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Simple indoline based donor–acceptor dye for high efficiency dye-sensitized solar cells

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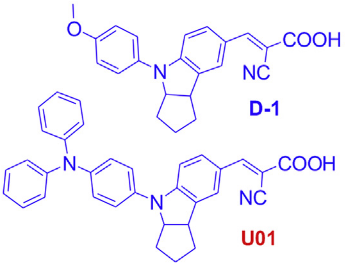
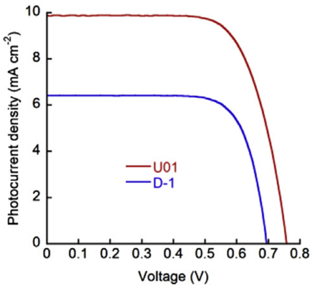
HIGHLIGHTS

- A simple and robust indoline-triphenylamine based sensitizer for DSCs.
- An overall conversion efficiency of 6.01% was obtained.
- Strong electron donor triphenylamine unit extends absorption spectrum.
- Simple and robust molecular design is a promising class of sensitizers.

GRAPHICAL ABSTRACT





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ABSTRACT

A simple metal-free donor–acceptor type sensitizer U01, bearing strong electron donor indoline-triphenylamine was synthesized for panchromatic sensitization of TiO_2 nanocrystalline film. Photovoltaic properties of U01 showed remarkably enhanced light harvesting due to the presence of strong electron donor and robust structure. The new U01 sensitized solar cell exhibited a photovoltaic performance: a short-circuit photocurrent density (J_{sc}) of 10.70 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 0.758 V and a fill factor (FF) of 0.74, corresponding to an overall conversion efficiency of 6.01% under standard global AM 1.5 solar light condition. Our results suggest that indoline-triphenylamine based robust D–A molecular architecture is a highly promising class of panchromatic sensitizers for improvement of the performance of dye-sensitized solar cells (DSCs).

1. Introduction

Dye-sensitized solar cells (DSCs) have received increasing attention due to their potential in low-cost renewable energy production, as well as application in flexible, colorful and light-weight devices [1–4]. Recently, a certified overall solar-to-electric energy conversion efficiency of 11.4% has been achieved under standard AM 1.5 conditions with DSCs based on ruthenium

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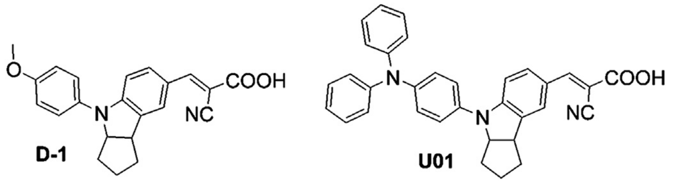


Fig. 1. Chemical structures of dyes **D-1** and **U01**.

sensitizers [5]. In view of the limited ruthenium resource, metal-free organic dyes have attracted considerable attention in the past several years due to their high molar extinction coefficients, flexible structural modifications, low costs and ease of tuning the band gap [6,7]. However, the overall conversion efficiencies of DSCs based on such organic dyes are low due to the larger zero–zero excitation ($E_{0\text{-}0}$) energy gap [6–9]. Our previous study showed that a minimum $E_{0\text{-}0}$ energy gap of 1.4 eV is sufficient for TiO_2 and I^-/I_3^- redox based DSCs which would furnish a highly panchromatic dye with greater total conversion efficiency [9,10]. The most common molecular architecture of organic dyes is built of three units including an electron donor (D) and an electron-acceptor (A) bridged by a π-conjugation linker (D–π–A) to tune the $E_{0\text{-}0}$ energy gap [4–11]. Although numerous studies focused on the modulation of the π-conjugation system and were successful in improving the light harvesting by producing red shift, their DSCs performances are not quite satisfactory as the molecular structure of these dyes tends to exhibit stronger intermolecular π–π interaction(s), higher flexibility and more potentials for aggregation on TiO_2 surface [12,13]. The high flexibility of a dye may increase the back-electron transfer rate resulting in a low photon-to-current conversion efficiency (IPCE). In addition, the synthesis of D–π–A type requires several steps compared to D–A types molecules. Therefore, besides thermodynamically favorable electronic states for efficient electron replenishment and electron injection, a simple D–A type molecule with robust molecular structure is also an essential requirement for the molecular design of efficient panchromatic metal-free organic dye for DSCs.

With the aforementioned in mind, we have attempted to improve the light harvesting efficiency of organic dye by increasing interaction between D and A of a dye without extending the π-conjugation linker. For a systematic study of this idea, we have selected here indoline-triphenylamine moiety as an electron donor as it has been used in organic sensitizers for strong and intense absorption bands in the visible region [14]. In addition, this unit has a tendency to reduce the π-stacked aggregation on the semiconductor surface [15,16]. Here, we report the molecular design, synthesis and characterization of a new D–A type organic sensitizer, **U01** (Fig. 1) containing triphenylamine substituted indoline as the strong electron donor and cyanoacrylic acid as the electron acceptor moiety. The photophysical properties, equilibrium molecular geometry calculations and the performance of DSCs based on this organic dye are reported and compared with its analog methoxyphenyl substituted indoline based dye **D-1** (Fig. 1) as a reference [17].

2. Experimental section

2.1. General information for materials synthesis

^1H NMR and ^{13}C NMR spectra were recorded on JEOL JMTC-270/54/SS (JASTEC, 400 MHz) and BRUKER (600 MHz) spectrometers. ^1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet and m = multiplet), and coupling constants (Hz). High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer. Column chromatography was carried out employing Silica gel 60N (spherical, neutral, 40–100 μm, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck). All other reagents and solvents commercially available were used without further purification unless otherwise noted. Compounds **1**–**3** (Scheme 1) were synthesized according to the literature method [18]. The compound **D-1** was synthesized according to the published procedures [19].

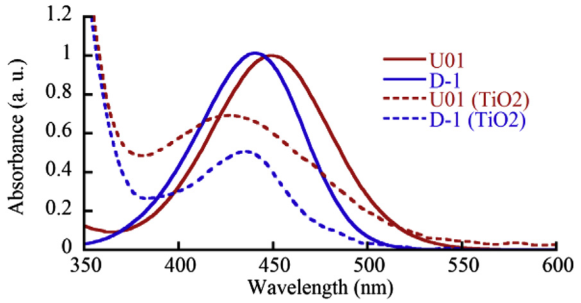
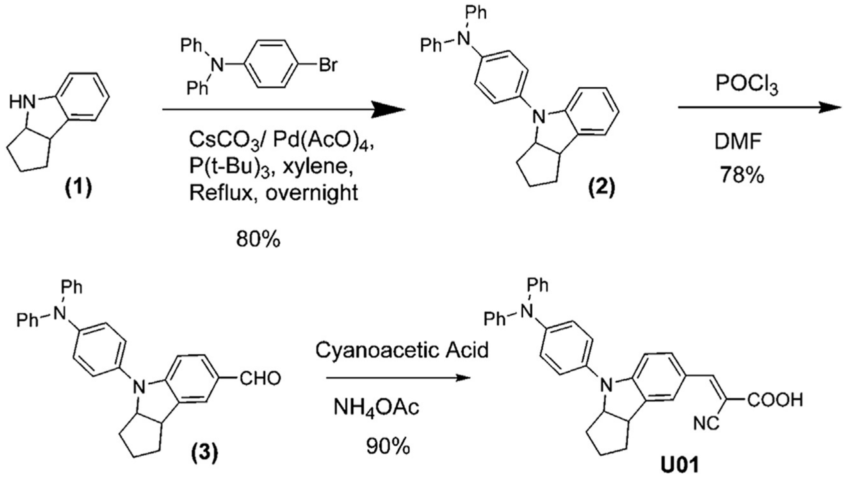


Fig. 2. Absorption spectra of **U01** and **D-1** in ethanol (solid line) and anchored on a transparent TiO_2 film (dashed line).



Scheme 1. Synthesis routes of dye **U01**.