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(Coordinatore Prof. Gaetano Guerra)

Cavity Filling and Chirality Effects in Calixarene Threading

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Abstract (English)

In 2010, the Prof. Neri's group showed that the calix[6]arene hosts were able to recognize dialkylammonium axles when they were coupled with the weakly coordinating **T**etrakis[3,5 bis(tri**F**luoromethyl)**P**henyl]**B**orate (TFPB^{-}) "*superweak anion*" that gives very loose ion-pairs with dialkylammonium cations in solution.[1] These interpenetrated structures have been defined in supramolecular chemistry as pseudorotaxane and can be considered as synthetic precursors of catenane and rotaxane architectures[2] which have showed appealing properties as molecular machines[3]. Interestingly, the threading of *directional* alkylbenzylammonium guests with calix[6]arene wheels, led to the stereopreference for the *endo*-alkyl complexation over the endo-benzyl one and this observed stereo-selectivity brought to the definition of the so called "*endo*-alkyl rule"[4]. On these basis we have studied the recognition abilities of calix[6]arene derivatives toward alkylbenzylammonium guests bearing aliphatic chains with different shape and length. In particular, we studied the validity of the *endo*-alkyl rule with alkylbenzylammonium axles bearing alkyl chains with different lengths and using guests bearing branched alkyl chains.

Then the thesis work has been extended to the threading of chiral systems. Special attention was paid to the possibility of obtaining, after threading, the chiral recognition of chiral alkylbenzylammonium ions using chiral calix[6]arene derivatives. The investigation techniques chosen for this purpose have been NMR spectroscopy and Mass Spectrometry by means of the "*Enantiomer Labelled Method*".

Finally the search for new and attractive potential chiral hosts resulted in the application of the "*p*-bromodienone route" for the first time on calix[6]arene derivatives[5] and the study of the optical and electronic properties of inherently chiral resorcin[4]arene derivatives.

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