# From Photoswitching to Instrically Responsive Supramolecular Structures

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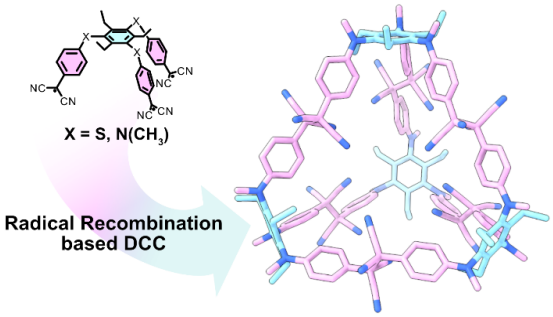
Dynamic covalent chemistry enables the selective synthesis of complex molecular architectures through reversible bond formation and error correction.[1] In our group, we exploit this dynamic behaviour to construct responsive two- and three-dimensional systems whose composition, topology, and function can be controlled by external stimuli, using two complementary dynamic covalent platforms based on imine formation and, now, radical recombination. In the first series, the reversible condensation of the visible-light photoswitchable azobenzene dialdehyde with chiral *R,R*-1,2-diaminocyclohexane and alkyldiamines generates libraries of imine macrocycles.[2] Extending from imine macrocycles to three-dimensional porous architectures, we introduce aryldicyanomethyl radical recombination as a dynamic covalent tool for constructing porous organic cages.[3] Systematic variation of a single substituent controls radical and σ-bond stability as well as cage topology: a thiophenoxy-substituted building block selectively forms a discrete $Tri^2$ cage, whereas its *N*-methylaniline-substituted analogue affords a tetrahedral $Tri^4$ architecture. The latter exhibits permanent porosity, while both cages display reversible mechano- and thermochromism. Moreover, their dynamic bonds and three-dimensional preorganisation enable efficient self-healing, which is strongly accelerated by exposure to THF vapour.




Together, these studies demonstrate how different reversible covalent bonds can translate molecular-level responsiveness into structural adaptation across dimensions. They establish design principles for light-controlled macrocycles and responsive porous cages, opening pathways towards adaptive molecular systems and self-healing functional materials.

Literature:

[1] M. Martínez-Fernández, Y. Hartmann, B. M. Schmidt, *Angew. Chem. Int. Ed.* **2025**, *64*, e202509618. [2] E. Nieland, J. Voss, A. Mix, B. M. Schmidt, *Angew. Chem. Int. Ed*. **2022**, *61*, e202212745. [3] Y. Hartmann, R. Oestreich, Y. Wada, P. de Bary, M. Kawano, C. Janiak, B. M. Schmidt, *Angew. Chem. Int. Ed.* **2026**, *65*, e7638565.