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Inorganic-organic covalent hybrid of polyoxometalate-calixarene:

Synthesis, characterization and enzyme mimetic activity

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Abstract: The inorganic-organic hybrid based on covalently attached trilacunary phosphotungstate and calixarene conjugate (POM-Calix hybrid) has been synthesized via facile click chemistry approach. The characterization studies showed that both the moieties are present together in the hybrid upon covalent modification. The morphology of the hybrid was studied by SEM, TEM and AFM analyses suggesting spherical shaped nanoparticles of 40-60 nm size for the hybrid. The POM-Calix hybrid was successfully employed to demonstrate peroxidase-like activity for the oxidation of the model substrate, viz., ophenylenediamine (OPD), for the enzyme. The activity of the POM-Calix hybrid was ~170% greater than that exhibited by simple POM and this is mainly attributed to the introduction of hydrophobic character by the covalently attached calixarene conjugate and the hydrophobicity is supported by the contact angle measurement. From the kinetic studies, the Michaelis constants, $K_{\rm m}$ and $V_{\rm max}$ were estimated to be 2.55 mM and 0.756 x 10⁻⁸ M sec⁻¹, respectively. It was observed that, the POM-Calix hybrid facilitates the formation of 'OH radicals when treated with H₂O₂ which eventually results in the oxidation of the substrate. The POM-Calix hybrid exhibits excellent enzyme-like activity over a wide pH range, which would enable its bio-applications at physiological conditions.

Keywords: Polyoxometalate-calixarene hybrid, peroxidase-like activity, detection of 'OH radical, *o*-phenylenediamine oxidation, thiol-ene click reaction

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