

Synthesis of a chiral-at-Pt(II)-Cu(I) complex with a bisphenanthroline macrocycle

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Chiral-at-metal complexes have been extensively studied due to their potential applications for chiroptical materials and enantioselective catalysts. Among them, chiral-at-metals multinuclear complexes are of particular interest due to some synergetic effects between the metal centers, but the examples are still limited especially for heteronuclear metal complexes due to the difficulty in controlling the product selectivity. In this regard, we have developed a novel method for synthesizing chiral-at-bimetals heterodinuclear complexes from bisphenanthroline macrocyclic ligands with two inward coordination sites. The heterodinuclear structure was constructed by first introducing a kinetically-stable cyclometalated Pt(II) center and then coordinating to the Cu(I) ion. Subsequently, ligand exchange with a C_s symmetrical 5-Ph-dpp ligand at the Cu(I) center afforded chiral-at-Pt(II)-Cu(I) heterodinuclear complexes (Figure 1a). Notably, the crystal structure of the $[\text{PtCuCl}(\text{H}_1\text{2})(5\text{-Ph-dpp})](\text{BF}_4)$ complex showed unprecedented diastereoselectivity for $(R)_{\text{Cu}}(S)_{\text{Pt}}/(S)_{\text{Cu}}(R)_{\text{Pt}}$ -isomers with chirality at both metal centers (Figure 1b–d). We also report the effect of the substituent at the 5-position of the dpp ligand on diastereoselectivity based on crystallographic and ^1H NMR spectroscopy.

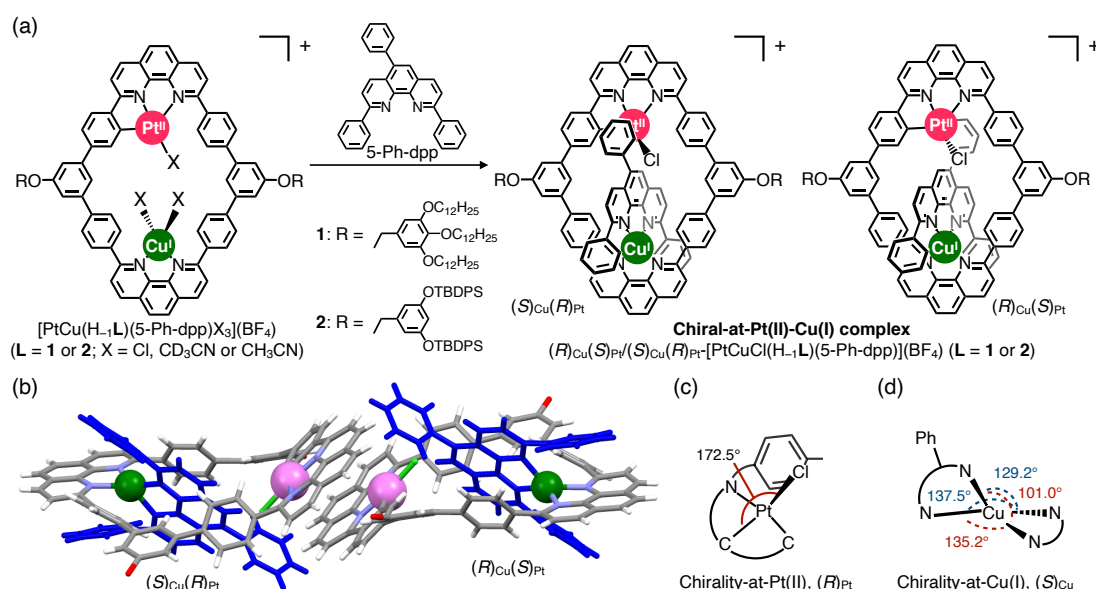


Figure 1. (a) Synthetic scheme for chiral-at-Pt(II)-Cu(I) complexes; (b) crystal structure of $(R)_{\text{Cu}}(S)_{\text{Pt}}/(S)_{\text{Cu}}(R)_{\text{Pt}}\text{-}[\text{PtCuCl}(\text{H}_1\text{2})(5\text{-Ph-dpp})]^+$ (5-Ph-dpp ligands are highlighted in blue.); (c) schematic representation of the chiral-at-Pt(II) structure; (d) schematic representation of the chiral-at-Cu(I) structure.