

Substituent effect on photophysical properties of bi-1,3,4-oxadiazole derivatives in solution



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ABSTRACT

A series of phenyl substituted bi-1,3,4-oxadiazole derivatives were designed and synthesized; the effect of substituent on the photophysical properties and molecular electronic structures was fully studied by the combination of experimental techniques and theoretical calculations. Compared to parent compound without any substituent (BOXD), fluoro-substituent shows little effect on the absorption and emission spectra, whilst a little larger spectral red-shift could be observed for methoxy-, nitro-substituted derivatives and thienyl-substituted bi-1,3,4-oxadiazole (TBOXD). These spectral changes can be well explained by theoretically calculated HOMO and LUMO energy level changes. All these molecules show high fluorescence quantum yield except for nitro-substituted derivative in dilute solutions. The quantum yield of BOXD changes with the concentration and exhibits a high value at the concentrated solution. This work revealed the influence of substituent on the photophysical properties of bi-1,3,4-oxadiazole derivatives in dilute solutions and provided guidance for designing molecules with potential application.

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1. Introduction

In recent years, organic fluorescent materials have been studied extensively, not only to explore their fundamental optical and electrical properties, but also to identify their potential applications in optoelectronic field, such as organic light-emitting diodes (OLED) [1–5], organic light-emitting field-effect transistors (OLE-FETs) [6–10], organic solid-state lasers [11–15] and organic fluorescent sensors [16–19]. Although there have been a lot of reports focusing on the organic fluorescent materials, many problems are still not solved. For instance, most molecules show a high fluorescence yield in their dilute solutions while exhibit an opposite situation in aggregated or condensed state [20–22]. It is reported that the fluorescence quenching may be caused by certain interactions among the adjacent molecules [22–24]. Moreover, some molecules have high charge carrier mobility for the existence of large extent of π - π interactions but show a very low fluorescence [25]. It is difficult to achieve the high fluorescence and the high charge carrier mobility simultaneously. The properties of organic light-emitting

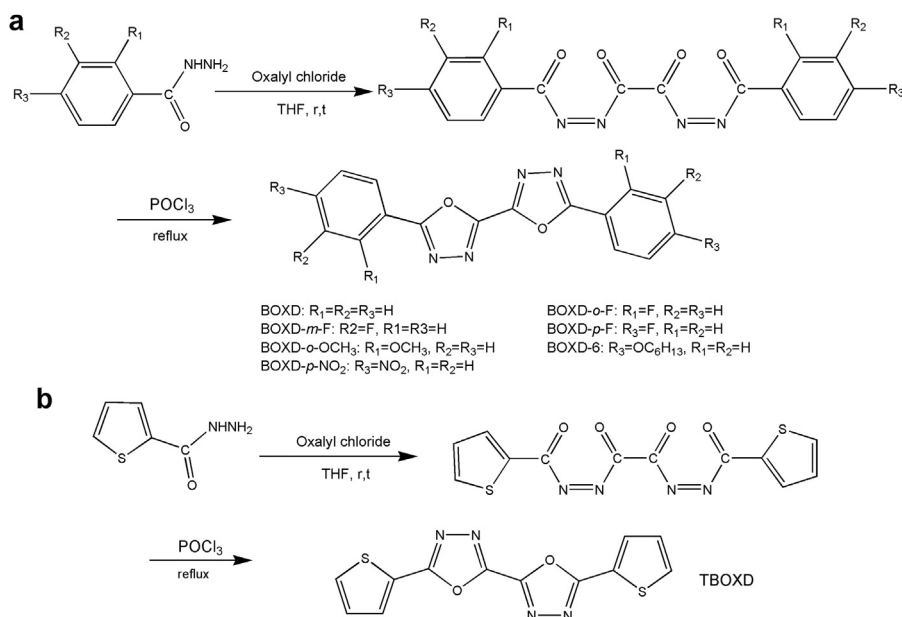
materials such as fluorescence and charge carrier mobility are not only decided by the molecular electronic structure but also by the packing modes and orientation [22,26,27]. How the molecular structure influences the photophysical properties and the mechanism is yet to be clear, which seriously restrict the applications of the organic light-emitting materials. In order to explore these problems, much more systematic research should be done. Thoroughly understanding the substituent effect is the basis to obtain high efficient solid state light-emitting materials and provides guidance for the molecular design of organic light-emitting materials.

Among the various π -conjugated systems, the phenyl substituted 1,3,4-oxadiazole (OXD) unit is an ideal mode to study the photophysical properties due to their tunable energy gap, high fluorescence quantum yield, good thermal and chemical stabilities [28–31]. However, systematically exploring the influence of substituent on the photophysical properties, the solid state molecular packing, and further more the solid state light-emission properties of 1,3,4-oxadiazole derivatives are still missing. Recently, we have designed and synthesis a series of phenyl substituted bi-1,3,4-oxadiazole (OXD) derivatives, where both the type and the position of the substituents are widely changed (Scheme 1). Here we will focus on the synthesis and photophysical properties of these

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Scheme 1. Synthetic routes to a series of bi-1,3,4-oxadiazole derivatives.

bi-1, 3, 4-oxadiazole derivatives in dilute solution. In order to get deep insight into the nature of the photophysical properties, experimental study and theoretical calculations were carried out jointly.

2. Experimental

2.1. Molecular design and synthesis

In designing a molecule, various substituents (-C₄H₃S (thiophene), -F, -OCH₃, -NO₂) with a range of electron-withdrawing and electron-donating properties and different substituted positions (Ortho-, *o*-; Meta-, *m*-; Para-, *p*-) were selected to assess their effects on these molecules (the molecular structures were shown in Scheme 1). In nomination, -F, -OCH₃ and -NO₂ indicate the substituents in the phenyl rings, -*o*-, -*m*-, and -*p*- indicate the substituted position, for example BOXD-*o*-F indicates that the phenyl ring in BOXD was *ortho*-substituted by -F; BOXD-6 [32] is a molecule that was *para*-substituted by -OC₆H₁₃ in BOXD; TBOXD represents a thienyl-substituted bi-oxadiazole derivative. All these compounds were obtained through the synthetic route in Scheme 1a, except for TBOXD in Scheme 1b. As shown in Scheme 1, firstly, the oxalyl chloride was slowly dropped into 50 mL tetrahydrofuran (THF) solution of the corresponding hydrazide derivative. The mixture was stirred at room temperature for about 10 h and the resulting solution was filtered, yielding oxalyl acid dihydrazide. The crude product was purified by washing with boiling ethanol. Secondly, oxalyl acid dihydrazide was dissolved in 50 mL phosphorous oxychloride (POCl₃). The mixture was stirred and heated to reflux for about 40 h. After the reaction, the resulting solution was cooled to room temperature and poured into 1000 mL ice water. At last, the product was collected by filtration and recrystallized from ethanol or dimethyl sulfoxide (DMSO) for further ¹H NMR, FT-IR measurements, and elemental analysis. The original ¹H NMR spectra of these bi-oxadiazole derivatives can be found in the supporting information (Figs. S1–S7).

2.1.1. 2,2-bis(phenyl)-bi-1,3,4-oxadiazole (BOXD)

Benzoyl hydrazine (3 g, 0.022 mol) and oxalyl chloride (1.4 g,

0.011 mol) were added. Yield >70%, melting point: 273–275 °C. ¹H NMR (300 MHz, DMSO), (ppm, from TMS): 8.17 (d, *J* = 6.82 Hz, 2H), 7.72 (m, *J* = 8.04 Hz, 3H). FT-IR (KBr, pellet, cm⁻¹): 3434, 3064, 2923, 2853, 2350, 1621, 1602, 1585, 1540, 1476, 1467, 1415, 1399, 1334, 1306, 1286, 1261, 1151, 1081, 1067, 1027, 993, 953, 907, 782, 707, 686. Elemental analysis: Found: C, 66.55; H, 3.34; N, 19.33. Calc. for C₁₆H₈N₆O₆: C, 66.20; H, 3.47; N, 19.30%.

2.1.2. 2,2-bis(2-fluorophenyl)-bi-1,3,4-oxadiazole (BOXD-*o*-F)

2-Fluorobenzoyl hydrazine (2.43 g, 0.016 mol) and oxalyl chloride (0.9 g, 0.007 mol) were added. Yield >70%, melting point: 215–217 °C. ¹H NMR (300 MHz, CDCl₃), (ppm, from TMS): 8.22 (t, *J* = 8.12 Hz, 1H), 7.64 (ddd, *J* = 7.30, 5.07, 1.58 Hz, 1H), 7.35 (td, *J* = 15.54, 8.30 Hz, 1H). FT-IR (KBr, pellet, cm⁻¹): 3434, 3084, 2921, 1614, 1588, 1541, 1468, 1436, 1269, 1231, 1161, 1153, 1120, 1062, 1085, 995, 952, 874. Elemental analysis: Found: C, 59.24; H, 2.36; N, 17.33. Calc. for C₁₆H₈F₂N₄O₂: C, 58.90; H, 2.47; N, 17.17%.

2.1.3. 2,2-bis(3-fluorophenyl)-bi-1,3,4-oxadiazole (BOXD-*m*-F)

3-Fluorobenzoyl hydrazine (2.45 g, 0.016 mol) and oxalyl chloride (1.0 g, 0.008 mol) were added. Yield >70%, melting point: 214–216 °C. ¹H NMR (300 MHz, DMSO), (ppm, from TMS): 8.01 (dd, *J* = 17.34, 8.42 Hz, 2H), 7.76 (dd, *J* = 14.03, 7.79 Hz, 1H), 7.62 (t, *J* = 8.49 Hz, 1H). FT-IR (KBr, pellet, cm⁻¹): 3434, 2921, 2852, 2316, 1617, 1593, 1545, 1485, 1466, 1424, 1383, 1335, 1314, 1292, 1274, 1208, 1164, 1145, 1090, 1065, 1010, 1002, 968, 954, 923, 878, 869, 833, 806, 728, 677. Elemental analysis: Found: C, 59.27; H, 2.39; N, 17.29. Calc. for C₁₆H₈F₂N₄O₂: C, 58.90; H, 2.47; N, 17.17%.

2.1.4. 2,2-bis(4-fluorophenyl)-bi-1,3,4-oxadiazole (BOXD-*p*-F)

4-Fluorobenzoyl hydrazine (2.44 g, 0.016 mol) and oxalyl chloride (1.0 g, 0.008 mol) were added. Yield >70%, melting point: 275–278 °C. ¹H NMR (300 MHz, DMSO), (ppm, from TMS): 8.24 (dd, *J* = 8.62, 5.38 Hz, 2H), 7.54 (t, *J* = 8.78 Hz, 2H). FT-IR (KBr, pellet, cm⁻¹): 3427, 2920, 2850, 1608, 1556, 1492, 1476, 1299, 1287, 1225, 1159, 1099, 1083, 1011, 953, 847, 828, 813, 786, 737, 696. Elemental analysis: Found: C, 59.24; H, 2.51; N, 17.25. Calc. for C₁₆H₈F₂N₄O₂: C, 58.90; H, 2.47; N, 17.17%.

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