

## Résumé en anglais

In this work, two new triarylamine-based hexaazaparacyclophane (HAPC) macrocycles were synthesized with three peripheral hydrogen-bonding amide groups having different relative arrangements. Weak interactions allow the obtained molecules to form one-dimensional columnar stacks, and the supramolecular polymerization mechanism of this process was investigated for the first time in HAPCs research with spectroscopy, microscopy, and DFT-calculations. It was found that amide substituents in positions 1,2,3 on the periphery of hexagonal macrocycles promote isodesmic mechanism and the formation of short rigid fibers, while the molecules with substituents in positions 1,3,5 form long flexible fibers in cooperative polymerization mechanism. The presence of six nitrogen atoms conjugated through phenyl rings implies multi-redox activity and potentially rich optoelectronic properties. The oxidation of self-assembled fibers showed delocalization of the generated polarons in the macrocyclic plane and along the supramolecular stacks, similar to the previously reported results. For the macrocycle with consecutive substitution, the data indicates a greater in-plane polaron delocalization at lower oxidation states, in comparison to the macrocycle with alternating and fully substituted peripheries. Such oxidized supramolecular fibers might serve as valuable materials with a high spin density in the domain of organic electronics.

Keywords: supramolecular chemistry, hydrogen bonds, self-assembly, supramolecular polymerization, oxidation, polaron delocalization, triarylamines, macrocycles, cross-coupling, DFT-calculations.