Poster

Molecular recognition of aromatics in spherical nanocages

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Due to the lack of efficient specific molecular interactions, achieving host-guest molecular recognition inside large and neutral metal organic cages (MOCs) is challenging. Preferential molecular recognition of aromatics using the internal binding sites of interlocked icosahedral (*i.e.*, spherical) $\mathbf{M_{12}L}$ [1] MOCs within poly-[*n*]-catenane (**1**) [2] is presented (Figure 1) [3]. The guest absorption has been monitored directly in the solid-state by consecutive single-crystal-to-single-crystal (SCSC) reactions in a gas-solid environment, using single-crystal X-ray diffraction (SC-XRD) crystallography. The guest uptake is preferential and is corroborated by Density Functional Theory (DFT) calculations by determining the host-guest interaction energy (E) with the nitrobenzene (NB) >> *p*-xylene (*p*-xy) >> *o*- dichlorobenzene (*o*-DCB) trend (*i.e.*, from 44 kcal/mol to 25 kcal/mol), assessing the crystallographic results. Combining SC-XRD, DFT and solid-state ^{13}C NMR, the exceptional stability of the $\mathbf{M_{12}L_8}$ cages, together with the guest exchange/release properties are rationalized by the presence of *mechanical bonds* (efficient π-π interactions) and by the pyridine's *rotor-like* behaviour (Figure 1). The structure-function properties of $\mathbf{M_{12}L_8}$ makes **1** a potential candidate in the field of molecular sensors and could be used as nanoreactor.

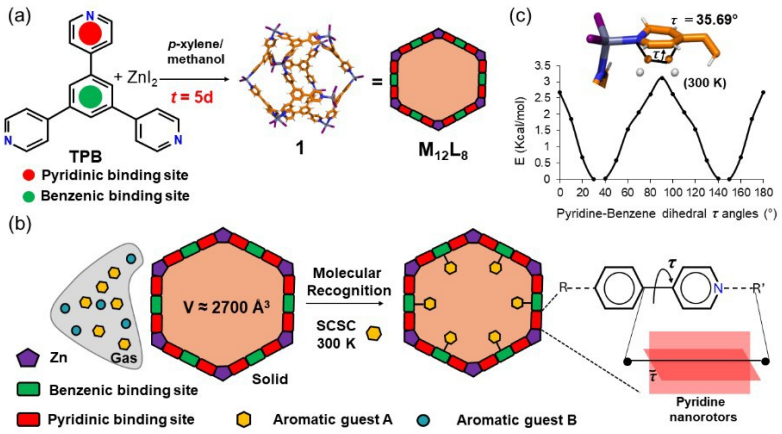

Figure 1. (a) Cartoon showing the synthesis of **1** using the TPB ligand and ZnI_2. For clarity, only one $M_{12}L_8$ nanocage without solvents is shown. (b) Molecular recognition of aromatic guest by $M_{12}L_8$ in **1** in a gas-solid reaction by means of a SCSC process. The pyridine rings act as nanorotors due to their low rotational E properties. (c) Actual SC-XRD structure of **1** containing nitrobenzene showing the pyridine disorder at 300 K, and plot of the potential energy barrier for the pyridine-benzene dihedral torsion angles calculated by DFT methods.

[1] Torresi, S., Famulari, A., Martí-Rujas, J. (2020). *J. Am. Chem. Soc.,* **142**, 9537.

[2] Martí-Rujas, J., Elli, S., Famulari, A. (2023). *Sci. Rep.*, **13**, 5605.

[3] Martí-Rujas, J., Elli, S., Zanotti, A., Famulari, A., Castiglione, F., (2023). *Chem. Eur. J.*, **29**, e2023022025. (Hot Paper)