Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.


# SUPPORTING INFORMATION

## Involvement of a unique chemodosimeter in selective estimation of noxious cyanide in common water hyacinth (*Eichhornia crassipes*): An environmental refinement

Shrabani Saha[a], Priyotosh Ghosh[a], Paritosh Mondal[b], Ansuman Chattopadhyay[b] and Prithidipa Sahoo[a*]

[a] S. Saha, P. Ghosh and Dr. P. Sahoo, Department of Chemistry, Visva-Bharati University, Santiniketan, 731235, India.

[b] P. Mondal and Dr. A. Chattopadhyay, Department of Zoology, Visva-Bharati University, Santiniketan, 731235, India.

E-mail: prithidipa@hotmail.com.

**1.Table S1** Performance comparison of existing methods and present method (colorimetric and fluorescence based chemosensor) for detection of $CN^-$

| Analytes | Method of detection | Sensor type | Detection limit | Sensitvity& Selectivity | Application | References |
|---|---|---|---|---|---|---|
| **$CN^-$** | **Colorimetry and Fluorescence based chemosensor** | **Naphthal dehyde-pyridoxal conjugate** | **81 nm** | **High** | **In common water hyacinth saplings** | **Current method** |
| **$CN^-$** | Colorimetry and Fluorescence based chemosensor | Coumarin-thiophene besedschif f base | 0.32 μM | Low | In water | Tetrahedron 74 (2018) 6897-6906 |
| **$CN^-$** | Colorimetryba sed chemosensor | 2-hydroxy-1-naphthald ehyde | 105 μM | Low | Nil | New J. Chem., 2015,39, 3900-3907 |
| **$CN^-$** | Colorimetryba sed chemosensor | 4-methylpyr idine and salicylalde hyde | 8.0 μM | Low | In water | Anal. Methods, 2015,**7**, 5239-5244 |
| **$CN^-$** | Colorimetryba sed chemosensor | 4-(*p*-tolyl)thiaz ol-2-amine | 19.4 μM | Moderate | In water | *New J. Chem.*, 2016,40, 7768-7778 |
| **$CN^-$** | Colorimetryba sedchemosens or | 2,3-Diaminom aleonitrile | 20 μM | Low | Nil | *Sensors and Actuators B: Chemical* 2015,211, 498-506 |

## 2. NMR Studies:

### $^{1}$H NMR of NPLC in DMSO-$d_6$ :

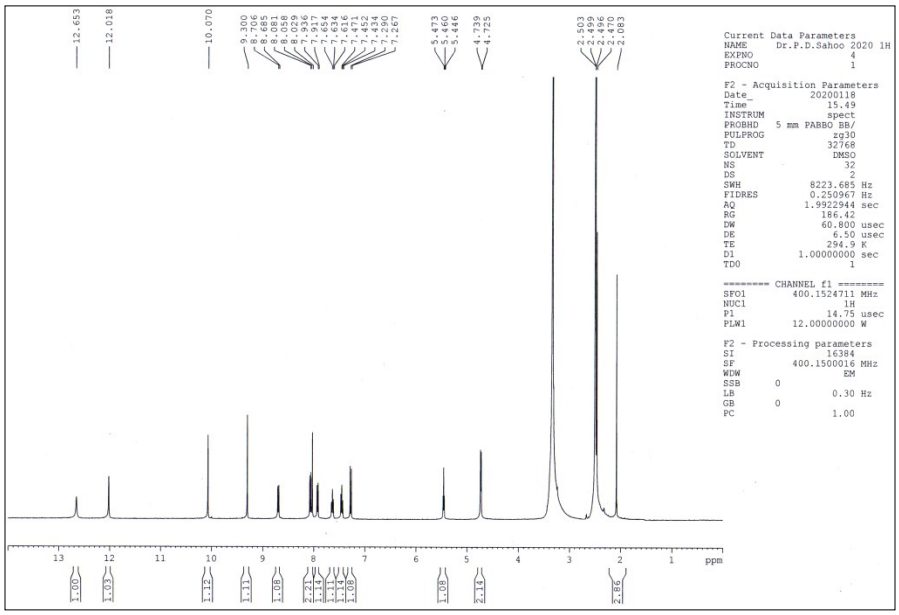

**Fig. S1.** $^{1}$H NMR of **NPLC** in DMSO-$d_6$ (400 MHz).

### $^{13}$C NMR of NPLC in DMSO-$d_6$:

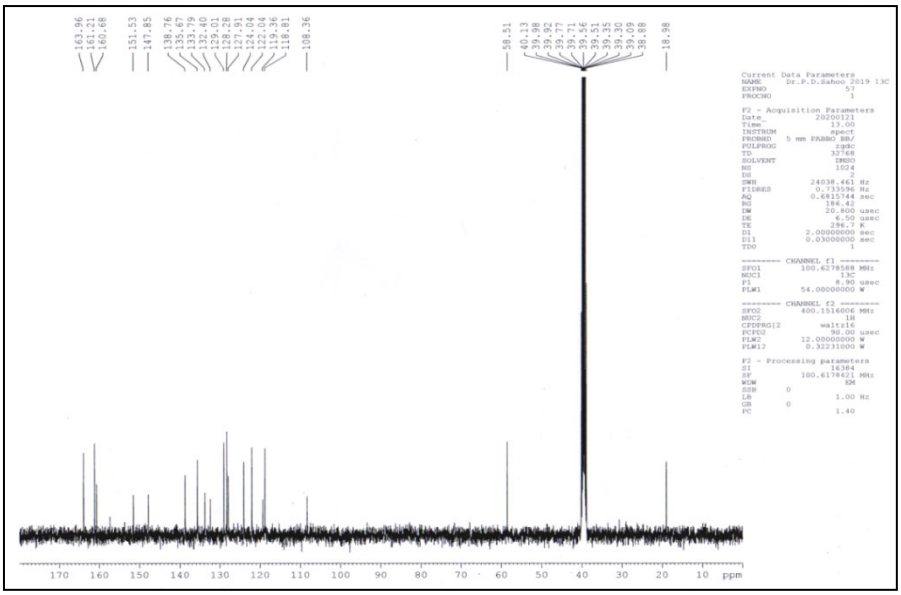

**Fig. S2.** $^{13}$C NMR of **NPLC** in DMSO-$d_6$ (400 MHz).

## 3. Materials and Instruments

All the reagents were purchased from Sigma-Aldrich Pvt.Ltd. Unless otherwise mentioned, materials were obtained from commercial suppliers and were used without further purification. Solvents werdried according to standard procedures. Elix Millipore water was used throughout all experiments. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker 400 MHz instrument. For NMR spectra, DMSO-$d_6$ and for NMR titration DMSO-$d_6$ and $D_2O$ were used as solvent using TMS as an internal standard. Chemical shifts are expressed in δ ppm units and $^{1}H$–$^{1}H$ and $^{1}H$–C coupling constants in Hz. The following abbreviations are used to describe spinmultiplicities in $^{1}H$ NMR spectra: s = singlet; d = doublet; t = triplet; m = multiplet.The mass spectrum (HRMS) was carried out using a micromass Q-TOF Micro™ instrument by using Acetonitrile as a solvent. Fluorescence spectra were recorded on a Perkin Elmer Model LS 55 spectrophotometer. UV spectra were recorded on a SHIMADZU UV-3101PC spectrophotometer. FT-IR data were recorded on Shimadzu IRAffinity-1S Fourier transform infrared spectrometer (Spectrum Two) by ATR technique.

Leica TCS SP8 laser scanning confocal microscope system was used for confocal microscopy. Images obtained through section scanning were analyzed by the LasX software with excitation at 425 nm monochromatic laser beam, and emission spectra were integrated over the range 542 nm (single channel) with 10X magnification.

**4. UV-vis and fluorescence titration.** A stock solution of **NPLC** (1 μM) was prepared in water-DMSO (1:1, v/v). **$CN^-$** solution of concentration 10 μM was prepared in Millipore water. All experiments were carried out in aqueous medium at neutral pH. During the titration, each time a 1 μM solution of **NPLC** was filled in a quartz optical cell of 1 cm optical path length and **$CN^-$** stock solution was added into the quartz optical cell gradually by using a micropipette. Spectral data were recorded at 1 min after the addition of **$CN^-$.**

## 5. Calculation of limit of detection (LOD) of NPLCwith $CN^-$:

The detection limit of the chemodosimeter **NPLC** for **$CN^-$** was calculated on the basis of fluorescence titration. To determine the standard deviation for the fluorescence intensity, the emission intensity of four individual receptors without **$CN^-$** was measured by 10 times and the standard deviation of blank measurements was calculated.

The limit of detection (LOD) of **NPLC** for sensing **$CN^-$** was determined from the following equation.

$$LOD = K \times SD/S$$

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

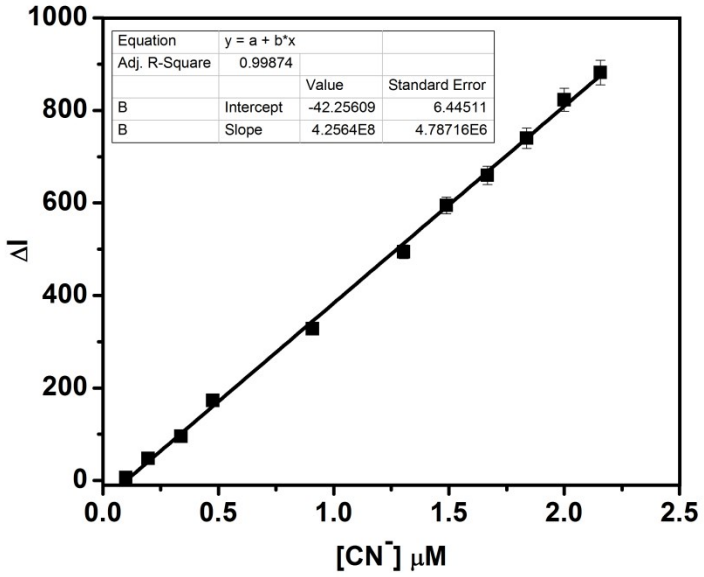


**Fig. S3** Linear fit curve of **NPLC** at 542 nm with respect to **CN**$^-$concentration. Standard deviations are represented by error bar (n=3).

For **NPLC** with **CN**$^-$**:**
From the linear fit graph we get slope = 4.2584× $10^8$, and SD value is 11.52605
Thus using the above formula we get the Limit of Detection = 8.12× $10^{-8}$ M, i.e 81 nM. Therefore **NPLC** can detect **CN**$^-$ up to this very lower concentration by fluorescence technique.

## 6. Job's plot for determining the stoichiometry of binding by fluorescence method:

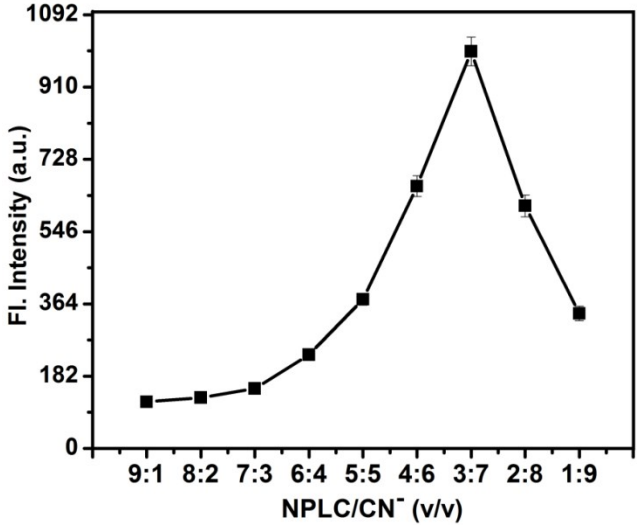

**Fig. S4** Job's plot of **NPLC** (1μM) with $CN^-$ (1μM) in DMSO-water (1:1, v/v), at neutral pH, by fluorescence method, which indicate 1:2 stoichiometry for **NPLC** with $CN^-$ ion. Standard deviations are represented by error bar (n=3).

## 7. pH Titration

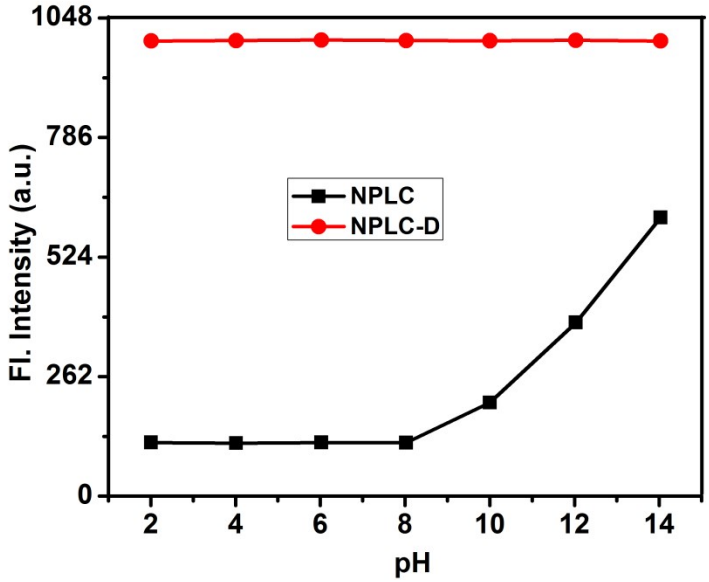


**Fig. S5** Fluorescence responses of probe **NPLC** (black) and **NPLC-D** (red) in different pH conditions in water-DMSO (1:1, v/v) ($\lambda_{ex}$= 425 nm).

## 8. Selectivity in presence of other analytes

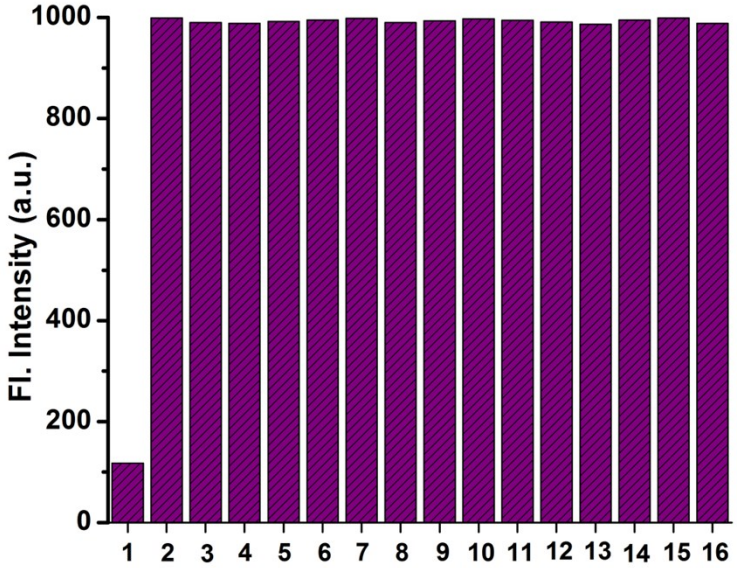

**Fig. S6** Histogram representing competitive fluorescence spectra of **NPLC** with different bio relevant anions at 542 nm ($\lambda_{ex}$= 425 nm) in DMSO-$H_2O$ (1:1, v/v), at neutral pH.[From left to right: 1) Only **NPLC**, **NPLC** with 2) $CN^-$, 3) $CN^-$+ $F^-$, 4) $CN^-$+ $Cl^-$, 5) $CN^-$+ $Br^-$, 6) $CN^-$+ $I^-$, 7) $CN^-$+ $SCN^-$, 8) $CN^-$+ $AcO^-$, 9) $CN^-$+ $SH^-$, 10) $CN^-$+ $H_2PO_4^-$, $CN^-$+ 11) $NO_3^-$, $CN^-$+ 12) $CN^-$+ $SO_4^{2-}$, 13) $CN^-$+ $PO_4^{3-}$, 14) $CN^-$+ $ClO_4^-$, 15) $CN^-$+ $NO_2^-$ and 16) $CN^-$+ $N_3^-$ in $H_2O$–DMSO (1:1 v/v, pH 7.0, 10 mM phosphate buffer) solution].

## 9. Energy minimized structures of NPLC, NPLC-D and keto-NPLC-D with bond distances

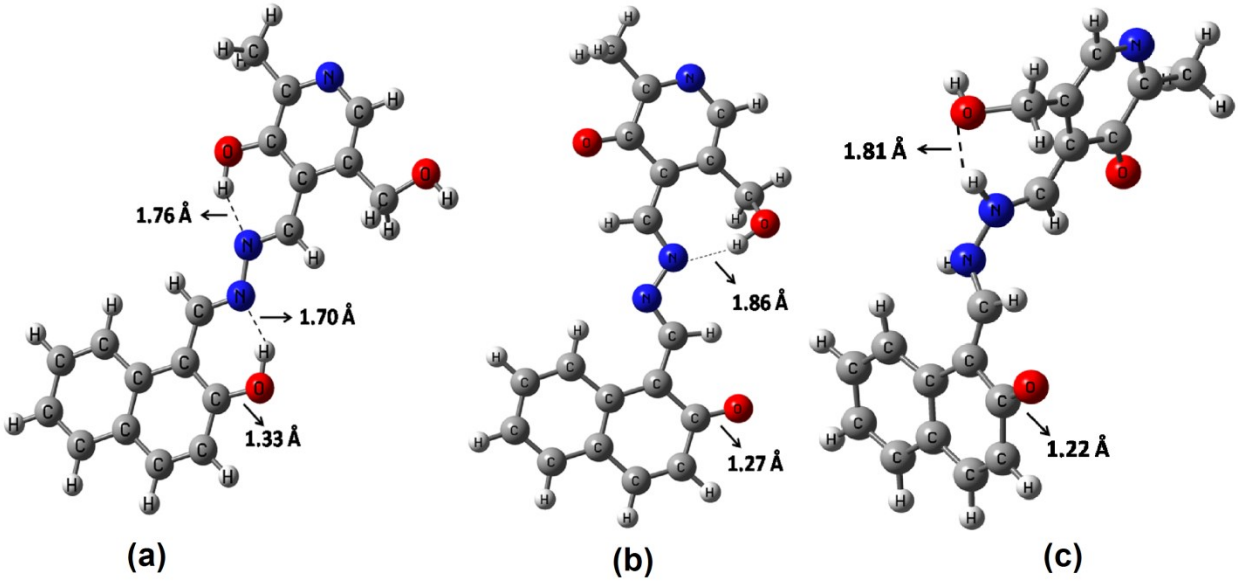


**Fig. S7** Energy minimized structures of **NPLC, NPLC-D** and **keto-NPLC-D** with important bond distances from B3LYP level

**10. Table S2** Details of the geometry optimization in Gaussian 09 program.

| Details | NPLC | NPLC-D | keto-NPLC-D |
|---|---|---|---|
| **Calculation method** | B3LYP | B3LYP | B3LYP |
| **Basis set** | 6-311G** | 6-311G** | 6-311G** |
| **E(CAM-B3LYP) (a.u.)** | -1124.4651 | -1123.5038 | -1124.4254 |
| **Charge, Multiplicity** | 0, 1 | -2, 1 | 0, 1 |
| **Solvent (CPCM)** | Water | Water | Water |

## 11. TDDFT Calulation

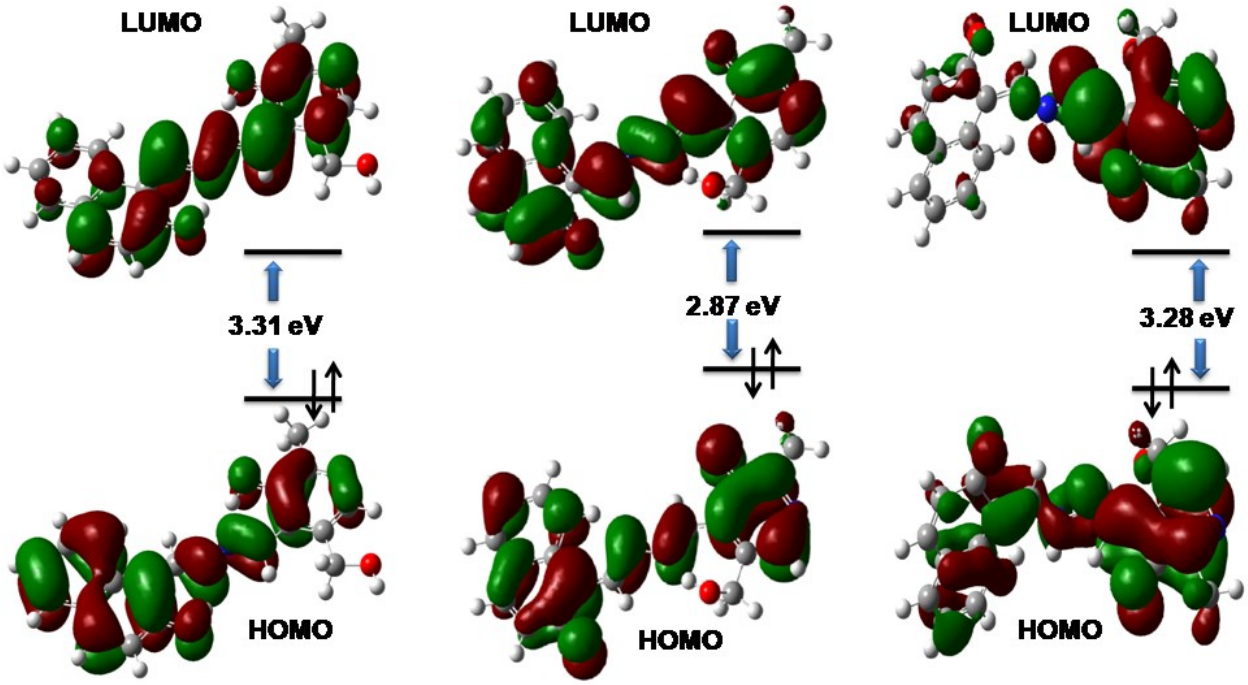


**Fig. S8** DFT optimized charge densities and the HOMO-LUMO energy gap of **NPLC, NPLC-D** and **keto- NPLC-D**

**12. Table S3.** Selected electronic excitation energies (eV), oscillator strengths (f), main configurations of the low-lying excited states of all the molecules and complexes. The data were calculated by TDDFT//B3LYP/6-311G(d,p) based on the optimized ground state geometries.

| Molecules | Electronic Transition | Excitation Energy[a] | f[b] | Composition[c](%) |
|---|---|---|---|---|
| **NPLC** | $S_0 \rightarrow S_1$ | 2.9068eV426.53 nm | 0.7811 | H → L (70%) |
| | $S_0 \rightarrow S_7$ | 4.0641eV305.07 nm | 0.2580 | H-4 → L (59%) |
| | | | | |
| **NPLC-D** | $S_0 \rightarrow S_1$ | 2.4983eV 496.27 nm | 0.8994 | H → L (70%) |
| | $S_0 \rightarrow S_6$ | 3.7415eV 331.38 nm | 0.0370 | H-1 → L+1(68%) |
| | | | | |

| | | | | |
|---|---|---|---|---|
| keto- **NPLC-D** | $S_0 \rightarrow S_2$ | 2.8323eV 437.75 nm | 0.2096 | H → L (59%) |
| | $S_0 \rightarrow S_3$ | 3.0152eV 411.19 nm | 0.1820 | H-1 → L (54%) |

[a]Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength.[b]Oscillator strength. [c]H stands for HOMO and L stands for LUMO.

**13. Table S4.** Energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)

| **Species** | **$E_{HOMO}$ (a.u)** | **$E_{LUMO}$ (a.u)** | **ΔE(a.u)** | **ΔE(eV)** | **ΔE(kcal/mol)** |
|---|---|---|---|---|---|
| **NPLC** | -0.21984 | -0.09822 | 0.12162 | 3.31 | 76.33 |
| **NPLC-D** | -0.15968 | -0.05423 | 0.10545 | 2.87 | 66.18 |
| Keto- **NPLC-D** | -0.21912 | -0.09862 | 0.1205 | 3.28 | 75.64 |

## 14. Plausible Mechanism

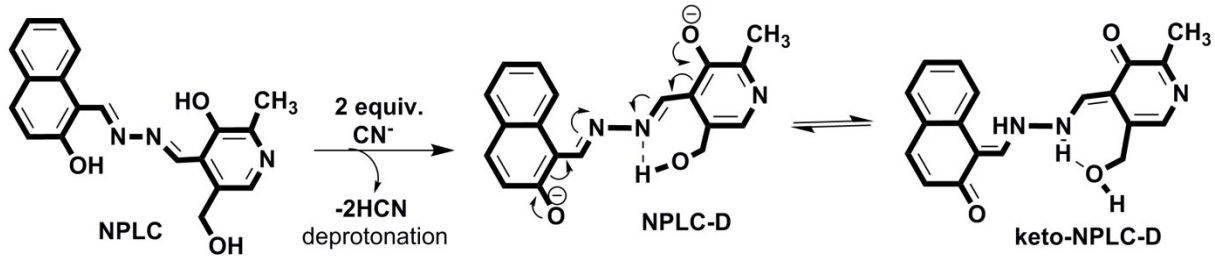


**Fig. S9** Plausible mechanism of interaction between **NPLC** and $CN^-$ ions and the formation of **NPLC-D** and **keto- NPLC-D**

## 15. Water hyacinth (*Eichhornia crassipes*) treatment in laboratory

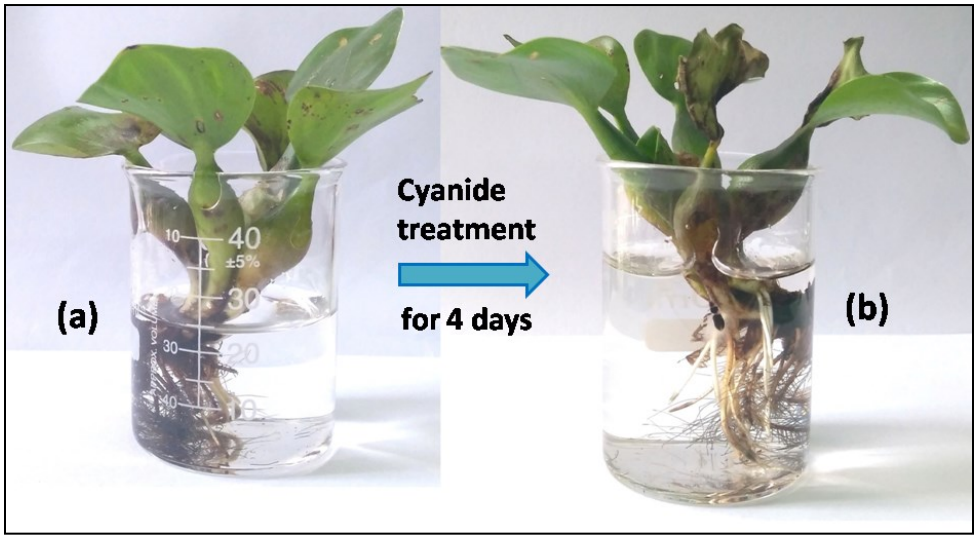


**Fig. S10** (a) Fresh water hyacinth (*Eichhornia crassipes*) sapling (b) sapling treated with aquous sodium cyanide for 4 days