Synthesis of rigid tridentate phosphine ligands and their application to emissive copper(I) complexes

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Keywords: copper complex; phosphine ligand; photoluminescence

Phosphine-coordinated Cu(I) complexes have been intensively studied as a promising candidate of next-generation luminophores due to their unique exciton dynamics that simultaneously enable fast radiative decay and theoretically 100 % electroluminescence efficiency[1]. However, the problems on these metal complex emitters are low emission quantum yield and extremely broad emission due to intramolecular motion, such as vibration or rotation during excitation[2]. Considering that the chelating ligand with rigid framework is effective in suppressing these unwanted motions, tridentate phosphine (TP) framework is expected to be a promising solution to these problems[3]. In this study, we have designed a series of new TP ligand derivatives, developed a library of copper complexes using them, and investigated their structural, electronic, and photophysical properties.

All the TP ligands can be synthesized in 1-4 steps from commercially available compounds. The ligands with indene backbone were synthesized by utilizing regioselective lithiations / electrophile trappings of 2,3-diiodo- 1*H*-indene specifically developed for this purpose. The emission color of the complexes can be controlled by tuning the LUMO level of the TP backbone, as DFT calculations indicated. The color tuning was experimentally achieved from green to red color range. PLQY of the complexes ranged from 20 to 90 %. The notable characteristic of these compounds is the emission FWHM of 60-70 nm, narrower than previously reported copper complexes emitting in the same color range. The single-crystal studies of the complexes showed, in addition to highly rigid and sterically hindered structure, all Cu-P bond length were 2.27 - 2.35 Å, indicating stable coordination geometry. The higher color purity of the complexes is attributed to these structural characteristics.

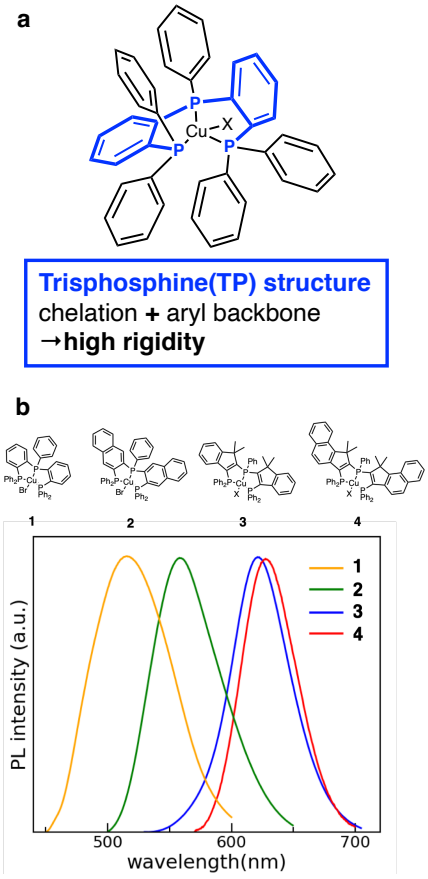

Figure. The luminescent trisphosphene Cu(I) complexes. a) chemical structure of TP-Cu*X* (*X* = Cl, Br, I). b) Photoemission spectra of the representative complexes.

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