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Asymmetric 1,3,4-oxadiazole derivatives containing naphthalene and stilbene units: Synthesis, optical and electrochemical properties



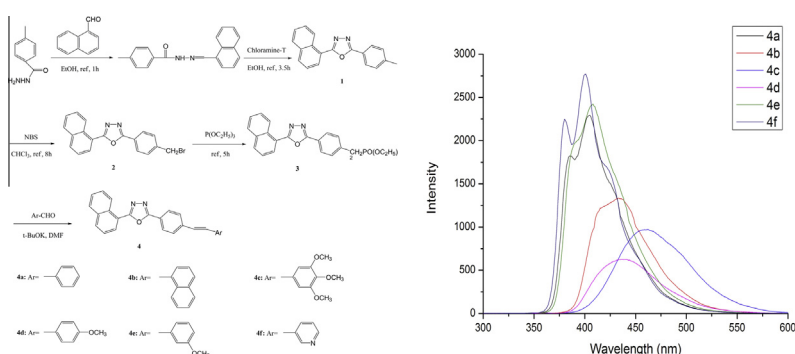
Huixiong Lu, Daohang He*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

HIGHLIGHTS

- Asymmetrical 1,3,4-oxadiazole dyes were efficiently synthesized.
- Structure–optical properties relationships were investigated.
- The compounds exhibit bright violet–blue emission with high fluorescence quantum yields.
- The high HOMO levels (−5.17 to −5.03 eV) are beneficial for hole-transporting.

GRAPHICAL ABSTRACT



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ABSTRACT

Six novel asymmetric 1,3,4-oxadiazole derivatives containing naphthalene and stilbene units have been efficiently synthesized and characterized by FT-IR, ^1H NMR, ^{13}C NMR, mass spectrometry and elemental analysis. The UV–vis absorption maximum wavelength, fluorescence excitation wavelength, fluorescence emission wavelength and fluorescence quantum yield were measured in dilute tetrahydrofuran solution. The solvent effect was also studied. The HOMO and LUMO levels of these compounds were calculated by density functional theory (DFT) (B3LYP, 6-31G*) method and cyclic voltammetry. They emit bright violet to blue emission with high fluorescence quantum yields (0.23–0.94) and large Stokes shifts (53–102 nm). These compounds possess high HOMO levels (−5.03 to −5.17 eV) and suitable band gaps, indicating that they could be benefit for hole injection. The results show that they have a potential for application in optoelectronic materials.

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Introduction

Organic dyes have been extensively investigated for versatile applications in coloring textiles, dye laser device, organic light emitting diodes and electroluminescent displays [1–4]. 1,3,4-Oxadiazoles are well known not only for their attraction in medicinal and pesticide chemistry [5–9], but also for their outstanding photoelectric properties such as electron-transporting capabilities, durability stability and high fluorescence quantum yields [10–12].

Many symmetrical 1,3,4-oxadiazole derivatives have actually been synthesized to use as TPA materials, polymers and organic electroluminescent (EL) devices [13–15]. However, it is well known that the large π -symmetrical system leads to poor solubility, which limits their synthesis, characterizations and applications [16]. Therefore, the synthesis of asymmetric 1,3,4-oxadiazole derivatives with high efficiency emitting are still in demand.

Naphthalene chromophore is an attractive π center, not only because it is planar, but it is also an excellent fluorophore. Though a great deal of excellent work has been reported on the naphthalene derivatives as organic electroluminescent (EL) materials [17,18], it is still meaningful to extend the research of such

* Corresponding author. Tel./fax: +86 20 87110234.

E-mail address: cehdh@scut.edu.cn (D. He).

materials. The naphthyl π systems attached to electron withdrawing groups are found to be effective photosensitive, and exhibit good electrochemical and optical properties [19,20].

The π -conjugated organic materials have attracted much attention owing to the increasing development of potentially active components for a wide range of electronic and optoelectronic devices [21]. Stilbene fluorescent compounds are an important class of fluorescent compounds with strong UV absorption, distinctive fluorescence emission and large Stokes shifts [22–24], which have developed as optical brighteners, TPA materials and electroluminescent materials [25–27]. The introduction of stilbene unit into the oxadiazole dyes not only builds a π -conjugated bridge, but also leads to a larger molecular length, which would make the electron-pair in the highest occupied molecular orbit possess a higher energy; the electron-pair could be excited easily to transit into a higher orbit [28].

On the basis of our previous studies on organic fluorescent materials [15,29,30], herein, we report six novel violet–blue asymmetric 1,3,4-oxadiazole dyes containing naphthalene chromophore with stilbene unit. As expected, the new dyes have good photoelectric properties such as strong fluorescence intensity, high HOMO levels and suitable band gaps. In addition, these compounds possess high fluorescence quantum yields, large Stokes shift and good electrochemical properties. The results will increase the knowledge to design and synthesis novel asymmetric 1,3,4-oxadiazole derivatives based on stilbene with excellent photophysical properties.

Experimental

Materials and instruments

All starting materials and reagents were commercially available and used without further purification. All solvents were carefully dried and freshly distilled according to common laboratory techniques. Melting points were determined using RY-1 melting point apparatus and were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 or $\text{DMSO}-d_6$ on a Bruker AVANCE-400 MHz NMR spectrometer using TMS as internal standard. FT-IR spectra were measured as KBr pellets on a Bruker TENSOR 27 in the region of $4000\text{--}400\text{ cm}^{-1}$. Mass spectra were obtained with a Bruker Esquire HCTplus (APCI). Elemental analyzes were performed on a Vario EL cube V2.1.0 elemental analyzer. UV–vis absorption spectra were recorded on a Hitachi UV-3010 spectrophotometer. Fluorescence spectra were obtained on a Hitachi F-4500 spectrophotometer at room temperature. The purity of the compounds was confirmed by TLC on silica gel 'G'-coated glass plates. Cyclic voltammetry was carried on a CHI830B electrochemical analyzer with three-electrode cell (Pt working electrode, Pt wire counter electrode and Ag/AgCl reference electrode) in CH_2Cl_2 solution in the presence of tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte.

Measurements

The fluorescence quantum yields (Φ) were determined according to the literature method [31,32].

$$\Phi_x = (A_s \times F_x \times n_x^2 \times \Phi_s) / (A_x \times F_s \times n_s^2)$$

Here, A is the absorbance at the excitation wavelength, F is the area under the fluorescence curve, n is the refraction index. Subscripts s and x refer to the standard and to the sample of unknown quantum yield, respectively. Quinine sulfate in 0.5 M sulfuric acid was used as fluorescence standard ($\Phi = 0.546$) [33].

Synthesis

The designed synthetic route for the target compounds are depicted in Scheme 1. The synthesis procedure and the analytical data of the compounds can be seen in Supplementary material.

Results and discussion

The synthesis and characterization

The reaction steps for the synthesis and the structures of the target molecules are shown in Scheme 1. Intermediate **1** was prepared through the oxidative cyclization of hydrazones derived from aromatic aldehydes and 4-methylbenzohydrazide by chloramine-T, and then reacted with N-bromosuccinimide under the catalysis of benzoyl peroxide to get compound **2**. Compound **2** and triethyl phosphite were mixed to prepare compound **3** through esterification. We then used compound **3** to react with various aldehydes, via Wittig–Horner reaction, to get a series of asymmetric 1,3,4-oxadiazole derivatives. Wittig–Horner reaction is an important synthetic route for the formation of an olefin functional group. The reaction procedure is convenient, takes place under mild conditions, and gives good yields. All new compounds were confirmed by ^1H NMR, ^{13}C NMR, MS, FT-IR and elemental analysis. The spectroscopic data of products are in accordance with the assigned structures. The FT-IR spectra show weak bands or shoulders located at $3100\text{--}3000\text{ cm}^{-1}$, a strong band at $1606\text{--}1608\text{ cm}^{-1}$ and at 1530 cm^{-1} which is assigned to aromatic C–H, C=N and aromatic C–C, respectively. IR spectra of **4c–4f** exhibit the stretching band at $2963\text{--}2826\text{ cm}^{-1}$ assigned to aliphatic groups and at 1130 cm^{-1} corresponding to aromatic C–O–C groups. Furthermore, the appearance of moderate intensity sharp C=C vibration band at 963 cm^{-1} indicate the existence of stilbene, which suggests the molecules are trans-structure [34]. In the ^{13}C NMR spectra, because of the electron withdrawing ability of the imine group, two resonance peaks appear at around 165 and 163 ppm which are assigned to two C atoms of 1,3,4-oxadiazole. In the ^1H NMR spectra of target compounds, the total number of hydrogen atoms is in good agreement with the proposed structure. The protons of the naphthyl and phenyl attached to oxadiazole are shifted to higher chemical shifts ($\delta = 9.30$ and 8.20 ppm) due to the electron-withdrawing ability of the oxadiazole lead to a decrease of the electron density. The doublet of CH=CH with $16.0\text{--}16.7$ Hz coupling constant in the ^1H NMR spectra of target compounds indicate the vinyl is trans-structure, but the multiplet of CH=CH appears in **4b** and **4e** owing to the doublet of vinyl is overlapped with the peaks of aromatic-H. In the mass spectra, the presence of characteristic molecular ion peaks $[M+1]$ confirm the proposed structures.

Optical properties

The optical data of the compounds were summarized in Table 1. The UV–vis absorption spectra and emission spectra of the compounds are given in Figs. 1 and 2 ($1 \times 10^{-5}\text{ mol L}^{-1}$ in tetrahydrofuran solution). It can be observed that these compounds have similar absorption spectra owing to their molecular structures. As is apparent in Fig. 1, all derivatives exhibit intense CT absorptions in the visible region from 345 nm to 357 nm, which is attributed to an intramolecular charge transfer transition ($S_0 \rightarrow \text{CT}$). The compound **4c** exhibits the largest maximum absorption peak at 357 indicating the introduction of electron-donating methoxy group into the phenyl results in bathochromic shift. It is also noted that the red-shift effect of the methoxy substituent is related to the numbers of methoxy and the substituent position. When the

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