LUMINESCENT PHOSPHINE-PHOSPHINITE/-PHOSPHINATE COINAGE METAL COMPLEXES

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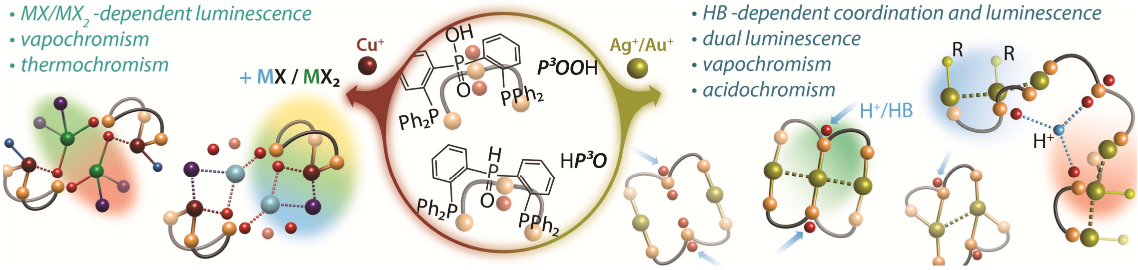
Bifunctional ligands combining chemically different metal-binding sites with adaptable coordination offer rich opportunities to generate new multinuclear architectures and functionalities.[1] The complexes of copper subgroup d^{10} ions, known for their diverse structural and photophysical behaviors, are often built of soft donor phosphines. Despite their extensive use in coordination chemistry of coinage metals, hybrid heterodentate ligands of the P,O-type are scarcely encountered among d^{10} compounds.[2]

In our work, we have reported a series of photoluminescent silver(I) and gold(I) complexes of various nuclearity derived from anionic diphosphine-phosphide oxide (phosphinite) $^{-}\boldsymbol{P^{3}O}$. The coordinated phosphide oxide (or phosphinite) in $^{-}\boldsymbol{P^{3}O}$ ligand undergoes selective oxidation promoted by strong protic acids to give phosphine-phosphinate ($\boldsymbol{P^{3}OO}^{-}$) complexes.[3] The assembly, reactivity and optical properties of resulting clusters strongly depend on acid-base interactions and hydrogen bonding (HB) that involve the $^{-}P{=}O$ and POO^{-} functions. In particular, polynuclear gold(I) species, composed of both $^{-}\boldsymbol{P^{3}O}$ and $\boldsymbol{P^{3}OO}^{-}$ ligands and stabilized with $PO^{\cdots}H^{\cdots}OP$ bonding, demonstrate solvent/H^{+}-dependent conformational diversity in the solid state, leading to unconventional variable dual phosphorescence.

While analogous copper(I) complexes of $^{-}\boldsymbol{P^{3}O}$ and $\boldsymbol{P^{3}OO}^{-}$ anionic ligands appeared to be unstable, introducing simple metal halides to the $\{Cu(\boldsymbol{P^{3}OO})\}_{n}$ synthon affords a range of copper(I)–M (M = Li to Cs, Mn, Zn) heteronuclear phosphine-phosphinate assemblies, which obey hard-soft acid-base principle. These bimetallic aggregates show intense solid-state luminescence, governed by intramolecular interactions (M–π/M–halide for M = alkali metals) or coordination geometry (M = Mn(II)). The perturbation of ligand environment induced by thermal transformation and vapors of organic solvents leads to contrasting switching of photoemission energies. The titled ligands thus provide versatile complexation modes adjustable to specific preferences of given metal ions. This allows for the construction of heterometallic stimuli-responsive systems based on the flexibility of coordination sphere.



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[2] V. R. Naina, F. Krätschmer, P. W. Roesky, *Chem. Commun.* **2022**, *58*, 5332.

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