Survey of Liquid Coumarin Dyes and Their Fluorescence Properties

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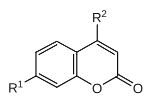
Novel liquid 7-dioctylamino-, 7-(didecylamino)-, 7-(1-butylpentyloxy)-, and 7-(1-octylnonyloxy)-4-methylcoumarins were found. They showed melting points in the range of −55.1 to −42.8 °C as a metastable liquid phase followed by rearrangement in the range of 1.7 to 20.0 °C to form stable liquid phase. The 7-dialkylamino and 7-alkoxy derivatives showed fluorescence maxima at around 440 and 400 nm with fluorescence quantum yields ca. 0.16 and 0.06 in neat form, respectively.

Dyes are usually solid. To our knowledge, no liquid dyes in which auxochrome(s) such as dialkylamino or alkoxy groups are included in a chromophore have been obtained yet. Coumarins are important and interesting compounds used as fluorescent labeling reagents,[1] sensors,[2] laser dyes,[3] and emitters in OLED.[4] We report herein the systematic survey of liquid coumarin dyes and their fluorescent properties.

Coumarin dyes **1**–**22** used in this study are shown in Table 1. 7-(Dialkylamino)coumarins **2**–**13** were obtained by the reaction of 3-(dialkylamino)phenols with ethyl alkanoylacetates. 7-Alkoxy-4-methylcoumarins **15**–**22** were prepared by the reaction of 7-hydroxy-4-methylcoumarin (**14**) with alkyl iodides. Solid products were recrystallized from hexane. Liquid products were purified by column chromatography. The purity of liquid products was checked by gas chromatography and ^{1}H NMR spectra (Figures S1–S4).[12] Even after storing the liquid products **4**, **5**, **20**, and **21** at −30 °C for 1 month, they did not solidify. Their DSC analysis is shown in Figure 1. The characteristic endothermic peak was observed at around −50 °C, followed by exothermic peak at around 10 °C. No peak was observed at higher temperature. The peak at around −50 °C corresponds to change from solid to metastable liquid phase and the peak at around 10 °C changes from the metastable liquid to stable liquid phase.

Table 1. Physical properties of coumarins



Compd	R^1	R^2	Mp/°C	In dichloromethane $\lambda_{max}(\varepsilon)$ /nm	F_{max} /nm	Φ_f[b]	Neat form[a] F_{max} /nm	Φ_f[c]
1	NH_2	CH_3	220–224[d]	326 (17300)	397	0.77	451	0.01
2	$N(C_2H_5)_2$	CH_3	88–89[e]	372 (24100)	424	0.90	432	0.29
3	$N(C_4H_9)_2$	CH_3	37.4[f]	374 (24900)	427	0.94	430	0.16
4	$N(C_8H_{17})_2$	CH_3	−47.1[g]	375 (24800)	426	0.93	439[h]	0.14[h]
5	$N(C_{10}H_{21})_2$	CH_3	−50.6[g]	375 (25700)	426	0.96	442[h]	0.18[h]
6	$N(C_{14}H_{29})_2$	CH_3	42.5[f]	375 (25400)	425	0.94	423	0.04
7	$N(C_{18}H_{37})_2$	CH_3	57.8[f]	375 (26800)	427	0.98	424	0.05
8	NH_2	CF_3	218.8[f]	360 (19600)	439	0.93	476	0.01
9	$N(C_2H_5)_2$	CF_3	80–81[i]	401 (23300)	478	0.87	522	0.40
10	$N(C_4H_9)_2$	CF_3	100.7[f]	405 (23100)	480	0.84	496	0.37
11	$N(C_8H_{17})_2$	CF_3	59.7[f]	405 (23100)	479	0.87	481	0.29
12	$N(C_{10}H_{21})_2$	CF_3	46.1[f]	404 (21900)	480	0.95	479	0.33
13	$N(C_{18}H_{37})_2$	CF_3	67.0[f]	404 (22400)	479	0.91	478	0.29
14	OH	CH_3	188–190[j]	317 (11400)	369	0.01	384	0.01
15	OCH_3	CH_3	164–165[k]	320 (15000)	378	0.03	393	0.33
16	OC_4H_9	CH_3	41–43[l]	322 (15400)	377	0.05	384	0.18
17	$OC_{10}H_{21}$	CH_3	40–42[l]	322 (15900)	380	0.04	385	0.21
18	$OC_{18}H_{37}$	CH_3	76–77[m]	321 (15400)	377	0.05	391	0.27
19	$OCH(CH_3)_2$	CH_3	86–87[k]	322 (17000)	379	0.07	395	0.54
20	$OCH(C_4H_9)_2$	CH_3	−42.8[g]	324 (16100)	377	0.08	422[h]	0.05[h]
21	$OCH(C_8H_{17})_2$	CH_3	−55.1[g]	324 (17700)	381	0.10	406[h]	0.07[h]
22	$OCH(C_{11}H_{23})_2$	CH_3	41.5[f]	323 (17300)	377	0.10	398	0.09

[a]Measured in the solid state unless otherwise cited. [b]Determined using quinine sulfate in 0.1 mol dm^{-3} sulfuric acid as a reference ($\Phi_f = 0.55$, $\lambda_{max} = 366$ nm) at 25 °C. [c]Determined with a Hamamatsu Photonics Absolute PL Quantum Yield Measurement System C9920-02. [d]Reference 5. [e]Reference 6. [f]Measured by TG/DTA. [g]Measured by DSC. [h]Measured in liquid state. [i]Reference 7. [j]Reference 8. [k]Reference 9. [l]Reference 10. [m]Reference 11.

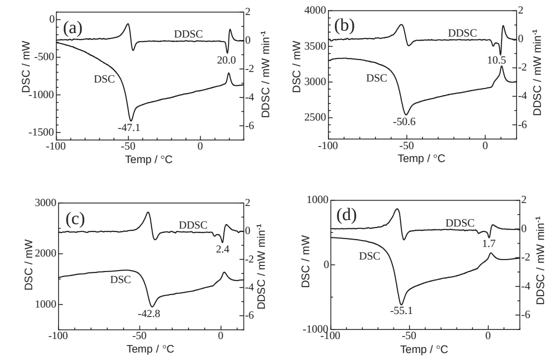


Figure 1. DSC of (a) **4**, (b) **5**, (c) **20**, and (d) **21**. The samples were cooled to −100 °C for 5 min, then heated at 10 °C min^{-1}.

The relationship between melting point and the number of carbon atoms at the 7-position is shown in Figure 2. In a series of 7-dialkylamino-4-methylcoumarins **1**–**7**, the melting point becomes lower with increasing number of total carbon atoms, showing the lowest melting point, and then becomes higher. The melting point of **4** and **5** was observed at −47.1 and −50.6 °C, respectively. The higher melting point of **6** and **7** could come from intermolecular interactions between longer alkyl groups. In a series of 7-dialkylamino-4-(trifluoromethyl)-coumarins **8**–**13**, the lowest melting point was observed for **12**, being 46.1 °C. It has been reported that the 7-diethylamino-4-methyl and -4-trifluoromethyl derivatives **2** and **9** are packed in isolated monomer and dimer forms, respectively.[13,14] This suggests that the 4-trifluoromethyl derivatives have stronger intermolecular interactions than the 4-methyl derivatives to form solid. In a series of 7-(*n*-alkyloxy)-4-methylcoumarins **14**–**18**, compound **17** showed the lowest melting point of 44–45 °C, being solid at room temperature. In a series of 7-(*iso*-alkoxy)-4-methylcoumarins **19**–**22**, compounds **20** and **21** were liquid, the melting point being −42.8 and −55.1 °C, respectively. Thus, a branched substituent at the 7-position is essential to show metastable liquid phase.

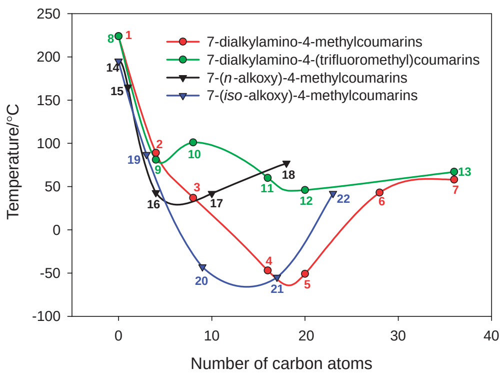


Figure 2. Relationship between melting point and number of carbon atom at the 7-position in coumarins.

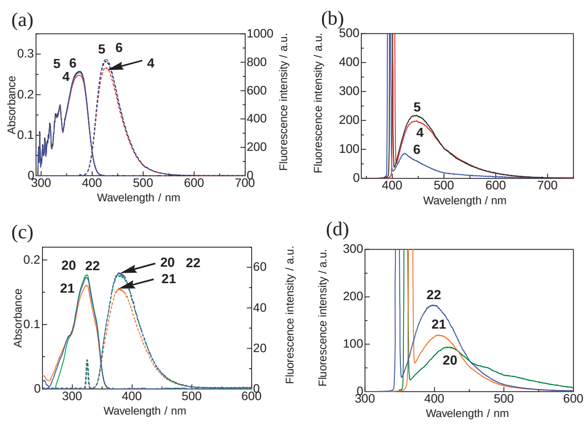


Figure 3. UV–vis absorption and fluorescence spectra (a) **4**, **5**, and **6** in dichloromethane, (b) **4**, **5**, and **6** in neat form, (c) **20**, **21**, and **22** in dichloromethane, and (d) **20**, **21**, and **22** in neat form. In (a) and (c), solid and dotted lines indicate UV–vis absorption and fluorescence spectra, respectively.

The UV–vis absorption and fluorescence spectra of **4**, **5**, and **6** are shown in Figures 3a and 3b. The results are also listed in Table 1. Figure 3a shows that the UV–vis absorption (λ_{max}) and fluorescence maxima (F_{max}) were observed at around 375 and 425 nm in dichloromethane, respectively. No significant difference in molar absorption coefficients (ε) and fluorescence quantum yields (Φ_f) were observed among them. Coumarin **6** showed F_{max} at 423 nm with Φ_f 0.04 in the solid state. Interestingly, liquid coumarins **4** and **5** also showed F_{max} at around 439 and 442 nm with Φ_f 0.14 and 0.18 in neat form, respectively, as shown in Figure 3b. The fluorescence intensity depends on the crystal rigidity. Therefore, it is surprising that these liquid coumarins show medium fluorescence intensity in neat form.

Figure 3c depicts the UV–vis absorption and fluorescence spectra of **20**, **21**, and **22** in dichloromethane. No remarkable differences in the spectra were observed among them. Liquid coumarins **20** and **21** also showed fluorescence in neat form with Φ_f 0.05 and 0.07, respectively, as shown in Figure 3d.

The pictures of liquid coumarins as well as their fluorescence upon UV-irradiation are shown in Figure 4. It is clear that

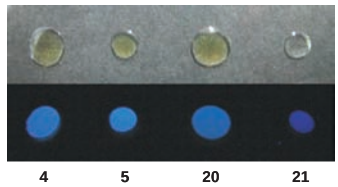


Figure 4. Appearance and fluorescence of liquid coumarins **4**, **5**, **20**, and **21**.

these coumarins are liquid at room temperature and show fluorescence in neat form.

In conclusion, novel 7-dioctylamino-, 7-didecylamino-, 7-(1-butylpentyloxy)-, and 7-(1-octylnonyloxy)-4-methylcoumarins are liquid at room temperature, showing F_{max} at 439, 442, 411, and 396 nm with Φ_f 0.14, 0.18, 0.05, and 0.07, respectively. It is required for liquid coumarin dyes to have a branched substituent at the 7-position. Medium carbon chain length is also essential to become liquid. This is the first report that liquid coumarins are obtained and they show fluorescence in neat form.

References and Notes

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http//www.csj.jp/journals/chem-lett/index.html: ^{1}H NMR spectra of **4**, **5**, **20**, and **21**.
13 Deposited cif file of **2** (CCDC 690558). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
14 Deposited cif file of **9** (CCDC 690559).

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