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# THE SERIES OF 4 INVENTIONS CONCERNING OBTAINING NEW NANOMATERIALS FOR RENEWABLE ENERGY SOURCES

## P. 439060, P. 439061, P. 442236, P. 442237

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### INNOVATION

The subject of the invention are innovative solutions dedicated to renewable energy sources, in particular technologies in the field of organic electronics and photovoltaics

### **APEX STRATEGY FOR PERYLENE AND BISANTHENE PI-EXPANSION**

Diels-Alder cycloaddition into perylene and its derivatives bay region belongs to singlestep annulative pi-extension (APEX) reactions and represents the maximum in synthetic efficiency for the constructions of pi-extended polycyclic aromatic hydrocarbons (PAHs), including functionalised ones, nanographenes, and pi-extended fused heteroarenes. This innovative strategy was used to obtain the nanomaterials described in inventions 3 and 4. The product obtained according to the invention no. 3, which is a derivative of 7,14-di(mesityl)bisanthene, was prepared from the above-mentioned precursor – it has interesting luminescent properties and is already a small nanographene. Whereas, the product of invention no. 4 is a precursor for the synthesis of a whole range of nanomaterials, including monomers for the production of concductive polymers. What is important, both nanomaterials can be target materials themselves, but they can also easily undergo further modifications, especially pi-expansion of the perylene moiety. This is especially innovative in terms of importance of perylene, bisanthene and their derivatives for modern technology: solar cells, OLEDs, OFETs.

(OLEDs, solar cells, OFETs, and others). The presented inventions concern obtaining new electroactive nanomaterials (nanographenes), whose structure is based on a pervlene core. Perylene and bisanthene moieties are the leading motifs in materials dedicated to sustainable technologies, because these moieties largely affect the properties of the final nanomaterial. The innovation concerns both structures and synthesis methods. The latest synthetic strategies, especially APEX and bottom-up, were used in the synthesis of the materials according to the inventions. The obtained nanomaterials are soluble in organic liquid and thermally stable up to over 200°C, and therefore meet the initial requirements for materials dedicated to organic electronics and photovoltaics.

#### **BUILDING BLOCKS**

The product of the first two inventions is a precursor for the synthesis of various perylene derivatives – a leading structure for dye technology and, above all, organic electronics. Currently, there are no such 'bricks' on the market to produce complex target structures, so the invention will certainly be of interest to scientists dealing with the synthesis of new nanomaterials. For example, the inventive precursor is described in the literature as a starting material for the synthesis of 7,14-di(mesityl)bisanthene. However, when it comes to the knows methods of synthesizing 10,10'-di(mesityl)-9,9'-bisanthracene, it is a complicated and inefficient way leading to the expected product [A. Konishi, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, Facile Synthesis and Lateral  $\pi$ -Expansion of Bisanthenes, Chem. Lett., 2013, 42(6), 592-594]. The aim of the inventors of the presented invention was to develop a two-step, efficient method for obtaining 10,10'-di(mesityl)-9,9'-bisanthracene from commercially available 10,10'-dibromo-9,9'bisanthracene and mesitylboronic acid.



Fig. 3. Synthetic path for perylene and bisanthene derivatives

### **APPLICATION**

Attractiveness of perylene, benzo[ghi]perylene, coronene, naphto[1,2,3,4-ghi]perylene, bisanthene and others polycyclic aromatic hydrocarbons (PAHs) equipped with various functional groups are almost unlimited for both academic science and many modern technologies. We believe, that our innovations will extend the opportunities of PAHs (especially perylene and bisanthene) applications in above mentioned technologies, especially in organic electronics.



*Fig. 1.* Former synthetic path: 5 steps, overall yield < 10%



Fig. 4. The presence of Bromine atoms importance: further functionalization of aromatic scaffold became almost unlimited



Fig. 2. Innovative synthetic path: 2 steps, overall yield 30%

The invention includes developed and proven methods for obtaining nanomaterials on a laboratory scale. The recipient and, at the same time, a potential producer of nanomaterials will be Syntal-Chemicals from Gliwice. The inventions are the result of cooperation with Syntal-Chemicals as a part of two NCN grants (OPUS 17 'From perylene to functionalized nanagraphenes with expected properties' and OPUS 18 'APEX strategy for the synthesis of functionalized nanographenes from 1,4-diaryl-1,3-butadiynes, perylene and its derivatives: new Diels-Alder cycloaddition-cycloisomerization domino type reactions') oraz programme Innovation Incubator 4.0 (these were pre-implementation works).









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