

Depolymerization Kinetics of Self-Immolative Polymers

Category

Synthesis of
Materials and
Unnatural Products

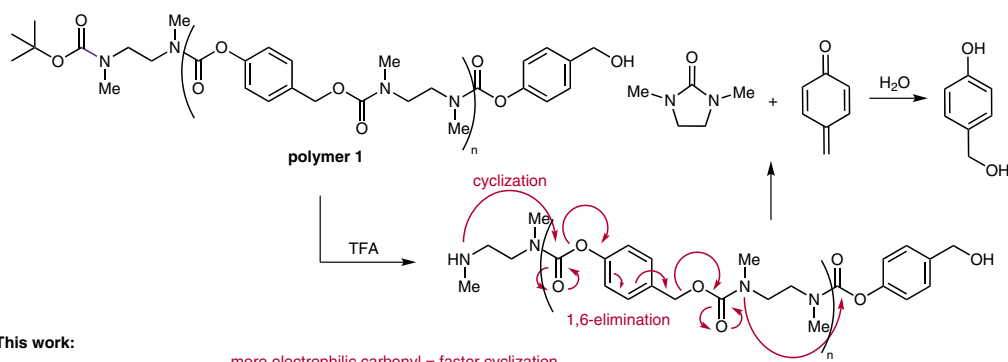
Key words

degradable
polymers

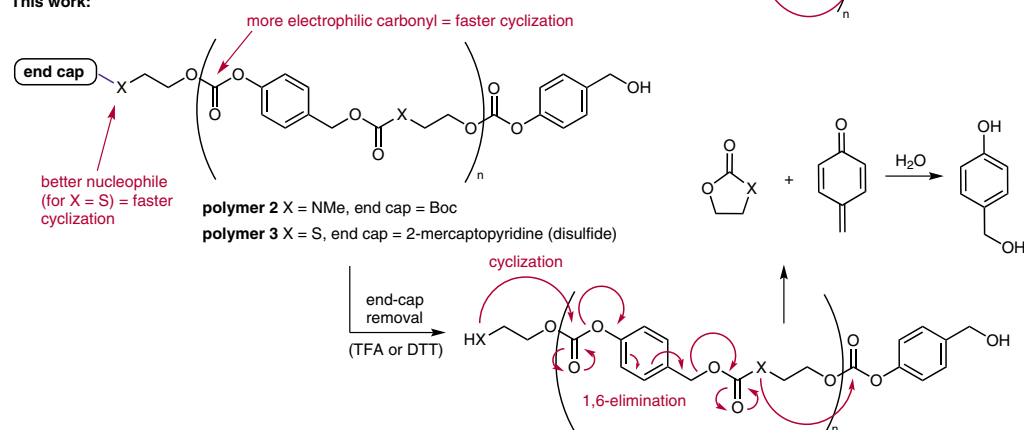
controlled
depolymerization

cyclization kinetics

Previous work (*J. Am. Chem. Soc.* **2009**, *131*, 18327):



This work:



overall depolymerization rates: polymer 3 ($7.8 \times 10^{-2} \text{ min}^{-1}$) > polymer 2 ($2.6 \times 10^{-2} \text{ min}^{-1}$) > polymer 1 ($6.8 \times 10^{-2} \text{ h}^{-1}$)

Significance: Self-immolative polymers are materials that degrade into small molecules by an intramolecular cascade reaction upon removal of an end-capping group. Due to their backbones primed for degradation, self-immolative polymers require strategic design and synthesis. Here, Gillies and co-workers have synthesized two new self-immolative polymers with different degradation rates by altering the nucleophilicity and electrophilicity of the functional groups participating in the intramolecular cascade reaction.

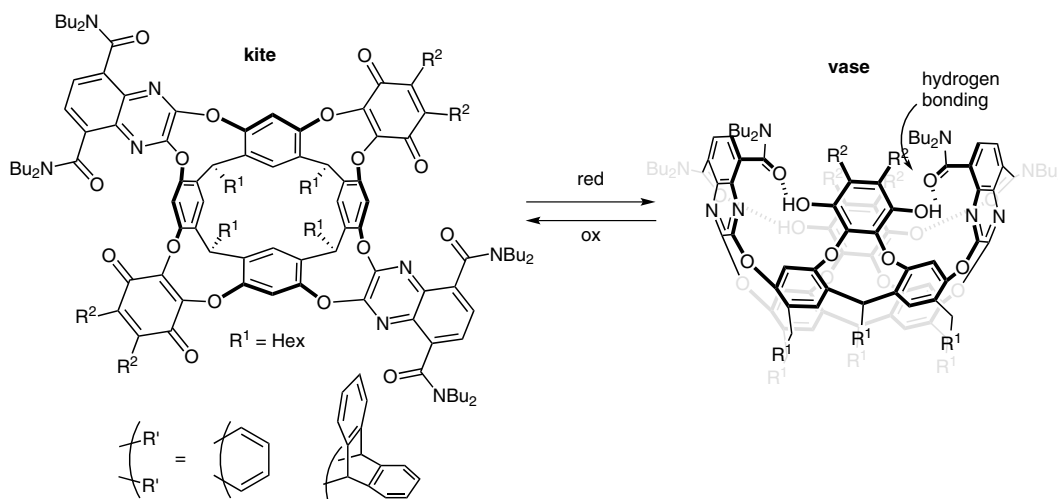
Comment: Previously reported self-immolative polymer **1** depolymerizes through a cyclization–1,6-elimination pathway with the cyclization being the rate-determining step. By increasing the electrophilicity of the carbonyl by changing it from a carbamate to a carbonate, as seen in polymer **2**, the rate of depolymerization was increased 500-fold. A further increase in depolymerization was achieved when the nucleophile was changed from an amine to a thiol (polymer **3**). Polymer **3** is of particular interest due to its redox-sensitive depolymerization, which could be used for cytosolic drug delivery.

SYNFACTS Contributors: Timothy M. Swager, Ellen M. Sletten
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DOI: 10.1055/s-0032-1317890; **Reg-No.:** S13812SF

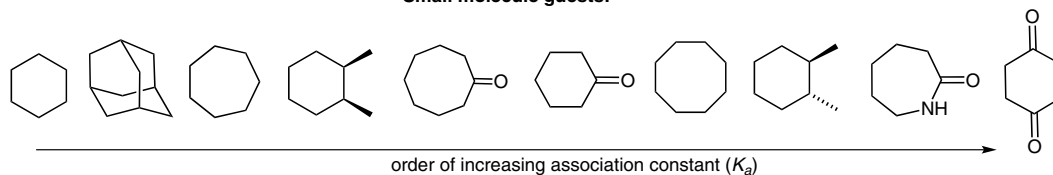
I. POCHOROVSKI, M.-O. EBERT, J.-P. GISSELBRECHT, C. BOUDON, W. B. SCHWEIZER, F. DIEDERICH* (ETH ZÜRICH, SWITZERLAND AND UNIVERSITÉ DE STRASBOURG, FRANCE)

Redox-Switchable Resorcin[4]arene Cavitands: Molecular Grippers
J. Am. Chem. Soc. **2012**, *134*, 14702–14705.

Redox-Switchable Cavitands: Molecular Grippers



Small molecule guests:

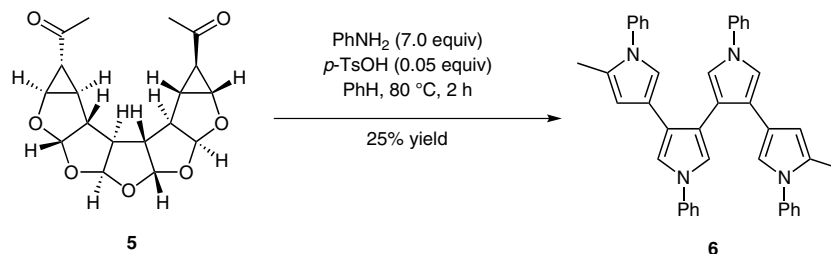
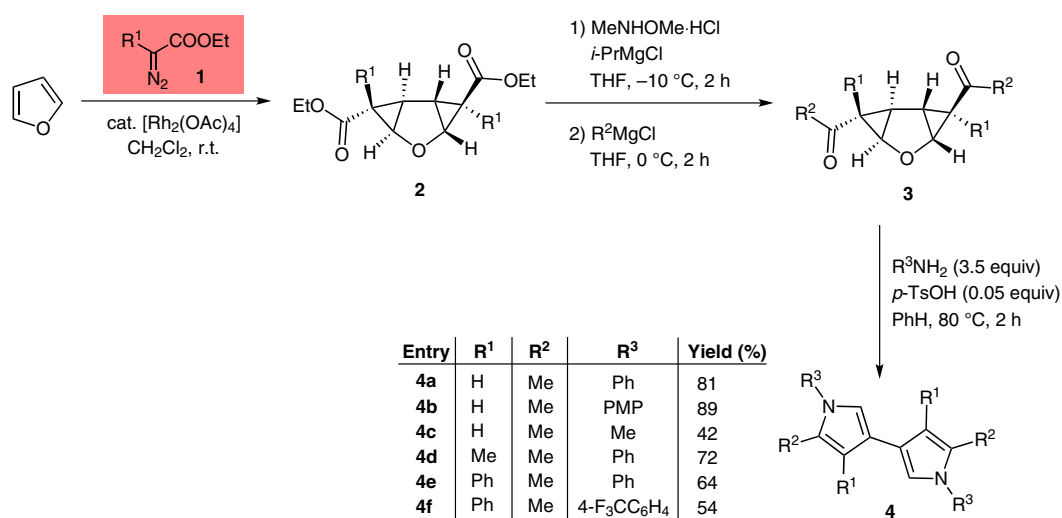


Significance: Here, a diquinone-based resorcin[4]arene cavitand goes from a kite to a vase form when reduced. The vase forms via hydrogen bonding between the central diols and the oxygens of the amides. This vase is stable even at $-80\text{ }^\circ\text{C}$ and can be used to capture the small molecule guests shown above. The molecules are shown in order of increasing association constant K_a . The vase cavitand releases the guests upon oxidation.

Comment: Both the kite and vase form are stable in deuterated chloroform, tetrahydrofuran, and mesitylene. After two to four days, the reduced form reverts into the oxidized form. A crystal structure of the reduced form has a 7.3° cavity, which allows it to encapsulate the solvent molecule mesitylene, as well as the larger guest molecules.

SYNFACTS Contributors: Timothy M. Swager, Markrete Krikorian
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Precisely Defined Electron-Rich Oligopyrroles

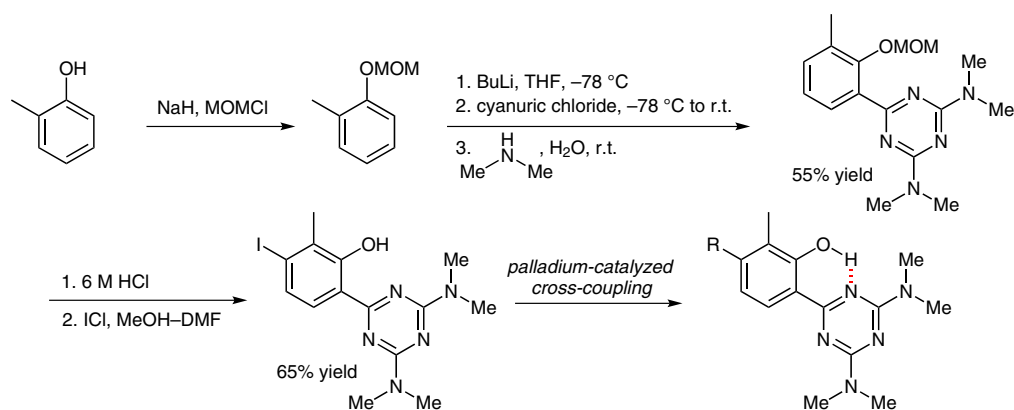


Significance: The authors report the synthesis of 3,3'-linked oligopyrroles through the domino ring-enlargement of cyclopropanes. In one step, furan is converted into **2**, which is subsequently transformed into diketone **3** via Weinreb-ketone synthesis. Refluxing with catalytic acid in benzene with an aniline, yielded the desired bispyrrole products **4**. Unsurprisingly, the electron-rich anilines provided significantly higher yields than the electron-poor anilines.

Comment: Extended oligoacetalic diketone **5** was synthesized and subsequently converted into quarter-pyrrole **6** in 25% yield. This is the first electron-rich, precisely defined oligopyrrole reported and it is noteworthy due the inherent instability of electron-rich oligopyrrolic systems.

S. RIHN, P. RETAILLEAU, A. DE NICOLA, G. ULRICH, R. ZIESSEL* (UNIVERSITÉ DE STRASBOURG AND LABORATOIRE DE CRYSTALLOCHIMIE, GIF-SUR-YVETTE, FRANCE)
Synthetic Routes to Fluorescent Dyes Exhibiting Large Stokes Shifts
J. Org. Chem. **2012**, *77*, 8851–8863.

Large Stokes Shift from Triazine–*o*-Phenol Dyes



Selected chromophores:

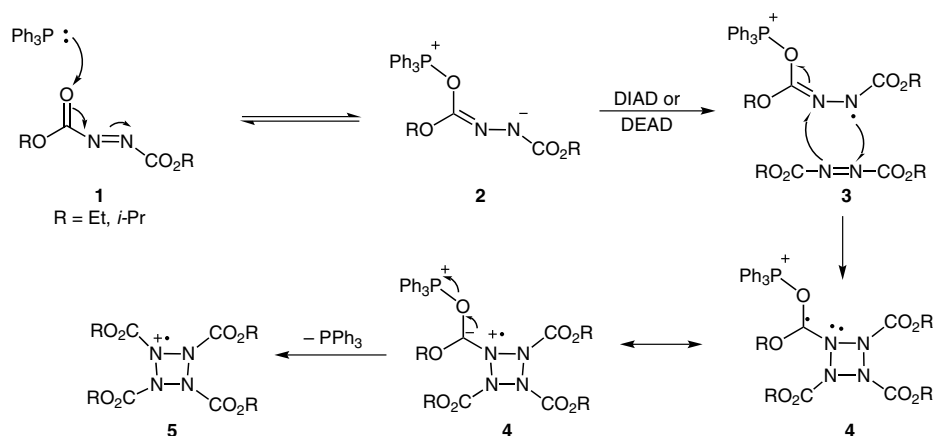
R	Yield of the cross-coupling step	Quantum yield, Φ	Stokes shift, cm^{-1}
H	–	0.28	10900
	31%	0.25	9100
	90%	0.23	9700
	40%	0.21	12000
	41%	0.46	6000
	48%	0.46	570

Significance: Fluorescent dyes exhibiting large Stokes shifts are of great interest for a multitude of applications. The authors report a straight-forward synthesis of a series of phenol–triazine dyes that exhibit hydrogen bonding in the ground state and undergo excited state intramolecular proton transfer (ESIPT), leading to the observation of large Stokes shifts.

SYNFACTS Contributors: Timothy M. Swager, Silvia V. Rocha
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DOI: 10.1055/s-0032-1317886; **Reg-No.:** S13412SF

Comment: An exception to the observation of a large Stokes shift is the perylene-substituted dye; in this case, the perylene is responsible for the emission observed and the energy transfer occurs from the keto form to the perylene moiety. Also noteworthy is the large range of absorption and emission maxima exhibited by the family of dyes in this report.

Formation of an Unusual Four-Membered Nitrogen Ring



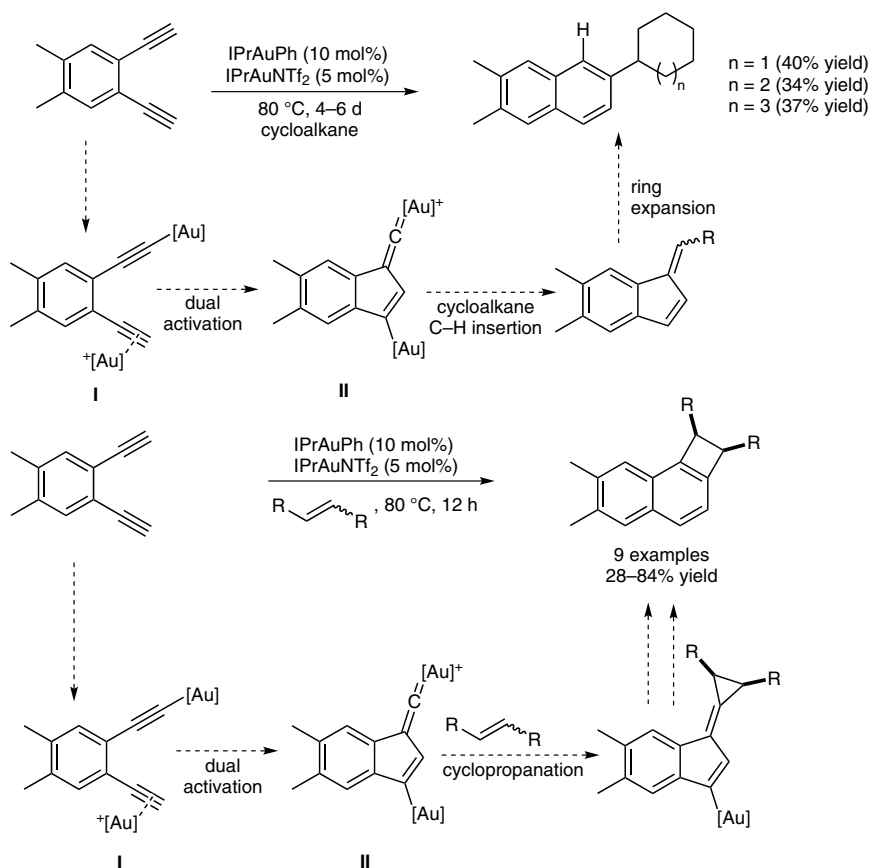
Significance: Above is one of three proposed mechanisms for the formation of the new radical cationic nitrogen four-membered ring **5**. This tetrazetidine forms from allowing triphenylphosphine and diisopropyl azodicarboxylate to react. Previous studies had shown cursory evidence for the formation of a tetrazetidine by other methods, while this work offers more conclusive evidence in the form of EPR spectra and DFT calculations.

Comment: The reaction was monitored by EPR spectroscopy, which showed the presence and disappearance of **3** followed by the formation of **5**. Thus, the authors claim that the above mechanism is the most plausible. The DFT calculations show electron density on the methine or methylene protons ($\text{R} = \text{Et}, i\text{-Pr}$), which helps to rationalize hydrogen hyperfine coupling seen on the EPR spectra.

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Gold Vinylidene Complexes: Intermolecular C(sp³)–H Insertions and Cyclopropanations Pathways
Angew. Chem. Int. Ed. **2012**, *51*, 10633–10637.

Intermolecular Reactions of Gold–Vinylidene Complexes



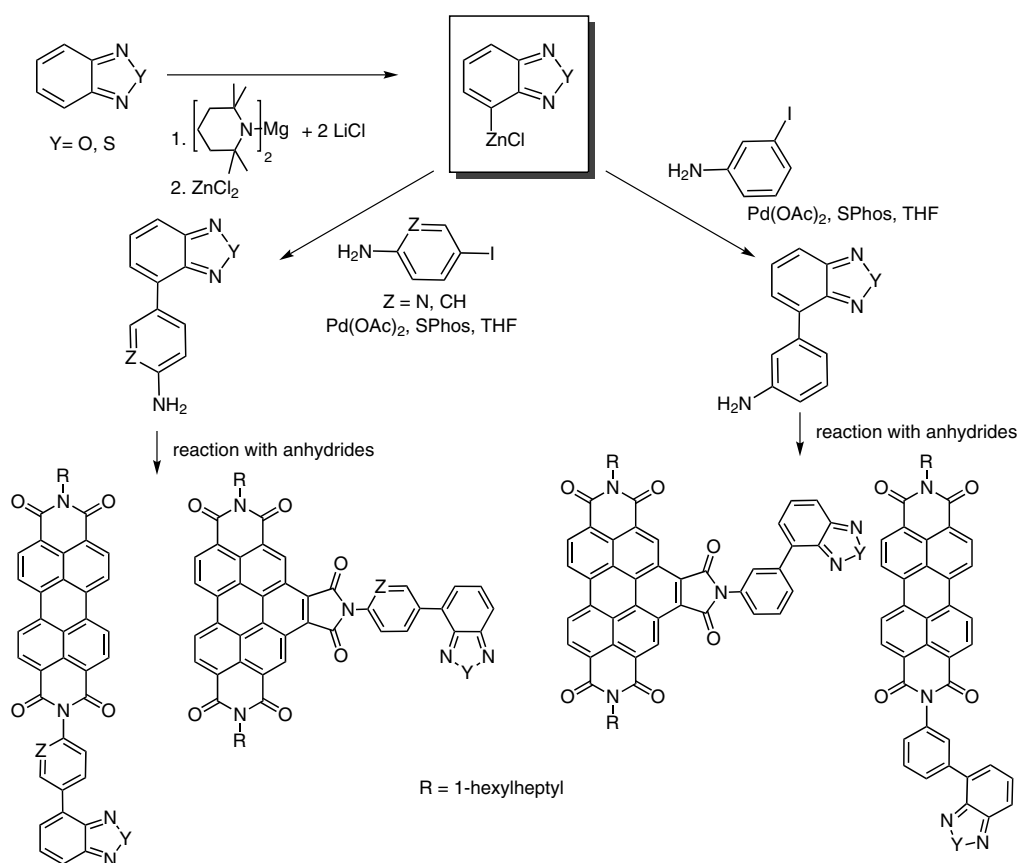
Significance: This communication reports the application of gold–vinylidene complexes in intermolecular C(sp³)–H insertion reactions and cyclobutene syntheses. Vinylidene complex **II** is accessed via dual activation of the dialkyne starting material. In the presence of a cycloalkane, the authors found that **II** follows a C(sp³)–H insertion pathway to form the corresponding cycloalkylated products. However, the complex undergoes cyclopropanation with an alkene to eventually generate the benzocyclobutene derivative shown.

Comment: The authors comment on the high stereoselectivity of the conversion of the dialkyne into benzocyclobutene, particularly noting that the stereochemical configuration of the alkenes used is cleanly reflected in the product. Additional experiments whose results are in favor of a stereospecific cyclopropanation pathway are discussed along with a proposed mechanism of the process.

SYNFACTS Contributors: Timothy M. Swager, Gregory D. Gutierrez
 Synfacts 2013, 9(1), 0040 Published online: 17.12.2012

DOI: 10.1055/s-0032-1317884; **Reg-No.:** S13212SF

Shape Matters: Creating Amorphous Semiconductors



Significance: This work reports efficient synthetic procedures for the connection of two of the best electron-acceptor units (benzothiadiazoles or benzoxadiazoles and perylenes dimides) to create structures that are of irregular shape that do not crystallize. The combined cross-coupling and condensation yields allow for quantities of materials to be produced and the authors also demonstrated direct cross-coupling of the key zinc reagent on functional perylene dimides.

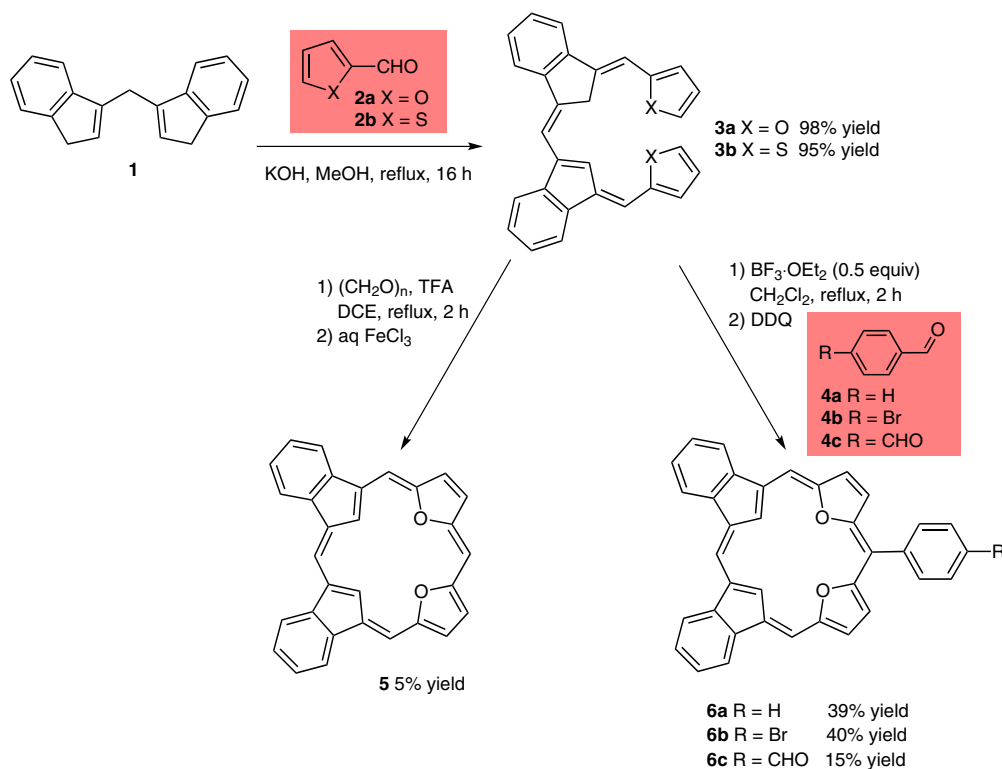
Comment: Organic semiconductors are often insoluble crystalline materials that are difficult to process. Crystalline materials are problematic for the formation of devices because mechanical or thermal stress can create cracks in the structures. As a result, general routes to molecular semiconductors with amorphous solid-state structures are desirable. It will be interesting to see, if the transport properties of these materials compare to crystalline materials.

T. D. LASH,* A. D. LAMMER, G. M. FERRENCE (ILLINOIS STATE UNIVERSITY, NORMAL, USA)

Two-Step Synthesis of Stable Dioxadibaporphyrins from Bis(3-indenyl)methane

Angew. Chem. Int. Ed. **2012**, *51*, 10871–10875.

Nitrogen-Free [18]Porphyrinoids in Two Steps



Significance: The researchers synthesized substituted and unsubstituted dioxadibaporphyrins, which are the first examples of porphyrinoids with adjacent indenes. Bis(3-indenyl)methane **1** was reacted with various aryl aldehydes to yield compounds **3**. Reaction with formaldehyde or an aryl aldehyde followed by oxidation led to the formation of dioxadibaporphyrins **5** and **6**, respectively. These bilin analogues are interesting as natural products as well as organic opto-electronic materials.

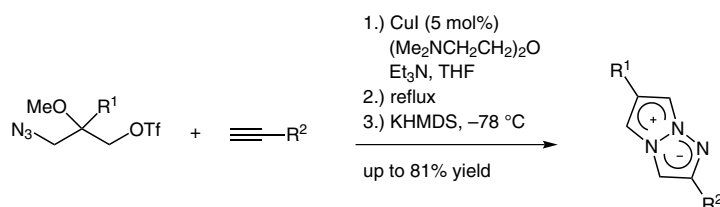
Comment: The reaction of bis(3-indenyl)methane **1** with aryl aldehydes was expected to give a symmetric difulvene; however, the fully conjugated derivative **3** was obtained instead and confirmed with 2D NMR and X-ray crystallography. The ¹H NMR spectra of the porphyrinoids **5** and **6** displayed that the macrocycles are diatropic, as expected from the [18]annulene core.

SYNFACTS Contributors: Timothy M. Swager, Jonathan G. Weis
Synfacts 2013, 9(1), 0042 Published online: 17.12.2012

DOI: 10.1055/s-0032-1317882; **Reg-No.:** S13012SF

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Tuning The Quantum Yield of Fluorescent 2,5-Disubstituted-1,3a,6a-triazapentalene



	R ¹	R ²	Product	Yield (%)
1	OMe	Ph	1a	64
2	OMe		1b	60
3	Me		1c	63
4	CN		1d	57
5 ^a	Ph		1e	19
6	Me		1i	72
7	Me		1j	27

^a The triflate was generated in situ and used without purification.

Significance: Rational design of organic molecules with improved photo-physical properties, such as high quantum yields and tunable fluorescence wavelength, is of great interest in modern science and technology. In this paper, the authors report a one-pot synthesis of 2,5-disubstituted-1,3a,6a-triazapentalenes. By a cascade sequence utilizing a copper(I)-catalyzed 1,3-dipolar cycloaddition followed by intramolecular cyclization and elimination, the authors managed to obtain the desired 1,3a,6a-triazapentalene skeleton.

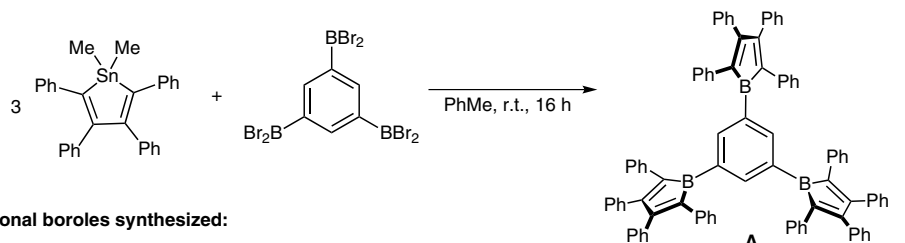
Comment: The authors report the synthesis of a series of 2,5-disubstituted-1,3a,6a-triazapentalenes. These novel compounds allowed the authors to probe the effects of electron-donating and -withdrawing substituents on the photo-physical properties of 1,3a,6a-triazapentalene derivatives. Introduction of substituents in the 5-position led to a dramatically increased quantum yield. A correlation between the Hammett σ_p -value of the R²-substituent and the quantum-yield tendency could furthermore be estimated.

SYNFACTS Contributors: Timothy M. Swager, Jens B. Ravensbæk
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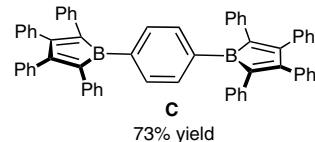
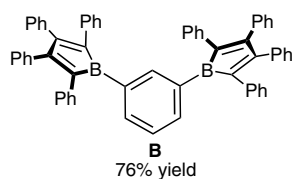
DOI: 10.1055/s-0032-1317891; **Reg-No.:** S13912SF

H. BRAUNSCHWEIG,* C.-W. CHIU, A. DAMME, B. ENGELS, D. GAMON, C. HÖRL, T. KUPFER, I. KRUMMENACHER, K. RADACKI, C. WALTER (JULIUS-MAXIMILIANS-UNIVERSITÄT WÜRZBURG, GERMANY AND NATIONAL TAIWAN UNIVERSITY, TAIPEI, TAIWAN)
Oligo(borolyl)benzenes—Synthesis and Properties
Chem. Eur. J. **2012**, *18*, 14292–14304.

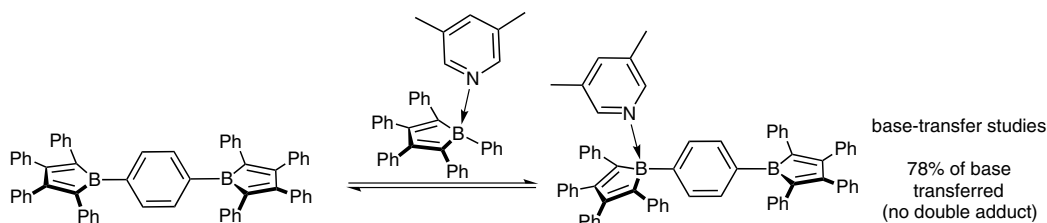
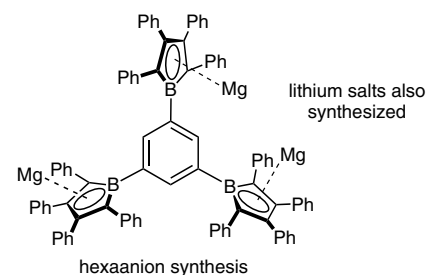
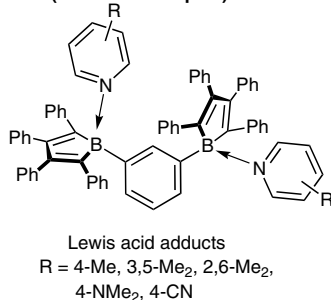
Synthesis of New Borolylbenzenes



Additional boroles synthesized:



Experimental studies (selected examples):

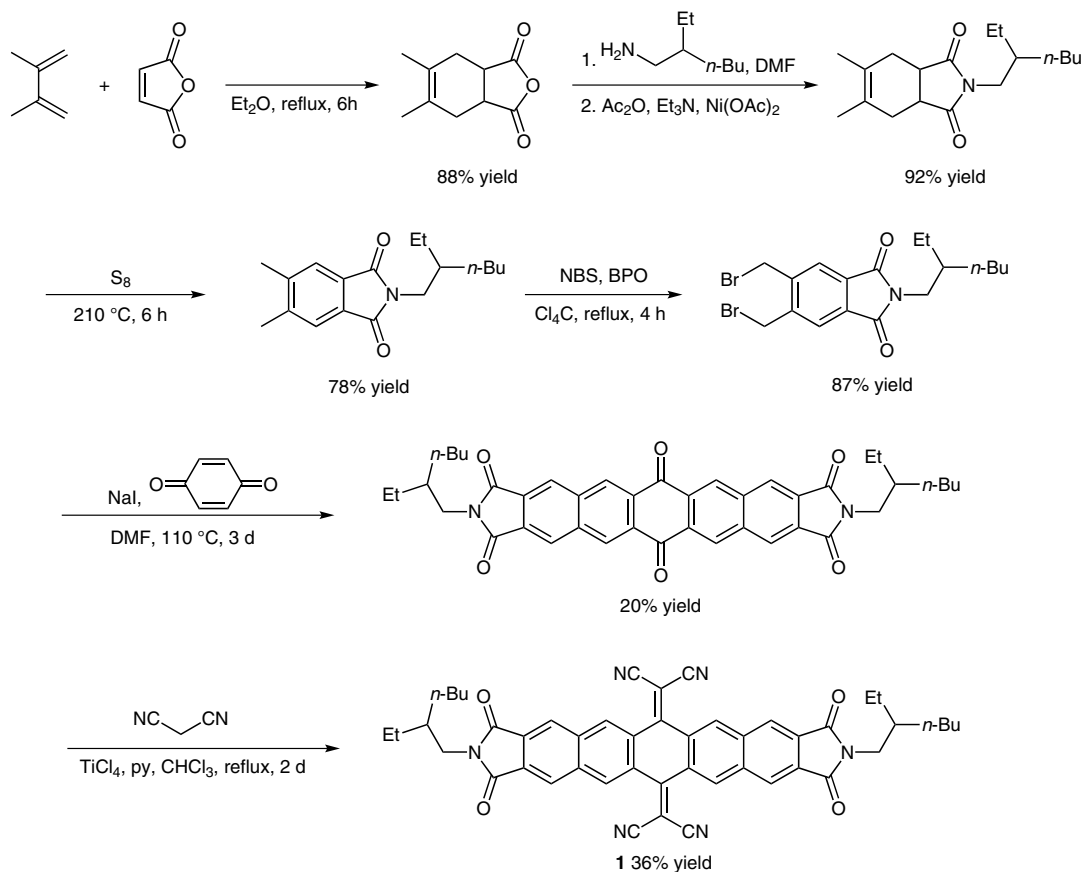


Significance: The synthesis and properties of a new class of oligoboroles are reported. These compounds represent the first examples of antiaromatic borolyl moieties connected by an organic π -conjugated system (i.e. benzene) and are synthesized via tin–boron exchange. Adducts of the oligoboroles with various pyridine derivatives and their hexaanion salts with magnesium and lithium are reported and extensively studied.

Comment: The Lewis acidities of boroles **B** and **C** are assessed by base-transfer studies with a pentaphenylborole–3,5-lutidine adduct. The authors conclude that there is an effective electronic communication between the *para*-functionalized borolyl groups of **C** because its double adduct is not observed during the exchange experiment. However, base-transfer studies of **B** indicate the formation of both single and double adducts, thus suggesting less interaction between the *meta*-substituted boroles.

SYNFACTS Contributors: Timothy M. Swager, Gregory D. Gutierrez
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DOI: 10.1055/s-0032-1317883; Reg-No.: S13112SF

Electron-Acceptor Pentacene Derivative



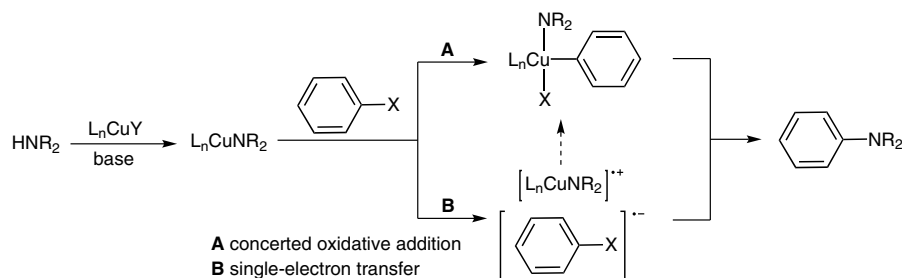
Significance: This paper reports the synthesis of an extended tetracyanoquinodimethane (TCNQ) analogue, **1**. Although this is not the first report of a TCNQ-like acene, the method reported by the authors consists of only six steps, including a double Diels–Alder reaction and a Knoevenagel condensation as key steps. The presence of the diimide substituents not only increases the solubility of the final molecule, but also has implications on its electronic properties.

Comment: Electron-acceptor molecules are essential in organic electronic materials, and an important property of such molecules is the LUMO energy level. The authors report a LUMO level of -4.03 eV for **1**, which makes this molecule and derivatives of it, good candidates for a variety of applications.

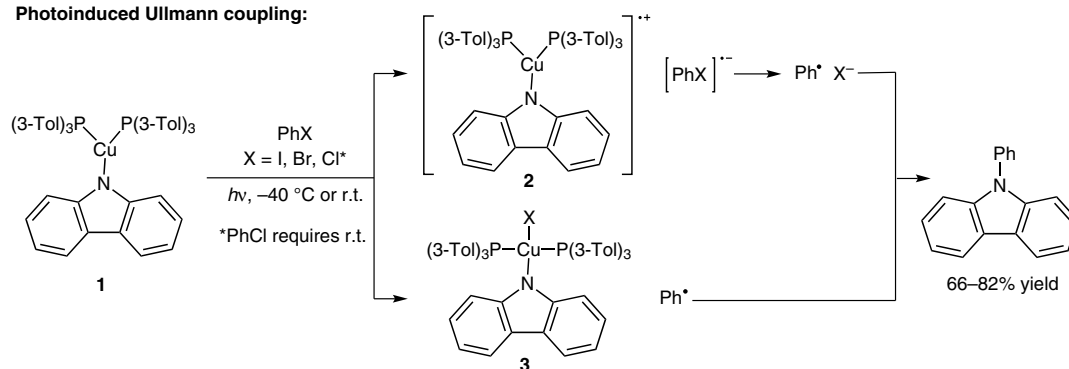
S. E. CREUTZ, K. J. LOTITO, G. C. FU,* J. C. PETERS* (CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA AND MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, USA)
Photoinduced Ullmann C–N Coupling: Demonstrating the Viability of a Radical Pathway
Science **2012**, 338, 647–651.

C–N Bond Formation Through a Single-Electron Transfer Pathway

Ullmann coupling and possible mechanistic pathways:



Photoinduced Ullmann coupling:

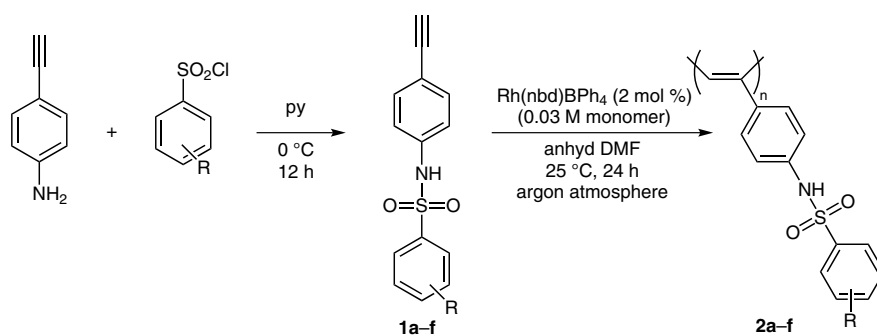


Significance: For the last century, Ullmann couplings have been used to synthesize anilines from amines and aryl halides, despite the relatively harsh conditions necessary for C–N bond formation (stoichiometric copper under high temperatures). Although many groups have focused their attention on improving the traditional Ullmann coupling, the mechanism of aryl halide bond cleavage has remained unsettled within the chemical community. Two possible mechanistic pathways include concerted oxidative addition (**A**) and single-electron transfer (**B**). In this report, Peters, Fu and co-workers provide the first experimental evidence for a single-electron transfer mechanism.

Comment: Radical intermediates were able to be observed for the first time during an Ullmann reaction by the development of a mild, photo-induced coupling of aryl halides and carbazole. Carbazole-containing copper complex **1** is excited with 300–400 nm light, which promotes an electron-transfer reaction, ultimately leading to an aryl radical. Reaction of the aryl radical with the resulting copper-carbazole complex (**2** or **3**) leads to C–N bond formation. It was shown that this transformation proceeds at -40°C with phenyl iodide or phenyl bromide. For coupling to phenyl chloride, longer reaction times at room temperature were necessary. The coupling does not occur in the dark and kinetic isotope effects, radical traps, competition experiments, by-product formation analysis, and EPR spectra all support one-electron chemistry in the photo-induced Ullmann coupling.

SYNFACTS Contributors: Timothy M. Swager, Ellen M. Sletten
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Poly(phenylacetylene)s with Pendant Sulfonamide Receptors for Anion Detection



	R	Yield		R	Yield	Mn × 10 ⁻⁵	PDI
1a	H	90%	2a	H	86%	0.9	1.97
1b	4-O ₂ N	87%	2b	4-O ₂ N	68%	4.77	5.65
1c	3,5-(CF ₃) ₂	92%	2c	3,5-(CF ₃) ₂	84%	2.44	3.54
1d	4-Me	95%	2d	4-Me	85%	2.91	2.57
1e	4- <i>t</i> -Bu	88%	2e	4- <i>t</i> -Bu	81%	1.2	3.33
1f	4-OMe	72%	2f	4-OMe	82%	1.64	4.99

Significance: Development of colorimetric sensors capable of detecting anions in aqueous medium is of great interest. In this paper, the authors describe the synthesis of a series of poly(phenylacetylene)s bearing pendant sulfonamide side chains. The sulfonamide moiety is demonstrated to act as an anion receptor via a deprotonation mechanism, allowing sensing of anions in aqueous environment.

Comment: In this paper, the authors report a two-step protocol leading to a series of poly(phenylacetylene)s containing pendant sulfonamide moieties with electron-withdrawing or electron-donating substituents (**2a-f**). The obtained polymers showed varied PDIs (see Table above) in agreement with known rhodium-catalyzed polymerizations of acetylenes. They furthermore demonstrate the utility of these polymers as anion sensors. **2b** showed clear red-shifted absorption upon addition of fluoride in mixed solvents with 20% water content.