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## COMMUNICATION

# Size-dependent patterned recognition and extraction of metal ions by a macrocyclic aromatic pyridone pentamer†

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**A macrocyclic aromatic pyridine pentamer was found to exhibit patterned recognition of metal ions and efficiently extract larger ions such as Cs<sup>+</sup>, Ba<sup>2+</sup>, Tl<sup>+</sup>, Au<sup>+</sup>, K<sup>+</sup> and Rb<sup>+</sup> preferentially over the other 18 smaller metal ions from aqueous phase into chloroform layer.**

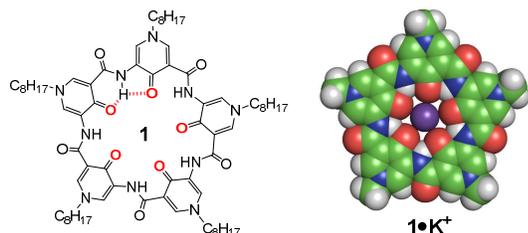
Over the recent years since 2006,<sup>1</sup> we have been developing H-bonded macrocyclic aromatic pentamers that possess unique aesthetically pleasing fivefold symmetry in terms of structures,<sup>2</sup> their rapid syntheses<sup>3</sup> and functions.<sup>2b,2c,4</sup> In particular, circularly folded pyridone pentamers such as **1** now can be made by BOP-mediated H-bonding-assisted one-pot macrocyclization reactions with yields of up to 25% in about a day,<sup>3c</sup> greatly facilitating their subsequent functional elaborations. With its suitably sized non-collapsible cavity of 1.4 Å in radius formed by five convergently aligned interior-pointing carbonyl O-atoms, pentamer **1** has been recently found to be capable of high-affinity binding of 10<sup>8</sup> M<sup>-1</sup> toward alkali metal ions in the water–CHCl<sub>3</sub> system (Table S1)<sup>2c</sup> and catalyzing highly efficient transition metal-free arylations of unactivated arenes with the use of potassium *tert*-butoxide.<sup>4b</sup> These functional investigations are in line with and add into the growing list of interesting functions (guest recognition,<sup>5a-e</sup> ion transportation,<sup>5f</sup> stabilization of G-quadruplex structures,<sup>5g</sup> etc) that arise from a number of H-bonded macrocyclic foldamers with their shape-persistent macrocyclic frameworks similarly rigidified by strong intramolecular H-bonds.<sup>1,6</sup>

In this communication, we have thoroughly investigated the

ion-differentiating ability of **1** toward 24 metal ions, and report here its selective recognition and efficient extraction of several larger ions in the decreasing order of Cs<sup>+</sup> > Ba<sup>2+</sup> > Tl<sup>+</sup> > Au<sup>+</sup> > K<sup>+</sup> > Rb<sup>+</sup> in the presence of many other smaller metal ions using biphasic water–CHCl<sub>3</sub> system. The patterned extraction displayed by **1** appears to be size-dependent with better efficiencies than 18-crown-6, 21-crown-7 and valinomycin containing six or more oxygen-donor atoms.<sup>7</sup>

Previously, we obtained very high binding affinities toward alkali metal ions from Li<sup>+</sup> to Cs<sup>+</sup> in their picrate salts by **1** at 10 mM by using Cram's method (Table S1)<sup>8</sup> The binding constants seem to correlate well with the ionic radii with the smallest one being bound the most tightly. Given the organic nature of the picrate anions and that binding constants might vary among counter anions of various types, there is a poor link between the binding data compiled in Table S1 and the practical applications including selective ion extraction and transportation by **1**. This necessitates the re-investigations of the ion-binding abilities of **1** toward not only alkali metal ions but also environmentally significant transition metal ions in order to discern its comprehensive ion-differentiating profiles and hopefully to provide certain pragmatic guiding principles for designing other closely related potentially ion selective metameric macrocycles for eventual practical applications.

With these application-oriented motivations in mind, we first tested the differential binding abilities of **1** toward a total of 18 metal ions in the form of nitrate salts by using inductively coupled plasma mass spectrometry (ICP-MS) that allows the measurement of ion concentrations at the ppb level. In a typical experimental set-up using biphasic water–CHCl<sub>3</sub> extraction system, the concentration of each of 18 metal ions is set constant at 0.10 mM in H<sub>2</sub>O, and that of **1** is variable, ranging from 0.12 mM to 1.80 mM in CHCl<sub>3</sub>. The ratio of the concentration of the host, [**1**], over that of individual metal ion, [individual metal ion], therefore varies from 1.2 to 18. Equal volumes of H<sub>2</sub>O containing 1.80 mM metal ions and CHCl<sub>3</sub> containing 0.12 – 1.80 mM of host **1** were mixed and shaken



**Table 1** Extraction efficiencies (%) of 18 metal ions in their nitrate salts by macrocyclic host **1**, 18-crown-6 ether, 21-crown-7 ether and valinomycin as determined by inductively coupled plasma mass spectrometry (ICP).<sup>a</sup>

		Cs <sup>+</sup>	Ba <sup>2+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Ag <sup>+</sup>	Na <sup>+</sup>	Hg <sup>2+</sup>	Pb <sup>2+</sup>	Ca <sup>2+</sup>	Cu <sup>2+</sup>	Li <sup>+</sup> , Mg <sup>2+</sup> , Al <sup>3+</sup> , Mn <sup>2+</sup> , Fe <sup>3+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup>	Total Extraction <sup>b</sup>
<b>1</b>	0.12 mM	31	6	-	-	-	-	-	-	-	-	-	37
<b>18-crown-6</b>		-	-	11	-	-	-	-	-	14	-	-	25
<b>1</b>	0.54 mM	97	90	74	47	23	14	17	-	10	8	-	380
<b>18-crown-6</b>		-	-	61	-	-	46	-	11	30	-	-	148
<b>1</b>	0.90 mM	>99	>99	89	83	60	53	32	13	14	15	-	557
<b>18-Crown-6</b>		-	-	96	-	-	88	6	8	71	-	-	249
<b>1</b>	1.80 mM	>99	>99	>99	>99	85	86	71	94	55	52	-	839
<b>18-Crown-6</b>		-	-	98	-	9	95	16	8	98	-	-	324
<b>21-Crown-7</b>	3.60 mM	29	-	11	21	-	14	-	-	9	-	-	84
<b>Valinomycin</b>		9	-	8	12	20	-	-	9	-	-	-	58

<sup>a</sup> The concentration of each metal ion is set at 0.10 mM in H<sub>2</sub>O, and that of macrocyclic hosts **1** and 18-crown-6 ranges from 0.12 mM to 1.80 mM in CHCl<sub>3</sub>, while the concentration of 21-crown-7 and valinomycin is 3.60 mM. Extractions were carried out in a biphasic system using equal volumes of H<sub>2</sub>O containing metal ions and CHCl<sub>3</sub> containing organic host at 25 °C. All the reported data are averaged values over six runs with relative errors within 3%, and only extraction efficiencies of ≥ 6% are listed. <sup>b</sup> Total extraction is the sum of all the measurable extraction efficiencies for the ions.

for 24 hours at 25 °C. Ion extractions from aqueous phase to chloroform layer were monitored by measuring the residual concentrations of various metal ions in H<sub>2</sub>O layer. To ensure that the data obtained are consistent and reproducible, the measurements for the same extracted solution were repeated three times, and the whole experiment including preparation of a new batch of sample solutions, extractions and measurements were repeated one more time. Averaging the data over 6 measurements gave the final extraction data with relative errors of ≤ 3% (Table 1).

At 0.12 mM of **1**, Cs<sup>+</sup> ion with an extraction efficiency of 31% is singled out as the most preferred species among 18 metal ions for binding by **1** at a [**1**]/[individual metal ion] ratio of 1.2, which is possibly followed by Ba<sup>2+</sup> (6%), and extractions of the other 16 metal ions apparently remain at the undetectable levels within the instrument's capacity. By considering a relative error of 3%, the extraction efficiency for Cs<sup>+</sup> is at least 2-fold higher than that of Ba<sup>2+</sup>. At the same concentration and ratio, 18-crown-6 displays marginal extractions of 11% and 14% for K<sup>+</sup> and Ca<sup>2+</sup>, respectively.

With an increase in concentration from 0.12 mM to 0.54 mM for **1** and in ratio of [**1**]/[individual metal ion] from 1.2 to 5.4, the extraction efficiencies for Cs<sup>+</sup> and Ba<sup>2+</sup> dramatically increase to 97% and 90%, respectively, with significant extractions of K<sup>+</sup> (74%) and Rb<sup>+</sup> (47%) and poor or no extractions of the other 14 metal ions. Under identical conditions, extractions of K<sup>+</sup>, Na<sup>+</sup> and Ca<sup>2+</sup> by 18-crown-6 also increase to 61%, 46% and 30%, respectively. By summing up the extraction efficiencies for all the metal ions at the measurable level, **1** demonstrates a total extraction capacity of 380% that is two and half times that of 148% for 18-crown-6 at 0.54 mM. This shows that despite 18-crown-6 being more selective, it is less general and capable **1**. This is remarkable given that 18-crown-6 carries one more oxygen-donor atom than **1** but it turns out to be less able to bind metal ions. Such a difference in ion binding ability presumably can be attributed to

(1) the convergently aligned properly spaced oxygen-donor atoms and (2) the higher electron density at carbonyl O-atoms in **1** than that of the O-atoms in 18-crown-6 due to electron-donating effect from N-atoms at *para*-positions in **1** via an aromatic resonance structure in which N-atoms are positively charged and carbonyl O-atoms each carries a negatively charge.

The comparative trend where **1** displays a much higher total cation-binding capacity than 18-crown-6 persists with increasing concentrations of **1** and 18-crown-6 at a ratio of [host]/[individual metal ion] of either 9 or 18. Quantitative removals of Cs<sup>+</sup>/Ba<sup>2+</sup> and K<sup>+</sup>/Rb<sup>+</sup> were achieved with the use of 0.9 mM and 1.80 mM of **1**, respectively. These were followed by extractions of 71 – 94% for Ag<sup>+</sup>, Na<sup>+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup>, and 52 – 55% for Ca<sup>2+</sup> and Cu<sup>2+</sup>. Significantly, no noticeable extractions take place for many other transition metal ions including Mn<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> by **1** at 1.80 mM. For comparison, nearly quantitative extractions were observed for K<sup>+</sup> (98%), Na<sup>+</sup> (95%) and Ca<sup>2+</sup> (98%) by 18-crown-6 at 1.80 mM while all the other metal ions remain poorly extracted.

It is worth noting that both 21-crown-7 and valinomycin exhibit very poor extractions of various metal ions from water into chloroform layers even at a higher concentration (Table 1).

As shown in Table 2, by examining **1**-mediated individual extractions of the aforementioned metal ions and six additional ones (Tl<sup>+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup> in their nitrate salts, and Au<sup>+</sup>, Pt<sup>2+</sup> and Pd<sup>2+</sup> in their chloride salts), **1** is consistently found to possess higher extraction capacities toward various ions than 18-crown-6 that only extracts K<sup>+</sup>, Na<sup>+</sup> and Ca<sup>2+</sup> to significant extents, and further demonstrates good extractions of Au<sup>+</sup> and Pd<sup>2+</sup> while Co<sup>2+</sup>, Cr<sup>3+</sup> and Pt<sup>2+</sup> were found to be completely nonextractable.

A more careful inspection of Table 2 reveals a remarkable correlation between the extraction efficiency and the ionic radius. Specifically, at 0.30 mM of **1**, high capacity extractions of >90% are achieved for all the metal ions with a radius of >1.30 Å (e.g., Cs<sup>+</sup>, Ba<sup>2+</sup>, Au<sup>+</sup>, K<sup>+</sup> and Rb<sup>+</sup>), and moderate extractions of 37% - 63% occur for ions with a radius of about

**Table 2** Extraction efficiencies (%) of 24 metal ions by host **1** as determined by inductively coupled plasma mass spectrometry (ICP).<sup>a</sup>

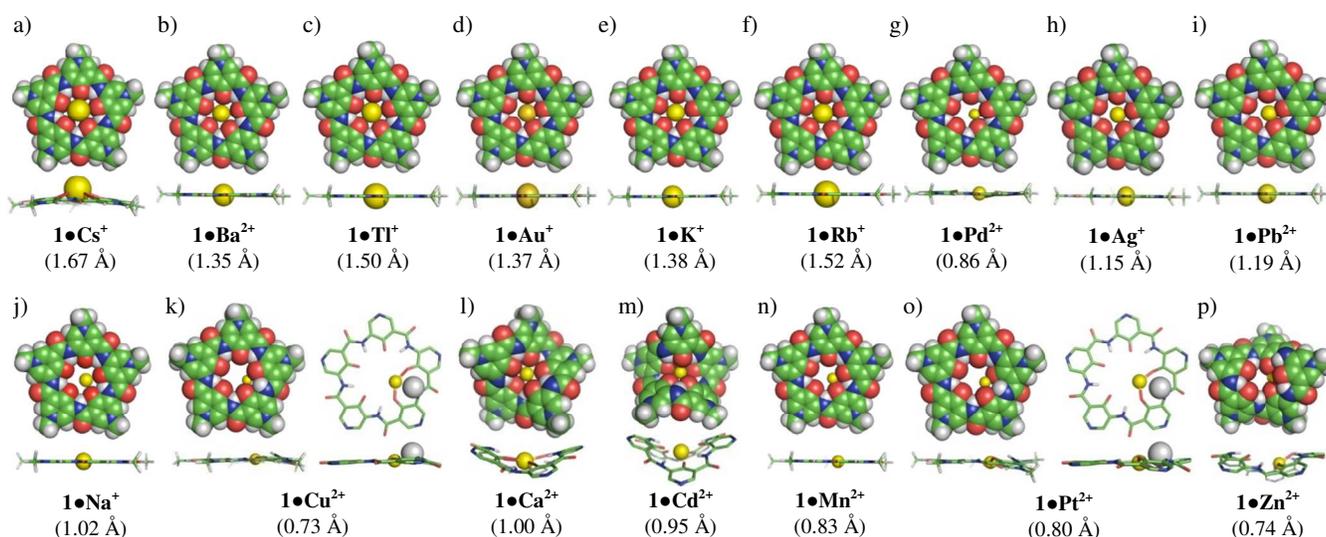
M <sup>nt+</sup> (0.10 mM)	Radius <sup>b</sup> (Å)	Host <b>1</b>			
		0.10 mM	0.20 mM	0.30 mM	0.40 mM
Cs <sup>+</sup>	1.67	69	92	>99	>99
Ba <sup>2+</sup>	1.35	51	86	97	>99
Tl <sup>+</sup>	1.50	41	84	97	>99
Au <sup>+</sup>	1.37	36	78	97	>99
K <sup>+</sup>	1.38	34	61	91	97
Rb <sup>+</sup>	1.52	30	63	92	98
Pd <sup>2+</sup>	0.86	24	43	63	80
Ag <sup>+</sup>	1.15	24	42	56	78
Pb <sup>2+</sup>	1.19	15	27	47	69
Na <sup>+</sup>	1.02	13	23	39	59
Cu <sup>2+</sup>	0.73	11	21	43	57
Ca <sup>2+</sup>	1.00	7	17	37	52
<b>Non-extractable ions</b>					
Cd <sup>2+</sup> (0.95), Mn <sup>2+</sup> (0.83), Pt <sup>2+</sup> (0.80), Li <sup>+</sup> (0.76), Co <sup>2+</sup> (0.75), Zn <sup>2+</sup> (0.74), Mg <sup>2+</sup> (0.72), Ni <sup>2+</sup> (0.69), Fe <sup>3+</sup> (0.645), Cr <sup>3+</sup> (0.62), Al <sup>3+</sup> (0.535)					

<sup>a</sup> Extractions were carried out in a biphasic system using equal volumes of H<sub>2</sub>O containing 0.10 mM metal ion and CHCl<sub>3</sub> containing 0.10 to 0.40 mM host **1** at 25 °C. All the reported data are averaged values over six runs with relative errors within 3%. <sup>b</sup> Ions are 6-coordinate unless indicated.<sup>9</sup>

1 Å, while ions whose radii stay significantly below 1 Å generally become non-extractable with the exceptions of Pd<sup>2+</sup> and Cu<sup>2+</sup>. In other words, the patterned recognition and extraction of ions by **1** are primarily governed by the ionic radius with the larger ions extracted to more substantial extents than smaller ions. This finding markedly deviates from our original postulate that **1**, arising from its five inward-pointing,

convergently aligned and highly electron-rich carbonyl O-atoms, might be able to bind and extract all types of metal ions.

To understand the size-dependent patterned recognition of ions by **1**, a total of 44 structures for 1:1 complexes **1**•M<sup>nt+</sup> possibly formed between **1** and ions of various sizes with or without coordinated water molecules<sup>10</sup> were computationally optimized at the B3LYP/6-31G(d,p) level that has consistently allowed us to predict and verify the structures of H-bonded oligomers (Figure 1).<sup>2a,11</sup> From the computed structures, a few points can be noted. First, an enclosed cavity of 2.85 Å in radius measured from the center of nucleus of O-atoms to the center of the cavity in **1** is able to accommodate a metal ion as large as Rb<sup>+</sup> with a radius of 1.52 Å, still producing a distortionless planar complex **1**•Rb<sup>+</sup> (Figure 1f). Second, larger ions of ≥ 1.3 Å in radius can form five strong coordination bonds with the five interiorly arrayed O-atoms with Au<sup>+</sup> being skewed to one side and in closer contacts with three O-atoms (Figure 1a-f), and the binding energy released seems to be sufficiently large to “strip” off four water molecules occupying the planar geometry around the metal ions and subsequently bring the ions from aqueous phase to chloroform layer. Third, being kept at bay from the three essentially nonmobile inward-pointing carbonyl O-atoms in **1**, smaller ions of ≤ 1.20 Å mostly forms only two coordination bonds with the remaining two O-atoms (Figure 1g-p and Figure S1), leading to moderate, low or no apparent extractions by **1**. In the only three cases where three to five coordination bonds are possibly formed in **1**•Ca<sup>2+</sup> (Figure 1l), **1**•Cd<sup>2+</sup> (Figure 1m) and **1**•Zn<sup>2+</sup> (Figure 1p), dramatic distortions of macrocyclic backbones seen in these complexes apparently disfavour concurrent binding of three or more O-atoms by the ions. An additional factor that contributes into the poor recognition of the smaller ions lies in the repulsive interactions between ions and one of the five amide H-atoms. Such repulsions become very pronounced for



**Fig. 1** The computationally optimized structures of **1**•M<sup>nt+</sup> at the level of B3LYP/6-31G(d,p) in chloroform. All the CPK models were built based on the van der Waals radius (Gray: H = 1.20 Å; Green: C = 1.70 Å; Blue: N = 1.55 Å; Red: O = 1.52 Å). The yellow atoms in all the structures refer to metal cations whose radii were specified in the respective parenthesis.<sup>9</sup> The structures in a)-l) are arranged in a decreasing order of extraction efficiencies. With ions being forced into the vicinity of one of the five partially positively charged amide H-atoms in k) and o), the amide H-atom is also forced to point away from the molecular plane due to the repulsions between ions and H-atom.

**1**•Cu<sup>2+</sup> (Figure 1k), **1**•Pt<sup>2+</sup> (Figure 1o), **1**•Ni<sup>2+</sup> (Figure S1d), **1**•Cr<sup>3+</sup> (Figure S1f) and **1**•Al<sup>3+</sup> (Figure S1g), eventually disallowing concurrent binding of the two interior O-atoms by these smaller ions and subsequently preventing them from favorably binding and entering the interior cavity of **1**. Nevertheless, the fact that Cu<sup>2+</sup> ions (Table 2) can be extracted to a good extent still remains somewhat mysterious to us.

To summarize, pentameric host **1**, having a rigid macrocyclic backbone whose interior is decorated by five convergently aligned oxygen donor atoms, makes possible the size-dependent patterned recognition and extraction of ions with the larger ions such as Cs<sup>+</sup>, Ba<sup>2+</sup>, Au<sup>+</sup>, K<sup>+</sup> and Rb<sup>+</sup> as the most extractable ones. The first principle computations at the B3LYP/6-31G(d,p) level provide the structural insights into the behavioral origins of **1** being that the “rigid” framework in **1** discourages or even prohibits concurrent binding of its three or more interior O-atoms toward smaller ions whose binding is additionally disfavored by the substantial repulsions from the vicinity amide H-atom. Our current systematic investigation has laid a solid foundation for us to pursue more challenging issues, focusing on the speedy evolution of circularly folded hybrid pentamers derived from monomeric pyridone,<sup>2c,3c</sup> methoxybenzene,<sup>2a,2b</sup> fluorobenzene,<sup>2d,4a</sup> or pyridine<sup>11b-c</sup> building blocks for highly selective recognition of metal ions.

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† Electronic Supplementary Information (ESI) available: Experimental procedures and computationally optimized structures. See DOI 10.1039/b000000x/

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