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Influence of the terminal electron donor in D–D– π –A phenothiazine dyes for dye-sensitized solar cells



PIGMENTS

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ABSTRACT

We report three new molecularly engineered push–pull dyes based on phenothiazine (PTZ) as a π conjugating linker and arylamine moiety as donor and compared with a simple phenothiazine derived reference dye. Absorption spectra, electrochemical cyclic voltammetry, theoretical calculations, current –voltage curves and electrochemical impedance spectroscopy were performed to understand the terminal electron donor influence on the performance of D–D– π –A PTZ dyes. Among these four dyes, the dye incorporating a 9-hexyl-9H-carbazole shows the best photovoltaic performance: a short-circuit photocurrent density of 14.02 mA cm⁻², an open-circuit photovoltage of 748 mV, and a fill factor of 0.68, corresponding to an overall conversion efficiency of 7.13% under standard global AM 1.5 solar light conditions.

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1. Introduction

Significant attention has been attracted by dye-sensitized solar cells (DSSCs) as alternatives to traditional solar cells, owing to their low-cost fabrication combined with high photovoltaic performance [1]. Upon irradiation, light is absorbed by the sensitizer, which results in electron injection from the photoexcited dye into the conduction band of the semiconductor. Studies have demonstrated that the performance of DSSCs strongly depends on the nature of sensitizer(s). DSSCs based on ruthenium sensitizers have reached overall solar-to-electric power-conversion efficiency (PCE) of 11.4% under standard air mass 1.5 G illumination. At the same time, the research activity has increased in the design and synthesis of metal-free organic dyes because of their lower cost, high molar extinction coefficients and good flexibility of molecular tailoring [2–33].

In general, organic sensitizers are constituted with the donor– π –acceptor (D– π –A) configuration. This push–pull structure can induce an efficient intramolecular charge transfer (ICT) from the donor to the acceptor. Based on this strategy, a series of arylamine electron donors have been employed to develop highly efficient organic dyes. Phenothiazine (PTZ) exhibits a well-known

electron donor effect due to its electron-rich sulfur and nitrogen heteroatoms. Furthermore, the phenothiazine ring is non-planar with a butterfly conformation in the ground state, which can impede the molecular aggregation and the formation of intermolecular excimers. The features make the PTZ-based dyes promising candidates for high efficiency DSSCs [34–49].

Originally, Yang, Hagfeldt, Sun and co-workers have synthesized a series of PTZ dyes for DSSCs. A prominent solar energy-toelectricity conversion efficiency of 5.5% was achieved in a DSC based on T2-1 dye which is simple in structure and easy to synthesize [34]. To extend the range of π -electron delocalization and increase the molar absorptivity of the PTZ dyes, π -linkers such as thiophene derivates was introduced in PTZ dyes. However, it is worth noticing that in contrast to the triphenylamine dyes, the increasing conjugation length of the PTZ dyes decreases the performance of DSSCs [3,35,36]. On the other hand, rational design of the terminal electron donor has very recently led to consecutive efficiency progress of DSSCs based on PTZ organic photosensitizers with D–D– π –A structure [36,37]. For example, Hua et al. developed a series of PTZ dyes their structure features of (4-hexyloxy) phenyl donor moiety at the C(7) position of phenothiazine, which extends the π -conjugation of the chromophore, therefore enhancing the performance of DSSCs [37]. This molecular design strategy was demonstrated to effectively improve the photovoltaic performance with the best PCE up to 8.18%, under simulated AM



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Fig. 1. Chemical structures of WR7, WR8, WR9, WR10 and T2-1.

1.5G irradiation. These results highlight the great potential of $D-D-\pi-A$ PTZ arylamine dyes for high efficiency DSSCs.

To design more powerful D–D– π –A PTZ dyes, it is of great significance to understand the influences of the terminal electron donors on the light-harvesting, electrochemical, interfacial kinetic parameters, as well as their joint contribution to the photovoltaic performance. Herein, we employ three PTZ dyes (WR8, WR9 and WR10, see Fig. 1) based on different arylamine electron donors, i.e., 9-hexyl-9*H*-carbazole (HCBZ), bis(4-(2-phenylpropan-2-yl)phenyl) amine (BPPA) and *N*-phenyl-9,9-dipropyl-*N*-(9,9-dipropyl-9*H*-fluoren-2-yl)-9*H*-fluoren-2-amine (DPFA), to investigate the electron donor influence on photovoltaic performance. For comparison the simple, amine donor free dye, WR7 with the D– π –A structure was prepared as a reference [34]. Our work provides a new insight into the terminal electron donor related structure–property relationship of PTZ dyes for DSSCs.

2. Results and discussion

2.1. Design and synthesis

Carbazole and its derivatives have been widely used as a functional building block in the fabrication of the organic photoconductors, nonlinear optical materials, and photorefractive materials due to their specific optical and electrochemical properties [50]. The excellent photoelectric function of the carbazole unit makes it a promising type of terminal electron donor for PTZ dyes. On the other hand, aiming to tune both the electronic trait and packing mode of dye molecules chemisorbed on titania nanocrystals of DSSCs, BPPA and DPFA have been incorporated to the terminal electron donor in WR9 and WR10, respectively.

The synthetic procedure to WR8, WR9 and WR10 is depicted in Scheme 1. Starting from 7-bromo-10-hexyl-10H-phenothiazine-3-carbaldehyde, the terminal electron donor was introduced by a transition metal-mediated coupling reaction, yielding the aldehyde precursors **3**, **5** and **7**. Finally, the conventional Knoevenagel condensation yielded the dyes WR8, WR9 and WR10 with cyano-acetic acid in the presence of piperidine.

2.2. Absorption spectra

UV/Vis absorption spectra of the resulting dyes in a diluted solution of CH₂Cl₂ are shown in Fig. 2 and the corresponding photophysical data are summarized in Table 1. The maximum absorption peaks for WR7, WR8, WR9 and WR10 are 453, 470, 478 and 464 nm, respectively. Compared with WR7, the λ_{max} of WR8, WR9 and WR10 is red-shifted by 17, 25 and 11 nm, respectively. Moreover, WR8-WR10 exhibited higher molar extinction coefficients than that of WR7. Obviously, the introduction of a terminal donor extends the π -conjugation of the chromophore, and therefore red-shifts the maximum absorption peak and enhances molar extinction coefficient. Scrutinizing the dyes with different



Scheme 1. Synthetic route for WR8, WR9 and WR10.



Fig. 2. Absorption spectra of the dyes in dichloromethane.

terminal donors, it is apparent that the molar extinction coefficient of WR10 is lower than those of the WR8 and WR9. This may be caused by the different electronic coupling parallel to the electronic transition dipole moment between the HOMO and LUMO (see computational analysis).

Fig. 3 displays the absorption spectra of the dyes anchored on transparent mesoporous titania film (3 µm). Note that, the absorption of WR9 sensitized film was found to be lower than that of the WR8 and WR10, despite the fact WR9 possesses the highest maximum molar absorption coefficient in solution. This observation indicates that incorporation of BPPA unit may reduce the WR9 loading amount significantly. The validity of this deduction was confirmed by comparing the amounts of the dyes adsorbed on the TiO₂ surface (12 µm, the thickness employed to devices). The dye load amount was evaluated by desorbing the dyes with a 0.01 M solution of KOH in methanol, and the dye loading amount was estimated to be 1.8 \times 10⁻⁷, 1.7 \times 10⁻⁷, 1.1 \times 10⁻⁷ and $1.5 \times 10^{-7} \mbox{ mol cm}^{-2}$ for WR7, WR8, WR9 and WR10, respectively. Apparently, loading amount of WR9 is quite limited by its 3D structure of BPPA unit. By contrast, WR8 adopts dense packing on the nanoparticle surface, which can be attributed to its small terminal electron donor, HCBZ.

2.3. Electrochemical properties

The redox potentials of WR7-WR10 dyes, measured by cyclic voltammetry (CV) are shown in Fig. 4 and the values are presented in Table 1. The first oxidation potential ($E_{D/D+}$), corresponding to the HOMO level of dyes, decrease in the order of WR7 (1.01 V) > WR10 (1.00 V) > WR8 (0.88 V) > WR9 (0.82 V). Attaching the terminal donor significantly extends the π -conjugation of the donor in WR8–WR10, which raises the HOMO energy and facilitates their oxidation. As a consequence, WR8–WR10 exhibit relative lower oxidation potentials as compared to the reference dye WR7. It is

Table 1	
Photophysical and electrochemical data for dyes.	

Dye	$\lambda_{\max}^{a}/nm \ (\epsilon/M^{-1} \ cm^{-1})$	E_{0-0}/eV	$E_{D/D+}^{b}/V$	$E_{D^*/D^+}^c/V$
WR7	453 (16,500)	2.29	1.01	-1.28
WR8	470 (23,200)	2.24	0.88	-1.36
WR9	478 (25,800)	2.28	0.82	-1.46
WR10	464 (17,600)	2.36	1.00	-1.36

^a The absorption spectra were measured in CH₂Cl₂ solutions.

^b The $E_{D/D+}$ (vs NHE) were measured in acetonitrile.

^c E_{D^*/D^+} were estimated from calculated from $E_{D^*/D^+} = E_{ox} - E_{0-0}$.



Fig. 3. Absorption spectra of sensitized electrodes (3 µm film).

also valuable to note that the WR9 possesses the smallest $E_{D/D+}$ of 0.82 V relative to other dyes, demonstrating the stronger electrondonating ability of the BPPA donor.

As shown in above, the HOMO levels of these dyes are more positive than I^-/I_3^- redox couples (0.4 V vs NHE [2]), indicating the driving forces for dye regeneration are sufficient for the iodine cells. On the other hand, the excited-state potential (E_{D^*/D^+}), reflecting the LUMO level of the dye, can be derived from the ground-state oxidation potential and the zero-zero excitation energy (E_{0-0}). The LUMO levels of these dyes are much more negative than the conduction band (CB) of the TiO₂ level (-0.5 V vs NHE [2]), ensuring an efficient electron injection process from the excited state of the dyes into the TiO₂ electrode.

2.4. Computational analysis

To gain further insight into the molecular structures of the PTZ dyes, density functional theory (DFT) calculations were performed and the resulting geometries are shown in Fig. 5. From the side view of the PTZ dyes (Fig. 5(a)), the geometry of phenothiazine is found to present a butterfly shape, endowing the PTZ dyes with reduced the dye-aggregation and attenuated internal charge recombination rate in DSSCs [37]. Note that, WR9 is more bulky than WR8/WR10 regarding their side view, which makes the whole molecule occupy a larger surface area than a molecule of linear



Fig. 4. CV lines of dyes sensitized electrodes.



Fig. 5. (a) The side view of the PTZ dyes; (b) B3LYP/6-31G molecular geometries of dyes as resulted from DFT calculations.

shape, therefore leading to the reduction of loading capacity. Furthermore, the terminal electron donor alteration from HCBZ/ DPFA to BPPA results in a decreased distance between the triarylamine nitrogen and the carboxylic acid of the anchoring group (Fig. 5(b)). The distance for WR8/WR10 is about 15.46 Å, while that for WR9 is only 12.17 Å. This may render back-electron transfer in WR9 based DSSCs owing to a closer contacts to the TiO₂ surface [32].

To clarify the terminal donor-correlated absorption and electrochemical properties in these dyes, time-dependent DFT (TDDFT) excited state calculations at the B3LYP/6-31G level in vacuo with the B3LYP/6-31G optimized ground-state geometries were performed. The charge distribution in the frontier molecular orbitals can be depicted in Fig. 6. WR8–WR10 exhibit a typical donor–acceptor-type architecture with the HOMO concentrated on the terminal electron donor or the PTZ unit, and the LUMO on the electron accepting cyanoacrylic acid anchor. Thus, the electrons of could be successively transferred to acceptor part and then injected into the conduction band of TiO₂ after being illuminated by the light.

Computed excitation energies, oscillator strength (f) and transition assignment of the lowest excited state for the PTZ dyes in vacuo are summarized in Table 2. The results have shown that the absorption characteristics and excited state features will mainly be dominated by charge transfer transitions from the HOMO to LUMO and HOMO-1 to LUMO. In spectroscopy, oscillator strength (f) is a dimensionless quantity that expresses the probability of absorption or emission of electromagnetic radiation in transitions between energy levels of an atom or molecule. The oscillator strength of excited state 1 for WR8, WR9 and WR10 are calculated to be 0.24,



Fig. 6. Computed frontier orbitals of WR8, WR9 and WR10.

Table 2
Computed excitation energies, oscillator strength (f) and transition assignment of
the lowest excited state for the PTZ Dyes in vacuo.

Dyes	Excited state	Calculated energy (eV, nm)	Oscillator strength (<i>f</i>)	Transition assignment ^a
WR8	1	2.35, 525	0.24	$\mathrm{H} \rightarrow \mathrm{L}(91.6\%)$
	2	2.79, 444	0.10	$H-1 \rightarrow L(88.4\%)$
WR9	1	2.09, 591	0.18	$H \rightarrow L (94.1\%)$
	2	2.84, 436	0.17	$H-1 \rightarrow L(86.0\%)$
WR10	1	1.94, 639	0.06	$H \rightarrow L (99.0\%)$
	2	2.58, 479	0.32	$\text{H-1} \rightarrow \text{L} (95.2\%)$

^a H means HOMO, and L means LUMO.

0.18 and 0.06, respectively. Note here that the oscillator strength for WR10 is much lower than that of WR8/WR9, indicating the probability of the corresponding absorption (HOMO to LUMO) is very low. This may be caused by the different electronic coupling parallel to the electronic transition dipole moment between the HOMO and LUMO. For the WR8 and WR9 dyes HOMO and LUMO have the overlapping extension on the PTZ fragment, while the corresponding overlap is markedly reduced in WR10. As a consequence, the molar extinction coefficient of WR10 is lower than that of WR8 and WR9. In spite of that, introduction of the DPFA unit into the dye structure evidently influenced the absorption features of WR10, leading to red-shifted absorption peak and an enhanced molar extinction coefficient.

2.5. Photovoltaic performance of DSSCs

The incident photon-current conversion efficiencies (IPCEs) for WR7-WR10 sensitized DSSCs are plotted in Fig. 7. The electrolyte was composed of 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPImI), 0.1 M LiI, 0.05 M I₂, and 0.5 M 4-tertbutylpyridine (TBP) in acetonitrile. These cells exhibit a broad IPCE plateau from 400 to 600 nm with comparable IPCE maxima (around 80%), implying a saturated light absorption in this wavelength. With respect to the WR8-WR10 sensitized DSSCs, WR7 sensitized solar cell gives a relatively narrow IPCE action spectrum because of its narrow absorption, resulting in a relatively low short-circuit photocurrent density (J_{SC}) of 12.96 mA cm⁻². These results revealed that incorporation of the strong auxiliary electron-donating unit at the end of PTZ dyes can successfully broaden the IPCE response area. On the other hand, WR9 based DSSC shows a lower and narrower IPCE as compared to that of WR8, which was attributed to the lower amount of WR9 adsorbed on the TiO₂ surface, consistent



Fig. 7. IPCE spectra of DSSCs made with the four dyes.



Fig. 8. J-V curves for DSSCs based on the dyes under illumination of AM 1.5G simulated sunlight (100 mW cm⁻²).

with observations from the contrasting absorption between the dye in solution and on the TiO_2 film (see Figs. 2 and 3).

The same DSSCs employed for IPCE measurements have been tested under standard conditions (AM 1.5G, 100 mW cm⁻²) in order to investigate the photovoltaic performance of the dyes. To prevent inflated photocurrent arising from stray light, a black metal mask surrounded the active area [51]. The photocurrent density voltage curves (I-V) of the DSSCs based on these dyes are shown in Fig. 8. The detailed parameters of short-circuit current density (I_{SC}) , opencircuit voltage (V_{OC}), fill factor (ff), and power-conversion efficiency (PCE) are collected in Table 3. When compared with WR8 $(J_{SC} = 14.02 \text{ mA cm}^{-2})$, WR7 shows lightly lower J_{SC} values of 12.96 mA cm^{-2} due to the narrower IPCE responsive area. Furthermore, DSSCs fabricated using WR8 gave a high V_{OC} of 748 mV, achieving an overall PCE of 7.13%, an evident improvement compared to the WR7 (PCE = 6.63%) with D- π -A structure. In contrast, the introduction of BPPA unit in WR9 resulted in significantly attenuated photocurrent ($J_{SC} = 12.63 \text{ mA cm}^{-2}$) and photovoltage ($V_{OC} = 705 \text{ mV}$), correspondingly, relative lower efficiency of 6.14% was attained. The influence of the DPFA unit seems to be beneficial since the J_{SC} and V_{OC} of WR10 are better than those of WR7. Nevertheless, the positive effect of the DPFA unit on the performance of D–D– π –A PTZ dyes is limited by its low molar absorption coefficient, which intimately correlates to the probability of the corresponding absorption (HOMO to LUMO).

2.6. Electrochemical impedance spectroscopy

To elucidate the correlation between the V_{OC} of the cell and the dye structure, electrochemical impedance spectroscopy (EIS) was carried out in the dark. Typical EIS Nyquist plots (Fig. 9(a)) and Bode phase plots (Fig. 9(b)) for DSSCs based on the WR7–WR10 measured in the dark under a forward bias of 0.7 V. Some important parameters can be obtained by fitting the EIS spectra to an electrochemical model [39]. R_S , R_{rec} , and R_{CE} represent the series

able 3			
photovoltaic parameters	for	studied	DSSCs

	1			
Dye	$J_{\rm SC}/{\rm mA~cm^{-2}}$	V _{OC} /mV	FF	PCE/%
WR7	12.96	710	0.71	6.63
WR8	14.02	748	0.68	7.13
WR9	12.63	705	0.69	6.14
WR10	13.01	734	0.68	6.49

 $^{\rm a}$ lodine electrolyte: 0.6 M DMPImI, 0.1 M LiI, 0.05 M I_2, and 0.5 M TBP in acetonitrile.



Fig. 9. Electrochemical impedance spectroscopy for the studied DSSCs (a) Nyquist plots and (b) Bode plots.

resistance, the charge-transfer resistance at the dve/TiO₂/electrolyte interface, and the charge-transfer resistance at the counter electrode (CE), respectively. The R_{rec} obtained by EIS is on the order of WR9 ($R_{\rm rec}$ = 74 Ω) < WR7 ($R_{\rm rec}$ = 75 Ω) < WR10 $(R_{\rm rec} = 134 \,\Omega) < WR8 \,(R_{\rm rec} = 146 \,\Omega)$, implying increasing resistance to charge recombination. By fitting the EIS curves, another important parameter for DSSCs, electron lifetime, could be obtained by multiplying the $R_{\rm rec}$ by the chemical capacitance. The fitted electron lifetime increases in the order of WR9 < WR7 < WR10 < WR8, indicating a sequence of lifetime increasing (Fig. 10). These results are in agreement with the observed shift in the V_{OC} value under standard global AM 1.5 illumination. Interestingly, the WR9 exhibits much shorter electron lifetime compared to WR7/WR8 despite with the more bulky terminal electron donor, BPPA unit. This is in striking contrast with other arylamine dyes such as triarylamine dyes. For example, truxene based triarylamine dyes prolong electron lifetime in the DSSCs, benefiting from their steric hindrance of the alkyl functionalized truxene group. The results from EIS reveal the dominant role of dense packing of PTZ dyes on TiO₂ surface, which in turn suppress the charge recombination and lengthens electron lifetime in DSSCs.

3. Conclusions

In summary, three new organic dyes, WR8, WR9 and WR10, featuring HCBZ, BPPA and DPFA terminal electron donors, respectively, were designed and synthesized to investigate the effects of



Fig. 10. Electron lifetime of the studied DSSCs as a function of bias voltage.

the terminal electron donor on the light-harvesting, electrochemical properties and performance of PTZ dves. The introduction of these additional electron donors extends the conjugation of the PTZ dyes, leading to the red-shifts of their absorption spectra and enhanced molar extinction coefficient. Interestingly, WR10 exhibits a lower molar extinction coefficient compared to that of WR8/WR9, a shortcoming limits the photoperformance of WR10. Theoretical calculations revealed that the probability of HOMO to LUMO transition for WR10 is much lower than that of WR8/WR9, which could induce a weakly absorption. In contrast, WR8 with HCBZ unit gave a better light-harvesting, leading to an improved photovoltage, photocurrent and efficiency of DSSCs compared to those of the reference dye, WR7. However, WR9 (containing BPPA unit) shows lower JSC values and thus lower efficiency owing to a decreased amount of dye. The electron lifetime of WR9 is even slightly lower than that of WR7, indicating the bulky structure of the terminal electron donor in PTZ dyes may not be advantageous. In conjunction with the iodine electrolyte, WR8 sensitized DSSCs affords a short-circuit photocurrent of 14.02 mA cm⁻², an open-circuit voltage of 748 mV, and a fill factor of 0.68, corresponding to an overall conversion efficiency of 7.13% under standard AM 1.5 sunlight. Our work provides a new insight into the terminal electron donor related structure-property relationship of PTZ arylamine dves for DSSCs.

4. Experimental

4.1. Materials and instruments

The synthetic routes for dyes are shown in Scheme 1 n-Butyllithium, Pd(PPh₃)₄, Pd(OAc)₂, t-BuOK, (t-Bu)₃P and cyanoacetic acid were purchased and used without purification. All other solvents and chemicals used in this work were analytical grade and used without further purification.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer. The reported chemical shifts were against TMS. The mass spectra were conducted on a 4700 Proteomics analyzer spectrometer. The absorption spectra were measured with a Jasco V-570 UV–vis spectrophotometer. Fluorescence spectra were acquired on Hitachi F-4500 spectrophotometers.

The cyclic voltammograms were measured on a CHI660B electrochemical workstation (CH Instruments) using a normal threeelectrodes cell with a dye loaded TiO₂ electrode as working electrode, a Pt wire auxiliary electrode, and Ag/AgCl reference electrode in saturated KCl solution, 0.1 M tetrabutylammonium perchlorate was used as supporting electrolyte. The redox potential of dyes on TiO₂ was measured in CH₃CN with a scan rate at 50 mV s⁻¹. After the measurement, ferrocene was added as the internal reference for calibration. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 100 mHz to 100 kHz in the dark with the alternate current amplitude set at 10 mV.

4.2. DSSCs fabrication and characterization

A transparent conducting substrate (F-doped SnO₂, 14 Ω /sq, >90% transparency in the visible region, Nippon Sheet Glass, Hyogo, Japan) was subsequently washed with detergent, distilled water, acetone, and EtOH ultrasonically, then treated with TiCl₄ (aqueous, 40 mM) at 70 °C for 30 min, followed by twice screenprinting and once doctor-blading a paste consisted of TiO₂ (18%), ethyl cellulose (9%), and terpinol (73%). The film was successively fired at 450 °C under air for 30 min, treated with TiCl₄ solution (aqueous, 40 mM), and fired again to give a ~12 μ m thick mesoscopic TiO₂ film. When cooled to 80 °C, the TiO₂ electrode was immersed in a dye solution (5 \times 10⁻⁴ M in THF) for 24 h in the dark and then rinsed with methanol and dried under an Air flow. The counter electrode was prepared by spin-coating H_2PtCl_4 (50 mM in isopropyl alcohol) on an FTO substrate and sintering at 390 °C under air for 40 min. The DSSCs had an active area of 0.18 cm² and electrolyte composed of 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPImI), 0.1 M LiI, 0.05 M I₂, and 0.5 M tertbutylpyridine (TBP) in acetonitrile.

An AM 1.5 solar simulator-Oriel 91160-1000 served as the light source for photovoltaic measurements of the DSSCs. The photocurrent–voltage (J–V) characteristics were recorded using a Keithley 2400 Source meter under 100 mW cm⁻² simulated air mass (AM 1.5) solar light illumination. The action spectra of monochromatic incident phototo-current conversion efficiencies (IPCEs) for the solar cells were performed by using a commercial setup (Oriel-74125 system, Newport, USA).

4.3. Synthesis

The synthetic procedures of the dyes WR8, WR9 and WR10 are depicted in Scheme 1. Corresponding aldehyde derivatives were synthesized by coupling reaction. Subsequently, the target dyes WR8, WR9 and WR10 were obtained via Knoevenagel condensation reaction of the respective aldehydes with cyanoacetic acid in the presence of a catalytic amount of piperidine.

4.3.1. 10-Hexyl-7-(9-hexyl-9H-carbazol-3-yl)-10H-phenothiazine-3-carbaldehyde (**3**)

A mixture of compound 1 (1.56 g, 4.15 mmol), compound 2 (1.62 g, 4.15 mmol), Pd(PPh₃)₄ (50 mg, 0.042 mmol), and Na₂CO₃ (2.2 g, 20.75 mmol) dissolved in THF (15 mL)/H₂O (8 mL) was refluxed under nitrogen for 8 h. After cooling the solution, the solvent was removed in vacuo. Dichloromethane was added. The organic layer was separated and washed three times with water, dried over anhydrous MgSO₄, and filtered. The crude product was then purified by silica gel chromatography with petroleum/ethyl acetate (10/1) as eluent to give a yellow oil **3** (1.27 g, 55%). ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3)$: δ 9.82 (s, 1H), 8.26 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.63-7.69 (m, 3H), 7.43-7.52 (m, 5H), 7.27 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.97J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 4.33 (t, J = 7.0 Hz, 2H), 3.95 (t, J = 7.0 Hz, 2H), 1.85–1.94 (m, 4H), 1.30–1.41 (m, 10H), 0.87–0.95 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ 189.9, 150.5, 141.6, 140.8, 139.8, 138.0, 131.1, 130.6, 130.2, 128.6, 126.1, 125.7, 124.6, 123.4, 122.8, 120.5, 119.0, 118.3, 116.3, 114.8, 108.9, 48.2, 43.3, 31.6, 31.4, 29.0, 26.9, 26.5, 22.6, 14.0. HRMS (ESI) calcd for C₃₇H₄₀N₂OS (M+H⁺): 561.2939, found: 561.2933.

4.3.2. 2-Cyano-3-(10-hexyl-7-(9-hexyl-9H-carbazol-3-yl)-10Hphenothiazin-3-yl)acrylic acid (WR8)

To a stirred solution of compound 3 (112 mg, 0.2 mmol) and cyanoacetic acid (25.5 mg, 0.3 mmol) in acetonitrile (8 mL) was added chloroform (4 mL) and piperidine (51.1 mg, 0.6 mmol). The reaction mixture was refluxed for 10 h and then acidified with 1 M hydrochloric acid aqueous solution (30 mL). The crude product was extracted into CH₂Cl₂, washed with water and dried over anhvdrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (CH₂Cl₂/methanol (15: 1) as eluent) to give desired product WR8 (Red powder, 101.7 mg, 81% yield). mp 92–94 °C. ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3)$: δ 8.25 (s, 1H), 8.14 (d, J = 8 Hz, 1H), 8.07 (s, 1H), 7.90 (d, J = 8 Hz, 1H), 7.69 (s, 1H), 7.63 (d, J = 9 Hz, 1H), 7.42–7.52 (m, 5H), 7.26 (t, J = 8.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.87 (d, I = 8.0 Hz, 1H), 4.31-4.34 (m, 4H), 1.82-1.95 (m, 4H), 1.25-1.39 (m, 10H), 0.86–0.94 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ 167.6, 141.0, 139.8, 132.5, 131.0, 128.8, 126.0, 125.7, 124.4, 123.4, 122.9, 120.4, 118.9, 118.3, 108.9, 108.7, 65.6, 31.6, 30.5, 26.9, 26.6, 22.5, 19.2, 13.9. HRMS (ESI) calcd for C₄₀H₄₁N₃O₂S (M+H⁺): 628.2997, found: 628.2995.

4.3.3. 7-(Bis(4-(2-phenylpropan-2-yl)phenyl)amino)-10-hexyl-10H-phenothiazine-3-carbaldehyde (**5**)

To a 100 mL two neck round-bottom flask was added compound 2 (1.63 g, 4.20 mmol), compound 4 (1.62 g, 4.00 mmol), Pd(OAc)₂ (60 mg), t-BuOK (600 mg), P(t-Bu)₃ (0.60 mL) and toluene (30 mL). The reaction mixture was refluxed overnight under nitrogen. After cooling to room temperature, saturated NH₄Cl was added and extracted with ethyl acetate (3 \times 10 mL). The combined organic layers were washed with brine and then dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to give the crude product, which were purified by column chromatograph packed with silica gel using petroleum ether/ethyl acetate (15:1) as eluent to afford a light-yellow oil of compound **5** (1.28 g, 45%). ¹H NMR (400 MHz, CDCl₃): δ 9.73 (s, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.52 (s, 1H), 7.18-7.29 (m, 8H), 7.04-7.16 (m, 7H), 6.95 (d, I = 8.5 Hz, 1H), 6.75–6.84 (m, 5H), 6.71 (s, 1H), 3.85 (t, J = 6.5 Hz, 2H), 1.58 (s, 12H), 1.34 (t, J = 7.0 Hz, 2H), 1.16–1.26 (m, 5H), 0.76–0.82 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 191.0, 150.6, 150.4, 145.0, 144.9, 143.6, 138.6, 131.0, 130.7, 128.5, 128.3, 127.9, 126.8, 126.01, 123.9, 123.7, 123.2, 122.8, 117.7, 115.7, 47.5, 42.4, 31.2, 30.8, 26.4, 26.1, 22.5, 14.3. HRMS (ESI) calcd for C₄₉H₅₀N₂OS (M+H⁺): 715.3722, found: 715.3718.

4.3.4. 3-(7-(Bis(4-(2-phenylpropan-2-yl)phenyl)amino)-10-hexyl-10H-phenothiazin-3-yl)-2-cyanoacrylic acid (WR9)

Compound WR9 was synthesized according to the same procedure of WR8, giving a red powder (78% yield). mp 109–112 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.92 (s, 1H), 7.75 (d, *J* = 8.0°Hz, 1H), 7.63 (s, 1H), 7.18–7.26 (m, 8H), 7.10–7.15 (m, 2H), 7.03–7.07 (m, 5H), 6.89–6.94 (m, 1H), 6.68–6.81 (m, 6H), 3.82 (t, *J* = 6.5 Hz, 2H), 1.56 (s, 12H), 1.33 (t, *J* = 7.0 Hz, 2H), 1.15–1.25 (m, 5H), 0.75–0.82 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 150.6, 147.9, 145.0, 143.4, 138.8, 131.1, 128.6, 128.0, 126.8, 126.0, 124.1, 123.6, 123.1, 122.8, 118.9, 117.4, 115.8, 47.4, 42.5, 31.2, 30.8, 26.5, 26.2, 22.7, 14.3. HRMS (ESI) calcd for C₅₂H₅₁N₃O₂S (M+H⁺):782.3780, found: 782.3786.

4.3.5. 7-(4-(Bis(9,9-dipropyl-9H-fluoren-2-yl)amino)phenyl)-10hexyl-10H-phenothiazine-3-carbaldehyde (7)

Compound **7** was synthesized according to the same procedure of **3**, giving a yellow powder (78% yield). mp 89–92 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.81 (s, 1H), 7.58–7.69 (m, 6H), 7.39–7.46 (m, 3H), 7.31–7.37 (m, 5H), 7.27–7.30 (m, 3H), 7.23–7.25 (m, 2H), 7.17–7.22 (m, 2H), 7.06 (d, *J* = 8.4°Hz, 2H), 6.91 (t, *J* = 8.5 Hz, 2H),

3.93 (t, J = 6.5 Hz, 2H), 1.82–1.96 (m, 8H), 1.42–1.53 (m, 3H), 1.31–1.40 (m, 5H), 0.85–0.94 (m, 6H), 0.67–0.74 (m, 17H). ¹³C NMR (100 MHz, CDCl₃): δ 190.1, 152.2, 150.5, 147.6, 146.8, 142.1, 140.9, 136.5, 136.3, 130.2, 128.4, 127.0, 126.8, 126.3, 125.6, 125.3, 124.5, 124.1, 123.4, 122.7, 120.3, 119.1, 118.9, 116.1, 114.7, 55.3, 48.2, 42.8, 31.4, 26.6, 22.6, 17.4, 14.5, 14.1. HRMS (ESI) calcd for C₆₃H₆₆N₂OS (M+H⁺): 899.4974, found: 899.4977.

4.3.6. 3-(7-(4-(Bis(9,9-dipropyl-9H-fluoren-2-yl)amino)phenyl)-10-hexyl-10H-phenothiazin-3-yl)-2-cyanoacrylic acid (WR10)

Compound WR10 was synthesized according to the same procedure of WR8, giving a red powder (65% yield). mp 113–116 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.04 (s, 1H), 7.83 (d, J = 8.0°Hz, 1H), 7.53–7.69 (m, 5H), 7.41 (d, J = 8.0 Hz, 2H), 7.21–7.35 (m, 9H), 7.17 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 8.5 Hz, 2H), 3.83 (t, J = 6.5 Hz, 2H), 1.78–1.95 (m, 8H), 1.39–1.49 (m, 3H), 1.26–1.37 (m, 5H), 0.84–0.93 (m, 6H), 0.64–0.73 (m, 17H). ¹³C NMR (100 MHz, CDCl₃): δ 152.3, 150.7, 147.7, 147.2, 147.0, 141.0, 136.4, 127.1, 126.8, 126.3, 125.4, 125.3, 124.6, 124.1, 123.5, 123.3, 122.8, 120.3, 119.1, 118.9, 55.3, 48.0, 42.7, 31.4, 29.7, 26.6, 22.6, 17.4, 14.5, 14.0. HRMS (ESI) calcd for C₆₆H₆₇N₃O₂S (M+H⁺):966.5032, found: 966.5038.

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References

- O'Regan B, Grätzel M. A low-cost high efficiency solar cell based on dye sensitized colloidal titanium dioxide films. Nature 1991;353:737–40.
- [2] Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-sensitized solar cells. Chem Rev 2010;110:6595–663.
- [3] Liang M, Chen J. Arylamine organic dyes for dye-sensitized solar cells. Chem Soc Rev 2013;42:3453–88.
- [4] Hua Y, Wang H, Zhu X, Islam A, Han L, Qin C, et al. New simple panchromatic dyes based on thiadiazolo[3,4-c]pyridine unit for dye-sensitized solar cells. Dyes Pigments 2014;102:196–203.
- [5] Wan ZQ, Jia CY, Zhang JQ, Duan YD, Lin Y, Shi Y. Triphenylamine-based starburst dyes with carbazole and phenothiazine antennas for dye-sensitized solar cells. J Power Sources 2012;199:426–31.
- [6] Al-Eid M, Lim SH, Park KW, Fitzpatrick B, Han CH, Kwak K, et al. Facile synthesis of metal-free organic dyes featuring a thienylethynyl spacer for dye sensitized solar cells. Dyes Pigments 2014;104:197–203.
- [7] He J, Hua J, Hu G, Yin XJ, Gong H, Li C. Organic dyes incorporating a thiophene or furan moiety for efficient dye-sensitized solar cells. Dyes Pigments 2014;104:75–82.
- [8] Li H, Yang L, Tang R, Hou Y, Yang Y, Wang H, et al. Organic dyes incorporating N-functionalized pyrrole as conjugated bridge for dye-sensitized solar cells: convenient synthesis, additional withdrawing group on the π-bridge and the suppressed aggregation. Dyes Pigments 2013;99:863–70.
- [9] Iqbal Z, Wu WQ, Zhang H, Hua PL, Fang X, Kuang DB, et al. Impact of hydroxy and octyloxy substituents of phenothiazine based dyes on the photovoltaic performance. Dyes Pigments 2013;99:299–307.
- [10] Duan T, Fan K, Fu Y, Zhong C, Chen X, Peng T, et al. Triphenylamine-based organic dyes containing a 1,2,3-triazole bridge for dye-sensitized solar cells via a 'Click' reaction. Dyes Pigments 2012;94:28–33.
- [11] Verbitskiy EV, Cheprakova EM, Subbotina JO, Schepochkin AV, Slepukhin PA, Rusinov GL, et al. Synthesis, spectral and electrochemical properties of pyrimidinecontaining dyes as photosensitizers for dye-sensitized solar cells. Dyes Pigmets 2014;100:201–14.
- [12] Zhao J, Jin T, Islam A, Kwon E, Akhtaruzzaman M, Asao N, et al. Thieno[2,3-a] carbazole-based donorepeacceptor organic dyes for efficient dyesensitized solar cells. Tetrahedron; 2014. http://dx.doi.org/10.1016/j.tet.2014.01.001.
- [13] Velusamy M, Thomas KRJ, Lin JT, Hsu YC, Ho KC. Organic dyes incorporating low-band-gap chromophores for dye-sensitized solar cells. Org Lett 2005;7: 1899–902.
- [14] Yu X, Ci Z, Liu T, Feng X, Wang C, Ma T, et al. Influence of different electron acceptors in organic sensitizers on the performance of dye-sensitized solar cells. Dyes Pigments 2014;102:126–32.

- [15] Baheti A, Tyagi P, Thomas KRJ, Hsu YC, Lin JT. Simple triarylamine-based dyes containing fluorene and biphenyl linkers for efficient dye-sensitized solar cells. | Phys Chem C 2009;113:8541–7.
- [16] Tamilavan V, Kim AY, Kim HB, Kang M, Hyun MH. Structural optimization of thiophene-(N-aryl)pyrrole-thiophenebased metal-free organic sensitizer for the enhanced dye-sensitized solar cell performance. Tetrahedron 2014;70: 371–9.
- [17] Cai S, Hu X, Han J, Zhang Z, Li X, Wang C, et al. Efficient organic dyes containing dibenzo heterocycles as conjugated linker part for dye-sensitized solar cells. Tetrahedron 2013;69:1970–7.
- [18] Matsui M, Shiota T, Kubota Y, Funabiki K, Jin J, Yoshida T, et al. N-(2-Alkoxyphenyl)-substituted double rhodanine indoline dyes for zinc oxide dye-sensitized solar cell. Tetrahedron 2012;68:4286–91.
- [19] Duan T, Fan K, Zhong C, Chen X, Peng T, Qin J. A new class of organic dyes containing b-substituted 2, 20-bithiophenene unit as a π-linker for dyesensitized solar cells: structural modification for understanding relationship of structure and photovoltaic performances. J Power Sources 2013;234:23–30.
- [20] Chen H, Huang H, Huang X, Clifford JN, Forneli A, Palomares E, et al. High molar extinction coefficient branchlike organic dyes containing di(p-tolyl) phenylamine donor for dye-sensitized solar cells applications. J Phys Chem C 2014;114:3280–6.
- [21] Liang M, Xu W, Cai F, Chen P, Peng B, Chen J, et al. New triphenylamine-based organic dyes for efficient dye-sensitized solar cells. J Phys Chem C 2007;111: 4465–72.
- [22] Li H, Hou Y, Yang Y, Tang R, Chen J, Wang H, et al. Attempt to improve the performance of pyrrole-containing dyes in dye sensitized solar cells by adjusting isolation groups. ACS Appl Mater Interfaces 2013;5:12469–77.
- [23] Pei K, Wu Y, Islam A, Zhang Q, Han L, Tian H, et al. Constructing high-efficiency D–A–π–A–featured solar cell sensitizers: a promising building block of 2,3-Diphenylquinoxaline for antiaggregation and photostability. ACS Appl Mater Interfaces 2013;5:4986–95.
- [24] Li G, Liang M, Wang H, Sun Z, Wang L, Wang Z, et al. Significant enhancement of open-circuit voltage in indoline-based dye-sensitized solar cells via retarding charge recombination. Chem Mater 2013;25:1713–22.
- [25] Lu M, Liang M, Han H, Sun Z, Xue S. Organic dyes incorporating bishexapropyltruxeneamino moiety for efficient dye-sensitized solar cells. J Phys Chem C 2011;115:274–81.
- [26] Zhang Y, Zhang YF, Wang Z, Liang M, Jia D, Wu Q, et al. Effects of different alkyl chains on the performance of dye-sensitized solar cells with different electrolytes. J Power Sources 2014;253:167–76.
- [27] Zong X, Liang M, Fan C, Tang K, Li G, Sun Z, et al. Design of truxene-based organic dyes for high-efficiency dye-sensitized solar cells employing cobalt redox shuttle. J Phys Chem C 2012;116:11241–50.
- [28] Wang Z, Liang M, Hao Y, Zhang Y, Wang L, Sun Z, et al. Influence of substituent of dithieno[3,2-b:2',3'-d]pyrrole (DTP) spacer and the adsorption time on the photovoltaic properties of arylamine organic dyes. J Mater Chem A 2013;1: 11809–19.
- [29] Zeng W, Cao Y, Bai Y, Wang Y, Shi Y, Zhang M, et al. Efficient dye-sensitized solar cells with an organic photosensitizer featuring orderly conjugated ethylenedioxythiophene and dithienosilole blocks. Chem Mater 2010;22: 1915–25.
- [30] Zhang M, Wang Y, Xu M, Ma W, Li R, Wang P. Design of high-efficiency organic dyes for titania solar cells based on the chromophoric core of cyclopentadithiophene-benzothiadiazole. Energy Environ Sci 2013;6:2944–9.
- [31] Cao Y, Cai N, Wang Y, Li R, Yuan Y, Wang P. Modulating the assembly of organic dye molecules on titania nanocrystals via alkyl chain elongation for efficient mesoscopic cobalt solar cells. Phys Chem Chem Phys 2012;14: 8282-6.
- [32] Ying W, Yang J, Wielopolski M, Moehl T, Moser JE, Comte P, et al. New pyrido [3,4-b]pyrazine-based sensitizers for efficient and stable dye-sensitized solar cells. Chem Sci 2014;5:206–14.
- [33] Wang S, Guo J, He L, Wang H, Zhao J, Lu C. Influence of thiophene and benzene unit in triphenylamine dyes on the performance of dye-sensitized solar cells. Synth Met 2013;168:1–8.
- [34] Tian H, Yang X, Chen R, Pan Y, Li L, Hagfeldt A, et al. Phenothiazine derivatives for efficient organic dye-sensitized solar cells. Chem Commun; 2007:3741–3.
- [35] Liu J, Yang X, Zhao J, Sun L. Tuning band structures of dyes for dye-sensitized solar cells: effect of different p-bridges on the performance of cells. RSC Adv 2013;3:15734–43.
- [36] Yang CJ, Chang YJ, Watanabe M, Hona YS, Chow TJ. Phenothiazine derivatives as organic sensitizers for highly efficient dye-sensitized solar cells. J Mater Chem 2012;22:4040–9.
- [37] Hua Y, Chang S, Huang D, Zhou X, Zhu X, Zhao J, et al. Significant improvement of dye-sensitized solar cell performance using simple phenothiazine-based dyes. Chem Mater 2013;25:2146–53.
- [38] Cheng M, Yang X, Zhang F, Zhao J, Sun L. Tuning the HOMO and LUMO energy levels of organic dyes with N-Carboxomethylpyridinium as acceptor to optimize the efficiency of dye-sensitized solar cells. J Phys Chem C 2013;117: 9076–83.
- [39] Cheng M, Yang X, Chen C, Zhao J, Tana Q, Sun L. Effect of the acceptor on the performance of dye-sensitized solar cells. Phys Chem Chem Phys 2013;15: 17452–9.
- [40] Kim SH, Kim HW, Sakong C, Namgoong JW, Park SW, Ko MJ, et al. Effect of five-membered heteroaromatic linkers to the performance of phenothiazinebased dye-sensitized solar cells. Org Lett 2011;13:5784–7.

- [41] Cao D, Peng J, Hong Y, Fang X, Wang L, Meier H. Enhanced performance of the dye-sensitized solar cells with phenothiazine-based dyes containing double D–A branches. Org Lett 2011;13:1610–3.
- [42] Hart AS, Bikram KCC, Subbaiyan NK, Karr PA, D'Souza F. Phenothiazinesensitized organic solar cells: effect of dye anchor group positioning on the cell performance. ACS Appl Mater Interfaces 2012;4:5813–20.
- [43] Wu W, Yang J, Hua J, Tang J, Zhang L, Long Y, et al. Efficient and stable dyesensitized solar cells based on phenothiazine sensitizers with thiophene units. J Mater Chem 2010;20:1772–9.
- [44] Chang YJ, Chou PT, Lin YZ, Watanabe M, Yang CJ, Chin TM, et al. Organic dyes containing oligo-phenothiazine for dye-sensitized solar cells. J Mater Chem 2012;22:21704–12.
- [45] Iqbal Z, Wu WQ, Kuang DB, Wang L, Meier H, Cao D. Phenothiazine-based dyes with bilateral extension of π-conjugation for efficient dye-sensitized solar cells. Dyes Pigments 2013;96:722–31.
- [46] Iqbal Z, Wu WQ, Zhang H, Han L, Fang X, Wang L, et al. Influence of spatial arrangements of π -spacer and acceptor of phenothiazine based dyes on the performance of dye-sensitized solar cells. Org Electron 2013;14:2662–72.

- [47] Chen C, Liao JY, Chi Z, Xu B, Zhang X, Kuang DB, et al. Metal-free organic dyes derived from triphenylethylene for dye-sensitized solar cells: tuning of the performance by phenothiazine and carbazole. J Mater Chem 2012;22: 8994–9005.
- [48] Marotta G, Reddy MA, Singh SP, Islam A, Han L, Angelis FD, et al. Novel carbazole-Phenothiazine dyads for dye-Sensitized solar cells: a combined experimental and theoretical study. ACS Appl Mater Interfaces 2013;19: 9635–47.
- [49] Wan Z, Jia C, Duan Y, Zhou L, Lin Y, Shi Y. Phenothiazine–triphenylamine based organic dyes containing various conjugated linkers for efficient dyesensitized solar cells. J Mater Chem 2012;22:25140–7.
- [50] Zhao Z, Xu X, Wang H, Lu P, Yu G, Liu Y. Zigzag molecules from pyrenemodified carbazole oligomers: synthesis, characterization, and application in OLEDs. J Org Chem 2008;73:594–602.
- [51] Ito S, Nazeeruddin MK, Liska P, Comte P, Charvet R, Péchy P, et al. Photovoltaic characterization of dye-sensitized solar cells: effect of device masking on conversion efficiency. Prog Photovoltaics 2006;14:589–601.