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N-fused ring strategy toward orange/yellow light-emitting liquid crystalline molecules

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ABSTRACT

A new synthetic procedure for fluorinated N-fused ring, 2F-fluorazone (1,2-difluoro-9H-pyrrolo[1,2]-indol-9-one), has been developed. It connected with acetylene to obtain the first example of fluorinated N-fused rings luminescent liquid crystals (LLCs). CH_3O-fluorazone-2F and CH_3O-fluorazone display yellow and orange fluorescence respectively, and their properties can be tuned by the substitution pattern.

1. Introduction

Luminescent liquid crystals (LLCs) are fascinating materials gaining tremendous interest for optoelectronic applications, because of their unique combination of ordered alignment and photophysics property [1–4]. The reported LLCs materials basically based on fluorescent materials, phosphorescent materials, and lanthanide complexes, and the liquid crystal molecules generally have a larger aspect ratio [5–12]. Based on simple design, the fluorophores connected with some linear molecular framework, as tolane for example, are widely used in the construction of liquid crystals. Nevertheless, the problem of conventional luminophores quenching in the condensed phases have great impact in brightness and quantum efficiency of LLCs. Tang and coworkers have proposed a strategy that AIE or AEE type molecule can solve the problems effectively [13,14]. Chi [15,16] and Wang [17] developed LLCs materilas based on AIE molecules. Hosokai [18,19] and Zeng [20–22] also designed a series of fluorine containing rod-shape organic molecules showing excellent luminous performance (Fig. 1a and b). However, the color of reported LLCs molecules based on tolane are mostly blue to green, even though some organometallic complexes [23] and few conjugated derivatives, e.g. benzothiadiazoles bridged with diacetylene, can achieve red emission LLCs [24–26]. The simple and straightforward approach to achieve orange or red emission LLCs are rare. To overcome these above disadvantages, extensive efforts should be devoted to developing a new class of luminophores.

Fluorazone (9H-pyrrolo[1,2-a]indol-9-one) containing compounds are an important framework for the synthesis of various complex molecules. As concerned to electronic perspective, the fixation of aromatic and heteroaromatic rings in the same plane in a fused ring can significantly increase their conjugation system [27]. As for fluorescent materials, the electronic acceptor and donor groups are usually connected by π bond to obtain controllable luminescent compounds, and fluorine or fluorine-containing substituents are used in LCs display devices. Fluorine as an important auxochrome, it show typical hyperchromic effect leads to red-shift emission in solution also in solid state [28]. Considering to these specifics, the preparation and fluorine functionalization of the fluorazone core have been the subjected to significant synthetic efforts. However, studies concerning the extension of its conjugate systems and the enhancement of its photophysical properties are rare.

In this work, we provide a synthetic route to obtain new fluorinated N-fused ring, **2F-fluorazone** (compound **4**), which contains two electron-withdrawing fluorine substituents will causes a significant electronic effect and high polarity. We introduce the **2F-fluorazone** in designing and synthesizing a series of D-π-A type phosphors based on phenylacetylene for the first time (Fig. 1), further successfully combined luminescence and liquid crystal properties into one molecule. The fused ring, 2F-fluorazone, with the lateral two fluoro substituents at out-edge position has a completely different mesomorphism and luminescence character to the comparable fluorazone, and it can be further transformed by reaction the carbonyl group to obtain the derivatives. It appears to be very simple and straightforward route to orange/yellow luminescent liquid crystal. Here, we report their optical and liquid crystal properties to better understand the fused ring based luminescence liquid crystal.

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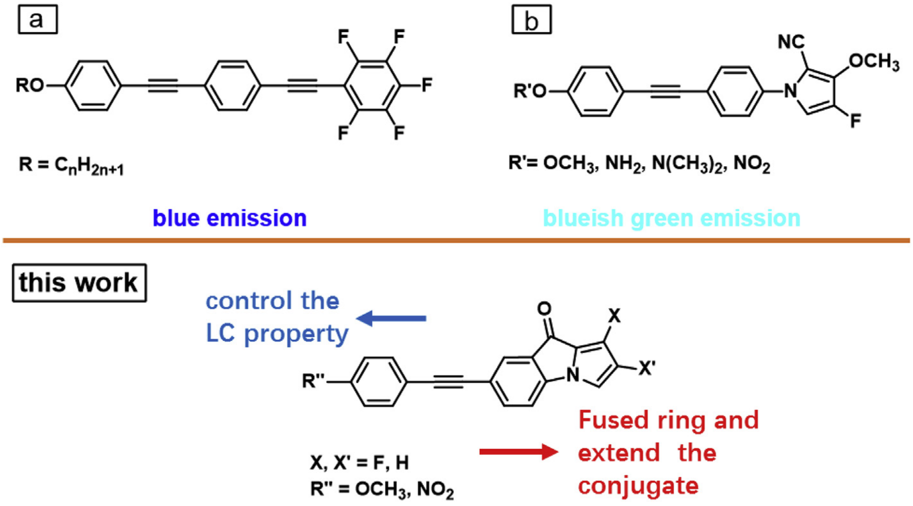
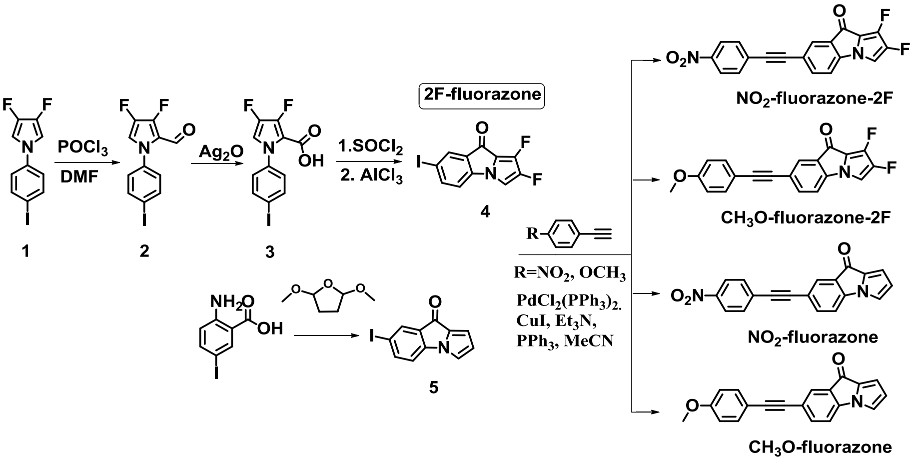


Fig. 1. Model of LLCs molecular.



Scheme 1. Synthetic route for the compounds NO_2-fluorazone-2F, CH_3O-fluorazone-2F, NO_2-fluorazone and CH_3O-fluorazone.

2. Results and discussion

2.1. Synthesis

Our strategy for the synthesis of LLCs is outlined in Scheme 1. Detail of the synthesis and characterization of materials are given in the electronic supporting information.

The intermediate **1** and **2** was synthesized according to our previous work [20]. The aldehyde **2** was oxidized into the corresponding acid under Ag_2O condition to give **3** at 85% yield. The key product **4** was prepared by two procedures in one pot. **3** was firstly treated with excess $SOCl_2$ to obtain the acyl chloride product, then adding $AlCl_3$ as a catalyst to give the intramolecular cyclization product **4** (**2F-fluorazone**) in 42% yield. The **5** was produced from the commercially available material 2-amino-5-iodobenzoic acid and 2, 5-dimethoxytetrahydrofuran with 85% yield, according to the literature [29]. Finally, **4** and **5**, respectively coupled with 1-ethynyl-4-nitrobenzene, and 1-ethynyl-4-methoxybenzene to yield the LLCs, **NO_2-fluorazone-2F**, **CH_3O-fluorazone-2F**, **NO_2-fluorazone** and **CH_3O-fluorazone**, in 80–95% yield.

2.2. Fluorescent property

The UV–vis absorption and fluorescence spectroscopic data in THF solution (10^{-5} mol/L) and in the solid state of compound **NO_2-fluorazone-2F**, **CH_3O-fluorazone-2F**, **NO_2-fluorazone** and **CH_3O-fluorazone** are shown in Fig. 2. The corresponding photophysical properties are summarized in Table 1. It can be seen that, UV–vis spectra of the all compounds in dilute THF solution (Fig. 2c) exhibit two absorption bands, which is the typical dualband spectra of D-π-A compound. As for **CH_3O-fluorazone-2F** and **CH_3O-fluorazone**, both compounds exhibit two absorption bands in the ranges of 300–400 nm and 422–433 nm, the shorter wavelength absorption can be ascribed to the π-π* transition, whereas the longer band is corresponded to the intramolecular charge transfer (ICT) transition between the donor and acceptor units. The UV/Vis absorption and photoluminescence (PL) spectra of **CH_3O-fluorazone-2F** and **CH_3O-fluorazone** were recorded in various solvents with different polarities (Fig. S4). The absorption spectra seldom changed, but the emission spectra are gradually redshift as the polarity of solvent increased, exhibiting an obvious bathochromic effect. The emission peak of **CH_3O-fluorazone-2F** changed from 517 nm in hexane to 561 nm in acetonitrile, meanwhile the change from 514 nm in