Synthesis and photochemistry of new “ternary” quinone-pool molecules containing TEMPO (2,2,6,6-tetramethylpiperidinyloxy), porphyrin, and quinones are described, as a new model for plant photosynthesis. The quinones were successfully reduced by irradiation in the presence of 4-tert-butylthiophenol.

Key words: synthetic quinone-pools, artificial photosynthesis, porphyrin, quinone, TEMPO

1. INTRODUCTION

Plant photosynthesis is one of the most important biological activities on this planet. Its primary function is to capture solar energy and to produce high-energy chemical substances (dioxygen and carbohydrates). Although solar energy can also be converted to other useful forms of energy by various physical processes (e.g. wind energy, hydroelectric energy, solar cells), photosynthesis is still the only known system for direct conversion of solar energy to chemical free energy. Therefore it is of interest, both academic and industrial, to mimic this process by artificial chemical systems.

To achieve this goal, it is useful for chemists to mimic individual processes of photosynthesis by use of artificial molecules [1-6]. This will allow us to "learn" from Nature, and help us to build up new systems for light-to-chemical energy conversion. The most successful attempts were the studies on photoinduced electron transfer in artificial donor-acceptor molecules [7-9]. More recently, models of light-harvesting antenna systems [10-12] and oxygen evolving complexes [13-16] are actively studied. Nevertheless, there are still many other features of photosynthesis that are yet unexplored by model chemists.

The quinone pool is one of such disregarded features. The quinone pools in biological systems consist of a collection of quinones embedded in special membranes, and they work as buffers between the redox enzymes embedded in the same membranes. This is a smart trick for biological systems to smoothly combine independent redox processes with different inherent reaction rates. In plant photosynthesis, the quinone pool connects the two important redox enzymes, photosystem II and cytochrome b6f complex [17].

Previously we reported our research on building a “single-molecular” quinone pool by use of synthetic dendrimer molecules [18,19]. The characteristic feature of this molecule is that the quinone groups are appended at multiple internal positions of the tree-like architecture. By irradiation in the presence of reducing agent (thiols), the quinones were converted to quinols, thus mimicking the key feature of the quinone pool in photosynthesis. Our “single molecular” quinone pool, however, lacked one important aspect. After giving an electron to the quinone, the oxidized porphyrin must receive an electron from the electron donor directly (Figure 1a). This is not always easy, because one-electron oxidation of a closed-shell molecule often requires high overpotential. To overcome this difficulty, it is desirable...
that the porphyrin has a neighboring catalytic site that oxidizes the substrate (electron donor) with low overpotential and supply electrons to the porphyrin (Figure 1b). This is exactly what the plant photosynthesis does; water is oxidized at the oxygen evolving complex, and the obtained electrons are routed to the photooxidized chlorophyll pigments (Figure 1c) [20].

In this paper, we present the first preparation of “ternary” quinone-pool molecules. As the electrocatalytic site, we featured TEMPO (2,2,6,6-tetramethylpiperidinooxy free radical), which is known to catalyze oxidation of various organic substrates including alcohols, thiols, and alkenes [21,22]. Recently we found that the TEMPO/porphyrin/quinone ternary system was effective for photochemical oxidation of alcohols, and proposed a mechanism in which the photoinduced electron transfer from porphyrin to quinone occurred first followed by one-electron oxidation of TEMPO to produce the reactive oxaammonium species [23]. In the light of this work, we designed the ternary molecules consisting of TEMPO, porphyrin, and quinones (Figure 2). In the following sections, we will describe synthesis and basic photochemical properties of such molecules.

2. MATERIALS
General equipments/procedures for synthesis, spectroscopic measurements and molecular dynamics calculations were already described [18]. Abbreviations: EDC•HCl, N-ethyl-N'-(3-dimethylaminopropyl)carbodiimide hydrochloride; DMAP: 4-dimethylaminopyridine; THF: tetrahydrofuran.

Scheme 1. Synthesis of the ternary quinone pool molecules.

Figure 2. The “ternary” quinone-pool molecules in this work.

and washed with EtOAc. The filtrate was evaporate to give white solid. Yield: 90% (74% for 2 steps).

Porphyrin-Boc, compound (5). A mixture of 3 (150 µmol), 4 [26] (50 µmol), EDC•HCl (200 µmol), DMAP (200 µmol) in CH2Cl2 (2 ml) was stirred at room temperature for 14 h. A solution of washed with aqueous 5% KHSO4 and saturated aqueous NaHCO3, dried over Na2SO4, and evaporated. The residue was purified by column chromatography (SiO2, CH2Cl2/acetone/MEOH = 100/0-80/15/5 (v/v/v)). Yield: 80%.

TEP-porphyrin-Boc, compound (6). The compound 5 (40 µmol) was dissolved in THF (2 ml) and MeOH (0.5 ml), and a solution of KOH (120 µmol) in H2O (0.2 ml) was added. The mixture was stirred at room temperature for 14 h. A solution of KHSO4 (200 µmol) in H2O (0.2 ml) was added, and the mixture was evaporated to dryness. Water (2 ml) was added and the red-violet solid was collected by filtration and dried in a vacuum. The product was mixed with 4-amino-TEMPO (100 µmol), EDC•HCl (100 µmol), DMAP (200 µmol) in CH2Cl2 (2 ml), and the mixture was stirred at room temperature for 3 days in the dark, washed with 5% aqueous KHSO4 and saturated aqueous NaHCO3, dried, and evaporated. The residue was purified by column chromatography (SiO2, CH2Cl2/MEOH = 90/10 (v/v)). Yield: 95% for 2 steps.

TEP-porphyrin-diquinone compound (7). The compound 6 (39 µmol) was dissolved in CH2Cl2 (1 ml) and CF3CO2H (1 ml) and stirred at room temperature for 2 h. The mixture was evaporated, and the residue was treated with aqueous 5% NaHCO3. After the color changed from green to red, the solid was collected by filtration and washed with water. The red solid was dissolved in CHCl3, and the mixture was dried over Na2SO4 and evaporated. The product was mixed with the
quinone-carboxylic acid 8 [19] (100 μmol), EDC•HCl (100 μmol), and DMAP (200 μmol) in CH₂Cl₂ (2 ml), and the mixture was stirred at room temperature for 14 h. The mixture was washed with aqueous 5% KHSO₄ and aqueous 5% NaHCO₃, dried over Na₂SO₄, and evaporated. The residue was purified by column chromatography (SiO₂, CH₂Cl₂/acetone/ MeOH = 100/0/80/15/5 (v/v/v)). The product was dissolved in CHCl₃ (2 ml), a suspension of Zn(OAc)₂•2H₂O (460 μmol) in MeOH (1 ml) was added, and heated at 80 °C for 2 h. The mixture was washed with water, dried over Na₂SO₄, evaporated, and purified by column chromatography (SiO₂, CH₂Cl₂/acetone/ MeOH = 100/0/70/23/7 (v/v/v)). Yield: 41% for 3 steps.

3. RESULTS AND DISCUSSION

Synthesis. The synthesis is outlined in Scheme 1. Because this was our first attempt to build the ternary quinone-pool molecule, we targeted the simplest compound, i.e., n = 2 (Figure 2). The key compound is 5, that contains one benzyl ester group and two Boc-amino groups; the former and latter are eventually converted to TEMPO-amide and quinone-amides, respectively. The ester and Boc groups can be removed by alkaline hydrolysis and acid treatment, respectively. Because the quinone groups were introduced. The TEMPO group was intramolecular electron transfer such as TEMPO-P-Q⁺ → TEMPO-P-Q⁻ is involved in the photoreaction. Detailed analysis of this photoreaction, as well as the synthesis of more elaborate compounds, is currently under investigation.

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Figure 5. (a) The spatial distribution of the TEMPO and quinone groups in relative to the porphyrin ring. In order to show the porphyrin-TEMPO or porphyrin-quinone distances correctly, the horizontal offset from the porphyrin center is presented in the bottom axis. The horizontal offsets of quinones and TEMPO are (arbitrarily) plotted as positive and negative values. (Note: this picture cannot correctly represent the TEMPO-quinone distances.) (b) The histogram of the TEMPO-quinone center-to-center distances.

5. REFERENCES

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