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Photostability, Laser Energy Conversion Efficiency and Absorption of IR Heptamethine Cyanine Dyes Absorbing Beyond 1 μm

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ABSTRACT

The optical absorption, photostability and energy conversion efficiency of a series of heptamethine IR dyes are reported and results related to chemical structure. The high photostability and high laser energy conversion efficiency of several of the dyes indicate potential use in IR dye lasers.

INTRODUCTION

The stability of IR-absorbing pyrylium dyes can be considerably improved by suitable rigidization of the molecular structure; most such dyes have an electron-withdrawing group (halogen atom) on the *meso* carbon atom of the polymethine chain.[1] A series of new heptamethine pyrylium dyes containing a disubstituted amino donor group on the *meso* position in the bridged polymethine chain have been recently described.[2] With the development of optical fibers, emission around 1·30 μm has prompted considerable interest in the synthesis of this type of dye.[3] Of special interest is the high photostability of these compounds, which make them useful as IR-lasing dyes.

In this paper, we report on a series of heptamethine cyanine dyes, the preparation of which has been described.[4,5] The optical absorption, laser energy conversion efficiency and photostability have now been investigated and the relationship of these properties to the molecular structure is outlined.

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TABLE 1
Dye and Electronic Spectra Data

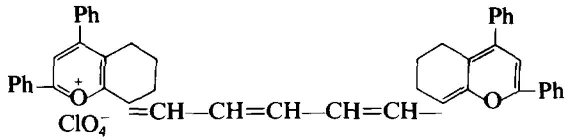
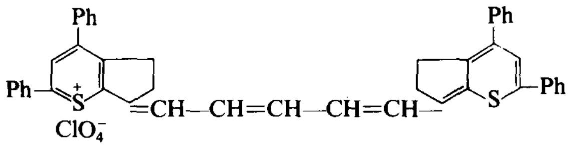
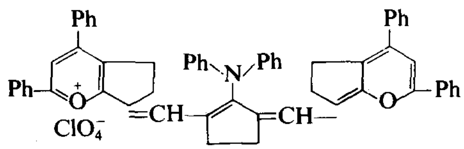
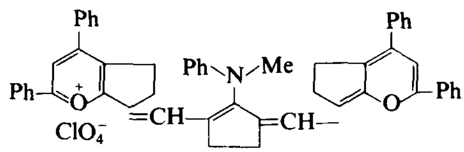
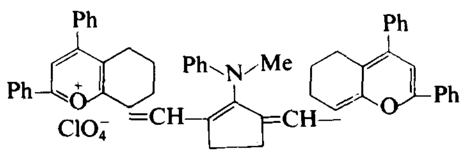
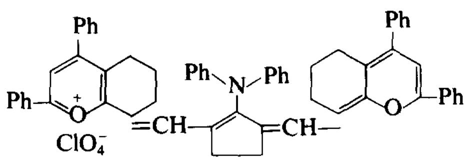
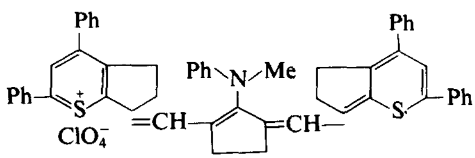
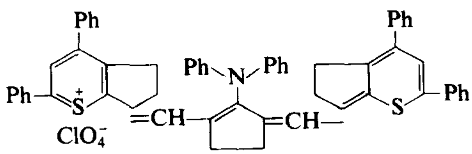
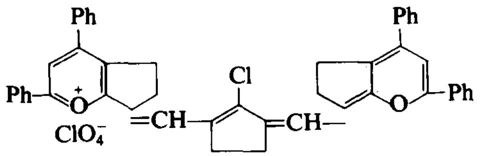
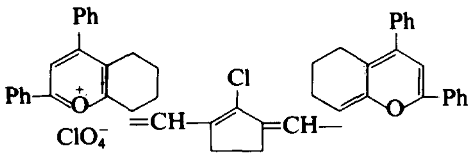
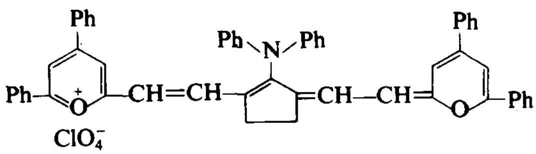
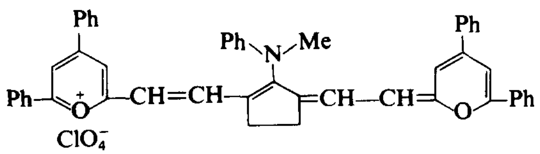
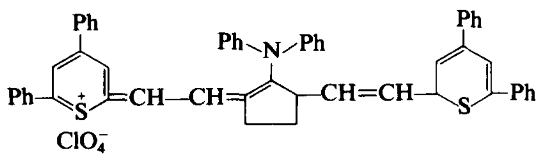
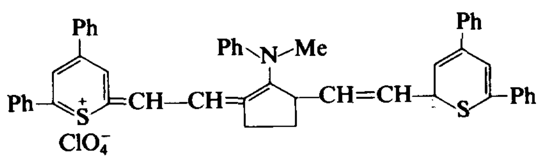
Dye No.	*Structure*	λ_{max} *(nm)*	ε_{max} $(\times 10^{-3})$
D-1 (Kodak 9740)		1055	125
D-2		1175	127
D-3		1160	126
D-4		1162	138
D-5		1150	140
D-6		1145	108
D-7		1245	175
D-8		1218	180

TABLE 1—*contd.*

Dye No.	*Structure*	λ_{max} *(nm)*	ε_{max} $(\times 10^{-3})$
D-9		1180	112
D-10		1145	143
D-11		1073	133
D-12		1071	117
D-13		1110	152
D-14		1112	145

EXPERIMENTAL

The structures of dyes D-1–D-14 are shown in Table 1. Absorption spectra were recorded using a Shimadzu UV-365 from dye solutions in 1,2-dichloroethane at a concentration of 5×10^{-6} M.

Photostability of the dye was determined by irradiating the sample with a high pressure xenon lamp, eliminating wavelengths below 700 nm with an appropriate filter. The irreversible bleaching of the dyes at the

TABLE 2
Relative Photostabilities of the Dyes in 1,2-Dichloroethane

Dye no.	*D-1*	*D-2*	*D-3*	*D-4*	*D-5*	*D-6*	*D-7*	*D-8*	*D-9*	*D-10*	*D-11*	*D-12*	*D-13*	*D-14*
Relative photostability	1	3	80	50	100	85	89	93	39	48	36	38	50	42

absorption peak was monitored as a function of time. In Table 2, the photostability of the dyes in relation to the dye Kodak 9740 is shown.

In our laser experiments, a Q-switched Nd : YAG laser served as pumping source; the duration of the pump pulse was 10 ns and the pulse energy was about 30 mJ.

The cavity for measuring energy conversion efficiency consisted of an $8 \times 8 \times 30$ mm^3 quartz dye cell with one aluminium-coated side. About 1·5 ml of dye solution were added without stirring, the concentration of which was 2×10^{-3} M in 1,2-dichloroethane. The energy conversion efficiency was calculated using the following equation:

$$y = E_d/E_p \times 100\%$$

in which y is the energy conversion efficiency, E_d is the output energy of the tested dye laser per pulse, and E_p is the pumping energy per pulse.

RESULTS AND DISCUSSION

From Table 1 it is apparent that the optical absorptions vary significantly within the dyes investigated. The dyes studied are heptamethine cyanine dyes, the structures, absorption maximum and extinction coefficients of which are shown in Table 1. One of these dyes, viz. No. 9740 (D-1), has been commercially available for more than a decade.

From Table 1, it can be seen that the absorption spectrum is displaced to longer wavelength when oxygen is substituted by sulfur (cf. D-1 and D-2; D-3 and D-8; D-4 and D-7; D-11 and D-13; D-12 and D-14). Substituents, such as methyl or phenyl in the *meso* amino group, do not significantly affect the spectrum. (cf. dyes D-11 and D-12; D-13 and D-14; D-3 and D-4; D-7 and D-8). When the dyes have a six-membered or five-membered ring rigidly attached to the pyrylium or thiapyrylium rings λ_{max} is shifted to longer wavelength (cf. dyes D-3, D-6 and D-11; D-4, D-5 and D-12; D-7 and D-14; D-8 and D-13).

The photostabilities of the dyes are shown in Table 2. The pyrylium and thiapyrylium dyes show higher photostability when parts of the methine

TABLE 3
Energy Conversion efficiency of the Dyes (2×10^{-3} mol l^{-1} in 1,2-dichloroethane)

Dye no.	*D-2*	*D-3*	*D-4*	*D-5*	*D-6*	*D-7*	*D-8*	*D-9*	*D-10*	*D-11*	*D-12*	*D-13*	*D-14*
Energy conversion efficiency	3·0	9·6	0·5	7·8	8·2	4·3	4·8	0	0·95	0	0	0	0

groups are incorporated in rings instead of straight chains (D-1 and D-5, D-6; D-2 and D-7, D-8; D-11 and D-3, D-6; D-12 and D-5, D-4; D-13 and D-8; D-14 and D-7). Pyrylium and thiapyrylium dyes containing a six-membered ring are more stable than those containing a five-membered ring. (cf. dyes D-3 and D-6; D-4 and D-5; D-9 and D-10).

The laser energy conversion efficiencies of the dyes are shown in Table 3. Dyes D-3, D-5, D-6, D-7 and D-8 show high lasing efficiency; D-2, D-4 and D-10 show a medium lasing efficiency and dyes D-9, D-11, D-12, D-13 and D-14 show the lowest lasing efficiency.

CONCLUSIONS

Dyes D-2, D-4 and D-10 have middle lasing efficiency and lower photostability. They are unsuitable for use as effective laser dyes. Dyes D-9, D-11, D-12, D-13 and D-14 have a comparatively lower lasing energy conversion efficiency and lower photostability and therefore also are of little value as laser dyes.

Dyes D-3, D-5, D-6, D-7 and D-8, however, have both higher lasing energy conversion efficiency and higher photostability and these dyes are very effective laser dyes.

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