

Synthesis and properties of annulenic subunits of graphyne and graphdiyne nanoarchitectures*

Michael M. Haley

Department of Chemistry and the Materials Science Institute, University of Oregon, Eugene, OR 97403-1253, USA

Abstract: This report describes the synthetic strategies toward and optoelectronic properties of substructures of the non-natural, planar carbon networks graphyne and graphdiyne, which are based on the dehydrobenzo[12]annulene and dehydrobenzo[18]annulene framework, respectively.

Keywords: carbon-rich; allotropes; alkynes; macrocycles; optoelectronic materials.

INTRODUCTION

For thousands of years, the only recognized crystalline forms of carbon were graphite and diamond. Only recently though have these forms found important technological uses [1]. Graphite, comprised of planar sheets of sp^2 -hybridized carbon atoms, is used in pencils, as a solid lubricant, as a moderator in nuclear reactors, as a component in electrodes, and as a reinforcement material in carbon fiber composites [2]. Diamond, a three-dimensional network of sp^3 -hybridized carbon atoms, is used in jewelry and as drilling heads in the petrochemical industry. More recently, diamond thin films generated by vapor deposition methods have been used extensively as protective coatings of tools and materials and in electronic devices [3].

Despite the rapidly emerging importance of these carbon allotropes, the study of other carbon-rich systems was limited for most of the 20th century. In 1968, a visionary group of theoreticians led by Alexandru Balaban published an article in which they put forth a variety of imaginative and aesthetically attractive two- and three-dimensional, non-natural carbon allotropes [4]. Although formation of many of these structures would be energetically prohibitive, some networks seemed more reasonable and thus might potentially be within the realm of synthetic endeavors. Over the next two decades, numerous two- and three-dimensional all-carbon networks were proposed in the literature, many of which were predicted to exhibit interesting electrical, optical, and structural properties [5].

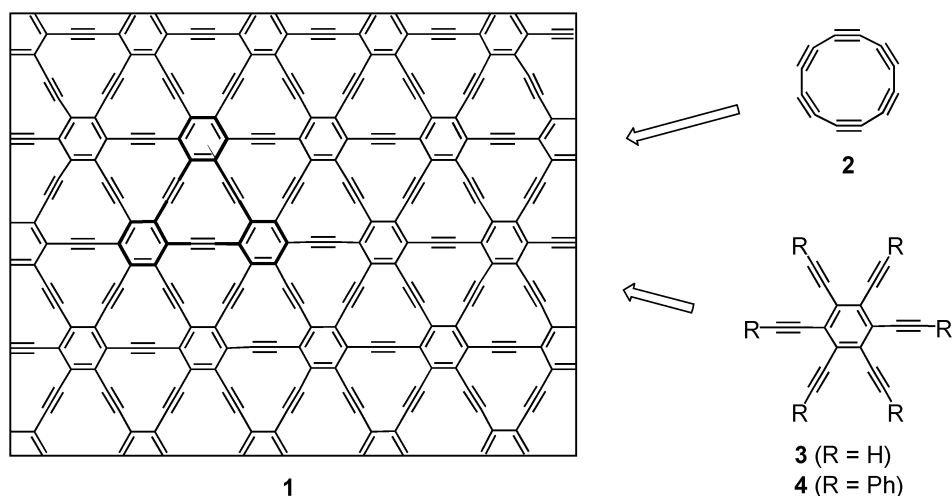
The landmark event that energized the study of carbon allotropes was the isolation and confirmation of the structure of C_{60} (buckminsterfullerene) in 1990 [6]. Although postulated by Kroto and Smalley in 1985 [7], it was not until five years later that Krätschmer and Huffman reported the isolation of macroscopic amounts of material, from which they were able to ascertain the now well-established icosahedral structure [8]. Over the ensuing 17+ years since the latter report, a plethora of publications has appeared, dealing with a burgeoning number of carbon-rich and all-carbon molecules. A vast majority of the research has centered on the construction of monomeric and oligomeric substructures of natural *and* non-natural, planar sp^2 and/or sp carbon networks. A number of excellent reviews

*Paper based on a presentation at the 12th International Symposium on Novel Aromatic Compounds (ISNA-12), 22–27 July 2007, Awaji Island, Japan. Other presentations are published in this issue, pp. 411–667.

have appeared from the leading protagonists in some of the respective subareas [9]. This report is limited to recent studies of two hypothetical carbon allotropes and their associated model substructures.

GRAPHYNE

Similar to purely sp^2 -hybridized networks, a wide range of planar allotropes combining sp and sp^2 carbon atoms can be envisaged. For instance, replacement of one-third of the carbon–carbon bonds of graphite with acetylene units results in the formation of a network composed entirely of phenyl rings and triple bonds, dubbed *graphyne* (**1**). In their seminal paper predicting structural, thermodynamic, and electronic properties for planar sheets equally occupied by sp and sp^2 carbon atoms, Baughman et al. postulated that **1** would exhibit interesting nonlinear optical behavior [10]. Furthermore, alkali metal charge-transfer complexes of **1** were expected to be metallic. Accompanying the expectations of interesting materials properties [11], graphyne was also predicted to be a large bandgap semiconductor ($E_g = 1.2$ eV). The calculated heat of formation [$\Delta H_f(g,C)$] for **1** is 12.4 kcal per g-atom C, which is comparable to the experimentally determined values for C_{60} and C_{70} (10.16 and 9.65 kcal per g-atom C, respectively) [12]. Despite this thermodynamic instability, the crystalline fullerenes are kinetically stable molecules, and require high temperature and pressure conditions to force their conversion to the more stable forms of graphite and diamond; thus, it is reasonable to anticipate that graphyne could exhibit similar kinetic stability and thus be resistant to graphitization.



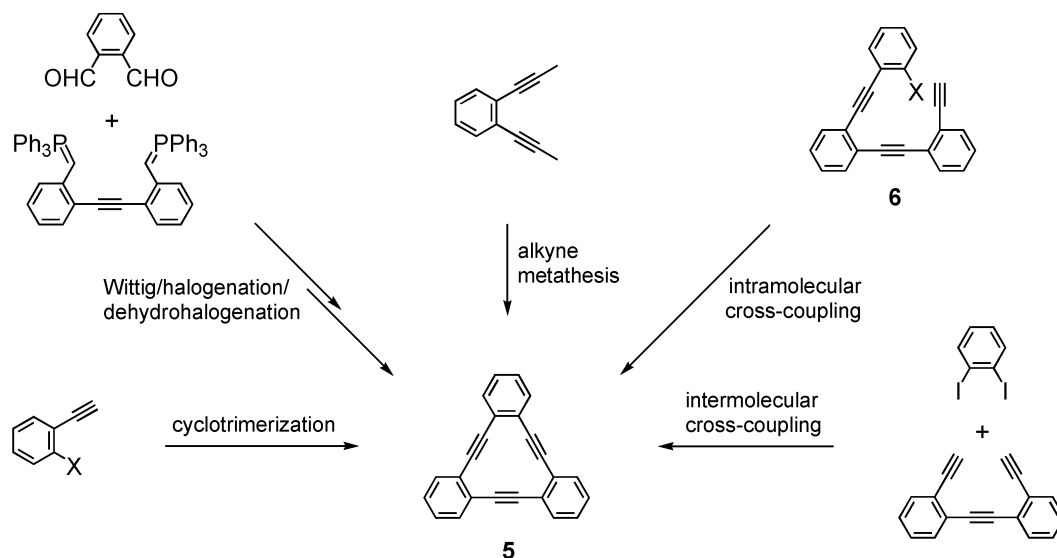
Synthetic strategies toward graphyne subunits

Synthetic accessibility is the primary deterrent to graphyne-related research. Controlled oligotrimerization of cyclo[12]carbon (**2**) could conceivably be a route to **1**; however, the synthesis (detection) of **2** outside a mass spectrometer has proven elusive [13]. The simplest graphyne subunit within the realm of synthetic accessibility is hexaethynylbenzene, which can be viewed as an acetylenic scaffold off of which graphyne mimics could be built. The parent hydrocarbon (**3**) was first prepared by Vollhardt et al. in 1986 using Sonogashira cross-coupling between hexabromobenzene and trimethylsilylacetylene followed by protodesilylation [14]. The resultant molecule proved to be highly sensitive to both heat and oxygen, a common problem found in perethynylated π -systems. Not surprisingly, this instability has limited studies utilizing **3**. Since the initial report, substituted hexaethynylbenzenes have been prepared which incorporate D_{6h} [15], D_{3h} [16], and C_{2v} [17] symmetries, yet the latter two systems require considerably involved syntheses. Of these compounds, the most “advanced” graphyne subunits are the

hexakis(phenylethynyl)benzenes (**4**). Also prepared from hexabromobenzene, molecule **4** was found to have a large third-order nonlinear susceptibility, a property predicted for the bulk graphyne network (*vide supra*) [15b]. The incorporation of long alkyl chains on the exterior phenyl rings of **4** produced molecules that exhibited discotic liquid-crystalline behavior [15a].

An alternative method to the use of acetylenic scaffolding is to prepare macrocyclic segments as network mimics. Dehydrobenzoannulenes (DBAs) [18] are a class of molecules that are well suited for this purpose. In addition to being subunits of synthetic carbon allotropes, DBAs have garnered tremendous interest in recent years as ligands for organometallic chemistry, as hosts for binding guest molecules, as probes for investigating weak induced ring currents, and as precursors to fullerenes, “bucky” tubes, “bucky” onions, and other carbon-rich materials [19]. More importantly, the annulenic compounds tend to be more stable to heat, light, and oxygen.

In the specific case of graphyne, hexadehydrotribenzo[12]annulene ([12]DBA, **5**) is the smallest macrocyclic unit. Triyne **5** has been synthesized in low to moderate overall yields via a variety of ways [19] (Scheme 1) over the 40+ years since its initial preparation [20]. Nonetheless, an improved version of the Cu-mediated intermolecular cyclotrimerization, the original approach, remains the easiest and most direct route, furnishing **5** in 47 % yield along with an 8 % yield of tetramer and traces of hexamer [21].



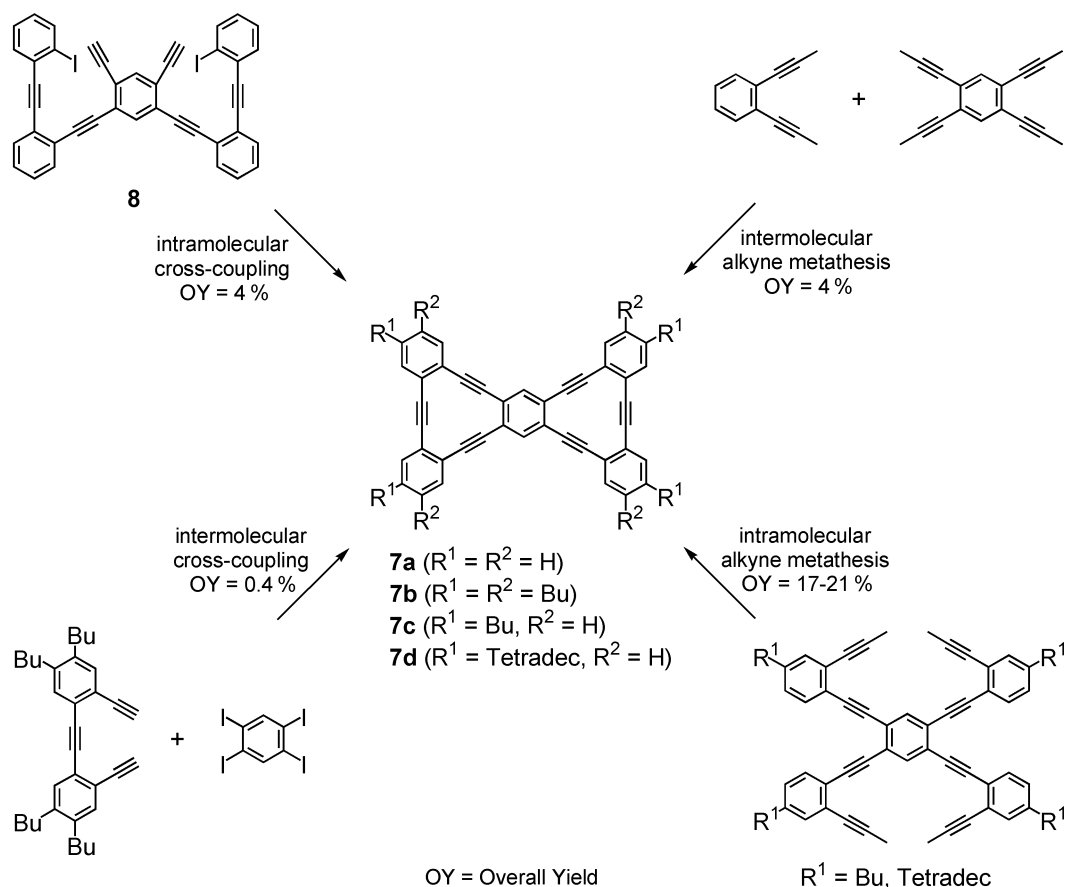
Scheme 1

The concomitant isolation of tetramer and hexamer along with **5** highlights a major drawback of intermolecular strategies. While simple in execution, an unavoidable pitfall of such syntheses is formation of additional cyclooligomeric and/or polymeric products, often affording low yields of material. Depending upon the substituents, trimeric, tetrameric, or even highly strained dimeric species can predominate [19]. Owing to their similarity in composition, structure, and solubility, it is often difficult (or impossible) to isolate a specific macrocycle from the mixture. Despite its shortcomings, the cyclotrimerization strategy has been utilized to furnish a variety of functionalized [12]DBA derivatives [19b].

To minimize the formation of side products, DBA **5** can be assembled via an intramolecular approach [22]. Sequential Sonogashira cross-coupling reactions and manipulation of iodines masked as triazenes represent most of the chemistry involved in construction of **6**. Intramolecular alkynylation with $\text{Pd}(\text{dba})_2$ under high dilution conditions furnished **5** as the sole product. Although this route re-

quired six more steps from commercially available materials, the overall yield was 35 %, which compared favorably with the yields of the other routes depicted in Scheme 1. More importantly, larger cyclooligomeric macrocycles were not detected, facilitating product isolation and purification.

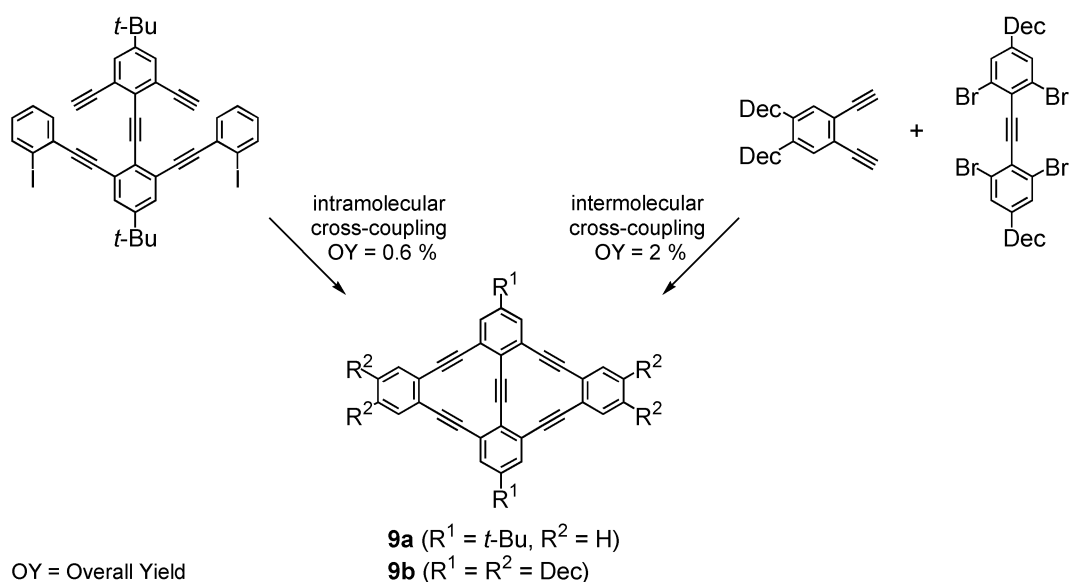
An intramolecular cyclization strategy is indispensable for the construction of more complex substructures of the graphyne network, such as bis[12]DBA **7** (Scheme 2). Our initial attempt at **7** focused on a double intramolecular Sonogashira reaction of **8**, which was prepared efficiently [22]. Cyclization, however, proceeded poorly and afforded **7a** in very low isolated yield. Subsequent to our 2000 publication, other groups showed that while it is possible to synthesize the carbon-rich backbone of **7a–b** by intermolecular routes, the overall yields are extremely low [23].



Scheme 2

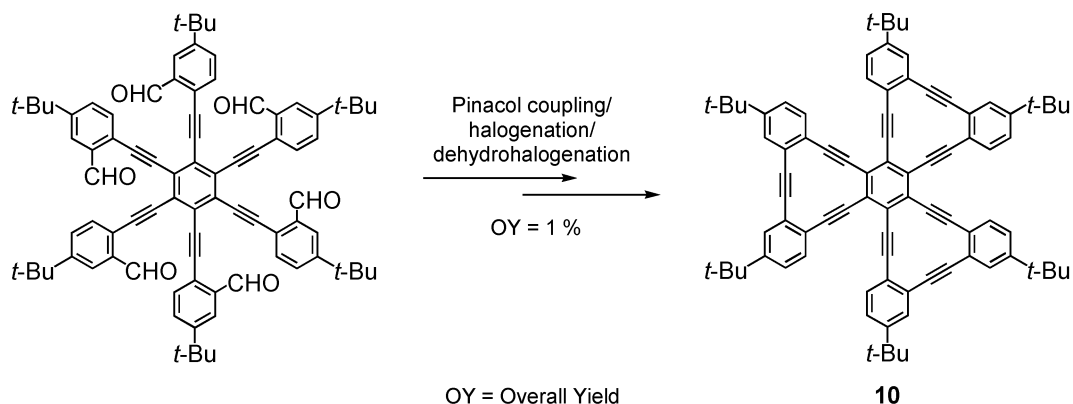
We recently returned our attention to the “bow-tie” bis[12]DBA core, utilizing an intramolecular approach where alkyne metathesis is the ring-forming method of choice. Alkyne metathesis has seen an extensive increase in catalyst development and use in macrocyclization in recent years [24]. By combining the efficiency of alkyne metathesis with pre-organized propynyl groups, this new route provides superior access to graphyne substructures, affording **7c–d** with appended solubilizing alkyl groups in ca. 20 % overall yield [25].

“Diamond” substructure **9** can be constructed by both intra-[22] and intermolecular [26] variants of the Sonogashira reaction (Scheme 3). This molecule is one of the few cases where the intramolecular

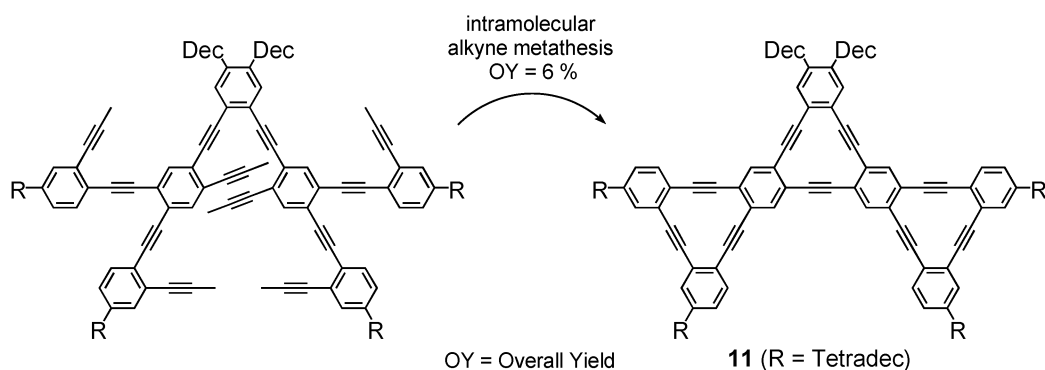
**Scheme 3**

synthetic route had a lower overall yield; however, neither method is suitable to prepare large amounts of material.

“Trefoil” subunit **10** contains three [12]DBAs fused to a central benzene core (Scheme 4) [27]. The carbon skeleton is first assembled by a sixfold Sonogashira reaction with hexabromobenzene. The annulene rings are then formed by sequential intramolecular pinacol coupling of the aldehydes, conversion of the resultant hydroxyls to chlorides, and double HCl elimination with strong base in ca. 1 % overall yield.

**Scheme 4**

Isomeric tris[12]DBA **11**, which possesses the longest linear chromophore of the known graphyne subunits, is readily available via directed alkyne metathesis (Scheme 5) in ca. 6 % overall yield [25]. Attempts to make the corresponding “linear” tetrakis[12]DBA substructure (analogous to “linear” tetrakis[18]DBA **27**) using alkyne metathesis have so far been unsuccessful, with only three of four rings being formed [25].



Scheme 5

Properties of graphyne substructures

Since the above graphyne subunits are based on the anti-aromatic [12]DBA core, all of these compounds possess paratropic ring currents and thus exhibit pronounced upfield shifts of the aromatic proton resonances ($\Delta\delta \approx 0.2\text{--}0.6$ ppm) upon macrocyclization. The largest $\Delta\delta$ values are associated with the internal arene rings of **7** and **11** and agree with calculations [11e], indicating decreased aromaticity from fusion with multiple paratropic [12]DBAs.

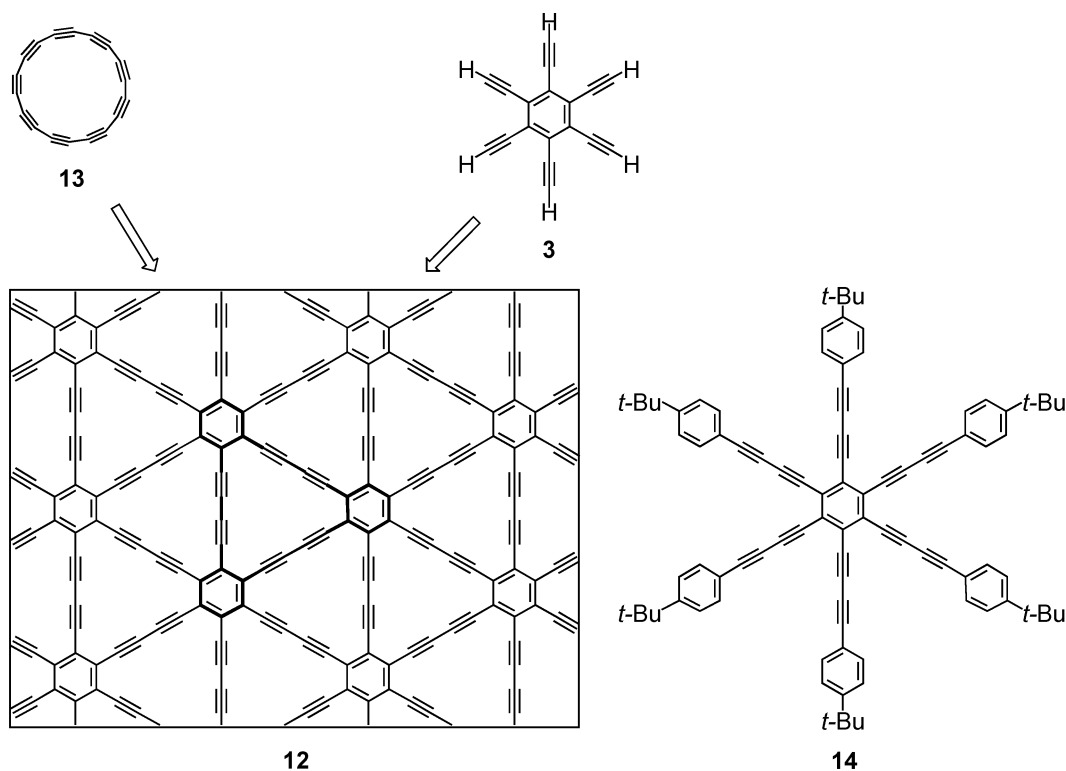
The absorption spectra of macrocycles **5**, **7**, and **11** show increased molar absorptivity and bathochromic shifts in both λ_{cutoff} and λ_{max} upon successive fusion of [12]cyclyne subunits, i.e., upon extension of the longest linear chromophore [25]. Unlike **10**, which is calculated to deviate from planarity, substructures **7** and **11** retain the characteristic vibronic spectral pattern of **5**, indicative of rigid, planar macrocycles. Highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) bandgaps calculated for **7** (~ 2.73 eV) and **11** (2.43 eV) from the lowest energy absorption λ_{max} coincide with computed values [11e]. [12]DBAs **7** and **11** exhibit large Stokes shifts (89–104 nm) as well as bathochromic λ_{em} and increased fluorescent quantum yield (**7**: $\Phi_{\text{F}} = 0.19\text{--}0.21$; **11**: $\Phi_{\text{F}} = 0.27$) upon extension of the linear conjugation pathway. Substructure **11** contains the longest linear diphenylacetylene conjugation pathway and highest quantum yield for graphyne substructures based on the [12]cyclyne subunit. Comparison of the data of **11** (absorption $\lambda_{\text{cutoff}} = 525$ nm, $\lambda_{\text{em}} = 515$ nm, $\Phi_{\text{F}} = 0.27$) with structurally isomeric trefoil **10** ($\lambda_{\text{cutoff}} \sim 500$ nm, $\lambda_{\text{em}} \sim 500$ nm, $\Phi_{\text{F}} = 0.03$) readily illustrates the dominance of the longest linear phenylacetylene conjugation pathway in electronic properties.

The graphyne substructures are robust molecules, possessing melting points in excess of 250–300 °C, and exhibit little or no sensitivity to heat-, light-, or oxygen-induced decomposition at room temperature. In fact, solid samples of **7a** and **9a** packaged under air have remained unchanged at -30 °C for over a decade! Although solid-state structures exist for **5** and derivatives, the only structural data for larger graphyne subunits was recently obtained by Tobe et al. The two-dimensional crystal structure of bisDBA **9b** forms the first example of a highly unusual Kagomé lattice at the liquid (1,2,4-trichlorobenzene)/solid (highly oriented pyrolytic graphite) interface, and is attributable to the “diamond”-shaped core of **9** [28].

GRAPHDIYNE

Extension of the linkages of graphyne by an additional triple bond generates another theoretical sp-sp^2 carbon allotrope called *graphdiyne* (**12**). While the calculated heat of formation [$\Delta H_{\text{f}}(\text{g,C})$] for **12** is 18.3 kcal per g-atom C, graphdiyne is predicted to be the most stable of the various diacetylenic non-natural carbon allotropes studied to date. Calculations predict **12** to retain all of the properties of

graphyne, e.g., high third-order nonlinear optical susceptibility, conductivity, or superconductivity when doped with alkali metals, and enhanced redox activity [11a]. In addition, the extra alkyne unit increases the pore size of the network to approximately 2.5 Å. This may make through-sheet transport of smaller ions possible, and thus possibly afford a method of dopant storage that is unavailable to graphite, namely, intrasheet intercalation.

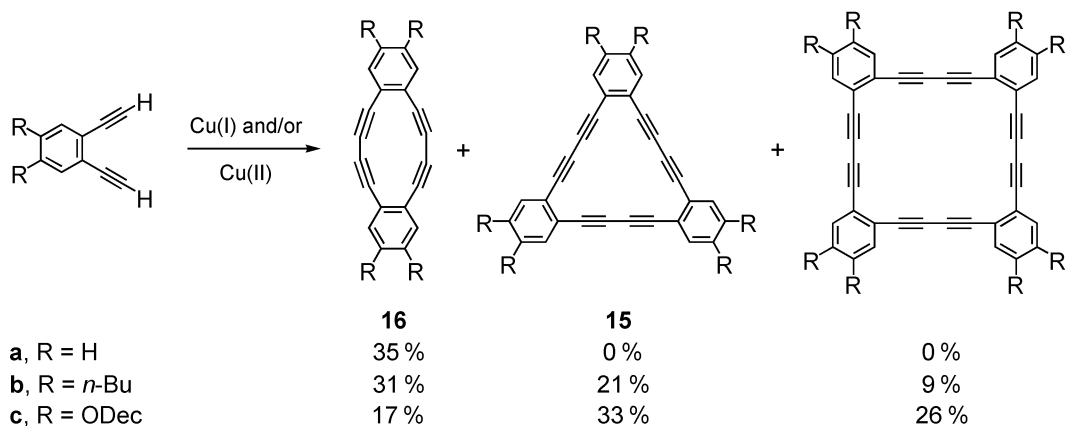


Synthetic strategies toward graphdiyne subunits

Analogous to graphyne, the synthetic routes to network **12** are beyond the limits of current methods. Whereas controlled oligotrimerization of cyclo[18]carbon (**13**) could conceivably furnish **12**, attempts to generate macroscopic amounts of this material have been unsuccessful [29]. Ideally, hexaethynylbenzene (**3**) would also be a suitable monomer for **12**. Instead of ordered polymerization via Cu-mediated oxidative homocoupling, the aforementioned instability problems result in random cross-linking and incomplete homocoupling, thus eliminating scaffold **3** as a viable network precursor. Additionally, defects from incomplete reductive elimination of the copper and from intersheet coupling are possible. Similar to **3**, the corresponding hexabutadiynylbenzene derivatives can be prepared in low to modest yield from hexabromobenzene via Sonogashira coupling [30]. Attempts to prepare the parent hydrocarbon by protidesilylation failed due to its instability. A more “advanced” graphdiyne model (**14**) was recently synthesized from hexaiodobenzene and *p*-*t*-butylphenylbutadiyne in 42 % yield using the highly reactive catalyst Pd[P(*o*-tol)₃]₂ [31].

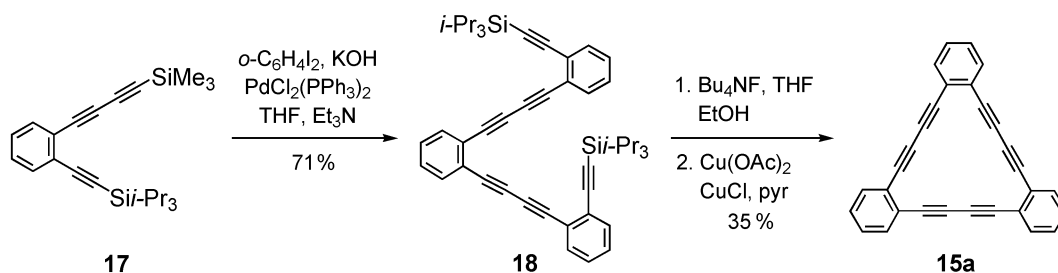
Once again, the best strategy for reliable correlation of structure and properties becomes the preparation and characterization of well-defined macrocyclic “oligomer” segments. By monitoring a variety of physical properties as a function of oligomer size, extrapolation toward the behavior of the bulk network may be possible. The smallest stable macrocyclic substructure of network **12** is do-

decadehydrotribenzo[18]annulene (**15a**), which has been pursued as a synthetic target since the late 1950s [32]. Similar to [12]DBA **5**, the primary approach to the preparation of **15a** and derivatives has been through the cyclooligomerization route. Cu-mediated cyclization of a 1,2-diethynylbenzene generates the desired macrocycle in low to moderate yield; however, the trimeric structure must be separated from a mixture of cyclooligomers (Scheme 6). Whereas it is possible to manipulate the ratio of dimer, trimer, and tetramer by varying the reaction conditions, a mixture is almost always isolated. Surprisingly, the purported exception to this is formation of the parent macrocycle **15a**. The only compound identified from the reaction was highly strained cyclodimer **16a** [32]; however, inclusion of alkyl or alkoxy groups on the starting diethynylarene did produce a mixture of products from which structures **15b–c** could sometimes be isolated in pure form only after repeated chromatography and/or recrystallization [33]. Subsequent reexamination of the conditions for reaction workup showed that the use of halocarbon solvents did indeed lead to isolation of **15a** in ca. 10 % yield [34].



Scheme 6

Analogous to the synthesis of larger graphyne substructures, utilization of an intramolecular cyclization in macrocycle construction assures the formation of a single product. Such an approach, however, necessitates the manipulation of phenylbutadiyne moieties, which are often highly reactive species and thus difficult to manipulate. Our group developed a method for coupling reactive phenylbutadiyne derivatives with iodoarenes by means of an in situ deprotection of the sensitive terminal alkynyl groups under typical Sonogashira coupling conditions [35], which is illustrated by the successful synthesis of **15a** (Scheme 7) [36]. Under pseudo-high dilution conditions, the smaller, more labile SiMe₃ group of triyne **17** is removed in situ and the resultant butadiyne is coupled to 1,2-diiodobenzene in 71 % yield. Protodesilylation of **18** with Bu₄NF followed by intramolecular homocoupling with CuCl and Cu(OAc)₂ in pyridine furnished **15a** as the sole product in modest 35 % yield. The in situ protodesilylation/alkynylation protocol has proven to be versatile and has led to the preparation of a large family of derivatized [18]annulenes [37] as well as numerous other dehydroannulene and DBA topologies [18,19b].



Scheme 7

The in situ deprotection/cross-coupling protocol is essential for the construction of all multi-macrocyclic graphdiyne substructures. The wavy lines and the bold lines shown on the “generation 1” mimics **19–23** [31,34] depict the key bonds formed by the protodesilylation/alkynylation and intramolecular homocoupling reactions, respectively. Given the poor solubility of **15a** (and thus the likely reason for its elusiveness prior to our 2000 work), inclusion of solubilizing decyl chains was necessary in order to manipulate the molecules.



by standard techniques to afford asymmetric cross-coupling unit **25**. Further synthetic elaboration furnished the second-generation targets **26–29** [38]. As before, the wavy lines and the bold lines in **26–29** show the key bonds formed by the protiodesilylation/alkynylation and intramolecular homocoupling reactions, respectively. For the latter transformation, both Cu-mediated [39] and Pd-catalyzed [40] macrocyclization conditions were explored (1–49 % yields).

The “G2” targets and all intermediate structures feature appended 3,5-di-*t*-butylphenyl groups. While this increased molecule crystallinity, the planarized products exhibited extremely poor solubility and were produced in minute quantities. Nonetheless, these compounds, which possess core diameters in the nanometer regime of ca. 5–6 nm, are the largest subunits of a non-natural carbon network yet made.

Properties of graphdiyne substructures

The above graphdiyne subunits are based on the aromatic [18]DBA core and therefore show small but distinct downfield shifts ($\Delta\delta \approx 0.15\text{--}0.35$ ppm) of the aromatic protons upon cyclization. As with the graphyne subunits, the largest $\Delta\delta$ values are associated with the internal arene rings. All of the substructures exhibit exothermic decomposition above 200 °C with broader or more disordered transitions associated with the larger “G2” systems (**26–29**).

The electronic absorption data for “G1” targets **15a** and **19–23** exhibit a characteristic pattern of four absorption bands, which are assigned primarily to $\pi \rightarrow \pi^*$ transitions in the [18]annulene skeleton [41]. These peaks shift to longer wavelengths and possess greater intensities as the number of longer 1,4-bis(phenylbutadiynyl)benzene chromophores is increased. Compared to **15a**, the peaks of “trefoil” **23** are shifted nearly 100 nm toward lower energy, thus reflecting the increased linear π -conjugation. Within structurally related systems, “bowtie” **19** ($\lambda_{\text{max}} = 413, 431$ nm), which contains two linear bis(phenylbutadiynyl)benzene pathways, exhibited bathochromic absorption beyond constitutional isomer **20** ($\lambda_{\text{max}} = 404, 420$ nm), which contains only one linear tetrayne pathway, and the more highly conjugated “half-wheel” **21** ($\lambda_{\text{max}} = 411, 426$ nm). Interestingly, the λ_{max} of **15a** and **19–23** all show the effect of locking the π -electron-rich backbone into planarity. This effect is most pronounced in **23**, in which the λ_{max} is red-shifted nearly 60 nm compared to its acyclic precursor.

The above trends are further amplified in “G2” targets **26–29**. Substructure **27**, the largest carbon-rich single molecule based on the graphdiyne network, exhibited electronic absorption ($\lambda_{\text{cutoff}} = 462$ nm, $\log \epsilon = 5.59$) that fell only 23 nm short of the calculated saturation wavelength for graphdiyne [38]. Structures **26**, **28**, and **29** all possess a longest, linear-conjugated “hexayne” pathway and show little variance in the wavelength of the lowest-energy λ_{max} of 454, 447, and 448 nm, respectively; however, a striking difference is observed in their molar absorptivities, which increase dramatically with the number of “hexayne” pathways present in the macrocycle (one in **26**, two in **28**, and three in **29**). Taken as whole, the UV–vis data of the graphdiyne substructures clearly indicate that the λ_{max} , or HOMO–LUMO bandgap energy, is dictated more by the length of the longest linear conjugated pathway, while the molar absorptivity is dictated more by the number of long pathways present.

“G2” compounds **26–29** are also quite fluorescent ($\lambda_{\text{em}} \approx 510\text{--}520$ nm, $\Phi_{\text{F}} \approx 0.30\text{--}0.60$) [38]. The increased conjugation due to planarization and cyclization generally resulted in an increase of two to three times the quantum efficiency and a slight bathochromic shift of the emission λ_{max} of ca. 10 nm. Solvent polarity showed little effect on λ_{em} or quantum yield between CH_2Cl_2 and PhMe. As with the absorption spectra, increasing the number of long linear chromophores had a pronounced effect on the emission spectra. With macrocycles **26**, **28**, and **29**, as the number of like pathways increased, a quantum efficiency increase of ~10 % and a bathochromic shift of ~5 nm resulted from each additional pathway. Comparatively, “linear” **27**, containing a longer “octayne” conjugated pathway, showed an emission spectrum only slightly hypsochromically shifted from that of **29**. These data indicate that for emission properties in the graphdiyne substructures, three “hexayne” pathways behave similarly to one “octayne”.

One of the most exciting aspects of graphdiyne research has been the recent confirmation of the materials potential of the substructures. In the area of nonlinear optics, organic multi-chromophore systems such as organic dendrimers have been utilized for two-photon absorption (TPA) effects which may have applications in optical limiting, imaging and photodynamic therapy [42]. Our graphdiyne mimics, which are multi-chromophore structures composed of repeated building block molecules, exhibit intramolecular coupling interactions among the multiple chromophores [41] and thus should lead to enhanced two-photon cross-sections. In addition, the various structures in hand allow us to investigate the influence of symmetry on the characteristics of the ground and excited states that are accessible by one- and two-photon processes, ultimately giving information about the mechanism(s) of the large TPA effect found in related systems. For the “G1” molecules, “trefoil” **23** possesses the largest TPA cross-section ($\delta = 1350 \text{ GM}$) followed by “bowtie” **19** ($\delta = 700 \text{ GM}$), with the remaining structures having considerably lower values [43]. The observed results, which are unusual for purely hydrocarbon compounds, suggest that molecules possessing higher symmetry give rise to larger TPA cross-sections. Additional linear and nonlinear optical measurements showed that the increase in symmetry of the annulenic systems enhances the TPA cross-sections by virtue of higher excited-state transition dipole moments. Ongoing TPA studies on the “G2” subunits should further corroborate these findings and result in even higher TPA values.

CONCLUSION

Tremendous strides have been made since 1990 on the construction of monomeric model systems and more advanced macrocyclic segments of non-natural graphyne and graphdiyne carbon allotropes. A vast majority of these successes can be attributed to the discovery of high-quality synthetic procedures. Intrinsic to the work discussed above has been the extensive development and utilization of metal-catalyzed cross-coupling, homocoupling, and metathesis reactions. Despite these advances, chemists have a long way to go. Issues concerning the development of high-yielding, *multiple intramolecular* homocoupling and metathesis reactions and the characterization of the resultant, often insoluble products must be addressed and overcome (or at least minimized) if the field is to continue to grow. Nevertheless, if the rapid expansion of this area over the last decade is any indication, the 21st century holds tremendous promise for the discovery and/or synthesis of new phases of carbon and related substructures.

ACKNOWLEDGMENTS

I would like to thank the University of Oregon graduate and undergraduate students who made our work on graphyne/graphdiyne substructures possible. I also thank Prof. Ted Goodson III (Michigan) and his group for a fruitful collaboration examining the photophysical properties of the graphdiyne subunits. The National Science Foundation, the ACS Petroleum Research Fund, and the University of Oregon are gratefully acknowledged for past and/or continuing support of this research.

REFERENCES

1. (a) R. E. Kirk, D. F. Othmer, M. Grayson, D. Eckroth. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed. 1978–1984, Vol. 4, p. 556, John Wiley, New York (1978); (b) B. T. Kelly. *Physics of Graphite*, Applied Science Publishers, New Jersey (1981); (c) J. E. Fields (Ed.). *The Properties of Diamond*, Academic Press, London (1979).
2. (a) E. Fitzer (Ed.). *Carbon Fibers and Their Composites*, Springer, Berlin (1985); (b) M. C. Reisch. *Chem. Eng. News* **65**, 9 (1987); (c) A. M. Thayer. *Chem. Eng. News* **68**, 37 (1990); (d) *Carbon* Vol. **27**, Issue 5 (1989); (e) J. B. Donnet, R. C. Bosnsal. *Carbon Fibers*, Marcel Dekker, New York (1984); (f) J. Delmonte. *Technology of Carbon and Graphite Fiber Composites*, Van Nostrand-Reinhold, Princeton (1981); (g) G. M. Jenkins, K. Kawamura. *Polymeric Carbons: Carbon Fibre, Glass and Char*, University Press, Cambridge (1976).
3. (a) P. K. Bachman, R. Messier. *Chem. Eng. News* **67**, 24 (1989); (b) M. Simpson. *New Sci.* **117**, 50 (1988).
4. A. T. Balaban, C. C. Rentia, E. Ciupitu. *Rev. Roum. Chim.* **13**, 231 (1968).
5. Inter alia: (a) R. Hoffmann, T. Hughbanks, M. Kertész, P. H. Bird. *J. Am. Chem. Soc.* **105**, 4831 (1983); (b) R. L. Johnston, R. Hoffmann. *J. Am. Chem. Soc.* **111**, 810 (1989); (c) A. T. Balaban. *Comput. Math. Appl.* **17**, 397 (1989); (d) R. H. Baughman, D. S. Galvão. *Nature* **365**, 735 (1993); (e) S. A. Best, P. A. Bianconi, K. M. Merz Jr. *J. Am. Chem. Soc.* **117**, 9251 (1995); (f) D. J. Klein, H. Zhu. In *From Chemical Topology to Three-Dimensional Geometry*, A. T. Balaban (Ed.), p. 297, Plenum Press, New York (1997); (g) A. T. Balaban. In *Theoretical Organic Chemistry*, C. Párkányi (Ed.), Elsevier, Amsterdam (1998).
6. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman. *Nature* **347**, 354 (1990).
7. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley. *Nature* **318**, 162 (1985).
8. J. M. Hawkins. *Acc. Chem. Res.* **25**, 150 (1992).
9. Inter alia: (a) A. C. Grimsdale, K. Müllen. *Angew. Chem., Int. Ed.* **44**, 5592 (2005); (b) U. H. F. Bunz, Y. Rubin, Y. Tobe. *Chem. Soc. Rev.* **28**, 107 (1999); (c) Y. Rubin. *Chem.—Eur. J.* **3**, 1009 (1997); (d) U. H. F. Bunz. *Synlett* 1117 (1997); (e) F. Diederich. *Nature* **369**, 199 (1994).
10. R. H. Baughman, H. Eckhardt, M. J. Kertész. *J. Chem. Phys.* **87**, 6687 (1987).
11. Inter alia: (a) N. Narita, S. Nagai, S. Suzuki, K. Nakao. *Phys. Rev. B* **58**, 11009 (1998); (b) N. Narita, S. Nagai, S. Suzuki, K. Nakao. *Phys. Rev. B* **62**, 11146 (2000); (c) N. Narita, S. Nagai, S. Suzuki. *Phys. Rev. B* **64**, 245408 (2001); (d) Y. Zhou, S. Feng. *Solid State Commun.* **122**, 307 (2002); (e) K. Tahara, T. Yoshimura, M. Sonoda, Y. Tobe, R. V. Williams. *J. Org. Chem.* **72**, 1437 (2007).
12. (a) H.-D. Beckhaus, C. Rückhardt, M. Kao, F. Diederich, C. S. Foote. *Angew. Chem., Int. Ed. Engl.* **31**, 63 (1992); (b) H.-D. Beckhaus, S. Verevkin, C. Rückhardt, F. Diederich, C. Thilgen, H.-U. ter Meer, H. Mohn, W. Müller. *Angew. Chem., Int. Ed. Engl.* **33**, 996 (1994).
13. Y. Tobe, H. Matsumoto, K. Naemura, Y. Achiba, T. Wakabayashi. *Angew. Chem., Int. Ed. Engl.* **35**, 1800 (1996).
14. R. Diercks, J. Armstrong, R. Boese, K. P. C. Vollhardt. *Angew. Chem., Int. Ed. Engl.* **25**, 268 (1986).
15. (a) K. Praefcke, B. Kohne, D. Singer. *Angew. Chem., Int. Ed. Engl.* **29**, 177 (1990); (b) K. Kondo, S. Yasuda, T. Sakaguchi, M. Miya. *J. Chem. Soc., Chem. Commun.* 55 (1995).
16. J. E. Anthony, S. I. Khan, Y. Rubin. *Tetrahedron Lett.* **38**, 3499 (1997).
17. (a) Y. Tobe, K. Kubota, K. Naemura. *J. Org. Chem.* **62**, 3430 (1997); (b) J. D. Tovar, N. Jux, T. Jarrosson, S. I. Khan, Y. Rubin. *J. Org. Chem.* **62**, 3432 (1997).
18. J. A. Marsden, G. J. Palmer, M. M. Haley. *Eur. J. Org. Chem.* 2355 (2003).
19. (a) C. S. Jones, M. J. O'Connor, M. M. Haley. In *Acetylene Chemistry: Chemistry, Biology, and Materials Science*, F. Diederich, P. J. Stang, R. R. Tykwinski (Eds.), p. 303, Wiley-VCH, Weinheim (2005); (b) E. L. Spitler, C. A. Johnson II, M. M. Haley. *Chem. Rev.* **106**, 5344 (2006).

20. (a) I. D. Campbell, G. Eglinton, W. Henderson, R. A. Raphael. *J. Chem. Soc., Chem. Commun.* 87 (1966); (b) H. A. Staab, F. Graf. *Tetrahedron Lett.* 751 (1966).
21. D. Solooki, J. D. Ferrara, D. Malaba, J. D. Bradshaw, C. A. Tessier, W. J. Youngs. *Inorg. Synth.* **31**, 122 (1997).
22. J. M. Kehoe, J. H. Kiley, J. J. English, C. A. Johnson, R. C. Petersen, M. M. Haley. *Org. Lett.* **2**, 969 (2000).
23. (a) O. S. Miljanic, K. P. C. Vollhardt, G. D. Whitener. *Synlett* 29 (2003); (b) M. Iyoda, S. Sirinintasak, Y. Nishiyama, A. Vorasingha, F. Sultana, K. Nakao, Y. Kuwatani, H. Matsuyama, M. Yoshida, Y. Miyake. *Synthesis* 1527 (2004).
24. (a) R. R. Schrock. *Polyhedron* **14**, 3177 (1995); (b) W. Zhang, J. S. Moore. *Adv. Synth. Catal.* **349**, 93 (2007).
25. C. A. Johnson II, Y. Lu, M. M. Haley. *Org. Lett.* **9**, 3725 (2007).
26. M. Sonoda, Y. Sakai, T. Yoshimura, Y. Tobe, K. Kamada. *Chem. Lett.* **33**, 972 (2004).
27. T. Yoshimura, A. Inaba, M. Sonoda, K. Tahara, Y. Tobe, R. V. Williams. *Org. Lett.* **8**, 2933 (2006).
28. K. Tahara, S. Furukawa, H. Uji-i, T. Uchino, T. Ichikawa, J. Zhang, M. Sonoda, F. C. De Schryver, S. De Feyter, Y. Tobe. *J. Am. Chem. Soc.* **128**, 16613 (2006).
29. (a) F. Diederich, L. Gobbi. *Top. Curr. Chem.* **201**, 43 (1999); (b) Y. Tobe. In *Advances in Strained and Interesting Organic Molecules*, B. Halton (Ed.), Vol. 7, p. 153, JAI Press, Greenwich, CT (2000).
30. R. Boese, J. R. Green, J. Mittendorf, D. L. Mohler, K. P. C. Vollhardt. *Angew. Chem., Int. Ed. Engl.* **31** 1643 (1992).
31. W. B. Wan, M. M. Haley. *J. Org. Chem.* **66**, 3893 (2001).
32. (a) G. Eglinton, A. R. Galbraith. *Proc. Chem. Soc.* 350 (1957); (b) O. M. Behr, G. Eglinton, R. A. Raphael. *Chem. Ind.* 699 (1959); (c) G. Eglinton, A. R. Galbraith. *J. Chem. Soc.* 3614 (1960).
33. Q. Zhou, P. J. Carroll, T. M. Swager. *J. Org. Chem.* **59**, 1294 (1994).
34. W. B. Wan, S. C. Brand, J. J. Pak, M. M. Haley. *Chem.—Eur. J.* **6**, 2044 (2000).
35. M. M. Haley, M. L. Bell, J. J. English, C. A. Johnson, T. J. R. Weakley. *J. Am. Chem. Soc.* **119**, 2956 (1997),
36. M. M. Haley, S. C. Brand, J. J. Pak. *Angew. Chem., Int. Ed. Engl.* **36**, 835 (1997).
37. J. J. Pak, T. J. R. Weakley, M. M. Haley. *J. Am. Chem. Soc.* **121**, 8182 (1999).
38. J. A. Marsden, M. M. Haley. *J. Org. Chem.* **70**, 10213 (2005).
39. P. Siemsen, R. C. Livingston, F. Diederich. *Angew. Chem., Int. Ed.* **39**, 2632 (2000).
40. J. A. Marsden, J. J. Miller, M. M. Haley. *Angew. Chem., Int. Ed.* **43**, 1694 (2004).
41. S. Anand, O. Varnavski, J. A. Marsden, M. M. Haley, H. B. Schlegel, T. Goodson III. *J. Phys. Chem. A* **110**, 1305 (2006).
42. Inter alia: (a) M. Albota, D. Beljonne, J.-L. Bredas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Rockel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu, C. Xu. *Science* **281**, 1653 (1998); (b) T. Kogej, D. Beljonne, F. Meyers, J. W. Perry, S. R. Marder, J.-L. Bredas. *Chem. Phys. Lett.* **298**, 1 (1998); (c) D. Beljonne, W. Wenseleers, E. Zoger, Z. Shuai, H. Vogel, S. J. K. Pond, J. W. Perry, S. R. Marder, J.-L. Bredas. *Adv. Funct. Mater.* **12**, 631 (2002); (d) T. Lin, S. Chung, K. Kim, X. Wang, G. S. He, J. Swiatkiewicz, H. E. Pudavar, P. N. Prasad. *Adv. Polym. Sci.* **161**, 157 (2003); (e) Y. Wang, G. S. He, P. N. Prasad, T. Goodson III. *J. Am. Chem. Soc.* **127**, 10128 (2005); (f) T. Goodson III. *Acc. Chem. Res.* **38**, 99 (2005).
43. A. Bhaskar, R. Guda, M. M. Haley, T. Goodson III. *J. Am. Chem. Soc.* **128**, 13972 (2006).