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ORIGINAL ARTICLE

Probing the molecular orientation of chemically polymerized polythiophene-polyrotaxane via solid state NMR

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Abstract Polyrotaxanes have attracted significant attention of scientific community and are being explored towing to its electro-optical properties. The orientation and the molecular structure of polyrotaxanes influence its final properties. Thus a, detail understanding of the structure of such compounds at the molecular level will provide an opportunity to further tune and optimize their properties. Here chemically polymerized polythiophene polyrotaxane i.e. Thiophene [2]Rotaxane which is the rotaxane like compound consisting of several macrocycle, was studied in the powdered form. This allowed us to investigate the molecular structure of polyrotaxane and to obtain the detail insights into its structure property relationship via solid state NMR. The as-obtained polymer has also been characterized via various other techniques including UV spectroscopy, solution NMR and so on. We elucidated the structure of the Thiophene [2]Rotaxane monomer remained intact even after polymerization.

1. Introduction

Polythiophenes are one of the most promising (semi)conducting materials for organic electronics, owing to its application in many devices such as organic field-effect transistors (OFET), organic light-emitting diode (OLED), photo-voltaic materials or electrochromic materials. This has gained momentum due to the ease of flexibility and rather simple processability of this type of materials (Osaka and McCullough, 2008; McCullough, 1998; Gohier et al., 2013; Zhang et al., 2011; Yaman et al., 2014; Irimia-Vladu, 2014; Shao et al., 2013). Sincere efforts are devoted to investigate insulated molecular wires in which conducting polymers are wrapped with insulating substituents or macrocyclic compounds (Li and Shi, 2013; Jeong et al.,

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2012). The insulating layer suppress strong molecular and electronic interactions between the conductive polymers, which results in better solubility in the organic solvents and higher quantum yield of the fluorescence emission (Zhou et al., 2006; Kuo et al., 2013; Cochran et al., 2013). Notably, such insulated molecular wires comprised of tetracationic cyclophanes cyclobis(paraquat-p-phenylene)s (CBPQT4 + s) and polythiophene (Fig. 1) were recently introduced (Ikeda et al., 2009).

In addition, thin layers of insulated molecular wires on electrode surfaces obtained through electrochemical polymerization of the thiophene [2]Rotaxane were described (Ikeda et al., 2011). The [*n*]rotaxane is the compound consisting of the macrocycle topologically entrapped by the dumbbell-shaped molecule. Here the number *n* in the square bracket indicates the number of the units (macrocycle and dumbbell-shaped compound) in the rotaxane compound (Yildiz et al., 2008). Polyrotaxanes are rotaxane-like compounds consisting of many macrocycles and dumb bell-shaped moieties and thus were dubbed "polythiophene polyrotaxanes" (Ikeda et al., 2009). In this work, we report the structure and characterization of polythiophene polyrotaxanes obtained from chemical polymerization of the thiophene [2] Rotaxane. The main aim of this study was to investigate the nature of the orientation of the macrocycle within the compound and its impact on the physicochemical properties, unraveling the corresponding structure property relationship via solid state NMR while putting forward the definition of rotaxane molecules. In particular, the powdered samples merely derived from chemical polymerization provided the opportunity to analyze its properties in more realistic ways. All as-prepared samples were further characterized by solution NMR, and their preliminary charge transport properties were estimated from conductivity measurements and localized level properties.

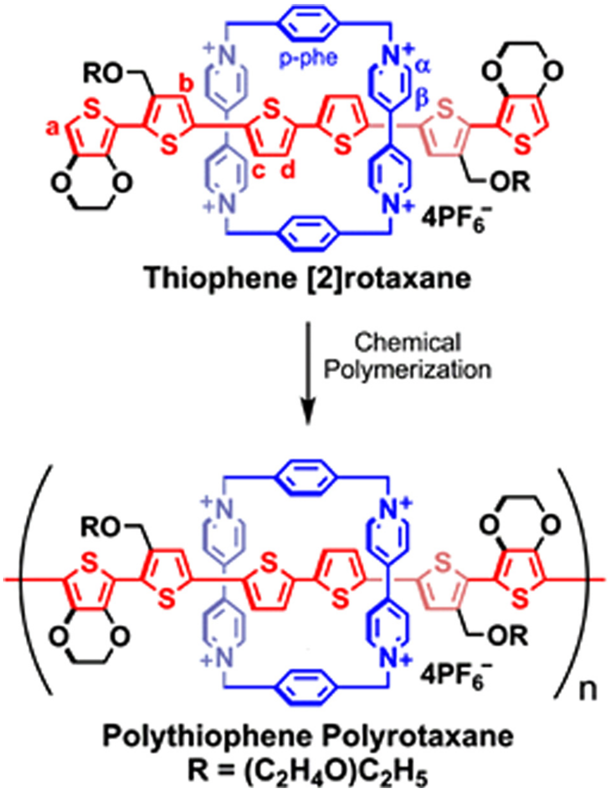

Fig. 1 Schematic illustration of the chemical polymerization of thiophene [2]Rotaxane to polythiophene polyrotaxane.

2. Materials and methods

2.1. Materials used

The thiophene [2]Rotaxane was synthesized according to a previous report (Ikeda et al., 2009). The chemical oxidant nitrosonium hexafluorophosphate ($NOPF_6$) was purchased from Acros Organics. The other chemicals and solvents were obtained from commercial sources and used as received. UV/Vis spectra were recorded at room temperature on a UV-2550 UV–Visible spectrophotometer (Shimadzu Co.). ^1H NMR spectra were recorded at room temperature on an Avance 250 FT NMR system (Bruker) with residual solvent as the internal standard. Acetonitirile (MeCN) and methyl alcohol (MeOH) were purchased from Sigma Aldrich.

2.2. Chemical polymerization of thiophene [2]Rotaxane

The thiophene [2]Rotaxane (25 mg, 1.2×10^{-5} mol) was dissolved in dry MeCN (0.4 mL). The solution was cooled to −10 °C with an ice bath. $NOPF_6$ (260 mg, 1.5 mmol) was dissolved in dry MeCN (5 mL). The $NOPF_6$ solution (0.20 mL) was added to the thiophene [2]Rotaxane solution. The reaction mixture was stirred at −10 °C for five minutes. After adding pyridine (1 mL) to reduce the product, the solution was diluted by acetone (5 mL). The solution was added dropwise to 2 N NH_4PF_6 aqueous solution (100 mL) to precipitate the product. The product was recovered by filtration and washed by dichloromethane (DCM). Subsequently the solid product was dissolved in acetone again and added dropwise in MeOH (100 mL) to precipitate the product. The product was recovered by filtration and dissolved in acetone again and then the solution was transferred to small flask and the solvent was removed by evaporation. Finally the product was dried under reduced pressure to afford deep red purple solid. [Yield: 22 mg (88%)].

2.3. Characterization

2.3.1. Solid-state NMR

Proton solid-state single-pulse and double-quantum (DQ) magic-angle spinning (MAS) (^1H, 850.1 MHz) as well as carbon cross-polarization (CP) and heteronuclear correlation (HETCOR) MAS NMR spectra (^{13}C, 213.8 MHz) were recorded at a 20 T magnet equipped with a Bruker Avance III console. Additional nitrogen CPMAS spectra (^{15}N, 30.4 MHz) were recorded at a Bruker Avance II 300 machine. All experiments were carried out at room temperature using commercially available Bruker 2.5 mm or 4 mm double-resonance MAS probes, respectively, at spinning frequencies of either 30 kHz or 5 kHz. Typical $\pi/2$-pulse lengths were adjusted to 2.5 µs (corresponding to B_1-fields of 100 kHz) and recycle delays of 15 s. The ^1H and ^{13}C MAS NMR spectra were referenced with respect to tetramethylsilane (TMS) using solid adamantane as secondary standard (1.84 ppm for ^1H and 29.456 ppm for ^{13}C); ^{15}N spectra were referenced with respect to solid $^{15}NH_4Cl$ (−341.0 ppm). The back-to-back (BaBa) (Geen et al., 1994; Gottwald et al., 1995; Sommer et al., 1995; Feikeet al., 1996; Saalwächter et al., 1999; Saalwächter et al., 2001) recoupling sequence was used to excite and reconvert double-quantum coherences, applying States-TPPI (Marion et al., 1989) for phase sensitive detection.

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