

## Evolution of Platinum(II) Based OLED Phosphors; Tuning Emission from Purple to Near Infrared

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This presentation is aimed at the current research progression of an unique class of Pt(II) metal complexes bearing the azolate-containing bidentate chelate. The azolate fragment, either pyrazolate or triazolate, can link to a neutral aromatic fragment or another anionic azolate unit in forming bidentate chelates, such as monoanionic 3-pyridyl-1*H*-pyrazolate and derivatives, and dianionic 3,3'-bi-1*H*-pyrazolate, 3,3'-(1-methylethylidene)-bis-1*H*-pyrazolate and analogues. These azolate-containing chelates readily reacted with variety of Pt(II) source reagents to afford the corresponding bis-bidentate Pt(II) complexes. Majority of them were highly emissive in solution, doped polymer matrix, thin film, and even as crystal or powder, due to the high ligand field strength exerted by these chelates and high propensity in forming the singular square-planar architecture and intermolecular aggregates with substantially strengthened Pt...Pt interaction. Dependent to their molecular designs, their emission can cover a very broad spectral range from ultraviolet and purple, all the way to saturated red and near infrared. The blue shifted emission is typically caused by enlarging the HOMO/LUMO energy gap within the molecule while preventing the intermolecular stacking interaction at the same time. In sharp contrast, the red shifted emission is principally induced by occurrence of excessive intermolecular Pt...Pt stacking interaction.

More specifically, Pt(II) metal complexes with a general formula [Pt(C<sup>∧</sup>C)(X<sup>∧</sup>X)], to which the charge-neutral dicarbene C<sup>∧</sup>C chelate and dianionic azolate X<sup>∧</sup>X chelate are represented by 1,1'-methylene bis(3-methyl-imidazol-2-ylidene) and 5,5'-di(trifluoromethyl)-3,3'-bipyrazolate, are capable to exhibit bright solid-state emission ranging from purple to sky blue color. Time-dependent density functional theory (DFT/TD-DFT) calculations confirmed that their emission characteristics were dominated by the combined <sup>3</sup>LLCT/<sup>3</sup>LMCT/<sup>3</sup>IL transition character, where

LLCT and LMCT and IL stand for ligand-to-ligand charge transfer, ligand-to-metal charge transfer, and intra-ligand  $\pi\pi^*$  transition processes. At the other extreme of longer emission wavelength, a series of Pt(II) metal complexes flanked by dual pyridyl pyrimidinate chelates, which are also akin to the azolate chelates, were synthesized and tested as efficient OLED emitters. The reduced  $\pi\pi^*$  energy gap of these pyrimidinate chelates, and strong intermolecular stacking interaction and high crystallinity in vacuum deposited thin films engendered strong intermolecular charge transfer (ICT) transition including metal-metal-to-ligand charge transfer (MMLCT) process. Thereby, these emitters exhibited efficient photoluminescence with emission peak maxima between 700 - 900 nm, i.e. into the genuine region of near infrared (NIR). Consequently, NIR OLEDs based on these Pt(II) complexes are fabricated, The corresponding OLEDs emit light with a 930 nm peak wavelength and a high external quantum efficiency up to 2.14% and a radiance of  $41.6 \text{ W sr}^{-1}\cdot\text{m}^{-2}$ , both are at least one order of magnitude higher than those documented in literature.

Therefore, based on these recorded performances, the relevant Pt(II) metal based phosphors should possess bright prospective in both academic and industrial arena, particularly to the fabrication of commercial viable NIR-emitting organic light-emitting diodes.