TOWARDS AN UNDERSTANDING OF THE REORIENTATION DYNAMICS OF RIGID AND NON-RIGID SIZABLE ANISOTROPIC MOLECULES CONSTITUTING A NEW CLASS OF GLASS-FORMING MATERIALS WITH PECULIAR RELAXATION PROPERTIES REVEALED IN DIELECTRIC RELAXATION STUDIES

The observed increase in the structural complexity of newly synthesized chemical compounds translates into their ability to generate more and more complex molecular motions. This is a consequence of striving to produce new materials with the desired characteristics for increasingly demanding applications. As an example materials for organic light-emitting diodes (OLEDs) can be given which become a popular light source being used in many everyday electronic devices. This technology is used in flexible displays, TV sets, etc. Biologists and physicists teach us that basic life processes (such as metabolism) are sustained by the generation of molecular motions by objects called biomolecular machines. Inspired by nature in its quest to create increasingly complex objects, chemists have long been interested in the design and synthesis of artificial molecular systems capable of precise mechanical operation and energy transfer. The common feature of these systems is the secret of their structural and dynamic complexity, hidden in objects of considerable size and directional properties. The molecular cores of such systems are a collection of rigid heterocyclic moieties connected in a way that ensures the optimal path for electron transport. Considering such systems from the point of view of their dynamics raises many fundamental questions about the influence of anisotropy and large size (significant moment of inertia) on their motion. To explore this issue, we need extraordinary tools and pioneering solutions. Therefore, **we proposed a new concept of sizable molecules** with the glass-forming ability. Our idea concerns systems that are a set of many rigid and semi-rigid heterocyclic groups functionalized with flexible chains and a small polar group, which have properties suitable for many attractive applications (e.g. in optoelectronics), but at the same time allow us to refer to the above-mentioned fundamentally important issues.

The main goal of the project is to investigate how factors such as size, shape anisotropy, structural complexity, orientation, and dipole moment value influence the reorientation dynamics of large glass-forming molecules studied with broadband dielectric spectroscopy (BDS). During dielectric measurements, dipole fluctuations triggered by the electric field allow the study of molecular motions on many scales, from internal side group rotations to the reorientation of whole molecules. The only necessary condition is the presence of a polar group in the material. Therefore, in the project, we intend to modify the non-polar backbone of large molecules by attaching a small polar group at different places. Such systematic modifications will lead to the creation of a virtual library of sizable molecules, differently "labeled" with a dipole. Using this original approach, we will obtain a tool that allows us to address previously unexplored issues related to the reorientation of large and anisotropic molecules with significant moments of inertia and we will explain to what extent the properties of the probe sampling their motion, i.e. the dipole (its position, size, and direction) affect the picture of reorientation dynamics of sizable molecules studied by broadband dielectric spectroscopy. The results of the planned research will have a significant impact on understanding the nature of many fundamental issues related to the supercooled state. These cognitive breakthroughs will be discussed in the context of the newly constituted class of glass-forming materials. Sizable molecules cannot be simply regarded as entities containing a large number of atoms (molar masses *approx*. 600 g/mol, number of atoms > 80) that will bridge the gap between low-molecular-weight glasses and polymers. The most important circumstance justifying their separate classification is a peculiar dielectric behavior different from that observed so far for other glass-forming materials. One of such features is the tremendous sensitivity of dynamics to compression. Our preliminary results showed that sizable molecules are unique in this context and could represent a breakthrough in the study of free volume models as a new class of materials with dynamics mainly driven by density fluctuations.

Another pioneering result of the project will be the direction of dielectric research into new application areas related to the study of the reorientation of molecule fragments "labeled" with dipoles. This is unattainable for small molecules with a dipole moment reflecting the motion of the entire system. The complex molecular dynamics of several moving parts within one molecule make the proposed sizable systems a platform of materials that is an intriguing starting point for the dielectric research of these complex objects mentioned above. This could be an important step that will facilitate the understanding of the movements of complex molecular and biomolecular systems in the future and open up new possibilities for studying them using the dielectric method.