Proceedings of the 9th World Congress on Recent Advances in Nanotechnology (RAN 2024)
London, United Kingdom –April 8 – 10, 2024
Paper No. ICNNFC 147
DOI: 10.11159/icnnfc24.147

New Molecular Nanographenes for Modern Technologies: (Electro) Chemical Synthesis and Properties Characterization

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Extended Abstract

Nanographenes play a very important role in the modern world of electronic devices. This is due to its unique thermal, emission and electrochemical properties[1]. Graphene itself has been known and used for some time – because of its unique advantage of high mobility at room temperature. On the other hand, it has a zero energy gap between the valence band and the bandgap, which prevents its use in the electronic context[2]. Functionalized molecular nanographenes can help solve this problem.

From the point of view of organic chemistry, molecular nanographene can be any polycyclic aromatic hydrocarbon (PAH). This applies not only to PAHs that consist only of carbon atoms, but also to those whose skeleton also contains heteroatoms. There are two methods of nanographene synthesis: bottom-down and bottom-up. The first one involves obtaining smaller fragments from larger ones through their selective destruction (molecular cutting)[3]. However, this method has several drawbacks, including the inability to control the size and composition of the obtained structures. The bottom-up method involves expanding smaller structures (in a controlled manner) until the expected polyaromatic systems are obtained[4]. The synthetic tool used to expand the pi-electron structure is Diels-Alder cycloaddition, especially cycloaddition in the perylenebisimide bay region[5]. The most crucial element is selecting the appropriate starting structure - the research focused on PAHs, whose skeleton is based on a perylene core.

The research began with synthesising a nanographene precursor, i.e. cis-dibenzoperylenebisimide (cis-DBPDI), through dimerisation of the starting anthracene substrate using classical chemical synthesis and electrochemistry. Then, cis-DBPDI was subjected to further functionalisation, i.e. pi-expansion using the APEX strategy, via cycloaddition and tandem cycloaddition-cycloisomerisation of acetylenes and butadiynes into its bay region. Several pi-extended derivatives were obtained, for which the following were performed: DFT calculations of frontier orbitals, NMR, HRMS and physicochemical measurements: UV-Vis spectroscopy, photoluminescence and electrochemistry. Structural studies allowed us to observe the lack of aromatisation of the obtained cycloadducts. On the other hand, other studies allowed us to confirm the expansion of the pi-electron structure and observe the unique properties represented by each structure.

References

[1] Y. Gu, Z. Qiu, K. Müllen, "Nanographenes and graphene nanoribbons as multitalents of present and future materials science", *J. Am. Chem. Soc.*, 26, 2022, 11499-11524.
[2] A. Narita, X. Y. Wang, X. Feng, K. Müllen, "New advances in nanographene chemistry", *Chem. Soc. Rev,* 18, 2015, 6616-6643.
[3] Z. Liu, S. Fu, X. Liu, A. Narita, P. Samorì, M. Bonn, H. I. Wang, "Small Size, Big Impact: Recent Progress in Bottom-Up Synthesized Nanographenes for Optoelectronic and Energy Applications", *Adv. Sci.*, 19, 2022, 2106055.
[4] L. Shi, B. Wang, S. Lu, "Efficient bottom-up synthesis of graphene quantum dots at an atomically precise level", *Matter*, 2023.
[5] A. Kurpanik, M. Matussek, G. Szafraniec-Gorol, M. Filapek, P. Lodowski, B. Marcol-Szumilas, S. Krompiec APEX Strategy Represented by Diels–Alder Cycloadditions—New Opportunities for the Syntheses of Functionalised PAHs. *Chem. Eur. J.*, 53, 2020, 12150-12157