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Graphical Abstract



We have successfully developed sensor **CPPB**, which exhibited distinct aggregation induced emission (AIE) effect, and detected CN^- based on naked-eye colorimetric and fluorescent sensing with high selectivity and great sensitivity.

A new carbazole-based colorimetric and fluorescent sensor with

Aggregation induced emission for detection of cyanide anion

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Abstract

A new carbazole-based naked-eye colorimetric and fluorescent sensor CPPB with aggregation induced emission (AIE) effect was successfully synthesized. The solid powder of **CPPB** emitted intense yellow fluorescence, and its emission wavelength and fluorescence intensity in DMSO/H₂O solution varied with the percentage of water (f_w) . Nano-aggregates of **CPPB** molecules were prepared by increasing f_w of DMSO/H₂O solution, and the optimal aggregation state of CPPB was reached in 99% aqueous DMSO solution with the maximum fluorescence intensity. Moreover, CPPB displayed high selectivity and sensitivity toward cyanide anions (CN⁻) in 99% aqueous DMSO solution even in the presence of other competitive anions (CN⁻, F⁻, Cl⁻, AcO⁻, NO₃⁻, I⁻, CO₃²⁻, HCO₃⁻, HSO₃⁻, SO₄²⁻, S²⁻, HS⁻, OH⁻, H₂PO₄⁻ and HPO_4^{2-}) and the reactive oxygen species (H₂O₂, O₂, O_2 , t-BuOOH and \cdot OH). The sensing mechanism for CN⁻ was confirmed by optical spectral studies, ¹H NMR titration, HRMS spectra, Job's plot analyses and DFT calculations. Sensor CPPB for CN⁻ detection revealed extremely low detection limit (67.4 nM), high anti-interference ability, wide pH response range $(3.0 \sim 10.0)$ as well as the immediate response (15 s). Furthermore, the CPPB-based test strips were applied to detect CN⁻ qualitatively and quantitatively in 100% aqueous solution.

Keywords: Aggregation induced emission, Colorimetric, Fluorescent, Cyanide anion, test strips.

1. Introduction

With the development of science, the safety of the living environment and food has attracted wide concern. The cyanide anions have received a great deal of attention since it is incredibly harmful and venomous to the human body ^[1–8]. Cyanide anions are mainly associated with metal ions in cytochrome P450, which lead to losing its ability to transmit electrons in the respiratory chain, followed by damaging on the central nervous system. Even so, cyanide is widely used in many aspects of the modern industry, such as wet smelting of gold and silver, electroplating technology, synthetic fiber, herbicides and so on, which cause cyanide anions to enter the human body through water and the food chain [9-13]. Nevertheless, the World Health Organization (WHO) stipulates that the maximum safe concentration level allowed in drinking water is 1.9 μ M^[14]. Therefore, the development of a low-cost, simple, great sensitive and highly selective colorimetric and fluorescent chemical sensor for the detection of cyanide ions in the environment is necessary ^[15-29]. A number of colorimetric and fluorescent chemosensor for CN⁻ has been developed, based on several mechanisms, such as intra-molecular charge transfer (ICT)^[30,31], excited state intra-molecular proton transfer (ESIPT)^[32], and photoinduced electron transfer (PET) ^[33], et al. However, most sensing materials for CN⁻ detection are readily soluble in organic solvents but insoluble in water, while the most significant number of CN⁻ exists in water, such as industrial waste water, drinking water and experimental discharge water, et al ^[34-37]. So it is critical to developing the sensors for CN⁻ in aqueous solution.

The sensing materials with aggregation induced emission (AIE) effect may be a good candidate for detecting CN^- in aqueous solution. AIE-active materials emit no fluorescence in solution, while it is highly emissive in aqueous solution due to the formation of aggregates ^[38]. However, only a limited number of sensing materials with both AIE effect and good sensing performance for CN^- have been reported. Therefore, research on sensing materials for CN^- detection with AIE effect is still of great challenge.

Herein, we reported an AIE-active compound CPPB (Scheme 1), which was an

ICT-based D- π -A type sensor with carbazole as an electron-donating group and barbituric acid as an electron-withdrawing group. Sensor **CPPB** exhibited highly sensitive and good selective for CN⁻ detection based on naked-eye colorimetric and fluorescent sensing in 99% aqueous DMSO solution. Sensor **CPPB** for CN⁻ detection displayed fast response speed, high anti-interference ability and low detection limit of 67.4 nM. Moreover, **CPPB**-based test paper strips revealed excellent and high sensitivities for detection of CN⁻ in 100% aqueous solution.

Scheme 1

2. Experimental

2.1. Materials and apparatus

All chemicals and solvents were obtained as the analytical grade by commerce and used without further purification. Anions (CN⁻, F⁻, Cl⁻, AcO⁻, NO₃⁻, Γ , CO₃²⁻, HCO₃⁻, HSO₃⁻, SO₄²⁻, S²⁻, HS⁻, OH⁻, H₂PO₄⁻ and HPO₄²⁻) from their tetrabutylammonium salts and reactive oxygen species (H₂O₂, O₂⁻⁻, ¹O₂, t-BuOOH and \cdot OH)^[39,40] were prepared, which was diluted to 1.0 mM by deionized water to obtain the stock solution. NMR spectra were measured on Bruker Avance II 400 using TMS as an internal standard spectrometer in DMSO-*d*₆. Infrared spectra of **CPPB** and **CPPB-CN⁻** were recorded on Bruker ALPHA FT-IR spectrometer using KBr pellets. High-resolution mass spectra (HRMS) were obtained from Agilent 6510 Accurate-Mass Q-TOF LC/MS system. UV-vis and fluorescent spectra were carried out on a Shimadzu UV-2600 and Hitachi F-4600 fluorescence spectrophotometer, respectively.

2.2. Synthesis of the sensor CPPB

Compounds 2 and 3 were prepared by the previously reported procedures (**Scheme** 1)^[41]. Compound 3 (0.5 g, 2.1 mmol) and barbituric acid (0.27 g, 2.1 mmol) were mixed in distilled ethanol (10 mL) and stirred under reflux for 5 h, then the mixture was cooled down and filtered off to obtain the compound **CPPB**, which was then washed with ethanol and dried in vacuum as an orange solid (0.68 g, yield 93%). ¹H NMR: (400 MHz, DMSO-*d*₆) δ = 11.22 (s, 1H), 11.10 (s, 1H), 9.21 (s, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.44 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.62-7.68 (m, 2H), 7.45 (t, *J* =

8.0 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 4.35 (t, J = 8.0 Hz, 2H), 1.71-1.77 (m, 2H), 0.80 (t, J = 4.0 Hz, 3H); ¹³C NMR: (100 MHz, DMSO– d_6) $\delta = 164.18$, 162.37, 156.82, 150.23, 143.20, 140.80, 133.23, 129.48, 126.67, 123.42, 122.34, 120.46, 120.40, 114.06, 110.27, 109.30, 44.01, 21.85, 11.23; FT-IR: (KBr, cm⁻¹) v = 3423 (H₂O), 3210 (N–H), 3057 (C–H), 1726 (C=O), 1665 (C=C), 1137 (C–N); HRMS (ESI): m/z: [M+H]⁺ calcd for: C₂₀H₁₇N₃O₃: 348.1348, found: 348.1340.

2.3. Spectroscopic experiments

The sensor **CPPB** was dissolved in DMSO to obtain a stock solution of 1.0 mM. The testing anions were dissolved in deionized water to obtain the stock solutions of 1.0 mM. The standard solution of **CPPB** (50 μ L) was added to 5 mL of deionized water containing various amount of CN⁻. A blank solution without any CN⁻ was prepared as the same procedure. The testing solutions contained 10 μ M of **CPPB**. The UV-vis absorption spectra were recorded in the wavelength range of 250 to 600 nm using a quartz cell of 1 cm. The fluorescence emission spectra were recorded in the wavelength at 627 nm. Both the excitation and emission slits were set at 5 nm.

2.4. The determination of DL

The detection limit (DL) was determined according to the formula (1) by emission data of sensor **CPPB** upon gradual addition of CN^{-} .

$$DL=3\delta/S$$
 (1)

where δ was the standard deviation of blank ample, *S* represented the absolute value of the slope between fluorescence intensity and CN⁻ concentration ^[42,43].

2.5. ¹H NMR titration

A solution of sensor **CPPB** (5 mM) was prepared in DMSO- d_6 . To a 0.5 mL of sensor solution, equivalents of tetrabutylammonium bromide (from a stock of 10 mM in DMSO- d_6) were added to an NMR tube through a micropipette, and the spectra were recorded.

2.6 Computational Procedures for HOMO-LUMO energy gap

The HOMO-LUMO energy gap for **CPPB** and **CPPB-CN**⁻, as well as its complexes, were calculated by density functional theory (DFT) using Gaussian 09W.

The DFT based B3LYP/6-31G* model was performed for C, N, O, H atoms. After obtaining the converged geometries, the TD-B3LYP/6-31G* was used to calculate the vertical excitation energies.

3. Results and discussion

3.1 Synthesis and characterization

The compound **CPPB** prepared refluxing between was by 9-Propyl-9H-carbazol-3-carbaldehyde and barbituric acid in EtOH (Scheme 1). The synthetic route of CPPB was simple, and the yield is very high. The structure was confirmed by ¹H NMR, ¹³C NMR, HRMS and FT-IR spectra (**Fig S1–S4**). ¹H NMR spectrum of **CPPB** exhibits singlet signal at 11.22 ppm and 11.10 ppm ascribed to NH and 9.21 ppm ascribed to vinyl C=CH proton, respectively. FT-IR spectrum of CPPB displays stretching at 3210 cm⁻¹ for N–H, 3057 cm⁻¹ for saturated hydrocarbon C–H, 1726 cm⁻¹ for amide C=O and 1665 cm⁻¹ for vinyl C=C group. HRMS spectrum of **CPPB** shows a parent peak at m/z 348.1340 corresponding to the $[M+H]^+$ fragment.

3.2 AIE activity of sensor CPPB

AIE activity of **CPPB** was investigated by UV-vis spectra and fluorescence (FL) spectra. As shown in **Fig. 1**, the absorption bands ranging between 270 and 350 nm were assigned to π - π * electronic transition of the barbituric acid and carbazole unit. Additionally, the **CPPB** molecule exhibited a sharp absorption peak at 434 nm, which can be attributed to intra-molecular charge transfer (ICT) from the carbazole to the barbituric acid.

Fig. 1

The FL spectra of sensor **CPPB** in pure DMSO solvent, as well as those in DMSO/H₂O mixture, were recorded (**Fig. 2a**). Since water is a poor solvent, aggregation of **CPPB** can be promoted by adding water to DMSO, leading to enhanced emission. Therefore, the mixture of DMSO and water was used for the preparation of nano-aggregates of **CPPB** by increasing the percentage of water (f_w). Different FL spectra with different f_w were exhibited (**Fig.2(a)**, (**b**)) depicted the variation trend of FL intensity and wavelength of **CPPB** under different f_w .

As observed in Fig. 2a, sensor CPPB showed weak emission in pure DMSO

solvent ($C_{CPPB} = 10 \ \mu$ M), while the powder of **CPPB** emitted strong fluorescence. These observations indicated a strong AIE activity of **CPPB**. In addition, the FL intensity of **CPPB** in pure DMSO ($f_w = 0\%$) was very weak. When f_w was less than 80%, the FL intensity of **CPPB** decreased as water content increased. However, it began to increase when f_w was increased to 90%. Moreover, the FL intensity reached a maximum at $f_w = 99\%$, which has increased by 5.7 times compared to the FL intensity in pure DMSO solvent ($f_w = 0\%$). These data demonstrated **CPPB** is AIE-active molecule ^[44-51].

From Fig. 2(b), it can be observed that the emission peak of CPPB was red-shifted from 547 to 623 nm when f_w increased from 0% to 99%. The large red-shifted may be attributed to the π - π staking when CPPB molecules aggregated at high water content. When f_w was no more than 90%, the addition of water enhanced the polarity of the mixed solvent which caused ICT, and thus the fluorescence became weakened as f_w increased. As f_w reached 90%, CPPB molecules started to aggregate, resulting in nanoparticles. Thus its fluorescence was significantly enhanced due to the AIE activity.

Fig. 2

The fluorescence emission of CPPB in mixed DMSO/H2O (fw = 0% ~ 99%) under UV lamp (365 nm) were observed in **Fig. 3**. The fluorescence enhanced when f_w increased from 0% to 80%, and then weakened obviously when f_w increased from 90% to 99%. The fluorescence color was significantly changed from yellow-green to orange. These observations were consistent with the data in **Fig. 2**.

Fig. 3

3.3 Sensing performance of CPPB

3.3.1. Selectivity and anti-interference of anions

A series of anions (F⁻, Cl⁻, Br⁻, Γ , NO₃⁻, AcO⁻, HCO₃⁻, CO₃²⁻, SO₄²⁻, HSO₄⁻, S²⁻, HS⁻, OH⁻ H₂PO₄⁻, HPO₄²⁻ and CN⁻) and the reactive oxygen species (H₂O₂, O₂⁻⁻, ¹O₂, t-BuOOH and ·OH) were respectively added to the solution containing **CPPB** (1 mM), and the changes in the spectra as well as the FL spectra with each addition were monitored. The solutions containing the common anions but CN⁻ showed yellow in

daylight and orange fluorescence at UV lamp (365 nm), while the solution containing only CN⁻ displayed no color in daylight and blue fluorescence at 365 nm (**Fig. 4**). These observations indicated that the sensor is highly selective towards CN⁻. It was found that the UV-vis spectra and FL spectra ($\lambda_{ex} = 440 \text{ nm}$, $\lambda_{em} = 625 \text{ nm}$) of CPPB did not show significant change, even upon adding 10 equiv. of each anions except for CN⁻ (**Fig. 5**). In the presence of CN⁻, the intensity of the absorption band of **CPPB** at longer wavelength (436 nm) was attenuated, while a new band appeared at 260 nm, and the intensity of the emission peak for **CPPB** at 625 nm was significantly enhanced. Such spectral changes suggest changes in the chemical structure of **CPPB**. This may be due to the fact that the reaction of cyanide with **CPPB** might have switched-off the ICT transition, which in turn affects its spectral properties ^[52].

Fig. 4

Fig. 5

To further explore the utility of **CPPB** as an ion-selective fluorescent sensor for CN^- , the anti-interference experiment of sensor **CPPB** was carried out upon addition of 2.0 equiv. of various anions in 99% aqueous DMSO solution (**Fig. 6**). The results indicate that common anions has no effect on sensor **CPPB** for CN^- detection and **CPPB** could be used as a fluorescent sensor for CN^- detection with excellent selectivity and good anti-interference.

Fig. 6

3.3.2. Detection performance of sensor CPPB to CN⁻

The changes of absorption spectrum of **CPPB** upon adding different amounts of CN^- in 99% aqueous DMSO solution can be seen in **Fig. 7**. As the concentration of CN^- increased from 0.5 to 2.0 equiv., all the absorption peaks at 280nm, 333nm and 440nm decreased remarkably. Additionally, a new absorption band appeared at 263 nm and increased significantly with the concentration of CN^- increasing. These results indicate that the reaction between **CPPB** and CN^- occurs and the conjugated system of **CPPB** was broken by CN^- . An iso-absorbance spot was observed at 275 nm indicating that the reaction between **CPPB** and CN^- produced a new complex. These speculations have been experimentally proved in the next section.

Fig. 7

The sensing performance of **CPPB** to different amounts of CN^- in 99% aqueous DMSO solution was further studied by fluorescence emission spectroscopy (Fig.8). As shown in **Fig. 8a**, with the amount of CN^- (0.5 ~ 2.0 equiv.) increasing, the emission peak at 625 nm gradually decreases due to the interruption of intra-molecular charge transfer (ICT) of **CPPB**. The inset in **Fig. 8a** is a plot of the fluorescence intensity of CPPB at 625 nm as a function of the concentration of CN^- (0 ~ 2.0 equiv). It can be seen that the FL intensity decreases remarkably when C_{CN}^- increases from 0 to 10 μ M. When C_{CN}^- is larger than 10 μ M, the FL intensity almost remains unchanged, indicating that CN^- is saturated in the solution. The detection limit (DL) of sensor **CPPB** for CN^- was determined to be 67.4 nM with a linear range of concentration to be 0 ~ 10 μ M (**Fig. 8b**), which far below the allowable content of CN^- in drinking water.

Fig. 8

The stability of **CPPB** and **CPPB-CN**⁻ under different pH in 99% aqueous DMSO solution was studied by FL spectra (**Fig. 9**). **CPPB** had a stable emission intensity as pH changed from 1.0 to 10.0, while the emission intensity dropped sharply when the pH was more than 10.0. Contrastingly, the emission intensity of **CPPB-CN**⁻ in the pH range of $1.0 \sim 10.0$ was weaker than **CPPB** and showed a sharply decreasing tendency when pH increased from 1.0 to 10. It can be seen that the different emission intensity between **CPPB-CN**⁻ and **CPPB** were relatively large at pH = $3.0 \sim 10.0$, indicating that **CPPB** may exhibits excellent fluorescence response to CN⁻ at this pH range.

Fig. 9

The reaction time of **CPPB** towards CN^- was investigated by time-dependent fluorescence spectrum (**Fig. 10**). The FL intensity of **CPPB** increased rapidly within the first 15 s when CN^- was added. Afterward, the FL intensity of **CPPB-CN**⁻ almost kept unchanged in the next 25 s. Conclusively, the reaction between **CPPB** and CN^- could accomplish within 15 s at room temperature. The rapid response of **CPPB** towards CN^- provides a favorable condition for practical applications.

Fig. 10

3.4 Detection mechanism

The detection mechanism was investigated by ¹H NMR titration, HRMS spectra and Job's titration. ¹H NMR spectrum of sensor CPPB displayed two stretching vibration bands at 11.20 ppm and 9.20 ppm, which were assigned to Ha of barbituric acid and H_1 of vinylidene (Fig. 11). Nevertheless, in the ¹H NMR spectrum of **CPPB-CN**⁻, the band at 9.20 ppm corresponding to H₁ disappeared completely, while a new peak at 5.60 ppm which was assigned to H_2 was observed. Meanwhile, the peak of Ha at 11.20 ppm moved to high frequency of 9.15 ppm that was assigned to Hb. Furthermore, some other peaks corresponding to aromatic protons move slightly to high frequencies upon CN⁻ addition, owing to the breaking of the original structure. The investigation confirmed that CN⁻ with strong nucleophilicity attacked the C=C bond and interrupted the ICT between the electron donor and the electron acceptor of sensor **CPPB**^[53]. To further confirm the detection mechanism, the HRMS spectra of CPPB and CPPB-CN⁻ were researched. As shown in Fig S5, a distinct upfield shift was observed for the vinylic proton H1 of CPPB upon addition of CN⁻. The vinylic proton H₁ shifted upfield from 325.1457 ppm to 392.1485 ppm (denoted H₂), indicating that the nucleophilic addition reaction between CPPB and CN⁻ was completed. Fig. 12 displayed the results of Job's titration derived from fluorescence emission spectra, which indicated the 1:1 stoichiometric reaction between sensor CPPB and CN⁻. Therefore, the detection mechanism of sensor CPPB for CN⁻ has been confirmed to be that CN⁻ with strong nucleophilicity attacked the vinylidene of CPPB (Scheme 2).

Fig. 11 Fig. 12 Scheme 2

3.5. Theoretical Calculations

To further investigate the detection mechanism of **CPPB** for CN⁻, the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed at the B3LYP/6-31G* level of the Gaussian 09 program

^[44-47] on the structure, electron distribution and optical properties of **CPPB** and **CPPB-CN**⁻. The optimized structure of **CPPB** and **CPPB-CN**⁻ was depicted in **Fig. 13.** Molecule **CPPB** showed a rigid planar conformation by sp² hybridization, however, **CPPB-CN**⁻ displayed a V-shaped conformation by sp³ hybridization. The result indicated that distinct structural differences between **CPPB** and **CPPB-CN**⁻ leaded to no ICT of **CPPB-CN**⁻ and caused significant changes of the conjugated system, which resulted in significant changes in their fluorescence properties.

Fig. 13

To grasp more about the colorimetric and fluorescent sensing mechanisms of CPPB, the time dependent DFT calculations were figured out (Fig. 14). For CPPB molecule, the electron distribution of LUMO was mainly concentrated in the entire barbituric acid and a part of the carbazole group, while that of the HOMO was distributed in the part of the barbituric acid and the entire carbazole group. However, for the CPPB-CN⁻ molecule, the electron distribution of LUMO and HOMO were both distributed over the carbazole group, which implied the interruption of ICT stage, resulted in obvious fluorescence weaken and brought about a new absorption band of **CPPB-CN**⁻. Moreover, the break of the π -conjugated system caused the increased HOMO-LUMO energy gap of CPPB-CN⁻ (4.63 eV) relative to the sensor CPPB (3.41 eV), which can be interpreted for the appearance of the new absorption band (263 nm). Furthermore, the calculated excitation wavelengths of CPPB and CPPB-CN⁻ were 402 nm and 268 nm respectively, which were almost consistent with the experimental results (Fig. 5). Therefore, these DFT and TD-DFT calculations verified that the CN⁻ was combined with the vinylidene of sensor CPPB which lead to the fluorescence quenching of CPPB.

Fig. 14

3.6 Test strips for CN⁻ detection in 100% aqueous

For convenient use of sensor **CPPB** for CN^- detection, the test strips of **CPPB** toward CN^- in 100% aqueous was prepared. Sensor **CPPB** (20 μ M, H₂O/DMSO (9:1; v/v)), has been coated on filter paper, and dried in a dry box, followed by adding different concentrations of CN^- in 100% aqueous. As observed in **Fig. 14**, significant

color changes under UV light from orange to blue turn out with different concentration of CN^- (0 ~ 20 μ M). It proved that the test strips can be applied to detect CN^- qualitatively and quantitatively.

Fig. 15

4. Conclusions

In summary, we have successfully developed sensor **CPPB** for CN^- detection based on naked-eye colorimetric and fluorescent sensing in 99% aqueous DMSO solution with high selectivity and great sensitivity, which exhibits interesting AIE effect. Moreover, sensor **CPPB** for the detection of CN^- revealed extremely low detection limit (67.4 nM), high anti-interference ability, wide pH response range as well as immediate response (15 s), which indicated that **CPPB** may be promising candidates for sensing CN^- in water.

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Declarations of interest

None.

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Figure captions

Scheme 1. The synthetic route of the sensor CPPB

Fig. 1. The UV-vis absorption spectra of sensor CPPB $(10 \mu M)$ in pure DMSO.

Fig. 2. (a) The FL spectra of sensor **CPPB** (10 μ M) in DMSO/H₂O (v/v) mixtures with different water fraction (f_w) at $\lambda_{ex} = 440$ nm; (b) Plot of relative FL peak wavelength (blue) and emission intensity (purple) of **CPPB** versus the f_w . (The blue line belongs to the wavelength, and the red line belongs to the FL intensity.)

Fig. 3. Photographs of sensor **CPPB** at $f_w = 0\%$ to 99% under 365 nm UV light.

Fig. 4. Color changes induced upon addition of 2.0 equiv. of various anions and reactive oxygen species to **CPPB** solution in 99% aqueous DMSO solution under sunlight and 365 nm UV light. (The first row shows the color change under sunlight, and the second row shows the color change under 365 nm UV light)

Fig. 5. (a) The UV-vis spectra of CPPB (10 μ M) with various anions and reactive oxygen species (2.0 equiv.) in 99% aqueous DMSO solution; (b) The FL spectra of CPPB (10 μ M) with various anions and reactive oxygen species (2.0 equiv.) in 99% aqueous DMSO solution.

Fig. 6. Competitive experiments in the **CPPB-CN**⁻ system with interfering anions $(\lambda_{ex} = 440 \text{ nm})$. Blue bars represent other anions and reactive oxygen species solution (1 mM) and red bars represent other anions and reactive oxygen species solution with CN⁻ (1 mM).

Fig. 7. The UV-vis spectra upon titration CN^- (0 ~ 2.0 equiv.) at various concentration in 99% aqueous DMSO solution.

Fig. 8. (a) The FL titration spectra of **CPPB** (10 μ M) with the increasing concentration of CN⁻ (0 ~ 2.0 equiv.) in 99% aqueous DMSO solution, **Inset**: plot of the FL intensity of **CPPB** at 625 nm as a function of CN⁻ concentration (0 ~ 2.0 equiv.); (b) The detection limit of **CPPB** for CN⁻.

Fig. 9. The FL intensity of CPPB (10 μ M) as a function of pH (1.0 ~ 14.0) in the absence and presence of CN⁻ ($\lambda_{ex} = 440$ nm).

Fig. 10. The time-dependent FL spectrum of CPPB toward CN⁻.

Fig. 11. The ¹H NMR spectra of CPPB (red) and CPPB-CN⁻ (navy) in DMSO- d_6

upon the addition of 2.0 equiv. CN⁻.

Fig. 12. Job's plot for CPPB towards CN^- in 99% aqueous DMSO solution (The total concentration was 10 μ M).

Scheme 2. The sensing mechanism of sensor CPPB for CN⁻.

Fig. 13. Optimized structures of CPPB and CPPB-CN⁻.

Fig. 14. HOMO and LUMO energy levels of CPPB and CPPB-CN⁻.

Fig. 15. The photographs of **CPPB** upon addition of CN⁻ under 365 UV light on filter paper.

Scheme 1









Fig. 5



Fig. 6



Fig. 7





Scheme 2



Fig. 13



7 μΜ

9 µM

 $10 \ \mu M \quad 20 \ \mu M$

0 µM

3 μΜ

5 μΜ

Highlights

Carbazole-based colorimetric and fluorescent sensor CPPB was designed and synthesized, which exhibited obvious aggregation induced emission (AIE) effect.

The sensor CPPB detected CN^- in 99% aqueous DMSO solution, and the test strips of CPPB recognized CN^- in 100% aqueous solution.

The detection limit of sensor CPPB for CN⁻ were at nanomolar level in 99% aqueous DMSO solution.

Colorimetric responses of sensor CPPB toward CN⁻ were visible with the naked eyes under sunlight and UV lamp (365 nm).