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SYNTHESIS AND CHARACTERIZATION OF A NAPHTHALIMIDE DERIVATIVE BASED CU^{2+}-SELECTIVE FLUORESCENT PROBE

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ABSTRACT

A fluorescent probe derived from naphthalimide was successfully synthesized and characterized as an "off-on" type Cu^{2+}-selective fluorescent probe. A prominent fluorescence enhancement at 430 nm was observed in the presence of Cu^{2+} in ethanol-water solution (5:5, v:v, pH 6.8, 50 mM HEPES). With the optimized experimental conditions, the probe exhibited a dynamic response rangeof 7.0×10^{-7}-9.0×10^{-6} M for Cu^{2+}, and the detection limit is2.3×10^{-7} M.

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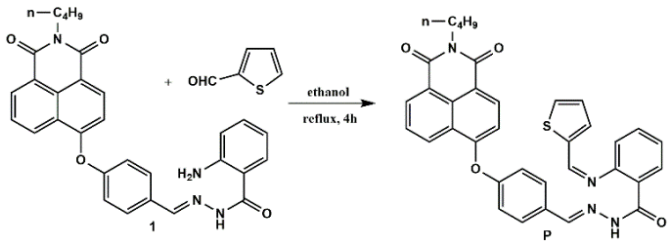
INTRODUCTION

Detection of cations, anions and molecular species is one of the challenging areas of current research. Among them, $Cu^{2+}$is an interesting target, because it exhibits toxicity under overloading conditions, which can causes neurodegenerative diseases (Lovstad *et al.*, 2004).Therefore, the detection of $Cu^{2+}$is important. Among the detection methods, the fluorescent probes method seems to be an ideal candidate due to the high selectivity, fast analysis (Quangand Kim, 2010; Guo *et al*., 2014).The design and synthesis of new Zn^{2+}-selective "off-on" probes is still attractive (Guo *et al.* 2014; Huang *et al.* 2011). Probes derived from naphthalimidehave excellentphotophysical properties, such as strong absorption band in the visible region, large Stokes shifts, high fluorescence quantum yields and stability, which have been widely used for the detection of environment samples (Dai *et al.* 2015; Zhang and Yu 2014; Zhang *et al.* 2012).

Herein a Cu^{2+}-selective probe derived from Naphthalimidewas designed and characterized (Scheme 1).



Scheme 1. Synthesis route of the proposed probe P

Experimental Section

Reagents and Instruments: All of the materialswereanalytical reagent gradeand used without further purification. MSspectra were recorded on a Thermo TSQ Quantum Access Agillent 1100.NMRspectra were measured with TMS as an internal standard. Fluorescence emission spectra were conducted on a

Hitachi 4600 spectrofluometer. The pH values were measured with a pH-meter PBS-3C.

Synthesis

Compound 1 (Yu and Zhang, 2014) (50.6mg, 0.1mmol) and 2-thenaldehyde (11.2μL, 1.1mmol) were mixed in ethanol (30 mL). The reaction mixture was stirred at 80 °C for 4 h, and then cooled to room temperature. The white precipitate so obtained was filtered and used directly. Yields: 83.4 %. MS (ES+) m/z: 601.45 $[M+H]^+$.^{1}H NMR (d_6-DMSO, δ ppm): 11.55 (s, 1H), 8.54 (d, 1H, *J* = 8.35), 8.45 (d, 1H, *J* = 8.15), 8.45 (t, 2H, *J* = 7.25), 8.33 (s, 1H), 7.90 (t, 1H, *J* = 7.82), 7.85 (d, 1H, *J* = 8.20), 7.69 (d, 1H, *J* = 7.25),7.65 (d, 1H, *J* = 7.50), 7.58 (d, 1H, *J* = 7.85), 7.36 (d, 2H, *J* = 8.35), 7.21 (t, 1H, *J* = 7.65), 7.13 (d, 1H, *J* = 8.25), 6.77 (d, 1H, *J* = 8.30), 6.59 (t, 1H, *J* = 7.47), 4.04 (t, 2H, *J* = 7.32), 1.62 (m, 2H, *J* = 7.45), 1.36 (m, 2H, *J* = 7.30), 0.93 (t, 3H, *J* = 7.25). ^{13}C NMR (d_6-DMSO, δ ppm): 163.46, 163.22, 163.11 (C=O), 158.53, 155.84, 151.44, 149.88, 147.63, 133.03, 132.84, 132.35, 131.78, 129.64, 128.87, 128.54, 127.68, 123.87, 122.56, 120.98, 117.12, 116.89, 115.11, 112.67, 36.24, 30.12, 20.26, 14.19.

General spectroscopic methods

All of the fluorescence spectra were recorded at 25 °C.Test solutions were prepared by placing 50μL of the P stock solution (1 mM) and an appropriate aliquot of individual ions stock solution into a test tube, and then diluting the solution to 5 mL with ethanol-water (5:5, v:v, pH 6.8,50mMHEPES).For all fluorescent measurements, excitation and emission slit widths were 5/10 nm, respectively. Excitation wavelength was 355 nm.

RESULTS AND DISCUSSION

pH effectson P with Cu^{2+}

The titration experiment was firstly carried out to test the pH effect of probe P for Cu^{2+} sensing (Figure 1). The results showed that the emission intensity at 430 nm rapidly reached to a maximum in the pH 6.8 after the addition of Cu^{2+}. Therefore, further fluorescent studies were carried out in ethanol–water solution at pH 6.8(5:5, v:v, 50 mM HEPES).

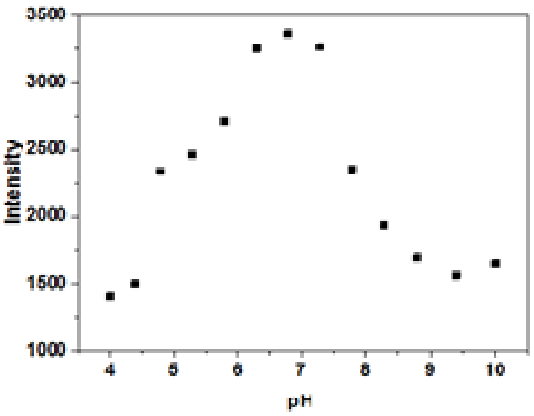


Figure 1. Influences of pH on the fluorescence spetra of P (10 μM) plus Cu^{2+} (10 μM)in ethanol-water solution (5:5, v:v). The pH was modulated by adding 1 M HCl or 1 M NaOH in HEPES buffers

Fluorescence spectral response of P

The fluorescent spectra (ex=355 nm) of P (10 μM) in ethanol–water solution (5:5, v:v, pH 6.8, 50 mM HEPES) with the addition of respective metal ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, Pb^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Ni^{2+}, Hg^{2+}, Cr^{3+} and Fe^{3+}, 10 equiv.) was investigated to evaluate the selectivity of probe P(Figure2). Compared to other examined ions, only Cu^{2+}generated a significant "turn-on" fluorescent response at 430 nm. It suggested that P has a higher selectivity toward Cu^{2+}than other metal ions.

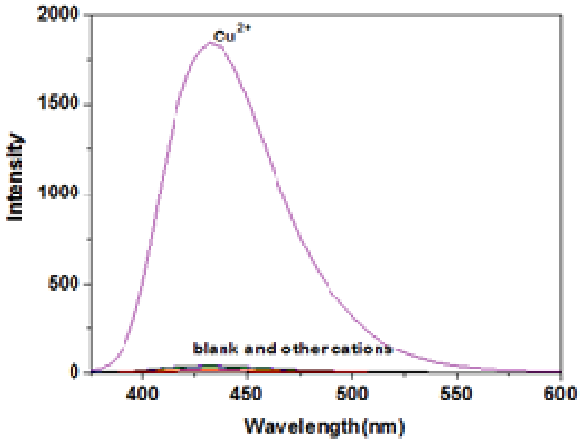


Figure 2. Fluorescence response of P (10 μM) with different metal ions (100 μM) in ethanol-water solution (5:5, v:v, pH 6.8, 50 mM HEPES)

Further investigation of the interaction of $Cu^{2+}$with the proposed probe was carried out by fluorescent titration experiment.Upon titration with Cu^{2+}, the fluorescence intensity of the monomer peak at 430 nm increased gradually (Figure3), and the fluorescent intensity of P was proportional to the concentration of Cu^{2+} in the range of 7.0×10^{-7}-9.0×10^{-6} M(R^2=0.996) with a detection limit of 2.3×10^{-7} MCu^{2+}. This clearly demonstrated that probePcould sensitively detect environmentally relevant levels of Cu^{2+}.

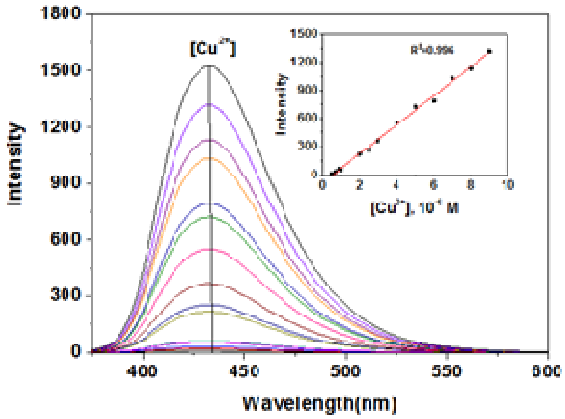


Figure 3. Fluorescence response of P (10μM) with different concentrations of Cu^{2+} in ethanol-water solution (5:5, v:v, pH 6.8, 50 mM HEPES). Inset: the fluorescence of P (10 μM) as a function of Cu^{2+} concentrations (0.7–9μM)

Proposed binding mode of P with Cu^{2+}

The linear dependence of the intensity at 430 nm within the equivalent range of the Cu^{2+}showed that a 1:1 complex was formedbetween P andCu^{2+}. Moreover, binding analysis using the method of continuous variations (Job's plot) was measured(Figure4), and a maximum fluorescent intensity at 430 nm was observed when the molecular fraction of P was

close to 0.5, which established the 1:1 complex formation between P and Cu^{2+}.Thus, according to the obtained results, the binding mode of P and Cu^{2+} was proposedas shown in Scheme 2.

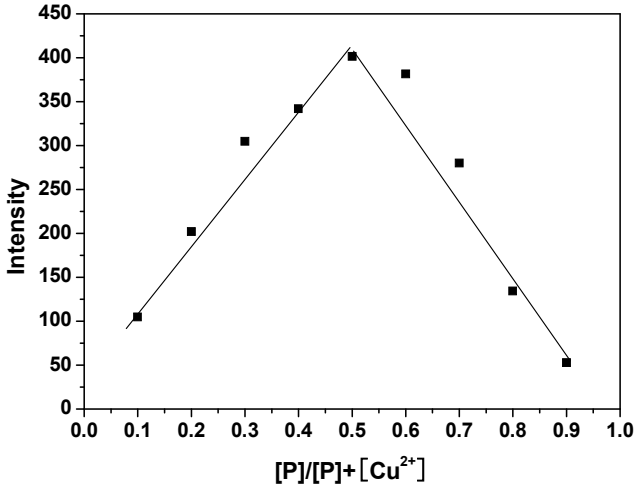
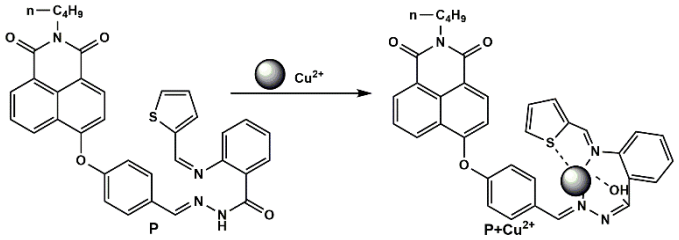


Figure 4. Job's plot curve of P with Cu^{2+} in ethanol-water solution (5:5, v:v, pH 6.8, 50 mM HEPES).The total concentration of P and $Cu^{2+}$was kept 10 μM



Scheme 2. Proposed binding mode of P with Cu^{2+}

Conclusions

In summary, an "off-on" type Cu^{2+}-selective probe P was characterized. The conception may expand a promising approach to develop selective detection method for Cu^{2+} and lead to the development of "off-on" type probes for other metal ions.

Acknowledgments

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