Coordination-Mediated Nonlinear Catalytic Feedback in Enzyme-Like Copper-Tyrosine Self-Assembled Networks

Prabhjot Singh[a,*], Amit Dubey[b], Neelam[c,g,h], Aleksander Piasecki[d], Simranjeet Sandhu[a], Saima[e], Jan Paczesny[d], Tejwant Singh Kang[f], Nishima Wangoo[g]

[a] Department of Chemistry, Akal University, Talwandi Sabo, Bathinda, Punjab-151302, India

[b] Center for Global Health Research, Saveetha Medical College and Hospitals, Saveetha Institute of Medical and Technical Sciences, Chennai, Tamil Nadu-600077, India

[c] Shaheed Major Harminderpal Singh Government College, S.A.S Nagar, Mohali. Punjab-160055, India

[d] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

[e] School of Advanced Chemical Sciences, Shoolini University of Biotechnology and Management Sciences, Solan-173229, India

[f] Department of Chemistry, UGC-Centre for Advanced Studies - II, Guru Nanak Dev University, Amritsar, 143005, India

[g] Department of Chemistry & Centre for Advanced Studies in Chemistry, Panjab University, Sector 14, Chandigarh-160014, India

[h] Department of Applied Sciences, University Institute of Engineering and Technology (U.I.E.T.), Panjab University, Chandigarh-160014, India

Abstract

The cooperativity and nonlinear dynamics are among the fundamental characteristics of life. Haemoglobin oxygen binding, actin polymerisation, microtubule dynamic assembly, and Ca^{2+} ion channels are a few assembly-coupled cooperative phenomena in living systems. Natural enzymes rely on the supramolecular environment and non-covalent interactions for their function; however their tuning and application under robust conditions remain challenging. To date, only a limited number of studies explored a dynamic metal-coordinated system coupled to supramolecularly regulated enzyme-like functions. Inspired by such principles, we investigated enzyme-like catalysis in copper-tyrosine self-assembled networks (CuYs) as a model system for coordination-driven nonlinear catalytic regulation. The structural organisation of CuYs supramolecular structures was comprehensively characterised using analytical and theoretical techniques. Further, the Michaelis-Menten parameters and the nonlinear dynamics were studied using the o-phenylenediamine oxidation reaction, demonstrating peroxidase-like catalytic activity. Finally, the CuY system showed an EDTA-dependent reorganisation, resulting in a nonlinear response, as demonstrated by experimental observations and supported by molecular dynamics simulations. The emergence of enzyme-

like function and coordination-driven adaptability in a minimal non-proteinaceous metal-ligand assembly provides a potential prebiotic link between inanimate matter and living chemical networks, opening new avenues for designing life-like functional systems.

Keywords: supramolecular chemistry, nonlinearity, metal-organic networks, self-assembly, nanozyme, enzyme-like catalysis

Corresponding authors:
Dr Prabhjot Singh: prabhjot_chm@auts.ac.in