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Effects of aromatic π -conjugated bridges on optical and photovoltaic properties of *N*,*N*-diphenylhydrazone-based metal-free organic dyes

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ABSTRACT

A series of novel D- π -A hydrazone dyes (**HB**, **HP**, **HF** and **HT**) containing an N.N-diphenvlhydrazone donor and 2-cyanoacetic acid acceptor linked by a different aromatic bridge (benzene, pyrrole, furan, and thiophene) have been designed and synthesized to evaluate the aromatic bridge effects on the photophysical, electrochemical and the photovoltaic properties of the hydrazone-sensitized TiO₂ solar cells. Each of the hydrazone-based dyes exhibited different adsorption behavior, frontier molecular orbitals, and photovoltaic performance depending on the identity of aromatic π -conjugated bridges. Specifically, **HP**-sensitized TiO₂ solar cell showed an obviously higher photocurrent, photovoltage, and power conversion efficiency than other three dyes. We interpret that these results were stemmed from light-harvesting abilities, the charge recombination rate and electron lifetime of different aromatic bridges. Optical spectroscopy, cyclic voltammetry, density functional theory calculations, electrochemical impedance spectra, and photovoltaic measurements were employed to support our proposal. With the addition of 1 mM chenodeoxycholic acid (CDCA) as the coadsorbent, a maximum power conversion efficiency of a DSSC based on HP was 7.74% (J_{sc} = 16.17 mA/cm², V_{oc} = 0.69 V, FF = 0.694) under simulated AM 1.5 G solar irradiation (100 mW/cm²). This work suggests that N,N-diphenylhydrazone and N-(2-ethylhexyl) substituted pyrrole moieties can be used as an alternative and effective donor and π -conjugated bridge, respectively, in the construction of efficient D- π -A organic dyes.

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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) are a potentially lowcost alternative to conventional silicon photovoltaic devices [1]. The photoactive dyes play a crucial role for highly efficient DSSCs and they can be broadly classified into two separate classes: organometallic dyes which

* Corresponding author at: College of Chemistry and Key Laboratory of Advanced Functional Polymeric Materials, College of Hunan Province, Xiangtan University, Xiangtan 411105, PR China. include a transition metal in the structure and metal-free organic dyes. At present, the most efficient DSSCs are based on TiO₂/Ru-bipyridyl dye systems, with the highest power conversion efficiency (PCE) up to 11.7% being achieved with a ruthenium dye (C106) [2]. Compared with the traditional ruthenium dyes, metal-free organic dyes have many advantages such as lower cost, easier structural modification, and higher molar extinction coefficient. 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 compounds has been found to possess photoinduced intramolecular charge transfer (PICT) properties [3], which makes them as ideal



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dyes for DSSCs application. Using this strategy, many novel D– π –A metal-free dyes with various donor moieties, such as coumarin [4], indoline [5], triarylamine [6], [bis(dimethylfluorenyl)amino]phenyl [7], phenothiazine [8], tetrahydroquinoline [9], carbazole [10], porphyrin [11], dithieno[3,2-*b*:2',3'-*d*]thiophene [12], and pyrrole [13], have been designed and synthesized as efficient sensitizers for DSSCs in recent years. PCEs up to ~9% have been achieved for DSSCs using these metal-free dyes [4]. Moreover, highly impressive PCEs (~10%) and excellent stability were also reported in very recent publications [14]. Developing novel and highly efficient metal-free organic dyes applied in DSSCs is thus an area of strong current research activity [3].

The π -conjugated bridge connecting the donor and acceptor in the dye 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. Aromatic moiety is usually used as efficient bridge in the design of dye molecules. Thiophene-based aromatic compounds have been demonstrated as the effective π -conjugated bridges by several research groups [15], including ours [6g]. Imahori et al. [16] investigated the effects of 5-membered heteroaromatic bridges on structures of porphyrin films and photovoltaic properties of porphyrin-based DSSCs. Recently, Wang and co-workers [17] also studied the influence of different heteroaromatic bridges on photovoltaic properties of triphenylamine-based organic dyes.

Aromatic hydrazone compounds are widely studied and used as organic nonlinear optical materials [18] and organic hole-transport materials for electrophotographic photoreceptors [19]. The main advantages of such compounds are the simple synthesis and high enough charge mobilities [19b]. Many triphenylamine-[20], carbazole- [21] and thiophene-based hydrazone [22] compounds were synthesized and used as glassforming hole-transport materials. Squaraine-based compounds containing *N*,*N*-diphenylhydrazone moiety were synthesized and applied as efficient small molecule donors in bulk-heterojunction solar cells [23]. In addition, Tran-Van et al. recently reported on the synthesis and application of biscarbazole and terthiophene derivatives containing hydrazone functional groups as hole-transport materials in solid-state DSSCs [24]. 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 another try of our efforts to explore new metal-free dyes, we herein report on the design and synthesis of four D– π –A dyes (**HB**, **HP**, **HF**, and **HT**, as shown in Fig. 1) consisting of an *N*,*N*-diphenylhydrazone donor, a 2-cyanoacetic acid acceptor, and a different aromatic bridge, i.e., benzene, pyrrole, furan, and thiophene. The effects of the π -conjugated bridges on the photophysical, electrochemical and photovoltaic properties of these dyes were investigated in detail. To the best of our knowledge, this is the first time to develop hydrazones-based compounds as me-

tal-free organic dyes used in DSSCs. Once again, our results indicate that π -conjugated bridge would have a large impact on photoelectronic properties of the metal-free dyes sensitized TiO₂ cells.

2. Experimental

2.1. Materials and reagents

1,1-Diphenylhydrazine hydrochloride, terephthalaldehyde, 2-furaldehyde, 2-thienaldehyde, thiophene, pyrrole, and 2-ethylhexyl bromide were purchased from commercial suppliers (Pacific ChemSource and Alfa Aesar) in analytical grade. 2-Carbaldehyde-*N*-ethylhexyl-pyrrole was synthesized according to the previous published procedure [25]. Toluene 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. Characterization

¹H NMR spectra was recorded on a Bruker Avance 400 instrument. Ultraviolet-visible (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 were 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 [6a]. The solutions were purged with argon and stirred for 15 min before the measurements. Electrochemical impedance experiments for DSSCs were carried out in the dark with an electrochemical workstation (ZAHNER ZENNIUM) at room temperature. Electrochemical impedance spectra (EIS) were scanned in a frequency range of 10^{-1} –100 kHz with applied potential set at open-circuit. The alternate current (AC) amplitude was set at 10 mV. Geometry optimization and electronic structure calculations of the hydrazonebased dyes were performed using B3LYP functional and 3-21G* basis set implemented in the Gaussian 03 program package. Molecular orbitals were visualized by GaussView 3.0 software.



Fig. 1. Molecular structures of the dyes HB, HP, HF, and HT.

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 the literature procedure [4]. 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 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 CH₃CN solution with 0.5 mM dyes (and 1 mM chenodeoxycholic acid as a coadsorbent) 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 for photovoltaic 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 cm^2 . 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.

2.4. Synthesis

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

2.4.1. 4-Carbaldehyde-benzene-N,N-diphenylhydrazone (1)

Under nitrogen atmosphere, a solution of *N*,*N*-diphenylhydrazine hydrochloride (0.88 g, 4 mmol) in 30 mL of THF was added dropwise into the mixture of terephthalaldehyde (0.94 g, 7 mmol), sodium acetate (0.82 g, 10 mmol) and anhydrous MeOH (20 mL) at the room temperature. The mixture was refluxed for 24 h and the color changed gradually from yellow to dark brown. After cooling, the resulting mixture was guenched with 40 mL distilled water and extracted with chloroform. The combined organic laver 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 (5/1, v/v) as eluent to yield **1** as a yellow solid. Yield: 67% (0.85 g). FT-IR (KBr, cm^{-1}): 1667 ($v_{C=0}$). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.97 (s, 1H), 7.83–7.85 (d, 2H, J = 8.0 Hz), 7.73–7.75 (d, 2H, J = 8.0 Hz), 7.48-7.44 (m, 4H), 7.25-7.23 (m, 6H), 7.15 (s, 1H). Elem. Anal. Calcd. for C₂₀H₁₆N₂O: C, 79.98%; H, 5.37%; N, 9.33%. Found: C, 79.70%; H, 5.85%; N, 9.56%.

2.4.2. The general synthetic procedure of (2)

In a 100 mL three-necked flask, a solution of *N*-ethylhexylpyyrole-2-carbaldehyde (or 2-furaldehyde or 2-thien aldehyde, 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.

2.4.2.1. N-Ethylhexylpyrrole-2-carbaldehyde-N,N-diphenylhydrazone (**2a**). Yield: 76% (1.42 g). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.46–7.42 (m, 5H), 7.24–7.17 (m, 5H), 7.10 (s, 1H), 6.88 (s, 1H), 6.67–6.65 (m, 2H), 4.34 (d, 2H, J = 5.6 Hz), 1.31–1.01 (m, 9H), 0.85 (t, 3H, J = 7.3 Hz), 0.72 (t, 3H, J = 7.2 Hz). Elem. Anal. Calcd. for C₂₅H₃₁N₃: C, 80.39%; H, 8.37%; N, 11.25%. Found: C, 80.40%; H, 8.47%; N, 11.66%.



Scheme 1. Synthesis of the HB, HP, HF, and HT dyes.

2.4.2.2. Furan-2-carbaldehyde-N,N-diphenylhydrazone (**2b**). Yield: 70% (0.92 g). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.43–7.39 (m, 6H), 7.20–7.27 (m, 5H), 7.08 (s, 1H), 6.46–6.42 (m, 2H). Elem. Anal. Calcd. for C₁₇H₁₄N₂O: C, 77.84%; H, 5.38%; N, 10.68%. Found: C, 77.52%; H, 5.47%; N, 10.80%.

2.4.2.3. Thiophene-2-carbaldehyde-N,N-diphenylhydrazone (**2c**). Yield: 72% (1.0 g). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.44–7.42 (m, 4H), 7.31 (s, 1H), 7.27 (s, 1H), 7.22–7.20 (m, 6H), 7.97–7.93 (m, 2H). 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%.

2.4.3. The general synthetic procedure of (3)

In a 100 mL three-necked flask, compound **2** (2 mmol) and dried DMF (0.23 mL, 3 mmol) were dissolved into 1,2-dichloroethane (20 mL). After the solution was cooled to 0 °C, POCl₃ (0.27 mL, 3 mmol) was added dropwise. The mixture was stirred at room temperature for 0.5 h and then heated up to reflux for another 12 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 resulting mixture was washed with distilled water and brine, dried over anhydrous MgSO₄. Solvent was removed by rotary evaporation, and the crude product was purified by silica gel column chromatography with petroleum ether/dichloromethane (5/1, v/v) as eluent.

2.4.3.1. 5-Formyl-N-ethylhexypyrrolel-2-carbaldehyde-N,Ndiphenylhydrazone (**3a**). Yield: 83% (0.67 g). FT-IR (KBr, cm⁻¹): 1666 ($v_{C=0}$). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.45 (s, 1H), 7.46–7.42 (m, 5H), 7.24–7.17 (m, 5H), 7.09 (s, 1H), 6.90 (d, 1H, *J* = 4.1 Hz), 6.67 (d, 1H, *J* = 4.2 Hz), 4.33 (d, 2H, *J* = 5.8 Hz), 1.26–1.03 (m, 9H), 0.83 (t, 3H, *J* = 7.1 Hz), 0.70 (t, 3H, *J* = 7.4 Hz). Elem. Anal. Calcd. for $C_{26}H_{31}N_3O;$ C, 77.77%; H, 7.78%; N, 10.46%. Found: C, 77.40%; H, 7.97%; N, 10.66%.

2.4.3.2. 5-Formyl-furan-2-carbaldehyde-N,N-diphenylhydrazone(**3b**). Yield: 81% (0.39 g). FT-IR (KBr, cm⁻¹): 1665 ($\nu_{c=0}$). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.56 (s, 1H), 7.46–7.43 (m, 6H), 7.26–7.23 (m, 4H), 7.19 (d, 1H, *J* = 3.5 Hz), 7.07(s, 1H), 6.81 (d, 1H, *J* = 3.2 Hz). Elem. Anal. Calcd. for C₁₈H₁₄N₂O₂: C, 74.47%; H, 4.86%; N, 9.65%. Found: C, 74.32%; H, 4.77%; N, 9.80%.

2.4.3.3. 5-Formyl-thiophene-2-carbaldehyde-N,N-diphenylhydrazone (**3c**). Yield: 85% (0.52 g). FT-IR (KBr, cm⁻¹): 1668 ($v_{C=0}$). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.86 (s, 1H), 7.63 (d, 1H, *J* = 3.5 Hz), 7.62 (s, 1H), 7.48 (d, 1H, *J* = 3.5 Hz), 7.47–7.45 (m, 4H), 7.27–7.21 (m, 2H), 6.99– 6.98 (m, 4H). 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%.

2.4.4. The general synthetic procedure of sensitizers

Under nitrogen atmosphere, a mixture of compound **1** (or **3**, 1.2 mmol), 2-cyanoacetic acid (0.21 g, 2.4 mmol), piperidine (0.5 mL), and CH₃CN (30 mL) was refluxed at 80 °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 dyes.

2.4.4.1. 5-(2-Cyanoacrylicacid-3-yl)-benzene-2-carbalde-hyde-N, *N*-diphenylhydrazone (HB). Yield: 72% (0.32 g). FT-IR (KBr, cm⁻¹): 2227 ($v_{C=N}$), 1693 ($v_{C=O}$). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.27 (s, 1H), 7.85 (s, 1H), 7.76–7.55 (m, 4H), 7.30–7.26 (m, 6H), 7.24–7.19 (m, 4H). Elem. Anal. Calcd. for C₂₃H₁₇N₃O₂: C, 75.19%; H, 4.66%; N, 11.44%. Found: C, 75.30%; H, 4.97%; N, 11.60%.

2.4.4.2. 5-(2-Cyanoacrylicacid-3-yl)-N-ethylhexylpyrrole-2carbaldehyde-N,N-diphen-ylhydrazone (HP). Yield: 74% (0.42 g). FT-IR (KBr, cm⁻¹): 2210 ($v_{C=N}$), 1670 ($v_{C=0}$). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.04 (s, 1H), 7.84 (d, 1H, J = 4.5 Hz), 7.08 (s, 1H), 7.52–7.44 (m, 4H), 7.21–7.17 (m, 6H), 6.82 (d, 1H, J = 4.6 Hz), 4.05 (d, 2H, J = 7.4 Hz), 1.55–1.11 (m, 9H), 0.84 (t, 3H, J = 7.0 Hz), 0.75 (t, 3H, J = 7.3 Hz). Elem. Anal. Calcd. for C₂₉H₃₂N₄O₂: C, 74.33%; H, 4.88%; N, 11.96%. Found: C, 74.10%; H, 4.97%; N, 11.60%.

2.4.4.3. 5-(2-Cyanoacrylicacid-3-yl)-furan-2-carbaldehyde-N, N-diphenylhydrazone (HF). Yield: 72% (0.31 g). FT-IR (KBr, cm⁻¹): 2221 ($\nu_{C=N}$), 1685 ($\nu_{C=0}$). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.96 (s, 1H), 7.48–7.44 (m, 6H), 7.28–7.26 (m, 4H), 7.22 (d, 1H, *J* = 3.5 Hz), 7.03 (s, 1H), 6.82 (d, 1H, *J* = 3.5 Hz). Elem. Anal. Calcd. for C₂₁H₁₅N₃O₃: C, 70.58%; H, 4.43%; N, 11.76%. Found: C, 70.30%; H, 4.57%; N, 11.80%.

2.4.4.4. 5-(2-Cyanoacrylicacid-3-yl)-thiophene-2-carbalde-hy de-N,N-diphenylhydrazone (HT). Yield: 74% (0.33 g). FT-IR (KBr, cm⁻¹): 2213 ($v_{C=N}$), 1673 ($v_{C=O}$). ¹H NMR (400 MHz, DMSO- d_6): δ (ppm) 8.36 (s, 1H), 7.82 (d, 1H, J = 3.4 Hz), 7.52 (s, 1H), 7.50 (d, 1H, J = 3.5 Hz), 7.37–7.26 (m, 6H), 7.19–7.17 (m, 4H). 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 HB, HP, HF, and HT is outlined in Scheme 1. The three dyes HP, HF, and HT were synthesized by the similar stepwise synthetic protocol. Firstly, the five-membered heterocyclic aldehyde (2-furaldehyde, 2-thienaldehyde or 2-carbaldehyde-N-ethylhexyl-pyrrole) reacted with N,N-diphenylhydrazine hydrochloride to afford fivemembered heterocycle-based hydrazone 2a, 2b or 2c according to the previous reports [22,23] in high yields. Then Vilsmeier formylation of 2a, 2b and 2c afforded the key intermediates 3a, 3b and 3c with good yields (81-85%), respectively. Finally, Knoevenagel condensation reactions of aldehyde derivatives 3a, 3b or 3c with twofold excess of cyanoacetic acid afforded the target dyes HP, HF, or HT in acetonitrile using piperidine as catalyst. Compared to the former three dyes, the dye HT with the phenyl unit as the conjugated bridge was synthesized by a relatively simple procedure. N,N-Diphenylhydrazine hydrochloride was reacted with excess terephthalaldehyde to afford compound 1. Then 1 reacted with cyanoacetic acid by Knoevenagel condensation to give the dye HT. The structures of all dye molecules were characterized unambiguously with FT-IR, ¹H NMR spectroscopy and elemental analyze.

3.2. Optical properties

In DSSCs, sensitizer is a key and unique component with a function of light harvesting. Its spectral response overlapped with the solar emission will affect the device photocurrent to a large extent; thus, we measured the ultraviolet–visible (UV–vis) absorptions of the dyes **HB**, **HP**, **HF**, and **HT** both in THF solutions and on TiO_2 films (Fig. 2 and Fig. 3, respectively). The characteristic data are collected in Table 1.

All the dyes exhibit two distinct absorption bands (Fig. 2): one absorption band is in the UV region (280–350 nm) corresponding to the π - π * electron transitions of the conjugated molecules; and the other is in the visible region (380-550 nm) that can be assigned to an intramolecular charge transfer (ICT) between the N,Ndiphenylhydrazone donating unit and the cyanoacrylic acid acceptor moiety [26]. It can be seen that the maximum absorption (λ_{max}) of the visible region red-shifts from 425 nm to 452 nm, 465 nm, and 469 nm for HB, HF, HT and HP, respectively. This red-shifted phenomenon may be ascribed to the different aromatic ability of the three five-membered heteroaromatic bridges. The aromatic ability of furan is larger than that of thiophene and pyrrole due to the stronger electronegative of oxygen element than that of nitrogen and sulphur elements. We can see that the λ_{max} values in the visible region shift to a lower energy with the decreased electronegativity of heteroatoms, which is in accordance with results of Wang et al. [17].

As depicted in Table 1, the molar extinction coefficient (ε) of the ICT bands of the four dyes (15.9–24.6 × 10³ M⁻¹ cm⁻¹) are higher than that of the standard N719 sensitizer (14.2 × 10³ M⁻¹ cm⁻¹) [27], indicating a better ability of light harvesting of these new *N*,*N*-diphenylhydrazone-based metal-free organic dyes than that of classical organometallic dyes. Moreover, the ε of the ICT bands increases in the order of **HB** < **HT** < **HF** < **HP**, which suggests that **HP** should hold the best ability of light harvesting. The higher ε of the organic dyes allows a correspondingly thinner nanocrystalline film so as to avoid the decrease of the film mechanical strength. This also benefits the electrolyte diffusion in the film and reduces the recombination possibility of the light-induced charges during transportation [28].

When the dyes were attached on TiO_2 films, the absorption spectra may shift more or less as compared with that



Fig. 2. Absorption spectra of the four dyes in THF solutions $(10^{-5}\,\text{M})$ at 25 °C.



Fig. 3. Absorption spectra of the four dyes adsorbed on TiO₂ surface.

 Table 1

 Maximum absorption and emission data of the four dyes.

Dye	$\lambda_{\rm max}^{\rm a}$ (^c ϵ/M^{-1} cm	$\lambda_{\max}^{a} (c \epsilon/M^{-1} cm^{-1})$		
HB	425(15,900)	295(9300)	418	
HP	469(27,000)	310(5300)	457	
HF	452(24,600)	304(15,800)	437	
HT	465(18,300)	295(8500)	469	

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

^b Maximum absorption on TiO₂ films.

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

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 *I*-aggregation for the red shift. From Figs. 2 and 3 and Table 1, it can be seen that absorption spectra of the dyes HB, HP, and HF on TiO₂ films displayed broader and a blue shift of 7 nm, 12 nm, and 15 nm, respectively, compared to those in THF solutions due to H-aggregation. However, the absorption spectrum of **HT** on TiO₂ film red shifted (4 nm) slightly in comparison with that in solution, indicating the dye possesses the *I*-aggregation on semiconductor surface. Another noteworthy feature in the spectra of dyes adsorbed on TiO₂ surfaces is an apparent tailing toward longer wavelength region (Fig. 3). In solutions the low energy edge of absorption bands does not exceed 550 nm (Fig. 1), yet on TiO_2 the absorption threshold extends to 750 nm. The long wavelength absorption should be result from the formation of a certain degree of aggregates on the surface of TiO₂. The absorption of aggregates is responsible for the induction of photocurrent in the regions of ≥600 nm (Fig. 5).

3.3. Electrochemical properties

While a good light absorption is an essential requirement for photovoltaic cells, the following charge generation from the closely bound electron-hole pair (Frenkel exciton) confined in a single organic molecule [29] also determines device operation. This process is triggered at the interface between a donor component and an acceptor component (dye and titania in DSSC), featuring a favorite energy alignment, although a hot electron injection is also possible [30]. Here we measured the oxidation potential of the four dyes by means of cyclic voltammetry (CV) to evaluate the possibility of electron transfer from the excited dye molecule to the conductive band of TiO₂. CV was performed in CH₃CN with 0.1 M Bu₄NPF₆ as a supporting electrolyte (Fig. 4). Table 2 summarizes all the electrochemical properties of the four dyes.

The first oxidation potential vs. NHE (E_{ox}), which corresponds 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 first oxidation potentials of the four dyes HB, HP, HF, and HT were measured as 1.23, 1.15, 1.28, and 1.29 V, respectively. It is easy to see that the negative shifts of the E_{ox} (0.08, 0.13, and 0.14 V) were observed for HB, HF, and HT vs. HP, respectively, which means that HP has the lowest HOMO level among the four dyes. The decrease of HOMO levels of the dyes could show a positive effect on the DSSCs performance due to the narrower gap between the HOMO level and the redox potential of iodine/iodide leading to less waste of energy [17]. We also can see that all the HOMO levels of four dyes are more positive than the iodide/triiodide redox couple (\sim 0.42 V vs. NHE), indicating that the oxidized dyes formed after electron injection into the conduction band of TiO₂ could accept electrons from I⁻ ions in the electrolyte thermodynamically.

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 **HB**, **HP**, **HF**, and **HT** were -1.33, -1.36, -1.21, and -1.09 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 [4a], these driving



Fig. 4. 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	$E_{\rm gap}/V$
HB	485	2.56	1.23	-1.33	0.83
HP	495	2.51	1.15	-1.36	0.86
HF	498	2.49	1.28	-1.21	0.71
HT	520	2.38	1.29	-1.09	0.59

^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_{0x} 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 $E_{0x}-E_{0-0}$. E_{gap} is the energy gap between the E_{red} of we and the CB level of TiO₂ (-0.5 V vs. NHE).

forces are sufficiently large for effective electron injection. Therefore, the four dyes used as sensitizers will have sufficient driving force for electron transfer from the excited dye molecules to the CB of TiO₂ electrode. Noticeably, the relatively large E_{gap} of the dyes allow for the addition of the 4-tertbutylpyridine (TBP) into the electrolyte, which can shift the conduction band of TiO₂ negatively about 0.3 V and consequently improve the open-circuit voltage (V_{oc}) and total power energy conversion efficiency (PCE) [31]. The E_{gap} of the four dyes ranges from 0.59 (**HT**) to 0.86 eV (**HP**) (Table 2). Accordingly, an increased E_{gap} may yield higher V_{oc} and enhance the PCE considerably, which predicts the dye **HP** may give a higher V_{oc} and PCE.

These above-discussed results indicate that the introduction of aromatic cycles (benzene, pyrrole, furan and thiophene) in π -conjugated bridges could easily tune the absorption spectra and HOMO and LUMO energy levels of the dyes.

3.4. Molecular orbital calculations

In order 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 aromatic π -conjugated 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

DSSCs were fabricated using these dyes as the sensitizers, with an effective area of 0.196 cm^2 , TiO_2 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. 5 shows incident photonto-electron conversion efficiency (IPCE) as a function of the wavelength for the sandwiched DSSCs based on the four dves as sensitizers. As shown in Fig. 5, the IPCE of HP sensitizer exceeds 60% in the spectral region from 400 to 520 nm, reaching its maximum over 80% at 425 nm, while other three dyes produce maximum IPCE about 60%. The relatively higher maximum IPCE for HP compared with other three dyes is well in agreement with the tendency of UV-vis absorption properties. In comparison with HB and HF, HT exhibits a broader IPCE spectrum. These results imply that HP 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. 5. We believe that this feature should be ascribed two reasons: one is the weak absorption band of the dyes on TiO_2 films at the range of 650–750 nm (see Fig. 3), which is consistent with our and the other reports [32]; the other is the effect of light scattering by TiO₂ nanoparticles, which increases the photocurrents for the weak absorption in that region.

Fig. 6 shows current density-voltage (I-V) characteristics of devices based on the four dyes. The detailed photovoltaic parameters of the short-circuit photocurrent density (I_{sc}) , open-circuit photovoltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE) are listed in Table 4. According to Fig. 6, it is clear that the photovoltaic performances of the DSSCs can be evidently affected by the aromatic bridges in the dye molecules. The PCE increases in the order of HB (4.39%) < HF (4.66%) < HT (5.29%) < HP (7.18%). HP exhibits the best PCE due to both the highest J_{sc} (14.76 mA/cm²) and $V_{\rm oc}$ (0.69 V) values. Obviously, the tendency of a gradually increased PCEs for the four dyes with various aromatic bridges shows be along with the increase of J_{sc} . Consistent with the increased tendency of IPCE, the measured Jsc increases in the order of **HB** $(9.64 \text{ mA/cm}^2) < \text{HF} (10.62 \text{ mA}/cm^2)$ cm²) < HT (11.04 mA/cm²) < HP (14.76 mA/cm²). In view of the similar configuration and anchoring mode of the four sensitizers, we compare their ratios of molar extinction coefficients and the absorptivities of dye coated titania films, deducing that **HB** has a lower surface coverage than those of other three dyes. In addition, the remarkably increased J_{sc} value of **HP** compared with other three dyes can be ascribed to its relatively better light harvesting ability, reflecting in its better IPCE spectrum.

Generally, V_{oc} becomes low along with the decrease of aromatic ability of aromatic π -conjugated bridges. The improved V_{oc} value (0.69 V) of **HP** compared to other three dyes (0.61–0.67 V) could be attributed to the following two aspect reasons. One is that the additional hydrophobic alkyl chain of pyrrole bridge in **HP** can effectively retard the charge recombination between injected electron and I₃⁻ ions in the electrolyte, which is favorable for increasing the electron lifetimes and hence to improve V_{oc} [33a,6i,6h,11b]. We will discuss it in detail as the following electrochemical impedance spectroscopy studies. The other reason can be attributed to the comparatively lower-lying HOMO of the **HP** (estimated from the CV), which offers enough larger driving force for the reduction of the oxidized dye. This, in turn, will lead to a slower back



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



electron transfer from TiO_2 to the dye and result in a lager V_{oc} value [33b].

It has been reported that chenodeoxycholic acid (CDCA) can enhance the performance of the DSSCs because CDCA can reduce the aggregation of the dyes on the TiO₂ surface [6g,8b,9a,34]. To investigate the influence of aggregation of dyes on the photovoltaic performance, CDCA was added into the dye solution as a coadsorbent and the relative photovoltaic data are also collected in Table 4. As shown in Table 4, after the addition of CDCA (1 mM) to the dye bath, PCEs of DSSCs based on the four dyes are increased by 16%, 8%, 19%, and 10% for **HB**, **HP**, **HF**, and **HT** respectively,

which results from the significant improvement of J_{sc} values. The obviously improved PCEs of **HB** (5.11%) and **HF** (5.54%) indicate that CDCA plays a important role in suppressing the aggregation conformation of dyes on TiO₂ surface. In the case of **HP** (7.74%), the relatively little increase implies that the CDCA has a slight impact on the aggregation the dye, which can be ascribe to effectively inhibiting aggregation of alkyl group to pyrrole unit [6g,10a,33a]. The above photovoltaic results indicate strongly that coadsorption of CDCA is effective to improve solar cell performance by suppressing the aggregation conformation of dyes on TiO₂ surface.



Fig. 5. IPCE plots for the DSSCs based on the four dyes.



Fig. 6. The J-V characteristics for DSSCs based on the four dyes.

Table 4Photovoltaic performance of DSSCs based on the four dyes.

Dye	$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}$ (V)	FF	PCE (%)
HB ^a	9.64	0.67	0.680	4.39
HB ^b	11.35	0.66	0.682	5.11
HP ^a	14.76	0.69	0.705	7.18
HP ^b	16.17	0.69	0.694	7.74
HF ^a	10.62	0.61	0.719	4.66
HF ^b	12.78	0.62	0.699	5.54
HT ^a	11.04	0.64	0.749	5.29
НТ ^ь	12.69	0.65	0.707	5.83

^a Dye bath: CH_3CN solution (0.5 mM).

 b Dye bath: CH₃CN solution (0.5 mM) with addition of CDCA (1 mM). For all cells, the double-layer TiO₂ films are composed of ${\sim}14\,\mu m$ transparent layer and ${\sim}5\,\mu m$ scatter layer.

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 elucidate correlation of $V_{\rm oc}$ with those dyes. The Nyquist plots of DSSCs with four dyes are shown in



Fig. 7. EIS Nyquist plots for DSSCs based on the four dyes measured in the dark under -0.65 V bias.



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

Fig. 7. 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 [33]. 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. $R_{\rm rec}$ 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 $R_{\rm rec}$ means the small charge recombination rate and vice versa. The $R_{\rm rec}$ values for HP and **HB** were estimated to be 186 and 97 Ω , respectively. In contrast, HF and HT were found to have relatively smaller $R_{\rm rec}$ values at 84 and 57 Ω , respectively. The result appears to be consistent with the larger $V_{\rm oc}$ values for the dyes HP (0.69 V) and **HB** (0.67 V). The significantly increased R_{rec} values of HP and HB imply the retardation of the charge recombination between injected electron and I_3^- ions in the electrolyte, with a consequent increase of $V_{\rm oc}$.

At the same time, DSSCs based on **HP** and **HB** produced higher V_{oc} than **HF** and **HT**, which can be explained by the

electron lifetime. Fig. 8 shows the Bode plot for DSSCs based on **HB**, **HP**, **HF**, and **HT**. Two peaks in Fig. 8 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. 7). The reciprocal of the peak frequency for the middle-frequency peak is regarded as the electron lifetime since it represents the charge transfer process at the $TiO_2/dye/electrolyte$ interface. It is evident that the electron lifetime for the DSSC based on **HT** and **HF** is smaller than those for DSSCs based on **HT** and **HF** to **HP** and **HB**.

4. Conclusions

In summary, we have designed and synthesized a series of novel hydrazone-based D- π -A dyes (**HB**, **HP**, **HF**, and **HT**), by employing different aromatic π -conjugated bridges such as benzene, pyrrole, furan, and thiophene in combination with the hydrophobic N,N-diphenylhydrazone donor and the hydrophilic cyanoacrylic acid acceptor. The effects of the aromatic π -conjugated bridges on the photophysical, electrochemical and photovoltaic properties of these dyes were extensively investigated. It was found that the absorption spectra and HOMO and LUMO energy levels can be conveniently tuned by alternating the aromatic bridges. Molecular orbital calculations showed that the HOMO-LUMO excitation could readily move the electron distribution from the N,N-diphenylhydrazone donor to the cyanoacrylic acid acceptor via aromatic π -conjugated bridges. We have also studied the influence of aromatic bridges on photovoltages through the electrochemical impedance experiments and achieved a preliminary conclusion that the high $V_{\rm oc}$ of HP based DSSC resulted from the relatively small charge recombination rate and long electron lifetime due to the additional hydrophobic alkyl chain of pyrrole bridge. DSSCs based on these dyes have achieved 5.11-7.74% PCEs when CDCA (1 mM) was added into the dye bath as a coadsorbent. For the first time we have proved that N.N-diphenylhydrazone and N-(2-ethylhexyl)-substituted pyrrole units can be employed as the effective and promising donor and π -conjugated bridge, respectively in D- π -A dyes, which expands the selection scope of building blocks for further dye design. Further structural modification of the π -conjugated bridge based on the series sensitizers to improve the photovoltaic performance is just ongoing.

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References

- [1] M. Grätzel, Nature 414 (2001) 338.
- [2] Q. Yu, Y. Wang, Z. Yi, N. Zu, J. Zhang, M. Zhang, P. Wang, ACS Nano 4 (2010) 6032.
- [3] Y. Ooyama, Y. Harima, Eur. J. Org. Chem. (2009) 2903;
 (b) A. Mishra, M.K.R. Fischer, P. Büerle, Angew. Chem. Int. Ed. 48 (2009) 2474;

- (c) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chem. Rev. 110 (2010) 6595.
- [4] (a) K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, J. Phys. Chem. B 107 (2003) 597;
 (b) Z. Wang, Y. Cui, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, Adv.

(c) Z. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo, K. Hara, J.

Phys. Chem. C 111 (2007) 7224.

[5] (a) S. Ito, M. Zakeeruddin, R. Hummphrey-Baker, P. Liska, R. Charvet, P. Comte, M.K. Nazeeruddin, P. Péchy, M. Takata, H. Miura, S. Uchida, M. Grätzel, Adv. Mater. 18 (2006) 1202; S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P.

Pechy, M. Grätzel, Chem. Commun. (2008) 5194.

 [6] (a) D.P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt, L. Sun, Chem. Commun. (2006) 2245;
 (b) S. Hwang, J.H. Lee, C. Park, H. Lee, C. Kim, C. Park, M.H. Lee, W.

Lee, J. Park, K. Kim, N.G. Park, C. Kim, Chem. Commun. (2007) 4887;

(c) D.P. Hagberg, T. Marinado, K.M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt, L. Sun, J. Org. Chem. 72 (2007) 9550;

(d) W. Xu, B. Peng, J. Chen, M. Liang, F. Cai, J. Phys. Chem. C 112 (2008) 874;

(e) G. Zhang, Y. Bai, R. Li, D. Shi, S. Wenger, S.M. Zakeeruddin, M. Grätzel, P. Wang, Energy Environ. Sci. 2 (2009) 92;

(f) L.-Y. Lin, C.-H. Tsai, K.-T. Wong, T.-W. Huang, L. Hsieh, S.-H. Liu, H.-W. Lin, C.-C. Wu, S.-H. Chou, S.-H. Chen, A.-I. Tsai, J. Org. Chem. 75 (2010) 4778;

(g) P. Shen, Y. Liu, X. Huang, B. Zhao, N. Xiang, J. Fei, L. Liu, X. Wang, S. Tan, Dyes Pigm. 83 (2009) 187;

(h) H. Chen, H. Huang, X. Huang, John N. Clifford, A. Forneli, E. Palomares, X. Zheng, L. Zheng, X. Wang, P. Shen, B. Zhao, S. Tan, J. Phys. Chem. C 114 (2010) 3280;

(i) W. Zhu, Y. Wu, S. Wang, W. Li, X. Li, J. Chen, Z. S Wang, H. Tian, Adv. Funct. Mater. 21 (2011) 756.

[7] (a) S. Kim, J.K. Lee, S.O. Kang, J. Ko, J.H. Yum, S. Fantacci, F. DeAngelis, D. Dicenso, M.K. Nazeeruddin, M. Grätzel, J. Am. Chem. Soc. 128 (2006) 16701;

(c) I. Jung, J.K. Lee, K.H. Song, K. Song, S.O. Kang, J. Ko, J. Org. Chem. 72 (2007) 3652;

H. Choi, J.K. Lee, K. Song, S.O. Kang, J. Ko, Tetrahedron 63 (2007) 3115;

- (d) H. Choi, C. Baik, S.O. Kang, J. Ko, M.S. Kang, M.K. Nazeeruddin, M. Grätzel, Angew. Chem. Int. Ed. 47 (2008) 327.
- [8] (a) H.N. Tian, X.C. Yang, R.K. Chen, Y.Z. Pan, L. Li, A. Hagfeldt, L. Sun, Chem. Commun. (2007) 3741;

(b) D. Cao, J. Peng, Y. Hong, X. Fang, L. Wang, H. Meier, Org. Lett. 13 (2011) 1610.

 [9] (a) R. Chen, X. Yang, H. Tian, X. Wang, A. Hagfeldt, L. Sun, Chem. Mater. 19 (2007) 4007;
 (b) D. Cheng, Y. Yang, H. Fing, L. Sun, L. Bhattachan, Dhattachial, A. Chang, M. Stark, J. Sun, J. Bhattachang, Bhattachial, A. Chang, J. Sun, J. Bhattachang, Bhattachial, A. Chang, J. Sun, J. Sun,

(b) R. Chen, X. Yang, H. Tian, L. Sun, J. Photochem. Photobiol. A Chem. 189 (2007) 295.

[10] (a) N. Koumura, Z.S. Wang, S. Mori, M. Miyashita, E. Suzuki, K. Hara, J. Am. Chem. Soc. 128 (2006) 14256;

[b] D. Kim, J.K. Lee, S.O. Kang, J. Ko, Tetrahedron 63 (2007) 1913;

(c) C. Zafer, B. Gultekin, C. Ozsoy, C. Tozlu, B. Aydin, S. Icli, Sol. Energ. Mater. Sol. Cells 94 (2010) 655.

[11] (a) S.-L. Wu, H.-P. Lu, H.-Ti.Yu, S.-H. Chuang, C.-L. Chiu, C.-W. Lee, E.W.-G. Diau, C.-Y. Yeh, Energy Environ. Sci. 3 (2010) 949;
(b) Y. Liu, N. Xiang, X. Feng, P. Shen, W. Zhou, C. Weng, B. Zhao, S. Tan, Chem. Commun. (2009) 2499;
(c) C.-P. Hsieh, H.-P. Lu, C.-L. Chiu, C.-W. Lee, S.-H. Chuang, C.-L. Mai, W.-N. Yen, S.-J. Hsu, Eric W.-G. Diau, C.-Y. Yeh, J. Mater. Chem. 20 (2010) 1127;
(d) T. Bessho, S.M. Zakeeruddin, C.-Y. Yeh, Eric W.-G. Diau, M.

Grätzel, Angew. Chem. Int. Ed. 49 (2010) 6646.

- [12] H.-Y. Yang, Y.-S. Yen, Y.-C. Hsu, H.-H. Chou, J.T. Lin, Org. Lett. 12 (2010) 16.
- [13] (a) Y.-S. Yen, Y.-C. Hsu, J.T. Lin, C.W. Chang, C.-P. Hsu, D. Yin, J. Phys. Chem. C 112 (2008) 12557;
 (b) J.A. Mikroyannidis, M.S. Roy, G.D. Sharma, J. Power Sources 19
- (2010) 5391.
 [14] (a) G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu, P. Wang, Chem. Commun. (2009) 2198;
 (D) W. Taren G. Bei, Y. Wang, Y. Chi, M. Zhang, C. Bag, C.

(b) W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan, P. Wang, Chem. Mater. 22 (2010) 1915.

[15] (a) W.-H. Liu, I.-C. Wu, C.-H. Lai, P.-T. Chou, Y.-T. Li, C.-L. Chen, Y.-Y. Hsu, Y. Chi, Chem. Commun. (2008) 5152; (b) H. Qin, S. Wenger, M. Xu, F. Gao, X. Jing, P. Wang, S.M. Zakeeruddin, M. Grätzel, J. Am. Chem. Soc. 130 (2008) 9202;
(c) M. Xu, S. Wenger, H. Bala, D. Shi, R. Li, Y. Zhou, S.M. Zakeeruddin,

- M. Grätzel, P. Wang, J. Phys. Chem. C 113 (2009) 2966. [16] S. Eu, S. Hayashi, T. Umeyama, A. Oguro, M. Kawasaki, N. Kadota, Y.
- Matano, H. Imahori, J. Phys. Chem. C 111 (2007) 3528. [17] R. Li, X. Lv, D. Shi, D. Zhou, Y. Cheng, G. Zhang, P. Wang, J. Phys. Chem.
- C 113 (2009) 7469. [18] O.-P. Kwon, M. Jazbinsek, H. Yun, I.-I. Seo, E.-M. Kim, Y.-S. Lee, P.
- Günter, Cryst. Growth Des. 8 (2008) 4021. [19] (a) V. Getautis, M. Daskeviciene, T. Malinauskas, V. Gaidelis, V.
- Jankauskas, Z. Tokarski, Synth. Met. 155 (2005) 599;
 (b) J.V. Grazulevicius, Polym. Adv. Technol. 17 (2006) 694;
 (c) R. Lygaitis, V. Getautis, J.V. Grazulevicius, Chem. Soc. Rev. 3 (2008) 770.
- [20] R. Budreckiene, G. Buika, J.V. Grazulevicius, V. Jankauskas, Z. Tokarski, Synth. Met. 156 (2006) 677.
- [21] (a) G. Bubnienea, T. Malinauskasa, A. Stanisauskaitea, V. Jankauskasb, V. Getautis, Synth. Met. 159 (2009) 1695;
 (b) A. Michaleviciute, J. Ostrauskaite, G. Buika, R. Lygaitis, J.V. Gražulevičius, V. Jankauskas, Synth. Met. 159 (2009) 218.
- [22] (a) R. Lygaitis, J.V. Gražulevičius, F. Tran Van, C. Chevrot, V. Jankauskas, D. Jankunaite, J. Photochem. Photobiol. A: Chem. 181 (2006) 67;
 - (b) A. Michalevičiutė, R. Lygaitis, J.V. Gražulevičius, G. Buika, V. Jankauskas, A. Undzėnas, E. Fataraitė, Synth. Met. 159 (2009) 223.
- [23] F. Silvestri, M.D. Irwin, L. Beverina, A. Facchetti, G.A. Pagani, T. Marks, J. Am. Chem. Soc. 130 (2008) 1764.
- [24] R. Aich, F. Tran-Van, F. Goubard, L. Beouch, A. Michaleviciute, J.V. Gražulevičius, B. Ratier, C. Chevrot, Thin Solid Films 516 (2008) 7260.
- [25] D.X. Liu, B. Zhao, P. Shen, H. Huang, L.M. Liu, S.T. Tan, Sci. China Ser. B-Chem. 52 (2009) 1198.

- [26] S. Roquet, A. Cravino, P. Leriche, O. Alévêque, P. Frère, J. Roncali, J. Am. Chem. Soc. 128 (2006) 3459.
- [27] P. Wang, B. Wenger, R. Humphry-Baker, J.-E. Moser, J. Teuscher, W. Kantlehner, J. Mezger, E.V. Stoyanov, S.M. Zakeeruddin, M. Grätzel, J. Am. Chem. Soc. 127 (2005) 6850.
- [28] (a) A.C. Khazraji, S. Hotchandani, S. Das, P.V. Kamat, J. Phys. Chem. B 103 (1999) 4693;
 (b) K. Sayama, K. Hara, N. Mori, M. Satsuki, S. Suga, S. Tsukagoshi, Y. Abe, H. Sugihara, H. Arakawa, Chem. Commun. (2000) 1173.
- [29] M. Pope, C.E. Swenberg, Electronic Processes in Organic Crystals and Polymers, 2nd ed., Oxford University Press, Oxford, 1999.
- [30] (a) R.T. Ross, A.J. Nozik, J. Appl. Phys. 53 (1982) 3813;
 (b) S. Ardo, G.J. Meyer, Chem. Soc. Rev. 38 (2009) 115.
- [31] K. Hara, T. Sato, R. Katoh, A. Furube, T. Yoshihara, M. Murai, M. Kurashige, S. Ito, A. Shinpo, S. Suga, H. Arakawa, Adv. Funct. Mater. 15 (2005) 246.
- [32] (a) P. Shen, Y. Tang, S. Jiang, H. Chen, X. Zheng, X. Wang, B. Zhao, S. Tan, Org. Electron. 12 (2011) 125;
- (b) Y.J. Chang, T.J. Chow, Tetrahedron 65 (2009) 9626.
 [33] (a) Z. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube, K. Hara, Chem. Mater. 20 (2008) 3993;
 (b) K.R.J. Thomas, Y.-C. Hsu, J.T. Lin, K.-M. Lee, K.-C. Ho, C.-H. Lai, Y.-M. Cheng, P.-T. Chou, Chem. Mater. 20 (2008) 1830;
 (c) C. Longo, A.F. Nogueira, M.-A. De Paoli, H. Cachet, J. Phys. Chem. B 106 (2002) 5925;
 (d) R. Kern, R. Sastrawan, J. Ferber, R. Stangl, J. Luther, Electrochim. Acta 47 (2002) 4213;
 (e) F. Fabregat-Santiago, G. Garcia-Belmonte, I. Mora-Seró, J.
 - Bisquert, Phys. Chem. Chem. Phys. 13 (2011) 9083.
- [34] W. Xu, J. Pei, J. Shi, S. Peng, J. Chen, J. Power Sources 183 (2008) 792.