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Synthesis, Characterization, and Optical Properties of Novel 2,5-Bis[4-(2-(-arylvinyl)phenyl]-1,3,4-oxadiazoles

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Six novel 2,5-bis[4-(2-arylvinyl)phenyl]-1,3,4-oxadiazoles were synthesized by introducing 1,3,4-oxadiazole moiety into the stilbene skeleton. The synthesis route included the cyclization of *p*-toluic acid and hydrazine hydrate catalyzed by polyphosphoric acid (**PPA**), bromination of 1,3-dibromo-5,5-dimethylhydantoin (**DBDMH**), esterification, and the Wittig-Horner reaction. All the title compounds were characterized by ^{1}H-NMR, MS, and elemental analysis. UV-Vis absorption and fluorescence emission spectra in THF solution were investigated; the compounds may have potential for use in organic optical materials.

Key Words: Stilbene, 1,3,4-oxadiazole, synthesis.

Introduction

Research on stilbene skeleton derivatives has attracted considerable interest because of their diverse biological activity, including anti-microbial and anti-tumor,[1,2] insecticidal,[3] and insect baculovirus synergist.[4,5] Moreover, they are also important organic electroluminescent materials that have received a great deal of attention due to their application in full-color flat-panel displays and optical data storage materials.[6–8] Small conjugated molecules based on stilbene skeleton derivatives that demonstrate distinctive blue light-emitting properties are currently the subject of intense research;[9,10] however, their use is still limited by unresolved problems, including the luminous efficiency of fluorescence, the short fluorescence lifetime, and the weak luminous intensity

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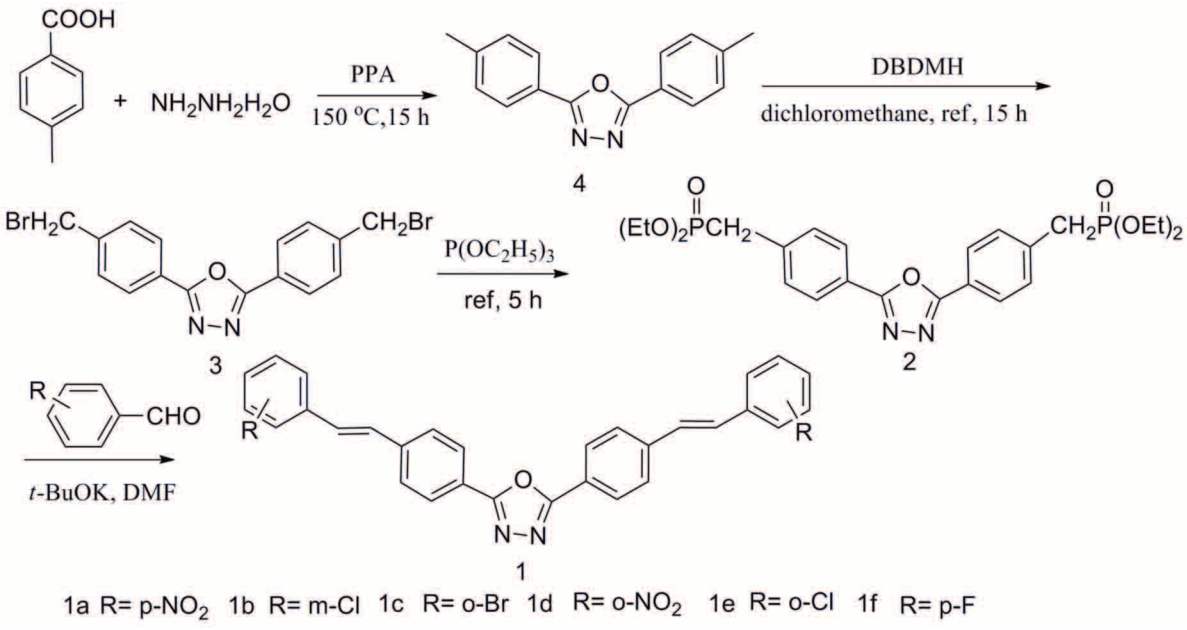
of fluorescence. In particular, a well-balanced injection of positively (hole) and negatively (electron) charged carriers into an emitting layer is considered a prerequisite for high luminous efficiency. Recent research has been carried out to enhance performance suitable for practical use.[11,12] Accordingly, there is an urgent need to explore efficient electroluminescent materials induced blue fluorescent emission.[13] Based on the fact that the 1,3,4-oxadiazole unit has good hole-transporting capability, durability, and thermal stability—especially high fluorescence quantum yields—it is envisioned that the introduction of the 1,3,4-oxadiazole unit into the stilbene skeleton can improve their photoelectric properties, durability, and thermal stability.[14,15] Herein, we report the synthesis of 6 novel 2,5-bis[4-(2-arylvinyl)phenyl]-1,3,4-oxadiazoles via the Wittig-Horner reaction. The cyclization and bromination procedures were designed in order to obtain a good yield. All the title products reported were characterized on the basis of MS, ^{1}H-NMR, and elemental analyses. UV-Vis absorption and fluorescence emission spectra in THF solution were also investigated. The synthesis route is outlined in the Scheme.



Scheme. Synthesis route of compounds **1a-f.**

Experimental

General

Melting points were determined using an RY-1 melting point apparatus and were uncorrected. ^{1}H-NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker AVANCE-600 MHz NMR spectrometer using TMS as the internal standard. Mass spectra were obtained with a HPLC/MS LCQDECA spectrometer (APCI). Elemental analysis was performed on a Vario EL III CHN elemental analyzer. UV-Vis absorption spectra were recorded with a Hitachi UV-3010 spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-4500 spectrophotometer at room temperature. The purity of the compounds was confirmed by TLC on silica gel 'G'-coated glass plates.

Synthesis of 2,5-di-p-tolyl-1,3,4-oxadiazole 4

p-Toluic acid (17 g, 125 mmol) and 80% hydrazine hydrate (4 mL, 66 mmol) were added to 60 mL of stirred phosphoric acid, consecutively; the reaction proceeded at 150 °C for 15 h until the disappearance of the starting material by TLC. The cooled mixture was poured into cold water, neutralized by 5% Na_2CO_3, and filtered; the residue was then recrystallized from $CHCl_3$/methanol, giving 9.4 g of compound **4** as white crystals. Yield 60%, mp 176-177 °C; ^{1}H-NMR ($CDCl_3$): δ 2.43 (s, 6H, CH_3), 7.32 (d, J = 8.4 Hz, 4H, $C_6H_4$3,5-H), 8.01 (d, J = 8.4 Hz, 4H, $C_6H_4$2,6-H); APCI MS (m/z) 251 (M + 1, 100), 252 (M + 2, 18).

Synthesis of 2,5-bis(4-(bromomethyl)phenyl)-1,3,4-oxadiazole 3

To a stirred solution of **4** (5 g, 20 mmol) in carbon dichloride (70 mL) was added DBDMH (4 g, 20 mmol); the reaction proceeded with refluxing for 15 h and then the excess solvent was removed. The resulting mixture was filtered and washed with ethanol. The residue was recrystallized from THF/ethanol, giving 6 g of compound **3** as white crystals. Yield 75%, mp 227-228 °C; ^{1}H-NMR ($CDCl_3$): δ 4.55 (s, 4H, CH_2Br), 7.57 (d, J = 8.4 Hz, 4H, $C_6H_4$3,5-H), 8.13 (d, J = 8.4 Hz, 4H, $C_6H_4$2,6-H); APCI MS (m/z) 409 (M + 1, 100).

Synthesis of diethyl 4-(5-(4-(diethoxyphosphino)methyl)phenyl)-1,3,4-oxadiazol-2-yl)-benzyl-phosphonate 2

A mixture of compound **3** (5 g, 14.7 mmol) and triethyl phosphite (13 mL, 76.6 mmol) was refluxed for 5 h. The excess triethyl phosphate was evaporated under reduced pressure and then filtered by the addition of hexane. The residue was recrystallized from THF/hexane, giving 6.2 g of compound **2**. Yield 80%, mp 111-112 °C; ^{1}H-NMR ($CDCl_3$): δ 1.27 (t, J = 7.2 Hz, 12H, CH_3), 3.43 (d, J = 22.2 Hz, 4H, CH_2), 4.02∼4.08 (m, 8H, OCH_2), 7.49 (dd, J = 2.4 Hz, J = 8.4 Hz, 4H, $C_6H_4$3,5-H), 8.09 (d, J = 8.4 Hz, 4H, $C_6H_4$2,6-H).

Typical procedure for the synthesis of compounds 1

To a stirred solution of aromatic aldehydes (3.4 mmol) and the intermediate **2** (0.9 g, 1.7 mmol) in anhydrous N,N-dimethylformamide (15 mL) under nitrogen atmosphere a solution of*t*-BuOK (2 g, 3%) in ethanol was added dropwise. The reaction proceeded at room temperature overnight. Then, the resulting mixture was filtered and washed with ethanol. The residue was recrystallized from ethanol/DMSO, giving compounds **1a-f**. Analytical and spectral data were obtained from all compounds.

1a: Yield 81%, mp > 300 °C; ^{1}H-NMR($CDCl_3$) δ 7.28 (d, J= 4.0 Hz, 4H, CH=CH), 7.66(d, J= 8.4 Hz, 4H, C_6H_4 2,6-H), 7.69 (d, J= 8.4 Hz, 4H, C_6H_4 3,5-H), 8.16 (d, J= 8.0 Hz, 4H, C_6H_4 2,6-H), 8.23 (d, J= 8.0 Hz, 4H, C_6H_4 3,5-H); APCI MS (m/z) 517 (M + 1, 100), 518 (M + 2, 32). Analysis: Calc. for $C_{30}H_{20}N_4O_5$(516.5): C, 69.76; H, 3.90 N, 10.85; found: C, 68.61; H, 3.95; N, 10.42.

1b: Yield 95%, mp 257.5-258.9 °C; ^{1}H-NMR ($CDCl_3$) δ 7.28 (d, J= 7.6 Hz, 2H, CH=CH), 7.33 (t, J = 2.4 Hz, 2H, C_6H_4 5-H), 7.41 (d, J = 7.6 Hz, 2H, CH=CH), 7.55 (s, 2H, C_6H_4 2-H), 7.67 (d, J= 2.4 Hz, 2H, C_6H_4 4-H), 7.69 (d, J = 2.0 Hz, 4H, C_6H_4 2,6-H), 8.15 (d, J = 2.0 Hz, 4H, C_6H_4 3,5-H), 8.17 (d, J = 2.4 Hz, 2H, C_6H_4 6-H); APCI MS (m/z) 495.4 (M+, 100), 497 (M + 2, 70). Analysis: Calc. for $C_{30}H_{20}Cl_2N_2O$ (495.4): C, 72.73; H, 4.07; N, 5.65; found: C, 72.58; H, 4.12; N, 5.69.

1c: Yield 67%, mp 240.1-240.9 °C; ^{1}H-NMR ($CDCl_3$) δ 7.04 (d, J = 16.0 Hz, 2H, CH=CH), 7.12 (t, J = 7.6 Hz, 2H, C_6H_4 4-H), 7.30 (t, J = 7.6 Hz, 2H, C_6H_4 5-H), 7.56 (d, J = 16.0 Hz, 2H, CH=CH), 7.58 (d, J = 7.6 Hz, 2H, C_6H_4 3-H), 7.67 (d, J = 8.4 Hz, 4H, C_6H_4 2,6-H), 7.68 (d, J = 7.6 Hz, 2H, C_6H_4 6-H), 8.12 (d, J = 8.4 Hz, 4H, C_6H_4 3,5-H). APCI MS (m/z) 585 (M + 1, 100), 587 (M + 2, 54). Analysis: Calc for $C_{30}H_{20}Br_2N_2O$ (584.3): C, 61.67; H, 3.45; N, 4.79; found: C, 61.01; H, 3.49; N, 4.82.

1d: Yield 96%, mp > 300 °C; ^{1}H-NMR ($CDCl_3$) δ 7.13 (d, J = 16.0 Hz, 2H, CH=CH), 7.46 (d, J = 16.0 Hz, 2H, CH=CH), 7.65 (t, J = 8.0 Hz, 2H, C_6H_4 3-H), 7.72 (s, 4H, C_6H_4 2,6-H), 7.75 (s, 4H, C_6H_4 3,5-H), 7.79 (t, J = 8.0 Hz, 2H, C_6H_4 4-H), 8.03 (d, J = 8.0 Hz, 2H, C_6H_4 6-H), 8.19 (d, J = 8.0 Hz, 2H, C_6H_4 3-H). APCI MS (m/z) 517 (M + 1,100), 518 (M + 2, 35). Analysis: Calc. for $C_{30}H_{20}N_4O_5$ (516.5): C, 69.76; H, 3.90; N, 10.85; found: C, 68.99; H, 4.01; N, 10.37.

1e: Yield 77%, mp 227.8-228.5 °C; ^{1}H-NMR ($CDCl_3$) δ 7.13 (d, J= 16.4 Hz, 2H, CH=CH), 7.24 (t, J = 7.6 Hz, 2H, C_6H_4 5-H), 7.31 (t, J = 7.6 Hz, 2H, C_6H_4 4-H), 7.43 (d, J = 7.6 Hz, 2H, C_6H_4 6-H), 7.65 (d, J = 16.4 Hz, 2H, CH=CH), 7.72 (d, 4H, J = 8.4 Hz, C_6H_4 3-H), 7.74 (d, J = 7.6 Hz, 4H, C_6H_4 2,6-H), 8.17 (d, J = 8.4Hz, 4H, C_6H_4 3,5-H). APCI MS (m/z) 495 (M +, 100), 497 (M + 2, 68). Analysis: Calc. for $C_{30}H_{20}Cl_2N_2O$ (495.4): C, 72.73; H, 4.07 N, 5.65; found: C, 71.85; H, 4.14; N, 5.69.

1f: Yield 90%, mp 280.3-281.9 °C; ^{1}H-NMR ($CDCl_3$) δ 7.04 (d, J = 16.4 Hz, 2H, CH=CH), 7.16 (d, J= 16.4 Hz, 2H, CH=CH), 7.49 (d, J = 5.6 Hz, 4H, C_6H_4 3,5-H), 7.51 (d, J = 5.6 Hz, 4H, C_6H_4 2,6-H), 7.62 (d, J = 8.4 Hz, 4H, C_6H_4 2,6-H), 8.11 (d, J = 8.4 Hz, 4H, C_6H_4 3,5-H). APCI MS (m/z) 463 (M + 1, 100), 464 (M + 2, 30). Analysis: Calc for $C_{30}H_{20}F_2N_2O$ (462.5): C, 77.91; H, 4.36; N, 6.06; found: C, 77.81; H, 4.37; N, 6.07.

Results and discussion

Synthesis of the 2,5-bis[4-(2-arylvinyl)phenyl]-1,3,4-oxadiazoles started from the reaction of *p*-toluic acid and 80% hydrazine hydrate, which were cyclized directly by polyphosphoric acid at 150 °C, giving 2,5-dip-tolyl-1,3,4-oxadiazole **4**. 2,5-Bis(4-(bromomethyl)phenyl)-1,3,4-oxadiazole **3** was synthesized using an inexpensive 1,3-dibromo-5,5-dimethylhydantoin as the brominating agent via refluxing in carbon tetrachloride for 23 h. It is possible that 2,5-dip-tolyl-1,3,4-oxadiazole **4** had a low solubility in the nonpolar solvent (carbon tetrachloride); therefore it was refluxed again in carbon dichloride and a yield of 75% was obtained after 15 h. The title compounds **1a-f,** synthesized via the Wittig-Horner reaction, were characterized with spectral and analytical methods. The ^{1}H-NMR spectra of compounds **1a-f** show that the proton chemical shifts of the benzene ring ranged from δ 7.04 to δ 8.23 ppm. A doublet of CH=CH was obtained between δ 7.0 and δ 7.4 ppm. According to the coupling constant, it was determined that 2 protons had different chemical environments because of the effect of substituents belonging to the trans-structure, which could stably exist in stilbene derivatives. The mass spectra of compounds **1a-f** show the intense molecular ion peaks and the characteristic ion peaks. These molecular ion peaks were consistent with their molecular formulae.

The Table shows the UV-Vis absorption and fluorescence emission spectra in dilute THF solution; the absorption spectra of compounds **1a-1f** show maximum absorption at λ_{max} = 373, 357, 348, 342, 353, and 356 nm, respectively. Compared with the fluorescence characteristic emission wavelengths of the other compounds, the maximum fluorescence emission wavelength of compound **1a** had a greater shift towards higher wavelengths

than the other compounds. The fluorescence quantum yields $\Phi_x = (A_s \times F_x \times n_x^2 \times \Phi_s)/(A_x \times F_s \times n_s^2)$, where A is the absorbance at the excitation wavelength, F is the area under the fluorescence curve, and n is the refraction index. Subscripts s and x refer to the standard and to the sample of unknown quantum yield, respectively. Rhodamine B in ethanol ($\Phi = 0.89$) was taken as the standard.[16] It can be seen that compound **1f** had the greatest fluorescence quantum yield, which can be explained by the space steric effect. The substituent F had a smaller atom space, which was attributed to the increased conjugation length of the molecule.

Table. Absorption and fluorescence characteristics of the title compounds in dilute THF solution at room temperature (concentration: 1×10^{-5} mol/L).

Compound	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**
UV-Vis λ_{max}/nm	373	357	348	342	353	356
$10^{-4}\varepsilon/(L{\cdot}mol^{-1}{\cdot}cm^{-1})$	9.37	11.05	8.79	15.2	9.23	8.49
PLλ_{max}/nm	429	412	414	413	414	413
f	0.278	0.578	0.307	0.194	0.624	0.796

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References

1. Cardile, V.; Lombardo, L.; Spatafora, C.; Tringali, C. *Bioorg. Chem.* **2005**, *33*, 22-33.
2. Pettit, G.; Minardi, M.; Rosenberg, H.; Hamel, E. *J. Nat. Prod.* **2005,** *68*, 1450-1458.
3. Ioset, J. R.; Andrew, M.; Mahabir, P. G..; Kurt, H. *J. Nat. Prod.* **2001**, *64*, 710-715.
4. Shapiro, M.; Argauer, R. *J. Econ. Entomol.* **1997**, *90*, 899-904.
5. Argauer, R.; Shapiro, M. *J. Econ. Entomol.* **1997**, *90*, 416-420.
6. Strukjelj, M.; Jordan, R.; Dodabalapur, A. *J. Am. Chem. Soc.* **1996**, *118*, 1213-1214.
7. Rothberg, L. J.; Lovinger, A. *J. Mater. Res.* **1996**, *11*, 3174-3187.
8. Pu, S. Z.; Yang, T. S.; Liu, G.; Fan, C. B.; Yao, B. L. *J. Mat. Sci. Eng.* **2007**, *25*, 837-845.
9. Li, J. Y.; Liu, D.; Li, Y. Q.; Lee, C. S.; Kwong, H. L.; Lee, S. *Chem. Mater.* **2005**, *17*, 1208-1212.
10. Stuhr-Hansen, N.; Christensen, J. B.; Harrit, N.; Bjørnholm, T. *J. Org. Chem.* **2003**, *68*, 1275-1282.
11. Li, Z. H.; Xia, P. F.; Sun, K.; Huang, W. C. *Chin. J. Org. Chem.* **2002**, *22*, 141-144.
12. Chen, Y.; Liao, C. K.; Wu, T. Y. *Polymer.* **2002**, *43*, 4545-4555.
13. Shao, P.; Li, Z.; Qin, J. G.; Gong, H. M.; Ding, S.; Wang, Q. Q. *Aust. J. Chem.* **2006,** *59*, 49-52.
14. Zhang, J. X.; Cui, Y. P.; Wang, M. L.; Xu, C. X.; Zhong, Y.; Liu, J. Z. *Chem. Lett.* **2001**, 824-825.
15. Zhang, T. L.; Li, H. H.; Yuan, Z. L. *Chin. J. Org. Chem.* **2005**, *25*, 997-1000.
16. X. Yang, Z. T. Pan, Y. Ma, *J. Anal. Sci.* **2003**, *19*, 588-601.