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π-Conjugation Control

Trinitroxide-Trioxytriphenylamine: Spin-State Conversion from Triradical Doublet to Diradical Cation Triplet by Oxidative Modulation of a π-Conjugated System**

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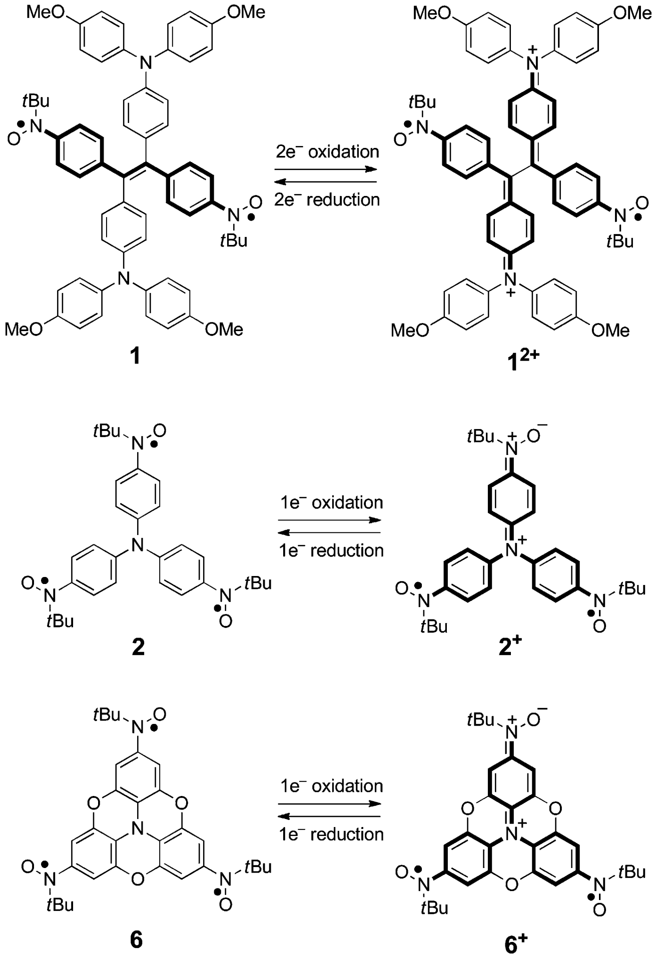
Organic-based open-shell molecules are promising components for next-generation electronic devices because of their wide diversity in molecular design, structural flexibility, and processability.[1–6] Continuous research in this field has led to interesting findings on the use of these species as spin sources and/or redox-active species: for example, molecule-based magnets,[1,3] electrical conductors,[3,6,7] radical-based batteries,[3,4,8] spintronics devices,[3,5,6] and molecular spin-based quantum computers.[4c–e] In these studies, control of the ferromagnetic or antiferromagnetic couplings between spin sources plays an important role in their unique magnetic properties.[6,9–12] Electron-donor molecules substituted with stable neutral radical species have frequently been used to construct high-spin molecules.[6,11–13] Selective oxidation of the electron-donor moieties of these molecules gives radical-substituted radical cation species, as demonstrated in the design of magnetic-field-responsive charge transport and ferrimagnets.[6,11,12]

Oxidation of the electron donor in a system composed of radicals and a π-donor could alter the π-conjugation network, affecting the magnetic interaction. Tanaka and co-workers reported tetraphenylethene derivative **1**,[14] where the exchange interaction between two nitroxides is switched from an antiferromagnetic interaction ($J/k_B \approx -66$ and -93 K for stereoisomers) to a very weak interaction ($J/k_B \approx 0$ K) by two-electron oxidation. This oxidation converts the π-conjugated system into a tetramethyleneethane system that is known to be weakly antiferromagnetic (Scheme 1).[15]

Trinitroxide-substituted triphenylamine **2**, synthesized by Iwamura and co-workers,[16] was reported to be in a doublet ground state with $J/k_B \approx -135$ K in its neutral state. Interestingly, the cyclic voltammogram of **2** shows a reversible one-electron redox wave owing to the oxidation of triphenylamine.[16c] The oxidized cationic species $\mathbf{2}^+$ is expected to have a trimethylenemethane-type π-conjugated system in a triplet ground state (Scheme 1)[17] with a large exchange interaction



Scheme 1. Switching of the π-conjugation networks of **1**, **2**, and **6** with their oxidized analogues.

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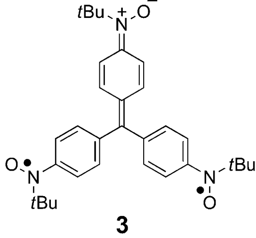
similar to the carbon analogue **3**[16a,b,18] and Yang's diradical **4**.[19] However, the oxidized species could not be isolated because of the poor stability of the radical cations, and the exchange interaction remains unanswered.



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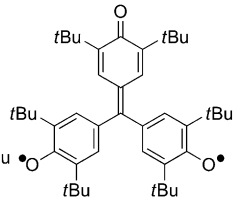

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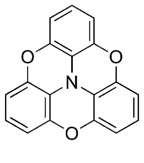

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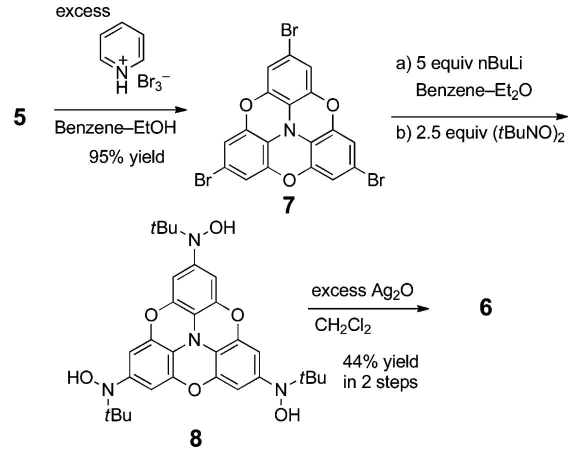
On the other hand, trioxytriphenylamine (TOT) **5**[20] is easily oxidized and gives a stable radical cation both in solution and in the crystalline state in air. These findings led us to design *N-tert*-butylnitroxide-substituted TOT **6**. Herein, we report an oxidative spin-state conversion from a triradical doublet ground state (**6**) to diradical cation triplet ground states ($\mathbf{6}^+$). We also determined the crystal structures of **6** and $\mathbf{6}^+$; the spin properties of these compounds were extensively clarified with theoretical analyses of zero-field splitting and *g* tensors.

Triradical **6** was prepared from **5** in three steps (Scheme 2). Compound **5** was converted into the tribromo derivative **7** with a 95% yield. Tri-lithiation by *n*-butyllithium in a mixture of benzene and ether followed by treatment with 2-methyl-2-nitrosopropane dimer gave trihydroxylamine **8**. Oxidation of **8** with an excess of Ag_2O gave triradical **6** in 44% yield from **7**.



Scheme 2. Synthesis of triradical **6**.

The ESR spectrum of triradical **6** was measured in degassed toluene at 293 K (see the Supporting Information). The ESR spectrum was composed of septet lines centered at $g = 2.0059$ with an intensity ratio of 1:3:6:7:6:3:1, which was attributed to the three equivalent nitrogen nuclei. The line splitting was estimated to be 0.385 mT by spectral simulation. The value is similar to that of triradical **2** (0.406 mT in 2-methyltetrahydrofuran)[16] and is approximately one-third of the hyperfine coupling constant of phenyl-*tert*-butylnitroxide ($|a_N| = 1.208$ mT in toluene),[21] indicating that the absolute value of the intramolecular exchange interaction is much larger than the hyperfine interaction.

Single crystals of **6** suitable for X-ray crystal analysis were obtained by recrystallization from CH_2Cl_2/Et_2O.[22] The X-ray crystal structure is shown in Figure 1. The TOT skeleton of **6** has a shallow bowl structure similar to the structure of **5**.[20a] The N–O bonds in *tert*-butyl nitroxide are oriented in a pseudo-C_3-symmetry (not crystallographic symmetry). Note that the dihedral angles between the nitroxide C_{sp^2}-N-O planes and the attached benzene rings are in the range of 5–26°.

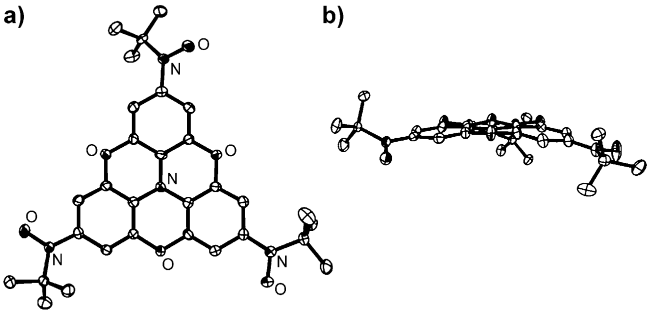


Figure 1. Crystal structure of **6**: a) top view; b) side view. Hydrogen atoms are omitted for clarity. Ellipsoids at 50% probability.

Bulk magnetic properties of **6** were investigated by magnetic susceptibility measurements using a SQUID magnetometer (Figure 2). The observed $\chi_p T$ value at 300 K (ca. 0.5 emu K mol^{-1}) was significantly smaller than the expected value for a magnetically independent three-spin system ($\chi_p T = 1.125$ emu K mol^{-1} assuming $g = 2$), suggesting the presence of a relatively large antiferromagnetic interaction in the crystalline state. Upon lowering temperature, the $\chi_p T$ values gradually decreased. The observed $\chi_p T$–T curve was analyzed using the spin Hamiltonian based on a symmetrical triangle model: $H = -2J(S_1S_2 + S_2S_3 + S_3S_1)$.[23] The use of a single J value is based on the pseudo-C_3-symmetric structure, as obtained from the crystal structure analysis. The expression of $\chi_p T$ is shown in Equation (1).[23] The exchange interaction J and the unspecified magnetic interaction θ were

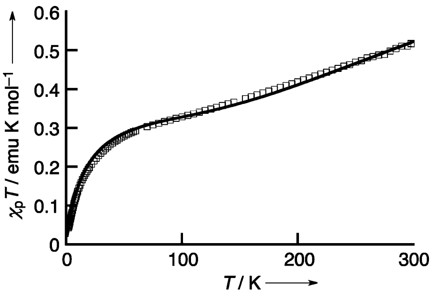


Figure 2. Temperature dependence of $\chi_p T$ for **6** in the polycrystalline state. The solid line shows the simulated curve based on the symmetrical triangle model: $2J/k_B = -410$ K and $\theta = -16$ K.

obtained as $2J/k_B = -410$ K and $\theta = -16$ K, respectively. The large $|J|$ value can be assigned to the intramolecular magnetic interaction between the *tert*-butyl nitroxides. The θ value is attributable to an intermolecular exchange interaction. Thus, triradical **6** was found to be in a doublet ground state. The observed $|J|$ value is much larger than that of triradical **2**,[16] implying the importance of the planarity in controlling the exchange interaction in **6**.

$$\chi_p T = \frac{N_A g^2 \mu_B^2}{3k_B}\frac{1}{T-\theta}\frac{15e^{3J/2k_BT} + 3e^{-3J/2k_BT}}{4e^{3J/2k_BT} + 4e^{-3J/2k_BT}}T \tag{1}$$

Triradical **6** showed a reversible one-electron oxidation wave at $E_{ox} = -0.29$ V vs Fc/Fc$^+$ in the cyclic voltammogram (see the Supporting Information). The E_{ox} value was considerably lower than those of **5** (+0.12 V)[20] and **2** (ca. −0.17 V).[16c] The electrochemical oxidation process of **6** can be monitored by absorption spectroscopy using a thin-layer cell. The UV/Vis absorption spectrum of triradical **6** in CH_2Cl_2 showed weak and broad absorptions in the 500–1000 nm region. Figure 3 shows the spectral changes in the electrochemical oxidation with an applied potential of −0.09 V versus Fc/Fc$^+$, which is sufficiently high to oxidize **6**. During the oxidation, new absorption peaks at $\lambda_{max} = 360$, 530, and 710 nm appeared with isosbestic points. The new absorption peaks were ascribed to the generation of **6**$^+$. The strong absorption at 710 nm is due to the quinoidal structure in **6**$^+$. The observed spectral change was reversible, and the neutral compound **6** was reproduced by the electrochemical reduction of **6**$^+$. This observation confirms that the conversion between **6** and **6**$^+$ constitutes a new molecule-based switch involving a spin-state conversion from the ground-state doublet (**6**) to triplet (**6**$^+$), as described below.

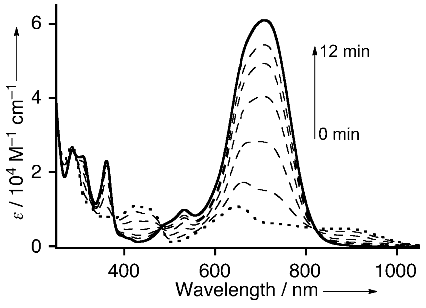


Figure 3. UV/Vis spectral change during the electrochemical oxidation of **6**: The dotted and solid lines show the spectra of neutral **6** and generated **6**$^+$, respectively. The dashed lines show intermediate states.

We isolated **6**$^+$ in an almost pure form by chemical oxidation. Treatment of a CH_2Cl_2 solution of **6** with an equivalent amount of tris(4-bromophenyl)aminium hexachloroantimonate afforded the desired salt **6**$^+$•$SbCl_6^-$ as a blue solid.[24] Single crystals of **6**$^+$•$SbCl_6^-$ were obtained by slow evaporation from a hexane/CH_2Cl_2 solution.[25,26] The X-ray crystal structure is shown in Figure 4. The TOT skeleton of **6**$^+$ has a planar structure, in contrast to the neutral compound **6**. Furthermore, one of the nitroxides is oriented in a different direction from the pseudo-C_3-symmetry. The dihedral angles between the nitroxide C_{sp^2}-N-O planes and the attached benzene rings are smaller (2–4°) than those of **6** (5–25°), which suggests that **6**$^+$ possesses a trimethylenemethane-type π-conjugation network with the quinoidal structure.

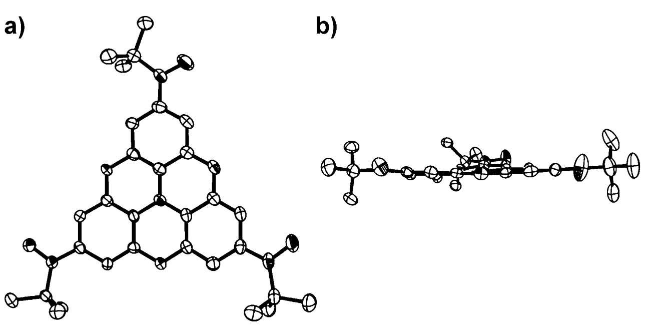


Figure 4. Crystal structure of **6**$^+$•$SbCl_6^-$: a) top view; b) side view. The counterion $SbCl_6^-$ and the hydrogen atoms are omitted for clarity. Ellipsoids at 50% probability. The whole molecule is of pseudo C_s symmetry owing to the asymmetric orientation of nitroxides around the axis normal to the ring. For atom labeling, see Figure 1.

The X band ESR spectrum of **6**$^+$•$SbCl_6^-$ in a diethyl phthalate rigid glass at 200 K is shown in Figure 5. The ESR spectrum is composed of two triplet species with similar *D* values, but one has a vanishing *E* value and their *g* anisotropies are quite different. The spin-forbidden transition (ΔMs = ±2) was clearly observed in a $g = 4$ region of the resonance field (see the Supporting Information). A quite similar spectrum was observed in frozen butyronitrile. The observed triplet ESR spectrum was satisfactorily reproduced by two sets of spin-Hamiltonian parameters: The triplet species **6**$^+$**a** ($S = 1$, $g_x = 2.0080$, $g_y = 2.0080$, $g_z = 2.0030$, $|D|/hc = 0.00575$ cm^{-1}, $|E|/hc = 0$ cm^{-1}), with the vanishing *E* value, corresponds to the simulated spectrum in Figure 5c.

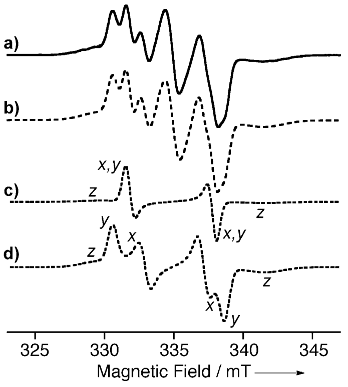
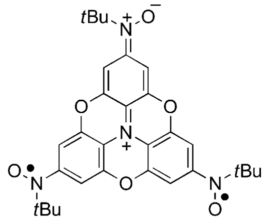
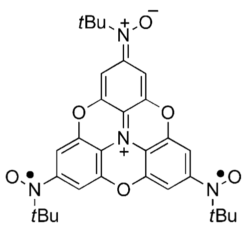


Figure 5. ESR spectra of **6**$^+$•$SbCl_6^-$: a) observed spectrum in a frozen diethyl phthalate rigid glass at 200 K (microwave frequency = 9.410117 GHz); b) superposition of the simulated spectra (c, d, and spin-doublet impurity); c) simulated spectrum of the triplet species attributed to **6**$^+$**a** ($S = 1$, $g_x = 2.0080$, $g_y = 2.0080$, $g_z = 2.0030$, $|D|/hc = 0.00575$ cm^{-1}, $|E|/hc = 0$ cm^{-1}); d) simulated spectrum attributed to **6**$^+$**b** ($S = 1$, $g_x = 2.0051$, $g_y = 2.0107$, $g_z = 2.0030$, $|D|/hc = 0.00570$ cm^{-1}, $|E|/hc = 0.00055$ cm^{-1}). The only spin-allowed transitions (ΔMs = ±1) are shown. The broad absorption line around 335 mT is due to a spin-doublet impurity. The assignments of the canonical orientations denoted by *x*, *y*, and *z* are given in the simulation spectra.

The other is the species $\mathbf{6}^{+}\mathbf{b}$ ($S=1$, $g_x=2.0051$, $g_y=2.0107$, $g_z=2.0030$, $|D|/hc=0.00570\ \text{cm}^{-1}$, $|E|/hc=0.00055\ \text{cm}^{-1}$), with a non-vanishing E value and a larger g anisotropy, corresponding to the simulated spectrum in Figure 5d. These results suggest that triplet $\mathbf{6}^{+}\mathbf{a}$ has a C_3-based symmetry, as observed in the crystalline state of the neutral species (**6**), and triplet $\mathbf{6}^{+}\mathbf{b}$ has a C_S symmetry, as shown in the crystal structure of $\mathbf{6}^{+}$. To chemically identify the triplet species $\mathbf{6}^{+}\mathbf{a}$ and $\mathbf{6}^{+}\mathbf{b}$, we have invoked quantum chemical calculations of the zero-field splitting **D** and **g** tensors[27] for both cations ($\mathbf{6}^{+}\mathbf{a}$ and $\mathbf{6}^{+}\mathbf{b}$) and supramolecular chemical entities corresponding to the ion pairs ($\mathbf{6}^{+}\mathbf{a}\cdot\text{SbCl}_6^{-}$ and $\mathbf{6}^{+}\mathbf{b}\cdot\text{SbCl}_6^{-}$). The theoretical evaluation of the tensors reasonably explains the experimental D, E and g values, and the relative orientation between the **D** and **g** tensors, which are needed to acquire complete spectral simulations (see the Supporting Information).



$\mathbf{6^{+}\,a}$



$\mathbf{6^{+}\,b}$

Thus, $\mathbf{6}^{+}$ in frozen solution was shown to exist as an equilibrium mixture of $\mathbf{6}^{+}\mathbf{a}$ and $\mathbf{6}^{+}\mathbf{b}$, whereas $\mathbf{6}^{+}$ in the crystalline form has the structure of $\mathbf{6}^{+}\mathbf{b}$, as confirmed by the X-ray analysis (Figure 4). Also, the electrospray ionization (ESI-MS) of $\mathbf{6}^{+}$ in acetonitrile (ca. 10^{-5} M) exhibited a peak of 1425 m/z (1% intensity) that corresponds to two $\mathbf{6}^{+}$ plus SbCl_6^{-} with a base peak of 545 m/z ($\mathbf{6}^{+}$), indicating the presence of a dimer in solution even at low concentration. Furthermore, the Curie plots using the ESR signal intensities I for the $\Delta Ms=\pm 2$ transition, I–$1/T$, resulted in a non-linear curve, suggesting the presence of diradical species possibly involving low-spin ground states in solution.

To obtain clear insight into the intramolecular exchange interaction, we have measured the magnetic susceptibility of the polycrystalline sample of $\mathbf{6}^{+}\cdot\text{SbCl}_6^{-}$. The temperature dependence of the paramagnetic susceptibility is shown in Figure 6. The $\chi_p T$ value at room temperature was approximately 0.8 emu K mol^{-1} and almost constant down to 150 K. This $\chi_p T$ value is larger than the theoretical value for a magnetically independent two-spin system, suggesting the occurrence of a sizable ferromagnetic interaction. Below 150 K, the $\chi_p T$ value dropped sharply. The observed $\chi_p T$–T curve can be simulated using the Curie–Weiss law for $S=1$ [Eq. (2)] with a purity factor f of 0.82 and antiferromagnetic

$$\chi_p T = f\frac{2N_A g^2 \mu_B^2}{3k_B}\frac{1}{T-\theta}T \qquad (2)$$

interaction θ of -11.5 K. A weak antiferromagnetic interaction θ is ascribed to an intermolecular magnetic interaction. The purity of the polycrystalline sample can also be estimated

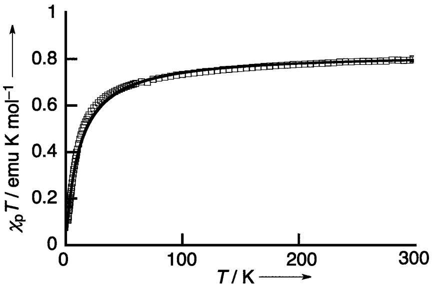


Figure 6. Temperature dependence of $\chi_p T$ for $\mathbf{6}^{+}\cdot\text{SbCl}_6^{-}$. The solid line is simulated based on the Curie–Weiss law [Eq. (2)] with $f=0.82$ and $\theta=-11.5$ K.

by the UV/Vis spectrum in solution, giving a consistent value (ca. 80%) assuming a quantitative transformation in the electrochemical oxidation. Thus, the magnetic behavior of the diradical cation $\mathbf{6}^{+}$ is best explained by assuming a triplet ground state with a strong magnetic interaction of $J/k_B \gg 300$ K between the two nitroxide radicals. The large positive J value ($J/k_B \gg 300$ K) is also consistent with theoretical calculations.[28]

In summary, trinitroxide-substituted TOT **6** showed a novel spin-state conversion from a neutral triradical doublet into diradical cation triplet states by the oxidative modulation of the π-conjugated TOT skeleton in their ground state. These observations are useful in the development of molecular electronic and spintronic devices using related spin-incorporated π-electronic systems. We also emphasize that the low-spin preference in **6** with the strong antiferromagnetic exchange coupling and the location of the excited quartet state with an expected small D value provide important insights into an improved and extended approach to quantitative quantum-chemical evaluations for the exchange couplings in high-spin chemistry. Our research along this line is currently underway.

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[22] Crystallographic data for **6**: orthorhombic, space group *Pbca* (no.61), $a = 8.6097(6)$, $b = 24.973(2)$, $c = 24.370(2)$ Å, $V = 5239.7(8)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.383\,\mathrm{g\,cm^{-3}}$, $T = 150(2)$ K, $R1 = 0.0951$, $wR2 = 0.2018$, GOF = 1.339. CCDC 833099 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[23] The spatial symmetry of the spin Hamiltonian should be set as the asymmetric triangle model with three unequal J values according to the crystallographic symmetry of **6**. However, the temperature dependence of $\chi_p T$ was calculated using the more symmetric equilateral triangle model with a single J value and with an unspecified magnetic interaction (θ) to avoid overparameterization. See Ref. [16b,c] for an asymmetric triangle model.

[24] The chemical oxidation using other tris(4-bromophenyl)aminium salts (ClO_4^-, PF_6^-) and thianthrenium tetrachlorogallate (see, Ref. [20b]) were examined. **6**$^{+}$•$SbCl_6^-$ exhibited good crystallinity and thus gave the highest purity.

[25] Crystallographic data of **6**$^{+}$•$SbCl_6^-$: triclinic, space group: $P\bar{1}$ (no.2), $a = 9.2100(15)$, $b = 13.430(3)$, $c = 16.620(3)$ Å, $\alpha = 84.400(14)$, $\beta = 75.470(12)$, $\gamma = 74.690(12)$°, $V = 1918.3(6)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.524\,\mathrm{g\,cm^{-3}}$, $T = 150(2)$ K, $R1 = 0.0981$, $wR2 = 0.2286$, GOF = 1.149. CCDC 833100 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[28] The ground states of **6**$^{+}$**a** and **6**$^{+}$**b** were theoretically evaluated by the broken-symmetry approach (see K. Yamaguchi, T. Kawakami, Y. Takano, Y. Kitagawa, Y. Yamashita, H. Fujita, *Int. J. Quantum Chem.* **2002**, *90*, 370–385): The exchange interactions for **6**$^{+}$**a** and **6**$^{+}$**b** were found to be large positive values ($>+10^3$ K, triplet ground state) for both species.