

## Frustrated ion-pair binding by heteroditopic macrocyclic receptors

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A series of  $\text{Ag}^+$  complexes of the macrocyclic heteroditopic receptor, 4-phenylurea-benzo-15-crown-5 (**1**) have been prepared from hydrophobic- ( $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ) and oxo- ( $\text{NO}_3^-$ ,  $\text{CF}_3\text{SO}_3^-$ ) anion salts. These complexes contain the  $\text{Ag}^+$  cation, partially interacting with the macrocyclic cavity and the anions H-bonded to urea moieties. Additional interactions of the  $\text{Ag}^+$  cation with a  $-\text{C}=\text{O}$  moiety of a neighbouring receptor **1** molecule or with the oxo-anions ( $\text{NO}_3^-$ ,  $\text{CF}_3\text{SO}_3^-$ ) have been observed.  $K_{\text{ass}}$  values calculated for the resulted ion-pair macrocyclic complexes  $\text{1}\cdot\text{Ag}^+-\text{BF}_4^-$ ,  $\text{1}\cdot\text{Ag}^+-\text{PF}_6^-$ ,  $\text{1}\cdot\text{Ag}^+-\text{CF}_3\text{SO}_3^-$ ,  $\text{1}\cdot\text{Ag}^+-\text{NO}_3^-$  were fitted with 1:1 model and correspond to the values of 140, 255, 660 and  $980\text{ M}^{-1}$ , respectively. The cooperative anion/urea and cation/macrocycle binding and their interaction favour the whole recognition process. This synergism is amplified by self-assembly and depends on the structural features of the anion. In the combined system, the cation–anion interactions are favourable for the stability of the whole system.

**Keywords:** ion-pair recognition; crown-ethers; silver salts; H-bonding; urea; self-assembly

### Introduction

Molecular recognition of ion-pair salts by neutral macrocyclic cation-carriers is greatly affected by the structural behaviours of the co-transported anion and vice versa (*1*). A large number of macrocyclic receptors have been evaluated for their abilities to recognise cations (*2, 3*) and increased attention has been directed towards various receptors for anions (*4, 5*). However, the target salts exist as associated ion-pairs which can influence or hinder the single-ion recognition by one receptor. One strategy to circumvent this problem is to design heteroditopic receptor molecules with specific cation and anion binding sites, which can simultaneously/synergistically bind both of the salt ions (*6–20*). Numerous heteroditopic receptors have been designed to recognise in solution or in the solid state, the inorganic ion-pair salts (*6–12*), or the zwitterionic amino acids (*13–19*). Active transport processes fuelled by concentration gradients of the cations have been described to pump hydrophilic anionic amino acids, adenosine triphosphate and organic carboxylates through polarised membranes (*17–20*).

During the last years, we reported various synthetic (ureido)crown-ether receptors (*21*). These neutral heteroditopic macrocycles can self-organise in solution (*22*), in bilayers (*23*) and in the solid state (*20, 24, 25*) into H-bonded ribbon-type superstructures, providing the evidence for a hybrid carrier and channel transport mechanism. Heteroditopic 4-phenylurea-benzo-15-crown-5

receptor (**1**) is able to extract solid  $\text{NaX}$  ( $\text{X} = \text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{CF}_3\text{SO}_3^-$ ) salts into  $\text{CDCl}_3$  and  $\text{CH}_3\text{CN}$ , consistent with formation of the receptor–salt complexes. The fittest cation  $\text{Na}^+$  binds the 15-crown-5 macrocycle and the counter-anions are usually H-bonded via the urea moieties (Figure 1(a)). Despite such progress, one aspect attracts our attention: no quantitative studies dedicated to the synergetic ion-pair binding chemistry of salts by such macrocyclic receptor for which the diameters of the cation and of the macrocycle are not dimensionally compatible (i.e.  $\text{Ag}^+$  cation and 15-crown-5)<sup>1</sup> or the nature of the anion imposes low H-bonding to the urea moiety.

Thus, we therefore decided to pursue these studies and to present here the ion-binding properties of 4-phenylurea-benzo-15-crown-5 receptor **1** of various silver salts. The salt-binding properties of heteroditopic receptor **1** might be strongly dependent on the interactional behaviours of the anion: (a) coordination to low-coordinated  $\text{Ag}^+$  cation or (b) H-bonding to urea moiety (Figure 1(b)) (*26–28*).

### Experimental section

#### Materials and methods

The 4-phenylurea-benzo-15-crown-5 receptor (**1**) has been synthesised as previously reported (*21*). All other reagents were obtained from commercial suppliers and used without further purification. All organic solutions were

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