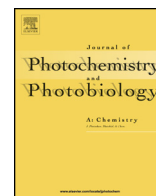




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Effect of π -spacers on the photovoltaic properties of D– π –A based organic dyes



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ABSTRACT

Three new triphenylamine based D– π –A (TPC, TSC and TOC) dyes with different π -spacers have been synthesized and analysed their significance on the photophysical properties and photovoltaic applications. The synthesized dyes were characterized by NMR, mass, melting point, absorbance and electrochemical measurements. In these dyes, triphenylamine moiety was utilized as electron donor and cyanoacetic acid acts as an electron acceptor. By keeping phenyl acetonitrile as one π -spacer and another π -spacer is varied by benzene/furan/thiophene group and their consequences on the photophysical, electrochemical and photovoltaic properties were analysed. Photovoltaic parameter such as short circuit current density (J_{SC}) and open circuit voltage (V_{OC}) is found to be significantly varied by changing the π -spacer. The maximum absorption was observed for TSC with thiophene linker which results in high J_{SC} value than TPC and TOC. However, a high V_{OC} of TPC results in better photovoltaic performance of 3.52% among other dyes. The outcome from the photophysical and photovoltaic measurements implies that the phenyl and thiophene spacer yields higher power conversion efficiency when compared to the furan bridged dye. The observed results will provide basic information for future designing of sensitizers with different π -spacers for photovoltaic applications.

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1. Introduction

Dye sensitized solar cells (DSSCs) have contributed significantly in energy conversion devices, due to their high performance and low production cost [1]. DSSCs are flexible, colorful, transparent, work at different angles with low light intensity and have lower CO₂ emission making it as environmental friendly technique among other high cost solar cell techniques. Among the major components in DSSCs, sensitizer plays a crucial role in achieving high power conversion efficiency and has been intensively studied. To overwhelm the high cost of ruthenium complex, metal free organic dyes are extensively explored in recent years. Zinc porphyrins achieved a maximum power conversion efficiency of 13% till date [2]. Generally, the organic molecules are composed of donor (D), spacer (π) and acceptor (A) as the common system [3].

Wide absorption in the visible region is an important criterion for a sensitizer. Tuning the absorption to longer wavelength region has been achieved so far either by increasing the electron donating ability of donor or expanding the spacer and enhancing the electron withdrawing ability of acceptor. For the past decades, donor fragments such as triarylamine [4], carbazole [5], phenothiazine [6], pyrene [7], indoline [8], fluorene [9], coumarin [10] and π -spacers such as thiophene, furan, benzene, isoxazole, thiazole, quinoline act as π -spacers [11] and acceptor parts such as cyanoacetic acid, carboxylic acid and rhodanine acetic acid have been employed in the D– π –A systems. Among this, triarylamine has the good electron donating ability in many sensitizers and enhances the photovoltaic performance. Cyanoacetic acid has proven to be an excellent candidate as acceptor fragment due to its strong electron withdrawing cyano group and carboxylic acid anchoring group on the TiO₂ surface. The π -spacer plays an important role in D– π –A systems to extend the π -conjugation from donor to acceptor which results in bathochromic shift in the absorption spectrum. Huang et al. [12] introduced cyanovinyl entity as π -spacer to increase the absorption wavelength of the dyes for better light harvesting. Qin et al. [13] introduced

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4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one as a strong acceptor between the donor and acceptor groups results in achieving panchromatic absorption of the sensitizer. Menzel et al. [14] introduced 4-methoxy-1,3-thiazole and thiophene as π -spacer for photovoltaic applications. Hence, tuning the bridging part of donor and acceptor parts assist in achieving better performance.

Based on this, we designed three (D- π - π -A) sensitizers with triphenylamine as the donor and cyanoacetic acid act as acceptor. These two moieties are bridged by vinyl phenyl acetonitrile as common π -spacer and varying the second π -spacer by benzene/furan/thiophene group to form TPC, TOC and TSC, respectively. All the new triphenylamine dyes were synthesized and characterized by spectroscopic techniques. The impact of different π spacers on the photophysical and photochemical properties were analysed using absorption, emission and cyclic voltammetric measurements. Photovoltaic parameter such as short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) is found to be significantly varied by changing the π -spacer.

2. Experimental methods

All chemicals were purchased from standard companies like Aldrich, Alfa Aesar, Merck Ltd., and used without further purification. 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (X-phos) and tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3) were used as ligand and catalyst for Buchwald reaction and were purchased from Alfa Aesar. All solvents were of spectrometric grade used without further purification. Methanol dried over 3 Å molecular sieves for 5 days and distilled before use. Thin layer chromatography checking was done using precoated silica gel sheets obtained from Merck Germany. All melting points were taken in open capillaries on a Buchi 530 apparatus and are uncorrected. 1H NMR and ^{13}C NMR spectrum was recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ -d or $DMSO-d_6$ solvent with tetramethylsilane as internal standard. Mass spectra were obtained with Bruker daltonics, FT-ICR/APEX II, ESI mode. MALDI-TOF mass spectra were recorded using Micromass ToF Spec 2E instrument. High-resolution mass spectra were obtained at the École Polytechnique Fédérale de Lausanne mass spectrometry laboratory (EPFL). Absorption spectra were generated using JASCO 300 UV-vis spectrometer. Emission and excitation spectra were recorded using a JASCO FP-6500 spectrofluorimeter with each 10 nm excitation and emission slit width and 500 nm/min scan rate in a 1 cm cell length at ambient temperature. Redox potentials were obtained by cyclic voltammetry using a three electrode system (platinum working electrode, Ag/AgCl reference electrode and platinum wire counter electrode) in an electrochemical workstation (SP-50 model potentiostat). Tetrabutyl ammonium hexafluoro phosphate ($TBAPF_6$, 0.1 M) is used as supporting electrolyte for TC, TPC, TSC and TOC compounds in acetonitrile (ACN) solvent. Ferrocene were used as internal reference. All samples were deaerated by bubbling with nitrogen gas for ca. 5 min at room temperature. All measurements were done at ambient temperature.

A 450 W xenon lamp (Oriel, USA) was used as a light source to study the current–voltage characteristics of the DSSC. The spectral output of the lamp was filtered using a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) to reduce the mismatch between the simulated and actual solar spectrum to less than 2%. The Keithley model 2400 digital source meter (Keithley, USA) was used for data acquisition. The photo-active area of 0.16 cm^2 was defined by a black mask of $6 \times 6\text{ mm}^2$. Incident photon-to-current conversion efficiency measurements were measured using the mono chromated visible photons, from Gemini-180 double monochromator Jobin Yvon Ltd. (UK), powered by a 300 W xenon light source (ILCTechnology, USA) superimposed on a 10 mW/cm^2 LED light. The monochromatic

incident light was passed through a chopper running at 2 Hz frequency and the on/off ratio was measured by an operational amplifier.

2.1. Device fabrication

A screen-printed double layer of nanocrystalline TiO_2 particles was used as the photoelectrode. The FTO glass plates were immersed in a 40 mM aqueous $TiCl_4$ solution at 70°C for 30 min and washed with water and ethanol. A $8\text{ }\mu\text{m}$ thick film of 20 nm sized TiO_2 particles was then printed on the FTO conducting glass and further coated with a $5\text{ }\mu\text{m}$ thick second layer of 400 nm light-scattering TiO_2 particles (400 nm diameters, Catalysts & Chemicals Ind., Co., Ltd. (CCIC), HPW-400). Sintering was carried out at 500°C for 15 min, which was gradually heated. The working electrode was prepared by immersing the $13.0\text{ }\mu\text{m}$ ($8.0\text{ }\mu\text{m}$ thick transparent layer + $5.0\text{ }\mu\text{m}$ thick scattering) TiO_2 film into the dye solution for 12 h. To prepare the counter electrode, Pt catalyst was deposited on cleaned FTO glass by coating with a drop of H_2PtCl_6 solution (10 mM in 2-propanol solution) with heat treatment at 400°C for 15 min. For the assembly of DSSCs, the dye-containing TiO_2 electrode and Pt counter electrode were assembled into a sandwich-type cell and sealed with a hot-melt gasket of $25\text{ }\mu\text{m}$ thickness made of the ionomer Surlyn 1702 (Dupont). Devices were completed by filling the electrolyte by pre-drilled holes in the counter electrodes and finally the holes were sealed with a Surlyn sheet and a thin glass cover by heating. A black mask ($6 \times 6\text{ mm}^2$) was used in the subsequent photovoltaic studies.

2.2. Synthesis and characterization

2.2.1. 4-Diphenylamino-benzaldehyde (TA)

To a 25 ml round bottom flask was charged with a solution of DMF (2.01 mol ratio) and 1,2-dichloroethane (3 ml) at 0°C . $POCl_3$ (1.25 mol ratio) was slowly added to the mixture. Triphenylamine (5 g, 1 mol ratio) in 1,2-dichloroethane (3 ml) was added drop wise to the above mixture. The mixture was stirred for 12 h at 90°C . Next, it was poured into ice water and the compound was filtered and dried to give yellow color TA. Yield – 88.9%, 1H NMR, (400 MHz, $CDCl_3$ -d): δ = 9.80 (s, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.34 (t, J = 7.6 Hz, 4H), 7.18 – 7.15 (m, 6H), 7.01 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR, (100 MHz, $CDCl_3$ -d): δ = 190.46, 153.39, 146.18, 131.34, 129.76, 129.13, 126.34, 125.15, 119.37 ppm.

2.2.2. 2-(4-Bromo-phenyl)-3-(4-diphenylamino-phenyl)-acrylonitrile (TA-BrP)

To compound TA (0.500 g, 1 mol ratio), 4-bromophenylacetonitrile (0.430 g, 1.2 mol ratio) was dissolved in dried methanol (34 volume) under stirring. To the mixture potassium tert-butoxide (0.287 g, 1.4 mol ratio) was added and kept reflux for 3 h. A bright yellow color solid was thrown out during the reaction, filtered and dried under vacuum to afford bright lemon yellow solid (TA-BrP). Yield – 92.5% 1H NMR, (400 MHz, $CDCl_3$ -d): δ = 7.76 (d, J = 8.4 Hz, 2H), (q, 4H), 7.39 (s, 1H), 7.32 (t, J = 8 Hz, 4H), 7.17 – 7.11 (m, 6H), 7.04 (d, J = 8.8 Hz, 2H) ppm. ^{13}C NMR, (100 MHz, $CDCl_3$ -d): δ = 150.24, 146.52, 142.04, 134.09, 132.13, 130.81, 129.64, 127.18, 126.03, 125.84, 124.57, 122.62, 120.70, 118.45, 106.39 ppm. Mass spectra (ESI): calculated for $C_{27}H_{19}N_2Br$ [$M + H$] = 450.07, found = 451.33.

2.2.3. 3-(4-Diphenylamino-phenyl)-2-[4-(5-formyl-thiophen-2-yl)-phenyl]-acrylonitrile (TABS)

A 25 ml round neck bottom flask was charged with dimethoxy ethane (50 volume) and H_2O (10 V) under N_2 atmosphere. Add TA-BrP (0.521 g, 1.2 mol ratio), 5-formylthiophene-2-yl boronic acid (0.150 g, 1 mol ratio) and Na_2CO_3 (0.306 g, 3 mol ratio) to the above mixture and stir 10 min. A $Pd(PPh_3)_2Cl_2$ (0.034 g, 0.05 mol ratio)

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