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Metal-free organic dyes containing benzo[b]phenothiazine were synthesized and effectively used for dye-sensitized visible-light-driven photocatalytic hydrogen production. The materials exhibited high stability and hydrogen production when numerous π-conjugated bridges were inserted as spacers between the donor and the anchor moiety. Photocatalytic hydrogen production was investigated in a TiO$_2$/dye/Pt structure using triethanolamine as the sacrificial reagent. Compound dye 3, which had the longest spacer between the donor and the acceptor, exhibited the best hydrogen production performance of the series examined in this study. It displayed a turnover number (TON) of 4460, a turnover frequency of 278 after 16 h, and a photo quantum efficiency of 1.65% at 420 nm. Furthermore, it showed the longest electron injection lifetime because its coordination structure was considered to be vertically standing on the TiO$_2$ surface by theoretical calculations. On the other hand, dye 1 showed the lowest hydrogen production performance with a TON of 483 and very short electron injection lifetime. This observation may suggest from the computation result, which showed the lying geometry of 1 with monodentate coordination of the dye with respect to the TiO$_2$ surface. This spacer effect–property relationship study may provide a good strategy for the development of metal-free organic dyes for dye-sensitized photocatalytic water splitting.

Introduction

Production of hydrogen is the key to establishing clean energy systems, because hydrogen can be employed as a clean energy source in fuel cells. Since the Honda–Fujishima water splitting effect using a rutile TiO$_2$ and a Pt black system was reported in 1972, hydrogen gas production by photocatalytic water splitting has been investigated with TiO$_2$ and other semiconductors, because it is one of the ideal hydrogen production methods. However, visible-light-driven photocatalytic water splitting is proven difficult to accomplish because almost all semiconductors have a wide band gap, whereas a visible-light-driven photocatalyst requires a band gap of less than 3.0 eV ($\lambda > 415$ nm).

Although some semiconductors have shown satisfactory visible-light-driven photocatalytic activity, many challenges still persist. These challenges include improving the water splitting efficiency and stability of catalysts through the engineering of semiconductors. Alternatively, dye-sensitized photocatalytic water splitting systems may achieve hydrogen production under visible light. Ruthenium complex dyes have displayed high efficiencies in dye-sensitized photocatalytic hydrogen production from water. In particular, a dimer of ruthenium complex Ru$_2$(bpy)$_4$(BL)(ClO$_4$)$_2$ showed good hydrogen production performance in a visible-light-driven Pt/dye/TiO$_2$ system with a turnover number (TON) of 75340 after 27 h. Other metal complex dyes, such as metal complex porphyrin (TON = 400), have also presented good hydrogen production rates. These metal complex dyes benefit from metal-to-ligand charge transfer abilities, which enhance the electron injection rate from the dye to the semiconductor. A wide
variety of organic dyes such as derivatives of coumarin, cyanine, xanthene dyes, imide and 1,1′-bi-2-naphthol (BINOL) have been reported in the literature. Compared to metal-containing materials, these dyes have the advantage of being environmentally friendly, abundant, cheap and flexible but have exhibited low hydrogen production rates (TON ~ 40) in similar Pt/dye/TiO<sub>2</sub> system. Performance enhancement of these metal-free complexes in water hinges on the design of new efficient sensitizers.

The environment between sensitizers and semiconductor surfaces has recently been reported to improve efficiency. Han et al. have demonstrated that hydrophilic substituents on sensitizers enhanced charge recombination lifetimes because aqueous media induced the relaxation of the dye from its excited state.

Lee et al. have reported that N-substitution by long alkyl chains improved the hydrogen productivity of phenothiazine derivatives by establishing a good electron injection pathway. These substituents changed the aggregation conformation of the dye on TiO<sub>2</sub> and/or prevented the undesired decomposition reaction in the excited state, resulting in a good performance of these metal-free dye systems (TON ~ 1026). These results indicate that the selection of an appropriate dye structure can increase hydrogen production. Donor–spacer–acceptor dyad systems have exhibited remarkable quantum efficiency in dye-sensitized solar cells. In these dyads, donor and spacer structures have played an important role in improving favourable electron injection into a semiconductor and achieving a slow charge recombination between semiconductor and dye.

In this study, the visible-light-driven photocatalytic activity of a novel donor–spacer–acceptor dye system was investigated with a focus on the relationship between hydrogen production and spacer length. The spacer can not only extend the absorption bands of visible light but also provide long charge recombination states by separating electron donor and acceptor sites. Substituents, such as hydrophilic groups, were introduced on the sensitizers to study the spacer effect. Benzo[h]phenothiazine was chosen as the electron donor because phenothiazine derivatives exhibit good electron donating ability and electrochemical stability in dye-sensitized solar cell systems.

**Results and Discussion**

**Synthesis**

Dyes 1–3 were synthesized using benzo[h]phenothiazine (4) as the starting material. The secondary amine of 4 was methylated using an excess amount of MeI in K<sub>2</sub>CO<sub>3</sub>/THF. Formylation at the 11-position of the methylated compound (5) moiety by the Vilsmeier–Haack reaction produced aldehyde 6. The reduction of 6 by NaBH<sub>4</sub> formed alcohol 7, which was subsequently treated with triphenylphosphine hydrobromide to give the phosphonium salt (8). Knoevenagel condensation of 8 with cyanoacetic acid afforded dye 1 in 48% yield. The cyanoacrylic acid moiety acted as the acceptor unit in dye 1.

The distance between donor and acceptor was further elongated by addition of another aromatic moiety. The Wittig reagent (8) reacted with thiophene-2,5-dicarboxaldehyde and [2,2′-bithiophene]-5,5′-dicarbaldehyde, 18-crown-6, K<sub>2</sub>CO<sub>3</sub>, DMF, 50%–56%.

with thiophene-2,5-dicarboxaldehyde and [2,2′-bithiophene]-5,5′-dicarbaldehyde in the presence of 18-crown-6-ether to give aldehydes 9 and 10, respectively, in 50%–56% yield. The presence of an aldehyde group in these intermediates was confirmed by the detection of <sup>1</sup>H NMR signals around 9.89–10.40 ppm. Similar to the synthesis of dye 1, Knoevenagel condensation of these aldehydes with cyanoacetic acid produced the corresponding spacer-extended dyes 2 and 3 in 70%–75% yield. The <sup>13</sup>C NMR spectra of the final compounds displayed peaks at 163–164 ppm, indicating the presence of a carboxyl acid group. IR spectra also showed peaks at 1686–1693 cm<sup>-1</sup> which corresponded to the carboxylic acid group stretching bands. The formation of dyes 2 and 3 was further confirmed by HR-FAB-MS spectra.

**Physical Properties**

The absorption spectra of organic dyes 1–3 in THF are shown in Fig. 2. Each compound displayed two major absorption bands at 250–330 nm and 350–550 nm. Short wavelength bands were assigned to π–π* and n–π* transitions.
transitions and long wavelength bands to internal charge-transfer (ICT) transitions. The ICT bands experienced a bathochromic shift with increasing number of thiophene spacers, i.e. 3 (443 nm) > 2 (391 nm) > 1 (363 nm). In addition, the ICT intensities increased with the number of thiophene spacers. Dyes 2 and 3 exhibited ICT excitation coefficients of 20312 nm/M·cm⁻¹ and 22239 nm/M·cm⁻¹, respectively, indicating a significant electron interaction between the donor and the acceptor via the thiophene spacer moieties. On the other hand, the very weak excitation coefficient of 1 (5122 nm/M·cm⁻¹) may be explained by weak electron coupling interactions caused by steric hindrance from the N-methyl substituent.

**Figure 2. Absorption spectra of dyes 1-3 in THF (1.0 × 10⁻⁴M)**

Dyes 1–3 presented similar absorption spectra on TiO₂ films as in THF, with the exception of a blue shift of ca. 20–30 nm for the ICT bands (Fig. 3 and Table 1). When the TiO₂ films 1–3 were measured in the THF, no shift of absorption was found (Fig. S2). These results suggested that dyes 1–3 of blue shift was occurred from electronic interaction with TiO₂. ²⁵

**Figure 3. Absorption spectra of dyes 1–3 on TiO₂ films.**

These absorption spectra suggested that the gaps between the highest occupied (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of these dyes would become narrower as the number of spacers increased. To investigate the electronic properties, cyclic voltammetry was conducted in THF in the presence of Bu₄NPF₆ (0.1 M) using Fe/C as an internal standard (Fig. 4). Reversible one-electron oxidation potentials (vs. NHE) were observed at a E_{ox}^{1/2} value of +1.16 V for 1, +1.07 V for 2 and +0.85 V for 3. On the other hands, the reduction potentials of the LUMO levels of dye 1-3 could not estimate by cyclic voltammetry, due to one-electron irreversible reduction processes, i.e. the potentials (vs. NHE) found at a E_{red}^{1/2} value of −1.33 V for 1, −1.09 V for 2 and −1.07 V for 3 (Fig. S3). The LUMO levels of the sensitzers were estimated from their E_{ox}^{1/2} value and the edge of their absorption spectra. When the number of the spacers increased, the LUMO energies (vs. NHE) decreased in the order 1 (−1.18 V), 2 (−1.15 V) and 3 (−1.14 V). These potentials of trends were agreed with cyclic voltammetry results. All LUMO levels displayed high potentials compared to the conduction band of TiO₂ (−0.4 V vs. NHE), which is required to drive electron injection into TiO₂. Furthermore, the reversible oxidations implied that the benzophenothiazine-containing dyes were highly stable during the oxidation–reduction process. These results suggest that dyes 1–3 may be suitable for photocatalytic reactions.

**Figure 4. Cyclic voltammograms of 1–3 in 0.1 M Bu₄NPF₆-containing THF solutions. The scan rate was 100 mV/s.**

**Theoretical Study**

The donor–acceptor interactions of dyes 1–3 were further investigated through theoretical computations. Density functional theory (DFT) computations at the B3LYP/6-31G(d) level by Gaussian 09 program. ²⁶ The result indicated that the cyano group of dye 1 must have a large dihedral angle (92°) with respect to the olefin bond to prevent steric effects between the olefin and the cyanoacrylic acid. On the other hand, the computational models showed much smaller dihedral angles for 2 (42°) and 3 (52°) because the insertion of the thiophene rings reduced the steric effects. Molecular orbitals (MOs) generated by DFT computations (B3LYP/6-31G(d) level) showed that the HOMO of 1 was located on the donor moiety but was not delocalized on the olefin bonds, indicating weak electronic interactions between the donor and olefin bonds and supporting the experimental results.

**Figure 5. Generated molecular orbitals of HOMO and LUMO geometries from optimized structure of 1–3 at the B3LYP/6-31G(d) level.**
Table 1. Calculated (TDDFT/M06/6-31G(d)), experimental absorption (in THF and on TiO$_2$), and electrochemical parameters for organic dyes.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>$\lambda_{max}$ / $f$ (nm/M$^2$cm$^{-1}$)$^a$</th>
<th>$\lambda_{max}$ / $f$ (nm/M$^2$cm$^{-1}$)$^b$</th>
<th>$\lambda_{onset}$ (nm)$^c$</th>
<th>$\lambda_{max}$,TiO$_2$ (nm)</th>
<th>$\Delta\lambda_{max}$,Solv.-TiO$_2$ (nm)</th>
<th>HOMO/LUMO</th>
<th>HOMO/LUMO $V_{vs}$ NHE$^d$</th>
<th>HOMO/LUMO (eV)$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>388 (0.158)</td>
<td>363 (5122)</td>
<td>530</td>
<td>336</td>
<td>27</td>
<td>1.16/-1.18</td>
<td>-6.95/-1.81</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>446 (0.501)</td>
<td>391 (20312)</td>
<td>560</td>
<td>361</td>
<td>30</td>
<td>1.07/-1.15</td>
<td>-6.59/-2.28</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>451 (1.26)</td>
<td>443 (22239)</td>
<td>621</td>
<td>425</td>
<td>18</td>
<td>0.85/-1.14</td>
<td>-6.53/-2.36</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ obtained by TDDFT at the M06/6-31G(d) level. $^b$ oscillator strength for the lowest energy transition. $^c$ $\varepsilon$: absorption coefficient. $^d$ measured in THF. $^e$ calibrated according to Fe/Fc$^+$ = −0.63 V vs. NHE. $^f$ obtained by TDDFT at the M06/6-31G(d) level.

On the other hand, the HOMO levels showed good electronic coupling between the donor and spacer moieties for molecules 2 and 3, consistent with efficient charge-transfer interactions between donor and acceptor (Fig. 5). Time-dependent (TD) DFT computations (M06/6-31Gd level) showed that trends observed in the computed HOMO–LUMO energy, lowest excitation energy and oscillator strengths for 1–3 were in good agreement with the experimental results. The physical properties of 1–3 are summarized in Table 1.

Water Splitting Reaction

To assess the performance of these dyes for photocatalytic water splitting reaction, the hydrogen production of TiO$_2$/dye/Pt systems containing dyes 1–3 was investigated in 10% triethanolamine (TEA) of water (pH = 7). The TiO$_2$/dye/Pt catalysts were fabricated on commercially available TiO$_2$ anatase particles by Pt photodeposition in methanol using a Xe lamp (300 W). After this photodeposition, the dye was loaded onto the TiO$_2$/Pt particles by solution processing in the presence of a 0.30 mM dye solution in methanol at room temperature for 12 h. The reflectance absorption spectra of the TiO$_2$ particles showed peaks at the same wavelengths as for dye–TiO$_2$ films (Fig. S1), confirming the appropriate loading of the dyes. The dye loading amounts on the TiO$_2$ catalyst were 0.65 µmol/33 mg for 1, 0.91 µmol/33 mg for 2 and 0.96 µmol/33 mg for 3. The low loading amount of dye 1 may be explained by its molecular structure. The N-methyl group of the donor moiety is very close to the cyanocarboxylic acid acceptor in 1, reducing the ability of the dye to connect with the TiO$_2$ surface. On the other hand, in 2 and 3, donor and acceptor moieties are separated by a bridge of thiophene spacers. Competition in the hydrogen production performances between dyes 2 and 3 is worth mentioning. After 16 h, dye 2 produced 1597 µmol of hydrogen gas, whereas dye 3 produced 2141 µmol. As a result, dye 3 exhibited higher turnover number (TON) and frequency (TOF) (TON = 4460; TOF = 278) than dye 2 (TON: 3510; TOF: 219) after 16 h. The hydrogen production performance of dye 1 was very low (TON: 483; TOF: 30) after 16 h (Fig. 6 and Table 2). One probable reason for the low production amount of hydrogen in dye 1 is its low loading amount on TiO$_2$ compared with those of the other dyes. Another reason may be the low excitation frequency and of dye 1 upon light stimulation over 420 nm. In solution, dye 1 displayed a low excitation coefficient (5122 nm/M$^2$cm$^{-1}$) at its maximum absorption peak ($\lambda$ = 380 nm) and this coefficient became even weaker at 420 nm (3503 nm/M$^2$cm$^{-1}$).

The single component of wavelength at 420 nm was used to determine the quantum efficiency for hydrogen conversion of water (Fig. S4 and table S1). We estimated the efficiency at 420 nm (7.36 mW/cm$^2$) was 1.65% for 3, 1.46% for 2, and very small yield of 0.03% for 1 was found, respectively. Even the effects of absorption range and excitation coefficient are considered by TON and quantum yield, hydrogen production rate at 1 is quite smaller than that of others. The difference of quantum efficiency at single wavelength suggested that the other factor should dominate for the rate of hydrogen production.

Time-resolved absorption spectra and theoretical studies of dyes on TiO$_2$

A protecting group such as a long alkyl chain may enhance dye stability and performance in solar cell systems. All model dyes are on a TiO$_2$ surface, i.e. benzophenothiazine donors without any bulky substituents, which may lead to the dyes
having similar stability in the hydrogen production process. However, dyes 2 and 3 exhibited a higher TON than dye 1. Time-resolved absorption spectra were measured for dyes 1–3 on TiO₂ to investigate different behaviors in their stabilities. Figure 7 shows typical spectra obtained for dye 3 on TiO₂. In dye 3 solutions, a broadband radical cation with a maximum at 630 nm appeared within a few picoseconds (Fig. S5). This change in structural behavior may result from vibrational relaxation and solvent reorganization. The time-resolved absorption spectra of 3 on TiO₂ film showed positive absorption above 620 nm for the radical cation species of 3 and a negative absorption difference below 620 nm induced by ground-state bleach. The decay profiles monitored at 699 nm showed multicomponent decay up to after 300 ps, including shorter components (< ca. 5 ps) and longer component (> ca. 5 ps). The decay could be conveniently fitted with triple exponential decay functions for 2 and 3, while single exponential decay function for 1. The time decay constants of 3 were evaluated as τ₁ (0.60 ps), τ₂ (7.00 ps), and τ₃ (85.4 ps). Similar experiments for dye 2 gave time constants of τ₁ (0.31 ps) τ₂ (3.64 ps), and τ₃ (47.0 ps) (Figure 8, and Figs. S6 and S7). Dye 1 only presented one time constant τ₁ of 0.18 ps as a shorter component, while no longer component over ca. 5 ps was found (Fig. 8a, and Figs. S6 and S7).

Table 2 Photocatalytic performance and the decay lifetimes of dyes 1–3 on TiO₂⁺.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Dye loading amount (µmol/33 mg)</th>
<th>Amoun of H₂ (µmol)</th>
<th>TON</th>
<th>TOF</th>
<th>Φ (%)</th>
<th>τ₁ (ps)</th>
<th>τ₂ (ps)</th>
<th>τ₃ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.65</td>
<td>157</td>
<td>483</td>
<td>30</td>
<td>0.03</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.91</td>
<td>1597</td>
<td>3510</td>
<td>219</td>
<td>1.46</td>
<td>0.31</td>
<td>3.64</td>
<td>47.0</td>
</tr>
<tr>
<td>3</td>
<td>0.96</td>
<td>2141</td>
<td>4460</td>
<td>278</td>
<td>1.65</td>
<td>0.60</td>
<td>7.00</td>
<td>85.4</td>
</tr>
</tbody>
</table>

<ref>A 300 W Xe lamp was used and wavelengths below 420 nm were cut off using an optical filter. H₂ produced after 16 h. TON = (2 × amount of H₂ / dye loading amount after 16 h) / amount of dye. Values after 16 h. 420 nm (7.36 mW/cm²) of single wavelength was used. t < ca. 5 ps was used to evaluate. Not determined and single exponential decay fitting used because of the short decay profile of 1 at t > 5 ps.</ref>

In the dye-loaded TiO₂ system, the multicomponent decay occurs in the transient have been reported, due to various charge recombination processes were occurred between oxidised dye and reduction band or trap site on TiO₂ surface. The electron injection into TiO₂ is started ~100 fs scale at trap sites of TiO₂, and electron injection into TiO₂ at the conduction bands and/or trapping into the TiO₂ site are occurred over 100 ps. Han et al. suggested that the decay component within < ca. 5 ps is charge recombination process between radical anion of TiO₂⁻ at surface and/or shallow trap state and radical cation of dye⁺, while a component > ca. 5 ps can be injected the electron into the TiO₂ of conduction bands and/or trapping site. In the components of slower decay should play an important process to reduce the water to hydrogen, because of this major component may have the longer life time electrons at TiO₂ site. The dye 1 showed shorter decay charge recombination component of τ₁ (0.18 ps) only, and could not find longer decay.
component of $t_2$, $t_3$. On the other hands, the dye 2 and 3 showed both shorter ($t_1$) and longer ($t_2$ and $t_3$) components. In the dye 3 of major component $t_3$ (85.4 ps) is longer than that of dye 2 (47.0 ps). Clearly, the time profiles of dyes 1–3 indicate that the lifetime of both radical cation species ($t_1$ for 1, $t_1$, $t_2$, and $t_3$ for 2 and 3) increased when the number of spacers between donor and acceptor increased. This fact suggests that the spacer effect extended the charge recombination lifetimes between dye and TiO$_2$, because the separation provided by the thiophene ring spacers enhanced the time taken by the TiO$_2$ electron to return to the dye or donor site. Therefore the dye 1 showed small TON and quantum efficiency. The longer decay component ($t_3$) in 2 and 3 can be provide the long-lived electron in TiO$_2$, thus the rate of hydrogen production can be improved.

To estimate the coordination structure of dyes on TiO$_2$, calculations were performed with DFT/BP86 functional for TiO$_2$ cluster and dye-molecules adsorbed on its surface. The coordinates of the TiO$_2$ atoms were kept fixed, while the coordinates of the dyes were fully relaxed. The calculations were performed with the DFT/BP86 functional and def-sv(p) basis set implemented in the Turbomole program. Owing to the large size of the models calculations with hybrid DFT functional could not be applied. The Dyes 2 and 3 showed biadentate with carboxylate type coordination structure on TiO$_2$, because of the both carboxylate distances to TiO$_2$ are almost same (2.1–2.3 Å for 2@TiO$_2$, and 2.1–2.4 Å for 3@TiO$_2$ in Fig. 9 and Fig. S8). In this geometry, the dye molecules stand on the semiconductor surface, leading to a good separation between benzo[b]phenothiazine donor moieties and semiconductor. On the other hand, dye 1 displayed a monodentate with carboxylate type coordination (3.3 Å and 2.2 Å for Dye1@TiO$_2$ in Fig. 9 and Fig. S8). We already discussed that the dye-loading amount of dye 1 (0.65 μmol) was much smaller than others cases (0.91 μmol for 2 and 0.96 μmol for 3, in table 2), suggested difficulty of the dye 1 of carboxylate coordination on TiO$_2$ surface. Coordination of different of dye 1 probably came from to avoid a repulsive steric effect toward TiO$_2$ surface due to the rotation of the donor site itself and/or the N-methyl group of the donor moiety. In this structure, the dye molecule lies on the semiconductor surface, resulting in a short distance between donor moiety and semiconductor. The molecular orbital of HOMOs of dye 1–3@ (TiO$_2$)$_{82}$ and LUMOs of dye 2–3@ (TiO$_2$)$_{82}$ were similar to their corresponding HOMO and LUMO geometries obtained without TiO$_2$ (Fig. 5). However, the LUMO of dye 1@ (TiO$_2$)$_{82}$ showed that most molecular orbitals did not cover the dye but were delocalized on the semiconductor. This result suggested that many electrons were trapped in the TiO$_2$ surface via through-space electron injection from the donor because of the close proximity between the dye and the semiconductor surface. As a result, efficient charge injection into TiO$_2$ by the spacer effects can reduce the number of times the charge recombination to the ground state without the excited dyes conducting charge injection into TiO$_2$. Thus, the biadentate with carboxylate type coordination structure of dyes 2 and 3 of the TON were enhanced. Dye 1 exhibited a small TON and its $t_2$ and $t_3$ values was not evaluated because of its fast decay. This may be explained by the difference of monodentate coordination with other dyes 2 and 3, and/or short coordination distance between the donor and TiO$_2$, which allowed the charge recombination to occur without an effective charge injection into TiO$_2$.

**Conclusion**

In conclusion, novel donor–spacers–acceptor dyads containing benzo[b]phenothiazine as the donor unit were synthesized. Thiophenes attached at the 10-position of the benzo[b]phenothiazine reduced the dihedral angle between donor and acceptor, readily increasing the charge-transfer electronic coupling between these units. The benzo[b]phenothiadine-containing dyes exhibited good donating ability and stability and their physical properties could be explained by DFT computations. Dyes 1–3 were incorporated in TiO$_2$/dye/Pt catalysts and the visible-light-driven photocatalytic hydrogen production of these catalysts was assessed at pH 7 in 10% aqueous TEA. The highest hydrogen production was observed for 3, which showed hydrogen production rate of 4460 TON and 278 TOF after 16 h, with 1.65 % at 420 nm of quantum efficiency for hydrogen conversion of water. Time-resolved absorption spectra of the dye 1 displayed single-decay component of a short cation radical decay, while the dyes 2 and 3 on TiO$_2$ showed multi-decay components that presented longer decays when the number of spacers increased. The computation results dye 1–3@ (TiO$_2$)$_{82}$ with the DFT/BP86 functional and def-sv(p) basis set suggested that the dyes 2 and 3 showed standing geometry on TiO$_2$ with bidentate structure, while lying geometry on TiO$_2$ due to monodentate structure. In our water splitting reaction and time-resolved results combined with theoretical computation suggested that the spacer can be reduced the charge combination from TiO$_2$ and enhanced charge injection into TiO$_2$, and making a bidentate
binding mode due to reduce the steric effect between the donor moiety and TiO₂ site. Dye 3 showed superior hydrogen production performance, which showed great value as a metal-free organic dye for water splitting cell in TiO₂/dye/Pt system.

Further studies of new dyes are currently underway to improve dye stability for visible-light-driven photocatalytic hydrogen production in aqueous media.

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Notes and references

Experimental Section

General Information
The $^1$H and $^{13}$C NMR were recorded on a Bruker AV500 (500 MHz) and AV 600 (400 MHz). The $^1$H and $^{13}$C NMR chemical shifts were reported as $\delta$ values (ppm) relative to internal Me$_4$Si. The coupling constants ($J$) were given in hertz. MALDI mass spectra were recorded on a Bruker Autoflex. The sample was dissolved in dichloromethane first, then an equal amount of matrix solution (1.0 μL) and a dithranol in dichloromethane (DIT, 1.0 μL) was spotted onto the stainless steel sample plate for injection together. High resolution mass spectra were recorded on a JEOL LMS-HX-110 spectrometer. FAB MS spectra were measured with 3-nitrobenzyl alcohol (NBA) as the matrix. Analytical thin layer chromatography (TLC) was performed on Silica gel 60 F$_{254}$ Merck. Column chromatography was performed on KANTOSil60N (neutral). Absorption spectra were recorded on a SIMAZU IR spectrophotometer. IR spectra were recorded on a SHIMAZU spectrometer. Redox potentials were carried out on a BAS-100B/W electrochemical analyzer. CV measurements were performed using a cell equipped with glassy carbon as the working electrode, platinum wire as the counter electrode, and Ag/AgNO$_3$ as the reference electrode. All electrochemical measurements were performed under an Ar atmosphere at room temperature in THF solution (5 × 10$^{-4}$ M) containing 0.1 M tetra-n-butylammoniumhexafluorophosphate (Bu$_4$NPF$_6$) as a supporting electrolyte at a scan rate of 100 mV/s. The ferrocene/ferrocinium (Fc/Fc') couple was used as an internal standard. THF was distilled from sodium benzenophenyl ketyl. Toluene was distilled from CaH$_2$. Other solvents and reagents were of reagent grade, purchased commercially, and used without further purification.

Dye-loaded 1.0 wt% Pt-TiO$_2$ nanoparticle
The procedure of 1.0 wt% Pt-loaded TiO$_2$ nanoparticle was followed reiterately. The commercially available of TiO$_2$ source (1.0 g, < 25 nm, anatase) was added MeOH (25 mL) and H$_2$PtCl$_6$ (0.25 mL, 8 wt%). The mixture was irradiated the Xe lamp (300 W) at 25 min., produced TiO$_2$-Pt nanoparticle. The TiO$_2$-Pt nanoparticle was separated by centrifuge (3600 rpm 20 min), then separated TiO$_2$-Pt nanoparticle was filtrated, washed MeOH successively. This was dried under vacuum, gave Pt-loaded TiO$_2$ nanoparticle.

1.0 wt% Pt-loaded TiO$_2$ (100 mg) was immersed in a MeOH solution containing 3 × 10$^{-4}$ M dye sensitizers (10 mL) for at least 12 h under the dark, centrifuged (3600 rpm 20 min), rinsed with anhydrous MeOH and dried under vacuum.

Water splitting reaction
The photocatalytic water splitting experiment was performed with a conventional closed circulating system with a dead volume of approximately 500 mL. The Pt/dye/TiO$_2$ catalyst 33 mg was suspended in 10 mL of 10 v/v% triethanol amine water (pH= 7.0, adjust with HClaq). A quartz reaction cell was irradiated by an external light source comprising a 300 W Xe lamp (Ushio Inc., Japan) with < 420 nm cutoff glass filter. During the H$_2$O photochemical reaction, reaction mixture was mixed with a magnetic stirring bar. Amounts of H$_2$ gas amount was measured with a TCD gas chromatograph (GC-8A, Shimadzu Corp., Japan, which was connected to a conventional volumetric circulating line with a vacuum pump.

To determine the quantum efficiency for hydrogen conversion of water. We estimated the efficiency by changing the light source equipment for using a single wavelength at 420 nm (7.36 mW/cm$^2$) (ASAHI SPECTRA MAX-303). The reaction surface area were 17.34 cm$^2$. The calculation of the quantum efficiency at 420±10 nm was used as equation 1.

$$\phi = \frac{\text{Number of electrons}}{\text{Number of incident photons}} \hspace{1cm} (1)$$

Time resolved absorption spectroscopy
The titania-oxide pastes of Ti-nanoxide T/SP that was purchased from Solaronix. The quartz plate (transmission > 90% in the visible) was used as substrate. A thin film of TiO$_2$ (8–10 mm) was coated on a quartz substrate. It was immersed in an anhydrous MeOH solution containing 3 x 10$^{-4}$ M dye sensitizers for at least 12 h, then rinsed with anhydrous MeOH and dried. Time resolved absorption spectra of dyes on thin-film or in solution were performed in an ambient atmosphere. The femtosecond time resolved absorption data were collected with a pump and probe time-resolved absorption spectroscopy system (Ultrafast Systems, Helios). The pump light (400 nm) was used from an amplified Ti:sapphire laser system (Spectra-Physics, Solstice)100F, < 100 fsec, 5 kHz). The UV/Vis range (450–750 nm) was detected with a sapphire laser system (Ultrafast Systems, Helios). The pump light (400 nm) was used as substrate. A thin film of TiO$_2$ (8–10 mm) was coated on a quartz substrate. It was immersed in an anhydrous MeOH solution containing 3 x 10$^{-4}$ M dye sensitizers for at least 12 h, then rinsed with anhydrous MeOH and dried. Time resolved absorption spectra of dyes on thin-film or in solution were performed in an ambient atmosphere. The femtosecond time resolved absorption data were collected with a pump and probe time-resolved absorption spectroscopy system (Ultrafast Systems, Helios). The pump light (400 nm) was used from an amplified Ti:sapphire laser system (Spectra-Physics, Solstice)100F, < 100 fsec, 5 kHz). The UV/Vis range (450–750 nm) was detected with a linear CCD array (Ocean Optics, S2000). The fitting was used triple exponential decay fitting as equation 2 for dye 2 and 3, while single exponential decay fitting as equation 3 for dye 1.

$$\Delta OD = A_1 \exp\left[\frac{-(t-t_0)}{\tau_1}\right] + A_2 \exp\left[\frac{-(t-t_0)}{\tau_2}\right] + A_3 \exp\left[\frac{-(t-t_0)}{\tau_3}\right] + A_{off} \hspace{1cm} (2)$$

$$\Delta OD = A_1 \exp\left[\frac{-(t-t_0)}{\tau_1}\right] + A_{off} \hspace{1cm} (3)$$

where $A_{off}$ is off-set of intensity at the fitting range of decay.

Synthetic Procedure
12-methyl-12H-benzo[b]phenothiazine 5
A mixture of 12H-benzo[b]phenothiazine 4 (3.05 g, 12.2 mmol) and THF (100 mL) were added the tBuOK (2.06 g, 18.4 mmol) at 0 °C in N$_2$ atmosphere. After 30 min, MeI (1.53 mL, 24.6 mmol) was added one portion and the mixture was stirred overnight at room temperature in N$_2$ atmosphere. The mixture was quenched with water, extracted with CH$_2$Cl$_2$, washed by anhyd. MgSO$_4$. Silicagel chromatography with CH$_2$Cl$_2$:hexane=1:3 to give 12-methyl-12H-benzo[b]phenothiazine 5 (1.42 g, 44 %) as pale yellow solid.

Phthalic acid of 5: Mp184–186°C. $\delta$$_H$ (CDCl$_3$, 500 MHz) 3.49 (s, 3H), 6.88 (d, $J$ = 6.6 Hz, 1H), 6.94-6.96 (m, 1H), 7.06 (s 1H), 8.07 (s, 1H), 8.38 (s, 1H).
251.56, 125.6, 126.3, 126.37, 126.4, 127.0, 127.2, 127.3, 128.2, 130.7, 131.0, 134.6, 146.2, 146.3; MS (MALDI) m/z [M+H]+: calcd for C17H16NO2S; 292: found: 292.

The mixture of aldehyde 6 (1.28 g, 4.39 mmol) and dried THF (373 mg, 9.80 mmol) at 0 °C in N2 atmosphere. After 1 h, the reaction mixture was quenched with water, extracted with CH2Cl2. Organic layer was washed with water, and dried with anhyd MgSO4. Silicagel chromatography with CH2Cl2-hexane:1=5:1 to give 12-methyl-12H-benzo[b]phenothiazine-11-carbaldehyde 6 (1.18 g, 84%).

The mixture of thiophene)2,5)dicarboxyaldehyde 5 (1.32 g, 5.01 mmol) was added and heated at 60 °C for 36 h. The reaction mixture was poured into ice-water, extracted with CH2Cl2. Organic layer was washed with water, and dried with anhyd MgSO4. Silicagel chromatography with CH2Cl2-hexane:1=1:1 to give 12-methyl-12H-benzo[b]phenothiazine-11-carbaldehyde 6 (1.14 g, 78%) as pale yellow solid.

Physical data of 6: Mp104-105°C. δH (CDCl3, 500 MHz) 3.74 (s, 3H), 7.01-7.05 (m, 1H), 7.11-7.16 (m, 2H), 7.22-7.26 (m, 1H), 7.36-7.39 (m, 1H), 7.48-7.52 (m, 1H), 7.60 (d, J = 7.95, 1H), 7.64 (s, 1H), 8.88 (d, J = 4.6, 1H), 10.4 (s, 1H) δC (CDCl3, 125 MHz) 47.0, 118.4, 119.3, 123.8, 124.4, 125.4, 125.5, 126.6, 127.0, 127.5, 128.3, 129.5, 130.2, 131.0, 145.6, 150.4, 190.4; MS (MALDI) m/z [M+H]+: calcd for C17H16NO2S; 292: found: 292.

The mixture of thiophene)2,5)dicarboxyaldehyde 5 (1.32 g, 5.01 mmol) and methyl)4)methyl)12)methyl)12)benzaldehyde 6 (1.28 g, 4.39 mmol) in DMF (30 mL) over 3h at 70 °C in N2 atmosphere. After 1 h, the reaction mixture was quenched with water, extracted with CH2Cl2. Organic layer was washed with water, and dried with anhyd MgSO4. Silicagel chromatography with CH2Cl2-hexane:1=5:1 to give aldehyde 6 (484 mg, 50%).

The mixture of [2,2'-bithiophene]-5,5'-dicarbaldehyde 10 (444 mg, 2.00 mmol), 18-crown-6 (28 mg, 0.11 mmol), K2CO3 (550 mg, 3.98 mmol), and DMF (30 mL) was dropwised the mixture of adduct 8 (1.24 g, 2.00 mmol) in DMF (30 mL) over 3h at 70 °C in N2 atmosphere. The reaction mixture was stirred further 3h at 70 °C. The reaction mixture was quenched with water, extracted with CH2Cl2. The organic layer was washed with brine, and dried with anhyd MgSO4. Silicagel chromatography with CH2Cl2-hexane:1=1:1 to give aldehyde 10 (484 mg, 50%).

A mixture of aldehyde 6 (633 mg, 1.58 mmol), cyanoacetic acid (820 mg, 9.64 mmol), ammonium acetate (36 mg, 0.45 mmol), and glacial acetic acid (70 mL) was heated at 90 °C for overnight in N2 atmosphere. After reaction mixture was cooled, the reaction was quenched with water, extracted with THF. The organic layer was washed with brine, and dried with anhyd Na2SO4. Silica gel chromatographed with CH2Cl2-CsOH:ACOH=40:1 to give target compound 1 (268 mg, 48%) as red colored solid.

A mixture of thiophene)2,5)dicarboxyaldehyde 9 (1.18 g, 8.42 mmol), 18-crown-6 (30 mg, 0.11 mmol), K2CO3 (570 mg, 4.12 mmol), and DMF (30 mL) was dropwised the mixture of adduct 8 (1.30 g, 2.10 mmol) in DMF (30 mL) over 3h at 70 °C in N2 atmosphere. The reaction mixture was stirred further 3h at 70 °C. The reaction mixture was quenched with water, extracted with CH2Cl2. The organic layer was washed with brine, and dried with anhyd MgSO4. Silicagel chromatography with CH2Cl2-hexane:1=1:1 to give aldehyde 11 (442 mg, 56%).

A mixture of [2,2'-bithiophene]-5,5'-dicarbaldehyde 10 (444 mg, 2.00 mmol), 18-crown-6 (28 mg, 0.11 mmol), K2CO3 (550 mg, 3.98 mmol), and DMF (30 mL) was dropwised the mixture of adduct 8 (1.24 g, 2.00 mmol) in DMF (30 mL) over 3h at 70 °C in N2 atmosphere. The reaction mixture was stirred further 3h at 70 °C. The reaction mixture was quenched with water, extracted with CH2Cl2. The organic layer was washed with brine, and dried with anhyd MgSO4. Silicagel chromatography with CH2Cl2-hexane:1=1:1 to give aldehyde 10 (484 mg, 50%).

The mixture of [2,2'-bithiophene]-5,5'-dicarbaldehyde 10 (444 mg, 2.00 mmol), 18-crown-6 (28 mg, 0.11 mmol), K2CO3 (550 mg, 3.98 mmol), and DMF (30 mL) was dropwised the mixture of adduct 8 (1.24 g, 2.00 mmol) in DMF (30 mL) over 3h at 70 °C in N2 atmosphere. The reaction mixture was stirred further 3h at 70 °C. The reaction mixture was quenched with water, extracted with CH2Cl2. The organic layer was washed with brine, and dried with anhyd MgSO4. Silicagel chromatography with CH2Cl2-hexane:1=1:1 to give aldehyde 10 (484 mg, 50%).

The mixture of thiophene)2,5)dicarboxyaldehyde 9 (1.18 g, 8.42 mmol), K2CO3 (570 mg, 4.12 mmol), and DMF (30 mL) was dropwised the mixture of adduct 8 (1.30 g, 2.10 mmol) in DMF (30 mL) over 3h at 70 °C in N2 atmosphere. The reaction mixture was stirred further 3h at 70 °C. The reaction mixture was quenched with water, extracted with CH2Cl2. The organic layer was washed with brine, and dried with anhyd MgSO4. Silicagel chromatography with CH2Cl2-hexane:1=1:1 to give aldehyde 11 (442 mg, 56%).
Na₂SO₄. Silica gel chromatographed with CH₂Cl₂-
CH₂Cl₂:AcOH=40:1 to give target compound 2 (342 mg, 70%) as
red colored solid.

Physical data of 2: Mp261-263°C (decomp.). δH (CDCl₃, 500
MHz) 3.44 (s, 3H), 6.84 (t, J = 15.9 Hz, 1H), 6.94 (t, J= 6.6 Hz,
1H), 7.00 (t, J = 7.6 Hz, 1H), 7.13-7.20 (m, 2H), 7.28-7.33 (m,
2H), 7.36 (t, J = 7.5 Hz, 1H), 7.58 (s, 1H), 7.64 (d, J = 7.3 Hz,
1H), 7.77-7.85 (m, 2H), 8.01 (d, J = 7.6 Hz, 1H), 8.38 (s, 1H).δC
(CDCl₃, 100 MHz) 43.7, 100.2, 116.5, 118.8, 233.9, 123.9,
124.7, 125.3, 126.8, 127.0, 127.1, 127.8, 128.1, 128.3, 130.4,
131.2, 132.7, 133.8, 136.3, 142.7, 146.4, 149.9, 152.6,
164.0.; ν(KBr) 1686 (C=O), 2220 (C≡N), cm⁻¹; HRMS (FAB)
m/z [M]+: calcd for C₁₂H₁₅O₉N₂S₂466.0810; found: 466.0812

(E)-2-cyano-3-(5′-((E)-2-(12-methyl-12H-
benzo[b]phenothiazin-11-yl)vinyl)-[2,2′-bithiophen]-5-yl)acrylic
acid 3

A mixture of aldehyde 12 (460 mg, 0.96 mmol), cyanoacetic
acid (107 mg, 1.24 mmol), ammonium acetate (23 mg, 0.29
mmol), and glacial acetic acid (70 mL) was heated at 90°C for
overnight in N₂ atmosphere. After reaction mixture was cooled,
the reaction was quenched with water, extracted with THF. The
organic layer was washed with brine, and dried with anhyd
Na₂SO₄. Silica gel chromatographed with CH₂Cl₂-
CH₂Cl₂:AcOH=40:1 to give target compound 3 (395 mg, 75%) as
red colored solid.

Physical data of 3: Mp226-228°C (decomp.). δH (CDCl₃, 500 MHz) 3.45 (s,
3H), 6.75 (d, J = 15.7 Hz, 1H), 6.94 (t, J = 6.9 Hz, 1H), 7.01 (d, J
= 7.5 Hz, 1H), 7.12-7.21 (m, 2H), 7.26-7.32 (m, 2H), 8.35 (t, J =
7.5 Hz, 1H), 7.44 (s, 1H), 7.47 (s, 1H), 7.54-7.60 (m, 2H), 7.64
(d, J = 7.4 Hz, 1H), 7.80 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 8.35 (s,
1H). δC (CDCl₃, 125 MHz) 43.6, 100.0, 116.6, 118.8, 123.3,
123.8, 124.8, 125.0, 125.3, 125.6, 126.7, 127.1, 127.11, 127.2,
127.8, 128.0, 128.2, 128.4, 128.8, 129.0, 131.6, 132.8, 133.9,
135.8, 135.9, 140.1, 42.5, 146.2, 147.1, 149.1, 164.0.; ν(KBr)
1686 (C=O), 2216 (C≡N), cm⁻¹; HRMS (FAB) m/z [M]+: calcd
for C₁₅H₁₅O₉N₂S₂548.0687; found: 548.0680