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ORIGINAL PAPER

Synthesis, Fluorescence Properties and Theoretical Calculations of Novel Stilbene Derivatives Based on 1,3,4-Oxadiazole Bearing Anthracene Core

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Abstract Two novel stilbene derivatives bearing anthracene core based on 1,3,4-oxadiazole were efficiently synthesized and characterized by ^{1}H-NMR, mass spectrometry and elemental analysis. The optical properties of the title compounds were investigated by UV–vis absorption and fluorescence emission spectra in different solvents. Chemical calculations were performed by density functional theory (DFT) at the (B3LYP)/6-31G* level. The results show the two compounds exhibit strong green fluorescence emission ranged from 489–493 nm, and the fluorescence quantum yield ranged from 0.78–0.92. Their HOMO and LUMO levels are (−5.44 eV, −2.25 eV) and (−5.45 eV, −2.28 eV), respectively. The influence of the solvent on the fluorescence intensities was also discussed.

Keywords Synthesis · Stilbene · 1,3,4-Oxadiazole · Anthracene · Fluorescence properties · DFT

Introduction

Over the past few years, π-conjugated organic materials have attracted much attention due to the increasing development of potentially active components for a wide range of electronic and optoelectronic devices [1]. As an important class of five-membered hetero cyclic compounds, 1,3,4-oxadiazoles are well-known not only for their considerable biological and medical activities, which include anti-inflammatory, antifungal, anti-HIV, anticancer, and antimicrobial activities [2–5], but also for their sufficient fluorescence in the visible light range, large Stokes shifts, high quantum yields [6–8], and so on. Another feature of the 1,3,4-oxadiazole derivatives is that the photophysical and spectroscopic properties can be readily modified by the introduction of substituents in the structure of the oxadiazole, giving more flexibility to fit well in various applications [9]. In addition, oxadiazole unit can improve electron injection and transport properties of the molecules. Thus, many 1,3,4-oxadiazole derivatives with good hole-transporting capabilities and high fluorescence emission, have actually been used as electron-injection materials [10]. Nowadays, compounds with blue luminescence are highly desirable because of their wide applicability in organic materials to tune the emission colours in the entire region of visible spectrum [11]. The fluorescent characteristics mainly depend on molecular structure, such as conjugate system, coplanarity and rigidity. The longer the conjugate system is, the stronger the fluorescent intensity and greater emission wavelength will be [12]. Anthracene derivatives have rigid structure, wide energy gaps and high fluorescent quantum efficiency [13, 14]. Moreover, anthracene derivatives have been extensively utilized as fluorescence sensors for metal ions and biological molecules [15]. Great deals of compounds which contain anthracene core electroluminescent materials have been developed till now.

In continuation of our work in organic fluorescent materials [16–18], herein, two novel stilbene derivatives bearing

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anthracene core based on 1,3,4-oxadiazole were synthesized by introducing anthracene core and 1,3,4-oxadiazole unit into the stilbene skeleton. The fluorescence properties of the title compounds are investigated by UV–vis absorption and fluorescence emission spectra in dimethylformamide (DMF), chloroform ($CHCl_3$) and tetrahydrofuran (THF). Quantum-chemical calculation was performed to obtain their optimized structures and the electron distribution. The synthetic route is outlined in Scheme 1.

Experimental

Instrumentation

Melting points were determined using RY-1 melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE-400 MHz NMR spectrometer using TMS as internal standard. Mass spectra were obtained with a HPLC/MS LCQDECA spectrometer(APCI). Elemental analyses were performed on a Vario EL Ш CHN 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.

Synthesis

Synthesis of 2-(anthracen-9-yl)-5-(p-tolyl)-1,3,4-oxadiazole (1)
Synthesis of 2-(anthracen-9-yl)-5-(4-(bromomethyl) phenyl)-1,3,4-oxadiazole(2)
Synthesis of 4-(5-(anthracen-9-yl)-1,3,4-oxadiazol-2-yl)benzylphosphonate(3)

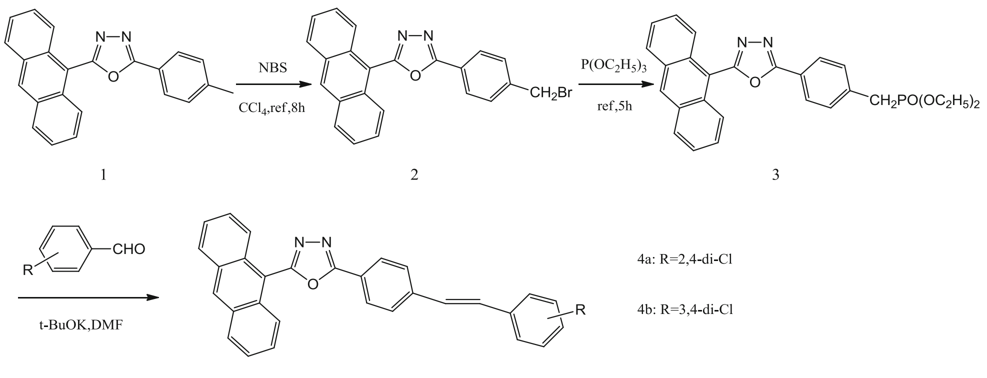
Intermediates of compounds **1**, **2** and **3** were prepared by the reported methods [17].

Typical Procedure for the Synthesis of Compounds(4)

To a stirred solution of aromatic aldehydes (1.7 mmol) and the intermediate **3** (0.9 g, 1.7 mmol) in anhydrous N, N-dimethylformamide (15 mL) under nitrogen atmosphere was added dropwise a solution of *t*-BuOK (2 g, 3 %) in ethanol. The reaction proceeded at room temperature overnight. Then the resulting mixture was filtered and washed with ethanol. The residue was recrystallized from ethanol/DMSO.

2-(anthracen-9-yl)-5-(4-(2,4-dichlorostyryl)phenyl)-1,3,4-oxadiazole (4a), yellow crystals, yield 92.5 %; m.p. 256–257 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H, anthracen-H), 8.21 (d, *J*=8.4 Hz, 2H, C_6H_4 2,6-H), 8.14–8.00 (m, 4H, anthracen-H), 7.71 (d, *J*=8.4 Hz, 2H, C_6H_4 3,5-H), 7.65 (d, *J*=8.5 Hz, 1H, C_6H_3 6-H), 7.61–7.52 (m, 4H, anthracen-H), 7.57 (d, *J*=16.2 Hz, 1H, CH=CH), 7.44 (d, *J*=2.1 Hz, 1H, C_6H_3 3-H), 7.28 (d, *J*=8.5 Hz, 1H, C_6H_3 5-H), 7.12 (d, *J*=16.3 Hz, 1H, CH=CH); APCI MS: *m/z*, 493(M+, 100), 495(M+2, 80), 496(M+3, 20); Anal. Calcd. for $C_{30}H_{18}Cl_2N_2O$ (493.2):C, 73.03; H, 3.68; N, 5.68; Found: C, 73.41; H, 3.65; N, 5.72.

2-(anthracen-9-yl)-5-(4-(3,4-dichlorostyryl)phenyl)-1,3,4-oxadiazole (4b), yellow crystals, yield 91.2 %; m.p. 253–254 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H, anthracen-H), 8.20 (d, *J*=8.2 Hz, 2H, C_6H_4 2,6-H), 8.15–8.02 (m, 4H, anthracen-H), 7.68 (d, *J*=8.3 Hz, 2H, C_6H_4 3,5-H), 7.63 (s, 1H, C_6H_3 2-H), 7.61–7.51 (m, 4H, anthracen-H), 7.45 (d, *J*=8.3 Hz, 1H, C_6H_3, 5-H), 7.37 (d, *J*=8.4 Hz, 1H, C_6H_3 6-H), 7.14 (s, 2H, CH=CH); APCI MS: *m/z*, 493(M+, 100), 495(M+2, 70), 496(M+3, 25); Anal. Calcd. for $C_{30}H_{18}C_{12}N_2O$(493.2):C, 73.03; H, 3.68; N, 5.68; Found: C, 72.99; H, 3.75; N, 5.76.



Scheme 1 The synthetic route of the title compounds

Table 1 The fluorescence characteristics of the title compounds in $CHCl_3$, THF, and DMF solution at room temperature (concentration: 1×10^{-5} mol/L)

compound	solution	λ_{max}(nm)	$\times10^{-4}\varepsilon_{max}$	λ_{ex}(nm)	λ_{em}(nm)	Stockes shifts	Φ_x
4a	DMF	336	4.79	341	493	152	0.81
	THF	338	5.07	340	489	149	0.78
	$CHCl_3$	335	4.43	343	489	146	0.88
4b	DMF	338	5.22	341	493	152	0.91
	THF	337	6.15	341	489	148	0.71
	$CHCl_3$	337	4.92	342	489	147	0.92

Results and Discussion

^{1}H NMR Spectra

In the ^{1}H NMR spectra of two compounds, 4a showed two fine doublets corresponding to the olefinic protons (CH=CH) from stilbene at δ: 7.57 ppm and 7.12 ppm (J=16.3 Hz). At δ: 7.65, 7.28, and 7.44 ppm, two doublets and a singlet could be assigned to 6-H, 5-H and 3-H from aromatic protons (C_6H_3-protons), respectively. At δ: 8.71, 8.14–8.00, and 7.61–7.52 ppm, two multiplets and a singlet could be assigned to the protons of anthracen. In addition, another two downfield doublets were also found at δ: 8.21 and 7.71 ppm which could be assigned to the contribution of aromatic protons (C_6H_4-protons). In contrast, the compound 4b in its ^{1}H NMR spectrum showed the similar resonance peaks accountable to the protons of anthracen and aromatic protons (C_6H_4-protons), respectively, only a singlet was found corresponding to the olefinic protons (CH=CH) from stilbene at δ: 7.14 ppm . From the ^{1}H NMR spectra of two compounds, it was found that their olefinic protons (CH=CH) from stilbene had different coupling, which indicated the different substituents on benzene had an effect on olefinic proton-proton coupling.

Fluorescence Properties

The data of fluorescence properties for compounds 4a and 4b are summarized in Table 1. It can be seen that compounds 4a and 4b had the similar optical properties such as the maximum absorption wavelengths, the maximum emission wavelengths, the Stokes shift and the fluorescence quantum yields, indicating that the different position Cl have a limited effect on their fluorescence properties. In Table 1, compared with λ_{max} and ε_{max} for the same compound in DMF, $CHCl_3$ and THF, the maximum absorption wavelengths of the two compounds had little change in different solvents, especially, in DMF and $CHCl_3$, the absorbency is lower than that in THF. This is because the dispersion force, permanent dipole and induction of dipole

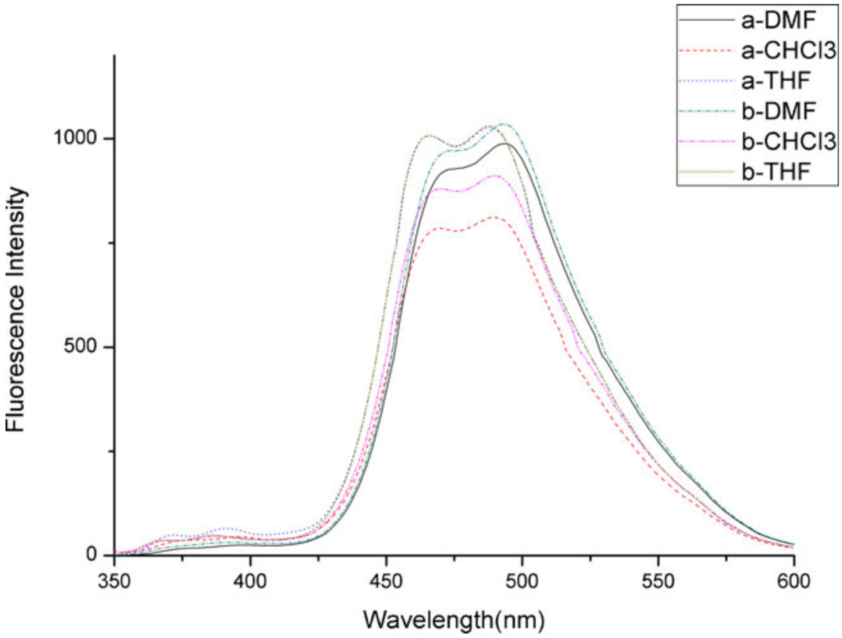


Fig. 1 The fluorescence emission spectra of the compounds 4a, 4b in $CHCl_3$, THF, and DMF solvent at room temperature (concentration: 1×10^{-5} mol L^{-1})

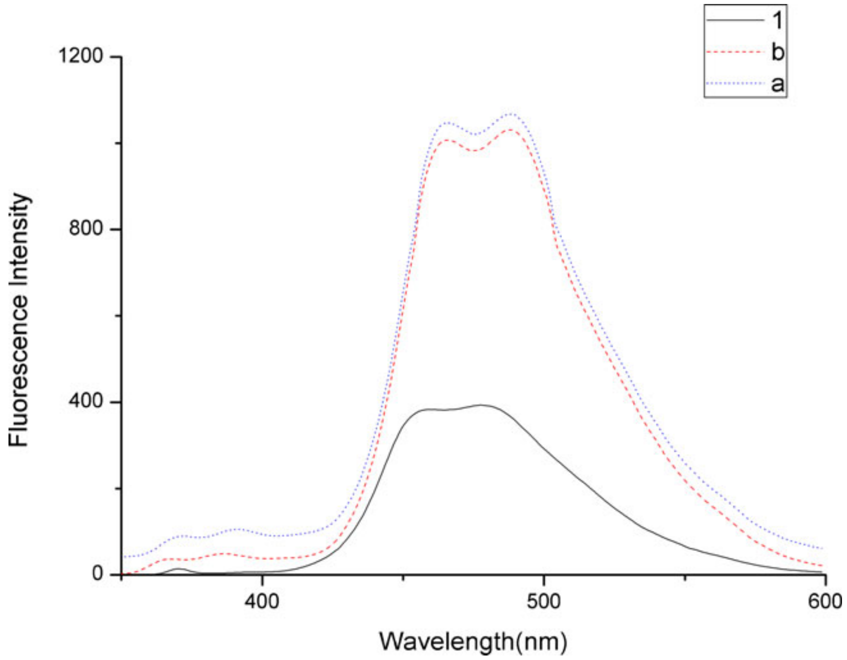


Fig. 2 The fluorescence emission spectra of the compounds 1, 4a and 4b in THF(concentration: 1×10^{-5} mol L^{-1})

in the strongly polar THF with stilbene derivatives are stronger than that in DMF and $CHCl_3$, which makes λ_{max} have a little red-shift.

Figure 1 showed fluorescence emission spectra of two stilbene derivatives in $CHCl_3$, THF, and DMF (Concentration: 1×10^{-5} mol/L). The influence of solvent on the fluorescence intensities of the 4a and 4b was investigated. We could see that the emission wavelengths and fluorescence intensity of the two compounds were different in three solvents at the same concentration. The fluorescence intensity of the two compounds in $CHCl_3$ was lower than that in the other solvents. All these indicated that the solutions molecules had strong coordination effect and the environment played an important role in determining the fluorescence intensity of the compounds. As shown in Fig. 2, compared with the fluorescence characteristic emission wavelengths of the title compounds in THF solvent, the maximum fluorescence emission wavelength of compound 4a and 4b had a greater shift (12 nm) towards higher wavelengths than the intermediate of compound **1** owing to increasing the conjugation length of the molecule, which would make the electron-pair in the highest occupied molecular orbit possess a lower energy; the electron-pair could be excited easily to

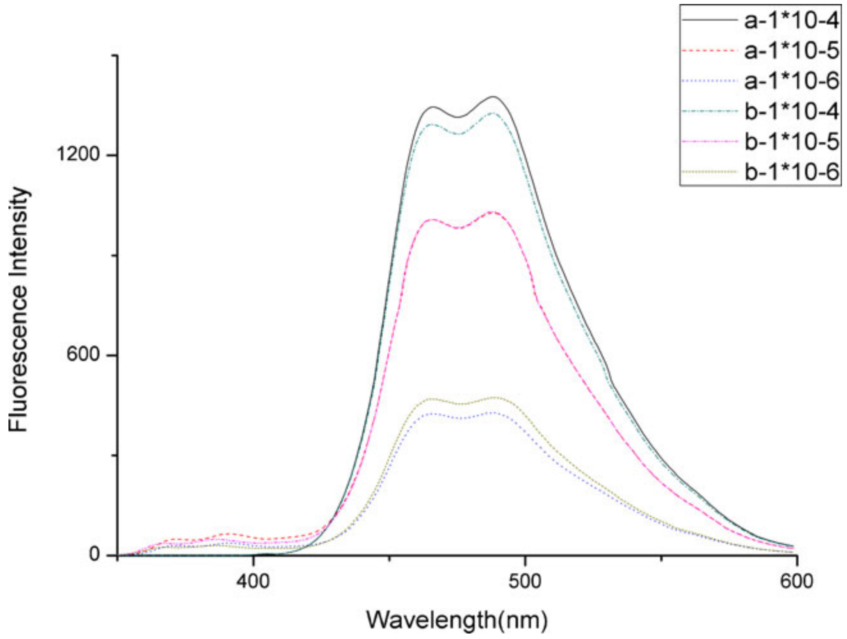


Fig. 3 The fluorescence spectra of compounds 4a and 4b at different concentration of THF(1.0×10^{-4} mol/L; 1.0×10^{-5} mol/L; 1.0×10^{-6} mol/L)

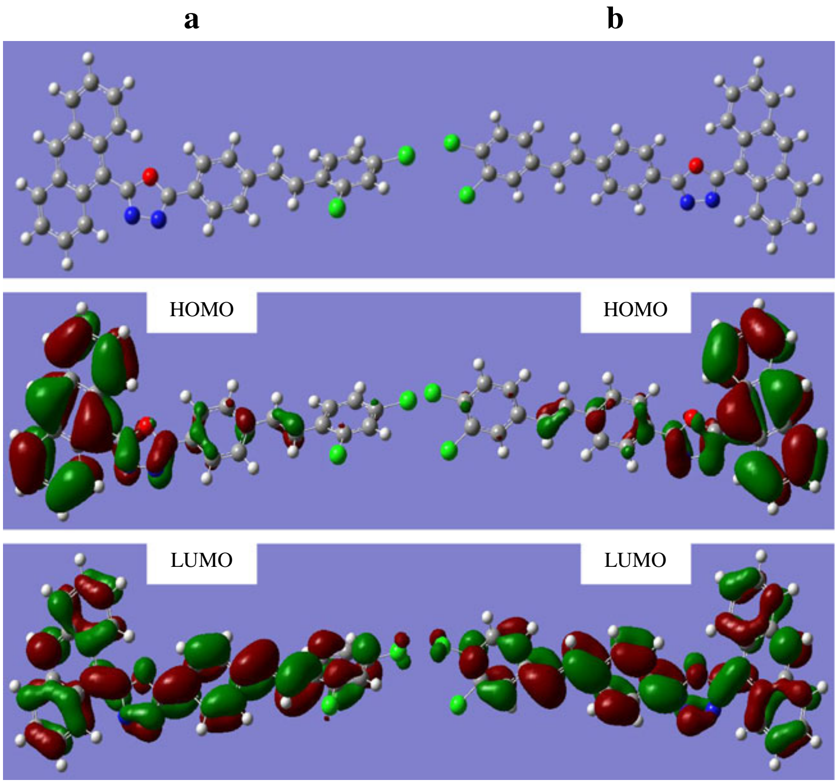


Fig. 4 Optimized geometric structure and frontier molecular orbital profiles of 4a and 4b

transit into a higher orbit. The influence of concentration on fluorescence intensity of the two compounds was also studied (Fig. 3). It can be seen that the emission intensity of fluorescence were greatly decreased with gradual increasing in concentration of 4a and 4b in THF. The fluorescence quantum yields: $\Phi_x = \frac{A_s \times F_x \times n_x^2 \times \Phi_s}{A_x \times F_s \times n_s^2}$ where A is the absorbance at the excitation wavelength, F the area under the fluorescence curve and n the refraction index. Subscripts *s* and *x* refer to the standard and to the sample of unknown quantum yield, respectively. Rhodamine B in ethanol (Φ=0.89) was taken as the standard [19]. The two compounds had a large fluorescence quantum yield (Φ), which was due to the conjugative effect. The molecular structure containing stilbene, anthracene core and 1,3,4-oxadiazole unit can increase the conjugation length and rigid structure of the molecule.

Theoretical Study

The geometries and electronic structures of molecules 4a and 4b were studied by density function theory (DFT) calculations at the B3LYP/6-31G* level [20]. The optimized structures and the frontier molecular orbital profiles of 4a and 4b are shown in Fig. 4. As expected, molecules 4a and 4b both have non-planar, twisted structures attributed to steric hindrance imposed by the 1,3,4-oxadiazole, anthracene skeleton, π-bridges, linkages and dihedral angles between two units. The dihedral angle of two molecules between anthracene and 1,3,4-oxadiazole is around 134°, and the dihedral angle in 4a between vinyl and 2,4-dichlorobenzene is 21°. Thus the -Cl group attached to the *o*-position phenyl seems to affect the planarity of the molecules. In both cases, the HOMO are mainly localized on the anthracene and 1,3,4-oxadiazole, while the LUMO are delocalized along the whole molecules, indicating that these molecules posses intramolecular charge transfer ability. It also implies that the anthracene core and 1,3,4-oxadiazole unit play an important part in their emission. Two molecules possess a high HOMO energy level (−5.44 and −5.46 eV), which could lead to their better hole-transport properties. Their LUMO energy level (−2.25 and −2.28 eV) is supposed to facilitate the acceptance of electrons from the cathode [21]. The band gaps are 3.19 eV and 3.18 eV, respectively. Two energy gaps are close, indicating they have the similar the emission spectra which agree well with the experimental observations.

Conclusions

Two novel stilbene derivatives bearing anthracene core based on 1,3,4-oxadiazole were synthesized, characterized by spectral studies, theoretical calculations and their fluorescence spectra were recorded in order to study the changes in the photophysical properties with different solvents. The results showed the compounds exhibited strong green fluorescence emission with high fluorescence quantum yield (0.78–0.92). The influence of solvent on the fluorescence intensities of the compounds indicated that the solvents played an important role in determining the fluorescence intensity of the compounds. The DFT calculations establish that they possess good charge-transport characteristics. Thus, they may serve as potential applications in organic electroluminescent materials.

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