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Minimal Requirements for One-Dimensional Aggregation in Simple Coarse-Grained Models of Charged Porphyrinoid Units

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Área temática: B. Autoensamblado

Understanding the minimal physical requirements that enable directional supramolecular growth is essential for the rational design of porphyrin-based nanomaterials. Here, we present a coarse-grained Monte Carlo study aimed at identifying the balance of interactions required for one-dimensional aggregation in oppositely charged porphyrinoid systems. The model captures two dominant driving forces of ionic porphyrin self-assembly: long-range screened electrostatic attraction, represented by a Debye–Hückel potential, and short-range cohesive interactions associated with π–π stacking, modeled through an isotropic Lennard–Jones (LJ) potential acting on neutral aromatic cores.

Our simulations reveal that electrostatic interactions alone are insufficient to sustain aggregation, leading only to dispersed particles or transient dimers.[1] In contrast, the introduction of a modest short-range cohesion induces a sharp cooperative transition. A critical LJ well depth between 1.5 and 2 k_{BT} marks the onset of ordered one-dimensional nanowire-like assemblies, separating disordered clusters from elongated supramolecular structures. This transition is quantitatively supported by radial distribution functions, cluster-size distributions, and a charge alternation index that captures local ionic ordering.

Above this threshold, the competition between Coulombic attraction and cohesive interactions drives the spontaneous emergence of linearly ordered aggregates. At intermediate cohesion, opposite-charge alternation is maximized, favoring directional growth. However, stronger cohesive interactions eventually introduce packing defects and partial loss of charge alternation, revealing an optimal interaction window for wire formation.

We further show that increasing ionic strength weakens long-range electrostatic attraction through Debye screening, shifting the aggregation threshold toward higher cohesive energies and delaying nanowire formation. Nevertheless, sufficiently strong short-range cohesion can still sustain one-dimensional growth even under strong screening conditions, highlighting the robustness of the cooperative mechanism.

These findings establish a generic thermodynamic design principle for charged aromatic self-assembly: directional growth requires not only electrostatic complementarity but also a minimum cohesive threshold capable of stabilizing persistent axial contacts. Beyond porphyrin systems, this framework provides mechanistic insight into the emergence of aniso

REFERENCIAS

1. Hamer, Mariana, *et al.*, *Phys. Chem.* 28 (2026) 5796-5806