Structurally rigid trisphosphine Cu(I) complexes with sharp red emission enabled by introduction of strains

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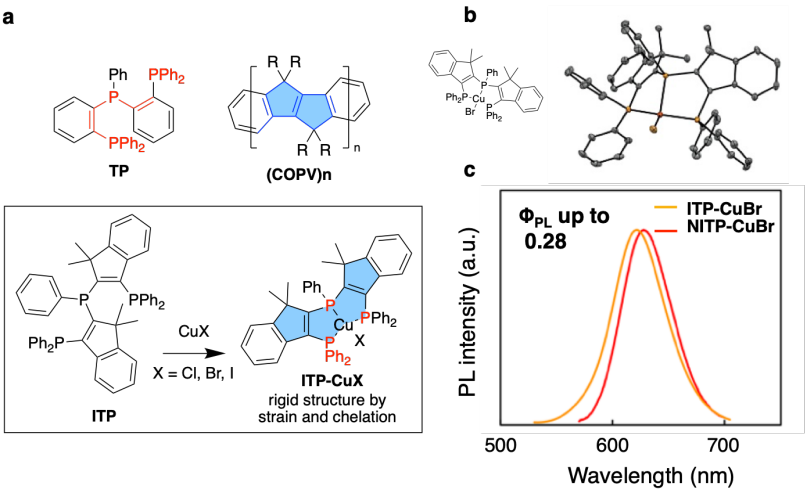
Luminescent Cu(I) complexes have been intensively studied due to the superior photophysical properties arising from the fast and efficient conversion of both singlet and triplet into photons.[1] However, the developments of red-emitting Cu(I) complexes still face low photoemission quantum yield (PLQY) and low color purity due to the structural flexibility of the Cu(I) complex. The reports on red-emitting Cu(I) complexes with high PLQY above and narrow full-width at half maximum (FWHM) (< 100 nm) are still limited.[2] We consider that the structural rigidity by introducing ring strain offers a solution for improved emission. Inspired by our previous works on rigid 1,4-dihydropentalene congeners featuring high structural rigidity endowed from fused five-membered rings[3] and the emissive properties of Cu(I) trisphosphine (**TP**) complexes,[4] we herein report the design of chelating bis- and trisphosphines incorporating two *1H*-indene backbones as ligands. The bidentate and tridentate indene-based ligands were synthesized in four steps utilizing the stepwise, regioselective lithiation-electrophile trapping of diiodoindene. These ligands formed stable complexes with Cu(I) halides and the complexes showed orange to red emission. Especially, the Cu(I) complexes of trisphosphine of *1H*-indene backbones (**ITP**) possessing four fused five-membered rings chelating Cu(I) generate a rigid skeleton. The structural strain in *1H*-indene-based Cu(I) complexes was demonstrated by the reduced P–C=C bond angles after coordination and the molecular rigidity has been supported by TD-DFT calculations, in which **ITP-CuX** showed almost minimum structural reorganization after excitation. The **ITP-CuX** showed narrow photoluminescence spectra peaking at 628 nm with FWHM of 56 nm and a PLQY of 28 %, presenting the smallest FWHM among known red emitting Cu(I) complexes reported, and a high PLQY among the red-emitting Cu(I) complexes. This work demonstrated strain-based structural rigidification for enhancing luminescence properties in metal complexes.



Figures. (a) molecular design of ligands and complexes (b) crystal structure of ITP-CuBr (c) Photoemission spectra of the ITP complexes

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