

Organic compounds are generally insulators because all electrons in molecules are paired, so no free electrons exist to conduct the electricity (radicals, the species with unpaired electrons are, as a rule, unstable for using them as materials). Since 1970s, specific classes of organic compounds (small molecules or their complexes, and then π -conjugated polymers) have been discovered and studied to “overcome the fundamental historical rule” and to demonstrate that organic compounds can be semiconductors or even show metallic type of conductivity. This opened a door for a new technological era of “organic electronics”. Following several decades of intense academic research, organic semiconductors have begun to impact on commercial sector (light-emitting devices (OLEDs), field-effect transistors (OFETs), organic solar cells (OSC), lasers, electro- and photochromics, batteries and supercapacitors, memory, switches and logic devices, sensors and biosensors, nanotechnologies, etc.). Many hi-tech devices based on organic electronic materials are now around us as consumer products (OLED TV, displays in mobiles and laptops, touch screens, disposable sensors, etc).

Such materials commonly possess an expanded system of π -electron orbitals, which form a cloud of delocalized electron density over the molecule bringing specific electronic and optical properties. Many different classes of aromatic/heteroaromatic molecules with different molecular symmetry, shape, size, ability to donate or accept electrons (from/to) their π -system have been used as building blocks to design organic electronic materials. This allows not only control (or tune) the processes of charge and/or electron transfer in such systems (and consequently their properties toward certain electronic applications), but also to construct materials of different dimensionality (1D, 2D, 3D). The great interest and challenge here lie in how to expand the conjugation in such systems from 1D (as in “classical” conjugated polymers) to star-shaped architectures and to 2D (as in graphene).

Azatriangulenes, a class of C_3 -symmetry molecules with central nitrogen atom bonded to 3 benzene rings that are bridged to each other by C or O atoms to form planar structure, represent fascinating cores to construct a wide range of star-shaped conjugated architectures and number of π -functional materials have been developed on their basis.

The main aim of this project is to elaborate synthetic methodologies to design azatriangulenes with $-\text{SO}_2-$, $-\text{S}-$ and $-\text{NH}-$ / $-\text{NR}-$ bridges (not easy but very challenging task). When the success in such synthesis is achieved, a wide range of functionalized materials based on these novel azatriangulene cores can (and will) be developed. The key idea behind the proposed design is that by changing the nature of the bridges from strongly electron-withdrawing groups (SO_2) to strongly electron-donating groups (NR) we can tune the frontier orbital energies in azatriangulene cores in extremely wide range. Another important feature is a wide palette of possible further functionalization (at C atoms of benzene rings or at nitrogen bridges) to construct star-shaped π -functional materials on their basis (from small molecular systems to covalent organic frameworks / 2D conjugated polymers), to bring the desired electronic properties for various electronic applications. Thus, we plan to construct hole transporting materials based on azatriangulenes with $-\text{NR}-$ bridges, and charge-transfer materials based on both $-\text{SO}_2-$ and $-\text{NR}-$ bridged azatriangulenes. Particularly, we predict an existence multiresonance intramolecular charge transfer in functionalized ATA-3 SO_2 compounds and expect to obtain (based on them) efficient materials with thermally activated delayed fluorescence (TADF) for OLED applications. Last but not least, we plan to perform broad photophysical, electrochemical and structural investigations of synthesized molecules for deep insight in their electronic structures and π -functionality to expand our academic knowledge on this fascinating class of molecules.