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A Novel Hybrid of Bi-Based High-T_c Superconductor and Molecular Complex

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Molecular complex HgI_2Py_2 (Py = pyridine) was intercalated into the Bi-based high-T_c cuprate by intercalative complexation. The intercalation method adopted in this work is based on the new concept, where a neutral ligating agent is diffused into the preintercalated HgI_2 layer leading to a charge transfer-type complex formation between the Bi_2O_2 double layers of $Bi_2Sr_2CaCu_2O_y$.

The unit layers of Bi-based high-T_c cuprate superconductor are stacked by the van der Waals interaction to form a mica-like structure, allowing guest species to be intercalated between the Bi_2O_2 double layers.[1−4] It has been reported that small atoms or inorganic molecules could be intercalated into Bi-based cuprates,[1,2] and organic cations such as alkyl-pyridinium and sulfonium could also be incorporated with superconducting cuprate.[3,4] Such hybrids of organic moiety and Bi-based cuprate will help us not only to better understand the nature of high-T_c superconductivity but also to design a new class of nanohybrids. For low-T_c superconductors, strongly anisotropic or two-dimensional superconductivity has been studied using transition-metal dichalcogenides MX_2 (M = Ta, Nb, X = S, Se) intercalated with organic molecules.[5−7] In this work, we report the synthesis of Bi-based superconductor $Bi_2Sr_2CaCu_2O_y$ (Bi2212) interstratified with an insulating complex of di-iodobis(pyridine)mercury(II), HgI_2Py_2.

The molecular complex/superconductor hybrid was prepared according to the following process. The pristine Bi2212 compound[8] was synthesized by conventional solid state reaction with the nominal composition of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_y$, where in the final synthetic step the sample was annealed at 500 °C for 72 h in air to ensure an unbroken Cu−O network within the superconductive CuO_2 layers.[9] The intercalation of molecular complex HgI_2Py_2 was achieved by stepwise reaction. First, the HgI_2-intercalated Bi2212 (HgI_2−Bi2212) was prepared by heating the guest HgI_2 and the pristine Bi2212 in a vacuum-sealed Pyrex tube, as reported previously.[2] Then the post-intercalation of the pyridine molecule was achieved by reacting the HgI_2-intercalate with pyridine vapor, where the two reactants were separately put in a T-shaped tube in order to avoid direct contact with each other. The tube was vacuum-sealed, while pyridine in the downward branch was being frozen in a liquid-nitrogen bath and heated in an oven at 80 °C for 40 h allowing the pyridine vapor to react with HgI_2-intercalate. After cooling it down to room temperature, the sample was washed with hexane to remove free pyridine molecules on the sample surface. Then the sample was vacuum-dried and characterized.

The structural evolution in each intercalation process was analyzed by the powder X-ray diffraction using nickel filtered Cu Kα radiation with a graphite monochromator. Figure 1 shows the powder XRD patterns for the pristine Bi2212 and its HgI_2- and HgI_2Py_2-intercalates. The XRD analyses indicate that the basal spacing increases from 19.5 Å (Δd = 7.2 Å) for the HgI_2-intercalate to 26.5 Å (Δd = 11.2 Å) for the HgI_2Py_2-intercalate. The basal increment (Δd) upon

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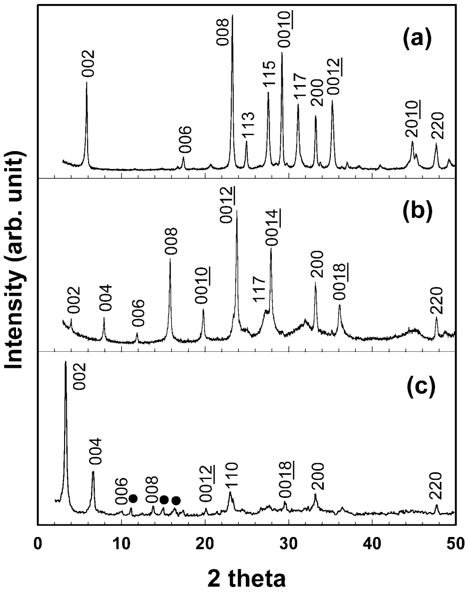

Figure 1. Powder X-ray diffraction patterns for (a) pristine Bi2212, (b) HgI_2−Bi2212, and (c) HgI_2Py_2−Bi2212. Filled circles (●) in part c represent the XRD peaks for the free HgI_2Py_2.

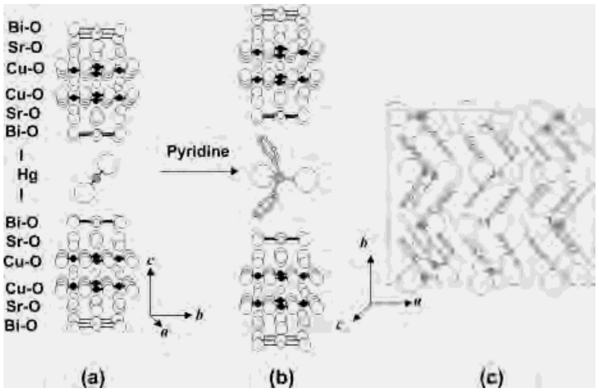

Figure 2. Schematic illustration of the interlayer complexation. The structures of (a) HgI_2−Bi2212, (b) HgI_2Py_2−Bi2212, and (c) free HgI_2Py_2 are represented.

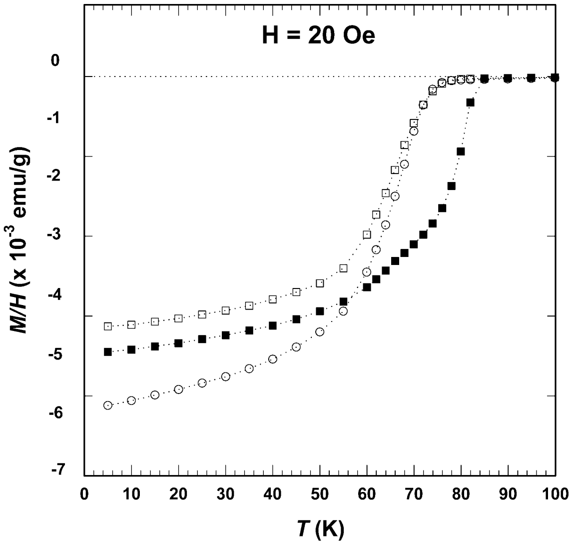

Figure 3. The temperature-dependent zero-field-cooled magnetizations for pristine Bi2212 (○), HgI_2−Bi2212 (□), and HgI_2Py_2−Bi2212 (■), respectively. All the measurements were carried out in an applied field of 20 Oe. In the SQUID data, the diamagnetic magnetization for the HgI_2Py_2−Bi2212 is slightly underestimated, since the sample contains a small amount of free HgI_2Py_2. The dotted-line is the guide to the eye.

HgI_2Py_2 intercalation with respect to the pristine compound is comparable to the projected molecular size of the complex molecule in the free HgI_2Py_2 crystal (Figure 2 c),[10] confirming the formation of a periodic sequence of Bi2212/HgI_2Py_2/Bi2212 along the *c*-axis. Despite basal increment upon intercalation, the in-plane (*a* and *b*) lattice parameters are invariant to those of the pristine within the detection limit of X-ray diffraction analysis. Taking into account the increase of layer separation and the pseudotetrahedral geometry of HgI_2Py_2 molecule, it is suggested that the iodine atoms in close contact with Bi−O layer (Figure 2a) move to the middle of interlayer gallery upon post-intercalation of pyridine (Figure 2b). The impurity phase in the XRD pattern (Figure 1c) results from the free HgI_2Py_2, which is expelled from the Bi2212 lattice upon post-intercalation of pyridine into the pre-intercalated HgI_2 layer due to the size difference between the HgI_2 molecule and the HgI_2Py_2 one. In an intention to completely remove the free HgI_2Py_2, the sample was rigorously washed with solvents that can dissolve the complex molecule. Unfortunately, however, any trial of removing the free molecular complex inevitably accompanied partial deintercalation of the intercalant (HgI_2Py_2) from the Bi2212 lattice probably due to the weak interaction between the molecular complex and the cuprate block, which hampered the accurate elemental analyses for HgI_2Py_2−Bi2212. At this point, the intercalation compound (HgI_2Py_2−Bi2212) can be represented as $(HgI_2Py_2)_x$Bi2212 ($x < 0.5$).

The black color and metallic nature of the host lattice (Bi2212) also prevented the characterization of the intracrystalline HgI_2Py_2 by using infrared (IR) spectroscopy. Instead, we have monitored the changes in the geometric and electronic structures of the guest by measuring bulk-sensitive X-ray absorption spectroscopy (XAS). The structural and electronic evolution of the guest upon interlayer complexation have been probed by the Hg L_{III}-edge and I L_I-edge X-ray absorption near structure (XANES) spectra, respectively (Supporting Information).

The superconducting properties were investigated by measuring the temperature-dependent magnetic susceptibilities using a dc SQUID (superconducting quantum interference device) magnetometer. Figure 3 represents the zero-field-cooled (ZFC) dc magnetizations of the pristine Bi2212, the HgI_2−Bi2212, and the HgI_2Py_2−Bi2212, where the applied magnetic field is 20 Oe. Upon HgI_2 intercalation, the T_c is nearly invariant to that of the pristine Bi2212 ($T_c \approx 78$ K), which is most probably due to the pristine material annealed at moderate temperature, distinguished from the previous reports.[2−4] However, the T_c is slightly increased to 82 K for HgI_2Py_2−Bi2212 despite increased layer separation ($\Delta d = 11.2$ Å). This phenomenon is very interesting in the viewpoint of interlayer coupling theory of high-T_c superconductivity,[11] in which T_c should decrease with increasing layer separation. Here it is worth noting that the T_c variation

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[10] Canty, A. J.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 15.

is solely dependent on the chemical nature of guest species irrespective of the basal increment. In this respect, the T_c variation is well understood as a change of hole concentration in the CuO_2 plane at each intercalation step.[12] According to the previous reports on the iodine and HgI_2 intercalated Bi2212,[2,13] it was revealed that there occurs electronic charge transfer from the host to the guest. It is, therefore, considered that the Bi2212 lattice acts as soft Lewis base and the electronegative guest acts as soft Lewis acid, respectively.

In the present case, electron-pair donating pyridine and electron-accepting mercury atom of the HgI_2 form a complex molecule with a charge-transfer type (Hg−N) bond. As a result of this donor−acceptor interaction between mercury and pyridine, the formation of HgI_2Py_2 can be explained by Lewis acid−base terminology.[14] Since the complex formation reaction proceeds between Bi_2O_2 double layer upon post-intercalation of pyridine, the two-dimensional cuprate sheet and pyridine molecule can be regarded as competing soft Lewis bases for the pre-intercalated HgI_2. But the electron-donating ability of pyridine molecule is superior so as to form a coordinative bond with Hg. Since the resultant HgI_2Py_2 is a molecular complex without any significant electron-donating or accepting property, post-intercalation of pyridine gives rise to a backward electronic charge transfer compared to the case of HgI_2-intercalation, in other words, electronic charge transfer from the guest to the host. Therefore, it is naturally anticipated that the hole concentration of CuO_2 plane is modified upon HgI_2Py_2 formation due to the electron transfer from the intercalant layer to the cuprate lattice, which is responsible for the slight increase of the T_c value.

From the comparative I L_I-edge XANES analyses for the HgI_2−Bi2212 and the HgI_2Py_2−Bi2212 (Supporting Information), it is revealed that the pyridine molecule coordinates via the nitrogen atom to the mercury, in which the electron transferred from the pyridine to the Hg consequently fills the I 5p empty states through strong covalent mixing between Hg 6s and I p_z orbitals.[15] In this respect, it is naturally expected that the electrons donated from the cuprate lattice to the intercalant HgI_2 layer should be given back to the host, recovering or possibly reducing the hole concentration within the CuO_2 plane. This interpretation asserts that the post-intercalation of pyridine changes the electronic structure of the intracrystalline HgI_2 as well as the host lattice.

In the present HgI_2Py_2/Bi2212 hybrid material, the 15.3 Å-thick cuprate layer and the 11.2 Å-thick molecular complex one are alternately stacked to form superconducting−insulating−superconducting (S−I−S) multilayer, which is distinguished from the oxide superlattices prepared by the conventional deposition methods.[16] In addition, the HgI_2Py_2−Bi2212 is considered as a high-T_c analogue of pyridine intercalated low-T_c metal chacogenide superconductors in its structure and property.

In summary, we have prepared a novel hybrid of molecular complex and cuprate superconductor through an intercalative complex formation reaction, where the molecular complex of HgI_2Py_2 is immobilized between the Bi_2O_2 double layers of two-dimensional oxide lattices. The T_c value of superconducting intercalates mainly depends on the nature of the guest species but is insensitive to the separation between the superconducting blocks, indicating that the high-T_c superconductivity is confined to the two-dimensional metallic layers and mainly dependent on the intrinsic hole concentration of CuO_2 plane.[17] In the viewpoint of chemistry, we were able to realize a molecular complex−superconductor nanohybrid by successfully inducing a complex formation reaction in the interlayer space of the cuprate slabs. Such an interlayer complexation reaction might be a useful strategy in designing and developing hybrid materials with unusual physicochemical properties,[18] which might be derived from combining the benefits of the (super)conducting inorganic lattice and the functional organic molecules or ions.

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Supporting Information Available: Figures depicting the changes in the geometric and electronic structures of the guest species through I L_I-edge and Hg L_{III}-edge XANES analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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