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Benzimidazoloindocarbocyanines: Aggregation Behavior, Redox Potential and Photographic Properties

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ABSTRACT

The aggregation behavior of some benzimidazoloindocarbocyanines in water-methanol and on silver halide emulsion strip were investigated by measuring the UV–Vis absorption spectrum and the reflectance spectrum. Frontier molecular orbital energies of the dyes were estimated from their redox potential. The photographic performance in silver halide emulsion was examined and a correlation of photographic performance with physicochemical properties of the dyes is discussed. The experimental results indicate that most of the dyes readily form J-aggregates in solution, have suitable adsorption capacity on AgBrI emulsion strip, have a redox potential appropriate to AgBrI microcrystal and cause the emulsion used to sensitize more or less. © 1998 Elsevier Science Ltd

Keywords: dye, cyanine dye, aggregation behavior, redox potential, spectral sensitization.

INTRODUCTION

In addition to their use as spectral sensitizers cyanine dyes have also been used for laser recording [1], fluorescent probes [2], chemical sensors [3], and in pharmaceutical applications [4]. A variety of spectral sensitizers have been examined from various aspects e.g. the aggregation state on silver halide substrates [5], adsorptive properties [6–8], evaluation of their LUMO and HOMO energy [9,10], and measurements of their absorption, fluorescence and phosphorescence properties etc [11–13]. The relationship between the physicochemical properties of sensitizers with their effect of spectral sensitization has been widely investigated [14,15]. Many good sensitizers, desenesitizers and supersensitizers have been found and most of them, regardless of their being symmetrical or asymmetrical dyes, were derived from heterocycles having mediate basicity or having near equal basicity. Whilst many research papers on such dyes have appeared, unsymmetrical benzimidazoloindocarbocyanines containing two heterocycles having larger different basicity have received more limited attention, although they have been described as sensitizers and supersentizers in several patents [16–18]. This investigation attempts to provide insight into the physicochemical properties of substituted benzimidazoloindocarbocyanines and to evaluate the relationship between the structure of the sensitizer and its application performance. We have studied the electrochemical properties, the adsorption behavior on AgBr microcrystal and the photographic performance of 15 benzimidazoloindocarbocyanines. The general formula of the dyes studied is shown in Fig. 1. The synthesis, purification and characterization of these dyes have been previously reported [19].

RESULTS AND DISCUSSION

Aggregation behavior

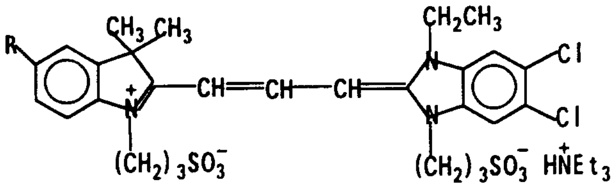
Some cyanine dyes tend to associate, in solution and on the adsorption layer forming different aggregates so that the maximum absorption wavelength of the dyes shifts red or blue; H-aggregates show a hypsochromic shift and J-aggregates have a bathochromic shift with respect to the dye monomer. To investigate the nature of the aggregates of these dyes, and also the relation, between the formed aggregate with various environmental conditions, we measured the absorption and reflectance spectra of dye solution and silver halide emulsion strip sensitized by these dyes.

(a) Aggregation behavior in aqueous-methanol

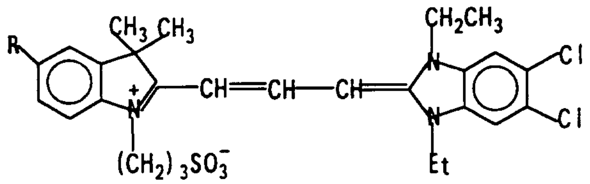
It can be seen from Table 1 that the absorption spectra of the dyes in water-methanol solution varies with dye concentration, and the λ_{max} values

TABLE 1
Spectra of **Dyes 1–5** At Various Concentrations

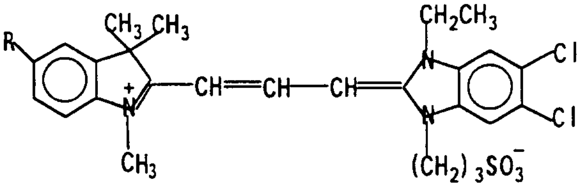
Dye	λ_{max}*(nm)* *(1×10^{-5} mol l^{-1})*	λ_{max}*(nm)* *(1×10^{-3} mol l^{-1})*	λ_{max} *(nm)* *(1×10^{-2} mol l^{-1})*
1	510(m)	515(m) + 574(J)	574(J)
2	500(m)	510(m) + 574(J)	574(J)
3	496(m)	500(m) + 540(J)	546(J)
4	492(m)	500(m) + 570(J)	572(J)
5	492(m)	500(m) + 570(J)	570(J)



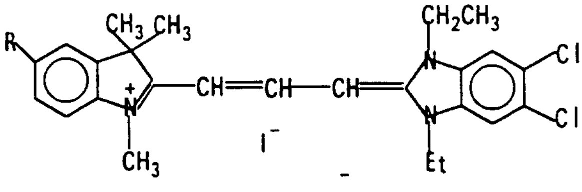
Series I: dye 1 R = OCH_3, dye 2 R = CH_3
dye 3 R = H, dye 4 R = Br
dye 5 R = Cl, dye 6 R = NO_2



Series II: dye 7 R = OCH_3, dye 8 R = CH_3
dye 9 R = H, dye 10 R = Br
dye 11 R = Cl, dye 12 R = NO_2



Dye 13 R= CH_3CONH
Dye 14 R= H



Dye 15 R = H

Fig. 1. Structural formulae of cyanine dyes.

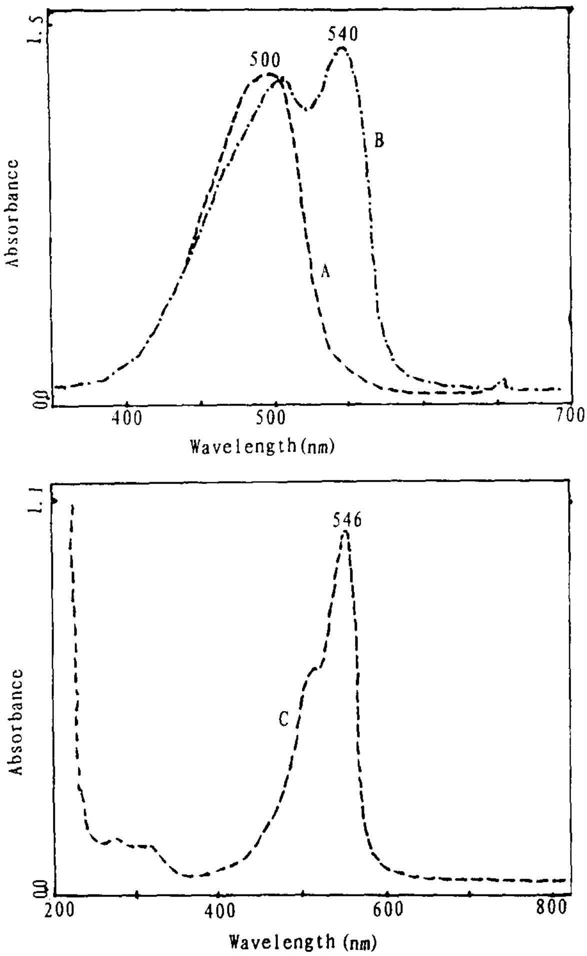


Fig. 2. The absorption spectra of dye 3 in methanolic solution. a; the dye conc. is 10^{-4} mol l^{-1}, (only monomer state exists); b: the dye conc. is 10^{-3} mol l^{-1}, (both J-state and monomer exist); c: the dye conc. is 10^{-2} mol l^{-1}, (only the J-aggregate is formed).

increase as the concentration of the dyes increases. As shown in Fig. 2, the peak at 500 nm (curve A) is the absorption band of the monomer **dye 3**; when the concentration of **dye 3** was increased to 1×10^{-3} mol l^{-1}, the λ_{max} was about 540 nm (curve B), corresponding to dye J-aggregation. The M-aggregates and J-aggregates come to equilibrium. On increasing the dye concentration to 1×10^{-2} mol l^{-1}, only the peak at 546 nm appears, *viz*, these dye molecules exist in J-aggregation states. The J-band (curve C) has a smaller half-band width than the M-band (curve A).

When the concentration of the dyes was gradually increased from 10^{-4} to 10^{-2} mol l^{-1}, the blue shift peak was not observed, indicating that no

H-aggregates form during the process of increasing dye concentration. However, the peak for J-aggregation is very evident for the series of dyes, J-aggregation is characterized by the sharp J-band in the absorption spectrum and by resonance fluorescence. It is therefore apparent that these dyes directly form J-aggregates, without any H-aggregation.

Finally, it can be seen from Table 1 that the absorption wavelength of the dyes in dilute solution (10^{-4}–10^{-5} mol l^{-1}) varies with changes in the substituent on the heterocycle, but, in more concentrated solution (10^{-2} mol l^{-1}), apart from **dye 3**, the values are almost equal. This suggests that the λ_{max} (J) values are related not only to the structure of the molecule, but also to the nature of the assembly of the molecule and the amount of molecules forming J-aggregation.

Figure 3 shows the absorption spectra of **dye 2** measured at different temperatures at constant dye concentration. Curve A shows only a peak for the dye monomer and curve B shows two peaks, one for the monomer and another for the J-aggregate. This shows that lowering the temperature of the dye solution is beneficial to the assembly of these dye molecules. It is assumed that the "velocity of hot motion" of the molecule decreases as the temperature of dye solution decreases, thus favouring interaction of the dye molecule and the formation of assembly states. It was also found that the addition of an inorganic salt results in an increase in the dielectric constant of the dye solution thus decreasing the repelling force between the dye molecules, and as a result, expediating the dye molecule to assemble.

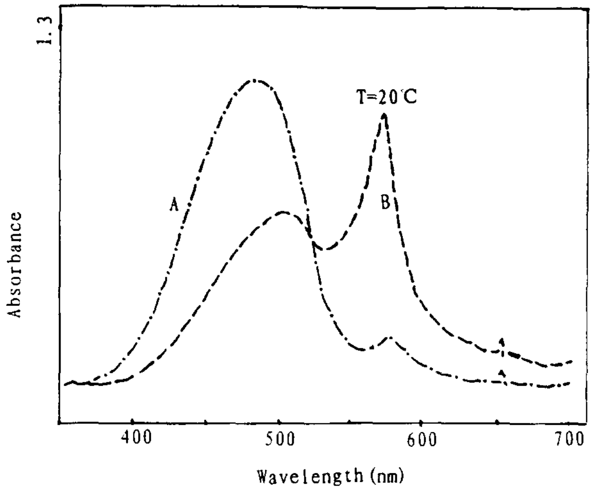


Fig. 3. The absorption spectra of dye 2 at different temperatures: curve A, T = 40°C; curve B, T = 20°C (dye conc. in methanol-water is 2×10^{-3} mol l^{-1}).

(b) Aggregation on dyed emulsion strip

The electronic spectra of the dyed emulsion strip is related to the spectral sensitization of the dyes, and reflects the state in which the dyes exist on film strip and the factor which influences the spectral sensitization effect. As shown in Table 2, they can form J-aggregates on base and exhibit a strong peak of J-aggregation (540–570 nm). It can also be observed from Fig. 4 that the proportion of J-aggregation is lowered after the dye concentration optimum for aggregation comes to a certain value. This indicates that a limit of the growth of J-aggregaties exists and that there is a saturate or critical concentration for J-aggregation of these dyes.

Again, as shown in Table 2, the peak at 490–530 nm corresponding to Ma state and B state absorption,(except **dyes 6, 8, 11, 12, 14** and **15**,) always exist in a certain proportion, no matter how the amount of dyes added is changed. Further, all of the emulsion strip dyed with the 15 dyes exhibited a sharp stronger J-band. However, it seems not to be possible for most of these dyes to completely exist in the J-state on the film strip, in contrast to indocarbocyanine dyes [20].

Redox potential

Dyes carrying the same coupling moiety and group on the heterocyclic nitrogen atom and different substituents in the 5-position of the indolenine

TABLE 2
Electronic Spectroscopic Data For Unsymmetrical **Dyes 1–15**

		$C \approx 1\times 10^{-5}$ mol l^{-1}		*Dyed emulsion strip*			
			$\varepsilon\times 10^{-4}$	*λ_{max}(nm)*	*Main existent state*		
Dye	*R*	*λ_{max}(nm)*	*(l mol cm^{-1})*	*(Second peak)*	*M*	*H*	*J*
1	OCH_3	510	7.43	600 (530)	V		V
2	CH_3	505	3.26	562 (520)	V		V
3	H	498	2.71	544 (515)	V		V
4	Br	486	3.01	550 (510)	V		V
5	Cl	485	2.60	545 (520)	V		V
6	NO_2	478	4.02	620			V
7	OCH_3	510	9.29	590 (550)	V		V
8	CH_3	501	3.59	560			V
9	H	495	3.19	546 (515)	V		V
10	Br	482	2.94	545 (515)	V		V
11	Cl	484	2.89	542			V
12	NO_2	474	5.02	520			V
13	$NHCOCH_3$	504	5.95	570 (520)	V		V
14	H	496	6.15	545			V
15	H	495	8.30	546			V

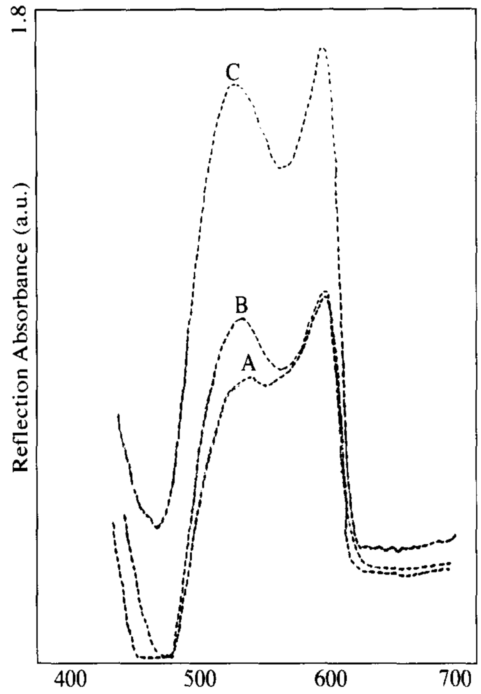


Fig. 4. The reflection absorption spectra of emulsion strip dyed with dye 1. A: 1 mg dye 50 g^{-1} emulsion; B: 2 mg dye 50 g^{-1}; C: 3 mg dye 50 g^{-1} emulsion.

ring, have somewhat different oxidation potential and reduction potential, as indicated in Table 3. Methoxyl and methyl substitutents which increase the electron density on the chromophore facilitate the oxidation of **dyes 1** and **2**. As a result, they have a lower oxidation and reduction potential than **dye 3** (R = H). Chloro and Bromo substitutents, which slightly decrease the electron density on the chromophore, resulted in **dyes 4** and **5** having a higher oxidation and reduction potential and these dyes are oxidized more difficultly than the unsubstituted **dye 3**. The nitro substitutent has a strong electron attracting character so that the electron density on the dye chromophore is greatly decreased, rendering **dyes 6** and **12** to be hardly oxidized; **dyes 6** and **12** have highest reduction potential of the dyes studied.

Further, the reduction–oxidation of the dyes is irreversible under our test conditions, e.g. Fig. 5 shows the cyclic voltammeter curve of **dye 2**; there is only an oxidation wave and no reduction wave is apparent. Although the redox potential measurement might deviate slightly from the actual value, the redox potential as measured by polarographic cyclic voltommetry methods, reflect basically the effect of the substituent on the electrochemical properties of the dyes, and can also explain some related problems. As shown in Table 3 the values of the redox potential change with the nature of

TABLE 3
E-Donating and *E*-Accepting Property

AgBrI: E_{CB} −3.23 ev E_{VB} > −5.76 ev

Dye	R	$E_{tr}(ev)$	$E_{red(VS.SFC)}$	$E_{OX(VS.\ SFC)}$	$E_{LU}(ev)$	$E_{HO}(ev)$	σ_p
1	OCH_3	2.42	−1.62	0.81	−2.89	−5.34	−0.27
2	CH_3	2.48	−1.59	0.89	−2.92	−5.40	−0.17
3	H	2.50	−1.60	0.91	−2.90	−5.42	0.00
4	Br	2.51	−1.57	0.92	−2.94	−5.44	0.23
5	Cl	2.52	−1.54	0.93	−2.97	−5.44	0.23
7	OCH_3	2.43	−1.64	0.80	−2.87	−5.31	−0.27
8	CH_3	2.48	−1.62	0.83	−2.89	−5.34	−0.17
9	H	2.51	−1.62	0.86	−2.89	−5.37	0.00
10	Br	2.57	−1.57	0.90	−2.94	−5.41	0.23
11	Cl	2.56	−1.58	0.92	−2.93	−5.43	0.23
12	NO_2	2.62	−1.35		−3.16	−5.70	0.78
13	MeCONH	2.46	−1.56	0.75	−2.95	−5.26	
14	H	2.50	−1.53	0.86	−2.98	−5.37	
15	H	2.51	−1.51	0.89	−3.00	−5.40	

the substituent on the 5-position of indolenine ring despite the change of the redox potential being not great. Figure 6 shows the relationship between the reduction potential and oxidation potential plotted vs the Hammett σ constant (σ_p), the correlation coefficients were 0.9424 and 0.9875, respectively. The lowest vacant and the highest occupied electronic energy levels of dyes, E_{LV} and E_{HO} are respectively estimated as follows [21]:

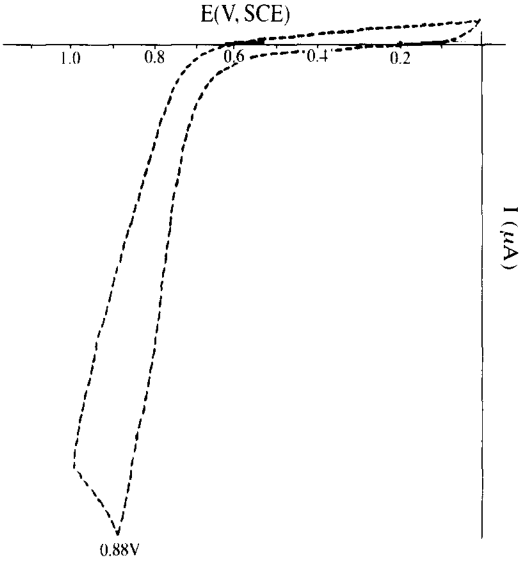


Fig. 5. Cyclic valtammetry curve of dye 2 (methanol, scan rate: 10 sv s^{-1}, 20°C).

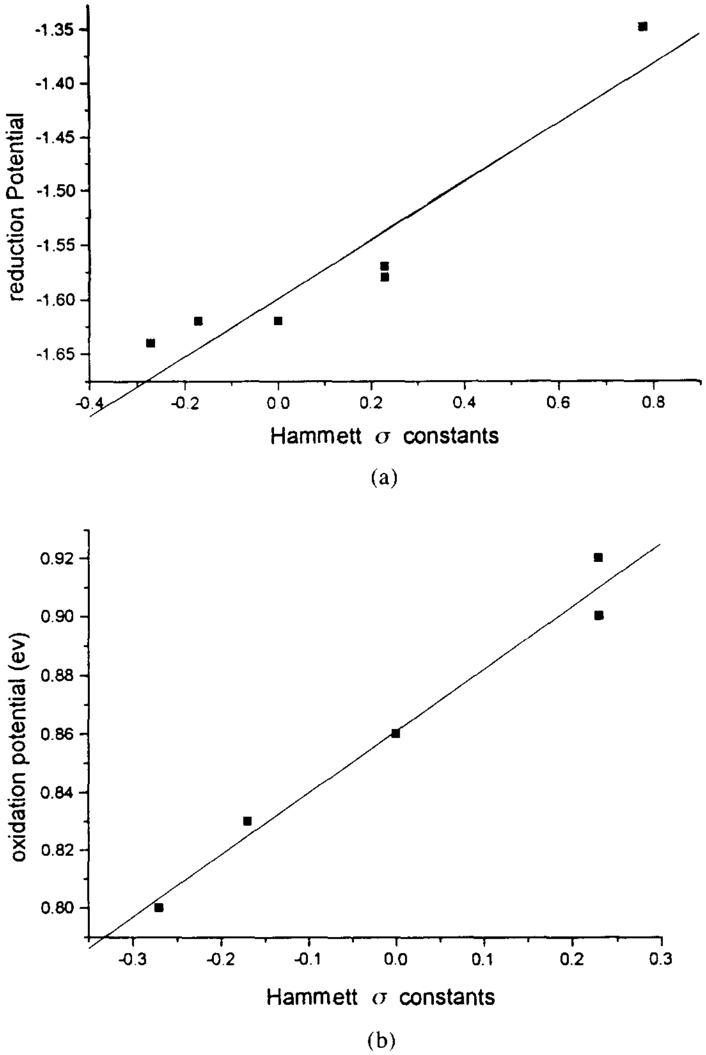


Fig. 6. (a) Correlation of the reduction potentials of dyes in series II and the Hammett σ constants of substitutents R. (Correlation coefficient 0.9424). (b) Correlation of the oxidation potential of dyes in series II and the Hammett σ constants of substituents R. (correlation coefficient 0.9875).

$$E_{LV} = -E_{red} - 4.51$$

$$E_{HO} = -E_{ox} - 4.51$$

The data are summarized in Table 3. It is estimated that the energy of the conduction band of AgBrI (E_{CE}) is lower than -3.23 ev and the energy of the valence band of AgBrI (E_{VB}) is higher than 5.76 ev.[22] E_{CB} and E_{VB} of AgBrI approximate to −3.23 ev and −5.76 ev respectively, appropriate energy level diagrams of the sensitizing dyes and silver lodobromide are plotted as in Fig. 7. Figure 7 shows that HOMO of these dyes is higher than the maximum of the valence bands of AgBrI and the LUMO of the dyes is also higher than the lowest of the conduction band. The relative energy level between the frontier molecule orbital of the dyes and the energy bands of AgBrI shows that the high excited electron of these dyes can easily transfer from dye to AgBrI, and hence these dyes enable AgBrI to spectrally sensitize.

Photographic performance

It can be noted from Table 4 that **dyes 1** and **7** having a methoxyl group on the indolenine ring, cause the emulsion strip to induce extreme fog under the experimental conditions. The main cause of this is that the dyes have a lower relative oxidation potential than other dyes in the series. They easily expedite the growth of the fogging centers, and bring out severe development fog, being entirely blackened. As far fogging is concerned, dyes in series I, apart from **dye 1**, show a decreased fog of the emulsion strip, but, dyes in series II (except **dye 7**) show a slight increase in the fog emulsion strip. This result is due to the difference in the number of sulfopropyl introduced into the heterocyclic nitrogen atom e.g. **dyes 3**, **8** and **15** have the same substituents on the 5-position of the indolenine ring and different substituents on the heterocyclic nitrogen atom, *viz* **dye 3** in series I has two sulfopropyl groups and

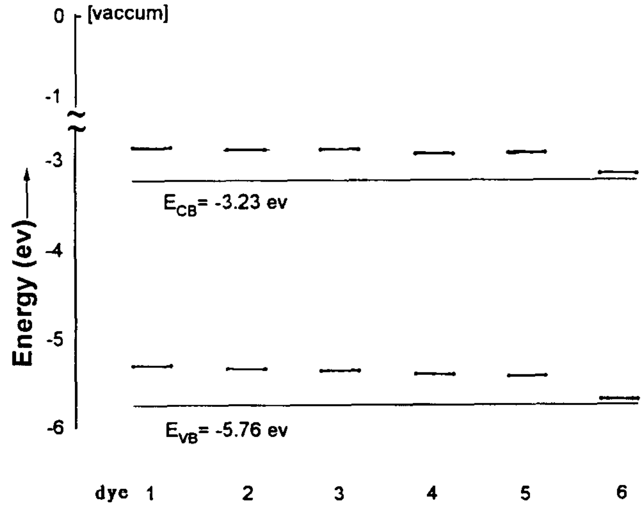


Fig. 7. Electron energy levels of sensitizing dyes and AGBrI.

TABLE 4
Photographic Performance of **Dyes 1–6**

Dye	*R*	*Vml*	*Do*	D_{max}	*S*	Δ*S*	*Contrast*	*Residual colour*
		0	0.07	7.10	320		4.00	No
								No
1	OCH_3	1	>6					No
		2	>6					No
		4	>6					No
		5	>6					No
2	CH_3	1	0.5	>7.00	400	+80	3.67	No
		2	0.05	>7.00	320	0	3.30	No
		3	0.06	>7.00	160	−160	3.50	No
		5	0.04	>7.00	125	−195	3.30	No
3	H	1	0.06	>7.00	400	+80	3.50	No
		2	0.06	>7.00	400	+80	3.90	No
		4	0.06	>7.00	400	+80	4.30	No
		5	0.07	>7.00	400	+80	4.30	No
4	Br	1	0.04	>7.00	320	0	3.20	No
		2	0.05	>7.00	320	0	3.50	No
		3	0.05	>7.00	320	0	3.60	No
5	Cl	1	0.06	>7.00	320	0	4.40	No
		2	0.06	>7.00	320	0	4.30	No
		4	0.05	>7.00	320	0	4.20	No
		5	0.06	>7.00	320	0	4.30	No
6	NO_2	2	0.04	>7.00	320	0	3.15	No
		3	0.04	>7.00	320	0	3.10	No
		5	0.05	>7.00	320	0	3.66	No
7	OCH_3	2	>6					
		3	>6					
		5	>6					
8	CH_3	2	0.08	>7.00	320	0	4.10	
		3	0.10	>7.00	320	0	4.03	
		5	0.10	>7.00	400	+80	4.12	Yes
9	H	2	0.08	>7.00	400	+80	4.20	

Table 4—*contd*

		3	0.07	> 7.00	400	+ 80	4.00	
		5	0.11	> 7.00	400	+ 80	4.00	
10	Br	1	0.08	> 7.00	320	0	4.10	
		2	0.08	> 7.00	320	0	4.10	
		3	0.09	> 7.00	320	0	4.00	
		5	0.08	> 7.00	400	+ 80	4.80	
11	Cl	2	0.09	> 7.00	400	+ 80	4.20	
		3	0.12	> 7.00	400	+ 80	3.90	
		5	0.12	> 7.00	500	+ 120	3.90	Yes
12	NO_2	1	0.07	> 7.00	320	0	5.00	
		3	0.08	> 7.00	320	0	4.50	Slightly have
		5	0.08	> 7.00	200	− 120	3.80	
13	MeCONH	2	0.15	> 7.00	320	0	4.30	
		3	0.15	> 7.00	320	0	4.30	
		5	0.14	> 7.00	320	0	4.50	
14	H	2	0.09	> 7.00	400	> 7.00	3.67	
		3	0.09	> 7.00	400	> 7.00	3.67	
		5	0.12	> 7.00	320	> 7.00	3.33	
15	H	2	0.12	> 7.00	400	> 7.00	3.10	
		3	0.13	> 7.00	400	> 7.00	2.90	
		5	0.14	> 7.00	320	> 7.00	3.00	Yes

V(ml), the number of milliliters of 0.1% methanol solution of dye added to 50 g emulsion.
D_0, D_{max}, the minimum and maximum spectra density of film strip.
S, the sensitivity is defined by the following equation:

$$S = 101\ g(1/H_{Do+0.1})$$

in which H represents the amount of exposure necessary to obtain a density of 0.1 above fog sensitivity.

dye 8 in series II has one sulfopropyl group on the heterocyclic nitrogen atom. The fog of the emulsion strip dyed with **dye 8** is heavier than that of the emulsion strip dyed with **dye 3**. **Dye 15**, having only alkyl and no sulfopropyl groups on the heterocyclic nitrogen atom shows the heaviest fog in these three dyes. Hence, the sulfopropyl groups on the heterocyclic nitrogen atom of these dyes have the effect of decreasing the fog of the emulsion strip.

It can also be seen from Table 4 that the residual colour for the emulsion strip dyed with dyes of series II (carrying a sulfopropyl groups) is readily shown up, but that it is difficult for the emulsion strip sensitized by dyes of series I (having two sulfopropyl groups on the heterocyclic nitrogen atom) to induce the residual colour. The main cause may be, or must be, that the sulfopropyl group introduced into the heterocyclic ring renders these dyes more readily soluble in water. The residual dye molecule adsorbed on the strip can be dissolved in water in the process of development, fixation and washing so that the residual colour induced by the dyes can disappear.

Those dyes (**dyes 8–11** in particular) whose LUMO is 0.3–0.36 higher than the lowest value of E_{CB} (AgBrI) show some sensitizing effect, the sensitivity gain being up to 80–120. **Dye 11** has the highest sensitivity gain. In the case of **dye 12**, the energy level difference between the dye LUMO and the bottom of E_{CB} (AgBrI), or between the dye HOMO and the top of $E_{VB(AgBr)}$, is too small, and no sensitivity gain was observed practically. In contrast, with further increase of the dye amount added, it became a desensitizer. These results are coincident with the general concept of the electron transfer of spectral sensitization.

EXPERIMENTAL

Photographic tests

A thick tabular iodobromide (AgI 2 mol%) grain emulsion was precipitated using the double-jet method with automated control of pAg, at initial gelatin concentration of 2%, temperature 60°C, pBr = 1.0 and for a period of 40 min. It was then coagulated, washed, redispersed, chemically sensitized with S + Au sensitizers, spectrally sensitized with **dyes 1-15** in various milliliters of 0.1% methanol dye solution at 40°C, for a given 50 g of emulsion. It was then coated on a film base, dried, exposed sensitometrically (1/20 s. Xian Feng sensitometer, Shanghai, China), developed in D-19b developer at 20°C for 5 min. fixed in an F-11 fixing bath at 25°C for 1 h, and sensitometrically measured on CMT Densito (China). The resulting data are given in Table 2. The pH and pAg of the emulsion were 6.5 and 7.8 respectively. The average grain size was 1.0 μ.

Uv–Vis spectra

The reflectance spectrum of the dyed emulsion strips made as above were measured on a Hitachi-557 spectrophotometer. The visible absorption spectra of the dyes in solution were recorded on a Hitachi UV-8451A spectrophotometer. The experimental results are compiled in Tables 1 and 2 and are shown in Figs 2 and 3.

Reduction potential

The reduction potentials were determined on an Oscilloscope Polarographer (Shichun, China, JP-2). The construction and the operational procedures are consistent with these given in ref. [23] with the exception that a dropping mercury electrode was used in present study as the working electrode. The concentration of dye in aqueous methanol (the percentage of water was 5%) was approximately 10^{-4} mol l^{-1}, KCI (0.2%) was added to the dye solution as the support electrolyte. A three-electrode system incorporating a dropping mercury electrode, a platinum counter electrode and a 212 saturated calomel reference electrode were used and operated at 25°C.

The oxidation potential measurements were made using a combination of a Princetion applied research potentiostat (Galvanostat Model 273 Cyclic instrument) and type 3036 X-Y recorder (Sichuan, China), with an approximately 10^{-4} mol l^{-1} dye solution in dry methanol, 0.1 mol l^{-1} LiCl was used as support electrolyte and a pyrolytic graphite electrode was used as working electrode. The other two electrodes were the same as those described above.

The solution was deaerated for 10 min before measurement under nitrogen. The experimentally found values of the redox potential are listed in Table 3.

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