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Colorimetric and ratiometric fluorescent chemosensor for fluoride ion based on perylene diimide derivatives

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ABSTRACT

Based on a perylene diimide derivatives(PDIs) platform, AM-PDIs was rationally designed and synthesized as a new colorimetric and ratiometric fluorescent sensor for naked-eye detection of fluoride ion with high selectivity over other halide ions. Addition of fluoride ion to a dichloromethane(DCM) solution of AM-PDIs resulted in an obvious color change (from red to blackish green) because of a large red shift (151 nm) in absorption. The recognition mechanism was attributed to the intermolecular proton transfer between a hydrogen atom on the amide N position of sensor and the fluoride anion. The detection limit was calculated to be 0.14 μ M.

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1. Introduction

The design and construction of sensory molecules for recognition and sensing of anions has received considerable attention in recent years [1–6], as anions play a fundamental role in a wide range of chemical, biological, medical, and environmental processes [7–9]. Among the anions, fluoride, the smallest anion with a high charge density, is an attractive target for sensor design due to its association with nerve gases, the analysis of drinking water, and the refinement of uranium used in nuclear weapons manufacture [10–12]. Fluoride is a strong hydrogen bond acceptor and has a high affinity to silicon and boron. These unique chemical properties have been widely deployed in the design and development of many fluorescent sensors for fluoride anions [13-19]. However, many of them are based on fluorescence measurement at a single wavelength, which may be influenced by variations in the sample environment. To increase the selectivity and sensitivity, ratiometric fluorescent sensors are used, which involves the observation of changes in the ratio of the intensities of the

* Corresponding author. Tel./fax: +86 21 64253881. E-mail address: wanglimin@ecust.edu.cn (L.M. Wang). absorption or the emission at two wavelengths. Thus, ratiometric fluorescent sensors can provide a built-in correction for environmental effects [20].

Perylene dianhydride (PTCDA) and its derivatives Perylene diimide derivatives (PDIs) represent a class of strongly fluorescent high performance pigments that have excellent chemical, thermal, photo, and weather stability [21]. Recently, significant progress has been made to use PDIs-containing materials in organic fieldeffect transistors (OFETs), fluorescent solar, collectors, electrophotographic devices, dye lasers, organic photovoltaic cells (OPVs), and optical power Limiters [22-24]. Also, PDIs show good optical and electrical properties due to their high photoluminescence efficiency and good chemical and thermal stability [25,26], Which indicates they could be good platforms for the fluorescent sensors. Therefore, many work about fluorescent sensors based on the PDIs has been reported. But most of these fluorescent sensors reported before were for cations and biomolecules [27–34], few of these sensors were for anions. To the best of our knowledge, there were no reports on the colormetric and ratiomeitric fluorescent sensors based on PDIs for fluoride ion. Herein, we designed and synthesized a new colorimetric and ratiometric fluorescent sensor for naked-eve detection of fluoride ion. The sensor exhibited a large red shift (151 nm) in absorption and it also exhibited a high selectivity for fluoride ion over other anions in DCM. The detection

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limit was calculated to be 0.14 uM due to our rational design. The synthesis of AM-PDIs started from PTCDA 1, via Imidization, nitration, reduction and acetylation steps, AM-PDIs was obtained, as shown in Scheme 1.

2. Materials and methods

2.1. Experimental

2.1.1. General

Reagents and solvents were reagent grade, used as received unless otherwise noted. All solvents used in water–sensitive reactions were freshly distilled: THF from K/benzophenone, CH₂Cl₂ from CaH₂. Reactions were monitored by TLC. Flash chromatography separations were carried out using silica gel (200–300 mesh). Yields are of purified product and were not optimized. ¹HNMR were recorded at 400 MHz. Infrared spectra was measured on the Fourier Transform Infrared (FT-IR) Spectroscopy (Nicollet, Thermo Scientific, USA). Absorption spectra was carried out on a Thermo UV–Vis spectrophotometer and Fluorescence spectra was measured on a Thermo Fluorescence spectrophotometer.

2.2. Synthesis

2.2.1. Synthesis of N,N'-dicyclohexyl-perylene-3,4,9,10tetracarboxylic acid bisimide **2**

PTCDA **1** (5 g, 9 mmol) was placed in a 250-mL round-bottomed flask, and cyclohexane (86 g, 870 mmol) was added with stirring. The mixture was heated to reflux for 15 h. The precipitate was filtered, washed with 5% (w/w) NaOH (100 mL) and ethanol (50 mL), Then dried to give 4.5 g of compound 2 (93%) as a red solid. compound **2**: ¹HNMR (CDC l₃): 8.01 (d, J = 10.8 Hz, 4H), 7.83 (d,





Scheme 1. The synthetic route of AM-PDIs.



Fig. 1. (a): UV–vis absorption spectra of AM-PTCDI (1×10^{-5} M) in DCM upon addition of 0–12 equiv of TBAF. b: Emission spectra of AM-PTCDI (1×10^{-5} M) in DCM upon the addition of 0–12 equiv of TBAF.

J = 10.8 Hz, 4H), 5.01 (m, 2H), 2.53 (m, 4H), 1.92 (m, 4H), 1.75 (m, 6H), 1.44 (m, 6H).

2.2.2. Synthesis of N,N'-dicyclohexyl-(1-nitro)perylene-3,4,9,10tetracarboxylic acid bisimide **3**

Compound **2** (2.5 g,4.5 mmol), cerium (IV) ammonium nitrate (CAN) (3 g, 5.5 mmol), nitric acid (3.25 mL, 80 mmol) and dichloromethane (350 mL) were stirred at 25 °C under N₂ for 2 h. The mixture was neutralized with 10%(w/w) KOH and extracted with CH₂Cl₂. After the solvent was removed, the crude product was purified by silica gel column chromatography with the eluent



Scheme 2. Intermolecular Proton Transfer between AM-PDIs and the Fluoride Ion.



Fig. 2. Partial ¹HNMR spectra of sensor AM-PDIs in CDCl₃ in the presence of 0 equiv, and 12 equiv of TBAF.

CH₂Cl₂ to afford compound **3** in 95% yield. compound **3**: ¹HNMR (CDCl₃): 8.74 (d, J = 6.4 Hz, 1H),8.62–8.69 (m, 4H), 8.55 (d, J = 6.0 Hz, 1H), 8.18 (d, J = 6.0 Hz, 1H), 5.00 (m, 2H), 2.54 (m, 4H), 1.47–1.91 (m, 14H), 1.34 (m, 2H).

2.2.3. Synthesis of N,N'-dicyclohexyl-(1-amino)perylene-3,4,9,10-tetracarboxylic acid bisimide **4**

Compound **3** (2.0 g, 3.3 mmol) was added to a previously prepared solution of THF (40 mL) containing 4.8 g of Zn (70 mmol) and aerated with ethylic acid(3 mL, 50 mmol). The reaction mixture was stirred at 25 °C under N₂ for 12 h. After the removal of the solvent and washing of the residue with 5% NaOH (30 mL \times 3), Compound **4** was obtained as purple solid in 95% yield. compound **4**: ¹HNMR(CDCl₃): 8.77(d, J = 8.4 Hz, 1H), 8.55–8.57(m, 2H),



Fig. 3. Partial infrared spectra of sensor AM-PDIs in the presence of 0 equiv, and 12 equiv of TBAF.



Fig. 4. (a): Plot of the absorbance ratio of AM-PDIs between 681 nm and 530 nm (A_{681nm}/A_{497nm}) vs concentration of F⁻ in DCM. b: Plot of the emission intensity ratio of AM-PDIs between 588 nm and 480 nm $(I_{480 nm}/I_{588 nm})$ vs concentration of F⁻ in DCM.

а

0.5

8.39–8.40(m, 2H), 8.35(d, *J* = 8.0 Hz, 1H), 8.07(s, 1H), 5.15(s, 2H), 4.34–4.37(m, 2H), 1.73–1.79(m, 12H), 1.22–1.28(m, 8H).

2.2.4. Synthesis of AM-PDIs

Acetylchloride (0.24 g, 3 mmol) was dissolved in THF (10 mL) and added dropwise to a solution of THF (40 mL) containing 0.57 g of compound 4 (1 mmol) and 0.3 mL pyridine (3.6 mmol). The reaction mixture was stirred at 55 °C under N₂ for 12 h. After the solvent was removed, This crude product was purified by silica gel column chromatography with 1:100 CH₂Cl₂:CH₃OH to give 0.2 g (33%) of a red solid. compound **AM-PDIs**: ¹HNMR(CDCl₃): 8.93(s, 1H), 8.32(d, J = 6.8 Hz, 1H), 8.18(d, J = 9.6 Hz, 1H), 7.96(d, J = 7.2 Hz, 1H), 7.87(d, J = 6.0 Hz, 1H), 7.69(d, J = 7.2 Hz, 1H), 7.17(m, 1H), 4.88(m, 2H), 2.41–2.48(m, 8H), 1.61–1.64(m, 6H), 1.25–1.38(m, 6H). MS: m/z = 611.2411, (calcd. 611.2420).

3. Result and discussion

 $n-Bu_4NF$ (TBAF) as a fluoride source was gradually added to a DCM solution of the sensor AM-PDIs. The deprotonated abilities of sensor AM-PDIs with the fluoride ion were investigated by the UV–vis absorption and fluorescence spectra, when TBAF was added to the DCM solution of sensor AM-PDIs, an obvious color

change from red to blackish green in ambient light, which could be observed by naked eyes. In the absence of anions, the maximum absorption wavelength of AM-PDIs is at about 530 nm. Upon progressive addition of TBAF, the peak at 530 nm decreased gradually, and a large bathochoromic shift (151 nm) of the maximum could be observed and increased (Fig. 1a), meanwhile a totally new band at 681 nm is developed with two clear isosbestic points at 564 nm and 455 nm, which indicated the formation of new compound. Upon excitation at 455 nm, the free sensor showed an intense emission at 588 nm, however, the addition of the flourion led to a drastic decrease at 588 nm and simultaneous appearance of a new emission band at 480 nm, attributed to the local emission(LE) [35], as shown in the Fig. 1b.

As a result, the sensor provided a ratiometric fluorescent response (I_{480}/I_{588}) to F anions. Thinking of the above facts, a possible explanation for the F.

anion-triggered spectroscopic changes was the intermolecular proton transfer (IPT) process between the amide moiety and fluoride ion and its change from electronically neutral (PDIs–NH–AC) without a fluoride ion to negatively charged (PDIs-N⁻-AC) with a fluoride ion [36] (Scheme 2).

To confirm this assumption, ¹HNMR titrations and infrared spectrum were carried out (Fig. 2 and Fig. 3). It was found that the amide N–H proton signal (8.93 ppm)-single peak and N–H

or AM-PDIs



Sensor AM-PDIs +F Sensor AM-PDIs+F +other anion Absorbtion 0.0 400 500 600 700 800 900 Wavelength(nm) b 35000 30000 25000 ensor AM-PDIs Intensity(au) 20000 15000 Sensor AM-PDIs+F +other anion 10000 AM-PDIs+ 5000 0 600 500 700 800 Wavelength(nm)

Fig. 5. (a): Absorbance ratiometric response of AM-PDIs between 681 nm and 530 nm to the halide ions (12 equiv). (b): Emission ratiometric response of AM-PDIs to the halide ions (12 equiv). The emissions were at 588 nm and 480 nm and excited at 455 nm.

Fig. 6. a): UV–Vis absorption spectra of sensor AM-PDIs $(1 \times 10^{-5} \text{ M})$ to F anions(12 equiv) in the presence of 12 equiv of each relevant analyte (Cl, Br, I) in DCM. (b): Fluorescent spectra of sensor AM-PDIs $(1 \times 10^{-5} \text{ M})$ to F anions(12 equiv) in the presence of 12 equiv of each relevant analytes (Cl, Br,I) in DCM.



Fig. 7. Color (a, left) and fluorescence (b, right) change of sensor AM-PDIs (from left to right: AM-PDIs only; AM-PDIs + F⁻; AM-PDIs + Cl⁻; AM-PDIs + Br⁻; AM-PDIs + I⁻).

stretching vibrational absorption(3294.93 $\rm cm^{-1}$) disappeared with addition of F⁻, which confirmed the deprotonation of N–H by F⁻.

Fig. 4a showed a near–linear correlation of AM-PDIs between intensity ratios of absorbance at 681 nm to those at 530 nm (A₆₈₁/ A₅₃₀) vs fluoride ion concentration in DCM.This demonstrated the potential utility of sensor AM-PDIs for calibrating and determining fluoride ion concentration in DCM. Furthermore, a corresponding correlation between emission ratiometric response of AM-PDIs at 580 nm and 488 nm (I₄₈₈/I₅₈₀) and fluoride ion concentration in DCM was obtained in Fig. 4b, thus, AM-PDIs could also serve as a ratiometric fluorescent sensor for F⁻. The linear equation was found to be $y = 533.22 \times 10^5 x + 25.309$ (R = 0.9652), where y was the absorbance at 681 nm measured at a given F₁ concentration and x represented the concentration (10⁻⁵ mol/L) of F added. According to IUPAC, the detection limit was determined from three times the standard deviation of the blank signal (3s) as 0.14 µM.

Sensor AM-PDIs was treated with all the halide ions to investigate the selectivity. AM-PDIs showed a large ratiometric response ($A_{681}/A_{530} = 1.67$, $I_{480}/I_{588} = 1.54$) for the fluoride anion,while the other analytes only induced a minimum ratiometric response with $A_{681}/A_{530} < 0.01$, $I_{480}/I_{588} < 0.01$, as shown in Fig. 5. These results indicate that the sensor is highly selective to F⁻ over other halide ions tested. The high selectivity to fluoride anion may be because fluoride anion was a much stronger hydrogen bond acceptor than other halide ions. Thus, only the flouride anion could induceintermolecular proton transfer (IPT) process between the amide moiety and fluoride ion while other halide ions could not.

To examine whether sensor AM-PDIs could still retain the sensing response to F^- under the potential competition of relevant analytes, the sensor was treated with F^- in the presence of Cl^- , Br^- and I^- . As displayed in Fig. 6a and Fig. 6b, all the relevant analytes tested have virtually no influence on the detection of F^- . Thus, sensor AM-PDIs seemed to be useful for selectively sensing F^- , even with these relevant analytes. Notably, the big red shift combined with large ratiometric absorbtion and fluorescent response rendered the sensor suitable for detection of F^- anions by simple visual inspection (Fig. 7).

4. Conclusions

In summary, we have designed and synthesized sensor AM-PDIs as a novel colorimetric and ratiometric fluorescent sensor for fluoride anions based on the PDIs rationally. The sensor exhibited a large red shift(151 nm) in absorption and the detection limit was calculated to be 0.14μ M. In addition, the sensor is highly

selective for fluoride anions over other halid ions. The large red shift in the absorption and the ratiometric fluorescent response render the sensor suitable for detection of F anions by simple visual inspection.

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