



Blue luminescent cyanopyridone based molecular architectures: A structure-property study

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ARTICLE INFO

Article history:

Received 29 November 2017

Received in revised form 18 January 2018

Accepted 21 January 2018

Available online xxxx

Keywords:

Luminescent

Liquid crystal

Cyanopyridone

Cyclic voltammetry

ABSTRACT

A new class of molecular architecture made of five conjugated rings carrying terminal methyl or variable alkoxy (chain lengths of 4, 6, 8, or 16) substituted at para positions has been synthesized. Among the five rings, two rings are of cyanopyridones utilized as an electron deficient N-heterocycle along with blue luminescent motif, and the rest of them are phenylene motifs. All the compounds produced good yield and ATR-IR, NMR and Mass spectroscopy confirmed their structures. Further, the compounds were stable up to ≈ 200 °C and the degradation occurs at higher temperature as evident from the TGA analysis. The mesomorphic study reveals that compound is only having very long terminal *n*-hexadecyloxy substituents appeared in-layers liquid crystalline organization as confirmed by POM and variable temperature XRD analysis. Further, the compounds showed intense blue fluorescence in both solution as well as solid state and their fluorescence quantum yields are dependent on the length of alkoxy chains. Calculated HOMO/LUMO levels by cyclic voltammetry measurements revealed that the compounds are ambipolar in nature and cited as an ideal candidates for electroluminescent applications.

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1. Introduction

In the recent years, tuning of photophysical properties of organic moieties based on their state, size, molecular framework, and change in functionalities have drawn a lot of interest, as tuning of these properties allows to achieve organic moieties with desired characteristic behavior. However, the field concerning the synthesis of new luminescent organic moieties showing emission over a wide range in the solid state is still challenging and is of great interest to many researchers. In this context, a number of recent research has confirmed that alkyl chain length could greatly influence the molecular conformations, intermolecular interactions and packing modes in solid state, thus, altering their solid state optical and optoelectronic properties [1–5]. Hence, variation in alkyl chain lengths has a functional role in determining the solid-state aggregation and optoelectronic behavior of organic motifs. The extensively studied luminescent materials exhibiting alkyl length-reliant fluorescence properties contains twisted conformations, usually displaying aggregation induced emission (AIE) [6], mechanochromic luminescence [7–9] phenomenon and weak solution fluorescence quantum yield. In the literature, some of the

cyanopyridone derivatives were reported to be electron deficient and strong blue emitters with high quantum yields [10–12]. Because of these exquisite properties, the present study concerns the luminescent cyanopyridone core bearing methyl and linear alkoxy substituent and their photo-physical properties in various solvent mixtures being inquisitive about the emission behavior upon aggregation.

On the other hand, quite handful of reports are available on liquid crystalline cyanopyridones with a rod-shaped molecular structure and polymerisable cyanopyridones [13]. Also, it is well established fact that the incorporation of cyanopyridone unit helps to attain high polarity and high positive values of the dielectric anisotropy mainly due to the presence of cyano and keto groups at adjacent positions in the ring [14]. Cyano group being a well-known electron withdrawing substituent, the incorporation of cyano group as a substituent in the molecular framework further increases the molecular dipole moment and thereby, minimize the repulsive interactions between adjacent aromatic π -systems and promotes the formation and stabilization of mesophase [15]. In addition, pyridone motifs have the greater tendency to self-assemble into columnar discotic mesophase via hydrogen bond interactions [16,17]. In contrast, polycatenar mesogens, particularly the penta-catenar compounds showed interesting mesophases viz. smectic, cubic and columnar phases. These mesophase formations are generally assisted by the number of rings present in the core, the type

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and number of terminal chains, the nature of the bridging groups etc. [18]. Keeping in line with all the above facts and the availability of such limited reports on the luminescent cyanopyridone unit, we have designed new five ring system carrying two cyanopyridones based molecular architecture in the present work.

In the present study, we have incorporated two 3-cyanopyridone units as luminescent core to achieve five ring molecular framework. Both the terminals of molecular frameworks have been substituted by the methyl or linear alkoxy groups (length of chain = 4, 6, 8, or 16) at their *para* position to get new cyanopyridone derivatives (**AC1–5**). These molecules were prepared from one pot synthesis method by reacting 4-methyl acetophenone/4-alkoxy acetophenone, terephthalaldehyde, ethyl cyanoacetate and ammonium acetate. Later, ATR-IR, NMR and Mass spectroscopy elucidated their chemical structures. Their photophysical properties were determined by UV-visible absorption and fluorescence emission studies. The synthesized compounds were subjected to TGA (thermogravimetric analysis), DSC (differential scanning calorimetry), POM (polarized optical microscopy) and variable temperature X-ray diffraction (XRD) analysis to check their underlying thermal stability as well as liquid crystalline behavior. Surface features of thin films of selected compounds were extracted with the help of AFM. Finally, electrochemical band gap, LUMO and HOMO energy levels were determined using cyclic voltammetry method.

2. Results and discussion

2.1. Synthesis and characterization

The systematic synthetic route for the preparation of the target molecules is depicted in Scheme 1. The general procedure for the preparation of long chained alkoxyacetophenones (**1b–e**) are same as reported earlier [19]. Target bicyanopyridone compounds (**AC1–5**) were synthesized by a one pot method by reacting the mixtures of methyl/alkoxyacetophenones (**1a–e**) with terephthalaldehyde (**2**), ethyl cyanoacetate and ammonium acetate (0.16 mol) in 1,4-dioxane under 80 °C for 8 h. All the target compounds were obtained in good yield (>70%). The structures of all the target molecules were confirmed using ATR-IR, NMR spectroscopy and Mass analysis.

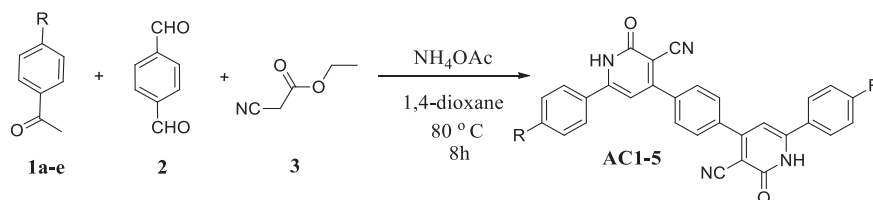
2.2. Thermal behavior

Thermal stability of all the target compounds was investigated with the help of thermogravimetric analysis (TGA) and using POM. Cyanopyridone derivatives (**AC1–5**) were unstable above 200 °C as evident by the TGA plot (Fig. 1). The temperature degradation depends on the terminal chain lengths, but this fact did not allow to fix their melting temperatures as cyanopyridone derivatives decompose before melting, with the exception of **AC5** that decomposes before passing to isotropic liquid from mesophase as discussed in detail latter.

2.3. Photophysical properties

Solution state UV-visible absorption spectra of **AC1–5** compounds were recorded at the concentration 1×10^{-5} M in DMSO. The values of absorption maximum of **AC1–5** are given in Table 1 and their absorption spectra is depicted in Fig. 2. As can be seen, the absorption spectra obtained for the solutions of **AC1–5** showed a single absorption layer, maximum in a range of 385–394 nm and these absorption bands can be attributed to the spin allowed π - π^* transitions in them. In general, more the planar molecular framework greater the extent of delocalization of π electrons, which narrows the band gap and shifts the absorption wavelength to longer wavelength region (red shift). However, the obtained absorption values for compounds **AC1–5** in DMSO are almost same when compared to our earlier report of the three ring system containing a central cyanopyridone core [20]. Further, compounds exhibited larger values of molar absorption coefficient (ϵ) $> 17,000$ L mol⁻¹ cm⁻¹ and showed how strongly these substances absorb light. The variation of alkoxy chain lengths in the compounds affects the absorption wavelength and molar extinction coefficient. Among **AC1–5**, the highest absorption wavelength and molar extinction coefficient are obtained for **AC3** (carrying n-hexyloxy chains) and **AC2** (carrying n-butyloxy chains), respectively. It is interesting to note that, as we varied the alkoxy chain lengths from n-butyloxy to n-hexyloxy chains, the bathochromic shift occurs, but later on the further increase of chain lengths n-hexyloxy to n-octyloxy or n-hexadecyloxy chains exhibited a hypsochromic shift. This can be accounted on the basis of steric factor, wherein, the presence of higher alkoxy chains causes a greater steric hindrance leading to attain a highly distorted chain conformation with shorter π -conjugation length in the molecule [21]. Thus, the extent of molecular planarity is noticeably recorded more in case of **AC3** (carrying n-hexyloxy chains) than the rest of compounds, which resulted in the absorption at longer wavelength region [22].

Fluorescence emission spectra of cyanopyridone compounds (**AC1–5**) were recorded in DMSO (Conc. 1×10^{-5} M) by exciting the solutions of these compounds at their absorption maxima, leading to emissions band with their maxima centered at around 456–474 nm (Fig. 3) and displaying large Stokes shift (range: 69–81 nm) values. In solution state, all the compounds are blue emissive in nature. Further, their relative quantum yield (Φ_f) in solution state were determined using quinine sulphate in 0.1 M sulfuric acid as a standard ($\Phi_f = 0.54$) [23–25]. The compounds displayed a varied quantum yields ($\Phi_f = 0.08$ –0.36), among themselves. In particular, compound **AC4** exhibited a highest quantum yield. It is observed that, the fluorescence quantum yield improved with the increase of alkoxy chain lengths till n-octyloxy chain, thereafter, no drastic change was noted with the n-hexadecyloxy chain [26]. Also, UV-visible absorption spectra of **AC1–5** were recorded in thin film state (Fig. S15) and showed a slight hypsochromic shift in their absorption band to that of solution state. Further, their optical band gaps (E_g) were estimated by considering the wavelength of absorption edge in their thin film state and they were found to be in the



where, R = $-\text{CH}_3$ for **1a** and **AC1**
 R = $-\text{OC}_4\text{H}_9$ for **1b** and **AC2**
 R = $-\text{OC}_6\text{H}_{13}$ for **1c** and **AC3**
 R = $-\text{OC}_8\text{H}_{17}$ for **1d** and **AC4**
 R = $-\text{OC}_{16}\text{H}_{33}$ for **1e** and **AC5**

Scheme 1. Synthetic route for **AC1–5**.

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