Mechanism of Photocurrent Generation by ITO Electrodes Modified with Self-Assembled Monolayers of *meso,meso*-linked Porphyrins

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Self-assembled monolayers (SAMs) of porphyrins have been attracted much attention in relevance to artificial photosynthesis and molecular photonic devices. However, poor absorptivity of such monolayers has precluded further improvement of incident photon-to-current efficiency (IPCE). *Meso,meso*-porphyrin arrays are promising candidates as new type of light-harvesting molecules because of their unique linear structure and photophysical properties. In particular, they absorb visible light more widely than a linear combination of the corresponding porphyrin monomer due to the exciton coupling of the porphyrins.

We report herein a systematic series of ITO electrodes modified with self-assembled monolayers (SAMs) of porphyrin monomers (**H_2P**/ITO) and porphyrin dimer ((**$H_2P)_2$**/ITO), which provide valuable insight into the development of artificial photosynthetic devices (Figure 1).

Photoelectrochemical measurements were carried out in an argon-saturated 0.1 M Na_2SO_4 aqueous solution containing triethanolamine (TEA) and methyl viologen (MV^{2+}) acting as an electron carrier in a three electrode system including the modified ITO electrodes, respectively (denoted as ITO/**H_2P** or **$(H_2P)_2$**/TEA/Pt cell). A stable cathodic and anodic photocurrent appeared immediately upon irradiation of the ITO electrode as shown in Figure 2. The action spectrum of porphyrin dimer SAM exhibits photocurrent generation in a wide wavelength region. The relative integrated value of the action spectrum as well as the quantum yield of photocurrent generation of ITO/**$(H_2P)_2$**/TEA/Pt cell are improved as compared to those of ITO/**H_2P**/TEA/Pt cell (Figure 3). This improvement of photoconversion efficiency may be explained by π-electron delocalization of porphyrin dimer radical anion relative to the monomer radical anion, which is indicated by the ESR measurements of the radical cations. The mechanism of the photocurrent generation by ITO electrodes modified with SAMs of *meso,meso*-linked porphyrins is discussed based on the photocurrent and fluorescence lifetime measurements.

The present results are highly promising for the further improvement of photoconversion efficiency.

References

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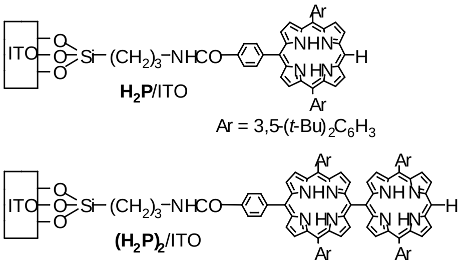

Figure 1. Self-assembled monolayers of porphyrins on ITO in this study.

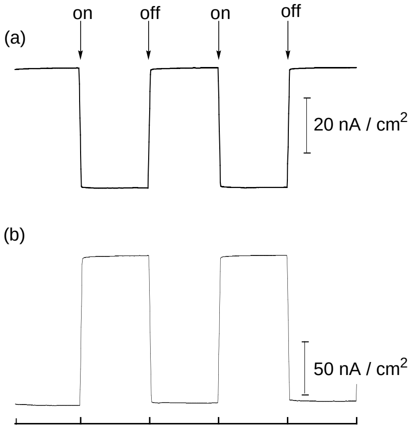

Figure 2. Photoelectrochemical response of ITO/**$(H_2P)_2$**/TEA/Pt cellwith illumination at 420 nm; electrolyte solution: an argon-saturated 0.1 M Na_2SO_4 aqueous solution containing (a) 5 mM MV^{2+} as electron carrier; input power 1 mW cm^{-2};applied potential: -200 mV vs Ag/AgCl (sat. KCl) (b) 50 mM TEA as electron carrier;input power 500 μW cm^{-2};applied potential:+400 mV vs Ag/AgCl (sat. KCl).

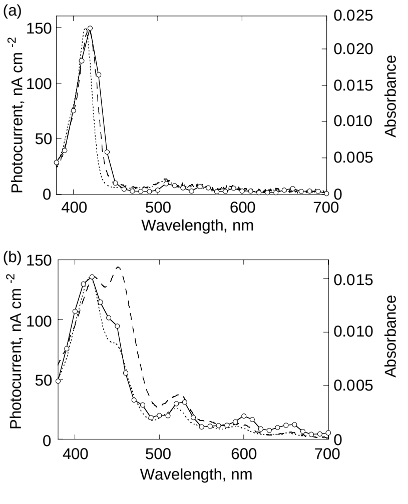

Figure 3. Absorption spectra of (a) **H_2P**/ITO (solid line) and (b) **$(H_2P)_2$**/ITO (solid line)and excited spectra of (a) **H_2P**/ITO (dotted line) and (b) **$(H_2P)_2$**/ITO (dotted line). The spectra are normalized at the Soret band for comparison. Action spectra of (a)ITO/**H_2P**/TEA/Pt cell and (b) ITO/**$(H_2P)_2$**/TEA/Pt cell are shown as dashed line with circles; Applied potential : +400 mV vs Ag/AgCl (sat. KCl); an argon-saturated 0.1 M Na_2SO_4 aqueous solution containing 50 mM TEA.