Molten Metal Synthesis of Nanographenes

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ABSTRACT: This manuscript describes a simple and effective method to cyclodehydrogenate arenes using liquid alkali metals. Direct reaction between molten potassium and arenes forms 6-membered rings and zig-zag edged structures within polyarenes. The approach is extended to integration of pyridinic nitrogen and 5-membered rings to arene structures and synthesis of larger, open-shell nanographenes.

Efficient intramolecular cyclodehydrogenation of polyarenes is critical for the bottom-up synthesis of polycyclic aromatic hydrocarbons (PAHs), nanographenes, and other carbon-based nanomaterials.[1–5] There are two broad strategies for synthesis of nanographenes: solution-based syntheses and on-surface syntheses (**Figure 1a**). Solution-based syntheses, such as the Scholl oxidation, typically subject the polyaromatic to strongly Lewis acidic and oxidizing conditions for extended periods of time.[3,6] Moreover, to maintain solubility and processibility, the molecules are heavily functionalized with solubilizing groups, which often dictate the assembly and properties of the nanographenes. Solution-based approaches, however, are scalable, and relatively large amounts of the product can be isolated. Surface-based syntheses typically employ noble metal surfaces to mediate a thermally induced cyclodehydrogenation. These on-surface reactions proceed with high selectivity and are applicable to a wide range of substrates. Using these methods, it is possible to form 5-membered rings, cyclize strained moieties (e.g., bianthryls), and build zig-zag edges from methylated PAHs. [1,2,7–9] Unfortunately, the sub-monolayer scale of these reactions makes it difficult to isolate sufficient material for properties measurements in the absence of the surface. This manuscript marries the two approaches, using reactive liquid metal surfaces to achieve the scope of the on-surface synthesis with the scalability of the solution-based approach.

Our studies build from solution-phase alkali metal mediated cyclodehydrogenation reactions. Despite their unique reactivity and selectivity,[10–17] alkali metal mediated approaches are mostly restricted to ethereal solvents in which reactants, products, intermediates, and the alkali metal have limited solubility. As such, only a few structures have been realized using these protocols (**Figure 1b**).[10–13,18–22] We reasoned that the scope of these reactions could be improved if the solvent was removed completely. The malleability and low melting point of the alkali metals (e.g., Na and K) enable a facile mixing with the reaction substrates without the need for solvent nor concerns about solubility – an issue that plagues nanographene syntheses. Moreover, molten alkali metal provides a fluid, regenerable surface on which the reactions can turn over and provide large amounts of the product. We find that performing reactions with neat, molten potassium at elevated temperatures (100 – 200 °C) promotes a facile formation of 6-membered rings, 5-membered

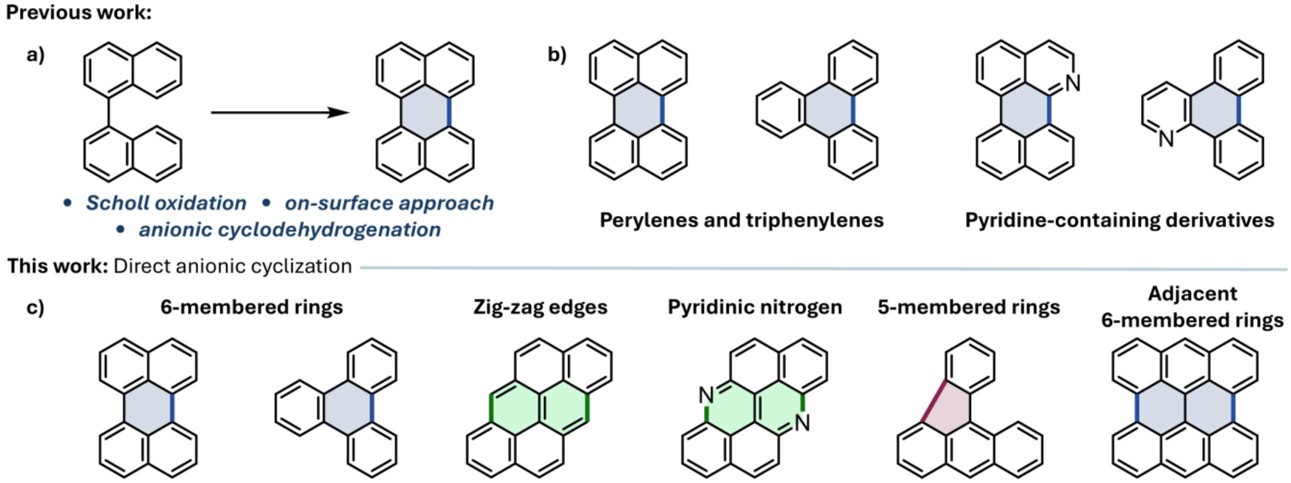
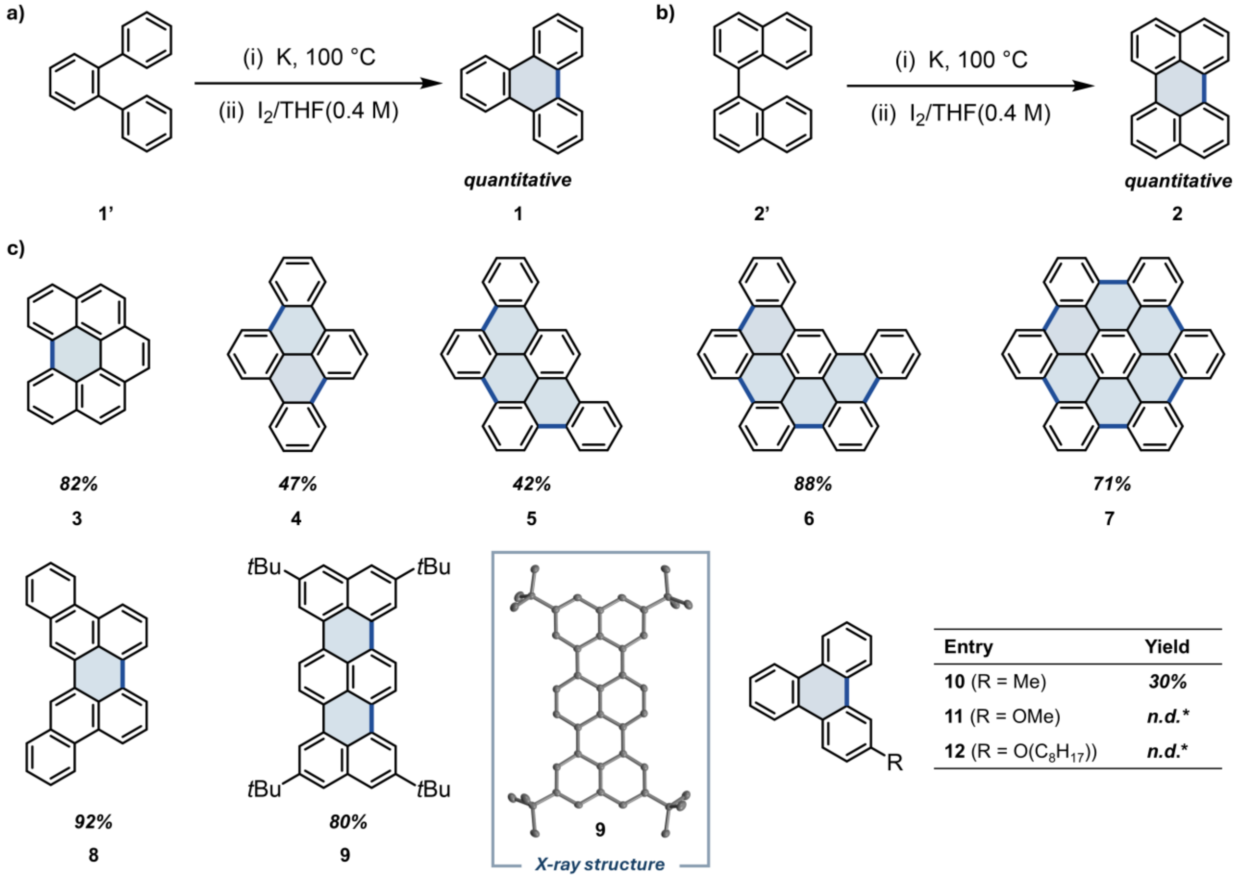


Figure 1. (a) Prototypical cyclodehydrogenation of polyarenes. (b) Reported structural motifs formed using solution-based anionic cyclodehydrogenation: perylenes and triphenylenes,[10,11] and pyridine-containing derivatives.[10,13] (c) Direct anionic cyclodehydrogenation with liquid alkali metal reported here.



Entry	Yield
10 (R = Me)	***30%***
11 (R = OMe)	***n.d.****
12 (R = $O(C_8H_{17})$)	***n.d.****

Figure 2. Cyclization *via* arene-arene coupling to form 6-membered rings. (a) Cyclization of *o*-terphenyl, (b) cyclization of 1,1'-binaphthyl, and (c) scope of 6-membered ring formation. Isolated yields, bold blue bonds represent bonds formed, shaded rings represent cycles formed, n.d. = not detected. ***1** is observed in low yield.

rings, in bianthryl subunits (**Figure 1c**). As a demonstration of the power of this methodology, we create a large nanographene with open-shell electronic character.

We first describe prototypical electrocyclizations of *o*-terphenyl (**1'**) and 1,1'-binaphthyl (**2'**), forming 6-membered rings (**Figure 2a,b**). When we grind elemental potassium (K) with *o*-terphenyl and then heat to 100 °C, triphenylene (**1**) forms quantitatively within an hour. The product is isolated after neutralization with I_2 in tetrahydrofuran (THF). Similarly, we find that the reaction of 1,1'-binaphthyl (**2'**) with molten K produces perylene (**2**) in quantitative yield. It is important to note that these reactions could be run on a gram scale, and there is no reason they could not be scaled further.

We note that the quenching of the reaction with I_2 is critical for obtaining the fully aromatized product. For example, in the reaction of **2'**, if isopropyl alcohol (*i*PrOH) is used to quench the reaction, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (MS) shows the corresponding di-, tetra- and hexa-hydro- compounds along with **2** (See Figure S1). Analogously, if *i*PrOD is used the di-, tetra- and hexadeuterio- compounds are observed. Similar protonation has been observed upon Birch reduction of both triphenylene and perylene, illustrating that the neutralization step should be performed in the absence of protic groups.[15,23,24]

We next surveyed 6-membered ring-forming reactions for a range of nanographenes (**Figure 2c**). Benzo[*ghi*]perylene (**3**), for example, forms from the cyclization of 5-helicene in 82% yield – indicating that the cyclization can be applied to contiguous aromatic systems.[14] Turning to the construction of larger nanographenes involving multiple cyclizations, **4** is obtained in 47% yield from *o*-quaterphenyl, while we form (**5**), (**6**) and (**7**) in 42-88% isolated yield from the corresponding phenylated aromatic precursors. Hexabenzocoronene (**7**) is an important subunit in the construction of many nanographenes.[25–27] The actual yields are higher in many cases but limited by the solubility of the products and byproducts.

8 and **9** provide a direct comparison of our molten metal process to published studies using the solution-based alkali metal approach and the Scholl cyclization. For the molten metal synthesis, **8** is obtained in 92% yield after 1 hour. This is a comparable yield to an extended (10 h) reaction with K in dimethoxyethane (DME) (reported yield: 90%) and represents a remarkable improvement over the mechanochemical approach with Li in THF (17% yield) and Scholl conditions (50% yield).[10,28,29] For the formation of terrylene **9** using molten potassium, the ternaphthyl precursor fuses twice, forming **9** in 80% yield (See **Figure 2c** for crystal structure). For comparison, previously reported conditions using K in DME yield only 24% of the product. Under Scholl conditions, **9** is not formed from the same precursor due to both isomerization and debutylation.[30,31] Using Scholl conditions, **9** could only be formed from the corresponding naphthyl perylene precursor in (42% yield).[30,31] These comparisons emphasize the remarkable efficacy of the molten metal reactions.

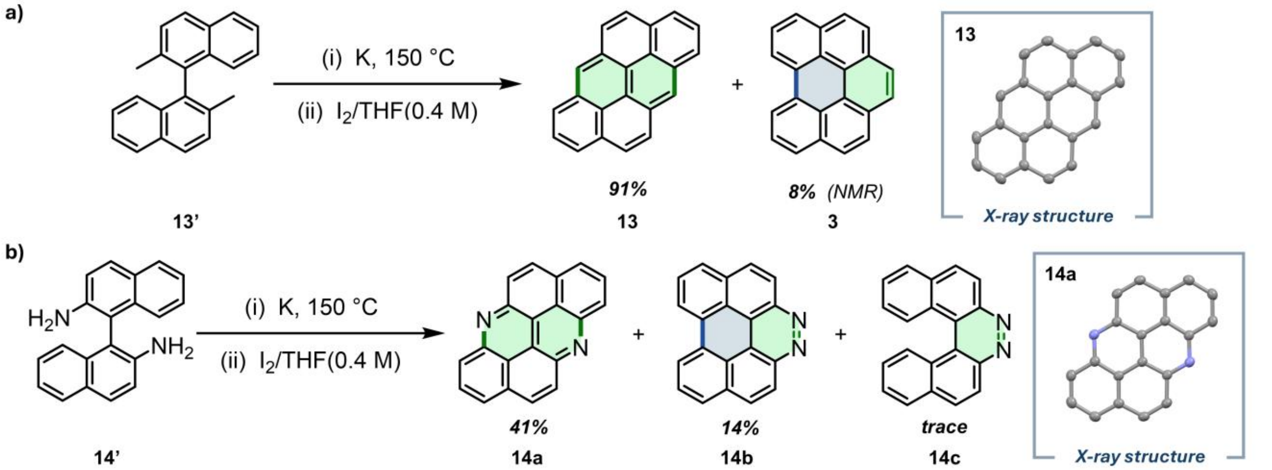


Figure 3. Zig-zag edges *via* incorporation of pendant groups. (a) Zig-zag edges through methyl group incorporation, (b) N-terminated edges from primary amines. We report isolated yields unless it states (NMR), indicating that product was detected by NMR but not isolated. In those cases, the yield is based on the amount relative to the major product. Green bonds represent bonds formed via incorporation of pendant methyl or amino groups, bold blue bonds represent bonds formed by arene-arene coupling, shaded rings represent cycles formed.

A counterintuitive aspect of these molten metal reactions is that they are able to tolerate functional groups. For example, rylene **9** contained *tert*-butyl substituents.[10,12,13,31] We used the cyclization of mono-substituted *o*-terphenyl to test whether methyl or ether substituents were tolerated. Indeed, 2-methyltriphenylene (**10**), is isolated in 30% yield. Interestingly, the other major product from this reaction (26% yield), was the triphenylene dimer resulting from a homocoupling at the benzylic position (See Figure S8 for crystal structure). Conversely, for arylalkyl ethers (**11** and **12**) we find that the major product is the defunctionalized PAH, triphenylene (**1**), suggesting that the reaction conditions employed are incompatible with alkoxy-substituents.[32]

Based on the observation that **10** formed and dimerized in significant quantities under our reaction conditions, we chose to explore the incorporation of pendant methyl groups into PAH precursors as a potential strategy for generating zig-zag edged nanographenes (**Figure 3a**)[33–36]. The prototype reaction of 2,2′-dimethyl-1,1′-binaphthalene (**13’**, **Figure 3a**) with molten potassium at 150 °C results in full conversion of starting material. We form anthanthrene (**13**) and benzo[*ghi*]perylene (**3**) in a ratio of 12:1, with trace oligomeric products also observed. We isolate **13** in 91% yield and crystallize it from hot toluene as red-orange crystals suitable for SCXRD (**Figure 3a**).[37] To further manipulate the zig-zag edge structure, we explored the creation of nitrogen-terminated nanographene structures, through incorporation of pendant amino groups (**Figure 3b**). When we treat [1,1’-binaphthalene]-2,2’-diamine (**14’**) with potassium at 150 °C, we isolate **14a** and **14b** in yields of 41% and 14%, respectively (**Figure 3b** shows the SCXRD structure for **14a**, while the structure of **14b** is shown in Figure S11). We note that under oxidative conditions the same transformation from a diamine has previously been used to form a diimide-functionalized derivative of this motif.[38] The protocol presented produces significant amounts of otherwise difficult to prepare, nitrogen-terminated nanographenes,[8] though A key finding here is that the reactivity of potassium’s dissolvable surface mirrors what is observed on the surface of noble metals such as Au.[8,35,36]

Inspired by the similarities between cyclizations on noble metal and molten potassium surfaces, we tested 5-membered ring formation (**Figure 4**).

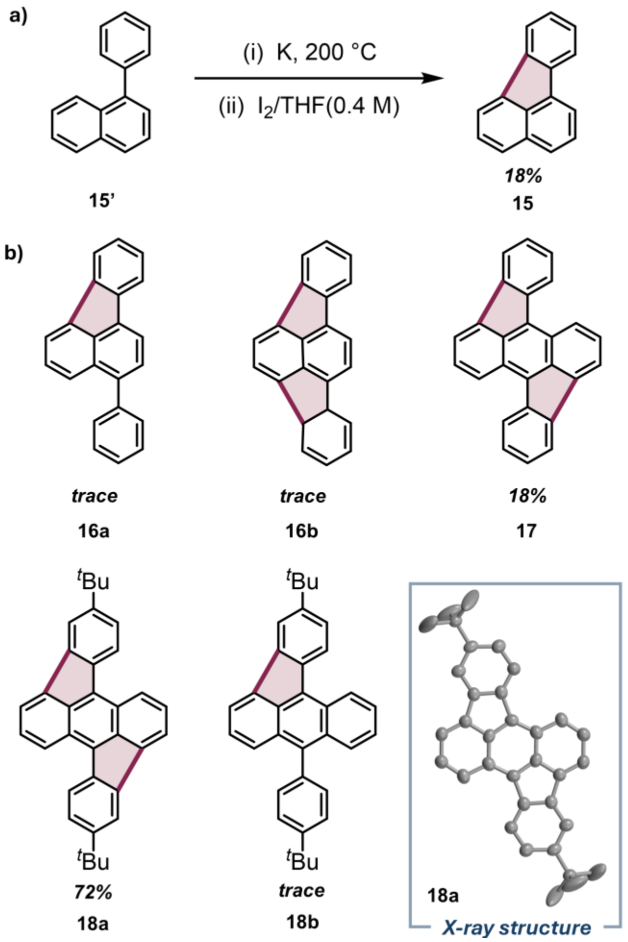


Figure 4. 5-membered ring formation *via* arene-arene coupling. (a) Reaction of 1-phenylnaphthalene, (b) scope of 5-membered ring formation. Isolated yields, bold burgundy bonds represent bonds formed, shaded rings represent cycles formed, n.d. = not detected.

After subjecting 1-phenylnaphthalene (**15'**) to potassium at 200 °C, we isolate fluoranthene (**15**) in 18% yield (**Figure 4a**). Interestingly 1,4-diphenylnaphthalene yields only trace amounts of **16a** and **16b** (**Figure 4b**) and conversion to a polymeric material. 9,10-diphenylanthracene yields rubicene (**17**) in 18% yield. We note that the corresponding isorubicene is not observed.[39] Similarly, when we treat 9,10-bis(4-*tert*-butyl)phenylanthracene with potassium at 200 °C, 5,12-di-*tert*-butylrubicene **(18a)** is the major product, isolated in a yield of 72% (**Figure 4b** displays the structure from SCXRD). We observe trace amounts of the partially fused product **(18b**, **Figure 4b)**, with the remaining material being unconverted starting material. Again, the corresponding isorubicene was not detected. Typically, approaches for the embedding of 5-membered rings into nanographenes rely on carbon-halogen bonds as directing groups,[12,39–42] Scholl oxidation reactions with limited success,[43–45] or noble-metal surfaces.[9,35,46] The transformations in **Figure 4** represent the first examples of an alkali-metal induced 5-membered ring formation within a PAH core, delivering significant synthetic utility.[9,36–38]

To further demonstrate the parallels between the molten potassium reaction and on-surface approaches, we describe the dehydrogenative cyclization of the sterically encumbered bianthryl motif shown in **Figure 5a**. Anthracenyl groups linked at the 9-position and the corresponding oligoanthrenes have been used extensively as precursors to graphene nanoribbon fragments, both on-surface and in solution.[2,3,5,9,47] This cyclization, however, is notoriously difficult due to the near orthogonal nature of the two anthracene moieties, and isolation of products can be challenging.[10,34,47–50] We find that (4-*tert*-butyl)phenyl capped bianthryl substrate (**19'**, **Figure 5a**) reacts on molten potassium to form a green-brown solid after workup and isolation. The product of this reaction (**19**) is isolated in 15% yield, mass spectrum shown in **Figure 5b**. Mass spectrometry of the crude reaction mixture also reveals minor peaks at m/z = 612, 614, and 616 for partially cyclized material. (See ESI for further details).

To form **19**, **19'** must formally lose 8 hydrogen atoms, form two 5-membered rings, and fuse the bisanthene core (**19**, **Figure 5a**). The formation of **19** is analogous to the on-surface synthesis of related benzo[*a*]fluoranthene-capped nanographenes.[9] We propose that **19** is a mixture of the *cis*- and *trans*- isomers (***cis*-/*trans*-19**), but we have yet to confirm this because **19** is ^{1}H NMR silent, even at temperatures down to –80 °C. DFT predicts only a small thermodynamic energy difference of the ground states (<1 kcal mol^{-1}) in favor of the *trans*-isomer (***trans*-Me-19**), supporting that both isomers form during the reaction (See ESI S6).

Electron paramagnetic resonance (EPR) spectroscopy of ***cis*-/*trans*-19** at 30 °C gives a broad signal centered at g = 2.0022 (**Figure 5c**). This is consistent with a thermally accessible open-shell electron configuration. Density functional theory (DFT) calculations of the triplet state for a truncated model of ***cis***- and ***trans*-19** (***cis*-Me-19** and ***trans*-Me-19;** B3LYP-D3/Def2-SVP level of theory) suggest a delocalized spin-density that is concentrated on quaternary carbon atoms embedded in the 5-membered ring (**Figure 5d**), explaining the absence of observable hyperfine features.[47,51] The UV-vis spectrum of the product (**Figure 5e**) shows a broad band centered in the near-IR (NIR) range at 806 nm (FWHM ca.

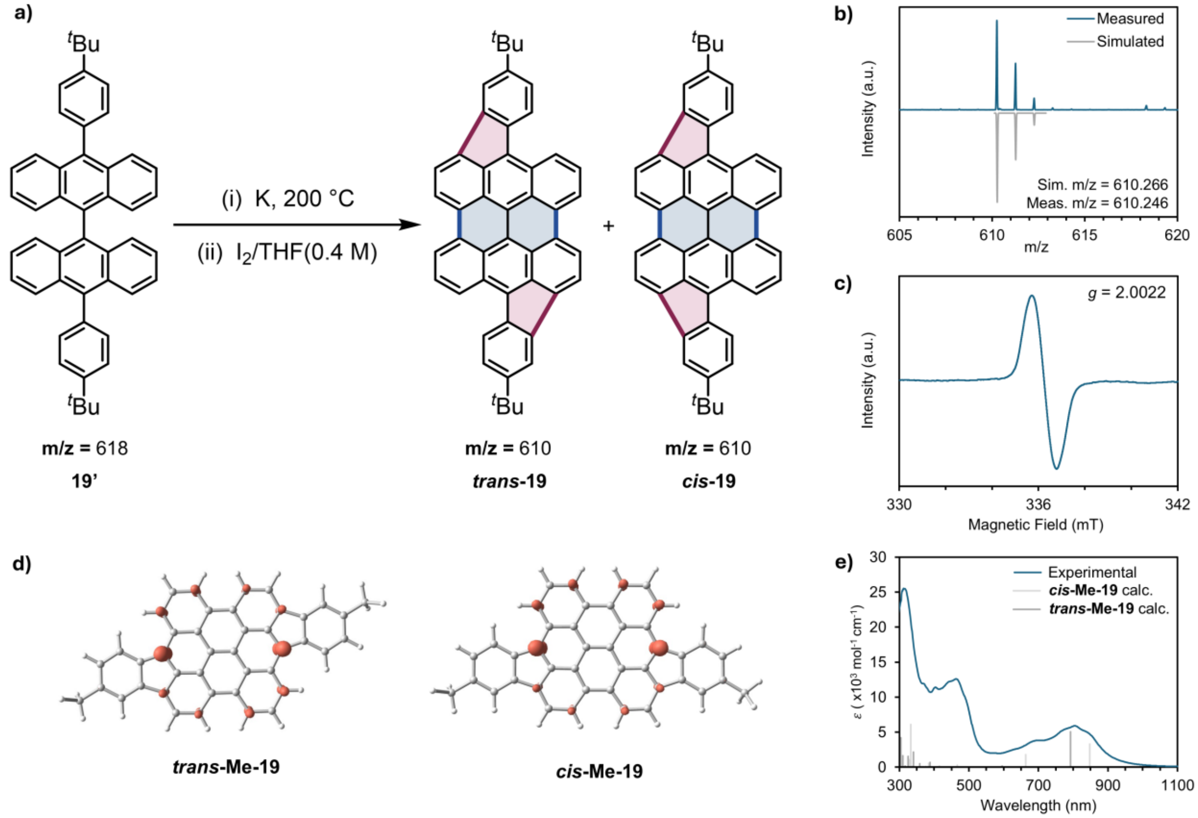


Figure 5. Cyclodehydrogenation to form the large nanographene **19** as a mixture of *cis*- and *trans* isomers. (a) overall reaction scheme; (b) measured and simulated MALDI for **19**; (c) X-band EPR spectrum of **19**; (d) spin density maps (DFT; B3LYP-D3/Def2SVP; isovalue = 0.015) of the triplet states for **19** (*tert*-butyl groups were reduced to methyl) (e) UV-vis absorption spectrum and calculated electronic transitions for ***cis*-/*trans*-Me-19** (B3LYP/Def2-TZVP).

150 nm), which is consistent with the simulated values obtained by TD-DFT (see **Figure 5e**). The ease of creating and isolating **19**, an interesting open-shell PAH, speaks to the power of this method and its applicability to larger nanocarbon systems.

In summary, we have revealed a new method to create nanographenes using molten alkali metals with both 5- and 6-membered rings using molten alkali metals. Furthermore, we show the formation of zig-zag-edged structures through incorporation of pendant methyl and amino groups. The study culminates with the formation of an open-shell bisanthene nanographene. Importantly, we are able to extend perylene both laterally (bisanthene) and longitudinally (terrylene), allowing the formation of extended nanographenes with interesting properties. In demonstrating the diverse reactivity of this system, we highlight the similarities between this reactivity and that of noble metal surfaces. This molten metal approach enables a broad range of scalable, bottom-up syntheses of novel nanographenes and nanoribbons.

Note on Synthesis

Due to the non-traditional nature of the reaction, and the high reactivity of some reagents, a detailed description of the experimental procedure and an additional safety note can be found in the ESI (S1). In our experience, this approach, performed on the scale outlined in this work, is controlled and safe when performed with adequate caution under inert (water and oxygen free) conditions.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/

Materials, experimental methods, and characterization, including NMR Spectroscopy, Mass Spectrometry, single crystal data, UV-Vis spectroscopy, and DFT calculations.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

REFERENCES

(1) Fischer, F. R. Bottom-up Synthesis of Graphene Nanoribbons on Surfaces. *Advances in Polymer Science* **2017**, *278*, 33–65. https://doi.org/10.1007/12_2017_2.

(2) Cai, J.; Ruffieux, P.; Jaafar, R.; Bieri, M.; Braun, T.; Blankenburg, S.; Muoth, M.; Seitsonen, A. P.; Saleh, M.; Feng, X.; Müllen, K.; Fasel, R. Atomically Precise Bottom-up Fabrication of Graphene Nanoribbons. *Nature* **2010**, *466*, 470-473. https://doi.org/10.1038/nature09211.

(3) Shekhirev, M.; Sinitskii, A. Solution Synthesis of Atomically Precise Graphene Nanoribbons. *Physical Sciences Reviews* **2017**, *2*, 20160108. https://doi.org/10.1515/psr-2016-0108.

(4) Mccurdy, R. D.; Jacobse, P. H.; Piskun, I.; Veber, G. C.; Rizzo, D. J.; Zuzak, R.; Mutlu, Z.; Bokor, J.; Crommie, M. F.; Fischer, F. R. Synergetic Bottom-Up Synthesis of Graphene Nanoribbons by Matrix-Assisted Direct Transfer. *J. Am. Chem. Soc* **2021**, *143*, 59. https://doi.org/10.1021/jacs.1c01355.

(5) Chen, Z.; Narita, A.; Müllen, K.; Graphene Nanoribbons: On-Surface Synthesis and Integration into Electronic Devices. *Advanced Materials* **2020**, *32*, 2001893. https://doi.org/10.1002/ADMA.202001893.

(6) Narita, A.; Feng, X.; Hernandez, Y.; Jensen, S. A.; Bonn, M.; Yang, H.; Verzhbitskiy, I. A.; Casiraghi, C.; Hansen, M. R.; Koch, A. H. R.; Fytas, G.; Ivasenko, O.; Li, B.; Mali, K. S.; Balandina, T.; Mahesh, S.; De Feyter, S.; Müllen, K. Synthesis of Structurally Well-Defined and Liquid-Phase-Processable Graphene Nanoribbons. *Nature Chemistry* **2014**, *6*, 126-132. https://doi.org/10.1038/NCHEM.1819.

(7) Treier, M.; Pignedoli, C. A.; Laino, T.; Rieger, R.; Müllen, K.; Passerone, D.; Fasel, R. Surface-Assisted Cyclodehydrogenation Provides a Synthetic Route towards Easily Processable and Chemically Tailored Nanographenes. *Nature Chemistry* **2011**, *3,* 61-67. https://doi.org/10.1038/NCHEM.891.

(8) Blackwell, R. E.; Zhao, F.; Brooks, E.; Zhu, J.; Piskun, I.; Wang, S.; Delgado, A.; Lee, Y.-L.; Louie, S. G.; Fischer, F. R. Spin Splitting of Dopant Edge State in Magnetic Zigzag Graphene Nanoribbons. *Nature* **2021**, *600,* 647-652. https://doi.org/10.1038/s41586-021-04201-y.

(9) Jacobse, P. H.; Daugherty, M. C.; Čerņevičs, K.; Wang, Z.; McCurdy, R. D.; Yazyev, O. V.; Fischer, F. R.; Crommie, M. F. Five-Membered Rings Create Off-Zero Modes in Nanographene. *ACS Nano* **2023**, *17,* 24901–24909. https://doi.org/10.1021/ACSNANO.3C06006.

(10) Fujishiro, K.; Morinaka, Y.; Ono, Y.; Tanaka, T.; Scott, L. T.; Ito, H.; Itami, K. Lithium-Mediated Mechanochemical Cyclodehydrogenation. *J Am Chem Soc* **2023**, *145* (14), 8163–8175. https://doi.org/10.1021/jacs.3c01185.

(11) Rickhaus, M.; Belanger, A. P.; Wegner, H. A.; Scott, L. T. An Oxidation Induced by Potassium Metal. Studies on the Anionic Cyclodehydrogenation of 1,1′-Binaphthyl to Perylene. *Journal of Organic Chemistry* **2010**, *75,* 7358–7364. https://doi.org/10.1021/JO101635Z.

(12) Borioni, J. L.; Baumgartner, M. T.; Puiatti, M.; Jimenez, L. B. 1-Substituted Perylene Derivatives by Anionic Cyclodehydrogenation: Analysis of the Reaction Mechanism. *ACS Omega* **2022**, *7,* 21860–21867. https://doi.org/10.1021/ACSOMEGA.2C02017.

(13) Wang, C. S.; Sun, Q.; García, F.; Wang, C.; Yoshikai, N. Robust Cobalt Catalyst for Nitrile/Alkyne [2+2+2] Cycloaddition: Synthesis of Polyarylpyridines and Their Mechanochemical Cyclodehydrogenation to Nitrogen-Containing Polyaromatics. *Angewandte Chemie International Edition* **2021**, *60,* 9627–9634. https://doi.org/10.1002/ANIE.202017220.

(14) Ayalon, A.; Rabinovitz, M. Reductive Ring Closure of Helicenes. *Tetrahedron Lett* **1992**, *33,* 2395–2398. https://doi.org/10.1016/S0040-4039(00)74221-3.

(15) Solodovnikov, S. P.; Ioffe, S. T.; Zaks, Yu. B.; Kabachnik, M. I. On the Formation of Perylene When Metallic Potassium Reacts with 1,1′-Dinaphthyl in 1,2-Dimethoxyethane. *Bulletin of the Academy of Sciences of the USSR Division of Chemical Science* **1968**, *17*, 442–443. https://doi.org/10.1007/BF00908472.

(16) Tamarkin, D.; Beny, D.; Rabinovitz, M. Phenanthrenchinon Aus Benzil: Eine Neuartige Synthese Mit Kalium-Graphit-Interaclationsverbindungen. *Angewandte Chemie* **1984**, *96,* 594–595. https://doi.org/10.1002/ange.19840960809.

(17) Firmansyah, D.; Banasiewicz, M.; Gryko, D. T. Vertically-Expanded Imidazo[1,2-a]Pyridines and Imidazo[1,5-a]Pyridine via Dehydrogenative Coupling. *Org Biomol Chem* **2015**, *13,* 1367–1374. https://doi.org/10.1039/C4OB02383H.

(18) Kawasumi, K.; Mochida, K.; Kajino, T.; Segawa, Y.; Itami, K. Pd(OAc)$_2$/o-Chloranil/M(OTf)$_n$: A Catalyst for the Direct CÀH Arylation of Polycyclic Aromatic Hydrocarbons with Boryl-, Silyl-, and Unfunctionalized Arenes. *Organic Letters* **2012**, *14*, 418-421. https://doi.org/10.1021/ol203235w.

(19) Markiewicz, J. T.; Wudl, F. Perylene, Oligorylenes, and Aza-Analogs. *ACS Appl Mater Interfaces* **2015**, *51,* 28063–28085. https://doi.org/10.1021/acsami.5b02243.

(20) Zhou, Z.; Egger, D. T.; Hu, C.; Pennachio, M.; Wei, Z.; Kawade, R. K.; Üngör, Ö; Gershoni-Poranne, R.; Petrukhina, M. A.; Alabugin, I. V. Localized Antiaromaticity Hotspot Drives Reductive Dehydrogenative Cyclizations in Bis-and Mono-Helicenes. *J. Am. Chem. Soc* **2022**, *144,* 12321–12338. https://doi.org/10.1021/jacs.2c03681.

(21) Eaton, S. W.; Miller, S. A.; Margulies, E. A.; Shoer, L. E.; Schaller, R. D.; Wasielewski, M. R. Singlet Exciton Fission in Thin Films of Tert-Butyl-Substituted Terrylenes. *The Journal of Physical Chemistry A* **2015**, *119,* 4151-4161. https://doi.org/10.1021/acs.jpca.5b02719.

(22) Zhang, X.; Li, D.; Tan, C. C. H.; Hanindita, F.; Hamamoto, Y.; Foster, A. S.; Kawai, S.; Ito, S. Synthesis of Azahexabenzocoronenium Salts through a Formal [3 + 3] Cycloaddition Strategy. *Nature Synthesis* **2024**, *3,* 1283–1291. https://doi.org/10.1038/s44160-024-00595-5.

(23) Paskovich, D. H.; Das, N. C. Formation of Substituted Phenalenes from the Reduction of Pyrene and Perylene. *Chemical Communications* **1967**, *1,* 39–40. https://doi.org/https://doi.org/10.1039/C19670000039.

(24) Eisenstein, O.; Mazaleyrat, J. P.; Tordeux, M.; Welvart, Z. Regio- and Stereoselectivity of Chiral Binaphthyl Reductive Aminoalkylation. Rotational Conformation and Electron Distribution of Alkali-Metal Biarylides. *J Am Chem Soc* **1977**, *99*, 2230–2235. https://doi.org/10.1021/ja00449a033.

(25) Huo, G.; Xu, W.; Hu, J.; Han, Y.; Fan, W.; Wang, W.; Sun, Z.; Yang, H.; Wu, J. Perylene-Embedded Helical Nanographenes with Emission up to 1010 Nm: Synthesis, Structures, and Chiroptical Properties. *Angewandte Chemie International Edition* **2024**, e202416707. https://doi.org/10.1002/anie.202416707.

(26) Watson, M. D.; Jäckel, F.; Severin, N.; Rabe, J. P.; Müllen, K. A Hexa-Peri-Hexabenzocoronene Cyclophane: An Addition to the Toolbox for Molecular Electronics. *J Am Chem Soc* **2004**, *126*, 1402–1407. https://doi.org/10.1021/ja037520p.

(27) Zhang, Z.; Zhu, H.; Gu, J.; Shi, H.; Hirose, T.; Jiang, L.; Zhu, Y.; Zhong, D.; Wang, J. Nonplanar Nanographene with a Large Conjugated π-Surface. *J Am Chem Soc* **2024**, *146*, 24681–24688. https://doi.org/10.1021/jacs.4c09167.

(28) Benshafrut, R.; Hoffman, R. E.; Rabinovitz, M.; Müllen, K. An Unusual Charge Umpolung: Synthesis of the Bay Region Diketone 2,3:10,11-Dibenzoperylene-1,12-Dione. *Journal of Organic Chemistry* **1999**, *64,* 644–647. https://doi.org/10.1021/jo981562s.

(29) Clar, E.; Zander, M. 378. 1 : 12-2 : 3-10 : 11-Tribenzoperylene. *J Chem Soc* **1958**, 1861–1865. https://doi.org/10.1039/jr9580001861.

(30) Bohnen, A.; Koch, K. -H; Lüttke, W.; Müllen, K. Oligorylene as a Model for "Poly(Perinaphthalene)." *Angewandte Chemie International Edition in English* **1990**, *29,* 525–527. https://doi.org/10.1002/anie.199005251.

(31) Koch, K. -H; Müllen, K. Polyarylenes and Poly(Arylenevinylene)s, V. Synthesis of Tetraalkyl-Substituted Oligo(1,4-naphthylene)s and Cyclization to Soluble Oligo(Peri-

naphthylene)s). *Chem Ber* **1991**, *124*, 2091–2100. https://doi.org/10.1002/cber.19911240935.

(32) Birch, A. J. The Reduction of Organic Compounds by Metal-Ammonia Solutions. *Quarterly Reviews, Chemical Society* **1950**, *4* , 69. https://doi.org/10.1039/qr9500400069.

(33) Rizzo, D. J.; Veber, G.; Jiang, J.; McCurdy, R.; Cao, T.; Bronner, C.; Chen, T.; Louie, S. G.; Fischer, F. R.; Crommie, M. F. Inducing Metallicity in Graphene Nanoribbons via Zero-Mode Superlattices. *Science* **2020**, *369*, 1597-1603. https://doi.org/10.1126/SCIENCE.AAY3588.

(34) Shen, T.; Dijkstra, D.; Farrando-Pérez, A.; Boj, P. G.; Villalvilla, J. M.; Quintana, J. A.; Zou, Y.; Hou, X.; Wei, H.; Li, Z.; Sun, Z.; Díaz-García, M. A.; Wu, J. Fused Triangulene Dimers: Facile Synthesis by Intramolecular Radical-Radical Coupling and Application for Near-Infrared Lasers. *Angewandte Chemie International Edition* **2023**, *62*, e202304197. https://doi.org/10.1002/ANIE.202304197.

(35) Ruffieux, P.; Wang, S.; Yang, B.; Sanchez-Sanchez, C.; Liu, J.; Dienel, T.; Talirz, L.; Shinde, P.; Pignedoli, C. A.; Passerone, D.; Dumslaff, T.; Feng, X.; Müllen, K.; Fasel, R. On-Surface Synthesis of Graphene Nanoribbons with Zigzag Edge Topology. *Nature* **2016**, *531*, 489–492. https://doi.org/10.1038/nature17151.

(36) Gröning, O.; Wang, S.; Yao, X.; Pignedoli, C. A.; Borin Barin, G.; Daniels, C.; Cupo, A.; Meunier, V.; Feng, X.; Narita, A.; Müllen, K.; Ruffieux, P.; Fasel, R. Engineering of Robust Topological Quantum Phases in Graphene Nanoribbons. *Nature* **2018**, *560*, 209–213. https://doi.org/10.1038/s41586-018-0375-9.

(37) Smith, G. W.; Stalley, J. C. Anthanthrene. *Acta Crystallographica Section A: Cryst.Phys.,Diffr.,Theor.Crystallogr.* **1975**, *31*, S122.

(38) Tajima, K.; Matsuo, K.; Yamada, H.; Seki, S.; Fukui, N.; Shinokubo, H. Acridino[2,1,9,8-*klmna*]Acridine Bisimides: An Electron-Deficient π-System for Robust Radical Anions and N-Type Organic Semiconductors. *Angewandte Chemie International Edition* **2021**, *60* (25), 14060–14067. https://doi.org/10.1002/anie.202102708.

(39) Wegner, H. A.; Scott, L. T.; De Meijere, A. A New Suzuki-Heck-Type Coupling Cascade: Indeno[1,2,3]-Annelation of Polycyclic Aromatic Hydrocarbons. *Journal of Organic Chemistry* **2003**, *68* , 883–887. https://doi.org/10.1021/jo020367h.

(40) Wegner, H. A.; Reisch, H.; Rauch, K.; Demeter, A.; Zachariasse, K. A.; De Meijere, A.; Scott, L. T. Oligoindenopyrenes: A New Class of Polycyclic Aromatics. *Journal of Organic Chemistry* **2006**, *71*, 9080–9087. https://doi.org/10.1021/JO0613939.

(41) Lombardi, F.; Lodi, A.; Ma, J.; Liu, J.; Slota, M.; Narita, A.; Myers, W. K.; Müllen, K.; Feng, X.; Bogani, L. Quantum Units from the Topological Engineering of Molecular Graphenoids. *Science* **2019**, *366*, 1107–1110. https://doi.org/10.1126/SCIENCE.AAY7203.

(42) Allemann, O.; Duttwyler, S.; Romanato, P.; Baldridge, K. K.; Siegel, J. S. Proton-Catalyzed, Silane-Fueled Friedel-Crafts Coupling of Fluoroarenes. *Science* **2011**, *332*, 574–577. https://doi.org/10.1126/SCIENCE.1202432.

(43) Kawamura Eiji Tsurumaki Shinji Toyota, M. Facile Synthesis of Rubicenes by Scholl Reaction. *Synthesis (Stuttg)* **2018**, *50*, 134–138. https://doi.org/10.1055/s-0036-1588570.

(44) Toyota, S.; Ban, S.; Hara, M.; Kawamura, M.; Ikeda, H.; Tsurumaki, E. Synthesis and Properties of Rubicene-Based Aromatic π-Conjugated Compounds as Five-Membered Ring Embedded Planar Nanographenes. *Chemistry – A European Journal* **2023**, *29*, e202301346. https://doi.org/10.1002/CHEM.202301346.

(45) King, B. T.; Kroulík, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. Controlling the Scholl Reaction. *J Org Chem* **2007**, *72*, 2279–2288. https://doi.org/10.1021/jo061515x.

(46) Liu, J.; Dienel, T.; Liu, J.; Groening, O.; Cai, J.; Feng, X.; Mü, K.; Ruffieux, P.; Fasel, R. Building Pentagons into Graphenic Structures by On-Surface Polymerization and Aromatic Cyclodehydrogenation of Phenyl-Substituted Polycyclic Aromatic Hydrocarbons. *The Journal of Physical Chemistry C* **2016**, *120*, 17588–17593. https://doi.org/10.1021/acs.jpcc.6b05495.

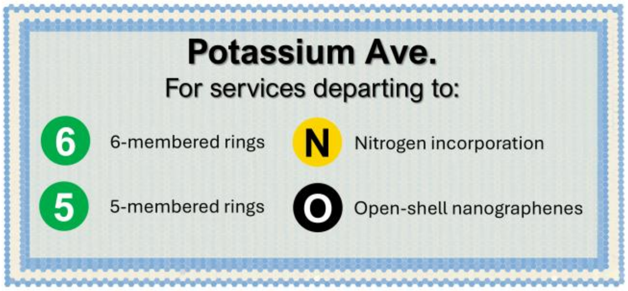
(47) Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kishi, R.; Shigeta, Y.; Nakano, M.; Tokunaga, K.; Kamada, K.; Kubo, T. Synthesis and Characterization of Quarteranthene: Elucidating the Characteristics of the Edge State of Graphene Nanoribbons at the Molecular Level. *J Am Chem Soc* **2013**, *135*, 1430–1437. https://doi.org/10.1021/JA309599M.

(48) Fort, E. H.; Scott, L. T. Facile Air-Oxidation of Large Aromatic Hydrocarbon Bay Regions to Bay Region Quinones: Predicted Oxygen-Sensitivity of Hydrogen-Terminated Carbon Nanotubes. *Org Biomol Chem* **2012**, *10*, 5747–5749. https://doi.org/10.1039/C2OB25208B.

(49) Fort, E. H.; Donovan, P. M.; Scott, L. T. Diels-Alder Reactivity of Polycyclic Aromatic Hydrocarbon Bay Regions: Implications for Metal-Free Growth of Single-Chirality Carbon Nanotubes. *J Am Chem Soc* **2009**, *131*, 16006–16007. https://doi.org/10.1021/ja907802g.

(50) Li, J.; Zhang, K.; Zhang, X.; Huang, K.-W.; Chi, C.; Wu, J. Meso-Substituted Bisanthenes as Soluble and Stable Near-Infrared Dyes. *J. Org. Chem* **2010**, *75*, 856–863. https://doi.org/10.1021/jo902413h.

(51) Zeng, Z.; Sung, Y. M.; Bao, N.; Tan, D.; Lee, R.; Zafra, J. L.; Lee, B. S.; Ishida, M.; Ding, J.; López Navarrete, J. T.; Li, Y.; Zeng, W.; Kim, D.; Huang, K. W.; Webster, R. D.; Casado, J.; Wu, J. Stable Tetrabenzo-Chichibabin's Hydrocarbons: Tunable Ground State and Unusual Transition between Their Closed-Shell and Open-Shell Resonance Forms. *J Am Chem Soc* **2012**, *134*, 14513–14525. https://doi.org/10.1021/ja3050579.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