

Carbazole-based Diradicals for Dynamic Covalent Chemistry

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Dynamic covalent chemistry (DCC) is focused on the creation of structural scaffolds based on chemical components that interact through strong but reversible bonds. In fact, dynamic covalent bonds receive lot of attention because of their unique feature to become reversible under mild conditions.¹ π -conjugated diradical compounds has emerged as essential building blocks in DCC.² In this work, we will review our most recent works on the formation of stimuli-responsive cyclophanes by self-assembly of carbazole-based diradicals. To this end, we use a combined experimental and theoretical approach that links vibrational spectroscopy with DFT calculations. In this sense, it is interesting to note that we have recently demonstrated the potential of a para-substituted carbazole with terminal dicyanomethylene (DCM) groups to act as building blocks in DCC.³ This quinoid carbazole monomer transforms to a macrocycle cyclophane upon soft external stimuli (temperature, pressure, light), showing strong chromic features. In addition, we have also recently explored how the different DCM substitution position affects the interesting chromoactive properties of carbazole compounds.⁴ Finally, we are currently exploring the effect of the elongation of the carbazole backbone on the formation of stimuli-responsive cyclophanes.

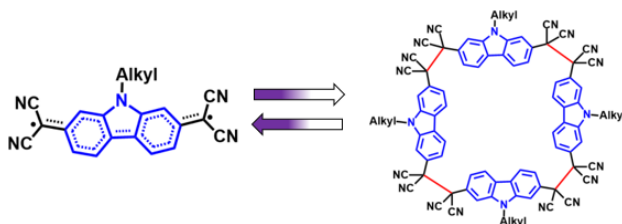


Figure 1. Equilibrium between an isolated carbazole-based monomer ascribed to the open-shell (OS) singlet state and its corresponding cyclophane aggregate.

References

1. Lehn J.M., *Chemical Society Reviews*. 2007, **36**, 151
2. Kohei, O et al *Angewandte Chemie International Edition*. 2017, **56**, 16597.
3. Wang D., et al, *Chemistry European Journal* 2017, **23**, 1.
4. Badía-Domínguez, I., et al *ACS Omega* 2019, **4**, 4761