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Synthesis, characterisation and photophysical studies of oxadiazolyl coumarin: A new class of blue light emitting fluorescent dyes

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ABSTRACT

A library of novel 1, 2, 4-oxadiazole linked coumarin dyes have been synthesised *via* condensation of corresponding acid **6** and *N*′-hydroxybenzimidamide **8**. This new class of organic compounds were examined for their fluorescent properties and found to emit blue light in the visible region of the spectrum with very high Stoke's shift values. Most of these compounds demonstrated high quantum yields and fluorescence life time in *nano*-second range which makes them quite lucrative to be used as new fluorescent probes. The highest quantum yield of 0.68 was shown by compound **9j** which also shows high Stoke's shift value. The electronic structure of these coumarin-based donor–π–acceptor (D–π–A)-type organic dyes have been examined by Density Functional Theory (DFT). TGA analysis of few of the compounds show that they are stable up to temperature range of 0–245 °C. The synthesised compounds were characterised by NMR and mass spectrometry and the structure of two of these compounds have been confirmed by X-ray crystallography.

1. Introduction

Coumarins and their analogues are not only known for their excellent biological activities [1] but also well known for their outstanding optical properties. Coumarin shows good spectral response, have high photostability [2] and are also recognised as highly efficient fluorophores with high quantum yield [3], decent extinction coefficient [4] and large Stokes shift [5]. Moreover, because of such exceptional optical properties, coumarin derivatives are known to find a diverse range of applications as fluorescent dyes [6], fluorescent probes [7], emission layers in organic light-emitting diodes (OLED) [8], optical brighteners, nonlinear optical chromophores, fluorescent whiteners, fluorescent indicators, optical recording and solar energy collectors [9].

The absorption and emission behaviour of coumarin vary significantly depending upon the substituent present on the coumarin ring [10]. The resonance contribution to the electron-accepting 2-pyranone moiety is responsible for this substituent effect [11]. Coumarin itself has a very low quantum yield but with an appropriate substitution on the coumarin moiety, the derivatives of coumarin can show strong fluorescence in the blue-green region (400–550 nm) with a precisely good quantum yield. This is attributed to the enhancement of intramolecular charge transfer (ICT) upon substitution at desired position. For instance, 7-amino-4-methylcoumarin (AMC) is commonly used as an important laser dye emitting in the blue region [12]. It has been reported in several literature that presence of electron donating group at 7-position of coumarin and various substitutions at 3-position modify the fluorescent property of coumarins to a larger extent [13]. Literature guided survey revealed that, the fluorescence spectral study of 4-substituted coumarins have not been much explored yet. Also, it has been reported in few instances that the oxadiazole moiety itself have been used as potential fluorescent dopants [14] and fluorescent chemosensors [15]. Zhang *et. al.* reported the synthesis of bismaleimides bearing 2,5-diphenyl-1,3,4-oxadiazole chromophores which exhibited good fluorescent properties including excellent quantum yield [16].

In this context, as a part of the foregoing research in our group, we have planned the synthesis of a hybrid molecule *viz.* 1, 2, 4-

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oxadiazolyl coumarin with the oxadiazole ring substituted at the 4-position of coumarin. Hence, a synergistic effect in the fluorescent property of this hybrid molecule is expected by the linkage of these two fluorescent heterocyclic moieties. Moreover, 2-(5-alkyl-1,3,4-oxadiazol-2-yl)-3*H*-benzo[*f*]chromen-3-ones *i.e.* 1,3,4 oxadiazole substituted at 3-position of coumarin have been reported to exhibit excellent fluorescence properties [17].

2. Experimental

2.1. Materials and methods

Analytical TLCs were performed on Merck silica gel 60_{F254} plates. All liquid column chromatographic separations were performed on column chromatography. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer at Department of Chemistry, University of Delhi. The ^{1}H and ^{13}C NMR spectra (in $CDCl_3$ and DMSO-d_6) were recorded on a JEOL ECX-400P NMR at 400 MHz and 100 MHz, respectively at USIC, University of Delhi and Department of Organic Chemistry, Ghent University, Belgium. TMS was used as internal standard. The high-resolution mass spectral data was obtained using Agilent technologies 1100 series LC/MSD system at Department of Organic Chemistry, Ghent University, Belgium. The absorption and florescence emission spectra were recorded by Hitachi U-2010 UV–Vis spectrophotometer and Varian Cary Eclipse Fluorescence Spectrophotometer respectively at Department of Organic Chemistry, Ghent University, Belgium. The fluorescence decay measurements were recorded by HORIBA Jobin Yvon Fluorohub at USIC, University of Delhi, Inda. The absorption, the fluorescence emission and fluorescence decay measurements of the synthesised compounds were recorded at 10^{-5} M concentration in chloroform and ethanol. Thermogravimetric analysis (TGA) was performed on TA instruments Q50 device at Department of Organic Chemistry, Ghent University, Belgium. Melting points were recorded on a Buchi M - 560 melting point apparatus and are uncorrected. The crystal data was collected on Oxford Xcalibur S diffractometer (4-circle kappa goniometer, Sapphire-3 CCD detector, omega scans, graphite monochromator, and a single wavelength Enhance X-ray source with MoKα radiation). The structures were solved by direct methods using SIR 9233 which revealed the atomic positions, and refined using the SHELX-97 program package34 and SHELXL9735 (within the WinGX program package). All the chemicals and reagents like substituted benzonitriles, ethylchloroformate, β-keto-esters, resorcinol *etc.* were purchased from commercial sources and used as received unless otherwise indicated.

2.2. Synthesis

2.2.1. Synthesis of coumarin (*4*)

Substituted hydroxy coumarin **3** were synthesized by known Pechmann condensation [18] and the methoxy/ethoxy coumarin **4**(**a**,**b**) were obtained from hydroxy coumarin *via* methylation/ethylation in presence of potassium carbonate [19].

2.2.2. Synthesis of 7-alkoxy-2-oxo-2H-chromene-4-carbaldehyde 5(a-b)

Compound **4** (98 mmol, 1eq.) was dissolved in 1,4-dioxane and selenium dioxide (117 mmol, 1.2 eq.) was added to the solution [20]. The reaction mixture was refluxed for 48 h. After the completion of reaction, the reaction mixture was filtered to remove the insoluble selenium. The crude product was purified by column chromatography (50% EtOAc/$CHCl_3$) over silica gel to yield the desired products. Compound **5a** was obtained as yellow solid in 55% yield, m.p. 193–195 °C (lit. m.p. 194–196 °C) [21] and **5b** was obtained as a bright yellow solid in 58% yield, m.p.164–168 °C. **IR** (KBr) (cm^{-1}): *ν* 2989, 1708, **^{1}H NMR** (DMSO-d_6, 400 MHz): *d* (ppm) 1.36 (3 H, t, *J* = 6.87 Hz), 4.14 (2 H, q, *J* = 7.63 Hz), 6.98 (1 H, s), 6.99–7.07 (2 H, m), 8.38 (1 H, d, *J* = 9.16 Hz), 10.09 (1 H, s); **^{13}C NMR** (DMSO-d_6, 100 MHz): *d* (ppm) 14.59, 64.30, 101.68, 108.30, 113.38, 121.48, 127.14, 143.75, 156.13, 160.67, 162.08, 193.99; **HRMS**: Found: $[M+H]^+$ 219.0655; 'molecular formula $C_{12}H_{10}O_4$' requires $[M+H]^+$ 219.0579.

2.2.3. Synthesis of 7-alkoxy-2-oxo-2H-chromene-4-carboxylic acid 6(a-b)

The aldehyde **5** (73.5 mmol, 1 eq.) was dissolved in DMF (60 mL). Oxone (110 mmol, 1.5 eq.) was added in one portion and stirred at room temperature for 3 h. After the completion of the reaction, the reaction mixture was poured into ice-cold water. The solid obtained was filtered and dried. The desired products **6a** and **6b** were obtained in 74% and 79% yield respectively and were used in the next reaction without further purification [22]. Compound **6a** was obtained as bright yellow solid in 74% yield, m.p. 217–221 °C (lit. m.p. 219 °C) [23]. Compound **6b** was obtained as bright yellow solid in 79% yield, m.p. 163–164 °C. **IR** (KBr) (cm^{-1}): *ν* 3424, 2926, 1734; **^{1}H NMR** (DMSO-d_6, 400 MHz): *d* (ppm) 1.35 (3 H, t, *J* = 6.87 Hz), 4.12 (2 H, q, *J* = 6.87 Hz), 6.61 (1 H, s), 6.92–6.99 (2 H, m), 8.03–8.07 (1 H, m); **^{13}C NMR** (DMSO-d_6, 100 MHz): *d* (ppm) 14.60, 64.31, 101.61, 109.25, 113.20, 114.30, 128.11, 144.28, 155.97, 160.22, 162.08, 165.79; **HRMS**: Found: $[M+H]^+$ 235.0591; 'molecular formula $C_{12}H_{10}O_5$' requires $[M+H]^+$ 235.0528.

2.2.4. Synthesis of N′-hydroxybenzimidamide 8(a-e)

N′-hydroxybenzimidamide **8**(**a-e**) were obtained in very good yields using literature reported procedure [24].

2.2.5. General procedure for synthesis of coumarin-linked oxadiazole derivatives 9(a-j)

The carboxylic acid **6**(**a-b**) (2.3 mmol, 1 eq.) was stirred in dichloromethane for 10 min followed by addition of potassium carbonate (3.4 mmol, 1.5 eq.). The resulting mixture was stirred for 30 min at room temperature. Ethyl chloroformate (3.4 mmol, 1.5 eq.) was added to the reaction mixture and it was stirred again for 30 min. Lastly, *N*′-hydroxybenzimidamide {**8**(**a-e**)} (2.3 mmol, 1 eq.) was added and reaction mixture was refluxed for 6–8 h. After completion of the reaction, the mixture was extracted with dichloromethane (3 × 30 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (5% Hexane/EtOAc) over silica gel to yield the desired products **9(a–j)** in moderate yields.

*2.2.5.1. 7-Methoxy-4-(3-phenyl-1,2,4-oxadiazol-5-yl)-2H-chromen-2-one (**9a**).* It was obtained as yellow solid having m. p. 170–171 °C in 43% yield. **IR** (KBr) (cm^{-1}): *ν* 2933, 1708, 1618, 1375; **^{1}H NMR** ($CDCl_3$, 400 MHz): *d* (ppm) 3.93 (3 H, s), 6.92 (1 H, d, *J* = 2.44 Hz), 7.01 (1 H, dd, *J* = 9.16, 2.44 Hz), 7.15 (1 H, s), 7.49–7.62 (3 H, m), 8.17–8.23 (2 H, m), 8.74 (1 H, d, *J* = 8.54 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): *d* (ppm) 55.89 101.27, 108.48, 113.28, 115.59, 125.92, 127.61, 128.28, 129.05, 131.82, 135.61, 156.39, 159.76, 163.52, 169.30, 171.73; **HRMS**: Found: $[M+H]^+$ 321.0868; 'molecular formula $C_{18}H_{12}N_2O_4$' requires $[M+H]^+$ 321.0797.

*2.2.5.2. 4-(3-(3-bromophenyl)-1,2,4-oxadiazol-5-yl)-7-methoxy-2H-chromen-2-one (**9b**).* It was obtained as yellow solid having m. p. 112–113 °C in 41% yield. **IR** (KBr) ν_{max} (cm^{-1}) = 2936, 1734, 1611, 1400, 488; **^{1}H NMR** ($CDCl_3$, 400 MHz): *d* (ppm) 3.94 (3 H, s) 6.93 (1 H, d, *J* = 2.20 Hz) 7.02 (1 H, dd, *J* = 8.79, 2.20 Hz) 7.15 (1 H, s) 7.44 (1 H, t, *J* = 8.05 Hz) 7.72 (1 H, d, *J* = 8.05 Hz) 8.15 (1 H, d, *J* = 8.05 Hz)