Supporting Information

Polyoxomolybdate Layered Crystals Hybridized with a Heterocyclic Surfactant: Syntheses, Pseudopolymorphism and Introduction of Metal Cations

1. Synthesis and Characterization of C_{12}py-Mo_8 by the Reoxidation of Reduced POM

1.1. Synthesis

C_{12}py-Mo_8 was synthesized by another method utilizing gradual reoxidation of reduced molybdenum POM hybridized with C_{12}py cation (C_{12}py-red-Mo). The C_{12}py-red-Mo hybrid was prepared as follows; $Na_2MoO_4{\cdot}2H_2O$ (2.6 g, 11 mmol) was dissolved in H_2O (10 mL), and the pH level was adjusted to 4.0 with 6 M HCl. To this colorless solution was added solid ascorbic acid (0.1 g, 0.5 mmol) as reducing reagent. After stirring for 40 min, the solution color turned dark blue indicating the formation of reduced POM species, and sequentially a water/ethanol (10 mL, 1:2 (v/v)) solution of $C_{12}pyCl{\cdot}H_2O$ (0.42 g, 1.5 mmol) was added to the solution with stirring for 10 min. Resultant suspension was filtered to obtain blue precipitate of C_{12}py-red-Mo. Colorless block crystals of C_{12}py-Mo_8 was grown by slow evaporation of *N*,*N*-dimethylformamide/acetone (15 mL, 2:1 (v/v)) solution of C_{12}py-red-Mo. CHN elemental analysis: Calcd for $C_{74}H_{138}N_4Mo_8O_{29}$: C: 38.39, H: 6.01, N: 2.42%. Found: C: 38.93, H: 5.74, N: 2.58%. IR (KBr disk): 954 (w), 927 (s), 914 (s), 844 (m), 823 (m), 800 (m), 779 (m), 713 (m), 685 (m), 663 (m), 555 (w), 525 (w), 480 (w), 456 (w), 411 (w) cm^{-1}.

1.2. Crystal Structure Deteramination

Diffraction data were collected and processed on a Rigaku R-AXIS RAPID diffractometer by using graphite monochromated Mo Kα radiation with PROCESS-AUTO. The diffraction data recorded at the 2D beamline in the Pohang Accelerator Laboratory (PAL, South Korea) confirmed the same crystal structure. Crystal structure was solved by SUPERFLIP, and refined by the full-matrix least-squares using SHELXL (Version 2018/3) through CrystalStructure software package. Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms on C atoms were located in calculated positions. CCDC 2153849.

2. Structure of C_{12}py-Mo_8 by the Reoxidation of Reduced POM

Gradual reoxidation of initially blue solution containing C_{12}py-red-Mo endowed colorless single crystals of C_{12}py-Mo_8. The IR spectrum and powder XRD pattern of the obtained crystal (Figure S2) were similar to those of the C_{12}py-Mo_8 precipitate and crystal prepared from conventional method using $Na_2MoO_4{\cdot}2H_2O$ or $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ as a molybdenum source (Figures 1a, 1b, 2a, 2b). In Figure S2b, the powder XRD patterns measured for obtained crystal and calculated from the result of crystal structure analysis were slightly different in the peak position and intensity probably because of pre-ferred orientation derived from the distinct layered structures of C_{12}py-Mo_8. In addition, the crystal structure of C_{12}py-Mo_8 obtained from C_{12}py-red-Mo (Table S1, Figure S3) was the same as that of the C_{12}py-Mo_8 crystal prepared from the conventional method (Figure 3a, 3c).

Table S1. Crystallographic data for C_{12}py-Mo_8 prepared from C_{12}py-red-Mo.

Compound	C_{12}py-Mo_8
Chemical formula	$C_{68}H_{120}N_4Mo_8O_{26}$
Formula weight	2177.23
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	10.4334(6)
b (Å)	11.6760(6)
c (Å)	20.1877(10)
α (°)	77.7581(14)
β (°)	75.7242(15)
γ (°)	68.5309(14)
V (Å^3)	2197.64(19)
Z	1
ρ_{calcd} (g cm^{-3})	1.645
T (K)	296
Wavelength (Å)	0.71075
μ (mm^{-1})	1.171
No. of reflections measured	35543
No. of independent reflections	10042
R_{int}	0.0642
No. of parameters	525
R_1 ($I > 2\sigma(I)$)	0.0546
wR_2 (all data)	0.1416

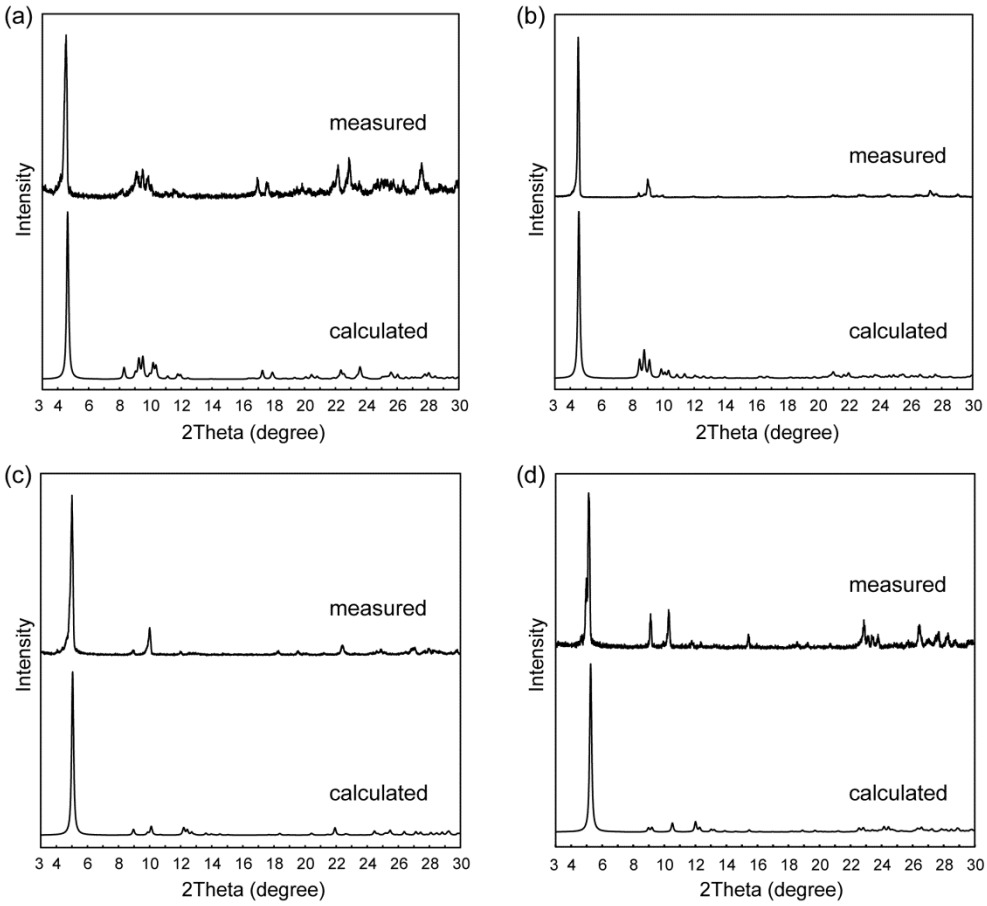


Figure S1. Measured and calculated powder X-ray diffraction patterns of C_{12}py-Mo_8 and related hybrid crystals. Measured patterns were obtained at ambient temperature. Calculated patterns were obtained from the structure revealed by single-crystal X-ray diffraction: (**a**) C_{12}py-Mo_8; (**b**) C_{12}py-Mo_8-AN; (**c**) C_{12}py-Rb-Mo_8; (**d**) C_{12}py-Cs-Mo_8.

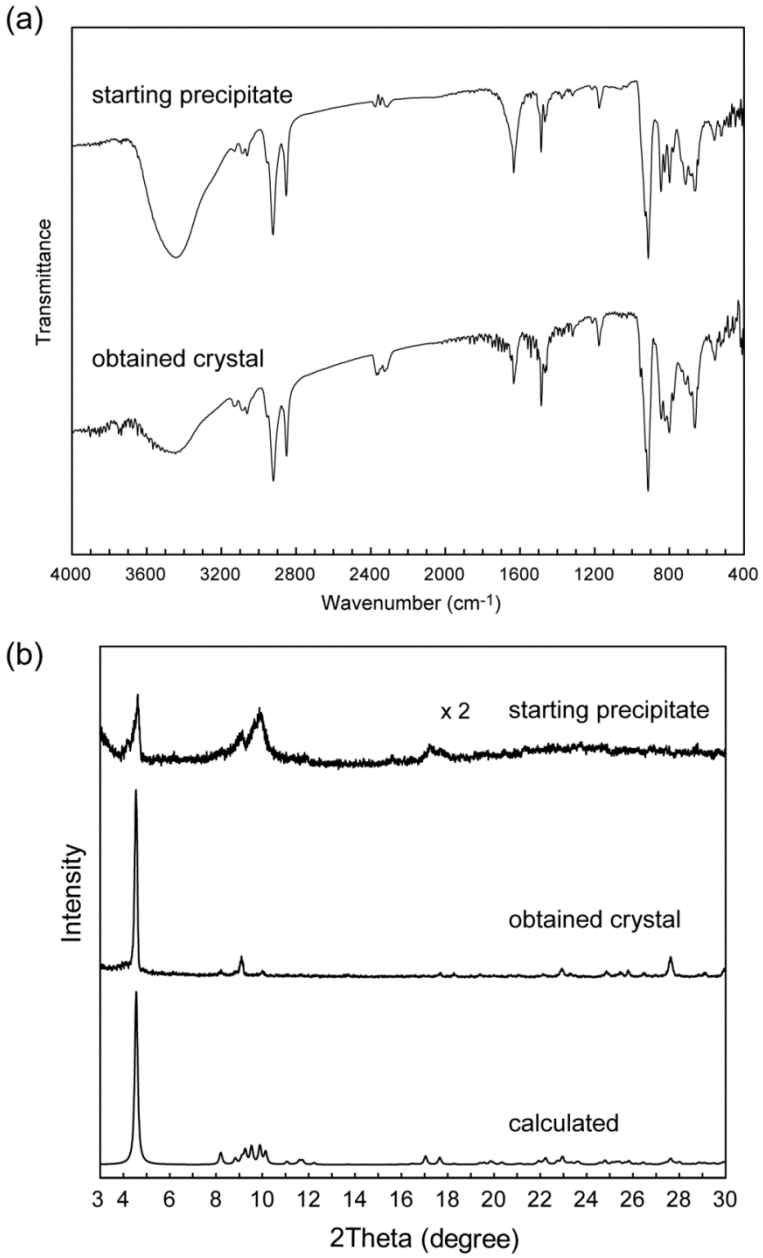


Figure S2. Structural information of C_{12}py-Mo_8 hybrid crystal prepared by the reoxidation of C_{12}py-red-Mo: (**a**) IR spectra of starting precipitate and obtained crystal; (**b**) Measured powder XRD patterns of starting precipitate and obtained crystal together with the pattern calculated from the structure revealed by single-crystal X-ray diffraction.

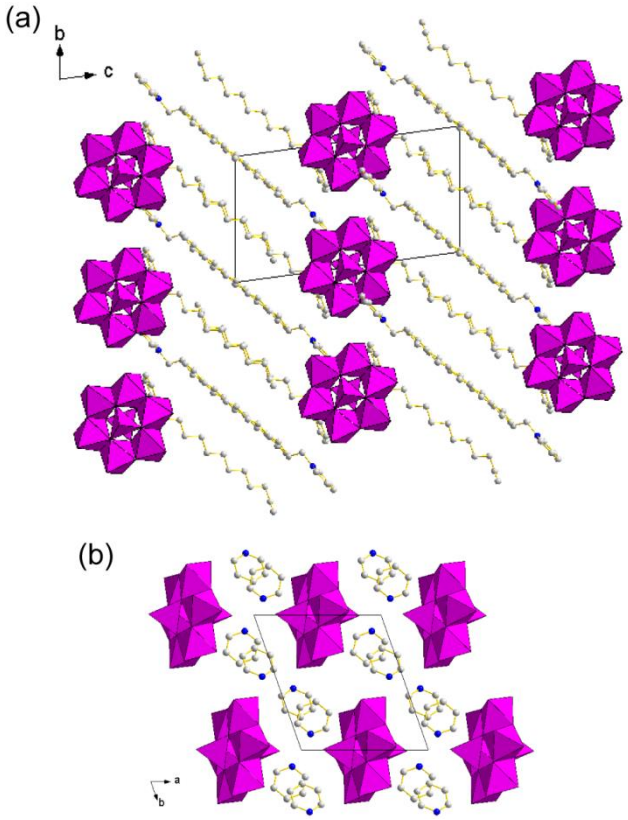


Figure S3. Crystal structure of C_{12}py-Mo_8 hybrid crystal prepared by the reoxidation of C_{12}py-red-Mo (C: gray, N: blue; α-Mo_8 in purple polyhedrons). H atoms and disordered atoms are omitted for clarity: (**a**) Packing diagram of C_{12}py-Mo_8 along the *a* axis; (**b**) Molecular arrangements in the inorganic layers (*ab* plane).

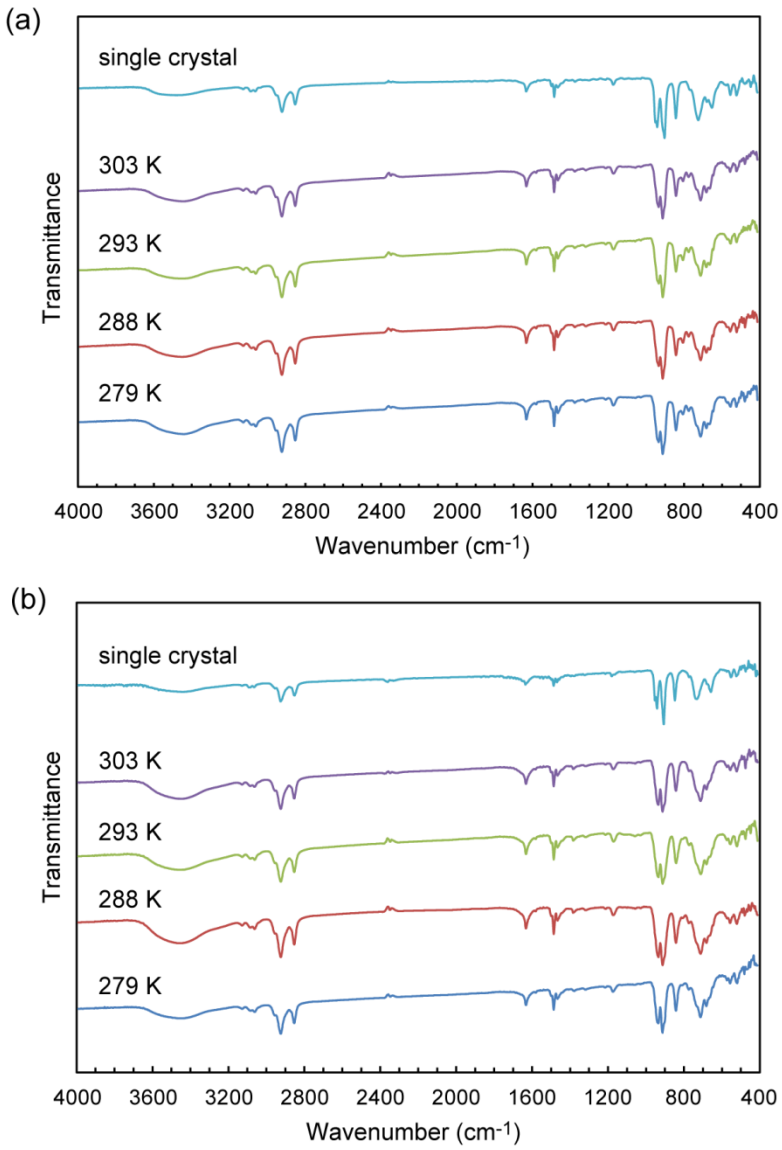


Figure S4. IR spectra of metal cation-introduced C_{12}py-Mo_8 hybrid crystals obtained at various crystallization temperatures: (**a**) C_{12}py-Rb-Mo_8; (**b**) C_{12}py-Cs-Mo_8.