

A One-Step Synthesis of a Poly(iptycene) through an Unusual Diels–Alder Cyclization/Dechlorination of Tetrachloropentacene

Dmitrii F. Perepichka, Michael Bendikov, Hong Meng, and Fred Wudl*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

Received May 16, 2003; E-mail: wudl@chem.ucla.edu

There is a continuous interest in polycyclic aromatic compounds mostly as materials for optoelectronic applications (LED, FET, photovoltaics, etc.), but also as building blocks in construction of supermolecular systems such as fullerenes, nanotubes, and triptycenes (tribenzo[2.2.2]bicyclohexadiene, Tr).¹ In the latter, the intramolecular cavities allows for strong, noncovalent binding to suitably sized species, which can be used in sensing of, e.g., nitric oxide.² Even more specific cavities have been synthesized with dendritic molecules, “superiptycenes”, containing up to nine Tr units connected by rigid benzene rings.³ Recently, the special geometry of Tr was recognized as a way to control the supramolecular architecture in liquid crystals and polymer matrices.⁴ Several polymers incorporating iptycene moieties, connected by (phenylene ethynylene) or (phenylene vinylene) units, have been synthesized and shown to possess improved order and electronic properties.⁵ To the best of our knowledge, there was only one preliminary report on polymers incorporating triptycene as the only repeating unit.^{5b} In principle, it can be constructed via [4 + 2] cycloaddition of acenes if both reactive centers — diene and dienophile — can be activated in the same molecule. Even though they could be considered aromatic, polyacene compounds (e.g., anthracene and pentacene) are excellent dienes for Diels–Alder (DA) synthesis of a Tr system. Very little, however, is known about polyacene compounds as dienophiles.⁶ Here we report the unusual cycloaddition followed by dechlorination reaction of 2,3,9,10-tetrachloropentacene (Cl₄Pn), leading to a novel aromatic ladder polymer, poly(iptycene) (PP1).

In a quest for novel materials for organic field-effect transistors (FET),⁷ we have synthesized Cl₄Pn by condensation of 4,5-dichlorophthalaldehyde with cyclohexane-1,4-dione and reduction of the resulting pentacenequinone with aluminum cyclohexanolate in the presence of HgCl₂ and CCl₄. Much to our surprise, we found absolutely no FET activity in this material.⁸ A possible explanation came from the thermal analysis, which showed instability of this compound at temperatures above 350 °C (sublimation at ~350 °C was used in device preparation) (Figure 1).

Heating Cl₄Pn (purified by vacuum sublimation at 300 °C) in nitrogen above 350 °C results in a rapid loss of weight down to a plateau, corresponding to liberation of two chlorine atoms, giving product PP1. On further heating, a second weight loss is seen above 600 °C (followed by stabilization at ~720 °C), corresponding to the loss of another two chlorine atoms and hydrogen atoms, as well as some decomposition (product PP2), and only minor gradual weight loss occurs up to 1400 °C. A perfect fit of the elemental analysis of the PP1 product to the formula C₂₂H₁₀Cl₂ (i.e., Cl₄Pn–2Cl),⁹ together with a well-defined two-stage TGA curve, suggested a relatively clean chemical reaction. Interestingly, the light color (from yellowish-green to brownish, depending on conditions) of the PP1 product (as compared to the dark blue color of Cl₄Pn) and complete disappearance of the characteristic pentacene vibronic band at 500–750 nm in the UV–vis spectra indicates decreased

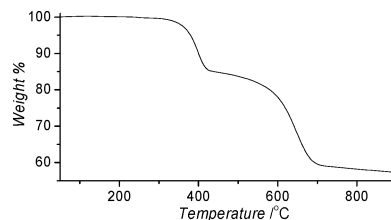


Figure 1. Thermal gravimetric analysis monitoring of the thermal decomposition of Cl₄Pn.

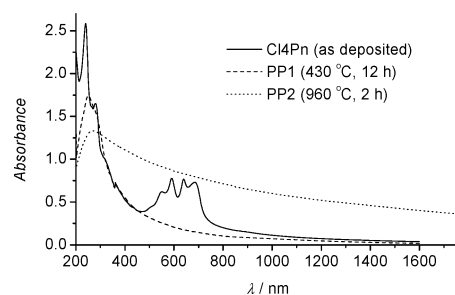


Figure 2. UV–vis–NIR spectra of thin films of Cl₄Pn and its pyrolysis products, PP1 and PP2.

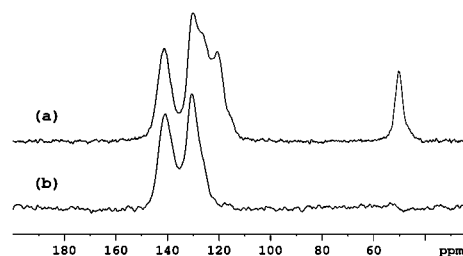
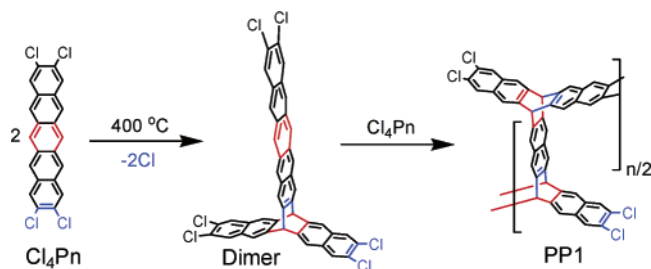


Figure 3. (a) CP and (b) NQS MAS ¹³C NMR spectra of PP1.

conjugation due to the disruption of the pentacene system (Figure 2).¹⁰ The λ_{max} at 250 nm corresponds to naphthalene moieties. Despite a strong ESR signal (a broad symmetric line with $g = 2.0035$, $\Delta H_{\text{p-p}} = 10$ G, spin concentration ~1%),⁹ PP1 gives well-resolved NMR spectra.¹¹ The CPMAS ¹³C NMR solid-state spectrum of PP1 (Figure 3) shows a wider range of chemical shifts of the aromatic carbons, as compared to Cl₄Pn,⁹ and, more importantly, a new peak at 50 ppm reveals sp³-hybridized carbons. The disappearance of this signal (as well as few other aromatic signals) in a nonquaternary suppression (NQS) CP MAS ¹³C NMR experiment allows their assignment to H-substituted carbon atoms.¹² Integration of the CPMAS spectrum⁹ gives a 10.7:1 ratio between the aromatic carbons at 110–150 ppm and aliphatic carbons at 50 ppm; i.e., only one out of five pentacene rings undergoes reaction to produce two sp³ carbons. On the basis of the above, we assigned a poly(iptycene) structure to the PP1 product, formed by [4 + 2] cycloaddition of Cl₄Pn molecules (Scheme 1).⁶ The complete lack of solubility of PP1, the absence of pentacene electronic absorbance,

Scheme 1. Thermal Polymerization of Cl₄Pn

the absence of oligomer molecular fragments in the mass spectra, and the elemental analysis showing precise loss of two chlorine atoms suggest a polymerization rather than a short-length oligomerization. At higher temperatures, it is unlikely to have a selective polymerization direction; i.e., an initial “dimer” may act as both a diene and a dienophile. Consequently, hyperbranching polymerization, competing with linear chain growth, should give an extended 2D structure of poly(iptycene).

Loss of the two residual chlorine atoms above 600 °C is accompanied by gradual dehydrogenation (as evidenced by elemental analysis), resulting in a highly conducting material (pressed pellet $\sigma_{\text{rt}} \approx 10^{-3}$ S/cm for the material obtained at 730 °C, and ≈ 5 S/cm for the material obtained at 960 °C by the two-probe method), possibly graphitic, though further characterization will be done in due course. This temperature is remarkably lower than the normal graphitization temperatures (2000–3000 °C) and in the range of a claim of graphitization of high-molecular-weight polycyclic aromatics.¹³ The UV–vis–NIR spectrum of PP2 is characterized by a broad, intense absorbance band through the entire spectral region (200–2000 nm), similar to that of graphite. The FT-IR spectrum of PP2, unlike PP1, which is very similar to starting Cl₄Pn, lacks any characteristic vibronic bands, but very intense broad electronic “conduction” bands give rise to IR absorbance of the material. The strong ESR signal seen in PP1 almost completely disappears on heating above 600 °C. Scanning electron microscopy of PP2 indicates a smooth surface and does not provide enough information to distinguish it from glassy carbon.⁹

To shed light on this unusual transformation of Cl₄Pn to poly(iptycene) PP1, we performed DFT (B3LYP) calculations using the 6-31G(d) basis set.⁹ Our first hypothesis was dechlorination of Cl₄Pn to give a benzyne species which could be trapped in a DA reaction with another Cl₄Pn molecule, which, however, had to be discarded due to extremely high energy requirements (111.7 kcal/mol for elimination of Cl₂ from Cl₄Pn, similar to 111.3 kcal/mol for elimination of Cl₂ from 2,3-dichloronaphthalene). An alternative mechanism included a DA reaction between the peripheral double bond (C2–C3) of Cl₄Pn itself (acting as dienophile)¹⁴ and the central ring of another Cl₄Pn molecule (acting as diene). The [4 + 2] cycloaddition product is expected, at the reaction temperature, to dechlorinate readily, due to aromatization resulting in an iptycene structure. The calculated activation energy of the concerted DA addition, keeping C_s symmetry, is 64.7 kcal/mol. The frequency analysis indicated a second-order saddle point. Indeed, when the wave function was allowed to become unrestricted and symmetry constraints were released, calculation of the asymmetric reaction mechanism through a formation of a biradical, rotation, and finally

cyclization showed its preference versus the concerted mechanism by 13.8 kcal/mol (for unsubstituted pentacene),⁹ leading to an overall activation barrier of ca. 50 kcal/mol, very reasonable for a reaction occurring at 400 °C. A DA adduct involving the *second* benzene ring as a diene is higher by 4.2 kcal/mol, which should result in $\sim 3\%$ of this byproduct. Once the pentacene has undergone cycloaddition, the terminal double bond loses its dienophilicity (calculations show that naphthalene has a higher activation energy, by 5.8 kcal/mol, toward cycloaddition with pentacene than pentacene itself).⁹ The overall reaction of the dechlorinating “dimerization” of Cl₄Pn is endothermic by 12.3 kcal/mol. To our knowledge, this is the first example of (i) a DA reaction between two acene molecules and (ii) the asymmetric biradical DA reaction mechanism for symmetric reagents. The mechanism of this unusual reaction will be discussed in detail in a forthcoming paper.

To conclude, we have discovered the first reaction of a substituted pentacene molecule as a dienophile. A surprisingly clean DA self-coupling of Cl₄Pn leads to a novel ladder polymer, poly(iptycene), which can be converted to a conducting carbon at relatively low temperature (600–900 °C). Theoretical calculations of the former reaction suggest a biradical asymmetric mechanism, despite highly symmetric reactants.

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Supporting Information Available: Experimental details for synthesis of Cl₄Pn, PP1, and PP2, their characterization, and DFT calculations; DSC, FTIR, ESR, and ¹³C NMR solid-state spectra of Cl₄Pn; SEM micrograph of the product PP2; schemes of the calculated reaction pathway (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Presumably, the ESR signal shall be attributed to the intermediate and/or side reaction radical species.
- The sp³ carbon of parent Tr resonates at 54.0 ppm in ¹³C NMR (in CDCl₃).
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- The calculated C2–C3 bond in Cl₄Pn (1.442 Å) is relatively long, relatively weaker, and hence more reactive.

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