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The sensitivity and selectivity properties of a fluorescence sensor based on quinoline-Bodipy

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ABSTRACT

A novel florescence sensor (***Q-BODIPY***) based on quinoline-Bodipy (quinoline-boradiazaindacene) was prepared by 'click chemistry' in several stages. The sensing actions of **Q-BODIPY** were confirmed by UV–vis titration, emission and excitation spectroscopic studies in presence of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Sn^{2+}, Hg^{2+}, Pb^{2+}, La^{3+}, Ga^{3+}, Er^{3+} and Yb^{3+} ions in methanol:H_2O (1:1) medium. Whereas some metal ions can only cause quenching effect on the fluorescence intensity of ***Q-BODIPY***, some of them show an increase in fluorescence intensity. The stoichiometry of host–guest complexes formed was determined by Job's plot method. The binding constants were calculated by Stern–Volmer method. As a fluorescence sensor, ***Q-BODIPY*** shows the best selectivity performance against Zn^{2+} ions in according to all spectroscopic data.

1. Introduction

A lot of literatures report to the design, synthesis and sensing action of novel fluorescence sensor bearing structural moieties like Schiff bases [1,2], Bodipy [3–7], Phthalocyanines [8], Porphyrins [9], etc. Among the fluorescence sensors, Bodipy sensors have been developed owing to their unique photophysical properties such as sharp emission–absorption peaks [10]. The Bodipy-derived ligands generally have a strong fluorescence and upon binding with metal ions exhibit weaker/stronger fluorescence and good photo-stability [11,12]. The Bodipy sensors show a shift in absorption and an increasing-quenching in emission intensity upon binding with cations. Although sensing of d group metal ions by fluorometric method (based on Bodipy) has developed owing to the great concern with medicine and environment, the fluorometric sensing of p and f block metal ions have rarely studied [13–15]. A few studies show dual or trio responsive property by sensing both d and p and f group metal ions [16]. Quinoline derivatives (metal-sensing) as an excellent electron donor have been widely exploited for design and preparation of metal sensors. For example, Tian's group reported a selective fluorescent probe of Hg^{2+} based on triazole linked 8-oxyquinoline calix [4] arene by click chemistry [17]. The metal sensing of quinolone-propargyl derivatives is particularly attractive for lanthanides due to their multiple coordination [18].

In recent years, azido-cycling form click reaction has been frequently used to construct ligands with cation chelating ability [19]. Such synthetic strategies to produce quinoline-propargyl and azido-Bodipy ligands with metal ion coordinating ability offer a new approach for the design of novel fluorescence sensors [20].

In this paper, we have presented to Bodipy-quinoline (***Q-BODIPY***) synthesized using click chemistry as two of the key intermediate reactions. In the first step, azido-Bodipy (**3**) was prepared by treating 3-ethyl-2,4-dimethylpyrrole and a functionalized aldehyde with using trifluoroacetic acid (TFA). 8-(Prop-2-ynyloxy) quinoline (**4**) was prepared via propargylation of 8-hydroxyquinoline. Azido-Bodipy, **3**, and alkyne-quinoline, **4**, were combined by copper sulfate-catalysed cycloaddition (click chemistry) to obtain a functional metal cation fluorescent sensor.

2. Experimental section

2.1. Materials and instruments

All reagents used for synthesis were obtained commercially and used without further purification. In the absorption and emission experiments, all the metal ions were added in the form of nitrate salts, which were purchased from Sigma-Aldrich and Acros, stored in a vacuum desiccator containing self-indicating silica and dried fully before using. Dichloromethane (DCM) was dried using CaH_2 and then distilled in reduced pressure. UV–vis spectra were recorded in 1 cm path length quartz cell using *Perkin Elmer Lambda 25 UV–vis spectrophotometer*. Emission spectra and excitation spectra were

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recorded in *PerkinElmer LS 55 spectrofluorimeter*. ^{1}H–NMR spectra were recorded on *a Varian* (400 MHz). FT-IR spectra were obtained from *Perkin-Elmer spectrometer* (400–4000 cm^{-1}) without using KBr pellet. The mass measurement was recorded by a *Bruker Compass Data Analysis 4.0* (*ESI-TOF-MS*) (The mass spectrometers used were a micrOTOFQ and a maXis quadrupole time-of-flight mass spectrometer).

2.2. The synthesis of 4-(3-bromopropoxy)benzaldehyde (1) and 4-(3-azidopropoxy) benzaldehyde (2)

One and two were prepared according to known procedures [21–23] and used by purification techniques.

2.3. The synthesis of 4,4-difluoro-8-(4-(3-azidopropoxy))phenyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (3)

Two (1.03 g, 5 mmol) and 3-ethyl-2,4-dimethylpyrrole (1.5 equiv) were dissolved in dry DCM (200 mL) and degassed with nitrogen for 15 min. TFA (0.1 mL) was added and the solution stirred at r.t. under nitrogen for 30 min. After DCM was removed by evaporation in vacuo, the dark oily residue was purified by eluent DCM to give dark-red oil in column. To a solution of this oil in ether (35 mL), was added DDQ (470 mg, 2.00 mmol) in ether/methanol (6:4 mL), the reaction was allowed to proceed at room temperature-dark ambient under an inert atmosphere for 15 min. The claret-red residue was obtained after evaporation and purified by column chromatography (by difficult-tiring procedure).

Toluene (100 mL) was degassed in a three-necked flask for 30 min under nitrogen atmosphere. Eight equivalents triethylamine was added to final residue. The solution was heated to 70 °C for 30 min after 5 equiv. boron trifluoride etherate was added in four portions. A white fume was occurred and the reaction was refluxed for overnight. The solution was concentrated in evaporator and the black residue re-dissolved in a minimal amount of dichloromethane and carefully purified by column chromatography (DCM:petroleum ether) a single red–orange band was observed which yielded a ruby solid. Yield; 27% (0.647 g). ^{1}H–NMR [400 MHz, $CDCl_3$]: 7.26 (d, 2H, ArH), 7.07 (d, 2H, ArH), 4.13 (t, 2H, CH_2), 3.57 (t, 2H, CH_2), 2.52 (s, 6H,CH_3), 2.30 (q, 4H, CH_2), 2.12 (m, 2H, CH_2), 1.35 (s, 6H, CH_3), 0.98 (t, 6H, CH_3). ^{11}B–NMR [128.3 MHz, $CDCl_3$]: 0.00 (s, 1B); ^{19}F NMR [376.83 MHz, $CDCl_3$]: −145.8224, −145.908, −145.9943, −146.0864 (dd, 2F); ^{13}C–NMR [100 MHz $CDCl_3$]: 159.2, 152.4, 139.8, 133.1, 132.9, 130.0, 128.8, 115.7, 64.5, 48.1, 28.8, 17.0, 14.6, 12.5, 11.8. Anal. Calc. for (%) $C_{26}H_{32}BF_2N_5O$; C, 65.14; H, 6.73; N, 14.61; Found; C, 65.19; H, 6.88; N, 14.44.

2.4. The synthesis of 8-(prop-2-ynyloxy)quinolone (4)

A sample of 0.73 g (5 mmol) 8-hydroxyquinoline was solved in acetonitrile (100 mL), K_2CO_3 (5 equiv.) was added to this solution. The excess of propargyl bromide (2 equiv. 10 mmol) was gradually added to this mixture and the mixture was refluxed for overnight and completion of the reaction was monitored by TLC. After filtration and evaporation, a brown oily residue was obtained and purified by using column chromatography on silica gel using eluent petroleum ether. The residue was re-crystallized in ethanol (brown solid). Yield (0.67 g, 75%).

^{1}H NMR [400 MHz, $CDCl_3$]: 8.90 (d, 1H, ArH), 8.14 (d, 1H, ArH), 7.40–7.50 (m, 3H, ArH), 7.22 (d, 1H, ArH), 5.09 (s, 1H, CH), 2.58 (s, 2H, CH_2). ^{13}C NMR [100 MHz, $CDCl_3$]: 210.2, 154.3 149.7, 141.4, 136.4, 128.5, 126.3, 122.4, 121.1, 110.0, 78.6, 76.3, 56.4. Anal. Calc $C_{12}H_9NO$; C, 78.67; H, 4.95; N, 7.65. Found: C, 78.84; H, 5.09; N, 7.41.

2.5. The synthesis of Q-BODIPY

A sample of 1.1. equiv. of **3** (0.526 g, 1.1 mmol) was added to a mixture of **4** (0.183 g, 1 mmol) in $CHCl_3$:EtOH:H_2O (ratio; 10:1:1). Then, 0.3 equiv. of sodium ascorbate was added to this mixture and stirred for 15 min, followed by 0.15 equiv. of $CuSO_4 \cdot 5H_2O$. The heterogeneous mixture was stirred vigorously for 72 h. (until TLC analysis indicated to the consumption of the starting material). After completion of the reaction, the solvents were evaporated and the residue was extracted with ethylacetate–water (3 times). The combined organic phase was concentrated and purified by column chromatography (ethylacetate, as an eluent) (0.537 g, 81% yield).

^{1}H NMR [400 MHz, $CDCl_3$]: 8.95 (d, 1H, ArH), 8.14 (d, 1H, ArH), 7.75 (s, 1H, CH), 7.4 (m, 5H, ArH), 7.08 (d, 1H, ArH), 6.95 (d, 2H, ArH), 5.55 (s, 2H, CH_2), 4.53 (t, 2H, CH_2), 4.02 (t, 2H, CH_2), 2.52 (s, 6H,CH_3), 2.30 (q, 4H, CH_2), 2.22 (m, 2H, CH_2), 1.30 (s, 6 H, CH_3), 0.99 (t, 6H, CH_3). ^{13}C NMR [100 MHz, $CDCl_3$]: 221.2, 159.2, 151.3, 142.7, 141.4, 139.8, 136.3,

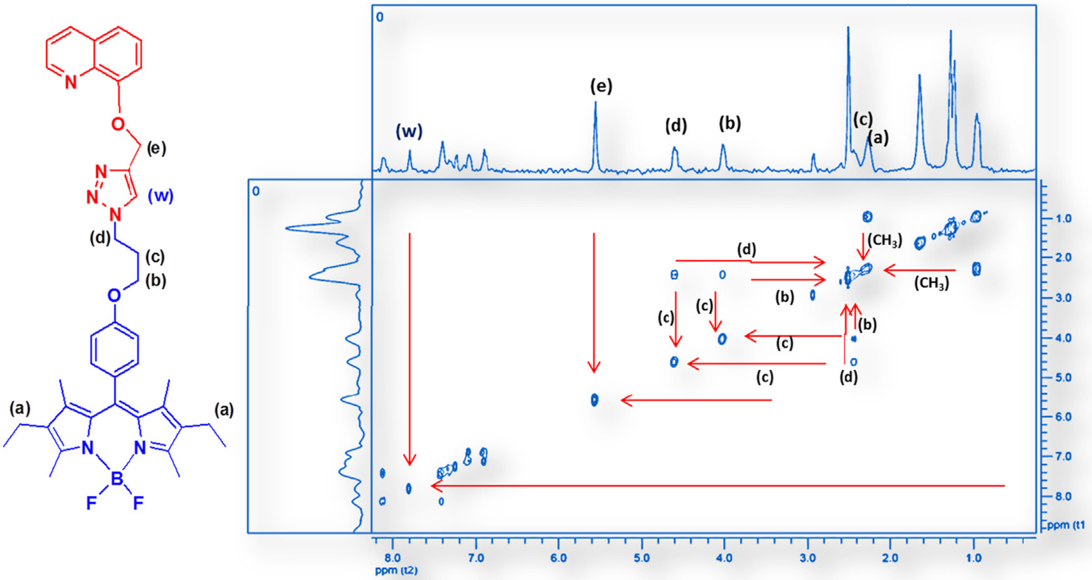

Fig. 1. The protons of neighbor carbon in COSY-NMR.