An Efficient Photochemical Synthesis of Conformationally Restricted Quinone-substituted Porphyrins

Atsuhiro Osuka,[a] Soichi Morikawa,[a] Kazuhiro Maruyama,*[a] Satoshi Hirayama,[b] and Takaaki Minami[b]

[a] *Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan*
[b] *Faculty of Textile Science, Kyoto Institute of Technology, Kyoto 606, Japan*

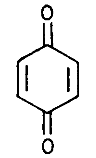
Quinone-substituted porphyrins were synthesized by the self-photosensitized reaction of porphyrins including phenol groups; intramolecular fluorescence quenching was inefficient in the conformationally restricted systems.

Despite the extensive studies on photoinduced electron transfer reactions between porphyrins and quinones,[1] there have been few reported irreversible reactions of synthetic interest so far. We now report a highly efficient synthesis of quinone-linked porphyrins based on self-photosensitization of porphyrin. Quinone-substituted porphyrins have received increasing attention recently as models of the primary electron transfer in photosynthesis.[2] Model compounds with well defined geometries are especially interesting.[3]

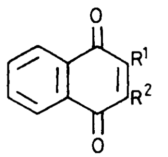
Typically, irradiation ($\lambda > 590$ nm) of a chloroform solution of 5-(2-hydroxyphenyl)-10,15,20-tris(4-tolyl)porphyrin (**2**) (0.5 mM) in the presence of 2,3-dichloro-1,4-naphthoquinone (**3c**) (5 mM) under argon for 10 h followed by flash column chromatography (silica gel, $CHCl_3$–C_6H_6, 50:50) gave the quinone-substituted porphyrin (**5c**)† in 32% yield, along with recovered (**2**) (66%). Photoinduced coupling of quinones to the porphyrins (**1**) and (**2**) proceeded cleanly and the yields of quinone-substituted porphyrin based on the amounts of the starting porphyrin consumed are generally >90% at low conversions (<30%) (Table 1). The present photochemical synthesis of quinone-substituted porphyrins has several advantages: (i) quinone protection is unnecessary, (ii) a variety of quinones having a wide range of electrochemical

---

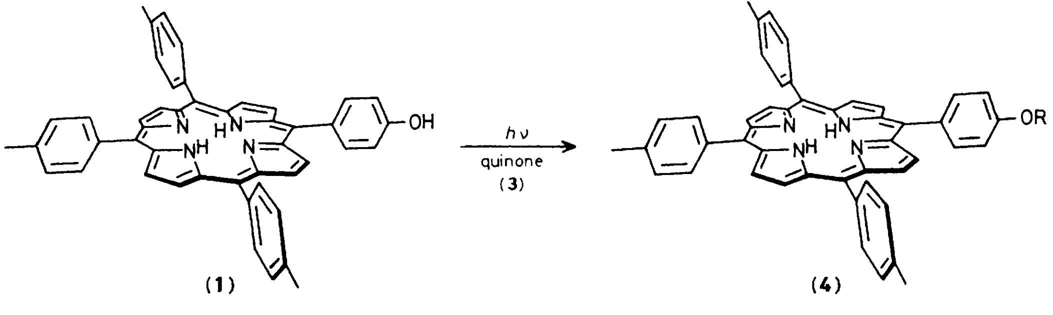
† All new compounds gave satisfactory spectral data consistent with the assigned structure.



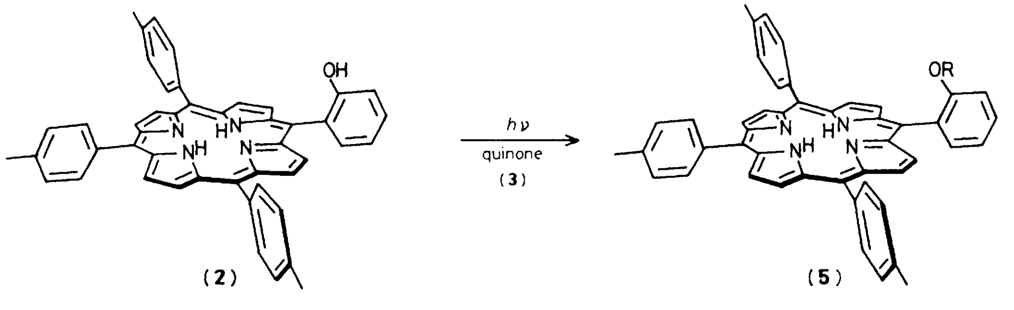
(3a)



(3b-e)



(1) **(4)**



(2) **(5)**

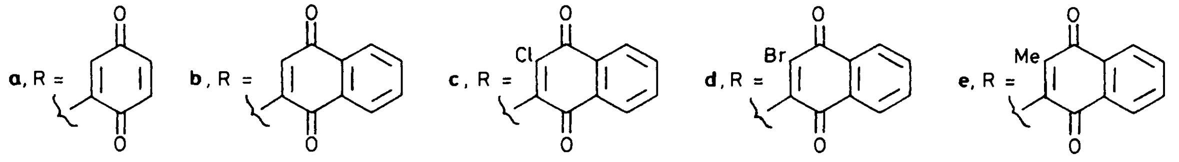


Table 1. Photochemical synthesis of quinone-linked porphyrins.

Porphyrin	Quinone	R^1	R^2	Conv. (%)	Photo-product	Yield[a] (%)
(1)	**(3a)**	—	—	16	**(4a)**	94
(1)	**(3b)**	H	Cl	28	**(4b)**	93
(1)	**(3c)**	Cl	Cl	41	**(4c)**	90
(1)	**(3d)**	Br	Br	18	**(4d)**	91
(1)	**(3e)**	Me	Br	20	**(4e)**	90
(2)	**(3a)**	—	—	6	**(5a)**	91
(2)	**(3b)**	H	Cl	21	**(5b)**	94
(2)	**(3c)**	Cl	Cl	34	**(5c)**	93
(2)	**(3d)**	Br	Br	6	**(5d)**	90
(2)	**(3e)**	Me	Br	7	**(5e)**	90

[a] Isolated yield of quinone-linked porphyrin based on the starting porphyrin consumed.

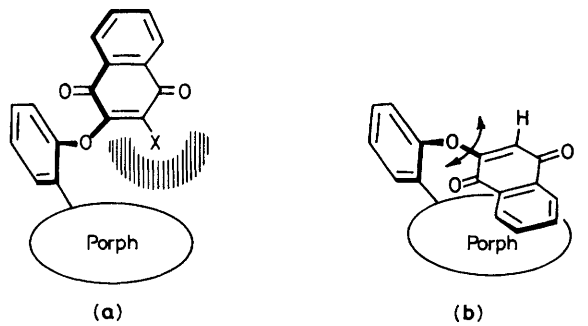
Table 2. One-electron redox potentials[a] of **(4)** and **(5)**.

	$E^{+}_{1/2}$	$E^{-}_{1/2}$	ΔE		$E^{+}_{1/2}$	$E^{-}_{1/2}$	ΔE
(4a)	0.51	−0.95	1.46	**(5a)**	0.47	−0.94	1.41
(4b)	0.54	−1.18	1.72	**(5b)**	0.52	−1.17	1.69
(4c)	0.48	−0.98	1.46	**(5c)**	0.48	−1.02	1.48

[a] Redox potentials (V *vs.* ferrocene/ferrocenium) were measured by cyclic voltammetry at a Pt electrode, in dichloromethane containing 10^{-3} M $Bu^{n}_{4}NClO_4$ at 20 °C.

and stereochemical properties can be employed, providing a series of compounds, and (iii) the reaction can be carried out in a one-pot photochemical procedure.

The relative fluorescence quantum yields of quinone-substituted porphyrins and the one-electron redox potentials for **(4)** and **(5)** are listed in Tables 2 and 3. The difference $(E^{+}_{1/2} - E^{-}_{1/2})$ between the redox potentials for oxidation of the donor and reduction of the acceptor, ΔE, which can be regarded as a good estimate of the radical ion pair energy level, is similar in each pair of **(4)** and **(5)**. The positions of the absorption and fluorescence bands of the porphyrins are not perturbed by the presence of the appended quinones and are almost identical with those of 5,10,15,20-tetraphenylporphyrin (TPP). However, the fluorescence of the porphyrin was greatly quenched by the appended quinone in **(4)** and **(5)** (Table 3). More efficient fluorescence quenching in **(5a)** than **(4a)** is in accordance with the shorter donor–acceptor centre-to-centre separation in **(5a)** than in **(4a)**. Similarly, the relative fluorescence yield of **(5b)** is less than that of **(4b)**. In marked contrast, fluorescence quenching in **(5c—e)** which have 3-substituted 2-naphthoquinone end units is less efficient than that in **(4c—e)**, regardless of much shorter donor–acceptor separation in **(5c—e)**.



(a) (b)

Figure 1

Table 3. Relative fluorescence quantum yields from (**4**) and (**5**).[a]

Compound	I/I_0	Compound	I/I_0	(**4**)/(**5**)[b]
(**4a**)	0.014	(**5a**)	0.0026	5.4
(**4b**)	0.025	(**5b**)	0.0098	2.6
(**4c**)	0.0070	(**5c**)	0.0165	0.42
(**4d**)	0.0058	(**5d**)	0.032	0.18
(**4e**)	0.019	(**5e**)	0.022	0.86

[a] The measured values are relative to the absolute value (0.11) of TPP taken from ref. 4. All samples were 10^{-7} M in dichloromethane in a 1-cm path-length cell under aerobic conditions. Excitation wavelength: 515 nm. [b] Ratios of fluorescence yields of (**4**) to (**5**).

Corey–Pauling–Koltum (C.P.K.) molecular models show that the orthogonal conformation shown in Figure 1(a) is only permitted for (**5c**—**e**) because of the severe steric hindrance due to the 3-substituents in the 2-naphthoquinonyl groups. The restricted orthogonal conformations of (**5c**—**e**) are also illustrated by their 400 MHz ^{1}H n.m.r. spectra; typically, the 3-chloro-2-naphthoquinone end unit in (**5c**) is weakly shielded by the porphyrin ring current and appears at δ 7.75 (d), 8.08 (d), 8.17 (dd), and 8.19 (dd), while the 2-naphthoquinone end unit in (**5b**) is much more greatly shielded and appears at δ 5.94 (s), 6.52 (d), 6.94 (d), 6.51 (dd), and 6.72 (dd). In the restricted orthogonal conformation of (**5c**—**e**), the dihedral angle between the porphyrin and quinone rings is nearly 90°. This situation presumably minimizes the π–π electronic interaction between the porphyrin and the quinone end. In contrast, the quinone end in (**5b**) can rotate freely around the C–O bond and accordingly can adopt a nearly coplanar orientation, Figure 1(b), where the intramolecular fluorescence quenching of the porphyrin by the quinone end unit may take place very rapidly.‡

Another advantage of the present synthesis consists particularly of the synthesis of conformationally restricted quinone-linked porphyrins, which should be useful for studies on intramolecular electron-transfer reactions.

Received, 21st October 1986; Com. 1499

References

1 G. Tollin and G. Green, *Biochim. Biophys. Acta*, 1962, **60**, 524; G. Tollin, *J. Phys. Chem.*, 1976, **80**, 2274; A. Harriman, G. Porter, and N. Searle, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 1515; K. Maruyama, H. Furuta, and T. Otsuki, *Chem. Lett.*, 1980, 857; 1981, 709.

2 For a comprehensive list of recent references, see: G. M. Sanders, M. van Dijk, A. van Veldhuizen, and H. C. van der Plas, *J. Chem. Soc., Chem. Commun.*, 1986, 1311.

3 R. J. Cave, P. Siders, and R. A. Marcus, *J. Phys. Chem.*, 1986, **90**, 1436; P. Siders, R. J. Cave, and R. A. Marcus, *J. Chem. Phys.*, 1984, **81**, 5613.

4 P. G. Seybold and M. Goutermann, *J. Mol. Spectrosc.*, 1969, **31**, 1.

---

‡ Preliminary measurements of the fluorescence lifetimes of (**5b**) using the picosecond time-correlated single photon counting technique revealed a very short-lived decaying component (110 ps), while a slightly longer-lived (200 ps) component was found for (**5c**). The short-lived components for (**4b**) and (**4c**) had lifetimes of 1.24 ns and 200 ps, respectively.