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# An effective fluorescent optical sensor: Thiazolo-thiazole based dye exhibiting anion/cation sensitivities and acidochromism

Zeynep Dikmen<sup>a</sup>, Onur Turhan<sup>b</sup>, Müjgan Yaman<sup>c</sup>, Vural Bütün<sup>c,\*</sup>

<sup>a</sup> Faculty of Engineering, Department of Biomedical Engineering, Eskisehir Osmangazi University, 26040 Eskisehir, Turkey
 <sup>b</sup> Institute of Science, Polymer Science and Technology Department, Eskisehir Osmangazi University, 26040 Eskisehir, Turkey

<sup>c</sup> Faculty of Science and Letters, Department of Chemistry, Eskischir Osmangazi University, 26040 Eskischir, Turkey

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#### ABSTRACT

Fluorescent 2,5-bis(4-hydroxyphenyl)thiazolo[5,4-d]thiazole (**HPhTT**) sensor molecule consisting of thiazolothiazole (**TTz**) binding central unit and phenolic signalling side groups was synthesized with a symmetric structure. The selectivity, sensitivity and reversibility properties of optical sensor towards cations and anions were investigated. **TTz** unit of the sensor was responsible from cation and proton interactions resulting with fluorescent quenching, while phenolic–OH groups were sensitive to anions with a deprotonation mechanism. The fluorescence quenching in the presence of Au<sup>3+</sup> with high selectivity, sensitivity and fast response, making it clear that the sensor was very effective in detecting Au<sup>3+</sup>. Fluorescent sensor (**HPhTT**) was also found to be able to recognize AcO<sup>-</sup>, F<sup>-</sup> and CN<sup>-</sup> anions accompanied by obvious UV–vis absorption change and fluorescence switch-on response, and exhibited enhanced intramolecular charge transfer (ICT) strongly depending on the forming conjugated acid after addition of anions. Ratiometric detection and reversible usage of the sensor for AcO<sup>-</sup>, F<sup>-</sup> and CN<sup>-</sup> anions were also possible. The sensor showed remarkable detection ability in a pH > 9 media and it has also been demonstrated that it can be used successfully as a pH sensor in an aqueous media. A colour calculator study using F<sup>-</sup> anion to estimate colour change, colour purity and colour coordinates under UV light excitation with I<sub>550</sub>/I<sub>444</sub> ratio indicated that **HPhTT** dye had a promising potential for fluorescent sensor studies.

## 1. Introduction

Fluorescence spectroscopy has become one of the most popular and challenging analytical methods in the last two decades with the demonstration of its highly functional use in biological systems as enzyme substrates, biomolecular labels, environmental indicators and cellular stains [1], biochemistry, biomedical engineering, biophysics and optical sensors. Determination of an analyte by fluorescence enables high sensitivity and biochemical measurements without radioactive agents [2]. After the improvement of this highly convenient method in bioimaging systems, fluorescent sensor dyes exhibiting selective optical response towards the analyte have been one of the major interest in the literature. Selective detections of cations [3-13], anions [14-20], acids bases [21-23], solvents and more specific chemicals [24-29] by using fluorescent sensor dyes have major interest in the literature. These smart molecules can be creatively used in the determination of calcification in soft tissue [30], fluorescent sensors for detection of analyte in live cells [31–35], optical detection of nerve agent [36].

Small molecules and macromolecules containing thiazolo[5,4-*d*] thiazole (**TTz**) unit are promising structures for many applications such as solar cells [37–40], organic light emitting diodes [41], nonlinear optics [42], photocatalysis [43,44], fluorescent metal–organic frameworks [45], electrochromic devices [46], and even for biological applications [47]. These wide range applications result from superior photo luminescent, solvatochromic [48], electrochromic [49,50] properties of **TTz** unit which has remarkable photo-chemical stability [51–53]. Eventhough the superior properties, reports on usage of **TTz** containing molecules as fluorescent sensor is very limited in the literature [54–56].

Live cell imaging of Au<sup>3+</sup> ions may present novel information about the binding mechanism to the biological molecules, because Au<sup>3+</sup> ions can bound to proteins and DNA resulting with broken down and damage of the liver, kidney, and nervous system [57,58]. Eventhough there are lots of studies on Au<sup>3+</sup> sensing by using photoluminescent BODIPY and rhodamine based fluorescent sensors in the literature, any study has not been found on thiazolo[5,4-d]thiazole containing fluorescent sensor for

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<sup>\*</sup> Corresponding author at: Faculty of Science and Letters, Department of Chemistry, Eskisehir Osmangazi University, 26040 Eskisehir, Turkey. *E-mail address:* vbutun@ogu.edu.tr (V. Bütün).

## Au<sup>3+</sup> sensing.

Eventhough synthesis of HPhTT molecule has been reported before, there has not been found a view on the optical and fluorescent sensor properties of the fluorophore [59,60]. As first reported herein, HPhTT is a TTz containing small molecule that exhibits a multiple optical response. Due to HPhTT has many advantage such as one step synthesis, easy purification, high photo-chemical stability, determination of superior properties of the dye would bring new usage areas such as sensors, bioimaging etc. Here in, we report synthesis and usage of a dye as multi – responsive fluorescent sensor for the detection of both Au<sup>3+</sup> and Fe<sup>3+</sup> cations via fluorescent quenching and piperidine, AcO<sup>-</sup>, CN<sup>-</sup> and F<sup>-</sup> anions via emission wavelength shifts. This dye also exhibits acidochromic property. TTz unit of this molecule serve as ligand for metal cations and electron serving cite for protons while phenolic-OH groups act as anion and base sensitive part of the molecule. As a result of these multiple stimuli responsive parts of the HPhTT, the dye can be used for the detection of different kinds of analytes. Herein, for the first time, we report an optical view of the photoluminescent sensing properties of HPhTT dye to determine its possible usage areas.

#### 2. Experimental

#### 2.1. Materials and instrumentation

All chemical solvents, reagents, cationic salts and anionic salts were supplied commercially and used without any further purification. 4-Hydroxy benzaldehyde (98%), dithiooxamide (97%), trifluoroacetic acid (TFA, 99%), hydrochloric acid (HCl, 37%), H<sub>3</sub>BO<sub>3</sub> (99.5%), KOH (85%), pyridine (ACS Reag.), piperidine (99%), cyclohexanone (CHp, ACS Reag.) were purchased from Sigma-Aldrich. AgNO<sub>3</sub> (99.5%), AlCl<sub>3</sub> (99%), ZnCl<sub>2</sub> (99%), FeCl<sub>3</sub> (99%), SnCl<sub>2</sub> (98%), NiCl<sub>2</sub> (99.5%), CuCl<sub>2</sub> (99%), Hg(NO<sub>3</sub>)<sub>2</sub> (98.5%), CdCl<sub>2</sub> (99.9%), dimethyl formamid (DMF, 99.8%), acetonitrille (ACN, 99.8%) and tetrabutylammonium salts (TBAX): F<sup>-</sup> (75%, in H<sub>2</sub>O), Cl<sup>-</sup> (97%), I<sup>-</sup> (99%), AcO<sup>-</sup> (99%), CN<sup>-</sup> (95%), HSO<sub>4</sub> (97%), H<sub>2</sub>PO<sub>4</sub> (99%) were purchased from Sigma-Aldrich. KAuCl<sub>4</sub>.3H<sub>2</sub>O (98%) and TBABr (99%) were purchased from Acros Organics. MgCl<sub>2</sub> (99%), Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (98%), CoCl<sub>2</sub> (98%), HCl (37%) were purchased from Merck. Acetic acid (AcOH, 100%), KH<sub>2</sub>PO<sub>4</sub> (99%) was supplied from Reidel-de Haen. Dichloromethane (DCM, 99.9%), dimethylsulfoxide (DMSO, 99.9%) were supplied from Carlo Erba and tetrahydrofuran (THF, 99.9%) was from Honeywell. <sup>1</sup>H NMR spectrum was recorded with Jeol ECZ 500R spectrometer at 80 °C. UV-vis spectra were recorded on Perkin-Elmer Lambda 35. Photoluminescence (PL) spectra were recorded with Perkin-Elmer LS-55 spectrophotometer in the solid state by using a permeable filter due to high fluorescent intensities of samples.

# 2.2. Synthesis

**HPhTT** dye was synthesized according to the literature by modifications [60,61]. A solution prepared with 4-hydroxybenzaldehyde (120.0 mmol, 15.0 g) and dithiooxamide (41.6 mmol, 5.0 g) was refluxed in 10 mL pyridine for 5 h. The mixture was then cooled to room temperature and precipitated with ethanol. **HPhTT** compound was filtered and recrystallized in cyclohexanone as yellow needle like crystals (yield: 74%). **HPhTT** product was characterized with <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>: d = 10.16 ppm (–OH), 7.79–6.88 (8H-m, <sup>3</sup>J = 9.00 Hz) (Fig. S1).

## 2.3. Photophysical characterization and titrations of HPhTT

The photophysical properties of **HPhTT** solutions were determined via UV–vis and fluorescent spectroscopies in four different solvents (THF, DMF, DMSO, CHp) having different polarities. It is also worth to mention that the solvents to study were very limited because of solubility limitation of the **HPhTT**. Due to the better solubility in DMSO, DMF was used for all spectral analysis. First, 1  $\mu$ M HPhTT solution in DMSO was prepared as a fluorophore stock solution for further UV–vis titration studies and 0.1  $\mu$ M HPhTT stock solution was prepared for fluorescent studies.

An appropriate amount of corresponding cation and anion salts were dissolved in DMSO to prepare 10 mM stock solutions of the metal ions. A quartz cuvette of 10  $\mu$ M **HPhTT** solution was titrated by related metal stock solutions via addition of desired equivalent of cation solutions till a plateau is reached in the collected spectra. Anion and piperidine titration studies were carried out as the same method. All measurements were performed at room temperature.

## 2.4. Anion selectivity study

In order to determine the selectivity of different anions towards **HPhTT** dye in DMSO, UV–vis and fluorescence spectroscopic studies were carried out by using the tetrabutylammonium (TBA) salts of anions (TBAX where  $X = F^-$ ,  $Cl^-$ ,  $I^-$ , Br<sup>-</sup>, AcO<sup>-</sup>,  $CN^-$ , HSO<sup>-</sup><sub>4</sub> and H<sub>2</sub>PO<sup>-</sup><sub>4</sub>). Optical response to titration of the **HPhTT** with anion salt solutions was also examined by UV–vis absorption and fluorescent spectra in DMSO.

#### 2.5. Cation selectivity study

Cation selectivity of the **HPhTT** dye was determined by using metal salt solutions prepared in DMSO. UV–vis and fluorescence spectra were recorded to determine its selectivity on various cations. **HPhTT** dye was also titrated with the studied cations in DMSO by recording the optical response via UV–vis and fluorescence spectral analysis. Cations used for all of the measurements were obtained as chloride or nitrate salts (Au<sup>3+</sup>, Ag<sup>+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, Mg<sup>2+</sup>, Sn<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Hg<sup>+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup>) and their solvents were prepared in DMSO.

#### 2.6. Acidochromic property of the HPhTT

UV–vis and fluorescence spectra of **HPhTT** solutions in different pH buffer and acid-base solutions (pH = 1, 3, 5, 7, 9, 11, 12, 13) were recorded to show the acidochromic behaviour. Buffer solutions of AcOH/AcOK for pH = 5; KH<sub>2</sub>PO<sub>4</sub>/ K<sub>2</sub>HPO<sub>4</sub> for pH = 7; H<sub>3</sub>BO<sub>3</sub>/KH<sub>2</sub>BO<sub>3</sub> for pH = 9 were used for the experiments. Buffer solutions were prepared with procedures well described by using Perrin's description [62]. **HPhTT** solution in piperidine was also examined to observe the effect of an organic base.

## 3. Results and discussions

A fluorescence sensor was designed to generate signal changes resulting from substrate interaction with the thiazolo-thiazole core conjugated to phenolic -OH. The design of such thiazole based dye is important because of the relatively more sensitive fluorescent switches and electron or charge transfer (CT) of the TTz core. This fluorescence sensor acts as donor-acceptor-donor (D-A-D) type sensor consisting para-substituted phenols as donors (D) and TTz chromophore as acceptor (A), thus, this structure significantly affects the switching process, absorption and emission wavelengths. The synthesized fluorescence sensor is a thiazolo-thiazole dye substituted symmetrically with the receptor sensitive to analytes on the chromophore part. TTz based sensor dye that is containing cation-acid sensitive part composing from thiazolo-thiazole bicyclic ring, and anion-base sensitive phenolic-OH part was designed and examined towards various analytes to exhibit its multiresponsive properties. The sensitivity to the cationic analyte is based on the nitrogen atoms of the TTz groups while the phenol groups act as receptors. In order to test the possible applications of  $\ensuremath{\text{TTz}}$  chromophoric derivatives having strong and analytically valuable effects on the absorption and emission behaviour, the photophysical changes of HPhTT dye were examined as a fluorescence sensor upon various anion interaction and complexation of various metal cations in DMSO. TTz ring in the structure is acceptor group while phenol ring is donor group of the dye. Optical properties of an intramolecular charge transfer (ICT) fluorophore is strongly dependent on the nature of the donor and acceptor groups.Protonation of nitrogen atoms in the **TTz** ring by weakening the donor capacity of side phenol groups and causing an increase of acceptor strength of central rings results with fluorescent quenching as depicted in Fig. 1 [63]. In our designed D–A–D dye, thiazolo-thiazole acceptor unit is responsive to acid and metal cations while phenolic–OH group acting as donor is sensitive to anions and base. The base interacted form of the molecule has oxygen anions that is a stronger donor than the phenolic group causing red shift of emission wavelength maxima [64]. Possible mechanisms for the **HPhTT** dye is depicted in Fig. 1.

Eventhough TTz functional backbone containing molecules are used in a large variety of studies, mostly based on optoelectronics [37,39–42], there are very limited studies about their sensing properties [54–56]. Herein we report a D-A-D type ICT fluorophore containing TTz ring which is sensitive to multi-analytes. The optical response of the fluorophore against Au<sup>3+</sup>, makes it a promising candidate as sensor probe with remarkable (54.7  $\mu$ M) LOD value. The probe also gives opportunity to detect anions in diluted and concentrated mediums. We also determined linear color change dependence of fluorophore with increasing anion amounts. In this context, white light emission can also be obtained by changing amount of additive anions. This property might be used in optoelectronics.

#### 3.1. Effect of cations on photophysical properties of HPhTT

Effects of solvents with different polarities (DMSO, DCM, THF, ACN and CHp) in the dye (1.0  $\mu$ M for absorption and 0.1  $\mu$ M for fluorescence emission) at room temperature were examined via absorption and fluorescence spectroscopies (Fig. S2). In a low polarity solvent such as cyclohexanone, the emission occurs only from an locally excited (LE) state, whereas in a more polar solvent such as DMSO, an ultra-fast excited state charge transfer reaction occurs to the hydroxyl donating basic chromophore. This results in strong quenching of the LE emission and the emergence of a batchromically shifted emission from a lower CT state. In complexation with the cation, it inhibits the CT process and reopens the LE emission; ultimately, it can be used to generate a very efficient fluorescence key with very large fluorescence enhancement factors. Since the thiazolo-thiazole ICT sensor is essentially donor-acceptor-substituted fluorophores with strong solvent-dependent behaviour, DMSO was used as the solvent for all spectrometric measurements. The UV-vis absorption and emission behaviour of towards variety of metal ions has been investigated in DMSO at room temperature, absorption (1.0  $\mu$ M) and emission (0.1  $\mu$ M) spectra are given in Fig. 2a-b. HPhTT dye has an absorption wavelength region centered at 382 nm and emission wavelenght maxima ( $\lambda_{max}$ ) of 446 nm.

Fig. 2a shows the absorption spectrum of free ligand complexes of  $Al^{3+}$ ,  $Au^{3+}$ ,  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Fe^{3+}$ ,  $Ag^+$ ,  $Hg^+$ ,  $Mg^{2+}$ ,  $Sn^{2+}$ ,  $Hg^{2+}$ ,  $Zn^{2+}$  (10 mM) to the **HPhTT** dye in DMSO. The figure shows blue shift accompanying with a fluorescent quenching through the binding of the  $Au^{3+}$  metal ion. There is no shift when interacting with  $Al^{3+}$ ,  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Fe^{3+}$ ,  $Ag^+$ ,  $Hg^{2+}$ ,  $Mg^{2+}$ ,  $Sn^{2+}$ ,  $Zn^{2+}$ cations, whereas complexing with  $Au^{3+}$ ,  $Cu^{2+}$ ,  $Hg^+$  have new absorption band formation at 327, 296 nm and 279 nm respectively. These absorption peaks are related with

interaction of metal cations with DMSO as we investigated from spectroscopic titration of  $Au^{3+}$  cation in DMSO in absence of **HPhTT** (Fig. S3).

In absorption spectra of **HPhTT** dye after addition of  $Au^{3+}$ ,  $Cu^{2+}$  and Hg<sup>1+</sup> cations, an intense band in short wavelength region that are related to DMSO and cation interaction was observed while all other metals have almost the same absorbance in the presence of HPhTT (Fig. 2a).  $Au^{3+}$  addition resulted with an absorption band at 382 nm related with interaction between thiazolo[5,4-d]thiazole ring and Au<sup>3+</sup> cation. The complexation-induced effects of metal cations on emission spectra are shown in Fig. 2b. Eventhough Fe<sup>3+</sup> cations causes fluorescent quenching of the dye, HPhTT dye exhibits more sensitive fluorescent response towards Au<sup>3+</sup> as shown in fluorescence intensity comparison graph (Fig. 2c). From the photo daylight is given in Fig. 2d and the digital image in Fig. 2e, it can be concluded that the complexations of dye with both  $Au^{3+}$  and  $Fe^{3+}$  ions are fluorescently quenched; it is seen that this dye shows much higher selectivity to  $Au^{3+}$  than other metals. Fluorometric response of HPhTT towards all other cations were almost the same; except  $Fe^{3+}$  and  $Au^{3+}$  ions.

Moreover, the absorption and fluorescent titration profiles of HPhTT dve with increasing concentrations of  $Au^{3+}$  and  $Fe^{3+}$  ions were also examined. The intensities of all absorption bands decreased gradually with increasing concentrations of both  $Au^{3+}$  and  $Fe^{3+}$  ions (Fig. 3a-d). The absorption intensities attained saturation after addition of 38 equiv. of Au<sup>3+</sup> and 23 equiv. of Fe<sup>3+</sup> ions and did not change. Fluorescent intensities of **HPhTT** obtained via titration with increasing Au<sup>3+</sup> and Fe<sup>3+</sup> ions decreased that indicated fluorescent quenching. The fluorescence intensities attained saturation after addition of 76 equiv. of  $Au^{3+}$  and 25 equiv. of Fe<sup>3+</sup> ions and did not change. There was downward curvature between the fluorescence intensities and concentrations for Au<sup>3+</sup> while linear curve good fitting for  $\mathrm{Fe}^{3+}$  over a large range of concentrations as given in Fig. 3c-f. Stern–Volmer plot [(F<sub>0</sub>/F) versus concentration] was an upward curvature for  $Au^{3+}$  (Fig. 3c) [61]. The limit of detection of  $Au^{3+}$  was determined as 54.7  $\mu M.$  Stern–Volmer plot for  $Fe^{3+}$  titration was a linear curve. Titration curves of HPhTT dye towards other metals without a remarkable change are given in Figs. S4 and S5. The limit of detection of Fe<sup>3+</sup> was determined as 57.3 µM. Photoinduced electron transfer (PET) is offered for the quenching of the fluorophore resulting from the interaction between the fluorophore and  $Au^{3+}$ ,  $Fe^{3+}$  ions in which electron density diminished upon metal binding [65].

### 3.2. Effect of anions on photophysical properties of HPhTT

Spectrophotometric and spectrofluorometric titrations were carried out to investigate anion sensing ability of **HPhTT** (1.0  $\mu$ M in DMSO) by titrating dye with tetrabutylammonium (TBAX) salts (X: AcO<sup>-</sup>, Br<sup>-</sup>, CN<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub>, HSO<sub>4</sub> and I<sup>-</sup>, 10 mM in DMSO). The titration results were given in Fig. 4. A new absorption band with 460 nm  $\lambda_{max}$  after addition of F<sup>-</sup>, CN<sup>-</sup> and AcO<sup>-</sup> anions were occured originated from stronger ICT mechanism as a result of deprotonation of phenol segment of the dye. Any remarkable change in the absorbance and fluorescence spectra has not been observed after addition of other anions (Figs. S6 and S7). Anion sensitivity properties were also determined by performing emission titration studies of **HPhTT** (0.1  $\mu$ M in DMSO) with the anions. The emission spectra observed by titration of **HPhTT** with AcO<sup>-</sup>, CN<sup>-</sup> and F<sup>-</sup> is shown in Fig. 4b-c. In the emission spectra, it is clearly seen that the



Fig. 1. Schematic illustration of ICT mechanisms of HPhTT in various media.



Fig. 2. UV–vis spectra of HPhTT (a), fluorescent spectra of HPhTT (b) and fluorescent intentisies of HPhTT at  $\lambda_{max}$  (c) before and after addition of metal salt solutions. Digital images of HPhTT (c = 10  $\mu$ M in DMSO) after addition of 25 equiv. (c = 250  $\mu$ M) of various metal cation solutions under day-light (d) and under UV-light (e).



**Fig. 3.** UV–vis spectra of **HPhTT** dye–Au<sup>3+</sup> solutions (a), fluorescent spectra of **HPhTT** dye–Au<sup>3+</sup> solutions (b), C–I curve and Stern–Volmer plot of **HPhTT** dye–Au<sup>3+</sup> solutions (c), UV–vis spectra of **HPhTT** dye–Fe<sup>3+</sup> solutions (d), fluorescent spectra of **HPhTT** dye–Fe<sup>3+</sup> solutions (e), C–I curve and Stern–Volmer plot of **HPhTT** dye–Fe<sup>3+</sup> solutions (f).

fluorescence intensity changes with the addition of AcO<sup>-</sup>, CN<sup>-</sup> and F<sup>-</sup> to the medium. This remarkable change shows that the fluorophore interacts with these anions, resulting in a new emission band at a longer wavelength (550 nm). Moreover, the color of the solutions were slightly changed from bright into yellowish color after addition of F<sup>-</sup>, CN<sup>-</sup> and AcO<sup>-</sup> anions.

A new shoulder peak at 550 nm  $\lambda_{max}$  after addition of AcO<sup>-</sup>, F<sup>-</sup> and CN<sup>-</sup> anions was occured and this shoulder emission peak was observed after increasing excitation wavelenght from 375 nm to 420 nm as given in Fig. 4c. After F<sup>-</sup> addition a broader sholuder occured at 485 nm. Bathochromic shift of absorption and emission wavelenghts maxima in the spectra originates from enhanced ICT. Anion addition results with deprotonation of phenolic–OH group causing formation of oxygene anion as stronger donor. Titration of **HPhTT** with anions was studied till

absorption and fluorescent intensities attained saturation. AcO<sup>-</sup>, CN<sup>-</sup> and F<sup>-</sup> addition resulted with a new band at 550 nm with increasing intensity and a decrease on the peak at 444 nm due to the concentration increases. Moreover, while there were yellow color alteration under the daylight in Fig. 4d., the emission color became white under UV light in Fig. 4e. Deprotonation of **HPhTT** is observed in two steps. After diluted TBAX (X: AcO<sup>-</sup>, CN<sup>-</sup> and F<sup>-</sup>) addition, anion-phenolic-OH group interactions were observed [66] while deprotonation of phenolic-OH groups was observed after the concentrated TBAX addition. <sup>1</sup>H NMR spectra of HPhTT with increasing TBAF concentration (concentrated TBAF was used) were given in Figure S11. The spectrophotometric titration studies with concentrated the AcO<sup>-</sup>, CN<sup>-</sup> and F<sup>-</sup> anions are given in Fig. S8. The spectrophotometric analysis indicates possible deprotonation of the phenolic-OH group through dipole-anion interactions



Fig. 4. UV-vis spectra of HPhTT dye-anion solutions (a), fluorescent spectra of HPhTT dye-anion solutions,  $\lambda_{exc} = 375$  nm (b), fluorescent spectra of HPhTT dye-anion solutions,  $\lambda_{exc} = 420$  nm (c), digital images of anion-HPhTT dye solution under daylight (d), and under UV-light (e).

between Ph-OH and  $F^{-}$  ion, forming the intramolecular charge transfer (ICT) state in the conjugated system of phenoxide anion with thiazolo-thiazole.

The plots of intensity ratios (I<sub>550</sub>/I<sub>444</sub>) versus concentration showed ratiometric fluorescent response as given in Fig. 5a-f. The dye interacts with AcO<sup>-</sup>, CN<sup>-</sup> and F<sup>-</sup> anions through mechanism of deprotonation of the phenolic OH following dipole-anion interactions between Ph-OH and anions. While the emission peak ( $\lambda_{max} = 444$  nm) of the dye in DMSO is 460 nm, it is observed that the fluorescence intensity at 444 nm decreases as a result of the F<sup>-</sup> addition while a new emission band is formed at long wavelength (550 nm). It has shown that the dye has a

potential to be used as a fluorescence sensor due to its interaction with AcO',  $CN^-$  and  $F^\cdot$  anions.

#### 3.2.1. Reversibility

Reversibility and reusability of the sensor are particularly important for applications in real environments. To test the applicability of **HPhTT**, titration studies were performed by the addition of trifluoroacetic acid (TFA) via using absorption and fluorescence spectroscopy techniques. After adding 10 equiv. of the anions (only AcO<sup>-</sup>, F<sup>-</sup> and CN<sup>-</sup>) to the **HPhTT** solution, a new band was observed at 464 nm. When 10 equiv. of TFA was added to the mixture, the absorption maxima of the



**Fig. 5.** Fluorescent spectra of F<sup>-</sup> anion titration curves of **HPhTT** dye solution (a), fluorescent spectra of CN<sup>-</sup> anion titration curves of **HPhTT** dye solution (b), fluorescent spectra of AcO<sup>-</sup> anion titration curves of **HPhTT** dye solution,  $\lambda_{exc} = 375$  nm (c),  $I_{550}/I_{444}$ -concentration plot of F<sup>-</sup> titration (d),  $I_{550}/I_{444}$ -concentration plot of CN<sup>-</sup> titration (e),  $I_{550}/I_{444}$ -concentration plot of AcO<sup>-</sup> titration (f).

dye had hypochromic effect and the dye immediately shifted to the original maxima (Fig. 6a-f). Color switching of **HPhTT** dye under UV-light excitation from blue to yellowish and then back to blue with addition of TFA shows the change of the fluorescence behaviour as shown in Fig. 6a-c. Additionally, the repeated display of the visual colour change shows the precise recycling and reusability of the dye.

#### 3.3. Acidochromic properties of HPhTT

In order to understand better the effect of acidic and basic environments on the **HPhTT** dye, photophysical response of the dye in different pH buffer solutions was studied. The pH dependent spectral properties of the dye were evaluated in Perrin's description buffer solutions with pH values ranging from 1, 3, 5, 7, 9, 11 and 13. The acid and base effect on photophysical properties of **HPhTT** dye was observed with the absorption and emission spectra as shown in Fig. 7a-b.

The absorption spectra of the HPhTT dye showed the maxima wavelength at 330 nm between pH 1 and 7, while the wavelength maxima shifted to 415 nm between pH 9 and 11. When the pH range changed from 7 to 9, it was noticed with the naked eye in daylight that the absorption color of the dye changed from transparent to yellow with significant color change. The pH dependent spectroscopic study appeared to give a clear response in absorption. It was observed that the change of pH had a great influence on the absorbance of the dye and caused an absorption maximum at 68 nm between pH 7-10. According to the emission spectra, the fluorescence intensity of the dye increased significantly with increasing pH from 7 to 10. Turn on mechanism of the dve from acidic pH ranges to pH 10 in aqueous medium can be clearly seen in Fig. 7a-b. In particular, it is clearly seen that the HPhTT dye is vellow in daylight in a basic media and colourless in an acidic media (Fig. 7c). The fluorescence intensity increased dramatically and consequently indicated a charge transfer (CT) at pH 10. As it can be seen in Fig. 7d, deprotonation of hydroxyl group in the basic media (pH > 9) caused enhanced ICT while protonation of N atoms in the TTz ring and weakening of electron donating ability of phenolic-OH at acidic medium resulted with quenching of fluorescence. In aqueous basic media, bathochromic shift in both the absorption wavelength maxima at 412 nm  $\lambda_{max}$  and the emission wavelenght at 498 nm was observed. The

bathochromic shift was obtained instead of a new band formation with the addition of base, that results from different optical properties in aqueous media. UV–vis and fluorescence spectra of **HPhTT** after  $H_2O$ addition measurements and digital images of the solutions under daylight and UV-light are given in Fig. S9. Importantly, the dye display different optical response against OH<sup>-</sup> anions in aqueous media.

An increase of I550/I444 ratio resulted with more obvious color change under UV light excitation, as expected. After addition of diluted bases (piperidine, F<sup>-</sup>, CN<sup>-</sup>, AcO<sup>-</sup>, OH<sup>-</sup>), the color changes were determined in blue region as shown in Fig. 7e, resulting from the dipole-ion interractions between -OH and anions. In concentrated basic media, the color changes were determined in yellow-green region as shown in Fig. 7e, resulting from phexoide ion formation leading to enhanced ICT. Eventhough the chromaticity diagrams are commonly used to estimate color purity and color coordinates for LED researches, usage of such softwares in fluorescent sensor studies may help to estimate usability of the fluorescent sensor under UV excitation. We demonstrate usability of color calculator software after titration of **HPhTT** with F<sup>-</sup> anion as given in Fig. 8a-b. The color change of the HPhTT solutions titrated with F anion and calculated colors are given in Fig. 8a. The images shows good estimation of color by the Color Calculator Software. Increasing F<sup>-</sup> anion concentration resulted with linear color change in the chromaticity diagram (Fig. 8b). The x and y values calculated for each concentration of F was graphed and a linear curve was obtained (Fig. 8c). The related concentrations of F were also graphed with increasing I550/I444 ratio and given in Fig. 8d. After addition of 25 equivalent AcO<sup>-</sup>, F<sup>-</sup> and CN<sup>-</sup> anions and piperidine in HPhTT solution, the I550/I444 ratios were calculated as 0.172, 0.208, 0.301, 2.169 respectively. Moreover, obvious color change under UV light excitation was observed with concentrated piperidine (2 M). UV-vis spectra and fluorescent spectra of the HPhTT dye before and after titration with both concentrated and diluted piperidine were also recorded and digital images of the solutions under daylight UV-light are given in see, FigS10. Spectroscopic results indicated a linear change on  $\mathrm{I}_{550}/\mathrm{I}_{444}$  ratio with concentration.

Filter papers were interacted with HPhTT/PVA solution in 0.01 M NaOH and in 0.1 M NaOH to prepare sensor papers (Fig. 9). The sensor papers emitting blue light (prepared with 0.01 M NaOH) were used to determine anion sensitivity, they are not sensitive against cations as



Fig. 6. Before and after TFA addition: UV-vis spectra of ACO<sup>-</sup>-HPhTT solution (a), UV-vis spectra of CN<sup>-</sup>-HPhTT solution (b), UV-vis spectra of F<sup>-</sup>-HPhTT solution (c), fluorescent spectra of ACO<sup>-</sup>-HPhTT solution (d), fluorescent spectra of CN<sup>-</sup>-HPhTT solution (e), fluorescent spectra of F<sup>-</sup>-HPhTT solution (f).



Fig. 7. UV–vis spectra of HPhTT dye in different pH values (a), fluorescent spectra of HPhTT dye in different pH values (b), digital images of HPhTT dye solutions in different pHs under daylight (c), under UV-light (d), and ICE 2015 chromaticity diagram of the fluorescent sensor dye before and after addition of analytes.



**Fig. 8.** Digital images of **HPhTT** dye titrated with different equivalents of F<sup>-</sup> and good fitting calculated colors in CIE 2015 chromaticity diagram (a), CIE coordinations of **HPhTT** dye with increasing equivalent of F<sup>-</sup> (b), x-y coordinates of CIE 2015 chromaticity diagram with increasing [F<sup>-</sup>] (c), I<sub>550</sub>/I<sub>444</sub> versus [F<sup>-</sup>] (d).

shown in Fig. 9. Interestingly, the paper was observed selectively interacted with CN<sup>-</sup> anion. The sensor papers emitting green light (prepared with 0. 1 M NaOH) were used to detect cations. Au<sup>3+</sup> (in DMSO) treatment resulted in blue shift, while Au<sup>3+</sup> (in H<sub>2</sub>O) treatment resulted in quenching of fluorescence.

## 4. Conclusion

In this study, a fluorescence symmetric sensor with thiazolo-thiazole (**TTz**) core, namelly 2,5-bis(4-hydroxyphenyl)thiazolo[5,4-d]thiazole

(HPhTT), is synthesized and its selectivity and sensitivity to multiple analytes has been investigated. The synthesis of fluorescent sensor dyes with superior properties reported in the literature involves stepwise reactions or long syntheses in many studies [4,21,67,68]. One–step synthesis, easy purification and superior optical properties of HPhTT is reported in here, that makes the dye an attractive candidate for many sensing applications.

The selectivity and sensitivity of **HPhTT** to cations and anions and its photophysical behaviour in aqueous, acidic and basic mediums were determined. Ratiometric sensing of both  $Au^{3+}$  and  $Fe^{3+}$  cations is



Fig. 9. Digital images of HPhTT dye modified filter papers after interacted with anions and cations.

possible with HPhTT, while ratiometric anion sensing is also possible via enhanced ICT mechanism even in concentrate mediums. We also proposed gradually increasing ICT enhancement to explain various I550/I444 ratios depending on dipole-ion interactions between Ph-OH and ions and followed by deprotonation of phenolic-OH. The chemosensor dye is responsive against AcO-, CN- and F- anions in both diluted and concentrated media. We also showed usability of color calculator to estimate color change of the sensor after addition of analyte. Moreover, the fluorescence of the dye showing remarkable changes in acidic and basic aqueous pH buffer solutions can be used as a potential pH sensor. It has been found that it is a Turn-ON / Turn-OFF type sensor with its acidochromic effect in an aqueous media. As a result, in the context of fluorescence and colorimetric sensor development and application focussed on the detection of multiple analytes, the thiazolo-thiazole (TTz) dye systems can be used selectively to identify both cations and anions as dual sensor.

#### CRediT authorship contribution statement

Zeynep Dikmen: Conceptualization, Methodology, Writing - original draft, Visualization, Validation. Onur Turhan: Methodology, Data curation, Formal analysis. Müjgan Yaman: Methodology, Investigation, Writing - original draft. Vural Bütün: Supervision, Writing - review & editing, Funding acquisition.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jphotochem.2021.113456.

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