Supporting information

Tunable Thermal Conductivity of π-Conjugated Two-Dimensional Polymers

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The thermal conductivity of 2D polymers can be calculated based on equation 4 in the main text. Note that $k = (k_x + k_y)/2$. We can only estimate the average group velocity because we do not have a complete set of mode-dependent phonon properties in the first Brillouin zone. Since our EMD simulations fall into the classical limit, the total volumetric heat capacity can be calculated by $c_v = 3k_B N/V$, where k_B is the Boltzmann constant, N is the total number of atoms, and V is the corresponding volume. Acoustic phonon group velocities can be extracted based on the slope of phonon dispersions. Here we assumed linear phonon dispersion of acoustic branches and the phonon group velocity was estimated using the following equation: $v = \frac{\omega(M)}{q(M)}$, where $\omega(M)$ and $q(M)$ are the angular frequency and the wavevector at M point in Figure 5. The average phonon group velocity $(\bar{v})$ [1, 2] is calculated by $\frac{1}{2}\bar{v}^2 = [\frac{v_{LA} + v_{TA1} + v_{TA2}}{3}]^2$, where v_{LA}, v_{TA1}, and v_{TA2} represent phonon group velocities of longitudinal acoustic (LA) modes and two transverse acoustic (TA) modes from Figure 5 , respectively. Given k, c_v, and $\bar{v}$, phonon lifetime ($\bar{\tau}$) can be obtained from equation (R1) and phonon mean free path ($\bar{l}$) can be calculated by $\bar{l} = \bar{v}\bar{\tau}$. All the results are summarized in Table SI. Phonon group velocity of all DPG is larger than 4000 m/s and phonon mean free path is smaller than 2.0 nm.

Table SI. Porosity, in-plane thermal conductivity (k), volumetric heat capacity (c_v), average phonon group velocity $(\bar{v})$, average phonon phonon mean free path $(\bar{l})$, and rotation factor (RF) of all three 2D polymers.

	Porosity (%)	k (W/(mK))	c_v ($J\cdot cm^{-3}\cdot K^{-1}$)	$\bar{v}$ (m/s)	$\bar{l}$ (nm)	RF (Å)
DPG-1	3.2	97.6	8.4	5898.2	2.0	0.24
DPG-2	35.4	8.8	2.4	4393.4	0.8	0.60
DPG-3	53.8	3.3	1.5	4407.7	0.5	0.68

We plotted average phonon group velocity $(\bar{v})$, average phonon phonon mean free path $(\bar{l})$ as a function of porosity, respectively, as shown in Figure S1. It is shown that both phonon group

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velocities and mean free paths of DPG decrease as the porosity increases. In other words, large porosity in DPG can lead to small phonon group velocities and reduced average phonon mean free path by increasing phonon scatterings, resulting in small thermal conductivity.

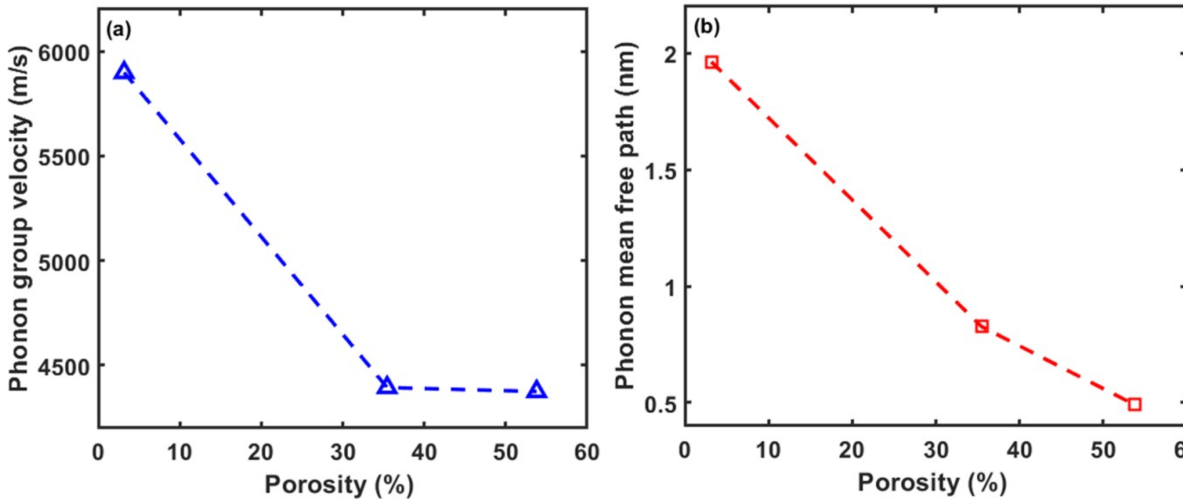

Figure S1. (a) Phonon group velocities as a function of porosity of DPG at 300 K. (b) Phonon mean free path as a function of porosity of DPG at 300 K.

Segmental rotation factor of 2D polymers was calculated based on equation 6 in the main text. The results are shown in Table SI. We have plotted the segmental rotation factor as a function of porosity; averaged phonon group velocity, averaged phonon mean free path as a function of porosity in Fig S2. It is shown that segmental rotation factor of DPG increase with porosity increases and phonon group velocities and mean free paths of DPG decrease as the rotation factor increases.

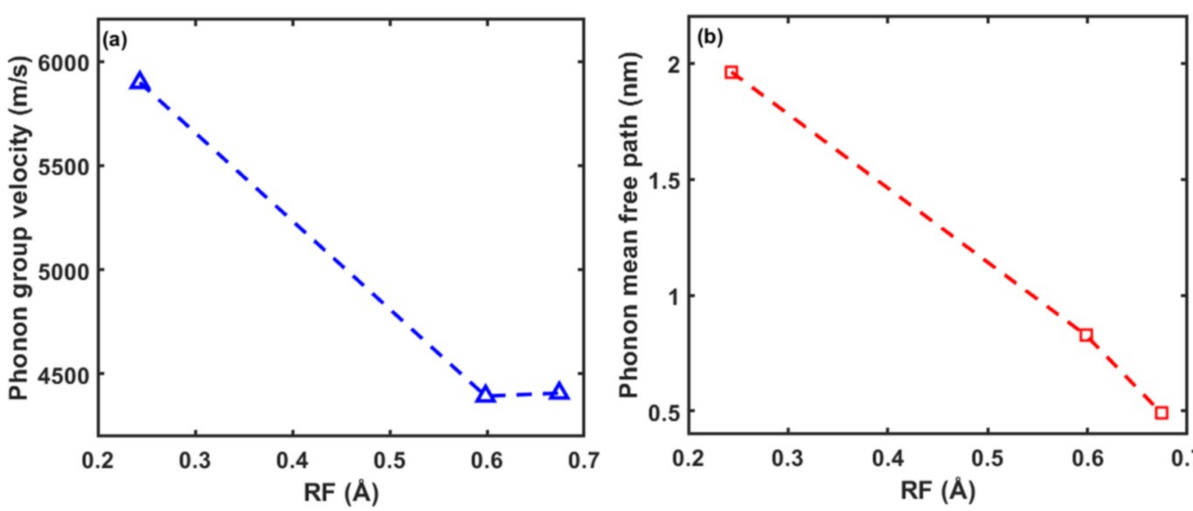

Figure S2. (a) Phonon group velocity vs. porosity of DPG at 300 K. (b) Phonon mean free path vs. porosity of DPG at 300 K.

References

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2. T. Zhang, X. Wu and T. Luo, *The Journal of Physical Chemistry C*, 2014, **118**, 21148-21159.