

Scalable Synthesis of Cholesteric Glassy Liquid Crystals

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Abstract

Capable of non-absorbing circular polarization of unpolarized incident light, cholesteric glassy liquid crystals consisting of hybrid chiral-nematic pendants to volume-excluding cores are potentially useful for the fabrication of various robust optical devices. As illustrated in this study, the well-oriented glassy film of enantiomeric *Bz3ChN*, with a glass transition at 73 °C and a cholesteric-to-isotropic transition at 295 °C, exhibits a selective reflection band centered at approximately 410 nm, an exceptional set of properties well suited for optical device exploration. To enable sustainable, large-scale synthesis of this material class for widespread applications, a productive strategy has been established, requiring a mere three-step scheme with an overall yield, atom economy, and reaction mass efficiency at 34, 33 and 12 %, respectively. While amenable to improvements, the resultant green chemistry metrics are encouraging as the first attempt.

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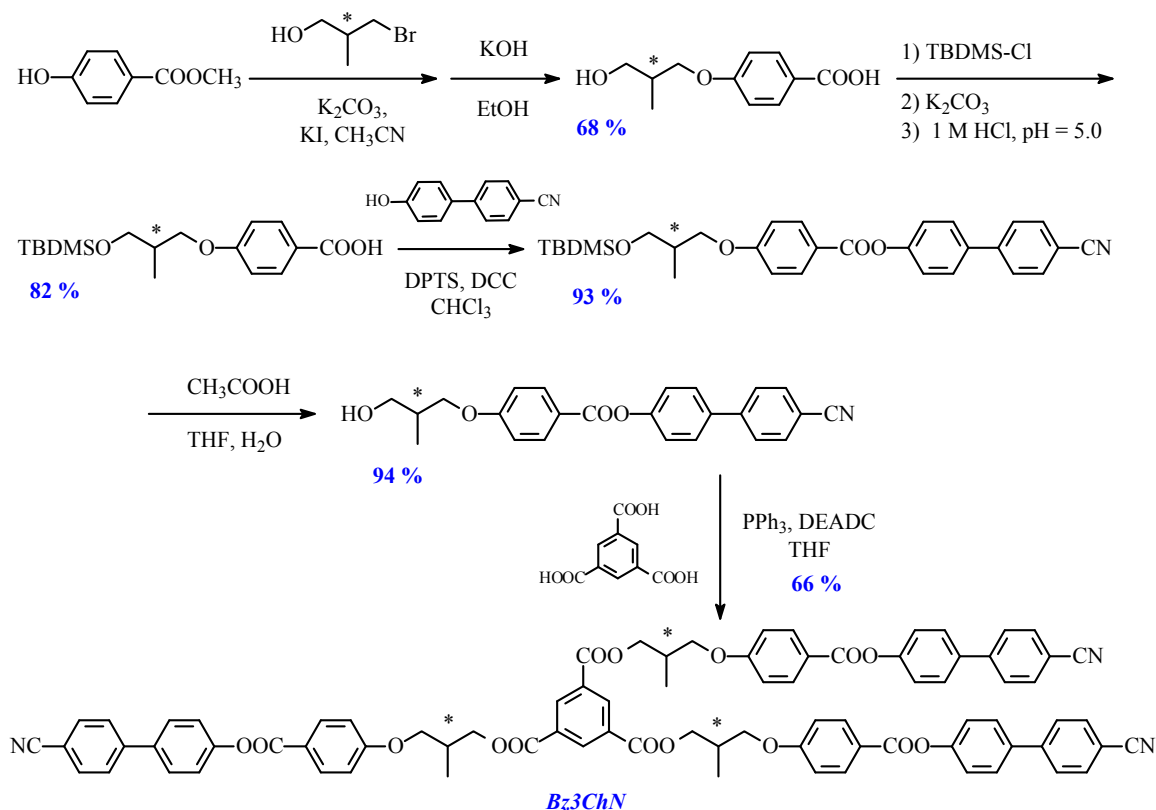
Introduction

The polarization state of light is a crucial consideration for most optics and optical systems. Polarization control impacts every day devices for communication, imaging, information displays, and medical needs, to name a few [1]. In the quest to produce more powerful lasers, one technique among many relies on manipulating the polarization of multiple laser beam into coherent orthogonal states which leads to an extremely efficient beam combination [2]. Liquid crystals have become important materials for polarization control devices such as circular polarizers and waveplates [3]. To improve device robustness, glassy liquid crystals, GLCs, have emerged as a superior material class via vitrification of liquid crystals below their glass transition temperatures without altering morphology. This materials concept was first demonstrated by Tsuji and Soai [4]. In the subsequent decades, numerous empirical approaches had been attempted with limited success in developing practically useful materials. A Physics Nobel Laureate, Philip Anderson [5], and a renowned polymer physicist, Karl Freed [6], stated that one of the most challenging and unresolved issues in solid state theory is to account for the nature of glass and glass transition. Indeed, no theoretical or computational frameworks have been formulated for molecular design of isotropic and mesomorphic organic glasses. Nevertheless, a modular approach based on the excluded-volume concept has been successfully implemented for developing GLCs with glass transition and clearing point up to 130 and 350 °C, respectively [7], with morphological stability against crystallization spanning over two decades and counting. Of particular interest are cholesteric glassy liquid crystals, *Ch-GLCs*, capable of selective wavelength reflection in thin films [8]. Various device concepts have been explored using selected materials, including non-absorbing polarizers, polarized lasers, notch filters, mirrors, and reflectors [7].

Molecules of *Ch-GLCs* normally consist of independent chiral and nematic pendants chemically bonded to a volume-excluding core to prevent crystallization from the glassy state [9]. The synthetic methodologies have evolved from the laborious statistical approach [10] through four generations of deterministic approaches [11], all incurring the stoichiometric control of chiral

versus nematic pendants to target the specific spectral range for selective wavelength. The most efficient and elegant approach involves a single pendant comprised of the hybrid chiral-nematic character [11d], thereby substantially facilitating the synthesis of *Ch-GLCs* as illustrated with *Bz3ChN* in **Reaction Scheme 1** while still demanding a total of five steps including the protection and deprotection routines for etherification and esterification reactions. In keeping with the spirit of green chemistry, attempts are made herein to perform esterification, as demonstrated by Guillon *et al.* [12], and etherification by taking advantage of the reactivity enhancement of the aromatic over aliphatic hydroxy groups in both reactions.

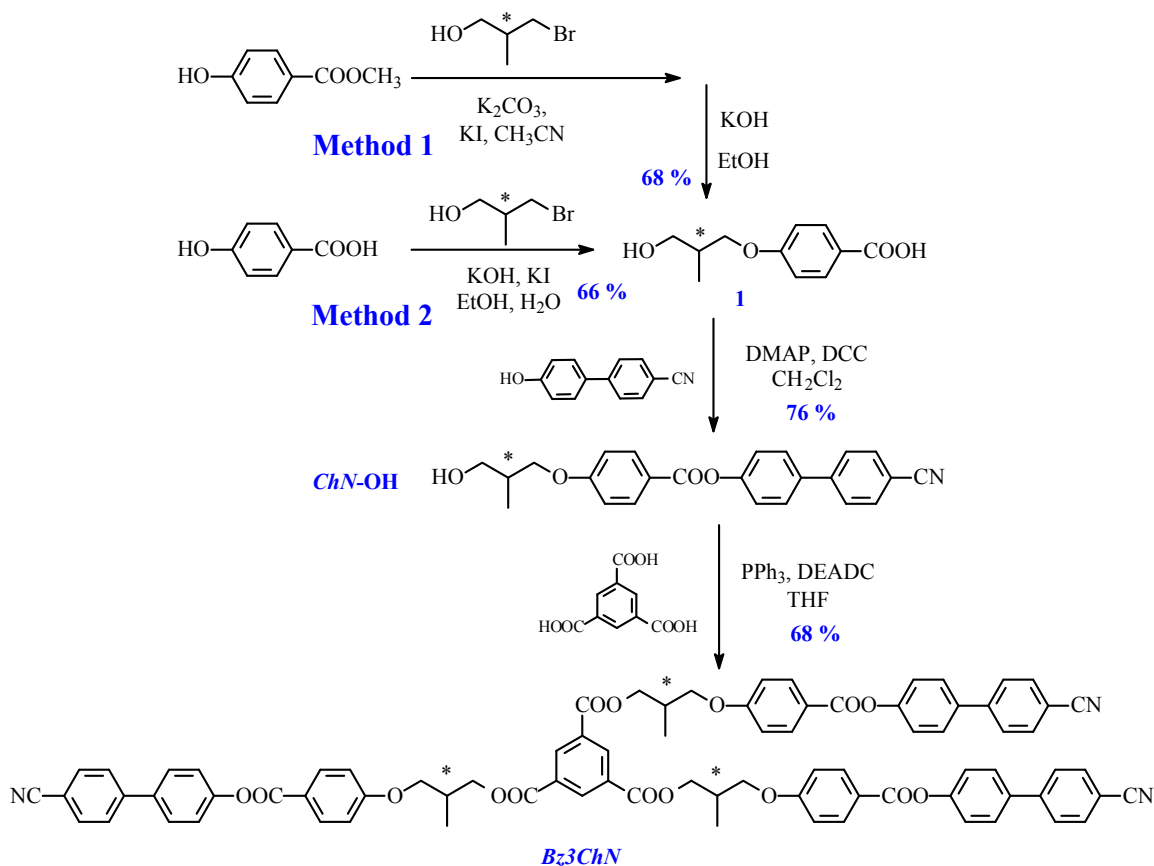
Reaction Scheme 1. Base-Line Synthesis of *BzCh3N*, i.e. Compound II in [11d], Being Improved with Green Chemistry Metrics



Results and Discussion

Two new methods depicted in **Reaction Scheme 2** are tested in this study. Method 1 calls for methyl 4-hydroxybenzoate as the starting material for direct etherification of the aromatic hydroxy group with the aliphatic bromide followed by deprotection of the methyl ester for esterification with aromatic hydroxy group of 4'-cyano-4-hydroxybiphenyl to form *ChN*-OH. Method 2 calls for *p*-hydroxybenzoic acid without protection and de-protection routines, and hence the most economical of all three approaches to *Bz3ChN* evaluated in **Reaction Schemes 1 and 2**.

Reaction Scheme 2. Scalable Synthesis Strategies



The purity and molecular structure of *Bz3ChN* were elucidated by proton-NMR spectroscopy and elemental analysis. The overall yields of **Reaction Scheme 1** and Methods 1 and 2 under **Reaction Scheme 2**, viz. 34 ± 2 %, are within experimental uncertainties of one another. In fact, yields are less relevant to green chemistry. Defined as the ratio of the desired product's molecular weight to the sum of all reactants' molecular weights multiplied by their stoichiometric coefficients, the atom economy values [13] increase from 26 to 33 % for **Reaction Schemes 1** and **2**. Nevertheless, atom economy does not account for the actual stoichiometric excesses and yields of all steps. As the more advanced metric of green chemistry, the reaction mass efficiency [14] is evaluated as the desired product's mass over the sum of all reactants' and reagents' masses. The resulting 6, 8, and 12 % for Reaction Scheme 1 and Methods 1 and 2 under **Reaction Scheme 2**, respectively, definitively quantify process sustainability albeit without accounting for solvents used as part of the inevitable chemical wastes.

The potential of *Bz3ChN* was appraised by the combination of differential scanning calorimetry and hot-stage polarizing optical microscopy that yielded a glass transition temperature and a clearing point at 73 and 295 °C, respectively, with nothing but cholesteric mesomorphism in between; moreover, a selective reflection band centered at approximately 410 nm for a well-oriented film as shown in Figures 1 and 3 of Ref. [11d]. Relevant points in a broader context are summarized as follows: (1) The left- and right-handed *Ch-GLCs* result from with (*S*)-(+)- and (*R*)-(–)-3-bromo-2-methylpropanol, respectively, as the chiral building block; (2) Fabricated into disclination-free films, the enantiomeric *Bz3ChN* films have exactly the same selective reflection bands; (3) Single-handed *Bz3ChN* films can serve as non-absorbing circular polarizers; (4) Mixtures of enantiomeric *Bz3ChN* samples give rise to selective reflection through the visible and infrared spectrum at an increasing off-balance composition with handedness determined by the major component in the mixture; (5) A stack of *Bz3ChN* films with opposite handedness tuned at the same selective reflection wavelength can serve as high-performance optical notch filters, reflectors, and mirrors; and (6) Ultimately the mixture loses selective reflection property in the limit of nematic mesomorphism at a 1:1 mass ratio. Alternatively,

nematic glassy liquid crystals can be readily prepared using racemic 3-bromo-2-methylpropanol or 3-bromo-propanol as the spacer instead of enantiomeric 3-bromo-2-methylpropanol . The scalable synthesis strategy introduced herein is generally applicable to chemically activated phenolic hydroxy groups and a host of additional volume-excluding cores [7, 9] for optimization of thermotropic and optical properties serving practical applications.

Experimental Section

(S)-(+)-4-(3-Hydroxy-2-methylpropoxy)benzoic acid, **1.**

Method 1: Methyl 4-hydroxybenzoate (11.8 g, 77.7 mmol), potassium carbonate (16.3 g, 118 mmol), potassium iodide (0.26 g, 1.6 mmol), and (S)-(+)-bromo-2-methylpropanol (13.7 g, 90.0 mmol) were put in a 250 mL round bottom flask. Acetonitrile (170 mL) was added and the reaction mixture was refluxed for 18 h. After cooling, the reaction mixture was filtered to remove solid residue and then the filtrate was evaporated to dryness under reduced pressure. To the resultant solid, potassium hydroxide (30.9 g, 550 mmol) and ethanol (600 mL) were added and this mixture was refluxed for 2 h. After evaporating off solvent under reduced pressure, the solid was dissolved in 400 mL of water and acidified to pH at about 1.0 with hydrochloric acid. The crude product was collected by filtration and recrystallized in chloroform to yield a white solid, **1** (11.1 g, 68 %).

Method 2: 4-hydroxybenzoic acid (8.2 g, 59 mmol), potassium hydroxide (9.0 g, 160 mmol), and potassium iodide (1.0 g, 5.9 mmol) were dissolved in ethanol (25 mL) and water (1.6 mL) and heated to 85°C. Over 30 minutes, (S)-(+)-bromo-2-methylpropanol (9.5 g, 62 mmol) was added dropwise, and then the reaction mixture was refluxed for 24 h. After cooling, the reaction mixture was filtered to remove residue then evaporated into a pale pink solid under reduced pressure. The resultant solid was dissolved in water (100 mL) and acidified with 10 % hydrochloric acid. The crude product was collected by filtration and recrystallized in a 1:1 mixture of ethanol and water to yield a white solid, **1** (8.3 g, 66 %). ¹H NMR spectral data (400

MHz, DMSO-d₆): δ (ppm) 0.95 (d, 3H, -CH₃), 1.98 (m, 1H, -CH₂CH(CH₃)CH₂-), 3.40 (s, 2H, HOCH₂-), 3.93 (m, 2H, -CH₂OAr), 4.57 (s, 1H, HO-), 6.99 (d, 2H, aromatics), 7.86 (d, 2H, aromatics), 12.57 (s, 1H, -COOH).

(S)-(+)-4-(3-Hydroxy-2-methylpropoxy)benzoic acid 4'-cyanobiphenyl-4-yl ester, *ChN*-OH.

Intermediate **1** (5.00 g, 23.7 mmol), 4'-hydroxy-4-biphenylcarbonitrile (4.76 g, 24.4 mmol), 4-(dimethylamino)pyridine (3.02 g, 24.7 mmol), and dicyclohexylcarbodiimide (8.34 g, 40.4 mmol) were added to a dry round bottom flask and put under argon. Anhydrous dichloromethane (300 mL) was added by cannulation and the reaction mixture was stirred under argon for 20 h at room temperature. The reaction mixture was then filtered to remove solid residue before evaporating to dryness. The resultant solid was recrystallized in ethanol and then further purified by flash column chromatography on silica gel with 10:1 dichloromethane:ethyl acetate to yield *ChN*-OH (6.99 g, 76 %). ¹H NMR spectral data (400 MHz, CDCl₃): δ (ppm) 1.07 (d, 3H, -CH₃), 1.64 (s, 1H, HO-), 2.24 (m, 1H, -CH₂CH(CH₃)CH₂-), 3.74 (m, 2H, HOCH₂-), 4.05 (m, 2H, -CH₂OAr), 7.01 (d, 2H, aromatics), 7.33 (d, 2H, aromatics), 7.64 (d, 2H, aromatics), 7.69 (d, 2H, aromatics), 7.74 (d, 2H, aromatics), 8.16 (d, 2H, aromatics).

1,3,5-Benzenetricarboxylic Acid, tris[(*R*)-3-[4-[(4'-Cyanobiphenyl-4-yl)oxycarbonyl] phenoxy]-2-methylpropyl] Ester, *Bz3ChN*.

To a solution of *ChN*-OH (1.7 g, 4.4 mmol), 1,3,5-benzenetricarboxylic acid (0.27 g, 1.3 mmol), and triphenylphosphine (1.15 g, 4.4 mmol) in anhydrous tetrahydrofuran (66 mL), a 40 wt % solution of diethyl azodicarboxylate (DEADC) in toluene (2.4 mL, 5.3 mmol) was added dropwise. The reaction mixture was stirred under argon at room temperature overnight. The reaction mixture was evaporated under reduced pressure, dissolved in a minimum amount of dichloromethane and precipitated into 500 mL of methanol. The resultant solid was purified by gradient column chromatography on silica gel with 0 to 2 % acetone in dichloromethane. The product was collected by precipitation from a minimum amount of dichloromethane into 300 mL of methanol to yield *Bz3ChN* (1.2 g, 68 %). Elemental analysis was carried out at the CENTC Elemental Analysis Facility, University of Rochester. Anal. Calcd. C, 73.79; H, 4.82; N, 3.19. Found: C, 73.24; H, 4.75; N, 2.95. ¹H NMR spectral data (400 MHz, CDCl₃): δ (ppm) 1.22 (d, 9H, -

CH_3), 2.55 (m, 3H, $-CH_2CH(CH_3)CH_2-$), 4.07 (d, 6H, $-CH_2OAr$), 4.49 (m, 6H, $-COOCH_2$), 6.99 (d, 6H, aromatics), 7.31 (d, 6H, aromatics), 7.62 (d, 6H, aromatics), 7.67 (d, 6H, aromatics), 7.73 (d, 6H, aromatics), 8.15 (d, 6H, aromatics), 8.86 (s, 3H, aromatics, benzene core). All the obtained analytical data are consistent with those acquired for Compound II [11d] intended for developing a scalable synthesis scheme in this study.

Summary

Cholesteric glass liquid crystals have found numerous potential optical device applications, including non-absorbing polarizers, polarized lasers, notch filters, mirrors, and reflectors. From the molecular structure standpoint, independent chiral and nematic pendant groups at an optimized stoichiometric ratio are chemically bonded to a volume-excluding core to form cholesteric glass liquid crystals. This traditional view entails sophisticated deterministic synthesis. The more elegant approach incorporates both chiral and nematic characters in a single hybrid pendant, e.g. *Bz3ChN* as illustrated in this study, which substantially reduces the synthesis and purification efforts and hence facilitates process scale-up. To further promote chemical sustainability, *p*-hydroxybenzoic acid carrying a chemically activated phenolic hydroxy group toward esterification and etherification is adopted as a building block to obviate the protection-deprotection routines, thereby serving a synthesis scheme in three steps compared to five with an atom economy and reaction mass efficiency improved from 26 to 33 % and 6 to 12 %, respectively. Nonetheless, all three strategies are generally applicable to the synthesis of nematic, cholesteric, and smectic glassy liquid crystals comprising diverse combinations of volume-excluding core and mesogenic pendant.

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