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Synthesis and Characterization of Some Stabilized Indocarbocyanine Dye Complex Colorants for Optical Recording Media

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ABSTRACT

Several stabilized cyanine dye complexes in which a cyanine dye cation is stabilized by a transient metal chelate anion have been synthesized. The structure of the complexes was confirmed by elemental analysis, visible/near-infra red absorption, ^{1}HNMR, and IR spectroscopy, and correlations between the constitution and properties of the dyes have been studied. The stabilized cyanine dye complex coloring matters exhibit an enhanced resistance to light, heat and moisture, in comparison with non-stabilized cyanine dye compounds, and are thus of potential interest for use in optical recording media. © 1997 Elsevier Science Ltd

Keywords: stabilized cyanine dye complex, quenchers, transient metal chelate complexes, erasing media, optical disk.

INTRODUCTION

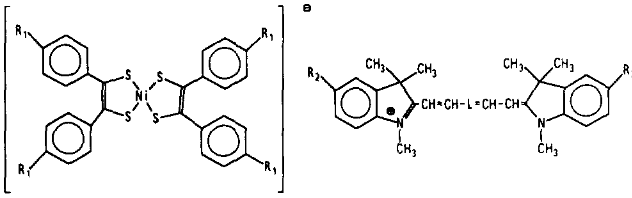
In recent years, with the rapid development of data recording and storage materials, increasing attention has been paid to the application of cyanine dyes for use in storage disk laser systems [1–3]. Cyanine dyes are cheap, easy to synthesize, and show very good optical properties, but their stability is not good, since the semiconductor laser sensitive cyanine dye undergoes a photo-oxidation reaction during illumination. The coloring matter used in such systems must have a high chemical stability (shelf life), so that in a recording-type medium the colorant has a high durability to repeated reading operations, and in an erasable-type medium, the colorant exhibits a high durability to repeated recording and erasing operations. Therefore, it is of value to study and resolve the problem of the photostability of cyanine dyes with respect to the development of high density optical recording and storage materials of organic dye media.

Addition of transient metal chelate compounds as quenchers to cyanine dyes enhances their photostability, and essentially inhibits their decolorization by light [4–6]. However, cyanine dyes normally have anions such as I^- and $C10_4^-$; transient metal chelate compounds as quenchers are coupled with cations such as the ammonium ion. When the cyanine dyes and quenchers above are combined in recording layers, such unnecessary paired cations are inevitably contained in the recording layers and on hydrolysis they tend to produce acids and alkalies. Thus, these recording layers have presented a problem with respect to resistance to moisture. Further, the inclusion of such unnecessary moieties results in an increase of the molecular weight, and a proportional decrease in the absorbance and reflectance per unit weight, and therefore the S/N ratio and sensitivity decease.

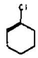
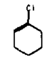
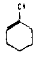
A stabilized cyanine dye complex without other anion and cation therein overcomes the above disadvantages [7–8]. Since the dye cation and the quencher anion are linked by an ionic bond, the stabilized cyanine dye complex has a much higher resistance to light, heat and moisture than the mixture of the cation and the anion.

Indocarbocyanine dyes have a high solubility in solvents, undergo minimal crystallization, offer thermal stability, and have a high reflectance [1–3]. However, stabilized cyanine dye complexes of the indolenine type have not been extensively studied.

This paper reports the synthesis and characterization of a series of some new stabilized indocarbocyanine dye complex coloring matters of general formula $I(B^-A^+)$, and also structure–property relationships of the dyes on the basis of their visible/near-infra red absorption, ^{1}HNMR and IR spectra. In formula 1, *A* represents a cation moiety, and *B* represents an anion moiety, paired with the cation moiety *A*.



(I)

	1a	1b	1c	1d	1e	1f
R_1	H	Cl	CH_3	H	CH_3	Cl
R_2	Cl	Cl	Cl	H	H	CH_3
L	CH=CHCH	CH=CHCH	CH=CHCH			

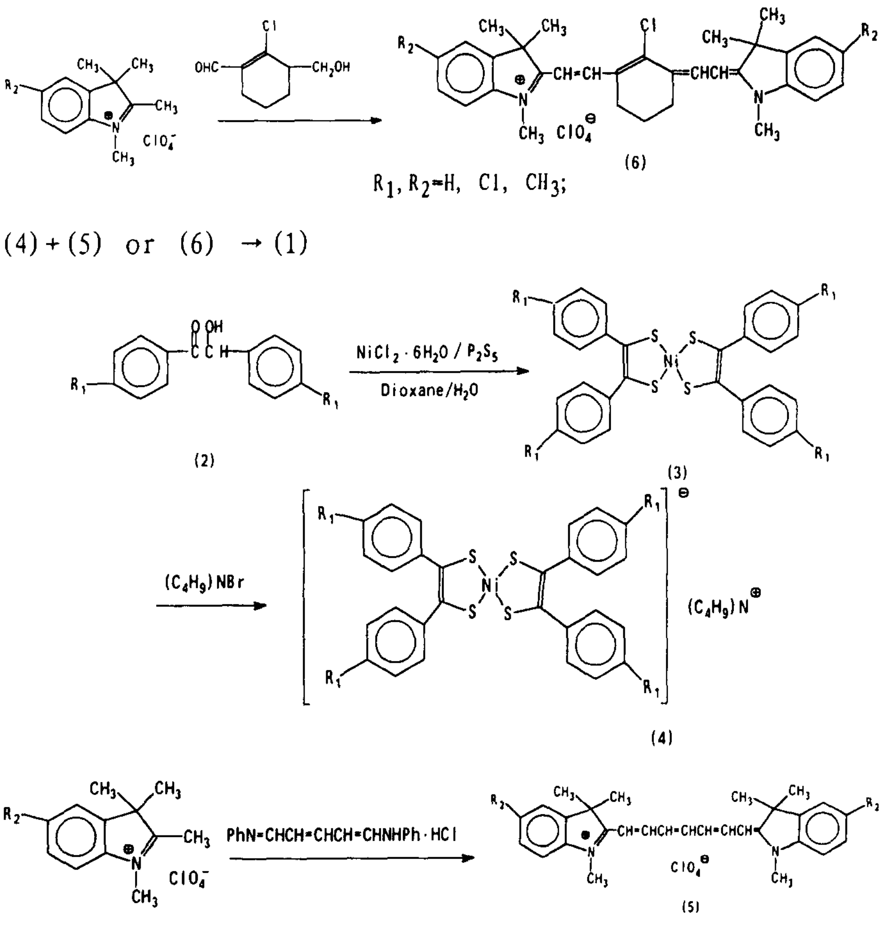
RESULTS AND DISCUSSION

Preparation of the stabilized indocarbocyanine dye complex coloring matters

The stabilized indocarbocyanine dye complex coloring matters 1a–f were prepared according to modified literature procedure [6] by a paired ion-exchange reaction of formula:

$$(B-X)+(A-Y)\rightarrow(B-A)+(X-Y)$$

wherein A and B are defined as above, X represents a cation, for example, ammonium ions, and Y represents a cation, for example, I^- and $C10_4^-$. The paired ion-exchange reaction was carried out at 70°C for 3 h in DMF. The general procedures used to prepare the stabilized indocarbocyanine dyes are shown in Scheme 1.



Scheme 1

TABLE 1
Yields, Melting Points and Elemental Analyses for Dyes (1a–f)

Dye	*M.P. (°C)*	*Yield (%)*	*Molecular formula*	*E.A. (%)*		
				C(calc.)	*H(calc.)*	*N(calc.)*
1a	219	90	$C_{57}H_{51}Cl_2N_2S_4Ni$	66.80 (66.70)	4.89 (5.03)	2.95 (2.74)
1b	241	90	$C_{57}H_{47}Cl_6N_2S_4Ni$	62.64 (59.04)	4.85 (4.56)	2.51 (2.42)
1c	228	92	$C_{61}H_{59}Cl_2N_2S_4Ni$	67.69 (67.97)	5.13 (4.95)	2.71 (2.42)
1d	216	95	$C_{60}H_{56}ClN_2S_4Ni$	70.13 (69.25)	5.44 (5.49)	2.91 (2.73)
1e	218	94	$C_{64}H_{64}ClN_2S_4Ni$	71.11 (70.94)	5.78 (5.95)	2.59 (2.88)
1f	233	93	$C_{62}H_{56}Cl_5N_2S_4Ni$	52.64 (52.37)	4.93 (4.73)	2.06 (2.35)

The precursory transition nickel complexes of formula 4, usable for the preparation of the stabilized indocarbocyanine dye complexes (B^-A^+), were synthesized according to the literature [9]; bis(dithiobenzil)nickel complexes 3 [10] and indotricarbocyanine dyes 5 and 6 were obtained according to literature procedures [11, 12]. Data on yields, melting points and elemental analyses are given in Table 1.

Characterization

Relevant visible/near-infra red absorption spectra, IR and ^{1}HNMR data for the complexes 1a–f are shown in Tables 2 and 3. The IR spectra showed typical aromatic absorption (C = C, 1600–1610, 1500, 1400(s) cm^{-1}, δH, 700–900 cm^{-1}), resonance conjugated unsaturated stretching modes in the chromophore (C = C, C = N, 1380–1480 cm^{-1}(s)) and bands at 1144–1150 cm^{-1} may be assigned to a vibration involving the perturbed C = S stretching.

TABLE 2
Visible/Near-Infra Red and IR Spectra Data of Dyes

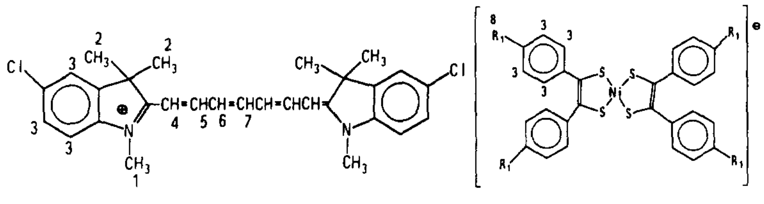
Dye	*λ max (nm)*^{a}	*ε(× 10^{-5} l cm^{-1} mol^{-1})*	*IR data (cm^{-1})*
1a	757	3.35	2965, 1658, 1589, 1507, 1482, 1235, 1387, 1309, 1145,
	855	0.41	1086, 1064, 1033, 1012, 918, 790, 744, 696
1b	757	3.37	2965, 1650, 1483, 1435, 1386, 1144, 1086, 1063, 1032,
	860	0.45	1012, 918, 789, 707
1c	757	3.35	2965, 1650, 1590, 1503, 1483, 1439, 1388, 1355, 1310,
	879	0.55	1146, 1086, 1066, 1034, 1013, 966, 919, 790, 708
1d	787	3.26	2965, 1587, 1545, 1503, 1448, 1426, 1391, 1365, 1241, 1165,
			1150, 1104, 1059, 1038, 1016, 923, 802, 696
1e	787	3.18	2965, 1644, 1541, 1504, 1450, 1426, 1390, 1360, 1240,
	879	0.56	1164, 1149, 1106, 1060, 1037, 1017, 966, 769, 713
1f	798	3.35	2965, 1650, 1541, 1485, 1430, 1386, 1353, 1245, 1215, 1180,
			1150, 1060, 1035, 966, 935, 815, 805, 735

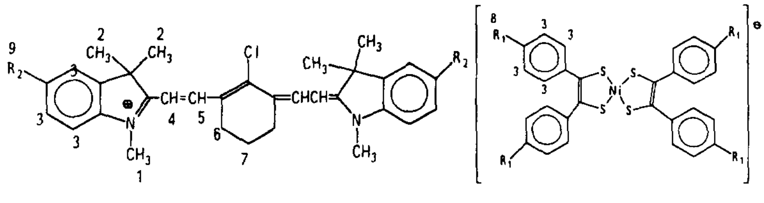
^{a}Concentration: 1.0–5.0 × 10^{-6}; solvent: CH_2Cl_2.

TABLE 3
^{1}HNMR Spectroscopy Data of Dyes

	1a	*1b*	*1c*	*1d*	*1e*	*1f*
1-H	3.70(s, 6H)	3.75(s, 6H)	3.75(s, 6H)	4.35(s, 6H)	4.35(s, 6H)	3.75(s, 6H)
2-H	1.70(s, 12H)	1.70(s, 12H)	1.70(s, 12H)	1.50(s, 12H)	1.50(s, 12H)	1.65(s, 12H)
3-H	6.9–7.5 (m, 26H)	6.9–7.5 (m, 22H)	6.9–7.5 (m, 22H)	7.1–7.5 (m, 28H)	7.0–7.5 (m, 24H)	6.9–7.5 (m, 22H)
4-H	6.35(d, 2H)	6.30(d, 2H)	6.30(d, 2H)	6.35(d, 2H)	6.35(d, 2H)	6.25(d, 2H)
5-H	7.85(t, 2H)	7.85(t, 2H)	7.85(t, 2H)	8.35(d, 2H)	8.35(d, 2H)	8.30(d, 2H)
6-H	6.50(t, 2H)	6.50(t, 2H)	6.50(t, 2H)	2.75(t, 4H)	2.80(t, 4H)	2.70(t, 4H)
7-H	7.75(t, 1H)	7.80(t, 1H)	7.80(t, 1H)	1.85(m, 2H)	1.85(m, 2H)	1.85(m, 2H)
8-H			2.35(s, 12H)		2.35(s, 12H)	
9-H						2.40(s, 6H)

The λ max values of the stabilized cyanine dye complexes in dichloromethane were essentially the same as those of the cyanines and the quenchers used as the raw materials. However, the absorption peaks of the quenchers in the stabilized cyanine dye complexes 1d and 1f were masked by those of the cyanines.





EXPERIMENT

Instrumental

Melting points were measured on an X4 micro-melting point apparatus and are uncorrected. IR spectra were taken on a Perkin-Elmer 683 spectrometer, visible/near-infra red spectra on a Shimadzu UV-160A UV-vis recording spectrophotometer. The ^{1}HNMR Spectra were recorded on a Brucker Ac-200, using TMS as internal standard and $CDCl_3$ as solvent.

Synthesis of the stabilized indocarbocyanine dye complex colorant 1a

After 168 mg (0.25 mmol) of bis(dithiobenzil)nickel(II) tetra-n-butyl ammonium salt and 144 mg (0.25 mmol) 1,1′ 3, 3, 3′ 3′-hexamethyl-5, 5′-dichloroindotricarbocyanine perchloride were dissolved in 20 ml of DMF it was left to react at 70°C for 3 h. The resultant reaction solution was then poured into cold water and the precipitate so formed was filtered, washed with water and dried under vacuum. The product was dissolved in hot DMF (10 ml) and, after addition of hot ethanol (30 ml), allowed to crystallize.

The synthesis of the other stabilized indocarbocyanine dye complex colorants was similarly effected.

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