Design of (NHC) Copper(I) complexes bearing dipyridylamine ligands for application in luminescent materials

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Design of (NHC) Copper(I) Complexes bearing Dipyridylamine Ligands for Application in Luminescent Materials.

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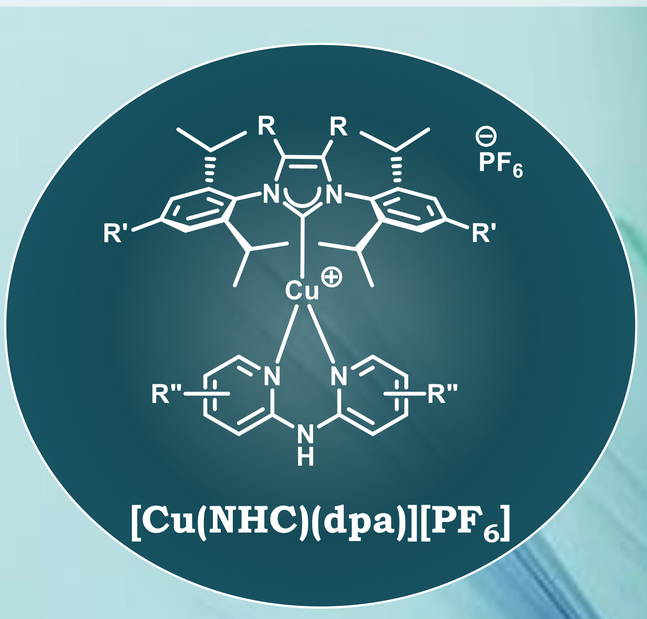
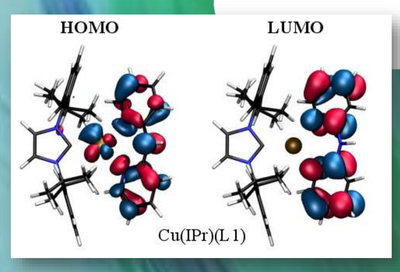
We developed new cationic tricoordinated copper complexes bearing an NHC and a bidentate dipyridylamine (dpa) ligand [Cu(NHC)(dpa)][X] which exhibit luminescence at solid state.[1,2] Varying the electronic properties of both NHC and dpa ligands, we established a structure – properties relationship, supported by structural, photophysic and TD-DFT studies. Thermally Activated Delayed Fluorescence coupled with phosphorescence was highlighted as the specific luminescence of the copper complexes [Cu(NHC)(dpa)][X] and the high quantum yield of some of them permitted to consider their application in luminescent materials. Light emitting Electrochemical Cells are thin electroluminescent films based on luminescent ions. Our copper complexes appeared as good candidates for this technology and, to the best of our knowledge, we are presenting here the first blue LEC device incorporating copper complexes. [2]

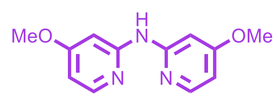
Luminescence of the complexes : modulation of the PLQY and the emission λ.



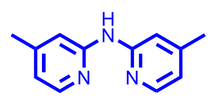
[Cu(NHC)(dpa)][PF$_6$]



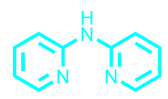
Tuning on dpa → different λ with EDG or EWG



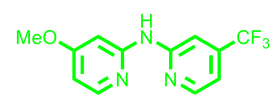
L1 λ_{em} = 420 nm



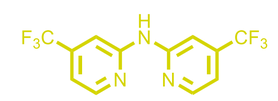
L2 λ_{em} = 455 nm



L3 λ_{em} = 463 nm



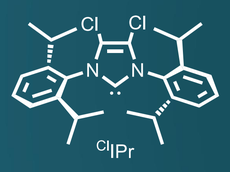
L4 λ_{em} = 521 nm



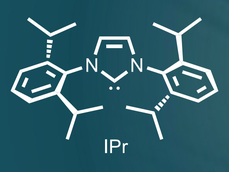
L5 λ_{em} = 550 nm

DFT calculations (ωB97XD)

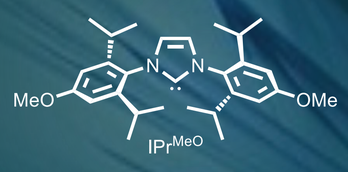
Tuning on NHC → structural changes and PLQY improvement up to 64 %



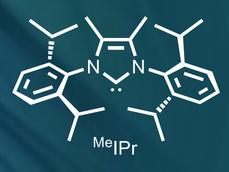
^{Cl}IPr
λem = 467 nm
ϕ_{em} = 0.17



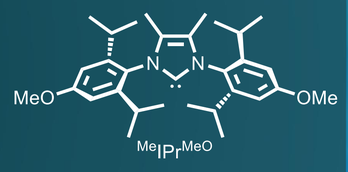
IPr
λem = 463 nm
ϕ_{em} = 0.22



IPr^{MeO}
λem = 481 nm
ϕ_{em} = 0.31



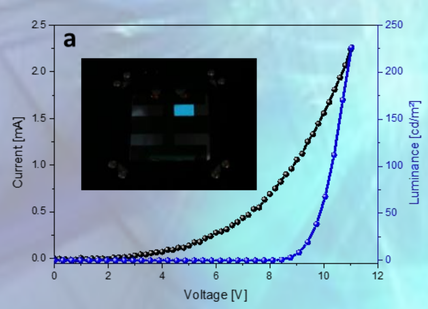
^{Me}IPr
λem = 475 nm
ϕ_{em} = 0.48



^{Me}IPr^{MeO}
λem = 479 nm
ϕ_{em} = 0.64

Application in LECs devices with [Cu(IPr)(L2)][PF$_6$].

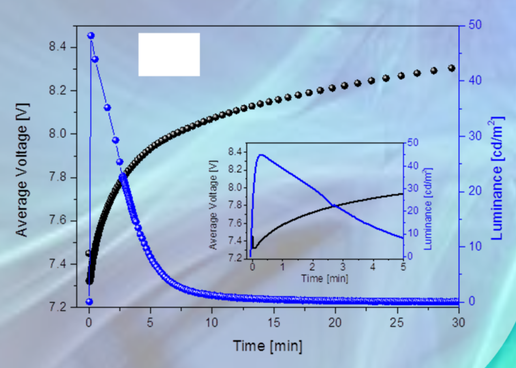
A Device as Efficient as Blue LECs incorporating [Ir] complexes!



LIV-scans of devices at a scan rate of dV/dt = 0.2V/s in a voltage range of 0-11V. Inset picture shows the blue LEC during the first LIV cycle.

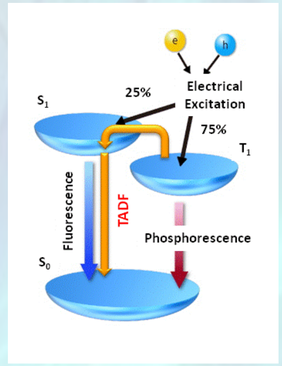
Table of the figures of merits for the LEC device incorporzting the copper complexe [Cu(IPr)(L2)][PF$_6$].

Current density [mA/cm²]	Luminance [cd/m²]	Efficacy [cd/A]	$T_{1/2}$ [min]
9.97	22.2	0.22	16.5
16.65	48.2	0.29	2.7
33.20	80.3	0.24	3.0

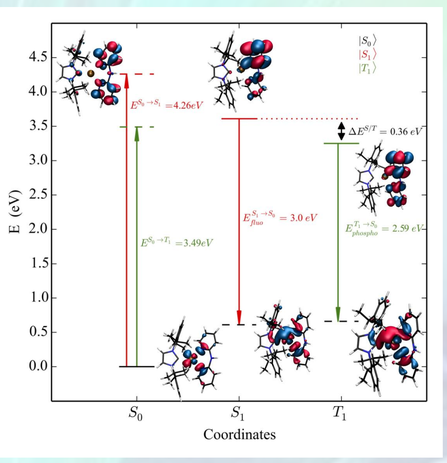


Lifetime measurement in galvanostatic pulsed driving mode at 2.5mA of the device. Inset features the initial voltage response and displaying the typical LEC-behavior (left).

Experimental Proofs of Thermally Activated Delayed Fluorescence (TADF)

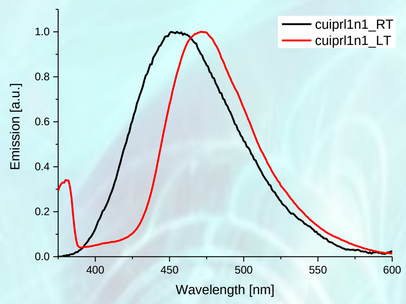


(ωB97XD)

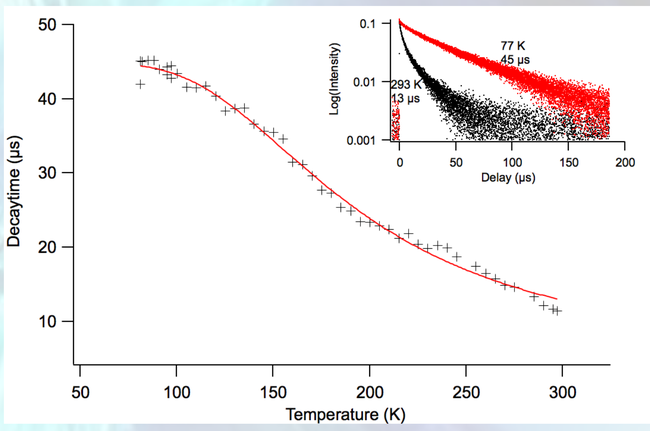


Calculated ΔE^{S-T} < 0.39 eV

Emission spectra in solid state at 298 K and 77 K.



Decay profil in solid state at 295 K and 77 K (inset) and temperature dependance of the excited state lifetime.



Temperature dependence of λ and τ proves that the copper complexes exhibit a mixed luminescence : phosphorescence and TADF!

[1] Marion, R.; Sguerra, F.; Di Meo, F.; Sauvageot, E.; Lohier, J.-F.; Daniellou, R.; Renaud J.-L.; Linares, M.; Hamel, M. Gaillard, S. *Inorg. Chem.* 2014, *53*, 9181-9191
[2] Elie, M.; Sguerra, F.; Di Meo, F.; Weber, M. D.; Marion, R.; Grimault, A.; Lohier, J.-F.; Stallivieri, A.; Brosseau, A.; Pansu, R. B.; Renaud, J.-L.; Costa, R. D.; Linares, M.; Hamel, M.; Gaillard, S. (Submitted)