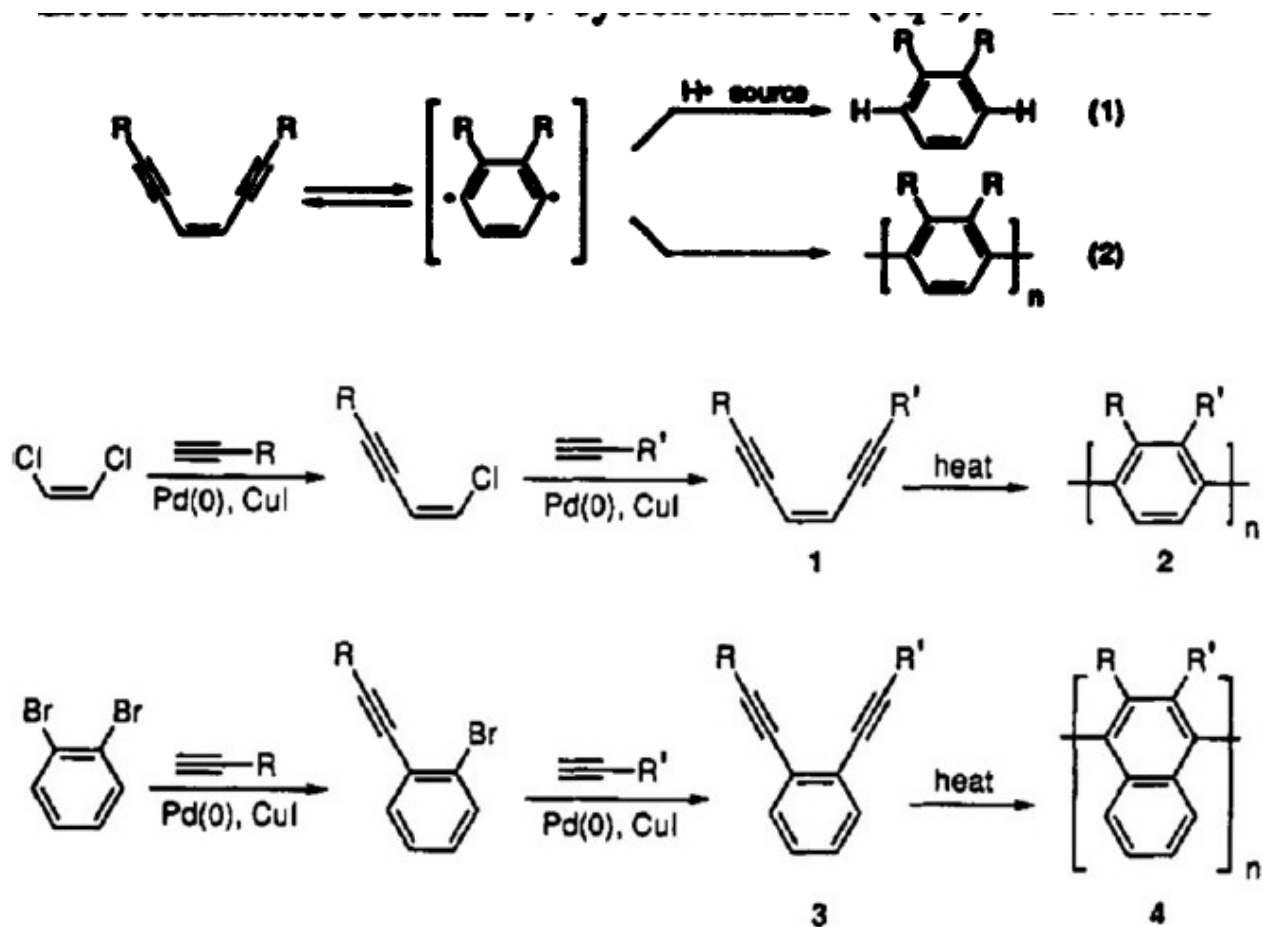


Bergman Cyclization based Acenes, Polyacenes and PDI derivatives

By: Robert B. Login rloginconsulting.com

The Bergman cyclization(BC) has been employed to prepare various polymers. BC enediynes rearrange to aromatic intermediate diradicals which can abstract protons or if none are readily available, couple to form polymers.



John, J. A., & Tour, J. M. (1994). Synthesis of polyphenylenes and polynaphthalenes by thermolysis of enediynes and dialkynylbenzenes. *Journal of the American Chemical Society*, 116(11), 5011-5012.

Shah, H. V., Babb, D. A., & Smith Jr, D. W. (2000). Bergman cyclopolymerization kinetics of bis-ortho-diynearenes to polynaphthalene networks. A comparison of calorimetric methods. *Polymer*, 41(12), 4415-4422.

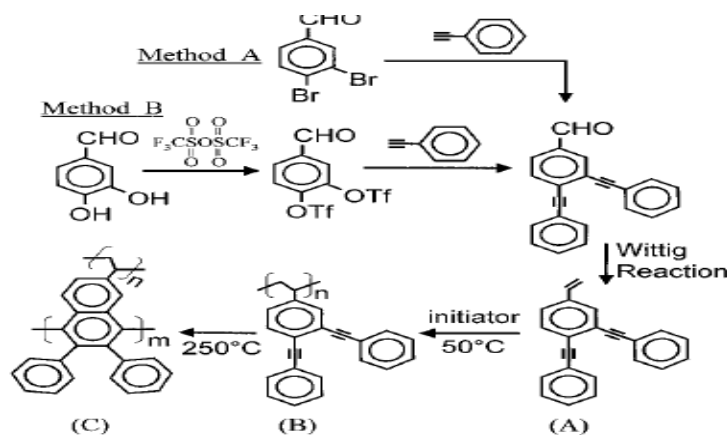
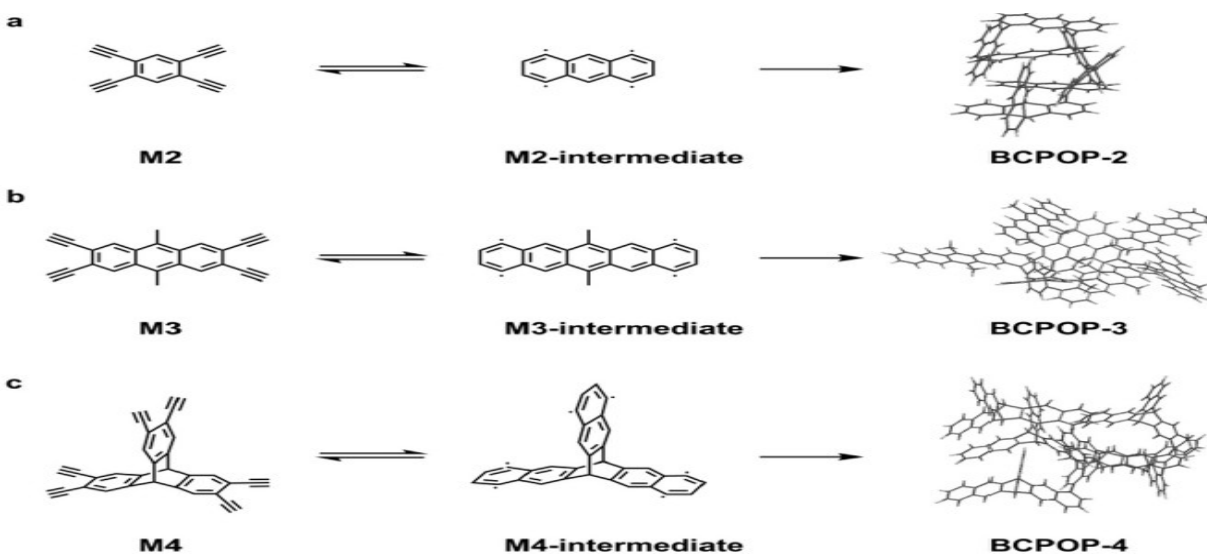


Figure 2. Synthetic route to formation of 3,4-bis(phenylethynyl)styrene followed by polymerization.

Chen, X., Tolbert, L. M., Hess, D. W., & Henderson, C. (2001). A Bergman cyclization approach to polymers for thin-film lithography. *Macromolecules*, 34(12), 4104-4108.

The above reference shows that BC can be used to post cross-link a free radical generated polymer or any polymer where a suitable enediyne can be incorporated. In fact the BC can initiate FR polymerization by itself.



Scheme 1. Synthesis route to a) BCPOP-2, b) BCPOP-3, and c) BCPOP-4.

Zhang, X. M., Ding, X., Hu, A., & Han, B. H. (2017). Synthesis of Bergman cyclization-based porous organic polymers and their performances in gas storage. *Polymer*, 118, 249-255.

BC polymer reviews:

Xiao, Y., & Hu, A. (2011). Bergman cyclization in polymer chemistry and material science. *Macromolecular rapid communications*, 32(21), 1688-1698.

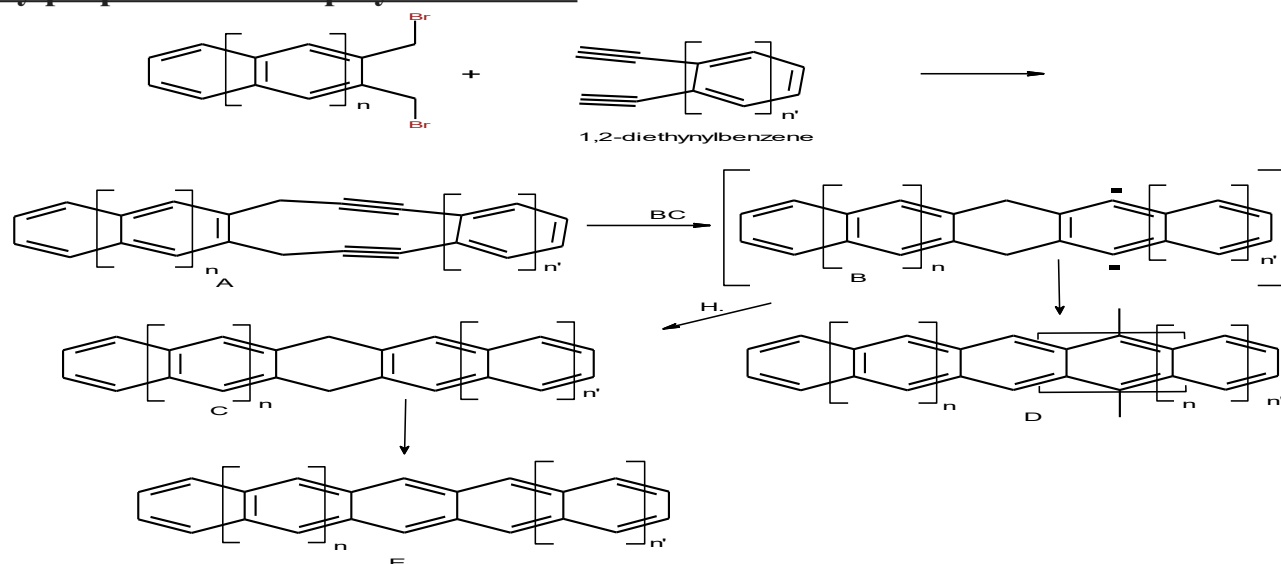
Wang, Y., Chen, S., & Hu, A. (2017). Construction of Polyarylenes with Various Structural Features via Bergman Cyclization Polymerization. In *Polymer Synthesis Based on Triple-bond Building Blocks*(pp. 97-126). Springer

Wang, C., Chen, S., Zhou, H., Gu, J., & Hu, A. (2018). Palladium-catalyzed cycloaromatization polymerization of enedynes. *Chinese Journal of Polymer Science*, 36(2), 237-243.

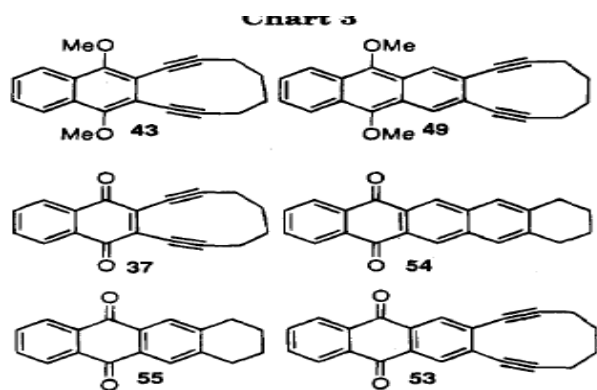
Prof. Hu is a leading BC polymer authority. He and his colleagues in the above references review BC mechanism and problems with BC chemistry but the essential

diradical mechanism can still explain most of this chemistry.

My proposals for BC polymerization:



Scheme 1: The starting compounds are well known. C is the proposed product when a source of protons are available. If not then a polymeric pentacene would form D (after aromatization) and mild oxidation would result in E. Scheme 1 is inherent in BC but I have not been able to find acene synthesis references to the above except for the following reference?

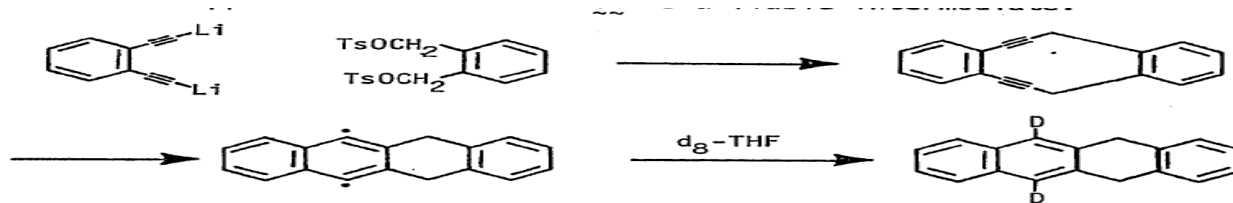


Semmelhack, M. F., Neu, T., & Foubelo, F. (1994). Arene 1, 4-diradical formation from o-dialkynylarenes. *The Journal of Organic Chemistry*, 59(17), 5038-5047. 49 starting compound for 54.

Although one could visualize there BC approach as a way to larger acenes, the cyclohexane ring is terminal. **Notice that in scheme 1(C) it interrupts the acenes resulting in stability!**

Possible negatives might be solubility and or stability problems where the BC reaction would be facile at unacceptably low temperatures? **But this is exactly why I think these are valuable proposals because of low or room temperature BC! BC can be conducted at temperatures that would not damage a sensitive substrate that they could be cast upon.**

Base catalyzed condensation of the alkynes and bromomethylbenzenes can be achieved at very low temperatures with very strong bases. These low temperatures would prevent BC. Work-up and warming would facilitate the BC in a controlled way. This would make the proposals in schemes 1-12 possible based on lower temperature BC.



H. N. C. Wong, and F. Sondheimer, Tetrahedron Lett. 217 (1980).

Nicolaou, K. C., Zuccarello, G., Riemer, C., Estevez, V. A., & Dai, W. M. (1992). Design, synthesis, and study of simple monocyclic conjugated enediynes. The 10-membered ring enediyne moiety of the enediyne anticancer antibiotics. *Journal of the American Chemical Society*, 114(19), 7360-7371.

Obviously Wong and Sondheimer had no trouble preparing the above followed by BC **which occurred at RT**. My claim is that this reaction can be controlled at lower temperatures.

Their Li-salt reacted with the tosylate is another synthesis approach that would probably also work with my proposals.

The following are reviews of BC:

Grissom, J. W., Gunawardena, G. U., Klingberg, D., & Huang, D. (1996). The chemistry of enediynes, enyne allenes and related compounds. *Tetrahedron*, 52(19), 6453-6518.

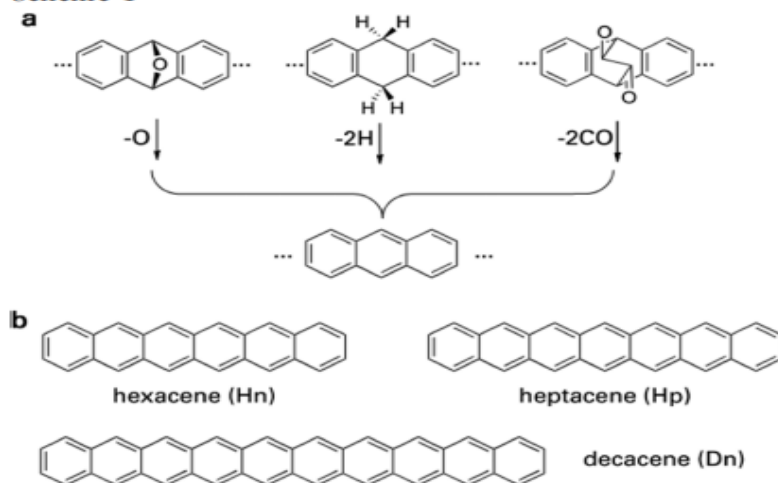
Wang, K. K. (1996). Cascade radical cyclizations via biradicals generated from enediynes, enyne-Allenes, and enyne-ketenes. *Chemical reviews*, 96(1), 207-222.

Kar, M., & Basak, A. (2007). Design, synthesis, and biological activity of unnatural enediynes and related analogues equipped with pH-dependent or photo triggering devices. *Chemical reviews*, 107(7), 2861-2890.

Kraka, E., & Cremer, D. (2014). Enediynes, enyne-allenes, their reactions, and beyond. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 4(4), 285-324.

On-Surface Synthesis of Acenes. On-surface chemistry allows to produce molecular compounds that cannot be prepared by standard solution-based methods due to their low solubility and instability.^{18–21} On a surface maintained in ultrahigh vacuum, the high chemical reactivity of long acenes can be kept under control by inducing the final steps of the synthesis through deoxygenation,^{11–13} dehydrogenation,¹⁴ or decarbonylation^{15,16} (see Scheme 1). Choosing the Au(111)

Scheme 1^a



^a(a) On-surface generation of large acenes starting from three different types of precursors: epoxyacenes (left), hydroacenes (center), and α -diketone (right) precursors. (b) Large acenes obtained and studied on Au(111) through on-surface deoxygenation.

surface as substrate has the advantage that the electronic coupling between acenes and surface is relatively weak, in contrast to Cu(111)^{22,23} or Ag(111).¹⁶ In the experiments

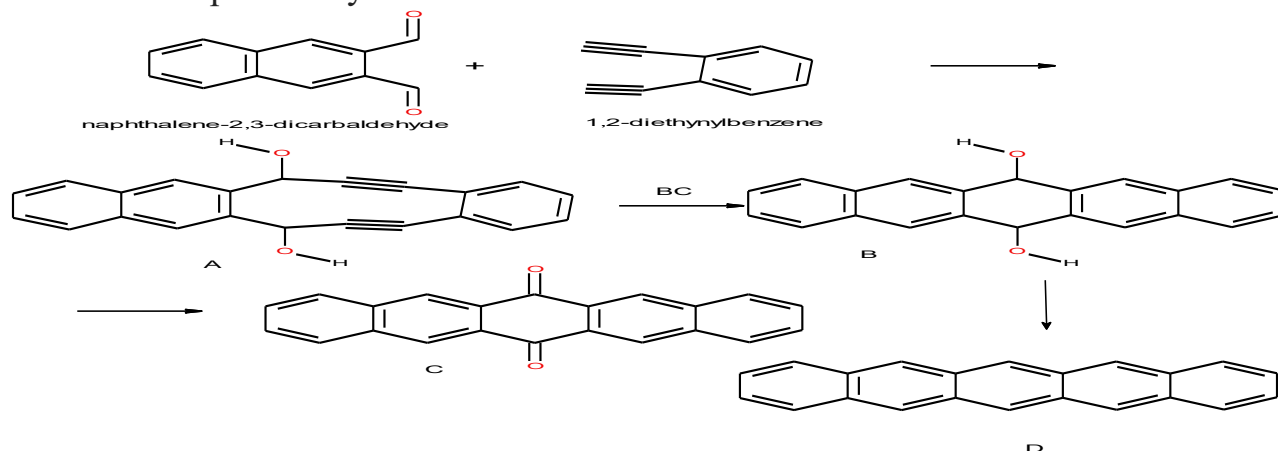
The above copied from:

Krüger, J., Eisenhut, F., Skidin, D., Lehmann, T., Ryndyk, D. A., Cuniberti, G., ... & Peña, D. (2018). Electronic Resonances and Gap Stabilization of Higher Acenes on a Gold Surface. *ACS nano*, 12(8), 8506-8511.

The above can be applied to my proposals should more conventional synthesis approaches prove unacceptable.

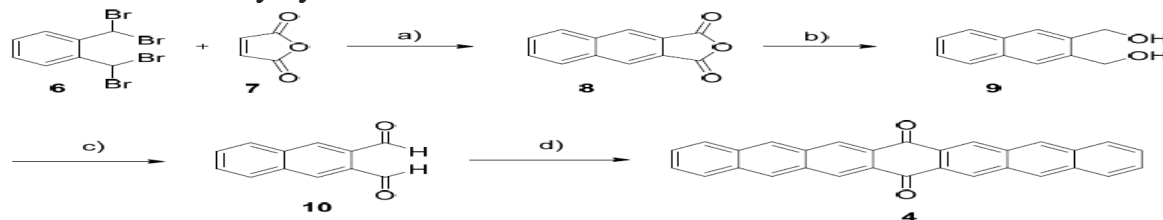
Wang, T., & Zhu, J. (2019). Confined on-surface organic synthesis: strategies and mechanisms. *Surface Science Reports*.

Another acene possibility:



Scheme 2: In this proposal, if protons are available then B would result. Mild oxidation would afford C and dehydration, D. The following reference shows how to prepare acenes with chemistry that can be applied to my proposals. I believe the above enediynes would undergo BC at relatively low temperatures.

The RM's are easily synthesized:

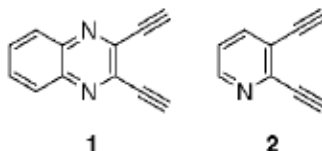


Scheme S1. Synthesis of 7,6-heptacenequinone (**4**). A) NaI, DMF, 4.5h/70 °C, 50 %; b) LAH, THF, 77 %; c) oxalylchloride, DMSO, dichloromethane, -80 °C, 99 %; d) 1,4-cyclohexanedione, KOH, H₂O, EtOH, reflux, 78 %.

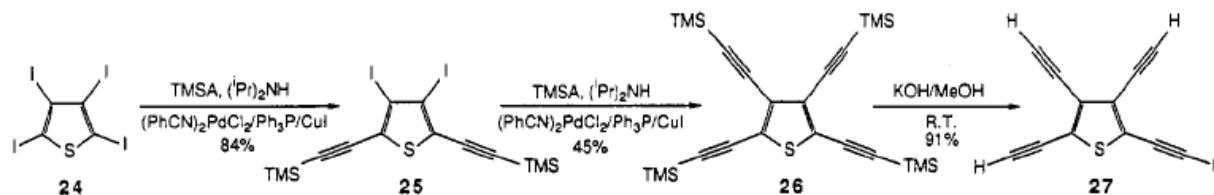
Einholz, R., Fang, T., Berger, R., Grüninger, P., Früh, A., Chassé, T., ... & Bettinger, H. F. (2017). Heptacene: characterization in solution, in the solid state, and in films. *Journal of the American Chemical Society*, 139(12), 4435-4442.

Note: 6 is commercially available and 9 can be converted to the di-Br derivative(scheme 1).

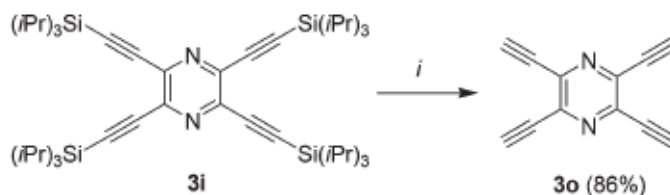
As an aside, let me point out that the starting compounds can be heterocyclics.



Kim, C. S., & Russell, K. C. (1998). Rapid Bergman cyclization of 1, 2-diethynylheteroarenes. *The Journal of Organic Chemistry*, 63(23), 8229-8234.

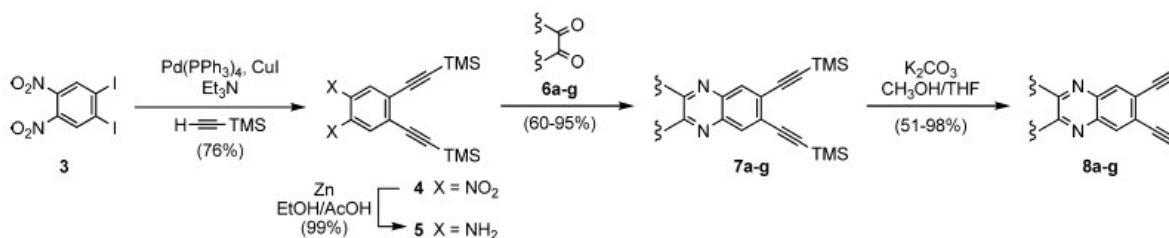


Neenan, T. X., & Whitesides, G. M. (1988). Synthesis of high carbon materials from acetylenic precursors. Preparation of aromatic monomers bearing multiple ethynyl groups. *The Journal of Organic Chemistry*, 53(11), 2489-2496.

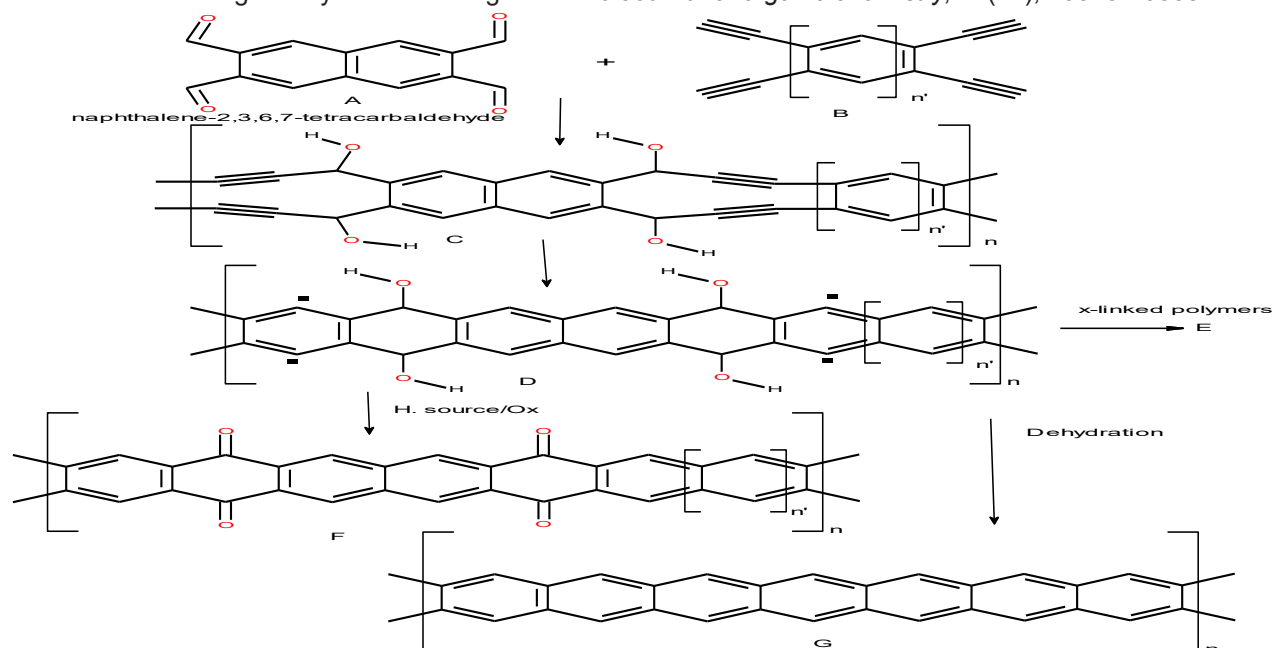


Scheme 4 Synthesis of **3o**; conditions: *i*: TBAF, THF, 0 → 20 °C, 2 h.

Petrosyan, A., Ehlers, P., Surkus, A. E., Ghochikyan, T. V., Saghyan, A. S., Lochbrunner, S., & Langer, P. (2016). Straightforward synthesis of tetraalkynylpyrazines and their photophysical properties. *Organic & biomolecular chemistry*, 14(4), 1442-1449.

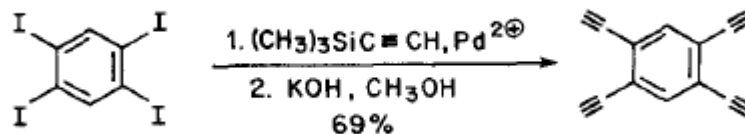


Spence, J. D., Rios, A. C., Frost, M. A., McCutcheon, C. M., Cox, C. D., Chavez, S., ... & Gherman, B. F. (2012). Syntheses, thermal reactivities, and computational studies of aryl-fused quinoxalenediynes: effect of extended benzannelation on Bergman cyclization energetics. *The Journal of organic chemistry*, 77(22), 10329-10339.



Scheme 3: The starting compounds are known (Lin, Y. C., Lin, C. H., Chen, C. Y., Sun, S. S., & Pal, B. (2011). Synthesis of electron deficient acene derivatives via a bidirectional iterative elongation reaction. *Organic & biomolecular chemistry*, 9(12), 4507-4517.

Zhang, X. M., Ding, X., Hu, A., & Han, B. H. (2017). Synthesis of Bergman cyclization-based porous organic polymers and their performances in gas storage. *Polymer*, 118, 249-255.



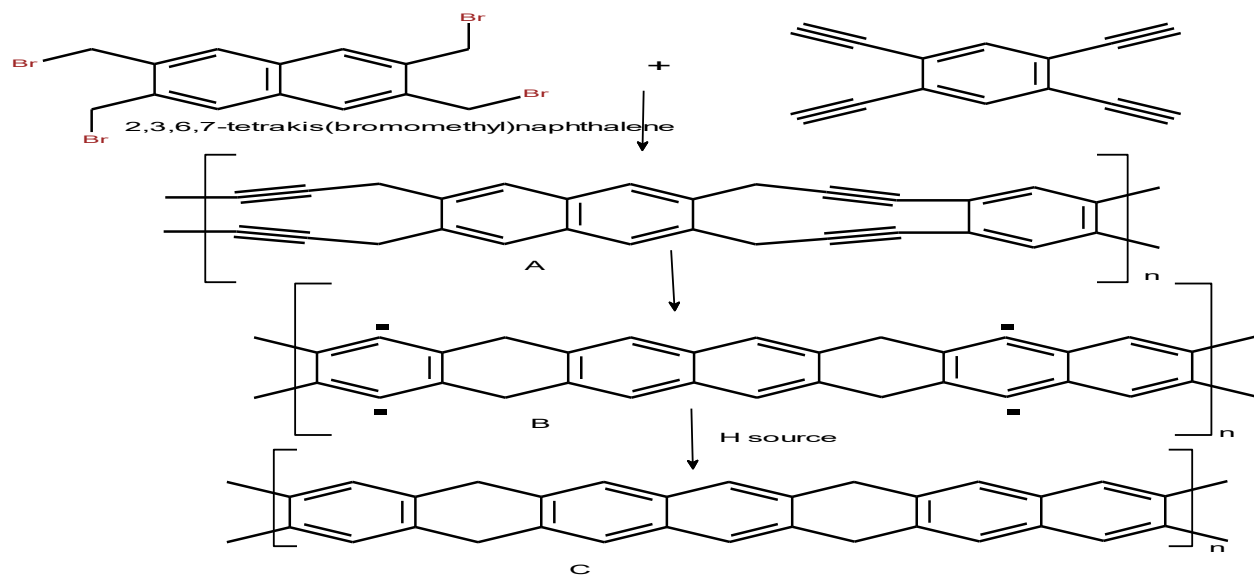
Vollhardt, K. P. C. (1984). Cobalt-Mediated [2+ 2+ 2]-Cycloadditions: A Maturing Synthetic Strategy [New Synthetic Methods (43)]. *Angewandte Chemie International Edition in English*, 23(8), 539-556.

Obviously the solvent/base needed to form C are undefined and would require experimentation. In the above case (scheme 3) the solvent would need to have a source of protons to prevent the BC from undergoing cross-linking polymerization. The alcohols can be oxidized (F) or removed (dehydrated) in favor of the aromatic (G) derivative. G apparently is very unstable if not on a gold surface as mentioned above while F should be stable.

Athans, A. J., Briggs, J. B., Jia, W., & Miller, G. P. (2007). Hydrogen-protected acenes. *Journal of Material Chemistry*, 17(25), 2636-2641.

Zuzak, R., Dorel, R., Kolmer, M., Szymonski, M., Godlewski, S., & Echavarren, A. M. (2018). Higher Acenes by On-

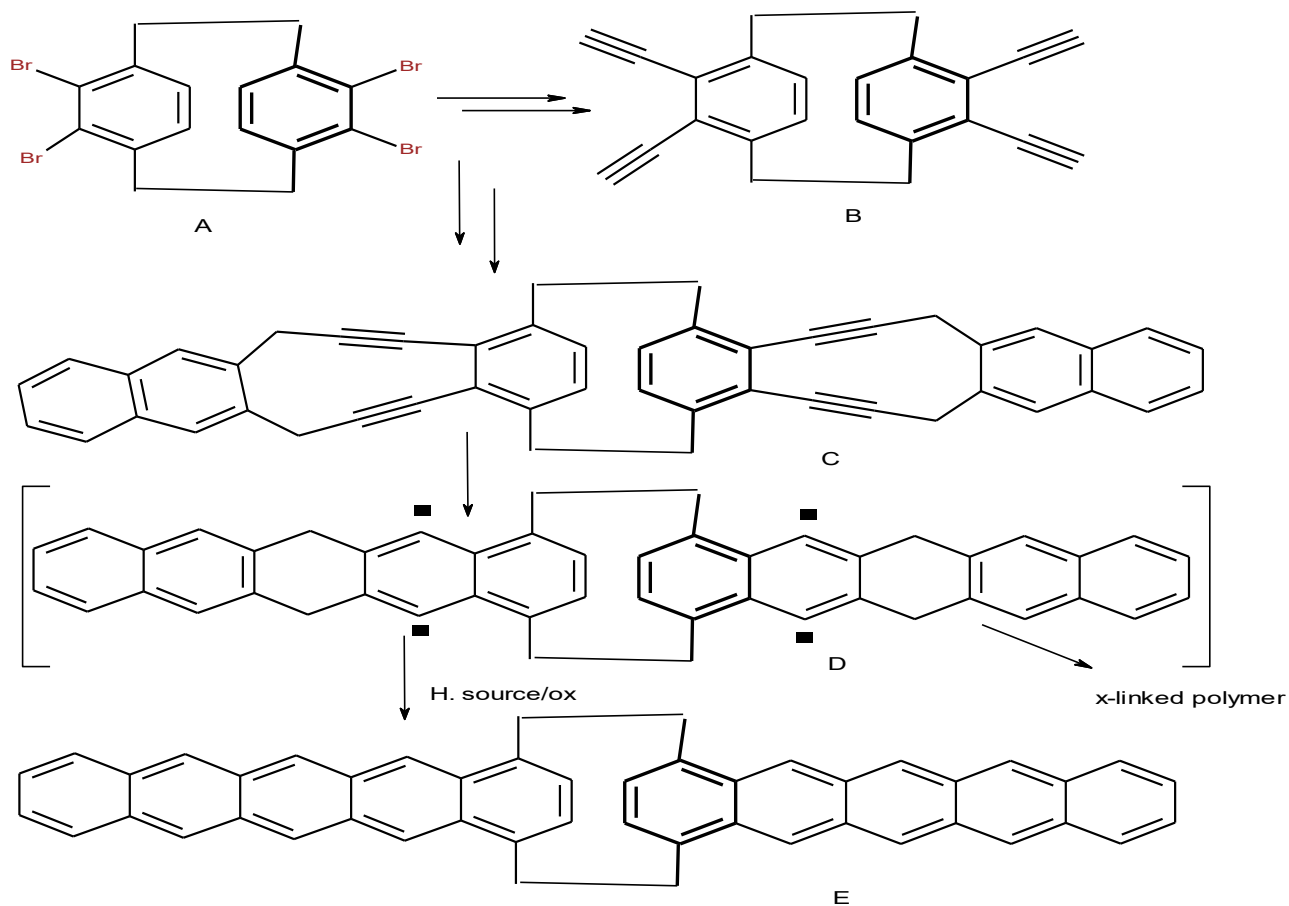
Surface Dehydrogenation: From Heptacene to Undecacene. *Angewandte Chemie International Edition*, 57(33), 10500-10505.



Scheme 4: Reaction leading to stable interrupted acene. I believe that the BC starting intermediate A would be stable at some lower temperature this would allow the BC to occur on the surface of say a silicone or organic semiconductor after warming, where subsequent controlled oxidation would result in the acene derivative. Encapsulation would stabilize the acene from further degradation. This could be a way to obtain singlet fission. This is the point of these ideas, that unlike other BC reactions that require relatively high temperatures that would destroy a substrate that they were coated on, these proposals undergo BC at room or lower temperatures. (Note: starting tetra-bromo compound is a known compound.)

Otsubo, T., Aso, Y., Ogura, F., Misumi, S., Kawamoto, A., & Tanaka, J. (1989). Synthesis, Structure, and Properties of Triple-Layered [2.2][2.2] Naphthalenophane. *Bulletin of the Chemical Society of Japan*, 62(1), 164-170.

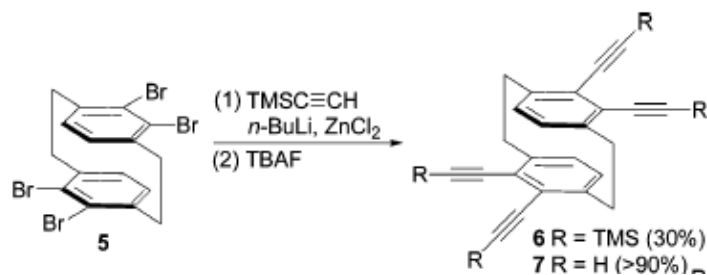
Carey, T. J., Miller, E. G., Gilligan, A. T., Sammakia, T., & Damrauer, N. H. (2018). Modular synthesis of rigid polyacene dimers for singlet fission. *Organic letters*, 20(2), 457-460.



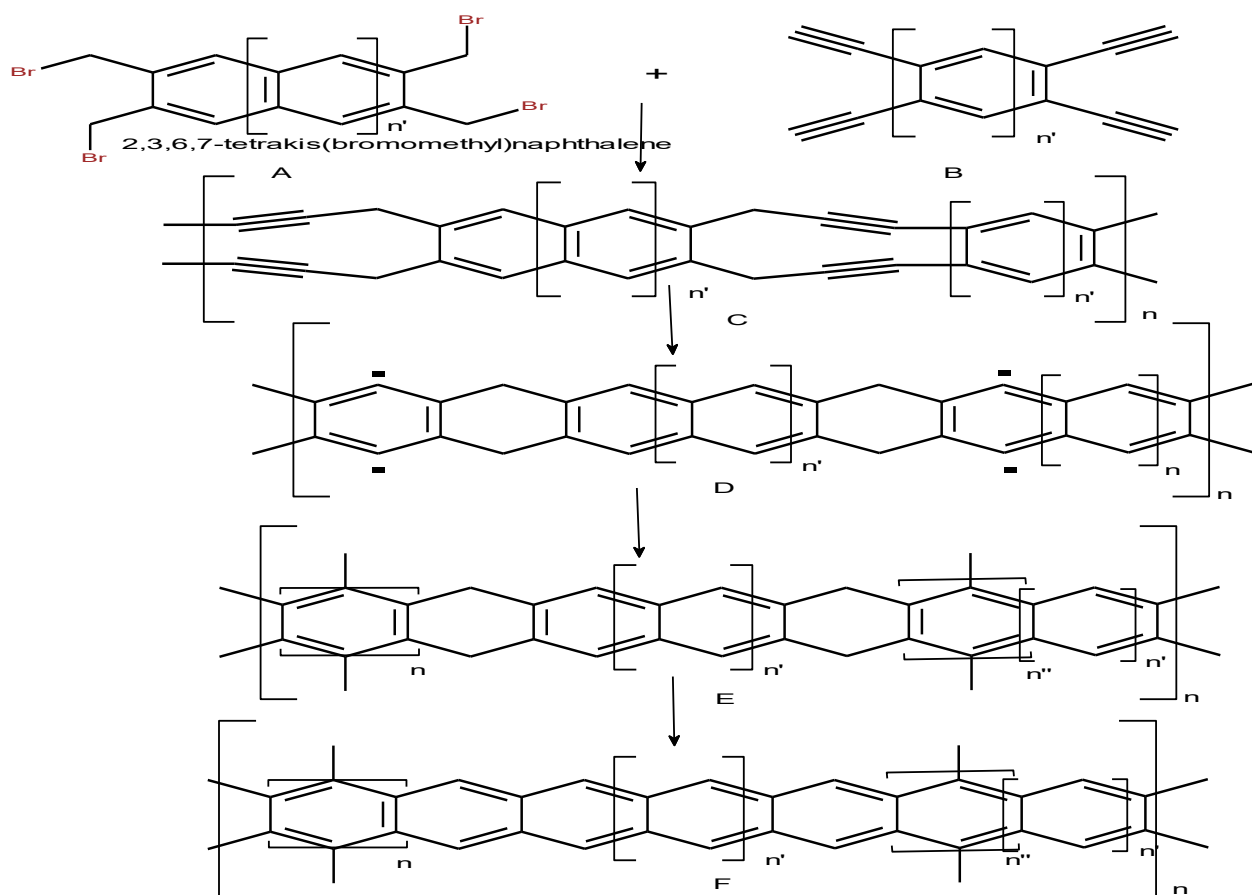
Scheme 5: In this case, the pentacenes are separated by the [2,2]paracyclophane and this might be a good approach to singlet fission. Although [2,2]paracyclophanes are shown, it might be necessary to tune the SF by further separation of the [n,n']paracyclophanes.

Synthesis of starting compounds see:

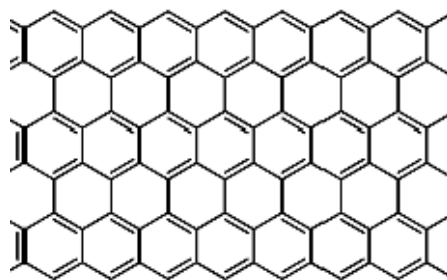
SCHEME 1



Leung, M. K., Viswanath, M. B., Chou, P. T., Pu, S. C., Lin, H. C., & Jin, B. Y. (2005). The Phane Properties of a nti-[2.2](1, 4) Biphenylenophane. *The Journal of organic chemistry*,70(9), 3560-3568.



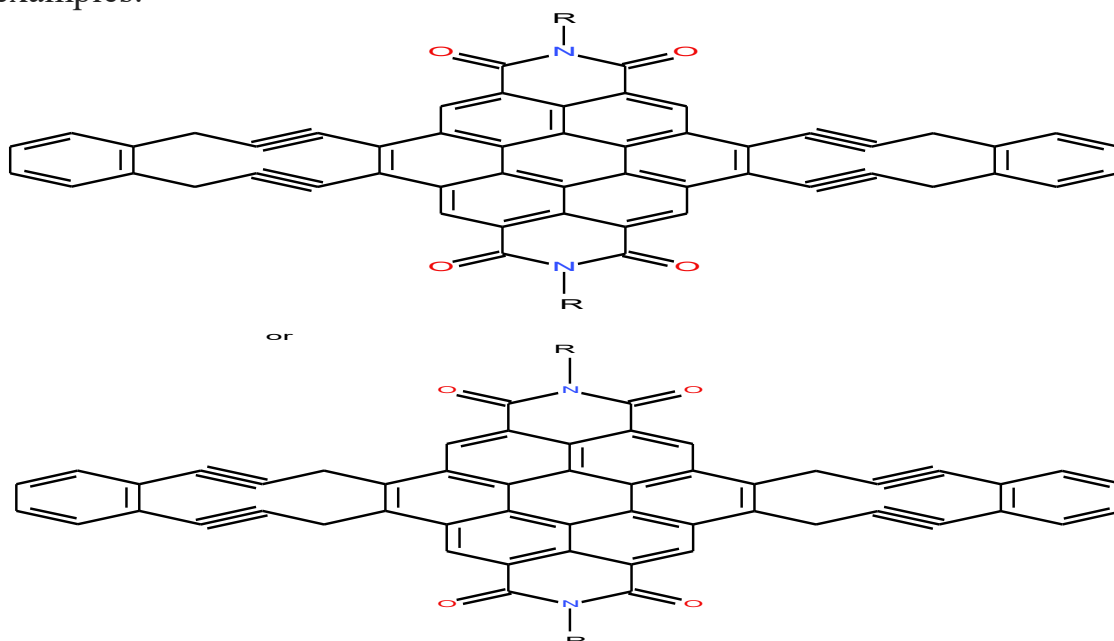
Scheme 6: In this idea the conditions do not afford a source of protons so the intermediates undergo cross-linking polymerization. Subsequent oxidation would afford the acene. Compound C should be stable enough to be cast onto a solid surface where it can be both cross-linked and oxidized to an acene. If done on a semiconducting silicone or an organic Solar Cell, it could function as a source of singlet fission resulting in the solar cells exhibiting greater efficiency.



It's possible that Scheme 6 D can be further reacted, for example with FeCl_3 , to form graphenes. However, random cross-linked porous resins, possibly suitable for CO_2 storage, are more likely.

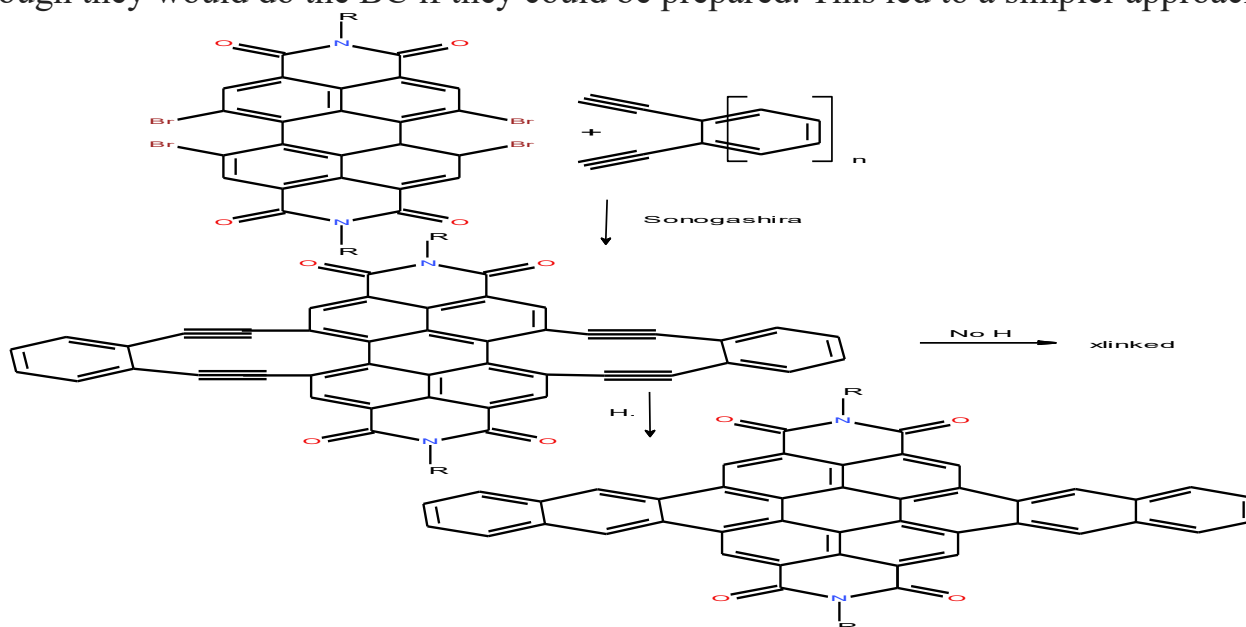
Wang, X. Y., Yao, X., & Müllen, K. (2019). Polycyclic aromatic hydrocarbons in the graphene era. *Science China Chemistry*, 1-46.

My proposals are based on known BC chemistry but in new contexts.
 More examples:

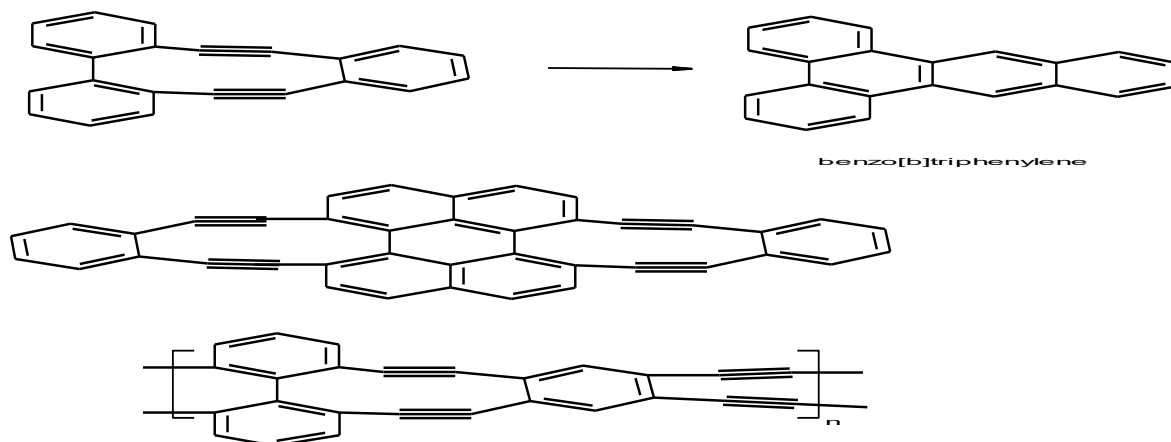


Scheme 7: Rather than drawing starting compounds and potential products, I'm just showing the key intermediate. A polymeric versions of the above can also be visualized either through the imides or by difunctional BC components.

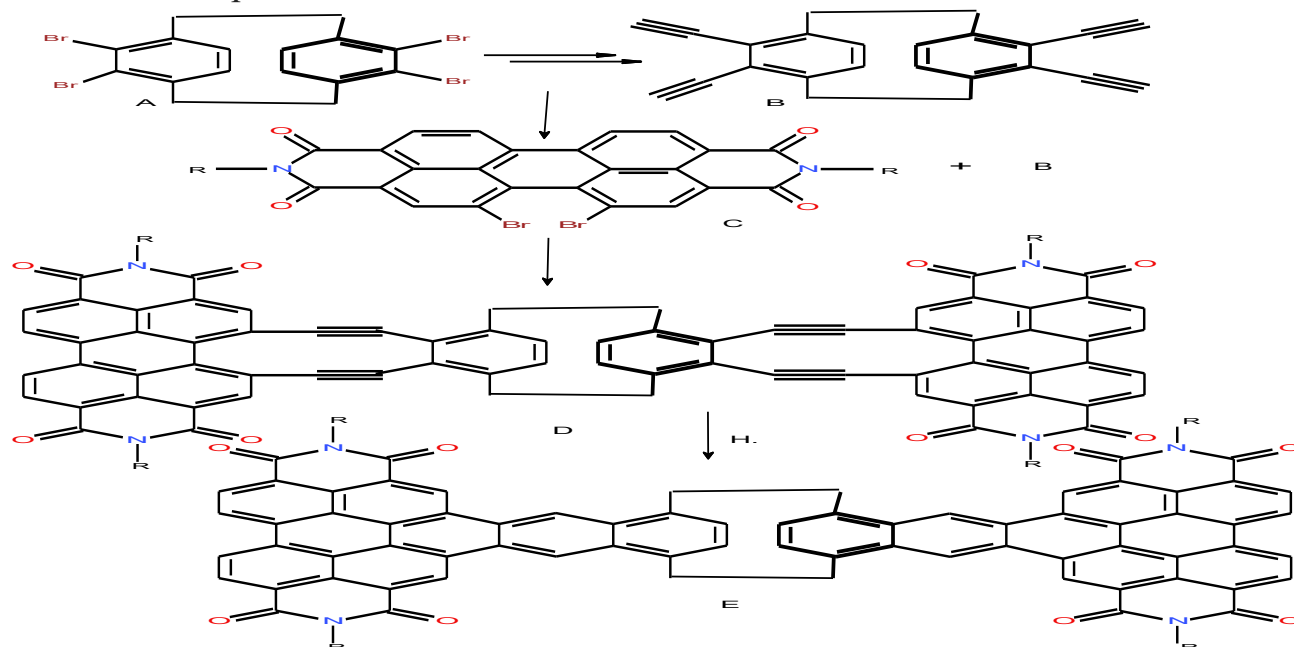
Thinking about scheme 7, it might be difficult to synthesize these compounds, even though they would do the BC if they could be prepared. This led to a simpler approach.



Scheme 8: The tetra-bromo derivative, as is the alkyne are wellknown RM's. The coupling reaction typically is high yield. The bay position is ideal for a ten-membered BC and no oxidation is required. Also it is unlikely that the BC would go the other way resulting in an 8membered and 4 membered rings.



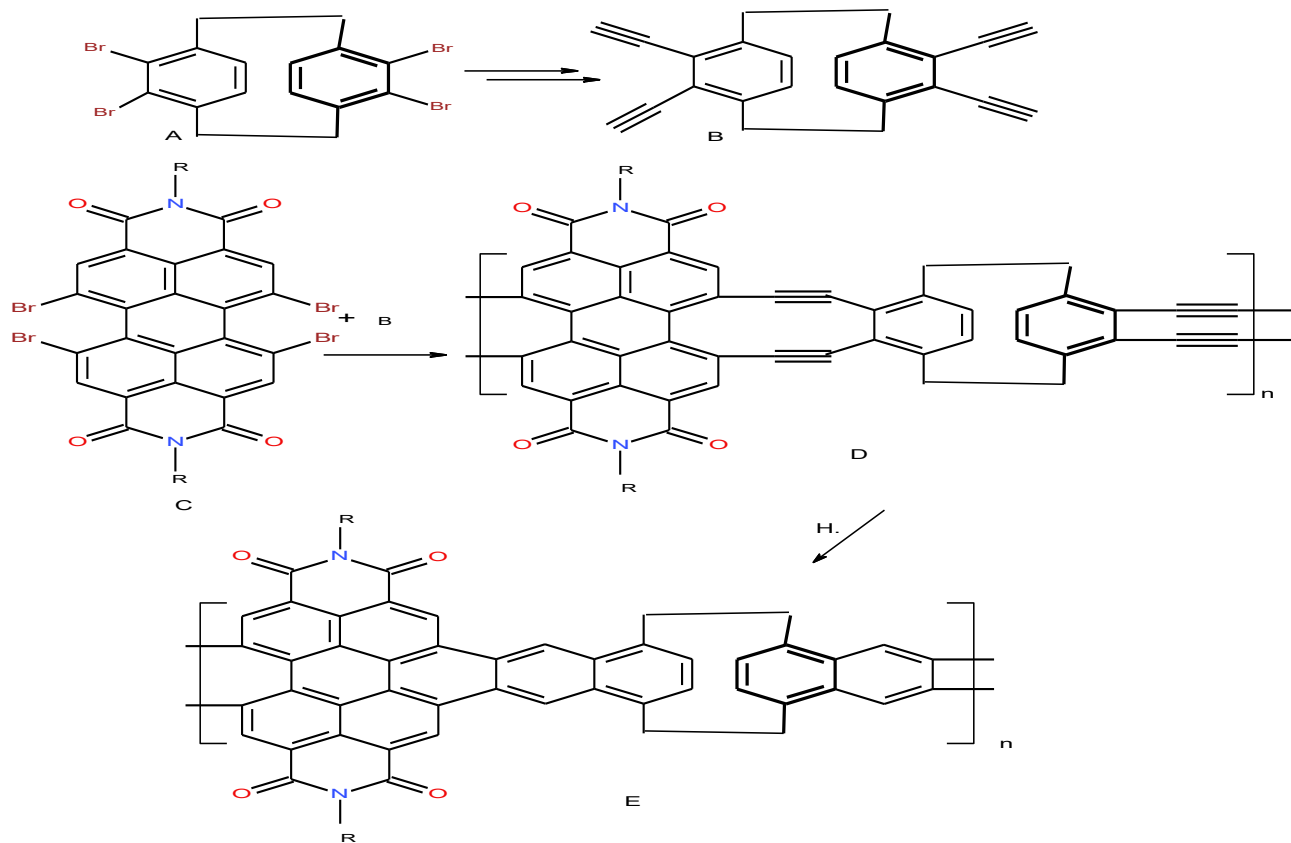
Scheme 9: These reactions can be applied to most compounds with bay positions. Just a few examples are shown, however.



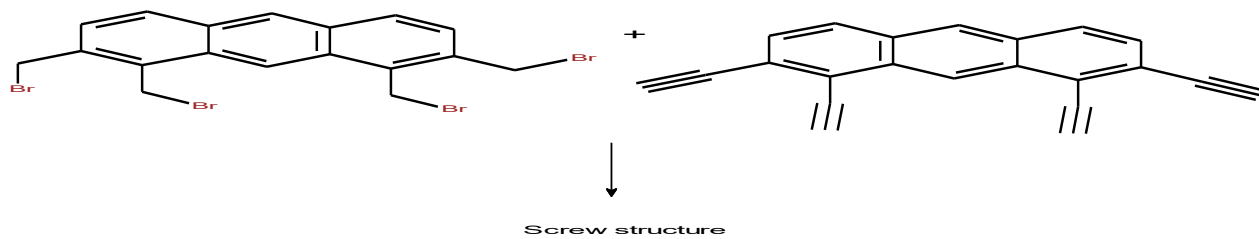
Scheme 10: [2,2]paracyclophane possibility that could exhibit singlet fission.

Nowak-Król, A., & Würthner, F. (2019). Progress in the synthesis of perylene bisimide dyes. *Organic Chemistry Frontiers*, 6(8), 1272-1318.

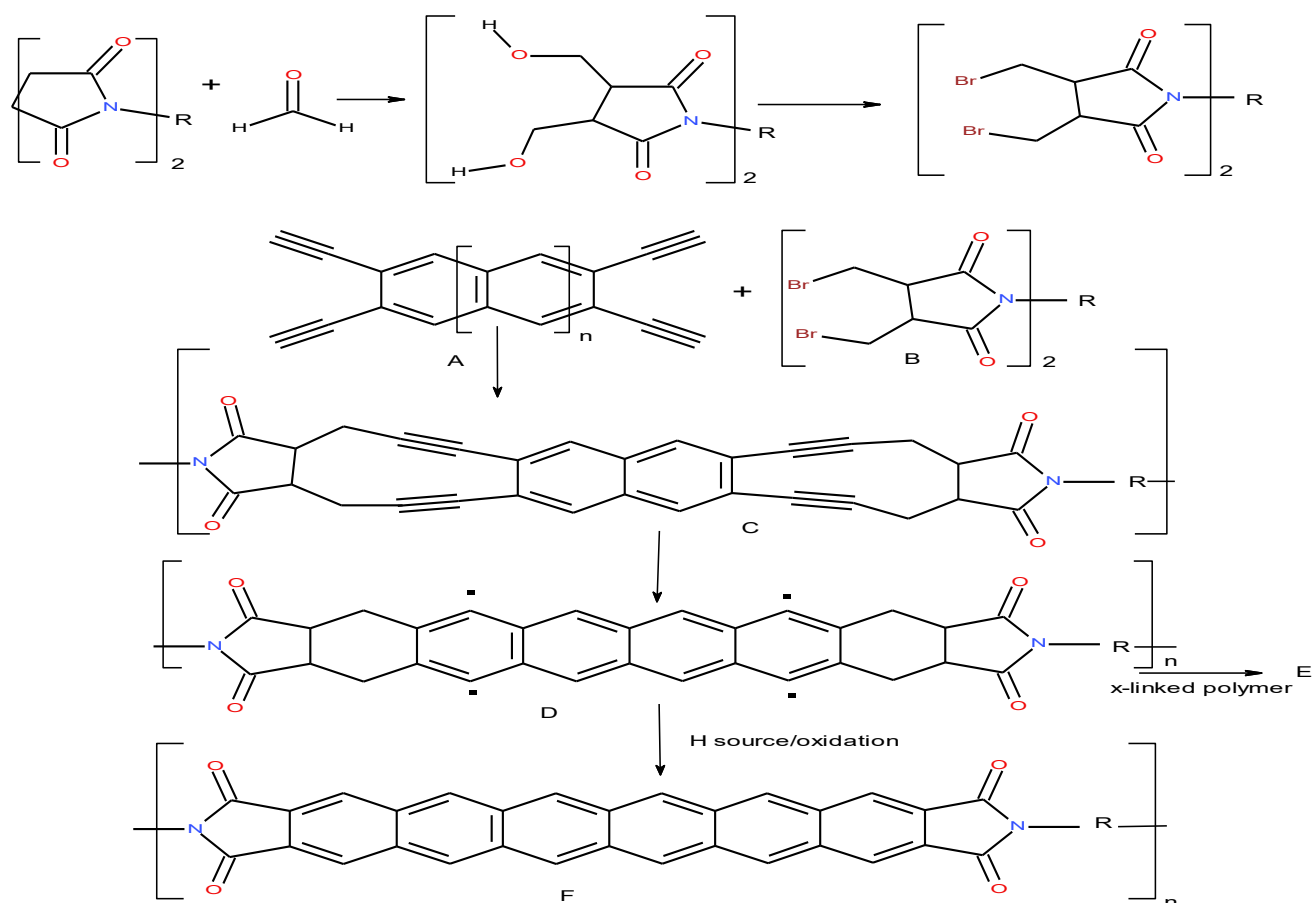
Li, C., Lin, Z., Li, Y., & Wang, Z. (2016). Synthesis and Applications of π -Extended Naphthalene Diimides. *The Chemical Record*, 16(2), 873-885.



Scheme 11: Polymeric version of scheme 10.



Scheme 11 : This polymerization should lead to a cyclic or screw like helicene structure.

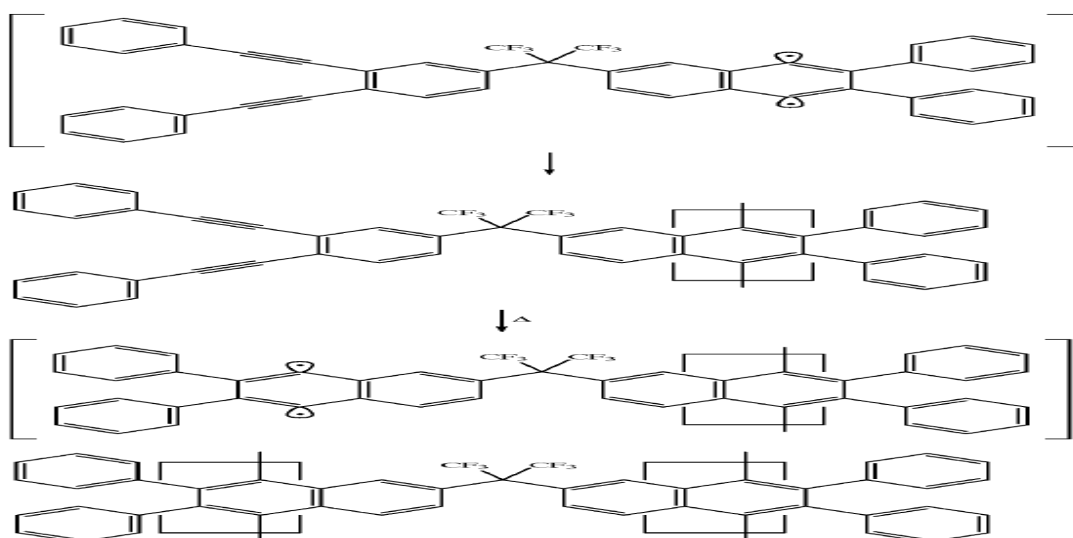


Scheme 12: Examples show A $n=1$ but could be bigger depending on stability of derivatives through F. I show a polymeric example but obviously the imides don't have to be attached.

Li, C., Lin, Z., Li, Y., & Wang, Z. (2016). Synthesis and Applications of π -Extended Naphthalene Diimides. *The Chemical Record*, 16(2), 873-885.

In all of these proposals, the possibility of intermolecular Diels-Alder reactions that would also lead to cross-linked polymers is possible.

I should point out that one problem with the above schemes is that the intermediate radicals must line-up for polymerization to produce anything but oligomers. One way around this problem is to connect the two BC structures with a flexible linker. For example: USP 6,121,495



Such flexible linkers afford greater opportunity for polymerization. In defense of my proposals, I point out that the acenes are very crystalline and should organize quickly. This may allow the diradicals to “see each other”. The unpolymerized acene proposals are unaffected by this potential problem because the diradicals are eliminated by readily available protons.

Thank you for reading these proposals!

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