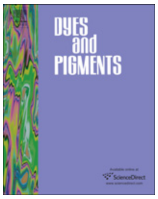
Dyes and Pigments 87 (2010) 109–118

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



The synthesis, structure and photoluminescence of coumarin-based chromophores

Yi-Feng Sun [a],*, Shu-Hong Xu [b], Ren-Tao Wu [a], Zhu-Yuan Wang [b], Ze-Bao Zheng [a], Ji-Kun Li [a], Yi-Ping Cui [b]

[a] *Department of Chemistry, Taishan University, Taian 271021, China*
[b] *Advanced Photonics Center, School of Electronic Science and Engineering, Southeast University, Nanjing 210096, China*

ARTICLE INFO

Article history:
Received 2 December 2009
Received in revised form
27 February 2010
Accepted 1 March 2010
Available online 15 March 2010

Keywords:
Coumarin
Azo
Pyrazoline
Crystal structure
Photoluminescence
Quantum chemical calculations

ABSTRACT

Coumarin-based chromophores with azo and pyrazoline moieties were synthesized and their structures and properties elucidated using spectroscopy. The coumarins were luminescent, having solid state emission at wavelengths ranging from 400 to 750 nm, depending on structure. The relationships between the solid state photoluminescence and both chemical and crystal structures are discussed.

1. Introduction

Coumarin derivatives have long been recognized to possess multiple biological activities [1–5], especially antioxidant and anti-inflammatory activities and the coumarin unit can be found in many natural and synthetic drug molecules. Moreover, as an important class of organic heterocyclic dyes, coumarin derivatives exhibit unique photochemical and photophysical properties, which render them useful in a variety of applications such as optical brighteners, laser dyes, non-linear optical chromophores, solar energy collectors, fluorescent labels and probes in biology and medicine, as well as two-photon absorption (TPA) materials [6–12]. More importantly, coumarin dyes have also been used as blue, green and red dopants in organic light-emitting diodes (OLEDs). For example, 10-(2-benzothiazolyl)-1,1,7,7 -tetrainethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]benzo pyrano[6,7,8-*ij*]quinolizin-11-one (**C-545T**) (Fig. 1), which belongs to the highly fluorescent class of coumarin laser dyes, is one of the best green fluorescent dopants, and has widely been used as a doped green emitter in OLEDs [13–16].

Similarly, pyrazoline derivatives generate strong interest stemming from their broad spectrum of pharmacological activities, including antimicrobial, anticonvulsant, anti-inflammatory, analgesic, anticancer, antitubercular and herbicidal [17,18]. Furthermore, pyrazolines show strong fluorescence and have a high hole-transport efficiency and excellent blue emitting properties. Therefore, pyrazoline derivatives have widely been used as whitening or brightening reagents for synthetic fibers, as fluorescence probes in chemosensors, as fluorescent chemosensors for recognition of transition metal ions, as hole-transport materials in electrophotography and electroluminescence fields [19–22]. For instance, 1,5-diphenyl-3-(1-naphthyl)-2-pyrazoline (**DPNPZ**) (Fig. 1) has a strong blue fluorescence emission, and can be used as an emissive dopant in an electroluminescent (EL) device [23].

On the other hand, azo compounds, while being a well-documented class of commercial dyes, are attracting ever increasing attention in the areas of optical data storage, non-linear optical materials, photoswitches, photoprobes, ink-jet printing, biochemical assays, and photocontrol of biological processes [24–26]. The main reason is that these azo chromophores can undergo light-driven, reversible *trans*–*cis* isomerisation of the azo bond with concomitant change of the structure, dipole moment and optical properties [27].

In view of the considerable importance of these compounds work, the focus of the current research workers turned towards the synthesis of coumarin derivatives containing an azo or pyrazoline

---

* Corresponding author. Tel.: +86 538 6715546; fax: +86 538 6715536.
E-mail address: sunyf50@yahoo.com.cn (Y.-F. Sun).

0143-7208/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2010.03.003

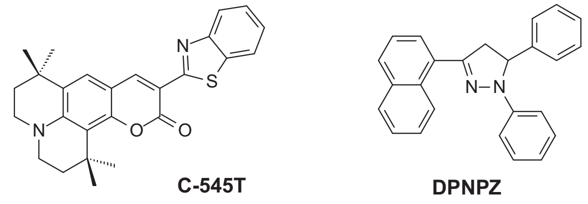


Fig. 1. The structures of C-545T and DPNPZ.

moiety. It was envisaged that compounds containing these moieties in the same molecule may show enhanced biological and optical properties. In previous papers we have reported the synthesis, crystal structures and preliminary spectroscopic properties of various coumarin derivatives [28–30]. However, as the solid state photoluminescence properties of the dyes have not been investigated, in keeping with our interest in the synthesis, crystallography and optical evaluation of coumarin-based chromophores, this paper concerns the synthesis and spectroscopic characterization of novel, coumarin-based chromophores based either on an azo or pyrazoline core. In addition, the photoluminescence properties of the compounds are discussed in the solid state and the structures of **2c** and **4a** were studied both experimentally and theoretically. The synthetic pathway and the structures of target molecules are shown in Figs. 2–4.

2. Experimental

2.1. General

^{1}H NMR spectra were recorded with a Bruker AVANCE-400 or Varian INOVA-600 NMR spectrometer and chemical shifts expressed as δ (ppm) values with TMS as internal standard. The IR spectra were measured on a Nicolet/Nexus-870 FT-IR spectrometer with KBr pellets in the range 4000–400cm^{-1}. Element analysis was taken with a Perkin–Elmer 240 analyzer. Mass spectra (MS) were measured on an LCQ Advantage MAX or VG ZAB-HS mass spectrometer. The melting points were determined with a WRS-1A melting point apparatus and are uncorrected. The Raman spectra were recorded using a Horiba Jobin-Yvon LabRam HR800 Raman microspectrometer, with an excitation laser at 514 nm, and a 600 groove mm^{-1} diffraction grating. Signals were recorded in the range from 200–2500 cm^{-1}. The UV–vis absorption spectra were recorded using a Helios Alpha UV–Vis scanning spectrophotometer. The photoluminescence spectra were measured using a Horiba Jobin-Yvon LabRam HR800 Raman microspectrometer under a 325 nm He–Cd laser excitation. Single crystal was characterized by Bruker Smart 1000 CCD X-ray single crystal diffractometer. All the chemicals are commercially available and they were used without further purification.

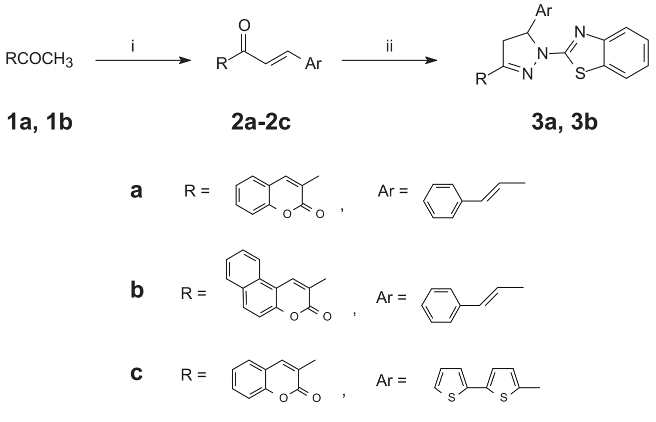


Fig. 2. Synthesis of coumarin–pyrazoline hybrids. Reagents and reaction conditions: (i) ArCHO, Piperidine, EtOH, reflux; (ii) 2-Hydrazino-1,3-benzothiazole, Ethylene glycol, MW.

2.2. Synthesis of the coumarin–chalcone hybrids (**2**)

Three coumarin–chalcone hybrids were synthesized from 3-acetyl coumarins and cinnamaldehyde or 2,2′-bithiophene-5-carbaldehyde in the presence of piperidine in ethanol under microwave irradiation following the method reported previously [28]. 3-((5-Phenyl)pent-2,4-dienoyl)-2*H*-1-naphtho[2,1-*b*] pyran-2-one (**2b**) and 3-(3-(2-(thiophen-2-yl)thiophen-5-yl) prop-2-enoyl)-2*H*-1-benzopyran-2-one (**2c**) have been reported in previous papers [28,31].

2.2.1. 3-((5-Phenyl)pent-2,4-dienoyl)-2H-1-benzopyran-2-one (**2a**)

Recrystallization from ethanol–acetone gave the title compound **2a** as yellow crystals, yield 62%; mp 182–184 °C; ^{1}H NMR (400 MHz, CDCl$_3$/TMS) δ: 7.02–7.10 (m, 2H), 7.31–7.40 (m, 5H), 7.47–7.52 (m, 3H), 7.63–7.70 (m, 3H), 8.56 (s, 1H); IR (KBr) ν: 1732, 1651, 1612, 1574, 1451, 1348, 1232, 1183, 1143, 997, 751, 689, 577 cm^{-1}. Anal. calcd. for $C_{20}H_{14}O_3$: C 79.46, H 4.67; found C 79.25, H 4.74.

2.3. Synthesis of the coumarin–pyrazoline derivatives (**3**)

Two coumarin–pyrazoline derivatives were synthesized from coumarin–chalcone hybrids (**2**) and 2-hydrazino-1,3-benzothiazole in ethylene glycol under microwave irradiation according to the method reported previously [29].

2.3.1. 1-(Benzothiazol-2-yl)-3-(-2-oxo-2H-1-benzopyran-3-yl)-5-styryl-2-pyrazoline (**3a**)

Recrystallization from chloroform gave the title compound **3a** as yellow solid, yield 63%; mp > 240 °C; ^{1}H NMR (400 MHz, CDCl$_3$/TMS) δ: 3.62 (dd, J = 5.6, 18.6 Hz, 1H), 3.98 (dd, J = 11.7, 18.6 Hz, 1H), 5.46–5.53 (m, 1H), 6.41 (dd, J = 6.6, 15.9 Hz, 1H), 6.76 (d, J = 15.9 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.24–7.42 (m, 8H), 7.57–7.71 (m, 4H), 8.51 (s, 1H). IR (KBr) ν: 1728, 1601, 1567, 1551, 1533, 1455, 1443, 1360, 1277, 1243, 1139, 1106, 959, 881, 747, 720, 697, 638 cm^{-1}. MS m/z: 450.6 (M + 1). Anal. calcd. for $C_{27}H_{19}N_3O_2S$: C 72.14, H 4.26, N 9.35; found: C 72.38, H 4.61, N 9.13.

2.3.2. 1-(Benzothiazol-2-yl)-3-(-2-oxo-2H-1-naphtho [2,1-b]pyran -3-yl)-5-styryl-2-pyrazoline (**3b**)

Recrystallization from chloroform gave the title compound **3b** as red solid, yield 52%; mp 216 °C (decompose); ^{1}H NMR (600 MHz, CDCl$_3$/TMS) δ: 3.65 (dd, J = 5.4, 18.6 Hz, 1H), 4.02 (dd, J = 11.7, 18.6 Hz, 1H), 5.50–5.53 (m, 1H), 6.41 (dd, J = 6.6, 15.6 Hz, 1H), 6.76 (d, J = 15.6 Hz, 1H), 7.07–8.42 (m,15H), 9.25 (s, 1H). IR (KBr) ν: 1726, 1598, 1568, 1527, 1440, 1281, 1214, 1143, 994, 810, 743, 687 cm^{-1}. MS m/z: 500.2 (M + 1). Anal. calcd. for $C_{31}H_{21}N_3O_2S$: C 74.53, H 4.24, N 8.41; found: C 74.33, H 4.37, N 8.26.

2.4. Synthesis of the coumarin–azo derivatives (**4**)

Azocoumarins were prepared according to the method described earlier [30] which was modified. Aromatic amines (10 mmol) were dissolved in 6 M HCl (8 mL) and diazotised using sodium nitrite (12 mmol in 5 mL of water) solution at 0 °C with stirring. On completion of diazotization (30–40 min), the resulting diazonium salt solution was added dropwise to a cold, alkaline solution of salicylaldehyde (or 3-methoxysalicylaldehyde) (10 mmol) in 2% aq