Synthesis and Photochromism of Dibenzylviologen Coupled with 5,10,15,20-Tetraphenylporphyrin or Its Metal Complex via a Carbonyloxy Spacer

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Synopsis. 1,1′-Dibenzyl-4,4′-bipyridinium (viologen) coupled with 5,10,15,20-tetraphenylporphyrin or its metal complex via a carbonyloxy spacer was prepared by modification of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin. The viologens in polar aprotic media brought about increases in the visible absorption characteristic of, but different in stability from, those of the conventional viologen radical cations upon irradiation with visible light (photochromism).

It is known that 4,4′-bipyridinium salts (viologens) in polar aprotic media such as poly(1-vinyl-2-pyrrolidone) (**PVP**) matrix film exhibit deep visible colors reversibly with irradiation by light of the solar level (photochromism).[1-4)]

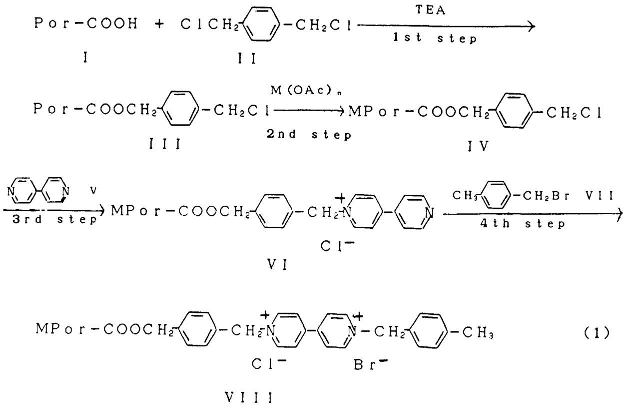
Light of wavelengths shorter than 400 nm, i.e. UV-light, is usually required in this case, however, to obtain satisfactory results.

In the present study, dibenzylviologen was coupled with 5,10,15,20-tetraphenylporpyrin or its metal complex, which could be excited by visible light, via a carbonyloxy spacer and the photochromic behavior of the resulting compound in polar aprotic media induced by visible light, to which conventional viologens were almost inert, was investigated.

Porphyrin- or metalloporphyrin-coupled viologens of various structures have so far been reported,[5-9)] but the synthesis and photochemistry of **VIII** appear to have never been reported before.

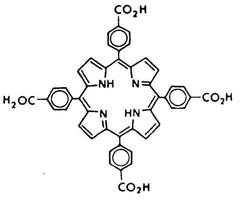
Experimental

Porphyrin- or metalloporphyrin-coupled viologen (**VIII**) was prepared starting with 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (**I**) following the reaction sequence shown in Eq. 1.



Por-COOH:

I



were M represents either none or a central metal atom of valence *n* in metalloporphyrin, such as Zn(II), Ni(II), Mn(II), Fe(III), and Sn(IV). The second step of the reaction sequence was omitted for the preparation of **VIII** without the central metal atom. 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrin (**1**) was synthesized from pyrrole and 4-formylbenzoic acid in the conventional manner.[10)]

5,10,15,20-Tetrakis[4-[4-(chloromethyl)benzyloxycarbonyl]phenyl]porphyrin (III). A solution of **I** (1.6 g, 2.0 mmol), triethylamine (TEA; 1.1 mL, 8.0 mmol), and *p*-bis(chloromethyl)benzene (II, 2.8 g 16.0 mmol) in DMF (50 mL) was stirred at 80 °C for 72 h. The reaction mixture was poured into a large amount of a saturated aq NaCl solution. The resulting precipitate was separated by centrifugation and dissolved in $CHCl_3$ (100 mL), followed by a working up. Recrystallization from $CHCl_3$–MeOH provided purple crystalline powder in a 69% yield. Calcd for $C_{76}H_{58}N_4O_8Cl_4$: C, 71.38; H, 4.31; N, 4.16%. Found: C, 71.31; H, 4.34; N, 4.12%. IR (KBr) 1720 and 1260 cm^{-1}. ^1H NMR ($CDCl_3$) δ=4.6 (s, 8H), 5.5 (s, 8H), 7.2—8.6 (m, 32H), and 8.8 (s, 8H).

Introduction of a Metal Atom into III. Carried out in a manner similar to that in a previous study.[11)] Thus, a saturated aq solution of a metal acetate (100 mmol), except for Sn(IV) and Fe(III) where the respective chlorides were used instead of the acetates, was added to a refluxing solution of **III** (0.3 g, 0.2 mmol) in acetic acid (5 mL), followed by stirring for one hour. The reaction mixture was poured into ice water and let stand overnight to afford a precipitate of **IV**.

Preparation of 4-Pyridylpyridinium Salt VI from IV and 4,4′-Bipyridine. A solution of **IV** (0.14 mmol) and 4,4′-bipyridine (**V**; 0.17 g, 1.1 mmol) in DMF (5 mL) was stirred at 80 °C for 48 h. The reaction mixture was precipitated into ether to give **VI** in about a 90% yield. IR (KBr) 1720, 1680, and 1270 cm^{-1}. ^1H NMR (DMSO-d_6) δ=5.6 (s, 8H), 6.0 (s, 8H), and 7.0—9.8 (m, 72H).

Completion of the Porphyrin- or Metalloporphyrin-Coupled Viologen (VIII). A solution of **VI** (0.2 g, 0.1 mmol) and 4-(bromomethyl)toluene (0.1 g, 1 mmol) in DMF (5 mL) was stirred at 80 °C for 48 h. The reaction mixture was precipitated into ether to afford **VIII** in about a 75% yield. The precipitate was soluble in DMF and insoluble in water and alcohols. IR (KBr) 1720, 1650, and 1260 cm^{-1}. ^1H NMR (DMF-d_7) δ=2.1 (s. 12H), 5.5 (s, 8H), 6.2 (s, 16H), and 7.0—10.2 (m, 88H). λ_{max} (Soret band in DMF): M=none, 418 nm (ε=10.7×10^4 mol^{-1} dm^3 cm^{-1}); Zn(II), 422 (15.6); Sn(IV), 420 (39.2); Fe(III), 420 (30.0); Ni(II), 419 (24.0); Mn(II), 420 (16.9).

Preparation of Thin Film. The procedure described in previous papers[1-4] was modified as follows. Thus, a DMF solution of poly(*N*-vinyl-2-pyrrolidone) (**PVP**; MW, 40000), **VIII** (2 wt% on the basis of **PVP**), and, when required, triethanolamine (**TEOA**; 10 wt% based on **PVP**) was spread over a glass plate, which was kept at 40 °C overnight so as to afford a thin film approximately 0.01 mm in thickness.

Evaluation of the Photosensitivity of VIII. DMF solutions and films bearing **VIII** were exposed to light at a distance of 2.5 cm from the lamp house of a 150 W Xenon lamp (Tohshiba) for 10 and 5 min, respectively. A glass filter cutting off UV light was inserted in front of the lamp. Visible absorption increases thus induced were recorded on a Hitachi 215 spectrophotometer.

Results and Discussion

For converting **I** into **III** by an esterification reaction (1st step in Eq. 1), a large excess of *p*-bis(chloromethyl)benzene (**II**) on the basis of **I** was employed to prevent further occurrence of the reaction between the chloromethyl group of **III** once produced and the remaining carboxylato group on another porphyrin. Analytical results for the product thus obtained were satisfactory.

Introduction of metal atoms into the porphyrin ring were then carried out for **III** in the 2nd step, since previous attempts to introduce metal atoms into **VIII** [M=none] had failed.

The 3rd step consisting of the monoquaternization of 4,4′-bipyridine (**V**) with the chloromethyl group of **IV** was carried out successfully also with a large excess of **V** to exclude the possible diquaternization of **V**.

The completion of the projected 4,4′-bipyridinium structure, i.e. the 4th step, was also effected with a large excess of **VII** to provide porphyrin- or metalloporphyrin-coupled viologen **VIII** in a reasonable yield.

Compound **VIII**, either in DMF solutions or embedded in the **PVP**-matrix film, was exposed to visible light and the resulting absorption increases were investigated. The shapes of the difference spectra thus obtained having λ_{max} around 610 nm clearly indicated that the portion of **VIII** responsible for the absorbance increase was the 4,4′-bipyridinium (viologen) moiety,[1-3] although conventional viologens were inert to visible light even in the presence of **TEOA**. This fact suggested that the visible light energy absorbed by the MPorphyrin (**MPor**) moiety was somehow transfered to the **viologen**-moiety to generate a highly colored radical cation from the latter.[1-4]

A feature of the difference spectra was that absorptions attributable to the associated viologen radical cations,[12] usually found between 500 and 550 nm, were hardly observed, suggesting that the radical cations (λ_{max}, ca. 610 nm) generated from **VIII** existed in less associated forms, probably for steric reasons.

Table 1. Absorption Increase for **VIII** in DMF Solution[a] Induced by Visible Light under N_2

Exp. No.	M in **VIII**	Molar absorptivity (ε) at 610 nm $dm^3 mol^{-1} cm^{-1} \times 10^4$ Before irradiation ε_0	Immediately after[b] irradiation ε_{10}	$\varepsilon_{10}-\varepsilon_0$
1	None (H)	0.040	0.230	0.190
2	Zn(II)	0.185	0.700	0.515
3	Ni(II)	0.195	0.280	0.085
4	Mn(II)	0.720	1.146	0.426
5	Fe(III)	0.256	0.277	0.021
6	Sn(IV)	0.235	0.747	0.512

a) **VIII**, 4 mg; TEOA, 100 mg; DMF, 10 mL. Irradiations and absorbance measurements were carried out through a 10 mm band pass length. b) Complete recovery took place within 10 min upon standing in the dark at 20 °C.

Table 2. Absorption Increase for **VIII** Embedded in PVP Matrix Film[a] Induced by Visible Light

Exp. No.	M in **VIII**	Absorbance[b] at 610 nm Before irrad. A_0	Immediately after irrad. A_5	Recovery[c] 20 min after	 60 min after	Absorbance increase by irrad. A_5-A_0
11-1	None(H)	0.048	0.120	0.102	0.086	0.072
11-2	H $2PF_6^-$	0.050	0.083	0.067	0.056	0.033
11-3	H $2PF_6^-$[d]	0.047	0.071	0.066	0.061	0.024
11-4	H $2BF_4^-$	0.052	0.069	0.059	0.052	0.017
11-5	H $2BF_4^-$[d]	0.057	0.070	0.068	0.066	0.013
12	Zn(II)	0.112	0.192	0.140	0.112	0.080
13	Ni(II)	0.112	0.174	0.166	0.130	0.062
14	Mn(II)	0.254	0.466	0.442	0.374	0.212
15	Fe(III)	0.172	0.195	0.172	0.172	0.023
16	Sn(IV)	0.168	0.544	0.472	0.304	0.376

a) With TEOA. b) Value for 0.01 mm film thickness and 1.0wt% **VIII**/**PVP**. c) Standing in the dark at 20 °C. d) For air-tight glass-sandwiched film.

Effects of **M** in **VIII** in DMF solutions on the absorption increase (λ_{max}=610 nm) induced by visible light are summarized in Table 1.

It was recognized that the absorbance increase $\varepsilon_{10}-\varepsilon_0$ at λ_{max} was profoundly affected by **M**. Thus, Zn(II), Mn(II), and Sn(IV) provided much larger values (Exp. 2, 4, and 6) of $\varepsilon_{10}-\varepsilon_0$ than **VIII** [none] did (No. 1), whereas Ni(II) and especially Fe(III) provided much smaller ones (Exp. 3 and 5).

A similar tendency was also found in Table 2, where the results obtained for **III** embedded in the **PVP**-matrix film are summarized.

Thus, Mn(II) and Sn(IV), and Fe(III) as **M** afforded much larger and smaller A_5-A_0 values for 0.01 mm film thickness and 1 wt% **VIII/PVP** (Exp. 14, 16, and 15), respectively, than **VIII** [none] did (Exp. 11-1), whereas Zn(II) and Ni(II) afforded similar values (Exp. 12 and 13). Besides these, the exchange of the counter anion (Cl^- and Br^-) in the viologen moiety of **VIII** [none] with PF_6^- or BF_4^- was found to bring about significant decreases in A_5-A_0 (Exp. 11-1—11-5), suggesting that the counter anion highly activated in polar aprotic media such as DMF and **PVP** film might be the principal attacking species against the viologen dication also activated to generate the radical cation, as shown in previous studies.[1-3,13,14] As is known from comparative data (Exp. 11-2, -3 and 11-4, -5) with glass-sandwiched films, oxygen accelerates the recovery by oxidation.

As could also be guessed from data (Exp. 11-3, -5) for the glass-sandwiched films, stabilities of the radical cations appeared to be inferior to that from 1,1′-dibenzyl-4,4′-bipyridinium, which was stable for more than a year under the same film-forming conditions.[13]

It is not clear within the scope of the present study, whether any interactions between the **MPor**- and **viologen** moieties within a **VIII** molecule exist or not.

It can be concluded, however, that the dependence characteristic of the photosensitivity of conventional 1,1′-dibenzyl-4,4′-bipyridinium on irradiation wavelength as well as the dark stability of the radical cation generated from it by irradiation, i.e. photochromic behavior by a redox mechanism, not to mention waterproofness,[14] was remarkably affected by coupling with a porphyrin or metalloporphyrin unit.

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