



Novel organic dyes with anchoring group of barbituric/thiobarbituric acid and their application in dye-sensitized solar cells



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ABSTRACT

New bi-anchoring donor- π -acceptor metal-free organic dyes based on diphenylamine as donor, and barbituric acid and thiobarbituric acid as the acceptor/anchor were synthesized, characterized and used in dye-sensitized solar cells applications. Among the fabricated dye sensitized solar cells, device based on the diphenylamine as donor, and barbituric acid as the acceptor exhibits a high power conversion efficiency of 1.53% with a short circuit current density of 3.71 mA cm^{-2} , an open-circuit photo voltage of 0.55 V and a fill factor of 0.75% under AM 1.5 illumination (85 mW cm^{-2}) compared to the other fabricated devices. The structure of synthesized dyes was optimized and their electronic structures studied.

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1. Introduction

The supply and demand of energy has been considered as the most significant problem in human life. The energy concerns especially for the next generation led to increased interest and demand for renewable energy sources. One of the promising candidates for them is solar energy that is renewable, clean, and inexhaustible resource.

Dye-sensitized solar cells (DSSCs) have attracted the attention of researchers since they were introduced by O'Regan and Grätzel [1]. Since then, DSSCs have been widely explored as a matter of tremendous interest to academic and commercial researchers due to their low cost fabrication and relatively high conversion efficiencies (>10%) [2–4]. Conventional DSSCs consist of a dye-sensitized mesoporous TiO_2 film interpenetrated by a liquid electrolyte containing an iodine/iodide redox couple [1–4]. In order to further improve the performances of DSSCs, extensive efforts are ongoing for each of its constituent components including nanocrystalline semiconductors [5], dye molecules [6],

electrolytes [7] and counter electrodes [8,9]. After the successful exploration by Grätzel and co-worker [1,10], DSSCs based on Ru-photosensitizers, such as N3 and N719, have been extensively investigated and developed [11,12]. So far, the impressive solar-to-electrical power conversion efficiency values of $\sim 11\%$ have been reported for the Ru sensitizers [11–16]. However, in addition to high cost of rare Ru metal, the ruthenium dyes featuring relatively low molar extinction coefficients and tedious purification processes [12]. Recently, these problems made scientists to think and develop the metal-free organic sensitizers. In the way to overcome these difficulties, great progress has been made in this field; however, reaching higher efficiencies of metal-free sensitizers remained a challenge. Various metal-free organic dyes, such as coumarin [17], indoline [18,19], cyanine [20,21], merocyanine [22], perylene [23], thiophene [24], and fluorine [25,26], have been reported as efficient sensitizers for DSSCs, where the higher molar extinction coefficients of metal-free organic dyes enhanced the net light harvesting. Although, the pure organic dyes have just attracted considerable attention, they do not surpass the conversion efficiency of the Ru-based sensitizers [27]. Enormous studies have been devoted to design novel structural dyes, to clarify the relationship between the structure and properties and to optimize the DSSC devices [28,29]. In the present work, we report the synthesis, exhaustive structural characterization, and

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investigation of the electrochemical, photophysical and photovoltaic properties of four novel organic dyes (**BA**, **TBA**, **DBA** and **DTBA** shown in Fig. 1) based on amine (diphenylamine) framework as donor and barbituric acid and thiobarbituric acid as the acceptor/anchor. In order to reduce the aggregation and enhance the solubility of the sensitizer, the hydrophobic octyl groups [30,31] are attached to the donor group (Fig. 1).

2. Experimental

2.1. Equipments and materials

^1H and ^{13}C NMR spectra were recorded on Bruker 400 Ultra-shield NMR and CDCl_3 or DMSO-d_6 was used as solvent. In some cases, a Bruker Avance ultra shield 500 MHz was used. FT-IR spectra were recorded in the matrix of KBr with a JASCO FT-IR-680 plus spectrometer. Elemental analyses were performed with a Heraeus CHN-O-Rapid analyzer. Mass spectra of the products were obtained with a HP (Agilent Technologies) 5937 Mass Selective Detector. Melting points were measured on an electrothermal KSB1N apparatus. Chemicals were purchased from Aldrich, Fluka and Merck chemical companies.

2.2. Synthesis and characterization of compounds

2.2.1. Synthesis of *N*-octyl-*N*-phenylaniline (**1a**)

Synthesis of this compound was carried out based on a previously reported method with some modifications [32]. 1-Bromo octane (3.926 g, 0.02 mol), phenylaniline (2.0 g, 0.012 mol) and sodium hydroxide (4.0 g, 0.10 mol) were dissolved in dimethylsulfoxide (DMSO) (30 ml), followed by heating at 110°C for 12 h. After cooling to room temperature, the resulting mixture was extracted with ethyl acetate/water and then dried with sodium sulphate (Na_2SO_4). The solvent was evaporated and the resulting liquid was purified by column chromatography on neutral alumina by using hexane as solvent to give a colorless liquid with yield 90.4% (3.1 g). ^1H NMR (500 MHz, CDCl_3 , TMS) δ 7.27–7.24 (m, 4H, Ar), 6.98 (d, $J=7.5$ Hz, 4H, Ar), 6.93 (t, $J=7.5$ Hz, 2H, Ar), 3.67 (t, $J=7.5$ Hz, 2H), 1.68–1.62 (m, 2H), 1.30–1.26 (m, 10H), 0.87 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 148.1, 129.2, 121.0, 120.9, 52.4, 31.8, 29.4, 29.3, 27.5, 27.1, 22.6, 14.1.

2.2.2. Synthesis of 4-(*N*-octyl-*N*-phenylamino)benzaldehyde (**1b**) and 4,4'-(octylazanediyldibenzaldehyde (**1c**)

The compounds **1b** and **1c** were prepared by the previously reported method [33]. Procedure for the synthesis of **1b**: to a

mixture of **1a** (3.12 g, 12.23 mmol) and DMF (40 ml) at 0°C was added POCl_3 (1.2 ml, 12.87 mmol) dropwise with stirring. The resulting mixture was stirred at $95\text{--}100^\circ\text{C}$ under nitrogen for 20 h when TLC analysis showed that no starting material existed. The mixture was then cooled to room temperature, poured into ice-water (150 ml) and neutralized with 4M NaOH solution. The solid was collected, washed with water, and dried. Purification by column chromatography on neutral alumina using a mixture of ethyl acetate/*n*-hexane (1:5, v/v), to give a pale yellow liquid (yield = 75%).

For the synthesis of compound **1c**, freshly distilled POCl_3 (23.1 ml, 25 eq) was added dropwise to DMF (17.6 ml, 23 eq) under an atmosphere of N_2 at 0°C , and then was stirred for 1 h. Compound **1a** (2.5 g, 9.9 mmol) was added to the above solution, and the resulting mixture was stirred for 4 h at 95°C . After cooling to room temperature, the mixture was poured into a beaker containing ice-cube and then basified with 4M NaOH. Afterward, the solid was filtered and extracted with ethyl acetate/brine. After evaporating organic solvent, the crude product was purified by column chromatography on neutral alumina using a mixture of ethyl acetate/*n*-hexane (1:4, v/v), to give a yellow liquid (1.5 g, yield = 49%).

The spectral data for **1b**: FT-IR (cm^{-1}): 2925, 2854, 2728, 1685, 1602, 1587, 1515, 1450, 1384, 1234, 1166, 1027, 821, 700; ^1H NMR (DMSO-d_6 , 400 MHz): 9.67 (s, 1H), 7.65 (d, $J=8.0$ Hz, 2H), 7.48 (t, $J=8.0$ Hz, 2H), 7.31 (t, $J=8.0$ Hz, 1H), 7.24 (d, $J=8.0$ Hz, 2H), 6.73 (d, $J=8.0$ Hz, 2H), 3.73 (t, $J=8.0$ Hz, 2H), 1.53–1.59 (m, 2H), 1.19–1.27 (m, 10H), 0.83 (t, $J=8.0$ Hz, 3H); ^{13}C NMR (DMSO-d_6 , 100 MHz) δ 190.3, 153.3, 145.7, 131.9, 130.6, 127.6, 126.7, 126.4, 113.6, 52.3, 31.7, 29.2, 29.1, 27.2, 26.7, 22.5, 14.4.

The spectral data for **1c**: FT-IR (cm^{-1}): 2925, 2854, 2730, 1693, 1587, 1509, 1369, 1232, 1164, 823; ^1H NMR (DMSO-d_6 , 400 MHz): δ 9.86 (s, 2H), 7.85 (d, $J=8$ Hz, 4H), 7.26 (d, $J=12$ Hz, 4H), 3.90 (t, $J=7.5$ Hz, 2H), 1.56–1.63 (m, 2H), 1.26–1.30 (m, 10H), 0.84 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (DMSO-d_6 , 100 MHz) δ 190.96, 151.34, 131.33, 130.09, 120.55, 51.48, 31.12, 28.65, 28.59, 26.93, 26.11, 22.01, 13.89.

2.2.3. Synthesis of 5-(4-(*N*-octyl-*N*-phenyl amino)benzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**1h**, **BA**)

4-(*N*-Octyl-*N*-phenylamino)benzaldehyde (1.238 g, 4 mmol) **1b** and barbituric acid **1d** (0.512 g, 4 mmol) were dissolved in absolute ethanol (25 ml). The reaction mixture was refluxed for 6 h. The orange solid obtained was filtered and washed with ethanol. The obtained dye **BA** was purified by crystallization from ethyl acetate/hexane. (Yield = 85.2%); m.p. = $209\text{--}211^\circ\text{C}$; FT-IR (cm^{-1}): 3420, 3182, 3044, 2926, 2851, 1728, 1687, 1497, 1485, 1443, 1388, 1308, 1182, 1132, 828, 543; ^1H NMR (DMSO-d_6 , 400 MHz): δ (ppm): 11.13 (s, 1H), 11.00 (s, 1H), 8.36 (d, $J=8.0$ Hz, 2H), 8.14 (s, 1H), 7.54 (t, $J=8.0$ Hz, 2H), 7.39 (t, $J=8.0$ Hz, 1H), 7.32 (d, $J=8.0$ Hz, 2H), 6.70 (d, $J=8.0$ Hz, 2H), 3.81 (t, $J=4.0$ Hz, 2H), 1.57–1.64 (m, 2H), 1.22–1.32 (m, 10H), 0.86 (t, $J=8.0$ Hz, 3H); ^{13}C NMR (DMSO-d_6 , 100 MHz): 164.5, 162.6, 155.1, 152.8, 150.2, 144.4, 138.6, 130.2, 127.4, 126.9, 121.2, 112.7, 110.9, 51.9, 31.1, 28.7, 28.6, 26.9, 26.1, 22.0, 13.9. Mass: $m/z = 419$ ($M+1$), 320, 104, 77. Anal. Calcd. for $\text{C}_{25}\text{H}_{29}\text{N}_3\text{O}_3$: C 71.57, H 6.97, N 10.02, O 11.44; found: C 71.54, H 6.95, N 10.00, O 11.41.

2.2.4. Synthesis of 5-(4-(*N*-octyl-*N*-phenylamino)benzylidene)-2,4,6(1*H*,3*H*,5*H*)-dihydro-2-thioxopyrimidine-4,6(1*H*,5*H*)-dione (**1i**, **TBA**)

It was synthesized according to the procedure of **1h** compound. The obtained product was a light red solid. (Yield = 84.2%); m.p. $206\text{--}208^\circ\text{C}$; FT-IR (cm^{-1}): 3422, 2921, 1649, 1479, 1387, 1184, 515, 446; ^1H NMR (DMSO-d_6 , 400 MHz): δ (ppm): 12.22 (s, 1H), 12.12 (s, 1H), 8.41 (d, $J=8.0$ Hz, 2H), 8.14 (s, 1H), 7.56 (t, $J=8.0$ Hz, 2H), 7.41 (t, $J=8.0$ Hz, 1H), 7.34 (d, $J=8.0$ Hz, 2H), 6.71 (d, $J=8.0$ Hz, 2H), 3.84 (t, $J=8.0$ Hz, 2H), 1.57–1.65 (m, 2H), 1.22–1.32 (m, 10H), 0.86

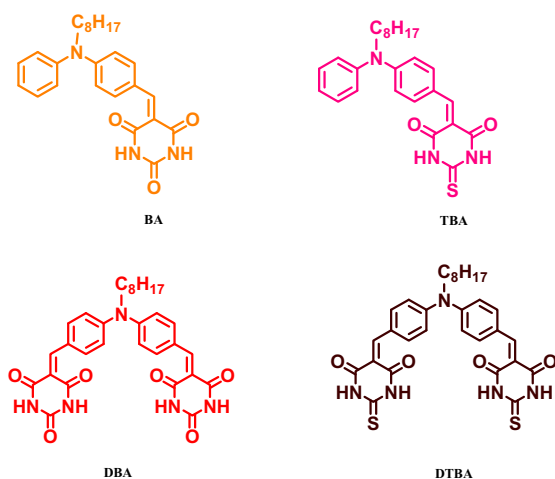


Fig. 1. Molecular structures of **BA**, **TBA**, **DBA** and **DTBA** dyes.

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