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## **A new carbazole-benzothiazole based chemodosimeter for chromogenic and fluorogenic detection of $\text{CN}^-$**

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### **Abstract**

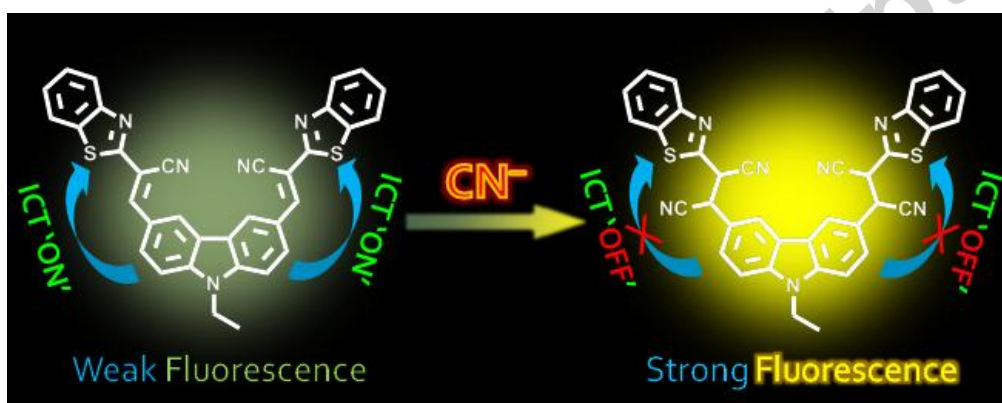
A hybrid carbazole-benzothiazole based chemodosimeter (CB) has been synthesized for the colorimetric and fluorogenic detection of cyanide ion ( $\text{CN}^-$ ). Intra-molecular charge transfer (ICT) played important role for the detection of  $\text{CN}^-$  in DMSO-water (4/1, v/v, pH=7.2) solution. Upon treatment of  $\text{CN}^-$  to the probe solution, results bleaching of the original yellow color of the probe with a large blue shift in absorption spectra. A large enhancement of the fluorescence intensity with a slight red shift is observed after addition of  $\text{CN}^-$  to the probe (CB). Here, the nucleophilic addition of  $\text{CN}^-$  inhibits the intra-molecular charge transfers (ICT) process responsible for the large enhancement of emission. The chemical reaction involved behind the sensing of  $\text{CN}^-$  has been confirmed through  $^1\text{H}$  NMR and mass spectroscopic studies. The density function theory (DFT) and time-dependent density function theory (TDDFT) has also been conducted to support the experimental findings.

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### **Graphical Abstract:**

The synthesized carbazole-benzothiazole based chemodosimeter (CB) is selectively used for the colorimetric and fluorogenic detection of cyanide ion ( $\text{CN}^-$ ). Both intra-molecular charge

transfer (ICT) and aggregation induced emission enhancement (AIEE) played important role for the detection of  $\text{CN}^-$  in DMSO-water (4/1, v/v, pH=7.2) solution. Upon treatment of  $\text{CN}^-$  to the probe solution, results bleaching of the original yellow color of the probe with a large blue shift in absorption spectra. A large enhancement of the fluorescence intensity with a slight red shift is observed after addition of  $\text{CN}^-$  to the probe (CB).



*Key words:* Chemodosimeter; Carbazole; Benzothiazole; ICT; Colorimetric and fluorogenic;  $\text{CN}^-$ ; DFT and TDDFT.

## 1. Introduction

Cyanide is one of the most well-known poisonous material [1]. It can damage our heart, brain and finally causes death. According to the World Health Organization (WHO) the acceptable level of cyanide in drinking water is up to 1.9  $\mu\text{M}$  concentration [2]. Cyanide binds to heme unit in the active site of cytochrome a3 and inhibits cellular respiration leading to unconsciousness, vomiting, convulsion and eventual death [3,4]. On the other hand cyanide is one of the most

useful anion among the other, used in industrial process of making papers, plastics. During gold-extraction from its ore cyanide salt is used [5]. Herbicide [6], synthetic fibers and resins industry [7] also use cyanide salts for their purpose. From industrial waste it contaminates water and reaches to living beings through food chain. So it is necessary to develop a low-cost, simple, selective and sensitive colorimetric and fluorescent chemosensor for the detection of cyanide anion ( $\text{CN}^-$ ) to monitor the presence of  $\text{CN}^-$  in environmental samples [8].

A number of colorimetric and fluorescent chemosensor for  $\text{CN}^-$  has been developed yet, based on intra-molecular charge transfer (ICT) [9-14], intra-molecular photon transfer (IPT) [15-17], photoinduced electron transfer (PET) [18-21], complex formation with metal ions and boron derivatives [22-24], hydrogen bonding interactions [25], attachment to quantum dots [26], and supramolecular self-assembly [27], mechanisms. Recently, some cyanide fluorescence probes have been developed depending on the nucleophilic attack of cyanide anion on the electrophilic functional group such as dicyano-vinyl [28-33], aldehyde [34-38], indolium [39-45], and trifluoroacetyl group [46], causing changes in conjugated system and followed by the spectroscopic properties.

Most of the sensors, with double activated acceptor, have low fluorescence quantum yield in aqueous medium and suffer from aggregation-caused quenching (ACQ) effect [47]. They have to operate in either pure organic solvent or solution containing large amount of organic solvent [48]. So it is challenging to synthesis a selective  $\text{CN}^-$  chemodosimeter which shows aggregation-induced emission enhancement (AIEE) effect and is highly emissive in aqueous solution despite of aggregation [49, 50].

Herein, we have designed and synthesized a new fluorescence chemodosimeter consist of an acceptor- $\pi$ -donor- $\pi$ -acceptor (A- $\pi$ -D- $\pi$ -A) skeleton in which two terminal benzothiazole-

2-acetonitrile group act as acceptor and carbazole derivative acts as donor. Upon addition of cyanide anion the intra molecular charge transfer (ICT) between A- $\pi$ -D- $\pi$ -A get inhibited. Cyanide acts as a good nucleophile, attacks to the electrophilic center of the probe to suppress the  $\pi$ -conjugation resulting rapid change in color and fluorescence.

## 2. Experimental

### 2.1. Material and methods

Carbazole and 2-aminothiophenol were purchased from Sigma Aldrich and used without further purification. All other reagents and solvents were purchased from commercial sources and used without any further purification.

2400 Series-II CHN analyzer, Perkin Elmer, USA, was used for elemental analysis of the synthesized probe. HRMS mass spectra were taken by Waters (Xevo G2 Q-TOF) mass spectrometer. Preparing a pellets of the probe with KBr, infrared spectrum was recorded on a RX-1 Perkin Elmer spectrophotometer. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 25 spectrophotometer. Emission spectra were taken by Shimadzu RF-6000 fluorescence spectrophotometer. NMR spectra were recorded with a Bruker (AC) 300 MHz FTNMR spectrometer of ~0.06 M solutions of the compounds in DMSO- $d_6$ .

### 2.2. Synthesis of the probe CB

9-ethylcarbazole-3,6-dicarbaldehyde [51] and 2-(1, 3-benzothiazol-2-yl)-acetonitrile [52] were prepared by following the procedure reported previously.

To a stirred solution of 9-ethylcarbazole-3,6-dicarbaldehyde (0.5 g, 2.0 mmol) and 2-(1, 3-benzothiazol-2-yl)-acetonitrile (0.7 g, 4.0 mmol) in EtOH (15 ml), piperidine (0.25 ml) was added. The whole mixture stirred under refluxing condition for seven hours in inert atmosphere.

After completion of the reaction, the reaction mixture is allowed to cool to room temperature. A yellow color precipitate is appeared which is collected through filtration. The compound is pure enough therefore no further column chromatography is performed to purify the compound. The probe (CB) is characterized by Elemental analysis,  $^1\text{H}$  NMR and HRMS. Yield: (0.95g) 80%.

Anal. Calcd for  $\text{C}_{34}\text{H}_{21}\text{N}_5\text{S}_2$ , C, 72.44%; H, 3.76%; N, 12.42%; S, 11.38%; Found C, 72.38%; H, 3.82%; N, 12.47%; S, 11.31%. IR ( $\text{cm}^{-1}$ , KBr):  $\nu(\text{C}\equiv\text{N})$  2211  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  1.39 (t,  $J = 6.37$  Hz, 3H), 4.57 (q,  $J = 6.7$  Hz, 2H), 7.54 (m, 4H), 7.93 (d,  $J = 8.5$  Hz, 2H), 8.06 (d,  $J = 7.5$  Hz, 2H), 8.15 (d,  $J = 7.8$  Hz, 2H), 8.36 (d,  $J = 9.2$  Hz, 2H), 8.57 (s, 2H), 8.95 (s, 2H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  161.07, 152.73, 150.21, 144.37, 135.87, 135.56, 131.59, 129.76, 127.87, 127.03, 126.09, 124.95, 117.07, 116.51, 115.25, 110.90, 22.87, 14.21 (18 carbon peak). HRMS: Calcd. for  $\text{C}_{34}\text{H}_{21}\text{N}_5\text{S}_2$  [ $\text{M} + \text{H}$ ] $^+$  (m/z): 564.1317; found 564.1310

### 2.3. UV-Vis study

For UV-Vis titrations, stock solution of CB (20  $\mu\text{M}$ ) in [(DMSO /  $\text{H}_2\text{O}$ ), 4:1, v/v, pH=7.2] (at 25°C) was prepared using HEPES buffered solution in deionised water. The solutions of the guest anions were prepared using their sodium salts in the order of  $2 \times 10^{-4}$  M in deionized water. Spectra were recorded using the solutions containing probe and increasing concentration of guest anions. All these solutions were prepared individually.

### 2.4. Fluorescence study

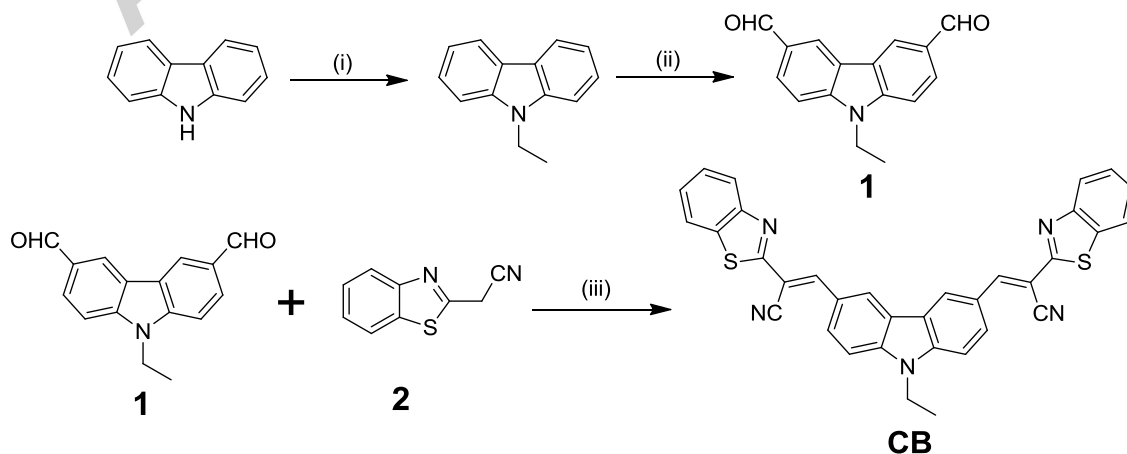
Stock solution of the chemodosimeter CB (20  $\mu\text{M}$ ) in [(DMSO /  $\text{H}_2\text{O}$ ), 4:1, v/v, pH=7.2] (at 25°C) was prepared using HEPES buffered solution in deionised water. To it tetrabutyl ammonium cyanide (40  $\mu\text{M}$ ) solution was gradually added and fluorescence spectra were recorded. Sodium salts of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SCN}^-$ ,  $\text{HSO}_4^-$ ,  $\text{N}_3^-$  in deionized water of 40  $\mu\text{M}$  concentration were also added to the 20  $\mu\text{M}$  CB solution and fluorescence spectra were

recorded. To it further  $\text{CN}^-$  ( $40 \mu\text{M}$ ) solution was added and spectra recorded. For fluorescence study excitation wavelength used was 375 nm (excitation slit = 5.0 and emission slit = 5.0). The detection limit was calculated using the fluorescence titration data. To determine the S/N ratio, the emission intensity of CB without the ion ( $\text{CN}^-$ ) was measured by 10 times and the standard deviation of blank measurements was determined. The detection limit of CB for  $\text{CN}^-$  was determined using,  $\text{LOD} = K \times \text{SD}/S$ , where SD is the standard deviation of the blank solution and S is the slope of the linear response curve.

### 3. Results and discussion

#### 3.1. Synthesis of the probe (CB)

Synthesis of the chemodosimeter (CB) involves the condensation of 2-(1,3-benzothiazole-2-yl)-acetonitrile and 9-ethylcarbazole-3,6-dicarbaldehyde in ethanol solution under reflux condition (Scheme 1). The structure of CB has been characterized by NMR, elemental and mass spectral analysis (Figs. S8-S11).



Scheme 1. Synthesis of the probe CB. Reagents and conditions: (i)  $K_2CO_3$ , ethyl iodide, Acetone, reflux, 6 h; (ii) DMF/ $POCl_3$ ,  $70^{\circ} - 80^{\circ}C$ , 12 h; (iii) EtOH, Piperidine, reflux, 7h.

### 3.2. IR, NMR and mass spectral analyses

The nitrile ( $-C\equiv N$ ) stretching frequency appears at  $2211.46\text{ cm}^{-1}$  and the  $-C=N$  stretching frequency of the benzothiazole moiety appears at  $1557$  and  $1574\text{ cm}^{-1}$ . In  $^1H$  NMR two singlet protons appear at  $\delta$  8.93 and  $\delta$  8.57 ppm and the other aromatic protons appear in the region  $\delta$  8.37–  $\delta$  7.48 ppm respectively (Fig. S8). After reaction with cyanide, two singlet protons shifted to upfield. One proton shifts from  $\delta$  8.93 to  $\delta$  8.10 ppm and other from  $\delta$  8.57 to  $\delta$  5.60 ppm respectively. All other aromatic protons also shift to the upfield region from  $\delta$  8.37–  $\delta$  7.48 ppm to  $\delta$  7.61 -  $\delta$  6.67 ppm (Fig. S12), which can clearly explained the formation of cyanide adduct with CB. Mass spectrum shows  $m/z$  peak corresponding to CB at  $m/z$  564.1310 (Fig. S10). For CB-CN there appear two new peaks at  $m/z$  591.1430 and 618.1534 correspond to  $[CB + CN^-]$  and  $[CB + 2CN^-]$  (Fig. S13) also support the adduct formation.

### 3.3. Anion sensing studies of CB

#### 3.3.1. UV-Vis study

The UV-vis spectra of the CB ( $20\ \mu M$ ) displays a low energy band at 440 nm and two high energy band at 389 nm and 342 nm due to intra molecular charge transfer (ICT) from carbazole moiety to electron deficient benzothiazole moiety and  $\pi-\pi^*$  transition respectively in DMSO- $H_2O$  (4/1, v/v, pH = 7.2) solution.



Upon addition of cyanide (40  $\mu\text{M}$ ) the yellow color of the probe solution become colorless indicates the nucleophilic addition of cyanide to the electron deficient part of CB results gradually lay off ICT transition and form a band with low absorbance and slight blue shift from 440 nm to 423 nm. Along with a new band appeared at 353 nm with a distinct isosbestic point at 373 nm (Fig. 1). UV-Vis spectrum of CB is also studied in presence of other anions such as  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SCN}^-$ ,  $\text{HSO}_4^-$  and  $\text{N}_3^-$  but no significant changes are observed (Fig. 2).

### 3.3.2. Fluorescence study

Chemodosimeter (CB) showed a very weak emission band with maxima at 522 nm upon excitation at 375 nm. Gradual addition of  $\text{CN}^-$  (0–40  $\mu\text{M}$ ) to the probe solution (20  $\mu\text{M}$ ) an excellent enhancement of fluorescence intensity at 531 nm is observed (Fig. 3). To monitor the reaction time of the probe with  $\text{CN}^-$  fluorescence spectra were recorded depending on time (Fig. S3). The experiment shows that after 9 minutes there is no significant change in the emission intensity indicates the completion of the reaction.

The limit of detection of CB for  $\text{CN}^-$  is found to be  $3.73 \times 10^{-9}$  M (Fig. S4). This result clearly exhibits that the chemodosimeter is highly efficient in sensing  $\text{CN}^-$  even in very minute level. Emission intensity of CB (20  $\mu\text{M}$ ) is also studied in presence of other anions i.e.  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SCN}^-$ ,  $\text{HSO}_4^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HSO}_3^-$ ,  $\text{SH}^-$ ,  $\text{HCO}_3^-$ , and  $\text{N}_3^-$  (40  $\mu\text{M}$ ) in DMSO- $\text{H}_2\text{O}$  (4/1, v/v) and there is no significant change in emission intensity of CB is observed (Fig. 4). To establish the selectivity of CB for cyanide detection we also execute fluorescence titration in presence of other anions (Fig. S5). It shows high-class  $\text{CN}^-$  sensing aptitude even in the presence of all co-existing anions in the same solution phase. Among the all anion only cyanide reacts with the probe to change the electronic property in compared to other anions studied.

For extending the scope of experimentation of synthesized probe, we have studied the pH dependent emission spectral changes of the probe (CB) in absence and presence of  $\text{CN}^-$  in DMSO- $\text{H}_2\text{O}$  (4/1, v/v). Spectra showed, in different pH conditions the emission intensity of the probe is almost unaffected in absence of  $\text{CN}^-$ . In presence of  $\text{CN}^-$ , there is a significant enhancement of emission intensity occur at near neutral pH range (Fig. 5). From this experiment, it is concluded that the probe shows most effective sensing of  $\text{CN}^-$  at neutral pH medium.

Excited state behaviour of the synthesised probe (CB) and the cyanide adduct (CB-CN) are examined by nano-second time resolved fluorescence technique. The fluorescence decay curves of the probe and cyanide adduct are obtained by using the mono-exponential functions with good  $\chi^2$  values (Fig. 6). For CB,  $\tau = 5.25$  ns ( $\chi^2 = 1.16$ ), and for CB-CN adduct,  $\tau = 38.13$  ns ( $\chi^2 = 1.14$ ). Radiative rate constant  $K_r$  and total non radiative rate constant  $K_{nr}$  have been calculated using the equation  $\tau^{-1} = K_r + K_{nr}$  and  $K_r = \Phi_f / \tau$  (Table S1). The change in the value of  $\tau$ ,  $K_r$  and  $K_{nr}$  indicates the adduct formation of cyanide with the probe CB to form a new fluorogenic compound CB-CN which have higher lifetime than the probe itself.

### 3.4. Aggregation-Induced Emission Enhancement (AIEE) study

Aggregation-Induced Emission Enhancement (AIEE) of our synthesized probe (CB) is studied in DMSO solvent with increasing volume percentage of water (Fig. 7). The concentration of the probe solution in DMSO-water mixture was kept constant at 20.0  $\mu\text{M}$ . As volume percentage of water of water-DMSO solution increases from 0% to 60% emission maximum shift from 521 nm to 614 nm ( $\lambda_{\text{ex}} = 375$  nm), with dramatically enhancement of emission intensity. It is observed that aggregation of the probe in DMSO-water solution begins from near 30% of water fraction. The fluorescence intensity reached to maximum value at 60% of water content. All of these suggest that CB is AIEE active compound. UV-Vis absorption spectral study is also done in the

same way as reported for emission study. A new broad band is generated at ~490 nm as volume percentage of water of water-DMSO solution increases from 40% to 99% (Fig. S7).

The single bond rotation in the probe CB is the reason for not viewing AIEE activity in DMSO solution. Free intra molecular rotation around single bond quenches the emission through non-radiative decay. This intra-molecular rotation quenches the emission in solution state, but in aggregate state where rotation is restricted, shows high emission enhancement with red-shift of about 93 nm [53-55]. Strong emission enhancement with red shift is maybe caused by planer geometry.

### 3.5. Probable sensing mechanism

The possible sensing mechanism of the probe is investigated by  $^1\text{H}$  NMR spectroscopy. The resonance signal at  $\delta$  8.57 ppm of the probe (CB), corresponds to vinylic proton which disappear in the resonance spectra of CB-CN adduct and a new signal generate at  $\delta$  5.60 ppm (Fig. S12) supports the formation of the adduct. Due to development of negative charges in CB-CN adduct, all other proton resonance signals also shifted to up-field region (Fig. 8). The formation of adduct after addition of  $\text{CN}^-$  is also confirmed by HRMS spectroscopy. Spectrum shows a peak at (m/z) 564.1310 for the probe itself (Fig. S10). However, two peaks at m/z 591.1430 and 618.1534 for the cyanide adduct of the probe confirm the formation of (CB+ $\text{CN}^-$ ) and (CB+2 $\text{CN}^-$ ) adducts respectively (Fig. S13). These results reveals the nucleophilic addition of  $\text{CN}^-$  to the  $\beta$ -position of C=C bond and conversation of  $\text{sp}^2$  hybridized carbon to  $\text{sp}^3$  hybridization (Fig. 9).

The previously reported chemodosimeters, where  $\text{CN}^-$  reacts with the probe as Michael type addition are given in table 1. Comparing the all reported chemodosimeters in terms of their

solvent system, reaction time and detection limit it is concluded that our probe has very low LOD with high selectivity.

### 3.7. DFT studies

To interpret the sensing mechanism of the chemodosimeter (CB) for the detection of  $\text{CN}^-$ , geometry optimization of CB and CB-CN were carried out by DFT/B3LYP/6-31+G(d) method. The optimized geometries are shown in Fig. 10. Geometry of the probe is almost planer with  $\pi$ -conjugation which is the reason for ICT from carbazole moiety to the benzothiazole moiety in the molecule. Upon interaction with  $\text{CN}^-$ , the geometry of the molecule changes to twisted form and as a result  $\pi$ -conjugation breakdown, leads to decrease ICT transition. Contour plots and energies of selected molecular orbitals are given in Figs. S14-15. The HOMO-LUMO energy gap is significantly increased in CB-CN adduct (3.504 eV) compared to CB (3.051 eV) (Fig. 11) which is well reflected in the changes in UV-vis spectra. To further support the fact TDDFT calculation by CPCM method were carried out and summarized in table 2. The calculated transitions are well supported the blue shift in UV-vis spectra of CB upon addition of  $\text{CN}^-$ .

### 4. Conclusion

In summary, we have reported herein the synthesis and characterization of a new, simple and inexpensive colorimetric and fluorescence 'turn on' chemodosimeter for the selective detection of cyanide anion in mixed aqueous medium. The LOD is found to be 3.73 nM for the detection of  $\text{CN}^-$  which is very much lower than the WHO regulation for tolerable level of  $\text{CN}^-$  in drinking water. The probe is almost silent in presence of other relevant competing anions indicates its high selectivity towards  $\text{CN}^-$ . The ICT based sensing mechanism of CB for the detection of  $\text{CN}^-$  is further confirmed by theoretical studies.

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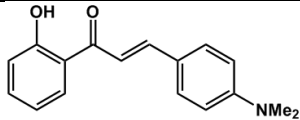
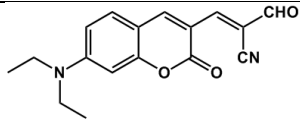
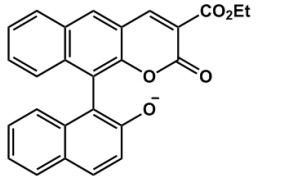
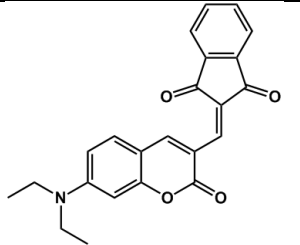
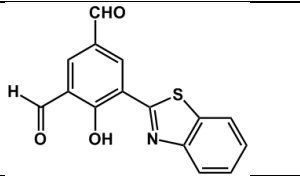
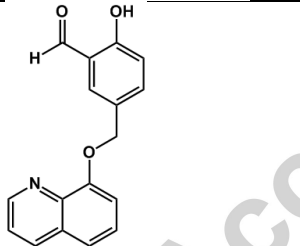
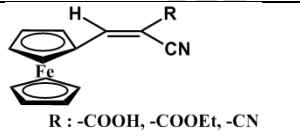
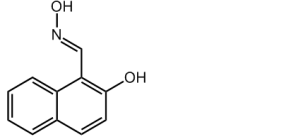
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Table 1. Comparison of the present probe (CB) with the reported chemodosimeters for the selective detection of  $CN^-$

Probe	Solvent system	Detection limit	Reaction time	Reference
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	CH <sub>3</sub> CN	1.7 μM	9h	<i>Chem. Commun.</i> , 2010, 46, 9197–9199
	CH <sub>3</sub> CN	0.328 μM	60 s	<i>Org. Lett.</i> 2011, 13, 3730–3733
	THF	2.28 μM	30 min	<i>Org. Lett.</i> , 2012, 14, 130–133
	CH <sub>3</sub> CN	1.8 μM	60 s	<i>Dyes Pigm.</i> 2012, 95, 168–173.
	CH <sub>3</sub> CN-H <sub>2</sub> O (1:1, v/v)	1.6 μM	-	<i>Chem. Commun.</i> , 2013, 49, 2912-2914
	H <sub>2</sub> O	0.20- 0.21 μM	50-60 min	<i>Tetrahedron Lett.</i> 2014, 55, 1052–1056
 R : -COOH, -COOEt, -CN	H <sub>2</sub> O-CH <sub>3</sub> CN (4:1, v/v)	0.14–0.49 μM	-	<i>Sens. Actuators B</i> 2015, 221, 1441–1448.
	CH <sub>3</sub> OH-H <sub>2</sub> O (1:9, v/v)	0.95 μM	-	<i>J. Lumin.</i> 2015, 167, 413-417.

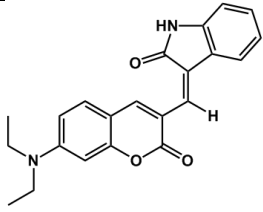
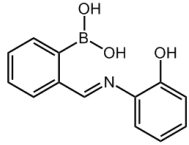
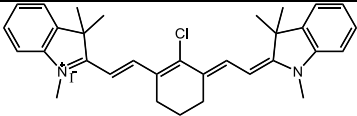
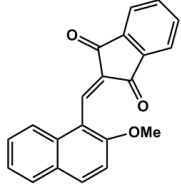
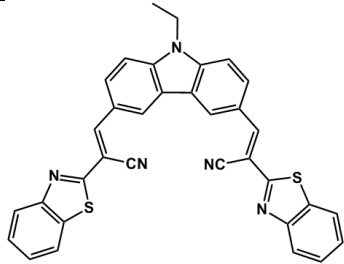
	DMSO-H <sub>2</sub> O (95:5, v/v)	0.51 μM	5 h	<i>Spectrochim. Acta Part A</i> 2015, 138, 164–168.
	CH <sub>3</sub> CN-H <sub>2</sub> O (2:8, v/v)	0.002 μM	-	<i>J. Lumin.</i> 2016,173, 25-29.
	CH <sub>3</sub> CN-H <sub>2</sub> O (9:1, v/v)	0.017 μM	-	<i>J. Lumin.</i> 2017,185 286–291
	H <sub>2</sub> O-DMF (9:1, v/v)	1.15–1.2 nM	10-30 s	<i>Sens. and Actuators B</i> 2017, 245, 74–80
	DMSO-H <sub>2</sub> O (4:1, v/v)	3.75 nM	9-10 min	This work

Table 2. Vertical electronic transitions of CB and CB-CN calculated by TDDFT/CPCM method

Comps.	$\lambda$ (nm)	E (eV)	Osc.	Key excitations	$\lambda_{\text{expt.}}$ (nm)
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	Strength (f)				
	462.3	2.6818	1.4243	(98%)HOMO→LUMO	440
CB	390.6	3.1743	0.9606	(72%)HOMO→LUMO+1	389
	351.9	3.5238	0.2389	(88%)HOMO-3→LUMO	342
CB-CN	342.6	3.6187	0.2698	(69%)HOMO→LUMO+1	353
	328.5	3.7741	0.5414	(37.6%)HOMO→LUMO+2	

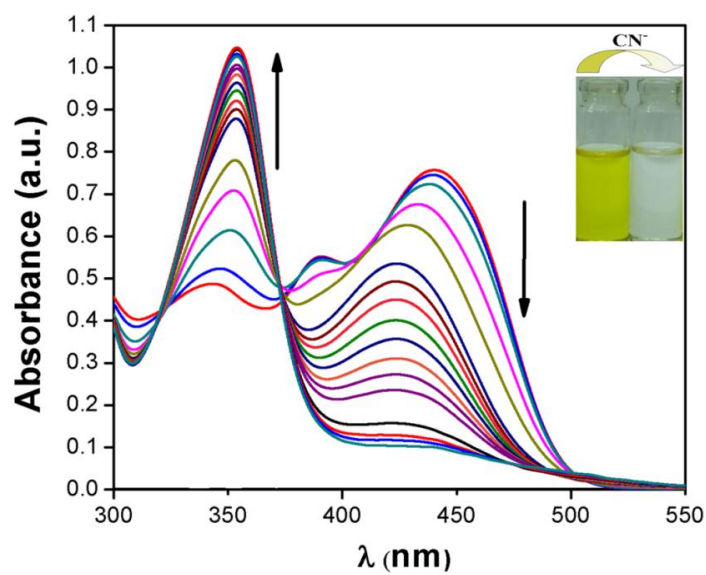


Fig. 1. Change in UV-Vis spectrum of CB (20  $\mu\text{M}$ ) upon gradual addition of  $\text{CN}^-$  (0–40  $\mu\text{M}$ ) in DMSO- $\text{H}_2\text{O}$  (4/1, v/v, pH = 7.2). Inset: The visual change of addition of  $\text{CN}^-$  (40  $\mu\text{M}$ ) to CB in ambient light.

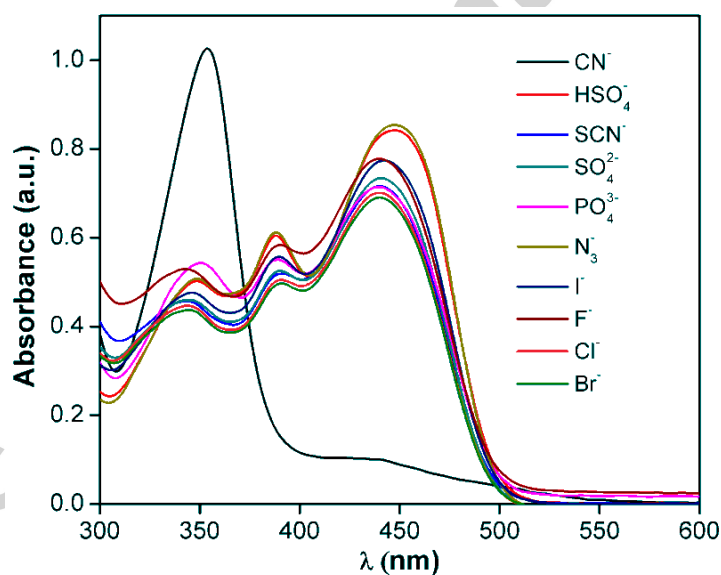


Fig. 2. Change in absorption spectrum of CB (20  $\mu\text{M}$ ) upon addition of different anions (40  $\mu\text{M}$ ) in DMSO- $\text{H}_2\text{O}$  (4/1, v/v, pH=7.2) solution.



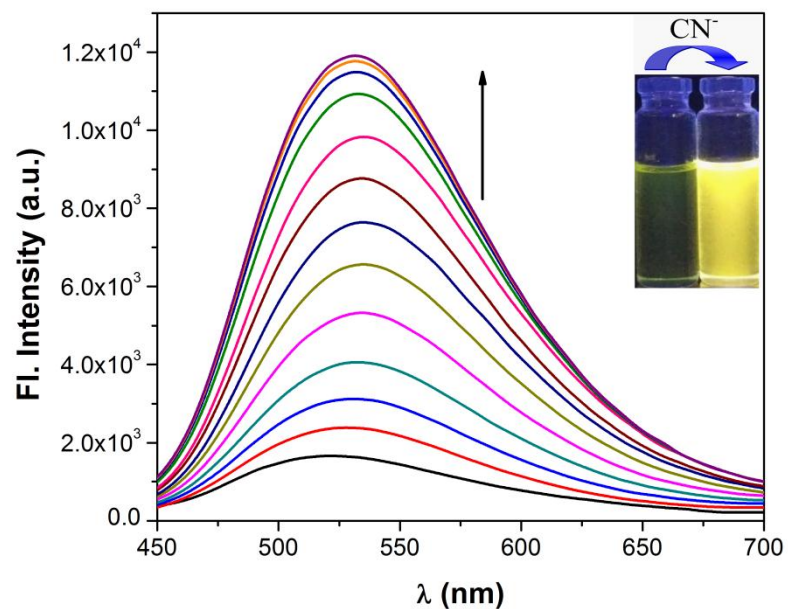


Fig. 3. Change in emission spectrum of CB (20  $\mu\text{M}$ ) upon gradual addition of  $\text{CN}^-$  (0–40  $\mu\text{M}$ ) in DMSO- $\text{H}_2\text{O}$  (4/1, v/v, pH = 7.2) solution ( $\lambda_{\text{ex}} = 375$  nm). Inset shows the visual effect of addition of  $\text{CN}^-$  to CB under UV light.

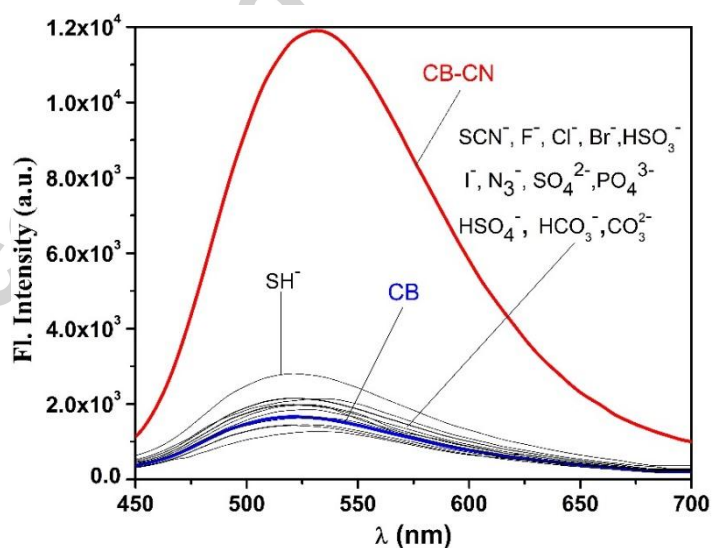


Fig. 4. Change in emission spectrum of CB (20  $\mu\text{M}$ ) upon addition of different anions (40  $\mu\text{M}$ ) in DMSO- $\text{H}_2\text{O}$  (4/1, v/v, pH=7.2) solution ( $\lambda_{\text{ex}} = 375$  nm).

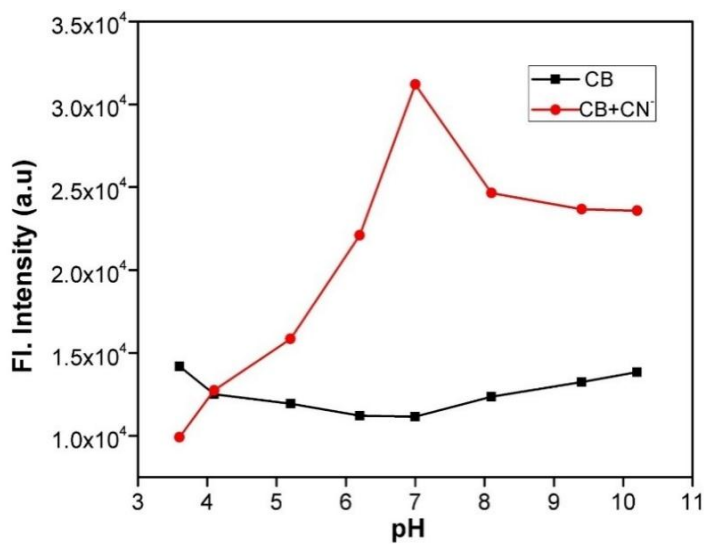


Fig. 5. Fluorescence response of CB (-■-■-) and CB-CN (-●-●-) as a function of pH in DMSO/H<sub>2</sub>O (4/1, v/v), pH is adjusted by using aqueous solutions of 1 M HCl or 1 M NaOH.

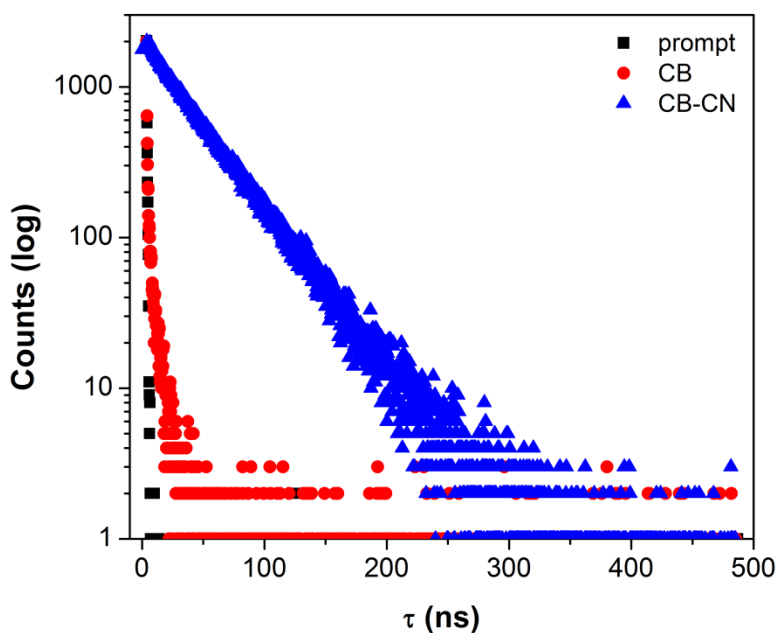


Fig. 6. Time-resolved fluorescence decay of CB (●●●), CB-CN complex (▲▲▲) and prompt (■■■) ( $\lambda_{\text{ex}} = 370 \text{ nm}$ ).

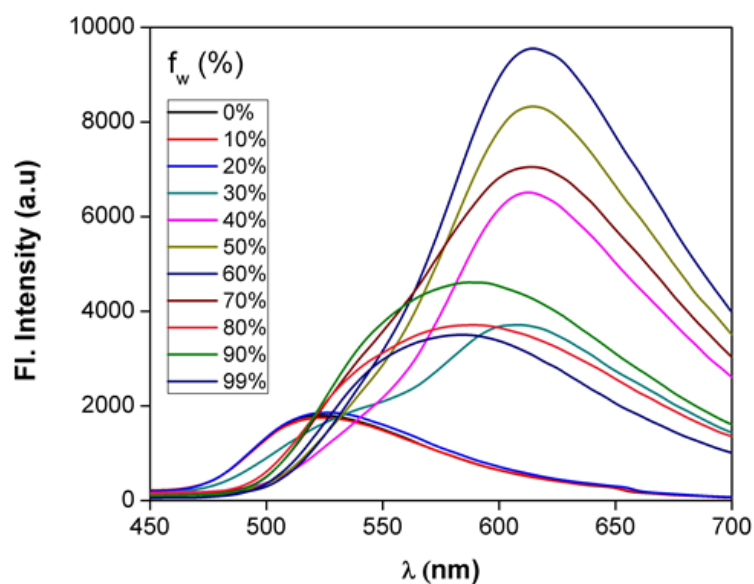


Fig. 7. Emission spectra of the probe in DMSO/water solution with different fraction of water in DMSO solvent.

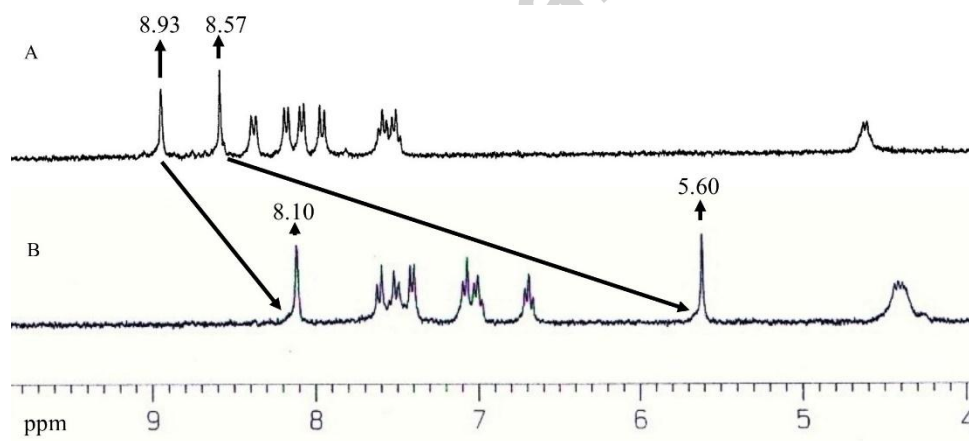


Fig. 8. Partial <sup>1</sup>H NMR spectra of (a) CB and (b) CB-CN recorded in DMSO-d<sub>6</sub>

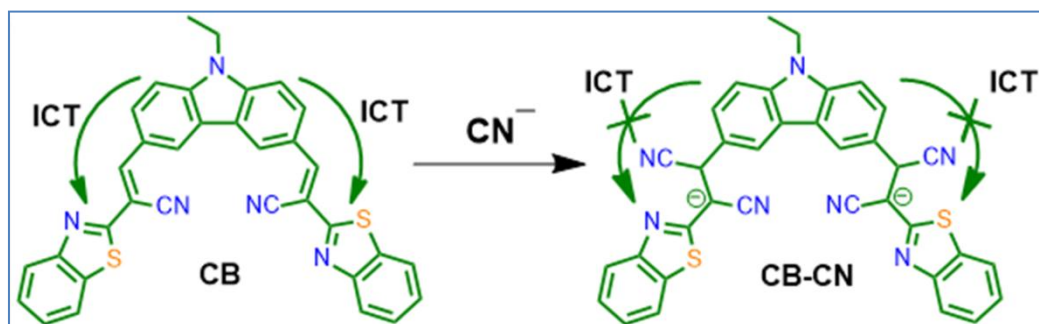


Fig. 9. Probable Sensing mechanism of the chemodosimeter (CB)

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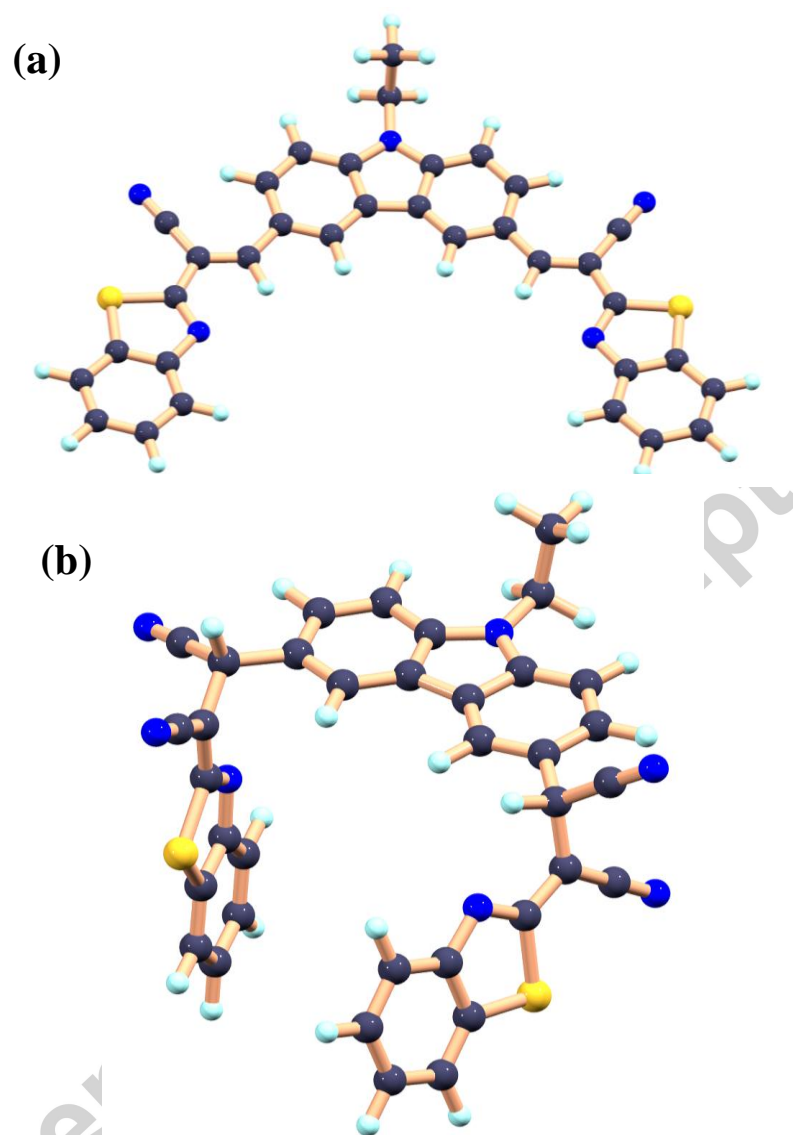


Fig. 10. Optimized structures of (a) CB and (b) CB-CN adduct calculated by DFT/B3LYP method.

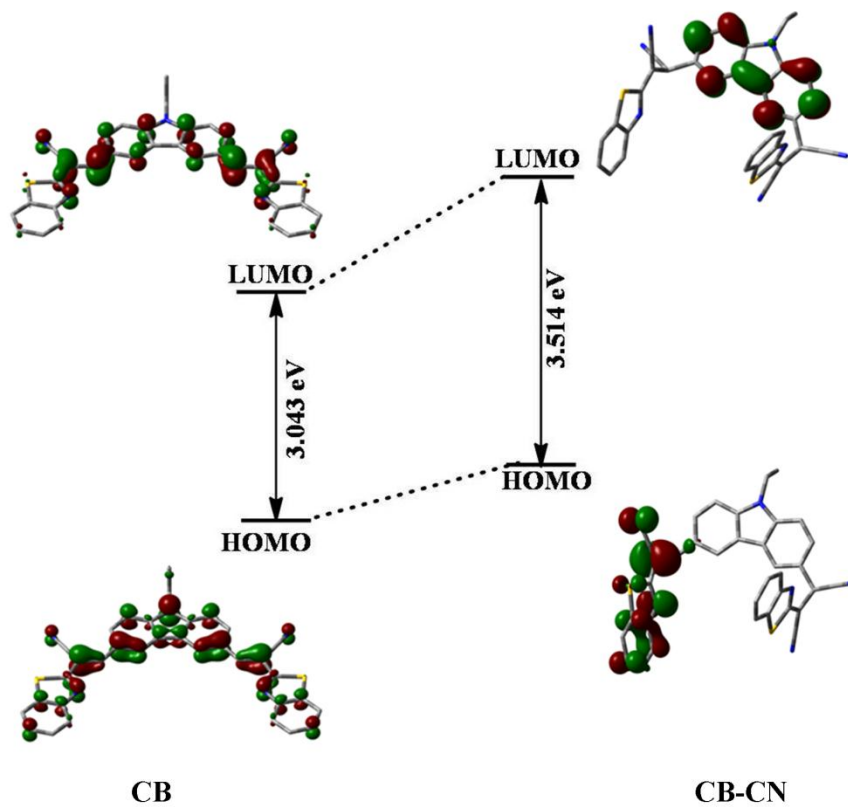


Fig. 11. Contour plots of HOMO, LUMO and HOMO-LUMO energy gap in CB and CB-CN complex