

Research Article

Steric and Solvent Effect in Dye-Sensitized Solar Cells Utilizing Phenothiazine-Based Dyes

Hany Kafafy,^{1,2} Hongwei Wu,¹ Ming Peng,¹ Hsienwei Hu,¹ Kai Yan,¹
Reda M. El-Shishtawy,³ and Dechun Zou¹

¹ Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

² Dyeing, Printing and Textile Auxiliaries Department, Textile Research Division, National Research Center, Dokki, Cairo 12622, Egypt

³ Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

Correspondence should be addressed to Dechun Zou; dczou@pku.edu.cn

Received 11 December 2013; Accepted 14 February 2014; Published 17 March 2014

Academic Editor: Chuanyi Wang

Copyright © 2014 Hany Kafafy et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Three phenothiazine-based dyes have been prepared and utilized as dye-sensitized solar cells (DSSCs). The effects of dye-adsorption solvent on the performances of dye-sensitized solar cells based on phenothiazine dyes were investigated in this study. The highest conversion efficiency of 3.78% was obtained using ethanol (EtOH) and 2.53% for tetrahydrofuran (THF), respectively, as dye-adsorption solvents. Cell performance using EtOH as a dye-adsorption solvent showed relatively higher performance than that using THF. Electrochemical and photochemical tests of phenothiazine dyes in solution and adsorbed on the TiO₂ surface showed less dye loading and coverage on the TiO₂ surface during adsorption in the case of THF, which decreased the solar cell performance of the DSSC using THF as adsorption solvent compared with using EtOH as adsorption solvent. Meanwhile, the steric effect of phenothiazine-based (PT1–3) dyes was also investigated. Dye with longer and branched aliphatic chain in the order of PT1, PT2, and PT3 showed an increased resistance of the recombination reaction and electron lifetime, thereby increasing V_{oc} and enhancing the overall cell performance because of the sterically hindered conformation of the phenothiazines.

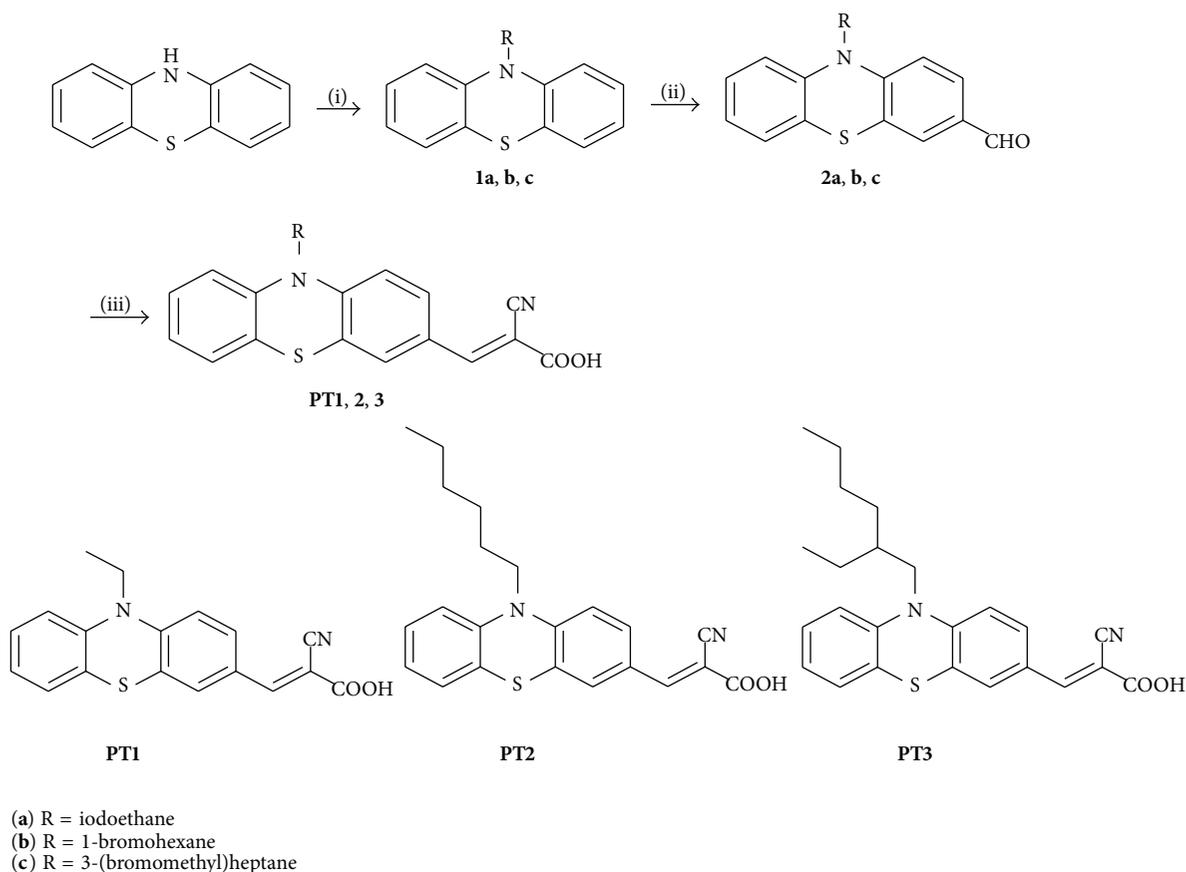
1. Introduction

The increasing consumption of fossil and the more serious crisis of environment pollution have led us to the search for new and renewable energy sources. Solar energy is widely recognized as the most promising candidate in helping solve this problem. Dye-sensitized solar cells (DSSCs), also known as Grätzel cells, offer a viable alternative to conventional all-inorganic solar cells because of their lower production cost. During the past decades, DSSCs have attracted significant attention as an alternative to silicon solar cell because they use environmentally benign materials through low cost process and exhibit commercially realistic energy-conversion efficiency [1–3]. The photon-to-current conversion of DSSCs is achieved by ultrafast electron injection from a photoexcited dye into the conduction band of the TiO₂, followed by dye regeneration and hole transportation to

the counter electrode. To enhance the performance of the DSSC, extensive research has been performed on semiconductor nanocrystalline TiO₂ electrodes [4–6], dye molecule [7–10], electrolytes [11–14], and counter electrodes [15].

Compared with the rare and expensive metal complexes, organic dyes have the advantages of being eco-friendly, having flexible and diverse form of molecular structures, lower cost, generally high molar extinction coefficients, and easier preparation and purification. Metal-free organic dyes have been widely investigated recently, many of which exhibited an energy-to-electricity conversion efficiency close to that of N719 [16–21].

The design of organic dyes for DSSCs is important to improve the value of the short-circuit current (J_{sc}) and the open-current voltage (V_{oc}). The π -conjugation of the J_{sc} must be improved so the organic chromophore can harvest light energy to a large extent. An effort of reducing the rate of



SCHEME 1: Synthesis route of phenothiazine (PT). Dyes: (i) KOC (CH₃)₃, THF, 66°C, 18 h; (ii) DMF, CHCl₃, 0°C, phosphorus oxychloride, reflux overnight; (iii) cyanoacetic acid, NH₄OAc, AcOH, 90–100°C.

charge recombination is necessary for the V_{oc} to minimize current leakage.

Whether the low voltages from organic dyes may be due to fast recombination kinetics is still being debated [22, 23]. A strong interaction between organic dye and iodine in the electrolyte has been proposed to be responsible for accelerating recombination [24, 25]. Also, the lack of electron donating moiety in the oxidized organic dye has also been proposed to have an influence on fast recombination reaction, compared with N719 with electron donating NCS ligand [26]. In addition, dye aggregation due to planar or sterically less-hindered structure has also been proposed as one of major factors for the lowering voltage [27, 28]. Thus, a molecular structure of organic dye must be designed to reduce recombination and/or prevent dye aggregation. Recently, heterocyclic phenothiazine (PT), originally used in drug applications [29, 30], has been adopted as a novel electron donor in organic dye because PT contains electron-rich sulfur-nitrogen heteroatoms and its ring has sterically hindered nonplanar butterfly conformation. In addition, the incorporation of PT derivatives in organic dye backbone is expected to inhibit molecular aggregation.

Most studies have focused on enhancing the properties of the photoelectrode, specifically the dye, which is responsible for most light absorption. Some of the important properties that need to be considered when designing sensitizers for

DSSCs are the geometric structures, molecular orbital energy, absorption profiles, and aggregation states of the dye [31, 32].

In this study, the effect of THF and EtOH on the absorption and solar cell performance was studied and evaluated. The synthesis and application of three dyes composed of N-substituted phenothiazine units (PT1–3) shown in Scheme 1 as sensitizers in dye-sensitized solar cells have been investigated. A cyanoacrylate group was attached to one side of the compound, acting as an electron acceptor. We envisioned that the nonplanar conformation of phenothiazine can reduce the rate of charge recombination and molecular aggregation. The synthetic procedures of PT1–3 are described in Scheme 1. All structures have been confirmed by their NMR, MS, and spectroscopic data. The photovoltaic performance and electrochemical properties of devices based on the three dyes using THF and EtOH solvents were evaluated by different spectroscopic techniques.

2. Experimental Section

2.1. Materials and Synthesis

2.1.1. General Considerations. Reagents, catalysts, ligands, and solvents were purchased reagent grade and used without further purification. The details of the synthetic procedure

of the **PT1–3** dyes were prepared according to the literature procedures, as shown in Scheme 1 [33–35]. N-alkylation of phenothiazine followed by Vilsmeier-Haack formylation and then Knoevenagel condensation between the carbaldehyde and cyanoacetic acid in the presence of ammonium acetate affords the desired dyes. Column chromatography was made using silica gel 60, mesh 70–230. TLC silica gel plates, 60 F₂₅₄, were also used. Lithium perchlorate (LiClO₄, 99%) and 4-tert-butylpyridine (TBP) were obtained from Sigma-Aldrich. Acetonitrile (AN) solvent as purchased from Siyou Inc., Tianjin, China. The substance I₂ (AR) was acquired from the Beijing Chemical Reagent Company. FTO glasses and TiO₂ paste (DSL-18NR-T), with diameter of 20 nm, and the electrolyte components were obtained from Heptachroma Inc., Dalian, China.

2.2. Characterization and Measurement. UV-Vis absorbance spectra were recorded on a lambda 35 UV/Vis Spectrometer (Perkin Elmer). All dyes were dissolved in THF and EtOH solution as bath solvent, and the concentrations of solutions used in the absorption experiment were set as 5×10^{-5} M. ¹H NMR and ¹³C NMR spectra were measured at room temperature on a 400 MHz (Bruker) spectrometers, respectively, using DMSO-d₆ or CDCl₃ as the solvents. The electrospray ionization mass spectra (ESI-MS) were characterized on an APEX IV Fourier transform ion cyclotron resonance mass spectrometer (Bruker).

2.3. Fabrication of DSSCs. The TiO₂ paste (DSL-18NR-T, diameter: 20 nm) was created on FTO glasses by screen printing. The obtained FTO glasses were sintered at 150°C for 15 min in a muffle furnace and then at 450°C for 30 min sequentially. The thickness of the TiO₂ film is approximately 3.5 μm after one screen printing. Through reciprocating the above steps three times, the TiO₂ film can reach up to 10.5 μm thick. After the last heated process, the TiO₂ electrodes were cooled to 100°C and then immersed into dye bath solution. After 24 h, the sensitized TiO₂ photoanodes were taken out from the dye solution, eluted by methanol to remove the excess dye from the TiO₂ surface, and were kept in vacuum drying oven at room temperature overnight. The counter electrode with a Pt film (thickness: approximate 50 nm) on the FTO glasses was prepared by magnetic sputtering. The obtained dye-adsorbed photoanodes (test area: ca. 0.25 cm²) and the Pt counter cathodes were assembled to form DSSCs and isolated by 25 μm thick hot-melt ionomer film (Surlyn, Dupont). The electrolytes were then injected into solar cells by preset pores in the counter electrode. Finally, the devices were sealed by Surlyn film to enhance the stability of the DSSCs.

2.4. Dye Bath Solutions. In this study, EtOH and THF bath solutions of **PT1–3** dyes (5×10^{-4} M) were prepared. The devices were soaked in EtOH and THF solution sensitizers for 24 h, respectively.

2.5. Measurement of Absorption Spectra in TiO₂. The TiO₂ paste was made on FTO glasses by screen printing.

The obtained FTO glasses were sintered at 150°C for 15 min in a muffle furnace and then at 450°C for 30 min sequentially. The thickness of the TiO₂ film was approximately 3.5 μm after one screen printing. The TiO₂ films were cooled to 100°C, and then immersed into different dye bath solutions. After 24 h, the sensitized TiO₂ photoanodes were taken out from the dye solution and eluted by methanol to remove the excess dye from the TiO₂ surface. The sensitized TiO₂ photoanodes were then immersed in 0.1 M solution of (CH₃)₄NOH base in ethanol overnight to extract the dye from the TiO₂ film. The film area was 0.64 cm² and thickness 10.5 μm and it was extracted in 9 mL of the (CH₃)₄NOH base in ethanol solution. The absorption spectra of the dyes in the extraction solution were then obtained.

2.6. Components of Electrolytes. The electrolyte used was iodide liquid electrolyte that was composed of acetonitrile solution of 0.03 M iodine, 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.05 M lithium perchlorate (LiClO₄), and 0.5 M 4-tert-butylpyridine (TBP).

2.7. Characterization of the Photoelectrochemical and Photovoltaic Properties. The photovoltaic performance of the devices was measured under AM 1.5 simulated sunlight illumination with a light intensity of 100 mW/cm². The simulated sunlight source was YSS-50A (Yamashita DESO). The electrochemical impedance spectra (EIS) were implemented on the Autolab (Frequency range: 100 kHz to 10 mHz). Two parameters, namely, chemical capacitance (C_m) and charge recombination resistance (R_{rec}), were obtained by fitting the EIS at different reverse biases with Z-View software according to the transmitting line mode. The incident photon-to-current efficiency (IPCE) was measured from 300 nm to 800 nm under SolarCellScan-100 (Beijing ZOLIX Corp.).

3. Results and Discussion

3.1. Synthesis. **PT1–3** dyes were prepared according to the literature procedures [33–37]. The sequence of reaction steps proceeds smoothly and efficiently to give a good yield of the product. Thus, N-alkylation of phenothiazine with different alkyl groups afforded the corresponding compounds **1a–c**, which upon Vilsmeier-Haack formylation gave the carbaldehyde **2a–c**. Knoevenagel condensation between **2a–c** and cyanoacetic acid in the presence of ammonium acetate produced the desired phenothiazine dyes **PT1–3**. All chemical structures were characterized by their spectroscopic data.

3.2. Absorption Spectra. The UV-Vis absorption spectra of all dyes in the EtOH and THF solutions are shown in Figure 1. Table 1 shows all the parameters; all the dyes exhibited broad absorption in the range of 250–350 nm and 370–525 nm. The short wavelength region at 280–340 nm is attributed to the localized $\pi-\pi^*$ and $n-\pi^*$ transitions, whereas the long wavelength region in the range of 390–510 nm is attributed to the charge transfer transitional energy of the delocalized $\pi-\pi^*$ transition as a result of donor- π -acceptor system. Compared with THF, the absorption bands of all dyes are relatively

TABLE 1: Absorption properties of **PT1-3** dyes in the EtOH and THF solutions.

Dye	EtOH		THF	
	ϵ ($M^{-1} cm^{-1}$)	λ_{max} (nm)	ϵ ($M^{-1} cm^{-1}$)	λ_{max} (nm)
1	9993	436	12027	447
2	10090	428	12719	447
3	10082	414	11014	436

TABLE 2: Photovoltaic performances of **PT1-3** dyes in different adsorption solutions.

Device	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE
E1	691	6.08	0.693	2.91%
E2	726	6.29	0.697	3.18%
E3	779	6.66	0.730	3.78%
T1	644	4.08	0.698	1.83%
T2	676	4.62	0.680	2.12%
T3	726	4.83	0.720	2.53%

E: EtOH; T: THF solutions. Photovoltaic performance was measured under AM 1.5 simulated sunlight illuminations with the light intensity $100 mW/cm^2$. Soaking time was 24 h. Electrolyte: mixture of 0.03 M iodine, 0.6 M (BMII), 0.05 M ($LiClO_4$), and 0.5 M (TBP) dissolved in AN.

blue-shifted using EtOH. This behavior would be attributed to the solvent effect. As **PT1-3** dyes are donor- π -acceptor system, charge transfer absorption band is destabilized in protic solvent such as ethanol due to hydrogen bonding interactions between ethanol and the donor and/or acceptor moieties [38, 39]. On the other hand, THF is aprotic solvent and less polar than EtOH; such effect does not exist and thus transfer absorption band is more favorable in this solvent than EtOH.

3.3. Photovoltaic Performance. Figure 2 shows the photocurrent-voltage curves and IPCE spectra for the **PT1-3** sensitized DSSCs in the EtOH and THF adsorption solvent. The corresponding photovoltaic parameters are listed in Table 2. The device performance of **PT1-3** dyes indicates that the devices using EtOH show a higher J_{sc} and a significantly higher V_{oc} than those obtained using THF, with a higher light conversion efficiency of **PT3** dye compared with those of **PT2** and **PT1**. The reasons for this inferior performance for the dyes using THF solution as mentioned before would be attributed to the smaller amount of adsorbed dye in the TiO_2 semiconductor due to the propensity of dye molecules to exist more in THF solvent rather than to get adsorbed and also due to the hydrogen bond interaction of the oxygen of the tetrahydrofuran and the hydrogen of the carboxylic acid of the dyes [40, 41]. Meanwhile, it was also noted that dyes with more branched alkyl groups show higher V_{oc} and J_{sc} in both EtOH and THF dye-bath solvent. We will discuss these afterwards.

The incident photon-to-current efficiency (IPCE) spectra as a function of the wavelength for DSSCs based on the **PT1-3** dyes in THF and EtOH is shown in Figure 4(c). The IPCE values of DSSCs based on **PT1-3** dyes when using EtOH exceeded 80% from 425 nm to 500 nm (with the highest value

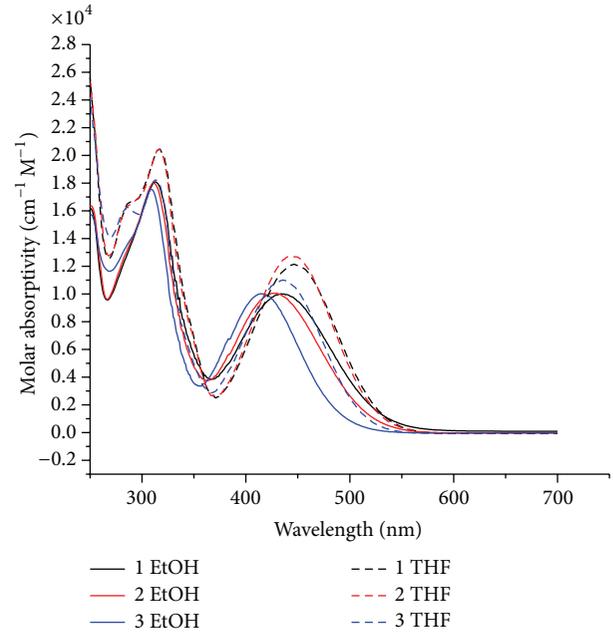


FIGURE 1: Absorption spectra of 5×10^{-5} M solutions of **PT1-3** dyes in EtOH and THF, respectively.

of 80.5% at 460 nm for **PT3** sensitized), whereas using THF only exceeded 50% from 425 nm to 475 nm (with the highest value of 55% at 430 nm **PT3** sensitized). The higher IPCE for **PT1**-, **2**-, and **3**-sensitized solar cells using EtOH can be ascribed to the larger adsorbed amount of **PT1-3** dyes compared with those obtained using THF, which is consistent with the obtained photovoltaic data for the **PT1-3** sensitizers under the same conditions, wherein the J_{sc} for the devices that use EtOH are much higher than those obtained using THF as dye-adsorption solvent.

The absorption spectra of all dyes extracted from the surface of TiO_2 film are shown in Figure 3. The absorption band displayed a blue shift of ca. 1–38 nm with respect to those in the solutions. The blue shift appeared to be a result of deprotonation of the carboxylic acid when anchored onto the titanium oxide surface. Similar to the case of ethanol effect on the absorption compared with THF, it is anticipated that deprotonation of the carboxylic group would lower its acceptability for electrons and thus would lead to the observed blue shift upon anchoring with TiO_2 . Additionally, a possible formation of H-aggregation for these dyes in the surface of TiO_2 would also lead to the observed blue shift [42].

3.4. Effect of the Adsorption Solvent on DSSC Performance.

The adsorption solvent has an indispensable role in the efficiency of solar cells that influences the dye loading on the TiO_2 surface and also has an important role in the formation of dye solvent- TiO_2 complex [43]. The cell performances of the **PT1**, **2**, and **3** dyes using EtOH and THF as dye-adsorption solvents are listed in Table 2. All the photovoltaic parameters, such as the J_{sc} , V_{oc} , and FF, were affected by the adsorption solvent. THF provides lower photovoltaic values

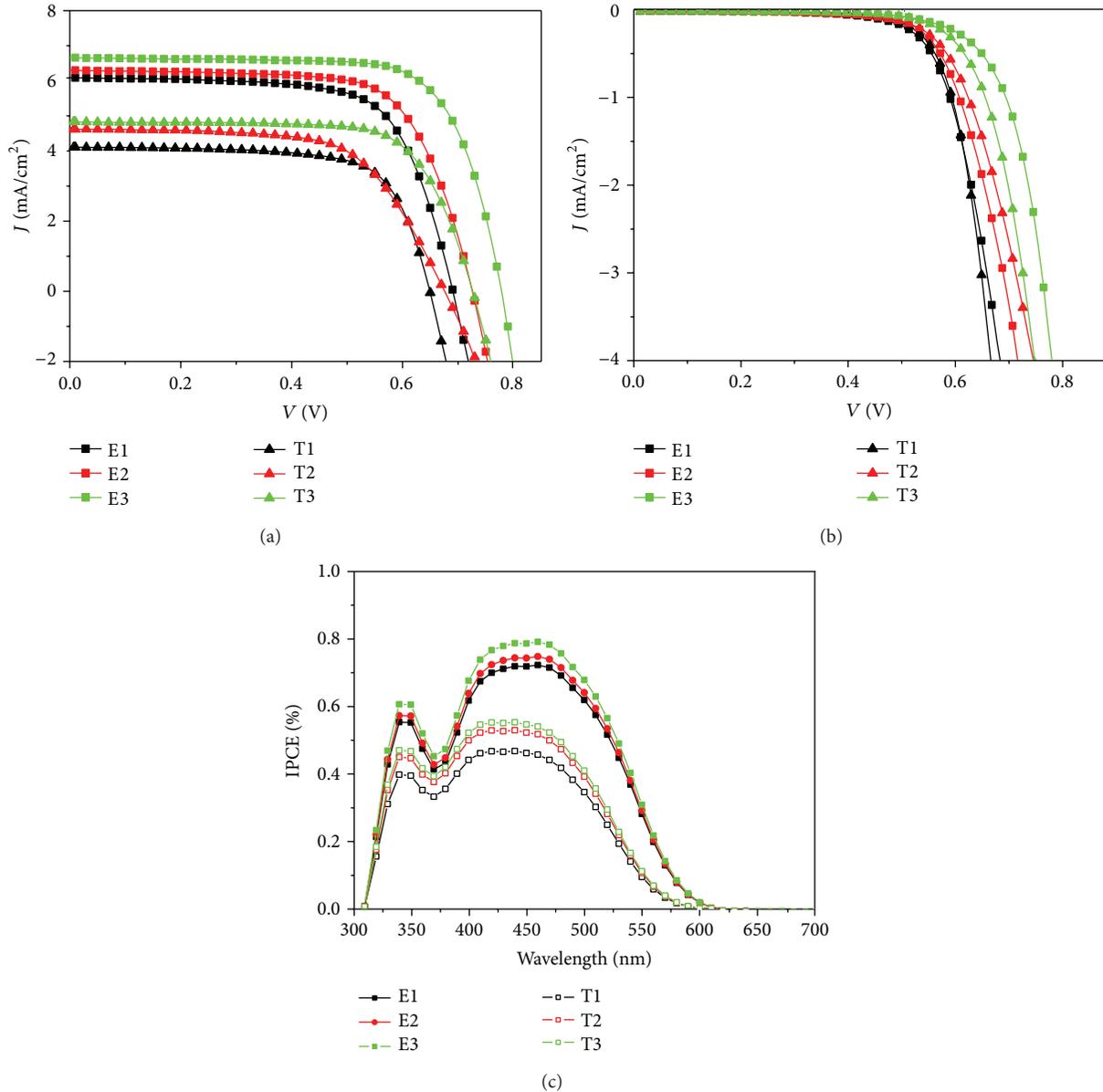


FIGURE 2: J - V plots under (a) simulated standard sunlight and (b) dark condition; (c) IPCE of devices E1-3 and T1-3.

compared with the EtOH measured under AM 1.5 simulated sunlight illuminations with the light intensity 100 mW/cm² conditions.

The use of THF as adsorption solvent decreases the photovoltaic efficiencies with respect to EtOH, which can be ascribed to the less dye loading from THF solution on the TiO₂ surface relative to EtOH, as shown in Figure 3. The use of THF as adsorption solvent decreases the photovoltaic efficiencies compared with EtOH case, which could be ascribed to the less dye loading from THF solution on the TiO₂ surface as shown in Figure 3. Compared with THF, EtOH seems favorable medium for dye loading onto TiO₂ owing to its high polarity that would facilitate better dye adsorption onto TiO₂ surface. The dye loading for **PT1-3** in EtOH and THF is 439 nmol/cm² (**PT1-EtOH**), 432 nmol/cm²

(**PT2-EtOH**), 337 nmol/cm² (**PT3-EtOH**), 288 nmol/cm² (**PT1-THF**), 266 nmol/cm² (**PT2-THF**), and 205 nmol/cm² (**PT3-THF**), respectively. Meanwhile, the conversion efficiency strongly depended on the dielectric constant of the dye-adsorption solvent. The amount of dye adsorption increased as the dielectric constant of the dye-adsorption solvent increased [44]. The higher conversion efficiency obtained when EtOH was used as dye-adsorption solvent can also be attributed to the higher dielectric constant for ethanol ($k = 24.5$) compared with THF ($k = 7.8$). Table 2 shows that the J_{sc} of the device using EtOH as dye-adsorption solvent are drastically higher than those using THF as dye-adsorption solvent. Thus, a higher IPCE value of DSSCs based on **PT1-3** dyes was obtained using EtOH, which exceeded 80% from 425 nm to 500 nm, compared with using THF,

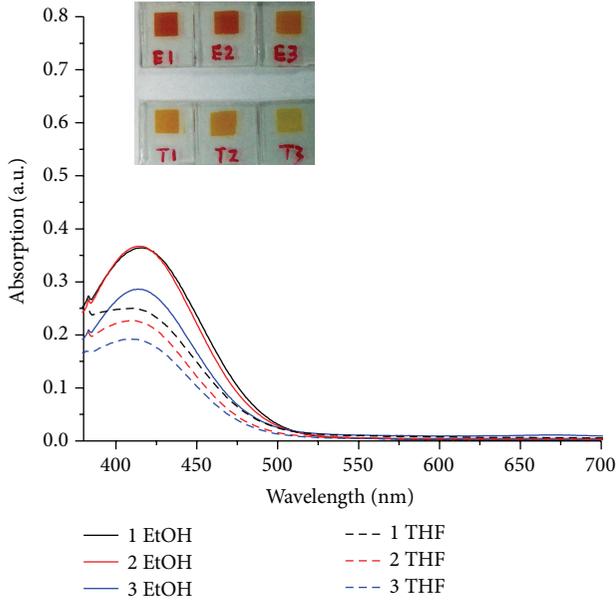


FIGURE 3: UV-vis absorption spectra of **PT1-3** dyes extracted from the surface of TiO_2 film in EtOH and THF.

which only exceeded 50% from 425 nm to 475 nm, as shown in Figure 2(c).

Meanwhile, the dye loading in case of **PT3** was relatively less than **PT1** and **PT2** in both cases of THF and EtOH solution but the J_{sc} values and the overall conversion efficiency were comparatively higher for **PT3** more than **PT1** and **PT2** in both dye-bath solvents EtOH and THF, indicating that the steric hinder effect of **PT3** dye with the branched aliphatic chain has the ability of decreasing the dye aggregation on the TiO_2 film as well as decreasing the electron recombination reaction rate at the interfaces between TiO_2 /dye and the electrolyte species, hence increasing the performance of the device.

To further elucidate the lower performance of the DSSC sensitized by **PT1-3** that uses THF, the electron lifetime and EIS were implemented on the Autolab (Frequency range: 100 kHz to 10 mHz). Two parameters, namely, chemical capacitance (C_m) and charge recombination resistance (R_{rec}), were obtained by fitting the EIS at different reverse biases with Z-View software, according to the transmitting line mode. Figures 4(a) and 4(b) show the Nyquist plot and recombination resistance, where the applied voltage is 0.65 V under dark condition for the **PT1-3** sensitizers using EtOH and THF as dye-adsorption solvents. In the Nyquist plots, a major semicircle was observed for all dyes, which is related to the electron recombination transport process at the interfaces between TiO_2 and the electrolyte/dye [45]. The data listed in Table 3 is related to the electron lifetime (τ), the electrochemical capacity (C), and the electron recombination (R_{rec}); for example, a smaller R_{rec} indicates faster electron recombination and hence a larger dark current as shown in Figure 2(b).

The recombination resistance (R_{rec}) decreased in the order of **PT3** ($154.4 \Omega\text{-cm}^2$) > **PT2** ($35.68 \Omega\text{-cm}^2$) > **PT1**

TABLE 3: Recombination resistance, electron life time, and the electrochemical capacity for the **PT1-3**-sensitizers using EtOH and THF as dye-adsorption solvents.

Device	R_{rec} ($\Omega\text{-cm}^2$)	C (F/cm^2)	T (ms)
E1	18.23	0.001638	29.86
E2	35.68	0.001572	56.09
E3	154.4	0.001442	222.64
T1	6.606	0.001582	10.45
T2	13.63	0.001529	20.84
T3	57.26	0.001476	84.52

($18.23 \Omega\text{-cm}^2$) in EtOH, consistent with the values of the V_{oc} that significantly increased using EtOH **PT3** (779 mV), **PT2** (726 mV), and **PT1** (691 mV), much more than that using THF **PT3** (726 mV), **PT2** (676 mV), and **PT1** (644 mV) as dye-adsorption solvent, and that could be ascribed to the bent and the sterically hindered conformation of phenothiazine with a branched and long aliphatic chain for **PT3** > **PT2** > **PT1**; the longer and branched aliphatic chain can prevent the direct contact between the electrolyte and the TiO_2 surface as well as inhibits or reduces dye aggregation. This behavior was clearly observed in case of using EtOH as the dye-adsorption solvent because of the higher dye loading and coverage on the TiO_2 surface and can thus reduce the charge recombination reaction rate.

Figure 4(c) shows the electron lifetime for all devices. A larger value of V_{oc} corresponds to the significantly longer electron lifetime for all sensitizers in EtOH $\tau = 222.64$ ms, 56.09 ms, and 29.86 ms for **PT3**, **PT2**, and **PT1**, respectively, whereas, that of THF, V_{oc} was comparatively lower than EtOH because of the comparatively lower electron lifetime $\tau = 8452$ ms, 20.84 ms, and 10.45 ms for **PT3**, **PT2**, and **PT1**, respectively, which can be attributed as mentioned above to the sterically hindered conformation of phenothiazine with a branched and long aliphatic chain of phenothiazine on one hand and on the other hand because of the higher dye loading when using EtOH more than that when using THF as dye-adsorption solvent.

4. Conclusion

Three phenothiazine-based sensitizers, namely, **PT1**, **PT2**, and **PT3**, were synthesized, and the photovoltaic performances of the three dyes were tested in EtOH and THF solution as dye-adsorption solvents, and it was found that the three sensitizers were influenced by the dye-adsorption solvent condition. The highest conversion efficiency 3.78% was obtained in the case of using EtOH as dye-bath solvent. The conversion efficiency of the DSSC was found to strongly depend not only on the kind of solvent but also on the steric hindered effect of the dye structure. The DSSCs that used dye with higher steric hindered effect showed higher J_{sc} value and higher overall conversion efficiency than the DSSCs that used dye with lower steric hindered effect.

The device that used THF as a dye-bath solvent showed lower J_{sc} value and lower conversion efficiency than

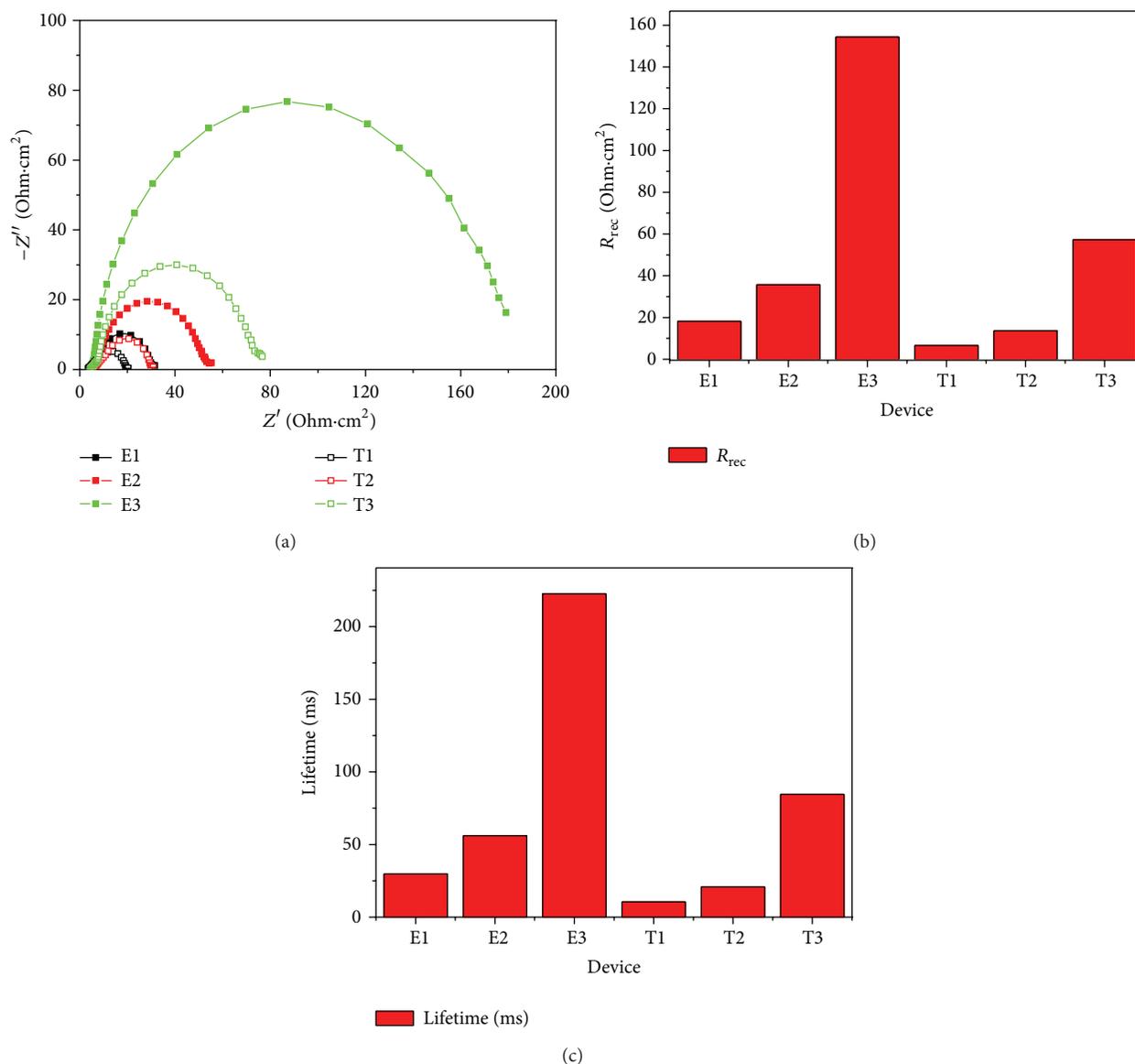


FIGURE 4: (a) Electrochemical impedance spectra (Nyquist plots) applied voltage is 0.65 V under dark condition, (b) recombination resistance (R_{rec}), and (c) lifetime for the DSSCs using EtOH and THF as a dye bath solvent, respectively.

the device that used EtOH, due to increase in the dye aggregates at the TiO₂ surface during the adsorption process in case of using THF and consequence lowering the overall cell performance which is attributed mainly to less dye loading on the TiO₂ surface in case of THF, the lower dielectric constant for the THF, the hydrogen bond interaction of the oxygen of the tetrahydrofuran, and the hydrogen of the carboxylic acid moiety of the dye.

This study revealed that designing of phenothiazine dyes with longer and branched aliphatic chain increases the steric hindered effect which was mainly responsible for increasing the electron lifetime and decreases the dye aggregation as well as increasing the electron recombination resistance rate at the TiO₂-dye-electrolyte interface, hence, enhancing the overall cell performance. Moreover the dye-bath solvent has a

significant role for the overall cell performance and choosing a compatible dye-adsorption solvent leads to enhancement of the performance of DSSCs.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work is jointly supported by the Ministry of Science and Technology (no. 2011CB933300), the Ministry of Education of China (no. 20120001140010), the National Natural Science

Foundation of China (no. 91333107), and the fund from Beijing (no. Z121100001312009).

References

- [1] M. Grätzel, "Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells," *Journal of Photochemistry and Photobiology A*, vol. 164, no. 1–3, pp. 3–14, 2004.
- [2] B. O'Regan and M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films," *Nature*, vol. 353, no. 6346, pp. 737–740, 1991.
- [3] S. Kambe, K. Murakoshi, T. Kitamura et al., "Mesoporous electrodes having tight agglomeration of single-phase anatase TiO₂ nanocrystallites: application to dye-sensitized solar cells," *Solar Energy Materials and Solar Cells*, vol. 61, no. 4, pp. 427–441, 2000.
- [4] A. Kay and M. Grätzel, "Dye-sensitized core-shell nanocrystals: improved efficiency of mesoporous tin oxide electrodes coated with a thin layer of an insulating oxide," *Chemistry of Materials*, vol. 14, no. 7, pp. 2930–2935, 2002.
- [5] Z.-S. Wang, C.-H. Huang, Y.-Y. Huang et al., "A highly efficient solar cell made from a dye-modified ZnO-covered TiO₂ nanoporous electrode," *Chemistry of Materials*, vol. 13, no. 2, pp. 678–682, 2001.
- [6] Z.-S. Wang, H. Kawauchi, T. Kashima, and H. Arakawa, "Significant influence of TiO₂ photoelectrode morphology on the energy conversion efficiency of N719 dye-sensitized solar cell," *Coordination Chemistry Reviews*, vol. 248, no. 13–14, pp. 1381–1389, 2004.
- [7] M. K. Nazeeruddin, P. Péchy, T. Renouard et al., "Engineering of efficient panchromatic sensitizers for nanocrystalline TiO₂-based solar cells," *Journal of the American Chemical Society*, vol. 123, no. 8, pp. 1613–1624, 2001.
- [8] T. Renouard, R.-A. Fallahpour, M. K. Nazeeruddin et al., "Novel ruthenium sensitizers containing functionalized hybrid tetradentate ligands: synthesis, characterization, and INDO/S analysis," *Inorganic Chemistry*, vol. 41, no. 2, pp. 367–378, 2002.
- [9] S. M. Zakeeruddin, M. K. Nazeeruddin, P. Pechy et al., "Molecular engineering of photosensitizers for nanocrystalline solar cells: synthesis and characterization of Ru dyes based on phosphonated terpyridines," *Inorganic Chemistry*, vol. 36, no. 25, pp. 5937–5946, 1997.
- [10] A. Islam, H. Sugihara, M. Yanagida et al., "Efficient panchromatic sensitization of nanocrystalline TiO₂ films by β -diketonato ruthenium polypyridyl complexes," *New Journal of Chemistry*, vol. 26, no. 8, pp. 966–968, 2002.
- [11] Y. Saito, W. Kubo, T. Kitamura, Y. Wada, and S. Yanagida, "I⁻/I₃⁻ redox reaction behavior on poly (3,4-ethylenedioxythiophene) counter electrode in dye-sensitized solar cells," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 164, no. 1–3, pp. 153–157, 2004.
- [12] Z. Kebede and S.-E. Lindquist, "Donor-acceptor interaction between non-aqueous solvents and I₂ to generate I₃⁻, and its implication in dye sensitized solar cells," *Solar Energy Materials and Solar Cells*, vol. 57, no. 3, pp. 259–275, 1999.
- [13] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, and H. Arakawa, "Influence of electrolytes on the photovoltaic performance of organic dye-sensitized nanocrystalline TiO₂ solar cells," *Solar Energy Materials and Solar Cells*, vol. 70, no. 2, pp. 151–161, 2001.
- [14] F. Cecchet, A. M. Gioacchini, M. Marcaccio et al., "Solvent effects on the oxidative electrochemical behavior of *cis*-bis(isothiocyanato)ruthenium(II)-bis-2,2'-bipyridine-4,4'-dicarb oxylie acid," *Journal of Physical Chemistry B*, vol. 106, no. 15, pp. 3926–3932, 2002.
- [15] E. Olsen, G. Hagen, and S. Eric Lindquist, "Dissolution of platinum in methoxy propionitrile containing LiI/I₂," *Solar Energy Materials and Solar Cells*, vol. 63, no. 3, pp. 267–273, 2000.
- [16] Z.-S. Wang, Y. Cui, K. Hara, Y. Dan-Oh, C. Kasada, and A. Shinpo, "A high-light-harvesting-efficiency coumarin dye for stable dye-sensitized solar cells," *Advanced Materials*, vol. 19, no. 8, pp. 1138–1141, 2007.
- [17] D. Kuang, S. Uchida, R. Humphry-Baker, S. M. Zakeeruddin, and M. Grätzel, "Organic dye-sensitized ionic liquid based solar cells: remarkable enhancement in performance through molecular design of indoline sensitizers," *Angewandte Chemie*, vol. 47, no. 10, pp. 1923–1927, 2008.
- [18] S. Ko, H. Choi, M.-S. Kang et al., "Silole-spaced triarylamine derivatives as highly efficient organic sensitizers in dye-sensitized solar cells (DSSCs)," *Journal of Materials Chemistry*, vol. 20, no. 12, pp. 2391–2399, 2010.
- [19] J. J. Cid, J. H. Yum, S. R. Jang et al., "Molecular cosensitization for efficient panchromatic dye-sensitized solar cells," *Angewandte Chemie*, vol. 46, no. 44, pp. 8358–8362, 2007.
- [20] C.-L. Mai, W.-K. Huang, H.-P. Lu et al., "Synthesis and characterization of diporphyrin sensitizers for dye-sensitized solar cells," *Chemical Communications*, vol. 46, no. 5, pp. 809–811, 2010.
- [21] A. Yella, H.-W. Lee, H. N. Tsao et al., "Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency," *Science*, vol. 334, no. 6056, pp. 629–634, 2011.
- [22] L. M. Peter, "Dye-sensitized nanocrystalline solar cells," *Physical Chemical Physics*, vol. 9, no. 21, pp. 2630–2642, 2007.
- [23] S. E. Kooops, P. R. F. Barnes, B. C. O'Regan, and J. R. Durrant, "Kinetic competition in a coumarin dye-sensitized solar cell: injection and recombination limitations upon device performance," *Journal of Physical Chemistry C*, vol. 114, no. 17, pp. 8054–8061, 2010.
- [24] B. C. O'Regan, I. López-Duarte, M. V. Martínez-Díaz et al., "Catalysis of recombination and its limitation on open circuit voltage for dye sensitized photovoltaic cells using phthalocyanine dyes," *Journal of the American Chemical Society*, vol. 130, no. 10, pp. 2906–2907, 2008.
- [25] K. Hara, K. Miyamoto, Y. Abe, and M. Yanagida, "Electron transport in coumarin-dye-sensitized nanocrystalline TiO₂ electrodes," *Journal of Physical Chemistry B*, vol. 109, no. 50, pp. 23776–23778, 2005.
- [26] N. Robertson, "Optimizing dyes for dye-sensitized solar cells," *Angewandte Chemie*, vol. 45, no. 15, pp. 2338–2345, 2006.
- [27] A. Mishra, M. K. R. Fischer, and P. Büerle, "Metal-Free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules," *Angewandte Chemie*, vol. 48, no. 14, pp. 2474–2499, 2009.
- [28] G. Li, K.-J. Jiang, Y.-F. Li, S.-L. Li, and L.-M. Yang, "Efficient structural modification of triphenylamine-based organic dyes for dye-sensitized solar cells," *Journal of Physical Chemistry C*, vol. 112, no. 30, pp. 11591–11599, 2008.
- [29] J. M. Vanderkooi, "Photoreduction of membrane bound cytochrome C by excited state phenothiazine," *Biochemical and Biophysical Research Communications*, vol. 69, no. 4, pp. 1043–1049, 1976.

- [30] L. Levy, T. N. Tozer, L. D. Tuck, and D. B. Loveland, "Stability of some phenothiazine free radicals," *Journal of Medicinal Chemistry*, vol. 15, no. 9, pp. 898–905, 1972.
- [31] P. J. Walsh, K. C. Gordon, D. L. Officer, and W. M. Campbell, "A DFT study of the optical properties of substituted Zn(II)TPP complexes," *Journal of Molecular Structure*, vol. 759, no. 1–3, pp. 17–24, 2006.
- [32] R. M. El-Shishtawy, "Functional dyes, and some Hi-Tech applications," *International Journal of Photoenergy*, vol. 2009, Article ID 434897, 21 pages, 2009.
- [33] T. Meyer, D. Ogermann, A. Pankrath, K. Kleinermanns, and T. J. J. Müller, "Phenothiazinyl rhodanylidene merocyanines for dye-sensitized solar cells," *Journal of Organic Chemistry*, vol. 77, no. 8, pp. 3704–3715, 2012.
- [34] S. S. Park, Y. S. Won, Y. C. Choi, and J. H. Kim, "Molecular design of organic dyes with double electron acceptor for dye-sensitized solar cell," *Energy and Fuels*, vol. 23, no. 7, pp. 3732–3736, 2009.
- [35] Y. J. Chang, P.-T. Chou, Y.-Z. Lin et al., "Organic dyes containing oligo-phenothiazine for dye-sensitized solar cells," *Journal of Materials Chemistry*, vol. 22, pp. 21704–21712, 2012.
- [36] T.-Y. Wu, M.-H. Tsao, F.-L. Chen et al., "Synthesis and characterization of organic dyes containing various donors and acceptors," *International Journal of Molecular Sciences*, vol. 11, no. 1, pp. 329–353, 2010.
- [37] S. Agrawal, M. Pastore, G. Marotta et al., "Optical properties and aggregation of phenothiazine-based dye sensitizers for solar cells applications: a combined experimental and computational investigation," *The Journal of Physical Chemistry C*, vol. 117, no. 19, pp. 9613–9622, 2013.
- [38] A. Baheti, P. Tyagi, K. R. J. Thomas, Y.-C. Hsu, and J. T. Lin, "Simple triarylamine-based dyes containing fluorene and biphenyl linkers for efficient dye-sensitized solar cells," *Journal of Physical Chemistry C*, vol. 113, no. 20, pp. 8541–8547, 2009.
- [39] P. Singh, A. Baheti, K. R. Justin Thomas, Ch.-P. Lee, and K.-C. Ho, "Fluorene-based organic dyes containing acetylene linkage for dye-sensitized solar cells," *Dyes and Pigments*, vol. 95, no. 3, pp. 523–533, 2012.
- [40] M. P. Balanay, K. H. Kim, S. H. Lee, and D. H. Kim, "Tuning the photovoltaic parameters of β -substituted porphyrin analogues: an experimental and theoretical approach," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 248, pp. 63–72, 2012.
- [41] M. J. Griffith, M. James, G. Triani, P. Wagner, G. G. Wallace, and D. L. Officer, "Determining the orientation and molecular packing of organic dyes on a TiO₂ surface using X-ray reflectometry," *Langmuir*, vol. 27, no. 21, pp. 12944–12950, 2011.
- [42] Y. Hua, H. Wang, X. Zhu et al., "New simple panchromatic dyes based on thiadiazolo[3,4-c]pyridine unit for dye-sensitized solar cells," *Dyes and Pigments*, vol. 102, pp. 196–203, 2014.
- [43] H. Imahori, S. Kang, H. Hayashi et al., "Photoinduced charge carrier dynamics of Zn-Porphyrin-TiO₂ electrodes: the key role of charge recombination for solar cell performance," *Journal of Physical Chemistry A*, vol. 115, no. 16, pp. 3679–3690, 2011.
- [44] H. Ozawa, M. Awa, T. Ono, and H. Arakawa, "Effects of dye-adsorption solvent on the performances of the dye-sensitized solar cells based on black dye," *Chemistry*, vol. 7, no. 1, pp. 156–162, 2012.
- [45] D. Kim, M.-S. Kang, K. Song, S. O. Kang, and J. Ko, "Molecular engineering of organic sensitizers containing indole moiety for dye-sensitized solar cells," *Tetrahedron*, vol. 64, no. 45, pp. 10417–10424, 2008.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

