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Phenothiazine-based organic dyes with two anchoring groups on TiO_2 for highly efficient visible light-induced water splitting[†]

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New phenothiazine-based organic dyes with two anchoring groups at 3,7 positions and systematic alkyl chains on nitrogen were prepared. Their TiO_2 -Pt composites showed excellent photo-catalytic activities in visible light-induced water splitting. Interestingly, phenothiazine dyes with longer alkyl chains showed better stability in catalytic systems.

As renewable energy resources become an important issue, use of solar energy for diverse chemical transformations has been an attractive research subject.¹ Especially, the production of hydrogen from water using solar energy has attracted special attention from scientists.² Since the early 1970s, it has been known that photo energy from ultraviolet (UV) light can be used to split water into hydrogen and oxygen using wide-bandgap semiconductors such as TiO₂.³ Moreover, utilizing the appropriate dyes with semiconductors, visible light can be used for water splitting.⁴ Although there has been some progress in the development of dyes, there should definitely be more extensive studies for more active systems.

As visible light sensitizers on TiO_2 , ruthenium-based dyes have been extensively used for water splitting.⁵ Although there have been recent studies on organic dye systems, efficient systems are rare due to the relative instability of organic systems.^{4,6} During the operation of catalytic systems, the photo-excited dyes transfer electrons to semiconductor materials to form transient cationic radical species which retrieve electrons from additional sacrificing compounds. In this process, the dyes are subject to decomposition, resulting in low turnover number (TON). Thus, more exploration for stable and efficient dyes is required.

Phenothiazines are cyclic compounds with amine and sulfide moieties.⁷ One of the interesting aspects of phenothiazines is the intriguing stability of their cationic radical formed by one electron oxidation⁷ (Fig. 1). Thus, it can be speculated that the phenothiazine-based dyes can have enhanced stability in photo-induced electron transfer from dyes to TiO₂. Based on this unique redox



Fig. 1 Structural analysis of the phenothiazine-based organic dyes used in this study and an illustration of visible light-driven water splitting.

behavior, diverse redox devices including electrochromic displays have been developed using phenothiazines.^{7,8} However, as far as we are aware, the application of phenothiazine derivatives for photocatalytic water splitting has not been reported.

For controlling the chemical surroundings, diverse functional groups can be easily introduced at the nitrogen of phenothiazines. It is noteworthy that the substituents in dyes such as long alkyl chains could enhance electrochemical performance.9 In addition, two anchoring groups can be introduced at the 3 and 7 positions of phenothiazine systems. The multi-anchoring groups can enhance the stability of catalytic systems during the photocatalytic reactions.¹⁰ Usually, N-substituted simple phenothiazines are colorless and cannot absorb visible light. However, further introduction of electron withdrawing groups into aromatic rings in phenothiazines can induce shift of the absorption band into the visible light region. It has been reported that phenothiazine-based dyes with a directly connected anchoring group showed higher visible light harvesting efficiencies in dye-sensitized solar cells than typical donor-acceptor type dyes with additional π -conjugated bridges.¹¹ Thus, we designed the straightforward phenothiazine-based dyes (P1-P5) with two anchoring groups, as shown in Fig. 1.

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In this work, we report on the preparation of phenothiazinebased organic dyes with systematic alkyl chains and two anchoring groups, their TiO₂–Pt composites, and the promising photo-catalytic activities in visible light-induced water splitting.

For preparation of the target dyes, alkyl groups were first introduced into nitrogen by reaction of phenothiazine with alkyl halides (Scheme 1). Through Vilsmeier reaction,¹² two formyl groups were introduced at the 3 and 7 positions. Then, Knoevenagel condensation¹² with cyanocarboxylic acid in the presence of base resulted in target dyes with two anchoring groups. The introduction of cyanocarboxylic acid to *N*-alkyl-phenothiazines induced a color change from colorless to deep red.

Fig. 2, Fig. S1 in the ESI[†] and Table 1 show optical and electrochemical properties of the prepared dyes (P1, N-ethyl; P2, N-butyl; P3, N-octyl; P4, N-dodecyl; P5, N-hexadecyl). The dyes P1-P5 showed maximum absorption peaks at 476-463 nm in UV/vis absorption spectroscopy, corresponding to deep red color. The optical properties of dyes were retained on TiO₂ (Fig. 2a). Cyclic voltammetry of dyes revealed reversible one-electron oxidation behavior (Fig. 2b). The length of alkyl chains on nitrogen showed little effect on the optical and electrochemical properties. Based on UV/vis absorption spectra and cyclovoltammograms of P1-P5, the HOMO and LUMO values were calculated. The 0-0 transition energies of dyes were calculated in the range of 2.19-2.23 eV, indicating suitable values for visible light absorption. The locations of HOMO and LUMO were calculated as -5.4 and -3.2 eV respectively. Considering the location of conduction



Scheme 1 Synthetic route for the phenothiazine-based organic dyes used in this study.



Fig. 2 UV-vis absorption spectra and cyclic voltammograms of dyes.

Table 1 Optical and electrochemical properties of P1-P5

| Dyes | $\lambda_{\max}/\epsilon^a$ (nm/M ⁻¹ cm ⁻¹) | $\begin{array}{c} E_{0-0}{}^{b}\\ (eV)\end{array}$ | $\begin{array}{c} E_{\mathrm{ox1/2}}{}^{c}\\ \mathrm{(V)} \end{array}$ | HOMO ^d (eV) | LUMO ^e (eV) |
|------|---|--|--|---------------------------|---------------------------|
| P1 | 476/13 200 | 2.19 | 0.52 | -5.40 | -3.21 |
| P2 | 467/13 400 | 2.21 | 0.54 | -5.42 | -3.21 |
| P3 | 466/13 300 | 2.23 | 0.55 | -5.43 | -3.20 |
| P4 | 464/13 600 | 2.23 | 0.55 | -5.43 | -3.20 |

^{*a*} UV-vis absorption band obtained in γ-butyrolactone (GBL). ^{*b*} 0–0 Transition energy measured at the onset of absorption spectra. ^{*c*} Oxidation potential (*vs.* ferrecene, Fc/Fc⁺) measured using 0.10 M Bu₄NPF₆ in GBL, ITO and Ag/Ag⁺ as the electrolyte solution, working and reference electrode respectively. ^{*d*} HOMO value calculated using potential value of oxidative waves. ^{*e*} LUMO value calculated by HOMO + E_{0-0} .

and valence bands of TiO_2 ,¹³ **P1–P5** are suitable as dyes for visible light-driven water splitting through complexation with TiO_2 .

To develop the visible light-driven catalytic systems for water splitting, Pt nanoparticles were loaded on commercial TiO₂ nanoparticles by a known method in the literature.¹⁴ Then, the prepared dyes were adsorbed on TiO₂-Pt composites by treating composites with 3×10^{-4} M methanolic solutions of the dyes. The concentration of the dyes was optimized by screening concentrations (see Fig. S2 in the ESI⁺). After retrieving the dye-TiO₂-Pt composites by centrifugation, the remaining solution became colorless, indicating that the used dves were completely adsorbed on TiO₂-Pt nanoparticles. Using the dye-adsorbed TiO₂-Pt composites, photocatalytic performances were investigated in aqueous solution with a 200 W xenon lamp and triethanolamine (TEOA) as sacrificing reagents (see the ESI[†] for details). Light with wavelengths shorter than 420 nm was cut off with an optical filter. For comparison experiments, dye-TiO2-Pt composite materials were prepared using commercial N719 and eosin Y via the same experimental procedure. Fig. 3 shows the photocatalytic performances of the prepared catalytic systems.

According to Fig. 3 and Table 2, the photocatalytic activities are summarized by two striking features. First, the phenothiazine-based dyes showed significantly higher TONs (380-1026 after 5 hours) than N719 (120 TON after 5 hours) and eosin Y (160 TON after 5 hours). It is noteworthy that a TON result (100 after 8 hours) similar to ours for N719 was reported in recent ruthenium-based water splitting.¹⁵ Moreover, P2 and P5 with two anchoring groups showed the higher TONs than dyes with one anchoring group (see Fig. S3 in the ESI[†]). The higher TON values of the P1-P5 could have originated from the stability of cationic species of phenothiazine-based dyes, as shown in their electrochemical behavior. Second, the photocatalytic activities of P1-P5 were quite dependent on the alkyl groups on nitrogen. As the length of alkyl chains on nitrogen became longer, higher turnover numbers (TON) were observed. Thus, among the prepared dyes, the P5 with the hexadecyl group on nitrogen of phenothiazine showed the best result with 254 µmol H₂ generation after 5 hours, corresponding to 1026 TON. These observations imply that the longer alkyl chains play a positive role in maintaining the stability of catalytic cycles.

Recently, it was reported that the introduction of long alkyl chains to ruthenium dyes enhanced the performance of solar cells.⁹



Fig. 3 Photocatalytic activities of the dyes (P1–P5, N719 and eosin Y) in visible light-driven water splitting; reaction conditions: 5 mL 10% (v/v) TEOA, 16.5 mg dye–TiO₂–Pt composites (0.495 μ mol dye), pH 7.0.

 Table 2
 Photocatalytic performances of dyes (P1-P5)^a

| Dyes | Amount of $H_2^{\ b}$ (µmol) | TON^c | $TOF^{d}(h^{-1})$ |
|------|------------------------------|---------|-------------------|
| P1 | 94 | 380 | 76 |
| P2 | 109 | 440 | 88 |
| P3 | 150 | 606 | 121 |
| P4 | 198 | 800 | 160 |
| P5 | 254 | 1026 | 205 |

^{*a*} A 200 W Xe lamp was used (the light below 420 nm was cut off by an optical filter). ^{*b*} Amount of H₂ after 5 hours. ^{*c*} TON = $(2 \times \text{amount of H}_2)$ /amount of dye after 5 hours. ^{*d*} Values after 5 hours.

It has been reported that the long alkyl chains retard the decomposition of excited states by blocking the possible reactions with unfavorable chemical quenchers.⁹ We speculate that a similar effect can be valid for this work. Moreover, the alkyl groups on nitrogen can induce a favorable orientation of dyes on TiO_2 , which may result in the efficient electron injection from excited dyes to TiO_2 .⁹ As shown in Fig. 4, density functional theory (DFT) calculation was performed for **P5**. The major electron densities of HOMO and LUMO states of the **P5** are located on the phenothiazine ring and cyanoacetate groups, respectively. Thus, it is expected that photo-excitation can induce intramolecular charge transfer from the phenothiazine ring to cyanoacetate groups.

In conclusion, phenothiazine-based organic dyes were prepared and showed highly efficient performances in visible light-driven water splitting. The alkyl chains on the nitrogen of the phenothiazine ring further enhanced the TON values up to 1016 after 5 hours. This work shows that phenothiazines are promising building blocks for visible light harvesting materials in photocatalytic water splitting.



Fig. 4 HOMO and LUMO states of P5 and their electron densities.

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