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# Synthesis of Ladder-type Graphene Ribbon Oligomers from Pyrene Units

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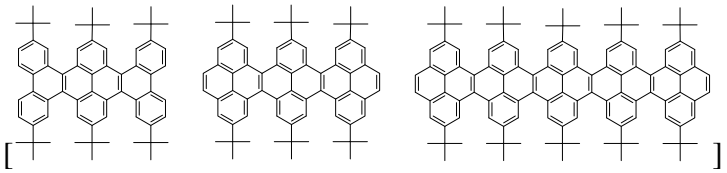
*Supporting Information*



ARTICLE INFO

*Keyword:* Graphene; Pyrene; Ladder-type

ABSTRACT

A series of ladder-type graphene ribbon oligomers have been synthesized through DDQ/acid-mediated oxidative cyclization. The oligomers present a bright blue light emission, and the new oligomers were clearly characterized by NMR and MALDI-TOF.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) as well defined "piece of graphite" [1-4] have been exploited in various organic electronic devices including field-effect transistors,[5-7] photovoltaic devices,[8-10] and light-emitting diodes.[11-13] A representative example of PAHs developed by Müllen et al is hexa-peri-hexabenzocoronene (HBC),[14,15] HBC and its derivatives were known for their unique self-organization into columnar superstructures and exhibit one of the highest charge-carrier mobilities for mesogens.[16-20] Various devices based on nanographene molecules with different structures and functionalities have been well developed by organic synthetic or supramolecular protocols, such as Aida's nanotubes,[21-23] Li's graphene quantum dots,[24,25] and Müllen's graphene nanoribbons and large graphenes.[1] Ladder or ribbon-type polymers and oligomers possessing two dimensionally planar conformation, high electron delocalization, and functional optic-electronic properties attract great scientific interest considering their potential applications in areas such as electroluminescence, plastic lasers, and molecular electronics.[26-29]

Pyrene, which has been widely investigated for its unique properties, is a promising building block to develop new extended π-systems for organic optoelectronics.[4, 30-36] As the smallest peri condensed polynuclear benzenoid aromatic hydrocarbon, pyrene has been used to architecture ladder or ribbon-type polymers and oligomers.[37, 29] By comparison to polymers, monodisperse conjugated oligomers can be free from structural defects, possessing high purity from conventional purification methods, are more suitable for detailed structure-property relationships studies.[38-43] However, in spite of their unique material properties, the synthesis and characterization of defect-free, soluble hydrocarbon ribbon molecule is still one of the ongoing challenges. Although a few pyrene derivatives fused at the K-region were developed, and they exhibited interesting properties, long-range ribbon-type oligomers are more attractive and seldom.[44]

In this paper we design a series of π-conjugated graphene ribbon oligomers (**1**-**4**) with increasing length through fusion at the K-region. The synthesis of the oligomers was in the way of the typical strategy of PAH production: first, the design and synthesis of soluble polyphenylene precursor molecules and second, the formation of aromatic C-C bonds by cyclodehydrogenation. Thus, appropriate polyphenylene precursor structures can be converted in a single reaction step into the desired planarized PAH structures. For a successful cyclodehydrogenation toward large graphene ribbon, the well defined precursors (**7**, **10**, **16**, **19** and **22**) containing pyrene and biphenyl units as repeated units were synthesized, they can be converted into planar ribbon-type graphene pieces by cyclodehydrogenation.

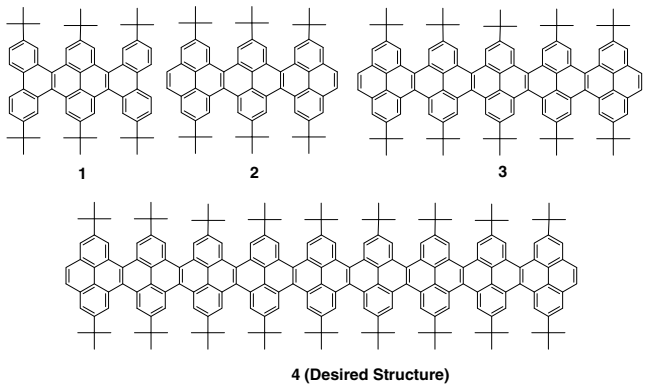



**Figure 1.**the structure of ladder-type graphene oligomers.

The synthetic route to oligomers **1**, **2** and **14** was shown in scheme 1. The precursor **7** was obtained from palladium-catalyzed Suzuki coupling reaction between