Selective Crystallization of Rare Earth Ions into Cationic Metal-Organic Frameworks for Rare Earth Separation

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Dedication ((optional))

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Abstract: For rare-earth separation, selective crystallization into metal-organic frameworks (MOFs) offers new opportunities. Especially important is the development of MOF platforms with high selectivity toward target ions. Here we report a MOF platform (CPM-66) with low-coordination-number environment for rare-earth ions. This platform is highly responsive to the size variation of rare-earth ions and shows exceptional ion-size selectivity during crystallization. CPM-66 family are based on M_3O trimers (M = 6-coordinated Sc, In, Tm-Lu) that are rare for lanthanides. We show that the size matching between urea-type solvents and metal ions is crucial for their successful synthesis. We further show that CPM-66 enables a dramatic multi-fold increase in separation efficiency over CPM-29 with 7-coordinated ions. This work provides some insights into methods to prepare low-coordinate MOFs from large ions and such MOFs could serve as high-efficiency platforms for lanthanide separation, as well as other applications.

Lanthanide elements are essential in modern technologies. In nature, they often coexist, making their separation challenging due to similarity in properties.[1] Various methods have been developed, including fractional crystallization, solvent extraction, and ion exchange. The subtle differences in ionic radii play a key role in separation efficiency of these methods.[2] To further improve separation efficiency, it is desirable to develop chemical platforms that are highly responsive to the size variation of rare-earth ions and have large potential to amplify the effects caused by the difference in ionic radii.[3] Towards this end, metal-organic frameworks (MOF) provide new opportunities due to the broad selection of ligands and a high degree of control over the assembly of coordination networks.[4]

We reason that rare-earth MOF structures with low coordination number (< 7) might offer superior separation efficiency because the low-coordination-number environment might amplify generally observed selectivity for smaller ions. Unfortunately, while lanthanide MOFs with high coordination number (> 6) are commonplace,[5] few are known with only 6-coordinated environments that are desired here for studying the effect of coordination environment on separation efficiency.[6] In fact, in the absence of targeted synthetic strategies, a typical synthesis involving lanthanide ions would in all likelihood lead to structures with high coordination numbers (> 6).[7]

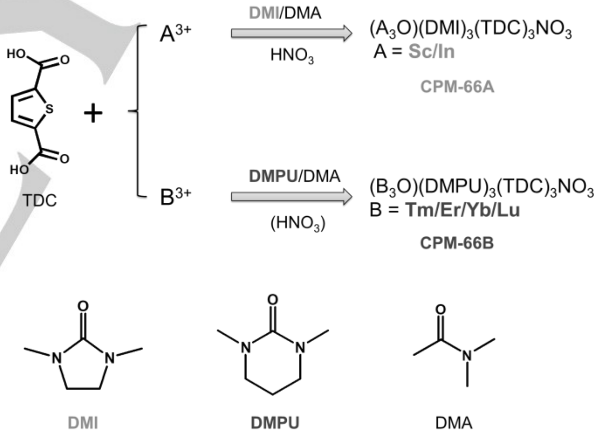

Figure 1. The ring size of DMI and DMPU matches with ionic radii of different M^{3+} ions, leading to a family of CPM-66.

$M_3(O)(RCOO)_6$ trimers are a recurring phenomenon in MOF synthesis and are especially suitable for targeting 6-coordinate MOFs.[8] Yet, identifying synthetic parameters to crystallize trimer-based MOFs across a broad range of ionic radii from Al^{3+} to lanthanides remains hard.[9] The question remains as to what is the upper limit of the ionic radii in trimer-MOFs. Addressing this fundamental question of trimer-MOF chemistry and the effect of coordination environment on separation efficiency, would require exploratory synthesis to investigate effects of ligands, solvent, additives, and extra-framework pore-filling and charge-balancing species. Ultimately, a confluence of these factors will lead to the synthesis of desired materials that stretch the limit of metal trimers in compositions, structures, and applications.[10]

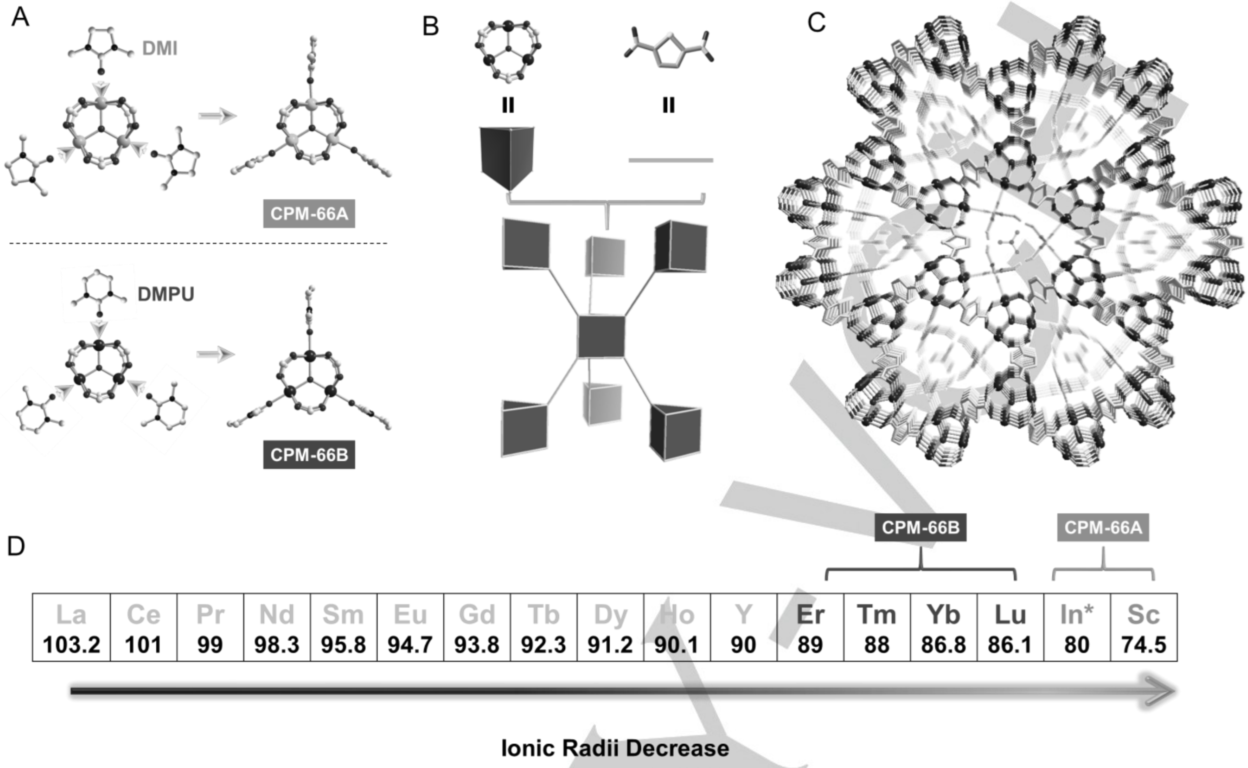

Figure 2. Structures of CPM-66. (a) the formation of trimer building blocks in CPM-66A and CPM-66B; (b) acs topology of CPM-66; (c) the framework of CPM-66B viewed along c direction; (d) rare-earth ions with their corresponding ionic radii (unit: pm) at coordination number of 6 (In^{3+} is also included). In/Sc, light blue; Er/Tm/Yb/Lu, violet; O, red; N, blue; C, gray; S, yellow..

In this work, a series of MOFs (CPM-66) with 6-coordinated rare-earth ions and 6-connected trimers are presented as a platform for studying effects of more restrictive coordination environment on the selectivity of separation. We show that this platform with at least two sub-families has unique crystallization recognition (CPM-66A for Sc/In and CPM-66B for Er/Tm/Yb/Lu). Specifically, a smaller 5-ring-based urea solvent (DMI) directs the synthesis of CPM-66A while the use of larger-sized 6-ring-based DMPU leads to CPM-66B (Figure 1).

Taking advantage of this synthetic success, we further performed a series of separation experiments using CPM-66B as the platform. Consistent with our initial reasoning, we found that the separation efficiency is indeed dramatically enhanced with 6-coordinated CPM-66B, compared with CPM-29 with 7-coordinated rare-earth ions. Furthermore, considerable separation efficiency is observed in rare-earth mixtures with adjacent atomic numbers (Yb-Tm), lending support to the aforementioned application effect of lower coordination environment.

One novel finding from this work that could help stretching the upper limit of ionic radii in trimers is the size matching effect between urea derivative solvents/ligands and trivalent metal ions (which translate into the size of trimer). It was observed that the choice of urea solvents for CPM-66A and CPM-66B was mutually exclusive (i.e., we could not synthesize CPM-66A with DMPU or CPM-66B with DMI). The smallest member of this family, CPM-66A-Sc, was prepared at 100 °C from scandium nitrate hydrate and 2,5-thiophenedicarboxylic acid (H_2TDC) in the mixed solvent of DMI and DMA with the addition of nitric acid. Located about half way between Sc^{3+} and Lu^{3+} in terms of ionic radii, is In^{3+} which was also a match for DMI. The crystallization of the In^{3+} phase can be effected at the same temperature. A further increase in ionic radii to Lu^{3+} or larger lanthanides, led to clear solution under the synthetic condition of CPM-66A. DMI appears not large enough to establish needed steric interactions (with crosslinking TDC^{2-} and/or charge-balancing/pore-filling NO_3^-) to stabilize larger rare-earth ions in the low coordination number of 6 (Figure S1). Subsequently, replacing DMI with a larger-sized urea solvent (DMPU) restores the needed steric interactions and leads to the synthesis of CPM-66B with four late lanthanides from Er to Lu.

The successful synthesis of CPM-66 was confirmed by single-crystal and powder X-ray diffraction (Table S1, Figure S2). CPM-66 crystallize as $[(M_3O)(TDC)_3L_3(NO_3)]$ (M = Sc or In, L = DMI for CPM-66A, M = Er, Tm, Yb, or Lu, L = DMPU for CPM-66B) in hexagonal system with space group *P*-62*c*. There was a good linear fit between the average M-O bond lengths and ionic radii (Figure S4-5 & Table S2).

CPM-66 are based on regular metal trimers and have a MIL-88/MOF-235 type framework with acs topology (Figure 2).[11] Unlike common MIL-88 structures with linear crosslinking ligands, the trimers in CPM-66 were joined by bent TDC ligand. Open metal sites of the trimers are occupied by urea solvents through M-O bond. Two kinds of pores exist in CPM-66 and one of them is filled with pendant urea solvents and nitrate ions (Figure S6).

While metal-trimer building block is common for metal ions with ionic radii from 53.5 pm (Al^{3+}) to 80 pm (In^{3+}),[12] the Ln-based trimers are rare in MOFs.[6] Currently, there are few strategies in MOFs to prevent the tendency for large-sized Ln ions (from 86.1 pm to 103.2 pm) to go higher in coordination numbers, even though in molecular complexes, the use of bulky ligands is a standard practice to achieve low coordination number. This work shows a possible path through structure directing effect and temperature effect (described below), both of which correlate with the increase in ionic radii. In fact, the $[M_3O(RCOO)_6]^+$ trimer (M = Er, Tm, Lu) with octahedral coordination is likely the first of its kinds for each respective element in MOFs and perhaps in all coordination compounds.

CPM-66 have cationic frameworks due to +3 oxidation state of metals in the trimer and neutral pendent DMI or DMPU. The 3-D cationic framework is charge-balanced by nitrate ions. Indicative of a co-structural directing effect, the nitrate ions can be unambiguously located from single-crystal X-ray analysis. Each nitrate group is positioned in a specific orientation within the cavity defined by six pendent urea solvents and three TDC ligands. The formation of CPM-66 with NO_3^- as extra-framework anions can also occur in the presence of competing anions such as Cl^- or ClO_4^- introduced by either using the corresponding metal salts in place of nitrate salts or alternatively by replacing HNO_3 with HCl in the synthesis. This suggests the likely co-templating effect by nitrates through directional H-bonding effects.

In this work, the achievable ionic radii of M^{3+} for the formation of CPM-66 cover the range from 74.5 pm for Sc^{3+} to 89 pm for Er^{3+}. CPM-66 based on Y^{3+}/Ho^{3+} (~90 pm) or larger lanthanides have yet to be synthesized. Thus, CPM-66B-Er contains the largest M^{3+} ion among the M_3O-trimer-based MOFs known so far. Given the observed size-matching effect and new understanding learned from the formation of CPM-66A and CPM-66B, it can be reasoned that CPM-66 based on pre-Er lanthanides (i.e., Y/Ho-La) may be accessible through intelligent design of one or more non-metal components with a size increase commensurate with the increase in the ionic radii of metals. This reasoning is supported by the fact that M_3O-based MOFs are already known for ionic radii up to 95 pm (for Cd^{2+}) in the case of divalent metal ions.[13] Excluding for already successful Lu-Er elements, at least 6 additional rare-earth elements fall into the size range (from 53.5 pm for Al^{3+} to 95 pm for Cd^{2+}) currently known for trimer MOFs.[14]

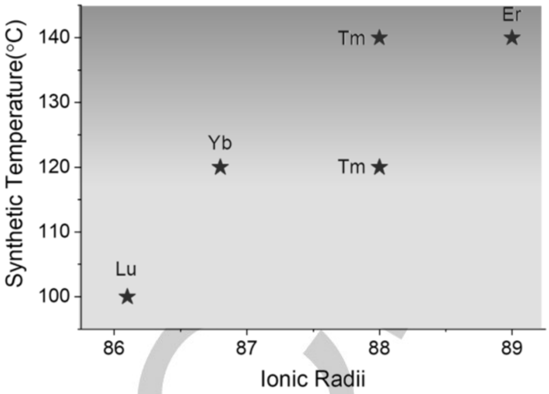

Figure 3. Dependence of synthetic temperature on ionic radii for CPM-66B.

Another finding of this work that may help the further development of M_3O-based trimer MOFs is the clear correlation between ionic radii of metal ions and crystallization temperature. Specifically, for the four lanthanides of CPM-66B, higher crystallization temperature is progressively more helpful as lanthanides get larger from Lu^{3+} to Er^{3+} (Figure 3). This is despite of the fact that the change in ionic radii is only about 1 pm between adjacent elements, less than 0.5% of the M-L bond length. This observation of the temperature-radius dependence can be interpreted as a direct experimental evidence for the amplification effect of low coordination environment.

CPM-66B was used as a platform for separation experiments. A binary mixture of Yb^{3+} and another rare-earth ion (i.e., La to Tm, Lu, and Y) in 1:1 molar ratio was used to grow MOFs under the synthetic condition of Yb-CPM-66B. As expected, the mixture resulted in the crystallization of CPM-66B (Figure S11), albeit with the possibility for having both lanthanide elements in different ratios.

CPM-66B showed high separation capability based on elemental analysis of CPM-66B samples crystalized out of binary mixtures by energy dispersive X-ray spectroscopy (EDS) (Figure S12). The EDS results, together with the separation factors, were given in Table S4. For this particular set of combinations, Yb^{3+} is preferred in all cases except Yb-Lu, in which Lu^{3+} has a smaller ionic radius. The separation results show that smaller Ln^{3+} is preferred in CPM-66, consistent with the observation in CPM-29.[5e] This is in line with the knowledge that smaller Ln3+ tends to form more stable metal complexes in the solution. In the cases of Yb-M (M =Eu, Sm, Nd, Pr, Ce, La), the separation is nearly complete, with only trace amount of secondary ions being detected. The separation factors decrease when the difference in ionic radii becomes smaller (Figure 4a). Nevertheless, reasonable separations could still be obtained for most combinations. Even for Yb-Tm with adjacent atomic numbers and a mere 1.2 pm difference in ionic radii, the molar fraction of Yb can still reach as high as 61.6%, with separation factor of 1.63. Such a high separation capability is advantageous, compared with solvent extraction and ion exchange method.[15] The recovery of purified rare earth is expected to be realized by dissolution of the crystals followed by precipitation. Our preliminary results indicated that CPM-66B could easily be dissolved in HCl solution (around 1M).

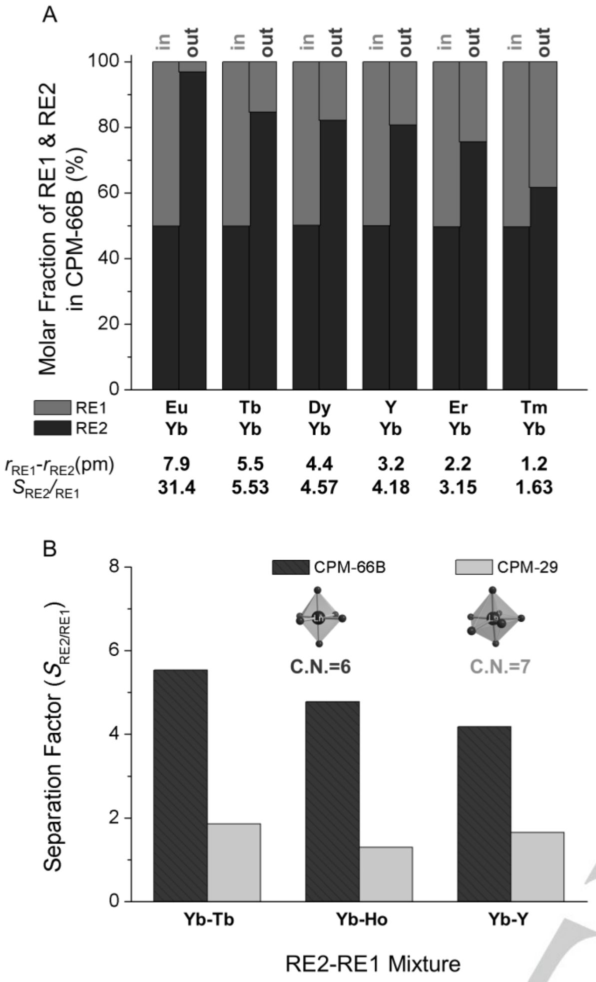

Figure 4. (a) Selective crystallization of CPM-66B from six binary RE ions mixtures. "in" and "out" indicate the molar fraction in the raw materials and the final crystals, respectively. (b) Comparison of separation factors between CPM-66 and CPM-29 with coordination number (C.N.) being 6 and 7, respectively.

Compared with CPM-29 with 7-coordinated rare-earth ions (Figure S13), CPM-66B showed a dramatic increase in separation factors for multiple binary combinations (Figure 4b & Table S5). For Yb-Sm combination, the separation factor of CPM-66B is almost ten times of that of CPM-29. There is also a 205%, 197%, 244%, 268%, 153%, and 209% increase for the combinations of Yb-Gd, Yb-Tb, Yb-Dy, Yb-Ho, Yb-Y and Yb-Er, respectively.

The EDS results were verified by ICP tests (Table S6) and were further supplemented by crystallographic site occupancy refinement using single-crystal X-ray data. For crystal refinement purpose, Yb-Y and Lu-Y combinations were chosen to further confirm the high selectivity of CPM-66B. Y^{3+} is an ideal stand-in for Ho^{3+}, because they have the identical ionic radii and behave the same in chemical systems where ionic radii play a critical role. The advantage of Y^{3+} over Ho^{3+} is that the electron density of Y^{3+} differs greatly from other lanthanides (e.g., Yb^{3+} or Lu^{3+}), rendering the crystallographic refinement of metal site occupancies very reliable. The X-ray refinement results are consistent with the EDS results (Table S4).

Since the M-L bond lengths also correlate, in nearly linear fashion,[16] with the metal site occupancy, they provide an alternative method to analyze the metal site occupancy. Based on the average M-O bond lengths in pure and binary phases, the molar fraction of Yb is determined to be 81.7% and 66.7% in Yb-Y and Yb-Tm crystals, respectively, close to the EDS result (80.7% and 61.6%) (Figure S14). It should be noted that for Yb-Tm crystal, the site occupancy cannot be reliably refined using single crystal X-ray diffraction data due to their similar electron density.

In conclusion, through the synthesis of a family of 6-coordinate rare-earth MOFs (CPM-66) that spans a broad range of ionic radii, we have gained important insight into the structure-directing and size-matching effects of urea-type solvents and co-structure-directing effect of nitrate anions. Using the CPM-66 platform, we have discovered that the crystallization of different lanthanide ions exhibits large and significantly amplified difference, even for adjacent elements as evidenced by their synthetic conditions and high separation efficiency during crystallization. This work demonstrates the great potential of lanthanide MOF with low-coordination-number environment for efficient rare-earth separation, and therefore it highlights the significance of the synthetic development of low-coordination-number rare-earth MOFs as reported here. More generally, it is hoped that this work would further boost the prospect of developing new strategies to create MOFs with lower coordination number from larger metal ions, which would lead to new or highly efficient applications.

Acknowledgements

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Keywords: MOFs • trimer • rare-earth separation • low-coordination number • urea solvents

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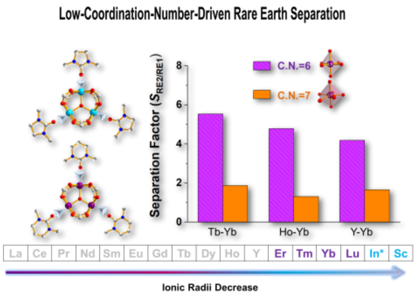

6-Coordinated and 6-Connected for Period 6 Elements A family of 6-connected trimer-based MOFs with 6-coordinated metals has been developed from rare-earth elements. A confluence of factors have been identified to lead to such unusual low-coordinate rare-earth MOFs that prove to be a powerful platform enabling dramatically enhanced efficiency for rare-earth-separation.