

# 铜系元素的可控配位组装与限域识别

## 摘要

铜系配位化学在核燃料循环体系优化中具有关键科学意义和应用潜力。本研究聚焦铜系元素的配位行为调控与新型分离材料开发，通过多齿配体与金属离子的协同配位效应，成功构建了过氧桥接二核铀酰功能化修饰的铀酰-雷索羟四羧酸胶囊型配位笼。基于该体系提出了一种新型放射性核素分离策略，采用多维表征技术（单晶 X 射线衍射、核磁共振波谱及质谱分析）系统阐明了配位笼与碱/碱土金属离子的主-客体作用机制，发现其对  $\text{Sr}^{2+}$  离子展现出显著特异性识别能力（分配系数  $K_d = 1.36 \times 10^7 \text{ mL g}^{-1}$ ），性能指标优于现有报道材料。理论分析表明，该优异选择性源于配位空腔中供体原子的几何排布与  $\text{Sr}^{2+}$  离子半径（1.16 Å）及配位环境的精准匹配。本研究不仅揭示了铜系配位笼在放射性核素分离领域的独特优势，更建立了通过配位空腔微环境工程化设计高选择性分离材料的新方法，为复杂体系中战略金属资源的高效回收提供了新思路与技术支撑

## 关键词

铜系元素、超分子笼、可控配位、核素分离

## Abstract

The investigation of actinide coordination chemistry holds pivotal scientific significance and application potential for optimizing nuclear fuel cycle systems. Elucidating the coordination behavior of actinides and developing novel separation materials not only advance fundamental theories in actinide chemistry but also offer innovative solutions for critical radioactive nuclide separation. Herein, we demonstrate a synergistic coordination strategy between polydentate ligands and metal centers to precisely control ligand conformation and metal-binding preferences, enabling the programmable assembly of polynuclear uranium/thorium coordination cages. Building upon this approach, we propose a groundbreaking methodology utilizing actinide coordination cages for selective extraction of key elements from nuclear fission products. Through modular design, we successfully constructed a peroxo-bridged diuranium-functionalized uranyl-calix[4]resorcinarene capsule system. Comprehensive characterization via NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction revealed its host-guest interaction mechanism with alkali/alkaline-earth metal ions, demonstrating exceptional  $\text{Sr}^{2+}$  selectivity with a remarkably high distribution coefficient ( $K_d = 1.36 \times 10^7 \text{ mL g}^{-1}$  under low-concentration conditions), surpassing existing  $\text{Sr}^{2+}$  adsorbents. This superior performance originates from the geometric complementarity between the precisely arranged donor atoms in the cage cavity and the ionic radius (1.16 Å) of  $\text{Sr}^{2+}$ , coupled with optimal coordination environment matching. Our findings not only validate the unique advantages of actinide coordination cages in radionuclide separation but also establish a new paradigm for designing high-selectivity separation materials through cavity microenvironment engineering, offering both theoretical insights and technical frameworks for strategic metal recovery in complex systems. The investigation of actinide coordination chemistry holds pivotal scientific significance and application potential for optimizing nuclear fuel cycle systems. Elucidating the coordination behavior of actinides and developing novel separation materials not only advance fundamental theories in actinide chemistry but also offer innovative solutions for critical radioactive nuclide separation. Herein, we demonstrate a synergistic coordination strategy between polydentate ligands and metal centers to precisely control ligand conformation and metal-binding preferences, enabling the programmable assembly of polynuclear uranium/thorium coordination cages. Building upon this approach, we propose a groundbreaking methodology utilizing actinide coordination cages for selective extraction of key elements from nuclear fission products. Through modular design, we successfully constructed a peroxo-bridged diuranium-functionalized uranyl-calix[4]resorcinarene capsule system. Comprehensive characterization via NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction revealed its host-guest interaction mechanism with alkali/alkaline-earth metal ions, demonstrating exceptional  $\text{Sr}^{2+}$  selectivity with a remarkably high distribution coefficient ( $K_d = 1.36 \times 10^7 \text{ mL g}^{-1}$  under low-concentration conditions), surpassing existing  $\text{Sr}^{2+}$  adsorbents. This superior performance orig-

inates from the geometric complementarity between the precisely arranged donor atoms in the cage cavity and the ionic radius (1.16 Å) of Sr<sup>2+</sup>, coupled with optimal coordination environment matching. Our findings not only validate the unique advantages of actinide coordination cages in radionuclide separation but also establish a new paradigm for designing high-selectivity separation materials through cavity microenvironment engineering, offering both theoretical insights and technical frameworks for strategic metal recovery in complex systems.

## Keywords

Actinides, Supramolecular cage, Controlled coordination, Radionuclide separation

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