Tetrahedron 70 (2014) 1230–1235

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis and self-assembly of oligomers containing cruciform 9,10-bis(arylethynyl)anthracene unit: formation of supramolecular nanostructures based on rod-length-dependent organization

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ARTICLE INFO

Article history:
Received 14 September 2013
Received in revised form 13 December 2013
Accepted 24 December 2013
Available online 31 December 2013

Keywords:
Anthracene
Self-assembly
Cruciform molecule
Coil-rod-coil
Supramolecular structure

ABSTRACT

Conjugated rod-coil molecules, incorporating flexible and rigid blocks, have a strong affinity to self-organize into various supramolecular nanostructures in the bulk state.In this study, we report synthesized oligomers containing cruciform 9,10-bis(arylethynyl)anthracene units and characterized their self-assembly behavior. The molecular structures were characterized with ^{1}H, ^{13}C NMR, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy. An investigation of the supramolecular nanostructures of these molecules using differential scanning calorimetry, thermal polarized optical microscopy, and small-angle X-ray scattering revealed that the rod length of coil-rod-coil molecules with identical rod to coil volume ratios dramatically influences self-assembly behavior in the bulk state. Molecules **2** and **3** with relatively longer rod lengths self-assemble into lamellar structures in the solid state, whereas, molecules **1** and **4** self-assemble into two-dimensional (2-D) oblique columnar structures in the liquid crystalline phase, in addition, on heating, molecule **1** transforms from the oblique columnar phase to the nematic phase.

1. Introduction

Synthesis of supramolecular units through self-assembly is one of the most exciting interdisciplinary researches areas involving chemistry, biology, and material science.[1] Among self-assembling molecular systems, rod-coil block molecules consisting of an elongated rigid rod and a flexible coil have attracted attention as interesting self-assembling soft materials given the possibility of synthesizing novel functional materials by combining their self-assembling capability and functional uniqueness.[2] Self-assembly studies concerning supramolecular structures and their intriguing properties have been reported, with a focus on the various shapes of the rigid conjugated rod segment, such as Y-,[3] T-,[4] O-,[5] K-,[6] propeller-,[7] and dumbbell-shaped[8] rod-coil molecules. Precise control over a supramolecular nanostructure with a well-defined shape and size is of critical importance for their application in photoelectronic self-organizing materials. This control is achieved by adjusting the cooperative effects of various molecular parameters such as volume fraction of rod to coil segment, rod anisotropy, and coil cross-sectional area.[9] Anthracene-centered cruciform compounds have been studied widely, with a focus on their two-photon absorption (TPA) properties;[2b,10] however, there are few studies on the self-assembling behavior of anthracene-centered cruciform derivates that explore the relationship between molecular aggregates and their unique physical properties. Therefore, it is interesting to design and synthesize new types of cruciform compounds possessing excellent TPA properties and study their self-assembling behavior for improving molecular photoelectronic properties.

With this in mind, we synthesized coil-rod-coil molecules **1**–**4** (Scheme 1) with conjugated rod building blocks and investigated their self-assembly behaviors in the bulk state with differential scanning calorimetry (DSC), thermal polarized optical microscopy (POM), and small-angle X-ray scattering (SAXS).

2. Results and discussion

2.1. Synthesis and characterization of molecules 1–4

The synthetic route of cruciform 9,10-bis(arylethynyl)anthracene derivatives consisting of 9,10-bis(arylethynyl)anthracene as

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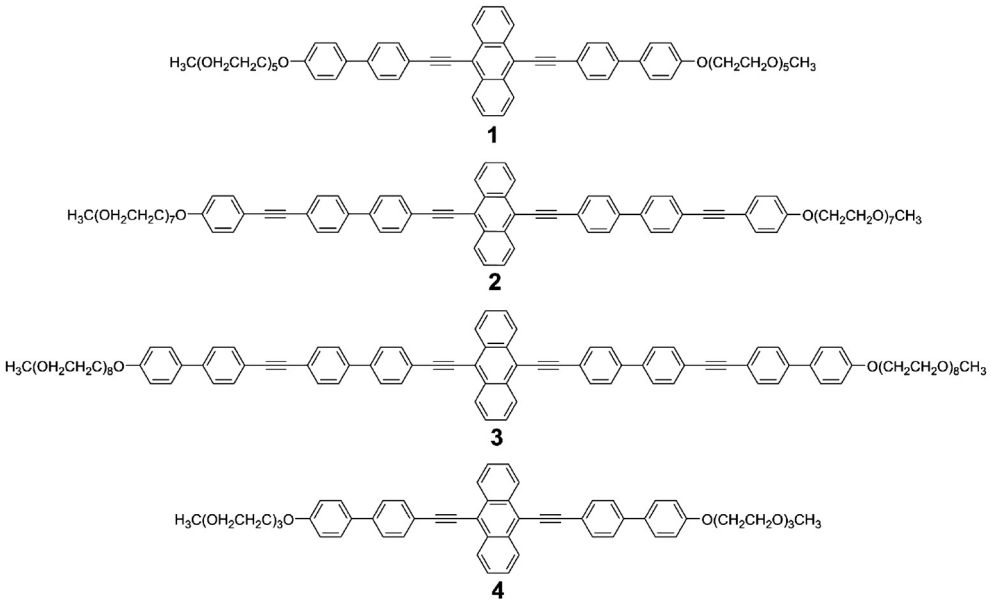
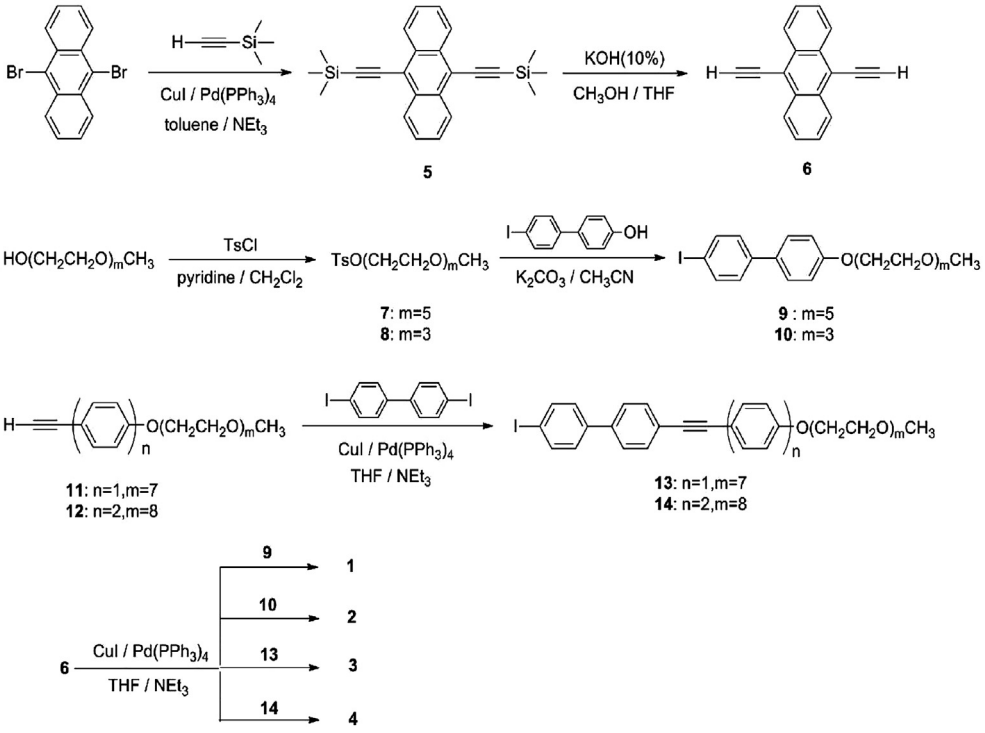
0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.12.072



Scheme 1. Chemical structures of the molecules **1**–**4** based on anthracene aromatic rod building block.

a rigid rod segment connecting poly(ethylene oxide) (PEO) chains of different lengths is outlined in Scheme 2. Target molecules were obtained through successive reaction steps including tosylation, substitution reaction, methylation, demethylation reaction, and Sonogashira coupling reaction. Target molecules **1**–**4** were characterized with ^{1}H, ^{13}C NMR and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy and were shown to be in full agreement with the structures presented in Scheme 1. A representative ^{1}H NMR spectrum analysis of molecule **1** is shown in Fig. 1 (three other molecular ^{1}H, ^{13}C NMR spectra are shown in Figs. S1–7, and ^{1}H–^{1}H COSY and NOESY spectra of molecule **1** are shown in Figs. S8 and 9, see Supplementary data). As confirmed by ^{1}H NMR spectroscopy, the ratio of the aromatic protons of the rod block to the alkoxyl protons is consistent with the calculated value, and the MALDI-TOF mass spectra of the molecules show three signals that can be assigned to H^{+}, Na^{+}, and K^{+} labeled molecular ions (Fig. S10, see Supplementary data). The experimental mass based on peak positions in the spectrum is well matched with the theoretical molecular weight of each molecule.



Scheme 2. Synthetic route of molecules **1**–**4**.