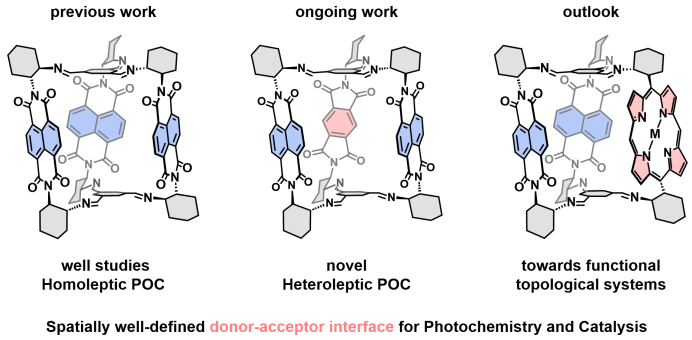
Heteroleptic Covalent Organic Cages

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Over the past decade, the field of porous organic cages (POCs) based on dynamic covalent chemistry (DCC) has emerged, offering access to a wide range of crystalline microporous materials.[1] Molecular organic materials distinguish themselves from porous bulk polymers by absence of intermolecular bonding in the solid-state. This characteristic provides higher degrees of accessibility for functionalization and superior solution processability.[1] With their combination of diverse optoelectrical properties, shape-persistent porosity, and ease of handling, POCs present an intriguing platform for further investigations. Šolomek and colleagues developed porous organic cages (POCs) based on photophysically and redox-active rylene diimide dyes leading to properties including long-lived charge separation, delayed fluorescence, and the selective adsorption of gases.[1-4]



Due to supramolecular self-sorting, as a consequence of the thermodynamic reaction control in DCC, the formation of POCs has been limited to the formation of homoleptic cages of higher symmetry. However, decreasing the symmetry holds the potential to introduce desirable properties for photochemistry and catalysis, leveraging the directional electronic field between well-arranged donor-acceptor interfaces. Recent scrambling experiments suggest that the selective formation of heteroleptic porous, shape-persistent POCs are achievable through kinetic reaction control. The current work focuses on selectively forming heteroleptic POCs by better understanding the stabilities of key synthetic intermediates. Recently the desired target molecules have been observed by means of HR-MS and NMR spectroscopy, albeit in a mixture with competing homoleptic POCs. To overcome this challenge, efforts are being made to minimize competing decay processes of key synthetic intermediates, which have hindered selectivity thus far. By doing so, it should be possible to obtain the desired heteroleptic POCs in sufficient purities, allowing for structural characterization and subsequent investigations of their physical, electronic, and photochemical properties. Allowing to access a novel class of POCs with extraordinary physical properties, which can be tuned for specific tasks at hand with.

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