

# Division of Environmental Chemistry – Molecular Materials Chemistry –

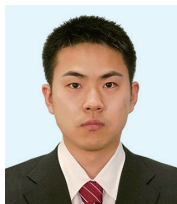
<http://molmat.kuicr.kyoto-u.ac.jp/index-e.html>



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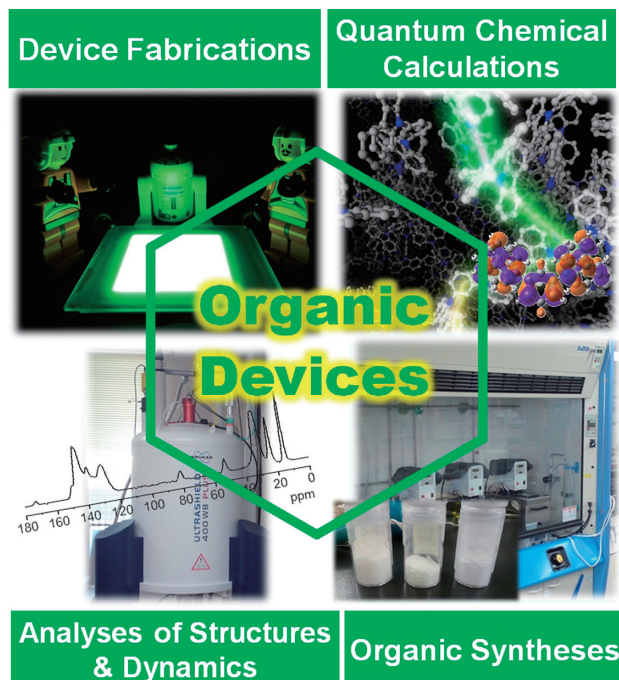
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## Scope of Research

Our research goal is to develop high-performance organic electroluminescence devices, organic solar cells, and polymer materials. Toward this, we carry out syntheses, device fabrications, precise structure characterizations, and quantum chemical calculations for high functional organic materials. Along with exploring novel synthetic routes and novel devices, we perform detailed analyses of structures and dynamics, mainly by sophisticated solid-state NMR spectroscopy, in order to obtain structure–dynamics–property relationships.

### KEYWORDS

Organic Light-Emitting Diodes  
Solid-State NMR  
Quantum Chemical Calculation  
Amorphous Materials  
Dynamic Nuclear Polarization Enhanced NMR



## Recent Selected Publications

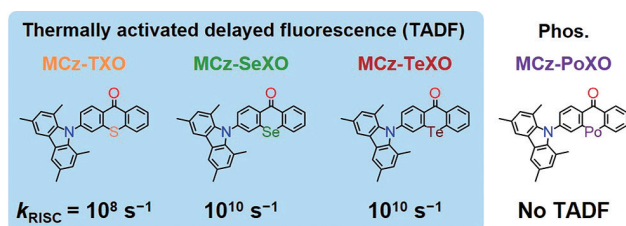
Shizu, K.; Ren, Y.; Kaji, H., Promoting Reverse Intersystem Crossing in Thermally Activated Delayed Fluorescence via the Heavy-Atom Effect, *J. Phys. Chem. A*, **127**, 439–449 (2023).

Tanaka, H.; Mizuhata, Y.; Tokitoh, N.; Miyamoto, R.; Kanamori, K.; Kaji, H., Multiple Stimuli-Responsive Supramolecular Organic Framework under Concomitant Emission Color Changes, *J. Phys. Chem. C*, **127**, 20459–20465 (2023).

Suzuki, K.; Kaji, H., Torsion Angle Analysis of a Thermally Activated Delayed Fluorescence Emitter in an Amorphous State Using Dynamic Nuclear Polarization Enhanced Solid-State NMR, *J. Am. Chem. Soc.*, **145**, 16324–16329 (2023).

## Promoting Reverse Intersystem Crossing in Thermally Activated Delayed Fluorescence via the Heavy-Atom Effect

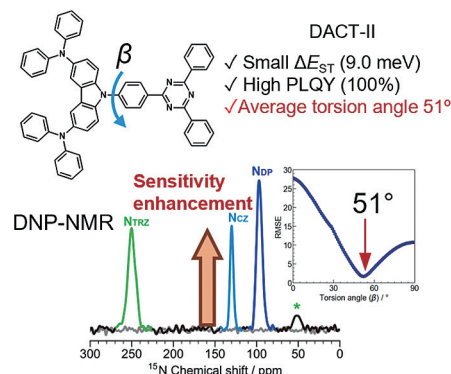
Fast reverse intersystem crossing (RISC) in thermally activated delayed fluorescence (TADF) is an effective approach to improving the device lifetime of organic light-emitting diodes. In this study, we reported the heavy-atom effect on TADF and a molecular design for accelerating RISC. We reproduced all the relevant rate constants of a sulfur-containing molecule ( $k_{\text{RISC}}$  of  $10^8 \text{ s}^{-1}$ ) using density functional theory and revealed the role of the heavy-atom effect on the rapid RISC. Then, we predicted much larger  $k_{\text{RISC}}$  ( $>10^{10} \text{ s}^{-1}$ ) for selenium- and tellurium-containing molecules. We also predicted that a polonium-containing molecule would promote phosphorescence without exhibiting TADF, indicating that a too strong heavy-atom effect is disadvantageous for achieving both rapid RISC and efficient TADF. A moderate heavy-atom effect was found to be essential for fast RISC in TADF.



**Figure 1.** Promoting Reverse Intersystem Crossing in Thermally Activated Delayed Fluorescence.

## Torsion Angle Analysis of a Thermally Activated Delayed Fluorescence Emitter in an Amorphous State Using Dynamic Nuclear Polarization Enhanced Solid-State NMR

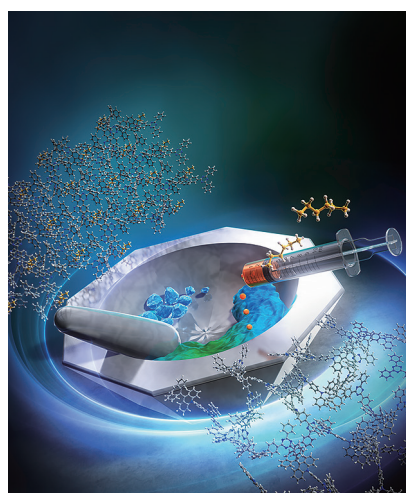
The torsion angle between donor and acceptor segments of a thermally activated delayed fluorescence (TADF) molecule is one of the most critical factors in determining the performance of TADF-based organic light-emitting diodes (OLEDs) because the torsion angle affects not only the energy gap between the singlet and triplet but also the oscillator strength and spin-orbit coupling. However, the torsion angle is difficult to analyze, because organic molecules are in an amorphous state in OLEDs. Here, we determined the torsion angle of a highly efficient TADF emitter, DACT-II, in an amorphous state by dynamic nuclear polarization-enhanced solid-state NMR measurements. From the experimentally obtained chemical shift principal values of  $^{15}\text{N}$  on carbazole, we determined the average torsion angle to be  $52^\circ$ . Such quantification of the torsion angles in TADF molecules in amorphous solids will provide deep insight into the TADF mechanism in amorphous OLEDs.



**Figure 2.** Torsion angle analysis of TADF emitter by DNP-NMR.

## Multiple Stimuli-Responsive Supramolecular Organic Framework under Concomitant Emission Color Changes

A stimuli-responsive luminophore embedding an overcrowded bistricyclic aromatic ene structure with a heptagon=hexagon central ring, DCHA-TRZ, has been designed and synthesized. In a single-crystalline solid, DCHA-TRZ constructed a supramolecular organic framework (SOF) including *n*-hexane molecules as a guest molecule. The crystalline SOF ( $\alpha$  phase) exhibited reversible crystalline ( $\alpha$ )-to-amorphous-to-crystalline ( $\alpha$ ) solid-state phase transitions triggered by external stimuli of mechanical grinding and treatment with a *n*-hexane solvent, in which release and inclusion of the guest molecules played an important role. Moreover, the thermal annealing of the amorphous ground solid afforded a bluish green-emitting solid with a different crystalline phase ( $\beta$ ). The combination of the three external stimuli of the mechanical grinding, thermal annealing and solvent treatment enables the reversible and cyclical phase transitions among three solid-state phases (crystalline  $\alpha$ ,  $\beta$  and amorphous) under concomitant emission color changes.



**Figure 3.** Multiple stimuli-responsive SOF under concomitant emission color changes on the mortar.