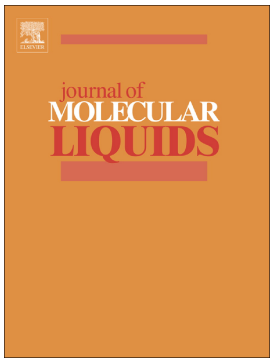

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Shengjie Jiang, Hongyu Guo, Shuyun Zhu, Fafu Yang

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Novel columnar liquid crystalline oligomers: Triphenylene tetramers with rigid aromatic Schiff-bases and hydrogen-bonding spacers *via* click chemistry

Shengjie Jiang [1], Hongyu Guo[1*], Shuyun Zhu[1], and Fafu Yang[1,2, 3*]

[1]*College of Chemistry and Chemical Engineering, Fujian Normal University, Fuzhou 350007, P. R. China*
[2]*Fujian Key Laboratory of Polymer Materials, Fuzhou 350007, P. R. China*
[3]*Fujian provincial Key Laboratory of Advanced Materials Oriented Chemical Engineering, Fuzhou 350007, China*
**Corresponding author; e-mail: yangfafu@fjnu.edu.cn; Tel.: +0086-591-83465225; fax: +0086-591-83465225;*

Abstract Three novel triphenylene tetramers with triazole bridges, rigid aromatic Schiff-bases and hydrogen-bonding spacers were designed and synthesized in yield of 73~78%. Their structures were confirmed by IR, NMR and MS. Their mesomorphic properties were studied by polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction. These novel triphenylene tetramers possessed the hexagonal columnar mesophase and exhibited excellent mesomorphic properties with melting points at 30~60^{o}C, which was first observed near room temperature for triphenylene tetramers. This study suggested that the mesomorphic properties of triphenylene oligomers could be tuned conveniently by the structures of spacers.

Keywords
Triphenylene ·Tetramer ·Synthesis ·Mesophase ·Room temperature

Introduction

Columnar discotic liquid crystals, possessing a rigid polyaromatic cores with several peripheral alkyl chains, have attracted much research interests in recent years due to their extensive application prospects, such as organic light-emitting diodes, organic photovoltaic cells, one dimensional conductors, organic field-effect transistors, gas sensors, photocopying machines, *etc* [1-4]. Triphenylene with six aliphatic arms were the important discotic liquid crystals and exhibited high tendency to form the required columnar phases [1-7]. Many triphenylene liquid crystals were synthesized and their interesting mesomorphic properties were investigated so far [8-21].

For the purpose of transferring liquid crystalline monomer to macromolecular material, much attention has been paid to liquid crystal oligomers. The liquid crystalline oligomers were good model molecules for polymeric materials due to the similarities in their transitional behaviors. Moreover, they had the advantage of simple purification and characterization, and some of them exhibited special fluid phases with interesting functions. Up to now, many triphenylene liquid crystalline dimers with various soft or rigid spacers, and some triphenylene liquid crystalline trimers were designed and synthesized [22-36]. Their mesomorphic properties were greatly influenced by the structures of both triphenylene units and spacers. However, as to triphenylene tetramer which might be more similar to polymeric material, only a few examples were presented. Kumar reported the triphenylene tetramers bridged by rufigallol.[21] Markovitsi's group synthesized the tetramers with siloxane core [37]. Laschat and his co-workers prepared the triphenylene tetramers with spiro-carbon spacer [35]. These tetramers were good liquid crystals with low phase transition temperatures (-60^{o}C~-40^{o}C), although many room-temperature liquid crystals with one or two triphenylene units were prepared. On the other hand, it had been proved that the large rigid spacer and hydrogen-bonding spacer could enhance obviously the melt points of discotic liquid crystals [39-45]. For examples, the rigid triazole bridges based on click chemistry had been used efficiently to construct the triphenylene liquid crystals with high phase transition temperatures [16, 36, 46-47]. However, the influences of rigid spacer and hydrogen-bonding spacer on the mesophase of triphenylene tetramer were not reported