# Surface Bottom-up Fabrication of Porphyrin-terminated Metal Complex Molecular Wires with Photo-electron Conversion Properties on ITO

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We fabricated photoelectron conversion system with porphyrin-terminated "molecular wires" on an ITO surface synthesized using stepwise metal–terpyridine complexation reactions. The efficiency and the electrode potential singnificantly depended on the metal center of the bis(terpyridine) complex unit in the molecular wire.

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Molecular assembling has attracted attention in the formation of functional devices and materials. Among the technologies of molecular assembling, "self-assembled monolayer (SAM)" provides effective alternatives to obtain target functions in a simple way using solutions. SAM is especially used for photochemistry as a means to arrange functional molecules, since the arrangement of photoreceptors, donors, and acceptors significantly controls the efficiency of photoelectric conversion. For example, Imahori et al. have reported achieving high quantum efficiency and long life with a photoelectrode with donor–photosensitizer–acceptor triad molecules.[1]

Recently, preparation of layer-by-layer assembled multilayers by stepwise chemical bond formation on the surface is beeing developed extensively.[2] Especially, coordination reactions are useful to synthesize oligomeric molecular wires with the desired number of complex units and the desired hetero-layered structures. When we use a linear bis(terpyridine) complex as a "molecular wire," it shows a one-dimensional ordered structure and exhibits redox conduction through the molecular wire using its redox-active d orbital electrons.[3] This type of electron transfer is also expected to provide efficient photo-electron transport using the d orbitals in the wire. In the present study, we designed ITO electrodes modified with $M(tpy)_2$ (tpy = 2,2′:6′,2″-terpyridine, M = Co, Fe, and Zn) complex wires with a terminal porphyrin moiety as a photosensitizer for studying photo-electron-transfer behavior from porphyrin to ITO through the "molecular wire" by changing the metal element in the $M(tpy)_2$ moieties.

We fabricated the modified ITO electrodes[4] by a combination of SAM formation with a terpyridine derivative and stepwise metal–terpyridine coordination reactions in a manner similar to that described in our previous reports (Figure 1).[3] 4-[(2,2′:6′,2″-Terpyridin)-4″-yl]benzoic acid (**1**) was immobilized on cleaned ITO[5] by immersing them in a 0.1 mmol dm$^{-3}$ solution of **1** in chloroform for 12 h in order to anchor the carboxyl group to ITO.[6,7] The modified ITO was immersed in the aqueous solution of 0.1 mol dm$^{-3}$ $CoCl_2$, $Fe(BF_4)_2$, or $Zn(BF_4)_2$ for 2–3 h to form metal–terpyridine coordination reactions. Finally, the metal-coordinated ITO was immersed in a 0.1 mmol dm$^{-3}$ acetonitrile solution of a terpyridine-functionalized porphyrin, **2**, to give the target molecular wires, **4**, on electrodes (Chart 1). In addition, a carboxylate-functionalized porphyrin, **3**, was immobilized on cleaned ITO to afford a modified ITO, **5**, by immersing them in a 0.1 mmol dm$^{-3}$ ethanol solution of the porphyrin as a reference.[8]

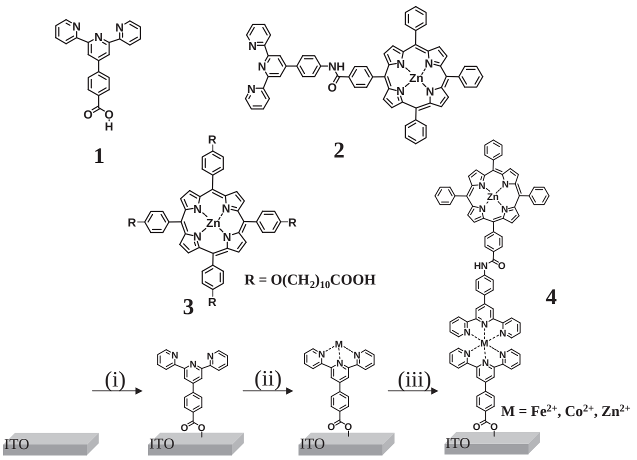

**Chart 1.** Chemical structure of the ligands used in this study, and stepwise coordination methods for the preparation of modified ITO electrodes: (i) immobilization at carboxylic acid **1**, (ii) complexation with metal ion, and (iii) complexation with **2**.

Cyclic voltammetry (CV) of **4** and **5** was carried out in $Bu_4NClO_4$–$CH_2Cl_2$ in order to estimate the surface coverage. The adsorbed amount of terpyridine-functionalized porphyrin was found to be $1.8 \times 10^{-12}$ mol cm$^{-2}$ for the Co complex (**4-Co**), $1.1 \times 10^{-11}$ mol cm$^{-2}$ for the Fe complex (**4-Fe**), $1.2 \times 10^{-11}$ mol cm$^{-2}$ for the Zn complex (**4-Zn**), and $2.8 \times 10^{-11}$ mol cm$^{-2}$ for **5** by calculation from the peak area of the porphyrin and $M(tpy)_2$.

The absorption spectra of **4-Co** and **2** in acetonitrile show the Soret band of porphyrin, while that of the former was broader than that of the latter. The $\lambda_{max}$ value of the Soret band of **4-Co** was nearly identical to that of **2** in methanol, but 12-nm red shift was observed. These spectral changes could be due to partial aggregation of porphyrin moieties, according to a previous study which shows similar broadening and a red shift for porphyrin SAMs on ITO and gold.[9] The adsorbed amount of **4-Co** calculated from the absorption spectra was $1.9 \times 10^{-12}$ mol cm$^{-2}$. This value is consistent with that derived from CV.

Photoelectrochemical measurements using the modified ITO as working electrodes were carried out in an argon-saturated 0.1 mol dm$^{-3}$ $Na_2SO_4$ aqueous solution containing 50 mmol dm$^{-3}$ triethanolamine (TEA) as an electron sacrificer.[10] A stable photocurrent appeared immediately upon irradiation of monochromatic light with a 28-nm width between 400 and 600 nm for **4** and **5**. The magnitude of the anodic photocurrent showed a dependence on the applied potential and the excitation wavelength (Figure 1). The dependency of the wavelength is

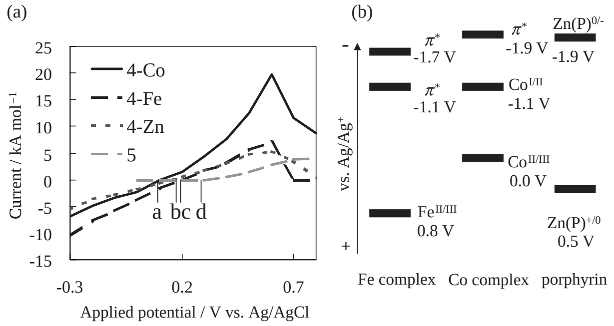

**Figure 1.** Potential dependence of the anodic photocurrent of modified ITO electrodes excited at 410 nm (a) and the energy diagram (b); a–d refers to $E_F$ (**4-Co**), $E_F$ (**4-Zn**), $E_F$ (**4-Fe**), and $E_F$ (**5**), respectively.

similar for all the modified electrodes. However, the potential at which the photocurrent intersected at zero ($E_F$) was different for each electrode (Figure 1a). The potential became more positive as follows: **4-Co** < **4-Zn** ≈ **4-Fe** < **5**. These results indicate that photo-electron transfer is related to the molecular orbital levels of the molecular wires. The molecular wires with bis(terpyridine)metal complexes have two possible photo-electron pathways. One is through the d orbital of the central metal ion, and the other is through the $\pi^*$ orbital of the terpyridine moieties (Figure 1b). In the case of **4-Co**, the level of the $Co^{I/II}$ orbital is considered to be located between the level of the $S_1$ state of porphyrin and the ground state. In contrast, in the case of **4-Fe**, the possible photo-electron-transfer pathway is the terpyridine $\pi^*$ orbital only, since the d-orbital level of the Fe complex moiety is higher than the ground state of porphyrin. The $\pi^*$ orbital level was estimated from the data with a similar $Fe(tpy)_2$ complex in the previous study.[11] Unlike **4-Co** and **4-Fe**, **4-Zn** with a $Zn(tpy)_2$ moiety and **5** without $M(tpy)_2$ moiety have no molecular orbital between the excited state and the ground state of porphyrin. Considering these molecular orbitals and that the zero current of the Co complex shows the most negative potential, the d orbital seems to conduct photo-electrons more effectively than the $\pi^*$ orbital of the molecular wire. In addition, the similarity of the zero-current voltage of **4-Fe** and **4-Zn** indicates that the $\pi^*$ orbital level of terpyridine has less influence on photo-electron transfer. Nevertheless, the $\pi$-conjugated chain of terpyridine transfers photo-electrons more effectively than the alkyl chain of **5**, which is derived from the comparison between the data of **4-Zn**, **4-Fe**, and **5**.

The results of the quantum efficiency also supported these assertions. **4-Co** showed the highest quantum efficiency, 0.57%, while those of **4-Zn** and **5** were 0.20% and 0.15%, respectively. The absorption spectra of the electrode with **4-Fe** cannot be acquired because of the spectral change that occurred after the immersion in $Fe(BF_4)_2$ aq, probably due to the interaction between Fe and glass or ITO.[12] The results regarding the quantum efficiency are in accordance with the obtained potentials of zero photocurrent. Both results indicate that the molecular wire transfers photo-electrons more effectively than the alkyl chain. In addition, the d orbital assists the photo-electron transfer more effectively than the $\pi^*$ orbital in the molcular wire.

In conclusion, we fabricated ITO electrodes modified with porphyrin-terminated $M(tpy)_2$ complex wires by the stepwise coordination method, and demonstrated that the electronic nature of the molecular wire is critical to the photo-electron transfer from the porphyrin to ITO. These results indicate a new facile fabrication method of molecular assemblies effective for construction of photo-electron-transfer systems. This system will be upgraded by increasing the wire length, making the redox potential step in the wire, and/or incorporating donors and acceptors. Experiments along this line are in progress.

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