

Self-Assembly of Cyclohelicate $[M_3L_3]$ Triangles Over $[M_4L_4]$ Squares, Despite Near-Linear Bis-terdentate L and Octahedral M



Ross Hogue



Sebastien Dhers



Ryan Hellyer



Jingwei Luo



Garry Hanan



David Larsen



Anna Garden



Sally Brooker



Invited for the cover of this issue is the collaborative team of Anna L. Garden, Sally Brooker and co-workers at the University of Otago (New Zealand), along with collaborators from Victoria and Montreal (Canada). The image depicts the entropic balancing act between 4 triangles and 3 squares, an argument which must be used with caution. Read the full text of the article at 10.1002/chem.201702153.

What was the biggest surprise in the course of this study?

The formation of triangles, not the squares anticipated on the basis of the diamide analogues we had worked with previously, was very unexpected given the linear (ligand) and right angle (metal) directing geometries of the reaction components. These surprising architectures warranted careful inspection and analysis. In particular, the use of DFT calculations—something we would not have done had the anticipated squares been observed—provided useful insights into the entropic factors that influence the self-assembly process.

What is the most significant result of this study?

That predicting self-assembly outcomes by particle counting is too simplistic to be correct all of the time. DFT studies on triangles versus squares show that whilst the rotational and translational entropic contributions follow as expected by simple particle counting, the vibrational contribution to the total entropy is an order of magnitude larger and is similar for triangles versus squares. For cyclohelicates, the dominant vibrational modes to the total entropy should therefore be considered very carefully when assessing the entropic outcome of molecular self-assembly processes.

What was the biggest challenge (on the way to the results presented in this paper)?

The synthesis of the pyrazine-2,5-dicarbaldehyde (1) precursor. For a relatively simple building block, it is quite challenging synthetically. There are already a few reported routes in the literature, however none are straightforward. The hard yards of this paper were the development of an ester route, and improvement of the existing ozonolysis route, to 1. We report two reliable syntheses to this key precursor, which will enable its future use in a wider range of self-assembled designer molecular architectures.

Who designed the cover?

Sally provided our graphic design whizz, Michael Crawford (Dunedin), with a concept, which he then added his amazing magic to, generating this striking image.

