



|              |   |
|--------------|---|
| Title        | Stimuli-Induced Controls of Magnetic and Photophysical Properties Using Liquescent Open-Shell Ionic Molecular Systems |
| Author(s)    | Suzuki, Shuichi; Tanaka, Ritsuki; Shu, Ruifeng et al.   |
| Citation     | ChemPlusChem. 2024, 89(7), p. e202400132  |
| Version Type | VoR   |
| URL          | <a href="https://hdl.handle.net/11094/95746">https://hdl.handle.net/11094/95746</a>                                   |
| rights       | This article is licensed under a Creative Commons Attribution 4.0 International License.                              |
| Note         |   |

*The University of Osaka Institutional Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

# Stimuli-Induced Controls of Magnetic and Photophysical Properties Using Liquescent Open-Shell Ionic Molecular Systems

Shuichi Suzuki,<sup>\*,[a]</sup> Ritsuki Tanaka,<sup>[a]</sup> Ruifeng Shu,<sup>[a]</sup> and Takeshi Naota<sup>[a]</sup>

This study explores the remarkable properties of liquescent open-shell ionic molecular systems, emphasizing the magnetic and photophysical characteristics arising from their associated structures in the condensed state under various conditions. Well-investigated open-shell molecules, namely, phenothiazine, dihydrophenazine, and tetrathiafulvalene radical cations, and bis(malononitriledithiolato)nickel(III) anionic complexes were

examined, and the concept of liquescent open-shell ionic molecular systems was devised. Transformations in their associated structures are induced by external stimuli, resulting in significant variations in their physical properties. These experimental findings open new avenues for exploring and applying stimuli-responsive molecule-based materials.

## 1. Introduction

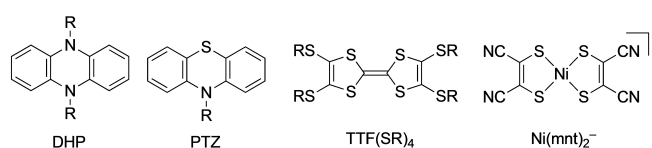
Open-shell molecular compounds have garnered considerable attention in both fundamental and applied research because they exhibit intriguing functionalities derived from their spin, redox, and photophysical properties.<sup>[1–6]</sup> The associated structures of these compounds exert profound influences on their magnetic,<sup>[1,5]</sup> electric,<sup>[2]</sup> and photophysical properties.<sup>[5,6]</sup> In solution, certain open-shell molecules exhibit dynamic changes in their spin and photophysical properties, attributed to their associated and dissociated characteristics.<sup>[7]</sup> These remarkable species could serve as molecule-based functional materials that exhibit simultaneous modulations of magnetic and electronic properties. This applicability depends on whether their associated structures in the condensed states would undergo changes induced by external stimuli and/or environmental factors. Such phenomena have been observed in studies using open-shell molecules, where the related properties exhibit diverse variations depending on the associated structures.<sup>[8]</sup> However, these stimuli-responsive systems generally require prolonged stimulation to alter the entire surface area of the compounds. In addition, the stimulated states require dissolution using an appropriate solvent to return to their initial states. This is due to the restricted conformational and translational motion of the molecular units in the condensed states. Recently, we attempted to establish methods to overcome the restrictions on the motion of molecules, even in condensed states, and to promote changes in their alignments in the entire

system triggered by external stimuli and/or environments.<sup>[9]</sup> These systems have the potential for application in new materials, allowing the precise control of physical properties to develop highly sophisticated magnetic materials,<sup>[11]</sup> advanced optical filters,<sup>[10]</sup> and multifunctional materials with multiple channels.<sup>[11]</sup> To understand these intriguing properties under ambient conditions, we have revisited well-investigated and stable open-shell ionic molecules (Scheme 1), dihydrophenazine (DHP),<sup>[5b,9,12]</sup> phenothiazine (PTZ),<sup>[5a,12,13]</sup> and tetrakis(alkylthio)-substituted tetrathiafulvalene [TTF(SR)<sub>4</sub>] radical cations,<sup>[14]</sup> and bis(malononitriledithiolato)nickel(III) anionic complex [Ni(mnt)<sub>2</sub>]<sup>−</sup>.<sup>[15]</sup> Accordingly, we have postulated that liquescent salt systems,<sup>[16]</sup> composed of open-shell ionic molecules and flexible counter ions are promising candidates for new stimuli-responsive materials. Within these systems, transformations of the condensed states are projected to cause significant changes in their associated structures without any solution state, as described below (Figure 1):

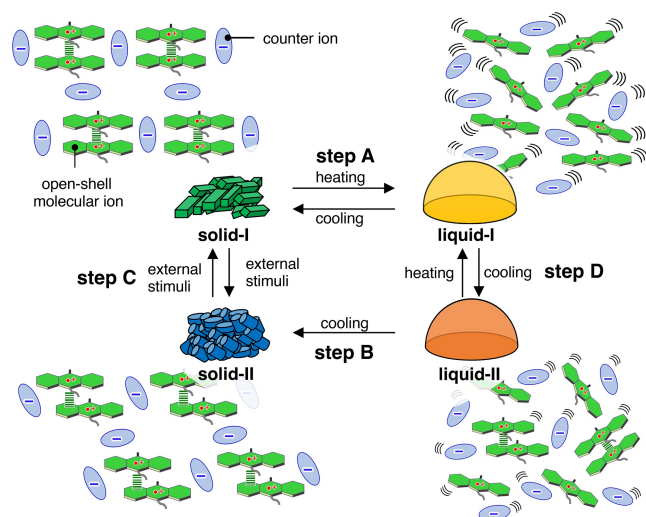
- Step A: Solid-liquid phase transitions upon heating/cooling;
- Step B: Liquid-solid phase transition upon cooling, kinetically generating associated structures from the liquid state;
- Step C: Solid-solid phase transition, wherein the kinetically generated associated structures change to thermodynamically stable configurations owing to external stimuli, including environmental changes;
- Step D: Thermal equilibrium with different associated structures in the liquid state.

[a] Prof. Dr. S. Suzuki, R. Tanaka, R. Shu, Prof. Dr. T. Naota  
Department of Chemistry, Graduate School of Engineering Science,  
Osaka University  
Toyonaka, Osaka, 560-8531, Japan  
E-mail: suzuki.shuichi.es@osaka-u.ac.jp

© 2024 The Authors. ChemPlusChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.



**Scheme 1.** Chemical structures of dihydrophenazine (DHP), phenothiazine (PTZ), and tetrakis(alkylthio)-substituted tetrathiafulvalene [TTF(SR)<sub>4</sub>], and bis(malononitriledithiolato)nickel(III) complex [Ni(mnt)<sub>2</sub>]<sup>−</sup>.



**Figure 1.** Schematic representations for associated structures of open-shell ionic molecules and counter ions in condensed states (for instance, radical cationic species). The green broken lines denote intermolecular interactions between the open-shell species.

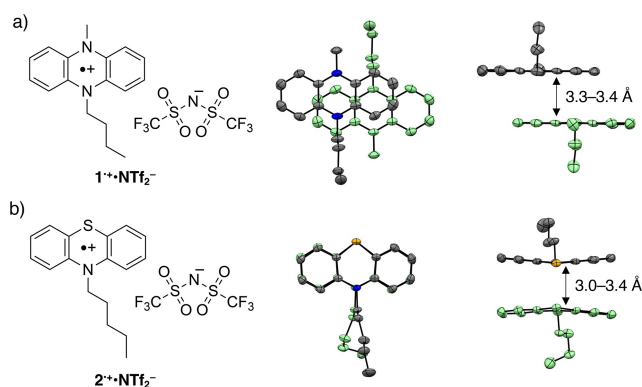
These transformations are expected to induce drastic changes in the physical properties related to the intermolecular interactions of the open-shell species and counter ions. Herein, we present recent findings on liquescent open-shell ionic molecular systems.<sup>[9,17–22]</sup>

## 2. Liquescent DHP and PTZ Radical Cation Salts

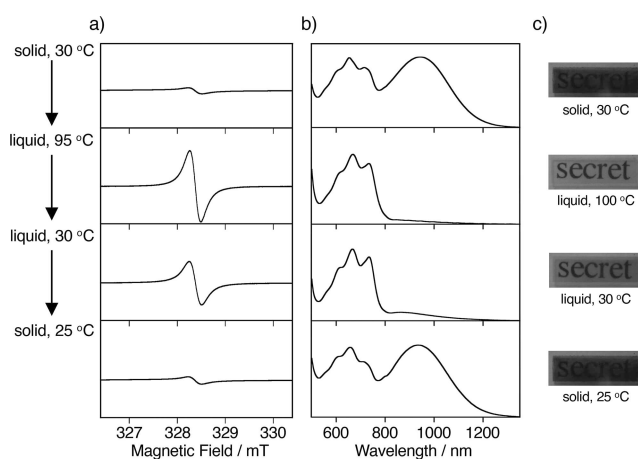
Under certain conditions, DHP and PTZ radical cations can adopt associated structures in condensed states, such as  $\pi$ -bonded dimers ( $\pi$ -dimers). In contrast to the monomeric form,  $\pi$ -dimers exhibit distinct optical absorptions and magnetic properties due to pronounced intermolecular interactions. We hypothesize that modulating functionalities derived from associated structures of radical cation species are achievable by inducing deformation and/or dissociation of  $\pi$ -dimer structures through external stimuli or environmental changes, even in condensed states. A significant challenge arises from the difficulties associated with the mobility of molecular species within such states, as highlighted in the introduction. To

overcome this issue, we developed a methodology that leverages solid-liquid phase transitions, capitalizing on the inherent stability of radical cations. Consequently, compounds  $1^{+\bullet} \cdot \text{NTf}_2^-$  and  $2^{+\bullet} \cdot \text{NTf}_2^-$  ( $\text{NTf}_2^-$ : bis(trifluoromethanesulfonyl)imide ion),<sup>[23]</sup> in which the radical cations formed  $\pi$ -dimer structures (Figure 2), were found to melt under ambient conditions. Furthermore, they exhibited significant changes in their photophysical and magnetic properties, as outlined by a process involving steps A, B, and C (Figure 1).<sup>[17,18]</sup>

In the case of  $1^{+\bullet} \cdot \text{NTf}_2^-$ , its magnetic and near-infrared (NIR) absorption properties underwent significant changes during the solid-liquid phase transitions with hysteretic behavior (Figure 3).<sup>[17]</sup> Compound  $1^{+\bullet} \cdot \text{NTf}_2^-$  transformed from the solid state, exhibiting weak electron spin resonance (ESR) signals, to an ESR-active liquid at 95 °C (Figure 3a). Polarized optical microscopy (POM) images of the liquid were dark,



**Figure 2.** Chemical structures and Oak Ridge Thermal-Ellipsoid Plot (ORTEP) views of their  $\pi$ -dimer structures for a)  $1^{+\bullet} \cdot \text{NTf}_2^-$  and b)  $2^{+\bullet} \cdot \text{NTf}_2^-$ . The figures at the side of the chemical structures are ORTEP views. The frameworks colored light green are located at behind and bottom for the top and side views, respectively. Images in Figure 2 are reproduced from Ref. [9] with modifications and permission from the Society of Synthetic Organic Chemistry, Japan.



**Figure 3.** a) ESR and b) electronic spectra of  $1^{+\bullet} \cdot \text{NTf}_2^-$  on changing the temperature. The y-axis denotes arbitrary units. c) Photographs showing the transparency of  $1^{+\bullet} \cdot \text{NTf}_2^-$  thin film under irradiation of 940 nm LED light. The images in Figure 3 are reproduced from Ref. [9] and Ref. [17] with modifications and permission from Wiley-VCH and the Society of Synthetic Organic Chemistry, Japan.



Shuichi Suzuki received his Ph.D. in 2006 from Osaka University under the supervision of Prof. Dr. Kazuhiro Nakasuji and Prof. Dr. Yasushi Morita. In 2006, he moved to Osaka City University as Assistant Professor. Then he was promoted to Lecturer in 2010 at Osaka City University. In 2015, he moved to Osaka University as Associate Professor. His current research interests focus on developing molecule-based assemblies with exotic physical properties and functions based on syntheses of organic molecules and organic-inorganic hybrid materials.

suggesting that the solid changed to an isotropic liquid phase. The liquid persisted after cooling to 30 °C, transforming into the ESR-inactive solid state at 25 °C. In addition, the phase transitions were accompanied by changes in the electronic spectra (Figure 3b). A robust NIR absorption band was observed in the solid state, but not in the liquid state or solution, demonstrating that the band is attributable to the  $\pi$ -dimers. Additionally, observations in the liquid state revealed the generation of monomers through the dissociation of the  $\pi$ -dimers. We also achieved controlled readability of letters under 940 nm-light by using  $1^{++} \cdot \text{NTf}_2^-$  (Figure 3c). This change in letter readability has potential applications for security filters and inks.<sup>[24]</sup>

The phase transition behavior of  $2^{++} \cdot \text{NTf}_2^-$  was notably different from that of  $1^{++} \cdot \text{NTf}_2^-$  (Figure 4). Compound  $2^{++} \cdot \text{NTf}_2^-$  exhibited distinctive color changes in conjunction with phase transitions (Figure 4a).<sup>[18]</sup> A green crystal of  $2^{++} \cdot \text{NTf}_2^-$  was transformed into an orange liquid upon heating to 100 °C. Upon cooling to 50 °C, the orange liquid changed to an orange solid, which gradually transformed into a green solid at 30 °C. Interestingly, the orange solid state changed to the green solid state upon indirect mechanostress, whereas the orange solid state remained unchanged without mechanostress at 50 °C. These phase transitions were not observed for other counterions. Therefore, the  $\text{NTf}_2^-$  ion is important for developing distinctive phase transitions.

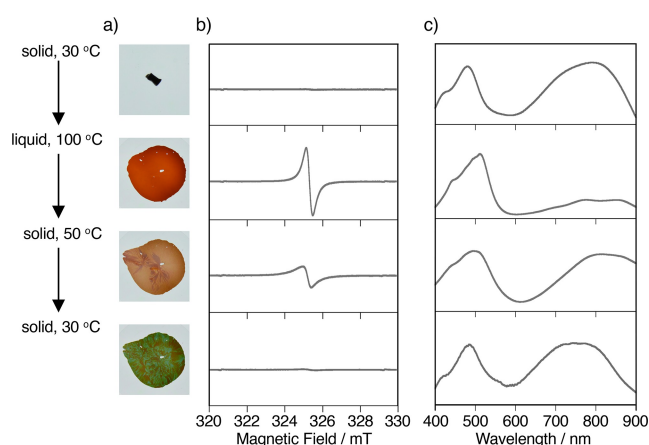
The magnetic properties of  $2^{++} \cdot \text{NTf}_2^-$  also changed significantly during the phase transition (Figure 4b). The ESR signal of the initial green solid was extremely weak, whereas it was visible in the orange liquid state. The orange solid obtained by cooling the liquid state was found to be in the ESR-active state, whereas the green solid generated by further cooling was in the ESR-inactive state. These observations indicate that (i) radical cation  $2^{++}$  in the green solid states formed  $\pi$ -dimer with strong antiferromagnetic interactions; (ii) radical cation  $2^{++}$  in the orange liquid and solid states interacted weakly with each other. The electronic spectra also demonstrated the formation

of  $\pi$ -dimers in the green solid and monomers in the orange liquid (Figure 4c). In the kinetically-generated orange solid state, radical cation  $2^{++}$  was expected to form an offset stacking dimer based on the experimental results of other analogues of the PTZ radical cation salts.<sup>[18]</sup>

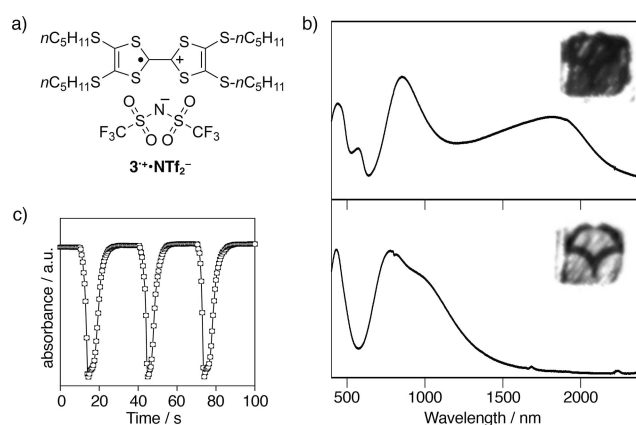
### 3. TTF(SR)<sub>4</sub> Radical Cation Salt Exhibiting Low Melting Points

The liquescent salts of the DHP and PTZ radical cations showed unprecedented changes in their physical properties in the neat liquid state, as described previously. Accordingly, we hypothesized that the associated structures in open-shell ionic molecular systems with low melting points would facilitate the deformation of their configuration by external stimuli, including environmental changes, even in the solid state at room temperature (illustrated as step C in Figure 1). We focused on TTF(SR)<sub>4</sub> radical cations to observe these phenomena.<sup>[14]</sup> These radical cations associate and form columnar structures through  $\pi$ - $\pi$  interactions and S-S contacts. Furthermore, the electronic spectra of the TTF(SR)<sub>4</sub> radical cations depend on these associated structures. Consequently, our investigations revealed that  $3^{++} \cdot \text{NTf}_2^-$ , melted at 68–70 °C, showed rapid transparent property changes in the NIR (700–1000 nm) and short-wave infrared (SWIR: 1000–2500 nm) regions (Figure 5).<sup>[19]</sup>

The photophysical characteristics of  $3^{++} \cdot \text{NTf}_2^-$  in the solid states were investigated using electronic spectral measurements under ambient conditions and dichloromethane vapor (Figure 5b). Initially, compound  $3^{++} \cdot \text{NTf}_2^-$  exhibited strong absorption bands from the visible to the NIR/SWIR regions under ambient conditions. Exposure to dichloromethane vapor resulted in the disappearance of absorption in the SWIR region. Upon the cessation of exposure, the electronic spectrum reverts to its initial state (Figure 5c). The electronic spectra before and



**Figure 4.** a) Photographs of  $2^{++} \cdot \text{NTf}_2^-$  under white light during phase transitions on changing the temperature. Temperature-dependent b) ESR and c) electronic spectra of  $2^{++} \cdot \text{NTf}_2^-$  in the corresponding states. The images in Figure 4 are reproduced from Ref. [9] with modifications and permission from the Society of Synthetic Organic Chemistry, Japan.

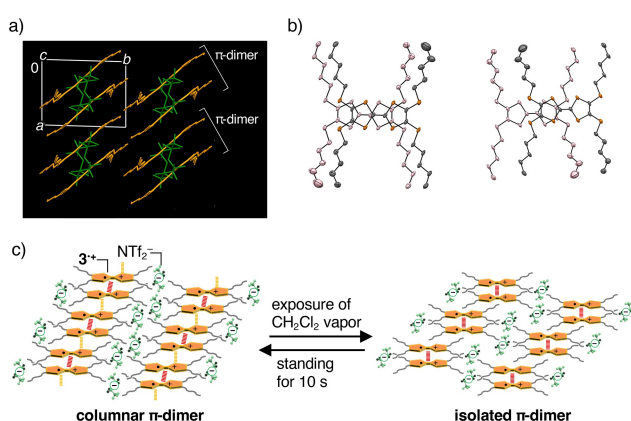


**Figure 5.** a) Chemical structure of  $3^{++} \cdot \text{NTf}_2^-$ . b) Electronic spectra without (top) and with (bottom) exposure to dichloromethane vapor. The y-axis denotes arbitrary units. The inset figures show photographs using the SWIR detection camera using 1450-nm light under ambient (top) and dichloromethane vapor (bottom). c) Time profile of the absorbance at 1650 nm detected by optical waveguide spectrometry. The images in Figure 5 are reproduced from Ref. [19] with modification and permission from Wiley-VCH.

after exposure to dichloromethane vapor differed from those of  $3^{++} \cdot \text{NTf}_2^-$  in dichloromethane solution, confirming that the SWIR absorption is attributable to the associated structures of  $3^{++}$ .

The crystal structure analyses of  $3^{++} \cdot \text{NTf}_2^-$  revealed the formation of a columnar  $\pi$ -dimer structure (Figure 6). The radical cations exhibited efficient overlap, providing sufficient proximity for interactions between the radical cations (Figure 6b). Similar chromic behaviors were observed in other TTF(SR)<sub>4</sub> radical cation salts, forming columnar  $\pi$ -dimer structures. Therefore, the columnar  $\pi$ -dimer structure emerges as a pivotal motif contributing to the chromic behaviors. Additionally, the electronic spectrum of  $3^{++} \cdot \text{NTf}_2^-$  under exposure to dichloromethane vapor was similar to those of the TTF(SR)<sub>4</sub> radical cation salts, which formed isolated  $\pi$ -dimer structures.<sup>[19]</sup> These experimental findings suggested that the SWIR-transparency/absorption of  $3^{++} \cdot \text{NTf}_2^-$  in the solid states was modulated by the structural transformations of the associated structure with transitions between columnar and isolated  $\pi$ -dimer structures under the corresponding conditions.

We then visualized the rapid changes in the SWIR absorption/transparency of  $3^{++} \cdot \text{NTf}_2^-$  by using the solid film prepared from the liquid state (Figure 5b, inset). Placing the solid film of  $3^{++} \cdot \text{NTf}_2^-$  on a paper depicting the Osaka University logo rendered the logo invisible under 1450-nm light. Upon exposing the solid film to dichloromethane vapor for several seconds, the logo became visible under 1450-nm light. The subsequent cessation of dichloromethane vapor exposure restored the initial invisible state. A change in the transparency was also observed under mechanostress, which was achieved by scratching the surface with a steel spatula.<sup>[19]</sup>

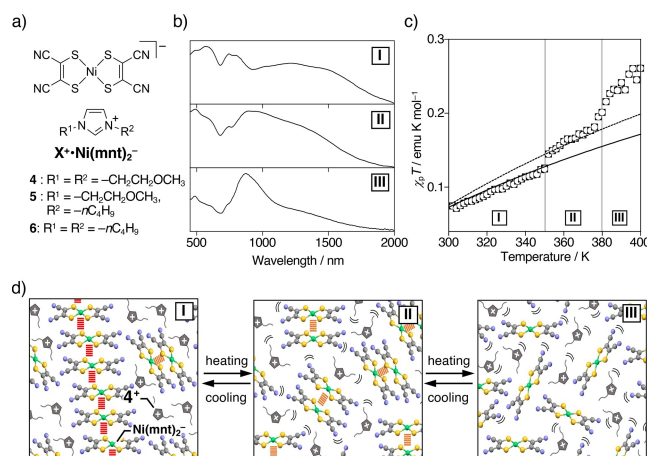


**Figure 6.** a) Packing of  $3^{++} \cdot \text{NTf}_2^-$  in the crystal along the *c* axis. Molecular frameworks of radical cation species and counter ions are shown in orange and green colors. b) ORTEP views of the stacking modes of intra- $\pi$ -dimer (left) and inter- $\pi$ -dimer (right). The pink frameworks are located behind the front ones. c) Proposed associated structures during changes in SWIR light transparency for  $3^{++} \cdot \text{NTf}_2^-$ . The red and orange broken lines denote interactions in intra- $\pi$ -dimer and inter- $\pi$ -dimer. The images in Figure 6 are reproduced from Ref. [19] with modification and permission from Wiley-VCH.

## 4. Liquescent Ni(mnt)<sub>2</sub> Anion Salt

The liquescent salts with DHP and PTZ radical cations exhibited monomer behavior in the liquid state. The development of liquescent open-shell ionic molecules capable of manipulating their associated structure, even in the liquid state under specific conditions, represents a crucial pursuit for multi-stage control of spin and related functionalities (illustrated as step D in Figure 1). Open-shell ionic molecular species with stronger intermolecular interactions are promising candidates for controlling the associated structures in liquid states. However, these species are generally considered to have high melting points. To address this challenge, we devised a solution involving a combination of imidazolium ions as counter cations owing to their ease of design and synthesis and anionic open-shell metal complexes as stable spin sources with aggregated properties. Consequently, we focused on salts of imidazolium ions and the anionic metal complex, Ni(mnt)<sub>2</sub>.<sup>[15]</sup> We found that nickel salt  $4^+ \cdot \text{Ni}(\text{mnt})_2^-$  exhibited changes in the electronic spectra even in the SWIR-region through solid-liquid phase changes and shifts of the dimer-monomer equilibrium in the liquid state achieved via temperature modulations (Figure 7).<sup>[20]</sup>

The electronic spectra of  $4^+ \cdot \text{Ni}(\text{mnt})_2^-$  showed stepwise changes in the SWIR photophysical properties (Figure 7b). In the solid state, complex  $4^+ \cdot \text{Ni}(\text{mnt})_2^-$  exhibited broad absorption bands from 1800 nm to the visible-light region (State-I). Upon heating to 90 °C, it transformed into a liquid state (State-II), accompanied by a slight blue-shift in absorption compared to State-I. Furthermore, the electronic spectra changed upon further heating to 150 °C (State-III), characterized by weak absorption in the SWIR region.<sup>[25]</sup> Intriguingly, the electronic spectra in State-II and -III were similar to those of  $5^+ \cdot \text{Ni}(\text{mnt})_2^-$  and  $6^+ \cdot \text{Ni}(\text{mnt})_2^-$  in the solid state, respectively. Therefore, crystal structure analyses provided insights into the underlying



**Figure 7.** a) Chemical structure of  $4^+ \cdot \text{Ni}(\text{mnt})_2^-$ ,  $5^+ \cdot \text{Ni}(\text{mnt})_2^-$ , and  $6^+ \cdot \text{Ni}(\text{mnt})_2^-$ . b) Electronic spectra in State-I, -II, -III (top to bottom), respectively, measured at 30, 90, and 150 °C. c) Temperature-dependent  $\chi_p T$  plots of  $4^+ \cdot \text{Ni}(\text{mnt})_2^-$ . The solid and dashed line show simulation based on singlet-triplet models. d) Proposed associated structures of  $4^+ \cdot \text{Ni}(\text{mnt})_2^-$  in State-I, -II, and -III. The red and orange broken lines show intra-columnar and intra-dimer interactions, respectively. The images in Figure 7 are reproduced from Ref. [20] with modification and permission from Wiley-VCH.



mechanisms of the spectral changes. Comparative analyses of the packing in the crystals revealed that the  $\text{Ni}(\text{mnt})_2^-$  species in  $4^+ \cdot \text{Ni}(\text{mnt})_2^-$ ,  $5^+ \cdot \text{Ni}(\text{mnt})_2^-$  and  $6^+ \cdot \text{Ni}(\text{mnt})_2^-$  formed columnar, dimer, and monomer structures, respectively. These structural variations probably account for the broad SWIR absorptions observed in the longer-wavelength regions of State-I and -II, which are attributable to the columnar and dimer structures of the  $\text{Ni}(\text{mnt})_2^-$  entities. Additionally, the NIR absorption of State-III was ascribed to the monomer structure of the  $\text{Ni}(\text{mnt})_2^-$  unit.

The magnetic susceptibility measurements provided additional insights into the changes in the SWIR absorption of  $4^+ \cdot \text{Ni}(\text{mnt})_2^-$  (Figure 7c). The  $\chi_p T$  values in State-I gradually increased upon heating. This value increased abruptly at the melting point. Subsequently, the  $\chi_p T$  values in State-II gradually increased again upon heating. Then, the  $\chi_p T$  values in State-III further increased again on heating. The observed  $\chi_p T$  values in State-I and -II were smaller than the calculated value for the  $S = 1/2$  system, suggesting the presence of considerable antiferromagnetic interactions between the  $\text{Ni}(\text{mnt})_2^-$  species. The  $\chi_p T$ - $T$  curves for State-I and -II can be reproduced using the appropriate singlet-triplet models. These results indicate that the chromic behavior in the SWIR region was due to a sequential dissociation of the associated structures of the  $\text{Ni}(\text{mnt})_2^-$  species as follows (Figure 7d): dissociation from columnar to dimer structures during the solid-liquid phase transition (State-I to State-II), followed by a shift of the dimer-monomer equilibrium in the liquid state (State-II to State-III).

## 5. Summary and Outlook

Herein, we propose stimuli-responsive functionalities using liquescent open-shell ionic molecular systems. The platforms of these species are known to be stable. By incorporating certain substituents and flexible counter ions into conventional open-shell ionic entities, we revealed unprecedented functionalities arising from solid-liquid phase transitions and unusual condensed states generated from the liquid states. In particular, changes in magnetic and NIR/SWIR transparency/absorption properties derived from the spins and singly-occupied molecular orbitals of the open-shell molecular species have not been achieved by chemical species with closed-shell entities, such as typical organic compounds. Our experimental results indicate that the conformational and translational dynamics of the molecular units in the liquescent open-shell ionic molecular systems remain unimpeded in both liquid and solid states, as evidenced by the significant conversions of the functionalities prompted by comparatively weak stimuli. These findings can pave the way for developing intricately designed molecular architectures with functionalities previously deemed unattainable under standard ambient conditions.

## Acknowledgements

This work was supported by JSPS KAKENHI (grant numbers, JP20H02692 and JP21H05486 to S.S.), and Tokyo Ohka Foundation for The Promotion of Science and Technology (to S.S.). We thank Dr. Hiroyasu Sato (Rigaku Corporation) for the help of the X-ray crystal structure analysis, Prof. Dr. Yoshiaki Uchida (Osaka University) for measurements of the ESR spectra, Prof. Dr. Daisuke Shiomi for measurements of the magnetic susceptibility, and Dr. Hiromi Takahashi (ATR Scientists Partners Inc.) for helpful discussions about optical waveguide spectroscopy.

## Conflict of Interests

The authors declare no conflict of interest.

**Keywords:** Liquescent molecular system · Open-shell compounds · Magnetic Property · Photophysical property · Stimuli-responsive material

- [1] a) *Magnetism: Molecules to Materials II* (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**; b) C. Shu, Z. Yang, A. Rajca, *Chem. Rev.* **2023**, *123*, 11954.
- [2] a) S. K. Pal, M. E. Itkis, F. S. Tham, R. W. Reed, R. T. Oakley, R. C. Haddon, *Science* **2005**, *309*, 281; b) T. Sugawara, H. Komatsu, K. Suzuki, *Chem. Soc. Rev.* **2011**, *40*, 3105; c) T. Suemune, K. Sonoda, S. Suzuki, H. Sato, T. Kusamoto, A. Ueda, *J. Am. Chem. Soc.* **2022**, *144*, 21980.
- [3] a) Y. Morita, S. Nishida, T. Murata, M. Moriguchi, A. Ueda, M. Satoh, K. Arifuku, K. Sato, T. Takui, *Nat. Mater.* **2011**, *10*, 947; b) K. Hatakeyama-Sato, K. Oyaizu, *Chem. Rev.* **2023**, *123*, 11336.
- [4] S. Nishida, Y. Morita, K. Fukui, K. Sato, D. Shiomi, T. Takui, K. Nakasuji, *Angew. Chem. Int. Ed.* **2005**, *44*, 7277.
- [5] a) T. Tahara, S. Suzuki, M. Kozaki, D. Shiomi, K. Sugisaki, K. Sato, T. Takui, Y. Miyake, Y. Hosokoshi, H. Nojiri, K. Okada, *Chem. Eur. J.* **2019**, *25*, 7201; b) A. Nagata, S. Hiraoka, S. Suzuki, M. Kozaki, D. Shiomi, K. Sato, T. Takui, R. Tanaka, K. Okada, *Chem. Eur. J.* **2020**, *26*, 3166.
- [6] a) Y. Ikabata, G. Wang, T. Yoshikawa, A. Ueda, T. Murata, K. Kariyazono, M. Moriguchi, H. Okamoto, Y. Morita, H. Nakai, *npj Quantum. Mater.* **2017**, *2*, 27; b) J. S. Park, J. Park, Y. J. Yang, T. T. Tran, I. S. Kim, J. L. Sessler, *J. Am. Chem. Soc.* **2018**, *140*, 7598.
- [7] a) J.-M. Lü, S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2003**, *125*, 12161; b) S. Suzuki, Y. Morita, K. Fukui, K. Sato, D. Shiomi, T. Takui, K. Nakasuji, *J. Am. Chem. Soc.* **2006**, *128*, 2530; c) T. Nishinaga, Y. Sotome, *J. Org. Chem.* **2017**, *82*, 7245.
- [8] a) T. Kobashi, D. Sakamaki, S. Seki, *Angew. Chem. Int. Ed.* **2016**, *55*, 8634; b) K. Oda, S. Hiroto, H. Shinokubo, *J. Mater. Chem. C* **2017**, *5*, 5310; c) T. Nishiuchi, S. Aibara, H. Sato, T. Kubo, *J. Am. Chem. Soc.* **2022**, *144*, 7479.
- [9] S. Suzuki, M. Kozaki, T. Naota, *J. Synth. Org. Chem. Jpn.* **2022**, *80*, 843.
- [10] I. H. Song, C. H. Rhee, S. H. Park, S. L. Lee, D. Grudin, K. H. Song, J. Choe, *Org. Process Res. Dev.* **2008**, *12*, 1012.
- [11] M. E. Itkis, X. Chi, A. W. Cordes, R. C. Haddon, *Science* **2002**, *296*, 1443.
- [12] K. Yoshida, S. Suzuki, M. Kozaki, K. Okada, *Bull. Chem. Soc. Jpn.* **2019**, *92*, 1902.
- [13] a) D. Sun, S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2004**, *126*, 1388; b) S. Suzuki, K. Yoshida, M. Kozaki, K. Okada, *Angew. Chem. Int. Ed.* **2013**, *52*, 2499; c) I. S. Pereteanu, T. J. J. Müller, *Org. Biomol. Chem.* **2013**, *11*, 5127; d) A. Karimata, S. Suzuki, M. Kozaki, K. Okada, *RSC Adv.* **2017**, *7*, 56144.
- [14] *TTF Chemistry* (Eds.: J. Yamada, T. Sugimoto) Kodansha, Tokyo, **2004**.
- [15] a) P. I. Clemenson, *Coord. Chem. Rev.* **1990**, *106*, 171; b) N. Robertson, L. Cronin, *Coord. Chem. Rev.* **2002**, *227*, 93.
- [16] The open-shell ionic molecular systems reported here are found to show solid-liquid phase transitions. The tending toward liquid states, so-called *liquescent* properties, enable us to focus on the properties of the designed salts in both solid and ionic liquid states. Thus, we used

- the terms such as “*liquescent salt*” and “*liquescent open-shell ionic molecular system*” in this paper.
- [17] S. Suzuki, D. Yamaguchi, Y. Uchida, T. Naota, *Angew. Chem. Int. Ed.* **2021**, *60*, 8284.
- [18] S. Suzuki, R. Maya, Y. Uchida, T. Naota, *ACS Omega* **2019**, *4*, 10031.
- [19] S. Suzuki, T. Sakai, S. Takagi, T. Naota, *Angew. Chem. Int. Ed.* **2023**, *62*, e202308570.
- [20] S. Suzuki, R. Shu, T. Naota, *Small* **2024**, *20*, 2305668.
- [21] Some other fluid open-shell molecules with localized spin-systems have been reported to show interesting physical properties. For instance, a) Y. Uchida, S. Oki, R. Tamura, T. Sakaguchi, K. Suzuki, K. Ishibashi, J. Yamauchi, *J. Mater. Chem.* **2009**, *19*, 6877; b) S. Nakagami, T. Akita, D. Kiyohara, Y. Uchida, R. Tamura, N. Nishiyama, *J. Phys. Chem. B* **2018**, *122*, 7409; c) T. Inagaki, T. Mochida, *Chem. Lett.* **2010**, *39*, 572; d) T. Inagaki, T. Mochida, M. Takahashi, C. Kanadani, T. Saito, D. Kuwahara, *Chem. Eur. J.* **2012**, *18*, 6795; e) Y. Funasako, T. Mochida, T. Inagaki, T. Sakurai, H. Ohta, K. Furukawa, T. Nakamura, *Chem. Commun.* **2011**, *47*, 4475; f) T. Tominaga, T. Mochida, *Chem. Eur. J.* **2018**, *24*, 6239.
- [22] There are a few examples of radical ionic systems with low melting points. See, following references; a) V. A. Starodub, E. M. Gluzman, K. I. Pokhodnya, M. Y. Valakh, *Theor. Exp. Chem.* **1994**, *29*, 240; b) A. Otsuka, G. Saito, *Synth. Met.* **1988**, *27*, B575; c) K. Nishimura, G. Saito, *Synth. Met.* **2005**, *153*, 385; d) G. Saito, Y. Yoshida, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1.
- [23] a) T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2015**, *115*, 11379; b) K. Dong, X. Liu, H. Dong, X. Zhang, S. Zhang, *Chem. Rev.* **2017**, *117*, 6636; c) *Ionic Liquids Completely Uncoiled* (Eds.: N. V. Plechkova, K. R. Seddon) John Wiley & Sons, Inc., New Jersey, **2015**.
- [24] a) M. Yousaf, M. Lazzouni, *Dyes Pigm.* **1995**, *27*, 297; b) P. M. Beaujuge, S. Ellinger, J. R. Reynolds, *Nat. Mater.* **2008**, *7*, 795; c) R. J. Mortimer, *Annu. Rev. Mater. Res.* **2011**, *41*, 241; d) K. Tahara, T. Kadowaki, J.-i. Kikuchi, Y. Ozawa, S. Yoshimoto, M. Abe, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 1630.
- [25] The images of polarized optical microscopy (POM) of State-II and -III were dark, suggesting that these states were found to be in isotropic liquid phases.

---

Manuscript received: February 15, 2024

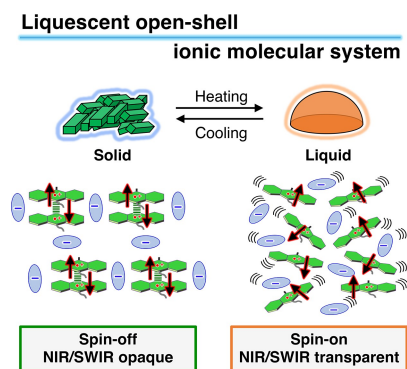
Revised manuscript received: March 28, 2024

Accepted manuscript online: March 28, 2024

Version of record online: ■■, ■■

## CONCEPT

This concept presents liquescent open-shell ionic molecular systems that exhibit fascinating switching magnetic and near-IR/short-wave-IR absorption/transparency properties by external stimuli under condensed and ambient conditions. These property variations originate from the significant transformations of their associated structures caused by phase transitions or related state changes.



*Prof. Dr. S. Suzuki\*, R. Tanaka, R. Shu,  
Prof. Dr. T. Naota*

1 – 7

**Stimuli-Induced Controls of  
Magnetic and Photophysical Proper-  
ties Using Liquescent Open-Shell  
Ionic Molecular Systems**