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ARTICLE TYPE

Tetraphenylethylene Imidazolium Macrocycle: Synthesis and Selective Fluorescence Turn-On Sensing of Pyrophosphate Anion

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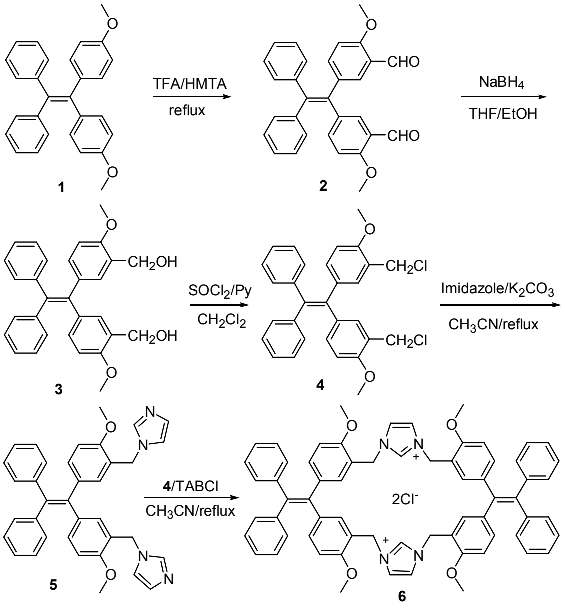
A new imidazolium macrocycle based on tetraphenylethylene (TPE) was synthesized. This positive macrocycle showed a typical aggregation-induced emission (AIE) effect but could not be induced fluorescence emission by common inorganic anions in aqueous solution, including pyrophosphate bearing four negative charges. However, in the presence of half equivalent of zinc (II) ions, the addition of pyrophosphate anion could arouse a strong fluorescence while other common inorganic anions gave almost no response. The macrocycle had an inherent cavity with a proper size for binding pyrophosphate anion, so that pyrophosphate anion easily aggregated together with the macrocycle and zinc cation, which selectively triggered a turn-on fluorescence.

Introduction

Anions are important chemical species that have great impact on life and environment. Among a large variety of anions, phosphate anions especially attract interest due to their important role in life. For example, Arthritis and Mönckeberg's arteriosclerosis are related to the abnormal level of phosphate and pyrophosphate anions in blood serum.[1] In addition, the signal and energy transduction also require the participation of phosphate anions.[2] Various techniques, such as colorimetric,[3] electro-chemiluminence,[4] have been employed to detect the phosphate anions. Fluorometric method, due to its high sensitivity, low cost and easy operation, has a greater potential in analysis of compounds including anions. During the past decades, many fluorescence receptors for the sensing of phosphate anions have been developed.[5] However, the fluorescence probe with high selectivity for the pyrophosphate anions is still scarce.

In 2001, Tang's group reported a new class of organic compounds with an amazing fluorescence property, that is, they had no emission in solution but emitted strong fluorescence in aggregation state or solid.[6] This novel fluorescence phenomenon was coined as aggregation-induced emission (AIE) and a probable mechanism of restriction of intramolecular rotation (RIR) for the fluorescence was suggested. Since then, the AIE fluorophores have attracted great deal of attention due to the potential application in bio/chemosensors and solid emitter.[7] Especially, due to the significant fluorescence change between aggregation and deaggregation, the AIE compounds were received more researches as bio/chemosensors.[7,8] However, the research work for the sensing of phosphate anions by AIE effect,[9] especially for selective sensing of the anions in aqueous solution,[10] is very rare. The reason behind this might be the solvent competing effect in highly polar solvent.[11] Herein, we report the synthesis of imidazolium macrocycle based on tetraphenylethylene (TPE). The macrocycle could selectively detect pyrophosphate anion in aqueous solution in the presence of zinc (II) ion.



Scheme 1 The synthesis of tetraphenylethylene macrocycle **6**.

Result and discussion

As shown in scheme 1, the TPE derivative **1**, a known AIE compound,[12] was used as starting material and was easily transferred into dialdehyde **2** by Duff reaction. With dialdehyde **2** in hand, dialcohol **3** and dichloride **4** were obtained by a reduction with NaBH$_4$ followed by chlorinating reaction with thionyl chloride. Upon a nucleophilic substitution with imidazole, dichloride **4** was converted into diimidazole **5**. Finally, the target product imidazolium macrocycle **6** containing TPE units was obtained in 24% yield by the reaction of dichloride **4** and diimidazole **5** in the presence of tetrabutylammonium chloride template.[13]

Fortunately, the single crystal of compound **6** was obtained by slow evaporation of its solution in THF/H$_2$O. The crystal structure is a monoclinic one with C2 space group symmetry and the cell parameters of a = 33.698, b = 8.9588, c = 10.793 Å and α = γ = 90°, β = 107.81°.[14] The distance between two opposite nitrogen atom of **6** is 5.836 Å as showed in Fig. 1. The macrocycle forms a rectangle cavity approximately with 8.294 × 5.836 Å^2 size (Fig. 1A). As an interesting packing mode, the cavities can stack each other to form a channel which is filled with solvents and counter ions. The channels arrange in parallel to give the 3-dimmentional newworks (Fig. 1B).

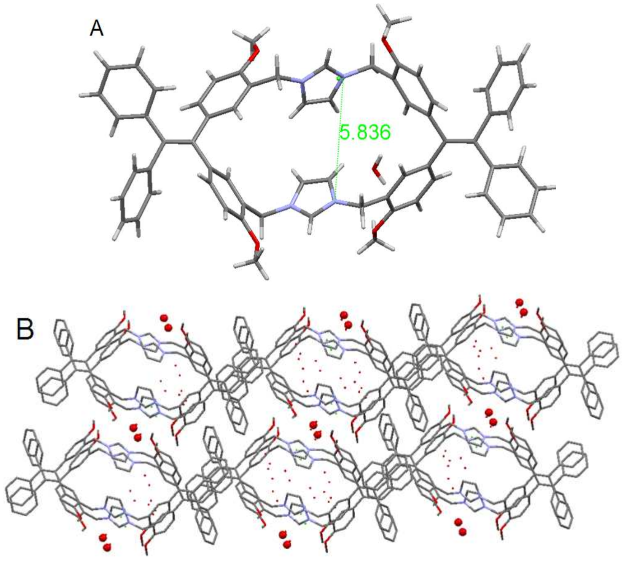


Fig. 1 (A) The crystal structure of **6**. (B) The crystal packing pattern of **6**, hydrogen atoms were hidden for clarity.

The imidazolium macrocycle **6** was soluble in highly polar solvents such as acetonitrile and methanol but was not dissolved in less polar solvents, such as hexane. Hence, its AIE effect could be observed in the mixed solvent of THF and hexane (Fig. S1). The solution of **6** in THF (containing 0.5% acetonitrile) was not light emitting, but it appeared fluorescence at 472 nm after 50% hexane (volume percentage, the same below) was added and a cloudy started to be observed. After that, the fluorescence became stronger with the continued addition of hexane.

Similarly, the aqueous solution of **6** (5.0 × 10^{-5} M) in water containing 0.5% DMSO exhibited almost no emission. By addition of various anions, such as pyrophosphate $P_2O_7^{4-}$ (PPi), PO_4^{3-} (Pi), HPO_4^{2-} (HPi), $H_2PO_4^-$ (H$_2$Pi), SO_4^{2-}, SO_3^{2-}, NO_3^-, NO_2^-, HCO_3^-, CO_3^{2-}, $C_2O_4^{2-}$, F$^-$, Cl$^-$, Br$^-$ and I$^-$ (counter ion, Na$^+$), no obvious enhancement of the emission could be observed. However, upon addition of one equivalent of Zn(OAc)$_2$ before or after the addition of anions, the pyrophosphate anion gave rise to a strong blue emission while other anions resulted in almost no emission under 365 nm lamp light (Fig. 2). This clearly indicated that **6** could be used as selective turn-on sensor for pyrophosphate anion in the presence of Zn (II). It was found that other some divalent transition metal ions, such as Cu (II), Ni (II), Pb (II), Co (II), and Cd (II), also changed the emission intensity but the effect was much less than that of Zn (II) (Fig. S2). The titration of **6** (5×10^{-5} M) with Zn (II) in the presence of two equivalents of PPi showed that the fluorescence intensity had a maximum after addition of 0.5 equivalent of Zn (II) (Fig. S3), which was 25 times larger than that without Zn (II).

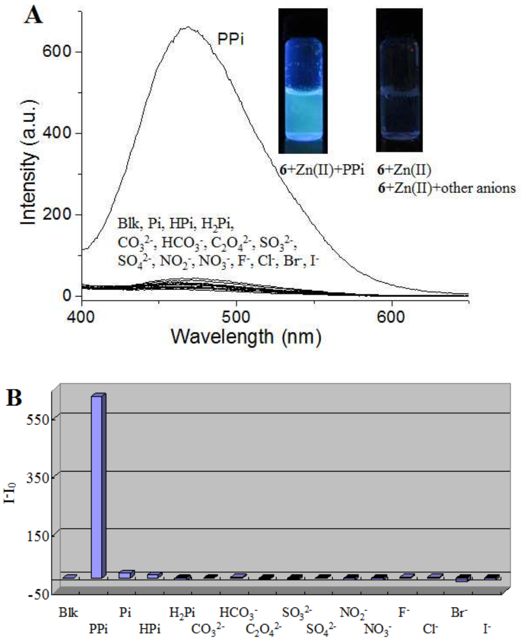


Fig. 2 (A) The fluorescence spectra of **6** in water containing 0.5% DMSO with addition of different anions in the presence of zinc (II). Insets, photos of the solutions under 365 nm lamp light; λ_{ex} = 347 nm, ex/em slits = 5/5 nm. (B) Diagram of the emission at 472 nm of **6** in the presence of zinc(II) and different anions. [**6**] = 2[Zn(OAc)$_2$] = 1/2[anion] = 5.0 × 10^{-5} M.

Moreover, even in the presence of a mixture of other anions with each anion one equivalent to **6**, PPi anions aroused a strong fluorescence while the mixture of the other anions without PPi only gave rise to a very weak fluorescence (Fig. 3). The intensity difference between the mixtures of anions with and without PPi was more than 10 times. In addition, the fluorescence aroused by PPi in the presence of other anions was almost same as that in the absence of the other anions. This result demonstrated that other anions did not interfere with the detection of PPi by this fluorescence receptor.

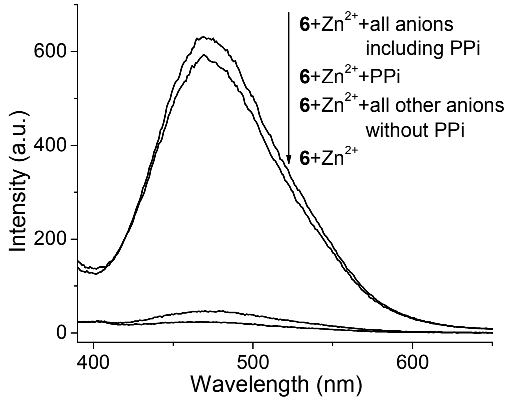


Fig. 3. The fluorescence spectra of **6** in water containing 0.5% DMSO with addition of anion mixture in the presence of zinc (II). λ_{ex} = 354 nm, ex/em slit width = 5/5 nm, [**6**] = [each other anion] = 1/2[PPi] = 2[Zn(II)] = 5 × 10^{-5} M.

Fluorescent titration of **6** (5×10^{-5} M) with pyrophosphate anion in the presence of Zn (II) (2.5×10^{-5} M) in H$_2$O containing 0.5%

DMSO was also tested (Fig. 4). When small amount of pyrophosphate anions was added, the enhancement of fluorescence was not significant. This might result from the solubility of the complex formed upon addition of pyrophosphate anion. In the range of 0.6–2.0 equivalents of pyrophosphate anions, the fluorescence intensity rapidly increased with the added anions. After that, the increase of the fluorescence intensity became slow and finally stopped until 2.4 equivalents of pyrophosphate anions were added.

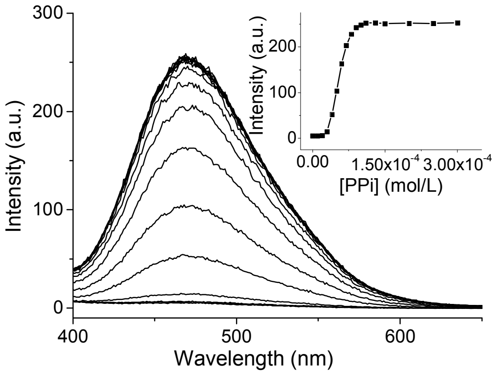


Fig. 4 The fluorescence change of **6** with PPi in the presence of zinc (II) in water containing 0.5% DMSO. Inset, curve of the intensity at 472 nm vs. the concentration of PPi. λ_{ex} = 347 nm, ex/em slits = 5/5 nm. [**6**] = 2[Zn(OAc)$_2$] = 5.0 × 10^{-5} M.

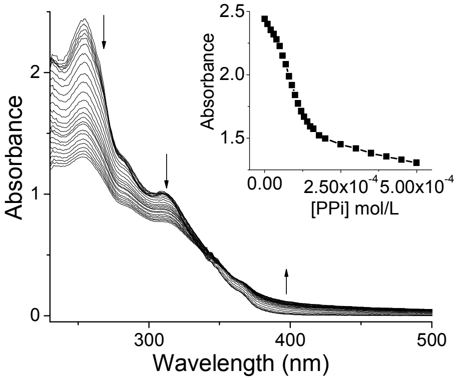


Fig. 5 Change of the absorption spectra of **6** in water containing 0.5% DMSO with PPi. Inset, curve of the absorbance at 253 nm vs. the concentration of PPi. [**6**] = 5.0 × 10^{-5} M.

The UV-Vis titration confirmed the interaction between **6** and pyrophosphate anion (Fig. 5). With addition of pyrophosphate anion, the absorption peaks both at 253 nm and 313 nm were decreased while a new absorption band at about 400 nm increased. Moreover, the absorption at 313 nm had a small bathochromic shift toward 320 nm with the anion. This obvious change demonstrated the formation of stable complex between **6** and pyrophosphate anion even without zinc (II). The association constant of the complex, according to a 1:1 molar ratio of the complex between **6** and pyrophosphate, was calculated to be (1.41 ± 0.10) × 10^4 M^{-1} by nonlinearly curve fitting of absorbance at 253 nm vs. concentration of pyrophosphate (Fig. S4).[15] In the presence of Zn (II), the UV-Vis titration of **6** with PPi was very similar to that of without Zn (II) (Fig. S5), indicating that the metal ions did not directly interact with the macrocycle but only with the anion ions.

From the above absorption spectra, it was known that the mixing of **6** and PPi easily aroused the formation of **6**-PPi complex probably because the two negative charges at the two ends of one pyrophosphate anion (one end one phosphate unit) had a so proper distance that could just bind the two positive charge on the molecule of **6** (Fig. 6). As discussed early in the crystal structure of **6**, the distance between nitrogen atoms at each imidazolium unit of **6** is about 5.836 Å while the longest distance between oxygen atoms at each phosphate unit of PPi is 5.36 Å. Therefore, the cavity of **6** composed of two imidazolium units is suitable for inclusion of one molecule of PPi to form **6**-PPi complex after driving by an electrostatic attraction (Fig. 6). The new absorption peak at about 400 nm of **6** upon addition of PPi demonstrated that PPi had a so strong interaction with **6** that the acidic proton on the imidazolium unit was probably removed by pyrophosphate anion. In the presence of zinc cation, the two-component **6**-PPi complex was transferred into a five-component (**6**-PPi)$_4$-Zn complex due to one zinc cation that was coordinated by two **6**-PPi complexes. With continued coordination, aggregate of (**6**-PPi)$_4$-Zn complexes formed, therefore, it gave a strong fluorescence.

In addition, both the emission spectrum and the excitation one of suspension of **6** in THF/hexane 10:90 were similar with that of **6**-PPi-Zn mixture in aqueous solution, hinting the complex of **6**-PPi-Zn existed in aggregation state (Fig. S6). The dynamic light scattering (DLS) diagram corroborated that the mixture of **6**, PPi and Zn (II) in water formed aggregates with an average diameter up to 2800 nm (Fig. S7). Due to being soluble in water, **6**-PPi complex was no light emitting, but the five component (**6**-PPi)$_4$-Zn complex had a low solubility so that it could emitted a strong fluorescence (Fig. 6). The formation of **6**-PPi complex with 1:1 molar ratio was confirmed by the ESI$^+$ HRMS spectrum of the mixture of **6** and sodium pyrophosphate (Calcd for $C_{66}H_{58}N_4Na_3O_{11}P_2$ 1213.3270 [**6**-PPi + 3Na$^+$]$^+$, found 1213.3265 [**6**-PPi + 3Na$^+$]$^+$) (Fig. S8).

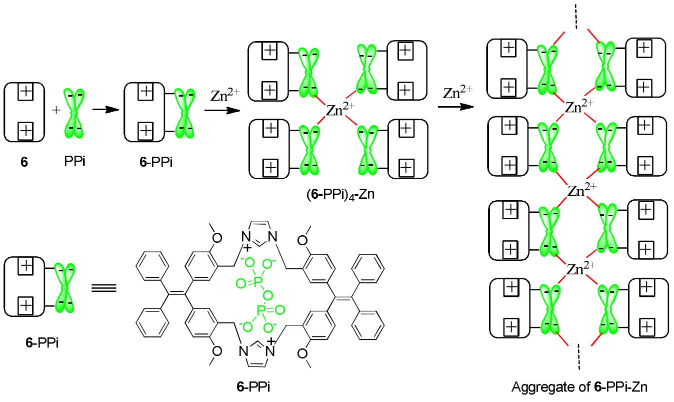


Fig. 6 The AIE mechanism of **6** aroused by PPi in the presence of Zn (II).

Conclusions

In conclusion, a novel imidazolium macrocycle based on tetraphenylethylene (TPE) was synthesized. It was found that this macrocycle had an inherent cavity with a proper size for binding pyrophosphate anion. Without addition of zinc cation, the **6**-PPi complex was soluble and could not emit light. In the presence of zinc cation, **6**-PPi complex could form aggregates because of coordination to zinc, which resulted in strong fluorescence. Therefore, this macrocycle could act as selective probe for pyrophosphate anion in aqueous solution. By selective inclusion of an analyte into the cavity of macrocycle bearing TPE units which could lead to a turn-on fluorescence provides a new approach to the design of selective fluorescence probs.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis of compounds and additional spectrum, ^{1}H NMR, ^{13}C NMR, IR, HRMS spectra of compounds **2** – **6**. See DOI: 10.1039/b000000x/

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Table of contents entry

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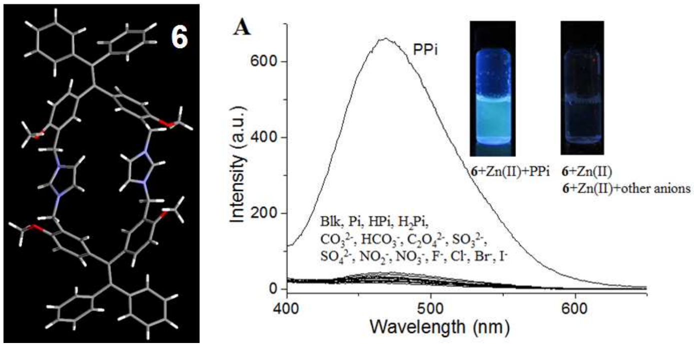

A novel tetraphenylethylene imidazolium macrocycle was found to be able to form aggregate with pyrophosphate anion in water which given the characteristic aggregation-induced emission fluorescence.