Supplementary Material to the article "Anisotropy of electron mobility in two-dimensional biphenylene network"

1. CALCULATION DETAILS

Ribbons. Electron mobility is defined as

$$\mu = \left|\frac{\sigma}{en}\right|, \tag{S1}$$

where σ is the conductivity, n - electron density, and e is electron charge. In a one-dimensional case one has

$$n = \frac{1}{a_z}\int_{E_F}^{\infty} d\varepsilon \rho(\varepsilon) f(\varepsilon), \tag{S2}$$

with $\rho(\varepsilon) = 4a_z/h \sum_n v_n^{-1}(\varepsilon)\theta(\varepsilon - E_C^n)$ being the density of electronic states per unit cell, E_C^n the bottom of the conduction band of nth branch, E_F the Fermi level, $v_n(\varepsilon) = \partial E_n/\partial p$ the group velocity, and a_z the length of the translation vector along the ribbon. In our calculations, the Fermi level was set at the level of the bottom of the conduction band. The number of branches involved depends on the width of the ribbon. In the range of widths we considered (2-15 hexagons, which roughly corresponds to 6-56 Å), only one branch was taken into account, since the others are located significantly further than $4k_BT \approx 0.1$ eV and cannot participate in transport for energy reasons. The density of states was calculated both through the definition (with the replacement of delta functions by Gaussian functions) and using group velocities using the DFTB+ functional, and the results were the same.

Conductivity is written as [1, 2, 3, 4]

$$\begin{aligned}\sigma &= \frac{2e^2}{a_z}\sum_n \int_{-\pi/a_z}^{\pi/a_z} \frac{dk}{\Omega_{BZ}}\left[-\frac{\partial f_n(k)}{\partial \varepsilon}\right] v_n^2(k)\tau_n(k) \\ &= \frac{4e^2}{h}\sum_n \int_{E_C^n}^{\infty} d\varepsilon \left[-\frac{\partial f(\varepsilon)}{\partial \varepsilon}\right] v_n(\varepsilon)\tau_n(\varepsilon).\end{aligned} \tag{S3}$$

Here $\tau_n(\varepsilon)$ is the relaxation time for the nth branch and $\Omega_{BZ} = 2\pi/a_z$. The main difficulty lies in the calculation of $\tau(\varepsilon, T, E_F)$. In SERTA approximation one has [5, 4]

$$\begin{aligned}\tau_n^{-1}(\mathbf{k}) = \sum_m \int \frac{d\mathbf{q}}{\Omega_{BZ}} \frac{2\pi}{\hbar} \sum_\lambda |g_{mn}^\lambda(\mathbf{k},\mathbf{q})|^2 \\ \times \Big[\Big(n(\omega_\lambda(\mathbf{q})) + 1 - f(\varepsilon_m(\mathbf{k}+\mathbf{q}))\Big) \\ \times \delta(\varepsilon_m(\mathbf{k}+\mathbf{q}) - \varepsilon_n(\mathbf{k}) + \hbar\omega_\lambda(\mathbf{q})) \\ + \Big(n(\omega_\lambda(\mathbf{q})) + f(\varepsilon_m(\mathbf{k}+\mathbf{q}))\Big) \\ \times \delta(\varepsilon_m(\mathbf{k}+\mathbf{q}) - \varepsilon_n(\mathbf{k}) - \hbar\omega_\lambda(\mathbf{q}))\Big]\end{aligned} \tag{S4}$$

with λ being the phonon branch idex, m, n indices of electron branches, $n(\omega)$ Bose-Einstein distribution function, and $\mathbf{k}$ and $\mathbf{q}$ the wave vectors of electrons and phonons, respectively. $|g_{nm}^\lambda|$ is the electron-phonon coupling (EPC) matrix.

In the non-orthogonal tight-binding approximation, which underlies both the DFTB method and the DFTB+ package, the electron subsystem is described by the Hamiltonian matrix $\mathbf{H}(\mathbf{k})$ and the overlap matrix $\mathbf{S}(\mathbf{k})$. The matrix elements in these matrixes are obtained by expanding the hopping integrals $H_{\mu s,\nu s'}(l,l')$ and the overlap integrals of the wave functions $S_{\mu s,\nu s'}(l,l')$ into a Fourier series with respect to the index of the unit cell l. s numbers the atoms within the unit cell, μ and ν number the orbitals of the atoms, and l numbers the unit cells.

The energy spectrum can be obtained from the following eigenvalue problem:

$$\mathbf{H}(\mathbf{k})\vec{A}_n = \varepsilon_n(\mathbf{k})\mathbf{S}(\mathbf{k})\vec{A}_n, \tag{S5}$$

where n, as before, denotes the branch (zone) number. By writing the equations of motion for such a system and considering the changes in the hopping integrals and overlap integrals due to phonon vibrations of the atoms as a time-dependent perturbation, in a linear approximation with respect to displacements, one can obtain the electron-phonon interaction matrix in the following form (see [6, 7, 8] for details)

$$g^{\lambda}_{nm}(\mathbf{k},\mathbf{q}) = \sqrt{\frac{\hbar}{2\omega_{\lambda}(\mathbf{q})}} \sum_{s,\mu,s',\nu} A^{*}_{n,s\mu}(\mathbf{k}+\mathbf{q}) \qquad \text{(S6)}$$
$$\times \left[\left(\widetilde{\nabla H}_{s\mu,s'\nu}(\mathbf{k}) - \varepsilon_m(\mathbf{k}) \widetilde{\nabla S}_{s\mu,s'\nu}(\mathbf{k}) \right) \frac{\mathbf{e}^{\lambda}_{s}(\mathbf{q})}{\sqrt{m_s}} \right.$$
$$- \left(\widetilde{\nabla H}_{s\mu,s'\nu}(\mathbf{k}+\mathbf{q}) - \varepsilon_n(\mathbf{k}+\mathbf{q}) \widetilde{\nabla S}_{s\mu,s'\nu}(\mathbf{k}+\mathbf{q}) \right)$$
$$\left. \times \frac{\mathbf{e}^{\lambda}_{s'}(\mathbf{q})}{\sqrt{m_{s'}}} \right] A_{m,s'\nu}(\mathbf{k}).$$

Here $\omega(\mathbf{q})$ is the phonon frequency, $\mathbf{e}^{\lambda}(\mathbf{q})$ is the polarization vector, and m_s is the mass of atom s. $\widetilde{\nabla H}_{s\mu,s'\nu}(\mathbf{k})$ is the three-dimensional gradient vector. To obtain it, it is necessary to find the derivative of the hopping parameter $H_{\mu s,\nu s'}(l,l')$ with respect to the displacement of atom s in the x, y, and z directions, and then perform the Fourier transform with respect to l, going to $\mathbf{k}$. A similar procedure is carried out to find $\widetilde{\nabla S}_{s\mu,s'\nu}(\mathbf{k})$.

The algorithm implemented in the DFTBephy package (described in detail in [8]) involves constructing a unit cell and optimizing it. A sufficiently large supercell is then created, consisting of an odd number of unit cells. Typically, this number ranges from 5 to 9 cells; the number is chosen to include the maximum coordination sphere for which the applied set of tight-binding parameters is calculated. A finite mesh is selected for $\mathbf{k}$ and $\mathbf{q}$. The electron eigenvalue problem is solved. Using this supercell, the required phonon properties, $\omega^{\lambda}(\mathbf{q})$ and $\mathbf{e}^{\lambda}(\mathbf{q})$ are calculated using Phonopy. To find $\widetilde{\nabla H}_{s\mu,s'\nu}(\mathbf{k})$ and $\widetilde{\nabla S}_{s\mu,s'\nu}(\mathbf{k})$, the same supercell and finite-difference scheme with a bias parameter of 0.001Å are used. Next, the matrix (S6) is calculated, and then the scattering rate (S4). In this case, the delta functions are replaced by Gaussian functions with a width $\sigma = 0.003$ eV.

We perform optimization by using the following parameters: SCC tolerance was 10^{-9}, the maximum force tolerance was 10^{-7} a.u., the Fermi filling temperature was 100 K, and $\mathbf{k}$-mesh was 1×1×220. The separation distance in the x and y directions was set to 7 nm. In our Phonopy calculations, we employed 1×1×7 supercell, k-mesh was 1×1×23. The charges for DFTBephy were calculated using the same parameters. For scattering rates calculation the DFTBephy was set up with the following parameters: q-mesh: 1×1×1000 on full BZ.

$\tau(k)$ calculations were performed for first π-branch in conduction band. We used a mesh of 300 k-points. To study a small segment of the Brillouin zone from the Γ-point toward the Z-point, we used a refinement factor of 10 and a shift of $(0, 0, 0.05)$. The default values were kept for all unspecified parameters.

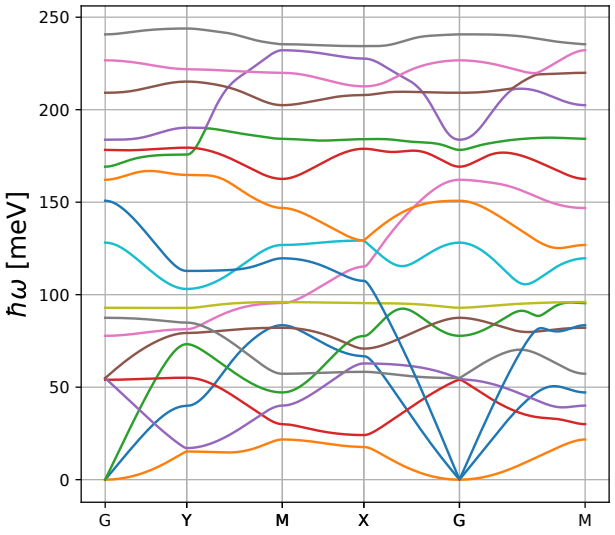

Fig. S1. Phonon dispersion of a two-dimensional biphenylene network

Two-dimensional biphenylene network. In this case, mobility acquires indices that characterize the direction of current flow:

$$\mu_{\alpha\beta} = \left| \frac{\sigma_{\alpha\beta}}{en} \right|. \qquad \text{(S7)}$$

where α and β take a set of values $\{x, y\}$. The conductivity tensor can be found as

$$\sigma_{\alpha\beta} = \frac{2e^2}{S_{uc}} \sum_{n} \int \frac{dk_x dk_y}{\Omega_{BZ}} \left[-\frac{\partial f_n(\mathbf{k})}{\partial \varepsilon} \right] \qquad \text{(S8)}$$
$$\times v_{n\alpha}(\mathbf{k}) v_{n\beta}(\mathbf{k}) \tau_n(\mathbf{k}),$$

where 2 comes from summation over spins and S_{uc} is the area of the unit cell. In the sum over n, we retained only one term, that is, we considered only the band that formed an intersection with the Fermi level in the vicinity of the Γ point. The electron density was calculated by

$$n_e = \frac{2}{S_{uc}} \sum_{n} \int \frac{dk_x dk_y}{\Omega_{BZ}} f(\varepsilon_n(\mathbf{k}), E_F, T). \qquad \text{(S9)}$$

Here also only one branch was considered. The electroneutrality point was taken as $E_F = 0$.

For optimization, a 150×150×1 mesh was chosen. When calculating phonons, a 7×7×1 supercell and a 22×22×1 k-mesh were used. The phonon spectrum is shown in Fig. S1. When calculating $\tau(\mathbf{k})$, a q-mesh of size 400×400×1 centered at Γ-point was used. The mesh

shape coincided with the BZ mesh, but was stretched over the reciprocal lattice vectors reduced by a factor of 2. For electrons, the k-mesh was 100×100×1, stretched over the vectors reduced by a factor of 4, also centered at Γ-point.

The energy spectrum of $\varepsilon(\mathbf{k})$ and the group velocities $v_{\alpha\alpha}(\mathbf{k})$ were calculated on a 400×400×1 mesh on the full BZ. When calculating the integrals (S8)-(S9) for the quantities determined on the mesh, i.e., $\varepsilon(\mathbf{k})$, $v_{\alpha\alpha}(\mathbf{k})$, and $\tau_n(\mathbf{k})$, triangulation with linear interpolation was used.

1. T. Fang, A. Konar, H. Xing, and D. Jena, "Mobility in semiconducting graphene nanoribbons: Phonon, impurity, and edge roughness scattering," *Phys. Rev. B*, vol. 78, p. 205403, Nov 2008.
2. Y. Zhao, A. Liao, and E. Pop, "Multiband mobility in semiconducting carbon nanotubes," *IEEE Electron Device Letters*, vol. 30, no. 10, pp. 1078–1080, 2009.
3. S. Poncé, W. Li, S. Reichardt, and F. Giustino, "First-principles calculations of charge carrier mobility and conductivity in bulk semiconductors and two-dimensional materials," *Reports on Progress in Physics*, vol. 83, p. 036501, feb 2020.
4. E. Unsal, A. Pecchia, A. Croy, and G. Cuniberti, "Charge carrier mobilities in γ-graphynes: a computational approach," *Nanoscale*, vol. 17, pp. 24591–24600, 2025.
5. R. Claes, S. Poncé, G.-M. Rignanese, and G. Hautier, "Phonon-limited electronic transport through first principles," *Nature Reviews Physics*, vol. 7, no. 2, pp. 73–90, 2025.
6. C. M. Varma, E. I. Blount, P. Vashishta, and W. Weber, "Electron-phonon interactions in transition metals," *Phys. Rev. B*, vol. 19, pp. 6130–6141, Jun 1979.
7. V. N. Popov and P. Lambin, "Intraband electron-phonon scattering in single-walled carbon nanotubes," *Phys. Rev. B*, vol. 74, p. 075415, Aug 2006.
8. A. Croy, E. Unsal, R. Biele, and A. Pecchia, "Dftbephy: A dftb-based approach for electron–phonon coupling calculations," *Journal of Computational Electronics*, vol. 22, no. 5, pp. 1231–1239, 2023.