



obtained by decimation techniques. And then, the total transmission function with coupling matrices  $\Gamma_{L(R)} = i[\Sigma_{L(R)} - \Sigma_{L(R)}^\dagger]$  can then be computed from the Caroli formula:

$$T(E) = \text{Tr}[\Gamma_R G_C^r \Gamma_L G_C^a] \quad (5)$$

## 2. Thermoelectric parameters calculation

Once the transmission function is obtained, the Seebeck coefficient ( $S$ ), conductance ( $\sigma$ ) and electrical thermal conductance ( $\kappa_e$ ) can be obtained by:<sup>3</sup>

$$S(\mu, T) = -\frac{1}{eT} \left( \frac{L_1}{L_0} \right) \quad (6)$$

$$\sigma(\mu, T) = -\frac{2e^2}{h} L_0 \quad (7)$$

$$k_e(\mu, T) = -\frac{2}{hT} \left( L_2 - \frac{L_1^2}{L_0} \right) \quad (8)$$

where  $h$  is Plank constant,  $T$  is temperature,  $e$  is elementary charge, and  $L_n$  is Lorentz function, which expressed as:

$$L_n(\mu, T) = \int_{-\infty}^{\infty} T(E)(E - \mu)^n \frac{\partial f_E}{\partial E} dE \quad (9)$$

where  $f_E$  is Fermi-Dirac distribution function. Since the phonon thermal conductance is uncorrelated to chemical potential  $\mu$ , it is a constant value at a specific temperature. Finally, the  $ZT$  value is determined by the well-known relations:

$$ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_p} T \quad (10)$$

## 3. Individual phonon mode transmission probability

The transmission probability of individual phonon modes that originated from graphene leads are given by the transmission matrix:<sup>4,5</sup>

$$t_{mn} = \frac{2i\omega}{a_L a_R} \sqrt{V_R} [U_R^r]^{-1} \mathbf{j} [U_R^{a\dagger}]^{-1} \sqrt{V_L} \quad (11)$$

where  $\mathbf{j} = d_R^{00} K_{RC} D_C^r K_{CL} d_L^{00}$ , and the  $a_{L(R)}$  is the lattice constant of left (right) leads along the transport direction,  $m$  and  $n$  is the vibration degree of freedom of the left and right leads respectively. The eigenvector matrices  $U_{L(R)}^{a(r)}$  are obtained from diagonalizing the Bloch matrices:

$$F_{L(R)}^{a(r)} U_{L(R)}^{a(r)} = \Lambda_{L(R)}^{a(r)} U_{L(R)}^{a(r)} \quad (12)$$

where

$$F_L^a = \left[ (H_L^{10} \mathbf{g}_L^r)^{-1} \right]^\dagger \quad (13)$$

$$F_R^r = \mathbf{g}_R^r H_R^{10} \quad (14)$$

and the velocities matrices are given by:

$$V_{L(R)} = \frac{a_{L(R)}}{2\omega} U_{L(R)}^{a(r)} \Gamma_{L(R)}^{00} U_{L(R)}^{a(r)} \quad (15)$$

where  $\Gamma_{L(R)}^{00} = i \left[ \Pi_{L(R)}^{00} - (\Pi_{L(R)}^{00})^\dagger \right]$ . In addition, this method can also apply to calculate electronic transport. The transmission probability that contribute from different phonon mode of left or leads is read as:

$$T_L^m(\omega) = \sum_n |t_{mn}|^2$$

$$T_R^n(\omega) = \sum_m |t_{mn}|^2$$

Equivalent to Caroli's formula, the total phonon transmission of left and right leads is given by:

$$T_L(\omega) = T_R(\omega) = Tr(tt^\dagger) = Tr(t^\dagger t)$$

#### 4. Phonon transmission eigenchannel decomposition

To better understand the phonon interference effect, it is necessary to clarify the phase change of propagating lattice wave. For this purpose, we adopt the phonon transmission eigenchannel decomposition method as described in manuscript.<sup>6</sup> For simplicity, we skip the theoretical derivation and go straight to the key steps of numerical calculation. It starts with the spectral function  $A_C$ , which is given by terms of the Green's functions as follows:

$$A_C = A_C^B + \sum_{Z=L,R} A_C^Z = i \left[ D_C^r - D_C^{r\dagger} \right]$$

$$= \sum_{L,R} D_C^r \Gamma_{L(R)} D_C^{r\dagger} + 4i\eta\omega D_C^r D_C^{r\dagger} \quad (16)$$

Where  $A_C^Z$  is contributed from left/right leads, and  $A_C^B$  is contributed from the bound state of central molecular. Then, the spectral function of specific leads ( $L$  or  $R$ ) can be decomposed for:

$$A_C^{L(R)}(\omega) = \sum_m \mathcal{G}_m^L(\omega) \lambda_m(\omega) \mathcal{G}_m^L(\omega)^\dagger$$

$$= \frac{\pi}{\omega} \sum_m \mathcal{G}_m^L(\omega) \mathcal{G}_m^L(\omega)^\dagger \quad (17)$$

Diagonalizing the spectral function matrix we can obtain the eigenvalues  $\lambda_m$  and the scattering state  $\mathcal{G}_m^L(\omega)$ . Then the transmission probability matrix is given by:

$$\tau_{mn} = \frac{\pi}{\omega} \mathcal{G}_m^L(\omega)^\dagger \Gamma_R \mathcal{G}_n^L(\omega) = \frac{\pi}{\omega} [U^L(\omega)^\dagger \Gamma_R U^L(\omega)]_{mn} \quad (18)$$

where  $U(\omega) = [\xi_1, \xi_2, \dots, \xi_m]$ . Diagonalizing this transmission probability matrix, we will obtain the transmission eigenvector  $c_{m\mu}$  and transmission eigenvalue  $\tau_\mu$ . In this way, the total phonon transmission spectra are decomposed into the contribution of different phonon transmission eigenchannels in the central region of device. And the eigenchannel  $\Psi_\mu$  in central region is given by:

$$\Psi_{\mu}(\omega) = \sum_m c_{m\mu}(\omega) \frac{\rho_m(\omega)}{z_m(\omega)} \quad (19)$$

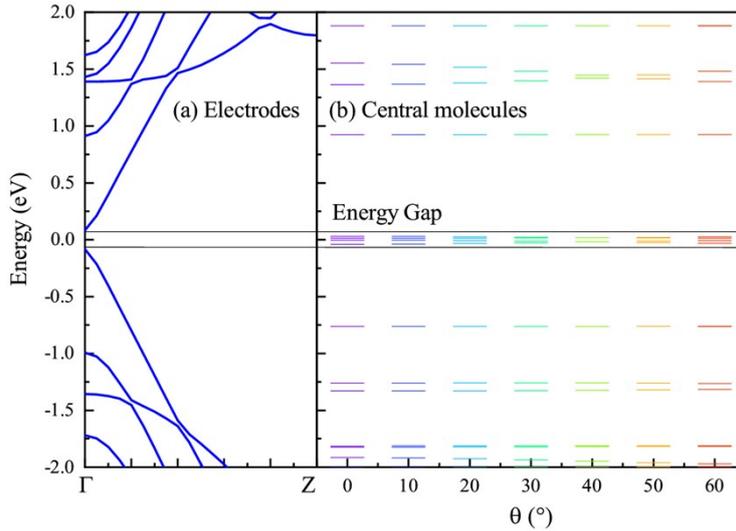
Finally, the complex displacements of eigenchannels are given by:

$$Q_{\mu}(\omega) = \sum_{i \in C, \alpha} \frac{s(\omega)}{\sqrt{m_i}} |\Psi_{\mu}(\omega)| e^{i\theta_{i\alpha, \mu}(E)} \quad (20)$$

where  $s(\omega)$  is a frequency dependent scaling factor of complex displacement vector,  $m_i$  is mass of  $i$ -th atom. Here, the  $\theta_{i\alpha, \mu}(E)$  is the phase angle of transmission eigenchannel. This information is included in the imaginary part of the complex displacement of eigenchannels  $\Psi_{\mu}$ .

## 5. Band structure and molecular energy spectrum

To illustrate the electronic properties are less affect by the twist angle, we calculated the band structure of graphene leads and molecular energy spectrum of central molecules, as shown in left panel of Figure. S1. The band structure of graphene leads clearly show semiconducting property (with around 0.2 eV band gap). The central molecular energy spectrum as a function of twist angles are calculated, as shown in the right panel of Figure. S1. For convenience, we aligned the molecular energy levels and band structure of graphene (Fermi level as the reference). One can see that molecular energy levels near Fermi level are located within the band gap of graphene. This illustrated the zero electronic transmission of the intermediate coupling molecular junction near the Fermi level. In addition, the isolated discrete energy level leads to localization of electronic state and thus results in the slope of transmission function changes in every discrete energy levels. Therefore, the Seebeck coefficient will undergo the unsystematic changes on the upper and lower sides of every discrete energy levels. In addition, one can see that the molecular energy spectrum is almost unaffected by twist angle.



**Figure. S1** (a) Band structure of graphene leads. (b) Molecular energy spectrum of central molecules.

## References

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