Syntheses and Structures of Keggin-Type Polyoxometalate Crystals Hybridized with a Polymerizable Ionic-Liquid

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Keggin-type polyoxometalate clusters were successfully hybridized with a polymerizable ionic-liquid having methacryloyl group and imidazolium moieties (denoted as MAImC₁). Metatungstate ([H₂W₁₂O₄₀]⁶⁻, H₂W₁₂) and dodecamolybdophosphate ([PMo₁₂O₄₀]³⁻, PMo₁₂) anions were firstly employed to obtain inorganic-organic hybrid crystals. Their compositions and structures were clearly revealed by single crystal structure analyses.

Key words: Inorganic-organic, Hybrid crystal, Polymerizable, Ionic-liquid, Polyoxometalate

1. INTRODUCTION

Ionic-liquids are an attractive class of organic molten electrolytes having characteristic properties such as conductivity, catalysis, and separation abilities [1–8]. The combination of ionic-liquids with other inorganics bringing additional properties can lead to the construction of functional inorganic-organic hybrid materials [9–12]. Polyoxometalate (POM) clusters having several physicochemical properties are promising counter parts [13–24]. Keggin-type POMs have been well-known as catalysts or proton conductors [25–28], and their hybridization with ionic-liquids or polymer matrices has been achieved [29–37].

Such ionic liquid-POM hybrids sometimes have ill-ordered or disordered molecular arrangements in the solid states. This may be disadvantage to exploit their characteristic functions. Recently, we designed a polymerizable ionic-liquid of [$\{CH_2=C(CH_3)COO(CH_2)_2C_3H_3N_2(CH_3)\}^+$] (denoted as MAImC₁, Fig. 1a) having imidazolium and methacryloyl group. MAImC₁ can be hybridized with several POMs as single crystals [38–40]. MAImC₁-POM hybrid crystals are well-defined in an atomic level, and polymerizable to obtain conductive hybrid polymers. In these cases, dodecatungstophosphate ([PW₁₂O₄₀]³⁻, PW₁₂) and dodecatungstosilicate ([SiW₁₂O₄₀]⁴⁻, SiW₁₂) anions were utilized as Keggin-type POMs.

We report here the first syntheses of MAImC₁ hybrid crystals with other Keggin-type clusters. Metatungstate ([H₂W₁₂O₄₀]⁶⁻, H₂W₁₂, Fig. 1b) and dodecamolybdophosphate ([PMo₁₂O₄₀]³⁻, PMo₁₂, Fig. 1b) anions were employed. Structures of both hybrid crystals were revealed by single crystal X-ray structure analyses.

Fig. 1. (a) Molecular structure of MAImC₁. (b) Molecular structure of metatungstate (H₂W₁₂, left) and dodecamolybdophosphate (PMo₁₂, right).

2. EXPERIMENTAL

2.1 Materials and methods

All chemical reagents were used as received from commercial sources except for polymerizable ionic-liquid imidazolium cation (MAImC₁). MAImC₁ was obtained as iodide salt according to our previous studies [38–40].

IR spectra (as KBr pellet) were measured on a Jasco FT/IR-4200ST spectrometer. Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku MiniFlex300 or a Bruker AXS D8 ADVANCE diffractometer (Cu K α radiation, $\lambda = 1.54056$ Å) at ambient temperature. CHN elemental analyses were performed with a PerkinElmer 2400II elemental analyzer.

2.2 Synthesis of MAImC₁-H₂W₁₂ hybrid crystal

Sodium metatungstate (Na₆[H₂W₁₂O₄₀] (Na-H₂W₁₂), 0.90 g (0.3 mmol)) was dissolved in 10 mL of ethanol/water (1:1 (v/v)), and insoluble solids were removed by filtration. To the obtained clear colorless filtrate was added an ethanol solution (5 mL) of MAImC₁-I (0.50 g, 1.55 mmol). Resulting colorless precipitates were filtered off, washed by water, and dried under ambient atmosphere to obtain colorless powder of

MAImC₁-H₂W₁₂ (0.24 g, yield: 17%). Colorless plate crystals of MAImC₁-H₂W₁₂ were grown from the washing solution of the MAImC₁-H₂W₁₂ precipitates. Some amounts of ethanol molecule seemed to remain in or onto the MAImC₁-H₂W₁₂ precipitates. Elemental analysis calcd (%) for C₆₈H₁₁₆N₁₂W₁₂O₅₆: C, 19.42; H, 2.78; N, 4.00. Found: C, 20.12; H, 2.12; N, 3.88. IR, ν (KBr disk, cm⁻¹): 3138 (w), 2957 (w), 2924 (w), 2853 (w), 1725 (m), 1631 (s), 1578 (w), 1546 (w), 1445 (w), 1314 (w), 1289 (w), 1156 (w), 1085 (w), 1031 (w), 933 (m), 878 (m), 771 (s), 669 (w), 623 (w), 507 (w).

2.3 Synthesis of MAImC₁-PMo₁₂ hybrid crystal

Dodecamolybdophosphoric acid *n* hydrate (H₃[PMo₁₂O₄₀] $\cdot$ *n*H₂O (H-PMo₁₂), 1.1 g (0.6 mmol)) was dissolved in 10 mL of ethanol. To the obtained clear yellow solution was added an ethanol solution (5 mL) of MAImC₁-I (0.50 g, 1.55 mmol). Resulting dark-green precipitates were filtered off, washed by ethanol, and dried under ambient atmosphere to obtain dark-green powder of MAImC₁-PMo₁₂ (0.85 g, yield: 56%). Yellow-green block crystals of MAImC₁-PMo₁₂ were grown from the hot acetonitrile (10 mL) or acetonitrile/ethanol (10 mL, 1:1 (v/v)) solution of the MAImC₁-PMo₁₂ precipitates. Some amounts of ethanol molecule seemed to remain in or onto the MAImC₁-PMo₁₂ precipitates. Elemental analysis calcd (%) for C₃₂H₅₁N₆PMo₁₂O₄₇: C, 15.66; H, 2.09; N, 3.42. Found: C, 15.95; H, 1.80; N, 3.41. IR, ν (KBr disk, cm⁻¹): 3152 (w), 3116 (w), 2960 (w), 2927 (w), 1720 (m), 1636 (w), 1561 (w), 1450 (w), 1316 (w), 1296 (w), 1164 (m), 1063 (m), 957 (s), 879 (m), 801 (s), 738 (m), 649 (w), 621 (w), 500 (w), 465 (w), 436 (w), 412 (w).

2.4 Crystal structure determination

Single crystal X-ray diffraction measurements were performed with an ADSC Q210 CCD area detector by using a synchrotron radiation ($\lambda = 0.63000$ – 0.70000 Å) at 2D beamline in Pohang Accelerator Laboratory (PAL, a synchrotron radiation facility in Pohang, Republic of Korea). The processing of diffraction images was performed with HKL3000 [41]. Absorption correction was done with PLATON [42] or HKL3000. The structures were solved by the direct methods (SHELXS97 or SHELXS(Version 2013/1)) [43], and refined by the full-matrix least-squares method on F^2 (SHELXL(Version 2014/7)) [43] with the usage of CrystalStructure software package [44].

3. RESULTS AND DISCUSSION

3.1 Syntheses

MAImC₁ hybrid crystals were synthesized by cation-exchange reaction in the solution of prescribed Keggin-type POM anions depicted in Fig. 1b. IR spectra of MAImC₁-H₂W₁₂ hybrid crystals (Fig. 2b) exhibited characteristic peaks for MAImC₁ (methylene groups in 2800–3000 cm⁻¹ and methacryloyl group in 1200–1800 cm⁻¹) together with the peaks of H₂W₁₂ anion (400–1000 cm⁻¹) as observed for the starting Na-H₂W₁₂ (Fig. 2a). This indicates successful hybridization of MAImC₁ and H₂W₁₂. IR spectra of MAImC₁-PMo₁₂ (Fig. 2d) showed distinct peaks of PMo₁₂ (400–1100 cm⁻¹) as shown in the starting H-PMo₁₂ (Fig. 2c), demonstrating the successful hybridization of MAImC₁ and PMo₁₂.

XRD patterns of MAImC₁-H₂W₁₂ and MAImC₁-PMo₁₂

Fig. 2. IR spectra of (a) Na-H₂W₁₂, (b) MAImC₁-H₂W₁₂, (c) H-PMo₁₂, and (d) MAImC₁-PMo₁₂.

Fig. 3. Powder X-ray diffraction patterns of MAImC₁-POM hybrid crystals. (a) Precipitate of MAImC₁-H₂W₁₂, (b) calculated pattern of MAImC₁-H₂W₁₂ using the result of single-crystal structure analysis, (c) precipitate of MAImC₁-PMo₁₂, and (d) calculated pattern of MAImC₁-PMo₁₂ using the result of single-crystal structure analysis.

hybrid crystals (Fig. 3a and 3c) were almost identical to the patterns calculated from the results of single crystal X-ray analysis (Fig. 3b and 3d). This demonstrates that both MAImC₁-H₂W₁₂ and MAImC₁-PMo₁₂ were precipitated as single phase with the same composition and structure as the single crystals. Differences in the peak intensity and position of the patterns may be due to the difference in the measurement temperature (powder: ambient temperature, single crystal: 100 K).

3.2 Structure of MAImC₁-H₂W₁₂ hybrid crystal

Single crystal X-ray analysis revealed the molecular structure of MAImC₁-H₂W₁₂ hybrid crystal [45], which was formulated to be [MAImC₁]₆[H₂W₁₂O₄₀]. Fig. 4 shows asymmetric unit and crystal packing, which verified the presence of Keggin-type metatungstate anion of H₂W₁₂ (Fig. 1b) [46–49] in MAImC₁-H₂W₁₂. The crystal contained no solvent molecule of crystallization.

All the counter cations of starting Na-H₂W₁₂ were exchanged, and six MAImC₁ cations surrounded one H₂W₁₂ (Fig. 4a). The imidazolium rings and C=C bonds

Fig. 4. Crystal structure of MAImC₁-H₂W₁₂. H atoms are omitted for clarity. (a) Asymmetric unit. (b) Packing diagram along *a* axis.

Fig. 5. Crystal structure of MAImC₁-PMo₁₂. H atoms are omitted for clarity. (a) Asymmetric unit. The PMo₁₂ anion is completed by symmetry operation (0.5-*x*, 0.5-*y*, -*z*). (b) Packing diagram along *b* axis. Selected disordered MAImC₁ cations are omitted for clarity.

with π electrons were located in the vicinity of each H₂W₁₂. The H₂W₁₂ anions surrounded by MAImC₁ may be reduced to colored species under photoexcitation [17,50], and MAImC₁-H₂W₁₂ possibly behave as photochromic materials.

3.3 Structure of MAImC₁-PMo₁₂ hybrid crystal

Molecular structure and crystal packing of MAImC₁-PMo₁₂ were clarified as shown in Fig. 5 [51]. The chemical formula was [MAImC₁]₃[PMo₁₂O₄₀] without any crystallization solvent. The protons of starting H-PMo₁₂ were fully exchanged, and three MAImC₁ cations were associated with one PMo₁₂. The asymmetric unit contained two MAImC₁ cations and a half of PMo₁₂ anion (Fig. 5a). One crystallographically independent MAImC₁ with a site occupancy of 0.5 was disordered around 2-fold axis. The PMo₁₂ anion was located on the inversion center, and exhibited a common type of disorder for Keggin anion [52]. MAImC₁-PMo₁₂ was isostructural to that of hybrid crystal comprising MAImC₁ and PW₁₂ anion having the same charge (3-) as PMo₁₂ [38].

Each PMo₁₂ anion was isolated and surrounded by MAImC₁ in the yellow-green crystals (Fig. 5b). The crystal color indicates that slight amount of PMo₁₂ anions were reduced to dark blue-colored species [13,17,25] in

most non-reduced yellow PMo₁₂ anions. This may be because the PMo₁₂ anion is more easily reduced than H₂W₁₂ [13,18]. The MAImC₁-PMo₁₂ hybrid crystal could be considered as a weak charge-transfer salt [53].

4. CONCLUSIONS

Polymerizable ionic-liquid (MAImC₁) was firstly hybridized with Keggin-type polyoxometalates of metatungstate (H₂W₁₂) and dodecatungstophosphate (PMo₁₂) as single crystals. Their molecular and crystal structures were clearly revealed that each H₂W₁₂ or PMo₁₂ anion was isolated by the π electron-rich MAImC₁ cations. The charge-transfer from MAImC₁ to H₂W₁₂ or PMo₁₂ may be result in the emergence of photochromic property. In principle, these hybrid crystals can be polymerized derived from the polymerizable MAImC₁ cation, which would pave a way to another class of inorganic-organic hybrid functional polymers.

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