

Charge-separated sensitizers with enhanced intramolecular charge transfer for dye-sensitized solar cells: Insight from structure-performance relationship

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ABSTRACT

A series of charge-separated (CS) sensitizers with various donor modules and pyrimidine as acceptor were synthesized and employed to explore the effect of donor structure engineering on the properties of CS sensitizers and photovoltaic performances of dye-sensitized solar cells (DSSCs). Using previously reported CS sensitizer **MTPA-Pyc** or **YD-Pyc** as the model molecule, cyano group or benzotriazole were incorporated into the donor module and the electrochemical, spectral and photophysical properties were investigated. Incorporating electron-withdrawing structures enhances the intramolecular charge transfer (ICT) and conjugation of the donor module which leads to not only remarkably red-shifted absorption spectra, but also elongated lifetime of CS state of the sensitizers, thus resulting in an over 30% increase of power conversion efficiency (PCE) of the DSSCs. Combination of an electron-withdrawing benzotriazole with a strong electron-donating indoline moiety in the donor module produces the best PCE of 7.41% for DSSC based on **YDBT-Pyc**. Our results provide not only the rational design principles for CS sensitizers, but also insight into the feasibility of CS sensitizers for high performance photovoltaic applications.

1. Introduction

The construction and utilization of novel charge-separated (CS) organic compounds have been attractive areas of research within the study of organic photoelectronic materials. Inspired by the natural photosynthetic system, long-lived CS states were employed to promote the conversion process of light into electrical or chemical energy [1]. Various electron donor–acceptor (D–A) systems with a CS state lifetime ranging from 80 ns to 2 h have been acquired [2–11]. However, the photovoltaic performances of solar cells fabricated with long-lived CS organic compounds were shown to be far from satisfactory [6,9,12–21]. The possible reasons for the poor performance involve inappropriate device structures for CS materials, such as the single-layer solar cells [6,9] and heterojunction solar cells [12], and the inefficient electron injection at the interfaces between the organic compounds and the adjacent metal oxide substrate [18,21]. Considering that dye-sensitized solar cells (DSSCs), promising alternatives for

traditional photovoltaic devices over the last two decades [22–29], possess a more favorable device structure for interfacial charge transfer, two CS sensitizers with long-lived CS states and anchoring groups for the DSSC, namely **MTPA-Pyc** and **YD-Pyc**, were designed to overcome the two issues listed above [30]. It has been demonstrated that CS sensitizers could improve electron injection efficiencies and slow down charge recombination. Thus, a high internal quantum efficiency (IQE) of devices was achieved, showing the superiority of CS sensitizers over charge-transfer (CT) sensitizers of which the CS states could not be detected in a nanosecond instrument.

Another discovery of the CS sensitizers is that **YD-Pyc**, which has a stronger donor moiety of methylphenyl indoline, shows red-shifted absorption spectrum and elongated lifetimes of CS state. This leads to higher photovoltaic performance in comparison to that of **MTPA-Pyc** with triphenylamine donor moiety. The result suggests that molecular structural tuning of the donor module could provide an improved photophysical and photovoltaic properties of the CS sensitizers.

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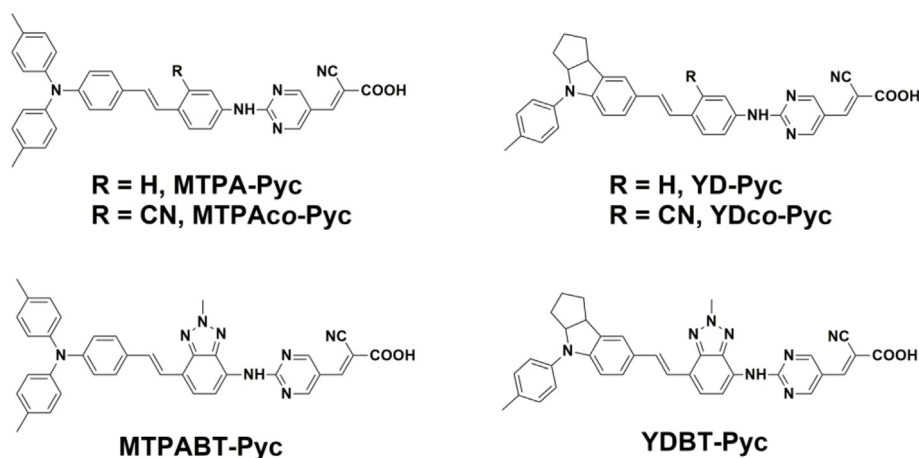


Fig. 1. Chemical structures of the sensitizers.

Structural modification of metal-free sensitizers involves the aspects including light harvesting [31], electron injection [32], dye regeneration [33] and charge recombination [34]. Although molecular designing principles for general metal-free sensitizers have been extensively investigated and concluded [35,36], they are mostly applied in CT sensitizers. Therefore, the relationship between the structural characters of the CS sensitizers and their properties as well as the photovoltaic performance of DSSCs based on these sensitizers still remains unclear.

Aiming at exploring the effect of structural tuning of CS sensitizers on their properties and achieving better feasibility in DSSCs, we herein synthesized a series of CS sensitizers (Fig. 1) with long-lived CS states and an anchoring group. A cyano group was introduced into the phenyl ring between electron-donating triphenylamine or indoline moiety and pyrimidine acceptor module [37–39] of previously reported CS sensitizers **MTPA-Pyc** and **YD-Pyc** (Fig. 1) [30] to produce **MTPAco-Pyc** and **YDco-Pyc**. Meanwhile, benzotriazole unit was employed in replacement of the phenyl ring and the novel sensitizers were denoted as **MTPABT-Pyc** and **YDBT-Pyc**. Cyano group [40] and benzotriazole [41] unit have been applied in CT sensitizers and showed their ability to extend the absorption range and facilitate charge transfer due to their electron-withdrawing property. The synthetic procedures of these dyes were given in Scheme 1. The electrochemical and photophysical properties of the CS sensitizers were investigated using electrochemical measurements, DFT calculations and both steady state and transient UV-Vis and fluorescence measurements. On this basis, DSSCs were fabricated employing these CS sensitizers, and their photovoltaic performances were investigated and correlated to their structural features. Finally, the effects of structural tuning of the donor module of CS sensitizers on their electrochemical, spectral and photophysical properties and the photovoltaic performances of their DSSCs were concluded.

2. Experimental section

2.1. Materials

4-*N,N*-bis(4-methylphenyl)aminostyrene (**1a**) [42], 4-(4-methylphenyl)-7-vinyl-1,2,3,3a, 4,8 b-hexahydrocyclopenta [b]indole (**1b**) [30], 2-chloro-5-(1,3-dioxolan-2-yl)pyrimidine [43] and 4,7-dibromo-2-methyl-2H-benzo [d] [1–3]triazole [44,45] were prepared according to the previous reports. 2-bromo-5-nitrobenzonitrile, 2-aminopyrimidine-5-carbaldehyde, ethanediol, *p*-toluenesulfonic acid, 2-cyanoacetic acid and the reagents involved were commercially available and used as acquired. All solvents were in reagent grade and were purified by the standard methods.

2.2. Synthesis

2.2.1. Synthetic methods of the sensitizers

Synthetic routes of novel CS sensitizers **MTPAco-Pyc**, **MTPABT-Pyc**, **YDco-Pyc** and **YDBT-Pyc** are outlined in Scheme 1. The detailed synthetic methods and characterizations of the intermediates are given in the supplementary information.

For **MTPAco-Pyc** and **YDco-Pyc**, the palladium catalyzed Heck reaction of **1a** or **1b** and 2-bromo-5-nitrobenzonitrile gives vinyl triphenylamine or indoline coupled nitrobenzonitrile **2a** or **2b** in good yield. The nitro group was then reduced by SnCl₂·2H₂O to afford amino intermediate **3a** or **3b** with a yield of 70–80%. **4a** or **4b** was prepared through Buchwald–Hartwig coupling of **3a** or **3b** with 2-chloro-5-(1,3-dioxolan-2-yl)pyrimidine, followed by an acidic hydrolysis procedure to give the pyrimidine carbaldehyde intermediates **5a** or **5b**. Finally, **5a** or **5b** were converted into **MTPAco-Pyc** or **YDco-Pyc** by Knoevenagel condensation with cyanoacetic acid in good yield.

For **MTPABT-Pyc** and **YDBT-Pyc**, 2-amino-5-(1,3-dioxolan-2-yl)pyrimidine was coupled with dibromobenzotriazole to afford intermediate **8** in high yield of over 80%. Then vinyl triphenylamine (**1a**) or vinyl indoline (**1b**) moiety was incorporated through Heck reaction with compound **8** to afford intermediate **9a** or **9b**. The subsequent procedure to obtain the final sensitizers **MTPABT-Pyc** and **YDBT-Pyc** via hydrolysis and condensation was similar to those in the preparation of **MTPAco-Pyc** and **YDco-Pyc**.

2.2.2. Synthesis of (*E*)-2-cyano-3-(2-((*E*)-4-(2-(4-*N,N*-bis(4-methylphenyl)aminophenyl)vinyl)-5-cyanophenylamino)pyrimidine-5-yl)acrylic acid (**MTPAco-Pyc**)

A mixture of compound **5a** (180 mg, 0.34 mmol), 2-cyanoacetic acid (168 mg, 1.7 mmol) and three drops of piperidine in acetonitrile (20 mL) was stirred in a Schlenk tube at 80 °C for 8 h in an Ar atmosphere. After cooling to room temperature, the reaction mixture was concentrated by rotary evaporation and purified by the column chromatography on silica gel with DCM/methanol (10:1 v/v) as the eluent to give a reddish orange solid (150 mg, 72%). ¹H NMR (500 MHz, DMSO-*d*₆, δ): 10.58 (s, 1H), 9.04 (s, 2H), 8.30 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.84 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 16.0 Hz, 1H), 7.15–7.12 (m, 5H), 6.96 (d, *J* = 8.0 Hz, 4H), 6.89 (d, *J* = 8.5 Hz, 2H), 2.28 (s, 6H). ¹³C NMR (125.7 MHz, DMSO-*d*₆, δ): 168.08, 161.16, 159.93, 148.39, 148.50, 145.44, 145.20, 133.17, 131.55, 130.24, 130.15, 129.44, 127.73, 126.43, 125.14, 122.31, 122.10, 120.20, 119.71, 118.68, 117.77, 115.00, 111.64, 105.04, 21.16. HRMS (ESI) *m/z*: [M - H]⁻ calcd for C₃₇H₂₈N₆O₂, 587.2201; found, 587.2200. Anal. calcd for C₃₇H₂₈N₆O₂: C 75.49, H 4.79, N 14.28, O 5.44; found: C 75.71, H 4.70, N 14.13, O 5.46.

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