



Rational design of triphenylamine dyes for highly efficient p-type dye sensitized solar cells



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ABSTRACT

Two new sensitizers based on triphenylamine-dicyanovinylene have been synthesized and used for p-type dye-sensitized solar cells. The best performance amongst solar cells was achieved by the dye with a ter-thiophene bridge ligand between carboxylic acid group and the triphenylamine part (with power conversion efficiency of 0.19%, short circuit current of 4.01 mA cm^{-2} , open circuit voltage at 144 mV, and fill factor of 0.33). Results indicate that the ter-thiophene groups in the dyes strongly affects both charge recombination and hole injection in the photoelectrode. In addition, the hexyl chains on the bridged thiophene rings also help to avoid dye aggregation on the nickel oxide film and block I^- in electrolyte from approaching the surface of nickel oxide, which leads to a reduction in the charge recombination between nickel oxide semiconductor and electrolyte. This study suggested that modification of the bridge moiety between triphenylamine and the carboxylic group by increasing thiophene units is a promising way for preventing charge recombination and increasing the power conversion efficiency.

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1. Introduction

Dye sensitized solar cells (DSSCs) as one of the most promising photovoltaic devices have attracted much attention due to their low material cost, device flexibility and simple manufacturing process compared to the silicon-based photovoltaic devices [1,2]. DSSCs using sensitized n-type semiconductors such as TiO_2 as a photoelectrode (n-DSSCs) are mostly studied and have achieved high photon conversion efficiency (PCE) [3–6]. As their inverse model, p-type DSSCs (p-DSSCs) injecting holes to the valence band of a p-type semiconductor such as NiO from the excited state of a sensitizer are rarely studied, and their overall efficiency is much lower than n-DSSCs [7–11]. Fundamentally and practically, it is very necessary to investigate p-DSSCs for inexpensive tandem solar cells, in which both electrodes are photoactive to offer great potential for significant improvement of the existing solar cell efficiency [12–14].

In p-DSSCs, the dye molecules absorbs photons and generates holes and electrons, followed by hole-transport from the acceptor to the donor, then injecting through the carboxylic group into the

valence band (VB) of NiO semiconductor. Fast charge recombination between the injected holes and the reduced sensitizer is a major challenge to greatly limit the power conversion efficiencies [15–17]. Rational design of the dye molecules could help to overcome this limitation. The organic sensitizer has advantages such as high molar absorption coefficients, facile molecular design and cost-effectiveness [18]. Since Lindquist and co-workers' first demonstration for generation of cathodic photocurrent with an erythrosine-sensitized NiO cathode [19], numerous organic sensitizers such as coumarin, perylene monoimide and porphyrin derivatives have been explored [20–22]. "Push–pull" dyes with an anchoring group on the triphenylamine donor were first developed by Sun [7]. The p-DSSCs based on these dyes exhibit high incident photon-to-current conversion efficiencies (IPCEs), among which 4-(bis-{4-[5-(2,2-dicyanovinyl)-thiophene-2-yl]-phenyl}amino)benzoic acid (P1) shows the highest efficiency (η) ($\sim 0.15\%$) [7,11]. Inspired from this work, various "push–pull" dyes have been developed. Diketopyrrolopyrrole (DPP) based novel dyad gives promising efficiency of 0.07% with I^-/I_3^- electrolyte, and a PCE of 0.18% is obtained with cobalt complex as a redox shuttle [9]. Yen et al. increased the amount of anchoring groups on triphenylamine donor to facilitate hole injection, resulting in η of 0.08%–0.09% [23]. Organic dyads comprising a perylene monoimide (PMI) dye connected to a naphthalene diimide (NDI) or a fullerene (C_{60}) with a

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cobalt electrolyte in p-DSSCs has accomplished a PCE of 0.14% [24]. The performance has been further increased to 1.3% when Tris(1,2-diaminoethane)Cobalt(II)/(III) based electrolytes were introduced [25]. More efficient sensitizers by varying the length of the oligothiophene bridge ligands between triphenylamine donor and PMI acceptor unveil long-lived charge separated excited states to result in the most efficient p-DSSCs up to date ($\eta = 0.43\%$) [9]. However, most of the reported arylamine dyes show PCE still lower than 0.1% [26,27].

Quite recently we have synthesized a novel dye T1 based on a triphenylamine donor and dicyanovinyl acceptor (Scheme 1) [28]. Compared to P1 reported by Sun et al. [7], a thiophene ring is inserted between triphenylamine and carboxylic acid group. Results show that T1 outperforms P1 under the same test condition. In light of this work, herein we design and synthesize two new dyes T3 and T4, in which the conjugation length between triphenylamine and carboxylic group further increased by inserting ter-thiophene and fluorene units respectively (Scheme 1). Hexyl chains on the bridged thiophene rings in T3 and T4 are introduced to maintain solubility, which are also expected to play an important role in preventing dye aggregation and blocking of I^- in electrolyte approaching the NiO surface for charge recombination. The influences of different linkages toward the photovoltaic properties of these organic dyes were investigated in detail to provide valuable knowledge for rational design of high performance dyes for p-DSSCs.

2. Experimental details

The 1H NMR and ^{13}C NMR spectra were recorded on a BRUKER AVANCE 300 MHz NMR Instrument in $CDCl_3$, CD_3COCD_3 and $DMSO-d_6$, using tetramethylsilane as an internal reference. GC-MS was recorded on a GCMS-QP2010 Plus Spectrometer. MALDI-TOF was performed on a Bruker Autoflex instrument, using 1,8,9-trihydroxyanthracene as a matrix. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlorerba-1106 microanalyzer. UV–Vis absorption spectra were recorded on Shimadzu 160A spectrophotometer. Electrochemical experiments were performed using a CH Instruments electrochemical

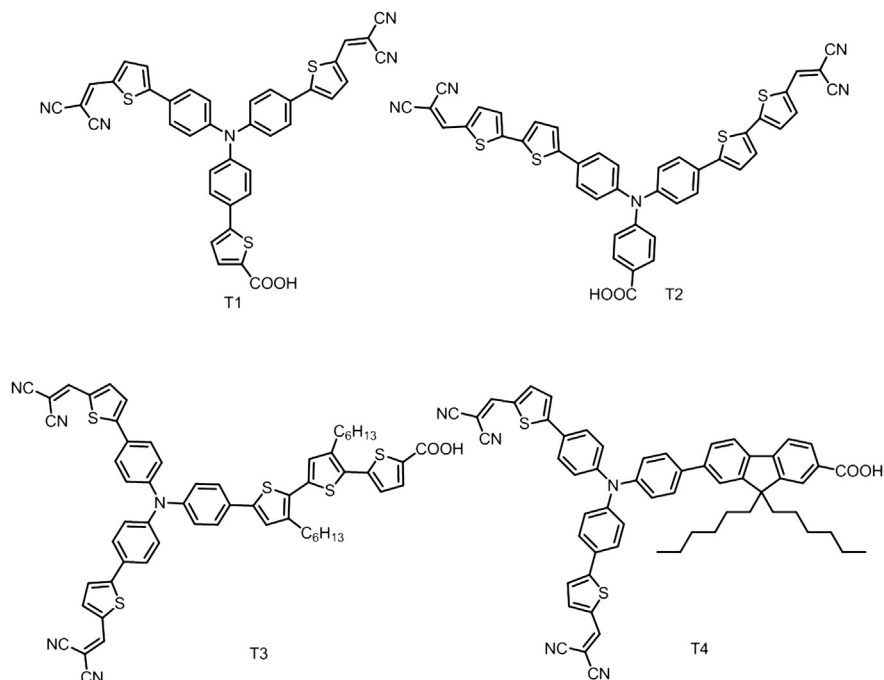
workstation (model 660A). The potentials are quoted against the ferrocene internal standard.

2.1. Synthesis

The synthetic procedures for intermediates of T3 and T4 are shown in the electronic Supplementary information. T3 and T4 were synthesized by Suzuki Coupling reaction between brominated triphenylamine and thiophene boronic acid before finally undergoing a Knoevenagel reaction with malononitrile as reported for dye T1 (Synthetic routes shown in Scheme 2) [28]. The final products were fully characterized by 1H and ^{13}C NMR spectroscopy, MALDI-TOF spectrometry and elemental analysis as well (detailed synthetic routes, see ESI).

2.1.1. Synthesis of dye T3 (5''-(4-(bis(4-(5-(2,2-dicyanovinyl)thiophen-2-yl)phenyl)amino)phenyl)-3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carboxylic acid)

To a solution of compound 7 (200 mg, 0.22 mmol) in degassed toluene (120 mL) were added malononitrile (44 mg, 0.66 mmol) and 0.1 mL Et_3N . The mixture was stirred at 90 °C overnight under an Ar atmosphere. After cooled to room temperature, water (100 mL) was added, the solution was extracted with $CHCl_3$, and dried over anhydrous sodium sulfate. The solvent was evaporated, the residue was purified by column chromatography over silica gel using $EtOH/CHCl_3$ (1:7, v/v) as the eluent to give the final product T3 (170 mg, 77%) as a dark red solid. 1H NMR (300 MHz, CD_3OCD_3): δ (ppm): 8.35 (brs, 1H), 7.93 (brs, 1H), 7.76–7.65 (m, 8H), 7.48–7.17 (m, 12H), 2.82 (brm, 4H), 1.71 (brm, 4H), 1.32 (brm, 12 H), 0.89 (brm, 6H). ^{13}C NMR (75 MHz, CD_3OCD_3): δ (ppm): 180.17, 168.43, 158.27, 155.29, 151.55, 148.33, 141.81, 141.38, 133.90, 132.51, 130.01, 127.17, 126.68, 126.18, 125.30, 124.47, 124.10, 114.41, 113.75, 75.09, 35.28, 31.50, 30.25, 30.17, 29.71, 29.46, 22.44, 13.50. MALDI-TOF-MS: m/z 1019.55 (M^+). Anal. calcd for $C_{59}H_{49}N_5O_2S_5$ (%): C, 69.45; H, 4.84; N, 6.86. Found: C, 69.80; H, 4.76; N, 6.39. IR, ν (cm^{-1}): 2225 ($C\equiv N$), 1699 ($C=O$), 1600, 1560 (aromatic rings).



Scheme 1. Molecular structures of T1, T2, T3 and T4.

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