Charge-Directed Self-Assembly of Fe–Cu and Fe–Ni Porphyrins into Functional Biomimetic 3D Nanoarchitectures

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Área temática: B. Autoensamblado

The charge-directed self-assembly of Fe-, Cu-, and Ni-metalloporphyrins into three-dimensional nanoarchitectures provides a powerful biomimetic platform to investigate cooperative electronic communication in natural metalloenzymes. Binary systems such as FeTMPyP–CuTPPS, CuTMPyP–FeTPPS, NiTMPyP–FeTPPS, and FeTMPyP–NiTPPS reproduce, within a controllable supramolecular framework, the spatial proximity and functional coupling of metal centers with complementary electronic roles.

From a biomimetic standpoint, these nanoassemblies emulate how natural redox proteins—including cytochromes, oxidases, and photosynthetic reaction centers—arrange multiple metal cofactors to enable sequential electron transfer, charge separation, and stabilization of long-lived intermediates. Iron contributes redox and spin-state flexibility, closely resembling heme enzymatic sites, while Cu and Ni modulate electron density, coordination environment, and π–π interactions, thereby tuning the collective response of the assembly.

Their spontaneous formation in water generates adaptive 3D supramolecular networks, where the emergent architecture depends not only on electrostatic attraction between oppositely charged porphyrins but also on the identity of the central metal ion.[1] This mirrors the way biological scaffolds regulate metal–metal distances, redox potentials, and electron-transfer pathways through precise structural organization. Accordingly, subtle variations in Fe/Cu or Fe/Ni pairing produce distinct UV–vis, Raman, and morphological signatures, reflecting a cooperative response analogous to allosteric modulation in multimetallic biological systems.

A particularly attractive feature of these heterometallic nanoarchitectures is their ability to stabilize persistent or metastable electronic states, likely associated with supramolecular defects, charge delocalization, and slow structural reorganization. This behavior makes them excellent biomimetic models for transient redox memory, accumulation of reducing equivalents, and prolonged activation phenomena found in natural energy-conversion processes.

Overall, Fe–Cu and Fe–Ni nanoassemblies offer a versatile framework for understanding how self-organization, heterometal incorporation, and cooperative electronic coupling generate emergent properties resembling those of complex biological systems, with strong potential in redox catalysis, artificial photosynthesis, sensing, and adaptive molecular electronics.

REFERENCIAS

1. Medforth C. J. , *et. al*. *Chem. Commun.* (2009) 7261–7277