Selective binding of weakly coordinating anions: exploring the conformational space of flexible receptors

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Recently, the multifaceted studies of anion receptors have emerged into an

integral part of recognition and separation processes in chemistry or industry.¹ In general two types of receptors are used: *preorganized receptors* which often exhibit high peak-selectivity and *flexible receptors*, which are able to sculpture specific response to anion's needs (various geometries, pH-sensitivity etc.).² The later often have problems with affinities in contrast to their rigid counterparts, but are very useful in the development of various fields which employ supramolecular systems (sensors, signallers etc.).³

Over the past years we have studied binding and recognition of environmentally relevant anions to polyamine receptor which showed remarkable selectivity towards inorganic or organic anions.^{4a,c} Selectivity in separation was conducted in a series of competitive crystallization experiments. Later, the selectivity trend was extended for the solid state, surpassing the solubility problems of investigated acids.^{4b,c,5} Structural aspects of binding of weakly coordinating anions (such as perchlorate) will be presented and discussed in the context of the conformational space of prepared receptors. In several cases crystals of supramolecular complexes were obtained from gel-phase (preliminary results, emphasize the importance of structural characterization of such phases). Taken altogether, results show how the receptor utilizes its flexibility to ensure the optimal environment for inclusion of target anions in the crystal structure.

1. R. Custelcean, Chem. Soc. Rev., 2010, 39, 3675-3685.

2. N. Gimeno, R. Vilar, Coord. Chem. Rev., 2006, 250, 3161-3189.

3. (a) K. Ariga, T. Kunitake, *Supramolecular Chemistry*, Springer-Verlag, Berlin, Heidelberg, 2006. (b) A. T. Wright, E. A. Anslyn, *Chem. Soc. Rev.*, **2006**, *35*, 14-28; (c) R. Custelcean, *Chem. Commun.*, **2013**, *49*, 2173-2182.

4. (a) K. Užarević, I. Đilović, D. Matković-Čalogović, D. Šišak, M. Cindrić, *Angew. Chem. Int. Ed.* 2008, 47, 7022-7025; (b) K. Užarević, I. Đilović, N. Bregović, V. Tomišić, D.
Matković-Čalogović, M. Cindrić, *Chem Eur. J.*, 2011, 17, 10889-10897; (c) K. Užarević, I.
Halasz, I. Đilović, N. Bregović, M. Rubčić, D. Matković-Čalogović, V. Tomišić, *Angew. Chem. Int. Ed.* 2013, 52, 5504-5508.

5.I. Đilović, K. Užarević, CrystEngComm, 2015, 17, 3153-3161.