Ab initio investigation of thermoelectric properties of two-dimensional MOFs

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ABSTRACT

Metal–organic frameworks (MOFs) have the potential to be used as thermoelectric materials. Thermoelectric materials enable direct conversion between thermal and electrical energy. The main motivation for this project is to further our knowledge of thermoelectric properties in MOFs and find which available self-consistent-charge density functional tight-binding (SCC-DFTB) method can best predict (at least trends in) the electronic, phononic and therefore thermoelectric properties of MOFs at a lower computational cost than standard density functional theory (DFT). In the case of the electronic properties, we compare SCC-DFTB/3ob and SCC-DFTB/mio (based on available Slater-Koster files), GFN1-xTB and GFN2-xTB against PBE and hybrid DFT (HSE06) for $Zn_3C_6O_6$, Zn-NH-MOF, $Ni_3(HITP)_2$ and $Cd_3C_6O_6$ MOFs for the monolayer and stacked AA, serrated and AB structures. We also calculate the phononic contribution to the thermal conductivity using SCC-DFTB/3ob(mio) and GFN-xTB. Our results suggest that while GFN-xTB is adequate to predict the MOFs' electronic properties, DFTB-mio and GFN2-xTB are adequate to predict the MOFs' phononic properties. We find that while $Zn_3C_6O_6$, Zn-NH-MOF and $Cd_3C_6O_6$ MOFs are predicted to have a higher power factor than the $Ni_3(HITP)_2$ MOF (one of the highest performing synthesized thermoelectric MOFs), thermal transport is substantially lower for Zn-NH-MOF, leading to the highest ZT among the group.

MOTIVATION

An estimated two thirds of all the energy produced in the world is wasted as heat. Thermoelectric (TE) materials can convert wasted heat into useful electricity and vice-versa. The challenge to create efficient TE materials lies in achieving simultaneously high electronic conductivity (σ), high Seebeck coefficient (S) and low thermal conductivity (κ) in the same solid [1]. These properties define the dimensionless TE figure of merit $ZT=(S^2\sigma/\kappa)T$, where T is the temperature. The research goal of this reasearch is to develop the fundamental knowledge to predict key quantitative (QSPR) structure-property relationships to inform the rational design of thermoelectric metal–organic frameworks (MOFs).

METHODS

We use the Vienna *Ab Initio* Simulation Package (VASP) [2-4], a computer program which uses density functional theory (DFT) for atomic scale materials modelling. Using VASP is computationally expensive. DFTB+ [5] is a fast and versatile software package, here used to implement SCC-DFTB and GNFn-xTB. These semiempirical methods lead to up to two orders of magnitude increase in speed with only a small loss in accuracy. All the electrical transport coefficients (*S* and *σ)* are determined by solving the Boltzmann transport equation as implemented in BoltzTraP2 [6]. Second-order force constant phonon properties using both DFT and SCC-DFTB/GFNn-xTB were determined through the PHONOPY code [7]. To get the third-order force constant phonon contributions to the thermal conductivity (κ_L), the PHONO3PY code was employed [8-9].

CONCLUSION

While GFN1-xTB electronic properties are closer to DFT-PBE, the phonon dispersions using GFN2-xTB and DFTB-3ob/mio better resemble those from DFT-PBE. We therefore expect that the lattice thermal conductivities from GFN2-xTB and, to a lesser extent, DFTB-3ob/mio are closer to DFT-PBE. Curiously, GFN2-xTB did not converge for most unstable geometries (i.e., those with negative phonon modes) and was found to converge for all but one of the stable geometries.

The $Zn_3C_6O_6$, Zn-NH-MOF, $Ni_3(HITP)_2$, and Cd3C6O6 maximum electrical conductivity, Seebeck coefficient, and PF computed with DFT and SCC-DFTB are shown in Fig 1. The phonon properties of the monolayer, AA-stacked and serrated Zn-NH-MOF MOF results have been presented here due to its high ZT results (Fig 2). This work has been published [10-11].

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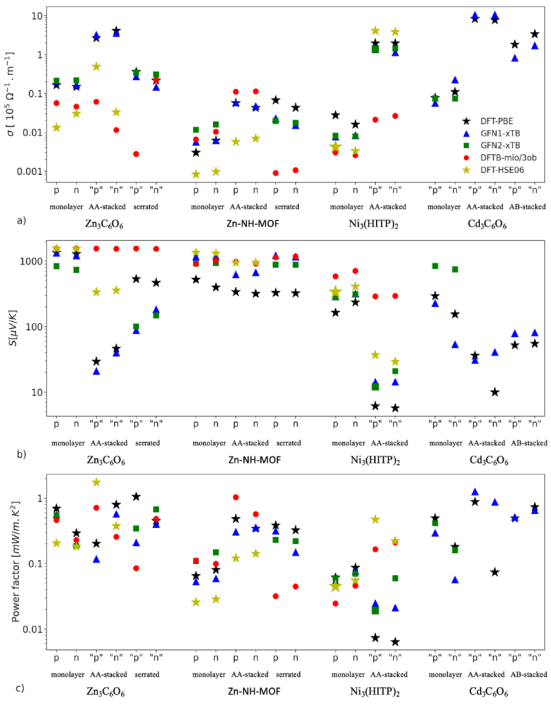

Fig. **1**. The maximum a) electrical conductivity (σ), b) the Seebeck coefficient (S) and c) the power factor (PF) of the $Zn_3C_6O_6$, Zn-NH-MOF, Ni_3(HITP), and $Cd_3C_6O_6$. The black stars, red circles, blue triangles, green squares, and yellow stars correspond to the DFT-PBE, DFTB, GFN1-xTB, GFN2-xTB and DFT-HSE06 results. Figure reproduced from [10].

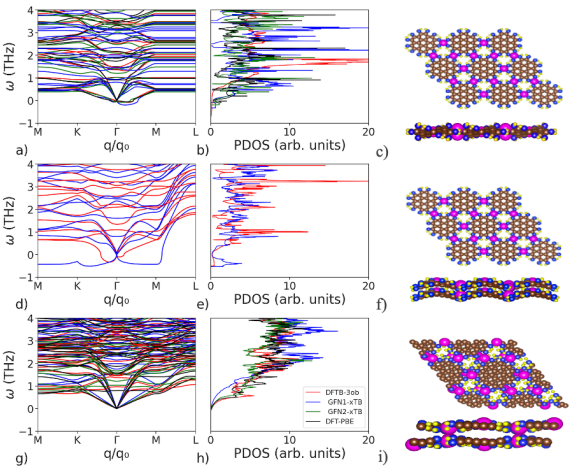

Fig. 2. a) The phonon dispersion and b) density of states of e) the wavy Zn-NH-MOF monolayer. f) The phonon dispersion and g) density of states of h) Zn-NH-MOF AA-stacked. i)The phonon dispersion and j) density of states of k) Zn-NH-MOF serrated. Zn, C, N and H are pink, brown, blue, and yellow, respectively. Figure reproduced from [11].