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Dipicolylamine styryldiazine derivatives: Synthesis and photophysical studies

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ABSTRACT

Different D–π–A push–pull molecules in which dipicolylamine (DPA) is used as the donor group, different diazines as the acceptor groups, and styryl as the π-conjugated spacer have been synthesized in a straightforward manner by aldol condensation of 4-(di-2-picolylamino)benzaldehyde and the appropriate methyldiazine. All of the compounds showed π–π* transitions in the UV or visible region and the emission of yellow-green light upon irradiation. Significant red shifts were observed in the fluorescence emission maxima of these compounds on increasing the solvent polarity, a finding that suggests the formation of an intramolecular charge-separated emitting state that is also supported by semi-empirical calculations. In some cases, protonation led to marked color changes, thus showing the ability of these molecules to function as colorimetric pH sensors. The DPA and diazine units can act as coordination sites for metal cations such as Zn^{2+}, Cd^{2+} or Hg^{2+}, leading to a blue or red shift in the fluorescence spectra due to the change in the intramolecular charge transfer properties. This phenomenon could become a powerful tool for the creation of multiple emission colors with a single molecule after suitable design.

1. Introduction

During the past decade, donor–π–acceptor (D–π–A) push–pull systems that incorporate diazine rings as electron-attracting units have been widely studied for their luminescence and non-linear optical properties [1]. The fluorescence of these molecules relies heavily on the nature of the donor and acceptor parts, and it can be easily modulated by several external stimuli. For example, diazine derivatives have been developed as fluorescent sensors for polarity [2], pH [2a,c,e,3], metal cations [4], proteins [5] and particular forms of DNA [6]. Most recently, 1,3-benzodiazine (quinazoline) units were used as electron-deficient segments in D–π–A dyes that displayed solid-state white photoluminescence (PL) and electroluminescence (EL) by doping a certain amount of acid into thin films, which has a potential application in the fabrication of white organic light emitting diodes (OLEDs) [7].

In general, D–π–A push–pull systems are highly sensitive to metal coordination, which can occur not only in the acceptor part of the molecule but also in the donor part [8]. Binding in the A unit leads to a red shift in the emission spectra due to stronger stabilization of the LUMO than the HOMO, which results in a lower HOMO–LUMO energy gap. In contrast, interaction with the D unit results a blue shift of the fluorescence because the metal coordination stabilizes the HOMO more strongly than the LUMO. Of particular interest are molecules that possess metal-binding sites on both the electron-donor and -acceptor parts because such systems can show multiple fluorescence colors in response to several metal cation inputs [9]. In this context, Shiraishi et al. described a styrylquinoline dye with a dipicolylamine (DPA) moiety that showed multicolor fluorescence upon addition of different metal cations. For the first time, near white fluorescence was created by the addition of a mixture of Cd^{2+} and Pb^{2+} in an appropriate ratio [8a].

The diazine ring is an excellent candidate to be incorporated in such structures because of its high electron-withdrawing character and potential ligand properties. Thus, taking advantage of our experience in the synthesis of arylvinyl (styryl) diazines and benzodiazines [2a,b,e,6a,10], we report here the straightforward preparation of a series of D–π–A push–pull molecules in which DPA is used as a donor group and different diazine-based groups [pyridazine, pyrimidine, pyrazine, quinoxaline and di(pyridin-2-yl) pyrimidine] are used as acceptors. The DPA group is a strong

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electron donor that can act as a coordination site for metal cations and this unit has been widely used for the design of new fluorophores [8a,11]. On the other hand, we previously showed that 4-arylvinyl-2,6-di(pyridyn-2-yl)pyrimidines can coordinate various metal cations, such as Zn^{2+}, Sn^{2+} and Ca^{2+}, to give a red-shifted emission [12].

The photophysical properties of the prepared compounds are also reported, including solvatochromism and the effect that treatment with acid and selected metal cations (Zn^{2+}, Cd^{2+}, Hg^{2+}) has on the luminescence properties.

2. Experimental

2.1. General

4-(Di-2-picolylamino)benzaldehyde (**1**) [13] and 4-methyl-2,6-dipyridin-2-yl-pyrimidine [10e] were obtained as described previously. In air- and moisture-sensitive reactions, all glassware was flame-dried and cooled under nitrogen. NMR spectra were acquired at room temperature on a Bruker AC-300 spectrometer. Chemical shifts are given in parts per million relative to TMS (^{1}H, 0.0 ppm) and $CDCl_3$ (^{13}C, 77.0 ppm). Acidic impurities in $CDCl_3$ were removed by treatment with anhydrous K_2CO_3. High resolution mass analyses were performed at the "Centre Regional de Mesures Physiques de l'Ouest" (CRMPO, University of Rennes1) using a Bruker MicroTOF-Q II apparatus. UV/vis spectra were recorded on a Jasco V-530 spectrophotometer using standard 1 cm quartz UV cells. Fluorescence spectra were recorded on a Jasco FP-750 spectrofluorimeter. Compounds were excited at their absorption maxima (band of lowest energy) to record the emission spectra. The Φ_F values were calculated using a well-known procedure with two different standards, quinine sulfate in 0.1 M H_2SO_4 and 9,10-diphenylanthracene in cyclohexane [14]. Stokes shifts were calculated by considering the lowest energetic absorption band.

2.2. General procedure for the synthesis of arylvinyldiazine (styryldiazines)

4-(Di-2-picolylamino)benzaldehyde (**1**) (110 mg, 0.36 mmol) and the appropriate methyldiazine derivative (0.72 mmol; 0.36 mmol for 4-methyl-2,6-dipyridin-2-yl-pyrimidine; 0.18 mmol for 4,6-dimethylpyrimidine) were dissolved in anhydrous THF (15 mL). K^{t}BuO (1.44 mmol, 161 mg, 4 eq.) was slowly added at room temperature and the solution was heated under reflux for 15 h. The mixture was allowed to cool and water was added. THF was evaporated and the mixture was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was removed under vacuum. The crude product was purified by flash chromatography.

2.2.1. 4-[2-(4-Di-2-picolylaminophenyl)vinyl]pyrimidine ***2a***

The crude product was purified by flash chromatography (alumina, eluent:petroleum ether/ethyl acetate 1:1). Orange solid: 61% (82 mg). Mp: 144–145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.87 (s, 4H), 6.73 (d, 2H, J = 8.7 Hz), 6.81 (d, 1H, J = 15.9 Hz), 7.20 (d, 1H, J = 2.1 Hz), 7.25–7.23 (m, 4H), 7.42 (d, 2H, J = 8.7 Hz), 7.67–7.61 (m, 2H), 7.76 (d, 1H, J = 15.9 Hz), 8.63–8.56 (m, 3H), 9.07 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 162.9 (C), 158.1 (C), 156.8 (CH), 149.81 (CH), 149.76 (CH), 149.4 (C), 137.5 (CH), 136.9 (CH), 129.4 (CH), 124.7 (C), 122.3 (CH), 121.2 (CH), 120.8 (CH), 118.0 (CH), 112.7 (CH), 57.2 (CH_2). HRMS (ESI/ASAP): m/z calculated for $C_{24}H_{22}N_5$ $[M+H]^+$ 380.1875, found 380.1882.

2.2.2. 4-[2-(4-Di-2-picolylaminophenyl)vinyl]-2,6-dipyridin-2-yl-pyrimidine ***2b***

The crude product was purified by flash chromatography (alumina, eluent:ethyl acetate/isopropanol 9:1) followed by crystallization from CH_2Cl_2/n-heptane. Orange solid: 64% (123 mg). Mp: 84–86 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.90 (s, 4H), 6.75 (d, 2H, J = 8.4 Hz), 7.26–7.17 (m, 5H), 7.43 (t, 2H, J = 6.0 Hz), 7.51 (d, 2H, J = 8.4 Hz), 7.67 (t, 2H, J = 7.5 Hz), 7.97–7.88 (m, 3H), 8.44 (s, 1H), 8.64–8.62 (m, 2H), 8.77–8.67 (m, 3H), 8.90 (d, 1H, J = 4.2 Hz). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 165.6 (C), 163.4 (C), 163.0 (C), 158.2 (C), 155.6 (C), 154.5 (C), 150.0 (CH), 149.8 (CH), 149.4 (CH), 149.3 (C), 137.6 (CH), 137.0 (CH), 136.9 (CH), 136.8 (CH), 129.4 (CH), 125.2 (CH), 125.2 (C), 124.5 (CH), 123.9 (CH), 122.8 (CH), 122.2 (CH), 122.1 (CH), 120.8 (CH), 112.6 (CH), 112.2 (CH), 57.2 (CH_2). HRMS (ESI/ASAP): m/z calculated for $C_{34}H_{28}N_7$ $[M+H]^+$ 534.2406, found 534.2413.

2.2.3. 2-[2-(4-Di-2-picolylaminophenyl)vinyl]pyrazine ***2c***

The crude product was purified by flash chromatography (alumina, eluent:petroleum ether/ethyl acetate 1:1). Yellow solid: 63% (85 mg). Mp: 150–151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.87 (s, 4H), 6.72 (d, 2H, J = 8.7 Hz), 6.91 (d, 1H, J = 15.9 Hz), 7.24–7.17 (m, 4H), 7.42 (d, 2H, J = 8.7 Hz), 7.65–7.59 (m, 3H), 8.31 (d, 1H, J = 2.4 Hz), 8.46 (d, 1H, J = 2.4 Hz), 8.55 (s, 1H), 8.62–8.60 (m, 2H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 158.3 (C), 149.8 (CH), 149.0 (C), 144.1 (CH), 143.4 (CH), 142.0 (C), 141.4 (CH), 136.9 (CH), 135.1 (CH), 128.8 (C), 125.3 (CH), 122.2 (CH), 120.8 (CH), 119.9 (CH), 112.7 (CH), 57.3 (CH_2). HRMS (ESI/ASAP): m/z calculated for $C_{25}H_{22}N_5$ $[M+H]^+$ 380.1875, found 380.1880.

2.2.4. 2-[2-(4-Di-2-picolylaminophenyl)vinyl]quinoxaline ***2d***

The crude product was purified by flash chromatography (alumina, eluent:petroleum ether/ethyl acetate 1:1). Yellow solid: 84% (129 mg). Mp: 112–113 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.88 (s, 4H), 6.75 (d, 2H, J = 8.7 Hz), 7.13 (d, 1H, J = 15.9 Hz), 7.21–7.18 (m, 2H), 7.27–7.24 (m, 2H), 7.48 (d, 2H, J = 8.7 Hz), 7.68–7.62 (m, 4H), 7.75 (d, 1H, J = 15.9 Hz), 8.03–7.99 (m, 2H), 8.62–8.60 (m, 2H), 8.97 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 158.2 (C), 151.4 (C), 149.9 (CH), 149.2 (CH), 144.5 (CH), 142.6 (C), 141.2 (C), 136.9 (CH), 136.4 (CH), 130.1 (CH), 129.1 (CH), 128.9 (CH), 128.6 (CH), 125.3 (C), 122.2 (CH), 121.2 (CH), 120.8 (CH), 112.7 (CH), 57.2 (CH_2). HRMS (ESI/ASAP): m/z calculated for $C_{28}H_{23}N_5Na$ $[M+Na]^+$ 452.1851, found 452.1851.

2.2.5. 3-[2-(4-Di-2-picolylaminophenyl)vinyl]pyridazine ***2e***

The crude product was purified by flash chromatography (alumina, eluent:petroleum ether/ethyl acetate 1:1). Yellow solid: 64% (86 mg). Mp: 171–172 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.88 (s, 4H), 6.74 (d, 2H, J = 8.7 Hz), 7.13 (d, 1H, J = 16.2 Hz), 7.22–7.18 (m, 2H), 7.37 (dd, 1H, J_1 = 4.8 Hz, J_2 = 8.7 Hz), 7.44 (d, 2H, J = 8.7 Hz), 7.59–7.54 (m, 2H), 7.68–7.62 (m, 2H), 8.62–8.61 (m, 2H), 8.97 (dd, 1H, J_1 = 1.5 Hz, J_2 = 4.8 Hz). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 159.0 (C), 158.9 (C), 158.3 (C), 149.8 (CH), 148.5 (CH), 136.9 (CH), 135.0 (C), 128.9 (CH), 126.2 (CH), 125.2 (C), 123.4 (CH), 122.2 (CH), 121.0 (CH), 120.8 (CH), 112.7 (CH), 57.3 (CH_2). HRMS (ESI/ASAP): m/z calculated for $C_{24}H_{22}N_5$ $[M+H]^+$ 380.1875, found 380.1879.

2.2.6. 4,6-Bis[2-(4-di-2-picolylaminophenyl)vinyl]pyrimidine ***3***

The crude product was purified by flash chromatography (alumina, eluent:petroleum ether/ethyl acetate 1:1). Orange solid: 52% (64 mg). Mp: 110–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.87 (s, 8H), 6.72 (d, 4H, J = 8.7 Hz), 6.80 (d, 2H, J = 15.9 Hz), 7.10 (s, 1H), 7.22–7.18 (m, 8H), 7.42 (d, 4H, J = 8.7 Hz), 7.66–7.60 (m, 4H), 7.73 (d, 2H, J = 15.9 Hz), 8.61–8.59 (m, 4H), 8.95 (s, 1H). ^{13}C NMR and JMOD (75 MHz, $CDCl_3$): δ 163.0 (C), 158.2 (C), 149.2 (C), 136.9 (CH), 136.6