Encapsulation in Chalcogen-Bonded vs Hydrogen-Bonded Cages

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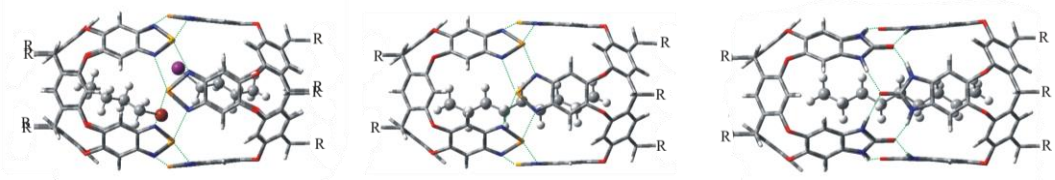
Supramolecular capsules present many diverse applications in sensing, transport, catalysis, material science and separation technologies. In addition, they are desirable containers for the study of molecular behavior in small spaces. The molecules are isolated from the bulk solution and as a result reactive intermediates can be stabilized, even species unknown in solution.[1] The cages can be assembled by a variety of forces including hydrogen bonding,[2] metal−ligand interactions,[3] halogen bonding,[4] chalcogen bonding,[5] and even purely hydrophobic effects.[6] All these supramolecular systems have different properties.

In this presentation, theoretical data on encapsulation of small guests on homo-cavitands and hetero-cavitands chalcogen bonded container capsules and on hydrogen-bonded analogues are presented.[7,8] Theoretical DFT calculations in agreement with available experimental data show that the chalcogen-bonded capsule features enhanced magnetic anisotropy. This causes an unexpected feature of the chalcogen-bonded capsules compared to hydrogen-bonded analogues: the magnetic environment of the former caused larger upfield shifts for the guest nuclei, particularly near the center of the capsule, than in the latter. These observations are attributed to different factors depending on which chalcogen is involved in the capsules.



References:

1. Q. Zhang, L. Catti, K. Tiefenbacher, *Acc. Chem. Res.* **51** 2107 (2018).
2. D. Tzeli, G. Theodorakopoulos, I. D. Petsalakis, D. Ajami, and J. Rebek J. Am. Chem. Soc. 133, 16977 (2011).
3. Y. Hatakeyama, T. Sawada, M. Kawano, M. Fujita, *Angew. Chem., Int. Ed.* **48,** 8695 (2009).
4. C. Gropp, B. L. Quigley, F. Diederich, *J. Am. Chem. Soc.* **140**, 2705 (2018).
5. F.-Ur Rahman, D. Tzeli, I. Petsalakis, G. Theodorakopoulos, P. Ballester, J. Rebek, Jr., Y. Yu, *J. Am. Chem. Soc.* 1**35**, 5876 (2020)
6. K. Wang, X. Cai, W. Yao, D. Tang, R. Kataria, H. S. Ashbaugh, L. D. Byers, B. C. Gibb, *J. Am. Chem. Soc.* **141**, 6740 (2019).
7. D. Tzeli, I. D. Petsalakis, G. Theodorakopoulos, F.-U. Rahman, P. Ballester, J. Rebek, Jr., Y. Yu, *ChemPhysChem* **21**, 2187-2195 (2020)
8. D. Tzeli, I. D. Petsalakis, G. Theodorakopoulos, F.-U. Rahman, J. Rebek, Jr., *submitted.*