

Synthesis, Crystal Structure and Photophysical Properties of a Novel Molecule Containing a Triarylamine and an Oxadiazole Units

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2-{3-[2-(4-*N,N*-di-*p*-tolylaminophenyl)ethenyl]phenyl}-5-(4-bromophenyl)-1,3,4-oxadiazole (**1**) containing triarylamine and 2,5-diaryl-1,3,4-oxadiazole units was prepared by Horner-Witting reactions. The structure of the compound was confirmed by ¹H NMR, IR, MS and elemental analyses. The crystal structure of **1** was determined by X-ray diffraction analysis. UV absorption spectra and photoluminescent spectra were measured.

Keywords synthesis, triarylamine, oxadiazole, crystal structure, electron-transport, hole-transporting

Introduction

Electroluminescence (EL) from small organic molecules¹ and polymers² forms the basis for their use in light-emitting diodes (LEDs). A LED produces light via the recombination of electrons and holes, injected from electrodes on opposite sides of the film. To achieve high luminescence efficiency, the electron and hole currents must be balanced. However, typical organic molecules and polymers are not simultaneously good conductors for both electrons and holes.

2,5-Diaryl-1,3,4-oxadiazole ring, which has extremely high thermal and oxidative stability, functions well as an electron-transport moiety.³⁻⁷ Triphenylamine was characterized by a high hole-transporting ability and a bulk volume,⁸⁻¹⁰ which is appropriate for the compound to realize both high fluorescence efficiency in the solid state and high hole mobility. It might be possible to develop

new organic EL materials by satisfactory combination of triphenylamine and 2,5-diaryl-1,3,4-oxadiazole groups through appropriate molecular design and synthesis. Optical and electrical properties of thin films of conjugated materials are known to be strongly dependent on the coplanarity of the conjugated π -system and on the inter-chain distance of conjugated segments. A useful tool to predict these influences is the single-crystal X-ray analysis of model compounds. Advantage of this technique is the possibility to get an insight into packing of the molecules and structural organization of the related compounds and thus a help to explain the mechanisms of luminescence phenomena. We report here, for the first time, the synthesis, single-crystal X-ray structure and the photophysical properties of 2-{3-[2-(4-*N,N*-di-*p*-tolylaminophenyl)ethenyl]phenyl}-5-(4-bromophenyl)-1,3,4-oxadiazole (**1**) (Scheme 1).

Experimental

Materials

All starting materials were commercially available and of analytical grade. The intermediates of 2-(4-bromophenyl)-5-(3-methylphenyldiethylphosphonate)-1,3,4-oxadiazole (**2**) and 4-*N,N*-di-*p*-tolylaminobenzaldehyde (**3**) were prepared according to the reported procedures.¹¹⁻¹⁵

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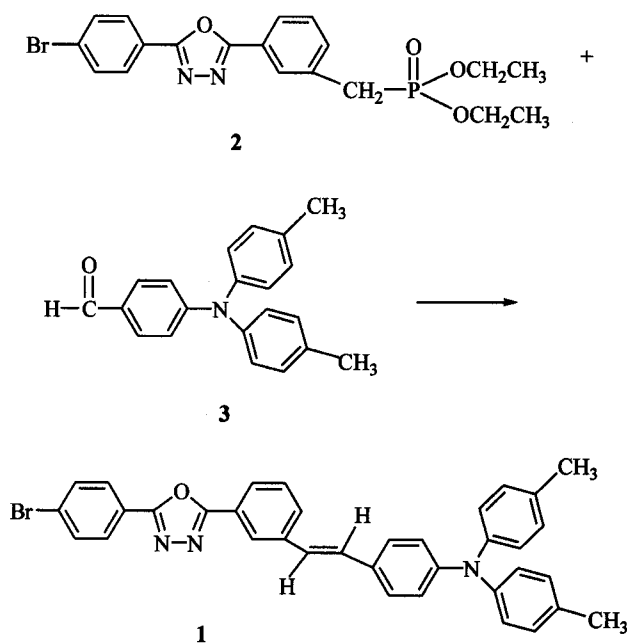
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Synthesis of compound 1

A solution of compound 2 (1 mmol) and compound 3 (1 mmol) in THF (26 mL) was cooled to $-3\text{ }^{\circ}\text{C}$ under N_2 . A solution of potassium *tert*-butoxide (1.1 mmol) in THF (6.5 mL) was added at such a rate as to keep the temperature below $0\text{ }^{\circ}\text{C}$. The reaction mixture was aged at $0\text{ }^{\circ}\text{C}$ for 4 h, warmed to $60\text{ }^{\circ}\text{C}$ and stirred for 24 h. The resulting mixture was then diluted with water (10 mL) and the insoluble reaction product was collected by filtration, washed with water and purified by column chromatography on a silica gel column (petroleum ether: ethyl acetate, 5:1 as the eluent) to give a greenish yellow solid (yield 75%). M. p. $214\text{--}215\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (CDCl_3 , 200 MHz) δ : 2.32 (s, 6H), 7.02–8.10 (m, 22H); IR (KBr) ν : 3060, 3030, 1600, 1500, 1258, 1320, 1015, 962, 820 cm^{-1} ; MS m/z (%): 598 (M^+ , 100). Anal. calcd for $\text{C}_{36}\text{H}_{28}\text{BrN}_3\text{O}$: C 72.24, H 4.72, N 7.02; found C 72.34, H 4.71, N 7.04.

Scheme 1



Physical measurements

IR spectra were obtained on a Shimadzu-IR 435 spectrometer. $^1\text{H NMR}$ spectra (with TMS as the internal standard) were recorded on a Bruker AC-P200 spectrometer. Elemental analysis was performed on a Yanaco MT-3 instrument. Mass spectra were measured on a HP 5989

instrument (EI). Melting points were determined with a model Yanaco MP-500 apparatus and uncorrected. Absorption and emission spectra were taken with a Hitachi UV-3010 absorption spectrophotometer and Hitachi F-4500 fluorescence spectrophotometers, respectively.

X-Ray structural determination

The single crystal suitable for X-ray analysis were obtained from a solution of the mixed solvent of ether and DMF by slow evaporation at room temperature. The crystals were mounted on a fine-focus sealed tube and used for data collection. The determination of unit cell and the data collection were performed with $\text{Mo K}\alpha$ radiation ($\lambda = 0.071073\text{ nm}$) on a BRUKER SMART 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection using ω scan mode. Unit cell dimensions were obtained with least squares refinements using the programs SHELXS-97¹⁶ and the structure was solved by direct methods using SHELXL-97 program.¹⁷ The data collection parameters and determined crystallographic data are summarized in Table 1. All hydrogen atoms were located by calculation geometry and took part in refinement. The selected bond lengths and angles are collected in Table 2.

Results and discussion

Crystal structure

The crystal structure of compound 1 shows that the moiety of 2,5-diaryl-1,3,4-oxadiazole has a nearly coplanar structure (Fig. 1) as seen in the torsion angles 4.0° and 3.3° for 4-bromophenyl and *m*-substituted phenyl rings, respectively, relative to the oxadiazole ring. The torsion angle between $\text{C}(13)\text{--C}(15)\text{--C}(16)\text{--C}(17)$ is -175.8° , indicating the configuration at the $\text{C}(15)=\text{C}(16)$ double bond is *E*. Parameters most important for conjugation are the torsion angle between the planar aromatic and olefinic moieties. The torsion angles between $\text{C}(14)\text{--C}(13)\text{--C}(15)\text{--C}(16)$ and $\text{C}(15)\text{--C}(16)\text{--C}(17)\text{--C}(18)$ are -11.3° and -9.7° , respectively, indicating the presence of conjugation. Structure analysis also indicates that oxadiazole moiety and all the three benzene planes except the two tolyl rings of triarylamine were approximately coplanar in 1. The triarylamine group has three non-coplanar benzene rings, contributing to the steric hindrance of the molecule.

Table 1 Data collection parameters and crystal data for **1**

Empirical formula	C ₃₆ H ₂₈ BrN ₃ O
Formula weight	598.52
<i>a</i> (nm)	0.727(3)
<i>b</i> (nm)	1.519(6)
<i>c</i> (nm)	1.602(6)
α (°)	61.78(7)
β (°)	85.73(7)
γ (°)	77.23(7)
Space group	<i>P</i> -1 (no. 2)
Crystal system	Triclinic
<i>Z</i>	2
Volume (nm ³)	1.520(10)
Crystal size (mm)	0.25 × 0.20 × 0.10
Density (calculated) (mg/m ³)	1.308
Temperature (K)	293
θ range for data collection (°)	1.45–25.02
Index range	−8 ≤ <i>h</i> ≤ 8, −18 ≤ <i>k</i> ≤ 12, −19 ≤ <i>l</i> ≤ 19
Absorption coefficient (mm ^{−1})	1.385
<i>F</i> (000)	616
Number of collected reflections	6147
Number of unique reflections	5232
<i>R</i> _{int}	0.0545
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5232/0/370
Goodness-of-fit on <i>F</i> ²	0.993
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0623, <i>wR</i> ₂ = 0.1223
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0758, <i>wR</i> ₂ = 0.1609
Largest diff. peak and hole (e/nm ³)	398 and −328

Table 2 Selected bond lengths (nm) and angles (°) with e. s. d. s. in parentheses for **1**

Br(1)—C(1)	0.1904(8)	C(7)—O(1)—C(8)	102.6(5)
O(1)—C(7)	0.1373(8)	C(7)—N(1)—N(2)	106.5(6)
N(1)—N(2)	0.1407(7)	C(20)—N(3)—C(30)	117.6(5)
N(2)—C(8)	0.1286(8)	C(20)—N(3)—C(23)	122.4(4)
N(3)—C(20)	0.1429(7)	C(30)—N(3)—C(23)	119.7(4)
C(4)—C(5)	0.1381(10)	C(6)—C(1)—Br(1)	120.4(6)
C(4)—C(7)	0.1459(8)	C(3)—C(4)—C(7)	122.6(6)
C(8)—C(9)	0.1459(9)	N(1)—C(7)—O(1)	111.7(5)
C(12)—C(13)	0.1395(9)	N(1)—C(7)—C(4)	130.0(6)
C(13)—C(15)	0.1473(8)	O(1)—C(7)—C(4)	118.3(6)
C(15)—C(16)	0.1317(8)	N(2)—C(8)—C(9)	130.3(5)
C(16)—C(17)	0.1486(8)	O(1)—C(8)—C(9)	117.6(5)
C(17)—C(18)	0.1384(8)	C(12)—C(13)—C(15)	119.4(6)
C(23)—C(28)	0.1391(7)	C(16)—C(15)—C(13)	127.5(6)
C(30)—C(31)	0.1379(8)	C(15)—C(16)—C(17)	128.8(6)
C(26)—C(29)	0.1538(9)	C(22)—C(17)—C(16)	120.8(5)
C(33)—C(36)	0.1519(9)	C(21)—C(20)—N(3)	120.7(5)

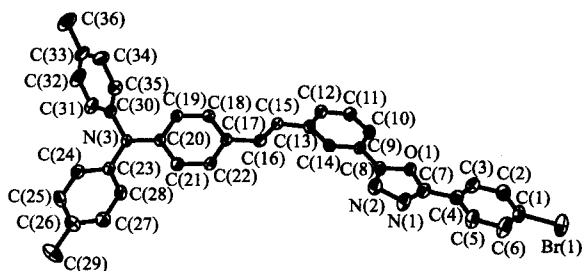


Fig. 1 ORTEP drawing of compound 1 with 30% probability thermal ellipsoids.

The molecules of **1** form stacks in a head-to-tail manner (Fig. 2). The molecules are inclined to *b*-axis by *ca.* 30°. No intermolecular hydrogen bond exists between the stacks. The molecules exhibit intermolecular π - π interactions. The dihedral angle between planes A (ring: C(9)-C(10)-C(11)-C(12)-C(13)-C(14)) is 0.03° and the center-to-center distance between rings A is 0.39 nm. The intermolecular π - π interactions suggest that compound **1** can possess charge/hole transport property, thus making it a promising candidate for EL material.

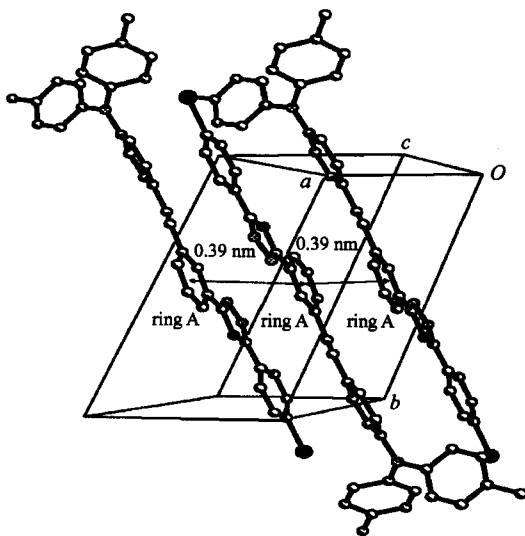


Fig. 2 Packing diagram of compound 1.

Photophysical properties

The wavelengths of the UV-vis absorption maximum (λ_{\max}) in four solvents (1×10^{-5} mol/L) are: 292, 380 nm (hexane); 290, 380 nm (acetic ether); 290, 380 nm (alcohol) and 293, 390 nm (chloroform). The two

absorption peaks at *ca.* 290 and *ca.* 380 nm may be attributed to the oxadiazole-*trans*-stilbene¹⁸ and the triarylamine moieties, respectively.

Because photoluminescence (PL) has almost the same mechanism as EL, fluorescent properties of the compound were investigated to estimate its EL spectra. The PL emissions in solutions (1×10^{-5} mol/L) and in the spin-coated film state are shown in Fig. 3. Compound **1** exhibits strong solvatochromism. The emission maximum in hexane occurs at 420 nm, whereas in alcohol, the emission maximum moves to the green region at 503 nm. Since molecules in the S_0 and locally excited (LE) states have similar dipole moments, the solvent effects on these states are expected to be similar, resulting in the observation of only a small shift in electronic absorption spectra when solvent polarity is changed. On the other hand, molecules in the charge transfer (CT) state have larger dipole moments than those in the S_0 and LE states. Therefore, the relative energy of the CT state against that of the LE state depends on the solvent polarity.¹⁹ This means that great stability of the CT state can be obtained by increasing the polarity. Thus, a polar solvent contributes much more to the stability of the excited state than to the ground state. Compound **1** emits a bright blue-green color in the spin-coated film state at $\lambda_{\max} = 492$ nm when irradiated by UV light, whereas in a CHCl_3 solution, the emission maximum of **1** is at $\lambda_{\max} = 482$ nm. The red shift of emission energy from solution to solid state is clearly caused by intermolecular π - π interactions in the solid state as confirmed by the crystal structure of **1**. The molecule crystal structure showed that compound **1** is rather flat except the two tolyl groups of the triarylamine

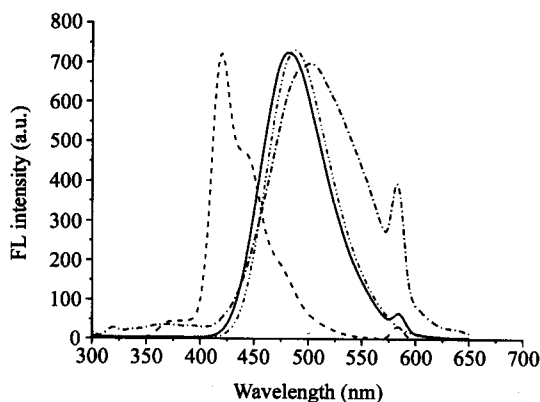


Fig. 3 Photoluminescence spectra of compound **1** in different solutions: — in CHCl_3 ; ··· in $\text{CH}_3\text{COOC}_2\text{H}_5$; - - - in hexane; - · - in $\text{C}_2\text{H}_5\text{OH}$; that in film: - - -.

unit. The strong π - π stacking interactions evident in the X-ray crystal structure clearly affect its excited-state electronic structure. Excimer formation²⁰ is the likely explanation of the solid state emission spectra.

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