Dyes and Pigments 101 (2014) 67-73

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

A comparative study on properties of two phenoxazine-based dyes for dye-sensitized solar cells



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ARTICLE INFO

Article history: Received 5 June 2013 Received in revised form 4 September 2013 Accepted 6 September 2013 Available online 6 October 2013

Keywords: Phenoxazine Conjugated direction Phenyl ring Alkyl chain Dye-sensitized solar cells Photovoltaic performances

1. Introduction

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ABSTRACT

Two phenoxazine (POZ)-based organic D $-\pi$ -A sensitizers (**POZ-1** and **POZ-2**) were synthesized. Then these two dyes were applied in dye-sensitized solar cells (DSSCs) to investigate the influence of different conjugated direction, extra phenyl ring and alkyl chain on the light-harvesting, energy level and photovoltaic properties through a joint spectral, electrochemical and photovoltaic study. The result shows that dye **POZ-2** exhibits higher power conversion efficiency ($\eta = 6.5\%$) than dye **POZ-1** ($\eta = 2.4\%$) under standard illumination (Global Air Mass 1.5). Besides, the geometries of the dyes were optimized to gain insight into the molecular structure and electron distribution. The charge extraction and transient photovoltage decay measurements were further performed to understand the alterative order of efficiency.

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concept of the organic dyes is donor $-\pi$ -linker–acceptor (D $-\pi$ –A) structure, in which the electron donor plays a vital role in determining the molecular energy level, which affects the light-harvesting capacity of a sensitizer and thus the ultimate overall conversion efficiency.

Due to the strong electron donating ability and easy structure modification of phenoxazine (POZ) unit, it has been utilized for the DSSCs and has attained satisfying performance [35,36]. In this report, two POZ-based metal-free organic dyes were synthesized (**POZ-1**, **POZ-2** [39] shown in Fig. 1) to evaluate the performance of the dyes with different structural modification, such as different conjugated directions, extra phenyl ring and alkyl chain. The thiophene moiety was introduced as π linker. Finally, these two sensitizers were applied to DSSCs, and the structures related photovoltaic properties were deeply investigated through joint electrical, photophysical and computational studies.

2. Experimental section

2.1. Materials

Acetonitrile (AN) and tetrahydrofuran (THF) were distilled before use. Phenoxazine were purchased from Inno-Chem Science

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Dye-sensitized solar cells (DSSCs) have attracted considerable

scientific interests due to their promising efficiency and potentially

low cost since developed by Grätzel and coworkers [1]. As a critical

component in DSSCs, the sensitizer plays a crucial role in influ-

encing on the performance of solar cell. In recent years, more

attention has been paid to metal-free organic dyes because of their

easy synthesis, high molar extinction coefficients as well as less

environmental issues compared with metal-complex sensitizers

[2-6]. Up to now, many kinds of metal-free organic dyes based on coumarin [7-9], merocyanine [10-12], indoline [13-15], polyene

[16], hemicyanine [17,18], fluorine [19–21], triphenylamine (TPA)

[22–28], tetrahydroguinoline [29,30], carbazole [31] and hetero-

anthracene (phenothiazine and phenoxazine) [32–38] have been

developed and showed good performance. The traditional design

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Fig. 1. Chemical structures of POZ-1 and POZ-2.

Technology Co., Ltd. N-bromosuccinimide (NBS), cyanoacetic acid, piperidine, copper powder, 5-formyl-2-thiopheneboronic acid, 1-bromo-4-iodobenzene and 1-bromo-iso-octane were purchased from Energy-Chemical. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), 1-ethyl-3-methylimidazoliumbis(trifluoromethane-sulfonyl)imide (EMITFSI), 1,3-dimethylimidazolium iodide (DMII), guanidinium thiocyanate (GNCS) and 4-tert-butylpyridine (TBP) were purchased from Sigma–Aldrich.

2.2. Synthesis

POZ-1 was synthesized by the Suzuki cross-coupling of bromine substituted aromatic compound 1 and 5-formyl-2thiopheneboronic acid. Then the widely employed Knoevenagel condensation was used to construct the cyanoacrylic acid dye (Scheme 1). **POZ-2** was synthesized according to a previous publication [37], and the details of synthesis and characterization of **POZ-2** are provided in the electronic Supplementary information (ESI).

2.2.1. Synthesis of (4-bromophenyl)-10H-phenoxazine(1)

Potassium carbonate (7.8 g, 60 mmol), copper powder (0.5 g, 8 mmol), 4-iodo-bromobenzene (12.4 g, 44 mmol), and phenoxazine (8 g, 40 mmol) were added to a 100 mL one-port roundbottomed flask. The mixture was heated to 170 °C for 7 h. The reaction mixture was cooled to 130 °C and ethyl acetate was added. The resulting mixture was stirred for 30 min at 130 °C and then filtered. The filtrate was evaporated to remove the solvent. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford white solid (3.6 g, 25%). ¹H NMR (CDCl₃, 400 MHz), (TMS, ppm):7.59 (d, 2H), 7.13–6.98 (m, 6H), 6.82–6.75 (m, 4H). GC-MS: m/z = 337.3.

2.2.2. Synthesis of 5-(4-(10H-phenoxazin-10-yl)phenyl)thiophene-2-carbaldehyde (**2**)

Compound **1** (1.06 g, 3 mmol) and 5-formylthiophene-2-boronic acid (0.624 g, 4 mmol) were dissolved in THF (50 mL). Then potassium acetate solution (0.98 g, 2 mol/L) and Pd(PPh₃)₄ (0.20 g, 0.165 mmol) were added under argon. The mixture was stirred for 24 h at 70 °C. After THF was removed by evaporation under vacuum, the reaction mixture was poured into water and extracted with dichloromethane several times. The organic phase was dried



Scheme 1. Synthesis route of **POZ-1**. Reagents: i) Cu, K₂CO₃, 1-Bromo-4-iodobenzene; ii) 5-Formyl-2-thiopheneboronic acid, KOAc, THF, Pd(pph₃)₄; iii) Piperidine, Cyano-acetic acid.

over anhydrous magnesium sulfate. The solvent was removed, and then the product was purified using column chromatography on a silica gel with dichloromethane/hexane (1:4 v/v). The product was obtained as crimson solid. Yield: 0.845 g (76%). ¹H NMR (CDCl₃, 400 MHz), (TMS, ppm): 9.95 (s, 1H), 8.11–8.08 (m, 3H), 7.87–7.86 (d, 1H), 7.55–7.53 (d, 2H), 6.76–6.75 (m, 2H), 6.69–6.67 (m, 4H), 5.96–5.94 (m, 2H). GC-MS: m/z = 369.1.

2.2.3. Synthesis of POZ-1

POZ-1 was prepared following the procedures described for **POZ-2** (ESI). The product was obtained as orange-red powder (50.0%). ¹H NMR (DMSO, 400 MHz), (TMS, ppm): 8.22 (s, 1H), 8.04–8.02 (d, 2H), 7.84–7.78 (m, 2H), 7.53–7.51 (d, 2H), 6.77–6.71 (m, 2H), 6.69–6.67 (m, 4H), 5.97–5.94 (m, 2H). GC-MS: m/z = 436.1.

2.3. UV-vis, photoluminescence and voltammetric measurements

Electronic absorption spectra were measured on an Agilent G1103A spectrometer. Emission spectra were recorded with a Perkin Elmer LS55 luminescence spectrometer. The emitted light was detected with a Hamamatsu R928 red-sensitive photomultiplier. A computer-controlled CHI660C electrochemical workstation was used for square-wave voltammetric measurements with a threeelectrode electrochemical cell. All potentials were reported against the ferrocene/ferrocenium (Fc/Fc⁺) reference.

2.4. Computation details

The ground state geometries were optimized employing the hybrid B3LYP [40] function and a 6-31G** basis set. Vertical excitation energies were calculated by time-dependent density functional theory (TD-DFT) at MPW1K [41]/6-31G** and levels of theory. The effect of the solvent (THF) on the geometries and absorption spectra has been simulated by the C-PCM method [42]. All the calculations were carried out with Gaussian 09 program packages [43].

2.5. Cell fabrication

A screen-printed double layer film of interconnected TiO₂ particles was used as the mesoporous negative electrode. A 7 μ m thick transparent layer of 20 nm sized titania particles were first printed on the fluorine-doped SnO₂ (FTO) conducting glass electrode and further coated by a 5 μ m thick scattering layer of 400 nm sized



Fig. 2. UV-vis absorption spectra of POZ-1 and POZ-2 in THF.

Table 1Photophysical and electrochemical data of POZ-1 and POZ-2 in THF.

Dye	λ ^{abs} a [nm]	${}^{\mathcal{E}^{abs}_{max}a}_{[10^3 M^{-1} cm^{-1}]}$	λ ^{pl} a [nm]	E_{0-0}^{b} [eV]	<i>E_{D/D+}</i> ^c [V]	
POZ-1	371	23.5	418	3.12	0.33	-2.79
POZ-2	465	16.1	593	2.30	0.25	-2.05

^a The maximum absorption wavelength (λ_{max}^{abs}) and maximum molar absorption coefficient (ϵ_{max}^{abs}) , and PL maximum wavelength (λ_{max}^{pl}) were derived from the static electronic absorption and emission spectra in THF solution.

^b The zero–zero transition energy (E_{0-0}) was estimated from the intersection points of normalized absorption and emission spectra.

^c The ground-state redox potential (E_{D/D^+}) was reported with Fc/Fc⁺ as reference. ^d The excited-state redox potential (E_{D^+/D^+}) was estimated by equation $E_{D^+/D^+} = E_{D/D^+} - E_{0-0}/e$ without considering any entropy change during the light excitation.

titania particles. Preparation procedures of titania nanocrystals, screen-printing pastes, and nanostructured titania films were very similar to those described in a previous paper [44]. The thickness of film was measured by a benchtop Ambios XP-1 stylus profilometer. A cycloidal TiO₂ electrode ($\sim 0.28 \text{ cm}^2$) was stained by immersing it into a dye solution containing POZ-1 and POZ-2 sensitizers (150 uM) respectively in THF/AN (v/v, 1/1) for 10 h. After being washed with acetonitrile and dried by air flow, the sensitized titania electrode was assembled with a thermally platinized FTO electrode. The electrodes were separated by a 35 µm thick Bynel (DuPont) hot-melt gasket and sealed up by heating. The internal space was filled with a liquid electrolyte using a vacuum backfilling system. The electrolyte-injecting hole on the counter electrode glass substrate, made with a sand-blasting drill, was sealed with a Bynel sheet and a thin glass cover by heating. The infiltrated electrolyte is composed of 1.0 M DMII, 0.02 M iodine (I₂), 1.0 M TBP, 0.1 M GNCS and 0.05 M LiI in AN.

2.6. Photovoltaic measurements

A Keithley 2400 source meter and a Zolix Omni-λ300 monochromator equipped with a 500 W xenon lamp were used for the measurements of photocurrent action spectra, with a wavelength sampling interval of 10 nm and a current sampling time of 2 s under the full computer control. A Hamamatsu S1337 1010BQ silicon diode used for IPCE measurements was calibrated in National Institute of Metrology, China. During the photocurrent action spectrum measurements, a white light-emitting diode was used to bias a testing cell with \sim 1.0 mA cm⁻² background current. A model LS1000 4S-AM1.5G-1000-W solar simulator (Solar Light Company, USA) in combination with a metal mesh was employed to give an irradiance of 100 mW cm⁻². The light intensity was tested with a PMA2144 pyranometer and a calibrated PMA 2100 dose control system. J-V characteristics were obtained by applying a bias potential to a testing cell and measuring photocurrent with a Keithley 2602 source meter under the full computer control. The measurements were fully automated using Labview 8.0. A metal mask with an aperture area of 0.158 cm² was covered on a testing cell during all measurements. An antireflection film (λ < 380 nm, ARKTOP, ASAHI Glass) was adhered to the DSSC photoanode during IPCE and I-V measurements. The short-circuit photocurrent densities measured under this solar simulator were well consistent with the integral of IPCEs over the AM1.5G spectrum (ASTM G173 03), within 5% errors.

2.7. Transient photovoltage decay and charge extraction measurements

Transient photoelectrical experiments were measured with an Autolab-PGSTAT302N electrochemical workstation. The steady and



Fig. 3. Square-wave voltammograms of dyes in THF with 0.1 M 1-ethyl-3methylimidazolium bis(trifluoromethanesulfonyl)imide supporting electrolyte.

perturbing lights on the photoanode side of a testing cell were supplied with white and red light-emitting diodes, respectively. We used the red light to generate a photovoltage perturbation near the open-circuit photovoltage of a testing cell under a certain white light and measured the voltage decay process thereafter. The modulated photovoltage by the red pulse of a testing cell was below 5 mV. Normally, the transient signal follows monoexponential decay, thus the electron lifetime can be obtained by fitting an exponential function to the photovoltage decay. The electron density was estimated by the charge extraction method. A testing cell was first kept at open circuit under white light and subsequently the white light was turned off upon switching the cell from open circuit to short circuit to record the resulting current transient, and the electron density was obtained by current integration.

3. Results and discussion

3.1. Photophysical and electrochemical properties

The light-harvesting capacities at the molecular level were first compared by recording the UV–visible absorption spectra (Fig. 2) of **POZ-1** and **POZ-2** in THF. The detailed parameters were compiled in Table 1. **POZ-1** has a maximum absorption wavelength (λ_{max}^{abs}) at 371 nm, but **POZ-2** has two distinct absorption peaks at



Fig. 4. Normalized electronic absorption and emission spectra of the POZ-1 and POZ-2 in THF.



Fig. 5. Energy diagram of frontier orbitals of POZ-1 and POZ-2.

336 and 465 nm upon changing the conjugated direction between donor (phenoxazine) and π -unit. The extra phenyl ring does not broaden the absorption spectrum.

To fabricate efficient DSSCs, the optimum energy-offsets of dye molecules with respect to the titania nanocrystals and redox electrolytes are very important. The ground-state redox potentials (E_{D/D^+}) of these two dyes were measured in THF with the Fc/Fc⁺ redox couple as reference, which can be accurately derived by averaging the anodic and cathodic peak potential of square-wave voltammograms (Fig. 3), being 0.33 V and 0.25 V for **POZ-1** and **POZ-2** respectively. The E_{0-0} (zero-zero transition energies) were estimated from the intersection points of normalized absorption and emission spectra (Fig. 4) of 150 μ M dye solution, being 3.12 eV, 2.30 eV for **POZ-1** and **POZ-2** respectively. Then the excited-state redox potentials (E_{D^*/D^+}) were further calculated by equation $E_{D^*/D^+} = E_{D/D^+} - E_{0-0}/e$ without considering any entropy change



Fig. 7. Calculated absorption spectra of POZ-1 and POZ-2 in THF.

during light excitation. The E_{D^*/D^+} values of **POZ-1** and **POZ-2** were -2.79 V and -2.05 V.

3.2. Computational analysis

Calculation based on density functional theory (DFT) was used to gain insight into the molecular structure and electron distribution. As we can see from the frontier orbitals of **POZ-1** and **POZ-2** (Figs. 5 and 6), they have the similar HOMOs and LUMOs. The HOMO is mainly distributed on the POZ unit and the LUMO is mainly distributed on the anchoring group (carboxylic acid) and thiophen-conjugate unit.

According to further analyses on the calculated $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitation based upon the TD-DFT simulation, the lowenergy absorption band of **POZ-2** mainly includes the transitions



Fig. 6. Distribution of frontier molecular orbitals involving $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions for POZ-1 and POZ-2 in THF. All the isodensity surface values are fixed at 0.04.

Table 2

Calculated $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2 \lambda_{max}$, oscillator strengths (f) and main transition assignments for **POZ-1** and **POZ-2**.^a

Dye		λ _{max} [nm]	f	Transition assignments
POZ-1	$S_0 \rightarrow S_1$	461	0.0189	$H_{-0} \rightarrow L_{-0}(96\%)$
	$S_0 \rightarrow S_2$	371	1.1622	$H_{-1} \rightarrow L_{-0}(100\%)$
POZ-2	$S_0 \rightarrow S_1$	480	0.9679	$H_{-0} \rightarrow L_{-0}(95\%)$
	$S_0 \rightarrow S_2$	342	0.4175	$H_{-1} \rightarrow L_{-0}(98\%)$

^a H \rightarrow HOMO; L \rightarrow LUMO.



Fig. 8. Optimized molecular geometries of POZ-1 and POZ-2.

of HOMO–LUMO and HOMO – 1–LUMO which can be assigned to the intramolecular charge transfer from the POZ donor and its adjacent conjugated unit to cyanoacrylic acid acceptor. But for **POZ-1**, the transition of $S_0 \rightarrow S_1$ is prohibited and there is no obvious absorption (f = 0.0189, Fig. 7 and Table 2) in the corresponding theoretical absorption wavelength (461 nm) of HOMO–LUMO. The transition of HOMO – 1 to LUMO is the main low-energy absorption band of **POZ-1**, so the transition energy of **POZ-1** is higher than **POZ-2**, which results in the weak light-harvesting capacity of **POZ-1**. That's in good agreement with the UV–vis absorption spectra of **POZ-1** and **POZ-2**. The main reason leading to this phenomenon is



Fig. 9. Photocurrent action spectra of POZ-1 and POZ-2.



Fig. 10. Absorption percentage of a cell possessing a transparent 7-µm-thick mesoporous titania film grafted with **POZ-1** or **POZ-2** in contact with the electrolyte for cell fabrication.

that the strong rigidity of POZ contributes to an 83° torsion angle between POZ and extra phenyl ring when conjugated along with 'N' atom for **POZ-1** (Fig. 8). Moreover, the dihedral angle between benzene and thiophen (24°) in **POZ-1** is larger than that between



Fig. 11. (A) J-V characteristics measured under irradiation of 100 mW cm⁻², simulated AM1.5 sunlight. (B) Plots of open-circuit photovoltage as a function of short-circuit photocurrent density. Cells were tested using a metal mask with an aperture area of 0.158 cm⁻². An antireflection film was adhered to a testing cell during measurements.

Table 3

Photovoltaic parameters of cells measured at an irradiation of 100 mW $\rm cm^{-2},$ simulated AM1.5 sunlight.^a

Dye	$V_{\rm oc} [{\rm mV}]$	$J_{\rm sc}$ [mA cm ⁻²]	FF	η [%]
POZ-1	660	4.83	0.74	2.4
POZ-2	730	12.82	0.69	6.5

^a The validity of our photovoltaic data is confirmed by comparing the calculated j_{sc} via wavelength integration of the product of the standard AM1.5 emission spectrum (ASTM G173-03) and measured IPCE spectra with the experimental j_{sc} showing a less than 5% error. Also note that all our cells show a linear dependence of photocurrent on light intensity.

POZ and thiophen (16°) in **POZ-2**. So, the weak planarity and delocalization ability of **POZ-1** lead to the prohibition of POZ do-nor's charge transporting to the accepter unit.

3.3. Photovoltaic performance of DSSCs

Fig. 9 shows the photocurrent action spectra of DSSCs which made from 7 + 5 µm thick bilayer titania films coated with **POZ-1** and **POZ-2** in THF/AN(v/v 1/1). The onsets of IPCE spectra increase in the order **POZ-1** < **POZ-2**, and the **POZ-2** cell has a much broader and higher IPCE peak which is in good agreement with the absorption spectra of **POZ-1** and **POZ-2** dye in 7 µm transparent TiO₂ with electrolyte (Fig. 10). Though **POZ-2** features a smaller dye loading amount on titania surface $(2.4 \times 10^{-8} \text{ mol cm}^{-2} \text{ µm}^{-1})$ compared to that of **POZ-1** ($3.1 \times 10^{-8} \text{ mol cm}^{-2} \text{ µm}^{-1}$), the cell with **POZ-2** possesses stronger absorption owing to the higher absorptivity character of **POZ-2**.

As presented in Fig. 11A, the photocurrent density–voltage (*J*–*V*) characteristics were recorded under simulated AM1.5G illumination (100 mW cm⁻²) and the detailed photovoltaic parameters were collected in Table 3. The **POZ-1** and **POZ-2** cells display power conversion efficiencies (η) of 2.4% and 6.5% respectively. Note that the efficiency of the N719 dye under the same device condition is 6.7%. The great improvement of efficiency from **POZ-1** to **POZ-2** is mainly related to the short-circuit photocurrent density (*J*_{sc}) increasing from 4.83 mA cm⁻² to 12.82 mA cm⁻². This increase is due to the better light-harvesting capacity of **POZ-2** than **POZ-1** when the conjugated direction has been changed and the alkyl chain was added in **POZ-2** which can restrain the charge recombination. That's in good agreement with the absorption and IPCE spectra. Moreover, there is a very small efficiency decrease of these

cells placed on the lab bench for over two months. Assuming J_{sc} is proportional to photocarrier generation flux, we further measured the current density–voltage (J–V) curves of these two cells at various light intensities and plotted V_{oc} as a function of J_{sc} in Fig. 11B. At a given J_{sc} , the photovoltage increase in the order **POZ-1** < **POZ-2**.

For a certain redox electrolyte in DSSCs, it is well recognized that a rise or fall of V_{oc} stems from a shift of electron quasi-Fermi-level ($E_{F,n}$) in titania, which could be related to a variance of titania conduction-band edge (E_c) and/or a fluctuation of electron density [45,46]. At a given photocarrier generation flux, the electron density is controlled by the interfacial recombination of titania electrons with electron accepting species in electrolyte and/or dye cations. Thus, we further performed charge extraction and transient photovoltage decay measurements to understand the alterative order of V_{oc} .

As depicted in Fig. 12A, at the same V_{oc} or potential bias the **POZ-1** and **POZ-2** cells have different extracted electron density (d_e). With respect to the **POZ-2**, there is an upward shift of ~ 17 mV in the **POZ-1** cell of the titania conduction-band edge against the electrolyte Fermi-level. However, the relatively higher conduction-band edge of the **POZ-1** cell does not lead to improved V_{oc} , owing to a shortened charge recombination lifetime (τ) at a given d_e as presented in Fig. 12B. At the same d_e , the charge recombination lifetime (τ) of **POZ-2** are more longer than **POZ-1**, it's possibly due to the flexible alkyl chains of **POZ-2** which can restrain the charge recombination of titania electrons with electron accepting species in the electrolyte. Thereby, the interfacial charge recombination is a crucial influential factor of the rise or fall of V_{oc} . It's in good agreement with the alterative order of V_{oc} .

4. Conclusions

In summary, we have comparatively studied the properties of two POZ-based dyes which have different conjugated directions, extra phenyl ring and alkyl chain. The results of UV–vis, IPCE, *J*–*V*, transient photovoltage decay and charge extraction measurements have suggested that the conjugative and delocalization ability of **POZ-2** were better than **POZ-1** when the phenyl ring was added in **POZ-1** and the conjugated direction has been changed from along with 'N' atom to along with 2-position of POZ unit. Nearly 90° of the dihedral angle between POZ and phenyl ring unit in **POZ-1** leads to the intramolecular charge transfer transition (HOMO–LUMO)



Fig. 12. (A) Extracted electron density in titania against open-circuit photovoltage. (B) Electron lifetime as a function of extracted electron density for cells made with titania films coated by POZ-1 and POZ-2.

being prohibited from the POZ donor to thiophen-conjugated unit and cyanoacrylic acid acceptors. Also, the interfacial charge recombination is a crucial influential factor of $V_{\rm oc}$.

Acknowledgments

This work was supported by grants from the Natural Science Foundation of China (NOs. 20976199, 21204103 and 51103146) and the National 973 Program (No. 2011CBA00702).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.09.039.

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