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Design and synthesis of covalently tethered “isoG-star” as a recyclable host for selective cesium separation†

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The isoguanosine self-assembled pentamer (isoG-star) exhibits remarkable selectivity for Cs⁺ binding over competing alkali and alkali earth metal cations, rendering it a promising extractor for radioactive waste ¹³⁷Cs separation. However, to make isoG-star a practical material for Cs⁺ isolation, the development of a recyclable isoG-star material is required. In this study, a systematic screening of functional isoG derivatives was performed. By employing well-defined complex formation and post-assembly modification, a covalently tethered isoG₅-star was prepared through olefin metathesis, utilizing a designed isoG monomer. The application of this newly developed covalently linked isoG-star enabled selective Cs⁺ extraction, followed by controlled solvent-induced H-bond dissociation. This resulted in the creation of a recyclable Cs⁺ extractor, demonstrating excellent cation selectivity and good reusability (over seven cycles) for the first time. Consequently, this new supramolecular macrocycle offers a practical new platform for the treatment of radiocesium (¹³⁴Cs and ¹³⁷Cs) in an environmentally friendly and highly effective manner.

Introduction

Radiocesium ions represent significant constituents of radioactive wastewater in nuclear power plants, necessitating efficient treatment and isolation methods for cesium (Cs) ions.^{1–3} In 2011, the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident resulted in the release of substantial amounts of radiocesium (¹³⁴Cs and ¹³⁷Cs with half-lives of 2.07 and 30.1 years, respectively) into the environment, further highlighting the requirement for novel systems to effectively extract Cs cations from aqueous solutions with a focus on eco-

logical security and sustainable development.^{4–7} Considering the abundant existence of sodium (Na) and potassium (K) cations in aqueous solutions, along with their chemical similarities, achieving selective separation of Cs⁺ from such solutions can pose significant challenges.^{8–11} Crown ethers and calixarene derivatives are typical receptors for Cs⁺ separation. Reinhoudt and Ungaro made a fundamental contribution to the hybrids of calix[4]arene and crown ethers as excellent Cs⁺ selective ionophores.^{12–15} Selective binding is the first part of recognition and subsequent controlled release is critical for practical application. Although certain crown ether and calixarene derivatives can selectively coordinate with Cs⁺ through ion–dipole interaction or cation– π interaction, making them promising Cs⁺ extractants, concerns arise regarding their limited operating pH range and poor recyclability for practical applications. Sessler and co-workers developed calix[4]pyrrole which could extract Cs⁺ from an aqueous phase while allowing its subsequent release by the addition of K⁺. Calix[4]pyrrole-containing diblock copolymers are demonstrated to be more effective as extractants than the corresponding free ion pair receptors.^{16–21} The development of new systems exhibiting high Cs⁺ binding selectivity and practical operational conditions is thus of paramount importance for environmental protection and energy sustainability.

Molecular self-assembly is a prevalent process in nature that gives rise to various receptors, providing a powerful approach for designing selective ionophores.^{22–24} Guanosine (G) rich nucleic acids are recognized for their ability to coordinate alkali and alkaline earth cations through the formation of a hydrogen-bonded G₄-quartet motif.^{25–33} This rigid macrocyclic structure exhibits a high binding affinity towards K⁺, Sr²⁺, and Ba²⁺.^{34–39} However, despite its structural reversibility, the H-bonding supramolecular architecture lacks flexibility and tends to maintain a fixed size to maximize H-bonding interactions. Consequently, the G₄-quartet demonstrates no binding affinity towards Cs⁺ due to a size mismatch. Interestingly, the structural isomer of G, known as isoguanosine (isoG, also referred to as 2-hydroxy-adenosine) features a

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successful extraction of Cs^+ into the organic layer. Interestingly, the BARF^- anion led to the formation of a different Cs^+ complex, $[(3\mathbf{a})_5\text{Cs}]^+(\text{BARF}^-)$, with a 5:1 integration ratio, suggesting a specific role of the BARF anion in this assembly. Additionally, isoG **3b**, with one extra carbon on the side chain, could also form similar Cs^+ complexes, $[(3\mathbf{b})_{10}\text{Cs}]^+(\text{BPh}_4^-)$ and $[(3\mathbf{b})_5\text{Cs}]^+(\text{BARF}^-)$. The detailed NMR spectra are provided in Fig. S3 and S4.†

Following isoG-star formation, we proceeded with the supramolecular weaving process in an attempt to covalently link the isoG-star through olefin metathesis. Both the decamer and pentamer from **3a** and **3b** were treated with the Hoveyda-Grubbs-II (HG-II) catalyst, and the reaction process was monitored by MALDI-TOF. Subsequent analysis through NMR and MS confirmed the occurrence of metathesis when treating $[(3\mathbf{a})_{10}\text{Cs}]^+(\text{BPh}_4^-)$ and $[(3\mathbf{a})_5\text{Cs}]^+(\text{BARF}^-)$ with HG-II. However, a mixture of oligomers was observed, and the desired formation of pentameric isoG₅-star did not materialize. Our hypothesis is that the ester linker might not be sufficiently long to establish a connection with neighboring isoG units. As expected, treating $[(3\mathbf{b})_{10}\text{Cs}]^+$ with HG-II led to the detection of alkene-linked cyclic isoG₅ by MALDI-TOF with an MW of 2829.15. However, the resulting cyclic structure showed very poor solubility in CHCl_3 , precipitating from the reaction mixture, which makes it unsuitable for the proposed Cs^+ extraction application.

To address the solubility issue, we investigated the metathesis reaction with 2'-deoxy isoG derivatives **4a–4c**. Fig. 2A illustrates the treatment of deoxy isoG derivatives **4a** and **4b** in

CDCl_3 solution with CsCl and NaBARF aqueous solution, leading to the formation of simple complexes exhibiting a single set of signals in the ^1H NMR spectra. Diffusion NMR experiments with deoxy isoG derivatives confirmed the presence of C₅-symmetric decamers with the formulas $[(4\mathbf{a})_{10}\text{Cs}_2]^{2+}(\text{BARF}^-)_2$ and $[(4\mathbf{b})_{10}\text{Cs}_2]^{2+}(\text{BARF}^-)_2$. This finding establishes that the enhanced CDCl_3 solubility of these deoxy-isoG derivatives enables effective Cs^+ extraction into the organic layer through straightforward procedures. Moreover, it is noteworthy that these deoxy-isoG derivatives can also form isoG-star structures with both Na^+ and K^+ . To assess the binding selectivity of these alkene-modified isoG compounds, extractions of Cs^+ in the presence of competing Na^+ and K^+ were performed. The summarized results are presented in Fig. 2B and C.

As anticipated, the ^1H NMR spectra demonstrated excellent Cs^+ cation binding selectivity over Na^+ and K^+ cations. At a Cs^+/Na^+ ratio of 1:50, the deoxy isoG derivative **4b** formed over 99% Cs^+ complex, with minimal Na^+ complex formation being observed. Slightly reduced Cs^+ selectivity was observed when treating **4b** with a large excess of K^+ , resulting in 80% Cs^+ complex formation with a 1:50 Cs^+/K^+ mixture. Other alkaline earth metal cations (Mg^{2+} , Ca^{2+} , and Ba^{2+}) were applied to investigate their influence on the selectivity of Cs^+ . Nearly zero amount of Mg^{2+} , Ca^{2+} , and Ba^{2+} was extracted in the competition experiments with a 1:100 $\text{Cs}^+/\text{alkaline earth metal ion}$ mixture separately. Remarkably, at a $\text{Cs}^+/\text{Mg}^{2+}$ ratio of 1:150, the Cs^+ complex was still dominant in solution. Slightly reduced Cs^+ selectivity was observed when treating **4b** with a large excess of Ca^{2+} , resulting in 90% Cs^+ complex formation with a 1:150 $\text{Cs}^+/\text{Ca}^{2+}$ mixture (Fig. S9–S11†).

Remarkably, the resulting Cs^+ complexes derived from isoG **4b** remain stable even at a very low concentration (0.0001 M) with no significant dissociation. Variable-temperature NMR (VT-NMR) experiments confirmed that these Cs^+ complexes maintained stability even at an elevated temperature (55 °C, see dilution and VT NMR in Fig. S8†). These results strongly support the potential of using deoxy isoG **4** as a new host for Cs^+ extraction even in the presence of excess alkali metal and alkaline earth metal cations.

Following the confirmation of Cs^+ binding selectivity, excellent solubility, and good complex stability, we investigated the possibility of forming covalently-linked isoG-star using the deoxy-isoG derivatives **4a–4c**. Complexes derived from these compounds were treated with the HG-II catalyst, and the metathesis reactions were monitored using NMR and MALDI-TOF. As depicted in Fig. 3A, both the isoG ligand and the Cs^+ complex $[(4)_{10}\text{Cs}_2]^{2+}(\text{BARF}^-)_2$ were treated with the HG-II catalyst (5 mol%). Interestingly, no olefin metathesis products were observed while reacting with monomer **4**, likely due to the catalyst being quenched by the purine moiety. In the presence of the complex $[(4)_{10}\text{Cs}_2]^{2+}(\text{BARF}^-)_2$, the metathesis reaction was observed with complete consumption of the terminal olefin within 8 h in CHCl_3 at 55 °C. Monitoring the process with MALDI-TOF suggested the formation of an isoG trimer and tetramer with allyl ether **4a**, indicating that the chain

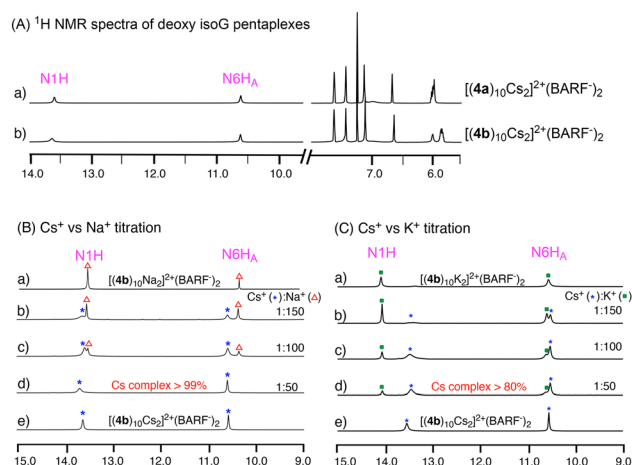


Fig. 2 (A) Self-assembly experiments of **4a** and **4b**: (a) ^1H NMR spectrum of $[(4\mathbf{a})_{10}\text{Cs}_2]^{2+}(\text{BARF}^-)_2$ in CDCl_3 and (b) ^1H NMR spectrum of $[(4\mathbf{b})_{10}\text{Cs}_2]^{2+}(\text{BARF}^-)_2$ in CDCl_3 . (B) ^1H NMR experiments of **4b** with a Cs^+ and Na^+ mixture at 25 °C in CDCl_3 , (a) $[(4\mathbf{b})_{10}\text{Na}_2]^{2+}(\text{BARF}^-)_2$, with a $\text{Cs}^+:\text{Na}^+$ molar ratio of: (b) 1:150, (c) 1:100, (d) 1:50, and (e) $[(4\mathbf{b})_{10}\text{Cs}_2]^{2+}(\text{BARF}^-)_2$. The concentrations of Cs^+ in aqueous solution are the same in all cases. (C) ^1H NMR experiments of **4b** with a Cs^+ and K^+ mixture at 25 °C in CDCl_3 , (a) $[(4\mathbf{b})_{10}\text{K}_2]^{2+}(\text{BARF}^-)_2$, with a $\text{Cs}^+:\text{K}^+$ molar ratio of (b) 1:150, (c) 1:100, (d) 1:50, and (e) $[(4\mathbf{b})_{10}\text{Cs}_2]^{2+}(\text{BARF}^-)_2$. The concentrations of Cs^+ in aqueous solutions are the same in all cases. Partial ^1H NMR spectra for the region correspond to N1H and N6H_A peaks.

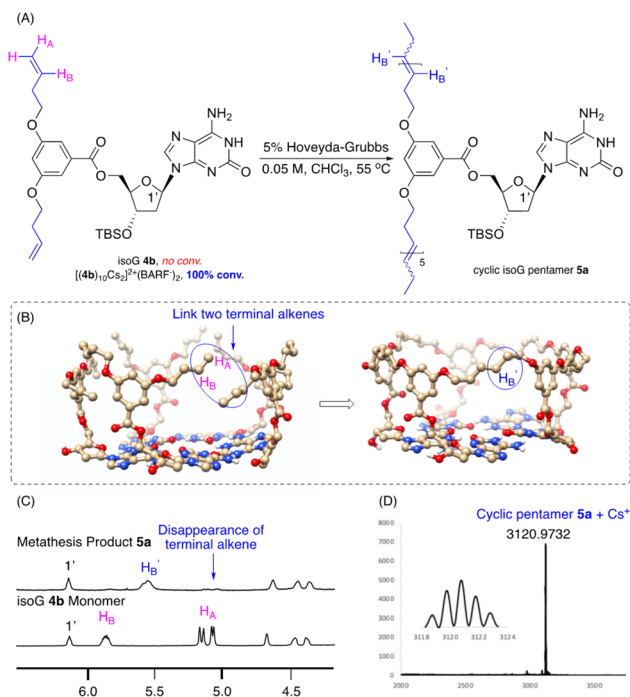


Fig. 3 Chemical structure, model and characterization of cyclic deoxy isoG pentamer **5a**. (A) Macrocyclization process through olefin metathesis; (B) computational model of the cyclic pentamer; (C) ^1H NMR spectra of the deoxy isoG **4b** monomer and the metathesis product, cyclic deoxy isoG pentamer **5a** in DMSO; (D) MALDI-TOF spectrum showing the effective extraction of Cs^+ from the aqueous phase.

length was not sufficient enough to accommodate isoG₅-pentamer cyclization, leading to complex dissociation after pentamer formation. With a longer linker, the desired cyclic pentamer was successfully observed with $m/z = 3120.9732$, consistent with the covalently linked cyclic isoG₅ containing one Cs cation ($\text{C}_{145}\text{H}_{195}\text{N}_{25}\text{O}_{35}\text{Si}_5\text{Cs}^+$, Fig. 3D). The overall yield was over 90%, forming the cyclic deoxy isoG pentamer **5a** as the dominant product. Compound **5a** could be readily purified through column chromatography, with no terminal olefin signals observed in the ^1H NMR spectra. Similar cyclic isoG-pentamer structures were observed with **4c**, with the ligand containing an even longer chain. However, complex NMR was obtained, likely due to the overly flexible side arms.

Having successfully prepared cyclic-isoG **5a**, aqueous extraction experiments to evaluate its Cs^+ extraction capabilities were performed. As expected, this covalently-linked isoG-star effectively extracts Cs^+ from the aqueous solution, forming Cs^+ complexes in CHCl_3 . The formation of new complexes was confirmed by ^{133}Cs NMR, where 25 ppm and 53 ppm signals clearly proved the coordination between Cs^+ and the cyclic pentamer product. In recyclability experiments, protic solvent MeOH can disrupt the H-bond in the deoxy isoG pentamer and cause the decomposition of the isoG complex. Upon treating the complex MeOH, complex dissociation occurred, resulting in the release of Cs^+ . The fact that cyclic pentamer **5a** is not soluble in MeOH leads to its precipitation from solution.

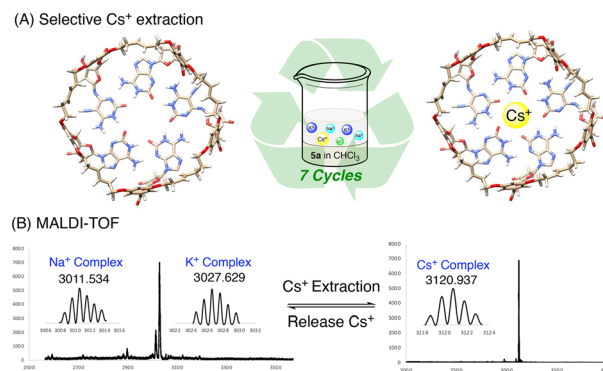


Fig. 4 Selective Cs^+ extraction by cyclic pentamer **5**. (A) 7 cycles of extraction without a significant efficiency decrease; (B) MALDI-TOF spectra of Cs^+ extraction and release.

The receptor itself can be regenerated after filtration. In this way, Cs^+ can be released or stored in another container by adding MeOH solvent, giving $\text{C}_{145}\text{H}_{195}\text{N}_{25}\text{O}_{35}\text{Si}_5\text{Na}^+$ and $\text{C}_{145}\text{H}_{195}\text{N}_{25}\text{O}_{35}\text{Si}_5\text{K}^+$ on MALDI-TOF. The resulting recycled cyclic isoG **5a** could be reapplied for Cs^+ extraction by dissolving it in CHCl_3 and reacting it with Cs^+ containing aqueous solution. Remarkably, this process was performed for multiple cycles (7 times) without losing Cs^+ selectivity and binding affinity (Fig. 4). The detailed results for each cycle are provided in Fig. S14.† Furthermore, the influence of pH on Cs^+ selective extraction was investigated, showing effective extraction of Cs^+ between pH = 1 and pH = 14. The effective pH range covers a broad region, making the cyclic deoxy isoG pentamers widely applicable ionophores. To the best of our knowledge, this is the first covalently-linked isoG-star that has been synthesized, and its ease of operation for effective Cs^+ extraction demonstrates its potential as a promising strategy for the treatment of radioactive Cs^+ waste.

Conclusion

In summary, we have successfully developed the first covalently-linked isoG-star through olefin metathesis with selected deoxy-isoG derivatives. The resulting cyclic isoG-star has demonstrated exceptional performance in Cs^+ extraction and separation with ease of operation and excellent recyclability. This breakthrough not only offers a novel material for potential Cs^+ -containing radioactive nuclear waste treatment, but also introduces a new strategy for the preparation of extra-large macrocycles through post-assembly modification. We anticipate that this strategy will be applicable in the development of new supramolecular hosts, and our ongoing investigations in the laboratory are currently exploring its potential applications.

Author contributions

M. L. conducted the experiments, performed the characterization, and analyzed the results and data; Y. H. analyzed the

results and data; L. W. solved and refined the crystal structures; X. S. conceived the original idea, set research directions, and designed the experiments.

Conflicts of interest

There are no conflicts to declare.

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