Modulation of Hydrogen Bonding through Redox Chemistry of Quinones and Urea-functionalized Porphyrin

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Quinones play a crucial role in photosynthetic energy conversion.[1,2] The redox potentials of the bound quinones shift positively up to 300 mV compared with those obtained for the free quinones in biological systems.[1,3] It was described that the hydrogen bonding interactions between quinones and proteins in biological systems are responsible for adjusting the redox potentials of the quinones.[4] Hydrogen bonding provides reliably molecular recognition, regulation of bond strength, and structural backbones in molecular assembly. Recently there has been increasing interest in utilizing hydrogen bonding for molecular recognition[5] and structural backbones.[6] It was reported that the control of hydrogen bonding strength was possible by electrochemistry of redox-dependent receptors such as quinones[7] and flavins.[8] The positive shifts in the redox potential of quinones bound to host compounds relative to uncomplexed quinones are less than 200 mV in previous reports.[7] In this work we describe electrochemically the modulation of bonding strength through hydrogen bondings of quinones and urea-functionalized porphyrin. Urea-functionalized porphyrin as a host of quinone was synthesized,[9] and 1,4-bezoquinone derivatives were used as guests of porphyrins.

The uncommon effect of hydrogen bonding on the reduction of quinone is clearly manifested with 2,6-dimethoxy-1,4-benzoquinone (Q1) as a guest and *meso*-($\alpha,\alpha,\alpha,\alpha$)-tetrakis(2-(pentafluorophenylurea)phenyl)porphyrin (TPPP) as a host receptor. The effects of interaction with host receptor on the reduction of quinones were studied electrochemically using cyclic voltammetry (CV). Figure 1 shows unusual effects on CVs of Q1 in the presence of TPPP in CH_2Cl_2 solutions. One-electron reduction of Q1 to the radical anion is reversible, with an $E_{1/2}$ of -0.72 V *vs* Ag/AgCl. In the presence of 0.5 equiv. receptor TPPP, the voltammetric response of Q1 exhibits the original wave corresponding to the uncomplexed Q1, and the new wave with an $E_{1/2}$ of -0.00 V. As the concentration of TPPP increases, the current related to the new wave increases at the expense of the original current.

Finally, the original wave disappears in the presence of excess equivalent receptor because of the binding property between Q1 and TPPP, and there is only the new wave ascribed to the complexed Q1 with TPPP. The new wave attributed to the reduction of complexed Q1 is 722 mV positive relative to the original wave, and the second reduction of complexed Q1 seems to begin at the negative end of the scan. The voltammetric behavior exhibited by Q1 in the presence of P1 distinctly reveals that host-guest complexation makes the reduction of quinone more easily. As shown in Figure 1, the observation of two waves at less than 1 equiv of TPPP supports clearly that receptor TPPP binds with guest Q1 in CH_2Cl_2 solutions. The strong binding between quinones and TPPP is observed in visible spectroscopy and NMR experiments, and the binding constant for Q1 and TPPP is 2.4×10^5 (M^{-1}) in CH_2Cl_2 solution.[10] Most of complexes of quinones and TPPP reveals moderate binding constants within the range of 10^4-10^5 in CH_2Cl_2 solutions. We want to discuss the interactions of quinones and TPPP. The remarkable potential shift ($\Delta E = E^{0'}_{bound} - E^{0'}_{free}$ = 722 mV) for the reduction of Q1 in the presence of TPPP relative to uncomplexed Q1 has been observed in CH_2Cl_2 solutions as shown in Figure 1, indicating the production of powerful

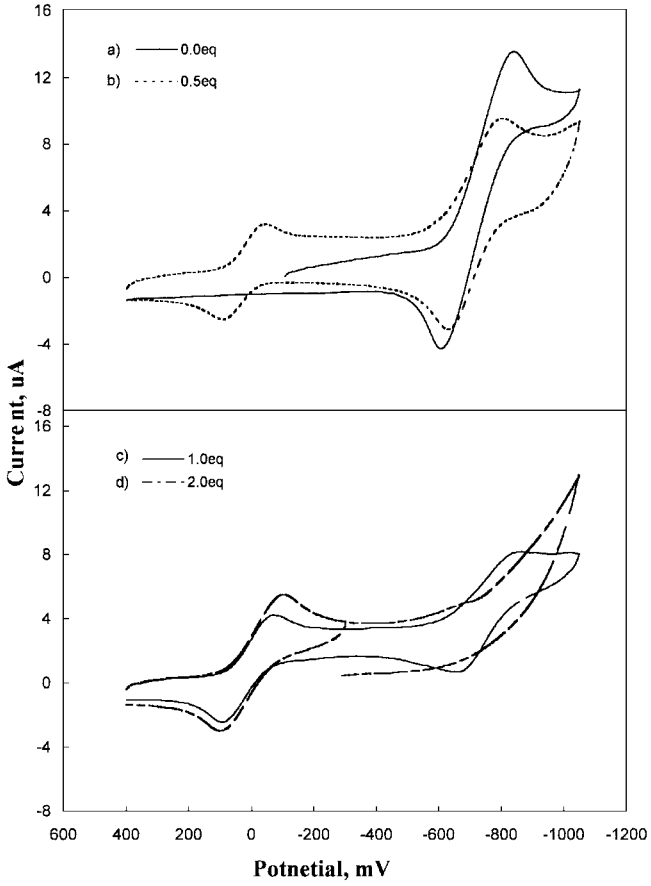

Figure 1. Cyclic voltammograms on the reduction of Q1 in the absence (a), and presence [(b) 0.5 eq, (c) 1.0 eq, (d) 2.0 eq] of TPPP in CH_2Cl_2 solutions under Ar atmosphere; scan rate = 50 mVs^{-1}.

Table 1. Potential shifts on the first reduction of quinones in the presence of TPPP in organic solvents

Quinones	ΔE (mV)	
	CH_2Cl_2	DMF
Q1	722	193
Q2	703	
Q3	394	71
Q4	105	
Q5	656	
Q6	321	60
Q7	95	
Q8	155	
Q9	59	

hydrogen bonding between the reduced Q1 and TPPP. According to above equation (1), the binding constant (K_{red}) upon the reduction of Q1 to its radical anion by one-electron transfer with TPPP increases remarkably by about 10^{12} times relative to K_{ox}. In order to confirm the unusual potential shift, many quinones are investigated in the presence of TPPP, and summarized in Table 1. Likewise Q1, the result (ΔE = 703 mV) of 2,5-dimethoxy-1,4-benzoquinone (Q2) having non-vicinal dimethoxy group to the 1,4-benzoquinone ring is similar to that of Q1, but those of 2,3-dimethoxy-5-methyl-1,4-benzoquinone (Q3) and ubiquinone (Q4), which are very important in biological systems, having vicinal dimethoxy group show the smaller potential shift (394 mV and 105 mV, respectively) relative to Q1. Meanwhile, 1,4-benzoquinone (Q6) shows the moderate potential shift (321 mV), and 2-methoxy-1,4-benzoquinone (Q5) containing mono-methoxy group provides large shift (656 mV). According to these results, the methoxy group bonded to benzoquinone ring is very important for the increase of binding properties, but the structure of vicinal dimethoxy group is non-effective. Ubiquinone and 2,3,4,5-tetrachloro-1,4-benzoquinone (Q7) are used to test the steric effect, and Q7 shows very small potential shift (95 mV). The small potential shifts for Q4 and Q7 are attributed to the steric hindrance of long alkyl chain and chloro group bonded to the benzoquinone ring. The effect of four N-H hydrogen bondings to both carbonyls compared with two N-H hydrogen bondings to both carbonyls is tested using 1,4-naphthoquinone (Q8) and 1,2-naphtho-quinone (Q9). Q8 gives geometrically cofacial four N-H hydrogen bondings to both carbonyls, but Q9 produces structurely two N-H hydrogen bondings to both carbonyls. Based on the results, the potential shift (155 mV) on reduction of Q8 is higher value than that (59 mV) of Q9, indicating clearly that four N-H hydrogen bondings to both carbonyls are essential to strong binding on quinone reduction. Cofacial set of two N-H bonds in urea-function-alized porphyrin are basically well-oriented to two carbonyl oxygens of quinones. The more important feature is the participation of methoxy group bound to benzoquinone ring for their binding. The positive shift depends on the number of methoxy groups as well as the position of methoxy substituents. The remarkable shift for Q1 compared with that for Q3 indicates that two non-vicinal methoxy substituents interact simultaneously with the two N-H bonds positioned in both side of the urea-functionalized porphyrin, and their bonding strength increases by simultaneous hydrogen bond-ing between methoxy substituent and two N-H bonds. To test solvent effect, CVs of Q1 with TPPP are measured in DMF, the observed shifts are much smaller than those in CH_2Cl_2, but they are still very great despite the strongly solvating feature. The effect of other hydrogen-bonding receptors on the reduction potential of Q1 is in the presence of host receptor. Unlikely urea groups in TPPP, 1,3-diphenylurea gives a negligible shift (~5 mV) in CH_2Cl_2. *meso*-($\alpha,\alpha,\alpha,\alpha$)-tetrakis (2-hydroxy-1-naphthyl)porphyrin, which strongly binds with quinones in toluene,[11] produces also a negligible shift (~10 mV) and a prewave in CH_2Cl_2. This results imply that cofacial set of two N-H hydrogen bondings to both carbonyls of 1,4-benzoquinones and the participation of methoxy group are very effective to the unusual potential shift on the reduction of quinones.

In conclusion, 1,4-benzoquinone derivatives combine with *meso*-($\alpha,\alpha,\alpha,\alpha$)-tetrakis(2-(pentafluorophenylurea)phenyl)-porphyrin through four hydrogen bondings between cofacial set of two N-H bonds and both carbonyls in CH_2Cl_2. The remarkably potential shift (722 mV) on the reduction of Q1 is observed in the presence of TPPP, and the highest shift is by far the largest reported in synthetic host-guest complex-ation. It is very important that redox chemistry of electroactive species can switch a moderate host-guest complex to a powerful one. This feature due to electron transfer can apply to molecular recognition, molecular transfer, and molecular assembly or disassembly in biological systems.

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9. *meso*-($\alpha,\alpha,\alpha,\alpha$)-tetrakis(2-(pentafluorophenylurea)phenyl)porphyrin (TPPP) in $CDCl_3$: Yield, 70%; mp 240 °C, dec; UV/vis ($CHCl_3$) λ_{max}(ln): 422 (12.13), 518 (9.47), 522 (8.54), 588 (8.64), 644 (7.78); ^{1}H NMR -2.54 (br s, 2H) 6.35 (br s, 4H) 6.70 (br s, 4H) 7.66 (t, 4H, *J* = 7.59 6.63 Hz) 7.88 (t, 4H, *J* = 7.86 7.44 Hz) 8.18 (d, 4H, *J* = 7.26 Hz) 8.26 (d, 4H, *J* = 6.81 Hz) 8.86 (s, 8H).
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