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SYNTHESIS AND BLUE DYEING ABILITY FOR POLYPROPYLENE FABRICS OF VARIOUS 3,7-BIS(DIALKYLAMINO)PHENOXAZIN-5-IUM SALTS AND THE SULFUR AND SELENIUM ANALOGS

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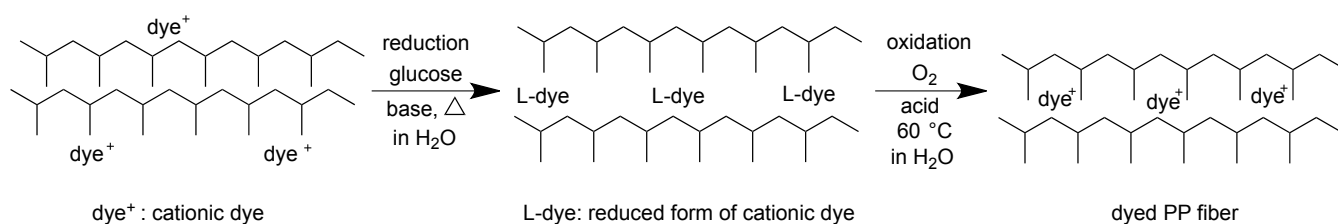
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Abstract – 3,7-Bis(dialkylamino)phenoxazin-5-ium salts having different amino groups (dimethylamino, diethylamino, dipropylamino, dibutylamino, and pyrrolidyl) and counter anions (chloride, bromide, iodide, hydrogensulfate, and nitrate) were synthesized in up to 80% isolated yield as blue cationic dyes. In addition, 3,7-bis(diethylamino)phenothiazin-5-ium and 3,7-bis(diethylamino)phenoselenazin-5-ium iodides were also synthesized in 20% and 17% isolated yields, respectively. Polypropylene fabrics were dyed with the above synthesized blue cationic dyes. As an evaluation result, it has been found that the moderate size such as diethylamino groups at the 3 and 7 positions of phenoxazinium salts is suitable for the dyeing ability.

INTRODUCTION

Polypropylene (PP) fibers have various excellent characteristics such as small specific gravity, heat resistance, rigidity, transparency, water resistance, chemical resistance, and good insulation. However, it is difficult to use PP fabrics for fashionable apparels due to the poor dyeing properties.¹⁻³ This main disadvantage is attributed that PP has no dyeing site owing to the simple molecular structure. Various methods for dyeing of PP fibers have been studied and performed so far, for examples, spin-dyeing,⁴ mixing of a good-dyeing resin,⁵⁻⁷ surface modification method,⁸ and supercritical fluid method.⁹ Nevertheless some problems have been still remained, i.e. lack of color saturation, changes in physical

properties, and increases in manufacturing and dyeing costs. To solve these problems, we investigated a novel dyeing method for PP fibers utilizing the colorless reduced form (leuco form, L-dye) of a cationic dye (Scheme 1).¹⁰ In our method, the permeability and affinity of the cationic dye for PP fibers would have been enhanced by reduction of the cationic dye with a reducing agent in basic aqueous solution followed by reoxidation of the adsorbed L-dye with an oxidizing agent in acidic conditions. The reduced compound (L-dye) of a cationic dye is very sensitive to air and is easily reoxidized. As a result, the cationic dye was strongly adsorbed onto the PP fibers. Thus, our method made it possible to dye PP fibers with various kinds of colors using some cationic dyes simply and inexpensively. In our previous report, we evaluated the dyeing ability for PP fiber using only commercially available cationic dyes, in which Basic Blue 3 (3,7-bis(diethylamino)phenoxazin-5-ium chloride) was the most effective for blue dyeing (Figure 1).¹⁰ Hence, we herein report the synthesis of several blue cationic dyes having different amino groups or counter anions compared with Basic Blue 3 and their blue dyeing abilities for PP fiber. In addition, 3,7-bis(diethylamino)phenothiazin-5-ium and 3,7-bis(diethylamino)phenoselenazin-5-ium iodides, which are sulfur and selenium analogs of phenoxazin-5-ium salt, respectively, were also synthesized and their dyeing abilities were investigated.



Scheme 1. Estimated mechanism for dyeing of PP fiber with a cationic dye

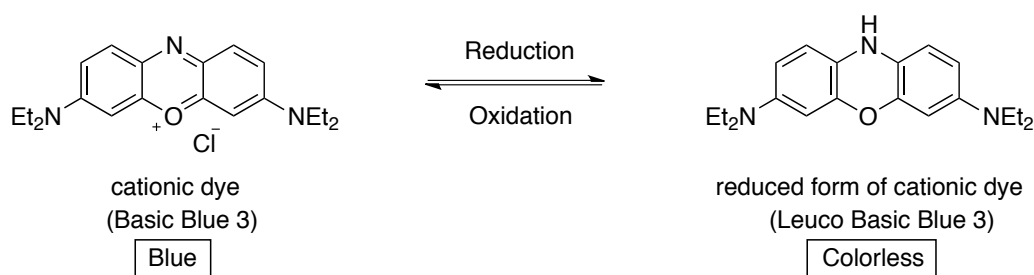
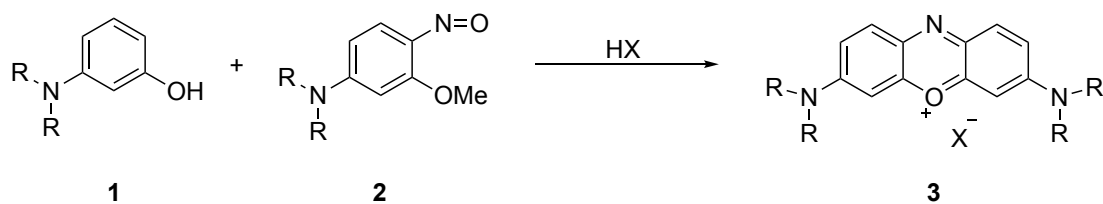


Figure 1. Basic Blue 3 and its reduced form

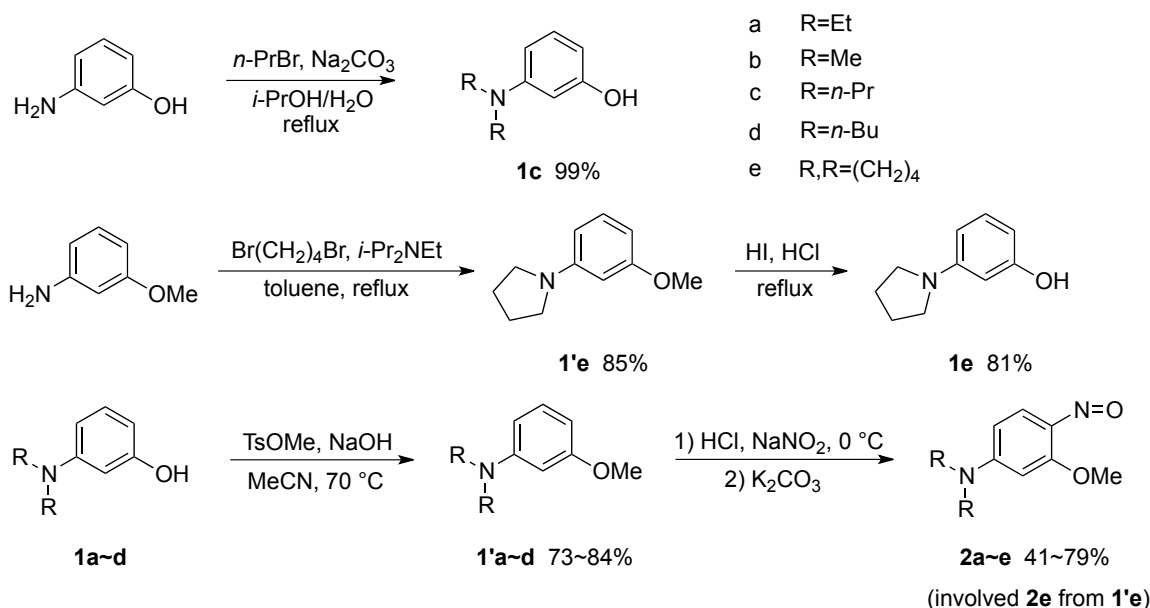
RESULTS AND DISCUSSION

3,7-Bis(dialkylamino)phenoxazin-5-ium salt derivatives **3** were synthesized by the treatment of 3-dialkylaminophenols **1** and *N,N*-dialkyl-3-methoxy-4-nitrosoanilines **2** in acidic solutions, modifying the method reported by Ihara *et al.* (Scheme 2).¹¹ Compounds **1a**, **1b** and **1d** are commercially available.

The synthesis of 3-dipropylaminophenol **1c**, 3-(pyrrolidin-1-yl)phenol **1e**, and nitroso-substituted compounds **2** are shown in Scheme 3. 3-Dipropylaminophenol **1c** was prepared by *N,N*-dipropylation of 3-aminophenol in 99% yield.¹² 3-(Pyrrolidin-1-yl)phenol **1e** was obtained by cleavage of the corresponding methoxy derivative **1'e** by use of HI in 81% yield, which was prepared by *N*-alkylation of 3-methoxyaniline with dibromopropane in 85% yield.^{13,14} *N,N*-Dialkyl-3-methoxy-4-nitrosoanilines **2** were synthesized by *O*-methylation of 3-dialkylaminophenol **1** followed by nitrosation using NaNO₂ and HCl in good yields. The reaction of compounds **1** and **2** obtained by the above method gave the targeted blue cationic dyes **3** in the presence of protic acid in 90% *i*-PrOH.



Scheme 2. Synthetic method of 3,7-bis(dialkylamino)phenoxazin-5-ium salts

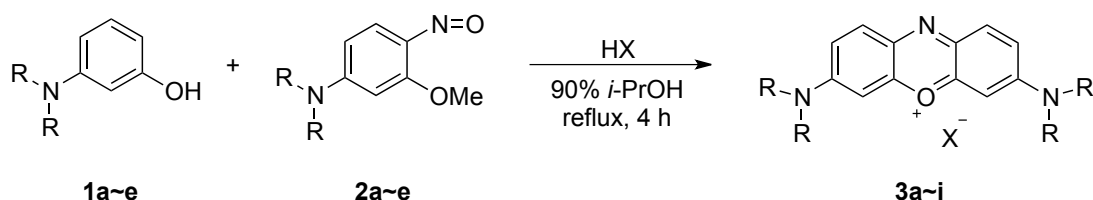


Scheme 3. Synthesis of 3-dialkylaminophenols and *N,N*-dialkyl-3-methoxy-4-nitrosoanilines

The results are summarized in Table 1. Compound **3a** (X=Cl) is commercially available and named by “Basic Blue 3”. The obtained blue cationic dyes **3** were purified by column chromatography with silica gel followed by recrystallization in moderate to good yields. The blue cationic dyes (R=Et) with an alterable anion such as chloride, bromide, iodide, hydrosulfate, and nitrate were synthesized (Entries 1-5). Three resonance structures (**3A-C**) are possible for phenoxazin-5-ium salts **3** as shown in Figure 2. To investigate the effect of substituents on nitrogen atom in imminium cation structures (**3A** and **3C**) for dyeing ability, phenoxazin-5-ium chlorides having dimethylamino, dipropylamino, dibutylamino, and

pyrrolidyl groups were also synthesized (Entries 6-9). Unfortunately, the synthesis of compound **3** having more bulky amino groups ($R=i\text{-Pr}$) was not achieved, because the corresponding precursor, 3-diisopropylaminophenol, was not efficiently and purely obtained owing to the steric effect, accompanied by the formation of a large amount of 3-isopropylaminophenol.

Table 1. Synthesis of 3,7-bis(dialkylamino)phenoxazin-5-ium salts



Entry	R	Aminophenol 1a-e	Nitrosoaniline 2a-e	X	Product 3a-i	Yield (%) ^{a)}
1	Et	1a	2a	Cl	3a (Basic Blue 3)	60
2	Et	1a	2a	Br	3b	68
3	Et	1a	2a	I	3c	78
4	Et	1a	2a	HSO ₄	3d	36
5	Et	1a	2a	NO ₃	3e	73
6	Me	1b	2b	Cl	3f	72
7	<i>n</i> -Pr	1c	2c	Cl	3g	80
8	<i>n</i> -Bu	1d	2d	Cl	3h	80
9	-(CH ₂) ₄ -	1e	2e	Cl	3i	78

a) Isolated yield.

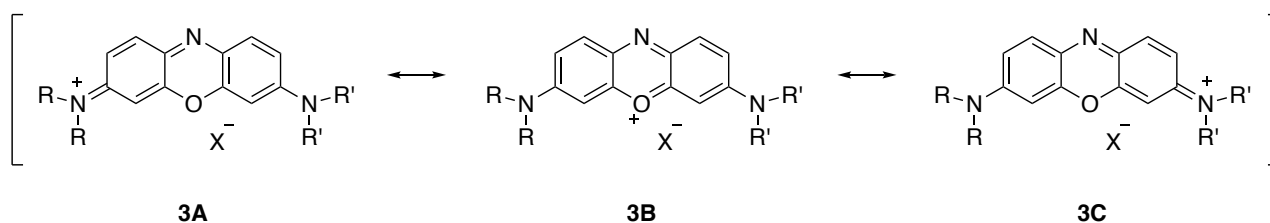
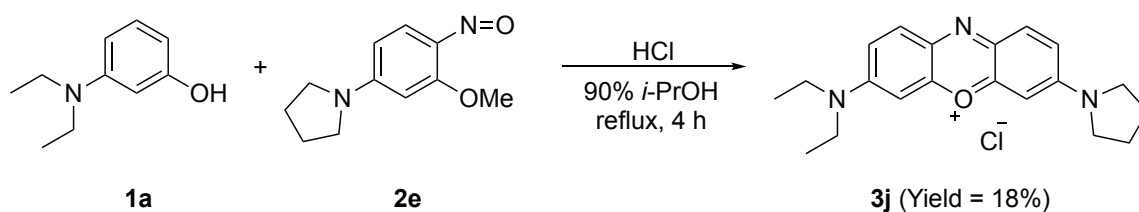


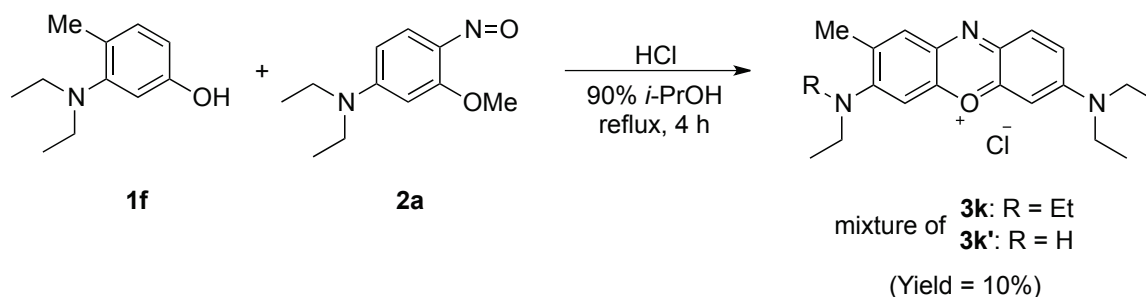
Figure 2. Resonance structures of phenoxazininium salts **3**

Next, we examined the synthesis of two unsymmetrical cationic dyes (Schemes 4 and 5). The reaction of compound **1a** with compound **2e** in the presence of HCl gave the unsymmetrical compound **3j** with different amino groups at the 3 and 7 positions in 18% isolated yield (Scheme 4). The cause of this low yield may be difficulty of the recrystallization of **3j**. Phenol derivative **1f** obtained by *N,N*-diethylation of 3-amino-4-methylphenol reacted with nitroso compound **2a** to afford another unsymmetrical cationic dye **3k** in low yield, accompanied by the formation of by-product **3k'** with monodeethylation on the nitrogen

atom (Scheme 5). The steric hindrance between neighboring methyl and diethylamino groups in **3k** may lead to low yield of **3k**.

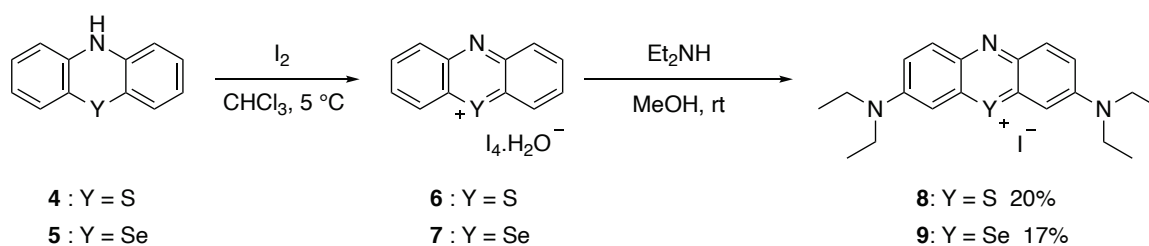


Scheme 4. Synthesis of unsymmetrical compound **3j** with different amino groups at the 3 and 7 positions



Scheme 5. Synthesis of another unsymmetrical cationic dye **3k**

We then examined the synthesis of sulfur and selenium analogs (**8** and **9**) of phenoxazin-5-ium salts **3** as shown in Scheme 6. Methylene Blue (3,7-bis(dimethylamino)phenothiazin-5-ium chloride) is well known as a cationic dye having a phenothiazine skeleton (Figure 3), and the preparation of Methylene Blue analogs having different dialkylamino groups has been reported.¹⁵ The sulfur and selenium analogs (**8** and **9**) were synthesized according to the method reported by Mellish *et al.*¹⁵ The reaction of commercially available 10*H*-phenothiazine **4** with iodine gave quantitatively the corresponding tetraiodine hydrate **6** which was successively treated with diethylamine to afford the desired 3,7-bis(diethylamino)phenothiazin-5-ium iodide **8** via nucleophilic attack of diethylamine at the 3 and 7 positions in 20% yield. On the other hand, 10*H*-phenoselenazine **5** was prepared by reaction of diphenylamine with selenium monochloride,¹⁶ and the obtained **5** reacted with iodine followed by the treatment of diethylamine to give the selenium analog **9** in 17% yield.



Scheme 6. Synthesis of sulfur and selenium analogs of cationic dyes **3**

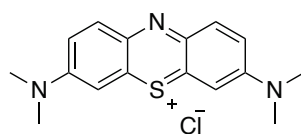
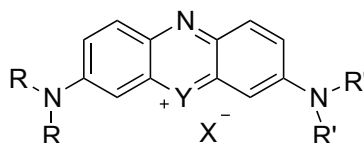


Figure 3. Structure of Methylene Blue

Absorption property of the synthesized cationic dyes at a concentration of 3.0×10^{-5} M in MeOH is listed in Table 2. The absorption maximum (λ_{\max}) was hardly shifted, regardless of the counter anions on cationic dyes **3** (Entries 1-5). On the other hand, the shift to longer wavelengths in λ_{\max} was observed as an alkyl chain length on nitrogen atom of amino group increases (Entries 1 and 6-8). Compared to λ_{\max} of compounds **3**, those of the sulfur and selenium derivatives (**8** and **9**) were shifted to longer wavelengths as the size of group 16 atoms becomes larger. In addition, the extinction coefficients (ϵ) of compounds **3c**, **8**, and **9** decreased in order of X=O, S, and Se (Entries 3 and 11-12).

Table 2. Absorption data for synthesized cationic dyes

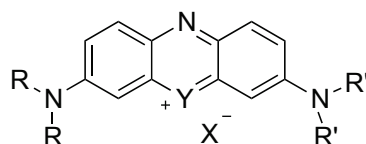


Entry	Cationic Dye	R	R'	X	Y	λ_{\max} (nm) ^{a)}	ϵ (M ⁻¹ cm ⁻¹) ^{a)}
1	3a	Et	Et	Cl	O	643	106000
2	3b	Et	Et	Br	O	642	112000
3	3c	Et	Et	I	O	642	112000
4	3d	Et	Et	HSO ₄	O	643	101000
5	3e	Et	Et	NO ₃	O	643	106000
6	3f	Me	Me	Cl	O	638	97000
7	3g	<i>n</i> -Pr	<i>n</i> -Pr	Cl	O	649	97000
8	3h	<i>n</i> -Bu	<i>n</i> -Bu	Cl	O	650	100000
9	3i	-(CH ₂) ₄ -	-(CH ₂) ₄ -	Cl	O	643	98000
10	3j	Et	-(CH ₂) ₄ -	Cl	O	643	112000
11	8	Et	Et	I	S	652	61000
12	9	Et	Et	I	Se	658	38000

a) 3.0×10^{-5} M in MeOH. Absolute errors, λ_{\max} : 1 nm, ϵ : 1000 M⁻¹cm⁻¹.

We next performed the dyeing of PP fabric using synthesized blue cationic dyes **3a-j**, **8** and **9**. The dyeing procedure is as follows. First, a PP fabric, water and a dye were put into a container, and subsequently a reducing agent (glucose) and NaOH were added to the container. Then the container was heated at boiling temperature for 30 minutes. By this operation, the cationic dye was reduced, and the colorless reduced dye (leuco form) permeated and diffused inside the PP fibers. Next, the PP fabric treated as mentioned above was subjected to 3% acetic acid aqueous solution at 60 °C for 30 minutes, whereby the dye inside the PP fiber was reoxidized and fixed. The color measurement results of blue-dyed PP fabrics are summarized in Table 3. It should be noted that the closer to 0 an L^* value gets, the darker a color is. Accordingly, a lower L^* value indicates that PP fabric was deeply dyed, being good result.

Table 3. Color measurement results of dyed PP fabrics



Entry	R	R'	X	Y	Dye	L^*	a^*	b^*
1 ^{a)}	—	—	—	—	—	79.10	2.47	-8.47
2	Et	Et	Cl	O	3a	27.97	0.86	-33.29
3	Et	Et	Br	O	3b	28.80	2.28	-32.44
4	Et	Et	I	O	3c	33.87	0.53	-34.92
5	Et	Et	HSO ₄	O	3d	31.15	-1.01	-32.20
6	Et	Et	NO ₃	O	3e	25.63	2.05	-32.43
7	Me	Me	Cl	O	3f	40.16	10.24	-31.83
8	<i>n</i> -Pr	<i>n</i> -Pr	Cl	O	3g	37.11	-5.79	-33.29
9	<i>n</i> -Bu	<i>n</i> -Bu	Cl	O	3h	54.41	-5.27	-25.06
10	-(CH ₂) ₄ -	-(CH ₂) ₄ -	Cl	O	3i	44.92	-3.96	-20.87
11	Et	-(CH ₂) ₄ -	Cl	O	3j	29.22	-0.48	-31.16
12	Et	Et	I	S	8	67.50	-2.77	-11.26
13	Et	Et	I	Se	9	66.37	0.58	-10.82

L^* values indicate degree of lightness from black to white (range = 0 - 100). Negative b^* is blue, positive b^* is yellow; negative a^* is green and positive a^* is red. Both a^* and b^* values range from -127 to +127.

a) Entry 1 is the result of color measurement of a gray state fabric. Absolute errors of a gray state fabric, L^* : 0.81, a^* : 0.07, b^* : 0.37.

CONCLUSIONS

Various 3,7-bis(dialkylamino)phenoxazin-5-ium salts having different amino groups such as dimethylamino, diethylamino, dipropylamino, dibutylamino, and pyrrolidinyl at the 3 and 7 positions and counter anions such as chloride, bromide, iodide, hydrogensulfate, and nitrate were synthesized in up to 80% isolated yields as blue cationic dyes. In addition, as sulfur and selenium analogs of the above cationic dyes, 3,7-bis(diethylamino)phenothiazin-5-ium and 3,7-bis(diethylamino)phenoselenazin-5-ium iodides were also synthesized in 20% and 17% isolated yields, respectively. Through a series of our dyeing procedure (reduction-reoxidation processes with PP fabrics) using the above synthesized cationic dyes, it was found that the size of dialkylamino groups at the 3 and 7 positions in 3,7-bis(dialkylamino)phenoxazin-5-ium salts is responsible for dyeing ability and a moderate size such as diethylamino group is suitable in the blue dyeing for PP fabrics. On the other hand, the sulfur and selenium analogs (**8** and **9**) of phenoxazin-5-ium salts were not suitable for the dyeing of PP fabrics because of the instability of reduced forms under basic conditions.

EXPERIMENTAL

General. Melting points were determined on Mettler Toledo, FP90 with FP82HT. ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-EC S400 spectrometer. Tetramethylsilane (TMS) was used as an internal standard for ^1H NMR and solvent peak was used as an internal standard for ^{13}C NMR. Coupling constants (J) were reported in hertz (Hz). Following abbreviations were used to designate the multiplicities: s=singlet; d=doublet; t=triplet; q=quartet; br=broad; m=multiplet. IR spectra were determined on a JASCO FT/IR-6200. HPLC were carried out by Shimadzu LC-10Avp on a Luna 3μ CN (150 x 2.0 mm) column with a pre-column filter (ODS), eluted with MeCN-H₂O (70:30, v/v) containing HCOOH (1%). LC-MS (ESI) spectra were recorded with a Shimadzu LCMS-2010 spectroscope. Absorption spectra were taken on Shimadzu UV-2450 UV-visible spectrophotometer. Flash column chromatography was carried out using FUJIFILM Wako Pure Chemical Wakogel C-200. The $L^*a^*b^*$ was measured under a D65 light source, a visual field of 10°, and an SCE mode by a Konica Minolta CM-3600d spectrophotometer. Unless otherwise noted, starting materials were obtained from FUJIFILM Wako Pure Chemical, Aldrich Company and Tokyo chemical Industry Company and used as received.

Dyeing Method.

Put a PP knit fabric (DTY 300 dtex / 72 F, 0.5 g), distilled water (100 mL) and a dye (15 mg) into a container. Subsequently, D-(+)-glucose (0.2 g) and NaOH (0.1 g) were added to the container; then the container was capped and heated at boiling temperature for 30 min. The PP fabric treated as above was subjected to 0.3% acetic acid aqueous solution at 60 °C for 30 min. The PP fabric was washed with

enough water, and then the PP fabric was soaping with 0.3% HIPOM MC-2300 aqueous solution at 80 °C for 20 min. The PP fabric was washed with enough water and dried at room temperature.

Typical Procedure for the Preparation of Dialkylaminophenols 1c and 1f.

Dialkylaminophenols were synthesized according to the literature 12.

3-Dipropylaminophenol (1c). Purple oil; yield 99%; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 0.91 (t, 6H, $J = 7.6$ Hz, $2 \times \text{CH}_3$), 1.55-1.65 (m, 4H, $2 \times \text{CH}_2$), 3.20 (t, $J = 7.8$ Hz, 4H, $2 \times \text{CH}_2\text{N}$), 6.07-6.12 (m, 2H, Ar-H), 6.23 (dd, $J = 8.2, 2.3$ Hz, 1H, Ar-H), 7.03 (t, $J = 8.2$ Hz, 1H, Ar-H).

3-Diethylamino-4-methylphenol (1f). Pale pink oil; yield 79%; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 0.98 (t, 6H, $J = 7.1$ Hz, $2 \times \text{CH}_3$), 2.19 (s, 3H, CH_3), 2.94 (q, 4H, $J = 7.0$ Hz, $2 \times \text{CH}_2$), 6.45 (dd, $J = 8.2, 2.8$ Hz, 1H, Ar-H), 6.57 (d, $J = 2.3$ Hz, 1H, Ar-H), 7.00 (d, $J = 8.2$ Hz, 1H, Ar-H).

3-Diisopropylaminophenol. Purple pink oil; yield 9%; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 0.89 (d, 6H, $J = 6.9$ Hz, $4 \times \text{CH}_3$), 2.03-2.14 (m, 2H, $2 \times \text{CH}$), 3.11 (d, $J = 7.3$ Hz, 4H, $2 \times \text{CH}_2\text{N}$), 6.00-6.31 (m, 3H, Ar-H), 7.03 (t, $J = 8.0$ Hz, 1H, Ar-H).

3-Isopropylaminophenol. Reddish brown oil; yield 50%; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 0.96 (d, 6H, $J = 6.9$ Hz, $2 \times \text{CH}_3$), 1.82-1.92 (m, 1H, CH), 2.89 (d, 2H, $J = 6.9$ Hz, CH_2), 6.07-6.19 (m, 3H, $3 \times \text{Ar-H}$), 6.99 (t, 1H, $J = 8.0$ Hz, Ar-H).

Typical Procedure for the Preparation of 3-Methoxy-*N,N*-dialkylanilines 1'a~d.

Compounds 1'a~d were synthesized according to the literature 11.

***N,N*-Diethyl-3-methoxyaniline (1'a).** Reddish brown oil; yield 78%; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 1.15 (t, 6H, $J = 7.1$ Hz, $2 \times \text{CH}_3$), 3.33 (q, $J = 7.0$ Hz, 4H, $2 \times \text{CH}_2$), 3.78 (s, 3H, OCH_3), 6.20-7.14 (m, 4H, Ar-H).

***N,N*-Dimethyl-3-methoxyaniline (1'b).** Reddish brown oil; yield 73%; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 2.93 (s, 6H, $2 \times \text{CH}_3$), 3.79 (s, 3H, OCH_3), 6.20-6.44 (m, 4H, Ar-H), 7.15 (t, $J = 8.0$ Hz, 1H, Ar-H).

***N,N*-Dipropyl-3-methoxyaniline (1'c).** Brown oil; yield 84%; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 0.91 (t, 6H, $J = 7.3$ Hz, $2 \times \text{CH}_3$), 1.56-1.65 (m, 4H, $2 \times \text{CH}_2$), 3.21 (t, $J = 7.6$ Hz, 4H, $2 \times \text{CH}_2$), 3.78 (s, 3H, OCH_3), 6.11-6.36 (m, 3H, $2 \times \text{Ar-H}$), 7.10 (t, $J = 8.0$ Hz, 1H, Ar-H).

***N,N*-Dibutyl-3-methoxyaniline (1'd).** Brown oil; yield 81%; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 0.92-0.96 (m, 6H, $2 \times \text{CH}_3$), 1.29-1.39 (m, 4H, $2 \times \text{CH}_2$), 1.52-1.60 (m, 4H, $2 \times \text{CH}_2$), 3.21-3.25 (m, 4H, $2 \times \text{CH}_2$), 3.77 (s, 3H, OCH_3), 6.19-7.12 (m, 4H, Ar-H).

Preparation of 1-(3-Methoxyphenyl)pyrrolidine (1'e).

Compound 1'e was synthesized according to the literature 13.

1'e: Reddish brown oil; yield 85%; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 1.96-1.99 (m, 4H, $2 \times \text{CH}_2$), 3.25-3.28 (m, 4H, $2 \times \text{CH}_2\text{N}$), 3.79 (s, 3H, OCH_3), 6.10-6.25 (m, 3H, Ar-H), 7.12 (t, $J = 8.2$ Hz, 1H, Ar-H).

Preparation of 3-(Pyrrolidin-1-yl)phenol (1e).

Compound **1e** was synthesized according to the literature 14.

1e: Pale pink powder; yield 81%; mp 123-124 °C; ¹H NMR (400 MHz, CDCl₃) δ_{ppm}: 1.89-2.05 (m, 4H, CH₂), 3.01-3.48 (m, 4H, 2 × CH₂N), 5.99-6.18 (m, 3H, Ar-H), 7.05 (t, *J* = 8.0 Hz, 1H, Ar-H).

Typical Procedure for the Preparation of *N,N*-Dialkyl-3-methoxy-4-nitrosoanilines 2a~e.

Compounds **2a~e** were synthesized according to the literature 11.

***N,N*-Diethyl-3-methoxy-4-nitrosoaniline (2a).** Light green powder; yield 79%; mp 73-74 °C; ¹H NMR (400 MHz, CDCl₃) δ_{ppm}: 1.30 (t, 6H, *J* = 7.1 Hz, 2 × CH₃), 3.53 (q, 4H, *J* = 7.2 Hz, 2 × CH₂), 4.17 (s, 3H, OCH₃), 6.13 (d, 1H, *J* = 2.8 Hz, Ar-H), 6.18 (dd, 1H, *J* = 9.4, 2.5 Hz, Ar-H), 6.77 (brs, 1H, Ar-H).

***N,N*-Dimethyl-3-methoxy-4-nitrosoaniline (2b).** Light green powder; yield 76%; mp 129-130 °C; ¹H NMR (400 MHz, CDCl₃) δ_{ppm}: 3.19 (s, 6H, 2 × CH₃), 4.18 (s, 3H, OCH₃), 6.05-6.23 (m, 2H, Ar-H), 6.69 (brd, 1H, *J* = 9.2 Hz, Ar-H).

***N,N*-Dipropyl-3-methoxy-4-nitrosoaniline (2c).** Light green powder; yield 41%; mp 79-80 °C; ¹H NMR (400 MHz, CDCl₃) δ_{ppm}: 1.01 (t, 6H, *J* = 7.6 Hz, 2 × CH₃), 1.63-1.81 (m, 4H, 2 × CH₂), 3.32-3.48 (m, 4H, 2 × CH₂), 4.17 (s, 3H, OCH₃), 6.04-6.19 (m, 2H, Ar-H), 6.62-6.79 (1H, Ar-H).

***N,N*-Dibutyl-3-methoxy-4-nitrosoaniline (2d).** Deep green oil; yield 63%; ¹H NMR (400 MHz, CDCl₃) δ_{ppm}: 1.01 (t, 6H, *J* = 7.3 Hz, 2 × CH₃), 1.37-1.46 (m, 4H, 2 × CH₂), 1.62-1.78 (m, 4H, 2 × CH₂), 3.33-3.56 (m, 4H, 2 × CH₂), 4.17 (s, 3H, OCH₃), 6.03-6.19 (m, 2H, Ar-H), 6.71 (brs, 1H, Ar-H).

1-(3-Methoxy-4-nitrosophenyl)pyrrolidine (2e). Light green powder; yield 74%; mp 137-138 °C; ¹H NMR (400 MHz, CDCl₃) δ_{ppm}: 2.02-2.17 (m, 4H, 2 × CH₂), 3.40-3.56 (m, 4H, 2 × CH₂), 4.16 (s, 3H, OCH₃), 6.00 (d, 1H, *J* = 2.3 Hz, Ar-H), 6.04 (dd, 1H, *J* = 9.2, 2.3 Hz, Ar-H), 6.72 (brs, 1H, Ar-H).

Typical Procedure for the Preparation of 3,7-Bis(dialkylamino)phenoxazin-5-ium Salts 3a~j.

The mixture of dialkylaminophenol (0.5 mmol) and 90% *i*-PrOH (10 mL) was stirred at 70 °C in a 100 mL three-neck bottle with distilling apparatus filled with argon. A suspended solution of *N,N*-dialkyl-3-methoxy-4-nitrosoaniline (0.5 mmol) and acid (0.5 mmol) in 90% *i*-PrOH (10 mL) was injected with syringe to the above mixture in four portions during 45 min. The temperature rose to reflux. When about 10 mL volume of the solvent was distilled out, 10 mL of 90% *i*-PrOH was added to the reaction mixture; this procedure was repeated three times during 4 h. The dark blue solution was evaporated and the residue was purified by column chromatography with silica gel, eluting by CHCl₃/MeOH from 10:1 to 10:3 (v/v) and the dark blue solution was evaporated. To a solution of the residue MeOH (1 mL), was added AcOEt (10 mL). After ultrasonication for 10 min, the mixture was filtrated. The powder was washed by AcOEt and Et₂O then dried under vacuum.

3,7-Bis(diethylamino)phenoxazin-5-ium Chloride (3a). Green powder; yield 63%; mp 176-179 °C; ¹H NMR (400 MHz, CDCl₃) δ_{ppm}: 1.41 (t, *J* = 7.3 Hz, 12H, 4 × CH₃), 3.82 (q, *J* = 7.1 Hz, 8H, 4 × CH₂), 7.15

(d, $J = 2.3$ Hz, 2H, 2 × Ar-H), 7.19 (dd, $J = 9.6, 2.7$ Hz, 2H, 2 × Ar-H), 7.75 (d, $J = 9.6$ Hz, 2H, 2 × Ar-H); ^{13}C NMR (101 MHz, CD_3OD) δ_{ppm} : 13.3 (4 × CH_3), 48.9 (4 × CH_2), 97.5 (2 × Ar CH), 118.7 (2 × Ar CH), 135.7 (2 × Ar CH), 135.7 (2 × Ar CH), 151.0 (2 × Ar C), 157.9 (2 × Ar C); IR(neat) ν (relative intensity) = 2969 (w), 2928 (w), 2870 (w), 1590 (s), 1498 (m), 1397 (s), 1144 (s) cm^{-1} ; MS (LC-ESI): m/z : 324 $[\text{M}-\text{Cl}]^+$.

3,7-Bis(diethylamino)phenoxazin-5-ium Bromide (3b). Green powder; yield 68%; mp 189-190 °C; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 1.40 (t, $J = 7.3$ Hz, 12H, 4 × CH_3), 3.81 (q, $J = 7.0$ Hz, 8H, 4 × CH_2), 7.10 (d, $J = 2.8$ Hz, 2H, 2 × Ar-H), 7.19 (dd, $J = 9.6, 2.8$ Hz, 2H, 2 × Ar-H), 7.74 (d, $J = 9.6$ Hz, 2H, 2 × Ar-H); ^{13}C NMR (101 MHz, CD_3OD) δ_{ppm} : 13.3 (4 × CH_3), 47.9 (4 × CH_2), 97.6 (2 × Ar CH), 118.7 (2 × Ar CH), 135.7 (2 × Ar C), 135.7 (2 × Ar CH), 150.9 (2 × Ar C), 157.8 (2 × Ar C); IR(neat) ν (relative intensity) = 2963 (w), 2929 (w), 1591 (s), 1497 (m), 1398 (s), 1147 (s) cm^{-1} ; MS (LC-ESI): m/z : 324 $[\text{M}-\text{Br}]^+$.

3,7-Bis(diethylamino)phenoxazin-5-ium Iodide (3c). Green powder; yield 78%; mp 200-207 °C; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 1.42 (t, $J = 7.3$ Hz, 12H, 4 × CH_3), 3.80 (q, $J = 7.2$ Hz, 8H, 4 × CH_2), 7.04 (d, $J = 2.3$ Hz, 2H, 2 × Ar-H), 7.19 (dd, $J = 9.6, 2.8$ Hz, 2H, 2 × Ar-H), 7.76 (d, $J = 9.6$ Hz, 2H, 2 × Ar-H); ^{13}C NMR (101 MHz, CD_3OD) δ_{ppm} : 13.4 (4 × CH_3), 48.1 (4 × CH_2), 97.7 (2 × Ar CH), 118.9 (2 × Ar CH), 135.7 (2 × Ar C), 135.7 (2 × Ar CH), 150.8 (2 × Ar C), 157.8 (2 × Ar C); IR(neat) ν (relative intensity) = 2964 (w), 2923 (w), 2869 (w), 1588 (s), 1497 (m), 1393 (s), 1143 (s) cm^{-1} ; MS (LC-ESI): m/z : 324 $[\text{M}-\text{I}]^+$.

3,7-Bis(diethylamino)phenoxazin-5-ium Hydrosulfate (3d). Green powder; yield 36%; mp 204-207 °C; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 1.40 (t, $J = 7.1$ Hz, 12H, 4 × CH_3), 3.83 (q, $J = 7.2$ Hz, 8H, 4 × CH_2), 7.01 (d, $J = 2.8$ Hz, 2H, 2 × Ar-H), 7.44 (dd, $J = 9.6, 2.8$ Hz, 2H, 2 × Ar-H), 7.84 (d, $J = 9.6$ Hz, 2H, 2 × Ar-H); ^{13}C NMR (101 MHz, CD_3OD) δ_{ppm} : 13.3 (4 × CH_3), 47.9 (4 × CH_2), 97.6 (2 × Ar CH), 118.7 (2 × Ar CH), 135.7 (2 × Ar C), 135.7 (2 × Ar CH), 151.0 (2 × Ar C), 157.9 (2 × Ar C); IR(neat) ν (relative intensity) = 2968 (w), 2932 (w), 2868 (w), 1591 (s), 1499 (m), 1399 (s), 1145 (s) cm^{-1} ; MS (LC-ESI): m/z : 324 $[\text{M}-\text{HSO}_4]^+$.

3,7-Bis(diethylamino)phenoxazin-5-ium Nitrate (3e). Green powder; yield 73%; mp 176-179 °C; ^1H NMR (400 MHz, CD_3OD) δ_{ppm} : 1.36 (t, $J = 7.1$ Hz, 12H, 4 × CH_3), 3.78 (q, $J = 6.4$ Hz, 8H, 4 × CH_2), 6.95 (brs, 2H, 2 × Ar-H), 7.36 (brs, 2H, 2 × Ar-H), 7.75 (brs, 2H, 2 × Ar-H); ^{13}C NMR (101 MHz, CD_3OD) δ_{ppm} : 13.3 (4 × CH_3), 47.9 (4 × CH_2), 97.6 (2 × Ar CH), 118.7 (2 × Ar CH), 135.6 (2 × Ar C), 135.6 (2 × Ar CH), 151.0 (2 × Ar C), 157.9 (2 × Ar C); IR(neat) ν (relative intensity) = 2971 (w), 2933 (w), 2874 (w), 1591 (s), 1499 (m), 1400 (s), 1144 (s) cm^{-1} ; MS (LC-ESI): m/z : 324 $[\text{M}-\text{NO}_3]^+$.

3,7-Bis(dimethylamino)phenoxazin-5-ium Chloride (3f). Green powder; yield 72%; decomposed at 184 °C; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 3.57 (s, 12H, 4 × CH_3), 7.12 (brs, 2H, 2 × Ar-H), 7.24-7.27 (m,

2H, 2 × Ar-H), 7.77 (brs, 2H, 2 × Ar-H); ^{13}C NMR (101 MHz, CD_3OD) δ_{ppm} : 42.0 (4 × CH_3), 97.7 (2 × Ar CH), 118.8 (2 × Ar CH), 135.3 (2 × Ar C), 135.6 (2 × Ar CH), 150.5 (2 × Ar C), 159.4 (2 × Ar C); IR(neat) ν (relative intensity) = 2936 (w), 1599 (s), 1489 (m), 1395 (s), 1151 (s) cm^{-1} ; MS (LC-ESI): m/z : 268 $[\text{M}-\text{Cl}]^+$.

3,7-Bis(dipropylamino)phenoxazin-5-ium Chloride (3g). Green powder; yield 80%; mp 165-167 °C; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 1.07 (t, $J = 7.6$ Hz, 12H, 4 × CH_3), 1.76-1.85 (m, 8H, 4 × CH_2), 3.68 (brs, 8H, 4 × CH_2N), 7.12-7.19 (m, 4H, 4 × Ar-H), 7.72 (dd, 2H, 2 × Ar-H); ^{13}C NMR (101 MHz, CD_3OD) δ_{ppm} : 11.6 (4 × CH_3), 22.3 (4 × CH_2), 55.2 (4 × CH_2), 97.8 (2 × Ar CH), 118.9 (2 × Ar CH), 135.6 (2 × Ar C), 135.7 (2 × Ar CH), 150.9 (2 × Ar C), 158.3 (2 × Ar C); IR(neat) ν (relative intensity) = 2960 (w), 2932 (w), 2872 (w), 1589 (s), 1495 (m), 1397 (s), 1148 (s) cm^{-1} ; MS (LC-ESI): m/z : 380 $[\text{M}-\text{Cl}]^+$.

3,7-Bis(dibutylamino)phenoxazin-5-ium Chloride (3h). Green powder; yield 80%; mp 153-155 °C; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 1.01 (t, $J = 7.3$ Hz, 12H, 4 × CH_3), 1.44-1.53 (m, 8H, 4 × CH_2), 1.70-1.78 (m, 8H, 4 × CH_2), 1.44-1.53 (m, 8H, 4 × CH_2), 3.71 (brs, 8H, 4 × CH_2N), 7.08 (d, $J = 2.4$ Hz, 2H, 2 × Ar-H), 7.17 (dd, $J = 9.6, 2.7$ Hz, 2H, 2 × Ar-H), 7.73 (d, $J = 9.6$ Hz, 2H, 2 × Ar-H); ^{13}C NMR (101 MHz, CD_3OD) δ_{ppm} : 14.4 (4 × CH_3), 21.3 (8 × CH_2), 53.5 (4 × CH_2), 97.8 (2 × Ar CH), 118.9 (2 × Ar CH), 135.6 (2 × Ar C), 135.8 (2 × Ar CH), 150.9 (2 × Ar C), 158.2 (2 × Ar C); IR(neat) ν (relative intensity) = 2954 (w), 2929 (w), 2869 (w), 1591 (s), 1496 (m), 1400 (s), 1147 (s) cm^{-1} ; MS (LC-ESI): m/z : 436 $[\text{M}-\text{Cl}]^+$.

3,7-Di(pyrrolidin-1-yl)phenoxazin-5-ium Chloride (3i). Green powder; yield 78%; decomposed at 168 °C; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 2.22 (brs, 8H, 2 × $(\text{CH}_2)_2$), 3.79, 3.85 (brs, 8H, 2 × $(\text{CH}_2)_2\text{N}$), 7.00 (brs, 2H, 2 × Ar-H), 7.37 (dd, $J = 9.4, 2.5$ Hz, 2H, 2 × Ar-H), 7.73 (d, $J = 9.2$ Hz, 2H, 2 × Ar-H); ^{13}C NMR (101 MHz, CD_3OD) δ_{ppm} : 26.5 (2 × CH_2), 26.7 (2 × CH_2), 51.2 (2 × CH_2), 51.5 (2 × CH_2), 98.4 (2 × Ar CH), 119.8 (2 × Ar CH), 135.6 (2 × Ar C), 135.6 (2 × Ar CH), 150.6 (2 × Ar C), 156.8 (2 × Ar C); IR(neat) ν (relative intensity) = 2970 (w), 2868 (w), 1601 (s), 1485 (m), 1396 (s), 1151 (s) cm^{-1} ; MS (LC-ESI): m/z : 320 $[\text{M}-\text{Cl}]^+$.

3-Diethylamino-7-(pyrrolidin-1-yl)phenoxazin-5-ium Chloride (3j). Green powder; yield 18%; decomposed at 164 °C; ^1H NMR (400 MHz, CD_3OD) δ_{ppm} : 1.36 (t, $J = 7.3$ Hz, 6H, 2 × CH_3), 2.18 (q, $J = 6.8$ Hz, 4H, 2 × CH_2), 3.74-3.80 (m, 8H, 4 × CH_2), 6.81 (d, $J = 2.7$ Hz, 1H, Ar-H), 6.95 (d, $J = 2.7$ Hz, 1H, Ar-H), 7.26 (dd, $J = 9.6, 2.3$ Hz, 1H, Ar-H), 7.37 (dd, $J = 9.6, 2.7$ Hz, 1H, Ar-H), 7.76 (d, $J = 5.0$ Hz, 1H, Ar-H), 7.79 (d, $J = 5.0$ Hz, 1H, Ar-H); ^{13}C NMR (101 MHz, CD_3OD) δ_{ppm} : 13.2 (4 × CH_3), 26.2 (CH_2), 26.5 (CH_2), 47.8 (2 × CH_2), 51.1 (CH_2), 51.3 (CH_2), 97.5 (Ar CH), 98.2 (Ar CH), 118.5 (Ar CH), 119.9 (Ar CH), 135.3 (Ar C), 135.6 (Ar CH), 135.7 (Ar CH), 136.2 (Ar C), 150.8 (Ar C), 151.0 (Ar C), 156.9

(Ar C), 157.8 (Ar C); IR(neat) ν (relative intensity) = 2974 (w), 2930 (w), 2870 (w), 1593 (s), 1498 (m), 1396 (s), 1143 (s) cm^{-1} ; MS (LC-ESI): m/z : 322 $[\text{M}-\text{Cl}]^+$.

Preparation of 3,7-Bis(diethylamino)phenothiazin-5-ium Iodide (8).

Phenothiazine (1 mmol) was stirred at 5 °C in CHCl_3 (20 mL). A solution of iodine (3.2 mmol) in CHCl_3 (30 mL) was added dropwise to the phenothiazine. The reaction was stirred for an additional 30 min, and the resulting precipitate was filtered, washed with CHCl_3 (3×20 mL) and dried to quantitatively give a tetraiodide hydrate. The tetraiodide hydrate salt (1 mmol) was dissolved at room temperature in MeOH (20 mL). A solution of the diethylamine (4 mmol) in MeOH (5 mL) was added to the tetraiodide hydrate solution, and stirring was continued for 3 h. When the reaction was judged to have proceeded to completion by TLC, the MeOH was removed under vacuum and the residue dissolved in CH_2Cl_2 (15 mL). The solution was transferred to a separating funnel and washed with dilute hydrochloric acid (3×15 mL) and dilute sodium hydroxide (15 mL). The organic phase was collected and evaporated off using a rotary evaporator, and then purified by column chromatography with silica gel, eluting by $\text{CHCl}_3/\text{MeOH}$. The resulted phenothiazinium iodide was dissolved in CH_2Cl_2 and then precipitated by adding an excess of Et_2O . The final products were filtered and washed with Et_2O . **8**: dark blue powder; yield 20%; decomposed at 147 °C; IR(neat) ν (relative intensity) = 2970 (w), 2928 (w), 2865 (w), 1594 (s), 1576 (s), 1482 (m), 1407 (s), 1128 (s) cm^{-1} ; MS (LC-ESI): m/z : 340 $[\text{M}-\text{I}]^+$.

Preparation of 10*H*-Phenoselenazine (5).

To a suspension of selenium monochloride (1.6 mmol) in toluene (10 mL) was added, over 1 h, a solution of diphenylamine (3.3 mmol) in toluene (15 mL). Once the addition was complete, the reaction was refluxed for 5 h. After this time, the reaction mixture was purified by column chromatography with silica gel, eluting by AcOEt/Hexane. **5**: pale yellow solid; yield 12%; mp 158-161 °C; ^1H NMR (400 MHz, CDCl_3) δ_{ppm} : 6.97-7.14 (m, 8H, $8 \times \text{Ar-H}$); MS (LC-ESI): m/z : 248 $[\text{M}+\text{H}]^+$.

Preparation of 3,7-Bis(diethylamino)phenoselenazin-5-ium Iodide (9).

To a solution of phenoselenazine (0.5 mmol) in CHCl_3 (10 mL) cooled to <5 °C was added, over 90 min, a solution of iodine (3 mmol) in CHCl_3 (30 mL). Following the addition, the reaction was stirred for a further 30 min before filtration. 3,7-Diiodo-phenoselenazinium iodide hydrate was collected to quantitatively, washed with copious volumes of CHCl_3 and dried. Next, to a solution of the 3,7-diiodophenoselenazinium iodide hydrate (0.5 mmol) in MeOH (30 mL) was added triethylamine (10 mL) followed by diethylamine (2 mmol). The reaction was stirred for 48 h. The residue remaining after removal of the methanol was taken up in CH_2Cl_2 and washed with dilute hydriodic acid (5% w/w) followed by water. The organic phase was isolated and dried (MgSO_4). Column chromatography with silica gel, eluting by $\text{CHCl}_3/\text{MeOH}$ was performed on the crude material. After isolation of the desired fractions and removal of MeOH, the product was dissolved in CH_2Cl_2 (1 mL). Addition of an excess of

Et₂O resulted in precipitation of the product. The product was collected by filtration, washed with Et₂O and dried to give **9**. **9**: dark blue powder; yield 17%; decomposed at 145 °C; IR(neat) ν (relative intensity) = 2967 (w), 2928 (w), 2865 (w), 1592 (s), 1574 (s), 1479 (m), 1407 (s), 1133 (s) cm⁻¹; MS (LC-ESI): m/z : 562 [M+H+HCO₂H]⁺.

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