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Synthesis and fluorescent property of some novel bischromophore compounds containing pyrazoline and naphthalimide groups

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Abstract

A series of novel bischromophore compounds containing pyrazoline and naphthalimide were synthesized, and their structures were confirmed by means of IR, ^{1}H NMR, UV and elementary analysis. The fluorescent spectrum showed that these compounds had good green fluorescence. The fluorescence emission wavelengths varied from 520 to 540 nm.

Keywords: Pyrazoline; Naphthalimide; Bischromophore compounds

1. Introduction

Since Tang and Vanslyke [1] first reported the usage of multi-layer organic thin films for light-emitting devices (LEDs), organic electroluminescent devices (OELDs) have gained more and more interest all over the world. OLEDs are given more attention because of their potential applications in various displays [2−7]. The organic electroluminescent devices have shown several advantages over inorganic ones, such as low cost, high luminous efficiency, wide selection of emission colors via molecular design of organic materials, and easy processing. As an important part of luminescent and fluorescent materials, some bis- and tri-chromophore light-emitting compounds [8,9] were synthesized.

Pyrazoline derivatives have been investigated in many respects due to their blue light emission with high quantum yield [10−14], ready accessibility, and easily being used as carrier transporting as well as emitting materials [15]. Many have been reported as hole transporting or emitting materials in organic EL devices [16−18]. And also it is well known that the naphthalimide usually exhibits strong fluorescent emission on irradiation, which usually acts as supermolecular moieties for the study of photo-induced electron transfer [19,20], fluorescence switcher [21] or liquid crystal displays [22]. Recently, naphthalimide derivatives utilized as EL materials have been reported [23,24], whose fluorescence emission can be widely tuned (from blue to yellow, green and even red) with amino- and alkoxy-groups at the 4-position of naphthalimide. Many multichromophore compounds have been synthesized [9,25].

Our group has previously reported the synthesis of several benzothiazoyl pyrazoline derivatives containing aromatic heterocycle, which have good blue fluorescence. In this paper, we synthesized a series of novel bischromophore compounds containing pyrazoline and naphthalimide groups using 4-hydrazinenaphthalimides and chalcones (Scheme 1), which had good green light fluorescence. These bischromophore compounds have seldom been reported previously.

2. Experimental

2.1. General

Melting points were recorded on an electrothermal digital melting point apparatus and were uncorrected. ^{1}H NMR

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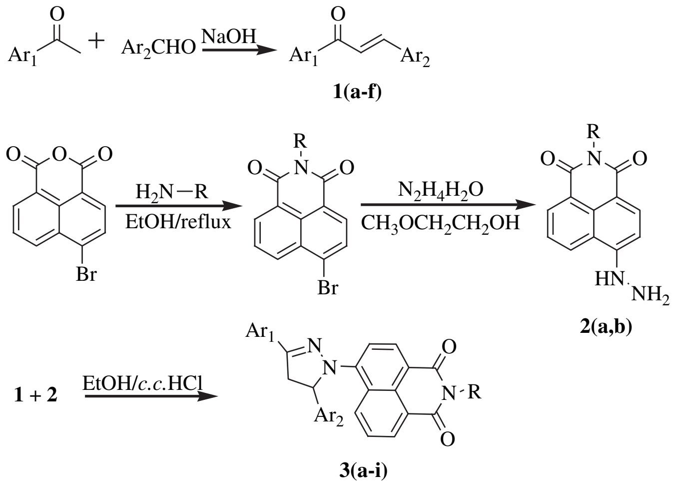
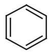
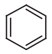
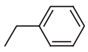
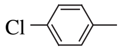
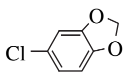
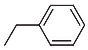
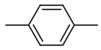
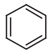
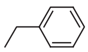
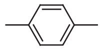
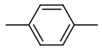
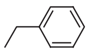
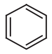
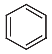
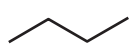
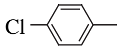
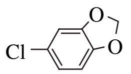
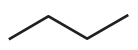
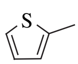
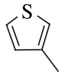
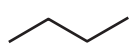
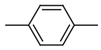
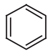
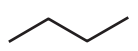
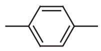
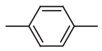
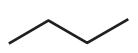


Scheme 1.

Table 1
The synthesis of bischromophore compounds **3**(**a**–**i**)

Entry	Ar_1	Ar_2	R	Time (h)	Product	Yield[a] (%)
1				10	**3a**	38
2				6	**3b**	57
3				9	**3c**	61
4				10	**3d**	50
5				12	**3e**	47
6				9	**3f**	72
7				8	**3g**	83
8				10	**3h**	86
9				9	**3i**	84

[a] Recrystallization yields.

(400 MHz) spectra were recorded on a Varian Mercury MHz spectrometer in $CDCl_3$. IR spectra were obtained on a Nicolet FT-IR500 spectrophotometer using KBr pellets. Elemental analyses were performed by a Carlo–Erba EA1110 CNNO-S analyzer.

2.2. Syntheses

First, the chalcones **1**(**a**–**f**) and compounds **2**(**a**, **b**) were prepared according to literature [26], which served as our starting materials for further synthetic studies. Then, compounds **3**(**a**–**i**) were synthesized by **2**(**a**, **b**) with chalcones **1**(**a**–**f**) as the following procedure: a mixture of **2**(**a**, **b**) (1 mmol) and chalcone **1** (1 mmol) in ethanol (5 ml) and 0.5 ml 37% HCl was refluxed for 6–12 h. The resulting mixture was cooled down and the precipitates were filtered to afford the crude products, which can be purified by recrystallization from ethanol/tetrahydrofuran (v:v = 1:1). The results are shown in Table 1.

2.2.1. 1-(2-Benzyl-benzo[de]isoquinoline-3-dione)-3,5-bisphenyl-2-pyrazoline (*3a*)

M.p.: 232–235 °C. Anal. Calcd. (%) for $C_{34}H_{25}N_3O_2$: C, 80.45; H, 4.96; N, 8.28. Found (%): C, 80.73; H, 5.21; N, 8.17. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.72 (d, $J = 8.8$ Hz, 1H), 8.65 (d, $J = 6.4$ Hz, 1H), 8.30 (d, $J = 8.8$ Hz, 1H), 7.21–7.80 (m, 16H), 6.77 (d, $J = 8.4$ Hz, 1H), 5.68–5.73 (m, 1H), 5.35 (s, 2H), 3.88–3.95 (m, 1H), 3.30 (dd, $J_1 = 17.2$ Hz, $J_2 = 7.6$ Hz, 1H). IR (KBr, cm^{-1}): 1577, 1643, 1685, 3031, 3119.

2.2.2. 1-(2-Benzyl-benzo[de]isoquinoline-1,3-dione)-3-(4-chloro-phenyl)5-(3′,4′-methylendioxyphenyl)pyrazoline (*3b*)

M.p.: 206–207 °C. Anal. Calcd. (%) for $C_{35}H_{24}ClN_3O_4$: C, 71.73; H, 4.13; N, 7.17. Found (%): C, 71.68; H, 4.40; N, 6.73. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.70 (d, $J = 8.4$ Hz, 1H), 8.64 (d, $J = 7.6$ Hz, 1H), 8.33 (d, $J = 8.4$ Hz, 1H), 6.73–7.73 (m, 14H), 5.90 (d, $J = 12$ Hz 2H), 5.59–5.64 (m, 1H), 5.35 (s, 1H), 3.79–3.86 (m, 1H), 3.23 (dd, $J_1 = 17.0$ Hz, $J_2 = 7.8$ Hz, 1H). IR (KBr, cm^{-1}): 1577, 1645, 1686, 2886, 3030, 3117.

2.2.3. 1-(2-Benzyl-benzo[de]isoquinoline-1,3-dione)-3-(p-tolyl)-5-(phenyl)-2-pyrazoline (*3c*)

M.p.: 212–214 °C. Anal. Calcd. (%) for $C_{35}H_{27}N_3O_2$: C, 80.59; H, 5.22; N, 8.06. Found (%): C, 80.82; H, 5.07; N, 8.31. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.73 (d, $J = 8.8$ Hz, 1H), 8.63 (d, $J = 7.2$ Hz, 1H), 8.28 (d, $J = 8.4$ Hz, 1H), 7.18–7.72 (m, 15H), 6.73 (d, $J = 8.8$ Hz, 1H), 5.64–5.69 (m, 1H), 5.35 (s, 2H), 3.88 (m, 1H), 3.26 (dd, $J_1 = 17.4$ Hz, $J_2 = 7.4$ Hz, 1H). 2.41 (s, 3H). IR (KBr, cm^{-1}): 1573, 1645, 1681, 3029.

2.2.4. 1-(2-Benzyl-benzo[de]isoquinoline-1,3-dione)-3,5-bis(tolyl)-2-pyrazoline (*3d*)

M.p.: 247–250 °C. Anal. Calcd. (%) for $C_{26}H_{29}N_3O_2$: C, 80.72; H, 5.46; N, 7.84. Found (%): C, 80.60; H, 5.94; N, 7.34. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.73 (d, $J = 8.8$ Hz, 1H), 8.64 (d, $J = 7.2$ Hz, 1H), 8.30 (d, $J = 8.4$ Hz, 1H), 7.10–7.72 (m, 14H), 6.75 (d, $J = 8.8$ Hz, 1H), 5.62–5.67 (m, 1H), 5.35 (s, 2H), 3.83–3.90 (m, 1H), 3.25 (dd, $J_1 = 17.4$ Hz, $J_2 = 7.4$ Hz, 1H). 2.42 (s, 3H), 2.29 (s, 3H). IR (KBr, cm^{-1}): 1575, 1640, 1675, 2922.

2.2.5. 1-(2-Butyl-benzo[de]isoquinoline-1,3-dione)-3,5-bisphenyl-2-pyrazoline (*3e*)

M.p.: 229–231 °C. Anal. Calcd. (%) for $C_{31}H_{27}N_3O_2$: C, 78.62; H, 5.75; N, 8.87. Found (%): C, 78.05; H, 5.92; N, 8.94. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.69 (d, $J = 8.8$ Hz, 1H), 8.63 (d, $J = 7.2$ Hz, 1H), 8.28 (d, $J = 8.4$ Hz, 1H), 7.25–7.79 (m, 11H), 6.76 (d, $J = 8.4$ Hz, 1H), 5.66–5.71 (m, 1H), 4.14 (t, $J = 7.6$ Hz, 2H), 3.87–3.94 (m, 1H), 3.29 (dd, $J_1 = 16.8$ Hz, $J_2 = 7.6$ Hz, 1H), 1.64–1.70 (m, 2H), 1.1.39–1.47 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H). IR (KBr, cm^{-1}): 1576, 1649, 1691, 2955.

*2.2.6. 1-(2-Butyl-benzo[de]isoquinoline-1,3-dione)-3-(4-chloro-phenyl)5-(3′,4′-methylendioxyphenyl)pyrazoline (**3f**)*

M.p.: 217–220 °C. Anal. Calcd. (%) for $C_{32}H_{26}ClN_3O_4$: C, 69.62; H, 4.75; N, 7.61. Found (%): C, 69.63; H, 4.89; N, 7.64. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.55 (d, $J = 8.4$ Hz, 1H), 8.63 (d, $J = 7.2$ Hz, 1H), 8.32 (d, $J = 8.4$ Hz, 1H), 7.68–7.74 (m, 3H), 7.43 (d, $J = 8.4$ Hz, 1H), 6.74–6.85 (m, 4H), 5.91 (d, 2H), 5.60–5.64 (m, 1H), 4.15 (t, $J_1 = 7.4$ Hz, 2H), 3.80–3.87 (m, 1H), 3.24 (dd, $J_1 = 17.2$ Hz, $J_2 = 8.0$ Hz, 1H), 1.65–1.73 (m, 2H), 1.25–1.47 (m, 2H), 0.96 (t, $J = 7.2$ Hz, 3H). IR (KBr, cm^{-1}): 1576, 1644, 1681, 2363, 2956.

*2.2.7. 1-(2-Butyl-benzo[de]isoquinoline-1,3-dione)-3-(2-thiophene)-5-(3-thiophene)-2-pyrazoline (**3g**)*

M.p.: 222–224 °C. Anal. Calcd. (%) for $C_{27}H_{23}N_3O_2S_2$: C, 67.78; H, 4.77; N, 8.65. Found (%): C, 67.64; H, 4.88; N, 8.88. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.49 (d, $J = 8.4$ Hz, 1H), 8.61 (d, $J = 7.2$ Hz, 1H), 8.32 (d, $J = 8.0$ Hz, 1H), 7.70 (t, $J = 7.4$ Hz, 1H), 7.44 (d, $J = 4.4$ Hz, 1H), 7.23–7.27 (m, 2H), 7.17 (s, 1H), 7.10 (s, 1H), 7.00 (d, $J = 4.4$ Hz, 1H), 6.88 (d, $J = 8.4$ Hz, 1H), 5.79 (m, 1H), 4.15 (t, $J = 7.2$ Hz, 2H), 3.81–3.87 (m, 1H), 3.32 (dd, $J_1 = 16.8$ Hz, $J_2 = 6.8$ Hz, 1H), 1.65–1.71 (m, 2H), 1.40–1.46 (m, 2H), 0.96 (t, $J = 7.2$ Hz, 3H). IR (KBr, cm^{-1}): 1576, 1689, 2956, 3101.

*2.2.8. 1-(2-Butyl-benzo[de]isoquinoline-1,3-dione)-3-(p-tolyl)-5-(phenyl)-2-pyrazoline (**3h**)*

M.p.: 182–184 °C. Anal. Calcd. (%) for $C_{32}H_{29}N_3O_2$: C, 78.82; H, 5.99; N, 8.62. Found (%): C, 79.03; H, 5.86; N, 8.95. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.72 (d, $J = 8.8$ Hz, 1H), 8.63 (d, $J = 7.2$ Hz, 1H), 8.27 (d, $J = 8.4$ Hz, 1H), 7.26–7.74 (m, 10H), 6.75 (d, $J = 8.4$ Hz, 1H), 5.64–5.69 (m, 1H), 4.14 (t, $J = 7.4$ Hz, 2H), 3.85–3.92 (m, 1H), 3.27 (dd, $J_1 = 17.2$ Hz, $J_2 = 7.6$ Hz, 1H), 2.42 (s, 3H), 1.64–1.72 (m, 2H), 1.38–1.47 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H). IR (KBr, cm^{-1}): 1576, 2864, 2926.

*2.2.9. 1-(2-Butyl-benzo[de]isoquinoline-1,3-dione)-3,5-bis(tolyl)-2-pyrazoline (**3i**)*

M.p.: 187–189 °C. Anal. Calcd. (%) for $C_{33}H_{31}N_3O_2$: C, 79.01; H, 6.23; N, 8.38. Found (%): C, 78.88; H, 6.33; N, 8.54. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.71 (d, $J = 8.8$ Hz, 1H), 8.63 (d, $J = 7.2$ Hz, 1H), 8.28 (d, $J = 8.4$ Hz, 1H), 7.11–7.73 (m, 9H), 6.76 (d, $J = 8.4$ Hz, 1H), 5.62–5.67 (m, 1H), 4.14 (t, $J = 7.4$ Hz, 2H), 3.83–3.90 (m, 1H), 3.25 (dd, $J_1 = 17.0$ Hz, $J_2 = 7.4$ Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H), 1.62–1.70 (m, 2H), 1.40–1.45 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H). IR (KBr, cm^{-1}): 1573, 1676, 2334, 2958, 3124.

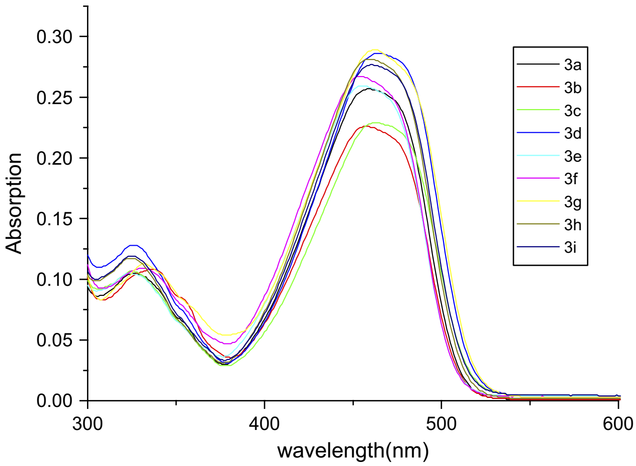


Fig. 1. The normalized UV–vis spectra of compounds **3**(**a**–**i**) in tetrahydrofuran solution with the concentration of 1×10^{-5} M.

3. Results and discussion

3.1. Absorption spectra

The UV–vis spectrums of **3**(**a**–**i**) are shown in Fig. 1. The absorptions of the compounds were the results of the interaction between two chromophores, and their absorption bands ranged from 310 to 465 nm. The absorption of **3d** was located at 465 nm and others appeared from 455 to 465 nm.

The difference of absorption was due to *N*- on 4-position of 1,8-naphthalimide and different groups on 3- and 5-position of pyrazoline.

3.2. Fluorescence

Fig. 2 presents the emission spectrums of **2**(**a**, **b**), and Fig. 3 presents the emission spectrums of **3**(**a**–**i**) in tetrahydrofuran solution (1×10^{-5} M). Their excitation wavelengths were all fixed at 450 nm. It can be found that their intensity of

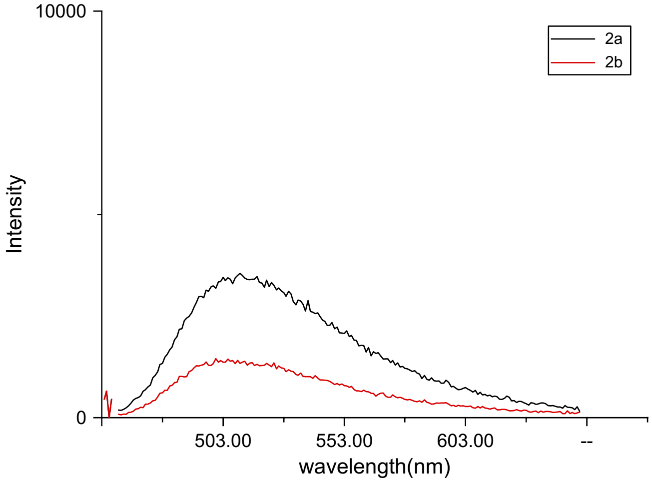


Fig. 2. The emission spectra of compound **2** in tetrahydrofuran solution with the concentration of 1×10^{-5} M.

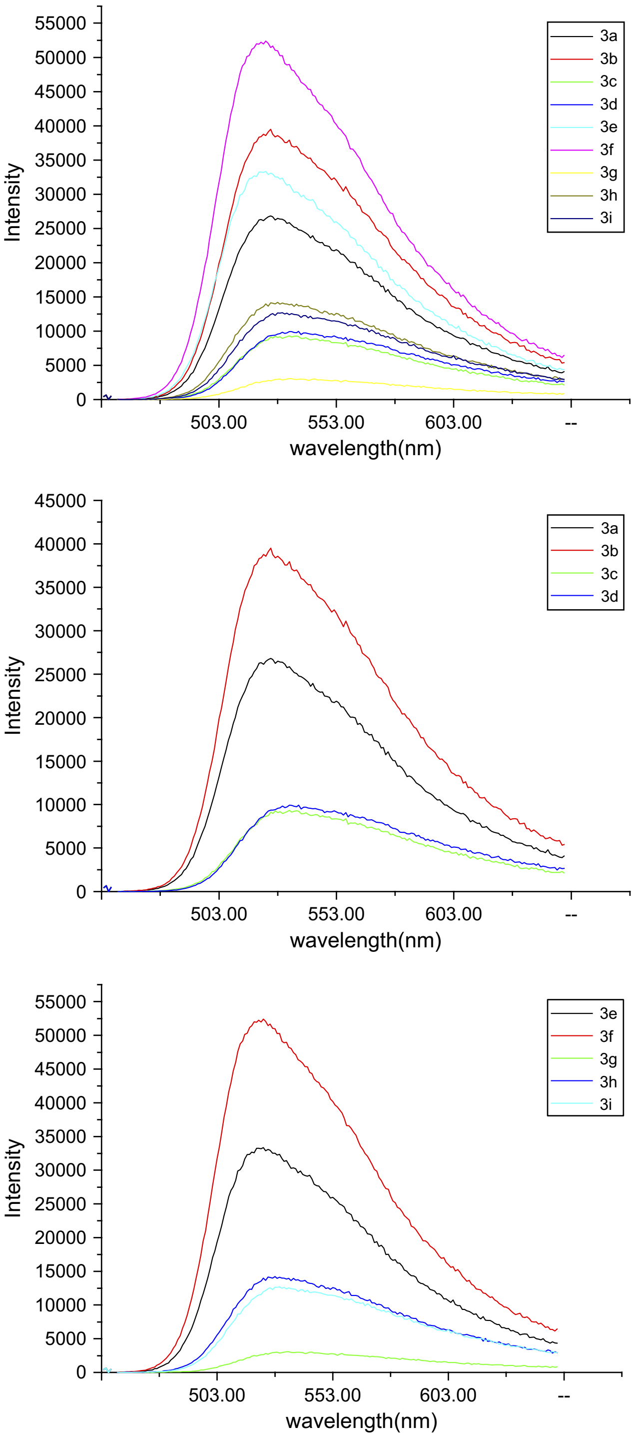


Fig. 3. The emission spectra of compound **3** in tetrahydrofuran solution with the concentration of 1×10^{-5} M.

Table 2
Absorption and fluorescence spectra of compounds **3**(**a**–**i**)

Compound	$\lambda_{\max}^{\mathrm{em}}$ (nm)	$\lambda_{\max}^{\mathrm{abs}}$ (nm)
3a	525	460
3b	525	458
3c	533	463
3d	537	465
3e	523	456
3f	521	454
3g	533	462
3h	528	460
3i	530	461

fluorescence differed from each other. From the fluorescence of **3**(**a**–**i**), it can also be found that these bischromophore compounds have red-shift phenomenon compared with **2a** and **2b**. Since the emission wavelength of 4-amino-1,8-naphthalimide derivatives is red-shifted from blue to red region [27] and many 1,3,5-triaryl-2-pyrazolines have been reported as blue emitting materials [10–14], we concluded that these compounds containing naphthalimide and pyrazoline chromophores interacted with each other in a manner leading to a red-shift of these bischromophore compounds.

As shown in Table 2, the maximal emission bands were all in the range of 520–540 nm. Comparing the fluorescence of **3a** with **3e**, **3d** with **3i**, it was found that they had similar fluorescence wavelengths. Then we concluded that different carbon chain groups at *N*-position of 1,8-naphthalimide had little influence on the excitation wavelengths.

From **3f**, **3e**, **3h** and **3i** whose emission wavelengths were 521, 523, 528 and 530 nm, it was found that they were red-shifted. We concluded that groups at 3- and 5-position with electron-donating substituents such as methyl could lead to a red-shifted phenomenon, with electron-withdrawing ones could lead to a blue-shifted phenomenon. Meanwhile, when we compared these novel bischromophore compounds with other pyrazoline derivatives whose 1-position had phenyl, a red-shifted phenomenon was found. So it was concluded that the groups at both positions 1 and 3 had very strong influence on the emission fluorescence of these compounds.

4. Conclusion

A series of novel bischromophore compounds containing pyrazoline and naphthalimide groups were synthesized and also their absorption and photoluminescence in tetrahydrofuran solution were studied. Moreover, we found groups on 3- and 5-, and especially on 1-position of pyrazoline influenced the emission wavelength of these novel bischromophore compounds. Since they have different emitting fluorescence wavelengths, ranging from 520 to 540 nm, these bischromophore compounds may serve as good green light-emitting materials.

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