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A highly selective and sensitive probe based on benzo[1,2-b:4,5-b′] dithiophene: synthesis, detection for Cu(II) and self-assembly

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ABSTRACT

A novel turn-off probe for copper(II) containing benzo[1,2-b:4,5-b′]dithiophene (BDT) and two picolinamide units was synthesized. In this probe, two picolinamide units complex with one Cu^{2+} ion and two nitrogen atoms in each picolinamide unit coordinate with Cu^{2+}, which is verified by DFT calculation. Its fluorescence quantum yield is 0.43 and the detection limit is as low as 2.4×10^{-8} mol/L. The results show that the probe displays good selectivity for Cu^{2+} over other ions (Mn^{2+}, Pb^{2+}, Cr^{3+}, Zn^{2+}, Ni^{2+}, K^{+}, Ca^{2+}, Ag^{+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Hg^{2+}, Al^{3+}, Cd^{2+}, Pd^{2+}, Co^{2+}). Furthermore, the probe induced by Cu^{2+} and the π−π interaction of the aromatic unit can also form rod structure assembly, which can be observed by scanning electron microscopy (SEM).

1. Introduction

The design and synthesis of efficient artificial receptors for various ions have received much interest in the last decade due to their essential roles in many places.[1–10] Among these ions, copper(II) is the third most abundant transition-metal ion in the human body, and it plays an important role in many biological and environmental processes.[5] Up to now, much effort has been made to detect copper(II) ions based on different analytical strategies,[11–22] among which fluorometric methods have attracted considerable attention.

Benzo[1,2-b:4,5-b′]dithiophene (BDT) unit has been the most popular donor for designing bulk heterojunction solar cells for its favor light harvesting and thermal stability.[23] In our previous work, BDT unit was formed copolymer with benzodithiophene and its photoelectric properties were studied.[24] Then we found that BDT unit has strong fluorescence. However, to the best of our knowledge, there are few researches for designing probe containing BDT as fluorophore.

At the same time, molecular self-assembly based on rational control of non-covalent interactions such as hydrophobic interactions, hydrogen bonding, aromatic stacking or metal coordination interactions, provides the design of self-assembly molecules from nanometer to micrometer scale.[25] Among these non-covalent interactions for molecular self-assembly, co-ordination compounds of metal ions with the organic ligands can result in interesting structures such as spherical particles,[26] rigid rods,[27] nanotubes[28] and springs[29] of micro to even nano dimension.

In this work, a novel probe was designed and synthesized, in which benzo[1,2-b:4,5-b′]dithiophene (BDT) unit is used as fluorophore and two picolinamide units are used as metal-binding sites. To develop the probe of fluorophore—π conjugate spacer—receptor form, phenyl group is elongated the π-conjugation. Picolinamide unit has been utilized as a receptor and a suitable *p*-conjugated bridge. It is anticipated that the external metallic cations stimulus with picolinamide unit could modulate the intramolecular charge transfer, resulting in changes in the absorption spectra and fluorescence emission, thus the compound can be used as turn-off sensor for Cu^{2+} in a flash way, furthermore, transition metal Cu^{2+} can induce the compound to form metallosupramolecular assembly.

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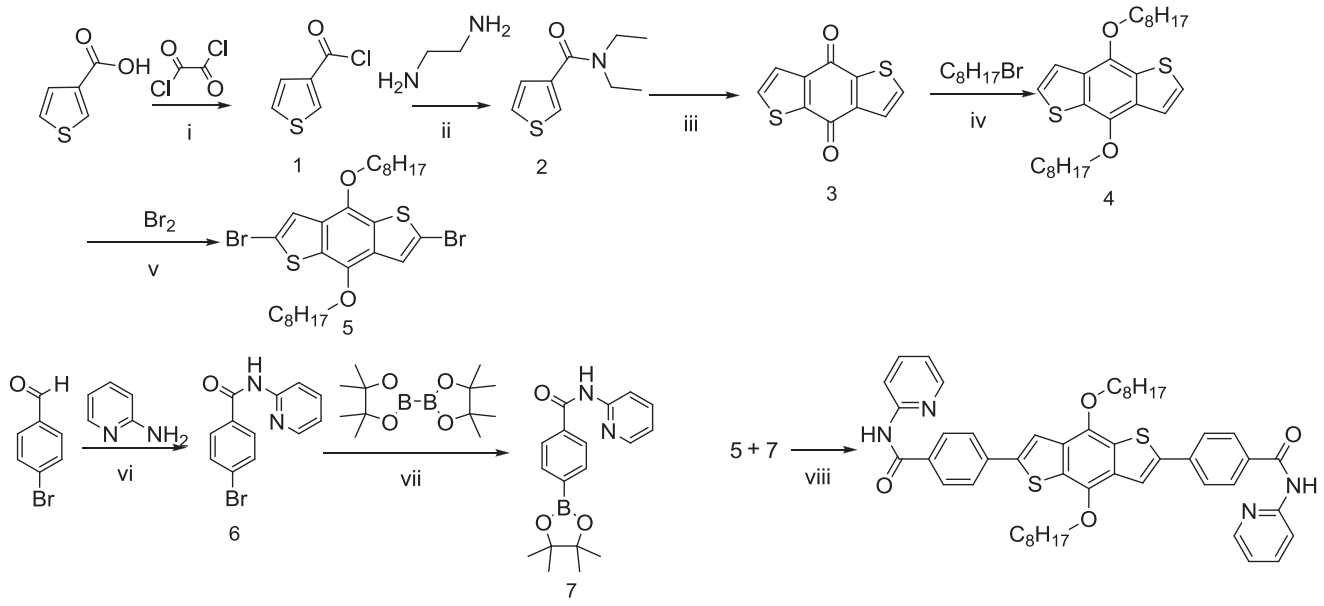
2. Results and discussion

2.1. Synthesis

The synthesis route of BDT-BPBA was shown in Scheme 1. BDT-BPBA was synthesized by Suzuki coupling reaction of 4-bromo-*N*-(pyridin-2-yl)benzamide and *N*-(pyridin-2-yl)-4-(4,4,5, 5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide in 54% yield. The chemical structure of BDT-BPBA was confirmed by ^{1}H NMR, ^{13}C NMR and mass spectroscopic data (As shown in Fig. S1–S9).

the fluorescence intensity at a particular concentration of Cu^{2+}, the ratio of the final fluorescence intensity to the initial fluorescence intensity was found to be 0.03.

From the titration experiment, it can be estimated that Cu^{2+} and picolinamide unit formed complex with a ratio of 1:2, and the ratio was confirmed by the Job's Plot (Fig. 4). The change in Job's Plot happened at $[Cu^{2+}]/([Cu^{2+}]+[BDT\text{-}BPBA])=0.33$, which meant that Cu^{2+} and BDT-BPBA formed a complex with a ratio of 1:2. It can be deduced that two picolinamide units of two BDT-BPBA molecules are in complex with one Cu^{2+} and two nitrogen atoms in each picoli-



(i) CH_2Cl_2, r.t., overnight. (ii) CH_2Cl_2, r.t., 30min, 84%. (iii) THF/n-BuLi, r.t., 30min, 71%. (iv) H_2O/Zn/NaOH/TBAB, relux, 7h, 74%. (v) CH_2Cl_2, r.t., 6h, 87%. (vi) DMF/CuI, 80°C, 24h, 63%. (vii) dioxane/KOAc/ $Pd(dppf)Cl_2$, 100°C, overnight, 72%. (viii) toluene/H_2O/K_2CO_3/ $Pd(PPh_3)_4$, reflux, 24h, 54%.

Scheme 1. The synthesis of BDT-BPBA.

2.2. Sensing response of BDT-BPBA for Cu^{2+}

The UV–vis spectra of BDT-BPBA with different amount of Cu^{2+} were investigated. As shown in Fig. 1, BDT-BPBA in DMSO/H_2O (v:v=4:1) showed that two absorption peaks were centered at 358 nm and 422 nm. Upon additional of 0.5 equiv Cu^{2+} into the solution of BDT-BPBA, the two peaks were red-shift to 380 nm and 440 nm. The change of the UV–vis spectra can be explained by internal charge transfer (ICT) mechanism, which refers to the push–pull effect of the electron-donating and electron-withdrawing groups. That is, the red shift indicates that the energy gap of ICT band decreases, upon binding Cu^{2+} to the electron withdrawing moieties.[30]

For fluorescence spectra (Fig. 2a), the emission wavelength of BDT-BPBA was appeared at 546 nm in DMSO/H_2O (v:v=4:1) when excited by 410 nm photon. The fluorescence quantum yield can reach at 0.43. The fluorescence intensity was found to quench with the addition of Cu^{2+}. The quenching continues till addition of 0.5 equiv Cu^{2+} and remains constant thereafter. Under the common TLC-UV light, λ=365 nm, the yellow fluorescence quenching was observed by naked eyes when 0.5 equiv of Cu^{2+} was added to a 2×10^{-5} mol/L BDT-BPBA solution in DMSO/H_2O (v:v=4:1) (Fig. 2b). The plot of F/F_0 as a function of Cu^{2+} concentration was shown in Fig. 3, where F_0 is the initial fluorescence intensity and F is

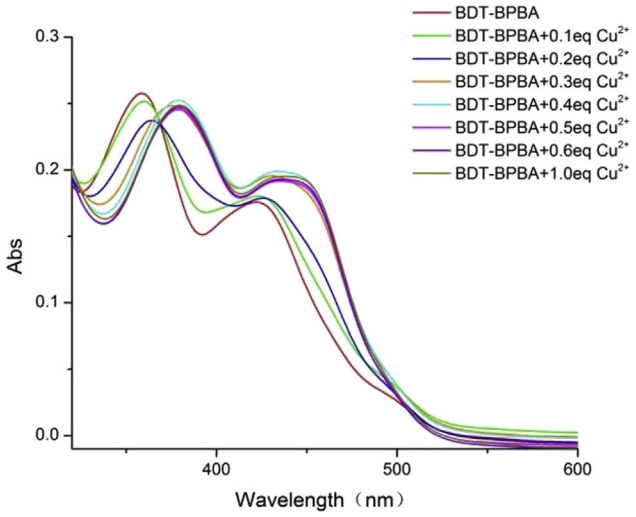


Fig. 1. UV–vis spectra of BDT-BPBA in DMSO/H_2O (v:v=4:1) (2×10^{-5} mol/L) upon addition of 0.1–1.0 equiv of $CuCl_2$.