Dyes and Pigments 136 (2017) 480–487

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Full color emissions based on intramolecular charge transfer effect modulated by formyl and boron-dipyrromethene moieties

Xiaodong Wei [a, 1], Lulu Bu [a, 1], Xin Li [b], Hans Ågren [b], Yongshu Xie [a, *]

[a] Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Meilong 130, Shanghai, 200237, China
[b] Department of Theoretical Chemistry and Biology, School of Biotechnology, KTH Royal Institute of Technology, Stockholm, Sweden

ARTICLE INFO

Article history:
Received 16 August 2016
Received in revised form
31 August 2016
Accepted 31 August 2016
Available online 1 September 2016

Keywords:
Boron-dipyrromethenes
Intramolecular charge transfer
Full color emission

ABSTRACT

From the simple one-pot Vilsmeier formylation of 9-diphenylaminoanthracence, mono-, di- and tri-formyl products were successfully synthesized and the yields for the individual products can be optimized by varying the equivalents of the Vilsmeier reagent and changing the reaction temperature. The four obtained aldehydes exhibit distinct optical properties, with the emission maxima varying in a large wavelength range of 455–593 nm, despite their similar structures. The intramolecular charge transfer effect can be effectively modulated by varying the numbers and positions of the formyl groups, resulting in the observed distinct optical properties. Based on the aldehydes, the corresponding boron-dipyrromethenes were also synthesized. Similarly, the intramolecular charge transfer effect and the optical properties can be effectively modulated by the numbers and positions of the boron-dipyrromethene moieties. To further modulate the intramolecular charge transfer effect and red shift the emission, the dimethoxy-substituted 9-diphenylaminoanthracence was also used for synthesizing the corresponding aldehyde and boron-dipyrromethene. Thus, full color emissions within the wavelength range of 455–704 nm were successfully achieved based on modulating the intramolecular charge transfer.

1. Introduction

Developing high performance organic fluorescent dyes is of great importance because of their wide applications in biomedical and materials science, such as living cell fluorescent imaging, biosensors and organic light-emitting diodes (OLEDs) [1–20]. Among various approaches for achieving this goal, modulation of intramolecular charge transfer (ICT) effects of the dyes has been intensively investigated because of the easy design and effective modulation of the absorption and emission of various luminophores [21–32]. However, in these cases, the ICT effects are modulated by successively introducing various electron donating and withdrawing substituents into certain fluorophores, which usually requires tedious synthetic procedures. In this work, starting from the well known 9-diphenylaminoanthracene [33–38], its multiple reactive sites were employed for introducing electron withdrawing formyl groups. Thus, through a simple one-pot Vilsmeier reaction, four mono-, di- and tri-formyl products (**1a**-**4a,** Scheme 1) were successfully synthesized.

It is noteworthy that the ICT effect can be effectively modulated simply by varying the numbers and positions of the formyl groups, and thus the emission behavior can be effectively modulated. To further elucidate the effect of ICT on the emission behavior, the monoaldehyde **5a** was also synthesized. Furthermore, all the aldehydes were used for synthesizing the corresponding boron-dipyrromethenes (BODIPYs **1b**-**5b**) (Scheme 2), which further modulate the ICT effect and the emission behavior. Thus, full color emissions were successfully achieved.

2. Experimental section

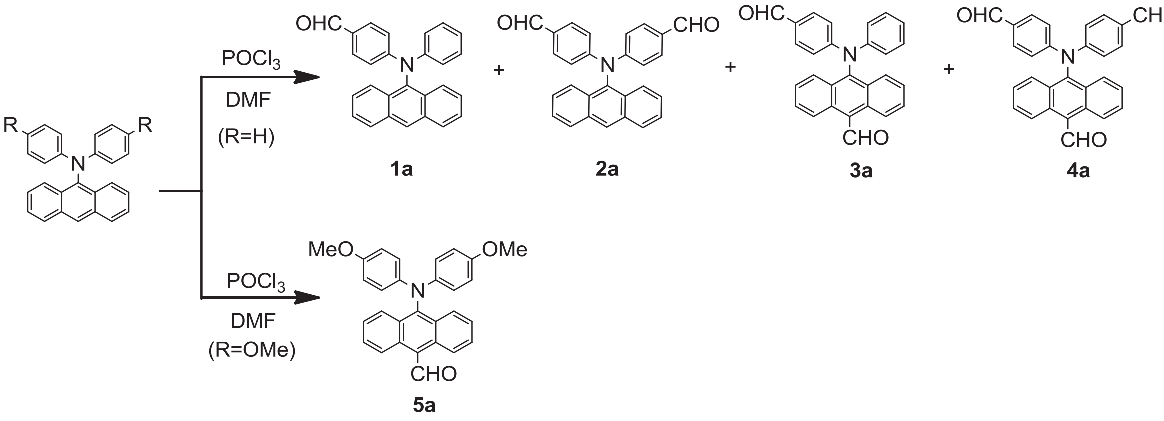
2.1. Materials and instrumentation

Commercially available solvents and reagents were used as received. Deuterated solvents for NMR measurements were available from Aldrich. 9-diphenylaminoanthracence (**A**) and 9-bis(4-methoxyphenyl)aminoanthracene (**B**) were synthesized according

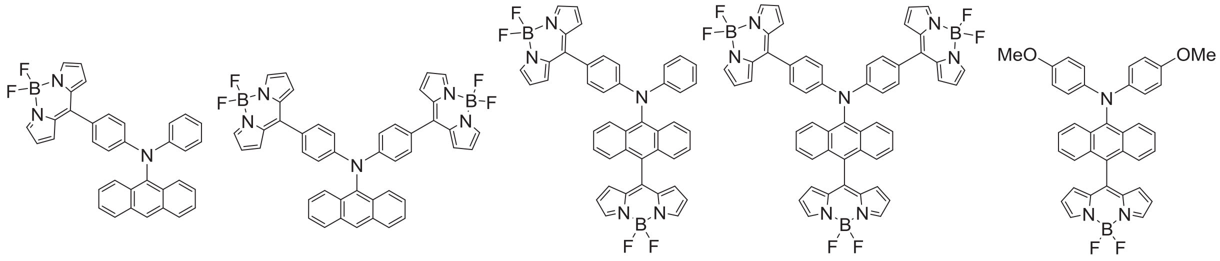
---

* Corresponding author.
E-mail address: yshxie@ecust.edu.cn (Y. Xie).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.dyepig.2016.08.069



Scheme 1. Preparation of the aldehydes.



Scheme 2. Chemical structures of the BODIPYs.

to the reported procedures [39–44]. UV-vis absorption spectra were recorded on a Varian Cary 100 spectrophotometer and fluorescence spectra were recorded on a Varian Cray Eclipse fluorescence spectrophotometer, with a quartz cuvette (path length = 1 cm). ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker AM 400 spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were carried out on a Waters LCT Premier XE spectrometer. Column chromatography was carried out in air using silica gel (200–300 mesh). The reactions were monitored by thin-layer chromatography.

2.2. UV-vis absorption spectra measurements

The absorption spectra of **1a**-**5a**, **A** and **B** (10 μM) were measured at 25 °C in dichloromethane. The absorption spectra of **1b**-**5b** (10 μM) were measured at 25 °C in toluene.

2.3. Fluorescence emission spectra measurements

The fluorescence emission spectra of **1a**-**5a**, **A** and **B** (10 μM) were measured at 25 °C in dichloromethane with excitation at 373 nm for **A**, 378 for **B**, 349 nm for **1a**, 375 nm for **2a**, 345 nm for **3a**, 367 nm for **4a** and 401 nm for **5a**. The fluorescence emission spectra of **1b**-**5b** (10 μM) were measured at 25 °C in toluene with excitation at 502 nm for **1b**, 504 nm for **2b**, 503 nm for **3b**, 504 nm for **4b** and 508 nm for **5b**. The slit width was 5 nm, and the PMT voltage was 600 V except that a PMT voltage of 800 V was used for **5b**.

2.4. Quantum yield measurements

The relative fluorescence quantum yields were determined using optically matching solutions of 9,10-bis(phenylethynyl) anthracene ($\Phi_f = 1$ in cyclohexane) [45], rhodamine 6G ($\Phi_f = 0.95$ in ethanol) [46], and tetraphenylporphyrin ($\Phi_f = 0.11$ in toluene) [47,48] as the standards. The quantum yields were calculated using the following equation: $\Phi_s = \Phi_r(A_rF_s/A_sF_r)(n_s/n_r)^2$, where A_s and A_r are the absorbance of the sample and the reference, respectively. At the excitation wavelength, F_s and F_r are the corresponding relative integrated fluorescence intensities, and n is the refractive index of the solvent.

2.5. DFT calculations

Density functional theory (DFT) calculations were employed to optimize the geometries of the compounds using the hybrid B3LYP functional and the 6-31G(d,p) basis set [49]. At the optimized geometries, time-dependent (TD) DFT calculations were carried out to gain insight into the low-lying excited states, using the range-separate CAM-B3LYP density functional and the 6-311 + G(d,p) basis set. Solvent effects of CH_2Cl_2 were taken into account by the polarizable continuum model throughout the calculations. All calculations were carried out using the Gaussian09 program package [50].

2.6. General procedure for preparation of the aldehydes

In a 100 mL round bottom flask, phosphorus oxychloride (17 mL, 183 mmol) was added dropwise to a vigorously stirred anhydrous DMF (28 mL) under nitrogen. The mixture was stirred at 0 °C for 30 min to afford the Vilsmeier reagent. In another 500 mL round bottom flask, 9-diphenylaminoanthracence (2.53 g, 7.32 mmol) was added to 1,2-dichloroethane (210 mL), and then the previously prepared Vilsmeier reagent was added into the flask dropwise under nitrogen. The solution was stirred at 0 °C for 1 h, then kept stirring at 50 °C for 12 h. After that, the solution was carefully