Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Bradshaw, Jerald S. , Izatt, Reed M. , Savage, Paul B. , Bruening, Ronald L. and Krakowiak, Krzysztof E.(2000) 'The Design of Ion Selective Macrocycles and the Solid-Phase Extraction of Ions Using Molecular Recognition Technology: A Synopsis', Supramolecular Chemistry, 12: 1, 23 — 26
To link to this Article: DOI: 10.1080/10610270008029802
URL: http://dx.doi.org/10.1080/10610270008029802

SUPRAMOLECULAR CHEMISTRY, Vol. 12, pp. 23-26
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The Design of Ion Selective Macrocycles and the Solid-Phase Extraction of Ions Using Molecular Recognition Technology: A Synopsis

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(In final form February 01, 1999)

We have combined organic synthesis and the study of cation complexation properties of the crown ethers in an effort to design and prepare macrocyclic ligands that will selectively bind specific cations.[1-3] The bis-phenol-containing diazacrown ethers allow a great number of possibilities for designing ion selectivity into macrocyclic ligands. In these cases, the macrocyclic ligand can be varied as can the type and position of attachment of the phenolic group. Any of these variations can have profound effects on complexation properties. For example, ligand **1** (see Figure 1), where two 5-chloro-8-hydroxyquinoline (CHQ) groups are attached through their positions 7, is selective for Mg^{2+} over other alkali and alkaline earth metal ions (see Table I).[4] On the other hand, ligand **2**, where the two CHQ groups are attached through their positions 2, exhibits remarkable selectivity for K^+ and Ba^{2+} over all other metal ions studied. The chemical shifts of the CHQ protons in the ^1H NMR spectra of K^+- and Ba^{2+}- complexes with **2** shift significantly upfield in relation to the free ligand. These shifts are indicative of an overlap of the two CHQ substituents. Indeed, the crystal structure of the Ba^{2+}-**2** complex shows that Ba^{2+} is in the center of a pseudo-cryptand with the diazacrown forming two arms and the two overlapping CHQ groups forming the third.[4,5] This pseudo-cryptand formation accounts for the fact that the K^+-**2** and Ba^{2+}-**2** complexes are so stable in comparison to complexes of **2** with the other alkali and alkaline earth cations.

TABLE I Log *K* (CH_3OH) Values Valid at 25°C for the Interactions of Ligands **1** and **2** with Various Cations[a]

Ligand	Na^+	K^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Co^{2+}
1	2.89	3.39	b	6.82	5.31	4.43	3.60	5.14
2	3.74	6.61	2.70	c	4.71	4.67	12.2	4.8

a. Data from reference 4.
b. No measurable heat.
c. Formed precipitate.

The relatively strong complex of Mg^{2+} with **1** is probably a result of the inability of the OH and quinoline nitrogen atoms of the two CHQ groups to completely interact with a cation

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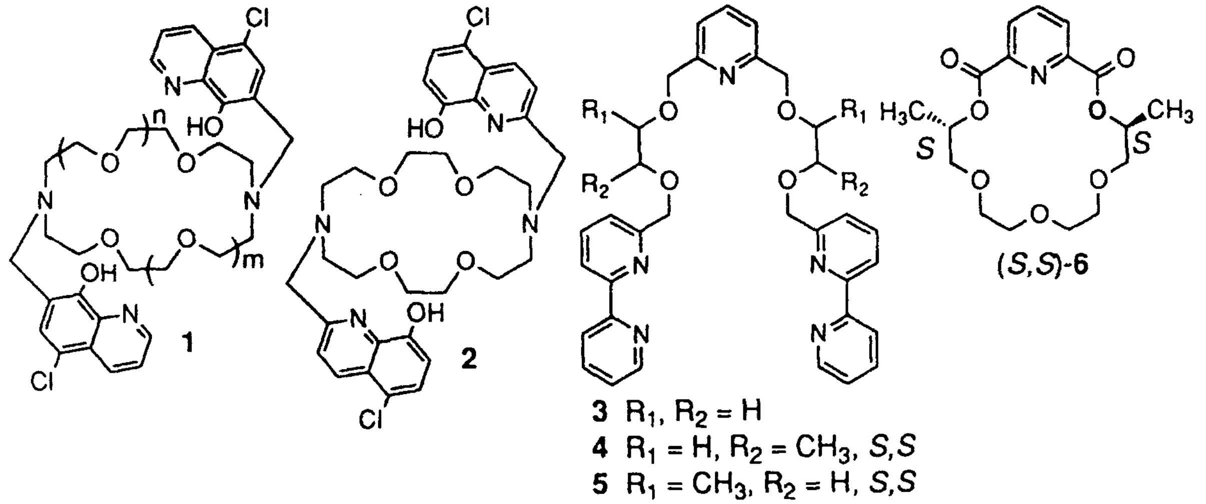

FIGURE 1 Ligands discussed in this paper

bound within the macroring. In this case, the OH groups sterically prevent the quinoline nitrogens from approaching the macroring. Thus, the two CHQ groups interact with $Mg^{2+}$and the macroring is merely a template keeping the two CHQ groups in proper positions to interact. It is interesting that a new peak at 265 nm appears in the UV spectrum for the Mg^{2+}-**1** complex. A remarkable increase in the intensity of the fluorescence spectrum of **1** occurs when Mg^{2+} is introduced even in the presence of much higher amounts of the alkali and other alkaline earth cations (see Figure 2).[6] Thus, ligand **1** can be used as a sensor for Mg^{2+} ions.

We recently prepared a series of open-chain bis(2,2′-bipyridine)-containing ligating agents (**3**–**5**) which interact with primary ammonium salts after being organized by interaction with Cu(I).[7] Thus, ligand **3** does not interact with α-phenylethylammonium perchlorate in the absence of Cu(I). With Cu(I) present, the log *K* value for formation of the **3**-Cu(I)-RNH_3^+ complex is 3.56. Chiral ligands *S,S*-**4** and *S,S*-**5** form stronger complexes with the *R*-form of α-phenylethylammonium perchlorate (log *K* 3.38 and 3.25) than does chiral pyridino-18-crown-6 (*S,S*-**6**) (log *K* 2.33). The degree of recognition of chiral **4** and **5** ligands for the *S*- and *R*-forms of α-phenylethylammonium perchlorate as measured by differences in log *K* values (0.26 for **4** and 0.17 for **5**) is similar to that of **6** (0.22).

In 1988, we reported that crown ethers immobilized on silica gel displayed metal ion dissociation constants which were nearly identical to those of the unbound crown ethers.[8] Thus, a macrocycle which interacted selectively with a specific metal ion could be attached to a solid support and used to remove that ion from aqueous solutions.[9] This process is not the same as ion exchange chromatography since the crown ligand does not interact with all cations but only with specific metal ions. The crown ether-containing solid is packed into a column and an aqueous solution containing a mixture of metal ions including the one to be separated is passed through the column. Selectivity for the desired ion is so great that only that ion is captured by the bound crown ether molecules. For example, diaza-18-crown-6 interacts very strongly with Hg^{2+} and Pb^{2+} (log $K = 15.38$ and 8.39, respectively), but not with alkali and alkaline earth cations. Thus, ppb amounts of Hg^{2+} and Pb^{2+} were

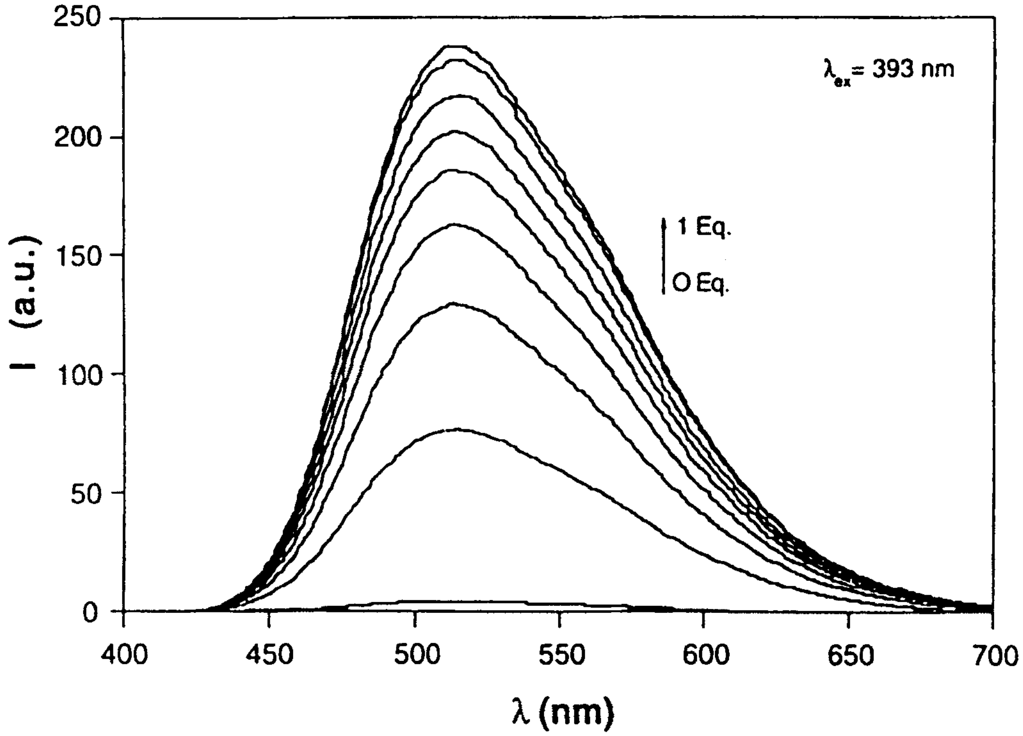

FIGURE 2 Fluorescence spectra[6] of **1** (1×10^{-5} *M*) in methanol-water (1:1 vol:vol) with increasing amounts of Mg^{2+}. λ_{ex}=393 nm

completely removed from a solution also containing ppm amounts of Ca^{2+}, Mg^{2+}, Na^{2+} and K^+ by a diaza-18-crown-6-bound silica gel column.[9]

These dramatic separations results prompted Izatt and Bradshaw in 1988 to found IBC Advanced Technologies, Inc. to develop this technology for commercial use. Over the past 10 years, IBC has developed solid phase extraction materials to remove and/or purify a variety of metal ions from various metal ion mixtures. Some of the separations systems include the following.

1. Removing and purifying Pt and Rh from mixtures of platinum group metals.
2. Removing unwanted Bi and Sb from Cu concentrates in Cu refineries.
3. Removing Hg from concentrated H_2SO_4.
4. Recovery of Cu and other valuable metals from mine waste waters.
5. Removing and concentrating radioactive Cs and Sr from radioactive waste storage solutions.

A typical example of an IBC environmental separation process is the recovery and partial purification of Cu, Fe, Al, Sn, and Mn from the Berkeley Pit waste waters in Butte, Montana. The Berkeley Pit is a large body of mine drainage water from underground and open pit mining operations over the past century. Table II shows the concentrations of the five desired metal ions as well as that for unwanted Cd and As which needed to be removed for environmental cleanup purposes. The data from pilot-plant scale separations experiments in Table II show that all the metals were removed to very low concentrations and the five desired metals were recovered in good to excellent purities.

TABLE II Separation and purification of Berkeley Pit metal constituents[2]

Metal	*Feed concentration (mg L^{-1})*	*Treated effluent concentration[a] (mg L^{-1})*	*Recovery (%)*	*Eluant Purity (%)*
Cu	180	<0.02	>99	96–98
Fe	994	<0.1	>99	99.5
Al	270	<1	>99[b]	97–98
Sn	554	<0.05	>99	99–99.5
Mn	194	<1	>99	75–80[b]
Cd	2	<0.02	NA[c]	NA[c]
As	0.3	<0.1	NA[c]	NA[c]

a. All below detection by analytical methods used.
b. Some Al slipped past the Al system but was recovered with the Mn. Total Al recovery was >99%.
c. Not analyzed.

The metal ion separations processes being developed by IBC have a bright future for the industrial scale separations of unwanted trace impurities, the recovery of metals from waste solutions, or the purification of valuable metals. This new technology demonstrates the power of supramolecular chemistry in meeting current and future industrial and environmental separations needs.

Acknowledgements

This research was supported in part by the Office of Naval Research.

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