

Domino Dehydrative π -Extension: A Facile Path to Extended Perylenes and Terrylenes

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Abstract: Herein, we report a new method for synthesis of extended perylenes and terrylenes. The technique is based on the cascade dehydrative π -extensions (DPEX) of aryl aldehydes, in which stepwise annulations activate previously “dormant” substituents. Two- and fourfold cyclizations of 3-aryl-biphenyl-2,2'-dicarbaldehydes offer a rapid path to unsymmetrical perylenes and elusive terrylene derivatives, respectively. DPEX of 3,3''-(phenanthrene-1,8-diyl)bis (([1,1'-biphenyl]-2,2'-dicarbaldehyde)) leads to the biradical structure, which proceeds in situ into oxidative electrocyclization at room temperature. The described domino process complements and expands DPEX approach to a large family of fused acenes and related PAHs.

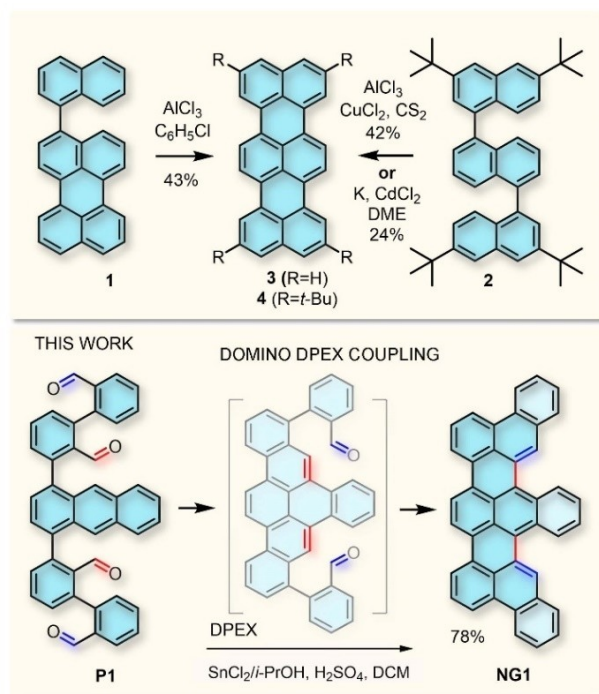
Nanographenes (NGs) or extended polycyclic aromatic hydrocarbons have received well-deserved emphasis thanks to their outstanding optical and physical properties.^[1–3] The possibility of controlling the properties of NGs by adjusting their shape, width and edge topologies is the key feature enabling the flexible design of new carbon-based materials. Thus, NGs are constantly reported to have superior properties in the fields of photovoltaics,^[4–6] OLEDs,^[7–9] OFETs,^[10,11] liquid crystals,^[12] single-molecule spectroscopy,^[13] etc. To attain atomically precise control over the structure of NGs, organic chemists actively develop and exploit different bottom-up strategies based on C–C coupling techniques such as the Scholl reaction,^[14,15] APEX,^[16,17] alkyne benzannulations,^[18–20] aryne trimerizations,^[21] cross-coupling reactions,^[22–25] Diels–Alder cycloadditions,^[26] etc.

Domino folding of the respective precursors into NGs is an attractive pathway to reduce the overall complexity of its

synthesis. Directed formation of multiple C–C bonds in one step helps to avoid purification of intermediates and solubility issues of the target NGs. However, only a few C–C coupling techniques are suitable for the synthesis of NGs in a domino fashion. Among them are examples of the Scholl reaction,^[27–29] alkyne benzannulations described by Alabugin,^[30–35] and Chalifoux,^[36] and the HF-zipping approach described by Amsharov et al.^[37–39]

Rylene diimides belong to the most utilized structures in material chemistry.^[40–45] Meanwhile, their parent hydrocarbons are less represented in the literature, apparently, due to the lack of synthetic methods. To the best of our knowledge, there are only two reported methods for synthesis of terrylene, that is, Scholl reaction of 1-naphthylperylene (1)^[46] and anionic cyclo-dehydrogenation of trisnaphthalene 2^[47,48] (Scheme 1). Synthesis of extended analogs of perylene and terrylene are even scarcer^[49] and are mentioned almost exclusively by Clar.^[50]

Herein, we describe a new domino approach towards extended perylenes and terrylenes based on the recently developed DPEX reaction.^[51,52]



Scheme 1. Reported synthesis of terrylene (top) and the synthesis of tribenzo terrylene NG1 (bottom) demonstrating the efficiency of the domino DPEX approach.

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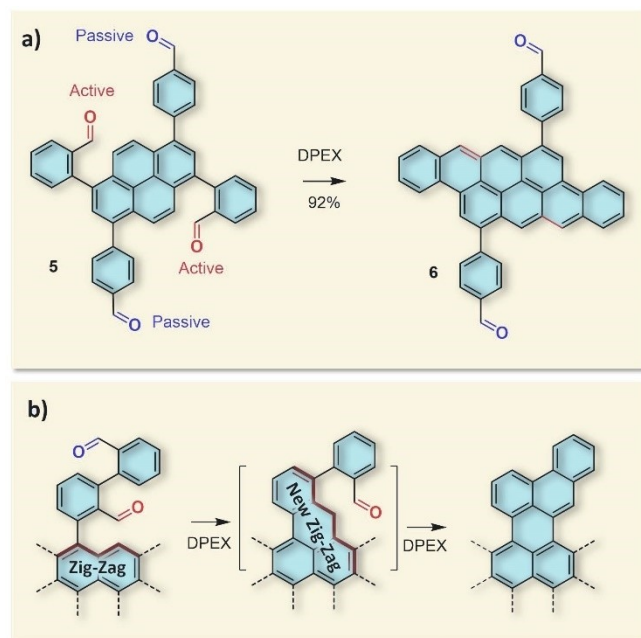
Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202103098>

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Our approach exploits aldehydes as key functional groups, the positions of which unambiguously dictate the path of the domino reaction. This technique is based on an important prerequisite characteristic of DPEX, namely, regioselective activation of aldehyde groups. Thus, DPEX leaves aldehyde substituents intact if the intramolecular cyclization with closure to the six-membered ring is impossible (transformation from **5** to **6**).^[52] In other words, aldehyde can be activated for the cyclization if it placed close to the zigzag region (L-region), as depicted in Scheme 2a. It is worth mentioning that DPEX enables the synthesis of NGs with newly constructed zigzag regions. We were excited to realize that this unique combination could provide the possibility to carry out the extension process in a truly domino fashion. We, therefore, envisioned that the “dormant” aldehyde groups can be activated by the new zigzag region that appears during the reactions as is shown schematically in Scheme 2b.

To demonstrate this possibility we choose biphenyl-2,2'-dicarboxaldehyde block which attachment to the PAH with zigzag periphery (Scheme 2b) will meet the requirements (i.e., presence of active and “dormant” aldehydes, whereas the latter will be activated after the first cyclization).

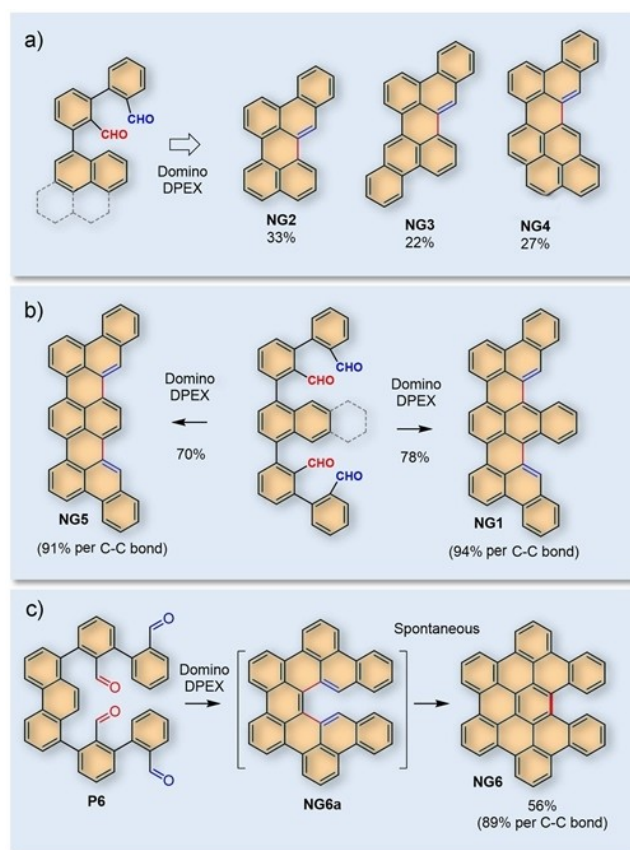
To test our suggestion, we have prepared several aryl aldehydes containing 3-[1,1'-biphenyl]-2,2'-dicarbaldehyde moiety (Scheme 2b). The precursors **P2–P4** have been synthesized in a modular approach by using 3-bromo-[1,1'-biphenyl]-2,2'-dicarbaldehyde (**6**) or 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-2,2'-dicarbaldehyde (**7**) as building blocks which were attached to different PAHs cores by Suzuki coupling. It was found that upon exposure to the DPEX condition, **P2–P4** can be transformed into the target extended



Scheme 2. a) Synthesis of fused acene demonstrating tolerance towards “misplaced” formyl groups under DPEX conditions. b) Description of Domino DPEX.

perylene **NG2–NG4** in only moderate 22–33% yields. We were surprised to observe that in sharp contrast to these examples of twofold cyclization, a fourfold cyclization of 1,4-disubstituted naphthalene **P5** and anthracene **P1** results in symmetric extended terrylene in substantially higher yields. Thus, the yield of dibenzoterrylene **NG5** was found to be 70% which corresponds to 91% per each C–C coupling (Scheme 3b). Although **NG5** was found to be rather unstable in solution, we were able to perform immediate HPLC analysis which has demonstrated high purity of the target compound. Unfortunately, low solubility prevented the registration of NMR spectra at room temperature, whereas a rapid degradation disabled NMR measurements at elevated temperatures. In contrast, tribenzoterrylene **NG1** was found to be stable presumably due to the presence of two cove regions, which also remarkably improved solubility of **NG1** allowing NMR spectra to be recorded at room temperature. Worth mentioning that the NMR signals were slightly broadened which is presumably connected to the significant biradical character of **NG1**.

Furthermore, to demonstrate the efficiency of the domino-DPEX approach we decide to generate **NG6a** with a high biradical character. Due to pronounced biradical character, this compound is expected to undergo further cyclization into **NG6** in a spontaneous 6π -electrocyclization.^[53] Our experiment

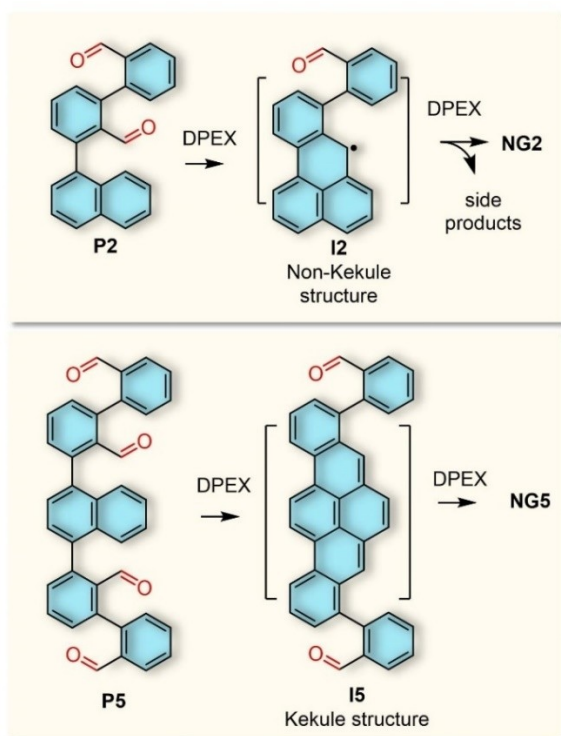


Scheme 3. Synthesis of extended perylene and terrylene by a) twofold, and b) fourfold cyclization. c) Synthesis of **NG6** in a fivefold domino-DPEX accompanied by spontaneous electrocyclization. Conditions of domino-DPEX: SnCl_2 , $i\text{PrOH}$, H_2SO_4 , CH_2Cl_2 .

demonstrated that doubly substituted phenanthrene **P6** indeed undergoes smooth domino transformation directly into **NG6** with 56% yield (Scheme 3c). Since the domino transformation, in this case, is extended to the formation of five new C–C bonds the efficiency of every single coupling can be estimated to be close to 90%.

These observations give certain insights into the plausible mechanism of the transformation.

Firstly, we were puzzled by the drastically different yields of **NG2–NG4** and **NG1**, **NG5**. The appearance of the intermediates **I2** and **I5** might account for these seemingly contradicting results (Scheme 4). In the case of **NG2**, the domino process includes the formation of benzophenalenyl radical **I2**, which due to its high reactivity leads to the set of difficult to characterize oxygen-containing by-products. On the other hand, **NG5** has an opportunity to circumvent the formation of non-Kekule structures by concerted annulation on both sides that leads to stable Kekule PAH **I5**. Considering good yields of the transformation, we conclude that the first two annulation steps take place quickly one after another, which also accounts for the excellent yields observed in previous studies.^[51–53] It is important to note that the respective domino-DPEX reaction of biphenyl-2,2'-dicarbaldehyde with zigzag periphery can be described as a formal analog of [3+3] *peri*-annulation of phenanthrene.^[22] However, we have ruled out the formation of the phenanthrene moiety as only starting material was recovered upon exposure of [1,1'-biphenyl]-2,2'-dicarbaldehyde to DPEX conditions (see the Supporting Information).



Scheme 4. Comparison of two- and fourfold Domino-DPEX explaining the low yield in the case of twofold cyclisation as a result of the formation of highly reactive intermediates.

The orbitals of the obtained NGs show the same spatial structure associated with the perylene moiety (Figures S40–S44 in the Supporting Information). The electronic structural data obtained from DFT calculations and UV/vis measurements are summarized in Table 1. The pattern of the UV spectra was found to be similar for all compounds (Figure 1). However, the typical acene-like vibronic feature with three distinct bands shifts towards infrared regions, while absorption maximum reaches 640 nm in the case of **NG1**. Such big shift of the absorption maxima results in significant biradical character, which theoretical value for **NG1** (0.45) was obtained from the broken symmetry calculation at the UHF/6-31+G(d,p) level of theory.

In summary, we have presented a conceptually novel example of the domino reaction in which identical moieties, that is, aldehyde substituents, enter the transformation in a stepwise manner. The unique ability of DPEX to form pristine zigzag regions serves as a key to the success of the transformation. Coupling of 3-bromo-[1,1'-biphenyl]-2,2'-dicarbaldehyde building block with L-region-containing PAH cores allows precursors suitable for the two- and fourfold domino cyclizations to be designed. The outcome of the domino process is the elusive extended perylenes and terrylenees with a range of absorption maxima of 450–650 nm. Moreover, we have demonstrated that the cascade transformation can be rationally accompanied by electrocyclization, thus allowing the highly effective formation of five C–C bonds in one synthetic step.

Compound	DFT HOMO-LUMO gap [eV]	Optical gap [eV]
NG1	1.98	1.92
NG2	3.05	2.83
NG3	3.10	2.87
NG4	2.74	2.61
NG5	2.29	2.20

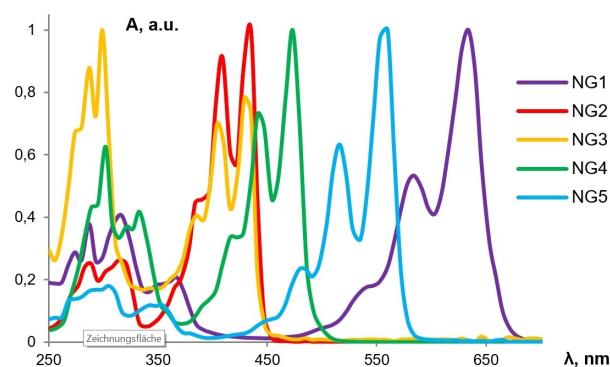


Figure 1. UV/vis spectra of **NG1–NG5**. The spectra were recorded in CH_2Cl_2 .

Acknowledgements

Funded by the Deutsche Forschungsgemeinschaft (DFG)—Projektnummer 182849149—SFB 953, AM407. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: domino reactions · perylenes · pi-extension · polycyclic aromatic compounds · terrylenes

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Manuscript received: August 31, 2021

Accepted manuscript online: September 23, 2021

Version of record online: November 10, 2021