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New benzo[e]indolinium cyanine dyes with two different fluorescence wavelengths

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Abstract

Three compounds, which comprise of benzo[e]indolinium luminophores with two different fluorescence wavelengths, have been synthesized. Those compounds have been prepared by condensation of benzo[e]indolinium and their counterpart aldehydes, and they were confirmed by H-NMR, MS, IR. The absorption and fluorescence spectra of them were tested. The influences of pH value and various solvents on their absorption and fluorescence spectra were summarized. At the same time, self-condensation of benzo[e]indolinium was found in the synthesis of three compounds above.

Keywords: Benzo[e]indolinium; Fluorescence; Condensation; Synthesis; Cyanines

1. Introduction

Methine cyanine dyes have attracted much attention because of their potential applications in organic functional materials [1–5]. In recent years, they have been used extensively as optical recording materials [6–8]. Cyanine dyes with short methine chains are readily soluble in common organic solvents such as ethanol and acetone. However, a convenient method for synthesis of these short methine chains still needs to be developed. The majority of methine cyanines reported for use in optical recording materials belong to the class of symmetrical cyanine dyes, whereas unsymmetrical methine cyanines have superior optical properties and alcohol solubility [9]. During previous investigations into the syntheses of methine cyanines, we have accessed the methine chain system via an expeditious condensation reaction of (1,3,3-trimethyl-1,3-dihydro-indol-2-ylidene)-acetaldehyde with methylpyridinium iodide [10]. This route would allow access to methine cyanine dyes with unsymmetrical structures. Benzo[e]indolinium derivative is an important part of cyanine dyes. Here, three novel unsymmetrical cyanines named A, B, C respectively, which have two different fluorescence wavelengths and comprise of benzo[e]indolinium luminophores were synthesized. Compound A comprises of a 3-sulphonaphthalimide unit and benzo[e]indolinium, which would be expected to show two identical emission peaks with different excited wavelengths and would be used for identical

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addresses with fluorescent probe. Recently, we used the 4-amino-1,8-naphthalimide fluorophore to design dual-mode protons/electrochromic molecular switches and functional fluorescent imaging polymers [11–13]. Compounds B and C consist of the typical hole transporting units- *N*,*N*′-di(4-butylphenyl)-*N*,*N*′-diphenyl-phenanthrene-9,10-diamine and triphenylamine [14], respectively. A self-condensation product (D) of 1,1,2,3-tetramethyl-1H-benzo[e]indolinium was also synthesized.

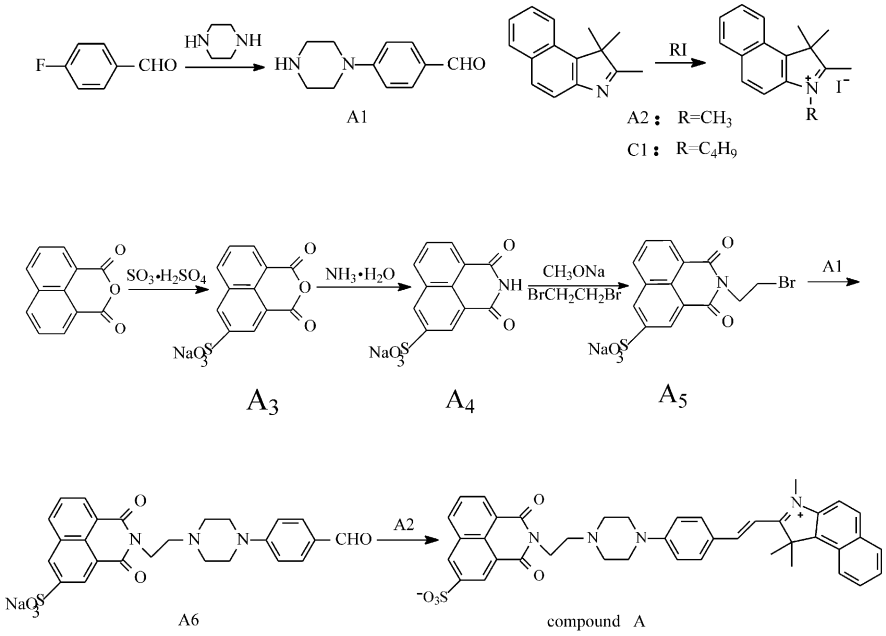
2. Syntheses

The synthesis of compounds A, B, C and D, along with their precursors, was illustrated in Schemes 1–4. Scheme 1 demonstrates the synthesis of compound A, which has two luminophores, 1,8-naphthalimide and styrene-benzo[e]indolinium. 1,8-Naphthalimide recrystallized from acetic anhydride was used as the starting material for the preparation of compound A. 1,8-Naphthalimide was sulfonated to give A3, which reacted with ammonia to afford A4. A4 was reacted with sodium methanol and 1,2-dibromoethane to give A5. A6 was obtained by the reaction of A5 and 4-pierazino-benzylalhedyde (A1). Then A6 condensed with 1, 1, 2, 3-tetramethyl-1H-benzo[e]indolinium iodide (A2) to afford the target compound A.

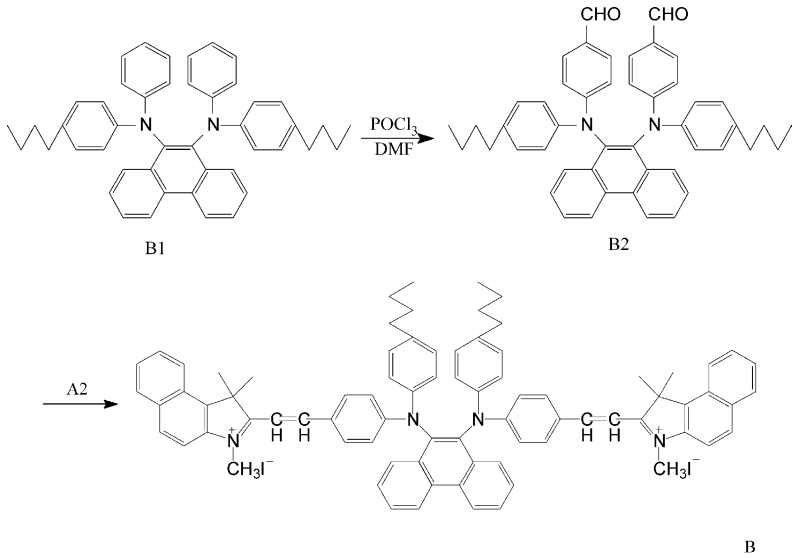
Scheme 2 shows the process of synthesizing compound B, a dication cyanine. *N*,*N*′-di(4-butylphenyl)-*N*,*N*′-diphenyl-phenanthrene-9,10-diamine (B1) has previously been described [14,15] and was aldehyded to give dialdehyde (B2), which condensed with A2 to afford compound B.

This reaction was extended to synthesize compound C (Scheme 3), which has a triphenylamine luminophore and a styrene-benzo[e]indolinium luminophore. *N*-2-Ethyl-6-methylphenyl-*N*-phenyl-4-aldehyde-phenylamine (C2) was synthesized according to a patent [16] and condensed with 1,1,2-trimethyl-4-butyl-1H-benzo[e]indolinium iodide (C1) to give compound C.

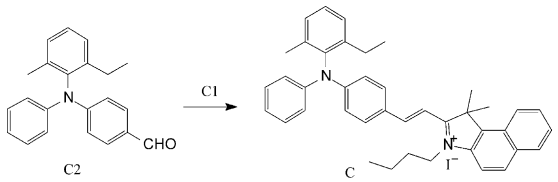
In the process of synthesizing compounds A, B and C, self-condensation of A2 was also found. Several experiments were done to prove this case. A2 was used as the starting material, and H_2O, ethanol, pyridine was used as solvents respectively. The experiments show that the basicity of pyridine makes it very fit to be the solvent of self-condensation.



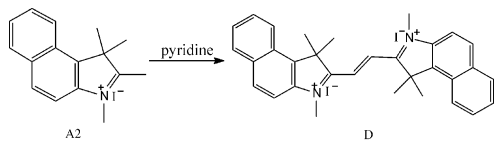
Scheme 1. Synthetic procedure for compound A.



Scheme 2. Synthetic procedure for compound B.



Scheme 3. Synthetic procedure for compound C.



Scheme 4. Synthetic procedure for compound D.

Scheme 4 shows the synthesis of compound D, a self-condensation of A2. ^{1}H-NMR and MS also confirmed its presence.

3. Experimental section

3.1. General methods and materials

^{1}H-NMR spectra were recorded on a Brucker DRX instrument at 300 and 500 MHz, and Mass spectra were obtained with HP5989A, Mariner API time of flight (TOF, TIS ion source, PE Corp.) and API2000 (TIS, PE Corp.) spectrometers. Infrared spectra were measured on a Nicolet Magna IR550. UV–vis-NIR spectra were recorded on a Varian Cary500. Fluorescence spectroscopy was recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer. An elementar vario EL III (made in Germany) analyzer was used for element analysis. All chemicals except triphenylamine were purchased from commercial suppliers and used with purification.

3.2. Experimental

3.2.1. Synthesis of 4-pierazino-benzylalhedyde (A1)

Piperazine (15 g, 0.174 mol), 4-fluorobenzaldehyde (5 ml, 46.4 mmol) were mixed and dissolved in H_2O (18 ml) and 2-methoxyethanol (25 ml). Then the mixture was refluxed for 3 h. After cooling down to room temperature, the mixture was poured into H_2O (200 ml) to afford a yellow precipitate. After being filtered, the filter cake was dissolved in 10% hydrochloric acid (150 ml), then filtering to remove the residue, the solution of 20% sodium hydroxide was added to the filtrate until the pH value was 10. The dichloromethane (3×80 ml) was added to the mixture to

extract the product. The organic layer was washed with H_2O (50 ml), dried with anhydrous sodium sulfate and concentrated in vacuum to afford a yellow product (6.0 g, 68%), m.p. 177–178 °C.

3.2.2. Synthesis of 1,1,2,3-tetramethyl-1H-benzo[e]indolinium iodide (A2) [17]

The mixture of 1,1,2-trimethyl-1H-benzo[e]-indole (10.5 g, 50 mmol) and methyl iodide (3.5 ml, 100 mmol) in toluene (50 ml) was refluxed for 7 h to afford a white solid. After cooling and filtering, the filter cake was washed with ethanol and dried in vacuum to give a white solid (15.8 g, 90%), m.p.159–160 °C.

3.2.3. Synthesis of 1,8-naphthalic anhydride-3-sulfonate sodium (A3) [13,18,19]

1,8-Naphthalic anhydride (7.7 g, 39.09 mmol), 98% concentrated sulfate acid (9.1 ml), 50% fuming sulfonic acid (15 ml) were mixed and stirred at 90 °C for 0.5 h. After cooling down to room temperature, the mixture was poured into ice-water (200 ml). Sodium chloride (30 g) was added to the solution, and a white deposit was filtered and washed with 10% sodium chloride and ethanol. Intensive drying gave 11 g A3 (94.3%), m.p. > 300 °C.

3.2.4. Synthesis of 1,8-naphthalimide-3-sulfonate sodium (A4)

A3 (4.7 g, 5.7 mmol) was dissolved in 16% ammonia solution (40 ml), then the mixture was stirred at 90 °C for 2 h. After cooling, the deposited white solid was filtered. The solid was stirred in 50 ml ethanol for 1 h. After being filtered, the filter cake was washed with ethanol and dried to afford a white product (4.5 g, 96%), m.p. > 300 °C.

3.2.5. Synthesis of N-(2-bromoethyl)-1,8-naphthalimide-3-sulfonate sodium (A5)

Na 0.36 g (15.5 mmol) was dissolved in methanol (20 ml). Then the solution of sodium methanol was added to a stirred solution of A4 (4.5 g, 15.05 mmol) in dry DMF (80 ml). The mixture was stirred for 0.5 h. Then 1,2-dibromoethane (6.8 ml, 77.5 mmol) was added quickly and stirred for 2 h. The mixture was poured into 20% sodium chloride solution (300 ml). The deposited white solid was filtered and washed with 10% sodium chloride solution and ethanol respectively to afford A5 (3 g, 53.5%), m.p. > 300 °C.

^{1}H-NMR (D_2O): δ (ppm) 3.78 (t, $J = 5.7$ Hz, 2H), 4.20 (t, $J = 5.7$ Hz, 2H), 7.75 (t, $J_1 = 7.81$ Hz, $J_2 = 6.75$ Hz, 1H), 8.31 (d, $J = 7.81$ Hz, 1H), 8.41 (d, $J = 6.75$ Hz, 1H), 8.61 (s, 2H).

3.2.6. Synthesis of N-{2-[4-(4-formylphenyl)-piperazino-1-yl]-ethyl}-1,8-naphthalimide-3-sulfonate sodium (A6)

A1 (1.7 g, 8.95 mmol), potassium carbonate (2 g, 4.6 mmol), DMF (20 ml) was mixed and stirred at 120 °C for 0.5 h. Then A5 (1.2 g, 2.96 mmol) was added and the mixture was heated for 4 h under Ar. After cooling down to room temperature, the mixture was poured into 10% hydrochloric acid (100 ml). The solid deposited was filtered and the filter cake was dissolved in 10% sodium hydroxide (100 ml), and filtered to remove the solid components, and the solution was acidified with hydrochloric acid to precipitate yellow solid. After being filtered, the filter cake was washed with ethanol and moved to a mixture of sodium hydroxide (0.4 g), H_2O (5 ml) and ethanol (50 ml). The mixture was stirred for 20 h at room temperature. The solid was filtered and dried to give A6 (0.5 g, 32%), m.p. > 300 °C.

3.2.7. Synthesis of compound A

The mixture of A6 (0.3 g, 0.57 mmol) and A2 (0.3 g, 0.86 mmol) in H_2O (90 ml) was heated to 70 °C and potassium carbonate was added to adjust pH value to 8. The solution was maintained at 70 °C for 24 h under an atmosphere of Ar gas. After cooling down to room temperature, the red solid deposited was filtered and washed with ethanol. The solid was purified by column chromatography (silica, DMF:acetone = 1:2) to afford A (0.2 g, 50.8%), m.p. > 300 °C.

^{1}H-NMR (DMSO-d6): δ (ppm) 1.96 (s, 6H), 3.33 (t, 8H), 3.50 (t, 2H), 4.13 (s, 3H), 4.25 (t, 2H), 5.76 (d, $J = 8.75$ Hz, 2H), 7.15 (d, $J = 7.44$ Hz, 2H), 7.36 (d, $J = 15.51$ Hz, 1H), 7.7 (t, $J_1 = 7.62$ Hz, $J_2 = 7.26$ Hz, 2H), 7.88 (t, $J_1 = 7.73$ Hz, $J_2 = 7.33$ Hz, 1H), 7.99 (d, $J = 8.84$ Hz, 1H), 8.07 (d, $J = 8.29$ Hz, 1H), 8.16 (d, $J = 8.29$ Hz, 1H), 8.22 (d, $J = 8.75$ Hz, 1H),

8.37 (t, $J_1 = 8.06$ Hz, $J_2 = 14.86$ Hz, 1H), 8.50 (d, $J = 7.09$ Hz, 1H), 8.56 (d, $J = 8.49$ Hz, 1H), 8.67 (s, 2H). MS-ES + (%): m/z, 699.2([M + 1], 100), 625(58).

3.2.8. Synthesis of compound N,N′-Bis-(4-butylphenyl)-N,N′-di-p-benzylaldehyde-phenanthrene-9,10-diamine (B2)

Phosphorus oxychloride (15 g) was added into DMF (10 ml) under ice-bath to maintain 0–10 °C, then a solution of *N*,*N*′-di(4-butylphenyl)-*N*,*N*′-diphenyl-phenanthrene-9,10-diamine (B1, 1.5 g) DMF (25 ml) was added dropwise slowly into the previous solution. After dropping, the mixture was stirred for 10 h at 90 °C and poured into ice-water (150 ml). Sodium hydroxide was added to adjust pH value to 8. Then the mixture was heated to 80 °C and stirred for 20 min. After cooling, the solid deposited was filtered and the solid was recrystallized from chloroform/hexane to give yellow product B2 (1.0 g, 73.7%), m.p.194 °C.

MS (EI,%): m/z, 680(82).IR (KBr): 3070, 2970, 2910, 2820, 2450, 1700, 1600, 1570, 1500, 1300, 1220, 1170, 820, 760, 720.

3.2.9. Synthesis of compound B

B2 (0.4 g, 0.59 mmol) and A2 (0.413 g, 1.18 mmol) was mixed and dissolved in pyridine (25 ml). The solution was stirred under reflux for 5 h. After cooling down to room temperature, the solid deposited was filtered and washed with pyridine and H_2O respectively to afford black product (0.12 g, 12.5%), m.p. > 300 °C.

^{1}H-NMR ($CDC1_3$): δ (ppm) 0.88 (t, 6H), 1.24 (m, 4H, CH_2), 1.4 (m, 4H, CH_2), 1.97 (s, 12H), 2.4 (m, 4H, CH_2), 3.78 (t, 6H), 5.46 (d, 4H), 6.55–6.60 (m, 16H), 7.54 (t, 2H), 7.69 (t, 2H), 7.82 (d, 2H, $J = 8.24$), 8.14 (m, 8H), 8.31 (m, 4H), 8.58 (t, 2H, $J = 8.35$).

3.2.10. Synthesis of 3-butyl-1,1,2-trimethyl-1H-benzo[e]indolinium iodide (C1)

The mixture of 1,1,2-trimethyl-1H-benzo[e]-indole (4 g, 0.019 mol) and butyl iodide (3.5 g, 0.019 mmol) in butanol (50 ml) was refluxed for 20 h. After cooling and filtering, the filter cake was washed with ethanol and dried in vacuum to give white solid (3.6 g, 54%), m.p. 114–115 °C.

^{1}H-NMR($CDCl_3$): δ (ppm) 1.0 (t, 3H, CH_3), 1.52 (m, 2H), 1.84 (s, 6H), 2.0 (m, 2H), 3.2 (s, 3H), 4.7 (t, 2H), 7.67 (t, 1H), 7.75 (t, 1H), 7.8 (d, 1H,), 8.05–8.15 (m, 10H).

3.2.11. Synthesis of N-2-ethyl-6-methylphenyl-N-phenyl- {4-[2-(1,3,3-trimethyl-1H-benzo[e]indolinium-2-yl)-vinyl]-phenyl}-amine iodide (C)

The mixture of *N*-2-ethyl-6-methylphenyl-*N*-phenyl-4-aldehyde-phenylamine (C2, 5 g, 0.016 mmol) and C1 (6.5 g, 0.016 mmol) in ethanol (80 ml) was stirred under reflux for 2 h. After cooling, the solid deposited was filtered and recrystallized from ethanol to afford purple crystal (5.6 g, 51%), m.p. 186–187 °C.

^{1}H-NMR($CDCl_3$): δ (ppm) 0.98 (m, 6H), 1.62 (m, 4H), 1.96 (m, 2H), 2.05 (s, 3H), 2.12 (s, 6H), 2.46 (m, 2H), 5.01 (t, 2H), 6.98 (d, 2H), 7.13 (m, 3H), 7.21 (d, 1H), 7.23 (d, 1H), 7.30 (m, 3H), 7.62 (m, 2H), 7.70 (d, 1H), 7.73 (t, 1H), 8.06 (m, 4H), 8.20 (m, 2H).

3.2.12. Synthesis of D

A2 (2 g, 5.73 mmol) was dissolved in pyridine (20 ml) and the solution was heated to 100 °C for 20 h under an atmosphere of Ar gas. The solvent was removed in vacuum. The residue was purified by column chromatography (silica, acetic acid:-acetone = 50:1) to afford purple solid D (0.5 g, 26%), m.p. 210–212 °C.

^{1}H-NMR (CD_3COCD_3) δ (ppm): 2.10 (s, 12H), 3.92 (s, 6H), 6.65 (d, $J = 13.63$ Hz, 2H), 7.57 (t, $J_1 = 7.14$ Hz, $J_2 = 7.43$ Hz, 2H), 7.71 (t, $J_1 = 7.22$ Hz, $J_2 = 7.07$ Hz, 2H), 7.79 (d, $J = 8.9$ Hz, 2H), 8.10 (d, $J = 8.18$ Hz, 2H), 8.14 (d, $J = 8.82$ Hz, 2H), 8.14 (d, $J = 8.5$ Hz, 2H). MS (EI,%): m/z, 218 (80), 233.2 (21).

4. Absorption and fluorescence properties

4.1. Absorption and fluorescence properties of compound A

Table 1 shows the relevant data of the absorption and fluorescence spectra of compound A when various kinds and different concentrations of

Table 1
Absorption and fluorescence data of compound A (1×10^{-5} mol/l) at different ion solutions ($CH_3OH:H_2O = 1:1$ v/v)

Ion ($\times10^{-5}$ mol/l)		λ^{ab}_{max} (log ε)	λ^{flu}_{max} (intensity)	
			$\lambda_{ex} = 330$	$\lambda_{ex} = 532$
0		337 (4.196), 532 (4.127)	391.8 (20.27)	607.9 (42.22)
Co^{2+}	2	337 (4.196), 531 (4.137)	390.9 (20.18)	607 (44.46)
	4	332 (4.230), 527 (4.155)	388.9 (21.13)	607 (45.00)
	6	332 (4.223), 527 (4.152)	388.9 (21.13)	607 (44.75)
	8	331 (4.230), 527 (4.137)	390 (22.03)	607 (43.27)
Cu^{2+}	2	336 (4.204), 529 (4.152)	389.9 (20.25)	605 (43.57)
	4	335 (4.204), 528 (4.130)	389.9 (20.76)	607 (45.09)
	6	336 (4.201), 529 (4.149)	390.9 (21.9)	607 (43.91)
	8	336 (4.196), 529 (4.107)	388.9 (22.64)	607 (39.42)
Mn^{2+}	2	337 (4.196), 531 (4.137)	391.8 (19.99)	605 (23.27)
	4	336 (4.201), 529 (4.149)	389.8 (20.73)	607.5 (39.02)
	6	336 (4.207), 529 (4.155)	391.8 (20.38)	605 (41.28)
	8	336 (4.207), 529 (4.158)	388.9 (21.33)	604 (35.74)
Ni^{2+}	2	332 (4.204), 527 (4.146)	387.8 (20.96)	607 (30.40)
Zn^{2+}	2	337 (4.204), 531 (4.064)	391.8 (21.31)	606.2 (38.29)
Fe^{2+}	2	337 (4.196), 531 (4.137)	390.9 (21.52)	607 (31.84)

ions are present. As seen from Table 1, ions have little influence on the spectra of compound A. Two identical fluorescent peaks obtained at the different excited wavelengths result from the two fluorescent units in compound A, i.e. 3-sulphonaphthalimide moiety (short wavelength region) and a styrene-benzo[e]indolinium luminophore (longer wavelength region).

A further measurement was done to investigate the influence of pH, because the difference of pH value may influence the spectra of cyanine part in compound A. We used methanol and H_2O (1:1) as solvent, and the relevant data of the spectra at different pH values (2–12) have been collected and listed in Table 2. Figs. 1 and 2 show the absorption and fluorescence spectra respectively. As

Table 2
Absorption and fluorescence data of compound A (1×10^{-5}mol/l) at different pH value solutions (CH_3OH: $H_2O = 1:1$ v/v)

pH	λ^{ab}_{max} (log ε)	λ^{flu}_{max} (intensity)	
		$\lambda_{ex} = 330$	$\lambda_{ex} = 530$
3	338.4 (4.46), 529.4 (3.892)	393 (26.03)	594 (71.19)
4	337.4 (4.405), 528.4 (4.290)	392.2 (25.03)	594.9 (74.77)
5	336.4 (4.365), 529.8 (4.366)	379.8 (25.89)	596.9 (76.89)
6	337.4 (4.365), 531.8 (4.377)	383.1 (24.41)	605.7 (69.10)
7	337.8 (4.366), 529.8 (4.384)	389.8 (21.86)	604.9 (73.13)
8	337.2 (4.377), 528.2 (4.398)	388 (20.59)	606 (71.07)
9	333 (4.378), 522.4 (4.415)	396.9 (25.56)	607 (72.22)
10	329.6 (4.410), 504 (4.511)	378 (26.87)	606 (69.34)
11	330.4 (4.413), 501 (4.516)	394 (23.75)	607.9 (37.48)
12	331.8 (4.447), 497.8 (4.535)	389.8 (23.67)	595.7 (4.38)

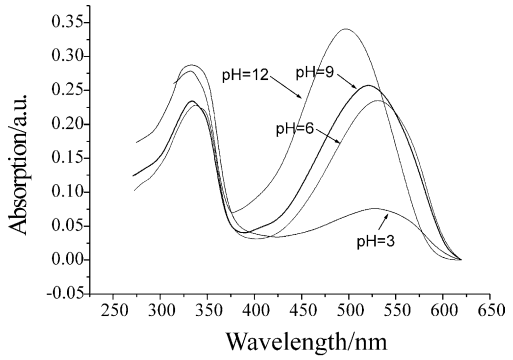


Fig. 1. Absorption spectra of compound A (1×10^{-5} mol/l) at different pH value solutions (CH_3OH:H_2O = 1:1 v/v).

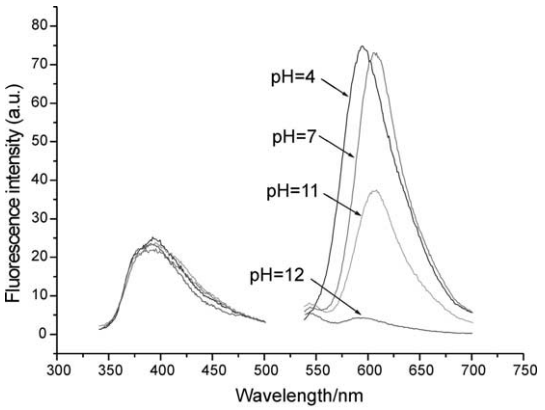


Fig. 2. Fluorescence spectra of compound A (1×10^{-5} mol/l) at different pH value solutions (CH_3OH:H_2O = 1:1 v/v). (Left curves: 3-sulphonaphthalimide unit. Right: the ones of styrene-benzo[e]indolinium part).

shown in Fig. 1, the peak at around 330–340 nm is due to the absorption of the 3-sulphonaphthalimide unit and the peak at around 500–530 nm is due to the absorption of styrene-benzo [e]indolinium group. The pH values affect little on the absorption spectra of 3-sulphonaphthalimide part but much on styrene-benzo[e]indolinium part. At the absorption band of 450–560 nm, the value of ε becomes intensive and the absorption wavelength has an distinctive blue-shift when pH value changes from 3 to 12. The compound does not absorb above 450–560 nm by and large when pH value is 3. The changes of the fluorescence spectra are similar, as shown in Fig. 2. On one hand, the peak shapes of the 3-sulphonaphthalimide unit are nearly the same when the pH value changes from 3 to 12; on the other hand, the fluorescence spectrum of styrene-benzo[e]indolinium part is influenced obviously when pH value is 11 and 12. When pH value is 3–10, the change in fluorescence spectra is relative small. But the fluorescence was quenched obviously (shown in Fig. 2) when pH value changes from 11 to 12. Those changes are probably due to the change of the structure of styrene-benzo[e]indolinium part. When compound A is in an acid or a weak base environment, it exists, shown in Fig. 3, in form **a**. When in an intensive base environment, compound A changes to form **b** structure. The places of donor and acceptor in the system are changed which results in the blue shift of the absorption spectrum and the quenching of the fluorescence.

4.2. Absorption and fluorescence properties of compound B

Compound B as a cyanine—its absorption and fluorescence spectra may be influenced very much in different solvents and different concentrations, which is known as solvatochromism [20]. Table 3 shows the data of the absorption spectra in DMF solution of different concentrations. It can be seen that, when the solution was diluted from 1.96×10^{-5} M to 1.96×10^{-6} M, a peak in the short wave region increases and the peak in the long wave region disappears. Fig. 4 shows the absorption spectra of compound B in different solvents. As seen, though the peak shapes are

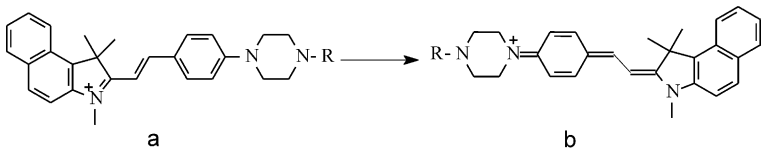


Fig. 3. The suggested structural change of compound A in the environment.

similar, the absorption curves are different from each other, that is, the colors of the solutions are different.

Besides the solvatochromism, concentration quenching effect was studied. As shown in Fig. 5, the fluorescence intensity in DMF solution increases first and decreases later with the accretion of the concentration. For the small concentration of the compound (below 1.0×10^{-5} mol/l), the higher the dispersing degree in the solvents, the more intensive the fluorescence has. For relatively high concentration (greater than 1.0×10^{-5} mol/l), the fluorescence decreases with the increasing of the concentration. The changes of the fluorescence spectra (Fig. 6) and the fluorescence intensity (Fig. 7) in acetone solution are similar.

The fluorescence spectra of compound B in various solvents are shown in Fig. 8 when excited at 342 nm. As we can see, the peak shapes are same. But the fluorescence in acetic acid is different from others. The fluorescence wavelength in acetic acid is shorter (415 nm) than one in dichloromethane (470 nm) and the fluorescence was quenched in CH_3COOH. This is probably due to the interaction

Table 3
Absorption data of compound B in DMF solutions

Concentration (M)	1.96×10^{-5}		7.85×10^{-6}		1.96×10^{-6}	
λ_{max}^{ab} (nm)	329	551	342	548	342	545
log ε	–	4.35	4.65	4.36	4.61	–

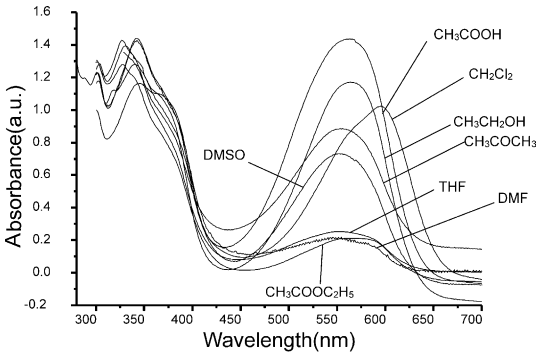


Fig. 4. Absorption spectra of compound B (1×10^{-5} mol/l) in different solvents.

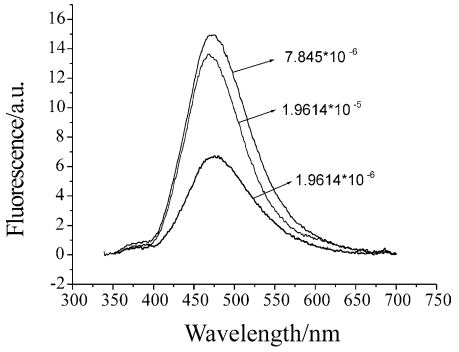


Fig. 5. Fluorescence spectra of compound B in DMF solutions of different concentrations ($\lambda_{ex}=342$ nm).

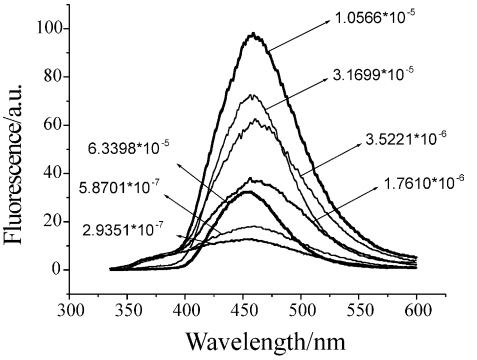


Fig. 6. Fluorescence spectra of compound B in acetone solutions of different concentrations ($\lambda_{ex}=325$ nm).

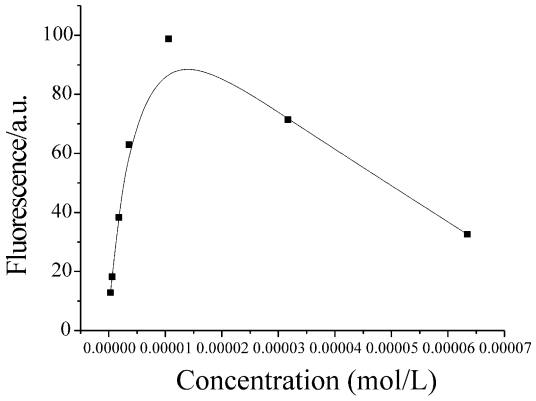


Fig. 7. Fluorescence intensity change of compound B at different concentrations.

of acetic acid and cyanine molecule. The fluorescence spectrum in acetic acid solution was different from that in other solvents when the excitation was at 595 nm (Fig. 9). Comparing Figs. 8 and 9, two fluorescent peaks obtained at the different excited wavelengths are identified with each other, which indicates that compound B could be used as a special fluorescent probe with two addresses of emission. In addition, the emission peaks of compound B were very sensitive to the proton, which might be used as a probe for proton with two excited wavelengths.

4.3. Absorption and fluorescence properties of compound C

Fig. 10 shows the absorption and fluorescence spectra of compound C. Compound C absorbs at 360 and 585 nm and has an emission wavelength at 653 nm, and the fluorescence intensity is weak because of low quantum efficiency of cyanine and the reabsorption in the spectral region.

4.4. Absorption and fluorescence properties of compound D

Compound D is a product of self-condensation of benzo[e]indolinium. It absorbs in 596.6 and 556.8 nm in chloroform solution. The dication of compound D might also result in its water solubility, which is very useful for biological probing. The absorption in other solvents such as methanol, acetone and H_2O were also measured. The relevant data have been collected and listed in Table 4. The fluorescence was also measured and the data were shown in Fig. 11. With the increasing of the polarity of the solvents ($CHCl_3 < CH_3COCH_3 < CH_3OH < H_2O$), the maximum absorption wavelength of

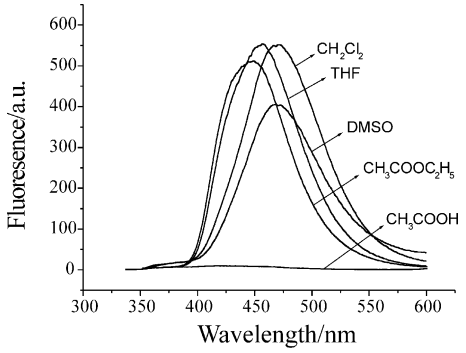


Fig. 8. Fluorescence spectra of compound B in various solvents (1×10^{-5} mol/l, $\lambda_{ex} = 342$ nm).

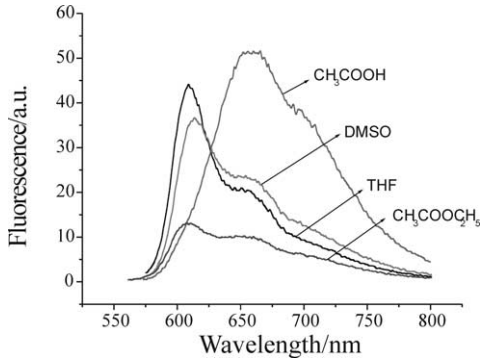


Fig. 9. Fluorescence spectra of compound B in various solvents (1×10^{-5} mol/l, $\lambda_{ex} = 555$ nm).

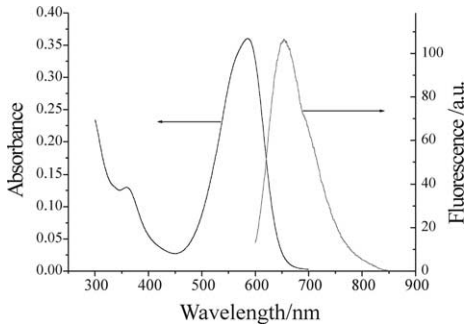


Fig. 10. Absorption and fluorescence spectra of compound C in $CHCl_3$ (1×10^{-5} mol/l).

Table 4
Absorption and fluorescence data of compound D in different solvents. Absorption: 1.0×10^{-5} M; fluorescence: 2.0×10^{-6} M

Solvent	Absorption	Fluorescence	
	λ^{ab}_{max} (log ε)	λex (nm)	λem (intensity)
$CHCl_3$	596.6 (5.06); 556.8 (4.84)	597	610.88 (601.5)
CH_3COCH_3	584.2 (5.02); 547.8 (5.14)	584	604.5 (528.8)
CH_3OH	584.4 (5.02); 547.2 (4.87)	584	602.5 (372.4)
H_2O	579.2 (4.91); 542.1 (4.76)	579	596.4 (91.5)

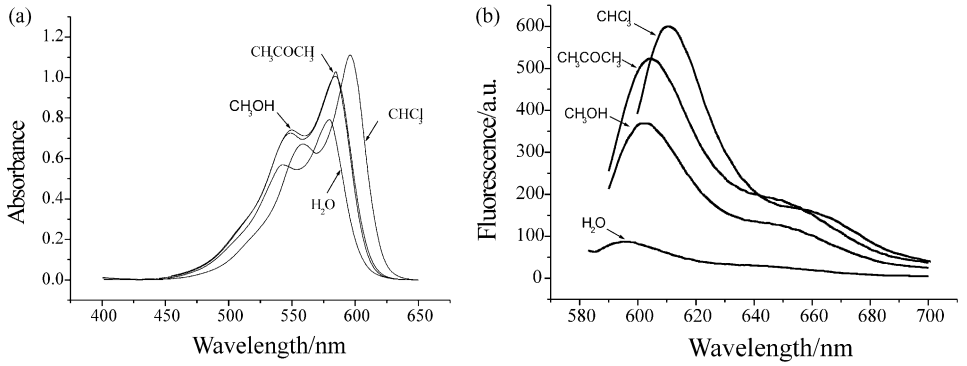


Fig. 11. (a) Absorption spectra of compound D in various solvents. (b) Fluorescence spectra of compound D in various solvents.

compound D has a blue-shift of 17.4 nm, and the fluorescence intensity decreases. As seen from Table 4 and Fig. 11, the Stokes shifts of compound D in various solvents were small (less than 20 nm), which would result in a low fluorescence quantum yield due to the inevitable reabsorption.

5. Conclusions

Three novel methine cyanine dyes, which comprise of benzo[e]indolinium luminophores, have been synthesized using a new synthetic strategy of condensation reaction. They show two different fluorescence emission peaks and might be used as a special fluorescent probe with two addresses of emission. Compound D with dication, a water soluble product self-condensed of benzo[e]indolinium, was also synthesized by a concise simple route. The absorption spectra and fluorescence spectra were investigated and the influences on the spectra by pH value, ions and solvents were discussed.

Acknowledgements

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