Summary

Ph.D. thesis entitled: "Cyclometalated and ethynyl complexes of iridium(III) and platinum(II) - synthesis and photophysical properties" is devoted to the synthesis and studying of physicochemical properties (electronic, absorption and luminescence) of ethynyl and cyclometalated complexes of iridium(III) and platinum(II). The obtained compounds can be divided into three groups: bis-cyclometalated iridium(III) complexes, aryl-ethynyl NCN cyclometalated iridium(III) complexes, and aryl-ethynyl NCN cyclometalated platinum(II) complexes.

In the first group of compounds, five heteroleptic (cationic and neutral) bis-cyclometalated complexes of iridium(III), which have not been described in the literature, were obtained in which the cyclometalating CN ligands were the following: 2-(2,2'-bithiophene-5-yl)-4-phenylquinolinate (**q-bt-Ph**) and 2-(2,2'-bithiophene-5-yl)-4-methylquinolinate (**q-bt-Me**). The accessory ligands in these complexes were: acetylacetonate (**acac**) and 2-pyridinecarboxylate (pic) in neutral complexes and 1,10-phenanthroline (**phen**) and 2,2'-bipyridine (**bpy**) in cationic complexes. The obtained bis-cyclometalated complexes of iridium(III) absorb light in a very wide range - from 270 to 536 nm, where the cationic complexes (with **bpy** and **phen** ligands) show absorption in a narrower range than neutral. All obtained compounds in a solution of CH_2Cl_2 emit light at about 700 nm.

Furthermore, the following precursors of the NCN cyclometalating and aryl-ethynyl ligands were obtained: 1,3-bis(2-pyridyl)benzene (**pir-fen**), 2,4-difluoro-1,5-bis(2-pyridyl)benzene (**pir-fen-F2**), 2,4-difluoro-1,5-bis[4-(2,2-dimethylpropyloxy)2-pyridyl]benzene (**pyr-OAlk-fen-F2**), 2,4-difluoro-1,5-bis(benzothiazol-2-yl)benzene (**bz-fen-F2**); 5-ethynyl-2,2'-bithiophene (**bt**), 9,9-dibutyl-2-ethynylfluorene (**fl**) and N-butyl-3-ethynylcarbazole (**kb**). Synthesized precursors (both of the above-mentioned ligands) were used to synthesize of the next two groups of iridium(III) and platinum(II) compounds.

The second group of target complexes was aryl-ethynyl NCN cyclometalated iridium(III) complexes with general formula [Ir(NCN)(ppy)(C≡C-Ar)]. Four complexes of this type were obtained - **Ir-1 – Ir-4**, which absorb light in the range from 237 to 451 nm, and in a solution emit light at a wavelength from 406 to 560 nm. The presence of the pyridine ligand in the cyclometalated iridium(III) complexes (**Ir-1**, **Ir-2**) causes the emission of light at shorter wavelengths and much shorter luminescence decay times in comparison to the complexes with the benzothiazole ligand - **Ir-3**, **Ir-4**. The emission of the **Ir-2**, **Ir-3** and **Ir-4** complexes takes place from the mixed LC and MLCT states. For all compounds (except **Ir-3**) the maximum emission in the solid state is batochromically shifted in relation to the maximum emission value in the solution.

The third group of the obtained complexes was aryl-ethynyl NCN cyclometalated platinum(II) complexes with the general formula [Pt(NCN)(C≡C-Ar)]. The aryl-ethynyl platinum(II) complexes that have not yet been described in the literature and two new chloride NCN cyclometalated platinum(II) complexes were obtained. Ethynyl platinum(II) **- Pt-1 – Pt-10** complexes absorb light in the range from 280 to 440 nm and emit (in solution) from 413 to 580 nm. There were significant changes in the wavelength of emitted light depending on the nature of the substituents in the NCN cyclometalating ligand. The subtle structure of luminescence spectra at diversified lifetimes of excited states for **Pt-1 – Pt-10** complexes indicates emission from the mixed LC and MLCT states. The emission in the solid state of aryl-ethynyl NCN cyclometalated platinum complexes (except one compound) occurs from the excited state of so-called excimer, hence it is strongly batochromically shifted (590 – 630 nm) in relation to the emission in the solution. All the obtained compounds were characterized by ^1H NMR and ^{13}C NMR spectroscopy, and by the high-resolution mass spectrometry (HRMS). Quantum mechanical calculations supported to correlate photophysical properties of compounds with their chemical structure.

mgr inż. Grażyna Szafraniec-Gorol

Dissertation supervisor: prof. zw. dr hab. inż. Stanisław Krompiec

Auxiliary supervisor: dr Piotr Lodowski