Selective VOC Uptake in Smart Crystals Based on Homothiacalix[4]arene

Renny Maria Losus[a], Sem Bleus[b], Wim Dehaen[b], Liliana Dobrzańska[a]

[a] *Faculty of Chemistry, Nicolaus Copernicus University in Toruń, 87-100 Toruń, Poland.*

[b] *Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.*

contact: renny@doktorant.umk.pl

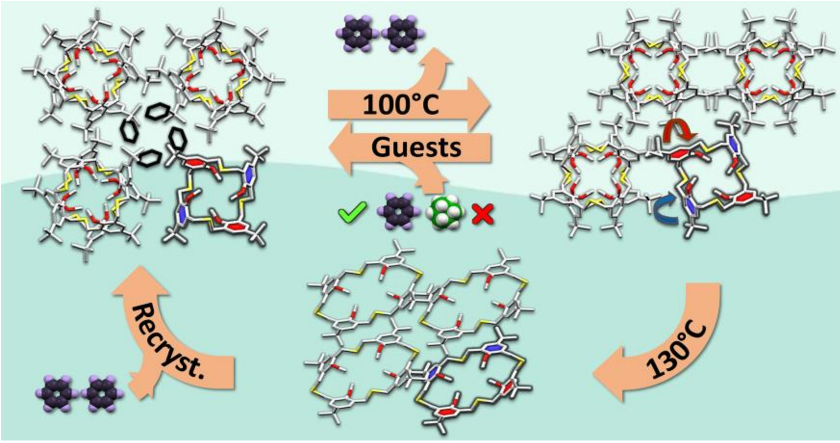

Figure: SC-SC and conformational transformations taking place in HTCA.

Porous materials have increasingly gained importance in materials science, particularly due to their applications in greener chemical processes such as adsorption and separation.[1] While zeolites, MOFs, and COFs play key roles, porous materials based on molecular crystals offer unique advantages. These include flexible supramolecular frameworks that underpin adaptive behavior and straightforward synthetic procedures that allow for the production of pure materials with minimal effort. This makes them highly promising for advanced applications.[2]

In this context, we present, a unique responsive and selective behavior of homothiacalix[4]arene crystals.[3] A benzene disolvate adopting the 1,3-*alternate* conformation (HTCA-s1,3) can be converted to a guest-free non-porous phase (HTCA-a1,3) upon heating, with the host molecules retaining the same 1,3-*alternate* conformation. The process is reversible, with non-porous apohost crystals 'opening up' upon exposure to benzene vapor to reaccommodate the solvent molecules, as confirmed by SCXRD and sorption studies monitored in situ via PXRD analysis. The gate opening mechanism is selective, preventing cyclohexane molecules from passing through, which creates the opportunity to apply this system, for example, in benzene capture/separation. Furthermore, with a higher energy boost, the crystal of the HTCA-a1,3 apohost undergoes a significant conformational change, resulting in HTCA-a1,2, an apohost in which the host molecules adopt the 1,2-*alternate* conformation.

References

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[2] M. A. Little and A. I. Cooper, Adv. Funct. Mater., **2020**, 30, 1909842.

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