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Photoresponsive Coordination Assembly with a Versatile Logs-Stacking Channel Structure Based on Redox-Active Ligand and Cupric Ion

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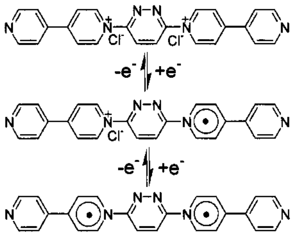
After the great success[1] in such molecular architecture based on coordination polymers, the next generation of supramolecules should acquire their own functions specific to the assembly structures, as a molecule consisting of atoms shows its own electronic structure. The magnetic property is one of the most powerful probes to elucidate the electronic structure including interaction pathway of the assembly. Especially, spin manipulation upon external stimuli will be potentially applied to sensors, molecular switching, and information storage media.[2] There have been several photoinduced spin manipulation systems[3−6] prepared by assembling paramagnetic metal ions or organic neutral radicals with multidentate ligands or π-conjugated blocks. Along this line, we demonstrated four-step redox processes and their corresponding spin manipulation of pyridazylene- and pyrimidylene-conjugated viologen dimers[7] as minimal models of the spin-tunable assemblies. In this communication, we report a new coordination polymer assembling a redox-active bidentate ligand, 3,6-bis(4′-pyridyl-1′-pyridinio) pyridazine (**BPyP**) dichloride,[8] with cupric ion. A logs-stacking structure with giant channels and phototunable magnetic properties of the crystal are described.



The coordination polymer, **CuCl$_4$−BPyP**, was obtained as needle crystal by self-assembly of $CuCl_2$ and **BPyP**$(Cl^-)_2$ in aqueous solution. X-ray single-crystal analysis reveals that the **CuCl$_4$−BPyP** has a logs-stacking structure with multichannels along *c*-axis (Figure 1), including several disordered structures.[9]

Each **BPyP** ligand coordinates to hydrated $CuCl_2$ to give one-dimensional infinite chains in the *ab* plane, which are stacked alternately in orthogonal configuration along the *c* axis to form a desired channel structure. The largest channel is 12x12 Å^2 in inner size, comparable to the porous or grid-like coordination polymers reported so far.[10,11] Here, special emphasis should be laid on the two-step 1D-to-3D assembling mode, that is, the stacking of the first assembled **CuCl$_4$−BPyP** logs to afford the multichannel structure. This two-step assembling may solve a problem of self-interpenetration commonly found in the construction of coordination framework containing giant channel/cavity.[12] The layer structure with ca. 3.29 Å of spacing is reinforced by $\pi-\pi$ interaction of the orthogonally stacked pyridyl moieties. The thermogravimetric analysis indicated that the framework was kept up to 430 K with the loss of most of crystalline water molecules in the unit lattice. Furthermore, the multichannel structure withstood either dehydration in a vacuum at 383 K or rehydration under high humid atmosphere, judging from unchanged main peaks of X-ray powder diffraction during these thermal treatments.

The magnetic susceptibility of the crystal under 5000 Oe of field was evaluated with a SQUID magnetometer (Quantum Design, MPMS-XL) in a range of 2−300 K (Figure 2). The crystal is paramagnetic. The constant χT value (0.38 cm^3 K/mol) in a high-temperature region is consistent with the value (0.375 cm^3 K/mol) expected on one cupric ion ($S = {}^1/_2$) per the formula. The χ-T curve obeys Curie equation with antiferromagnetic interaction (−4.15 K of Weiss constant), suggesting an appreciable spin-exchange interaction between the nearest cupric ions in the smaller channel, not the distant ones at both ends of **BPyP** (23.5 Å).[13] After irradiation at 100 K,[14] the magnetic susceptibility in a high-temperature region increased by a factor of 15%. The crystal was tinged with blue, but little change was observed in the X-ray powder diffraction pattern. This color change was confirmed by UV−vis absorption spectra in solid state, indicating

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(9) Crystal data for **CuCl$_4$−BPyP**: $[CuCl_2(C_{24}H_{18}N_6)](2Cl)(11.275H_2O)$, formula weight = 798.99, monoclinic, space group *C*2/*c* (no. 15), a = 33.295(2) Å, b = 33.289(2) Å, c = 6.5856(4) Å, β = 90.0490(10)°, V = 7299.2(8) Å^3, Z = 8, T = 103 K, D_{calcd} = 1.454 g/cm^3, μ = 0.951, R_1 = 0.066 for unique 6882 reflections ($I > 2\sigma(I)$), and 0.075 for all 8161 reflections (R_{int} = 0.029). The details of the disorders are described in Supporting Information.

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(13) Cu−Cu distance between two close logs is 8.82 Å in *ab* plane, 6.58 Å along the *c* axis.

(14) The sample was irradiated through an optical guide inside the SQUID magnetometer with a 500 W Xe lamp without optical filter. The intensity of incident light was 2 mW/cm^2.

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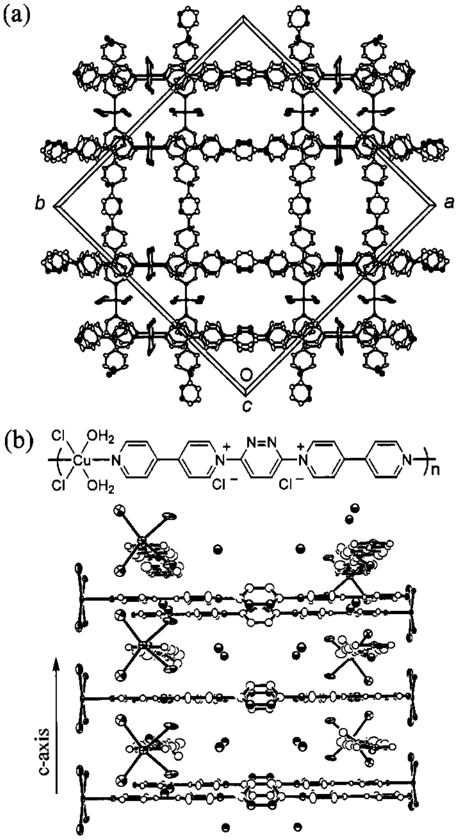

Figure 1. Packing arrangement for the logs-stacking structure of **$CuCl_4$−BPyP** crystal. (a). A view of the multichannel from [001] direction. (b). A view of the alternation chains between layers from [110] direction. The disordered structures[9] were simplified, and crystalline water molecules were also omitted for clarity.

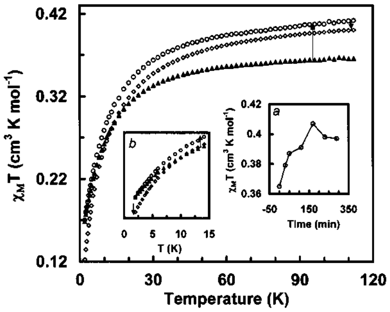

Figure 2. Temperature dependence of the magnetic susceptibility at 5000 Oe of **$CuCl_4$−BPyP** crystal before (▲) and after irradiated for 170 min (○) and 290 min (◇) at 100 K. The insets show (a) the time course of magnetic susceptibility change at 100 K under irradiation and (b) the figure enlarged in a low-temperature region.

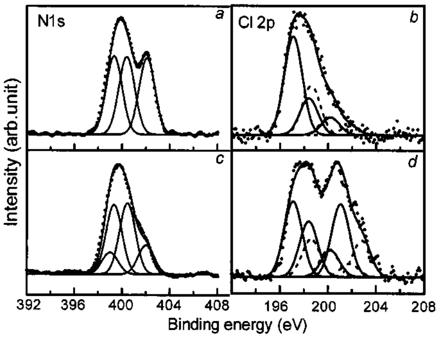

Figure 3. N 1s and Cl 2p XPS core-level spectra of **$CuCl_4$−BPyP** crystal before (a, b) and after (c, d) irradiation (10 mW/cm^2, 4 h) with a 500 W Xe lamp. In the Cl 2p spectra, solid Gaussian peak components correspond to the Cl 2p$_{3/2}$ of spin−orbit-split doublets, and dashed components correspond to the Cl 2p$_{1/2}$.

photoreduction of **BPyP** to form the pyridyl radical. The photoreduction was also confirmed in a **BPyP**(Cl^-)$_2$ ligand crystal by UV−vis spectra and ESR measurement, while little change was observed after **BPyP**(Cl^-)$_2$ anion exchange with Br^-, I^-, SCN^-, or NO_3^-. Therefore, chloride ion would play a role as electron donor in the photoreduction of **$CuCl_4$−BPyP**. Actually, the photoinduced electron transfer in the **$CuCl_4$−BPyP** crystal was successfully proved by XPS measurement.

The N 1s core-level spectrum (Figure 3a) of the as-prepared crystal could be fitted by three well-resolved components at 402.1, 400.4, and 399.3 eV, assigned to the nitrogens of the pyridinium, the coordinated pyridine, and the pyridazine, respectively.[15] After irradiation (Figure 3c), the pyridinium component at 402.1 eV became weak, and a new component appeared at 399.0 eV, assigned to the nitrogen of neutral pyridyl radical.[15] This change strongly suggested the photoreduction of **BPyP** in the coordination polymer. What is an electron donor? After irradiation, a new pair of prominent components appeared in the Cl 2p core-level spectra (Figure 3d), with the binding energy for the Cl 2p$_{3/2}$ peak lying at about 201.1 eV, indicating the formation of neutral chlorine atom or molecule.[16] The ESR signal ($g = 2.135$) assigned to cupric ion was never changed after irradiation, so that the cupric ion did not participate in the photoinduced electron transfer. These results clearly illustrated that the photoinduced electron transfer should take place from Cl^- to **BPyP**. It should be noted that the successful XPS study owes a great deal to selective analysis on only the topmost surface in which any photochemical process is prominent in the solid state. A further irradiation resulted in a gradual decrease in the χT value. This up-and-down change in the χT value in a high-temperature region was demonstrated as a function of irradiation time (inset a, Figure 2). An enhanced antiferromagnetic behavior was suggested in a low-temperature region (inset b). The decrease of magnetization in a prolonged irradiation may be explained by a contribution of 2-electron-reduced **BPyP**, of which two spins are coupled antiferromagnetically. An additional noticeable aspect is an effective anion-exchangeable property due to the positively charged skeleton of the assembly. This treatment with various anionic guests allows us to widely derivatize the multichannel coordination assembly, which is now under investigation. The redox-active building blocks will open a new avenue in the coming coordination assemblies with specific electronic functions, through their valence control by external stimuli.

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Supporting Information Available: Tables of crystal data and structure refinement data, positional and thermal parameters, bond lengths and angles for **$CuCl_4$−BPyP** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Each spectrum of N 1s and Cl 2p was fitted with Gaussian component peaks with reference to: (a) Tan, K. L.; Tan, B. T. G.; Kang, E. T.; Neoh, K. G. *Phys. Rev. B* **1989**, *39*, 8070. (b) Neoh, K. G.; Kang, E. T.; Tang, K. L. *J. Phys. Chem.* **1991**, *95*, 10151. (c) Alvaro, M.; Garcia, H.; Garcia, S.; Marquez, F.; Scaiano, J. C. *J. Phys. Chem. B* **1997**, *101*, 3043. (d) Sampanthar, J. T.; Neoh, K. G.; Ng, S. W.; Kang, E. T.; Tan, K. L. *Adv. Mater* **2000**, *12*, 1536.

(16) The crystal involves three kinds of chloride species, i.e., coordinated Cl^-, hydrogen-bonded Cl^-, and free Cl^-. Before irradiation, the Cl 2p core-level spectrum is resolved into three spin−orbit-split doublets (Cl 2p$_{1/2}$ and Cl 2p$_{3/2}$), with the binding energy for the Cl 2p$_{3/2}$ peaks lying at 197.1, 198.4, and 200.2 eV (also see ref 15).