## Supporting Information

## Hierarchically Hydrogen-Bonded Graphene/Polymer Interfaces with Drastically Enhanced Interfacial Thermal Conductance

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**Fig. S1**. System setup for nonequilibrium molecular dynamics (NEMD) simulations (green: PMMA; yellow: PVA; blue: graphene). Atoms in the frozen region were fixed. Temperatures of the heat source and the heat sink were fixed at 400 K and 250 K, respectively. Periodic boundary conditions (PBC) were applied in all three directions.



Fig. S2. Heat energy added to the heat source by the Langevin thermostat versus time in NEMD.



**Fig. S3.** Temperature contours of graphene and a pair of PVA chains in G-32PVA. PVA chains shown in (a)-(d) were randomly chosen for a total of 32 pairs. Distance between the grafting points of two PVA chains in a pair is comparable to that in G-1PVA.



**Fig. S4.** Contour plots of the atomic number density of graphene and selected pairs of PVA chains in G-32PVA.



**Fig. S5.** Axial atomic number density distributions of (a) PVA and (b) PMMA along the direction perpendicular to the surface of graphene. Atoms were binned into cells of 0.2 Å along the *z*-direction starting from the surface of graphene. Over 8000 frames were analyzed and averaged. PVA in G-32PVA shows long-range ordering until 16 Å away from the graphene surface. This distance is very close to the length of a relaxed straight PVA chain employed for this study (19.9 Å), proving the highly extended configuration of PVAs in G-32PVA. With less PVA chains in the system, the ordering length is only slightly reduced, suggesting extended configurations even at low grafting densities.



Fig. S6. Local Herman's orientation for polymer main chains in G-XPVA at different PVA grafting densities: (a, c, e, g) PVA and (b, d, f, h) PMMA. From top to bottom: X = 1, 8, 16 and 32.



**Fig. S7.** Geometric criteria used to identify a hydrogen bond: (1) the distance between the hydrogen bond donor (D) and the acceptor (A) is smaller than 3.0 Å; and (2) the angle of D-H (hydrogen)-A is smaller than 25°.



**Fig. S8.** Hydrogen bonds formed in four selected pairs of PVA chains in G-32PVA. Grey color dots show the atomic number density. Red dots show hydrogen bonds formed between PVA and PMMA, while blue dots show those formed between and within PVA chains.



**Fig. S9.** Number of hydrogen bonds versus time: (a) hydrogen bonds between PVA and PMMA and (b) hydrogen bonds between and within PVA chains.



**Fig. S10.** An atomistic model for MD simulation of the pull-out process. Atoms of PMMA (green) to the left of plane "1" are fixed. Atoms of PVA (yellow) to the right of plane "2" are fixed. Atoms of graphene (ice blue) and those between "1" and "2" are movable. The center of mass (COM) of graphene and the rigid part of PVA as a whole is moved at a constant velocity along the +z direction. The simulation was performed in the NVT ensemble with the time step of 0.1 fs. The pulling force was sampled at different separations. Work of adhesion was evaluated by integrating the force-displacement curve.



**Fig. S11.** Pull-out force versus interfacial separation for G-*X*PVA with different PVA grafting densities. G represents pristine graphene/PMMA interface.