

Two novel rhodamine-perylenediimide fluorescent probes: Synthesis, photophysical properties, and cell imaging



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ARTICLE INFO

Article history:

Received 30 June 2015

Received in revised form 14 September 2015

Accepted 14 January 2016

Available online 1 February 2016

Keywords:

Perylenediimide

Rhodamine

Photoinduced electron transfer

Dual-switch

ABSTRACT

In this study, two novel dual-switch fluorescent chemosensors based on rhodamine-perylenediimide have been designed and synthesized. The dual-switching behaviors of the sensors were based on the structural transformations of rhodamine and an intramolecular photoinduced electron transfer (PET) process from rhodamine to perylenediimide. These probes exhibited excellent sensitivity to protons with enhanced fluorescence emission from 500 nm to 580 nm. The fluorescence changes of probes were reversible within a wide range of pH values from 2.0 to 11.0. Moreover, the sensors exhibited high selectivity, short response time, and long lifetime toward protons. The possible mechanism was investigated by the DFT calculation and ^1H NMR. According to the experiment of confocal laser scanning microscopy, these probes could be used to detect the acidic pH variations in living cells.

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1. Introduction

As common cations, protons play key roles in both of metabolism and cellular events, such as cell growth, calcium regulation chemotaxis, and cell adhesion [1]. Many detection methods in the determination of pH have resulted in the research of pH sensors [2–11]. Among these methods, fluorescent probes are regarded as outstanding detection systems due to their terms of high sensitivity, selectivity, and more convenient operation in many applications [12–14]. So far, strenuous efforts have been made to the development of efficient fluorescent chemosensors for the detection of pH [15–19]. Rhodamine derivatives have been widely used for detection of various metal ions due to their high photostability, high quantum yield, and special structure [20–27]. The sensing mechanism is based on fluorescence enhancement caused by spirolactam ring-opening of rhodamine derivatives [28]. The spirolactam structure is also sensitive to the pH value of the environment. Under neutral or basic conditions, the spirolactam remains closed and the rhodamine derivatives are non-fluorescent, while under acidic conditions, proton leads to spirolactam ring-opening and the rhodamine derivatives exhibit strong fluorescence emission [29–31]. Thus, rhodamine derivatives are suitable to

monitor the pH value in acidic environment with enhanced fluorescence signals. This type of rhodamine-based pH probes have been prepared and attained considerable effects [30–34], while pH-sensitive rhodamine derivatives as pH fluorescence probes are less common. Among these rhodamine-based probes, dual-switch pH sensors that emit fluorescence with dual emission wavelengths and enable a built in correction for the undesired environmental effects have received more and more concerns.

Perylene tetracarboxylic diimides (PDI) have also generated great interest in the fields of sensors because of their excellent photo-stability, chemical stability, and high electron-accepting ability [35–44]. Most perylenediimide fluorometric sensors were designed to sense photophysical changes produced upon complexation, including photoinduced electron transfer (PET), intramolecular charge transfer (ICT) [45], and fluorescence resonance energy transfer (FRET) [46]. In these sensors, the PET-based PDI fluorometric sensors [47,48] have been widely utilized in the design of sensors due to the inherently higher sensitivity of PET in comparison with the normal fluorescence quenching motif. However, PET-based PDI fluorometric sensors with dual-switch sensor for proton have not been reported before.

Herein, based on the unique structural transformations of rhodamine in acid media and the high electron-accepting ability of PDI, two novel dual-switch fluorescent probes **4** and **5** were designed and synthesized as shown in Fig. 1. In these probes, the perylene diimide chromophore plays as an electron acceptor;

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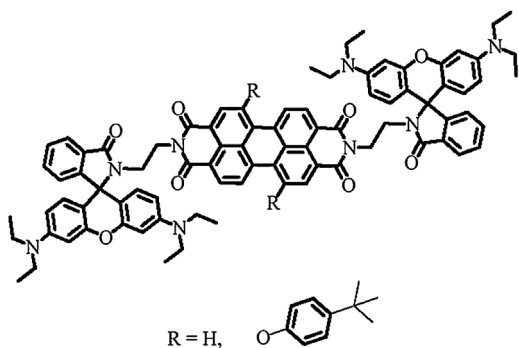


Fig. 1. Structure of the compounds **4** and **5**.

the rhodamine units serve as electron donors, and the ethylenediamine plays as spacer, which separates the two units. In order to improve the solubility of PDI-core in probes, two PDI cores have been prepared *via* modifying the bay region of perylene diimides with 4-*tert*-butylphenol. In these cases, A PET process can occur accompanying with the spiroactam ring-opening of rhodamine. The probes represent off-state when the rhodamine units are in spirocyclic, the protonation coordination of the amine fluorophore would generate the rhodamine ring-open. At the same time, the PET process should be blocked and the probes represented “switched on” state.

2. Experimental

2.1. Materials

Commercially available rhodamine B, ethylenediamine and perylene-3,4,9,10-tetracarboxylic acid bisanhydride were used without purification. The starting compounds **3** [49] and (1,7-bis(4-*tert*-butylphenoxy)perylen-3,4,9,10-tetracarboxylic acid bisanhydride) **2** [50,51] were prepared according to the reported procedures. All solvents used in spectroscopic measurements were of analytical grade. Reactions were monitored by thin layer chromatography using Merck TLC Silica gel 60 F254. Silica gel column chromatography was performed over Merck Silica gel 60. Dilute hydrochloric acid or sodium hydroxide was used for tuning pH values.

2.2. Methods

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX 300 NMR spectrometer and a Bruker ADVANCE 500 NMR spectrometer in CDCl_3 with tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. HRMS were recorded on an Ultraflex II MALDI-TOF mass spectrometer. UV-visible absorption spectra were determined on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were measured on a HORIBA FL-4 Max spectrometer. FT-IR spectra were recorded on a Nicolet 750 series in the region of $4000\text{--}400\text{ cm}^{-1}$ using KBr pellets. DFT calculations of compounds were performed using the Gaussian 03 program package. The calculations were optimized at the B3LYP/6-31G (d) level of theory. The molecular orbitals were visualized using GaussView.

2.3. Synthesis of amino-functional rhodamine B (**3**)

Rhodamine B 5.0 g (11.2 mmol) and ethylenediamine 9.0 mL (134.8 mmol) were dissolved in ethanol (50 mL) in a 250 mL flask, then the mixture was heated at $80\text{ }^\circ\text{C}$ for 7 h. After ethanol was removed under vacuum, the residue was purified by column

chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 10:1) to give **3** as a pale yellow powder 4.7 g, yield: 85%. M.p. $216\text{--}218\text{ }^\circ\text{C}$ (the reference value $217\text{--}219\text{ }^\circ\text{C}$), yield: 75%. ^1H NMR (CDCl_3 , ppm): δ 7.89 (m, 1H), 7.42 (m, 2H), 7.07 (m, 1H), 6.40 (dd, 4H, $J = 8.9$, 2.6 Hz), 6.26 (dd, 2H, $J = 8.8$, 2.7 Hz), 3.32 (m, 8H), 3.18 (t, 2H, $J = 6.6$ Hz), 2.40 (t, 2H, $J = 6.6$ Hz), 1.15 (t, 12H, $J = 6.9$ Hz).

2.4. Synthesis of 1,7-bis(4-*tert*-butylphenoxy)perylen-3,4,9,10-tetracarboxylic acid bisanhydride (**2**)

- (1) A mixture of 5.0 g (13 mmol) of perylene-3,4,9,10-tetracarboxylic acid bisanhydride (**1**) and sulfuric acid (100 mL) was stirred at $50\text{ }^\circ\text{C}$ for 12 h, and subsequently I_2 (0.56 g) was added. The reaction mixture was heated to $80\text{ }^\circ\text{C}$, and bromine 2.2 g (15 mmol) was added dropwise over a time period of 2 h. After bromine addition, the reaction mixture was heated for an additional 48 h, the excess bromine was removed by saturated aqueous solution of K_2CO_3 , and water (100 mL) was added carefully. The precipitate was separated by filtration, washed with water (100 mL), and dried in a vacuum to give a red powder 6.0 g. Without further purification it was used to the next reaction.
- (2) A mixture of compound 1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisanhydride 2.0 g (3.6 mmol), 4-*tert*-butylphenol 1.8 g (12.0 mmol), and K_2CO_3 2.4 g (6.8 mmol) in dry DMF (120 mL) was heated at the refluxing temperature for 4 h under an N_2 atmosphere. The reaction mixture was poured into water (100 mL) and neutralized with aqueous 1.2 mol/L HCl solutions. The formed precipitate was collected by filtration and washed with water and methanol to give crude product **2** 3.1 g, yield: 92%. As this product showed poor solubility in common organic solvents, it was used for the next reaction without further purification.

2.5. Rhodamine-perylenediimide (**4**)

Compound **3** 1.1 g (2.3 mmol), compound **2** 0.42 g (0.6 mmol), and $\text{N}(\text{C}_3\text{H}_7)_3$ (0.5 mL) were dissolved in DMF (25 mL), the mixture was heated at $120\text{ }^\circ\text{C}$ for 12 h under nitrogen and the reaction was followed by TLC (DCM: methanol = 10:1). On completion of the reaction the solvent was removed under reduced pressure, a red-black solid got, washed with waters (100 mL), dry in $60\text{ }^\circ\text{C}$, a more rigorous purification was then carried out *via* column chromatography (DCM/methanol = 20:1) to give a purple solid **4** 0.79 g, yield: 80%. m.p. $> 300\text{ }^\circ\text{C}$. FT-IR (KBr, cm^{-1}): 3422 (ν_{NH}), 2950–2863 (ν_{CH}), 1696 ($\nu^{\text{as}}_{\text{N-C=O}}$), 1665 ($\nu^{\text{s}}_{\text{N-C=O}}$), and 1578 ($\nu_{\text{N-C=O}}$). ^1H NMR (CDCl_3 , ppm): δ 8.53 (s, 2H), 8.33 (d, 4H, $J = 8.1$ Hz), 7.79–7.71 (m, 2H), 7.43–7.41 (m, 8H), 7.14 (s, 2H), 7.05 (d, 2H, $J = 6.0$ Hz), 6.96 (d, 4H, $J = 8.4$ Hz), 6.62–6.60 (m, 4H), 6.43–6.40 (m, 4H), 6.29–6.26 (m, 4H), 3.74 (t, 4H, $J = 4.5$ Hz), 3.52 (t, 4H, $J = 4.5$ Hz), 3.28 (m, 16H), 1.65 (s, 18H), 1.13 (t, 24H, $J = 6.3$ Hz); ^{13}C -NMR (CDCl_3): δ 168.4, 163.2, 155.7, 153.8, 152.8, 147.0, 132.8, 131.1, 128.8, 127.8, 126.5, 123.7, 122.9, 122.7, 120.1, 119.5, 119.2, 44.4, 44.3, 44.2, 39.4, 34.3, 31.6, 31.4, 29.6, and 12.5. MALDI-TOF-MS: m/z . Calcd.: $[\text{M} + \text{H}]^+ = 1621.7635$, found: 1621.7639.

2.6. Compound **5**

Compound **5** was prepared according the same method of compound **4**. A oxblood red solid **5** was got 1.1 g, yield: 84%. m.p. $= 292\text{--}294\text{ }^\circ\text{C}$. FT-IR (KBr, cm^{-1}): 3423 (ν_{NH}), 2969–2863 (ν_{CH}), 1695 ($\nu^{\text{as}}_{\text{N-C=O}}$), 1616 ($\nu^{\text{s}}_{\text{N-C=O}}$), 1592 ($\nu_{\text{N-C=O}}$). ^1H NMR (300 MHz): δ 8.45 (m, 8H, $J = 8.1$ Hz), 7.94–7.85 (m, 2H), 7.45–7.36 (m, 4H), 7.02 (dd, 2H, $J = 5.1$, 4.2 Hz), 6.5 (d, 4H, $J = 8.7$ Hz), 6.31 (d, 4H, $J = 2.1$ Hz), 6.03 (dd, 4H, $J = 8.7$, 1.8 Hz), 4.25 (t, 4H, $J = 3.2$ Hz), 3.57 (t, 4H, $J = 3.2$ Hz), 3.12 (m, 16H), 1.04 (t, 24H, $J = 6.9$ Hz);

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