

Supplementary Information of

“Bimetallic Cu(I) complex with a pyridine-bridged  
bis(1,2,3-triazole-5-ylidene) ligand”

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S-1. NMR and MS spectra of 3a and 4

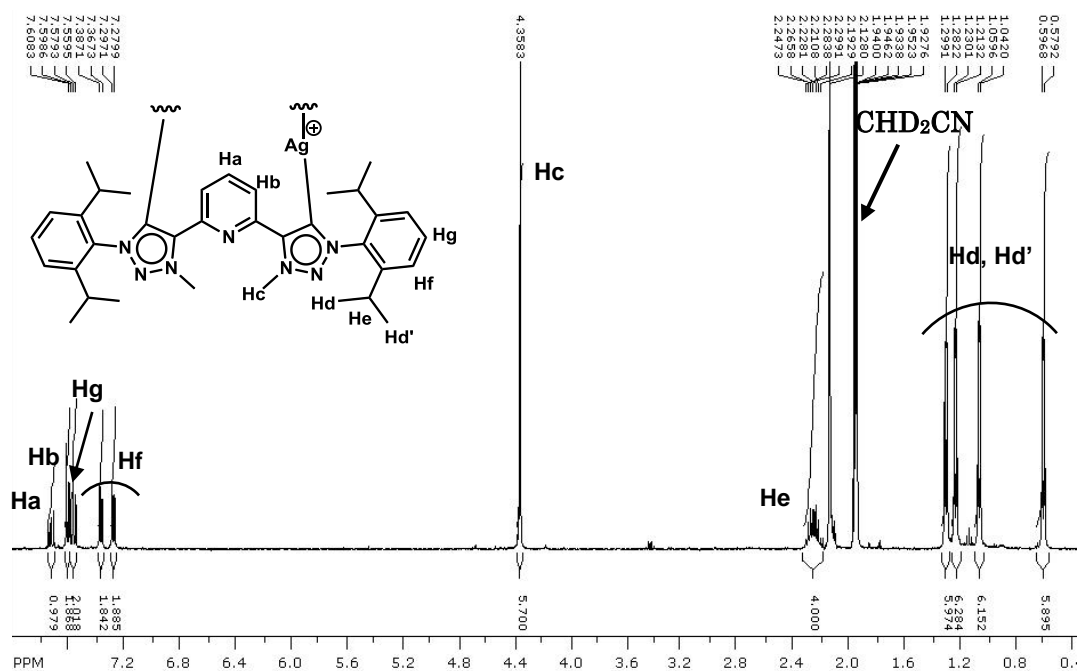


Figure S-1-1. <sup>1</sup>H NMR spectrum for 3a (acetonitrile-d<sub>3</sub>, 400 MHz)

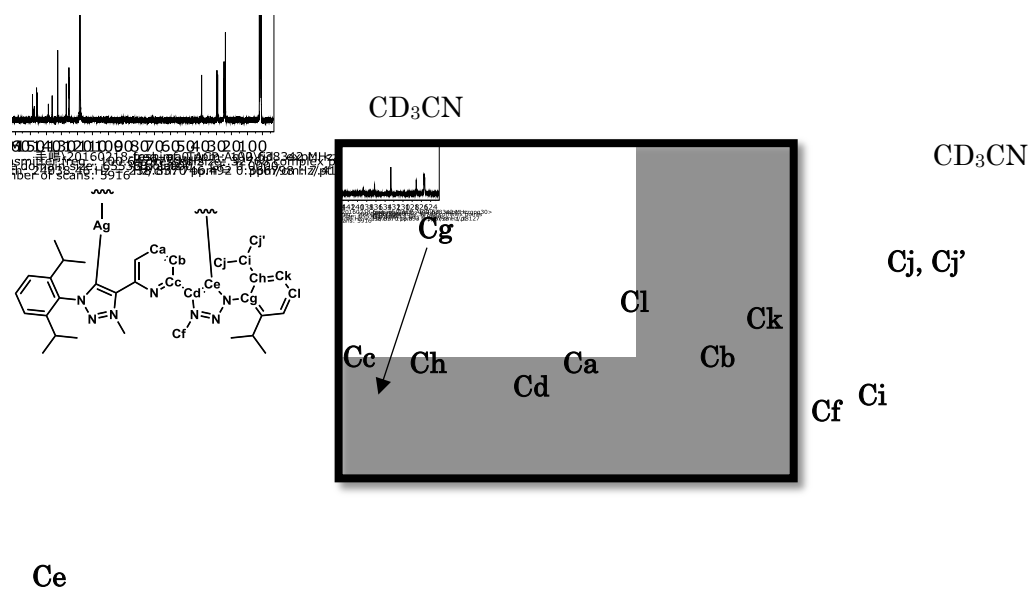


Figure S-1-2. <sup>13</sup>C NMR spectrum of 3a (acetonitrile-d<sub>3</sub>, 100 MHz)



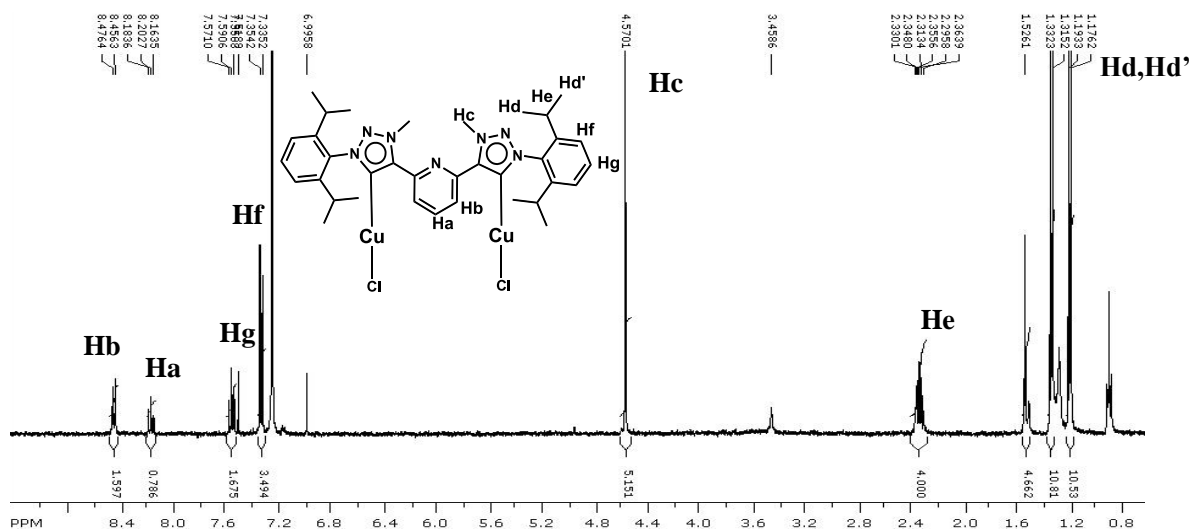


Figure S-1-5.  $^1\text{H}$  NMR spectrum of **4** (chloroform- $d$ , 400 MHz)

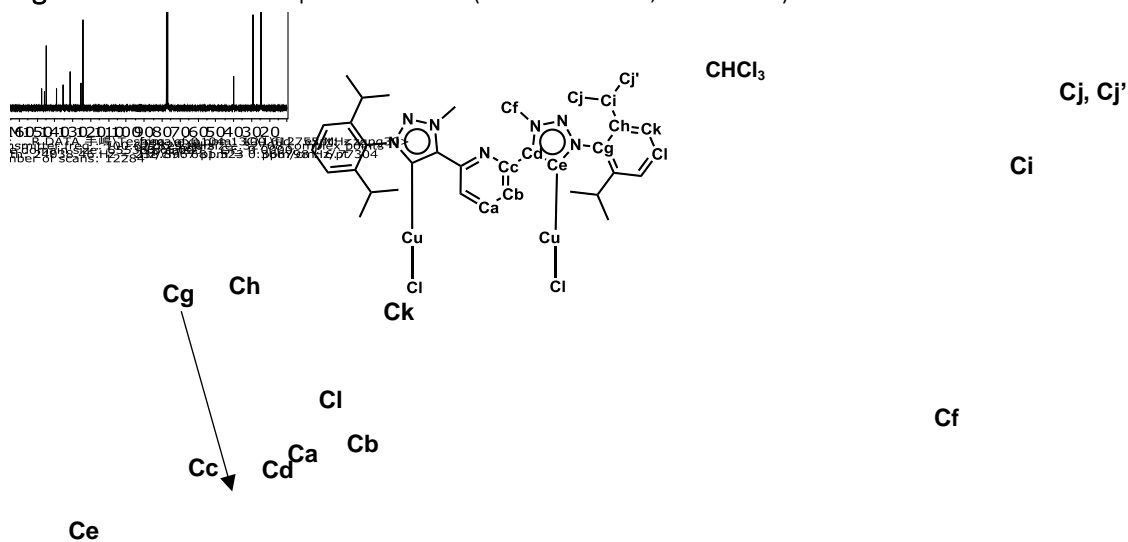


Figure S-1-6.  $^{13}\text{C}$  NMR spectrum of **4** (chloroform- $d$ , 100 MHz)

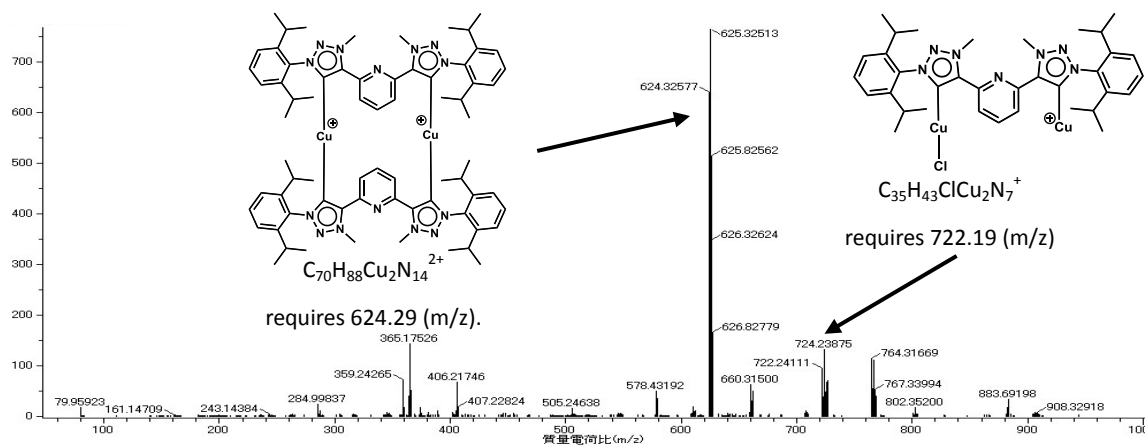


Figure S-1-7. ESI-MS spectrum of the acetonitrile solution of **4**.

## S-2. DFT calculations

### S-2-1. Computational details

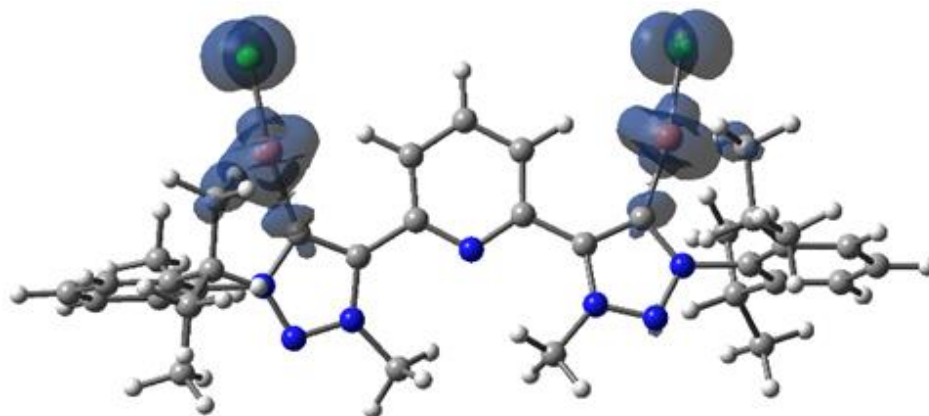
All the calculations were performed using the GAUSSIAN 09 package.<sup>1</sup> The geometry optimization was initially performed on the electronic ground states of different forms of MIC and its copper complex using the density functional theory (DFT) with the B3LYP functional<sup>xx2</sup> without symmetry restriction. Two basis sets of 6-31G(d) and 6-31+G(d) were selected according to the calculated system size. For simplicity, the solvent effect by polarizable continuum model (PCM) was ignored. In order to check the nature of stationary points at the optimized geometries, that is local minimum or saddle point, a harmonic vibrational frequency analysis was carried out at the same calculation level as the optimization. Estimating the relative energies ( $\Delta E$ s) for the various optimized isomers was corrected with the zero-point vibrational energies (ZPE). The computation was carried out using the computer facilities at Research Institute for Information Technology, Kyushu University.

The geometry optimizations starting from several different structures of MIC-(copper chloride)<sub>1</sub> complex were examined. As a result, they were mainly relaxed to three geometries; one is the most stable monodentate-MIC isomer which is analogous to the experimentally obtained complex **4**. The second is ( $\eta^1$ -MIC)CuCl in Fig. 3, which was obtained by the geometry optimization starting from “T-shaped” cyclometalated geometry of copper(I) complex, where both the distances from copper to nitrogen atom in the pyridine ring and carbon atom in the triazolylidene were initially set to less than 2 Å and the other triazolylidene ring was oriented perpendicularly to the pyridine ring. Within optimization, the coordinate bond to nitrogen atom in the initial T-shape was broken, because the triazolylidene ring was likely to move to out-of-plane direction resulting from the steric repulsion between methyl group and pyridine ring. The third is tridentate-MIC, where three coordinate bonds between copper and MIC nearly lay in the flat. The former two show the almost same stability ( $\Delta E = 0.86$  kcal/mol), meanwhile the tridentate-MIC complex is unstable by +13.06 kcal/mol than

the global minimum, despite the number of coordinate bonds.

### S-2-2. Calculated results of ionic states

The energy differences from neutral to monovalent cation and divalent cation of **4** corresponding to the first and second ionization energies, namely two step electron oxidation potentials were calculated to be 6.58 and 15.50 eV with B3LYP/6-31G(d) level. Though the calculated ionization potentials fairly seemed to coincide with the experimentally observed values in the cyclic voltammogram, 0.204 and 0.688 V, because of ignoring some effects such as solvents, electrode surface, and so on, the tendency of the calculated results was correlated to them. The calculated result of the largely separated redox potentials may indicate that monovalent cation of **4** formed a mixed-valent state. The spin density of monovalent cation **4** showed the delocalization between two Cu orbitals (Figure S-2-1), which strongly suggested the validity of our prediction of the mixed-valent state. This delocalization was considered to be attributed to the inter-atomic interaction through  $\pi$ -bond or the extended  $\pi$ -conjugation despite slightly twisted triazolylidene rings. Here, the dihedral angles between central pyridine ring and them in the optimized geometry were 17.7° and 9.1°.



**Figure S-2-1.** A spin density (isosurface value of 0.001) of the monovalent cation of **4** calculated with B3LYP/6-31G(d) level.

## References

- (1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. *Gaussian 09, Revision D.01*; Gaussian, Inc.: Wallingford CT, 2013.
- (2) B. Miehlich, A. Savin, H. Stoll, H. Preuss, "Results obtained with the correlation-energy density functionals of Becke and Lee, Yang and Parr," *Chem. Phys. Lett.* 1989, **157**, 200-206.