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Preparation of new redox-active polyionenes with porphyrin units in the main chain

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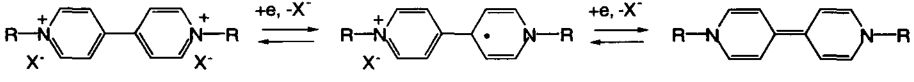
Summary

Quaternization of *trans*-dipyridylporphyrin with 1,4-butaneditrifluoromethanesulfonate affords new polyionenes containing porphyrin units in the main chain. The polymers exhibit chemical and electrochemical reversible redox activities. Weitz-type two-step redox processes similar to those of viologens account for the redox properties of the polymers.

Introduction

Porphyrins have high functionality and play an important role in living systems such as photosynthetic reactions, oxygen carrier, and enzyme systems. For an elucidation of the functions, a large number of porphyrin derivatives including polymeric porphyrin systems have been investigated (1). For example, tetraarylporphyrin derivatives have been copolymerized with acrylic acid and a quinone derivative to form polymers with structured porphyrin-quinone orientation designed to model photosynthesis (2). Various π-conjugated polymers having the porphyrin structure in the main chains as well as in pendant groups also have been explored as photoconducting, paramagnetic, and nonlinear optical materials (3).

On the other hand, 4,4'-bipyridinium salts, viologens, usually show Weitz-type two-step redox behaviors (4). Owing to the interesting redox phenomena, various viologen-type polyionenes have been synthesized and applied to making modified electrodes as well as photochromic and electrochromic devices (5).



(1)

Recently, Okura et al. (6) have reported synthesis of viologen linked porphyrins, and found that they took part as both a photosensitizer and an electron carrier in the same molecule for photoinduced hydrogen evolution systems. On these bases, we have prepared new polyionenes containing porphyrin units in the main chain. These polyionenes consist of quaternized *trans*-dipyridylporphrin units, and these units are expected to show Weitz-type two-step redox behavior similar to that of viologens. Although similar linked porphyrin systems have been reported by Fleischer et al. (7), little attention has been paid to chemical and electrochemical redox properties of the polymeric porphyrin systems. In this

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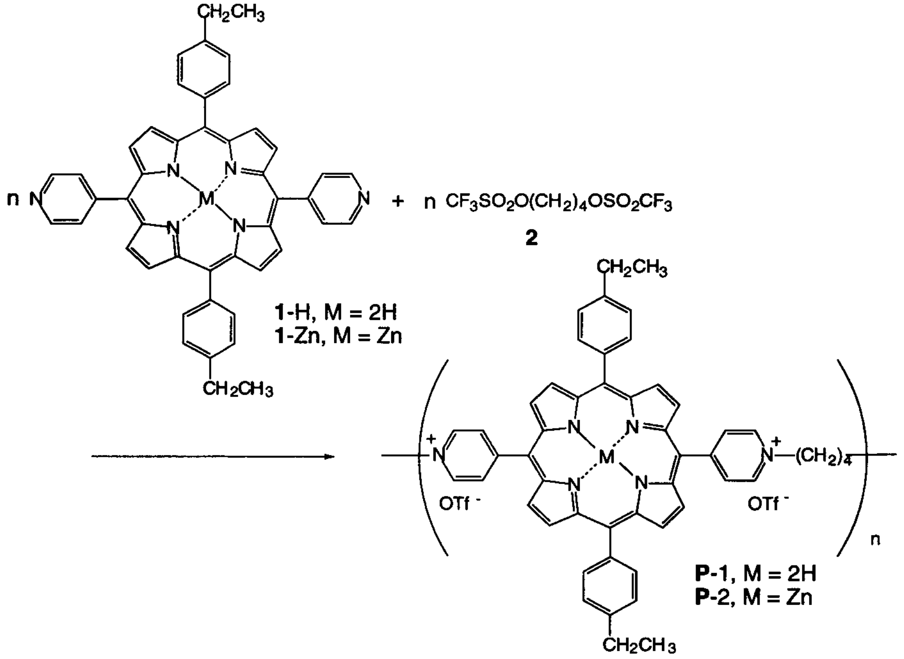
paper, we report preparation of the polyionenes and chemical and electrochemical redox properties of the polymers.



(2)

Experimental

Materials

Synthesis of 5,15-di(4-ethylphenyl)-10,20-dipyridylporphyrin, **1**-H, was carried out according to literature methods for the formation of porphyrin ring (8). The zinc(II) complex of **1**-H, **1**-Zn, was synthesized under reflux with zinc(II) acetate in DMF (8c). 1,4-Butaneditrifluoromethanesulfonate, **2**, was prepared according to the literature (9).

Polymerization

1-H (67 mg, 0.1 mmol) and **2** (35 mg, 0.1 mmol) were dissolved in $CHCl_3$ (20 ml). The solution was refluxed for 24 h to yield a deep purple precipitate of **P**-1. The precipitate was separated by filtration and washed thoroughly with $CHCl_3$ (81 mg, 79% yield). IR (KBr, cm^{-1}): 3453, 3120, 2964, 1635, 1461, 1256, 1161, 1029, 801, 638. ^1H NMR (DMSO-d_6, ppm): 9.7 (4H), 9.2 (12H), 8.2 (4H), 7.7 (4H), 5.2 (4H), 3.0 (4H), 2.7 (4H), 1.5 (6H), -2.9 (2H).

The preparation of **P**-2 was carried out analogously by using **1**-Zn (74 mg, 0.1 mmol) and **2** (35 mg, 0.1 mmol) (95 mg, yield 87%). IR (KBr, cm^{-1}): 3119, 2965, 1631, 1457, 1256, 1162, 1029, 795, 638. ^1H NMR (DMSO-d_6, ppm): 9.6 (4H), 9.0 (12H), 8.1 (4H), 7.7 (4H), 5.2 (4H), 3.0 (4H), 2.5 (4H), 1.5 (6H).

Model compound of **P**-1, 5,15-di(4-ethylphenyl)-10,20-di(N-methylpyridinium)-porphyrin ditrifluoromethanesulfonate, **3**, was also prepared analogously by using **1**-H (67 mg, 0.1 mmol) and methyl trifluoromethanesulfonate (41 mg, 0.25 mmol). Purification was carried out by column chromatography (85 mg, 85% yield). IR (KBr, cm^{-1}): 3419, 3112, 2965, 1643, 1461, 1262, 1159, 1032, 968, 808, 639. ^1H NMR (DMSO-d_6, ppm): 9.4 (q, 4H), 9.0 (m, 12H), 8.1 (d, 4H), 7.7 (d, 4H), 4.7 (s, 6H), 3.1 (q, 4H), 1.5 (t, 6H), -2.9 (s, 2H).

A viologen-type polyionene, poly[4,4'-bipyridine-1,1'-diyl-tetramethylene di(trifluoromethanesulfonate)], **VP**, was prepared according to the literature (5).

Measurements

IR spectra, NMR spectra, and fluorescence spectra were recorded on a JASCO FT/IR-230 spectrometer, a JEOL JNM-A400 NMR spectrometer, and a Hitachi 650-10S spectrometer, respectively. Cyclic voltammetry was carried out in a nitrogen-filled H-shaped three-electrode cell with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko KB-104 function generator. A platinum plate (1 x 1 cm) was used as a working electrode, and a platinum plate (1 x 2 cm) and a Ag wire/0.1 M $AgNO_3$ electrode were used as a counter electrode and a reference electrode, respectively. In the case of a film of **P**-1, spreading 10 µl of a DMF solution of **P**-1 (*ca.* 1 mg/1 ml, *ca.* 1×10^{-3} M of monomer unit) on an platinum plate and evaporation of DMF under vacuum afforded a platinum electrode coated with the film of **P**-1 (*ca.* 1×10^{-5} g cm^{-2}); with this electrode the cyclic voltammogram was measured. The preparation of films of **P**-2 and **VP** was carried out analogously. UV-visible absorption spectra were measured with a Shimadzu UV-265FS spectrometer. After absorption spectra of the polymers were measured in a DMF solution under nitrogen, the polymers were reduced by adding a drop of an aqueous solution of $Na_2S_2O_4$ (0.2 M). The visible spectra of the reduced polymers in DMF were also measured under nitrogen.

Results and Discussion

The reactions of **1**-H and **1**-Zn with **2** afforded **P**-1 and **P**-2 in good yields, respectively, while the reactions of **1**-H with 1,4-diiodobutane and 1,8-octanedi(*p*-toluenesulfonate) gave only small amounts of precipitates. **P**-1 and **P**-2 are soluble in polar solvents such as DMSO, NMP, and DMF, and partially soluble in acetonitrile and acetone. Intrinsic viscosity [η] values of **P**-1 and **P**-2 are 0.19 and 0.14 dLg^{-1}, respectively, as determined in 0.1 M LiBr/DMSO at 30 °C.

A UV-visible absorption spectrum of **P**-1 in DMF exhibits a strong Soret band at 425 nm and Q bands at 519, 557, 591, and 649 nm, while **P**-2 shows a Soret band at 435 nm and Q bands at 565 and 628 nm. **P**-1 and **P**-2 exhibit red shifts of the Soret and Q bands compared to the corresponding monomers (Soret band: 417 nm for **1**-H and 421 nm for **1**-Zn), which are considered to result from electron-withdrawing character of quaternized pyridine units (10). The DMF solutions of **P**-1 and **P**-2 show strong fluorescence with a peak at 656 and 645 nm, respectively, when excited at the Soret band. IR spectra of **P**-1 and **P**-2 essentially resemble those of model compound **3**. The bands due to ν(C-F) (1029 cm^{-1}), ν_{as}(S=O) (1256 cm^{-1}), and ν_s(S=O) (1161 cm^{-1}) are observed in the IR spectra of the products.

Figure 1 shows a ^1H NMR spectrum of **P**-1 in DMSO-d_6. Assignment of the peaks was carried out by comparison of the peak positions of **1**-H with those of model compound **3**. In Figure 1, a peak attributable to the N-H proton of the pyrrole ring is observed at δ -2.89 ppm, and a peak at δ 5.19 ppm is assigned to the quaternized N-methylene protons. The ratios of the peak area assist the structure suggested for **P**-1. The ^1H NMR spectrum of

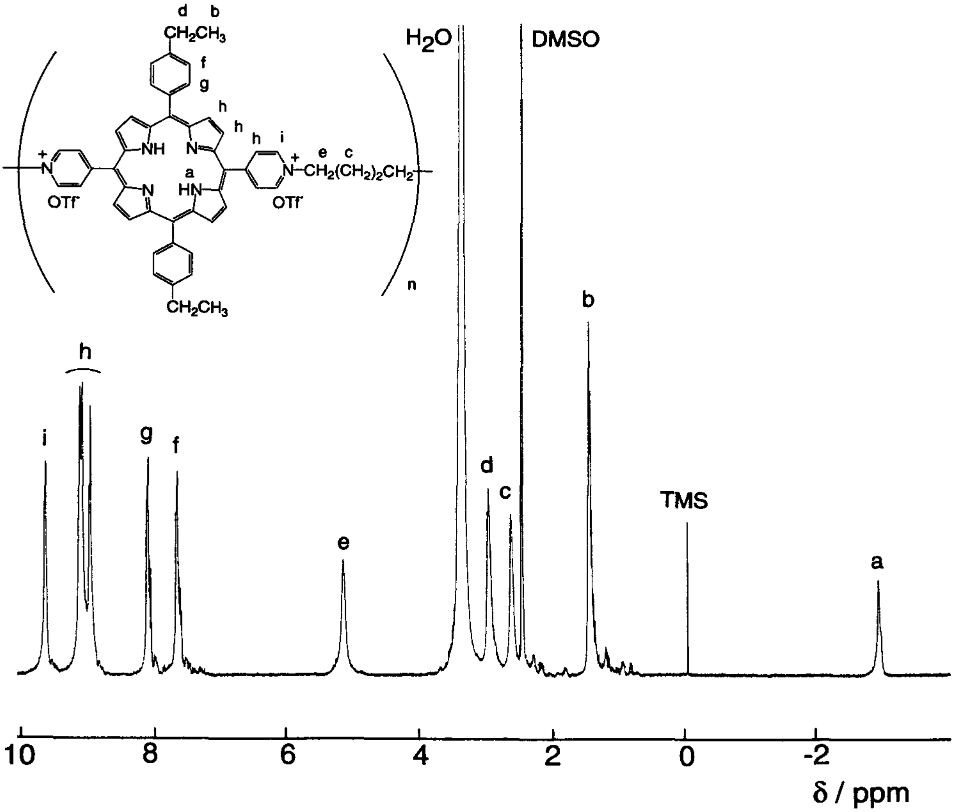


Figure 1. ^{1}H NMR spectrum of **P**-1 in DMSO-d_6.

P-2 is similar to Figure 1, and no peak assignable to the N-H proton of the pyrrole ring is observed.

The polyionenes give mechanically strong films by casting from their solutions. Figure 2 depicts cyclic voltammograms (CV's) of the cast films of **P**-1 and **VP** in a THF solution of *n*-Bu_4NBF_4 (0.1 M) and model compound **3** dissolved in a DMF solution of *n*-Bu_4NBF_4 (0.1 M). As shown in Figure 2(a), **P**-1 film gives rise to an electrochemically active cycle, showing two reduction peaks at -1.29 and -1.70 V *vs.* Ag/Ag^+ and two oxidation peaks at -1.07 and -0.95 V. The color of **P**-1 (purple) becomes deep blue during the reduction. The polymer film was stable and gave the same CV curves and color change in the repeated scanning.

The CV results and the electrochemical color change of **P**-1 resemble those of **VP** (Figure 2(b)) which undergoes the Weitz-type electrochemical redox reaction, showing two reduction peaks at -0.82 and -1.30 V *vs.* Ag/Ag^+ and two oxidation peaks at -0.94 and -0.58 V. Model compound **3** (Figure 2(c)) also gives rise to an electrochemically active cycle with two reduction peaks at -1.20 and -1.35 V *vs.* Ag/Ag^+ and two oxidation peaks at -1.29 and -1.16 V. These results indicate **P**-1 has reversible Weitz-type electrochemical redox activity expressed by Scheme 1.

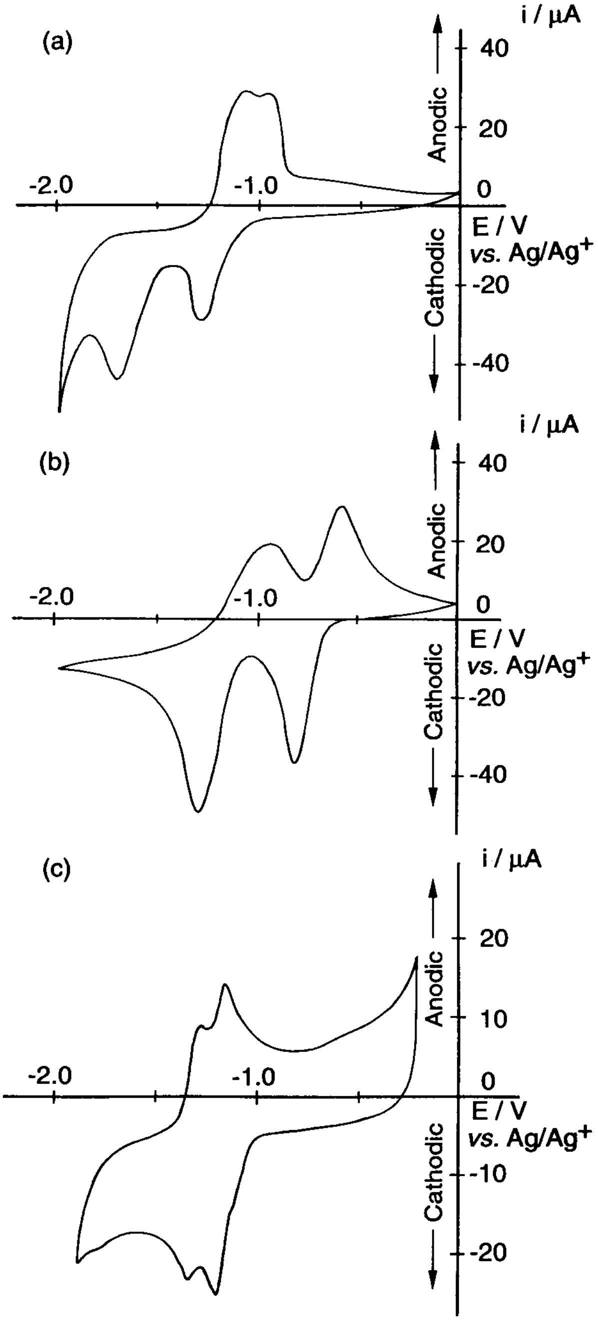
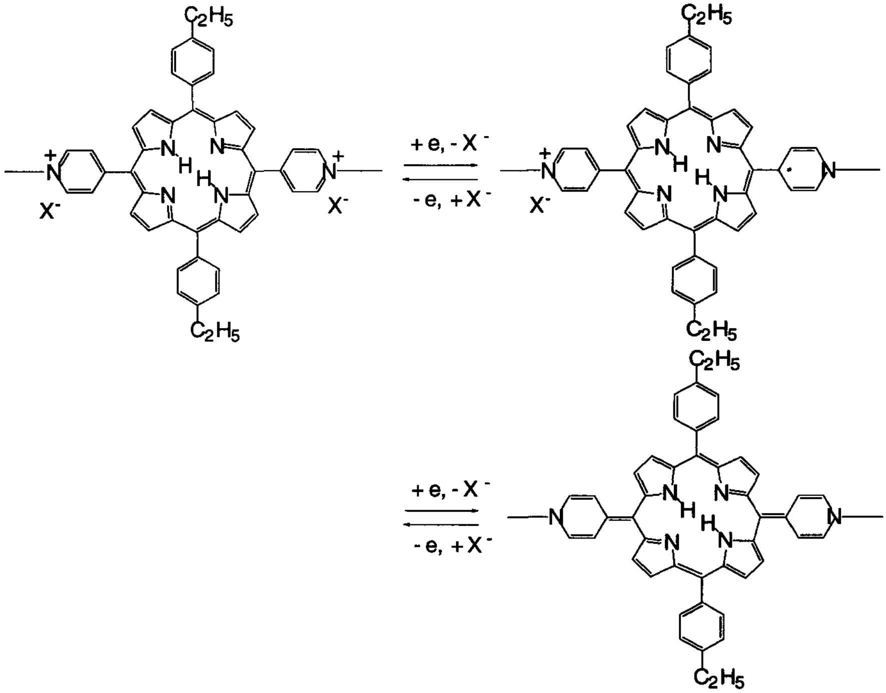


Figure 2. Cyclic voltammograms of films of (a) **P**-1 and (b) **VP** on platinum plates in a THF solution of 0.1 M *n*-Bu_4NBF_4 at scanning rate of 10 mV s^{-1}. (c) Cyclic voltammogram of **3** (2 x 10^{-4} M) in a DMF solution of 0.1 M *n*-Bu_4NBF_4 at scanning rate of 100 mV s^{-1}.

Scheme 1



As shown in Scheme 1, the *trans*-dipyridyl porphyrin unit will form a cation radical in the first-step reduction and a neutral quinoid in the second-step reduction. This redox behavior is similar to that of viologens. The observations that the redox reactions of **P**-1 take place at lower potentials than those of **VP** indicate that a larger energy is required to reduce the *trans*-dipyridylporphyrin unit to form a coplanar conformation. Fleischer et al. (11) have reported a crystal structure of 5-pyridyl-10,15,20-triphenylporphyrinatozinc(II), showing the pyridine ring almost perpendicular to the porphyrin plane. The large energy required to form the coplanar quinoid structure is accounted for by steric hindrance between the pyridine ring and the hydrogen atoms of the pyrrole ring in the porphyrin unit.

Monomer **1**-H dissolved in a THF solution of *n*-Bu_4NBF_4 (0.1 M) exhibits a pair of redox peaks with a cathodic peak at -2.15 V *vs.* Ag/Ag^+ and a broad anodic peak at -2.05 V due to reduction of the porphyrin ring. When the CV measurement of **P**-1 was carried out at lower potentials (up to -2.5 V *vs.* Ag/Ag^+), another pair of redox peaks with a cathodic peak at -2.20 V and a broad anodic peak at -2.10 V was observed, which would be considered to correspond to the further reduction of the porphyrin ring in **P**-1. However, the redox current decreased with repeated scanning, which may be due to the instability and high reactivity of the porphyrin cation radical in the polymer at the further reduction condition.

Figure 3 shows the change in the UV-visible spectra of **P**-1 by reduction with $Na_2S_2O_4$. Addition of $Na_2S_2O_4$ led to a decrease in the Soret band at 425 nm and the

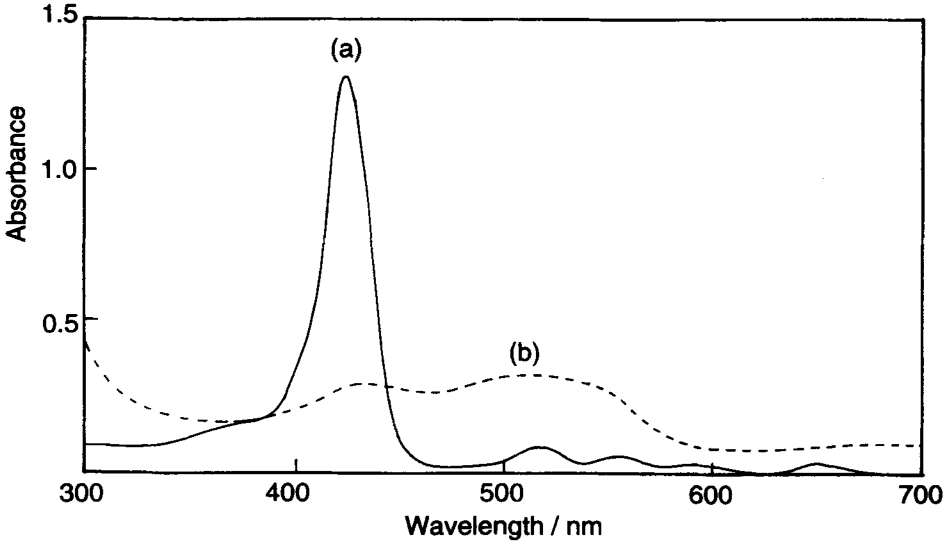


Figure 3. UV-vis absorption spectra of (a) **P**-1 and (b) reduced **P**-1 formed by adding $Na_2S_2O_4$ (aq) in DMF under N_2.

appearance of a new broad peak at about 500-550 nm. The spectrum was restored by exposure to air. It has been reported that the solutions of viologen cation radicals show an absorption peak at ca. 550-600 nm (4,5b-e), and a decrease in the intensity of the Soret band of porphyrin is observed in the generation of porphyrin cation radicals (10,12). These results indicate that the change in the UV-visible spectra in Figure 3 is reasonably explained by the formation of the Weitz-type cation radical in the reaction of **P**-1 with $Na_2S_2O_4$.

P-2 also displays an electrochemically active cycle with a broad cathodic peak at -1.76 V and a broad anodic peak at -1.14 V *vs.* Ag/Ag^+, as well as a similar change in the UV-visible spectra by reduction with $Na_2S_2O_4$. These results indicate **P**-2 also has the Weitz-type redox activity.

As described above, new polyionenes containing quaternized *trans*-dipyridylporphyrin units exhibit the Weitz-type two-step redox behavior similar to that of viologens. Although the optical properties of the porphyrin units such as photoexcited lifetime and photosensitivity are not clear in the present study, the polymers are expected to provide a new class of multiporphyrin systems which could serve as both the photosensitizer and the electron carrier in the same molecule. The scope of the preparation and application of the polymeric porphyrin systems are in progress.

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