

Molecular Diradicals

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Diradicals are defined as molecules with two unpaired electrons which define distinctive manifolds of singlet and triplet states. Diradicals have been recently shown to be fruitful candidates for applications such as enhanced non-linear optical chromophores, sensitizers for singlet exciton fission in photovoltaics, or electrically ambipolar substrates in organic field effect transistors, etc. [1]. Quinoidal-based oligothiophenes produced by double dicyanomethylene substitution through the 1,4 positions of the thiophenes have been demonstrated to be diradical precursors [2]. Solid-state structure and supramolecular interactions are key ingredient to have enhanced properties in the substrates for organic electronics. Quinoidal compounds display typical p-p stacking aggregation and, as such, are able to form p-dimers and s-dimers depending on the degree of diradical character [3]. Another intrinsic molecular property of quinoidal molecules is their inherent tendency for reductive redox processes given the stabilization by aromatization upon acceptance of electrons. [4].

In this contribution, we describe an example of tetracyano substituted oligothiophenes with the central thiophenes substituted at the beta positions of the central units with pyrrolo diones groups, from a dimer to a pentamer. In this series of quinoidal oligomers, a transition from closed-shell to open-shell (diradical) structures is described, accompanied in parallel with a change in the mode of supramolecular aggregation from herringbone π - π stacking to cholesteric-type in the neutral state allowing the maximization of the electrical conductivity, an unprecedented stability upon *n*-type doping and excellent thermoelectric performance.

References

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4. Casado, J.; et al. *J. Am. Chem. Soc.* **2002**, *124*, 12380.