Significance of Hydrophilic Characters of Organic Dyes in Visible-Light Hydrogen Generation Based on TiO$_2$

Su-Hyun Lee,[†] Yiseul Park,[‡] Kyung-Ryang Wee,[†] Ho-Jin Son,[†] Dae Won Cho,[†] Chyongjin Pac,[†,*] Wonyong Choi,[‡] and Sang Ook Kang*,[†]

Department of Materials Chemistry, Sejong Campus, Korea University, Chung-Nam 339-700, South Korea, and School of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang, 790-784, South Korea

jjpac@korea.ac.kr; sangok@korea.ac.kr

ABSTRACT
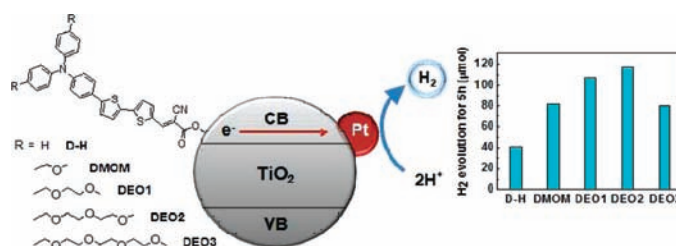
A series of dyes were synthesized to examine the roles of the hydrophilic characteristics of R in sensitized hydrogen generation by dye-grafted Pt/TiO$_2$ under visible light irradiation. The hydrogen-generation efficiencies and optimum amounts of the dyes grafted to Pt/TiO$_2$ were affected substantially by the hydrophilic and steric effects of R; moderately hydrophilic DEO1 and DEO2 showed higher sensitization activity at a lower loading than hydrophobic D-H.

Considerable attention has been paid to semiconductor TiO$_2$ in connection to the creation of clean energy,[1] typically hydrogen evolution from water[2] and electricity generation by solar cells under solar-light illumination.[3] Due to little visible-light absorption by TiO$_2$, dye modification has been used to make TiO$_2$ active to visible-light excitation, typically in dye-sensitized solar cells (DSSCs)[4] and in dye-sensitized H$_2$ generation using platinized TiO$_2$ particles (Pt/TiO$_2$).[5] Such modifications are usually performed by chemical bonding of a functional group (e.g., CO$_2$H[6] or PO$_3$H$_2$[7]) of dyes to the TiO$_2$ surface. While ruthenium(II) polypyridine complexes have been used for such modifications, organic dyes are also considered to be potentially attractive due to the availability of versatile functional molecules associated with tuning of the electronic and chemical properties. While DSSCs using organic dyes have been developed,[8] little

† Korea University.
‡ Pohang University of Science and Technology.
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systematic investigation has been carried out on the application of organic dyes to sensitized H_2 generation from water. In 1985, Shimidzu et al. reported that H_2 generation can be sensitized by xanthene dyes under visible-light irradiation using Pt-loaded metal-oxide particles and triethanolamine as a sacrificial electron donor.[9] In recent years, considerable improvements in H_2-generation efficiency have been achieved with similar reaction systems, in which Pt/TiO$_2$ or related solid catalysts are modified with organic dyes, particularly Eosin Y.[10] In general, neutral chromophoric cores of conventional organic dyes are intrinsically hydrophobic. Consequently, the poor water miscibility should give rise to complex features in the dye/TiO$_2$ interface with the water phase as well as in the conformation/aggregation behavior of the dyes adsorbed on the hydrophilic TiO$_2$ surface, which have critical effects on the electron-transfer and chemical processes involved in H_2 generation.

Scheme 1. Synthetic Routes to the Dyes **6R**
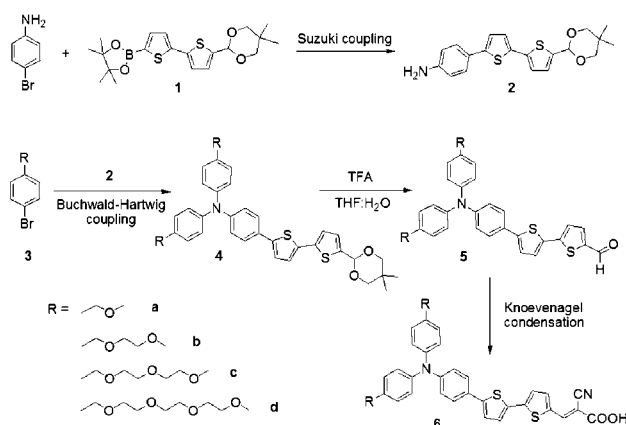
This study aims to explore the significance of hydrophilic and steric characteristics of organic dyes in sensitized H_2 generation based on Pt/TiO$_2$ catalysts using a series of (*E*)-3-[5-(4-(*p*,*p'*-bis(R-phenyl)amino)phenyl)-2,2'-bithiophen-2'-yl]-2-cyanoacrylic acid dyes, which are the hydrophobic parent dye (R = H, **D-H**), slightly hydrophilic **DMOM** (R = CH$_2$OCH$_3$,), and hydrophilic **DEO1**−**3** (R = CH$_2$−(OCH$_2$CH$_2$)$_n$−OCH$_3$, $n = 1$−3). It was found that Pt/TiO$_2$ particles modified with the dyes work as effective catalysts for visible-light-induced H_2 evolution from water

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with the efficiencies depending on the substituent R. Moderately hydrophilic **DEO1** and **DEO2** showed substantially higher sensitization activities at a lower loading than hydrophobic **D-H**, whereas intermediate behavior was observed in the cases of slightly hydrophilic **DMOM** and most hydrophilic **DEO3**.

Table 1. Photophysical Properties of the Dyes in THF

dye	λ_{abs}[a] (nm)	ε[b] (M^{-1} cm^{-1})	λ_F[c] (nm)	τ_F[d] (ns)	Φ_F[e]
D-H	433	27,360	552	1.18	0.23
DMOM	432	26,730	561	1.25	0.24
DEO1	433	31,580	559	1.26	0.22
DEO2	433	27,550	557	1.31	0.24
DEO3	432	35,460	557	1.19	0.21

[a] Absorption maxima. [b] Molar absorption coefficients. [c] Fluorescence maxima. [d] Fluorescence lifetimes. [e] Fluorescence quantum yield was measured using rhodamine B as a reference at rt.
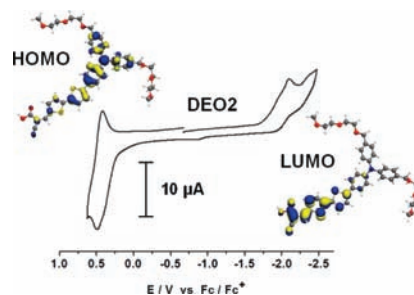
Figure 1. CV trace in THF using [*n*-Bu$_4$N]PF$_6$ (0.1 M) as a supporting electrolyte and Fc/Fc$^+$ reference and DFT-generated population densities of the HOMO and LUMO for **DEO2**.

Scheme 1 summarizes the synthetic routes for the dyes; the experimental details for the synthetic procedures and spectroscopic data for identification are given in the Supporting Information (SI). The dyes in tetrahydrofuran (THF) commonly reveal the visible absorption maxima at 432−433 nm and relatively strong fluorescence at 552−561 nm with lifetimes of 1.18−1.31 ns (Table 1). Cyclic voltammetry (CV) measurements for THF solutions of the dyes show clear one-electron oxidation/reduction peaks, as shown in Figure 1 for a typical CV trace of **DEO2**. The apparent half-wave oxidation and reduction potentials of the dyes are commonly +(0.46−0.49) V and −(2.06−2.08) V, respectively, vs the Fc/Fc+ reference (see Figure S4 in SI). From the CV data coupled with the longest absorption edge, the HOMO and LUMO levels of the dyes were estimated to be (5.26−5.29) eV and (2.78−2.82) eV below the vacuum level, respectively. DFT MO calculations of the dyes indicated that the HOMO and LUMO largely populate on the diphenylaminophenyl-2,2'-bithiophene donor and cyanoacrylic acid acceptor, respectively, as shown in Figure 1 for **DEO2** as a typical example. Therefore, the electronic properties of the dyes are essentially identical independent of the substituent R.

After Pt had been loaded on TiO_2 particles (Hombikat UV-100, primary particle size of 16 nm, BET surface area of 348 m^2/g) according to a published method,[11] the Pt/TiO_2/ Dye catalysts were obtained by adsorption of the dyes (0.5−10 μmol) on Pt/TiO_2 (0.1 g) in 1:1 MeCN:*t*-BuOH (10 mL) at rt. The dye adsorption on the Pt/TiO_2 particles was complete because the filtrates obtained after the adsorption treatment were transparent. Figure 2a shows diffuse reflectance spectra (DRS) of the Pt/TiO_2/**DEO2** catalyst, which are significantly broader than the solution spectrum but showed little dependence of the spectral shape on the amount of dye-adsorption. This spectral broadening might be attributable to charge transfer between the adsorbed dyes and TiO_2,[12] and/or to multiple reflections. In the case of Pt/TiO_2/ **D-H**, however, a further red shift in the DRS was observed (Figure 2b), suggesting that the hydrophobic dye molecules should more or less undergo molecular stacking on the hydrophilic TiO_2 surface, whereas the ethylene−oxide chains of **DEO2** might sterically hinder the dye-core stacking.
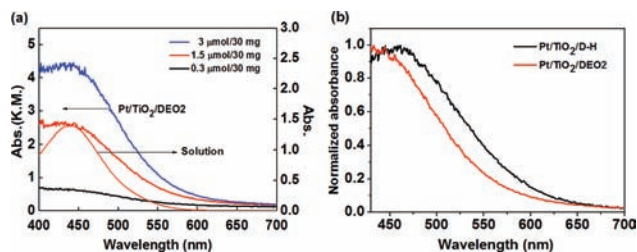

Figure 2. (a) DRS of Pt/TiO_2/**DEO2** and absorption spectrum of a THF solution. (b) DRS of Pt/TiO_2/**D-H** compared to that of Pt/TiO_2/**DEO2** (1.5 μmol dye/30 mg Pt/TiO_2).

Water suspensions containing the catalysts (30 mg/30 mL) and EDTA (10 mM) were adjusted at pH = 3, bubbled with an N_2 stream, and then irradiated at λ > 420 nm. The generated amounts of H_2 were determined by gas chromatography with $\leq$3 μmol error. Figure 3 shows temporal plots for the H_2 generation using the catalysts of 0.3 μmol dye/30 mg Pt/TiO_2. This clearly shows that the **DEO1** and **DEO2** catalysts bearing the hydrophilic ethylene−oxide substituents are ~3 times more active than the hydrophobic **D-H**. Moreover, even the slightly hydrophilic methoxymethyl groups in **DMOM** are significantly effective in enhancing the sensitization activity. Interestingly, the catalyst activity uniquely depends on the hydrophilic chain length such that **DEO1** and **DEO2** showed significantly higher catalyst activities than **DEO3** with the longest hydrophilic chain.

These observations clearly suggest that the hydrophilic chains of **DEO1** and **DEO2** are particularly effective in enhancing H_2 generation. In general, the H_2-generation efficiencies should be controlled by the following major processes; electron injection from the excited-state dyes into
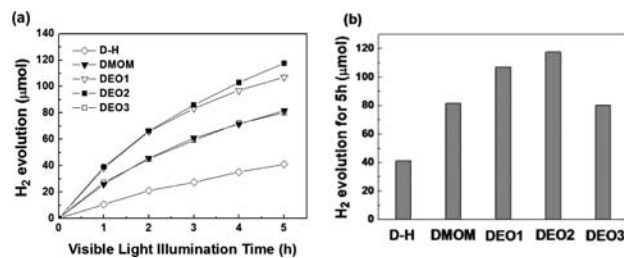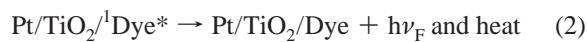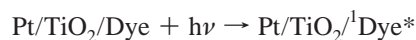
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Figure 3. (a) Temporal plots for H_2 generation by irradiation of water suspensions of the catalysts (0.3 μmol dye/30 mg Pt/TiO_2) at >420 nm and (b) the amounts of H_2 generated after 5 h irradiation; pH_i = 3 and $[EDTA]_i$ = 10 mM.

the conduction band of TiO_2 (process 1) in competition with the excited-state decay to the ground state (process 2), recombination between the injected electron and the dye radical cation (process 3), and the reduction of the dye radical cation by EDTA (process 4) that facilitates the collection of electrons injected at Pt sites to result in net H_2 generation (process 5).

$$Pt/TiO_2/Dye + h\nu \rightarrow Pt/TiO_2/{}^1Dye*$$

$$Pt/TiO_2/{}^1Dye* \rightarrow Pt/TiO_2(e^-)/Dye^{\bullet+} \quad (1)$$

$$Pt/TiO_2/{}^1Dye* \rightarrow Pt/TiO_2/Dye + h\nu_F \text{ and heat} \quad (2)$$

$$Pt/TiO_2(e^-)/Dye^{\bullet+} \rightarrow Pt/TiO_2/Dye \quad (3)$$

$$Pt/TiO_2(e^-)/Dye^{\bullet+}(+EDTA) \rightarrow Pt/TiO_2(e^-)/Dye \quad (4)$$

$$Pt/TiO_2(e^-)/Dye + H^+ \rightarrow Pt/TiO_2/Dye + 1/2H_2 \quad (5)$$

The dyes adsorbed on Pt/TiO_2 exhibited virtually no fluorescence. The fluorescence decay occurred in a time domain of the excitation laser pulse (~30 ps). The fluorescence quenching can be mainly attributed to the dominant occurrence of process 1 over process 2. Process 5 depends primarily on the electron mobility in TiO_2, electron-collection efficiency at the Pt sites, and H_2 formation rate on the Pt surface. These factors should be not affected significantly by the dye substituent unless the Pt sites are covered with dye molecules. Consequently, the observed effects of substituent R on the H_2-generation effciency should mainly arise from the competition between processes 3 and 4. However, process 3 should be essentially independent of the substituent R because the driving force for electron transfer between the dye-core radical cation and injected electron in TiO_2 are certainly identical for all the dyes.

Process 4 requires the diffusional approach of hydrophilic EDTA molecules to the dye radical cation at an effective distance. In this regard, it should be noted that the positive charge of the dye radical cation largely develops on the

diphenylaminophenyl moiety to which the substituents (R) attach. In the cases of **DEO1** and **DEO2**, the hydrophilic ethylene−oxide chains should make the dye surface miscible with the aqueous phase so that process 4 might be facilitated by approaching of EDTA molecules close to the radical-cation center. Such enhancement effects should be weaker, but not negligible, with the slightly hydrophilic methoxym-ethyl groups of **DMOM**. Another benefit of the hydrophilic chains might be due to possible hydrogen bonding of EDTA molecules with the ethylene-oxide chains. This is certainly favorable for process 4 to proceed. In contrast, the interface between hydrophobic **D-H** and the water phase should be substantially different, thus forming an unfavorable environment for electron transfer from hydrophilic EDTA to the hydrophobic dye radical cation. Moreover, the molecular stacking of **D-H** might open a rapid decay channel from the excited state, but this is less important for the hydrophilic dyes. However, in the case of **DEO3**, irrespective of the hydrophilic character, the long triglyme chains might steri-cally inhibit the approach of EDTA to the radical-cation core and/or cover the Pt sites.
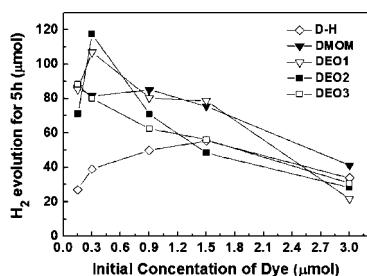

Figure 4. Dependences of the sensitized H_2 generation on the dye loading (μmol on 30 mg Pt/TiO$_2$). The experimental conditions are the same as those in Figure 3.

Another interesting observation is the complex dependence of the catalyst activity on the amounts of dye fixed to Pt/TiO$_2$ particles, as shown in Figure 4. The catalyst activity for **D-H** increases with increasing amount of dye to show a maximum at a dye amount of 1.5 μmol/30 mg Pt/TiO$_2$ and a slight decrease at 3 μmol/30 mg Pt/TiO$_2$. On the other hand, the **DMOM** catalyst exhibits a weak dependence of the activity on the dye loading at $\leq$1.5 μmol/30 mg Pt/TiO$_2$ but a relatively large drop at 3 μmol/30 mg Pt/TiO$_2$. In the cases of **DEO1** and **DEO2**, the H_2-generation efficiency reaches a maximum at a significantly lower dye loading (0.3 μmol/30 mg Pt/TiO$_2$) and decreased rapidly at higher amounts. In contrast, **DEO3** showed a continuous decrease in catalyst activity from the minimum dye amount (0.15 μmol/30 mg Pt/TiO$_2$).

In general, the fraction of incident light absorbed by the dyes increases with increasing dye loading to saturate at a certain level. However, as the dye loading is increased further, the penetration depth of incident light should decrease and limit the effective utilization of incident light by the whole reaction system. Moreover, the dye coverage over the Pt/TiO$_2$ surface should become high enough to have unfavorable effects on process 5 proceeding over the Pt site. At high levels of dye adsorption, stabilization of the dye radical cation can occur by charge delocalization over the closely packed dye molecules to retard process 4. Such counterbalancing effects would control the optimum dye loading for the maximum H_2-generation efficiency, for example, 1.5 μmol/30 mg Pt/TiO$_2$ for **D-H** and 0.9 μmol/30 mg Pt/TiO$_2$ for **DMOM**. In the cases of **DEO1** and **DEO2**, the ethylene-oxide chains are intrinsically capable of enhancing H_2 generation due to their hydrophilic nature, but can form a dense layer at high dye loadings to impart steric effects on processes 4 and 5. The hydrophilic effect should prevail at lower dye loadings to allow rapid increases in H_2 generation with increasing dye loading from 0.15 μmol to 0.3 μmol, whereas the steric effects might be increasingly dominated at higher dye loadings. On the other hand, the longer triglyme chains of **DEO3** form a dense layer, even at lower concentrations, giving greater steric effects that might cancel the hydrophilic effect at $\geq$0.15 μmol.

In summary, a series of dyes (hydrophobic **D-H**, slightly hydrophilic **DMOM**, and hydrophilic **DEO1**-**DEO3**) were synthesized and applied to sensitized hydrogen generation based on Pt/TiO$_2$/Dye catalysts. The moderately hydrophilic **DEO1** and **DEO2** catalysts showed substantially higher H_2-generation efficiencies at a low dye adsorption than the hydrophobic **D-H** catalyst, whereas either slightly hydrophilic **DMOM** or **DEO3** with the longest ethylene-oxide chains showed intermediate sensitization ability. The optimum grafted amounts of the dyes (μmol/30 mg Pt/TiO$_2$) for maximizing H_2 generation were considerably different: $\leq$0.15 for **DEO3**, $\sim$0.3 for **DEO1** and **DEO2**, 0.15−0.9 for **DMOM**, and $\sim$1.5 for **D-H**. The dependence of the catalyst activity on the substituent was interpreted in terms of the intrinsic enhancement effects of the hydrophilic character canceled by the steric and/or coverage effects. These results strongly suggest that the optimization of hydrophilic character coupled with the minimization of steric effects is a key issue associated with the general guideline for designing organic dyes with high sensitization capability in H_2 generation based on TiO$_2$ and related semiconductors.

Supporting Information Available: Experimental details and characterization data (^{1}H, ^{13}C NMR), CVs, and DFT-calculation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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