

Effect of counterion on the mesomorphic behavior and optical properties of columnar pyridinium ionic liquid crystals derived from 4-hydroxypyridine



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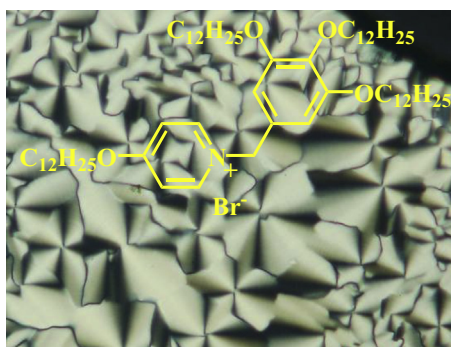
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HIGHLIGHTS

- ILC pyridinium salts derived from 4-hydroxypyridine were prepared and studied.
- *N*-3,4,5-tridodecyloxybenzyl-4-pyridone shows a monotropic Col_h phase.
- Bulkier counterions (BF₄⁻ or PF₆⁻) destabilize the LC phase.
- 3,4,5-Tridodecyloxybenzyl pyridinium bromide salt shows two LC columnar phases.

GRAPHICAL ABSTRACT

Influence of counterion on the mesomorphic behavior and photophysical properties of columnar pyridinium ionic liquid crystals derived from 4-hydroxypyridine



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ABSTRACT

A series of 3,4,5-tridodecyloxybenzyl pyridinium salts derived from 4-hydroxypyridine has been designed and prepared. The liquid crystalline properties of these compounds were investigated by polarized optical microscopy, differential scanning calorimetry and powder X-ray diffraction while their thermal stability was studied by thermogravimetric analysis. The *N*-3,4,5-tridodecyloxybenzyl-4-pyridone intermediate shows a monotropic columnar hexagonal mesophase ranging from 56 °C down to room temperature while the corresponding bromide dodecyl *O*-alkylated pyridinium salt shows one enantiotropic columnar mesophase and one additional monotropic columnar phase at lower temperatures. Replacing bromide ion (Br⁻) with other counterions (NO₃⁻, BF₄⁻ and PF₆⁻) resulted in mesophase suppression. These luminescent pyridinium salts show weak emission in dichloromethane solutions at room temperature and a pronounced red-shifted emission in solid state. Photoluminescent properties of the pyridinium salts do not depend significantly on the nature of counterion employed.

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Introduction

Ionic liquid crystals (ILC) are a special class of materials that combine in a unique manner the liquid crystal (LC) and ionic liquid (IL) properties. They are closely related to ionic liquids (IL) that show very interesting properties such as low volatility, nonflammability and high-ionic conductivity. In this respect, they are regarded as good candidates to replace conventional organic solvents in organic reactions. The most attractive and investigated ILC systems include ammonium, phosphonium, imidazolium, pyridinium and pyrrolidinium salts. The anisotropic ionic conductivity is one of the most interesting features of ILC, due to the presence of ionic units in the liquid crystal phase. Several reviews covering this topic were published in the recent years [1,2]. Amongst them, pyridinium-based ILC, whose mesomorphism has been known since long time, show similar properties with the related imidazolium based ILC [3].

In this work we report preliminary studies regarding the synthesis and LC investigation of a series of pyridinium ionic liquid crystals derived from 4-hydroxypyridine with different counterions such as bromide (Br^-), nitrate (NO_3^-), tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-). It is worth mentioning that 4-hydroxypyridine is a very appealing starting material as it can be either *N*- or *O*-alkylated in the first step [4–6], yielding either 4-pyridones or *O*-substituted pyridines respectively, followed by a second alkylation step to yield desired ILC materials. This represents a big advantage as different mesogenic groups can be introduced separately in the molecule with the aim of finely tune the liquid crystalline properties. For instance, Lin et al. [7] reported ILC based on 4-hydroxypyridine motif with simple alkyl chains, both *O*- and *N*-alkylated pyridinium salts. Generally, all these ILC show a SmA phase whose stability depends on the alkyl chain length and the counterion employed. On the other hand, there are only several examples of pyridinium based ILC that display columnar phases. One representative example has a classical hexaalkoxytriphenylene moiety connected via a flexible alkyl spacer to the pyridinium ring [8]. There is a growing interest in the discovery of new materials showing columnar liquid crystal phases as they found their applications in electronic or optoelectronic devices, in particular due to their ability to display improved anisotropic charge transportation [9]. 3,4,5-trialkylbenzyl bromide is a well-known alkylation reagent for imidazole or pyridinium units that can lead to LC materials able to display columnar phases depending on alkyl chains length employed [10–12]. We were interested to investigate the structure – mesomorphic properties relationship of a series of pyridinium salts with different counterions, having on one side the 3,4,5-trialkylbenzyl moiety and an alkyl chain group at the other side of the molecule. The emission properties of these salts were also studied in solution and solid state.

Experimental

All the chemicals were used as supplied. 3,4,5-tridodecyloxybenzyl bromide was synthesized as reported elsewhere [12]. C, H, N analyses were carried out with a Perkin Elmer instrument. IR spectra were recorded on a Bruker spectrophotometer using ATR technique. UV–Vis absorption spectra were recorded by using a Jasco V-660 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 BB spectrometer operating at 300 MHz, using CDCl_3 as solvent. ^1H chemical shifts were referenced to the solvent peak position, δ 7.26 ppm. The phase assignments and corresponding transition temperatures for the 4-pyridone intermediate and the pyridinium salts were determined by polarizing optical light microscopy (POM) using a Nikon

50iPol microscope equipped with a Linkam THMS600 hot stage and TMS94 control processor. These observations were made on untreated glass slides. Temperatures and enthalpies of transitions were investigated using differential scanning calorimetry (DSC) with a Diamond DSC Perkin Elmer instrument. The materials were studied at different scanning rates after being encapsulated in aluminum pans. Two or more heating/cooling cycles were performed on each sample with variable scanning rate (2, 5 and $10^\circ\text{C}/\text{min}$). Mesophases were assigned by their optical texture and powder X-ray diffraction data. The powder X-ray diffraction measurements were made on a D8 Advance diffractometer (Bruker AXS GmbH, Germany), in parallel beam setting, with monochromatized $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$), scintillation detector, and horizontal sample stage. The measurements were performed in symmetric (θ – θ) geometry in the 2θ range from 1.5° to 10° or 30° in steps of 0.02° , with measuring times per step in the 5–40 s range. The temperature control of the samples during measurements was achieved by adapting a home-made heating stage to the sample stage of the diffractometer. Variable temperature emission spectra in solid state were recorded with an OceanOptics QE65PRO spectrometer attached to the microscope and using a Nikon Intensilight excitation source. Fluorescence spectra in solution were recorded on a Jasco FP-6300 spectrofluorometer (operating parameters: band width – 5 nm; data pitch – 0.5 nm; scanning speed – $100 \text{ nm}/\text{min}$; spectrum accumulation – 3; path length – 10 mm by using Quartz SUPRASIL cells) in dichloromethane solution. Thermogravimetric analysis was performed on a TA Q50 TGA instrument using alumina crucibles and nitrogen as purging gas. The heating rate employed was $10^\circ\text{C min}^{-1}$ from room temperature (approximately 25°C) to 550°C .

Synthesis of 2

To a mixture of 4-hydroxypyridine (1.06 g, 11.2 mmol) and tetrabutylammonium bromide (0.36 g, 1.1 mmol) in tetrahydrofuran, an aqueous 2 N NaOH solution (NaOH equivalent to 4-hydroxypyridine) was added. After the mixture became homogenous, the bromide derivative **1** (6.5 g, 8.9 mmol) was added and the mixture was heated under reflux and nitrogen atmosphere for 2 days. After cooling, the solvent was removed by rotary evaporation under reduced pressure and the crude product was extracted with a mixture of $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ 1/0.8. The organic layers were collected and dried over anhydrous Na_2SO_4 . The solvent was removed in vacuum and the residue was purified on a silica gel chromatography column using as eluent a mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (95/5). Yield 67%, white waxy solid. Anal. Calcd. for $\text{C}_{48}\text{H}_{83}\text{NO}_4$: C%78.10, H%11.33, N%1.90. Found: C%77.83, H%11.58, N%1.68. ^1H NMR (CDCl_3 , 300 MHz): 7.32(d, 2H, $J = 7.4 \text{ Hz}$), 6.41(d, 2H, $J = 7.4 \text{ Hz}$), 6.30(s, 2H), 4.82(s, 2H), 3.94–3.87(m, 6H), 1.80–1.60(m, 6H), 1.50–1.20(m, 54H), 0.86(m, 9H). ^{13}C NMR (CDCl_3 , 75 MHz): 179.1; 154; 140.1; 138.7; 129.6; 119.0; 105.9; 77.6; 77.4; 77.2; 76.8; 73.7; 69.4; 60.5; 56.3; 32.1; 30.5; 29.9; 29.8; 29.6; 26.2; 22.8; 14.3. IR(ATR, cm^{-1}): 2957, 2916, 2851, 1640, 1574, 1505, 1467, 1435, 1381, 1211, 1116, 847, 720.

Synthesis of 3

The 4-pyridone **2** (1 g, 1.35 mmol) was dissolved in acetonitrile (50 mL). 1-Bromododecane (0.97 mL, 4.05 mmol) was added and the reaction mixture was heated under reflux in a nitrogen atmosphere for two days. After this period, the solvent was removed by rotary evaporation under reduced pressure. The residue was purified by column chromatography using $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (95/5) mixture followed by crystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to yield a white powder. Yield 74%, white solid. Anal. Calcd. for $\text{C}_{60}\text{H}_{108}\text{BrNO}_4 \cdot 0.5\text{H}_2\text{O}$: C%72.40, H%10.94, N%1.41. Found: C%72.25,

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