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Multifunctional quinoxaline containing small molecules with multiple electron-donating moieties: Solvatochromic and optoelectronic properties

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ABSTRACT

Two multifunctional quinoxaline containing small molecules (designated as: SD-1 and SD-2) composed of electron-donating (D) moieties both in vertical and horizontal directions to an electron-accepting (A) quinoxaline at the central position have been synthesized. In both SD-1 and SD-2, the dimethylaminobenzene (DMAB) and triphenylamine (TPA) groups were used as an electron-donor in the vertical direction, and dihexyloxy-functionalized TPA was adapted as an additional donor in the horizontal direction. The unique donor (D)–acceptor (A) structures around the central quinoxaline moiety impart special solvatochromic and optoelectronic features to the SD-1 and SD-2. Photovoltaic cells (PVCs) and organic light-emitting diodes (OLEDs) were fabricated from SD-1 and SD-2 by solution processing (*i.e.* spin-coating). While PVCs with a structure of ITO/PEDOT:PSS/SD-1 or SD-2:$PC_{71}BM$/Al show the power conversion efficiencies of 0.31% and 0.45%, respectively, OLEDs with a structure of ITO/PEDOT:PSS/SD-1 or SD-2/LiF/Al exhibit a maximum luminance (efficiency) of 7.42 cd/m^2 (0.034 cd/A) and 48.84 cd/m^2 (0.032 cd/A) with a turn-on voltage of 3.6 and 2.4 V, respectively. Furthermore, the Commission Internationale de L'Eclairage (CIE) chromacity coordinates of the OLED device with SD-2 were (0.67, 0.32), which are very close the CIE chromacity coordinates (0.67, 0.33) of National Television Society Committee (NTSC) for red color. Owing to their promising stimuli-responsive properties and device performances, these D–A molecules with unique structures can be considered as good candidates for multifunctional sensory and optoelectronic applications.

1. Introduction

Materials with combined electron-donor (D) and electron–acceptor (A) units connected *via* π-bridge(s) have been extensively studied for last two decades due to their potential applications in nonlinear optics (NLO) [1,2], organic thin film transistors (OTFTs) [3,4], organic light emitting diodes (OLEDs) [5–7], and photovoltaic cells (PVCs) [8–10]. One of the most significant features for the D-π–A molecules is their low band gaps induced by efficient electron delocalization *via* partial intramolecular charge transfer (ICT) between the donor and acceptor units along the conjugated molecular chain [10]. As a consequence, unique solvatochromic properties [11–13] have been observed for certain D–π–A molecules. Various electron donors, such as triphenylamine [14,15] carbazole [16,17] and fluorine [18,19], and acceptors, including benzothiadiazole [20,21] and quinoxaline [14,22,18] have been used for the design and synthesis of various functional D-π-A compounds. Meanwhile, thienyl, vinyl, and phenyl moieties have been utilized as the π-bridge between donor and acceptor units. Due to excellent electron-donating and nonaggregation properties associated with the non-planar molecular configuration [14,15], triphenylamine has been an important donor for many applications. Similarly, quinoxaline has been widely used in conjugated polymers as a strong electron–acceptor because of its high electron affinity originated from the two symmetric nitrogen atoms in the pyrazine ring [23–25].

Recently, solution-processable small molecular semiconductors have received great attention as active materials in optoelectronic devices, such as bulk heterojunction (BHJ) PVCs [26–29] and OLEDs [30–33]. Comparing with polymeric active materials, small molecules have several advantages, including their well-defined mono-dispersed chemical structures for reproducible materials synthesis and device performance as well as straightforward structure and property characterization. More specifically, great improvement in the PVCs power conversion efficiencies (up to 4.4% for diketopyrrollopyrrole (DPP) derivatives [34]) has been

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achieved with D–π–A small molecules since the important work reported by Roncali et al. in 2006 [35–37]. Along with the extensive studies on small molecules with D–π–A structures in PVCs [26–29,34–37], their applications in OLEDs have also been demonstrated to be promising with the recent availability of red emissive small molecules [30–33]. Although several multifunctional polymers, which can be used in PVCs and OLEDs as active materials simultaneously, have been investigated [38–41], there is no report on the multifunctional solution processable small molecules with the same purpose to our best knowledge. Therefore, it is interesting, though still quite challenging, to develop solution-processable small molecules with special D–π–A structures (*e.g.*, **SD-1**, **SD-2**) for optoelectronic device (*e.g.*, PVCs, OLEDs) and other applications.

Herein, we report the synthesis of two model compounds with electron-donating moieties in both vertical and horizontal directions to an electron-accepting quinoxaline core. It has been previously demonstrated that the synthesis of two-dimensional D-A structures around quinoxaline core in both *vertical* and *horizontal* directions and their applications for dye sensitized solar cells (DSSCs) [14] and OPVs [42]. The high population of active components in one molecule and the efficient formation of D-π-A structures through multi-directions are advantageous for optoelectronic applications. Our synthetic strategy involved that the dimethylaminobenzene (DMAB) and TPA connected with phenylene–vinylene linkage were used as donors in vertical direction for **SD-1** and **SD-2**, respectively. Consequently, dihexyloxy-functionalized TPA was adapted as an additional donor in the horizontal direction for both **SD-1** and **SD-2** (Fig. 1). A quinoxaline moiety has been selected as an acceptor due to the strong electron-withdrawing capability of its pyrazine ring and the ease with which structural modifications can be performed on 2 and 3-phenyl rings. In this study, we have investigated the interesting solvatochromic properties of **SD-1** and **SD-2** originated from their unique D-π-A conjugated structures around the quinoxaline central moiety, along with their potential applications in photovoltaic and electroluminescent devices. The observed interesting stimuli-responsive properties and device performance make these newly-synthesized small molecules with unique D–π–A structures attractive for multifunctional applications in various sensing and optoelectronic devices.

2. Experimental

2.1. Materials and measurements

1,2-Bis(4-dimethylaminophenyl)-1,2-ethandione was purchased from TCI. All other reagents and solvents were purchased from Aldrich. The compounds, **1** [43], **3** [14] and **5** [44] (Scheme 1) were synthesized according to literature procedures. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Varian VNMRS 600 spectrometer. UV–vis and photoluminescent spectra were measured using Perkin-Elmer Lambda 35 and LS 35, respectively. Cyclic voltammetry (CV) measurements were performed on a VersaSTAT3 potentiostat (Princeton Applied Research). For the CV measurements, a platinum electrode coated with a thin layer of small molecules and platinum wire were used as working and counter electrode, respectively. Ag wire was used as a pseudo-reference electrode with the ferrocene/ferrocenium redox pair as an external standard.

2.2. Syntheses and characterizations

4-(5,8-Dibromo-2-(4-(dimethylamino)phenyl)quinoxaline-3-yl)-*N*,*N*-dimethylbenzeneamine (**2**). **1** (0.50 g, 1.88 mmol) and 1,2-bis(4-dimethylaminophenyl)-1,2-ethandione (0.56 g, 1.88 mmol) were dissolved in 10 ml toluene and 10 ml acetic acid. The reaction mixture was heated under reflux overnight. After cooling to room temperature, the mixture was poured into distilled water and extracted with chloroform. The organic layer was separated and dried over $MgSO_4$ and filtered. The filtrate was dried on a rotary evaporator and the solid residue was recrystallized from chloroform/ethanol (1/4, v/v) mixture to give 0.71 g (72% yield) of **2** as a yellowish powder. MS (MALDI-TOF) *m*/*z* 524.88, calcd 524.02. ^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm) = 7.75 (s, 2H), 7.71 (d, 4H), 7.67 (d, 4H), 3.01 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) = 153.8, 151.2, 138.7, 131.7, 131.3, 126.1, 123.1, 111.6, 40.2.

***N*-(4-(4-(2-(4-(4-(Diphenylamino)styryl)phenyl)-5)-8-dibromoquinoxaline)-3-yl)-*N*-phenylamine** (**4**). **1** (0.15 g, 0.56 mmol) and **3** (0.42 g, 0.56 mmol) were dissolved in 10 ml toluene and 10 ml acetic acid. The reaction mixture was refluxed overnight. After cooling to room temperature, the mixture was poured into distilled water and extracted with chloroform. The organic layer was separated and dried over $MgSO_4$ and filtered. The filtrate was dried on a rotary evaporator and the solid residue was recrystallized from chloroform/ethanol (1/4, v/v) to give 0.35 g (65% yield) of **4** as an orange powder. MS (MALDI-TOF) *m*/*z* 977.97, calcd 978.81. ^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm) = 7.90 (s, 2H), 7.71 (d, 4H), 7.50 (d, 4H), 7.39 (d, 4H), 7.25–7.28 (m, 8H), 7.11–7.14 (m, 8H), 7.02–7.06 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) = 153.6, 147.7, 147.5, 139.2, 139.0, 136.6, 132.9, 131.0, 130.6, 129.6, 129.3, 127.6, 126.3, 126.1, 124.7, 123.6, 123.3, 123.2.

4-(Bis(4-hexyloxy)phenyl)aminobenzaldehyde 6). Phosphorous oxychloride (1.82 g, 11.72 mmol) was slowly added to dimethyl formamide (1.71 g, 23.40 mmol) at 0 °C. After stirring for 2 h, **5** (5.21 g, 11.70 mmol) in dichloroethane was added in one portion and the mixture was stirred at 90 °C for 2 h. The mixture was poured into ice water and neutralized with 2 M sodium hydroxide. The organic layer was separated and dried over $MgSO_4$ and filtered. The filtrate was dried on a rotary evaporator and the residue was purified by column chromatography (ethyl acetate/hexane, 1/10, v/v) to produce 3.60 g (65% yield) of **6** as a yellowish viscous liquid. MS (MALDI-TOF) *m*/*z* 473.09, calcd 473.29. ^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm) = 9.75 (s, 1H), 7.62 (d, 2H), 7.11 (d, 4H), 6.88 (d, 4H), 6.84 (d, 2H), 3.95 (t, 4H), 1.78 (m, 4H), 1.47 (m, 4H), 1.35 (m, 8H), 0.92 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) = 190.2, 156.9, 154.1, 138.6, 131.4, 128.0, 127.7, 116.7, 115.6, 68.3, 31.4, 29.3, 25.7, 22.6, 14.0.

4-(Hexyloxy)-(*N*-(4-hexyloxy)phenyl)-*N*-(4-vinylphenyl)benzenamine (7). Potassium *t*-butoxide (0.71 g, 6.33 mmol) was added to methyltriphenylphophonium iodide (2.86 g, 6.32 mmol) solution in 20 ml dry THF. After stirring for 15 min at room temperature, **6** (1.5 g, 3.17 mmol) in 10 ml dry THF was added dropwise. The solution was further stirred at room temperature for 6 h. Finally, the solid by-product was removed by filtration and the filtrate was concentrated and purified by column chromatography (ethyl acetate/hexane, 1/15, v/v) to produce 1.19 g (80% yield) of **7** as a yellow viscous liquid. MS (MALDI-TOF) *m*/*z* 471.13, calcd 471.31. ^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm) = 7.21 (d, 2H), 7.03 (d, 4H), 6.87 (d, 2H), 6.81 (d, 4H), 6.62 (q, 1H), 5.57 (q, 1H), 5.08 (q, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) = 154.4, 147.5, 139.6, 135.3, 128.8, 125.8, 125.5, 119.3, 114.2, 109.9, 67.2, 30.5, 28.3, 24.7, 21.6, 13.0.

***N*-(4-((1E)-2-(5-(Bis(4-(hexyloxy)phenyl)amino)styryl)-2,3-bis(4-(dimethylamino)phenyl)quinoxaline-8-yl)vinyl)phenyl)-4-(hexyloxy)-*N*-(4-(hyxyloxy)phenyl)benzenamine (SD-1)**. **2** (0.10 g, 0.19 mmol), **7** (0.19 g, 0.40 mmol), palladium acetate (0.003 g, 0.01 mmol), potassium carbonate (0.067 g, 0.38 mmol), and tetra-*n*-butylammoniumbromide (0.062 g, 0.19 mmol) were mixed with 9 ml dry DMF. After degassing for 30 min with Ar, the mixture was heated under Ar at 90 °C for 2 days. The resultant black