

Synthesis of Furo-fused BINOL derived 17-Crown-5 and its application as a cation Sensor

Sandeep B. Kotwal^{*a}

^aDepartment of Chemistry,

Smt. Chandibai Himathmal Mansukhani College, Ulhasnagar, Thane, Maharashtra, India 421003.

Abstract

Furo-fused BINOL derived 17-crown-5 was developed and was evaluated as a cation sensor. This crown exhibited good binding to Cu^{2+} ion. Selective "Turn-Off" type fluorescence changes were observed upon the addition of Cu^{2+} . The fluorescence intensity quenching was ascribed to the complex formation between furo-fused BINOL derived 17-Crown-5 and Cu^{2+} .

Keywords

Furo-fused BINOL, cation sensor, fluorescence, 17-crown-5, quenching.

1. INTRODUCTION

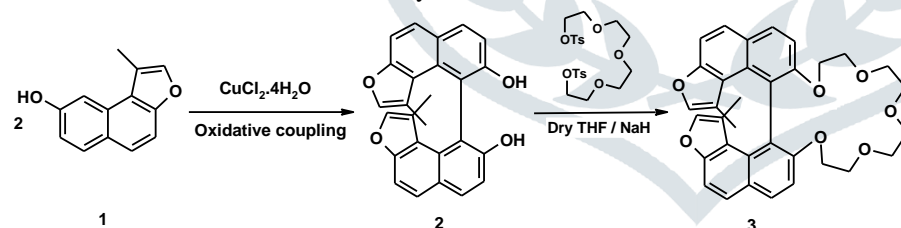
Ever since the chiral applications of BINOL was reported by Noyori¹, the chemist community has been consistently engaged in developing structural modification of the basic BINOL moiety in search of better applications². The chemical and stereochemical properties can be tailored by suitable placement of various groups at C-3, C-4, C-5, C-6, C-7 and C-8 positions of BINOL. In the recent past a new furo-fused BINOL was developed³. This molecule was found to exhibit good levels of chiral molecular recognition. Introduction of furan ring at 7, 8, 7', 8'-positions of BINOL was considered to be responsible for the significant molecular recognition achieved. The literature search indicated that the BINOLs based macromolecules have exhibited a great deal of promise as selective metal ions⁴ as well.

The development of fluorescence responsive sensors for various biologically and chemically important ions has seen a phenomenal growth in the past two to three decades⁵. Cu^{2+} is one of the heavy and soft metal ions which display considerable biological activity⁶. Cu^{2+} exhibits beneficial as well as toxic effects⁷. Designing an efficient chemosensor largely selective for copper is an important research goal from biological and environmental view point. An array of Cu^{2+} probes displaying either fluorescence 'on-off' or 'off-on' signaling modes have been preferred for sensitivity and experimental convenience. Numerous Cu^{2+} selective fluorescence sensors are available in the literature.⁸

The BINOL motif is endowed with a groove and electron rich aryl rings. New macrocycles, based on this unit, naturally could be expected to exhibit good levels of binding to cations. It was therefore of interest to carry out studies to find out whether such unit was capable of exhibiting selective binding to a particular metal cation. Due to the enormous significance of selective metal sensors, it was considered to evaluate the potential of the furo-fused BINOL derived crown as a selective metal sensor.

2. RESULT AND DISCUSSION

A furo-fused BINOL derivative was synthesized.⁹



Scheme-1

The two furo-naphto units were almost perpendicular to each other. The feature we were looking for as the much desired groove due to substantial dihedral angle.

The furo-fused derived 17-crown-5 (3) was obtained by reaction of 2 with tetra ethylene glycol ditosylate in presence of NaH and with high dilution protocol.

The furo-fused derived 17-crown-5 molecular framework thus offered a platform for metal ion coordination via its O-atoms. The fluorescence emission at 457 nm was relatively unaffected by pH values from 4 to 9. Thus, the compound furo-fused derived 17-crown-5 was found to be organic solvent-stable, pH-stable and therefore offered potentially useful chemosensor material. Fig. 1 shows the fluorescent spectra of host 3 in the presence of various metal ions Na^+ , Ba^{2+} , Hg^{2+} , Zn^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} and Pb^{2+} at 1:1 equivalent ratio.

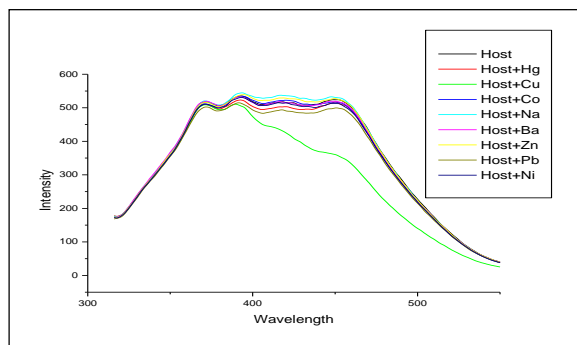


Fig. 1 Fluorescent spectra of **3** (5×10^{-5} M) in the presence of various metal ions (1mM) in acetonitrile

The concentration of **3** in acetonitrile was fixed at 5×10^{-5} M, and the final concentration of metal ions was fixed at 1×10^{-3} M. It was observed that Cu^{2+} lead to an efficient fluorescence quenching of **3**. The other metal ions such as Na^+ , Ba^{2+} , Hg^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} and Pb^{2+} displayed a slight fluorescence quenching of **3**. The fluorescence quenching of **3** in the presence of different metal ions can be ascribed to the existence of crown part as the furo-fused BINOL **2** did not exhibit any quenching with any of the above-mentioned metal ions.

The competition experiment was carried out by adding Cu^{2+} (1×10^{-3} M) to the acetonitrile solution of **3** (5×10^{-5} M) in the presence of another metal ion, shown in **Fig.2** For all measurements, the excitation wavelength was set at 306 nm and the emission was monitored at 457 nm.

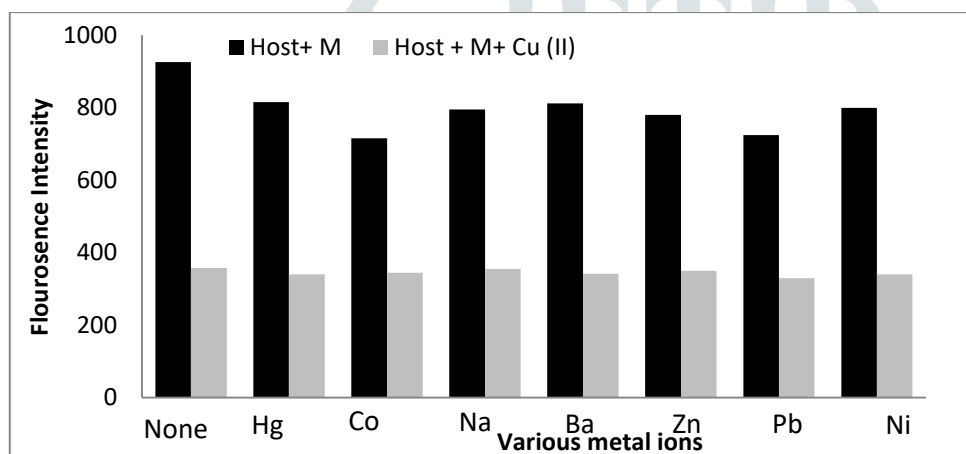


Fig. 2 Fluorescent response of **3** (5×10^{-5} M) with various metal ions. Dark bars represents complexation of **3** (5×10^{-5} M) with various metal ions (1 equiv), grey bars represent subsequent addition of Cu^{2+} (1 equiv) to the respective complexes.

With the help of aforementioned data, it could be concluded that **3** was a useful fluorogenic sensing material for detection of Cu^{2+} ions.

To study the quenching behavior of Cu^{2+} ion in details, we investigated the decrease in fluorescence intensity upon successive addition of aliquots of Cu^{2+} (1×10^{-3} M) in Acetonitrile to **3** (5×10^{-5} M) solutions in acetonitrile. As shown in **Figure 3** quenching of photoluminescence was observed at a moderate level of Cu^{2+} , and the fluorescent intensity decreased upon the increase in the concentration of Cu^{2+} .

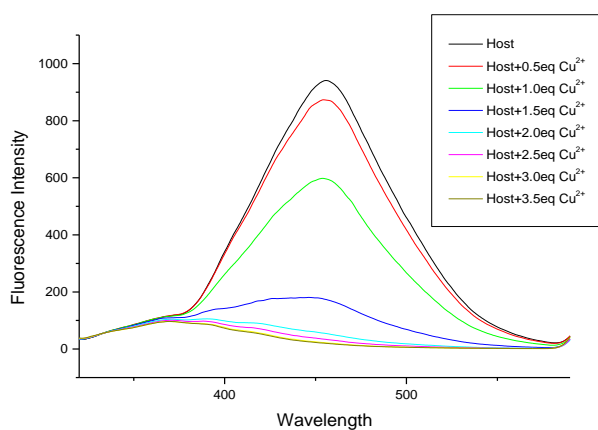


Fig.3 Fluorimetric titration of **3** (5×10^{-5} M) with Cu^{2+} (1×10^{-3} M) in acetonitrile (2.5×10^{-5} to 17.5×10^{-5} M) at 306 nm.

Initially we used 1equivalent Cu^{2+} ions solution ($1 \times 10^{-3}\text{M}$) that caused 7% quenching of fluorescence emission of **3**. When the equivalence of Cu^{2+} increases up to 3.5 ($1 \times 10^{-3}\text{M}$) almost no luminescence was observed. Thus **3** is a good “turn-off” type Cu^{2+} -induced fluorescence quencher. The Job’s plot analysis shows formation of 1:1 complex between **3** and Cu^{2+} in Figure 4.

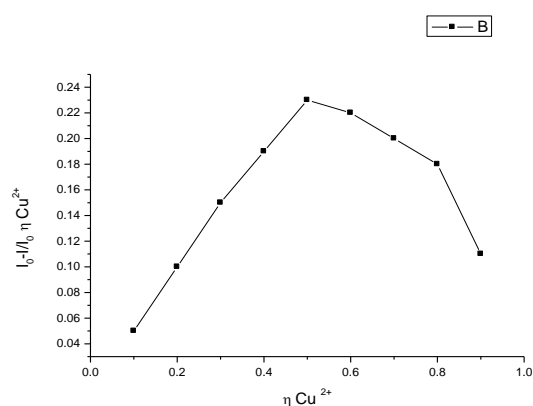


Fig.4 Job’s Plot analysis of **3** ($5 \times 10^{-5}\text{M}$) with Cu^{2+}

The quenching efficiency is related to the Stern-volmer constant, K_{sv} , and is determined by monitoring measurable changes in the fluorescence via Stern-volmer plot of **3** with Cu^{2+} . A reasonably good binding and selectivity was observed, as indicated by $K_{sv} = 5.9 \times 10^6 \text{M}^{-1}$ Figure 5.

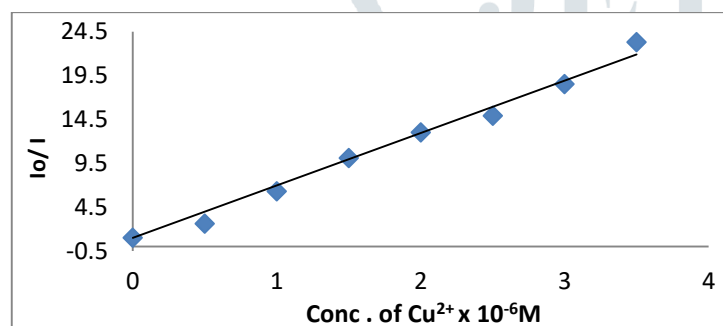


Fig.5 Stern-volmer plot **3** ($5 \times 10^{-5}\text{M}$) with Cu^{2+}

From the spectrophotometric titrations we calculated the detection limit of Cu^{2+} to be $1.7 \times 10^{-7}\text{M}$, which was comparable with the values reported for several Cu^{2+} selective sensors.

3.MATERIALS AND METHODS:

Spectral grade solvents were purchased from S. D. fine Chemicals (India) and used as received. UV-Vis. spectra were recorded using SHIMADZU UV-Vis. recording spectrophotometer, model no. UV-2401PC. Fluorescence studies were carried out using Perkin-Elmer LS-55 Spectrofluorophotometer. The slit width was set at 2 nm for both excitation and emission and the PMT detector voltage was 700 V. IR spectra were recorded on PERKIN ELMER FTIR Spectrometer and ^1H NMR spectra were recorded on 300 MHz Bruker, AV II 300 of 300 MHz, using TMS as internal standard. Chemical shifts were given in ppm relative to internal reference for CDCl_3 ^{13}C NMR spectra were recorded on 75 MHz Bruker, AV II 300 spectrometer. GC-MS spectrum were recorded on Thermo Finnigan LCQ DECA XP (Ion Trap). Reagents were of AR grade and used with out further purification. Column chromatography was performed on silica gel 60-120 mesh. Melting points reported are uncorrected.

4. EXPERIMENTAL SECTION

Synthesis of furo-fused-BINOL derived 17-crown-5 (**3**)

In a 100 mL three-necked round bottomed flask fitted with a reflux condenser alongwith a calcium chloride guard tube and N_2 inlet was taken dry THF (30 mL). Then sodium hydride (0.004 g, 0.174 mmol) was added. To the refluxing solution was added slowly in 1 h, a 1:1 mixture of furo-fused BINOL (**2**). (0.1 g, 0.349 mmol) and tetraethylene ditosylate (0.175 g, 0.349mmol) in dry THF (30 mL). After complete addition, the mixture was further refluxed for 4 h (monitored by TLC), and finally, the THF was concentrated under reduced pressure and the oily residue obtained was added to 100 g of ice. The solid was separated and was filtered, dried, and purified by column chromatography using petroleum ether and ethyl acetate (60:40) as eluents to afford a white solid (**3**) (0.07 g, 0.126 mmol, 50%).

FTIR (KBr): 2907, 1742, 1617, 1529, 1450, 1418, 1371, 1219, 1062 cm^{-1} .

^1H NMR (300MHz, CDCl_3) δ : 2.44 (s,3H; CH_3), 3.53-3.66 (m,4H,2 CH_2), 3.66-3.69 (m,4H, 2 CH_2), 7.04-7.07 (d,1H,ArH, $J=8.7\text{Hz}$), 7.46-7.49 (d,1H,ArH, $J=9.0\text{Hz}$), 7.52 (s,1H,ArH), 7.60-7.63 (d,1H,ArH, $J=9.0\text{Hz}$), 7.84-7.87 (d,1H,ArH, $J=9.0\text{Hz}$)

^{13}C NMR (75 MHz, CDCl_3) δ : 11.14, 68.67,69.25, 70.53, 70.71,

106.25,109.54,110.44,115.13,117.41,121.07,125.22,125.74,130.30,130.78,140.73,153.84.

ESI MS :m/z:[M] $^+$ 552.

5. CONCLUSION

In summary, we have described a new TURN-OFF fluorogenic probe for copper(II) cation in acetonitrile.

REFERENCES:

- [1] (a) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R., Synthesis of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), an atropisomeric chiral bis(triaryl)phosphine, and its use in the rhodium(I)-catalyzed asymmetric hydrogenation of α -(acylamino)acrylic acids, *J. Am. Chem. Soc.* 102 (1980) 7932-7934.
 (b) Yamakawa, M.; Noyori, R., An Ab Initio Molecular Orbital Study on the Amino Alcohol-Promoted Reaction of Dialkylzincs and Aldehydes, *J. Am. Chem. Soc.* 117 (1995) 6327.
 (c) Noyori, R.; Kitamura, M., Enantioselective addition of organometallic reagents to carbonyl compounds: chirality transfer, multiplication and amplification, *Angew. Chem., Int. Ed. Engl.* 30(1991) 49.
- [2] (a) Nishizawa, M.; Yamada, M.; Noyori, R., Highly enantioselective reduction of alkynyl ketones by a binaphthol-modified aluminum hydride reagent. Asymmetric synthesis of some insect pheromones, *Tetrahedron Lett.* 22 (1981) 247.
 (b) Hutchins, R. O.; Abdel-Magid, A.; Stercho, Y. P.; Wambsgans, A., Asymmetric reduction of phosphinyl imines with hydride reagents. Enantioselective synthesis of chiral primary amines, *J. Org. Chem.* 52(1987) 702.
 (c) Bougauchi, M.; Watanabe, S.; Arai, T.; Sasai, H.; Shibasaki, M., Catalytic Asymmetric Epoxidation of α,β -Unsaturated Ketones Promoted by Lanthanoid Complexes *J. Am. Chem. Soc.* 119(1997) 2329.
- [3] (a) Anil V. Karnik, Sunil P. Upadhyay and Manish G. Gangrade, [9,9']Bi[naphtho(2,1-*b*)furanyl]-8,8'-diol, a furo-fused BINOL derivative: synthesis, resolution and determination of absolute configuration, *Tetrahedron: Asymmetry*, 17(2006) 1275-1280.
 (b) Sunil P. Upadhyay, Raghuvir R. S. Pissurlenkar, Evans C. Coutinho, and Anil V. Karnik*, Furo-Fused BINOL Based Crown as a Fluorescent Chiral Sensor for Enantioselective Recognition of Phenylethylamine and Ethyl Ester of Valine, *J. Org. Chem.*, 72(2007)5709-5714.
- [4] (a) Lin Pu *Acc. Chem. Res.*, Enantioselective Fluorescent Sensors: A Tale of BINOL, 45(2012) 150–163 .
 (b) Xia Yang, Xuechao Liu, Kang Shen, Chengjian Zhu, and Yixiang, A Chiral Perazamacrocyclic Fluorescent Sensor for Cascade Recognition of Cu(II) and the Unmodified α -Amino Acids in Protic Solutions, *Cheng Org. Lett.*, 13(2011) 3510–3513.
 (c) Ji-Ting Hou, Qin-Fang Zhang, Bang-Yu Xu, Qiao-Sen Lu, Qiang Liu, Ji Zhang, Xiao-Qi Yu, A novel BINOL-based cyclophane via click chemistry: synthesis and its applications for sensing silver ions, *Tetrahedron Letters*, Volume 52, Issue 38, 21 September 2011, Pages 4927-4930
 (d) Tian-Hua Ma, Ai-Jiang Zhang, Ming Dong, Yu-Man Dong, Yu Peng, Ya-Wen Wang, A simply and highly selective “turn-on” type fluorescent chemosensor for Hg²⁺ + based on chiral BINOL-Schiff’s base ligand, *Journal of Luminescence*, 130(2010) 888-892.
- [5] (a) H.N. Kim, M.H. Lee, H.J. Kim, J.S. Kim, J. Yoon, A new trend in rhodamine-based chemosensors: application of spiro lactam ring-opening to sensing ions, *Chem. Soc. Rev.* 37 (2008) 1465.
 (b) D.T. Quang, J.S. Kim, Fluoro- and Chromogenic Chemodosimeters for Heavy Metal Ion Detection in Solution and Biospecimens *Chem. Rev.* 110 (2010) 6280.
 (c) A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Signaling Recognition Events with Fluorescent Sensors and Switches, *Chem. Rev.* 97 (1997) 1515.
 (d) J.F. Zhang, Y. Zhou, J. Yoon, J.S. Kim, Recent progress in fluorescent and colorimetric chemosensors for detection of precious metal ions (silver, gold and platinum ions), *Chem. Soc. Rev.* 40 (2011) 3416.
- [6] Koval, I. A.; Gamez, P.; Belle, C.; Selmechi, K.; Reedijk, Synthetic models of the active site of catechol oxidase: mechanistic studies *J. Chem. Soc. Rev.* 35(2006) 814.
- [7] (a) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E., Signaling Recognition Events with Fluorescent Sensors and Switches, *Chem. Rev.* 97(1997) 1515-1566.
 (b) Amendola, V.; Fabbrizzi, L.; Foti, F.; Licchelli, M.; Mangano, C.; Pallavicini, P.; Poggi, A.; Sacchi, D.; Taglietti, A., Light-emitting molecular devices based on transition metals *Coord. Chem. Rev.* 250(2006) 273-299.
- [8] (a) Singhal, N. K.; Ramanujam, B.; Mariappanadar, V.; Rao, C. P., Carbohydrate-Based Switch-On Molecular Sensor for Cu(II) in Buffer: Absorption and Fluorescence Study of the Selective Recognition of Cu(II) Ions by Galactosyl Derivatives in HEPES Buffer *Org. Lett.* 8(2006) 3525-3528.
 (b) Qi, X.; Jun, E. J.; Xu, L.; Kim, S.-J.; Joong Hong, J. S.; Yoon, Y. J.; Yoon, J. J. *Org. Chem.* 71(2006) 2881-2884.
 (c) Xu, Z.; Xiao, Y.; Qian, X.; Cui, J.; Cui, D., Ratiometric and Selective Fluorescent Sensor for Cu(II) Based on Internal Charge Transfer (ICT), *Org. Lett.* 7(2005) 889-892.
 (d) Park, S. M.; Kim, M. H.; Choe, J.-I.; No, K. T.; Chang, S.-K., Cyclams Bearing Diametrically Disubstituted Pyrenes as Cu²⁺- and Hg²⁺-Selective Fluoroionophores, *J. Org. Chem.* 72(2007) 3550-3553.
 (e) Xiang, Y.; Tong, A.; Jin, P.; Ju, Y., New Fluorescent Rhodamine Hydrazone Chemosensor for Cu(II) with High Selectivity and Sensitivity, *Org. Lett.* 8(2006) 2863-2866.
 (f) Zhang, X.; Shiraiishi, Y.; Hirai, T., Cu(II)-Selective Green Fluorescence of a Rhodamine-Diacetic Acid Conjugate, *Org. Lett.* 9(2007) 5039-5042.
- [9] Sandeep B Kotwal, Anita D Pandey, Vaibhav N Khose Anil V Karnik, A convenient route to enantiomerically enriched furo-fused BINOL derivative, *Indian Journal of Chemistry*, 54(2015) 940-943.