



# Synthesis, optical, electrochemical and photovoltaic properties of organic dyes containing trifluorenylamine donors



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## ABSTRACT

Two new organic dyes based on trifluorenylamine donor and cyanoacrylic acid acceptor have been synthesized and characterized by optical and electrochemical measurements and density functional theory calculations. It is found that the trifluorenylamine donor is beneficial to red-shift the absorption and to lower the oxidation potential when compared to the triphenylamine donor. The variations in the photovoltaic performance of the dyes are corroborated by the dye loading data, incident photon to current conversion efficiency and the interfacial kinetic parameters estimated from the intensity modulated photovoltage/photocurrent spectral measurements. A dye with fluorene and bithiophene segments in the  $\pi$ -linker exhibited device efficiency up to 5.8%. The enhanced power conversion efficiency exhibited by this dye when compared to its analogue containing diphenylaminofluorene donor is attributed to its superior anti-aggregation ability and the comparatively prolonged electron lifetime.

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## 1. Introduction

Ever since the pioneering work of O'Regan and Grätzel [1], dye-sensitized solar cell (DSSC) [2] fabricated using organic and organometallic dyes has received immense attention due to their potential advantages such as low cost, facile chemical modifications to fine-tune the functional properties and environmental friendliness. Typically, a DSSC is constituted by four major components namely mesoporous nanocrystalline semiconductor oxide such as titanium dioxide or zinc oxide based photoanode, an organic or organometallic sensitizer, redox shuttle in an electrolyte solution and a counter electrode. The sensitizer acts as light harvester and electron generator. The absorption of sun light by the sensitizer leads to an intramolecular charge transfer (CT) electronic excitation followed by electron injection into the conduction band (CB) of semiconductor oxide. Finally, the oxidized sensitizer is regenerated by the redox mediator. Ground and excited state potentials of the sensitizer predominantly affect the efficiency of the DSSC as they are directly related to the photocurrent generation and dye regeneration kinetics. Wealth of knowledge on the structural features affecting the ground and excited state properties are available

in recent literature dealing with the structure-property relationship investigations on different classes of sensitizers including ruthenium polypyridyl complexes [3], porphyrins [4] and metal-free organic dyes [5]. Among these sensitizers, metal free organic dyes are most attractive due to their easy synthesis, higher molar extinction coefficient for the charge transfer absorption, lower cost and environment compatibility. An organic dye is typically composed of three functionally unique structural elements: donor (D), acceptor (A) and  $\pi$ -linker. A large number of organic dyes with D- $\pi$ -A configuration and possessing amine donors such as triphenylamine [6], carbazole [7], indoline [8], phenothiazine [9], phenoxazine [10], etc. have been explored as sensitizers in DSSC. Polycyclic fused heteroaromatics have also been demonstrated as decent donors [11]. Heterocyclic rings possessing reduced aromaticity have been found to be beneficial for CT from the donor to acceptor [11,12]. Also, the presence of electron accepting units such as benzothiadiazole [13], benzotriazole [14], thienopyrazine [15], quinoxaline [16], diketeopyrrolopyrrole [6a,17], triazine [18], cyanovinyl [19], etc., has been found to alter the excited state energetics of the dyes and consequently the light harvesting properties. Despite the wealth of design rules evolved for organic dyes, most of the dyes known till now suffer from one or more of the detrimental processes such as dye aggregation at the surface of TiO<sub>2</sub>, enhanced charge recombination at the TiO<sub>2</sub>/electrolyte interface and the inherently narrow absorption below 600 nm. It has been found that

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the presence of electron rich donor groups produce red-shift in the absorption spectrum [8a,20] and introduction of longer alkyl/alkoxy chains on the donor [21] or  $\pi$ -linker [22] can in principle retard the electron recombination and dye aggregation. Alternatively, externally added co-adsorbants [23] have been used to inhibit  $\pi$ – $\pi$  stacking interactions of the organic dyes at the expense of the dye loading.

Ko and co-workers [24] have designed several organic dyes containing fluorene units in the donor part and found to efficiently function as sensitizer in DSSC. Difluorenylaniline moiety was found to display enhanced photo- and thermal-stability when compared to the corresponding triphenylamine-based dyes. Herein, we report two new organic dyes (Fig. 1) possessing trifluorenylamine donor and cyanoacrylic acid acceptor. We believe that the presence of fluorene moiety will be advantageous for several reasons: (a) Due to electron-richness and elongated conjugation fluorene will modulate the donor acceptor interactions and red-shift the corresponding CT transition. (b) The rigidity of the fluorene segment will suppress the vibrational relaxation pathways in the excited state [25]. (c) Furthermore, the alkyl chains on the fluorene nucleus may help to inhibit the dye aggregation and interfacial electron recombination processes. (d) Finally, the dye cations formed after electron injection is expected to be stabilized by fluorene unit due to delocalization of the charge and prolong the lifetime of the charge separated state. This will be beneficial for the electron injection from the dye to the TiO<sub>2</sub> CB [26]. We have used thiophene units in the conjugation pathway to increase the CT transition probability and hence the molar extinction coefficients for the longer wavelength absorption. The light harvesting properties of the new dyes (JA1 and JA2) are also compared with the known dyes (D1 and D2) featuring diphenylaminofluorene donor [27].

## 2. Experimental details

### 2.1. Materials and methods

All the chemicals were commercially available and they were used without further purification. All the solvents were dried using standard methods prior to use. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on a spectrometer operating at 500.13 and 125.77 MHz, respectively. Deuterated chloroform (CDCl<sub>3</sub>) and dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) were used as solvent. UV–vis spectra were recorded at room temperature in quartz cuvettes using a spectrophotometer for dichloromethane (DCM). The cyclic voltammetry (CV) recorded on an electrochemical workstation in DCM by using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The experiments were performed at room temperature with a three-electrode cell consisting of a platinum wire as auxiliary electrode,

a non-aqueous Ag/AgNO<sub>3</sub> reference electrode and a glassy carbon working electrode. Mass spectra were recorded in positive-ion mode on an ESI TOF high-resolution mass spectrometer.

### 2.2. Synthesis

#### 2.2.1. Synthesis of 7-bromo-*N,N*-bis(9,9-diethyl-9H-fluoren-2-yl)-9,9-diethyl-9H-fluoren-2-amine (1)

In a pressure tube bis(9,9-diethyl-9H-fluoren-2-yl)amine (1.1 g, 2.4 mmol), 2,7-dibromo-9,9-diethyl-9H-fluorene (1.82 g, 4.8 mmol) was mixed with sodium *t*-butoxide (0.35 g, 3.61 mmol), Pd(dba)<sub>2</sub> (27.6 mg), 1,2-bis(diphenylphosphino)ferrocene, (26.6 mg) in toluene (10 mL) under nitrogen atmosphere. This was heated at 80 °C for 36 h. After the completion of the reaction the volatiles were removed by evaporation. The residue was triturated with water and extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate and evaporated in vacuum to produce a crude product. It was adsorbed on silica gel and purified by column chromatography by using hexane/dichloromethane mixture as eluant. White solid. Yield: 0.90 g (50%). mp 203–205 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.35–0.38 (m, 18H), 1.82–2.01 (m, 12H), 7.09 (d, *J* = 7.5 Hz, 3H), 7.15–7.17 (m, 3H), 7.25–7.34 (m, 6H), 7.40–7.44 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.53–7.55 (m, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H); <sup>13</sup>C NMR (125.77 MHz, CDCl<sub>3</sub>)  $\delta$  152.0, 151.3, 150.9, 149.7, 148.1, 147.4, 141.4, 140.5, 136.6, 135.1, 130.0, 126.9, 126.4, 126.1, 123.2, 122.9, 122.8, 120.4, 120.3, 120.1, 119.1, 118.8, 118.3, 56.4, 56.1, 32.8, 32.7, 8.7. HRMS calcd. for C<sub>51</sub>H<sub>50</sub>BrN [M + Na<sup>+</sup>] *m/z* 788.3204 found 788.3200.

#### 2.2.2. Synthesis of 5-(7-(bis(9,9-diethyl-9H-fluoren-2-yl)amino)-9,9-diethyl-9H-fluoren-2-yl)thiophene-2-carbaldehyde (2a)

A mixture of (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane (0.58 mmol) and 7-bromo-*N,N*-bis(9,9-diethyl-9H-fluoren-2-yl)-9,9-diethyl-9H-fluoren-2-amine, **1** (0.400 g, 0.52 mmol) were taken in dry DMF (4 mL) and degassed with nitrogen followed by the addition of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (4 mg). The reaction mixture was heated at 80 °C for 24 h under nitrogen. After that, it was poured into water and extracted with dichloromethane. The organic layer was washed with brine solution followed by water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the solid residue was dissolved in glacial acetic acid (5 mL). The acetic acid solution was stirred for 30 min at 60 °C then water 10 mL was added. Heating was continued for 6 h. Then after cooling it up to room temperature water was added and extracted with dichloromethane. The organic layer was washed liberally with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent, the residue obtained was purified by column chromatography on silica gel using hexane/dichloromethane as eluant. Orange solid. Yield:

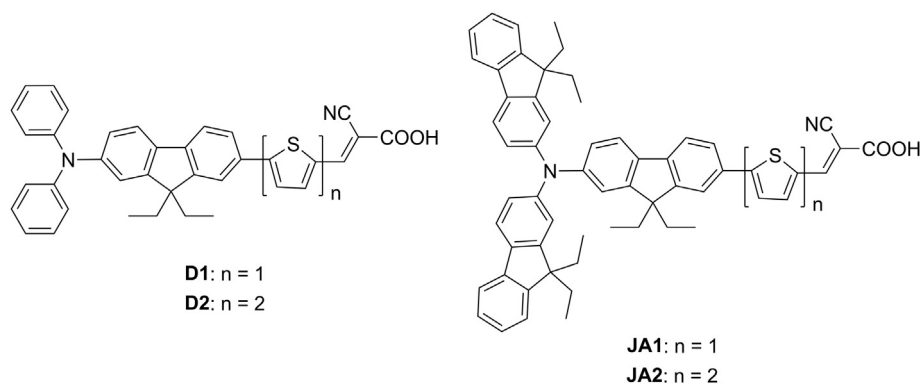


Fig. 1. Structures of the dyes.

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