Supplementary Information for

Investigation of interfacial thermal transport across graphene and an organic semiconductor using molecular dynamics simulations

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1. Potential parameters in the simulation

The general AMBER force field (GAFF)[1] is employed to describe the intermolecular and intramolecular interactions of DNTT molecules. In GAFF, the total energy of the system, E_{pair}, includes five components: the bond, angle, dihedral, van der Waals interaction (Lennard-Jones potential, L-J potential) and electrostatic terms, as presented below:

$$E_{pair} = \sum_{bonds} k_r \left(r_b - r_{b,eq}\right)^2 + \sum_{angles} k_\theta \left(\theta - \theta_{eq}\right)^2 + \sum_{dihedrals} \frac{v_n}{2} \times \left[1 + \cos\left(n\varphi - \gamma\right)\right] + \sum_{i<j} 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \sum_{i<j} C \frac{q_i q_j}{r_{ij}} \quad \text{(S1)}$$

where, r_b and θ are the bond length and angle, respectively; subscript "*eq*" represents the equilibrium condition; k_r, k_θ and v_n are force constants; n is multiplicity and γ is phase angle for dihedral angle parameters; r is the distance between atoms; ε is the depth of potential well; σ is the zero energy separation distance; C is an energy-conversion constant; q is the charge; subscripts "*i*" and "*j*" represent atoms. The cutoff distances for L-J potential and electrostatic terms are 10 Å. The detailed GAFF parameters used in the simulation are shown in Tables S1-S7.

The second-generation reactive empirical bond order (REBO) potential is applied to describe the C-C interaction in graphene.[2] The L-J potential is also employed to describe the van der Waals interaction of graphene and DNTT as below:

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$$E_{LJ} = 4\chi\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad \text{(S2)}$$

where, χ is the coupling strength factor to tune the interaction strength between graphene and DNTT. The cutoff distances for the van der Waals interaction of graphene and DNTT are 10 Å. The L-J potential parameters for interaction of graphene and DNTT are calculated from the universal force field (UFF)[3] as shown in Table S8.

Table S1 List of atom types

Atom	Type	Description
Carbon	CA	Aromatic carbon in DNTT molecule
	CB	Aromatic carbon at junction of 5- and 6-membered rings and attached to sulfur in DNTT molecule
	CC	Aromatic carbon at junction of 5- and 6-membered rings and unattached to sulfur in DNTT molecule
	CS	Carbon at junction of two 5-membered rings in DNTT molecule
	CG	Graphene carbon
Hydrogen	HA	H attached to aromatic carbon in DNTT molecule
	HG	H attached to graphene carbon
Sulfur	S	Sulfur in 5-membered ring in DNTT molecule

Table S2 List of bond parameters of GAFF

Bond	k_r (eV/Å^2)	$r_{b,eq}$ (Å)
CA-CA	20.028748	1.3980
CA-CB	21.300848	1.3790
CA-CC	21.830059	1.3715
CA-HA	15.371818	1.0800
CB-CC	18.032574	1.4310
CB-S	12.190098	1.7345
CS-CC	18.032574	1.4310
CS-CS	22.748275	1.3590
CS-S	12.190098	1.7345

Table S3 List of angle parameters of GAFF

Angle	k_θ (eV/rad^2)	θ_{eq} (°)
CA-CA-CA	2.873818	120.3300
CA-CA-CB	2.926188	119.6500
CA-CA-CC	2.875878	120.8500
CA-CA-HA	2.102674	119.6600
CB-CA-HA	2.107006	120.2000
CC-CA-HA	2.137473	119.6000
CA-CB-CC	2.825984	121.0000
CA-CB-S	2.477234	126.1000
CC-CB-S	2.259073	132.2500
CA-CC-CB	2.909368	119.4000
CA-CC-CS	2.909368	119.4000
CB-CC-CS	3.405900	109.2500
CC-CS-CS	3.204438	114.0000
CC-CS-S	2.259073	132.2500
CS-CS-S	3.061716	113.6000
CB-S-CS	4.449848	90.2800

Table S4 List of dihedral angle parameters of GAFF

Dihedral angle	$\frac{v_n}{2}$ (eV)	n	γ (°)
X-CA-CA-X	0.157192	2	180
X-CA-CB-X	0.151772	2	180
X-CA-CC-X	0.151772	2	180
X-CB-CC-X	0.236331	2	180
X-CB-S-X	0.014453	3	0
X-CC-CS-X	0.072634	2	180
X-CS-CS-X	0.288367	2	180
X-CS-S-X	0.014453	3	0

Table S5 List of improper dihedral angle parameters of GAFF

Improper dihedral angle	$\frac{v_n}{2}$ (eV)	n	γ (°)
X-X-X-X	0.047700	2	180

Table S6 List of Lennard-Jones potential parameters of GAFF

Atom type	ε (eV)	σ (Å)
CA	0.003729	3.4000
CB	0.003729	3.4000
CC	0.003729	3.4000
CS	0.003729	3.4000
HA	0.000650	2.6000
S	0.010841	3.5640

Table S7 List of charge parameters of atoms in DNTT

Atom type	q
CA (attached to H)	-0.1270
CA (unattached to H)	0.0000
CB	-0.0130
CC	0.0000
CS	-0.0130
HA	0.1270
S	0.0260

Table S8 List of Lennard-Jones potential parameters of UFF

Pair type	ε (eV)	σ (Å)
CG-CA	0.004553	3.4309
CG-CB	0.004553	3.4309
CG-CC	0.004553	3.4309
CG-CS	0.004553	3.4309
CG-HA	0.002947	2.9700
CG-S	0.007355	3.5119
HG-CA	0.002947	2.9700
HG-CB	0.002947	2.9700
HG-CC	0.002947	2.9700
HG-CS	0.002947	2.9700
HG-HA	0.001908	2.5711
HG-S	0.004761	3.0402

2. Effect of DNTT orientation on TBR of graphene and DNTT

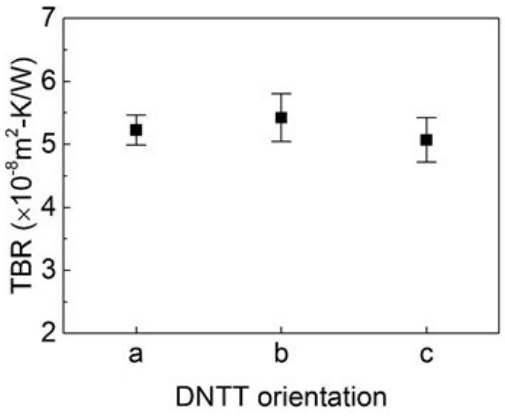

Fig. S1 TBR variation of graphene and DNTT at different DNTT orientations (*a*, *b* and *c* directions). There is no dependence of TBR on DNTT orientation.

3. Verification of TBR of graphene and DNTT without graphene lattice constant modification

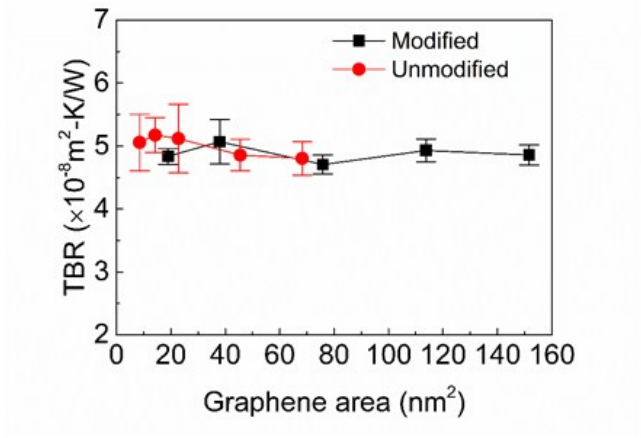

Fig. S2 TBR variation of graphene and DNTT at different graphene areas. The black square symbols represent the TBR with graphene lattice constant modification and the periodic boundary conditions are applied in in-plane direction during the simulation. The red dot symbols represent the TBR without graphene lattice constant modification and the free boundary conditions are applied in in-plane direction during the simulation.

4. Contributions of "C" and "H" of hydrogenated graphene to the TBR of hydrogenated graphene and DNTT

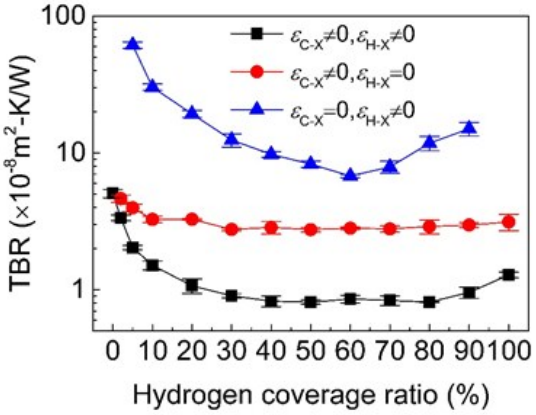

Fig. S3 Contributions of "C" and "H" of hydrogenated graphene to the TBR of hydrogenated graphene and DNTT. "C", "H" and "X" represent the carbon atoms of hydrogenated graphene, hydrogen atoms of hydrogenated graphene and atoms (carbon, hydrogen, or sulfur) of DNTT, respectively. "$\varepsilon_{C\text{-}X} \neq 0$" and "$\varepsilon_{H\text{-}X} \neq 0$" (black square symbols) represent both "C" and "H" in hydrogenated graphene participate in the interfacial thermal transport with DNTT; "$\varepsilon_{C\text{-}X} \neq 0$" and "$\varepsilon_{H\text{-}X} = 0$" (red dot symbols) represent only "C" in hydrogenated graphene participates in the interfacial thermal transport with DNTT and the interaction between "H" of hydrogenated graphene and DNTT is turned off; "$\varepsilon_{C\text{-}X} = 0$" and "$\varepsilon_{H\text{-}X} \neq 0$" (blue triangle symbols) represent only "H" in hydrogenated graphene participates in the interfacial thermal transport with DNTT and the interaction between "C" of hydrogenated graphene and DNTT is turned off. It can be observed that the contribution from "C" of hydrogenated graphene to interfacial thermal transport is much larger than that from "H" of hydrogenated graphene.

5. Phonon DOS of graphene and DNTT with DNTT vacancies

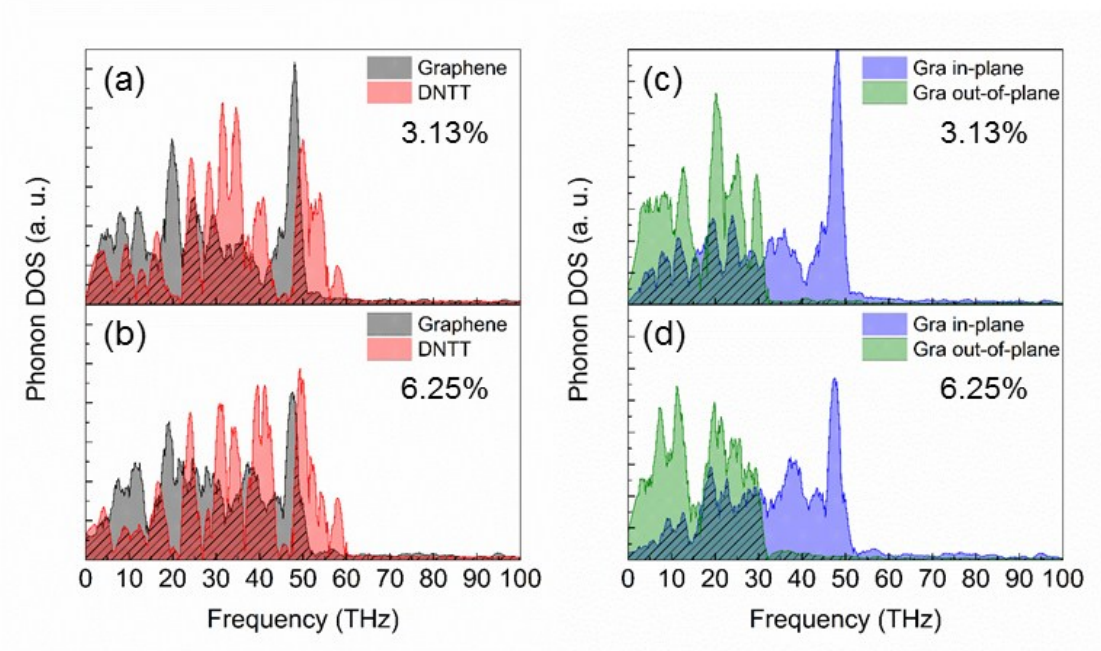

Fig. S4 (a)-(b) Phonon DOS of total graphene and DNTT at DNTT vacancy concentration of 3.13% and 6.25%. (c)-(d) Phonon DOS of in-plane and out-of-plane graphene at DNTT vacancy concentration of 3.13% and 6.25%. Slanted line areas denote overlap of phonon DOS. The phonon overlapping factors of graphene and DNTT are 0.597 and 0.604 at DNTT vacancy concentration of 3.13% and 6.25%; and the phonon overlapping factors of in-plane and out-of-plane phonons in graphene are 0.451 and 0.455 at DNTT vacancy concentration of 3.13% and 6.25%.

References

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2. W. B. Donald, A. S. Olga, A. H. Judith, J. S. Steven, N. Boris and B. S. Susan, *J. Phys. Condens. Matter*, 2002, **14**, 783.
3. A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024-10035.