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 frustrated spins in molecular crystals. The anisotropic assembly of open-shell molecules in crystalline states can afford unusual electronic states attributed to the frustrated spins, providing exotic electrical and magnetic properties.

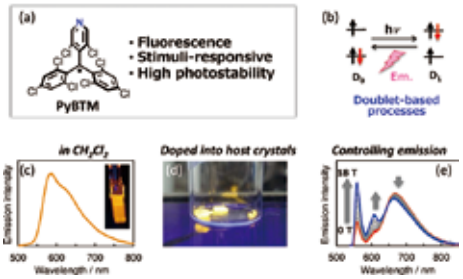

Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH_2Cl_2. (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

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. NIR Emission and Acid-Induced Intramolecular Electron Transfer Derived from a SOMO–HOMO Converted Non-Aufbau Electronic Structure

Some organic radicals violate the Aufbau principle and possess peculiar electronic structures in which the energy level of the SOMO (Singly Occupied Molecular Orbital) is formally lower than that of the highest occupied molecular orbital (HOMO). Radicals with such SOMO–HOMO converted electronic structures are attracting growing interest as promising candidates for unique stimulus-controlled molecular functions, which cannot be achieved using conventional radicals or closed-shell molecules. We prepared a novel organic radical with a SOMO–HOMO converted electronic structure, TPA-R$^{\bullet}$, a novel electron donor–acceptor hybrid of triphenylamine (an electron donor) and a stable polychlorinated diphenyl(4-pyridyl)methyl radical (an electron acceptor).[1] TPA-R$^{\bullet}$ exhibited fluorescence in the near-infrared region (λ_{max} = 910 nm) in cyclohexane from a polar intramolecular charge-transfer excited state. Cyclic voltammetry, absorption spectroscopy, and DFT calculation revealed the inversion of the SOMO and HOMO levels in the electronic structure of TPA-R$^{\bullet}$. Addition of trifluoromethanesulfonic acid to TPA-R$^{\bullet}$ caused a two-step change. Protonation initially occurred on the diphenylpyridylmethyl radical moiety to form TPA-[RH]$^{\bullet+}$. Further addition of the acid caused unprecedented intramolecular electron transfer from the triphenylamine moiety to the protonated radical moiety, generating [TPA]$^{\bullet+}$-RH. TPA-[RH]$^{\bullet+}$ and [TPA]$^{\bullet+}$-RH could be switched by changing the acidity of the solution. These results constitute the first example of the multistep switching behavior stimulated by a single external stimulus in the SOMO–HOMO converted non-Aufbau electronic structure and demonstrate its great potential for realizing unique molecular photonic and electronic functions.

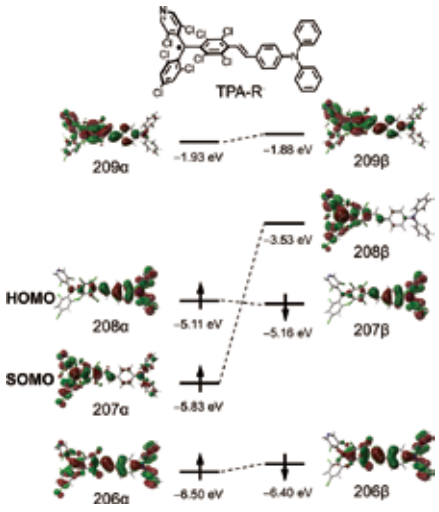

Figure 2. MO diagram of TPA-R$^{\bullet}$ calculated using DFT (uB3LYP/6-31G*).

2. 1D Cu^{II}–Radical Heterospin System: Temperature-Dependent Jahn–Teller Distortion Correlated to π-Conjugation and Magnetic Properties

Jahn–Teller (JT) and pseudo-JT distortions modulate coordination geometry around the metal ion to decrease the energy of an electronic system, thereby affecting the physical properties of materials. Controlling the JT distortion is one promising approach to develop tunable physical properties or to reveal structure–property relationships. We prepared a new class of 1D chain complexes $[Cu^{II}(hfac)_2(bisPyTM)]_n$ (hfac = hexafluoroacetylacetonato; bisPyTM[2] = bis(3,5-dichloro-4-pyridyl)(2,4,6-trichlorophenyl)methyl radical).[3] In the crystal, bisPyTM bridges two Cu^{II} ions via the nitrogen atoms to form a 1D –Cu^{II}(hfac)$_2$–bisPyTM– type zigzag chain structure (Figure 3). Importantly, the coordination geometry around the Cu^{II} atom continuously changes with temperature, where the JT axis rotates from the Cu–N1 bond direction at 298 K to the Cu–O1 bond direction at 93 K. This structural change induces changes in the mode of π-conjugation in the hfac moieties. Magnetic investigations revealed ferromagnetic (FM) interaction between spins on bisPyTM and Cu^{II}. The FM interaction was enhanced below 90 K due to the reorientation of the spin orbital (d_{x2-y2} orbital) accompanied by the rotation of the JT axis on the Cu^{II} atom. The reorientation of the spin orbitals was supported by ESR spectroscopy and DFT calculation. Namely, the JT distortion, degree of freedom of π-conjugation, and magnetic properties in $[Cu^{II}(hfac)_2(bisPyTM)]_n$ were coupled, resulting in unique temperature-dependent properties. The present study expands the scope of JT-active magnetic molecular compounds displaying controllable properties.

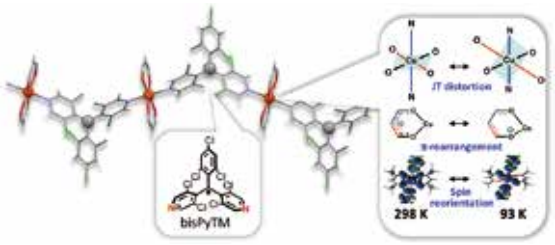

Figure 3. 1D chain structure of $[Cu^{II}(hfac)_2(bisPyTM)]_n$. CF_3 groups in the hfac ligands are omitted for clarity.

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