

Formation and Characterization of Keggin Based Hybrid Molecular Materials

Mohd Vikaruddin Ansari¹

¹ Research Scholar, Department of Chemistry, P. K. University, Shivpuri, M.P., India.

Prof. Dr. A. Vinay Chandra²

² Professor, Department of Chemistry, P. K. University, Shivpuri, M.P., India.

ABSTRACT

A strong framework for hybridization with organic or inorganic components may be found in Keggin-type heteropolyanions, which are usually metal-oxygen frameworks with oxyanions around a core atom. Using phosphotungstic acid Keggin anions and we created a stable hybrid molecular material from 1-butyl 3-methyl imidazolium cations. CHN, FTIR, XRD, and TGA analysis fully characterize it. The compound's FTIR spectrum shows fingerprint vibrational bands for keggin molecular anions and imidazolium cations. C-H vibrational breakdowns were detected using infrared spectroscopy., which were indicative of strong electrostatic contacts between the imidazolium cation and the Keggin anion, and powder X-ray diffraction (PXRD) studies revealed a multilayer structure.

Keywords: *Imidazolium, Hybrid Molecular, Phosphotungstic Acid, Keggin Anion, Ionic Liquid.*

I. INTRODUCTION

An interesting family of molecules that connect the inorganic and organic chemistry domains, keggin-based hybrid molecular materials have a lot of potential for breakthroughs in many scientific and technological applications. The Keggin structure, a famous polyoxometalate (POM) archetypal with a strong tetrahedral framework and great chemical flexibility, is the basis of these materials. A unique cluster with great symmetry is formed by four groups of three transition metal-oxygen octahedra, with a center heteroatom (such silicon or phosphorus) encircling the structure. This arrangement was first found in 1934 by J.F. Keggin. Keggin structures can be fine-tuned for electrical, catalytic, and optical characteristics by accommodating a range of heteroatoms and transition metals, which is what makes them adaptable. Hybrid molecular materials, which blend organic and inorganic components to provide new capabilities, rely on their exceptional structural and functional flexibility.

The unique combination of organic or polymeric ligands with the polyoxometalate cluster is the central component of hybrid materials based on Keggin. Scientists can make materials with better characteristics and several uses by combining these two components. Organic Keggin units bring tunability, solubility, and flexibility to the table, while their inorganic counterparts provide a host of desired properties including high acidity, thermal stability, and redox activity. Several synthetic methods, including as ionic

interactions, supramolecular assembly, and covalent grafting, are used to accomplish this fusion. A wide variety of crystalline frameworks, thin films, and amorphous composites are among the resulting materials' structural features. Catalysis, energy storage, medicine, and environmental cleanup are just a few of the many uses made possible by their remarkable versatility.

The use of Keggin-based hybrid materials has been greatly advanced in several areas, perhaps none more so than catalysis. Keggin ions are excellent catalysts because of their redox activity and proton storage and release capabilities. Scientists have created more active, selective, and stable catalysts by attaching Keggin units to organic scaffolds or porous materials. Oxidation processes, including hydrocarbon and alcohol oxidation, and acid-catalyzed transformations are two areas where these materials have shown promise. The chemical industry has found new uses for catalysts that incorporate Keggin clusters into porous networks, such as metal-organic frameworks (MOFs). These catalysts have a larger surface area and are easier to access.

Hybrid materials based on Keggin have recently gained attention as potential components of next-generation fuel cells, supercapacitors, and batteries. By combining Keggin structures with conductive polymers and carbon-based materials, their reversible redox transition capabilities allow for efficient charge storage and transfer, and their structural stability and conductivity are further improved. Examples of potential electrode materials for lithium-ion and sodium-ion batteries include Keggin-polymer composites, which have shown promising results in terms of cycle stability and high specific capacities. Their use in supercapacitors has also shown remarkable performance, with features like high energy density and fast charge-discharge rates. These materials have been studied as electrolytes that conduct protons in fuel cells, taking use of the acidic properties of Keggin clusters to make proton transport efficient.

II. REVIEW OF LITERATURE

Hidalgo, Gabriel et al., (2022) In a detailed study, the effects of bipyridine isomers on the physicochemical properties and production of two new hybrid materials, , composed of bipyridine and Keggin phosphotungstic acid (PTA), are described. The synthesis of the hybrids was confirmed by powder X-ray diffraction, and the structural preservation of the polyoxometalate (POM) was validated by infrared spectroscopy (IR). Using thermogravimetric analysis-mass spectrometry, we were able to determine the hybrids' stoichiometric composition and thermal stability, and we also discovered that they had gained hydrophobic characteristics. Both hybrids' POM skeleton units were found to be deformed in comparison to POM in PTA, as shown by Raman and IR spectroscopies.

Mohammadi Zonoz, Farrokhzad et al., (2013) We created a soluble polyoxotungstate-based inorganic-organic hybrid and examined it using element analysis, infrared spectroscopy, ^1H NMR, and single-crystal X-ray diffraction. Hybrid frameworks are shown in X-ray crystallography. By cyclic voltammetry, tungsten center redox activities were discovered. In electrocatalytic activities, 1 reduced -2NONO_2- more effectively than $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ heteropolyacid.

Masteri-Farahani, Majid et al., (2012) We provide a new microemulsion-based approach for the efficient one-pot synthesis of a hybrid nanomaterial of the Keggin type $(\text{CTA})(3)\text{PMo}_{12}\text{O}_{40}$ (where CTA stands for cetyltrimethylammonium cation). The finished product looked and behaved like small, uniform spheres of 20-30 nm in diameter.

Chimamkpan, Emmanuel et al., (2009) An emerging class of materials that is gaining more and more attention from researchers is organic-inorganic hybrids. Despite POMs offering almost infinite options for composite materials owing to their varied structural motifs and high application potential, relatively little research into POM-polymer combinations has been conducted thus far. Therefore, we have studied the PAni-[AsW₉O₃₃]9- unusual reactivity, which combines building-block capabilities with a heteroatom's lone pair, in detail. Various analytical methods were used to characterize the composite material that was produced, and the impact of reaction circumstances on the nanoscale structure was studied. Even more encouraging for potential future uses is the fact that the POM-PAni composites that were recently produced have a steady temperature-dependent resistivity.

T., Rajkumar et al., (2008) White hybrid molecular compound from silicotungstic acid and 1-butyl 3-methylimidazolium bromide ionic liquid. DMSO and other polar organic solvents dissolve it, but not water. The FTIR fingerprint vibrational bands of imidazolium and Keggin ions of silicotungstic acid reflect a hybrid molecule. In IL-SiWA's UV-vis DR spectra and imidazolium C-H band IR spectrum splitting, Keggin anions and cations interact. The heteropoly acid-ionic liquid hybrid loses some crystallization water, as visible in near-infrared spectra.

III. EXPERIMENTAL SETUP

Synthesis of BmImBr Ionic Liquid for Advanced Applications

This laboratory procedure generated. This mixture was swirled for 24 hours at 80°C. Washing it twice with ethyl acetate removes the unreacted starting material from the upper phase of the two phases. Therefore, the bottom phase bearing the IL product is devoid of unreacted material. Infrared, ¹H, and ¹³C NMR spectroscopy verified the yellowish IL product production after heating the BmImBr liquid to 50°C to remove dissolved ethyl acetate solvent.

Design of 1-Butyl-3-Methyl Imidazolium Phosphotungstate for Catalytic Reactions

In a 3:1 mole ratio, an ionic liquid of imidazolium bromide was mixed with an aqueous solution of phosphotungstic acid to make one mole of phosphotungstate salt. While agitating at ambient temperature, three grams of imidazolium bromide were slowly added to a solution of 14.5 grams of PWA. The white precipitate from scheme 1 was washed with distilled water and dried overnight at 80°C until the AgNO₃ test showed it was bromine-free.

The hybrid molecular compound was formed by reacting one mole of Keggin anions of PW₁₂O₃₃ and three moles of imidazolium cations, according to CHN analysis of the white solid. Replace water with DMSO to dissolve.

Characterization

Shimadzu XD-D1 diffractometer using CuK α -radiation ($\lambda = 1.5418 \text{ \AA}$). The materials' infrared spectra (400-4000 cm⁻¹) were acquired using a Perkin Elmer spectrometer with a 4 cm⁻¹ resolution, utilizing KBr pellets. The Perkin-Elmer TGA-7 was used to TGA the IL-PWA hybrid material. For thermal stability testing, the sample was heated at 20°C/min using 30 ml/min of pure N₂ gas.

IV. EXPERIMENTAL RESULTS

Results of Powder XRD

In our imidazolium-based ionic liquid template, the massive $\text{PW}_{12}\text{O}_{40}^{3-}$ anion substitutes the Br^- ion. This molecular solid has organic and inorganic characteristics due to the Keggin anion and imidazolium cation. Elemental analysis of the sample (C-H-N) yields $[(\text{C}_{8+x}\text{N}_2\text{H}_{15-y})_3]:\text{C}_{24.90}\text{H}_{41.93}\text{N}_{6.23}\text{PW}_{12}\text{O}_{40}$, with the right chemical notation. This compound is a white, non-porous solid with $2.8 \text{ m}^2/\text{g}$ surface area. Figure 1 shows the PXRD pattern of the $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid material, which is 1-butyl-3-methyl imidazolium phosphotungstate and pure hydrated phosphotungstic acid. Three 1-butyl-3-methyl imidazolium cations replace most water molecules and three acidic protons in phosphotungstic acid, causing structural changes. The $[\text{BmIm}]_3[\text{PW}_{12}\text{O}_{40}]$ hybrid has a more complicated PXRD structure than pure PWA salt. The Keggin polyanions are commonly hydrogen bonded with sandwiched water molecules (H_3O^+ and H_5O_2^+), however the PXRD pattern does not indicate their presence. This shows that 1-butyl-3-methyl imidazolium cations may change phosphotungstic acid's secondary structure. The PXRD data shows host-guest structural alterations, including a peak at $2\theta = 9.4^\circ$, indicating a multilayered molecular structure.

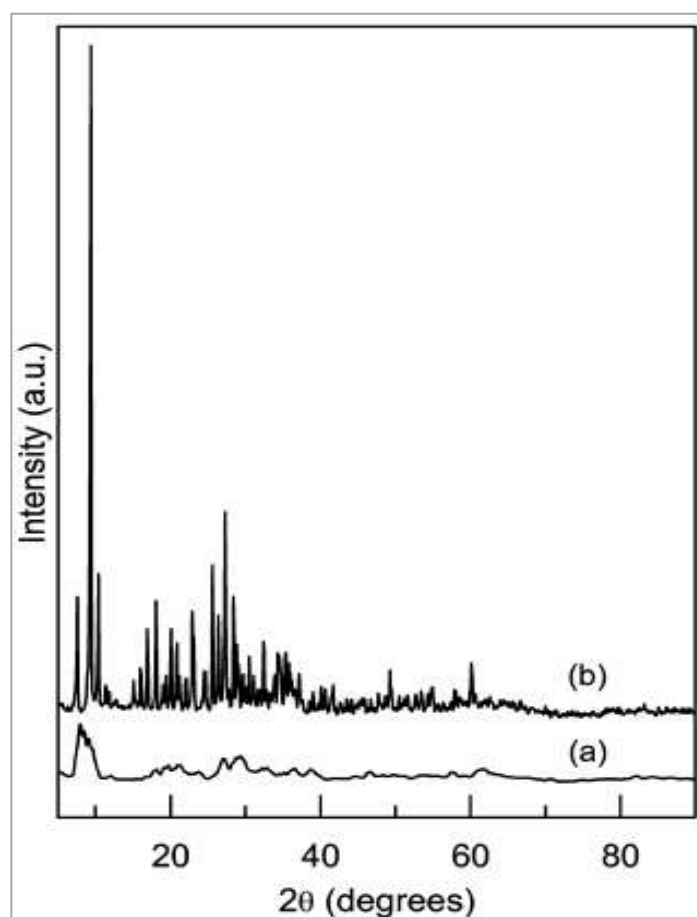


Figure 1: Powder XRD Structures of Hybrid Molecular Material

Results of FTIR

In [BmIm]₃[PW₁₂O₄₀] hybrid FTIR spectra, Keggin unit structure and bonding vary. The P-O stretching vibration is at 1083 cm⁻¹, while the W-O terminal stretching is at 987 cm⁻¹. The W-Oc-W interbridging mode was seen at 891 cm⁻¹ in PW₁₂O₃-40. Fig. 2 compares ILPWA, parent BmImBr, and H₃PW₁₂O₄₀nH₂O IR spectra. Five PW₁₂O₃-40 infrared characteristics. In the hybrid material's 475-1120 cm⁻¹ stretching region, discrete ion clusters reveal the 1-butyl 3-methyl imidazolium phosphotungstate holds its Keggin structure.

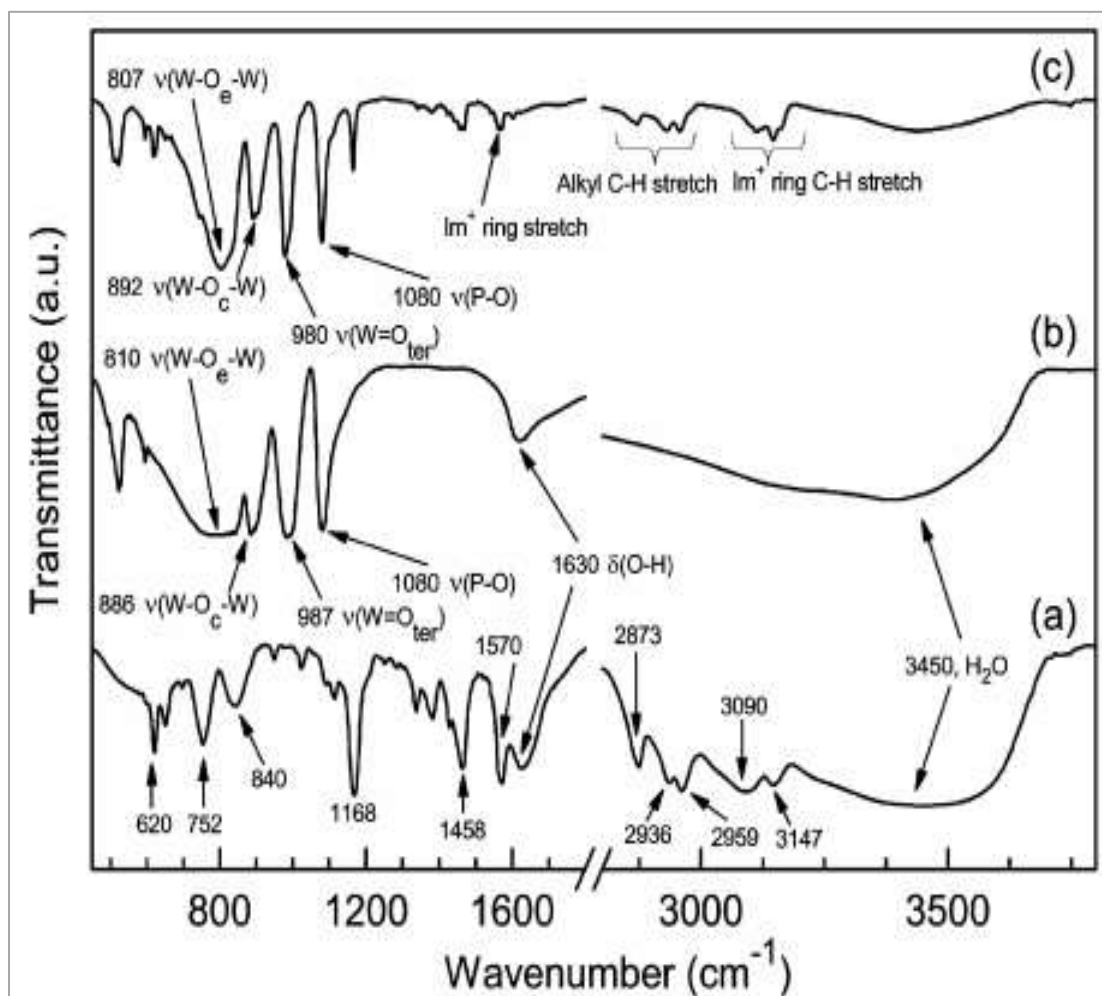


Figure 2: FTIR Spectra of The Selected Hybrid Molecular Material

There is a substantial electrostatic contact between the BmIm⁺ cation and the big Keggin anion. The interaction between the two compounds causes the [BmIm]₃ [PW₁₂O₄₀] hybrid molecular salt to split the two C-H stretching peaks of the imidazolium ring of BmImBr into five vibrational peaks. Figure 2c shows that the imidazolium ring vibrates differently depending on the intensity. This C-H split is the result of an interaction between the big Keggin anion and the BmIm cation.

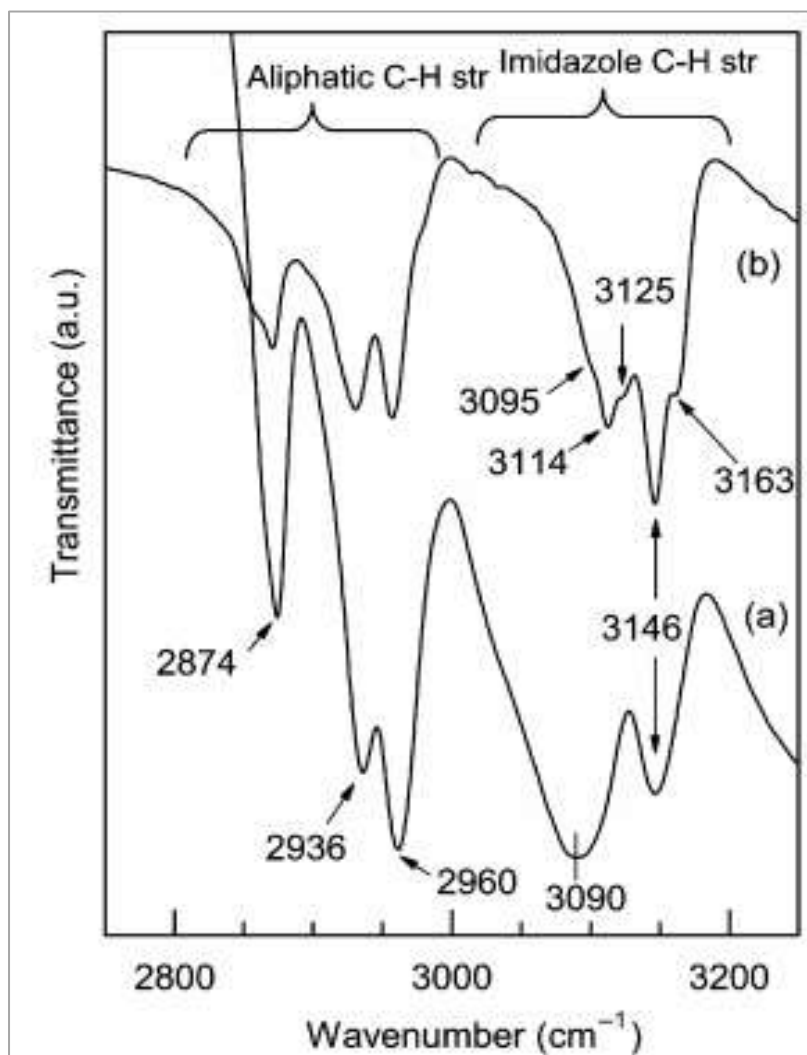
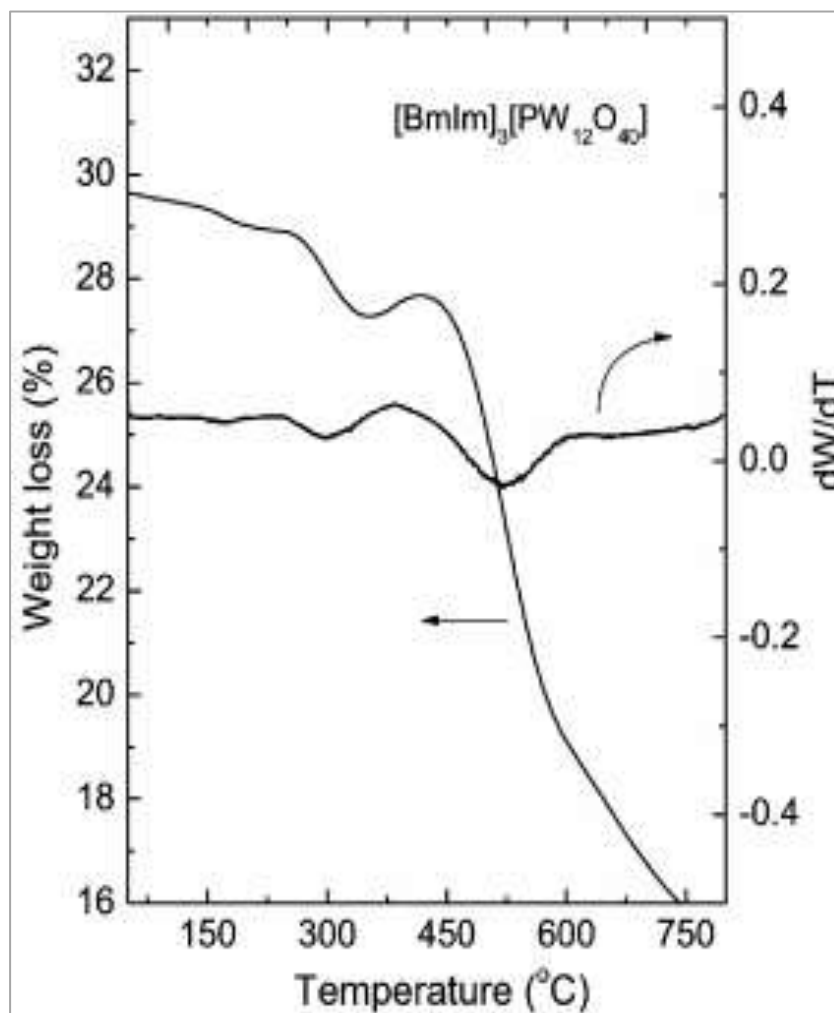


Figure 3: C–H Stretch Regions of Hybrid Molecular Material

Results of TGA

In Figure 4, is shown. At 140–250°C, 250–420°C, and above 420°C, TGA indicates weight loss. In low-water samples, TG loss starts at low temperatures. Key weight loss mechanism, including BmIm's organic component, declines around 250–420°C. A TGA curve weight drop above 420°C suggests a shift in imidazolium ring Keggin ion breakdown temperature because pure PWA dissolves at 550°C. Keggin units break degraded into WO₃ and P₂O₅ at 420°C, causing rapid weight loss. Molecular hybrid material BmIm⁺ moieties change Keggin units' thermal stability and Bronsted acidity.

**Figure 4: TGA of Hybrid**

V. CONCLUSION

Its ionic liquid, [BmIm]⁺[PW₁₂O₄₀]⁻, were produced using well-established techniques in the research. The presence of a new organic-inorganic hybrid molecular structure was verified by the XRD, FTIR, and TGA analysis of the produced materials. An unusual layered structure was discovered in the Keggin unit as a consequence of structural change as shown by XRD analysis. This transformation was caused by the interaction of imidazolium cations with phosphotungstic acid. By splitting in the C-H and imidazolium ring vibrations, FTIR spectra revealed significant electrostatic contacts between the bulky Keggin anion and the BmIm⁺ cation, highlighting the preservation of the Keggin unit's fundamental structure. The TGA analysis provided further evidence of the hybrid material's thermal stability and degradation profile, suggesting a substantial interaction between the inorganic and organic components. Taken together, the results provide light on the thermal and structural characteristics of hybrid materials based on imidazolium, which might have far-reaching implications in fields as diverse as catalysis and materials science.

REFERENCES

1. G. Hidalgo, M. Devillers, and E. Gaigneaux, "Hybrid Materials Based on Keggin Phosphotungstate and Bipyridine with Valuable Hydrophobic and Redox Properties," *Inorg. Chem.*, vol. 61, no. 32, 2022, doi: 10.1021/acs.inorgchem.2c00342.
2. M. Yang, S. Rong, X. Wang, H. Ma, H. Pang, L. Tan, Y. Jiang, and K. Gao, "Preparation and Application of Keggin Polyoxometalate-based 3D Coordination Polymer Materials as Supercapacitors and Amperometric Sensors," *ChemNanoMat*, vol. 7, no. 3, pp. 1–5, 2021, doi: 10.1002/cnma.202000654.
3. A. Ucar, M. Findik, N. Kocak, A. Çolak, and O. Şahin, "Hydrothermal synthesis and crystal structures of a novel Keggin-type polyoxometalate based on 1,10-phenanthroline," *Cumhuriyet Sci. J.*, vol. 42, no. 1, pp. 22–29, 2021, doi: 10.17776/csj.812164.
4. S. U. Khan, M. Akhtar, F. U. Khan, J. Peng, A. Hussain, H. F. Shi, J. Du, G. Yan, and Y. G. Li, "Keggin Polyoxometalates," *J. Coord. Chem.*, vol. 71, pp. 16–18, 2018.
5. L. J. Xu, W. Z. Zhou, L. Y. Zhang, B. Li, H. Y. Zang, Y. H. Wang, and Y. G. Li, "Polyoxometalate-Based Crystals," *CrystEngComm*, vol. 17, pp. 3708–3714, 2015.
6. F. Mohammadi Zonoz, A. Jamshidi, and S. Tavakoli, "Preparation, characterization and electrochemical investigation of a new inorganic–organic hybrid material based on Keggin-type polyoxometalate and organic imidazole cation," *Solid State Sci.*, vol. 17, no. 1, pp. 83–89, 2013, doi: 10.1016/j.solidstatesciences.2012.10.029.
7. J. W. Zhao, D. Y. Shi, L. J. Chen, P. T. Ma, J. P. Wang, J. Zhang, and J. Y. Niu, "Polyoxometalate Hybrid Structures," *Cryst. Growth Des.*, vol. 13, pp. 4368–4377, 2013.
8. L. Rodriguez-Albelo, G. Rousseau, P. Mialane, J. Marrot, C. Mellot-Draznieks, A. R. Ruiz-Salvador, S. Li, R. Liu, G. Zhang, B. Keita, and A. Dolbecq, "ε-Keggin-based coordination networks: Synthesis, structure and application toward green synthesis of polyoxometalate@graphene hybrids," *Dalton Trans.*, vol. 41, no. 3, pp. 9989–9999, 2012, doi: 10.1039/c2dt30537b.
9. M. Masteri-Farahani and S. Shahbazi, "Preparation of Keggin-type polyoxometalate hybrid nanomaterial with one pot multicomponent reaction in reverse micelle nanoreactors," *Inorg. Chem. Commun.*, vol. 15, pp. 297–300, 2012, doi: 10.1016/j.inoche.2011.11.007.
10. Z. G. Han, S. Li, J. J. Wu, and X. L. Zhai, "Hydrothermal synthesis and structural characterization of two new polytungstate-based hybrids," *J. Coord. Chem.*, vol. 64, no. 1, pp. 1525–1532, 2011.
11. F. Santos, P. Brandão, V. Felix, A. Cavaleiro, E. Gomes, and M. Belsley, "Synthesis and structural characterization of Keggin polyoxometalate compounds with argininium(2+) cations," *J. Mol. Struct.*, vol. 963, no. 2–3, pp. 267–273, 2010, doi: 10.1016/j.molstruc.2009.11.002.
12. E. Chimamkam, F. Hussain, A. Engel, A. Schilling, and G. Patzke, "Synthesis and Characterization of Hybrid Materials Derived from Polyaniline and Lacunary Keggin-type Polyoxotungstates," *Z. Anorg. Allg. Chem.*, vol. 635, no. 4–5, pp. 624–630, 2009, doi: 10.1002/zaac.200801394.



13. L. J. Dolomanov, R. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, "Crystallography Tools," *J. Appl. Cryst.*, vol. 42, pp. 339–341, 2009.
14. T. Rajkumar and R. R. Gangavarapu, "Synthesis and characterization of hybrid molecular material prepared by ionic liquid and silicotungstic acid," *Mater. Chem. Phys.*, vol. 112, no. 3, pp. 853–857, 2008, doi: 10.1016/j.matchemphys.2008.06.046.
15. Y. Feng, Z.-G. Han, J. Lu, B. Xue, L. Li, H. Ma, and E. Wang, "Fabrication and characterization of multilayer films based on Keggin-type polyoxometalate and chitosan," *Mater. Lett.*, vol. 60, no. 13, pp. 1588–1593, 2006, doi: 10.1016/j.matlet.2005.11.069.