doi:10.1246/cl.2011.1335

ON–OFF Switching of the Solvatochromic Behavior of a Copper(II)–Hydrazone Complex Induced by Protonation/Deprotonation

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(Received August 17, 2011; CL-110684; E-mail: mkato@sci.hokudai.ac.jp)

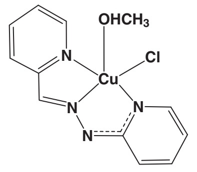
A new copper(II)–hydrazone complex, [Cu(paph)Cl(CH_3-OH)] (Hpaph: 2-pyridinecarboxaldehyde 2-pyridylhydrazone) (**1**) has been synthesized and characterized by single-crystal X-ray diffraction and UV–vis spectroscopy. This complex shows distinctive color changes by the protonation/deprotonation and exhibits interesting ON–OFF switching of solvatochromic behavior on the basis of the protonation/deprotonation of the hydrazone moiety.

Solvatochromism, which is a phenomenon of reversible color changes caused by various solvents, has been widely studied and utilized to develop various chemical sensing devices.[1] Transition-metal complexes often show solvatochromic behavior originating from the structural changes around the metal center due to the coordination of solvent molecules.[2] For example, copper(II) complexes with diketonato and diamine derivatives have been investigated for their solvatochromic behaviors which are responsible for the shift of the d–d transition bands depending on the donor or acceptor numbers of solvents.[3] Metal complexes with charge-transfer transition bands in the visible region are also good candidates exhibiting distinctive solvatochromic behavior as well as various organic dyes.[4] In addition, solvatochromism can provide an approach to understand the solvent behavior and the role of solvents in chemical and biological applications.[5] However, there are few reports on the control of solvatochromic behavior by external stimuli.

Substituted hydrazones of the type $R^1HC{=}NNHR^2$ (R^1, R^2 = alkyl, aryl, acyl, etc.) are known as colorimetric reagents, and their metal complexes have attracted much attention for the acid–base behavior accompanied by remarkable color changes.[6] We recently reported that the acidity of hydrazone complexes strongly correlates to the coordination geometries.[7] The planar coordination to metal ions makes the NH proton of the hydrazone ligand more active because of the stronger coordination than that in the tetrahedral geometry. In this work, aiming at the control of the chromic behavior by using protons as external stimuli, we newly synthesized a deprotonated Cu^{II}–hydrazone complex, [Cu(paph)Cl(CH_3OH)] (Hpaph: 2-pyridinecarboxaldehyde 2-pyridylhydrazone) (**1**) (Chart 1) and found that **1** shows interesting ON–OFF switching of colorful solvatochromism driven by the protonation/deprotonation at the hydrazone part.

The complex **1** was obtained by the reaction of [Cu(Hpaph)Cl_2] with an excess amount of triethylamine in methanol.[8] Brick red crystals formed after a few days by spontaneous evaporation. X-ray diffraction revealed the structure of the neutral complex **1** with the deprotonated hydrazone.[9] The geometry around the copper(II) ion is a distorted square-pyramid occupied by three nitrogen atoms (N1, N3, and N4) and one chloride ion in a basal plane with an oxygen atom of methanol locating at the apical site (Figure 1). The Cu–O bond distance (2.32(2) Å) is close to the typical distance between a copper(II) ion and a neutral methanol molecule rather than the methoxide ion.[10] Compared to the protonated complex [Cu(Hpaph)Cl_2],[11] the N1–C5 bond distance of **1** (1.358(3) Å) is longer by about 0.014 Å, whereas the C5–N2 bond (1.375(3) Å) is shorter by about 0.01 Å. The C5–N2–N3 bond angle (109.7(2)°) is also smaller by about 5.0° than that of the protonated form (114.6(3)°). These differences suggest that the electronic delocalization is expanded in the deprotonated paph ligand. Similar structural differences between the protonated and deprotonated forms were observed in the bis(hydrazone)iron(II) complex, [Fe(pbph)$_2$] (Hpbph: 2-(diphenylphosphino)benzaldehyde 2-pyridylhydrazone) and mono(hydrazone)palladium(II) complex, [PdBr(mtbhp)] (Hmtbhp: 2-{2-[2-(methylthio)benzylidene]hydrazinyl}pyridine).[12] As shown in Figure 1, two complex molecules are dimerized by two hydrogen bonds between the OH group of coordinated methanol and the N site of hydrazone part of the adjacent molecule. These dimerized molecules form a one-dimensional column along the *a* axis by moderate π–π stacking interactions (3.376(3) and 3.379(2) Å).

To estimate the acid–base properties of **1**, we measured the electronic absorption spectra at various pH in methanol. As



[Cu(paph)Cl(CH_3OH)] (**1**)

Chart 1.

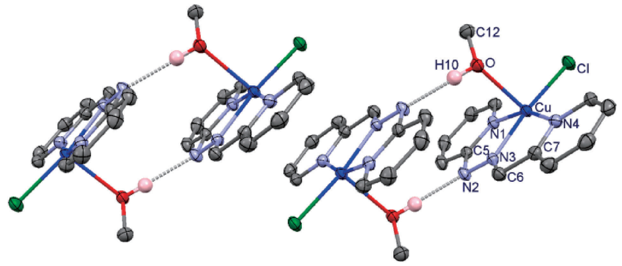


Figure 1. Hydrogen-bonded dimerized structures and their π–π stacking of **1**. Thermal ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted for clarity. Dotted lines show hydrogen bonds.

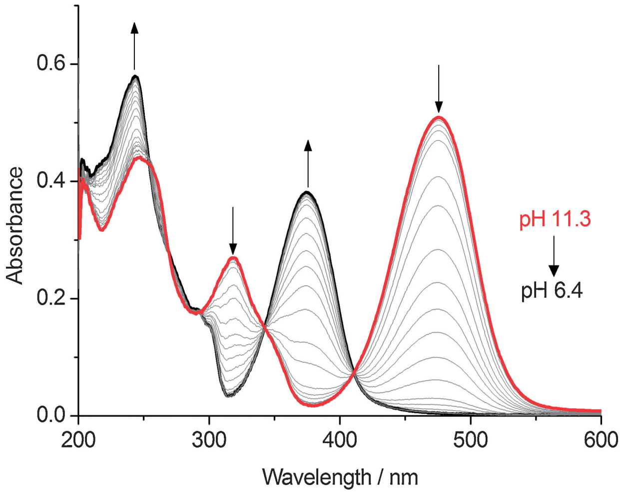


Figure 2. Absorption spectral changes of **1** at various pH in methanol.

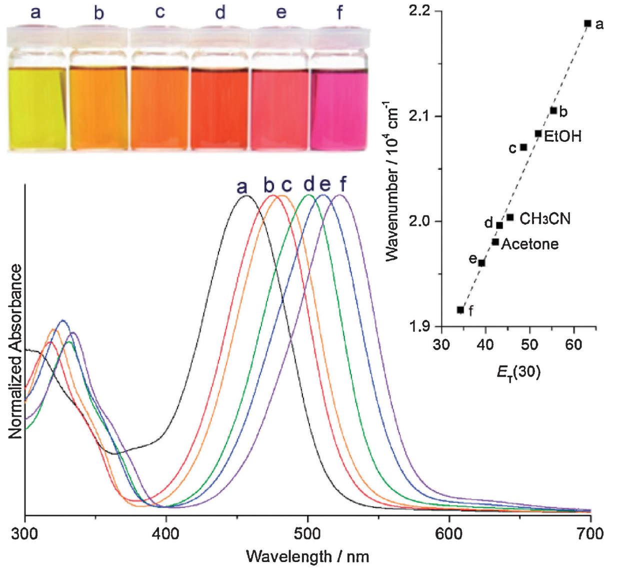


Figure 3. Bright field images and UV–vis absorption spectra of **1** in (a) water, (b) CH_3OH, (c) 2-propanol, (d) DMF, (e) $CHCl_3$, and (f) benzene. Inset shows the linear relationship between the wavenumber of absorption muximum and $E_T(30)$. Dotted line is drawn for a guide.

shown in Figure 2, the deprotonated Cu^{II}–hydrazone complex **1** showed an intense intraligand charge-transfer (ILCT) transition band at 476 nm. By the titration of a methanolic hydrochloric acid solution, the decrease in the band was accompanied by an appearance of a new absorption band at 375 nm, showing the color change from orange to yellowish green. The isosbestic points were maintained at 343 and 411 nm, indicating that the protonation reaction proceeds without any decomposition in this system. The original spectrum of **1** recovered completely by the addition of a base such as potassium hydroxide. Such spectral changes were also observed by adding the other strong acids such as $HClO_4$, HNO_3, and H_2SO_4 (Figure S1[8]). Thus, these spectroscopic results indicate that this complex exhibits reversible acid–base behavior. The acid dissociation constant (pK_a) is determined to be 9.0 ± 0.1 (details are given in Figure S2[8]) which is smaller by about 2.4 than that of [Cu(Hpbph)I] with tetrahedral geometry.[7] It should be attributed to the higher planarity of the hydrazone ligand of the divalent copper complex **1**.

As mentioned above, the color of the metal–hydrazone complexes are highly pH-sensitive by the protonation/deprotonation of the NH part in the hydrazone ligand. In addition, we found that the complex **1** exhibits colorful solvatochromic behavior in the range of yellow to violet as shown in Figure 3. As shown in the inset graph of Figure 3, the energies of the ILCT transition increased linearly with the increase of Dimroth–Reichardt $E_T(30)$ values.[4] This negative solvatochromism suggests that the complex **1** has higher polarity in the ground state than that in the excited state, and larger electrostatic stabilization of the ground state occurs in the solvents with higher polarity. Interestingly, this solvatochromic behavior almost disappeared by the addition of acid. As mentioned above, the complex **1** can receive one proton at the hydrazone part to form the protonated form $[Cu(Hpaph)Cl]^+$. In the protonated form, the solvatochromic shifts of the absorption band were found to be much smaller (Figure S3 and Table S2 in the Supporting Information[8]). These results clearly indicate that the solvatochromic behavior of the complex **1** can be switched by the proton. This switching behavior is attributable to the change of the bonding character of the hydrazone nitrogen (N2) by protonation. In other words, much smaller solvent effect for the protonated form would be due to smaller extent of the charge transfer in the restricted delocalized system. In contrast, larger charge transfer is possible for the deprotonated form, which could give rise to distinct solvent effects. It should be noted that coordinated methanol does not affect this solvatochromic behavior, because the methanol-removed complex [Cu(paph)Cl] also showed the same solvatochromic behavior even in non-coordinating solvents such as benzene (Figure S4[8]).

In summary, we newly synthesized a deprotonated Cu^{II}–hydrazone complex, $[Cu(paph)Cl(CH_3OH)]$ and found that the complex exhibits reversible protonation/deprotonation and colorful solvatochromism in various solvents. Utilizing the protonation ability of the hydrazone moiety, we have succeeded in the ON–OFF switching of the solvatochromic behavior. Further work to develop the hydrogen-bonded proton-transfer assemblies based on this complex is now in progress.

This study was supported by a Grant-in-Aid for Scientific Research (B) (No. 23350025), Coordination Programming (No. 2107), Young Scientists (B) (No. 19750050), and the Global COE Program (Project No. B01: Catalysis as the Basis for Innovation in Materials Science) from MEXT, Japan.

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8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 Crystal data for **1**: [Cu(paph)Cl(CH_3OH)], $T = 150(1)\,K$, $P2_1/c$, $a = 8.8168(19)\,Å$, $b = 8.9742(19)\,Å$, $c = 17.035(4)\,Å$, $\beta = 105.111(3)°$, $V = 1301.3(5)\,Å^3$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 7.6\,\text{mm}^{-1}$. The final R_1 and $wR(F^2)$ were 0.0458 and 0.1209, respectively. CCDC-No. 838660.

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