

# Novel Fluorescent Molecular Clips: Selective Recognition Towards Fe<sup>3+</sup> in Aqueous Solution

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**Abstract** In this paper, we report the synthesis, characterization and Fe<sup>3+</sup>-sensing properties of a series of new artificial fluorescent molecular clips, and structure of clip **1** is confirmed by X-ray crystallography. All these molecular clips had the ability to bind and sense Fe<sup>3+</sup> selectively through decrease fluorescence responses in THF-MeOH-Water. Fluorimetric titration experiment indicated that the quenching of these compounds' fluorescence upon Fe<sup>3+</sup> probably arises from the electron/energy transfer between Fe<sup>3+</sup> and the excited chemosensors. The limit of detection, linear concentration range and selectivity of the fluorescent molecular clips were evaluated in this study as well.

**Keywords** Chemosensor · Fluorescence quenching · Fe<sup>3+</sup> · Diethoxycarbonyl glycoluril derivative

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## Introduction

Iron is an essential element for nearly all living systems. It is a catalyst in some important biological processes such as oxygen metabolism and synthesis of DNA and RNA [1–3]. Abnormal level of iron could be related to some serious diseases, such as Huntington's, Parkinson's and Alzheimer's diseases [4]. Therefore, it is necessary to develop accurate and rapid detection methods to selectively detect and quantify iron in environmental and biological samples.

The past decade has witnessed significant advances in the development of fluorescent chemical sensors for Fe<sup>3+</sup> ion [5–13]. Fluorescence has an intrinsic advantage of 'zero background' that can be translated into high sensitivity, but selectivity is a nagging problem as other metal ions can elicit a nonspecific turn-off quenching response. Among the reported fluorescent sensors for Fe<sup>3+</sup>, some of them were interfered by other transition metals cations such as Cu<sup>2+</sup> or Cr<sup>3+</sup> [14–17]. Grabchev et al. proposed a sensitive and convenient fluorimetric procedure for the determination of Fe<sup>3+</sup> with bis-1, 8-naphthalimide as the fluorogenic reagent, which was unfortunately interfered by Cr<sup>3+</sup> [14].

Recently, glycoluril has received considerable attention for its potential to synthesize highly efficient and selective receptors [18–22]. In a previous study we described the glycoluril molecular clips exhibited selective fluorescent quenching for Fe<sup>3+</sup> in the THF-MeOH [18]. It seems reasonable that the weak noncovalent interactions in the system are crucial for the molecular recognition. The polarized carbonyl groups and the electron-rich nitrogen atoms in the cavity of glycoluril may play an important role in such interactions. Those molecular clips are believed to bind metal ions by means of coordination interaction and

the so-called ‘cavity-effect’ [20]. In addition, drastic changes in their photophysical properties of the molecular clips can be observed in the intramolecular charge transfer [23, 24].

Seeking to confirm our hypothesis and develop new fluorescence sensors, we reasoned that modifying the size and electron density of the sidewall group of the clips would allow a facile synthesis of various derivatives and influence the guest binding. Herein we present the design, synthesis, and characterization of a series of fluorescent molecular clips **1–3** as shown in Scheme 1. All of those clips displayed a highly selective and sensitive fluorescent response towards  $\text{Fe}^{3+}$  in THF-MeOH-Water (9:1:10, v/v/v).

## Experimental

### Reagents

All starting materials and catalysts were obtained commercially and used without further purification. Most of the solvents were distilled under  $\text{N}_2$  over appropriate drying reagents (sodium or calcium hydride). THF and MeOH in chromatographic grade and newly double-distilled water were used throughout the experiments. Some manipulations were performed under an argon atmosphere by standard Schlenk techniques. Whenever possible, reactions were monitored by thin-layer chromatography polygram SIL G/UV254 0.2 mm silica gel with fluorescent indicator. Column chromatography: silica gel 200–300 mesh. KCl,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{HgCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{CrCl}_3$ , while  $\text{AgNO}_3$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Bi}(\text{NO}_3)_3$  and  $\text{La}(\text{NO}_3)_3$  were employed as sources for metal cations.

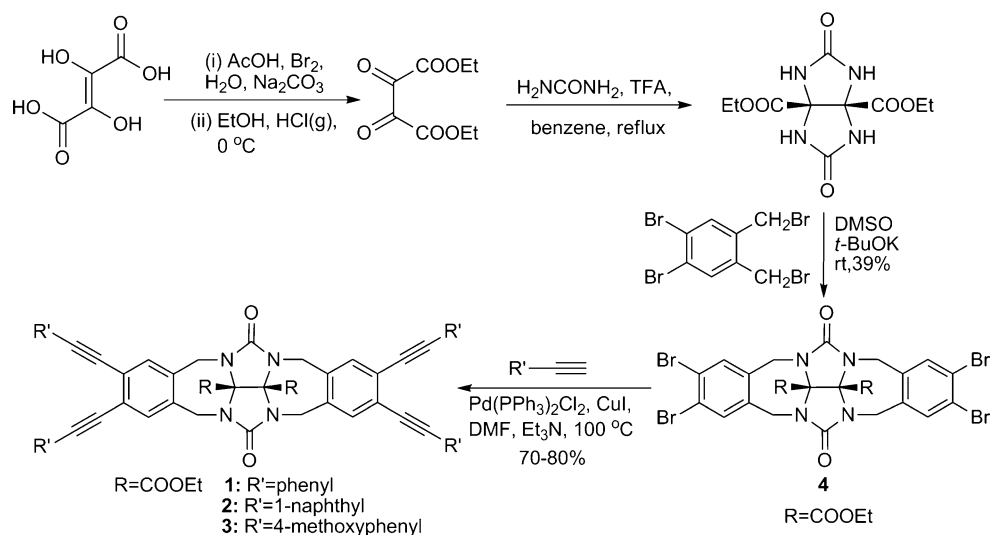
### Apparatus

Absorption spectra were determined on an UV-2501 PC spectrophotometer. Fluorescence spectra measurements were performed on a FluoroMax-P spectrofluorimeter equipped with a 150 W xenon discharge lamp, 1 cm quartz cells at room temperature (about 298 K). Typical scanning parameters were integration time of 0.1 s per point, intervals of 1 nm, and excitation/emission slits set at 2 nm. NMR spectra were measured on a Varian Mercury 400 spectrometer operating at 400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$  relative to tetramethylsilane as an internal standard. MS spectra were obtained on a Finnigan Trace MS spectrometer or by the ESI method on a Quattro LCZ instrument (Waters-Micromass, Manchester, UK) with nanospray inlet. IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption reported in  $\text{cm}^{-1}$ . The X-ray crystal structure determination of **1** was obtained on a Bruker SMART APEX CCD system. Melting points were determined on an XT-4A Meltemp apparatus and were uncorrected.

### Synthesis of **4**

The synthesis of **4** is shown in Scheme 1, and diethoxycarbonyl glycoluril was prepared according to a reported procedure [25]. Diethoxycarbonyl glycoluril (2.86 g, 10 mmol) was dissolved in anhydrous DMSO (40 mL) under argon, and *t*-BuOK (4.48 g, 40 mmol) was added. After the reaction had been stirred for 15 min, 1, 2-dibromomethyl-4, 5-dibromo benzene (8.44 g, 20 mmol) was added in one portion and the stirring continued for another 6 h. The reaction mixture was poured into 0.1N HCl (1 L) and extracted with EtOAc ( $3 \times 400$  mL). The extracts were washed with brine and dried over anhydrous  $\text{MgSO}_4$ . After

**Scheme 1** Synthetic routes to compounds **1–3** from Bis(ethoxycarbonyl)glycoluril



filtration and rotary evaporation, the residue was purified by flash chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>) to give **4** (3.14 g, 39%) as a white solid.

**4** M.p.: >300°C. IR ( $\nu_{\max}$ , KBr, cm<sup>-1</sup>): 2924, 2854, 1738, 1722, 1566, 1449, 1,422 s, 756, 690. <sup>1</sup>H NMR (*d*<sub>6</sub>-DMSO),  $\delta$  (ppm): 7.99 (s, 4H, Ar–H), 5.21 (d, *J*=16.0 Hz, 4H, CH<sub>2</sub>), 4.64 (d, *J*=16.0 Hz, 4H, CH<sub>2</sub>), 4.26 (q, *J*=6.8 Hz, 4H, COOCH<sub>2</sub>CH<sub>3</sub>), 1.27 (t, *J*=6.8 Hz, 6H, COOCH<sub>2</sub>CH<sub>3</sub>). ESI mass spectrometry: *m/z* 807 (100% [M + H]<sup>+</sup>); M<sup>+</sup> calculated 806.

#### General Procedure for Preparing Compounds 1, 2 and 3

**Compound 1:** To a solution of bis(triphenylphosphine) palladium(II) dichloride (35.1 mg, 0.05 mmol), copper(I) iodide (19.1 mg, 0.1 mmol) and compound **4** (403 mg, 0.5 mmol) in DMF (50 ml) and Et<sub>3</sub>N (5 ml) under argon was added phenylacetylene (408 mg, 4 mmol). After stirring at 100°C for 14 h, the solvent was evaporated in vacuo and palladium salts were eliminated through a short column of SiO<sub>2</sub>(CHCl<sub>3</sub>/CH<sub>3</sub>OH, 25:1). The crude product was purified by column chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>) to give **1** (356 mg, 0.4 mmol, 80%) as a white solid.

- M.p.: 268–269°C. IR ( $\nu_{\max}$ , KBr, cm<sup>-1</sup>): 2922, 2852, 1757, 1725, 1570, 1455, 1421, 1252, 755, 688. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 7.51–7.28(m, 24H, Ar–H), 4.80 (d, *J*=16.4 Hz, 4H, CH<sub>2</sub>), 4.44 (d, *J*=16.4 Hz, 4H, CH<sub>2</sub>), 4.33 (q, *J*=7.2 Hz, 4H, COOCH<sub>2</sub>CH<sub>3</sub>), 1.36 (t, *J*=7.2 Hz, 6H, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 165.6, 155.5, 136.0, 132.8, 131.6, 128.4, 128.3, 125.6, 123.1, 94.4, 87.7, 79.9, 63.5, 45.0, 14.0. ESI mass spectrometry: *m/z* 891 (100% [M + H]<sup>+</sup>); M<sup>+</sup> calculated 890.
- M.p.: >300°C. IR ( $\nu_{\max}$ , KBr, cm<sup>-1</sup>): 3054, 297, 1757, 1722, 1584, 1457, 1424, 1255, 1134, 1017, 799, 773. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 8.42 (d, *J*=8.8 Hz, 4H, Ar–H), 7.78 (d, *J*=8.8 Hz, 4H, Ar–H), 7.77–7.66 (m, 12H, Ar–H), 7.38–7.30 (m, 8H, Ar–H), 7.02–6.97 (m, 4H, Ar–H), 4.91 (d, *J*=16.0 Hz, 4, CH<sub>2</sub>), 4.52 (d, *J*=16.0 Hz, 4H, CH<sub>2</sub>), 4.37 (q, *J*=6.8 Hz, 4H, COOCH<sub>2</sub>CH<sub>3</sub>), 1.40 (t, *J*=6.8 Hz, 6H, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 165.7, 155.6, 136.3, 133.2, 133.1, 132.9, 130.9, 129.0, 127.9, 126.8, 126.5, 126.3, 125.6, 125.1, 120.5, 92.6, 92.5, 80.0, 63.6, 45.1, 14.1. ESI mass spectrometry: *m/z* 1113 ([M + Na]<sup>+</sup>); M<sup>+</sup> calculated 990.
- M.p.: 293–294°C. IR ( $\nu_{\max}$ , KBr, cm<sup>-1</sup>): 2976, 2838, 2208, 1759, 1724, 1603, 1514, 1458, 1290, 1250, 1176, 1026, 830. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 7.43 (s, 4H, Ar–H), 7.42 (d, *J*=8.4 Hz, 8H, Ar–H), 6.83 (d, *J*=8.4 Hz, 8H, Ar–H), 4.78 (d, *J*=16.0 Hz, 4H, CH<sub>2</sub>), 4.42 (d, *J*=16.0 Hz, 4H, CH<sub>2</sub>), 4.32 (q, *J*=7.2 Hz, 4H, COOCH<sub>2</sub>CH<sub>3</sub>), 3.80 (s, 12H, CH<sub>3</sub>), 1.36 (t, *J*=7.2 Hz, 6H, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 165.7,

159.7, 155.5, 135.6, 133.1, 132.6, 125.7, 115.4, 114.0, 94.4, 86.7, 80.0, 63.5, 55.3, 45.1, 14.0. ESI mass spectrometry: *m/z* 1012 ([M + H]<sup>+</sup>); M<sup>+</sup> calculated 1011.

#### X-ray Diffraction Analysis of Compound 1

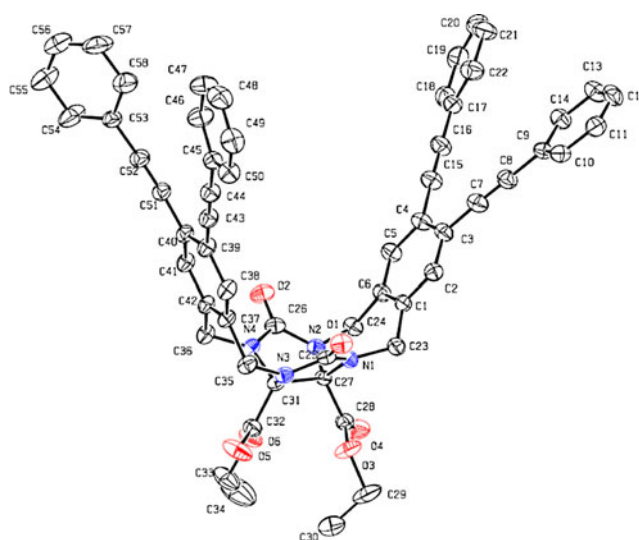
The crystals of **1** that were suitable for X-ray crystal structure analysis were grown by slow evaporation of solutions of the compounds in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>CN (20:1, *v/v*) mixture. Details of the crystal data are available in the archive of Cambridge Crystallographic Data Centre with Supplementary Publication No. CCDC 779333.

#### General Procedures for Determination of Spectroscopic and Photophysical Properties

A 1.0 × 10<sup>-5</sup> M of stock solution of **1** was prepared in THF-MeOH (9:1, *v/v*). The cationic stocks were all in THF-MeOH-Water (9:1:10, *v/v/v*) with a concentration of 3.0 × 10<sup>-3</sup> M for fluorescence and UV-Vis spectra analysis. Each time a 3 mL solution of **1** was filled in a quartz cell of 1 cm optical path length, and different stock solutions of cations were gradually added into the quartz cell with the help of a micro-syringe. Excitation wavelength was 320 nm and the temperature was 25°C. Spectral analysis of model compounds **2** and **3** was the same as that of **1**, but the excitation wavelength was 353 nm for **2** and 329 nm for **3**.

Fluorescence quantum yield values were determined by comparing the emission intensity of the samples with that of a fluorescence standard with the following equation:

$$\Phi_u = \Phi_s \times A_s \times F_u \times n^2 / A_u \times F_s \times n_0^2$$



**Fig. 1** The crystal structure of **1**. Hydrogen atoms and solvent molecules omitted for clarity

**Table 1** Parameters obtained from the photophysical characterizations of compounds **1–3** in THF

Compound	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm)	$\Delta\lambda_{\text{ST}}$ (nm)	$\Phi_{\text{F}}^a$
1	320	365	45	0.51
2	353	402	49	0.74
3	329	383	54	0.83

<sup>a</sup>  $\Phi_{\text{F}}$ : Quantum Yields referenced to quinine that has a reported quantum yield of 0.546 in 0.5 M aqueous sulfate as a standard

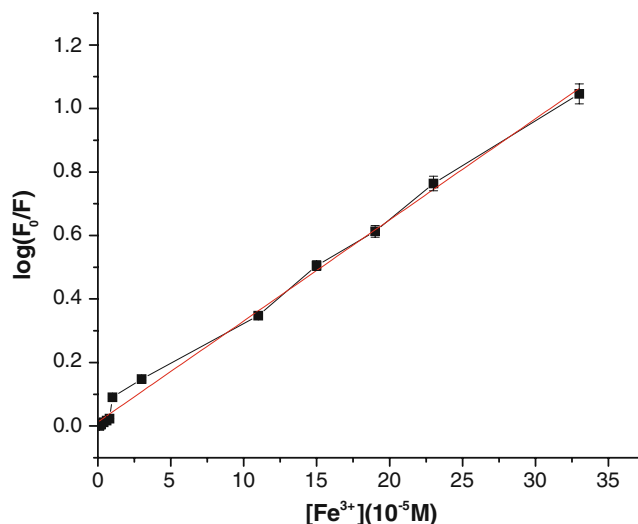
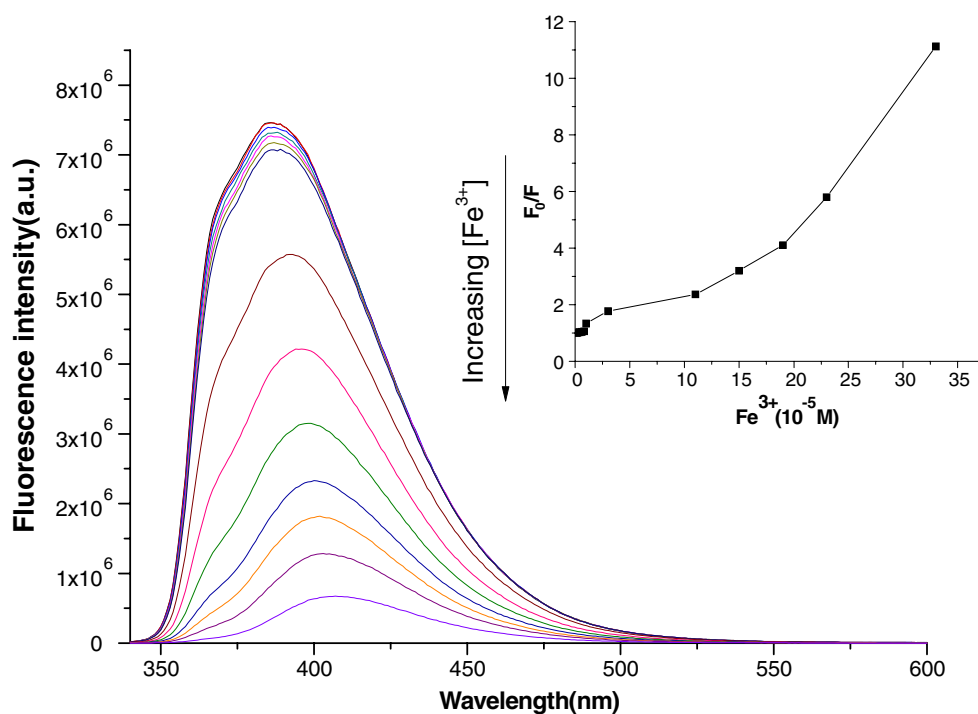
where  $\Phi_{\text{u}}$  and  $\Phi_{\text{s}}$  denote quantum yield of the sample and reference,  $F_{\text{u}}$  and  $F_{\text{s}}$  are the integrated area under the corrected fluorescence spectra of the sample and reference,  $A_{\text{u}}$  and  $A_{\text{s}}$  are the absorbance of the sample and reference,  $n$  and  $n_0$  are the refractive indexes of the solvents used in the sample and reference, respectively. Fluorescence quantum yield of the reference, the quinine sulfate dihydrate in sulfuric acid (0.1 N), was used as a standard ( $\Phi_{\text{s}}=0.546$ ) [22, 26].

## Results and Discussion

### Synthesis and Structural Characteristics of Molecular Clips

The fluorescent molecular clips **1–3** were synthesized in excellent yield from compound **4** and terminal aryl alkynes by using Sonogashira cross-coupling reaction (Scheme 1) [27, 28]. Their molecular structures were confirmed by infrared, NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) and mass spectrometry.

**Fig. 2** Fluorescent spectra (excitation at 329 nm) of **3** (10  $\mu\text{M}$ ) in THF-MeOH (9:1, v/v) in the presence of 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 3.0, 11.0, 15.0, 19.0, 23.0, 33.0 equiv of  $\text{Fe}^{3+}$  predisolved in THF-MeOH-Water (9:1:10, v/v/v); Inset: Stern-Volmer plot for interaction between **3** and  $\text{Fe}^{3+}$  ions



**Fig. 3** Modified Stern–Volmer relationship between **3** and  $\text{Fe}^{3+}$  ion

In addition, the structure and conformation of **1** were determined by single crystal X-ray diffraction (Fig. 1). The X-ray crystallographic analysis of **1** indicates that it possesses a deep cavity defined by two aromatic sidewalls with aryl alkyne conjugated to the benzene moieties of this molecule. In fluorescent molecular clip **1**, the carbonyl groups of the glycoluril moiety, which are hydrogen-bond acceptor sites, are separated by 5.7 Å. The dihedral angle between the two phenyl rings of the sidewalls is 52.01°, and the distance between the centroids of the two phenyl rings of the sidewalls amounts to 6.9 Å. The length of the cavity arm is 10 Å and the height of the cavity is 8.6 Å.

**Table 2** Analytical parameters for the determination of Fe<sup>3+</sup>

Compound	Linear range (mol L <sup>-1</sup> )	Detection limit (mol L <sup>-1</sup> )	Correlation coefficient	Binding constant (M <sup>-1</sup> )
1	9.7×10 <sup>-7</sup> –3.5×10 <sup>-4</sup>	9.4×10 <sup>-7</sup>	0.9959	1.31×10 <sup>4</sup>
2	9.6×10 <sup>-7</sup> –3.7×10 <sup>-4</sup>	9.1×10 <sup>-7</sup>	0.9972	9.63×10 <sup>3</sup>
3	8.5×10 <sup>-7</sup> –4.9×10 <sup>-4</sup>	7.3×10 <sup>-7</sup>	0.9956	1.19×10 <sup>4</sup>

These compounds were expected to possess features that can act as good receptors for cations. The molecular clips may turn off the fluorescent emission when the target cation is bound.

#### Photophysical Properties of the Sensors

Table 1 shows that the molecular clips **1–3** in THF exhibit strong blue fluorescence with high quantum yields ranging from 0.51 to 0.83. Compared to **1** that exhibits an emission peak at 365 nm, **2** exhibits an emission maxima with 37 nm red shift due to the larger  $\pi$ -conjugation of naphthyl than the phenyl groups. The red shift (18 nm) of **3** with respect to **1** is presumably attributed to the more electron-donating property of 4-methoxyphenyl than the phenyl groups.

The Stokes shift between the absorption and emission of a chromophore reflects the displacement in potential surface between the ground and excited states and the loss of vibrational energy in the excited state [29–31]. A high Stokes shift value allows clear differentiation of the emitted fluorescence photons from the excitation photons, and can lead to low background signals. Owing to its enhanced electron density of the mobilized electrons, the Stokes shift value of compound **3** increased to 54 nm, which is higher than the 45 nm for compound **1**.

#### Response to Fe<sup>3+</sup> Ion

Strong fluorescence signals in the range around 370 nm could be observed by the sensors alone in THF-MeOH

(Fig. 2). However, addition of Fe<sup>3+</sup> to the solution of **3** markedly diminished the fluorescence intensities with a red shift (~20 nm). As the Fe<sup>3+</sup> concentration increased, the fluorescence intensity at 385 nm progressively decreased. When the concentration of Fe<sup>3+</sup> was increased to up to 330  $\mu$ M (33 equiv relative **3**), the fluorescence intensity was reduced to 8.9% of the initial one.

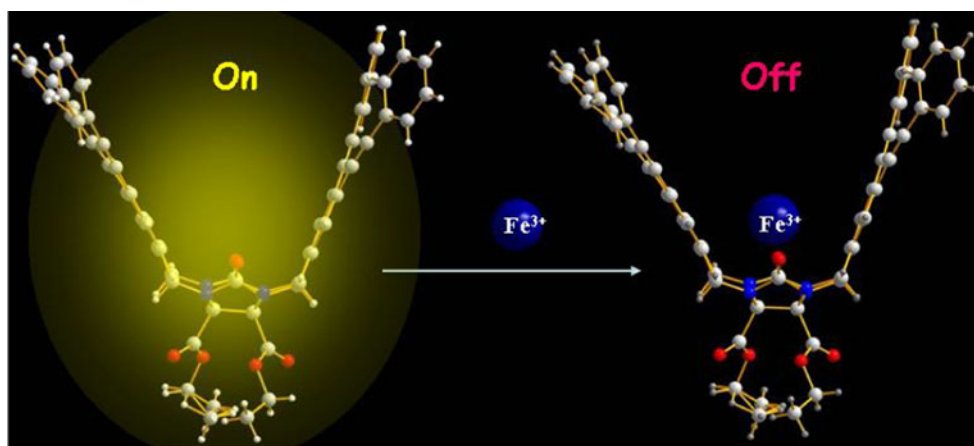
For a homogeneous medium that has only a single component exponential decay, the concentration of the quencher can be calculated using the Stern-Volmer equation [32, 33]. Interestingly, the plots of  $F_0/F$  versus Fe<sup>3+</sup> ion concentration did not fit a conventional linear Stern-Volmer equation (Insert of Fig. 2). The steep upward curvature may suggest a more complex quenching model which may involve both dynamic and static quenching simultaneously [34, 35].

The data, however, could be fitted to the following empirical equation [36, 37]:

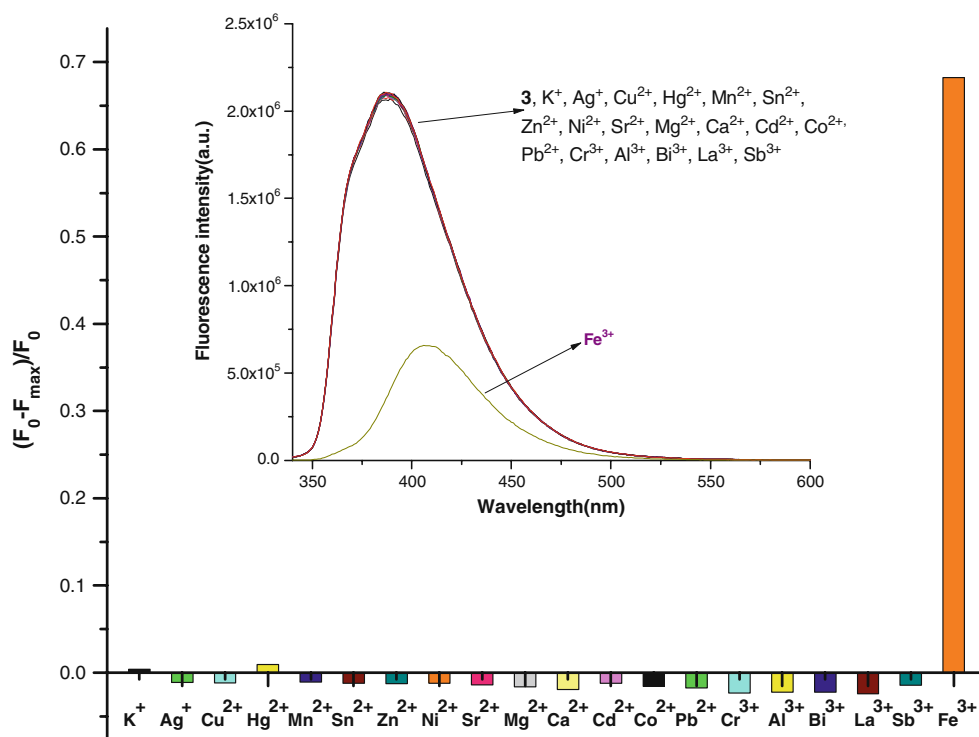
$$\log[(F_0/F)] = K_{sv}[Q] + C$$

The calibration plot of  $\log [(F_0/F)]$  versus [Q] shows a good linear relationship ( $R^2=0.9956$ ) for Fe<sup>3+</sup> ion concentration (Fig. 3). From the slope and intercept of the calibration plot, the  $K_{SV}$  and  $C$  could be evaluated as  $3.2 \times 10^{-4} \text{ M}^{-1}$  and 0.0125 respectively. The limit of detection of **3** is found to be  $7.3 \times 10^{-7} \text{ M}$ , which is calculated using  $3\delta/S$  [38], where  $\delta$  was the standard deviation of the blank signal, and  $S$  was the slope of the linear calibration plot (Table 2). Those achieved the level of the current published fluorescence detection papers [6, 16,

**Fig. 4** Proposed binding model of sensors **1–3** with Fe<sup>3+</sup>



**Fig. 5** Effect of  $10^{-4}$  M relevant cations on the fluorescence intensity of **3**, Inset: Fluorescent emission changes of **3** ( $10 \mu\text{M}$ ) in THF-MeOH-Water (9:1, v/v/v) in the presence of 40 equiv various metal ions (Excitation Wavelength was 329 nm)



39]. Meanwhile, the Job plot for the binding between sensor **3** and  $\text{Fe}^{3+}$  shows a 1:1 stoichiometry [40]. The binding constant ( $K_a$ ) was determined to be  $1.19 \times 10^4 \text{ M}^{-1}$  by a standard algorithm for competitive binding in the presence of excess in THF-MeOH-Water at  $25^\circ\text{C}$  [41, 42].

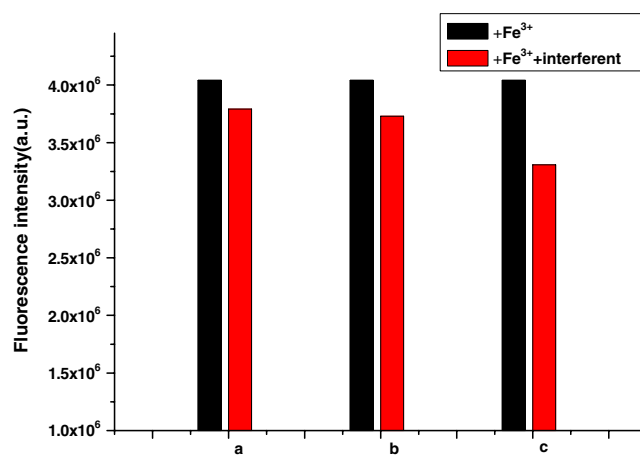
Based on the fluorimetric titration experiments, UV-Vis spectra (Fig. S5–7) and the X-ray crystal structure of **1**, we speculated that the fluorescent molecular clips would form a 1:1 complex with  $\text{Fe}^{3+}$  in the THF-MeOH-Water (Fig. 4) [18]. It should be noted that  $\text{Fe}^{3+}$  may establish coordinative interactions with the ureidyl carbonyl groups in their cavities and cation- $\pi$  interactions with aromatic sidewalls. The capture of  $\text{Fe}^{3+}$  may cause the electron or energy transfer from the excited aromatic sidewalls with aryl alkynes conjugated to the benzene ring to the ureidyl carbonyl groups and  $\text{Fe}^{3+}$ , in consequence resulting in the quenching of the fluorescent aromatic sidewalls [43, 44].

#### Evaluation of Selectivity

To test the selectivity of the fluorescent molecular clips, complexation of the molecular clips with different ions were evaluated. The tested ions included alkali and alkaline-earth cations  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , first-row transition-metal ions  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$ , Group 12 metal ions  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$ , the P block metal ions  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Bi}^{3+}$ , the lanthanide series metal ion  $\text{La}^{3+}$  and common heavy-metal contaminants  $\text{Ag}^+$  and  $\text{Hg}^{2+}$ . The results showed that the molecular

clips retain excellent selectivity for  $\text{Fe}^{3+}$  ions over these common environmental and biological metal ions (Fig. 5, Figs. S1 and S2)

Competition experiments were also carried out to test the practical applicability of the molecular clips for  $\text{Fe}^{3+}$  detection. A fixed concentration of  $1 \times 10^{-5} \text{ M}$  was used for  $\text{Fe}^{3+}$  and the fluorescence intensity was recorded before and after the adding of interferents into the  $\text{Fe}^{3+}$  solution. Only small changes were observed for the fluorescence intensities and the caused relative error for



**Fig. 6** Changes of the fluorescence intensity of the proposed sensor **3** before and after adding interferents into the  $\text{Fe}^{3+}$  solution. a)  $\text{Cr}^{3+} 1 \times 10^{-5} \text{ M}$ ; b)  $\text{Cd}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Cr}^{3+} 1 \times 10^{-5} \text{ M}$ ; c)  $\text{Cd}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Cr}^{3+} 1 \times 10^{-4} \text{ M}$

the determination of  $\text{Fe}^{3+}$  concentration was less than  $\pm 5\%$  (Fig. 6, Figs. S8 and S9). These results suggested that molecular clips 1–3 could be used as  $\text{Fe}^{3+}$  selective fluorescent chemosensors.

## Conclusions

In summary, we have described the synthesis and properties of three fluorescent molecular clips for  $\text{Fe}^{3+}$  ion in aqueous solution. They featured high Stokes shift, excellent  $\text{Fe}^{3+}$  specificity over a wide range of metal ions. The selective complexation of these molecules with  $\text{Fe}^{3+}$  makes them potential to be a fluorimetric chemosensors toward  $\text{Fe}^{3+}$  ion. More studies about other chemical species responsive to these fluorescent molecular clips and a better insight into the mechanisms are in progress.

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