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NOVEL SYNTHESES OF PHENOSELENAZINEQUINONE INFRARED DYES

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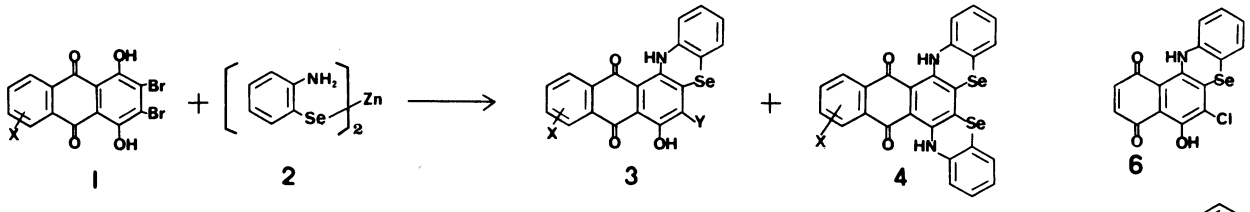
New series of phenoselenazinequinone infrared dyes for optical recording medium have been synthesized by the ring-closure reaction between 2,3-dihalogenoquinones and zinc 2-aminobenzeneselenate. These dyes absorbed near infrared light at 700-830 nm.

There is a current interest in the development of the new infrared dye for optical information recording medium for semiconductor laser.[1] Recently, some of the infrared dye such as squarylium and pentamethine dyes have been reported as dyes for diode-laser optical storage.[2] We reported that 5-amino-8-arylamino-2,3-dicyano-1,4-naphthoquinones which absorb infrared light at 750-800 nm have superior properties as a dye medium.[3]

In this paper, we wish to report the novel syntheses of phenoselenazinequinone infrared dyes by the ring-closure reaction of 2,3-dibromoquinizarins (**1**) with zinc 2-aminobenzeneselenate (**2**). An ethanol (50 ml) solution of **2** (0.28 mmol) and potassium hydroxide (10 mg) was added dropwise to a suspension of **1a** (0.25 mmol) in ethanol (10 ml) at 80 °C. The mixture was stirred at 80 °C for 6 h under nitrogen atmosphere to give the mixture of **3** and **4**, 11,12-diselena-6H,17H-6,17-diazadinaphtho[3,2a][2,3c]anthra-5,18-quinone. The naphthazarin analogues **6** and **7**, 10,11-diselena-5H,16H-5,16-diazadinaphtho[3,2a][2,3c]naphtho-1,4-quinone, could be synthesized by the reaction of 2,3-dichloronaphthazarin **5** with **2**. Results are summarized in Table 1.



1

a, X=H
b, X=Cl_4
c, X=F_4

2

3

a, X=H, Y=H
b, X=H, Y=Br
c, X=Cl_4 Y=Br
d, X=F_4 Y=Br

4

a, X=H
b, X=Cl_4
c, X=F_4

6

7

Table 1. Reaction of halogenoquinones with **2** under nitrogen atmosphere

Run	Reactant	Solvent	Temp /°C	Time/h	Product (yield/%)[a]	
1	**1a**	EtOH	80	6	**3b** (12)	**4a** (8.4)
2	**1a**	DMF	150	6	**3a** (11)	**4a** (0)
3	**1b**	DMF	150	6	**3c** (10.2)	**4b** (12.4)
4	**1c**	EtOH	80	6	**3d** (7.2)	**4c** (8.1)
5	**5**	EtOH	80	0.5	**6** (0)[b]	**7** (48)

a) Yield of isolated product after chromatography based on reactant.

b) Dye **6** was obtained in 25% yield at 25 °C for 0.5 h.

The absorption spectra are shown in Figure 1 and some properties of phenoselenazinequinone infrared dyes are as follows. Phenoselenazinequinone dyes absorbed at much more longer wavelength than the corresponded phenothiazinequinone dyes.

3a : Mp 268 °C ; UV λmax (nm) ($CHCl_3$), ($\varepsilon \times 10^{-4}$) : 645(1.21), 700(1.32) ; Found : C, 60.86 ; H, 2.70 ; N,2.92%. Calcd for $C_{20}H_{11}NO_3Se$: C, 61.07 ; H, 2.80 ; N, 3.56%. **3b** : Mp 272 °C ; UV ($CHCl_3$) : 645(1.27), 705(1.15). **3c** : Mp >300 °C ; UV ($CHCl_3$) : 700(1.13), 760(0.98). **3d** : Mp >300 °C ; UV ($CHCl_3$) : 700(1.26), 755(1.41). **4a** : Mp >300 °C ; UV ($CHCl_3$) : 665(1.42), 720(1.27) ; Found : C, 57.47 ; H, 2.52 ; N, 4.87%. Calcd for $C_{26}H_{14}N_2O_2Se_2$: C, 57.14 ; H, 2.56 ; N, 5.13%. **4b** : Mp >300 °C ; UV ($CHCl_3$) : 710(1.27), 765(1.42), 830^{s}(1.02). **4c** : Mp >300 °C ; UV ($CHCl_3$) : 725(1.31), 780(1.48). **6** : Mp 275 °C ; UV (DMF) : 664(0.97), 719(0.99) ; Found : C, 50.67 ; H, 2.25 ; N, 3.78%. Calcd for $C_{16}H_8NO_3ClSe$: C, 51.02 ; H, 2.14 ; N, 3.72%. **7** : Mp 212 °C ; UV (DMF) : 680(0.62), 730(0.51).

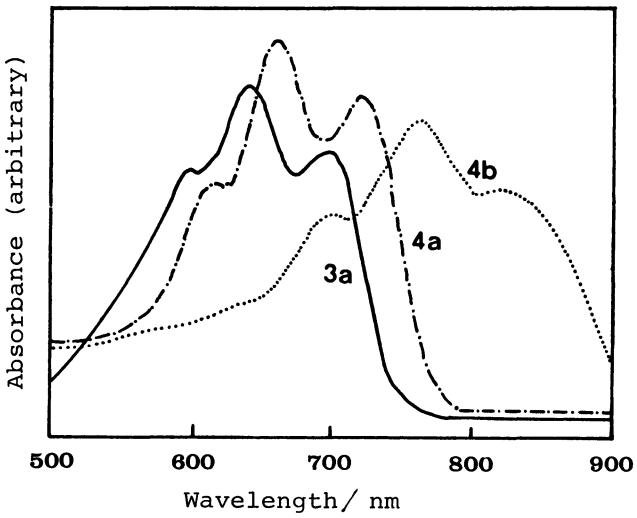


Fig. 1. Absorption spectra of infrared dyes in chloroform.

References

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