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FUNCTIONALIZATION OF PHENOTHIAZINE DERIVATIVES BY AMMONIUM BRIDGE

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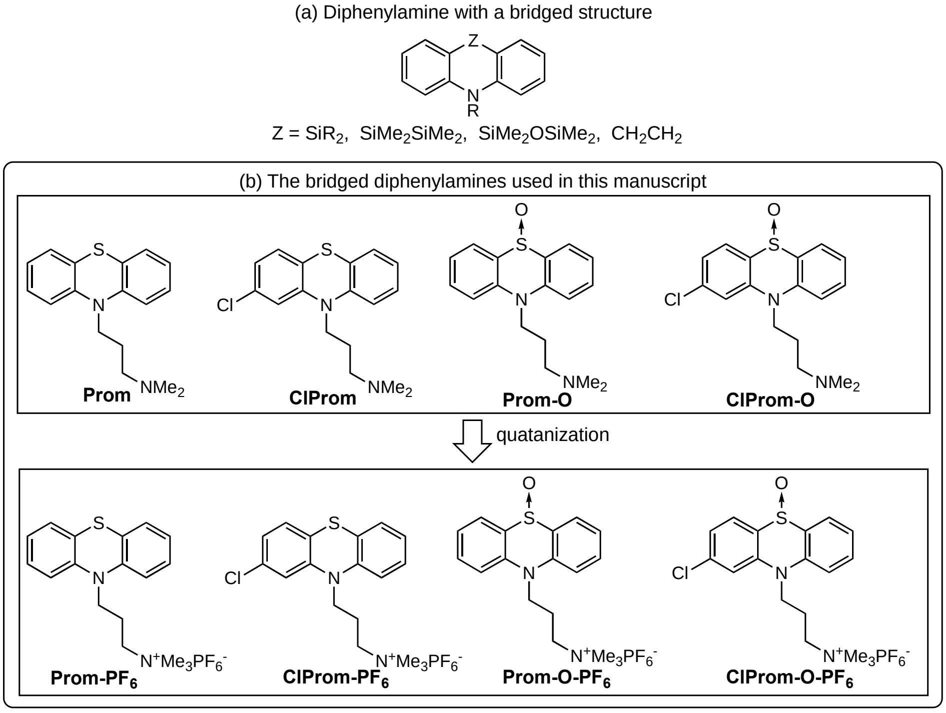
Abstract - Ammonium-bridged bis(promazine) type compounds (**BA-PF$_6$**: $[\mathrm{Y\text{-}N^{+}Me_2\text{-}CH_2\text{-}R\text{-}CH_2\text{-}N^{+}Me_2\text{-}Y}]^{2+}[\mathrm{PF_6}^{-}]_2$, Y = 3-(phenothiazin-10-yl)propyl, 3-(5-oxophenothiazin-10-yl)propyl, 3-(2-chlorophenothiazin-10-yl)propyl, and 3-(5-oxo-2-chlorophenothiazin-10-yl)propyl; R = octane-1,8-diyl, 1,4-phenylene, biphenylene-4,4'-diyl, and 2,2'-bipyridine-4,4'-diyl) were prepared and the effects of the central R unit and side Y unit were investigated. The products' optical and electrochemical properties showed the effect of the central and side unit, suggesting that the products had two independent functional groups in one molecule. X-Ray crystallographic analyses indicated that the spatial placement of the compounds was controlled by the central R unit, which behaves as a spacer without changing the properties of the molecules.

INTRODUCTION

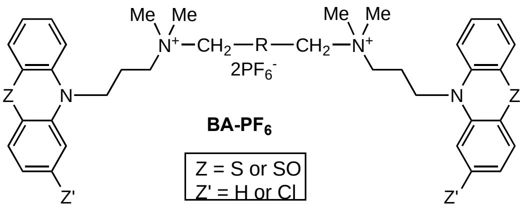
Diphenylamines with a bridged structure are interesting as functional materials and are widely researched. We previously reported the preparation, properties, and applications of monosilane,[1-5] disilane,[1,2] and ethylene[6,7] unit-bridged diphenylamine derivatives (Scheme 1(a)). These compounds are available to introduce various substituents and can be expected to prepare various functional materials.

We focused on promazine (10-[3-(dimethylamino)-1-propyl]phenothiazine **Prom**, Scheme 1(b))[8,9] and chlorpromazine (2-chloro-10-[3-(dimethylamino)-1-propyl]phenothiazine **ClProm**, Scheme 1(b))[9,10] because they are easily available, since they are studied for medical use. We have previously investigated the development of functional materials based on **Prom** and **ClProm** derivatives. In the manuscripts, n-type properties appeared by the formation of *S*-oxide (**Prom-O**, Scheme 1(b)),[11] and phenothiazine dimer was obtained by the coupling reaction of **ClProm** and its *S*-oxide analog (**ClProm-O**, Scheme 1(b)).[12]



Scheme 1

On the other hand, organic ammonium compounds were generally prepared by the reaction of organic halide and amine.[13] Therefore, the development of functional materials seems to be expected by introducing the functional group.[5] We have investigated the ammonium salts (**BA-PF$_6$**, Scheme 2) obtained by the reaction between alkyl monohalide and monoamine[11,12] or diamine.[12] In this study, the properties of the ammonium salts obtained from the reaction between alkylene dihalide and monoamine shown in Scheme 1(b) were investigated. Development of interesting functional materials and further chemical modification is expected by preparation of a dimer with a cross-linked structure.



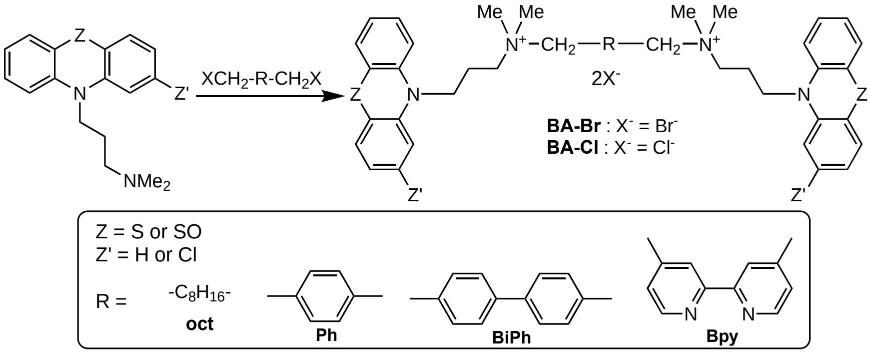
Scheme 2

RESULTS AND DISCUSSION

Functionalization of promazine derivative

Reaction with α,ω-alkylene dihalide and promazine derivatives afforded bis(ammonium) type compounds

(**BA-Br** and **BA-Cl**) as shown in Scheme 3. The ESI-MS spectrum of the product suggested that the target molecule was formed because the signal based on $[M-2X^{-}]^{2+}$ was observed. ^{1}H and ^{13}C NMR spectra also agreed with the structure.



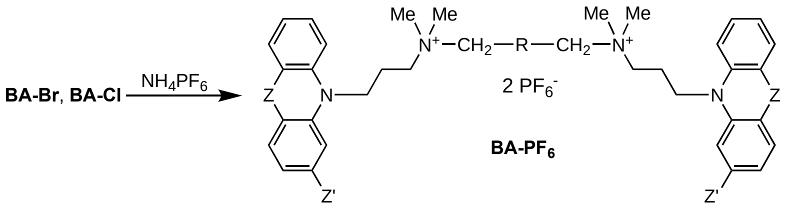
Scheme 3

Table 1. Preparation results of **BA-X**

Product	X	R	Z [a]	Z’ [a]	Yield %
Oct-Prom-Br	Br	**Oct**	S	H	94
Oct-Prom-O-Br	Br	**Oct**	SO	H	57
Oct-ClProm-Br	Br	**Oct**	S	Cl	68
Oct-ClProm-O-Br	Br	**Oct**	SO	Cl	86
Ph-Prom-Br	Br	**Ph**	S	H	94
Ph-Prom-O-Br	Br	**Ph**	SO	H	99
Ph-ClProm-Br	Br	**Ph**	S	Cl	75
Ph-ClProm-O-Br	Br	**Ph**	SO	Cl	>99
BiPh-Prom-Br	Br	**Biph**	S	H	98
BiPh-Prom-O-Br	Br	**Biph**	SO	H	97
BiPh-ClProm-Br	Br	**Biph**	S	Cl	87
BiPh-ClProm-O-Br	Br	**Biph**	SO	Cl	>99
Bpy-Prom-Cl	Cl	**Bpy**	S	H	82
Bpy-Prom-O-Cl	Cl	**Bpy**	SO	H	89
Bpy-ClProm-Cl	Cl	**Bpy**	S	Cl	90
Bpy-ClProm-O-Cl	Cl	**Bpy**	SO	Cl	71

[a] See Scheme 3.

The anions of **BA-Br** and **BA-Cl**, Br^{-} and Cl^{-}, were converted to PF_6^{-} by modified reported method[14] as shown in Scheme 4, because such a halide anion may prevent observing oxidation potential of the phenothiazine unit.[11,15] The results of anion exchange are shown in Table 2. The anion exchange proceeded efficiently.



Scheme 4

Table 2. Preparation results of **BA-PF$_6$**

BA-PF$_6$	Starting material	Z [a]	Z' [a]	R[a]	Yield %
Oct-Prom-PF$_6$	**Oct-Prom-Br**	S	H	**Oct**	91
Oct-Prom-O-PF$_6$	**Oct-Prom-O-Br**	SO	H	**Oct**	97
Oct-ClProm-PF$_6$	**Oct-ClProm-Br**	S	Cl	**Oct**	97
Oct-ClProm-O-PF$_6$	**Oct-ClProm-O-Br**	SO	Cl	**Oct**	99
Ph-Prom-PF$_6$	**Ph-Prom-Br**	S	H	**Ph**	95
Ph-Prom-O-PF$_6$	**Ph-Prom-O-Br**	SO	H	**Ph**	99
Ph-ClProm-PF$_6$	**Ph-ClProm-Br**	S	Cl	**Ph**	93
Ph-ClProm-O-PF$_6$	**Ph-ClProm-O-Br**	SO	Cl	**Ph**	90
BiPh-Prom-PF$_6$	**BiPh-Prom-Br**	S	H	**Biph**	98
BiPh-Prom-O-PF$_6$	**BiPh-Prom-O-Br**	SO	H	**Biph**	93
BiPh-ClProm-PF$_6$	**BiPh-ClProm-Br**	S	Cl	**Biph**	94
BiPh-ClProm-O-PF$_6$	**BiPh-ClProm-O-Br**	SO	Cl	**Biph**	94
Bpy-Prom-PF$_6$	**Bpy-Prom-Cl**	S	H	**Bpy**	92
Bpy-Prom-O-PF$_6$	**Bpy-Prom-O-Cl**	SO	H	**Bpy**	81
Bpy-ClProm-PF$_6$	**Bpy-ClProm-Cl**	S	Cl	**Bpy**	95
Bpy-ClProm-O-PF$_6$	**Bpy-ClProm-O-Cl**	SO	Cl	**Bpy**	87

[a] See Scheme 3.

Figure 1 shows ORTEP drawings of **Oct-Prom-O-PF$_6$**, **Oct-ClProm-O-PF$_6$** and **Bpy-Prom-PF$_6$**. Each molecule is a diammonium, linked by a bridging unit with two **Prom**, **Prom-O** or **ClProm-O** units, consistent with the result obtained from the NMR measurement. **Oct-Prom-O-PF$_6$** and **Oct-ClProm-O-PF$_6$** have a two-fold axis in the center of the bridging octylene unit, and **Bpy-Prom-PF$_6$** has it in the center of its **Bpy** unit. Each molecule has an S-shaped structure, and two phenothiazine units are located in the opposite direction.

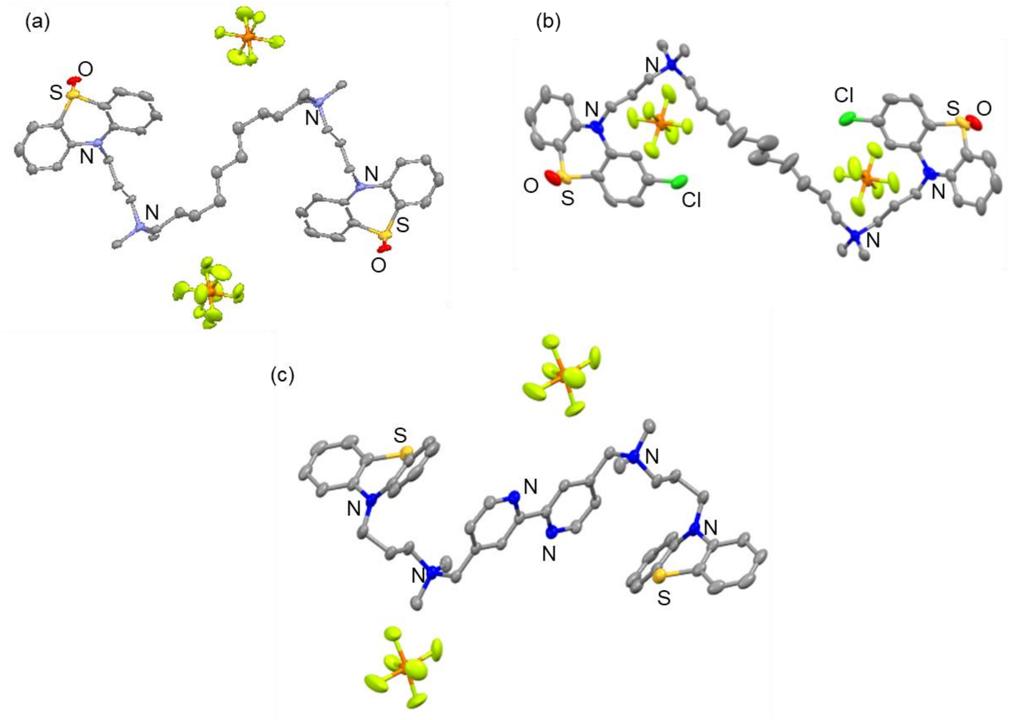


Figure 1. ORTEP drawings of (a) **Oct-Prom-O-PF$_6$**, (b) **Oct-ClProm-O-PF$_6$**, (c) **Bpy-Prom-PF$_6$**. Hydrogen atoms and disordered atoms are omitted for clarity.

The dihedral angle of the central **Bpy** unit of **Bpy-Prom-PF$_6$** is 0°, indicating that the two pyridine rings have a co-planar structure. The **Bpy** unit forms π–π stacking with the phenyl ring in the phenothiazine moiety of the neighboring molecule as shown in Figure 2. The distance of centroid$_{\text{phenyl}}$ (red ring in Figure 2) and C21 in the neighboring molecule is 3.598 Å, and the dihedral angle between the two aromatic rings is 11.5°.

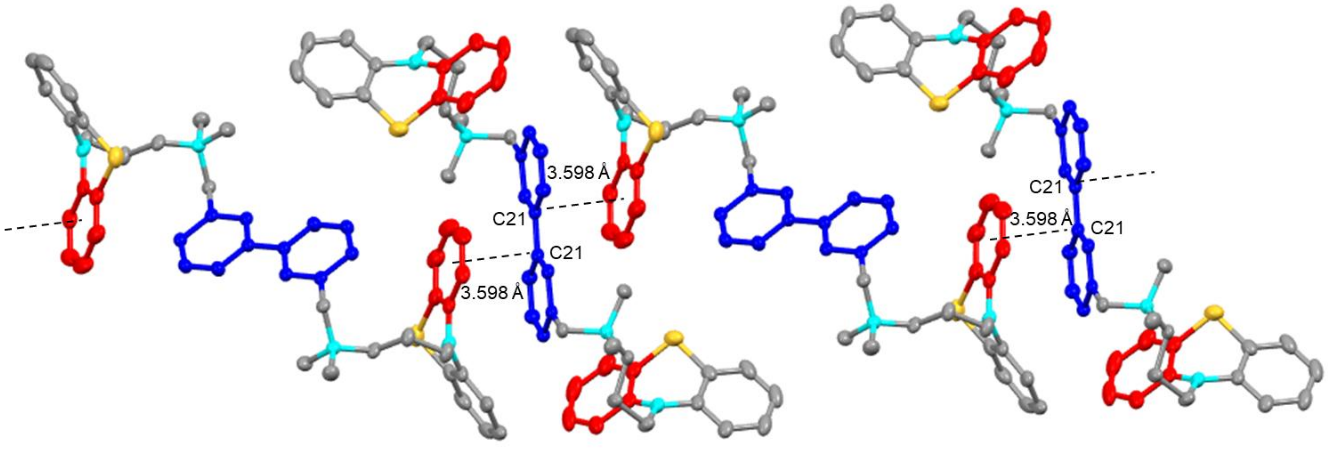


Figure 2. Packing diagram of **Bpy-Prom-PF$_6$**

Optical properties

The absorption spectra of **BA-PF$_6$** are shown in Figure 3, and the data are summarized in Table 3. The absorption λ_{max} of the products were almost the same as the corresponding monophenothiazine derivatives, suggesting that the connecting units of the compounds did not affect their optical properties. Usually, *N*-substituted diphenylamines show absorption λ_{max} corresponding to the π-π* transition at ca. 300 nm: for example, diphenylamine (λ_{max} = 297 - 305 nm)[16] and phenazasiline (λ_{max} = 295 nm).[3] In agreement with the literature, the π-π* transition of monopromazine derivatives is observed at λ_{max} = ca. 305 nm. However, the π-π* transition in monopromazine oxide derivatives is red-shifted by ca. 30 nm due to the narrow π-π* gap resulting from the electron-withdrawing *S*-oxide unit, as previously reported.[11,12,17]

The fluorescence spectra of **BA-PF$_6$** are shown in Figure 4, and the data are summarized in Table 4. As shown in Figure 4, the fluorescence intensity of phenothiazine oxide-type compounds (**###-Prom-O-PF$_6$** and **###-ClProm-O-PF$_6$**) were stronger than those of corresponding phenothiazine type compounds (**###-Prom-PF$_6$** and **###-ClProm-PF$_6$**). We have reported fluorescence intensity of phenothiazine type compounds is much weaker than that of relative phenothiazine oxide.[11,12] Especially, as shown in Figures 4(c) and 4(d), bis(arylene) (**BiPh** and **Bpy**)-phenothiazine (**Prom** and **ClProm**)-type compounds showed significantly weak fluorescence. The introduction of **BiPh** and **Bpy** seems to affect the difference in fluorescence intensity between phenothiazine type compounds and phenothiazine oxide-type compounds.

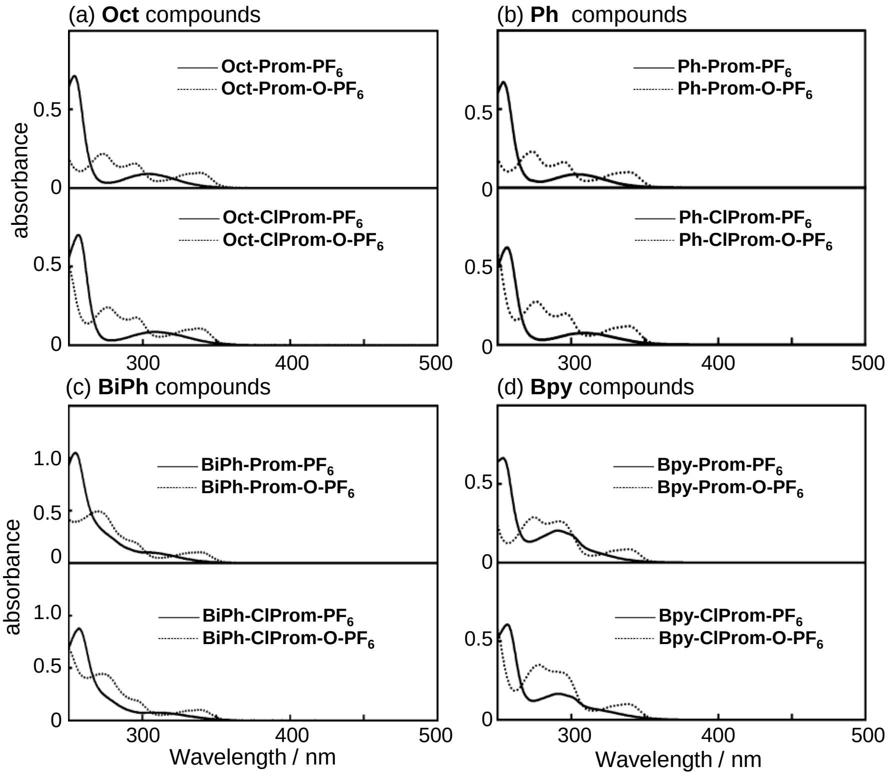
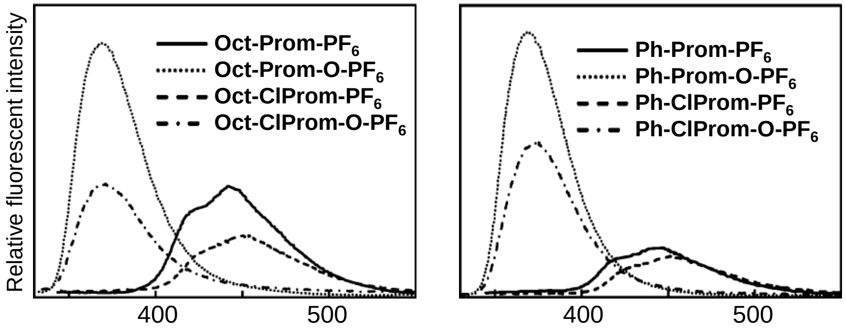


Figure 3. Absorption spectra of (a) **Oct-**, (b) **Ph-**, (c) **BiPh-**, and (d) **Bpy-** containing **BA-PF$_6$** in 10 μM MeCN solution

(a) **Oct** compounds (b) **Ph** compounds



(c) **BiPh** compounds (d) **Bpy** compounds

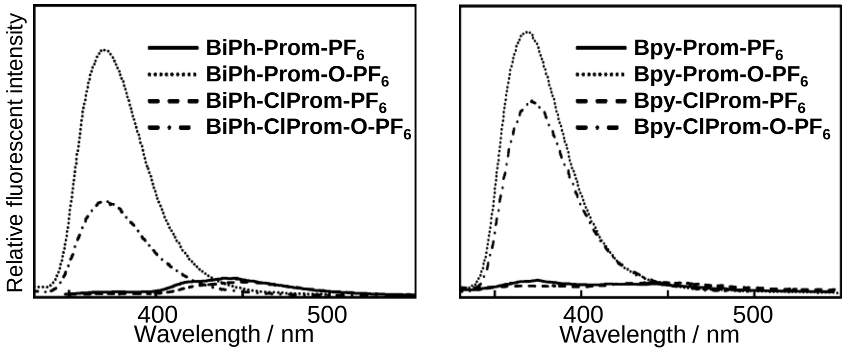


Figure 4. Fluorescent spectra of (a) **Oct-**, (b) **Ph-**, (c) **BiPh-**, and (d) **Bpy-** containing **BA-PF$_6$** in 10 µM MeCN solution

Table 3. Optical data of **BA-PF$_6$**

compound	UV λ_{max}/ nm [a,b]	PL λ_{max}/ nm [a,c]
Oct-Prom-PF$_6$	304 (8.0x10^3), 254 (5.8x10^4)	442
Oct-Prom-O-PF$_6$	339 (1.0x10^4), 294 (1.6x10^4), 274 (2.3x10^4)	371
Oct-ClProm-PF$_6$	308 (8.5x10^3), 258 (7.1x10^4)	450
Oct-ClProm-O-PF$_6$	338 (9.6x10^3), 296 (2.0x10^4), 277 (2.2x10^4)	371
Ph-Prom-PF$_6$	304 (8.4x10^3), 254 (6.7x10^4)	443
Ph-Prom-O-PF$_6$	340 (1.0x10^4), 295 (1.6x10^4), 274 (2.3x10^4)	369
Ph-ClProm-PF$_6$	308 (7.7x10^3), 257 (6.2x10^4)	452
Ph-ClProm-O-PF$_6$	339 (1.2x10^4), 296 (1.6x10^4), 276 (2.8x10^4)	373
BiPh-Prom-PF$_6$	255 (9.9x10^4)	440
BiPh-Prom-O-PF$_6$	339 (1.0x10^4), 270 (4.9x10^4)	370
BiPh-ClProm-PF$_6$	308 (7.6x10^3), 257 (8.3x10^4)	449
BiPh-ClProm-O-PF$_6$	339 (1.0x10^4), 273 (4.4x10^4)	373
Bpy-Prom-PF$_6$	291 (2.1x10^4). 254 (6.7x10^4)	[d]
Bpy-Prom-O-PF$_6$	339 (8.5x10^4), 292 (2.6x10^4), 275 (2.9x10^4)	369
Bpy-ClProm-PF$_6$	291 (1.8x10^4), 256 (6.2x10^4)	[d]
Bpy-ClProm-O-PF$_6$	339 (9.3x10^3), 278 (3.4x10^4)	370
Prom-MePF$_6$ [e]	306 (6.2x10^3), 254 (5.0x10^4)	442
Prom-O-MePF$_6$ [e]	338 (8.7x10^3), 294 (1.4x10^4), 273 (1.9x10^4)	370
ClProm-MePF$_6$ [e]	307 (4.3x10^3), 256 (3.5x10^4)	450
ClProm-O-MePF$_6$ [e]	339 (5.5x10^3), 296 (8.9x10^3), 276 (1.3x10^4)	369

[a] 10 µM MeCN solution. [b] The ε value is shown in the parentheses. [c] Excited at UV λ_{max}.. [d] Very weak. [e] See lit.[12]

Electrochemical behavior

The electrochemical behavior of the products was studied using cyclic voltammetry (CV). The redox responses of the compounds are shown in Figure 5 and Figures S1-3, and the data are summarized in Table 4. The peaks that seem to originate from the phenothiazine unit are indicated by "○" marks, and those from the central unit are indicated by "#" marks.

First, the oxidation or reduction of the terminal phenothiazine unit described as "○" was compared. The **Prom**-containing compounds showed a reversible oxidation process at about $E_{1/2}$ = +0.35 V (vs. Fc$^+$/Fc). The $E_{1/2}$ values are similar to those of previously reported **Prom-Me-PF$_6$** ($E_{1/2}$ = +0.33 V *vs.* (Fc$^+$/Fc)), as shown in Table 4.[12] The other type compounds also showed oxidation and/or reduction peaks at the same potentials, as reported phenothiazine type compounds (**Prom-O** (*ca.* 1.1 and -2.8 V), **ClProm** (*ca.* 0.5 and -2.9 V), and **ClProm-O** (*ca.* -2.4 and -2.9 V)), respectively.[12] Reversibility of CV based on phenothiazine unit ("○" in the figure) was same as that of monomeric phenothiazine derivatives[12] (**Prom-PF$_6$**, **Prom-O-PF$_6$**, **ClProm-PF$_6$**, and **ClProm-O-PF$_6$** in Table 4).

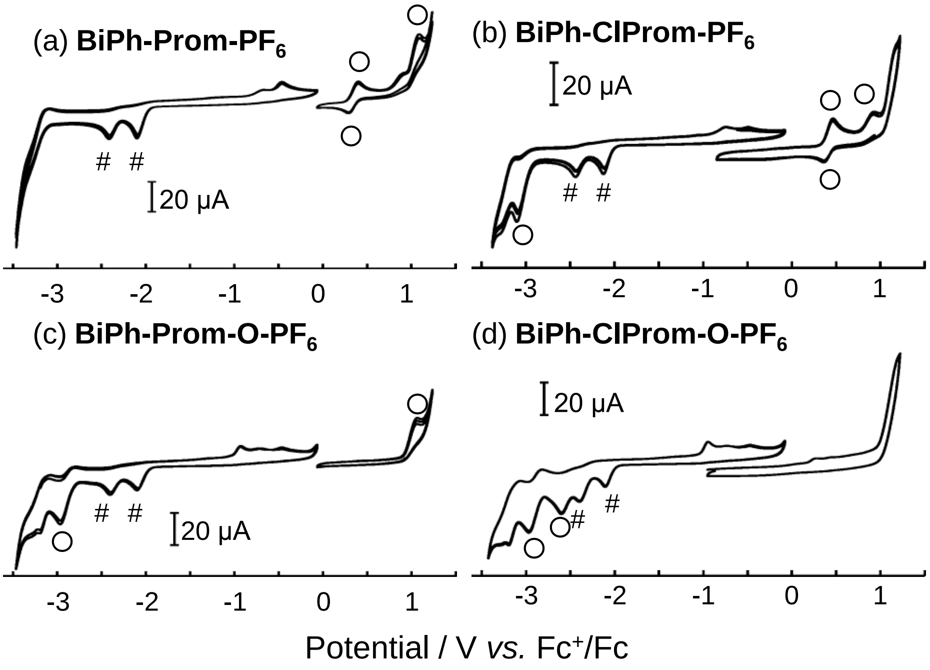


Figure 5. CV of **BiPh**-containing **BA-PF$_6$**. DMF was used as the solvent.

Table 4. Electrochemical data of **BA-PF$_6$**

compound	Oxidation potential [a]		Reduction potential [a]	
	E_{pa}	E_{pc}	E_{pc}	E_{pa}
Oct-Prom-PF$_6$	0.41	0.28	-3.36	[b]
Oct-Prom-O-PF$_6$	[b]	[b]	-2.83 -3.32	[b] [b]
Oct-ClProm-PF$_6$	0.49 0.60	0.36 [b]	-2.97	[b]

compound	Oxidation potential [a]		Reduction potential [a]	
	E_{pa}	E_{pc}	E_{pc}	E_{pa}
Oct-ClProm-O-PF$_6$	[e]	[e]	-2.36	[b]
			-2.85	[b]
Ph-Prom-PF$_6$	0.40	0.28		
	0.88	[b]	2.41	[b]
	1.09	[b]		
Ph-Prom-O-PF$_6$	1.12	[b]	-2.45	[b]
			-2.99	[b]
Ph-ClProm-PF$_6$	0.48	0.37	-2.47	[b]
	0.94	[b]	-3.12	[b]
Ph-ClProm-O-PF$_6$	[e]	[e]	-2.40	[b]
			-2.66	[b]
			-2.97	-2.81
BiPh-Prom-PF$_6$	0.40	0.29	-2.10	[b]
	1.09	[b]	-2.41	[b]
BiPh-Prom-O-PF$_6$	1.07	[b]	-2.11	[d]
			-2.41	[d]
			-2.97	[d]
BiPh-ClProm-PF$_6$	0.48	0.37	-2.12	[b]
	0.94	[b]	-2.44	[b]
			-3.10	[b]
BiPh-ClProm-O-PF$_6$	[c]	[c]	-2.11	[b]
			-2.41	[b]
			-2.61	[b]
			-2.97	-2.82
Bpy-Prom-PF$_6$	0.40	0.28	-1.97	[b]
	1.08	[b]	-2.14	[b]
			-2.75	-2.63
Bpy-Prom-O-PF$_6$	1.09	[b]	-1.98	[b]
			-2.13	[b]
			-2.75	-2.63
			-2.99	-2.82
Bpy-ClProm-PF$_6$	0.49	0.35	-1,98	[b]
			-2.15	[b]
			-2.74	-2.61
			-3.17	[b]
Bpy-ClProm-O-PF$_6$	[c]	[c]	-2.13	[b]
			-2.60	[b]
			-2.75	[b]
			-2.99	[b]
Prom-MePF$_6$ [d]	0.38	0.27	[c]	[c]
	0.89	[b]		
	1.04	[b]		
Prom-O-MePF$_6$ [d]	1.03	[b]	-2.82	[b]
ClProm-MePF$_6$ [d]	0.46	[b]	-2.85	[b]
ClProm-O-MePF$_6$ [d]	[c]	[c]	-2.36	[b]
			-2.86	[b]

[a] *vs* Fc$^+$/Fc. [b] Irreversible. [c] Not observed. [d] See lit.[12]

The redox potentials of the central unit of each compound were also compared. The reduction peak, which is considered to be based on the **BiPh** unit, was observed at *ca.* E_{pc} = -2.1 and -2.4 V (*vs.* Fc^+/Fc) shown in Figure 5. As shown in Table 3 and Figures S1-3, reduction peaks which seem to be based on **Ph** (about -2.4 V, Figure S2) and **Bpy** (*ca.*-2.0, -2.1, and -2.75 V, Figure S3) were observed, respectively. On the other hand, **Oct**-containing compounds did not show peaks based on the central unit (Figure S1). The potentials based on both ○ and # were independent of the content of the compounds. This agreed with the result of the optical properties.

CONCLUSION

Bis(ammonium) compounds prepared from a reaction between alkylene dihalide and diamine had functionality. The obtained compounds had properties originated from both the side and central groups. Further functionalization of promazine will be expected by chemical modification.

EXPERIMENTAL

Materials

Promazine oxide (**Prom-O**)[11] and chlorpromazine oxide (**ClProm-O**)[12] were prepared by the reported procedure. Promazine (**Prom**) and chlorpromazine (**ClProm**) were prepared by neutralizing the corresponding hydrochlorides (**Prom-HCl** and **ClProm-HCl**), respectively. 1,10-Dibromodecane ($BrCH_2$-**Oct**-CH_2Br), 1,4-bis(bromomethyl)benzene, ($BrCH_2$-**Ph**-CH_2Br), 4,4'-bis(bromomethyl)biphenyl ($BrCH_2$-**BiPh**-CH_2Br), and 4,4’-bis(chloromethyl)-2,2’-bipyridine ($ClCH_2$-**Bpy**-CH_2Cl) were used as purchased. Other chemicals were also used as purchased.

Instruments

NMR spectra were taken by using a Bruker AVANCEIII400HD spectrometer. Absorption spectra were measured by using a JASCO V-570 spectrometer. Fluorescence spectra were measured by using a Hitachi 4010 spectrometer. Fluorescence spectra were excited at the absorption λ_{max} light. ESI-MS was measured by the LC-MS system: Shimadzu Nexera X3 was used for LC and Shimadzu LCMS-8045 was used for MS.

Cyclic voltammetry (CV) was measured as follows. A conventional three-electrode configuration was used, with a glassy carbon electrode (BAS PFCE 3 carbon electrode), a platinum wire auxiliary electrode (Tokuriki, special order), and 0.1 M $AgNO_3/Ag$ reference (BAS RE-5). Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1}. The sample concentration was 1 mM in DMF containing 0.1 M n-Bu_4NPF_6 as the supporting electrolyte.

Crystal Structure Determination

Crystals for X-ray analyses were obtained from an acetone-Et_2O mixed solvent. Data collection was performed at –160 °C on a Rigaku XtaLaB Synergy-DW dual wavelength X-ray diffractometer with an HPC X-ray detector. The structures were solved by using the OLEX2 software package.[18] Refinements were performed anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Deposition Numbers 2257042 (for **Oct-Prom-O-PF$_6$**), 2257043 (for **Oct-ClProm-O-PF$_6$**), and 2257044 (for **Bpy-Prom-PF$_6$**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Preparation

*Preparation of 1,10-bis(3-(10H-phenothiazin-10-yl)propane)dimethylammoniodecane dibromide (**Oct-Prom-Br**)*

BrCH$_2$-**Oct**-CH$_2$Br (0.22 g, 0.73 mmol) was added to an acetonitrile solution (10 mL) of **Prom** (0.50 g, 1.76 mmol), and stirred for 24 h at 70 °C. Then, the acetonitrile was evaporated and the residue was dissolved to CHCl$_3$ to reprecipitate from hexane. The precipitate was separated by filtration, and dried in vacuo to afford **Oct-Prom-Br** (0.61g, 0.70 mmol) as a pale red powder in 94% yield.

^{1}H NMR (CD$_3$OD, 400 MHz) δ 7.15-7.4 (m, 8H), 6.9-7.15 (m, 8H), 4.11 (t, 4H), 3.4-3.5 (m, 4H), 3.1-3.2 (m, 4H) 2.98 (s, 12H), 2.1-2.3 (m, 4H), 1,4-1,6 (m, 4H), 1.0-1.4 (m, 12H). ESI-MS: *m/z* 354 $[M-2Br^-]^{2+}$.

*Preparation of 1,10-bis(3-(5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniodecane dibromide (**Oct-Prom-O-Br**)*

BrCH$_2$-**Oct**-CH$_2$Br (0.16 g, 0.53 mmol) was added to MeCN solution (10 mL) of **Prom-O** (0.38 g, 1.26 mmol), and stirred for 24 h at 70 °C. Then, the precipitate was separated by filtration and the powder was washed with hexane. After filtration, the powder was dried in vacuo to afford **Oct-Prom-O-Br** (0.28 g, 0.31 mmol) as a colorless powder in 57% yield. ^{1}H NMR (CD$_3$OD, 400 MHz) δ 7.99 (d, 4H), 7.7-7.85 (m, 8H), 7.3-7.4 (m, 4H), 4.66 (t, 4H), 3.2-3.4 (m, 4H), 3.0-3.2 (m, 4H), 2.89 (s, 12H), 2.2-2.4 (m, 4H), 1.4-1.6 (m, 4H), 1.0-1.3 (m, 12H). ESI-MS: *m/z* 370 $[M-2Br^-]^{2+}$ ($z = 2$).

*Preparation of 1,10-bis(3-(2-chloro-10H-phenothiazin-10-yl)propane)dimethylammoniodecane dibromide (**Oct-ClProm-Br**)*

The reaction of BrCH$_2$-**Oct**-CH$_2$Br (0.19 g, 0.62 mmol) and **ClProm** (0.48 g, 1.51 mmol) by the same preparation method as **Oct-Prom-O-Br** afforded **Oct-ClProm-Br** (0.40 g, 0.42 mmol) as a colorless powder in 68% yield. ^{1}H NMR (CD$_3$OD, 400 MHz) δ 6.9-7.4 (m, 14H), 4.11 (t, 4H), 3.4-3.5 (m, 4H), 3.15-3.25 (m, 4H), 3.01 (s, 12H), 2.1-2.3 (m, 4H), 1.4-1.6 (m, 4H), 1.1-1.3 (m, 12H). ESI-MS: *m/z* 388 [M-2Br$^-$]$^{2+}$ (*z* = 2).

*Preparation of 1,10-bis(3-(2-chloro-5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniodecane dibromide (**Oct-ClProm-O-Br**)*

The reaction of BrCH$_2$-**Oct**-CH$_2$Br (0.30 g, 1.0 mmol) and **ClProm-O** (0.75 g, 2.4 mmol) by the same preparation method as **Oct-Prom-O-Br** afforded **Oct-ClProm-O-Br** (0.84 g, 0.86 mmol) as a colorless powder in 86% yield. ^{1}H NMR (CD$_3$OD, 400 MHz) *δ* 7.9-8.1 (m, 4H), 7.7-7.9 (m, 6H), 7.3-7.5 (m, 4H), 4.55-4.8 (br, 4H), 3.2-3.4 (m, 4H), 3.0-3.2 (m, 4H), 2.89 (s, 12H), 2.2-2.4 (m, 4H), 1.4-1.5 (m, 4H), 1,1-1.3 (m, 12H). ESI-MS: *m/z* 405 [M-2Br$^-$]$^{2+}$ (*z* = 2).

*Preparation of 1,4-bis(3-(10H-phenothiazin-10-yl)propane)dimethylammoniomethylbenzene dibromide (**Ph-Prom-Br**)*

The reaction of BrCH$_2$-**Ph**-CH$_2$Br (0.11 g, 0.43 mmol) and **Prom** (0.27 g, 0.95 mmol) by the same preparation method as **Oct-Prom-O-Br** afforded **Ph-Prom-Br** (0.34 g, 0.41 mmol) as a colorless powder in 94% yield. ^{1}H NMR (CDCl$_3$, 400 MHz) *δ* 7.51 (s, 4H), 7.2-7.3 (m, 4H), 7.05-7.15 (m, 4H), 6.9-7.0 (m, 8H), 5.14 (s, 4H), 4.09 (t, 4H), 3.5-3.6 (m, 4H), 2.99 (s, 12H), 2.4-2.6 (m, 4H). ESI-MS: *m/z* 336 [M-2Br$^-$]$^{2+}$ (*z* = 2).

*Preparation of 1,4-bis(3-(5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniomethylbenzene dibromide (**Ph-Prom-O-Br**)*

The reaction of BrCH$_2$-**Ph**-CH$_2$Br (0.14 g, 0.51 mmol) and **Prom-O** (0.34 g, 1.13 mmol) by the same preparation method as **Oct-Prom-O-Br** afforded **Ph-Prom-O-Br** (0.44 g, 0.51 mmol) as a colorless powder in 99% yield. ^{1}H NMR (CD$_3$OD, 400 MHz) *δ* 8.00 (d, 4H), 7.7-7.85 (m, 8H), 7.3-7.4 (m, 4H), 7.28 (s, 4H), 4.71 (t, 4H), 4.33 (s, 4H), 3.3-3.4 (m, 4H), 2.88 (s, 12H), 2.3-2.5 (m, 4H). ESI-MS: *m/z* 352 [M-2Br$^-$]$^{2+}$ (*z* = 2).

*Preparation of 1,4-bis(3-(2-chloro-10H-phenothiazin-10-yl)propane)dimethylammoniomethylbenzene dibromide (**Ph-ClProm-Br**)*

The reaction of BrCH$_2$-**Ph**-CH$_2$Br (0.076 g, 0.29 mmol) and **ClProm** (0.21 g, 0.64 mmol) by the same reaction as **Oct-Prom-Br** afforded **Ph-ClProm-Br** (0.20 g, 0.22 mmol) as a colorless powder in 75% yield. ^{1}H NMR (CD$_3$OD, 400 MHz) *δ* 7.42 (s, 4H), 7.2-7.4 (m, 2H), 7.1-7.2 (m, 8H), 6.9-7.1 (m, 4H), 4.54 (s, 4H), 4.14 (t, 4H), 3.4-3.5 (m, 4H), 3.01 (s, 12H), 2.2-2.4 (m, 4H). ESI-MS: *m/z* 370 [M-2Br$^-$]$^{2+}$ (*z* = 2).

*Preparation of 1,4-bis(3-(2-chloro-5-oxo-10H-phenothiazin-10-yl)propane)-dimethylammoniomethylbenzene dibromide (**Ph-ClProm-O-Br**)*

The reaction of BrCH$_2$-**Ph**-CH$_2$Br (0.13 g, 0.50 mmol) and **ClProm-O** (0.37 g, 1.10 mmol) by the same preparation method as **Oct-Prom-O-Br** afforded **Ph-ClProm-O-Br** (0.48 g, 0.51 mmol) as a colorless powder in quantum yield. ^{1}H NMR (CD_3OD, 400 MHz) δ 7.9-8.1 (m, 4H), 7.7-7.9 (m, 6H), 7.3-7.5 (m, 4H), 7.32 (s, 4H), 4.6-4.8 (m, 4H), 4.41 (s, 4H), 3.39 (t, 4H), 2.94 (s, 12H), 2.3-2.5 (m, 4H). ESI-MS: *m/z* 352 $[M\text{-}2Br^-]^{2+}$ (*z* = 2).

*Preparation of 4,4'-bis(3-(10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-1,1'-biphenyl dibromide (**BiPh-Prom-Br**)*

The reaction of $BrCH_2$-**BiPh**-CH_2Br (0.17 g, 0.50 mmol) and **Prom** (0.32 g, 1.13 mmol) by the same preparation method as **Oct-Prom-O-Br** afforded **BiPh-Prom-Br** (0.44 g, 0.49 mmol) as a colorless powder in 98% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, 4H), 7.15-7.3 (m, 4H), 7.0-7.1 (m, 8H), 6.9-7.0 (m, 8H), 5.24 (s, 4H), 4.12 (t, 4H), 3.5-3.65 (m, 4H), 3.06 (s, 12H), 2.3-2.5 (m, 4H). ESI-MS: *m/z* 374 $[M\text{-}2Br^-]^{2+}$ (*z* = 2).

*Preparation of 4,4'-bis(3-(5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-1,1'-biphenyl dibromide (**BiPh-Prom-O-Br**)*

The reaction of $BrCH_2$-**BiPh**-CH_2Br (0.17 g, 0.50 mmol) and **Prom-O** (0.34 g, 1.13 mmol) by the same preparation method as **Oct-Prom-O-Br** afforded **BiPh-Prom-O-Br** (0.42 g, 0.44 mmol) as a colorless powder in 89% yield. ^{1}H NMR (CD_3OD, 400 MHz) δ 8.01 (d, 4H), 7.7-7.9 (m, 8H), 7.6-7.7 (m, 4H), 7.3-7.5 (m, 8H), 4.69 (t, 4H), 4.40 (s, 4H), 3.3-3.5 (m, 4H), 2.88 (s, 12H), 2.3-2.5 (m, 4H). ESI-MS: *m/z* 390 $[M\text{-}2Br^-]^{2+}$ (*z* = 2).

*Preparation of 4,4'-bis(3-(2-chloro-10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-1,1'-biphenyl dibromide (**BiPh-ClProm-Br**)*

The reaction of $BrCH_2$-**BiPh**-CH_2Br (0.21 g, 0.62 mmol) and **ClProm** (0.46 g, 1.44 mmol) by the same preparation method as **Oct-Prom-O-Br** afforded **BiPh-ClProm-Br** (0.52 g, 0.53 mol) as a colorless powder in 87% yield. ^{1}H NMR (CD_3OD, 400 MHz) δ 7.69 (d, 4H), 7.51 (d, 4H), 7.2-7.3 (m, 2H), 6.9-7.2 (m, 12H), 4,56 (s, 4H), 4,15 (t, 2H), 3.4-3.5 (m, 4H), 3.02 (s, 12H), 2.3-2.4 (m, 4H). ESI-MS: *m/z* 409 $[M\text{-}2Br^-]^{2+}$ (*z* = 2).

*Preparation of 4,4'-bis(3-(2-chloro-5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-1,1'-biphenyl dibromide (**BiPh-ClProm-O-Br**)*

The reaction of $BrCH_2$-**BiPh**-CH_2Br (0.34 g, 1.00 mmol) and **ClProm-O** (0.75 g, 2.35 mmol) by the same preparation method as **Oct-Prom-Br** afforded **BiPh-ClProm-O-Br** (1.06 g, 1.05 mmol) as a colorless powder in quantum yield. ^{1}H NMR (CD_3OD, 400 MHz) δ 7.9-8.1 (m, 4H), 7.7-7.9 (m, 6H), 7.69 (d, 4H), 7.3-7.5 (m, 8H), 4.4-4.6 (m, 4H), 4.40 (s, 4H), 3.2-3.5 (m, 4H), 2.90 (s, 12H), 2.3-2.5 (m, 4H). ESI-MS: *m/z* 424 $[M\text{-}2Br^-]^{2+}$ (*z* = 2).

*Preparation of 4,4'-bis(3-(10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-2,2'-bipyridine dichloride (**Bpy-Prom-Cl**)*

The reaction of $\mathrm{ClCH_2}$-**Bpy**-$\mathrm{CH_2Cl}$ (0.11 g, 0.43 mmol) and **Prom** (0.27 g, 0.95 mmol) by the same preparation method as **Oct-Prom-O-Br** afforded **Bpy-Prom-Cl** (0.29 g, 0.35 mmol) as a colorless powder in 82% yield.

^{1}H NMR ($\mathrm{CD_3OD}$) δ 8.64 (d, 2H), 8.51 (s, 2H), 7.4-7.5 (m, 2H), 7.1-7.25 (m, 4H), 6.95-7.1 (m, 8H), 6.89 (t, 4H), 4.66 (s, 4H), 4.13 (t, 4H), 3.4-3.6 (m, 4H), 3.04 (s, 12H), 2.2-2.4 (m, 4H). ESI-MS: *m/z* 375 $[\mathrm{M\text{-}2\ PF_6^-}]^{2+}$ ($z = 2$).

*Preparation of 4,4'-bis(3-(5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-2,2'-bipyridine dichloride (**Bpy-Prom-O-Cl**)*

The reaction of $\mathrm{ClCH_2}$-**Bpy**-$\mathrm{CH_2Cl}$ (0.13 g, 0.52 mmol) and **Prom-O** (0.34 g, 1.13 mmol) by the same reaction of preparation of **Oct-Prom-O-Br** afforded **Prom-O-bpy-Cl** (0.40 g, 0.46 mmol) as a colorless powder in 89% yield.

^{1}H NMR ($\mathrm{CD_3OD}$) δ 8.67 (d, 2H), 8.44 (s, 2H), 7.97 (d, 4H), 7.7-7.9 (m, 8H), 7.3-7.5 (m, 6H), 4.69 (t, 4H), 4.50 (s, 4H), 3.4-3.5 (m, 4H), 2.96 (s, 12H), 2.4-2.5 (m, 4H). ESI-MS: *m/z* 391 $[\mathrm{M\text{-}2\ PF_6^-}]^{2+}$ ($z = 2$).

*Preparation of 4,4'-bis(3-(2-chloro-10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-2,2'-bipyridine dichloride (**Bpy-ClProm-Cl**)*

The reaction of $\mathrm{ClCH_2}$-**Bpy**-$\mathrm{CH_2Cl}$ (0.11 g, 0.44 mmol) and **ClProm** (0.31 g, 0.97 mmol) by the same preparation method of **Oct-Prom-O-Br** afforded **Bpy-ClProm-Cl** (0.36 g, 0.40 mmol) in 90% yield.

^{1}H NMR ($\mathrm{CD_3OD}$) δ 8.65 (d, 2H), 8.49 (s, 2H), 7.6-7.7 (m, 2H), 7.1-7.3 (m, 2H), 6.7-7.1 (m, 12H), 4.70 (s, 4H), 4.08 (t, 4H), 3.4-3.55 (m, 4H), 3.06 (s, 12H), 2.2-2.4 (m, 4H). ESI-MS: *m/z* 410 $[\mathrm{M\text{-}2Cl^-}]^{2+}$ ($z = 2$).

*Preparation of 4,4'-bis(3-(2-chloro-5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-2,2'-bipyridine dichloride (**Bpy-ClProm-O-Cl**)*

The reaction of $\mathrm{ClCH_2}$-**Bpy**-$\mathrm{CH_2Cl}$ (0.13 g, 0.52 mmol) and **ClProm-O** (0.37 g, 1.1 mmol) by the same preparation method of **Oct-Prom-O-Br** afforded **Bpy-ClProm-O-Cl** (0.33 g, 0.35 mmol) in 71% yield.

^{1}H NMR ($\mathrm{CD_3OD}$) δ 8.67 (d, 2H), 8.41 (s, 2H), 7.7-8.0 (m, 10H), 7.2-7.5 (m, 6H), 4.64 (t, 4H), 4,54 (s, 4H), 3.41 (t, 4H), 2.98 (d, 12H), 2.3-2.5 (m, 4H). ESI-MS: *m/z* 425 $[\mathrm{M\text{-}Cl^-}]^{2+}$ (z = 2)

*Preparation of 1,10-bis(3-(10H-phenothiazin-10-yl)propane)dimethylammoniodecane bis(hexafluorophosphate) (**Oct-Prom-PF$_6$**)*

$\mathrm{NH_4PF_6}$ (0.22 g, 1.35 mmol) was added to a mixture of MeOH-water (50:50 v/v, 10 mL) of **Oct-Prom-Br** (0.26 g, 0.30 mmol). The generated white precipitate was collected by filtration, washed with water, and dried in vacuo. **Oct-Prom-PF$_6$** was obtained as a colorless powder in a 91% yield (0.276 g, 0.28 mmol).

^{1}H NMR (CD_3CN) δ 7.15-7.4 (m, 8H), 6.9-7.1 (m, 8H), 4.05 (t, 4H), 3.2-3.4 (m, 4H), 3.0-3.1 (m, 4H), 2.88 (s, 12H), 2.1-2.3 (m, 4H), 1.4-1.6 (m, 4H), 1.0-1.3 (m, 12H). ^{19}F NMR (acetone-*d*$_6$) δ -72.71 (d, *J* = 707 Hz). ESI-MS: *m/z* 354 $[M\text{-}2PF_6^-]^{2+}$ (*z* = 2).

*Preparation of 1,10-bis(3-(5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniodecane bis(hexafluorophosphate) (**Oct-Prom-O-PF$_6$**)*

The reaction of NH_4PF_6 (0.14 g, 0.86 mmol) and **Oct-Prom-O-Br** (0.18 g, 0.20 mmol) by the same preparation method of **Oct-Prom-PF$_6$** afforded **Oct-Prom-O-PF$_6$** (0.19 g, 0.19 mmol) as a colorless powder in 97% yield.

^{1}H NMR (CD_3CN) δ 7.9-8.0 (m, 2H), 7.6-7.8 (m, 8H), 7.3-7.4 (m, 4H), 4.54 (t, 4H), 3.2-3.3 (m, 4H), 2.9-3.0 (m, 4H), 2.74 (s, 12H), 2.2-2.4 (m, 4H), 1.0-1.5 (m, 16H). ^{19}F NMR (CD_3CN) δ -72.82. ESI-MS: *m/z* 370 $[M\text{-}2\ PF_6^-]^+$ (*z* = 2).

*Preparation of 1,10-bis(3-(2-chloro-10H-phenothiazin-10-yl)propane)dimethylammoniodecane bis(hexafluorophosphate) (**Oct-ClProm-PF$_6$**)*

The reaction of NH_4PF_6 (0.22 g, 1.35 mmol) and **Oct-ClProm-Br** (0.33 g, 0.35 mmol) by the same preparation method of **Oct-ClProm-PF$_6$** afforded **Oct-ClProm-PF$_6$** (0.37 g, 0.34 mmol) as a colorless powder in 97% yield. ^{1}H NMR (acetone-*d*$_6$) δ 7.0-7.3 (m, 14H), 4.20 (t, 4H), 3.6-3.8 (m, 4H), 3.4-3.5 (m, 4H), 3.25 (s, 12H), 2.3-2.5 (m, 4H), 1.7-1.9 (m, 4H), 1.2-1.4 (m, 12H). ^{19}F NMR (acetone-*d*$_6$) δ -72.36 (d, *J* = 707 Hz). ESI-MS: *m/z* 388 $[M\text{-}2\ PF_6^-]^{2+}$ (*z* = 2).

*Preparation of 1,10-bis(3-(2-chloro-5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniodecane bis(hexafluorophosphate) (**Oct-ClProm-O-PF$_6$**)*

The reaction of NH_4PF_6 (0.37 g, 4.22 mmol) and **Oct-ClProm-Br** (0.52 g, 0.54 mmol) by the same preparation method of **Oct-Prom-PF$_6$** afforded **Oct-ClProm-O-PF$_6$** (0.59 g, 0.54 mmol) as a colorless powder in 99% yield.

^{1}H NMR (acetone-*d*$_6$) δ 7.9-8.1 (m, 4H), 7.7-7.85 (m, 6H), 7.3-7.5 (m, 4H), 4.77 (t, 4H), 3.4-3.6 (m, 4H), 3.2-3.4 (m, 4H), 3.03 (s, 12H), 2.2-2.4 (m, 4H), 1.5-1.65 (m, 4H), 1.1-1.4 (m, 12H). ^{19}F NMR (acetone-*d*$_6$) δ -72.38 (d, *J* = 708 Hz). ESI-MS: *m/z* 404 $[M\text{-}2\ PF_6^-]^{2+}$ (*z* = 2).

*Preparation of 1,4-bis(3-(10H-phenothiazin-10-yl)propane)dimethylammoniobenzene bis(hexafluorophosphate) (**Ph-Prom-PF$_6$**)*

The reaction of NH_4PF_6 (0.14 g, 0.86 mmol) and **Ph-ClProm-oct-Br** (0.17 g, 0.20 mmol) by the same preparation method of **Oct-Prom-PF$_6$** resulted **Ph-Prom-PF$_6$** (0.18 g, 0.19 mmol) as a colorless powder in 95% yield.

^{1}H NMR (acetone-*d*$_6$) δ 7.63 (s, 4H), 7.2-7.3 (m, 8H), 7.12 (d, 4H), 7.02 (t, 4H), 4.79 (s, 4H), 4.20 (t, 4H), 3.6-3.8 (m, 4H), 3.23 (s, 12H), 2.5-2.6 (m, 4H). ^{19}F NMR (acetone-*d*$_6$) δ -72.38 (d, *J* = 708 Hz). ESI-MS: *m/z* 336 $[M\text{-}2\ PF_6^-]^{2+}$ (*z* = 2).

*Preparation of 1,4-bis(3-(5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniobenzene bis(hexafluorophosphate) (**Ph-Prom-O-PF$_6$**)*

The reaction of NH$_4$PF$_6$ (0.14 g, 0.86 mmol) and **Ph-Prom-O-Br** (0.18 g, 0.20 mmol) by the same preparation method of **Oct-Prom-PF$_6$** afforded **Ph-Prom-O-PF$_6$** (0.18 g, 0.18 mmol) as a colorless powder in 90% yield.

^{1}H NMR (CD$_3$CN) δ 7.95 (d, 4H), 7.6-7.8 (m, 8H), 7.3-7.4 (m, 4H), 7.17 (s, 4H), 4.58 (t, 4H), 4.15 (s, 4H), 3.1-3.3 (m, 4H), 2.68 (s, 12H), 2.2-2.4 (m, 4H). ^{19}F NMR (CD$_3$CN) δ -72.91 (d, J = 706 Hz). ESI-MS: *m/z* 352 [M-2 PF$_6^-$]$^+$ (Z = 2).

*Preparation of 1,4-bis(3-(2-chloro-10H-phenothiazin-10-yl)propane)dimethylammoniobenzene bis(hexafluorophosphate) (**Ph-ClProm-PF$_6$**)*

The reaction of NH$_4$PF$_6$ (0.14 g, 0.86 mmol) and **Ph-ClProm-Br** (0.15 g, 0.17 mmol) by the same preparation method of **Oct-Prom-PF$_6$** resulted **Ph-ClProm-PF$_6$** (0.16 g, 0.16 mmol) as a colorless powder in 93% yield. ^{1}H NMR (acetone-*d$_6$*) δ 7.68 (s, 4H), 7.0-7.4 (m, 14H), 4.84 (s, 4H), 4.23 (t, 4H), 3.7-3.9 (m, 4H), 3.26 (s, 12H), 2.5-2.7 (m, 4H). ^{19}F NMR (acetone-*d$_6$*) δ -72.21 (d, J = 708 Hz). ESI-MS: m/z 370 [M-2 PF$_6^-$]$^{2+}$ (z = 2).

*Preparation of 1,4-bis(3-(2-chloro-5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniobenzene bis(hexafluorophosphate) (**Ph-ClProm-O-PF$_6$**)*

The reaction of NH$_4$PF$_6$ (0.17 g, 1.04 mmol) and **Ph-ClProm-O-Br** (0.24 g, 0.25 mmol) by the same preparation method of **Oct-Prom-PF$_6$** afforded **Ph-ClProm-O-PF$_6$** (0.24 g, 0.23 mmol) as a colorless powder in 90% yield.

^{1}H NMR (acetone-*d$_6$*) δ 8.02 (d, 4H), 7.7-7.9 (m, 6H), 7.3-7.5 (m, 8H), 4.80 (t, 4H), 4.50 (s, 4H), 3.4-3.6 (m, 4H), 2.99 (s, 12H), 2.5-2.6 (m, 4H). ^{19}F NMR (acetone-*d$_6$*) δ -72.18 (d, J = 709 Hz). ESI-MS: *m/z* 386 [M-2 PF$_6^-$]$^{2+}$ (*z* = 2).

*Preparation of 4,4'-bis(3-(10H-phenothiazin-10-yl)propane)dimethylammoniobiphenyl bis(hexafluorophosphate) (**BiPh-Prom-PF$_6$**)*

The reaction of NH$_4$PF$_6$ (0.17 g, 1.04 mmol) and **BiPh-Prom-Br** (0.20 g, 0.22 mmol) by the same preparation method of **Oct-Prom-PF$_6$** afforded **BiPh-Prom-O-PF$_6$** (0.23 g, 0.22 mmol) as a colorless powder in 97% yield.

^{1}H NMR (acetone-*d$_6$*) δ 7.82 (d, 2H), 7.69 (d, 2H), 7.1-7.4 (m, 12H), 7.02 (t, 4H), 4.8 (s, 12H), 4.23 (t, 4H), 3.6-3.8 (m, 4H), 3.27 (s, 12H), 2.5-2.7 (m, 4H). ^{19}F NMR (acetone-*d$_6$*) δ -73.85 (d, J = 708 Hz). ESI-MS: *m/z* 374 [M-2PF$_6^-$]$^{2+}$ (z = 2).

*Preparation of 4,4'-bis(3-(5-oxo-10H-phenothiazine-10-yl)propane)dimethylammoniobiphenyl bis(hexafluorophosphate) (**BiPh-Prom-O-PF$_6$**)*

The reaction of NH_4PF_6 (0.23 g, 1.35 mmol) and **-BiPh-Prom-O-Br** (0.30 g, 0.32 mmol) by the same preparation method of **Oct-Prom-PF$_6$** afforded **BiPh-Prom-O-PF$_6$** (0.32 g, 0.30 mmol) as a colorless powder in 93% yield.

^{1}H NMR (acetone-*d$_6$*) δ 8.01 (d, 4H), 7.7-7.9 (m, 12H), 7.55 (d, 4H), 7.38 (m, 4H), 4.78 (t, 4H), 4.53 (s, 4H), 3.5-3.7 (m, 4H), 3.01 (s, 12H), 2.5-2.7 (m, 4H). ESI-MS: *m/z* 390 $[M\text{-}2\ PF_6^-]^+$ (*z* = 2).

*Preparation of 4,4'-bis(3-(2-chloro-10H-phenothiazin-10-yl)propane)dimethylammoniobiphenyl bis(hexafluorophosphate) (**BiPh-ClProm-PF$_6$**)*

The reaction of NH_4PF_6 (0.30 g, 1.84 mmol) and **BiPh-ClProm-Br** (0.41 g, 0.42 mmol) by the same preparation method of **Oct-Prom-PF$_6$** resulted **BiPh-ClProm-PF$_6$** (0.43 g, 0.39 mmol) as a colorless powder in 94% yield. ^{1}H NMR (acetone-*d$_6$*) δ 7.84 (d, 4H), 7.72 (d, 4H), 7.0-7.4 (m, 14H), 4.83 (s, 4H), 4.27 (t, 4H), 3.7-3.9 (m, 4H), 3.30 (s, 12H), 2.5-2.7 (m, 4H). ^{19}F NMR (acetone-*d$_6$*) δ -72.41 (d, *J* = 708.1 Hz). ESI-MS: *m/z* 408 $[M\text{-}2\ PF_6^-]^{2+}$ (z = 2).

*Preparation of 4,4'-bis(3-(2-chloro-5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniobiphenyl bis(hexafluorophosphate) (**BiPh-ClProm-O-PF$_6$**)*

The reaction of NH_4PF_6 (0.49 g, 3.01 mmol) and **BiPh-ClProm-O-Br** (0.72 g, 0.71 mmol) by the same preparation method of **Oct-Prom-PF$_6$** afforded **BiPh-ClProm-O-PF$_6$** (0.76 g, 0.68 mmol) as a colorless powder in 94% yield.

^{1}H NMR (acetone-*d$_6$*) δ 8.0-8.1 (m, 2H), 7.7-7.9 (m, 10H), 7.57 (d, 4H), 7.3-7.5 (m, 4H), 4.83 (t, 4H), 4.56 (s, 4H), 3.5-3.7 (m, 4H), 3.05 (s, 12H), 2.5-2.7 (m, 4H). ^{19}F NMR (acetone-*d$_6$*) δ -72.48 (d, *J* = 708 Hz). ESI-MS: *m/z* 424 $[M\text{-}2\ PF_6^-]^{2+}$ (*z* = 2).

*Preparation of 4,4'-bis(3-(10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-2,2'-bipyridine bis(hexafluorophosphate) (**Bpy-Prom-PF$_6$**)*

The reaction of NH_4PF_6 (0.14 g, 0.86 mmol) and **Bpy-Prom-Cl** (0.17 g, 0.20 mmol) by the same preparation method of **Oct-Prom-PF$_6$** afforded **Bpy-Prom-PF$_6$** (0.19 g, 0.19 mmol) as a colorless powder in 92% yield.

^{1}H NMR (acetone-*d$_6$*) δ 8.77 (d, 2H), 8.71 (s, 2H) 7.63 (d, 2H), 7.1-7.3 (m, 12H), 6.98 (t, 4H), 4.93 (s, 4H), 4.22 (t, 4H), 3.7-3.9 (m, 4H), 3.34 (s, 12H), 2.5-2.7 (m, 4H). ^{19}F NMR (acetone-*d$_6$*) δ -72.33 (d, *J* = 708 Hz). ESI-MS: *m/z* 375 $[M\text{-}2\ PF_6^-]^{2+}$ (*z* = 2).

*Preparation of 4,4'-bis(3-(5-oxo-10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-2,2'-bipyridine bis(hexafluorophosphate) (**Bpy-Prom-O-PF$_6$**)*

The reaction of NH_4PF_6 (0.14 g, 0.86 mmol) and **Bpy-Prom-O-Cl** (0.18 g, 0.21 mmol) by the same preparation method of **Oct-Prom-PF$_6$** afforded **Bpy-Prom-O-PF$_6$** (0.18 g, 0.17 mmol) as a colorless powder in 81% yield.

^{1}H NMR (acetone-d_6) δ 8.68 (d, 2H), 8.52 (s, 2H), 7.98 (d, 4H), 7.7-7.9 (m, 8H), 7.47 (d, 2H), 7.34 (t, 4H), 4.80 (t, 4H), 4.66 (s, 4H), 3.6-3.8 (m, 4H), 3.09 (s, 12H, -NMe_3), 2.5-2.7 (m, 4H). ^{19}F NMR (acetone-d_6) δ -72.40 (d, J = 707 Hz). ESI-MS: m/z 391 [M-2 PF_6^-]$^{2+}$ (z = 2).

Preparation of 4,4'-bis(3-(2-chloro-10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-2,2'-bipyridine bis(hexafluorophosphate) ***(Bpy-ClProm-PF$_6$)***

The reaction of NH_4PF_6 (0.14 g, 0.86 mmol) and **Bpy-ClProm-Cl** (0.18 g, 0.20 mmol) by the same preparation method of **Oct-Prom-PF$_6$** resulted **Bpy-ClProm-PF$_6$** (0.21 g, 0.19 mmol) as a colorless powder in 95% yield.

^{1}H NMR (acetone-d_6) δ 8.78 (d, 2H), 8.71 (s, 2H), 7.66 (d, 2H) 6.9-7.3 (m, 14H), 4.95 (s, 4H), 4.24 (t, 4H), 3.6-3.7 (m, 4H), 3.35 (s, 12H), 2.5-2.7 (m, 4H). ^{19}F NMR (acetone-d_6) δ -72.29 (d, J = 708 Hz). ESI-MS: m/z 409 [M-2 PF_6^-]$^{2+}$ (z = 2).

Preparation of 4,4'-bis(2-chloro-5-oxo-3-(10H-phenothiazin-10-yl)propane)dimethylammoniomethyl-2,2'-bipyridine bis(hexafluorophosphate) ***(Bpy-ClProm-O-PF$_6$)***

The reaction of NH_4PF_6 (0.14 g, 0.86 mmol) and **Bpy-ClProm-O-Cl** (0.19 g, 0.20 mmol) by the same preparation method of **Oct-Prom-PF$_6$** afforded **Bpy-ClProm-O-PF$_6$** (0.20 g, 0.17 mmol) as a colorless powder in 87% yield.

^{1}H NMR (acetone-d_6) δ 8.69 (d, 2H), 8.52 (s, 2H), 7.98 (d, 2H), 7.7-7.9 (m, 6H), 4.19 (d, 2H), 7.3-7.4 (m, 6H), 4.81 (t, 4H), 4.67 (s, 4H), 3.6-3.7 (m, 4H), 3.35 (s, 12H), 2.5-2.7 (m, 4H). ^{19}F NMR (acetone-d_6) δ -72.30 (d, J = 708 Hz). ESI-MS: m/z 425 [M-2 PF_6^-]$^{2+}$ (z = 2).

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