



New *N*-methyl pyrrole and thiophene based D– π –A systems for dye-sensitized solar cells

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ABSTRACT

Dye-sensitized solar cells (DSSCs) containing novel **DP-T** and **DP-P** organic sensitizers having thiophene and *N*-methyl pyrrole moieties as π bridges in a D– π –A system were assembled and characterized. Incorporation of a thiophene bridge to give sensitizer **DP-T** enhanced solar energy capture, while impedance spectroscopy showed a much longer electron recombination lifetime (τ) for the DSSCs based on pyrrole containing sensitizer **DP-P**. The observed kinetics led to increased open circuit voltage (V_{oc}) for the device based on **DP-P**, regardless of types of additives (TBP or DCA) employed in the devices. Better photovoltaic performance was achieved using **DP-T**.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are of great interest because their construction involves low cost components and they are relatively simple, affording them the potential to compete with fossil fuel-based electricity generation, a non-renewable process. Ru (II) based polypyridyl complexes for DSSCs attracted early attention in this arena, by giving a photon-to-current conversion efficiency (η) of $\sim 12\%$ [1]. Studies aimed at metal-free dye sensitizers led to merocyanine [2], oligoene [3,4], coumarin [5,6], indoline [7,8], and cyanine dyes [9,10], with an efficiency (η) up to 10% achieved by using metal-free dye C219 containing ethylenedithiophene and dithienosilole blocks [11]. Although the performance of DSSCs based on metal-free organic dyes has not exceeded that of solar cells based on Ru-complexed dyes, metal-free types remain of interest for DSSCs due to advantages that include high absorption coefficients resulting from intramolecular π – π^* transitions, straightforward synthesis, color tuning, structural modification for desired physical and photochemical properties, and their economy. Typical metal-free sensitizers are based on

a donor–spacer–acceptor system (D– π –A), to achieve effective charge separation and transfer. Molecular engineering of donor groups has evolved from the use of a simple triphenylamine moiety to a starburst phenylene based moiety [12,13], to control electronic levels or molecular geometry and to afford effective charge transfer. A π bridging unit has been a common design feature, to influence HOMO/LUMO energy levels and/or spectroscopic properties [14]. Generally, increased conjugation path length using oligoene [4] or oligothiophene [5] was adopted as a basic way to achieve a red shift. However, a flexible extended chain length had a negative effect on charge separation or efficient generation of photons, thus counteracting the positive effect of red shifted absorption spectra contributing to large solar capture [15]. On the other hand, it was reported that the presence of a rigid spacer [16,17] or introduction of an alkyl group [18] as a side chain affected dye aggregate and/or charge recombination and, consequently, photovoltaic performance. Results from another recent study showed that the even a small change in the bridging unit caused a significant change in photovoltaic parameters [19]. In addition, aryl amine based donors [20,21] have been used to give efficient charge separation and/or control charge recombination. In view of these different results, the rigid *N*-methyl pyrrole system, having both electron rich character and low delocalization energy [22], attracted our attention and led us to investigate its effect on photovoltaic parameters relative to the thiophene ring system commonly incorporated into DSSC

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sensitizers. The present paper reports the photovoltaic performance of DSSCs sensitized with two new metal-free sensitizers in which a diphenylamino-substituted indole moiety and cyanoacrylic acid were connected using either thiophene or *N*-methyl pyrrole to form a D- π -A system (cf. Fig. 1), as a part of a larger study in which heterocyclic systems in place of a benzene spacer and a bulky *bis*-carbazoleaminor donor in place of diphenylamine were examined for DSSC dye development [23].

2. Methods

2.1. Materials

All reagents were purchased from Sigma–Aldrich, TCI, or Fisher Scientific. All chemicals used in this study were of reagent-grade quality and solvents purchased from commercial suppliers were used without further purification. Moisture-sensitive reactions were performed under either nitrogen or argon gas. All reactions were followed by thin-layer chromatography (TLC) using Analtech silica gel GHLF plates. The N719 sample used for fabrication of the reference solar cell was received as a gift from Dyesol and used without further purification.

2.2. Characterizations

2.2.1. Structure confirmation

¹H NMR spectra were recorded on a 300, 400, or 500 MHz Bruker Advance spectrometer using DMSO-*d*₆ or CDCl₃ as a solvent. ¹³C NMR spectra were recorded on a 500 MHz Bruker Advance spectrometer. 2-Dimensional NMR spectra including COSY, HSQC, and HMBC were recorded on a 500 MHz or 700 MHz Bruker Advance spectrometer. High resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI), in the positive mode, on an Agilent Technologies (Santa Clara, California) 6210 LC-TOF mass spectrometer.

2.2.2. Spectroscopic analysis

UV–Vis spectra in solution and in dye-loaded TiO₂ film were recorded on a Varian Cary 300 UV–Vis spectrophotometer. Photoluminescence of dye solutions was recorded using a fluorometer (Fluorolog[®]-3, HORIBA, USA) equipped with a 450 W xenon lamp (FL-1039/40, HORIBA, USA). The concentration of dye solutions for emission spectra was constrained to have absorbance of ~0.2. Fluorescence lifetime of each dye in THF was measured by a system using a TCSPC (time-correlated single photon counting) controller. LED (NanoLED-460, HORIBA) having a peak wavelength of 460 nm was used as an excitation source and Ludox[®] in distilled water was used as an internal reference. The instrument response was measured below the 200 ns of time period. The decay curve obtained was fitted to the multi-exponential function represented by $A + B1\exp(-i/T1) + B2\exp(-i/T2)$. In order to predict the amount of dye adsorbed on the TiO₂ surface, dyes on TiO₂ film were desorbed into a solution of 0.1 M NaOH in THF–H₂O (v/v, 1:1) followed by measurement of UV–Vis spectra and calculation of the adsorbed amount of dye using Beer–Lambert's law. Thickness of dye loaded TiO₂ film for all characterizations was 6 μ m.

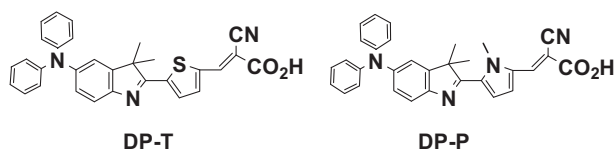


Fig. 1. Chemical structures of DP-T and DP-P.

2.2.3. Voltammetry and impedance measurements

The oxidation potential of dye adsorbed on TiO₂ films was measured using a three electrode electrochemical cell in acetonitrile containing 0.1 M TBAPF₆ (tetrabutylammonium hexafluorophosphate) at a scan rate of 100 mV s⁻¹. Dye coated TiO₂ film was used as a working electrode and Ag/Ag⁺ electrode and Pt wire were employed as a reference and counter electrode, respectively. The potential of the working electrode was calibrated with ferrocene as an internal reference.

The impedance spectroscopy of the cell was recorded using an impedance analyzer connected to a potentiostat (reference 600TM, Gamry Instruments, USA) in a frequency range of 0.1 Hz–10⁵ Hz at room temperature under dark condition. The applied forward bias was –0.65 V and AC amplitude was set to 10 mV.

2.2.4. Photovoltaic measurements

Photocurrent–voltage characteristics of DSSCs were measured using a Keithley 2400 source meter under illumination of AM 1.5 G solar light coming from solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). The incident light intensity was calibrated using a reference Si solar cell (Newport Oriel, 91150V) to set 1 Sun (1 mW/cm²). The current–voltage curve of the cell was obtained by applying external voltage bias and the measuring generated photocurrent. The measurement was fully controlled under Oriel IV Test Station software. A mask (0.30 cm²) was covered on the testing cell during photocurrent and voltage measurement. The photo active area of cell was 0.5 × 0.4 cm.

IPCE (incident monochromatic photon to current conversion efficiency) experiments were carried out using a system (QEX10, PV Measurements, USA) equipped with a 75 W short arc xenon lamp (UXL-75XE, USHIO, Japan) as a light source connected to a monochromator. Calibration of incident light was performed using a silicone photodiode (IF035, PV Measurements). Monochromatic quantum efficiency was recorded at short circuit conditions under AC mode with white-light bias. Wavelength sampling interval was 10 nm. The beam size of monochromatic light illuminated on DSSCs was 0.1 × 0.5 cm and chopping speed of AC was set to 10 Hz.

2.3. Synthesis of target dye sensitizers

2.3.1. (2E)-2-cyano-3-(5-(5-(diphenylamino)-3,3-dimethyl-3H-indol-2-yl)thiophen-2-yl)acrylic acid (DP-T)

To a solution of compound **1c** (0.3 g, 0.70 mmol) and 2-cyanoacetic acid (0.07 g, 0.85 mmol) in acetonitrile (70 ml) was added a few drops of piperidine under N₂ gas flow. The reaction mixture was then stirred under reflux at 80 °C. The precipitate formed during reaction was collected by filtration and dried. Pure DP-T was obtained by column chromatography (dichloromethane/methanol, 12/1, v/v) on silica gel, to give a red solid. Yield: 87%, ¹H NMR (300 MHz, DMSO-*d*₆) δ = 8.13 (s, 1H), 7.87 (d, 1H, *J* = 3.9 Hz), 7.76 (d, 1H, *J* = 3.6 Hz), 7.54 (d, 1H, *J* = 8.4 Hz), 7.33–7.28 (m, 4H), 7.21 (d, 1H, *J* = 2.1 Hz), 7.06–7.01 (m, 6H), 6.93 (dd, 1H, *J* = 8.2 Hz, 2.1 Hz), 1.47 (s, 6H). ¹³C NMR (500 MHz, DMSO-*d*₆) δ = 176.35, 162.84, 148.97, 148.39, 147.44, 145.84, 141.09, 140.07, 139.56, 135.83, 129.54, 129.52, 123.66, 123.56, 122.90, 121.25, 118.83, 117.23, 111.53. HRMS-ESI: calculated for C₃₀H₂₃N₃O₂S (M + H)⁺/z 490.1584, Found: 490.1579.

2.3.2. (2E)-2-cyano-3-(5-(5-(diphenylamino)-3,3-dimethyl-3H-indol-2-yl)-1-methyl-1H-pyrrol-2-yl)acrylic acid (DP-P)

To a stirred solution of **2d** (0.13 g, 0.31 mmol) and 2-cyanoacetic acid (0.05 g, 0.61 mmol) in ethanol (20 ml) was added NaOH (0.05 g, 1.22 mmol) under N₂ gas flow. The reaction mixture was then stirred under reflux at 80 °C. The mixture formed during reaction was filtered and product was dried. Pure DP-P was obtained by

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