SYNTHESIS AND OPTICAL PROPERTIES RESEARCH OF SOME NOVEL TRICHROMOPHORE COMPOUNDS CONTAINING COUMARIN, PYRAZOLINE AND NAPHTHALIMIDE GROUPS

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Abstract – A series of novel trichromophore compounds containing coumarin, pyrazoline and naphthalimide groups were synthesized and their properties were elucidated using absorption and fluorescence. In chloroform solution, their maximal absorption bands and the maximal emission bands slightly varied from 478 to 485 nm and from 559 to 565 nm, respectively.

INTRODUCTION

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. More importantly, coumarin dyes have also been used as blue, green and red dopants in organic light-emitting diodes (OLEDs).

Similarly, 1, 3, 5-triaryl-2-pyrazolines, with their rigid but only partly unsaturated central pyrazoline ring, are well-known fluorescent compounds widely used for the optical brightening of textile fiber, plastics and paper. Pyrazoline derivatives have not only excellent hole-transfer performance but also excellent emitting blueness property. The fluorescence properties of these pyrazoline derivatives were reported by studying the effect of substituents on the absorption and fluorescence properties of this class of compounds.

On the other hand, naphthalimide usually exhibits strong fluorescent emission on irradiation, which usually acts as supermolecular moieties for the study of photo-induced electron transfer, fluorescence switcher, liquid crystal displays and EL materials.
In view of the considerable importance of these compounds work, we envisaged that compounds containing these moieties in the same molecule may show enhanced optical properties. In this paper, we synthesized a series of novel trichromophore compounds containing coumarin, pyrazoline and naphthalimide groups and researched their optical properties.

RESULTS AND DISCUSSION

The synthetic route of trichromophore compounds was shown in Scheme 1. Compound 2 was prepared from 4-bromo-1,8-naphthalic anhydride through two-step reaction in 84% yield. Compound 4(a-g) were synthesized from 3-acetylcoumarins and different aromatic aldehyde in the presence of piperidine in chloroform under reflux in 85-90% yields. The trichromophore compounds 5(a–g) were obtained by the reaction of compound 2 with substituted chalcones 4(a–g) in AcOH solution under reflux temperature in 78–85% yields. The structures of the compounds 5(a–g) were determined by IR, NMR, EI-MS and Elemental analyses.

Scheme 1. The synthesis of trichromophore compounds 5(a-g)

The UV-vis spectrums of naphthalimide 2 and coumarin chalcones 4(a-g) in chloroform solution with the concentration of 1×10⁻⁵M were shown in Figure 1. Their absorption wavelength maxima and molar extinction coefficient (ε) values were presented in Table 1. As shown in Table 1, compounds 2 showed
UV absorption maxima at 412 nm and the absorption peaks of 4(a–g) varied from 344 to 372 nm, which indicated that given various electron-withdrawing and electron-donating substituent on the aryl ring had an obvious effect on the electronic structure of these π-conjugation molecules. Compared with 2 and 4(a–g), the absorption spectrum of trichromophore compounds 5(a–g) showed strong bathochromic shift effect. As shown in Figure 2 and Table 2, compounds 5(a–g) showed UV absorption maxima at 478–485 nm, indicating that naphthalimide group and pyrazoline ring extended their π-conjugation system.

![Figure 1.](image1.png)

**Figure 1.** UV-vis spectra of compounds 2 and 4(a–g) in CHCl₃ with the concentration of 1×10⁻⁵ M

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>ε (10⁴ M⁻¹ cm⁻¹)</th>
<th>Compound</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>ε (10⁴ M⁻¹ cm⁻¹)</th>
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<td>2</td>
<td>412</td>
<td>2.22</td>
<td>4d</td>
<td>346</td>
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</tr>
<tr>
<td>4a</td>
<td>348</td>
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<td>4e</td>
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<tr>
<td>4b</td>
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<td>4g</td>
<td>344</td>
<td>1.91</td>
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</table>

From the Figure 2 and Table 2, it can be seen that the absorption spectra of compounds 5(a–g) were very similar because of their same structure unit of pyrazoline, which confirmed that given substituent Ar of C5 of pyrazoline ring had an negligible effect on the electronic structure of the molecules, because aromatic (Ar) in C5 cannot extend to the π-conjugation system. The molar coefficient of 5d was slightly
larger than other trichromophore compounds, it maybe because the substituent Cl atom on the benzene ring had better auxochrome effect than other atoms.

Figure 2. UV-vis spectra of compounds 5(a-g) in CHCl₃ with the concentration of 1×10⁻⁵ M

Figure 3. The fluorescence excitation and emission spectra of compounds 5(a-g) in CHCl₃ with the concentration of 1×10⁻⁵ M

Figure 3 showed the fluorescence spectra of compounds 5(a-g) in chloroform solution with concentration of 1×10⁻⁵ M. As shown in Table 2, these compounds had good red fluorescence and high quantum yields,
the quantum yields of 5(a-g) varied from 0.615 to 0.928. The maximal excitation bands and the maximal emission bands of compound 5(a-g) varied from 480 to 484 nm and from 559 to 565 nm, respectively, indicating that substituent phenyl group in 5- position of pyrazoline ring had little influence on the excitation and emission wavelengths, because aromatic (Ar) in C5 cannot extend to the π-conjugation system. However, we found that the substituent Ar affected the fluorescence quantum yields of compounds 5(a-g). As listed in Table 2, when Ar was p-(Me) phenyl group, the fluorescence quantum yield was higher than that when Ar was p-(F) phenyl group.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{max}^{abs}(nm)</th>
<th>ε (10^4 M^{-1} cm^{-1})</th>
<th>λ_{max}^{ex}(nm)</th>
<th>λ_{max}^{em}(nm)</th>
<th>Δν(cm^{-1})</th>
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<td>561</td>
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<td>5b</td>
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<td>5c</td>
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<td>481</td>
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<tr>
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<td>484</td>
<td>560</td>
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<td>5g</td>
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<td>1.67</td>
<td>483</td>
<td>562</td>
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In conclusion, a series of novel trichromophore compounds containing coumarin, pyrazoline and naphthalimide groups were designed and synthesized, and their absorption and fluorescence spectral characteristics were investigated in chloroform solution. The results showed their maximal absorption bands and the maximal emission bands varied from 478 to 485 nm and from 559 to 565 nm, respectively. These compounds maybe serve as good red light-emitting materials.

**EXPERIMENTAL**

Melting point was determined with XT4A micromelting point apparatus and was uncorrected. The 1H NMR was recorded on a Bruker 300 spectrometer with TMS as internal reference and CDCl3 as solvent. IR were recorded on a Perkin–Elmer PE–983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. MS were obtained with Finnigan Trace MS instrument using EI method. UV spectra were measured on a SP-1900 spectrophotometer. Fluorescence spectra were determined on a Hitachi F-4500. The fluorescent quantum yield of these compounds was measured by comparing with rhodamine B as the standard compound in ethanol solution (λ_{ex} 495 nm; A (Absorption), <0.01; Φ_F = 0.89)^{19}
Starting materials. 2-Ethyl-6-hydrazinobenzo[de]isoquinoline-1,3-dione 2,21 3-acetyl-2H-chromen-2-one (3),21 coumarin-chalcone hybrids 4(a-f)22 and 4g23 were prepared according to literature. All other chemicals used in this study were commercially available.

General procedure for the synthesis of trichromophore compounds 5: A mixture of 2 (1 mmol) and chalcone 4 (1 mmol) in AcOH (15 mL) was refluxed for 8 h. The progress of the reaction was monitored by TLC. Then the reactant was poured into water, dried and consequently recrystallized from THF: EtOH (1:1, v/v) to afford 5 as red solid.

1-(2-Ethylbenzo[de]isoquinoline-1,3-dione-6-yl)-3-[(2-oxo-2H-1-benzopyran-3-yl)-5-(phenyl)-2-pyrazoline (5a) : mp 272–273 °C; IR (vmax, KBr, cm⁻¹): 1733, 1681, 1639, 1574, 1415, 1382, 1097, 764; H NMR (CDCl3, δ ppm): 9.59-9.62 (m, 1H, Ar-H), 8.48 (dd, 2H, J = 6.9, 6.9 Hz, Ar-H), 7.72-7.78 (m, 1H, Ar-H), 7.60 (dd, 2H, J = 2.7, 2.7 Hz, Ar-H), 7.31 (m, 8H, Ar–H), 5.72 (dd, 1H, J = 5.1, 5.1 Hz, pyrazoline-H), 4.17-4.25 (m, 2H), 4.12 (dd, 1H, J = 12.0, 12.0 Hz, pyrazoline-H), 3.50 (dd, 1H, J = 8.1, 8.1 Hz, pyrazoline-H), 1.28-1.37 (t, J = 3H, 6.9 Hz, CH3-H); 13C NMR (CDCl3), δ (ppm): 13.35, 35.26, 44.12, 66.63, 111.49, 115.01, 116.63, 119.02, 119.96, 122.63, 123.69, 124.94, 125.18, 125.83, 128.27, 129.34, 130.50, 131.31, 132.13, 132.49, 133.78, 139.46, 139.71, 145.11, 148.08, 153.83, 159.11, 163.67, 164.45. EI mass spectrometry: m/z 513.00. M* calculated 513.17. Anal. Calcd for C32H23N3O4: C 74.84, H 4.51, N 8.18. Found: C 74.80, H 4.49, N 8.16.

1-(2-Ethylbenzo[de]isoquinoline-1,3-dione-6-yl)-3-[(2-oxo-2H-1-benzopyran-3-yl)-5-(p-tolyl)-2-pyrazoline (5b) : mp 270–271 °C; IR (vmax, KBr, cm⁻¹): 1735, 1682, 1641, 1575, 1382, 1098, 752, 472; H NMR (CDCl3, δ ppm): 9.60 (dd, 1H, J = 1.17 Hz, Ar-H), 8.64 (dd, 1H, J = 1.14 Ar-H), 8.30-8.32 (m, 1H, Ar-H), 7.71-7.77 (m, 1H, Ar-H), 7.55-7.61 (m, 2H, Ar-H), 7.30-7.38 (m, 2H, Ar–H), 7.09-7.19 (m, 4H, Ar–H), 6.85-6.88 (m, 1H, Ar–H), 5.69 (dd, 1H, J = 8.1, 8.1 Hz, pyrazoline-H), 4.21 (dd, 2H, J = 7.2, 7.2 Hz, CH3-H), 4.09 (dd, 1H, J = 11.4, 11.4 Hz, pyrazoline-H), 3.48 (dd, 1H, J = 8.4, 8.4 Hz, pyrazoline-H), 2.29 (s, 3H), 1.30 (t, 3H, J = 6.9 Hz, CH3-H); 13C NMR (CDCl3), δ (ppm): 13.32, 21.04, 35.21, 44.08, 66.43, 111.48, 114.84, 116.59, 119.00, 119.98, 122.58, 123.62, 124.87, 125.09, 128.49, 129.94, 130.46, 131.24, 132.11, 132.41, 133.82, 136.69, 138.04, 139.33, 145.08, 148.03, 153.77, 159.02, 163.63, 164.42. EI mass spectrometry: m/z 527.01. M* Calculated 527.18. Anal. Calcd for C33H25N3O5: C 75.13, H 4.78, N 7.96. Found: C 75.09, H 4.76, N 7.80.

1-(2-Ethylbenzo[de]isoquinoline-1,3-dione-6-yl)-3-[(2-oxo-2H-1-benzopyran-3-yl)-5-(p-methoxyphenyl)-2-pyrazoline (5c) : mp 230–231 °C; IR (vmax, KBr, cm⁻¹): 1731, 1679, 1640, 1574, 1383, 1244, 1098, 766, 477; H NMR (CDCl3, δ ppm): 9.56-9.58 (m, 1H, Ar-H), 8.62-8.65 (m, 1H, Ar-H), 8.31-8.34 (m, 2H, Ar-H), 7.72-7.77 (m, 1H, Ar-H), 7.55-7.61 (m, 2H, Ar-H), 7.22-7.39 (m, 6H, Ar–H), 6.80-6.89 (m,2H, Ar–H), 5.68 (dd, 1H, J = 8.1, 8.1Hz, pyrazoline-H), 4.21 (dd, 2H, J = 7.2, 7.2Hz, -CH2 ), 4.08 (dd,
1H, J = 10.4, 10.4Hz , pyrazoline-H). 3.75 (s, 3H, OCH₃), 3.48 (dd, 1H, J = 8.1, 8.1Hz, pyrazoline-H), 1.29 (t, 3H, J = 6.9 Hz, -CH₃); ¹³C NMR (CDCl₃), δ (ppm): 13.35, 35.26, 44.14 , 55.26, 66.25, 111.48, 114.84, 116.59, 119.00, 120.03, 122.60, 123.76, 124.92, 125.15, 127.10, 128.54, 130.46, 131.29, 131.64, 132.12, 132.45, 133.74, 139.39, 145.20, 148.10, 153.81, 159.12, 159.39,163.69, 164.47. EI mass spectrometry: m/z 542.91. M⁺ calculated 543.18. Anal. Calcd for C₃₃H₂₅N₅O₅: C 72.92, H 4.64, N 7.73. Found: C 72.89, H 4.62, N 7.70.

1-(2-Ethylbenzo[de]isoquinoline-1,3-dione-6-yl)-3-((2-oxo-2H-1-benzopyran-3-yl)-5-(4-chlorophenyl)pyrazoline (5d) : mp 279–280 °C; IR (vmax, KBr, cm⁻¹): 1733, 1681, 1641, 1574, 1384, 1299, 1097, 748,476; ¹H NMR (CDCl₃), δ (ppm): 9.51 (dd, 1H, J = 1.2, 1.2 Hz, Ar-H), 8.65 (dd, 1H, J = 12, 12 Hz, Ar-H), 8.32-8.35 (m, 2H, Ar-H), 7.73-7.78 (m, 1H, Ar-H), 7.56-7.62 (m, 2H, Ar-H), 7.27- 7.39 (m, 5H, Ar–H), 6.83 (d, J = 8.4, 8.4 Hz, 1H, Ar–H), 5.70 (dd, 1H, J = 8.4, 8.4 Hz, pyrazoline-H), 4.21 (dd, 2H, J = 7.2, 7.2 Hz, -CH₂), 4.11 (dd, 1H, J = 8.7, 8.7Hz, pyrazoline-H), 3.49 (dd, 1H, J = 8.4, 8.4 Hz, pyrazoline-H), 1.31 (t, 3H, J = 6.9Hz, CH₃-H); ¹³C NMR (CDCl₃), δ (ppm): 13.35, 35.29, 44.11, 53.41, 66.03, 111.57, 115.46, 116.66, 118.98, 119.79, 122.72, 123.80, 124.98, 125.32, 127.30 128.60, 129.03, 129.30, 129.55, 130.45, 131.36, 132.01, 132.59, 133.49, 134.12, 138.21, 139.62, 144.96, 148.08, 153.87, 159.14, 163.58, 164.37. EI mass spectrometry: m/z 547.02. M⁺ Calculated 547.13. Anal. Calcd for C₃₂H₂₂ClN₃O₄: C 70.14, H 4.05, N 7.67. Found: C 70.11, H 4.03, N 7.65.

1-(2-Ethylbenzo[de]isoquinoline-1,3-dione-6-yl)-3-((2-oxo-2H-1-benzopyran-3-yl)-5-(4-bromo-phenyl)pyrazoline (5e) : mp 292–293 °C; IR (vmax, KBr, cm⁻¹): 1733, 1678, 1640, 1573, 1298, 1099, 748, 474; ¹H NMR (CDCl₃), δ (ppm): 9.51-9.54 (m, 1H, Ar-H), 8.65 (dd, 1H, J = 1.2, 1.2 Hz, Ar-H), 8.56-8.67 (m, 1H, Ar-H), 7.73-7.78 (m, 1H, Ar-H), 7.56-7.62 (m, 2H, Ar-H), 7.01-7.45 (m, 8H, Ar–H), 6.81-6.84 (m, 1H, Ar–H), 5.69 (dd, 1H, J = 8.7, 8.7Hz, pyrazoline-H), 4.26 (dd, 2H, J = 6.9, 6.9Hz, -CH₂), 4.16 (dd, 2H, J = 6.9, 6.9Hz, pyrazoline-H), 3.48 (dd, 1H, J = 8.4, 8.4 Hz, pyrazoline-H), 1.31 (t, 3H, J = 6.9 Hz, CH₃-H); ¹³C NMR (CDCl₃), δ (ppm): 13.35, 35.30, 44.06, 66.07, 111.55, 115.45, 116.66, 118.97, 119.76, 122.18, 122.71, 123.79, 124.99, 125.34, 127.62, 128.61, 129.52, 130.45, 131.38, 131.97, 132.03, 132.50, 132.61, 133.49,138.72, 139.65, 144.93, 148.08, 153.86, 159.16, 163.59, 164.38. EI mass spectrometry: m/z 591.06. M⁺ calculated 591.08. Anal. Calcd for C₃₂H₂₂BrN₅O₄: C 64.87, H 3.74, N 7.09. Found: C 64.83, H 3.70, N 7.05.

1-(2-Ethylbenzo[de]isoquinoline-1,3-dione-6-yl)-3-((2-oxo-2H-1-benzopyran-3-yl)-5-(4-fluorophenyl)pyrazoline (5f) : mp 268–269 °C; IR (vmax, KBr, cm⁻¹): 1732, 1678, 1641, 1575, 1519, 1386, 1298, 1097, 751, 474; ¹H NMR (CDCl₃), δ (ppm): 9.51 (dd, 1H, J = 1.2, 1.2Hz, Ar-H), 8.65 (dd, 1H, J = 1.2, 1.2Hz, Ar-H), 8.32-8.34 (m, 2H, Ar-H), 7.75 (m, 1H, dd, 1H, J = 7.2, 7.2Hz, Ar-H), 7.56-7.61 (m, 2H, Ar-H), 7.22-7.39 (m, 3H, Ar–H), 6.97-7.02 (m, 2H, Ar–H), 6.83-6.86 (m, 1H, Ar–H), 5.71 (dd, 1H, J = 8.1, 8.1Hz, pyrazoline-H), 4.21 (dd, 2H, J =7.2, 7.2Hz, -CH₂ ), 4.11 (dd, 1H, J = 10.4, 10.4Hz,
pyrazoline-H), 3.49 (dd, 1H, J = 8.4, 8.4 Hz, pyrazoline-H), 1.29 (t, 3H, J = 6.9 Hz, -CH3 ); 13C NMR (CDCl3), δ (ppm): 13.31, 35.26, 44.16, 66.00, 111.62, 115.37, 116.15, 116.44, 116.62, 118.97, 119.83, 122.68, 123.82, 124.94, 125.26, 127.55, 127.66, 128.56, 130.42, 131.32, 131.99, 132.53, 133.48, 135.42, 135.46, 139.54, 145.02, 148.06, 153.84, 154.27. EI mass spectrometry: m/z 531.01. M+ Calculated 531.16. Anal. Calcd for C32H22F3N3O4: C 72.31, H 4.17, N 7.91. Found: C 72.29, H 4.15, N 7.87.

1-(2-Ethyl-benzo[d]isoquinoline-1,3-dione-6-yl)-3-(2-oxo-2H-1-benzopyran-3-yl)-5-(2-thiophene)-2-pyrazoline (5g) : mp 270–271 °C; IR (νmax, KBr, cm–1): 1734, 1683, 1640, 1574, 1421, 1380, 1301, 1247, 1097, 910, 766; 1H NMR (CDCl3), δ (ppm): 9.26-9.29 (m, 1H, Ar-H), 8.64 (dd, 1H, J = 0.9, 0.9 Hz, Ar-H), 8.37-8.41 (m, 2H, Ar-H), 7.72-7.78 (m, 1H, Ar-H), 7.55-7.62 (m, 2H, Ar-H), 7.33-7.39 (m, 2H, Ar-H), 7.12-7.15 (m, 2H, Ar-H), 6.97-6.98 (m, 1H, Ar-H), 6.84-6.87 (m, 1H, Ar-H), 5.98-5.99 (m, 1H, pyrazoline-H), 4.21 (dd, 2H, J=6.9, 6.9 Hz, -CH2), 4.13 (dd, 2H, J = 8.1, 8.1 Hz, pyrazoline-H), 3.69 (dd, 1H, J = 8.1, 8.1 Hz, pyrazoline-H), 1.31 (t, 3H, J = 6.9 Hz, CH3-H ); 13C NMR (CDCl3), δ (ppm): 13.35, 35.31, 44.50, 62.92, 113.02, 116.22, 116.64, 119.03, 119.88, 122.72, 124.48, 124.96, 125.38, 125.45, 125.69,128.64, 130.16, 131.30, 131.95, 132.54, 132.92, 139.69, 142.47, 145.68, 148.49, 153.91, 159.29, 163.69, 164.37. EI mass spectrometry: m/z 519.00. M+ calculated 519.13. Anal. Calcd for C30H21N3O4S. C 69.35, H 4.07, N 8.09. Found: C 69.31, H 4.04, N 8.05.

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REFERENCES