SYNTHESIS OF NEW SPIROPYRANS AND SPIROOXAZINES HAVING A HETEROAROMATIC PENDANT AND THEIR PHOTOCHROMIC BEHAVIOR

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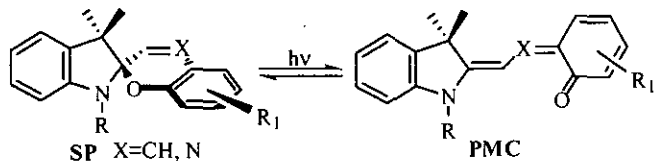
Abstract — Two series of novel spiropyrans and spirooxazines having a heteroaromatic pendant were synthesized using two convenient methods. Their photochromic behaviors were investigated with the aid of absorption spectral measurements. The compounds showed several features different from the parent spiro compounds, including an inhibitory effect on the fatigue during the photochromic process of spiropyrans.

INTRODUCTION

Photochromism involving reversible change in the visible absorption spectrum has attracted much attention in the last decades due to the various potential applications of the photochromic systems.[1~4] Spiropyrans and spirooxazines, the important classes of photochromic materials, have been extensively investigated.[5~16] The photochromic processes of these compounds are accompanied by intramolecular pericyclic reactions (Scheme 1).[4,17,18] The reversible transformation between the closed spiro form (SP) and the open photomerocyanine form (PMC) results in a color change.

Scheme 1



SP X=CH, N **PMC**

It is well known that the photochromic behaviors of these compounds are affected by their structures and the media. The λ_{max} and the stability of compounds in the open form showed remarkable substituent effects.[19~22] As for the media effect, it has been reported that many factors such as temperature, solvent, pH, concentration, coexisting ion, etc., could influence on the photochromic behaviors, such as the rate of color change, the λ_{max} of the colored form, aggregation of the compounds, especially the stability of the open form.[23~26] Such factors might change the microenvironment of the photochromic compounds. We were interested to see how a particular group linked as a pendant to a spiro-compound through a number of s-bonds affects its photochromic behavior.

With this aspect, we report here on the synthesis of a series of new spiropyrans and spirooxazines containing a heteroaromatic group and their photochromic behavior in solution with the aid of the UV-VIS absorption spectral measurements.

RESULTS AND DISCUSSION

Synthesis

The reference compounds (**1**)[27] and (**2**)[28] were synthesized according to the literatures and used for comparisons with a series of spiropyrans and spirooxazines.

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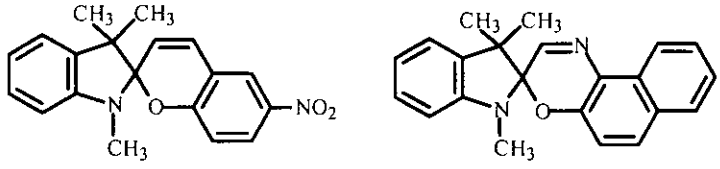
Scheme 1

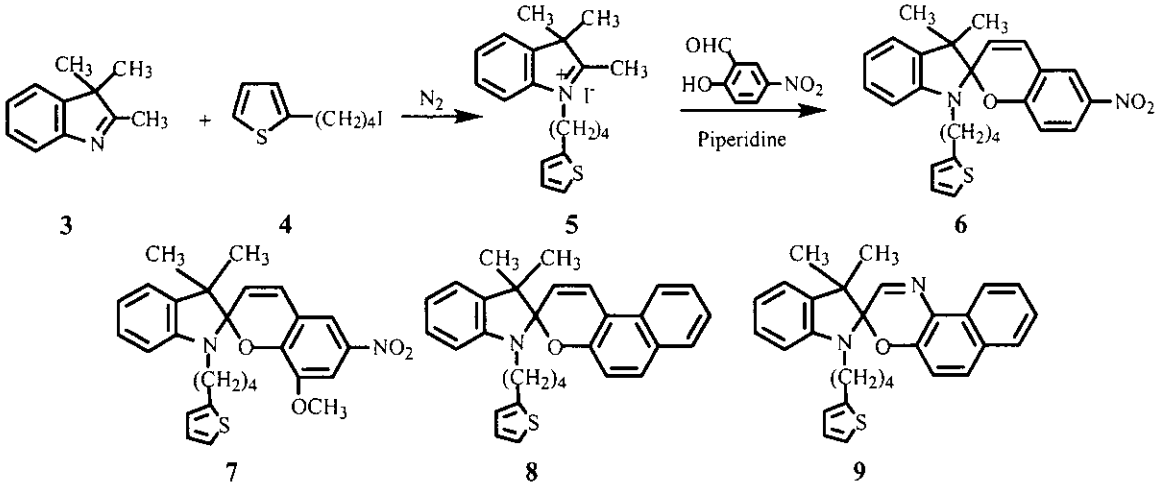


1 **2**

Various heteroaromatic groups such as thiophene (Scheme 2), quinoline, coumarin, etc. including some aromatic groups such as naphthalene (Scheme 3) were selected as the pendants. These groups were connected to the indolenine nitrogen of a photochromic spiro compound through a butylene chain or a propionic acid side chain, which makes unconjugated between the photochromic part and the heteroaromatic part. As the general procedure of synthesizing spiropyrans and spirooxazines having a heteroaromatic pendant, we used two methods.

The first method is shown in Scheme 2; namely a 4-(2-thienyl)butyl iodide (**4**) was first linked to 2,3,3-trimethylindolenine (**3**) to give an indoleninium iodide (**5**), which was condensed with a salicylaldehyde derivative to give a spiro-photochromic compound (**6**, **7**, **8**, or **9**) in 14~40% yield. These compounds were characterized by the spectral and elemental analyses to confirm their structures (see **Experimental**).

Scheme 2

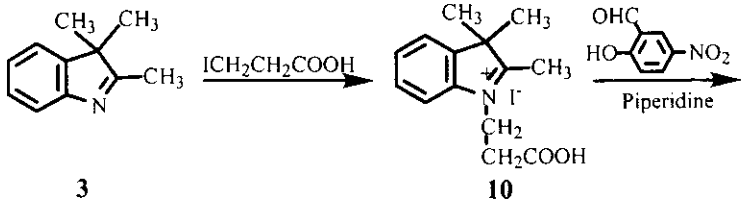


3 **4** **5** **6**

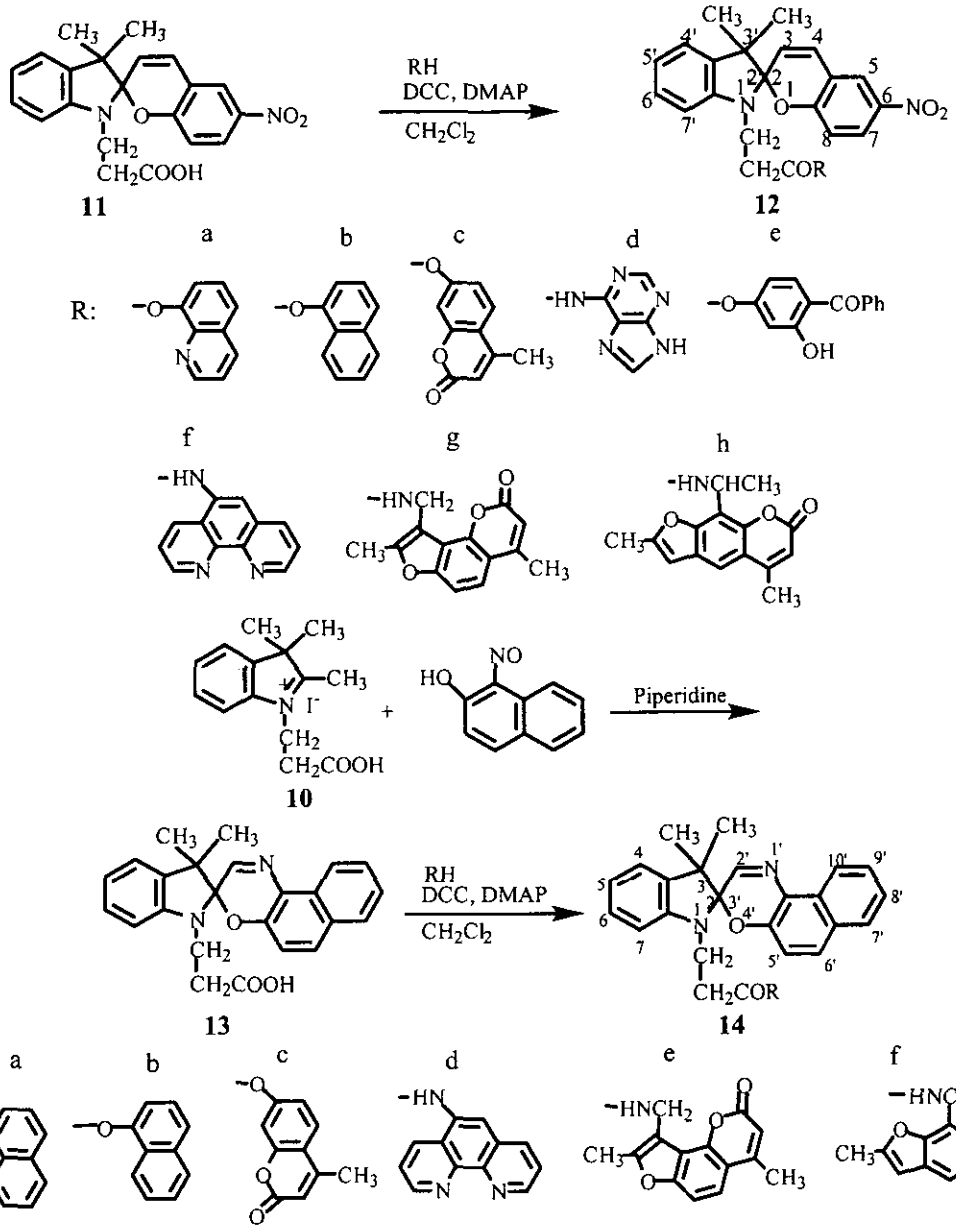
7 **8** **9**

The second method involved two steps (Scheme 3): in the first step, the condensation of 1-(2-carboxyethyl)-2,3,3-trimethylindoleninium iodide (**10**) with 5-nitrosalicylaldehyde and 2-hydroxy-1-nitrosonaphthalene gave **11** and **13**, respectively, which contain a carboxyl group. Considering the structural features of the final spiro-photochromic compounds and heteroaromatic compounds having an OH or NH group, the reaction in the second step should be performed under mild conditions. We selected DCC in the presence of DMAP, a reagent for synthesizing peptides,[29] as the condensation reagent between **11** (or **13**) and the heteroaromatic compounds. The reaction proceeded at room temperature to form **12** (or **14**) (Scheme 3).

Scheme 3



3 **10**



With this second method, two series of new spiropyrans (**12a~12h**) and spirooxazines (**14a~14f**) containing a heteroaromatic group were obtained in the yields of 43~93%, providing an effective method for preparing the spiro-photochromic compounds containing various functional groups. These compounds were also characterized by the spectral and elemental analyses to confirm their structures.

Photochromism

The photochromic behaviors of the compounds synthesized were briefly investigated with the aid of absorption spectral measurements, giving several features on the photochromism of these spiropyran and spirooxazine derivatives. Table 1 shows the UV spectral data for these spiropyrans (**6~8**) and (**12a~12h**) and spirooxazines (**9**) and (**14a~14f**) in the closed form (SP form of Scheme 1) in various solvents, together with those of the parent reference compounds (**1**) and (**2**). They exhibited absorption maxima near 240, 270 and 340 nm as exemplified by the curves of **1** and **12a** of Figures 1 and 2. We observed

only small shifts of their absorption maxima due to solvent polarity.

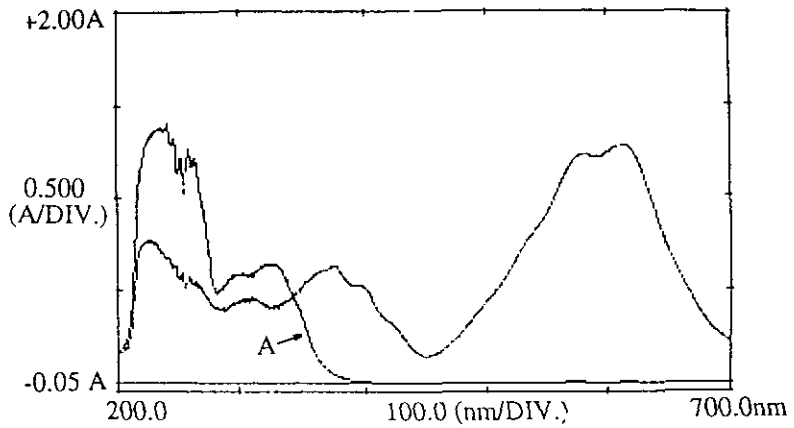


Figure 1. The UV-VIS spectra of compound (**1**) in cyclohexane solution (c = 5.0×10^{-4} mol L^{-1}) before (Curve A) and after irradiation for 30 sec with a 400 W high-pressure mercury lamp.

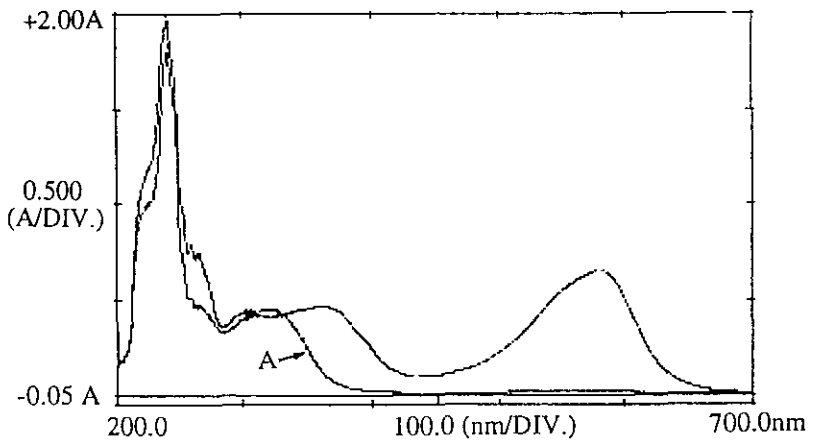


Figure 2. The UV-VIS spectra of compound (**12a**) in cyclohexane solution (c = 5.0×10^{-4} mol L^{-1}) before (Curve A) and after irradiation for 30 sec with a 400 W high-pressure mercury lamp.

Table 1 The absorption maxima (λ_{max})data of the spiro-photochromic compounds in closed spiro form in various solvents and in PMMA (polymethylmethacrylate) matrix

Compounds	Solvent (E value[a])				
	Methanol(55.5)	Acetonitrile(37.5)	Acetone(20.7)	Cyclohexane(2.02)	PMMA(-)
1	237.5, 171, 339.5	236.5, 270, 339	341	238, 271.5, 335.5	340
6	240.5, 269.5, 340	239.5, 270.5, 341	342	241.5, 273, 337.5	341.5
7	241, 273, 347.5	240.5, 270.5, 343.5	346	243, 275, 338.5	337.5
8	242, 275, 341	239, 273.5, 342.5	344	239, 271.5, 342	339.5
12a	241, 271.5, 339.5	240.5, 273, 340.5	340	242.5, 335.5	335
12b	239.5, 272, 341.5	240.5, 271.5, 341	340	240.5, 271.5, 340	346
12c	241.5, 275, 340.5	240.5, 274.5, 342	330	239.5, 273.5, 340.5	334
12d	235.5, 272.5, 339.5	239, 270.5, 341.5	346	240.5, 271, 342.5	340.5
12e	241.5, 273, 342.5	240.5, 273.5, 339.5	341.5	240, 271.5, 344.5	338.5
12f	245, 271.5, 340.5	241.5, 270.5, 343.5	338.5	—	340
12g	243.5, 273.5, 345.5	241.5, 270, 342.5	338	241.5, 270.5, 341.5	340
12h	241.5, 272.5, 343.5	240.5, 271, 340.5	338.5	240.5, 270.5, 341.5	340.5
2	241, 269.5, 342.5	240.5, 271, 340.5	346	240.5, 270.5, 340.5	323

9	239.5, 273.5, 343	240.5, 271.5, 339.5	339.5	239, 270.5, 339.5	318.5
14a	240.5, 271.5, 342	241.5, 270.5, 341.5	347	240, 271.5, 340.5	319
14b	238.5, 271.5, 341.5	240, 273.5, 341.5	346	239.5, 274, 342.5	320
14c	240.5, 270.5, 342	241.5, 272.5, 340.5	332.5	241.5, 273.5, 341	325.5
14d	241, 270.5, 342.5	239, 272.5, 341.5	338.5	240.5, 270.5, 342.5	326
14e	240.5, 273, 343.5	241.5, 271.5, 345	341.5	240.5, 271.5, 340	328
14f	242.5, 271.5, 340.5	239.5, 272.5, 341.5	343.5	239.5, 272.5, 339.5	327.5

a: Dimroth's solvent polarity parameter E, were taken from S. L. Murov, " Handbook of Photochemistry", M. Dekker, New York, 1973.

The spiropyran (**6~8** and **12a~12h**) and spirooxazine (**9** and **14a~14f**) derivatives showed a broad band in the visible region by the irradiation of their solution with a high-pressure mercury lamp, indicating the formation of their open colored form (PMC form of Scheme 1). The absorption maxima of these open colored forms measured in various solvents and in PMMA (polymethylmethacrylate) matrix are listed in Table 2. The absorption spectra of these spiro compounds having a heteroaromatic pendant are similar to those of the parent reference compounds (**1**) and (**2**), implying that no intramolecular spatial interaction occurred between the π-electrons of the photomerocyanine part and the heteroaromatic part.

Table 2 The λ_{max} of the spiro-photochromic compounds in different solvents and in PMMA (polymethylmethacrylate) matrix after UV irradiation

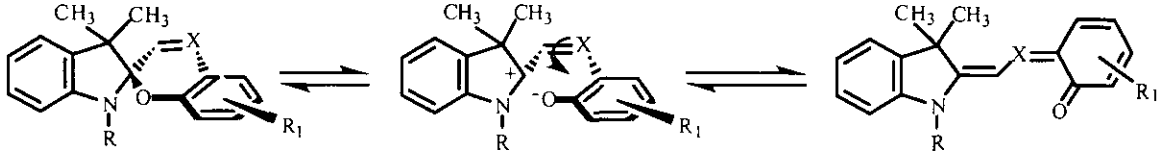
Compounds	Solvent (E value[a])				
	Methanol(55.5)	Acetonitrile(37.5)	Acetone(20.7)	Cyclohexane(2.02)	PMMA matrix(-)
1	524.5	555	570	580.5, 612	582
6	545	562	572	581, 616	582
7	536.5	560	553	582	571.5
8	539	563.5	568	579.5	576
12a	535.5	560	580	580.5	348, 571
12b	533.5	569	585	604.5	352, 588
12c	537.5	568.5	580	575	587
12d	532.5	563	581	580.5	569
12e	531.5	564.5	557	583	570
12f	534	566	572	—	574
12g	538	562.5	566.5	581.5	572.5
12h	536.5	565	571	583	577.5
2	611	600.5	584	578.5	587
9	603.5	598	583	575.5	583.5
14a	605	601	585	584	585
14b	608	596	588	578.5	587
14c	607	598	586.5	581	583.5
14d	603	595	589	582	586
14e	604.5	598	581.5	578.5	583
14f	602.5	595.5	580	579	581.5

a: Dimroth's solvent polarity parameter E, were taken from S. L. Murov, " Handbook of Photochemistry", M. Dekker, New York, 1973.

We observed that the solvent polarity effect on the absorption maximum position is in contrast between the sipropyrans and the spirooxazines. Thus, the visible absorption maxima of spiropyrans (**6~8**) and (**12a~12h**) underwent a hypsochromic shift in more polar solvents similar to that of the parent spiropyran (**1**), while those of spirooxazines (**9**) and (**14a~14f**) did a hyperchromic shift similar to that of the parent spirooxazine (**2**) (Table 2). This indicates that the introduction of a pendant group through a methylene chain into spiro-compounds did not alter the spectral properties of the open colored form.
Whereas the parent spiropyran (**1**) showed two peaks at 580.5 and 612 nm in cyclohexane, only spiropyran (**6**) showed similar splitting peaks among other spiropyran and spirooxazine derivatives (**6~9**,

12a~12h and **14a~14f**). There have been a number of reports on the photochromic mechanism for spiro-compounds in solution,[4,30~32] which argued the formation of the configurational isomers, cis and trans forms for the open colored form as Scheme 4. The appearance of the splitting peak may imply the formation of both of cis and trans isomers on irradiation in particular cases.

Scheme 4



A qualitative study on the decoloration process of the open colored form of the spiropyran derivatives was carried out. Typical examples are given in Figures 3 and 4, which illustrate the change of the absorption spectra of the open form of spiropyrans (**1**) and (**12a**), respectively, taken at 5.0×10^{-4}mol L^{-1} concentration in cyclohexane, in comparison with the spectral curve of each closed form (curve A). These figures show that the decoloration process of **12a** was virtually the same as that of **1**. The decoloration processes of other spiropyran derivatives (**6~8**) and (**12b~12h**) also showed the similar results. In the case of the spirooxazine derivatives (**9**) and (**14a~14f**), the decoloration process was found to so fast, that the measurement of the decoloration process of the open colored form was difficult on the available spectrophotometer.

It should be noted that for the decoloration process of the parent reference compound (**1**) the peak intensity of the maximum at 240 nm of the final stage was weaker than that of the closed form (Figure 3). The result indicates that some degradation process occurred simutaneously during the reversible coloration-decoloration process of **1**. However, in the case of the decoloration of the colored form of spiropyran (**12a**) (Figure 4), the coloration-decoloration process occurred without degradation process, indicating that the introduction of a heteroaromaitic pendant into the spiropyran (**1**) provides an inhibitory effect in the photochromic process.

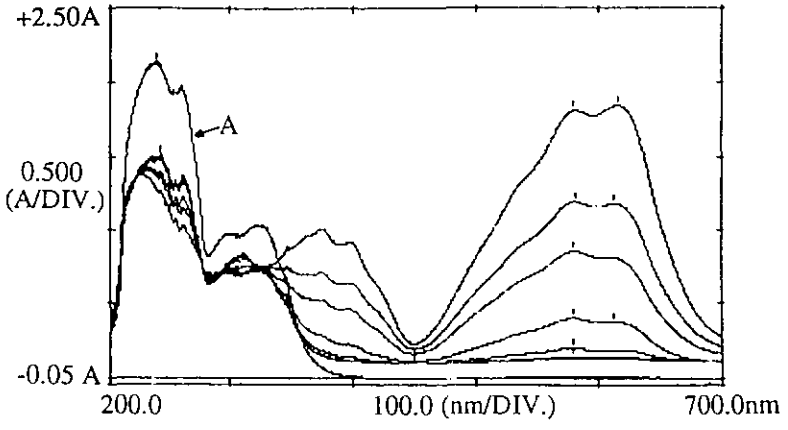


Figure 3. The spectral change for the decoloration process of compound (**1**) in cyclohexane solution ($c=5.0\times10^{-4}$ mol L^{-1}) after irradiation for 30 sec with a 400 W high-pressure mercury lamp. Curve A denotes the spectrum of the closed form. Time interval of measurements, 3 min for the first two and 5 min for the others. The solution became colorless after 2 h.

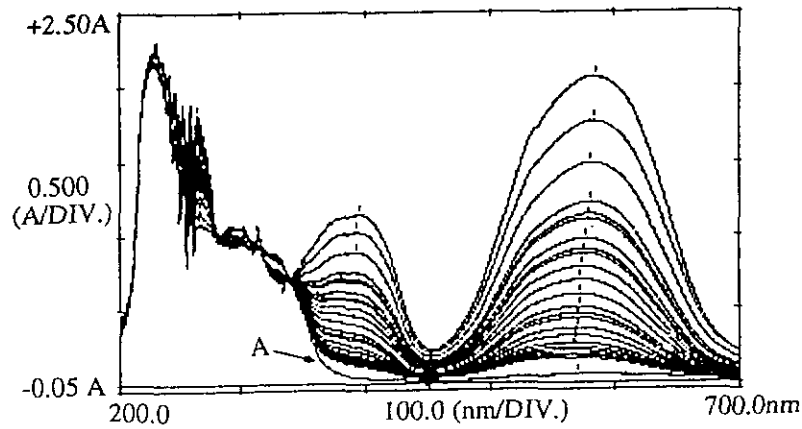


Figure 4. The spectral change for the decoloration process of compound (**12a**) in cyclohexane solution ($c=5.0\times10^{-4}$mol L^{-1}) after irradiation for 30 sec with a 400 W high-pressure mercury lamp. Curve A denotes the spectrum of the closed form. Time interval of measurements, 1 min. The solution became colorless after 1.5 h.

EXPERIMENTAL

All melting points were uncorrected. The spectral and microanalytical data were recorded with the following instruments: the IR spectra, Bio-Rad FTS135 spectrophotometer (with KBr pellets); the ^{1}HNMR spectra, Bruker AC-P200 spectrometer; the UV spectra, Shimadzu UV-160A UV-VIS spectrophotometer; the mass spectra, 7070E-HE spectrometer, and elemental analysis, YANACO CHN CORDER MT-3 analyzer.

4-(2-Thienyl)butyl iodide (**4**) was prepared according to the literatures using thiophene and succinic anhydride as the starting materials. [33-35]

Synthesis of 1-(4-(2-thienyl) butyl)-2,3,3-trimethyl-indoleninium iodide (5)

A mixture of 2.9 g (0.011 mol) of 4-(2-thienyl)butyl iodide (**4**) and 1.8 g (0.011 mol) of 2,3,3-trimethylindolenine (**3**) was heated on a water bath for 16 h under nitrogen atmosphere. To the mixture petroleum ether (60~90°C) and ethanol were added, and a pink solid precipitated. After recrystallization from ethanol-petroleum ether (60~90°C), product (**5**) was obtained as pale pink crystals, 2.5 g (54%), mp 134~136°C (lit.,[28] mp 132~133°C).

Synthesis of compound(6)

A solution of 1.5 g (3.5 mmol) of 1-(4-(2-thienyl)butyl)-2,3,3-trimethylindoleninium iodide (**5**), 0.36 mL (3.5 mmol) of piperidine and 0.6 g (3.6 mmol) of 5-nitrosalicylaldehyde in 12 mL of absolute ethanol was refluxed for 11 h under nitrogen atmosphere. After cooling, a yellow solid precipitated which was recrystallized from acetone to give **6** as yellow crystals, 0.6 g (40%), mp 134~136°C. ^{1}H NMR ($CDCl_3$) δ 1.17, 1.28 (2s, 6H, $2CH_3$), 1.69 (m, 4H, $2CH_2$), 2.81 (m, 2H, CH_2), 3.19 (m, 2H, CH_2), 5.86 (d, J=10.8 Hz, 1H, -CH=), 6.53~7.21 (m, 9H, 8ArH and 1-CH=), 8.00~8.10 (m, 2H, ArH, 5-H and 7-H). IR(KBr) 3050, 2945, 2840, 1605, 1510, 1478, 1338, 1271, 1132, 1082, 951 cm^{-1}. MS m/z(%): 446 (M^+) (22.7), 323 (30.3), 321 (20.3), 307 (4.8), 291 (5.8), 283 (2.2), 217 (8.0), 168 (2.7), 158 (22.2), 144 (10.8), 130 (8.7), 115 (6.9), 97 (100). Anal. Calcd for $C_{26}H_{26}N_2O_3S$: C 69.93, H 5.87, N 6.27. Found: C 69.61, H 5.95, N 5.99.

Synthesis of compound (7)

Following the procedure used to prepare compound (**6**), compound (**7**) was prepared from 1.3 g (3.1 mmol) of **5** and 0.6 g (3.1 mmol) of 5-nitro-3-methoxysalicylaldehyde. Yellow crystalline product (**7**) was obtained, 0.2 g (14%), mp 159~162°C (EtOH). ^{1}H NMR ($CDCl_3$) δ 1.28, 1.38 (2s, 6H, $2CH_3$), 1.72 (m,

4H, $2CH_2$), 2.70 (m, 2H, CH_2), 2.96 (m, 2H, CH_2), 4.01 (s, 3H, OCH_3), 5.82 (d, J=10.8 Hz, 1H, -CH=), 6.32~7.20 (m, 8H, 7ArH and 1-CH=), 7.79, 7.92 (2s, 2H, ArH, 5-H and 7-H). IR(KBr) 3040, 2950, 2860, 1610, 1509, 1481, 1332, 1269, 1135, 1078, 950 cm^{-1}. MS m/z(%): 477 (M+1) (91.3), 476 (M^+) (23.1), 461 (41.6), 409 (31.5), 352 (4.5), 324 (18.1), 283 (15.4), 282 (16.2), 200 (31.4), 174 (54.4), 172 (48.1), 158 (63.8), 144 (42.6), 139 (10.1), 130 (21.7), 117 (13.2), 115 (14.8), 97 (100). Anal. Calcd for $C_{27}H_{28}N_2O_4S$: C 68.04, H 5.92, N 5.88. Found: C 68.13, H 6.17, N 5.73.

Synthesis of compound (8)

Following the procedure used to prepare compound (**6**), compound (**8**) was prepared from 0.8 g (1.9 mmol) of **5** and 0.33 g (1.9 mmol) of 2-hydrox-1-naphthaldehyde. Product (**8**) was obtained as pale pink needle crystals, 0.4 g (37%), mp 106~107°C (acetone). ^1H NMR ($CDCl_3$) δ 1.20, 1.31 (2s, 6H, $2CH_3$), 1.66 (m, 4H, $2CH_2$), 2.76 (m, 2H, CH_2), 3.20 (m, 2H, CH_2), 5.78 (d, J=10.8 Hz, 1H, -CH=), 6.50~7.80 (m, 13H, 12ArH and 1-CH=), 8.05 (d, J=8.1 Hz, 1H, ArH). IR(KBr) 3060, 2960, 2850, 1610, 1590, 1480, 1284, 1165, 1081, 950 cm^{-1}. MS m/z(%): 451 (M^+) (100), 436 (16.8), 326 (16.1), 296 (26.9), 283 (20.5), 267 (15.1), 181 (18.8), 168 (19.7), 158 (61.1), 144 (24.5), 139 (15.2), 97 (84.6). Anal. Calcd for $C_{30}H_{29}NOS$: C 79.78, H 6.47, N 3.10. Found: C 79.52, H 6.65, N 3.11.

Synthesis of compound (9)

A mixture of 2.2 g (5.2 mmol) of 1-(4-(2-thienyl)butyl)-2,3,3-trimethylindoleninium iodide (**5**), 0.52 mL (5.2 mmol) of piperidine, 1.0 g (5.8 mmol) of 2-hydrox-1-nitrosonaphthalene and 15 mL of dry trichloroethylene was refluxed for 41 h. The crude reaction product was purified by chromatography over silica eluting with petroleum ether (60~90°C)-acetone (v/v=3:1) to give product (**9**) as green crystals, 0.6 g (27%), mp 115~117°C (EtOH). ^1H NMR ($CDCl_3$) δ 1.32 (s, 6H, $2CH_3$), 1.68 (m, 4H, $2CH_2$), 2.77 (m, 2H, CH_2), 3.20 (m, 2H, CH_2), 6.54~7.80 (m, 13H, 12ArH and -CH=N), 8.58 (d, J=9.0 Hz, 1H, ArH, 10'-H). IR(KBr) 3050, 2955, 2840, 1627, 1604, 1590, 1481, 1310, 1276, 1171, 1082, 957, 821, 745 cm^{-1}. MS m/z(%): 452 (M^+) (80.4), 437 (39.5), 327 (37.3), 297 (12.2), 283 (37.1), 268 (20.2), 182 (12.4), 170 (25.5), 158 (58.5), 144 (34.1), 139 (10.6), 130 (17.5), 128 (13.9), 115 (32.6), 97 (100). Anal. Calcd for $C_{29}H_{28}N_2OS$: C 76.95, H 6.24, N 6.19. Found: C 76.69, H 6.16, N 6.07.

Synthesis of 1-(2-carboxyethyl)-2,3,3-trimethylindoleninium iodide (10)

A mixture of 3.2 g (0.02 mol) of 2,3,3-trimethylindolenine (**3**) and 4.0 g (0.02 mol) of 3-iodopropionic acid were thoroughly agitated and heated on a water bath for 4 h under nitrogen atmosphere. The mixture was dissolved in water, and the solution was washed with chloroform. After the removal of water under reduced pressure, the residue was recrystallized from acetone-ether to afford **10** as pale yellow microcrystals 6.6 g (92%), mp 189~190°C (lit.,[28] mp 189.5~191°C).

Synthesis of compound (11)

A mixture of 3.6 g (0.01 mol) of 1-(2-carboxyethyl)-2,3,3-trimethylindoleninium iodide (**10**), 1.7 g (0.01 mol) of 5-nitrosalicylaldehyde, 30 mL of butanone and 1.0 mL (0.01 mol) of piperidine was refluxed for 5h under nitrogen atmosphere. After cooling, 2.9 g (76%) of product (**11**) was obtained as pale yellow crystals, mp 206°C (EtOH). ^1H NMR ($CDCl_3$) δ 1.19 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 2.53 (t, J=6.3 Hz, 2H, CH_2), 3.61 (t, J=6.3 Hz, 2H, CH_2), 5.89 (d, J=10.8 Hz, 1H, -CH=), 6.62~7.28 (m, 6H, 5ArH and 1-CH=), 7.97~8.09 (m, 2H, ArH, 5-H and 7-H). IR (KBr) 3060, 2960, 1704(s), 1605, 1505, 1480, 1330, 1270, 1164, 1086, 1026, 945, 802, 750 cm^{-1}. m/z(%): 381 (M+1) (9), 380 (M^+) (25), 365 (M-CH_3) (12), 347 (3), 335 (M-NO_2) (12), 321 (8), 319 (6), 307 (4), 291 (22), 217 (45), 216 (15), 202 (13), 164 (5), 158 (100), 144 (40), 130 (33), 117 (18), 115 (31), 91 (19), 89 (15), 77 (25). Anal. Calcd for $C_{21}H_{20}N_2O_5$: C 66.30, H 5.30, N 7.37. Found: C 66.19, H 5.25 N, 7.20.

Synthesis of compound (12a)

A solution of 0.38 g (1.0 mmol) of compound (**11**), 0.15 g (1.0 mmol) of 8-hydroxyquinoline, 12 mg (0.1 mmol) of DMAP and 0.21 g (1.0 mmol) of DCC in 20 mL of dry dichloromethane was stirred in the dark at rt for 24 h. The solid was removed by filtration. The solution was successively washed by a saturated

aqueous Na_2CO_3 solution and water, dried with anhydrous Na_2SO_4. After removing the solvent, the residue was submitted to silica gel chromatography using CH_2Cl_2 as the eluent. A white solid product (**12a**) was obtained, 0.45 g (89%), mp 153°C (EtOH). ^{1}H NMR ($CDCl_3$) δ ($CDCl_3$) 1.19, 1.27 (2s, 6H, $2CH_3$), 2.16 (q, J=6.3 Hz, 2H, CH_2), 2.76 (q, J=6.3 Hz, 2H, CH_2), 5.98 (d, J=10.8 Hz, 1H, -CH=), 6.72~8.24 (m, 13H, 12ArH and 1-CH=), 8.83 (d, J=2.7 Hz, 1H, 2-H of quinoline). IR (KBr) 3052, 2958, 2927, 2857, 1769, 1607, 1512, 1477, 1335, 1270, 1165, 1135, 1082, 950, 805, 746 cm^{-1}. MS m/z(%): 508 (M+1) (3.70), 507 (M^+) (10.98), 492 (M-CH_3) (60.15), 363 (14.15), 362 (30.08), 347 (22.88), 345 (63.80), 334 (24.53), 321 (41.19), 319 (29.34), 307 (75.68), 291 (28.79), 275 (12.43), 259 (13.63), 246 (13.06), 230 (13.03), 217 (12.35), 200 (29.77), 196 (15.68), 168 (12.45), 157 (61.73), 146 (100), 130 (17.87), 117 (51.50), 89 (28.77), 77 (8.46), 63 (12.67), 55 (42.53). *Anal. Calcd for* $C_{30}H_{25}N_3O_5$: C 70.99, H 4.97, N 8.28. Found: C 70.62, H 5.05, N 8.28.

Synthesis of compound (12b)

Following the procedure used to prepare **12a**, compound (**12b**) was prepared from 0.38 g (1.0 mmol) of **11** and 0.15 g (1.0 mmol) of α-naphthol. Product (**12b**) was obtained as pale yellow crystals, 0.50 g (99%), mp 122°C (acetone-petroleum ether). ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 3.12 (q, J=7.2 Hz, 2H, CH_2), 3.73 (q, 2H, J=7.2 Hz, CH_2), 5.92 (d, J=10.8 Hz, 1H, -CH=), 6.70~8.08 (m, 15H, 14ArH and 1-CH=). IR (KBr) 3040, 2960, 2850, 1760, 1602, 1510, 1476, 1332, 1269, 1135, 950, 748 cm^{-1}. MS m/z(%): 507 (M+1) (7.90), 506 (M^+) (21.19), 363 (38.08), 321 (100), 309 (13.80), 307 (8.11), 291 (5.44), 275 (12.09), 246 (6.36), 245 (5.02), 217 (4.94), 199 (6.68), 158 (39.35), 144 (21.15), 127 (4.45), 115 (24.68), 89 (4.00), 77 (3.25), 55 (17.10). Anal. Calcd for $C_{31}H_{26}N_2O_5$: C 73.50, H 5.17, N 5.53. *Found: C 73.36, H 5.55, N 5.58.*

Synthesis of compound (12c)

Following the procedure used to prepare **12a**, compound (**12c**) was prepared from 0.38 g (1.0 mmol) of **11** and 0.18 g (1.0 mmol) of 7-hydroxy-4-methylcoumarin. Product (**12c**) was obtained as pale yellow crystals, 0.53 g (98%), mp 184°C (EtOH). ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.96 (q, J=5.4 Hz, 2H, CH_2), 3.68 (q, J=5.4 Hz, 2H, CH_2), 5.91 (d, J=10.8 Hz, 1H, -CH=), 6.16 (s, 1H, -COCH=), 6.64~7.35 (m, 8H, 7ArH and 1-CH=), 7.58 (d, J=9.0 Hz, 1H, 8-H of coumarin), 7.95~8.05 (m, 2H, ArH, 5-H and 7-H). IR (KBr) 3060, 2960, 1766, 1725, 1609, 1570, 1510, 1479, 1334, 1270, 1130, 950, 805, 740 cm^{-1}. MS m/z(%): 539 (M+1) (6.46), 538 (M^+) (19.07), 523 (M-CH_3) (4.10), 380 (3.50), 363 (8.72), 335 (19.85), 321 (19.40), 319 (9.83), 309 (12.34), 307 (17.68), 291 (79.53), 276 (20.80), 246 (16.51), 230 (26.02), 217 (12.08), 199 (4.31), 177 (17.09), 176 (73.09), 158 (61.92), 148 (75.73), 147 (62.35), 145 (22.19), 144 (21.64), 130 (13.59), 115 (12.35), 91 (30.83), 77 (13.15), 65 (15.74), 55 (100). Anal. Calcd for $C_{31}H_{26}N_2O_7$: C 69.14, H 4.87, N 5.20. Found: C 68.85, H 5.10, N 5.27.

Synthesis of compound (12d)

Following the procedure used to prepare **12a**, compound (**12d**) was prepared from 0.38 g (1.0 mmol) of **11** and 0.14 g (1.0 mmol) of adenine. A pale yellow solid product (**12d**) was obtained, 0.30 g (59%), mp 163~4°C (acetone-petroleum ether). ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 2.7 (m, 2H, CH_2), 3.52~3.66 (m, 2H, CH_2), 3.94 (br s, 1H, NH), 5.10 (br s, 1H, NH), 5.89 (d, J=10.8 Hz, 1H, -CH=), 6.65~7.44 (m, 8H, 7ArH and 1-CH=), 7.98~8.10 (m, 2H, ArH, 5-H and 7-H). IR (KBr) 3320, 3030, 2921, 2850, 1680, 1655, 1624, 1572, 1507, 1480, 1330, 1266, 1218, 1088, 1020, 949, 805, 749 cm^{-1}. MS m/z(%): 446 (7.64), 335 (13.9), 321 (10.8), 307 (100), 292 (5.83), 259 (4.28), 230 (3.47), 204 (2.39), 168 (3.27), 158 (17.47), 144 (8.42), 130 (6.17), 115 (3.26), 97 (7.10), 82 (8.54), 67 (7.83), 55 (19.98). Anal. Calcd for $C_{26}H_{23}N_7O_4$: C 62.77, H 4.66, N 19.71. Found: C 62.53, H 4.61, N 19.47.

Synthesis of compound (12e)

Following the procedure used to prepare **12a**, compound (**12e**) was prepared from 0.38 g (1.0 mmol) of **11** and 0.22 g (1.0 mmol) of 2,4-dihydroxybenzophenone. A pale yellow solid product (**12e**) was obtained,

0.35 g (61%), mp 154°C (acetone-petroleum ether). ^{1}HNMR ($CDCl_3$) δ 1.13 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 2.57~2.74 (m, 2H, CH_2), 3.41~3.84 (m, 2H, CH_2), 5.80 (d, J=9.8 Hz, 1H, -CH=), 6.58~7.21 (m, 9H, 8ArH and 1-CH=), 7.43~7.71 (m, 5H, ArH), 7.93~8.01 (m, 2H, ArH, 5-H and 7-H). IR (KBr) 3040, 2930, 2850, 1695, 1650, 1610, 1516, 1484, 1335, 1273, 1090, 952, 809, 745 cm^{-1}. MS m/z(%): 577 (M+1) (1.20), 576 (M^+) (3.41), 561 (2.05), 471 (8.22), 380 (4.41), 363 (7.25), 347 (12.1), 307 (5.10), 217 (11.20), 202 (5.73), 158 (22.71), 144 (9.32), 130 (11.29), 105 (100), 77 (65.28). Anal. Calcd for $C_{34}H_{28}N_2O_7$: C 70.82, H 4.89, N 4.86. Found: C 70.51, H 4.75, N 4.90.

Synthesis of compound (12f)

Following the procedure used to prepare **12a**, compound (**12f**) was prepared from 0.38 g (1.0 mmol) of **11** and 0.20 g (1.0 mmol) of 5-amino-1,10-phenanthroline. A pale yellow solid product (**12f**) was obtained, 0.35 g (63%), mp 168~9°C (EtOH). ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 2.81~3.05 (m, 2H, CH_2), 3.61 ~3.92 (m, 2H, CH_2), 5.80 (d, J=10.8 Hz, 1H, -CH=), 6.59~6.92 (m, 3H, 2ArH and 1-CH=), 7.09 (d, J=7.4 Hz, 2H, ArH), 7.25~7.68 (m, 3H, ArH), 7.60~8.33 (m, 5H, ArH), 9.04 (s, 2H, 2-H and 9-H of phenanthroline). IR (KBr) 3325, 3050, 2970, 2850, 1709(s), 1610, 1575, 1510, 1484(s), 1442, 1335, 1274, 1166, 1090, 1030, 950(s), 806, 754(s) cm^{-1}. MS m/z(%): 408 (3), 380 (6), 365 (3), 362 (10), 347 (14), 344 (8), 335 (10), 328 (12), 319 (5), 307 (20), 248 (21), 224 (56), 219 (27), 217 (13), 205 (19), 193 (11), 180 (11), 174 (10), 165 (18), 158 (45), 150 (52), 143 (66), 130 (17), 128 (12), 122 (14), 115 (14), 108 (243), 99 (52), 91 (12), 89 (6), 82 (49), 77 (19), 70 (29), 69 (23), 67 (22), 56 (100). Anal. Calcd for $C_{33}H_{27}N_5O_4$: C 71.08, H 4.88, N 12.56. Found: C 69.77, H 4.65, N 12.31.

Synthesis of compound (12g)

Following the procedure used to prepare **12a**, compound (**12g**) was prepared from 0.38 g (1.0 mmol) of **11** and 0.24 g (1.0 mmol) of 4'-aminomethyl-4,5'-dimethylisopsoralen. A white solid product (**12g**) was obtained, 0.28 g (46%), mp 140°C (Et_2O-petroleum ether). ^{1}H NMR ($CDCl_3$) δ 1.10, 1.20 (2s, 6H, $2CH_3$), 2.43 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 2.78~2.93 (m, 2H, CH_2), 3.37~3.60 (m, 2H, CH_2), 4.40~4.50(m, 2H, CH_2), 5.70 (d, J=10.8 Hz, 1H, -CH=), 6.20 (s, 1H, =CH-CO-), 6.50~7.48 (m, 8H, 7ArH and 1-CH=), 7.90~8.02 (m, 2H, ArH, 5-H and 7-H). IR (KBr) 3380, 3040, 2940, 2850, 1709, 1607,1570, 1509, 1480, 1331, 1265, 1080, 950, 805, 745 cm^{-1}. MS m/z(%): 606 (M+1) (6.02), 605 (M^+) (16.03), 590 (M-CH_3) (16.41), 588 (33.88), 364 (6.68), 363 (5.10), 346 (3.78), 345 (5.17), 335 (21.32), 321 (16.72), 308 (14.44), 307 (75.99), 292 (9.55), 291 (5.70), 242 (31.98), 227 (100), 217 (7.80), 216 (8.06), 202 (5.41), 198 (12.37), 185 (4.72), 184 (7.92), 172 (9.72), 158 (43.36), 144 (20.77), 130 (15.21), 128 (16.65), 115 (9.94), 102 (3.85), 91 (5.10), 89 (2.74), 77 (4.14). Anal. Calcd. for $C_{35}H_{31}N_3O_7$: C 69.41, H 5.16, N 6.94. Found: C 69.42, H 5.60, N 6.93.

Synthesis of compound (12h)

Following the procedure used to prepare **12a**, compound (**12h**) was prepared from 0.38 g (1.0 mmol) of **11** and 0.26 g (1.0 mmol) of 8-(1-aminoethyl)-4,5'-dimethylpsoralen. A white solid product (**12h**)was obtained, 0.23 g (49%), mp 147~148°C (Et_2O-petroleum ether). ^{1}H NMR ($CDCl_3$) δ 1.15, 1.22 (2s, 6H, $2CH_3$), 1.52 (d, J=7.0 Hz, 3H, CH_3), 2.44 (s, 6H, $2CH_3$), 2.46~2.59 (m, 2H, CH_2), 3.47~3.57 (m, 3H, CH, CH_2), 5.77 (br s, 1H, NH), 5.91~5.95 (m, 1H, -CH=), 6.19 (s, 1H, =CH-CO-), 6.37 (s, 1H, -CH=C-O-), 6.56~7.06 (m, 6H, 5ArH and 1-CH=), 7.53 (s, 1H, ArH), 7.86~7.97 (m, 2H, ArH, 5-H and 7-H). IR (KBr) 3380, 3060, 2940, 2860, 1710, 1650, 1605, 1580, 1510, 1475, 1335, 1270, 1085, 946, 804, 745 cm^{-1}. MS m/z(%): 620 (M+1) (4.81), 619 (M^+) (11.96), 604 (M-CH_3) (24.58), 603 (28.10), 602 (61.26), 470 (2.86), 456 (2.90), 378 (4.51), 347 (2.24), 345 (6.13), 335 (23.77), 319 (8.91), 317 (3.60), 307 (68.56), 292 (13.72), 286 (10.27), 256 (16.36), 242 (34.81), 241 (100), 228 (10.86), 217 (2.35), 215 (3.93), 214 (5.17), 171 (8.62), 158 (29.24), 130 (7.63). Anal. Calcd for $C_{36}H_{33}N_3O_7$: C 69.78, H 5.37, N 6.78. Found: C 69.66, H 5.25, N 6.49.

Synthesis of compound (13)

To a gently refluxing mixture of 4.0 g (0.023 mol) of 2-hydroxy-1-nitrosonaphthalene and 40 mL of

absolute ethanol, a solution of 7.2 g (0.023 mol) of 1-(2-carboxyethyl)-2,3,3-trimethylindoleninium iodide (**10**) and 6.0 mL of triethylamine in 30 mL of absolute ethanol was added dropwise. The mixture was further refluxed with stirring for 3 h. After removal of the ethanol, the residue was purified by flash chromatography over silica gel with petroleum ether-acetone (v/v=2:1) to give a pale yellow solid product (**13**), 2.7 g (35%), mp 186~187°C (EtOH). ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 6H, $2CH_3$), 2.70 (t, J=6.3 Hz, 2H, CH_2), 3.60 (t, J=6.3 Hz, 2H, CH_2), 6.69 (d, J=10.8 Hz, 1H, ArH), 6.88~7.83 (m, 9H, 8ArH and -CH=N), 8.64 (d, J=7.2 Hz, 1H, ArH, 10'-H). IR (KBr) 3050, 2970, 2867, 2510(br), 1725, 1607, 1595, 1514, 1485, 1310, 1230, 1081, 1045, 1004, 818, 744 cm^{-1}. MS m/z(%): 387 (M+1) (4), 386 (M^+) (18), 371 (M-CH_3) (11), 342 (M-CO_2) (1), 327 (9), 312 (13), 298 (6), 297 (6), 217 (62), 202 (26), 182 (7), 170 (24), 169 (23), 158 (100), 144 (62), 130 (45), 128 (40), 115 (94), 101 (30), 91 (22), 89 (21), 77 (49). Anal. Calcd for $C_{24}H_{22}N_2O_3$: C 74.59, H 5.74, N 7.25. Found: C 74.32, H 5.41, N 7.08.

Synthesis of compound (14a)

A solution of 0.39 g (1.0 mmol) of compound (**13**), 0.15 g (1.0 mmol) of 8-hydroxyquinoline, 12 mg (0.1 mmol) of DMAP and 0.21 g (1.0 mmol) of DCC in 20 mL of dry dichloromethane was stirred in the dark at rt for 24 h. The solid was removed by filtration. The solution was washed by an aqueous saturated Na_2CO_3 solution and water successively, and dried with anhydrous Na_2SO_4. After removing the solvent, the residue was submitted to silica gel chromatography using CH_2Cl_2 as the eluent. A white solid product (**14a**) was obtained, 0.47 g (91%), mp 175°C (EtOH). ^{1}H NMR ($CDCl_3$) δ 1.33, 1.36 (2s, 6H, $2CH_3$), 3.20 (q, J=7.2 Hz, 2H, CH_2), 3.82 (q, J=7.1 Hz, 2H, CH_2), 6.76~7.80 (m, 13H, ArH), 7.85 (s, 1H, -CH=N), 8.15 (dd, J=9.0 Hz, J=1.8 Hz, 1H, ArH), 8.55 (dd, J=9.0 Hz, J=1.8 Hz, 1H, ArH), 8.80 (dd, J=3.6 Hz, J=1.8 Hz, 1H, ArH). IR (KBr) 3054, 2926, 2856, 1758, 1620, 1605, 1590, 1486, 1453, 1356, 1308, 1241, 1158, 1081, 1039, 1000, 823, 783, 746 cm^{-1}. MS m/z(%): 514 (M+1) (1.25), 513 (M^+) (3.72), 498 (M-CH_3) (1.30), 368 (36.12), 353 (15.58), 340 (36.65), 327 (18.63), 325.20 (100), 311 (99.90), 297 (13.06), 282 (5.08), 269 (14.32), 200 (5.25), 182 (8.14), 170 (19.85), 168 (8.61), 158 (54.00), 146 (77.18), 145 (48.42), 144 (35.25), 130 (12.63), 128 (14.70), 117 (30.91), 115 (28.25), 101 (5.20), 89 (18.14), 77 (6.33), 55 (15.84). Anal. Calcd for $C_{33}H_{27}N_3O_3$: C 77.17, H 5.30, N 8.18. Found: C 76.92, H 5.03, N 7.98.

Synthesis of compound (14b)

Following the procedure used to prepare **14a**, compound (**14b**) was prepared from 0.39 g (1.0 mmol) of **13** and 0.15 g (1.0 mmol) of α-naphthol. Product (**14b**) was obtained greenish yellow crystals, 0.41 g (80%), mp 150°C (acetone-petroleum ether). ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 6H, $2CH_3$), 3.14 (q, J=7.2 Hz, 2H, CH_2), 3.78 (q, J=7.2 Hz, 2H, CH_2), 6.76 (d, J=7.2 Hz, 1H, ArH), 6.94~7.90 (m, 16H, 15ArH and -CH=N), 8.58 (d, J=9.0 Hz, 1H, ArH, 10'-H). IR (KBr) 3050, 2965, 2860, 1752, 1624, 1602, 1590, 1480, 1455, 1380, 1302, 1224, 1166, 1130, 1080, 965, 805, 735 cm^{-1}. MS m/z(%): 513 (M+1) (10.41), 512 (27.94), 497 (M-CH_3) (17.54), 369 (3.09), 353 (5.28), 328 (14.32), 327 (51.72), 313 (31.70), 312 (25.28), 311 (100), 297 (9.61), 283 (4.45), 269 (11.30), 241 (2.38), 199 (10.52), 182 (7.15), 170 (14.27), 158 (68.09), 144 (45.68), 115 (70.15), 103 (3.47), 102 (3.35), 91 (3.46), 89 (8.05), 55 (11.20). Anal. Calcd for $C_{34}H_{28}N_2O_3$: C 79.67, H 5.51, N 5.46. Found: C 79.29, H 5.34, N 5.58.

Synthesis of compound (14c)

Following the procedure used to prepare **14a**, compound (**14c**) was prepared from 0.39 g (1.0 mmol) of **13** and 0.18 g (1.0 mmol) of 7-hydroxy-4-methylcoumarin. A white solid product (**14c**) was obtained, 0.51 g (93%), mp 223°C (EtOH). ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 6H, $2CH_3$), 2.40 (s, 2H, CH_3), 2.98 (m, 2H, CH_2), 3.75 (m, 2H, CH_2), 6.26 (s, 1H, =CH-CO), 6.71 (d, J=8.1 Hz, 1H, ArH), 6.87~7.81 (m, 12H, 11ArH and -CH=N), 8.58 (d, J=8.1 Hz, 1H, ArH, 10'-H). IR (KBr) 3050, 2970, 2865, 1760, 1715, 1623, 1609, 1480, 1381, 1360, 1314, 1260, 1146, 1125, 1079, 1011, 976, 952, 855, 831, 750 cm^{-1}. MS m/z(%): 545 (M+1) (8.05), 544 (M^+) (22.45), 529 (M-CH_3) (14.81), 375 (13.37), 369 (1.73), 353 (4.83), 328 (7.09), 327 (27.74), 313 (20.88), 312 (26.11), 311 (100), 297 (10.47), 269 (8.97), 199 (5.00), 182 (6.60),

177 (22.06), 170 (12.66), 158 (83.86), 144 (24.19), 130 (11.42), 128 (9.61), 115 (22.82), 91 (13.48), 77 (7.76), 55 (18.59). Anal. Calcd for $C_{34}H_{28}N_2O_5$: C 74.99, H 5.18, N 5.14. Found: C 75.02, H 5.04, N 4.88.

Synthesis of compound (14d)

Following the procedure used to prepare **14a**, compound (**14d**) was prepared from 0.39 g (1.0 mmol) of **13** and 0.20 g (1.0 mmol) of 5-amino-1,10-phenanthroline. A pale yellow solid product (**14d**) was obtained, 0.37 g (65%), mp 197°C (EtOH). ^{1}H NMR ($CDCl_3$) δ 1.22, 1.32 (2s, 6H, $2CH_3$), 2.78~2.92 (m, 2H, CH_2), 3.81~3.95 (m, 2H, CH_2), 6.71 (d, J=8.4 Hz, 1H, ArH), 6.81~6.84 (m, 2H, ArH), 7.08 (d, J=7.4 Hz, 2H, ArH), 7.35~8.11 (m, 10H, 9ArH and -CH=N), 8.53 (d, J=8.4 Hz, 1H, ArH, 10'-H), 9.03 (s, 2H, ArH, 2-H and 9-H of phenanthroline). IR (KBr) 3200, 3030, 2954, 1675, 1605, 1590, 1530, 1480, 1415, 1245, 1078, 995, 810, 736 cm^{-1}. MS m/z(%): 564 (M+1) (1), 563 (M^+) (3), 548 (M-CH_3) (18), 349 (4), 340 (5), 325 (13), 312 (46), 311 (31), 298 (12), 297 (35), 281 (4), 269 (5), 249 (56), 222 (44), 21 (28), 207 (14), 195 (100), 170 (18), 169 (15), 167 (58), 158 (45), 144 (60), 130 (33), 114 (29). Anal. Calcd for $C_{36}H_{29}N_5O_2$: C 76.71, H 5.19, N 12.43. Found: C 76.87, H 5.01, N 12.20.

Synthesis of compound (14e)

Following the procedure used to prepare **14a**, compound (**14e**) was prepared from 0.39 g (1.0 mmol) of **13** and 0.24 g (1.0 mmol) of 4'-aminomethyl-4,5'-dimethylisopsoralen. A pale yellow solid product (**14e**) was obtained, 0.26 g (43%), mp 173~174°C (acetone-petroleum ether). ^{1}H NMR ($CDCl_3$) δ 1.12, 1.14 (2s, 6H, $2CH_3$), 2.47, 2.49 (2s, 6H, $2CH_3$), 2.89~3.08 (m, 2H, CH_2), 3.75~3.90 (m, 2H, CH_2), 4.46 (d, J=5.4 Hz, 2H, NCH_2), 6.17 (s, 1H, -COCH= of psoralen), 6.53 (d, J=8.0 Hz, 2H, ArH), 6.83~7.69 (m, 11H, 10ArH and -CH=N), 8.52 (d, J=8.1 Hz, 1H, ArH, 10'-H). IR (KBr) 3325, 3045, 2960, 2840, 1710, 1690, 1630, 1590, 1505, 1480, 1460, 1265, 1180, 1081, 1025, 998, 814, 745 cm^{-1}. MS m/z(%): 612 (M+1) (2.81), 611 (M+) (7.90), 596 (20.33), 370 (12.47), 327 (9.58), 313 (35.25), 311 (46.10), 298 (5.79), 297 (4.13), 269 (4.78), 242 (28.91), 227 (100), 216 (6.51), 198 (8.92), 172 (8.41), 158 (17.90), 144 (10.09), 130 (13.47), 128 (11.25), 115 (6.88), 91 (7.26), 89 (3.49), 77 (18.98). Anal. Calcd for $C_{38}H_{33}N_3O_5$: C 74.62, H 5.44, N 6.87. Found: C 74.38, H 5.51, N 6.95.

Synthesis of compound (14e)

Following the procedure used to prepare **14a**, compound (**14f**) was prepared from 0.39 g (1.0 mmol) of **13** and 0.26 g (1.0 mmol) of 8-(1-aminoethyl)-4,5'-dimethylpsoralen. A pale yellow solid product (**14f**) was obtained, 0.28 g (45%), mp 203~204°C (acetone-petroleum ether). ^{1}H NMR ($CDCl_3$) δ 1.12, 1.16 (2s, 6H, $2CH_3$), 1.37 (d, J=6.8 Hz, 3H, CH_3), 2.33 (s, 6H, $2CH_3$), 2.32~2.51 (m, 2H, CH_2), 3.35~3.78 (m, 2H, CH_2), 5.93 (m, J=6.8 Hz, 1H, -NCH-), 6.08 (s, 1H, =CH-CO), 6.26(s, 1H, -CH=C-O), 6.59 (d, J=8.0 Hz, 1H, ArH), 6.71~6.89 (m, 4H, ArH), 7.26~7.63 (m, 6H, 5ArH and -CH=N), 8.50 (d, J=8.0 Hz, 1H, ArH, 10'-H). IR (KBr) 3318, 3050, 2950, 2920, 2850, 1725, 1695, 1665, 1605, 1588, 1505, 1480, 1460, 1345, 1270, 1245, 1180, 1078, 1026, 995, 810, 742 cm^{-1}. MS m/z(%): 626 (M+1) (3.59), 625 (M^+) (9.11), 610 (9.91), 370 (10.44), 327 (4.50), 313 (23.22), 311 (21.44), 298 (4.70), 297 (4.21), 269 (3.05), 241 (100), 170 (9.80), 169 (5.27), 158 (18.30), 144 (21.56), 130 (5.62), 128 (7.76), 115 (11.01), 77 (2.69). Anal. Calcd for $C_{39}H_{35}N_3O_5$: C 74.86, H 5.64, N 6.72. Found: C 74.82, H 5.56, N 6.89.

Determination of the photochromism of the synthesized compounds

The solutions of spiropyrans in different solvents (methanol, acetonitrile, acetone and cyclohexane) and in PMMA poly(methylmethacrylate)] matrix with the concentration of 1×10^{-5} mol L^{-1} ~ 1×10^{-4} mol L^{-1} were prepared, respectively. The UV spectrum of each solution before and after irradiation with a 400W high-pressure lamp for 30sec was recorded on a Shimadzu UV-160A UV-VIS spectrophotometer, and the λ_{max} of the compounds were listed in Table 1 and Table 2, respectively.

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