

Energy-resolved Collision-induced Dissociation of Non-Covalent Ions: Charge- and Guest-dependence of the Decomplexation Reaction Efficiencies

**Glenn Carroy,^{a,b,c} Vincent Lemaux,^c Julien De Winter,^a Lyle Isaacs,^d Edwin De Pauw,^b Jérôme Cornil,^c
Pascal Gerbaux^{a,*}**

^a Organic Synthesis and Mass Spectrometry Laboratory, Interdisciplinary Center for Mass Spectrometry, Research Institute for Science and Engineering of Materials, University of Mons, UMONS, 23 Place du Parc, 7000 Mons, Belgium

^b Mass spectrometry Laboratory, University of Liège, B-4000 Liège, Belgium

^c Laboratory for Chemistry of Novel Materials, Center of Innovation and Research in Materials and Polymers, Research Institute for Science and Engineering of Materials, University of Mons, UMONS, 23 Place du Parc, 7000 Mons, Belgium

^d Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

SUPPLEMENTARY INFORMATION

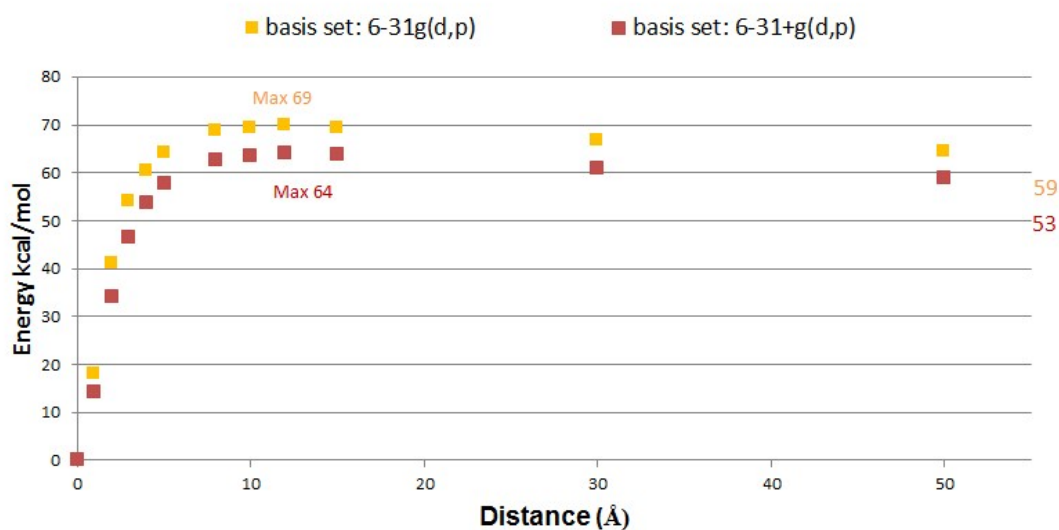


Figure SI 1: Extraction curves for the protonated PXD loss from the doubly charged ternary complexes, $[ns\text{-}CB[10]+2PXD+2H]^{2+}$, calculated at the 6-31G(d,p) and 6-31+G(d,p) levels of theory (see experimental section) : influence of the basis set on the profile of the extraction curves. For each curve, the specified energy value corresponds to the relative energy difference between the equilibrium distance (0Å) and infinity.

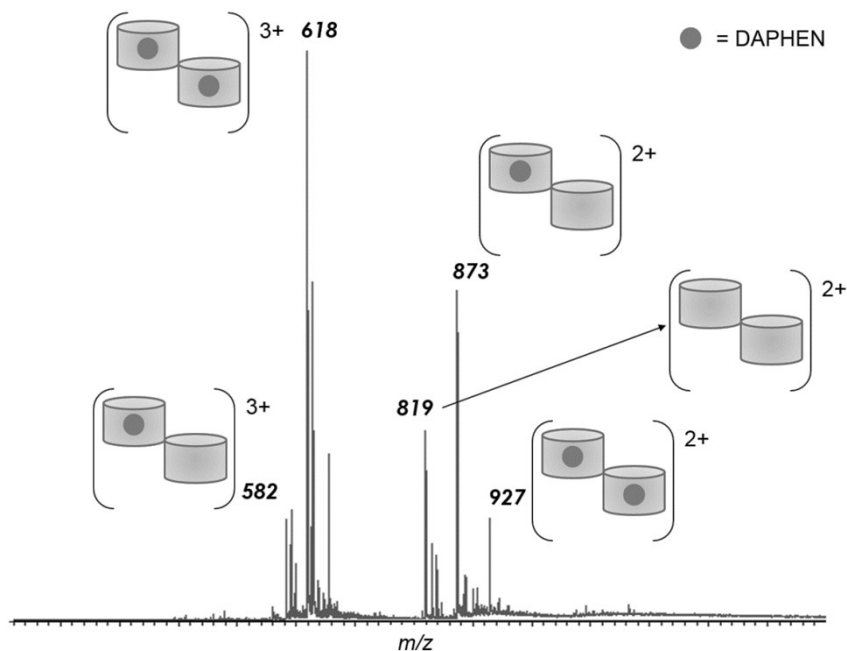


Figure SI 2: ESI-MS spectrum (Waters Q-ToF2, CV=40V, in source-pressure 6 mbar) obtained for a mixture of DAPHEN ($5.10^{-5}M$) and ns-CB[10] ($10^{-5}M$, solvent: water/methanol, 80/20 v/v).

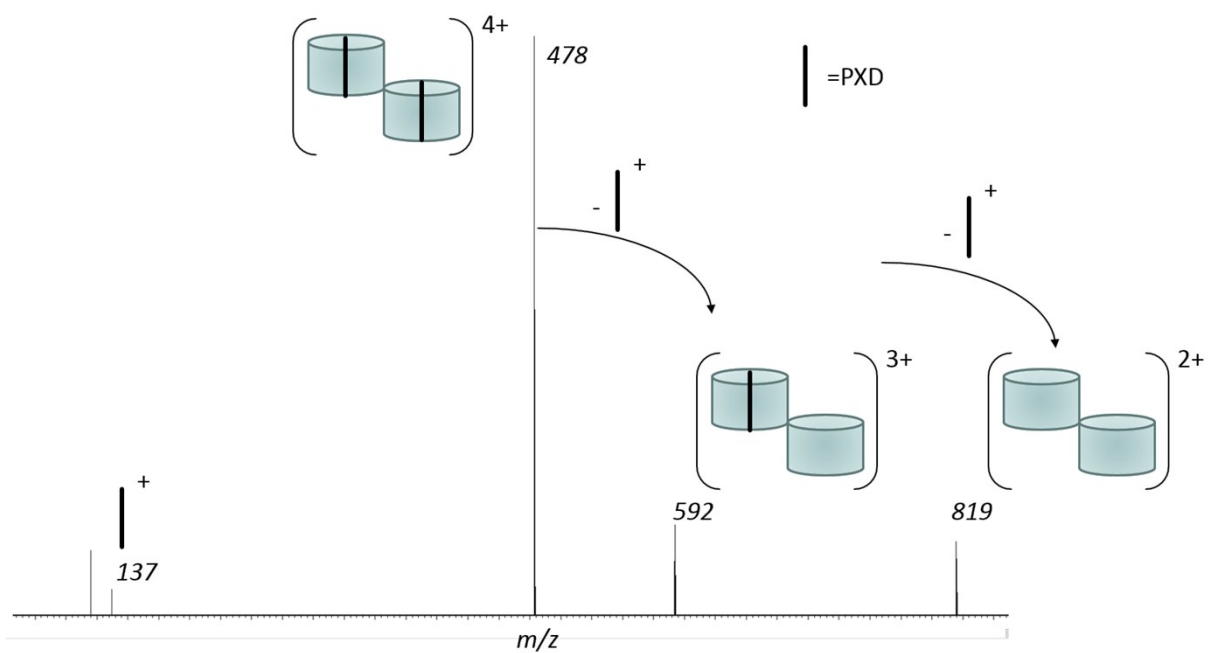
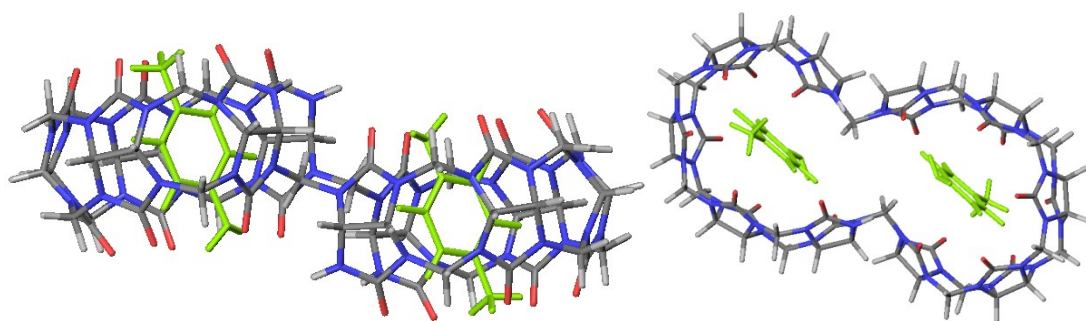
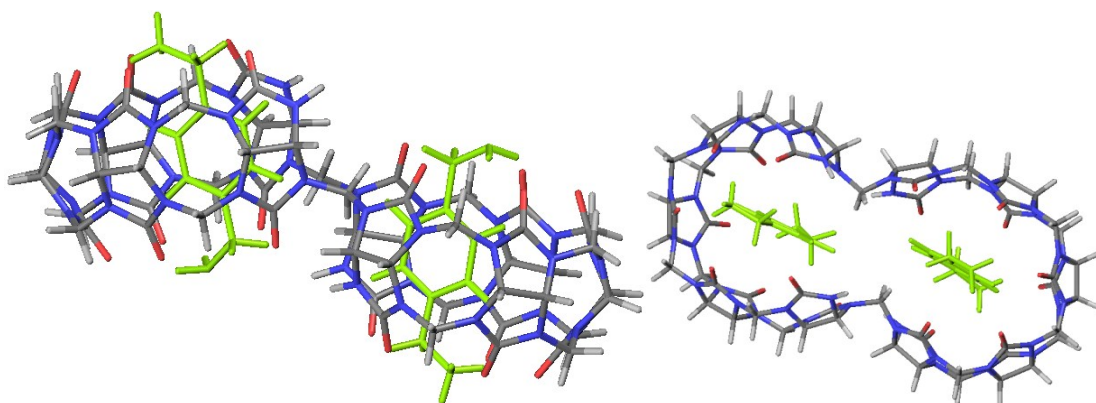


Figure SI 3: ESI-MS/MS analysis of the m/z 478 (Source pressure 7.4 mbar, CV = 40V, CE = 15V) ternary complexes associating para-xylylenediamine to the bitopic receptor.

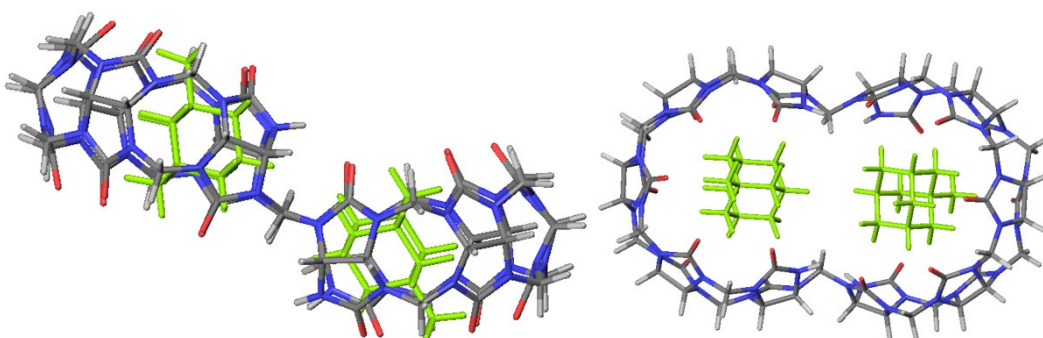
[ns-CB[10]+2DAPHEN+2H]²⁺



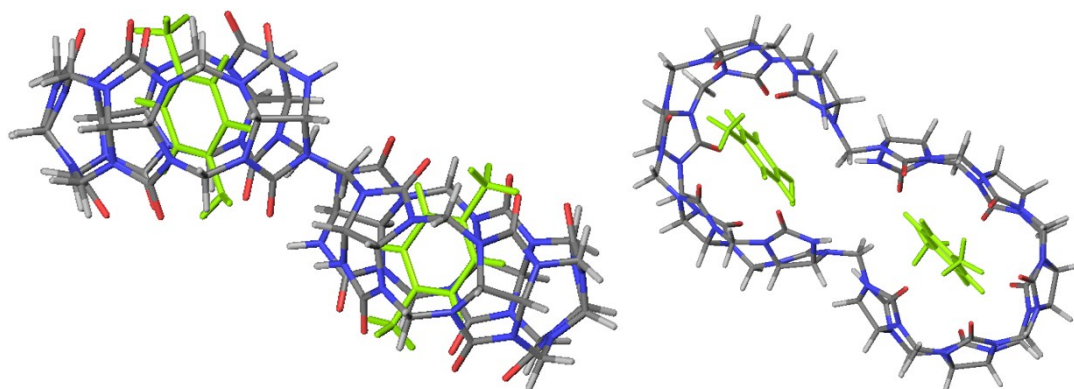
[ns-CB[10]+2PXD+2H]²⁺



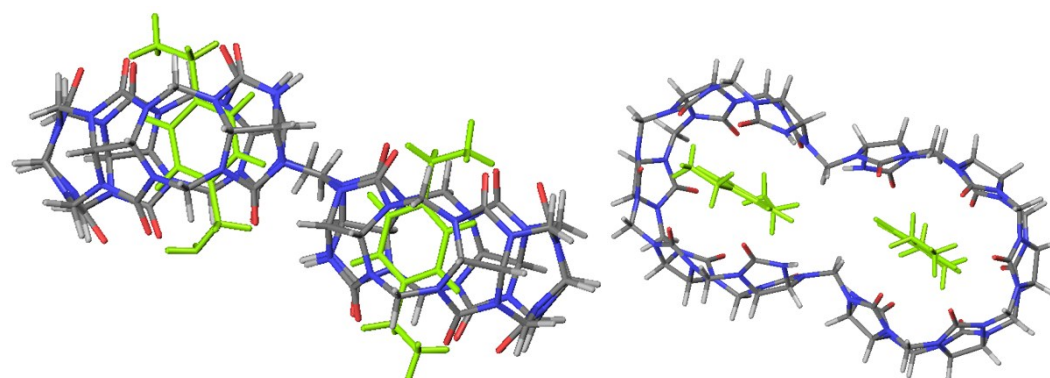
[ns-CB[10]+2ADAM+2H]²⁺



$[\text{ns-CB}[10]+2\text{DAPHEN}+3\text{H}]^{3+}$



$[\text{ns-CB}[10]+2\text{PXD}+3\text{H}]^{3+}$



$[\text{ns-CB}[10]+2\text{ADAM}+3\text{H}]^{3+}$

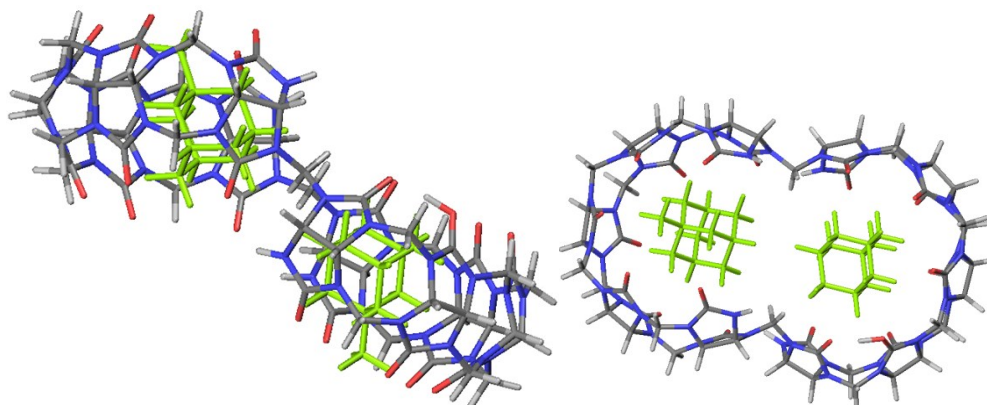


Figure SI 4: 2+ and 3+ ternary complexes associating DAPHEN, PXD and ADAM to the bitopic ns-CB[10] receptor. Structures optimized at the DFT level using the B97D functional and a 6-31g(d,p) basis set from reference 3.

Proton transfer starting from the optimized exclusion structures:

As a typical example of our procedure to estimate the energy involved in the proton transfer reaction, we present here the case of PXD for both the doubly and triply charged complexes. In both cases, the starting point corresponds to the exclusion structures optimized at the DFT level (B97D, 6-31G(d,p)). In those structures, all charges are carried by the PXD guests (*Figure SI 5*).

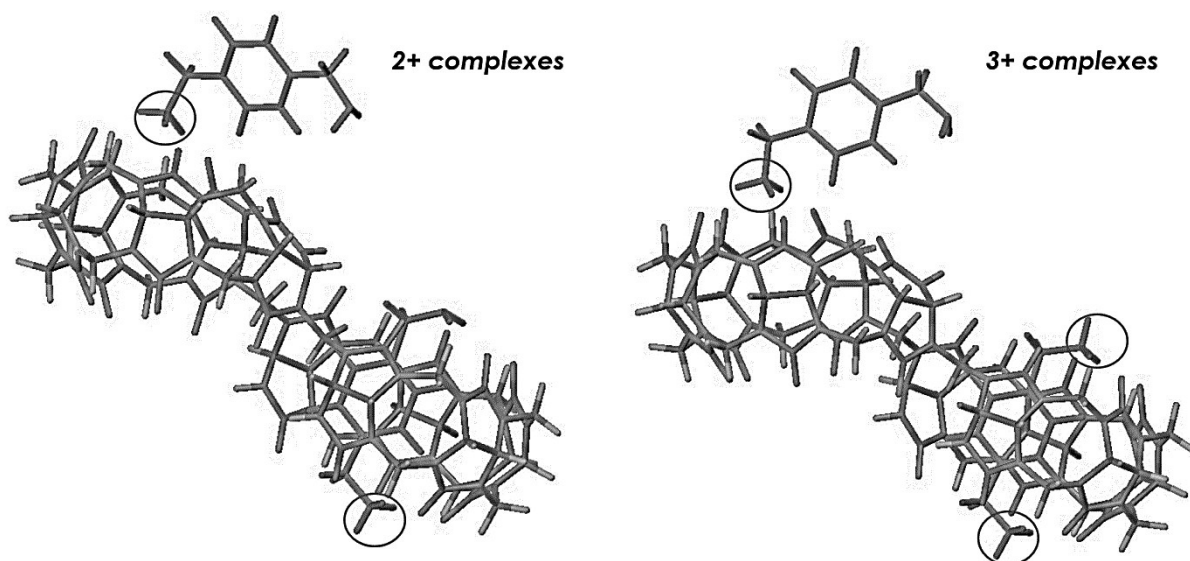


Figure SI 5: DFT-optimized structures of the doubly and triply charged exclusion complexes of PXD and ns-CB[10] (B97D, 6-31G(d,p)). Charge locations are noticed in circles.

Figure SI 6 illustrates the method used to determine the energy cost for the proton transfer. Starting from the optimized structure of the exclusion complex, single point calculations have been performed by increasing the distance between the proton and the nitrogen atom of the leaving guest amine function from the equilibrium distance up to 1 Å, upon freezing all the other atom coordinates including the O-N distance (3.1 Å) in the optimized complex (see the black arrow on **Figure SI 6**), with O the nearest oxygen atom.

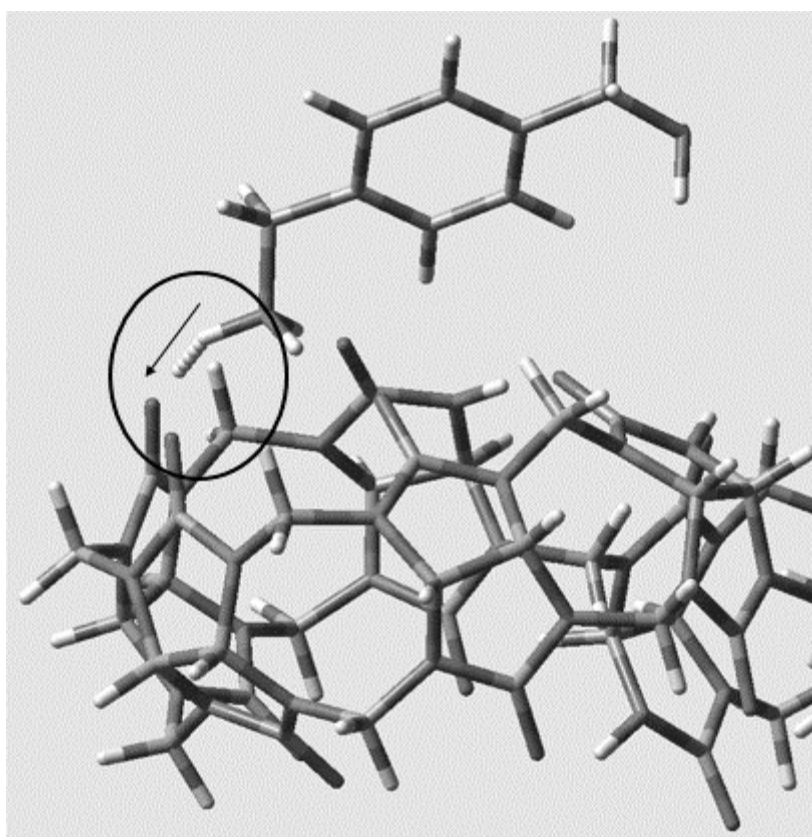


Figure SI 6: Illustration of the method used to evaluate the energy cost for a proton transfer from the guest to a cage carbonyl function (see black circle).

Figure SI 7 displays the evolution of the relative energies obtained for the doubly charged and triply charged associations between ns-CB[10] and PXD as a function of the distance. The same procedure was conducted on the other complexes and the data are presented in **Table SI 1**. The relative energies determined by this method can be considered as the upper limit for the energy required for transferring the proton from the ammonium group to the carbonyl rim since no optimization has been performed.

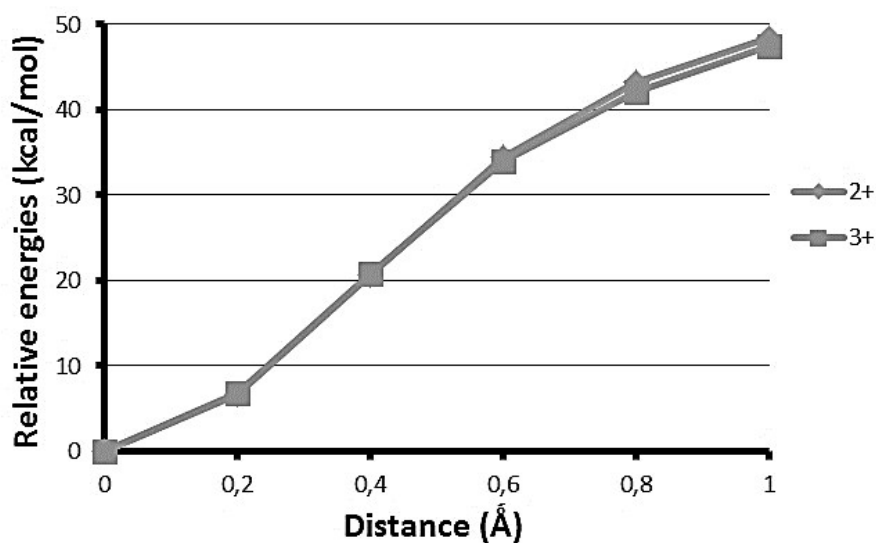


Figure SI 7: Proton transfer curves obtained with single-point calculations (DFT, B97D 6-31G(d,p)) for the doubly and triply charged complexes of PXD and ns-CB[10].

<i>Guest</i>	Maximum energy required for the proton transfer (kcal/mol)	
	2+	3+
<i>PXD</i>	48	47
<i>DAPHEN</i>	44	44
<i>ADAM</i>	46	50

Table SI 1: Relative energies obtained for the proton transfer reaction for the 6 studied complexes without geometric relaxation effects thus preventing any link with the actual basicity