

Cyclophane self-assembly from carbazole-based diradicals

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The investigation of π -conjugated diradical compounds, featuring radical centers in the ground state, is key to understanding the nature of chemical bonds.^[1] Occasionally, these systems can form long σ C-C bonds between two unpaired electrons resulting in macrocyclic or staircase oligomers or polymers by self-assembly processes. Furthermore, these new C-C bonds are longer than an ordinary bond between two sp^3 carbon resulting in reversible dissociation/formation behavior between isolated radical species and cyclophane structures. Therefore, these materials are potential building blocks for dynamic covalent chemistry (DCC).^[2] Hereinto, we present an experimental and theoretical study of carbazole and indolocarbazole-based diradicals (Figure 1) with dicyanomethylene (DCM) groups in different positions (para-DCM or meta-DCM) to identify new building blocks to obtain multi-responsive materials.^[3-5] To this end, we investigated the dynamic interconversion between the isolated diradical and the cyclophane structures under external stimuli such as temperature, pressure and so on. Specifically, our main aim is to study how the DCM substitution and the elongation of the conjugated core affect the diradical character and to understand the connection between this parameter and the cyclophanes stability. In addition, we want to investigate if this transformation is reversible or not.

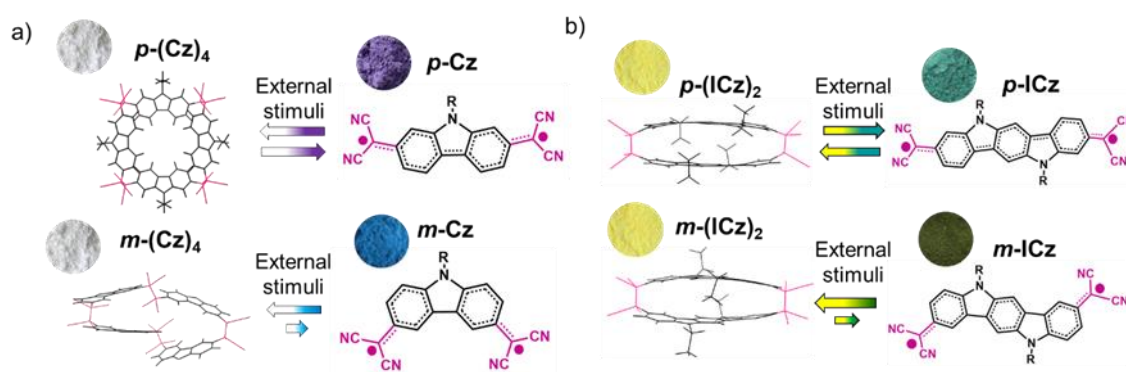


Figure 1. Equilibrium between cyclophane and their isolated diradicals

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