Host–Guest systems

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Highly Selective Na^+-Templated Formation of [2]Pseudorotaxanes Exhibiting Significant Optical Outputs**

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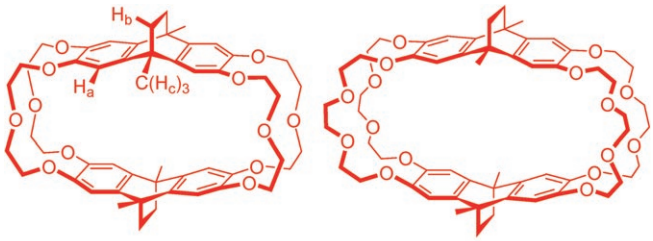
The diverse range of binding geometries exhibited by metal ions and their relatively stable interactions with ligands can be exploited for the efficient template-directed synthesis of macrocycles,[1] supramolecular architectures,[2] and interlocked molecules.[3] Although the formation of rotaxanes or pseudorotaxanes has been demonstrated using transition-metal ions coordinated to four (tetrahedral and square planar),[4] five (trigonal bipyramidal and square pyramidal),[5] and six (octahedral)[6] donor atoms, alkali-metal ions, which are useful templates for the synthesis of crown ethers,[7] are rarely used to direct the construction of such complexes. In one example, Li^+ ions have been used to assist the formation of a unique donor–acceptor pseudorotaxane,[8] but it appears that Na^+ ions play a similar role in that system.[9] We became interested in forming pseudorotaxanes in solution with high efficiency and selectivity toward a single species of alkali-metal ion—especially if we could differentiate between the physiologically important,[10] but chemically similar, Na^+ and K^+ ions.[11] Herein, we report a new molecular recognition system based on the molecular cage **1** (Scheme 1) and two different threadlike molecules (anthraquinone and squaraine), each of which forms a pseudorotaxane complex with **1** in the presence of templating Na^+ ions and exhibits high selectively over the other alkali-metal ions tested. This ion-specific templating effect was easy to monitor because the complexation and decomplexation of the pseudorotaxane complexes in solution occurred with color changes that were detectable to the naked eye. It appears from the solid-state structures that the dramatic Na^+/K^+ selectivity in this supramolecular system results from the different positions and ligand complexation geometries of the metal ions bound by the crown ether motifs of the molecular cage.



1 2

Scheme 1. Molecular cages **1** and **2**.

Previously, we demonstrated that molecular cage **2** and anthraquinone (**3**, Scheme 2) can form pseudorotaxane-like complexes in solution when K^+ ions are present.[12] We suspected that greater ion-selective templating behavior would arise if we replaced the two openings resembling dibenzo[24]crown-8 (DB24C8) in **2** with two relatively smaller and more rigid units resembling dibenzo[18]crown-6 (DB18C6, Scheme 2). Thus, we synthesized the corresponding molecular cage **1** in three steps from 2,3,6,7-tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene (see the Supporting Information).

The ^{1}H NMR spectrum (Figure 1B) of a mixture of macrocycle **1**, anthraquinone, and $NaClO_4$ (2:2:4 mM) in $CDCl_3/CD_3CN$ (1:1) exhibits three sets of resonances: 1) those of the Na^+-complexed molecular cage **1** (Figure 1A), 2) the free anthraquinone (Figure 1C), and 3) the complex formed between **1**, anthraquinone, and Na^+ ions. This finding implies that the rates of complexation and decomplexation are both slow on the ^{1}H NMR spectroscopic timescale at 400 MHz and 298 K. The upfield shifts of the signals of the aromatic protons of both components imply that stacking of their aromatic rings occurs within the supramolecular complex. By using a single-point method,[13] we determined the association constant (K_a) of this system to be 660 M^{-1} in $CDCl_3/CD_3CN$ (1:1). In contrast, the ^{1}H NMR spectrum of a mixture of macrocycle **1**, anthraquinone, and KPF_6 (2:2:4 mM) in $CDCl_3/CD_3CN$ (1:1) exhibits negligible shifts of the anthraquinone signals relative to those of the uncomplexed molecule, which suggests that K^+ ions are very poor templates for the formation of the corresponding pseudorotaxane complex (Figure 1D).

We grew single crystals suitable for X-ray crystallography by liquid diffusion of diisopropyl ether into a solution of molecular cage **1**, $NaClO_4$, and anthraquinone (1:2:1) in CH_3CN. The solid-state structure (Figure 2) reveals the expected [2]pseudorotaxane binding geometry of the complex $[\mathbf{3}\subset\mathbf{1}\supset Na_2]^{2+}$;[14,15] the rodlike anthraquinone unit penetrates through the two 28-membered rings while its two

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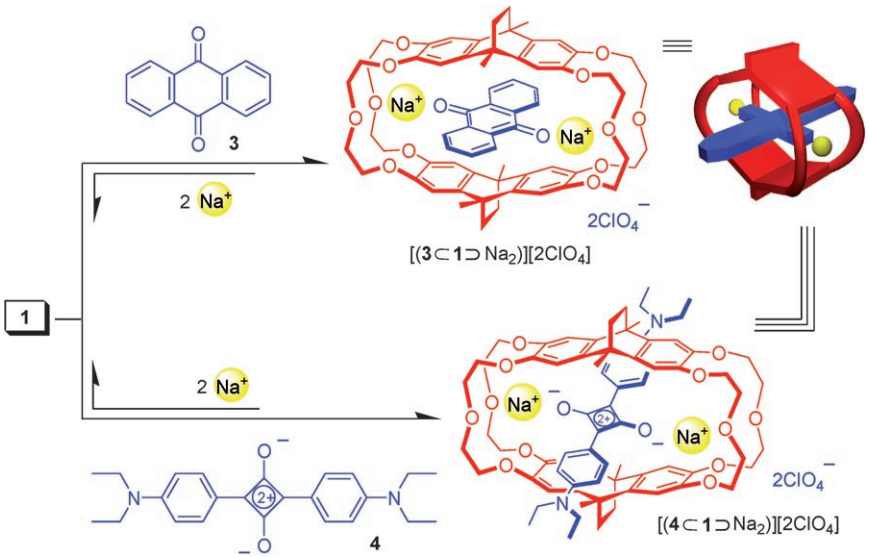

Scheme 2. Complexation of molecular cage **1** with threadlike guests **3** and **4** in the presence of templating Na^+ ions.

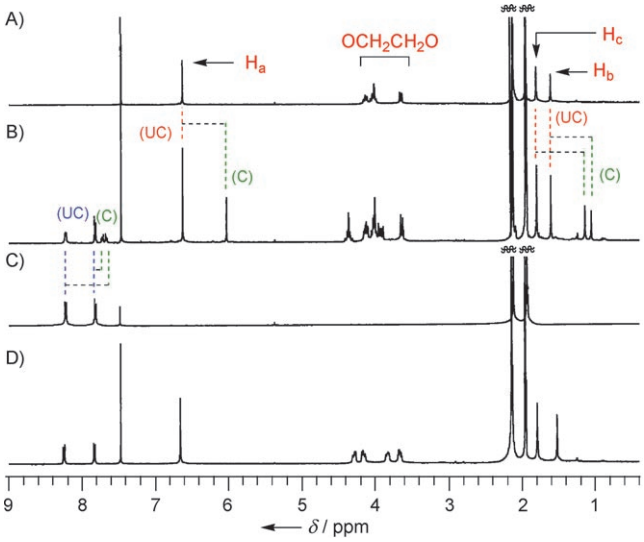

Figure 1. Partial ^1H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ (1:1), 298 K) of A) a mixture of **1** (2 mM) and $NaClO_4$ (4 mM), B) a mixture of **1** (2 mM), **3** (2 mM), and $NaClO_4$ (4 mM), C) **3**, and D) a mixture of **1** (2 mM), **3** (2 mM), and $KClO_4$ (4 mM). The descriptors (C) and (UC) refer to the signals of the complexed and uncomplexed states of the components, respectively.

oxygen atoms coordinate to the two Na^+ ions, which are themselves bound within the [18]crown-6 units of the molecular cage.

The solution of **1**, **3**, and $NaClO_4$ (4:4:8 mM) in $CDCl_3/CD_3CN$ (1:1) displayed a clearly observable orange color, possibly as a result of charge-transfer interactions between the molecular cage and the anthraquinone in the pseudorotaxane-like complex (Figure 3). The addition of Li^+, K^+, or Cs^+ ions at the same concentration did not cause a noticeable color change of the molecular cage/anthraquinone solution, thus suggesting that Na^+ ions templated the formation of the pseudorotaxane-like complex quite selectively among these common alkali-metal ions. As the absorption arising from charge-transfer interactions between the electron-rich phenol units of the molecular cage and the electron-deficient anthraquinone was not very striking to the naked eye, we turned our attention toward complexes formed using the rodlike squaraine (**4**, Scheme 2), which is an important near-IR dye with potential applications in many areas, such as nonlinear optics, photovoltaics, biological labeling, and photodynamic therapy.[16]

The ^1H NMR spectrum of a solution of macrocycle **1**, squaraine, and $NaClO_4$ (2:2:4 mM) in $CDCl_3/CD_3CN$ (1:1) exhibits proton shifts that are similar to those of the $[\mathbf{3}\subset\mathbf{1}\supset Na_2][2\,ClO_4]$ system, which suggests that the geometry of the complex $[\mathbf{4}\subset\mathbf{1}\supset Na_2][2\,ClO_4]$ is likely to

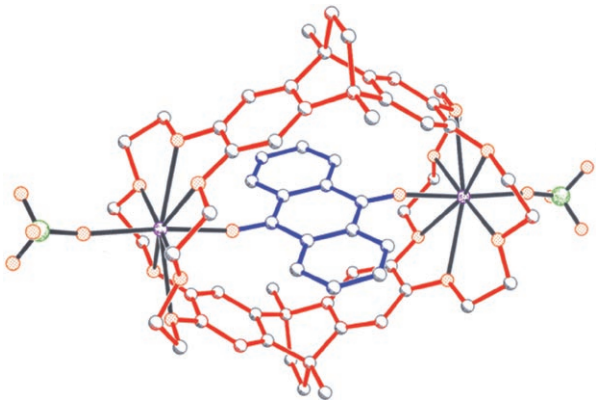

Figure 2. Ball-and-stick representation of the solid-state structure of $[\mathbf{3}\subset\mathbf{1}\supset Na_2][2\,ClO_4]$. Atom labels: C, gray; O, orange; Na, purple; Cl, green.

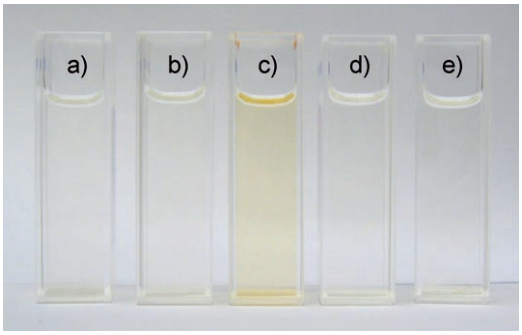

Figure 3. Photograph of vials containing solutions of **1** and anthraquinone (4 mM each) in $CDCl_3/CD_3CN$ (1:1) in the a) absence and b)–e) in the presence of b) Li^+, c) Na^+, d) K^+, and e) Cs^+ ions (8 mM each).

be that of a pseudorotaxane (see the Supporting Information). The Na^+ ions templated the formation of the complex $[\mathbf{4}\subset\mathbf{1}\supset Na_2][2\,ClO_4]$ much more efficiently than they did the

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corresponding anthraquinone complex; the binding constant (K_a) between the Na-complexed molecular cage **1** and squaraine in $CDCl_3/CD_3CN$ (1:1) was 9600 M^{-1},[13] which is more than tenfold higher than that of the anthraquinone complex. The stronger binding affinity of squaraine to the Na-complexed molecular cage **1**, relative to that of anthraquinone, may be the result of greater steric compatibility and/or the greater electron densities of the oxygen atoms of **4**.

We obtained single crystals of the complex suitable for X-ray crystallography by liquid diffusion of diisopropyl ether into a solution of molecular cage **1**, $NaBF_4$, and squaraine (1:2:1) in CH_3CN. The solid-state structure (Figure 4) confirms the expected [2]pseudorotaxane binding geometry of the complex $[\mathbf{4}\subset\mathbf{1}\supset Na_2]^{2+}$,[17] in which the rodlike squaraine unit penetrates through the two 28-membered rings, while its two oxygen atoms coordinate to the two Na^+ ions, which are themselves complexed to the two [18]crown-6 units of **1**.

Figure 5 illustrates that, among all of the alkali-metal ions tested, the blue color of the solution of **1** and squaraine turned red only in the presence of Na^+ ions. The quantum yield of squaraine dye at a wavelength of approximately 650 nm decreases significantly in polar solvents.[18] Thus, the color of a squaraine solution is related to the polarity of the solvent system; for example, $CHCl_3$ solutions of squaraine and its mixture with molecular cage **1** displayed similar red-to-blue color changes when the more-polar CH_3CN was added (see the Supporting Information). This finding suggests that the red color of the $CHCl_3/CH_3CN$ (1:1) solution of molecular cage **1**, squaraine, and Na^+ ions results from the formation of the corresponding pseudorotaxane-like complex in solution; that is, the relatively nonpolar molecular cage protects the squaraine dye from solvation by polar CH_3CN molecules.

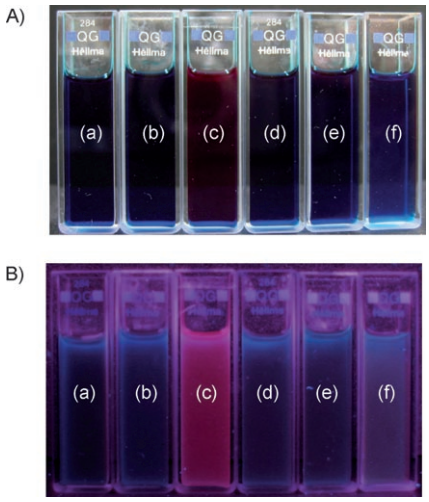

Figure 5. Photographs of the A) visible and B) fluorescence (excitation at 354 nm) behavior of mixtures of **1** and **4** (2 mM each) in $CHCl_3/CH_3CN$ (1:1) in the a) absence and b)–f) presence of 2 equiv of b) Li^+, c) Na^+, d) K^+, and e) Cs^+ and f) 2 equiv of Na^+ and 20 equiv of K^+ ions.

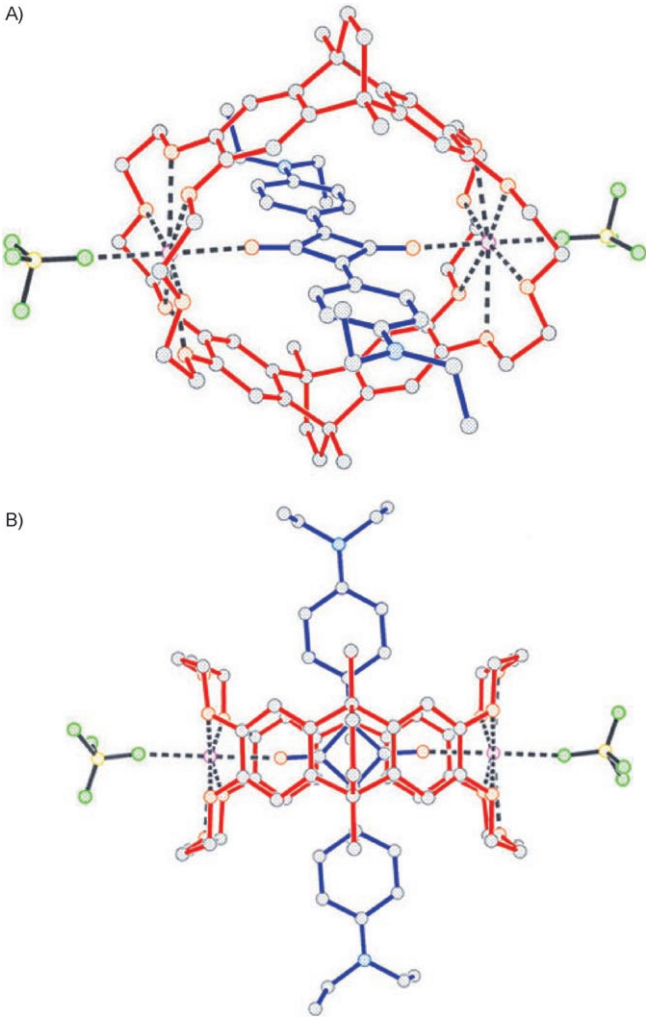

Figure 4. Ball-and-stick representations of the solid-state structure $[\mathbf{4}\subset\mathbf{1}\supset Na_2][2\,BF_4]$. Atom labels: C, gray; O, orange; N, blue; Na, purple; B, yellow; F, green.

Figure 6 provides a comparison of the emission spectra observed after adding Na^+ and K^+ ions (2 equiv), respectively, to an equimolar (1.3×10^{-4} M) solution of molecular cage **1** and squaraine **4**; it is clear that the presence of Na^+ ions enhanced the fluorescence of squaraine substantially. Interestingly, the addition of 20 equivalents of K^+ ions to the red solution of $[\mathbf{4}\subset\mathbf{1}\supset Na_2][2\,ClO_4]$ led to a substantial degree of

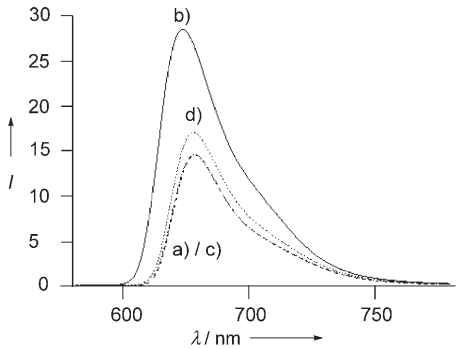

Figure 6. Fluorescence spectra ($CDCl_3/CD_3CN$ (1:1), 298 K; excitation at 400 nm) of a) an equimolar mixture (1.3×10^{-4} M) of **1** and **4**, b) the system in (a) after the addition of 2 equiv of $NaClO_4$, c) the system in (a) after the addition of 2 equiv of KPF_6, and d) the system in (b) after the addition of 20 equiv of KPF_6.

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dissociation of the pseudorotaxane complex: the color of the solution turned immediately from red to blue (compare vials f in Figure 5 A,B). This result suggests that while K^+ ions can compete with Na^+ ions for complexation to **1** in solution, the K^+-complexed molecular cage displays a much weaker binding affinity to the squaraine thread.

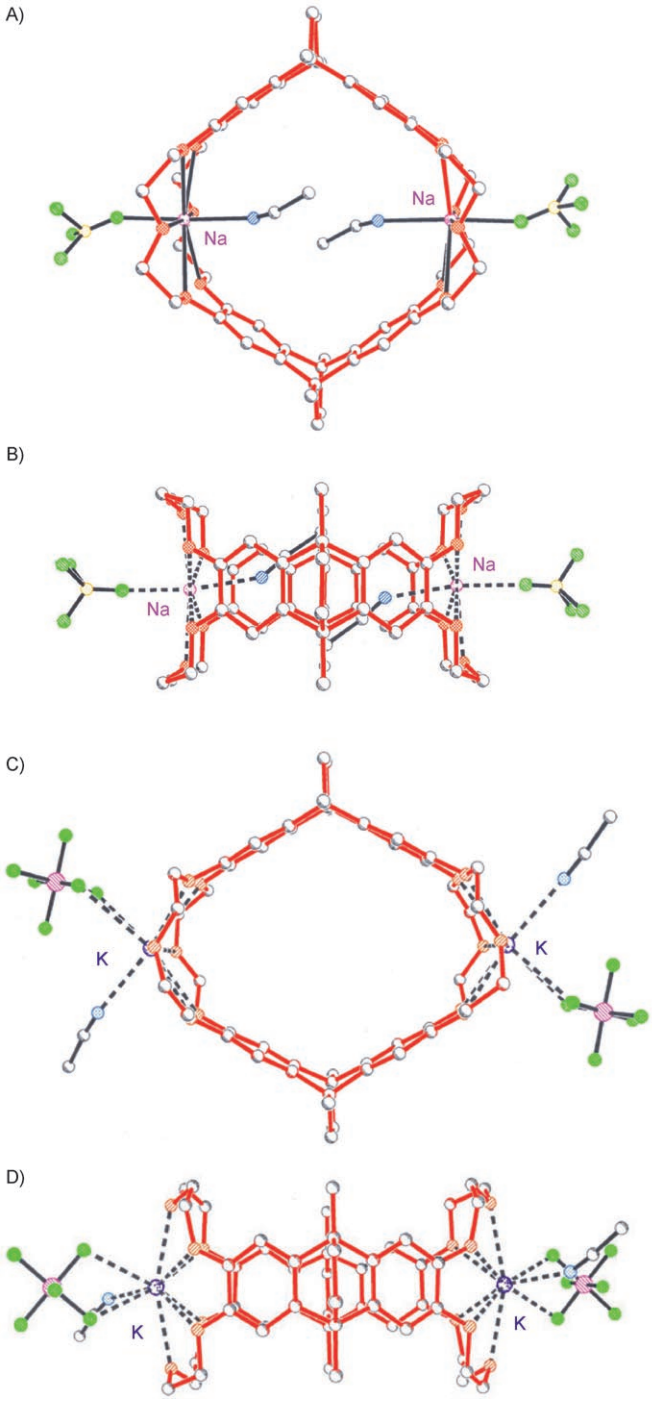

Figure 7. Ball-and-stick representations of the solid-state structures of $[(\mathbf{1}\supset Na_2)\cdot 2\,MeCN][2\,BF_4]$: a) side view; b) top view, and $[(\mathbf{1}\supset K_2)\cdot 2\,MeCN][2\,PF_6]$: c) side view; d) top view. Atom labels: C, gray; O, orange; N, blue; Na, light purple; B, yellow; P, pink; K, purple; F, green.

Our finding that the metal-templating motifs in anthraquinone and squaraine (that is, the aromatic rings with two carbonyl groups) both highly favor Na^+ over K^+ ions in templating the formation of their respective [2]pseudorotaxanes seems puzzling, as they are of different sizes. To determine how the molecular cage **1** coordinates to these two metal ions we grew single crystals suitable for X-ray crystallography by liquid diffusion of diisopropyl ether into solutions of molecular cage **1** and $NaBF_4$ or KPF_6 (1:2 molar ratio) in CH_3CN. The solid-state structures reveal that each Na^+ (Figure 7 A,B) and K^+ (Figure 7 C,D) ion is bound to all six oxygen atoms of the individual crown ether units of molecular cage **1**.[19,20] The [18]crown-6-complexed Na^+ ions are also coordinated by labile CH_3CN ligands located within the cavity of molecular cage **1**; clearly these ligands could be replaced by bidentate ligands such as anthraquinone and squaraine. In contrast, the crown ether motifs of the molecular cage **1** position their K^+ ions outward from the internal cavity, thereby leaving no internal coordination sites for templating bidentate ligands. Thus, it seems that differences in the coordination geometries and ligand binding sites of the complexed metal ions are responsible for molecular cage **1** forming [2]pseudorotaxane structures in the presence of Na^+ ions, but not K^+ ions, even when the bidentate ligands have different sizes.

We have demonstrated that Na^+ ions behave as highly selective templates, relative to K^+ and other alkali-metal ions, for the formation of pseudorotaxanes from the molecular cage **1** and two threadlike molecules (anthraquinone and squaraine) in $CD_3CN/CDCl_3$ (1:1). In addition to this ion-specific binding, the complexation and decomplexation of the pseudorotaxane-like complexes in solution is observable by the naked eye. We believe that rotaxanes constructed from **1** and squaraine derivatives will protect this sensitive dye from decay;[16f,g] furthermore, they have potential for application as chemosensors and molecular switches that exhibit significant optical outputs. Such systems are currently under investigation.

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[15] CCDC-617617 $[(\mathbf{3}\subset\mathbf{1}\supset Na_2)\cdot 4\,MeCN][2\,ClO_4]$, CCDC-617618 $[(\mathbf{1}\supset K_2)\cdot 3\,MeCN][2\,PF_6]$, CCDC-617619 $[(\mathbf{4}\subset\mathbf{1}\supset Na_2)\cdot 4\,MeCN][2\,BF_4]$, and CCDC-617620 $[(\mathbf{1}\supset Na_2)\cdot 2\,MeCN\cdot CH_2Cl_2\cdot H_2O][2\,BF_4]$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[17] Crystal data for $[(\mathbf{4}\subset\mathbf{1}\supset Na_2)\cdot 4\,MeCN][2\,BF_4]$: $[C_{84}H_{100}O_{14}N_6Na_2][BF_4]_2$, $M_r = 1637.30$, triclinic, space group $P\bar{1}$, $a = 13.5847(2)$, $b = 13.7701(2)$, $c = 14.2357(2)$ Å, $V = 2230.43(6)$ Å^3, $\rho_{calcd} = 1.219$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.101$ mm^{-1}, $T = 295(2)$ K, orange cubes; 7859 independent measured reflections, F^2 refinement, $R_1 = 0.0730$, $wR_2 = 0.2305$.

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[19] Crystal data for $[(\mathbf{1}\supset Na_2)\cdot 2\,MeCN\cdot CH_2Cl_2\cdot H_2O][2\,BF_4]$: $[C_{57}H_{66}O_{13}N_2Cl_2Na_2][BF_4]_2$, $M_r = 1277.62$, trigonal, space group $P1c$, $a = 21.3476(4)$, $b = 21.3476(4)$, $c = 26.1494(4)$ Å, $V = 10320.3(3)$ Å^3, $\rho_{calcd} = 1.233$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.184$ mm^{-1}, $T = 295(2)$ K, colorless plates; 6056 independent measured reflections, F^2 refinement, $R_1 = 0.1487$, $wR_2 = 0.4145$.

[20] Crystal data for $[(\mathbf{1}\supset K_2)\cdot 3\,MeCN][2\,PF_6]$: $[C_{58}H_{69}O_{12}N_3K_2][PF_6]_2$, $M_r = 1368.30$, monoclinic, space group $P2_1/n$, $a = 15.5177(8)$, $b = 15.0057(9)$, $c = 15.1762(8)$ Å, $V = 3211.9(3)$ Å^3, $\rho_{calcd} = 1.415$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.292$ mm^{-1}, $T = 295(2)$ K, colorless plates; 7246 independent measured reflections, F^2 refinement, $R_1 = 0.0980$, $wR_2 = 0.2431$.

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