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A non-symmetric pillar[5]arene based on triazole-linked 8-oxyquinolines as a sequential sensor for thorium(IV) followed by fluoride ions†

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A novel non-symmetric pillar[5]arene bearing triazole-linked 8-oxyquinolines at one rim was synthesized and demonstrated as a sequential fluorescence sensor for thorium(IV) followed by fluoride ions with high sensitivity and selectivity.

Functional groups mounted on pillararenes[1] often leads to unique properties that greatly stimulates the interest of chemists of various fields.[2] This has been demonstrated by their application in host–guest chemistry, self-assembly systems and construction of supramolecular smart materials.[3] Structurally, these behaviors are based on the functionalization of a pillar framework that comprises a cyclic array of hydroquinone units linked by methylene bridges at *para* positions. Despite numerous reports on complexation of organic species,[2,3h,j] the use of host–guest interactions involving pillararenes and metal ions remains very limited. Dipyridyl functionalized pillar[5]arene and di-Pt(II) acceptors have been utilized to prepare metallacycles through metal–ligand coordination.[4] More recently, the introduction of terpyridine moieties into a pillar[5]arene-based [c2]daisy chain endows the molecule with efficient formation of a metallo-coordination supramolecular polymer.[5] Our recent study showed that pillar[5]arenes functionalized with organophosphorus ligands exhibited pronounced selectivity for actinide cations and even mercury(II).[6] Furthermore, pre-organizing diglycolamide moieties on the pillararene platform resulted in high efficiency towards partitioning of Eu(III) and Am(III).[7] Intriguingly, only one metal ion was found to bind to most of these pillararene ligands under extraction conditions. This stimulated our interest in probing the metal complexation behavior of non-symmetric pillararene (NSP) with just one rim being functionalized. So far, only a few publications

involve NSP.[8] Surprisingly, to the best of our knowledge, recognition of metal ions by functionalized NSP as receptors has been unexplored to date.

Thorium (Th) is a naturally occurring radioactive actinide element that often coexists with lanthanides and other transition metal ions in soil and rocks.[9] The chemistry of the thorium element has received renewed attention in recent years because of its use as a uranium resource and as a model of other more radioactive tetravalent actinides.[10] The design of artificial receptors with fluorescence properties for selective recognition of Th^{4+} from lanthanides still represents a challenging task due to its high coordination numbers (CN) (CN > 8) and the similarity in ionic radii and chemical behavior of these two block elements. So far, only a few reports have been associated with fluorescent detection of Th^{4+}.[11] In the meantime, it is of interest to develop receptors with dual functions for the selective recognition of thorium and fluoride allowing for the importance of fluoride in the biological systems.[12] Thus, we envisaged that tethering quinoline units, which are recognized as an excellent fluorophore for metal sensors,[13] onto pillar[5]arene would produce a preorganization effect and cooperative coordination for fluorescent recognition towards specific cations. With our continued interest in recognition of organic molecules and metal cations,[11c,14] we report herein on the design and synthesis of a functionalized NSP **1** (Scheme 1), which showed sequential fluorescent sensing for Th(IV) followed by fluoride ions. Hitherto, pillararene-based fluorescent chemosensors have been developed only for organic guests and anions,[15] and no report on functionalized pillararenes designed for fluorescent sensors towards metal ions has been published. As far as we know, this is the first example of selective fluorescent recognition towards metal ions, especially actinide cations, in the field of pillararene chemistry.

The functionalized NSP **1** was designed to contain five triazole-linked 8-oxyquinolines at one rim and five alkyl chains at the other (Scheme 1). The key precursor **4a** was achieved by only a one-step condensation reaction of compound **3** and para-formaldehyde under Lewis acid catalyzed conditions following a similar prior procedure (Scheme S1, ESI†).[1a] Subsequent

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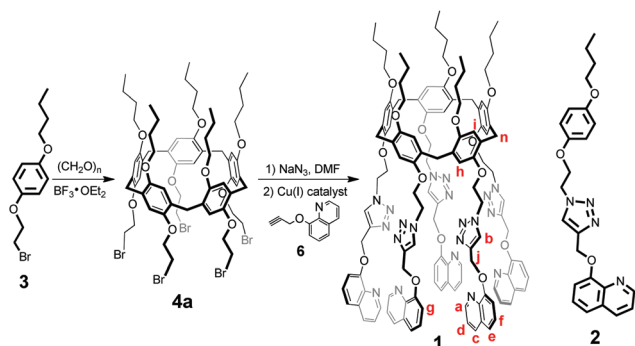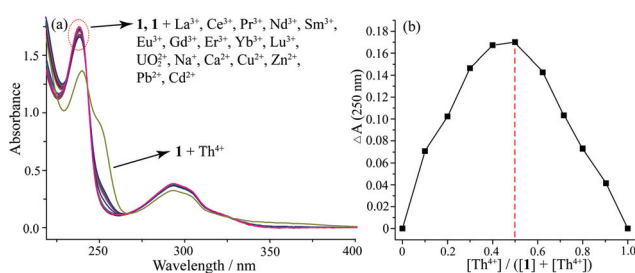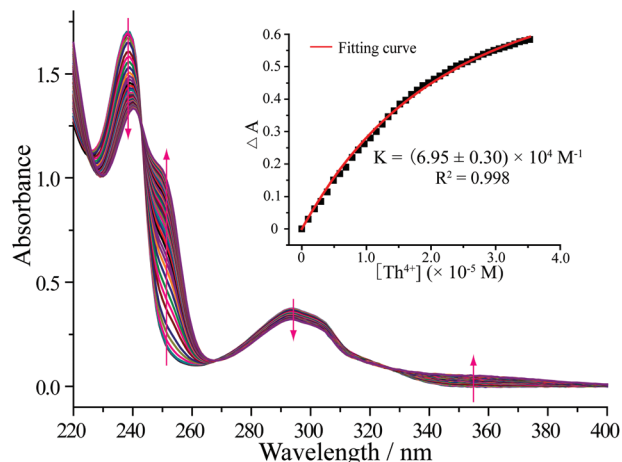
Scheme 1 Synthesis of the NSP functionalized with triazole-linked 8-oxyquinoline **1** and the chemical structure of the acyclic monomeric analog **2**.
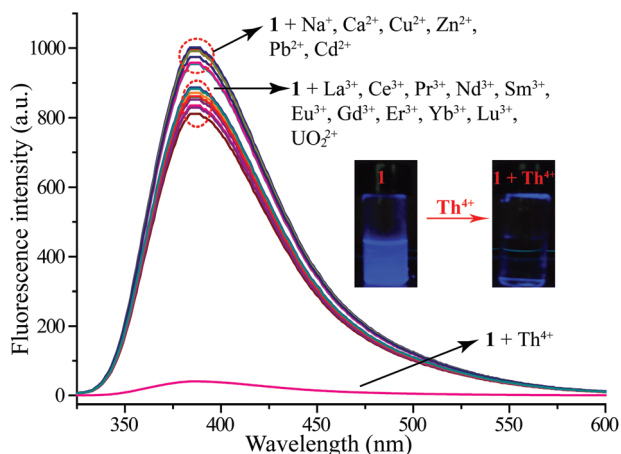

Fig. 2 UV-vis titration of ligand **1** (10 μM) upon addition of Th^{4+} (0–3.5 equiv.) in a mixed aqueous medium (CH$_3$CN–H$_2$O, v/v = 9 : 1). Inset: non-linear fitting curve of **1** with increasing concentration of Th^{4+}.

nucleophilic substitution of the resulting **4a** with NaN$_3$ in DMF at 90 °C produced the azide almost quantitatively, which was further applied in the Cu(ɪ)-catalyzed 1,3-dipolar cyclo-addition reaction with 8-(prop-2-ynyloxy)quinoline **6** to obtain the desired compound **1** in a 72% isolated yield. The acyclic monomeric analog **2** was also prepared as a control for comparison. All the target molecules and intermediates were characterized by ^{1}H NMR, ^{13}C NMR and HRESI-MS (Fig. S1–S14, ESI†). ^{1}H NMR spectrum of the NSP **1** recorded in CDCl$_3$ shows characteristic signals for H$_b$ of the 1,2,3-triazole moiety at 7.93 ppm and methylene hydrogens H$_j$ adjacent to the O atoms of quinoline groups at 5.47 ppm. Two singlets at 6.63 and 6.48 ppm are observed for the aromatic protons H$_h$ and H$_i$ respectively, suggesting that **1** still holds in the initial non-symmetric conformation due to the difference in chemical environments of the phenyl protons from both sides.

In order to assess the recognition behavior of receptor **1** towards metal ions, screening of various nitrate metal salts (ten lanthanides: La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Er^{3+}, Yb^{3+} and Lu^{3+}; two actinides: UO$_2$$^{2+}$ and Th^{4+}; four transition metal ions: Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}; alkali metal Na$^+$ and alkali earth metal Ca^{2+}) was conducted in a mixed aqueous medium (CH$_3$CN–H$_2$O, 9 : 1) by the UV-vis absorption technique. A sharp absorption band centered at 238 nm and a broad one centered at 292 nm are attributed to the sum of π–π* transition of 8-methoxyquinoline and the 1,2,3-triazolyl moieties (Fig. 1a). Upon addition of 1.0 equiv. of the above-

mentioned set of metal cations to **1**, a noticeable change is observed for Th^{4+} as indicated by the decrease of the maximum absorption band at 238 nm and the concomitant formation of a new band shouldered at 250 nm. However, the absorption bands for all the other metal ions remain almost unchanged. These results indicate that NSP **1** is appropriate for selective recognition of Th^{4+}. An analysis of the Job plot afforded a metal mole fraction of 0.5, pointing to 1 : 1 stoichiometry of receptor **1** and Th^{4+} (Fig. 1b). The UV-vis titration of **1** with Th^{4+} reveals the presence of three well-defined isosbestic points at 244, 268 and 326 nm, suggesting the formation of a **1**–Th^{4+} complex (Fig. 2). The binding constant (K) between **1** and Th^{4+} in CH$_3$CN–H$_2$O (9 : 1, v/v) was calculated from UV-vis titration results to be $(6.95 \pm 0.30) \times 10^4$ M^{-1} using the non-linear curve fitting method at 250 nm. The HRESI-MS provides additional strong evidence for the 1 : 1 complex formation, where a highly intense ion peak at m/z 815.3346 (calculated: 815.3439) assigned to [**1** + Th^{4+} + NO$_3$$^-$]$^{3+}$ is observed with the isotope pattern being consistent with the simulated one (Fig. S15, ESI†).

The recognition properties of receptor **1** were then investigated by fluorescence spectroscopy in the same medium. Upon addition of 1.0 equiv. of the above-mentioned metal ions, a strong emission band at 390 nm characteristic of **1** is almost completely quenched by Th^{4+} (Fig. 3) (quenching efficiency at 390 nm, $(I_0 - I)/I_0 \times 100\%$ = 94%, Fig. S17, ESI†). The change can be easily distinguished by the naked eye when illuminating the solution with UV light (365 nm) (inset of Fig. 3 and Fig. S18, ESI†). Alkali, alkali earth and transition metal ions show marginal quenching of fluorescence (<5%). The other lanthanide and actinide ions induce fluorescence quenching (<20%), but only to a much lesser extent with respect to Th^{4+}. On the other hand, competition experiments were performed for **1** even in the presence of 10 equiv. each of the other selected metal ions. The results show that those background metal cations do not have any obvious interfering


Fig. 1 (a) Absorption spectra of **1** (10 μM) in the presence of various nitrate salts (1.0 equiv.) in a mixed aqueous medium (CH$_3$CN–H$_2$O, v/v = 9 : 1); (b) a Job plot of compound **1** and Th^{4+} ([**1**] + [Th^{4+}] = 10 μM).

Fig. 3 Fluorescence emission spectra of **1** (10 μM) in the presence of various metal ions (1.0 equiv.) in a mixed aqueous medium (CH_3CN–H_2O, v/v = 9 : 1; λ_{ex} = 310 nm, slit = 5 nm/5 nm). The inset photographs show the corresponding fluorescence changes (left: 50 μM **1**; right: 50 μM **1** + 50 μM Th^{4+}) upon excitation at 365 nm using a UV lamp.

effect on the fluorescence sensing of Th^{4+} (Fig. S19, ESI†), indicating a highly selective and sensitive response of sensor **1** toward Th^{4+} over other cations. Receptor **1** also exhibits the pH-dependent fluorescence behavior (pH 3.5–10) both in the absence and presence of Th^{4+}, indicative of persistence of the fluorescence sensing ability in the pH range examined (Fig. S20, ESI†). Consistent with the results from UV-vis data, **1** can form a 1 : 1 complex as confirmed by fluorescent titration of the receptor with Th^{4+} in the same mixed solvent (Fig. S21, ESI†). In addition, the detection limit (DL) was deduced to be 5.35×10^{-7} M (124 μg L^{-1}) toward Th^{4+} (Fig. S22, ESI†), which is much lower than the maximum level for Th^{4+} (246 μg L^{-1}) in drinking water specified by WHO guidelines.[16] In sharp contrast, acyclic monomeric analog **2** even at a ligand concentration with the triazole-linked 8-oxyquinoline functionality being equal to that of **1** only shows very poor fluorescence quenching for Th^{4+} (the quenching efficiency at 390 nm was 26%) under the same conditions (Fig. S24, ESI†), highlighting the importance of the preorganization of the pillar[5]arene platform on the recognition of thorium(IV) *via* the cooperative coordination in the supramolecular complex.

To obtain a better understanding of the mechanism for sensing of Th^{4+}, the interaction and binding behavior of sensor **1** with Th^{4+} were investigated by ^1H NMR experiments. All the protons (H_a and $H_{c–g}$) of quinoline units show downfield shifts (+0.06–0.13 ppm, Table S1, ESI†) upon addition of 1.0 equiv. of Th^{4+}. In contrast, both the protons (H_b) from the triazole moieties and methylene protons (H_j) adjacent to the quinoline units experience upfield shifts (−0.04 and −0.01 ppm, respectively), probably due to the increased shielding effect when the electron-rich quinoline units approach each other upon complexation. These observations suggest that **1** binds to Th^{4+} through the nitrogen atoms of quinoline moieties rather than the nitrogen atoms from triazole units. Thus, this may explain the Th^{4+}-induced quenching mechanism

that probably proceeds by the electron transfer from the quinoline nitrogen to the Th^{4+} in accordance with a metal ligand charge transfer (MLCT) effect.[17] In addition, much clearer splitting of the aromatic protons (H_h and H_i) of the pillar[5]-arene platform can be observed after complexation with Th^{4+}, suggesting that the coordination at one rim leads to reduced conformation freedom of pillar[5]arene. As a consequence, the constrained framework may favor the preorganization of multiple triazole-linked 8-oxyquinolines on the pillar[5]arene platform to achieve higher binding affinity towards softer thorium(IV) of higher coordination numbers, which partially accounts for the high selectivity and high sensitivity of sensor **1** towards Th^{4+}. However, other factors such as counter anions and hydration of metal ions may also play a role.

Since the *in situ* generated **1**–Th^{4+} complex exhibited almost complete fluorescence quenching, it is likely to exploit this ensemble as a turn-on fluorescent sensor for anions which are known to play important roles in a wide range of chemical and biological processes. Thus, the **1**–Th^{4+} complex, prepared by mixing an equal amount of **1** and $Th(NO_3)_4$ (10 μM) in the same mixed aqueous solution, was treated separately with 6 equiv. of different halides. When a fluoride ion is added to the **1**–Th^{4+} system, the fluorescence intensity is completely regenerated, as also indicated visually by the fluorescent color change (Fig. 4, inset). However, other halides (Cl^-, Br^- and I^-) show very little response. The observed fluorescence and color regeneration can be ascribed to the snatching of Th^{4+} from its chelated complexes by F^-, resulting in the formation of more stable species ThF_4 and the release of free ligand **1**. The fluorescent titration curve of the **1**–Th^{4+} complex toward the fluoride ion offers a good linear correlation at the concentration range 10–45 μM, from which the detection limit for fluoride is estimated to be 3.03×10^{-6} M (57.6 μg L^{-1}, Fig. S29, ESI†).
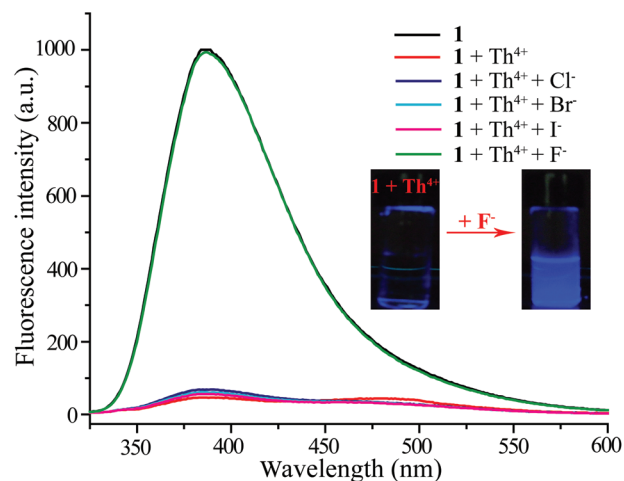
Fig. 4 Fluorescence emission spectra of **1** (10 μM) in the presence of Th^{4+} (1.0 equiv.) followed by addition of different halides (6.0 equiv.) in a mixed aqueous medium (CH_3CN–H_2O, v/v = 9 : 1, λ_{ex} = 310 nm). The inset photographs show the corresponding fluorescence changes (left: 50 μM **1**–Th^{4+} ensemble; right: 50 μM **1**–Th^{4+} ensemble + 6.0 equiv. F^-) upon excitation at 365 nm using a UV lamp.

This value is much lower than the limit concentration level (4.00 mg L^{-1}) in drinking water set by USEPA.[18] Control experiments of **1** even in the presence of 10 equiv. of each of the halides indicated the absence of interaction between **1** and halides in this solvent system (Fig. S25, ESI†). Competition experiments were conducted by adding fluoride (6 equiv.) to the solution of **1**–Th^{4+} in the presence of 100 equiv. of other halides (Fig. S30, ESI†). The fluorescence emission spectra display nearly an identical pattern to that with F$^-$ alone, suggesting that all of the tested anions do not interfere in the sensing of F$^-$. In addition, the fluorescent intensity could be turned off and on repeatedly with the alternate addition of Th^{4+} and F$^-$ ions at least in four cycles (Fig. S31, ESI†). All the above results indicate that the **1**–Th^{4+} ensemble could serve as an outstanding sensitive and selective fluorescent OFF–ON sensor for F$^-$.

In conclusion, by designing a non-symmetric pillar[5]arene, we demonstrated, for the very first time, the construction of receptor **1** anchored with five triazole-linked 8-oxyquinolines at one rim for sequential fluorescence sensing of Th^{4+} followed by F$^-$. The recognition ability of specifically binding to Th^{4+} from among 18 metal ions arises from the formation of a weak fluorescent **1**–Th^{4+} complex of 1 : 1 stoichiometry, which is confirmed by UV-vis, fluorescence, MS and NMR techniques. The resulting **1**–Th^{4+} ensemble can also act as a turn-on fluorescent sensor for fluoride ions over other halides in the same media without interference. The work shown here not only presents the fact of using pillararenes for selective fluorescent recognition towards both thorium(ⅳ) and fluoride in a sequential fashion, but more importantly, it implicates the potential of pillararene macrocycles for the design of fluorescent sensors towards other metal cations with tailored properties.

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