

# Studies on the Fluorescence Quenching of Anthracenes by Polysilane Copolymers

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## SYNOPSIS

In this article, the room-temperature solution fluorescence quenching of electron-deficient anthracenes such as 9-cyanoanthracene (CNA), 9,10-dicyanoanthracene (DCNA), and 9,10-dichloroanthracene (DCLA) by polysilane copolymers was studied. The fluorescence quenching data was in conformity with the Stern-Volmer equation  $F_0/F = 1 + K_{SV}[Q]$ , the  $F_0/F - [Q]$  straight lines were drawn, and the fluorescence quenching constants  $K_{SV}$  were obtained. By measuring the fluorescence lifetimes of the anthracenes, the fluorescence quenching rate constants  $k_q$  were calculated. Based on experiments and references, we tentatively proposed that for the same polysilane copolymer quencher the fluorescence quenching was caused mainly by the polysilane Si—Si chain and affected in a small degree by the side substituents attached to the Si—Si chain. In addition, it was observed that the order of the fluorescence quenching rate constants  $k_q$  of the above three electron-deficient anthracenes by the same polysilane copolymer was DCNA > CNA > DCLA, which is just in keeping with that of their electron deficiency. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polysilane, which, because of its Si—Si  $\sigma$  conjugation in the main chain, has many unique optical and electrical properties and may be potentially used as high-resolution photoresists,<sup>1</sup> nonlinear optical materials,<sup>2</sup> optical waveguides,<sup>3</sup> photoconductors, etc., has become a focus of worldwide scientists.

The photodegradation of polysilane is the most important theoretical foundation for polysilane microlithography.<sup>1</sup> The quantum yields for chain scission in the solid state are 1–2% those in solution,<sup>5</sup> which is probably attributed to the chain repair in the immobilizing medium. The inefficiency of the photoreactions in the solid state makes it necessary to investigate the effect of small molecule additives on the photophysics and photochemistry of polysilane derivatives. Wallraff et al. studied the fluorescence quenching of polysilane homopolymers by several small electron-deficient molecules and attributed the fluorescence quenching mechanism to

electron transfer.<sup>6</sup> To obtain more knowledge about the electron-transfer mechanism between the small electron-deficient molecules and the polysilane Si—Si  $\sigma$  conjugational segments, Miller et al. did research on the fluorescence quenching of 9,10-dicyanoanthracene (DCNA) by various polysilane homopolymers including those with strongly electron-donating side substituents.<sup>7,8</sup> Karatsu et al. studied the fluorescence quenching of 9-cyanoanthracene (CNA), DCNA, and triphenylpyridium tetrafluoroborate ( $\text{TPP}^+\text{BF}_4^-$ ) by similar polysilane homopolymers and found direct evidence of electron transfer from polysilane homopolymers to  $\text{TPP}^+$  through the observation of the transient absorption spectrum of pyryl radical ( $\text{TPP}$ ).<sup>9</sup> However, as is well known, the yields of the synthesis of polysilane homopolymers are usually low, while those of polysilane copolymers are often high,<sup>10</sup> which makes it practically important to investigate the photophysics of the polysilane copolymers. So, in this article, the authors studied the fluorescence quenching of such electron-deficient anthracenes as CNA, DCNA, and 9,10-dichloroanthracene (DCLA) by polysilane copolymers and obtained some new interesting results.

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## EXPERIMENTAL

### Materials

The quenchers poly(dimethylsilane-*co*-methylphenethylsilane) [ $P_{(PE)}$ ] and poly(dimethylsilane-*co*-cyclohexylmethylsilane) [ $P_{(CH)}$ ] were synthesized by Wurtz-type reductive condensation of their corresponding disubstituent-dichlorosilane monomers<sup>11,12</sup> and purified according to the literature procedures. The copolymerization ratios ( $m/n$ ) are both 1.25 and the molecular weights ( $\overline{M}_n$ ) are  $1.06 \times 10^5$  and  $2.15 \times 10^5$ , respectively. The solvent tetrahydrofuran (THF), analytically pure, was further purified just before use according to the reported methods.<sup>13</sup> The polysilane copolymer quenchers and the solvent have no absorption at the wavelength of excitation. All the electron-deficient anthracenes CNA, DCNA, and DCLA were of ultrapure grade and purchased from Tokyo Chemical Industry Co. The concentrations of CNA, DCNA, and DCLA were  $1.0 \times 10^{-5}$  M for all six systems and those of the polysilane copolymers were calculated by the number of the Si atoms, as shown in Table I.

### Instrumentation

The steady-state fluorescence spectra were recorded on a Hitachi MPF-4 fluorescence spectrophotometer, the UV absorption spectra were determined by a MP-8541A diode spectroscopic photometer, and the fluorescence lifetimes of the electron-deficient anthracenes were measured by a Hiraba NAES-1100 nanosecond fluorescence spectrophotometer. All experiments were carried out at the room temperature (20°C). The wavelengths of excitation for the above three anthracenes were 380, 400, and 380 nm, respectively.

## RESULTS AND DISCUSSION

As we know, the dynamic quenching, which includes energy-transfer quenching, electron-transfer

quenching, etc., can be described by the Stern–Volmer equation:

$$F_0/F = 1 + K_{SV}[Q] \quad (1)$$

where  $F_0$  and  $F$ , respectively, represent the fluorescence intensity without and with the addition of a quencher, and  $K_{SV}$  is the Stern–Volmer quenching constant, standing for the ratio of the bimolecular quenching rate constant to the unimolecular decay rate constant, i.e., the competition between the two processes.

As for the dynamic quenching, there also exists another equation:

$$K_{SV} = k_q\tau_0 \quad (2)$$

where  $k_q$  is the bimolecular quenching rate constant, and  $\tau_0$ , the average lifetime of the fluorescent molecules without the addition of a quencher. However, it is necessary to notice that there also exists a kind of static quenching where ground-state complexations are formed between the fluorescent molecules and the quencher molecules and the relationship between its fluorescence intensity and quencher concentration is in a form completely similar to that of the Stern–Volmer equation which is used to describe dynamic quenching. Therefore, it requires the measurement of the fluorescence lifetime to definitely differentiate dynamic quenching from static quenching. For static quenching, the existence of a quencher cannot change the lifetime of the excited state of the fluorescent molecules, i.e.,  $\tau_0/\tau = 1$ , while for dynamic quenching, the existence of a quencher reduces the fluorescence lifetime, i.e.,  $\tau_0/\tau = F_0/F$ . The solution fluorescence lifetimes ( $\tau_0$ ) of the electron-deficient anthracenes without adding the polysilane copolymer quenchers are shown in Table II.

Figure 1 shows the fluorescence quenching emission spectra for system 5. A similar situation also exists for the other five systems. From these spectra,

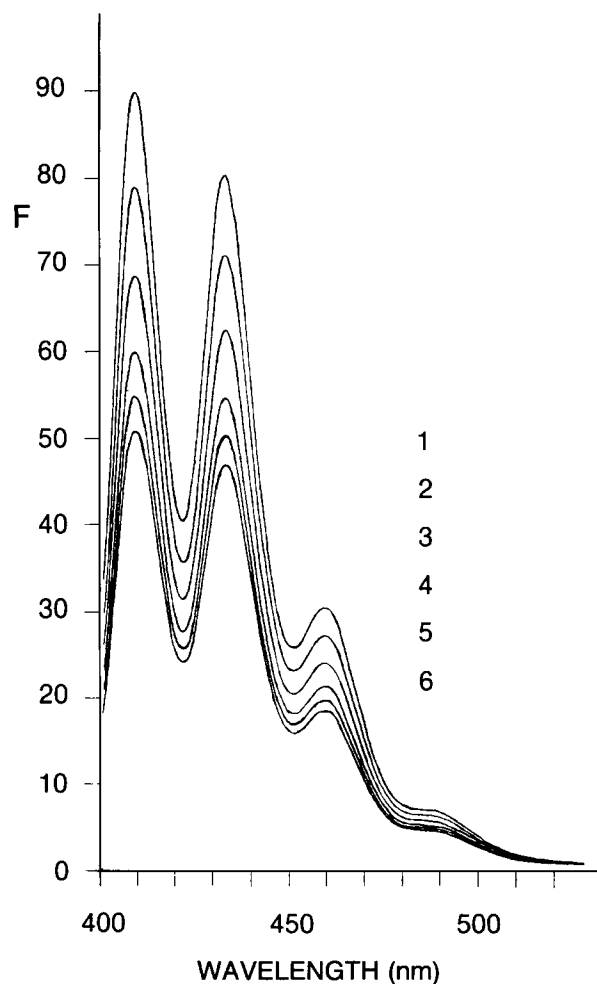
**Table I** The Concentrations of the Polysilane Copolymer Quenchers ( $M$ )

Systems	Anthracenes	Polysilane Copolymers						
			1	2	3	4	5	6
1	CNA	$P_{(PE)}$	0.000	0.040	0.080	0.120	0.160	0.200
2		$P_{(CH)}$	0.000	0.040	0.080	0.120	0.160	0.200
3	DCNA	$P_{(PE)}$	0.000	0.025	0.050	0.075	0.100	0.125
4		$P_{(CH)}$	0.000	0.026	0.050	0.075	0.100	0.125
5	DCLA	$P_{(PE)}$	0.000	0.040	0.080	0.120	0.160	0.200
6		$P_{(CH)}$	0.000	0.040	0.080	0.120	0.160	0.200

**Table II** The Stern–Volmer Fluorescence Quenching Constants  $K_{SV}$  and the Fluorescence Quenching Rate Constants  $k_q$  of the Electron-deficient Anthracenes by the Polysilane Copolymers

Systems	Anthracenes	Polysilanes	$K_{SV} (M^{-1})$	$\tau_0$ (ns)	$k_q (\times 10^9 M^{-1} s^{-1})$
1	CNA	$P_{(PE)}$	5.31	10.58	0.50
2		$P_{(CH)}$	4.01	10.58	0.38
3	DCNA	$P_{(PE)}$	7.24	9.39	0.77
4		$P_{(CH)}$	12.79	9.39	1.36
5	DCLA	$P_{(PE)}$	3.91	8.49	0.46
6		$P_{(CH)}$	2.63	8.49	0.31

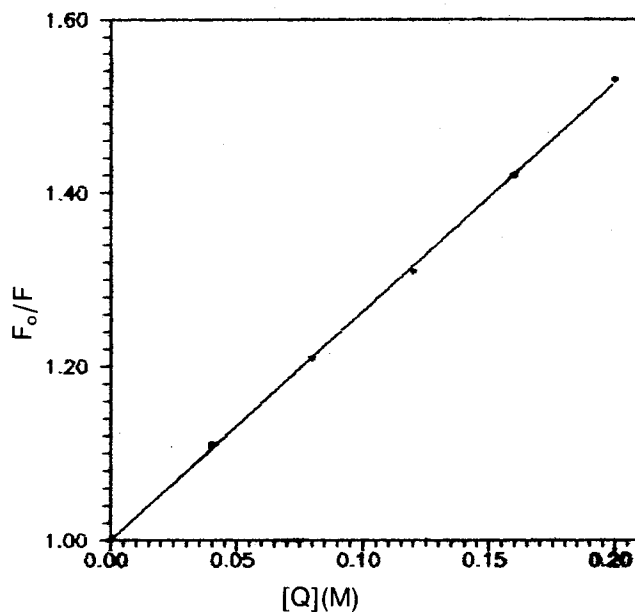
it can be seen that the room-temperature solution fluorescence of the electron-deficient anthracenes are quenched step by step with increase of the polysilane copolymer concentrations. In addition, the maximum emission wavelengths of CNA, DCNA, and DCLA are 440, 436, and 409 nm, respectively, and their fluorescence quenching at the


**Figure 1** The solution fluorescence quenching emission spectra of the anthracene DCLA by the polysilane copolymer  $P_{(PE)}$ .

maximum emission wavelengths was studied in this article.

Figure 2 shows the fluorescence intensity quenching ratios for system 6, i.e., the  $F_0/F-[Q]$  plot. From Figure 2, it can be seen that the  $F_0/F-[Q]$  plot is a straight line with excellent correlativity. A similar situation also exists for the other five systems. From these straight lines, we can calculate their slopes, i.e., the Stern–Volmer quenching constants  $K_{SV}$ . Moreover, in line with eq. (2), the fluorescence quenching rate constants  $k_q$  can be obtained. See Table II.

A number of studies have been concentrated upon the fluorescence quenching of such electron-deficient anthracenes as CNA and DCNA by the polysilane homopolymers including those with strongly electron-donating side substituents,<sup>7-9</sup> most of whose fluorescence quenching rate constants  $k_q$  are at the same scale with those in Table II, i.e., the  $10^8 M^{-1}$


**Figure 2** The fluorescence intensity quenching plot for system 6.

$s^{-1}$  scale. It states that for the same electron-deficient anthracene the fluorescence quenching may be caused chiefly by the polysilane Si—Si main chain and affected in a small degree by the side substituents. Perhaps, from an indirect source, it reflects the characteristics of the photophysics of the polysilanes, whose main chains all consist of the big-volume Si atoms.

The calculation of the concentrations of the polysilane copolymer quenchers is based on the number of the Si atoms. However, according to the chromophoric segmental model for polysilane, the effective electron donors of the polysilanes should be a variety of segments, which are composed of *trans* or nearly *trans* conformers separated by strong conformational twists or kinks and whose average length is about tens of the Si atoms.<sup>14,15</sup> If the calculation of the concentrations of the polysilane copolymer quenchers is based on the number of the segments, the actual fluorescence quenching rate constants  $k_q$  should be increased by one or two scales, i.e., the  $10^9$  or  $10^{10} M^{-1} s^{-1}$  scale.

Moreover, all the relevant studies have shown that the fluorescence quenching of the electron-deficient anthracenes by the polysilane homopolymers is in accordance with the electron-transfer mechanism.<sup>7-9</sup> From our experimental results, that by the polysilane copolymers may also conform to this mechanism.

From Table II, it can be seen that the order of the fluorescence quenching rate constants  $k_q$  of the electron-deficient anthracenes such as CNA, DCNA, and DCLA by the polysilane copolymer quencher  $P_{(PE)}$  is DCNA > CNA > DCLA for systems 1, 3, and 5, and the same situation exists for systems 2, 4, and 6, which are just in consistency with that of their electron deficiency.<sup>16,17</sup>

## CONCLUSION

The fluorescence quenching of such electron-deficient anthracenes as CNA, DCNA, and DCLA by the polysilane copolymers was studied in this article, most of whose fluorescence quenching rate constants  $k_q$  are at the same scale with those of CNA and DCNA by the polysilane homopolymers in the relevant references. It indicates that fluorescence quenching may be caused chiefly by the polysilane Si—Si chain and affected in a small degree by the

side substituents. Perhaps it reflects the characteristics of the photophysics of polysilane from an indirect source. In addition, the order of the fluorescence quenching rate constants  $k_q$  of the three anthracenes by the same polysilane quencher is DCNA > CNA > DCLA, which is just consistent with that of their electron deficiency.

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