



Pyrophosphate-triggered nanoaggregates with aggregation-induced emission



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ABSTRACT

A novel tetraphenylethene-based probe bearing bis-imidazolium anion donors is herein reported for pyrophosphate anion recognition. This probe can self-assemble finite, small sphere nanoaggregates with very weak emission in aqueous solution, and changes into large rod-like nanoaggregates with strong aggregation-induced emission upon binding with the pyrophosphate anion.

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1. Introduction

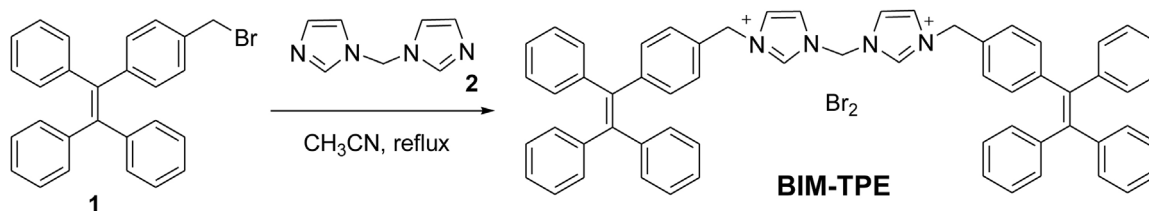
Fluorescent organic nanoparticles prepared by a self-assembly method have attracted much attention for their unique advantages, including low-cost, good photostability, good biocompatibility, and low cytotoxicity [1–4]. Recently, research has revealed that the fluorescent organic nanoparticles are good materials for detecting important analytes in environmental and biological systems [5–7]. Driven by weak intermolecular interactions such as electrostatic attraction, hydrogen bonds, π - π stacking, and hydrophobic interactions, the organic building blocks can self-assemble vesicle, fiber, worm, and sphere-shaped nanoaggregates. Compared with small molecular probes, nanoaggregates show more sensitivity to external stimuli and better biocompatibility. In addition, some impressive nanomaterials for detecting metal ions, anions, and biomolecules have been reported [8–13]. However, the detrimental aggregation-caused quenching (ACQ) issue often results in organic nanoparticles having weak fluorescence and/or poor photochemical stability.

Recently, research of aggregation-induced emission (AIE) fluorogens, first reported by Tang's group, has provided a new avenue for the preparation of fluorescent organic nanoparticles [14,15]. AIE fluorogens show very weak or no emission in the molecularly dissolved state, but give a strong emission in the aggregation state due to the restriction of intramolecular motions (RIMs). Therefore, different kinds of AIE fluorophores, including tetraphenylethene, siloles, arylbenzene, and arylethene, have been designed and used as fluorescent probes for the detection of various species [16–21]. In most cases, a fluorescence “switch on” response was observed for the analytes triggering self-aggregation. However, these probes often work in organic-water mixtures with strong emission background, which is not favorable for designing a useful “turn-on” fluorescence sensor. As one of the most important biological anions, pyrophosphate anion (PPi) plays a crucial role in several bioenergetic and metabolic processes [22–27]. However, high concentration of PPi in waterways can lead to eutrophication, a serious environmental problem. Thus, the development of PPi chemosensors with high sensitivity and selective functions is greatly desired. Today, fluorescence sensors of PPi with different anion-binding sites, such as neutral NH donors (urea, thiourea, amide, pyrrole), cationic (CH)⁺ (imidazolium and triazolium) and metal-ion-binding sites, have been established [28–30]. Owing to the high solvation energy ($\Delta G^\circ = -465 \text{ kJ mol}^{-1}$) of PPi in water, the bulk of the studies on PPi detection in aqueous and physiological conditions are confined to the metal complexes due to the strong interaction of PPi

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Scheme 1. the synthesis route of target compound **BIM-TPE**.

with metal ions [31–33]. Notably, organic receptors for PPI recognition in aqueous solution are rare [34–37].

Herein, we report a novel bis-imidazolium (BIM)-functionalized TPE (**BIM-TPE**, [Scheme 1](#)) for PPI recognition. In this system, two chelate imidazoliums were selected as the anion donors for their specific $(\text{CH})^+ \cdots$ anion interaction and good binding ability toward phosphate anions [38,39], while the typical AIE fluorogen tetraphenylethene was used as the signal unit. We found that this probe shows exclusive “turn-on” sensing of PPI over other anions in pure aqueous solution by changing its aggregation state, i.e., the free **BIM-TPE** can form finite, sphere-shaped nanoaggregation in pure aqueous solution with very weak emission, but changes into large, rode-like nanoaggregates with large enhancement upon binding with the PPI anion. The proposed binding mode between **BIM-TPE** and PPI was investigated in detail by using emission spectra, ^1H NMR titration, dynamic light scattering (DLS), and transmission electron microscopy (TEM) techniques.

2. Experimental section

2.1. General methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Most of chemicals were purchased from Aladdin, Aldrich and J&K. Solvents were purified by normal procedures and handled under moisture free atmosphere. The precursors 1-[(4-bromomethyl)phenyl]-1,2,2-triphenylethene (**1**) and di(1*H*-imidazol-1-yl)methane (**2**) were prepared by the literature methods [40,41]. NMR spectra were recorded by NMR spectra were recorded using a Varian instrument (400 MHz) with TMS as internal standard. MS spectra were recorded on MALDI-TOF MS Performance (Shimadzu, Japan) UV–vis spectra were recorded on an S-3100 spectrophotometer. Fluorescence spectra measurements were performed on a Hitachi F-4500 FL spectrophotometer (Hitachi Hi-Tech, Tokyo, Japan) Dynamic light scattering (DLS) measurements were performed on the Nano-ZS90 Light Scattering System (Malvern, England).

2.2. Synthesis of **BIM-TPE**

A solution of 1-[(4-bromomethyl)phenyl]-1,2,2-triphenylethene **1** (215.4 mg, 0.50 mmol) and di(1*H*-imidazol-1-yl)methane **2** (25 mg, 0.17 mmol) in 30 mL acetonitrile was heated at 90 °C for 48 h under nitrogen. After cooling to the room temperature, the precipitate was filtered and washed with petroleum ether for 3 times. Desired product compound **BIM-TPE** was obtained as a white solid (90.0 mg, 0.09 mmol) in 53% yield. ^1H NMR (DMSO- d_6 , 400 MHz): δ 9.54 (s, 2H), 8.00–7.94 (m, 2H), 7.78 (s, 2H), 7.10 (s, 22H), 7.02–6.97 (m, 4H), 6.97–6.88 (m, 12H), 6.62 (s, 2H), 5.38 (s, 4H). ^{13}C NMR (DMSO, 100 MHz) δ 144.07, 143.32, 143.30, 141.61, 140.18, 138.30, 132.74, 131.52, 131.00, 130.95, 128.35, 128.26, 128.18, 127.18, 127.09, 123.55, 123.07, 52.26. ESI-TOF-MS: 919.3174 ($\text{M}-\text{Br}^-+\text{H}^+$), 837.3932 ($\text{M}-2\text{Br}^-$).

3. Results and discussion

The synthesis route of the **BIM-TPE** probe has been depicted in [Scheme 1](#). Firstly, the two precursors, 1-[(4-bromomethyl)phenyl]-1,2,2-triphenylethene and di(1*H*-imidazol-1-yl)methane, were prepared according to the methods available in the literature. The precursors were then reacted in reflux acetonitrile solution to obtain **BIM-TPE** in 53% yield. The structure of **BIM-TPE** was fully confirmed by the ^1H NMR, ^{13}C NMR, and ESI-MS spectroscopic techniques.

The emission of **BIM-TPE** in THF/water mixtures, with different water fractions, and in the solid state was first investigated ([Fig. 1a](#)). This is a commonly used method for detecting the evidence of AIE. Normally, TPE-based fluorophores are nonfluorescent or weakly fluorescent in organic solvent due to their high solubility, and show strong emission with the increasing water percentage of the medium due to the lowering of the solubility. However, in the present case, the **BIM-TPE** probe showed very weak emission even in 100% aqueous solution, which may be attributed to the good solubility of the imidazolium salts in water, thus resulting in a poor aggregation in the checking condition. The critical AIE concentration value of **BIM-TPE** in an aqueous solution is determined to be 60 μM by the concentration-dependent fluorescence spectra method ([Fig. 1b](#)), which is larger than the checking concentration (10 μM). In contrast, the solid of the **BIM-TPE** showed typical strong green emission at the maximal wavelength of 465 nm for the restriction of intramolecular rotations (RIR) process of the surrounded phenyl group.

The recognition ability of **BIM-TPE** toward various anions (PPI , H_2PO_4^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , ClO_4^- , HCO_3^- , NO_2^- , HSO_3^- , F^- , Cl^- , Br^- , and I^-) was then investigated by emission spectra in pure aqueous solution ([Fig. 2](#)). A strong blue emission of **BIM-TPE** at 465 nm was observed upon the addition of PPI, with the intensity increasing by 46 fold when compared with that of the free probe **BIM-TPE**. In contrast, the addition of other anions leads to minimal fluorescence changes in the **BIM-TPE**. This result indicates that **BIM-TPE** can be used as a turn-on fluorescent sensor for PPI.

[Fig. 3](#) shows the fluorescence changes of **BIM-TPE** upon addition of various amounts of PPI. The fluorescence intensity of **BIM-TPE** was increased by the incremental addition of PPI, with saturation occurring at around 10 μM . The plot of fluorescence intensity against the equivalence of PPI reveals a 1:1 stoichiometric complexation between **BIM-TPE** and PPI, which can also be confirmed by the Job-plot ([Fig. S1](#)). On the basis of the emission titration data, the binding constant between **BIM-TPE** and PPI was calculated to be $7.14 \times 10^4 \text{ M}^{-1}$ by Benesi-Hildebrand method. Most importantly, the fluorescence intensity of **BIM-TPE** is linearly dependent on the concentration of PPI in the range 0–10 μM ($R^2 = 0.9912$, [Fig. S2](#)), showing a very low detection limit of 16 nM (based on $3\delta/k$). This indicates that the **BIM-TPE** probe has sufficient sensitivity to detect PPI in aqueous solution.

The conspicuous fluorescence increase of **BIM-TPE** with PPI can be attributed to the ionic hydrogen bonding interactions between the cationic imidazolium $(\text{C}-\text{H})^+$ donors and phosphate anion, which leads to increased aggregation of the receptor. To confirm

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