Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary to "Two-Dimensional Metal-organic Frameworks with High Thermoelectric Efficiency Through Metal Ion Selection"

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Methods

Ab initio calculation

The atomic structures of monolayer hexagonal $X_3(HITP)_2$ with X=Ni, Pd, or Pt were generated based on the experimental data for $Ni_3(HITP)_2$ [1], and then optimized using *ab initio* simulations. All electronic and structural optimization calculations were performed within the Kohn-Sham density functional theory (DFT) framework implemented in the Vienna *ab initio* simulation package (VASP)[2]. The Local Density Approximation (LDA)[3] for the exchange and correlation functional was used to describe the electrons of all atoms, except for Ni, for which the LDA+U[4] with U=6.0[5] was applied to better represent the strong correlation of the Ni *d* orbitals. Previous studies showed that the *d* orbitals of both Pd and Pt are less localized than that of Ni metal (i.e. U_{pd} =1.005 and U_{pt} =1.07)[6], hence we did not use LDA+U for Pd and Pt MOFs. We also calculated the band structures of the Pt MOF within the Generalized Gradient Approximation (GGA) using the PW91 functional including spin-orbit coupling to see the influence of relativistic effects on the band structure, and found that the calculated band structure is similar to that of LDA with a small rigid shift. The projector augmented wave (PAW) pseudo-potential[7] was chosen to describe the electron-core interactions, and a kinetic energy cutoff of 400 eV was defined for the plane-wave basis set. The Brillouin zone for all simulated systems was sampled with a Monkhorst-Pack grid[8] of 8x8x1 for both electronic structure and optimization calculations, while a grid of 16x16x1 was used for the calculations of thermal transport properties. To mimic a 2D MOF, we increased the length of the simulation cell along the Z direction up to ~8 Å to avoid image interactions. Since LDA generally underestimates the electronic band gap, HSE06[9] calculations were performed on the three 2D MOGs. All TE transport properties were calculated with the band gaps obtained using the HSE06 functional.

Thermoelectric transport model

The thermoelectric transport properties of three 2D MOGs were calculated using the Landauer formalism in the linear response regime[10]:

$$S = \left(-\frac{k_B}{e} \right) \frac{I_1}{I_0} \qquad (1)$$

$$\sigma / \lambda = \frac{1}{A} \left(\frac{2e^2}{h} \right) I_0 \qquad (2)$$

$$\kappa_e / \lambda = \left(\frac{1}{A} \right) \left(\frac{2k_B^2 T}{h} \right) \left(I_2 - I_1^2 / I_0 \right) \qquad (3)$$

$$I_j = \int \left(\frac{E - E_f}{k_B T} \right)^j \tilde{T}(E) \left(-\frac{\partial f_0}{\partial E} \right) dE \qquad (4)$$

where e is the electronic charge, k_B the Boltzmann constant, h the Planck constant, T the temperature, and A the area of the simulation cell perpendicular to the transport direction; $f_0(E) = 1/(1 + e^{(E-E_f)/k_B T})$ is the Fermi-Dirac distribution function with respect to the Fermi level E_f ; $\tilde{T} = T(E) M(E)$ with the transmission $T(E) = \lambda / L$, the density of tunnelling modes $M(E) = (h/2L) \sum_k | v_k^\alpha | \delta(E - E_k)$ and $\delta(E - E_k) = (1/w\sqrt{2\pi}) e^{-(E-E_k)^2/2w^2}$. The ratio of the mean free path λ and the length L of the system can be used to determine the carrier transport in ballistic or diffusive regime (i.e. $T(E) = 1$ for ballistic and $0 < T(E) < 1$ for diffusive regime).

Using the VASP code, we calculated the group velocities of the charge carriers by using the finite difference method $v_k^y = (1/h)(\Delta E_k / \Delta k_y)$ with a small value of Δk_y along the y direction. The carrier DOS was produced by using the Gaussian smearing $\delta(E - E_k) = (1/w\sqrt{2\pi}) e^{-(E-E_k)^2/2w^2}$ on a calculated full electronic band structure energy E_k with a k-point sampling of 16x16x1 over a whole Brillouin zone and a smearing width of

0.005 eV. The sum of the product of v_k^y and the DOS over all k-points yields the density of modes *M(E)*.

Classical molecular dynamics calculation

Classical molecular dynamics was used to simulate the phonon modes and their interactions given an empirical interaction potential. In this context, the heat flux J is defined as

$$J = \frac{1}{V}\sum_{\alpha}\left(\varepsilon_{\alpha} I + v_{\alpha}^{T}\right) v_{\alpha} \qquad (5)$$

and the thermal conductivity tensor κ was obtained from the Green-Kubo formula

$$\kappa = \frac{V}{k_B T^2}\int_0^{\infty} \langle J(0) \otimes J(t) \rangle dt \qquad (6)$$

where *V* is the system volume, ε_α is the per-atom energy, v_{α}^{T} is the per-atom virial, v_α is the velocity of atom α, *T* is the temperature, k_B is the Boltzmann constant, ⟨·⟩ denotes the canonical ensemble average, and ⟨J⟩ = 0 in equilibrium. The trajectories $\{x_\alpha(t)\}$ of the atoms were obtained by integrating Newton's equations of motion, $m_\alpha \ddot{x}_\alpha = f_\alpha$, given initial conditions, masses m_α, and forces f_α derived from an empirical potential

$$\Phi(x_\alpha, q_\alpha) = \frac{\epsilon}{2}\sum_{\alpha,\beta}\frac{q_\alpha q_\beta}{r_{\alpha\beta}^{2}} + \frac{1}{2}\sum_{\alpha,\beta}\varphi(r_{\alpha\beta}) + \sum_{a}\mathrm{B}_a(x_a) \qquad (7)$$

where q_α is the charge on atom α, and $r_{\alpha\beta} = |\mathbf{x}_\alpha - \mathbf{x}_\beta|$ is the distance between atoms α and β. The first term is the Coulomb potential, the second is a Lennard-Jones pair potential modelled with van der Waals interactions, and the third is comprised of pair, angle, and dihedral bonds.

The partial charges q_α for the long-range Coulomb interactions were calculated with DFT/B3LYP (CRYSTAL14) via the Mulliken method on the optimized monolayer. The majority of the other parameters and functional forms of the potential were obtained from the well-known unified AMBER potential[11]. To allow for realistic anharmonic interactions and hence thermal conductivity, Morse pair bonds were used with an exponent of 2 in $\mathrm{B}_{\alpha}$with the equilibrium distance and stiffness matched to the harmonic bonds specified by the AMBER parameterization. The stiffness of the metal X-N pair bond and N-X-N angle bond missing from the AMBER parameterization were tuned using a frozen phonon-like method where the frequencies of a set of modes were adjusted to match those obtained from DFT/B3LYP calculations on a model system containing a single square planar metal center with diaminobenzene linkers; the system has the same N-X-N environment. The frequency of the empirical model of a given mode $\boldsymbol{m}$ was calculated via

$$\omega^2 \approx -m \cdot M^{-1} \frac{1}{\varepsilon} f(\varepsilon m) \tag{8}$$

where $\boldsymbol{M}$ is a diagonal matrix of atomic masses and $\boldsymbol{f}$ is the vector of atomic forces resulting from a displacement $\varepsilon\boldsymbol{m}$ from equilibrium with ε being a small number. The modes of the minimal substructure that have the same N-X-N coordination where used to simultaneously tune the metal X pair and angle bonds. In particular, the lowest frequency predominantly in-plane stretching and a bending modes were used since these were deemed to be the most informative of the two missing parameters.

With the interatomic potential fully specified, the Green-Kubo method was used to calculate the in-plane thermal conductivity using a rectangular unit cell. The size of the cell (2x2) was chosen based on previous results by Huang et al.[12] (and in our preliminary studies, 3x3 and 4x4 supercells gave comparable results). To obtain the ensemble average of the flux correlations given in Eq. (6), the atomic trajectories of 10 replicas, with initial velocities drawn from a Boltzmann distribution, were simulated using constant energy dynamics for 3.2 ns after equilibrating at 300 K. These simulations were done with LAMMPS. The calculated thermal conductivity for the single sheet in the armchair direction was 0.97 ± 0.03 W/mK, and 1.25 ± 0.03 W/mK in the perpendicular direction, based on a sheet-to-sheet spacing of 0.3 nm.

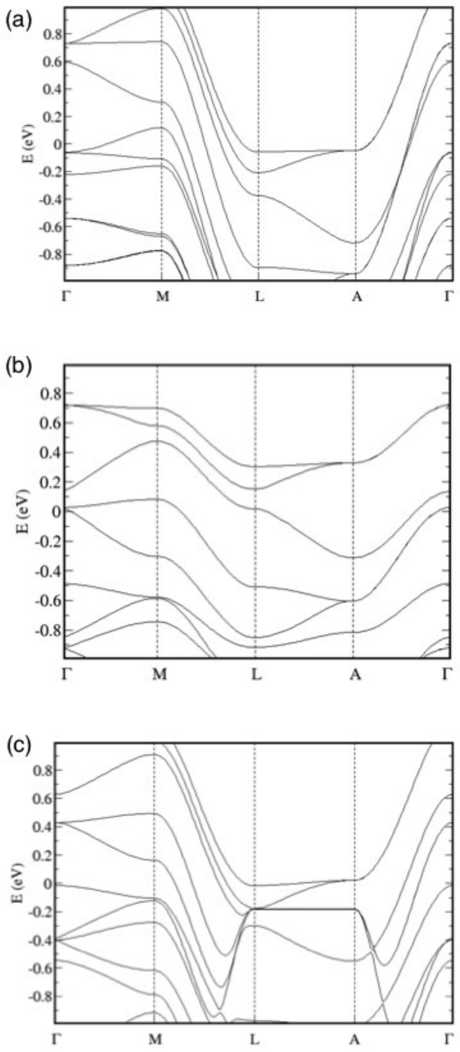

Figure S1. Calculated band structure of multi-layer $Ni_3(HITP)_2$ (a), $Pd_3(HITP)_2$ (b), $Pt_3(HITP)_2$ (c) using DFT+LDA. The multilayer system is formed by replicating a monolayer along the Z direction with the layer distance of 3.3 Å.

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