



# Thienyl diketopyrrolopyrrole as a robust sensing platform for multiple ions and its application in molecular logic system



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## ABSTRACT

3,6-Di(2-Thienyl)-2,5-dihydropyrrolo-[3,4-c]-pyrrole-1,4-dione (TDPP), a simple but versatile and stable dye, can effectively recognize four human health-related ions ( $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{F}^-$ ). TDPP-based elementary logic gates (OR, XOR, and INHIBIT) and a half-subtractor were fabricated. Results demonstrated that TDPP is a potential building block in designing novel and robust chemo/biosensors and molecular logic systems.

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## 1. Introduction

Insight into molecular logic gates by de Silva [1] has caused chemical and biological molecules with optical responses to multiple stimuli to gain extensive attention [2–4]. These molecular entities, upon chemical, photonic, or other stimuli, have been successfully used to imitate the function of logic operation, offering potential alternatives in information processing [5–10]. To date, studies on certain traditional dyes, such as rhodamine [11–13] and boron-dipyrromethene [14,15], have made important advances in fabricating optical logic systems. However, challenges still exist in building a simpler and more practical molecular logic system because the common strategy in molecular platform construction, which is the optimal combination of different functional groups, is accompanied with a bulky molecular structure that features low photo/thermostability and high cost. A better logical system is necessary to find a smart dye with a simple, stable structure and the ability to distinguish multiple stimuli.

Diketopyrrolopyrroles (DPPs), a class of commercially available and multifunctional pigments, exhibit exceptional

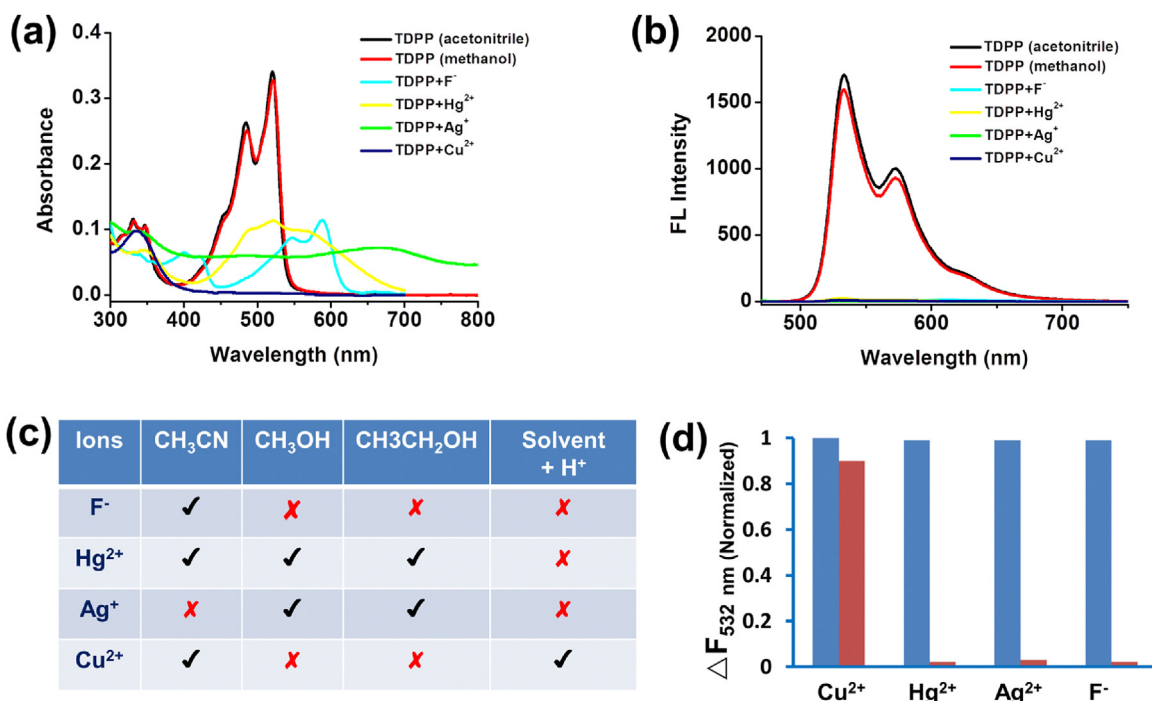
photo/thermostability and desirable spectroscopic properties [16–18]. To date, DPP pigments have been used successfully in many applications [19,20], including car paint pigments, transistors, and photovoltaic cells. However, reports on its utilization in sensing for chemical stimuli (e.g., ions) are rare [21,22]. DPP derivatives with the lactam-NH moiety are potential receptors for multiple transition metal ions [23]. DPPs with excellent photostability and strong fluorescence have recently shown great potential in bioconjugation [17]. Therefore, studies on these special compounds may benefit the design of novel, stable chemo/biosensors and logic systems. In this paper, we present a smart molecule, 3,6-di(2-Thienyl)-2,5-dihydropyrrolo-[3,4-c]-pyrrole-1,4-dione (TDPP), which shows active responses to four human health-related ions ( $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{F}^-$ ).

## 2. Results and discussion

DPPs with the lactam-NH moiety show fast and sensitive responses to fluoride [22,24,25]. As shown in Figs. 1 and S1, TDPP exhibited a bright fluorescence at 532 nm and characteristic UV–vis absorption with a shoulder peak at 485/520 nm. In the presence of fluoride, the fluorescence emission at 532 nm was eliminated because of lactam deprotonation. Simultaneously, the characteristic absorption signal of TDPP disappeared and new peaks at 546 and 587 nm emerged. TDPP could recognize fluoride in acetoni-

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**Fig. 1.** Changes in (a) absorption and (b) fluorescence ( $\lambda_{\text{ex}} = 450$ ) spectra of TDPP (10  $\mu\text{M}$ ) in the presence of Hg<sup>2+</sup> (20  $\mu\text{M}$ ), Cu<sup>2+</sup> (20  $\mu\text{M}$ ), Ag<sup>+</sup> (100  $\mu\text{M}$ ), and F<sup>-</sup> (60  $\mu\text{M}$ ). (c) The effects of solvent and acid to TDPP response. All solvents contain 1% *N,N*-dimethylformamide. ✓ indicates obvious changes in absorption (485 nm) and fluorescence (532 nm) intensity. (d) Changes in the fluorescence intensity of TDPP (10  $\mu\text{M}$ ) in solution with (brownish yellow) and without (blue) addition of H<sup>+</sup>. Cu<sup>2+</sup> was added in CH<sub>3</sub>CN and others were added in CH<sub>3</sub>OH. After the addition of H<sup>+</sup> (0 or 1 mM), metal ions were tested. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

trile but appeared “blind” in methanol or ethanol, indicating the pronounced effect of protic solvent to fluoride (Fig. S2a). Thus, acid water could be used to suppress fluoride efficiently in TDPP solution (Fig. S2b).

Since Lorenz et al. [23,26] observed complexation between phenyl DPP and transition metal complexes, metal ions may be detected using TDPP. Subsequently, the responses of TDPP (10  $\mu\text{M}$ ) to common metal ions (Hg<sup>2+</sup>, Ag<sup>+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>) were examined using ethanol, methanol, and acetonitrile. Only Hg<sup>2+</sup> and Cu<sup>2+</sup> (2 equiv.) caused remarkable changes in acetonitrile, whereas others (10 equiv.) resulted in negligible changes (Fig. S3). Both ions quenched the fluorescence of TDPP effectively but differed in absorption. Specifically, Hg<sup>2+</sup> decreased the absorption at 485/520 nm and induced a new band at 565 nm, whereas Cu<sup>2+</sup> only made the shoulder peaks at 485/520 nm completely disappear (Figs. 1 and S4). These findings indicated that TDPP could distinguish Hg<sup>2+</sup> and Cu<sup>2+</sup> from other tested metal ions in acetonitrile. TDPP could recognize Hg<sup>2+</sup> in all the test solvents, but respond to Cu<sup>2+</sup> only in acetonitrile (Fig. S3). Another transition metal ion, Ag<sup>+</sup>, showed similar behavior to Hg<sup>2+</sup> in TDPP solution (Figs. 1 and S4). However, TDPP appeared “apathetic” to Ag<sup>+</sup> in acetonitrile (Fig. S3), indicating that TDPP could be used to distinguish Hg<sup>2+</sup>, Ag<sup>+</sup>, Cu<sup>2+</sup>, and F<sup>-</sup> effectively by choosing a suitable solvent. Additionally, the effect of pre-addition of H<sup>+</sup> strongly contributed to the response of TDPP to Hg<sup>2+</sup>, Ag<sup>+</sup>, and F<sup>-</sup> but only slightly contributed to TDPP-Cu reaction (Fig. 1). Notably, TDPP showed a fast response to all the ions, displaying distinct optical changes within 1 min (Fig. S5). Therefore, TDPP is a novel and efficient receptor for distinguishing Hg<sup>2+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, and F<sup>-</sup> by varying the medium in detection.

The model of TDPP-based complexation was investigated. The FT-IR data (Fig. S6) indicated the direct involvement of lactam. Further information on the involved binding model was difficult to obtain because of the poor solubility of TDPP and TDPP-Hg/Ag com-

plex. Therefore, disubstituted TDPP, which can inhibit N-involved coordinate bond, was prepared. Disubstituted TDPP was unreactive to Hg<sup>2+</sup> but active to Cu<sup>2+</sup> in acetonitrile (Fig. S7), demonstrating the direct participation of the N-H moiety in TDPP-Hg/Ag complexation. In addition, both Hg<sup>2+</sup> and Ag<sup>+</sup> caused negligible changes in the absorption spectrum of phenyl DPP, which indicated the involvement of S atom in the complexation (Fig. S8). Given that DPP can bind to Cu<sup>2+</sup> with S and O atoms [27], we proposed the possible model of molecular reaction shown in Scheme 1. This proposed model conforms to the acid-sensitive sensing of TDPP to Hg<sup>2+</sup> or Ag<sup>+</sup>, because the N-H moiety that is easily protonated in acid medium may lose the ability to capture Hg<sup>2+</sup> or Ag<sup>+</sup>.

To explain the effects of complexation in the emission and absorption of TDPP, subsequent analysis was conducted. In TDPP-Cu, the changes in spectral properties of TDPP solution were possibly attributed to the paramagnetic nature of Cu<sup>2+</sup> [28,29]. However, the changes caused by Hg<sup>2+</sup> or Ag<sup>+</sup> were relatively complicated. Only Hg<sup>2+</sup> or Ag<sup>+</sup> could induce molecular aggregation, which, at some stage, produced nanoparticles (Fig. 2). Hg<sup>2+</sup>- or Ag<sup>+</sup>-triggered absorption bands were eliminated by simple filtration, which demonstrated the participation of molecular aggregation in sensing. Fluorophores (e.g., pyrene derivatives) with plane rigid structures have a high tendency for aggregation in some conditions and undergo optical changes (e.g., fluorescence quenching) because of  $\pi$ - $\pi$  intermolecular stacking [30]. TDPP, which possesses a nearly planar construction, may form a more rigid planar structure by the TDPP-Hg-TDPP (or TDPP-Ag-TDPP) reaction. This rigid system will induce molecular aggregation, which can lead to the particles. The DLS data described clearly the increase in size of Hg<sup>2+</sup>-/Ag<sup>+</sup>-triggered nanoparticles in the titration experiment (Fig. S9). The X-ray photoelectron spectroscopy data of both nanoparticles directly demonstrated the TDPP-Hg and TDPP-Ag complexation (Fig. S10). Interestingly, these nanoparticles were easily eliminated upon the addition of cysteine or S<sup>2-</sup> (Fig. S11), which could effectively break

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