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APEX strategy represented by Diels-Alder cycloadditions – new opportunities for the syntheses of functionalised PAHs

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Abstract: Diels-Alder cycloaddition of various dienophiles to PAHs bay region is particularly effective and useful tool for PAHs structure and finally properties modification. It is due to the fact that Diels-Alder cycloaddition belongs to single-step Annulative π -Extension (APEX) reactions and represents the maximum in synthetic efficiency for the constructions of π -extended PAHs including functionalised ones, nanographenes, and π -extended fused heteroarenes. Herein we report new applications of APEX strategy for the synthesis of derivatives of 1,2-diarylbenzo[ghi]perylene, 1,2diarylbenzo[ghi]perylenebisimide and 1.2-disubstitutedbenzo[j]coronene. Namely, so far unknown cycloaddition of 1,2diarylacetylenes into perylene and perylenebisimides bay region was used. 1,2-Disubstituted-benzo[j]coronenes were obtained via cycloaddition of benzyne into 1,2-diarylbenzo[ghi]perylenes using a new highly effective system for benzyne generation and/or high pressure conditions. Moreover, we report unprecedented Diels-Alder cycloaddition-cycloaromatisation domino-type reaction between 1,4-(9,9-dialkylfluoren-3-yl)-1,3-butadiynes and perylene. The obtained diaryl-substituted-core-extended PAHs were characterized by DFT calculation, electrochemical and spectroscopic measurements.

The Diels-Alder reaction is undoubtedly one of the most fundamental and useful tools available to organic chemists for the synthesis of structures with expected properties. One of the types of this reaction is cycloaddition of various dienophiles into PAHs (polyaromatic hydrocarbons and their functionalised derivatives) bay region. PAHs, including pervlene. benzoperylene, coronene, naphthoperylene, bisanthene and other hydrocarbons which structures can be derived from perylene and also their functionalised derivatives, attract increasing attention in many areas of chemistry, material science and finally in modern technology^[1]. It is worth to mention that Diels-Alder cycloaddition into perylene and its derivatives bay region belongs to single-step annulative π-extension (APEX) reactions and represents the maximum in synthetic efficiency for the constructions of π-extended PAHs, including functionalised ones, nanographenes, and π -extended fused heteroarenes^[2]. PAHs, particularly perylene, benzoperylene, coronene derivatives, especially perylenebisimides, have great and constantly increasing importance in optoelectronic devices such as solar cells^[3], light-emitting diodes^[4], field-effect transistors FETs^[5] and molecular electronics^[6]. PAHs, not only pure hydrocarbon but also heteroatom-doped π -scaffolds, are precursors of extended carbon networks, and their carbon skeletons (or carbon-heteroatom) can be seen as small pieces of graphene^[7]. As far as pervlene is concerned, structural modifications are realized in peri, ortho, bay and both ortho and bay region positions, which can be functionalised selectively. As for expansion and modification of perylene and other PAHs' structures, cycloaddition to bay region is of particular significance. So far, cycloaddition of various ethylenic dienophiles, anhydride^[8], namely maleic N-substituted maleimides^[9]. maleates^[10]. dialkyl alkyl acrylates and diazenedicarboxylates[11], benzoand naphtho-1.4anthraquionones^[12]. fumarodinitrile^[13], N-substituted 1,2,4triazoline-3,5-diones^[14] has been described. In the case of cycloaddition of dipolarophiles with triple bond, cycloaddition of acetylene (gaseous or masked)^[15], acetylenedicarboxylates^[13,16], arynes, i.e. unsubstituted or substituted benzynes, naphthynes, 9,10-phenanthryne and higher polyacynes are known^[17].

Herein we report new applications of APEX strategy for the of 1,2-diarylbenzo[ghi]perylene, synthesis 1,2diarylbenzo[ghi]perylenebisimide 1,2-disubstitutedand benzo[j]coronene derivatives. Namely, cycloaddition of 1,2diarylacetylenes into perylene and perylenebisimide derivatives region, and cycloaddition of benzyne bav into diaryl(disubstituted)benzo[ghi]perylenes, unknown before, was used. Moreover, unprecedented Diels-Alder cycloadditioncycloaromatisation domino type reaction between 1,4-(9,9dialkylfluoren-3-yl)-1,3-butadiynes and perylene was discovered.

Our research was started from DFT calculations using B3LYP functional. Activation energies of cycloaddition of various dienophiles $R^1-C\equiv C-R^2$ type to perylene, 3,4,9,10-tetraaminoperylene, 3,4,9,10-tetranitroperylene and benzo[*ghi*]perylene bay region, leading to cycloadducts were determined (Figure 1). For the first time in 2009, the cycloaddition reaction into PAHs bay region became the object

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of theoretical research using the DFT method^[15c]. Namely, Fort et al. hypothesised that activation energies of cycloaddition of maleic anhydride to bay regions of increasingly long PAHs should decrease in the series phenanthrene perylene bisanthene - tetrabenzocoronene, due to diminishing aromatic stabilization energies of the terminal "wing" benzene rings^[15c]. This hypothesis was supported by B3LYP/6-31G* calculations and confirmed experimentally: maleic anhydride undergoes cycloaddition to substituted bisanthene but not to perylene. The elegant approach to benzannulation of bay areas of large polyaromatic hydrocarbons, described by Fort and Scott^[15b], was discovered thanks to computational investigation of reactive dienophiles for this cycloaddition: nitroethene, at B3LYP/6-31G* level of theory, was predicted to be more reactive by four orders of magnitude. In this case, the calculated E_a activation energy for cycloaddition of nitroethene is lower by 8.8 kcal/mol in relation to energy barrier for reaction with phenyl-vinyl sulfoxide. It is worth to mention that calculations with the use of B3LYP functional and 6-31G* basis set but without the dispersion corrections leads to unsystematic errors, at the order of tens of kcal/mol^[15d].



Figure 1. Calculated energy barriers for transition state (ΔE_{TS}) in modeled cycloaddition reactions of R¹-C≡C-R² into perylene, 3,4,9,10-tetraamino-, 3,4,9,10-tetranitroperylene and benzo[*ghi*]perylene bay region, obtained by the DFT/B3LYP/def2-TZVP method. Result with superscript **a** refers to the cycloaddition of acetylenedicarboxylic acid. Moreover, the results with superscript **b** and **c** corresponds to the cycloaddition of acetylene into 3,4,9,10-tetraaminoperylene and 3,4,9,10-tetranitroperylene, respectively. Additionally, results shown in the superscript **d** and **e** correspond to cycloaddition of 1,3-butadiyne into perylene and diphenylacetylene into benzo[*gh*]perylene, respectively. Ar = *N*-methylphthaloimido-3-yl

Our calculations showed that activation energy of cycloaddition reaction of disubstituted acetylenes into perylene and its derivatives bay regions, surprisingly, depends mainly on the dienophile, not diene structure. It can be inferred, that the role and electronic influence of substituents in the positions 3,4,9 and 10 is low. The summary of this findings is presented in Figure 1.

The activation energies of the cycloaddition of acetylene into perylene, 3,4,9,10-tetraaminoand 3,4,9,10tetranitroperylene proved to be similar, despite the strong donor or strong acceptor character of NH₂ and NO₂ groups. On the contrary, the activation energy of cycloaddition of 1,2diphenylacetylene into benzo[ghi]perylene (46.0 kcal/mol) is considerably higher than for perylene (42.8 kcal/mol). In 1969 Zander published a work regarding the relative reactivity of perylene and another polycyclic aromatic hydrocarbons based on perylene core in cycloaddition reaction of maleic anhydride into bay region. It was shown that benzoperylene is 220 times less reactive than perylene^[18]. The results of our DFT calculations were crucial in planning the conditions of cycloaddition reaction of various acetylenes ($R^1-C\equiv C-R^2$ type) to perylene and its derivatives. From mechanistic point of view, the calculations also shown, that formation of $\boldsymbol{\sigma}$ bonds between two carbon atoms of acetylene motif in dienophiles (CAc) with respective carbon atoms of bay region perylene (CPe) has synchronous character. In first phase of reaction, both CAc atoms attack the perylene simultaneously and in transition state (TS) CAc...CPe distances for both pair of carbon atoms is the same. In Figure 2 the calculated potential energy surface as a functions of CAc-CPe distances is presented, for cycloaddition reaction of 1,2diphenylacetylene with perylene. As is visible on the figure, minimum energy path from reactants to transition state proceed along the diagonal of PES, so at each moment, formation of σ bonds between appropriate carbon atoms will have synchronous course. For relaxation from TS to transition product the same process character can be observed. For disubstituted acetylenes presented in Figure 2, in transition state the new formed C-C bonds have the same length if the R substituents in dienophile are the same. In the case when R are different, i.e. PhC=CCOOMe, calculated transition state geometry suggest that to some extend C-C bond formation can be asynchronous process. For mentioned-above dienophile, length difference between two CAc-CPe bonds is about 0.47 Å.



Figure 2. (a) Potential energy surface (PES) as a functions of $C_{Ac-}C_{Pe}$ distances for cycloaddition reaction of 1,2-diphenylacetylene with perylene. (b) Vertical projection of PES in the contour representation.

The calculation results showed that the activation energy of the cycloaddition of various R¹C≡CR² nucleophiles strongly depends on R and is the lowest for $R = CO_2R'$ (28,4 kcal/mol when R' = Hand 30,0 kcal/mol, when R' = Me) and the highest for R = Ph(42.8 kcal/mol). Due to this fact, it was decided to start our examinations from attempts to improve the formerly described results of cycloaddition of acetylenedicarboxylates into perylene region. 2009 cycloaddition bav In of diethvl acetylenedicarboxylate into bay region of perylene (toluene 150 °C, 3 days, 56% conversion, 25% isolated yield $^{\rm [15c]}$ was described. Our results proved to be fruitful since the perylene conversion was quantitative and isolated yields were over 95% -Scheme 1.



Scheme 1. Cycloaddition of acetylene dicarboxylates into perylene bay region (perylene/dienophile = 1/5; 100% perylene conversion, isolated yield 95% (R = Me) and 96% (R = Et)).

In the next step, we aimed to obtain the product of ethyl phenylpropiolate cycloaddition into perylene. It was rational because the value of activation energy of the cycloaddition of phenyl propiolate into perylene (36.3 kcal/mol) is situated between acetylene (35.0 kcal/mol) and 1,2-diphenylacetylene (42.8 kcal/mol) cycloaddition. However, instead of cycloaddition into perylene, the creation of the dimerisation of ethyl propiolate was observed (Scheme 2).

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Analogical results were reported by Fondjo et al. where the dimer of phenylpropiolate (with 30% yield) was created in the reaction of some 2-aminothiophene fused with coumarin motif with ethyl phenylpropiolate, instead of expected anellation product^{(19]}. The structure of dimerisation product of ethyl

phenylpropiolate was confirmed with the aid of an X-ray analysis (sup. info.).

The reaction shown in Scheme 1 was repeated without perylene and as a result naphthalene derivative was obtained with high yield. Results of our calculations suggest that in the first stage of this reaction [2 + 2] cycloaddition takes place.



Scheme 2. Dimerisation of ethyl phenylpropiolate into diethyl 1-phenyl-2,3-naphthalenedicarboxylate (Nph) (Q = CO₂Et; 80% isolated yield).

Next, the obtained cyclobutadiene derivative is transformed in several steps into naphthalene derivative. Importantly, the value of Δ_{ETS} + $_{\text{ZPE}}$ is more than 10 kcal/mol lower for [2 + 2] cycloaddition than for [4 + 2] cycloaddition. Due to this fact the reaction takes place very quickly in 185 °C, similarly to the cycloaddition of acetylenedicarboxylate into perylene ($\Delta_{\text{ETS}+\text{ZPE}}$ = 28.4 kcal/mol).

On the basis of the results of DFT calculations, we successfully performed several cycloadditions of 1,2diarylacetylenes into perylene bay region (Scheme 3 and Figure 3).



Scheme 3. Cycloaddition of Ar-C=C-Ar to perylene (perylene/dienophile = 10/1)

Such cycloadditions to PAHs bay region have not been described, so far. The reaction conditions were established thanks to the test reactions, i.e. cycloaddition of 1,2-diphenylacetylene into perylene bay region (Table 1, sup. info).

The highest yield of pure product was obtained at 285 °C, 72 h, in vacuum conditions (< 0.1 Pa), using excess of melted perylene. Reactions conducted in different conditions (air or argon atmosphere, higher or lower temperature, in solvent) were characterised by lower yields and larger amount and number of side products. Structures of some of the obtained benzoperylenes were confirmed *via* X-ray analysis (sup. info.). The only limitation of the reactions shown in the Scheme 3 and Table S3 is thermal stability of 1,2-diarylacetylenes. All of the above-mentioned dienophiles were stable in the cycloaddition conditions, which was verified with DSC (see sup. info.).



Figure 3. Cycloaddition of 1,2-diarylacetylenes into perylene bay region - list of obtained products (isolated yields in the parentheses).

The results of our calculations shown in the Figure 1 encouraged us to verify whether the cycloaddition of 1,2-



Scheme 4. Cycloaddition of 1,2-diarylacetylenes into N,N-bis(2-ethelhexyland 2,6-diisopropylphenyl)perylenebisimides bay region (diene/dienophile = 1/5).

diarylacetylenes to 3,4,9,10-tetrasubstituted perylene is really possible. The model compound was N,N-disubstituted perylenebisimide due to its thermal stability and importance for organic electronics. Moreover, it is common knowledge that perylenebisimides undergo various APEX-type modifications. The successfully performed cycloaddition reactions confirmed conclusions resulting from our DFT calculations. Namely, four new derivatives of N,N-disubstituted benzo[*ghi*]perylenebisimide with good yields were obtained – Scheme 4.

One should add that in cycloaddition of 1,2diarylacetylenes into perylene and perylenebisimides bay region the creation of cycloaddition products to both bay regions was not observed. This fact is strictly correlated with the results of DFT calculations, which showed that the cycloaddition activation energy of acetylene to benzo[*ghi*]perylene is higher than in the case of perylene.



Figure 4. Cycloaddition of 1,2-diarylacetylenes into perylenebisimides bay region - list of obtained products (isolated yields in the parentheses).

The possibility to perform cycloaddition of benzyne generated from 2-trimethylsilylphenyl triflate to selected 1,2diaryl(disubstituted dimethoxycarbonyl)benzo[*ghi*]perylenes was also verified, which allowed to obtain coronene derivatives – see Scheme 5. Similarly to the previous cases, we started from the determination of activation energy of cycloadduct creation. It was discovered that the activation energy of benzyne cycloaddition into benzoperylene (7.0 kcal/mol) is only slightly higher than in the case of cycloaddition of benzyne into perylene (6.0 kcal/mol). Therefore, coronene derivatives were easily obtained (see Scheme 6). Moreover, we claimed that benzyne cycloaddion to 1,2-di(methoxycarbonyl)benzo[*ghi*]perylene (see also Scheme 1) proceed very smoothly.



Scheme 5. Synthesis of benzo[*j*]coronenes *via* cycloaddition of benzyne into selected diarylbenzo[*ghi*]perylenes (R = aryl or -COOMe; diene/benzyne precursor/CsF = 1/4/4; succinonitrile/1,2-dimethoxyethane = 1v/1v).

Benzyne was *in situ* generated from commercially available precursor – 2-trimethylsilylphenyl trifluoromethanesulfonate – and a new very effective system, i.e. cesium fluoride and 1,2dicyanoethane in 1,2-dimethoxyethane. Using succinonitrile and 1,2-dimethoxyethane instead of standard THF and MeCN was crucial for reaching the quantitative conversion of 1,2diarylbenzo[*ghi*]perylenes and 1,2-bis(methoxycarbonyl)benzo-[*ghi*]perylene. The efficiency of a wide range of systems of benzyne generation and various reaction conditions, including reactions under high pressure was tested in the model cycloaddition of benzyne into perylene and 1,2-diphenylbenzo[*ghi*]perylene bay region (Table 2 in sup. info.).

We would like to emphasise the efficiency of dicyanoethane-dimethoxyethane system and unprecedented outcome of cycloaddition under high pressure. According to us, highly increased efficiency of 1,2-dicyanoethane in comparison to acetonitrile stems from the fact that Cs⁺ complex with 1,2dicyanoethane is much more stable than the one with acetonitrile. The consequence of higher stability of the abovementioned complex is increased fluoride anion activity in the substitution of OTf group. Importantly, reaction yields from the Scheme 6 were very low (< 10%) when benzyne was generated in the mixture of MeCN/THF. As far as cycloaddition under high pressure (1.8 GPa) is concerned, quantitative conversion in the test reactions was also reached, which is unprecedented for such reactions. However, due to technical simplicity, coronenes in the larger scale were prepared under atmospheric pressure.

The DFT calculations results suggested that the cycloaddition of 1,4-diaryl-1,3-butadiynes into perylene bay region is possible, as well. It was verified for 1,4-bis(9,9'-dibutylfluoren-3-yl)-1,3-butadiyne and 1,4-bis(9,9'-dioctylfluoren-3-yl)-1,3-butadiyne – see Scheme 6. To our surprise, we separated from the post-reaction mixture 6-((9,9-dibutyl- and 9,9-dioctyl)fluoren-2-yl)-9,9-dibutyl- and 9,9-dioctylfluoren-[a]naphtho[*ghi*]perylenes instead of expected products of one

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Figure 5. Cycloaddition of benzyne into 1,2-diaryl- and 1,2-dimethoxycarbonylbenzo[ghi]perylenes bay region – list of obtained products (isolated yields in the parentheses).

triple-bond cycloaddition. The mentioned isolated π -extended PAHs turned out to be products of consecutive cycloaromatisation of the semi-product presented in the Scheme 6 in the parenthesis. According to our best knowledge, the domino-type reaction, namely Diels-Alder cycloaddition-cycloaromatisation, presented in Scheme 7 is so far unknown. This reaction is useful for the synthesis of π -extended PAHs belonging to APEX strategy using Diels-Alder cycloaddition followed by cycloaromatisation of cycloadduct.



Scheme 6. Diels-Alder cycloaddition-cycloisomerisation domino-type reaction between of 1,4-di(9,9-dibutyl- or 9,9-dioctyl/fluoren-3-yl)-1,3-butadiynes and perylene (perylene/diyne = 10/1). Synthesis of 6-((9,9-dibutyl- and 9,9-dioctyl)fluoren-2-yl)-9,9-dibutyl- and 9,9-dioctyl/fluoren[a]naphtho[*ghi*]perylenes (with 10 and 8% isolated yield, respectively).

As it can be seen in Scheme 6, the first step of the domino-type Diels-Alder cycloaddition-cycloaromatisation is Diels-Alder cycloaddition of one carbon-carbon triple bond coming from diyne, followed by cycloadduct aromatization via H₂ elimination. In the second step, cycloaromatisation of the benzo[ghi]perylene derivatives takes place, which leads to further expansion of the aromatic system. The semi-product is not detected, which means that the second step is much faster than the first one. It can be noticed that the semi-product has a structure of masked dienyne, hence the second step is the cycloaromatisation of dienyne. Thermal and catalytic cycloaromatisation of open and masked conjugated dienynes is well-known and its importance for the synthesis of both carbo- and heterocycles synthesis cannot be overvalued [2d-g]. In this context, one should particularly enumerate recently described doublecycloaromatisation of 1,4-diaryl-1,3-butadiynes [2d-f], including domino reaction [2d]. However, it is still cycloisomerisation without Diels-Alder cycloaddition step. APEX strategy shown in Scheme 6 is unknown combining of cycloaddition and cycloisomerisation into a domino-type reactions leading to unique and complex structures would be unavailable in any other way.

For all of the obtained cycloaddition products and also for unsubstituted purposes), structures (for comparative DFT/B3LYP calculations were carried out. Additionally, optical and electrochemical measurements were performed for almost every structure - see sup. info. When it comes to the character, location and $\Delta E_{(HOMO- LUMO)}$ Kohn-Sham orbitals for obtained compound, the variability of the above-mentioned properties is great. In the case of the derivatives of 1,2-diarylbenzoperylene for **BP4** the HOMO is localised on the arvl substituent but LUMO on BP-core. For BP7 the orbitals localisation is reversed, it means that HOMO orbital is situated on BP-core whereas LUMO on Ar groups. For BP9 the HOMO is delocalised and involves both BP-core and Ar groups, but LUMO is highly located on the BP-core. For the remaining 1,2-diarylbenzo[ghi]perylenes the HOMO and LUMO location is similar to the one for BPO (unsubstituted benzo[ghi]perylene) and includes solely BP motif. For obtained 1,2-diarylbenzo[ghi]perylenes $\Delta E_{(HOMO-LUMO)}$ ranges from 2.89 to 3.51 eV. When it comes to PBI4 belonging to 1,2diarvl[ahilbenzopervlenebisimides its HOMO is placed on Ar groups but LUMO on BPI-core. In case of the remaining PBI, including BPIO (unsubstituted one), the frontier orbitals are localised only on BPI-core. The calculated $\Delta E_{(HOMO-LUMO)}$ for PBI ranges from 2.28 to 2.86 eV. Also for 1.2diaryl(dimethoxycarbonyl)benzo[j]coronenes remarkable influence of cycloaddition on frontier orbitals location and gap energies was observed. For BC3 the HOMO is situated on BCcore and LUMO on aryl groups. For ${\bf BC4}$ the HOMO can be found on BC-core and LUMO is delocalised on the entire structure. The $\Delta E_{(HOMO-LUMO)}$ gap for BC ranges from 3.19 to 3.61 eV.

The optical properties of the designed compounds in CH_2CI_2 were investigated with UV-Vis absorption and emission

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spectroscopy (Tables S5-S6 and Figures S43-S46 in ESI). For all the compounds, the lowest energy absorption band exhibits well-defined vibronic structure and its position is predominately governed by core-expanded perylene unit. A significant bathochromic shift of the absorption of 1,2diarylbenzo[ghi]perylenebisimides (PBI1-PBI4) in relation to other investigated systems is attributed to introduction of bisimide fragments into benzo[ghi]perylene core (Figure S44). Emission behaviour of the reported compounds is largely affected by expanded perylene core, but the impact of attached substituents can be also noticed (Figure S46). As illustrated for PBI1-PBI4, BP4 and BP7, addition of bisimide fragments or strong electron-donating triphenylamine induces dramatic bathochromic shifts of the emission. For the vast majority of the obtained compounds, the fluorescence spectra have welldefined vibronic structures, typically for locally excited state in extended π -conjugated aryl systems. On the contrary, the emission band of BP4 and BP7 becomes unstructured and broad. Prominent red-shift accompanied with change of emission profile from vibronically structured to broad unstructured is indicative for CT nature of the emitting states in BP4 and BP7. Significant enhanced fluorescence intensity was revealed for 1,2-diarylbenzo[ghi]perylene-bisimides (66-79%). exception in this group was PBI4, with fluorescence An quantum yield of 6.3%. In series of BP1-BP9, the introduction of triphenylamine moieties was found to be beneficial regarding emission quantum yield (Table S6).

All of the obtained compounds were also investigated electrochemically in their diluted CH₂Cl₂ solutions. By using cyclic voltammetry one can easily estimate molecule's HOMO and LUMO energy level (or rather, ionization potentials and electron affinities) and energy gaps, assuming the IP of ferrocene equal's -5.1 eV^[20]. First, behaviour of BP1-BP9 and FBPI1-FBPI2 compounds were evaluated. For each of abovementioned compounds oxidation (BP/BP+) is fully reversible process with peak onsets strongly depending on substituent nature. For example, compound possessing strongly π-donating TPA (triphenyl amine) group, i.e. BP4 exhibit lowest Eox value (0.31 V), while in the case of BP3 (with (p-trifluoromethyl)phenylene moiety) Eox is highest (0.82V). Only for BP9 electrochemical response is slightly different - oxidation occurs exclusively at carbazole fragments. On the other hand, reduction (BP/BP) takes place below -2.14V and is located at benzo[ghi]perylene core. The only exceptions are BP7 and BP8 for which reduction occurs at substituent's imide moieties (-1.82 V and -1.72 V, respectively). PBI's series exhibit typical for this type of compounds behaviour - i.e. two step, reversible reduction: E_{red1} (PBI/PBI) and E_{red2} (PBI/PBI²) an irreversible oxidation. It is worth noting that in the case of PBI4 oxidation occurs at carbazole moiety, as expected. Comparing BC1-BC4 compounds with their BP precursors one can easily observe that extension of fused benzene rings lowering both E_{ox} and E_{red} i.e. oxidation is easier (due to the fact that created carbocations are better stabilised) while reduction is harder.

In summary, using APEX strategy, nineteen new coreexpanded perylene derivatives, namely nine 1,2-diarylbenzo[ghi]perylenes, four 1,2-diarylbenzo[ghi]perylene-1,2-diarylbenzo[/]coronenes, bisimides. three 1.2di(methoxycarbonyl)benzo[j]coronene 6-((9,9and two dialkyl)fluoren-2-yl)-9,9-dialkylfluoren[a]naphtho[ghi]perylenes were successfully synthesized. 1,2-Diarylbenzo[ghi]perylenes and 1,2-diarylbenzo[ghi]perylenebisimides were synthesized via unprecedented Diels-Alder cycloaddition of 1,2-diarylacetylenes into perylene or perylenebisimides bav region. 1,2-Diarylbenzo[/]coronenes and 1,2-di(methoxycarbonyl)benzo[j]coronene were obtained via benzyne cycloaddition into 1,2-diarylbenzo[ghi]perylenes 1,2-di(methoxycarbonyl)or benzo[ghi]perylene bay region using new highly active system for benzyne generation, namely CsF + NCCH₂CH₂CN + MeOCH₂CH₂OMe. High pressure conditions for benzyne cycloaddition into perylene and 1,2-diarylbenzo[ghi]perylene

resulted in 100% diene conversion. According to our best knowledge, it is the first such spectacular pressure effect in aryne 6-((9,9-dialkyl)fluoren-2-yl)-9,9cycloaddition. Two dialkylfluoren[a]naphtho[ghi]perylenes were prepared via cycloaddition-cycloaromatisation unprecedented Diels-Alder domino type reaction between 1,4-diaryl-1,3-butadiynes and perylene. DFT calculations, optical and electrochemical measurements given for all the obtained cycloaddition products confirm that APEX strategy (in this work represented by Diels-Alder cycloaddition and cycloaddition-cycloaromatisation domino-type reaction) is able to generate m-expanded structures with broad spectrum of properties. All of the obtained derivatives can be further modified, including core-expansion via cycloaddition into the remaining bay region or/and via Scholltype dehydrocyclocondensation. Further works on the obtained molecules, namely testing in OLED or solar cells technology, are currently ongoing.

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It was shown, that APEX strategy represented by Diels-Alder cycloaddition of acetylenes and benzyne into perylenes bay region and also by a new domino-type reaction is able to generate π -expanded structures with broad spectrum of properties. New, highly active system for benzyne generation and high pressure conditions were unprecedentedly used. DFT calculations, optical and electrochemical measurements were given for all the obtained products.