Diradicals and their Driving Forces

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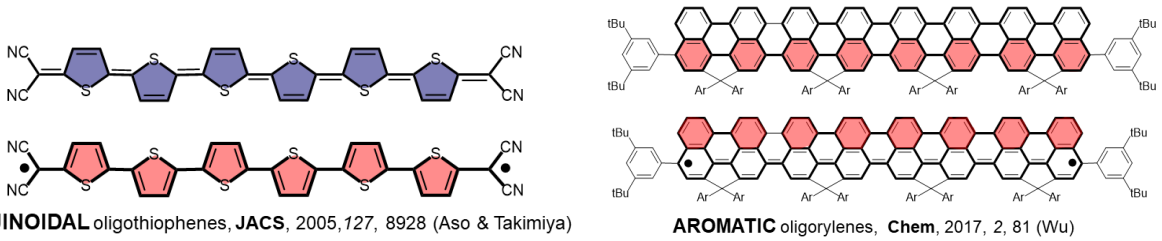
Several series of aromatic and quinoidal compounds, such as oligothiophenes (Scheme 1), oligophenylene-vinylenes, oligoperylenes (oligophenyls) and graphene nanoribbon derivatives, are studied in the common context of the capability to stabilize diradical structures. [1,2,3,4]. In this work, we try to clarify how several driving forces (i.e., thermodynamic and entropic) are responsible for the generation of diradical and diradicaloid structures.



QUINOIDAL oligothiophenes, **JACS**, 2005, *127*, 8928 (Aso & Takimiya)

AROMATIC oligorylenes, **Chem**, 2017, *2*, 81 (Wu)

Scheme 1. Left: Quinoidal oligothiophenes and their conversion into aromatic diradicals. Right: Aromatic oligorylenes and their conversion into non-aromatic diradicals.

A combination of different types of molecular spectroscopies (i.e., electronic absorption, electronic emission, excited state absorption, vibrational Raman, vibrational infrared, etc.) as well as hybridized with thermal and pressure-dependent techniques are shown to provide important information about the origin of the formation and stabilization of diradicals. From a conceptual point of view, we analyze these properties in the context of the oligomer approach which is the study of the evolution of these spectroscopic quantities as a function of the oligomer size.

References

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[2] J. Casado, R. Ponce Ortiz, J. T. Lopez Navarrete, *Chem. Soc. Rev.* **2012**, *41*, 5672.
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[4] J. Casado, *Para-quinodimethanes: A unified review of the quinoidal-versus-aromatic competition and its implications*. *Top. Curr. Chem.* **2017**, 375, 73.