Modulation of phosphine sulfonate ligands containing copper complexes emission properties: playing with solvato-, thermo-, and mechanochromism

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General Information:

All reactions were carried out under argon atmosphere using Schlenk tube techniques. Unless stated, reagents were purchased from commercial sources and used as received. Acetonitrile, was dried using a MBraun Solvent Purification System. Methanol HPLC grade was degassed and used as received. NMR spectra were recorded at room temperature on a Bruker Avance (400 MHz) spectrometer and reported in ppm. Data are reported as follows: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. Coupling constants are reported in Hz. ¹³C NMR spectra were recorded at 100.6 MHz on the same spectrometer and reported in ppm.

Solid state absolute quantum yield were measured with a Hamamatsu C9920-03G system. Optical microscopy investigations were performed on a Nikon H600L polarising microscope equipped with a Linkam "liquid crystal pro system" hotstage. The microscope is also equipped with a UV irradiation source (Hg Lamp, $\lambda = 340-380$ nm) and an ocean optic USB 2000+ UV-Vis-NIR spectrophotometer based on CCD detection technology. This set-up allows the recording of luminescence spectra on solids, liquids, liquid crystalline materials and gels from -196°C up to 420°C between 350 and 1100 nm.

Excitation and emission spectra were recorded on a FL920 Edingburgh Instruments spectrometer, equipped with a Xenon lamp (Xe900), double monochromators for the excitation and emission pathways, and photomultiplier (PMT-R928P) as detector. The emission was collected at right angles to the excitation source with the emission wavelength selected using a double grated monochromator and detected by a R928-P PMT. The excitation and emission spectra were fully corrected using the standard corrections supplied by the manufacturer for the spectral power of the excitation source and the sensitivity of the detector.

The luminescence lifetimes were measured on a FL920 Edingburgh Instruments spectrometer, via Multichannel Scaling Module using a μ F900 pulsed 60 W xenon microsecond flash lamp, with a repetition rate of 100 Hz. Low temperature measurements were performed with an Optistat cryostat with ITC controller (Liquid nitrogen).

Computational details : Computations have been performed using the B3PW91¹⁻³ functional together with the LANL2DZ⁴⁻⁷ basis set augmented with polarization functions on all atoms except hydrogens. The choice of this pair functional-basis set is coming from our previous calculations which led to satisfying geometries and accurate optical properties simulations (absorption, emission)⁸⁻¹². In order to accurately model our system, solvent effects (MeOH) were taken into account using implicit solvent (PCM) together with explicit molecules in the calculations.^{13,14} The geometries of the ground state and of the excited states have been relaxed and frequency calculations have been performed in order to check to be at the minimum of the potential energy surfaces. UV-vis absorption and emission for the singlet states have been performed within the TD-DFT ansatz using both the B3PW91 and the CAM-B3LYP functionals.¹⁵ The choice of the latter functional is assessed by the potential plots and spin density plots have been realized with the Gaussview package.¹⁶ Oscillator strengths analysis and bands assignments were performed thanks to the VMS package.¹⁷



Figure S1: Cyclic voltammogram of complex **Cu-1** in methanol. The two reduction peaks suggest a dimeric structure after the first oxidation. E_{ox1} = 810 mV (irr.)/ E_{0x2} = 980 mV (quasi rev.) and E_{red1} = 860 mV (quasi rev.)/ E_{red2} = 370mV (irr.)



Figure S2: Cyclic voltammogram of complex **Cu-2** in acetonitrile. The presence of one reduction peak suggest a non-dimeric form after oxidation of the first copper atom. $E_{ox1} = 670 \text{ mV} (\text{rev.})/E_{0x2} = 850 \text{ mV}$ (irr.) and $E_{red1} = 600 \text{ mV} (\text{rev.})$.



Figure S3: Effect of the solvent molecules toward rigidification via intramolecular interaction in **Cu-1** (top view) and contribution of acetonitrile in the lattice towards rigidification in **Cu-2**.



Figure S4: Evolution of the quantum yield of Cu-2



Figure S5 : TGA of (0-5 min. at 20°C) Cu-2



Figure S6 : TGA of Cu-2 after 5 min. (gradient 20°C-100°C)

	QuantumYield	
1 : t= 0	0.127	Pristine
2	0.129	powdered
3	0.126	
4 : t= 30 mins	0.168	addition of methanol
5	0.167	
6 : t= 60 mins	0.167	
7 : t= 16 h	0.033	
8	0.033	
9	0.033	

Figure S7 : Evolution of the quantum yield of Cu-4



Figure S8: Excitation scan of **Cu-1** (298K, λ_{max} = 368 nm) and Emissions at 78K λ_{max} = 515 nm and 298K λ_{max} = 515 nm of **Cu-1** (Ex at 360 nm)



Figure S9: decay profiles at 78K, 218K and 298K for Cu-1



Figure S10: Emission at 298K λ_{max} = 567 nm of **Cu-2** (Ex at 350 nm)



Figure S11: Emission at 298K λ_{max} = 550 nm of **Cu-3** (Ex at 350 nm)



Figure S12: Emission at 298K λ_{max} = 522 nm of **Cu-4** (Ex at 350 nm)



Figure S13: Emission at 298K $\lambda_{\text{max}}\text{=}$ 555 nm of Cu-5 (Ex at 350 nm)



Figure S14: Emissions at 78K λ_{max} = 508 nm and 298K λ_{max} = 515 nm of **Cu-6** (Ex at 360 nm)



Figure S15: Excitation scan and solid abs spectra of Cu-6 (298K, λ_{max} = 361 nm)



Figure S16: decay profiles at 78K and 298K for Cu-6



Figure S17: Emissions at 78K λ_{max} = 593 nm and 298K λ_{max} = 568 nm of **Cu-7** (Ex at 340 nm)



Figure S18: Excitation scan of and solid abs spectra Cu-7 (298K, λ_{max} = 344 nm)



Figure S19: decay profiles at 78K and 298K for Cu-7



Figure S20: Packing structure for Cu-6

Theoretical Part on Cu-1 taking into account solvent effects.

Geometry:

Optimized geometrical parameters of the binuclear complex obtained for the ground state S0 in the gas phase and in solution (in CH₃OH) as well as the X-ray ones are given in Table S1.

As it can be seen in Table S1, the S0 optimized geometry departs slightly from the symmetry of the X-ray structure. We remind that no symmetry constraint has been applied during the geometry optimization process of the complex. The agreement between the X-ray and computed structures is correct, the mean deviation between the computed bond lengths and the X-ray one being less than 5%. We checked that these small deviations can be reduced when using a more extended basis set. Not surprisingly, small deviations are observed between optimized dihedral angles and X-ray ones, packing effects being at work in the crystal, whereas deviations between bond angles is higher than expected, especially in the case of P-Cu-O angle, namely 117.3° and 114.7° for computed values *vs.* 133.4° for the X-ray ones.

Atoms (numbers)	S ₀ Calc.	X-ray	S_0 Calc.
	gaz		solvent
Cu-P (88-86)	2.244	2.153	2.255
Cu-P (44-42)	2.260	2.153	2.260
Cu-O (44-77)	2.061	2.099	2.065
Cu-O(88-33)	2.029	2.099	2.080
Cu-O (44-40)	2.271	2.190	2.317
Cu-O (88-84)	2.293	2.190	2.232
Cu-O(OHCH3) (44-34)	2.176	2.040	2.163
Cu-O(OHCH3) (88-78)	2.263	2.040	2.189
Cu-O-S (bridge:44-77-87)	119.76	121.96	124.42
Cu-O-S (bridge:88-84-87)	107.62	113.49	110.16
Cu-O-S (bridge:88-33-43)	121.67	121.96	124.21
Cu-O-S (bridge:44-40-43)	111.78	113.49	109.74

Table S1: X-ray and computed geometrical parameters of the ground state.

P-Cu-O (42-44-34)	117.33	133.43	119.83
P-Cu-O (bridge:42-44-40)	96.53	100.48	96.23
Cu-O-S-O (44-77-87-84)	-55.74	-52.97	-61.33
Cu-O-S-O (44-40-43-33)	36.36	46.15	35.29
P-Cu-O-S (42-44-77-87)	13.37	6.51	14.05
Cu-O-P-O (88-33-43-40)	48.03	52.97	60.64
Cu-O-P-O (88-84-87-77)	-32.17	-46.15	-34.90

The optimized structure has been shown to be thermodynamically stable thanks to the computations of the frequencies of its normal modes of vibration which were all real. Based on these satisfying results, it is now possible to discuss the ground state electronic structure of the complex (see manuscript).

Luminescence:

The luminescence wavelength has been deduced from the energy difference between the excited states and the ground state at the CAM-B3LYP level, considering the molecule in the gas phase. The energy of the relaxed triplet state has been estimated doing an unrestricted calculation. The emitting state is the first triplet ³MLCT state. The computed value is equal to 372 nm reminding that absorption is computed at 273 nm in the gas phase.

The complex emits only in the solid state, at *ca*. 515 nm whereas its maximum absorption is at 364 nm. The energy Stokes shift between absorption and emission is equal to 0.93 eV. Moreover, it must be reminded that a strong batochromic shift of the UV-visible absorption band is observed when comparing the spectra of the complex in solution and in the solid state, *i.e.* 270 vs. 364 nm. Thus, it is hard to compare optical properties observed for a complex in the solid state phase to those of a single complex in the gas phase or in solution. Anyway we compute an energy Stokes shift *i.e.* 1.20 eV for the complex which of the same order of magnitude as the observed one in the solid state.

Electrochemistry:

The frontier occupied MOs of the considered binuclear complex, *i.e.* HOMO and HOMO-1 exhibit a metallic character (*vide supra*). Moreover, the computed HOMO of the cation, after the geometry optimization, is also metallic. These results indicate that the first and the second oxidation processes are mainly localized on the metallic centres. In the case of the second ionization, this is fully confirmed by the spin density of the cation shown in Figure 3. In this Figure, one can see that the spin density is clearly centred on one copper atom, so that it is this one which will undergo ionization. It is worth noting that the cationic binuclear structure is thermodynamically stable in solution, as checked thanks to the computation of its normal modes of vibration. Furthermore, the computed adiabatic Gibbs first ionization energy, computed as the difference between the Gibbs energies of the neutral and cationic

species, is equal to 5.44 eV, all species being optimized in solution. Under the same conditions, the second adiabatic ionisation energy is computed to be equal to 6.72 eV.



Figure S21: Spin density plot of the cation, isovalue= 0.0009 au

































