Contents lists available at ScienceDirect



Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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



Aggregation-induced emission enhancement (AIEE)-active tetraphenylethene (TPE)-based chemosensor for CN⁻



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ARTICLE INFO

Article history: Received 11 July 2020 Received in revised form 25 August 2020 Accepted 5 September 2020 Available online 10 September 2020

Keywords: Aggregation-induced emission enhancement Mechanofluorochromic Fluorescent sensor Cyanide

ABSTRACT

An aggregation-induced emission enhancement (AIEE)-active fluorescent sensor has been successfully designed and synthesized, combining the AIE effect of tetraphenylethylene (TPE) with the cyanide acceptor of phenanthro [9,10-d]imidazole. The sensor exhibits not only the property of AIEE in DCM/*n*-hexane or THF/H₂O, but also the phenomenon of mechanofluorochromic (MFC). It displays large Stokes shift (107 nm) due to the intramolecular charge transfer (ICT) process. The cation of CN⁻ boosts the ICT process to make the greater Stokes shift (184 nm) with the fluorescent color vary from blue-green to sodium-yellow and visually turning from light yellow to dark yellow in the naked eyes. The results of Job's plot, ESI-MS and the DFT calculations provide the stoichiometric ratio and electronic properties of the sensor. Furthermore, the sensor could be applied to qualitative and quantitative detection of CN⁻ on test paper strips.

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1. Introduction

Cyanide compounds are vital in chemical, medicine, fuel industry and heavy industry fields, because of not only the wide range of sources but also the wide range of uses [1,2] such as gold mining, electroplating, metallurgy, synthetic fiber and resin industry [3]. However, cyanide compounds are one of the most toxic substances to the environment and human health [4,5]. Cyanide is absorbed through the skin, the eyes or gastrointestinal tract into the body, breaking down toxic cyanide ions, which can inhibit the activity of 42 enzymes in the cell [6–9] taking cytochrome oxidase, peroxidase and decarboxylase [10,11] for example. Among them, cytochrome oxidase is susceptible to prussiate which can easily bind to trivalent iron in oxidized cytochrome oxidase to inhibit its lessening to divalent iron, break the oxidation process of transmitting electrons, and eventually lead to respiratory failure and death [12-15]. Therefore, the urgent problem to be solved at present is how to quickly, efficiently and easily detect cyanide ions in the environment and daily life. Traditional methods for detecting cyanide ions require expensive instruments and complicate operations, which limit the application of these methods [16,17]. In recent years, colorimetric and fluoresent methods have become the research hotpot in ion detection field, because of their simple operation and cheap instrument [18,19]. Cyanide ions colorimetric and fluorescence sensors are usually combined by binding sites and signal groups in a certain way to achieve the purpose of detection [20,21]. According to the different binding modes, it is mainly divided into the following categories: hydrogen bonding type, deprotonation type, addition reaction type and coordination action type [22–25]. For example, Kasushik and co-works [26] reported that hydrogen-bond-based thiourea recognition sites would rapidly detect fluoride ions and cyanide ions in the naked eyes, but the disadvantage was that it would not achieve specific recognition [26]. Bhattacharya and group members synthesized sensor molecules with anthraquinone imidazoie as the framework [27]. The compound was indentified fluoride ions and cyanide ions in acetonitrile by intramolecular electron transfer mechanism, and achieved a single colorimetric recognition of cyanide ions by changing the solvent system [27].

With the research of colorimetric and fluorescent sensors, more and more sensors have been reported and proposed, such as imidazole derivatives, rhodamine derivatives and coumarin fluorescent derivatives, which have high fluorescent quantum yield, good photostability and molar extinction coefficient [28–30]. But they also exhibit fatal irrepressible drawbacks such as aggregation-caused quenching (ACQ), small stoke shifts (<10 nm) and background interference, limiting their practical applications [31,32].

Academician Tang Benzhong and members of his research group proposed aggregation-induced emission (AIE) for the first time in 2001 to overcome the notorious ACQ phenomenon [33–35]. Aggregation-induced emission was the opposite process of the aggregation-caused quenching, showing weak fluorescence or even no fluorescence in the non-aggregating state, but enhancing fluorescence

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in the aggregated state [36,37]. For instance, hydrazone imide derivatives, anthracene derivatives and tetraphenylene derivatives exhibited AlE phenomena and would be applied to biological detection [38,39]. Among them, tetraphenylene was the characteristics of simple synthesis and easy modification, so many tetraphenylene derivatives had been designed and proposed. For example, (E)-1,2-di([1,1':4',1"terphenyl]-4-yl)-1,2-diphenylethene [40], tetra(4-pyridylphenyl)ethylene [41], 9,9'-bixanthenylidene [42], but there were few studies on linking tetraphenyl to imidazole. Combination the application of imidazole derivatives in the field of ion detection with the advantages of tetraphenylene [43,44], An AIEE-active fluorescent sensor (Scheme 1) 2-(5-(4-(1,2,2-triphenylvin-yl)phenyl)thiophen-2-yl)-1*H*-phenanthro [9,10-*d*]imidazole (**TPI**) was designed and synthesized for cyanide ion identification.

2. Experimental

2.1. General methods

All chemicals and solvents were acquired the analytical grade by bargain and utilized without further purification. ¹H NMR and ¹³C NMR spectra were noted on a Bruker AV500 (500 MHz) NMR spectrometer utilizing tetramethylsilane as the internal standard. Mass spectra were obtained using an Agilent 1100 ion trap LC/MS MSD system. Fluorescence spectra and UV-Vis absorption spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer and an Agilent 8453 UV-Vis spectrophotometer, respectively. The fluorescence quantum yield was resolved the QYC11347-11 (absolute PL quantum yield spectrometer). XRD researches were performed in the Shimadzu XRD-6000 diffractometer with Ni-filtered and graphitemonochromated Cu K_a radiation ($\lambda = 1.54$ Å, 40 kV, 30 mA). Dynamic light scattering (DLS) studies were measured using Brookhaven NanoBrook 90 Plus and scanning electron microscopy (SEM) were recorded on a SEM, Zeiss, Sigma. Anions (CN⁻, F⁻, Cl⁻, CH₃COO⁻, NO₃⁻, I⁻, CO₃²⁻, HCO₃⁻, HSO₃⁻, SO₄²⁻, H₂PO₄⁻, SCN⁻, ClO₄⁻, HSO₄⁻, Br⁻, PO₄³⁻, $S_2O_3^{2-}$ and HPO_4^{2-}) from their tetrabutylammonium salts were prepared, which was diluted to 0.1 mol L^{-1} by deionized water to obtain the stock solution.

2.2. Synthesis of TPI

As shown in Scheme 1, synthesis of compound 1 by Suzuki coupling, compound 1 was prepared by reacting (2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene (0.800 g, 2 mmol) with (5-formylthiophen-2-yl) boronic acid (0.624 g, 4 mmol) in the presence of Pd(PPh₃)₄ and Na₂CO₃ (4 g, 38 mmol) in tetrahydrofolate (THF, 30 mL containing 10% water). Refluxing at 360 K was continued until TLC revealed that the reaction was complete, after being extracted with DCM. Purification by silica gel column chromatography in petroleum ether and ethyl acetate (45: 1) to compound 1 (56%) pale green solid after drying the solvent. ¹H NMR (500 MHz, DMSO-*d*₆): δ (ppm) 6.99–7.10 (m, 8H), 7.13–7.24 (m, 9H), 7.62 (d, 1H, *J* = 9.5 Hz), 7.71 (d, 1H, *J* = 4.5 Hz), 8.03 (d, 1H, *J* = 4.5 Hz), 9.91 (s, 1H). (Fig. S1).

Synthesis of TPI by compound 1 (0.1 g, 0.23 mmol) was dissolved in methanol (15 mL) and placed in a one-neck flask, and phenanthrene-9,10-dione (0.07 g, 0.3 mmol) and ammonium acetate (0.7 g, 9 mmol) were added to the solution to allow the reaction mixture to be at 360 K. The mixture was stirred at reflux temperature until a solid precipitated. It was cooled to room temperature, washed with methanol until no impurities, and dried to give a yellow solid (0.08 g, yield: 55%). ¹H NMR (500 MHz, DMSO- d_6): δ (ppm) 6.60 (d, 1H, J = 4 Hz), 6.99 (d, 3H, J = 7.5 Hz), 7.15-7.06 (m, 4H), 7.27-7.22 (m, 6H), 7.29 (d, 3H, J = 8.0 Hz), 7.33 (d, 1H, J = 7.0 Hz), 7.37 (t, 3H, J = 6.5 Hz),7.59 (d, 1H, I = 4.0 Hz), 7.81 (d, 3H, I = 25 Hz), 8.78 (d, 2H, I =7.5 Hz), 9.02 (d, 2H, I = 3.5 Hz), 13.76 (s, 1H,), ¹³C NMR (126 MHz, DMSO-*d*₆): δ (ppm) 122.30, 122.38, 122.56, 124.27, 124.68, 125.20, 125.76, 125.99, 127.08, 127.18, 127.27, 127.30, 127.36, 137.65, 127.73, 127.99, 128.03, 128.25, 128.31, 128.42, 128.51, 131.14, 131.19, 131.24, 131.80, 132.05, 133.35, 137.35, 140.42, 141.48, 143.48, 143.59, 144.47, 145.03. MS-ESI (m/z): 631.21 [M + H]⁺ (calcd 631.1) (Fig. S2).

3. Results and discussion

3.1. Optical characterization

The UV-Vis absorption spectrums of TPI in pure THF $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ and solid state were recorded in Fig. 1A. The absorption peaks of TPI in pure THF were 321 nm and 394 nm, in that a relatively weaker absorption peak at 321 nm was due to the π - π * transitions, and a main absorption peaks at 394 nm was due to the intramolecular charge transfer (ICT) process [38]. The absorption band of solid **TPI** ($\lambda_{max} = 401 \text{ nm}$) was slight red-shifted, compared with that of **TPI** ($\lambda_{max} = 394 \text{ nm}$) in pure THF, presumably on account of the aggregation formation and the intermolecular interactions occurrence in the solid state [45]. The fluorescence spectrum of TPI showed bright blue fluorescence at 501 nm in THF when excited at 394 nm (Fig. 1A), and exhibited large stock shift (107 nm), whereas this solid state showed bright blue-green fluorescence at 522 nm. The photograph of TPI in THF solutions and solid state were shown in Fig. 1B. In addition, the fluorescence lifetime of TPI was found to be 0.05 ns in THF solutions, whereas the fluorescence lifetime was found to be 0.49 ns in the solid state. The longer fluorescence lifetime could be due to the restriction of intramolecular rotations in the solid state [46]. At the same time photophysical data of TPI were summarized in Table 1.

3.2. Aggregation induced emission enhancement (AIEE) properties

To research the probable AIEE behavior of **TPI**, this spectral behavior was explored in the good and poor solvents. AIEE characteristics of compound **TPI** was based on emission and UV–Vis absorption spectral assessments in various *n*-hexane fraction ($f_h = 0-98\%$) of DCM/*n*-hexane mixtures (Fig. 2A). The emission of **TPI** was weak in DCM solution and increased slowly until the ratio of *n*-hexane increased to 80%. Afterwards, the remarkable emission enhancement was recorded for **TPI** at f_h of 90% and 98%, which were 2-fold (90%) and 6-fold (98%) higher than that in pure DCM, respectively. As f_h altered from 0 to



Scheme 1. Synthetic route of TPI.



Fig. 1. (A) The absorption and fluorescence spectra of TPI compound in pure THF solution and in solid states and (B) their photographic images under 365 nm UV light.

90%, the absorption bands of **TPI** in DCM/*n*-hexane had little changed compared to it in DCM solution. However, the absorption peak intensities of **TPI** slightly increased as f_h increasing to 98% (Fig. S3). Additionally, limiting the intramolecular motions of **TPI** in aggregation states made the fluorescence quantum yield of **TPI** remarkably increase from 0.042 ($f_h = 0\%$) to 0.101 ($f_h = 98\%$) and resulted in the emission improvement [47,48]. These results indicated that **TPI** displayed AIEE characteristics in DCM/*n*-hexane mixtures. Further, the morphological transition of the **TPI** in the DCM/*n*-hexane mixture solution ($f_h = 98\%$) was determined by scanning electron microscopy (SEM) and dynamic light scattering (DLS) as shown in Fig. S4 and Fig. S5. DLS result revealed that the particulate size of aggregates changed with increasing various *n*-hexane fraction in the DCM/*n*-hexane mixture. SEM images of **TPI** clearly indicated the morphological aggregates state.

Different luminescence response was present with the alteration of water, a polar and poor solvent, in THF solution (Fig. 2B). The fraction of water ranging from 0% to 20%, the emission intensity descended mildly. Subsequently the emission intensity ascended slowly with the f_w from 20% to 70%, the emission intensity improved dramatically with the f_w from 70% to 80%, and the f_w more than 80% the emission converted to decrease. The emission color appeared red-shift (34 nm) from blue-green (501 nm) to pure green (535 nm) with the reason that the dye molecules had different conformations and packing modes at the aggregation states [49]. In the mixture of the higher water content ($f_w > 80\%$), the dye molecules might rapidly agglomerated in an irregular way to induce less emission [50,51]. The fluorescence quantum efficiency of **TPI** raised from 0.039 ($f_w = 0\%$) to 0.09 ($f_w = 80\%$). Thus, TPI featured the unique AIEE characteristics in THF/water mixtures, also. In addition, the AIEE behavior could be further confirmed by DLS and SEM measurements, as shown in Fig. 2C and D. The Optical properties for TPI under different environment were summarized in Table S1.

Table 1Optical properties for TPI.

Sample	THF			$\Delta\lambda^e$	Solid		
	$\lambda_{max} (nm)^a$	$\lambda_{em}(nm)^b$	$\tau(ns)^{c}$		$\lambda_{max} (nm)^a$	$\lambda_{em}(nm)^{b}$	$\tau(ns)^{c}$
TPI	321, 394	501	0.05	107	290, 401	522	0.49

^a Absorption wavelength.

^b The wavelength of emission maximum.

^c The fluorescence lifetime.

3.3. Mechanofluorochromic behavior of TPI

The mechanofluorochromic characteristics of compound TPI were further investigated by emission spectral (Fig. 3A). The solid sample was then crushed with a pestle, and the fluorescence emission color of the sample changed (Fig. 3B). The blue green luminescence (521 nm) transformed into bright green luminescence (542 nm) with a moderate red-shift (21 nm) after crushing (Fig. 3C). Significantly, after treating the ground sample with DCM vapor, the fluorescence emission could be essentially reverted to its initial emission with the color changing (Fig. 3D). This mechanochromic luminescence transition of TPI would be repeated many times between the blue green luminescence and bright green luminescence by alternating grinding and fuming processes (Fig. S6). The powder X-ray diffraction (PXRD) technique was used to reveal the reason for the mechanofluorochromic behavior of **TPI**, and the results indicated that this phenomenon occurred due to the change in molecular packing modes [52]. As shown in Fig. S7, the diffraction patterns of the solid sample and the solvent fumed powders clearly exhibited sharp and intense reflections, indicating TPI form microcrystals. In contrast, the ground powders did not exhibit any noticeable diffraction in the PXRD profile, reflecting its amorphous.

3.4. Analytical studies of TPI

The binding ability of **TPI** with different anions including CN⁻, F⁻, Cl⁻, CH₃COO⁻, NO₃⁻, I⁻, CO₃²⁻, HCO₃⁻, HSO₃⁻, SO₄²⁻, H₂PO₄⁻, SCN⁻, CIO_4^- , HSO₄⁻, Br⁻, PO₄³⁻, S₂O₃²⁻ and HPO₄²⁻ was also investigated by fluorescence spectroscopy in DCM $(2.0 \times 10^{-5} \text{ mol } L^{-1})$ at room temperature. When excited at 441 nm, upon adding 9.0 equiv. of CN⁻, the fluorescence emission peak of TPI exhibited a theatrical enhancement (~8.3 folds) and transformed from 500 nm to 595 nm due to the TPI-CN⁻ complex form (Fig. 4A). Simultaneously, TPI-CN⁻ complex exhibited greater stock shift (184 nm) than that in TPI (107 nm), which would be easy to facilitate ICT processes [50]. The apparent fluorescence color turned from blue-green to sodium-yellow (Fig. 4C) with the visible color changing from light yellow to dark yellow (Fig. S7). After addition 9.0 equiv. of other anions, no obvious fluorescence variations were observed. The results indicated that TPI could be used as a fluorescent sensor for the naked-eye detection of CN⁻ in DCM. In order to evaluate the **TPI** anti-jamming capability for detecting CN⁻ in the presence of various anions (Fig. 4B), the experiment of anti-interference was carried out. There was scarcely any interference in the emission intensity was seen by addition CN⁻ (9.0 eq.) to TPI solution in the presence of various anions (10 eq.). Thus, these results indicated TPI could be served as an



Fig. 2. (A) The fluorescence spectra of **TPI** in THF/*n*-hexane with different fractions (inset: photos of **TPI** in DCM/*n*-hexane under 365 nm excitation and PL relative intensity of **TPI**). (B) The fluorescence spectra of **TPI** in THF/H₂O with different fractions (inset: photos of **TPI** in THF/H₂O under 365 nm excitation and the PL relative intensity of **TPI**). (C) Size distribution of **TPI** in THF/H₂O. (D) SEM images of **TPI** in THF/H₂O ($f_w = 99\%$).

excellent fluorescent sensor for CN⁻ detection with favorable selectivity and enjoyable anti-interference.

To further estimate the dose-dependent fluorescence response of **TPI** to CN^- was decided by fluorescence titration in DCM at room temperature (Fig. 5A). As the CN^- from 0 to 9.0 equiv. dropped into the

solution of TPI ($2.0 \times 10^{-5} \text{ mol } \text{L}^{-1}$), the peak at 595 nm ascended gradually with the peak at 500 nm descending (Fig. 5B). Accompanied by the fluorescent color of the solution transforming from blue-green to sodium-yellow, simultaneously the fluorescence quantum yield remarkable was increased from 0.042 (**TPI**) to 0.23 (**TPI**-CN⁻ complex).



Fig. 3. (A) Solid state fluorescence spectra of **TPI** before and after the grinding, and after treatment with DCM vapor ($\lambda_{em} = 400 \text{ nm}$). Photographic images of **TPI** under 365 nm UV light: (B) the solid sample, (C) the ground solid sample, (D) the solid sample after the treatment with DCM vapor.



Fig. 4. Alteration in the fluorescence spectra of **TPI** induced by the anions mentioned above in the DCM solution: (A) fluorescent spectral changes, (B) the change of fluorescence color induced by various ions (Photographic images under 365 nm UV light), (C) Competitive tests for the emission intensities of **TPI** in the presence of CN⁻ and other competing anions (9.0 eq.).

These results indicated that the sensor **TPI** could also be used as a latent CN^- fluorescent sensor application. For the CN^- in a concentration ranging from 0 to 9.0 eq., the emission intensities revealed a fine linear relationship (Y = 44.8*X + 68.02857, *R* = 0.99098) (Fig. 5C). The detection limit was calculated to be 0.09258 µm L⁻¹ based on reported means [53], which was much lower than the maximum contaminant level (1.9 µm L⁻¹) for CN⁻ in drinking water set by the WHO.

3.5. Detection mechanism for CN⁻

The ¹H NMR analysis further demonstrated the sensor **TPI** binding from with CN^- in DMSO- d_6 (Fig. 6). Upon gradual adding of CN^- , the -NH proton signal (located at 13.76 ppm) of **TPI** declined gradually until disappeared, which indicated the interaction of highly electronegative CN⁻ with –NH proton. To further verify the binding stoichiometry of TPI-CN⁻, Job's plot experiment was constructed by varying the molar fraction of CN⁻ from 0 to 1 under a constant total concentration $(2.0 \, \times \, 10^{-5} \mbox{ mol } L^{-1}).$ The concentration of $TPI \, + \, CN^{-}$ complex achieved the maximum when the molar fraction of [TPI]/ ([**TPI**] + [CN⁻]) was 0.5, which suggested stoichiometry between **TPI** and CN^- was 1:1 (Fig. S8). The formation of **TPI** + CN^- complex was further verified by the ESI mass spectrometry analysis (Fig. S9). TPI revealed a main peak at 631.1 m/z ([**TPI** + H]⁺) and another major peak produced at 656.6 m/z as 9 eq. of CN^- added owing to $[TPI-CN + H]^+$ (calculated 656.2). These results reinforced that the binding stoichiometry between **TPI** and CN⁻ was 1:1.

3.6. Practical application of aggregation induced emission

To further elucidate the effect of cyanide ion on the AIE behavior of **TPI**, the fluorescence changes of **TPI**- CN^- complex in DCM/*n*-hexane mixtures with the volume ratio of *n*-hexane were studied. The Fig. S10 shown the fluorescence intensity of **TPI**- CN^- complex gradually

increased with the addition of *n*-hexane until 80%. The emission wavelength was blue-shifted, meanwhile the maximum *n*-hexane content was 98%, the I/I_0 value probably reached to 4.3, and the fluorescence quantum yield were 0.23 and 0.419, respectively. The results indicated that **TPI**-CN⁻ complex also had an AIE behavior.

With the purpose of confirming the feasibility of practical application of sensor **TPI**, the test strips were made for the CN⁻ detection. Firstly, test strips were prepared by immersing filter papers into the DCM and *n*hexane solutions of **TPI** $(2 \times 10^{-5} \text{ mol } \text{L}^{-1})$ for 10s and then dried in air. As listed in Fig. S11, test paper strips showed that the blue-green fluorescence was visible in the naked eyes under the 365 nm UV light, and the result was consistent with the various *n*-hexane fraction. With the treating of CN⁻, the test strips quickly changed from blue-green to sodium-yellow in aggregation state and dark-yellow in non-aggregation state. The test strip in aggregation state was more suitable for the CN⁻ detection with more dramatic color changing than that in non-aggregation state (Fig. S12). After treating different anions into the test strips of aggregation state, it could be apparently noticed that only CN⁻ made a notable fluorescence color change from blue-green to sodium-yellow under the 365 nm UV light (Fig. 7A), and the color of the test strips gradually changed from dark yellow to light yellow under natural light (Fig. 7B). The result indicated that the sensor TPI could be served as facilitation test strips for a rapid detection of CN⁻. Furthermore, the fluorescent color of the test strips gradually turned from blue-green to sodiumyellow under the 365 nm UV light with the concentration of CN⁻ raising from 0 to 2.5×10^{-4} mol L⁻¹ (Fig. 7C). All the above results demonstrated the facilitation test strips of sensor TPI could be successfully used for quantitative detecting CN⁻.

3.7. The density functional theory (DFT)

To supplementary comprehended the relationship between the optical property and electronic structure, the density functional theory



Fig. 5. (A) The fluorescence variation of TPI induced by CN⁻. (B)The curve of fluorescent intensity ratio at 595 nm with the addition 0–9 eq. of CN⁻. (C) The limit of detection (LOD) was determined to be 0.09258 µm/L.

(DFT) calculations was by B3LYP/6-311G (d) basis set with the G09 program. As displayed in Fig. 8, for **TPI** molecule, the electron distribution of HOMO was a majority of localizing on 5-phenyl-thiophene, phenanthro [9,10-*d*]imidazole unit, while that of the LUMO was distributed in the part of the 5-phenyl-thiophene and imidazole unit. The electrons of LUMO orbital was mostly similar to the HOMO orbital electron distribution, which led to the certain restriction on intramolecular charge



Fig. 6. The ¹H NMR spectra of **TPI** (red), **TPI-CN**⁻ (blue) and **TPI-CN**⁻ (black) in DMSO-*d*₆ upon the addition of 0 eq., 5.0 eq. and 9.0 eq. CN⁻.

transfer [54,55]. Nevertheless, the **TPI**-CN⁻ compound, the electron distribution of HOMO was distributed the entire molecule. In contrast, the electron distribution of LUMO was distributed in 5-phenyl-thiophene and phenanthro[9,10-*d*]imidazole unit. Such a spatial frontier orbital distributions revealed that **TPI-CN**⁻ was easy to facilitate ICT processes [50,56]. The calculated HOMO and LUMO energy levels for **TPI** were – 0.19286 eV and – 0.06996 eV, respectively. However, **TPI-CN**⁻ exhibited a deeper HOMO (-0.20209) and LUMO (-0.08360) energy level. The HOMO-LUMO band gaps in the **TPI-CN**⁻ (0.11849 eV) was found to be lower than the **TPI** (0.1229 eV), which could be due to the **TPI-CN**⁻ strong electron-withdrawing ability. These results of investigations also corroborated, for instance, experimental observations of red-shifted emission and large Stokes shifts (Table S2).

4. Conclusion

In summary, a fluorescent sensor of CN^- was successfully synthesized based on a phenanthro[9,10-*d*]imidazole AlEgen-based (**TPI**), and its utilization in highly selective and sensitive real-time naked-eye detection was proved according to the transforming fluorescence and visible color. Meanwhile, the sensor could be applied to qualitative and quantitative detection of CN^- on test paper strips. The MFC behavior, AlEE properties in two different solvent systems (DCM/*n*-hexane and THF/H₂O), the large stokes shift, ICT process and outstanding optical properties strongly proved the feasibility of our sensor design strategy. The results in this paper would support new methods for the fluorescence sensors in practical application in the future.



Fig. 7. Photograph showing: (A) fluorescent color change of **TPI** on test paper strips after treating with various anions under 365 nm light, (B) visible color change of **TPI** on test paper strips after treating with various anions under natural light, (C) Fluorescence photos of different concentrations of $CN^{-}(\times 10^{-5} \text{ mol } L^{-1})$ on test paper strips.



Fig. 8. Optimized structures of TPI and TPI-CN⁻, HOMO and LUMO energy levels of TPI and TPI-CN⁻.

CRediT authorship contribution statement

Yilan Wang: Investigation, Writing - original draft. Hongliang Liu: Writing - review & editing, Supervision. Zhao Chen: Validation. Shouzhi Pu: Project administration, 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.

Acknowledgements

This research was financially supported by the Natural Science Foundation of China (41867053, 41867052, 21702079), the Project of Jiangxi Science and Technology Normal University Advantage Sci-Tech Innovative Team (2015CXTD002), the Science Funds of Jiangxi Education Office (GJJ190598, GJJ190613), and the Open Project Program of "Polymer Engineering Research Center", Jiangxi Science and Technology Normal University (KFGJ19019).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.saa.2020.118928.

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Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 245 (2021) 118928

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