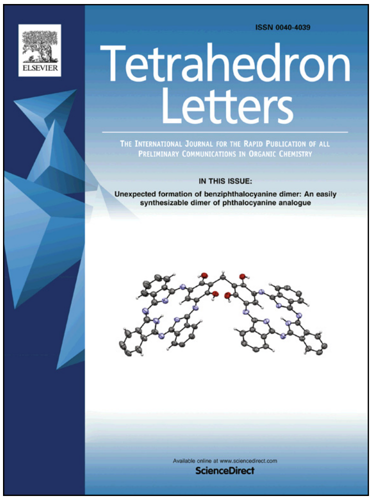


A dipyrromethane based receptor as a dual colorimetric sensor for F^- and Cu^{2+} ions

Pradeep K. Muwal, Aradhana Nayal, Manish K. Jaiswal, Pramod S. Pandey

PII: S0040-4039(17)31456-9
DOI: https://doi.org/10.1016/j.tetlet.2017.11.042
Reference: TETL 49485

To appear in: *Tetrahedron Letters*

Received Date: 27 September 2017
Revised Date: 2 November 2017
Accepted Date: 19 November 2017

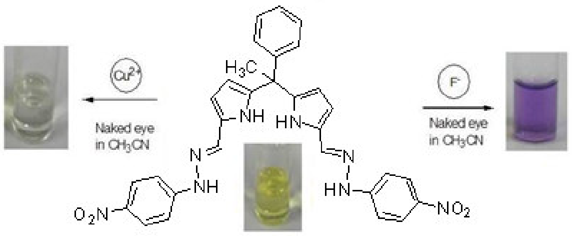
Please cite this article as: Muwal, P.K., Nayal, A., Jaiswal, M.K., Pandey, P.S., A dipyrromethane based receptor as a dual colorimetric sensor for F^- and Cu^{2+} ions, *Tetrahedron Letters* (2017), doi: https://doi.org/10.1016/j.tetlet.2017.11.042

Graphical Abstract

A dipyrromethane based receptor as a dual colorimetric sensor for F^- and Cu^{2+} ions

Pradeep K. Muwal, Aradhana Nayal, Manish K. Jaiswal and Pramod S. Pandey*

Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016



Tetrahedron Letters
journal homepage: www.elsevier.com

A dipyrromethane based receptor as a dual colorimetric sensor for F$^-$ and Cu^{2+} ions

Pradeep K. Muwal, Aradhana Nayal, Manish K. Jaiswal and Pramod S. Pandey*
Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India 110016
pramod@chemistry.iitd.ac.in, Mobile: 91-9910678428

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Dipyrromethane
Colorimetric sensor
***F$^-$** recognition*
Cu^{2+}recognition

ABSTRACT

A novel dipyrromethane based receptor has been synthesized. It works as a highly selective colorimetric sensor for F$^-$ andCu^{2+} ions, which can be used for their necked eye detection with evident colour change of its solution.

1. INTRODUCTION

Development of artificial receptors for the selective detection of biologically and environmentally relevant anions and metal ions has attracted considerable attention in recent years.[1,2] Among the anions, fluoride ions play important role in treatment in dental decay and osteoporosis. However, the excess of fluoride ions can lead to several diseases such as fluorosis, gastrointestinal and kidney disorders. Among the various metal ions, copper ions play significant role in many fundamental biological processes and enzyme-catalysed reactions involving superoxide dismutase, cytochrome c oxidase and tyrosinase. Moreover, Cu^{2+} is an environmental pollutant and its excess amount can cause serious health problems such as Alzheimer's and Parkinson's diseases. Hence, there has been continuously growing interest to design new sensors for F$^-$ and Cu^{2+} ions.[3,4]

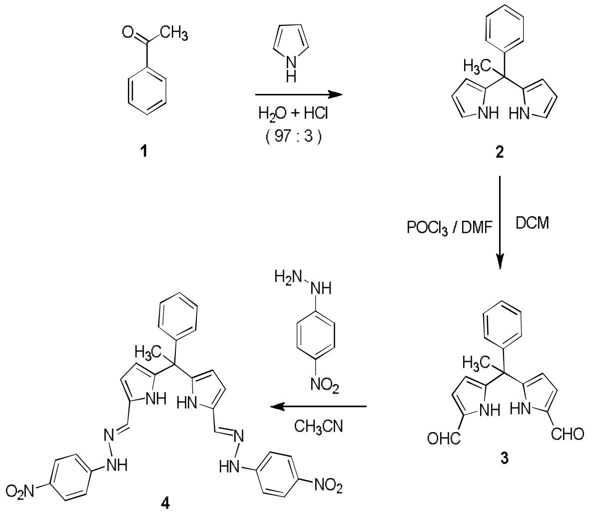
Recently, dipyrromethane and its derivatives have been found to show great potential for the design of receptors for anion and metal ion recognition. Sessler and co-workers synthesized various dipyrromethane based receptors which showed selective recognition of hydrogen sulphate, acetate, dihydrogen phosphate and pyrophosphate ions.[5] Jurazak and co-workers reported the binding ability of a series of 7,7'-diurido-2,2'-diindolylmethane derivatives towards $H_2PO_4^-$ ion.[6] Azamacrocyclic and azacryptand receptors containing dipyrromethane units were reported by Mani and co-workers showing their ability to bind fluoride ion.[7] Majerski and co-workers synthesized various admantane based dipyrromethane derivatives which were selective for fluoride and acetate ions.[8] Pandey and co-workers reported the binding ability of *meso*-glycosyl dipyrromethane derivatives which exhibited fluorescent 'turn on' and 'turn off' signaling for Cd^{2+} and Cu^{2+} ions.[9]

Our research group has considerable interest in anion and metal ion recognition.[10] Herein, we report a novel and easily accessible dipyrromethane based receptor as a colorimetric sensor for the dual sensing of F$^-$ as well as Cu^{2+} ions which can be used for the naked eye detection of these ions in acetonitrile solution.

2. RESULTS AND DISCUSSION

2.1. Synthesis

The dipyrromethane based receptor **4** was synthesized by following the sequence of reactions given in Scheme 1. Treatment of acetophenone **1** with pyrrole in the presence of HCl in water resulted in the formation of *meso*-methyl-*meso*-phenyl-2,2'-pyrromethane **2**.[11] The Vilsmeier reaction of compound **2** gave compound **3**.[12]The refluxing of the acetonitrile solution of **3** and *p*-nitrophenylhydrazine in 1:1 molar ratio led to the formation of compound **4**.



Scheme 1. Synthesis of dipyrromethane based receptor

2.2. Ions binding studies

The anion binding property of receptor**4** was investigated by UV-Vis titration method. The change in the absorbance bands after addition of $Bu_4N^+X^-$ (X = F, Cl, Br, I, HSO_4, H_2PO_4, CH_3COO) to the solution of receptor was monitored to determine the binding affinity of this receptor towards anions.

Receptor **4** showed the highest selectivity towards F^- ion. The binding affinity of receptor **4** towards F^- anion was investigated by monitoring the absorbance changes on addition of $Bu_4N^+F^-$ (1 mM) to the solution of compound **4** (1×10^{-5} M) in CH_3CN. As shown in Figure 1, the absorbance bands at 295 and 420 nm decreased and a new band around 531 nm developed with a isosbestic point at 462 nm, on incremental addition of F^- ion (0-1.2 equiv).

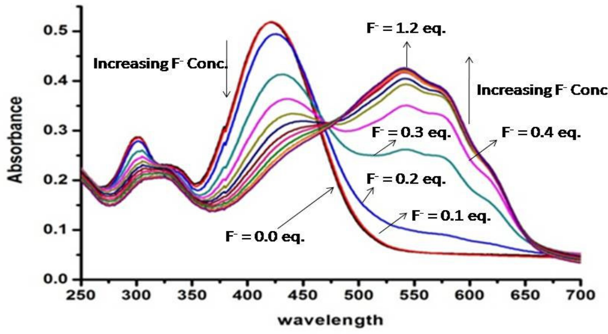


Figure 1: Absorbance spectra of compound **4** (1×10^{-5} M) in CH_3CN in the presence of F^- ion (0-1.2 equiv).

The binding constant was calculated using Hildebrand-Benesi equation[13]. The plot with $A_0/(A\text{-}A_0)$ *vs* $[G]^{-1}$ showed good linear relationship with correlation coefficient (R^2) = 0.99. The binding constant was obtained from the ratio of the y-intercept to the slope and found to be $6.02 \times 10^3\ M^{-1}$ (Fig. S8a). The Job's plot indicated the 1:1 complex formation between receptor **4** and F^- ion (Fig.S8b).

Significant spectral changes were also observed in the UV-Vis spectrum of receptor **4** on addition of $H_2PO_4^-$ anion (Fig. 2). As shown in Figure 2, the absorbance bands at 300 and 420 nm decreased and a new band around 450 nm developed with two isosbestic points at 436 and 560 nm, on incremental addition of $H_2PO_4^-$ ion (0-1.5 equiv). The binding constant was found to be $3.39 \times 10^3\ M^{-1}$ (Fig. S9a) with 1:1 complex formation between receptor **4** and $H_2PO_4^-$ anion (Fig. S9b).

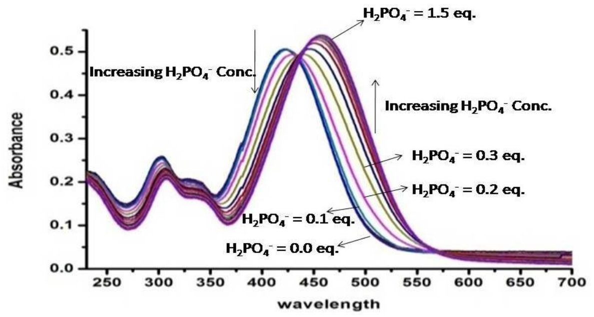


Figure 2: Absorbance spectra of compound **4** (1×10^{-5} M) in CH_3CN in the presence of $H_2PO_4^-$ ion (0-1.5 equiv).

However, no measurable change in its spectrum on addition of Cl^-, Br^-, I^-, HSO_4^- and CH_3COO^- anions was observed, suggesting no or very weak binding for these anions to receptor **4**. The colorimetric anion sensing ability of sensor **4** was examined by the anion-induced colour changes in the solution of sensor **4** in acetonitrile before and after the addition of an anion. Sensor **4** showed significant colour change in the presence of fluoride. Upon addition of 0.3 equivalents of fluoride ion (TBAF), the pale yellow solution of receptor **4** became violet, which can be used for the "naked-eye" detection of this anion. In the case of dihydrogen phosphate ion ($TBAH_2PO_4$), the pale yellow solution of receptor **4** became dark yellow after 5 equiv addition. No colour change was observed on addition of other anions such as chloride, bromide, iodide sulphate and acetate ions even up to 8 equiv (Fig. 3).

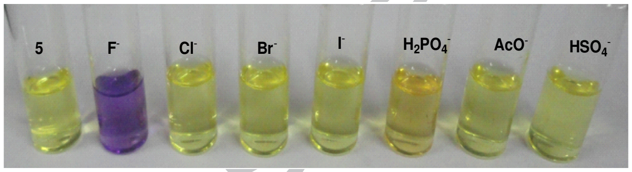


Figure 3: Photograph of receptor **4** (1×10^{-5} M) in CH_3CN and after addition of 0.3 equiv of F^-, 5 equiv $H_2PO_4^-$ and 8 equiv of Cl^-, Br^-, I^-, HSO_4^-, CH_3COO^-

The mode of binding of F^- ion with compounds **4** was ascertained by ^1H NMR spectroscopy. After addition of F^- ion to the solution of compound **4** (10 mM) in CD_3CN, N-H protons of pyrrole ring, amino and –N=CH protons of hydrazone group shifted downfield (Fig. 4), indicating their involvement in H-bonding with F^- ion. The NMR showed fast disappearance of –NH protons, however, there was no peak observed for HF_2^- at 12-16 ppm.

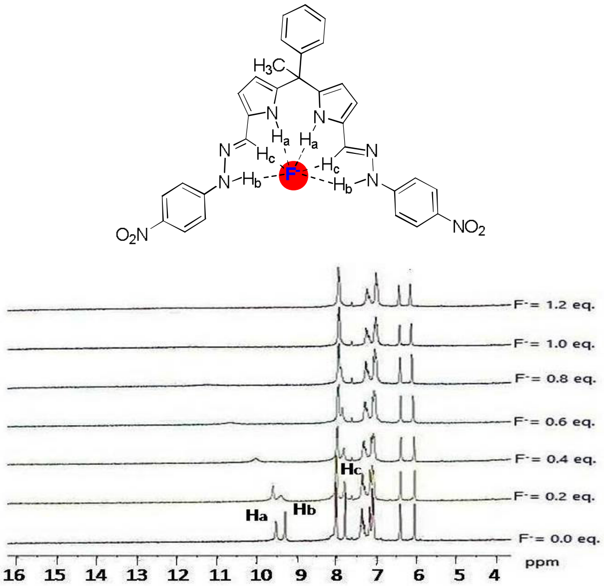


Figure 4: (i) Proposed mode of binding of F^- with **4** based on NMR data (ii) Partial ^1H NMR spectra (300 MHz, CD_3CN, δ in ppm) of **4** showing chemical shift change in the presence of incremental addition of TBAF (0-1.2 equiv).

Receptor **4** also showed high selectivity towards Cu^{2+} ion as indicated by the change in the UV-Vis spectrum of receptor **4** on addition of different metal ions. The binding affinity of receptor **4** towards Cu^{2+} ion was investigated by monitoring the absorbance changes on addition of $Cu(ClO4)_2$ (1 mM) to the solution of compound **4** (1×10^{-5} M) in CH_3CN. As shown in Figure 5, the absorbance band at 295 increased and at 420 nm decreased. A new band at 597 nm developed with a sharp isosbestic point at 509 nm, on the incremental addition of Cu^{2+} ion (0-1.2 equiv).

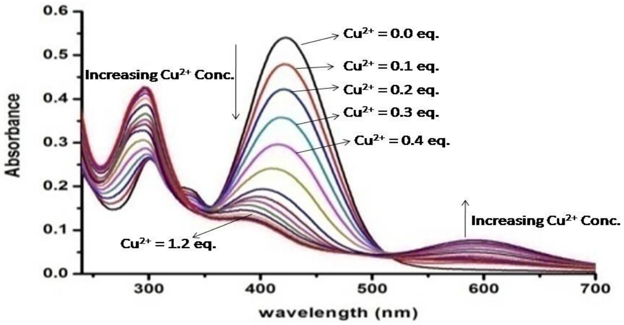


Figure 5: Absorbance spectra of compound **4** (1×10^{-5} M) in CH_3CN in the presence of Cu^{2+} ion (0-1.2 equiv).

The plot with A0/(A-A0) vs $[G]^{-1}$ showed good linear relationship with correlation coefficient $R^2 = 0.99$. The binding constant for complex formation between receptor **4** and Cu^{2+} ion was found as $K_a = 9.82 \times 10^3$ M^{-1} (Fig. S10a). The Job's plot indicated the 1:1 complex formation between receptor **4** and Cu^{2+} anion (Fig. S10b). However, no significant change was observed in the absorbance spectrum of compound **4** with other metal ions, suggesting no or very weak binding for these ions to receptor **4**.

The colorimetric metal sensing ability of sensor **4** was examined by the metal-induced colour change in the solution of sensor **4** in acetonitrile before and after the addition of a metal. Sensor **4** showed significant colour change in the presence of Cu^{2+} ion. Upon addition of 0.2 equivalents of Cu^{2+} the pale yellow solution of receptor **4** became colourless (pale blue) which can be used for the "naked-eye" detection of this cation. No colour change was observed on addition of other metal ions even up to 5 equiv (Fig. 6).

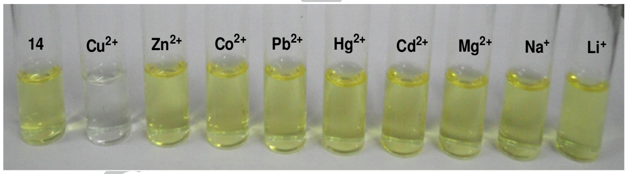


Figure 6:A photograph of (1×10^{-4} M) soln of receptor **4** in CH_3CN and after addition of 0.2 equiv of Cu^{2+} and 5 equiv of other metals.

The mode of binding of Cu^{2+} ion with compounds **4** was ascertained by ^1H NMR spectroscopy. After addition of Cu^{2+} ion to the solution of compound **4** (10 mM) in CD_3CN, N-H protons of pyrrole ring and -NH and -CH protons of hydrazone group shifted downfield, which showed the binding of Cu^{2+} ion with the receptor as shown in Figure 7.

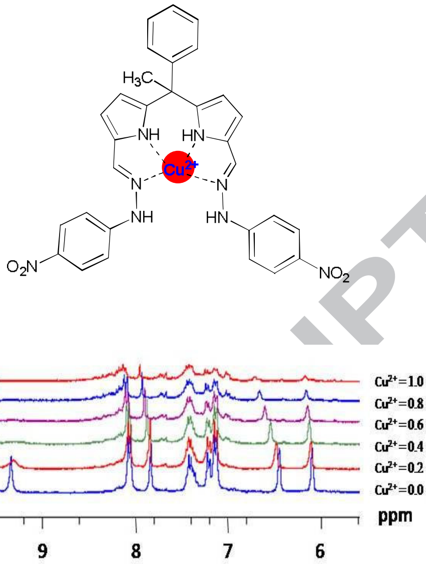


Figure 7: (i) Proposed mode of binding of Cu^{2+} with **4** based on NMR data.(ii) Partial ^1H NMR spectra (300 MHz, CD_3CN, δ in ppm) of **4** showing chemical shift change in the presence of incremental addition of Cu^{2+} ion (0-1.0 equiv).

3. CONCLUSION

A dipyrromethane based receptor containing two *p*-nitrophenylhydrazone groups has been synthesized. The receptor showed highly selective binding and colorimetric sensing towards F^- and Cu^{2+} ions, which can be used for the naked eye detection of these ions.

Acknowledgments

PKM and AN thank the Council of Science and Industrial Research, New Delhi, for the research fellowships.

Supplementary Material

Supplementary data (experimental details, characterization data for compounds, NMR spectra, Hildebrand-Benesi plots, Job's plots) associated with this article can be found, in the online version, at

References

1. (a) Gale, P. A. *Acc. Chem. Res.* **2006**, *39*, 465. (b) Sessler, J. L.; Gale, P. A.; Cho, W.-S. *Anion Receptor Chemistry*, Royal society of Chemistry: Cambridge, UK, **2006**. (c) Gale, P. A.; Garcia-Garrido, S. E.; Garric, J. *Chem. Soc. Rev.* **2008**, *37*, 151. (d) Caltagirone, C.; Gale, P. A. *Chem. Soc. Rev.* **2009**, *38*, 520.(e) Gale, P. A.; Gunnlaugsson, T. eds.: *Supramolecular chemistry of anionic species themed issue*, *Chem. Soc. Rev.* **2010**, *39*, 3595. (f) Wenzel, M.; Hiscock, J. R.; Gale, P. A. *Chem. Soc. Rev.***2012**, *41*, 480. (e) Busschaert, N.; Caltagirone, C.; Rossom, W. V.; Gale, P. A. *Chem. Rev.***2015**, *115*, 8038. (f) Pedro, P. M.; Zapata, F.; Caballero A. *Chem. Rev.***2017**, *117*, 9907.

2. (a) Hancock, R. D.; Melton, D. L.; Harrington, J. M.; McDonald, F. C.; Gephart, R. T.; Boone, L. L.; Jones, S.

B.; Dean, N. E.; Whitehead, J. R.; Cockrell, G. M. *Coord. Chem. Rev.***2007**, *251*, 1678. (b) Freisinger, E.; Sigel, R. K. O. *Coord. Chem. Rev.* **2007**, *251*, 1834. .(c) Nolan, E. M.; Lippard, S. J. *Chem. Rev.***2008**, *108*, 3443. (d) Nolan, E. M.; Lippard, S. J. *Acc. Chem. Res.* **2009**, *42*, 193. (e) Quang, D. T.; Kim, J. S. *Chem. Rev.* **2010**,*110,* 6280. (f) Xu, Z.; Yoon, J.; Spring, D. R. *Chem. Soc. Rev.* **2010**, *39*, 1996. (g) Kim, H. N.; Ren, W. X.; Kim, J. S.; Yoon, J. *Chem. Soc. Rev.* **2012**, *41*, 3210.

3. (a) Song, E. J.; Kim, H.; Hwang, I. H.; Kim, K. B.; Kim, A. R.; Noh, I.; Kim, C.; *Sens. Actuator B-Chem.* **2014**, *195*, 36. (b) Xu, Y.; Wang, Y.; Zhao, S.; Guan, R.; Cao, D.; Wu, Q.; Yu, X.; Sun Y.; *Inorg. Chem. Commun.* **2017**, *78*, 52. (c) You, D. K.; Lee, S. H.; lee, J.H.; Kwak, S.W.; Hwang, H.; Lee, J.; Chung, Y.; Park, M. H.; Lee, K. M. *RSC Adv.* **2017**, *7,*10345.

4. (a) Kumar, M.; Kumar, N.; Bhalla, V.; Sharma, P. R.; Kaur, T. *Org. Lett.,* **2012**, *14*, 406. (b) Ji, X. F.; Yao, Y.; Li, J. Y.; Yan, X. Z.; Huang, F. H. *J. Am. Chem. Soc.***2013**, *135*, 74. (c) Park, G. J.; Hwang, I.H.; Song, E.J.; Kim, H.; Kim, C. *Tetrahedron* **2014**, *70*, 2822 (d) Kim, H.; Na, Y.J.; Song, E.J., Kim, K.B.; Bae, J.M.; Kim, C., *RSC Adv.* **2014**, *4*, 22463. (e) Liu, Y.-W.; Chir, J.-L.; Wang, S.-T.; Wu, A.-T. *Inorg. Chem. Commun.*, **2014**, *45*, 112. (f) Udhayakumari, D.; Velmathi, S.; Venktesan, P.; Wu, S.- P. *J. Luminescence*, **2015**, *161*, 411.

5. (a) Sessler, J. L.; Roznyatovskiy, V.; Pantos, G. D.; Borisova, N. E.; Reshetova, M. D.; Lynch, V. M.; Khrustalev, V. N.; Ustynyuk, Y. A.; *Org. Lett.* **2005**, *7,* 5277. (b) Katayev, E. A.; Boev, N.; V.; Khrustalev, V. N.; Ustynyuk, Y. A.; Tananaev, I. G.; Sessler, J. L. *J. Org. Chem.* **2007**, *72,* 2887. (c) Sessler, J. L.; Cai, J.; Gong, H.-Y.; Yang, X.; Arambula, J. F.; Hay, B. P. *J. Am. Chem. Soc***.** **2010**, *132*, 14058. (d) Bill, N. L.; Kim, D. S.; Kim, S. K.; Park, J. S.; Lynch, V. M.; Young, N. J.; Hay, B. P.; Yang, Y.; Anslyn, E. V.; Sessler, J. L. *Supramol. Chem.* **2012,** *24*, 72.(e) Deliomeroglu, M. K.; Lynch, V. M.; Sessler, J. L. *Chem Comm.* **2014**, 50, 11863.

6. Dydio, P.; Zielinski, T.; Jurazak, J. *Org. Lett*. **2010**, *12*, 1076.

7. (a) Mani, G.; Guchhait, T.; Kumar, R.; Kumar, S. *Org. Lett*. ***2010*****,** *12*, 3910. (b) Guchhait, T.; Mani, G. *J. Org.Chem.* **2011**, *76*, 10114.

8. Aleskovi, M.; Basari, N.; Halasz, I.; Liang, X.; Qin, W.; Majerski. K. M. *Tetrahedron* **2013**, *69,* 1725.

9. Biswas, A.; Pandey, R.; Kushwaha, D.; Shahid, M.; Tiwari, V. K.; Misra, A.; Pandey. D. S. *Tetrahedron Lett.* **2013,** *54,* 4193.

10. (a) Khatri, V. K.; Shailesh, U.; Pandey, P. S. *Org. Lett.* **2006**, *8*, 1755.(b) Khatri, V. K.; Chahar, M.; Pavani, K.; Pandey, P. S. *J. Org. Chem.* **2007**, *72*, 10224.(c) Chahar, M.; Shailesh, U.; Pandey, P. S. *Tetrahedron.* **2007**, *63*, 171.(d) Chahar, M.; Pandey, P. S. *Tetrahedron.* **2008**, *64*, 6488.(e) Kumar, A.; Pandey, P. S. *Org Lett,* **2008***, 10,*165.(f) Kumar, A.; Pandey, P. S. *Tetrahedron Lett.,***2009**,*50*, 5842 (g) Chhatra, R. K.; Kumar, A.; Pandey, P. S. *J. Org. Chem.* **2011**, *76*, 9086. (h) Tripathi, A; Pandey, P. S. *Tetrahedron Lett.* **2011**, *52*, 3558. (i) Nayal, A.; Pandey, P. S. *Tetrahedron* **2015**, *71*, 6991. (j) Muwal, P. K.; Pandey, S.; Pandey, P.S. *RSC Adv*, **2014**, *4*, 21531.(k) Jaiswal, M. K.; Muwal P. K.; Pandey S.; Pandey, P. S. *Tetrahedron Lett.,* **2017**, *58*, 2153.

11. Alemayehu*, A.;* Conradie, M. M.; Ghosh, A. *J. Porphyrins Phthalocyanines* **2012**, *16*, 695.

12. (a) Geier, G. R.; Callinan, J. B.; Rao, P. D.; Lindsey, J. S.; *J. Porphyrins Phthalocyanines* **2001**, *5*, 810. (b) Bruckner C.; Posakony J. J.; Johnson C. K.; Boyle R. W.; James B. R; Dolphin D. *J. Porphyrins Phthalocyanines* **1998**, *2*, 455.

Highlights

- A dipyrromethane-based receptor containing two *p*-nitrophenylhydrazone groups has been synthesized.
- This receptor shows excellent colorimetric sensing for F^- as well as Cu^{2+} ions.
- The binding studies were carried out by UV-Vis and ^1H NMR spectroscopy.
- The binding studies show 1:1 complex formation in both cases.