# *Supporting Information*

## Resonance-assisted hydrogen bonding induced nucleophilic addition to hamper ESIPT: ratiometric detection of cyanide in aqueous media

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## CONTENTS

## 1. General:

Unless otherwise mentioned, chemicals and solvents were purchased from Sigma-Aldrich Chemicals Private Limited and were used without further purification. Melting points were determined on a hot-plate melting point apparatus in an open-mouth capillary and are uncorrected. $^{1}$H-NMR and $^{13}$C-NMR are recorded on Brucker 400 and 500 MHz instruments. For $^{1}$H-NMR and $^{13}$C-NMR spectra, $d_6$-DMSO and $CDCl_3$ are used as solvents respectively, TMS is used as an internal standard. Chemical shifts are expressed in $\delta$ units and $^{1}$H–$^{1}$H and $^{1}$H–C coupling constants in Hz. UV-vis titration experiments were performed on a JASCO UV-V530 spectrophotometer and fluorescence experiment was done using PTI fluorescence spectrophotometer using a fluorescence cell of 10 mm path. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer, using KBr discs.

## 2. General method of UV-vis and fluorescence titration:

### By UV-vis method

For UV-vis and fluorescence titrations, stock solution of the sensor was prepared (c = 1 x $10^{-5}$ $ML^{-1}$) in $CH_3CN$-$H_2O$ (1:1, v/v, 25°C). The solution of the guest anions using their salts in the order of 2 x $10^{-4}$ $ML^{-1}$ was prepared in $CH_3CN$ solvent. pH of the solution is adjusted at 7.1 by using 20 mM HEPES buffer. Solutions of various concentrations containing sensor and increasing concentrations of anions were prepared separately. The spectra of these solutions were recorded by means of UV-vis methods.

## 3. Determination of Detection Limit:

The detection limit DL of **BHI** for $CN^{-}$ was determined from the following equation. [S1]

DL = K* Sb1/S

Where K = 2 or 3 (we take 3 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

Thus using the formula we get the Detection Limit = 1.6 μM i.e. BHI can detect $CN^{-}$ in this minimum concentration.

**4. Methods for the preparation of the receptor i.e. BHI and BHI-CN:**

**Synthesis of 2-(benzo[d]thiazol-2-yl) phenol:** HBT was synthesized according to a previously reported method [S2] with a minor modification. A solution of 2-aminothiophenol (0.3 mL, 4.2 mmol) and salicyldehyde (500mg, 4.09 mmol) in EtOH (10 mL), aq $H_2O_2$ (30%, 18.0 mmol) and aq HCl (37%, 10.5 mmol) was stirred at rt for 2hr. The solution was quenched by 20 mL $H_2O$. The precipitate was filtered, washed with ethanol, dried under vacuum and recrystallizaed from EtOH to afford the desired product as a white solid (670mg, 70% yield).

**Synthesis of 5-(benzo[d]thiazol-2-yl)-4-hydroxyisophthalaldehyde (BHI):** 2-(benzo[d]thiazol-2-yl) phenol (550mg, 2.42mmol) was dissolved in toluene (15ml) and acetic acid (15ml). Hexamethylenetriamine (583mg, 4.16mmol) was added in one portion and the solution was refluxed until all the starting material was consumed (TLC monitor, 21 hrs.). Then the mixture was cooled to rt and poured into 6M HCl (30ml) and extracted with ethyl acetate. The combined organic extracts were washed with saturated brine. Next purification was done by column chromatography to get the pure product (115mg) (we used 100-200 mesh silica gel and ethyl acetate: petroleum ether $_=$ 5:1).

**$^1$H NMR (CDCl$_3$, 400 MHz):** δ (ppm): 13.33 (d, 1H, $J$ = 30.8 Hz), 10.55 (s, 1H), 9.95 (s, 1H), 8.26 (d, 1H, $J$ = 2.4 Hz), 8.07 (q, 1H, $J$ = 10.4 Hz), 7.94 (m, 1H), 7.5 (m, 2H), 7.09 (t, 1H, $J$ = 10 Hz).

**$^{13}$C NMR (CDCl$_3$, 125 MHz)**: δ (ppm): 190.01, 189.00, 165.08, 154.12, 151.88, 147.73, 132.98, 130.59, 128.38, 124.01, 123.13, 118.34, 105.42, 96.79.

**Elemental Analysis: C - 63.50%, H – 3.12%, N – 5.01% (** Calculated **C - 63.59%, H – 3.20%, N – 4.94%)**

**MS (ESI MS):** (m/z, %): 284.03 [(BHI+H$^+$), 100 %]

**Synthesis of Cyanide adduct BHI:** BHI is mixed with one equivalent KCN in acetonitrile at rt to give a green color solution. On removing the solvent, a brownish solid product was obtained which directly was used for NMR, MASS, Elemental analysis and IR spectroscopy.

**¹H NMR (d₆-DMSO), 400 MHz):** δ (ppm): 10.32 (s, 1H), 9.5 (s, 1H), 8.31 (d, 1H, $J = 4$ Hz), 7.89 (m, 1H), 7.82 (t, 2H), 7.41 (m, 1H), 7.23 (q, 1H, $J = 10$ Hz), 6.37 (s, 1H).

**Elemental Analysis: C – 62.15%, H – 3.01%, N – 9.11% (** Calculated **C - 62.13%, H – 2.93%, N – 9.06%)**

**MS (ESI MS):** (m/z, %): 333.03 [(BHI+Na+H⁺), 100 %]

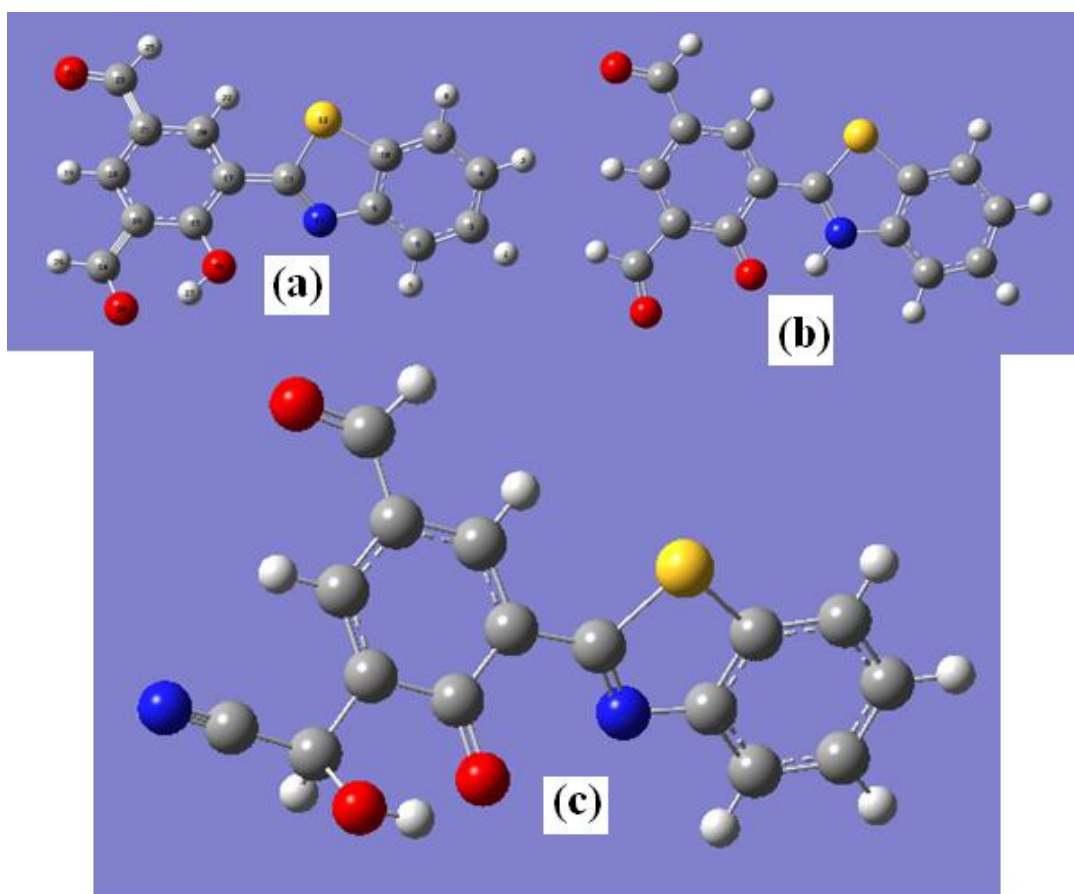**5. Energy minimized structure of BHI and its cyanide adduct product:**



**Figure S1:** Energy minimized structure of (a) BHI in enol form, (b) BHI in keto form and (c) BHI-CN adduct from DFT calculation.

## 6. Time-dependent absorption intensity of BHI with addition of KCN:
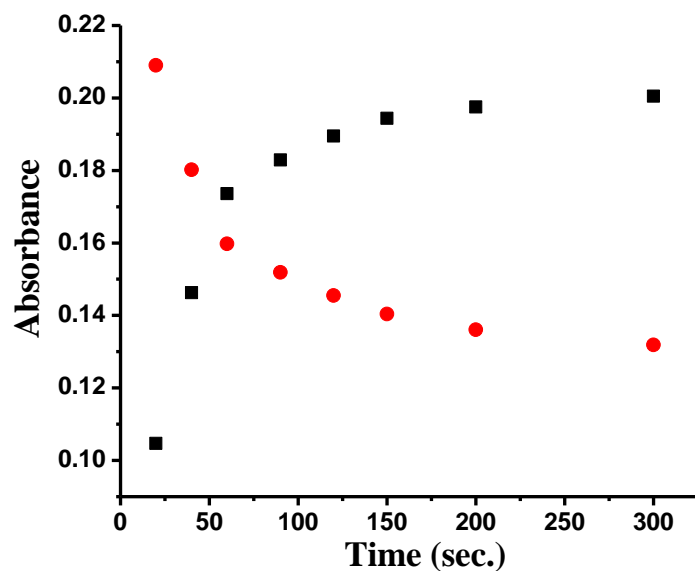


**Figure S2:** Time-dependent absorption intensity of BHI (10μM) at 346 nm (in red) and 438 nm (in black) in the presence of CN⁻ (2.0 equiv at a time) at pH 7.5 in $CH_3CN:H_2O$ = 1:1 (v/v).

## 7. $^1$H NMR, $^{13}$C NMR and ESI MS spectra of BHI and BHI + CN⁻:

### $^1$H NMR of Receptor i.e. BHI (in CDCl₃):
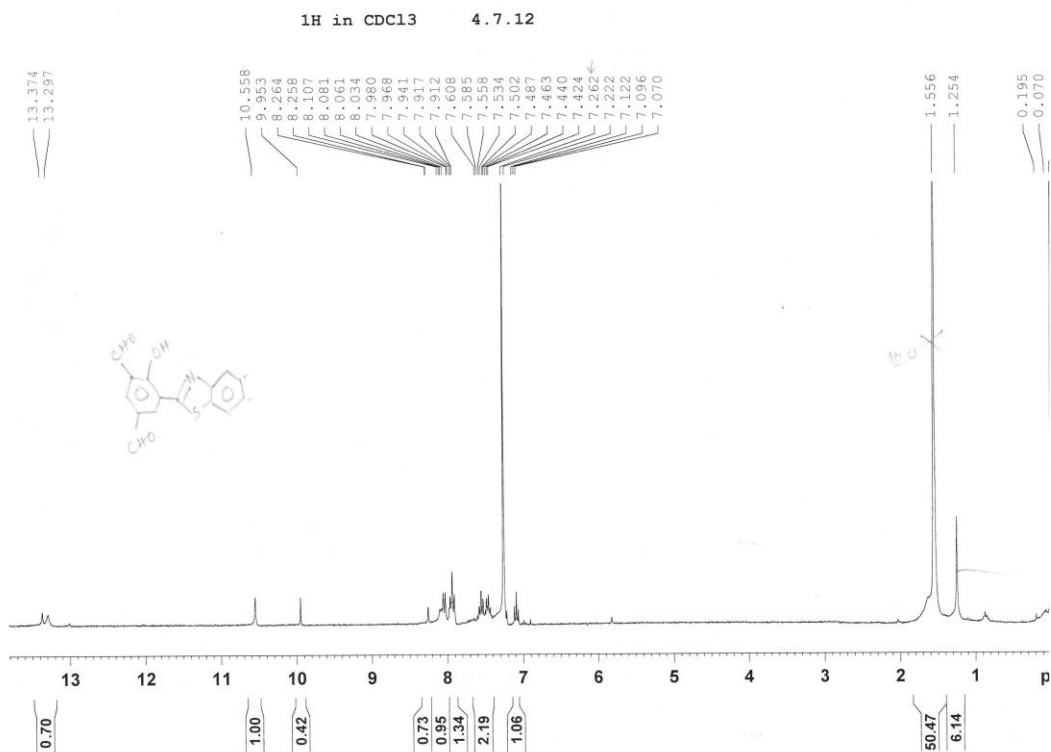
## Expansion of ¹H NMR:

1H in CDCl3      4.7.12
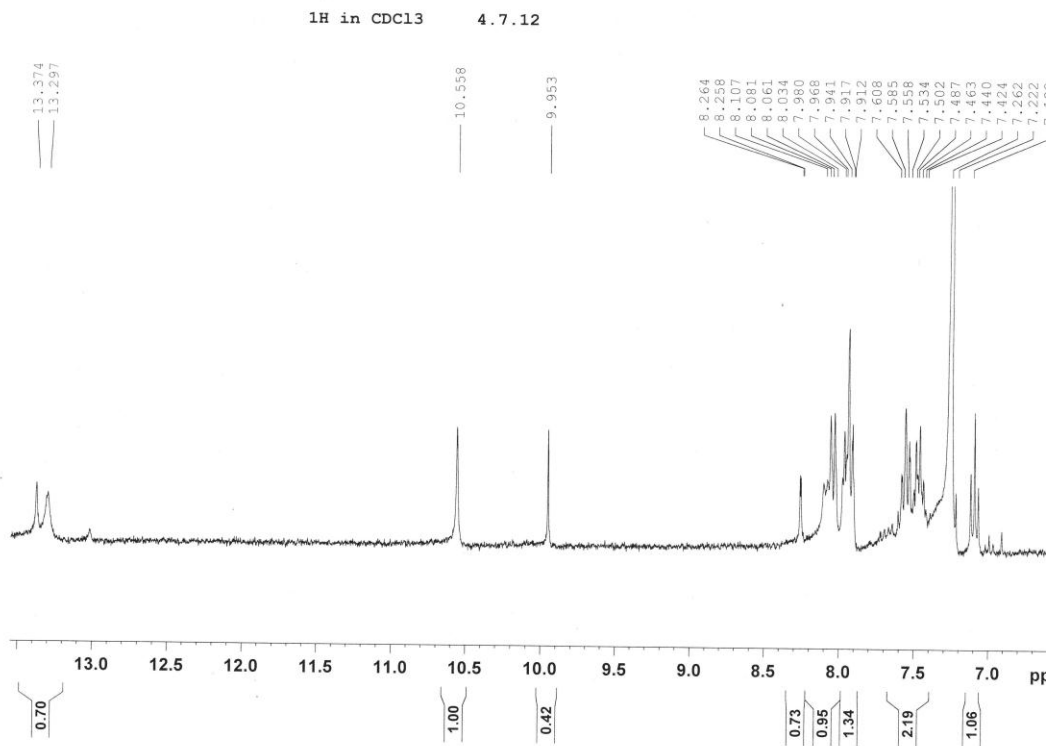


## ¹H NMR of Receptor i.e. BHI (in d₆-DMSO):



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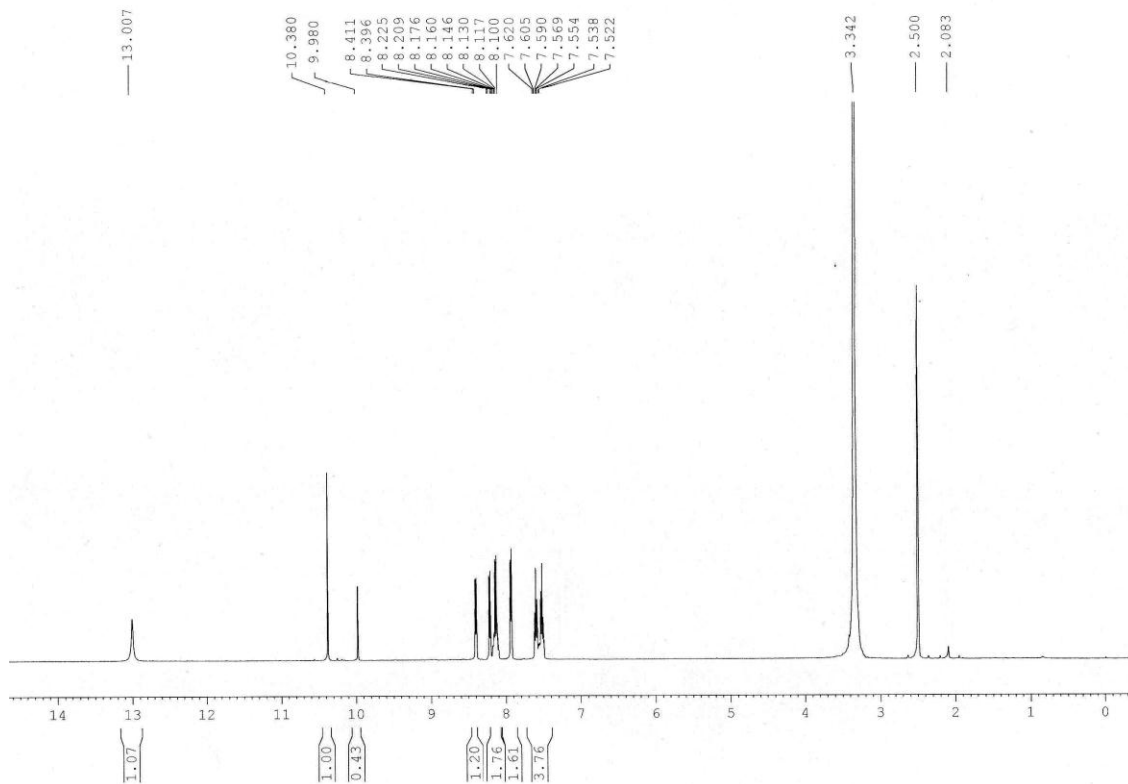
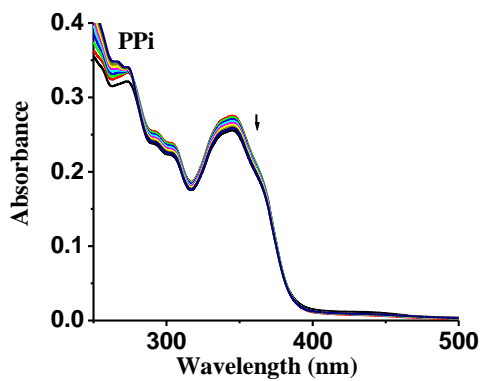## $^1$H NMR of BHI –CN (in $d_6$-DMSO):
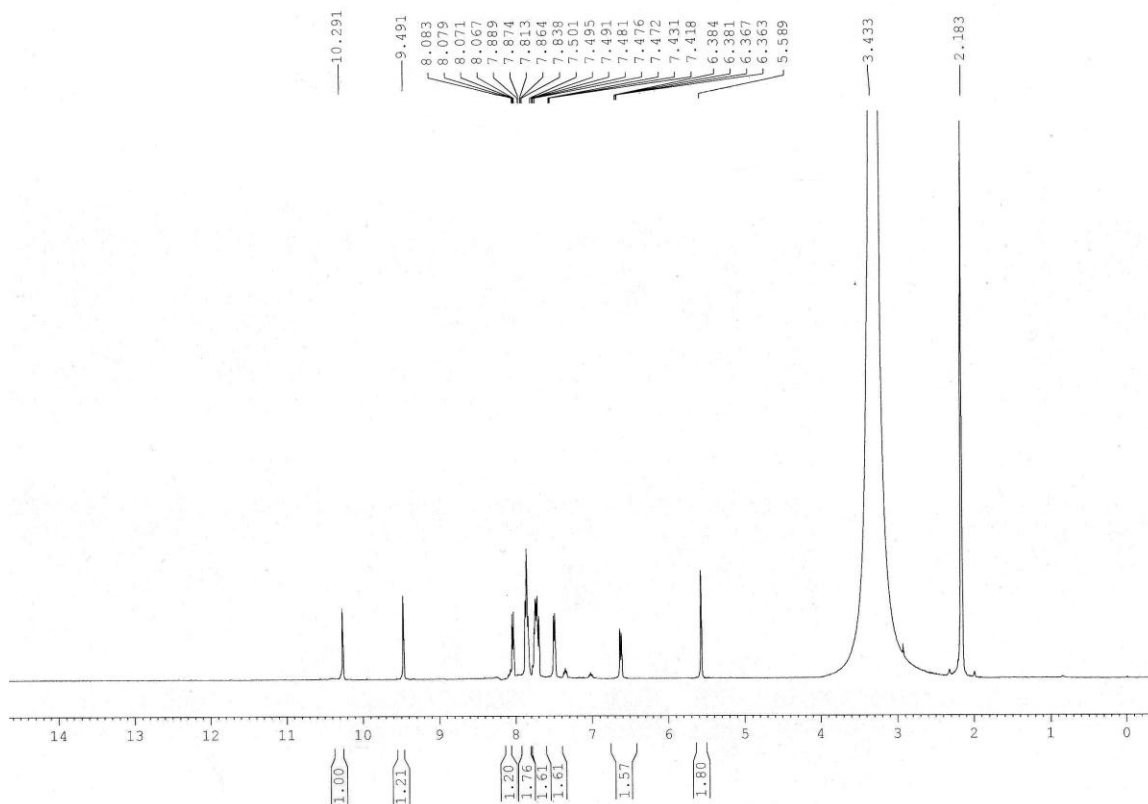


## $^{13}$C NMR of BHI:
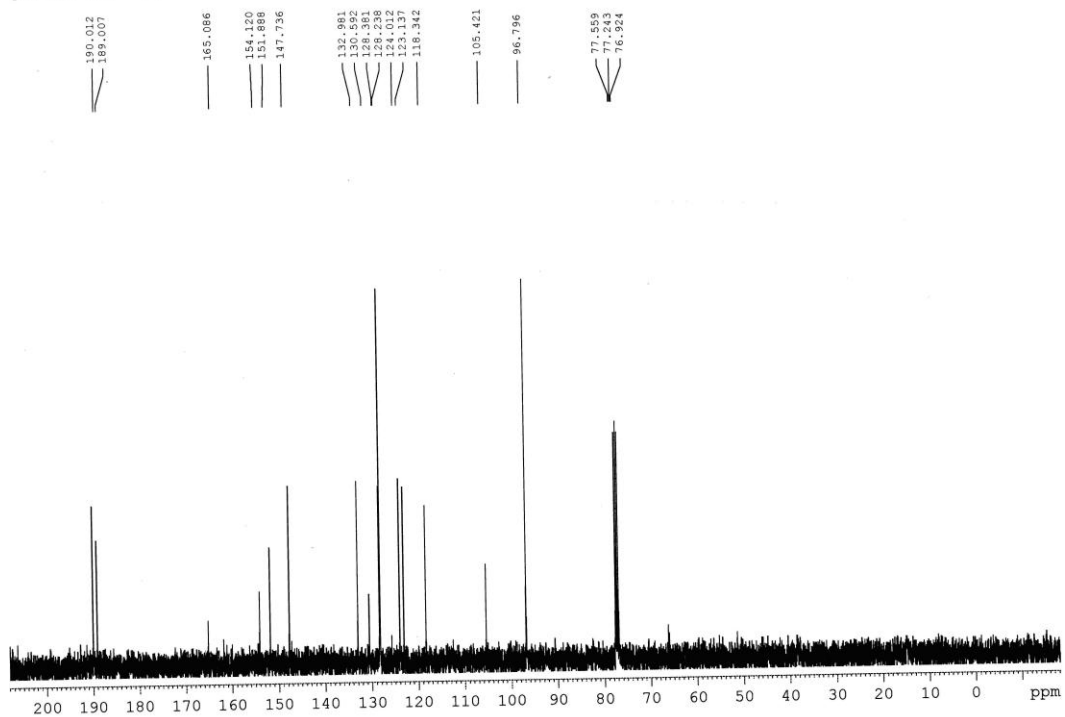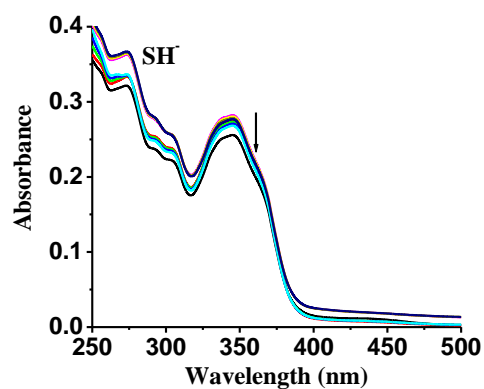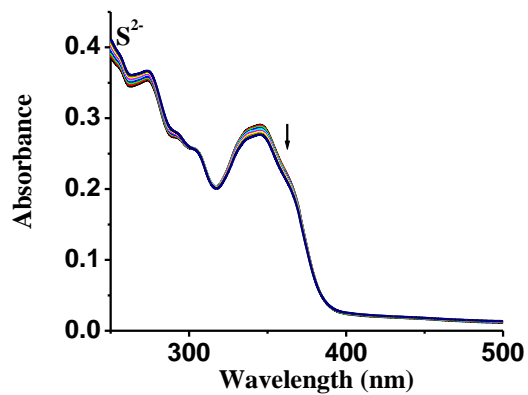
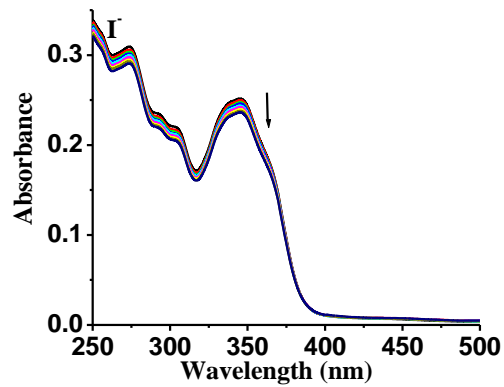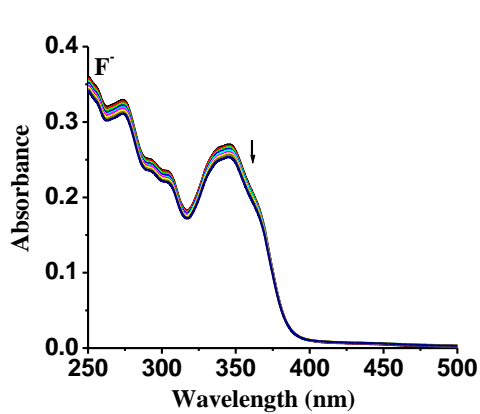## ESI MS spectra of BHI:
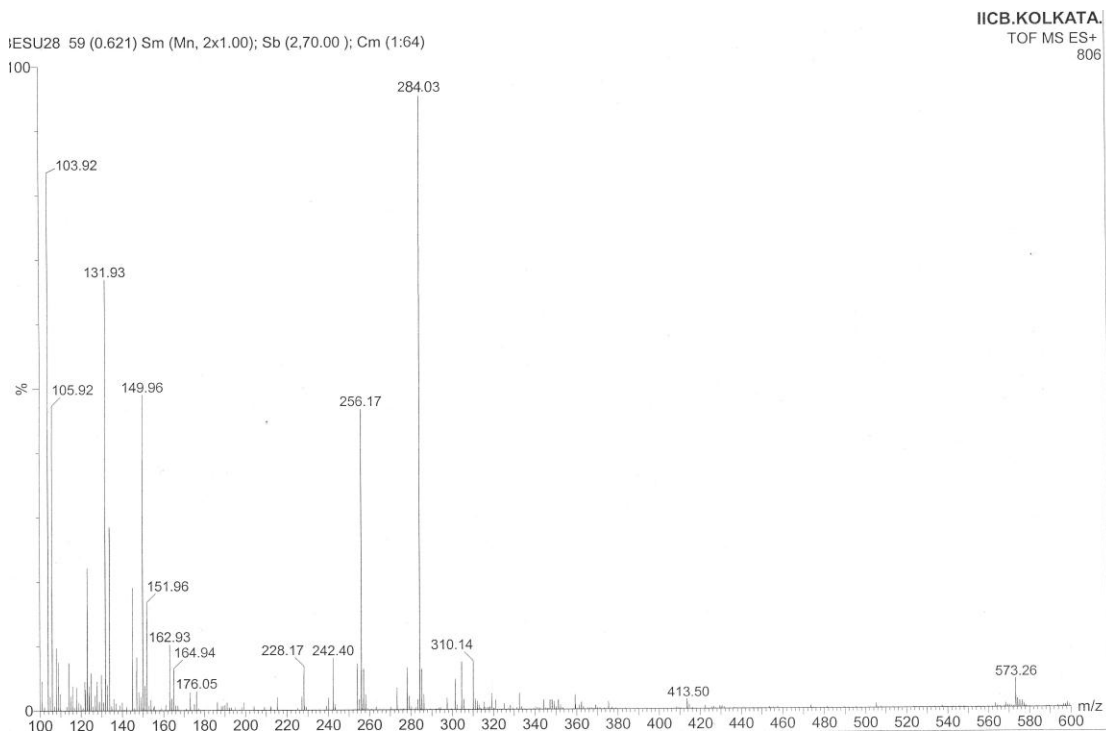


## ESI MS spectra of BHI + CN:
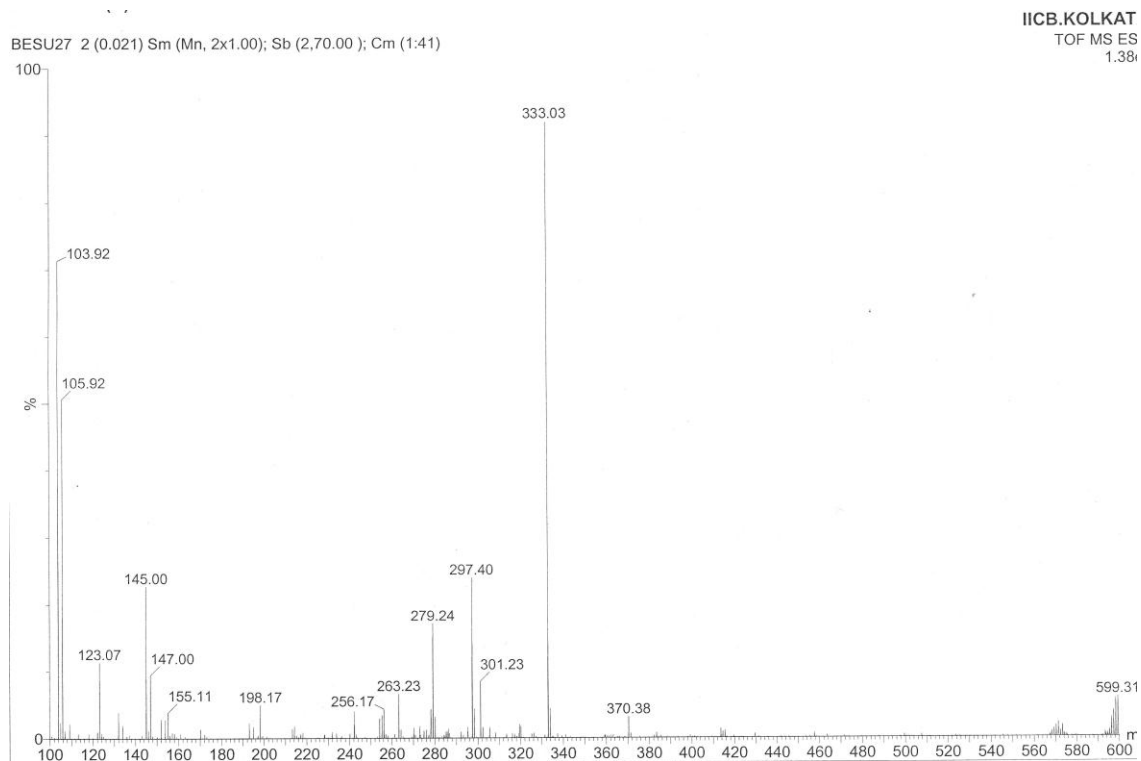
## 8. UV-vis and fluorescence titration spectra of BHI with different anions:

UV-vis titration spectra of BHI ($c$ = 1.0 x $10^{-5}$ M) with other anions except $CN^-$ i.e. $CH_3COO^-$, $Cl^-$, $Br^-$, $I^-$, $F^-$, $BzO^-$, $SH^-$, $H_2PO_4^{2-}$, $PO_4^{3-}$, $S^{2-}$, $N^{3-}$, $P_2O_7^{4-}$ and ADP ($c$ = 2.0 x $10^{-4}$ M) in $CH_3CN:H_2O$ = 1:1 at pH= 7.5.
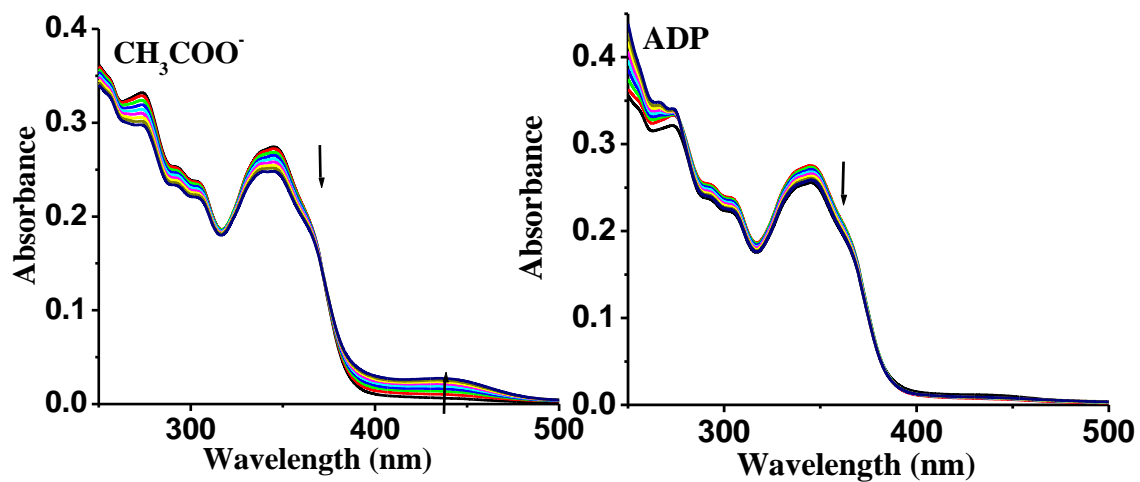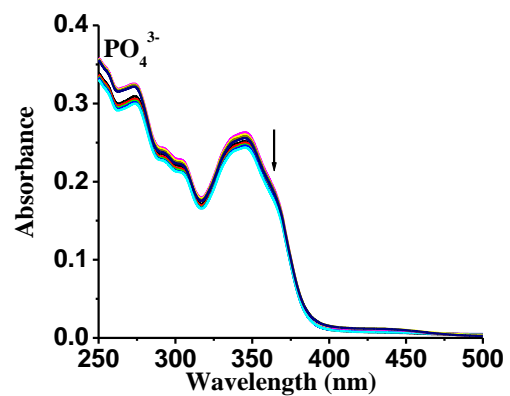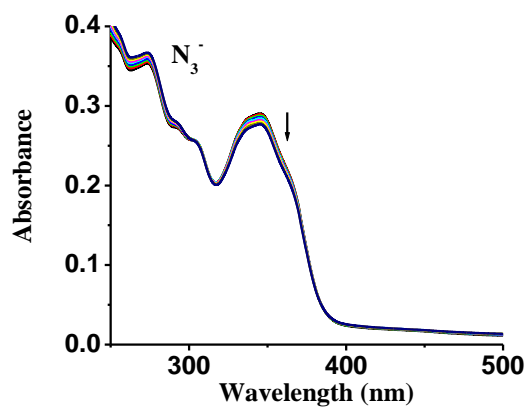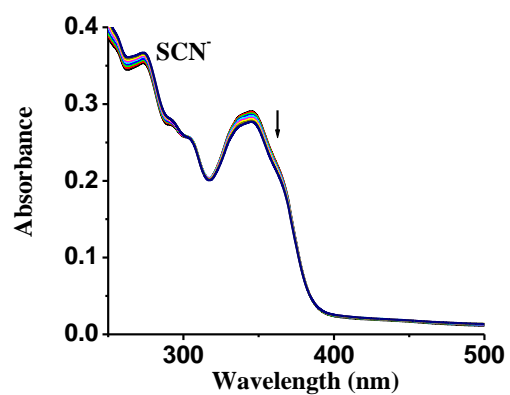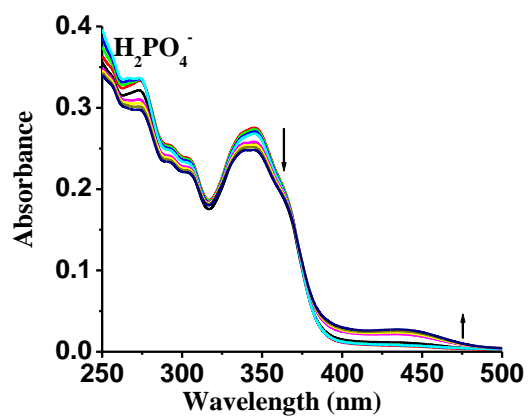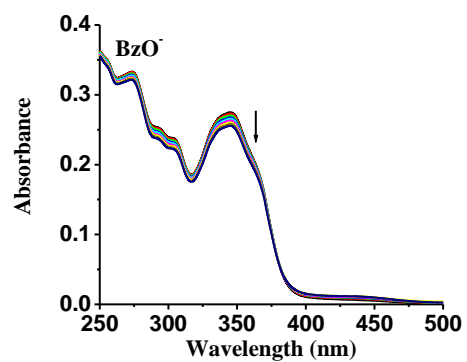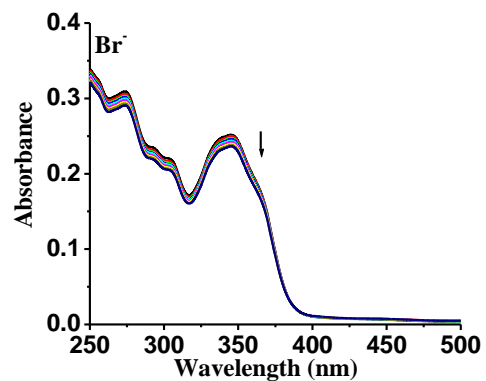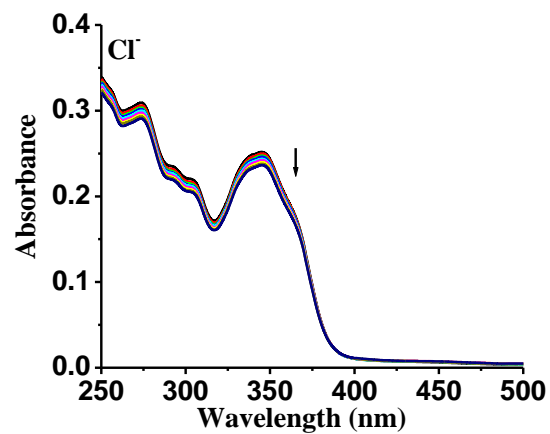
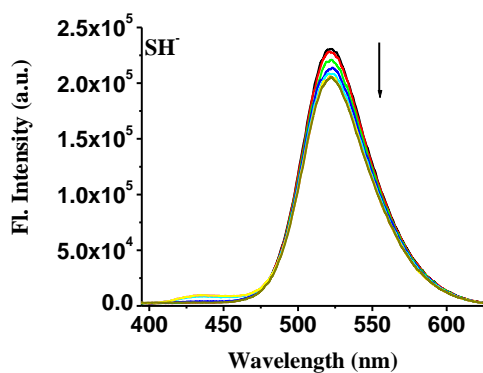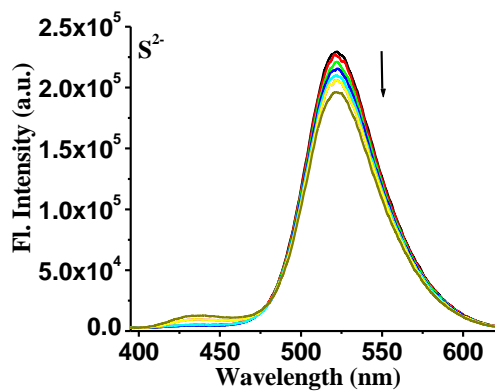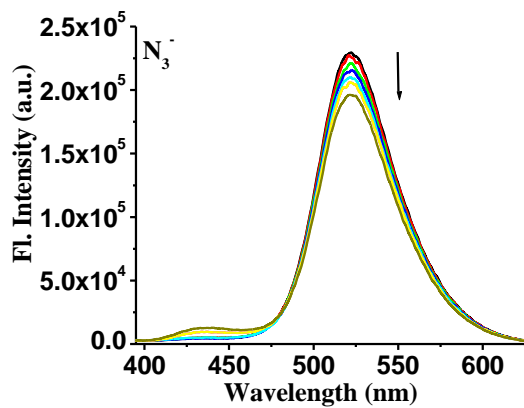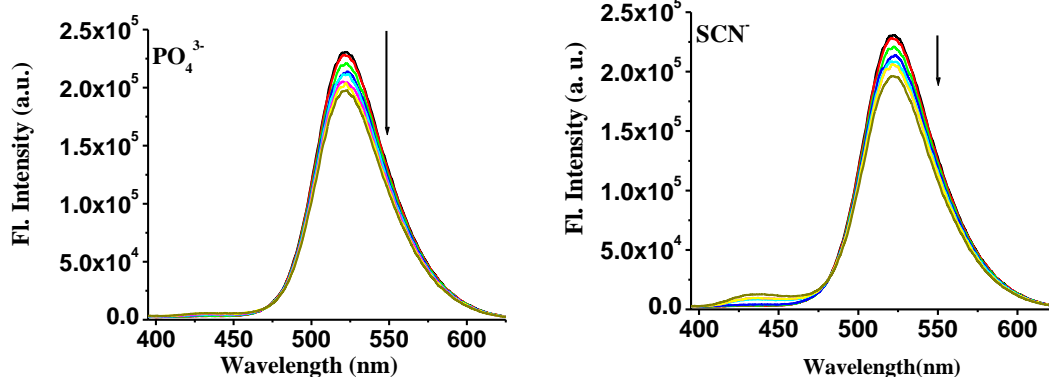Fluorescence titration spectra of BHI ($c$ = 1.0 x $10^{-5}$ M) with addition of 5 equivalent another tested anions except cyanide ($c$ = 2.0 x $10^{-4}$ M) in $CH_3CN:H_2O$ = 1:1 at pH= 7.5.
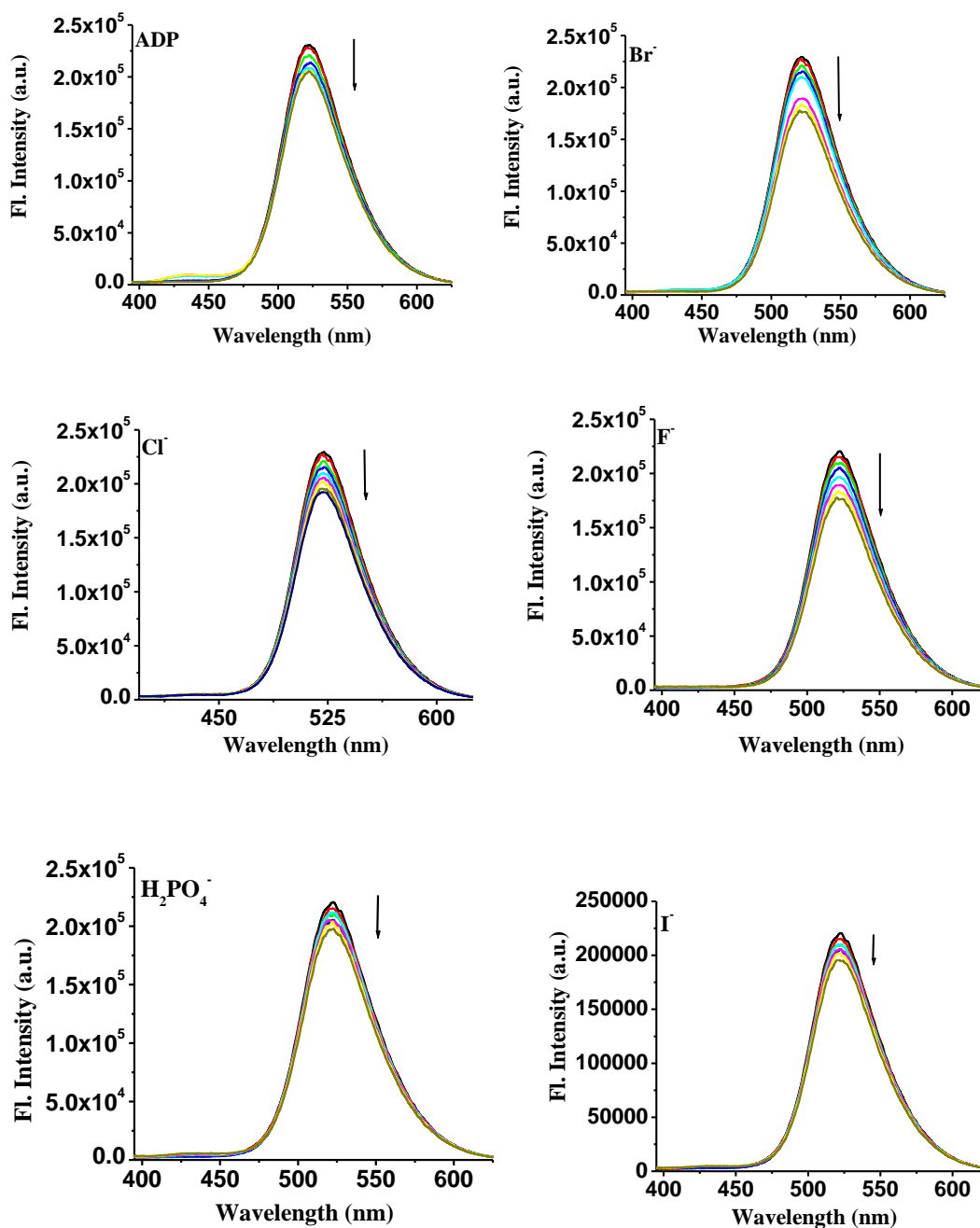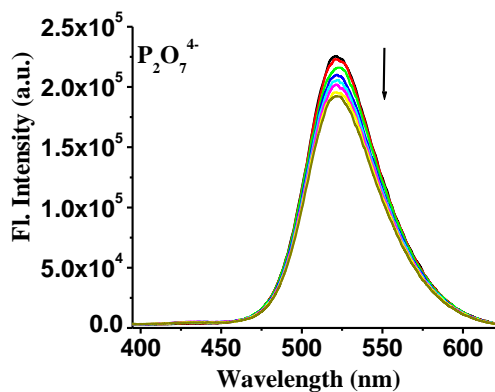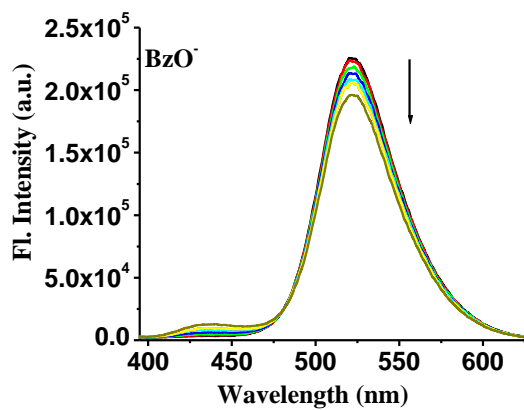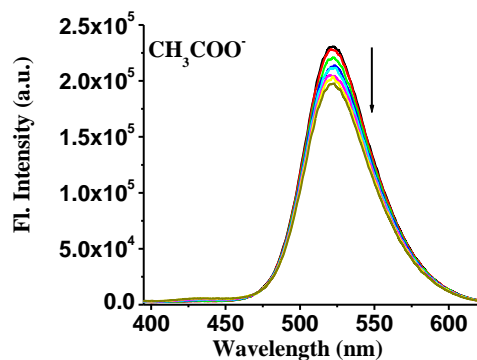
## 9. Method of Calculations:

The ground state geometry of BHI (isomers) and molecule BHI-CN has been fully optimized in acetonitrile (CH$_3$CN) solution by using the DFT functionals B3LYP (a hybrid exchange-correlation functional (Becke + Slater + HF exchange and LYP + VWN5 correlations)) [S3-S5] for the 6-311+G** basis set. The Hessian analysis showed energy minimum structures on the potential-energy hyper surface as confirmed by real frequencies obtained for all normal modes of vibration. The solvent effect on the ground state of the investigated molecules has been calculated by employing the polarizable continuum model (PCM) [S6,S7] of solvent at the B3LYP/6-311+G** level. The polarized solute-solvent interaction within the PCM model considers geometry relaxation of solute in equilibrium with the solvent reaction field.

The solvent-modified transition energy and the oscillator strength corresponding to 50 lowest lying singlet excited states have been calculated by using the PCM solvent model in the framework of time-dependent density functional (TD-DFT) method using the B3LYP functionals for the 6-311+G** basis set and the corresponding solvent-modified geometry of the molecule. All calculations have been carried out using the GAUSSIAN 09 package [S8].

## 10. References:

[S1]. M. Zhu, M. Yuan, X. Liu, J. Xu, J. Lv, C. Huang, H. Liu, Y. Li, S. Wang, D. Zhu, *Org. Lett.,* 2008**, 10***,* 1481.
[S2]. H. Y. Guo, J. C. Li, Y. L. Shang, *Chin. Chem. Lett.* 2009, *20*, 1408–1410.
[S3]. A. D. Becke, *J. Chem. Phys.,* 1993*,* **98**, 5648.
[S4]. P. J. Stephens, F. J. Devlin, C. F. Chablowski and M. J. Frisch, *J. Phys. Chem.* 1994, **98**, 11623.
[S5]. R. H. Hertwig and W. Koch, *Chem. Phys. Lett.,* 1997*,* **268**, 345.
[S6]. V. Barone, M. Cossi, *J. Phys. Chem. A*. 1998, *102*, 1995.
[S7]. M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comp. Chem*, 2003, **24**, 669.
[S8]. M. J. Frisch, et al. Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.