



Contents lists available at ScienceDirect

## Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: [www.elsevier.com/locate/saa](http://www.elsevier.com/locate/saa)

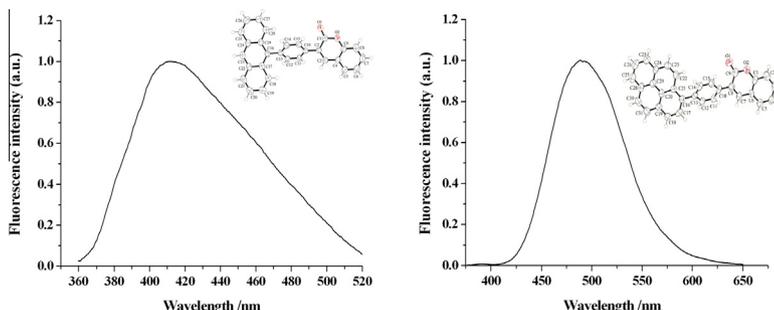
## Synthesis, crystal structures and photoluminescence of anthracen- and pyrene-based coumarin derivatives

Hui Zhang<sup>a</sup>, Hao Tong<sup>a</sup>, Yuling Zhao<sup>b</sup>, Tianzhi Yu<sup>a,\*</sup>, Peng Zhang<sup>a</sup>, Jianfeng Li<sup>a</sup>, Duowang Fan<sup>a</sup><sup>a</sup>Key Laboratory of Opto-Electronic Technology and Intelligent Control (Ministry of Education), Lanzhou Jiaotong University, 88 West Anning Road, Lanzhou 730070, China<sup>b</sup>School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

## HIGHLIGHTS

- Two new anthracen- and pyrene-based coumarin derivatives were synthesized and characterized.
- 3-(4-(Anthracen-10-yl)phenyl)-coumarin exhibits blue emission.
- 3-(4-(Pyrene-1-yl)phenyl)coumarin exhibits bright blue-green emission.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 15 January 2015

Received in revised form 24 April 2015

Accepted 4 May 2015

Available online 29 May 2015

## Keywords:

Synthesis

Coumarin derivative

Anthracene

Pyrene

Crystal structure

Photoluminescence

## ABSTRACT

Two new anthracen- and pyrene-based coumarin derivatives, 3-(4-(anthracen-10-yl)phenyl)coumarin (**4**) and 3-(4-(pyrene-1-yl)phenyl)coumarin (**5**), were synthesized and characterized by FT-IR, <sup>1</sup>H NMR, element analysis and single crystal X-ray crystallography. The UV-vis absorption and photoluminescence spectra of these coumarin derivatives were investigated. The results show that compound **4** and **5** exhibit blue and blue-green emissions, respectively, under ultraviolet light excitation. Compared with the compound **4**, the emission peak of compound **5** was bathochromically shifted by about 80 nm due to the more planar structure and larger  $\pi$ -conjugation.

© 2015 Elsevier B.V. All rights reserved.

## Introduction

Coumarins are considered among the most important classes of organic heterocyclic molecules with versatile applications in various fields of science and technology [1]. Many natural and synthetic coumarin derivatives exhibit several advantages such as interesting photophysical properties, good photostability, large Stokes shifts, high fluorescence quantum yields, and they are

usually used in detection laser dyes, effective fluorophores, fluorescent molecular probes, photosensitizers, electroluminescent materials, light-harvesting molecular assemblies, etc [2–6]. In the recent years, many coumarin-based fluorescent emitters have been designed and synthesized for several applications [7–10].

Anthracene and pyrene are well-known fluorescent chromophores, which contain three and four fused benzene rings, respectively. Anthracene and pyrene derivatives have rich electronic and photophysical properties such as high fluorescent quantum yields, good thermal stabilities and long lifetimes in non-polar media [11–15]. Due to their planar and rigid architecture,

\* Corresponding author. Tel.: +86 931 4956935; fax: +86 931 4938756.

E-mail address: [yutianzhi@hotmail.com](mailto:yutianzhi@hotmail.com) (T. Yu).

incorporation of anthracene or pyrene unit into molecular materials would offer an effective way to control the  $\pi$ - $\pi$  stacking interactions and the associated red shift in emission, and enhance charge migration in the solid state [16].

In this paper, two new anthracen- and pyrene-based coumarin derivatives, 3-(4-(anthracen-10-yl)phenyl)coumarin (**4**) and 3-(4-(pyrene-1-yl)phenyl)coumarin (**5**) were successfully synthesized and characterized. Our purpose was to extend the  $\pi$ -conjugation framework of the fluorophore, and investigate how anthracene and pyrene functional groups affect the photoluminescence properties of coumarin.

## Experimental

### Materials and methods

Salicylaldehyde, 4-bromophenylacetonitrile, BuLi, pyrene and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were analytical grade reagents from Alfa Aesar China (Tianjin) Co. Ltd. Other reagents and solvents were commercially available and used without further purification.

IR spectra ( $400$ – $4000$   $\text{cm}^{-1}$ ) were measured on Shimadzu IR Prestige-21 FT-IR spectrophotometer. C, H, and N analyses were obtained using Elemental Vario-EL automatic elemental analysis instrument.  $^1\text{H}$  NMR spectra were obtained on Unity Varian-500 MHz. The UV-vis absorption and photoluminescence spectra were recorded on UV-2550 spectrometer and Perkin-Elmer LS-55 spectrometer, respectively. Melting points were measured by using X-4 microscopic melting point apparatus in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

### Preparation of 3-(4-(anthracen-10-yl)phenyl)-coumarin (**4**) and 3-(4-(pyrene-1-yl)phenyl)coumarin (**5**)

The synthetic routes for compound **4** and **5** are shown in Scheme 1.

3-(4-Bromophenyl)coumarin (**1**) was prepared by modifying the procedure as previously described [17].

2-(Anthracen-10-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) and 2-(pyren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**) were synthesized according to the methods reported by us [18] and Yu [19].

Compound **1** (3 mmol) and **2** (3 mmol) as reactants, and  $(\text{PPh}_3)_4\text{Pd}(0)$  (0.06 mmol) as catalyst were dissolved in the mixture of 20 mL THF and 5 mL 2 M  $\text{Na}_2\text{CO}_3$  solution. Under argon, the resulting mixture was refluxed with stirring for 25 h, and then the mixture was extracted with EtOAc. The organic extracts were combined, dried over anhydrous  $\text{MgSO}_4$ , and concentrated under

reduced pressure. The residue was purified by column chromatography using EtOAc/petroleum ether (1/10, v/v) as the eluent to give the compound **4** as a yellow solid (yield 51%). m.p. 165–167 °C. IR (KBr pellet,  $\text{cm}^{-1}$ ): 1732(C=O), 1114(C–O–C), 750 (C–H–arom.).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.27–8.53 (m, 18H, Ar–H). Anal. calc. for  $\text{C}_{29}\text{H}_{18}\text{O}_2$  (%): C, 87.44; H, 4.52. Found: C, 87.56; H, 4.44.

The preparation of the compound **5** was similar to that of compound **4**. The reaction of compound **1** and **3** occurred to produce yellow solid compound **5** in 72% yield. m.p. 241–243 °C. IR (KBr pellet,  $\text{cm}^{-1}$ ): 1717(C=O), 1113(C–O–C), 841, 758 (C–H–arom.).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.44–8.25 (m, 18H, Ar–H). Anal. calc. for  $\text{C}_{31}\text{H}_{18}\text{O}_2$  (%): C, 88.15; H, 4.26. Found: C, 88.23; H, 4.19.

### Crystallography

The diffraction data of compound **4** and **5** were collected with a Bruker Smart Apex CCD area detector using a graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å) at 190(2) and 191(2) K, respectively. The structures were solved by using the program SHELXL and Fourier difference techniques, and refined by full-matrix least-squares method on  $F^2$ . All hydrogen atoms were added theoretically.

## Results and discussion

### IR spectra

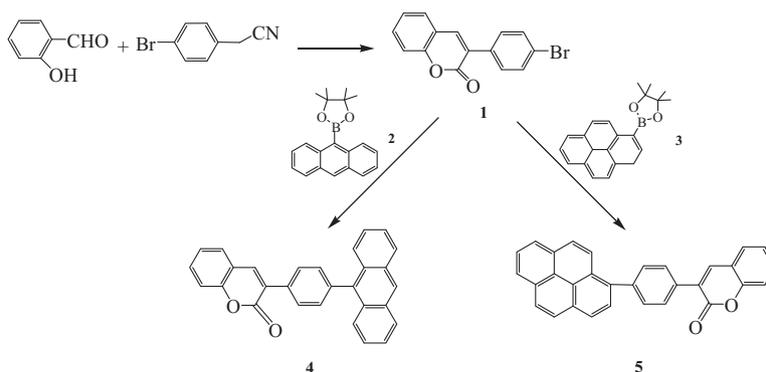
The important feature of the IR spectrum of compound **4** is the presence of the bands at 1732 and 1114  $\text{cm}^{-1}$ , which due to the C=O and C–O–C vibrations respectively. The 750  $\text{cm}^{-1}$  band are likely due to C–H out-of-plane bending vibrations of the adjacent H atoms on the rings [20].

For compound **5**, the very strong bands of 1717 and 1113  $\text{cm}^{-1}$  assigned to C=O and C–O–C stretching vibrations respectively. The 841 and 758  $\text{cm}^{-1}$  bands are assigned to C–H out-of-plane bending vibrations on the rings. For condensed ring systems containing 3 or more rings, bands near 750  $\text{cm}^{-1}$  arise from C–H bonds that are approximately parallel to the longer axis of the molecule [21].

### X-ray crystallographic analyses

The crystal data and experimental details of compound **4** and **5** are shown in Table 1. The selected bond lengths and bond angles of compound **4** and **5** are listed in Table 2.

The model of compound **4** is shown in Fig. 1. The crystal of compound **4** belongs to the monoclinic space group  $\text{P}2(1)/n$ ,  $a = 8.9400(6)$  Å,  $b = 17.1642(11)$  Å,  $c = 13.3874(8)$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 106.1300(10)^\circ$ ,  $U = 1973.4(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.341$  g/cm<sup>3</sup>,



Scheme 1. Structure and synthetic routes for anthracen- and pyrene-based coumarin derivatives.

Download English Version:

<https://daneshyari.com/en/article/1231621>

Download Persian Version:

<https://daneshyari.com/article/1231621>

[Daneshyari.com](https://daneshyari.com)