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Oligothiophene Bearing 1-Hydroxy-1-oxodithieno[2,3-*b*:3′,2′-*d*]phosphole as a Novel Anchoring Group for Dye-sensitized Solar Cells

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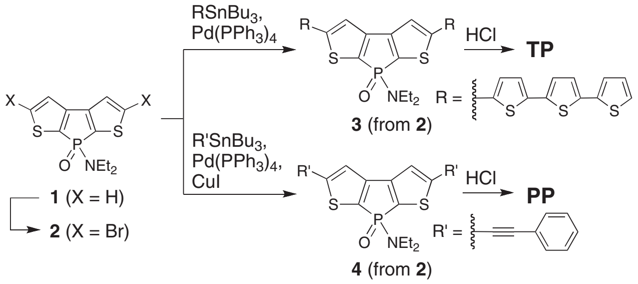
An oligothiophene bearing 1-hydroxy-1-oxodithieno[2,3-*b*:3′,2′-*d*]phosphole (**TP**) as a novel anchoring group has been synthesized for dye-sensitized solar cells (DSSC). Attenuated total reflectance-Fourier transform infrared and X-ray photoelectron spectroscopy measurements disclosed the bidentate binding of the phosphinic acid unit to a TiO_2 surface. A **TP**-sensitized TiO_2 cell yielded a maximum incident photon-to-current efficiency of 66% and a power conversion efficiency of 1.8%, indicating that 1-hydroxy-1-oxodithienophosphole is a potential unit as a new type of anchoring groups for DSSC.

Recently, studies on metal-free or inexpensive metal-based organic chromophores for DSSC have grown rapidly.[1] In this regard it is also essential to improve the binding ability of anchoring groups to a TiO_2 electrode as well as electron-transfer properties through them for highly efficient DSSC.[2] Nevertheless, the variations of the anchoring groups are still limited to carboxylic acid,[3] sulfonic acid,[4] phosphonic acid,[5] and others.[6] Herein, we report an oligothiophene bearing 1-hydroxy-1-oxodithieno[2,3-*b*:3′,2′-*d*]phosphole (**TP**) as a novel anchoring group for DSSC (Figure 1).

The electron density of the LUMO of 1-hydroxy-1-oxodithienophosphole is extended to the phosphinic acid group due to the effective σ^*–π^* orbital interaction in the phosphole moiety,[7] as predicted by DFT calculations (Figure S1).[15] In addition, it is worth noting that phosphole changes its electronic structure by the introduction of π-conjugative substituents at the P-connected *cis*-1,3-diene function.[7] Thus, we can expect the occurrence of fast electron injection from the dye excited state to the conduction band (CB) of the TiO_2 through the anchoring group by introducing electron-donating π-conjugative chromophores (i.e., oligothiophene) into the dithienophosphole core, resulting in the efficient photocurrent generation.

The synthetic route to **TP** is shown in Scheme 1. Dithienophosphole **1** was synthesized according to methods previously reported by Cristau et al.[8] Then, dithienophosphole **1** was treated with *N*-bromosuccinimide (NBS) to yield dibromodithienophosphole **2**. Terthiophene-linked dithienophosphole **3** was prepared by the Stille coupling of **2** with 5-tri(n-butyl)-stannyl-2,2′:5′,2″-terthiophene. Finally, hydrolysis of **3** afforded **TP**. Phenylethynyl-linked 1-hydroxy-1-oxodithienophosphole (**PP**) was also prepared by the Sonogashira coupling to compare the light-harvesting, optical, and photovoltaic properties with those of **TP**.



Scheme 1. Synthesis of **TP** and **PP**.

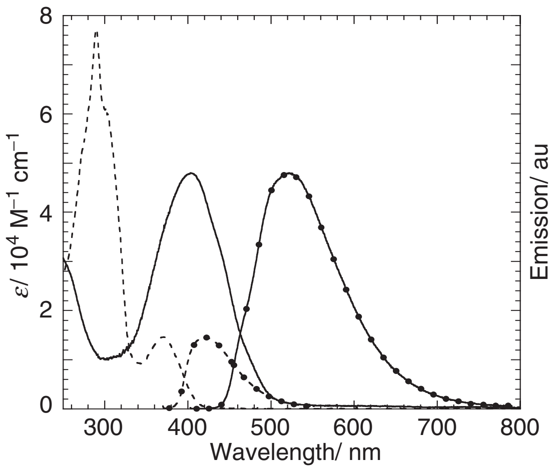


Figure 2. Absorption spectra of **TP** (solid line) and **PP** (dashed line) and normalized emission spectra of **TP** (solid line with circles) and **PP** (dashed line with circles) in THF. $\lambda_{ex} = 403$ nm for **TP**, 370 nm for **PP**.

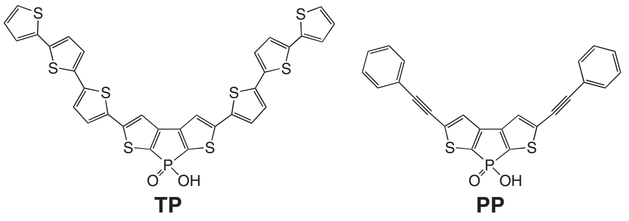


Figure 1. Molecular structures of the **TP** and **PP** sensitizers.

Figure 2 displays the UV–vis absorption and fluorescence spectra of **TP** and **PP** in THF. The absorption band of **TP** appears at 403 nm with a molar extinction coefficient (ε) of $4.80 \times 10^4\,M^{-1}\,cm^{-1}$, whereas the fluorescence of **TP** is centered at 522 nm. The absorption maximum of **TP** is red-shifted by 32 nm compared with that of **PP**. The fluorescence quantum yield (Φ_f) of **TP** (10%) is larger than that of **PP**. These results imply that the introduction of the electron-donating π-extended chromophores into the dithienophosphole core improves the light-harvesting and fluorescence properties in the visible region considerably. In addition, the absorption and fluorescence maxima of **TP** are significantly red-shifted relative to those of **1** ($\lambda_{abs} = 345$ nm, $\lambda_{em} = 422$ nm) and terthiophene ($\lambda_{abs} = 352$ nm, $\lambda_{em} = 428$ nm), supporting effective π-extension in **TP** (Figure S2).[15] The first one-electron oxidation potentials (E_{OX}) of **TP** (1.25 V vs. NHE) and **PP** (1.52 V vs. NHE) were determined by differential pulse voltammetry (Table S1).[15] From the E_{OX} and the excitation energy ($E_{0\text{–}0}$) values, the excited-state oxidation potentials ($E_{OX}{}^*$) of **TP** and **PP** were estimated to be -1.48 and -1.62 V vs. NHE (Table S1).[15] Taking into account the energy levels of the CB of TiO_2 (-0.5 V vs. NHE)[9] and $I^-/I_3{}^-$ couple (0.5 V vs. NHE),[9] electron injection from the dye excited singlet state to the CB of TiO_2 and charge shift from I^- to the resulting dye radical cation (1.25 V vs. NHE) are thermodynamically feasible both in the **TP** and **PP** cells. DFT calculations were employed to gain insight into the equilibrium geometry and electronic structures for the HOMO and LUMO of **TP** and the SOMO of **TP** radical cation (Figure S3).[15] The optimized geometry has no negative frequencies, implying that optimized geometries are in the global energy minima. The LUMO is localized mainly over the dithienophosphole including the anchoring group, whereas the HOMO of **TP** and the SOMO of **TP** radical cation are delocalized except for the anchoring group. For **TP**, 70% of the electron density in the HOMO is located on the two terthiophene units, and 10% of the electron density in the LUMO is distributed on the phosphinic acid group. For **PP**, 37% of the HOMO is localized on the two phenylacetylene units, and 14% of the LUMO lies on the phosphinic acid group. These results indicate that the HOMO–LUMO excitation of **TP** shifts the electron distribution from the chromophores to phosphinic acid group more obviously than **PP**, thus allowing an efficient photoinduced electron transfer from **TP** to the TiO_2 electrode and slow charge recombination from the electron in the CB to the dye radical cation due to the remoteness.[10]

TP and **PP** were sensitized onto mesoporous P-25 based TiO_2 electrodes with chenodeoxycholic acid (CDCA) (denoted as TiO_2/**TP** and TiO_2/**PP**, respectively). Little shift and broadening of the absorption peak of **TP** on the TiO_2 are noted in comparison with that in THF (Figure S4),[15] showing little aggregation of **TP** on the TiO_2 electrode. On the other hand, **3** did not bind to a bare TiO_2 electrode (Figure S5). Therefore, 1-hydroxy-1-oxodithienophosphole acts as an anchoring group to the TiO_2 surface through its phosphinic acid unit. To get information on the binding mode of the molecules adsorbed on the TiO_2 electrode, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were measured for powders of **TP** and **PP** as well as TiO_2/**TP** and TiO_2/**PP** (Figure S6).[15] ATR-FTIR spectra of **TP** and **PP** reveal the characteristic bands of ν(P=O) and ν(P–OH) of the phosphinic acid group at around 1200 and 960 cm^{-1}, respectively.[11] However, these bands disappear and a peak corresponding to ν(O–P–O) at around 1040–1060 cm^{-1} emerges for the spectra of TiO_2/**TP** and TiO_2/**PP**.[11] These results demonstrate that the two equivalent P–O bonds are formed through a bidentate coordination of the phosphinate to the TiO_2 surface.[11] To further shed light on adsorption state of the dyes on the TiO_2 surface, X-ray photoelectron spectroscopy (XPS) measurements were performed for TiO_2/**TP** and TiO_2/**PP** together with **TP** and **PP** (Figure S7).[15] The O1s XPS spectra of **TP** and **PP** were curve-fitted into two chemically different O1s subpeaks (Figures S7a and S7b and Table S2).[15] The peaks arising at around 531 and 533 eV can be assigned to the oxygen atoms of P=O and of P–OH in the phosphinic acid, respectively.[11c,12] The spectra of TiO_2/**TP** and TiO_2/**PP** also exhibit two different peaks, respectively (Figures S7c and S7d and Table S2).[15] The peaks at 530.2 eV stem from the oxygen atoms in TiO_2.[9,12] The peaks at 531.2–531.6 eV can be attributed to the oxygen atoms of P–O–Ti bonds.[12] It is noteworthy that the peaks derived from the O atoms of P–OH at around 533 eV disappear in the spectra of TiO_2/**TP** and TiO_2/**PP**. Consequently, we can conclude that the two oxygens in the phosphinate bind to the TiO_2 surface with the same binding energy through a bidentate coordination, which is in good agreement with the results of the ATR-FTIR measurements (vide supra). Given the surface area of P-25 ($54\,m^2\,g^{-1}$),[9] the packing densities (Γ) of **TP** and **PP** on the actual TiO_2 surface area are determined to be 1.9×10^{-10} and 2.0×10^{-10} $mol\,cm^{-2}$. Assuming that **TP** and **PP** molecules are densely packed onto the TiO_2 surface yielding a full monolayer without CDCA, the calculated Γ values are 2.4×10^{-10} and 3.2×10^{-10} $mol\,cm^{-2}$. The experimental Γ values are considerably lower than the calculated Γ values, implying that the dye molecules are isolated from each other by the intercalation of CDCA molecules, thereby reducing dye aggregation.

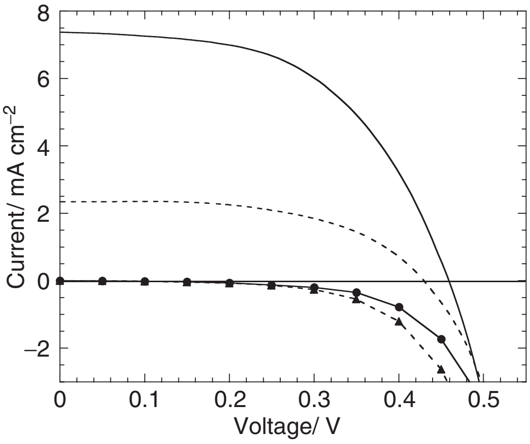


Figure 3. Current–voltage characteristics of the TiO_2/**TP** (solid line) and TiO_2/**PP** (dashed line) electrodes under an irradiation of $100\,mW\,cm^{-2}$ AM 1.5G sunlight and TiO_2/**TP** (solid line with circles) and TiO_2/**PP** (dashed line with triangles) electrodes in the dark. Electrolyte: 0.5 M LiI and 0.01 M I_2 in CH_3CN.

Current–voltage characteristics of the TiO_2/**TP** and TiO_2/**PP** electrodes were evaluated under standard AM 1.5 conditions ($100\,mW\,cm^{-2}$) (Figure 3). An $\eta = 1.8\%$ value of the **TP** cell was obtained with a J_{SC} of $7.4\,mA\,cm^{-2}$, a V_{OC} of 0.46 V, and a *ff* of 0.54, whereas an $\eta = 0.56\%$ value of the **PP** cell was obtained with a J_{SC} of $2.3\,mA\,cm^{-2}$, a V_{OC} of 0.44 V, and a *ff* of 0.54. The large η value of the **TP** cell relative to the **PP** cell is consistent with the difference in the light-harvesting properties of **TP** and **PP** (vide infra).

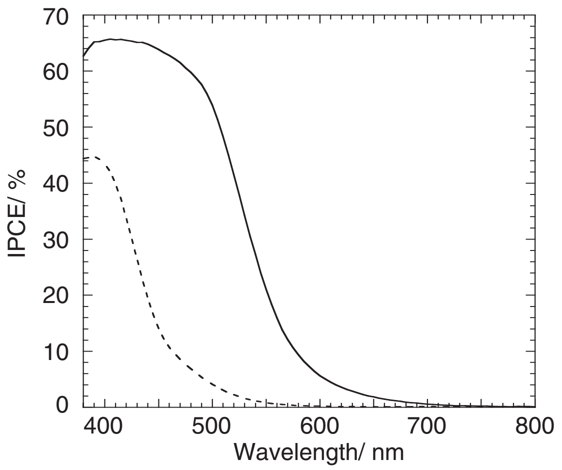


Figure 4. Photocurrent action spectra of the TiO_2/**TP** (solid line) and TiO_2/**PP** (dashed line) electrodes.

The photocurrent action spectra of the TiO_2/**TP** and TiO_2/**PP** electrodes are illustrated in Figure 4. The action spectra and the absorption spectra are virtually similar for the electrodes, implying the involvement of the dyes for the photocurrent generation. The TiO_2/**TP** electrode exhibits a maximum IPCE (incident photon-to-current efficiency) value of 66% at 400 nm. This IPCE value is comparable to that of N719-sensitized TiO_2 cell (72%) under our experimental conditions,[13] implying the occurrence of efficient electron injection from the **TP** excited singlet state to the CB of TiO_2 due to sufficient strong electronic coupling between 1-hydroxy-1-oxodithienophosphole and the 3d orbital of TiO_2. In contrast, the TiO_2/**PP** electrode reveals much lower IPCE values in the visible region (43% at 400 nm).

Similar difference is noted for APCE (absorbed photon-to-current efficiency) values of the TiO_2/**TP** (66%) and TiO_2/**PP** (44%) electrodes.[14] To address the effect of the charge recombination, we measured the current–voltage characteristics under dark conditions (Figure 3). The onset of the dark current for the **TP** cell appears at a higher potential than that for the **PP** cell, indicating that the degree of the charge recombination for the **PP** cell is higher than that for the **TP** cell. The differences in the APCE values and in the effect of the charge recombination between **TP** and **PP** may be attributed to those in fluorescence quantum yields as well as in the HOMO–LUMO distribution (vide supra).

In conclusion, we have successfully synthesized oligothiophene-bearing 1-hydroxy-1-oxodithienophosphole as a novel anchoring group for DSSC for the first time. The introduction of the oligothiophene moieties into 1-hydroxy-1-oxodithienophosphole was found to improve the light-harvesting property in the visible region, leading to significant enhancement in the cell performance relative to a reference device with a weak light-harvesting unit. We have also disclosed the binding mode of the novel anchoring group to a TiO_2 surface. These results corroborate the potential utility of 1-hydroxy-1-oxodithienophosphole as a novel anchoring group for DSSC. Further improvement of the cell performance may be possible by introducing excellent light-harvesting and electron-donating chromophores into the 1-hydroxy-1-oxodithienophosphole as well as improving the device structure.

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14 The APCE values are lower limits because we do not take into account the collection losses (e.g., reflection) in the TiO_2 films.

15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.