

## Impact of the Dicyanomethylene Substitution Position on the Cyclophane Macrocyclic Formation in Carbazole-based Biradicals

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$\pi$ -Conjugated biradical compounds, featuring unique unsaturated valences and radical centers in the ground state, are fundamentally important for understanding the nature of chemical bonds and have potential applications in material science.<sup>[1]</sup> Recently, it has been demonstrated that several  $\pi$ -conjugated mono- and biradicals systems form long strain  $\sigma$ -bonds between two unpaired electrons resulting in macrocyclic or staircase oligomers or polymers by self-assembly processes.<sup>[2]</sup> Therefore, these materials are potential building blocks for dynamic covalent chemistry (DCC) since the aggregates can be formed or broken upon soft external stimuli. For instance, 2,7-dicyanomethylene-9-(2-ethylhexyl)carbazole biradical (*p*-Cz-alkyl in Figure 1) reversibly converts upon soft stimuli (temperature, pressure, light) to a cyclophane tetramer as a result from the formation (or bond cleavage) of long C-C single bonds.<sup>[3]</sup> Here, we present an experimental and theoretical study in order to investigate how the *N*-substitution and the change from *para*- to *meta*-dicyanomethylene substitution on carbazole-based biradicals affects their biradical character and thus, their tendency to act as useful motifs for DCC (see Figure 1).

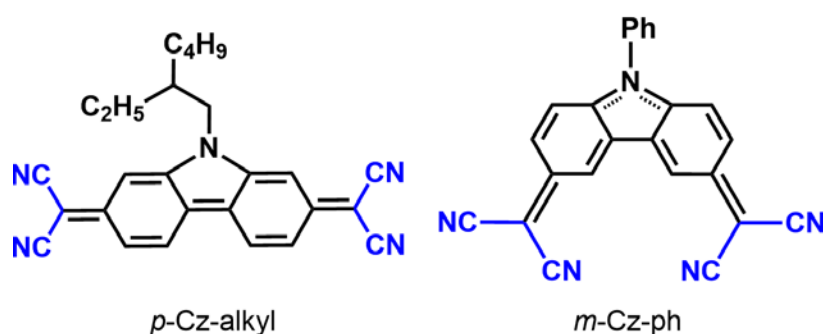


Figure 1. Carbazole-based biradical systems under study.

### References

- [1] M. Abe, Chem. Rev. 2013, 113, 7011 – 7088.
- [2] O. Kohei, H. Shota, I. Yuki, S. Daisuke, S. Shu, Ang. Chem. Int. Ed. 2017, 56, 16597-16601.
- [3] D. Wang, C. C. Ferrón, J. Li, S. G. Valenzuela, R. P. Ortiz, J. T. L. Navarrete, V. H. Jolin, X. Yang, M. P. Álvarez, V. G. Baonza, F. Hartl, M. C. R. Delgado, H. Li, Chem. Eur. J. 2017, 23, 13776 – 13783.