Diradical-mediated weak intermolecular sigma bond formation. Influence of the quinoidal-to-aromatic interplay on the reversible and giant chromism of a novel thienoquinoidal derivative.

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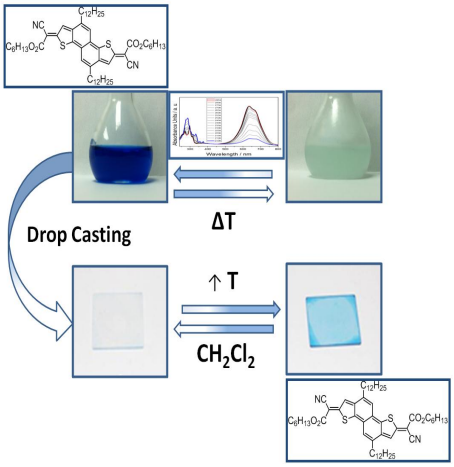

Fig 1. Reversible chromism of sample 1

Pro-aromatic molecular systems are well known as promising materials for applications in Organic Electronics due to their outstanding electronic, molecular and magnetic properties. One approach to obtain this kind of systems is by incorporating dicyanomethylene acceptor units at both ends of the molecules. Well known examples of these are series of quinoidal oligothiophenes to the hexamer [1], tetracyano-oligo(*N*-annulated perylene)quinodimethanes with the longest molecule having 12 *para*-linked benzenoid rings[2] and Tetracyano-(quater and hexarylene)quinodimethane derivatives [3]. All these systems display open shell ground electronic states achieved, among other effects, thanks to the proaromaticity of the core that leads to an additional stabilization of the structure with two electrons unpaired, each at both exomethylene groups, giving rise to open shell diradical-like species

Another interesting example of diradical-like molecules are stable benzoquinoid hydrocarbons with singlet open-shell ground states thermodynamically stabilized by exploiting the spin delocalizing character of the phenalenyl radical [4]. Interestingly, these molecules constitute one of the very first examples of the formation of stair-chain oligomeric and polymeric aggregates by co-facial coupling between the radicaloid center.

With this communication we present a novel thienoquinoidal molecule consisting of π-extended quinoidal naphtodithiophene core and ((alkoxy)carbonyl) cyanomethylene termini that presents giant and reversible chromism depending on the states: going from a deep blue color in solution to a colorless spin coated thin film. By means of different spectroscopic techniques, like VT-NMR, VT-Uv-Vis aborption or ICP–MS, supported by DFT calculations, we aim to explore the role of the quinoidal-to-aromatic interplay in the outstanding chromism observed, in the context of the possibility of a kinetically trapped intermolecular sigma bond formation mediated by a biradicaloid intermediate that is generated due to core aromatization of each original molecular entity.

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