

Structures, electronic properties and solid state luminescence of Cu(I) iodide complexes with 2,9-dimethyl-1,10-phenanthroline and aliphatic aminomethylphosphines or triphenylphosphine.

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The luminescent complexes of triphenylphosphine and two interesting aminomethylphosphines: $\text{P}(\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3)_3$ and $\text{P}(\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})_3$ with copper(I) iodide and 2,9-dimethyl-1,10-phenanthroline (dmp): $[\text{CuI}(\text{dmp})\text{PPh}_3]$, $[\text{CuI}(\text{dmp})\text{P}(\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3)_3]$ and $[\text{CuI}(\text{phen})\text{P}(\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})_3]$ are presented in this work. These complexes were characterized in solution by means of NMR spectroscopy and their structures were crystallographically determined in the solid state. All complexes crystallize as the discrete dimers bound by π -stacking interactions between dmp rings. The coordination geometry about the Cu(I) centre is pseudo-tetrahedral showing small flattening and large rocking distortions. The investigated compounds exhibit intense orange photoluminescence in the solid state (emission peaks at r.t.: $\lambda_{\text{max}} = 588\text{--}592\text{ nm}$; $\tau = 1.7\text{--}2.2$ and $6.4\text{--}10.0\text{ }\mu\text{s}$; at 77 K: $\lambda_{\text{max}} = 605\text{--}612\text{ nm}$; $\tau = 4.8\text{--}6.5$ and $32\text{--}47\text{ }\mu\text{s}$), which is several orders higher than the luminescence of the analogous complexes with 1,10-phenanthroline (phen). Electronic and structural properties of the $[\text{CuI}(\text{dmp}/\text{phen})\text{PR}_3]$ complexes were characterized using DFT methods to interpret their photophysics. On the basis of TDDFT calculations the broad CT bands observed in UV-Vis spectra are interpreted as the two mixed transitions from $\sigma(\text{CuI})$ bond with a small admixture of $\sigma(\text{CuP})$ bond to π^* phen or dmp ligand: $(\text{MX}, \text{MPR}_3)\text{LCT}$, while the emissions most probably occur from two triplet states which are in thermal equilibrium.

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