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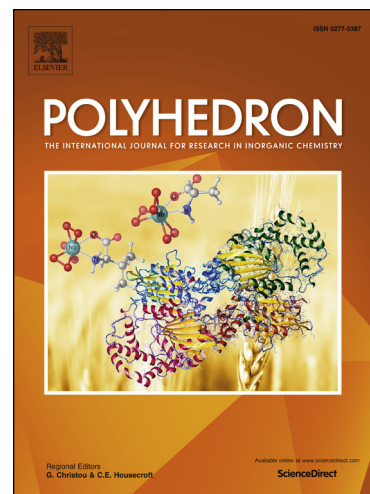
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Hydrophobic supramolecular assemblies of Keggin anions with lactam-lactim cationic tautomers

K. Shakeela^a, Vuppala Laxmi Sinduri^b, G. Ranga Rao^{a*}

^aDepartment of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

^bIIT Madras Summer Research Fellow 2013

Polyoxometalate-based materials are gaining importance in the fields of heterogeneous catalysis and materials chemistry. In this context, we have synthesized $(\text{H}(\text{CL})_2)_3\text{PMo}$ and $(\text{H}(\text{CL})_2)_3\text{PW}$ 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 $(\text{H}(\text{CL})_2)_3\text{PMo}$, 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

*Corresponding author Tel.: +91 44 2257 4226; Fax: +91 44 2257 4202

E-mail: grrao@iitm.ac.in (G. Ranga Rao)

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