



# The improved photovoltaic performance of phenothiazine-dithienopyrrole based dyes with auxiliary acceptors

Ming-Liang Han<sup>a,b</sup>, Yi-Zhou Zhu<sup>a,\*</sup>, Shuang Liu<sup>a</sup>, Qing-Long Liu<sup>a</sup>, Dan Ye<sup>a</sup>, Bing Wang<sup>a</sup>, Jian-Yu Zheng<sup>a,b,\*\*</sup>

<sup>a</sup> State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

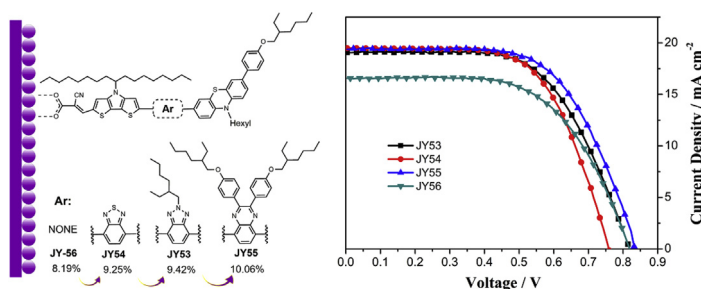
<sup>b</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China



## HIGHLIGHTS

- Dithienopyrrole was first used to construct phenothiazine-based D–A– $\pi$ –A type dyes.
- The  $J_{sc}$  values were obviously improved by inserted auxiliary acceptors.
- High  $V_{oc}$  has also been realized together with the improvement of  $J_{sc}$ .
- Over ten percent of PCE has been achieved for JY55-based device.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Dye-sensitized solar cell  
Phenothiazine  
Dithienopyrrole  
Auxiliary acceptor  
Iodine electrolyte  
Long alkyl-chain

## ABSTRACT

Incorporating alkyl chain decorated dithienopyrrole  $\pi$ -spacer with phenothiazine donor has proven to be efficient strategy for constructing novel dyes, which can achieve both large short-circuit current ( $J_{sc}$ ) and high open-circuit voltage ( $V_{oc}$ ) in dye-sensitized solar cells (DSSCs). To promote the light harvesting capability, auxiliary acceptors including benzotriazole (BTZ), benzothiadiazole (BTZ), and quinoxaline (Qu) have been inserted into the skeleton of dyes, and much improved  $J_{sc}$  have been realized. Meantime, the rational design of alkyl chains endows dyes JY53 and JY55 a good shielding effect from the penetration of electrolyte, guaranteeing a high  $V_{oc}$  (over 810 mV) through retarding unwanted interfacial charge recombination. As a result, with the assistance of introduced auxiliary acceptors and alkyl chains, the photovoltaic performance of devices have been significantly improved, and dye JY55 has achieved an excellent power conversion efficiency (PCE) of 10.06% with  $J_{sc}$  of 19.18 mA cm<sup>-2</sup>,  $V_{oc}$  of 829 mV, and FF of 0.63 under AM 1.5 G irradiation.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) have experienced extensive interdisciplinary investigation in the past two decades due to relatively high power conversion efficiency (PCE), low cost, ease of fabrication, intrinsic merit to be a portable and wearable energy supplier [1–5]. In order to improve the PCE of DSSC devices, the design of a superior

photosensitizer has always been one of the key challenges owing to its important effects on governing the photon harvesting, charge generation and separation processes at the semiconductor interface [6–8]. After continuous efforts on it, various structures such as metal-based dyes [9–11], porphyrin-based dyes [12–14], quantum dot-based dyes [15,16], natural dyes [17–20], and pure organic dyes [21–25] have been developed and successfully applied in this area. Although

\* Corresponding author.

\*\* Corresponding author. State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China.

E-mail addresses: [zhuyizhou@nankai.edu.cn](mailto:zhuyizhou@nankai.edu.cn) (Y.-Z. Zhu), [jy Zheng@nankai.edu.cn](mailto:jy Zheng@nankai.edu.cn) (J.-Y. Zheng).

impressive PCEs have been achieved in above-mentioned cases, there still exists a gap to meet the requirement of practical application. Recently, increasing attention has been attracted by metal-free organic sensitizers for their rich skeleton, good flexibility in molecular tailoring, tunable absorption spectra, and environmental friendliness [26,27].

Phenothiazine entities have been widely employed as a donor to construct efficient D- $\pi$ -A type organic dyes for DSSCs [28–32], in virtue of their strong electron-donating feature and non-planar butterfly configuration which are beneficial in facilitating intramolecular charge transfer (ICT) and impeding intermolecular aggregation, respectively [31]. Aiming to improve the relatively narrow absorption of phenothiazine, a large  $\pi$ -conjugate spacer is generally needed to extend the electron delocalization of resulting dye for better match to the spectral distribution of sunlight [33,34]. For the same reason, the introduction of auxiliary acceptor which has proven to be an effective approach to extend the spectral response, enhance ICT process, and optimize energy levels of photosensitizers [35–39], has been adopted in phenothiazine-based dye [40–43]. Unfortunately, the structural modification by inserting either benzothiadiazole (BTD) or quinoxaline (Qu) failed to give a relatively high short-circuit photocurrent density ( $J_{sc}$ ) and open-circuit voltage ( $V_{oc}$ ), although the resultant dyes all exhibit broadened absorption as expected. This might be ascribed to the induced deterioration of recombination by the insertion of uncovered rigid electron acceptor, which has been approved by their very short electron lifetime [40–43]. Taking account of the reported much higher  $V_{oc}$  for dyes containing alkoxy-decorated BTD against un-substituted BTD [44], and for alkoxy-substituted Qu relative to uncovered Qu [45], it is reasonable to expect this shortcoming would be overcome through wrapping the introduced rigid electron acceptor with suitable alkyl or alkoxy chains, finally achieving good spectral response together with enhanced  $J_{sc}$  and  $V_{oc}$ .

Altering the  $\pi$ -conjugate spacer is another way to extend the dye's electron delocalization and optimize the energy levels [46,47]. Di-thieno[3,2-b:2',3'-d]pyrrole (DTP) which possesses two fused thiophene rings, has been successfully applied as an efficient donor in bulk heterojunction solar cells [48,49] and  $\pi$ -spacer in organic dyes-based DSSCs [50,51]. The highly delocalized electronic structure of DTP endows the resultant dyes broadened light absorption and great intramolecular electronic communications, hence impressive photovoltaic performance [52,53]. Accordingly, DTP unit has been selected herein as  $\pi$ -conjugate spacer to construct dye molecule.

With that above-mentioned in mind, four dyes JY53–56 (Fig. 1) featuring phenothiazine donor and DTP spacer in skeleton have been designed and synthesized. Three different auxiliary acceptors including benzotriazole (BTZ), benzothiadiazole, and quinoxaline were inserted into dye molecule towards obtaining better light harvesting capability and understanding the difference. To avoid the serious charge recombination observed in the reported cases and achieve an actually promoted photovoltaic performance, alkyl or alkoxy chains were introduced onto BTZ and Qu units. Additionally, flexible alkyl or alkoxy chains were also decorated onto phenothiazine and DTP units to ensure a compact layer of dye formed at the TiO<sub>2</sub> surface and a good shielding

effect from the penetration of electrolyte.

## 2. Experimental section

### 2.1. Materials and characterization

All of the synthetic procedures were carried out under an argon atmosphere, using dry solvents unless otherwise noted. Tetrahydrofuran (THF) and toluene were pre-dried over Na/benzophenone and freshly distilled prior to use. *N,N*-Dimethylformamide (DMF), acetonitrile, and chloroform (TCM) were dried and freshly distilled from calcium hydride (CaH<sub>2</sub>). Compounds 3,6-dibromobenzene-1,2-diamine [54], 4-((2-ethylhexyl)oxy)phenylboronic acid [55], and 3,3'-dibromo-2,2'-bithiophene [56] were synthesized according to the reported procedures. Other reagents were directly used as received.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker 400 MHz spectrometer using TMS as the internal standard. HR-MS data were obtained on a Varian 7.0T FTMS. UV–Vis spectra were measured on a Varian Cary 300 Conc UV–Visible spectrophotometer. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) experiments were carried out on a Zennium electrochemical workstation (Zahner Corporation).

### 2.2. Cell fabrication and measurements

The working electrode was fabricated by repeated screen printing process with commercial TiO<sub>2</sub> paste (Heptachroma Corporation) with an average particle diameter of 20 nm for transparent layer (~10  $\mu$ m), and an average particle diameter of 200 nm for scattering layer (~4  $\mu$ m), respectively. Afterwards, the TiO<sub>2</sub> film was heated with a ramped temperature profile (kept at 125, 250, 325, 450, and 500 °C for 5, 5, 5, 15, and 15 min, respectively). The active area of dye-sensitized solar cells was 0.196 cm<sup>2</sup>. Then, a TiCl<sub>4</sub> post-treatment was performed, followed by another sintering process at 500 °C for 60 min. The concentration of dyes in a mixed solvent of TCM and EtOH (v/v = 1:1) used for sensitization is 3  $\times$  10<sup>-4</sup> M, and the photoanode was immersed in dye solutions for 12 h. The counter electrode was obtained by thermoplyrolysis of H<sub>2</sub>PtCl<sub>6</sub> (0.02 M in isopropanol) on the surface of FTO glass at 400 °C for 20 min. The electrolyte consists of 0.6 M DMPII, 0.1 M LiI, 0.03 M I<sub>2</sub>, 0.1 M guanidinium thiocyanate and 0.5 M 4-*tert*-butylpyridine in acetonitrile/valeronitrile (v/v = 85/15).

The DSSCs were illuminated by a solar simulator (CHF-XM-500W, Trusstech Co. Ltd.) under 100 mW cm<sup>-2</sup> irradiation, which was calibrated by a standard silicon solar cell (91150V, Newport Corporation). The photocurrent density-voltage ( $J$ - $V$ ) characteristic curves of the DSSCs were recorded using an electrochemical workstation (Zahner Corporation). The incident photon-to-current conversion efficiency (IPCE) was measured using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTECH, USA).

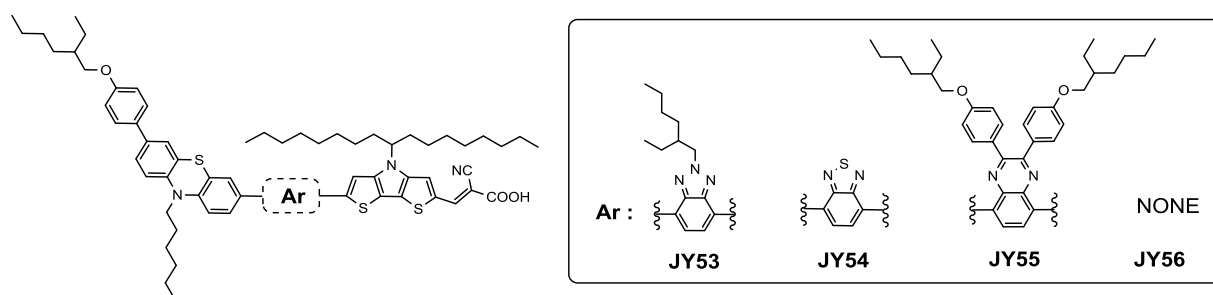


Fig. 1. Molecular structures of dyes JY53–56.

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