ASSEMBLY OF METAL−ORGANIC FRAMEWORK ON TEMPO-OXIDIZED CELLULOSE NANOFIBRILS: INSIGHTS FROM MOLECULAR DYNAMICS

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The integration of cellulose with metal-organic frameworks (MOFs) to create hybrid functional materials has attracted significant interest due to the synergistic combination of cellulose's substrate properties and MOFs' multifunctional features. However, the precise *in situ* assembly mechanism between the two materials remains unclear. In this study, we employed molecular dynamics simulations to explore the early-stage assembly of MOF precursors on 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-oxidized cellulose nanofibrils (TOCNF). The simulation mimics the experimental synthesis conditions, incorporating an 18-chain TOCNF crystal model and MOF precursors—zinc ions and the organic ligand terephthalic acid (BDC)—in N,N-dimethylformamide (DMF) solvent. We examined the coordination behavior between zinc ions and BDC ligands and investigated the time evolution of the cluster assembly on the TOCNF substrate. Our results reveal that the carboxylate groups in TOCNF can form coordination bonds with metal ions, directing the assembly of MOF clusters onto the TOCNF substrate. Additionally, the hydroxyl groups in TOCNF can form hydrogen bonds with the organic ligands, facilitating the attachment of MOFs to TOCNF. Our study provides fundamental insights into the synthesis mechanism of cellulose/MOF hybrid materials, thereby expanding the potential of cellulose as a sustainable polymer substrate for functional material design.