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

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ABSTRACT

Two phenoxazine (POZ)-based organic D–π–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.

1. Introduction

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 influencing 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], tetrahydroquinoline [29,30], carbazole [31] and hetero-anthracene (phenothiazine and phenoxazine) [32–38] have been developed and showed good performance. The traditional design concept of the organic dyes is donor–π-linker–acceptor (D–π–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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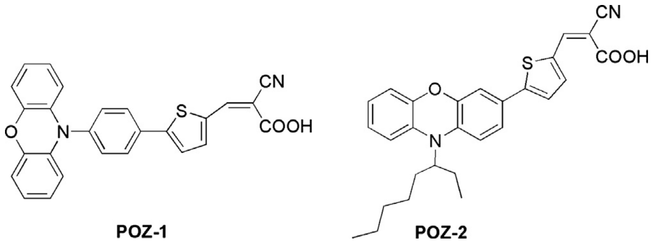


Fig. 1. Chemical structures of **POZ-1** and **POZ-2**.

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(trifluoromethanesulfonyl)imide (EMITFSI), 1,3-dimethylimidazolium iodide (DMII), guanidinium thiocyanate (GNCS) and 4-tert-butylpyridine (TBP) were purchased from Sigma–Aldrich.

2.2. Synthesis

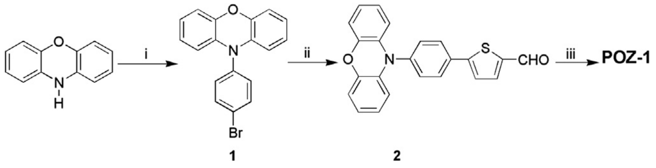
POZ-1 was synthesized by the Suzuki cross-coupling of bromine substituted aromatic compound 1 and 5-formyl-2-thiopheneboronic acid. Then the widely employed Knoevenagel condensation was used to construct the cyanoacrylic acid dye (Scheme 1). **POZ-2** was synthesized according to a previous publication [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 round-bottomed 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%). ^{1}H NMR ($CDCl_3$, 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 $Pd(PPh_3)_4$ (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 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%). ^{1}H NMR ($CDCl_3$, 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: $m/z = 369.1$.



Scheme 1. Synthesis route of **POZ-1**. Reagents: i) Cu, K_2CO_3, 1-Bromo-4-iodobenzene; ii) 5-Formyl-2-thiopheneboronic acid, KOAc, THF, $Pd(pph_3)_4$; iii) Piperidine, Cyanoacetic acid.

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%). ^{1}H 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 three-electrode 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 TiO_2 particles was used as the mesoporous negative electrode. A 7 μm thick transparent layer of 20 nm sized titania particles were first printed on the fluorine-doped SnO_2 (FTO) conducting glass electrode and further coated by a 5 μm thick scattering layer of 400 nm sized

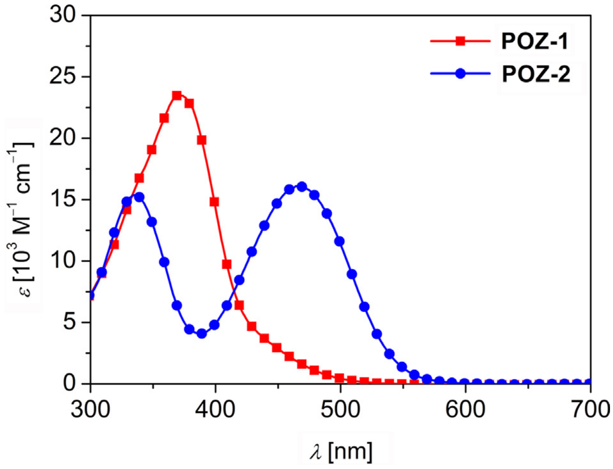


Fig. 2. UV–vis absorption spectra of **POZ-1** and **POZ-2** in THF.