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An approach towards artificial quinone pools by use of photo- and redox-active dendritic molecules

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Abstract

Molecules with one porphyrin and multiple quinone groups are described. The molecules are based on dendritic frameworks, with the quinone groups attached at the "internal" positions and the porphyrin attached at the focal point, leading to a characteristic layer architecture. When irradiated with visible light in the presence of 4-*tert*-butylthiophenol, the quinones were converted to quinols. Such a behavior mimics the function of quinone pools in photosynthesis.

Keywords: Quinone pool; Photoinduced electron transfer; Dendrimer; Porphyrin

1. Introduction

Mimicking individual processes of photosynthesis by use of artificial molecules is an interesting approach for chemists to build up new systems for light-to-chemical energy conversion [1–6]. It would also be beneficial for research in bioenergetics, where fundamental understanding of chemical energy conversion is a prerequisite. Particular success was achieved by studies on photoinduced electron transfer in artificial donor–acceptor molecules [7–9]. More recently, models of antenna systems [10–12] and oxygen evolving complexes [13–16] are being actively studied. However, many other features of photosynthesis are still unexplored by model chemists.

The quinone pool is one of such disregarded features. From the viewpoint of synthetic chemists, the quinone pool has not been an attractive target, mainly because it consists of a collection of unspecified number of molecules (quinones and quinols embedded in membranes) rather than a well-defined set of characteristic molecules as the reaction center. Nevertheless, the quinone pool is a very important and essential component in biochemical energy conversion. Chemists would find something to learn by mimicking the quinone pool with artificial molecules.

In this article, we will report our attempt to build a "single-molecular" quinone pool by use of synthetic molecules. The molecules (Fig. 1) are based on dendrimers, which are tree-like macromolecules with well-defined size and shape [17]. A porphyrin (photoactive group) is attached at the center, and multiple quinones are attached at internal positions of the dendrimer. We already reported similar molecules with attached ferrocenes [18], in which only photoinduced electron transfer was observed. This time we use quinones, so that we can expect real "chemistry" instead of reversible single-electron transfer. Indeed, we found that the quinones in these molecules were gradually reduced to quinols by irradiation in the presence of an electron donor.

2. Materials and methods

2.1. Preparation of the molecules

The target molecules, G1Q_2P, G2Q_6P, and G3Q_{14}P were synthesized according to the procedures in [18], with slight modifications. Representative procedures are described in the Supplementary Materials.

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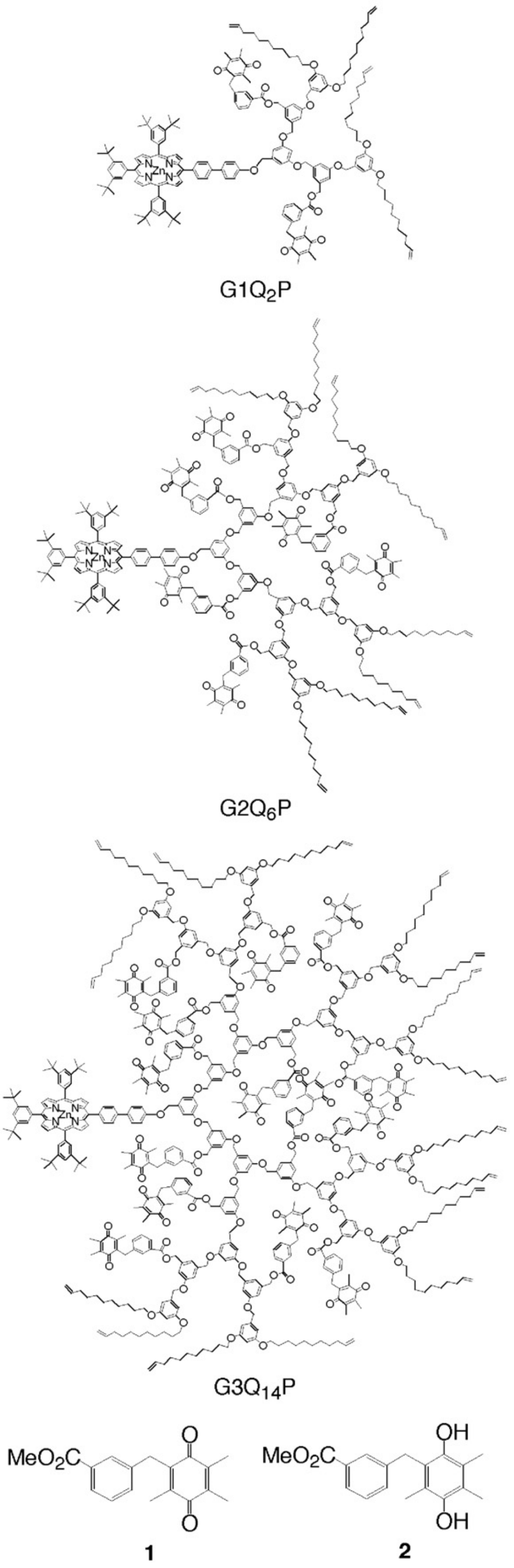

Fig. 1. The compounds used in this study.

2.2. Physical measurements

UV/visible absorption spectra and steady-state emission spectra were measured by a Shimadzu UV-2500PC spectrometer and a Shimadzu RF-5300PC spectrometer, respectively. A solution of about 1×10^{-6} mol dm^{-3} in CH$_2$Cl$_2$ was placed in a quartz cell (1 × 1 × 4 cm). No attempts were made to degas the solution. The emission intensity was normalized by the optical density at the excitation wavelength (550 nm).

Electrochemical measurements were carried out with an ALS/CHI Model 660 voltammetric analyzer under the following conditions: 0.1 mmol dm^{-3} in CH$_2$Cl$_2$ containing 0.1 mol dm^{-3} of Bu$_4$NClO$_4$, glassy carbon working electrode (0.1 mm diameter), platinum wire counter electrode, Ag/AgClO$_4$/CH$_3$CN reference electrode. The DPV (differential pulse voltammetry) parameters were as follows: pulse amplitude 50 mV, potential increment 4 mV, pulse width 50 ms, pulse period 200 ms.

2.3. Photoreactions

The photoreactions were performed with a standard “merry-go-round” type apparatus. Solutions of the porphyrin-quinone molecules (0.5 μmol), 4-*tert*-butylthiophenol (50 μmol) in CDCl$_3$ (0.6 mL) were placed in NMR tubes with J-Young valves. Argon was bubbled through the solutions for 5 min immediately before photoreaction. A 65-W halogen lamp (Toshiba JDR110V65WN/K5S) was used, with a colored glass filter (Asahi Techno Glass Y-52, 4 × 50 × 50 mm) that cuts off wavelength shorter than 500 nm. Temperature was kept at 30 ± 1 °C by circulating water.

The measurements of quantum yield were performed by the following setup. A DPSS laser (532 nm, 30 mW, Mitsui Chemical Corp. MDS-1000) was collimated and introduced into a 10 × 10 mm quartz cuvette, behind which a power meter was placed. The light intensity at the cuvette was 4.4 mW. The sample solutions (3 mL, the same concentration as above) were placed in the cuvette and Ar was bubbled for 20 min. After irradiation the solution was taken with a syringe and examined by ^{1}H NMR.

3. Results

3.1. Characterization of the target molecules

As we discussed in the previous report [18], the quinones in the target molecules G1Q$_2$P, G2Q$_6$P, and G3Q$_{14}$P are arranged in a layered structure (Fig. 2). The ^{1}H NMR of these compounds (Fig. 3) revealed that the three layers in G3Q$_{14}$P were observed separately. The changes in the peak positions are mainly attributed to the interaction with the central porphyrin (which has a large diamagnetic ring current [19]). Consequently, the observation of the separate signals for the different layers of quinones implies that the interaction of the quinones and the porphyrin is dependent on the layer number. This is easily

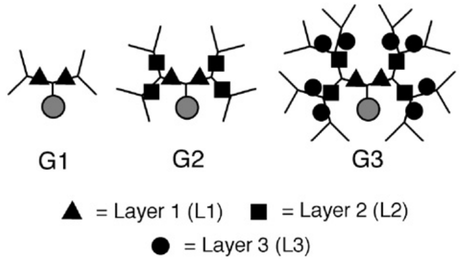

Fig. 2. A pictorial view of the layered structure of the quinone-dendrimer molecules. The shaded circle represents the porphyrin at the center. The symbols, triangle, square, and circle, represent the quinones in the first, second, and third layers, respectively.

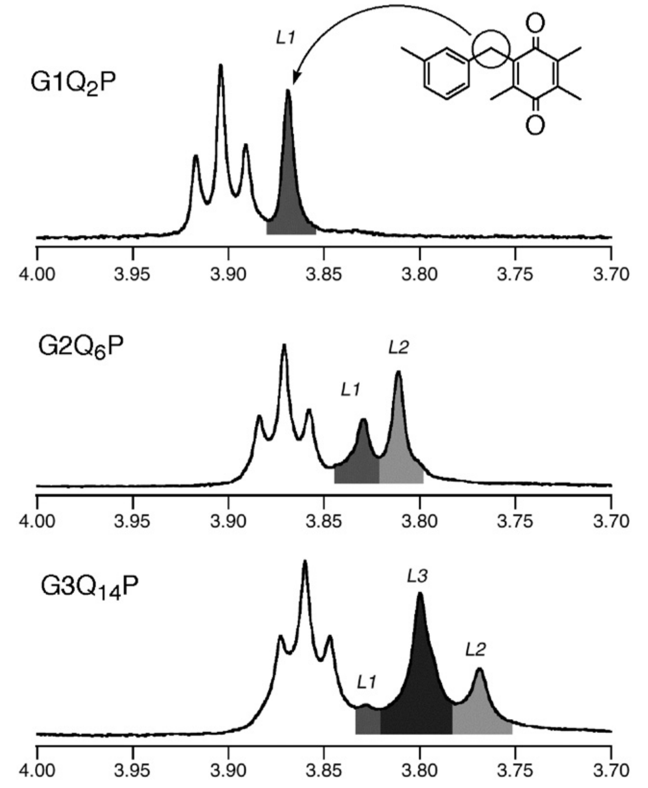

Fig. 3. Parts of the ^{1}H NMR spectra of G1Q$_2$P, G2Q$_6$P, and G3Q$_{14}$P in CDCl$_3$.

understood in light of the molecular structure (Figs. 1 and 2). Such layer-dependence was already observed in our previous study [18].

3.2. Photoreactions

When these molecules were irradiated with visible light ($\lambda > 500$ nm) in the presence of 4-*tert*-butylthiophenol in CDCl$_3$, the quinones were gradually converted to the corresponding quinols. Fig. 4 shows the time-dependent change of ^{1}H NMR of G3Q$_{14}$P under these conditions. The quinones were quantitatively converted to the quinols, with concurrent formation of bis (4-*tert*-butylphenyl) disulfide. Similar results for G1Q$_2$P and G2Q$_6$P are shown in the Supplementary Materials. The reaction is formulated as follows:

$$\mathrm{Q} + 2\mathrm{ArSH} \xrightarrow{h\nu,\text{Porphyrin}} \mathrm{QH_2} + \mathrm{ArSSAr} \tag{1}$$

This reaction did not proceed in the absence of light. Since the optical density of the quinone was less than 1% of that of the porphyrin in the region of $\lambda > 500$ nm, we can conclude that this reaction is triggered by photoexcitation of the porphyrin. This was further supported by the control experiment; when a solution of the quinone **1** and 4-*tert*-butylthiophenol in CDCl$_3$ (without porphyrin) were irradiated with the same light source, no quinol was generated after 2 h.

A particularly interesting observation in Fig. 4 is that the quinones of all layers in G3Q$_{14}$P were converted to quinols at similar apparent rates. Fig. 5 shows the time-dependent conversion from quinone to quinol for each layer in G1Q$_2$P, G2Q$_6$P, and G3Q$_{14}$P. The rates of conversion do not vary with the layer number in one molecule, whereas they do vary with the total size (or “generation”) of the molecule. The compounds of higher generation with more quinones showed slower conversion.

4. Discussion

There were preceding reports on the porphyrin-quinone molecules containing multiple quinones [20–23]. However, they were mainly concerned with photoinduced electron transfer, and no particular attention was paid to the subsequent chemical reactions. In this sense, this is the first report on mimicking the function of “quinone pools”, where multiple

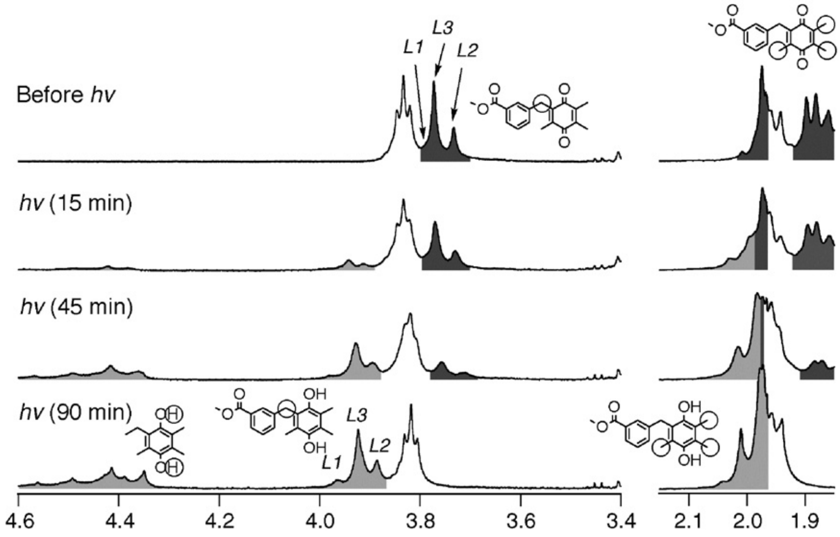

Fig. 4. Time-dependent change of the ^{1}H NMR of G3Q$_{14}$P during photoreaction with 4-*tert*-butylthiophenol. The marks “L1”, “L2” and “L3” denote the quinones belonging to the layer 1, layer 2 and layer 3, respectively.

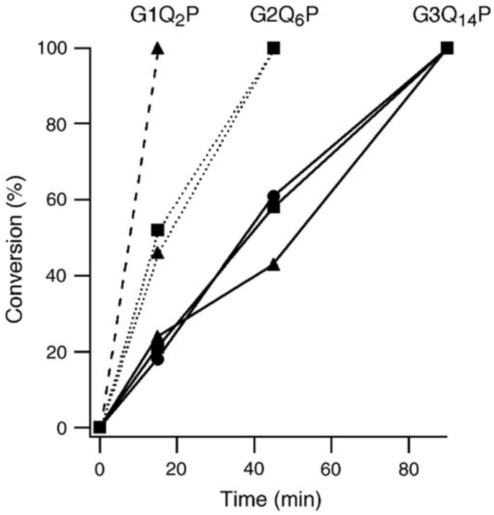

Fig. 5. Time-dependent conversion of quinones in each layer in $G1Q_2P$, $G2Q_6P$, and $G3Q_{14}P$. The symbols triangle, square, and circle denote the quinones in the first, second, and third layers, respectively.

quinones located in confined space are sequentially converted to quinols by the action of light.

The conversion of quinones to quinols in these reactions is triggered by photoexcitation of the porphyrin. We can safely assume that the first photochemical step is the electron transfer from the excited porphyrin to one of the quinones [23–26]. The electrochemistry and the fluorescence measurements were consistent with this assumption (see Supplementary Materials). The steps following the initial electron transfer can only be speculated at present. We propose the following reaction sequence:

$$P^* + Q \longrightarrow P^{+\bullet} + Q^{-\bullet} \tag{2}$$

$$Q^{-\bullet} + ArSH \longrightarrow QH^{\bullet} + ArS^- \tag{3}$$

$$P^{+\bullet} + ArS^- \longrightarrow P + ArS^{\bullet} \tag{4}$$

$$QH^{\bullet} + ArSH \longrightarrow QH_2 + ArS^{\bullet} \tag{5}$$

$$2QH^{\bullet} \longrightarrow Q + QH_2 \tag{5'}$$

$$2ArS^{\bullet} \longrightarrow ArSSAr \tag{6}$$

where $Q^{-\bullet}$ and $QH^{\bullet}$ are the anionic and neutral semiquinone radicals, respectively. When we used 1-dodecanethiol instead of 4-*tert*-butylthiophenol, the photoreaction was much slower. This is consistent with the above sequence, where protonation of the semiquinone anion radical (Eq. (3)) is the key step. Since 1-dodecanethiol ($pK_a = 10.57$) is a much weaker acid than 4-*tert*-butylthiophenol ($pK_a = 6.76$), we expect the protonation of the semiquinone anion is slower for 1-dodecanethiol.

It is intriguing that there is no apparent layer dependence in the rates of conversion from quinones to quinols in $G3Q_{14}P$ and $G2Q_6P$. The interaction between the quinone and the porphyrin cannot be the same for all layers, as shown in our previous study on ferrocene–dendrimer–porphyrin compounds [18], where we observed characteristic layer dependence. This inconsistency is clarified when we consider another photochemical process, a photoinduced exchange reaction between quinones and quinols, as shown in Eq. (7):

$$Q + Q'H_2 \xrightarrow{h\nu,\text{Porphyrin}} QH_2 + Q' \tag{7}$$

This type of exchange reaction was indeed observed when a mixture of $G1Q_2P$ (0.5 μmol) and the quinol 2 (2.5 μmol) was irradiated ($\lambda > 500$ nm) in $CDCl_3$ (0.6 mL). The quinol form of $G1Q_2P$ and the quinone 1 were generated and reached to a photostationary state after 10 min. In the absence of light, the reaction was very slow and completed only after 48 h. These observations strongly suggest that similar photoinduced exchange of quinone/quinol is responsible for the apparent layer independence of the conversion rates in $G3Q_{14}P$ and $G2Q_6P$.

To our disappointment, the quantum yields of these reactions were very low. In all three compounds, the quantum yields of a single quinone/quinol conversion were $2 \pm 1\%$. This is most likely due to the fast back electron transfer, since we made no attempts to make the long-lived charge-separated state. Certainly, there are many possible ways to improve these compounds [27,28], which should be the subject of our future research.

5. Conclusion

The molecules with one porphyrin and multiple quinones groups underwent quinone-to-quinol conversion when irradiated with visible light in the presence of thiophenol. Such a behavior mimics the function of the quinone pool in photosynthesis. Although the compounds have layer-like arrangements of the quinones, the apparent rates of conversion did not depend on the layer. This was ascribed to the photoinduced exchange of quinones and quinols. These molecules represent a new type of redox-active molecular devices, and will introduce an interesting possibility in constructing biomimetic energy-conversion systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bbabio.2006.11.006.

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