

# Merocyanine dye-based specific sensing cyanide anions in aqueous medium



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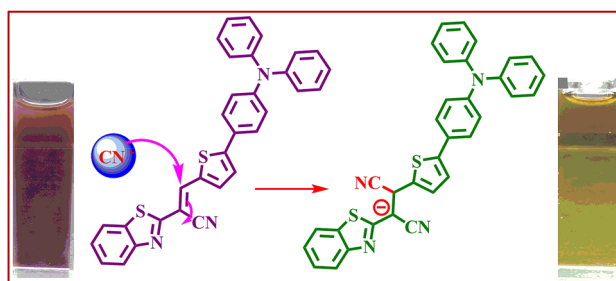
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## Abstract

The (E)-2-(benzo[d]thiazol-2-yl)-3-(5-(4-(diphenylamino) phenyl) thiophen-2-yl) acrylonitrile TP1 dye has been investigated as new fluorescent chemosensor for cyanide anions. The dye TP1 acted as strong turn on fluorescent sensor after addition of the cyanide anions. Upon addition of cyanide anions to dye TP1 solution induced a change in the solution color from red to green color under the naked-eye detection. While no color change could be observed in presence of other common-anions. The detection limit of dye TP1 for cyanide anions was found to be  $4.24 \times 10^{-8}$  M.

## Graphic abstract



**Keywords** Hemi cyanine · Colorimetric · Triphenylamine · Cyanides

## 1 Introduction

Anions are playing an important role in various biological and chemical processes, the development of optical chemosensors for anion detections are recently a great interest [1–7]. Thus, the design and synthesis of fluorophores for the optical sensors that can detect anions selectively are always of major interest. In particular cyanide anions are absorption through the lungs, skins, leading to vomiting,

convulsion, loss of consciousness and eventually death. On the other hand, cyanide ions widely used in the several industrial processes such as gold mining, electroplating, metallurgy and the synthesis of fibers and resins. Therefore, the many industries produce nearly 140,000 tons of cyanide per year worldwide. The World Health Organization (WHO) and the Environmental Protection Agency (EPA) have set the maximum [3, 4, 8–10], contaminant level (MCL) for cyanide to regular the safe level of drinking water

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system at  $< 1.9 \mu\text{M}$  and at  $0.2 \text{ mg L}^{-1}$  respectively. Hence, cyanide contamination is a very severe problem and there is a need for an efficient sensing to detect fluoride and cyanide environment and in living organisms [11, 12]. Therefore, industrial use of mass quantities of cyanide with its associated transportation through highly populated areas, drastically increases the risk of exposure. Uptake of toxic cyanide could occur through absorption by lungs, skin and also from contaminated food and polluted drinking water. Nowadays, environmental pollution caused by cyanide is becoming severe due to the aggravation of the industrialization process; convenient and efficient detection of cyanide anions is called for in the battle against such pollution [13–15]. Thus, the development of sensitive, selective and easy methods for cyanide anion detection, especially in water and physiological conditions [16–19].

Different kinds of mechanisms have been used to design the ratiometric fluorescent sensors for anions, such as intramolecular charge transfer (ICT), fluorescence resonance energy transfer (FRET) and nucleophilic reactivity are the most important characters of cyanide anion and decided the kind of receptors. Recent years, compared to the hydrogen bond donor–receptor and lewis acid–base pair recognition, cyanide chemodosimeters based on the nucleophilic reaction have attracted increasing attention. The second point for molecular design of chemical sensor and the structure of fluorophore which directly relate to the photochemical mechanism of recognition and the signal processing. “Off–on” fluorescence sensors always obtained more advantages over “on–off” type, because of their higher signal to-noise ratio and more recognizable optical changes suitable for naked-eye observation. In consideration of cyanide analysis in bio sample, red to near infrared (NIR) emission is preferable to ultra-visible range for the low photo toxicity, large stokes shift and the negligible auto fluorescence interference.

In the present study, we utilize this ICT mechanism based dye (E)-2-(benzo[d]thiazol-2-yl)-3-(5-(4-(diphenylamino) phenyl) thiophen-2-yl) acrylonitrile TP1 as the cyanide addition unit and reveal the selectivity-structure relationship and the triphenylamine unit is acceptor. The benzothiazole–triphenylamine based fluorophore is excellent photophysical properties with absorption wavelength at 550 nm and emission at 560 nm due to the strong intramolecular charge transfer process [17, 20–28]. However, their practical application was proved by test strip study. The dye TP1 acted as strong fluorescent sensor for cyanide anions and exhibited color change under the UV-lamb, which showed significant shift after addition of the cyanide anion. To best of our knowledge, benzothiazole–triphenylamine based dye as selective turn-off sensor for detection of cyanide anions at low concentration in aqueous medium is a new strategic one.

## 2 Experimental section

### 2.1 Materials and instrumental methods

All reagents and solvents are used without further purification. Absorption measurements were carried out using a JASCO-V630 spectrophotometer. Fluorescence spectra were recorded on an Agilent-8000 fluorescence spectrophotometer. The slit width was 2.5 nm for both excitation and emission. The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker (Advance) 300 MHz NMR instrument using TMS as internal standard DMSO- $d_6$  as solvent. Mass spectra were recorded in LCQ Fleet mass spectrometer, Thermo Fisher Instruments Limited, US. Electrospray ionization mass spectrometry (ESI–MS) analysis was performed in the positive ion and negative ion mode on a liquid chromatography ion trap.

### 2.2 Synthesis of dye TP1

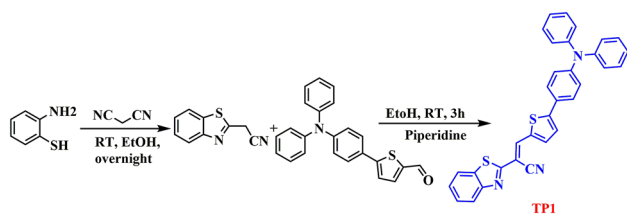
The compound was synthesized by condensation between 2-(1, 3-benzothiazol-2-yl) acetonitrile and their corresponding aldehyde in ethanol solution containing piperidine. The reaction mixture was allowed to stir for 3 h. Then the product was filtered and washed with cold ethanol and finally dried under vacuum.  $^1\text{H}$  NMR (800 MHz, DMSO- $d_6$ )  $\delta$  8.24 (s, 1H), 8.13 (s, 1H), 8.01 (d,  $J=4.0$  Hz, 1H), 7.85 (d,  $J=3.2$  Hz, 1H), 7.70 (dd,  $J=11.4, 8.4$  Hz, 1H), 7.62 (dd,  $J=11.6$ , Hz, 2H), 7.55–7.49 (m, 2H), 7.49–7.38 (m, 3H), 7.38–7.31 (m, 4H), 7.23 (t,  $J=7.4$  Hz, 1H), 7.16–7.05 (m, 4H), 7.01–6.93 (m, 1H).  $^{13}\text{C}$  NMR (200 MHz, DMSO- $d_6$ )  $\delta$  171.09, 162.98, 144.27, 130.23, 129.88, 129.80, 127.79, 127.59, 125.43, 124.91, 124.59, 124.49, 124.03, 122.62, 112.52, 112.41, 112.29. ESI–MS (positive mode,  $m/z$ ) Calculated for  $\text{C}_{32}\text{H}_{21}\text{N}_3\text{S}_2$ , 511.12. Found: 511.17.

### 2.3 UV–vis–fluorescence titration studies

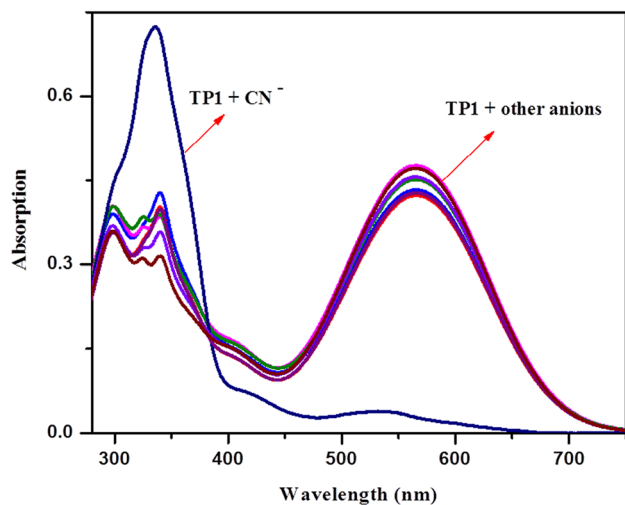
The absorption and emission performance of various anions towards the dye TP1 was examine by UV–vis spectroscopy and fluorescence spectroscopy correspondingly in ACN– $\text{H}_2\text{O}$  (1:9 v/v) using PBS buffered solution. All the ability was carried out in PBS buffer solution (pH 7.2).

## 3 Results and discussion

The (E)-2-(benzo[d]thiazol-2-yl)-3-(5-(4-(diphenylamino) phenyl) thiophen-2-yl) acrylonitrile were synthesized from readily available triphenylamine derivatives. The reaction of 2-(benzo[d]thiazol-2-yl) acetonitrile with



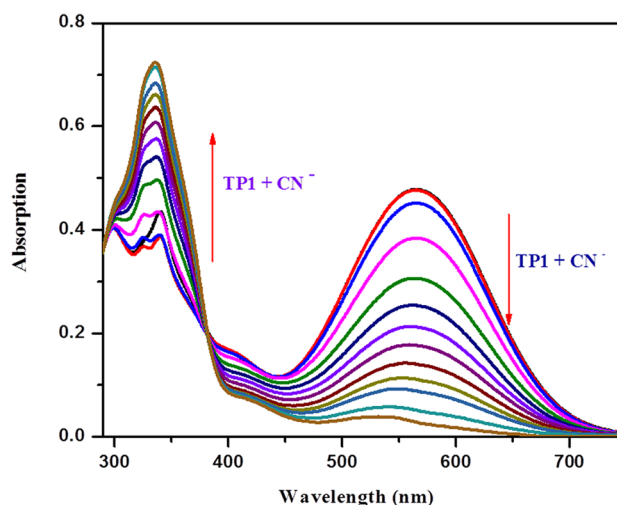
**Scheme 1** Synthetic routes of the merocyanine dye based TP1 derivative



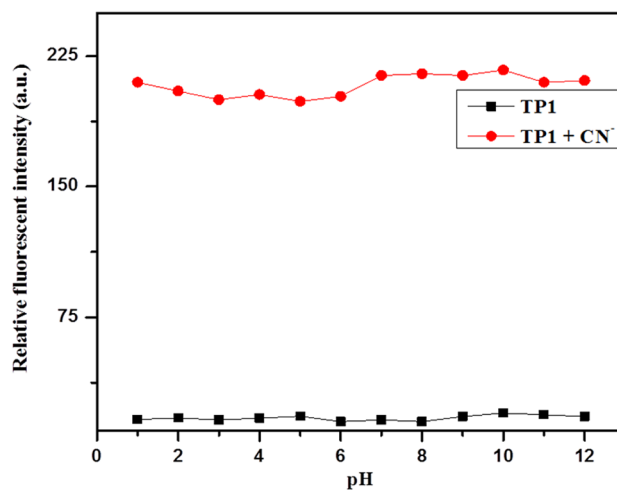
**Fig. 1** Absorption spectra of dye TP1 in the presence of various anions (50  $\mu\text{M}$ ) of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{SCN}^-$ ,  $\text{P}_2\text{O}_7^{4-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  in HEPES buffer (20 mM, pH 7.2) solution ( $\text{ACN-H}_2\text{O}=1:9$ )

5-(4-(diphenylamino) phenyl) thiophene-2-carbaldehyde in the presence piperidine gives merocyanine dye (TP1) are shown in scheme 1.

The synthesized compound was characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR are shown in Fig. S1–S2. In the merocyanine dye TP1, the  $^1\text{H}$  NMR clearly showed the disappearance of aldehyde proton and appearance of benzothiazole unit. The appearance of singlet at 7.4 ppm indicates the presence of alkene bond unit. The remaining aromatic protons have their corresponding chemical shift values. Similarly the  $^{13}\text{C}$  NMR also gives additional information. The peak at 120.5 ppm indicates the presence of cyanide and the peak at 160.6 ppm indicates the presence of benzothiazole core. The  $^1\text{H}$  NMR clearly showed the disappearance aldehyde proton and appearance of alkene unit. The chemosensing properties of merocyanine dye TP1 was investigated by UV–vis spectroscopy in PBS buffer (20 mM, pH 7.2) solution ( $\text{ACN-H}_2\text{O}=1:9$ ) with other anions. The cyanide anion was only that caused significant blue shift in absorption whereas other anions not shown significant effects on the absorption of merocyanine dye TP1 (Fig. 1).



**Fig. 2** Absorption spectrum of dye TP1 (10  $\mu\text{M}$ ) toward different concentrations of  $\text{CN}^-$  (0–50  $\mu\text{M}$ ) in HEPES buffer (20 mM, pH 7.2) solution ( $\text{ACN-H}_2\text{O}=1:9$ )



**Fig. 3** Effect of PH in the fluorescence response of dye TP1 and TP1 + cyanide ions

The UV–vis titration of the increasing addition of  $\text{CN}^-$ , a new absorption band wavelength 325 nm appeared with increasing intensity significantly, while that absorbance at 550 nm decreased sharply. After addition of 100  $\mu\text{M}$  of  $\text{CN}^-$ , the isosbestic points at 380 nm were observed shown in Fig. 2.

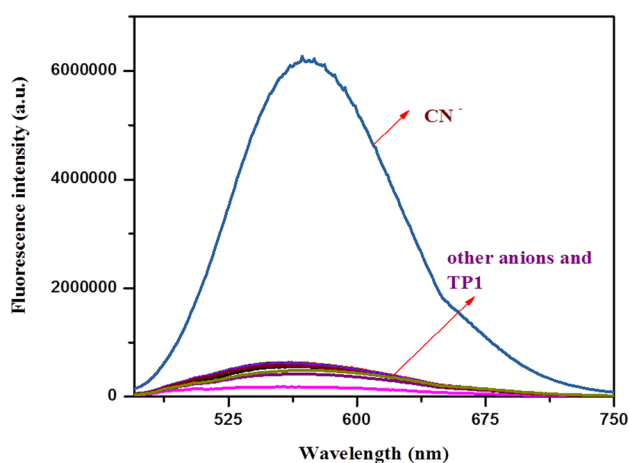
Then pH effect on fluorescent fluorophore nature of dye TP1 and TP1 + cyanide ions also analysis with different pH solutions (from 2 to 12) are shown in Fig. 3.

Since the pH adjusted from 2 to 12, there was no change in florescent intensity of dye TP1 and TP1 + cyanide anions. So these results indicated the dye TP1 and TP1 + cyanide anions are used broad pH range in the physiological and

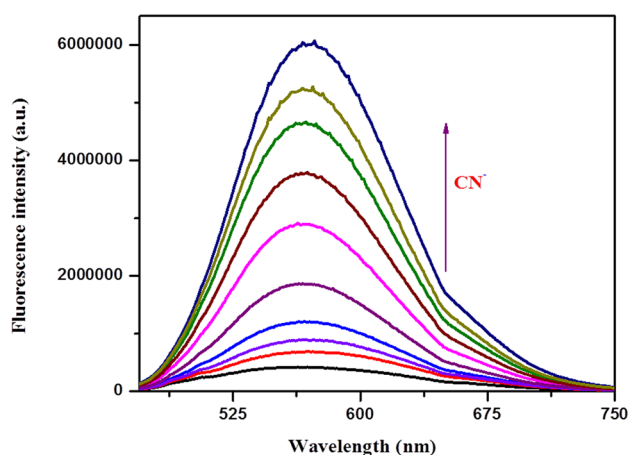
biological studies. Hence, the all absorption and fluorescence studies carried out in PBS at pH 7.2. The dye TP1 was treated with various analysts represented by  $\text{CN}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{SCN}^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in ACN–buffer. The dye 1 was displayed very low intense fluorescence emission at one main band 565 nm. The dye 1 show a turn-on fluorescence response with cyanide anions but other anions did not induce any significant change in fluorescence responses are shown in Fig. 4. These results indicate that the TP1 sensor is highly selective to cyanide anions over other anions tested.

The fluorescence titration spectra of probe TP1 (10  $\mu\text{M}$ ) in the presence of  $\text{CN}^-$  (0–100  $\mu\text{M}$ ) in PBS buffer (20 mM, pH 7.2) solution (ACN– $\text{H}_2\text{O}$  = 1:9) solution are exhibited in Fig. 5.

As it can be seen the addition of cyanide anions in the fluorescence emission intensity at 565 nm was gradually increased. The detection limit for probe TP1 was calculated based on the fluorescence titration method was found to be  $4.24 \times 10^{-8}$  M. For the low detection limit of  $4.24 \times 10^{-8}$  M along with the great linear detection range for cyanide anion was obtained and it's compared with the previous chemosensors reports (Table-S1). On the other hand, the presence of other competitive species did not induce any significant change in the emission peak at 565 nm. In addition, the competition experiments were also measured by addition of 100  $\mu\text{M}$  of  $\text{CN}^-$  to the solution of probe TP1 (10  $\mu\text{M}$ ) in the presence of 100  $\mu\text{M}$  of other anions are shown in Fig. 6. The apparent fluorescence emission color change of dye TP1 from violet to green color could be observed by under UV lamp and normal light observed fluorescence emission color change from violet to colorless by naked eye.



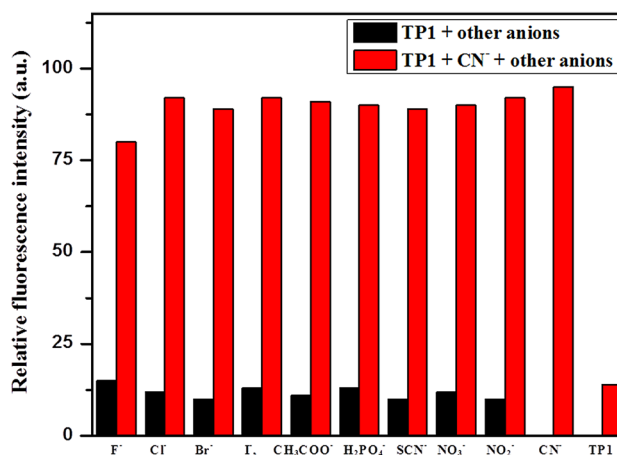
**Fig. 4** Fluorescence spectra of dye TP1 in the presence of various anions (50  $\mu\text{M}$ ) of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{SCN}^-$ ,  $\text{P}_2\text{O}_7^{4-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  in HEPES buffer (20 mM, pH 7.2) solution (ACN– $\text{H}_2\text{O}$  = 1:9) at excitation of 450 nm



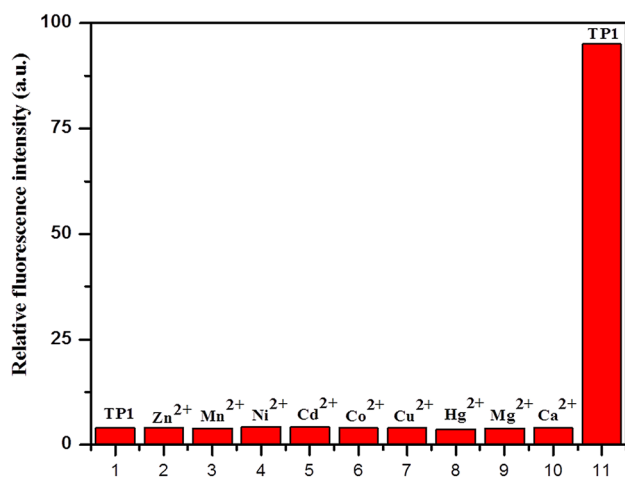
**Fig. 5** Fluorescence responses of dye TP1 (10  $\mu\text{M}$ ) toward different concentrations of  $\text{CN}^-$  (0–50  $\mu\text{M}$ ) in HEPES buffer (20 mM, pH 7.2) solution (ACN– $\text{H}_2\text{O}$  = 1:9) at excitation of 450 nm

The fluorescence intensity obtained from the competition experiments revealed that probe TP1 is highly selective to cyanide anions over other common anions. Meanwhile, the addition of important metal cations, no color changes and spectral changes was observed. These results indicate the metal doesn't interact with the merocyanine dye TP1 are shown in Fig. 7.

The jobs plot indicate the molar fraction of probe TP1 was around 0.5, the fluorescence value at 565 nm approached a maximum, indicating a definite 1:1 reaction mode between probe TP1 and cyanide anions are shown in Fig. S3. Further supported by the ESI–MS data of dye TP1 observed at 511.66 and dye TP1 + cyanide anions a new peak appears at  $m/z$  = 539.57. Therefore, merocyanine dye TP1 was shown a highly sensitivity and selectivity for cyanide anions. However; to date there has been no report



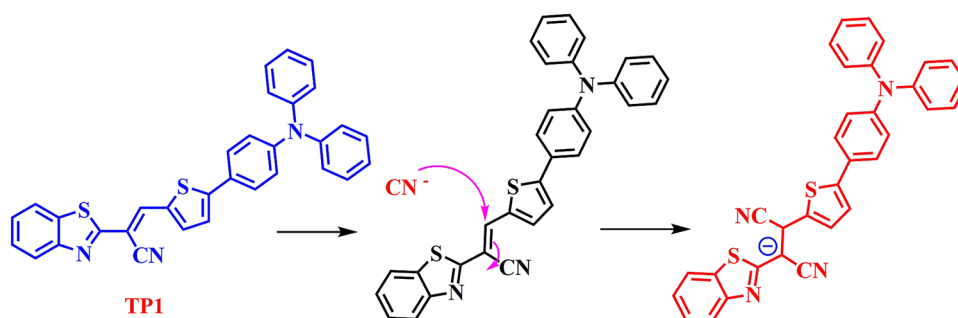
**Fig. 6** Fluorescence changes in the presence of the competing anions followed by cyanide anions



**Fig. 7** The cyanide anions selectivity of dye TP1 (10  $\mu\text{M}$ ) in HEPES buffer (20 mM, pH 7.2) upon addition other metals (100  $\mu\text{M}$ ) solution (ACN-H<sub>2</sub>O=1:9) at excitation of 450 nm

on the recognition of  $\text{CN}^-$  by receptor TP1 in aqueous solution. Furthermore, the reversibility nature of chemosensor TP1 was measured by adding a few drops of acetic acid ( $5 \times 10^{-2}$  M) solution to TP1.  $\text{CN}^-$  adduct, while the preferential protonation of the  $\text{CN}^-$  took place. The fluorescence emission intensity due to TP1 +  $\text{CN}^-$  probe returned to lower level of fluorescence intensity. The reversibility of the interaction was examined by the acid-induced loss of cyanide anions to give the original dye TP1 fluorescence spectrums are shown in Fig. S5. The binding ability of probe TP1 was further subjected to NMR titration experiment in ( $\text{CDCl}_3/\text{D}_2\text{O}$ , 1:1, V/V). The addition of cyanide anions to merocyanine dye TP1 resulted in the disappearance of aromatic signals corresponding to vinyl protons and new dicyanoethyl proton signals appeared at 5.00–5.45 ppm and then aromatic protons changed slightly. The suggested proposed mechanism for the detection of cyanide anions through the formation of internal charge transfer mechanism are shown in Scheme 2.

**Scheme 2** Probable mechanism for the observed ratio-metric response of the dye TP1 with cyanide anions

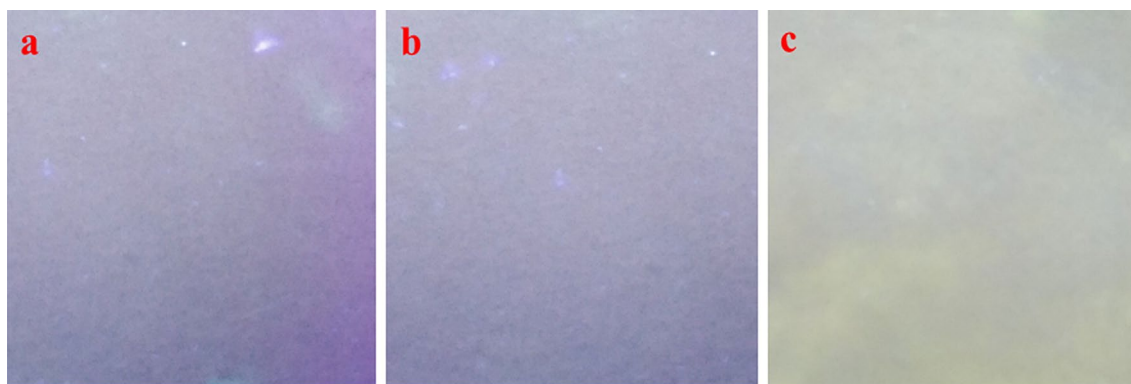


We have analyzed the merocyanine dye TP1 1, 2-adduct formation by adding trifluoroacetic acid. The dye TP1 + cyanide anions highly fluorescent after addition of drop trifluoroacetic acid, we obtained a fluorescence spectrum similar to the dye 1 without cyanide anions are shown Fig. S5. The practical application of color change of the system in solution, test strips were prepared by immersing filter papers in the ACN/H<sub>2</sub>O solution of dye TP1 ( $\mu\text{M}$ ) and then drying them in air. Then the colour changes was observed under UV lamp, when the dye TP1 based test strips were immersed in the aqueous media of cyanide anions solution, a clear color change from mild violet color to light yellow green color fluorescence. But no more color changes observed in dye with other interferes anions are shown in the Fig. 8. Hence, this result indicted the excellent selectivity fluorescence towards cyanide anions with dye TP1. Therefore, the dye TP1-based test trips can conveniently detect cyanide anions in solutions without any additional equipment.

## 4 Conclusion

We have developed a new turn-on fluorescent fluorophore for  $\text{CN}^-$  based on (E)-2-(benzo[d]thiazol-2-yl)-3-(5-(4-(diphenylamino) phenyl) thiophen-2-yl) acrylonitrile (TP1) merocyanine dye. The merocyanine dye TP1 was highly specific recognition of cyanide anions from aqueous solution of TBACN through the formation of ICT mechanism. The interaction with anions studied via UV-visible, fluorescence. Furthermore, the merocyanine dye TP1 displayed high selectivity for cyanide anions over other analytes including fluoride,  $\text{CH}_3\text{COO}^-$  and  $\text{H}_2\text{PO}_4^-$  anions. The cyanide anions could be detected at low ( $4.24 \times 10^{-8}$  M) levels in aqueous medium.





**Fig. 8** Photographs of test trips detections **a** dye TP1, **b** dye TP1 + other interfering anions, **c** dye TP1 + cyanide anions under the UV lamp

## Compliance with ethical standards

**Conflict interest** The authors declared that they have no conflict interest.

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