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Regioselective Synthesis of Nanographenes by Photochemical Cyclodehydrochlorination

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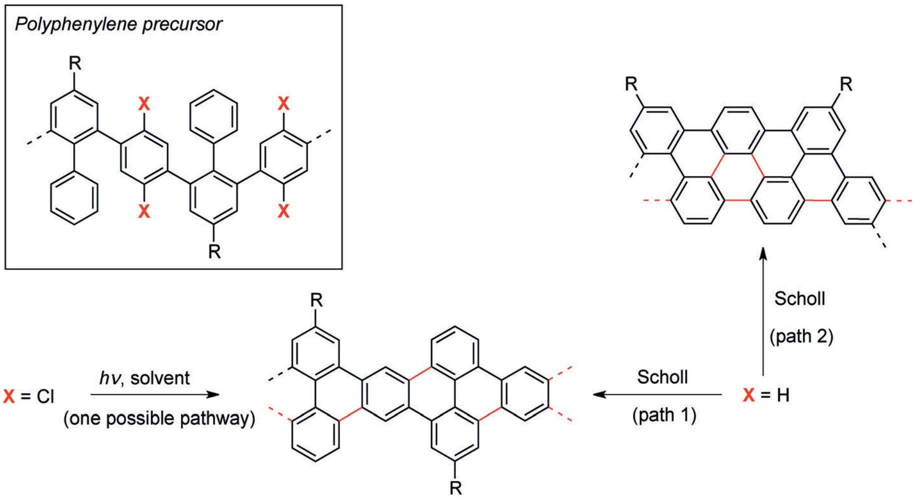
Abstract: *Novel nanographenes were prepared by a photochemical cyclodehydrochlorination (CDHC) reaction. Chlorinated precursors were irradiated in acetone in the presence of a base or in pure benzene and underwent multiple (up to four) regioselective cyclization reactions to provide rigid π-conjugated molecules. Pure compounds were recovered in good yields by simple filtration at the end of the reaction. The CDHC reaction showed compatibility with both electron-poor and electron-rich substrates, thus allowing the synthesis of pyridine- and thiophene-fused nanographenes. It also enabled the synthesis of sterically hindered contorted π-conjugated molecules without causing full aromatization. A kinetic study showed that the CDHC reaction under the conditions used is a very fast process, and some reactions are completed within minutes. The CDHC reaction thus shows great potential as an alternative to other reactions involving harsher conditions for the preparation of nanographenes.*

Bottom-up, solution-phase synthesis is arguably one of the most promising strategies for obtaining well-defined nanographenes and graphene nanoribbons (GNRs) with tunable electronic and optical properties.[1] Unlike well-known physical top-down methods in which GNRs are obtained by "unzipping" carbon nanotubes[2] or cutting stripes from graphene sheets,[3] bottom-up approaches enable precise control of the widths and edge configurations of nanographenes and GNRs. In their seminal studies, the Müllen group showed that it is possible to obtain nanographenes and GNRs with different widths and edge configurations through multiple Lewis acid catalyzed cyclodehydrogenation reactions, known as the Scholl reaction,[4] on polyphenylene precursors.[1] Although the usefulness of the Scholl reaction is widely acknowledged, it possesses some serious drawbacks that limit the structural diversity of the nanographenes and GNRs that can be prepared.[5] One of its most detrimental features is its poor regioselectivity, which results in structural defaults that affect the properties of the resulting materials. Other disadvantages include the formation of by-products by undesired rearrangements and the use of a metal-based catalyst.[5d] To overcome these problems, other techniques, such as palladium-catalyzed direct C–H arylation,[6] Al_2O_3-mediated HF elimination,[7] Yamamoto cyclotrimerization,[8] palladium-catalyzed [2+2+2] cycloaddition,[9] sequential I–Cl-induced cyclization and Mizoroki–Heck coupling,[10] and the Katz-modified Mallory reaction,[11] have been used for the cycloaromatization of the polyphenylene precursor. However, these methods may suffer from modest yields, lead to a significant amount of side products, or require a high metal-catalyst loading.

Herein we report a new solution-phase strategy for the preparation of novel nanographenes and GNR fragments by the photochemical cyclodehydrochlorination (CDHC) of various aryl chlorides (Scheme 1). The optical properties of the new nanographenes are also reported, along with the results of DFT and TD-DFT calculations.



Scheme 1. Different reaction paths for the CDHC (X = Cl) and Scholl (X = H) reactions. Newly formed bonds are shown in red.

The first reports of the formation of simple polycyclic aromatic hydrocarbons (PAHs) by the use of the CDHC reaction appeared in the early 1970s.[12] Surprisingly, very few articles have mentioned the use of this reaction for the synthesis of PAHs, as the Scholl reaction is seen as the "go-to" reaction for the synthesis of such compounds. Recently,

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Hartley and co-workers used this reaction to prepare simple PAHs with liquid-crystal properties,[13,14] whereas Schnapperelle and Bach employed it to prepare phenanthro[9,10-*c*]thiophenes.[15] A similar photochemical cyclodehydrofluorination reaction of aryl fluorides was also reported recently for the preparation of triphenylene and phenanthrene derivatives, but good yields were observed for the cyclization of polyfluorinated precursors only.[16]

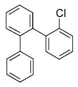
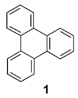
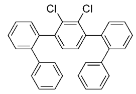
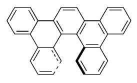
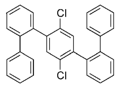
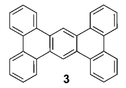
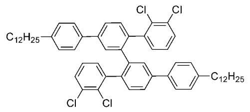
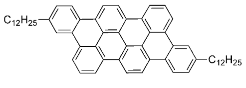
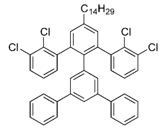
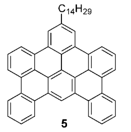
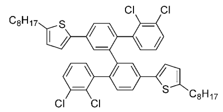
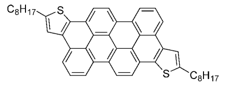
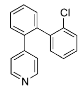
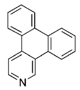
The CDHC reaction is very attractive for the synthesis of nanographenes for several reasons: 1) It is regioselective, meaning that new well-defined architectures that were not accessible with the Scholl reaction could potentially be prepared; 2) it provides better control over the edge configurations of the nanographenes; 3) it proceeds without the use of a metal catalyst, which is particularly important if electronic applications are targeted; 4) it proceeds cleanly without rearrangement or the formation of side products under appropriate conditions; 5) chlorine atoms can be introduced into polyphenylene precursors by careful design of the monomers; and 6) it is conducted under very mild conditions, thus enabling the introduction of different functional groups onto the nanographenes to modulate their properties. Scheme 1 highlights the difference in regioselectivity between the CDHC reaction and the oxidative cyclodehydrogenation (Scholl) reaction.

To investigate the usefulness of the CDHC reaction for the preparation of nanographenes, we undertook the synthesis of compounds **1**–**7** from their chlorinated precursors (Table 1; see the Supporting Information for synthetic details). The triphenylene **1** was prepared as a model compound, whereas the small nanographenes **2** and **3** were prepared to demonstrate the regioselectivity of the photochemical CDHC reaction. Nanographenes **4** and **5** were synthesized to assess the usefulness of the CDHC reaction in multiple cyclization processes and to evaluate its efficiency for the preparation of large nanographenes. Finally, molecules **6** and **7** were targeted to show the versatility of the CDHC reaction for the preparation of nanographenes fused with either electron-rich (thiophene, **6**) or electron-poor (pyridine, **7**) moieties.

The common building blocks for all these molecules are dichlorobenzene derivatives that are either commercially available (2,3-dichloroaniline) or can be synthesized on a gram scale in a few straightforward synthetic steps. 1,2-Dichloro-3,6-diiodobenzene was prepared from commercially available 2,3-dichloroaniline according to a reported procedure,[17] whereas 1,4-diiodo-2,5-dichlorobenzene was prepared in two steps from 2,5-dichloroaniline (see the Supporting Information). 1,2-Dichloro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)benzene was prepared in one step from the corresponding commercially available iodo derivative. A wide variety of nanographene precursors can be prepared from these building blocks by Suzuki–Miyaura coupling. All nanographenes are presented with the corresponding chlorinated precursor in Table 1.

In a typical photochemical CDHC reaction, a solution of the chlorinated precursor at a concentration of 5×10^{-5} M in acetone and aqueous Na_2CO_3 (0.1 M, 1 equiv per CDHC reaction) was prepared. This solvent system, which was reported for the formation of indole derivatives through cyclodehydrohalogenation,[18] was used as an alternative to benzene. We hypothesized that the sensitization effect of acetone as well as the presence of a base to quench the HCl formed during this reaction could be beneficial for this reaction. The solution was irradiated at room temperature with a medium-pressure 450 W Hg lamp for 2–5 h, depending on the substrate. Even under the conditions of relatively high dilution used, the desired products gradually precipitated from the solution, thus allowing the recovery of nanographenes **1**–**6** through simple filtration. In the case of compound **7**, a standard workup and column chromatography were necessary to isolate the product, as no precipitation was observed during the course of the reaction. In all other cases, simple filtration was enough to obtain the nanographenes in their pure form. A photoreactor equipped with 16 300 nm UV lamps (7.2 W) could also be used successfully for the CDHC reaction of our chlorinated precursors. When the photoreactor was used, the yields of formation for nanographenes **1**–**7** were very similar to those observed with the medium-pressure Hg lamp, although the reactions were generally slower. The all-benzene products **1**–**5** of the CDHC reaction

Table 1: Synthesis of nanographenes **1**–**7** by the CDHC reaction.[a]

Substrate	Product	Yield [%][b]
	 **1**	95
	 **2**	85 (92)
	 **3**	72 (85)
	 **4**	71 (92)
	 **5**	79 (94)
	 **6**	21 (68)
	 **7**	76

[a] Reaction conditions for the synthesis of nanographenes **1**, **2**, **3**, and **7**: 0.01 M, acetone, 0.1 M aqueous Na_2CO_3, 16×7.2 W lamps @300 nm, 48 h, room temperature. For compounds **4**–**6**, a 450 W medium-pressure mercury lamp was used instead, and the concentration of the reaction mixture was 5×10^{-5} M. [b] The yield per cyclization reaction is given in parentheses.

were isolated in relatively high yields of 79–95%. Unfortunately, the lack of solubility of these nanographenes did not enable us to perform HPLC experiments to determine the precise conversion of the precursors into the desired products. Nonetheless, monitoring of the reactions by thin-layer chromatography suggested that the chlorinated precursors reacted quickly.

We conducted a kinetic study of the CDHC reaction by monitoring the fluorescence of **5** as a function of the irradiation time of the corresponding chlorinated precursor. The experiment performed in an acetone/Na_2CO_3 mixture at 300 nm suggests that the CDHC reaction behaves like a zero-order process at the beginning of the reaction, as the emission intensity increased linearly with irradiation time from $t=0$ to $t=50$ s with a slope (k value) of 21.4 s^{-1} (Figure 1a; see also the Supporting Information).[19] After only 1 min, a significant decrease in the emission intensity was observed. This change can be attributed to the rapid precipitation of **5** and, hypothetically, to some degradation due to the light-induced formation of acetone radicals.[20] Interestingly, the CDHC reaction in the same solvent system was much faster at 300 nm than at 254 nm ($k=4.6$ s^{-1}). When benzene was used as the solvent at 300 nm, the reaction proceeded at a slower rate with $k=12.2$ s^{-1} (Figure 1b), although a higher yield was observed (96% isolated, 99% per CDHC reaction). Unlike that in acetone, the reaction in benzene did not lead to a decrease in the emission intensity, as compound **5** remained soluble. Also, degradation induced by benzene by-products is presumably less likely, since benzene is stable upon UV irradiation.[21] Nonetheless, we believe that side reactions involving acetone are negligible, since the desired nanographenes precipitated out of the solution quite rapidly, and the yields were generally good. None of the kinetic experiments showed distinct emission bands that could be associated with reaction intermediates. This result suggests that once a first CDHC reaction had occurred, the second was very fast and happened almost instantly in the time frame of our experiments.

To understand the role of the solvent in the CDHC reaction, we performed the synthesis of compound **2** in pure acetonitrile (without a base), which is known as a transparent, nonsensitizing solvent (see Table S1 in the Supporting Information). Interestingly, the yield was similar to that observed in pure acetone (87 versus 92%; see Table S1), thus indicating that the presence of a photosensitizer might not be necessary for the CDHC reaction. However, the formation of a small amount of polar by-products was observed when acetonitrile was used. Furthermore, the yield observed in pure acetone (92%) is comparable to that observed in the presence of Na_2CO_3 (85%), thus indicating that the presence of a base is neither necessary for nor detrimental to the success of the reaction. This feature is a significant advantage, since a base could be used to quench the HCl produced during the CDHC reaction of compounds bearing acid-sensitive moieties. Triethylamine was also tested as a base, but the yield was much lower (62%; see Table S1) as several by-products were formed, as observed by TLC analysis.

Previous mechanistic studies on chloro derivatives suggested that the CDHC reaction proceeds through a photo-

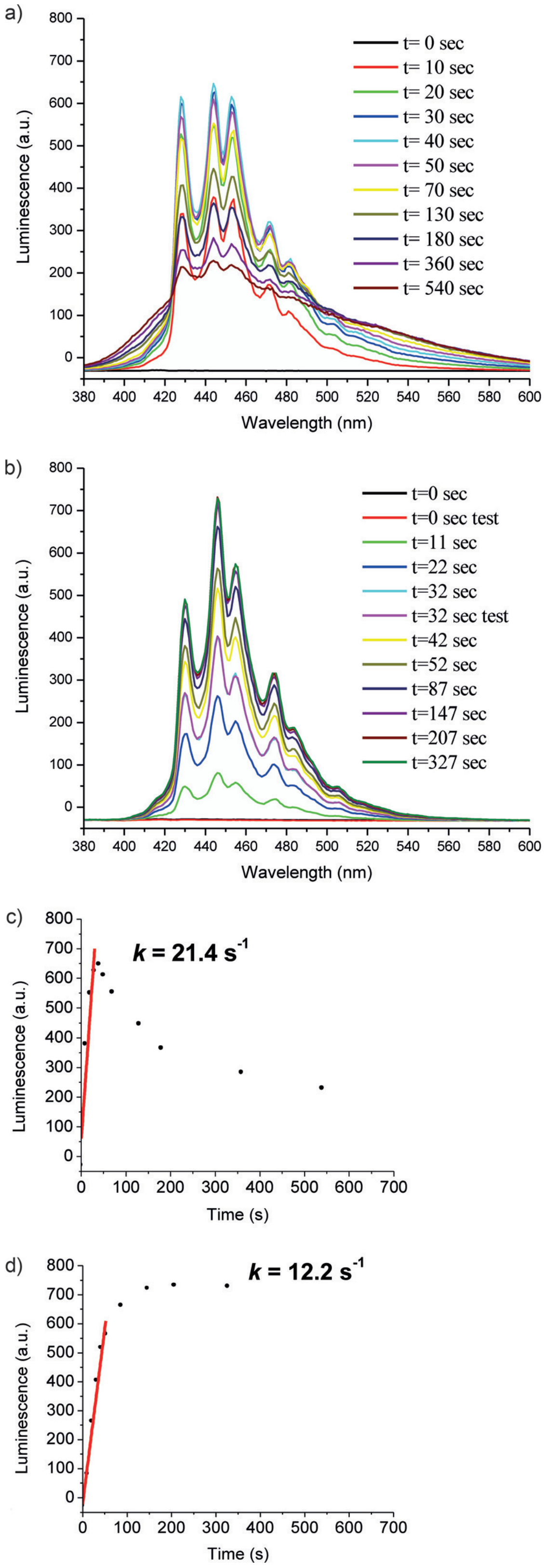


Figure 1. Photoluminescence kinetic study for the formation of nanographene **5** under irradiation at 300 nm in a) an acetone/Na_2CO_3 mixture and b) pure benzene. c,d) Plots showing the variation of emission intensity at 446 nm as function of time. The k values in (c,d) indicate the slope of the linear region of the plot for the reaction conducted in acetone/Na_2CO_3 and pure benzene, respectively.

chemical conrotatory $(4n+2)\pi$ electrocyclization, followed by the elimination of HCl.[12b,15,22] The other plausible mechanism involves the photolysis of the C−Cl bond to generate a phenyl radical intermediate, as observed for the corresponding bromo and iodo derivatives.[23] However, such a mechanism would also involve intermolecular side reactions with the solvent (e.g. hydrogen abstraction), which was not observed in any of our reactions. The greater strength of the C−Cl bond as compared to C−Br and C−I could also explain the nonradical mechanism of the CDHC reaction.[24] The very low amount of side products also points towards a non-radical-based mechanism.

As well as being a powerful tool to prepare planar nanographenes, such as **4** and **5**, the CDHC reaction is very efficient at forming sterically hindered, contorted nanographenes, such as **2**, which was prepared in 85 % yield through two CDHC reactions (92 % per CDHC reaction). Contorted polycyclic aromatic compounds are particularly interesting for organic electronics and supramolecular chemistry, since their twisted conformation can yield concave π surfaces and chiral materials, besides increasing their solubility in organic solvents.[25] The synthesis of nanographene **2** also demonstrates that the photochemical CDHC reaction enables improved control over the edge configurations of nanographenes as compared to that observed with the Scholl reaction, which converted the same precursor (without the chlorine atoms) exclusively into the completely cyclized compound.[1a] The synthesis of nanographene **3**, a structural isomer of **2**, demonstrates that the CDHC reaction is regioselective and that a simple change in the position of the chlorine atoms on the precursor can lead to different isomers.

The yield of the thiophene-containing compound **6** was much lower at 21 %, which corresponds to 68 % per CDHC reaction. This lower yield can be attributed to the various rearrangement reactions that can occur upon the irradiation of phenyl-appended thiophene derivatives.[26] We could not determine the exact nature of the side products, as they were not isolated. Although the efficiency of this reaction needs to be further optimized, the result demonstrates that substituted thiophenes are compatible with the photochemical cyclization process, which shows the versatility of the CDHC reaction. Likewise, compound **7** with an electron-poor fused pyridine unit was prepared in 76 % yield.

The optical properties of nanographenes **1**–**6** were studied by UV/Vis absorption and emission spectroscopy, and the spectra of nanographenes **4**–**6** are shown in Figure 2a. As usually observed for very rigid π-conjugated molecules, the UV/Vis spectra of nanographenes **4**–**6** exhibit a highly defined vibronic structure, within which the β-bands are the most intense.[27] For nanographene **5**, a set of three bands between 405 and 430 nm, associated with the α-bands in the Clar nomenclature,[28] were found with ε values below $3000\,\text{M}^{-1}\,\text{cm}^{-1}$ (Figure 2, inset). As expected, the absorption spectrum of nanographene **6**, containing two electron-rich fused thiophene units, is red-shifted (25 nm) relative to that of its phenyl analogue **4**, thus resulting in a lower optical band gap (2.82 eV) as compared to that of compound **4** (3.00 eV).

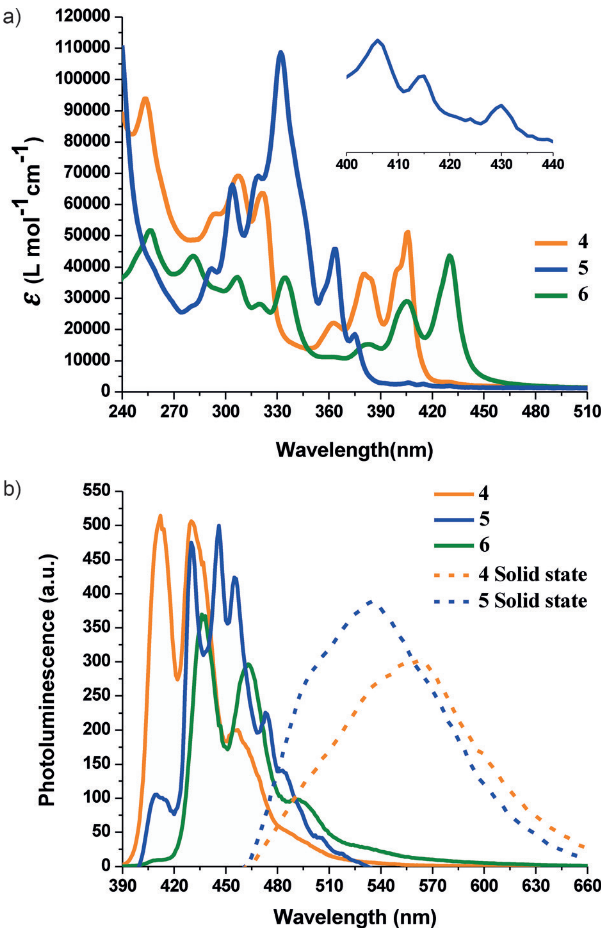


Figure 2. a) UV/Vis absorption spectra of nanographenes **4**–**6** in chloroform. The inset is a zoom of the 400–440 nm region of the spectrum of **5**. b) Photoluminescence spectra of nanographenes **4**–**6** in chloroform (solid lines) and in the solid state.

To further study the electronic properties of nanographenes **4**–**6**, we performed DFT and time-dependent DFT (TD-DFT) calculations at the commonly used B3LYP/6-311G(d,p) level of theory (see Figure S4 in the Supporting Information).[29] The optimized structures of nanographenes **4**–**6** show a highly planar conformation with HOMO and LUMO frontier orbitals delocalized over the entire molecule. For compound **4**, the calculated electronic transitions are in good agreement with those observed experimentally (see the Supporting Information). The HOMO–LUMO transition occurs at 404 nm (oscillator strength, $f=0.68$) versus 406 nm in the experimental spectrum, whereas the second-lowest energy transition, corresponding to a combination of the HOMO−1 to LUMO (54 %) and HOMO to LUMO+2 transitions (43 %), occurs at 380 nm ($f=0.01$). For compound **6**, the TD-DFT calculations are in good agreement with the experimental data for the lowest-energy transition, with a value of 431 nm ($f=0.71$), whereas slight discrepancies appeared at higher energy, as the second-lowest energy transition appeared at 390 nm (versus 405 nm in the absorption spectrum).

In conclusion, we have prepared several nanographenes by a photochemical cyclodehydrochlorination (CDHC) reaction. The reaction is efficient, even when multiple cyclization steps are necessary to provide the desired product. Unlike other aromatization methods, photochemical CDHC is compatible with both electron-rich and electron-poor moieties. Most importantly, this reaction is regioselective and allows the preparation of nanographenes with different edge configurations, including sterically demanding contorted PAHs. Our attention is now focused on the use of this reaction to prepare soluble graphene nanoribbons with well-defined edge configurations.

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