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Unusual binding selectivity with non-selective homoditopic pillar[5]arene oxime: serendipitous discovery of a unique approach to heterobinuclear metalation in solution

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A heterobinuclear complexation strategy on homoditopic pillar[5]arene was developed by using a pillar[5]arene with two rims decorated with benzaldehyde oximes. The unique selective recognition process was found to result from vesicular formation based on a controllable self-assembly, leading to binding of thorium (IV) only on one rim, with the other rim being unoccupied for subsequent complexation of a second different metal ion.

Pillararenes have gained significant popularity in the past years due to their ability to implement host-guest interactions with a wide range of neutral, cationic or anionic species.[1] These macrocyclic hosts are featured by its unique construction involving a certain number (n=5~15) of hydroquinone units linked by methylene (-CH_2-) groups at the 2,5-positions of aromatic rings.[2] Among them, functionalized homoditopic pillar[5]arenes (P5A), i.e., those with two rims fully decorated with same functional groups, have found widespread applications in molecular recognition,[3] catalysis,[4] separation technology,[5] transmembrane channels,[6] metallic or anionic sensor,[7] drug delivery,[8] and liquid-crystal materials,[9] and constructing mechanically interlocked structures [10] or supramolecular polymers.[11] Sometimes, use of one-rim on a pillar framework is desired to serve a specific purpose.[12] In this regard, synthesis of non-symmetric pillararenes (NSP) with just one rim being functionalized enables selective complexation of guests or construction of amphiphilic molecule.[13] However, low yield and tedious workup preclude NSP or heteroditopic pillararenes from being widely applied. This prompted us to raise the question: Is it possible to selectively exploit only one rim of homoditopic pillar[5]arenes in recognition process while the other rim remains untouched? In effect, it is a commonplace for a pillararene to bind one cationic species on one rim by controlling host/guest molar ratios.[14] In our previous work, preorganizing ten diglycolamide moieties on both sides of the pillararene platform was found to result in high efficiency towards partitioning of Eu(III) and Am(III) with only one metal ion binding to pillararene ligands under extraction conditions.[15] This is not unexpected given the extremely low concentration of radioactive metal ion. However, the presence of excessive metal ions still lead to binuclear complexation on both rims of the pillar.[14]

Selective binding of two different metal ions can be readily achieved at two different sites using heteroditopic ligands,[16] while it is difficult to do so with homoditopic ligands[17] in high specificity, particularly in the presence of excess metal ions. Installation of two different metal ions may have implications in biological enzymes where two metal ions display different functions.[18] So far, it is a demanding challenge to utilize homoditopic P5A for selective one-rim complexation. Herein we report on our discovery that this can be realized by using oxime-based pillar[5]arene **3** (Fig. 1) via a route based on bilayer vesicle formation. This work provides a useful strategy of utilizing homoditopically functionalized pillararene for one-rim host-guest interaction, which allows for subsequent

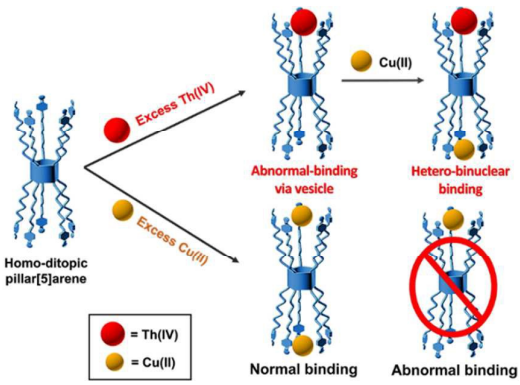

Fig. 1. Schematic representation of an approach to heterobinuclear complex from monothorium complex with homoditopic pillar[5]arene oxime **3** via vesicular formation (vide post). Excess thorium nitrate and cupric nitrate salts are used in the recognition process.

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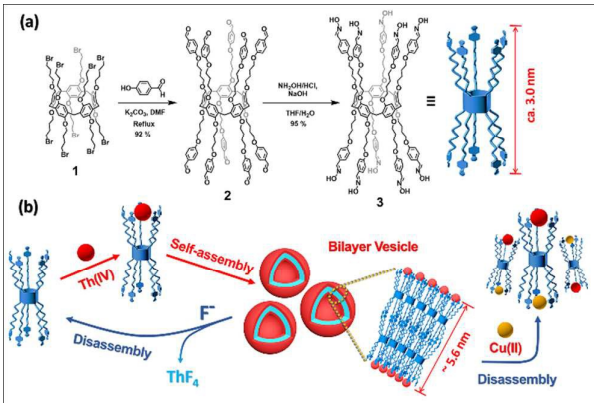
introduction of otherwise different metal ion on the other rim.

During our investigation on the recognition properties of organic molecules and metal cations with macrocyclic ligands,[19] homoditopic pillar[5]arenes were found to serve as an excellent molecular platform for preorganizing various functional groups such as N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA) and carbamoyl methylphosphine oxide (CMPO) for the extraction and separation of actinide/lanthanide elements.[14, 20] As a further step, oximes (R^i-CH=N-OR^{ii}), one of the widely used chelating agents for transition metal ions such as Cu^{2+}, Zn^{2+}, Co^{2+}, UO_2^{2+} and Th(IV),[21] are thus incorporated into a pillar[5]arene molecule in this work, which leads to the design of pillar[5]ararene based benzaldehyde oxime (**P5ABO**) **3** (Scheme 1a). Compound **3** was synthesized by coupling bromo-substitued pillar[5]arene with 4-hydroxybenzaldehyde, followed by reacting the resultant **2** with hydroxylamine hydrochloride. The yield is over 90% for each step.

Oxime-based ligands are known to have a strong coordination ability and a variety of coordination modes. A routine screening in acetonitrile of various lanthanide ions (La^{3+}, Nd^{3+}, Gd^{3+}, Pr^{3+}, Er^{3+}, Yb^{3+}, Sm^{3+}, $Lu^{3+}$and Eu^{3+}) and a typical actinide ion (Th^{4+}) (Fig. S3, ESI†) showed the preference of complexing Th(IV) by the macrocyclic ligand **3** over other metal ions. However, to our great surprise, absorptions of the complex in acetonitrile during UV-vis titration experiments were found to decrease at the outset of increasing the concentration of thorium nitrate, but soon cease to change beyond ca. 1.0 equiv. of the salt (Fig. S4, ESI†), implicating a 1:1 binding mode between **3** and Th(IV). Results from Job's plot experiments indicated a 1:1 stoichiometry for **3**⊃Th(IV) complex (Fig. S5, ESI†). The failure to observe the binding of two metal ions even in the presence of 3.0 equiv. of thorium nitrate is hardly rationalized given the two equivalent rims of the pillar[5]arene that are exposed to metal ions in solution. ^{1}HNMR titration experiments were then conducted in acetone-d_6/acetonitrile-d_3 (4:1, v/v) to further explore the complexation process. The hydroxyl proton (Ha in **3**) is diagnostic of the complexation between **P5ABO** and thorium ion (Fig. S6, ESI†). Binding saturation occurs after the addition of 1 equiv. of Th(IV), also indicating a 1:1 binding stoichiometry of the complex between **3** and Th(IV).

As generally found with homoditopic macrocycles,[22] the mononuclear complexes, once formed, show a marked tendency to encapsulate a second metal ion in solution, to give stable binuclear complexes, particularly when metal to ligand molar ratio is greater than 2:1.[14] Even at 1:1 molar ratio, the presence of both mononuclear and binuclear complexes is still often inevitable. Therefore, the question that follows is: how could it be possible for such a selectivity to be observed on a homoditopic pillar[5]arene even with addition of excess thorium ion? The first clue to the answer comes from the observation that an off-white solid precipitated out if an acetone solution of **3** and thorium(IV) nitrate (1:1) was allowed to stand for over 48 h, suggesting the possibility of aggregation in solution. Indeed, dynamic light scattering (DLS) revealed the presence of aggregates with the average size of 152 nm in acetone (Fig. S7, ESI†), indicating self-assembling of the monothorium complex. The critical aggregation concentration (CAC) in acetone was determined to be 1.9×10^{-5} M (Fig. S8, ESI†). Further experiments were performed at concentrations above its CAC. Scanning electron microscopy (SEM) experiments revealed spherical nanoscale particles at an average size of 138 nm. (Fig. S9, ESI†), which is consistent with the observations from atomic force microscopy (AFM) (Fig. S10, ESI†). Luckily, expanding the SEM image discloses a vesicle with a defect that a hole exists on the spherical particle, indicating its empty inside (Fig.2a & 2b). A more convincing evidence for forming vesicular assemblies is from transmission electron microscopy (TEM) images where a distinctly darker edge with a width of 5.6 nm is observed (Fig. 2c & 2d). Besides, encapsulating of rhodamine B also proved the existence of vesicles (Fig. S16, ESI†).

To verify the crucial role played by the presence of thorium ion in forming vesicles, fluoride anion was then added to the solution to disrupt the aggregation. Fluoride is known to react with Th(IV), forming an insoluble precipitate.[23] As anticipated, spherical assemblies disappeared in solution as shown by SEM technique. Upon adding Th(IV), vesicles were observed again (Fig. S11, ESI†). In contrast, macrocycle **3** alone was unable to form vesicles or aggregates in the chosen solvent system. This



Scheme 1 a) Synthesis route of **P5ABO 3**; b) schematic illustration of the proposed mechanism for thorium(IV)-induced vesicle formation and disassembly process in the presence of fluoride or a second metal ion.

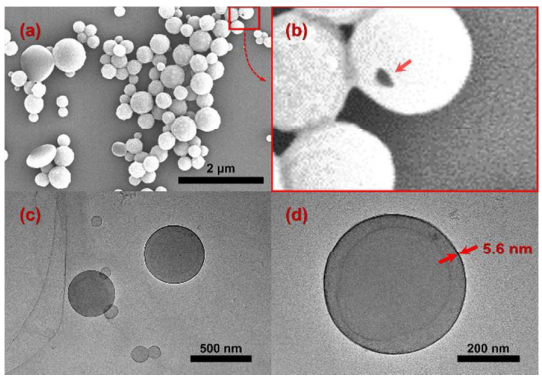


Fig. 2 SEM images (a, b) and TEM images (c, d) of **3**⊃Th(IV) vesicular aggregates from acetone-water (1:1, v/v) solution. b) and d) are the enlarged view.

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clearly indicates that the formation of the Th complex constitutes an important step towards production of vesicles. High resolution electrospray ionization (HR-ESI) MS experiments uncovered a peak with the highest intensity at m/z = 917.7, corresponding to the complex $[M+Th^{4+}-H^{+}]^{3+}$. The identity of the 1:1 complex is also corroborated by matching the isotope distribution with the simulated one (right inset in Fig. S12, ESI†). In addition, IR spectroscopy showed the strong band at 1606.6 cm^{-1} of ν(C=N) in **3**, which shifts to 1599.9 cm^{-1} in its Th complex, a change of 6.7 cm^{-1} (Fig. S13, ESI†). Particularly, the pronounced band shift of 42.4 cm^{-1} of N-O of the complexes with respect to **3** (Fig. S13, ESI†) strongly suggests that coordination occurs mainly through its oxygen atoms of N-O bonds of oxime groups. All these results, taken in concert, seem to present a scenario for the selective binding of only one metal ion on a non-selective homoditopic P5A: the macrocycle binds one thorium ion first to form amphililic **3**⊃Th(IV) complex, followed immediately by the self-assembly of this amphiphilic complex to form vesicles before proceeding to add a second thorium ion on the other rim of P5A.

To provide further evidence for the rationalized pathway through mononuclear Th-complex to vesicle formation, computational simulation was carried out at B3LYP/6-31G level (Fig. S17 & Table S1, ESI†). Since a **P5ABO** molecule is about 3.0 nm long as determined computationally, the wall of the vesicle is reasonably assumed to consist of two layers with each layer aligned with side-to-side complexes (Scheme 1). The analysis from theoretical calculations and the experimental results above only indicated the vesicles that are formed by mononuclear complex. As a control, the possibility of forming vesicles via binuclear complex was examined. Cupric(II) ion was selected to replace Th(IV) ion for the experiment because of its strong coordinating ability towards oximes.[24] UV-vis titration experiments showed a gradual decrease of absorbance with addition of cupric nitrate to a solution of **1** in acetonitrile till up to ca. 2.0 equiv. (Fig. S14, ESI†), suggesting the formation of dicopper complex. Job's plot offered 1:2 (ligand to metal) stoichiometry (Fig. S5, ESI†), which is consistent with HR-ESI data (Fig. S12C, ESI†). However, no sign of assemblies was observed from DLS profiles (Fig. S15b, ESI†). This again indicates that the selectivity for mononuclear complexation on one rim and vesicle formation are dependent on a specific metal ion, such as thorium(IV) used here. In addition, the fact that Cu(II) alone failed to form a mononuclear complex explains the non-aggregation behaviour of **P5ABO** in the presence of cupric(II) ion because the amphiphilicity of the complex is lost when two cupric(II) ions are introduced to both rims of the pillar.

With the other unoccupied rim on a Th-complex available for further complexation, we wondered if it is possible to make use of a homtoditopic pillar[5]arene for generating heterobinuclear complexes. We started to explore the possibility by a continuous UV-vis titration method.[25] The absorption of **3** at 264 nm decreases with increasing the amount of Thorium(IV) nitrate; however, a marginal change is observed beyond 1 equiv. of the salt (up to 2 equiv.), indicative of binding one Th(IV) ion. Further addition of cupric salt induces a continuous decrease in absorption until 1 equiv. of Cu(II) ion is added, beyond which a plateau is achieved (up to 4 equiv.) (Fig. 3a), suggesting addition of a

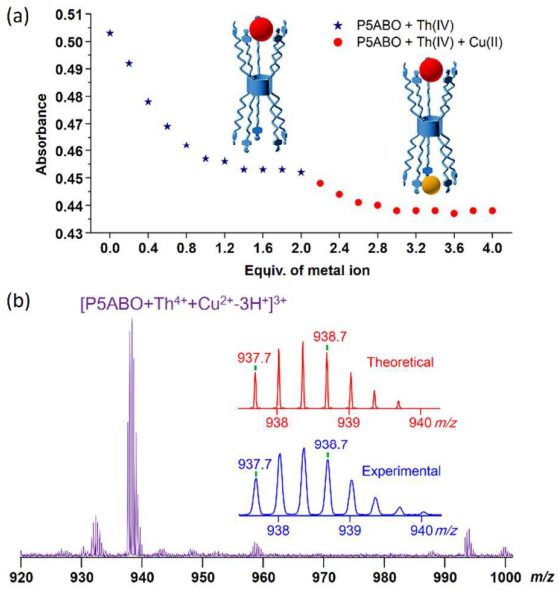

Fig.3 a) Plot of the UV-vis absorbance of **3** (2.5 μM) at 264 nm versus equivalents of metal nitrate when titrating first with Th(IV), and then with Cu(II) in acetonitrile); b) high-resolution ESI MS spectrum and simulated spectra (insert red) of heterobinuclear complex Th(IV)⊂**3**⊃Cu(II).

second metal ion to the other rim of pillararene platform. These results clearly demonstrate a stepwise binding process from mononuclear complex to heterobinuclear complex with homoditopic ligand **3**. The formation of the heterobinuclear complex was further corroborated by high resolution spectrometry of the sample prepared from a solution containing **3** (5.0 mmol) and 1 equiv. of thorium nitrate in acetone/methanol, which shows identical peaks (m/z = 938.4 $[M+Th^{4+}+Cu^{2+}-3H^{+}]^{3+}$) with isotopic distribution matching those observed for Th(IV)⊂**3**⊃Cu(II) complex (Fig. 3b & Fig. S12D, ESI †). The presence of aggregation prevents us from acquiring the accurate binding constants.[26] It should be noted that the results from DLS experiments revealed absence of aggregation when 2 equiv. of Cu(II) ions was added to a solution of aggregated **3**⊃Th(IV) complex (Fig. S15c, ESI†), indicating disruption of the vesicles in the presence of a second metal ion. The observed thorium(IV)-induced vesicular self-assembly and disassembly process underlines a mechanistic pathway for the formation of the heterobinuclear complex with a homoditopic pillar[5]arene (Scheme 1b). The significant difference in metal-ion-induced assembly between Th(IV) and Cu(II) ions may be ascribed to the discrepancy in their coordination ability, size of metal ions and the effect of solvents.[27]

In conclusion, we demonstrate a strategy that enables exclusive formation in solution of mononuclear complex by spontaneously assembling into vesicles with a homoditopic pillar[5]arene, and more importantly, subsequent formation of heterobinuclear complex. Our approach also circumvents

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limitations of homobinuclear complex formation when only mono-nuclear complex is desired. This represents the first example of complexation of two different metal cations on a homoditopic pillar[5]arene, which distinguishes it from other reported approaches that include the use of heterobinuclear ligands and varying molar ratios of ligand to metal ion. Given the uniqueness of such an approach, this strategy may shed light on possibilities of creating heteronuclear host-guest metal complexes with homoditopic receptors that are synthetically readily available.

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Notes and references

1 (a) T. Ogoshi, T.-a. Yamagishi and Y. Nakamoto, *Chem. Rev.*, 2016, **116**, 7937-8002.; (b) Y. Wang, G. Ping and C. Li, *Chem. Commun.*, 2016, **52**, 9858-9872.

2 (a) T. Ogoshi, S. Kanai, S. Fujinami, T.-a. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022-5023.; (b) D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang and H. Meier, *Angew. Chem. Int. Ed. Engl.*, 2009, **48**, 9721-9723. (c) Z. Zhang, B. Xia, C. Han, Y. Yu and F. Huang, *Org. Lett.*, 2010, **12**, 3285-3287.

3 (a) X.-B. Hu, L. Chen, W. Si, Y. Yu and J.-L. Hou, *Chem. Commun.*, 2011, **47**, 4694-4696.; (b) I. Nierengarten, M. Nothisen, D. Sigwalt, T. Biellmann, M. Holler, J.-S. Remy and J.-F. Nierengarten, *Chem. - Eur. J.*, 2013, **19**, 17552-17558. (c) G. Yu, J. Zhou, J. Shen, G. Tang and F. Huang, *Chem. Sci.*, 2016, **7**, 4073-4078. (d) S. Wang, Y. Wang, Z. Chen, Y. Lin, L. Weng, K. Han, J. Li, X. Jia and C. Li, *Chem. Commun.*, 2015, **51**, 3434-3437.

4 (a) T. Ogoshi, N. Ueshima and T.-a. Yamagishi, *Org. Lett.*, 2013, **15**, 3742-3745.; (b) D. G. Liz, A. M. Manfredi, M. Medeiros, F. Nome, R. Montecinos, B. Gomez-Gonzalez and L. Garcia-Rio, *Chem. Commun.*, 2016, **52**, 3167-3170.

5 (a) S.-Y. Zhou, N. Song, S.-X. Liu, D.-X. Chen, Q. Jia and Y.-W. Yang, *Microchim. Acta.*, 2014, **181**, 1551-1556.; (b) B. Bai, Y. Y. Fang, Q. Gan, Y. Y. Yang, L. H. Yuan and W. Feng, *Chin. J. Chem.* 2015, **33**, 361-367.; (c) S. N. Talapaneni, D. Kim, G. Barin, O. Buyukcakir, S. H. Je and A. Coskun, *Chem. Mater.*, 2016, **28**, 4460-4466.

6 W. Si, P. Xin, Z.-T. Li and J.-L. Hou, *Acc. Chem. Res.*, 2015, **48**, 1612-1619.

7 (a) P. Wang, Y. Yao and M. Xue, *Chem. Commun.*, 2014, **50**, 5064-5067.; (b) Q. Lin, F. Zheng, L. Liu, P.-P. Mao, Y.-M. Zhang, H. Yao and T.-B. Wei, *RSC Adv.*, 2016, **6**, 111928–111933.; (c) L. S. Yakimova, D. N. Shurpik and I. I. Stoikov, *Chem. Commun.*, 2016, **52**, 12462-12465.; (d) R. R. Kothur, J. Hall, B. A. Patel, C. L. Leong, M. G. Boutelle and P. J. Cragg, *Chem. Commun.,* 2014, **50**, 852-854.

8 (a) Y. Chang, K. Yang, P. Wei, S. Huang, Y. Pei, W. Zhao and Z. Pei, *Angew. Chem., Int. Ed. Engl.*, 2014, **53**, 13126-13130.; (b) X. Wu, Y. Li, C. Lin, X.-Y. Hu and L. Wang, *Chem. Commun.*, 2015, **51**, 6832-6835. (c) G. Yu, R. Zhao, D. Wu, F. Zhang, L. Shao, J. Zhou, J. Yang, G. Tang, X. Chen and F. Huang, *Polymer Chemistry*, 2016, **7**, 6178-6188.;

9 S. Pan, M. Ni, B. Mu, Q. Li, X.-Y. Hu, C. Lin, D. Chen and L. Wang, *Adv. Funct. Mater.*, 2015, **25**, 3571-3580.

10 (a) N. Sun, X. Xiao, W. Li and J. Jiang, *Adv. Sci.*, 2015, **2**, 1500082.; (b) W. Wang, B. Sun, X. Q. Wang, Y. Y. Ren, L. J. Chen, J. Ma, Y. Zhang, X. Li, Y. Yu, H. Tan and H. B. Yang, *Chem. Eur. J.*, 2015, **21**, 6286-6294. (c) S. H. Li, H. Y. Zhang, X. Xu and Y. Liu, *Nat. Commun.*, 2015, **6**, 7590.

11 (a) M. Hong, Y.-M. Zhang, Y.-C. Liu and Y. Liu, *Asian J. Org. Chem.*, 2016, **5**, 321-324.; (b) M. Ni, X.-Y. Hu, J. Jiang and L. Wang, *Monogr. Supramol. Chem.*, 2016, **18**, 157-186.

12 (a) Y. Yao, M. Xue, Z. Zhang, M. Zhang, Y. Wang and F. Huang, *Chem. Sci.*, 2013, **4**, 3667-3672.; (b) L. Luo, G. Nie, D. Tian, H. Deng, L. Jiang and H. Li, *Angew. Chem., Int. Ed. Engl.*, 2016, **55**, 12713-12716.

13 (a) X. Shu, W. Chen, D. Hou, Q. Meng, R. Zheng and C. Li, *Chem. Commun.*, 2014, **50**, 4820-4823.; (b) H. Zhang, X. Ma, K. T. Nguyen and Y. Zhao, *ACS Nano*, 2013, **7**, 7853-7863.; (c) T. Nishimura, Y. Sanada, T. Matsuo, T. Okobira, E. Mylonas, N. Yagi and K. Sakurai, *Chem. Commun.*, 2013, **49**, 3052-3054.; (d) K. Jie, Y. Zhou, Y. Yao and F. Huang, *Chem. 0457547Soc. Rev.*, 2015, **44**, 3568-3587.

14 Y. Y. Fang, X. Y. Yuan, L. Wu, Z. Y. Peng, W. Feng, N. Liu, D. G. Xu, S. J. Li, A. Sengupta, P. K. Mohapatra and L. H. Yuan, *Chem. Commun.*, 2015, **51**, 4263-4266

15 L. Wu, Y. Y. Fang, Y. M. Jia, Y. Y. Yang, J. L. Liao, N. Liu, X. S. Yang, W. Feng, J. L. Ming and L. H. Yuan, *Dalton Trans.*, 2014, **43**, 3835-3838.

16 A. Gasnier, J.-M. Barbe, C. Bucher, C. Duboc, J.-C. Moutet, E. Saint-Aman, P. Terech and G. Royal, *Inorg. Chem.*, 2010, **49**, 2592-2599.

17 J. Wahsner and M. Seitz, *Inorg. Chem.*, 2015, **54**, 9681-9683.

18 Tainer, J. A.; Getzoff, E. D.; Beem, K. M.; Richardson, J. S.; Richardson, D. C. *J. Mol. Biol.* 1982, 160, 181-217.

19 (a) X. W. Li, X. Y. Yuan, P. C. Deng, L. X. Chen, Y. Ren, C. Y. Wang, L. X. Wu, W. Feng, B. Gong and L. H. Yuan, *Chem. Sci.*, 2017. Advanced article, DOI: 10.1039/c6sc04714a.; (b) L. Mao, W. Pan, Y. Fu, L. Chen, M. Xu, Y. Ren, W. Feng and L. Yuan, *Org. Lett.*, 2017, **19**, 18-21.; (c) Y. Z. He, M. Xu, R. Z. Gao, X. W. Li, F. X. Li, X. D. Wu, D. G. Xu, H. Q. Zeng and L. H. Yuan, *Angew. Chem. Int. Ed. Engl.*, 2014, **53**, 11834-11839. (d) L. Chen, Z. Y. Peng, S. Liu, X. W. Li, R. Z. Chen, Y. Ren, W. Feng and L. H. Yuan, *Org. Lett.*, 2015, **17**, 5950-5953.

20 (a) Y. Y. Fang, L. Wu, J. L. Liao, L. Chen, Y. Y. Yang, N. Liu, L. T. He, S. L. Zou, W. Feng, and L. H. Yuan, *RSC Adv.*, 2013, **3**, 12376-12383. (b) C. X. Li, L. Wu, L. Chen, X. Y. Yuan, Y. M. Cai, W. Feng, N. Liu, Y. Ren, A. Sengupta, M. S. Murali, P. K. Mohapatra, G. H. Tao, H. Q. Zeng, S. D. Ding and L. H. Yuan, *Dalton Trans.*, 2016, **45**, 19299-19310.

21 (a) R. S. Forgan, J. E. Davidson, F. P. Fabbiani, S. G. Galbraith, D. K. Henderson, S. A. Moggach, S. Parsons, P. A. Tasker and F. J. White, *Dalton Trans.*, 2010, **39**, 1763-1770.; (b) A. P. S. Pannu, J. R. Stevens and P. G. Plieger, *Inorg. Chem.*, 2013, **52**, 9327-9337.; (c) N. Sehati, Z. Shiri-Yekta, A. A. Zamani, M. R. Yaftian and N. Noshiranzadeh, *Sep. Sci. Technol.*, 2012, **47**, 670-676.

22 J. Ma, Q. Meng, X. Hu, B. Li, S. Ma, B. Hu, J. Li, X. Jia and C. Li, *Org. Lett.*, 2016, **18**, 5740-5743.

23 Y. Y. Fang, C. X. Li, L. Wu, B. Bai, X. Li, Y. M. Jia, W. Feng, and L. H. Yuan, *Dalton Trans.*, 2015, **44**, 14584-14588.

24 L. K. Das, C. Diaz and A. Ghosh, *Cryst. Growth Des.*, 2015, **15**, 3939-3949.

25 J. Polster and H. Lachmann, *Spectrometric titrations*, VCH Weinheim, 1989.

26 (a) P. Thordarson, Chem. Soc. Rev., 2011, 40, 1305–1323; (b)E. N. W. Howe, M. Bhadbhade and P. Thordarson, *J. Am. Chem. Soc.*, 2014, **136**, 7505–7516.

27 (a) M. Melník, *Coord. Chem. Rev.*, 1982, **47**, 239-261.; (b) M. Rand, J. Fuger, I. Grenthe, V. Neck, D. Rai, F. J. Mompean, J. Perrone and M. Illemassène, *Chemical thermodynamics of thorium*, OECD Nuclear Energy Agency, 2008.