Introduction

Phenothiazines (PTZs) are typical electron donors and have been used in charge transporting materials, molecular spin materials, dye-sensitized solar cells, π-electron systems for photo-induced electron transfer, organic emitting devices, and charge transfer complexes. Tuning of the oxidation potential of these PTZs is important to widen their applicability. Several 3- or 3,7-substituted PTZs have been synthesized for various purposes. Müller reported the oxidation potentials and optical properties of various 3,7-diamino PTZs. Although PTZ derivatives with considerably low oxidation potentials have been synthesized, systematic substituent-effects based on their conformations confirmed by crystal structure analyses have not been reported.

In this paper, we investigated the diarylaminop (Ar₂N−) substituent effect on the oxidation potentials of 3,7-bis(diarylaminol)-10-methyl-10H'-phenothiazines (Ar₂N)₂-PTZ (1a–f: a: carbazolyl, b: dihydrodibenzoazepinyl, c: dibenzoazepinyl, d: diphenylamino, e: phenothiazinyl, and f: phenoxazinyl) is investigated, where the Ar₂N-substituent effects based on their oxidation moieties in the crystal structure of 1c* and 1e*, for which coplanar conformation is observed between the PTZ**-plane and the planes of the sp²-hybridized nitrogen atoms in Ar₂N-substituents through a large conformational change during the oxidation process of (Ar₂N)₂-PTZ.

Scheme 1: Chemical structures of (Ar₂N)₂-PTZ (1a–f) and Ar₂N-Ph (2a–f).

The influence of diarylamino (Ar₂N−) substituents on the oxidation potential of 3,7-bis(diarylamino)phenothiazines (Ar₂N)₂-PTZ (1a–f: a: carbazolyl, b: dihydrodibenzoazepinyl, c: dibenzoazepinyl, d: diphenylamino, e: phenothiazinyl, and f: phenoxazinyl) is investigated, where the Ar₂N-substituent sequence a→f is aligned in the increasing order of their electron-donating ability. Interestingly, a different sequence of electron-donating ability for Ar₂N-substituents was observed for the oxidation potentials of (Ar₂N)₂-PTZ: 1a (Eox = +0.35 V vs. Fe/Fe⁺) > 1f (+0.15 V) > 1e (+0.15 V) > 1d (−0.05 V) > 1c (−0.19 V) > 1b (−0.22 V). The observed sequence can be explained by the stereoelectronic effect of the Ar₂N-substituents to stabilize (Ar₂N)₂-PTZ**. Clear-cut examples are observed in the crystal structure of 1c* and 1e*, for which coplanar conformation is observed between the PTZ**-plane and the planes of the sp²-hybridized nitrogen atoms in Ar₂N-substituents through a large conformational change during the oxidation process of (Ar₂N)₂-PTZ.
Previously, we have reported a unique structure of the PTZ trimer radical cation, the 10-phenyl derivative instead of the 10-methyl derivative (1e); the PTZ trimer radical cation has a considerably deformed structure, which is stabilized by the conjugation between the inner PTZ\(^{+}\) moiety and the sp\(^2\) hybridized nitrogen atoms in the outer PTZs.\(^9\) This paper presents a more general relationship between structures and oxidation potentials using various Ar\(_2\)N-substituents; the proposed stereoelectronic stabilization is directly demonstrated by the crystal structure analyses of a series of \((\text{Ar}_2\text{N})_2\text{—PTZ}\)\(^{+}\).

### Results and discussion

**Syntheses of 3,7-bis(diarylamino)-10-methyl-10\(^{H}\)′-phenothiazines and their radical cationic species**

Compounds \((\text{Ar}_2\text{N})_2\text{—PTZ}\) were synthesized from 3,7-dibromo-PTZ 3 (Scheme 2). Compound 3 was prepared according to the reported method.\(^9\) Compound 3 was converted to the desired PTZ derivatives 1a–f by using Buchwald–Hartwig cross-coupling reactions with the corresponding diarylamines 4a–f.\(^7\) Single crystals of \((\text{Ar}_2\text{N})_2\text{—PTZ}\) were obtained by recrystallization under suitable conditions (see Experimental section). However, we failed to obtain single crystals of 1b. We could obtain the crystal structure of the model compound 1b′ (Scheme 3) using \(\text{N}_2\text{p}-\text{tolyl}\) group instead of the \(\text{N}-\text{methyl}\) group in 1b. The reference compounds 2a–f were also synthesized from the corresponding diarylamines and bromobenzene using Buchwald–Hartwig reactions.

We prepared the radical cationic species of \((\text{Ar}_2\text{N})_2\text{—PTZ}\) by chemical oxidation using suitable reagents (Scheme 2) to study their detailed molecular structures by X-ray crystal structure analysis. The compounds 1a, 1b, 1d, and 1e were oxidized using tris(4-bromophenyl)ammonium hexafluoroantimonate (TBPA\(^{+}\)–Sb\(_6\)F\(_{11}\)) to the corresponding radical cation salts (1a\(^{+}\)–Sb\(_6\)F\(_{11}\), 1b\(^{+}\)–Sb\(_6\)F\(_{11}\), 1d\(^{+}\)–Sb\(_6\)F\(_{11}\), 1e\(^{+}\)–Sb\(_6\)F\(_{11}\)). The single crystals of these radical cationic salts could be obtained by recrystallization from suitable solvents.\(^9\) Although we synthesized 1c\(^{+}\)–Sb\(_6\)F\(_{11}\) and 1f\(^{+}\)–Sb\(_6\)F\(_{11}\), we could not obtain their single crystals for crystal structure analysis. Alternatively, we could obtain single crystals of 1c\(^{+}\)–GaBr\(_4\) and 1f\(^{+}\)–GaBr\(_4\), which could be prepared from 1c and 1f by treatments with thianthrenium tetrabromogallate (TH\(^{+}\)–GaBr\(_4\)).\(^{11,12}\) These radical cationic species are quite stable for days, even under aerated conditions in both solution state and solid state.

**Oxidation potentials of 3,7-bis(diarylamino)-10-methyl-10\(^{H}\)′-phenothiazines**

The cyclic voltammograms are shown in Fig. 1 for 1a–e and Fig. S1 for 1f, and their oxidation potentials are listed in Table 1. In order to gain insight into the electron donating ability of the Ar\(_2\)N-substitutents, oxidation potentials of \((\text{Ar}_2\text{N})\text{—Ph}\) (2a–f) and N-methyl-10\(^{H}\)′-phenothiazine (5) were also measured (Table 1), which reflects the electron donating ability of the Ar\(_2\)N-substituent: \(E_{\text{ox}}\) for (2a–f) is aligned in the sequence of \(a < b < c < d < e < f\) (Table 1).

The oxidation potentials of \((\text{Ar}_2\text{N})_2\text{—PTZ}\) were considerably lower than those of \((\text{Ar}_2\text{N})\text{—Ph}\), except for 1f (Table 1). Compound 1a has a lower oxidation potential (+0.35 V vs. Fc/Fc\(^{+}\)) than that (+1.08 V) of 2a, because the oxidation in 1a occurs in the central

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**Scheme 2** Synthetic methods of \((\text{Ar}_2\text{N})_2\text{—PTZ}\) (1a–f) and \((\text{Ar}_2\text{N})_2\text{—PTZ}\)\(^{+}\) \(\text{X}^{(\pm)}\) (1a–f\(^{+}\) \(\text{X}^{(\pm)}\)).

**Scheme 3** Chemical structure of 1b′.

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**Fig. 1** Cyclic voltammograms of (a) 1a, (b) 1b, (c) 1c, (d) 1d, and (e) 1e in dichloromethane: conditions of cyclic voltammetry: \(\text{nBu}_{4}\text{N}^{+}\text{ClO}_4^{-}\) as an electrolyte; glassy carbon and Pt wire as a working and counter electrode; in CH\(_2\)Cl\(_2\); Fc/Fc\(^{+}\) = +0.49 V vs. SCE.
PTZ moiety rather than the outer carbazolyl-moieties (cf. $E_{\text{ox}}$ for 5 and 2a). The oxidation potentials of 1b and 1c with seven-membered ring systems ($E_{\text{ox}}$ ≈ −0.2 V) are considerably lower than those of 2b and 2c ($E_{\text{ox}}$ = +1.0 V) and even lower than that of 5 (+0.31 V). The observed sequence of the oxidation potentials in 1a-f ($E_{\text{ox}}$/1a > $E_{\text{ox}}$/1f > $E_{\text{ox}}$/1e > $E_{\text{ox}}$/1d > $E_{\text{ox}}$/1c > $E_{\text{ox}}$/1b) is totally different from those of the Ar2N-substituents.

X-ray diffraction studies revealed that the compounds with low oxidation potential (1b, 1c, and 1d) can adopt a coplanar conformation about the PTZ π-plane and the plane of sp2-hybridized nitrogen atom in the radical cation states by a structural change from the neutral states (vide infra), as observed in the PTZ trimer radical cation. However, 1a+f and 1f+ cannot undergo such conformational changes due to their rigid planar structures of Ar2N-substituents, which causes steric repulsion between H+ (H3) and H+ (H3) in the structure of (Ar2N)2−PTZ, as shown in Scheme 1.

It is to be noted that the oxidation wave for 1f (+0.3 V) is assigned to sequential two-electron oxidations of outer phenoxazines (Table 1, Fig. S1†). This assignment is compatible with the following three observations; (1) slightly lower oxidation potential of 2f (+0.24 V) than those of 2e (+0.26 V) and 5 (+0.31 V), (2) crystal structure of 1f+.GaBr4− exhibiting neutral PTZ with a butterfly structure (vide infra, Fig. 3[i] and S2†), and (3) UV-vis-NIR spectrum of 1f+.GaBr4− showing a strong absorption at ~500 nm assigned to the terminal phenoxazine radical cation (Fig. S3†). These results indicate that the oxidation potential of the central PTZ moiety in 1f should be more positive than +0.30 V.

**Table 1 Oxidation potentials of 5, (Ar2N)2−PTZ (1a−f), and Ar2N−Ph (2a−f) a**

| Compound | $E_{\text{ox}}$ [V vs. Fe/Fe+] | $E_{\text{ox}}$ [V vs. Fe/Fe+] |
|----------|-------------------------------|-------------------------------|
| 5        | +0.31                        | −                            |
| 1a       | +0.35                        | +0.75                        |
| 1b       | −0.22                        | +0.27                        |
| 1c       | −0.19                        | +0.30                        |
| 1d       | −0.05                        | +0.29                        |
| 1e       | +0.15                        | +0.36                        |
| 1f       | +0.30                        | −                            |
| 2a       | +0.10                        | −                            |
| 2c       | +0.08                        | −                            |
| 2d       | +0.80                        | −                            |
| 2e       | +0.26                        | −                            |
| 2f       | +0.24                        | −                            |

a Conditions of cyclic voltammetry: nBu4N+.ClO4− as an electrolyte; glassy carbon and Pt wire as a working and counter electrode, respectively; in dichloromethane; Fe/Fe+ = +0.49 V vs. SCE. b Half wave potential of a reversible oxidation wave. c Two-electron oxidation processes of phenoxazine moieties. d Peak potential, respectively. $E_{\text{ox}}$ 1a: first and second oxidation potentials.

*Fig. 2 Specific names of atoms and planes for discussion of crystal structures.*
from the oxidation of the adsorbed molecular edge of the Ar₂N moiety rather than the central PTZ moiety covered by the bulky groups to produce Ar₂N⁺–PTZ; it then quickly changes to more stable hole-shifted Ar₂N–PTZ⁺ with large conformational change. These processes occur very rapidly, so that the cyclic voltammograms exhibit usual reversible waves (Fig. 1). In order to obtain insight into such hole-shift processes, we previously investigated photo-induced electron transfer of a (PTZ trimer)–anthraquinone (PTZ3–PTZ2–PTZ1–B–AQ, B: bridge) dyad in which electron transfer via through-bond interaction from PTZ trimer to the excited anthraquinone (AQ) to give PTZ3–PTZ2–PTZ1¹⁺–B–AQ⁻. The hole shift process (PTZ3–PTZ2–PTZ1¹⁺–B–AQ⁻ → PTZ3–PTZ2⁺–PTZ1–B–AQ⁻) with large conformational change was directly monitored by the transient absorption spectroscopy using a time constant of 6 ns. Thus, the oxidation of (Ar₂N)₂–PTZ is associated with both neutral and radical cation geometries.

We also carried out theoretical calculation on the stereoelectronic effects by theoretical calculation using Gaussian 09 on the basis of (U)B3LYP/6-31G** level of theory in order to obtain a general relationship between structures and oxidation potentials. The calculated HOMO energy levels of 1a–e are not correlated to the oxidation potentials (HOMO energy of 1a (−5.18 eV) > 1c (−5.00 eV) > 1d (−4.58 eV) > 1b (−4.24 eV) > 1c (−4.19 eV)) (Fig. S6†). The calculated SOMO energy levels of 1a–e⁻ are in the order of 1a⁺⁺ (−7.92 eV) > 1c⁺⁺ (−7.64 eV) > 1c⁺⁺ (−7.54 eV) > 1b⁺⁺ (−7.53 eV) > 1d⁺⁺ (−7.46 eV) (Fig. S4†) are also not correlated to oxidation potentials; the sequence agrees with the experimentally observed oxidation potentials except for the position of 1d (Fig. 4, inset). This consideration also indicates the importance of radical cation geometry in the oxidation potentials of 1a–e. Finally, the stabilization-energy gain from the neutral to the radical cation state, i.e. the calculated heat of formation differences between optimized structures in neutral

![Fig. 3 ORTEP views along the N=S axis (50% probabilities): (a) 1a, (b) 1a⁺, (c) 1b, (d) 1b⁺, (e) 1c, (f) 1c⁺, (g) 1d, (h) 1d⁺, (i) 1e, (j) 1e⁺, (k) 1f, (l) 1f⁺, (m) hydrogen atoms, counter anions, and crystal solvents were omitted for clarity.](image)

**Fig. 4** The plots of $E_{ox}^{1}$ of 1a–e vs. calculated heat of formation difference ($\Delta H_F$) between 1a–e and 1a–e⁺. (inset) The plots of $E_{ox}^{1}$ vs. SOMO energy of 1a–e⁺.

| Table 2 | Selected bond lengths (averaged) and dihedral angles for (Ar₂N)₂–PTZ (1a–f) and (Ar₂N)₂–PTZ⁺ (1a–f)† |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| **Neutral species** | **Cationic species** | **Neutral species** | **Cationic species** | **Neutral species** | **Cationic species** |
| S–C1(12) [Å] | 1.76 | 1.76 | 1.77 | 1.77 | 1.76 | 1.75 | 1.73 | 1.73 |
| N1–C6(7) [Å] | 1.41 | 1.43 | 1.42 | 1.42 | 1.41 | 1.41 | 1.39 | 1.38 |
| N2(3)–C3(10) [Å] | 1.42 | 1.41 | 1.42 | 1.43 | 1.43 | 1.44 | 1.40 | 1.38 |
| Plane A/B [°] | 33.0 | 34.5 | 48.7 | 38.3 | 34.9 | 40.5 | 14.9 | 17.7 |
| Plane A/C [°] | 56.4 | 6.8 | 21.7 | 59.0 | 85.7 | 80.9 | 40.6 | 5.6 |
| Plane B/D [°] | 62.0 | 3.3 | 22.4 | 41.8 | 88.1 | 80.9 | 41.4 | 4.0 |

† See Fig. 2 for naming of atoms and planes in (Ar₂N)₂–PTZ. Dihedral angles between two planes. Averaged values of two crystallographically independent species. Averaged values of four crystallographically independent species.
and radical cation states (ΔHF) are considered: the plots of ΔHF
(−139.23 kcal mol\(^{-1}\) (1a), −119.70 (1b), −118.97 (1c), −124.98
(1d), −128.85 (1e)) vs. \(E_{\text{ox}}\) provides a good correlation (corre-
lation coefficient: \(R^2 = 0.983\); Fig. 4).

As apparent from the crystal structures of 1a-e\(^{\text{c}}\), the cen-
tral PTZ\(^{\text{c}}\) can be stabilized by the conjugation with the
nitrogen p-orbitals in Ar\(_2\)N-substituents. These π-conjugation
gives rise to broad and intense intramolecular charge transfer
(CT) bands in near infrared region: 1a\(^{\text{c}}\) (λ\(_{\text{max}}\) = 1200 nm in
dichloromethane), 1b\(^{\text{c}}\) (950 nm), 1c\(^{\text{c}}\) (918 nm), 1d\(^{\text{c}}\) (1118
nm), and 1e\(^{\text{c}}\) (963 nm) (Fig. 5). These differences are almost
consistent with the results of theoretical calculations by
TDDFT method (see, ESI†).

Conclusions

We designed and prepared a series of 3,7-bis(diarylamino)
phenothiazines (Ar\(_2\)N)\(_2\)-PTZ (1a-f) and investigated relation-
ship between their oxidation potentials and their molecular
structures. X-ray crystal structural analyses and theoretical
calculations indicated a unique stereoelectronic effect on PTZs,
which strongly depends on the conformation of Ar\(_2\)N-
substituent.

The oxidations of 1c and 1e are accompanied by the large
conformational changes. In compound 1a, the freedom of Ar\(_2\)N-
substituent is restricted only by rotation of the carbazolyl group.

Although the manner of stabilization of (Ar\(_2\)N)\(_2\)-PTZ\(^{\text{c}}\) (1a-e\(^{\text{c}}\))
is highly substituent-dependent, these substituent-dependent
oxidation potentials were shown to be proportional to the
energy gain from the neutral state to the radical cation state.

The radical cationic species (Ar\(_2\)N)\(_2\)-PTZ\(^{\text{c}}\) were quite stable
under aerobic conditions in both solution and the solid states.
In addition, the radical cationic species 1a-e\(^{\text{c}}\) showed intense
intermolecular CT bands in near infrared region.

Although this study was particularly investigated for the PTZ
derivatives, the observed stereoelectronic substituent-effect
must be uniformly applicable to electron rich aromatic or
benzo-condensed π-conjugated systems.

Experimental

General information

\(^1\)H and \(^13\)C NMR spectra were recorded on a Bruker NanoBay
300 spectrometer. MALDI-TOF-MS was measured on a Shi-
madzu-Kratos AXIMA-CFR Plus spectrometer using dithranol
as a matrix reagent. Absorption spectra were measured with a
JASCO V-750 UV-vis spectrometer and Hitachi U-3500L spec-
rometer. X-ray data were collected by a Rigaku Saturn CCD
system with graphite monochromated Mo-K\(_\alpha\) radiation.
Melting points were measured with a hot-stage apparatus and
the values are uncorrected. Redox potentials were measured
using ALS electrochemical analyzer MODEL 610A in a con-
temporary three-electrode cell equipped with a glassy carbon
as a working electrode and a platinum wire as a counter electrode
with a SCE reference electrode. The measurements were carried
out with a sweep rate of 100 mV s\(^{-1}\) in suitable solvent con-
taining 0.1 M tetra-n-butylammonium perchlorate (nBu\(_4\)-
N\(^{\text{f}}\)-ClO\(_4\)) as an electrolyte. The redox potentials were finally
corrected by the ferrocene/ferrocenium couple (Fc/Fc\(^{\text{c}}\)).

Silica gel 60 (100–200 mesh) was used for column chroma-
tography. All commercially available compounds were reagent
grade and used without further purification. Dichloromethane
(CH\(_2\)Cl\(_2\)), and acetonitrile (CH\(_3\)CN) were dried and distilled over
calcium hydride. Toluene, benzene, tetrahydrofuran (THF), and
diethyl ether (Et\(_2\)O) were dried and distilled over sodium.
Ethanol (EtOH) and methanol (MeOH) were dried and distilled
over magnesium.

Tris(4-bromophenyl)ammonium hexafluoroantimonate
(TBPA\(^{\text{c}}\)-Sb\(_6\)\(^{\text{f}}\)) was prepared from tris(4-bromophenyl)amine
and silver hexafluoroantimonate according to the literature
with some modification.\(^7\) 3,7-Dibromo-10-methyl-10H-phen-
thiazine (3) was prepared according to the literature.\(^8\) 5,5′-(10-
Tolyl-10H-phenothiazine-3,7-diyl)bis(10,11-dihydro-5H-dibenzo
[b,f]azepine) (1b) was prepared from 3,7-dibromo-10-p-tolyl-
10H-phenothiazine and 10,11-dihydro-5H-dibenzo[b,f]azepine
(4b) according to the synthetic method of 1b. Single crystals of
1b suitable for X-ray crystal structure analysis were obtained by
recrystallization from toluene–EtOH.

Synthetic procedures

Thianthrenium tetrabromogallate (TH\(^{\text{c}}\)-GaBr\(_4\)) Oxidant
TH\(^{\text{c}}\)-GaBr\(_4\) was prepared according to the same procedure of
C37H25N3S: C, 81.74; H, 4.64; N, 7.73. Found: C, 81.57; H, 4.58; N, 7.99%. Single crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from CH2Cl2 (2 : 1 v/v) as eluent to give 1a as a white solid (219 mg, 73%). Single crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from THF-MeOH. 1c: C41H32N4S; MW 595.76; mp 291 °C (decomp.); 1H NMR (300 MHz, DMSO-d6): δ (ppm) 7.57–7.41 (m, 16H), 6.87 (s, 4H), 6.52 (d, J = 8.8 Hz, 2H), 5.86 (dd, J = 8.8 and 2.8 Hz, 2H), 5.75 (d, J = 2.8 Hz, 2H), 2.99 (s, 3H); 13C NMR (75 MHz, THF-d6): δ (ppm) 144.43, 143.61, 138.36, 136.76, 130.52, 130.33, 130.29, 129.45, 126.82, 123.59, 112.93, 110.65, 110.51, 34.01; HRMS (MALDI-TOF+) m/z calc for C41H32N4S: 595.2082, found: 595.2076 [M+].

**10-Methyl-N,N,N',N'-tetraphenyl-10H-phenothiazine-3,7-diamine (1d).** A mixture of dibromophenothiazine 3 (188 mg, 0.507 mmol), diphenylamine (4d) (212 mg, 1.25 mmol), Pd2(dba)3-CHCl3 (21.0 mg, 0.002 mmol), a toluene solution of bBuP (30 mM, 0.014 mL, 0.004 mmol), NaOtBu (143 mg, 1.49 mmol), and toluene (5 mL) was stirred at 110 °C under a nitrogen atmosphere for 2 h. After cooling to room temperature, the insoluble material was removed by filtration using celite column, and the filtrate was concentrated. The residue was purified by alumina column chromatography using hexane–CH2Cl2 (10 : 1 v/v) as eluent to give 1d as a white solid (276 mg, 99%). Single crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from CH2Cl2–MeOH. 1d: C37H38N4S; MW 547.72; mp 219–220 °C; 1H NMR (300 MHz, DMSO-d6): δ (ppm) 7.26 (t, J = 7.7 Hz, 8H), 7.00–6.93 (m, 16H), 6.80 (s, 2H), 3.29 (s, 3H); 13C NMR (75 MHz, THF-d6): δ (ppm) 143.22, 139.30, 130.71, 127.70, 123.84, 123.81, 122.76, 121.42, 118.07, 117.75, 113.31, 107.57, 33.14; HRMS (MALDI-TOF+) m/z calc for C37H38N4S: 547.2082, found: 547.2077 [M+]; anal. calc for C37H38N4S: C, 81.14; H, 5.34; N, 7.67. Found: C, 80.88; H, 5.38; N, 7.52.

**10'-Methyl-10H,10,3',7',10'-'terphenothiazine (1e).** A mixture of dibromophenothiazine 3 (87.0 mg, 0.234 mmol), phenothiazine (4e) (119 mg, 0.597 mmol), Pd2(dba)3-CHCl3 (2.4 mg, 0.002 mmol), a toluene solution of bBuP (30 mM, 0.16 mL, 0.005 mmol), NaOtBu (68.1 mg, 0.709 mmol), and toluene (2 mL) was stirred at 110 °C under a nitrogen atmosphere for 2 h. After cooling to room temperature, the insoluble material was removed by filtration using celite column, and the
filtrate was concentrated. The residue was purified by silica column chromatography using hexane–CH$_2$Cl$_2$ (4:1 v/v) as eluent to give 1e as a white solid (161 mg, 82%). Single crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from toluene–hexane. 1e: C$_{37}$H$_{25}$N$_3$S$_3$; MW 607.81; mp 293 °C (decomp.); $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ (ppm) 7.34–7.24 (m, 6H), 7.05 (dd, $J$ = 7.5 and 1.4 Hz, 4H), 6.95 (td, $J$ = 7.5 and 1.4 Hz, 4H), 6.85 (td, $J$ = 7.5 and 1.4 Hz, 4H), 6.25 (dd, $J$ = 7.5 and 1.4 Hz, 4H), 3.48 (s, 3H); $^1$C NMR (75 MHz, THF-$d_8$): $\delta$ (ppm) 145.57, 143.96, 134.38, 133.89, 129.94, 128.86, 124.43, 123.35, 120.33, 118.22, 114.08, 113.95, 33.13; HRMS (MALDI-TOF$^+$) $m/z$ calcd for C$_{37}$H$_{25}$N$_3$S$_3$: 607.1206; HRMS (MALDI-TOF$^+$) $m/z$ found: 607.1211, 607.1206 [M$^+$]; anal. calcld for C$_{37}$H$_{25}$N$_3$S$_3$: C, 58.21; H, 3.74; N, 6.42.

Radical cation tetramethylphenoxyazine salt 1b$^+$-SaF$_6^-$. To a solution of compound 1b (20.0 mg, 0.033 mmol) in CH$_2$Cl$_2$ (2 mL) was added TBPA$^+$-SaF$_6^-$ (24.1 mg, 0.034 mmol) at room temperature, and the mixture was stirred at room temperature for 1 h. The mixture was concentrated under reduced pressure, then Et$_2$O was added to the residue. The precipitate was collected by filtration and dried under reduced pressure to give 1b$^+$-SaF$_6^-$ as a yellow solid (24.5 mg, 88%). Single crystals for X-ray structure analysis were obtained by recrystallization from chlorobenzene–pentane. 1b$^+$-SaF$_6^-$: C$_{41}$H$_{29}$N$_3$S$_3$-SaF$_6^-$ MW 835.55; yellow solid; mp 230 °C (decomp.); EPR (powder) $g$ = 2.0041; HRMS (MALDI-TOF$^+$) $m/z$ calcd for C$_{41}$H$_{29}$N$_3$S$_3$-SaF$_6^-$: 599.2395, found: 599.2389; HRMS (MALDI-TOF$^+$) $m/z$ calcd for SaF$_6^-$: 234.8942, found: 234.8947; anal. calcld for C$_{41}$H$_{29}$N$_3$S$_3$-SaF$_6^-$: C, 59.20; H, 4.01; N, 4.77. Found: C, 58.98; H, 4.12; N, 4.53.

Radical cation hexafluoroantimonate salt 1c$^+$-GaBr$_6^-$. To a solution of compound 1c (20.5 mg, 0.034 mmol) in CH$_2$Cl$_2$ (2 mL) was added TH$^+$-GaBr$_6^-$ (21.4 mg, 0.035 mmol) at room temperature, and the mixture was stirred at room temperature for 1 h. The mixture was concentrated under reduced pressure, then Et$_2$O was added to the residue. The precipitate was collected by filtration and dried under reduced pressure to give 1c$^+$-GaBr$_6^-$ as a green solid (26.0 mg, 77%). Analytically pure sample was obtained by recrystallization from CH$_2$Cl$_2$–Et$_2$O. Single crystals for X-ray crystal structure analysis were obtained by recrystallization from chlorobenzene–cyclohexane. 1c$^+$-GaBr$_6^-$: C$_{37}$H$_{25}$N$_3$S-GaBr$_6$ MW 985.10; green solid; mp > 300 °C; EPR (powder) $g$ = 2.0043; anal. calcld for C$_{37}$H$_{25}$N$_3$S-GaBr$_6$: C, 52.68; H, 2.99; N, 4.98. Found: C, 52.50; H, 3.42; N, 4.78.
Radical cation tetrabromogallate salt $1f^{+}\cdot\text{GaBr}_4^-$. To a solution of compound $1f$ [20.3 mg, 35.3 mmol] in CH$_2$Cl$_2$ (2 mL) was added THF$^+\cdot\text{GaBr}_4^-$ [21.4 mg, 35.3 mmol] at room temperature, and the mixture was stirred at room temperature for 1 h. The mixture was concentrated under reduced pressure, then Et$_2$O was added to the mixture. The precipitate was collected by filtration and dried under reduced pressure (30.6 mg, 90%). Single crystals for X-ray crystal structure analysis were obtained by recrystallization from CH$_2$Cl$_2$–cyclohexane. $1f^+\cdot\text{GaBr}_4^-: C_{37}H_{25}N_3O_2S\cdot\text{GaBr}_4$; MW 575.1661 [C$_{37}$H$_{25}$N$_3$O$_2$S$^+$]; anal. calcd for C$_{37}$H$_{25}$N$_3$O$_2$S $C$, 46.02; H, 2.61; N, 4.35. Found: C, 46.02; H, 2.74; N, 4.54.

Theoretical calculations

All calculations were carried out on the basis of DFT with the (U)B3LYP exchange–correlation functional and using Gaussian 09 program packages.$^{15}$ The basis set used was 6-31G** for all atoms. The criterion for the SCF convergence was 10$^{-9}$. Molecular orbitals for 1a–e and 1a–e$^+$ were calculated by using the molecular geometries obtained from the optimized structures. The transition energies of 1a–e$^+$ were estimated by TD-DFT calculation (UB3LYP/6-31G**).

Conflicts of interest

The authors declare no conflict of interest.

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