Phenanthroimidazole and dicyanovinyl-substituted triphenylamine for the selective detection of CN-: DFT calculations and practically applications



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Phenanthroimidazole and dicyanovinyl-substituted triphenylamine for the selective detection of CN⁻: DFT calculations and practically applications

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Graphical Abstract



Highlights

- Cyanide selective triphenylamine and phenanthroimidazole based a probe (TPMN) were developed
- **TPMN** indicated high selectivity and sensitivity for CN⁻ in the presence of most anions
- The limits of detection of **TPMN** for sensing CN^{-} is down to 0.23 μM
- The practical performance of **TPMN** was successfully observed on the TLC kits and water samples

Abstract

A novel CN⁻ selective fluorescent turn-on sensor (TPMN) possessing triphenylamine and phenanthroimidazole as signaling units and dicyanovinyl unit for the binding site was

designed and synthesized. TPMN exhibited a drastic change in its emission spectra with about 13-fold fluorescence enhancement when treated with CN^- , while other tested anions could not arouse the fluorescence enhancement. The experimental and theoretical calculation results showed that this increase in fluorescence intensity of TPMN in presence of CN^- is due to the large decrease in the ICT effect by the addition of CN^- ion to β -carbon of the dicyanovinyl moiety. TPMN could selectively detect CN^- with a detection limit of 0.23 μ M among the common anions. The CN^- -binding mode was well-characterized to be 1:1 by using Job's plot with an association constant of 5.36 (log*K*_a). Besides, the possible utilization of TPMN was successively tested in water samples and test kits.

Keywords: Triphenylanime, phenanthroimidazole, cyanide, fluorescent

1. Introduction

Cyanide (CN-) is one of the highly toxic species in environmental and biological systems due to its inhibition of cellular respiration [1]. In addition to presence in numerous foodstuffs and plants, cyanide is generally used in numerous chemical processes, such as metal plating and mining, medicines, the plastic-based materials and fertilizers [2]. Because the maximum permissive level of CN- in drinking water is as low as 1.9 μ M (WHO) [3], it is extremely necessary to efficiently and safely monitor a residual concentration of cyanide. Unlike other known analytical methods, chromogenic and fluorogenic sensors for the detection of cyanide by the naked eye have remarked much interest in consequence of the easy detection, fast usage, low cost, high sensitivity and remote control [4, 5].

Many strategies for detecting as fluorometric and colorimetric of CN– have been reported in recent years, involving the mechanism of coordination [6, 7], CdSe quantum dots [8, 9], the displacement approach [10], hydrogen-bond interactions [11], deprotonation [12], and nucleophilic addition reactions [13-15]. Among these methods, the nucleophilic addition reaction of CN- induces the formation of the new covalent bond and indicates high selectivity, anti-interference ability [16]. Some of these chemosensors have high limits of detection or show only moderate selectivity towards cyanide and, in some cases, cyanide cannot be determined in aqueous solution. Thus, fluorescent and colorimetric sensors with a low detection limit, high sensitivity, and selectivity for CN- in aqueous solutions are still needed. In the present study, we have synthesized a novel probe (TPMN) with common $D-\pi$ -A

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structural, which contain dicyanovinyl group as electron acceptor (A), and triphenylamine and phenanthroimidazole groups as the electron donor (D). Upon the nucleophilic Michael addition of cyanide anion to the dicyanovinyl unit, TPMN indicated good selectivity, sensitivity and short response time in MeCN/H₂O (v/v, 9/1) towards CN^- due to inhibited ICT effect.

2. Experimental

2.1. Materials and methods

Some materials such as triphenylamine, malononitrile, 9,10-phenanthrenequinone, TFA (trifluoroacetic acid) and HMTA (hexamethylenetetramine) were obtained from Sigma-Aldrich and ACROS. ¹H, ¹³C, and APT NMR analysis were carried out in DMSO- d_6 on a Bruker 400 MHz spectrometer. The fluorescence and UV-vis spectra were measured using a Perkin Elmer LS 55 and a Shimadzu 1280 spectrophotometer, respectively. Also, FTIR analysis were realized on a Bruker FTIR instrument. The excitation wavelength for fluorescence measurements was 390 nm.

2.2. Synthesis

2.2.1. N-(4-(1H-phenanthro[9,10-d]imidazol-2-yl)phenyl)-4-(1H-phenanthro[9,10-d]imidazol-2-yl)-N-phenylaniline (2)

For the synthesis of compound **2**, triphenylamine-dialdehyde derivative (1) was firstly synthesized via Vilsmeier-Haack reaction by using POCl₃ in DMF [17]. Then, a solution of compound **1** (300 mg, 1.0 mmol), 9,10-Phenanthrenequinone (420 mg, 2.0 mmol) and ammonium acetate (310 mg, 4.0 mmol) in acetic acid (20 mL) was refluxed for 6h. At the end of this period, the produced beige solid was filtered, and dried to give **2**. Yield: 84%; Mp > 350 °C ; ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.40 (br s, 2H, NH), 8.85 (d, 4H, *J*=8.62 Hz, ArH), 8.58 (d, 4H, *J*=8.62 Hz, ArH), 8.29 (d, 4H, *J*=8.71 Hz, ArH), 7.74 (d, 4H, *J*=7.68 Hz, ArH), 7.63 (d, 4H, *J*=7.68 Hz, ArH), 7.44 (t, 2H, *J*=8.06 Hz, ArH), 7.30 (d, 4H, *J*=7.68 Hz, ArH), 7.21-7.25 (m, 3H, ArH).

2.2.2. 4-(bis(4-(1H-phenanthro[9,10-d]imidazol-2-yl)phenyl)amino)benzaldehyde (3)

To solution of 2 (500 mg, 0.74 mmol) in TFA (50 mL), HMTA (620 mg, 4.44 mmol) was added under stirring. The resulting mixture was refluxed for 24 h to complete the reaction. Then, a solution of HCl (1.0 M, 100 mL) was interacted with this reaction mixture.

After the stirring for 1 h, the dark green colored product was precipitated. The filtered **3** was then recrystallized from ethanol. Yield: 67%; Mp:282-284 °C; FTIR: 1660 cm⁻¹ (CHO); ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.89 (s, 1H, CHO), 8.86 (d, 4H, *J*=8.30 Hz, ArH), 8.56 (d, 4H, *J*=8.30 Hz, ArH), 8.33 (d, 4H, *J*=8.41 Hz, ArH), 7.89 (d, 2H, *J*=8.73 Hz, ArH), 7.75 (d, 4H, *J*=7.35 Hz, ArH), 7.67 (t, 4H, *J*=7.35 Hz, ArH), 7.42 (d, 4H, *J*=8.60 Hz, ArH), 7.26 (d, 2H, *J*=8.73 Hz, ArH).

2.2.3.2-(4-(bis(4-(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)phenyl)amino)benzylidene) malononitrile (TPMN)

TPMN was obtained by Knoevenagel condensation reaction between 3 and malononitrile. For this, a solution of **3** (352 mg, 0.5 mmol) and malononitrile (33 mg, 0.5 mmol) in DMF (5.0 mL) was stirred in presence of Zn(OAc)₂·2H₂O (110 mg, 0.5 mmol) at room temperature. The color of the reaction mixture turned from light yellow to red in this period. After 2h, the reaction mixture was interacted with water (20 mL), and stirred for 1h. The product TPMN precipitated as red power was filtered, and then dried. Yield: 90%; Mp:255-257 °C; FTIR: 2220 cm⁻¹ (CN); ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.50 (br s, 2H, NH), 8.82 (d, 4H, *J*=8.71 Hz, ArH), 8.56 (d, 4H, *J*=7.68 Hz, ArH), 8.37 (d, 4H, *J*=8.36 Hz, ArH), 8.22 (s, 1H, C=CH), 7.84 (d, 2H, *J*=8.85 Hz, ArH), 7.72 (t, 4H, *J*=7.71 Hz, ArH), 7.61 (t, 4H, *J*=7.71 Hz, ArH), 7.43 (d, 4H, *J*=8.51 Hz, ArH), 7.10 (d, 2H, *J*=8.85 Hz, ArH). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 162.77, 159.84, 152.47, 148.88, 146.18, 133.46, 128.42, 128.14, 127.65, 126.80, 125.89, 124.71, 124.43, 122.44, 120.68, 115.67, 114.70, 75.86; Anal. Calcd for C₅₂H₃₁N₇ (753.26): C, 82.85; H, 4.15; N, 13.01. Found: C, 83.01; H, 4.22; N, 13.15.

2.3. Analytical measurements and theoretical calculations

The tetrabutylammonium forms of anions (F⁻, Cl⁻, Br⁻, I⁻, CN⁻, NO₃⁻, NO₂⁻, N₃⁻, HSO₄⁻, H₂PO₄⁻, ClO⁻, AcO⁻, OH⁻, SO₄²⁻, SCN⁻) were used to prepare their solutions (10.0 mM) in pure water. A stock solution (10 mM) of TPMN was prepared in DMSO. Then, it was diluted to 10 μ M and 20 μ M with MeCN/H₂O (9/1, v/v) for fluorescence and UV-vis studies, respectively. To perform the fluorescence and UV-vis titration experiments, the anion solutions were gradually added to a 3.0 mL solution of TPMN by using a micro-pipette. The obtained titration results were used in the determination of association constant (logK) and detection limit (DL) values. ¹H NMR titration experiments were realized by addition of CN⁻ (0.0, 0.5, 1.0, and 1.5 equiv.) to a solution of TPMN (0.079 M) in DMSO-*d*₆. Moreover, the nature of the sensing mechanism between TPMN with CN⁻ was determined by molecular

modeling. The density functional theory (DFT) calculations were accomplished for optimization of TPMN and TPMN-CN⁻ complex at the B3LYP/6-31G level (Gaussian 2016) [18].

3. Results and discussion

3.1. Production of TPMN

TPMN was successfully produced by Vilsmeier-Haack reaction [17], the formation of phenanthroimidazole [19], Duff reaction [20] and Knoevenagel condensation [21], respectively (Scheme 1). After the Vilsmeier-Hack reaction of triphenylamine, the reaction of the obtained triphenylamine's dialdehyde derivative (2) with 9,10-phenanthrenequinone in the presence of NH₄OAc generated the triphenylamine conjugated with two phenanthroimidazole groups (2) with a 68 % yield. The product 2 was then transformed to its aldehyde derivative (3) in the presence of HMTA and TFA by Duff reaction. Finally, compound 3 was condensed with malononitrile using Knoevenagel condensation in the presence of Zn(OAc)₂.2H₂O in DMF to provide TPMN in good yield (90%). The characterization of TPMN was made by using FTIR, ¹H, ¹³C, APT NMR and elemental analysis (Figs. S1–S7).

3.2. Optical properties of TPMN towards anions

To observe the optical properties, UV–vis and fluorescence spectroscopies of TPMN in MeCN/H₂O (v/v, 9/1) were recorded in absence or presence of anions (F⁻, Cl⁻, Br⁻, I⁻, CN⁻, NO₃⁻, NO₂⁻, N₃⁻, HSO₄⁻, HPO₄⁻, ClO⁻, AcO⁻, OH⁻, SO₄²⁻, SCN⁻). As shown in Fig. 1a, free TPMN (1.0 μ M) showed weak fluorescence emission at 430 and 435 nm due to the ICT effect from the triphenylamine and phenanthroimidazole units to the dicyanovinyl group via π -conjugation. Nevertheless, the addition of CN⁻ (10 equiv.) produced an effective emission enhancement at 430 and 435 nm, whereas other anions were induced no noticeable changes in the fluorescence spectrum of TPMN. This selectivity is the result of the nucleophilic addition of the CN⁻ ion to the β -position of the dicyanovinyl carbon in TPMN. The nucleophilic reaction of CN⁻ conducted to inhibiting the ICT process in TPMN due to disrupts the π conjugation between electron donor and acceptor groups [22]. On the other hand, the UV-vis properties of TPMN (10.0 μ M) towards anions were also studied. As depicted in Fig. 1b, the absorption bands of TPMN appeared at ~382 and 462 nm, which ascribed to the π - π^* or n- π^* transitions and the intramolecular charge transfer (ICT) processes, respectively. The absorption band at 462 nm disappeared after 10 equiv. CN⁻ was added, and the color of the solution converted from yellow to colorless (Fig. 1b, inset). However, no obvious UV-vis changes for TPMN were observed upon the addition of other anions. It may due to the nucleophilic addition of CN^{-} and destroyed the conjugated structure of TPMN.

To insight the interaction between TPMN and CN⁻, we carried out the UV-vis and fluorescence titration experiments of TPMN with varying equivalents of CN⁻. With the increasing concentration of CN⁻ from 0 to 20 µM, the fluorescence intensities at 430 and 445 nm of TPMN have exhibited a remarkable increase, indicating that TPMN was a turn-on fluorescent probe for CN⁻ (Fig.2a). The increase of fluorescence intensity was near to the maximum when about 20 equiv. of CN⁻ (20 µM) was added. At the same time, the titration curve showed an excellent linear relationship between the emission intensities and the concentrations of CN⁻. According to these data, the limit of detection (DL) was found to be 0.23 μ M based on 3 σ /k, suggesting that TPMN has a high sensitivity for CN⁻ (Fig. S8) [23]. The binding ratio between TPMN and CN⁻ was further determined by using Job's plot analysis (Fig. S9). As seen in Fig. S9, when the mole fraction of CN⁻ is 0.5, the change of fluorescence became maximum, which showed a 1:1 stoichiometric ratio between TPMN and CN⁻. The Benesi-Hildebrand plot was used to determine the association constant of TPMN for CN⁻, and it was also found to be 5.36 (log K_a) (Fig. S10) [24]. The quantum yield of TPMN ($\Phi_{\text{TPMN}} = 0.046$) reached to 0.522 for cyanide (Fig. S11). The results indicated that quantum yield of TPMN was increased ~11-fold for cyanide. Besides, the UV-vis changes were investigated by the addition of CN^{-} (0–200 µM) into 10 µM solution of TPMN. The absorption band centered at 462 nm gradually decreased and then completely disappeared without any blue shift by addition of CN⁻, and the bands at 382 and 388 nm slightly decreased and increased, respectively (Fig. 2b). Additionally, the formation of an isosbestic point at 418 nm indicated that the reaction of TPMN with CN⁻ was one-to-one conversion to form a new compound.

To investigate the photophysical properties of TPMN, the solvent effect in the absorption and emission spectra were also investigated. As shown in Fig. S12, solvent dependent shifts in the absorption and emission spectra of TPMN occurred. By plotting the Stokes shifts (Δv) against the solvent polarity parameter (Δf), show approximately a linear relationship according to the Lippert–Mataga plot [25], showing a positive slope and a good linear relationship (R = 0.9447). The change of the solvent polarity indicated the enhancement or diminished the electron density in the structure, as well as the intermolecular charge transfer (ICT) due to the interaction with the solvent.

3.3. Competition, kinetic studies, and practical applications

Selectivity and competition are important parameters for fluorescent sensors. Thus, to check the selectivity of TPMN for CN^- , a solution of TPMN was incubated with CN^- and 10 equiv. of other anions and their emission spectra were recorded. As shown in Fig.3, the TPMN indicated unaltered signaling for CN^- in the presence of other anions. These selective and anti-interference of the TPMN to CN^- was probably owing to the high reactivity of cyanide ion to the β -position of the dicyanovinyl moiety in TPMN. Therefore, TPMN could be utilized as an effective probe for CN^- detection in a complex environment. Compared with other reported probes including dicyanovinyl unit as receptor unit for fluorescence cyanide detection, the present method shows a comparable response due to its promising properties low detection limit, high selectivity and sensitivity, rapid response and environmental analysis [26-30]

To evaluate the performance of TPMN, time-dependent absorbance changes to TPMN (10.0 μ M) for CN⁻ (100.0 μ M) were recorded in MeCN/H₂O (v/v, 9/1). As shown in Fig. 4, upon the introduction of CN⁻, the absorbance intensities at 462 nm was gradually decreased depending on time and reached a maximum within about 10 s. After 10 s., any change in the absorbance intensity could not be observed. The reaction rate constant of TPMN with CN⁻ was found to be 0.119 min⁻¹ assuming pseudo-first-order kinetics (Fig.4, inset).

To control the accuracy of the proposed method, after the supernatant in water samples (i.e., tap, distilled and mineral water) were removed using a 0.45 μ m pore size membrane filter, different concentrations level of CN⁻ were spiked in water samples. The prepared water samples were then conducted to the presented procedure. As listed in Table 1, the recovery values were generally higher than 95%, and the RSD values were less than 3.6%, illustrating that TPMN could be used for direct detection of CN⁻ in relevant real water samples. On the other hand, the practical application of TPMN by high sensitivity and selectivity for CN⁻ was observed by simple test kits. TLC plates were immersed into the TPMN solution (10⁻⁶ M, 3 mL) for 2 min to produce the test kits and then dried in air. These test kits were interacted by CN⁻ solution with different concentrations. As depicted in Fig. 5, whereas the test kit coated TPMN showed no apparent emission, the test kits containing a different concentration of CN⁻ qualitatively and quantitatively.

3.4. ¹H NMR experiments and DFT calculations

¹H NMR titration of TPMN (0.079M) was realized by adding of CN⁻ in DMSO- d_6 at 25 °C in order to determine the interaction mechanism between TPMN and CN⁻, As illustrated in Fig 6, the vinyl (CH) and NH proton signals of TPMN were observed at δ 8.22 and δ 13.50 ppm without CN⁻, respectively. The NH protons appeared as two separate peaks due to probably hydrogen binding effect, and the vinyl CH signal was shifted downfield (δ 8.24 ppm) by the addition of 0.5 equiv. of CN⁻. Also, the different splits were observed for aromatic protons in TPMN. When the amount of CN⁻ was increased to 1.0 equiv., the NH signal was observed as one peak at δ 13.43 ppm, the vinyl CH signal at δ 8.24 ppm vanished and a new proton signal at 4.59 ppm emerged. This new peak support that the -C=C- bond is broken by the CN⁻ attack giving rise to the formation of the C–C single bond. Upon the addition of 1.5 equiv. of CN⁻, no obvious spectral changes were observed in ¹H NMR, indicating that the reaction is complete.

DFT calculations were carried out to evidence the ICT transition and further explain the changes of fluorescence intensity before and after the reaction between TPMN and CN⁻. The optimized structures and frontier HOMO-LUMO orbitals of TPMN and TPMN-CN⁻ are shown in Fig. 7 and 8, respectively. The optimized structures illustrated that there is a significant difference of π -conjugation between TPMN and TPMN-CN⁻. As seen in Fig. 7, the dihedral angle of dicyanovinyl and benzene of triphenylamine moiety in TPMN is 1.45°, which showed in-plane. The addition of CN⁻ induced to destroy of this planer geometry, then the dihedral angle converted to be 101.03°. It demonstrates that the interrupting of π conjugation and ICT transfer between triphenylamine-phenanthroimidazole groups and dicyanovinyl unit. Also, the bond distances and bond angles in TPMN and TPMN-CN⁻ were found to be 1.376 Å/114.134° and 1.540 Å/107.113°, which supports the change -C=C- bond to -C-C- bond, respectively.

The HOMO and LUMO orbitals of TPMN and TPMN-CN⁻ were illustrated in Fig. 8. In the case of TPMN, HOMO is primarily distributed on the triphenylamine and phenanthroimidazole ring whereas LUMO is majorly located on the dicyanovinyl group, showing the possible ICT pathway from donor to acceptor. However, the HOMO and LUMO orbitals of TPMN-CN⁻ distributed solely within the triphenylamine and phenanthroimidazole moieties which indicates the obstruction in the ICT process, resulting in enhanced fluorescence emission. The energy gap (ΔE) of TPMN was found to be 2.93 eV, and after cyanide addition, the ΔE increased significantly to 3.81 eV, which are in good agreement with the changes in the UV-vis spectra. Also, TD-DFT calculations showed that the excitation wavelengths of TPMN and TPMN-CN⁻ are 495 and 425 nm, respectively, supporting to the obtained results in experiments (462 and 390 nm). These theoretical calculations were in consistent with the experimental results, by means of complete disappearance of ICT band at 495 nm of when CN⁻ attack TPMN (Fig. S13).

4. Conclusion

In summary, the phenanthroimidazole and dicyanovinyl substituted triphenylamine derivative as a fluorescent probe was produced for selective CN^- detection. Only the addition of CN^- to TPMN induced a remarkable emission enhancement at 430 nm which results in restricting the donor-acceptor extended π -conjugation. TPMN also demonstrated a fast response time (~10 s) for CN^- , which could be effective for real-time detection. The sensing mechanism was characterized by ¹H NMR measurements and DFT/TD-DFT calculations. The limit of detection was found to be 0.23 μ M, which indicated good sensitivity to CN^- . Moreover, TPMN has successfully integrated into test strips for real-time detection of CN^- and applied to detect CN^- in water samples.

AUTHOR STATEMENT

Ahmet Ozdemir: Conceptualization, Investigation Serkan Erdemir: Conceptualization, Project administration, Writing – review and editing

Declaration of interests

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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Figure Captions

Scheme 1. Synthetic route for TPMN. Reagents and conditions (i): DMF, $POCl_3$ (ii): 9,10-Phenanthrenequinone, ammonium acetate, acetic acid, 6h (iii): HMTA, TFA, 24h (iv): malononitrile, $Zn(OAc).2H_2O$, 2h.

Fig. 1. Fluorescence (a) and UV-vis response (b) of TPMN in presence of various anions (10 equiv.) in MeCN/H₂O (v/v, 9/1).

Fig.2. Fluorescence emission (a) and UV-vis spectra of TPMN in MeCN/H₂O (v/v, 9/1) upon addition of various concentrations of CN^{-} .

Fig.3. Competitive experiments of TPMN (1.0 μ M) for CN⁻ (10.0 equiv.) in the presence of common anions (10.0 equiv.) in in MeCN/H₂O (v/v, 9/1) solution.

Fig.4. The kinetic study of TPMN (10 μ M) to CN⁻ at room temperature under pseudo-first-order condition.

Table 1. Determination of CN⁻ ions in spiked water samples using TPMN

Fig.5. Color changes of TLC plates containing TPMN for CN⁻ detection in different concentrations under 365 nm UV light

Fig.6. ¹H NMR spectra of TPMN in the absence and presence of CN^- (a=0.0, b=0.5, c=1.0 and d=1.5 equiv.) in DMSO-*d*₆

Fig. 7. DFT calculated optimized structures of TPMN and TPMN-CN⁻

Fig. 8. Frontier molecular orbital diagrams and energy levels of TPMN and TPMN-CN⁻⁻ by DFT at the B3LYP/6-31G /level using Gaussian 16



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Sample	Added CN ⁻ (µM)	Found (µM)	Recovery (%)	RSD (Relative standard
				deviation) (n=3) (%)
Tap Water	5.0	4.79 ± 0.3	95.8	2.4
	10.0	9.75 ± 0.3	97.5	3.3
Distilled water	5.0	4.95 ± 0.2	99.0	2.1
	10.0	10.12 ± 0.4	101.2	3.0
Mineral water	5.0	4.77 ± 0.3	95.4	3.6
	10.0	9.89 ± 0.5	98.9	2.5

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Fig.5. Color changes of TLC plates containing TPMN for CN⁻ detection in different concentrations under 365 nm UV light



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