ABSTRACT

In an era of intensive industrial progress, urban sprawl, agriculture, energy shortages and environmental problems are intensifying worldwide. Due to unrestricted exploitation and consumption over the past few decades, the world's primary energy source, fossil fuels, is rapidly depleting. Therefore, it is crucial to create modern devices which are highly energy-efficient and renewable. To meet the challenges of today's world, synthetic chemists are constantly working on ever-increasingly new chemical compounds exhibiting desirable properties (e.g., in relation to new energy sources). In this context, a significant group of compounds are perylene derivatives, perylenediimide in particular, whose applications are virtually limitless (solar cells, light-emitting diodes, biosensors). Perylene exhibits exciting physicochemical properties, but the products obtained through the expansion of its aromatic structure have great potential as materials used in organic electronics and photovoltaics.

One of the strategies to expand the perylene system is APEX, which is annulative π-extension. The ideal tool for this strategy is one of the fundamental reactions in organic chemistry, namely the Diels-Alder cycloaddition reaction. This thesis is devoted to the synthesis of new, functionalised molecular nanographenes (FMNs) based on the perylene structure via Diels-Alder cycloaddition (DAC) reactions and a virtually unknown version of this strategy, the domino cycloaddition-cycloisomerization (DAC-CI) reaction.

As part of this dissertation, I synthesised cis-DBPDI (cis-dibenzoperlenediimide) – a perylene derivative – using chemical and electrochemical methods (both patented). Next, by DAC reactions of disubstituted acetylenes into the cis-DBPDI bay region, I obtained a series of pi-expanded derivatives of the initial structure, belonging to FMNs. It is worth noting that such perylene derivatives are unknown in the literature, namely the DAC chemistry of cis-DBPDI is not known at all. I also obtained pi-expanded cis-DBPDI derivatives via a domino DAC-CI reaction involving 1.4-diaryl-substituted buta-1.3-diynes. All the obtained FMNs were subjected to physicochemical studies: optical, thermal, and electrochemical.

Furthermore, theoretical calculations using DFT allowed the analyse the structure-property relationship of the newly synthesised FMNs in depth. The properties of the synthesised FMNs will enable us to predict their use as nanomaterials for the fabrication of devices such as OLEDs and solar cells. Most importantly, the dissertation provided new knowledge on the APEX strategy, DAC, and DAC-CI reactions for the bay region of perylenediimides and their derivatives. Some cycloadducts did not undergo spontaneous thermal dehydrogenation, which is an extraordinary finding for DAC to the bay region of PAHs (Polyaromatic Hydrocarbons). Patents have been filed for the structures and syntheses of the new FMNs.