



Influence of *m*-fluorine substituted phenylene spacer dyes in dye-sensitized solar cells



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ABSTRACT

A series of new organic dyes based on fluorine substituted phenyl moiety, used as a π -linker in various dyes, were designed and synthesized for dye sensitized solar cell (DSSC) application. These dyes share same anchoring group (Cyano acrylic acid) with different donors such as carbazole, thiophene substituted carbazole, triphenylamine and phenothiazine moieties. For effective electron flow, the dyes were incorporated with novel D- π -A or D-A-A framework. The optical, electrochemical, time-resolved photoluminescence (TRPL) spectra and photovoltaic properties of the dyes were carefully studied. The results reveal that without addition of any co-adsorbent, among all fluoro-phenyl spacer dyes, the Cz-dye showed highest open circuit voltage (V_{oc}), short circuit current (J_{sc}) and exhibited enhanced PCE value of 4.2 (± 0.2) %, due to the deeper HOMO level of dye, planarity of backbone with better charge transfer occurring from D to A. The optimization calculations for the geometries of all the dyes with fluoro phenyl substituted π -linkers were ascertained by Density functional theory (DFT) using B3LYP/631G (d,p) basis set.

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1. Introduction

Due to the growing demand for green energy, researchers have been attracted towards sustainable energy resources and thereby a great deal of attention on efficient solar cells development is under investigation. DSSCs with remarkable performance initially developed by Grätzel and O'Regan have generated immense hope in harvesting solar energy [1]. Over the past decade unconventional solar cells have been developed, yet considerable efforts on developing efficient dye sensitized solar cell (DSSC) have been devoted due to the high solar energy to electric conversion efficiency and its potential for low cost production and easy fabrication process as compared to traditional silicon based solar cells [2–4]. In DSSCs, the key component is a sensitizer, due to its function of light harvesting and electron injection capacity [5,6]. Ruthenium-based sensitizers (N3, N719 and black dye) are the most representative and most successful in DSSCs due to their long term stability and

outstanding performances (PCE = >10% at AM 1.5 condition) [7,8]. However, these dyes are inconvenient for commercial applications as they are very expensive, challenging synthesis, tedious purification, lower molar extinction coefficient and environmental issues. On the other hand, organic dyes (metal-free) are gradually attracting researchers attention due to the multiple advantages of relatively lower cost, high molar extinction coefficient, easy synthesis and excellent flexibility in structure modification, easily tunable functionalities and the photophysical as well as photochemical properties of dyes [9–12]. In the recent past, donor- π -acceptor (D- π -A) structures based on organic sensitizers were constructed to achieve efficient solar energy harvesting. For efficient dye materials, different donor moieties such as carbazole, thiophene substituted carbazole, triphenylamine and phenothiazine are incorporated with cyanoacrylic acid as acceptor/anchoring group (Fig. 1). Because these donors have good electron donating ability and cyanoacrylic acid has efficient electron injection ability, it is believed that both can improve the overall performance of the dye molecules. Spacer/ π -linker in between the donor and acceptor also plays a crucial role for the superior performance of the cell [13–16].

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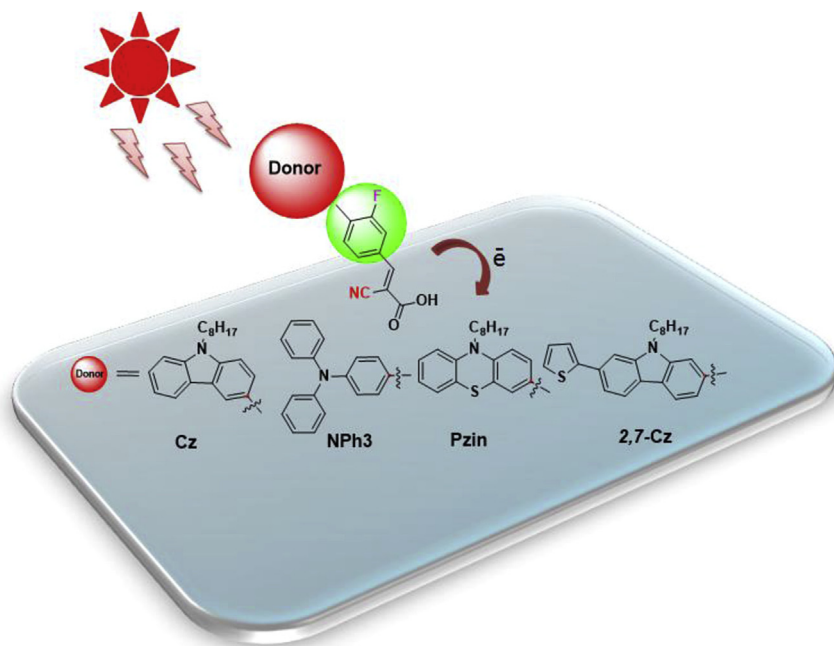


Fig. 1. Chemical structure of organic dyes.

Generally in DSSCs the photo-excited state of dye injects electrons into the conduction band of the semiconductor layer having nano-crystalline TiO_2 or ZnO [16,17]. Oxidized dye is regenerated by the redox shuttle of the electrolyte which injects electron into the HOMO of the oxidized dye. Some factors that control the power conversion efficiency (PCE) of the dye are light harvesting, electron injection, charge recombination and dye regeneration. Among them charge recombination with electrolyte (oxidized) and dye aggregation remain unresolved problems [18,19]. To inhibit the dye aggregation the bulky groups or alkyl chains were incorporated at the donor site. Addition of co-absorbents (antiaggregation agents) such as deoxycholic acid (DCA) or chenodeoxycholic acid (CDCA) suppress the dye aggregation on the TiO_2 layer [20].

Recently several groups have made tremendous efforts to design organic sensitizers to obtain higher PCE and have incorporated fluorine atom into the π -bridge of organic dyes. The advantage of fluorine atom containing π -bridge/spacer is to generally obtain the electron-withdrawing ability and drastically tune the dye molecule properties, like changing the energy levels, governed by charge distribution, charge transfer from D to A and improving the electron mobility. In addition, fluorine atom substituted π -bridge also has strong influence on the intra and inter molecular interaction through hydrogen-bonding and decrease the LUMO energy level of the dye [21]. Several organic dyes possessing fluorine substituents have been reported. Ortho substituted fluorine phenyl spacer with 4,4'-dialkyl Cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) were reported for efficient DSSCs [22]. Similarly, few other reports appeared where comparative study with and without fluorine substituted phenyl spacer for tuning electron flow in DSSC were studied, thereby explaining that ortho-fluorinated phenyl plays a very important role for improving the cell performance (especially improve open-circuit voltage) [23–25]. On the contrary, ortho-fluorinated phenyl that does not play any significant role for improving the device performance has also been reported [26].

For achieving optimized structure, meta-substituted fluoro phenyl (*m*-PhF) group was introduced as a π -linker, four different polycyclic aromatic moieties were employed as electron-donating groups and cyano acrylic acid moiety acts as anchoring group

(Scheme 1, Figs. S1–S32). Generally these kind of dyes are reported as acceptor molecules in solid state DSSCs [22]. To the best of our knowledge, carbazole based dyes (Cz-dye) showed superior results and may be applicable further in solid state DSSCs. We introduced linear octyl alkyl chains at the donor site to suppress the dye molecule aggregation and avoid close contact to the electrolyte on TiO_2 surface. Fluorine substituted phenyl as a spacer containing dye improves the intra and inter molecular interactions, but without addition of any co-absorbent (CDCA or DCA) on TiO_2 layer we achieved highest efficiency (PCE) of 4.2% by using a simple Cz-dye. These novel dyes have high open-circuit voltage (0.778 V) and short-circuit current (8.65 mA/cm^2) and highest PCE of $4.2 \pm 0.2\%$, corresponding to the simple D- π -A architecture of CZ-dye. This dye has a deep HOMO level, high molar absorption coefficient ($13,126 \text{ M}^{-1} \text{ cm}^{-1}$), planarity of backbone and long excitation life time value $\tau(\text{ns}) = 1.25, 2.80$ (Table 1) compared to other dyes. Comparatively, 2,7-Cz dye (molar absorption coefficient = $19,752 \text{ M}^{-1} \text{ cm}^{-1}$) has a similar architecture to Cz-dye, but due to blue shift in absorption spectral values weak charge transfer from donor to acceptor affected the cell efficiency with this dye. The NPh3 and Pzin dyes have lower efficiency values of $\eta = 2.9\%$ and 2.6% with the three dimensional triphenyl amine, two dimensional phenothiazine (Butterfly) structure as the charge recombination occurs between the high lying HOMO level of dye and electrolyte. High lying HOMO levels of NPh3 and Pzin dyes are 0.75 and 0.82 V (vs NHE) and these energy levels are close to I^-/I_3^- (0.4V vs NHE) redox shuttle (ESI Fig. S33). This series of novel dyes are characterized by NMR (^1H NMR, ^{13}C NMR, ^{19}F NMR), mass spectrometry (ESI) and the corresponding optical, electrochemical and photovoltaic properties are also presented and discussed elaborately.

2. Experimental section

The chemical structures of dyes are shown in Fig. 1 and the synthetic route is depicted in Scheme 1. Material Characterization and Fabrication of photovoltaic devices are available (ESI Page S3-S4).

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