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RESEARCH ARTICLE

Synthesis and Photochromic Properties of Spirobiindane Based Bis-coumarins

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Abstract A facile synthesis of spirobiindane bis-coumarin hybrid molecules with C4-alkyl, C3-acyl, C3-ethoxycarbonyl or C3-nitrile groups has been achieved. Absorption, emission and solvatochromic characteristics of the bis-coumarins were evaluated in comparison with 3-acetylcoumarin. Studies show that the bis-coumarins with C3-ester and C3-cyano group show more than tenfold increase in fluorescence emission than others in hexane and ethyl acetate. Unlike in the cases of the bis-coumarins with an electron withdrawing acyl or ester group at C3 position where methanol quenches fluorescence emission there is no significant solvent effect in the case of an alkyl group at C4 position.

Keywords Spirobiindane bisphenol · Bis-coumarin · Fluorescence

Introduction

Natural and synthetic coumarins find many applications as drug candidates, optical brighteners, energy storage materials, triplet sensitizers etc. [1–4]. Among coumarins, bis-coumarins, where two coumarin units are present in a single molecule are a unique class of compounds with wide ranging biological activities [5]. Many bis-coumarins, e.g. desertonine **1** (Fig. 1) where two coumarin units are covalently linked directly or by a tether occur in plants, microorganisms and animals. Such natural and synthetic bis-coumarins are flexible and exhibit innumerable rotomeric populations. Therefore they may not efficiently exhibit synergic properties due to both the coumarin units. Bis-coumarins located on a rigid molecular frame work, on the other hand, are better suited for exhibiting inter and intramolecular synergic properties particularly those related to photochromic absorption and emission. In continuation of our interest in the synthesis of coumarins [6–10], we have conceived of novel bis-coumarins like **2** (Fig. 1) present on a rigid molecular motif. While there have been directed synthetic efforts towards linked bis-coumarins, to our knowledge there are no reports on the synthesis of bis-coumarins incorporated on a rigid molecular frame work like the one present on spirobiindane bisphenol **2**. The spirobiindane bisphenol derivatives similar to **2** found use in the synthesis of foldamers [11–13], polymers [14], [15] and photo-electronic devices [16]. Such polymeric carbon networks were projected to have technological applications. Herein we describe synthesis, characterization and fluorochromic properties of bis-coumarins incorporated on the spirobiindane motif.

Experimental

The progression of all the reactions was monitored by TLC using hexanes (60–80 °C boiling mixture)/ethyl acetate mixture as eluent. Column chromatography was carried on silica gel (100–200 mesh SRL chemicals) using increasing percentage of ethyl acetate in hexanes. ^{1}H NMR spectra (400 MHz), ^{13}C NMR (100 MHz) and DEPT spectra were recorded for ($CDCl_3$ + CCl_4 1:1) solutions on a Bruker-400 spectrometer with tetramethylsilane (TMS) as internal standard and *J*-values are in Hz. IR spectra were recorded

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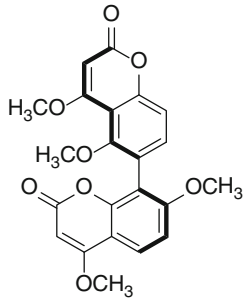

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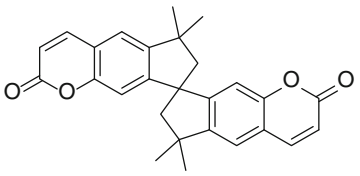
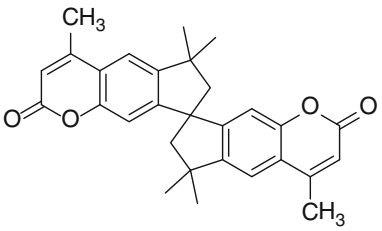


2

Fig. 1 Structures of desertonine **1** and spirobiindane bis-coumarin **2**

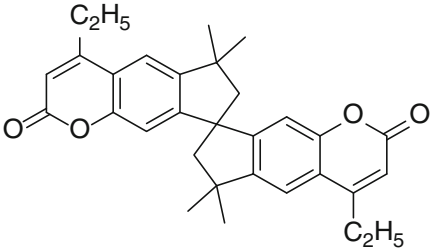
as KBr pellets on a Nicolet-6700 spectrometer. UV spectra were recorded using Hitachi ratio-beam spectrometer. Melting points were recorded using open-ended capillary tubes on VEEGO VMP-DS instrument. High resolution mass spectra were recorded on a Waters Micromass Q-TOF micro mass spectrometer using electron spray ionization mode. Organic solvents were distilled and dried before use.

Synthesis of 4-alkyl substituted spirocoumarin



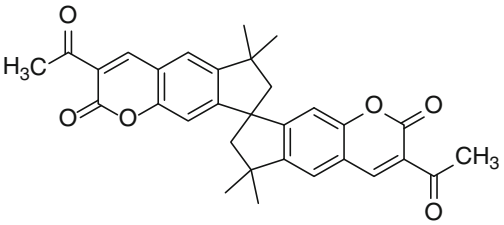
4,4′,6,6,6′,6′-Hexamethyl-6,6′,7,7′-tetrahydro-2H,2′H-8,8′-spirobi[cyclopenta[g]chromene]-2,2′-dione ***5a***

A stirred solution of spirobiindane bisphenol **3** (220 mg, 0.65 mmol) in 75 % H_2SO_4 (2 ml) ethyl acetoacetate **4a** (422 mg, 3.24 mmol) was added at 100 °C under the blanket of nitrogen atmosphere and refluxed for 2 h. After completion of reaction, mixture was diluted with ice cold water (10 ml) and extracted with DCM (3 × 10 ml). The combined organic layer was washed with saturated sodium bicarbonate solution (10 ml) for removal of excess H_2SO_4 and then washed with water (2 × 10 ml) and brine solution (10 ml) dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silicagel (100–200 mesh) using hexanes and EtOAC (8.2:1.8) as eluent to obtain bis-coumarin as reddish yellow colour solid, mp 101 °C, yield 68 %; IR (KBr) 2965, 2865, 1732, 1619, 1569, 1456, 1425, 1387, 1325, 1118, 886 cm^{-1}; ^1H NMR (400 MHz $CDCl_3 + CCl_4$) δ 7.34 (s, 1H), 6.70 (s, 1H), 6.23 (s, 1H), 2.49 (s, 3H), 2.32 (d, 1H, $J = 13.2$ Hz), 2.29 (d, 1H, $J = 13.2$ Hz), 1.49 (s, 3H), 1.41 (s, 3H) ppm; ^{13}CNMR (100 MHz, $CDCl_3 + CCl_4$) δ 160.1 (C), 154.5 (C), 153.7 (C), 151.5 (C), 148.2 (C), 119.7 (C), 117.4 (CH), 114.5 (CH), 112.5 (CH), 59.4 (CH_2), 57.6 (C), 43.5 (C), 32.0 (CH_3), 30.4 (CH_3), 18.8 (CH_3) ppm; LCMS 440.90 (100 %), 415, 218, 134.



4,4′-Diethyl-6,6,6′,6′-tetramethyl-6,6′,7,7′-tetrahydro-2H,2′H-8,8′spirobi[cyclopenta[g]chromene]-2,2′-dione ***5b***

Yellow color solid, mp 101 °C, yield 74 %; IR (KBr) 2968, 2861, 1730, 1621, 1565, 1452, 1402, 1393, 1321, 1120, 889 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3 + CCl_4$) δ 7.34 (s, 1H), 6.70 (s, 1H), 6.23 (s, 1H), 4.02 (q, $J = 4.8$ Hz, 2H), 2.49 (t, 3H, $J = 4.8$ Hz), 2.32 (d, 1H, $J = 13.2$ Hz), 2.29 (d, 1H, $J = 13.2$ Hz), 1.49 (s, 3H), 1.41 (s, 3H) ppm; ^{13}CNMR (100 MHz, $CDCl_3 + CCl_4$) δ 160.1 (C), 154.5 (C), 153.7 (C), 151.5 (C), 148.2 (C), 119.7 (C), 117.4 (CH), 114.5 (CH), 112.5 (CH), 59.4 (CH_2), 57.6 (C), 43.5 (C), 32.0 (CH_3), 30.4 (CH_3), 18.8 (CH_3) ppm; LCMS 454.90 (100 %), 425, 223.

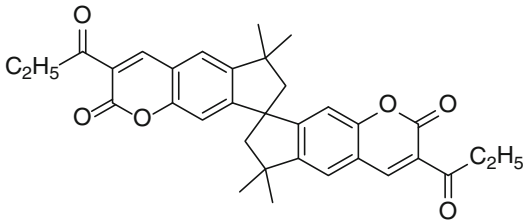


Synthesis of spirobiindane based bis-coumarins **7a–d**

3,3′-Diacetyl-6,6,6′,6′-tetramethyl-6,6′,7,7′-tetrahydro-2H,2′H-8,8′-spirobi[cyclopenta[g] chromene]-2,2′-dione ***7a***

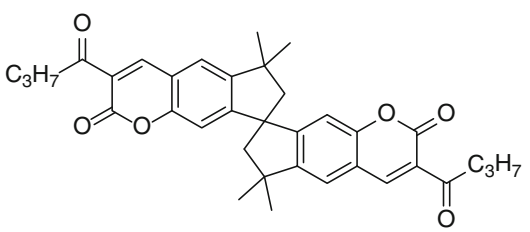
To a stirred solution of diformyl Spirobiindane bisphenol **6** (10 mg, 0.274 mmol) ethylacetoacetate **4a** (96 mg, 0.60 mmol) in EtOH (2 ml), piperidine (2.6 mg, 0.032 mmol) in dry ethanol (2 ml) was added over a period of 5 min drop wise at rt under the blanket of dry nitrogen. This reaction was heated at reflux condition in a pre heated oil bath (80 °C) for 5 h for completion of reaction (TLC, 20 % EtOAc in hexanes; $R_f = 0.3$). Reaction mixture diluted with ethanol (1 ml). Evaporation of solvent under reduced pressure resulted in crude product as light yellow colour solid. Reaction mixture was extracted DCM (25 ml) and the organic solution was washed subsequently with

water (3 × 25 ml) and brine (2 × 10 ml). This organic layer was dried over anhydrous Na_2SO_4. Crude product was subjected to column chromatography on SiO_2 (25 g: 30 cm × 2 cm) using increasing amounts of EtOAc in hexanes as eluant. Colourless solid, Yield 75 %, mp above 250 °C; IR (KBr) υ_{max} 3046, 2956, 2866, 1767, 1685, 1611, 1551, 1415, 1363, 1202, 1107, 974, 877, 769, 581, 456 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3 + CCl_4$) δ 8.48 (s, 1H), 7.43 (s, 1H), 6.71 (s, 1H), 2.66 (s, 3H), 2.41 (d, 1H, $J = 13.2$ Hz), 2.37 (d, 1H, $J = 13.2$ Hz), 1.47 (s, 3H), 1.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3 + CCl_4$) δ195.0 (C), 158.9 (C), 157.6 (C), 155.6 (C), 149.5 (C), 147.3 (CH), 123.8 (C), 123.6 (CH), 118.3 (C), 112.3 (CH), 59.2 (CH_2), 58.6 (C), 43.7 (C), 32.0 (CH_3), 30.6 (CH_3), 30.4 (CH_3) ppm; HRMS (ESI, *m/z*) 519.1784 calcd for $C_{31}H_{28}O_6$ (M+Na) found 519.1783.



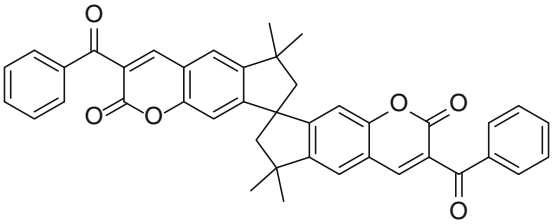
6,6,6′,6′-Tetramethyl-3,3′-dipropionyl-6,6′,7,7′-tetrahydro-2H,2′H-8,8′-spirobi[cyclopenta [g]chromene]-2,2′-dione ***7b***

Colourless solid, mp > 250 °C, yield 92 %; IR (KBr) υ_{max} 3037, 2960, 2870, 1733, 1684, 1614, 1550, 1458, 1416, 1366, 1250, 1181, 949, 808 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3 + CCl_4$) δ 8.50 (s, 1H), 7.44 (s, 1H), 6.72 (1H, s), 3.10 (q, 2H, $J = 10.0$ Hz), 2.41 (d, 1H, $J = 13.2$ Hz), 2.38 (d, 1H, $J = 13.2$ Hz), 1.47 (s, 3H), 1.39 (s, 1H), 1.15 (t, 3H, $J = 8.0$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3 + CCl_4$) δ 198.2 (C), 158.9 (C), 157.5 (C), 155.5 (C), 149.5 (C), 147.3 (CH), 123.7 (C), 123.5 (CH), 118.4 (C), 112.2 (CH), 59.2 (CH_2), 58.5 (C), 43.7 (C), 36.1 (CH_2), 32.0 (CH_3), 30.4 (CH_3), 8.1 (CH_3) ppm; HRMS (ESI, *m/z*) 547.2097 calcd for $C_{33}H_{32}O_6$ (M+Na) found 547.2092.



3,3′-Dibutyryl-6,6,6′,6′-tetramethyl-6,6′,7,7′-tetrahydro-2H,2′H-8,8′-spirobi[cyclopenta [g]chromene]-2,2′-dione ***7c***

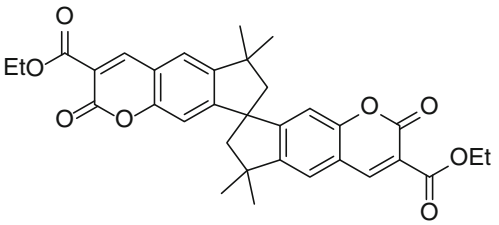
Colourless solid, mp > 250 °C, yield 94 %; IR (KBr) υ_{max} 3037, 2960, 2870, 1733, 1684, 1614, 1550, 1458, 1416, 1366, 1250, 1181, 949, 808 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3 + CCl_4$) δ 8.50 (s, 1H), 7.44 (s, 1H), 6.72 (1H, s), 3.10 (q, 2H, $J = 10$ Hz), 2.41 (d, 1H, $J = 13$ Hz), 2.38 (d, 1H, $J = 13$ Hz), 1.47 (s, 3H), 1.39 (s, 3H), 1.24-1.21 (m, 2H),1.15 (t, 3H, $J = 8$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3 + CCl_4$) δ 198.2 (C), 158.9 (C), 157.5 (C), 155.5 (C), 149.5 (C), 147.3 (CH), 123.7 (C), 123.5 (CH), 118.4 (C), 112.2 (CH), 59.2 (CH_2), 58.5 (C), 43.7 (C), 36.1 (CH_2), 32.0 (CH_3), 30.4 (CH_3), 9.2 (CH_2), 8.1 (CH_3) ppm; HRMS (ESI, *m/z*) 575.2609 calcd for $C_{33}H_{32}O_6$ (M+Na) found 575.2611.



3,3′-Dibenzoyl-6,6,6′,6′-tetramethyl-6,6′,7,7′-tetrahydro-2H,2′H-8,8′-spirobi[cyclopenta [g]chromene]-2,2′-dione ***7d***

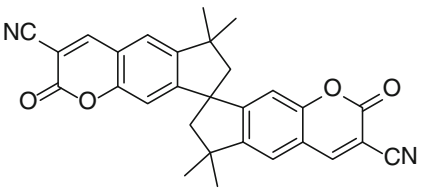
Yeild 89 %; mp 201 °C; IR (KBr) υ_{max} 3052, 2959, 286, 1731, 1660, 1612, 1557, 1268, 1215, 1163, 930, 860, 765, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3 + CCl_4$) δ 8.10 (s, 1H), 7.84 (d, 2H, $J = 8.0$ Hz), 7.58 (t, 1H, $J = 8.0$ Hz), 7.45 (t, 2H, $J = 8.0$ Hz), 6.78 (s, 1H), 2.46 (d, 1H, $J = 13.2$ Hz), 2.41 (d, 1H, $J = 13.2$ Hz), 1.48 (s, 3H), 1.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3 + CCl_4$) δ 191.7 (C), 158.1 (C), 157.0 (C), 155.1 (C), 149.5 (C), 145.4 (CH), 136.6 (C), 133.7 (CH), 129.7 (CH), 128.6 (CH), 126.5 (C), 122.4 (CH), 118.1 (C), 112.6 (CH), 59.2 (CH_2), 58.4 (C), 43.8 (C), 32.1 (CH_3), 30.2 (CH_3) ppm; HRMS (ESI, m/z) 643.2097 calcd for $C_{41}H_{32}O_6$ (M+Na) found 643.2098; Crystals obtained from CH_2Cl_2, molecular formula: $C_{41}H_{32}O_6$, monoclinic, space group P-1(No. 14), $a = 12.1947(14)$, $b = 14.2673(17)$, $c = 19.6415(15)$ Å, $\alpha = 73.579$ (9), $\beta = 82.205$ (9), $\gamma = 84.827$ (10), $V = 3244.1(10)$ $Å^3$, T = 293(2) K, $Z = 5$, $\rho_c = 1.427$ g cm^{-3}, $F(000) = 1630$, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), μ ($Mo_{K\alpha}$) = 0.106 mm^{-1}, colourless (0.5 × 0.4 × 0.2 mm^3), empirical absorption correction with SADABS (transmission factors: 1–0.8086), 2400

frames, exposure time 10 s, $2.60 \leq \theta \leq 26.00$, $-16 \leq h \leq 9$, $-19 \leq k \leq 17$, $-26 \leq l \leq 27$, 27648 reflections collected, 14809 independent reflections ($R_{int} = 0.1164$), solution by direct methods (SHELXS97[a]) and subsequent Fourier syntheses, full-matrix least-squares on F_o^2 (SHELX97), hydrogen atoms refined with a riding model, data/restraints/parameters = 14809/0/855, $S(F^2) = 1.103$, $R(F) = 0.0495$ and $wR(F^2) = 0.1140$ on all data, $R(F) = 0.3548$ and $wR(F^2) = 0.2051$ for 7514 reflections with $I > 2\sigma(I)$, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1167P)^2 + 1.646P]$ where $P = (F_o^2 + 2F_c^2)/3$, largest difference peak and hole 0.416 and -0.172 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-779835. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).



Diethyl 6,6,6′,6′-tetramethyl-2,2′-dioxo-6,6′,7,7′-tetrahydro-2H,2′H-8,8′-spirobi[cyclopenta [g]chromene]-3,3′-dicarboxylate ***9a***

Colourless solid, yield 75 %, mp 203 °C; IR (KBr) υ_{max} 3050, 2959, 2867, 1780, 1768, 1616, 1558, 1466, 1373, 1277, 1209, 876, 795 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3 + CCl_4$) δ 8.55 (s, 1H), 7.41 (s, 1H), 6.72 (s, 1H), 4.40 (q, 2H, $J = 8$ Hz, $J = 3$ Hz), 2.43 (d, 1H, $J = 13.2$ Hz), 2.39 (d, 1H, $J = 13.2$ Hz), 1.48 (s, 3H), 1.41 (s, 3H), 1.41 (t, 2H, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3 + CCl_4$) δ 163.3 (C), 157.6 (C), 156.5 (C), 155.4 (C), 149.4 (C), 148.7 (CH), 127.9 (C), 123.0 (CH), 117.9 (C), 112.3 (CH), 61.9 (CH_2), 59.2 (CH_2), 58.5 (C), 43.6 (C), 32.0 (CH_3), 30.4 (CH_3), 14.4 (CH_3) ppm; HRMS (ESI, *m/z*) calcd for $C_{33}H_{32}O_8$ (M+Na) 579.1995 and found 579.1996; Crystals obtained from CH_2Cl_2, molecular formula: $C_{33}H_{32}O_8$, monoclinic, space group $P2_1/c$, $a = 28.212$ (3), $b = 19.308$ (3), $c = 16.7559$ (18) Å, $\alpha = 90$, $\beta = 109.382$ (11), $\gamma = 90$, $V = 8610.0$ (18) Å^3, T = 293(2) K, $Z = 13$, $\rho_c = 1.395$ g cm^{-3}, F (000) = 3822, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), μ ($Mo_{K\alpha}$) = 0.100 mm^{-1}, colourless ($0.5 \times 0.4 \times 0.2$ mm^3), empirical absorption correction with SADABS (transmission factors: 1–0.8086), 2400 frames, exposure time 10 s, $2.53 \leq \theta \leq 29.30$, $-22 \leq h \leq 37$, $-25 \leq k \leq 22$, $-21 \leq l \leq 20$, 39145 reflections collected, 19689 independent reflections ($R_{int} = 0.1493$), solution by direct methods (SHELXS97[a]) and subsequent Fourier syntheses, full-matrix least-squares on F_o^2 (SHELX97), hydrogen atoms refined with a riding model, data/restraints/parameters = 19689/0/1126, S (F^2) = 1.103, R (F) = 0.0737 and wR (F^2) = 0.0739 on all data, $R(F) = 0.4973$ and wR (F^2) = 0.1328 for 7514 reflections with $I > 2\sigma(I)$, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1167P)^2 + 1.646P]$ where $P = (F_o^2 + 2F_c^2)/3$, largest difference peak and hole 0.135 and –0.153 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-780576. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).



6,6,6′,6′-Tetramethyl-2,2′-dioxo-6,6′,7,7′-tetrahydro-2H,2′H-8,8′-spirobi[cyclopenta [g]chromene]-3,3′-dicarbonitrile ***9b***

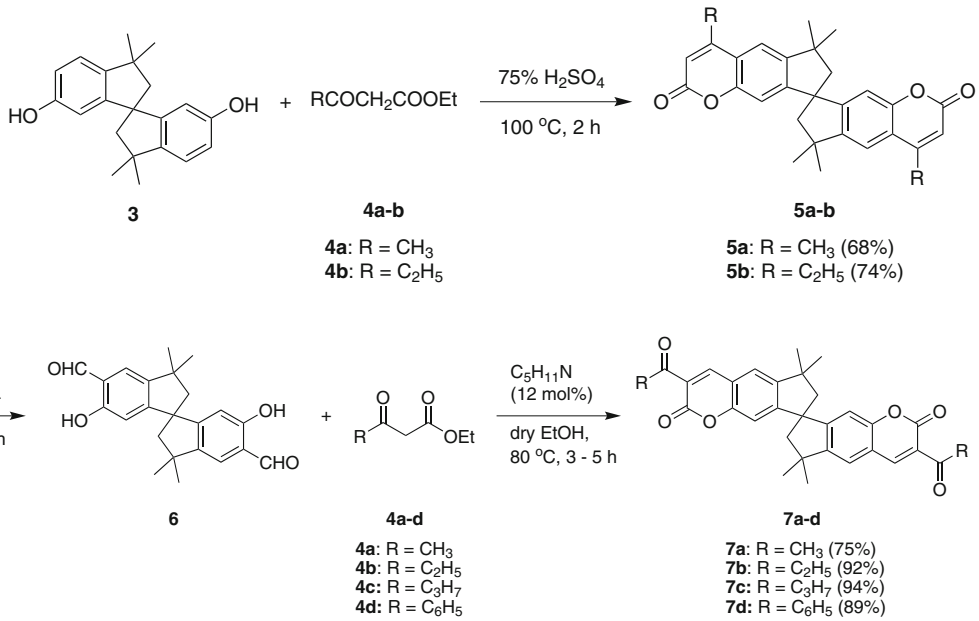
Colourless solid, yield 85 %, mp above 250 °C; IR (KBr) υ_{max} 3046, 2956, 2866, 2011, 1767, 1685, 1611, 1551, 1415, 1363, 1202, 1107, 974, 877. 769, 581, 456 cm^{-1}; ^{1}H NMR (400 MHz $CDCl_3 + CCl_4$) δ 8.55 (s, 1H), 7.41 (s, 1H), 6.72 (s, 1H), 2.47 (d, 1H, $J = 13.2$ Hz), 2.36 (d, 1H, $J = 13.2$ Hz), 1.48 (s, 3H), 1.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3 + CCl_4$) δ 157.6 (C), 156.5 (C), 155.4 (C), 149.4 (C), 148.7 (CH), 123.0 (CH), 117.9 (C), 117.5 (CH), 112.3 (C), 103.5 (C), 59.2 (CH_2), 58.5 (C), 43.6 (C), 32.0 (CH_3), 30.4 (CH_3) ppm; HRMS (ESI, *m/z*) 485.1572 calcd for $C_{29}H_{22}N_2O_4$ (M+Na) found 485.1570.

Results and Discussion

Synthesis of spirobiindane based bis-coumarins

Our first target in the synthesis of spirobiindane based bis-coumarins was the C4-alkyl courmains **5**, which can be generated by reacting alkyl acetoacetates with spirobiindane bisphenol **3** by double Von-Pechman condensation [17]. The bisphenol **3** was prepared by methanesulfonic acid catalyzed deep-seated rearrangement of bisphenol A [18]. The spirobiindane mounted bisphenol **3** underwent facile iterative Von-Pechmann condensation when treated with two equivalents of ethyl acetoacetate **4a** under

Scheme 1 Von-Pechmann condensation of spirobiindane bisphenol **3** with β-keto esters **4** to form bis-coumarins **5**



Scheme 2 Two-step synthesis of bis-3-acylcoumarins **7a–d** from bisphenol **3**

strongly acidic conditions to furnish the bis-coumarin **5a** in good yield (Scheme 1). Reflecting its C_2 symmetric nature, bis-coumarin **5a** exhibited three singlets for the methyl groups and a double doublet for the methylene group in its ^{1}H NMR spectrum. As anticipated the ^{13}C NMR spectrum of **5a** displayed 15 signals out of which six were in aliphatic region. The DEPT-135 spectrum, when analyzed along with the ^{13}C NMR spectrum, confirmed the assigned structure. The Von-Pechmann condensation of spirobiindane bisphenol **3** with β-keto esters **4** to form C4 alkyl bis-coumarin **5** was generalized by reacting β-keto ester **4b** with bisphenol **3** to provide **5b** in good yield (Scheme 1).

Next we targeted synthesis and characterization of bis-3-acylcoumarins **7**, as such coumarins are expected to exhibit useful flourochromic properties [19]. Initially, the spirobiindane bisphenol **3** was converted into bis-2-hydroxybenzaldehyde **6** by iterative Duff reaction (Scheme 2) [20]. Among the three options for conversion of bisphenol **3** to bis-2-hydroxybenzaldehyde **6**, namely Reimer Teimann reaction [21] and Vilsmeier reaction [22] and Duff reaction, last one worked well to provide **6** in good yield. The Knoevenagel condensation [23] of bis-2-hydroxybenzaldehyde **6** with 2 equivalents of ethyl acetoacetate **4a** in presence of a catalytic amount of piperidine provided spirobiindane based bis-coumarin **7a** (Scheme 2). The ^{1}H NMR spectrum of **7a** exhibited three singlets as anticipated from its C_2 symmetric nature. A singlet at δ 8.5 ppm was the diagnostic peak assignable to olefinic C4-H. In addition to other anticipated signals the ^{13}C NMR spectrum of **7a** exhibited two carbonyl carbon signals at δ 195 and 159 ppm. The conversion of bis-2-hydroxybenzaldehyde **6** into bis-coumarin **7a** proved to be general as we synthesized **7b–d** by employing three more β-keto esters **4b–d** (Scheme 2). In each case spectral data compared well with the parent bis-coumarin **7a**. Structure of the spirobiindane based 3-acylcoumarin **7d** was unequivocally established on the basis of single crystal X-ray diffraction data analysis (Fig. 2).

Next, we conducted the Knoevenagel condensation of spirobiindane bis-2-hydroxy benzaldehyde **6** with two more active methylene compounds namely diethyl melonate **8a** and ethyl cyanoacetate **8b** which provided spirobiindane based coumarins **9a** and **9b** respectively without any difficulty (Scheme 3). The ^{1}H, ^{13}C and DEPT-135 NMR Spectra of **9a–b** matched well with the bis-3-acetylcoumarin **7a**. In addition, single crystal X-ray diffraction data analysis of **9a** unambiguously confirmed its assigned structure (Fig. 3).

Photophysical Properties

3-Acylcoumarins, in general, exhibit rich photochemical and photophysical properties useful for many technological applications [24]. Upon excitation 3-acylcoumarins increase their dipole moment through contribution of resonance forms **B** and **C** as shown in Fig. 4. Owing to stabilizing dipolar nature of the resonance forms **B** and **C** (Fig. 4) coumarins with electron donating groups at C7 position show good solvatochromic effects, which can be exploited for the characterization of micelles [25]. We have recorded absorption and emission spectra of spirobiindane bis-coumarins **5a**, **7a**, **7b**, **7d**, **9a**, **9b** and compared the data with that of the parent 3-acetylcoumarin.

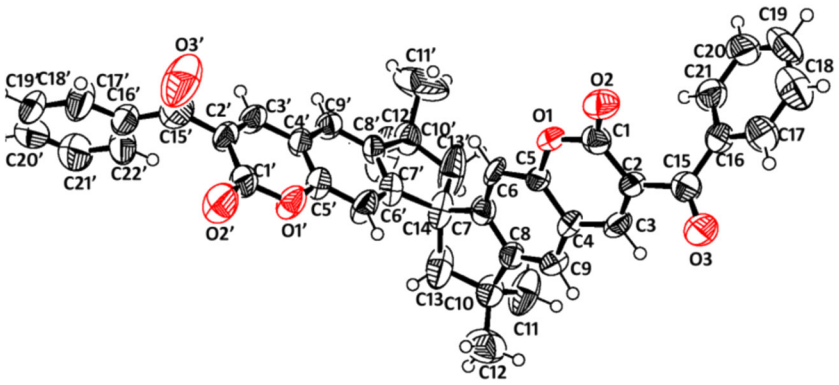
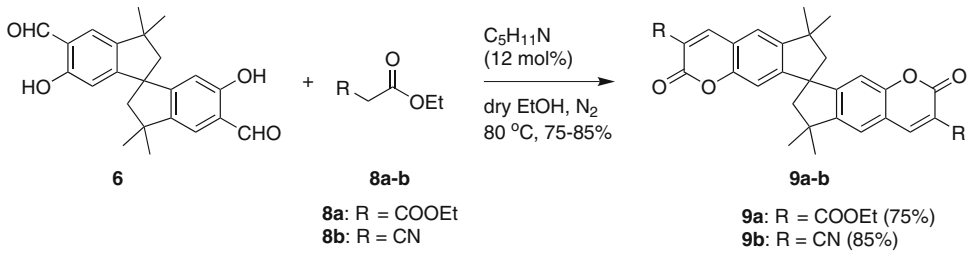


Fig. 2 X-ray crystal structure of 3,3′-dibenzoyl-6,6,6′,6′-tetramethyl-6,6′,7,7′-tetrahydro-2*H*,2′*H*-8,8′-spirobi[cyclopenta[*g*]chromene]-2,2′-dione **7d**

Scheme 3 Synthesis of spirobiindane based bis-coumarins **9a–b**



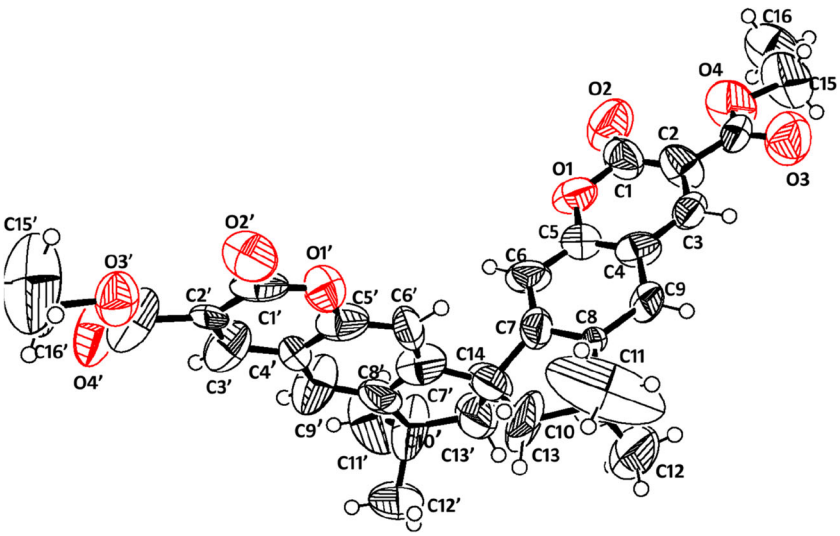


Fig. 3 X-ray crystal structure of diethyl 6,6,6′,6′-tetramethyl-2,2′-dioxo-6,6′,7,7′-tetrahydro-2*H*,2′*H*-8,8′-spirobi[cyclopenta[*g*]chromene]-3,3′-dicarboxylate **9a**

Fig. 4 Resonance forms (**A**–**C**) of 3-acylcoumarins

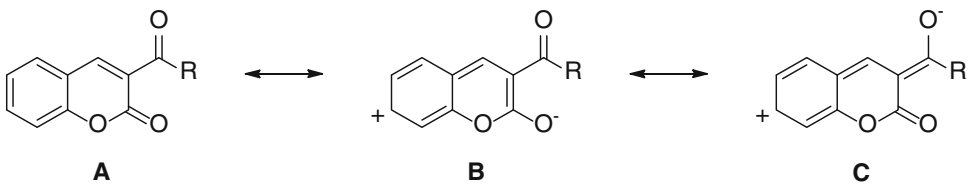


Table 1 Wavelength of the absorption maxima (nm) of spirobiindane bis-coumarin hybrids in different solvents

Coumarins	λ_{max} (abs) ε (cm^{-1} mol^{-1})		
	Hexane	Ethyl acetate	Methanol
5a	296 (74330)	302 (72020)	303 (73240)
	361 (78820)	356 (73800)	356 (76820)
7a	304 (74210)	298 (70430)	304 (76340)
	356 (76720)	352 (72120)	357 (77820)
7b	305 (74180)	300 (70440)	306 (76310)
	357 (76700)	354 (72150)	357 (77800)
7d	299 (79030)	296 (77680)	298 (81500)
	348 (81600)	344 (78400)	345 (82200)
9a	300 (83200)	297 (80010)	300 (84320)
	350 (84500)	349 (80200)	350 (85400)
9b	297 (92320)	301 (83210)	301 (91550)
	356 (90800)	350 (83400)	349 (91600)
3-Acetylcoumarin	304 (59060)	304 (54320)	308 (60260)
	344 (63320)	348 (55510)	350 (62480)

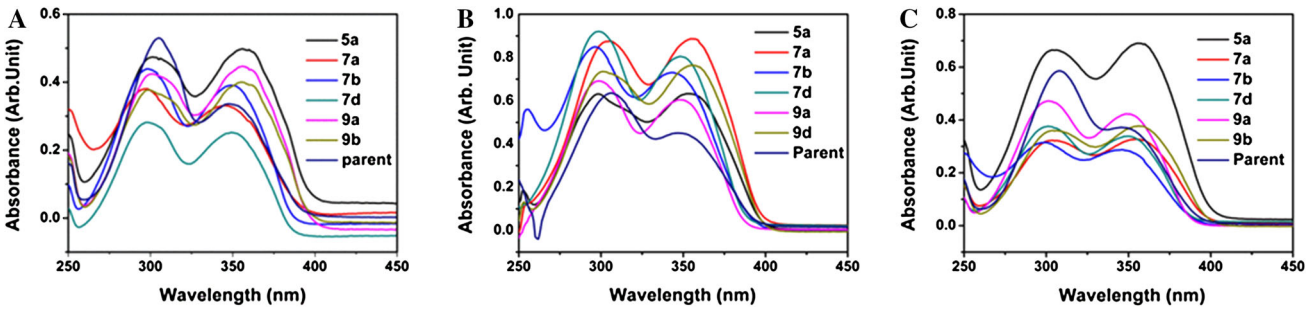


Fig. 5 Absorption spectra of **5a**, **7a**, **7b**, **7d**, **9a**, **9b** and 3-acetylcoumarin in hexane (**A**), EtOAc (**B**) and MeOH (**C**)

Table 2 Photo physical characteristics of spirobiindane based bis-coumarins in hexane, ethyl acetate and methanol

Coumarins	λ_{max} (emission)			$\Delta\lambda_{max}$ (hexane)	Φ		
	Hexane	EtOAc	MeOH		Hexane	EtOAc	MeOH
5a	420	432	440	59	0.024 (2.4 %)	0.024 (2.4 %)	0.044 (4.4 %)
7a	435	427	437	79	0.074 (7.4 %)	0.0165 (1.6 %)	0.0052 (0.5 %)
7b	434	427	437	79	0.074 (7.4 %)	0.015 (1.5 %)	0.0050 (0.5 %)
7d	420	428	424	72	0.031 (3.1 %)	0.0196 (1.9 %)	0.0049 (0.49 %)
9a	422	446	459	72	0.0888 (8.8 %)	0.116 (11.6 %)	0.0043 (4.3 %)
9b	440	444	424	84	0.0916 (9.1 %)	0.172 (17 %)	0.0102 (10 %)
3-acetylcoumarin	395	429	425	55	0.011 (1.1 %)	0.013 (1.3 %)	0.001 (0.1 %)

UV–Vis spectral analysis

3-Acetylcoumarins exhibit two intense UV absorption bands with λ_{max} located around 300 and 350 nm attributable to π–π* excitation of two major resonance forms **B** and **C** (Fig. 4) [26, 27]. The absorption spectral data of spirobindane bis-coumarins **5a**, **7a**, **7b**, **7d**, **9a**, **9b** and 3-acetylcoumrin in three solvents namely hexane (non-polar), ethyl acetate (EtOAc, moderately polar, aprotic) and methanol (MeOH, polar protic) are gathered in Table 1. Similar to the parent 3-acetylcoumrin, all the bis-coumarins prepared in this study show two almost equally intense bands located around 300 and 350 nm (Fig. 5). While the parent 3-acetylcoumrin exhibits bathochromic

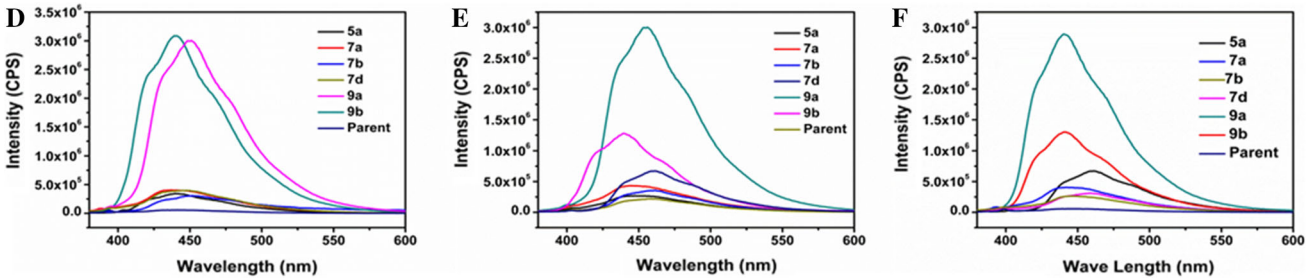


Fig. 6 Emission spectra of **5a**, **7a**, **7b**, **7d**, **9a**, **9b** and 3-acetylcoumarin in hexane (**D**), EtOAc (**E**) and Methanol (**F**)

shift and hypochromic effect on change of solvents from hexane to methanol there is no such trend for bis-coumarins which indicate that solvent does not interfere for the UV absorption of the molecule. However, the hyperchromic effect seen in bis-coumarins (Fig. 5; Table 1) may be attributable to the presence of two chromophores in close proximity.

Fluorescence Emission Spectral Analysis

The fluorescence emission spectral data of spirobiindane bis-coumarins **5a**, **7a**, **7b**, **7d**, **9a**, **9b** and 3-acetylcoumrin in three solvents namely hexane (non-polar), EtOAc (moderately polar, aprotic) and MeOH (polar protic) are gathered in Table 2 (see also Fig. 6). Fluorescence quantum yields for the newly made bis-coumarins **5a**, **7a**, **7b**, **7d**, **9a**, **9b** were measured with respect to 3-acetylcoumarin (0.011 in hexane) and were found to be in the range of 0.02–0.09 in hexane which indicates that spirobiindane based bis-coumarins exhibit better fluorescence emission (Fig. 6). Compared to 3-acetylcoumarin the bis-coumarins **9a** and **9b** which have ester and cyano substitutions at C3 position respectively exhibit ten-fold increase in fluorescence emission in hexane and about 15-fold increase in EtOAc. Excepting the bis-coumarin **5a** others **7a**, **7b**, **7d**, **9a**, **9b** exhibit about ten-fold quenching by the polar protic solvent (MeOH) in moving from the non-polar (hexane) solvent, which shows that the excited states are Inoue hard-anionic [28]. Among the bis-coumarins studied, one with C3 ester group **9a** exhibits maximum Stokes shift of 84 nm in hexane. The solvatochromic effect on **5a** includes a red shift of about 59 nm on emission maximum when the medium is changed from non polar (hexane) to polar protic solvent (MeOH) and the near absence of quenching on changing the solvent from hexane to methanol. These observations indicate Inoue soft-anionic character of the excited state of **5a**. Excepting the coumarin **7d** all other bis-coumarins exhibit large Stokes shift of 59–84 nm similar to that of the parent 3-acetylcoumarin. Since excitation increases the molecular dipole moment in the coumarin motif both reorganization of the solvent and conformational changes are expected to be involved in stabilization of the excited state, thus making Stokes shift larger [29].

Conclusion

Some perpendicularly disposed rigid bis-coumarins embedded on spirobiindane frame work were synthesized from spirobiindane bisphenol in two high yielding steps. Newly synthesized bis-coumarins possess electron-donating C4-alkyl group or electron-withdrawing C3-acyl/ester/cyano groups. Both absorption and emission characteristics of the bis-coumarins show that they have better photochromic properties compared to 3-acetylcoumarin which arise out of synergy between two perpendicularly disposed coumarin units.

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References

1. Hepworth J (1984) Comprehensive heterocyclic chemistry I. In: Katritzky AR, Rees CW (eds). Pergamon, Oxford, vol 3, pp 737–883
2. Geen GR, Evans JM, Vong AK (2005) Comprehensive heterocyclic chemistry II. In: Katritzky AR, Rees CW, Scriven EF (eds). Pergamon, Oxford, vol 5, pp 469–500
3. Padwa A (2008) Comprehensive heterocyclic chemistry III. In: Katritzky AR, Ramsden C, Scriven E, Taylor R (eds) Rhbne-Poulenc Rore, Dagenham, vol 5, pp 554–671
4. Murry RDH, Mendez J, Brown SA (1982) The natural coumarins: occurrence, chemistry and biochemistry. Wiley, New York
5. Hidayat H, Javid H, Ahmed AH, Karsten K (2012) The chemistry and biology of bicoumarins. Tetrahedron 68:2553–2578
6. Rao HSP, Sivakumar S (2006) Condensation of α-aroylketene dithioacetals and 2-hydroxyarylaldehydes results in facile synthesis of a combinatorial library of 3-aroylcoumarins. J Org Chem 71:8715–8723
7. Rao HSP, Vasantham K (2011) Nitroketene dithioacetal chemistry: synthesis of coumarins incorporating nitrothiophene moiety. J Chem Sci 123:411–420
8. Rao HSP, Swamy TV (2012) Synthesis of coumarin flavone hybrids. Lett Org Chem 9:218–220

9. Rao HSP, Swamy TV (2013) Synthesis and transformations of 4*H*-chromene 4-hydroxy-2*H*-pyran-2-one and 4*H*-chromene 4-hydroxycoumarin conjugates. J Chem Sci 125:777–790
10. Rao HSP, Swamy TV (2013) Synthesis of spirobiindane based bis-flavanones and bis-chroman-4-ones by Kabbe Reaction. Lett Org Chem 10:307–310
11. Ramesh V, Veera E (2011) Conformationally rigid aromatic amino acids as potential building blocks for abiotic foldamers. Org Biomol Chem 9:367–369
12. Kohler B, Enkelmann V, Oda M, Pieraccini S, Spada GP, Scherf U (2001) Novel chiral macrocycles containing two electronically interacting arylenechromophores. Chem Eur J 7:3000–3004
13. Kendhale AM, Rajesh G, Pattuparambil R, Rajamohanan K, Hoffmann HJ, Gangadhar J, Sanjayan R (2008) Unusual structural architecture from spirobi(indane) building blocks. Chem Commun 22:2541–2543
14. Fritsch D (2011) Synthesis and gas permeation properties of spirobischromane-based polymers of intrinsic microporosity. Mol Phys 212:1137–1146
15. Du N (2010) System and method of sensing and removing residual charge from a processed wafer. Advanced micro-fabrication equipment. PCT Int, Appl 20100271744
16. Liang Y (2009) Organic optoelectronic device and method for manufacturing the same. PCT Int, Appl 20090208776
17. Pechmann HV (1884) New buildings blocks of coumarin. Synthesis of daphnetins. Chem Ber 17:929–936
18. Faler GR, Lynch JC (1987) Preparation of spiro biindane bisphenol. U.S. 4701566
19. Jean B, Jacques P, Bernard V (1993) Ion-responsive fluorescent compounds. Effect of cation binding on the photophysical properties of a coumarin linked to monoaza and diaza-crown ethers. J Phys Chem 97:4552–4557
20. Duff JC, Bills EJ (1932) Reactions between hexamethylenetetramine and phenolic compounds. Part I. A new method for the preparation of 3 and 5-aldehydosalicylic acids. J Chem Soc 3:1987–1988
21. Reimer K, Tiemann F (1876) Formation of phenolic aldehydes from phenols, chloroform and alkali. Ber 9:1268–1285
22. Vilsmeier A, Haack A (1927) Vilsmeier reagent (chloromethylene) dimethyl ammonium chloride or DMF/$POCl_3$, or DMF/oxalyl chloride. Ber 60:119–123
23. Knoevenagel E (1898) Berichte der deutschen chemischen Gesellschaft. Chem Ber 31:2596–2619
24. Hyo SJ, Pil SK, Jeong WL, Jae IK, Chang SH, Jong WK, Shihai Y, Jin YL, Jung HL, Taiha J, Jong SK (2009) Coumarin-derived Cu^{2+}-selective fluorescence sensor: synthesis, mechanisms, and applications in living cells. J Am Chem Soc 131:2008–2012
25. Pavol H, Jana D, Henrieta S, Anton G (2010) Influence of polarity of solvents on the spectral properties of bichromophoric coumarins. Molecules 15:8915–8932
26. Jing L, Xiang GL, Shi RW (2002) Photo luminescent and theoretical studies of 3-acetyl-8-methoxycoumarin. Chin J Struct Chem 31:1003–1007
27. Azuma K, Uchiyama SS, Kajiro T, Santa T, Imai KA (2003) Study of the relationship between the chemical structures and the fluorescence quantum yields of coumarins, quinoxalinones and benzoxazinones for the development of sensitive fluorescent derivatization reagents. Photochem Photobiol Sci 2:443–449
28. Morimoto A, Yatsuhashi T, Shimada T, Biczok L, Tryk DA, Inoue H (2001) Radiation less deactivation of an intramolecular charge transfer excited state through hydrogen bonding: effect of molecular structure and hard-soft anionic character in the excited state. J Phys Chem A 105:10488–10496
29. Retsek JL, Gentemann S, Medforth CJ, Smith KM, Chirvony VS, Fajer J, Holten D (2000) Photo induced evolution on the conformational landscape of non planar dodecaphenylporphyrin: picosecond relaxation dynamics in the 1(π, π^*) excited state. J. Phys Chem. B 104:6690–6693