

Contents lists available at ScienceDirect

Dyes and Pigments



journal homepage: www.elsevier.com/locate/dyepig

A novel fluorescent sensor based on triphenylamine with AIE properties for the highly sensitive detection of CN⁻



Bin Zuo, Lian Liu, Xicheng Feng, Denghui Li, Wanfang Li, Mingxian Huang, Qinyue Deng*

College of Science, University of Shanghai for Science and Technology, Shanghai, 200093, China

ARTICLE INFO	A B S T R A C T	
Keywords: Fluorescent probes Cyanide anions Aggregation induced emission DFT Test strip	In this study, a novel fluorescent sensor 1 built on triphenylamine was designed for the extremely sensitive detection of trace cyanide anions. The UV absorbance and fluorescence emission intensity of sensor 1 with aggregation-induced emission (AIE) properties vary with water fraction (f_w). In the 1% DMSO aqueous solution, sensor 1 exhibits the optimal aggregation state and fluorescence intensity, and has high selectivity and sensitivity for cyanide ions (CN^-). From formula 3 δ /S, it is clear that sensor 1 has an extremely low limit of detection (LOD) for CN^- (LOD = 2.95×10^{-8} mol/L). Excellent anti-interference performance and broad pH response scope (1.0–9.0) are also advantages of sensor 1. Fluorescence spectroscopy, ¹ H NMR, ¹³ C NMR spectroscopy, HRMS, Job's plot analysis and density functional theory calculations have been employed to elucidate the sensing mechanism between TPEB and CN^- . Through colorimetry and fluorescence approach, the sensor 1 test strip can easily detect CN^- . Therefore, the novel sensor 1 provides a broad application prospect for detecting toxic environmental pollutants	

1. Introduction

With the development of science and technology, water pollution and food safety issues caused by poisonous anions have attracted widespread attention [1–5]. Cyanide and cyanide-containing compounds are currently extensively found in various areas of industrial manufacturing, including paint, electroplating, rubber, herbicides, and so on, causing CN⁻ to reach the organism through the drinkable water system [6–9]. In turn, cyanide is toxic and can cause damage to human health and the ecological environment [10–12]. However, the World Health Organization (WHO) specifies 1.9×10^{-6} mol/L as the permissible acceptable concentration of drinking water [13]. As a result, developing a quick, reliable, ultra-sensitive and selective detection method for CN⁻ is crucial for environmental science.

There are several methods for detecting CN^- , including electrochemical tests, colorimetric analyzers, and fluorescent probes [14–19]. Among these reported methods, fluorescent probes are regarded as the most promising detection methods due to their high sensitivity, high selectivity, low detection limits, simple operation, and online monitoring [20–22]. The significant advancements in the chemical characteristics and composition of fluorescent sensors make them more sensitive and selective than other tests [23–26]. For example, Li et al. synthesized a novel fluorescent probe built on tetraphenylethylene for detecting CN^{-} [27]. Wen et al. developed a triphenylamine-based sensor for the detection of CN^{-} and Hg^{2+} [28]. Therefore, the sensitivity and selective detection of fluorescent probes is an ongoing hot topic.

Currently, the majority of the fluorescent sensing probes are organic solvent-soluble rather than water-soluble [29–32]. However, CN^- often present in the aqueous phase of the industrial wastewater. Therefore, it is of great importance to design a fluorescence sensor capable of detecting CN^- in the aqueous phase. Since Tang and coworkers' discovery of the AIE phenomenon of organic molecules in 2001 [33], growing number of fluorescent probes with AIE effect has been published [34–37]. The construction of AIE fluorescent sensors for the identification of CN^- in the aqueous phase would become a current research trend relying on the special properties of AIE molecules [38, 39].

In this paper, sensor **1** was synthesized with triphenylamine (TPA) as an electron donor and two barbituric acids (BA) units as electron acceptors, while sensor **2** was formed with TPA as an electron donor and three BA units as electron acceptors (Scheme 1). The experimental results show that sensor **1** has good AIE and ICT effects in the DMSO-H₂O solution system, however, sensor **2** has weak ICT effects in the DMSO-H₂O solution system and therefore cannot detect CN⁻. Compared with

* Corresponding author. *E-mail address:* dqy1991@usst.edu.cn (Q. Deng).

https://doi.org/10.1016/j.dyepig.2021.109534

Received 28 April 2021; Received in revised form 27 May 2021; Accepted 3 June 2021 Available online 9 June 2021 0143-7208/© 2021 Elsevier Ltd. All rights reserved.



Scheme 1. The synthetic routes of sensor 1 and sensor 2.

the previously reported TPA fluorescent probe [28], sensor 1 has higher sensitivity to CN^- (LOD = 2.95×10^{-8} mol/L). Sensor 1 has an excellent selectivity and anti-interference capacity, and it has a well linear relationship with the CN⁻ concentration at 581 nm. NMR spectroscopy, HRMS, Job's plot analysis and DFT computation were utilized to study the sensing mechanism of sensor 1. Besides, we also prepared the detection test paper for CN⁻ based on sensor 1.

2. Material and methods

2.1. Chemicals and instruments

All reagents obtained from Sinopharm Chemical Reagent Co. Ltd. and Aladdin Reagent Shanghai Co. Ltd. are analytical grade without further purification in procedures except for special instructions. Anions $(F^-, Cl^-, Br^-, I^-, CO_3^{--}, NO_3, HSO_3, HSO_3, SO_4^{--}, H_2PO_4^{--}, HPO_4^{--}, AcO^{--}, OH^-, CN^{--})$ from their tetrabutylammonium salts were prepared, which was diluted to1.0 mM by deionized water to obtain the stock solution.

The sizes and morphologies of the aggregation states of sensor 1 and sensor $1+CN^-$ were observed in the scanning electron microscope (SEM, TESCAN). ¹H NMR and ¹³C NMR were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers, respectively. UV–Vis spectra and fluorescence spectra are recorded on a UV–Vis spectrophotometer (UV-3900, Hitachi, Japan) and fluorescence spectrometer (FL-7000, Hitachi, Japan), respectively. The pH data are obtained by a pH meter (pH400, Alalis Co. China). High-resolution mass spectra (HRMS) were obtained from Bruker solanX 70 FT-MS system.

2.2. Synthetic procedures

Synthetic procedures of the sensor 1. 4,4'-diformyltriphenylamine

was synthesized followed by Mallegol's procedure [40]. POCl₃ (9.5 mL, 101.9 mmol) was added dropwise at 0 °C under N₂ to DMF (7.3 mL, 93.8 mmol) and the reaction mixture was stirred for 1 h. Triphenylamine (1.0 g, 4.1 mmol) was added, and the resulting mixture was stirred at 95 °C for 4 h. After cooling to r. t., the mixture was poured into ice-water (200 mL), and basified with 1 M NaOH. After extraction with CH₂Cl₂ (200 mL), the organic layer was washed with water (3 × 50 mL), dried (Na₂SO₄) and filtered over a short pad of silica gel. 4,4'-diformyl-triphenylamine (brown solid, 85%): ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 9.90 (s, 2H), 7.78 (d, *J* = 8.7 Hz, 4H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.29–7.24 (m, 2H), 7.22–7.16 (m, 6H). ¹³C NMR (101 MHz, CDCl₃, 298 K): δ = 190.51, 151.99, 145.48, 131.29, 130.14, 128.49, 127.05, 126.25, 122.74.

Under nitrogen, a mixture of 4,4'-diformyltriphenylamine (0.3 g, 1.0 mmol) and BA (0.4 g, 3.1 mmol) in ethanol (10 mL) was refluxed for 4 h. The residue was purified using column chromatography on silica to afford the product as a red powder after vacuum drying at 50 °C overnight [41]. The sensor 1 (red solid, 91%): ¹H NMR (400 MHz, DMSO- d_6 , 298 K): $\delta = 11.31$ (s, 2H), 11.17 (s, 2H), 8.28 (d, J = 8.8 Hz, 4H), 8.19 (s, 2H), 7.48 (t, J = 7.7 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.25 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 8.7 Hz, 4H). ¹³C NMR (101 MHz, DMSO- d_6 , 298 K): $\delta = 164.27$, 162.48, 154.38, 150.62, 150.35, 145.00, 137.12, 130.83, 127.82, 127.42, 121.81, 116.44.

Synthetic procedures of the sensor 2. Tris (4-formylphenyl)amine was synthesized followed by Mallegol's procedure [40]. The 4, 4'-diformyltriphenylamine (0.3 g, 1.0 mmol) was added on an ice-cooled mixture of POCl₃ (3.0 mL, 32.2 mmol) and DMF (2.3 mL, 29.5 mmol). The resulting mixture was stirred at 95 °C for 1.5 h, and after cooling to r. t., poured into ice-water (100 mL), and basified with 1 M NaOH. After extraction with CH_2Cl_2 (100 mL), the organic layer was washed with water (3 × 50 mL) and dried (Na₂SO₄). After evaporation of the solvent,



Fig. 1. (a) Absorbance of the sensor 1 (1 × 10⁻⁵ mol/L) in DMSO/H₂O (v/v); (b) The fluorescence spectra of the sensor 1 (1 × 10⁻⁵ mol/L) in DMSO/H₂O (v/v) mixed solvent with varying f_w at $\lambda_{ex} = 365$ nm; (c) Sensor 1's fluorescent wavelength (red) and emission intensity (blue) against the f_w are plotted. (d) Absorbance of the sensor 2 (1 × 10⁻⁵ mol/L) in DMSO/H₂O (v/v); (e) The fluorescence spectra of the sensor 2 (1 × 10⁻⁵ mol/L) in DMSO/H₂O (v/v); (e) The fluorescence spectra of the sensor 2 (1 × 10⁻⁵ mol/L) in DMSO/H₂O (v/v); mixed solvent with varying f_w at $\lambda_{ex} = 365$ nm; (f) Sensor 2's fluorescent wavelength (red) and emission intensity (blue) against the f_w are plotted.

the crude product was purified by column chromatography (CH₂Cl₂) to a yellow solid. Tris (4-formylphenyl)amine (yellow solid, 80%): ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 9.95 (s, 3H), 7.85 (d, *J* = 8.6 Hz, 6H), 7.25 (d, *J* = 8.7 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃, 298 K): δ = 190.45, 151.17, 132.57, 131.48, 124.51.

Under nitrogen, a mixture of tris(4-formylphenyl)amine (0.2 g, 0.6 mmol) and BA (0.3 g, 2.3 mmol) in ethanol (10 mL) was refluxed for 4 h. The residue was purified using column chromatography on silica to afford the product as a red powder after vacuum drying at 50 °C overnight [41]. The sensor **2** (red solid, 82%): ¹H NMR (400 MHz, DMSO-*d*₆, 298 K): $\delta = 11.35$ (s, 2H), 11.30 (d, J = 6.9 Hz, 1H), 11.23 (d, J = 9.6 Hz, 2H), 11.17 (s, 1H), 8.28 (t, J = 7.2 Hz, 6H), 8.24–8.13 (m, 3H), 7.18 (t, J = 8.9 Hz, 5H), 7.04 (d, J = 8.8 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆, 298 K): $\delta = 164.11$, 162.37, 154.04, 150.62, 149.38, 136.84, 128.96, 123.86, 117.55.

2.3. Spectroscopic detections

A sensor **1** stock solution of 1×10^{-2} mol/L is prepared by DMSO and sensor 1. A series of 1×10^{-3} mol/L anionic stock solutions are obtained via different anions dissolved into deionized water. Except for special instructions, the typic fluorescence detection system with sensor 1 at 1 \times 10⁻⁵ mol/L is made from 0.01 mL TPEB stock solution, 0.09 mL DMSO, several anion stock solutions, dropped into the volumetric flask and added some deionized water to 10 mL. Meanwhile, the solution pH is adjusted to 7 by 0.01 mol/L hydrochloric acid solution and sodium hydroxide solution. The fluorescence emission spectra of all detection systems are recorded in the wavelength range from 400 to 800 nm under 365 nm excitation. In addition, the fluorescence spectra were measured more than 3 times, and the average values were used to determine the fluorescence intensity. The sensor 1+CN⁻: ¹H NMR (400 MHz, DMSO- d_6 , 298 K): $\delta = 9.08$ (s, 4H), 7.25 (dd, J = 18.1, 8.0 Hz, 6H), 6.98-6.91 (m, 3H), 6.89 (d, J = 8.5 Hz, 4H), 5.19 (s, 2H), 2.52-2.49 (m, 6H). ¹³C NMR (101 MHz, DMSO- d_6 , 298 K): $\delta = 163.62$, 152.38, 146.07, 133.99, 129.81, 128.70, 126.63, 123.86, 123.59, 122.75, 121.97, 81.50, 58.00.

2.4. Computational details

DFT and TD-DFT calculations of sensor 1 and sensor $1+CN^-$ are carried out in Gaussian 16 software package. The geometries of sensor 1 and sensor $1+CN^-$ are optimized by using density functional theory (DFT) calculations at the M06–2X/6–31 g(d) level of theory. Transition energy is calculated by using time-dependent density functional theory (TD-DFT). The binding pattern of sensor 1 with CN^- is further proposed from the calculation results using DFT/TDDFT.

2.5. Effect of pH on sensor 1

To investigate the effect of pH on the fluorescence properties of sensor 1 and sensor $1+CN^-$, the fluorescence spectra are measured at the same conditions shown in various acidity. The pH is adjusted by 0.01 mol/L sodium hydroxide and hydrochloric acid solution. Relevant data are recorded by the fluorescence spectrometer. In addition, the fluorescence spectra were measured more than 3 times, and the average values were used to determine the fluorescence intensity.

2.6. The determination of LOD

The detection limit (LOD) was determined according to formula (1) by emission data of sensor 1 upon gradual addition of CN^- .

$$LOD = 3\delta/S \tag{1}$$

where δ was the standard deviation of blank ample, S represented the absolute value of the slope between fluorescence intensity and CN^- concentration.

3. Results and discussion

3.1. The AIE effect of sensor 1 and sensor 2

Sensor 1 and sensor 2 are very soluble in the organic phase rather than the aqueous phase. We used DMSO/water as solvent systems in our quest for the best specific solvent for industrial application, and we



Fig. 2. Under sunlight and 365 nm UV light, color variations were caused by the addition of 2.0 equiv. of different anions to sensor **1** solution in 99% aqueous DMSO solution.

investigated the AIE behavior of sensor **1** and sensor **2** using UV–visible and fluorescence spectroscopy. As shown in Fig. 1a and d, sensor **1** and sensor **2** both have two absorption peaks in the UV–visible spectrum. The activated $\pi \rightarrow \pi^*$ electron transition of TPA and BA is primarily responsible for the absorption peak in the 350–400 nm region, while the intramolecular charge transfer (ICT) impact of TPA to BA is responsible for the absorption peak at 474 nm.

The addition of water to DMSO will facilitate aggregation of sensor 1 and sensor 2 as water is an undesirable solvent. The fluorescence variations of sensor 1 and sensor 2 are observed by modifying the DMSO to H₂O proportion in the solvent situation (Fig. 1b and e). The results show that sensor **1** (1 × 10⁻⁵ mol/L) has very weak fluorescence ($f_w = 0\%$) in pure DMSO under the irradiation of the 365 nm ultraviolet lamp. The enhancement of polarity when $f_w < 90\%$ leads to the ICT effect, so the fluorescence of sensor 1 will become very weak. However, when $f_w >$ 90%, sensor 1 aggregates, so it presents a fluorescence enhancement state. Besides, sensor 1 emits bright red fluorescence when $f_w = 90\%$ (Figure S1 in the ESI[†]). All these observations show that sensor 1 has AIE activity. According to related literature [42,43], as the proportion of water increases, the emission intensity of sensor 1 shifts to the long-wave direction, which may be caused by the electronic transition $(\pi - \pi^*)$ inside the sensor **1** (Fig. 1c). However, the fluorescence intensity of sensor 2 was weak in the DMSO-H₂O solution system and cannot be recognized by the machine. The possible reason was that sensor 2 has a locally symmetric molecular structure (three-arm BA units) and the ICT effects within the molecular structure cancel each other out, resulting in a significant decrease in the fluorescence intensity of sensor 2 compared to sensor 1 (two-arm BA units). In order to confirm the above point of view, we further studied the luminescence mechanism of sensor 2 in the DMSO-H₂O solution system and implemented it on the M06-2X/6-31G* level of the Gaussian 16 package. We found through calculations that the

electronic transition type of sensor **2** is HOMO to LUMO+1 (Figure S2 in the ESI†). Both sensor **1** and sensor **2** have charge separation, but the degree of charge separation of sensor **2** (f = 1.1645) is weaker than that of sensor **1** (f = 1.5774). It is speculated that the addition of the third BA may cause the local symmetry of sensor **2** molecule, which weakens the ICT effect, which leads to weaker fluorescence intensity. Therefore, we selected sensor **1** with good AIE and ICT effects as the fluorescence sensor for the detection of CN⁻.

3.2. The sensing performance of sensor 1

3.2.1. Selectivity and anti-interference of sensor 1

The fluorescence spectra of sensor 1 solution $(1 \times 10^{-5} \text{ mol/L})$ ($f_w = 99\%$) were documented with different anions (F⁻, Cl⁻, Br⁻, I⁻, CO₃²⁻, NO₃⁻, HCO₃⁻, HSO₃⁻, SO₄²⁻, H₂PO₄⁻, HPO₄²⁻, AcO⁻, OH⁻, CN⁻) (Fig. 2). Except for CN⁻, the tested anion solution is colorless under sunlight and pink fluorescence under ultraviolet light (365 nm). Only the sensor with CN⁻ added appears transparent under sunlight and non-fluorescence under 365 nm UV light. The results of the fluorescence intensity test in Fig. 3a also correspond to corresponding observations. According to these observations, sensor 1 has high selectivity for CN⁻. The results showed that the competing anions had little effect on the color of the solution.

We performed an anti-interference test on sensor **1** by adding 2.0 equivalents of different anions to DMSO/H₂O ($f_w = 99\%$) to further investigate its usefulness as an ion-selective fluorescence sensor for CN⁻ (Fig. 3b). But for the decline in the fluorescence intensity of OH⁻, the inclusion of other anions has little effect on the fluorescence intensity in the single intervening ion system. The fluorescence intensity in the coexistence system of disturbance ions system with CN⁻ is significantly lower than in the single intervening ion system. The results of the preceding study indicate that sensor **1** has strong selectivity and stable anti-interference capability for CN⁻.

3.2.2. Sensing ability of sensor 1 for CN^{-}

The scanning electron microscope (SEM) was utilized to study the aggregation state of sensor 1 after adding CN^- to the solution. As depicted in Fig. 4, sensor 1 had a granular morphology with a rough surface before the addition of CN^- and an aggregated form with a smooth surface after the addition of CN^- .

We further investigated the sensing performance of sensor 1 for different CN^- concentrations in 99% DMSO aqueous solution by fluorescence emission spectroscopy. As seen in Fig. 5a, the fluorescence intensity at 581 nm steadily decreased with increasing CN^- concentration (0.1–2.0 equiv.) due to the interruption of ICT of sensor 1. Fig. 5b shows the fluorescence intensity of sensor 1 at 581 nm as a function of



Fig. 3. (a) The fluorescence spectra of sensor 1 (1 × 10⁻⁵ mol/L) with multiple anions (2.0 equiv.) in 99% aqueous DMSO solution. (b) Competitive experiments in the sensor 1+CN⁻ system with interfering anions at $\lambda_{ex} = 365$ nm.



Fig. 4. The SEM images of sensor 1 (a, b) and sensor $1+CN^{-}$ (c, d).



Fig. 5. (a) The fluorescence spectra of sensor 1 (1 \times 10⁻⁵ mol/L) with steadily rising concentrations of CN⁻ (0–2.0 equiv.) in $f_w = 99\%$; (b) The detection limit of sensor 1 for CN⁻ (0–2.0 equiv.).

 $\rm CN^-$ concentration. The fluorescence intensity gradually decreases as the CN- concentration rises from 0 to 1.6×10^{-5} mol/L, with a strong linear relationship (y = 526.94–27.50x, R^2 = 0.998). As the concentration of CN^- > 1.6×10^{-5} mol/L, the fluorescence intensity remains almost constant, meaning that CN^- is surplus in the solution. According to equation 38/S, the LOD of sensor 1 for CN^- was determined to be

 2.95×10^{-8} mol/L (0–1.6 $\times 10^{-5}$ mol/L), which is significantly lower than the permitted amount of CN $^-$ in drinking water (1.9 $\times 10^{-6}$ mol/L). The conclusions demonstrate that the designed sensor 1 has enough sensitivity to detect CN $^-$ conveniently.



Fig. 6. (a) The influence of pH on the fluorescent intensity of the sensor 1 and sensor 1+CN⁻; (b) The time-dependent fluorescent intensity of sensor 1 toward CN⁻.



Fig. 7. 1 H NMR spectra of the sensor 1 and sensor 1+CN⁻.

3.2.3. Analysis of pH and reaction time toward sensor system

We used fluorescence spectroscopy to study the stability of sensor 1 and sensor $1+CN^-$ under different pH conditions (Fig. 6a). When the pH changes from 1.0 to 9.0, sensor 1 has a stable emission intensity, and as the pH rises above 9, the fluorescence intensity diminishes sharply. After adding CN^- to sensor 1, the fluorescent intensity is relatively stable in the pH range of 4.0–9.0. The fluorescence intensity changed considerably in the pH range of 5.0–8.0 before and after the addition of CN^- , meaning that sensor 1 can detect CN^- in the pH range and has a significant fluorescence response. In the following experimental testing, we preferred pH = 7 as the experimental condition.

We studied the fluorescence spectrum of sensor $1+CN^-$ over time (Fig. 6b). The fluorescence intensity of sensor $1+CN^-$ decreased rapidly after the addition of CN^- for the first 5 min, then stayed nearly constant for the next 30 min. The results show that at room temperature, the reaction time of sensor $1+CN^-$ can be completed within 5 min. Therefore, the swift response of sensor 1 to CN^- provides a promising application.

3.3. The detection mechanism of sensor 1

¹H NMR and Job's titration were used to investigate the process of



Fig. 8. Job's plot for sensor 1 in $f_{\rm w}=$ 99% (The total concentration was 1 \times 10⁻⁵ mol/L).

sensor 1 detecting CN⁻. In the ¹H NMR spectrum (Fig. 7), sensor 1 shows two proton peaks at 11.17 ppm and 8.19 ppm, respectively, corresponding to the H_a of BA and H₁ of the vinylidene. As CN⁻ were applied to sensor 1, the peak at H1 (8.19 ppm) vanished entirely, whereas a new peak at 5.19 ppm appeared, attributed to H₂. Simultaneously, the H_a (11.17 ppm) moved to the low-frequency magnetic field H_b (9.08 ppm). From Fig. 7, we can observe that the H_0 peak attributed to the BA group of sensor $1+CN^{-}$ is submerged by the water peak (3.34 ppm). Besides, the initial molecular structure is broken by the addition of CN-, and some of the proton peaks attached to the aromatic group move to a high field. The ICT between the electron donor (TPA) and the electron acceptor (BA) is blocked by CN⁻, which has nucleophilicity and attacks the C = C bond of sensor **1**. To further determine the detection mechanism, Job's titration experiment was conducted on sensor 1. As shown in Fig. 8, the stoichiometric ratio of sensor 1 to CN⁻ is 1–2. As a result, sensor 1 detects CN⁻ since it is a strong nucleophilicity that attacks vinylidene.

3.4. Theoretical calculations

The density functional theory (DFT) and time-dependent density functional theory (TDDFT) were used to compute the composition, electron density, and electronic structure of sensor 1 and sensor 1+ CN⁻ by the M06–2X/6-31G* level of the Gaussian 16 package to investigate

the intrusion detection between sensor 1 and CN^{-} [44,45].

Fig. 9 depicts the optimum structures of sensor 1 and sensor $1+CN^-$. By sp² hybridization of vinyl, the sensor 1 molecule exhibits a rigid planar configuration. Sensor $1+CN^-$, on the other hand, shows the non-planar confirmation through the sp³ hybridization of the carbon-carbon bond. The results show that the apparent structural difference between sensor 1 and sensor $1+CN^-$ leads to significant changes in the conjugate system, which leads to changes in its fluorescence properties.

Besides, Fig. 9 also lists the TD-DFT calculations. As an electron acceptor, the BA fragment has a strong electron-withdrawing ability in sensor 1. The electron distribution of HOMO in sensor 1 molecule was primarily distributed in triphenylamine and part of barbiturate, while that of LUMO was concentrated in the whole barbiturate and part of triphenylamine. However, for sensor $1+CN^-$ molecules, the electron distribution of LUMO and HOMO is limited to the unit, which means that the ICT phase is interrupted, resulting in a significant decrease in fluorescence. The results indicate that the addition of CN^- has an appreciable impact on the phase change performance. The disruption of the ICT mechanism is caused by the transition in the conjugate scheme, which is compatible with our previous discussion. Furthermore, the rupture of the π -conjugated structure results in a higher HOMO-LUMO energy difference for sensor $1+CN^-$ (6.91 eV) than sensor 1 (4.57 eV). As a result, theoretical calculations indicated that CN^- attacked the C =







Fig. 9. Calculation of HOMO and LUMO electron distributions for sensor 1 and sensor 1+CN⁻.

Table 1

Sensor 1 compared to other previously recorded probes.

Fluorescence sensors	Solvent system (v/v)	$LOD/mol L^{-1}$	References
	THF/H ₂ O (9:1)	2.1×10^{-6}	[46]
	H ₂ O/THF (9:1)	3.83×10^{-6}	[47]
	THF/H ₂ O (1985:15)	3.9×10^{-8}	[48]
$\bigcup_{i=1}^{OH} \bigcup_{i=1}^{CN} \bigcup_{$	DMSO/H ₂ O (7:3)	1.4×10^{-7}	[49]
	H ₂ O/THF (8:2)	$1.3 imes 10^{-7}$	[50]
	DMSO/H ₂ O (1:99)	$4.0 imes10^{-8}$	[28]
Sensor 1	DMSO/H ₂ O (1:99)	$2.95 imes 10^{-8}$	This work

C bond and interrupted the conjugation structure in the molecule, resulting in no ICT in sensor $1+CN^{-}$.

3.5. Test strips based on sensor 1

We prepared sensor 1 test strips to make the detection of CN⁻ easier. Sensor 1 (100 μ M) was applied on filter paper and dried in an oven to obtain test strips, and then OH⁻, CN⁻ and HCO₃²⁻ ($f_w = 100\%$) were added dropwise to the test strips to detect the anions. Fig. 10 reveals that when CN⁻ (50 μ M) is added dropwise to the filter paper, the fluorescence of the test strip based on sensor 1 varies from red to light blue under 365 nm UV light, which is readily visible with the naked eye. The fluorescence intensity of the test paper with drops of OH⁻ (50 μ M) and HCO₃²⁻ (50 μ M) was marginally weakened and improved, respectively, in contrast to the sensor 1-based test strips, which was compatible with the above fluorescence sensors performance. These observations showed that the sensor 1-based test strips can be used to detect CN⁻ in a qualitative manner by colorimetric method.

3.6. Sensor 1 compared to other previously recorded probes

According to standards of WHO on the cyanide concentration in

drinking water, the LOD of the first and second probes did not fulfill the actual detection demand, as shown in Table 1 [46,47]. The third and fourth probes have excellent selectivity and anti-interference performance for CN^- , but there are disadvantages such as poor linear fit and long-time process [48,49]. Despite the good linear fit of the last two probes, their LOD was poor compared with this work [28,50]. In contrast, sensor 1 synthesized in this work has the advantages of excellent selectivity, easy operation, and outstanding LOD.

4. Conclusions

To summarize, we have successfully produced a novel sensor 1 for the detection of CN⁻ that uses TPA as an electron donor and two BA as electron acceptors. The fluorescent sensor 1 has excellent AIE activity in DMSO/H₂O mixing system. Besides, the detection limit of sensor 1 for CN⁻ is extremely low (LOD = 2.95×10^{-8} mol/L), and it has the advantages of strong anti-interference ability, excellent selectivity, and easy operation. Theoretical calculations show that the sensing mechanism of sensor 1 is due to the addition of CN⁻, which interrupts the conjugated structure in the molecule and leads to the blocking of ICT. Sensor 1-based test strips can be used to detect CN⁻ in a qualitative manner by colorimetric method. Thus, sensor 1 offers a promising alternative for the detection of CN^- in water.

CRediT authorship contribution statement

Bin Zuo: Methodology, Writing – original draft. Lian Liu: Data curation, Software. Xicheng Feng: Investigation. Denghui Li: Validation. Wanfang Li: Investigation. Mingxian Huang: Investigation. Qinyue Deng: Supervision, Writing – review & editing.

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.

Acknowledgment

Financial support from the Shanghai Young Teachers Training and Support Program (No. slg20035), Shanghai Engineering Research Center for Food Rapid Detection and the College of Science, University of Shanghai for Science and Technology is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2021.109534.

References

- [1] Cheng D, Huu Hao N, Guo W, Chang SW, Dinh Duc N, Liu Y, Wei Q, Wei D. A critical review on antibiotics and hormones in swine wastewater: water pollution problems and control approaches. J Hazard Mater 2020;387:121682. https://doi. org/10.1016/j.jhazmat.2019.121682.
- [2] Mahmoud ME, Amira MF, Seleim SM, Mohamed AK. Amino-decorated magnetic metal-organic framework as a potential novel platform for selective removal of chromium (VI), cadmium (II) and lead (II). J Hazard Mater 2020;381:120979. https://doi.org/10.1016/j.jhazmat.2019.120979.
- [3] Zwolak I. The role of selenium in arsenic and cadmium toxicity: an updated review of scientific literature. Biol Trace Elem Res 2020;193(1):44–63. https://doi.org/ 10.1007/s12011-019-01691-w.
- [4] Zuo B, Deng Q, Shao H, Cao B, Fan Y, Li W, Huang M. Fe₃O₄@Mesoporous-SiO₂@ Chitosan@Polyaniline core-shell nanoparticles as recyclable adsorbents and reductants for hexavalent chromium. ACS Appl. Nano Mater. 2021;4(2):1831–40. https://doi.org/10.1021/acsanm.0c03235.
- [5] Zuo B, Li W, Wu X, Wang S, Deng Q, Huang M. Recent advances in the synthesis, surface modifications and applications of core-shell magnetic mesoporous silica nanospheres. Chem Asian J 2020;15(8):1248–65. https://doi.org/10.1002/ asia.202000045.
- [6] Sharma M, Akhter Y, Chatterjee S. A review on remediation of cyanide containing industrial wastes using biological systems with special reference to enzymatic degradation. World J Microbiol Biotechnol 2019;35(5):70. https://doi.org/ 10.1007/s11274-019-2643-8.
- [7] Yang W, Liu G, Chen Y, Miao D, Wei Q, Li H, Ma L, Zhou K, Liu L, Yu Z. Persulfate enhanced electrochemical oxidation of highly toxic cyanide-containing organic wastewater using boron-doped diamond anode. Chemosphere 2020;252:126499. https://doi.org/10.1016/j.chemosphere.2020.126499.
- [8] Kongsawadworakul P, Viboonjun U, Romruensukharom P, Chantuma P, Ruderman S, Chrestin H. The leaf, inner bark and latex cyanide potential of Hevea brasiliensis: evidence for involvement of cyanogenic glucosides in rubber yield. Phytochemistry 2009;70(6):730–9. https://doi.org/10.1016/j. phytochem.2009.03.020.
- [9] Grossmann K. Auxin herbicides: current status of mechanism and mode of action. Pest Manag Sci 2010;66(2):113–20. https://doi.org/10.1002/ps.1860.
- [10] Wan H, Xu Q, Gu P, Li H, Chen D, Li N, He J, Lu J. ATE-based fluorescent sensors for low concentration toxic ion detection in water. J Hazard Mater 2021;403: 123656. https://doi.org/10.1016/j.jhazmat.2020.123656.
- [11] Isigonis P, Critto A, Zabeo A, Ciffroy P. AMORE" decision support system for probabilistic ecological risk assessment-Part II: effect assessment of the case study on cyanide. Sci Total Environ 2019;648:1665–72. https://doi.org/10.1016/j. scitotenv.2018.08.227.
- [12] Madeira D, Andrade J, Leal MC, Ferreira V, Rocha RJM, Rosa R, Calado R. Synergistic effects of ocean warming and cyanide poisoning in an ornamental tropical reef fish. Front. Mar. Sci. 2020;7:246. https://doi.org/10.3389/ fmars.2020.00246.
- [13] Sobsey MD, Bartram S. Water quality and health in the new millennium: the role of the World health organization guidelines for drinking-water quality. Forum Nutr 2003;56:396–405.

- [14] Chen Z, Wagner J, Turq V, Hillairet J, Taberna P-L, Laloo R, Duluard S, Bernard J-M, Song Y, Yang Q, Lu K, Cheng Y. Surfactant-assisted electrodeposition of Au-Co/ WS2 self-lubricating coating from WS2 suspended cyanide electrolyte. J Alloys Compd 2020;829:154585. https://doi.org/10.1016/j.jallcom.2020.154585.
- [15] Gupta S, Mittal SK, Chhibber M. Triphenyl ether amide as a probe for electrochemical and optical sensing of copper, cyanide and arginine. J Electrochem Soc 2020;167(16):167506. https://doi.org/10.1149/1945-7111/abcbb0.
- [16] Tang L, Zhou L, Liu A, Yan X, Zhong K, Liu X, Gao X, Li J. A new cascade reactionbased colorimetric and fluorescence "turn on" dual-function probe for cyanide and hydrazine detection. Dyes Pigments 2021;186:109034. https://doi.org/10.1016/j. dyepig.2020.109034.
- [17] Wu Q, Wang S, Hao E, Jiao L. Highly selective, colorimetric probes for cyanide ion based on beta-formylBODIPY dyes by an unprecedented nucleophilic addition reaction. Spectrochim Acta A 2021;247:119102. https://doi.org/10.1016/j. saa.2020.119102.
- [18] Poongodi K, Kumar PS, Shanmugapriya R, Nandhini C, Elango KP. 2-Aminophenols based Schiff bases as fluorescent probes for selective detection of cyanide and aluminium ions-Effect of substituents. Spectrochim Acta A 2021;249:119288. https://doi.org/10.1016/j.saa.2020.119288.
- [19] Yue Y, Huo F, Yin C, Chao J, Zhang Y. A new "donor-two-acceptor" red emission fluorescent probe for highly selective and sensitive detection of cyanide in living cells, Sensor. Actuat. B-Chem. 2015;212:451–6. https://doi.org/10.1016/j. snb.2015.02.074.
- [20] Pak YL, Swamy KMK, Yoon J. Recent progress in fluorescent imaging probes. Sensors 2015;15(9):24374–96. https://doi.org/10.3390/s150924374.
- [21] Kaur M, Choi DH. Diketopyrrolopyrrole: brilliant red pigment dye-based fluorescent probes and their applications. Chem Soc Rev 2015;44(1):58–77. https://doi.org/10.1039/c4cs00248b.
- [22] Lin Q, Liu X, Chen P, Wei T, Zhang Y. Colorimetric and fluorescent cyanide anion sensors. Prog Chem 2013;25(12):2131–46.
- [23] Udhayakumari D. Chromogenic and fluorogenic chemosensors for lethal cyanide ion. A comprehensive review of the year 2016. Sensor Actuator B Chem 2018;259: 1022–57. https://doi.org/10.1016/j.snb.2017.12.006.
- [24] Wang F, Wang L, Chen X, Yoon J. Recent progress in the development of fluorometric and colorimetric chemosensors for detection of cyanide ions. Chem Soc Rev 2014;43(13):4312–24. https://doi.org/10.1039/c4cs00008k.
- [25] Ashton TD, Jolliffe KA, Pfeffer FM. Luminescent probes for the bioimaging of small anionic species in vitro and in vivo. Chem Soc Rev 2015;44(14):4547–95. https:// doi.org/10.1039/c4cs00372a.
- [26] Jun ME, Roy B, Ahn KH. Turn-on" fluorescent sensing with "reactive" probes. Chem Commun 2011;47(27):7583–601. https://doi.org/10.1039/c1cc00014d.
- [27] Li D, Ma J, Wang H, Liu L, Yang H. A novel barbituric-based fluorescent probe with aggregation induced emission for the highly sensitive ratiometric detection of cyanide anions. J Mater Sci 2021;56(2):1373–85. https://doi.org/10.1007/ s10853-020-05377-w.
- [28] Wen X, Yan L, Fan Z. A novel AIE active NIR fluorophore based triphenylamine for sensing of Hg²⁺ and CN and its multiple application. Spectrochim Acta A 2020; 241:118664. https://doi.org/10.1016/j.saa.2020.118664.
- [29] Erdemir S, Malkondu S. On-site and low-cost detection of cyanide by simple colorimetric and fluorogenic sensors: smartphone and test strip applications. Talanta 2020;207:120278. https://doi.org/10.1016/j.talanta.2019.120278.
- [30] Li J, Yuan S, Qin J-S, Pang J, Zhang P, Zhang Y, Huang Y, Drake HF, Liu WR, Zhou H-C. Stepwise assembly of turn-on fluorescence sensors in multicomponent metal-organic frameworks for in vitro cyanide detection. Angew Chem Int Ed 2020; 59(24):9319–23. https://doi.org/10.1002/anie.202000702.
- [31] Ma X-Q, Wang Y, Wei T-B, Qi L-H, Jiang X-M, Ding J-D, Zhu W-B, Yao H, Zhang Y-M, Lin Q. A novel AIE chemosensor based on quinoline functionalized Pillar 5 arene for highly selective and sensitive sequential detection of toxic Hg²⁺ and CN[°]. Dyes Pigments 2019;164:279–86. https://doi.org/10.1016/j.dyepig.2019.01.049.
- [32] Moghadam FN, Amirnasr M, Meghdadi S, Eskandari K, Buchholz A, Plass W. A new fluorene derived Schiff-base as a dual selective fluorescent probe for Cu²⁺ and CN⁻. Spectrochim Acta A 2019;207:6–15. https://doi.org/10.1016/j.saa.2018.08.058.
- [33] Hong Y, Lam JWY, Tang BZ. Aggregation-induced emission. Chem Soc Rev 2011; 40(11):5361–88. https://doi.org/10.1039/c1cs15113d.
- [34] Chua MH, Shah KW, Zhou H, Xu J. Recent advances in aggregation-induced emission chemosensors for anion sensing. Molecules 2019;24(15):2711. https:// doi.org/10.3390/molecules24152711.
- [35] Ghosh T, Mitra S, Maity SK, Maiti DK. Halogen-bonded bithiophene-based nanofibers for luminescent sensing. ACS Appl. Nano Mater. 2020;3(4):3951–9. https://doi.org/10.1021/acsanm.0c00886.
- [36] Santhiya K, Sen SK, Natarajan R, Murugesapandian B. Multifunctional behavior of bis-acylhydrazone: real-time detection of moisture in organic solvents, halochromism and aggregation induced emission. Dyes Pigments 2021;185: 108891. https://doi.org/10.1016/j.dyepig.2020.108891.
- [37] Wang Y, Liu H, Chen Z, Pu S. Aggregation-induced emission enhancement (AIEE)active tetraphenylethene (TPE)-based chemosensor for CN⁻. Spectrochim Acta A 2021;245:118928. https://doi.org/10.1016/j.saa.2020.118928.
- [38] Liu Y, Qin A, Tang BZ. Polymerizations based on triple-bond building blocks. Prog Polym Sci 2018;78:92–138. https://doi.org/10.1016/j.progpolymsci.2017.09.004.
- [39] Bozkurt S, Halay E. Synthesis, application and AIE properties of novel fluorescent tetraoxocalix 2 arene 2 triazine: the detection of a hazardous anion, cyanate. Tetrahedron 2020;76(46):131647. https://doi.org/10.1016/j.tet.2020.131647.
- [40] Mallegol T, Gmouh S, Meziane MAA, Blanchard-Desce M, Mongin O. Practical and efficient synthesis of tris(4-formylphenyl)amine, a key building block in materials chemistry. Synthesis-Stuttgart 2005;11:1771–4.

B. Zuo et al.

- [41] Shi W, Zhao S, Su Y, Hui Y, Xie Z. Barbituric acid-triphenylamine adduct as an AIEE-type molecule and optical probe for mercury(II). New J Chem 2016;40(9): 7814–20. https://doi.org/10.1039/c6nj00894a.
- [42] Sun T, Niu Q, Li Y, Li T, Hu T, Wang E, Liu H. A novel oligothiophene-based colorimetric and fluorescent "turn on" sensor for highly selective and sensitive detection of cyanide in aqueous media and its practical applications in water and food samples. Sensor Actuator B Chem 2018;258:64–71. https://doi.org/10.1016/ j.snb.2017.11.095.
- [43] Zou Q, Tao F, Wu H, Yu WW, Li T, Cui Y. A new carbazole-based colorimetric and fluorescent sensor with aggregation induced emission for detection of cyanide anion. Dyes Pigments 2019;164:165–73. https://doi.org/10.1016/j. dyepig.2019.01.023.
- [44] Dennington RK, Todd A, Millam JM. KS GaussView, vol. 6. Shawnee Mission: Semichem Inc.; 2016.
- [45] Frisch MJ, Trucks GW, Schlegel HB, et al, Gaussian 16 rev. A.03, Wallingford.
- [46] Chen K-Y, Lin W-C. A simple 7-azaindole-based ratiometric fluorescent sensor for detection of cyanide in aqueous media. Dyes Pigments 2015;123:1–7. https://doi. org/10.1016/j.dyepig.2015.07.012.

- [47] Li Y, Gu Z, He T, Yuan X, Zhang Y, Xu Z, Qiu H, Zhang Q, Yin S. Terpyridyl-based triphenylamine derivatives with aggregation-induced emission characteristics for selective detection of Zn²⁺, Cd²⁺ and CN⁻ ions and application in cell imaging. Dyes Pigments 2020;173:107969. https://doi.org/10.1016/j.dyepig.2019.107969.
- [48] Xie Z, Kong X, Feng L, Ma J, Li Y, Wang X, Bao W, Shi W, Hui Y. A novel highly selective probe with both aggregation-induced emission enhancement and intramolecular charge transfer characteristics for CN⁻ detection. Sensor Actuator B Chem 2018;257:154–65. https://doi.org/10.1016/j.snb.2017.10.167.
- [49] Malkondu S, Erdemir S, Karakurt S. Red and blue emitting fluorescent probe for cyanide and hypochlorite ions: biological sensing and environmental analysis. Dyes Pigments 2020;174:108019. https://doi.org/10.1016/j.dyepig.2019.108019.
- [50] Zhai B, Hu Z, Peng C, Liu B, Li W, Gao C. Rational design of a colorimetric and fluorescence turn-on chemosensor with benzothiazolium moiety for cyanide detection in aqueous solution. Spectrochim Acta A 2020;224:117409. https://doi. org/10.1016/j.saa.2019.117409.