

## Article

# Solid–Liquid Phase Transition-Induced Magnetic Property Changes in Tetrakis(ethylthio)tetrathiafulvalene Radical Cation Salt

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**Abstract:** We discovered that the radical cation salt  $[1^{\bullet+}][NTf_2^-]$ , composed of tetrakis(ethylthio)tetrathiafulvalene radical cation and bis(*N*-trifluoromethanesulfonyl)imide ion, exhibits significant changes in its magnetic properties during a solid–liquid phase transition. Single-crystal structure analysis revealed that the radical cation salt  $[1^{\bullet+}][NTf_2^-]$  forms an associated structure called a  $\pi$ -dimer in the crystalline phase. The extremely weak ESR signal in the crystalline state indicates strong antiferromagnetic interactions between unpaired electrons within the  $\pi$ -dimer. Upon heating, the crystalline phase transitions into a liquid state without decomposition at 144 °C (417 K). The ESR signals in the liquid state are significantly stronger than those in the solid state, suggesting the formation of a paramagnetic state with weak interactions between radical cations.

**Keywords:** tetrathiafulvalene; liquescent radical cation; magnetic property



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## 1. Introduction

Recent advances in open-shell molecules have demonstrated their potential as promising components in molecule-based magnetic materials [1–6], electronic materials [7–9], near-infrared absorbing materials [10–13], molecule-based batteries [3,14,15], and organic-based high-spin materials [4,5,16–26]. The association characteristics of such molecules are a major factor in determining their electronic, electrical, and magnetic properties [27–40]. In solution, some of these molecules have exhibited dynamic changes in spin properties, attributed to their association and dissociation [27–35]. The ability to utilize such properties depends on whether the associated structures in condensed states, where the motions of the molecules are restricted, can be altered by external stimuli or environmental factors [36–52]. Recently, we have attempted to establish methods to overcome the restrictions in condensed states and to promote changes in their alignments across the entire system triggered by external stimuli or environmental factors (e.g., temperature, vapors, mechanostress) [53–56]. Especially, we have focused on the liquescent materials for new stimuli-responsive materials. Within these systems, transformations of condensed states are projected to induce significant changes in their associated structures without requiring a solution state. Pioneering work on liquescent open-shell materials has been conducted using dithiadiazolyl and dithiazolyl neutral radicals [41,42], which are somewhat difficult to prepare as they often require purification by sublimation, likely due to their instability. Some nitroxide neutral radical derivatives have exhibited liquescent behavior [43–45], while their spins remain localized and protected by adjacent bulky substituents, leading to a paramagnetic state with weak intermolecular spin–spin interactions. Metal-free open-shell ionic compounds with

specific liquefaction points have also attracted interest because their electronic properties and associated structures can be easily modulated by changing their substituents and counterions [46,47]. In these cases, ionic nitroxide radical derivatives have also been designed and investigated, but they still exhibit weak intermolecular spin–spin interactions [48–50]. Conversely, 7,7,8,8-tetracyanoquinodimethane radical anions ( $\text{TCNQ}^{\bullet-}$ ) display intriguing phase transitions due to their tendency to form associated structures. Saito reported that molten salts composed of imidazolium derivatives and  $\text{TCNQ}^{\bullet-}$  undergo reversible changes in magnetic properties because of the dissociation and association of radical species during solid–liquid phase transitions, occurring exclusively under an inert atmosphere above 127 °C (400 K) [51,52]. Recently, we found that a tetra-*n*-decylammonium ion salt of  $\text{TCNQ}^{\bullet-}$  transforms from a blue solid to a green liquid at 90 °C (363 K) without decomposition, even under aerated conditions [53]. Accordingly, we have postulated that liquescent salt systems, composed of open-shell ionic molecules and flexible counter ions, represent promising candidates for new stimuli-responsive materials [53–56]. In this study, we have focused on tetrathiafulvalene (TTF) derivatives, which were prepared as strong electron-donor molecules for the development of electrically conducting materials [57–61]. The TTF derivatives have also been successfully used in the construction of supramolecular systems. These radical cations frequently form  $\pi$ -dimer structures in solid and solution states [35,56,60,61]. Consequently, we designed tetrakis(ethylthio)-substituted TTF radical cations, bearing a bis(trifluoromethanesulfonyl)imide anion,  $1^{\bullet+} \cdot \text{NTf}_2^-$  (Figure 1a), with the following features: (1) the stable TTF radical cation system provides variable electronic-spin structures depending on its association as described above, and (2) the flexibility and charge delocalization of the anion enhances molecular fluidity, increasing the controllability of phase transitions. We found that the magnetic and electronic properties of  $[1^{\bullet+}][\text{NTf}_2^-]$  were controllable via solid–liquid phase transitions.

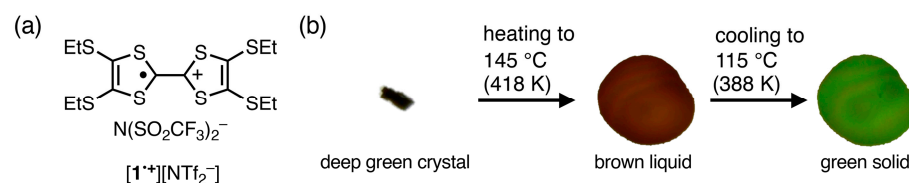


**Figure 1.** (a) Chemical structure of  $[1^{\bullet+}][\text{NTf}_2^-]$  and (b) photographs of  $[1^{\bullet+}][\text{NTf}_2^-]$  during the phase transitions from a crystal to a liquid, and then back to a solid. The material in the photographs was placed on a glass plate and covered with a thin glass.

## 2. Materials and Methods

### 2.1. General

Melting points were measured using a Yanaco MP-J3 apparatus (Kyoto, Japan) and were not corrected. The elemental analyses were performed at the Analytical Instrument Facility, Graduate School of Science, Osaka University. Electronic spectra were obtained on a JASCO V-670 spectrometer (Tokyo, Japan). Variable-temperature electronic spectra were carried out using a glass heater. ESR spectra were recorded with a JEOL JES-FE1XG spectrometer (Tokyo, Japan) and a JEOL JES-FE2XG spectrometer (Tokyo, Japan). The experiments were conducted at several microwave powers to ensure no signal saturation (Figure S1). Finally, microwave power of 1 mW and 100 kHz modulation frequency were used for the measurements. Single-crystal X-ray data were collected by a Rigaku XtaLAB P200 diffractometer (Tokyo, Japan) with graphite monochromated Mo- $K\alpha$  radiation ( $\alpha = 0.71075 \text{ \AA}$ ). The thermal gravimetric analyses were performed by a Hitachi NEXTA STA (Tokyo, Japan).

All reactions were performed under inert atmosphere. Tetrakis(ethylthio)tetrathiafulvalene, dehydrated dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), dehydrated diethyl ether ( $\text{Et}_2\text{O}$ ), and dehydrated

cyclohexane were obtained from common commercial suppliers and used without further purification. Tris(4-bromophenyl)aminium bis(trifluoromethanesulfonyl)imide ([**TBPA**<sup>•+</sup>][NTf<sub>2</sub><sup>−</sup>]) was prepared according to the literature [56].

## 2.2. Synthesis of **1**<sup>•+</sup>·NTf<sub>2</sub><sup>−</sup>

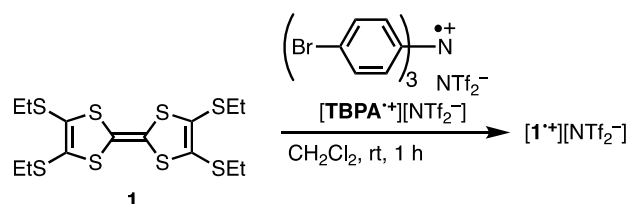
A suspension of tetrakis(ethylthio)tetrathiafulvalene (**1**) (105 mg, 0.236 mmol) and [**TBPA**<sup>•+</sup>][NTf<sub>2</sub><sup>−</sup>] (180 mg, 0.236 mmol) in dehydrated CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was stirred for 1 h at room temperature. The mixture was concentrated under reduced pressure. After dehydrated Et<sub>2</sub>O was added to the residue, the precipitate was collected using a membrane filter. The precipitate was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane to give the desired compound as deep green crystals (163 mg, 95%). [**1**<sup>•+</sup>][NTf<sub>2</sub><sup>−</sup>]: C<sub>16</sub>H<sub>20</sub>O<sub>4</sub>NF<sub>6</sub>S<sub>10</sub>; deep green crystals; MW 724.93; mp: 144–145 °C (417–418 K); MS (FAB<sup>+</sup>-MS): *m/z* 443.93 ([C<sub>16</sub>H<sub>20</sub>S<sub>8</sub>]<sup>+</sup>); MS (FAB<sup>−</sup>-MS): *m/z* 279.92 ([C<sub>2</sub>O<sub>4</sub>NF<sub>6</sub>S<sub>2</sub>]<sup>−</sup>); Anal. Calcd. for C<sub>16</sub>H<sub>20</sub>O<sub>4</sub>NF<sub>6</sub>S<sub>10</sub>: C, 26.51; H, 2.78; N, 1.93, found: C, 26.56; H, 2.79; N, 1.80; IR (KBr): 2970 (w), 2874 (w), 1452 (w), 1419 (m), 1340 (s), 1265 (s), 1192 (s), 1055 (s), 788 (s), 616 (s) cm<sup>−1</sup>. The single crystals of [**1**<sup>•+</sup>][NTf<sub>2</sub><sup>−</sup>] were obtained by recrystallization from dichloromethane–cyclohexane (CCDC No. 2417640).

## 2.3. Density Functional Theory Calculation for the $\pi$ -Dimer of **1**<sup>•+</sup>

The total energies of dimer-A,B for **1**<sup>•+</sup> in high-spin (HS) and low-spin (LS) states were calculated using *Gaussian 16* program (Revision C.01) at the uωB97X-D/6-31g(d,p) level of theory [62]. The dimer geometries were extracted from the crystal structure. The exchange interactions were estimated using the equation proposed by Yamaguchi and coworkers:  $2J_{\text{calc}} = 2 \times ({}^{\text{LS}}E - {}^{\text{HS}}E) / ({}^{\text{HS}}\langle S_2 \rangle - {}^{\text{LS}}\langle S_2 \rangle)$  [63].

## 3. Results and Discussion

Compound [**1**<sup>•+</sup>][NTf<sub>2</sub><sup>−</sup>] was obtained from compound **1** by treatment with [**TBPA**<sup>•+</sup>][NTf<sub>2</sub><sup>−</sup>] (Scheme 1). The compound exhibited intriguing color changes associated with phase transitions between solid and liquid states during heating and cooling processes (Figure 1b). A deep green crystal of [**1**<sup>•+</sup>][NTf<sub>2</sub><sup>−</sup>] was obtained by recrystallization from a dichloromethane/cyclohexane mixture. Upon heating to 144–145 °C (417–418 K), the crystal transformed into a brown liquid state. Subsequently, cooling the liquid to 115 °C (388 K) induced a return to the green solid state. Notably, thermogravimetric analysis (TGA) revealed no weight loss below 200 °C (473 K) under aerated conditions (1% weight loss at 211 °C (484 K)), indicating that [**1**<sup>•+</sup>][NTf<sub>2</sub><sup>−</sup>] did not decompose during the phase transitions (Figure 2a). The phase transitions were also observed as a peak at 141 °C (414 K) and 114 °C (387 K) in temperature-dependent differential scanning calorimetry (DSC) measurements (Figure 2b) [64,65].



**Scheme 1.** Synthesis of [**1**<sup>•+</sup>][NTf<sub>2</sub><sup>−</sup>].

The electronic spectra of [**1**<sup>•+</sup>][NTf<sub>2</sub><sup>−</sup>] in the solid and liquid states revealed significant differences in photophysical properties within the visible and near-infrared (NIR) regions (Figure 3). In the solid state, [**1**<sup>•+</sup>][NTf<sub>2</sub><sup>−</sup>] exhibited broad absorption between the visible to NIR regions, with  $\lambda_{\text{max}}$  values at 420 nm and 740 nm, and a shoulder band at 900 nm

(Figure 3a) [66]. The spectrum is similar to that of TTF radical cation having  $\pi$ -dimer structures [56], suggesting that  $1^{\bullet+}$  forms the similar  $\pi$ -dimer structure in the green solid state. Upon heating to 150 °C (423 K) to generate the liquid state, new absorptions appeared with a  $\lambda_{\max}$  at 440 nm, a shoulder band at 534 nm, and another  $\lambda_{\max}$  at 810 nm (Figure 3a). The spectrum in the visible and NIR regions resembled that of  $[1^{\bullet+}][NTf_2^-]$  in a dilute dichloromethane solution (Figure 3b), suggesting that  $1^{\bullet+}$  exists as monomers in the brown liquid state.

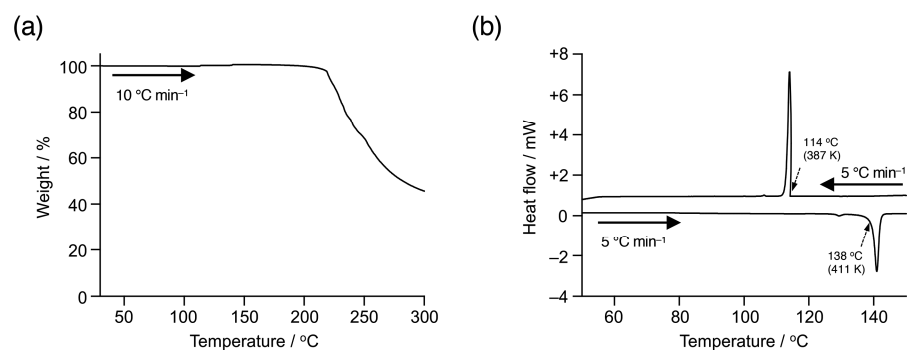


**Figure 2.** (a) Thermogravimetric diagram of  $[1^{\bullet+}][NTf_2^-]$  (scan rate = 10 °C min<sup>−1</sup>). (b) Differential scanning calorimetry diagrams of  $[1^{\bullet+}][NTf_2^-]$  during heating and cooling processes (scan rate = 5 °C min<sup>−1</sup>). The onset temperatures of the phase transitions during heating and cooling were found to be 138 °C and 114 °C, respectively.

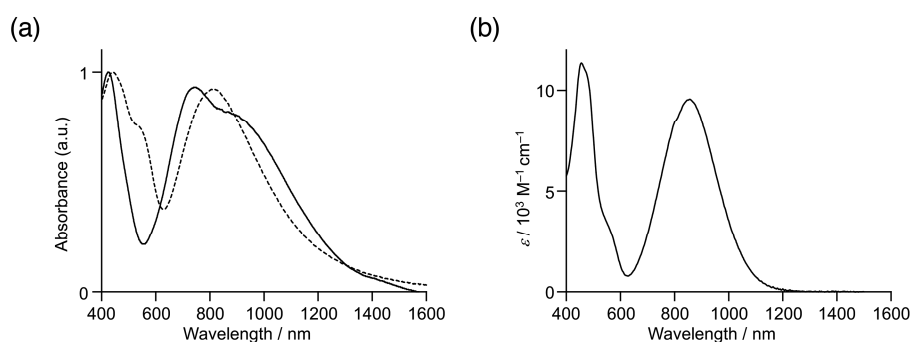


**Figure 3.** Electronic spectra of  $[1^{\bullet+}][NTf_2^-]$  for (a) the solid (at 30 °C (303 K), KBr pellet, solid line) and liquid states (at 150 °C (423 K), placed between quartz glasses, broken line) and (b) in  $CH_2Cl_2$  solution ( $2.87 \times 10^{-4}$  M).

Electron spin resonance (ESR) spectra of  $[1^{\bullet+}][NTf_2^-]$  provided important insights into the associated structures of  $1^{\bullet+}$  species (Figure 4). The ESR signal corresponding to  $1^{\bullet+}$  species appeared upon the phase transition from the green solid to the brown liquid. The significantly lower intensity of the ESR signal in the solid state at 50 °C (323 K) compared to that in the liquid state at 150 °C (423 K) indicated that  $1^{\bullet+}$  forms a singlet dimer structure in the solid state and exists as monomer species in the liquid state (Figure 4a). The ESR intensities above the melting point were found to slightly increase up to 190 °C (463 K), suggesting the existence of a dimer/monomer equilibrium (Figure S2).

A detailed investigation of the ESR spectra in the solid state revealed that signals originating from the thermally excited triplet species of  $1^{\bullet+}$  dimer at 80 °C (353 K) were observed (Figure 4b inset). These signals were successfully simulated using the following parameters:  $g_{xx} = 2.018$ ,  $g_{yy} = 2.003$ ,  $g_{zz} = 2.003$ ,  $|D/hc| = 0.0140$  cm<sup>−1</sup>, and  $|E/hc| = 0.000384$  cm<sup>−1</sup>. The zero-field splitting parameters were similar to those of  $NTf_2^-$  salt of tetrakis(*n*-propyl)tetrathiafulvalene radical cation recrystallized from dichloromethane/hexane, which were  $|D/hc| = 0.0138$  cm<sup>−1</sup> and  $|E/hc| = 0.000366$  cm<sup>−1</sup> [56]. These values are attributed to the thermally excited triplet species for a  $\pi$ -dimeric associated species of  $1^{\bullet+}$ .

Thus, the results suggest that  $1^{\bullet+}$  in  $[1^{\bullet+}][NTf_2^-]$  forms a  $\pi$ -dimer structure similar to that of the *n*-propyl analog. The observation is also consistent with the conclusions drawn from the electronic spectra. Finally, we estimated the exchange interaction ( $2J/k_B$ ) between the spins on the dimer species in the solid form to be  $-3.55(6) \times 10^3$  K using the singlet–triplet model based on the temperature dependence of the signal intensities (Figure 4b).

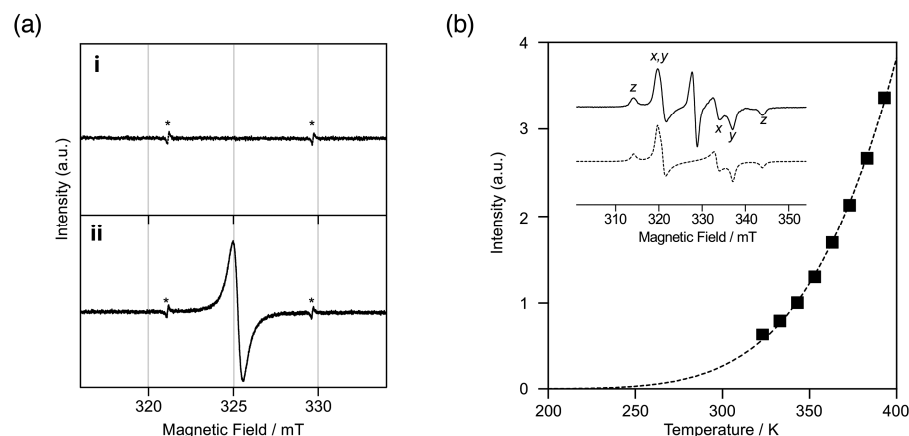


**Figure 4.** (a) ESR spectra of  $[1^{\bullet+}][NTf_2^-]$  in (i) the solid (at 50 °C (323 K); microwave frequency = 9.1403 GHz) and (ii) the liquid (at 150 °C (423 K); microwave frequency = 9.1403 GHz). The asterisks denote signals assigned to  $Mn^{2+}$  marker. (b) Temperature-dependent relative intensities (filled square) of the ESR spectra for  $[1^{\bullet+}][NTf_2^-]$  in the solid sample assigned to the thermally excited triplet species. The broken line represents the simulated curve calculated using the singlet–triplet model with  $-3.55(6) \times 10^3$  K. Inset: observed (at 80 °C (353 K), solid line; microwave frequency = 9.2097 GHz) and simulated (broken line) ESR spectra of the spin-allowed transition for  $[1^{\bullet+}][NTf_2^-]$  in the solid state. Assignments of the canonical orientations are denoted by *x*, *y*, and *z*. The signal at 330 mT originated from the spin-doublet species. The parameters for simulations are as follows;  $g_{xx} = 2.018$ ,  $g_{yy} = 2.003$ ,  $g_{zz} = 2.003$ ,  $|D/hc| = 0.0140$  cm<sup>−1</sup>, and  $|E/hc| = 0.000384$  cm<sup>−1</sup>.

Single-crystal X-ray structure analysis of  $[1^{\bullet+}][NTf_2^-]$  was conducted to elucidate the associated structure of  $1^{\bullet+}$  species in the solid state (Figure 5). The analysis revealed that  $1^{\bullet+}$  units form two kinds of crystallographically independent  $\pi$ -dimers, dimer-A and dimer-B. These  $\pi$ -dimer structures are quite similar. The distances between sulfur atoms in the  $\pi$ -dimer units, based on the crystal structure geometry, were found to be ca. 3.3–3.4 Å, which is shorter than the sum of the van der Waals radii of sulfur atoms (3.7 Å) [67]. The exchange interaction between  $1^{\bullet+}$  units in the  $\pi$ -dimer was calculated using density functional theory (DFT) and determined to be  $-4.45 \times 10^3$  K (for dimer-A) and  $-4.90 \times 10^3$  K (for dimer-B) (Table 1) [62,63]. The experimentally estimated exchange interaction, based on temperature-dependent ESR, was in good agreement with the calculated one, demonstrating that the  $\pi$ -dimerization significantly contributed to the diamagnetic properties of  $1^{\bullet+}$ .

**Table 1.** Calculated total energies of dimer-A,B for  $1^{\bullet+}$  in high-spin (HS) and low-spin (LS) states, and the calculated exchange interaction<sup>1</sup>.

|                      | Spin State         | <i>E</i> /Hartree | $\langle S^2 \rangle$ | $2J_{\text{calc}}/k_B/\text{K}$ |
|----------------------|--------------------|-------------------|-----------------------|---------------------------------|
| dimer-A <sup>2</sup> | HS ( <i>S</i> = 1) | −7460.5179844     | 2.021808              | −4453                           |
|                      | LS ( <i>S</i> = 0) | −7460.5275252     | 0.668801              |                                 |
| dimer-B <sup>2</sup> | HS ( <i>S</i> = 1) | −7460.4126425     | 2.022636              | −4897                           |
|                      | LS ( <i>S</i> = 0) | −7460.4238986     | 0.570847              |                                 |

<sup>1</sup> The calculations were carried out using the *Gaussian 16* program at the *uw97xd/6-31g(d,p)* level of theory [62], using an equation which was proposed by Yamaguchi and coworkers:  $2J_{\text{calc}} = 2 \times ({}^{\text{LS}}E - {}^{\text{HS}}E)/({}^{\text{HS}}\langle S^2 \rangle - {}^{\text{LS}}\langle S^2 \rangle)$  [63]. <sup>2</sup> The geometries of the dimer were extracted from the crystal structure.

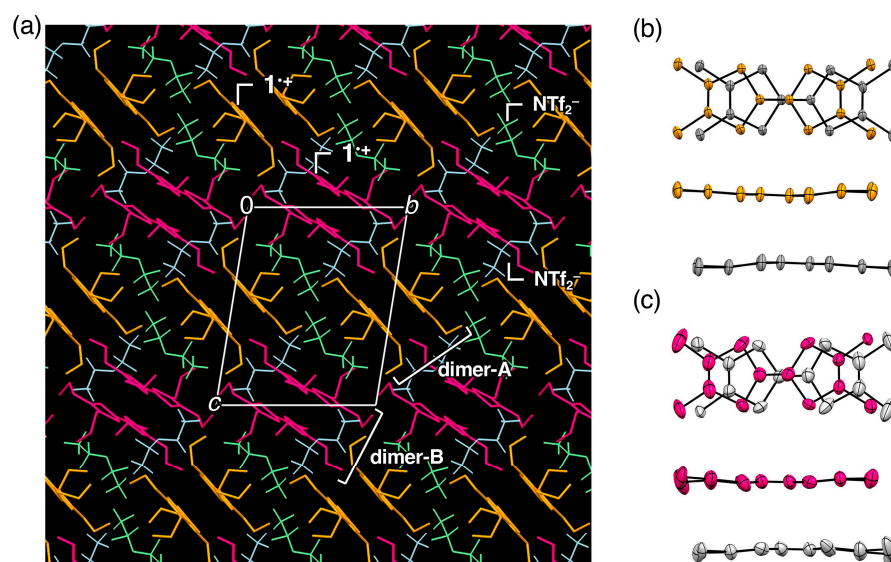


**Figure 5.** (a) Perspective view of the packing of  $[1^{\bullet+}][\text{NTf}_2^-]$  in the crystal structure along the *a*-axis. Two types of crystallographically independent  $1^{\bullet+}$  and  $\text{NTf}_2^-$  units are shown in orange and reddish-purple, light green and light blue, respectively. (b,c) ORTEP views of the stacking modes of (b) dimer-A and (c) dimer-B, respectively. The gray molecular units are located behind the front ones, which are denoted by the colors.

The changes in the physical properties of  $[1^{\bullet+}][\text{NTf}_2^-]$  can be explained by the following proposed mechanism (Figure 6). In the initial green solid state,  $1^{\bullet+}$  species form the diamagnetic  $\pi$ -dimer units (Figure 6I). The formation of the  $\pi$ -dimer structure is clearly evidenced by the results of single-crystal structure analysis and further supported by the observation of thermally excited triplet species in the ESR spectra. Upon heating above 144 °C (417 K), compound  $[1^{\bullet+}][\text{NTf}_2^-]$  transforms into the brown liquid state. In this ionic liquid state, compound  $[1^{\bullet+}][\text{NTf}_2^-]$  exhibits a paramagnetic property due to the presence of  $1^{\bullet+}$  monomers, as confirmed by measurements of the ESR spectra (Figure 6II). The electronic spectrum of  $[1^{\bullet+}][\text{NTf}_2^-]$  in the liquid state closely resembles that in solution, strongly suggesting the dissociation of the  $\pi$ -dimer structures. Cooling below 115 °C triggers the liquid–solid phase transition, inducing the association of monomers into the diamagnetic  $\pi$ -dimer units (Figure 6I). These results suggest that  $\text{NTf}_2^-$  ions, with high conformational flexibility, influence the dissociation and association behavior of  $1^{\bullet+}$  species in response to temperature changes.

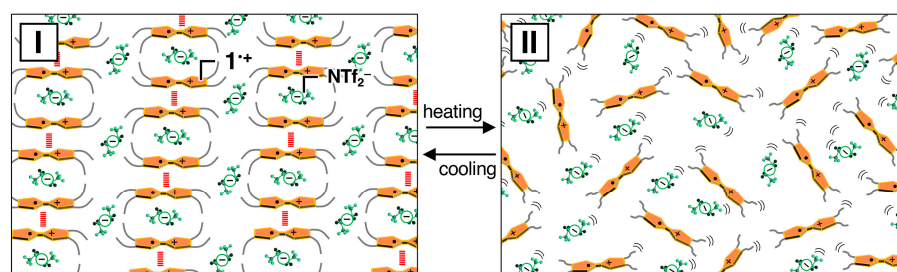


**Figure 6.** Schematic representation of the mechanism underlying the changes in the magnetic and photophysical properties of  $[1^{\bullet+}][\text{NTf}_2^-]$ . Phases I and II represent the diamagnetic crystalline (solid) and paramagnetic liquid states, respectively. Units in orange and light green color denote  $1^{\bullet+}$  and  $\text{NTf}_2^-$  molecules.

## 4. Conclusions

We reported a liquescent TTF radical cation salt,  $[1^{\bullet+}][NTf_2^-]$ , that undergoes reversible transformations between a diamagnetic solid and a paramagnetic liquid through a cycle of heating and cooling, accompanied by significant changes in photophysical properties. Radical cation salt  $[1^{\bullet+}][NTf_2^-]$  demonstrates remarkable thermal stability, even at high temperatures in an air atmosphere. These intriguing magnetic and photophysical properties are attributed to the dynamic dissociation and association of  $1^{\bullet+}$  species, facilitated by the incorporation of flexible  $NTf_2^-$  counterions.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemistry7020032/s1>, Figure S1: Microwave power dependence of ESR signal intensity for  $[1^{\bullet+}][NTf_2^-]$ , Figure S2: Temperature dependence of ESR signal intensity for  $[1^{\bullet+}][NTf_2^-]$ .

**Author Contributions:** Conceptualization, S.S.; methodology, S.S.; validation, T.S., S.K., T.N. and S.S.; formal analysis, T.S. and S.S.; investigation, T.S. and S.S.; data curation, T.S. and S.S.; writing—original draft preparation, S.S.; writing—review and editing, T.S., S.K., T.N. and S.S.; supervision, T.N. and S.S.; project administration, S.S.; funding acquisition, S.S. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The original contributions presented in the study are included in the article/Supplementary Materials, and further inquiries can be directed to the corresponding author.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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65. The TGA and DSC measurements also revealed that the results were consistent even when using samples prepared at different times.
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