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Organic dyes containing fluoreneamine donor and carbazole π-linker for dye-sensitized solar cells

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ABSTRACT

A series of new organic dyes containing fluoreneamine-based donor and carbazole π-spacer are reported. These dyes displayed longer wavelength charge transfer absorption when compared to that of the corresponding phenylamine analogs. Fluoreneamine-based donors shifted the lowest unoccupied molecular orbital upwardly which is beneficial for the injection of electrons from the excited dye into the conduction band of TiO_2 and lowered the oxidation potential of the dyes. The electronic perturbations caused by the fluorene unit have been confirmed by the density functional theoretical calculations. A device fabricated using a dye featuring difluorenylaminocarbazole donor and thiophene in the π-spacer exhibited promising power conversion efficiency (6.4%). The interfacial electron transfer kinetics has been elucidated by electrochemical impedance spectroscopy which showed the beneficial role of difluorenylamine unit in suppressing the electron recombination.

1. Introduction

Organic dyes have been intensively developed in the recent years for application as emitters in organic light-emitting diodes, electron donors in bulk heterojunction solar cells or perovskite solar cells and sensitizers in dye-sensitized solar cells (DSSCs) [1–4]. Organic dyes have also been utilized as semiconductors in thin-film transistors and developed as chromophores possessing unusual non-linear optical properties such as polarizability and two-photon absorption [5,6]. In order for a dye to function as sensitizer in DSSCs, it should possess excellent visible region absorption and facile photo-induced intramolecular charge transfer [4]. Several molecular configurations such as D–π–A, D_1-π-D_2-π-A, A_1-π-D-π-A_1, D–π–A_1-π-A_2 and A_2-π-D-π-A_1 featuring different electron donors (D) and electron acceptors (A) have been found to fulfill the above requirements [7]. For efficient functioning in DSSCs, besides possessing light harvesting capability, the sensitizers also need to inherit special qualities to retard the detrimental processes such as electron recombination and dye-aggregation [4]. Electronic property manipulations were demonstrated for the simple donor-acceptor dyes (D–π–A) by the introduction of additional donor (D_1-π-D_2-π-A) or acceptor (A_2-π-D-π-A_1) [7b–f]. Similarly, for the dianchoring dyes, several chromophoric configurations such as rigid rod (A-π-D-π-A), Y-shape (D-(π-A)$_2$) and H-shape ((D–π–A)$_2$) have been used and their benefits evaluated [8]. In a simple D–π–A configuration, nature of donor and linker segments can be changed to fine-tune the electronic energies or steric requirements [4].

Triarylamine donors are most attractive due to their promising photo- and redox stability [4b]. Triarylamine-based organic dyes containing polyaromatic/heteroaromatic chromophores such as fluorene [9], phenothiazine [10], phenoxazine [11], indoline [12], coumarin [13], cyclopentadithiophene [14], dithienothiophene [15], dithienopyrrole [16], etc. have been developed and found to function as effective sensitizers. Most of the units mentioned above are electron-rich in nature and enhance the charge transfer characteristics by increasing the donor strength of the molecule [10–16]. Also, these electron-releasing groups stabilize the oxidized dye generated due to the electron injection from the dye into the conduction band of TiO_2. Additionally, bulkiness of the polyaromatic chromophore combined with its hydrophobicity is helpful to hinder the close association of the dyes on the surface of TiO_2 and to forbid the approach of polar electrolyte components at the surface of TiO_2 [17]. In this regard, a classic example was provided by Chow and co-workers [18]. They found that replacement

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of diphenylamine unit by naphthylphenylamine in a dye led to significant increase in open circuit voltage (V_{OC}). This is attributed to the effectiveness of naphthylphenylamine in hindering the self-aggregation of the dyes on TiO_2 surface and facile stabilization of the oxidized dye. Thus, the organic dyes containing chromophores featuring sufficient steric bulk and extended conjugation are useful.

Organic dyes containing difluorenylamine donor have been extensively studied. Ko and co-workers for the first time introduced difluorenylamine donor in organic dyes and achieved high power conversion efficiency above 8% [9b]. Grätzel and co-workers further developed dyes based on thieno[3,2-*b*]thiophene linker and difluorenylamine donor and found to possess high molar extinction coefficients for the charge transfer transition [19]. Ko and co-workers reported dyes based on *p*-phenylenevinylene linker and difluorenylamine donor [20]. Organic dyes showing panchromatic absorption and featuring electron-deficient chromophores such as benzo[1,2,5]thiadiazole or squaraine and difluorenylamine donor were also reported [21]. Thomas and co-workers synthesized fluorene-based dyes which showed longer wavelength absorption when compared to dyes containing phenylene linker [22]. The superior efficiency of the fluorene-based dyes is attributed to the difluorenylamine unit which offers strong donating strength, bulky structure which suppresses the aggregation and keeps away the electrolyte from TiO_2 film. The beneficial properties of difluorenylamine unit are due to the following reasons: (1) bulky trigonal structure with rigidity and extended conjugation and (2) the presence of alkyl chains at C9-position. Also, it has been found that light harvesting potential of the dyes containing difluorenylamine donor is largely dependent on the nature of linker which crucially alters the donor-acceptor interactions.

In our earlier report, we successfully demonstrated 2,7-disubstituted carbazole-based sensitizers with promising power conversion efficiencies [23]. We felt that the introduction of difluorenylamine donor in the above design may be beneficial to increment the absorption properties and inhibit the detrimental processes such as electron recombination and molecular aggregation. To test this hypothesis, we have designed and synthesized new organic dyes featuring fluorenylphenylamine and difluorenylamine donors connected to the cyanoacrylic acid acceptor via 2,7-carbazole linker (Fig. 1). We studied the effect of fluorene present in the donor segment on the optical, electrochemical and photovoltaic properties. Introduction of fluorene in the donor moiety red-shifted the charge transfer absorption and imparted redox stability to the dyes. Also suppression of back electron transfer was identified by electrochemical impedance spectroscopy studies attributable to the presence of fluorene unit.

2. Experimental section

2.1. Materials and methods

The precursor chemicals were purchased from commercial sources and used as received. Solvents used in reactions and spectroscopy measurements were dried by following standard distillation methods. Column chromatography purifications were performed on silica gel (230–400 mesh) packed in a column measuring 40 cm long and 3.0 cm diameter. The IR spectra were recorded with a NEXUS FT-IR spectrometer (Thermonicolet) by using KBr pellets. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 3 spectrometer operating at 500.13 and 125.77 MHz respectively. Deuterated chloroform ($CDCl_3$) and dimethyl sulfoxide (DMSO-d_6) were used as solvent and the residual peaks at δ 7.26 and 2.52 for ^1H; 77.0 and 39.5 for ^{13}C, were used to calibrate the chemical shifts. Absorption and emission spectra were measured in spectroscopic grade solvents at room temperature in quartz cuvettes using a Cary 100 spectrophotometer and Shimadzu RF5301 spectrofluorimeter respectively. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using BASi Epsilon electrochemical analyzer. A standard three-electrode assembly containing glassy carbon working electrode, a non-aqueous $Ag/AgNO_3$ reference electrode and a platinum auxiliary working electrode was used. The experiments were performed at room temperature under nitrogen atmosphere in dichloromethane with Bu_4NClO_4 (0.1 M) as supporting electrolyte. The high resolution mass spectra were obtained from a Bruker micrOTOF-QII ESI mass spectrometer in the positive ion mode.

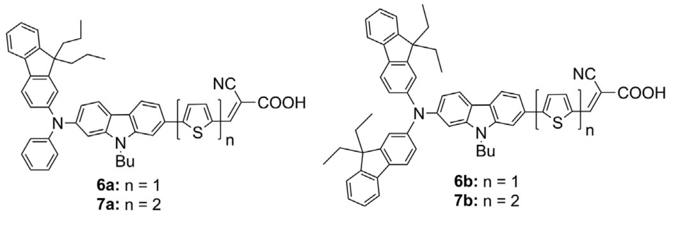

Fig. 1. Structures of the carbazole based dyes.

2.2. Synthesis

The precursors, 2,7-dibromo-9-butyl-9*H*-carbazole [24] (1), 2-bromo-9,9-diethyl-9*H*-fluorene [25] and 9,9-diethyl-9*H*-fluoren-2-amine [26] were synthesized by following the reported procedures.

2.2.1. *N-phenyl-9,9-dipropyl-9H-fluoren-2-amine (**2a**)*

A mixture of 2-bromo-9,9-diethyl-9*H*-fluorene (3.29 g, 10 mmol), aniline (1.12 g, 12 mmol), $Pd(dba)_2$ (0.05 g, 0.20 mmol), dppf (0.06 g, 0.20 mmol), sodium *tert*-butoxide (2.40 g, 25 mmol), and toluene (25 mL) was taken in a pressure tube and heated at 80 °C for 48 h under N_2 atmosphere. After completion of the reaction, the volatiles were removed under vacuum, and the resulting solution extracted with dichloromethane (3 × 60 mL). The combined organic extract was washed with brine solution, dried over Na_2SO_4, and concentrated to leave a yellow solid. Further, the crude product was purified by column chromatography on silica gel by using hexane/dichloromethane mixture (2:1 *v*/*v*) as an eluant. White powder; Yield 2.37 g (70%); mp 77–79 °C; ^1H NMR ($CDCl_3$, 500.13 MHz) δ 7.57–7.61 (m, 2H), 7.27–7.31 (m, 4H), 7.21–7.24 (m, 1H), 7.06–7.10 (m, 3H), 7.05 (dd, *J* = 7.5 Hz, *J* = 2.0 Hz, 1H), 6.91–6.95 (m, 1H), 5.82 (s, 1H), 1.86–1.93 (m, 4H), 0.64–0.73 (m, 10H); ^{13}C NMR ($CDCl_3$, 125.77 MHz) δ 152.5, 150.3, 143.7, 142.3, 141.3, 134.9, 129.5, 126.8, 126.0, 122.8, 120.7, 120.5, 118.9, 117.4, 117.2, 116.9, 113.1, 52.3, 43.0, 17.3, 14.6; HRMS calcd for $C_{25}H_{27}N$ $[M]^+$ *m/z* 341.2138, found 341.2123.

2.2.2. *Bis(9,9-diethyl-9H-fluoren-2-yl)amine (**2b**)*

It was prepared from 2-bromo-9,9-diethyl-9*H*-fluorene (3.01 g, 10 mmol) and 9,9-diethyl-9*H*-fluoren-2-amine (2.84 g, 12 mmol) by following a procedure described above for **2a**. White powder; Yield 2.92 g (64%); mp 160–162 °C; ^1H NMR (DMSO-d_6, 500.13 MHz) δ 8.45 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 4H), 7.05–7.09 (m, 4H), 6.98–7.01 (m, 2H), 6.96 (d, *J* = 1.5 Hz, 2H), 6.85 (dd, *J* = 7.5 Hz, *J* = 2.0 Hz, 2H), 1.73–1.84 (m, 8H), 0.13 (t, *J* = 2.0 Hz, 12H); ^{13}C NMR (DMSO-d_6, 125.77 MHz) δ 150.5, 148.6, 143.1, 141.3, 133.2, 126.8, 125.6, 122.6, 120.7, 118.6, 116.2, 111.1, 55.3, 32.0, 8.5; HRMS calcd for $C_{34}H_{35}N$ $[M]^+$ *m/z* 457.2764, found 457.2745.