Anomalous thermal transport and enhanced thermoelectric performance in 2D layered metal organic frameworks

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Two-dimensional metal–organic frameworks (2D MOFs) combine soft lattices and tunable interlayer coupling, making them an appealing platform to engineer directional heat transport and, potentially, thermoelectric response. Here we investigate lattice dynamics and thermal conduction in layered copper benzenehexathiolate (Cu_3BHT) as a function of stacking pattern (AA, AB, and C) using a first-principles workflow. Density-functional-theory simulations coupled with lattice dynamics reveal that AB stacking is dynamically unstable, while the C phase is the thermodynamic ground state and features Cu–S interlayer bridges that stiffen shear/breathing modes and enhance through-plane transport. Heat conduction is dominated by low-frequency interlayer modes, yielding ultralow thermal conductivity and pronounced anisotropy. Moreover, coherent (Wigner) contributions substantially increase κ and weaken the classical 1/T to $\kappa \propto T^{-\alpha}$ with $\alpha<1$, consistent with mixed particle-/wave-like transport in near-degenerate phonon manifolds.

To connect heat transport with thermoelectric performance, we complement the phonon picture with first-principles electronic transport based on electron–phonon coupling and the linearized Boltzmann transport equation. In pristine AA-stacked CuBHT, the metallic band structure leads to high electrical conductivity but very low Seebeck coefficients and a near-zero figure of merit zT, despite the ultralow lattice thermal conductivity. However, a robust route to enhanced thermoelectric response is obtained via charge modulation: adding three electrons (CuBHT–3e) induces a metal-to-semiconductor transition (small-gap at PBEsol, larger gap at HSE06), yielding a strong Seebeck enhancement and reduced electronic thermal conductivity; additional in-plane strain further boosts Seebeck (up to ~500 μV/K) and can raise zT up to ~0.6 at elevated temperature under 5% strain.

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