of the steady-state Stern–Volmer plot measured at 660 nm (1.88 eV) by 6.7×10^4 s^{-1}, which is the estimated value of $k_{nr} + k_r$ at 660 nm, as noted in the text.

Several complications arise from the fact that porous Si consists of an ensemble of emitters with a range of fluorescence lifetimes.[24] In general, the slope of the steady-state Stern–Volmer plot increases when measured at higher energies, implying that the rate of quenching is faster at a higher energetic driving force. For example, the Stern–Volmer slope for pyrene measured at 660 nm (Figure 1) is 2.5 times larger than the slope measured at 700 nm. However, the photoluminescence decay rate (sum of k_r and k_{nr} in eq 1) increases at shorter emission wavelengths, so the energy dependence of the steady-state data cannot be interpreted in a straightforward manner. Further experiments aimed at a quantitative analysis of the energy dependencies of PL quenching are needed. This report demonstrates that porous Si PL can be quenched via an energy transfer pathway, illustrating the potential for use of porous Si as a sensor for aromatic hydrocarbons and perhaps as a sensitizer for molecular triplet states.

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