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Design of organic dyes for dye-sensitized solar cells: Extending π-conjugation backbone via 'Click' reaction to improve photovoltaic performances

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ABSTRACT

The organic dyes have been synthesized via a 'Click' reaction and employed in dye-sensitized solar cells, in which an electron-deficient 1,2,3-triazole unit is introduced to connect the thienyl group and the phenoxyl group as π-linkers. Compared with the non-thiophene containing reference dye, these new dyes show stronger intramolecular charge transfer and higher molar extinction coefficient with incremental increase of thienyl groups. Thus, the short-circuit current of solar cells based on them is greatly increased. Moreover, the existence of 1,2,3-triazole unit is favorable for the charge separation that can retard the charge recombination and improve the open circuit voltage. Consequently, the solar cell based on the dithienyl containing dye presents the best performance with a J_{sc} of 10.00 mA cm^{-2}, a V_{oc} of 0.68 V and a *FF* of 0.71, corresponding to an overall conversion efficiency of 4.81% among them.

1. Introduction

In the past two decades, dye-sensitized solar cells (DSSCs) have been widely investigated due to their high photovoltaic performance and low-cost fabrication [1–8]. In DSSCs, the photosensitizer is a key component to harvest light and inject electrons. Until now, hundreds of photosensitizers have been designed and synthesized for improving the photovoltaic performance and exploring the relationship of structure and performance of DSSCs. Among them, the ruthenium complex dyes, such as N719, N3 and C101, have dominated the highly efficient DSSCs for many years [9–12]. For example, the efficiency of DSSC based on N719 has exceeded 12% [13]. However, the scarcity of ruthenium metal is a big problem for the future commercial development and applications. Compared with the metal complex dyes, the metal-free organic dyes have some advantages, such as the relative simplicity of synthesis and purification, convenient structural modification and high molar extinction coefficient. Thus, searching new metal-free organic dyes with excellent photovoltaic performance has attracted considerable attention. Many organic dyes, which exhibit comparably excellent photovoltaic performances to ruthenium complexes, have been designed and obtained [6,14–16].

However, designing the new organic dyes via simple and convenient synthetic routes is still a challenge in DSSCs. In last decade, various kinds of functional groups and their derivatives have been combined to generate D–π–A organic dyes. Among them, an arylamine group, thiophene derivatives and cyanoacrylic acid moiety are the most common subunits that act as an electron donor, π-linker, and an electron acceptor/anchoring group, respectively. Especially, the π-linker as a bridge that connects the donor and acceptor exerts a significant influence on the transmission and recombination of electron during the photo-electric conversion process in DSSCs [17–19]. Generally, the crucial step for the construction of D–π–A organic dyes is to connect the donor group and π-linker. The palladium-catalyzed carbon–carbon coupling reactions, such as Suzuki coupling [14] or Stille coupling [16], are the most common reactions employed to perform this step. But the palladium-catalysts are costly, and the reaction

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conditions are relatively harsh requiring an oxygen free atmosphere. Recently, a 'Click' reaction of Cu(I) catalyzed alkyne-azide cycloaddition developed by Sharpless and co-workers [20] has been widely used in the design and preparation of optoelectronic materials [21–23], so it can afford a good way to construct new organic dyes under the mild reaction condition for DSSCs. We have found that the introduction of 1,2,3-triazole group as an electron-deficient unit in the linear D–π–A organic dyes can effectively enhance the open-circuit voltage of the DSSCs with good efficiency [19]. Therefore, in order to improve the photovoltaic performance and also to explore the relationship of structure and photovoltaic properties, D-π-A-π-A organic dyes (**DH-S1** and **DH-S2** shown in Fig. 1) containing a 1,2,3-triazole unit have been designed and synthesized via the "Click" reaction. In these dyes, one or more electron-rich thienyl groups are introduced to act as a π-bridge to extend π-conjugation backbone. 1,2,3-Triazole group connects the thienyl ring and the phenoxyl ring to link a triphenylamine donor and a cyanoacrylic acid acceptor/anchoring group, respectively. Here, we present the synthesis and investigation on the photophysical properties and photovoltaic performance of DSSCs based on them.

2. Experimental section

2.1. Equipments and materials

^{1}H NMR and ^{13}C NMR spectra were measured with a Varian MERCURY-VX300 in $CDCl_3$ or in DMSO-d6 with TMS as internal reference. UV–vis Absorption spectrometry was performed on a Shimadzu UV-3600 spectrophotometer. The electrochemical behaviors of DH dyes were investigated by using cyclic voltammetry (CV) on a CHI600A electrochemical work station. The elemental analysis was carried out on a CARLOERBA-1106 microelemental analyzer. Mass spectra were recorded with a Bruker 320-MS triple quadrupole mass spectrometer.

Compound **1** [24], **2** [25], **3** [26], **4** [27] were prepared according to the corresponding literatures. The catalyst of $Pd(PPh_3)_4$ was synthesized in our own lab, anhydrous THF used in Schlenk system was purified by refluxing with Na–K alloy. The other reagents and solvents were commercially available and were used without further purification unless otherwise stated.

2.2. Synthesis of DH-1, DH-S1 and DH-S2

In a 50 mL of flask, a mixture of the terminal alkynes (**2**–**4**) (1.05 equiv.), organic azide (**1**) (1.0 equiv.), $NaHCO_3$ (0.05 equiv.) and ascorbic acid (0.05 equiv.) were dissolved in the solution of THF and H_2O (V/V = 5/1), and then an aqueous solution of $CuSO_4 \cdot 5H_2O$ (0.05 equiv.) was added to it. After stirring for 8 h under an argon atmosphere, the mixture was extracted with ether (10 mL × 3). The organic phase was dried over anhydrous Na_2SO_4. Then the solvent was removed and the residue was purified by a silica gel column eluted with toluene/methanol (V/V = 10/1) to give the target dyes.

2.2.1. 2-cyano-3-(3,4′,5′-tris(9-hexyl-9H-carbazol-3-yl)-2,2′-bithiophen-5-yl)acrylic acid (**DH-1**) [19].

Yellow powder, Yield: 85%. ^{1}H NMR (300 MHz, d6-DMSO): δ 8.87 (s, 1H), 8.32 (s, 1H), 7.93 (s, 1H), 7.83 (d, J = 8.1 Hz, 2H), 7.50 (s, 1H), 7.35 (t, J = 7.5 Hz, 4H), 7.10–7.04 (m, 8H), 4.10 (t, J = 7.5 Hz, 2H), 4.05 (t, J = 7.2 Hz, 2H), 1.75–1.69 (m, 4H), 1.42–1.19 (m, 12H), 0.86–0.75 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 151.4, 146.9, 146.7, 146.0, 142.8, 142.2, 128.9, 127.9, 126.93, 125.9, 123.8, 122.9, 122.7, 122.1, 121.3, 118.2, 113.1, 111.8, 108.0, 69.0, 68.7, 31.1, 30.7, 28.3, 28.2, 25.0, 24.8, 21.8, 13.5. MS (ESI-MS): m/Z = 683.6. $C_{42}H_{45}N_5O_4$ (M_w = 683.84): Calcd. C, 73.77; H, 6.63; N, 10.24; Found C, 73.83; H, 7.04; N, 10.67.

2.2.2. 2-cyano-3-(4-(4-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-1H-1,2,3-triazol-1-yl)-2,5-bis(hexyloxy)phenyl)acrylic acid (**DH-S1**)

Orange powder, Yield: 89%. ^{1}H NMR (300 MHz, d6-DMSO): δ 8.92 (s, 1H), 8.56 (s, 1H), 8.02 (s, 1H), 7.63–7.61 (m, 3H), 7.51 (d, J = 3.3 Hz, 1H), 7.46 (d, J = 3.6 Hz, 1H), 7.37 (t, J = 7.8 Hz, 4H), 7.12–7.06 (m, 6H), 7.01 (d, J = 8.4 Hz, 2H), 4.17 (t, J = 6.6 Hz, 2H), 4.05 (t, J = 6.3 Hz, 2H), 1.74 (br, 4H), 1.44–1.24 (m, 12H), 0.89–0.79 (m, 6H). MS (ESI-MS): m/Z = 765.1. $C_{46}H_{47}N_5O_4S$ (M_w = 765.96): Calcd. C, 72.13; H, 6.18; N, 9.14; Found C, 72.12; H, 5.87; N, 8.89.

2.2.3. 2-cyano-3-(4-(4-(5′-(4-(diphenylamino)phenyl)-2,2′-bithiophen-5-yl)-1H-1,2,3-triazol-1-yl)-2,5-bis(hexyloxy)phenyl) acrylic acid (**DH-S2**)

Brown red powder, Yield: 87%. ^{1}H NMR (300 MHz, d6-DMSO): δ 8.96 (s, 1H), 8.55 (s, 1H), 8.02 (s, 1H), 7.61–7.58 (m, 3H), 7.51 (d, J = 3.6 Hz, 1H), 7.41–7.32 (m, 7H), 7.12–7.06 (m, 6H), 7.00 (d, J = 7.5 Hz, 2H), 4.15 (t, J = 8.1 Hz, 2H), 4.10 (t, J = 7.2 Hz, 2H), 1.75 (br, 4H), 1.44–1.24 (m, 10H), 0.87–0.79 (m, 8H). MS (ESI-MS): m/Z = 847.6. $C_{50}H_{49}N_5O_4S_2$ (M_w = 848.09): Calcd. C, 70.81; H, 5.82; N, 8.26; Found C, 70.76; H, 5.69; N, 8.51.

Caution: The organic azides are potentially explosive hazards, they should be stored in a refrigerator and handled with great care!

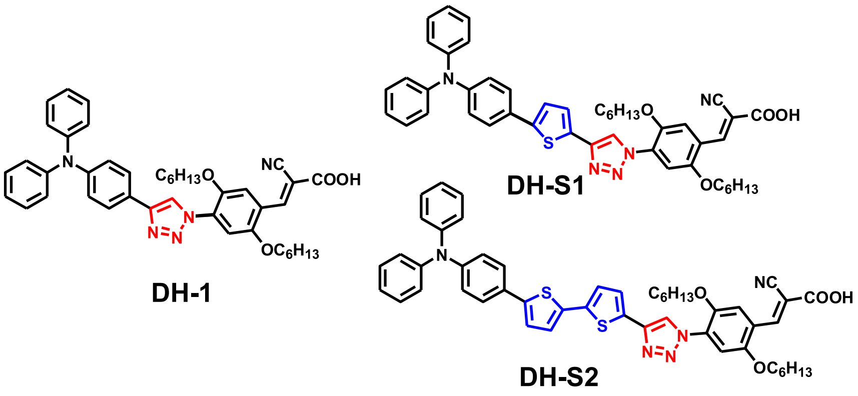

Fig. 1. The molecular structure of **DH-1**, **DH-S1** and **DH-S2**.