



New tetrazole-based organic dyes for dye-sensitized solar cells[☆]

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ABSTRACT

A series of new metal-free organic dyes that contain donors with triphenylamine or its derivatives and tetrazole-based acceptors were synthesized and characterized by photophysical, electrochemical, and theoretical computational methods. They were applied in nanocrystalline TiO₂ solar cells (DSSCs). It is found that the introduction of diphenylamine units as antennas in the as-synthesized dyes could improve photo-voltaic performance compared with phenothiazine and carbazole units as antennas in DSSCs. The dye with (2H-tetrazol-5-yl) acrylonitrile electron acceptor also displayed the highest solar-to-electrical energy conversion efficiency.

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1. Introduction

Since the discovery by Grätzel et al. in 1991, dye-sensitized solar cells (DSSCs) on organic and organometallic complexes have attracted considerable attention [1]. A typical DSSC is constructed using wide band gap semiconductor oxides such as TiO₂ or ZnO, a molecular sensitizer, a redox electrolyte and a Pt-coated counter electrode [2,3]. In the DSSCs system, the photoexcited electrons from dye inject into the conduction band (CB) of the TiO₂. The oxidized dye is reduced back to the ground state by electron transfer from the electrolyte. The photosensitizer is thus one of the critical components in DSSC to efficient light harvesting and electron generation/transfer [4].

Organic dyes have been used as photosensitizers in DSSCs, because of their many advantages, such as large absorption coefficients due to intramolecular $\pi-\pi^*$ transitions, inexpensiveness with no transition metals contained, environment-friendliness [5]. Generally, donor-linker-acceptor (D- π -A) structure is the common design of the organic sensitizer [6–10].

Electron-withdrawing anchoring groups such as the nitro group, aldehyde, 2-(1,1-dicyanomethylene) rhodanine, pyridine and 8-hydroxyquinoline as an alternative to conventional carboxyl groups

had already been used in DSSCs [11]. Recently, the effectiveness of the tetrazole functional group as a serious alternative anchoring group for organic photosensitizers in DSSCs has also been reported by Massin et al. [12]. Because of its highest value of ionization potential among azoles and its low HOMO value, this functional group is extraordinarily stable to both acids and bases as well as to oxidizing and reducing conditions [13–15]. They are used in coordination chemistry as a ligand, in pharmaceuticals as a metabolically stable surrogate for a carboxylic acid group, in materials science applications including propellants and explosives [16–18].

In this paper, we report on the synthesis and characterization of novel metal-free organic dyes (Fig. 1) that contain donors with triphenylamine or its derivatives and tetrazole-based acceptors and their application as sensitizers in DSSCs. In this design, **TD1** is the basic model, in which the triphenylamine unit was connected to the ethyl 2-(1H-tetrazol-5-yl) acetate by one double bond. Phenothiazine, carbazole and diphenylamine units as antenna groups were attached to the phenyl rings of **TD1**, leading to the structures of **TD2**, **TD3**, **TD4**. Therefore, new starburst dyes with D-D- π -A structure were synthesized by introducing starburst donor units into the D- π -A molecule. Such a starburst conformation probably minimizes the charge recombination processes of injected electrons with triiodide in the electrolyte [19]. The dyes **TD5** and **TD6** containing (2H-tetrazol-5-yl) acrylonitrile and 1H-tetrazole-5-acetic acid moieties as acceptor, for the purpose of comparison with **TD1** containing ethyl 2-(1H-tetrazol-5-yl) acetate were also synthesized and the effect of different tetrazole-based motifs as anchoring group on the performance of the dye-sensitized solar cells was studied.

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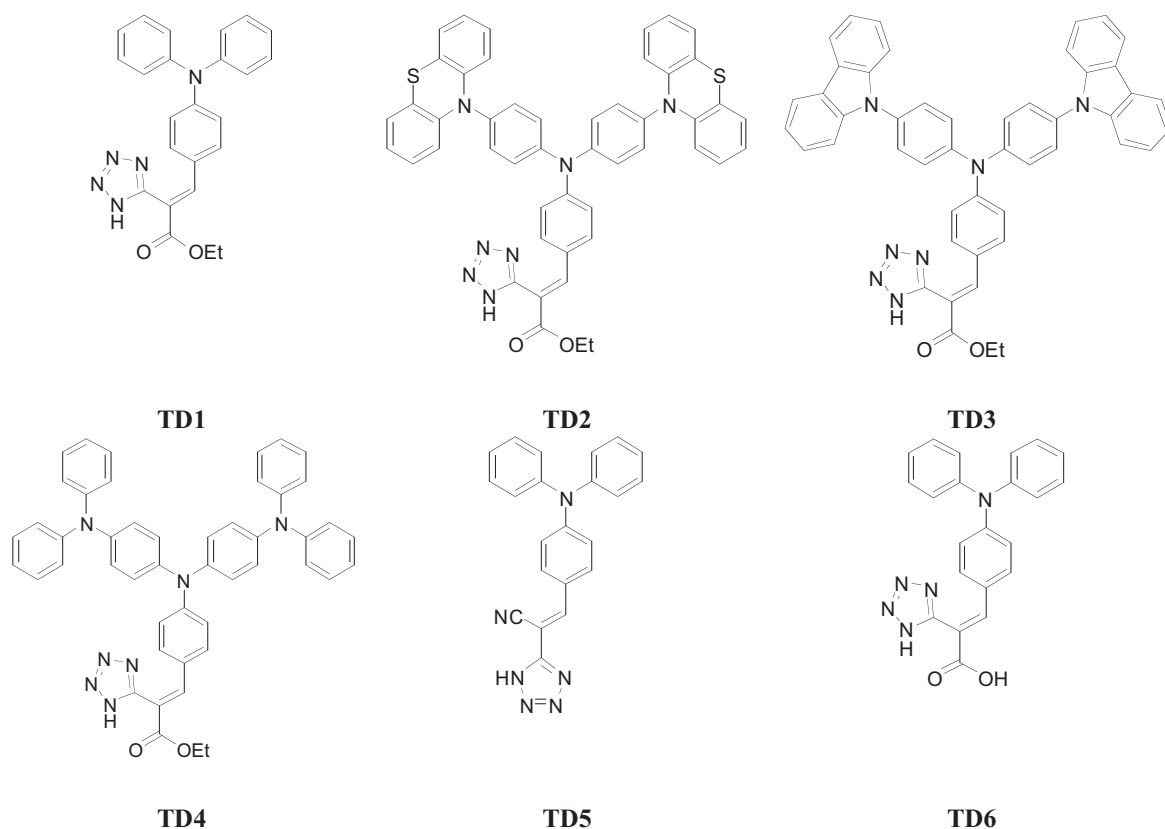


Fig. 1. Molecular structures of triphenylamine dyes.

2. Experimental

2.1. General methods

All solvents and chemicals used in this work were reagent grade and used without further purification and were obtained from commercially available sources. Phenothiazine and carbazole were purchased from Merck. All solvents and other chemical used in this work were purchased from Sigma–Aldrich. Solvents were dried from appropriate drying agents (calcium sulfate for dimethylformamide, calcium chloride for 1,2-dichlorobenzene, calcium hydride for acetonitrile and dichloromethane) and freshly distilled before use. The ^1H and ^{13}C NMR spectra were measured using Bruker 400 MHz spectrometers. Mass spectra (EI-MS) were measured with 5973 Network Mass Selective Detector (Agilent Technology (HP)). FTIR absorption spectra were recorded on a FTIR Jasco 680 plus spectrometer using KBr pellets. FTIR spectrum of TiO_2 nanoparticles was subtracted from the spectra of dyes on TiO_2 nanoparticles. The absorption spectra of the dyes in solution and adsorbed on TiO_2 films were measured with a Jasco-570 UV/vis spectrophotometer. The precursor compounds **1–3** (Scheme 1) and the acceptor moieties were synthesized according to the literature procedures [20–23]. Cyclic voltammetry experiments of the dyes were performed in SAMA 500 electroanalyzer system, SAMA research center, Iran, with a Pt working electrode, a Pt counter electrode, an Ag/AgCl reference electrode, and a scan rate of 0.1 V/s at room temperature under nitrogen in a CH_2Cl_2 solution that included 0.1 M tetrabutylammonium hexafluorophosphate. The potentials were calibrated against the ferrocene internal standard. DSSCs were constructed by Sharif Solar, with an effective area of 0.25 cm^2 and an iodine-based liquid electrolyte. The photo anodes were prepared by doctor blade and two layers of nanocrystalline TiO_2 particles. A transparent layer composed of 20 nm TiO_2 particles (Sharif

Solar) with thickness of $7\text{ }\mu\text{m}$ and a scattering layer of 150–300 nm TiO_2 particles with a thickness $5\text{ }\mu\text{m}$ to enhance the light harvesting and improve the device performance. The TiO_2 electrodes were immersed into a dichloromethane solution of dyes ($4 \times 10^{-4}\text{ M}$) for 20 h. Solar cells were illuminated by solar simulator (SIM-1000, Sharif Solar) to provide an incident irradiance of 100 mW/cm^2 at the surface of the device. *I–V* measurements were performed using a potentiostat (Palmsense, Netherlands). Action spectra of the incident photon-to-current conversion efficiencies (IPCE) were measured using a 100 W halogen lamp associated with a monochromator (Jarrell Ash monochromator) in DC mode. The amount of each dye loaded onto TiO_2 is calculated from the difference in concentration of each solution before and after TiO_2 film immersion. UV–visible absorption spectra of each solution before and after sensitization of TiO_2 film were recorded. The difference in concentration of each solution before and after TiO_2 film immersion was deduced from the difference between the two sets of data.

2.2. Synthesis

The dyes (TD1, TD5 and TD6) were prepared in two steps involving the Vilsmeier–Haack formylation of the triphenylamine followed by the Knoevenagel condensation of the resulting aldehydes with ethyl 2-(1H-tetrazol-5-yl) acetate, (2H-tetrazol-5-yl) acrylonitrile, or 1H-tetrazole-5-acetic acid (Scheme 1). The dyes (TD2–TD4) were synthesized from 4-(diphenylamino) benzaldehyde **1** following a three-step procedure. Iodination of aldehyde **1** led to 4-(bis(4-iodophenyl)amino) benzaldehyde **2**. Cu-catalyzed Ullmann coupling reaction of **2** with phenothiazine, carbazole or diphenylamine provided **3** which was subsequently reacted with ethyl 2-(1H-tetrazol-5-yl) acetate by a Knoevenagel condensation.

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