Sensor, Smart device

Development of diradical molecules exhibiting spin-correlated luminescence

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Abstract

Materials with open-shell electronic structures exhibit unique photofunctions based on their various spin states (i.e., spin-correlated photofunctions). In recent years, it has become clear that the luminescence of open-shell molecules possessing unpaired electrons (i.e., organic radicals) can be modulated in response to external stimuli such as magnetic fields. In this study, we designed and prepared a novel diradical emitter and found that this molecule displayed unique luminescence behavior responsive to magnetic fields and temperature at cryogenic temperatures. Detailed analysis revealed that these luminescence behaviors correlated with the magnitude of spin-spin interactions within the diradical molecule.

Background & Results

Luminescent materials with open-shell electronic structures have attracted significant attention due to their unique emission properties, which arise from the interplay between spin states and emission (i.e., spin-correlated luminescence). Recent studies have shown that open-shell molecules possessing unpaired electrons (i.e., radicals) can display distinctive emission behavior responsive to external stimuli such as magnetic fields in their aggregated states. Luminescent diradicals, which contain two spins within a single molecule, are considered useful model systems for the development and elucidation of spin-correlated emission. However, due to the limited number of reports on such systems, a comprehensive understanding of how the magnitude of intramolecular spin–spin interactions influences the emission properties of diradicals is still lacking. In this study, we synthesized a novel carbazole-containing diradical emitter **1** (Figure 1a) and investigated the magnetic-field and thermal effects on the luminescence properties of **1**.

Diradical **1** possesses a relatively large intramolecular spin–spin interaction and exhibits red emission under UV irradiation (Figure 1b). We found that diradical **1** dispersed in poly(methyl methacrylate) (PMMA) showed an increase in emission intensity under applied magnetic fields at cryogenic temperatures, i.e., a magnetic-field-responsive luminescence (Figure 2a). Furthermore, this PMMA dispersion exhibited thermally activated emission at temperatures below 100 K (Figure 2b). Comparison of the emission properties of **1** with those of a monoradical having a similar molecular skeleton suggested that the observed magnetic-field- and temperature-responsive luminescence is characteristic of diradicals. Detailed analyses revealed that the observed changes in emission intensity correlated with the magnitude of the intramolecular spin–spin interactions within the diradical molecule.

Significance of the research and Future perspective

Changes in emission properties in response to external stimuli such as magnetic fields, heat, and light have been extensively studied, as they enable potential applications in high-sensitivity imaging and sensing. In this study, we prepared a novel diradical emitter and found that the molecule exhibited pronounced emission changes in response to external magnetic fields and temperature. We also revealed that these unique photoluminescence behaviors correlated with the magnitude of the intramolecular spin–spin interaction. This study describes a novel diradical molecule displaying stimulus-responsive emission and elucidates its emission mechanism, thereby contributing to a fundamental understanding of the emission properties of luminescent radicals and demonstrating their potential as externally stimuli-responsive luminescent materials.

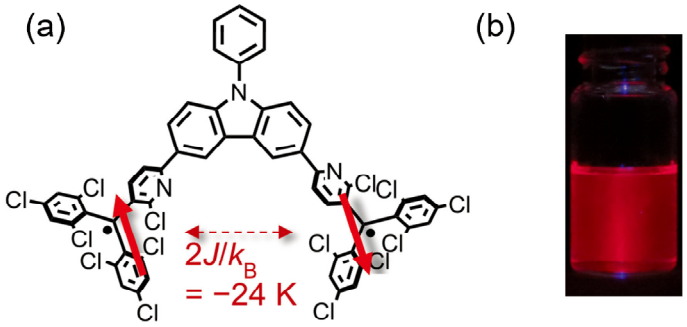

Fig. 1 (a) Structure of diradical **1** and (b) its emission under UV light.

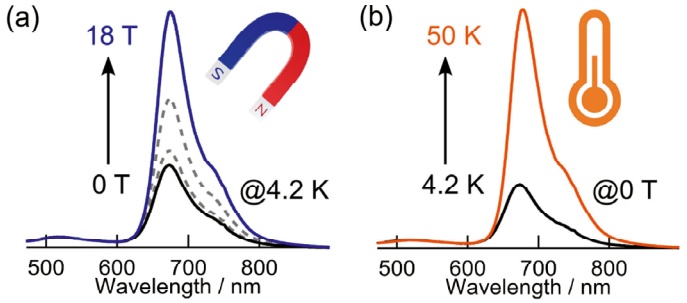

Fig. 2 Spin-correlated emission of diradical **1**: (a) magnetic field-responsive emission and (b) thermally activated emission.

Patent

Treatise Mizuno, Asato; Kusamoto, Tetsuro et al. Spin-correlated luminescence of a carbazole-containing diradical emitter: Single-molecule magnetoluminescence and thermally activated emission. J. Am. Chem. Soc. 2024, 146, 18470-18483. doi: 10.1021/jacs.4c03972

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