Organic electronic materials, Organic magnetic materials

Triplet diradical cation with near-infrared emission

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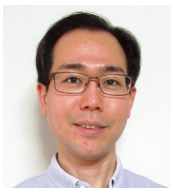


Abstract

Luminescent organic molecules have attracted attention as materials for organic light-emitting diodes and sensing devices. In addition to typical closed-shell molecules, luminescent organic radicals have recently been studied. On the other hand, triplet diradicals with two unpaired electrons aligned have attracted attention as magnetic materials. However, their optical properties remained to be clarified due to their high reactivity and instability, and only two triplet diradicals emitting UV-visible light have been reported to date.

We previously succeeded in designing and synthesizing a triangulene derivative, a triplet polycyclic hydrocarbon. In this study, we designed and synthesized a nitrogen-doped triangulene cation by replacing the central carbon atom of the triangulene derivative with a nitrogen cation. The nitrogen-doped triangulene cation had similar magnetic properties to the triangulene derivative but showed significantly different optical properties, exhibiting near-infrared absorption and emission.

Background & Results

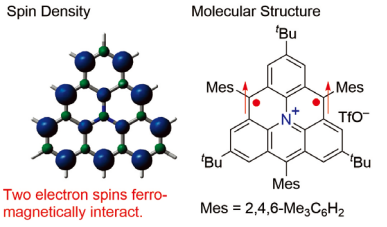
Luminescent organic molecules have attracted attention as materials for organic light-emitting diodes and sensing devices. In addition to typical closed-shell molecules, luminescent organic radicals have recently been studied. On the other hand, triplet diradicals with two unpaired electrons aligned have attracted attention as magnetic materials. However, their optical properties remained to be clarified due to their high reactivity and instability, and only two triplet diradicals emitting UV-visible light have been reported to date.

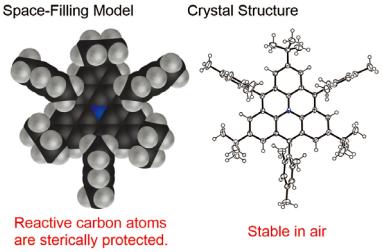
We previously succeeded in designing and synthesizing a triangulene derivative, a triplet polycyclic hydrocarbon, and experimentally elucidated that the two unpaired electrons aligned even at room temperature. In this study, we designed and synthesized a nitrogen-doped triangulene cation by replacing the central carbon atom of the triangulene derivative with a nitrogen cation to generate a stable triplet diradical. The nitrogen-doped triangulene cation was stable in air, and had similar magnetic properties to the triangulene derivative: two electrons were delocalized over the periphery of the molecule and aligned even at room temperature. The nitrogen-doped triangulene cation exhibited near-infrared absorption at 815 nm and emission at 846 nm because of its rigid core structure.

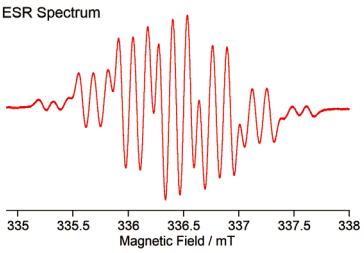
Quantum chemical calculations showed that the characteristic optical properties were caused by breaking the alternancy symmetry of triangulene by nitrogen doping, making the T_0–T_1 transition allowed. The doping of a nitrogen cation to triplet hydrocarbons would be a promising method to generate triplet diradical cation with magnetic properties similar to the parent hydrocarbons but with different optical properties.

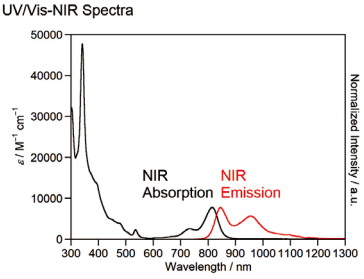
Significance of the research and Future perspective

This is the first study of a triplet diradical with near-infrared emission. On the basis of this study, various luminescent triplet diradicals would be generated, leading to the creation of functional organic materials with characteristic optical and magnetic properties.









Patent

Treatise Arikawa, Shinobu; Shimizu, Akihiro; Shintani, Ryo et al. A kinetically stabilized nitrogen-doped triangulene cation: Stable and NIR fluorescent diradical cation with triplet ground state. Angew. Chem., Int. Ed. 2023, 62(29), e202302714. doi: 10.1002/anie.202302714

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Keyword magnets, spins, radicals, organic molecules, near-infrared absorption