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Absorption spectra, aggregation and photofading behaviour of near-infrared absorbing squarylium dyes containing perimidine moiety

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Abstract

Representatives of a new class of squarylium dyes containing a perimidine moiety have been synthesized and characterized. Almost all of these dyes absorbed near infrared light over 800 nm. The light absorption characteristics of these dyes are well accounted for with the PPP-MO calculation. The photostability properties of the dyes were also investigated when hydroperinidine containing quinoline moiety was introduced, the photochemical stability being better than that of dihydroperimidine moiety. The aggregation of the dyes were also studied in different DMSO/water solution.

Keywords: Perimidine; Squarylium dye; NIR dye; Aggregation; Photofading; PPP-MO

1. Introduction

Development of the gallium–arsenic semiconductor laser that emits laser light at 780–830 nm has made possible development of new optoelectronic systems including laser optical recording systems, thermal writing display systems, laser printing systems, DNA-sequencing, and so on [1,2]. Medical applications of laser in photodynamic therapy for the treatment of cancer were also developed. In such systems, the near-infrared absorbing dyes (NIR dyes) are currently used as effective photoreceivers for diode lasers, and will become the key materials in high technology.

Recently some NIR dyes such as pentamethine cyanine, naphthoquinonoid, anthraquinonoid, phthalocyanine and nickel complex dye have been reported as functional dyes for optical recording media for semiconductor lasers [1].

Squarylium dyes and derivatives are 1,3-disubstituted compounds synthesized from squaric acid and two equivalents of various types of electron

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donating carbocycles or heterocycles such as azulene, pyrroles or heterocyclic methylene bases. Structural modification of squarylium dyes has been an active area of research since the compounds were found to be useful for xerographic organic photoreceptors, optical recording media, and organic solar cells, on account of their advantageous properties such as photoconductivity and their sharp and intense absorption in the visible or near-infrared regions.

We have previously reported the synthetic [3], electrochromic [4], electroluminescent [5] and electrophotographic [6] properties of squarylium dyes containing indoline moiety. In the search for aromatic electron donor groups, it was found that the dihydroperimidine system was very effective. This afforded dye **10**, which absorbed at about 800–810 nm, with ε_{max} values of about 15,000 l mol^{-1}cm^{-1} [7]. The ease of modifying the physical properties of these dyes by variation of the donor moiety R makes them attractive candidates for various applications.

In this study, we report the synthesis, absorption spectra, aggregation and photofading behaviour of squarylium dyes containing perimidine terminal group in the molecule.

2. Experimental

2.1. Characterization of products

Melting point were determined using an electrothermal IA 900 and are uncorrected. The visible spectra were measured using Shimadzu UV-2100 spectrophotometer. Elemental analysis were recorded on a Carlo Elba Model 1106 Analyzer. Mass spectra were recorded using a Shimadzu QP-1000 spectrometer with an electron energy of 70eV and direct sample introduction. H^1 NMR spectra were recorded in CDCl$_3$ using a Varian Unity Inova 300 MHz FT-NMR spectrometer using TMS as internal standard.

2.2. Synthesis of squarylium dye and intermediate

Intermediate **4** and dye **10** were prepared using a previously described procedure [8].

2.2.1. Intermediate *5*

A stirred mixture of 1,8-diaminonaphthalene **1** (11.4 g, 72 mmol), adamantanone **3** (10.8 g, 72 mmol), *p*-toluenesulfonic acid monohydrate (20 mg) and 100 ml of toluene was heated to reflux under a nitrogen atmosphere using a Dean–Stark trap to remove the water evolved from the reaction for 8 h. The mixture was then washed with saturated sodium bicarbonate solution and the organic layer was dried over anhydrous potassium carbonate. The solvent was removed under reduced pressure. The crude product was purified by recrystallization with a mixture of benzene/*n*-hexane (1:1/v:v).

Yield 14.22 g (68%). ^{1}H NMR (CDCl$_3$): δ 7.22 (2H, t), 7.12 (2H, d), 6.51 (2H, d), 4.95 (2H, s), 2.08–1.74 (14H, m): EA calcd; $C_{20}H_{22}N_2$ (C, 82.72; H, 7.64; N, 9.65), found; (C, 82.93; H, 7.55; N, 9.86); *m*/*z* (M$^+$); 290.

2.2.2. Intermediate *8*

Quinaldine **6** (4.29 g, 30 mmol) and selenium dioxide (4 g, 36 mmol) were heated under reflux for 5 h in 50 ml of dioxane containing 2 ml water and then hot filtered. To the above solution, 1,8-diaminonaphthalene **1** (4.74 g, 30 mmol) and acetic acid (0.5 ml) was added and the mixture was stirred under reflux for 3 h. The red solid appeared and filtered and was washed with acetone several times.

Yield 2.66 g (30%). ^{1}H NMR: δ 10.93 (12H, s), 8.57 (1H,d), 8.41 (1H, d), 8.26 (1H, d), 8.11 (1H, d), 7.91 (1H, t), 7.74 (1H, t), 7.23 (1H, t), 7.18 (1H, d), 7.14 (1H, t), 7.05 (1H, d), 6.85 (1H, d), 6.79 (1H, d): EA calcd; $C_{20}H_{13}N_3$ (C, 81.34; H, 4.44; N, 14.23), found; (C, 80.51; H, 4.43; N, 14.46); *m*/*z* (M$^+$); 295.

2.2.3. Squarylium dyes *10–12* (general method)

Squaric acid **9** (0.74 g, 6.5 mmol) and 13 mmol of the perimidine derivative **4**, **5** or **8** were heated under reflux for 3 h in a mixture of 64 ml of *n*-butanol/toluene (1:1/v:v). Water was removed azeotropically using a Dean–Stark trap. The reaction mixture was cooled and poured into 300 ml of petroleum ether. The product was filtered and washed with acetonitrile, DMF and acetone. Yields and physical properties are shown in Table 1.

Table 1
Some properties and indentifications of dyes **10–12**

Dye	Yield (%)	Mass (M^+)	$\lambda_{max}{}^a$ (nm)	ε^a ($\times 10^{-5}$)	MP (°C)	Analysis (%) found/calcd		
						C	H	N
10	88	530	826	4.5	278 (decomp.)	76.87	6.17	10.15
						76.95	6.46	10.56
11	80	658	826	10.8	>300	79.83	6.46	8.61
						80.21	6.43	8.50
12	60	668	858	2.2	>300	78.92	3.82	12.86
						79.03	3.62	12.57

[a] Measured in DMF.

2.3. *Photofading*

Solutions of dyes (4.5×10^{-6} mol/l) in DMF were prepared. These solutions (35 ml) were placed in Pyrex tubes. The solutions were then irradiated with a 500 W mercury lamp (Ushio Electronic, UM-501). The absorption spectra were measured before and after irradiation and relative percentage photofading (conversion) determined at the absorption maxima of each of the dyes.

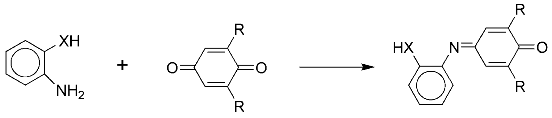
3. Results and discussion

Symmetrical squarylium dyes are normally synthesized by condensation of squaric acid and electron rich aromatic or heteroaromatic compounds.

Some dihydroperimidine squarylium dyes have been known for a number of years [7].

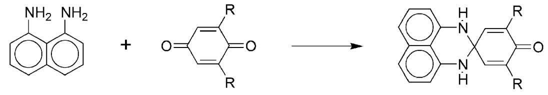
We now describe a new class of squarylium dyes with dihydroperimidine containing polycyclic alkane such as adamantly moiety and hydroperimidine containing quinoline moiety. Coupling carbonyl compounds with aromatic amines bearing amino, hydroxy, or thiol groups in *o*-positions is known to be a general method for the synthesis of 1,3-benzazoles. No heterocyclization occurs, however, in the reaction of *o*-phenylenediamines or *o*-aminophenoles with *p*-quinones. In these cases, the reaction stops at the stage of formation of the deeply coloured quinoneimine **13** [9] which is similar to that obtained by the reaction of a variety of *p*-substitued anilines with derivatives of *p*-benzoquinone [10].

These quinoneimines do not undergo cyclization under heating or irradiation of its solution.



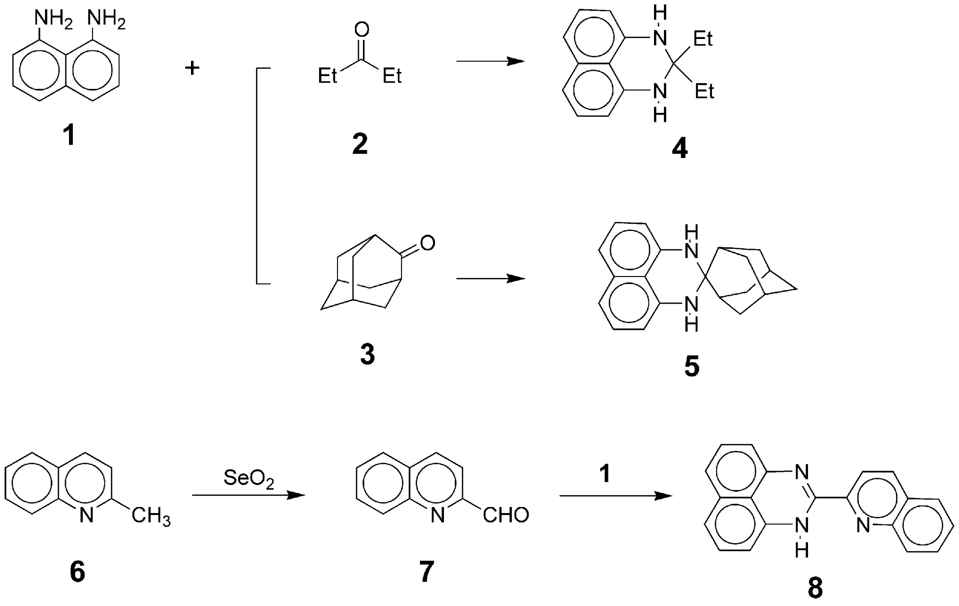
13
X = O, NR

In contrast to *o*-phenylenediamines, 1,8-diaminonaphthalene and most of its derivatives react with 2,6-di-*tert*-butyl-1,4-benzoquinone to give perimidinespirocyclohexa dienone. The reaction occurs readily under noncatalytic conditions when refluxing propanol or toluene solution of the components.

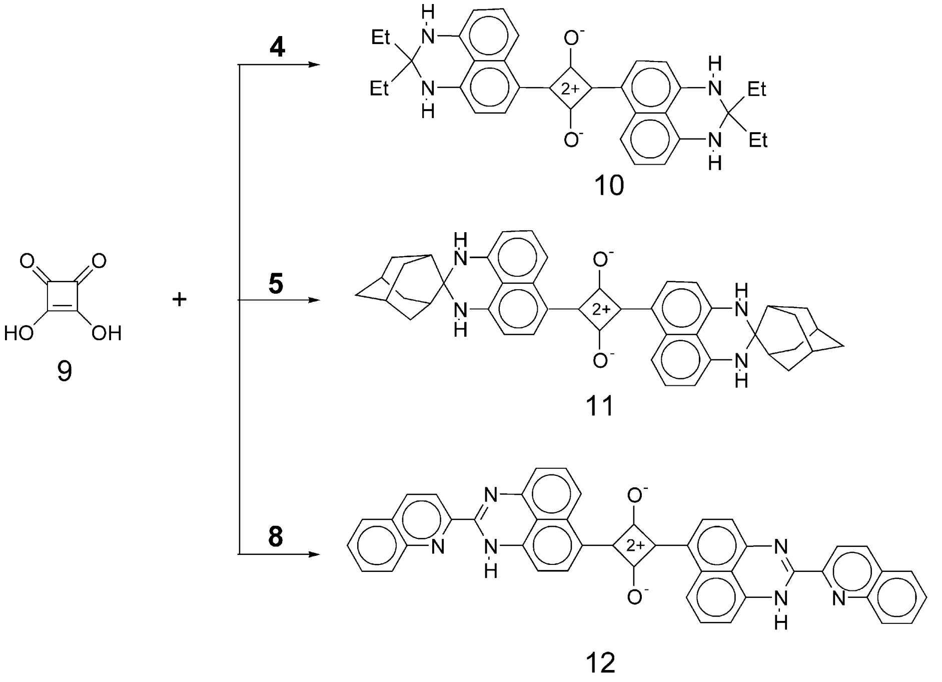


Compound **4** and **5** were prepared by condensing ketones such as **2** and **3** with a 1,8-diaminonaphthalene **1** in the presence of an acid catalyst in toluene under reflux conditions, with removal of water from the reaction mixture as it is formed. Methyl and methylene groups α to a carbonyl can be oxidized with selenium dioxide to give, respectively, α-ketoaldehydes and α-diketones. The reaction of quinaldine **6** with selenium dioxide in dioxane gives compound **7**. Reaction of **7** with 1,8-diaminonaphthalene **1** containing a small amount of acetic acid gave **8** (Scheme 1).

A mixture of **4** and squaric acid **9** in *n*-butanol/toluene (1:1/v:v) was reflux for 3 h to give dye **10**.



Scheme 1.



Scheme 2.

Dyes **11** and **12** were obtained by a similar reaction (Scheme 2). Absorption spectra and analysis data are shown in Table 1.

The effect of a heteroaromatic ring R on the $\lambda_{\max}$ of squarylium dye depends on its structure as shown in Scheme 1. The bathochromic effect of substituent R on the $\lambda_{\max}$ is in order of $a<b<c<d<e<f$, which is attributed to the longer π-system, followed by the electron-donating property of the heteroaromatic ring R.

Substitution by a strong electron-donating group such as hydroperimidine containing quinaldine moiety produced a large bathochromic shift compared to dihydroperimidine squarylium dye **11**. The PPP-MO calculation results were in accordance with both the observed absorption

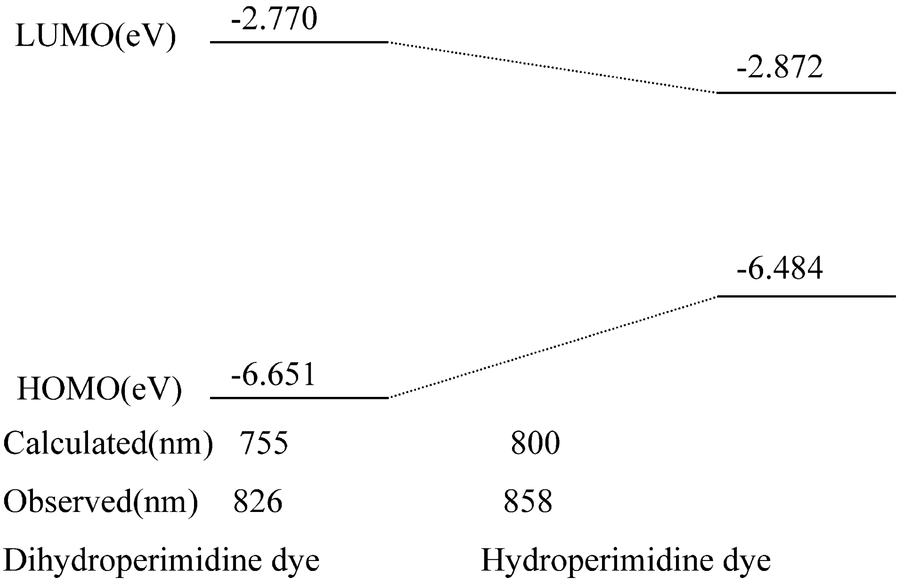


Fig. 1. Comparision between experimental and calculated visible absorption spectra of perimidine squarylium dyes.

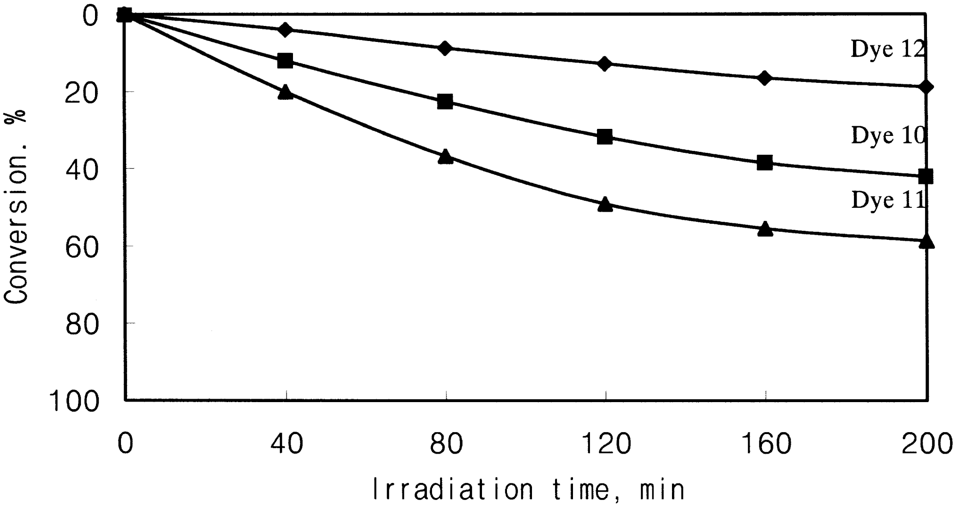


Fig. 2. Photofading behavior of dyes **10–12** in DMF.

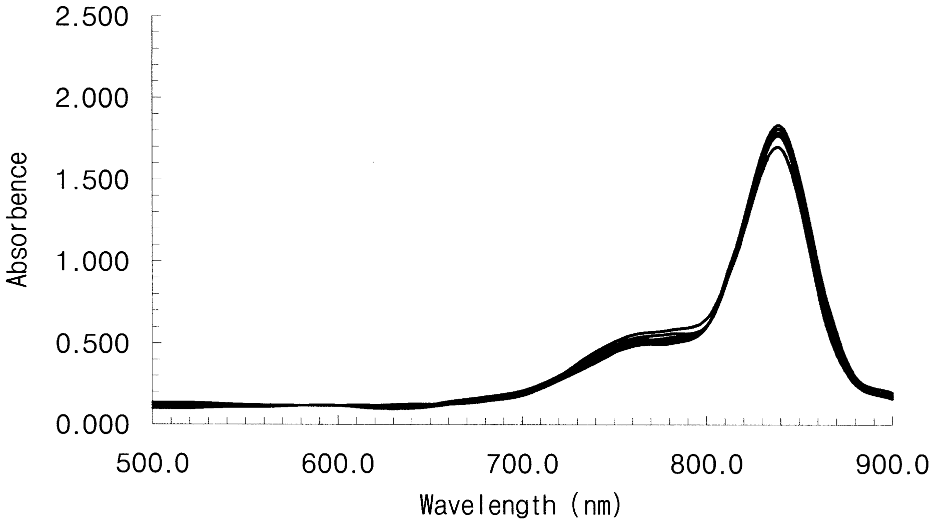


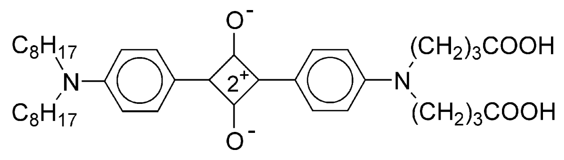
Fig. 3. Absorption spectra of dye **11** in DMSO–water solution (70–100% DMSO).

spectra and the bathochromic properties of the squarylium dyes (Fig. 1).

From these results it was apparent that the hydroperimidine moiety caused a large increase in the energy level of the highest occupied molecular orbital (HOMO) and a small decrease on that of lowest unoccupied molecular orbital (LUMO). The large increase of the HOMO compared with small decrease of the LUMO gave rise to the bathochromic effect. In this present work, the lightfastness behaviour of the perimidine squarylium dyes in solution was investigated. As shown by Fig. 2, a DMF solution containing squarylium dyes excessively faded on exposure to UV light. The order of photostability is as follows, **12**>**10**>**11**.

Introduction of an electron-donating group such as hydroperimidine containing quinaldine into the dye molecule afforded considerable protection against fading.

There have been several efforts to study the aggregation behaviour of the squarylium dyes and the mechanisms involved in the aggregation process [11–14]. Addition of dimethyl sulfoxide (DMSO) to an aqueous solution of certain squarylium dyes increases their solubility in general and results in a preference for monomer, compared to pure aqueous media. Chen et al. reported the formation of blue shifted aggregates of squarylium dye **14** with larger hydrophobic alkyl group substituents in DMSO–water mixtures when the percentage of water in the mixture was increased [11].



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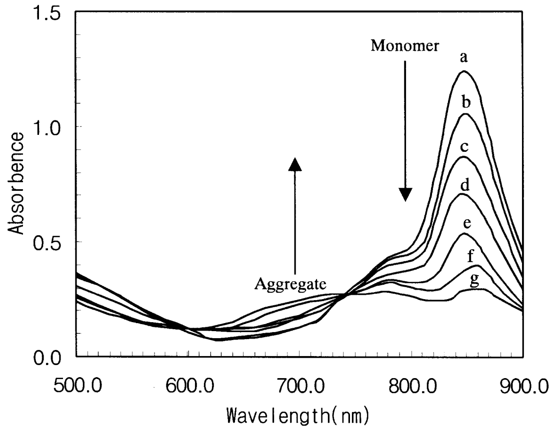

Fig. 4. Absorption spectra of dye **12** in DMSO–H_2O mixed solvent. DMSO/H_2O (v/v): (a) 100/0, (b) 95/5, (c) 90/10, (d) 85/15, (e) 80/20, (f) 75/25, (g) 70/30.

Dye **14** existed as the aggregate (530 nm), dimer (594 nm) and monomer (650 nm) in the binary solvent system.

The absorption spectra of dye **11** in DMSO–water are shown in Fig. 3. When dye **11** was added to DMSO–water mixtures in the range of 70–100% the DMSO, absorption band at 644 nm indicated the non-associated dye **11**.

For dye **12** carrying hydroperimidine moiety, the conversion between aggregate and monomer was observed by changing the percentage of DMSO in the mixture (Fig. 4). The results obtained were consistent with those reported by Kim et al. [14].

From the aggregation behavior we can conclude that the terminal group has significant influence on the formation of perimidine squarylium dye aggregate.

Acknowledgements

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