Metal-Ion Displacement Approach for Optical Recognition of Thorium: Application of a Molybdenum(VI) Complex for Nanomolar Determination and Enrichment of Th(IV)

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Supporting Information

ABSTRACT: An azine-based molybdenum (Mo(VI)) complex (M1) is exploited for selective detection of thorium (Th(IV)) ions through a metal-ion displacement protocol. Th(IV) displaces Mo(VI) from M1 instantly leading to the formation of the Th(IV) complex, having orange-red emission. Consequently, a red shift of the emission wavelength along with 41-fold fluorescence enhancement is observed. This unique method allows detection of Th(IV) as low as $1.5 \times 10^{-9}$ M. The displacement of Mo(VI) from M1 by Th(IV) is established by spectroscopic studies and kinetically followed by the stopped-flow technique. The displacement binding constant for Th(IV) is notably strong, $4.59 \times 10^{6}$ M$^{-1}$. Extraction of Th(IV) from aqueous solution to the ethyl acetate medium using M1 has been achieved. The silica-immobilized M1 efficiently enriches Th(IV) from its reservoir through solid-phase extraction. Computational studies (density functional theory) support experimental findings.

INTRODUCTION

In spite of significant contribution in NMR signalling, catalytic, biological, therapeutic, and imaging applications,1–25 selective recognition of actinides is relatively scarce compared to transition metal ions. Actinide complexes have charming characteristics including large Stokes transition metal ions. Actinide complexes have charming recognition of actinides is relatively scarce compared to accidental release from nuclear power plants.14,15 In addition, thorium to environment includes mining, processing, and enrichment of thorium is very relevant and time worthy.17

Metal displacement/exchange reactions that lead to thermodynamically more stable structures are extremely valuable in organometallic synthesis and catalytic cross-coupling like Stille, Suzuki, Sonogashira, and Negishi cross-coupling reactions.18–28 For in vivo metal displacement reaction, kinetic stability/inertness plays a key role over thermodynamic stability.29–32 Moreover, the metal displacement approach allows highly selective fluorescence detection of cations over a free organic probe leading to significant advancements in recognition research.33–36

It is well known that hydrazone-based metal complexes have been used as drugs for cancer and leprosy. They are also used as plasticizers, polymer stabilizers, antioxidants, polymerization inhibitors, herbicides, insecticides, and plant stimulating agents.37,38 Additionally, N–N-linked diimines known as azines, undergo a wide variety of chemical processes and are useful derivatives for isolation, purification, and characterization of many organic compounds.39,40

On the other hand, molybdenum complexes, precisely dioxo Mo(VI) complexes of N, O-donor hydrazone derivatives occupied a pivotal role in coordination chemistry,41 biological chemistry, and catalytic transformations.42,43 Thus, above discussion highlights the importance of Th(IV) recognition, azine-based Mo(VI) complex, and metal displacement approach.
for selective recognition of trace level Th(IV). So far the literature is concerned, few spectrophotometric probes are available for Th⁴⁺ determination. ⁶¹⁻⁶⁷

A β-diketone derivative undergoes marginal fluorescence enhancement in the presence of Th⁴⁺ at 500–530 nm (λₑₘ = 360 nm). ⁶⁸,⁶⁹ However, the probe fails to discriminate Th⁴⁺ from UO₂²⁺, La³⁺, Pb²⁺, and Cu²⁺. Moreover, the LOD (lowest detection limit) and apparent binding constant for Th⁴⁺ are very poor. A coumarin-containing oligoamide detects Th⁴⁺ (λₑₘ = 365 nm, λₑₙₘ = 505 nm); however, La³⁺, Tb³⁺, Ho³⁺, Tm³⁺, and Gd³⁺ interfere. Moreover, lengthy, hazardous synthetic route and poor LOD and binding constant limit its practical applications. ⁷⁰ It is indeed challenging to develop a fluorescence probe for heavy transition-metal ions for their quenching action through spin–orbit coupling or energy/electron transfer processes.

In this context, Th⁴⁺-assisted ratiometric fluorescence enhancement of a Mo(VI) complex via the metal displacement approach is undoubtedly a significant advancement for determination of trace level Th⁴⁺. ⁷¹⁻⁷³

Herein, an azine derivative (L), prepared by condensing hydrazine and 4-((N,N-diethylenimin)salicylaldehyde (Scheme S1), binds Mo(VI) through N and O donors, leading to the eight-coordinated oxo-bridged dinuclear Mo(VI) complex (M1), the structure of which is confirmed by single-crystal X-ray diffraction (SCXRD) analysis. Besides, various spectroscopic analyses firmly establish the binding interaction between Mo(VI) and L (Figures S1–S13 and Tables S1–S5). The density functional theory (DFT) studies have been performed to unfold the molecular-level interactions and origin of spectroscopic properties.

In addition, the resulting Mo(VI) complex (M1) is utilized for selective recognition of Th⁴⁺ via the metal-ion displacement approach, reflected in fluorescence enhancement and associated color change with the formation of the [L−Th⁴⁺] complex (M2). Spectroscopic and DFT studies authenticated the displacement process (Figures S1–S10 and Tables S1–S5). Moreover, M1 efficiently extracts Th⁴⁺ from the aqueous to ethyl acetate medium, allowing its enrichment. ⁶¹,⁶³ The silica-immobilized probe (M1) is suitable for solid-phase extractive enrichment of Th⁴⁺ from its reservoir. ⁶¹

Thus, the novelty of the present work lies in the fact that the new Mo(VI) complex is a dual-functioning material: it enables optical detection ⁶¹,⁶³ of nanomolar Th⁴⁺ via the highly selective metal-ion displacement protocol and allows extractive separation ⁶¹/3/enrichment of Th⁴⁺ from aqueous solution.

### CRYSTAL STRUCTURE OF THE M1 COMPLEX

Figure 1 displays the structure of the oxo-bridged dinuclear Mo(VI) complex (M1) along with the co-crystallized L derived from SCXRD analysis (Table S1). L plays an important role in crystal packing connecting hydrogen-bonded dimeric units, [Mo₂O₄(μ₂-O)(CH₃OH)₂(L)]₂⁺, having methanol–oxo interactions (Figure 2). The intermolecular hydrogen bonds exist between methanol, oxo center of M1, and two phenol hydrogen-bonded dimeric units, [Mo₂O₄(μ₂-O)(CH₃OH)₂(L)]₂⁺...[Mo₂O₄(μ₂-O)(CH₃OH)₂(L)]₂⁺...[Mo₂O₄(μ₂-O)(CH₃OH)₂(L)]₂⁺ while the circular region indicates L.

Figure 1. Single-crystal X-ray structure of M1.

### RESULTS AND DISCUSSION

**Spectroscopic Studies.** The spectroscopic properties of the Mo(VI) complex (M1) and its optical recognition of Th⁴⁺ have been thoroughly investigated. The methanol solution of M1 is absorbed at 267 nm (ε = 2.7 × 10³ M⁻¹ cm⁻¹) and 362 nm (ε = 9.8 × 10⁵ M⁻¹ cm⁻¹), assigned to π−π* and n−π* electronic transitions, respectively. ⁶²,⁶³ Upon addition of Mo(VI) to L, a new band that appears at 481 nm (ε = 141.45 M⁻¹ cm⁻¹). This angle is significantly smaller than reported di-oxo-(µ-oxo)-Mo(VI) dimers of monodentate ligands (L⁺⁻), (151–171°). ⁶¹ The difference in Mo−O−Mo angles between [Mo₂O₄(µ₂-O)-Cl₂(L)₄] and [Mo₂O₄(µ₂-O)(CH₃OH)₂(L)] is notable and may be due to higher degrees of freedom of the angles around Mo(VI) centers for the former.

ranges from ~1.92Å (terminal oxo group) to ~2.33Å (methanol). The two long bonds correspond to Mo−O₉ and Mo−N₉⁺ are trans-oxo groups to terminal oxo groups. Each Mo(VI) center is bonded to one L (as chelating N and O donors), one methanol, two terminal oxo groups, and a µ₂-bridged oxo group that imposes Mo−Mo bridging angle, ~141.45°. The Mo−O−Mo angle between [Mo₂O₄(µ₂-O)-Cl₂(L)₄] and [Mo₂O₄(µ₂-O)(CH₃OH)₂(L)] is notable and may be due to higher degrees of freedom of the angles around Mo(VI) centers for the former.
Lu\(^{3+}\), Yb\(^{3+}\), Y\(^{3+}\), Mn\(^{2+}\), and their mixture have no effect (\(\lambda_{EM} = 310\) nm) (Figures 3 and 4). The effect of pH on the emission characteristics of M1 in the presence and absence of Th\(^{4+}\) has directed us to perform the entire studies at pH \(\sim 7\) (Figure S1).

In the presence of Th\(^{4+}\), the green emission of M1 (\(\lambda_{EM} = 310\) nm, Figures 3 and S2) experiences red shift to orange-red and its intensity increases up to 41-fold with increasing amounts of Th\(^{4+}\) (Figure 3). The selectivity of M1 for Th\(^{4+}\) is further established by measuring the emission intensity of M1 in a mixture containing Th\(^{4+}\) along with various other metal ions (Figure S3). Thus, high selectivity of M1 for Th\(^{4+}\) in the binary mixture as well as in the “multicomponent” system is established.

Gradual addition of Th\(^{4+}\) lowers the emission intensity at 398 nm (\(\lambda_{EM} = 310\) nm), whereas the intensity of the new band at 557 nm (orange-red) gradually enhances (Figure S) up to 41 (\(\Phi = 0.72, 4.5\)-fold). Moreover, the ratiometric response is associated with an isoemissive point at 508 nm (Figure S2). Moreover, the ratio, \(F_{557nm}/F_{362nm}\) also experiences 41-fold enhancement (from 0.02469 to 1.01267, Figure S4). The emission intensity versus the [Th\(^{4+}\)] plot is sigmoidal having a linear region up to 0.97 \(\mu\)M Th\(^{4+}\) (Figure S5). The limit of detection (LOD) of M1 for Th\(^{4+}\) is \(1.5 \times 10^{-9}\) M (Figure S6). The corresponding displacement binding constant is \(4.59 \times 10^{6}\), calculated by applying the Hill equation\(^{21}\) on fluorescence titration data (Figure S7).\(^{66,67}\) On the other hand, the binding affinity of L for Th\(^{4+}\) calculated in a similar way is \(3.17 \times 10^{5}\) (\(\lambda_{EM} = 525\) nm; \(\lambda_{EX} = 338\) nm). The LOD of L for Th\(^{4+}\) is \(8.6 \times 10^{-8}\) M (Figure S8). Thus, the efficiency of M1 is higher than L for optical recognition of Th\(^{4+}\).

The UV–vis spectrum of M1 displays an intramolecular CT transition at 481 nm. Gradual adding of Th\(^{4+}\) (0–3000 \(\mu\)M) lowers the absorbance of the 362 nm band (\(e = 9.8 \times 10^{4}\) M\(^{-1}\) cm\(^{-1}\)) with appearance of two new bands at 267 nm (\(e = 9.6 \times 10^{4}\) M\(^{-1}\) cm\(^{-1}\)) and 485 nm (\(e = 2.3 \times 10^{5}\) M\(^{-1}\) cm\(^{-1}\)) involving two isosbestic points at 321 and 388 nm (Figures 6 and S9).\(^{64}\)

The plots of absorbance of M1 versus added Th\(^{4+}\) at three different wavelengths viz. 267, 362, and 485 nm are presented in Figure S9 (Supporting Information). The corresponding ratiometric plots, viz. \(A_{267nm}/A_{362nm}\) (0.01543–5.96655) and \(A_{267nm}/A_{362nm}\) (2.0986–0.17126) versus [Th\(^{4+}\)] are presented in Figure S10 (Supporting Information).

In the presence of Th\(^{4+}\), the green emission of M1 (\(\lambda_{EX} = 310\) nm, Figures 3 and S2) experiences red shift to orange-red and its intensity increases up to 41-fold with increasing amounts of Th\(^{4+}\) (Figure 3).

Plausible interference by relevant cations (M\(^{4+}\)) during Th\(^{4+}\) sensing is tested by competitive experiments in two different ways. In the first case, the [M1–Th\(^{4+}\)] system is titrated with different M\(^{4+}\) (100 \(\mu\)M), whereas for the other, the [M1–M\(^{4+}\)] mixture is titrated with Th\(^{4+}\) (Figure S3). In the first case, the emission intensity remains unaltered, whereas the emission intensity increased in the second case (Figure 3). The selectivity of M1 for Th\(^{4+}\) is further established by measuring the emission intensity of M1 in the presence and absence of Th\(^{4+}\) along with various other metal ions (Figure S3). Thus, high selectivity of M1 for Th\(^{4+}\) in the binary mixture as well as in the “multicomponent” system is established.

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Job’s plot from fluorescence titration data indicates 1:1 (mole ratio) binding between Th⁴⁺ and M1 (Figure S11), corroborated by the electrospray ionization mass spectrometry (ESI-MS) spectrum of the resulting mixture (calcd m/z, 777.48; found, 777.52 for [M + Na⁺]).

Similarly, Job’s plot and the ESI-MS spectrum reveal the composition of the [Mo(VI)–L] complex as 1:2 (mole ratio, Figures S11 and S28). In the presence of Th⁴⁺, green M1 turns orange-red (under UV light) and pale yellow to orange-red (bare eye) (Figures 3 and 4).

The weak emission of L may nicely be rationalized by DFT studies that reveal its planar geometry (Figure S12), allowing the photoinduced electron transfer (PET) process. Addition of Mo(VI) to L inhibits the PET through initiation of CHEF, resulting weak green fluorescence (Scheme 1). On the other hand, addition of Th⁴⁺ displaces Mo(VI) from the [L–Mo(VI)] complex (M1) to form the [L–Th⁴⁺] complex (M2), whereby green fluorescence turns orange-red (Scheme 1).

The interaction between L and Th⁴⁺ is further supported by ¹H NMR spectroscopy. Upon addition of Th⁴⁺ to L, the phenol proton (–OH) at 12.82 ppm disappears indicating deprotonation. Further, the imine proton (–CH==N–, “b”) at 8.52 ppm splits into two downfield shifted peaks, viz. 9.86 ppm (“d”) and 8.71 ppm (“c”) (Figure S13).

The experimental molecular-ion peak at 755.12 in the mass spectrum of the [L–Th⁴⁺] adduct is very close to the calculated m/z, 755.25. The notable difference between the Fourier transform infrared (FTIR) spectra of the [L–Th⁴⁺] adduct and L indicates the formation of the complex (Figure S14). All these support the CHEF process involving L and Th⁴⁺, and obviously, CHEF occurs via inhibition of the PET process.

Upon addition of Th⁴⁺ to M1, the absorbance increases at 362 nm ([ε = 9.8 × 10⁵ M⁻¹ cm⁻¹]) and 485 nm ([ε = 2.3 × 10⁶ M⁻¹ cm⁻¹]), attributed to LMCT from L to Th⁴⁺ (Figure 6).

The FTIR spectrum of M2 (Figure S15) displays ε(CH==N) at 1768 cm⁻¹ while the corresponding peak for M1 appears at 1615 cm⁻¹. The new peak at 2245 cm⁻¹ is due to −N==N−, originated from deprotonalization of π-electrons involving the hydrazone-N center. It is proposed that the dinuclear [L–Mo(VI)] complex is transformed to the mononuclear [L–Th⁴⁺] complex. In consequence, π-electrons on the N-donor site rearrange to form the −N==N− bond which is involved in LMCT observed in M2. Besides, splitting of the 2017 cm⁻¹ peak indicates involvement of the −NO₃⁻ group to form M2. Additionally, a new weak peak at 3486 cm⁻¹ (−O−H stretching) indicates the presence of H₂O in M2. The stretching at 2987 cm⁻¹ in solid-state FTIR spectra of M1 shifted to 2949 cm⁻¹ in M2, indicating the interaction of the Mo(VI) complex with Th⁴⁺ (Figure S15). The −N−O− stretching is found at 1380 cm⁻¹ in the FTIR spectra of M2.

To further establish the fact that Mo(VI) in M1 is displaced by Th⁴⁺ leading to M2, the energy dispersive X-ray fluorescence (EDXRF) spectra of M1 and M2 are compared (Figure S16). For this purpose, M2 is collected from the reaction mixture of M1 and Th⁴⁺ by partitioning between ethyl acetate and water. However, the residue collected after removal of the organic solvent is subjected to EDXRF, the aqueous layer is tested for Mo(VI). All of the results (Figures S16–S19) clearly establish the proposed sensing mechanism.

The ¹H NMR titration in DMSO-d₆ further strengthens the proposed interaction in solution (Figure 7). Upon addition of 2.0 equiv Mo(VI) to L, the imine proton (−CH==N, “b”) at 8.52 ppm is downfield shifted to 9.66 ppm, indicating the interaction of imine-N with Mo(VI). Moreover, the phenol proton (−OH) at 12.82 ppm disappears suggesting O-coordination via deprotonation (Figure 7).

On the other hand, upon addition of 2.0 equiv Th⁴⁺ to M1, the phenol proton [of L at 12.82 ppm that disappeared in presence of Mo(VI)] does not reappear, suggesting involvement of phenol oxygen to form the M₂ complex (Figure 7). However, other aromatic ring protons do not change significantly, except a small upfield shift, attributed to “through bond delocalization” or “diamagnetic shielding” of the negatively charged phenolate moiety. Interestingly, in the presence of 1.0 equiv Th⁴⁺, the imine proton (−CH==N−, “b”) for M1 at 9.66 ppm splits into two peaks (8.83 ppm, “c” and 9.82 ppm, “d”), whose intensity increases with increasing Th⁴⁺ concentration. This fact suggests “uncoordinated” of one imine-N (−CH==N−, “c”), corroborated from the mass spectrum of the [M₁ + Th⁴⁺] adduct (Figure S32). All these lead to propose the formation of a mononuclear [L–Th⁴⁺] complex involving N and O donors of L. Additionally, ¹H NMR, FTIR, and mass spectra of the isolated [Th(IV)−L] complex support its mononuclear status.

**Kinetics of Mo(VI) Displacement from M1 by Th⁴⁺**. The kinetic studies have been performed at 362 nm by monitoring the change of absorbance of M1 as a function of time on a stopped-flow spectrophotometer with varying amounts of Th⁴⁺ (Figure S20). Immediately after the pulse at 362 nm, a very rapid decay in absorbance is detected, attributed to very fast displacement of Mo(VI) by Th⁴⁺. Under the pseudo-first-order condition with respect to Th⁴⁺ in methanol, the absorbance remains unaltered just after ~0.30 s. At the same time, a strong absorbance is observed at 485 nm associated with an extinction coefficient, 2.3 × 10⁶ M⁻¹ cm⁻¹. The rate constant...
of the displacement reaction is \(7.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}\) (Figure S20).

## THEORETICAL STUDIES

The optimized geometry of M1 and M2 complexes has been generated using the correlation consistent cc-pVDZ basis set for C, N, H, and O atoms in the gas phase. For Th\(^{4+}\), the Stuttgart relativistic small-core effective core potentials and their companion basis sets are used. A set of \(8s7p6d4f\)/Th Gaussian basis functions are employed for rest of the electrons (Figure S12). The highest occupied molecular orbital—lowest unoccupied molecular orbital (HOMO—LUMO) energy gap for optimized M1 and M2 complexes are 0.09050 and 0.06742 eV, respectively, (Figure 8). Notably, DFT studies indicate ground-state CT from L to Th\(^{4+}\) in the gas phase. It is observed that the energy of both the HOMO and LUMO decreases in the Th\(^{4+}\) bound state with an overall decrease of the HOMO—LUMO gap by 0.02308 eV in M2 relative to M1. Moreover, the charge density at the LUMO of M1 is distributed throughout the molecule. Upon excitation, the charge density slightly shifted to the azine and Th\(^{4+}\) center. After binding to Th\(^{4+}\), the CT becomes more prominent at the vicinity of acceptors, azine bound to Th\(^{4+}\), observed from the LUMO.

As selectivity of the probe is highly solvent dependent, the emission characteristics of M1 in the presence of Th\(^{4+}\) have been tested in different solvents viz., MeOH, EtOH, dimethylformamide (DMF), CHCl\(_3\), CH\(_3\)CN, tetrahydrofuran (THF), EtOAc, dichloromethane (DCM), and dimethyl sulfoxide (DMSO). The sensitivity being highest in MeOH, entire studies have been performed in MeOH.

To examine the reversibility of binding between M1 and Th\(^{4+}\), ethylenediaminetetraacetic acid (200 \(\mu\)M) (\(\lambda_{\text{Ex}}\) 342 nm) is added to the mixture of M1 (20 \(\mu\)M) and Th\(^{4+}\) (100 \(\mu\)M). Interestingly, the emission intensity at 557 nm decreases, whereas it increases significantly at 398 nm, demonstrating reversibility of the binding process.

The emission characteristic of M2 being solvent dependent, coordinating solvents shift the emission to higher wavelength and lower the quantum yield (Table 1). These observations in combination with DFT results indicate that the HOMO—LUMO energy gap (\(E_g\)) may be tuned. Figure 8 shows solvent-dependent emission spectra and corresponding UV-light exposed colors of M2 (\(\lambda_{\text{Ex}} = 310\) nm).

### Table 1. Solvent-Dependent Emission and Quantum Yield of M2

| solvent     | \(\lambda_{\text{Em}, \text{nm}}\) | quantum yield (\(\phi_\text{f}, \%\)) |
|-------------|----------------------------------|-------------------------------------|
| DMSO        | 534                              | 1.1                                 |
| MeOH        | 557                              | 1.5                                 |
| EtOH        | 554                              | 1.6                                 |
| DCM         | 434                              | 3.1                                 |
| THF         | 480                              | 3.5                                 |
| CHCl\(_3\) | 479                              | 3.3                                 |
| DMF         | 548                              | 0.8                                 |
| ACN         | 534                              | 1.8                                 |
| EtOAc       | 539                              | 2.6                                 |
| **ETOH**    | **554**                          | **1.6**                             |
| **MeOH**    | **557**                          | **1.5**                             |
| **DCM**     | **434**                          | **3.1**                             |
| **THF**     | **480**                          | **3.5**                             |
| **CHCl\(_3\)** | **479**                        | **3.3**                             |
| **DMF**     | **548**                          | **0.8**                             |
| **ACN**     | **534**                          | **1.8**                             |
| **EtOAc**   | **539**                          | **2.6**                             |

### Table 2. Real Water Analysis

| river water | added (10\(^{-2}\) M) | found (10\(^{-2}\) M) | recovery (%) |
|-------------|------------------------|------------------------|--------------|
| R1\(^a\)   | 5.52                   | 4.85                   | 87.86 ± 1.13 |
| R2\(^a\)   | 10.36                  | 9.42                   | 90.96 ± 1.21 |
| R3\(^a\)   | 15.32                  | 14.02                  | 91.51 ± 1.01 |
| T1\(^b\)   | 5.21                   | 4.36                   | 83.68 ± 1.21 |
| T2\(^b\)   | 10.32                  | 9.32                   | 90.31 ± 2.11 |
| T3\(^b\)   | 15.36                  | 14.01                  | 91.21 ± 1.66 |
| I1\(^c\)   | 5.21                   | 4.99                   | 95.77 ± 1.21 |
| I2\(^c\)   | 10.22                  | 9.88                   | 96.67 ± 1.26 |
| I3\(^c\)   | 15.34                  | 14.96                  | 97.52 ± 2.01 |

\(^a\)River water. \(^b\)Tap water. \(^c\)Industrial water.

### APPLICATION

#### Analysis of Real Water Samples. The developed method is applied for determination of Th\(^{4+}\) in real water samples by the standard addition method. The accuracy of the method is checked by recovery studies using different concentration levels of Th\(^{4+}\) in the contaminated water. A known amount of Th\(^{4+}\) (as nitrate salt) is added to the contaminated water sample collected from Durgapur-Asansol Industrial area of West Bengal (India). Total concentration of Th\(^{4+}\) is measured using the developed method (Figure S21). Table 2 indicates the efficiency of the developed method.

#### Solid-Phase Extractive Recovery of Th\(^{4+}\) Using Immobilized M1. The immobilization of M1 on silica (100–200 mesh) is achieved by following the literature procedure. The mixture of M1 (1.5 g) and silica (10.1 g) is refluxed in methanol...
for 3 h. The solvent is removed under vacuum. The color of silica-immobilized M1 becomes light yellow. A glass column (15 cm × 1 cm) is filled with immobilized M1 up to 12 mL bed volume (Figure 10). Th4+ contaminated in real water is passed through the column at a flow rate of 1 mL min⁻¹.

Figure 10. Color of silica-immobilized M1 after Th⁴⁺ sorption.

To establish that silica-immobilized M1 binds to Th⁴⁺, its FTIR spectra are measured before and after sorption of Th⁴⁺. Figure S22 (Supporting Information) shows a red shift of the −CH=N− stretching from 1625 to 1990 cm⁻¹ after sorption of Th⁴⁺. Moreover, the 1386 cm⁻¹ band is red shifted to 1436 cm⁻¹. The absence of the 3219 cm⁻¹ (−O−H) band supports Th⁴⁺ binding on silica-immobilized M1.

Comparison of the scanning electron microscopy (SEM) images of silica-immobilized M1 before and after sorption of Th⁴⁺ (Figure 11) indicates micellial growth at the silica bead surface for later one, suggesting Th⁴⁺ sorption.

Table 3 indicates efficiency of silica-immobilized M1 toward Th⁴⁺ recovery from the mixture of other relevant cations. After passing the solution of Th⁴⁺ along with other cations (M⁺) through the column filled with silica-immobilized M1, the light yellow-colored bed turns orange-red suggesting Th⁴⁺ sorption. The sorbed Th⁴⁺ finally eluted with the hexane−ethyl acetate mixture (1:9, v/v).

Table 3. Recovery of Th⁴⁺ from the Mixture of Other Relevant Cations

| sample | added (10⁻² M) | found (10⁻² M) | recovery (%) |
|--------|---------------|---------------|--------------|
| S1     | 10.51         | 9.85          | 93.72 (±0.22) |
| S2     | 18.60         | 17.66         | 94.94 (±0.13) |
| S3     | 25.21         | 24.65         | 97.78 (±0.33) |

Table 4. Role of Solvents on Th⁴⁺ Extraction (%) Efficiency

| solvent  | extraction (%) |
|----------|----------------|
| CH₃COOC₂H₅ | 95.23 ± 1.23   |
| CHCl₃    | 93.36 ± 1.10   |
| CCl₄     | 91.12 ± 2.11   |
| DCM      | 88.69 ± 1.86   |

Table 4 indicates very high Th⁴⁺ extraction efficiency of M1 over other cations in a competing environment at a wide pH range in ethyl acetate (Figures 13 and S23). Concentration of M2 in the organic phase is monitored from the emission intensity (λₑm = 557 nm). Similarly, L also enables to extract Th⁴⁺ (82.56%) in EtOAc. However, M1 being a better extractor is used for extraction of Th⁴⁺ ions (95.23%).

Figure 12. Extraction of Th⁴⁺ by M1 from water into EtOAc.

Solvent Extraction of Th⁴⁺. The solvent extraction of Th⁴⁺ from the mixture of other relevant cations (M⁺) is carried out using M1. Different solvents like CH₃COOC₂H₅, CHCl₃, CCl₄, and DCM have been checked. Different concentrations of M1 (0.1 × 10⁻³, 0.3 × 10⁻³, 0.5 × 10⁻³, 1.0 × 10⁻³, and 1.5 × 10⁻³ M) are prepared and equilibrated with the abovementioned mixture containing Th⁴⁺. The system is allowed to equilibrate for 2 h at 298 K in an automatic shaker equipped with a temperature regulator. Then, the organic layer is separated and the concentration of Th⁴⁺ is measured using the calibration graph (Figure 12). The distribution coefficient (D) is calculated from

the equation, \( D = \frac{C_M(\text{org})}{C_M(\text{aq})} \), where \( C_M(\text{org}) \) and \( C_M(\text{aq}) \) are concentrations of Th⁴⁺ in organic and aqueous phases, respectively, after extraction. Table 4 indicates very high Th⁴⁺ extraction efficiency of M1 over other cations in a competing environment at a wide pH range in ethyl acetate (Figures 13 and S23). Concentration of M2 in the organic phase is monitored from the emission intensity (λₑm = 557 nm). Similarly, L also enables to extract Th⁴⁺ (82.56%) in EtOAc. However, M1 being a better extractor is used for extraction of Th⁴⁺ ions (95.23%).

CONCLUSIONS

An azine-based Mo(VI) complex (M1) is explored for selective detection of Th(IV) through orange-red emission. Th(IV) quickly displaces Mo(VI) from M1, resulting in red shift of the emission band and 41-fold fluorescence enhancement. The
LOD for Th(IV) is 1.5 × 10⁻⁹ M. The displacement binding constant of M1 for Th(IV) is 4.59 × 10⁴ M⁻¹. However, the structure of M1 is confirmed by SCXRD, the recognition of Th(IV) by the displacement approach using M1 is established firmly by spectroscopic studies and kinetically followed by the stopped-flow technique. Moreover, M1 efficiently extracts Th(IV) from aqueous solution to ethyl acetate. The silica-immobilized M1 efficiently enrichs Th(IV) from the mixture of other relevant cations through solid-phase extraction. DFT calculations on Th(IV) from aqueous solution to ethyl acetate. The silica-immobilized M1 is con

Materials and Equipment. HEPES buffer, 4-N,N-diethylaniline salicyaldehyde, and hydrazine hydrate (98%) are procured from Sigma-Aldrich (India). Thorium(IV) nitrate is bought from Merck (India). The spectroscopic grade solvents and other analytical grade reagents purchased from Merck (India) are used without further purification. Milli-Q Millipore (18.2 MΩ cm⁻¹) water is used whenever required.

A Multispec 2450 spectrophotometer and Prestige 21 CE FTIR spectrometer are used to measure respective spectra. A QTOF 60 Micro YA 263 mass spectrometer is utilized to measure the mass spectrum in the ES positive mode. The steady-state emission and excitation characteristics are monitored with a Hitachi F-4500 spectrophotometer. The solution pH is measured with a SYSTRONICS digital pH meter (model 335). The elemental analysis is carried out using the Bruker ETAX instrument in air. Kinetic experiment is carried out with an Applied Photophysics SX 17MV stopped-flow spectrophotometer (model OPT-622) in the symmetric mixing mode at 25 °C and ambient pressure. A Bruker ADVANCE III HD (400 MHz) spectrometer is used to record ¹H NMR spectra. Chemical shifts are reported in parts per million (ppm), and the residual solvent peak is used as an internal reference: proton (chloroform-δ 7.26), carbon (chloroform-δ 77.16), or tetramethyl silane (TMS-δ 0.00) is used as a reference. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), and bs (broad singlet). Coupling constants are reported in Hertz (Hz). The SCXRD analysis of M1 is carried out at 150 K on a Bruker SMART APEX CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å).

Synthesis. 6,6′-(1(E,1′E)-Hydrazine-1,2-diylidenebis-(methylidyline))bis(3-diethy lamino)phenol) (L). The mixture of hydrazine hydrate (0.0167 g, 0.2825 mmol) and 4-diethy lamino salicyaldehyde (0.108 g, 0.5595 mmol) is refluxed in methanol at 60 °C for 5 h (Scheme S1). The brown crystals collected after slow removal of the solvent are recrystallized from methanol to yield pure L. Anal. Calcd (%): C, 69.08; H, 7.91; N, 14.65. Found: C, 69.20; H, 7.88; N, 14.67. The crystal belongs to the P1 space group (Figure S24) with CCDC no. 1555280. Tables S3–S5 (Supporting Information) provide crystal refinement parameters. The QTOF–MS (ES⁺) (Figure S25): [M + H]^+ = 383.77 (calcld. 383.51), 100%; [H NMR (Figure S26) (400 MHz, DMSO-d₆): δ (ppm) 13.614 (1H, s), 8.379 (1H, s), 8.312 (1H, s), 7.259 (1H, s), 6.913–6.731 (m, J = 2.8), 4.116–3.671 (m, J = 6.8). FTIR (cm⁻¹) (Figure S27): 3226 ν(O–H); 3103, ν(C–H, aromatic); 1768, 1652, ν(–C=NH); 1536, ν(–C=N–stretch); 1375, ν(C=O–stretch); 1226, ν(C–N–stretch). UV–vis (Figure S28): λ (nm) in MeOH (ε, M⁻¹ cm⁻¹), 248 nm (6.3 × 10⁵) and 421 nm (7.9 × 10⁴).

Emission characteristics (Figure S29): λₑx = 338 nm, λₑm = 422 nm in MeOH.

M1 Complex. Solutions of MoO₂(acac)₃ (as 1% H₂O, 1.023 g, 2.39 mmol, 5 mL) and L (0.4554 g, 1.18 mmol, 10 mL) in MeOH/DCM (4/1, v/v) are mixed under stirring conditions at room temperature. Slow evaporation of solvent yielded brick-red crystals (yield, 97%, Scheme S1). The crystal has the P1 space group with CCDC no. 1553740. Table S1 (Supporting Information) provides the crystal refinement parameters. Elemental analysis (%): C, 51.15; H, 6.26; N, 9.94. Calcd: C, 51.04; H, 6.30; N, 10.01. The sharp peak at 719.49; 100% (calcld, 719.85) in the mass spectrum corresponds to Ca₆H₆Mo₃N₄O₁₁ (Figure S30) and the peak at m/z 383.46 is assigned to protonated L. Figure S31 (Supporting Information) shows ¹³C NMR of M1. FTIR (cm⁻¹) (Figure S27): 3256, ν(O–H); 2987 ν(C–H, aromatic); 1666, ν(–CH=NH); 1586, ν(–C=C–, stretch); 1464, ν(bending aromatic –C–H and aliphatic –C–H bond, respectively); 1382, ν(C–N); 1242, ν(C=O–stretch); 1026, ν(C=O–stretch). UV–vis (Figure S32): λ in MeOH (ε, M⁻¹ cm⁻¹), 267 nm (2.7 × 10³), 362 nm (9.8 × 10³) and 481 nm (2.6 × 10⁴). The emission spectrum is presented in Figure S33 (Supporting Information).

M2 Complex. The method is same as described for M1, including the solvent system. Only the reagents differ as mentioned here. Th(NO₃)₄ (1.023 g, 2.13 mmol, 5 mL) and M1 (1.53 g, 2.13 mmol, 15 mL). The yield is 97% (Scheme S2). Elemental analysis (%): found, C, 35.02; H, 4.01; N, 11.14. Calcd: C, 35.07; H, 3.99; N, 11.21. The peaks in the mass spectrum at 755.52 (20%) (calcld, 755.55) and 777.48 (100%) are assigned to C₂₂H₂₄ThN₄O₉ (M) and [M + Na]⁺, respectively, (Figure S34). Figure S31 (Supporting Information) shows the ¹³C NMR spectrum of the [M1 + Th³⁺] adduct. FTIR (cm⁻¹) (Figure S35): 3426, ν(O–H); 2909, ν(C–H, aromatic); 1734, ν(C=O); 1556, ν(C=C, stretch); 1386, ν(C–N). UV–vis (Figure S36): λ in MeOH (ε, M⁻¹ cm⁻¹), 267 nm, (8.3 × 10³), 372 nm (3.2 × 10⁵) and 485 nm (2.3 × 10⁴). The emission spectrum is presented in Figure S37 (Supporting Information).

ASSOCIATED CONTENT

3 Supporting information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01901.

¹H NMR, ¹³C NMR, and MS spectra; experimental details for determination of binding constants, LOD, interference studies, and so forth; and optimized structures of M1 and M2 along with theoretical bond lengths and angles (PDF)

Crystal refinement parameters of C₂₂H₂₄N₄O₉ (CIF)

Crystal refinement parameters of 2(C₂₂H₃₆Mo₃N₄O₉), C₂₂H₃₆N₄O₉ (CIF)

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Notes

The authors declare no competing financial interest.
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