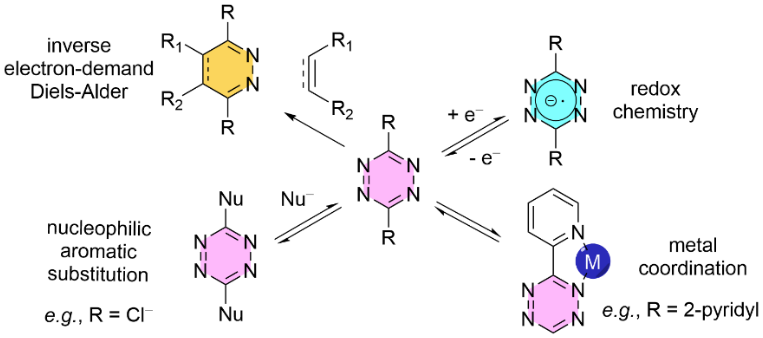
Tetrazines in Stimuli-Responsive Supramolecular Assemblies

Ben S Pilgrim

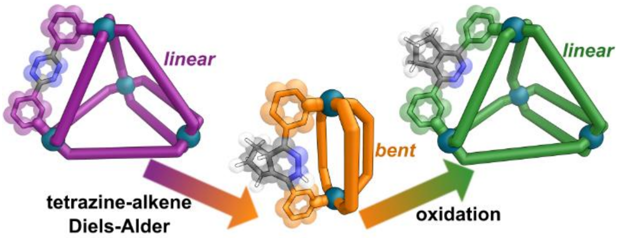
School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK
E-mail: ben.pilgrim@nottingham.ac.uk | Twitter: @BenSPilgrim | https://www.thepilgrimgroup.co.uk

Keywords: tetrazine, click chemistry, metal-organic cages

Self-assembly allows the construction of complex architectures from simple pieces by exploiting reversible non-covalent or dynamic-covalent bond formation. In the Pilgrim Group we are developing functional and stimuli-responsive self-assembled materials, notably those that respond to a chemical stimulus, and the response leading to the structure changing properties such as shape, size, or guest binding properties. We have a particular interest in the materials chemistry of tetrazines. Best known for their biorthogonal or 'click' chemistry capability, tetrazines are diverse and fascinating molecules. As aromatic rings isostructural to benzene, they can often readily replace the relatively rigid benzenes in existing ligand designs, allowing us to equip known structures with the interesting reactivity of tetrazines. Tetrazines have several orthogonal modes of reactivity which we can exploit. In addition to the inverse electron demand Diels-Alder click reaction with strained alkenes and alkynes, tetrazines can also undergo interesting redox chemistry with reversible reduction to radical anions, can act as ligands to metals, and can undergo reversible/dynamic nucleophilic aromatic substitution.



This talk will focus entirely on currently unpublished work and recent developments within the group. Incorporating tetrazine units within the panels for palladium-based metal-organic cages, we have been able to introduce structural transformations between architectures due to the greater flexibility of the non-aromatic dihydropyridazine intermediate formed after the reaction between a tetrazine and alkene, before oxidising the system restores aromaticity and planarity and thus induces a second structural change.



We have shown tetrazines as important additives to improve the lifetime of batteries through charge/discharge cycles in coin cell batteries. We have also incorporated them into a new series of macrocycles and are investigating the extra functionality they impart of these systems.

References

1. Pilgrim, B. S., Champness, N. R. *ChemPlusChem* **2020**, *85*, 1842-1856. **2.** Roberts, D. A., Pilgrim, B. S., Nitschke, J. R. *Chem. Soc. Rev.* **2018**, *47*, 626-644. **3.** Black, M., Bhattacharyya, S., Argent, S. Pilgrim, B. S. *Submitted*.

Biography

Ben Pilgrim studied for his undergraduate/masters (MChem) in Chemistry at St John's College, University of Oxford. Ben remained at Oxford for his postgraduate work, with Prof. Timothy Donohoe. Ben then moved to the University of Cambridge to undertake a Herchel Smith Research Fellowship with Prof. Jonathan Nitschke on the 'Post-assembly Modification of Metallosupramolecular Architectures'. Ben was subsequently awarded a Royal Commission for the Exhibition of 1851 Research Fellowship to study 'Stimuli-responsive Molecular Containers'. In October 2019, Ben moved to the University of Nottingham to start his own research group in the School of Chemistry as a Nottingham Research Fellow. In 2022 Ben was awarded a Royal Society University Research Fellowship and the position of Assistant Prof. (proleptic). In 2023 Ben was promoted to Associate Prof. (proleptic). Ben's research interests span supramolecular chemistry, self-assembly, metal-organic cages, and interlocked molecules. Ben is also a leading advocate for public engagement and outreach in chemistry. Ben is a key member of the UK Chemistry Olympiad Working Group of the RSC, coordinating the national and international rounds of the Chemistry Olympiad competition.