



Synthesis, structural and electrochemical characterization of benzimidazole compounds exhibiting a smectic C liquid crystal phase

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ABSTRACT

Mesomorphic benzimidazole compounds were prepared from a biphenyl benzoate based precursor by substitution reaction of alkyl bromide with 2-mercaptobenzimidazole. Molecular structures of the benzimidazole compounds were characterized by nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR) spectroscopy and elemental analysis. Differential scanning calorimetry (DSC) measurements and polarizing optical microscopic (POM) observations revealed that the benzimidazole compounds exhibited a thermotropic smectic C (S_C) phase. Temperature dependent X-ray diffraction (XRD) patterns suggested a tilted bilayer smectic structure in which intermolecular hydrogen bonds between benzimidazole moieties formed lamellar arrangement. Electrochemical impedance spectroscopy (EIS) characterization suggested that the S_C phase favored anhydrous proton conduction of the benzimidazole compounds and the proton conductivities showed an Arrhenius temperature dependence.

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1. Introduction

Proton conducting materials have great potential for a wide variety of applications such as fuel cells, chemical sensor, water electrolysis, and hydrogen separation [1–4]. The commercially available perfluorosulfonic acid materials, such as Nafion[®] 117, exhibited considerable proton conductivities under humidified conditions [5]. Water-assisted proton conduction through the vehicle mechanism was regarded as principal contribution to the resultant conductivities of these materials. Accordingly, they are only suitable for conducting protons at temperatures below the boiling point of water. Water-free proton conductors are becoming more attractive due to the improved performance of proton exchange membrane fuel cells at elevated temperatures (e.g., 100–200 °C) [6,7]. A few anhydrous proton conductive materials have been developed based on proton hopping between protic molecules through the Grotthuss mechanism [8,9].

Hydrogen-bonding chains in organic compounds are believed to act as effective pathways for the rapid translocation of protons over long distances [10]. Amphoteric nitrogen-heterocycles are optional candidates to prepare proton conductive materials because hydrogen-bonding networks could form by the heterocycles

themselves [11–17]. Based on X-ray single crystal structure analysis, Pangon et al. revealed that the benzimidazole derivatives with mono-, di- and tri-benzimidazole units formed perpendicular, parallel and helical hydrogen bond chains, respectively [18]. They suggested that anhydrous proton conductivities of the benzimidazole compounds depended on both packing structure and mobility of molecules. Chen et al. reported that comb-like benzimidazole polymers organizing into lamellar or columnar self-assemblies showed a dramatic enhancement in proton conductivity compared with the analogous materials that lacked regular molecular packing [19]. It seems that dynamic order of nitrogen-heterocycles plays a key role in obtaining efficient proton conduction.

In order to achieve both order and mobility for nitrogen-heterocycle compounds, we have prepared a series of liquid crystals whose terminal benzimidazole moieties were attached to biphenyl side of a rod-shaped biphenyl benzoate mesogen [20]. The compounds exhibited nematic and smectic A phases during the cooling process but only nematic phase was observed during the heating process. Nematic liquid crystal phase made limited contribution to anhydrous proton conduction owing to lack of molecular position order. With a view to tuning mesomorphic properties, we attached a terminal benzimidazole moiety to the benzoate side of the biphenyl benzoate mesogen through a flexible althio spacer to obtain benzimidazole liquid crystals (C_nBIm) in this research. Polarizing optical microscopic (POM) observations, X-

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ray diffraction (XRD) and differential scanning calorimetry (DSC) measurements revealed that **C_nBIm** exhibited smectic C (S_C) phase during both the heating and cooling processes. The tilted bilayer smectic order induced lamellar arrangement of intermolecular hydrogen bonds between the benzimidazole moieties. Temperature dependent electrochemical impedance spectroscopy (EIS) measurements suggested that the S_C phase favored anhydrous proton conduction and protons were transported through the hopping mechanism. It was revealed that formation of S_C phase was an optional strategy to promote anhydrous proton conductivities of protic compounds.

2. Experimental

2.1. Materials and reagents

The commercially available starting chemicals and solvents were purchased from Acros Ltd or TCI and used as received. All reactions were carried out under an oxygen-free nitrogen atmosphere. 4-(6-bromohexoxy) benzoic acid (**BABr**) and 4'-alkoxy-4-hydroxy biphenyl (**C_nBPh**) were synthesized according to the procedures described previously [21–23]. The synthetic route of the benzimidazole compounds (**C_nBIm**) bearing terminal alkoxy groups with different chain lengths is presented in Scheme 1.

2.2. Analytical measurements

The ¹H NMR spectra were obtained with a Bruker AV II-400 spectrometer in CDCl₃. The FT-IR measurements were conducted on a NEXUS 670 FTIR spectrometer. Elemental analyses were performed on a Euro EA3000 CHNS/O Elemental Analyzer. The DSC thermograms were collected on a TA modulated Netzsch DSC 204 F1 under a nitrogen atmosphere at a heating/cooling rate of 10 °C min⁻¹. The DSC measurement was performed in triplicate. The POM of thin film samples were observed on a Weitu XPL-30TF microscope fitted with a WT-3000 hot-stage. The XRD data were

measured on a 9 kW SmartLab Rigaku diffractometer equipped with Cu-Kα radiation. The EIS responses were recorded on an electrochemical workstation (EG&G Princeton Applied Research potentiostat/galvanostat model 273A and PAR lock-in-amplifier model 5210) linked to a PC running electrochemical impedance software (frequency range: 10 mHz to 100 kHz; applied voltage: 10 mV). Conductivity is computed as $\sigma = L/(RA)$, where *R*, *L* and *A* are sample's resistance to proton conduction (Ω), sample thickness (cm) and sample area (cm²), respectively.

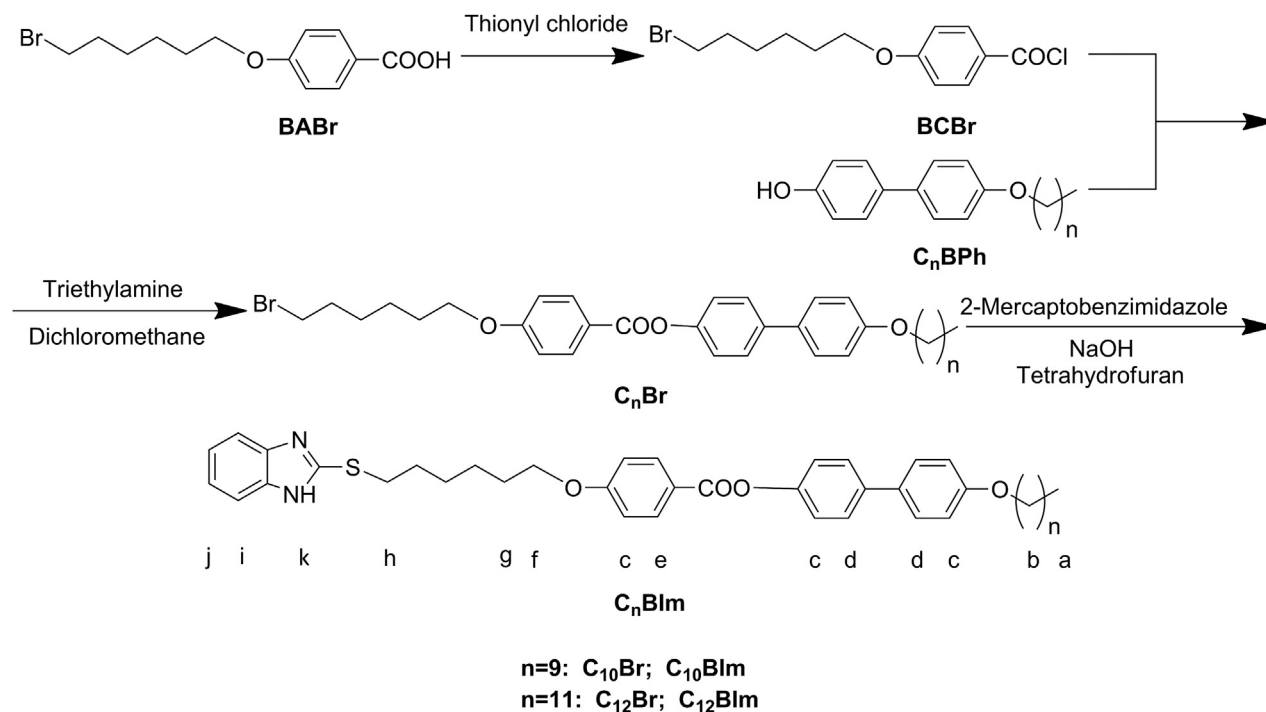
2.3. Synthesis

2.3.1. 4'-(alkoxy)-[1,1'-biphenyl]-4-yl 4-(6-bromohexoxy)benzoate (**C_nBr**)

Thionyl chloride was added dropwise to **BABr**. After the solution was stirred for 30 min at room temperature, 4-(6-bromohexoxy) benzoyl chloride (**BCBr**) was obtained by removing the excess of thionyl chloride under reduced pressure. A solution of **BCBr** was added dropwise to a solution of **C_nBPh** in dichloromethane containing a small amount of triethylamine. The reaction mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the residue was washed with methanol twice and further purified by flush column chromatography on silica gel (eluent: dichloromethane) to give **C_nBr** as a white powder.

C₁₀Br: ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.16 (d, 2H), 7.24 (m, 2H), 6.97 (m, 6H), 4.06 (m, 4H), 3.51 (m, 2H), 1.71 (m, 6H), 1.60–1.22 (m, 18H), 0.86 (t, 3H). FT-IR (KBr) ν: 2922, 2853, 1732 (C=O), 1473 (C–H), 1440, 1398 (C–H), 1079 (C–O), 1012, 848, 647 (C–Br). yield: 65%.

C₁₂Br: ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.16 (d, 2H), 7.24 (m, 2H), 6.96 (m, 6H), 4.06 (m, 4H), 3.52 (m, 2H), 1.72 (m, 6H), 1.61–1.22 (m, 22H), 0.86 (t, 3H). FT-IR (KBr) ν: 2923, 2853, 1732 (C=O), 1472 (C–H), 1440, 1397 (C–H), 1080 (C–O), 1012, 848, 645(C–Br). yield: 66%.



Scheme 1. Synthetic route of 4'-(alkoxy)-[1,1'-biphenyl]-4-yl 4-(6-(1H-benzo[d]imidazol-2-yl)thiohexoxy)benzoate.

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