



Green synthesis of fluorescent N,O-chelating hydrazone Schiff base for multi-analyte sensing in Cu^{2+} , F^- and CN^- ions

Neeraj Saini^a, Nicha Prigyai^a, Chidchanok Wannasiri^a, Vuthichai Ervithayasuporn^{a,*}, Suda Kiatkamjornwong^{b,c}

^a Department of Chemistry, Center of Excellence for Innovation in Chemistry (PERCH-CIC), Center for Inorganic and Materials Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Ratchathewi District, Bangkok 10400, Thailand

^b Faculty of Science, Chulalongkorn University, Phayathai Road, Bangkok 10330, Thailand

^c FRST, Division of Science, The Royal Society of Thailand, Sanam Suepa, Dusit, Bangkok 10300, Thailand

ARTICLE INFO

Article history:

Received 31 January 2018

Received in revised form 1 March 2018

Accepted 12 March 2018

Available online 13 March 2018

Keywords:

Dehydroacetic acid

1,8-Naphthalimide

Fluorescence

Copper

Fluoride

Cyanide

ABSTRACT

A colorimetric and fluorometric hydrazone Schiff's base derived from dehydroacetic acid by three-steps and high-yield syntheses under green approach employing ethanol as a solvent has been prepared. Multi-analyte sensing for both metal cation (Cu^{2+}) and anions (F^- and CN^-), with high sensitivity and competitive selectivity, was encountered. The sensing mechanism of anion detection found to be deprotonation of N—H and O—H moieties in the presence of ions. However, metal cation like copper(II) ions chelation with sensor, leads to diminish intra-molecular charge transfer (ICT) with chelation induced quenching of fluorescence (CHQF). Contrary, anionic interaction ensued in heightened ICT as well as photo-induced electron transfer (PET) processes. The Job's plots interpretation rendered stoichiometry of 2:1 with $\text{Cu}^{2+}/\text{F}^-$ and 1:1 with CN^- . Moreover, the detection limits of 0.962 ppm (Cu^{2+}), 0.023 ppm (F^-) and 0.073 ppm (CN^-) were much lower than WHO guidelines. Further, either water or methanol was employed to differentiate F^-/CN^- ions with sensor in THF, with prominent visible naked eye and fluorometric responses.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Constructing dual responsive chemosensors for the efficient and selective recognition of metal ions as well as anions simultaneously are still a challenging task for the scientific community [1–3]. Nowadays, research scenario has been focused more on developing optical signaling probes due to high competitive selectivity, rapid naked eye detection in ambient light and economical testing, over conventional detection methods [4,5]. Various receptor molecules interacting through unidirectional hydrogen bonding [6,7], ions induced Si-O bond cleavage reactions [8], molecular encapsulation [9], chelation [10] etc. displaying either colorimetric or fluorometric responses, have been contrived and tested toward ions [11]. But the majority of them exhibited severe limitations such as non-discrimination between fluoride and cyanide ions, interference from other competing ions specially acetate ions, long time to response and/or irreversibility [12–15]. On the other side, deprotonation

based sensing probes display higher selectivity with stable optical responses [16,17]. As an example, Pu et al. [18] accounted various diarylethene based chemosensors for fluoride and copper ions in acetonitrile. However, Wan and co-workers described a phenol derived indicator system with dual optical responses toward fluoride and risky cyanide ions. Even though, these systems were excellent examples of chemosensors but effective only in pure organic environments limiting their application to off-site detection. In addition, aqueous analysis suffers from solvent competition and probe insolubility, ensuing sensing of ions an uphill battle [19,20]. Probes that can effectively detect multiple ions in aqueous medium are highly desirable but still quite rare [21,22]. Further, synthetic methodologies followed in the previous reports involve the use of hazardous chemicals such as pyridines, dioxanes, nitrobenzene, etc. with high temperature and tedious extraction processes [1,15,18]. This puts a negative impact on the development of economical sensing probes as well as on human health.

It has been well demonstrated that both metal ions as well as anions are crucial constituents in various biological, manufacturing and metallurgical processes [23–26]. In particular, copper ions act as cofactor and active site constituent in various metalloenzymes due to its versatile redox and binding properties [27–29]. Also, fluoride ions

* Corresponding author.

E-mail address: vuthichai.erv@mahidol.ac.th (V. Ervithayasuporn).

have been a crucial constituent in toothpastes and drinking water. It precludes dental caries [30]. However, over intake of fluoride ions is deduced for many medical ailments such as fluorosis, osteoporosis or even urolithiasis [31,32]. Similarly, excess concentration of cyanide ions poses hazardous impingement on the living systems [33–35]. For these reasons, an impetus always exists for the development of economical optical probes that assist in maintaining a periodic check and in-turn regulate ion's concentration in the ecosystem [36,37].

Majorly, 1,8-naphthalimide moiety has been exploited as fluorophore unit in different sensing systems due to eminent quantum yields, proficient photo-stability and prominent Stokes' shift [38,39]. Moreover, pyran ring systems have evinced biocompatibility, scuttling unexampled dimensions of sensor application in biological system. Additionally, a pyrone derivative such as dehydroacetic acid based receptor system puts forth excellent chelation based sensing of metal ions [40,41]. Literature survey revealed that there is still paucity of dual responsive sensors that can selectively detect copper ions in addition to differentiating fluoride and cyanide ions within same measurement method. To work on this site, a cost efficient dual responsive chemosensor, based on 1,8-naphthalimide and hydroxypyrones ring system with a hydrazone linker, has been synthesized in ethanol under ambient temperature conditions. Apparently, due to paramagnetic behavior, Cu^{2+} ions N,O-chelation with **4**, resulted in diminished ICT process and complete quenching of emission intensity. Besides, anions induced deprotonation elicit the internal charge transfer (ICT) and PET processes. In the present report, NMR titration experiments delineated the deprotonation based recognition mechanism. Sensor **4** loaded paper strip experimentation revealed the practical applicability via portable sensor kit for on-site detection of multi-analytes in aqueous medium. Additionally, it has been demonstrated that both deionized water and methanol assisted in selective discrimination of F^- and CN^- ions with **4**, in THF. Indeed, the fluorescent N,O-chelation successfully demonstrated that an efficient sensing probe has been synthesized under a green solvent like ethanol that can effectively detect multiple analytes generating instantaneous optical responses.

2. Experimental

2.1. Materials and instrumentations

4-Bromo-1,8-naphthalic anhydride, *n*-butylamine, 2-methoxyethanol, 3-acetyl-4-hydroxy-6-methyl-pyran-2-one hydrazine hydrate (80%), DMSO- d_6 and chloroform- d_1 were incurred from Sigma Aldrich. Tetrabutylammonium salts of different anions and metal perchlorates were bought from TCI chemicals and dried prior to use. Ethanol and THF employed for the synthesis or analysis were used as supplied without further purification. Water utilized in the analysis processes was obtained from Millipore system and deionized prior to use. Commercially available toothpaste (Colgate) and mineral water (Nestle) were purchased and analyzed for ions. All the metal ions and anions were incurred by the dissolution of their respective TBA salts in deionized water. Melting point was measured with the open capillary tube method using a GALLENKAMP variable heater melting point apparatus. ESI-Mass (negative mode) was calculated employing a microTOF-Q III instrument. UV-vis spectra were measured using a slit width of 1.0 nm and matched quartz cells on a Shimadzu UV-2600 UV-vis spectrophotometer. Fluorescence spectra and quantum yield (filter glass 2.5, dark offset) were recorded with a HORIBA Fluoro Max Plus Spectrofluorometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were incurred on a Bruker 500 MHz spectrometry using TMS as an internal reference. NMR chemical shifts were reported in ppm and referenced to residual protonated solvent. Tetrabutylammonium

salts and metal perchlorates were used for anion and cation studies, respectively.

2.2. Preparations

2.2.1. Synthesis of 6-bromo-2-butyl-benzoisoquinoline-1,3-dione (**2**)

4-Bromo-1,8-naphthalic anhydride (0.277 g, 1 mmol) was dissolved in ethanol (20 mL). Later, *n*-butylamine (0.073 g, 1 mmol) was dropwise added to the ethanolic solution. The reaction mixture was refluxed with gentle stirring for 12 h, in an oil bath. The resulting mixture was allowed to cool to room temperature and concentrated under vacuum. The crude product was filtered down and washed 3–4 times by ethanol. Recrystallization of **2** in ethanol obtained a white crystalline solid. m.p. 103–104 °C. yield: 0.295 g (89%). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm): 8.63–8.61 (dd, 1H, ArH), 8.55–8.52 (dd, 1H, ArH), 8.39–8.37 (d, 1H, ArH), 8.02–8.00 (d, 1H, ArH), 7.83–7.79 (t, 1H, ArH), 4.16–4.12 (t, 2H, CH_2), 1.72–1.64 (m, 2H, CH_2), 1.46–1.36 (m, 2H, CH_2), 0.96–0.92 (t, 3H, CH_3) as shown in Fig. S1. $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm): 163.68 (C12), 163.66 (C1), 133.25 (C9/C3), 132.08 (C5), 131.27 (C8), 130.66 (C7), 130.26 (C4), 129.03 (C6), 128.17 (C2), 123.24 (C10), 122.38 (C11), 40.54 (C13), 30.32 (C14), 20.54 (C15), 14.01 (C16) as depicted in Fig. S2.

2.2.2. Synthesis of 2-butyl-6-hydrazinyl-benzoisoquinoline-1,3-dione (**3**)

Compound **2** (0.332 g, 1 mmol) was dissolved in 25 mL of ethanol followed by the addition of 80% hydrazine hydrate (0.3 mL, 3.3 mmol). The resulting solution was refluxed with stirring for 3 h in an oil bath. Finally, the precipitated orange colored crude product was collected under vacuum suction and washed with ethanol. Recrystallization of **3** was carried out in acetonitrile to obtain an orange crystalline solid. m.p. 220–223 °C. yield: 0.241 g (85%). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm): 9.10 (s, 1H, NH), 8.59–8.57 (d, 1H, ArH), 8.40–8.38 (d, 1H, ArH), 8.27–8.25 (d, 1H, ArH), 7.63–7.59 (t, 1H, ArH), 7.23–7.21 (d, 1H, ArH), 4.65 (s, 2H, NH_2), 4.01–3.97 (t, 2H, CH_2), 1.60–1.53 (m, 2H, CH_2), 1.36–1.27 (m, 2H, CH_2), 0.92–0.88 (t, 3H, CH_3) as shown in Fig. S3. $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm): 163.79 (C12), 162.94 (C1), 153.19 (C7), 134.22 (C9), 130.58 (C3), 129.30 (C5), 128.23 (C4), 124.13 (C2), 121.75 (C11), 118.45 (C6), 107.40 (C10), 104.01 (C8), 38.93 (C13), 29.86 (C14), 19.87 (C15), 13.77 (C16) as depicted in Fig. S4.

2.2.3. Synthesis of 2-butyl-6-(2-(1-(4-hydroxy-6-methyl-2-oxo-pyran-3-yl)-ethylidene)-hydrazinyl)-benzoisoquinoline-1,3-dione (**4**)

Compound **3** (0.283 g, 1 mmol) and 3-acetyl-4-hydroxy-6-methyl-pyran-2-one (0.168 g, 1 mmol) were added in ethanol (25 mL). The mixture was refluxed with continuous stirring at 100 °C. After refluxing for 12 h, the reaction mixture was left to cool at room temperature and concentrated under vacuum. The crude product was further purified by recrystallization with acetonitrile-hexane mixture (95:5) to give a novel compound **4** (0.345 g) as yellow crystalline solid. m.p. 253–254 °C. yield: 0.345 g (80%). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm): 15.52 (s, 1H, OH), 8.62–8.60 (d, 1H, ArH), 8.50–8.48 (d, 1H, ArH), 8.19–8.17 (d, 1H, ArH), 7.99 (s, 1H, NH), 7.74–7.70 (t, 1H, ArH), 7.13–7.11 (d, 1H, ArH), 5.89 (s, 1H, ArH), 4.15–4.11 (t, 2H, CH_2), 2.77 (s, 3H, $-\text{CH}_3$), 2.20 (s, 3H, $-\text{CH}_3$), 1.72–1.64 (m, 2H, CH_2), 1.46–1.36 (m, 2H, CH_2), 0.96–0.92 (t, 3H, $-\text{CH}_3$) as shown in Fig. S5. $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm): 178.62 (C17), 166.38 (C15), 164.39 (C14), 163.89 (C1/C12), 163.04 (C18), 144.78 (C7), 133.57 (C9), 131.68 (C3), 129.55 (C5), 126.40 (C4), 125.53 (C12), 123.74 (C11), 119.91 (C6), 115.59 (C10), 107.35 (C8), 104.30 (C16), 97.09 (C13), 40.42 (C19), 30.44 (C20), 20.61 (C23), 20.27 (C21), 15.99 (C22), 14.06 (C24) as depicted in Fig. S6. HRMS (ESI): $[\text{M} - \text{H}]^-$ calcd for $[\text{C}_{24}\text{H}_{22}\text{N}_3\text{O}_5]^-$, m/z 432.1559; found m/z 432.1583 (Fig. S7).

Download English Version:

<https://daneshyari.com/en/article/6492567>

Download Persian Version:

<https://daneshyari.com/article/6492567>

[Daneshyari.com](https://daneshyari.com)