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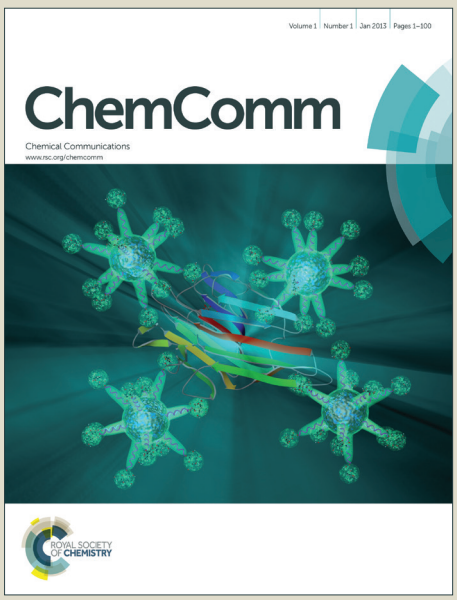

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An anthracene-appended 2:3 copillar[5]arene: synthesis, computational studies, and application in highly selective fluorescent sensing for Fe(III) ion†

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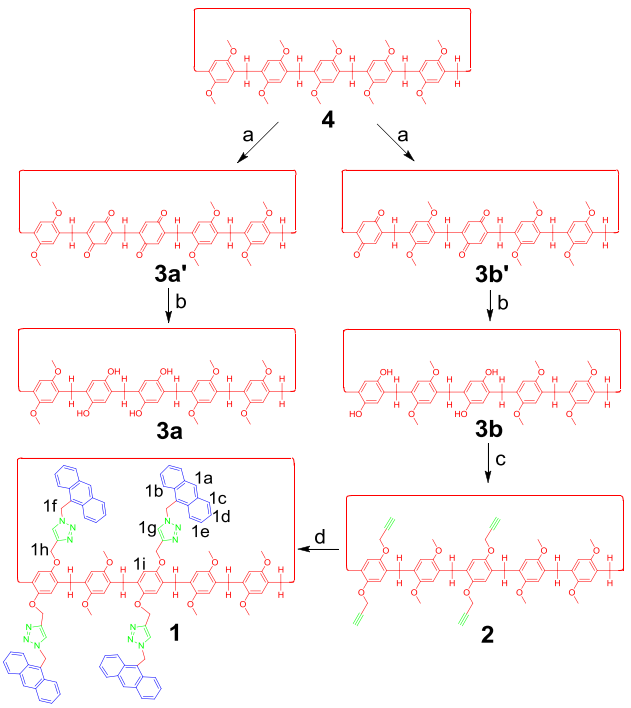
Herein an anthracene-appended 2:3 copillar[5]arene was prepared by CuAAC method, which was further used as a Fe^{3+}-selective fluorescent chemosensor over a wide range of metal ions.

The synthesis and functionalization of macrocyclic structures have been attracting a lot of interest in chemistry and materials science of late, not only because of topological importance of these novel structures, but also due to their wide applications in the construction of molecular machines, supramolecular polymers, and advanced functional materials.[1] Pillararenes, a new class of macrocycles, have a symmetric architecture with an overall cylindrical or pillarlike shape.[2] Because of this unique rigid structure and facile chemical modification, pillararenes have been shown to act as good hosts for a variety of guests and used to construct (supra)amphiphiles, mechanically interlocked structures, artificial transmembrane channels, supramolecular polymers, and liquid crystals.[3] Bearing this in mind, we envision that by proper functionalization, pillararenes can serve as platforms for preorganizing chelating groups for ion sensing to which little attention has been drawn to date.[4] Among various biologically important metals, iron is one of the most abundant essential elements found in the human body and is critical to sustain important physiological processes such as enzymatic catalysis, oxygen transport, and electron transfer *etc*.[5] Given the physiological implications of iron, its detection is very important.

A fluoroionophore is a fluorescent chemosensor for ions, consisting an ion recognition unit (ionophore) and a fluorogenic unit (fluorophore) which are combined together through a proper spacer.[6] As we know, the unsatisfactory selectivity for most of the chemosensors may be ascribed to the single-ion recognition unit. Fluoroionophores with multi-ion recognition units may overcome this disadvantage. The Huisgen-type copper(I)-catalyzed 1,3-dipolar azide-alkyne cycloaddition (CuAAC) has emerged as a valuable tool to fabricate complex functional materials not only because of its high efficiency and mild reaction conditions but also due to its function of introducing a new 1,2,3-triazole binding site.[7] The inherent physicochemical properties of 1,2,3-triazole would alter the electronic environment around the pillararene annulus and its three nitrogen atoms are expected to contribute more chelating sites which can be used as recognition units, while the anthracene groups can provide the fluorogenic units. Thus, we synthesized a novel anthracene-appended 2:3 copillar[5]arene by the CuAAC method, which was further used as a Fe^{3+}-selective fluorescent chemosensor over a wide range of metal ions in DMSO. The binding mode of this copillar[5]arene with Fe^{3+} was modeled by DFT and molecular dynamics (MD) computational calculations.



Scheme 1 Synthesis of 2:3 copillar[5]arene **2** and its anthracene-appended derivative **1**. Reagents and conditions: (a) $(NH_4)_2[Ce(No_3)_6]$, THF/H_2O, < 1% for 3a′ and 20% for 3b′; (b) $Na_2S_2O_4$, H_2O/CH_2Cl_2, 100% for both 3a and 3b; (c) 3-bromopropyne, K_2CO_3, CH_3CN, 95%; (d) 9-azidomethylanthracene, $CuSO_4•5H_2O$, sodium ascorbate, DMF/H_2O, 48%.

In the previous work, a new method for the synthesis of 2:3 copillar[5]arenes was reported *via* a partial oxidation/reduction strategy.[8] Pillar[5]arene **4** was used as the

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starting material and $(NH_4)_2[Ce(NO_3)_6]$ acted as the oxidant. By column chromatography, we successfully got pillar[3]arene[2]quinone isomers **3a′** and **3b′** as red solids with the yields of < 1% and 20%, respectively. Furthermore, upon reduction of **3a′** and **3b′** by $Na_2S_2O_4$, two isomeric tetrahydroxylated pillar[5]arenes **3a** and **3b** were obtained quantitatively. Then alkynyl groups were introduced by substitution reaction of **3b** with 3-bromopropyne to afford compound **2**. Reaction of **2** with 9-azidomethylanthracene resulted in the formation of fluoroionophore **1** (Scheme 1). By employing 2D COSY NMR and comparing the protons among **2**, 9-azidomethylanthracene, and **1**, partial signals from the skeleton and anthracene groups (or 1,2,3-triazole) of **1** were identified clearly (Figs. S11 and S12, ESI†).

All attempts to grow X-ray quality single crystals of **1** have so far proven unsuccessful. Fortunately, by slow evaporation of a solution of **2** in a dichloromethane/methanol mixture (1 : 1, *v*/*v*) at room temperature, crystals suitable for X-ray analysis were obtained (Fig. 1). The crystal structure gave direct proof that copillar[5]arene **2** contained three 1,4-dimethoxybenzene (DMB) units and two 1,4-bis(prop-2-yn-1-yloxy)benzene (DPYB) units. It clearly showed that two DPYB units were not neighboring. This crystal structure provided the possibility that the copillar[5]arene could be used as a multi-ion recognition fluoroionophore by functionalization with fluorogenic units.

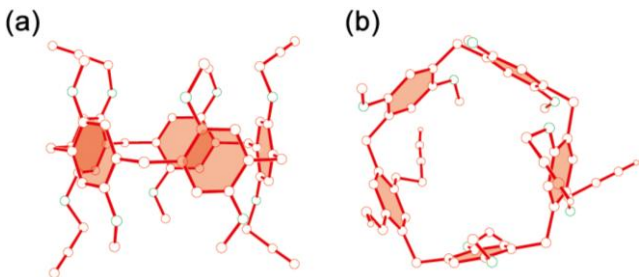

Fig. 1 The crystal structure of **2** (a) (side view) and (b) (top view). Hydrogens and solvent molecules were omitted for clarity. Carbon atoms are red and oxygen atoms are green.

To evaluate the binding ability of compound **1** toward Fe^{3+} ion, we carried out UV-vis experiments in DMSO by adding aliquots of Fe^{3+} as its perchlorate salt (Fig. S13, ESI†). The absorption spectrum of compound **1** (20 μM) exhibited a maximum absorption band at 370 nm. However, an obvious intensity increase took place upon treatment with 10 equiv of Fe^{3+}. This phenomenon confirmed the binding behaviour of Fe^{3+} by **1**.

In order to investigate the Fe^{3+} recognition ability of **1**, we carried out a series of host–guest recognition experiments. The recognition profiles of chemosensor **1** toward various ions, including Fe^{3+}, Cr^{3+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pd^{2+}, Zn^{2+}, Mg^{2+}, Hg^{2+}, and Ag^{+} ions, were primarily investigated by exciting the corresponding solutions at 370 nm and measuring the emission in 380−550 nm range in DMSO (Fig. 2a). When 10 equiv of Fe^{3+} was added to the DMSO solution of sensor **1**, the fluorescence emission band in 380–550 nm showed an obvious decrease. The apparent fluorescence emission change could be distinguished by the naked eye. Furthermore, sensor **1** could be considered as a good ON–OFF Fe^{3+} fluorescent switch. To validate the selectivity of sensor **1**, the same tests were also conducted using Cr^{3+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pd^{2+}, Zn^{2+}, Mg^{2+}, Hg^{2+}, and Ag^{+} ions, and none of these ions induced fluorescence quenching in the fluorescent spectra of the sensor (Fig. 2a). Therefore, in DMSO, **1** showed specific fluorescent selectivity to Fe^{3+}.

To further investigate the interaction between sensor **1** and Fe^{3+}, fluorescent spectrum variation of sensor **1** was monitored during titration with different concentrations of Fe^{3+} (Figs. S14 and S15, ESI†). It turned out that, in DMSO solution of **1**, with an increasing amount of Fe^{3+}, the fluorescence emission bands at 400, 420, and 444 nm decreased by an extent of ~75%.

To explore the utility of sensor **1** as an ion-selective chemosensor for Fe^{3+}, competitive experiments were carried out in the presence of 10 equiv of Fe^{3+} and 10 equiv of various other ions (Cr^{3+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pd^{2+}, Zn^{2+}, Mg^{2+}, Hg^{2+}, and Ag^{+}) in DMSO. Results of these studies have revealed that these competing ions exerted no or little influence on the fluorescent emission spectra of sensor **1** with Fe^{3+}, which further indicated that **1** had specific selectivity to Fe^{3+} (Fig. 2b).

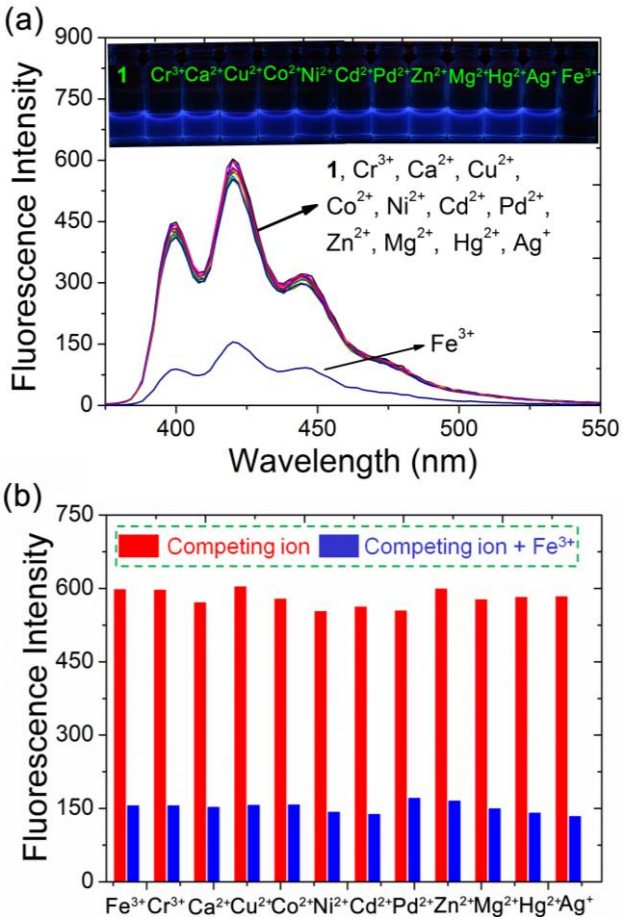

Fig. 2 (a) Fluorescence spectra responses of **1** (20 μM) in DMSO upon addition of 10 equiv of Fe^{3+}, Cr^{3+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pd^{2+}, Zn^{2+}, Mg^{2+}, Hg^{2+}, and Ag^{+} ions (λ_{ex} = 370 nm). Inset: photograph of **1** (20 μM) upon adding 10 equiv of various ions, which was observed under a UV-lamp (365 nm). (b) Fluorescence intensities of **1** (20 μM) in

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the presence of 10 equiv of various ions containing 10 equiv of Fe^{3+} in DMSO (λ = 420 nm).

Molecular dynamics (MD) simulations were carried out using the GROMACS 4.5.2 software package[9] to establish the binding mode and binding stoichiometry of **1** and ferric ion (Fig. 3). The force field parameters for ferric ion were taken from the previous study.[10] To develop the force fields for **1**, the initial structure of **1** was optimized using Guassian 03 package[11] at the B3LYP/6-31g(d,p) level of theory. The output obtained was given as the input file for the open source Antechamber suite of force field tools, which was used to assign the non-bonded and bonded force field parameters from generalized AMBER force field (GAFF).[12] Atomic point charges were calculated from results of ab initio calculations via Antechamber using the restrained electrostatic potential (RESP)[13] method. The **1** structure optimized at B3LYP/6-31g(d,p) was put into a cubic box. Then up to 1927 water molecules were used to solvate **1** and one hundred ferric ions were randomly added. For water molecules, the SPC model was used. The system was energy minimized with Steepest Descent (SD) method.[14] Subsequently, MD simulations under NVT condition of 6 ns were carried out with a time step of 2 fs. The Nosé–Hoover thermostat method[15] was used to keep the temperature at 300 K and the periodic boundary conditions were applied in the simulations.

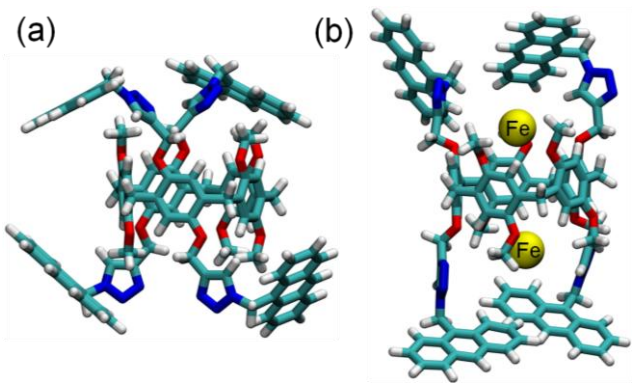

Fig. 3 The structures of (a) **l** and (b) **l**⊃Fe_2 based on DFT studies and molecular dynamic simulations, respectively.

The MD studies supported the formation of 1:2 complex between **1** and ferric ion (Fig. 3b). According to the system trajectory snapshots, it is implied that all the oxygen atoms of **1** play significant roles in the association of ferric ion to **1**. In the top half of the complex **1**⊃Fe_2, the five oxygen atoms formed a planar binding core which binds one ferric ion. The binding modes in the bottom part of the complex is similar. The study also shows conformational dynamism of the arms to accommodate ferric ion. From this MD study, we know that **1** is actually a fluoroionophore with multi-ion recognition units which endows this sensor satisfactory selectivity for Fe^{3+}.

In summary, a novel anthracene-appended 2:3 copillar[5]arene was synthesized and well characterized by various techniques. The single crystal structure of the precursor of **1** was obtained to confirm its constitution. Moreover, compound **1** could be used as a Fe^{3+}-selective fluorescent chemosensor, and other ions, including Cr^{3+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pd^{2+}, Zn^{2+}, Mg^{2+}, Hg^{2+}, and Ag^{+} had nearly no influence on the probing behavior in DMSO. The complexation between **1** and Fe^{3+} had been further addressed by DFT and molecular dynamics (MD) computational calculations, which confirmed that sensor **1** was a fluoroionophore with multi-ion recognition units. Given the physiological applications of Fe^{3+}, compound **1** could subsequently found practical applications in chemical and biological systems.

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Notes and references

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†*Electronic Supplementary Information (ESI) available: Synthetic procedures, characterizations, X-ray crystallographic file (CIF) for **2** and other materials. See DOI: 10.1039/b000000x/*
‡*These authors contributed equally to this work.*

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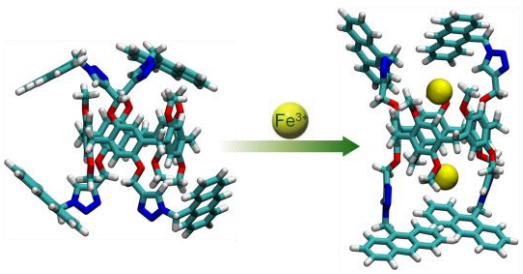

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