研究简报

化合物[2,6-bis(benzo[1,2-d:4,5-d′]diimidazole-2′-yl)pyridine]的合成、晶体结构和光物理性质

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Synthesis, Crystal Structure and Photophysical Properties of 2,6-bis (benzo[1,2-d:4,5-d′]diimidazole-2′-yl)pyridine

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A new tridentate benzimidazole derivative, 2,6-bis (benzo[1,2-d:4,5-d′]diimidazole-2′-yl) -pyridine (Bzdiimpy), was prepared from *o*-phenylenediamine in five steps with improved methods according to the literature in good yield. The crystal structure was determined by X-ray diffraction analysis. It crystallized in monoclinic, space group $P2_1/c$, with a=1.170 8(4) nm, b=2.479 6(9) nm, c=1.215 9(4) nm, β=114.641(7)°, Z=1, R=0.035 0, wR_2=0.089 0. The bzdiimp molecule displayed an almost planar structure and formed a zig-zag chain through weak interactions between imidazole-N and $[SnCl_6]^{2-}$-Cl. Its electronic absorption and emission spectra were measured and compared with the reported analogue 2,6-bis (benz[1,2-d:4,5-d′]imidazole-2′-yl)-pyridine (Bzp). CCDC: 239203.

Keywords: **benzimidazole** **crystal structure** **weak interaction** **fluorescence**

0 Introduction

Benzimidazole and its derivatives have attracted a great attention in the recent years due not only to their biological activities[1,2], but also strong coordination abilities as multidentate ligands and their metal complexes having a broad scope of properties. For example, pyridyl derivatives of benzimidazole exhibit excited-state proton transfer (ESPT) that can be used for proton transfer lasers[3~5], iron(Ⅱ) complexes with Bzps are typical spin crossover complexes[6~8], lanthanide complexes with chiral substituted Bzp have interesting chiro-optical properties which might be used for the sensing of chirality in biological substrates[9~11], manganese(Ⅱ) complex with Bzp is a potent superoxide dismutase mimic[12], the copper(Ⅰ) and copper(Ⅱ) complexes with Bzp serve as biomimetic models for the study of metal sites in complex biological system[13~15], and some vanadium complex with Bzp have been prepared to elucidate the biological role of vanadium[16].

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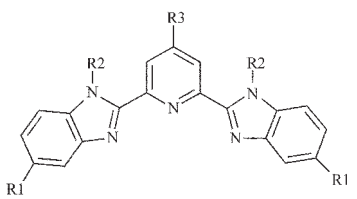
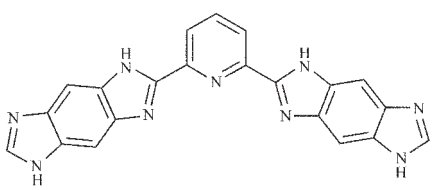
By varying the substituents on the benzimidazole rings, their structures, photophysical and photochemical properties can be tuned[17~19]. Generally, substitution in the R^2 position of the benzimidazole rings essentially controls the stability and the structure of the complexes, while substitution in the R^1 and R^3 affects the electronic and photophysical properties. However, benzodiimidazole and its derivatives were seldom studied; they are potentially antitumor agents[20] and its ruthenium complex exhibit charge-transfer excited state[21]. We present here the synthesis, crystal structure and spectroscopic properties of a new tridentate benzimidazole derivative, 2,6-bis (benzo[1,2-d:4,5-d′] diimidazole-2′-yl)pyridine.



Bzp



Bzdiimpy

1 Experimental

1.1 Instruments

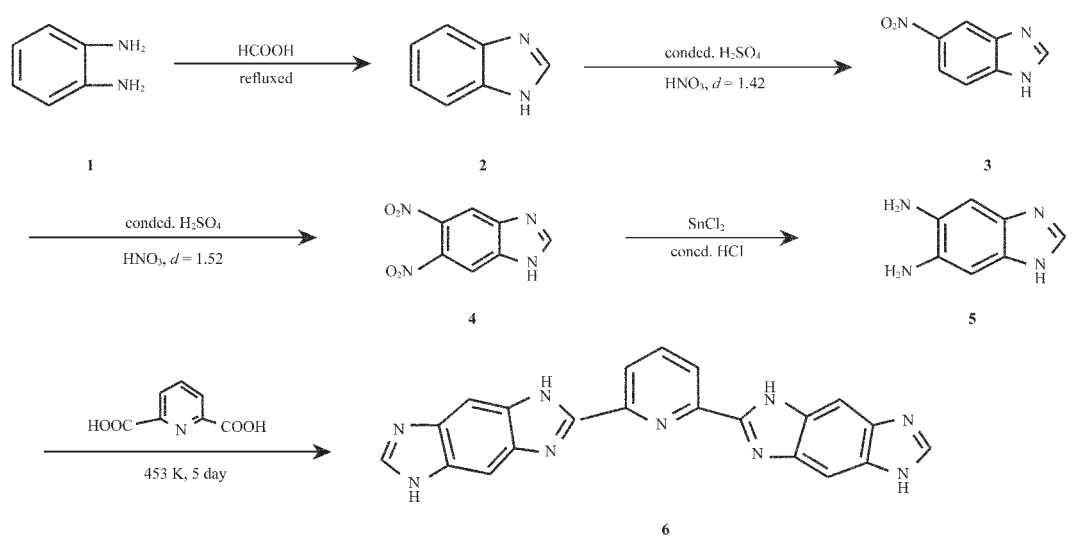
Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyzer. 1H NMR spectra were recorded on Bruker DAX 500. The IR spectra were recorded on a VECTOR 22 spectrophotometer with KBr discs in the 4 000~400 cm^{-1} region. UV-Visible spectra were carried out on a UV-3100 spectrophotometer. Fluorescence spectra were measured on an Aminco Bowman 2 Luminescence spectrophotometer with a xenon arc lamp as the light source.

1.2 Materials

All reagents and solvents were used as commercial sources without further purification.

1.3 Preparation of 2,6-bis(benzo[1,2-d:4,5-d′] diimidazole-2′-yl)pyridine

The synthetic route of Bzdiimpy adopted in this work is given in Scheme 1. The syntheses of benzimidazole, 5-nitrobenzimidazole and 5,6-dinitrobenzimidazole were referred to the previous literatures[22~24]. A minor change was the use of aqueous NaOH solution instead of ammonia during neutralization. Reduction of 5,6-dinitrobenzimidazole with stannichloride gave 5, 6-diamino-benzimidazole dihydrochloride. 5,6-diaminobenzimidazole dihydrochloride (2.21 g, 10 mmol) was mixed with 2,6-pyridinedicarboxylic acid (0.836 g, 5 mmol) in 6 $mol \cdot L^{-1}$ hydrochloric acid, this het-



1 2 3 4 5 6

Scheme 1 Synthetic route for bzdiimpy

erogeneous mixture was then placed in a Teflon-lined steel autoclave and heated at 180 ℃ for 5 days in the oven. Block-shaped colorless single crystals were obtained (yield ca. 30%). ^{1}H NMR (DMSO, 500 MHz) δ: 9.58 (s, 2H), 8.38 (s, 2H), 8.27~8.32 (m, 5H), 8.09~8.14 (m, 4H). IR (KBr) ν / cm^{-1}: 3 448, 3 026, 1 611, 1 577,1 507, 1 431; Anal. Calcd for $C_{21}H_{17}Cl_6N_9O_2SnNa_2$ (%): C 31.31, H 2.11, N 15.66; found (%): C 31.20, H 2.07, N 15.70.

1.4 X-ray Single Crystal Structure Determination

Single crystal of Bzdiimpy suitable for X-ray analysis was carefully selected and glued to a thin glass fiber with adhesive. The unit cell parameters and data were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo$K\alpha$ radiation (λ=0.071 073 nm) using the φ-ω scan mode. The data were corrected for Lorenz and polarization effects. The structure was solved by the direct method and refined on F^2 by full-matrix least-squares methods using SHELXTL. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as riding model. All computations were carried out on a computer using the SHELXTL program package[25]. Crystallographic data is summarized in Table 1.

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Table 1 Crystallographic Data and Structure Refinement for Bzdiimp

empirical formula	$C_{21}H_{17}Cl_6N_9O_2SnNa_2$
formula weight	804.80
crystal system	monoclinic
space group	$P2_1/c$
wavelength / nm	0.071 073
a / nm	1.170 8(4)
b / nm	2.479 6(9)
c / nm	1.215 9(4)
β / (°)	114.641(7)
V / nm^3	3.208 5(19)
Z	1
calculated density / (g·cm^{-3})	1.666
absorption coefficient / mm^{-1}	1.36
F(000)	1 584
crystal size / mm	0.2 × 0.2 × 0.3
θ / (°)	2.0 to 26.0
reflections collected/unique	16 841, 6 222, (R_{int}=0.069)
R_1, wR_2	0.035 0, 0.089 0
goodness-of-fit on F^2	1.07
largest diff. Peak and hole / (e·nm^{-3})	950, −660
refinement method	full-matrix least-squares on F^2

$w=1/[\sigma^2(F_o^2) + (0.020\,0P)^2]$, where $P=(F_o^2+2F_c^2)/3$

2 Results and Discussion

2.1 Synthesis

In general, benzimidazole derivatives were prepared by the condensation of carboxylic acid with a diamine in polyphosphoric acid solution at 150~250 ℃ according to the procedures developed by Thompson and others[26,27]. Whereas we described here for the first time that the condensation of 2,6-pyridinedicarboxylic acid with 5,6-diaminobenzimidazole was carried out under hydrothermal condition to give bzdiimpy in good yield.

2.2 Crystal Structure

An ORTEP drawing of the structure with atomic numbering and a perspective view of the crystal packing in the cell unit are shown in Figs.1~3, respectively. The selected bond length and angles are presented in Table 2.

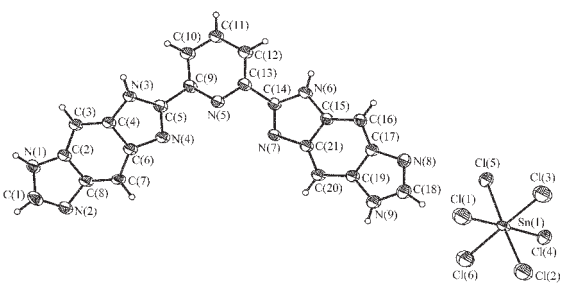

Fig.1 Molecular structure of Bzbiimpy showing 50% probability displacement ellipsoids

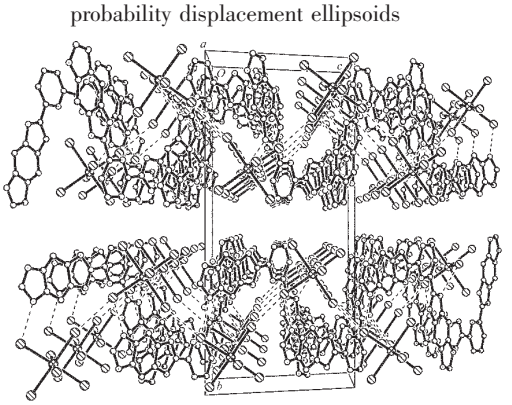

Fig.2 Packing diagram of Bzbiimpy in the unit cell along a axis

Table 2 Selected Bond Lengths (nm) and Torsion Angles (°)

Sn1-Cl1	0.239 59(18)	N6-C15	0.142 1(6)	C6-C7	0.138 4(5)
N1-C1	0.137 0(5)	N7-C14	0.132 8(5)	C7-C8	0.132 1(7)
N1-C2	0.136 2(5)	N7-C21	0.139 2(6)	C9-C10	0.140 8(6)
N2-C1	0.129 6(6)	N8-C17	0.139 9(6)	C10-C11	0.138 5(6)
N2-C8	0.142 7(5)	N8-C18	0.132 4(6)	C11-C12	0.136 3(7)
N3-C4	0.140 7(5)	N9-C18	0.132 5(6)	C12-C13	0.138 4(6)
N3-C5	0.132 7(6)	N9-C19	0.139 3(6)	C13-C14	0.147 8(7)
N4-C5	0.133 9(5)	C2-C3	0.139 6(5)	C15-C16	0.137 7(7)
N4-C6	0.141 4(5)	C2-C8	0.141 0(7)	C15-C21	0.142 7(5)
N5-C9	0.130 4(6)	C3-C4	0.135 1(7)	C16-C17	0.135 3(6)
N5-C13	0.132 4(5)	C4-C6	0.143 6(7)	C17-C19	0.138 0(5)
N6-C14	0.136 0(5)	C5-C9	0.148 1(6)	C19-C20	0.139 9(7)
C6-N4-C5-C9	−176.2(4)	C21-N7-C14-C13	−175.5(4)	C5-C9-C10-C11	−179.6(4)
N6-C15-C16-C17	−179.1(4)				

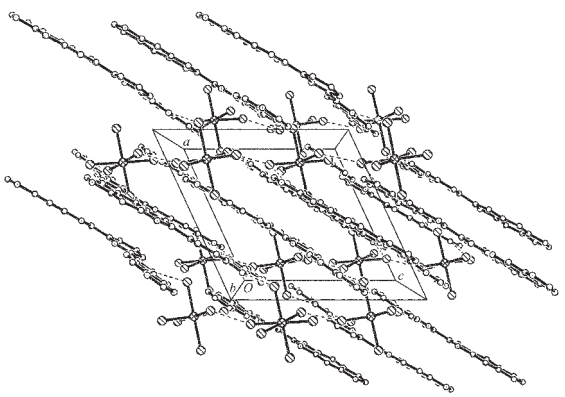

Fig.3 Packing diagram of Bzbiimpy in the unit cell along *b* axis

Structure analysis reveals that each unit cell consists of one 2,6-bis (benzodiimidazole-2′-yl) pyridine neutral molecule, one $Na_2[SnCl_6]$ molecule and two waters. The Bzdiimpy molecule has an almost planar structure. The bond length of N2-C1 (0.129 6(6) nm) in the benzodiimidazole group is shorter than that of N2-C8 (0.142 7(5) nm), N1-C1 (0.137 0(5) nm) and N1-C2 (0.136 2(5) nm), indicating that N2-C1 is a double bond. In addition, the bond length of N4-C5 (0.133 9(5) nm), N7-C14 (0.132 8(5) nm) and N8-C18 (0.132 4(6) nm) are also within the double bonds range, so that the two benzodiimidazole moieties are conjugated with pyridine unit.

A zig-zag chain was formed by the molecular bridge, hexachlorostannade, and were packed in direction of crystal face of (1,0,1) (Fig.2). There are two types of intermolecular interaction in the crystal structure. One is hydrogen bond, which occurs between imidazole-N and H_2O-O, $SnCl_6^{2-}$-Cl (as N1−H1A⋯O3 (0.271 4(7) nm), N3−H3A⋯Cl4 (0.328 8(4) nm), and also between two waters (such as O3−H3E⋯O4 (0.277 5(6) nm). Another is the π-π stacking interaction between imidazole ring (C1/C2/C8/N1 and N2) and pyridine ring (C9/C10/C11/C12/C13 and N5) in two molecules from upper and lower layers, respectively. The distance between the two adjacent aromatic rings is 0.339 19(4) nm.

2.3 UV-Visible and Fluorescence Spectra

The electronic absorption spectrum of Bzdiimp in DMF exhibits a maximum absorption band at 347.5 nm and two shoulder peaks at 361.5 nm and 335 nm (Fig.4), which is around 20 nm red-shifted compared to that of the 2,6-bis (benzimidazole-2′-yl)pyridine (Bzp) (λ_{max}=327.4 nm and $\lambda_{shoulder}$=340 nm and 308 nm in

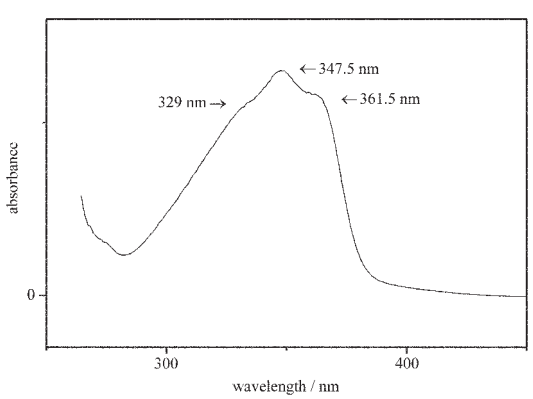

Fig.4 UV-Vis spectra of Bzbiimpy

methanol)[8]. This indicates that bzdiimp forms a planar structure between the central pyridine and benzodiimidazoles and the conjugation is increased by fusion with a second imidazole than Bzp.

Fig.5 shows the excitation and emission spectra of Bzdiimp in DMF (solid line) and in the solid state (dash line), respectively at room temperature. Bzdiimp exhibits a fluorescence band at 421 nm and 415 nm in the solution and in the solid state, respectively. The hydrogen bonding or other intermolecular interactions probably cause the small blue shift of the emission spectrum of bzdiimp in the solid state than that in the solution. The excitation spectrum monitored at 421 nm in DMF shows an intense band at 372 nm which reproduces well the $\pi \rightarrow \pi_1^*$ transition, indicating that the origin of the 421 nm fluorescence band is the $\pi \rightarrow \pi_1^*$ excited state. In addition, the fluorescence band of Bzdiimp is also red-shifted compared to that of Bzp (λ_{em}=374 nm), which is in accordance with the result of the electronic absorption spectra, confirming the increased conjugation and planar structure in Bzdiimp with respect to Bzp.

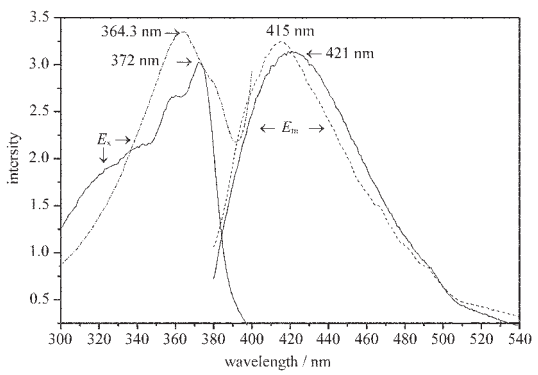

Fig.5 Excitation and emission spectra of Bzbiimpy in DMF (solid line) and in the solid states (dash line)

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