Synthesis, Crystal Structure and Fluorescence Behavior of 2,6-Di(thiophen-2-yl)-benzo[1,2-*d*:4,5-*d*′]bisoxazole

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An effective and clean new aerobic approach for the synthesis of 2,6-disubstituted benzobisoxazole by using a one-pot reaction of an organic aminoxyl radical as the catalyst is reported. 2,6-Di(thiophen-2-yl)-benzo[1,2-*d* : 4,5-*d*′]bisoxazole was synthesized with catalysis by the free radical 4-methoxy-TEMPO and characterized by ^{1}H and ^{13}C NMR spectroscopy, HRMS, as well as by elemental analysis, UV/Vis and emission spectroscopy. The crystal structure of the title compound has been determined by single-crystal X-ray diffraction. It crystallizes in the monoclinic space group *C*2/c with $a = 12.531(1)$, $b = 3.8960(2)$, $c = 28.733(2)$ Å, $\beta = 100.760(1)^\circ$, $Z = 4$. Through intermolecular weak C–H···O hydrogen bonding and π-π stacking interactions, a supramolecular 3D structure is formed.

Key words: 4-Methoxy-TEMPO Free Radical, 2,6-Dithiophene Disubstituted Benzobisoxazole, Synthesis, Crystal Structure, Fluorescence Behavior

Introduction

Aerobic oxygenation/oxidation of hydrocarbons, alcohols and amines catalyzed by aminoxyl radicals have been extensively studied [1, 2]. However, its application in the catalytic oxidative synthesis of heterocycles is rare. Recently, we reported an expeditious, one-pot, efficient method for the preparation of a series of asymmetric semicarbazides with heteroarene core [3 – 5].

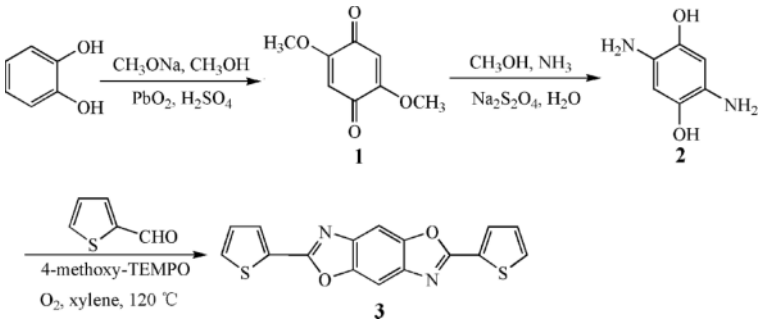
The advantages of using organic materials to fabricate electroluminescent (EL) devices are their high brightness, high efficiency and potential color tuning as well as their low cost of fabrication, which shows great commercial potential [6]. 2-(Biphenyl-4-yl)-5-(*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), was the first example and one of the most efficient electron transport materials in an organic EL device [7]. We are interested in developing benzobisoxazoles for their use as building blocks for novel organic semiconductors because conjugated small molecules and polymers based on benzobisoxazoles are well suited for use in organic semiconducting applications. These materials combine efficient electron transport, photoluminescence, and third-order nonlinear optical properties with excellent mechanical strength and thermal stability [8 – 10].

It has been reported that benzoxazole derivatives were widely used in thin membrane field effect transistors [11, 12], electrophosphorescent materials [13], light cells, molecular electrodes [14], high-performance fibers and in other fields [15 – 17]. Compared with benzoxazoles, 2,6-disubstituted benzobisoxazoles have larger conjugated systems. Herein, an effective and more eco-friendly new aerobic approach for the synthesis of 2,6-di(thiophen-2-yl)-benzo[1,2-*d*:4,5-*d*′]bisoxazole (**3**) by using a one-pot reaction of an organic aminoxyl radical as the catalyst and 2-thiophenecarboxaldehyde is reported.

Results and Discussion

*Synthesis of compound **3***

As shown in Scheme 1, the new compound 2,6-di(thiophen-2-yl)-benzo[1,2-*d*:4,5-*d*′]bisoxazole (**3**) was synthesized with 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy (4-methoxy-TEMPO) as a free radical catalyst starting from **1** and **2**. The 4-methoxy-



Scheme 1. The synthetic route to 2,6-di(thiophen-2-yl)-benzo[1,2-*d* : 4,5-*d′*]bisoxazole (**3**).

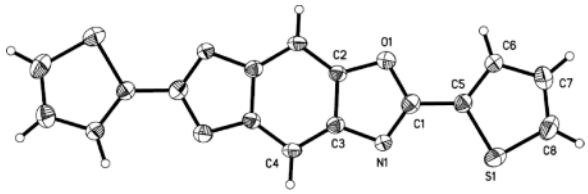


Fig. 1. Molecular structure in the crystal with atom numbering of compound **3**.

TEMPO radical is widely used for the selective oxidation of primary or secondary alcohols [18 – 20]. 4-Methoxy-TEMPOH can be slowly oxidized to the 4-methoxy-TEMPO radical in air at room temperature, so a strategy for the aerobic catalytic oxidative synthesis of benzoxazole using 4-methoxy-TEMPO as the catalyst was developed [21]. Moreover, the crystal structure of the new compound was determined by single-crystal X-ray diffraction.

As shown in Fig. 1, the X-ray crystallographic analysis (Table 1) of the title compound **3** revealed that the dihedral angles defined by the central benzo[1,2-*d*:4,5-*d′*]bisoxazole ring plane and the side thiophene planes is only 2.12(2)° , the planes defined by two side thiophene rings are parallel, and their distance is about 0.242(1) Å, showing that the title molecule has a good coplanar property owing to the absence of steric hindrance of alkyl chains [22]. Selected bond lengths and bond angles as well as hydrogen bonds parameters are listed in Tables 2 and 3, respectively [23].

As shown in Fig. 2, in the crystal structure of the title compound, the neighboring units are linked into an infinite chain by intermolecular hydrogen bonding C4–H4···O1 (Table 3) forming six-membered rings with a graph motif $R_2^2(6)$. Furthermore, in Fig. 4 the packing diagram shows that the title compound **3** forms a herringbone arrangement with abundant $\pi-\pi$ stacking interactions between neighboring thiophene rings, oxazole rings and benzene rings with distances between the centroids of 3.896(2) Å and 3.829(2) Å (Table 4 [24], Fig. 3).

Table 1. Crystal data and structure refinement for compound **3**.

Molecular formula	$C_{16}H_8N_2O_2S_2$
Molecular weight, g mol^{-1}	324.36
Crystal color, habit	colorless, needle-like
Crystal size, mm^3	0.49 × 0.12 × 0.09
Crystal system	monoclinic
Space group	*C*2/*c*
a, Å	12.5309(1)
b, Å	3.8960(2)
c, Å	28.733(2)
β, deg	100.7600(1)
V, Å^3	1378.10(2)
Z	4
T, K	298(2)
$D_{calcd.}$, mg m^{-3}	1.56
μ(MoK_α), cm^{-1}	3.9
F(000), e	664
hkl range	−14 : 10, ±4, −33 : 34
θ range for data collection, deg	2.889–25.919
Refl. collected / unique / R_{int}	3183 / 1212 / 0.0477
Data / restraints / parameters	1212 / 0 / 100
Final R_1/wR_2 [$I > 2\sigma(I)$]^a	0.0533 / 0.1414
Final R_1/wR_2 (all data)^b	0.0697 / 0.1527
Goodness-of-fit (F^2)^c	1.032
Largest diff. peak / hole, e Å^{-3}	0.263 / −0.406

^{a} $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; ^{b} $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2)+(AP)^2+BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2,0)+2F_c^2)/3$; ^{c} GoF $= [\Sigma w(F_o^2-F_c^2)^2/(n_{obs}-n_{param})]^{1/2}$.

UV/Vis and photoluminescence spectra

The UV/Vis absorption and photoluminescence spectra of the title compound **3** were determined in 5×10^{-5} mol L^{-1} CH_2Cl_2 solution at room tempera-

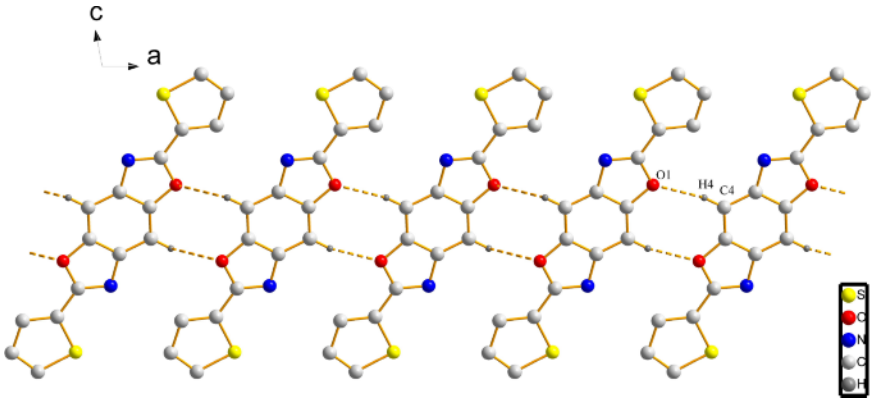


Fig. 2. Part of the infinite chain motif of compound **3** (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

Table 2. Selected bond lengths (Å) and bond angles (deg) for compound **3**.

Bond	Lengths	Bond	Lengths	Bond	Lengths
S(1)–C(8)	1.684(4)	S(1)–C(5)	1.722(3)	O(1)–C(1)	1.367(3)
O(1)–C(2)	1.380(3)	N(1)–C(1)	1.304(4)	N(1)–C(3)	1.404(4)
C(1)–C(5)	1.439(4)	C(2)–C(4)	1.383(4)	C(2)–C(3)	1.409(4)
C(3)–C(4)	1.385(4)	C(4)–C(2)	1.383(4)	C(5)–C(6)	1.386(4)
C(6)–C(7)	1.416(4)	C(7)–C(8)	1.367(5)		
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
C(8)–S(1)–C(5)	91.83(16)	C(1)–O(1)–C(2)	104.7(2)	C(1)–N(1)–C(3)	105.2(2)
N(1)–C(1)–O(1)	114.9(3)	N(1)–C(1)–C(5)	126.0(3)	O(1)–C(1)–C(5)	119.1(3)
O(1)–C(2)–C(4)	128.5(2)	O(1)–C(2)–C(3)	107.5(2)	C(4)–C(2)–C(3)	124.0(3)
C(4)–C(3)–N(1)	129.7(3)	C(4)–C(3)–C(2)	122.6(3)	N(1)–C(3)–C(2)	107.7(2)
C(2)–C(4)–C(3)	113.4(2)	C(6)–C(5)–C(1)	128.4(3)	C(6)–C(5)–S(1)	111.6(2)
C(1)–C(5)–S(1)	120.0(2)	C(5)–C(6)–C(7)	111.1(3)	C(8)–C(7)–C(6)	112.9(3)
C(7)–C(8)–S(1)	112.6(3)				

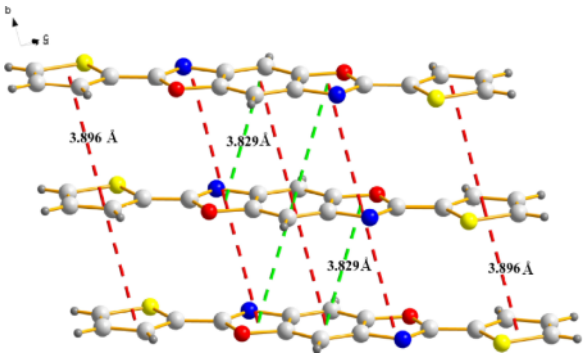


Fig. 3. Face-to-face π-π stacking diagram of compound **3**.

ture and are shown in Figs. 5 and 6, respectively. The absorption spectrum exhibits the maximum peak at about 361 nm, a shoulder peak at 344 nm and another peak at about 380 nm. Comparatively, the fluorescence spectrum shows a maximum peak at 408 nm, a shoulder peak at 428 nm and another peak at 387 nm (Table 5). The Stokes shift between the maximum wavelength of the absorbance and fluorescence spectrum is 47 nm.

Table 3. Weak hydrogen bond parameters for compound **3**[a].

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA
C4–H4···O1[i]	0.930	2.565	3.455	160.44

[a] Symmetry code: (i) $-1/2+x$, $-1/2+y$, z.

Conclusion

We have reported the synthesis and structural characterization of 2,6-dithiophene disubstituted benzobisoxazole. Future efforts will focus on the synthesis of other useful heterocycles based on these materials, as well as device construction and evaluation of the electronic and optical properties of oligomers and polymers containing the benzobisoxazole moiety.

Experimental Section

Materials and physical measurements

2,5-Dimethoxycyclohexa-2,5-diene-1,4-dione (**1**) and 2,5-diaminobenzene-1,4-diol (**2**) were prepared according to literature procedures [25]. Pyrocatechol and

Table 4. π-π Stacking interactions (Å, deg) for compound **3**[a].

Ring 1	Ring 2	α	DCC (Å)	CgI–perp (Å)	CgJ–perp (Å)	Slippage
Cg1	Cg1	0	3.896(2)	−3.476(1)	−3.476(1)	1.761
Cg2	Cg2	0	3.896(2)	−3.476(1)	−3.476(1)	1.761
Cg2	Cg3	0.27(15)	3.829(2)	3.4743(2)	−3.4689(2)	0
Cg3	Cg3	0	3.896(2)	−3.476(1)	−3.476(1)	1.761

[a] DCC = distance between ring centroids; α = dihedral angle between planes I and J; CgI–perp = perpendicular distance of Cg(I) from ring J; CgJ–perp = perpendicular distance of Cg(J) from ring I; slippage = distance between Cg(I) and perpendicular projection of Cg(J) on ring I; Cg1, Cg2 and Cg3 are the centroids of the thiophene ring S1-C5-C6-C7-C8, the oxazole ring O1-C1-N1-C3-C2 and the benzene ring C2-C3-C4-C2(a)-C3(a)-C4(a), respectively.

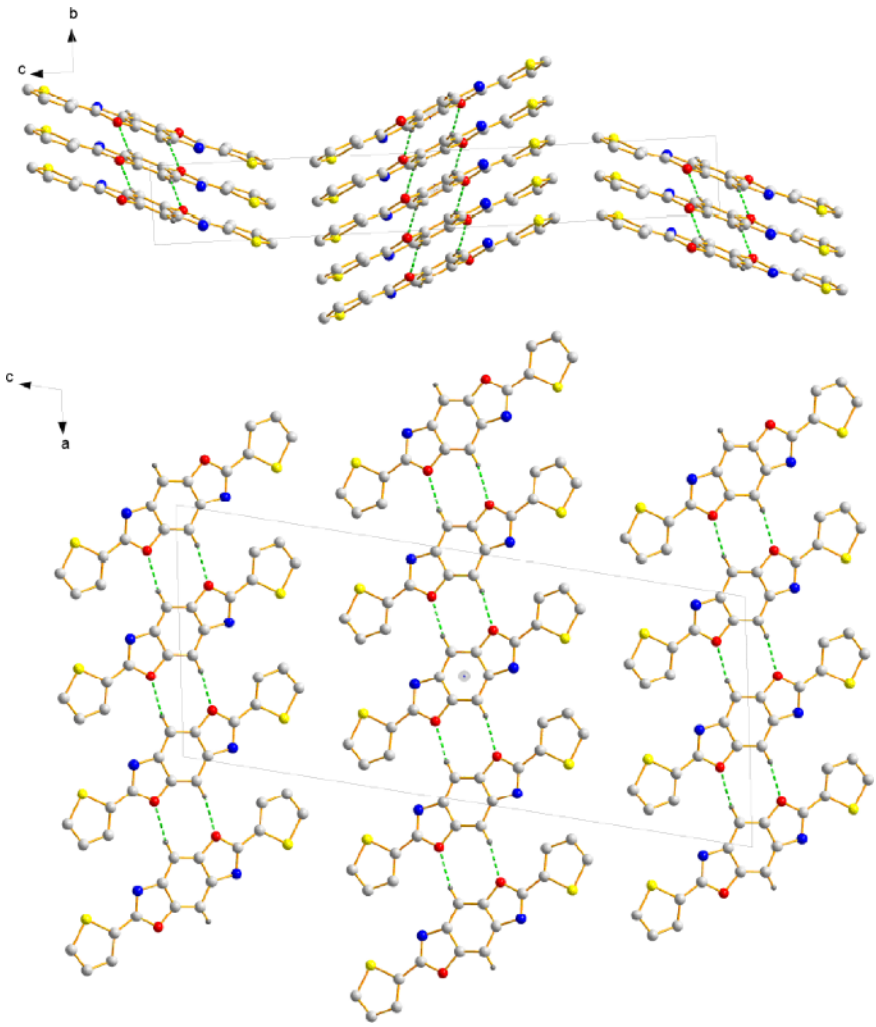


Fig. 4. Packing diagram of compound **3** viewed along the *a* and *b* axis, respectively.

2-thiophenecarboxaldehyde were purchased from Alfa Aesar. All chemicals were of analytical reagent grade and were used without further purification.

^{1}H and ^{13}C NMR spectra were measured on Mercury Plus (400 MHz) spectrometers. Chemical shifts of ^{1}H NMR were expressed in parts per million relative to the singlet ($\delta = 7.26$) for $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million relative to the central line of the triplet ($\delta = 77.0$ ppm) for $CDCl_3$ and TMS as internal standard. HRMS spectra were obtained with a Bruker APEX

Table 5. The absorption and fluorescence data for compound **3**.

Absorption		Fluorescene	
λ_{max} (nm)	ε (L mol^{-1} m^{-1})	λ (nm)	Relative intensity
344	46 494	387	433.0
361	58 180	408	546.3
380	43 508	428	360.0

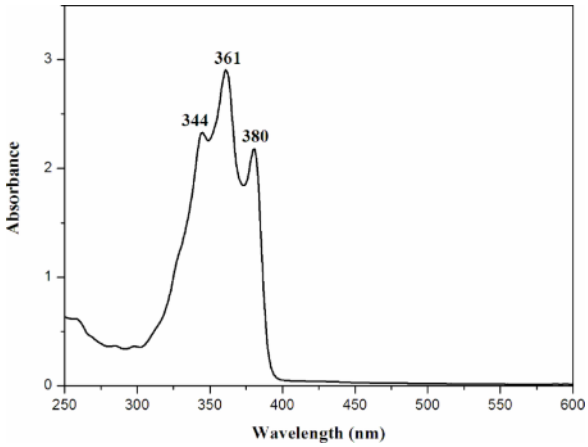


Fig. 5. UV/Vis absorption spectrum of compound **3** in CH_2Cl_2 solution (5.0×10^{-5} mol L^{-1}).

II FT-MS instrument using CD_2Cl_2 as solvent. UV/Vis spectra were recorded on a Shimadzu UV-2550 spectrometer. The fluorescence spectra were taken on a 970 CRT spectrofluorometer (Spectro, Shanghai/China) with 370 nm excitation. The single-crystal X-ray structure determination was carried out on a Bruker Smart 1000 CCD area detector diffractometer. Elemental analysis was performed on an Elementar Vario EL Elemental Analysis instrument.

*Preparation of compound **3***

2,5-Diaminobenzene-1,4-diol (**2**) (280.0 mg, 2.0 mmol) and 2-thiophenecarboxaldehyde (0.5 mL, 4.5 mmol) were reacted in *o*-xylene solution (25 mL) at 120 °C under argon atmosphere. The mixture was stirred for 5 h. After cooling to room temperature, 4-methoxy-TEMPO (47.0 mg, 5.0 mmol) was added to the mixture, which was stirred at 120 °C for 15 h under oxygen atmosphere. After removing the solvent under reduced pressure, the obtained crude product was extracted by chloroform (3 × 20 mL), washed with distilled water (3 × 20 mL) and dried over anhydrous Na_2SO_4. The residue was purified by chromatography using petroleum ether-ethyl acetate (3 : 2) to give a colorless crystalline solid (**3**) (535.9 mg). Yield: 87 %. The identidy and purity of the product was confirmed by ^{1}H and

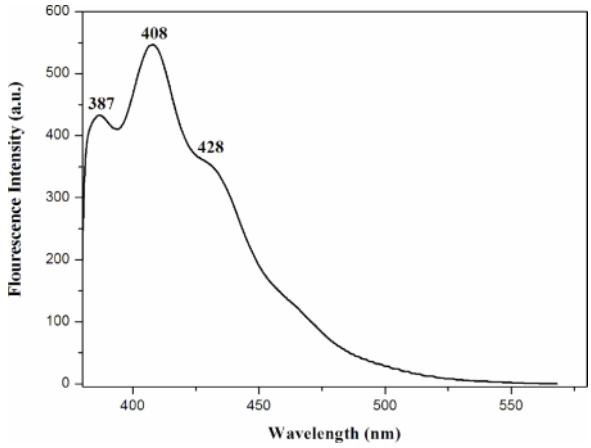


Fig. 6. Fluorescence spectrum of compound **3** in CH_2Cl_2 solution (5.0×10^{-5} mol L^{-1}, $\lambda_{ex} = 360$ nm).

^{13}C NMR spectroscopic analysis. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.97$ (q, $^1J = 4.8$ Hz, $^2J = 3.2$ Hz, 2H), 7.86 (s, 2H), 7.61 (q, $^1J = 6.4$ Hz, $^2J = 1.6$ Hz, 2H), 7.23 (q, $^1J = 10.8$ Hz, $^2J = 3.6$ Hz, 2H) ppm – ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 160.22$, 148.32, 140.28, 130.61, 130.17, 129.47, 128.40, 100.66 ppm. – MS (EI): $m/z = 324$ – Analysis for $C_{16}H_8N_2O_2S_2$ (324.36): calcd. C 59.24, H 2.49, N 8.64; found C 59.36, H 2.63, N 8.76.

Crystal structure determination

The title compound was recrystallized from trichloromethane-acetonitrile. After several days, many colorless needle-like single crystals suitable for X-ray diffraction were obtained. A crystal of **3** was mounted on a Bruker Smart 1000 CCD area detector diffractometer. Intensity data were collected using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structure was solved using the program SHELXS-97 [26, 27] and difference Fourier techniques, and refined by full-matrix least-squares methods on F^2 using the program SHELXL-97 [28, 29]. All hydrogen atoms were added in calculated positions. The crystal data and parameters pertinent to data collection and structure refinement are given in Table 1.

CCDC 879998 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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