



Invited Speaker

Triarylamine-based Supramolecular Polymers: Structures, Dynamics, and Functions

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Abstract:

Triarylamine molecules and triarylamine-based covalent polymers have been extensively investigated for more than sixty years in academics and industry because of their intriguing electronic and optical characteristics. However, despite the profusion of studies made on these derivatives, only very recently have the first examples of supramolecular polymers based on the triarylamine motif been described in the literature. Specifically, our research group has shown that, by adding supplementary hydrogen bonding moieties such as amide functions in their periphery, it becomes possible to tightly pack triarylamine molecules in columnar supramolecular stacks presenting a collinear arrangement of their central nitrogen atoms. These supramolecular polymers can self-assemble into various soft hierarchical structures such as helical fibers, nanorods, nanospheres, and nanoribbons in the sol and in the gel states, into liquid-crystalline mesophases, as well as into highly organized supramolecular frameworks and their single crystals thereof. Interestingly, the associated supramolecular polymerization mechanism involves a nucleation step of high activation energy which requires the flattening of the triarylamine core. Because of this singularity, and although dependent on the precise chemical nature of the building blocks, it has been demonstrated that their supramolecular polymerization can be triggered by original tools such as light irradiation or electrochemistry, and that it can display autocatalytic growth behaviors, remarkably strong amplifications of chirality, as well as complex and competing thermodynamic and kinetic self-assembly pathways. Further, from a functional point of view, it has been highlighted that a partial oxidation of the triarylamine molecules results in an enhanced through-space delocalization of the charge carriers along the π - π stacked supramolecular polymers, a feature that confers to these nanowires exceptional transport properties. Upon increasing the charge carrier concentration, the electronic nature of these soft materials can be switched from a semiconducting to a metallic behavior, and the presence of highly delocalized unpaired electrons in supramolecular polaronic band structures has been further exploited to implement plasmonic properties within subwavelength organic interconnects and microscopic optical waveguides. Finally, by making use of the unusual dynamics and functions of triarylamine-based nanostructures, it becomes possible to precisely address their self-construction within confined environments or within nano- and micrometer scale devices. This has been demonstrated for instance in between nanoparticles and in between electrodes, inside inorganic nanopores and inside phospholipid bilayers, as well as at the liquid-liquid interface. Such a meeting point between bottom-up and top-down technologies is of high interest to envision further developments and applications for this entirely new class of supramolecular polymers which combine a unique relationship between their structures, their dynamics, and their subsequent emerging functional properties.

Reference:

Moulin, E.; Armao IV, J.; Giuseppone, N. *Acc. Chem. Res.* **2019**, *52*, 975-983.