

DOCTORAL THESIS

Synthesis, characterization and photophysical properties of metal complexes with schiff-base and porphyrin ligands

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**Synthesis, Characterization and Photophysical Properties of
Metal Complexes with Schiff-Base and Porphyrin Ligands**

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**A thesis submitted in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy**

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Abstract

A series of a new class of D- π -A conjugated nonsymmetrical metallosalophen complexes have been synthesized and characterized. The two photon absorption cross-section $\sigma^{(2)}$ reached level as high as to 1754 GM, as measured by a femtosecond open-aperture Z-scan, which is among the highest value known for metallosalophen complexes to date. The similar $\sigma^{(2)}$ values 1465 GM of symmetric metallosalophen indicates the attachment of D and A fragments doesn't have much effect on electronic properties of this kind of nonsymmetrical metallosalophen complexes. DFT calculations also show the two photon absorption is slightly affected by D and A fragments. Such kind of D- π -A conjugated metallosalophen complexes can be further modified along the Y axis. These salophen complexes with moderate fluorescence quantum yields, larger two photon absorption cross-sections $\sigma^{(2)}$ and high stability are potential two-photon fluorophores applicable in tissue imaging which can be excited by NIR or longer wavelengths to increase penetration depth and reduce cell damage.

We synthesized a series of new di-nuclear Schiff-base (**L**) Complexes **ZnLnL** (**Ln**=La, Gd, Nd, Yb, Er, Eu, Tb, Ho) heterometallic iodine substituted Schiff-base complexes. Some of these complexes have been structurally characterized. The structures of **ZnEuL** and **ZnNdL** were ascertained by X-ray crystallography. Effective energy transfer was observed from the triplet state of the **ZnL** complex to the excited

state of lanthanide(III) ions, which emitted in the visible (Ln = Tb, Ho) and NIR (Ln = Nd, Er, Yb) region. The NIR luminescence of lanthanide ions can be enhanced by putting a heavy-atom such as iodine at the phenyl rings. The Eu(III) centered emission was quenched possibly because of the electron transfers from excited state of **ZnL** to the Eu^{3+} .

A series of platinum(II) Schiff-base complexes were synthesized and fully characterized. The low-energy absorption bands (400-600 nm) of the complexes were assigned to metal-to-ligand charge-transfer (MLCT): $^1[\text{Pt}(5d) \rightarrow \pi^*(\text{L})]$ mixed with $^1[\text{L}(\text{phenoxide}) \rightarrow \pi^*(\text{imine})]$ transitions. These complexes showed high emission quantum yields and good thermal stability. HOMO (-5.09 to -5.40 eV) and LUMO (-3.26 to -3.43 eV) energy levels had been determined by cyclic voltammetry. The energy gaps of these complexes were from 1.66-2.13 eV. Yellow and red organic light-emitting devices (OLEDs) were fabricated using these complexes as emitting materials. The maximum luminous efficiency, power efficiency, and brightness for the complexes doped OLEDs were 23 cd/A, 17 lm/W and 11106 cd/m^2 , respectively. Aggregation was successfully inhibited and the emission was not changed even at high concentrations in OLEDs device. The WOLEDs is further fabricated with maximum external quantum efficiency of 7.7%, maximum luminance efficiency of 21 cd A^{-1} and maximum power efficiency of 17.7 lm W^{-1} . This phenomenon indicates that these

platinum(II) Schiff-base complexes are good candidates for phosphorescence materials used in OLED devices.

We have synthesized porphyrin-salen-porphyrin triads (**H₆L³**, **ZnL³**, **H₆L⁴**, **ZnL⁴**, **H₂L⁵** and **ZnL⁵**). These products were characterized by ¹H NMR, IR, MALDI-TOF-MS and elemental analysis. The UV-visible absorption results of **H₆L³**, **ZnL³**, **H₆L⁴**, **ZnL⁴**, **H₂L⁵** and **ZnL⁵** supported that the porphyrin and Schiff-base moiety exist a profound electronic communication in the ground state. Comparing to the triads of **H₆L³**, **ZnL³**, **H₆L⁴** and **ZnL⁴**, the emission and absorption peak of **H₂L⁵** and **ZnL⁵** were red-shifted. This is probably due to the *meso*-position linked porphyrin-salen-porphyrin triads have a better conjugation than β -position linked porphyrin-salen-porphyrin triads. Energy transfer studies showed that the energy was transferred from Schiff-base (donor) to porphyrin (acceptor) effectively. HOMO (-4.95 to -5.31 eV) and LUMO (-3.25 to -3.40 eV) energy levels had been determined by cyclic voltammetry, which showed these products were low band gap materials. Furthermore, the highest PCE of 0.32% was achieved for **ZnL³** with a $V_{oc} = 0.65$ V, $J_{sc} = 1.72$ mA cm⁻² and $FF = 0.29$ under illumination of an AM 1.5 solar cell simulator in a 1000 rpm spinning speed. The light energy absorbed by the triads/PCBM blend film was to some extent converted into electricity. The present work demonstrates the potential application of porphyrin-salen-porphyrin triads for visible and near-infrared light power generation. However, the absorption

bands (Soret band) of these triads at 450 nm are narrow, and the Q-bands are still weak in the film absorption spectra. Therefore, the photovoltaic efficiency could be increased by improving the absorption property of porphyrin containing triads in the visible and near-infrared region.

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