The electronic structure of high molecular weight substituted silane polymers in solution: Fluorescence quenching studies

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ABSTRACT

A number of electron-deficient small molecule additives quench the fluorescence of substitute silane high polymers in solution in a fashion consistent with an electron transfer mechanism. The measured rate constants are, however, often much larger than expected for diffusion control. This effect has been attributed to rapid energy transfer among the chromophoric segments comprising the polymer chain. This hypothesis is further supported by quenching studies of photoexcited 9,10-dicyanoanthracene, where the excitation is localized, by ground state substituted silane polymers and oligomers.

INTRODUCTION

Polysilane high polymers which contain only silicon-silicon sigma bonds in the polymer backbone are old materials which have attracted considerable attention recently. The revival of interest over the last 10 years has resulted mainly from the synthesis of soluble homo- and copolymers amenable to characterization. As a result, many potential applications have been envisioned, e.g., broad spectrum photoinitiators, preceramic materials, lithographic resists, photo- and charge conductors and nonlinear optical materials [1].

$$- (R_1 R_2 Si)_n -$$

$$\underset{\sim}{1}$$
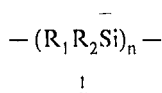
The curious electronic properties of high molecular weight Group XIV catenates in general and polysilanes in particular [1] have stimulated a large number of theoretical and experimental investigations. The polysilanes absorb strongly in the UV from $300 - 410$ nm. The absorption band is usually unstructured and inhomogeneously broadened. Extinction coefficients ranging from $3000 - 25,000$/SiSi have been measured and vary, to a point, with the degree of polymerization [2]. Similar molecular weight effects on the position of the long wavelength absorption (λ_{max}) have also been noted. The increase in both ϵ and λ_{max} seems to saturate around a degree of polymerization of $40 - 50$ [2].

Unlike many π-conjugated polymers, the σ-delocalized polysilanes are often strongly fluorescent both in solution and in the solid state (Φ_{fl} $0.1 - 0.8$) [3,4]. The fluorescence emission is usually narrower than the absorption and only slightly Stokes-shifted. The emission lifetimes are short ($75 - 250$ ps) and the fluorescence quantum yields depend markedly upon the excitation wavelength [4,5],.increasing rapidly for excitation wavelengths near and longer than the absorption maximum. In solution, the emission band shape also depends on the excitation energy, and the fluorescence lifetimes vary with the monitoring wavelength [4]. The fluorescence polarization anisotropy also depends strongly on the excitation wavelength; polarization memory is scrambled for short wavelength excitation and is retained for excitation at wavelengths longer than the absorption maximum [4 – 7]. A number of time regimes associated with fluorescence polarization decay have been reported [8,9].

On the basis of spectroscopic and photochemical studies (vide infra), a chromophoric segmental model has been proposed for the polysilane chain both in solution and in the solid state [4 – 7]. This model suggests that a polysilane chain is composed of a collection of loosely electronically coupled chromophores defined and restricted by the polymer chain conformations which when photoexcited communicate by rapid energy transfer. The absorption and emission properties of the segments depend on factors such as their length, segmental conformational flexibility, site-site variations, differential solvation, etc. The spectral properties of the chain are therefore a composite of those of the various individual segments. Emission studies on poly(di-n-hexylsilane) (PDHS) suggest that the longest emitting segments are in the $Si_{20} - Si_{35}$ range perhaps shorter [5,9]. It has been suggested that in room temperature solution, the segments are composed of trans or nearly trans conformers separated by

strong conformational twists or kinks [5–7], although an alternative worm-like chain structure has also been proposed especially for low temperatures [10,11].

The photochemistry of polysilanes in solution is similarly spectrally inhomogeneous. Although monomeric silylenes, chain silylenes and silyl radicals have all been implicated by trapping [12] and flash spectroscopic studies [13], the products of irradiation depend on the exposure wavelength [14,15]. For example, irradiation of alkyl polysilanes produces monomeric silylenes inefficiently upon irradiation at wavelengths longer than 300 nm, while silyl radicals are generated wherever the polymer absorbs the light. Irradiation results in rapid spectral bleaching and the formation of lower molecular weight fragments. Oxygen is often extensively incorporated into the photoproducts, but spectral bleaching and molecular weight reduction occurs even in an anaerobic atmosphere or under high vacuum. In solution, the quantum yields for chain scission are often high (0.5–1.0), with competitive crosslinking playing a lesser role depending on the nature and position of the substituents [1]. In all cases examined, both chain scissioning and crosslinking are markedly less effective in the solid state than in solution (50–100 times) presumably because of chain repair in the immobilizing medium. The inefficiency of the photoreactions in the solid state led us to investigate the effect of small molecule additives on the photophysics and photochemistry of polysilane derivatives.

Previously, we have described the solution fluorescence quenching of poly(methylphenylsilane) (PMPS) by a variety of small molecule quenchers [16]. In many cases, the measured fluorescence quenching was faster than that expected for diffusion control; a feature which was rationalized by the concept of rapid energy transfer within the polymer chain. Here we extend these quenching studies to include alkyl-substituted polysilanes and probe the role of energy transfer by studying the quenching effect of a variety of poly- and oligosilanes on the fluorescence of 9,10-dicyanoanthracene.

RESULTS

The oxidation of the σ-conjugated backbone of high molecular weight polysilane derivatives is quite facile. Cyclic voltammetry studies both on solid polymer films and in solution show that oxidation occurs between 0.6–1.5 V vs. SCE [17,18]. The position and shape of the oxidation wave depends on the nature of the substituents, with aromatic substitution directly on the polymer backbone facilitating oxidation. In each case, the shape of the oxidation wave suggests that the process is highly irreversible. During electrochemical oxidation, solid polymer films are completely stripped from the electrodes and spectral bleaching occurs in solution. Coulometry studies on the solid films suggested that approximately one electron is removed for every 8–10 silicon atoms in the chain [17].

The combination of the low oxidation potential and the relatively high photoexcitation energy (3.1–4.2 eV) suggested that photoexcited polysilane derivatives should be potent electron transfer reducing agents. The energetics of such electron-transfer reactions are described by the Rehm-Weller equation [19]

$$P + h\nu \rightarrow P^* + A \rightarrow P^+A^- \rightarrow \text{ Products}$$

Photoexcited $\Delta G_{ET}(\text{kcal/mol}) = 23.06[E^*_{1/2}(\text{ox}) - E_{1/2}(\text{red})]$
Donors

$$E^*_{1/2}(\text{ox}) = E^{ox}_{1/2} - E_{0,0}$$ (1)

where $E^{ox}_{1/2}$ is the oxidation potential of the polymer, $E_{0,0}$ is the excitation energy of the polymer in eV and $E_{1/2}(\text{red})$ is the reduction potential of the acceptor. A small coulombic term normally incorporated into the Rehm-Weller equation ($-e_0^2/\epsilon r$) has been omitted here because of the relatively low dielectric constant of the solvents employed (THF, CH_2Cl_2). In principle, the thermodynamic electropotentials utilized in equation 1 refer to reversible oxidation and reduction. Irreversible processes introduce additional uncertainties, since the true thermodynamic values are not known. In these cases, we have chosen the peak potentials for our calculations. Table I lists the $E^*(\text{ox})$ values for some typical polysilane derivatives calculated from Equation 1 and using oxidation peak potentials determined by cyclic voltammetry.

Table I. Excited State Oxidation Potentials

Polysilane	$E_{ox}(V)$	$E^*_{1/2}(\text{ox})$ (V)
$(MePhSi)_n$	0.9	−2.79
$(MeOPhMeSi)_n$	0.66	−2.85
$(Hex_2Si)_n$	1.25	−2.62

The kinetics of photochemical electron transfer processes are often studied by fluorescence quenching [20]. Purely diffusional quenching of a fluorescent material by a quenching additive often follows simple Stern-Volmer (SV) kinetics [21], as shown below, where the ratio of the fluorescence intensities respond linearly to the quencher concentration and k_q and τ_0 are the bimolecular quenching rate constants and the fluorescence lifetimes respectively. A more complicated situation exists for cases

$$F_0/F = 1 + k_q\tau_0[Q] \qquad K_{SV} = k_q\tau_0 \qquad (2)$$

where no diffusion is necessary for quenching (i.e., either ground state complex formation or Perrin active sphere quenching) [22]. In the latter, the assumption is that all molecules contained within the active sphere instantaneously quench the excitation without diffusion. In this situation, the quenching kinetics are described as shown in Equation 3, where

$$F_0/F = \exp([Q]vN/1000) \qquad (3)$$

v is the active quenching volume and N is Avogadro's number. The equation describing competitive diffusional and active sphere quenching is shown below [21].

$$F_0/F = \exp([Q]vN/1000)(1 + K_{SV}[Q]) \qquad (4)$$

The fluorescence quenching of a number of polysilane derivatives by a variety of electron-deficient small molecule additives was studied in THF solution. The measurements were conveniently conducted by front-face excitation of the concentrated polymer solutions, although comparison studies using right-angle, dilute solution techniques gave comparable results. The polymers were prepared as described previously [23] and the molecular weights of the materials employed ranged from $M_w = 10 - 50,000$ Daltons. Very high molecular weight samples were avoided wherever possible due to the high viscosities of the concentrated solutions. Excitation of the emission was performed at the absorption λ_{max} or longer and the emission intensity was monitored at the emission maximum. Solution fluorescence quenching data for poly(methylphenylsilane) (PMPS) in THF by a variety of small molecule additives are shown in Table II [16]. Similar studies were done on the alkyl polymers poly(cyclohexylmethylsilane) (PCHMS) and poly(di-n-hexylsilane) (PDHS) for comparison (see Table III). For the latter polymers, the measured quenching constants were lower than for PMPS by factors of 2−6 for comparable quenchers. The Stern-Volmer quenching plots of PMPS often curved strongly upward with increasing quencher concentration suggesting the possibility of significant static quenching at higher concentrations [16]. Analysis of the data by two parameter (v and K_{SV}) curve fitting to Equation 4 or by linear extrapolation of the plot of F_0/F vs [Q] at low quencher concentrations gave similar values for K_{SV}. Interestingly, the Stern-Volmer plots for the alkyl polymers were linear over concentration ranges where the PMPS data was strongly curved. No evidence of ground state complexes between the polymers and the additives was detectable by absorption spectroscopy.

The data in Tables II and III were obtained by fluorescence quenching of the photoexcited polysilane. It is also possible to use polysilane high polymers to quench the fluorescence of certain polycyclic aromatic derivatives such as 9,10-dicyanoanthracene (DCA) ($\tau_0 = 13$ ns). The energetics for electron

Table II. Fluorescence Quenching of Poly(Methylphenylsilane)

Quencher	$E_{1/2}^{red}$ (V)[a]	ΔG_{ET} (kcal/mol)	$k_q\tau_0$ (M^{-1})[b]	$k_q \times 10^{-10}$ (M$^{-1}\cdot$sec^{-1})
Phthalimidotriflate	-0.91	-41	17.1	19.8
Perchloropentacyclododecane	-1.44	-29	24.7	28.4
1,4-Dicyanobenzene	-1.51	-27	14.5	16.8
2,6-Dicyanotoluene	-1.79	-21	10.9	12.5
Ethyl-4-trifluoromethyl benzoate	-2.01	-16	5.8	6.7
Methyl benzoate	-2.25	-10	0.9	1.0
Benzonitrile	-2.43	-6	0.6	0.7
Anisole	-2.70	0	—	—

a. Measured in 0.1 M Et_4NBF_4 in CH_3CN versus SCE. b. Run in THF solution. The poly(PhMeSi) excited state lifetime (τ) is 86 ps.

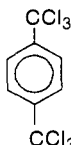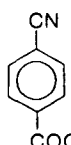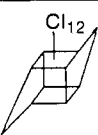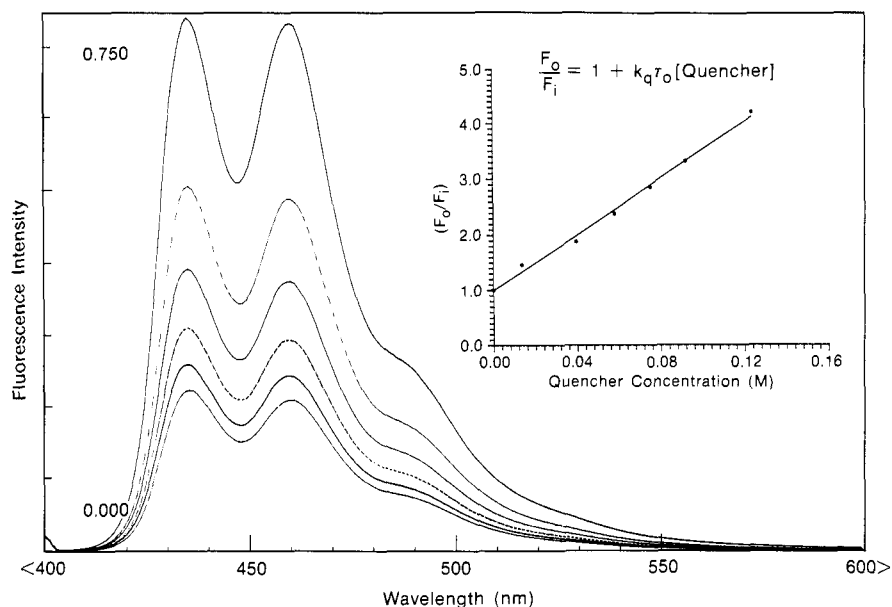transfer quenching of this type where the aromatic derivative is selectively excited are described below.

$$DCA + h\nu \rightarrow DCA^* + P \rightarrow DCA^{\bullet -}P^{\bullet +} \rightarrow \quad Products$$
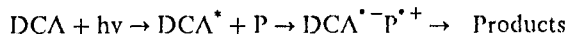
Photoexcited $\quad \Delta G_{ET}(kcal/mol) = 23.06[E_{1/2}(ox) - E^*_{1/2}(red)]$
Acceptors
$$E^*_{1/2}(red) = E^{red}_{1/2} + E_{0,0} \tag{5}$$

$E^*_{1/2}(red)$ for DCA as calculated above is 1.97 V. The fluorescence quenching of DCA* in THF by various silane polymers showed a good fit to the SV kinetic expression over the quencher concentration range employed (see Figure 1). In these cases, the polymer concentration [Q] was defined in terms of the monomer unit. The quenching data for photoexcited DCA by a number of silane high polymers is shown in Table III.

Table III. Comparison of Fluorescence Quenching Data for Aryl and Alkyl Polysilanes in THP

Quencher	Polymer	τ_0(ps)	$k_q \times 10^{-10}$ $(M^{-1} \cdot sec^{-1})$
CCl3 — ⬡ — CCl3	(PhSiMe)	86	19.8
	(CychexSiMe)	165	7.8
	(DihexSi)	130	4.2
CN — ⬡ — COOEt	(PhSiMe)	86	19.0
	(CychexSiMe)	165	5.8
	(DihexSi)	130	2.6
Cl12 (cube)	(PhSiMe)	86	28.4
	(CychexSiMe)	165	10.6
	(DihexSi)	130	6.1

Figure 1. The Fluorescence of DCA* Quenched by Poly(p-methoxyphenyl methylsilane) in THF

Finally, we have also examined the front-face fluorescence quenching of DCA* in THF by a number of oligomeric silanes with various catenation lengths and substitution patterns. Again the quenching reaction conformed to Stern-Volmer kinetics and the pertinent data are reported in Table V. As was observed earlier for the high polymers, the electrochemical oxidation of the oligosilanes is also highly irreversible, thus affecting somewhat the accuracy of the calculated ΔG_{ET} values.

DISCUSSION

The combination of low oxidation potentials and relatively high excitation energies suggests that excited substituted silane high polymers should be potent reducing agents. The data in Table I show that the electron transfer from a typical photoexcited polysilane to an acceptor whose reduction potential is more anodic than ~ -2.5 V would be exothermic. Even so, we anticipated difficulties with the quenching studies due to the short fluorescence lifetimes of the polymers (75 – 250 ps). For example, the additive half-quenching concentration for a typical photoexcited polymer where τ_0 is 10^{-10} sec (100 ps) would be ~ 1 M assuming a diffusion limited process (see Equation 2). Surprisingly, however, very efficient quenching was observed for a number of additives both in the solid state and in solution. In solution, strong fluorescence quenching was often observed for quencher concentrations of less than 0.1 M!

For PMPS, the Stern-Volmer quenching plots were often distinctly nonlinear curving upward at quencher concentrations greater than ~ 0.1 M [16]. The point of deviation from nonlinearity depended on the structure of the quencher. The upward curvature is consistent with the presence of a competitive static quenching component as described in Equation 4. The Stern-Volmer quenching constants (K_{SV}) (determined at low Q concentrations) are listed in Table II. Since the fluorescence lifetime of PMPS is 75 ps in THF, the bimolecular quenching constants (k_q) can be calculated from the measured values of K_{SV} and they also appear in Table II. The k_q values vary with the reduction potential of the quencher and hence the calculated exothermicity of the reaction, in a manner which is at least qualitatively consistent with that predicted for an electron transfer reaction [20]. We note here without further comment that perchloro $[5.1.0^{2,6}0.^{3,8}0^{5,9}]$ pentacyclodecane (denoted only as perchloropentacyclodecane in Table II) is an unusually efficient quenching additive for photoexcited PMPS. A similar effect was also observed for the quenching of the dialkyl polysilanes shown in Table III.

It is particularly striking that the quenching rate constants are often substantially larger than predicted for diffusion control. A typical diffusion controlled bimolecular quenching constant for two small molecules diffusing in toluene at room temperature is 1.1×10^{-10} m^{-1} sec^{-1} [24]. Since high molecular weight polymers (or even diffusing segments) are essentially stationary relative to the small quencher molecules, the effective diffusion controlled rate constant for the polymeric system should be somewhat less than 10^{10} m^{-1} sec^{-1}. For example, Guillet and Heskins have found that the rate constants for fluorescence quenching of two diffusing small molecules are 2 – 3 times larger than for photoexcited polymer quenched by a diffusing small molecule quencher [25]. The relative rate constants for quenching photoexcited dialkyl polysilanes (Table III) are somewhat smaller than measured for PMPS, but are still significantly larger than expected for diffusion controlled quenching. We tentatively attribute the large quenching rate constants observed for photoexcited polysilanes to rapid energy migration along the polymer chain. This hypothesis is also consistent with conclusions derived from the earlier fluorescence depolarization experiments [4 – 7].

Substituted silane high polymers also effectively quench the fluorescence of a variety of photoexcited polynuclear aromatics by electron transfer. The energetics of such a reaction are described by Equation 5. 9,10-Dicyanoanthracene can be selectively excited in the presence of polysilanes at wavelengths longer than 375 nm and the quenching of its fluorescence studied as a function of polymer concentration. For convenience, we have defined the polymer concentration in terms of the respective monomer unit. As before, front-face excitation is most convenient, although results obtained in dilute solutions with right angle geometries are comparable. The value of $E^*_{1/2}$(red) for photoexcited DCA is 1.97 V, and the excited state lifetime measured in THF without rigorous deoxygenation is 13 ns.

Electron transfer to DCA* from the polysilane derivatives should be quite exothermic and the fluorescence quenching shows good Stern-Volmer kinetics with no curvature in the plots for polymer concentrations up to 0.2 M ($F_0/F > 5$) when the emission was monitored at 435 nm (see Figure 1). The Stern-Volmer quenching constants (K_{SV}) and the related bimolecular rate constants (k_q) are reported in Table IV. Since the oxidation potentials of most substituted silane polymers cluster in the range 0.7 – 1.3 V, the calculated exothermicities for electron transfer to DCA* show less spread than in the previous examples and are uniformly quite large. As a result, the measured values of k_q vary over a narrower range. For the most part, the rate constants track with the oxidation potential of the polymer, and those polymers with aryl substituents directly bonded to the backbone tend to quench

Table IV. 9,10-Dicyanoanthracene Solution Fluorescence Quenching by Polysilanes

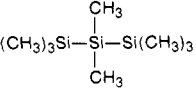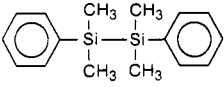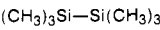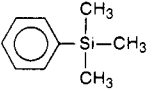| Polysilane Quencher	E^{ox} (Onset)[a] (Volts)	E^{ox} (Peak)[a] (Volts)	ΔG_{ET} (kcal/mol)	$k_q \tau_0$[b] (M^{-1})	$k_q \times 10^{-9}$ ($M^{-1} \cdot sec^{-1}$)
$(MeOPhSiMe)_n$	0.5	0.7	−29	25.4	1.94
$(MePhSi)_n$	0.75	0.9	−25	12.6	0.97
$(MePropylSi)_n$	0.9	1.0	−22	5.8	0.45
$(PhHexSi)_n$	1.0	1.15	−19	4.6	0.35
$(CychexMeSi)_n$	0.95	1.15	−19	5.8	0.45
$(Hex_2Si)_n$	1.1	1.25	−17	3.9	0.30
$(\beta\text{-TolylethylMeSi})_n$	1.05	1.3	−15	8.2	0.63
$(Tetradecyl_2Si)_n$[c]	—	—	—	6.9	0.53
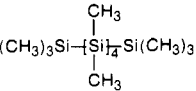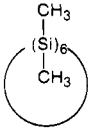
a. Measured in 0.1 M Et_4NBF_4 in CH_2Cl_2. All oxidations are irreversible, and potentials are reproducible to ±50 mV. b. The excited state lifetime of DCA (τ_0) is 13 ns. c. Insufficiently soluble for the determination of E^{ox}.

somewhat more efficiently than the alkyl substituted derivatives. The next to last example in Table IV, poly[β-tolylethylmethyl silane], is slightly more efficient than expected on the basis of its measured oxidation potential, but the significance of this small difference is questionable in light of the uncertainties involved in estimating the true oxidation potentials from irreversible oxidations. Poly(di-n-tetradecylsilane) was too insoluble in the methylene chloride-electrolyte mixture to yield a reproducible oxidation potential, although a quenching rate constant could be measured in THF. It is interesting that the measured oxidation potential of poly(n-hexylphenylsilane) is higher than for PMPS and the quenching rate is lower, suggesting that steric effects may play a role in the electron transfer process. It is significant that for comparable quenchers the quenching rate constants reported in Table IV are markedly smaller in every case than those reported in Tables II and III. Since, in the former, the photoexcitation is localized on the individual DCA molecules, this effect would be expected if rapid energy migration is the cause of the larger than diffusional rate constants observed for the photoexcited polymers. In each case, diffusion is dominated by the small molecules.

One potential complication in the interpretation of the data in Table IV is the definition of polymer concentration in terms of the monomer unit. If, for example, there is a minimum segment length of the polymer which is necessary for effective quenching of DCA*, the effective concentration of the polymer could be much lower and the quenching rates correspondingly higher. For this reason, we have studied the fluorescence quenching of DCA* by substituted silane oligomers of varying length and substitution pattern. Earlier, Horn and Whitenack [26] studied the fluorescence quenching of electron-deficient aromatic derivatives by hexamethyldisilane in a variety of solvents. Similarly, Sakurai et al. [27] have reported the fluorescence quenching of DCA* by the cyclic oligomer dodecamethylcyclohexasilane. In each case, the authors have concluded that fluorescence quenching occurs by an electron transfer mechanism.

The data in Table V suggest that for alkyl-substituted oligosilanes, quenching of DCA* becomes efficient at a catenation length around Si_3. Aryl substitution improves the efficiency so that even the disilane becomes an effective quencher of DCA*. Once again, the quenching efficiency tracks the oligosilane oxidation potential as expected for an electron transfer reaction. Consideration of the quenching data in Table IV in light of a proposed effective quenching segment length of Si_3 for the alkyl substituted derivatives and Si_2 for aryl substitution still supports the conclusion that the quenching of DCA* by ground state polysilanes is much less efficient than the quenching of photoexcited polysilanes by electron-deficient additives, even when the calculated electron transfer exothermicities are comparably large. These data further support the original conclusion that the very large measured quenching constants of photoexcited polysilane derivatives by many electron-deficient small molecule additives is a result of rapid energy transfer between the polymer chromophoric segments.

Table V. 9,10-Dicyanoanthracene Solution Fluorescence Quenching by Oligosilanes

Quencher	E^{ox} (Onset)[a] (Volts)	E^{ox} (Peak)[a] (Volts)	ΔG_{ET} (kcal/mol)	$k_q \tau_o$[b] (M^{-1})	$k_q \times 10^{-9}$ ($M^{-1} \cdot sec^{-1}$)
$(CH_3)_3Si\!-\![Si(CH_3)_2]_4\!-\!Si(CH_3)_3$	0.85	1.15	−19	134	10.3
cyclo-$[Si(CH_3)_2]_6$ (ring)	0.8	1.25	−17	104	8.0
$(CH_3)_3Si\!-\!Si(CH_3)_2\!-\!Si(CH_3)_3$	0.9	1.55	−9.7	32	2.5
$Ph\!-\!Si(CH_3)_2\!-\!Si(CH_3)_2\!-\!Ph$	0.9	1.6	−8.5	65	5.0
$(CH_3)_3Si\!-\!Si(CH_3)_3$	1.3	1.75	−5.1	5.3	0.41
$Ph\!-\!Si(CH_3)_2\!-\!CH_3$	2.0	2.9	21	1.34	0.10

a. Measured in 0.1 M Et_4NBF_4 in CH_3CN. All oxidations are irreversible, and potentials are reproducible to ±50 mV. b. The excited state lifetime of DCA (τ) is 13 ns.

In conclusion, we have found that the strong fluorescence of substituted silane polymers in solution is effectively quenched by a variety of electron-deficient small molecule additives. The rate constants for these processes roughly track the reduction potentials of the quenchers, and hence the calculated exothermicities, in a fashion consistent with that expected for an electron transfer reaction. The quenching rates are affected to some degree by polymer substitution, since aryl groups directly on the polymer backbone leads to larger quenching constants, as expected from the lower oxidation potentials. In all cases, however, when the calculated exothermicities for electron transfer are large, the quenching rates are considerably larger than would be expected for diffusion control. This effect has been attributed to rapid energy transfer among the chromophoric segments comprising the polymer chain, a proposal consistent with earlier fluorescence depolarization studies. This hypothesis is now further supported by quenching studies of photoexcited DCA, where the excitation is localized, by ground state substituted silane polymers and silane oligomers, in a reaction also believed to proceed via electron transfer.

Acknowledgements

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