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# Solvent-Performance Relationships of Phenothiazine-Based Organic Dye in Dye-Sensitized Solar Cell

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**Abstract.** In this paper, we study the impacts of solvent effects on the dye-sensitized solar cells' (DSSCs') performances. Initially, a new D-D- $\pi$ -A phenothiazine-based metal-free organic dye (WY5) was designed and synthesized. Afterwards, we assumed that the WY5 sensitized in different solvents N, N-dimethylformamide (DMF), methanol (MeOH) and tetrahydrofuran (THF) would affect the aggregations and the adsorption modes on TiO<sub>2</sub> surface and further affect the photovoltaic performances of corresponding DSSCs. The champion efficiency of 5.61% was obtained by the DSSC using MeOH as sensitization solvent. Our work provides a potential strategy for investigating the impacts of different sensitized solvents on the DSSCs' performances and further to screen the best suitable sensitized solvent for dye WY5.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) have rapidly jumped into the hot seat of academic research for next-generation photovoltaic devices due to its low-cost manufacturing and high photoelectric conversion efficiency ( $\eta$ ). The photon-to-current conversion of DSSC is achieved by ultrafast electron injection from a photoexcited dye into the conduction band of the TiO<sub>2</sub>, followed by dye regeneration and hole transportation to the counter electrode [1].

To obtain the well-performed DSSC, the development of the functional molecular in DSSC is confirmed as one of the most important methods [2]. Among them, phenothiazine (PTZ) unit with electron-rich sulfur and nitrogen heteroatoms in its structure is widely used as the electron donor in organic dyes [3]. Furthermore, the  $\eta$  of DSSC is also affected by the formation of dye aggregation on the TiO<sub>2</sub> surface which is uncontrollable. The aggregations are triggered by the electrostatic and non-covalent interactions between dye molecules [4]. Solvent properties such as the polarity, dipole moment, dielectric constant, and hydrogen bonding could modulate the interactions among the dye molecules and also between the dyes and the surface [5]. Previous studies focused primarily on how the adsorption geometry of organic dyes is configured on TiO<sub>2</sub> surface in the presence of solvents [6-8]. Although the surface density of some organic dyes at TiO<sub>2</sub> surfaces has been experimentally examined [9-11], however, the effect of different sensitization solvent on the aggregations and the adsorption modes onto TiO<sub>2</sub> surfaces has not been explored.

Understanding the solvent effects on molecular adsorption and electron-transfer at the particle surface is important for the optimization of the DSSC efficiency, hence, we designed, synthesized a



novel PTZ-based dye (WY5) with the structure of D-D- $\pi$ -A and further studied that the different sensitization solvent DMF/MeOH/THF affect WY5 dye's aggregations and the adsorption modes onto TiO<sub>2</sub> surface and the photovoltaic performances of corresponding DSSCs.

## 2. Experimental details

### 2.1. Materials

Cyanoacetic acid, N, N-dimethylformamide (DMF), tetrahydrofuran (THF) and methanol (MeOH) were purchased from Aldrich. PTZ, benzil and 4,4'-dimethoxybenzil were purchased from Astatech. The electrolyte consisted of 0.6 M 1, 2-dimethyl-3-propylimidazolium iodide (DMPII), 0.025 M LiI, 0.04 M I<sub>2</sub>, 0.05 M guanidium thiocyanate (GuSCN), and 0.28 M 4-tertbutylpyridine (TBP) in dry acetonitrile was purchased from Heptachroma. All solvents and other chemicals were reagent grade and used without further purification.

### 2.2. Preparation of DSSCs

TiO<sub>2</sub> electrodes were bought from Opvtech. When the TiO<sub>2</sub> electrodes were heated to 80 °C for 30 min, the electrodes were immersed in a dye bath containing  $2 \times 10^{-4}$  M WY5 in different solvent MeOH, DMF and THF, then left 12 h in the dark. The films were then rinsed in ethanol to remove excess dyes. In our experiment, open solar cells were fabricated in air by clamping the different sensitized electrodes with platinized counter electrodes. An electrolyte solution was injected into interlayer between two electrodes.

### 2.3. Photovoltaic characterization

Absorption spectra were measured with HITACH (model U-2910) *UV-vis* spectrophotometer. Emission spectra were recorded with HITACH (model F-4600) spectrophotometer. Cyclic voltammetry experiments were performed on a CH Instruments 660 C electrochemical workstation at a scan rate of 0.05 V s<sup>-1</sup> in DMF ( $5.0 \times 10^{-4}$  M) containing 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte, platinum as counter and work electrodes and Ag/AgCl as reference electrode. The irradiation source for the photocurrent action spectrum measurement is a photosource (CHF-XM-500W, Trusttech Co. Ltd., Beijing, China) with a CH Instruments 660 C electrochemical workstation (Shanghai CH Instruments Co., China). The incident light intensity was 100 mW cm<sup>-2</sup> calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.20 cm<sup>2</sup>. The action spectra of incident photon-to-electron conversion efficiency (IPCE) for solar cells were performed by using Newport 77890 IPCE measurement system. Electrochemical impedance spectroscopy (EIS) data were obtained in the dark under forward bias 0.75 V, scanning from 10<sup>-1</sup> to 10<sup>5</sup> Hz with ac amplitude of 0.01 V by using CH Instruments 660 C electrochemical workstation.

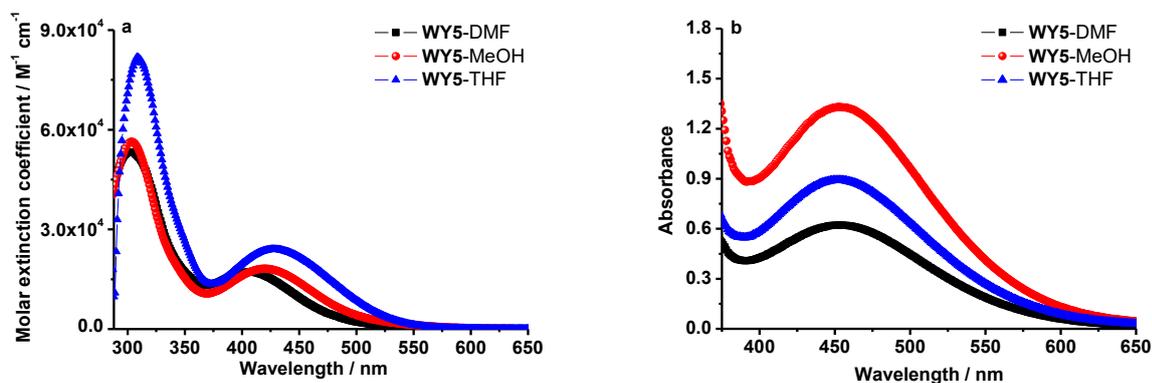
### 2.4. Synthesis

Compound WY5 was synthesized according to our previous report [12].

## 3. Results and discussions

Initially, the absorption spectra of the WY5 dye in different solvent DMF/MeOH/THF ( $2 \times 10^{-4}$  M) sensitized on nanocrystalline TiO<sub>2</sub> films, and the absorption spectra of the WY5 dye ( $5 \times 10^{-5}$  M) in different solvent DMF/MeOH/THF are shown in Figure 1, the corresponding data of the WY5 dye in different solvent DMF/MeOH/THF are summarized in Table 1. In Figure 1, it's obvious that all of the dyes exhibit two absorption bands. The first one appearing at 280~350 nm is assigned to the localized  $\pi$ - $\pi^*$  transition, another at the longer wavelengths pointing at 350~525 nm is attributed to intramolecular charge transfer (ICT) between donor and acceptor. The ICT peaks ( $\lambda_{max}$ ) for dye WY5 in DMF (406 nm) and MeOH (419 nm) exhibit a blue-shift compared with that in THF (427 nm). When WY5 dye sensitized on the TiO<sub>2</sub> films, the absorption spectra are red-shifted compared with that in different solvent, which widened its absorption scope. In addition, it is worth noting that the  $\lambda_{max}$

(453 nm) are almost completely consistent on the TiO<sub>2</sub> films, and the absorption intensities show obvious difference in different solvent. Among them, WY5 dye using MeOH as sensitization solvent sensitized on the TiO<sub>2</sub> film showed the strongest absorption, which also suggested that MeOH was conducive to WY5 dye adsorption on the surface of TiO<sub>2</sub>.



**Figure 1.** (a) The absorption spectra of the WY5 dye in different solvent DMF/MeOH/THF sensitized on nanocrystalline TiO<sub>2</sub> films, and (b) the absorption spectra of the WY5 dye in different solvent DMF/MeOH/THF.

**Table 1.** The UV-vis data of the WY5 dye in different solvent DMF/MeOH/THF.

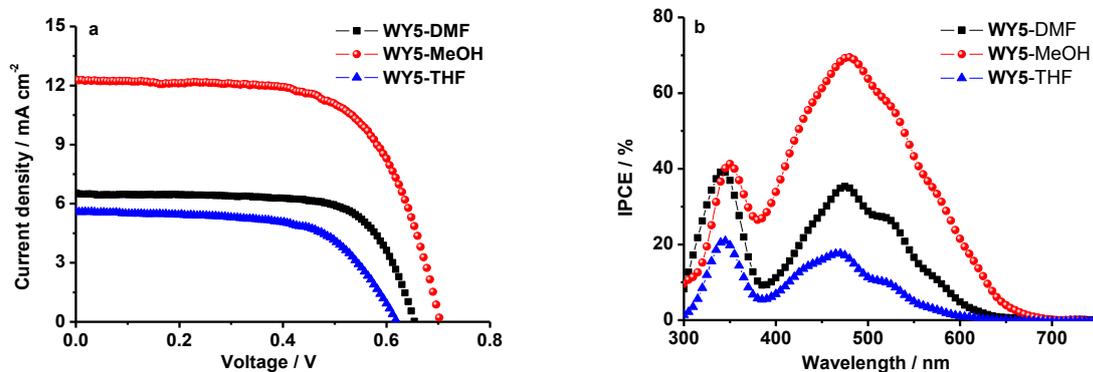
WY5 in different solvent	$\lambda_{max}^a$ (nm) $\varepsilon^b$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{max}^c$ (nm)
DMF	406 (17054)	453
MeOH	419 (18249)	453
THF	427 (24226)	453

<sup>a</sup> The absorption spectra of the WY5 dye in different solvent DMF/MeOH/THF (5 × 10<sup>-5</sup> M).

<sup>b</sup> Molar extinction coefficient ( $\varepsilon$ ) of  $\lambda_{max}$ .

<sup>c</sup>  $\lambda_{max}$  of WY5 dye on the TiO<sub>2</sub> film.

To study the impacts of different sensitization solvent on the performances of the DSSCs, WY5 in DMF/MeOH/THF sensitized on the photoanode, respectively. Further, we fabricated the corresponding DSSCs for the current-voltage ( $J$ - $V$ ) and IPCE measurements, the correlative curves are listed in Figure 2. The photoelectric data are summarized in Table 2. From Figure 2a, it can be concluded that photoelectric performance of DSSC is significantly affected by the sensitizing solvent. In particular, the sensitizing solvent would affect its short-circuit current density ( $J_{sc}$ ). The champion efficiency of 5.61% ( $J_{sc} = 12.31$  mA cm<sup>-2</sup>,  $V_{oc} = 0.70$  V and  $FF = 0.65$ ) was obtained by the DSSC using MeOH as sensitization solvent, which is mainly due to its higher  $J_{sc}$  than other two kinds of DSSCs using DMF/THF (2.98%/2.16%) as sensitization solvent. The enhanced  $J_{sc}$  can also be explained by the IPCE curves. In Figure 2b, the value (400~600 nm) reached 69% for the WY5-based DSSC using MeOH as sensitization solvent, while the values only reached 35% and 18% for the WY5-based DSSCs using DMF/THF as sensitization solvent under the same condition, respectively.



**Figure 2.** (a)  $J$ - $V$  and (b) IPCE curves of WY5-based DSSCs using DMF/MeOH/THF sensitization solvent.

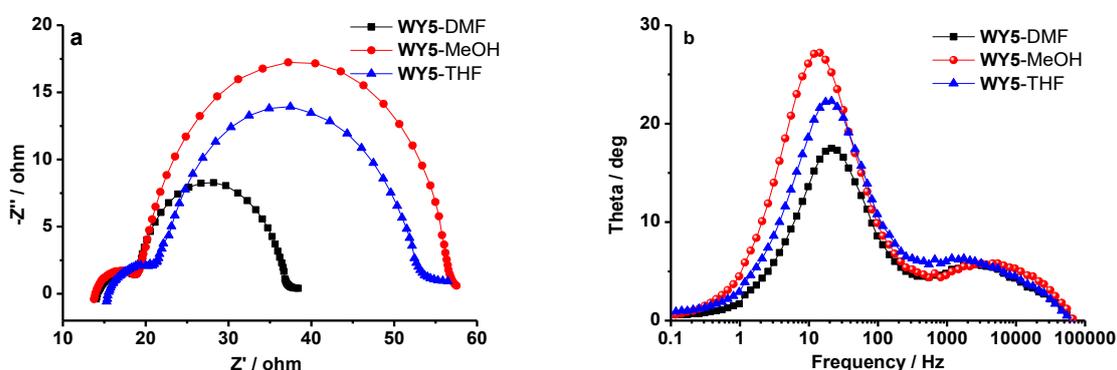
**Table 2.** The photoelectric data of WY5-based DSSCs using DMF/MeOH/THF sensitization solvent.

WY5 in different solvent	$J_{sc}$ / mA cm <sup>-2</sup>	$V_{oc}$ / V	$FF$	$\tau_e$ / ms	$\eta$ %
DMF	6.54	0.65	0.68	9.46	2.98
MeOH	12.31	0.70	0.65	14.10	5.61
THF	5.60	0.62	0.62	9.87	2.16

To further illuminate the relationships between photoelectric performance and sensitizing solvent, it is crucial to have an insight into the charge transfer properties of above-mentioned DSSCs. Therefore, EIS measurement was used to further explain the voltage change of WY5-based DSSCs using DMF/MeOH/THF sensitization solvent. Figure 3 shows the Nyquist and Bode diagrams of WY5-based DSSCs using DMF/MeOH/THF sensitization solvent under dark condition, respectively. In Nyquist diagram (Figure 3a), the radius (low frequency) decreases in the following order: WY5-MeOH > WY5-DMF > WY5-THF, which indicates that the charge transfer reorganization resistance ( $R_{ct}$ ) also reduces in the following order: WY5-MeOH > WY5-DMF > WY5-THF. These results are consistent with the  $V_{oc}$  of DSSCs. The electron lifetimes ( $\tau_e$ ), achieved by the Equation:

$$\tau_e = \frac{1}{2\pi f}$$

Where  $f$  is the frequency of the low-frequency peak in Bode diagram (Figure 3b), can also be used to explain the tendency of  $V_{oc}$ . The relatively longer  $\tau_e$  suggests an enhanced  $R_{ct}$ , a reduced dark current and an improved  $V_{oc}$ .



**Figure 3.** The EIS of WY5-based DSSCs using DMF/MeOH/THF sensitization solvent under dark condition: (a) Nyquist and (b) Bode diagrams, respectively.

#### 4. Conclusion

In this paper, we study that the impacts of solvent effects on the DSSCs' performances. The experimental result shows the WY5 dye sensitized in different solvents DMF, MeOH and THF would affect the aggregations and the adsorption modes on  $\text{TiO}_2$  surface and further affect the photovoltaic performances of corresponding DSSCs.

#### Acknowledgments

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