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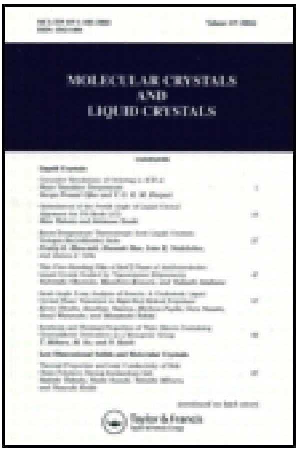

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# Donor-Acceptor Naphthylimide: Synthesis and Properties

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# Donor–Acceptor Naphthylimide: Synthesis and Properties

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*N-butyl-4,5-dibutylamine-1,8-naphthylimide with a donor–acceptor structure was successfully synthesized by one-pot method using 4,5-dibromo-1,8-naphthalic anhydride and butylamine as starting materials. The structure was characterized by NMR and elemental analyses, and the optical and electrochemical properties were investigated. The compound can be used to selectively bind $Cu^{2+}$, along with obvious blueshifts of fluorescence spectrum.*

**Keywords** $Cu^{2+}$ recognition; donor–acceptor system; naphthylimide; optoelectronic properties

## Introduction

Naphthalenediimides (NDIs) are widely used in electronically and optically induced electron transfer systems such as organic field-effect transistors, artificial biological mimics, solar energy converters and supramolecular self-assembling materials, owing to easy structural decoration, strong intermolecular stacking, and excellent electron transfer [1]. As an efficient n-type organic semiconducting materials, NDI and derivatives have been largely applied in organic field effect transistors (OFETs) due to the existence of strong deficient-electron carboxylic imide groups [2].

Meanwhile, NDI as a $\pi$-conjugated molecule possesses very strong fluorescence. Therefore, naphthalene monoimide was usually utilized as a versatile building block to construct novel fluorescent sensors. At present, there are a large number of small molecular fluorescent sensors based on naphthalene monoimide developed by chemists, and some sensors have displayed excellent selectivity and sensitivity [3]. Naphthalene monoimide also plays a favorable role to construct the novel molecules with donor–acceptor structure, which have been widely applied in organic photovoltaic solar cells and organic dyes [4]. Hence, an efficient synthetic method is very important. Herein, we reported a simple method to obtain N-butyl-4,5-dibutylamine-1,8-naphthylimide with a donor–acceptor structure, in which 4,5-dibromo-1,8-naphthalic anhydride [5] was treated with butylamine in a one-pot process. The structure was characterized, and the optical and electrochemical properties

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were investigated. The frontier molecular orbital energy level (HOMO and LUMO) was calculated by density functional theory (DFT). Furthermore, we also explored the binding toward metal ions. The results suggest that it can be used as a fluorescent sensor toward $Cu^{2+}$.

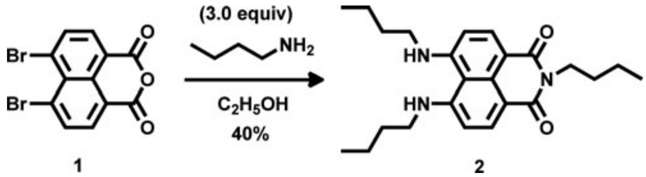
## Experimental

Unless otherwise mentioned, all commercial materials were used as received without further purification. The manipulations were carried out under an argon atmosphere by using standard Schlenk techniques. $^1H$ and $^{13}C$ NMR spectra were collected on an American Varian Mercury Plus 400 spectrometer 400 MHz. Chemical shifts ($\delta$) are reported in parts per million (ppm), using tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed by investigation of C, H, N at Central China Normal University (CCNU), Wuhan, P. R. China. UV–Vis spectra were obtained on a U-3310 UV Spectrophotometer. Fluorescence spectra were obtained on a FluoroMax-P. Electrochemical measurements were performed on a CHI660C potentiostat (CH Instruments, Austin, TX). A three-electrode one-compartment cell was used to contain the solution of the compound and supporting electrolyte in dry $CH_2Cl_2$. Deaeration of the solution was achieved by argon bubbling through the solution for about 10 minutes before measurement. Compound **2** and electrolyte ($Bu_4NPF_6$) concentrations were typically 0.001 and 0.1 mol·$L^{-1}$, respectively. A 500-$\mu$m-diameter platinum disk working electrode, a platinum wire counter electrode, and an $Ag/Ag^+$ reference electrode were used. The $Ag/Ag^+$ reference electrode contained an internal solution of 0.01 mol·$L^{-1}$ $AgNO_3$ in acetonitrile and was incorporated to the cell with a salt bridge containing 0.1 mol·$L^{-1}$ $Bu_4NPF_6$ in $CH_2Cl_2$. The electrochemical experiments were carried out under ambient conditions. The theoretical calculation in the present studies was performed at B3LYP/6-31G* level by using Gaussian 09 program.

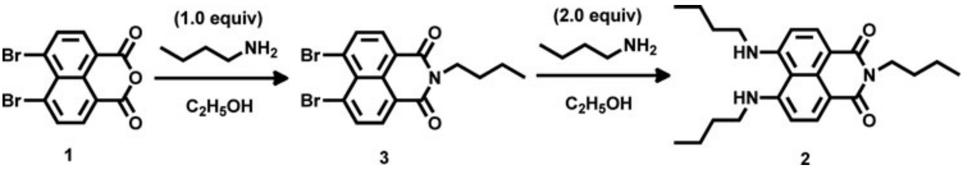
Synthesis of compound **2**: Compound **1** (0.50 g, 1.4 mmol) and butylamine (0.31 g, 4.2 mmol) in ethanol (20 mL) were stirred for 24 hours at 80°C. Then the reaction mixture was filtered, washed with ethanol, and dried ($Na_2SO_4$). The residue was purified by column chromatography (silica gel, eluted with acetic ether:petroleum ether = 4:1) to give yellow solid **2** (200 mg) in 40% yield. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.43–8.41 (d, 2H, PyH), 6.76–6.74 (d, 2H, PyH), 5.79 (d, 2H, NH), 4.16–4.12 (t, 2H, $CH_2$), 3.27–3.22 (dd, 4H, $CH_2$), 1.76 (m, 6H, $CH_2$), 1.58–1.54 (m, 6H, $CH_2$), 1.05–0.96 (m, 9H, $CH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 164.32, 152.44, 133.15, 131.75, 111.66, 111.25, 106.70, 77.31, 77.00, 76.68, 44.29, 39.54, 31.12, 30.22, 20.43, 20.36, 13.74. Elemental analyses: Anal. Calcd for $C_{24}H_{33}O_2N_3$: C, 72.88; H, 8.14, N, 10.62. Found: C, 72.78; H, 8.21; N, 10.58.

## Results and Discussion

The synthesis of naphthylimide **2** is outlined in Scheme 1. The 4,5-dibromo-1,8-naphthalic anhydride was synthesized according to a previously reported literature [5]. Compound **1** was treated with 3.0 equivalents butylamine in a one-pot process to afford the N-butyl-4,5-dibutylamine-1,8-naphthylimide with donor–acceptor structure in a 40% yield. In this case, this reaction contains the following process: (1) from anhydride to imide and (2) nucleophilic substituted reaction. For exploring the priority, we performed the further experiments. The treatment of compound **1** with 1.0 equivalent butylamine only produced bromide **3**, which was further reacted with 2.0 equivalents butylamine to generate the compound **2**. The results indicate that the step from anhydride to imide is prior to the nucleophilic substituted reaction, as shown in Scheme 2. The molecular structure compound **2** was confirmed by NMR and elemental analyses.



**Scheme 1.** Synthesis of naphthylimide **2**.



**Scheme 2.** Synthesis of naphthylimide 2 by two steps.

Because of the alkoxyl chains, the target molecule showed very good solubility in common solvents, which permitted it to be investigated by UV-Vis absorption and fluorescence spectra in solution. The UV-Vis absorption and fluorescence emission spectra of **2** in acetonitrile are presented in Fig. 1. As can be observed, the compound **2** showed three absorbance peaks at 244, 312, and 438 nm, respectively. Furthermore, the two absorbance peaks 312 and 438 nm overlapped a very broad absorbance bands from 310 nm to 500 nm in comparison with the naphthyldiimide [1], possible ascribing to the donor–acceptor structure of compound **2**. The emission spectrum of compound **2** was observed at 521 nm. According to Fig. 1, the compound **2** exhibited a 0.45 eV stoke shift. Subsequently, the

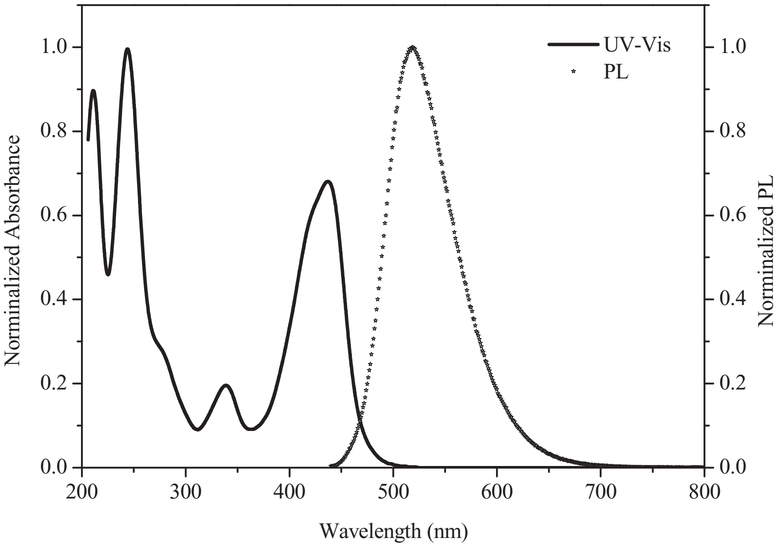


**Figure 1.** UV–Vis absorption and fluorescence spectra of **2** (10 $\mu$M) in acetonitrile.

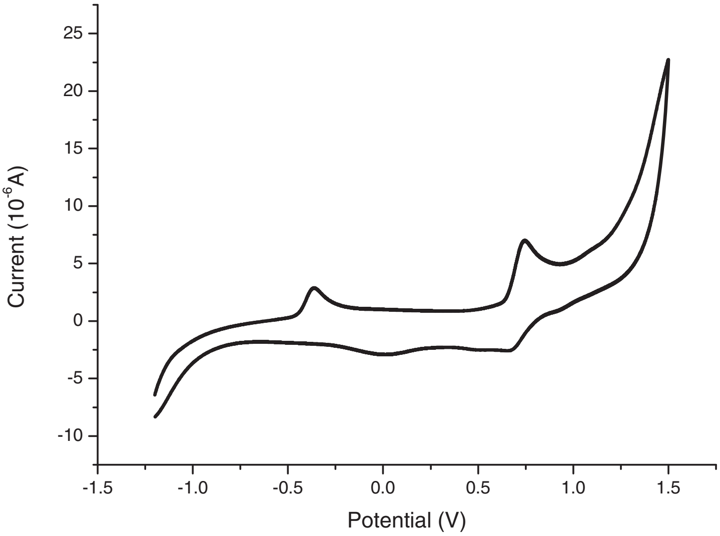


**Figure 2.** Cyclic voltammogram of **2** in $CH_2Cl_2/Bu_4NPF_6$ at $v = 0.1$ V·s$^{-1}$. Potentials are given relative to the $Ag/Ag^+$ standard.

electrochemical behavior was investigated under nitrogen atmosphere at room temperature. $Bu_4NPF_6$ was the supporting electrolyte. As can be observed in Fig. 2, two quasi reversible redox potential were found. In addition, the molecule was optimized by DFT calculation at the B3LYP/6-31G* level in a suite of Gaussian 09 programs as shown in Fig. 3. The theoretical value of energy gap is 3.5 eV, and HOMO and LUMO energy are −5.4 eV and −1.9 eV, respectively.

Subsequently, we further explored the effect of metal ions (such as $Li^+$, $Na^+$, $K^+$, $Cs^+$, $Ba^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $Ca^{2+}$, $Cd^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Ag^+$, $La^{3+}$, and $Hg^{2+}$) for the

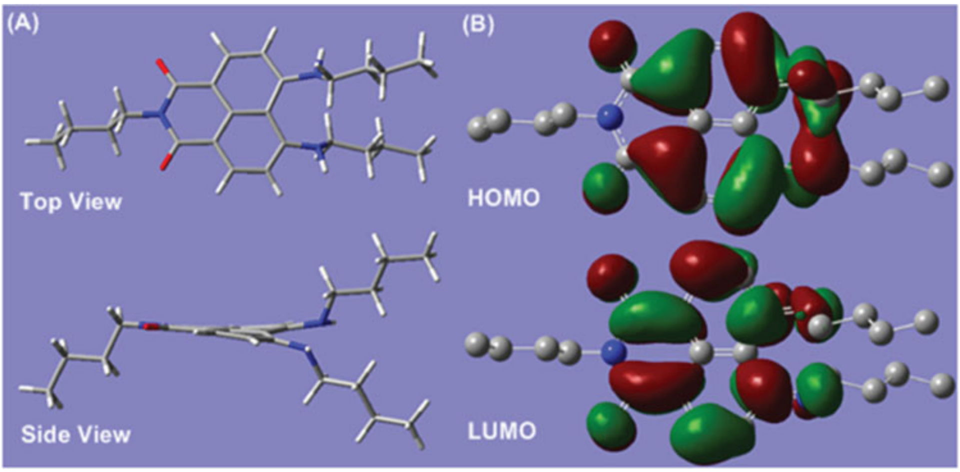


**Figure 3.** The structure and frontier molecular orbital profiles of molecule based on DFT (B3LYP/6-31G*) calculations.

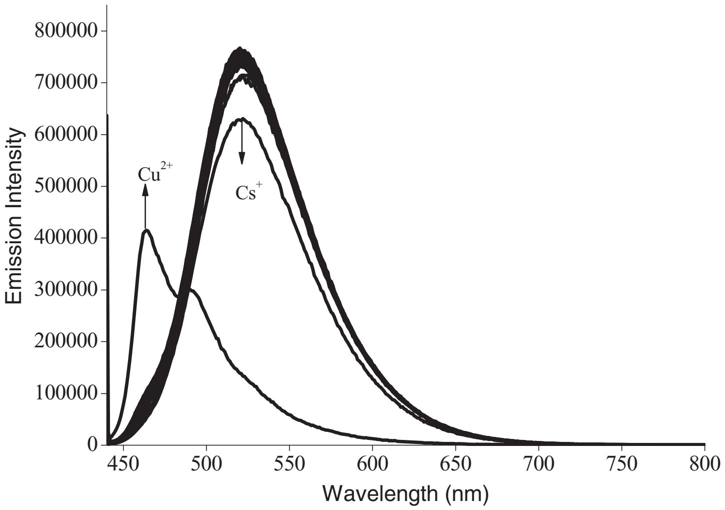


**Figure 4.** Fluorescence spectra of **2** (10 $\mu$M) under effects of different metal ions (30 eq).

fluorescence spectra of compound **2**. In the presence of $Cu^{2+}$, the color of the solution changed from yellow green to orange along with the obvious blueshift (60 nm) as depicted in Fig. 4. In addition, the fluorescent intensity was weakened when $Cs^{+}$ was added. While the other metal ions were added into the acetonitrile solution of **2** (10 $\mu$M), no observable color changes of the solution could be detected. Therefore, the change of fluorescence spectrum of compound can be used as a fluorescent sensor to detect $Cu^{2+}$. These results indicated that compound **2** could be used as a potential candidate of fluorescent chemosensor for $Cu^{2+}$ with very high selectivity.

## Conclusion

In conclusion, we have prepared N-butyl-4,5-dibutylamine-1,8-naphthylimide with a donor–acceptor structure and studied the optical and electrochemical properties, which shows a fluorescent response with a large blueshift emission that is useful for the easy detection of Cu (II) ion with very high electivity.

## Acknowledgments

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