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Direct Observation of Intramolecular Electron Transfer from Excess Electrons in a σ-Conjugated Main Chain to a Porphyrin Side Chain in Polysilanes Having a Tetraphenylporphyrin Side Chain by the Pulse Radiolysis Technique

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Summary: A novel polysilane having a tetraphenylporphyrin (TPP) side chain was synthesized. Intramolecular charge transfer between the σ-conjugated main chain and TPP side chain was investigated by the pulse radiolysis technique. The excess electrons are intramolecularly transferred to the TPP side chain with an apparent rate of electron transfer of >10^8 s^{-1}, although a hole in the σ-conjugated main chain of the polysilanes is not transferred to the TPP side chain.

Introduction

Intramolecular charge-transfer properties in conducting polymers have received considerable attention on the basis of potential applications as emitting layers in emitting diodes, semiconductor molecular wires, etc.[1,2] The one-dimensional semiconductor systems of σ-conjugated polysilanes are candidates for uses in these applications,[2−7] because of their large hole mobility well in excess of 0.1 $cm^2/(V\ s)$ on its isolated chains.[2] Polysilanes are silicon backbone polymers understood as a collection of conjugated helical segments separated by conformational disorder.

Porphyrins with excellent electronic and optical properties are intriguing molecules for incorporation into π-conjugated polymers. Polymers containing porphyrins and π-conjugated oligomers were designed and prepared for use in the investigation of electron and energy transfer and their potential application to optical and electronic devices.[8−14] However, there have been no reports about the studies of porphyrins linked with σ-conjugated polymers. Since porphyrins and polysilanes take part in reversible redox reactions and readily undergo one-electron oxidation and reduction, the polysilane−porphyrin linked molecules may give rise to effective charge-transfer systems or charge separation systems leading to potential use for optoelectronic devices. The investigation of intramolecular charge transfer in the molecules plays an important role in evaluating these systems.

In the present study, a novel polysilane having a tetraphenylporphyrin (TPP) side chain was synthesized in order to design a polysilane−porphyrin linked system. Intramolecular charge transfer between the σ-conjugated main chain and TPP side chain was investigated to evaluate the system using the pulse radiolysis technique.

Results and Discussion

In the electron-beam-induced reaction in THF solution, solvated electrons (e_{sol}^-) are formed; some of them are transferred to solute molecules, and the radical anions of solute molecules are selectively produced. Figure 1a provides the transient absorption spectrum of a 0.1 mM 5-(4-hydroxyphenyl)-10,15,20-tris(4-isopropylphenyl)porphyrin (**2**) solution in THF, measured at 100 ns after a pulse. The band around 700 nm is assigned to the radical anion of **2** (**2**$^{\bullet-}$). The compound **2** is shown in Scheme 1.

Radical ions in polysilanes show intense absorption bands based on σ-electrons delocalized over a silicon main chain in the near-ultraviolet (UV) region and near-infrared (IR) region.[15−22] Figure 1b provides transient

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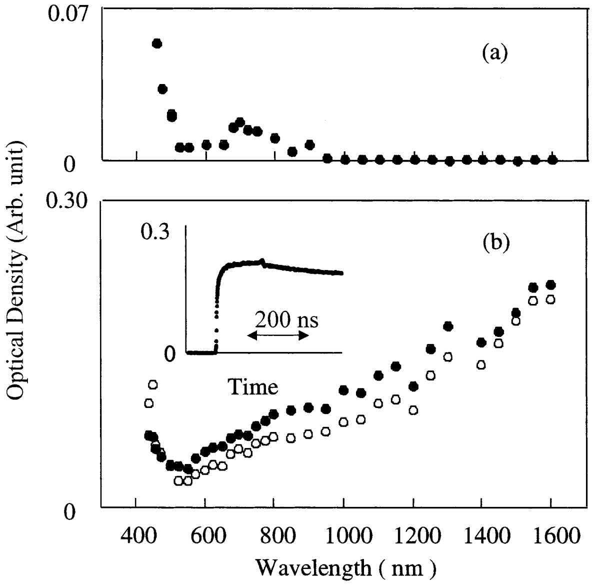
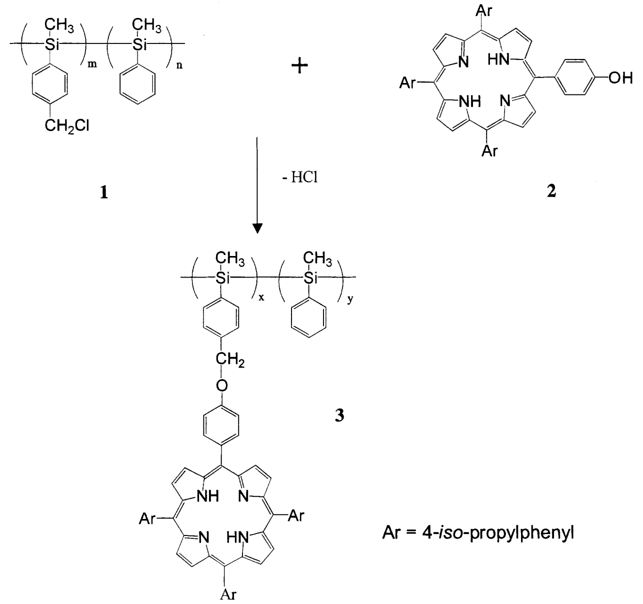


Figure 1. (a) Transient absorption spectrum of a 0.1 mM solution of **2** in THF, measured at 100 ns after a pulse. (b) Transient absorption spectra of a 50 mM (base mol unit) solution of PMPS in THF with 0.1 mM **2**: (●) immediately after a 8 ns pulse; (○) 250 ns after a pulse. The inset is the kinetic trace at 1600 nm.

Scheme 1



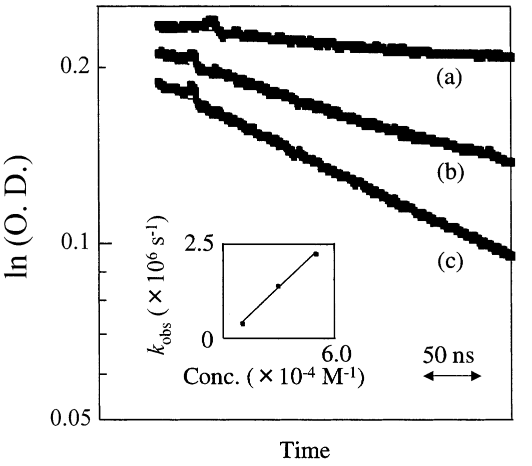


Figure 2. Pseudo-first-order plots of PMPS$^{•-}$ at 1600 nm in the presence of **2** in THF. The concentration of PMPS was 50 mM (base mol unit). Concentrations of **2**: (a) 0.1 mM; (b) 0.3 mM; (c) 0.5 mM. The inset denotes the dependence of the pseudo-first-order rate constant k_{obs} of PMPS$^{•-}$ vs the concentration of **2**.

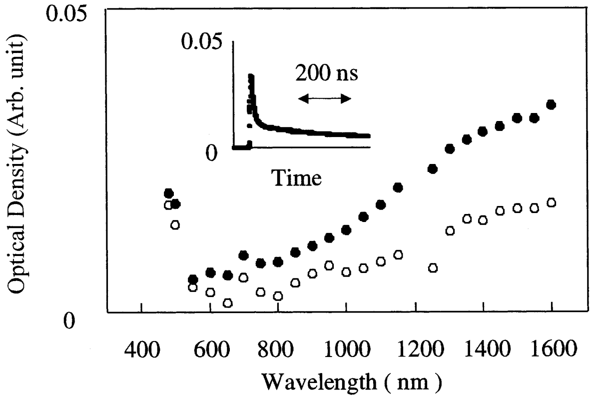


Figure 3. Transient absorption spectra of 5 mM (base mol unit) **3** solution in THF: (●) immediately after a 8 ns pulse; (○) 250 ns after a pulse. The inset is the kinetic trace at 1600 nm.

absorption spectra of a 50 mM (base mol unit) poly(methylphenylsilane) (PMPS) solution in THF with 0.1 mM **2**. The near-IR band is assigned to the radical anion of PMPS (PMPS$^{•-}$). The near-IR band shows a gradual decrease, as shown in the inset of Figure 1b, although PMPS$^{•-}$ does not decrease in the absence of porphyrin within a nanosecond time scale.[15-20] Figure 2 provides pseudo-first-order kinetic traces of PMPS$^{•-}$ in THF with 0.1–0.5 mM **2**, observed at 1600 nm. The pseudo-first-order rate constant k_{obs} is plotted against the concentration of **2**, as shown in the inset of Figure 2. The rate constant is proportional to the concentration of **2**, indicating that the decay of PMPS$^{•-}$ can be attributed to intermolecular electron transfer to **2**. The intermolecular electron-transfer rate constant is determined to be 4.6×10^9 M^{-1} s^{-1} from the slope of the plots.

A polysilane having a TPP side chain (**3**) was prepared by coupling of chloromethylated PMPS (**1**) and **2** (Scheme 1), to design a polysilane–porphyrin linked system and to investigate charge transfer between a σ-conjugated main chain and a TPP side chain. The weight-average molecular weight (M_w) of **3** was 2.2×10^4 with the molecular weight distribution $M_w/M_n = 6.7$. **2** is estimated to be incorporated into **3** with the ratio of **2** to Si repeating unit (R_{inc}) being 5×10^{-3}.

Figure 3 shows the transient absorption spectra of a 5 mM (base mol unit) solution of **3** in THF. The optical density abruptly decreases over the whole wavelength range observed (400–1600 nm). The near-IR band mainly reflects a transition from the interband level to the conduction band in the excess electrons in the σ-conjugated main chain, although the near-IR band may include the band of e_{sol}^-, because e_{sol}^- species ($\epsilon^{•-}$ = ca. 10^4 M^{-1} cm^{-1} at 1600 nm)[23] are rapidly captured by polysilanes with a rate constant of ca. 10^{10} M^{-1} s^{-1}

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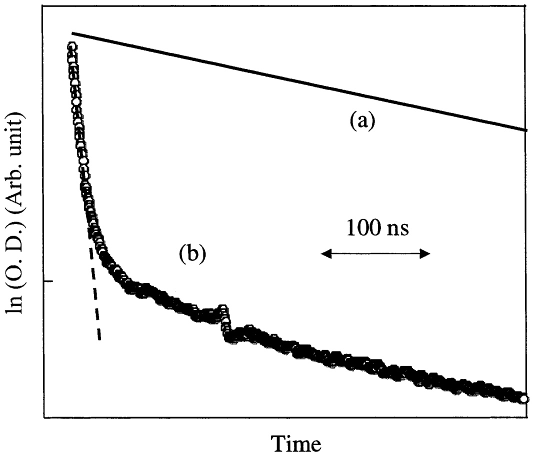

Figure 4. (a) Calculated trace of PMPS$^{\bullet-}$ in THF in the presence of **2** at 1600 nm, which is calculated by using $k = 4.6 \times 10^9$ M^{-1}s^{-1} as an intermolecular electron-transfer rate constant. The concentration of PMPS was 50 mM (base mol unit), and the concentration of **2** was 0.25 mM. (b) Kinetic trace of excess electrons in the σ-conjugated main chain of **3** in THF, observed at 1600 nm. The concentration of **3** was 50 mM (base mol unit), and the concentration of tetraphenylporphyrins was 0.25 mM. The dashed line is a single-exponential fitting and has a rate constant of 6×10^7 s^{-1}.

(for PMPS[24] and poly(methylpropylsilane)[15,17]) and then PMPS$^{\bullet-}$ species ($\epsilon^{\bullet-}$ = ca. 10^5 M^{-1} cm^{-1} at 1600 nm)[19] are produced. The transient absorption band around 700 nm can be assigned to excess electrons in the TPP side chain, which is interpreted from the absorption of **2**$^{\bullet-}$ (Figure 1b). Both the abrupt decrease of the near-IR band due to excess electrons in the σ-conjugated main chain and the appearance of a band (around 700 nm) due to excess electrons in the TPP side chain suggest intramolecular electron transfer from the excess electrons in the σ-conjugated main chain to the TPP side chain. The relative intensity at 700 nm may show good agreement with a small amount of doping with porphyrin (R_{inc}). Figure 4 provides a comparison between the calculated trace of PMPS$^{\bullet-}$ in THF in the presence of **2** (calculated trace (a)) and the kinetic trace of excess electrons in the σ-conjugated main chain of **3** (kinetic trace (b)). The calculated trace was done by using $k = 4.6 \times 10^9$ M^{-1} s^{-1} as an intermolecular electron-transfer rate constant between PMPS$^{\bullet-}$ and **2**. The kinetic trace (b) shows an abrupt decrease at first ($t <$ ca. 10 ns) and then a gradual decrease ($t >$ ca. 100 ns). The apparent rate of the kinetics in the first phase ($t <$ ca. 10 ns) is larger than 10^8 s^{-1}, which is obtained by assuming the kinetics ($t <$ ca. 10 ns) could be fitted by single-exponential decay. The decay of the excess electrons (kinetic trace (b) in Figure 4) is much faster than the decay of the PMPS$^{\bullet-}$ (calculated trace (a) in Figure 4) within 10 ns, although the calculated trace was done using the same TPP concentration as that in 50 mM **3** solution in THF (apparent trace (b) in Figure 4). This result supports the occurrence of intramolecular electron transfer from excess electrons in the σ-conjugated main chain to the TPP side chain. The gradual decrease of the excess electrons ($t >$ ca. 100 ns), shown in the kinetic trace (b) in Figure 4, may be due to intermolecular electron transfer from the excess electrons in the σ-conjugated main chain of one molecule to the TPP side chain of another.

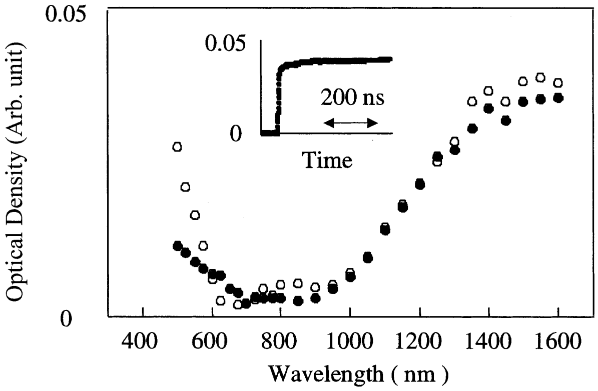

Figure 5. Transient absorption spectra of 5 mM (base mol unit) solution of **3** in CH_2Cl_2: (●) immediately after a 8 ns pulse; (○) 250 ns after a pulse. The inset gives the kinetic trace at 1600 nm.

Cationic species of solvent are formed in the electron-beam-induced reaction in CH_2Cl_2, and then radical cations of solute molecules are formed by hole transfer from cationic species of the solvent to solute molecules. Figure 5 shows transient absorption spectra of a 5 mM (base mol unit) solution of **3** in CH_2Cl_2. The near-IR band can be assigned to a hole in the σ-conjugated main chain, which is interpreted from the spectra of radical cations of polysilanes.[18] The near-IR band shows no decrease on the nanosecond time scale, indicating that a hole in the σ-conjugated main chain of **3** is stable on the nanosecond time scale.

The electrochemical half-wave reduction potentials of polysilanes have not been reported. In our previous reports, radical anions of polysilanes are effectively transferred to pyrene (−2.09 V, *N*,*N*-dimethylformamide, saturated calomel electrode (SCE)[25]).[19,20] The electrochemical half-wave reduction potential of pyrene is lower than that of H_2TPP (−1.05 V, 0.1 M $NClO_4$ in dimethyl sulfoxide, SCE).[26] Therefore, excess electrons in the σ-conjugated main chain can be transferred to the TPP side chain. On the other hand, the half-wave oxidation potential of PMPS (nearly equal to 0.78 V, acetonitrile, SCE[27]) is not higher than that of tetraphenylporphin (H_2TPP) (0.95 V, 0.1 M tetra-*n*-butylammonium hexafluorophosphate in CH_2Cl_2, saturated sodium chloride calomel electrode[28]). Therefore, a hole in the σ-conjugated main chain of polysilanes should not be transferred to the TPP side chain but should stay on the σ-conjugated main chain. However, a hole in the main chains might be transferred to the TPP side chain if the polysilane is linked with a suitable metallotetraphenylporphyrin such as Mg$^{\text{II}}$TPP,[29] having a lower oxidation potential than polysilanes.

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Conclusion

Intermolecular electron transfer from the radical anion of poly(methylphenylsilane) to tetraphenylporphyrins was investigated, using the pulse radiolysis technique. The intermolecular electron-transfer rate constant is determined to be 4.6×10^9 M^{-1} s^{-1}.

A novel polysilane having a TPP side chain was synthesized in order to design a polysilane–porphyrin linked system and to investigate intramolecular charge transfer between the σ-conjugated main chain and the TPP side chain by the pulse radiolysis technique. The excess electrons in the σ-conjugated main chain are randomly transferred to the TPP side chain intramolecularly and then captured by the side chain. In contrast to the fact that excess electrons in the σ-conjugated main chain are captured by the TPP side chain, a hole in this polymer is delocalized over the σ-conjugated main chain on the nanosecond time scale.

Experimental Section

PMPS was synthesized by a Wurtz-type coupling reaction with sodium metal. M_w and M_w/M_n values of PMPS were determined by gel permeation chromatography (GPC) with polystyrene calibration standards. The M_w value of PMPS was 6.5×10^5 with $M_w/M_n = 5.3$. **1** was prepared by the chloromethylation of PMPS by the method of Ban et al.[15] **3** was prepared by Williamson synthesis from **1** and **2**, as shown in Scheme 1. A 2.2 g amount of **1** was dissolved into 30 mL of THF. The solution was added into the reaction vessel with 11 g of K_2CO_3. The solution was stirred and maintained at 80 °C. Then the solution of **2** at 6.5 mM in THF (20 mL) was dropped into the reaction vessel. The reaction was carried out overnight. After the reaction, the resulting polymer was precipitated in methanol. The yield was 20–40%. **3** was characterized by ^{1}H NMR, UV–vis spectrometry, gel-permeation chromatography, and elemental analysis. The UV–vis spectrum was measured by a Shimadzu UV-3100PC instrument in THF at 0.1 mM. The maximum wavelength (λ_{max}) of the lowest transition in σ electrons of the main chain is $\lambda_{max} = 331$ nm, and that of the Soret band in TPP is $\lambda_{max} = 420$ nm. The elemental analyses were performed at the Institute of Scientific and Industrial Research, Osaka University. H, C, and N was measured to be 5, 60, and 0.5%, respectively. The M_w value of **3** was 2.2×10^4 with $M_w/M_n = 6.7$. **2** is estimated to be incorporated into **3** with $R_{inc} = 5 \times 10^{-3}$ on the basis of NMR spectrometry, UV–vis spectrometry, and elemental analysis.

The transient absorption spectra were obtained by the pulse radiolysis technique at room temperature. The samples were irradiated with an 8 ns single-pulse electron beam from the 28 MeV L-band linear accelerator instruments at Osaka University.[16]

NMR Spectroscopy for 3. ^{1}H NMR (270.05 MHz, $CDCl_3$): δ 0.01 (br), 1.54 (br), 3.04 (br), 4.45 (br), 7.10 (br), 7.55 (br), 7.61 (br), 8.87 (br).

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