Metal-Containing Conducting Polymers Built on Clathrochelate Metal Complexes: Caged Metal Centers for Interlayer Charge Transport and Electrocatalytic H_2 Production

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Metal-templated [2 + 3]-type condensation reactions between π-extended boronic acids and N,N'-bidentate dioxime ligands furnished a series of cage metal complexes, which were subsequently electropolymerized to prepare metal-containing conducting polymers (MCPs). Despite sharing essentially isostructural organic scaffolds, these materials display metal-dependent electrochemical properties as evidenced by different redox windows observed for M = Co, Fe, and Ru. Notably, consecutive electropolymerization using two different monomers produced well-defined bilayer MCPs, in which the bottom MCP layer in its oxidized form functions as redox mediator for vectorial charge transport to the top MCP layer having different metal center. In addition, MCP with M = Co in its reduced form can function as robust thin-film electrocatalyst for the production of H_2 in acidic organic media.