Acenaphthenoannulation Induced by the Dual Lewis Acidity of Alumina

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Abstract: We have discovered a dual (i.e., soft and hard) Lewis acidity of alumina that enables rapid one-pot π-extension through the activation of terminal alkynes followed by C—F activation. The tandem reaction introduces an acenaphthene fragment – an essential moiety of geodesic polyarenes. This reaction provides quick access to elusive non-alternant polyarenes such as π-extended buckybowls and helicenes through three-point annulation of the 1-(2-ethynyl-6-fluorophenyl)naphthalene moiety. The versatility of the developed method was demonstrated by the synthesis of unprecedented structural fragments of elusive geodesic graphene nanoribbons.

sp²-Carbon-based nanomaterials such as large polycyclic aromatic hydrocarbons (PAHs) or nanographenes (NGs), and graphene nanoribbons (GNRs) continue rapidly to gain the attention of the scientific community. Such interest is fueled not only by their unique electronic, optical, and magnetic properties[1–4] but also by the possibility of tuning these properties through atomically precise control over the structure. While the exact connectivity of the atoms strictly defines the chemical and physical properties of NGs it also places severe limitations on their preparation, where bottom-up techniques such as organic synthesis are by far the most reliable, and therefore common, methods enabling PAHs with a defined structure.

The development of such techniques requires new efficient synthetic tools for the rational construction of multiple C-(aryl)—C(aryl) bonds in one-step, enabling sophisticated targets from reasonably simple starting blocks. For example, the Scholl reaction has proved to be a powerful tool to generate numerous C(aryl)—C(aryl) bonds in one-step enabling an immense number of various structures.[5–7] However, this method frequently suffers from unexpected rearrangements leading to undesired products.[8] Although several other methods can provide rapid π-extension through inter- or intramolecular C—C coupling reactions, most developed reactions lead to alternant PAHs containing exclusively hexagons.[9–16] Meanwhile, only a handful of synthetic instruments enable the rapid synthesis of non-alternant PAHs.[17–23]

Thus, the incorporation of pentagons into the hexagonal lattice is accompanied by strain energies related to the deviation of the valence angles leading to the positive Gaussian curvature. Due to the similarity of the acquired shape with a bowl, this class of compounds is oftentimes referred to as buckybowls, which, despite recent advances,[21,23–27] remain extremely elusive targets. For example, incorporation of a pentagon (by indenoannulation) is a challenging reaction that can be implemented using only a few methods, such as flash vacuum pyrolysis,[28,29] Pd-catalyzed aryl-aryl coupling,[30] or C—F bond activation[31,32] using hard σ-Lewis acids such as silyl carboranes[33,34] or activated γ-alumina.[20]

Synthesis of benzo[ghi]fluoranthene's moiety (common fragment in the structure of buckybowls) is one of the key synthetic bottlenecks, that prevent some intriguing materials from being thoroughly investigated or even being obtained. Thus, a general and simple method such as one-step **a**ce**n**aph-theno**a**nnulation **π**-**ex**tension (ANAPEX) would open new venues to synthesize a number of hardly accessible or unavailable classes such as fully fused macrocycles or geodesic nano-

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ribbons, which may acquire shapes of various intriguing conformers, for example, snail (Figure 1B).

While one-pot construction of a pentagon and a hexagon appears as an optimal approach to solve this problem, to the best of our knowledge, there are no chemical conditions that would implement both transformations in one step (Figure 1A). Moreover, the sequence of these steps plays a crucial role as strain energies are to be introduced during the intermediate steps. Thus, once the hexagon is formed, incorporation of the pentagon is significantly facilitated into the cavity of energetically rich [4]helicene's structure (Figure 1A).

Our recent finding[35] demonstrates that activated γ-alumina can act as a soft π-Lewis acid enabling transformations of alkynes previously assigned primarily to noble metal homogeneous catalysts.[36] Here, a combination of Lewis acidic and Lewis basic sites is believed to efficiently mimic σ-dative and π-back-dative interactions of alkynes with transition metals. This mode of catalysis, inter alia, enables 6-endo cycloizomerization of biarylacetylenes generating functionalized [4]helicenes at ambient temperatures.[35,37] In the context of our previous reports,[20] this discovery renders alumina as an ideal material to induce ANAPEX of fluorinated aryl alkynes according to the scheme depicted in Figure 1.

In this work, we report that the dual (i.e., soft π- and hard σ-) Lewis acidity of alumina can be used for the rapid construction of non-alternant PAHs. Initially, we obtained 1-(2-ethynyl-6-fluorophenyl)naphthalene as a model compound, which was converted into benzo[ghi]fluoranthene (1) in excellent yields (Scheme 1). In principle, this type of π-extension could be employed for any 1-functionalized naphthalene moiety unsubstituted at 2- and 8-positions. To investigate the scope of this transformation, we have tested several precursors, which were obtained in two steps from readily available aryl bromides or boronic esters. Thus, some pristine PAHs (2–5) can be

constructed very efficiently in accordance with the suggested synthetic scheme. Moreover, we found that the method allows the synthesis of brominated PAHs (6 and 7), which can serve as valuable building blocks for more complex architectures owing to the broad utility of the C–Br functionality. The reaction is also suitable to generate π-extended helicenes (8 and 9). Noteworthy, ANAPEX efficiently extends buckybowls generating a fragment of a GNR composed of fused acenaphthene fragments. For example, buckybowl 10 was synthesized in good yields, while its structure was unambiguously confirmed by means of X-ray analysis. Due to non-planarity, 10 acquires chirality, while two enantiomers freely interconvert by bowl inversion. According to the X-ray data, alternating enantiomers pack into columnar arrays with some intercolumnar C–H contacts of 2.87 and 2.79 Å. Interestingly, crystal structure analysis reveals that, unlike similar less curved compounds,[22] the structure of 10 cannot provide effective intracolumnar π-interactions with only a few C–C contacts in the range of 3.28 and 3.35 Å.
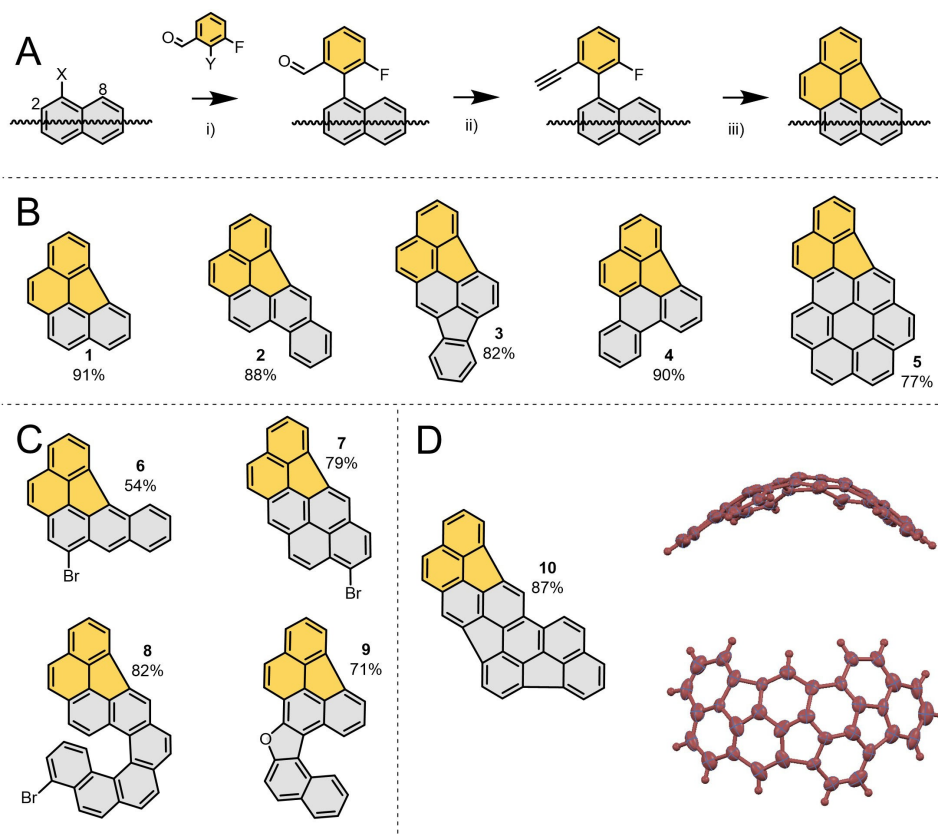
To investigate whether double-ANAPEX can be implemented, we exposed doubly functionalized naphthalene derivatives, which transformed into buckybowls 11 and 12 in reasonable yields (Scheme 2). This methodology enables substantially easier access to valuable building blocks such as buckybowl 11, which has been previously synthesized in nine steps.[38] The same approach is also suitable to extend other aromatic cores such as phenanthrene (13), pyrene (14), [4]heliecene (15), [6]helicene (16 and 17), and hetero[5]helicene (18). Noteworthy, it is also possible to generate differently coupled benzo[ghi]fluoranthene's dimers (19 and 20), where the latter was obtained from the conjugated diyne 20a. The yield of 19 was lower than expected compared to 1, probably, due to steric repulsion of the binaphthyl moiety.

We investigated optoelectronic properties (Table S1) of the obtained set of benzo[ghi]fluoranthene's derivatives. They feature visible light absorption and fluorescence properties, up to 550 nm and 650 nm, respectively. While the quantum yields of the molecules containing only one benzo[ghi]fluoranthene's unit show mediocre values in the range of 0.12–0.32, the larger compounds (e.g., 12, 14, 21–23) hardly fluoresce (quantum yields <0.1). This is likely connected to the multiple quenching possibilities, such as bowl inversion and aggregation in the ground and excited states. The oxygen-containing PAHs 9 and 18 possess good fluorescence induced by higher dipole moment. Noteworthy, 5 shows an interesting distinction of 150 nm Stokes shift and a zero overlap of the absorption and emission spectrum, which is interesting in future sensing applications.[39]

Considering the sequence of the cyclizations during ANAPEX, where the gradual introduction of strain energies is realized, we envisioned that the method could also allow the synthesis of strained systems containing multiple fused pentagons. Thus, we have successfully obtained π-extended [5]helicene 21. We also used the method to synthesize buckybowls 22 and 23. Although these two structures appear to face the border of processibility due to solubility issues preventing their proper characterization and yield estimation. ANAPEX allows the synthesis even of such strained moieties,
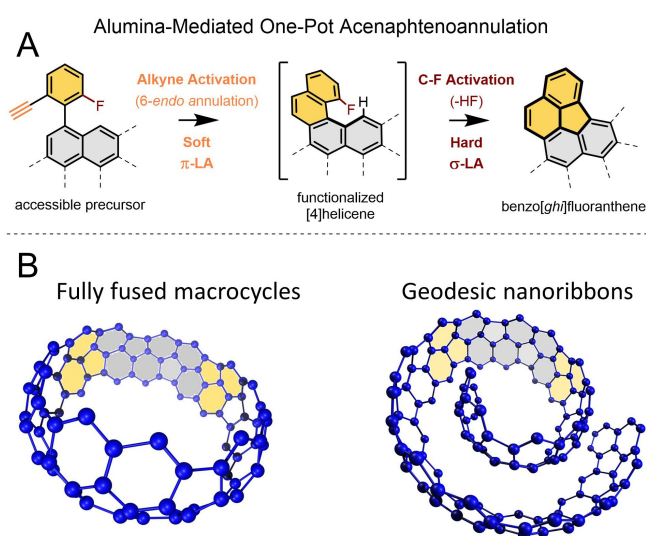
Figure 1. One-pot acenaphthenoannulation (acenaphthene fragment depicted in orange). A) Alumina-mediated annulation of fluorinated arylalkynes via helical intermediates. B) Elusive sp² nanomaterials consisting of fused acenaphthene units.

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Scheme 1. Three-point annulation of the 1-substituted naphthalene moiety. A) Synthetic scheme of the ANAPEX: i) Suzuki coupling: Pd(PPh$_3$)$_4$ 2.5 mol%, K$_2$CO$_3$, toluene/methanol/water, reflux, X=Br, Y=BPin or vice versa; ii) Ohira–Bestmann reagent, K$_2$CO$_3$, methanol, RT; iii) activated γ-alumina, o-dichlorobenzene, microwave reactor, 190 °C. B) Pristine planar PAHs containing a benzo[*ghi*]fluoranthene fragment obtained by ANAPEX. C) Brominated PAHs and π-extended helicenes. D) π-extended buckybowl and top and side views of its crystal structure (thermal ellipsoids are shown at the 50% probability level). Isolated yields for the ANAPEX step are given.
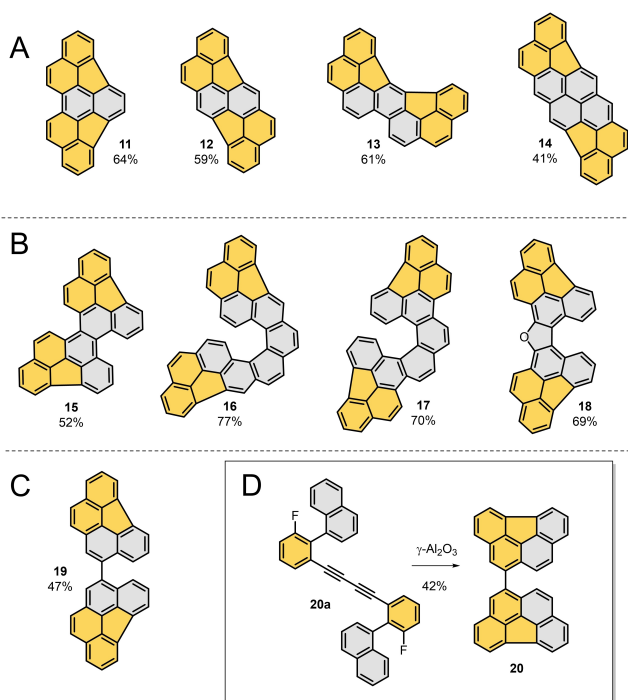
which were characterized by means of HRMS and UV-vis spectroscopy.

To strengthen our conclusions and to further investigate the optoelectronic properties of **21**–**23**, we carried out additional theoretical simulations of molecules **21**–**23**. Theoretical UV-vis spectra were simulated by performing time-dependent density functional theory (TD-DFT) calculations of the lowest 40 singlet discreet transitions from the ground state and broadened by Gaussian line shape functions to account for thermal and solvent effects. This allows a direct comparison of experimental and theoretical data on optoelectronic properties. As Figure 2 depicts, the calculated spectra are in excellent agreement with experimental counterparts, thus serving as an additional characterization tool. Detail analysis of the leading contributions to the most prominent discreet electronic transitions is given in Figures S207–S213.
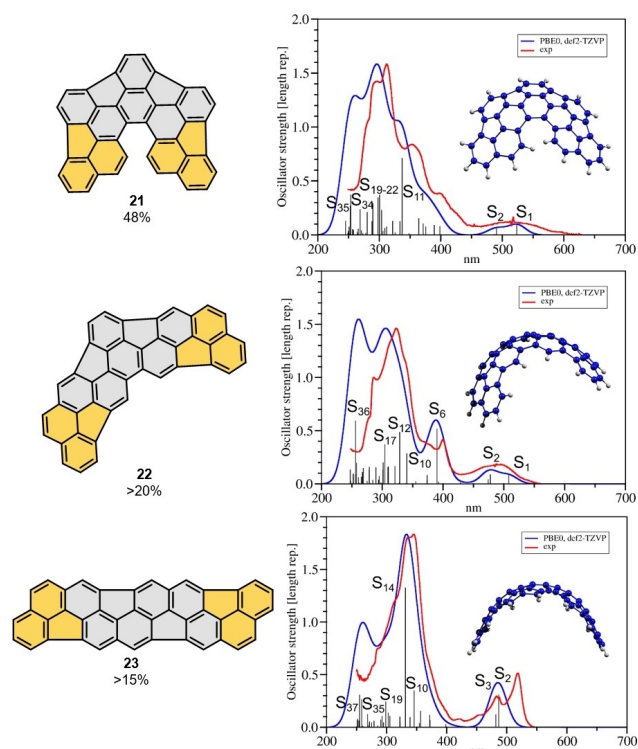
These molecules possess interesting shapes that allow referring to them as fragments of geodesic nanoribbons with different chain fusion of acenaphthene's units. Thus, **21** combines helical and bowl-shaped geometries. While both features can be inversed (DFT-level calculated values are 2.4 and 5.3 kcal/mol, respectively), the former renders **21** chiral. Meanwhile, the inversion of the bowl geometry does not invert

the helical configuration (Figure S213). Moreover, **21** has an interesting outer armchair periphery, where all *para*-conjugation π-electronic system is implemented (formally corresponding to the fragment of synthetically challenging nearly planarized cycloparaphenylenes showing some interesting electronic properties. Interestingly, the interplay of helical and bowl shapes lowers the inversion barriers with respect to similar compounds featuring either pure helical or pure bowl geometries.[22] Thus, according to the same level of theory **22**, featuring no helical moiety, it undergoes bowl-to-bowl inversion with a significantly larger barrier of 16.6 kcal/mol. Unlike **22**, **23** has no internal plane of symmetry and is not superposable on its mirror image. Thus, the most significantly curved **23** is chiral, whereas DFT calculations indicate that the enantiomers interconvert with the barrier of 17.2 kcal/mol. Another noteworthy feature of the bowl-to-bowl inversions occurring in **21**–**23** is that the transition states are nonplanar and have wave-like shapes (Figure S213).

In summary, we have taken synthetic advantage of γ-alumina's dual Lewis acidity to activate two functionalities, that is, the terminal alkyne and C–F bond leading to incorporation of a hexagon and a pentagon, respectively, in one step. This combination of reactivity constructs a acenaphthene fragment

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Scheme 2. Products of double ANAPEX. A) Facile synthesis of buckybowls. B) Synthesis of π-extended helicenes. C) and D) Synthesis of benzo[ghi]fluoranthene dimers. Isolated yields for the ANAPEX step are given.

and enables the creation of a comprehensive set of non-alternant PAHs. This technique gives facile access to elusive molecules such as π-extended helicenes and buckybowls, and represents an important step in the development of the rapid, rational, and atomically precise construction of sp²-carbon-based nanomaterials.

Crystal structures

Deposition Numbers 2149923 (for **11**), 2149924 (for **2**), 2149925 (for **10**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformations-zentrum Karlsruhe Access Structures service.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Figure 2. Towards geodesic nanoribbons. Structures obtained by double ANAPEX of buckybowls. Experimental and TD-DFT-calculated UV-vis spectra. DFT B3LYP- D3BJ/ 6–311 + G(d,p)-calculated structures are inset.

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RESEARCH ARTICLE

The dual Lewis acidity of γ-alumina is reported to enable rapid π-extension of readily available building blocks through the tandem activation of "soft" triple C—C bonds and hard C—F bonds. The reaction gives facile access to elusive non-alternant polycyclic aromatic hydrocarbons such as π-extended helicenes and geodesic carbon nanoribbon fragments.
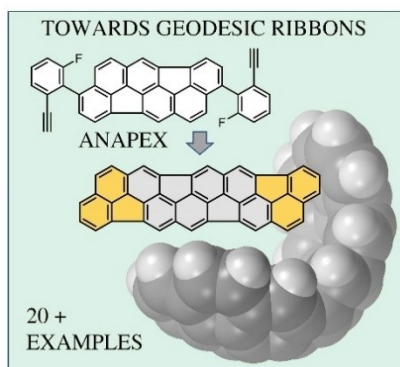
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