Creation of Novel Photonic-Electronic-Magnetic Functions Based on Molecules with Open-Shell Electronic Structures

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The molecules with open-shell electronic states can exhibit unique properties, which are difficult to achieve for conventional closed-shell molecules. Our group develops new open-shell organic molecules (= radicals) and metal complexes to create novel photonic-electronic-magnetic functions.

While conventional closed-shell luminescent molecules have been extensively studied as promising components for organic light-emitting devices, the luminescent properties of radicals have been much less studied because of its rarity and low chemical (photo-)stability. We have developed a novel luminescent organic radical PyBTM, which is highly stable at ambient condition and in the photoexcited state. We have also discovered that (i) PyBTM-doped molecular crystals exhibit photoluminescence with a room-temperature emission quantum yield of 89%, which is exceptionally high in radicals, and (ii) the doped crystals show drastic changes in the emission spectra by applying a magnetic field. This is the first observation of the magnetoluminescence in organic radicals. Our studies provide novel and unique insights in molecular photonics, electronics, and spintronics, and also contribute to developing applied science for light-emitting devices.

Our group focuses on strongly-interacted spins in molecular crystals. The anisotropic assembly of open-shell molecules in crystalline states enables unique molecular materials with exotic electrical and magnetic properties, such as superconductors, ferromagnets, and quantum spin liquids.

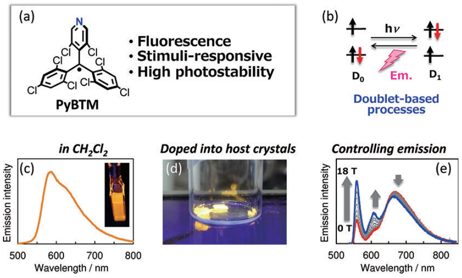

Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH_2Cl_2. (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

Selected Publications

- S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki and H. Nishihara, "Magnetoluminescence in a Photostable, Brightly Luminescent Organic Radical in a Rigid Environment," *Angew. Chem., Int. Ed.* **57**, 12711–12715 (2018).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Enhanced Luminescent Properties of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical by Coordination to Gold," *Angew. Chem., Int. Ed.* **54**, 3731–3734 (2015).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Luminescence, Stability, and Proton Response of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical," *Angew. Chem., Int. Ed.* **53**, 11845–11848 (2014).
- T. Kusamoto, H. M. Yamamoto, N. Tajima, Y. Oshima, S. Yamashita and R. Kato, "Bilayer Mott System with Cation···Anion Supramolecular Interactions Based on Nickel Dithiolene Anion Radical: Coexistence of Ferro- and Antiferro-Magnetic Anion Layers and Large Negative Magnetoresistance," *Inorg. Chem.* **52**, 4759–4761 (2013).

1. Construction of Supramolecular Two-Dimensional Network Mediated via Sulfur's σ-Holes in Conducting Molecular Crystals

Metal bis(dithiolato) complexes are attractive class of multi-functional molecular systems showing magnetic, conducting, and optical properties, such as superconductivity, ferromagnetism, quantum spin liquid, and NIR absorption. These properties depend highly on the arrangement of molecules in the solid state; therefore, controlling the arrangement (*i.e.*, crystal structure) plays a crucial role for achieving novel or desired properties. We have focused on a σ-hole bond as an efficient noncovalent supramolecular interaction to control the arrangement of metal bis(dithiolato) complexes, with a goal of developing exotic magneto-conducting phenomena in molecular system. The σ-hole bond is observed between electron-deficient region on an atomic surface, so-called σ-hole, and an electron-rich moiety in a molecule. Halogen and chalcogen atoms possess one and two σ-holes capable of forming supramolecular bonds with high directionality. We have developed novel conducting molecular solids based on platinum bis(dithiolato) complex anion radicals, $(\text{Et-4XT})_2[\text{Pt(mnt)}_2]_3$ (X = Br, I; Et-4BrT = ethyl-4-bromothiazolium, Et-4IT = ethyl-4-iodothiazolium, mnt = maleonitriledithiolato).[1,2] In their crystal structures, $\text{X}_{\text{cation}}\cdots\text{N}_{\text{anion}}$ and $\text{S}_{\text{cation}}\cdots\text{N}_{\text{anion}}$ σ-hole bonds (*i.e.*, halogen bond and chalcogen bond) were detected between the cation and the lone pairs of –CN moieties in the anion, forming a two-dimensional (2D) supramolecular network. The arrangement of the ions was similar in the two compounds (X = I and X = Br), while the orientation of the cations and the stacking manner of the anions along the direction perpendicular to the 2D supramolecular network were different (Figure 2). Such structural differences are attributed to the strength of the halogen bond, which is greater in iodine than in bromine, and resulted in distinct differences in their physical properties. For example, stronger trimerization of the anions in $(\text{Et-4IT})_2[\text{Pt(mnt)}_2]_3$ enhanced antiferromagnetic interaction between the spins on the anions. These results suggest that sulfur-mediated chalcogen bonds can be robust enough to dominate the primary arrangement of molecules and the resulted physical properties, even in the presence of the other noncovalent intermolecular interactions or even upon the atomic replacements. Sulfur-based chalcogen bonds would be effective to realize desired structures and properties in molecular materials, while understanding the hierarchy of the noncovalent interactions operated in the crystal would be important for the precise crystal engineering.

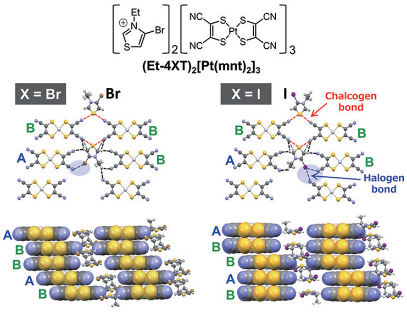

Figure 2. Chemical and crystal structures of $(\text{Et-4XT})_2[\text{Pt(mnt)}_2]_3$ (X = Br, I).

2. Magnetoluminescence as Unique Photofunctions of Open-Shell Molecules

Controlling the spin state of open-shell molecules is a promising strategy for developing unique photochemical and photophysical properties, which are difficult to realize with conventional closed-shell molecules. We have shown that PyBTM doped into α*H*-PyBTM molecular crystals demonstrates new luminescent properties for organic radicals attributed to interplay between spin and luminescence.[3] Crystals containing 10 wt% PyBTM displayed PyBTM monomer- and PyBTM excimer-centered emissions and magnetic-field-sensitive luminescence, *i.e.*, magnetoluminescence. We have revealed that changes in spin multiplicities of aggregated radicals contribute to the magnetic-field effect. To date, magnetoluminescence of stable radicals has been observed only in a few pure organic radicals. We are developing novel PyBTM-ligated metal complexes to expand the variety of materials showing magnetoluminescence behaviour, with a goal of realizing novel spin-sensitive photofunctions. We succeeded in observing excimer-like emission and magnetoluminescence behaviour in PyBTM-ligated zinc complexes doped into host crystals (Figure 3). Detailed investigations are in progress.

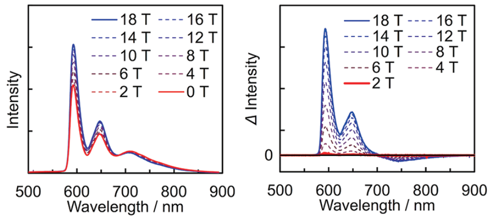

Figure 3. (left) Emission spectra of PyBTM-ligated zinc complex doped into host crystals at 4.2 K under magnetic fields. (right) Difference emission spectra (Δ intensity) under magnetic fields compared with the spectrum under 0 T.

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2) C. Ohde, T. Kusamoto and H. Nishihara, *J. Magn. Magn. Mater.* **497**, 165986 (2020).
3) S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki and H. Nishihara, *Angew. Chem., Int. Ed.* **57**, 12711–12715 (2018).

Award

KUSAMOTO, Tetsuro; Research Encouragement Award, Japan Society of Coordination Chemistry (2019).

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* carrying out graduate research on Cooperative Education Program of IMS with the University of Tokyo