

Hysteretic control of near-infrared transparency using stable radical cation

Department of Chemistry, Graduate School of Engineering Science

Associate Professor **Shuichi Suzuki**

Professor **Takeshi Naota**

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Abstract

Molecules that absorb near-infrared (near-IR) light (over 700 nm) have attracted as fundamental components of various practical applications, such as information-storage materials, optical filters, and security inks. In this study, we have succeeded in developing aggregates of radical cations that exhibit drastic changes in near-IR transparency by temperature control.

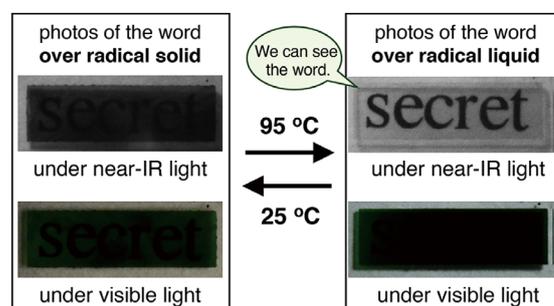
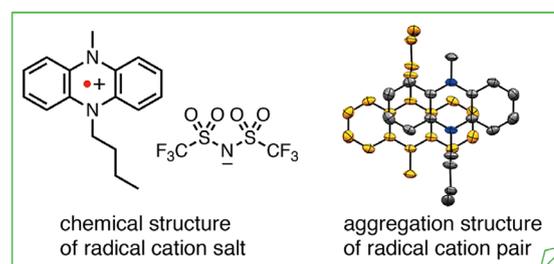
Background & Results

Radicals are chemical species that are used as reagents for organic synthetic reactions such as polymerization and intramolecular cyclization reactions. Their high reactivity generally promotes the disappearance of their unique functionality in the aggregated state. Fortunately, recent developments in related chemistry enabled us to design radical pairs exhibiting interesting electronic and magnetic properties derived from their unusual electronic structures. It is possible to modulate the radical function when the radicals consisting of the radical pair can be displaced even in condensed states. However, it is generally difficult to change the structure in the condensed state where molecular motions are remarkably restricted. We have succeeded in overcoming this difficulty by utilizing liquescent radical cations, and have found new properties of the radical molecules.

Radical molecules frequently exhibit long-wavelength absorption properties because of existence of the singly-occupied molecular orbitals. Furthermore, the radical pair species are known to show longer wavelength absorption until near-IR region due to the existence of relatively strong inter-radical interactions. We considered that molecule-based materials with controllable properties of near-IR absorption/transmission could be created when the changes in the structures of the radical pair could be induced by external stimuli/environment. Consequently, a bis(trifluoromethanesulfonyl) imide salt of dihydrophenazine radical cation was found to show hysteretic phase transitions over a wide-temperature range with drastic changes in the near-IR transparency under neat and ambient conditions without changes in visible color. During the heating and slow cooling process, its electronic and magnetic properties were altered clearly and repeatedly changed between solid and liquid states. The liquid state was transparent to near-IR light, but the solid state was opaque, despite both samples exhibiting a similar green color under room light. This feature allowed us to control visibility and legibility using visible and near-IR light under specific temperature conditions. UV/vis/near-IR and electron spin resonance spectroscopies revealed that these drastic changes were attributable to the dynamic dissociation and association of the π -dimer structure of the radical cation accompanying with the solid-liquid phase transitions even under the condensed conditions.

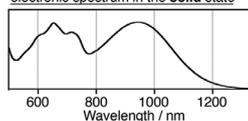
Significance of the research and Future perspective

By providing near-IR optical properties with “forward” and “backward” directional responses to stimuli, it is possible to achieve highly-complicated information processes for invisible optical sensors and security. The radical cation can be “painted” on various media and used in on-demand sensors, because they can be melted. Furthermore, radical molecules frequently show interesting magnetic properties and electrical conductivity by external stimuli, enabling them to be applied in many fields in materials chemistry.

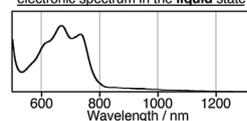


Photophysical properties

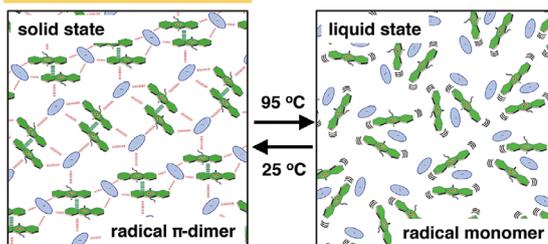
electronic spectrum in the **solid state**



electronic spectrum in the **liquid state**



Model of radical aggregate



Patent

Treatise

URL

Keyword

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<http://www.chem.es.osaka-u.ac.jp/soc/>
<https://youtube.com/playlist?list=PLAb-4nGLCCqs1uJkBWLSOcyudMOia7IcV>

open-shell molecule, stimuli responsiveness, liquescent molecule, near-IR property