



Fast and inexpensive synthesis of pentacene with high yield using 6,13-pentacenequinone as precursor



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ABSTRACT

Pentacene is an important semiconductor in the field of organic electronics. In this work is presented an alternative synthesis procedure to obtain pentacene from 6,13-pentacenequinone as a precursor. Synthesis of pentacene was performed in two reactions, Diels-Adler cycloaddition of 6,13-pentacenequinone followed by 6,13-pentacenequinone reduction to pentacene, employing LiAlH_4 as reducing agent. The products were characterized by Fourier Transform Infrared Spectroscopy (FTIR), ^1H -Nuclear Magnetic Resonance Spectroscopy ($^1\text{H-NMR}$), X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA) and Ultraviolet–Visible Spectroscopy (UV-VIS). In this work, 6,13-pentacenequinone was synthesized with a high yield (55%) using an alternative method. The optimization process resulted in an overall reduction of reaction time while exhibiting high yield. The method presented here provides an affordable pentacene synthesis route with high purity, which can be further applied for research and development of organic electronic applications.

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1. Introduction

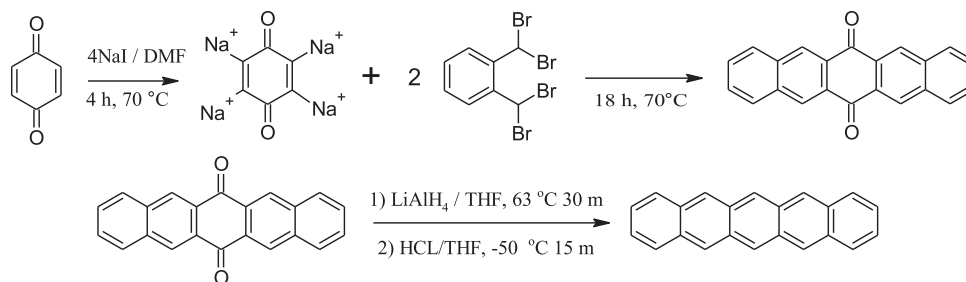
Pentacene is a well-known p-type semiconductor in the organic electronics field. Its high field effect mobility –around $2.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [1] and stability make it a remarkable material in the development of organic transistors. The first successful synthesis of pentacene was reported in 1929 by Clar and collaborators. Although, yield was not reported, pentacene was obtained via dehydrogenation of 6,14-dihydropentacene using phenanthraquinone [2]. Since the implementation of organic semiconductors in large area electronics, specifically in light switching speed transistors, pentacene became an alternative to amorphous silicon due to its similar performance to inorganic semiconductors [3]. Moreover, the use of

organic semiconductors greatly reduces the processing temperatures, hence enabling the use of polymeric substrates which are applied in flexible electronic devices. In order to further advance the development of such devices, active organic materials such as pentacene must be researched through simple and low cost routes. Cava and collaborators have reported that one of the precursors of pentacene is 6,13-pentacenequinone, as a byproduct in the synthesis of quinone compounds. The synthesis was conducted using TBOX as a reactive intermediate that cyclizes spontaneously with 1,4-benzoquinone in the presence of sodium iodide; 6,13-pentacenequinone was obtained with low yield (7%) [4]. Bruckner and Tomasz synthesized pentacene by continuous aldol condensations with two equivalents of *o*-phthalaldehyde and one equivalent of 1,4-cyclohexanodione. A mixture of Al in cyclohexanol or Al/HgCl₂ mixture in cyclohexanol/carbon tetrachloride. This synthesis required a long reaction time (48 h) involving toxic reactants (HgCl₂) [5]. (see Scheme 1)

Another example is the synthesis of pentacene with 92% yield reported from 5,14-dihydropentacene in the presence of Pd/C to produce hydrogenation [6]. Very high yield was obtained at the

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Scheme 1. Synthesis of pentacene. (a) Synthesis of 6,13-pentacenequinone, (b) 6,13-pentacenequinone reduction to pentacene.

expense of long reaction time (3 days) and use of a toxic catalyst. Vets and collaborators reported a synthesis route with 6,13-pentacenequinone using LiAlH₄ for the reduction of the carbonyl group to produce 6,13-pentacenediol followed by acid dehydrations to produce pentacene with a 54% yield. The procedure was done for each carbonyl group, first with LiAlH₄ to reduce the carbonyl groups to alcohol and then with HCl to expel water from the molecule [7]. The syntheses described in this introduction, involve the presence of a metallic catalyst (HgCl₂, Pd/C), long reaction time, inaccessible and expensive reactants or equipment. In this manuscript, we report the results on the synthesis of 6,13-pentacenequinone and pentacene. As reported by Clar and collaborators, 6,13-pentacenequinone was prepared from a Diels-Addler adduct; however, a higher yield (55%) was achieved through the optimization of reaction conditions and purification protocol of the final product. Pentacene was prepared by performing the reduction of both 6,13-pentacenequinone carbonyl groups in only one step, avoiding the isolation of a highly unstable intermediate (6,13-pentacenediol). The final product was obtained with a 51% yield. The advances presented in this work allow the simple and low cost production of pentacene enabling research laboratories to advance the organic and flexible electronics field.

2. Results and discussions

2.1. Chemical characterization

The attenuated total reflection of Fourier Transform Infrared (FTIR-ATR) spectrums of 6,13-pentacenequinone and pentacene are shown in Fig. 1. For the 6,13-pentacenequinone the principal

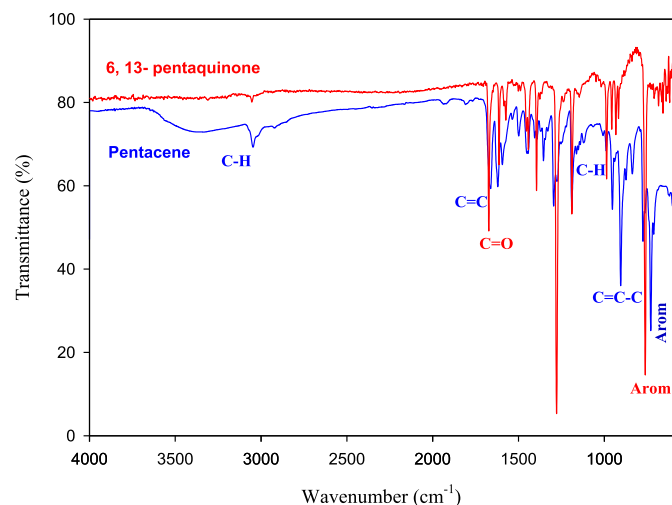


Fig. 1. FTIR Spectrum of 6,13-pentacenequinone and pentacene.

identification of conjugation with two carbonyl (C=O) groups in the same ring results in delocalization of the π electrons of both unsaturated groups. Conjugation of phenyl groups may cause a reduction in frequency of C=O band in the 1672 cm⁻¹ region, with extended conjugation. Steric effects of C=O groups reduces the coplanarity of the conjugated system.

The common region for carbonyl absorption band shows the two signature peaks; overtone of C=O stretch at 3350 cm⁻¹ and C=O stretch peak at 1672 cm⁻¹. Other absorption peaks in the 6,13-pentacenequinone spectrum are present and associated to a stretch of C-H aromatic bond at 3054 cm⁻¹, the C=C stretch corresponding to the ring consist of peaks at 1612 cm⁻¹, 1443 cm⁻¹ and 1396 cm⁻¹. The absorption of bending vibrations in the aromatic ketones (C-C=O-C) absorb at a higher frequency at 1277 cm⁻¹ than 1230-1100 cm⁻¹ region as the literature remark and an aromatic ring stretch of C=C-C at 758 cm⁻¹ [8,9]. For pentacene ¹H NMR spectroscopy was utilized to verify the structure and purity of the synthesized pentacene (see supplementary material). Furthermore, FTIR was also employed and the results can be seen also in Fig. 1. Pentacene spectrum exhibited bands assigned to vibration of C=C conjugated bond around 1632 cm⁻¹, a strong vibration stretch of aromatic C-H bond at 841 cm⁻¹, and strong signals corresponding to the aromatic conjugated C=C-C bond from 671 cm⁻¹ to 601 cm⁻¹, according to IR peaks identifications previously reported [10]. A peak for O-H stretching was observed at 3425 cm⁻¹ due to the presence of moisture in the pentacene sample.

2.2. Thermal stability

The TGA thermograms corresponding to 6,13-pentacenequinone and pentacene are depicted in Fig. 2. Thermogravimetric analysis revealed that the 6,13-pentacenequinone compound is thermally stable up to 330 °C, the latter is due to its intermolecular π - π stacking arrangement.

Yuan and collaborators reported a commercially available 6,13-pentacenequinone compound to be thermally stable up to 360 °C [11]. Furthermore, the TGA results for the 6,13-pentacenequinone compound synthesized in this work showed a singular deflection, indicating a simple process of decomposition which suggests a high purity obtained. The TGA thermogram obtained for pentacene indicates a dynamic process of degradation showing two important deflections. As shown, the pentacene sample starts to decompose around 150 °C with 7 wt% loss associated to CO removal. However, the pentacene shows to be stable up to 305 °C, before thermal decomposition occurs as a vaporization process [12].

2.3. Structural characterization

The structural analysis of 6,13-pentacenequinone and pentacene was performed using XRD (Fig. 3).

For 6,13-pentacenequinone (Fig. 3a) the diffraction peaks

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