ORGANIC LETTERS

2010
Vol. 12, No. 15
3406−3409

Specific Recognition and Sensing of CN^- in Sodium Cyanide Solution

Sukdeb Saha, Amrita Ghosh, Prasenjit Mahato, Sandhya Mishra, Sanjiv K. Mishra, E. Suresh, Satyabrata Das, and Amitava Das*

Central Salt & Marine Chemicals Research Institute (CSIR), Bhavnagar 364002, Gujarat, India

amitava@csmcri.org

Received June 10, 2010

ABSTRACT

Specific recognition of CN^- in sodium cyanide solution was achieved using two imidazole-based receptors (A and B). Visually detectable color changes were associated with the formation of hydrogen bonded adducts, A·CN^- and B·CN^-. Ratiometric fluorescence response was achieved for receptor A on binding to CN^-, and this reagent was used for imaging bacterial cells pre-exposed to 1.42 μM CN^- solution.

The cyanide ion is extremely toxic to mammals.[1,2] It inhibits the cellular respiration in mammals by interacting strongly with a heme unit in the active site of cytochrome a_3.[1] The cyanide ion also adversely affects vascular, visual, central nervous, cardiac, endocrine, and metabolic functions.[1,2] However, the use of cyanide salts has remained widespread, particularly in gold mining, electroplating, and metallurgy.[3] Despite safeguards and stringent norms set by different regulatory bodies, accidental releases of cyanide into the environment do occur.[4] Further, the possibility of its release in the environment for harmful purposes is also an added source of concern.[5] All of these factors necessitate the development of cyanide-selective receptors. Significant efforts have been put forward by researchers, active in the area of anion recognition, to address this issue. However, examples of chromogenic sensor molecules that are capable of recognizing cyanide ions in aqueous environments are much fewer compared to those that display sensing features in nonaqueous solvents.[6] Higher solvation energy of the cyanide ion in aqueous environments is known to affect adversely the hydrogen-bonded adduct formation between the receptor unit and the CN^-.[7] An alternate approach, adopted by many researchers, for recognition of CN^- in aqueous solution is based on chemodosimetric methodology. This involves coordination of free cyanide ion to a transition

(1) Holland, M. A.; Kozlowski, L. M. *Clini. Pharm.* **1986**, *5*, 737.
(2) (a) Baskin, S. I.; Brewer, T. G. In *Medical Aspects of Chemical and Biological Warfare*; Sidell, F.; Takafuji, E. T.; Franz, D. R., Eds.; TMM Publications: Washington, DC, 1997; Chapter 10, p271. (b) Kulig, K. W. *Cyanide Toxicity*; U.S. Department of Health and Human Services: Atlanta, GA, 1991. (c) Lee, C.-H.; Miyaji, H.; Yoon, D.-W.; Sessler, J. L. *Chem. Commun.* **2008**, 24. (d) Yoon, J.; Kim, S. K.; Singh, N. J.; Kim, K. S. *Chem. Soc. Rev.* **2006**, *35*, 355. (e) Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094. (f) Gale, P. A. *Acc. Chem. Res.* **2006**, *39*, 465. (g) Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 486. (h) Martinez-Manez, R.; Sancanon, F. *Chem. Rev.* **2003**, *103*, 4419. (i) Kim, S. K.; Lee, D. H.; Hong, J.-I.; Yoon, J. *Acc. Chem. Res.* **2009**, *42*, 23. (j) Lee, H. N.; Xu, Z.; Kim, S. K.; Swamy, K. M. K.; Kim, Y.; Kim, S.-J.; Yoon, J. *J. Am. Chem. Soc.* **2007**, *129*, 3828.

(3) Eisler, R. *Cyanide Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review*; U.S. Fish and Wildlife Service Patuxent Wildlife Research Center: Laurel, MD, 1991.
(4) Koenig, R. *Science* **2000**, *287*, 1737.
(5) Baud, F. J. *Hum. Exp. Toxicol.* **2007**, *26*, 191.

10.1021/ol101281x
Published on Web 07/09/2010

metal ion,[8] to a coordinatively unsaturated boron center,[7,9,10] or to an electrophilic carbonyl functionality.[7a] However, such examples have certain limitations such as delayed response, lack of reversibility, or use of elevated reaction temperature.[10] The few reports that describe the recognition of CN^- in aqueous solution, utilizing the hydrogen bond motif, suffer from lack of selectivity.[11] A recent report, based on a displacement method, describes a lowest detection limit of 0.31 ppm for cyanide ion,[12a] which is still higher than the permissible level (0.2 ppm) for drinking water as set by health advisory bodies such as the Environment Protection Agency (EPA).[12b]

Keeping this information in mind, we report herein the use of two relatively simple imidazole-based colorimetric receptors, **A** and **B**, which are capable of detecting $[CN^-]_{aq}$ as low as ~0.1 ppm. For receptor **B**, presence of a redox active ferrocene (Fc) moiety allows an additional handle in probing the CN^- binding process. Formation of the H-bonded adducts, **A**·CN^- and **B**·CN^-, results in a new charge transfer complex with novel spectral (electronic and/or fluorescence) properties. Receptor **A** constitutes a rare example of the ratiometric response to the CN^- binding process.[7b,e,13]

Methodologies adopted for synthesis of receptor **A** and **B** are shown in Figure 1. Receptor **A** was reported earlier;[14] however, the present methodology is different from that previously reported. Receptors **A** and **B** were characterized

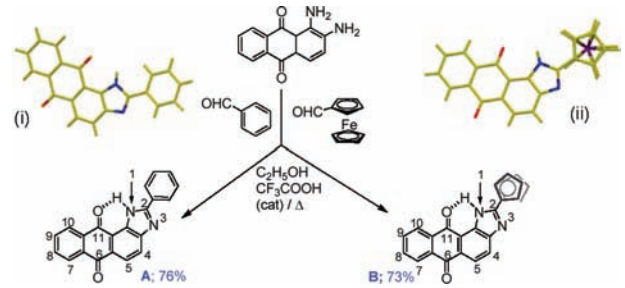

Figure 1. Synthesis of receptors **A** and **B**; (i) and (ii) are single crystal X-ray structures for receptors **A** and **B**, respectively.

using various analytical and spectroscopic techniques, apart from single crystal X-ray structures (Supporting Information).[15]

Both receptors were found to have limited solubility in water, and this compelled us to use these receptors in mixed solvent, such as CH_3CN/HEPES buffer (1:1, v/v), for recognition studies. Spectral response and visually detectable color changes of these receptors were tested with aqueous solutions of the sodium salt of all common anionic analytes such as F^-, Cl^-, Br^-, I^-, CN^-, SCN^-, CH_3COO^-, $H_2PO_4^-$, $P_2O_7^{3-}$, HSO_4^-, NO_3^-, and NO_2^- present in excess (0.1 mM) (Figure 2). Changes in spectral pattern, as well as visually detectable color (insert Figure 2) and fluorescence, were observed only in the presence of added CN^-. No change in spectral pattern for receptor **A** or **B** in the presence of other anions suggests either a very weak or no interaction between these anions and the respective receptor. Electronic spectra recorded for receptor **A** in CH_3CN/HEPES buffer (1:1, v/v) medium with increasing $[CN^-]$ revealed a successive increase in absorption at 474 nm along with a concomitant decrease at 393 nm. These changes were associated with the appearance of four simultaneous isosbestic points at 242, 275, 335 and 426 nm (Figure 3). In case of receptor **B**, these changes are as follows: decrease in absorbance around 390 nm, increase in absorbance around 552 nm and appearance of four simultaneous isosbestic points at 240, 278, 338 and 421 nm (Figure 3).

For both receptors, simultaneous appearance of isosbestic points signified the presence of two different species that remained in equilibrium. Absorption bands at ~390 nm for receptors **A** and **B** were attributed primarily to the anthraquinone/imidazole-based $\pi-\pi^*$ transition, whereas the

(6) (a) Hundnall, T. W.; Gabbai, F. P. *J. Am. Chem. Soc.* **2007**, *129*, 11978. (b) Männel-Croisé, C.; Zelder, F. *Inorg. Chem.* **2009**, *48*, 1272. (c) Tomasulo, M.; Sortino, S.; White, A. J. P.; Raymo, F. M. *J. Org. Chem.* **2006**, *71*, 744. (d) Lee, J. H.; Jeong, A. R.; Shin, I.-S.; Kim, H.-J.; Hong, J.-I. *Org. Lett.* **2010**, *12*, 764. (e) Hong, S.-J.; Yoo, J.; Kim, S.-H.; Kim, J. S.; Yoon, J.; Lee, C.-H. *Chem. Commun.* **2009**, 189. (f) Cho, D.-G.; Kim, J. H.; Sessler, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 12163.

(7) (a) Lee, K.-S.; Kim, H.-J.; Kim, G.-H.; Shin, I.; Hong, J.-I. *Org. Lett.* **2008**, *10*, 49. (b) Xu, Z.; Pan, J.; Spring, D. R.; Cui, J.; Yoon, J. *Tetrahedron* **2010**, *66*, 1678. (c) Abalos, T.; Royo, S.; Martinez-Manez, R.; Sancenon, F.; Soto, J.; Costero, A. M.; Gil, S.; Parra, M. *New J. Chem.* **2009**, *33*, 1641. (d) Jamkratoke, M.; Ruangpornvisuti, V.; Tumcharern, G.; Tuntulani, T.; Tomapatanaget, B. *J. Org. Chem.* **2009**, *74*, 3919. (e) Lou, X.; Zhang, L.; Qin, J.; Li, Z. *Chem. Commun.* **2008**, 5848. (f) Ren, J.; Zhu, W.; Tian, H. *Talanta* **2008**, *75*, 760. (g) Ajayakumar, M. R.; Mukhopadhyay, P.; Yadav, S.; Ghosh, S. *Org. Lett.* **2010**, *12*, 2646.

(8) (a) Lou, B.; Bian, Z.-Q.; Huang, C.-H. *New J. Chem.* **2010**, *34*, 132. (b) Chung,za, S.-Y.; Nam, S.-W.; Lim, J.; Park, S.; Yoon, J. *Chem. Commun.* **2009**, 2866. (c) Sarkar, D.; Mallick, A.; Haldar, B.; Chattopadhyay, N. *Chem. Phys. Lett.* **2010**, *484*, 168.

(9) Yoshino, J.; Kano, N.; Kawashima, T. *J. Org. Chem.* **2009**, *74*, 7497.

(10) (a) Huh, O.; Do, Y.; Lee, M. H. *Organometallics* **2008**, *27*, 1022. (b) Ros-Lis, J. V.; Martýnez-Máñez, R.; Sato, J. *Chem. Commun.* **2005**, 5260. (c) Todd, W.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2007**, *129*, 3635. (d) Ekmekci, Z.; Yilmaz, M. D.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 461. (e) Shang, L.; Zhang, L.; Dong, S. *Analyst* **2009**, *134*, 107. (f) Jin, W. J.; Fernández-Arğ uelles, M. T.; Costa-Fernández, J. M.; Sanz-Medel, A. *Chem. Commun.* **2005**, 883. (g) Touceda-Varela, A.; Stevenson, E. I.; Galve-Gasi'on, J. A.; Dryden, D. T. F.; Mareque-Rivas, J. C. *Chem. Commun.* **2008**, 1998.

(11) (a) Sun, S. S.; Lees, A. J. *Chem. Commun.* **2000**, 1687. (b) Miyaji, H.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 154. (c) Gimeno, N.; Li, X.; Durrant, J. R.; Vilar, R. *Chem.—Eur. J.* **2008**, *14*, 3006. (d) Anzenbacher, P.; Tyson, D. S.; Jursíková, K.; Castellano, F. N. *J. Am. Chem. Soc.* **2002**, *124*, 6232. (e) Tomasulo, M.; Sortino, S.; White, A. J. P.; Raymo, F. M. *J. Org. Chem.* **2006**, *71*, 744.

(12) (a) Li, Z.; Lou, X.; Yu, H.; Li, Z.; Qin, J. *Macromolecules* **2008**, *41*, 7433. (b) Regulatory body: Enviornment Protection Agency, USA; Drinking water quality legislation of the United States, 1974; Safe Drinking Water Act PL 93-523, Subchapter 6A of Title 42.

(13) Xu, Z.; Chen, X.; Kim, H. N.; Yoon, J. *Chem. Soc. Rev.* **2010**, *39*, 127.

(14) Peng, X.; Wu, Y.; Fan, J.; Tian, M.; Han, K. *J. Org. Chem.* **2005**, *70*, 10524.

(15) Crystal data. **A**: $C_{21}H_{21}N_2O$, formula weight = 324.33 monoclinic, *P*2/*c*; a = 15.444(4), b = 7.4809(17) c = 14.862(3) Å, β = 116.866(4)°, U = 1531.8(6) Å^{-3}, T = 293(2) K, Z = 4, D_c = 1.406 Mg m^{-3}, μ(Mo K$_\alpha$) 0.092 mm^{-1}, F(000) = 672, orange block 0.35 mm × 0.24 mm × 0.16 mm; 10477 reflections measured of which 2697 were unique (R_{int} = 0.0362), 223 parameters, wR_2 = 0.1720, $R1$ = 0.0934 (with $I > 2\sigma(I)$), S = 1.308, largest final difference peak/hole 0.249 and −0.192 Å^{-3}. **B**: $C_{25}H_{16}Fe_1N_2O_2$, formula weight = 432.25, orthorhombic, *Pbcn*, a = 27.672(5), b = 10.248(2), c = 13.417(3)Å, U = 3804.6(13) Å^{-3}, T = 295(2) K, Z = 8, D_c = 1.509 Mg m^{-3}, μ(Mo K$_\alpha$) 0.818 mm^{-1}, F(000) = 1776, wine red block 0.52 mm × 0.34 mm × 0.22 mm; 30419 reflections measured of which 4629 unique (R_{int} = 0.0283), 335 parameters, wR_2 = 0.1032, $R1$ = 0.0382 (with $I > 2\sigma(I)$), S = 1.044, largest final difference peak/hole 0.364 and −0.204 Å^{-3}.

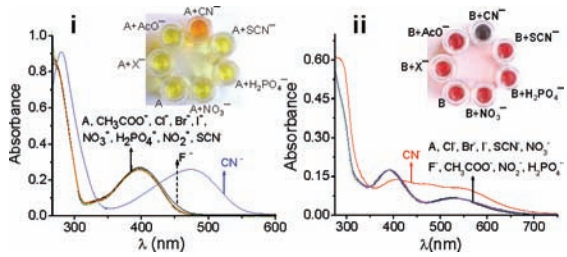

Figure 2. Change in electronic spectra for receptors (i) **A** (19 μM) and (ii) **B** (24 μM) in the presence of various anion (0.1 mM) in CH_3CN/HEPES buffer medium. (Insets) Change in color for receptors (i) **A** and (ii) **B** in the presence of different anionic analytes: X^- is $F^-/Cl^-/Br^-/I^-$.

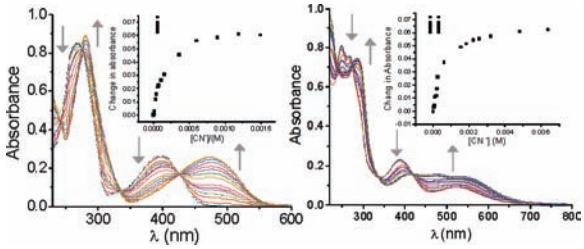

Figure 3. Spectrophotometric titrations for receptors (i) **A** (1.96×10^{-5} M) and (ii) **B** (2.48×10^{-5} M) in the presence of varying $[CN^-]$ ($0-8 \times 10^{-3}$ M) in CH_3CN/HEPES buffer medium. (Insets) Titration profiles for receptor **A** (i) and **B** (ii).

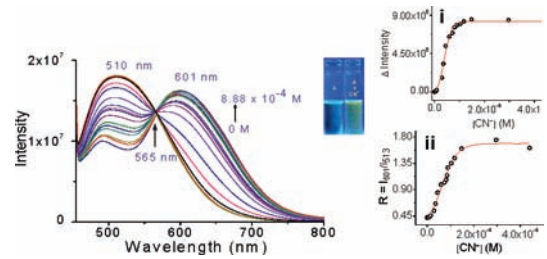

Figure 4. Emission titration of receptors (i) **A** (1.72×10^{-6} M) with varying $[CN^-]$ ($0-8.88 \times 10^{-4}$ M) in CH_3CN/HEPES buffer medium with $\lambda_{ext} = 427$ nm. (Insets) (i) Emission titration profile and (ii) a plot of the ratio of the emission intensities ($R = I_{601}/I_{510}$) at 601 and 510 nm for varying $[CN^-]$.

longer wavelength absorption band for receptor **B** at ~530 nm was assigned to the Fc-based metal to ligand charge transfer and intraligand $\pi-\pi^*$ transition. On binding to the CN^-, the new band (for receptor **A**) or the growth in absorbance (for receptor **B**) could be attributed to a $[\pi]_{imidazole} \rightarrow [\pi^*]_{anthraquinone}$ based intercomponent charge transfer (CT) band. CT nature of this band was further confirmed by its shift to longer wavelength with increase in solvent polarity. Interference studies reveal that spectral response for CN^- remains unaffected in the presence of 10 equiv of all other anions.

Receptor **A** was found to be luminescent with maxima at 510 nm ($\lambda_{ext} = 427$ nm); however, in the presence of increasing $[CN^-]$, a new emission band with $\lambda_{ems}{}^{max}$ of 602 nm appeared with an associated decrease in emission intensity at 510 nm and an isoemissive point at 565 nm. This new emission band for **A**·CN^- was assigned as the CT band. Emission intensity ratio (I_{601}/I_{510}) was found to increase with increase in $[CN^-]$, until the saturation point was reached, and allowed the ratiometric detection of CN^-. Binding efficiency for CN^- was evaluated using data obtained from fluorescence (for **A**) and spectrophotometric titration (for **A** and **B**) in CH_3CN/HEPES buffer medium following standard procedures (Supporting Information).[16] Aqueous solution of NaCN, as well as the acetonitrile solution of TBACN, were used for these studies. Values evaluated from UV−vis titration data are as follows (in CH_3CN/HEPES buffer (1:1, v/v): $K_{assoc}{}^{A} = 1.1 \times 10^4\ M^{-1}$, $K_{assoc}{}^{B} = 5.87 \times 10^2\ M^{-1}$. In CH_3CN these values are $K_{assoc}{}^{A} = 5.1 \times 10^4\ M^{-1}$ and $K_{assoc}{}^{B} = 2.08 \times 10^3\ M^{-1}$.

Respective binding affinities evaluated for receptor **A**, using a fluorescence titration method,[17] were $1.16 \times 10^4\ M^{-1}$ and $2.2 \times 10^4\ M^{-1}$ in CH_3CN/HEPES buffer (1:1, v/v) and CH_3CN medium. Most notably, a plot of I_{601}/I_{510} versus $[CN^-]$ (Figure 4, Inset ii) confirmed the ratiometric changes upon complexation of CN^-. In all cases binding stoichiometry was found to be 1:1 with respect to receptor (**A** or **B**) and CN^-. This was evaluated using either Job's plot or from the slope of the least-squares plot of the emission titration data (Supporting Information). Mass spectral data also corroborated the 1:1 adduct formation (Supporting Information).

The noninterfering absorption bands with significant wavelength shift and the possibility to probe the binding of CN^- in aqueous medium at two emission maxima at dual wavelength excitation (390 and 474 nm) make the receptor **A** a unique ratiometric probe. Ratiometric fluorescence response of **A** on binding to CN^- was also confirmed from the results of time-resolved emission studies (Supporting Information). Decay constants evaluated in the absence and presence of CN^- are shown in SI Table 1 in the Supporting Information. The emission decay lifetime for **A** at 485 nm was found to be single exponential with $\tau = 0.2 \pm 0.001$ ns, and this could be attributed to the fluorescence decay of the (AQ)-based excited state. Similar measurement at λ_{mon} of 565 nm (isoemissive point, Figure 4) was found to be biexponential with $\tau_1 = 0.22$ ns (96%) and $\tau_2 = 1.09$ ns (4%). The major component reflects an AQ-based emission decay process. However, decay traces with varying $[CN^-]$ could be fitted with a biexponential function with time constants of $\tau_1 \approx 0.21$ ns and $\tau_2 \approx 1.11$ ns; while contribution of the longer lived component increases with subsequent decrease in the shorter component on increase in $[CN^-]$ (Supporting Information). The

(16) (a) Lehrer, S. S.; Fashman, G. D. *Biochem. Biophys. Res. Commun.* **1966**, *2*, 133. (b) Chipman, D. M.; Grisaro, V.; Shanon, N. *J. Biol. Chem.* **1967**, *242*, 4388.

(17) Tedesco, A. C.; Oliveira, D. M.; Lacava, Z. G. M.; Azevedo, R. B.; Lima, E. C. D.; Morais, P. C. *J. Magn. Magn. Mater.* **2004**, *272−276*, 2404.

longer component could be attributed to the new CT emission state for the H-bonded adduct **A**·CN^-. This clearly reveals a ratiometric response in the presence of varying [CN^-].

Recognition of F^- by receptor **A** was reported earlier in acetonitrile;[14] however, to date there has been no report on the recognition of CN^- by receptor **A** in aqueous solution. Very high solvation energy for F^- in water ($\Delta H_{hyd} = -505$ kJ/mol) could account for the very weak/negligible binding of the receptor **A** or **B** with F^- in the present study. A similar argument may also be offered for studies on CH_3COO^- ($\Delta H_{hyd} = -375$ kJ/mol) and $H_2PO_4^-$ ($\Delta H_{hyd} = -260$ kJ/mol)[18] in aqueous environment. Thus, the much lower hydration energy for the CN^- ($\Delta H_{hyd} = -67$ kJ/mol) contributed primarily to the adduct formation (**A**·CN^- and **B**·CN^-) and thus its selective recognition. Absence of any deprotonation equilibria in the present study could be explained on the basis of the lower basicity of the partially aquated cyanide ion.[19] Presumably, the higher the acidity of the -N(H)imidazole hydrogen in **A** that could be accounted for the higher observed affinity of receptor **A** toward CN^-. Reversibility of the CN^- binding process could be demonstrated by adding a few drops of acetic acid (5×10^{-2} M) solution to either **A**·CN^- or **B**·CN^- adduct, while the preferential protonation of the CN^- took place and the original spectra of **A** or **B** was restored.

Upfield shifts observed in the ^{1}H NMR spectra (DMSO-d_6/D_2O, 1:1, v/v) for the phenyl (Ha,a′,b,b′,c) and imidazole (H4) ring hydrogen atoms for **A** or **B** on binding to CN^- ion suggest the increase in the electron density in respective rings through partial charge delocalization in the conjugated system in immediate proximity of the N^1-center. However, the absence of any signal for $[(CN)_2H]^-$ does not support the deprotonation phenomena. Further, the appearance of the ESI-Ms signal for **A**·CN^- or **B**·CN^- in the presence of excess NaCN (10 equiv (Supporting Information) corroborates the hydrogen bonded adduct formation and nullifies any possibility of the deprotonation process.

Presence of the Fc moiety offered us the posssibility to probe the CN^- binding process in **B** using differential pulse voltammometry, where a cathodic shift of 80 mV for Fc/$Fc^{+\bullet}$ couple was observed. Nonreversibility of this couple in aqueous media is well documented,[20] and no sensible cyclic voltammogram in CH_3CN-H_2O (1:1, v/v) could be obtained (Supporting Information).

The lowest detection limit of 0.06 ppm for **A** and 0.078 ppm for **B** with respect to CN^- (used in the form of aqueous solution of NaCN) was evaluated from the plots of the respective titration profile of two receptors. These concentration limits are much lower than the limit (0.2 ppm) set by Environment Protection Agency for drinking water.[10b] Thus, these receptors could be used for checking CN^- in drinking water following standard international norm.

Microorganism such as *Pseudomonas putida* utilize cyanide as the sole source of carbon and nitrogen, and thus

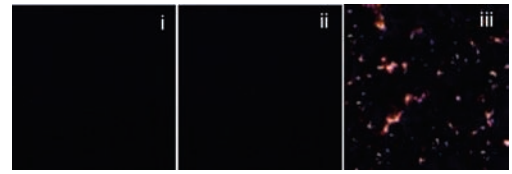

Figure 5. Fluorescence microscope images (FITC filter) of (i) cells of *Pseudomonas putida* (control), (ii) cells exposed to CN^- (1.42×10^{-6} M), (iii) cells exposed to aqueous solution of CN^- (1.42×10^{-6} M) for 5 min and then to **A** (2.14×10^{-6} M), CH_3CN/HEPES buffer medium (1:1, v/v).

NaCN is nontoxic to this organism.[21] We have used this microorganism for checking the possibility of using **A** as reagent for the detection of the uptake of CN^-. Bacterial cell suspensions, pre-exposed (0−5 m, 25 °C) (Supporting Information) to the 1.42 μM aqueous solution of NaCN were further treated with a 2.14 μM solution of **A** and viewed through fluorescence microscope (AxioImager Carl Zeiss).

Respective images of the control and cultures with CN^- and CN^- + **A** are shown in Figure 5. Fluorescent images could be observed when bacterial cell cultures were treated with CN^-_{aq} and then with the reagent **A**, and thus this experiment clearly demonstrates that **A** could be used for detection of CN^- adsorbed on the cell surface of microorganisms such as *Pseudomonas putida*.

In conclusion, we have demonstrated that two imidazole-based receptors (**A** and **B**) are highly specific for recognition of CN^- from aqueous solution of NaCN through the formation of a reversible H^- bonded adduct. This adduct formation produces an instant visually detectable color and fluorescence change. These receptors are suitable for detection of CN^- much lower than 0.2 ppm, the permissible concentration of CN^- for drinking water according to the standard set by EPA. Thus, we have shown that two unique receptors (**A** and **B**) are suitable for colorimetric detection of CN^- in aqueous solution and one of these, receptor **A**, was even suitable for detection of CN^- present in microbes.

Acknowledgment. DST and CSIR have supported this work. S.S., A.G., P.M., and S.K.M. acknowledge CSIR for JRF/SRF fellowship. CCDC 776987 (**A**) and 776988 (**B**) contain the crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: (+44) 1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.

Supporting Information Available: Synthetic details, analytical data for **A** and **B** and their spectra in different solvents, structural details, CIF files, evaluation of binding constants. This material is available free of charge via the Internet at http://pubs.acs.org.

OL101281X

(18) Sluys, W. G. V. D. *J. Chem. Educ.* **2001**, *78*, 111.
(19) Kim, D.-S.; Chung, Y.-M.; Jun, M.; Ahn, K. H. *J. Org. Chem.* **2009**, *74*, 4849.
(20) Monk, P. *Fundamentals of Electro-analytical Chemistry*; John Wiley: New York, 2001; 160 pp.
(21) Chapatwala, K. D.; Babu, G. R. V.; Vijaya, O. K.; Kumar, K. P.; Wolfram, J. H. *J. Ind. Microbiol. Biotechnol.* **1998**, *20*, 28.