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Photochromic properties of cationic merocyanine dyes. Thermal stability of the spiropyran form produced by irradiation with visible light†

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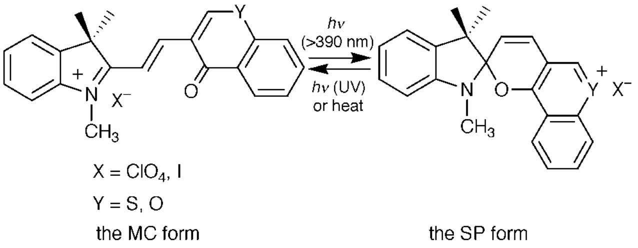
A series of novel cationic merocyanine dyes were prepared by condensation of 1,2,3,3-tetramethylindolium derivatives and 3-formyl-4*H*-1-benzothiopyran or -benzopyran derivatives, and their photochromic properties were investigated, especially focusing on the substituent effect in the indolium moiety. These dyes were converted into the spiropyran (SP) form so as to be colorless by irradiation with visible light, although, left under darkness, the colored merocyanine (MC) form was reproduced. The thermal coloration was affected by two factors: the substituent in the indolium moiety and the counter anion. An electron-donating substituent such as a methoxy group at the 5 position effectively retarded the thermal coloration, whereas an electron-withdrawing group such as a nitro group accelerated it. These substituent effects afforded good linearity for the Hammett rule with *para* σ parameters, indicating that decrease of the electron density in the indoline moiety of the SP form facilitated heterolytic cleavage of the bond between the spiro carbon and the oxygen of the pyran ring.

Introduction

Photochromic compounds have attracted much attention in terms of potential applications in erasable optical recording media,[1] materials for transmittance control,[2] photo-switching devices,[3] and so on. Among them, indolinospiropyrans as well as fulgides and diarylethenes are the most popular photochromic organic dyes, and their photochromic properties such as kinetic and thermodynamic profiles for interconversion between the merocyanine (MC) and spiropyran (SP) forms triggered by photoirradiation have been investigated in detail.[4] Unfortunately, spiropyrans possess a few points to be overcome: the MC form is less stable than the SP form, and thus, from the viewpoint of applications, *i.e.* achievement of interconversion in the photon–photon mode, the thermal stability of the MC form is essential. Attempts to stabilize the MC form have been demonstrated by formation of the J-aggregate,[5] chelation of a metal ion,[6] and copolymerization to polymer backbones.[7] As another defect, the limitation of synthetic methods to prepare a variety of spiropyran derivatives has afforded little chance for wider utilization. Thus, synthetic approaches to novel spiropyran derivatives and analogues and assessment of their photochromic properties are urgently required.

In the course of our researches to develop novel photochromic compounds,[8] we previously reported merocyanine dyes which are converted into the SP form by irradiation with visible light, changing from yellow-orange to colorless (Scheme 1).[9] The dyes can be regarded as analogues of the MC form of indolinospiropyran and afforded the possibility to design novel photochromic spiropyran derivatives. They are essentially stable in the MC form. In this paper, we report preparation of a series of cationic merocyanine dyes, their structural assignment and thermal stability, especially focusing on substituent effects on the indolium moiety.



Scheme 1

Results and discussion

Preparation of merocyanine dye

Merocyanine dyes were typically prepared in a similar manner to that reported previously.[9] As shown in Scheme 2, condensation of 5-substituted indolium salt **1**·X$^-$ (X = ClO_4, I or BPh_4) with 3-formyl-4*H*-1-benzothiopyran-4-one **2**, 3-formyl-4*H*-1-benzopyran-4-one **3**, or 3-formyl-2-phenyl-4*H*-1-benzothiopyran-4-one **4** afforded **5**–**10** and **13** in 23–81% yields. The dyes bearing more extended π conjugation, **11** and **12**, were prepared by condensation of benz[*c*,*d*]indolium perchlorate **16** with **2** and **3** in 17 and 46% yields, respectively. The merocyanine dyes discussed here and their absorption maxima are summarized in Table 1. For **5**–**8**, the substituent at the 5 position is varied from Hto MeO, Me, Br, and NO_2. Benzothiopyrano-merocyanine dyes exhibited absorption maxima at longer wavelengths than those of the benzopyrano-merocyanines: the bathochromic shifts in the benzothiopyrano series ranged from 38 to 64 nm among the dyes with the same substituent at the 5 position. The dyes **11** and **12** showed their absorption maxima at 522 and 488 nm, respectively, owing to the strong electron-donating property of the benzindolium moiety and the extension of the π-conjugation

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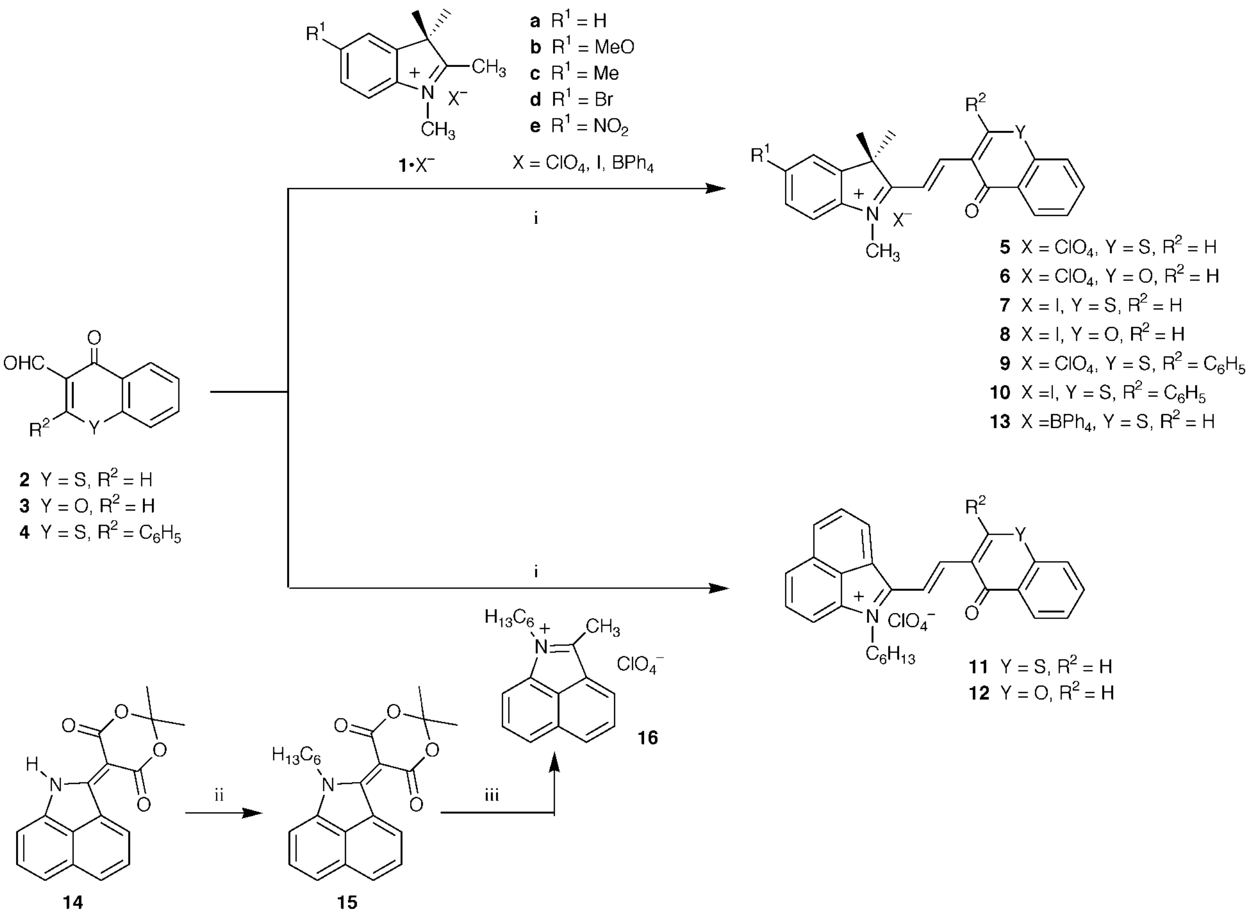
†Elemental analyses for compounds **6**–**10** and **13** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/jm/1999/2991/, otherwise available from BLDSC (SUPPL. NO. 57663, pp. 3) or the RSC Library.



Scheme 2 *Reagents and conditions*: i, EtOH, reflux; ii, 1-iodohexane, K_2CO_3, DMF, 80 °C; iii, 70% $HClO_4$, AcOH, reflux.

system. Substitution at the 5 position of **5a**–**8a** leads to bathochromic shifts of the absorption maxima, ranging from 2 to 31 nm. The effect of the introduction of a phenyl group to the benzothiopyran ring on the absorption maximum was small: the bathochromic shift was 7 nm, in comparison to that between **5a** (or **7a**) and **9** (or **10**). Each merocyanine dye was identified by ^{1}H NMR, UV-vis and IR spectra and elemental analysis.

Table 1 UV-vis absorption spectral features of compounds **5**–**11** in $CHCl_2CHCl_2$ at 20 °C

Compound	X	Y	R^1	R^2	λ_{max}/nm	log (ε/dm^3 mol^{-1} cm^{-1})
5a	ClO_4	S	H	H	456	4.54
5b	ClO_4	S	MeO	H	467	4.48
5c	ClO_4	S	Me	H	458	4.49
5d	ClO_4	S	Br	H	468	4.59
5e	ClO_4	S	NO_2	H	481	4.60
6a	ClO_4	O	H	H	403	4.48
6b	ClO_4	O	MeO	H	429	4.41
6c	ClO_4	O	Me	H	409	4.44
6d	ClO_4	O	Br	H	413	4.54
6e	ClO_4	O	NO_2	H	427	4.48
7a	I	S	H	H	456	4.58
7b	I	S	MeO	H	470	4.53
7c	I	S	Me	H	459	4.57
7d	I	S	Br	H	468	4.60
7e	I	S	NO_2	H	487	4.57
8a	I	O	H	H	403	4.51
8b	I	O	MeO	H	430	4.45
8c	I	O	Me	H	409	4.50
8d	I	O	Br	H	414	4.54
8e	I	O	NO_2	H	423	4.59
9	ClO_4	S	H	C_6H_5	460	4.33
10	I	S	H	C_6H_5	463	4.56
11	ClO_4	S	—	H	522	4.49
12	ClO_4	O	—	H	488	4.39
13	BPh_4	S	H	H	456	4.49

Molecular structure of merocyanine dyes

In the MC form of indolinospiropyrans, several stereoisomers are possible in terms of the photoisomerization of the central ethenyl double bond as shown in Fig. 1; (s-*trans*, s-*trans*), (s-*trans*, s-*cis*), (s-*cis*, s-*trans*) and (s-*cis*, s-*cis*) isomers. The molecular structure of the cationic merocyanine dye was confirmed by the X-ray structural analysis of **13**. The ORTEP

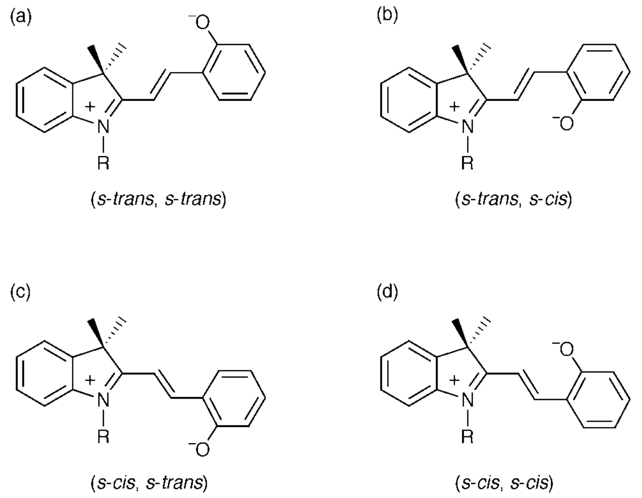


Fig. 1 Isomers of an indolinospiropyran: (a) (s-*trans*, s-*trans*), (b) (s-*trans*, s-*cis*), (c) (s-*cis*, s-*trans*) and (d) (s-*cis*, s-*cis*) isomers.

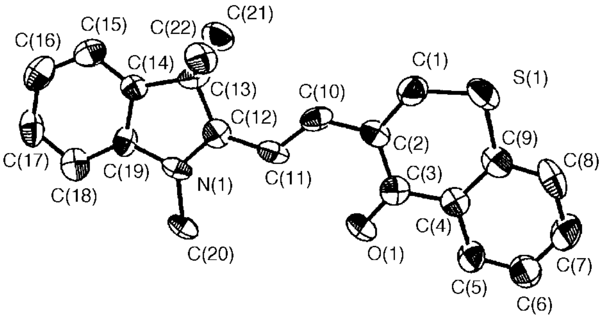


Fig. 2 The ORTEP drawing of compound **13**. All hydrogen atoms and the tetraphenylborate anion are neglected for clarity.

drawing of **13** is shown in Fig. 2. From the structural analysis, it was confirmed that the merocyanine dyes adopted the geometry resembling the (s-*trans*, s-*cis*) of the MC form of indolinospiropyrans. In the ^{1}H NMR spectra of **5**–**13**, coupling of the methyne protons of the central double bond was observed ($J = 16$ Hz), indicating the *trans* configuration of the bond. Thus, the structure obtained by the X-ray analysis is likely to be adopted in solution.

Substituent effects on isomerization to the spiropyran form by photoirradiation

As reported previously, merocyanine dyes **5a** and **6a** isomerized to the SP form on irradiation by visible light (>390 nm), confirmed by ^{1}H NMR spectra of the dyes just after photoirradiation. In the spectra the two methyne protons were magnetically coupled with each other ($J = 12$ Hz) and the peak of the *N*-methyl protons appeared at 3.0 ppm, which are characteristic of the SP form.[9] In the UV-vis spectrum, remarkable bleaching of the absorbance at λ_{max} was observed for each dye, and the original spectrum was recovered when left under darkness. Typical UV-vis absorption spectra of the merocyanine and the spiropyran forms are shown for **7c** in Fig. 3. The efficiency of decoloration was >65% for **5**–**8** and **13**. The other dyes also exhibited similar decoloration upon photoirradiation and thermal coloration, although conversion into the SP form was less effective for **9**–**12**. The thermal coloration obeyed first order kinetics, and the efficiency of decoloration upon irradiation and the rate constant k of the thermal coloration for each dye are summarized in Table 2. For nitro-substituted dyes **5e**–**8e** the rate constants could not be determined because the thermal isomerization was too fast. The rate of the thermal coloration was affected mainly by two factors: electron-donating or -withdrawing properties of the substituent at the 5 position and the character of the counter anion. The larger the electron-donating property of the substituent was, the more the rate of the thermal coloration was decreased: the rate constants of bromo-substituted dyes **5d**–**8d** were larger than those of the methoxy-substituted dyes by factors of 35–1240. As shown in Fig. 4, dealing with the Hammett *para* substituent constant σ_p afforded good linearity.[10] These results indicate that decrease of the elctron density in the indoline moiety accelerates heterolytic cleavage of the bond between the spiro carbon and the oxygen atom of the pyran ring.

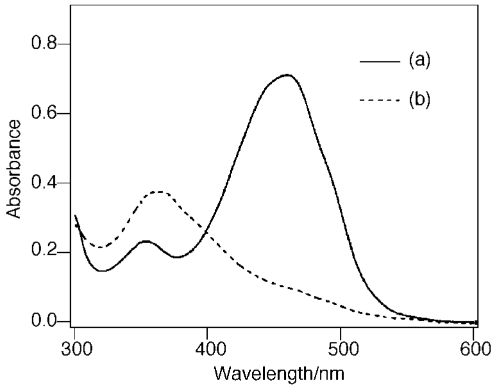


Fig. 3 UV-vis spectra of (a) the merocyanine and (b) the spiropyran forms of compound **7c** (1.9×10^{-5} mol dm^{-3}). Spectrum (b) was obtained upon irradiation by visible light ($\lambda > 390$ nm).

Table 2 Efficiency of the conversion of the merocyanine dyes **5**–**12** into the SP form upon photoirradiation and kinetic data for the thermal coloration[a]

Compound	Efficiency (%)[b]	$k/10^{-3}$ s$^{-1\,b,c}$
5a	88	0.449
5b	82	0.0120
5c	88	0.0247
5d	77	14.9
6a	93	0.170
6b	81	0.0151
6c	90	0.0471
6d	71	15.1
7a	76	3.89
7b	81	0.425
7c	85	0.995
7d	65	14.9
8a	84	2.44
8b	76	0.624
8c	85	0.801
8d	67	37.9
9	61	0.000458
10	65	0.0190
11	56	4.05
12	53	17.3
13	81	0.586

[a]In $CHCl_2CHCl_2$ at 20 °C. [b]Determined by UV-vis spectroscopy. [c]Standard deviations are <3%.

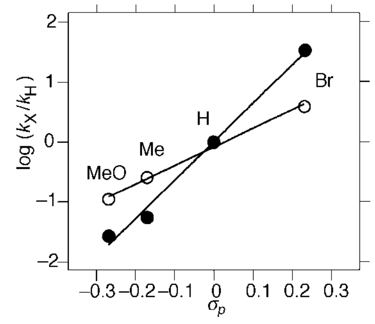


Fig. 4 Correlation between Hammett's substituent constant σ_p and log (k_X/k_H) (X = H, MeO, Me or Br) for compounds **5** (●) and **7** (○).

Effect of counter anions on thermal coloration

As mentioned above, the thermal coloration was also affected by the counter anion. Comparison between compounds **5** (or **6**) and **7** (or **8**) showed that exchange of the counter anion from perchlorate to iodide led to acceleration of the thermal coloration. The tetraphenylborate dye **13** exhibited a similar kinetic profile to the corresponding perchlorate dye **5a**, indicating that the iodide anion plays an important role in

Table 3 ρ Values for dyes **5**–**8** obtained by Hammett's plots

Dye	Counter anion	ρ
5	ClO_4^-	6.39 (±0.43)
6	ClO_4^-	5.88 (±0.86)
7	I^-	3.08 (±0.20)
8	I^-	3.63 (±0.58)

promoting the thermal coloration. The anion effect on the thermal coloration was clearly shown in the slopes of the Hammett plots for dyes **5**–**8** given in Table 3. The ρ values are similar for **5** and **6** and for **7** and **8**, respectively, where the perchlorate dyes yielded larger slopes than the iodides by a factor of *ca.* 2. Thus, the substituent effect at the 5 position of the indolium was more marked in the perchlorates than in the iodides. Although we can not offer a definitive answer for the effect of counter anions at this point, this might be due to the softer character of iodide anion than that of perchlorate.

Conclusion

The novel merocyanine dyes, **5**–**13**, were prepared as analogues of the indolinospiropyrans. The molecular structure was confirmed by X-ray crystallography showing that the geometry around the central olefin was (s-*trans*, s-*cis*). These dyes exhibited negative photochromic properties, and substitution at the 5 position of the indolium ring with an electron-donating group or introduction of a phenyl group at the 2 position of the benzothiopyran ring brought about retardation of the thermal coloration. The rate for thermal conversion from the SP form to the MC form was affected by the counter anion: the SP form of the perchlorate dye was converted more slowly than that of the iodide. Results obtained here should contribute to investigation of novel photochromic spiropyrans and their analogues.

Experimental

^{1}H NMR spectra (270 MHz) were recorded on a JEOL JNM-GX 270 spectrometer in $CDCl_3$, DMSO-d_6, CD_3CN and CD_3COCD_3 using TMS (0 ppm), CHD_2SOCD_3 (2.49 ppm), CHD_2CN (1.93 ppm) and CD_2HCOCD_3 (2.04 ppm) as internal standards, respectively, IR spectra were recorded on a Horiba FT-200 spectrometer for KBr disks of samples. Melting points were determined by differential thermal analyses with a Rigaku TAS 100 analyzer under nitrogen atmosphere (flow rate: 100 mL min^{-1}) by the use of Al_2O_3 as a reference. The temperature rate programmed was 10 °C min^{-1}.

Indolium salts **1**·X^- ($X = ClO_4$, I or BPh_4) were prepared by the conventional reaction of the corresponding 2,3,3-trimethylindolinine derivatives with methyl iodide followed by anion exchange in the cases of perchlorates and tetraphenylborate, each of which was confirmed by ^{1}H NMR spectra and elemental analyses. Compounds **2**,[11] and **3**[12] and **14**[13] were prepared by the reported procedures. The solvent used in UV-vis studies, $CHCl_2CHCl_2$, was of spectroscopic grade.

General procedure for the preparation of compounds 5–10 and 13

A mixture of indolium salt **1**·X^- (0.3 mmol) and the aldehyde **2**, **3** or **4** (0.33 mmol) in ethanol (5 mL) was heated at reflux for 7–42 h. After cooling, the solid was separated by filtration and washed with diethyl ether (50 mL × 3) to afford the merocyanine dye.

1,3,3-Trimethyl-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)-indolium perchlorate 5a. This compound was prepared by condensation of **1a**·ClO_4^- and **2**; yield 35%; mp 264 °C (decomp.); δ_H (DMSO-d_6) 1.79 (s, 6H), 4.10 (s, 3H), 7.63–7.67 (m, 2H), 7.78 (dt, $J = 1.2$ and 7.6, 1H), 7.85–7.96 (m, 3H), 8.07 (dd, $J = 1.2$ and 8.2, 1H), 8.15 (d, $J = 16.3$, 1H), 8.36 (d, $J = 16.3$, 1H), 8.53 (dd, $J = 1.2$ and 8.2, 1H), 9.63 (s, 1H); IR (KBr) 1623 cm^{-1} (C=O). Calc. (%) for $C_{22}H_{20}NO_5SCl$: C, 59.26; H, 4.52; N, 3.14. Found: C, 58.82; H, 4.43; N, 3.06.

5-Methoxy-1,3,3-trimethyl-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)indolium perchlorate 5b. This compound was prepared by condensation of **1b**·ClO_4^- and **2**; yield 51%; mp 251 °C (decomp.); δ_H (DMSO-d_6) 1.78 (s, 6H), 3.90 (s, 3H), 4.08 (s, 3H), 7.18 (dd, $J = 2.4$ and 8.9, 1H), 7.54 (d, $J = 2.4$, 1H), 7.77 (dt, $J = 1.2$ and 8.0, 1H), 7.84–7.90 (m, 2H), 8.05–8.11 (m, 2H), 8.38 (d, $J = 16.3$, 1H), 8.52 (dd, $J = 1.2$ and 8.0, 1H), 9.54 (s, 1H); IR (KBr) 1623 cm^{-1} (C=O). Calc. (%) for $C_{23}H_{22}NO_6SCl$: C, 58.04; H, 4.66; N, 2.94. Found: C, 58.14; H, 4.39; N, 2.81.

1,3,3,5-Tetramethyl-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)indolium perchlorate 5c. This compound was prepared by condensation of **1c**·ClO_4^- and **2**; yield 69%; mp 261 °C (decomp.); δ_H (DMSO-d_6) 1.77 (s, 6H), 2.47 (s, 3H), 4.08 (s, 3H), 7.46 (dd, $J = 0.6$ and 8.0, 1H), 7.71 (s, 1H), 7.74–7.84 (m, 2H), 7.87 (dt, $J = 1.4$ and 8.0, 1H), 8.05–8.14 (m, 2H), 8.32 (d, $J = 16.3$, 1H), 8.52 (dd, $J = 1.4$ and 8.0, 1H), 9.62 (s, 1H); IR (KBr) 1624 cm^{-1} (C=O). Calc. (%) for $C_{23}H_{22}NO_5SCl$: C, 60.06; H, 4.82; N, 3.05. Found: C, 59.78; H, 4.80; N, 3.25.

5-Bromo-1,3,3-trimethyl-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)indolium perchlorate 5d. This compound was prepared by condensation of **1d**·ClO_4^- and **2**; yield 63%; mp 284 °C (decomp.); δ_H (DMSO-d_6) 1.80 (s, 6H), 4.08 (s, 3H), 7.78 (dt, $J = 1.2$ and 8.0, 1H), 7.84–7.92 (m, 3H), 8.07 (dd, $J = 0.8$ and 8.0, 1H), 8.15 (d, $J = 16.3$, 1H), 8.23 (d, $J = 1.4$, 1H), 8.37 (d, $J = 16.3$, 1H), 8.52 (dd, $J = 1.2$ and 8.0, 1H), 9.66 (s, 1H); IR (KBr) 1626 cm^{-1} (C=O). Calc. (%) for $C_{22}H_{19}NO_5SBrCl \cdot H_2O$: C, 48.68; H, 3.90; N, 2.58. Found: C, 48.52; H, 3.52; N, 2.94.

1,3,3-Trimethyl-5-nitro-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)indolium perchlorate 5e. This compound was prepared by condensation of **1e**·ClO_4^- and **2**; yield 71%; mp 272 °C (decomp.); δ_H (DMSO-d_6) 1.88 (s, 6H), 4.12 (s, 3H), 7.79 (dt, $J = 1.0$ and 7.7, 1H), 7.89 (dt, $J = 1.4$ and 7.7, 1H), 8.08 (dd, $J = 1.0$ and 7.7, 1H), 8.17 (d, $J = 8.9$, 1H), 8.24 (d, $J = 16.3$, 1H), 8.46–8.57 (m, 3H), 8.88 (d, $J = 2.0$, 1H), 9.73 (s, 1H); IR (KBr) 1632 cm^{-1} (C=O). Calc. (%) for $C_{22}H_{19}N_2O_7SCl$: C, 53.83; H, 3.90; N, 5.71. Found: C, 53.55; H, 3.51; N, 5.85.

1,3,3-Trimethyl-2-(4-oxo-4*H*-1-benzopyran-3-ylethenyl)indolium perchlorate 6a. This compound was prepared by condensation of **1a**·ClO_4^- and **3**; yield 33%; mp 259 °C (decomp.); δ_H (DMSO-d_6) 1.80 (s, 6H), 4.06 (s, 3H), 7.62–7.68 (m, 3H), 7.83 (1H, dd, $J = 1.2$ and 8.3, 1H), 7.87–7.97 (m, 3H), 8.19 (d, $J = 16.4$, 1H), 8.22 (dd, $J = 1.2$ and 7.9, 1H), 8.49 (d, $J = 16.4$, 1H), 9.33 (s, 1H); IR (KBr) 1657 cm^{-1} (C=O).

5-Methoxy-1,3,3-trimethyl-2-(4-oxo-4*H*-1-benzopyran-3-ylethenyl)indolium perchlorate 6b. This compound was prepared by condensation of **1b**·ClO_4^- and **3**; yield 55%; mp 249 °C (decomp.); δ_H (DMSO-d_6) 1.78 (s, 6H), 3.90 (s, 3H), 4.04 (s, 3H), 7.18 (dd, $J = 2.4$ and 8.8, 1H), 7.54 (m, 1H), 7.64 (dt, $J = 0.8$ and 8.0, 1H), 7.82 (dd, $J = 0.8$ and 8.0, 1H), 7.87 (d, $J = 8.8$, 1H), 7.93 (dt, $J = 1.6$ and 8.0, 1H), 8.10 (d, $J = 16.3$, 1H), 8.21 (dd, $J = 1.6$ and 8.0, 1H), 8.42 (d, $J = 16.3$, 1H), 9.28 (s, 1H); IR (KBr) 1647 cm^{-1} (C=O).

1,3,3,5-Tetramethyl-2-(4-oxo-4*H*-1-benzopyran-3-ylethenyl)-indolium perchlorate 6c. This compound was prepared by condensation of **1c**·ClO_4^- and **3**; yield 77%; mp 259 °C (decomp.); δ_H (DMSO-d_6) 1.78 (s, 6H), 2.47 (s, 3H), 4.04 (s, 3H), 7.45 (dd, $J = 0.8$ and 8.3, 1H), 7.64 (dt, $J = 1.0$ and 7.8, 1H), 7.71 (s, 1H), 7.81–7.85 (m, 2H), 7.93 (dt, $J = 1.6$ and 7.8, 1H), 8.14 (d, $J = 16.3$, 1H), 8.21 (dd, $J = 1.6$ and 7.8, 1H), 8.45 (d, $J = 16.3$, 1H), 9.30 (s, 1H); IR (KBr) 1657 cm^{-1} (C=O).

5-Bromo-1,3,3-trimethyl-2-(4-oxo-4*H*-1-benzopyran-3-ylethenyl)indolium perchrorate 6d. This compound was prepared by condensation of **1d**·ClO_4^- and **3**; yield 71%; mp 277 °C (decomp.); δ_H (DMSO-d_6) 1.81 (s, 6H), 4.04 (s, 3H), 7.64 (dt, J = 1.0 and 7.7, 1H), 7.83 (dd, J = 1.0 and 8.0, 1H), 7.84–7.97 (m, 3H), 8.18–8.24 (m, 3H), 8.46 (d, J = 16.3, 1H), 9.34 (s, 1H); IR (KBr) 1655 cm^{-1} (C=O).

1,3,3-Trimethyl-5-nitro-2-(4-oxo-4*H*-1-benzopyran-3-ylethenyl)indolium perchlorate 6e. This compound was prepared by condensation of **1e**·ClO_4^- and **3**; yield 61%; mp 268 °C (decomp.); δ_H (DMSO-d_6) 1.89 (s, 6H), 4.09 (s, 3H), 7.66 (dt, J = 1.0 and 7.8, 1H), 7.84 (dd, J = 1.0 and 8.5, 1H), 7.95 (dt, J = 1.6 and 7.8, 1H), 8.18–8.24 (m, 2H), 8.36 (d, J = 16.1, 1H), 8.52 (dd, J = 2.2 and 8.9, 1H), 8.54 (d, J = 16.1, 1H), 8.89 (d, J = 2.2, 1H), 9.39 (s, 1H); IR (KBr) 1659 cm^{-1} (C=O).

1,3,3-Trimethyl-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)-indolium iodide 7a. This compound was prepared by condensation of **1a**·I^- and **2**; yield 75%; mp 256 °C (decomp.); δ_H (DMSO-d_6) 1.79 (s, 6H), 4.10 (s, 3H), 7.63–7.67 (m, 2H), 7.79 (dt, J = 1.2 and 7.6, 1H), 7.85–7.96 (m, 3H), 8.07 (dd, J = 0.9 and 8.2, 1H), 8.16 (d, J = 16.5, 1H), 8.37 (d, J = 16.5 , 1H), 8.53 (dd, J = 1.2 and 8.2, 1H), 9.64 (s, 1H); IR (KBr) 1624 cm^{-1} (C=O).

5-Methoxy-1,3,3-trimethyl-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)indolium iodide 7b. This compound was prepared by condensation of **1b**·I^- and **2**; yield 23%; mp 256 °C (decomp.); δ_H (DMSO-d_6) 1.78 (s, 6H), 3.90 (s, 3H), 4.08 (s, 3H), 7.18 (dd, J = 2.4 and 8.9, 1H), 7.55 (d, J = 2.4, 1H), 7.77 (dt, J = 1.0 and 8.0, 1H), 7.86 (d, J = 8.9, 1H), 7.88 (dt, J = 1.4 and 8.0, 1H), 8.05–8.11 (m, 2H), 8.28 (d, J = 16.3, 1H), 8.52 (dd, J = 1.4 and 8.0, 1H), 9.61 (s, 1H); IR (KBr) 1628 cm^{-1} (C=O).

1,3,3,5-Tetramethyl-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)indolium iodide 7c. This compound was prepared by condensation of **1c**·I^- and **2**; yield 44%; mp 264 °C (decomp.); δ_H (DMSO-d_6) 1.77 (s, 6H), 2.47 (s, 3H), 4.08 (s, 3H), 7.46 (dd, J = 0.6 and 8.0, 1H), 7.71 (s, 1H), 7.74–7.84 (m, 2H), 7.87 (dt, J = 1.4 and 8.0, 1H), 8.05–8.14 (m, 2H), 8.32 (d, J = 16.3, 1H), 8.52 (dd, J = 1.4 and 8.0, 1H), 9.60 (s, 1H); IR (KBr) 1624 cm^{-1} (C=O).

5-Bromo-1,3,3-trimethyl-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)indolium iodide 7d. This compound was prepared by condensation of **1d**·I^- and **2**; yield 35%; mp 281 °C (decomp.); δ_H (DMSO-d_6) 1.80 (s, 6H), 4.07 (s, 3H), 7.78 (dt, J = 1.2 and 8.0, 1H), 7.84–7.92 (m, 3H), 8.07 (dd, J = 0.8 and 8.0, 1H), 8.15 (d, J = 16.3, 1H), 8.23 (d, J = 1.4, 1H), 8.37 (d, J = 16.3, 1H), 8.53 (dd, J = 1.2 and 8.0, 1H), 9.65 (s, 1H); IR (KBr) 1624 cm^{-1} (C=O).

1,3,3-Trimethyl-5-nitro-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)indolium iodide 7e. This compound was prepared by condensation of **1e**·I^- and **2**; yield 70%; mp 260 °C (decomp.); δ_H (DMSO-d_6) 1.88 (s, 6H), 4.12 (s, 3H), 7.79 (dt, J = 1.0 and 7.7, 1H), 7.89 (dt, J = 1.4 and 7.7, 1H), 8.09 (dd, J = 1.0 and 7.7, 1H), 8.18 (d, J = 8.9, 1H), 8.24 (d, J = 16.3, 1H), 8.46–8.57 (m, 3H), 8.88 (d, J = 2.0, 1H), 9.77 (s, 1H); IR (KBr) 1630 cm^{-1} (C=O).

1,3,3-Trimethyl-2-(4-oxo-4*H*-1-benzopyran-3-ylethenyl)indolium iodide 8a. This compound was prepared by condensation of **1a**·I^- and **3**; yield 69%; mp 254 °C (decomp.); δ_H (DMSO-d_6) 1.80 (s, 6H), 4.06 (s, 3H), 7.62–7.68 (m, 3H), 7.83 (dd, J = 1.2 and 8.3, 1H), 7.87–7.97 (m, 3H), 8.19 (d, J = 16.4, 1H), 8.22 (dd, J = 1.2 and 7.9, 1H), 8.49 (d, J = 16.4, 1H), 9.33 (s, 1H); IR (KBr) 1651 cm^{-1} (C=O).

5-Methoxy-1,3,3-trimethyl-2-(4-oxo-4*H*-1-benzopyran-3-ylethenyl)indolium iodide 8b. This compound was prepared by condensation of **1b**·I^- and **3**; yield 80%; mp 260 °C (decomp.); δ_H (DMSO-d_6) 1.79 (s, 6H), 3.90 (s, 3H), 4.04 (s, 3H), 7.17 (dd, J = 2.4 and 8.8, 1H), 7.56 (d, J = 2.4, 1H), 7.63 (dt, J = 0.8 and 8.0, 1H), 7.82 (dd, J = 0.8 and 8.0, 1H), 7.88 (d, J = 8.8, 1H), 7.94 (dt, J = 1.6 and 8.0, 1H), 8.11 (d, J = 16.3, 1H), 8.21 (dd, J = 1.6 and 8.0, 1H), 8.42 (d, J = 16.3, 1H), 9.33 (s, 1H); IR (KBr) 1659 cm^{-1} (C=O).

1,3,3,5-Tetramethyl-2-(4-oxo-4*H*-1-benzopyran-3-ylethenyl)-indolium iodide 8c. This compound was prepared by condensation of **1c**·I^- and **3**; yield 61%; mp 254 °C (decomp.); δ_H (DMSO-d_6) 1.78 (s, 6H), 2.47 (s, 3H), 4.04 (s, 3H), 7.46 (dd, J = 0.6 and 8.5, 1H), 7.64 (dt, J = 0.8 and 7.8, 1H), 7.72 (d, J = 0.6, 1H), 7.82 (dd, J = 0.8 and 8.0, 1H), 7.83 (d, J = 8.5, 1H), 7.94 (dt, J = 1.6 and 8.0, 1H), 8.15 (d, J = 16.3, 1H), 8.22 (dd, J = 1.6 and 7.8, 1H), 8.45 (d, J = 16.3, 1H), 9.33 (s, 1H); IR (KBr) 1651 cm^{-1} (C=O).

5-Bromo-1,3,3-trimethyl-2-(4-oxo-4*H*-1-benzopyran-3-ylethenyl)indolium iodide 8d. This compound was prepared by the condensation of **1d**·I^- and **3**; yield 78%; mp 248 °C (decomp.); δ_H (DMSO-d_6) 1.81 (s, 6H), 4.04 (s, 3H), 7.65 (dt, J = 1.0 and 7.7, 1H), 7.83 (dd, J = 1.0 and 8.0, 1H), 7.84–7.97 (m, 3H), 8.18–8.24 (m, 3H), 8.46 (d, J = 16.3, 1H), 9.34 (s, 1H); IR (KBr) 1655 cm^{-1} (C=O).

1,3,3-Trimethyl-5-nitro-2-(4-oxo-4*H*-1-benzopyran-3-ylethenyl)indolium iodide 8e. This compound was prepared by the condensation of **1e**·I^- and **3**; yield 51%; mp 248 °C (decomp.); δ_H (DMSO-d_6) 1.89 (s, 6H), 4.09 (s, 3H), 7.66 (dt, J = 0.8 and 7.8, 1H), 7.84 (dd, J = 0.8 and 7.8, 1H), 7.95 (dt, J = 1.6 and 7.8, 1H), 8.18–8.24 (m, 2H), 8.36 (d, J = 16.1, 1H), 8.52 (dd, J = 2.2 and 8.8, 1H), 8.54 (d, J = 16.1, 1H), 8.89 (d, J = 2.2, 1H), 9.41 (s, 1H); IR (KBr) 1659 cm^{-1} (C=O).

1,3,3-Trimethyl-2-(4-oxo-2-phenyl-4*H*-1-benzothiopyran-3-ylethenyl)indolium perchlorate 9. This compound was prepared by condensation of **1a**·ClO_4^- and **4**; yield 70%; mp 243 °C (decomp.); δ_H (DMSO-d_6) 1.29 (s, 6H), 4.00 (s, 3H), 7.52–7.61 (m, 2H), 7.66 (d, J = 15.9, 1H), 7.70–7.78 (m, 6H), 7.81 (dt, J = 1.2 and 8.0, 1H), 7.88–7.95 (m, 2H), 8.07 (dd, J = 1.0 and 8.0, 1H), 8.42 (d, J = 15.9, 1H), 8.55 (dd, J = 1.2 and 8.0, 1H); IR (KBr) 1632 cm^{-1} (C=O).

1,3,3,-Trimethyl-2-(4-oxo-2-phenyl-4*H*-1-benzothiopyran-3-ylethenyl)indolium iodide 10. This compound was prepared by condensation of **1a**·I^- and **4**; yield 63%; mp 233 °C (decomp.); δ_H (DMSO-d_6) 1.30 (s, 6H), 4.00 (s, 3H), 7.57–7.61 (m, 2H), 7.66 (d, J = 15.9, 1H), 7.70–7.78 (m, 6H), 7.81 (dt, J = 1.2 and 8.0, 1H), 7.89–7.95 (m, 2H), 8.06 (dd, J = 1.0 and 8.0, 1H), 8.41 (d, J = 15.9, 1H), 8.55 (dd, J = 1.2 and 8.0, 1H); IR (KBr) 1626 cm^{-1} (C=O).

1,3,3-Trimethyl-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)-indolium tetraphenylborate 13. This compound was prepared by condensation of **1a**·BPh_4^- and **2**; yield 81%; mp 191 °C (decomp.); δ_H (DMSO-d_6) 1.79 (s, 6H), 4.09 (s, 3H), 6.78 (t, J = 7.3, 4H), 6.92 (t, J = 7.3, 8H), 7.15–7.21 (m, 8H), 7.63–7.66 (m, 2H), 7.78 (dt, J = 1.2 and 7.9, 1H), 7.84–7.95 (m, 3H), 8.07 (dd, J = 1.2 and 7.9, 1H), 8.15 (d, J = 16.5, 1H), 8.36 (d, J = 16.5 Hz, 1H), 8.53 (dd, J = 1.2 and 7.9, 1H), 9.62 (s, 1H); IR (KBr) 1633 cm^{-1} (C=O).

1-Hexyl-2-(4-oxo-4*H*-1-benzothiopyran-3-ylethenyl)[*c*,*d*]indolium perchlorate 11. A mixture of compounds **16** (0.25 mmol) and **6** (0.38 mmol) in ethanol (10 mL) was heated at reflux for 10 h. The hot reaction mixture was filtered to separate the resultant solid, which was dispersed in ether (30 mL) and stirred for 30 min. Filtration afforded **11** as a solid; yield 17%; mp 230 °C (decomp.); δ_H (CD_3CN) 0.87 (t, J = 7.3, 3H), 1.26–1.49 (m, 4H), 1.63 (quint, J = 7.3, 2H), 2.18 (quint, J = 7.3, 2H), 4.91 (t, $J=7.3$, 2H), 7.71 (dt, $J=1.2$ and 7.9, 1H), 7.80 (dt, $J=1.2$ and 7.9, 1H), 7.89 (dd, $J=1.2$ and 7.9, 1H), 7.99 (t, $J=7.9$, 1H), 8.20 (t, $J=7.9$, 1H), 8.36 (d, $J=7.9$, 1H), 8.44 (d, $J=7.9$, 1H), 8.55 (dd, $J=1.2$ and 7.9, 1H), 8.70 (d, $J=15.9$, 1H), 8.71 (d, $J=7.9$, 1H), 8.79 (d, $J=15.9$, 1H), 9.21 (d, $J=7.9$, 1H), 9.42 (s, 1H); IR (KBr) 1622 cm^{-1} (C=O). Calc. (%) for $C_{28}H_{26}NO_5SCl$: C, 64.18; H, 5.00; N, 2.67. Found: C, 64.26; H, 4.84; N, 2.58.

1-Hexyl-2-(4-oxo-4*H*-1-benzopyran-3-ylethenyl)benz[*c*,*d*]indolium perchlorate 12. This compound was prepared by the similar method to **11** using **3**; yield 46%; mp 239 °C (decomp.); δ_H (CD_3COCD_3) 0.88 (t, $J=7.3$, 3H), 1.28–1.50 (m, 4H), 1.64 (quint, $J=7.3$, 2H), 2.21 (quint, $J=7.3$, 2H), 4.93 (t, $J=7.3$, 2H), 7.65 (dt, $J=1.8$ and 7.9, 1H), 7.85 (d, $J=7.9$, 1H), 7.94 (dt, $J=1.8$ and 7.9, 1H), 8.06 (t, $J=7.9$, 1H), 8.24 (t, $J=7.9$, 1H), 8.32 (dd, $J=1.8$ and 7.9, 1H), 8.45 (d, $J=7.9$, 1H), 8.52 (d, $J=7.9$, 1H), 8.72 (d, $J=15.9$, 1H), 8.79 (d, $J=7.9$, 1H), 9.06 (d, $J=15.9$, 1H), 9.18 (s, 1H), 9.32 (d, $J=7.9$, 1H); IR (KBr) 1655 cm^{-1} (C=O). Calc. (%) for $C_{28}H_{26}NO_6Cl$: C, 66.21; H, 5.16; N, 2.76. Found: C, 66.25; H, 5.13; N, 2.80.

3-Formyl-2-phenyl-4*H*-1-benzothiopyran-4-one 4. A mixture of 3-hydroxy-2-phenyl-4*H*-1-benzothiopyran-4-one[14] (1.81 g, 6.75 mmol) and pyridinium dichromate (5.08 g, 13.5 mmol) in dry dichloromethane was stirred for 25 h at ambient temperature. Ether (50 mL) and anhydrous $MgSO_4$ were added and the mixture was stirred for 15 min, followed by filtration. The filtrate was washed with 5 M HCl, water and saturated brine, and dried over anhydrous $MgSO_4$. The solvent was removed by an evaporater, and the residue purified by silica gel column chromatography (dichloromethane–ethyl acetate, 20 : 1, v/v, as eluent). Further purification by recrystallization from benzene afforded compound **4** as ivory crystals; yield 39% (698 mg); mp 166 °C; δ_H ($CDCl_3$) 7.42 (m, 8H), 8.58 (dd, $J=1.8$ and 7.3, 1H), 10.2 (s, 1H); IR (KBr) 1701 cm^{-1} (HC=O), 1614 cm^{-1} (C=O); EI-MS (*m/z*) 266 (84, M^+), 237 (100%, $[M-CHO]^+$). Calc. (%) for $C_{16}H_{10}O_2S$: C, 72.16; H, 3.78. Found: C, 72.11; H, 3.55.

2-(2,2-Dimethyl-4,6-dioxo-1,3-dioxacyclohex-5-cylidene)-1-hexyl-1,2-dihydrobenz[*c*,*d*]indoline 15. A stirred mixture of compound **14** (2.22 g, 7.5 mmol), 1-iodohexane (3.18 g, 15 mmol) and K_2CO_3 (2.07 g, 15 mmol) in DMF (30 mL) was heated at 80 °C for 8 h. After cooling, the solvent was removed by an evaporator and water added to the residue, followed by extraction with dichloromethane ($\times 2$). The extracts were combined, washed with water ($\times 2$) and saturated brine, and dried over anhydrous $MgSO_4$. The solvent was removed by an evaporator, and the residue purified by silica gel column chromatography (hexane–ethyl acetate, 2 : 1, v/v, as eluent). Recrystallization from benzene–hexane afforded **15** as orange crystals; yield 80% (2.28 g); mp 165 °C; δ_H ($CDCl_3$) 1.34 (t, $J=7.3$, 3H), 1.25–1.36 (m, 6H), 1.83 (s, 6H), 1.89 (quint, $J=7.3$, 2H), 4.37 (t, $J=7.3$, 2H), 7.52 (d, $J=7.9$, 1H), 7.61 (t, $J=7.9$, 1H), 7.81 (t, $J=7.9$, 1H), 7.84 (d, $J=7.9$, 1H), 8.17 (d, $J=7.9$, 1H), 9.01 (d, $J=7.9$, 1H); IR (KBr) 1664 cm^{-1} (C=O); EI-MS (*m/z*) 379 (8.6, M^+), 236 (100%, $[M-C_6H_7O_4]^+$). Calc. (%) for $C_{23}H_{25}NO_4$: C, 72.80; H, 6.64; N, 3.69. Found: C, 72.85; H, 6.61; N, 3.22.

1-Hexyl-2-methylbenz[*c*,*d*]indolium perchlorate 16. To a refluxed solution of compound **15** (2.09 g, 5.5 mmol) in acetic acid (15 mL) was added dropwise perchloric acid (70%, 900 mg, 6.1 mmol). The reaction mixture soon changed to dark green, and carbon dioxide evolved. After the gas evolution ceased, the reaction mixture was cooled and poured into ice–water to yield a precipitate. Recrystallization of the precipitate from ethanol afforded **16** as crystals; yield 50% (0.97 g); mp 200 °C (decomp.); δ_H ($CDCl_3$) 0.87 (t, $J=7.3$, 3H), 1.25–1.38 (m, 4H), 1.43–1.51 (m, 2H), 2.01 (quint, $J=7.3$, 2H), 3.27 (s, 3H), 4.70 (t, $J=7.3$, 2H), 7.88 (t, $J=7.9$, 1H), 8.04 (t, $J=7.9$, 1H), 8.15 (d, $J=7.9$, 1H), 8.23 (d, $J=7.9$, 1H), 8.55 (d, $J=7.9$, 1H), 8.72 (d, $J=7.9$, 1H). Calc. (%) for $C_{18}H_{22}NO_4Cl$: C, 61.45; H, 6.30; N, 3.98. Found: C, 61.17; H, 6.35; N, 3.60.

X-ray structural analysis‡

A single crystal of compound **13** suitable for X-ray crystallographic analysis was obtained by recrystallization from ethanol–acetonitrile. All data were collected on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo-Kα radiation in the range $3 < 2\theta < 55°$ using ω–2θ scan mode. The structure was solved by direct methods and refined by full matrix least squares, using the TEXSAN crystallographic software.

The 26 non-hydrogen atoms were assigned anisotropic thermal parameters, and others isotropic thermal parameters. There were so few reflections that it was not meaningful to refine more than a limiting number of anisotropic thermal parameters.

Crystal data. $C_{46}H_{40}BNOS$, $M = 665.70$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.648(5)$, $b = 20.874(5)$, $c = 17.800(3)$ Å, $\beta = 94.32(3)°$, $V = 575(2)$ Å^3, $T = 296$ K, $Z = 4$, μ(Mo-Kα) = 1.21 cm^{-1}, 8750 reflections measured, 8259 unique ($R_{int} = 0.096$) which were used in all calculations. The final $wR(F^2)$ was 0.075, $R1 = 0.078$.

Photoirradiation studies

The molar absorption coefficient of each dye was measured with a solution which was left under darkness for more than 3 h. Irradiation by visible light was carried out with a solution of 2×10^{-5} mol dm^{-3}, using a Xe lamp (Ushio, 400 W) as a light source through a Toshiba L-39 glass filter. The cell holder of the spectrometer was kept at 20 °C during the measurement. Upon irradiation, a sample solution was kept at a distance of 45 cm from a light source. The rate constant k of the thermal coloration for each dye was confirmed by plotting $\log\{(A_\infty - A_0)/(A_\infty - A_t)\}$ against the time to afford good linearity, where A_∞ is the absorbance at λ_{max} at the time when no more spectral change occurs under darkness, A_0 that just after photoirradiation, and A_t that at time t (s) under darkness after photoirradiation is stopped.[15]

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