telectric effect observed in solid CO may arise from four mechanisms: (1) the permanent dipole moment changes and the associated stark shift between the *X* and *A* states; (2) the induced dipole change through polarizability difference between two states; (3) the change in degree of dipole orientation associated to the change in deposition temperatures; (4) electron-hole formation in the excited state of solid CO. Chen *et al*., reported the observation of Davydov splitting of solid CO that arose from a force field of CO lattice with cubic symmetry and supports the formation of electron-hole pairs in the excited state of solid CO. This crystal field results in the separation of the energy levels of the exciton into three components. They proposed a simple electrostatic model to describe how the spontelectric effect affects the separations of Davydov splitting. The experimental and theoretical results are in a good agreement on the spectral shifts along with various deposition temperatures. In contrast, solid nitrogen having no spontelectric field, shows no dependence between Davydov splitting and deposition temperature. This work explains the long-standing mystery for the sensitivity of the VUV spectra of the molecular solids on the various deposition temperatures correlating the formation of the Wannie-Mott excitons. (Reported by Yu-Jong Wu)

This report features the work of Yu-Jung Chen and his co-workers published in Phys. Rev. Lett. ***119****, 157703 (2017).*

TLS 03A1 BM – (HF-CGM) – Photoabsorption/ Photoluminescence

- VUV Absorption
- Molecular Science

Reference

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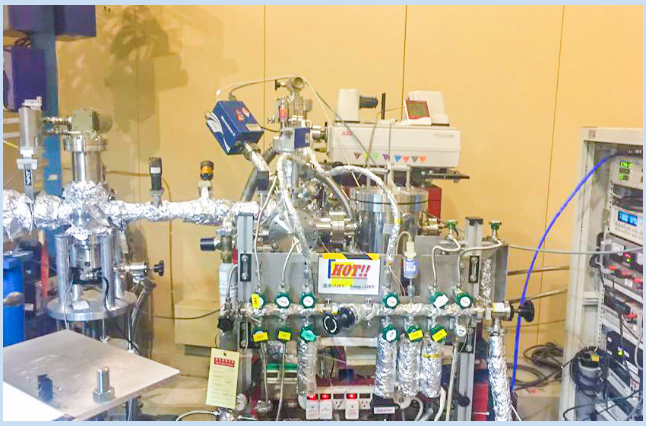

The Interstellar Photoprocessing System (IPS) connected to the **TLS 03A1** beamline.

Ultra-Bright Near-IR OLED

The Pt(II) complex-based OLEDs emitting at 740 nm possess very high efficiency and radiance. The external quantum efficiency can reach 24% in a normal planar structure.

Advances of light-emitting diodes (LEDs) since their discovery in the 60's have changed the way we light up our daily lives in the past decade. Amongst these advances is the development of electroluminescent material of the emissive layer, composed of organic compounds and called organic LEDs (OLEDs). Compared to the LEDs, the OLEDs possess many advantages for producing displays and/or lighting luminaires including their thin profile, flexible, wide view angle, high contrast and color gamut. Due to the technological needs of flat panel displays that are common in our daily life, the efficiency and radiance of OLEDs emitting in the visible light spectrum has matured rapidly in recent years. In contrast, the development of OLEDs emitting in the near-IR (NIR) is just beginning. The function of NIR emitters has a great importance for applications in optical signal processing, night vision technologies, bioimaging, photodynamic therapy, and so on.[1] However intrinsic quenching mechanisms via nonradiative processes limits the efficiency for NIR emissions of phosphors. If the energy between the electronic excited states and the ground state is close, particularly when the energy gap lies in the NIR region, the nonradiative process would be greatly enhanced through the coupling of vibrations in the two states; this is commonly called "energy gap law". Therefore, the best reported external quantum efficiency (EQE) of NIR OLEDs is lower than 14.5%.

To enhance the efficiency of NIR emission, strategies to suppress the quenching process have to be incorporated into the design of a material. This means the overlap of vibrations between electronic excited and ground states must be weakened. Following this designing idea, the joint research groups led by Hao-Wu Lin (National Tsing Hua University), Pi-Tai Chou (National Taiwan University), and Yun Chi (National Tsing Hua University) synthesized three novel Pt(II) complexes, as shown in **Fig.1**, which contain the various characters to enhance the NIR emission including extended π conjugations of the peripheral chelate and shallow and/or repulsive potential energy surface of the ground states.[2] The photoluminescence measurements showed the emission bands of these complexes to be at 740, 703, and 673 nm and the quantum yields were also determined to be 81, 55, and 82% for complexes (1)–(3) respectively. In packaging a normal planar OLED structure, the complex (1) emitting at 740 nm exhibited EQE of 24% and radiance of 3.6×10^5 mW sr^{-1} m^{-2}. The light out-coupling hemisphere structure further boosted the EQE up to 55%.[2] This is a remarkable improvement and both parameters are far ahead to the current NIR OLEDs. Further Grazing-incidence wide-angle X-ray scattering (GIWAXS) at **TLS 23A1** was performed to reveal the ordered aggregations of these Pt(II) complexes. The complexes (1) and (2) each possesses a similar emission dipole orientation distribution and tended to lie horizontally on the substrate surface, whereas complex (3) showed dipoles in random distribution, but preferred horizontal orientation on average. Theoretical studies reveal the aggregation property is *via* d_z2 and/or π interactions. A dominant d_z2 contribution in the highest occupied molecular orbital (HOMO) is expected on expanding the aggregation to infinity, while the lowest unoccupied molecular orbital (LUMO) is mainly located at the ligand π^* orbitals on aggregation. Such a metal-metal-ligand-charge-transfer (MMLCT) property along the linear Pt–Pt linkage can be recognized as an exciton-like model. The created exciton may have a long diffusion length and hence be much less susceptible to exciton-optical phonon coupling or exciton-vibrational coupling. This results in permitting the anomalously high NIR emission yield of these Pt(II) complexes. (Reported by Yu-Jong Wu)

*This report features the work of research groups of Hao-Wu Lin, Pi-Tai Chou, Yun Chi and their co-workers published in Nat. Photonics **11**, 63 (2017).*

TLS 23A1 IASW – Small/Wide Angle X-ray Scattering

- GIWAXS
- Photochemistry

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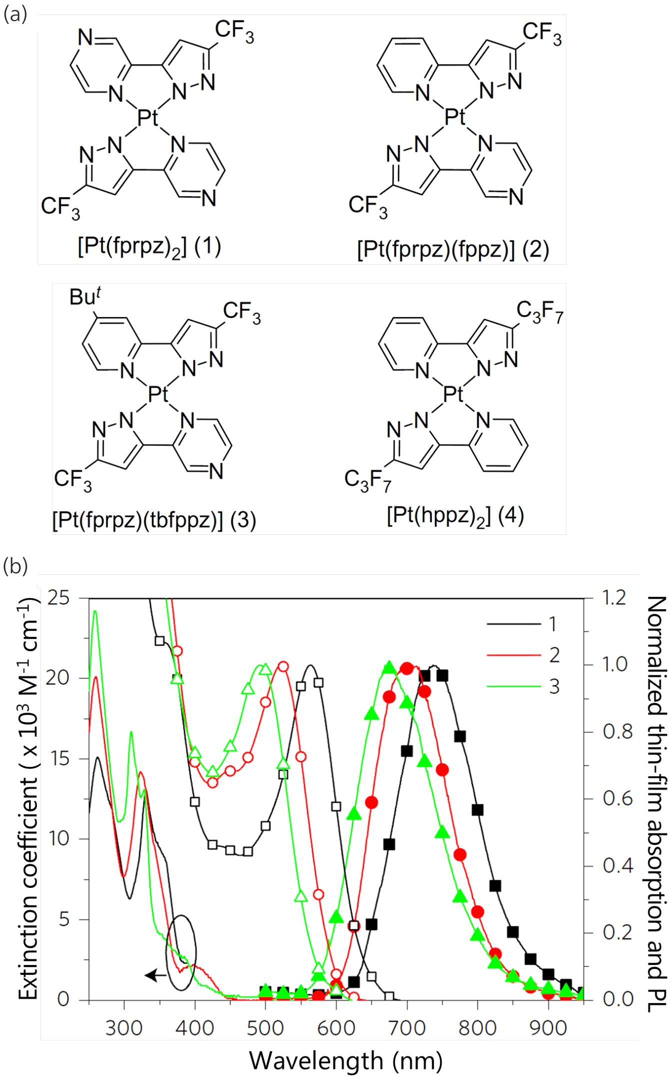
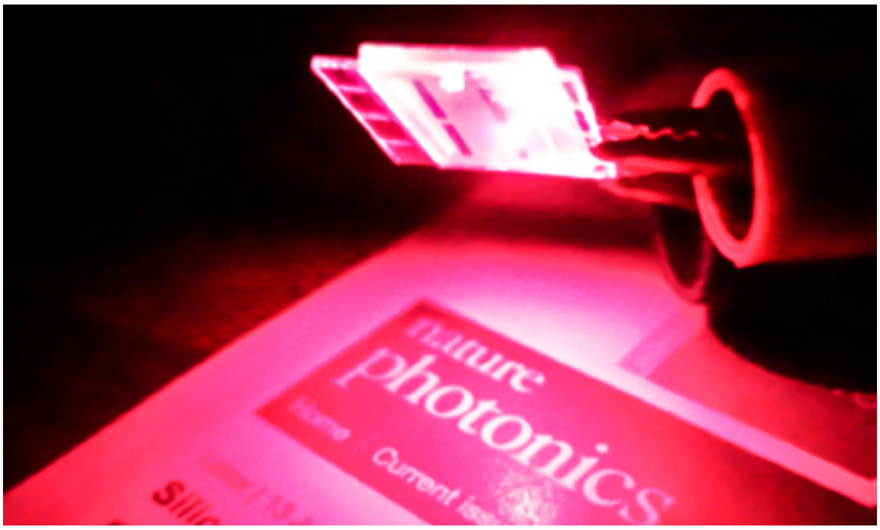


Fig. 1: Chemical structure and optical properties of Pt(II) complexes 1–3. (a) Pt(II) complexes 1–3. Structurally characterized [Pt(hppz)2] (4), whose packing arrangement was used to simulate the dimer and trimer of 1 in the solid state35 is also shown. (b) The absorption spectra of 1–3 in THF. The corresponding absorption (unfilled symbols, righthand *y* axis) and emission spectra in solid film (filled symbols, righthand *y* axis) normalized at the peak wavelength are also shown. [Reproduced from Ref. 2]



Operation of the ~740 nm OLED using Pt(II) complex 1. [Reproduced from Ref. 2]

Future Porous Materials: A Highly Flexible Inorganic Framework

In inorganic framework system, researchers have succeeded to develop an efficient method to perform a systematic reproducible synthesis of a flexible inorganic framework with different nanosized pores.

Over the past decade, chemists have endeavored to develop a series of practical porous materials for greenhouse gas capture and chemical catalysis. These porous materials include metal organic frameworks (MOFs),[1] covalent organic frameworks (COFs)[2] and inorganic frameworks. These materials are well known for their high thermal stability and exceptional surface area. In MOFs structures, the highly modular syntheses make modification of pore sizes possible and it is now known that the organic linker dominates the pore size. However, it is still a challenge to control inorganic frameworks in a similar manner to achieve a desirable pore sizes. In this work, Sue-Lein Wang (National Tsing Hua University) and her co-workers successfully developed a systematic synthesis procedure to control the pore size of an inorganic framework[3] and this work provided a new insight into the design of porous inorganic frameworks, with practical applications.

A series of five zinc phosphite-phosphate frameworks $(HA)_2[Zn_3(HPO_3)_{4-x}(HPO_4)_x]$ (A = $C_4H_9NH_3^+$, $C_5H_{11}NH_3^+$, $C_6H_{11}NH_3^+$, $C_6H_{13}NH_3^+$, and $C_8H_{15}NH_3^+$; $x = 0.3–1$) with nanometer-scale channels were synthesized. This kind of system has a low framework density (FD = 9.25), an extremely high surface area to volume (SAV) exceeding 60.3%, a large hydrophobic empty volume in the interior of the framework (20% of the unit cell). Inside the crystal, the organic template molecules were aligned parallel to the channel direction and the hydrogen bondings were found between the ammonium functional group of template molecules and the wall of frameworks, which leads a high temperature stability (up to 210°C).

The formation of different templates is critical. Three different template assemblies were generated, which leads to three products: hexagonal-rod-like, tetragonal-rod-like and bi-layer sheet-like structures (**Fig. 1(a)**). In this study, the ratio between Triethylene glycol (TEG) and water was manipulated to control these amine assemblies. For example, a high proportion of TEG facilitates the formation of the hexagonal phase structure.

It is rare that an inorganic framework system has flexibility due to the lack of adaptable structure units, such as organic ligand. Remarkably, as the unit cell volume increases while filling up with different amine template molecules, the void space expands significantly (**Fig. 1(b)**). More interestingly, from a crystallographic point of view, the bond distances remain similar in the five framework systems. However, the Zn–O–P bond angles were found to stretch (up to