

锥形构象含氟杯芳烃衍生物对铜离子的高选择性识别

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摘要: 合成了具有锥形构象的含氟功能基团的杯芳烃衍生物 **1~3**, 并用单晶 X 射线衍射和核磁共振证实了其锥形构象。在混合溶剂中, 研究了杯芳烃衍生物 **1~3** 对多种金属离子的识别行为。测试了化合物 **1~3** 的紫外-可见吸收光谱和荧光发射光谱, 结果显示铜离子对化合物 **1~3** 具有明显的荧光猝灭特性, 而其它金属离子(如 Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Fe^{3+} , Cd^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+})对化合物 **1~3** 的紫外-可见吸收光谱和荧光发射强度无显著的影响, 表明化合物 **1~3** 对铜离子的识别具有高选择性。

关键词: 杯[4]芳烃; 识别; 选择性; 含氟衍生物

中图分类号: O614.121

文献标识码: A

文章编号: 1001-4861(2019)07-1301-11

DOI: 10.11862/CJIC.2019.160

Highly Selective Recognition to Cu^{2+} Based on Fluorinated Calix[4]arene Derivatives in Cone Conformation

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Abstract: The fluorine derivatives of calix[4]arene, $\text{C}_{64}\text{H}_{52}\text{F}_{12}\text{O}_4$ (**1**), $\text{C}_{60}\text{H}_{52}\text{F}_4\text{O}_4$ (**2**), $\text{C}_{68}\text{H}_{48}\text{F}_{24}\text{O}_4$ (**3**), were synthesized, and their cone conformations were proved by single crystal X-ray diffraction and ^1H NMR spectroscopy. Their recognition behaviors were evaluated towards a variety of metal ions in mixed solvent. The UV-Vis absorption and fluorescence spectroscopy were measured and confirmed that copper ions resulted in fluorescence quenching of compounds **1~3**, while other ions such as Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Fe^{3+} , Cd^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} exerted hardly significant impact on the UV-Vis absorption and fluorescence intensity of **1~3**, exhibiting high selectivity of compounds **1~3** to copper ions. CCDC: 1900304, **1**; 1900303, **2**.

Keywords: calix[4]arene; recognition; selectivity; fluorinated derivatives

0 Introduction

During the past few years, the development of efficient sensors detecting metal ions has attracted wide attention. Some metal ions are strong toxic to the human body at very low concentration, such as mercury ions and palladium ions. Although some metal ions play a central part in our daily life and are

widely used in industry, excessive uptake can also have harmful effects. Therefore, it is meaningful to selectively identify related ions for human health. At present, many ion detection sensor materials have been developed, such as ion recognition responsive materials based crown ether^[1], ion recognition materials based coordination compounds^[2-3], ion recognition materials based calix[4]arene^[4].

收稿日期: 2019-03-01。收修改稿日期: 2019-05-13。

国家自然科学基金(No.21571110)、浙江省自然科学基金(No.LY18B010003)和宁波大学王宽诚幸福基金资助项目。

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Calix [4]arenes are highly applied into many fields, such as recognition, sensors, biomedicine^[5-9], because of their adjustable conformation and easy derivatization. Calix[4]arenes are especially prominent in sensors and selective receptors due to their functionalized structures and complexation possibilities^[10-12]. In the field of recognition of ions, the design of highly selective and multifunctional calix[4]arene derivatives has become an important branch and is also an interesting aspect of supramolecular chemistry^[13-18]. Chemical modification of calix [4]arenes is one of the methods to prepare derivatives^[19-20]. Calix[4]arene derivatives modified by different functional moieties are obtained by introducing characteristic groups, such as optical active groups and electrical active groups. Wong et al.^[21] investigated the property dependence of phenyl-calix[4]crown-4 on the upper rim substituent of methyl, fluorine or trimethylsilyl. Chawla et al.^[22] synthesized a series of para-substituted receptors which show selectivity to Cs⁺ and Rb⁺ ions by introducing arylazo, thiazolylazo, pyridylazo and β -naphthylazo groups into tetrathiacalix[4]arene. However, it was rarely reported that fluorine groups were introduced on the upper rim of calix[4]arene. It is due to the special properties of fluorine groups^[23-24] that few researchers synthesize fluorinated calix[4]arene derivatives. Herein, we synthesized fluorinated calix [4]arene derivatives by using Suzuki coupling reaction to modify the up-rim of calix[4]arenes and introduce fluorine and trifluoro-methyl groups into calix [4]arenes, and we studied their recognition properties.

1 Experimental

1.1 General

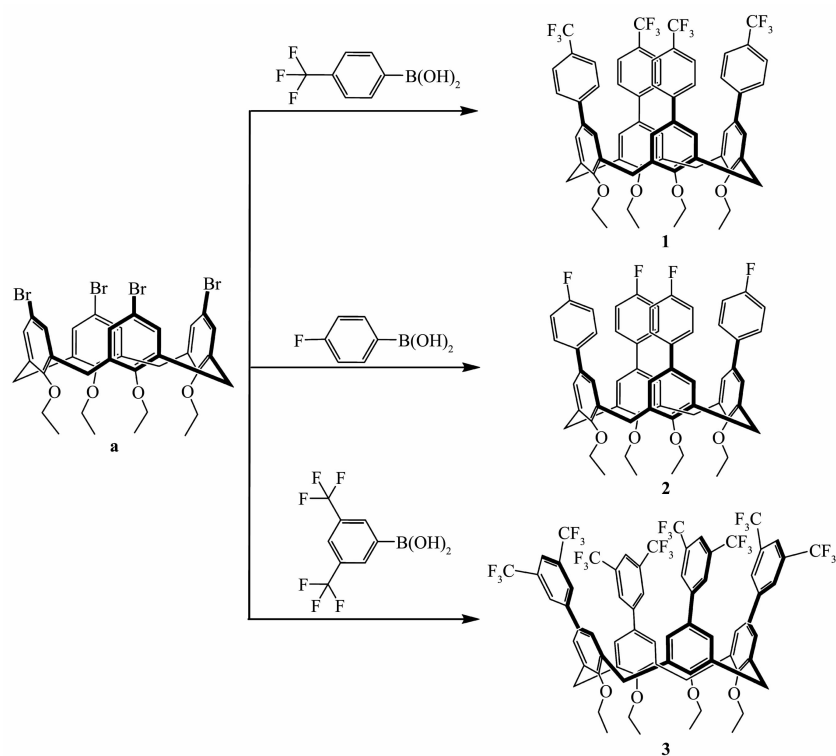
¹H NMR spectra in CDCl₃ were detected on a Bruker 400 MHz spectrometer. FT-IR spectra were obtained by a Nicolet 6700 FT-IR spectrometer. UV-Vis spectral studies were carried out by using a TU-1901 spectrophotometer (Beijing Purkinje General Instrument). Fluorescence spectra were recorded on a Hitachi F-4600 fluorescence spectrometer. All the reagents and chemicals were commercially available and analytical pure.

1.2 Synthesis of compound 1

5,11,17,23-Tetrabromo-25,26,27,28-tetraethoxycalix [4]arene (**a**, 0.425 7 g, 0.5 mmol), 4-(trifluoromethyl) phenylboronic acid (0.372 5 g, 2.0 mmol) and sodium carbonate (0.424 0 g, 4 mmol) were mixed in the mixed solvent of toluene/ethanol/water (20 mL/10 mL/2 mL). The mixture was added tetrakis (triphenylphosphine) palladium ((β -4)-platinum) after pumping vacuum and purging with nitrogen gas for three times. Subsequently, the mixture was heated at 80 °C to reflux under nitrogen protection and stirred for 24 h. The solution was stratified statically after the reaction completed. The inorganic layer was extracted with dichloromethane (6 mL \times 3), and the organic layer was washed with saturated salt water (6 mL \times 3). Successively, organic phases merged into one phase, which was dried with anhydrous sodium sulfate and concentrated by rotary evaporator. The raw solid was obtained. After the purification process by a silica gel column, the white solids of 5,11,17,23-tetra (4-trifluoromethylphenyl)-25, 26,27,28-tetraethoxycalix[4]arene were obtained (0.110 g, Yield: 19.8%). Elemental Anal. Calcd. C₆₄H₅₂F₁₂O₄ (%): C, 69.06; H, 4.70. Found (%): C, 70.20; H, 4.94. IR (KBr, cm⁻¹): ν_{\max} 1 328(CF₃). ¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, J =7.9 Hz, 4H, ArH), 7.27~7.18 (m, 5H, ArH), 6.95 (s, 4H, ArH), 4.59 (d, J =13.1 Hz, 2H, ArCH₂Ar), 4.12 (q, J =6.8 Hz, 4H, CH₂), 3.31 (d, J =13.2 Hz, 2H, ArCH₂Ar), 1.55 (t, J =6.7 Hz, 7H, CH₃).

1.3 Synthesis of compound 2

Compound **a** (0.426 7 g, 0.5 mmol) and 4-fluorophenylboronic acid (0.826 9 g, 2 mmol) were stirred in 32 mL of mixed solvents ($V_{\text{toluene}}:V_{\text{ethanol}}:V_{\text{water}}=10:5:1$) at ambient temperature. The sodium carbonate solution (2 mL, 2 mol \cdot L⁻¹) was added to the mixture. Then the mixture was added (β -4)-platinum after vacuuming and sparging nitrogen gas several times and heated at 80 °C to reflux for 24 h. Finally, the reaction mixture was extracted with CH₂Cl₂ and washed with saturated salt water. The product was purified by a silica gel column to give compound **2** as a white solid (0.100 g, yield 21.92%). Elemental Anal. Calcd. for C₆₀H₅₂F₄O₄(%): C, 78.93; H, 5.74. Found(%): C, 79.95; H, 6.56. IR (KBr, cm⁻¹): ν_{\max} 1 227 (Ar-F).

Scheme 1 Synthetic routes for compounds **1**~**3**

^1H NMR (400 MHz, CDCl_3): δ 7.04 (dd, $J=8.5, 5.4$ Hz, 2H, ArH), 6.86 (s, 2H, ArH), 6.80 (t, $J=8.7$ Hz, 2H, ArH), 4.55 (d, $J=13.1$ Hz, 1H, ArCH_2Ar), 4.08 (q, $J=7.0$ Hz, 2H, CH_2), 3.26 (d, $J=13.2$ Hz, 1H, ArCH_2Ar), 1.53 (dd, $J=13.5, 6.4$ Hz, 6H, CH_3).

1.4 Synthesis of compound **3**

A mixture of **a** (0.851 2 g, 1.0 mmol) and 3,5-bis(trifluoromethyl)benzeneboronic acid (1.038 8 g, 4 mmol) in the presence of Na_2CO_3 (2.218 9 g) as the templating base under nitrogen in mixed solvent was stirred. (β -4)-Platinum was added in the solution after vacuuming three times. After all reagents were added, the resulting mixture was refluxed at 90°C under the protection of nitrogen for 24 h. The solution was extracted with CH_2Cl_2 and washed with saturated salt water three times after reaction. The solution was dried with anhydrous sodium sulfate. Then, the crude product was obtained by concentrating with rotary evaporator. Compound **3** was obtained by the purification process (0.130 g, Yield: 9.40%). Elemental Anal. Calcd. for $\text{C}_{68}\text{H}_{48}\text{F}_{24}\text{O}_4$ (%): C, 58.97; H, 3.49. Found(%): C, 59.03; H, 3.51. IR (KBr, cm^{-1}): ν_{max} 1 272 (CF_3). ^1H NMR (400 MHz, CDCl_3): δ 7.58 (s, 1H, ArH), 7.43 (s,

2H, ArH), 6.94 (s, 2H, ArH), 4.60 (d, $J=13.2$ Hz, 1H, ArCH_2Ar), 4.12 (q, $J=7.0$ Hz, 2H, CH_2), 3.35 (d, $J=13.3$ Hz, 1H, ArCH_2Ar), 1.63~1.50 (m, 8H, CH_3).

1.5 General procedure for UV-Vis study and fluorescence study

Standard stock solutions ($0.01\text{ mol}\cdot\text{L}^{-1}$) of metal acetate salts and chloride salts (NaCl , KCl , CsCl , $\text{Cu}(\text{Ac})_2\cdot\text{H}_2\text{O}$, $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$, $\text{Zn}(\text{Ac})_2$, $\text{Mg}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$, $\text{Cd}(\text{Ac})_2\cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$, FeCl_3 , CaCl_2) were prepared in CH_3OH . The stock solutions ($0.1\text{ mmol}\cdot\text{L}^{-1}$) of compounds **1**~**3** were prepared with CH_2Cl_2 . The solution concentration of compounds **1**~**3** is $5\text{ }\mu\text{mol}\cdot\text{L}^{-1}$ with different concentrations of metal ions in the mixed solvent ($V_{\text{CH}_2\text{Cl}_2}:V_{\text{CH}_3\text{OH}}=1:1$) in the titration experiments for UV-Vis and fluorescent studies.

1.6 X-ray diffraction data collection and refinement

Crystallographic data for **1** and **2** were collected at room temperature on a Bruker Smart CCD area detector diffractometer equipped with a graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\text{ 073 nm}$) by ω - 2θ scan mode. All absorption corrections were

applied using the SADABS program^[25]. The Lp factor and empirical absorption were performed to correct the data, and to restore the data and correct the unit cell parameters by using SANIT and SMART software. The structures were solved by direct method and refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package^[26]. All non-hydrogen

atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed geometrically and were refined in a riding-model approximation. The crystallographic data of compound **1** and **2** are summarized in Table 1.

CCDC: 1900304, **1**; 1900303, **2**.

Table 1 Crystallographic data for compounds **1** and **2**

Compound	1	2
Empirical formula	C ₆₄ H ₅₂ F ₁₂ O ₄	C ₆₀ H ₅₂ F ₄ O ₄
Formula weight	1 113.06	913.02
Temperature / K	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a / nm	1.293 25(8)	1.371 7(3)
b / nm	1.534 64(9)	1.835 8(4)
c / nm	1.859 67(11)	1.899 4(4)
α / (°)	83.141(2)	
β / (°)	86.122(2)	95.660(7)
γ / (°)	71.506(2)	
Volume / nm ³	3.473 4(4)	4.759 8(17)
Z	2	4
D_c / (g·cm ⁻³)	1.064	1.274
$F(000)$	1 152	1 920
Absorption coefficient / mm ⁻¹	0.087	0.089
θ range for data collection / (°)	1.10~27.56	2.07~27.89
Reflection collected	54 847	24 449
Unique reflection	15 893	5 497
R_{int}	0.044 4	0.049 3
Data, restraint, parameter	15 893, 2, 726	5 497, 0, 300
Goodness-of-fit on F^2	1.346	1.047
R_1 indices [$I > 2\sigma(I)$]	0.128 5	0.066 3
wR_2 indices (all data)	0.414 2	0.210 2
Largest diff. peak and hole / (e·nm ⁻³)	949 and -527	544 and -355

2 Results and discussion

2.1 Synthesis of compounds **1**~**3**

Modifying up-rim of calix[4]arene was implemented according to the Scheme 1. Compound **a** as raw materials can be prepared by published procedure^[27]. Thus, the Suzuki coupling reaction of tetrabromocalix[4]arene with fluorine-containing phenylboronic acid produced fluorine-containing calix[4]arene derivatives. The structures of compounds **1**~**3** were proved by

respective IR, X-ray diffraction and ¹H NMR spectra.

¹H NMR spectroscopy can be used as a marker to identify the conformation of calix [4]arene derivatives because there are different characteristics with different conformations in ¹H NMR spectra^[28-30]. The conical conformation of the compound **1** can be confirmed by the presence of doublets at δ of 3.31 and 4.59 as an AB type proton signal of ArCH₂Ar in the ¹H NMR spectra. In the ¹H NMR spectra of compound **2**, there were two doublets at δ of 3.26 and

4.45 for ArCH_2Ar , which confirmed the compound **2** is in the cone conformation. Compound **3** adopts the cone conformation due to the proton signal of methylene bridges at δ of 3.35 and 4.60 in ^1H NMR spectra. The IR spectra of compounds **1**~**3** show characteristic bands at $1\,328\text{ cm}^{-1}$ (CF_3), $1\,227\text{ cm}^{-1}$ (Ar-F) and $1\,272\text{ cm}^{-1}$ (CF_3), respectively.

2.2 Single crystal structure

We successfully obtained colorless single crystals of compounds **1** and **2** from the mixed solvent (ethyl acetate/petroleum ether) and collected their structure data by single crystal X-ray diffractometer. As shown in Fig.1 and 2, X-ray diffraction analysis revealed that compound **1** and **2** adopts conical conformations. Single crystals suitable for X-ray diffraction analysis of **3** were not obtained presently.

Compound **1** shows an asymmetric distorted cone

conformation, in which the relatively long distance between the aromatic ring $\text{C1}\cdots\text{C6}$ and $\text{C29}\cdots\text{C34}$ is about 1.44 nm, and the short distance between the aromatic ring $\text{C15}\cdots\text{C20}$ and $\text{C43}\cdots\text{C48}$ is about 0.37 nm (Fig.1). The nearest distance (0.37 nm) is attributed to the strong π - π stacking interactions in **1**. The distance about 0.49 nm between the aromatic ring $\text{C21}\cdots\text{C26}$ and $\text{C49}\cdots\text{C54}$ displays hardly the π - π stacking interactions. The aromatic ring $\text{C21}\cdots\text{C26}$ are rotated relative to the aromatic ring $\text{C15}\cdots\text{C20}$, and torsion angle of C19-C18-C21-C26 is 37.2° . Similarly, torsion angle of C45-C46-C49-C50 is 40.5° .

Compound **2** with a cone conformation was obtained through substituents of 4-fluorophenyl groups on upper rim, similar to compound **1**. The distance between the aromatic rings $\text{C1}\cdots\text{C6}$ and $\text{C1A}\cdots\text{C6A}$ is about 0.35 nm, which results from strong π - π

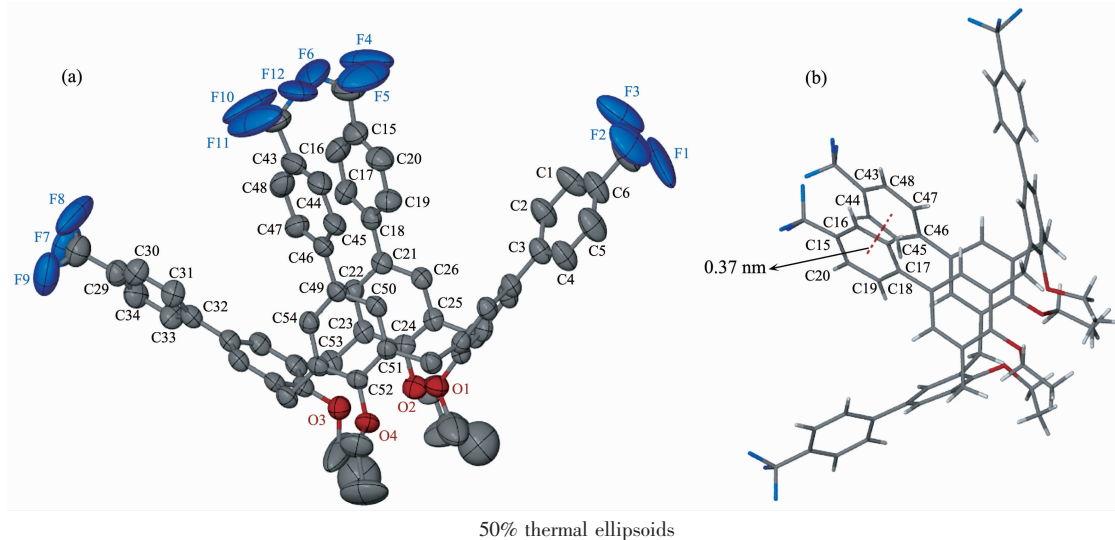
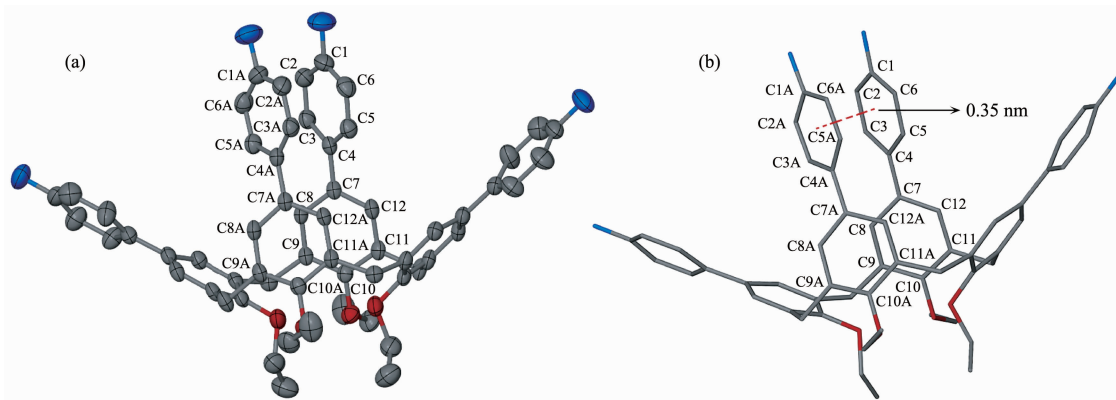


Fig.1 Crystal structure (a) and π - π stacking interaction (b) of compound **1**



All hydrogen atoms are omitted for clarity; 50% thermal ellipsoids; Symmetry codes: A: $2-x, y, 1/2-z$

Fig.2 Crystal structure (a) and π - π stacking interaction (b) of compound **2**

interactions in **2** (Fig.2). Torsion occurs between fluorophenyl-substituted aromatic rings C1...C6 and C7...C12, and torsion angle of C3-C4-C7-C8 is about 45.3°.

2.3 UV-Vis spectroscopic studies

Calix[4]arenes are considered to be perfect compounds for forming stable complexation with metal ions, such as Fe³⁺, Ni²⁺, Cu²⁺. Therefore, we studied and explored the fluorinated calix[4]arene for binding ability. The titration experiments were implemented to explore the interplay of compounds **1**~**3** with various metal ions and investigate its selectivity.

As shown in Fig.3, it can be found that the maximum ultraviolet absorption wavelength of compounds **1**~**3** are in a range of 220~270 nm in the mixed solvent ($V_{\text{CH}_2\text{Cl}_2}:V_{\text{CH}_3\text{OH}}=1:1$). The ultraviolet spectrum of compound **1** displayed strong peaks at 230 and 270 nm owing to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. There

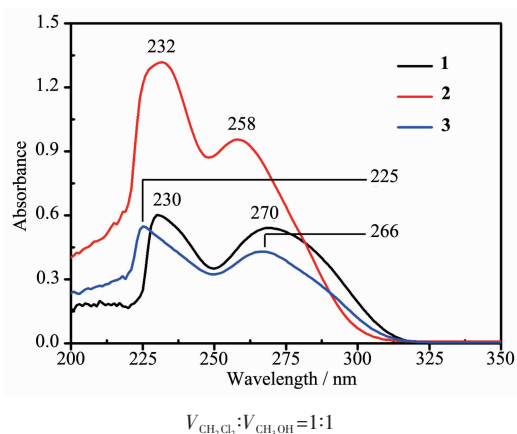


Fig.3 UV-Vis spectra of compounds **1**~**3** in mixed solvent CH₂Cl₂/CH₃OH

were two peaks at 232 and 258 nm in the ultraviolet spectrum of compound **2**, and the UV-Vis spectrum of **3** exhibited strong peaks at 225 and 266 nm.

The selectivity of **1**~**3** in mixed solvent (5 $\mu\text{mol} \cdot \text{L}^{-1}$) to different metal ions (0.5 $\text{mmol} \cdot \text{L}^{-1}$, excepted Fe³⁺) was preliminarily measured by UV-Vis spectroscopy. The wavelength with maximum absorbance upon the metal ion addition was listed in Table 2. On the basis of titration experiments, compound **1** exhibited a new band at 361 nm after adding Fe³⁺ (10 equiv.) (Fig.4). After adding copper ions (100 equiv.), the new band appeared at 246 nm while the original peaks disappeared as shown in Fig.4. Compared with the compound **1** in the absence of metal ions, the absorbance of the band enhanced greatly. Other metal ions, unlike iron or copper ions, only caused slight changes in absorption bands. Moreover, the color of

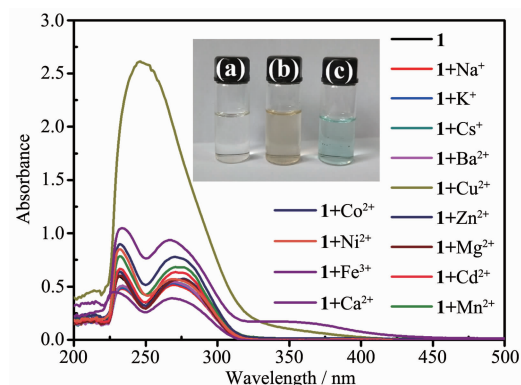


Fig.4 UV-Vis spectra of **1** with different metal ions (100 equiv. excepted Fe³⁺) in the mixed solvent CH₂Cl₂/CH₃OH

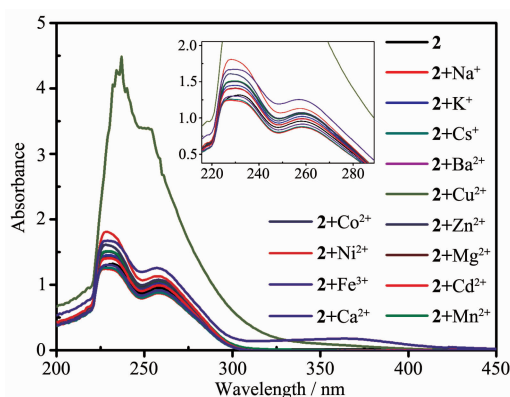
Table 2 Maximum absorbance wavelength of compounds **1**~**3** after titration with metals ions

Compound	$\lambda_{\text{max}} / \text{nm}$													
	Blank	Na ⁺	K ⁺	Cs ⁺	Ba ²⁺	Cu ²⁺	Zn ²⁺	Mg ²⁺	Cd ²⁺	Mn ²⁺	Co ²⁺	Ni ²⁺	Fe ³⁺	Ca ²⁺
1	230	234	234	234	234	246	232	232	232	232	232	232	234	229
	270	270	270	270	270		277	276	271	271	274	270	267	268
2	232	228	230	227	229	237	230	230	230	229	228	228	229	229
	258	258	258	258	258	240	258	258	258	258	258	258	257	258
3	225	227	227	227	229	246	230	230	230	230	226	226	226	230
	266	267	267	267	267		268	267	267	266	266	266	262	267
													361	
													362	

* $c_1 \sim c_3 = 5 \mu\text{mol} \cdot \text{L}^{-1}$, $c_{\text{Fe}^{3+}} = 50 \mu\text{mol} \cdot \text{L}^{-1}$, concentration of other metal ions: 0.5 $\text{mmol} \cdot \text{L}^{-1}$

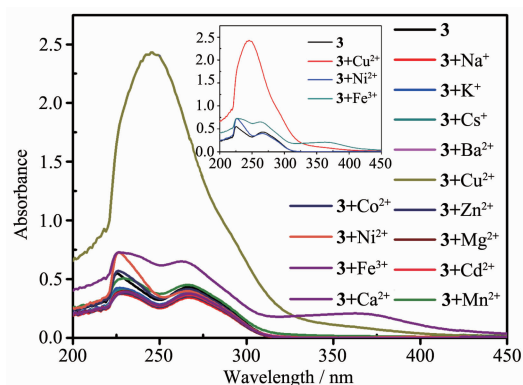
compound **1** changed to yellow green after adding Cu^{2+} for 24 h (Fig.4). The result reflects that **1** is more selective for Cu^{2+} ions.

The UV-Vis spectrum of compound **2** exhibited a significant increase of absorbance with the addition of Cu^{2+} (Fig.5), and the bands shifted to 237 nm. The change of bands indicates that compound **2** has the ability to interact with copper ions. With the addition of nickel ions, the absorbance of compound **3** enhanced remarkably at 226 nm and decreased at 266 nm, although the absorption bands did not shift significantly (Fig.6). In the presence of iron ions, the spectra showed gentle absorption peaks. In addition, it



$V_{\text{CH}_2\text{Cl}_2}:V_{\text{CH}_3\text{OH}}=1:1$; Inset: enlarged drawing of wavelength range of 200~350 nm

Fig.5 UV-Vis spectra of compound **2** with different metal ions (100 equiv., excepted Fe^{3+}) in the mixed solvent $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$



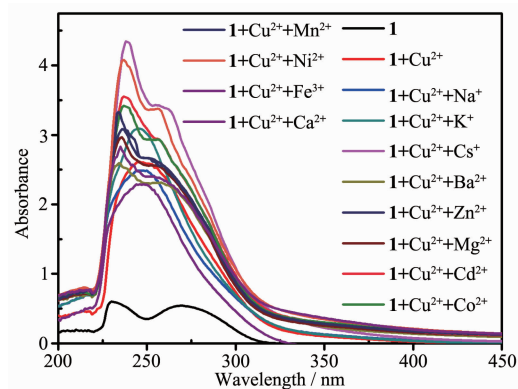
$V_{\text{CH}_2\text{Cl}_2}:V_{\text{CH}_3\text{OH}}=1:1$; Inset: UV-Vis spectra of **3** alone, **3** with Cu^{2+} , **3** with Ni^{2+} , **3** with Fe^{3+}

Fig.6 UV-Vis spectra of compound **3** with different metal ions (100 equiv., excepted Fe^{3+}) in the mixed solvent $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$

was visible that the new absorption band appeared at 246 and 362 nm, respectively, after copper and iron ions were added in the solution of compound **3** as shown in Fig.6. The results show that copper ions, iron ions and nickel ions can interact with compound **3**, especially copper ions have the most pronounced response.

Compounds **1~3** show different binding abilities to metal ions, which possibly result from the following two factors: different substituents and substitution sites on the upper edge of calix[4]arenes. It can be seen that the factors affecting the selectivity of ligands to metal ions are not only the hard or soft properties of metal ions, but also the radius of ions, the size of holes and even the conformation of compounds. Many factors lead to the selectivity of different compounds to specific ions^[31-35].

The selectivity of compounds **1~3** to copper ions was tested in existence of interfering ions by experiments adding Cu^{2+} ions and the other ions (1:1) (Fig. 7~9). It was found that other ions did not obviously interfere absorption spectra of the compounds with Cu^{2+} . In addition, the interference of other ions on the binding of compound **3** to iron ions was also examined (Fig.10). Other ions except Cu^{2+} did not affect the absorption spectra of compound **3** with iron ions. Adding copper ions broke down the binding of compound **3** to iron ions, which may be due to the higher binding efficiency of compound **3** to copper ions.



$V_{\text{CH}_2\text{Cl}_2}:V_{\text{CH}_3\text{OH}}=1:1$

Fig.7 Interference test of other ions on compound **1** with Cu^{2+} in the mixed solvent $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$

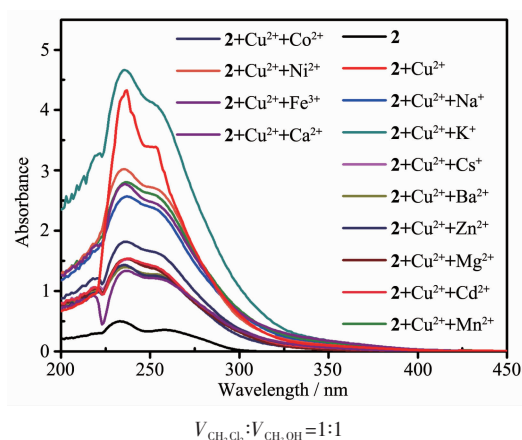


Fig.8 Interference test of other ions on compound **2** with Cu^{2+} in the mixed solvent $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$

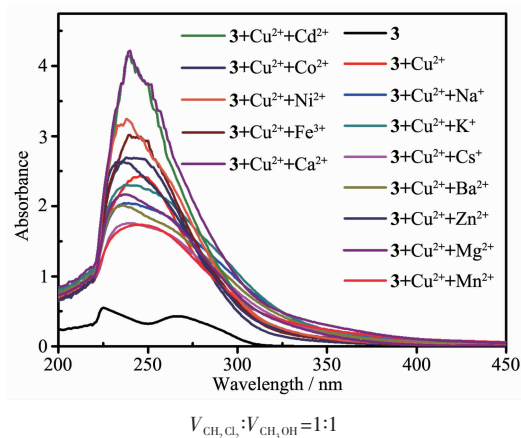


Fig.9 Interference test of other ions on compound **3** with Cu^{2+} in the mixed solvent $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$

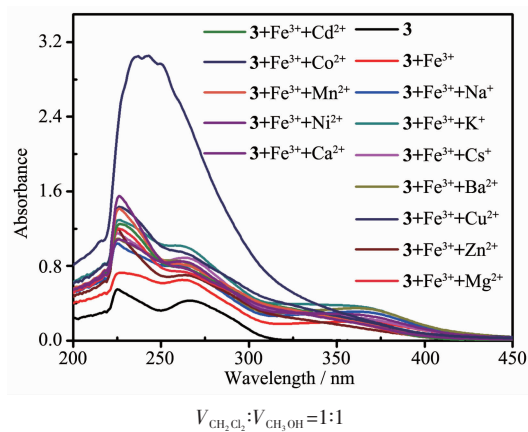


Fig.10 Interference test of other ions on compound **3** with Fe^{3+} in the mixed solvent $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$

2.4 Fluorescence studies

The fluorescence spectra of compounds **1~3** ($5 \mu\text{mol} \cdot \text{L}^{-1}$) were measured as shown in Fig.11. The emission peak of **1** was 360.4 nm under the excitation

of 294 nm, and there was a fluorescence peak of **2** at 348.4 nm when the exciting wavelength is 289 nm, while that of **3** was at 383.0 nm with excitation at 292 nm. The results from the fluorescence spectroscopy show that there is similarity in the optimum excitation wavelengths of the compounds.

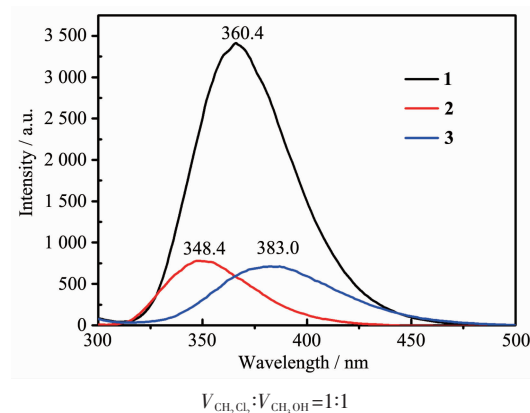


Fig.11 Fluorescence spectra of compounds **1~3** in the mixed solvent $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$

The binding of compounds **1~3** ($5 \mu\text{mol} \cdot \text{L}^{-1}$) towards various ions (100 equiv., excepted Fe^{3+}) was tested by fluorescence spectroscopy as showed in Fig. 12~14. The results of tests are consistent with those of ultraviolet spectra. The fluorescence intensity of compound **1** decreased sharply after adding copper ions, and there was obvious quenching in emission. The intensity of compound **2** decreased obviously in the existence of Cu^{2+} ions, while the other ions did not lead to remarkable changes. In the existence of copper and iron ions, the fluorescence intensity of compound **3** decreased. The intensity of compound **3**

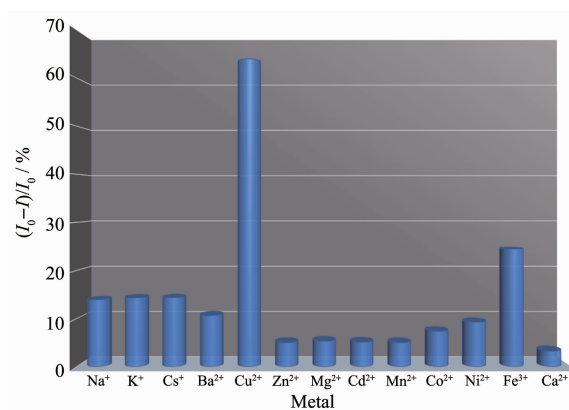


Fig.12 Selectivity of compound **1** towards Cu^{2+} upon addition of various metal ions

towards Cu^{2+} showed stronger quenching than that of compound **3** to Fe^{3+} . Compound **3** is more compatible to Cu^{2+} than Fe^{3+} . Upon addition of metal ions (100 equiv., except Fe^{3+}), all metal ions more or less affect the emission intensity of compounds **1~3** despite no changing in the band of compound **1~3**. In particular, the addition of copper and iron ions causes remarkable quenching in emission intensity. These results indicate that **1** and **2** only show high selectivity to Cu^{2+} , and **3** is highly selective to iron and copper ions due to their different groups.

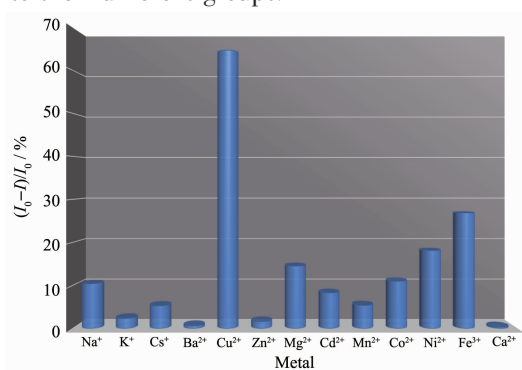


Fig. 13 Selectivity of compound **2** towards Cu^{2+} upon addition of various metal ions

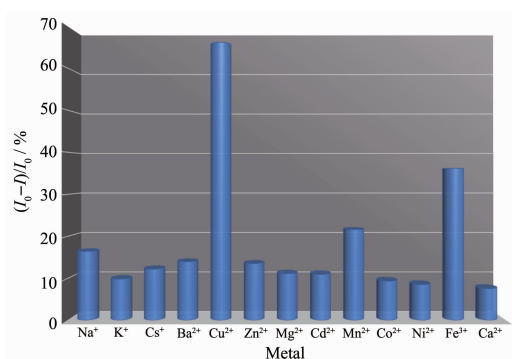


Fig. 14 Selectivity of compound **3** towards Cu^{2+} and Fe^{3+} upon addition of various metal ions

The selectivity of compounds **1~3** towards Cu^{2+} is further studied. The fluorescence quenching of compound **2** is more prominent, *i.e.* “Off state” (Fig. 13), compared to “On state” (Fig. 11), which has the highest selectivity to copper ions among compounds **1~3**. Quenching of fluorescence in emission caused by Cu^{2+} is owing to reverse photo-induced electron transfer (reverse PET)^[36-37].

In order to further observe the practical applicability of compounds **1~3** as fluorescent sensors

for Cu^{2+} or Fe^{3+} , we explored the interference of other ions. The competitive experiments were carried out on compounds **1~3** in the presence of copper ions (100 equiv.) or iron ions (10 equiv.) with an equal proportion of co-existing ions (Fig. 15~18). The results show that

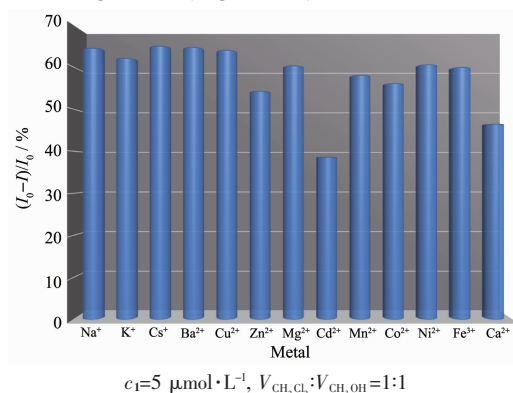


Fig. 15 Competitive selectivity of compound **1** towards Cu^{2+} in the presence of different cations in the mixed solvent $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$

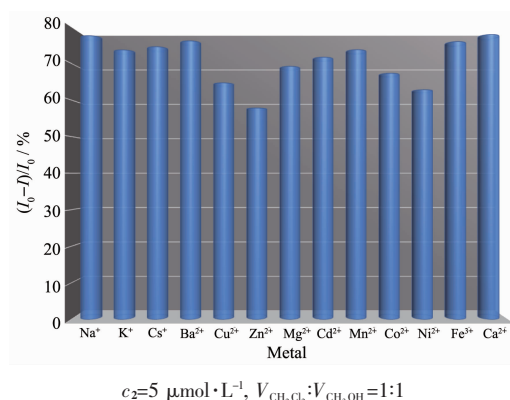


Fig. 16 Competitive selectivity of compound **2** towards Cu^{2+} in the presence of different cations in the mixed solvent $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$

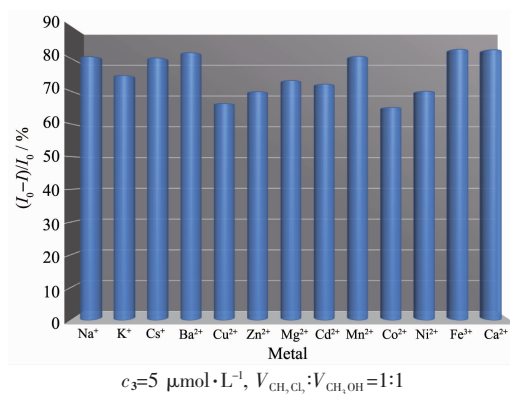


Fig. 17 Competitive selectivity of compound **3** towards Cu^{2+} in the presence of different cations in the mixed solvent $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$

the fluorescence responses of compounds **1**~**3** to copper ions do not change significantly in the existence of other ions, and the fluorescence response of compound **3** to iron ions except copper ions shows small changes.

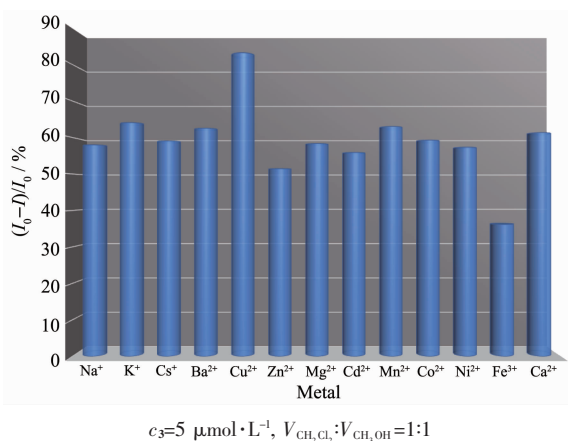


Fig.18 Competitive selectivity of compound **3** towards Fe³⁺ in the presence of different cations in the mixed solvent CH₂Cl₂/CH₃OH

3 Conclusions

In conclusion, we synthesized fluorinated calix[4]arene derivatives **1**~**3** in the cone conformation. The calix[4]arene derivatives were characterized by ¹H NMR, FT-IR, UV-Vis, fluorescence spectra analysis and so on. Compounds **1**~**3** show high significant selective nature to copper ions, which is indicated by UV-Vis and fluorescence techniques. The ultraviolet intensity of compounds **1**~**3** increased, new bands appeared and fluorescence quenching occurred in the presence of copper ions. At the same time, compound **3** exhibits higher selectivity to copper ions than iron ions. This kind of molecular switch may be utilized as a Cu²⁺ selective sensor.

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