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Fine-tuning of NHC Copper (I) Complexes bearing Dipyriddyamine Ligands: Application in Photoluminescence and LEC devices.

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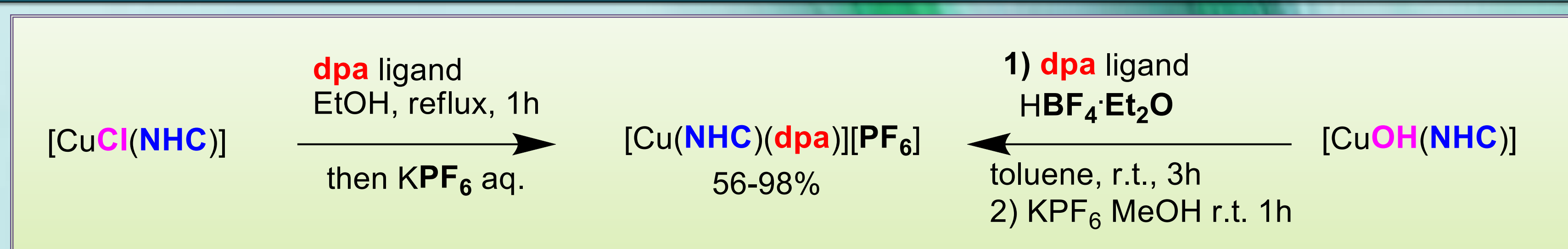
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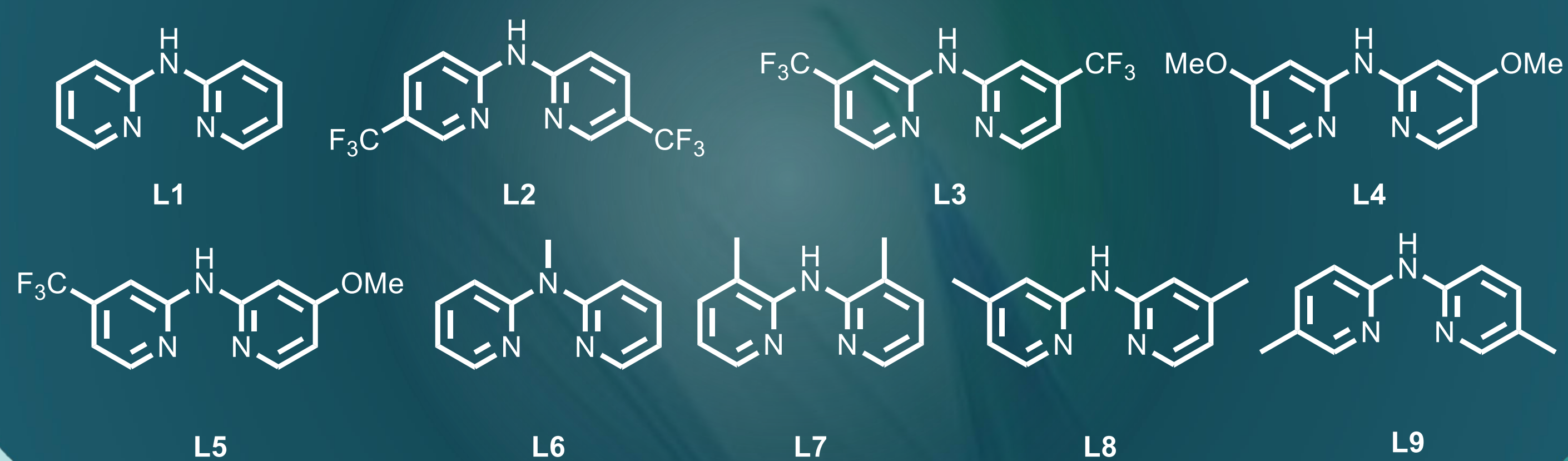
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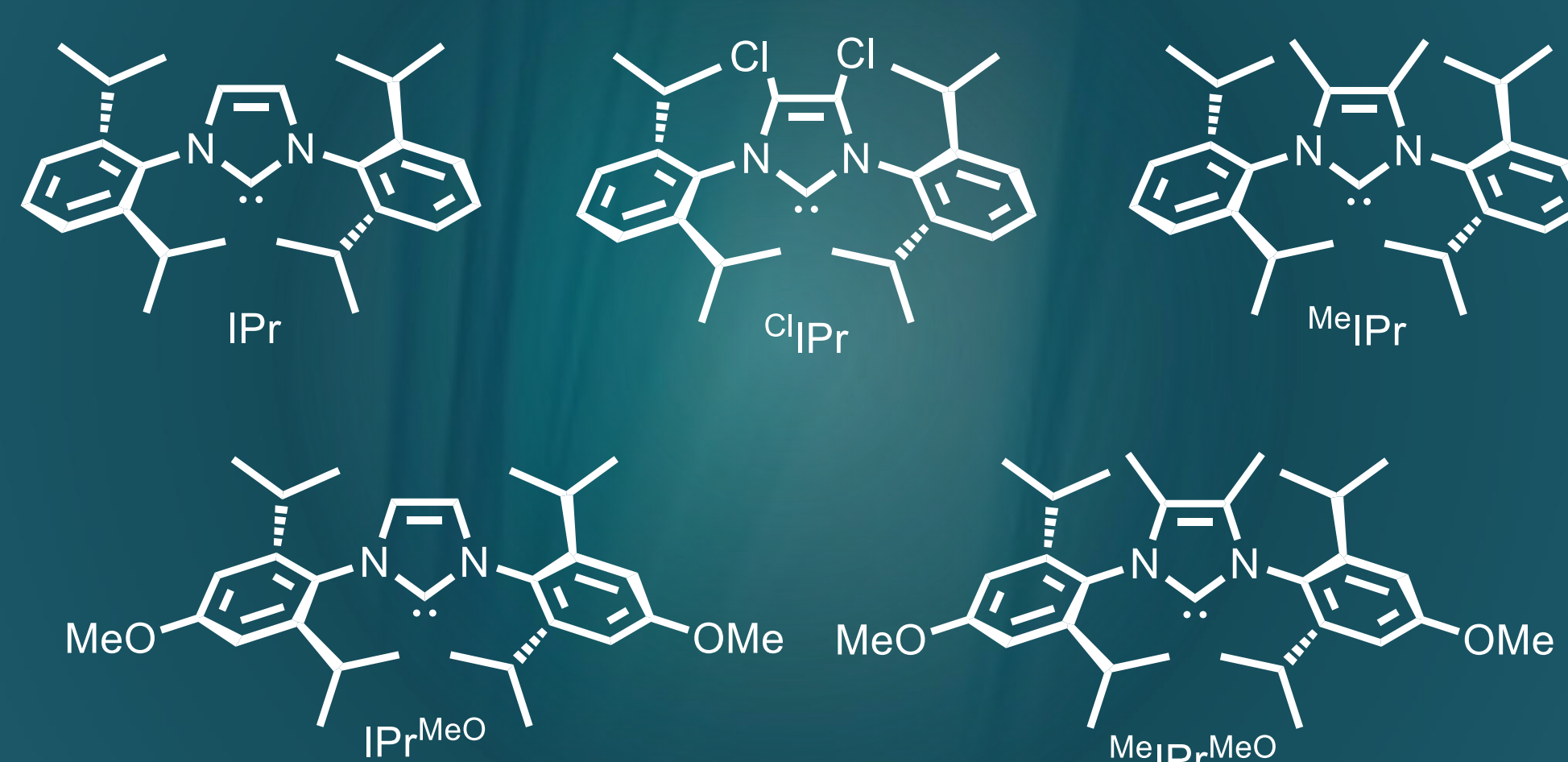
We present the synthesis of new cationic tricoordinated copper complexes bearing bidentate dipyriddyamine (dpa) ligands and NHC as ancillary ligands [Cu(NHC)(dpa)][X]. These copper complexes have been fully characterized by NMR, X-ray analysis, electrochemistry, and photophysics. Theoretical calculations were also undergone to rationalize the assignment of the photophysical properties. Some of these copper complexes exhibit very bright blue emission with high quantum yield at solid state. A variation of the electronic properties on both NHC and dipyriddyamine ligands, has been carried out and permitted to establish a structure – properties relationship, also supported by DFT and TD-DFT calculations. Since emissive cationic organometallic complexes can be good candidates for LEC (Light emitting Electrochemical Cells) applications, we presented here the proof of concept that our copper complexes of general formula [Cu(NHC)(dpa)][X] can be applied for LEC devices.^[1,2]



dpa ligands

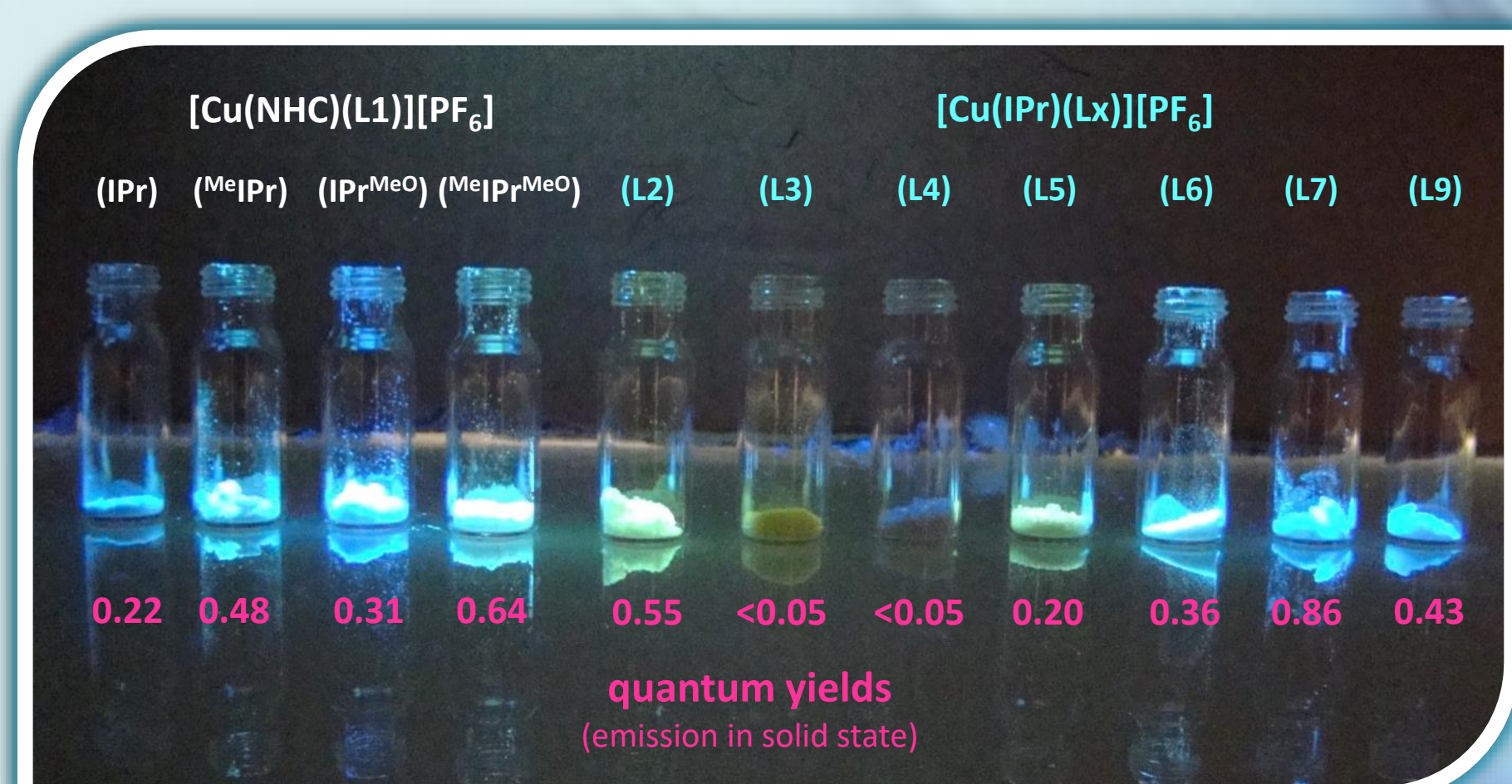


NHC Ligands



Photophysical Properties

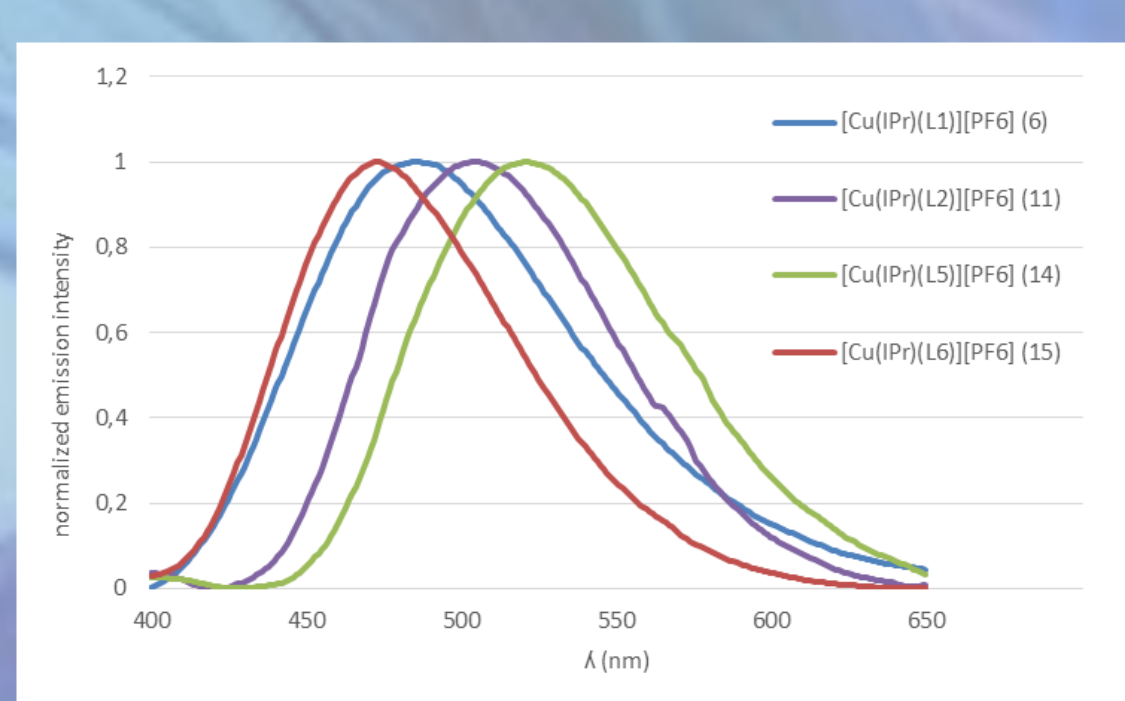
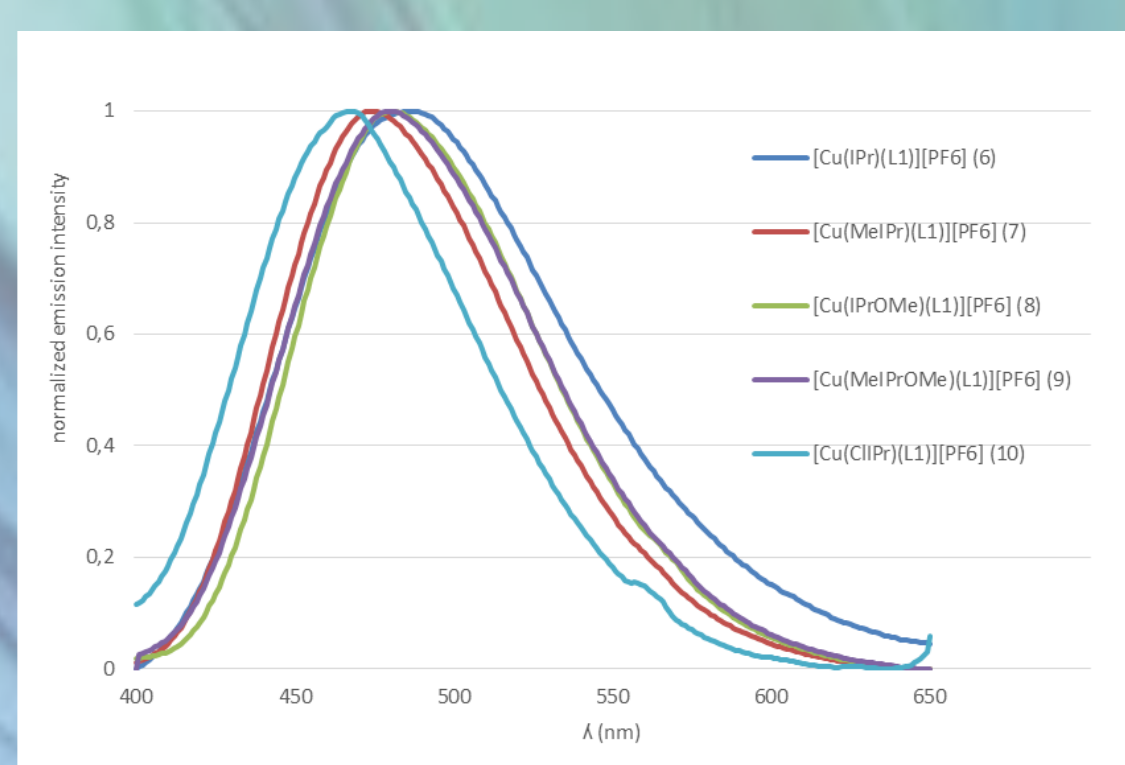
Copper complexes under UV radiation (366nm)



Tuning on NHC: quantum yields improvement

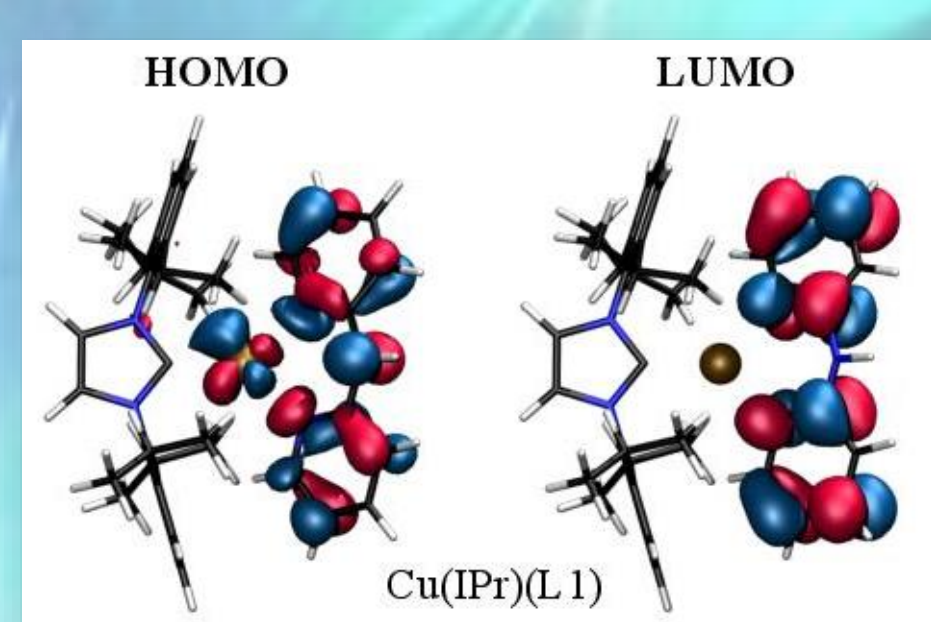
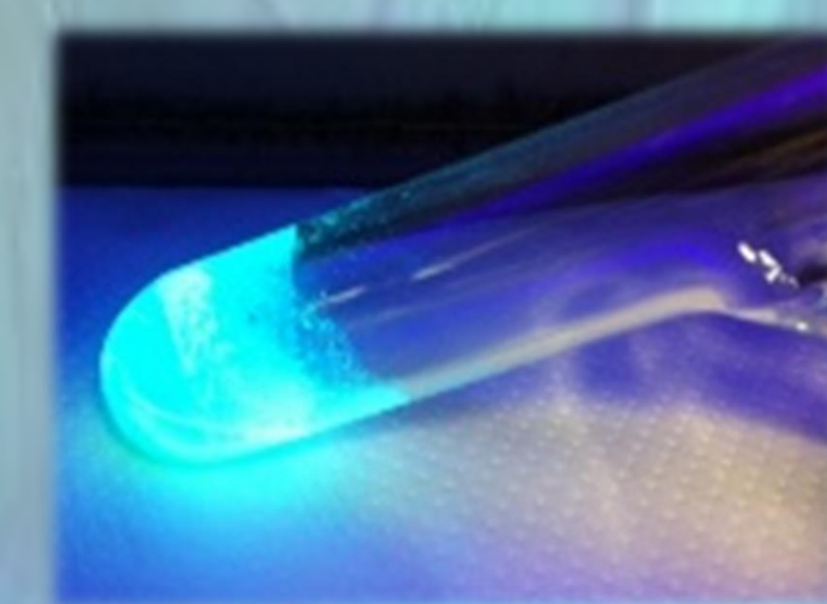
Tuning on dpa: emission wavelength modification

Emission spectra in solid state. Half life time of the excited state between 17 and 51 μs.

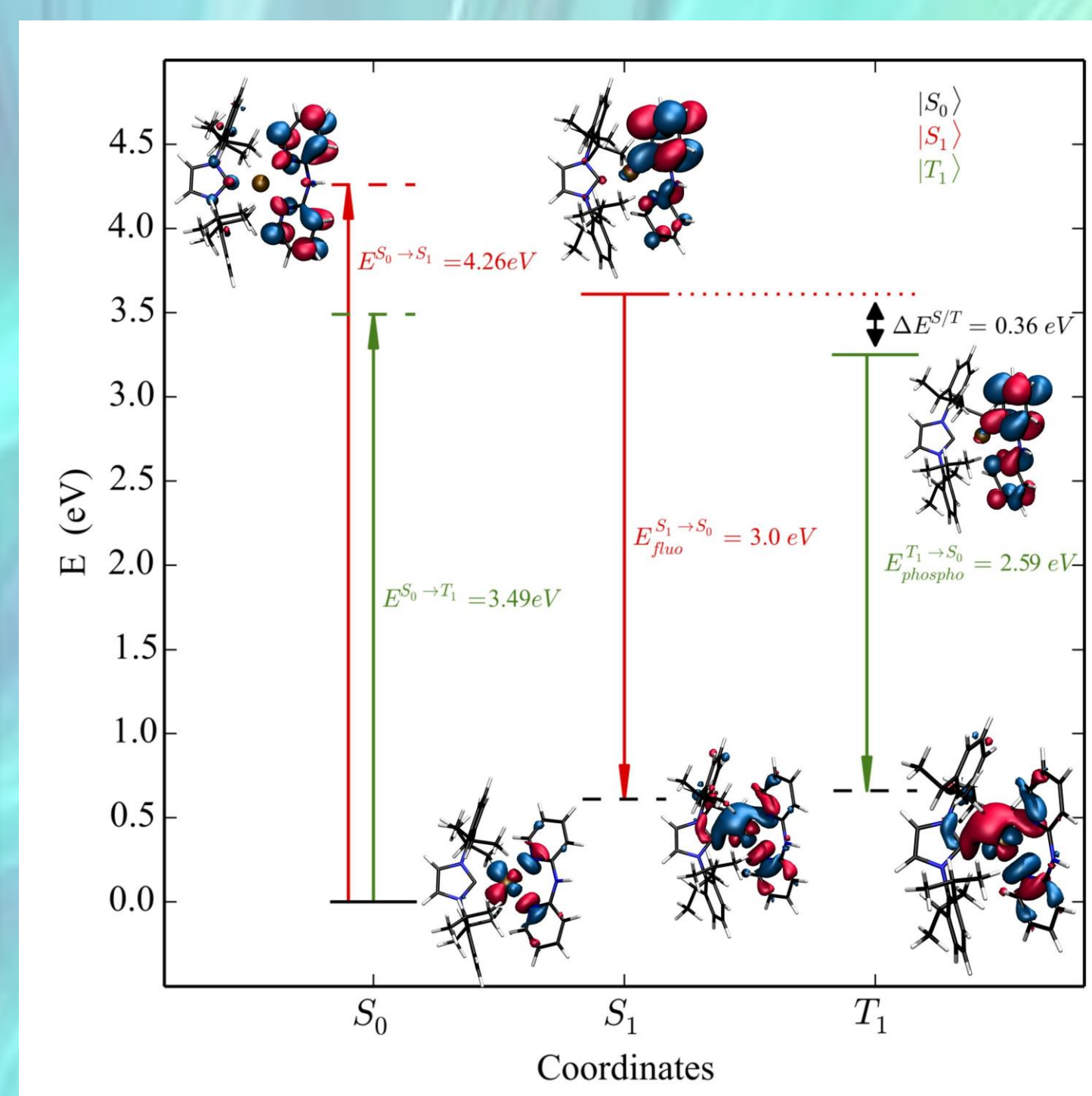


Theoretical study

Absorption – Emission Diagram of [Cu(IPr)(L1)]⁺

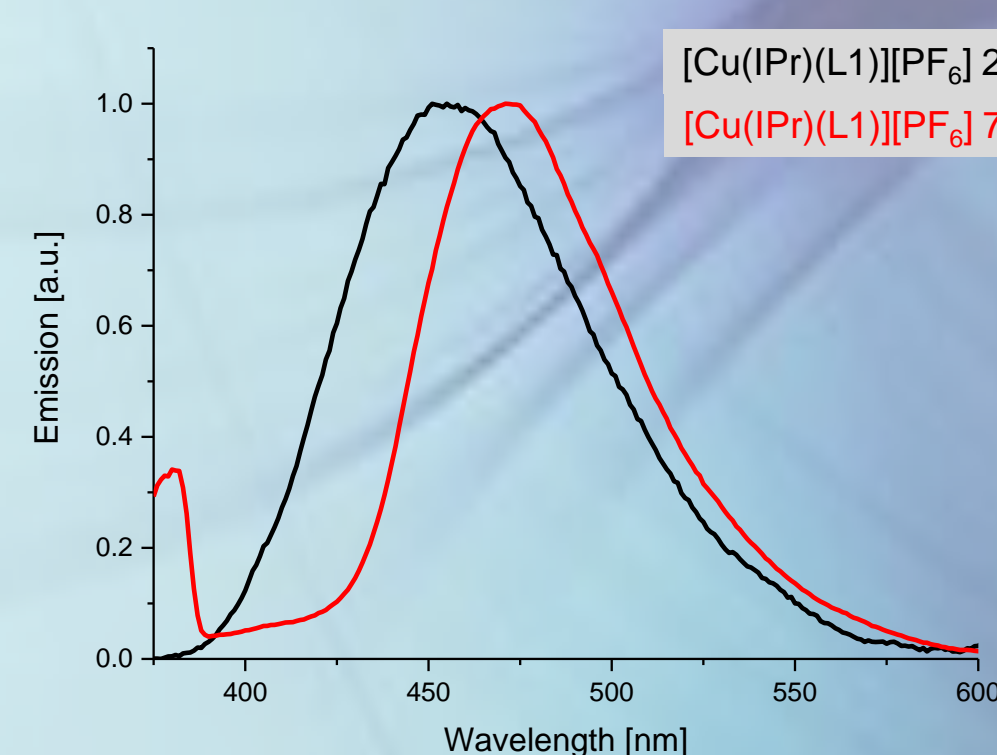


(TD-) DFT calculations (ωB97XD)



Thermally Activated Delayed Fluorescence (TADF)

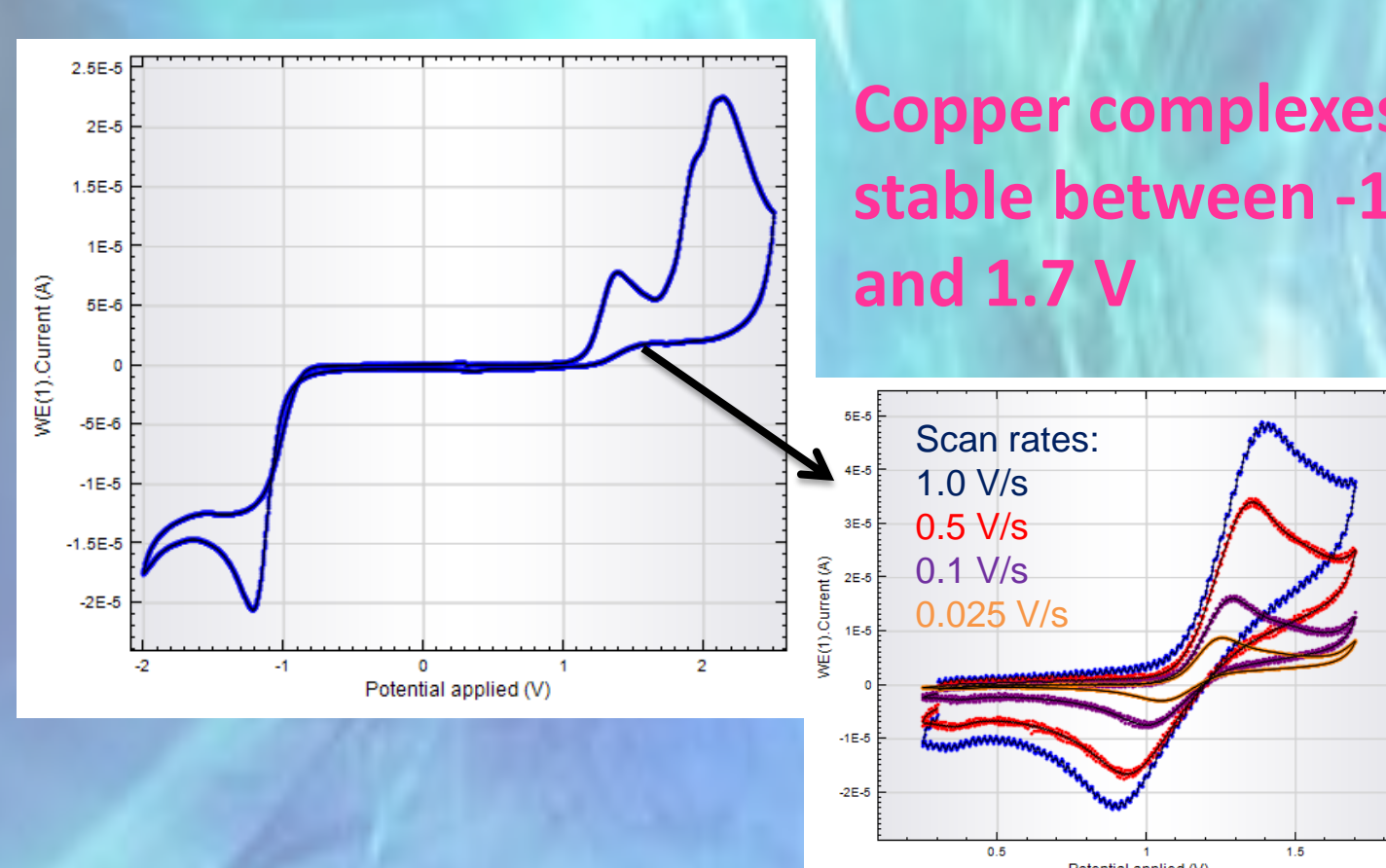
Emission spectra in solid state at 298 K and 77 K



Calculated ΔE^{ST}

[Cu(IPr)(L1)] ⁺	[Cu(MeIPr)(L1)] ⁺	[Cu(IPr-MeO)(L1)] ⁺	[Cu(MeIPr-MeO)(L1)] ⁺	[Cu(ClIPr)(L1)] ⁺
0.35	0.24	0.36	0.35	0.29
[Cu(IPr)(L2)] ⁺	[Cu(IPr)(L3)] ⁺	[Cu(IPr)(L4)] ⁺	[Cu(IPr)(L5)] ⁺	[Cu(IPr)(L6)] ⁺
0.36	0.37	0.12	0.36	0.24

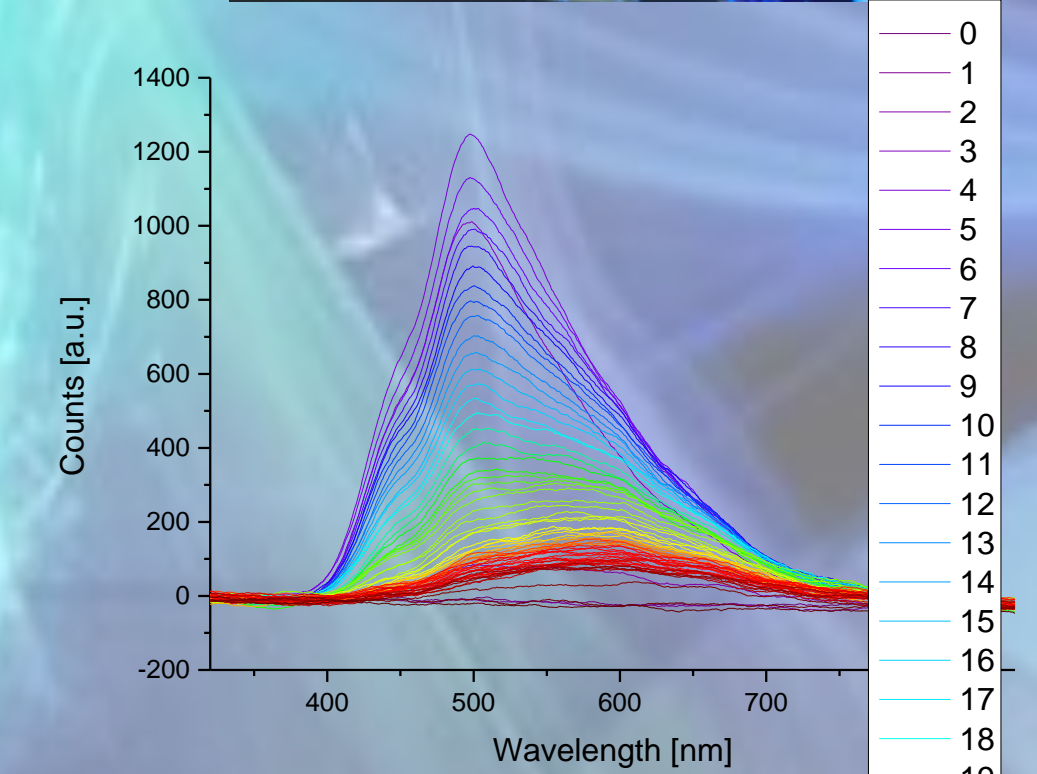
Redox Properties



Copper complexes are stable between -1.0 V and 1.7 V

Cyclic voltammogram of complex [Cu(IPr)(L1)][PF6] in CH₂Cl₂ containing 0.1 M NBu₄PF₆ between -2.0 and 2.5 V. Scan rate = 0.025 V.s⁻¹

Application in LEC devices



CONCLUSION

- Easy and robust syntheses for [Cu(NHC)(dpa)][X] complexes from [CuCl(NHC)] or [CuOH(NHC)].
- Tuning of the NHC ligand allows a better quantum yields

- Electronic properties of dpa ligand allows fine-tuning on the emission wavelengths (emission between 436 to 550 nm).
- TADF phenomenon assessed by the red-shift of the emission at 77K and TD-DFT calculations.

- Proof of concept for the use of [Cu(NHC)(dpa)][X] for the fabrication of LEC devices.