1-2-2. Metal Complexes

Overview

Metal complexes self-assembled due to metallophilic interactions exhibit unique photophysical properties strongly dependent on their aggregated and associated molecular structures. These features enable applications in functional molecular materials such as tunable luminescent systems and chemical sensors with molecular recognition capabilities. Recent studies have also focused on real-time observation of metal–metal bond formation and structural relaxation dynamics in photoexcited states of associated complexes.

Current Status and Frontiers

Since the 1970s, Japanese researchers have led studies in the photochemistry and photophysics of metal complexes. For an overview up to the early 2000s, refer to Section "1-2-2. Luminescent Metal Complexes" in the Photochemistry Div Report described in Japanese. URL: https://division.csj.jp/div-report/02/0210202.pdf

In recent years, research has expanded from applications in photo-functional materials to fundamental investigations of excited-state electronic structures, time evolution, and structural relaxation dynamics in aggregated and associated systems.

1. Electronic structure and photophysics of aggregated luminescent Pt(II) complexes

Aggregation of Pt(II) complexes induces overlap between 5dz² orbitals, forming Metal–Metal to Ligand Charge Transfer (MMLCT) bands in visible region. The emission wavelength from the MMLCT state is highly sensitive to the orbital overlap, facilitating applications in tunable emission, circularly polarized luminescence, and chemical sensing. Periodic MM/QM hybrid models have been proposed to understand the photophysics of one-dimensional stacked Pt complexes, with discussions on MMLCT state localization (Kato, Shinozaki, Sakaki).

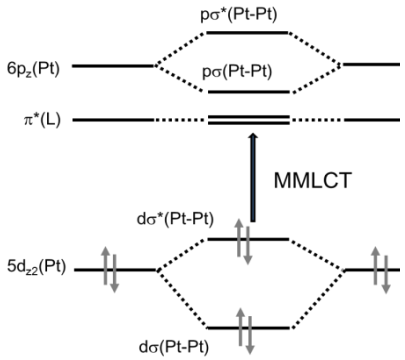

Figure 1. Schematic MO diagram for Pt(II) complex with Pt-Pt interactions.

2. Emission tuning and dynamics via association in solution

Photoexcitation of concentrated solutions of Pt(II) and Au(I) complexes induces the increase of metal-metal bonds, promoting stepwise aggregation with ground-state molecules to generate emissive oligomers. The resulting photophysical properties show strong concentration dependence, enabling applications in white-light emission and emission color tuning (Shinozaki, Iwamura).

3. Real-time observation of relaxation processes in photoexcited associates

Photoexcitation of oligomers of dicyanoaurate in aqueous solution induces electron transition from antibonding $5d_{z^2}$ orbitals to bonding $6p_z$ orbitals, causing a rapid ca. 0.5 Å shortening of Au–Au bonds. Iwamura et al. successfully observed quantum beats arising from simultaneous excitation of multiple vibrational modes and real-time structural relaxation in the excited oligomers, advancing kinetic studies of photoexcited dynamics.

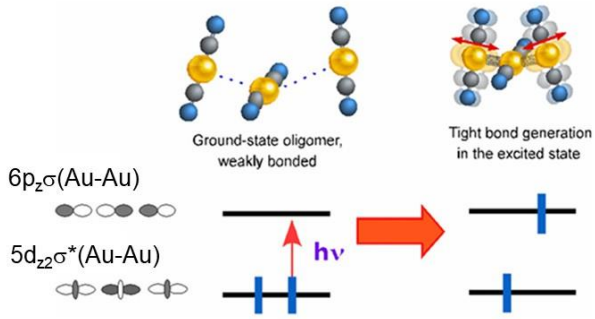

Figure 2. Tight bond formation and structural relaxation on photoexciation of ground-state oligomers of dicyanoaurate.

References

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Future Perspectives and Directions

Key challenges to be addressed within the next decade include: Development of novel luminescence materials based on 3d–4d orbital interactions. Advancement of quantum chemical models for simulating environmental responses and excited-state localization dynamics in aggregated luminescent systems. Progress in kinetic studies of excited-state structural changes and intersystem crossing rates through real-time observation.

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