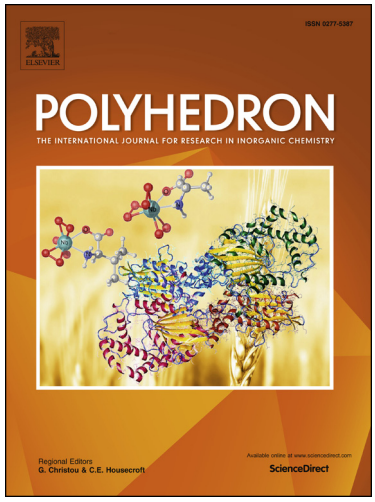

Hydrophobic supramolecular assemblies of Keggin anions with lactam-lactim cationic tautomers

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Hydrophobic supramolecular assemblies of Keggin anions with lactam-lactim cationic tautomers

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Polyoxometalate-based materials are gaining importance in the fields of heterogeneous catalysis and materials chemistry. In this context, we have synthesized $(H(CL)_2)_3PMo$ and $(H(CL)_2)_3PW$ novel hybrid materials using phosphomolybdic acid (PMoA) and phosphotungstic acid (PWA) as a source of Keggin anions, respectively, and ε-caprolactam (CL). The caprolactam molecules have undergone lactam-lactim tautomerisation in the presence of heteropolyacids forming cationic dimers. The hybrid materials are characterized by FTIR, XRD analyses, TGA, DSC, SEM and UV-DRS techniques. From single crystal X-ray analysis of $(H(CL)_2)_3PMo$, we find that the protonated caprolactam dimers replaced the protonated water molecules ($H_5O_2^+$) from hexahydrated state of heteropolyacids. These materials show increased band gaps in the semiconducting region, due to decrease in the crystallite size. The cyclic voltammograms recorded by immobilizing these materials on 6 mm glassy carbon electrodes have shown three consecutive two-electron redox couples.

Keywords: Polyoxometalate • caprolactam • tautomerism • optical band gap • cyclic voltammetry

1. Introduction

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