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Synthesis, characterization and optoelectronic properties of pyrrolopyrazine based Y-shaped color-tunable dipolar molecules

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ABSTRACT

A regioselective approach for the synthesis of functionalized dipolar Y-shaped chromophores is demonstrated. A series of dipolar pyrrolopyrazine based molecules were prepared in a straightforward manner. The key step in the preparation of the chromophores involves two-fold Sonogashira coupling reaction between the pyrrolopyrazine core and acetylene derivatives. Different electron-donors, including, NH_2, NMe_2, OMe and CF_3, CN acceptors were incorporated into the chromophores. By adjusting the substituents at 2, 3, and 6-position of the pyrrolopyrazine, dipolar tunable molecules with wide emission band are synthesized. The optical, thermal, and electrochemical properties of the materials are analysed and the results are supported with the DFT calculations. The preliminary studies of these engineered Y-shaped molecules indicate their potential as new building blocks in the fields of optoelectronic devices.

1. Introduction

The design and synthesis of functionalized tunable organic chromophores has been an area of great interest [1–5]. The ability to tune the optical property of an organic material is vital in designing light-emitting diodes [6–8], bioimaging probes [9], photoelectric devices [10], sensors [11–15] and nonlinear optical materials [16,17], mainly in the visible region. Various strategies have been established to achieve full color emitting materials which are based on intramolecular charge-transfer (ICT). Such strategies are used while designing novel fluorescent molecules. Recently, the introduction of a donor-acceptor moiety has played a crucial role in organic electronics based on ICT [18–21]. Furthermore, much effort has been devoted to develop highly efficient host materials [22]. Nevertheless, achieving a tunable material for high-performance devices remains a challenge. Moreover, understanding the structure property relationship is topic of on-going interest. The donor-acceptor interaction generates low energy molecular orbitals [21], which accounts for the unique properties of chromophores and plays a significant role in constructing tunable organic molecules that can exhibit a wide range of emission.

Pyrazine is a versatile fragment capable of acting as a powerful electron-withdrawing group. Besides their medical use, pyrazine derivatives have application in dye sensitized solar cells [23,24], luminescent materials [25], semiconductors [26–29], and sensors [30]. Due to its π-deficient aromatic character, the pyrazine scaffold can be used as an electron acceptor and a π-conjugated system. As the backbone pyrazine core can induce luminescent properties [31,32]. The ability of protonation, hydrogen bond formation and chelation of the nitrogen atom of pyrazine is of significant importance, and such derivatives could be used in sensors, as these chromophores are highly sensitive to acid and base. Linear structures incorporating pyrazine moieties exhibit interesting emission properties [32,33], in addition V-shaped [34] and T-shaped [35] structures with a pyrazine central core have also been reported as being good fluorescent chromophores. Pyrrole containing chromophores as π-bridge, were also found to show enhanced optical properties [36], which is attributed to the higher electron density in the pyrrole moiety. Pyrrolopyrazine based dipolar molecules would therefore exhibit interesting optical properties when functionalized with a strong donor and acceptor.

Continuing with the molecular engineering around the pyrazine core, we felt it would be worth preparing D-π-A molecules with a pyrrolopyrazine moiety. In this study, we designed a series of Y-shaped chromophores (push-push-pull) to investigate the influence of covalent donor and acceptor groups. Classical D-A moieties (NMe_2, NH_2, OMe, CF_3, and CN) have been introduced to tune the emitting color [37,38]. The functional groups were introduced at the 2, 3, and 6-positions of the pyrrolopyrazine moiety via Sonogashira cross-coupling reaction. We observed distinct optical properties in the solution. Broad and tunable emissions, from blue to yellow wavelengths, were achieved in a CH_2Cl_2 solution. The optical, thermal, electronic, and theoretical calculations indicate that this Y-shaped chromophore has potential for the design of full-color organic electrochromic devices and widens their scope as advanced functional materials.

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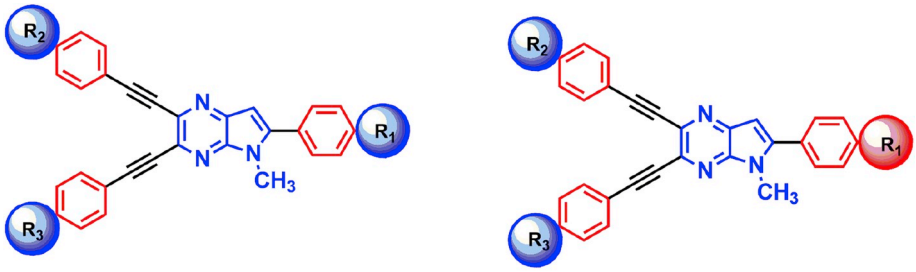

6a = $R_1 = R_2 = R_3 = H$
6b = $R_1 = R_2 = R_3 = OMe$
6c = $R_1 = R_2 = OMe$ $R_3 = NMe_2$
6d = $R_1 = R_2 = R_3 = NH_2$

6e = $R_1 = CF_3$ $R_2 = R_3 = NMe_2$
6f = $R_1 = CF_3$ $R_2 = R_3 = NH_2$
6g = $R_1 = CF_3$ $R_2 = R_3 = OMe$
6h = $R_1 = CN$ $R_2 = R_3 = OMe$

Fig. 1. Chemical structure of Y-shaped chromophore **6(a–h)**.

2. Experimental section

2.1. Materials and instrumentation

All chemicals used for synthesis were purchased from Sigma-Aldrich. NMR spectra measurements were carried out using Bruker 500 MHz for ^{1}H NMR and 126 MHz for ^{13}C NMR, using chloroform-d as the solvent. Chemical shifts were reported as δ (ppm) relative to a deuterated solvent as an internal reference and coupling constants (J) are reported in hertz (Hz). High-resolution mass spectrometry (HRMS) was performed using a 6550 iFunnel Q-TOF LC/MS system. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with the TGA 3 plus and DSC 2 STAR system, respectively, under nitrogen with a heating rate of 10 °C min^{-1}. UV–Vis spectra were recorded using the Varian cary-50 spectrophotometer. Fluorescence spectra were recorded using standard 1 cm quartz cells on Cary Eclipse Fluorescence Spectrophotometer (excitation slit 5 nm). The spectra were recorded by using freshly prepared dilute solution. Compounds were excited at their absorption maxima. Cyclic voltammetry (CV) was performed with a conventional three electrode configuration, Pt as a working electrode, Pt wire as a counter electrode and Ag wire as reference. Ferrocene was used as an internal standard at a scan rate of 50 mV s^{-1}. 0.1 M tetrabutyl ammonium hexafluorophosphate electrolyte was prepared in CH_2Cl_2. Single crystal X-ray analysis was performed using the Bruker D8 Discover X-ray Diffractometer.

2.2. Synthetic procedures

3-((4-aminophenyl)ethynyl)-5-bromo-6-chloropyrazin-2-amine (2e). To a solution of 3,5-dibromo-6-chloro-pyrazin-2-amine (3.0 g, 10.5 mmol) in anhydrous THF (60 mL) under nitrogen atmosphere, Pd$(PPh_3)_2Cl_2$ (0.74 g, 1.05 mmol), CuI (0.3 g, 1.05 mmol), TEA (3.2 mL, 30 mmol), were added subsequently. Then 4-ethynylaniline (1.53 mL, 10.5 mmol) was added and stirred for 2.5 h at RT. The reaction mixture was diluted with water and extracted with CH_2Cl_2, then the organic layer was concentrated in vacuum dried over anhydrous $MgSO_4$, then purified by silica column chromatography (25% EA/hexane) to afford the desired compound. Yield: 2.7 g (79%); brown powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 5.26 (s, 1H), 3.99 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.14, 153.08, 148.17, 144.86, 133.65, 123.96, 114.66, 109.80, 99.76, 81.06. LC-MS (ESI): m/z = 323 $[M+2]^+$.

4-(2-bromo-3-chloro-5*H*-pyrrolo [2,3-*b*] pyrazin-6-yl)aniline (3e). To a stirred solution of *t*-BuOK (1.87 g, 16 mmol) in NMP (20 mL), 3-((4-aminophenyl)ethynyl)-5-bromo-6-chloropyrazin-2-amine (2.7 g, 8.3 mmol) (dissolved in NMP) was added drop wise under nitrogen. The reaction mixture was heated at 70 °C for 2 h. The reaction mixture is then cooled to RT and diluted with CH_2Cl_2 and water. Organic layer washed with excess water and dried over anhydrous $MgSO_4$, filtered and concentrate to give the desired compound. The crude product was used directly without further purification. Yield: 2.3 g (85%); brown powder; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.56 (s, 1H), 7.70 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 1.6 Hz, 1H), 6.67 (d, J = 8.7 Hz, 2H), 5.75 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.33, 148.12, 141.00, 140.68, 136.90, 129.57, 128.03, 117.32, 114.22, 93.94. LC-MS (ESI): m/z = 323 $[M+2]^+$.

4-(2-bromo-3-chloro-5-methyl-5*H*-pyrrolo [2,3-*b*] pyrazin-6-yl) aniline (4e). 4-(2-bromo-3-chloro-5*H*-pyrrolo[2,3-*b*]pyrazin-6-yl)aniline (2.3 g, 7.1 mmol) was dissolved in DMF (40 mL) at 0 °C. NaH (0.28 g, 7.1 mmol) is added carefully under nitrogen and stirred for 30 min followed by addition of MeI (0.43 mL, 7.1 mmol) stirring continued for 2 h. The reaction mixture is quenched in ice-cold water and the precipitate is collected by vacuum filtration. The crude product is dissolved in EA and purified by silica gel column chromatography (20% EA/hexane). Yield: 2.1 g (87%); yellow crystals. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 8.7 Hz, 2H), 6.8 (d, J = 8.7 Hz, 2H), 6.58 (s, 1H), 3.97 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.90, 147.84, 140.36, 139.11, 138.65, 130.78, 130.38, 120.18, 114.94, 98.76, 30.26. LC-MS (ESI): m/z = 337 $[M+2]^+$.

2.2.1. General method: sonogashira cross-coupling reaction

5-methyl-6-phenyl-2,3-bis(phenylethynyl)-5*H*-pyrrolo [2,3-*b*] pyrazine (6a). 2-bromo-3-chloro-5-methyl-6-phenyl-5*H*-pyrrolo[2,3-*b*] pyrazine **(4a)** (300 mg, 0.93 mmol) was dissolved in DMF (8 mL). TEA (5.6 mmol), CuI (0.09 mmol), $Pd(PPh_3)_2Cl_2$ (0.09 mmol) and phenylacetylene (2.3 mmol) were subsequently added. The reaction mixture refluxed at 120 °C for 2 h under microwave condition. After cooling, the reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layer was concentrated in a vacuum and dried over $MgSO_4$. The resulting residue was purified using column chromatography. Repeated purification was required as a single cross-coupled product (**5a**) also formed in the reaction, which was also separated and characterized by NMR in a few compounds. Yield: 75 mg (41%); pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (m, 4H), 7.60 (d, J = 6.9 Hz, 2H), 7.55 (d, J = 6.8 Hz, 1H), 7.54–7.50 (m, 2H), 7.38 (d,