Supramolecular Chemistry of Aryl Extended Calix[4]pyrroles

Pablo Ballester

[a] *Catalan Institution for Research and Advances Studies (ICREA) Pg. Lluís Companys, 23, 08010-Barcelona, Spain and Institute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans, 16 43007-Tarragona, Spain.*

E-mail pballester@iciq.es

In this presentation, I will introduce two and four "wall" aryl-extended calix[4]pyrrole receptors as model systems for the experimental quantification of anion-π interactions in solution.[1]

I will comment on the preparation of water soluble aryl-extended calix[4]pyrroles i.e. **1** by installing ionizing groups at their upper or by functionalization at their lower rims.[2] I will show the use of a commercial instrument (BIA technology) that integrates microfluidics with surface plasmon resonance (SPR) detection for the kinetic and thermodynamic characterization of the interactions of water-soluble calix[4] pyrroles with surface-immobilized guests derived from pyridine N-oxide.[3]

I will describe the self-assembly of unprecedented receptors based on a bis-calix[4]-pyrrole cyclic component **2** and a linear bis-amidepyridyl-*N*-oxide unit **3** for the binding of ion pairs**.**[4] Suitable polyatomic anions induced the quantitative assembly of four-particle ion-paired complexes, TMA•OCN⊂**2•3**, displaying [2]pseudorotaxane topology. I will also present very recent results on the synthesis of closely related receptors displaying [2]rotaxane topology. Finally, I will disclose the unexpected properties of macrocycle **2** for the recognition of ion-pair dimers and ion-pair quartets.[5]

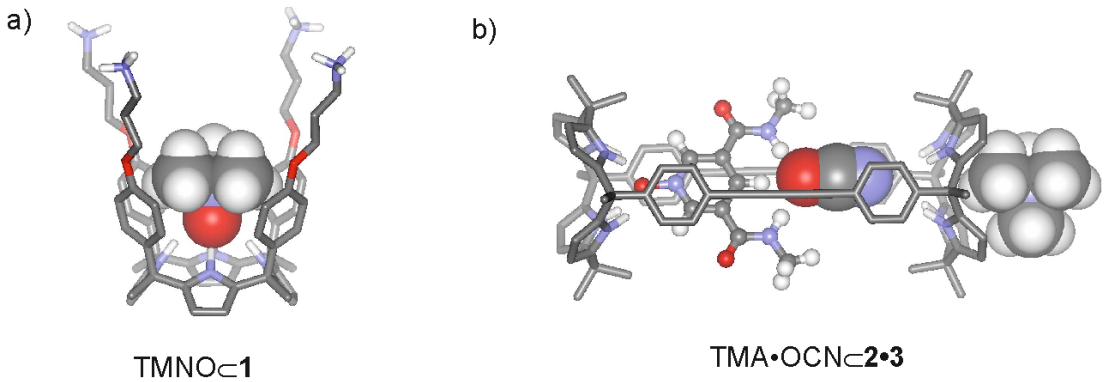

Fig.1. Examples of supramolecular systems based on aryl-extended calix[4]pyrrole scaffolds, a) inclusion complex of trimethylamine-*N*-oxide with a four "wall" receptor, b) interwoven four particle assembly with [2]pseudorotaxane topology. Some hydrogen atoms are omitted for clarity.

---

[1] a) Adriaenssens, L.; Gil-Ramírez, G.; Frontera, A.; Quiñonero, D.; Escudero-Adán, E. C.; Ballester, P., *J. Am. Chem. Soc.*, **2014**, *136*, 3208-3218; b) Ballester, P., *Acc. Chem. Res.*, **2013**, *46*, 874-884

[2] a) Verdejo, B.; Gil-Ramirez, G.; Ballester, P. *J. Am. Chem. Soc.* **2009**, *131*, 3178-3179; b) Hernandez-Alonso, D.; Zankowski, S.; Adriaenssens, L.; Ballester, P. *Org. Biomol. Chem.* **2015**, *13*, 1022-1029

[3] Adriaenssens, L.; Acero Sanchez, J. L.; Barril, X.; O'Sullivan, C.; Ballester, P. *Chem. Sci.* **2014**, *5*, 4210-4215.

[4] Valderrey, V.; Escudero-Adán, E. C.; Ballester, P., *J. Am. Chem. Soc.*, **2012**, *134*, 10733-10736

[5] a) Valderrey, V.; Escudero-Adán, E. C.; Ballester, P., *Angew. Chem., Int. Ed.*, **2013**, *52*, 6898-6902, b) Ciardi, M.; Galán, A.; Ballester, P. *J. Am. Chem. Soc.* **2015**, *137*, 2047-2055