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Colorimetric detection of *in situ* metal acetates and fluorides by a bipyridyl-linked Schiff base

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Here, we present a new bipyridyl moiety linked Schiff base (bipy-1) that is well characterized using spectroscopic techniques. Colorimetric and UV-vis titrations were used to study the photophysical properties of bipy-1 in the presence of various tetrabutyl ammonium salt of anions and metal salts containing different counter cations. bipy-1 showed selective recognition of dimethyl sulphoxide solution of tetrabutyl ammonium salt of F^- ion accompanied with a UV-vis band at 529 nm and interesting binding of aqueous Co, Ni, and Cu acetates/fluorides, as confirmed by distinct color changes from fluorescent green to pink or orange and a strong band around 480–510 nm in the UV-vis spectrum. However, in the presence of Co, Ni, and Cu countercations, any form of metal acetate/fluorides was found to be able to respond to similar color changes from fluorescent green to pink or orange, showing a band around 480–510 nm. This type of output clearly indicates that the *in situ* formation of Co, Ni, and Cu acetates/fluorides also coordinates with bipyridyl nitrogen atoms. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: bipyridyl Schiff base; colorimetric analysis; metal acetate/fluoride; *in situ* analyte detection

INTRODUCTION

Molecular recognition is a fascinating and growing research field for the identification of charged (Ghosh *et al.*, 2006; Mahapatra *et al.*, 2012; Tang & Cai, 2012; Guo *et al.*, 2013) and neutral analytes (Buryak & Severin, 2005; Zhou & Yoon, 2012) because they are cost effective, easy to create, selective for particular analytes, and show high sensitivity even at trace levels. Designing a single molecule for multiple analytes in the direct as well as in the *in situ* form is a highly interesting and new concept in the molecular recognition field. Among all metal ions, "d" block metal ions are capable of effective interaction with organic receptors. In particular, Co^{2+} (Maity & Govindaraju, 2011; Zhen *et al.*, 2011), Ni^{2+} (Aksuner *et al.*, 2012; Wang *et al.*, 2012), and Cu^{2+} (Hua *et al.*, 2013; Lin *et al.*, 2013) ions are biologically important species because of their extraordinary roles in living organisms. Similarly, fluorides and acetate ions (Zhang *et al.*, 2009; Hu *et al.*, 2011; Mahapatra *et al.*, 2011) are also biologically important anions with a wide range of application in medicine, food preservation, and in enzyme-catalyzed reactions. Deficiency of such charged analytes leads to severe health risks such as Alzheimer's disease, anemia, and heart and nerve problems. Although many reports are available regarding the individual detection of different types of metal ions or anions, the specific binding of metal acetates and fluorides is rarely reported. Recently, H. J. Zo *et al.* (Song *et al.*, 2013) reported the selective sensing of Zn$(OAc)_2$ using a bipyridyl-modified acetylene dye.

Many receptors for charged analytes have recently been designed using a binding site-signaling unit approach. When a particular analyte binds with the receptor unit, the electronic properties of the entire system are distorted upon a conversion into an optical signal. Common building blocks for charged analytes are nitrogen-containing compounds (Schiff base (Udhayakumari *et al.*, 2013), pyridine (Xue *et al.*, 2005), bipyridine (Beer *et al.*, 2004), and phenanthroline (Wang *et al.*, 2010)), NH group (pyrrole and indole (Suganya *et al.*, 2013; Martínez *et al.*, 2008), imidazole (Zapata *et al.*, 2009), quinoline (Basa & Sykes, 2012), triazole (Maity & Govindaraju, 2012), and naphthalimide (Satriano *et al.*, 2013)), coumarin (Jung *et al.*, 2009), and rhodamines (Zhou *et al.*, 2009). In this article, we demonstrate for the first time the synthesis of **bipy-1** and its binding property with $Co(OAc/F)_2$, $Ni(OAc/F)_2$, and $Cu(OAc/F)_2$ manifested by colorimetric analysis and UV-vis titration. The surprising concept is that the *in situ* formed metal acetates/fluorides can also bind effectively with **bipy-1**, showing results similar to those of the original metal acetates/fluorides. To the best of our knowledge, this is the first report of *in situ* formed metal acetate/fluoride binding with organic receptors. The dual-responsive nature of **bipy-1** also makes the system interesting with regard to the selective detection of tetrabutyl ammonium (TBA) salt of F^- ion in dimethyl sulphoxide (DMSO) medium.

EXPERIMENTAL SECTION

Materials and instruments used

Reagents such as o-amino phenol, 5,5′-dimethyl-2,2′-bipyridine, Bredereck's reagent, sodium periodate, TBA salt of anions, and metal salts were received commercially and were used as such without any further purification. The solvents DMSO, ethanol (EtOH), and dimethyl formamide, used for the spectroscopic experiments and synthesis process, were also

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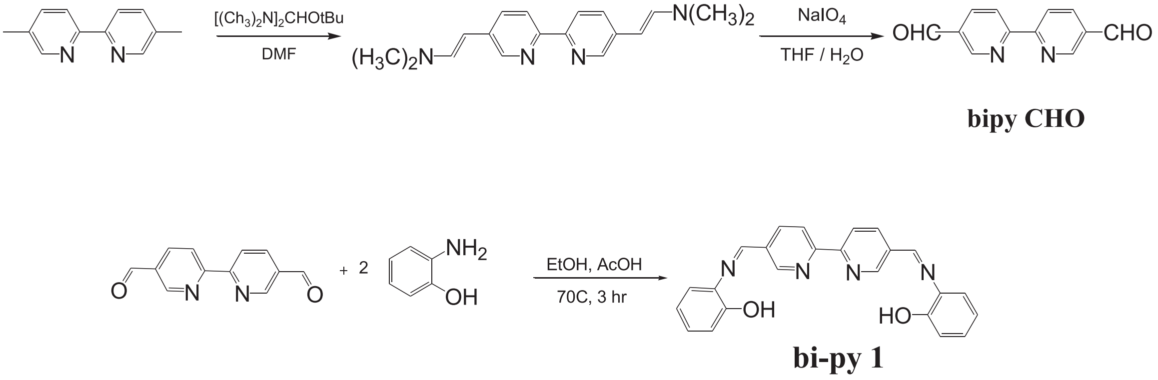

Scheme 1. Synthesis of **bipy-1**.

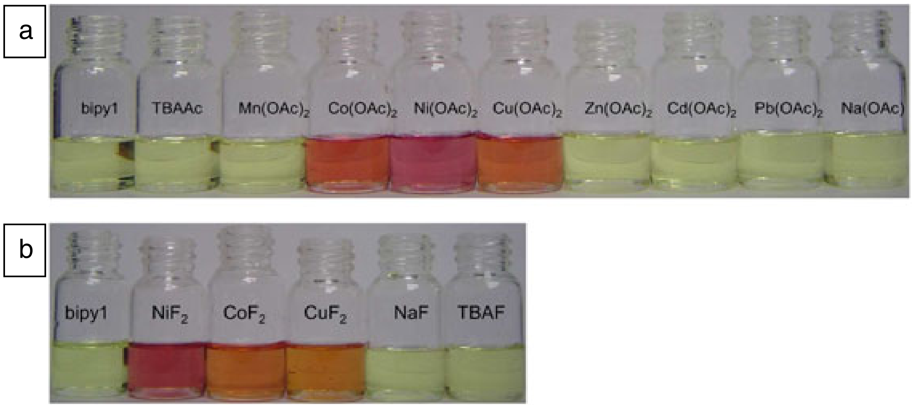

Figure 1. Color changes observed upon the addition of 2 eq of various metal (a) acetates and (b) fluorides (1.5×10^{-3} M in H_2O) to **bipy-1** (5×10^{-5} M in DMSO).

purchased and used as such. An Orbitrap Q Exactive mass spectrometer was used for the molecular weight analysis. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AV-III 300-MHz spectrometer using DMSO-d_6 as a solvent. The infrared (IR) spectra were recorded on a Nicolet IS5 instrument using KBr plates. The UV-vis spectra were recorded on a Shimadzu UV-2600 spectrophotometer with a quartz cuvette (path length = 1 cm) at room temperature (r.t.). For all the spectroscopic titrations, a 5×10^{-5} M solution of **bipy-1** in DMSO and 1.5×10^{-3} M of all TBA salt of anions in DMSO and metal salt of acetate, fluoride, chloride, and nitrate in H_2O were prepared and used.

Experimental procedure

2, 2′-Bipyridine-5,5′-dicarbaldehyde (bipy-CHO) was synthesized using reported procedure (Hodacova & Budesınsky, 2007). Then, **bipy-1** was prepared by reacting 1 mmol of o-amino phenol with 2 mmol of 2,2′-bipyridine-5,5′-dicarbaldehyde in EtOH medium. The reaction mixture was allowed to reflux for 3 h at 70°C. After cooling to r.t., the precipitate formed was filtered, washed with EtOH, and dried in a vacuum oven (Scheme 1). Yield: 70%; melting point: 265–270°C. IR (cm^{-1}, KBr): 3357.65, 1624.37, 1590.26, 1488.80, 1369.67, 1241.85, and 1150.69. ^1H NMR (300 MHz, DMSO-d_6, δ ppm): 9.26 (2H, OH, s), 9.13 (2H, CH=N, imine, s), 8.90 (2H, CH=N, pyridine ring, s), 8.59–8.62 (4H, aro, q), 7.29–7.33 (2H, aro, dd), 7.11–7.16 (2H, aro, t), 6.91–694 (2H, aro, dd), and 6.84–6.89 (4H, aro, t). ^{13}C NMR (75 MHz, DMSO-d_6, δ ppm): 153.93, 149.38, 148.35, 134.98, 134.15, 130.17, 125.93, 118.71, 117.26, 116.80, and 113.98. HRMS (M + 1): 395.1502 (calculated) and 395.1502 (observed).

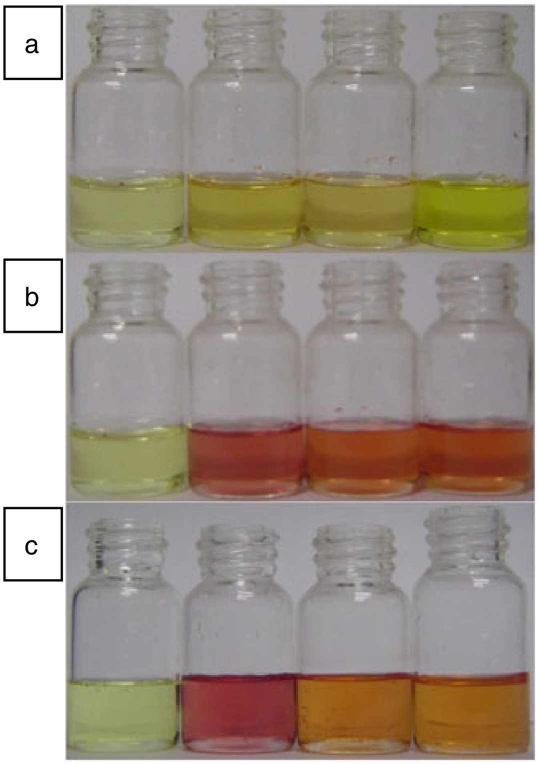

Figure 2. Color changes observed upon the addition of 2 eq of (a) $NiCl_2$, $CoCl_2$, and $CuCl_2$ to **bipy-1** (5×10^{-5} M in DMSO) and the addition of (b) $Ni(OAc)_2$, $Co(OAc)_2$, and $Cu(OAc)_2$ and (c) NiF_2, CoF_2, and CuF_2 (1.5×10^{-3} M in H_2O) to the solution of panel (a).

Figure 3. Color changes of **bipy-1** (5×10^{-5} M in DMSO) in the presence of Ni^{2+} ($NiCl_2$) counterion upon the addition of 2 eq of other metal (a) acetates and (b) fluorides (1.5×10^{-3} M in H_2O).

RESULTS AND DISCUSSIONS

Bipy-1 consists of an extended conjugation by means of a Schiff base at two ends of bipyridine ring, which can act as an excellent chromophore for specific metal acetate, fluoride, and anions interaction, showing output in the visible region. The metal acetate and fluoride binding of **bipy-1** was investigated through exposure to different aqueous metal acetates, fluorides, nitrates, and chlorides. Among the different metal salts, aqueous solution of Co$(OAc/F)_2$, Ni$(OAc/F)_2$, and Cu$(OAc/F)_2$ showed distinct color changes from fluorescent green to orange or pink (Figures 1(a)–1(b)). Whereas aqueous solution of other metal acetates/fluorides, other metal chloride and nitrate salt including Co, Ni, and Cu did not show any significant effect, even in the presence of excess quantities under aqueous and organic medium. However, in the presence of Co, Ni, and Cu chloride/nitrate, the addition of Co$(OAc/F)_2$, Ni$(OAc/F)_2$, and Cu$(OAc/F)_2$ produced a color change, fluorescent green to orange or pink. This finding implies that the formed *in situ* metal acetate/fluoride binding was successfully achieved by **bipy-1** without chloride and nitrate counteranion interference (Figures 2(a)–2(c)). In order to confirm the *in situ* metal acetate binding, a colorimetric titration was carried out with the addition of different metal acetate salts such as $Mn(OAc)_2$, $Co(OAc)_2$, $Cu(OAc)_2$, $Zn(OAc)_2$, Cd$(OAc)_2$, $Pb(OAc)_2$, Na(OAc), and TBAAc to the solution of **bipy-1: Ni^{2+}** complex. Similarly, CoF_2, CuF_2, NaF, and TBAF also used for the confirmation of *in situ* metal fluoride binding with **bipy-1**. In both cases, yellow color of the **bipy-1:Ni^{2+}** complex turned into pink or orange suggesting the peculiar binding of *in situ* metal acetate and fluoride (Figures 3(a)–3(b)). The colorimetric findings were further confirmed by spectroscopic methods.

For **bipy-1**, strong bands at 375 and 325 nm were observed, corresponding to the n–π^* and π–π^* transitions occurring within the molecule. No significant band was observed in the visible region for **bipy-1**. An addition of different metal acetate and fluoride solutions to **bipy-1**, Co$(OAc/F)_2$, Ni$(OAc/F)_2$, and Cu$(OAc/F)_2$ individually showed a readily apparent, characteristic band around 485–510 nm detailing the interaction with **bipy-1** through a charge or electron transfer process (Figures 4(a)–4(b)). For a complete understanding of the metal acetate binding of **bipy-1**, UV-vis titrations were carried out as incremental additions. Upon the addition of 0–2 eq of $Co(OAc)_2$, $Ni(OAc)_2$, and $Cu(OAc)_2$, a uniform formation of a new band at 487, 516 and 487 nm, respectively, was observed with a concomitant decrease in the bands at 375 and 325 nm (Figures 5(a)–5(c)).

To evaluate the counteranion, UV-vis titration was carried out with chloride and nitrate salts of Co, Ni, and Cu. No obvious changes in the absorption band of **bipy-1** were observed in the presence of Ni/$CoCl_2$ and Ni/$Co(NO_3)_2$; however, $CuCl_2$ and $Cu(NO_3)_2$ showed a reduction in the band at 375 nm (Figure 6). Similarly, the influence of the countercation was also evaluated in the presence of $NiCl_2$ with other metal

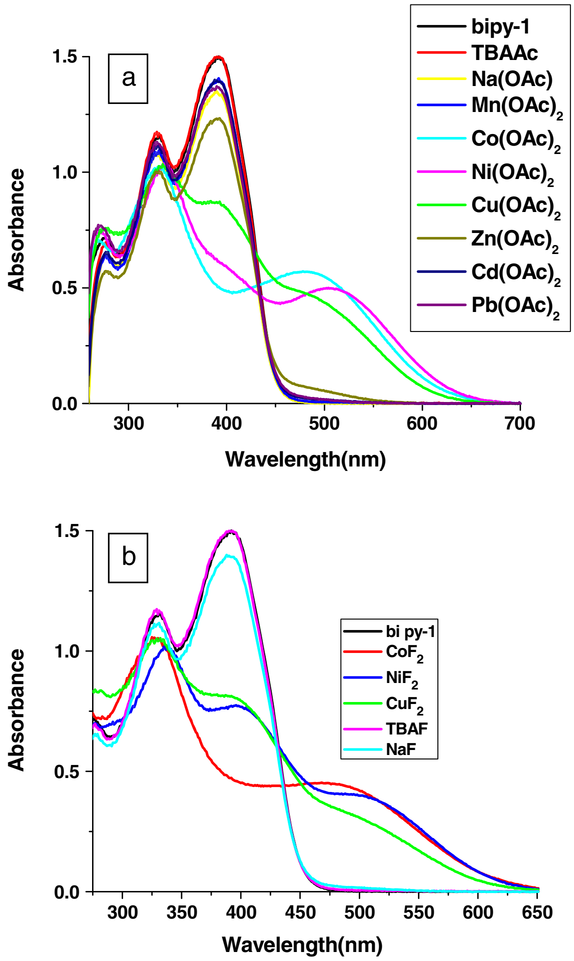

Figure 4. UV-vis changes observed upon the addition of 2 eq of various metal (a) acetates and (b) fluorides (1.5×10^{-3} M in H_2O) to **bipy-1** (5×10^{-5} M in DMSO).

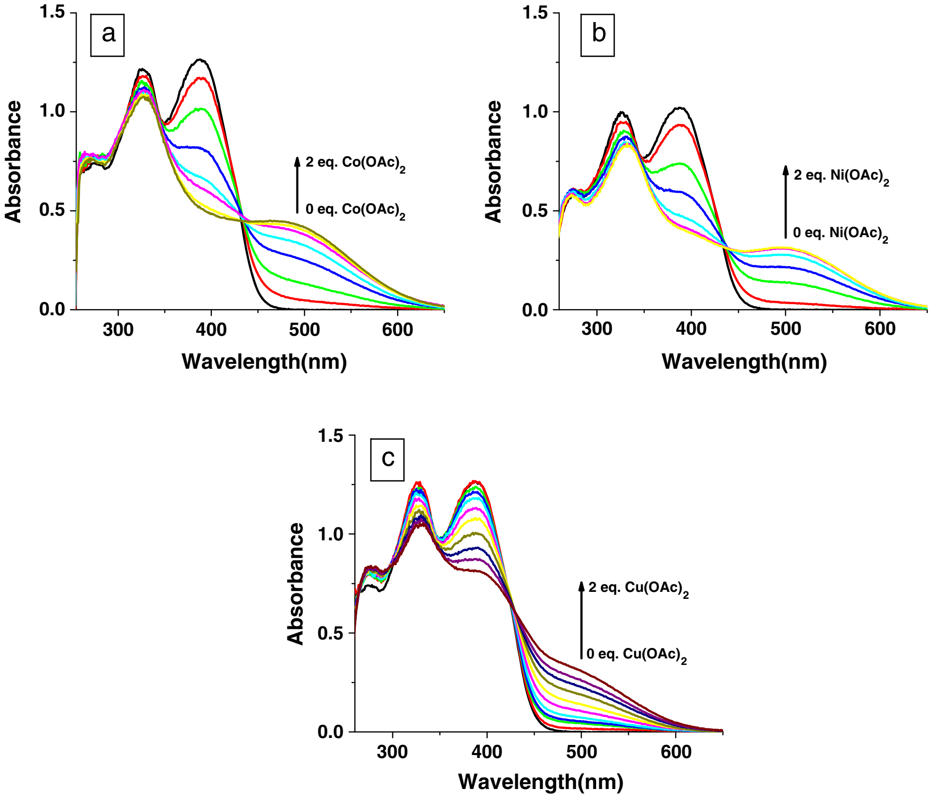

Figure 5. UV-vis changes observed upon the addition of 2 eq of (a) $Co(OAc)_2$, (b) $Ni(OAc)_2$, and (c) $Cu(OAc)_2$ (1.5×10^{-3} M in H_2O) to **bipy-1** (5×10^{-5} M in DMSO).

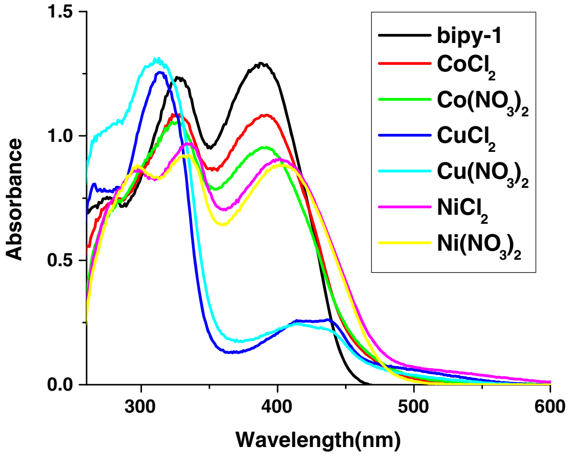

Figure 6. UV-vis changes observed upon the addition of 2 eq of various metal salts (1.5×10^{-3} M in H_2O) to **bipy-1** (5×10^{-5} M in DMSO).

acetates and fluorides; **bipy-1** responds with a band in the visible region, precisely matching the $Ni(OAc/F)_2$ complex of **bipy-1** without any countercation or anion interference (Figures 7(a)–7(b)). The same effect was reflected in the case of $Co/CuCl_2$ and $Ni/Co/Cu(NO_3)_2$. This type of metal acetate/fluoride binding even in the *in situ* form over other metal salts indicates that the structure of metal acetates/fluorides prefers to bind with the electron-rich **bipy-1**. In addition to the metal acetate/fluoride binding, **bipy-1** can selectively bind TBAF in DMSO

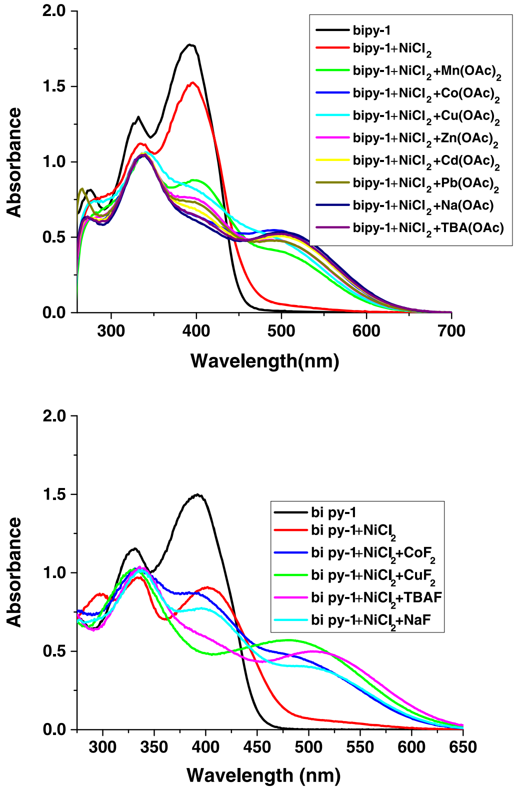

Figure 7. UV-vis changes of **bipy-1** (5×10^{-5} M in DMSO) in the presence of Ni^{2+} ($NiCl_2$) counterion upon the addition of 2 eq of different metal (a) acetates and (b) fluorides (1.5×10^{-3} M in H_2O).

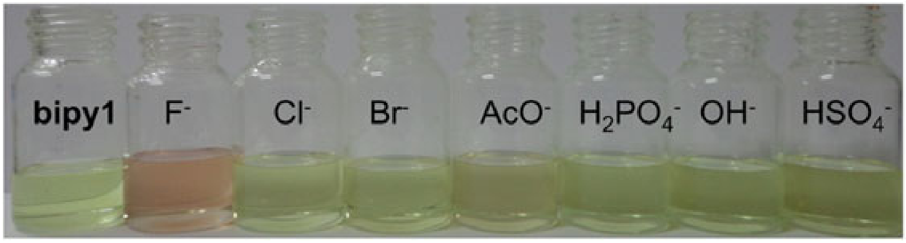

Figure 8. Color changes observed upon the addition of 2 eq of various TBA salt of anions (1.5×10^{-3} M in DMSO) to **bipy-1** (5×10^{-5} M in DMSO).

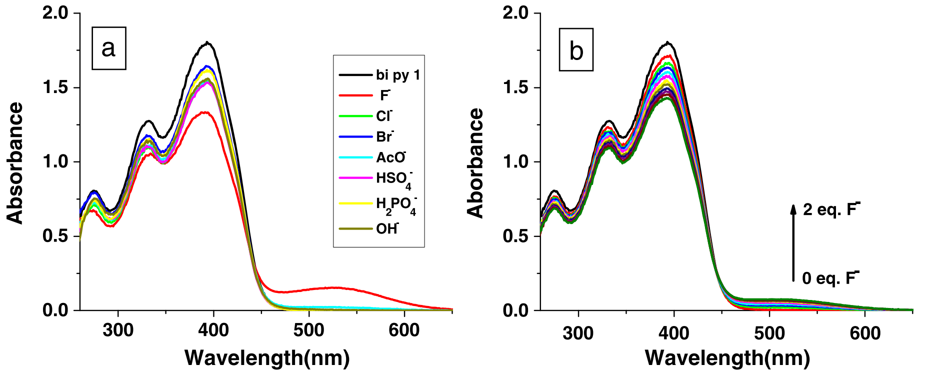

Figure 9. Absorption spectra upon the addition of (a) various TBA salt of anions (1.5×10^{-3} M) in DMSO to **bipy-1** (5×10^{-5} M) in DMSO and (b) 0–2 eq of TBA salt of F^- ion.

medium, as confirmed by the color changes from fluorescent green to light purple (Figure 8), causing the appearance of a band in the visible region around 529 nm. The remaining anions did not show any significant color or absorption changes (Figure 9(a)). To understand the uniform formation of the hydrogen-bond complex, UV-vis titration was carried out with incremental additions of F^- ions to the **bipy-1** solution (Figure 9 (b)). At the same time excluding TBAF, DMSO solution of any other metal acetates or fluorides including Co, Ni, and Cu shows no obvious colorimetric and UV-vis response. This result signifies that the **bipy-1** can be utilized for the detection of aqueous Co, Ni, and Cu acetates/fluorides and also the presence of aqueous medium with excellent binding.

^{1}H NMR is the powerful tool used for the further understanding of the TBA salt of F^- ion interaction with **bipy-1** in DMSO-d_6 medium. Three singlets at 9.26, 9.13, and 8.90 ppm suggest the presence of functional group in **bipy-1** as OH, CH=N (imine), and CH=N (pyridine ring), respectively. Also, the additional signal in the region at 6–8 ppm confirms the aromatic protons of **bipy-1**. Once TBAF was introduced into **bipy-1**, deprotonation of OH protons occurred even at 0.5 eq, which was confirmed by the disappearance of singlet at 9.26 ppm. Also, imine proton at 9.13 ppm was shifted into downfield region at 9.21–9.28 ppm upon the subsequent addition of TBAF. Simultaneously, the signal corresponds to the remaining aromatic protons that are shifted into upfield region upon the further addition of 0.5–2 eq of TBAF (Figure 10).

Absorption measurements also provide the binding constants and detection limit values for all guest–host complexes. Job's method was used to calculate the binding stoichiometry, and it reveals the formation of 2:1 complex of **bipy-1** with the specific metal acetates/fluorides, and 1:1 with TBAF is shown in Table 1. With the assistance of all findings from colorimetric, UV-vis, and ^{1}H NMR, the outcomes are summarized in Figure 11.

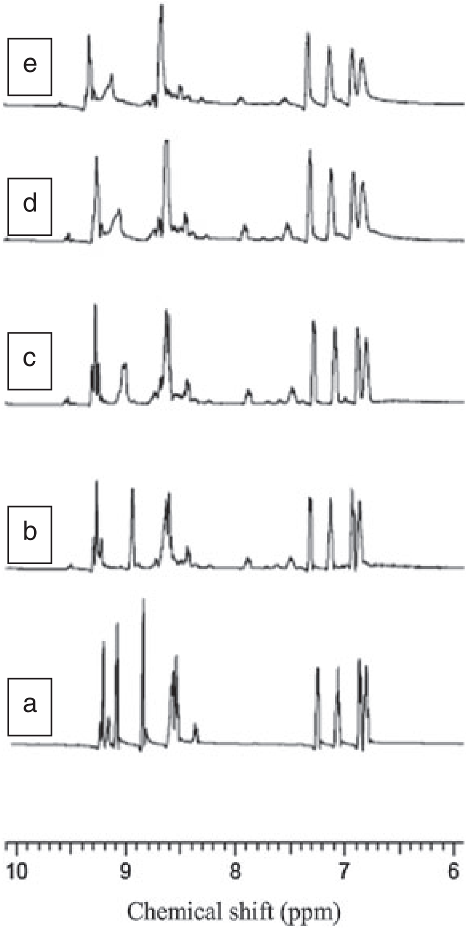

Figure 10. ^{1}H NMR spectra of **bipy-1** in DMSO-d_6 upon the gradual addition of TBA salt of F^- ion (a) 0, (b) 0.5, (c) 1, (d) 1.5, and (e) 2 eq.

Table 1. Data obtained from the UV-vis titration of **bipy-1** with the TBA salt of F⁻ ion, metal acetate, and fluorides

Analytes	Complex color and λ max (nm)	Isosbestic point (nm)	Binding constant (Ka)	Stoichiometry (M^{2+}: **bipy-1**)	Detection limit (μM)
$Co(OAc)_2$	Orange, 485	435	4.35×10^3	2:1	0.375
$Ni(OAc)_2$	Pink, 510	435	1.24×10^4	2:1	0.269
$Cu(OAc)_2$	Orange, 490	425	7.38×10^3	2:1	0.190
CoF_2	Orange, 485	435	1.02×10^4	2:1	0.681
NiF_2	Pink, 510	435	5.74×10^4	2:1	0.997
CuF_2	Orange, 490	425	3.74×10^4	2:1	0.492
TBAF	Purple, 529	443	2.47×10^3	1:1	0.2449

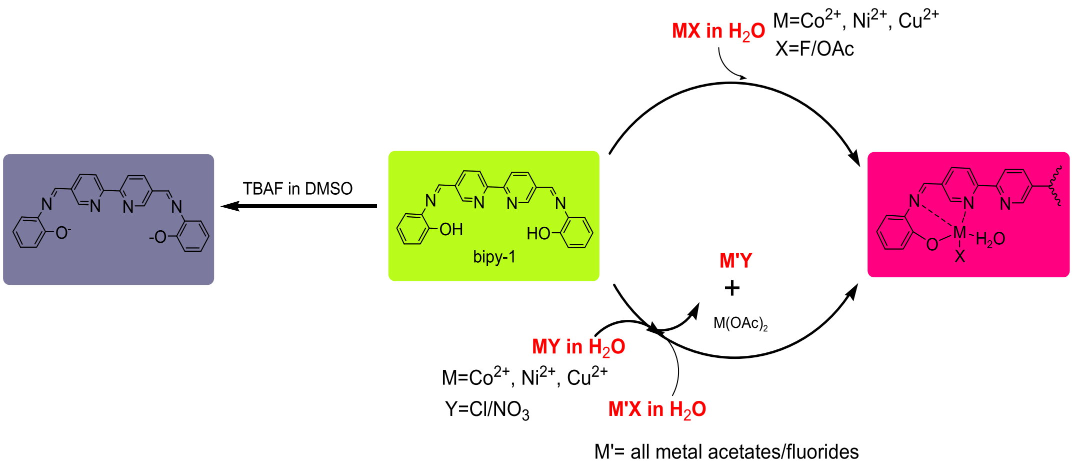

Figure 11. The proposed mechanism for the complex formed between **bipy-1** with original and *in situ* acetates/fluorides of different metals and TBA salt of F⁻ ion.

CONCLUSION

In summary, we demonstrated a new concept through bipyridyl-linked Schiff base **bipy-1** synthesis with utilization for the recognition of aqueous $Co(OAc/F)_2$, $Ni(OAc/F)_2$, and $Cu(OAc/F)_2$ over other acetates and fluorides as well as other metal salts. The effects of the counteranions of chlorides and nitrates of Co^{2+}, Ni^{2+}, and Cu^{2+} ions were also studied, with no significant responses observed. Simultaneously, the effect of countercations of Co^{2+}, Ni^{2+}, and Cu^{2+} was studied. The formed *in situ* complexes of $Co(OAc/F)_2$, $Ni(OAc/F)_2$, and $Cu(OAc/F)_2$ also showed excellent binding behavior with **bipy-1**. The selective sensing of TBAF was achieved by **bipy-1** in DMSO medium.

Acknowledgements

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REFERENCES

Aksuner N, Henden E, Yilmaz I, Cukurovali A. 2012. A novel optical chemical sensor for the determination of Nickel(II) based on fluorescence quenching of newly synthesized thiazolo-triazol derivative and application to real samples. *Sensor. Actuat B-Chem.* **166-167:** 269–274. DOI:10.1016/j.snb.2012.02.059.

Basa PN, Sykes AG. 2012. Differential Sensing of Zn(II) and Cu(II) via Two Independent Mechanisms. *J. Org. Chem.* **77**: 8428−8434. DOI: 10.1021/jo301193n.

Beer PD, Szemes F, Passaniti P, Maestri M. 2004. Luminescent ruthenium(II) bipyridine−calix[4]arene complexes as receptors for lanthanide cations. *Inorg. Chem.* **43:** 3965–3975. DOI: 10.1021/ic0499401.

Buryak A, Severin K. 2005. A chemosensor array for the colorimetric identification of 20 natural amino acids. *J. Am. Chem. Soc.* **127**: 3700–3701. DOI: 10.1021/ja042363v.

Ghosh T, Maiya BG, Samanta A. 2006. A colorimetric chemosensor for both fluoride and transition metal ions based on dipyrrolyl derivative. *Dalton Trans.* **35**: 795–801. DOI: 10.1039/B510469F.

Guo YY, Tang XL, Hou FP, Wu J, Dou W, Qin WW, Ru JX, Zhang GL, Liu WS, Yao XJ, 2013. A reversible fluorescent chemosensor for cyanide in 100% aqueous solution. *Sensor. Actuat B-Chem.* **181**: 202–208. DOI: 10.1016/j.snb.2013.01.053.

Hodacova J, Budesınsky M. 2007. New Synthetic Path to 2,2′-Bipyridine-5,5′-dicarbaldehyde and Its Use in the [3+3] Cyclocondensation with trans-1,2-Diaminocyclohexane. *Org. Lett.* **9:** 5641–5643. DOI: 10.1021/ol702612t.

Hu ZQ, Wang XM, Feng YC, Ding L, Li M, Lin CS. 2011. A novel colorimetric and fluorescent chemosensor for acetate ions in aqueous media based on a rhodamine 6G–phenylurea conjugate in the presence of Fe(III) ions. *Chem. Commun.* **47**: 1622–1624. DOI: 10.1039/C0CC04136J.

Hua S, Zhang S, Hua Y, Tao Q, Wu A. 2013 A new selective pyrazoline-based fluorescent chemosensor for Cu^{2+} in aqueous solution. *Dyes. Pigments.* **96:** 509–515. DOI: 10.1016/j.dyepig.2012.09.019

Jung HS, Kwon PS, Lee JW, Kim JI, Hong CS, Kim JW, Yan S, Lee JY, Lee JH, Joo T, Kim JS. 2009. Coumarin-derived Cu^{2+}- selective fluorescence sensor: synthesis, mechanisms, and applications in living cells. *J. Am. Chem. Soc.* **131**: 2008–2012. DOI: 10.1021/ja808611d.

Lin Q, Chen P, Liu J, Fu YP, Zhang YM, Wei TB. 2013. Colorimetric chemosensor and test kit for detection copper(II) cations in aqueous solution with specific selectivity and high sensitivity. *Dyes. Pigments.* **98:** 100–105. DOI: 10.1016/j.dyepig.2013.01.024.

Mahapatra AK, Hazra G, Roy J, Sahoo P. 2011. A simple coumarin-based colorimetric and ratiometric chemosensor for acetate and a selective fluorescence turn-on probe for iodide. *J. Lumin.* **131**: 1255–1259. DOI:10.1016/j.jlumin.2011.02.033.

Mahapatra AK, Roy J, Sahoo P, Mukhopadhyay SK, Chattopadhyay A. 2012. Carbazole–thiosemicarbazone–Hg(II) ensemble-based colorimetric and fluorescence turn-on toward iodide in aqueous media and its application in live cell imaging. *Org. Biomol. Chem.* **10**: 2231–2236. DOI: 10.1039/C2OB06792G.

Maity D, Govindaraju T. 2011. Highly selective colorimetric chemosensor for Co^{2+}. *Inorg. Chem.* **50**: 11282–11284. DOI: 10.1021/ic2015447.

Maity D, Govindaraju T. 2012. A differentially selective sensor with fluorescence turn-on response to Zn^{2+} and dual-mode ratiometric response to Al^{3+} in aqueous media. *Chem. Commun.* **48**: 1039–1041. DOI: 10.1039/C1CC16064H.

Martínez R, Espinosa A, Tárraga A, Molina P.′ 2008. Bis(indolyl)methane derivatives as highly selective colourimetric and ratiometric fluorescent molecular chemosensors for Cu^{2+} cations. *Tetrahedron* **64**: 2184–2191. DOI:10.1016/j.tet.2007.12.025.

Satriano C, Sfrazzetto GT, Amato ME, Ballistreri FP, Copani A, Giuffrida ML, Grasso G, Pappalardo A, Rizzarelli E, Tomaselli GA, Toscano RM. 2013. A ratiometric naphthalimide sensor for live cell imaging of copper(I). *Chem. Commun.* **49**: 5565–5567. DOI: 10.1039/C3CC42069H.

Song JY, Zo HJ, Velmathi S, Park JS. 2013. Highly selective response of bipyridyl-incorporated acetyelene dye for zinc acetate. *Talanta* **112**: 80–84. DOI: 10.1016/j.talanta.2013.03.063.

Suganya S, Udhayakumari D, Velmathi S. 2013. Heterocyclic thiosemicarbazones as fluorescent sensors for the selective recognition of cations in the aqueous phase. *Anal. Methods.* **5**:4179–4183. DOI: 10.1039/C3AY40381E.

Tang L, Cai M. 2012 A highly selective and sensitive fluorescent sensor for Cu^{2+} and its complex for successive sensing of cyanide via Cu^{2+} displacement approach. *Sensor. Actuat B-Chem.* **173**: 862–867. DOI: 10.1016/j.snb.2012.07.112.

Udhayakumari D, Suganya S, Velmathi S. 2013. Thiosemicabazone based fluorescent chemosensor for transition metal ions in aqueous medium. *J. Lumin.* **141**: 48–52. DOI: 10.1016/j.jlumin.2013.03.023.

Wang XL, Zheng WY, Liu GC, Lin HY. 2010. A turn-on fluorescent chemosensor for Hg^{2+} based on phenanthroline fluorophore. *J. Lumin.* **130**: 52–55. DOI:10.1016/j.jlumin.2009.07.018.

Wang L , Ye D, Cao D. 2012. A novel coumarin Schiff-base as a Ni(II) ion colorimetric sensor. *Spectrochim. Acta. Mol. Biomol. Spectrosc.* **90**: 40–44. DOI:10.1016/j.saa.2012.01.017.

Xue H, Tang XJ, Wu LZ, Zhang LP, Tung CH. 2005. Highly Selective Colorimetric and Electrochemical Pb^{2+} Detection Based on TTF-π-Pyridine Derivatives. *J. Org. Chem.* **70**: 9727–9734. DOI: 10.1021/jo051091r.

Zapata F, Caballero A, Espinosa A, Tárraga A, Molina P. 2009. Imidazole-annelated ferrocene derivatives as highly selective and sensitive multichannel chemical probes for Pb(II) cations. *J. Org. Chem.* **74**: 4787–4796. DOI: 10.1021/jo900533x.

Zhang YM, Lin Q, Wei TB, Wang DD, Yao H, Wang YL. 2009. Simple colorimetric sensors with high selectivity for acetate and chloride in aqueous solution. *Sensor. Actuat B-Chem.* **137**: 447–455. DOI:10.1016/j.snb.2009.01.015.

Zhen SJ, Guo FL, Chen LQ, Li YF, Zhang Q, Huang CZ. 2011. Visual detection of cobalt(II) ion in vitro and tissue with a new type of leaf-like molecular microcrystal. *Chem. Commun.* **47**: 2562–2564. DOI: 10.1039/C0CC03205K.

Zhou Y, Yoon J. 2012. Recent progress in fluorescent and colorimetric chemosensors for detection of amino acids. *Chem. Soc. Rev.* **41**: 52–67. DOI: 10.1039/C1CS15159B.

Zhou Y, Wang F, Kim Y, Kim SJ, Yoon J. 2009. Cu^{2+} selective ratiometric and "off-on" sensor based on the rhodamine derivative bearing pyrene group. *Org. Lett.* **11**: 4442–4445. DOI: 10.1021/ol901804n.