Supramolecular Machines

Towards Electrochemical Artificial Muscles: A Supramolecular Machine Based on a One-Dimensional Copper-Containing Organophosphonate System**

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Protein motors, such as myosin (from skeletal muscle) or kinesin (from the brain) are composed of mats of bipolar one-dimensional (1D) filaments. These filaments are set into motion either by an electrochemical reaction or by a chemical signal, which initiates a reversible contraction/stretched process.[1] To mimic the motions taking place in biological motors is very challenging. The mimetic nanofilaments should have mixed copper(II/I) centers and phosphate ligands and be self-assembled by much weaker π–π interactions. It is therefore of interest to explore the kind of supramolecular filaments that may be reversibly tuned simply by inserting and extracting ion species with an applied voltage. Such biomimetic concepts could lead to a new class of the battery-like actuations.[2–5]

Many inorganic 1D fibers, such as carbon nanotubes and conducting polymer, have been reported and investigated in the construction of smart actuator materials,[6,7] however, to date, relatively few examples of coordination-polymer-based artificial machines are known.[8] To maximize the potential of such supramolecular machines, we propose that the following are required: 1) the construction of a 1D supramolecular chain structure with redox active metal centers, especially mixed copper(II/I) centers,[9] 2) the introduction of metal-ion intercalation into the crystal at an arbitrary position, and 3) the introduction of crystal-volume change through an applied voltage.

Encouraged by our success in using ethylenediphosphate as a building block unit for the construction of extra-large molecular sieves under hydrothermal conditions,[10] we have turned our attention to the introduction of 1,10-phenanthroline (phen) units into the metal–organophosphate phases to

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create 1D chain structures (Figure 1 a). Green crystals of 1 DOP-Cu (Figure 1) were grown from a reaction mixture of $CuCl_2 \cdot 2\,H_2O$, ethylenediphosphate, phen, and water in molar ratios of 2:1:1:1778 that was heated at 180 °C for 48 h in an autoclave. This hydrothermal synthesis gives a yield of 48 % and is highly reproducible. The structure of 1 DOP-Cu was determined by single-crystal X-ray analysis (Figure 1 b–d). The structure reveals infinite 1D inorganic zigzag chains, $[\text{-Cu}^{II}\text{-O}_3\text{P-(CH}_2)_2\text{-PO}_3\text{-Cu}^{II}\text{-}]$, in which the phen ligands are bound to the metal centers. The chain structure of 1 DOP-Cu has three intriguing features. First, the backbone of 1 DOP-Cu consists of phosphonate groups, at which acid-functionalized groups may serve as carriers of protons, the phosphonate groups can also serve as a solid-state matrix for metal-ion transport. Second, the incorporated phen ligands play an important role in the construction of a π-stacked layer structure between adjacent crystallographically symmetry-related chains, which makes the layered framework conducting. Like natural muscle fibers, the corrugated sheets are composed of mats of individual chain-bundles joined by π–π interactions along the crystallographic *a* axis. Third, both the two crystallographically distinct Cu^{II} atoms have square-pyramidal coordination geometries, chelated by two nitrogen atoms of the phen ligands, two oxygen atoms from two distinct ethylenediphosphate groups, and one coordinated water molecule. The triggering signals of actuator of 1 DOP-Cu could be envisaged to be an electrochemical signal that initiates a redox process converting Cu^{II} into Cu^{I}. The proposed principle of the redox motion is shown in Figure 2.

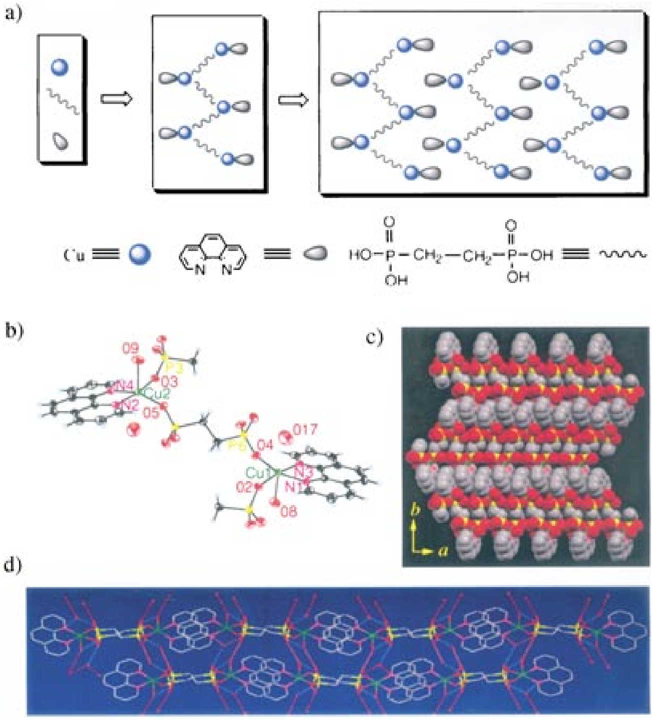

Figure 1. a) Schematic illustration of a macroscopic sheet generated by 1D chains. b) An ORTEP plot of a section of an infinite chain in 1 DOP-Cu (thermal ellipsoids set at 50 % probability). Selected bond lengths [Å]: Cu1–O2 1.934(3), Cu1–O4 1.936(4), Cu1–N1 2.002(4), Cu1–N3 2.020(4), Cu1–O8 2.391(4), Cu2–O3 1.945(3), Cu2–O5 1.940(3), Cu2–N2 2.011(3), Cu2–N4 2.025(4), Cu2–O9 2.277(4). c) Space-filling view of the *ab* plane showing the corrugated π–π network constructed from copper–ethylenediphosphate chains incorporating phen molecules. d) Perspective view of crystal packing along the *a* axis, showing adjacent layers are stacked on top of each other along the *c* axis and are held together by the hydrogen bonds. Green Cu, red O, pink N, yellow P, gray C.

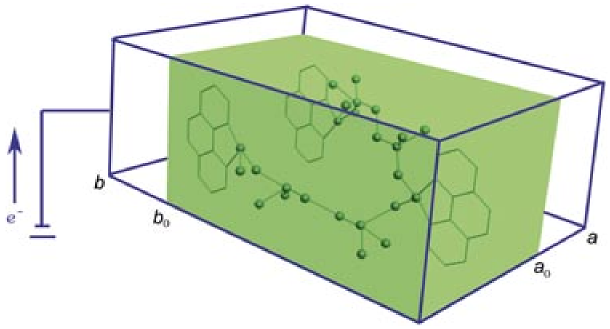

Figure 2. Schematic illustration of the increasing thickness of the sheet when it is charged negatively (green box 1 DOP-Cu, blue box Li@1 DOP-Cu). The strains, relative length change $\varepsilon_a = (a-a_0)/a_0 = \Delta a/a_0$, $\varepsilon_b = (b-b_0)/b_0 = \Delta b/b_0$, and the volume change $\varepsilon_V = (V-V_0)/V_0 = \Delta V/V_0$, are relative to the lattice parameters of 1 DOP-Cu. The electrochemical actuator is based on materials that change in shape and dimension when a potential is applied. Water molecules and Li^+ ions can be intercalated between the layers by applying a negative voltage to the organophosphonate sheet. We proposed that the electrochemical intercalation of Li^+ ions must be compensated by some reduction of Cu^{II} ions in the sheet. Thus, to maintain electroneutrality, partial Cu^{I} ions are formed, which are much larger than Cu^{II} ions (0.91 Å instead of 0.71 Å). Fundamentally, Cu^{I} prefers four-coordinate binding mode whereas Cu^{II} prefers five-coordinate square-pyramidal geometry. Therefore, the reduction of Cu^{II} ions leads to a strong deformation of the chain structure, leading to the mechanical deformation of the whole sheet.

To achieve a new battery actuator, a mechanically robust framework is necessary. The stability of the layered structure was therefore assessed by thermogravimetric analysis (TGA) and in situ synchrotron powder X-ray diffraction (XRD) studies. The results show that the phosphonate groups are stable up to 300 °C in the presence of air or nitrogen.

Because the phosphonate groups can act as a solid-state matrix for lithium ions to make crystalline phases with fast ion conduction, the insertion or doping of a lithium compound in 1 DOP-Cu was studied. Insertion was achieved by the recharge battery methodology[10] in the ionic liquid, $LiClO_4$, to give Li@1 DOP-Cu. Electrochemical studies show that the charge-state of 1 DOP-Cu was stable over a potential window of approximately 5 V, and especially a remarkable cyclabilty was traced between 3 and 5 volts (Figure 3). The electromechanical cycling of a battery shows an actuator response that can be detected during cyclic voltammetry, there are also concomitant changes in volume. It is evident from TGA analysis that the weight loss (9.8 %) of the Li-inserted phase (Li@1 DOP-Cu) is significantly larger than that (4.4 %) of 1 DOP-Cu upon heating up to 220 °C (Figure 4, inset). It is also of interest to compare the change in unit-cell volume.

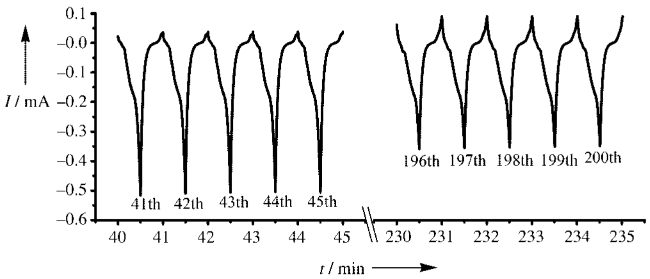

Figure 3. Current versus time plot for cyclic voltage changes in the range of 3–5 V for an anode graphite/cathode 1 DOP-Cu (**C**|1 DOP-Cu) cell employing 1 M $LiClO_4$ in an electrolyte mixture of ethylene carbonate, dimethyl carbonate, and methyl formate ($T = 30$ °C, scan rate 100 mV s^{-1}). The cyclability of 1 DOP-Cu by intercalating/de-intercalating lithium ions is shown (the numbers next to the peaks indicate the number of the cycle).

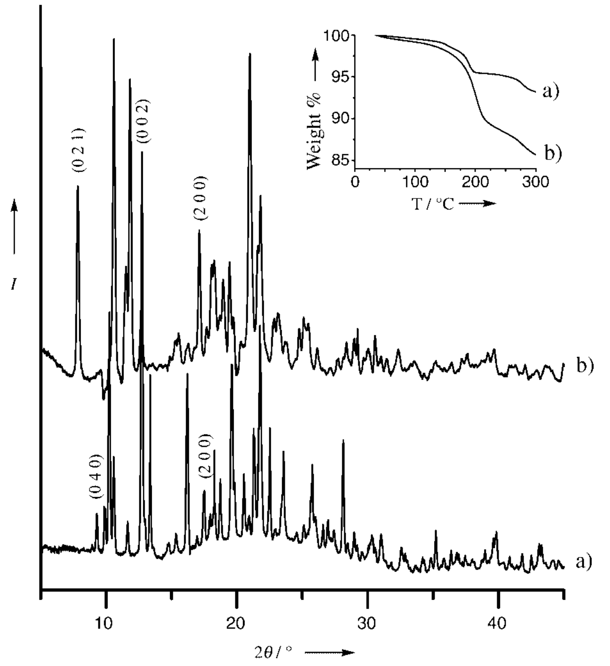

Figure 4. The XRD patterns (synchrotron radiation, $\lambda = 1.32633$ Å) of a) 1 DOP-Cu and b) Li@1 DOP-Cu. I is the X-ray intensity (arbitrary units). It is noteworthy that the simulated diffraction patterns based on the analysis of a single-crystal X-ray structure is in good agreement with the XRD patterns obtained for 1 DOP-Cu samples, which indicates that 1 DOP-Cu is a pure phase. (Li@1 DOP-Cu still has a monoclinic structure with the lattice constants $a = 9.51$, $b = 32.84$, $c = 12.88$ Å, $\beta = 110.5$, $V = 3767$ Å^3). The inset shows the corresponding weight loss of a) 1 DOP-Cu and b) Li@1 DOP-Cu, by TGA analysis.

According to the XRD patterns, the cell-volume strain $\Delta V/V_0$ change is 10.2 %. Phenomenologically, the actuator must produce the observed volume change by a change in the basal-plane dimension rather than in the distance between layers. The corresponding XRD spectra are presented in Figure 4. It is worth noting that the distance between layers (d_{002}) remains constant whereas the dimension of the unit cell of the corrugated sheets changes, which is caused by the uneven stress along the a and b axes. The variation of the strain $\Delta a/a_0$ and $\Delta b/b_0$ is 3.8 % and 6.2 %, respectively. The larger strain in the b axis direction during actuation could be due to the weakness of the π–π repulsions between chains. The whole thickness within the framework sheet increases owing to the strong deformation of the redox chain structure when it is charged negatively (see the Supporting Information movie file). This result may be similar to the battery-like actuation mechanism of conducting polymers where a redox reaction must occur to enable the flux of ionic dopant.[7,11]

Elucidating the mechanism of the deformation of the chain structure upon lithium insertion into crystals of 1 DOP-Cu is interesting for developing supramolecular machines. To address this problem, solid-state nuclear magnetic resonance (SSNMR) and X-ray absorption spectroscopy were used to elucidate the lithium-inserted state of 1 DOP-Cu. In ^{7}Li NMR spectrum, a chemical shift of $\delta = +1.8$ ppm for the Li^+ ion is small enough to assign the lithium residing in the phosphoric matrix as being in a highly ionic state rather than a metallic state. Moreover, it appears that the narrow line width (full width at half height, ≈400 Hz) offers a conclusive evidence for lithium-ion motion in crystalline Li@1 DOP-Cu.[12,13] Lithium-ion coordination contributes to the reversible charge–discharge reaction which takes place at the bonding orbitals of the Cu-O-P-O units. Evidence for the partial electronic reduction of Cu^{II} in Li@1 DOP-Cu was provided by ^{31}P-{^{1}H} MAS (magic-angle spinning) NMR data (Figure 5 a). Owing to the paramagnetic character of the bonding orbital of $Cu^{II}(d^9)$-O-P-O in 1 DOP-Cu, the ^{31}P NMR spectrum reveals a significant downfield chemical shift with associated spinning sidebands in the range $\delta = 200$–1000 ppm, whereas in the lithium-inserted state, Li@1 DOP-Cu ($Cu^{I}(d^{10})$-O-P-O···Li^+)

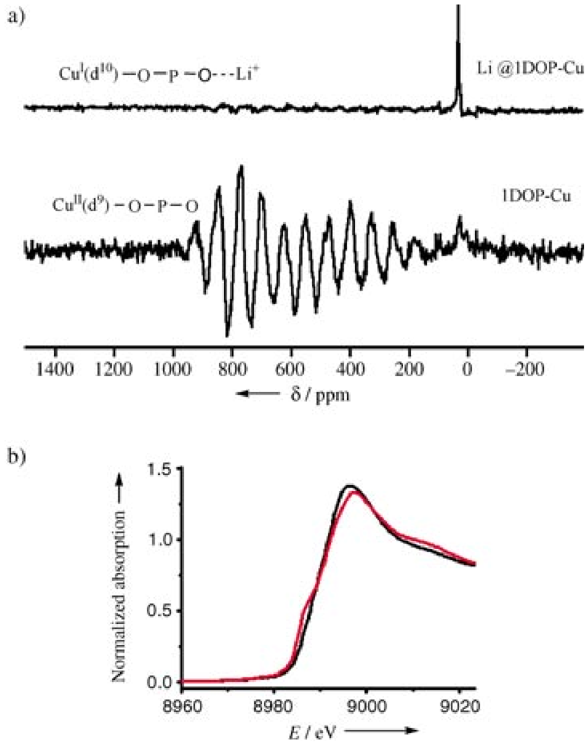

Figure 5. Monitoring the redox process in solid actuator by a) ^{31}P-{^{1}H} MAS NMR and b) XANES spectra. Red Li@1 DOP-Cu, black 1 DOP-Cu.

the chemical shift is $\delta = 31$ ppm. Finally, it is necessary to examine whether the coordination geometry of Cu^{II} or Cu^{I} is changed in the redox process, a key concept of artificial machines postulated by Sauvage.[9] X-ray absorption near edge spectra (XANES) is often used as a probe for the ligand-field geometry, electronic structure, and oxidation state of the metal center.[14] The synchrotron radiation XANES spectra for lithium (de)insertion states are shown in Figure 5b. A comparison of the XANES spectra reveals that the lithium-inserted state has a shoulder or partially resolved peak on the rising edge at 8985.4 eV in addition to $1s \rightarrow 3d$ pre-edge transition at 8991.8 eV, which suggests different environments in the geometry around the metal ions. It is observed that only a pre-edge peak from a $1s \rightarrow 3d$ transition is found in the XANES spectra of square-pyramidal copper-based 1DOP-Cu. For Li@1DOP-Cu the significant shoulder on the low-energy side of the edge was assigned to a $1s \rightarrow 4p_z$ transition in accordance with the destabilization of $4p_z$ metal orbital (z being the elongation axis), suggesting distortion from square-pyramidal into a square-planar geometry. It is reasonable to assume that 1DOP-Cu could afford machines that are electrochemically muscle-like, with basal planes that allow the conversion of the five-coordinate (Cu^{II}) geometry into the four-coordinate (Cu^{I}) arrangement and vice versa.

The electrochemical actuator process presented herein provides an approach for studying the actuating mechanism of natural molecular motor, this being one of the key goals for the progress of molecular motor technology. Not only could this work lead to the development of all-solid-state rechargeable lithium batteries, but also our approach could open the route for the design of new ionic-switched electrochemical artificial muscle systems.

Experimental Section

Synthesis of 1DOP-Cu: The reaction was carried out in a 23-mL teflon-lined acid digestion bomb (Parr), heated in a programmable electric furnace (Lindberg/Blue). A reaction mixture of $CuCl_2 \cdot 2H_2O$ (0.0850 g, 0.5 mmol), ethylenediphosphate (0.2850 g, 0.24 mmol), 1,10-phenanthroline monohydrate (0.0493 g, 0.24 mmol), and H_2O (8 mL) was sealed in a 23 mL teflon-lined stainless autoclave, heated at 100 °C for 2 h at $120\,^{\circ}C\,h^{-1}$, then heated at 180 °C for 48 h, then cooled to 70 °C at $9\,^{\circ}C\,h^{-1}$ and then allowed to cool to room temperatue. The resulting blue-green crystals were collected by filtration, and washed with deionized water. Yield 48 %.

The X-ray diffraction data were collected on a CCD Bruker AXS SMART-1000 diffractometer with monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) in the $\omega/2\theta$ scan. Crystal size $0.211 \times 0.277 \times 0.278$ mm, monoclinic, space group $P2(1)/n$, $a_0 = 9.1579(18)$, $b_0 = 30.916(6)$, $c_0 = 12.882(3)$ Å, $\beta_0 = 110.52(3)$; $V_0 = 3415.7(12)$ Å^3, $Z = 4$, $F(000) = 1864$, $\sigma = 1.796$ $Mg\,m^{-3}$, $2\theta max = 55°$; $R1 = 0.0778$, $wR_2(F^2) = 0.2586$, and $GOF = 1.086$; residual electron density between 2.499 and -1.353 e Å^{-3}. CCDC-228650 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax(+44)1223–336–033; or deposit@ccdc.cam.ac.uk).

All solid-state NMR spectra were recorded on a Bruker AVANCE-400 spectrometer with a standard Bruker double-tuned 4 mm probe; ^{31}P 161.73 mHz and ^{7}Li 155.45 MHz. A $\pi/2$ pulse length of 4 μs and a recycle delay of 10 s were used to acquire all the NMR spectra. ^{31}P MAS spectra were obtained under conditions of high-power proton decoupling. Chemical shifts of ^{31}P and ^{7}Li were externally referenced to 85 % H_3PO_4 and 1 M LiCl(aq), respectively.

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