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SYNTHESIS OF NOVEL BISPHENOL-BIPHENANTHROLINE-BASED MOLECULAR TWEEZERS

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Abstract

*A molecular "dugdugi" **8** derived from 1,10-phenanthroline was synthesized and characterized by using NMR, EIMS and UV studies. Bisphenol was alkylated with 1,3-dibromopropane and reacted with 4-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenol to obtain **8**. 30* $\mu molL^{-1}$ *solution of **8** was prepared in 10 % DMF in ethanol and was stirred for 30 min with 30* μL^{-1} *ethanolic solutions of* Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Ag^{+}, *and* Zn^{2+}, *all nitrates. Chemosensor **8** switched-on in the presence of* Fe^{3+} *by showing pink color while it remained turn-off in the presence of other metals. The UV spectra of the molecular "dugdugi" showed a peak at 279 nm which shifted to 290 nm after interacting with* Fe^{3+}*. A new peak also appeared at 524 nm.*

Keywords: Fe^{3+} chemosensor, imidazole, naked-eye chemosensors, molecular switch

MOLEKÜLER CIMBIZLAMAYA DAYALI YENİ BİR BISFENOL-BIPHENANTHROLINE SENTEZİ

ÖZET

1,10-fenantrolin'den elde edilen "dugdugi" 8 molekülü sentezlendi ve NMR, EIMS ve UV kullanılarak yapısı aydınlatıldı. Bisfenol 8'I elde etmek için 1,3-dibrompropan kullanılarak alkillendi ve 4-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenol ile reaksiyona sokuldu. Molekül 8'in 30 $\mu molL^{-1}$ *çözeltisi %10 DMF içeren etanolde hazırlandı, ve etanol ile hazırlanmış 30 m* L^{-1} Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Ag^{+}, *bir and* Zn^{2+} *çözeltisi ile 30 dakika karıştırıldı.Kemosensör 8,* Fe^{3+} *varlığında pembe renk vererek çalışırken, diğer metallerin varlığında ayırt edici bir renk gözlenmedi. "Dugdugi" nin moleküler UV spektrumunda 279 nm'de bulunan pik* Fe^{3+} *ile etkileştirilince 290 nm'ye kaydı. Ayrıca, 524 nm'de yeni bir pik oluştuğu görüldü.*

Anahtar Kelimeler: Fe^{3+} Kemosensör, İmidazol, Çıplak Gözle Kemosensör, Moleküler Anahtar

1 Introduction

Chemosensors and switches are promising candidates for the realization of innovative materials for information technology.[1] Molecular sensors[2-4] can sense metal cations,[5-7] anions,[8-10] amino acids[11] pesticides,[12, 13] proteins[14] etc. Schiff bases are reported as high sensitive and reversible chemosensor for gas phase HCl.[15] Metal pollution is of great concern due to their toxicity.[16] Development of suitable probes for sensing metal ion induced changes has assumed greater significance. Number of chemosensors have been reported for Zn^{2+},[17-19] Cd^{2+},[17, 18] Cu^{2+},[18] Ag,[20, 21] Hg^{2+},[20, 22] Mg^{2+},[23] Cr^{3+},[24]Cr^{4+},[25] Pb^{2+},[26] Al^{3+},[27] etc. Simplest form of metal detection is based on color change - also called naked-eye detection.[28-30] Despite the extensive work on chemosensors, fewer chemosensors for Fe^{3+} are reported.[31-33] Extensive efforts are going on to develop sensitive and selective Fe^{3+} chemosensors. [34-38] Fluorescence spectrometry is a sensitive technique for detection of metals having lower concentrations. However, due to its paramagnetic nature, fluorescent detection of Fe^{3+} is marred by quenching.

Colorimetric sensors [39, 40] containing combination of a receptor and a chromophore are more promising, requires less labor and inexpensive equipment than closely related fluorescent sensors. Up to now, a number of naked-eye sensors for transition metal ions have been reported [41, 42] but surprisingly, the reported Fe^{3+} selective fluorescent sensors are relatively rare despite the widespread applications of Fe^{3+}.[43]

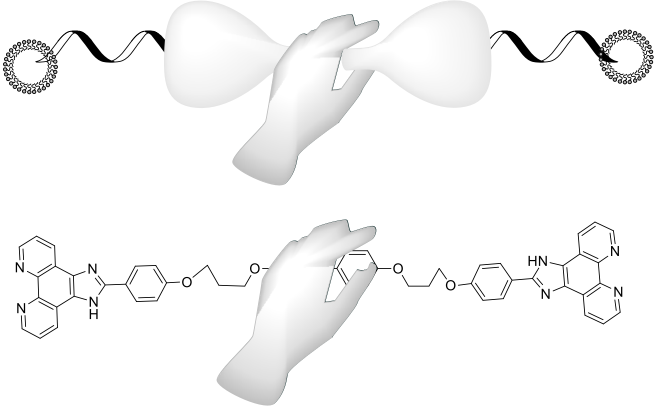


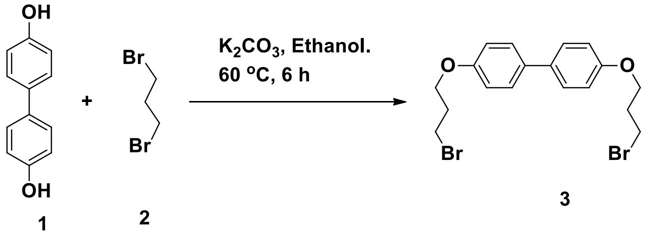
Figure 1. Monkey's drum (dugdugi) above and molecular dugdugi below

A molecular "dugdugi" is a molecule that is similar to the "dugdugi" of a monkey-charmer – also called monkey's drum. Dugdugi (Urdu language) has two goatskin drumheads that are tensioned with a threaded length of string, such that its pitch may be raised by squeezing the bunched strings at the dugdugi's waist.[44] A monkey charmer plays the drum by right-left movement. Our synthesized molecule is symmetrical and can be divided in two equal halves if cut from the middle – same as a "dugdugi" (Figure 1). Herein we report the synthesis of a naked-eye chemosensor for Fe^{3+} with efficient detection limit of up to >1 μmol L^{-1} concentrations. Nitrates of Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Ag^{+}, and Zn^{2+} were mixed with chemosensor **8**. The solution containing Fe^{3+} turned pink while other metals did not show any color change to naked eye. The same behavior was also observed in the UV-visible spectrum. The Fe^{3+} sensing properties were tested in 10 % DMF in ethanol with a concentration of 30 μmol L^{-1}.

2 Result and Discussion

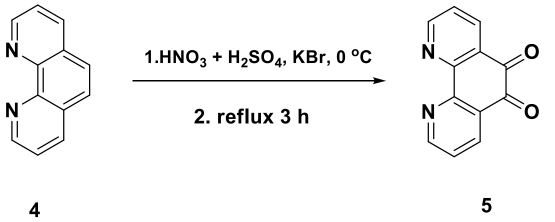
2.1 Synthesis

Our target flouregenic chemo-sensor **8** was synthesized in four steps. The first step was to elaborate flexible alkyl chain to the starting bisphenol **1.** The dialkylation of bisphenol **1** was carried out with the help of 1,3-dibromopropane **2**. The bisphenol was stirred with potassium carbonate at 50 °C (Scheme 1) which gave a greenish solution of the bisphenoxide ions. The reaction temperature was increased to 60 °C and excess of 1,3-dibromopropane was added. Excess of dibromopropane avoided the formation of undesired cyclophanes and bromsubstituted alkylated bisphenol **3** was obtained in excellent yield.



Scheme 1. Alkylation of bisphenol

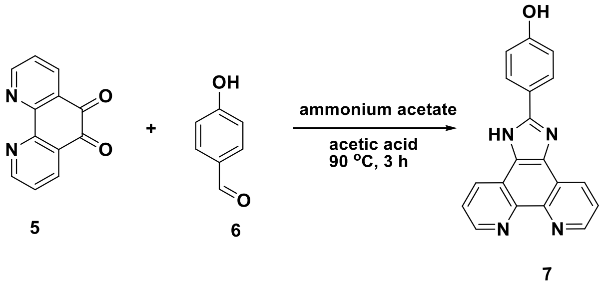
After having the flexible dialkylated bisphnol **3** in hand, our next requirement for the synthesis of target fluorescent compound **8** was to synthesize such a precursor which is flouregenic and must contain the functional group to substitute the bromines of **3** and to achieve the desired chemosensor molecule **8**. For this purpose compound **7** was chosen as a flouregenic precursor for the chemosensor **8**.



Scheme 2. Oxidation of 1,10-phenanthroline

Hydroxy-derivative of 1,10-phenanthroline **7** was synthesized according to literature procedure [45]. 1,10-Phenonthroline **4** was first oxidized to 1,10-phenanthroline-5,6-dione **5**. Phenanthroline **4** and KBr were taken in an ice cold flask. 10 mL of concentrated H_2SO_4 and 5 mL HNO_3 were added slowly with stirring at 0 °C and refluxed for 3h (Scheme 2). The color of mixture was changed to yellow and was poured into 500 mL of ice water and sodium hydroxide was added slowly to make the pH 4. The aqueous phase was extracted three times with dichloromethane and dried over Na_2SO_4. The solvent was evaporated under vacuum and required dione **5** was obtained with 96 % yield. The product was crystallized out from ethanol.

1,10-phenanthroline-5,6-dione **5** and 4-hydroxybenzaldehyde **6** were dissolved in glacial acetic acid. After stirring for 5 minutes at room temperature, ammonium acetate was added. Temperature was increased to 100 °C and then stirred at this temperature for three hours (Scheme 3). After the desired time, the mixture was poured in 50 mL of ice cold water and neutralized with ammonium hydroxide solution. Kept in freezer at -20 °C for overnight and then filtered, washed with water and then acetone successively. Our required product **7** was obtained as yellow powder in 65 % yield. The compound was dried under vacuum at 50 °C for 24 h.



Scheme 3. Synthesis of phen-imidazole

The highly fluorescent precursor **7** was then subjected to the last step of our target synthesis; it was dissolved in DMF and was added K_2CO_3 to stirrer for 40 min at 60 °C. Now the bromosubstituted dialkylated bisphenol **3** was added into the reaction mixture and the temperature was increased to 80 °C (Scheme 4). After 3 h TLC showed the completion of reaction and formation of highly polar product. The hot reaction mixture was poured in the ice water which gave yellow ppts which was washed with brine, ethanol and finally with acetone. The ppt was then dried under vaccum for 24 h and was characterized by NMR, EI-MS and ESI-MS as our required fluorogenic chemosensor **8.** Figure 3 shows the ^{1}HNMR spectra of compound **8**.

2.2 UV studies

The UV spectrum of molecular "dugdugi" **8** was obtained in 10 % DMF in ethanol with concentration of 30 μmol L^{-1}. The compound showed λ_{max} at 279 nm and no peak was observed in the range of 800 to 350 nm.

The molecular "dugdugi" was screened with different metals i.e. Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Ag^{+}, and Zn^{2+} through UV-visible spectroscopy for their sensing properties for these metals. Compound **8** was mixed in 1:1 ration with the stated metals with concentration of 30 μM and stirred in a 10 mL conical flask for 30 minutes. The flask having Fe^{3+} showed pinkish color while the solutions containing other metals did not show any color (Figure 2).

All these metals solutions were subjected for UV-visible studies. The spectrum of the solution containing Fe^{3+} showed a peak at 524 nm while the molecular "dugdugi" with other metals did not show a peak in that region as shown in figure 4.

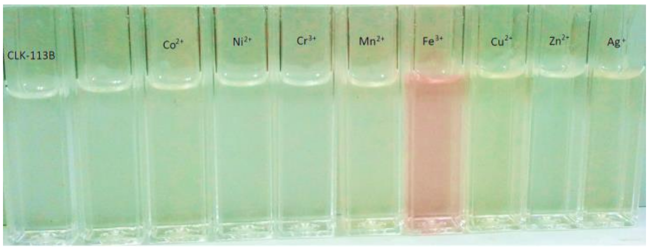
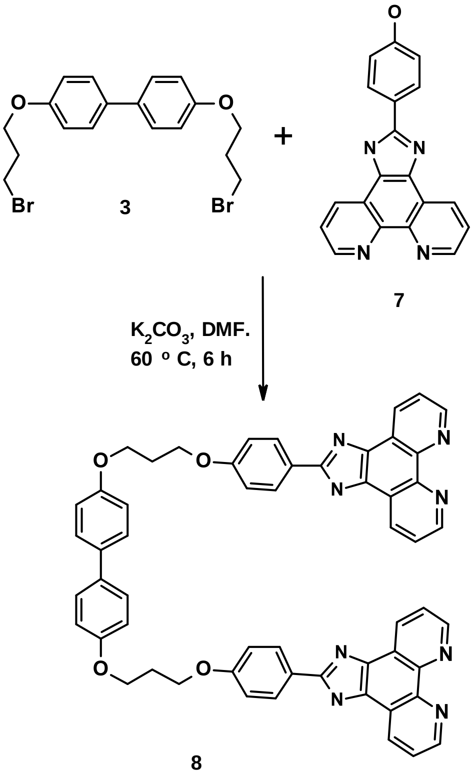


Figure 2. Naked-eye Chemosensing studies of compound 8



Scheme 4. Synthesis of Molecular "Dugdugi"

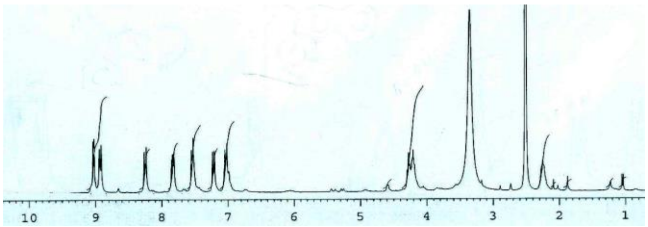


Figure 3: HNMR spectra of compound **8**

Also the λ$_{max}$ of the "dugdugi" which was observed at 279 nm was shifted to 290 nm after interacting with Fe^{3+}. Figure 5 shows a 3D optimized structure of chemosensor 8 hosting Fe^{3+}.

3 Experimental

3.1 Preparation of solutions

Stock solutions of 1 mM of nitrates of Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Ag^{+}, and Zn^{2+} were prepared in ethanol. For analytical study, 30 μM solutions were prepared by dilution with 10 % of DMF in ethanol. Stock solution of compound **8** was also prepared in 10 % DMF in ethanol with concentration of 1 mM which was diluted to 30 μM by 10 % DMF in ethanol for analytical studies.

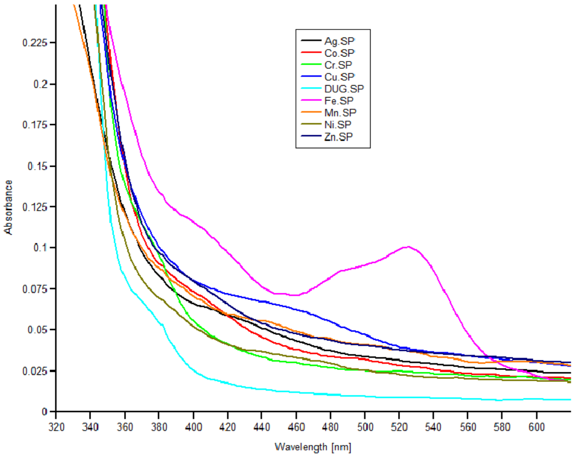


Figure 4: UV spectra of molecular "dugdugi" in the presence of different metals

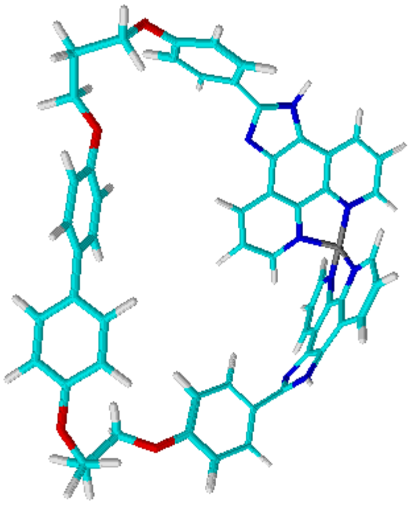


Figure 5: 3D optimized structure of molecular "dugdugi" hosting Fe^{3+}

3.2 UV-visible studies

UV-Visible spectra were obtained by using Perkin-Elmer's LAMBDA 35 UV/Vis Systems spectrophotometer in the range of 800-200 nm. 30 μM of chemosensor **8** was stirred with different metals (30 μM) for 30 min followed by UV-visible analysis.

3.3 Synthesis

3.3.1 4,4'-bis(3-bromopropoxy)-1,1'-biphenyl (3)

500 mg (2.69 mmol) of 4,4'-bisphenol **1** was taken in 50 mL round bottom flask in 30 mL acetone. 1.1 g (8.09 mmol) of K_2CO_3 was added and stirred for 40 minutes at 40^{0}C. 1,3-dibromopropane **2** was added in excess and then reaction mixture was stirred at 60 ^{0}C for 4 h. Solvent was evaporated and the crude product was extracted in triplicate with dichloromethane from aqueous phase. The organic phase was dried with $MgSO_4$ and purified on column chromatography by using silica get as stationary phase and 20 % ethyl acetate in hexane as eluent. The compound was obtained as colorless flat crystals which were submitted for XRD studies. EIMS m/e: 428.1; ^{1}HNMR 300 MHz $CDCl_3$δ: 7.46 (d, 4H, 3*J* = 8.7 Hz), 6.94 (d, 4H, 3*J* = 8.7 Hz), 4.13 (t, 4H, J = 6 Hz, $-CH_2-$), 3.61 (t, 4H, J = 6.3 Hz), 2.32 (pent, 4H, J = 6.3 Hz).

3.3.2 1,10-phenanthroline-5,6-dione (5):

1 g (5.5 mmol) of 1,10-phenanthroline and 1 g (8.4 mmol) of KBr were taken in an ice cold flask. 10 mL of concentrated H_2SO_4 and 5 mL HNO_3 were added slowly with stirring at 0 ^{o}C. The mixture was then refluxed for 3h. The color of mixture changed to yellow and was poured into 500 mL of ice water and sodium hydroxide was added slowly to make the pH 4. The aqueous phase was extracted three times with DCM and dried with Na_2SO_4. The solvent was evaporated under vacuum and 1.5 g of target compound was obtained with 96 % yield. The product was crystallized out from ethanol. M. p. 247–248 °C; EIMS *m/z*: 212 (M+2); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.12 (dd, 2H, 4*J* = 1.8 Hz, 3*J* = 4.8 Hz), 8.51 (dd, 2H, 3*J* = 7.8, 4*J* = 1.5 Hz), 7.69 (dd, 2H, 3*J* = 4.8, 4.8 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 178.7, 156.4, 152.9, 137.3, 129.7, 128.1, 125.6.

3.3.3 4-(1*H*-Imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)benzaldehyde (7):

201 mg (1.5 mmol) terephthalic aldehyde, 315 mg (1.5 mmol) of 1,10-phen-5,6-dione and 2.31 g (30 mmol) of ammonium acetate were taken in a 50 mL round bottom flask. 30 mL of glacial acetic acid was added slowly and refluxed for about 2 h. The reaction mixture was cooled to room temperature and 60 mL of distilled water was added. Ammonium hydroxide solution was added dropwise until pH 7. Yellow precipitate were formed which were collected and washed with water, and cold acetone. The compound was purified by column chromatography by using ethanol as eluent. The yellow solid obtained was dried by vacuum. Yield 0.351 g, 72.3 %. FT-IR: ν_{max} cm^{-1}; 3374m, 3064s, 1693s, 1609m, 1567m, 1482m, 1398m, 807s and 737s. EIMS *m/z*: 324; ^{1}H NMR (400 MHz, $DMSO_{d6}$): 10.096 (s,Ar-aldehyde, 1H), 9.05 (d, 2H, *4J* = 2.51 Hz), 8.94 (d, 2H, *3J* = 6.6 Hz), 8.51 (d, 2H, *3J* = 7.74 Hz), 8.14 (d, 2H, *3J* = 7.74 Hz), 7.85 (m, 2H, *3J* = 7.36 Hz), 1.92 (s, 1H, NH). ^{13}C NMR (400 MHz, CDCl3): Calculated: C, 70.2 %; H, 4.1 %; N, 16.4 %, Found: C, 70.1 %; H, 4.0 %; N, 16.1 %. $C_{20}H_{12}N_4O.H_2O$)

3.3.4 4,4'-bis(3-(4-(1H-imidazo[4,5-f][1,10] phenanthrolin-2-yl)phenoxy)propoxy)-1,1'-biphenyl (8)

Compound 6 (200 mg, 0.64 mmol) was dissolved in 5ml DMF in a 25 ml round bottom flask. It was then added K_2CO_3 (88 mg, 0.64 mmol) and stirred at 60 ^{o}C for 40 min. Then compound **3** (140 mg, 0.32 mmol) was added to the reaction mixture , the reaction temperature was increased to 80 ^{o}C and was stirred for 3 h. TLC showed the complete consumption of reactants and reaction was stopped. The hot reaction mixture was added to ice water which resulted in the formation of yellowish precipitates. The ppts were washed with brine, ethanol and acetone and dried in vacuum oven. The completely dried ppts were characterized as our required compound **8**. Calculated MS ($C_{56}H_{42}N_8O_4$) 890.33, ESI-MS M+1: 891.33, ^{1}HNMR (300 MHz DMSO d6): 9.01 (d, 4H, *J* = 3.3 Hz), 8.92 (d, 4H, *J* = 7.2 Hz), 8.24 (d, 4H, *J* = 8.7 Hz), 7.82 (dd, 4H, *J* = 8.1 Hz, *J* = 4.5 Hz), 7.53 (d, 4H, *J* = 8.4 Hz), 7.21 (d, 4H, *J* = 8.4 Hz), 6.99 (t, 4H, *J* = 8.7 Hz), 4.25 (t, 4H R–CH_2-), 4.19 (t, 4H R–CH_2-), 2.25 (t, 4H –CH_2-); ^{13}CNMR (300 MHz DMSO d6): 159.6, 157.5, 150.8, 147.5, 143.4, 132.4, 129.4, 127.7, 123.1, 12.8, 114.9, 64.5, 64.2, 28.6.

4 Conclusion

We have successfully synthesized 1,10-phenanthroline-based chemosensor molecules against Fe^{3+}. We will call it a molecular "dugdugi" due to its similarity with the monkeys drum used in Indo-Paki subcontinent. Chemosensor switched-on in the presence of Fe^{3+} by showing pink color while it remained turn-off in the presence of other metals. The UV spectra of the molecular "dugdugi" showed a peak at 279 nm which shifted to 290 nm after interacting with Fe^{3+}. A new peak also appeared at 524 nm.

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