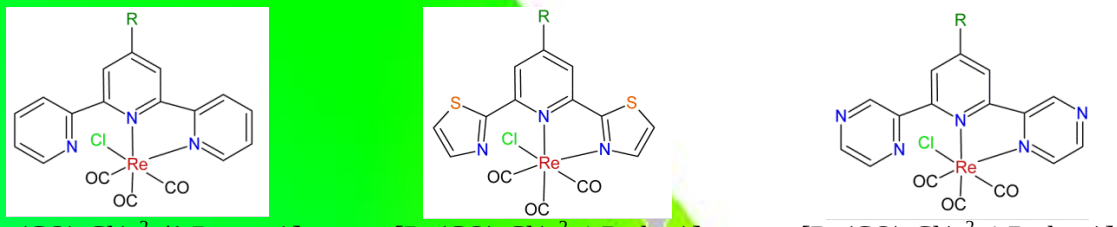
The objective of our research is to tune photo- and electroluminescent properties of Re(I) complexes of general formula [Re(CO)$_3$Cl(κ^2-N-N)] by variation and structural modification of triimine ligand coordinated to Re(I) center in a bidentate way (κ^2-N-N) in order to develop new efficient emitting materials of potential application in organic/organometallic light emitting diodes (OLEDs). Controlling of photo- and electroluminescent properties of Re(I) carbonyls will be realized by using suitable R substituents and three different triimine skeletons: 2,2':6',2''-terpyridine (4'-R-*terpy*), 2,6-di(thiazol-2-yl)pyridine (4-R-*dtpy*), and 2,6-di(pyrazin-2-yl)pyridine (4-R-*dppy*), coordinating to the central atom by two nitrogen atoms (scheme 1). The impact of the peripheral ring (pyridine, thiazole and pyrazine) of the triimine ligand will be examined by comparative analysis of the structural and spectroscopic properties of [ReCl(CO)$_3$(κ^2-*R-terpy*)], [ReCl(CO)$_3$(κ^2-R-*dtpy*)] and [ReCl(CO)$_3$(κ^2-R-*dppy*)] incorporating the same R substituents. This allows us to establish reliable structure–property relationships for [Re(CO)$_3$Cl(κ^2-N-N)] and understand the light-induced electron-transfer and electronic energy-transfer processes in this compounds, which is highly desirable to synthesize materials with pre-defined photophysical behaviour.

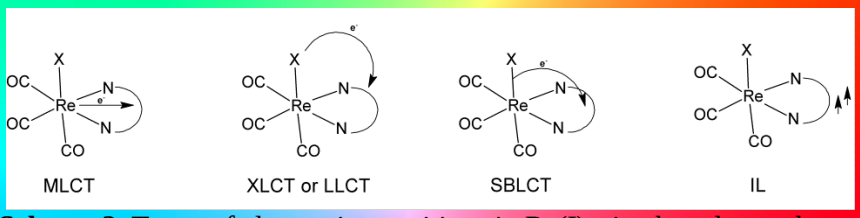


[Re(CO)$_3$Cl(κ^2-4'-R-*terpy*)] [Re(CO)$_3$Cl(κ^2-4-R-*dtpy*)] [Re(CO)$_3$Cl(κ^2-4-R-*dppy*)]

Scheme 1. Three groups of Re(I) complexes which will be investigated under this project.

The project hypothesis is based on the fact that various excited states can be generated and different electronic transitions are possible in this kind of compounds, depending on the relative energy levels of the metal and ligand orbitals:

- σ_L,π* (sigma-bond-to-ligand-charge-transfer (SBLCT) transition),
- π_{halide},π* (halogen-to-ligand-charge-transfer (XLCT)),
- π_L,$\pi_{N,N}$* states (ligand-to-ligand-charge-transfer (LLCT),
- d,π* states (metal-to-ligand-charge-transfer (MLCT)),
- π,π* or n,π* states (intraligand (IL) transition, either or L or N,N ligand).



Scheme 2. Types of electronic transitions in Re(I) tricarbonyl complexes.

To tune energies of the HOMO and LUMO and hence HOMO-LUMO gap and emission colour of the Re(I) carbonyls, three types of R substituents are planned to introduce into 2,2':6',2''-terpyridine, 2,6-di(thiazol-2-yl)pyridine and 2,6-di(pyrazin-2-yl)pyridine skeletons. First class comprises substituents possessing strong electron-releasing groups attached via phenyl ring. That group is expected to favour the energy transfer process from the substituents to the central pyridine ring of ligand. Second class contains substituents based on fused aromatic rings, such as naphthalene, anthracene and pyrene. They are expected to prolong the room-temperature excited-state lifetime of rhenium complexes due to the bichromophoric effect in which the triplet metal-to-ligand charge-transfer state is in equilibrium with the naphthalene/anthracene/pyrene triplet state. In the third one, alkoxy group/groups are attached to the phenyl, two or three fused benzene rings of the substituent to improve the solubility as well as to facilitate charge transfer processes.

The obtained rhenium(I) complexes will be also applied to construct OLEDs devices. Due to extraordinary photoluminescent properties, excellent electroluminescent performances, photochemical stability, thermal stability and easy synthesis, the Re(I) tricarbonyls are well suited to optoelectronic applications, they are good candidates for use in OLED devices, as emissive layers or dopants. On the other hand, the thickness and morphology of active layers, which influence the refractive index of the organic layers, will be controlled by methodology of OLEDs fabrication. The obtained compounds seems to be also interesting for medicine chemistry, catalysis, photosensitization of organic substrates, luminescence sensing and solar energy conversion.