



# Comparative analysis of fluorene and carbazole fused triphenylamine sensitizer donor units with new anchoring mode in dye-sensitized solar cells



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## ABSTRACT

Two fluorene- and carbazole fused triphenylamine-based metal-free organic polymer sensitizers that use 2-nitropyridine as a new acceptor anchoring mode but with different  $\pi$ -bridges of fluorene (FT04) and carbazole (CT04) have been designed, synthesized, and used as photosensitizers for dye-sensitized solar cells (DSSCs). Introduction of an imine unit into the  $\pi$ -bridge and extension of the  $\pi$ -bridge can dramatically improve the light-harvesting ability of DSSCs and suppress the electron recombination, thus uplifting their performance. The solar cell based on FT04 exhibited a broad incident photon-to-current conversion efficiency spectrum and high conversion efficiency ( $\eta = 4.95\%$ ). However, under the same measuring conditions, the polymer sensitizer CT04, which has a similar structure as that of FT04 but without the imine unit in the conjugated  $\pi$ -bridge, gave an  $\eta$  value of 3.50%, indicating that the sensitizers are promising candidates to improve the performance of DSSCs. The better cell performance of FT04 than that of CT04 can be attributed to better light harvesting and better dark current suppression.

## 1. Introduction

Polymer electronics is an emerging arena of intense research, where high performing organic semiconductors have the potential to deliver low-cost solutions, particularly in areas such as thin-film transistors, organic light-emitting diodes (OLEDs), and organic photovoltaics [1]. Dye-sensitized solar cells (DSSCs) are attractive as an alternate class of solar cells, and extensive research has been carried out in recent years [2]. In the recent years, numerous researchers have been captivated by structural engineering of sensitizers for DSSCs for the progression of next-generation solar cells because of their easy scale-up, economical production cost, and flexible structural modification [3]. Among the different types of sensitizers, metallo-organic dye sensitizers (MODs), such as ruthenium [4] and zinc porphyrin [5], show photo-conversion efficiency (PCE) between 11% and 13%. Instead, low-cost, metal-free organic dye sensitizers (MFODs), such as triphenylamine-derived dyes [6] and indoline-derived dyes [7], appear to be the most promising candidates for DSSCs.

To date, only a few examples of side-chain-functionalized polymers have been reported, mainly using triphenylamine-linked fluorene and carbazole as chromophores [8]. This calls for the design of new monomers with lower energy bandgaps, allowing extended absorption into the visible region. One methodology could be to increase the  $\pi$ -conjugation length of the pendant monomer. Although very useful, this

approach has its limitations as the molecular weights (MWs) of the monomers quickly become too high. Other methods include  $\pi$ -conjugated length alterations, increased aromaticity, substituent effects, and intermolecular interactions, which are often limited to fully conjugated polymer systems [9]. Another approach that provides a more feasible way of lowering the bandgap in pendant systems is the use of partial charge transfer/donor-acceptor (D-A) chromophores. These donor-acceptor (D-A) chromophores are formed when strong electron-donating and strong electron-withdrawing moieties interact through the high-lying HOMO of the donor and the low-lying LUMO of the acceptor [10]. The hybridization of these two orbitals results in new D-A orbitals with a smaller energy bandgap. The most commonly used dye anchoring group is a carboxylic acid moiety, which chemisorbs the dye on a  $\text{TiO}_2$  surface [11]. Lately, though its importance has been investigated and shown that it can affect both the DSSC stability, because of unwanted dye desorption, and power conversion efficiency, through back-electron transfer suppression [12]. In this respect, alternative anchoring groups to carboxylates have been shown to exhibit superior results [13]. Here, 2-nitropyridine as the electron-withdrawing unit has been successfully applied to this type of pendant chromophores.

Organic dyes commonly consist of donors,  $\pi$ -spacers, and acceptor groups (i.e., a D- $\pi$ -A molecular structure), and the properties of dye sensitizers can be finely tuned by altering different parts of the D- $\pi$ -A molecular architecture [14]. Triphenylamine and cyanoacrylic acid are

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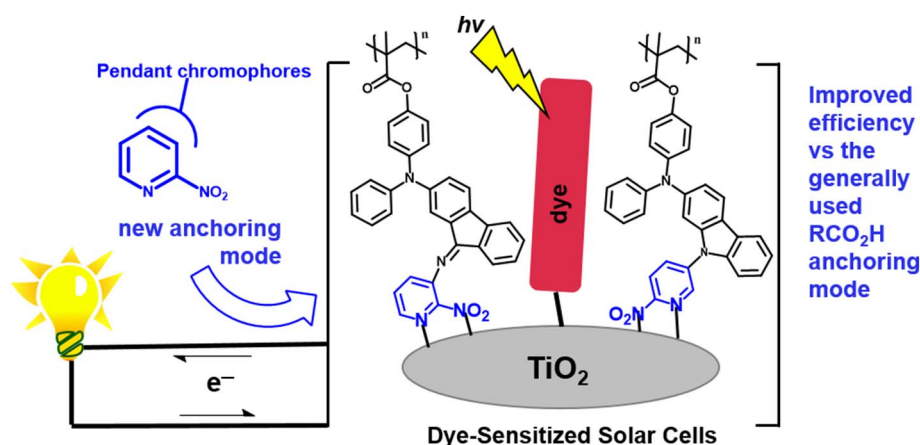


Fig. 1. Schematic representation of the synthesized polymers (FT04 and CT04), and the adsorption mode for anchoring group of 2-nitropyridine on  $\text{TiO}_2$  electrode surface.

often used as donor and acceptor, respectively, in conventional dye sensitizers. There are several factors such as the absorption range of sensitizers, aggregation of dye molecules on the  $\text{TiO}_2$  layer, and the delay time in dye regeneration after electron injection to the  $\text{TiO}_2$  conduction band, which affect the efficiency of resulting devices. The absorption and electrochemical properties can be tuned by a fine balance of donor-acceptor strength in the molecular dye architecture. In this regard, molecular modeling is a very important tool to design new efficient dyes [15]. Previously, we have studied the effect of the incorporation of picolinic acid as an acceptor on the photophysical properties of triphenylamine-based dyes [16]. In the present study, we report the effect of additional donors and different acceptor modes on the photophysical properties of the dyes and performance of these sensitizers in DSSC devices (Fig. 1).

In this contribution, we report the design and synthesis of new monomers based on electron-rich aromatic building blocks such as triphenylamine-linked fluorene (TFP) and carbazole (TCP) pendants and their radical polymerization with AIBN agent. Triphenylamine moiety with fluorene and carbazole substituents and nitropyridine were chosen as donor and acceptor-cum-anchoring group to the semiconductor surface, respectively. The twisted structure of the whole donor part may help to suppress dye aggregation on the  $\text{TiO}_2$  layer. This study also examined the thermal, photophysical, and electrochemical properties and photovoltaic performance of DSSCs.

## 2. Experimental section

### 2.1. Instruments

NMR spectra were taken with a Bruker-AVANCE-III 500 MHz FT-NMR spectrometer. FTIR spectra were obtained with a Bruker IFS 66 V Fourier Transform Spectrophotometer. High-resolution mass spectra were taken on a JEOL GCMATE II GC-MS. Polymer decomposition temperatures were studied by thermogravimetric analysis (TGA) using a Mettler 851e TGA under a nitrogen atmosphere. Molecular weights, average MWs, and poly dispersity index (PDI) were obtained by gel permeation chromatography (GPC) with tetrahydrofuran as an eluent and mono disperse polystyrene standards. UV-Vis absorption and fluorescence spectra were taken on a UV-1650PC Shimadzu UV-Visible spectrophotometer. The electrochemical measurement was carried out using an AUTOLAB PGSTAT302N electrochemical workstation in a typical three-electrode electrochemical system driven by the NOVA software package.

### 2.2. Materials and synthesis

The synthetic routes to FT04 and CT04 are shown in Scheme 1, and the synthetic procedure and characterization data are given in

Supporting Information (ESI<sup>†</sup>). All starting materials and solvents were commercially available and used without further purification (unless specially mentioned), and all reactions dealing with air- or moisture-sensitive compounds were carried out under nitrogen atmosphere using standard Schlenk techniques. Silica gel for column chromatography was 60–120 mesh. The fluorine-doped tin oxide (FTO) conducting glass used was washed successively with a detergent solution, deionized water, and ethanol/acetone under ultrasonication.

### 2.3. Preparation of $\text{TiO}_2$ /polymeric-dye hybrid films and device assembly

FTO-coated glass substrate (sheet resistance  $10 \text{ } \Omega \cdot \text{cm}^{-1}$ ; brought from BHEL, INDIA) was used to prepare dyed-titanium oxide electrodes. The FTO plate was immersed into the 40 mM aqueous titanium tetrachloride solution at  $70^\circ\text{C}$  for 30 min. A commercially available titanium oxide nanoparticle paste was coated onto the FTO glass by the doctor blade technique and subsequently sintered at  $500^\circ\text{C}$  for 15 min as described in the paper to prepare a mesoporous titanium oxide layer [17]. After immersing titanium oxide plates into the 40 mM aqueous titanium tetrachloride solution at  $70^\circ\text{C}$  for 30 min, the substrates were sintered at  $500^\circ\text{C}$  for 30 min. Thus, the obtained titanium oxide electrodes were immersed in the 0.15 mM dye solution (solvent: acetonitrile/*t*-butyl alcohol = 1:1 (v/v)) and kept in dark at  $25^\circ\text{C}$  for 24 h. Pt-sputtered FTO glass plates were used as counter electrodes. The dyed-titanium oxide electrode and counter electrode were then assembled into a sandwich-type cell (5 and 4 mm area, respectively). The electrolyte solution was composed of (0.5 M) LiI, (0.05 M) iodine ( $\text{I}_2$ ), and (0.5 M) 4-*tert*-butylpyridine (TBP) in 3-methoxypropionitrile which was injected in between the two electrodes.

### 2.4. Photoelectrochemical measurements

The two organic polymeric dye-sensitized  $\text{TiO}_2$  electrodes were tested under simulated AM 1.5 irradiation ( $100 \text{ mW}/\text{cm}^2$ ), and the photocurrent density-voltage (*J*-*V*) characteristics were recorded on a Keithley 4200 semiconductor characterization system (solar AAA simulator, oriel China, calibrated with a standard crystalline silicon solar). Monochromatic incident photon-to-current conversion efficiency (IPCE) for the solar cells was obtained using an Oriel 300 W Xe Arc lamp in combination with an Oriel Cornerstone 2601/4 monochromator. The monochromator was incremented through the visible spectrum to generate the IPCE spectra. A white light bias (1% sunlight intensity) was applied onto the sample during the testing with an AC model (10 Hz). Electrochemical impedance spectra (EIS) were scanned in a frequency ranging between 0.1 Hz and 10 kHz at the open circuit potential (OCP) at room temperature with an AUTOLAB PGSTAT302N analyzer.

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