

Effect of the Anchoring Group in Ru–Bipyridyl Sensitizers on the Photoelectrochemical Behavior of Dye-Sensitized TiO₂ Electrodes: Carboxylate versus Phosphonate Linkages

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The effects of the number of anchoring groups (carboxylate vs phosphonate) in Ru–bipyridyl complexes on their binding to TiO₂ surface and the photoelectrochemical performance of the sensitized TiO₂ electrodes were systematically investigated. Six derivatives of Ru–bipyridyl complexes having di-, tetra-, or hexacarboxylate (C2, C4, and C6) and di-, tetra-, or hexaphosphonate (P2, P4, and P6) as the anchoring group were synthesized. The properties and efficiencies of C- and P-complexes as a sensitizer depended on the number of anchoring groups in very different ways. Although C4 exhibited the lowest visible light absorption, C4–TiO₂ electrode showed the best cell performance and stability among C–TiO₂ electrodes. However, P6, which has the highest visible light absorption, was more efficient than P2 and P4 as a sensitizer of TiO₂. The surface binding (strength and stability) of C-complexes on TiO₂ is highly influenced by the number of carboxylate groups and is the most decisive factor in controlling the sensitization efficiency. A phosphonate anchor, however, can provide a stronger chemical linkage to TiO₂ surface, and the overall sensitization performance was less influenced by the adsorption capability of P-complexes. The apparent effect of the anchoring group number on the P-complex sensitization seems to be mainly related with the visible light absorption efficiency of each P-complex.

Introduction

For the past decade, dye-sensitized TiO₂ solar cells (DSSCs) have been extensively studied as a novel solar-to-electricity conversion system.^{1–4} A DSSC typically consists of a dye-coated porous TiO₂ electrode, a Pt-coated counter electrode, and a redox couple in nonaqueous electrolyte. Each component affects the overall energy conversion efficiency, but one of the most critical factors is related to the role of the dye. The ideal dye requires not only optimal optical properties for visible light absorption⁴ but also a stable interfacial electronic coupling with TiO₂.^{1,2,4} The electronic coupling through a covalent linkage between dyes and TiO₂ is significantly influenced by various physicochemical properties of dyes. It includes the type of ligand^{5,6} and anchoring group of the dye,^{7,8} the bridging distance between metal center and TiO₂,⁹ the surface coverage of the dye,¹⁰ and the type of central metal.^{11,12} Other properties of TiO₂ such as the crystallinity (anatase vs rutile)¹³ and its surface characteristics^{14,15} are also known to play a very important role in the overall energy conversion processes.

Typical anchoring groups for most metal-oxide-based semiconductors include phosphonate,^{2,4,6–8,16–19} carboxylate,^{2,4,5,7–14,20} silane (SiX₃), ether, acetylacetonate, salicylate,⁴ and so on. One of the most popular anchoring groups is the carboxylate (–COO[–]), and it has been known to bind to the TiO₂ surface mainly through the bidentate bridging mode;^{4,8,21–23} at least two

carboxylate groups are necessary for effective binding to the TiO₂ surface.^{8,10,14,21–25} N3, the most popular dye in DSSCs, is known to use only two carboxylate groups out of four, and which carboxylate groups are attached to TiO₂ surface has been discussed. For example, disagreeing views that the two carboxylates come from the different bipyridyl ligands^{14,21} or from the same bipyridyl ligand²⁶ have been reported. The dye anchoring in DSSCs is critical in achieving higher cell efficiencies, and a few previous studies have recently investigated the effects of the anchoring group in ruthenium sensitizers on the overall cell efficiency. Hara et al. observed that a Ru–phenanthroline complex with monocarboxylate was much less efficient than that with di- or tricarboxylates in the DSSC performance and concluded that two anchoring carboxylates are necessary for large and bulky complexes such as ruthenium polypyridyls.^{24,25} The phosphonate group instead of the carboxylate has been frequently used to enhance the surface binding strength. The surface binding constant of a Ru–bipyridyl complex with two phosphonate groups is approximately an order of magnitude higher than that with the two carboxylate groups.⁷ The terpyridyl ligand with one phosphonate group in a Ru complex exhibited much stronger adsorption on TiO₂ than the bipyridyl ligands with four carboxylate groups in N3.¹⁶

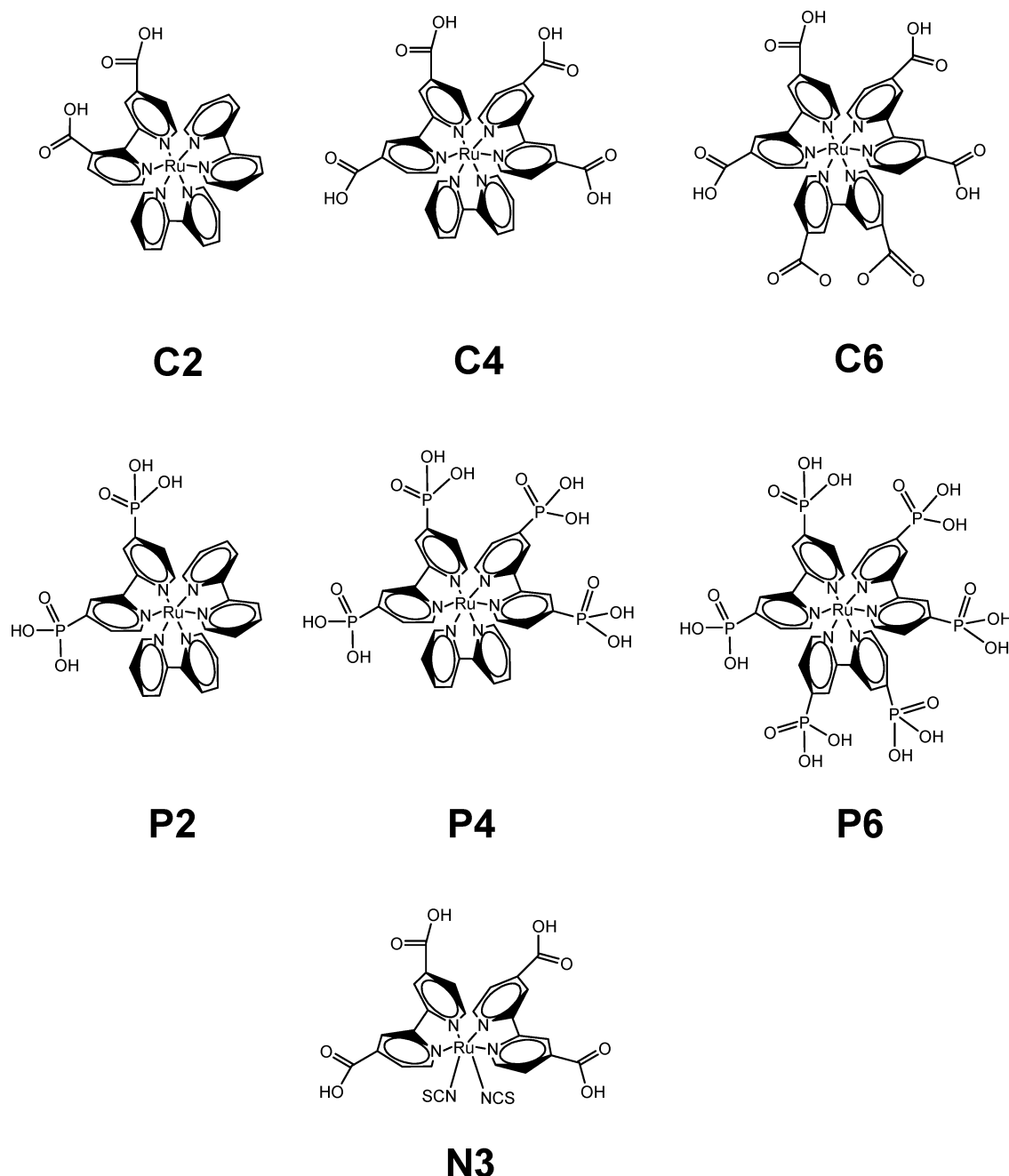
In this work, we have synthesized two different classes of the ruthenium bipyridyl derivatives to systematically study their effects on the overall cell efficiency: one with di-, tetra-, and hexacarboxylate (C2, C4, and C6, respectively) and the other with di-, tetra-, and hexaphosphonate (P2, P4, and P6, respectively) as the anchoring group (Chart 1). Among them, we have found that the C4- and P6-sensitized TiO₂ photoelectrode showed the best cell performance (C4 > C2 > C6 and P6 > P2 > P4). In general, the P-complexes showed higher photo-

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CHART 1: Structures of the Ruthenium Complexes Used in This Study^a

^a Note that C4 and P4 have the same symmetry as N3.

conversion efficiencies than the C-complexes, while the cell efficiency is highly influenced by the kind and the number of the anchoring group. The relation between the anchoring-group-dependent properties and the DSSC performance is discussed.

Experimental Section

Synthesis of Ruthenium Complexes Listed in Chart 1.

C2: $Ru(bpy)_2(dcbpy)(PF_6)_2$ [bpy = 2,2'-bipyridine; $dcbpy$ = 4,4'-dicarboxy-2,2'-bipyridine]. C2 was prepared by following the literature method.²⁷ The yield was ca. 78%.

C4: $Ru(bpy)(dcbpy)_2(PF_6)_2$. $Ru(dcbpy)_2Cl_2$ was prepared as described by Nazeeruddin et al.,^{28a} and then a bpy ligand was attached to the complex according to the method reported by Will et al.^{28b} The product was purified by recrystallization from a mixture of $CHCl_3$ and methanol (1:3). After removal of the solvent, 6 N HCl (20 mL) was added to the product, and the

resulting mixture was stirred for 4 h and concentrated by using a rotary evaporator. At the end of the reaction aqueous ammonium hexafluorophosphate was added, and the solution was refrigerated overnight. The precipitate was filtered and dried in a vacuum. The final recovery was 0.82 g (60%). ¹H NMR ($D_2O/NaOD$, δ): 7.34 (m, 2H), 7.56 (dd, 2H), 7.65 (dd, 2H), 7.78 (m, 4H), 7.94 (m, 2H), 8.33 (s, 2H), 8.41 (dd, 2H), 8.76 (s, 4H).

C6 and P2: $Ru(dcbpy)_3Cl_2$ and $Ru(bpy)_2(dpbbpy)Br_2$ [$dpbbpy$ = 4,4'-diphosphonate-2,2'-bipyridine]. These were prepared according to our previous method.⁸

P4: $Ru(bpy)(dpbpy)_2(PF_6)_2$. First, *cis*-dichlorobis(bis(ethyl ester phosphonate)-2,2'-bipyridine)ruthenium was synthesized as an intermediate for P4. 4,4'-Diethyl ester phosphonate-2,2'-bipyridine (300 mg, 0.7 mmol) and $RuCl_3(H_2O)_3$ (0.097 g, 0.47 mmol) were dissolved in 20 mL DMF under argon. The mixture

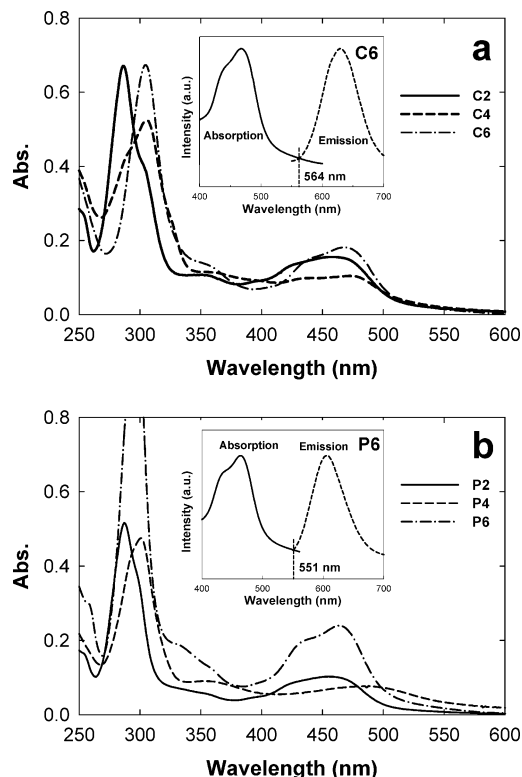


Figure 1. UV-vis absorption spectra of (a) C-complexes and (b) P-complexes. [Ru complex] = 10 μ M in water at pH 3. The insets compare the normalized absorption and emission bands of MLCT for C6 and P6, respectively.

was heated at 120 $^{\circ}$ C overnight and cooled to room temperature. Then, dichloromethane was added for precipitation, and the precipitate was filtered, washed with dichloromethane, and then dried in a vacuum. The yield of the intermediate was ca. 53%. For the preparation of P4, the product (206 mg, 0.2 mmol) and bipyridine (47 mg, 0.3 mmol) were dissolved in methanol (15 mL) in a round-bottomed flask, and then the solution was purged with argon. The flask was covered with aluminum foil and heated at reflux for overnight in the dark. After the flask cooled to room temperature, the solvent was evaporated completely, 6 N HCl (15 mL) was added, and the mixture was refluxed for 18 h. Then, the solvent was evaporated on a rotary evaporator. At the end of the reaction, aqueous ammonium hexafluorophosphate was added, and the solution was refrigerated overnight. The precipitate was filtered and dried in a vacuum (yield 15%). ^1H NMR ($\text{D}_2\text{O}/\text{NaOD}$, δ): 7.45 (m, 5H), 7.94 (m, 10H), 8.56 (m, 5H).

P6: $\text{Ru}(\text{dppbpy})_3(\text{PF}_6)_2$. 4,4'-Diethyl ester phosphonate-2,2'-bipyridine (300 mg, 0.7 mmol) and $\text{RuCl}_3(\text{H}_2\text{O})_3$ (0.052 g, 0.25 mmol) were dissolved in 20 mL of DMF under argon. The following steps were identical to those of P4. The yield was ca. 40%. ^1H NMR ($\text{D}_2\text{O}/\text{NaOD}$, δ): 7.45 (m, 6H), 7.69 (s, 6H), 8.57 (dd, 6H).

Characterizations of the Ruthenium Sensitizers and the Sensitized TiO_2 Particles. The solubilities and the degree of adsorption onto TiO_2 of six sensitizers were different in water and acetonitrile (MeCN). In general, all of them were easily dissolved in water, but only the five sensitizers (except C2) could be adsorbed on TiO_2 in an aqueous environment. C2 was hardly adsorbed on TiO_2 in water (Figure 2a) but could be adsorbed in MeCN. C4, C6, P4, and P6 were not dissolved in MeCN at all (Table 1). We have used water as the main solvent for dye adsorption on TiO_2 electrodes (except for C2 that was dissolved in MeCN) because it was the only solvent in which all six Ru

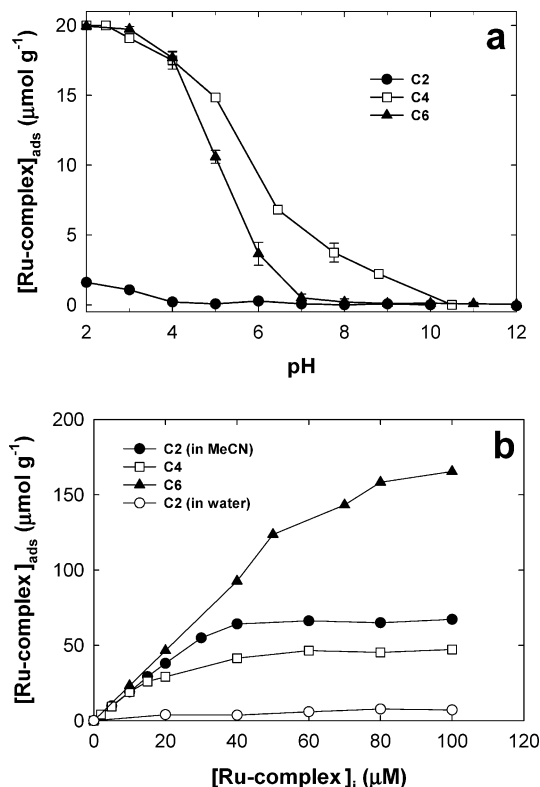


Figure 2. (a) pH-dependent adsorption and (b) adsorption isotherms of C-complexes. The adsorption of C2 on TiO_2 is compared between water and MeCN solvent. $[\text{TiO}_2] = 0.5 \text{ g/L}$; $[\text{Ru complex}]_i = 10 \mu\text{M}$ in part a; $\text{pH}_i = 3.0$ in part b.

complexes could be dissolved. Although the dye-adsorbed TiO_2 electrodes were prepared in water, their photoelectrochemical cell performances were measured in MeCN containing I^-/I_2 electrolytes (vide infra).

A UV-vis spectrophotometer (Agilent 8453) was used to quantify the concentration of the sensitizers through measuring the visible light absorption, and a spectrofluorometer (Shimadzu RF-5301) was used to obtain the emission spectra of the Ru complexes. The amount of the adsorption of each sensitizer on TiO_2 was estimated by comparison of the concentrations before and after the adsorption of the dye.

The surface charges of TiO_2 particles in water were measured at pH 3 using an electrophoretic light scattering spectrophotometer (ELS 8000, Otsuka) before and after the adsorption of the dyes.

Ground-state redox potentials of the Ru complexes were determined with a standard three-electrode setup by analyzing cyclic voltammograms and/or differential pulse voltammograms collected with the potentiostat/galvanostat (EG&G, 263A). The working, counter, and reference electrodes were a Pt disk, a Pt plate, and Ag/AgCl, respectively, and the supporting electrolyte was 1.0 M LiClO_4 in water.

Photoelectrochemical Measurements. A three-electrode-based small volume solar cell with Pt gauze and Pt wire as a counter and a reference electrode, respectively, has been designed to measure photoelectrochemical responses. The distance between the working and the counter electrode was 5 mm. A 3.5 mL solution of the redox electrolyte consisting of 0.5 M LiI, 0.04 M I_2 , 0.02 M pyridine, and 0.02 M pyridinium triflate in MeCN was injected into a homemade Teflon cell without headspace.

Degussa P25, a mixture of anatase and rutile (8:2) with surface area of 50 m^2/g , was used to construct a mesoporous

TABLE 1: Spectroscopic and Electrochemical Properties of the Ru Complexes

Ru complex	λ_{max} (nm) ^a		ϵ_{MLCT} (M ⁻¹ cm ⁻¹)	solubility in		$\text{pK}_{\text{a}}^{18,28}$	$E_{\text{H-L}}^{\text{c}}$ (eV)	E^{d} (V _{NHE})	$E^{*\text{e}}$ (V _{NHE})
	LC	MLCT		water	MeCN				
Ru ^{II} (bpy) ₃	285	452	14 400	○	×		2.12	1.26	-0.86
C2	286	457	15 500	○	○	1.75 (first-c, 1H) 2.85 (second-c, 1H)	2.16	1.31	-0.85
C4	306	472	10 400	○	×	1.80 (first-dc, 2Hs) 2.50 (second-dc, 2Hs)	2.14	1.40	-0.75
C6	305	467	21 200	○	×	1.70 (second-dc, 2Hs) 2.20 (third-dc, 2Hs)	2.20	1.39	-0.81
P2	287	455	10 200	○	△ ^f	1.0 (first-p, second H) 12.0 (second-p, 2Hs)	2.21	1.26	-0.95
P4	301	488	7740	○	×		2.19	1.40	-0.79
P6	297	464	23 900	○	×		2.25	1.27	-0.98

^a Measured in water. ^b Referring to the position and number of dissociable protons corresponding to pK_{a} ; c, dc, and p indicate carboxylate, dicarboxylate, and phosphonate group, respectively, and 2Hs means a concerted two-proton dissociation. Second H refers to the second proton dissociation: $(\text{bpy})_2\text{Ru}(\text{bpy})(\text{PO}_3\text{H}_2)(\text{PO}_3\text{H})^+ \rightarrow (\text{bpy})_2\text{Ru}(\text{bpy})(\text{PO}_3\text{H}_2)(\text{PO}_3) + \text{H}^+$. See refs 18 and 28 for more information. ^c HOMO–LUMO gap. ^d Ground-state reduction potential ($\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$). The determined potentials were estimated from the irreversible oxidation ($\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$). ^e Excited-state reduction potential ($\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}*}$), which was estimated from $E^* = E - E_{\text{H-L}}/q$. ^f Slightly soluble.

TiO₂ photoanode. TiO₂ paste was prepared by adding poly(ethylene glycol) (PEG, Aldrich, molecular weight 20 kDa) in an ethanol/water mixture (1:2 v/v) and spreading it out onto a fluorine-doped SnO₂ glass (FTO, Pilkington, 1.65 cm²) plate using a doctor-blade method. After the TiO₂-coated electrode was calcined at 450 °C for 30 min, it was cooled to room temperature and immediately followed by the immersion into a solution of each Ru complex over 12 h for adsorption of sensitizers. The dye solutions were typically prepared in water at pH 3 except for C2, which was dissolved in MeCN. The electrode was dried at 80 °C for 2 h under a N₂ gas stream.

The effective area of the dye-coated TiO₂ electrode in contact with the electrolyte was 0.65 cm². Light from a 450 W Xe arc lamp (Oriol) was passed through a cutoff filter ($\lambda > 420$ nm) and focused on the backside of the TiO₂ electrode. The intensity of the visible light ($420 < \lambda < 645$ nm, the wavelength range that the sensitizers absorb) was measured to be around 74 mW/cm² using a power meter (Newport 1830) equipped with a silicon diode detector and cutoff filters ($\lambda > 420$ and 645 nm). The estimated intensity was obtained by subtracting the measured light intensity of $\lambda > 645$ nm from that of $\lambda > 420$ nm.

Results

Spectroscopic and Electrochemical Properties of the Ru Complexes. Figure 1 compares the UV–vis absorption spectra of C- and P-complexes (10 μM) in water at pH 3. The absorption spectra of these complexes show an intense ligand-centered (LC) $\pi \rightarrow \pi^*$ transition band around 300 nm and a broad metal-to-ligand charge transfer (MLCT) ($d \rightarrow \pi^*$) band in the visible region around 460 nm.⁸ Table 1 lists the absorption band positions and the molar absorptivities of each complex, which are generally consistent with the values found in the literature.^{17,18,22,29,30} C4 and P4 are notable in that they showed the most red-shifted absorption (λ_{max} , C4 > C6 > C2 and P4 > P6 > P2) while their LC and MLCT absorptivities (ϵ_{max} , C6 > C2 > C4 and P6 > P2 > P4) were the smallest. Table 1 also summarizes the ground-state and excited-state reduction potentials ($E(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}})$ and $E^*(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}})$) of the six complexes along with those of $\text{Ru}(\text{bpy})_3^{2+}$. The highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap energy ($E_{\text{H-L}}$) and the ground-state reduction potentials (E) of the complexes were experimentally measured while the excited-state reduction potentials (E^*) were estimated from the equation $E^* = E - E_{\text{H-L}}/q$ (Table 1).²² $E_{\text{H-L}}$ was estimated by

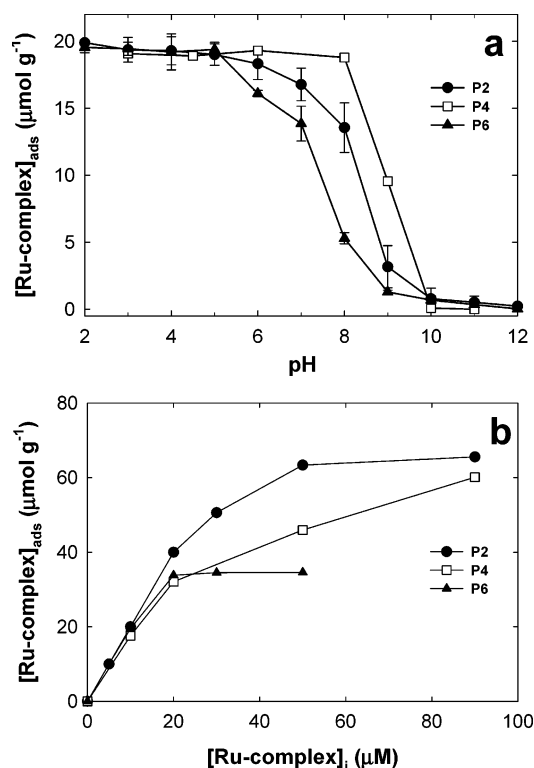


Figure 3. (a) pH-dependent adsorption and (b) adsorption isotherms of P-complexes. $[\text{TiO}_2] = 0.5$ g/L; $[\text{Ru complex}]_i = 10$ μM in part a; $\text{pH}_i = 3.0$ in part b.

determining the intersection point between the normalized absorption and emission spectrum of each Ru complex (see the inset of Figure 1). Both C4 and P4 exhibit more positive E and E^* than the others.

Adsorption. Figure 2 compares the adsorption behaviors among C-complexes in aqueous TiO₂ suspension. C4 and C6 are effectively adsorbed at $\text{pH} < 6$ whereas C2 hardly adsorbs on TiO₂ in aqueous environment (Figure 2a). However, C2 could be adsorbed on TiO₂ by changing the solvent from water to MeCN (Figure 2b). It was reported that the binding constant of C6 on TiO₂ in ethanol is around 4 times higher than that of C2.²² In this study, the maximum adsorption amount of C6 is far larger than that of C2 (Figure 2b).

All P-complexes were effectively adsorbed on TiO₂ over a wider range of pH than the C-complexes (Figure 3). It is well-known that the phosphonate group in a Ru complex can provide

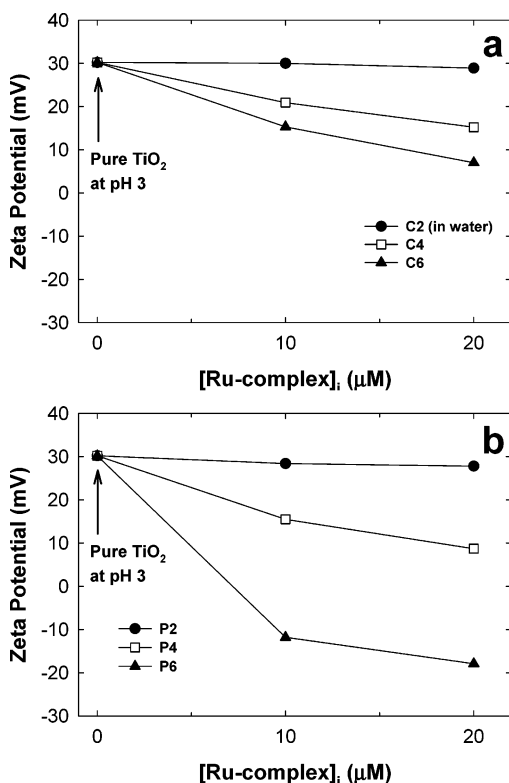


Figure 4. Effects of the Ru complex adsorption on the zeta potentials of the TiO₂ surface. (a) C-complexes and (b) P-complexes. [TiO₂] = 0.5 g/L; pH_i = 3.0.

a strong chemical attachment due to a high oxophilicity to Lewis acid metals such as Ti(IV), Zr(IV), or Sn(IV).^{6,7} As for the binding strength, P2 has been reported to have a surface binding constant that is 6 times as large as C2 in MeOH (1.3×10^5 vs 2.2×10^4 M⁻¹),⁷ which is consistent with this study. P4 showed the widest pH range of effective adsorption among the P-complexes such as C4 in the C-complexes. For both C- and P-complexes, the pH range for adsorption is the widest with four anchoring groups.

The adsorption of the complexes should change the surface charge of TiO₂. According to the electrostatic interaction model, the adsorption of anionic sensitizers should mask the positive surface charge on TiO₂ ($\equiv\text{Ti}-\text{OH}_2^+$) and therefore shifts the net surface charge to the negative direction. At pH 3, the surface charge of TiO₂ (~ 30 mV) progressively shifts toward the negative side with the increasing concentration of the C-complexes and also with the increasing number of anchoring groups (Figure 4a). A similar trend was observed for P-complexes (Figure 4b). The adsorption of P6 induces the largest change with even reversing the sign of the surface charge. It is interesting to note that both C2 and P2 have no effect on the surface charge. Because C2 hardly adsorbs on TiO₂, it is taken for granted that C2 induces no change in the surface charge. In contrast, P2 adsorbs quantitatively on TiO₂ but does not influence the surface charge, either.

Photoelectrochemical Responses of the Sensitized TiO₂ Electrode. Figure 5 shows the photoelectrochemical behaviors of the TiO₂ electrodes sensitized with C-complexes (C-TiO₂) under visible light ($\lambda > 420$ nm) irradiation. Under the identical surface concentration of the sensitizer (ca. 29 nmol/cm² based on the geometric area of the photoelectrode), C4-TiO₂ exhibited the best cell performance despite the lowest ϵ_{MLCT} value of C4. C2-TiO₂ (prepared in MeCN) was more efficient than C6-TiO₂. A similar trend was observed under the condition of

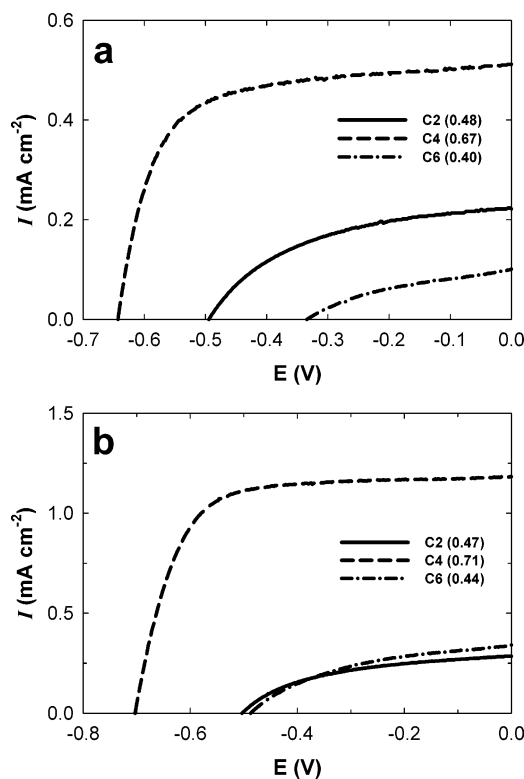


Figure 5. Photoelectrochemical *I*-*V* curves of C-TiO₂ electrodes (a) at an identical surface concentration (ca. 29 nmol/cm²) and (b) at saturated surface concentrations of C-complexes (ca. 41, 43, and 116 nmol/cm² for C2, C4, and C6, respectively). The numbers in parentheses refer to the fill factor. Note that the adsorption of C2 onto TiO₂ electrode was carried out in MeCN while the others were prepared in water. All cells were based on MeCN solvent.

saturated dye adsorption (Figure 5b). In both cases (Figures 5a and 5b), C4-TiO₂ had a fill factor of 70% or so and showed a stable photoelectrochemical performance over 11 h (Figure 6). The cell performances of the other two (C2-TiO₂ and C6-TiO₂) deteriorated instantly after the illumination. However, the TiO₂ electrodes sensitized with P-complexes (P-TiO₂) showed markedly different behaviors when compared to the C-TiO₂ electrodes. P6-TiO₂ was the most efficient (Figure 7) and stable (Figure 8) under both conditions (the identical surface coverage and the saturated coverage of dyes). P4-TiO₂ showed surprisingly poor performance. P2-TiO₂ exhibited a moderate activity and was as stable as P6-TiO₂. It seems that the stability of P-complexes is less influenced by the number of phosphonate groups unlike the case of C-complexes. The order of the overall cell performance among P-TiO₂ electrodes (P6 > P2 \gg P4) follows the order of the visible light absorptivity (ϵ_{MLCT}) whereas that of C-TiO₂ electrodes (C4 > C2 > C6) contradicts the order of ϵ_{MLCT} . In general, P-TiO₂ electrodes exhibited higher efficiencies than the corresponding C-TiO₂ electrodes. This agrees with our previous observation that the visible light photocatalytic reactivity of P2-TiO₂ is consistently higher than C6-TiO₂ in aqueous suspensions.⁸ However, both P2-TiO₂ and C6-TiO₂ as photocatalysts were not stable enough in aquatic environments unlike the present case of a DSSC application. Incidentally, the cell efficiencies obtained in this work were all very low (listed in Table 2) because the visible light absorption by all the sensitizers used is much lower than that of N3 and the cell geometry was not optimized at all. The primary purpose of this work is to compare the anchoring group effects in the C- and P-complex sensitization, not to achieve higher efficiencies.

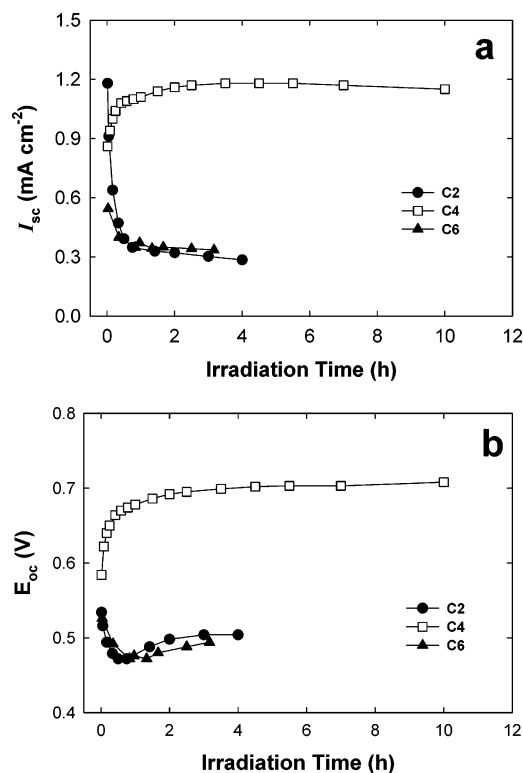


Figure 6. Time profiles of (a) I_{sc} and (b) V_{oc} with visible-light-irradiated C-TiO₂ electrodes at saturated surface concentrations.

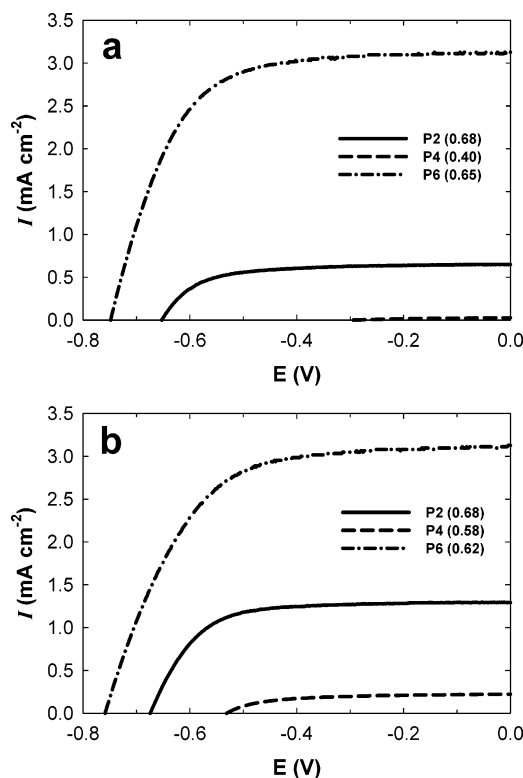


Figure 7. Photoelectrochemical I - V curves of P-TiO₂ electrodes (a) at an identical surface concentration (ca. 29 nmol/cm²) and (b) at saturated surface concentrations of P-complexes (ca. 45, 41, and 38 nmol/cm² for P2, P4, and P6, respectively). The numbers in parentheses refer to the fill factor.

Discussion

Binding of C-Complexes onto the TiO₂ Surface. It is known that two carboxylate groups are necessary for the stable adsorption of Ru-bipyridyl-based dyes on the TiO₂

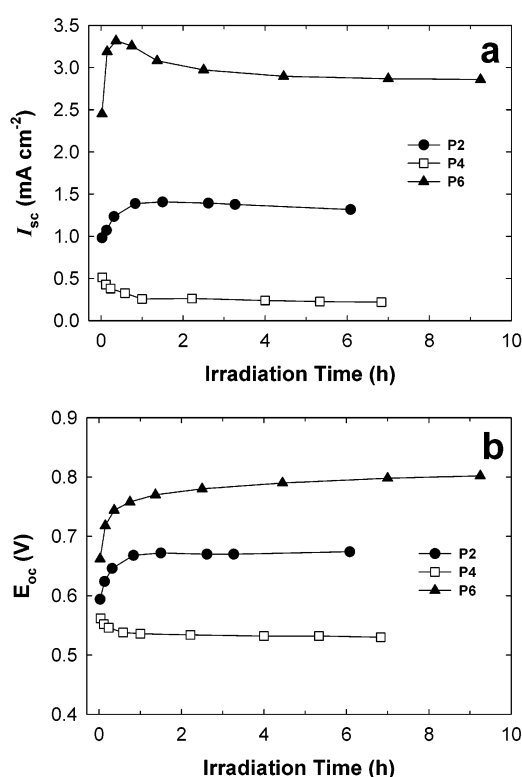


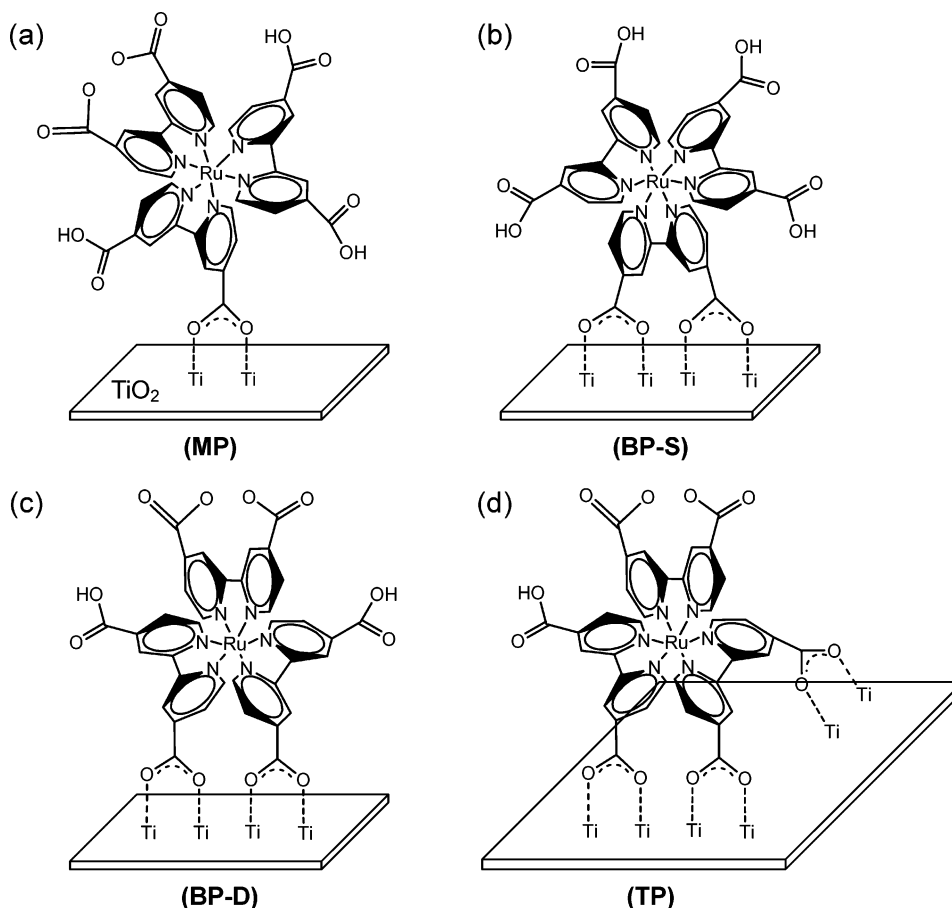
Figure 8. Time profiles of (a) I_{sc} and (b) V_{oc} of visible-light-irradiated P-TiO₂ electrodes at saturated surface concentrations.

TABLE 2: Photoelectrochemical Performances of the Sensitized TiO₂ Electrodes under Visible Light Irradiation

Ru complex	saturated surface coverage (nmol/cm ²)	V_{oc} (V)	I_{sc} (mA/cm ²)	fill factor	cell efficiency (%) ^a
C2	41	0.51	0.30	0.47	0.1
C4	43	0.71	1.18	0.71	0.8
C6	116	0.49	0.34	0.44	0.1
P2	45	0.67	1.36	0.68	0.8
P4	41	0.53	0.22	0.58	0.09
P6	38	0.80	2.87	0.62	1.9

^a Measured on the basis of the incident light (420–645 nm) intensity of 74 mW/cm².

surface.^{8,10,14,21–25} If we assume that the anchoring bond formation of C-complexes needs two carboxylate groups that come from different bipyridyl ligands as in N3,^{14,21} then C2 does not meet the requirement. This may explain the inefficiency of C2 adsorption in water, but not the fact that C2 can be adsorbed on TiO₂ in MeCN. In general, the sensitizer adsorption on TiO₂ should be driven by both surface-anchoring bond formation and electrostatic force. The latter can be sensitively dependent on the kind of solvent. C-complexes in water can be deprotonated, and the overall charge of the complex depends on the degree of deprotonation. All pK_a values of carboxylic acid groups in Ru complexes are reported to be less than 3 (Table 1), and the point of zero zeta potential (PZZP) of TiO₂ is around pH 6.³¹ Thus, the electrostatic attraction between the deprotonated carboxylate groups (–COO[–]) and the positively charged TiO₂ surface (mainly due to the presence of ≡Ti–OH₂⁺) prevails at pH < 6, and the adsorption of C4 and C6 (present primarily as anions) is favored. At basic pH where the surface charge of TiO₂ is negative, the adsorption of sensitizers (anions) is inhibited. This is fully consistent with the pH-dependent adsorption behavior shown in Figure 2a. In contrast, C2 cannot be present as anions, and the fully deprotonated C2

CHART 2: Simplified Binding Modes of C6 and C4 Complexes on TiO₂ Surfaces^a

^a It is assumed that all carboxylate groups are anchored onto the surface through a bidentate coordination: (a) monopod binding mode (MP); (b) bipod binding mode using two carboxylic groups coming from the same bipyridyl ligand (BP-S); (c) bipod binding mode using two carboxylic groups coming from different bipyridyl ligands (BP-D); (d) tripod binding mode (TP).

in water carries a net zero charge, and therefore the adsorption of C2 is negligible due to little electrostatic attraction between TiO₂ and C2. However, C2 in MeCN is much less likely to be deprotonated, and the surface charge on TiO₂ is not well developed in MeCN. Therefore, the electrostatic interaction is unimportant in MeCN, and the chemical bond formation should be the main mechanism for the sensitizer adsorption in the organic solvent. In an aquatic environment, the electrostatic attraction between TiO₂ and dyes can be considered as the dominant driving force for the adsorption of C-complexes. In addition, the surface chemical bond formation should not be much favored in water because the carboxylate linkage is intrinsically vulnerable to hydrolytic cleavage.

Herein, we consider the possible configurations of the binding mode in the C6/TiO₂ system as illustrated in Chart 2. It has been reported that two carboxylate groups originating from the neighboring bipyridyl ligands (BP-D; Chart 2c) are used for adsorption onto the TiO₂ surface^{14,21,22} and the binding with two carboxylate groups from the same bipyridyl ligand (BP-S; Chart 2b) is less favorable. The observed binding of C2 on TiO₂ in MeCN is expected to occur through either MP or BP-S mode, which is expected to be weaker than the BP-D mode. It has been previously proposed that N3 is adsorbed to the TiO₂ surface via a two-step mechanism, initial weak binding with one carboxylate group and the subsequent strong binding with two or more carboxylate groups.¹⁰ C2 binding in MeCN may have similar characteristics with the initial weak binding mode of N3. The weaker nature of C2 binding on TiO₂ has been consistently observed in previous desorption studies in various

solvent conditions.^{7,22} We also observed in this study that C2 desorbed more rapidly than C4 and C6 during photoelectrochemical tests, which reveals the weaker nature of C2 binding on TiO₂. Another mode of binding with three carboxylate groups (TP; Chart 2d) is also probable for C4 and C6,³² but we do not have any experimental evidence that can support or reject the presence of this binding mode.

The surface concentration of each sensitizer under saturation conditions is significantly different depending on the number of carboxylate groups. It reaches up to 170 $\mu\text{mol/g}$ for C6 while it was ca. 60 and 50 $\mu\text{mol/g}$ for C2 (in MeCN) and C4, respectively. For C2 in water, it was less than 10 $\mu\text{mol/g}$. The maximal sensitizer adsorption at a monolayer coverage for the bipod binding mode (Charts 2b and 2c) is roughly estimated to be 60 $\mu\text{mol/g}$ on the basis of a simple calculation and assumption that the amount of the surface hydroxyl groups present on P25 TiO₂ is ca. 250 $\mu\text{mol/g}$ ³³ and that four hydroxyl groups are to be consumed for the adsorption of each sensitizer molecule.^{14,21} The surface concentration of the C-complexes at a monolayer coverage should be close to this value, as observed for C2 and C4. However, the continuously rising uptake of C6 on TiO₂ with little sign of saturation suggests the formation of aggregates of C6 on TiO₂, which is (possibly) caused by the hydrogen bond formation between the dangling carboxylic acid groups in C6. Specifically, it seems that the two vertically oriented carboxylic acid groups in C6 attached onto TiO₂ are responsible for the aggregation. C4/TiO₂ that has fewer dangling carboxylic acid groups than C6/TiO₂ does not show any notable indication of the aggregation. (Figure 2b). The agglomerating tendency of

C6 was also observed in an aqueous solution of C6 in the absence of TiO_2 . Aqueous C6 flocculated and settled down at pH 3 after a few days in the dark whereas C2 and C4 remained relatively more stable at the same condition.

Binding of P-Complexes onto the TiO_2 Surface. The phosphonate anchoring groups are generally known to offer a very stable binding on TiO_2 over a wide pH range, and therefore they often have been employed in the studies of the pH-dependent electron-transfer dynamics between Ru complexes and TiO_2 .¹⁹ This study also shows that the P-complexes have a wider pH range for adsorption on TiO_2 than the structurally corresponding C-complexes. A stronger adsorption of the sensitizer is surely a necessary condition for the stable and efficient performance of a DSSC. The overall trends in the adsorption behaviors of P-complexes are not parallel with those of C-complexes. Adsorption of P2 on TiO_2 is highly efficient up to pH 8, whereas C2 hardly adsorbed over the whole pH region. P4 has the widest pH range for the adsorption on TiO_2 . The surface concentrations of all P-complexes at the saturation condition are not much beyond the monolayer coverage ($\sim 60 \mu\text{mol/g TiO}_2$). In particular, unlike C6, the surface concentration of P6 on TiO_2 at the saturation condition is the lowest among the P-complexes and not higher than $40 \mu\text{mol/g}$.

P-complexes can be anchored onto the TiO_2 surface via one, two, or three phosphonate groups as similarly illustrated in Chart 2, and each phosphonate group can be attached to the TiO_2 surface via mono-, bi-, or tridentate mode.⁸ It has been reported that the terpyridyl ligand with one phosphonate group in a Ru complex showed much stronger adhesion onto TiO_2 than the bipyridyl ligand with four carboxylate groups in N3,¹⁶ which implies that the surface anchoring through a single phosphonate group is strong enough to make the sensitizer adsorbed. It has been reported that the binding constant of P2 on TiO_2 is approximately an order of magnitude higher than that of C2.⁷ The present results are consistent with these previous observations and further indicate that the presence of additional phosphonate groups (more than two) does not increase the binding capability of the sensitizer. It seems that P-complexes are bound onto the TiO_2 surface primarily through a single phosphonate group regardless of the number of the phosphonate groups. Although we did not compare the binding properties of P-complexes (P2, P4, and P6) with those of P1, the surface charge variation shown in Figure 4b supports this claim. The observation that the adsorption of P2 on TiO_2 little changed the surface charge implies that P2 attached to the surface of TiO_2 carries a net zero charge. This indicates that two out of four P-OH groups in P2 are present as P-O⁻ and the other two should be involved in the surface-anchoring bond formation ($\equiv\text{Ti}-\text{O}-\text{P}-\text{O}-\text{Ti}\equiv$). According to $\text{p}K_a$ data listed in Table 1, the dissociation of the second phosphonic acid group in P2 is only significant above pH 12. The P2 (and other P-complexes as well) anchoring onto TiO_2 most probably uses only one phosphonate group.

C-Complex Sensitization. C4- TiO_2 showed the most efficient and stable cell performance among C- TiO_2 electrodes although the molar absorptivity of C4 is the lowest. This indicates that the overall electron-transfer process in the C4- TiO_2 system is far more efficient than that of other C- TiO_2 electrodes. C2 can bind through either MP or BP-S mode only whereas C4 can be anchored via all four modes in Chart 2. On the contrary, C6- TiO_2 in which all four binding modes are allowed, exhibited a lower efficiency than C2- TiO_2 . Furthermore, the performance of C6- TiO_2 still remained poor even with the much larger surface loading of C6 than the other two

under the saturation condition (Figure 5b). The most plausible explanation for the lower efficiency of C6 is that C6 molecules tend to form aggregates, not to adsorb uniformly on the surface of TiO_2 as we discussed previously. Agglomerated dyes would be inefficient in electron injection and the subsequent dye regeneration. To take a few examples, the aggregation of anionic dyes (Merocyanine 540) drastically reduced its photosensitization efficiency, but the use of an AOT micelle to minimize the dye aggregation significantly enhanced the photocurrent generation efficiency.³⁴ It has been also observed that Ru-complex aggregation made the photovoltaic efficiency lower.^{23,25,35} The aggregation of C6 sensitizers could be induced through the hydrogen bonding between unused carboxylic acid groups even below the saturation coverage.

It is also important to take into account the effects of electron-transfer-related kinetics and energetics on the cell performance among the structurally related sensitizers. Even though the interfacial electron-transfer kinetics was not investigated in this study, a previous study indicated no significant difference between C2- and C6-sensitized TiO_2 cells in most of the kinetics.³⁶ If we extend this to the current system, we can assume that the different binding modes do not significantly affect the overall interfacial electron-transfer kinetics in the C- TiO_2 electrode system. It seems that there is no distinct correlation between the number of anchoring groups and the measured redox potentials of C-complexes (Table 1). For example, even though C4 is the most active in the overall cell performance, it actually shows the smallest driving force for electron injection (i.e., with the least negative E^*). This is consistent with (or indirectly supports) one of the predictions from the recent analytical model of DSSCs.³⁷ In brief, it has been reported that the rate constant for the electron injection from an excited sensitizer to the TiO_2 conduction band (CB) is generally very fast, and therefore it is relatively insensitive to the variation of the redox potential of the excited sensitizer as long as it is sufficiently negative with respect to the TiO_2 CB.³⁷ Although the interfacial electron-transfer kinetics and the energetic properties are expected to depend on the structures of C-complexes, they do not seem to significantly influence the overall performance of the solar cell.

P-Complex Sensitization. The overall dependence of the cell performance of the P- TiO_2 system on the number of phosphonate groups is very different from that of the C- TiO_2 system. Among the six sensitizers used in this study, P6- TiO_2 exhibited the best photoelectrochemical performance ($V_{oc} = -0.8 \text{ V}$; $I_{sc} = 3.2 \text{ mA/cm}^2$) (Table 2). It could be attributed to both the highest MLCT absorptivity of P6 ($\epsilon = 24\,000 \text{ M}^{-1} \text{ cm}^{-1}$) and the stronger binding through the phosphonate group. In contrast to C6- TiO_2 system, P6- TiO_2 did not show a sign of the dye aggregate formation (Figure 3b). The marked difference between C6- TiO_2 and P6- TiO_2 systems might be caused by the difference in the surface binding affinities. P6 on TiO_2 also carries unused dangling phosphonate acid groups, which should interact with neighboring P6 molecules via hydrogen bonding. The sensitizer aggregation on TiO_2 should be favored when the attractive interaction between sensitizers is stronger or comparable to the strength of the sensitizer-surface binding. This seems to be the case for C6- TiO_2 . As for P6- TiO_2 , however, the surface binding between the phosphonate group and TiO_2 appears to be strong enough to inhibit the formation of P6 aggregates.

The comparison between C2 and P2 sensitization also reveals a marked difference. Although the MLCT absorptivity of P2 is about two-thirds that of C2 ($\epsilon_{\text{MLCT}}(\text{P2}) = 10\,200$ vs $\epsilon_{\text{MLCT}}(\text{C2})$

= 15 500 M⁻¹ cm⁻¹) and their surface coverages at saturation are similar, I_{sc} obtained with the P2–TiO₂ electrode is larger than that of C2–TiO₂ by a factor of 5. That is, P2 is a far more efficient sensitizer than C2. To take another example of dissimilarity between C- and P-sensitization, P4–TiO₂ showed the lowest cell performance (almost negligible) among the P–TiO₂ systems (P6 > P2 ≫ P4) in contrast to the fact that C4–TiO₂ was the best in the C–TiO₂ systems (C4 > C2 ≥ C6). The extremely low activity of P4–TiO₂ is particularly notable. Although it might be partly ascribed to the lowest visible light absorption by P4, the low absorbance alone does not seem to be a sufficient explanation for the unexpectedly poor performance. In this respect, it is also noted that P4 shows a marked red shift in the MLCT band. The origin of the poor performance of P4 despite its good surface binding remains to be understood.

The above comparison shows that changing the number of the anchoring groups affects the overall cell performance through different mechanisms between C- and P-complex sensitization. In C–TiO₂ systems, attaining the optimal surface binding mode that is sensitively dependent on the number of carboxylate groups seems to be the most important. Two carboxylate groups attached onto the same bipyridyl ligand (C2) are not sufficient to obtain the stable surface binding. However, C6 with six carboxylate groups may take an optimal binding mode but leaves unused anchoring groups that induce the agglomeration C6 on TiO₂. As a result, C4 with four anchoring groups shows the best cell performance despite the lowest visible light absorption. As for P–TiO₂ systems, however, the surface binding mode seems to be less important because all P-complexes (P2, P4, and P6) show sufficient affinities for surface adsorption. In this case, the visible light absorption by P-complexes that is indirectly related with the number of phosphonate groups seems to be the most dominant parameter in determining the overall cell performance.

Conclusions

We have investigated the effects of the anchoring group (carboxylate vs phosphonate) in ruthenium-bipyridyl-based complexes on the photoelectrochemical behaviors when they are used as sensitizers of DSSCs. The surface binding on TiO₂ and the overall cell performance were highly dependent on both the number and the kind of anchoring groups. The cell performance (or sensitization efficiency) of C–TiO₂ systems was primarily governed by the surface binding mode and stability of C-complexes on TiO₂, which is strongly influenced by the number of the carboxylate groups. As a result, the C4–TiO₂ system showed the best cell performance despite the lowest visible light absorption because the most effective surface binding mode is allowed with this structure. On the contrary, the photoelectrochemical behaviors of P–TiO₂ systems were not influenced much by the surface binding properties. This could be attributed to the intrinsically stronger binding capability of the phosphonate group than the carboxylate linkage. Since the surface binding of P-complexes is strong enough even with only one phosphonate group, the presence of additional anchoring groups does not make a significant difference in the sensitizer adsorption and the electronic coupling between the sensitizer and TiO₂. Therefore, the overall cell performance follows the order of the visible light absorptivity of P-complexes, which changes with the number of phosphonate groups.

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