

Enhancing solid-state phosphorescence in π -electronic molecules

January 31 2024

Photoluminescent molecules, capable of absorbing and re-emitting light, play an important role in the development of technologies such as light-emitting diodes, sensors, and displays. Among them, ordered arrangements of π -electronic molecules such as crystals of organoplatinum(II) complexes, where a platinum(II) ion is coordinated by organic ligands in a square-planar arrangement, stand out for their applications in energy-efficient flexible displays.

However, their luminescence in the solid state is short-lived due to the interaction between excitons (bound [electron-hole pairs](#)) of neighboring molecules. To address this issue, bulky foreign molecules are introduced into the [molecular structure](#) to prevent or minimize the electronic interactions between molecules.

Using this strategy, a research team led by Professor Hiromitsu Maeda from Ritsumeikan University, Japan, recently enhanced the solid-state phosphorescence in multiple organoplatinum(II) complexes, increasing the phosphorescence by up to 75 times.

"Spatially and electronically isolated ordered arrangement of emissive π -electronic molecules is a principal point for the preparation of emissive solid-state materials. This concept can be used in materials for organic electronics, particularly organic [light-emitting diodes](#) for flexible displays," explains Prof. Maeda.

In their study [published](#) in *Chemical Science* on December 5, 2023, the

research team synthesized dipyrrolyldiketone Pt^{II} complexes consisting of four different C^N ligands. These molecules display strong phosphorescence in solution but show extremely weak phosphorescence in the solid state due to self-association.

To enhance their luminosity in the solid state, the team introduced ion pairs consisting of a chloride anion and tetraalkylammonium counterions: TPA⁺ (tetrapropylammonium), TBA⁺ (tetrabutylammonium), and TPeA⁺ (tetrapentylammonium). This resulted in ion-pairing assemblies consisting of chloride ion-binding Pt^{II} complexes and counterions.

The [chloride ions](#) bind to the Pt^{II} complex via [hydrogen bonds](#), while the cations form layers between the π -electronic molecules. X-ray analysis confirmed the complex's rigid structure, where Pt^{II} complexes are separated by cations in charge-by-charge arrangements.

By isolating the π -electronic molecules from each other, the researchers enhanced the luminescent properties of the organoplatinum(II) complexes in the solid state. Compared to the original anion-free states where the complex is not bonded to the chloride ion, the relative intensity of phosphorescence in Cl⁻-binding Pt^{II} complexes with cations showed improvements ranging from 1% to 7.5%, a 75-fold increase over the original molecule.

The luminescence also lasts significantly longer, with certain ion-pairing assemblies achieving an emission lifetime nearly 200 times longer than the monomeric Pt^{II} complex. Theoretical studies using DFT calculations revealed that the charge-by-charge packing structure prevents the delocalization of the electron wavefunction over Pt^{II} complexes.

"To the best of our knowledge, such a room-temperature phosphorescence enhancement by anion binding and ion-pairing

assembly has not been demonstrated thus far," remarks Prof. Maeda.

Such a strategy can be used to design emissive materials and improve the phosphorescence of [solid-state materials](#) for novel applications.

"The chemistry of ion-pairing assembly of charged π -electronic molecules is a new topic in a research area of supramolecular chemistry. Understanding the interactions between charged species and the formation of assembled structures through research will affect in a further design and fabrication of functional ion-pairing assemblies such as efficient electric conductive materials, ferroelectric materials, and chiral transfer in ion pair and the ion-pairing assemblies exhibiting fascinating optical properties," concludes Prof. Maeda.

More information: Yohei Haketa et al, Enhanced solid-state phosphorescence of organoplatinum π -systems by ion-pairing assembly, *Chemical Science* (2023). [DOI: 10.1039/D3SC04564A](https://doi.org/10.1039/D3SC04564A)

Provided by Ritsumeikan University

Citation: Enhancing solid-state phosphorescence in π -electronic molecules (2024, January 31) retrieved 20 August 2024 from <https://phys.org/news/2024-01-solid-state-phosphorescence-electronic-molecules.html>

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