

Synthesis, helical columnar liquid crystalline structure, and charge transporting property of perylene diimide derivative bearing oligosiloxane chains



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ABSTRACT

A novel perylene diimide (PDI) derivative bearing four oligosiloxane chains was synthesized. The phase behavior, self-assembly structure and charge transport characteristic of the compound were elucidated via a sequence of experimental techniques such as UV/Vis and fluorescence spectra, differential scanning calorimetry, polarized optical microscopy, one- and two-dimensional X-ray diffraction as well as time-of-flight experiment. The experimental results reveal that the compound forms liquid crystalline (LC) helical supramolecular structure with two molecules coupled side-by-side in each column stratum at room temperature. Due to this unique structure, efficient charge transport occurs in the LC phase and the electron mobility reaches $1.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at ambient temperature in spite of the large π -stack spacing in the column.

1. Introduction

In the family of organic semiconductors, columnar liquid crystalline (LC) materials have attracted much attention due to their ability to self-assemble into the ordered architecture permitting one dimensional charge transport, which exhibit a high charge carrier mobility [1–3]. Hence, in the hope of developing and studying columnar discotic materials as hole- and electron-transport materials, extensive efforts have been directed [3]. The liquid crystalline and charge transport properties of p-type semiconducting materials, such as triphenylenes, phthalocyanine and hexabenzocoronene, are well studied in literature [4–6]. Unlike the extensively reported p-type semiconductors, the number of liquid crystalline compounds with good n-type semiconductivity is still limited [7–9].

Perylene diimide (PDI) derivatives are typical n-type organic semiconductors which have broad prospects of application in photovoltaic devices [10], light emitting diodes [11,12], and organic field effect transistors [13–15]. The engineering of supramolecular structure is essential for the PDI materials with excellent processability and

respectable charge-carrier mobility. With appropriate molecular design, the PDI derivatives can present a wide array of liquid crystalline phases [16–19]. In these LC phases, each column consists of a conducting stack of PDI cores surrounded by liquid-like alkyl chains. However, having only one molecule in each stratum may lead to the lack of both inter- and intra-column electronic coupling which makes charge carrier migration vulnerable to the occurrence of defect [20]. In 2011, Percec et al. reported the discovery of a novel class of self-repaired helical columns with a pair of PDI molecules arranged side-by-side in each stratum [21]. This self-assembled structure permits close and extended π -stacks in the column, which is potentially useful to circumvent defects in charge transport. In 2015, Jin et al. reported a novel bundled-stack LC phase which features several π -stacks bundled together in each column [22]. The bundled-stack structure allows inter-stack electronic coupling which enables the fabrication of highly efficient supramolecular electronics and photovoltaic cells.

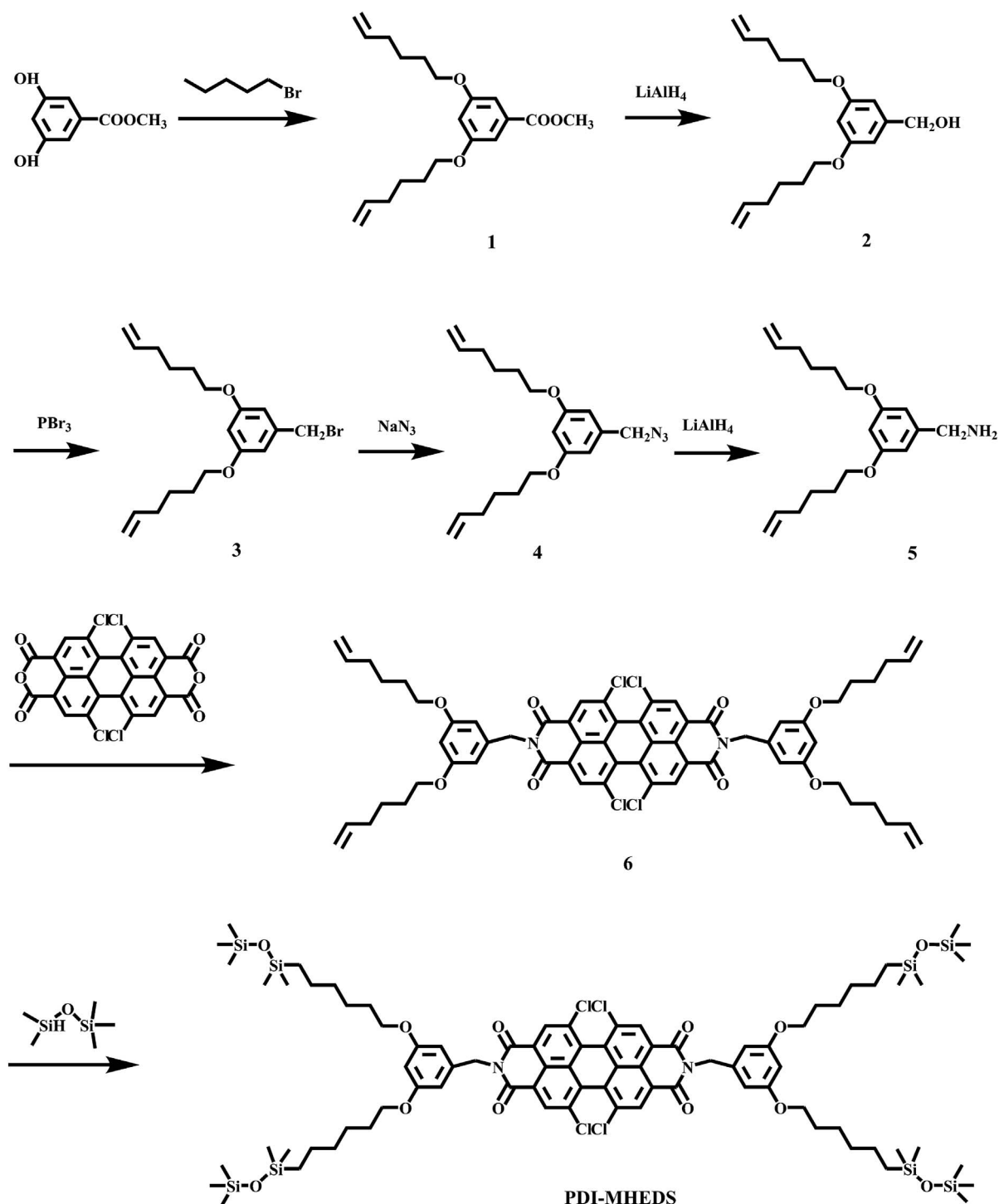
Recently, Funahashi et al. reported a series of nanosegregated LC semiconductors consisting of rigid nonchlorinated PDI core and oligosiloxane chains, exhibiting columnar phases and high electron

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Scheme 1. Synthetic route of PDI-MHEDS.

mobilities [23–25]. Nevertheless, all these compounds are based on the functionalization at imide position rather than at bay position, and the influence of bay region modification on their molecular packing is rarely reported yet. Moreover, it has been demonstrated that the non-planar, twisted and flexible tetrachlorinated PDI may provide a new route to generate room-temperature LC phase with enhanced electron affinity [26,27]. It has been shown by several research groups that the supramolecular structure of PDI derivatives can be modified by functionalization at both imide position and bay region [20–28]. Thus, it should be possible to fabricate oligosiloxane-substituted PDI compound capable of forming LC phase with extended π -stacks within the

columnar aggregates. However, until now, to the best of our knowledge, detailed studies of the complex supramolecular structure formed by the self-assembly of flexible tetrachlorinated PDI core with oligosiloxane substituents are not available.

In this publication, a novel tetrachloro-substituted PDI derivative bearing four oligosiloxane chains (PDI-MHEDS) was designed and synthesized (Scheme 1). This compound exhibits a unique LC phase at room temperature. Different to the reported columnar LC phase with one molecule in each column stratum, there are a pair of PDI-MHEDS molecules arranged side-by-side in each column stratum. These column strata then rotationally stack to form a 24-fold helical column, which

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