

## **Supplementary Information**

### **Autoxidation of thiol-containing amino acid to its disulfide derivative that links two copper(II) centers: the important role of auxiliary ligand**

Hiroyuki Seko, Kiyoshi Tsuge, Asako Igashira-Kamiyama, Tatsuya Kawamoto, and

Takumi Konno\*

## Synthesis of 1

To a light-blue solution containing 0.15 g (0.82 mmol) of  $\text{Cu}(\text{OAc})_2$  in  $15 \text{ cm}^3$  of water was added 0.13 g (0.83 mmol) of 2,2'-bipyridyl, followed by 0.12 g (0.83 mmol) of D-penicillamine. The mixture was stirred at room temperature for 2 h to give a deep-blue solution. After concentration to ca.  $4 \text{ cm}^3$ , a 1 M  $\text{NH}_4\text{PF}_6$  aqueous solution ( $2 \text{ cm}^3$ ) was added to the deep-blue solution. The resulting blue powder was filtered and then recrystallized from MeOH to give deep-blue plate crystals.

Yield: 0.22 g (48% based on Cu).

Anal. Calcd for  $[\text{Cu}_2(\text{bpy})_2(\text{D-pends})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2 \cdot 2\text{MeOH} = \text{C}_{32}\text{H}_{46}\text{Cu}_2\text{F}_{12}\text{N}_6\text{O}_8\text{P}_2\text{S}_2$ :

C, 34.19; H, 4.13; N, 7.48%. Found: C, 34.12; H, 4.17; N, 7.48%.

## Synthesis of 2

To a light-blue solution containing 0.15 g (0.82 mmol) of  $\text{Cu}(\text{OAc})_2$  in  $15 \text{ cm}^3$  of water was added 0.13 g (0.82 mmol) of 2,2'-bipyridyl, followed by 0.10 g (0.83 mmol) of L-cysteine. The mixture was stirred at room temperature for 2 h to give a deep-blue solution. After the concentration to ca.  $10 \text{ cm}^3$ , a 1 M  $\text{NaClO}_4$  aqueous solution ( $2 \text{ cm}^3$ ) and methanol ( $6 \text{ cm}^3$ ) were added to the deep-blue solution. Slow evaporation of the solution gave blue plate crystals.

Yield: 0.13 g (35% based on Cu).

Anal. Calcd for  $[\text{Cu}_2(\text{bpy})_2(\text{L-cysti})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} = \text{C}_{26}\text{H}_{28}\text{Cu}_2\text{Cl}_2\text{N}_6\text{O}_{13}\text{S}_2$ : C, 34.90; H, 3.16; N, 9.40%.

Found: C, 35.14; H, 3.21; N, 9.28%.

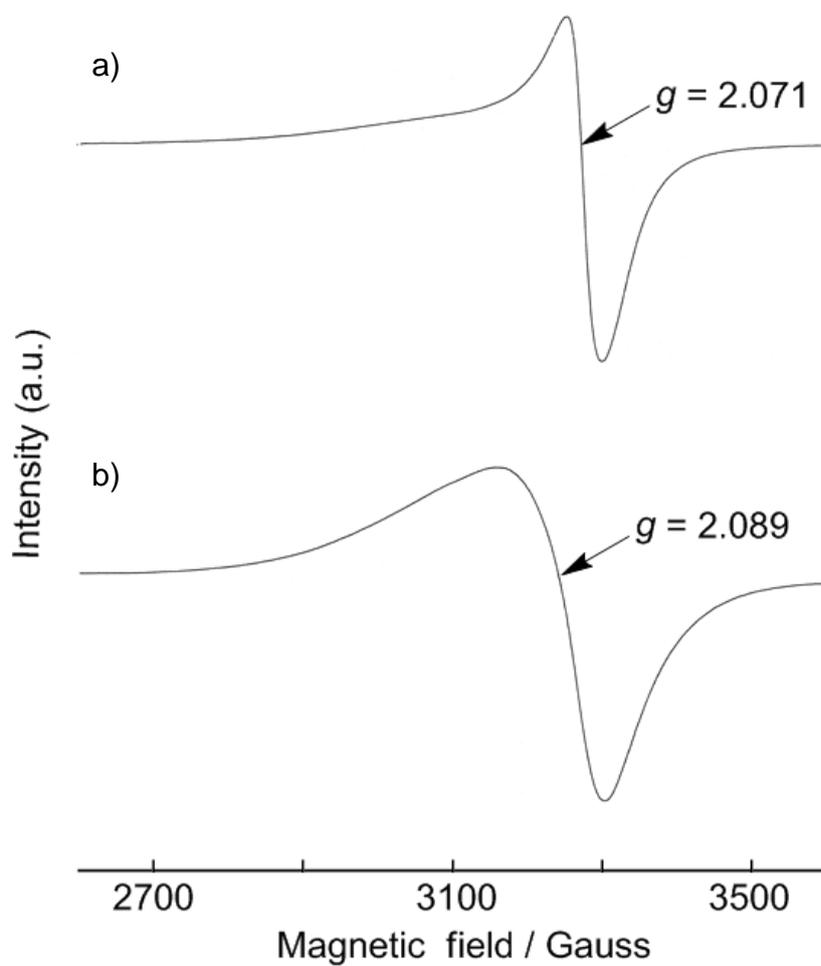
### Single crystal X-ray analysis of $[\text{Cu}_2(\text{bpy})_2(\text{D-pends})(\text{H}_2\text{O})_2](\text{PF}_6)_2 \cdot 2\text{MeOH}$ (**1**)

A crystal of **1** suitable for X-ray analysis was obtained by the recrystallized from MeOH. The crystal was mounted on a loop and measured at 200 K by a RIGAKU R-AXIS RAPID image plate diffractometer with graphite monochromated Mo  $K\alpha$  ( $\lambda = 0.71075 \text{ \AA}$ ). The intensities were corrected by Lorentz and polarized factors and an empirical absorption correction was applied. The lattice constant showed that crystal system is triclinic. Because the compound is chiral, the space group was determined as *P1*, with which the structure was successfully determined. All calculations were performed with CrystalStructure and SHELX-97. The crystal structure was solved by direct method and expanded by the conventional Fourier and difference Fourier techniques. The structure was refined with full-matrix least square method using SHELX-97. The chirality of ligands were confirmed by the Flack parameters (-0.016(17)). All non-hydrogen atoms were refined with anisotropic displacement factors except for four fluorine atoms on one  $\text{PF}_6$  anion. These fluorine atoms being disordered over two positions in a 6:4 ratio were refined with isotropic displacement factors. All hydrogen atoms are located on the calculated positions using riding model except for those of aqueous ligands. The C-O bond distances of EtOH were constrained to be 1.43  $\text{\AA}$  with s.u. of 0.01  $\text{\AA}$ .

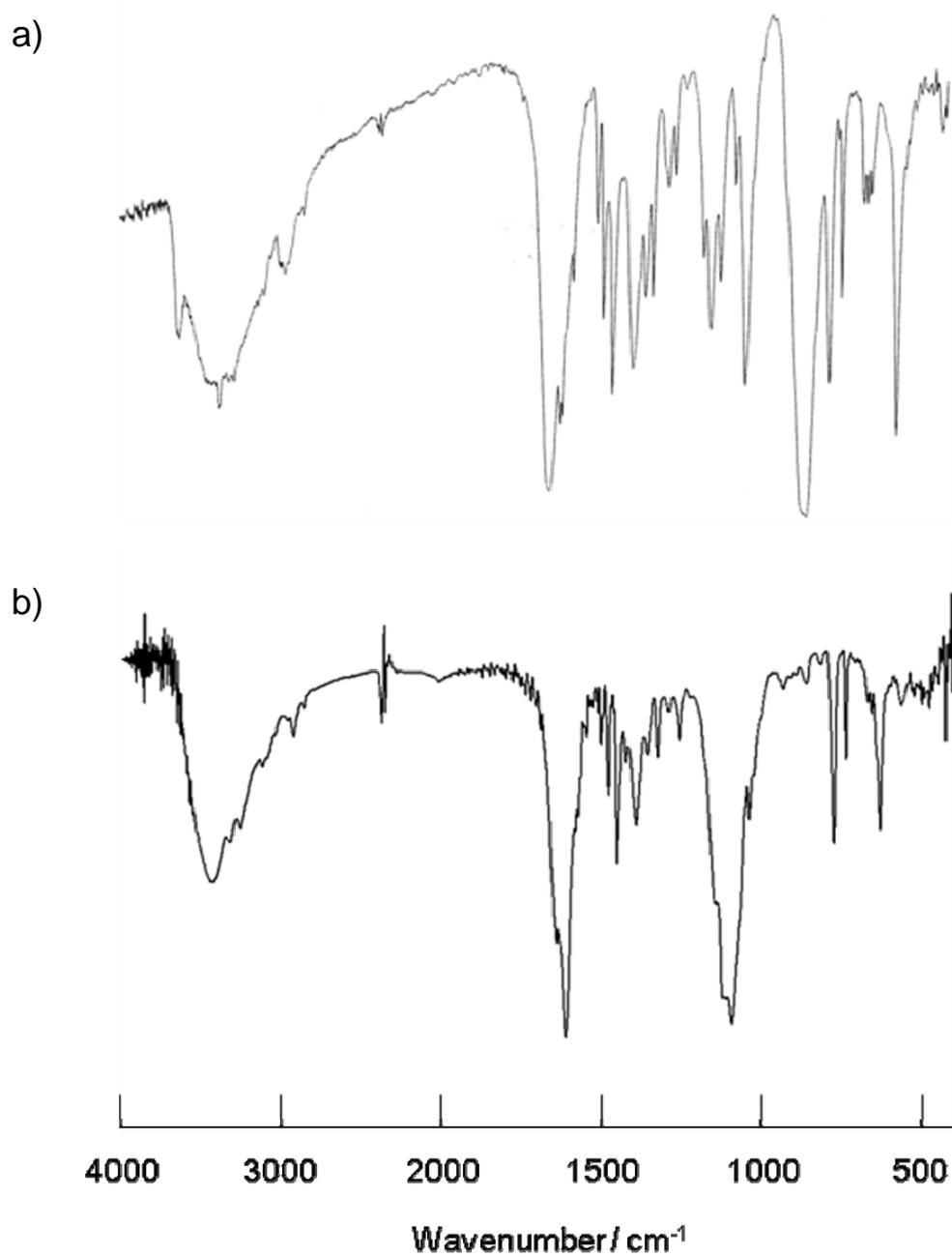
### Single crystal X-ray analysis of $[\text{Cu}_2(\text{bpy})_2(\text{L-cysti})](\text{ClO}_4)_2 \cdot 0.75\text{H}_2\text{O}$ (**2**)

Crystals of **2** for X-ray analysis were obtained by slow evaporation of the reaction mixture after the addition of  $\text{NaClO}_4$ . Because the crystals were thin and small, the intensity measurement was performed after the examination of several crystals. The crystal was mounted on a loop and measured at 200 K by a RIGAKU R-AXIS RAPID image plate diffractometer with graphite monochromated Mo  $K\alpha$  ( $\lambda = 0.71075 \text{ \AA}$ ). The intensities were corrected by Lorentz and polarized factors and an empirical absorption correction was applied. The lattice constant showed that crystal system is triclinic. Because the compound **2** is also chiral, the space group was assumed as *P1*, with which the structure was successfully determined. All calculations were performed with CrystalStructure and SHELX-97. The crystal structure was solved by direct method and expanded by the conventional Fourier and difference

Fourier techniques. The structure was refined with full-matrix least square method using SHELX-97. The chirality of ligands were confirmed by the Flack parameters (0.04(3)). In the asymmetric unit, two  $[\text{Cu}_2(\text{bpy})_2(\text{L-cysti})]^+$ , four  $\text{ClO}_4^-$  anions, and 1.5  $\text{H}_2\text{O}$  as crystal solvent existed. Water molecules were disordered over three positions with an occupation factor of 0.5. One  $\text{ClO}_4^-$  anion was disordered over two positions sharing three O atoms which was modelled to have same Cl-O bond distances with an s.u. of 0.01 Å. A sulfur atom in one disulfide unit was disordered over two positions in a 7:3 ratio. Because of the disorder and/or the relatively poor crystallinity, the bpy rings needed to be constrained as ideal aromatic rings by using an AFXI 66 command. Four C(methine)-C(methylene) distances in L-cysti were constrained to be an idealized value of 1.54 Å with an s.u. of 0.01 Å. All non-hydrogen atoms were refined with anisotropic displacement factors except for the oxygen atoms in the disordered  $\text{ClO}_4^-$  anion, carbon atoms neighboring to the disordered disulfide group, and disordered water molecules that were refined with isotropic displacement parameters. All hydrogen atoms were located on the calculated positions using riding models except for those of water molecules.

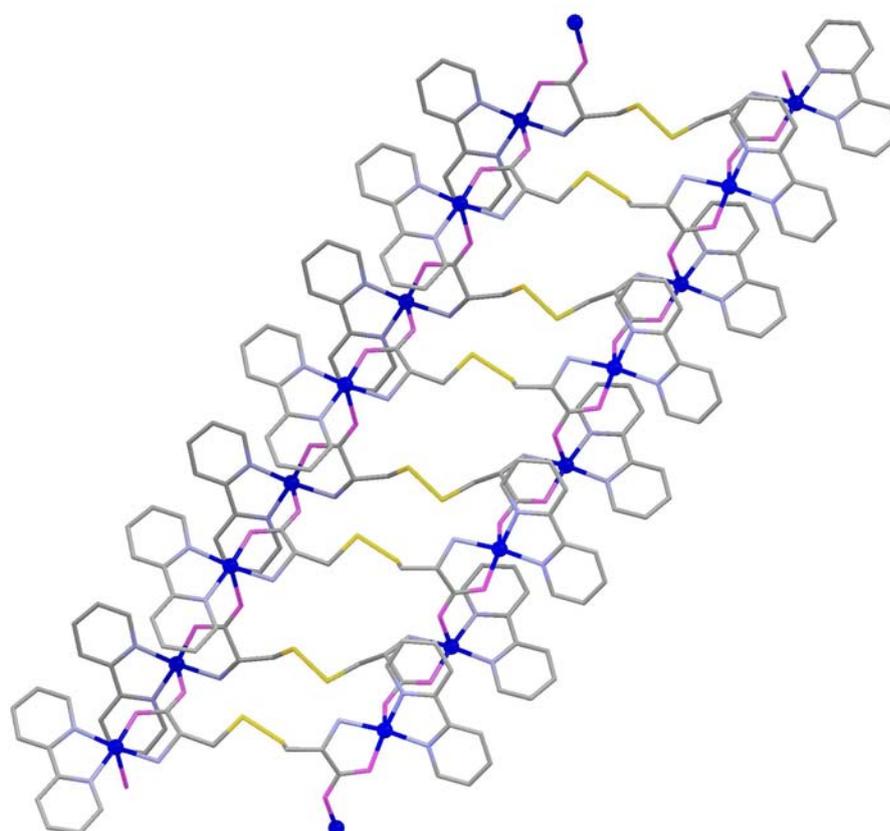
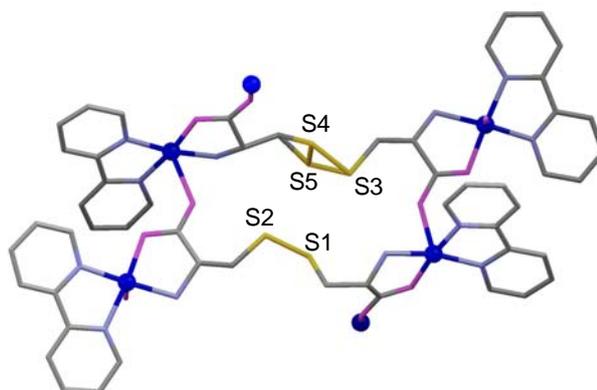


**Fig. S1** ESR spectra of a) **1** and b) **2** in the solid state at room temperature.

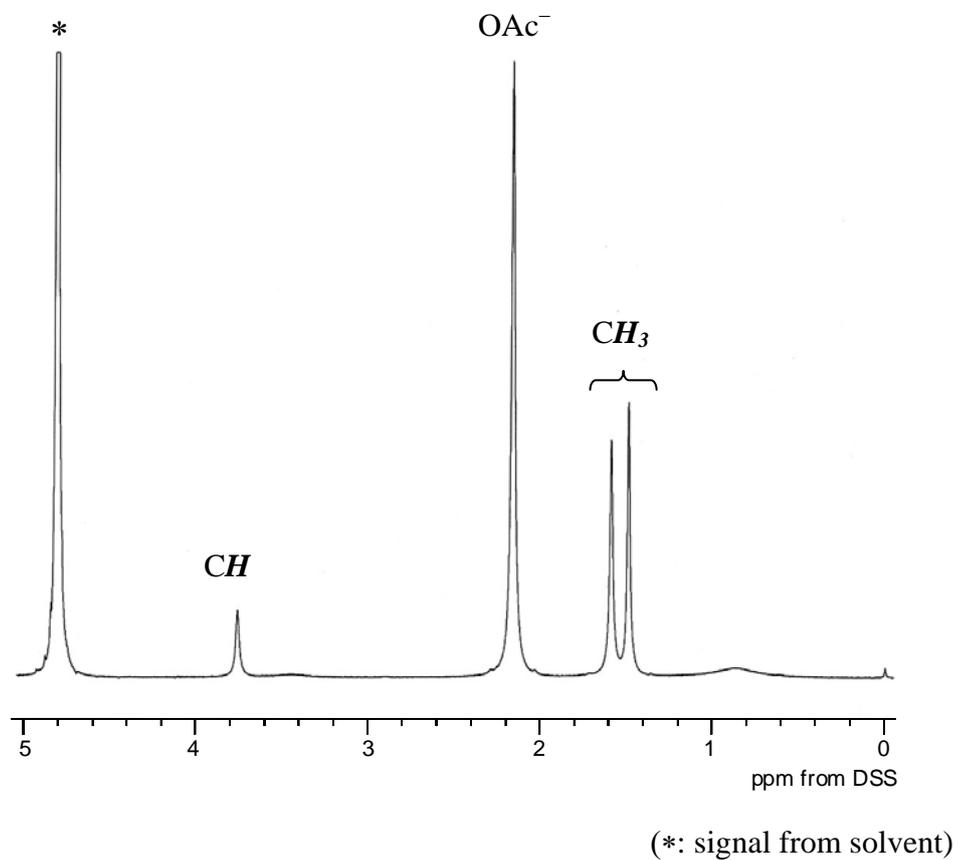


**Fig. S2** IR spectra of a) **1** and b) **2** (KBr pellet).

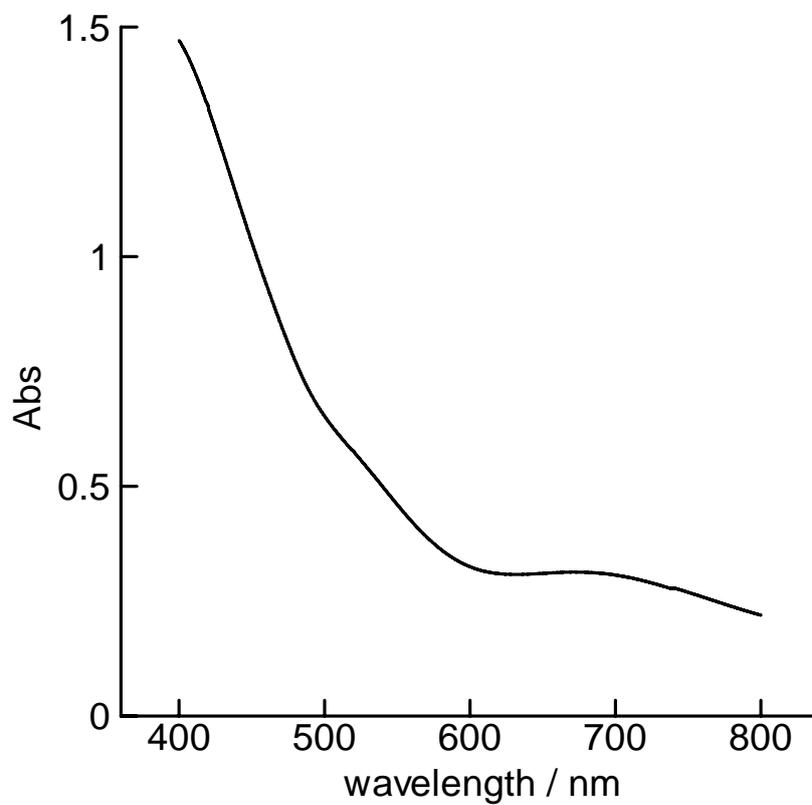
a)



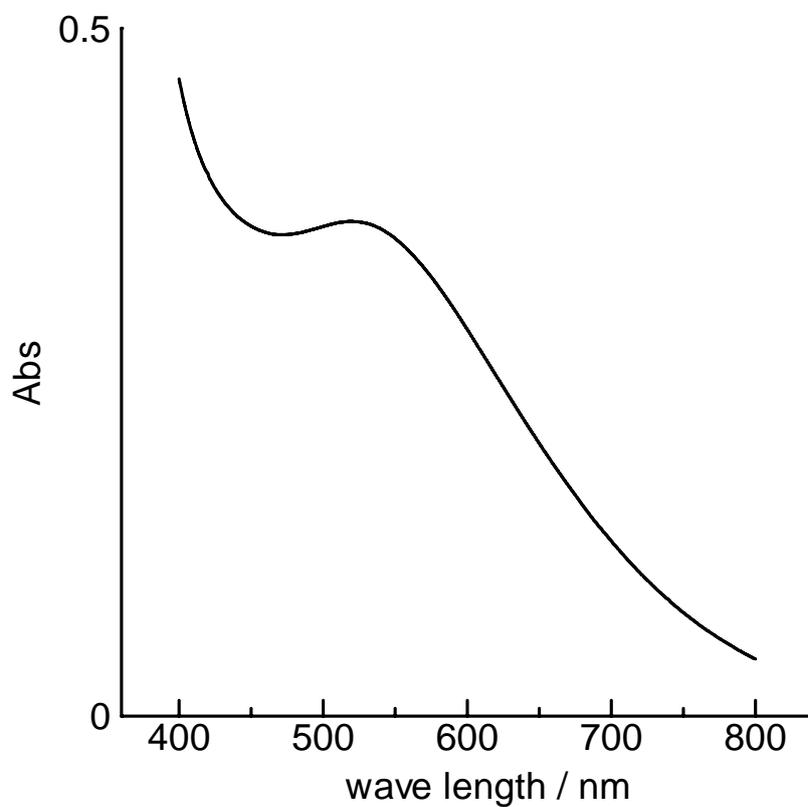
**Fig. S3** Perspective views of the cationic part of **2**. a) Asymmetric unit. Hydrogen atoms are omitted for clarity. b) Polymeric structure. Hydrogen atoms and a disordered sulfur atom (S5) are omitted for clarity.



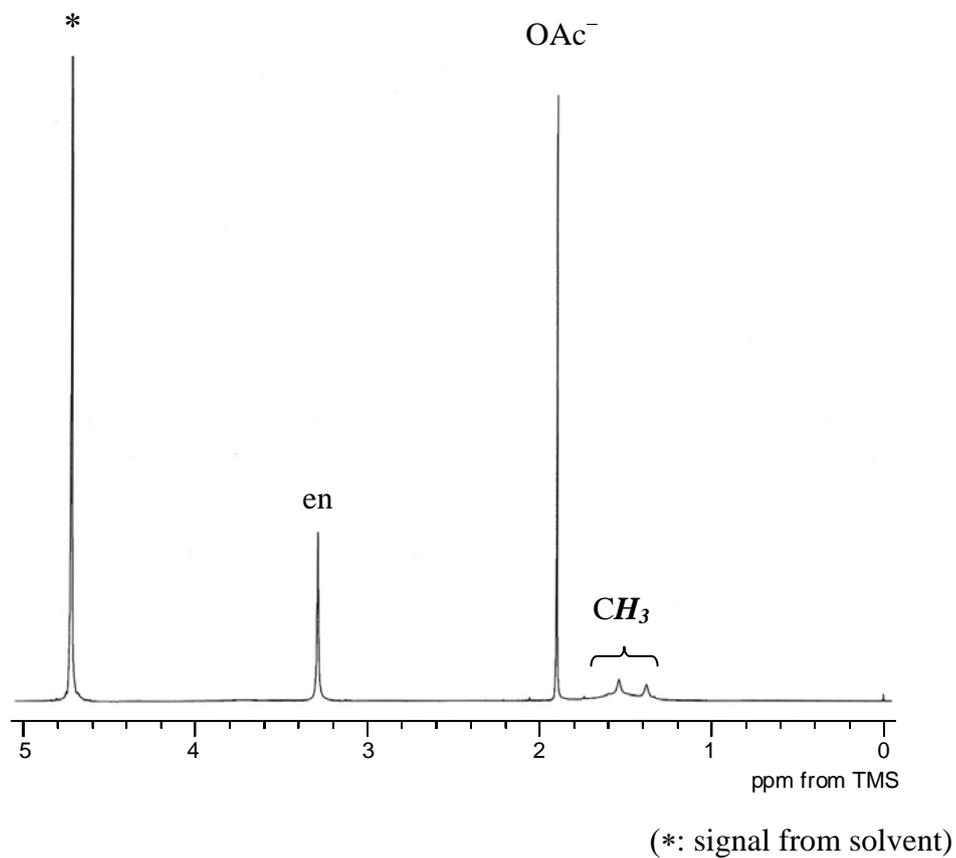
**Fig. S4** The  $^1\text{H}$  NMR spectrum of the reaction mixture containing  $\text{Cu}(\text{OAc})_2$ ,  
 $\text{bpy}$ , and  $\text{D-H}_2\text{pen}$  in 1:1:1 ratio in  $\text{D}_2\text{O}$  under  $\text{N}_2$ .



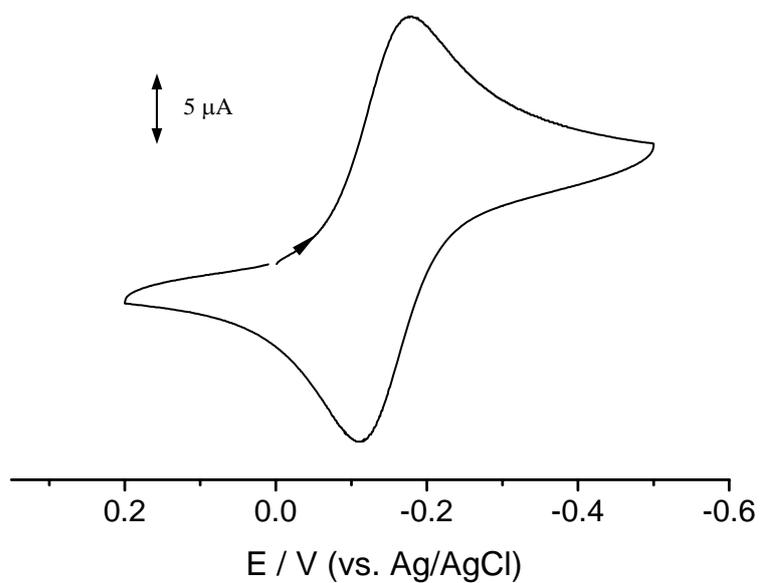
**Fig. S5** Electronic absorption spectrum of the reaction mixture containing  $\text{Cu}(\text{OAc})_2$ , bpy, and D- $\text{H}_2\text{pen}$  in 1:1:1 ratio in water under  $\text{N}_2$ .



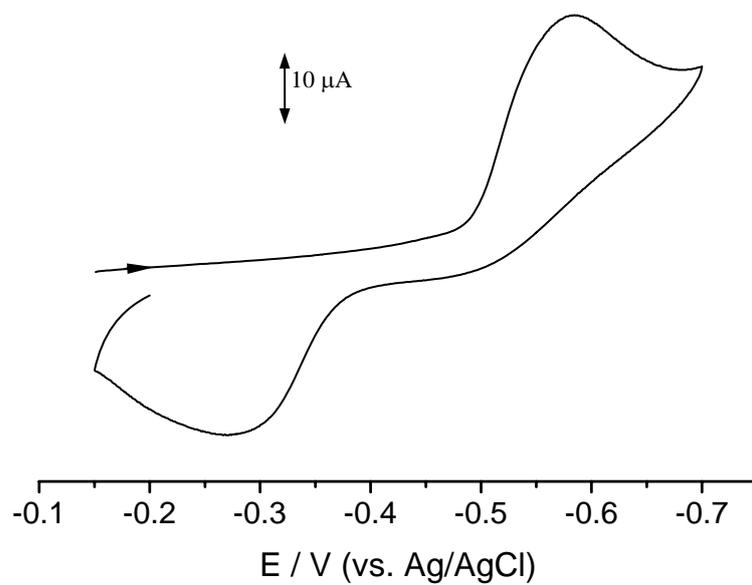
**Fig. S6** Electronic absorption spectrum of the reaction mixture containing  $\text{Cu}(\text{OAc})_2$ , en, and D- $\text{H}_2\text{pen}$  in 1:1:1 ratio in water under  $\text{N}_2$ .



**Fig. S7** The  $^1\text{H}$  NMR spectrum of the reaction mixture containing  $\text{Cu}(\text{OAc})_2$ ,  
 $\text{en}$ , and  $\text{D-H}_2\text{pen}$  in 1:1:1 ratio in  $\text{D}_2\text{O}$  under  $\text{N}_2$ .



**Fig. S8** Cyclic voltammogram of  $[\text{Cu}(\text{bpy})_2]^{2+}$  prepared *in situ* from  $\text{Cu}(\text{AcO})_2$  and 4 equiv of bpy in 0.1 M aqueous  $\text{KNO}_3$  as a supporting electrolyte.



**Fig. S9** Cyclic voltammogram of  $[\text{Cu}(\text{en})_2]^{2+}$  prepared *in situ* from  $\text{Cu}(\text{AcO})_2$  and 4 equiv of en in 0.1 M aqueous  $\text{KNO}_3$  as a supporting electrolyte.