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PII: S1010-6030(17)30258-7
DOI: http://dx.doi.org/10.1016/j.jphotochem.2017.09.022
Reference: JPC 10867

To appear in: *Journal of Photochemistry and Photobiology A: Chemistry*

Received date: 25-2-2017
Revised date: 9-9-2017
Accepted date: 10-9-2017

Please cite this article as: Mine Sulak, Ahmed Nuri Kursunlu, Burcu Girgin, Özlem Özen Karakuş, Ersin Güler, A highly selective fluorescent sensor for mercury (II) ion based on Bodipy and Calix[4]arene bearing triazolenaphthylene groups; synthesis and photophysical investigations, Journal of Photochemistry and Photobiology A: Chemistryhttp://dx.doi.org/10.1016/j.jphotochem.2017.09.022

A highly selective fluorescent sensor for mercury (II) ion based on Bodipy and Calix[4]arene bearing triazolenaphthylene groups; synthesis and photophysical investigations

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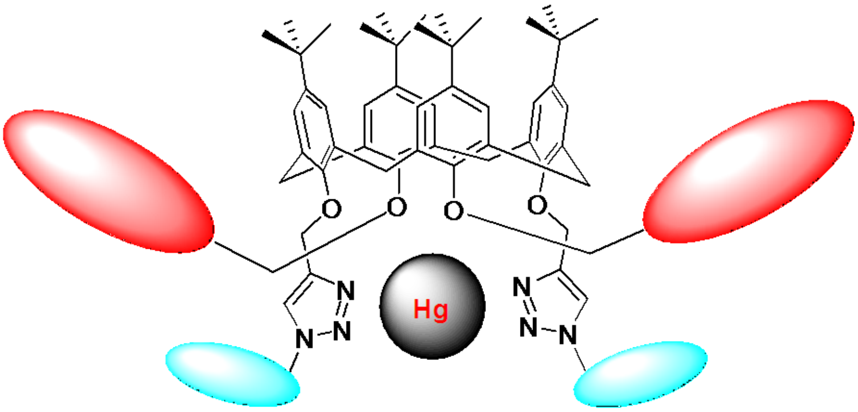
Graphical abstract



Highlights

- A highly selective and sensitive fluorescent sensor for mercury ion has been obtained from a combination of Bodipy and Calix[4]arene derived by click chemistry.
- *Calix [4]-B* can potentially serve a sensitive and selective ratiometric sensor for Hg (I).
- This chemosensor was performed by various spectroscopic methods.

Abstract

A highly selective and sensitive fluorescent sensor for mercury ion has been obtained from a combination of Bodipy and Calix[4]arene derived by click chemistry. The structural characterization of all compounds had been carried out by FT-IR, ^{1}H-NMR, ^{13}C-NMR, MS, elemental analysis or melting point. Calix[4]-B including a calix[4]arene and two Bodipy units is a good fluorescent sensor for Hg(II). It can be explained by the coordination between mercury and the triazole rings. In a co-solvent of methanol and water, the complexation ratio for Calix[4]-B/Hg(II) was determined as 1:1 and the binding constant was found to be 3.42×10^{7} M^{-1}. The detection of Hg (II) by Calix[4]-B works selectively in aqueous methanol mixture.

Keywords: *Bodipy, Calix[4]arene, fluorescence, sensor, mercury, complex*

Introduction

Sensors have a great importance in the detection of heavy metal ions due to their serious hazards toward the environment and biological systems [1-4]. Among transition metal ions, Hg (II) ion is a heavy metal that can cause harmful effects on the living organisms and environment owing to its high toxicitiy [5-8]. Mercury ions in the polluting water accumulate in the living cells by a soft-hard acid-base interaction, therefore, the removal and detection of

Hg (II) ion is important and necessary [9-12]. The researchers had published to some reports on Hg (II) ion sensors over last decade [13, 14].

On the other hand, the fluorescent probes (a class of chemosensors) are crucial for a lot of applications such as food analysis, process control, and medical diagnosis. The fluorescent chemosensors have to include both the detection of ionophore and the signaling of fluorophore units. The signaling units can convert into a signal expressed as the differences in the photophysical characteristics of the chemosensor, electron, charge (ICT) or energy transfer (PET) [15-17]. The chemosensors based-on cryptands, calixarene, cyclodextrins and crown-ether have received a remarkable attention in supramolecular chemistry [18-20]. These compounds can include some aromatic groups such as naphthalene, anthracene, pyrene, rhodamine, dansyl and BODIPY as a fluorescent probe [21-29].

Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction, known as “click reaction”, was reported by Meldal [30] and Sharpless [31], which five members heterocyclic 1,2,3-triazole occurred from the reaction between an organic azide and a terminal alkyne. In addition, it has also been demonstrated that the triazoles formed during the coupling reactions are excellent cation binding motifs [32,33].

This study reports to the synthesis of a calix[4]arene derived by the reaction of an azide and an alkyne to form a triazole binding site. Moreover, a Bodipy derivative with alkyl chloride terminal was prepared. Calix[4]arene based-on dual triazole-naphthalene and a Bodipy derivative were combined as ionophore group and fluorescent unit, respectively. The photophysical studies of target compound show that the sensor can be selectively used to the detection of Hg (II) ion in presence of other ones.

Experimental Section

2.1. Instruments and materials

^{1}H and ^{13}C-NMR spectra were recorded on Varian 400 MHz NMR. The infrared spectra were obtained from Bruker Fourier Transform Infrared FTIR (ATR). All components were supplied from Sigma-Aldrich (MO, USA), Fisher Scientific (USA) and Acros Organics (USA) in analytical grade and used as received, unless otherwise stated. The absorption data were recorded by Perkin Elmer Lambda 25 UV–vis spectrophotometer at room temperature. The emission results were taken from Perkin Elmer LS 55 spectrofluorimeter. The emission slits were set at 3 nm in a fixed excitation. The amounts of carbon, hydrogen and nitrogen were performed by using a TruSpec elemental analyzer. The solutions of **Calix[4]-B** ($5x10^{-7}$ M) and metal cation (1.10^{-5} M) were mixed.

2.2. *The synthesis of 5,11,17,23-tetra-t-butyl-25,26-bis(O-propargyl)calix[4]arene (2)*

p-*tert*-butylcalix[4]arene was classically synthesized as a known procedure [23]. Potassium carbonate (0.510 g, 3.69 mmol) and p-*tert*-butylcalix[4]arene (1 g, 1.54 mmol) was dissolved in acetone (100 mL) and stirred at room temperature for 1 h. Propargyl bromide (0.616 g, 5.18 mmol) was dropwise added into the mixture over 30 min. The reaction mixture was refluxed for 24 h and then allowed to cool down to room temperature. The mixture was then filtered over Celite to the removing of the insoluble particles and the filtrate was concentrated by a rotary evaporator. 50 mL of HCl (2 M) was added to the concentrated reaction mixture, and the product was extracted with dichloromethane/water (3 x 50 mL) for three times. The combined organic extracts were successively washed with water and brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness in vacuum. The crude product was recrystallized from CH_2Cl_2/CH_3OH to afford **2** as a white solid (Yield, 82%). mp 120–130 ◦C [34,35]. ^{1}H N-MR ($CDCl_3$, 400 MHz): 8.33 (s, 2H, OH), 7.04–7.00 (m, 8H, Ph-H), 4.81 (m, 4H, OCH_2), 4.37 (d, J = 13.4 Hz, 4H, Ph-CH_2-Ph), 3.40 (d, J = 13.2 Hz, 4H, Ph-CH_2-Ph), 3.38 (d, J = 13.5 Hz, 2H, Ph-CH_2-Ph), 2.67 (t, J = 2.4 Hz, 2H, OCH_2-CC-H), 1.24 (s, 18H, t-Bu), 1.17 (s, 18H, t-Bu); MS m/z for $C_{50}H_{60}O_4$: 724.45 $[M+H]^+$.

2.3. *The synthesis of 1-Azidonaphthalene (4)*

An ice-cold solution of sodium nitrite (210 mg, 3 mmol) in water was dropwise added to a cold solution of aryl amine (143 mg, 1 mmol) (**3**) in the concentrated hydrochloric acid in water (50 mL) at 0 ^oC over 10 min. The reaction mixture was slowly stirred for 10 min before an ice cold solution of sodium azide (195 mg, 3 mmol) in water (50 mL) was dropwise added at 0 ^oC over 10 min. After the mixture was stirred for 15 min. The resulting mixture was extracted with diethylether (3 x 20 mL) [36]. The organic layer was washed with water (3x 100 mL) and brine solution, dried over anhydrous Na_2SO_4, and then concentrated to pure aryl azide **4** (152 mg, yield 90%). ^{1}H- NMR ($CDCl_3$, 400 MHz): 8.0-8.2 (m, 3H, Ph-H), 7.4–7.9 (m, 4H, Ph-H).

2.4. *The synthesis of calix[4]arene-click-1-Azidonaphthalene (5)*

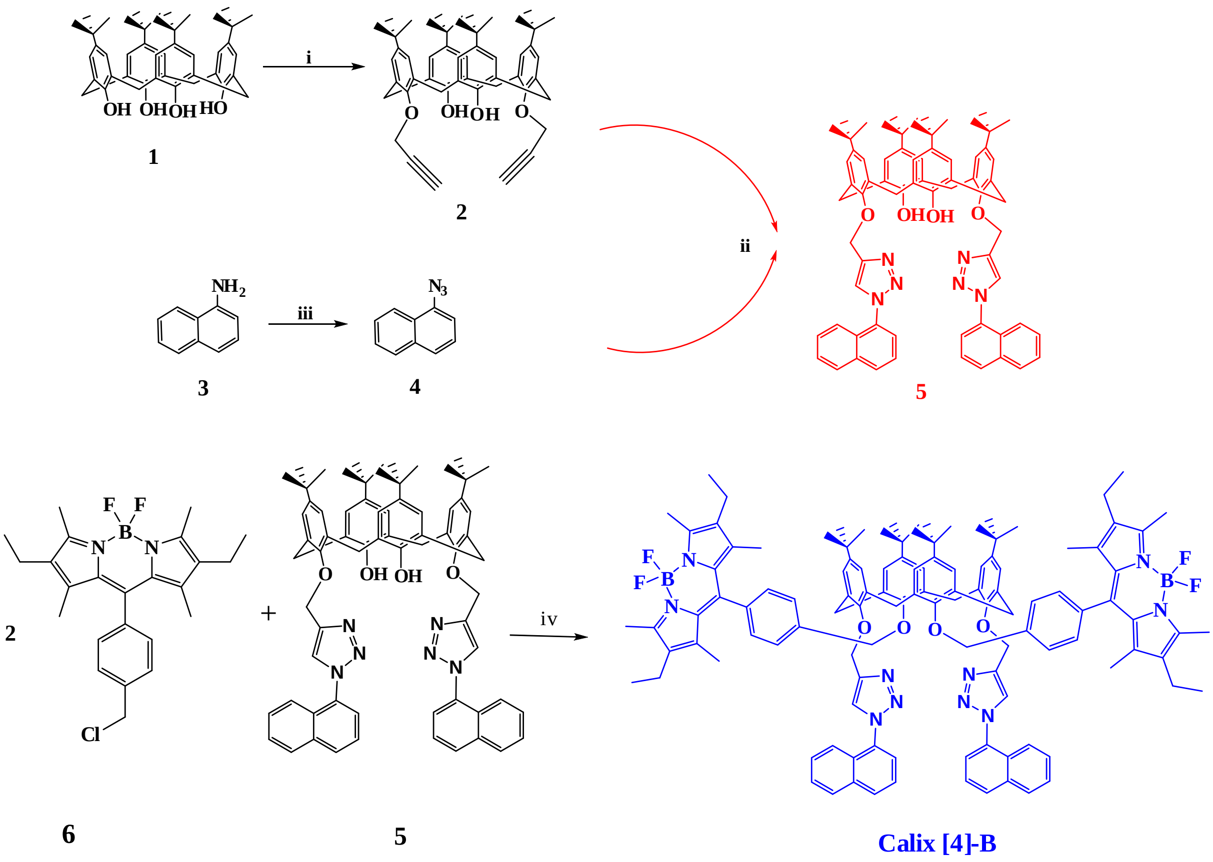
5,11,17,23-tetra-t-butyl-25,26-bis(O-propargyl)calix[4]arene (0.15g, 0.20 mmol) was solved in toluene (20 mL). A mixture of **4** (0.067 g, 0.40 mmol), CuI (0.021g, 0.11 mmol) and triethylamine (0.165 mL, 1.19 mmol) in DMF (20 mL) was added to this solution and refluxed for 24 h. The mixture was extracted with $CHCl_3$ /water for three times and the organic phase was combined. The organic phase was dried over $MgSO_4$ and the solvent was evaporated to give the solid crude product [20]. The solid product was eluted with ethyl acetate/hexane (v/v, 1:1) mixture and gave **5** (0.45 g, 72%) as a white solid, mp 241-242 ◦C; Rf = 0.3, ethyl acetate/hexane (v/v, 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.84 (s, 2H, OH), 7.75 (s, 2H, CCHN), 7.0-7.23 (m, 10H, naphthalene -H), 6.85 (d, J =2.4 Hz, 2H, Ph-H), 6.67 (d, J = 2.3 Hz, 2H, Ph-H), 7.04 (d, J = 2.3 Hz, 2H, Ph-H), 7.00 (d, J = 2.3 Hz, 2H, Ph-H), 4.93 (s, J = 11.5 Hz, 4H, OCH_2), 3.91 (d, J = 12.7 Hz, 4H, Ph- CH_2-Ph), 2.93 (d, J = 12.9 Hz, 4H, Ph-CH_2-Ph),.0.91 (s, 18H, t-Bu), 0.64 (s, 18H, t-Bu). Anal.Calc. for (%) $C_{70}H_{74}N_6O_4$: C, 79.06; H, 7.01; N, 7.90; Found; C, 79.46; H, 7.41; N, 7.77.

2.5. *The synthesis of 8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (6)*

6 was synthesized according to a known procedure [37,38]. 4-(chloromethyl)benzoyl chloride (0.938 g, 5 mmol) was added to a solution of 2,4-dimethyl-3-ethylpyrrole (1.35 mL, 10 mmol) in dry DCM (80 mL) at room temperature and under dark/N_2 medium. The solution was stirred at 55 ^oC for 3 h. After the cooling of the mixture, triethylamine (TEA) (5 equiv.) was injected to the residual solid, the mixture was stirred at room temperature for 1 h in inert medium and then $BF_3.OEt_2$ (8 equiv.) was added. The mixture was refluxed at 55 ^oC for 3 h and the final product was purified on column (petrolium ether-EtOAc; in 7:1). A red solid (0.885 g Yield 43%). ^{1}H-NMR [400 MHz, $CDCl_3$]: ^{1}H NMR [400 MHz, $CDCl_3$]: 7.41 (d, J = 2.3 Hz, 2H, Ph-H), 7.18 (d, J = 2.3 Hz, 2H, Ph-H), 4.63 (s, 2H, CH_2), 2.44 (s, 6H, CH_3) 2.21 (q, 4H, CH_2) 1.27 (s, 6H, CH_3) 0.89 (t, 6H, CH_3).^{13}C NMR [100 MHz, $CDCl_3$]: δ (ppm); 153.81, 139.42, 138.42, 136.12, 135.81, 132.83, 130.62, 129.02, 128.78, 45.59, 17.07, 14.43, 12.43, 11.62. Anal.Calc. for (%) $C_{24}H_{28}N_2F_2ClB$: C, 67.23; H, 6.58; N, 6.53; Found: C, 66.97; H, 6.98; N, 6.22. MS for $C_{24}H_{28}N_2F_2ClB$ m/z: 428.2 $[M+H]^+$.

2.6. The synthesis of Calix[4]-B

Calix[4]-B was prepared according to a known procedure [37] and purified by some purification techniques. A solution of potassium iodide (50 mg, 3 equiv.) in 10 mL dry DMF was poured to the solution of **5** (106 mg, 1 mmol) in 50 mL chloroform. The mixture was stirred at 95 ^{o}C for 24 hours. Chloro-Bodipy (86 mg, 2 mmol) and N,N-Diisopropylethylamine (DIPEA) (2 equiv.) was added to this mixture and was refluxed for 72 hours. The reaction mixture was poured to ice and the suspension was extracted with dichloromethane for five times (3 x 30 mL). The organic phase was evaporated and the purification of crude product was carried out with a mixture of ethylacetate/petroleum ether (1:2) in column, a red-orange solid was obtained (114 mg Yield: 62%).^{1}H NMR ($CDCl_3$, 400 MHz): 7.68 (d, J = 2.4 Hz, 2H, Ph-H) , 7.25 (d, J = 2.3 Hz, 4H, Ph-H), 7.20 (d, J = 2.3 Hz, 4H, Ph-H), 7.0-7.12 (m, 10H, naphthalene -H), 6.92 (s, , 2H, CCHN), 6.68 (d, J = 2.3 Hz, 2H, Ph-H), 6.48 (d, J = 2.3 Hz, 2H, Ph-H), 6.42 (d, J = 2.3 Hz, 2H, Ph-H), 5.38 (s, J= 11.5 Hz, 4H, OCH_2), 4.92 (s, 4H, CH_2), 4.28 (dd, J = 12.8 Hz, 2H, Ph- CH_2-Ph), 4.08 (dd, J = 12.8 Hz, 2H, Ph- CH_2-Ph), 3.25 (d, J = 12.8 Hz, 2H, Ph- CH_2-Ph), 3.17 (d, J = 12.8 Hz, 2H, Ph- CH_2-Ph), 2.50 (s, 12H, CH_3), 2.20 (q, 8H, CH_2), 1.21 (s, 12H, CH_3) , 1.17 (s, 18H, t-Bu), 1.11 (s, 18H, t-Bu), 0.93 (t, 12H, CH_3). ^{13}C-NMR [100 MHz, $CDCl_3$]: (ppm); 154.6, 147.2, 145.1, 143.2, 141.2, 139.2, 136.8, 135.2, 134.6, 134.0, 132.2, 132.1, 130.1, 129.8, 128.8, 128.1, 126.7, 126,0, 125.7, 125.0, 122.2, 120.0, 73.2, 71.2, 35.5, 32.5, 30.7, 18.3, 17.7, 14.3, 12.3, 11.6. Anal.Calc. for (%) $C_{118}H_{128}B_2F_4N_{10}O_4$: C, 76.69; H, 6.98; N, 7.58; Found: C, 76.82; H, 6.99; N, 7.50. MS for 1848,02 $[M+H]^+$.



Scheme 1. The preparing process of **Calix [4]-B**. (i) NaH, propargyl bromide, DMF, 70 °C, 2 h; (ii) 1-azidonaphthalene (4), CuI, Toluene/50 °C, 1 d;(iii) $NaNO_2$/HCl, NaN_3/H_2O, r.t., 15 min. (iv) DIPEA

3. Results and Discussion

3.1. The synthesis and characterization of compounds

The synthetic pathway for ligand, **Calix [4]-B**, was given in **Scheme 1**. The compound **2** was synthesized by the reaction of p-*tert*-butylcalix[4]arene and propargyl bromide in the presence of NaH in DMF. The compound **5** was obtained by a click reaction with Cu(I)-catalysis between **3** and **4**, which prepared from the diazotization of 1-aminonaphthalene. The target molecule, **Calix [4]-B**, was synthesized by the dually binding of chloro-Bodipy to **5** in presence of DIPEA. The structure of compounds synthesized in this work was characterized by ^{1}H-NMR spectra as well as Fourier Transform Infrared FTIR (ATR) and elemental analyses. The mass measurement was recorded by a Bruker Compass Data Analysis 4.0 (ESI-TOF-MS) (The mass spectrometers used were a micrOTOFQ and a maXis quadrupole time-of-flight mass spectrometer).

In FT-IR spectrum of **5**, the peaks were observed at 3367 cm^{-1}, 3057 cm^{-1}, 2964 cm^{-1}, 1598 cm^{-1}, 1515 cm^{-1} and 1481 cm^{-1} which can be referred to aromatic νO-H, aromatic νC-H, aliphatic νC-H, imine νC=N, νC-N and alkene νC=C, respectively. In spectrum of **Calix [4]-B**, new bands were especially observed around 1750 cm^{-1} that the peaks assigned to the νC=N vibrations of Bodipy.

^{1}H-NMR spectrum of **5** exhibits the evanescence of three terminal CCH hydrogens originally found in **2** leaving the new singlet peak revealing around δ = 6.91 ppm referring to two protons of the newly formed triazole skeleton. ^{1}H-NMR spectrum of **5** showed to two doublet-doublet signals at δ 3.98 and 2.90 ppm. These signals can be ascribed to a classical methylene-bridge protons of calix[4]arenes in **5** owing to its C_{2v} symmetry. These signals appeared as four doublets in ^{1}H-NMR spectrum of **Calix [4]-B**. These differences can be explained by the different conformation of two Bodipy fragments due to the steric hindrance occurred between Bodipy and triazoyl-naphtalene units. Therefore, the molecular symmetry of **Calix [4]-B** can be asserted as C_s. On the other hand, the peak -CH_2 of compound **6** at 4.63 ppm prominently shifted to 4.92 ppm depending on the effect of an electronegative atom and electron attractive groups. Other peak values of **6** and **5** around 0-2.5 ppm and aromatic area slightly changed and some signals hidden because of the overlapped peaks.

3.2. The spectroscopic studies of Calix [4]-B

As referred to previously, the synthesis of calixarenes containing ionophore groups is crucial in fluorescent sensor applications. Therefore, **Calix [4]-B** have been substituted with naphtalene groups and Bodipy units exhibiting ligand property and fluorescence character, respectively.

The fluorescence, excitation and absorption properties of **Calix [4]-B** were investigated in presence of some metal cations [Ga(III), Gd(III), Ni(II), Zn (II), Cu (II), Co (II), Cd (II), Cr (III), Mn (II), Yb (III), Hg (II), Ag (I), Tb (III)]. The concentrations of ligand and metal cations were adjusted as 5.10^{-7} M and 1.10^{-5} M, respectively.

In the fluorescence spectrum, we get to the band of **Calix [4]-B** with the longest wavelength as a reference that it appeared at 535 nm. Upon the addition of metal cations, a quenching effect was only observed in presence of Hg(II) ion. Other cations slightly affected to the emission intensity of **Calix [4]-B**. The evident change in the fluorescence intensity of sensor can be depended on the interaction between **Calix [4]-B** and Hg (II) ion. Compound **5** consists of two parts; the receptor fluorophore (Bodipy). **Calix [4]-B** has an efficient form binding sites of metal ion. The fluorescence measurements show that Hg (II) is most likely to bind **Calix [4]-B** via two N-atom pairs of the triazole ring. Actually, the complex formation was supported by the cavity occurred by the derivatization of calix[4]arene. The cationic size, charge and nature of donor atoms play a crucial role in the selective interaction of compound **Calix [4]-B** with only Hg (II) over other metal ions [Ga(III), Gd(III), Ni(II), Zn (II), Cu (II), Co (II), Cd (II), Cr (III), Mn (II), Yb (III), Ag (I), Tb (III)].

On the other hand, naphthyl derivatives are known as an effective precursor for the preparing of different fluorescent sensors due to its donor as well as acceptor sites [39]. Although the naphthyl groups have a good fluorescence character, they have a much lower emission wavelength (around 400 nm) and intensity when they compared with Bodipy (≥ 500 nm) [37,38]. However, in this study, both Bodipy units and naphthyl ring act as an electron donor toward Hg (II) ion. Therefore, the fluorescence intensity of **Calix[4]-B** bearing two naphthyl and two Bodipy fluorophores decreased in presence of Hg (II) ion. This turn-off fluorescence change indicated that an energy transfer carried out from the Bodipy-naphthyl excimer to mercury ion. In particular, calix[4]arene unit has attracted as a considerable interest because they form efficient excimer signal by the strong intramolecular π-π interactions between the two naphthyl groups.

The excitation spectra of **Calix[4]-B** and mixtures were performed at the fixed emission (535 nm). The excitation spectra specially show a So-S_1 band between 300-450 nm due to they have the lowest energy absorption features. The excitation curves of **Calix[4]-B** and **Calix[4]-B**/metal solutions in MeOH/H_2O mixture (v/v, 9:1) were obtained in the fixed emission (535 nm) (Fig.2). The five bands were observed in all spectra of the mixtures. The excitation curves almost superimposed except of **Calix[4]-B**/Hg(II) mixture. Although the excitations spectra are close for the Hg complex and the free ligand, the all excitation mounds of **Calix[4]-B** broadened in presence of Hg (II) cation owing to the strong ligand character of two triazolylnaphthalene units.

The absorption spectra of **Calix [4]-B** and **Calix [4]-B**/metal cations mixture were shown in Fig 3. The used metal cations [Ga(III), Gd(III), Ni(II), Zn (II), Cu (II), Co (II), Cd (II), Cr (III), Mn (II), Yb (III), Ag (I), Tb (III)] did not affect to the absorption properties of **Calix [4]-B**. Therefore, the absorption curves **Calix [4]-B** and **Calix [4]-B**/metal cations [except of Hg (II)] were represented with yellow cloudy-line. However, Hg (II) ion caused evidently to a blue-shift and the band of Bodipy (522 nm) and π-π transitions (around 360 nm) of **Calix [4]-B** appeared in lower wavelengths. A complexation reaction mechanism can be proposed between ligand and metal ion that mercury ion is encapsulated by calix-triazole-bodipy with triangle cavity. The shift in absorption bands can be explained with internal charge transfer (ICT) from Bodipy units. Uv-vis studies, just as the fluorescence and excitation, **Calix [4]-B** can be used as an effective fluorescent sensor in the selective and sensitive detection of Hg (II) ion. So, **Calix [4]-B** has a more attractive performance for the detection of mercury ion when compared to previous papers [40].

Job plot analysis was used for determine of the complex stoichiometry between **Calix[4]-B** and Hg (II). The mixtures of **Calix[4]-B** with Hg (II) approached a maximum when the molar fraction of ligand/metal cation was around 0.50, indicating a 1:1 ratio between sensor and mercury ion. The similar studies were carried out by the emission maxima and observed same ratio between metal and ligand as 1:1. The estimated binding mode of the complex was given in Fig. 4 that Hg(II) ion coordinated with two triazole fragments.

The quantum yields were determined by using rhodamine B as a criterion. The quantum yield of emission for **Calix[4]-B** and **Calix[4]-B**–Hg(II) complex were evaluated as 0.56 and 0.13 in methanol/water (9:1), respectively. The fluorescence quantum yield of Hg (II) solution (20 equiv.) was lower than of the free ligand. The lower quantum yield shows an energy transfer from **Calix[4]-B** to Hg (II) ion).

To determine the association constant, a solution of **Calix[4]-B** in MeOH:H_2O (9:1) was titrated with a solution of $HgCl_2$ in MeOH:H_2O (9:1) due to the solubility requirements (Fig. 5). The binding constant was calculated by Stern-Volmer relationship.

$I_0/I=1 + Ka[Q]$

where I_0 and I are the fluorescence intensities of **Calix[4]-B** in the absence and presence of mercury ion, respectively, Ka is the association constant of **Calix[4]-B**/Hg (II) ion and [Q] is the concentration of mercury cation. The concentration of **Calix[4]-B** was kept the constant during the whole experiment to a reliable measurement. The concentration of mercury salt was 2 times smaller (first mixture) and 19 times smaller (final mixture) that the association constant of **Calix[4]-B**/Hg (II) calculated as 3.42×10^{7} M^{-1} while other metal ions have lower association constants range of 2.5×10^4 -2.8×10^5 M^{-1}. The association constant can be depended on the strong chelating effect of a multi-dentate ligand on mercury ion. The value acceptable for the fluorescent sensors. Moreover, the quantum yield was calculated as 0.18 for the complex system.

To better investigate **Calix[4]-B** (5.10^{-7} M) as a selective sensor for Hg(II) ion in the practical applications, the competing ion studies were performed in the presence of Hg (II) ion (1.10^{-5} M) mixed with Ga(III), Gd(III), Ni(II), Zn (II), Cu (II), Co (II), Cd (II), Cr (III), Mn (II), Yb (III), Hg (II), Ag (I), Tb (III) at 1.10^{-5} M; as shown in Fig. 6., A remarkable interference in detection of Hg (II) ion with **Calix[4]-B** was not observed in the presence of most other competing metal ions except for the Hg (II) ion. Thus, these results assign that **Calix[4]-B** can be applied as a selective sensor for mercury ion in the presence of most competing metal cations.

Moreover, we studied to a sensing response time of the sensor toward various times of Hg (II) (0-20 minutes) (Fig. 7). By the addition of mercury solution, the fluorescence intensity of **Calix[4]-B** quickly decreased and reached to a maximum quenching effect in four minutes. The fluorescence intensity continued in a stable value after four minute though the increasing time. The response time is an ideal result for a selective sensor that **Calix[4]-B** can be applied for Hg (II) ion.

The peaks -CH_2 of compound **5** at 4.95 ppm clearly shifted to 5.38 ppm in the NMR spectrum of **Calix [4]-B** depending on the effect of an electron attractive groups. Other peaks of reagents between 0-2.5 ppm and aromatic area slightly changed and some signals hidden due to the overlapped peaks. To get first-hand information about the coordinating sites of receptor **Calix[4]-B** and Hg (II), ^{1}H-NMR of ligand was performed with $Hg(NO_3)_2$ (in DMSO-d6) (Fig. 8). Upon addition of Hg (II) ion, **Calix[4]-B** exhibited a considerable changes for the protons close to the triazole rings and Bodipy units that are supposed to serve as coordination sites. While -CH_2 protons close to the triazole and Bodipy groups appeared at 5.27 and 4.89 ppm, **Calix[4]-B**-Hg(II) complex gave singlet peaks for same protons at 5.8 and 5.1 ppm, respectively. Moreover, -CH protons in triazole ring shifted from 6.91 to 7.43 ppm.

The limit of detection (LOD) was calculated from the standard deviation of the blank and some parameters that the detection limit affected the accuracy of the model used to predict concentrations from the sole emission peak. LOD was evaluated by the emission intensities obtained from the mixture of **Calix[4]-B** (5.10^{-7} M) and the solutions of Cu (II) in different concentrations.

LOD= 3σ/F

In there, F is the false of the LOD curve, σ is the standard deviation of the blank solution; The LOD of **Calix[4]-B** towards Hg (II) calculated to be 2.8 (±0.2) × 10^{-7} M. When it compared with previous papers, **Calix[4]-B** has a lower LOD that it is useful for the detection of Hg (II) ions in half aqueous [40, 41].

Conclusion

An efficient sensor, **Calix[4]-B**, was produced from calix[4]arene−naphthalene derivative (**5**) obtained by click reaction and a fluorescent Bodipy with alkyl-chloride terminal. **Calix[4]-B** displayed a high selectivity for Hg (II) ion in MeOH/H_2O co-solvent. The studied competing ions [Ga(III), Gd(III), Ni(II), Zn (II), Cu (II), Co (II), Cd (II), Cr (III), Mn (II), Yb (III), Ag (I), Tb (III)] in the same solution did not cause to any hindrance to the enhancement or quenching in the fluorescence intensity of **Calix[4]-B**. The sensor having two azido-naphthalene groups turns out to have high affinity for Hg(II) and completely is quenched to the fluorescence intensity of the fluorophore. As result, the sensor, **Calix[4]-B**, can be usefully used in the detection of mercury (II) ion.

Acknowledgements

We thank to Selcuk University (BAP) (15401013) for financial support of this work.

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Figures

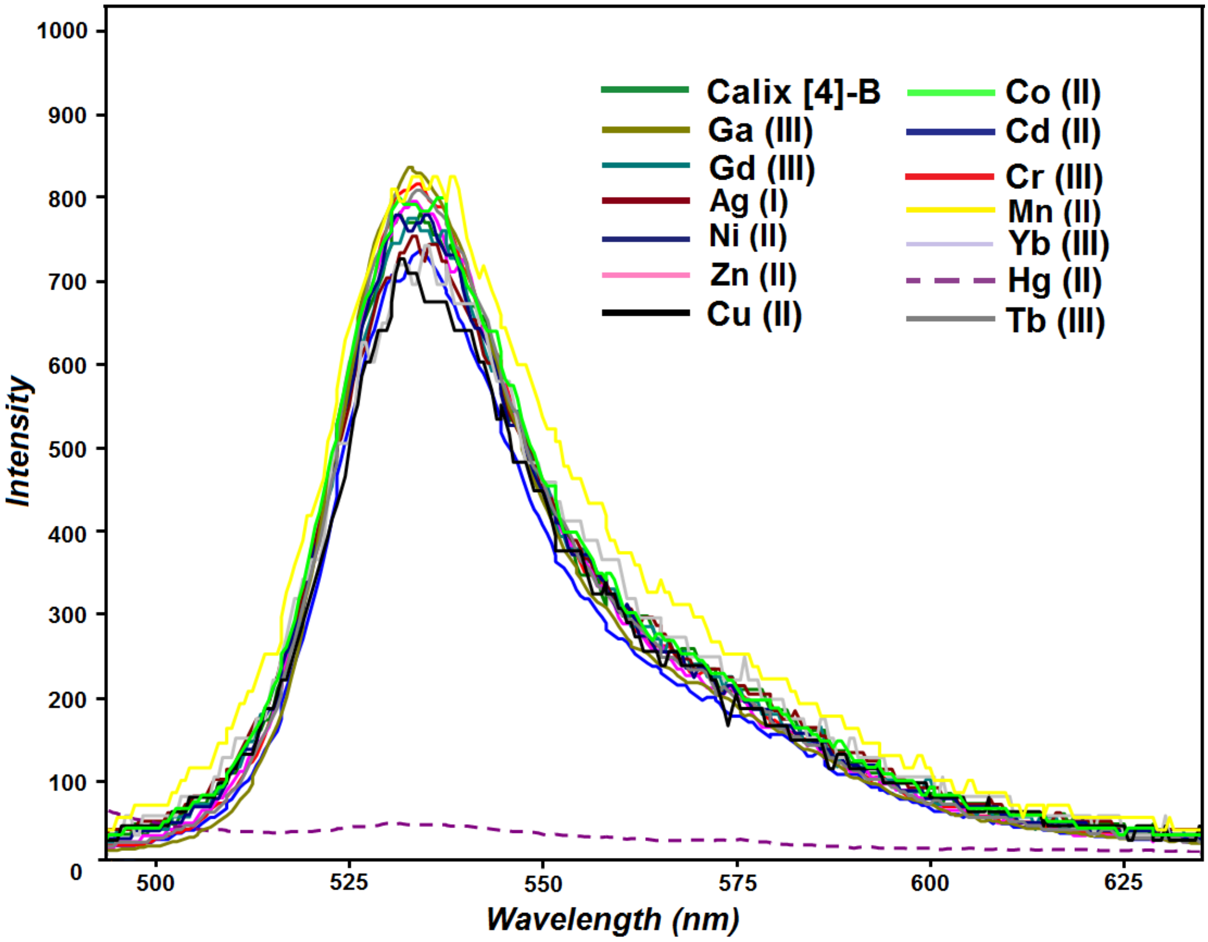

Fig.1 The fluorescence spectra (Λ_{exc}= 470 nm, slit:3) of **Calix [4]-B** (5.10^{-7} M) and **Calix [4]-B**/metal cations (1.10^{-5} M) in MeOH/H$_2$0(v/v, 9:1)

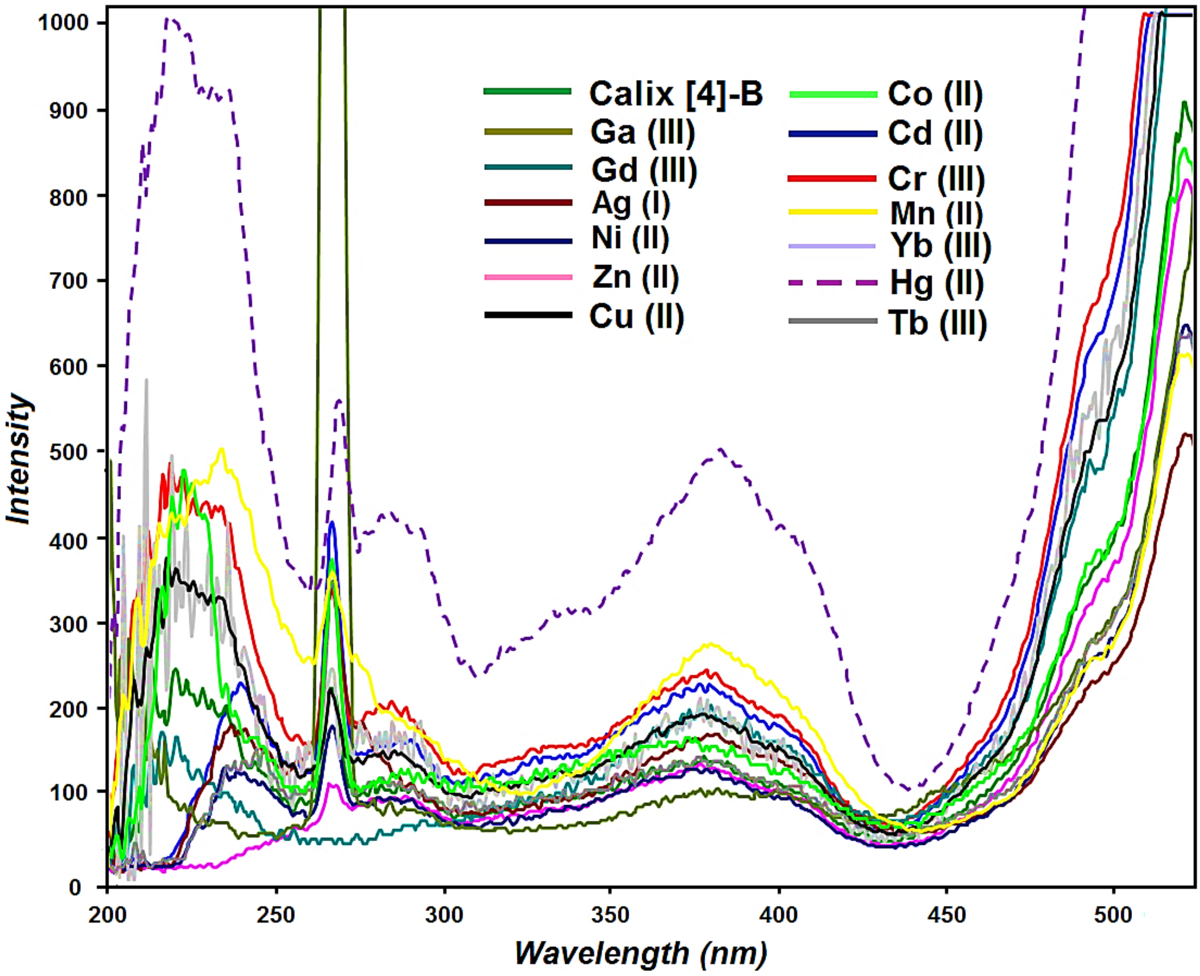

Fig.2 The excitation spectra (Λ_{em}= 535 nm, slit: 3) of **Calix [4]-B** (5.10^{-7} M) and **Calix [4]-B**/metal cations (1.10^{-5} M) in MeOH/$H_2$0(v/v, 9:1)

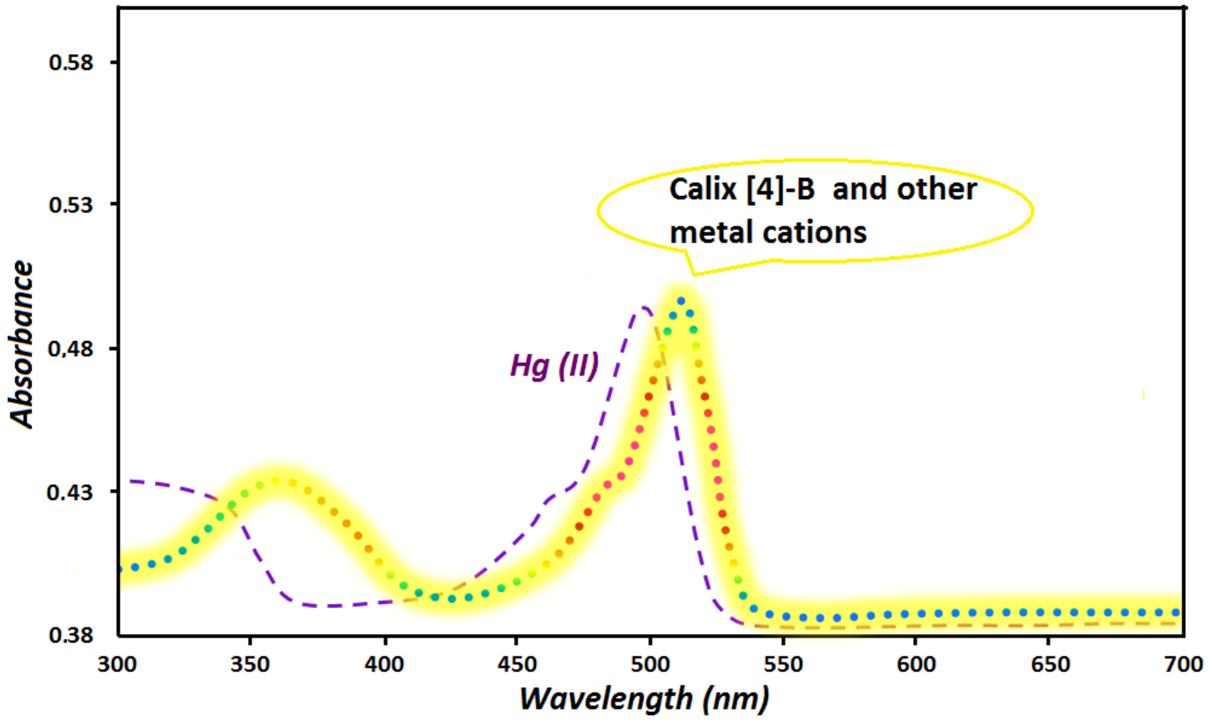

Fig.3 The absorption spectra of **Calix [4]-B** (5.10^{-7} M) and **Calix [4]-B**/metal cations (1.10^{-5} M) in MeOH/H$_2$0(v/v, 9:1)

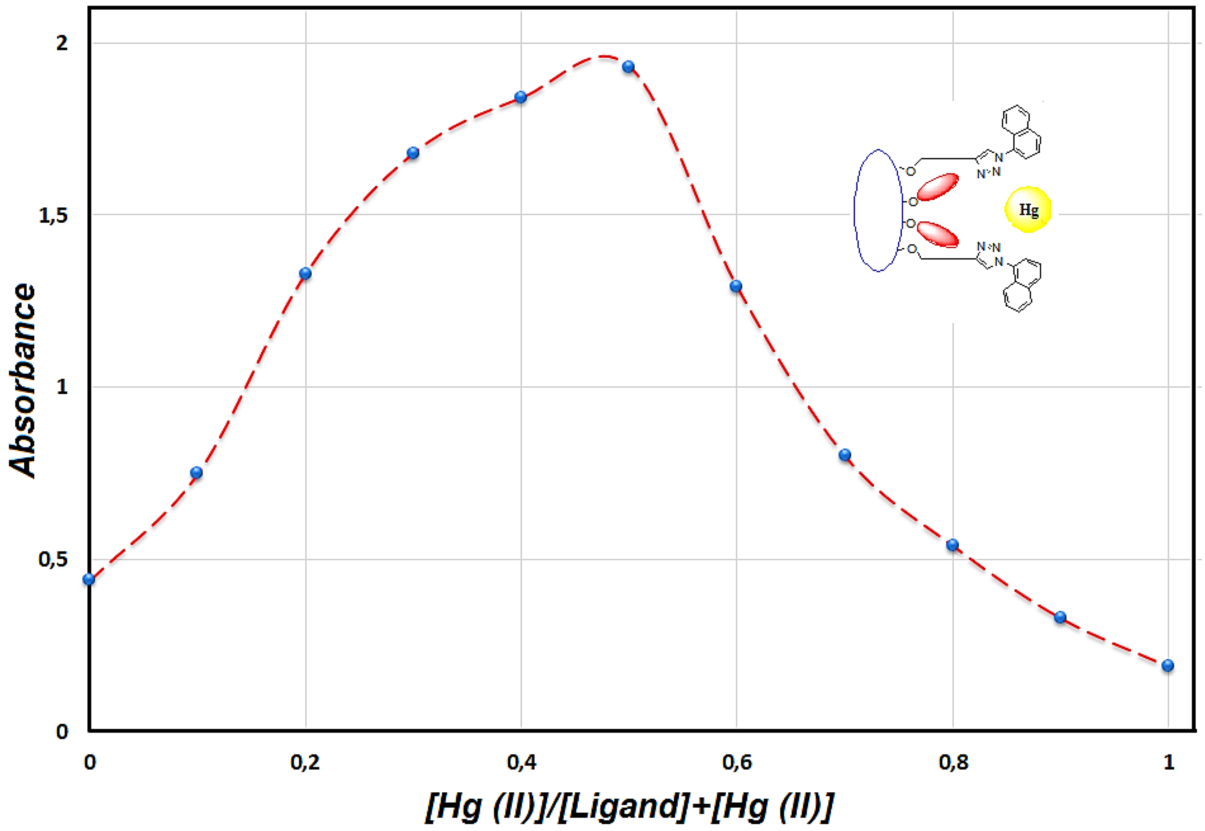

Fig. 4 Job's plot for **Calix[4]-B** (5.0×10^{-7} M) and Hg (II) complexation in a mixture of MeOH/H_2O (9:1, v/v).

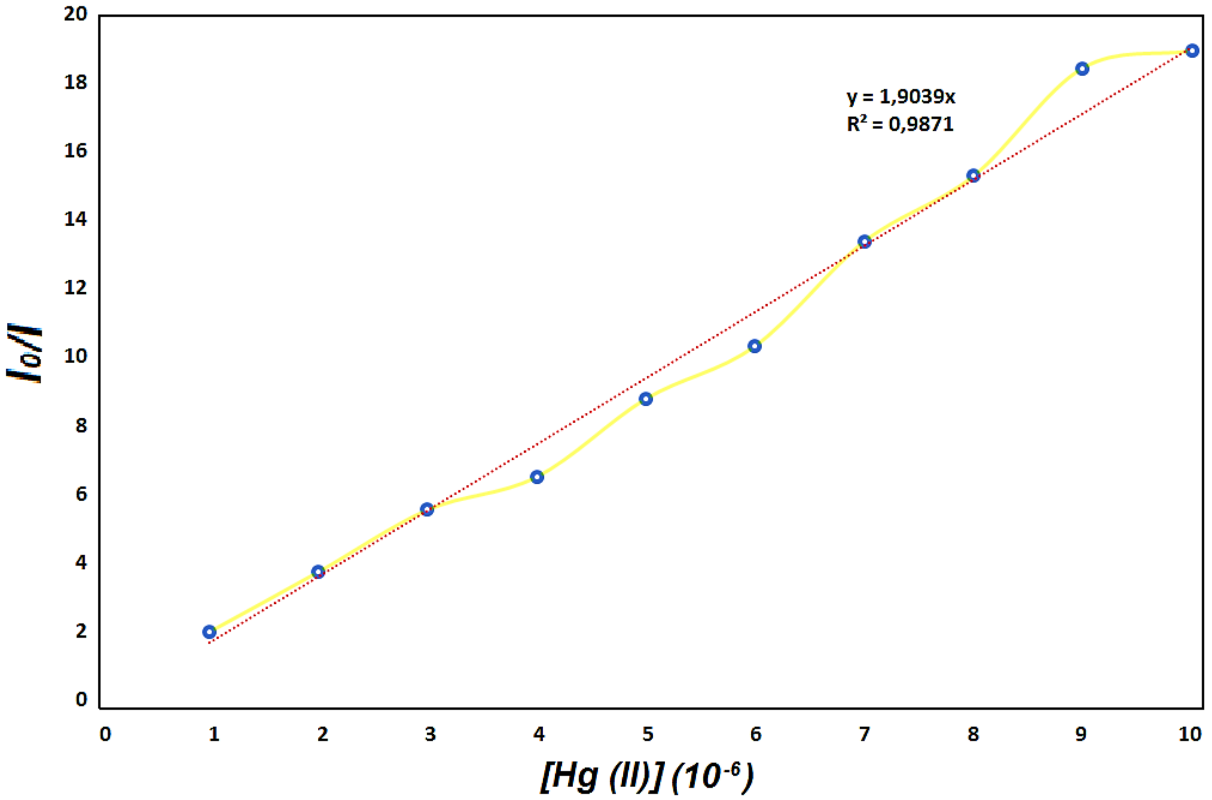

Fig.5 Stern-Volmer plot for changes of **Calix[4]-B** [5.10^{-7} M in MeOH/H_2O (9:1, v/v)] in the fluorescence intensity by the addition of Hg (II) ion in MeOH/H_2O (9:1)

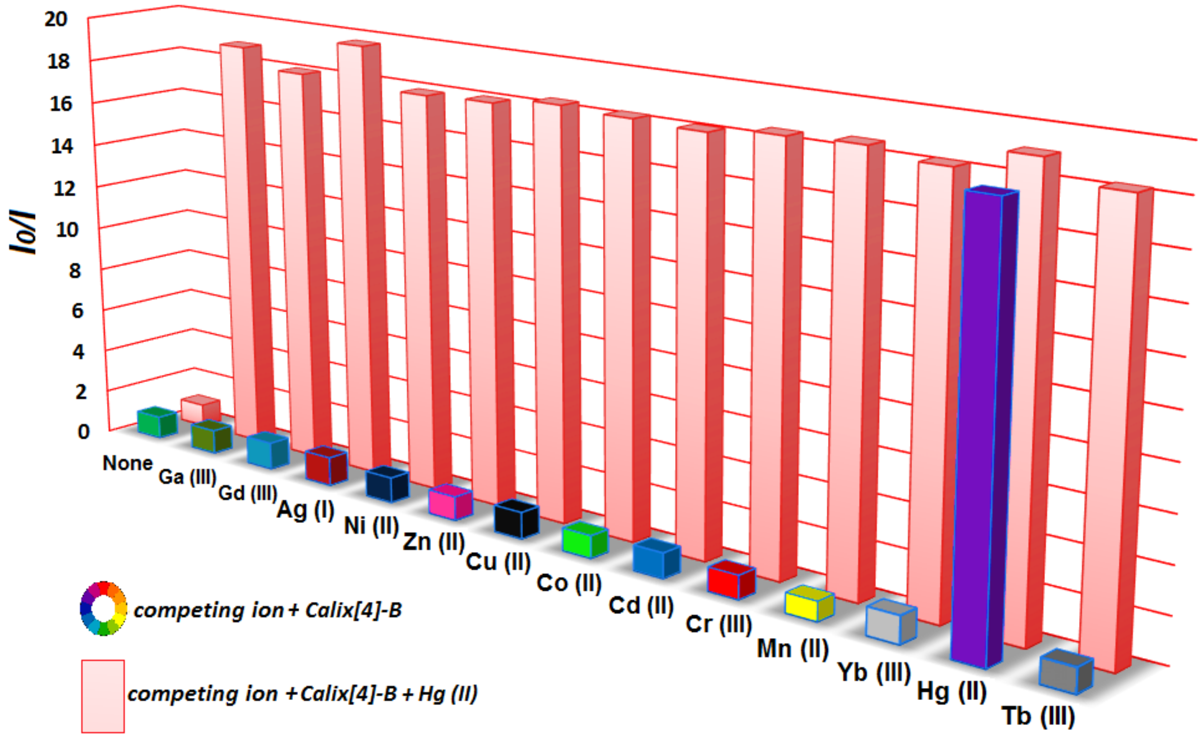

Fig. 6 The relative fluorescence intensity changes of **Calix[4]-B/**Hg(II) mixture [5.10^{-7} M, 1.10^{-5} M in MeOH/H_2O (9:1, v/v), respectively] at 298 K in presence of various competing metal ions (1.10^{-5} M). I_o is emission intensity at 535 nm for free receptors, and I is the emission intensities after adding metal cations with a fixed excitation at 470 nm.

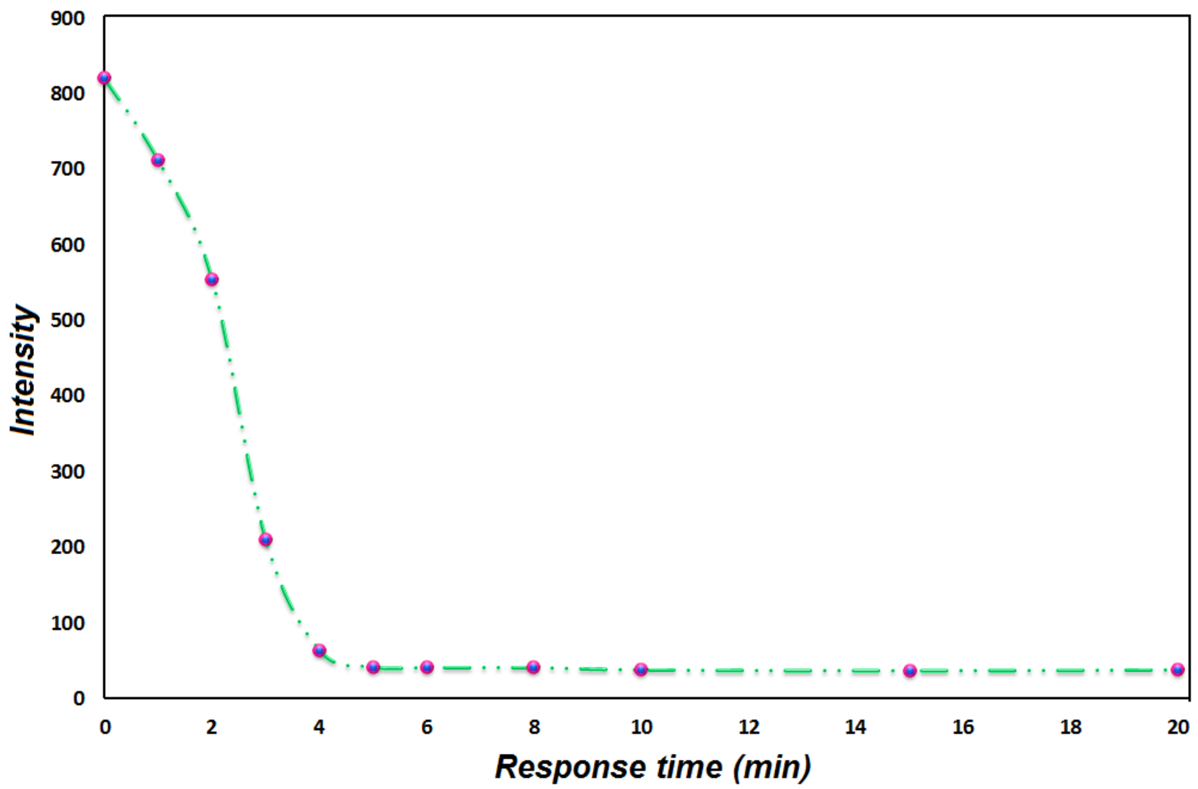

Fig. 7 The effect of response time to the fluorescence intensity of **Calix[4]-B** [5.10^{-7} M, 1.10^{-5} M in MeOH/H_2O (9:1, v/v)] in by the addition of Hg (II) ion [1.10^{-5} M in MeOH/H_2O (9:1, v/v), (ʎem: 535 nm)

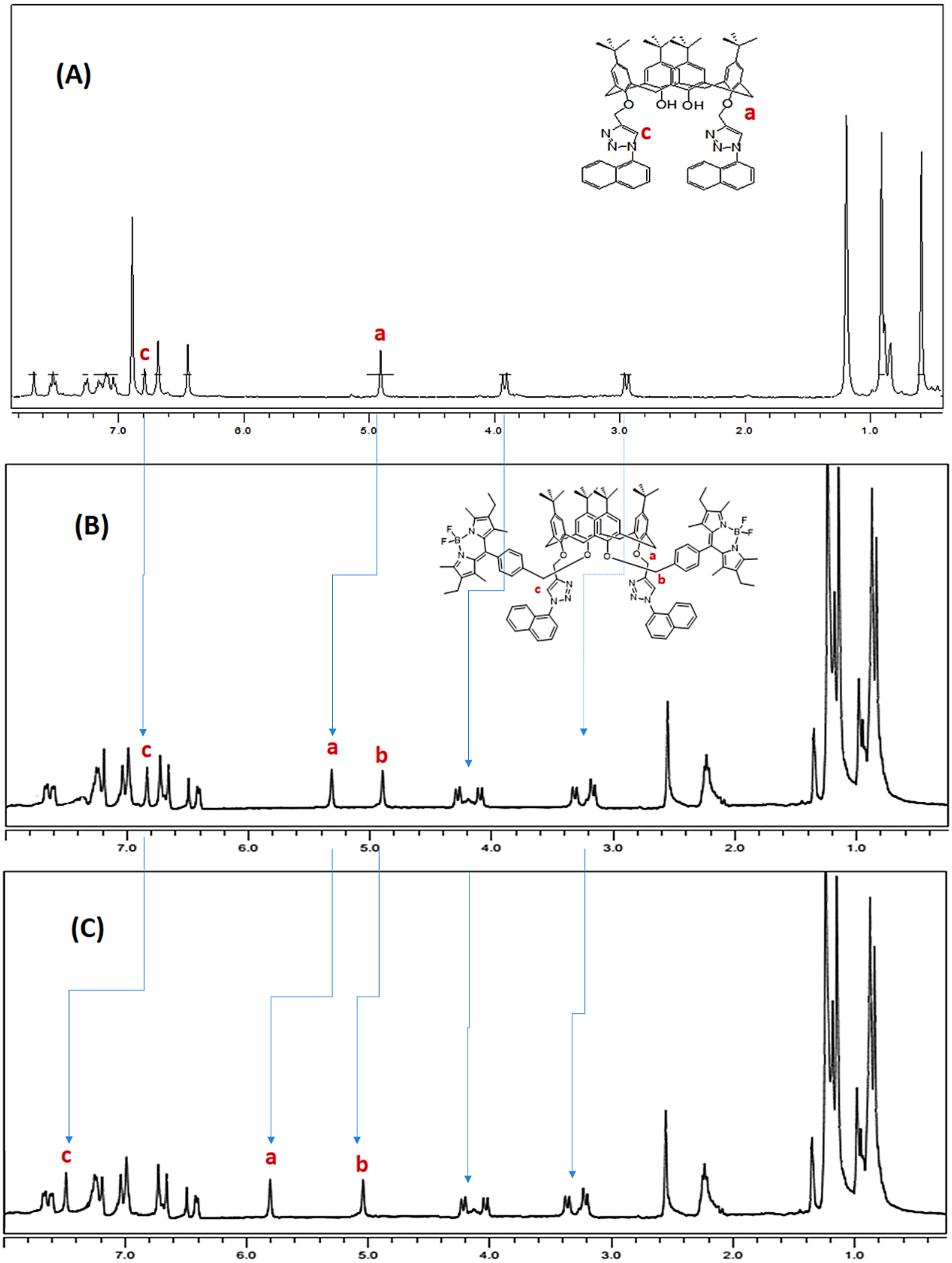

Fig. 8 The complexation of Hg (II) by **Calix[4]-B** A) ^{1}H-NMR spectrum of **Calix[4]-B** with signal assignment based on 2D spectra (400 MHz, DMSO, 298 K); B) **Calix[4]-B**–Hg(II) (2 equiv, 400 MHz, DMSO, 298 K)