Contents lists available at ScienceDirect

Organic Electronics

journal homepage: http://www.elsevier.com/locate/orgel

New tetrazole based dyes as efficient co-sensitizers for dsscs: Structure-properties relationship

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ARTICLE INFO

Keywords: Dve-sensitized solar cells Co-adsorbent Tetrazole

ABSTRACT

Two new compounds based on the phenyltetrazole system, 5-(4-decyloxyphenyl)tetrazole (LTz-4) and N,Ndiethyl-4-{[(2'-nitro-4'-tetrazoyl)phenyl]diazenyl}aniline (SD - 6), were synthesized and characterized as coadsorbents in Dye-Sensitized Solar Cells (DSSCs). The effects of hydrophobic chain length and anchoring group on the properties of DSSCs containing the previously reported dye HD-14 and compared with the benchmark deoxycholic acid (DCA) are described. The charge-transfer resistance of dye/TiO2 interface followed the order HD-14 - SD - 6 > HD-14 - LTz-4 > HD-14 - DCA. However, the V_{OC} for the dye HD-14 with coadsorbent DCA was 0.71 V, for the and the dye HD-14 with co-adsorbent LTz-4 was 0.70 V and for the dye HD-14 with co-adsorbent SD - 6 was 0.67 V. Co-adsorbents LTz-4 and SD - 6 achieved mean solar-to-power conversion efficiencies (%n), for three devices, of 9.20 and 7.48, respectively, compared to 9.14 for DCA under the same experimental device conditions. For LTz-4 co-adsorbent, the results can be attributed to the repellent effect of the long alkyl chain that prevents the charge recombination on the semiconductor surface. For SD - 6, the molecular volume of the co-adsorbent and the presence of the nitro group in a lateral position should make it difficult to form a more compact layer with the dye. The sum of these contributions would allow the electrolyte to approach, reducing the efficiency of electron injection into TiO2.

1. Introduction

Dve-sensitized solar cells (DSSCs) based on nanocrystalline oxide semiconductors are a type of solar cells that convert the sun's energy to electric energy using a sensitizing dye [1-3]. Among the fundamental concepts for the development of the dye-sensitive solar cell is the preparation of a highly porous nanocrystalline TiO₂ film (which provides a large area of inherent adsorptive surface), containing a dye with a high molar extinction coefficient anchored chemically to the surface, to form the working electrode of the solar cell [4]. In this concept, a typical DSSC consists of a nanoparticle TiO₂ photoelectrode sensitized by a ruthenium bipyridine complex and a platinum counter-electrode separated by an iodide-triiodide (I-1/I3-1) liquid electrolyte [5]. In DSSCs, the photosensitizer and its interactions with nanocrystalline TiO₂ film are the key point to obtain high photoconversion efficiency, this is, high efficiency to harvest light and inject electrons. Until now, hundreds of photosensitizers have been designed and synthesized for improving the photovoltaic performance and exploring the relationship of structure and performance of DSSCs. Among them, the ruthenium complex dyes, such as N719, N3, C101 and HD-14, have dominated the highly efficient DSSCs for many years [6-10]. For example, the efficiency of DSSC based on N719 has exceeded 12% [11]. However, the scarcity of ruthenium metal is a big problem for future commercial development and applications. Alternatives to ruthenium dyes are the porphyrin dyes, that have received widespread attention in DSSCs because of their prominent spectral bandwidth of 400-700 nm and easily modulated structures [12]. Despite the good results, the effectiveness of the cosensitization approach still needs further improvement [13]. Compared with the metal complex dyes, the metal-free organic dyes have some advantages, such as the relative simplicity of synthesis and purification, convenient structural modification, and high molar extinction coefficient.

Thus, searching new metal-free organic dyes with excellent photovoltaic performance has attracted considerable attention. Many organic dyes, which exhibit comparably excellent photovoltaic performances to

https://doi.org/10.1016/j.orgel.2020.105964

Received 7 August 2020; Received in revised form 5 September 2020; Accepted 11 September 2020 Available online 22 September 2020 1566-1199/© 2020 Elsevier B.V. All rights reserved.







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ruthenium complexes, have been designed and obtained [14]. However, designing the new organic dyes via simple and convenient synthetic routes is still a challenge in DSSCs. In last decade, various kinds of functional groups and their derivatives have been combined to generate D- π -A organic dyes. Among them, an arylamine group, thiophene derivatives and cyanoacrylic acid moiety are the most common subunits that act as an electron donor, p-linker, and an electron acceptor/anchoring group, respectively. Especially, the p-linker as a bridge that connects the donor and acceptor exerts a significant influence on the transmission and recombination of electron during the photoelectric conversion process in DSSCs [15,16]. The introduction of 1,2,3-triazole group as an electron deficient unit in the linear D-π-A organic dyes can effectively enhance the open-circuit voltage of the DSSCs with good efficiency [17]. The introduction of tetrazole group as an anchoring group has been pursued. The photovoltaic results further obtained with the tetrazole derivative outperformed those of the carboxylic analogue showing a significant increase in photovoltage for a device using the tetrazole dye [17].

Much effort has been paid to widen to the light absorption efficiency of the dyes and the charge transfer efficiency for the crystalline structure of TiO₂. Unfortunately, their photovoltaic performances are still not significantly improved yet due to their aggregation during the photoelectrode fabrication process. Thus, co-sensitization using two or more sensitizers is an effective approach to achieve panchromatic harvest [18-22]. Co-sensitization also termed as "dye-cocktail" method to DSSCs, is a widely followed strategy. Due to the complexity associated with the system formed by only one dye, like charge recombination, dye aggregation, and semiconductor surface protonation, that are important and unwanted processes, co-sensitization is employed [23-27]. The key criteria for a potential dye co-sensitizer includes (a) a lowest unoccupied molecular orbital (LUMO) energy level that lies above the semiconductor conduction band, (b) a highest occupied molecular orbital (HOMO) energy level that lie below the electrolyte redox potential, (c) presence of an anchor group to provide coupling between dye and semiconductor, (d) directed intramolecular charge transfer on photoexcitation from donor to semiconductor through the anchor, (e) good chemical compatibility between dye sensitizers, (f) reduced the charge recombination and (g) should be suitable for the competitive adsorption without aggregation on the working electrode (nanocrystalline TiO₂ film) surface [28]. The co-sensitizations of organic dyes have been extensively investigated, which exhibit an effective and promising photovoltaic performance [28-33].

In previous studies, the tetrazole group has been described for use in

DSSC both in the dye structure and in the structure of co-adsorbents [17, 28]. The optoelectronic and photovoltaic properties of the tetrazole-based molecules demonstrated the effectiveness of the tetrazole group as an important alternative anchoring group for both organic dyes and co-adsorbents in DSSCs. As an anchoring group of the dyes, the use of tetrazole has not shown significant differences to the carboxylic group yet, however, the use of the phenyl tetrazole system in coadsorbent for Ruteniun dyes has shown significant improvements in the efficiency of photoconversion in relation to the standard DCA. The mechanism of interaction between the dye and the phenyl tetrazole system is still unclear. Pi-stack interaction is suggested, which could induce photoelectron injection addition. On the other side, blocking the TiO₂ surface could prevent the electron recombination (dark current) too. Both effects can occur and be beneficial to the system. However, Pi-stack interaction can be an extra additive that contributes significantly to the efficiency of the dyes. In this work, we describe the synthesis of two new molecules in which we can distinguish these effects. Here we report the synthesis, photophysical and photovoltaic performance of DSSCs derived from co-sensitization of HD-14 and co-adsorbent SD - 6 and LTz-4 (Fig. 1).

2. Materials and methods

2.1. General information

The solvents and chemicals were purchased from Sigma-Aldrich, Fisher Scientific or TCI-America and used as received. The mass spectrometry analysis was carried out on a high-resolution mass spectrometer - Thermo Fisher Scientific Exactive Plus MS, a benchtop full-scan OrbitrapTM mass spectrometer using Heated Electrospray Ionization (HESI). Samples were dissolved in methanol and sonicated for 15 min. They were then diluted 1:1 with 20 mM ammonium acetate and analyzed via syringe injection into the mass spectrometer at a flow rate of 10 mL/min. The mass spectrometer was operated in negative ion mode. FT-IR (ATR) spectra were recorded on a Nicolet Nexus 470 F T-IR spectrometer (Thermo Scientific, USA) and UV-Visible spectra were measured by using Cary 300 spectrophotometer. Fluorescence, recorded at room temperature on a Fluorolog-3 spectrofluorometer (HORIBA Jobin Yvon Inc.). ¹HNMR (Hydrogen Nuclear Magnetic Resonance) and ¹³CNMR (Carbon Nuclear Magnetic Resonance) spectra were recorded in a Bruker 400 MHz spectrometer.



Fig. 1. Molecular structures of dye HD-14 and co-adsorbents: DCA, LTz-4 and SD - 6.

2.2. Synthesis

2.2.1. Synthesis of 2-nitro-4-(1-H-tetrazol-5-yl)-benzenamine (1)

The synthesis of the tetrazole system (1) was carried out as depicted in the literature [34,35]. To a solution of 3-nitro-4-aminobenzonitrile (1) (7.0 g, 0.043 mol) in 28 mL N,N-dimethyl formamide (DMF) was added sodium azide (11.0 g, 0.17 mol) and ammonium chloride (9.0 g, 0.17 mol). The mixture was stirred for 24 h maintaining the temperature at 120 °C. The reaction mixture was cooled to room temperature and was poured into 50 mL of ice cold water. The mixture was acidified with concentrated HCl to pH 2. The precipitate formed was filtered off and the product was recrystallized from ethanol giving yellow crystals. Yield 65%; mp 198–200 °C. FTIR-ATR $\nu_{max} = 3473$, 3431, 3335, 3185, 2710–2630 (br), 1633, 1556, 1515, 1356, 1256. ¹HNMR (400 MHz, DMSO- d_6) $\delta = 7.45$ (s, 1H, C₆H₃), 7.05 (d, J = 8.4 Hz, 1H, C₆H₃), 6.62 (d, J = 8.4 Hz, 1H, C₆H₃) 3.38 (br s, 1H, CN₄H). ¹³CNMR (100 MHz, DMSO- d_6): 154.6, 138.2, 134.7, 116.7 (1C), 113.4, 112.0, 110.7.

2.2.2. Synthesis of azo dyes N,N-diethyl-4-{[(2'-nitro-4'-tetrazoyl)-phenyl] diazenyl}aniline (SD - 6)

2-Nitro-4-(1H-tetrazol-5-yl)-benzenamine (1) (2.06 g, 0.01 mol) was dissolved in hydrochloric acid (20 mL) with stirring. After, the solution was cooled to 0 °C in an ice-bath. A solution of sodium nitrite (0.69 g, 0.01 mol) in 5 mL water, cooled to 0 °C was added. The mixture was stirred for 30 min at 0 °C to get the clear diazonium salt solution. The coupling component N,N-diethylaniline (1.60 g, 0.01 mol) was dissolved in NaOH (15 mL, 1 N) and then solution cooled 0 °C. To this well stirred solution, the above diazonium salt solution was added slowly so that temperature did not rise above 4 °C while maintaining the pH 4-5 b y the action of sodium acetate solution (10% w/v). The mixture was stirred for 3 h at 0 °C. After, the solid obtained was collected by filtration, washed three times with cold water and dried. The crude product was recrystallized from hexane:ethylacetate (1:1). Violet crystals, 3.04 g, yield 83% m. p. >300 °C. FTIR-ATR: 1381.4 cm⁻¹ and 1518.9 cm⁻¹ (N–O stretch), 1603.1 cm⁻¹ (C=C stretch). ¹H NMR (400 MHz, DMSO- d_6): 8.69 (s, 1H), 8.45 (d, J = 10 Hz, 1H), 7.96 (d, J = 10 Hz, 1H), 7.76 (d, *J* = 10 Hz, 2H), 6.87 (d, *J* = 10 Hz, 2H), 3.50 (q, *J* = 5 Hz, 4H), 1.15 (t, J = 5 Hz, 6H). ¹³CNMR (100 MHz, DMSO- d_6): 153.4 (1C), 152.0 (1C), 146.2 (1C), 143.1 (1C), 127.5 (1C), 126.7 (1C), 125.8 (1C), 123.0 (1C), 117.2 (2C), 111.5 (2C), 44.4 (2C), 12.5 (2C). HRMS (ESI Full) m/z: calcd for C₁₇H₁₉N₈O₂ [M+H]⁺, 367.1626; Found, 367.1636.

2.2.3. Synthesis of 5-(4-decyloxyphenyl)tetrazole (LTz-4)

To a round-bottomed flask were added 4-hydroxybenzonitrile (10.0 g, 0.084 mol), 1-bromodecane (18.6 g, 0.084 mol), KOH (46.4 g, 0.336 mol), and toluene/DMF (200 mL; 1:1) and the mixture was stirred under reflux for 6 h. The suspension was filtered and the solid was washed with toluene. The filtrate was concentrated and the obtained solid dissolved in diethylether. The organic phase was washed with NaOH (5%; 50 mL), HCl (5%; 50 mL), and H₂O (50 mL) and dried over anhydrous Na₂SO₄. The product was obtained after removal of the solvent, as a white solid. To this solid (compound 2) were added NaN₃ (13.50 g; 0.208 mol), NH₄Cl (11.10 g, 0.208 mol) and DMF (100 mL) and the mixture was refluxed for 20 h. The suspension was cooled to room temperature and poured into 400 mL of ice/water and acidified to pH 3 using HCl, (10%). The mixture was filtered and the solid was washed several times with water. Recrystallization from ethanol gave a white solid; 18.3 g, yield 72%, mp 164–166 °C, FT-IR ν_{max} = 3397, 2962, 2915, 2850, 3100–2600 (broad), 1613, 1500, 1256, 832.¹H NMR (acetone- d_6) δ ppm: 0.87 (t, J = 6.7 Hz, 3H, CH₃), 1.24–1.40 (m, 16H, -CH₂-), 1.50 (m, 2H, -CH₂-), 1.81 (qui, J = 6.6 Hz, 2H, -CH₂CH₂O-), 4.11 (t, J = 6.6 Hz, 2H, -CH₂O-), 7.14 (d, *J* = 9.0 Hz, 2H, Ar–H), 8.04 (d, *J* = 9.0 Hz, 2H, Ar–H). ¹³C NMR (DMSO-d₆) δ ppm: 13.62, 18.76, 24.22, 25.39, 27.69, 29.28, 31.20, 67.43, 114.74, 115.65, 129.06, 155.80.

2.2.4. Synthesis of HD-14. HD-14

Synthesis of **HD-14**. **HD-14** was synthesized according to the procedures reported by cheema et al. [10].

2.3. Measurements of ground state oxidation potential (GSOP) by cyclic voltammetry

The experimental HOMO and $E_{0.0}$ energy values for **SD** - **6** and **LTz**-4 were measured using a cyclic voltammetry (CV) whereas $E_{0.0}$ was determined from the absorption onset of the relevant compound. The CV was carried in DMF with 0.1 M [TBA][PF₆] as an electrolyte at a scan rate of 50 mV s⁻¹. Glassy carbon was used as the working electrode (WE), Pt wire as counter electrode and Ag/Ag⁺ in ACN was used as the reference electrode. Fc/Fc⁺ was used as internal references, voltage measured was converted to NHE by addition of 0.63 V.

2.4. TiO₂ electrode preparation and device fabrication

The photo-anodes composed of nanocrystalline TiO₂ and counter electrodes were prepared using a known procedure [11]. Fluorine-doped tin oxide (FTO) coated glasses (2.2 mm thickness, sheet resistance of 8 Ohm/cm², TEC 8, Pilkington) were washed with detergent, water, acetone and ethanol, sequentially. After this FTO glass plates were immersed into a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min and washed with water and ethanol. Thin layer (8-12 mm thick) of TiO₂ (Solaronix, Ti-Nanoxide D/SP) was deposited (active area, 0.18 cm²) on transparent conducting glass by squeegee printing. After drying the electrodes at 120 °C for 6 min, scattering layer (5 mm thick) TiO₂ particles (Solaronix, Ti- Nanoxide R/SP) were printed. The TiO₂ electrodes were heated under an airflow at 350 °C for 10 min, followed by heating at 500 °C for 30 min. After cooling to room temperature, the TiO₂ electrodes were treated with 40 mM aqueous solution of TiCl₄ at 70 °C for 30 min and then washed with water and ethanol. The electrodes were heated again at 500 $^\circ$ C for 30 min and left to cool to 80 $^\circ$ C before dipping into the dye solution. The dye solutions (HD-14, SD - 6 or LTz-4, 0.3 mM) were prepared in 1:1:1 acetonitrile/t-butyl alcohol/-DMSO. Deoxycholic acid (DCA), or SD - 6 or LTz-4, was added to the dye solution as a coadsorbent at a concentration of 20 mM. The electrodes were immersed in the dye solutions with active area facing up and then kept at 25 °C for 20 h to adsorb the dye onto the TiO2 surface. The amounts of dye loading on the TiO2 films were measured by using a Cary 300 spectrophotometer. The sensitized electrodes were immersed in a 0.1 M NaOH solution in a mixed solvent (H₂O/THF 1:1), which resulted in desorption of each dye. The amounts of dye loading can be estimated according to the following formula: $C = AV/\epsilon S_0$, where C stands for the amount of dye loading, A is the optical absorbance of the dye, V is the volume of desorption solution, ε is the molar extinction coefficients, and S_0 is the effective area of TiO₂ films. For preparing the counter electrode, pre-cut FTO glasses were washed with water followed by 0.1 M HCl in EtOH, and sonication in acetone bath for 10 min. These washed FTO were then dried at 400 °C for 15 min. Thin layer of Pt-paste (Solaronix, Platisol T/SP) on FTO was printed and the printed electrodes were then cured at 450 $^\circ$ C for 10 min. The dye sensitized TiO₂ electrodes were sandwiched with Pt counter electrodes and were sealed using a 40 μm Surlyn spacer through heating of the polymer frame. The electrolyte (Solaronix, Iodolyte AN-50) was then injected into the cell, while the two electrodes were held together with the clips.

2.5. Photo-electrochemical measurements

Photocurrent-voltage characteristics of DSSCs were measured using a Keithley 2400 source meter under illumination of AM 1.5 G solar light from solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91,160, Oriel). The incident light intensity was calibrated using a reference Si solar cell (Newport Oriel, 91150 V) to set 1 Sun (100 mW cm⁻²). The measurement was fully controlled by Oriel IV Test Station software. IPCE (incident monochromatic photon to current conversion efficiency) experiments were carried out using a system (QEX10, PV Measurements, USA) equipped with a 75 W short arc xenon lamp (UXL-75XE, USHIO, Japan) as a light source connected to a monochromator. Calibration of incident light was performed before measurements using a silicone photodiode (IF035, PV Measurements). All the measurements were carried out without the use of anti-reflecting film.

2.6. Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectra were measured with an impedance analyzer potentiostat (Bio-Logic SP-150) under illumination using a solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91,160, Oriel). EIS spectra were recorded over a frequency range of 100 mHz–200 kHz at room temperature. The applied bias voltage was set at the V_{oc} of the DSSCs, with AC amplitude set at 10 mV. The electrical impedance spectra were fitted using Z-Fit software (Bio-Logic).

3. Results and discussion

3.1. Synthesis of co-adsorbents

The synthetic routes for **SD** - **6** and **LTZ-4** are summarized in Scheme 1 and Scheme 2, and the synthetic products have been characterized with FT-IR, NMR, and mass spectrum. To prepare **SD** - **6**, was used 3-nitro-4-aminobenzonitrile as a starting reagent. It was converted to the tetrazole heterocycle by a Huisgen 1,3-dipolar cycloaddition with sodium azide. The phenyl tetrazole (1) was synthesized and used as the intermediates for AZo coupling reactions with the *N*,*N*-diethylaniline to afford the corresponding **SD** - **6**.

To prepare **LTz-4** we used 4-hydroxybenzonitrile as a starting reagent. It was initially alkylated with bromodecane and in the sequence, converted to tetrazole by a Huisgen 1,3-dipolar cycloaddition with sodium azide. The corresponding analytical data (IR, ¹H, and 13C NMR spectra and mass spectrum) are given in the Supplementary Information.

In order to determine the practical utility of the synthesized molecules (LTz-4 and SD - 6) as co-adsorbent in DSSCs, deoxycholic acid (DCA) was used as the standard and HD-14 was used as the dye. Nanocrystalline TiO₂ electrodes were prepared according to the procedure reported previously [11]. Fig. 12S (supplemental information) shows the photo anodes after desorption of dye (SD - 6 - DCA, LTz-4 -DCA, HD-14 – DCA, HD-14 – SD - 6 and HD-14 – LTZ-4) by dipping in solution of 1:1:1 acetonitrile/t-butyl alcohol/DMSO for 20 h. The visual difference in electrodes can be correlated to the interaction between dye and coadsorbent and their desorption capacity on the TiO2 surface. The desorption process of DH-14 and coadsorbent on the TiO2 surface can be demonstrated by FT-IR spectra of the photoanodes after desorption of dye (Fig. 13S, 14 S and 15S). The -NCS stretch is observed in both spectra (região de 2100 cm -1) and the stretch of functional groups belonging to coadsorbers SD - 6 (nitro group and tetrazole group) and LTz-4 (alkyl chain and tetrazole group) can be observed too. Sandwich types DSSCs were prepared from the stained photodiodes and Pt coated cathode. Photovoltaic measurements were carried out after introducing the electrolyte between the glass electrodes.

3.2. Photophysical measurements

The UV–Vis absorption and photoluminescence spectra of the coadsorbent **SD** - 6 and **LTz-4** in DMF (concentration of 1.8×10^{-5} M) are depicted in Fig. 2a and the corresponding photophysical data are summarized in Table 1.

In the electronic absorption spectra, the co-adsorbent **SD** - **6** and **LTz**-**4** exhibited a prominent band with the absorption maximum around 406 and 260 nm, respectively. The extinction coefficient are higher than 1.8 $\times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. Such absorption characteristics can be ascribed to the $\pi - \pi^*$ transition of the whole D- π -A conjugation backbone [36]. Similarly, the charge transfer emission maximum shifts from 600 nm for **SD** - **6**, 312 nm and 616 nm for **LTz**-4. These results suggest that **LTz**-4 dye possesses the strongest photoinduced intramolecular charge transfer ability over the π -conjugation backbone, leading to larger red shifts in absorption and emission spectra.

Fig. 16Sillustrates the absorption spectra of the HD-14 - DCA, HD-14 - SD - 6 and HD-14 - LTz-4 dyes on TiO2 thin films in comparison with HD-14 DCA dye in DMF (2×10^{-5} M). The TiO2 film sensitized with HD-14 - SD - 6 and HD-14 - LTz-4 dyes has displayed a λ_{max} of 415 nm, 555 nm and 403 nm, 542 nm respectively, in comparison with HD-14 DCA (400 nm, 539 nm) which were found to be a red shift of dyes by 15, 16, 3 and 3 nm upon adsorption on TiO2. Generally, this type of red shifted absorption spectra on TiO2 compared to the solution state absorption spectra have been observed for many dyes in organic, which could be attributed to the J-aggregation that benefits the capture of photons from an extended region [37].

The redox properties of the **SD** - **6** and **LTz**-**4** were investigated using cyclic voltammetry (CV) in DMF with 0.1 M [TBA][PF6] as an electrolyte at a scan rate of 50 mV s-1 (Fig. 2b) [38,39]. The cyclic voltammograms of **LTz**-**4** and **SD** - **6** show only one oxidation wave with the first oxidation potential ($E^{ox}_{1/2}$) at 1.06 and 0.55 V vs NHE, respectively, leading to HOMO energies of -6.35 eV for **LTz**-**4** and -5.84 eV for **SD** - **6**, respectively. Theses energy are very close to those measured for reference **HD**-**14** (-5.45 eV) and represent a stronger electron-donating ability of theses molecules in comparison to **HD**-**14**.

3.3. Molecular orbital calculations

The structures of co-adsorbent SD - 6 and LTz-4 were analyzed by using the B3LYP/6-31G (d,p) method. The true minima were characterized by calculating their vibrational modes at the same level of theory. All generated files from Gaussian 09 were analyzed with the Chemcraft program v1.8. The equilibrium molecular geometry and charge distribution in the frontier molecular orbitals can be depicted in Fig. 3 and the results are summarized in Table 2 [40-43]. It is clearly seen that the electron density of the highest occupied molecular orbitals (HOMO) is predominantly localized on the donor group for both co-adsorbent and diffusively distributed over the π -conjugation onto the system. For SD - 6, the electron density of the low unoccupied molecular orbital (LUMO) is predominantly localized on de nitro phenyl group, AZA bridge and diffusively distributed over the π -conjugation onto the donor group. No expressive electron density was observed on the tetrazole ring. The electron-withdrawing inductive effect of the nitro group and the low electron density on the tetrazole ring, suggests the reduction of resonance between the phenyl group and the heterocyclic tetrazole. Different from other studies where the tetrazole moiety was used as an



Scheme 1. Synthetic route of co-adsorbent SD - 6. Reaction conditions: (i) = NaN₃/NH₄Cl/DMF, yield 65%; (ii) = NaNO₂, HCl, 5 °C, C₆H₅N(C₂H₅)₂, yield 83%.



Scheme 2. Synthetic route of co-adsorbent LTz-4. Reaction conditions: (i) = $C_{10}H_{21}Br$, KOH, Toluene/DMF; (ii) = NaN₃/NH₄Cl/DMF, yield 72%.



Fig. 2. a) UV–Vis absorption (solid-lines) and emission spectra (dashed-lines) of SD - 6 and LTz-4 measured in DMF (1.8×10^{-5} M). b) Cyclic voltammetry of SD - 6 and LTz-4 in DMF with 0.1 M tetrabutylammonium hexafluorophosphate [TBA][PF₆] at a scan rate of 50 mV s⁻¹.

Table 1Photophysical date of co-adsorbent SD - 6 and LTz-4.

Compound	Absorption λ_{max} (nm)	$\epsilon (M^{-1} cm^{-1})$	Emission λ_{max} (nm)	Stokes shift (nm)	
SD - 6	406	34,400	600	194	
LTz-4	260	16,200	312 (and 616)	52 (and 356)	

anchor group on TiO_2 and gave a similar result to that presented by the carboxylic acid group [15], here the steric effects seem to have restricted the coplanarity of the system and anchoring by the tetrazole group [22, 44]. For LTz-4, the electron density of the low unoccupied molecular orbital (LUMO) is predominantly localized on the tetrazol group. This indicates that better p-orbital overlap is more likely in LTz-4 that of **SD** - **6**, which translates into slightly better charge transfer and hence slightly better photocurrent density in the former and that is consistent with the



Fig. 3. Energy level diagram for co-adsorbents SD - 6 and LTz-4.

Table 2

Excited state oxidation potential – ESOP (E^{*}), ground state oxidation potential (GSOP) and the lowest electronic transitions (E_{0-0}) for **SD - 6** and LTz-4.

Sensitizer	Experime	ental (eV)	^d Theoretical (eV)	
	^a E ₀₋₀	^{b,c} GSOP	ESOP (E*)	E ₀₋₀
SD - 6	2.63	-5.84	-3.21	2.87
LTz-4	4.80	-6.35	-1.55	5.00

^a E_{0-0} = calculated from the onset of absorption spectra (DMF).

 $^{\rm b}~{\rm GSOP} = {\rm ground}~{\rm state}~{\rm oxidation}~{\rm potential} = {\rm E}_{\rm HOMO}.$

^c GSOP was measured in DMF (1.8×10^{-5} M of dye) with 0.1 M [TBA] [PF6] and with a scan rate of 50 mV s⁻¹. It was calibrated with Fc/Fc⁺ as internal reference and converted to NHE by addition of 0.63 V, $GSOP = E^{ox}_{1/2} - E_{FC} + E_{NHE}$; Excited-state oxidation potential ESOP (E*) was calculated from: $E^* = GSOP + E_{0.0}$.

^d DFT calculations using Guassian 09 package [43].

measured efficiency.

3.4. Photovoltaic parameters of DSSCs

There are two widely used techniques for photovoltaic characterization: current-voltage measurements under simulated sunlight (producing J-V curves) and monochromatic light generated current measurements (producing incident photon-to-current conversion efficiency (IPCE) spectra). The photovoltaic parameters including shortcircuit photocurrent density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and overall power conversion efficiency (PCE) can be obtained by the current-voltage measurements. The IPCE value corresponds to the photocurrent density that is produced in the external circuit under monochromatic illumination of the cell divided by the photon flux that strikes the cell. The IPCE was determined by the light harvesting ability, the amount of adsorbed dyes on the TiO₂ surface, the overall charge collective efficiency and the overall electron injection efficiency. It is noted that the maximum IPCEs for DSSCs generally should be smaller than 90% because of the reflection and absorption loss due to the FTO glass. Fig. 4 shows the IPCE response as function of wavelength.

Incident photon to current conversion efficiency (IPCE) response of higher than 50% was exhibited by HD-14 – LTz-4 from 340 nm to 650 nm (reaching a maximum of 73% at 520–570 nm) and by HD-14 – SD - 6 from 390 nm to 560 nm (reaching a maximum of 55% at 410–420 nm). IPCE response high than 50% was achieved by HD-14 – DCA from 340 nm to 650 nm (reaching a maximum of 73% at 520–550 nm). These results indicate that, for this system, there is no direct relationship between amphiphilic characteristic and co-adsorbent effect for DSSCs. This possibility is confirmed by the result presented by the HD-14 - LTz-4 dye which one presented results very close to that presented by the HD-14 - DCA dye. On the other hand, the IPCE presented by the dye HD-14 – SD - 6 was inferior to the result presented by the dye HD-14 – DCA, this must be probably due to the difficulty of anchoring on TiO₂ surface.

The photovoltaic parameters including the short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factors (ff) and overall cell efficiencies (% η) are summarized in Table 3 and I-V results are shown in Fig. 5. HD-14 – DCA resulted in photocurrent densities (J_{sc}) of 19.50 mA cm⁻², HD-14 – LTz-4 resulted in J_{sc} of 19.71 mA cm⁻² and HD-14 – SD - 6 resulted in J_{sc} of 17.22 mA cm⁻², respectively. The fact that some compositions have higher values of photocurrent density can be attributed to the co-adsorbent favoring of photons capture and the more favorable injection of electrons into TiO₂. The dye HD-14 – DCA resulted in open-circuit photovoltage (V_{OC}) of 0.71 V, the dye HD-14 – LTz-4, resulted in V_{OC} of 0.70 V and the dye HD-14 – SD - 6, resulted in V_{OC} of 0.67 V.

The use of **LTz-4** as a co-adsorbent was shown to be more efficient. The dye **HD-14** - **LTz-4** resulted in a Jsc of 19.71 mA cm⁻² and Voc of 0.70 V, translating into a total conversion efficiency ($\%\eta$) of 9.21% and, the dye **HD-14** – **SD** - **6** resulted in a Jsc of 17.22 mA cm⁻² and Voc of 0.67 V, translating into a total conversion efficiency ($\%\eta$) of 7.48%, while the benchmark **HD-14** - **DCA** show a total conversion efficiency ($\%\eta$) of 9.22%. The use of **LTz-4** as a dye with **DCA** as a co-adsorbent show a total conversion efficiency ($\%\eta$) of 0.34% and the use of **SD** - **6** as a dye with **DCA** as a co-adsorbent show a total conversion efficiency ($\%\eta$) of 0.30%.

In previous studies, HD-14 and N719 with the DCA co-adsorbent on



Fig. 4. Photocurrent action spectra (IPCE) obtained with the dyes HD-14 – DCA, HD-14 – LTz-4, HD-14 – SD - 6, LTz-4 – DCA and SD - 6 – DCA. The concentration of the co-adsorbent used was 20 mM for all dyes.



Fig. 5. Photocurrent-voltage characteristics of DSSCs sensitized with HD-14 – DCA, HD-14 – LTz-4 and HD-14 – SD - 6. The concentration of the co-adsorbent used was 20 mM for all dyes.

a nanocrystalline TiO₂ electrode were studied under standard conditions [10]. HD-14 and N719 resulted in a J_{sc} of 18.71 and 16.15 mA cm⁻², respectively, corresponding to a conversion efficiency % η of 9.27 and 8.92, respectively. The experimentally obtained values for the HD-14 dye with the DCA co-adsorbent in this work are similar to those described in the literature (Table 1). The J_{sc} of 19.71 mA cm⁻² for HD-14 – LTz-4 is 5.3% higher than the J_{sc} of HD-14 – DCA, which can be attributed to the greater photon harvesting and more energetically favorable electron injection into TiO₂ provided by the co-adsorbent. The J_{sc} of 17.22 mA cm⁻² for HD-14 – SD - 6 is 8.0% lower than the J_{sc} of HD-14 – DCA.

3.5. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) successfully models the charge transfer and chemical capacitance at the interface of TiO_2 dye/electrolyte and Pt/electrolyte in DSSCs under operational conditions. Combination of charge transfer resistance (Rct) and chemical capacitance gives rise to a semi circle at the complex plan. Combination of charge transfer resistance and chemical capacitance give rise to a semi circle at the complex plan. In a typical EIS experiment, the first semicircle at high frequency corresponds to the cathode in a DSC, the middle semicircle corresponds to charge transfer resistance at the interface of dye/TiO₂ combined with chemical capacitance of electrons in TiO₂ (eTiO₂), and the third semicircle corresponds to finite Warburg impedance element [28]. The studies indicate that to the middle semicircle, the increase in its diameter is due to retardation of the charge recombination resistance (Rrec) at the interface of the TiO₂/dye/electrolyte. EIS was conducted with each of the different loading dye at an open-circuit potential (Fig. 6, Table 4).

 R_1 is the series resistance, R_{REC} is the recombination resistance of electrons in TiO_2 across the TiO_2-dye interface to an oxidized redox species, C_μ is the chemical capacitance for charge accumulation in TiO_2 , R_{CE} is the electron-transfer resistance at the counter electrode to an



Fig. 6. EIS Nyquist plots for DSSCs sensitized with HD-14 – DCA, HD-14 – LTz-4 and HD-14 – SD - 6.

oxidized redox species, and C_{CE} is the capacitance at the electrolytecounter electrode interface. $\eta_{CC}=1/(1+(R_{CE}/R_{REC}))$, where η_{CC} is the charge collection efficiency. $\tau_{TiO2}=1/(2\pi f)$, where τ_{TiO2} is the lifetime of injected electrons in TiO_2 and f is the peak frequency from the Bode plot for the lower frequency peak between 10 and 100 Hz (illustrated as gray lines in Fig. 7).

In Nyquist plot (Fig. 6), the order of increased charge recombination resistance is HD-14 - SD - 6 > HD-14 - LTz-4 > HD-14 - DCA. The higher the charge recombination resistance in Nyquist plot, the higher should be the photovoltage obtained from solar cells will be owing to slower charge recombination of electrons in TiO2 (eTiO2) and electron acceptors in electrolyte, resulting in higher eTiO2 lifetime [45-48]. Interestingly, charge recombination resistance (R_{REC}) was the lowest with the intermediate performing loading HD-14 – DCA system in DSC. This observation can be explained in terms of molecular polarity, in that, while aggregation is needed, the effect of the polarity of the co-adsorbent can alter the aggregation process, which can lowers device performances but more effectively blocks the TiO2 surface from recombination events. Considering that SD - 6 has a dipole moment perpendicular to the molecular axis and LTz-4 has a dipolar moment parallel to the molecular axis, SD - 6 is likely to provide more aggregation, which would reduce the performance the device. R_{RFC} was the higher with the lower performing loading HD-14 - SD - 6 system in DSC. Notably, the overall effect of varying RREC is low in these devices, which is apparent when analyzing the charge collection efficiency (η cc) via the equation, $\eta cc = 1/(1 + (RCE/Rrec))$, where RCE is the resistance at the counter electrode. Accordingly, all solvent systems have good ncc within the range of 68-72%. Analysis of the electron lifetime in TiO2 was undertaken via EIS with a Bode plot (Fig. 7). In this plot, the TiO2-dve interfacial electron transfer to the electrolyte is seen at frequencies between 10 and 100 Hz. The injected electron lifetime eTiO₂ can be determined by using the relation ($\tau_{TiO2}=1/(2\pi f),$ where τ is the lifetime of electrons in TiO₂ and f is the mid-frequency peak in Bode plots. eTiO₂ depends on the density of charge traps, which is ultimately related to V_{OC} [49]. In other words, the Bode plot results complement the Nyquist plot. The frequency peak of the DSSCs in the range of 1–100 Hz based on **HD-14**, with different co-adsorbents were at 53 Hz, corresponding to $eTiO_2$ of 3.0 m s, respectively, thus resulting in similar V_{OC} for different co-adsorbent, which correlates well with the actual V_{OC} reported for the solar cells (Table 3). A similar trend was also observed in the Nyquist plots (Fig. 6).

We measured the amounts of dye loading on TiO2, and the values of **HD-14 - DCA**, **HD-14 - SD - 6** and **HD-14 - LTz-4** are 2.06×10^{-6} M, 2.15×10^{-6} M and 2.12×10^{-6} M, respectively. Indeed, LTz-4 contributed to more efficient dye loading. In comparison with other studies described, the use of the phenyl tetrazole system as a base structure for co-adsorbent represents a superior gain in device efficiency [50].

The tetrazole system allows identification of two distinct effects that correlate with the magnification of the photovoltaic effect. The first one

Table 3

Photocurrent–voltage characteristics of DSSCs sensitized with HD-14 – DCA, HD14 – LTz-4 and HD-14 – SD - 6.

DYE ^a	$V_{OC}^{b}(V)$	Jsc ^b (mA/ cm ²)	Fill Factor ^b	Efficiency ^b (%)	Best Efficiency (%)
HD-14 –	0.70	19.52	0.67	9.2	-
DCA ^c					
HD-14 –	0.705 \pm	19.50 \pm	0.67 \pm	$\textbf{9.14} \pm \textbf{0.09}$	9.22
DCA	0.02	0.04	0.1		
HD-14 –	0.710 \pm	19.71 \pm	0.67 \pm	$\textbf{9.20} \pm \textbf{0.01}$	9.21
LTz-4	0.01	0.01	0.1		
HD-14 –	0.671 \pm	$17.22~\pm$	0.65 \pm	$\textbf{7.48} \pm \textbf{0.01}$	7.49
SD - 6	0.01	0.02	0.2		
LTz-4 –	0.404 \pm	1.65 \pm	0.44 \pm	$\textbf{0.34} \pm \textbf{0.04}$	0.37
DCA	0.04	0.05	0.3		
SD - 6 -	0.392 \pm	$1.73~\pm$	0.50 \pm	0.30 ± 0.02	0.34
DCA	0.03	0.12	0.2		

 $^{\rm a}$ Concentration of 0.3 mM in 1:1:1 acetonitrile/t-butyl alcohol/DMSO. The concentration of the co-adsorbent was 20 mM for all dyes, $^{\rm b}$ photoelectrode, TiO₂ (15 μm thickness acd 0.18 cm²).

^b Averages taken over 3 to 4 devices. .

^c Reference [10]. .



Fig. 7. EIS Bode plots for DSSCs sensitized with HD-14 - DCA, HD-14 - LTz-4 and HD-14 - SD - 6.

Table 4

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Device	R ₁ (Ohm)	R _{REC} (Ohm)	C _µ (mF)	R _{CE} (Ohm)	C _{CE} (mF)	η _{CC} (%)	τ _{TiO2} (ms)
HD-14 - DCA	16	12	$\begin{array}{c} 14 \times \\ 10^{-3} \end{array}$	5	0.3	71	3.0
HD-14 – SD - 6	24	15	$11 imes 10^{-3}$	6	0.3	72	3.0
HD-14 – LTz-4	26	13	$12 imes 10^{-2}$	6	0.2	68	3.0

is related to the amphiphilic characteristic of the co-adsorbent and the second effect is related to aggregation and the capacity of formation of the compact layer between co-adsorbent and dye.

Considering the amphiphilic character of co-adsorbent LTz-4, which has a 10-carbon alkyl chain, we believe that its greater contribution is due to the more protected monolayer formation capacity [49]. The hydrophobic end acts as a buffer between the semiconductor and the electrolyte, thus effectively preventing back-transfer of electrons from the semiconductor's CB to the redox couple or the oxidized dye molecules, so that unwanted re-combination is reduced [51–53]. On the other hand, the co-adsorbents **SD - 6** do not have an amphiphilic characteristic, which reduces its photoconversion efficiency, compared to that of the co-adsorbent **DCA**.

Long alkyl chain can suppress the dye aggregation on the TiO₂ film during dye uptake process and improve the device efficiency. Such an improvement is mainly observed in the organic dyes [54]. In case of Ru-based (octahedral) small size dyes, like HD-14, dye aggregation is not so strong and a compact monolayer on the TiO₂ film can form easily, resulting in a long electron lifetime [55]. One possible reason for the high efficiency HD-14 - LTZ-4 based DSC can be attributed to the bulkiness of the co-adsorbent dye set, leading to more compact monolayer formation, which hinders the recombination of conduction band electrons back to the electrolyte. Considering that the overall performance of DSSCs depends on the electron injection efficiency, we suggest that the improved IPCE performance of DSSCs based on the LTz-4 may arise from the prevention of the deactivation of the excited state via quenching processes between dye and co-adsorbent. These results clearly portray the advantage of using co-sensitizers in obtaining decreased recombination rate lifetime due to their small size and strong anchoring groups [50]. The back-electron recombination with the electrolyte or dye molecules was further prevented by the formation of a blocking layer covering the complete TiO2 nanoparticle due to increased dye loading [48,56]. This eventually led to decreased recombinations and increased Voc values, as evidently observed in case of experimentally co-sensitized DSSCs [57].

4. Conclusion

The development of new materials for DSSCs and understanding the interaction between them remains a major challenge in creating innovative hybrid materials with valuable functionality. In the present study, new phenyltetrazole derivatives were evaluated as co-adsorbents with HD-14 dye attached to TiO₂ thin films. The photovoltaic performance of phenyltetrazoles in DSSCs, were explored and compared to DCA coadsorbent. Overall, the results demonstrate the effectiveness of the tetrazole functional group as an alternative co-adsorbent moiety for organic photosensitizers. Structural characteristics of the evaluated coadsorbents allow the distinction of two effects that contribute to enhancing the efficiency of photo-injection in DSSCs. Theses effects allows more efficient charge transfer from dye to the phenyltetrazole system by π - π stacking interactions, that improves electron-injection efficiency into TiO₂. These results demonstrate a strong dependence of the electron injection process on TiO₂ to increase the efficiency of DSSCs.

Notes

The authors declare no competing financial interest.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported financially by CNPq. The authors wish to thank Dr. Hammad Cheema for providing the sample of **HD-14** used in this investigation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orgel.2020.105964.

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