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Colorimetric chemosensors based on diketopyrrolopyrrole for selective and reversible recognition of fluoride ions

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ABSTRACT

A series of colorimetric and reversible receptors for fluoride anions based on diketopyrrolopyrrole (DPP) were designed and synthesized successfully. The position of nitro substituent on the phenylhydrazide affected the alteration of photophysical properties to varying degrees. While the photoluminescence intensity of receptor **1** was weaker than that of receptor **2** and receptor **3** on account of the formation of intramolecular hydrogen bond deriving from oxygen atom of nitro substituent and hydrogen atom of hydrazide. The receptor **2** was a preferable chemosensor for responding fluoride anions. The fluorescence was quenched in the presence of fluoride anion resulted from the photo-induced electron transfer (PET) effect from the amide. The formation of deprotonation species, which produced by hydrazide N—H moiety and F^- was answerable for the spectral changes. Especially, the spectral and color responses of receptors could be switched back and forth successively by adding F^- and HSO_4^- anions in DMSO solution. These receptors could response fluoride anion sensitively, visually and selectively in a manner of reversible with a low determination.

1. Introduction

Recently, there has been a growing interest in recognition and detection of fluoride ions. These anions are associated with nerve gases, with pesticides, with the analysis of drinking water, with artificial blood, and with the refinement of uranium used in manufacture of nuclear weapons [1–12]. As the smallest anion with a high charge density, fluoride plays an important role in chemical, biological and medical processes [13]. Proper ingestion of fluoride was vital in many biochemical reactions with extraordinary role in preventing dental caries [14] as well as treatment for osteoporosis [15–17]. It is necessary to add fluoride to toothpaste and drinking water. Because fluoride is absorbed easily by the body and excreted slowly from the body, and fluoride ion with permeability in the body tissue could be combined with calcium ion and cause poisoning, the presence of excess fluoride ion resulted in dental and skeletal fluorosis, bone diseases, mottling of teeth, and lesions of the thyroid, liver, and other organs [18]. In addition, with the development of industry and the increase in the number and the scale of enterprises on fluorine products, the contamination of fluorine became more serious. As a result, there is a need to develop new selective and sensitive methods for fluoride detection in environments that are not easily served by conventional ion-selective electrodes.

As a detected anion, fluoride has the smallest ion radius, and the strongest electronegativity as proton transfer receptor group. It could binding amide derivatives containing proton transfer donor group [19–24]. A series of DPP derivatives for the detection fluoride anion were discovered, which has considerable benefits over other fluorescent chromophores such as brilliant fluorescence color, high fluorescence intensity, excellent light stability and so on [25–29]. Withal, it would be very profitable if a sensor could reversible and reusable during sensing fluoride anion. But most of sensors for the detection of fluoride were irreversible and unreducible, which restricted the application tremendously [30–35].

Just to make up for the above deficiencies, extend the application, enrich the system, a series of reversible and reducible diketopyrrolopyrrole (DPP) derivatives were designed and synthesized successfully. As well, our group already published three papers [11,12,36] on the detection of fluoride anions based on diketopyrrolopyrrole (DPP). It comes to light that the position and kinds of substituent groups could affect the nature of sensors. In this paper these receptors combined DPP with phenylhydrazide together to research the effect of nitro substituent's site of phenylhydrazide on their photophysical properties absence and presence fluoride anion. A hydrazide (—CO—NH—) possessed hydrogen donor moiety of NH, which was superior in binding anions. The results

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displayed that the synthesized receptors could detect fluoride anion sensitively and reversibly. The three receptors demonstrated prominent selectivity toward fluoride anion in the presence of various anions in both UV–vis and fluorescence spectra in DMSO solution. The fluorescence intensity of receptor **1** lower than other receptors due to the formation of hydrogen bond between oxygen atom offered by nitro and hydrogen atom provided by hydrazide. The fluorescent was quenched as the result of photo-induced electron transfer (PET) effect from amide and changes of the overall charge distribution. In brief, these receptors synthesized in this paper were could act as effective and colorimetric fluorescence sensors for fluoride selectively, sensitively and reversibly.

2. Experimental

2.1. Reagents and Chemicals

All the commercially available reagents and chemicals were purchased from Aladdin Shanghai Reagent Company and used without further purification unless otherwise noted. Reactions were monitored by TLC. Flash chromatography separations were carried out using silica gel (200–300 mesh).

2.2. Apparatus

^{1}H NMR and ^{13}C NMR spectra were collected on a Bruker Avance II 400 MHz spectrometer. UV–vis spectra were recorded on a Shimadzu 3100 spectrometer. And fluorescence spectra were carried out using an Edinburgh Instruments Ltd-FLS920 fluorescence spectrophotometer.

2.3. General Method

All UV–vis and fluorescence titration experiments were carried out at ambient temperature. To the 1×10^{-5} M dry DMSO solution of the receptor, the varying equivalents of the anions were added separately and the spectra were recorded. Titration plots were obtained by using Origin. The ^{1}H NMR titrations were carried out in DMSO d_6 using TMS as an internal reference standard. 3×10^{-3} M receptor solution in DMSO d_6 was added the varying equivalents of TBA^+F^- and the ^{1}H NMR spectra recorded after each addition.

2.4. Synthesis of Receptor *1*

To a solution of 2-nitrobenzohydrazide (199.0 mg, 1.10 mmol) in 20 mL ethanol, compound **4** (100.0 mg, 0.15 mmol) was added. After the reaction solution was refluxed for 2 h, the salmon pink solid was precipitated, collected and recrystallized from ethanol to afford compound receptor **1** (43.3 mg, 30%). ^{1}H NMR (400 MHz, DMSO d_6) δ (ppm) 12.28 (s, 2H), 8.21 (tt, $J = 9.1$, $J = 5.4$ Hz, 2H), 8.11–8.01 (m, 2H), 7.97–7.86 (m, 6H), 7.85–7.76 (m, 2H), 7.81–7.67 (m, 2H), 7.51 (dd, $J = 8.4$, $J = 6.2$ Hz, 4H), 3.66–3.09 (m, 30H). ^{13}C NMR (100 MHz, DMSO d_6) δ (ppm) 168.43, 162.14, 162.08, 147.54, 147.28, 143.89, 136.50, 134.91, 134.59, 131.50, 131.39, 131.31, 130.04, 129.88, 129.49, 129.14, 127.79, 127.18, 124.89, 124.00, 109.59, 71.71, 71.66, 70.23, 70.04, 70.01, 68.33, 58.49, and 58.43. HRMS-ESI: *m/z* calcd (%) for $C_{48}H_{50}N_8O_{14}$: 963.3400 [**1** + H]$^+$, found: 963.3514. IR (cm^{-1}, KBr): 3453, 3189, 2874, 1668, 1527, 1354, 1296, 1090, and 750. Element analysis for receptor **1** $C_{48}H_{50}N_8O_{14}$ (%): C 59.84, H 5.29, and N 11.59, calculated C 59.87, H 5.23, and N 11.64.

2.5. Synthesis of Receptor *2*

To a solution of 3-nitrobenzohydrazide (199.0 mg, 1.10 mmol) in 20 mL ethanol, compound **4** (100.0 mg, 0.15 mmol) was added. After the reaction solution was refluxed for 2 h, the salmon pink solid was precipitated, collected and recrystallized from ethanol to afford compound receptor **2** (92.4 mg, 64%). ^{1}H NMR (400 MHz, DMSO d_6) δ (ppm) 8.80 (s, 2H), 8.58 (s, 2H), 8.47 (d, $J = 8.7$ Hz, 2H), 8.40 (d, $J = 7.9$ Hz, 4H), 8.08 (d, $J = 8.2$ Hz, 4H), 7.95 (d, $J = 8.1$ Hz, 4H), 7.87 (t, $J = 8.0$ Hz, 2H), 3.66–3.09 (m, 30H). ^{13}C NMR (100 MHz, DMSO d_6) δ (ppm) 162.19, 161.55, 148.25, 148.14, 136.99, 135.07, 134.69, 130.84, 130.05, 129.49, 127.79, 126.97, 122.83, 109.70, 71.71, 70.27, 70.08, 68.41, 58.50, and 56.48. HRMS-ESI: *m/z* calcd (%) for $C_{48}H_{50}N_8O_{14}$: 963.3400 [**2** + H]$^+$, found: 963.3528. IR (cm^{-1}, KBr): 3444, 3205, 2874, 1660, 1536, 1519, 1354, 1279, 1098, 850, and 726. Element analysis for receptor **2** C48H50N8O14 (%): C 59.81, H 5.21, and N 11.62, calculated C 59.87, H 5.23, and N 11.64.

2.6. Synthesis of Receptor *3*

To a solution of 4-nitrobenzohydrazide (199.0 mg, 1.10 mmol) in 20 mL ethanol, compound **4** (100.0 mg, 0.15 mmol) was added. After the reaction solution was refluxed for 2 h, the salmon pink solid was precipitated, collected and recrystallized from ethanol to afford compound receptor **3** (46.2 mg, 32%). ^{1}H NMR (400 MHz, DMSO d_6) δ (ppm) 12.34 (s, 2H), 8.57 (s, 2H), 8.45–8.35 (m, 5H), 8.19 (d, $J = 8.6$ Hz, 4H), 8.07 (dd, $J = 8.6$, $J = 7.8$ Hz, 6H), 7.96 (d, $J = 8.2$Hz, 2 H), 3.66–3.09 (m, 30H). ^{13}C NMR (100 MHz, DMSO d_6) δ (ppm) 162.19, 149.81, 148.23, 139.37, 130.06, 129.72, 127.82, 124.18, 109.70, 71.71, 70.26, 70.08, 68.41, and 58.51. HRMS-ESI: *m/z* calcd (%) for $C_{48}H_{50}N_8O_{14}$: 963.3400 [**3** + H]$^+$, found: 963.3527. IR (cm^{-1}, KBr): 3450, 3213, 2883, 1668, 1594, 1519, 1354, 1288, 1089, and 850. Element analysis for receptor **3** $C_{48}H_{50}N_8O_{14}$ (%): C 59.83, H 5.31, and N 11.61, calculated C 59.87, H 5.23, and N 11.64.

2.7. Determination of the Limits of Detection (LOD)

The LOD was calculated on the basis of the fluorescence titration using the formula $3\sigma / k$, where σ was the standard deviation of blank (10 samples) and k was the slope between fluorescence intensity difference versus sample concentration. Sensors were employed at 1×10^{-5} M.

3. Results and Discussion

3.1. Synthesis of DPP-derivatives

DPP-derivatives were synthesized by one simple reaction through condensation of compound **4** and 2-nitrobenzohydrazide, 3-nitrobenzohydrazide or 4-nitrobenzohydrazide (Scheme 1). The compound **4** was synthesized according to a reported method [36].

The target products were explicitly characterized by ^{1}H NMR, ^{13}C NMR, ^{1}H—^{1}H COSY, ^{1}H—^{13}C HSQC and HRMS-ESI.

3.2. Photophysical Properties

The normalized UV–vis absorption and photoluminescence spectra of these three receptors in DMSO were depicted in Fig. 1. The receptor **1** showed an excitation peak at 495 nm and an emission peak at 578 nm. For receptor **2**, the excitation peak was at 498 nm, and the emission peak was at 578 nm. The receptor **3** indicated an excitation peak at 499 nm with an emission peak at 576 nm. The Stokes shift of these receptors **1**, **2** and **3** were 83, 80 and 77 nm respectively. Additionally, the photoluminescence intensity of these three receptors was different obviously, while the intensity of receptor **1** was weaker than others evidently. The distance between H atom in amide (—CO—NH—) group and O atom in —NO_2 group was too close in receptor **1**, which beneficial to form hydrogen bond and gave the excited state intramolecular proton transfer (ESIPT) [11]. So the receptor **1** showed pretty low intensity, partly imputing to the photoinduced electron transfer (PET) effect from the amide [11]. In respect of fluorescence