Taking the Dimers Out of Diazaheptacenes

**Significance:** The authors have successfully designed, synthesized, and isolated the first persistent diazaheptacene. The diazaheptacene in this work required four Si(s-Bu)3-ethynyl groups to effectively prevent dimerization upon oxidizing to the final product 4.

**Comment:** The key synthetic step was the fast oxidation using manganese oxide to convert 3 into 4, which was carried out for no longer than forty seconds. The product 4 was stable for approximately one hour, after which dimerization products were detected. Alternative trialkysilyl-ethynyl groups, such as the TIPS-ethynyl group, proved ineffective at impeding dimerization.
Regiospecific Synthesis of N2-Aryl 1,2,3-Triazoles from 2,5-Disubstituted Tetrazoles via Photochemically Generated Nitrile Imine Intermediates

**Synlett 2014, 25, 2480–2484.**

### Triazole Your Tetrazoles

**Significance:** Stewart, Harris, and Jamieson developed a one-step reaction to photochemically synthesize N2-aryl 1,2,3-triazoles from 2,5-diaryl tetrazoles. This method bypasses issues of regioselectivity by first preparing the appropriate N-arylated tetrazole, which under UV irradiation forms a nitrile imine intermediate that dimerizes and rearranges to produce the appropriate N2-aryl 1,2,3-triazole.

**Comment:** Electron-donating substituents and dilute conditions led to improved yields of the triazoles, while electron-deficient N-aryl substituents led to poor or zero conversion. Previous studies of similar starting materials identified tetrazine as the final product, but the authors indicate that the only other compound isolated in their study was the Wanzlick dimer, which can be converted into the final triazole with additional UV irradiation.

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**Selected examples of 5:**

- **OMe**
  - 67% yield
  - 16 h

- **OMe, MeO**
  - 38% yield
  - 30 h

- **CO2Et**
  - 90% yield
  - 7 h

- **MeO**
  - 14% yield
  - 23 h

- **NO2**
  - 19% yield
  - 24 h

- **CN**
  - 0% yield
  - >100 h

- **Cl, Cl**
  - 0% yield
  - 24 h

- **Cl, Cl**
  - 28% yield
  - 31 h
Twin Helicenes Twist Benzene

**Significance:** The authors report a new approach to construct distorted benzene rings by constraining a benzene ring between two opposing [5]helicenes. Double helicene 5 was synthesized via a tandem intramolecular phospha-Friedel–Crafts reaction. By X-ray crystallography, the central benzene ring of 5 was found to possess a bending angle of 23°, and the sulfur atoms were found to be in a cis arrangement.

**Comment:** Distorted double helicene 5 can be desulfurized with triethylphosphine to yield bis(phosphine) 7, which could find potential use as a $C_2^*$-symmetric ligand for bimetallic complexes, following separation of enantiomers.
Divergent Synthesis of Tricyclic Biselenophene-Based Derivatives

**Significance:** While tricyclic bithiophene-based materials have been extensively studied as an important class of organic semiconductors, the corresponding biselenophene-based analogues have not been reported. Cheng and co-workers demonstrate for the first time that biselenophene can be utilized as starting material for the synthesis of a new class of both sp<sup>3</sup>-bridged and sp<sup>2</sup>-bridged tricyclic biselenophene-based materials.

**Comment:** The six brominated molecules highlighted above can be used as monomers to create a new class of p- or n-type polymers for exploring biselenophene-based materials in various optoelectronic applications, such as organic field-effect transistors and polymer solar cells.
Having the Gall to Synthesize Conjugated Polymers Containing Gallium Atoms

**Significance:** The effect of gallium atoms in conjugated polymers is relatively unexplored, in part due to the air and moisture sensitivity of three-coordinate gallium centers. Tanaka, Chujo, and co-workers utilize a four-coordinate gallium monomer in which the gallium is stabilized by amine chelation and bears two 4-bromophenyl moieties. With Suzuki–Miyaura or Yamamoto coupling, a variety of air-stable π-systems containing gallium atoms are obtained. UV/Vis and DFT studies show that π-conjugation extends through the gallium atoms.

**Comment:** This study shows that gallium atoms can be incorporated into air-stable conjugated polymers. While typical aryl–aryl coupling conditions are employed in this study, relatively poor polymer yields and lengths are obtained. Future optimization of polymerization conditions could facilitate the development of gallium-containing polymers.
Phosgene as Key Reagent for Trifunctionalization of BODIPY Dyes

**Significance:** The functionalization of BODIPY fluorescent dyes allows the tuning of their photophysical, hydrophobic, and charge-transfer properties. Smith and co-workers utilize phosgene to access a 3,5,8-trichlorinated BODIPY. Exploiting the higher reactivity of the vinylic chloride in Stille couplings, regioselectively functionalized BODIPY dyes are synthesized.

**Comment:** Starting from a trichlorinated BODIPY and performing mixed Stille couplings with only four different organotin reagents, 14 new BODIPY dyes are reported in this paper. Photophysical properties are tunable via substitution at the 3-, 5-, and 8-positions. A plethora of regioslectively functionalized BODIPY dyes should be accessible through this strategy.
PB&J: Phosphorus and Boron at the Junction of Two $\pi$-Systems

Significance: The 1,1-alkenylboration of alkynes is an unique route to large conjugated $\pi$-systems. Erker and co-workers demonstrate that the 1,1-alkenylboration of diarylphosphino-enynes proceeds similarly to give hexatrienes 1. Upon thermolysis, two concurrent transformations occur: 6$\pi$-electrocyclic ring closure of the hexatriene moiety and nucleophilic aromatic substitution ($S_NAr$) of a pentafluorophenyl group by the phosphine nucleophile to yield heterotricyclic products 2.

Comment: These reactions are a convenient synthetic route to new molecules containing vicinal P/B Lewis pairs. Thermolysis products are only reported for 1a and 1b. Would the thermolysis of 1c and 1d, which contain bulky (Mes)$_2$P nucleophiles, result in electrocyclic ring closure without concurrent $S_NAr$?
A Diels–Alder Approach to Graphene Nanoribbon Precursors

**Significance:** Bottom-up approaches to graphene nanoribbons (GNRs) have been limited by the short length of nanoribbons produced (<50 nm) or the requirement for metal surfaces. The authors report a bottom-up approach to the synthesis of longer (>100 nm), structurally defined GNRs using an AB-type Diels–Alder polymerization to form nanoribbon precursors 8 that can be planarized to GNRs 9 by oxidative cyclodehydrogenation with FeCl₃.

**Comment:** Despite the formation of multiple regioisomers after the Diels–Alder polymerization of asymmetrical monomer 7, upon planarization, all isomers of 8 yielded an identical GNR structure (9). Polymerization of 7 was carried out both in solution and melt, with melt yielding GNR precursors of significantly higher $M_w$ (230,000–550,000 g/mol versus 42,000–78,000 g/mol for solution polymerization).

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Not-So-Triyne Route to Heteroarylene and Arylene Macrocycles

**Significance:** This is the first reported synthesis of macrocyclic π-conjugated structures featuring both benzene and heterocycle units. Isolated yields up to ~85% and stereochemical purity up to ~95% ee are reported, though it is difficult to achieve both simultaneously. Bis- and tri-thiophene substrates produce trimers. While absorbance maxima were red-shifted with increasing thiophene rings, fluorescence maxima were not, indicating poor conjugation through the benzene ring vertices. However, this resulted in large Stokes shifts (90–120 nm) for these structures.

**Comment:** Ligand selection was found to be crucial for stereoselectivity, with QuinoxP\* overall performing well. In trimer-forming systems, preference for dimer or trimer can also be tuned by ligand choice. The proposed mechanism is two rounds of metallacyclopentadiene formation followed by [2+2+2] cyclization. Stereochemistry is determined by the second [2+2+2] cyclization step. While thiophene-based systems performed well, attempts to use furans resulted in poor yields and stereoselectivity.

**Representative reaction:**

\[ \text{TsN}_2 \text{NTs}_2 \text{[Rh(cod)BF}_4 (10 \text{ mol}\%)] (R,R)-\text{QuinoxP*} (10 \text{ mol}\%) \]  
DCE, r.t. to 60 \degree C  
45% yield 52% ee

**Selected compounds:**

- **38% yield 69% ee**
- **47% yield >99% ee**
- **50% yield**

**Category:**
- Synthesis of Materials and Unnatural Products

**Key words:**
- electronic materials
- [2+2+2] cycloaddition
- rhodium catalysis

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Conducting Polyfurans by Electropolymerization of Oligofurans

**Chem. Sci. 2015, 6, 360–371.**

**Electropolymerization Furnishes Conducting Polyfuran Films**

**Significance:** Polyfurans have received less research attention than their pyrrole and thiophene analogues. This is due in part to the high oxidation potential of furan. Harsh electropolymerization conditions result in defect-rich, non-conducting polyfuran. To lower the potential required to form polyfuran, Sheberla and co-workers synthesize oligofurans 1–7. Potentiostatic polymerization for all of these monomers occurs at 0.75 V (vs. Ag/AgCl). The resulting polyfurans are found to have conductivities comparable with electropolymerized polythiophenes.

**Comment:** Electropolymerization of furan occurs at potentials in excess of 1.8 V (vs. Ag/AgCl). The onset oxidation potentials for 1–7 are under 0.7 V, and follow expected trends based on conjugation length and degree of alkyl substitution. The high-quality polyfurans also undergo oxidative doping at lower potentials than analogous poly(terthiophenes), resulting in increased stability under the operating conditions. This study may establish polyfuran as a competitor to other conducting polymers.
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Synthesis and Electronic Structure of Dicyanofulvene-Fused Electron Accepting Molecule Based on a 1,5-Dihydro-s-Indacene Framework


A High Cyano Content Indacene as a Stable Organic Electron Acceptor

Significance: The authors used rational design to target the reported structure, compound 1. The indacene framework was stabilized by the high degree of cyano functionalization without compromising ease of reduction, which has been an issue with indacenes stabilized by benzannulation. The high cyano content also lowered the LUMO to −5.8 eV. Cyclic voltammetry shows four reversible single electron transfers, and UV/Vis shows a band gap of ~1.9 eV.

Comment: The synthesis began from a previously reported compound (C. Adams et al. Inorg. Chim. Acta 2011, 366, 44), produced 330 mg of pure 3a, and should be scalable. Compound 3a was found to be generally stable both as a solid and in solution, possibly due to the low-lying LUMO.

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An Unusual Regioselective Di-, Tetra-, and Hexa-Bromination

Significance: Mastalerz and co-workers report an unusual even-numbered bromination of triptycene tris(thiadiazoles), yielding regioselectively di-, tetrabromo-, and hexabromotriptycenes with two bromines each on the same phenyl ring. These brominated compounds will be useful in the synthesis of π-conjugated polymers of intrinsic microporosity and small electron acceptors.

Comment: Given that the C–C bond lengths of the phenyl rings are alternating, and hence the phenyl rings exhibit more olefinic than aromatic character from X-ray single crystal structure of 1, the mechanism for this unusual even-numbered bromination is proposed to involve 1,4-addition of Br₂, followed by subsequent re-aromatization of the phenyl ring by oxidation by Br₂ or FeBr₃. It is also proposed that this 1,4-addition–oxidation sequence is favored over electrophilic aromatic substitution. Furthermore, to demonstrate the utility of these monomers in the synthesis of conjugated polymers, dibromotriptycene 2 has been shown to undergo facile Suzuki–Miyaura cross-coupling.