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Synthesis of new N, N-diphenylhydrazone dyes for solar cells: Effects of thiophene-derived π -conjugated bridge

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1. Introduction

The increasing energy demand and the concerns about climate changes have led to a great focus on environment friendly energy sources during the last years. Dye-sensitized solar cells (DSSCs) which emerged as a new generation of photovoltaic devices have attracted significant attention and have been studied extensively due to their high efficiency, low cost, and facile fabrication [1]. Although Ru-based complexes hold the record of validated efficiency of over 11% [2], they have encountered problems such as limited resources and difficult purification. On the other hand, metal-free organic dyes have also been developed for DSSCs because they have many advantages such as high molar absorption coefficient, low cost, simple synthesis, and easier structural modification [3,4]. A common strategy in the design of highly efficient metal-free dyes for DSSCs is the linking of electron donor/acceptor (D–A) systems through π -conjugated bridges, which is called the D- π -A molecular structure. This kind of D- π -A dyes has been

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ABSTRACT

Four novel $D-\pi-A$ hydrazone dyes (HT, HM, HE, and HO) with an *N*, *N*-diphenylhydrazone moiety as the electron donor, different thiophene-derived π -conjugated bridges and a cyanoacrylic acid moiety as the electron acceptor have been designed and synthesized for the application in dye-sensitized solar cells. The influences of thiophene-derived bridges on the photoelectrochemical and photovoltaic performance of these hydrazone dyes were investigated. Results demonstrate that the introduction of 3,4dialkyloxythiophene could red-shift the dye's absorption spectrum due to the enhancement of the electron-donating ability of π -conjugated bridges. Importantly, electrochemical impedance spectroscopy analysis reveal that 3,4-dialkyloxythiophene bridge could change the charge recombination resistance at the TiO₂/dye/electrolyte interface and as a result to improve the open-circuit photovoltage. Among the four dyes, HO exhibits the maximum power conversion efficiency of 5.83% ($V_{oc} = 0.65 \text{ V}$, $I_{sc} = 12.69 \text{ mA/cm}^2$, FF = 0.707) under simulated AM 1.5 irradiation (100 mW/cm²).

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found to possess photoinduced intramolecular charge transfer (ICT) properties [3.4], which makes these compounds as ideal dves for DSSCs application. Using this strategy, many D $-\pi$ -A metal-free dves with various donor moieties, such as coumarin [5,6], indoline [7,8], triarylamine [9–18], phenothiazine [19], and porphyrin [20,21], have been designed and synthesized as efficient sensitizers for DSSCs in recent years. Power conversion efficiencies (PCEs) up to \sim 9% have been achieved for DSSCs using these metal-free dyes [5,6]. Moreover, encouraging efficiencies up to 10% have been reported [22,23] in recent publications. Developing novel and highly efficient metal-free organic dyes applied in DSSCs is thus an area of strong current research activity [3,4].

In most dyes, the amine derivatives act as the electron donor while a 2-cyanoacrylic acid or rhodanine moiety acts as the electron acceptor. These two parts are connected by π -conjugated bridges such as the vinyl unit or thiophene chain. The π -conjugated bridge influences not only the region of light absorbed by the DSSCs but also the degree of electron injection from the dye's excited state to the TiO₂ surface. Consequently, even a small change in the conjugated bridge of the dye can cause a significant change in the solar cell performance [24-26]. Moreover, in our previous reports [14,15,27], we have proved that π -conjugated bridge has a great influence on the molecular structure and photoelectronic properities of the metal-free organic dyes.





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Changes in the electron-donating nature and structural variations of amine unit can result in a variation of electronic properties [28]. Aromatic hydrazones are widely studied and used as organic nonlinear optical materials [29] and hole-transport materials for electrophotographic photoreceptors [30-32]. The main advantages of such compounds are the simple synthesis and high enough charge mobilities [31]. Many triphenylamine [33]. carbazole [34,35] and thiophene-based hydrazone [36.37] compounds were synthesized and used as glass-forming hole-transport materials. Tran-Van et al. recently reported on the synthesis and application of biscarbazole and terthiophene derivatives containing hydrazone functional groups in solid-state DSSCs as hole-transport materials [38]. However, aromatic hydrazones compounds until now are few studied as photoactive dyes for DSSCs. Therefore, we became interested in constructing metal-free organic dyes with hydrazone moiety to make use of its excellent hole-transport property for the electron donor.

Expanding on the foregoing points and as part of our efforts to explore novel metal-free dyes, we herein report on the design and synthesis of a series of $D-\pi$ –A dyes (**HT**, **HM**, **HE**, and **HO**, as shown in Fig. 1) consisting of an *N*, *N*-diphenylhydrazone donor, a 2-cyanoacetic acid acceptor, and a thiophene-derived bridge. The effects of the π -conjugated bridges on the photophysical, electrochemical and photovoltaic properties of these novel dyes were investigated in detail. We found that the photoelectronic properties, especially power conversion efficiency is quite sensitive to the structural variations of the bridging thiophene moiety. Once again, our results indicate that the slight change of π -conjugated bridge would have a remarkable impact on structures and photoelectronic properties of organic dyes.

2. Experimental section

2.1. Materials and reagents

1,1-Diphenylhydrazine hydrochloride, 3,4-ethylendioxythiophene, 3,4-dimethoxythiophene, and thiophene-2-carbaldehyde (**3d**) were purchased from commercial suppliers (Pacific ChemSource and Alfa Aesar) in analytical grade. THF was dried and distilled over sodium/ benzophenone. DMF, CHCl₃, and CH₃CN were dried over by accustomed methods and distilled before using. All other solvents and chemicals used in this work were analytical grade and used without further purification. All chromatographic separations were carried out on silica gel (200–300 mesh).

2.2. Analytical instruments

¹H NMR spectra were recorded on a Bruker Avance 400 instrument. UV–vis spectra of the dyes were measured on a Perkin-Elmer Lamada 25 spectrometer. The PL spectra were obtained using

Perkin-Elmer LS-50 luminescence spectrometer. FT-IR spectra were obtained on Perkin-Elmer Spectra One spectrophotometer. The elemental analysis of all compounds was performed with a Perkin-Elmer 2400 analyzer for C, H, N, and S determination. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) using a three-electrode cell and an electrochemistry workstation (CHI830B, Chenhua Shanghai). The working electrode was a Pt ring electrode: the auxiliary electrode was a Pt wire, and saturated calomel electrode (SCE) was used as reference electrode. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) 0.1 M was used as supporting electrolyte in dry acetonitrile. Ferrocene was added to each sample solution at the end of the experiments, and the ferrocenium/ferrocene (Fc⁺/Fc) redox couple was used as an internal potential reference. The potentials of dyes versus NHE were calibrated by addition of 0.63 V to the potentials versus Fc^+/Fc . The solutions were purged with argon and stirred for 15 min before the measurements.

2.3. General procedure for fabrication and characterization of DSSCs

Fluorine-doped SnO₂ conducting glass (FTO) were cleaned and immersed in aqueous 40 mM TiCl₄ solution at 70 °C for 30 min, then washed with water and ethanol, sintered at 450 °C for 30 min, the TiO₂ colloid was prepared from 12 g P25 (Degussa AG, Germany) following a literature procedure [2]. First the 20–30 nm particles sized TiO₂ colloid was coated onto the above FTO glass by sliding glass rod method to obtain a TiO₂ film of 14 µm thickness after drying. Subsequently, the 200 nm particles sized TiO₂ colloid was coated onto the above FTO glass by sliding glass rod method to obtain a TiO₂ film of 14 µm thickness after drying. Subsequently, the 200 nm particles sized TiO₂ colloid was coated on the electrode by the same method, resulting in a TiO₂ light-scattering layer of 5 µm thickness. The double-layer TiO₂-coated FTO glass were sintered at 450 °C for 30 min, then treated with TiCl₄ solution and calcined at 450 °C for 30 min again. After cooling to 100 °C, the TiO₂ electrodes were soaked in a solution with 0.5 mM dyes and kept at room temperature under dark for 24 h.

The dye-adsorbed TiO₂ electrode washed with ethanol and dried. A drop of electrolyte solution was deposited onto the surface of the electrode and a Pt foil counter electrode was clipped onto the top of the TiO₂ electrode to assemble a dye sensitized solar cells forphotovoltaic performance measurements. The electrolyte consisted of 0.5 M LiI, 0.05 M I₂, and 0.5 M 4-*tert*-butylpyridine (TBP) in 3-methoxypropionitrile and the efficient irradiated area of cell was 0.196 cm². The photocurrent–voltage (*J*–*V*) characteristics of solar cells were measured using a Keithley 2602 Source meter under the 100 Mw/cm² irradiation of a 500 W Xe lamp with a global AM 1.5 filter for solar spectrum simulation. Meanwhile, the photoelectric conversion efficiency was calculated. The measurement of monochromatic incident photon-to-current conversion efficiencies (IPCE) was performed by a Zolix DCS300PA Data acquisition system and other optical system.



Fig. 1. Molecular structures of the dyes HT, HM, HE, and HO.

2.4. Synthesis

The synthetic routes to the four dyes are shown in Scheme 1. The detailed synthetic procedures are as follows.

2.4.1. 3,4-Dioctyloxythiophene (1)

3,4-Dimethoxythiophene (3.00 g, 21 mmol), *n*-octyl alcohol (11.9 g, 92 mol), and *p*-toluenesulfonic acid monohydrate (0.15 g) were added into a round-bottom flask equipped with a water knockout vessel. The mixture was stirred at 90 °C for 24 h with vacuum applied occasionally to remove side product methanol to drive the reaction to completion. Then the mixture was poured into a separatory funnel. The mixture was neutralized with dilute HCl and extracted with petroleum ether. The combined organic layer was washed with distilled water and dried over anhydrous MgSO₄, filtered, condensed by rotary evaporation. The crude product was purified by silica gel column chromatography (petroleum ether as eluent) to provide compound **1** (5.35 g, yield: 75%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 6.16 (s, 2 H), 3.97 (t, 4 H), 1.85–1.78 (m, 4 H), 1.43–1.28 (m, 20 H), 0.87 (t, 6 H).

2.4.2. The general synthetic procedure of (3)

In a 100 mL three-necked flask, compound **2** (20 mmol), 1,2dichloroethane (40 mL), dried DMF (4.65 mL, 60 mmol) and POCl₃ (5.54 mL, 60 mmol) were added sequentially under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 0.5 h and then heated up to reflux for another 4 h. After cooling to room temperature, saturated aqueous solution of NaOAc (20 mL) was added into the reaction mixture and stirred violently for 1 h. Then the reaction mixture was extracted with chloroform. The combined organic layer was washed with distilled H₂O and brine, dried over anhydrous MgSO₄. Solvents were removed by rotary evaporation, and the crude product was purified by silica gel column chromatography with petroleum ether/dichloromethane (4/1, v/v) as eluent to yield compound **3**.

2.4.2.1. 3,4-Dimethoxythiophene-2-carbaldehyde (**3a**). Yield: 63% (2.17 g). FT-IR (KBr, cm⁻¹): 1655 ($\nu_{C=0}$). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 10.01 (s, 1 H), 6.64 (s, 1 H), 4.12 (s, 3 H), 3.87 (s, 3 H).

2.4.2.2. 3,4-Ethylendioxythiophene-2-carbaldehyde (**3b**). Yield: 74% (2.52 g). FT-IR (KBr, cm⁻¹): 1649 ($v_{C=0}$). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 9.91 (s, 1 H), 6.80 (s, 1 H), 4.38–4.34 (m, 2 H), 4.31–4.27 (m, 2 H).

2.4.2.3. 3,4-Dioctyloxythiophene-2-carbaldehyde (**3c**). Yield: 69% (5.09 g). FT-IR (KBr, cm⁻¹): 1664 ($v_{C=0}$). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 9.99 (s, 1 H), 6.61 (s, 1 H), 4.32 (t, 2 H), 3.97 (t, 2 H), 1.82–1.72 (m, 4 H), 1.45–1.29 (m, 20 H), 0.88 (t, 6 H).

2.4.3. The general synthetic procedure of (4)

In a 100 mL three-necked flask, a solution of compound **3** (5 mmol) in 30 mL of THF was added dropwise into the mixture of *N*,*N*-diphenylhydrazine hydrochloride (1.54 g, 7 mmol), sodium acetate (0.82 g, 10 mmol) and anhydrous MeOH (20 mL) under nitrogen atmosphere. The mixture was refluxed for 24 h and the color turned gradually from yellow to dark brown. After cooling, the resulting mixture was quenched with 40 mL distilled water and extracted with chloroform. The combined organic layer was washed with distilled water and brine, dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography with petroleum ether/dichloromethane (4/1, v/v) as eluent.

2.4.3.1. 3,4-Dimethoxythiophene-2-carbaldehyde-N,N-diphenylhydrazone (**4a**). Yield: 75% (1.27 g). ¹H NMR (400 MHz, CDCl₃,



Scheme 1. Synthesis of the HM, HE, HO, and HT dyes.

 δ/ppm): 7.43–7.39 (m, 4 H), 7.28–7.26 (m, 2 H), 7.25 (s, 1 H), 7.23–720 (m, 4 H), 6.24 (s, 1 H), 4.12 (s, 3 H), 3.75 (s, 3 H). Elem. Anal. Calcd. for C₁₉H₁₈N₂O₂S: C, 67.43%; H, 5.36%; N, 8.28%; S, 9.47%. Found: C, 67.40%; H, 5.17%; N, 8.20%; S, 9.56%.

2.4.3.2. 3,4-Ethylendioxythiophene-2-carbaldehyde-N,N-diphenylhydrazone (**4b**). Yield: 71% (1.19 g). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.42–7.39 (m, 4 H), 7.25 (s, 1 H), 7.19–7.15 (m, 6 H), 6.25 (s, 1 H), 4.14 (m, 4 H). Elem. Anal. Calcd. for C₁₉H₁₆N₂O₂S: C, 67.84%; H, 4.79%; N, 8.33%; S, 9.53%. Found: C, 67.80%; H, 4.77%; N, 8.50%; S, 9.73%.

2.4.3.3. 3,4-Dioctyloxythiophene-2-carbaldehyde-N,N-diphenylhydrazone (**4c**). Yield: 70% (1.87 g). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.42–7.38 (m, 6 H), 7.34 (s, 1 H), 7.17–7.15 (m, 4 H), 6.06 (s, 1 H), 3.94–3.87 (m, 4 H), 1.77–1.74 (m, 4 H), 1.56–1.28 (m, 20 H), 0.88 (t, 6 H). Elem. Anal. Calcd. for C₃₃H₄₆N₂O₂S: C, 74.11%; H, 8.67%; N, 5.24%; S, 6.00%. Found: C, 74.10%; H, 8.37%; N, 5.27%; S, 6.15%.

2.4.3.4. Thiophene-2-carbaldehyde-N,N-diphenylhydrazone

(*4d*). Yield: 72% (1.00 g). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 7.44–7.42 (m, 4 H), 7.31 (s, 1 H), 7.27 (s, 1 H), 7.22–7.20 (m, 6 H), 7.97–7.93 (m, 2 H). Elem. Anal. Calcd. for C₁₇H₁₄N₂S: C, 73.35%; H, 5.07%; N, 10.06%; S, 11.52%. Found: C, 73.50%; H, 5.07%; N, 10.50%; S, 11.58%.

2.4.4. The general synthetic procedure of (5)

Compound **5** was synthesized according to the same procedure as that of compound **3**, except that compound **4** (0.68 g, 2 mmol) was used instead of compound **2**.

2.4.4.1. 5-Formyl-3,4-dimethyoxythiophene-2-carbaldehyde-N,N-diphenylhydrazone (**5a**). Yield: 84% (0.62 g). FT-IR (KBr, cm⁻¹): 1664 ($v_{C=0}$). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 10.00 (s, 1 H), 7.48–7.44 (m, 4 H), 7.28–7.26 (m, 2 H), 7.25 (s, 1 H), 7.21–7.19 (m, 4 H), 4.10 (s, 3 H), 3.73 (s, 3 H). Elem. Anal. Calcd. for C₂₀H₁₈N₂O₃S: C, 65.55%; H, 4.95%; N, 7.64%; S, 8.75%. Found: C, 65.80%; H, 4.97%; N, 7.60%; S, 8.83%.

2.4.4.2. 5-Formyl-3,4-ethylendioxythiophene-2-carbaldehyde-N,N-diphenylhydrazone (**5b**). Yield: 82% (0.60 g). FT-IR (KBr, cm⁻¹): 1666 ($v_{C=0}$). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 9.89 (s, 1 H), 7.47–7.43 (m, 4 H), 7.28–7.26 (m, 2 H), 7.25 (s, 1 H), 7.23–7.19 (m, 4 H), 4.34–4.33 (m, 2 H), 4.23–4.22 (m, 2 H). Elem. Anal. Calcd. for C₂₀H₁₆N₂O₃S: C, 65.92%; H, 4.43%; N, 7.69%; S, 8.80%. Found: C, 65.86%; H, 4.47%; N, 7.70%; S, 8.85%.

2.4.4.3. 5-Formyl-3,4-dioctyloxythiophene-2-carbaldehyde-N,N-diphenylhydrazone (**5c**). Yield: 83% (0.93 g). FT-IR (KBr, cm⁻¹): 1665 ($v_{C=0}$). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 9.95 (s, 1 H), 7.45–7.41 (m, 6 H), 7.24 (s, 1 H), 7.19 (d, 4 H), 4.24–4.20 (t, 2 H), 3.84–3.81 (t, 2 H), 1.76–1.73 (m, 4 H), 1.50–1.24 (m, 20 H), 0.90 (t, 6 H). Elem. Anal. Calcd. for C₃₄H₄₆N₂O₃S: C, 72.56%; H, 8.24%; N, 4.98%; S, 5.70%. Found: C, 72.60%; H, 8.26%; N, 4.80%; S, 5.90%.

2.4.4.4. 5-Formyl-thiophene-2-carbaldehyde-N,N-diphenylhydrazone (**5d**). Yield: 85% (0.52 g). FT-IR (KBr, cm⁻¹): 1664 ($\nu_{C=0}$). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 9.86 (s, 1 H), 7.63 (d, 1 H), 7.62 (s, 1H), 7.48 (d, 1 H), 7.47–7.45 (m, 4 H), 7.27–7.21 (m, 2 H), 6.99–6.98 (m, 4 H). Elem. Anal. Calcd. for C₁₈H₁₄N₂OS: C, 70.56%; H, 4.61%; N, 9.14%; S, 10.47%. Found: C, 70.50%; H, 4.67%; N, 9.16%; S, 10.53%.

2.4.5. The general synthetic procedure of sensitizers

Under nitrogen atmosphere, a mixture of compound **5** (1.2 mmol), 2-cyanoacetic acid (0.21 g, 2.4 mmol), piperidine (0.5 mL), and CH₃CN (30 mL) was refluxed at 80 $^{\circ}$ C for 24 h. After

cooling, most of solvent was removed under vacuum and the residue was dropped into a mixture of petroleum ether and HCl (0.1 M) to form a precipitation. The crude product was further purified by silica gel column chromatograph eluted with dichloromethane/methanol (15/1, v/v) to obtain the dye.

2.4.5.1. 5-(2-Cyanoacrylic acid-3-yl)-3,4-dimethyoxythiophene-2carbaldehyde-N,N-diphenylhydrazone (**HM**). Yield: 75% (0.39 g). FT-IR (KBr, cm⁻¹): 2216 ($v_{C=N}$), 1678 ($v_{C=0}$). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 8.44 (s, 1 H), 7.54 (s, 1 H), 7.50–7.42 (m, 6 H), 7.23–7.16 (m, 4 H), 4.05 (s, 3 H), 3.72 (s, 3 H). Elem. Anal. Calcd. for C₂₃H₁₉N₃O₄S: C, 63.73%; H, 4.42%; N, 9.69%; S, 7.40%. Found: C, 64.00%; H, 4.37%; N, 9.70%; S, 7.53%.

2.4.5.2. 5-(2-Cyanoacrylic acid-3-yl)-3,4-ethylendioxythiophene-2carbaldehyde-N,N-diphenylhydrazone (**HE**). Yield: 70% (0.36 g). FT-IR (KBr, cm⁻¹): 2214 ($\nu_{C=N}$), 1682 ($\nu_{C=0}$). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 8.39 (s, 1 H), 7.54 (s, 1 H), 7.51–7.47 (m, 6 H), 7.23–7.17 (m, 4 H), 4.36–4.35 (m, 2 H), 4.23–4.21 (m, 2 H). Elem. Anal. Calcd. for C₂₃H₁₇N₃O₄S: C, 64.03%; H, 3.97%; N, 9.74%; S, 7.43%. Found: C, 64.10%; H, 4.03%; N, 9.70%; S, 7.48%.

2.4.5.3. 5-(2-Cyanoacrylic acid-3-yl)-3,4-dioctyloxythiophene-2carbaldehyde-N,N- diphenylhydrazone (**HO**). Yield: 72% (0.54 g). FT-IR (KBr, cm⁻¹): 2215 ($v_{C=N}$), 1680 ($v_{C=0}$). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 8.43 (s, 1 H), 7.47–7.43 (m, 6 H), 7.24 (s, 1 H), 7.21–7.19 (d, 4 H), 4.18 (t, 2 H), 3.80 (t, 2 H), 1.74–1.71 (m, 4 H), 1.63–1.24 (m, 20 H), 0.90 (t, 6 H). Elem. Anal. Calcd. for C₃₇H₄₇N₃O₄S: C, 70.56%; H, 7.52%; N, 6.67%; S, 5.09%. Found: C, 70.80%; H, 7.57%; N, 6.70%; S, 5.23%.

2.4.5.4. 5-(2-Cyanoacrylicacid-3-yl)-thiophene-2-carbaldehyde-N,N-diphenylhydrazone (**HT**). Yield: 74% (0.33 g). FT-IR (KBr, cm⁻¹): 2213 ($v_{C=N}$), 1673 ($v_{C=0}$). ¹H NMR (400 MHz, DMSO- d_6 , δ /ppm): 8.36 (s, 1 H), 7.82 (d, 1 H), 7.52 (s, 1 H), 7.50 (d, 1 H), 7.37–7.26 (m, 6 H), 7.19–7.17 (m, 4 H). Elem. Anal. Calcd. for C₂₁H₁₅N₃O₂S: C, 67.54%; H, 4.05%; N, 11.25%; S, 8.59%. Found: C, 67.58%; H, 4.07%; N, 11.60%; S, 8.63%.

3. Results and discussion

3.1. Synthesis and characterization of sensitizers

The synthesis of the four hydrazone-based organic dyes **HM**, **HE**, **HO**, and **HT** is outlined in Scheme 1. The four dyes were synthesized by the similar stepwise synthetic protocol. First, 2-thienaldehyde or its derivatives (3a-c) reacted with *N*, *N*-diphenylhydrazine hydrochloride to afford thiophene-based hydrazone 4a-d according to the previous reports [20] in high yields. Then Vilsmeier formylation of 4a-d afforded the key intermediates 5a-d with good yields (82–85%). Finally, Knoevenagel condensation reactions of aldehyde derivatives 5a-d with two-fold excess of cyanoacetic acid afforded the four target dyes in acetonitrile using piperidine as catalyst. The structures of all important new compounds were characterized unambiguously with FT-IR, ¹H NMR spectroscopy and elemental analyze.

3.2. Photophysical properties

The ultraviolet–visible (UV–vis) absorption spectra of the four dyes in diluted THF solutions are shown in Fig. 2, and the corresponding data are collected in Table 1. All the dyes exhibit a strong absorption maximum (λ_{max}) in the visible region (460–490 nm) corresponding to the intramolecular charge transfer (ICT) between the *N*, *N*-diphenylhydrazone donating unit and the cyanoacrylic



Fig. 2. Absorption spectra of the four dyes in THF solutions (10⁻⁵ M) at 25 °C.

acid acceptor moiety [39] and a relatively weak peak in the near-UV region (290–315 nm) due to the $\pi - \pi^*$ electron transitions of the conjugated molecules. It can be seen that the λ_{max} in the visible region red-shifts from 465 nm to 479 nm, 483 nm, and 490 nm for HT, HM, HO and HE, respectively. This red-shifted phenomenon of λ_{max} in the visible region can be ascribed to the different electrondonating ability of the thiophene-derived bridges. Obviously, 3,4dialkoxyl substituted thiophene bridges (HM, HE, and HO) have more strong electron-donating ability than non-substituted thiophene bridge (HT), which enhances the ICT between the N, N-diphenylhydrazone donating unit and the cyanoacrylic acid acceptor moiety, and as a result to shift the λ_{max} to the long wavelength. For three 3,4-dialkoxyl substituted thiophene bridged dyes (HM, HE, and HO), we intend to understand the change regularity of their λ_{max} from the molecular modeling studies (Fig. 3) which is a common method to be widely used in other dyes [15,22,23]. The ground-state structures of HT, HM, HE, and HO have almost planar geometry with small twist angles of 0.012°, 1.32° , -1.60° and 1.62° , respectively, between N=C double bond and the adjacent thiophene-derived bridge. This result shows that the twist angles for these dyes are very similar which indicates that it is impossible to use the plananity of dye molecules to explain the change regularity of their λ_{max} . Moreover, the result also shows that hydrazone-based dyes have more coplanar geometry compared with tripheneylamine-based analogues [14] which benefits ICT between the donor and the acceptor moiety, thus red-shifting the λ_{max} in the visible region even though the influence of difference solvents is taken into consideration. Therefore, the red-shifts of λ_{max} for **HO** and **HE** compared to **HM** may attribute to more strong electron-donating ability of 3,4-ethylendioxythiophene and 3,4-dioctyloxythiophene bridges than 3,4-dimethyloxylthiophene bridge.

Table 1
Maximum absorption and emission data of the four dyes.

Dye	$\lambda_{max}^{a}/nm (\epsilon^{c}/M^{-1}c)$	m ⁻¹)	λ_{\max}^{b}/nm
HT	465(18300)	295(8500)	469
HM	479(23300)	309(16000)	476
HE	490(28000)	313(16600)	475
НО	483(29700)	312(19300)	496

^a Maximum absorption in THF solution (10^{-5} M) .

^b Maximum absorption on TiO₂ film.

^c ε is the molar extinction coefficient at λ_{max} of maximum absorption.

As depicted in Table 1, the molar extinction coefficient (ε) of the ICT bands of the four dyes ($18.3-29.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) are higher than that of the standard N719 sensitizer ($14.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) [2], indicating a better ability of light harvesting of these new *N*, *N*-diphenylhydrazone-based metal-free organic dyes than that of classical organometallic dye. Moreover, the ε of the ICT bands increases in the order of **HT** < **HM** < **HE** < **HO**, which suggests that the enhancing of electron-donating ability of the π -conjuagted bridge in a dye significantly increases the light harvesting efficiency.

When the dyes were attached on TiO₂ films, the absorption spectra may shift more or less as compared with those in solutions because of strong interactions between the dyes and the semiconductor surface, which can lead to form aggregates of the dyes on semiconductor surface, such as *H*-aggregation for the blue shift or J-aggregation for the red shift. Fig. 4 shows the absorption spectra of the four dyes adsorbed on the TiO₂ films, and the corresponding data are collected in Table 1. We can see that absorption spectra of the four dyes on TiO₂ films display a slight blue shift of 3 nm (HM) and 15 nm (HE), or a small red shift of 4 nm (HT) and 16 nm (HO), compared to those in THF solutions. The slight red or blue shift may be due to the reduction of intermolecular $\pi - \pi$ interaction. It cannot be concluded that the $\pi - \pi$ stack was broken up completely, but it is reasonable to presume that the intermolecular $\pi - \pi$ interaction is weakened and the dye aggregation is inhibit effectively. This implies that these N, N-diphenylhydrazone-based dyes have the relatively strong ability to inhibit possible intermolecular aggregation and retard the electron transfer from TiO₂ to the oxidized dye or electrolyte, thus possibly enhancing open-circuit voltage $(V_{\rm oc})$ [40,41]. It is noteworthy that the absorption spectra of those adsorbed on TiO₂ films show a markedly broad profile, which is beneficial to light-harvesting.

3.3. Electrochemical properties

To evaluate the possibility of electron transfer from the excited dye molecule to the conductive band of TiO_2 and the dye regeneration, cyclic voltammetry (CV) method was employed in acetonitrile solution, using 0.1 M Bu_4NPF_6 as a supporting electrolyte (Fig. 5), and the data are summarized in Table 2.

The first oxidation potential vs. NHE (E_{ox}) corresponding to the highest occupied molecular orbital (HOMO vs. NHE), was calibrated by addition of 0.63 V to the potential (vs. SCE) vs. Fc/Fc⁺ by CV (Table 2). The E_{ox} of the four dyes **HT**, **HM**, **HE**, and **HO** were measured as around 1.30 V, indicating no obvious effect on the E_{ox} for different the thiophene-derivatived bridges. We also can see that all the HOMO levels of four dyes are more positive than the iodide/triiodide redox couple (~0.42 V vs. NHE) [41], ensuring that there is enough driving force for efficient regeneration of the dye through the recapture of the injected electrons by the dye cation radical.

By neglecting any entropy change during light absorption, the reduction potential vs. NHE (E_{red}), which corresponds to the lowest unoccupied molecular orbital (LUMO vs. NHE), can be obtained from E_{ox} and E_{0-0} value determined from the intersection of absorption and emission spectra, namely, $E_{ox}-E_{0-0}$. The calculated LUMO levels of **HT**, **HM**, **HE**, and **HO** were -1.09, -1.06, -1.05, and -1.05 V vs. NHE (Table 2), respectively, which all are sufficiently higher than that of the conduction band (CB) level of TiO₂ (-0.5 V vs. NHE). Provided that energy gap (E_{gap}) between LUMO levels and CB level of TiO₂ of 0.2 eV is necessary for efficient electron injection [28], these driving forces are sufficiently large for effective electron injection. Noticeably, the slight positive shift of the reduction potentials in **HM**, **HE**, and **HO** compared to that of **HT** implies that the electron-donating 3,4-dialkyoxlythiophene bridges can heighten the LUMO levels of the dyes.



Fig. 3. Optimized structures calculated by TD-DFT using the B3LYP functional and the 3-21G* bases set for the four dyes.

These above-discussed results indicate that the photoelectrochemical properties of this series dyes could easily be tune by changing the thiophene-derived bridges.

3.4. Molecular orbital calculations

To gain an insight into the molecular structure and electron distribution, density functional theory (DFT) calculations were performed on the four dyes using the Gaussian 03 program package. In particular we used B3LYP as exchange-correlation functional and 3-21G* as basis set. The electron distribution of the HOMO and LUMO of the dyes is shown in Table 3. It is obvious that the electron density of HOMO is localized mainly on the N, N-diphenylhydrazone moiety and is extended along the π -conjugated bridge to the central region of the molecule. On the other hand, the LUMO is localized over the cyanoacrylic unit through aromatic bridges. We notice that the HOMO-LUMO excitation induced by light irradiation could move the electron distribution from the N, N-diphenylhydrazone unit to the cyanoacrylic acid moiety via π -conjugated thiophenederived bridges and the photo-induced electron transfer from the dyes to the TiO₂ electrode can occur efficiently by the HOMO-LUMO transition.

3.5. Photovoltaic performance of DSSCs based on the four dyes

DSSCs were fabricated using these dyes as the sensitizers, with an effective area of 0.196 cm^2 , TiO₂ particles on FTO, and the electrolyte composed of 0.5 M LiI, 0.05 M I₂, and 0.5 M 4-*tert*-butyl-pyridine (TBP) in 3-methoxy-propionitrile. Fig. 6 shows incident



Fig. 4. Normalized absorption spectra of the four dyes adsorbed on TiO₂ surface.

photon-to-electron conversion efficiency (IPCE) as a function of the wavelength for the sandwiched DSSCs based on the four dyes as sensitizers. The IPCEs action spectra for DSSCs based on HO and HE are broader than those of HT and HM, which are in accordance with their absorption spectra on the transparent TiO₂ films (Fig. 3). As shown in Fig. 6, the IPCEs of HO and HT sensitizers exceed 50% in the spectral region from 390 to 520 nm, reaching their maximum over 60%. The relatively higher maximum IPCE for HO compared with other three dyes is well in agreement with the tendency of UV-vis absorption spectra on TiO₂ films (Fig. 3). These results imply that HO and HT would show a relatively large photocurrent in DSSCs. Additionally, it should be noted that the four dyes still show weak IPCE response at the range of long wavelength region (650-750 nm), as shown in Fig. 6. We think this feature should be ascribed two reasons: one is the weak absorption band of the dyes on TiO₂ films at the range of 650–750 nm (see Fig. 4), which is consistent with the previous reports [42,43]; the other is the effect of light scattering by TiO₂ nanoparticles [44], which increases the photocurrents for the weak absorption in that region.

Fig. 7 shows current density–voltage (*J*–*V*) characteristics of devices based on the four dyes. The detailed photovoltaic parameters of the short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE) are listed in Table 4. According to Fig. 7, it is clear that the photovoltaic performances of the DSSCs can be evidently affected by the conjugated thiophene bridges in the dye molecules. The PCE increases in the order of **HE** (4.20%) < **HM** (4.70%) < **HT** (5.29%) < **HO** (5.83%). **HO** exhibits the best PCE due to both the



Fig. 5. Cyclic voltammograms of the three dyes: working electrode, Pt ring; auxiliary electrode, Pt wire; reference electrode, Hg/Hg₂Cl₂; scanning rate is 100 mV/s.

Table 2Electrochemical data of the four dyes.^a

Dye	λ_{int}/nm	E_{0-0}/eV	$E_{\rm ox}/V$ vs. NHE	$E_{\rm red}/V$ vs. NHE	$E_{\rm gap}/V$
HT	520	2.38	1.29	-1.09	0.59
HM	525	2.36	1.30	-1.06	0.56
HE	529	2.34	1.29	-1.05	0.55
HO	526	2.36	1.31	-1.05	0.55

^a E_{0-0} values were calculated from intersection of the normalized absorption and the emission spectra (λ_{int}): $E_{0-0} = 1240/\lambda_{int}$. The first oxidation potential (vs. NHE), E_{ox} was measured in acetonitrile and calibrated by addition of 0.63 V to the potential versus Fc/Fc⁺. The reduction potential, E_{red} , was calculated from E_{ox} – E_{0-0} . E_{gap} is the energy gap between the E_{red} of dye and the CB level of TiO₂ (-0.5 V vs. NHE).

highest J_{sc} (12.69 mA/cm²) and V_{oc} (0.65 V) values. The increased J_{sc} value of **HO** compared with other three dyes mainly derived from its relatively better light harvesting ability (broad absorption spectrum and high molar extinction coefficient), reflecting in its

better IPCE spectrum. In addition, consistent with the increased tendency of IPCE, the measured J_{sc} increases in the order of **HM** (10.20 mA/cm²) < **HE** (10.44 mA/cm²) < **HT** (11.04 mA/cm²) < **HO** (12.69 mA/cm²). The improved V_{oc} values of **HM** (0.66 V) and **HO** (0.65 V) compared with **HT** (0.64 V) and **HE** (0.62 V) could be attributed to the effective retardation of charge recombination between the injected electrons and I_3 ions in the electrolyte, which resulted from the hydrophobic dialkyloxyl-substitutes in the dyes **HM** and **HO** [14,15,27,45]. We will discuss it in detail as the following electrochemical impedance spectroscopy studies.

3.6. Electrochemical impedance spectroscopy studies

Electrochemical impedance spectroscopy (EIS) is a powerful technique of characterizing the important interfacial charge transfer processes in a DSSC. The EIS was measured in the dark to

Table 3

Frontier molecular orbitals of the HOMO and LUMO calculated with DFT on a B3LYP/3-21G* level of the four dyes.





Fig. 6. IPCE plots for the DSSCs based on the four dyes.

elucidate correlation of Voc with those dyes. The Nyquist plots of DSSCs with four dyes are shown in Fig. 8. Three semicircles are observed in the Nyquist plots. The small and large semicircles respectively located in the high- and middle-frequency regions, are assigned to the charge transfer at Pt/electrolyte and TiO₂/dye/ electrolyte interface, respectively [45-48]. Another small semicircle, which should have appeared at the low-frequency region, is overlapped by the middle-frequency large semicircle. The charge recombination resistance (R_{rec}) at the TiO₂ surface can be deduced by fitting curves from the range of the middle-frequency using a Z-view software. R_{rec} is related to the charge recombination rate between injected electron and electron acceptor (I_3^-) in the electrolyte, estimated by the large semicircle width. A large R_{rec} means the small charge recombination rate and vice versa. The R_{rec} values for HM and HO were estimated to be 133 and 115 ohm, respectively. In contrast, **HE** and **HT** were found to have relatively smaller R_{rec} values at 66 and 57 ohm, respectively. The result appears to be consistent with the larger V_{0c} values for the dyes **HM** (0.66 V) and



Fig. 7. The J-V characteristics for DSSCs based on the four dyes.

Table 4

Photovoltaic performance of DSSCs based on the four dyes.

Dye	$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}({ m V})$	FF	PCE (%)
HT	11.04	0.64	0.749	5.29
HM	10.20	0.66	0.698	4.70
HE	10.44	0.62	0.649	4.20
HO	12.69	0.65	0.707	5.83



Fig. 8. EIS Nyquist plots for DSSCs based on the four dyes measured in the dark under -0.65 V bias.

HO (0.65 V). The significantly increased R_{rec} values of **HM** and **HO** imply the retardation of the charge recombination between injected electron and I_3^- ions in the electrolyte, with a consequent increase of V_{oc} .

At the same time, DSSCs based on **HM** and **HO** produced higher V_{oc} than **HE** and **HT**, which can be explained by the electron lifetime. Fig. 9 shows the Bode plot for DSSCs based on these four dyes. Two peaks in Fig. 9 located at the high-frequency (right) and middle-frequency (left) respectively correspond to the small semicircle (left) and large semicircle (right) in the Nyquist plots



Fig. 9. EIS Bode plots for DSSCs based on the four dyes measured in the dark under $-0.65 \: V$ bias.

(Fig. 8). The reciprocal of the peak frequency for the middlefrequency peak is regarded as the electron lifetime since it represents the charge transfer process at the TiO₂/dye/electrolyte interface. It is evident that the electron lifetimes of the DSSCs based on **HM** and **HO** are larger than those based on **HE** and **HT**, thereby explaining the V_{0c} increase from **HM** and **HO** to **HE** and **HT**.

4. Conclusions

In summary, we have successfully designed and synthesized a series of novel $D-\pi$ -A hydrazone dyes (HT, HM, HE, and HO) with the same electron donor and acceptor groups and different π -conjugated thiophene bridges to apply in DSSCs. The influences of the various thiophene bridges on the photophysical, electrochemical, and photovoltaic properties of these hydrazone sensitizers were investigated. The results of calculation and experiments clearly demonstrate that photoelectrochemical properties can be regulated by introducing different π -conjugated thiophene bridges. Among the four synthesized dye molecules, hydrazone dye HO exhibits the maximum power conversion efficiency of 5.83%. Therefore, we have proved that N, N-diphenylhydrazone and 3,4-dialkyloxyl substituted thiophene units can be employed as the effective and promising donor and π -conjugated bridge, respectively in D- π -A dyes, which not only expands the selection scope of building blocks for further dye design but also provides a revelation to exploit highly efficient hydrazone sensitizers for DSSCs.

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