

Remarkable enhancement of photocurrent generation by ITO electrodes modified with a self-assembled monolayer of porphyrin†

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Quantum yield of the photocurrent generation by an ITO electrode modified with a self-assembled monolayer of porphyrin was remarkably enhanced by a factor of ca. 280, as compared to that of the corresponding porphyrin monolayer on a gold electrode.

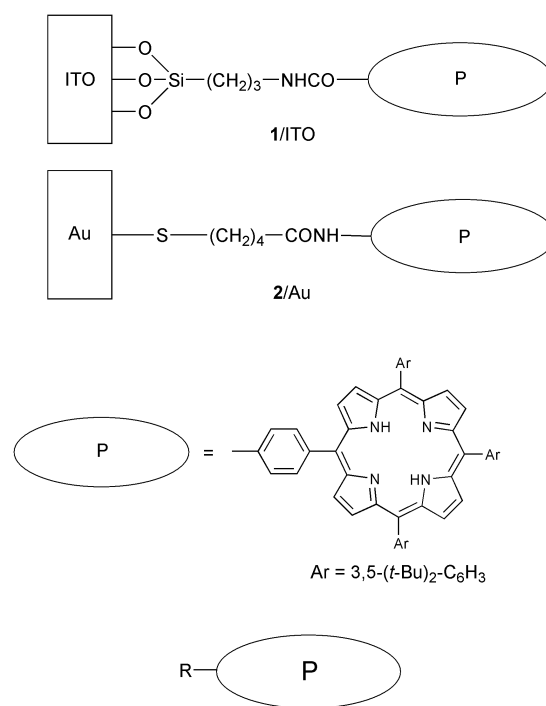
In recent years organized assemblies of porphyrins have attracted much attention directed toward the development of photovoltaic devices, catalysis, and sensors.¹ In particular, formation of self-assembled monolayers (SAMs)² of porphyrins on the material surface is a potential approach for fabricating highly ordered functional thin films. In this context, we^{3–5} and others⁶ have reported the photoelectrochemical properties of porphyrin and porphyrin-containing donor–acceptor SAMs on gold electrodes. However, the photocurrent generation, initiated from the porphyrin excited singlet state (¹P*) in the porphyrin SAMs on the gold electrodes, has been hampered by the competing energy transfer (EN) quenching of ¹P* by the gold surface. Such an undesirable EN process may be avoided by employing semiconductor electrodes such as indium tin oxide (ITO) instead of metal electrodes.^{7,8} However, there has so far been no report on the photoelectrochemical properties of porphyrin-containing donor–acceptor SAMs on conductive ITO support, although porphyrin SAMs on oxide surfaces or gold nanoparticles have been extensively studied.^{9–12} As such, no quantitative comparison of such quenching effect has ever been reported for porphyrin SAMs on semiconductor and metal electrodes.

We report herein the first quantitative comparison of photocurrent generation in porphyrin SAMs on ITO and gold electrodes. A remarkable 280-fold enhancement of photocurrent generation has been observed in the porphyrin SAM on the ITO, as compared to the corresponding porphyrin SAM on the gold surface. The present study thereby provides valuable information for the construction of highly efficient photovoltaic cells.

In order to evaluate the EN quenching effect accurately, we designed porphyrin SAMs where the porphyrin is tethered to ITO (denoted as **1**/ITO) and gold electrodes (denoted as **2**/Au) with a spacer of the same number of atoms, respectively, as shown in Fig. 1. Bulky *tert*-butyl groups were introduced into the *meta*-positions of the *meso*-phenyl groups on the porphyrin to preclude self-quenching of the ¹P* due to the porphyrin aggregation.^{4,13} The general strategy employed for synthesizing the SAMs is summarized in Scheme 1. ITO electrodes (1900–2000 Å ITO on transparent glass slides) were treated with aminopropyltrimethoxysilane by refluxing for 3 h in toluene.¹¹ Activated porphyrin **4**, prepared from porphyrin carboxylic acid **3** and pentafluorophenol,¹¹ was coupled to the aminopropylsilylated glass by refluxing for 3 h in toluene

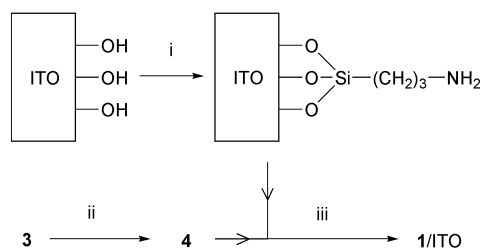
to give **1**/ITO.¹¹ **2**/Au was prepared by following the same procedures as described previously.⁴ Porphyrin references **5** and **6**⁴ were also synthesized.

Fig. 2 displays absorption spectra of **1**/ITO and reference **5** in CHCl₃. The Soret band of **1**/ITO becomes broader than that of reference **5** in CHCl₃. The λ_{max} value of the Soret band of **1**/ITO is nearly identical to that of **5** in CHCl₃, whereas the λ_{max} value of **2**/Au was reported to be red-shifted (4 nm) as compared to that of reference **6** in CHCl₃.⁴ This indicates that the porphyrin environment of **1**/ITO is less perturbed than that of **2**/Au.



3: R=CO₂H; **4:** R=CO₂C₆F₅; **5:** R=CONH-(4-CH₃)C₆H₄; **6:** NHCOCH₃

Fig. 1 **1**/ITO and **2**/Au and porphyrin derivatives used in this study.



Scheme 1 Reagents and conditions: i, (MeO)₃Si(CH₂)₃NH₂, isopropylamine, dry toluene, argon, reflux 3 h; ii, DCC, 4-pyrrolidinopyridine, pentafluorophenol, dry CH₂Cl₂, 96%; iii, dry toluene, argon, reflux 3 h.

† Electronic supplementary information (ESI) available: Fig. A cyclic voltammograms of **1**/ITO and **2**/Au. See <http://www.rsc.org/suppdata/cc/b0/b006108p/>

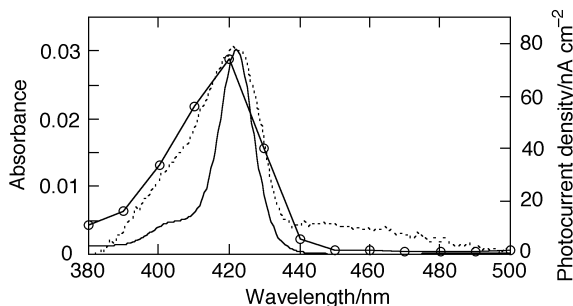


Fig. 2 UV-visible absorption spectra of **1**/ITO (dotted line) and **5** in CHCl_3 (solid line) and action spectrum of the ITO/1/TEA/Pt cell (solid line with circles); $100 \mu\text{W cm}^{-2}$, $+400 \text{ mV vs. Ag/AgCl}$, an argon-saturated $0.1 \text{ M Na}_2\text{SO}_4$ aqueous solution containing 50 mM TEA . The spectra are normalized at the Soret band for comparison.

A cyclic voltammetric experiment using **1**/ITO (electrode area, 0.48 cm^2) in CH_2Cl_2 containing $0.2 \text{ M Bu}^n_4\text{NPF}_6$ electrolyte with a sweep rate of 0.1 V s^{-1} was performed to estimate the surface coverage.^{4,5}† The adsorbed amount of the porphyrin on ITO was calculated from the anodic peak of the porphyrin as $2.4 \times 10^{-10} \text{ mol cm}^{-2}$ (69 \AA^2). Assuming that packing densities of the porphyrins are similar in **1**/ITO and **2**/Au ($1.0 \times 10^{-10} \text{ mol cm}^{-2}$, 170 \AA^2),⁴ the roughness factor of ITO is estimated as 2.5.

Photoelectrochemical measurements were carried out in an argon-saturated $0.1 \text{ M Na}_2\text{SO}_4$ aqueous solution containing 50 mM triethanolamine (TEA) as an electron sacrificialer using **1**/ITO or **2**/Au as the working electrode, Pt counter electrode, and Ag/AgCl (sat. KCl) reference electrode (hereafter represented by ITO/1/TEA/Pt and Au/2/TEA/Pt, respectively, where / denotes an interface).^{4,5} A stable anodic photocurrent from the electrolyte to the ITO appeared immediately upon irradiation of the ITO electrode with $\lambda = 419.5 \pm 5.3 \text{ nm}$ light with $100 \mu\text{W cm}^{-2}$. The photocurrent fell down instantly when the illumination was cut off. In the absence of TEA, the anodic photocurrent was negligible under otherwise the same experimental conditions. The anodic photocurrent increases monotonically with increasing positive bias to the ITO electrode (-0.2 – $+0.4 \text{ V}$), whereas the dark current remains constant, as shown in Fig. 3. This demonstrates that photocurrent flows from the electrolyte to the ITO electrode *via* the porphyrin SAM. The agreement of the action spectrum with absorption spectrum of **1**/ITO from 380 – 500 nm (Fig. 1) demonstrates clearly that the porphyrin is the photoactive species.

The photocurrent generation efficiency becomes much lower when the ITO/1/TEA/Pt cell was replaced by the Au/2/TEA/Pt cell under the same experimental conditions. The quantum yield (3.4%) of the ITO/1/TEA/Pt cell determined under the optimized conditions ($\lambda = 419.5 \pm 5.3 \text{ nm}$ light with $100 \mu\text{W cm}^{-2}$ and at $+0.4 \text{ V vs. Ag/AgCl}$)§ is *ca.* 280 times higher than the value (0.012%) for the Au/2/TEA/Pt cell.

Time-resolved, single-photon counting fluorescence studies were made for **1**/ITO and **2**/Au as well as **5** and **6** in solutions

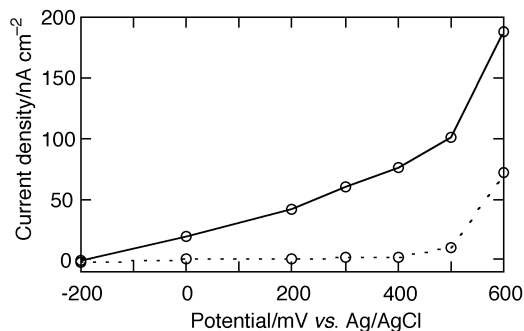


Fig. 3 Photocurrent vs. applied potential curves for the ITO/1/TEA/Pt cell (solid line with open circles): $\lambda = 419.5 \text{ nm}$ ($100 \mu\text{W cm}^{-2}$), an argon-saturated $0.1 \text{ M Na}_2\text{SO}_4$ aqueous solution containing 50 mM TEA . The dark current is shown as a dotted line with open circles.

with the excitation wavelength at 435 nm . In each case the decay of the fluorescence intensity due to the $^1\text{P}^*$ was monitored at 655 nm . The decay curve could be fitted as a single exponential except for the case of **1**/ITO. The fluorescence lifetimes of **1**/ITO (1.0 (74%) and 3.7 ns (26%))¶ are significantly longer than that of **2**/Au (15 ps), although the lifetimes are shorter than those of **5** (7.7 ns) and **6** (7.6 ns) in CHCl_3 .⁴ This clearly indicates that the EN quenching efficiency of $^1\text{P}^*$ on the ITO is much suppressed as compared to that on the gold surface. Based on the electrochemical data, it is concluded that an electron transfer takes place from TEA ($+0.61 \text{ V}$)¹⁵ to the singlet excited state $^1\text{P}^*$ ($+0.62 \text{ V vs. Ag/AgCl}$)¹⁴ rather than the excited triplet state $^3\text{P}^*$ ($+0.12 \text{ V vs. Ag/AgCl}$),¹⁴ yielding the porphyrin radical anion ($\text{P}^{\bullet-}$). The formation efficiency of $\text{P}^{\bullet-}$ in **1**/ITO should become much larger than that in **2**/Au as observed experimentally because of the suppression of undesirable EN quenching of $^1\text{P}^*$ by the electrode as compared to the **2**/Au system. The resulting $\text{P}^{\bullet-}$ ($-1.28 \text{ V vs. Ag/AgCl}$) gives an electron to the ITO electrode, resulting in the anodic photocurrent generation.

In conclusion, we have successfully demonstrated that the quantum yield of photocurrent generation for the porphyrin SAM cell on ITO becomes 280 times larger as compared to the quantum yield on the gold electrode due to the suppression of undesirable EN quenching of $^1\text{P}^*$ by the electrode.

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Notes and references

† For electrochemical and photoelectrochemical measurements, gold electrodes (**2**/Au) (roughness factor $R = 1.1$) were prepared by a vacuum deposition technique with titanium (5 – 10 nm) and gold (20 – 100 nm) in a sequence onto a Si(100) wafer, whereas for UV-visible absorption measurements, gold (20 nm) was evaporated onto a transparent glass slide to give **1**/Au ($R = 1.5$).^{4,5}

§ $\phi = (i/e)/[I(1 - 10^{-A})]$, $I = (W\lambda)/(hc)$ where i is the photocurrent density, e is the elementary charge, I is number of photons per unit area and unit time, λ is the wavelength of light irradiation, A is absorbance of the adsorbed dyes at $\lambda \text{ nm}$, W is light power irradiated at $\lambda \text{ nm}$, c is the light velocity, and h is the Planck constant; ITO/1/TEA/Pt: $i = 74 \text{ nA cm}^{-2}$, $A = 0.029$; Au/2/TEA/Pt: $i = 0.28 \text{ nA cm}^{-2}$, $A = 0.030$ (including the reflection at 419.5 nm).^{4,5}

¶ In the case of 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (TBP) and octadecylamine (ODA) Langmuir–Blodgett multilayers on a glass slide, two-component emission decay was observed with lifetimes of 1 – 2 ns and 2 – 4 ns at a high ratio of TBP–ODA (>0.11).¹³

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