Supporting Information (SI): Heat Transfer Enhancement in Tree-Structured Polymer Linked Gold Nanoparticle Networks

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The following items are available in this Supporting Information (SI): (i) Simulation model size in detail. (ii) Detailed molecular dynamics (MD) simulation force field parameters. (iii) Additional results and explanations.

S-1　This SI includes the following Tables and Figures:

• Tables S1 - S2 list the related force field parameters for polyethylene (PE) and poly(p-phenylene) (PPP) tree polymer network models.

• Figure S1 shows gold nanoparticle (AuNP), PE and PPP tree polymer models.

• Figure S2 shows the simulation model and network structures for PE trees with branch length C12.

• Figure S3 shows the up heat flux calculation set up in MD simulation.

• Figure S4 shows the positions of the randomly selected 20 carbons for calculating vibrational density of state (VDOS).

• Figure S5 shows the extended VDOS results, frequency up to 100 THz, for PE and PPP tree networks.

• Figure S6 shows the heat conductance results for PE C12 tree networks.

• Figures S7 and S8 show the PE and PPP cut tree networks.

S-2 Simulation Models and Methods

Smaller PE trees with C12 branches are less stable than larger PE trees with C50 branches. Because for PE branch length C12 trees, there is not enough space to link larger AuNPs, we have use 1 nm diameter AuNPs. However these 1 nm diameter AuNPs are too small, they are easily dragged by the polymer, and they are clustering to neighboring AuNPs during the simulation.

The AuNPs are constructed by the following steps: (1) We use Large-scale Atomic Molecular Massively Parallel Simulator (LAMMPS) script to construct a bulk gold crystal $5 \times 5 \times 5$ nm^3. (2) We use 2 nm as the radius cutoff to cut an AuNP of 4 nm in diameter, which contains 2117 Au atoms. (3) We replicate and move the AuNPs to connect them on to the polymer tails. The bulk gold is a FCC crystal with lattice constant 4.078 Å. The Lennard-Jones (LJ) force field derived by Heinz et al. is used to describe Au-Au interactions in AuNPs.[1]

The VDOS $(D(\omega))$ is calculated by Fourier transform of the velocity autocorrelation function.[2]

$$D(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\langle \vec{v}(t) \cdot \vec{v}(0) \rangle}{\langle \vec{v}(0) \cdot \vec{v}(0) \rangle} e^{i\omega t} \, dt \tag{1}$$

Fourier transform is performed using the fast Fourier transform (fft) function in Matlab. The actual integration time for the velocity autocorrelation function is from 0 to 500 ps. The velocity profile for each atom $(\vec{v}_i(t))$ is generated from MD simulations. The velocity autocorrelation $(\vec{v}_i(t) \cdot \vec{v}_i(0))$ is calculated by a Matlab code. Using N atoms, we get the averaged velocity autocorrelation:

$$\langle \vec{v}(t) \cdot \vec{v}(0) \rangle = \frac{1}{N} \sum_{n=1}^{N} \vec{v}_i(t) \cdot \vec{v}_i(0) \tag{2}$$

Here the velocity profiles of the selected $N = 20$ carbons are calculated at every 0.25 fs time

step for 1 ns simulation time. The 20 atoms are randomly selected and they are in the middle part of the polymer tree to reduce the effect from the thermostat; see Fig. S4. In MD simulation, to get velocity profiles, we set the temperature of AuNPs at 300 K using Langevin thermostat and the polymers are not applied with thermostat. We only use 1 trajectory and 20 different atoms to calculate the averaged velocity autocorrelation function. To improve the VDOS result, using more different atoms and trajectories can be helpful. However, this calculation computational intensive and hard to know how many is good enough.

AuNP: D = 4 nm

50 carbons
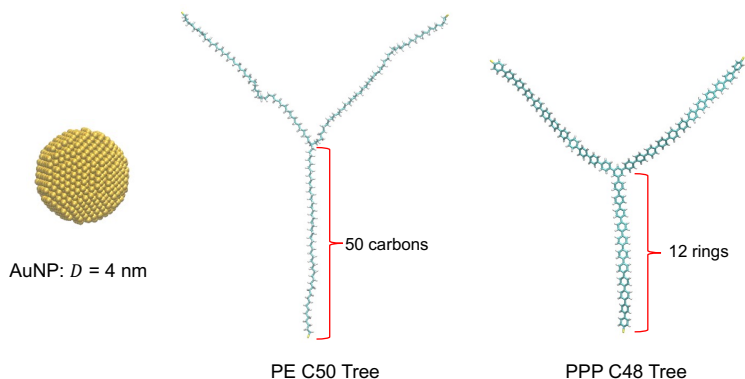
PE C50 Tree

12 rings

PPP C48 Tree

Figure S1: Schemes of the 4 nm diameter AuNP, Level 1 PE tree with a branch chain length of C50, and Level 1 PPP tree with a branch chain length of C48 (12 rings).
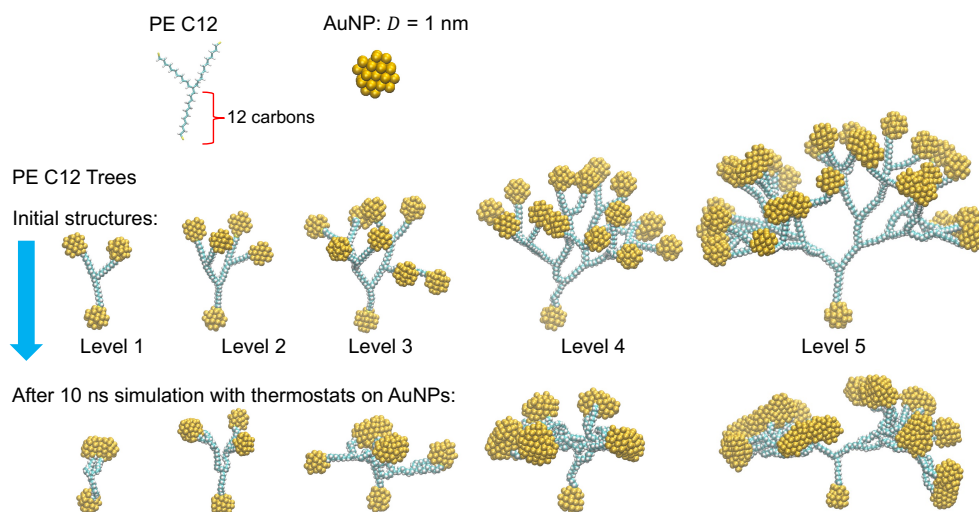
Figure S2: Schemes shorter PE trees with a branch chain length of C12 and the AuNP diameter is 1 nm. The initial trees have AuNPs more separated from each other (upper 5 structures). After 10 ns simulation of the heat flux calculation, the AuNPs migrated and merged to each other (bottom 5 structures).

Table S1: Force field parameters of PE tree network models.[1,3–6]

Atom types	Mass	LJ-ε (kcal/mol)	LJ-σ (Å)	Charge (e⁻)
c	12.011	0.066	3.5	-0.12
c next to s	12.011	0.066	3.5	0.06
h	1.008	0.03	2.5	0.06
s	32.06	0.25	3.55	-0.18
Au	196.967	5.29	2.951	0
Mixing LJ pairs	LJ-ε (kcal/mol)	LJ-σ (Å)		
Au-c	0.050734604	3.2175		
Au-h	0.034205263	2.7175		
Morse potential	D_0 (kcal/mol)	α (1/Å)	r_0 (Å)	r_c (Å)
Au-s	8.763	1.47	2.65	8
Harmonic Bond	K_b (kcal/mol/Å)	r_0 (Å)		
c-c	268.0	1.529		
c-h	340.0	1.09		
c-s	222.0	1.81		
Harmonic Angle	K_a (kcal/mol/degree)	θ_0 (degree)		
c-c-c	58.35	112.7		
c-c-h	37.5	110.7		
h-c-h	33.0	107.8		
h-c-s	35.0	109.5		
c-c-s	50.0	108.6		
OPLS dihedral	K_1 (kcal/mol/degree)	K_2 (kcal/mol/degree)	K_3 (kcal/mol/degree)	K_4 (kcal/mol/degree)
c-c-c-c	1.3	-0.05	0.2	0.0
c-c-c-s	1.262	-0.198	0.465	0.0
c-c-c-h	0.0	0.0	0.3	0.0
h-c-c-h	0.0	0.0	0.3	0.0
h-c-c-h with c-s	0.0	0.0	0.452	0.0

Table S2: Force field parameters of PPP tree network models.[1,3–6]

Atom types	Mass	LJ-ε (kcal/mol)	LJ-σ (Å)	Charge (e⁻)
cp	12.011	0.07	3.55	-0.115
cp next to s	12.011	0.07	3.55	0.18
h	1.008	0.03	2.42	0.115
s	32.06	0.25	3.55	-0.18
Mixing LJ pairs	LJ-ε (kcal/mol)	LJ-σ (Å)		
Au-cp	0.052249402	3.2425		
Au-h	0.034205263	2.6775		
Harmonic Bond	K_b (kcal/mol/Å)	r_0 (Å)		
cp-cp	469.0	1.4		
cp-h	367.0	1.08		
cp-s	250.0	1.74		
Harmonic Angle	K_a (kcal/mol/degree)	θ_0 (degree)		
cp-cp-cp	63.0	120.0		
cp-cp-h	35.0	120.0		
cp-cp-s	70.0	120.0		
OPLS dihedral	K_1 (kcal/mol/degree)	K_2 (kcal/mol/degree)	K_3 (kcal/mol/degree)	K_4 (kcal/mol/degree)
cp-cp-cp-cp	0.0	7.25	0.0	0.0
cp-cp-cp-s	0.0	7.25	0.0	0.0
cp-cp-cp-h	0.0	7.25	0.0	0.0
s-cp-cp-h	0.0	7.25	0.0	0.0
h-cp-cp-h	0.0	7.25	0.0	0.0
Harmonic improper	K_i (kcal/mol/degree)	χ_0 (degree)		
cp-(h-)cp-cp	2.5	180.0		

The right column of the table shows the PPP structure with "cp and h" labeled, and sulfur (S) atoms on both ends, labeled PPP.
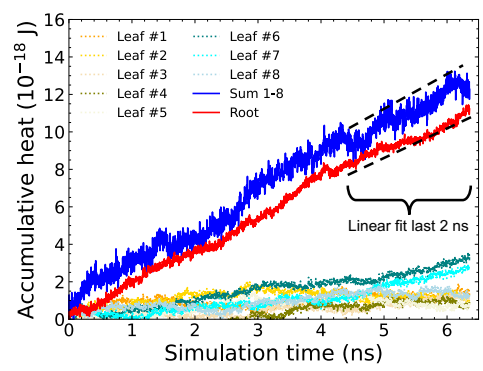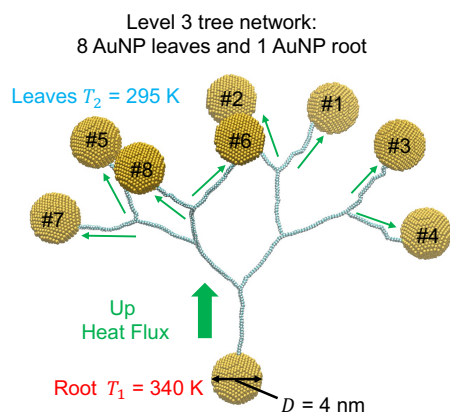

Figure S3: The left scheme shows a representative structure of a level 3 PE tree linked with 8 AuNPs as leaves and 1 AuNP as the root. Each PE branch has 50 carbons in length. The inverse heat flux is induced by setting the 8 AuNP leaves at 295 K and the 1 AuNP root at 340 K, using Langevin thermostats. The right figure shows the accumulated energy added at 8 different AuNP leaves separately in 8 different dotted lines, the accumulative energy subtraction at the 1 AuNP root in red line, and the sum of the 8 leaves in blue line.
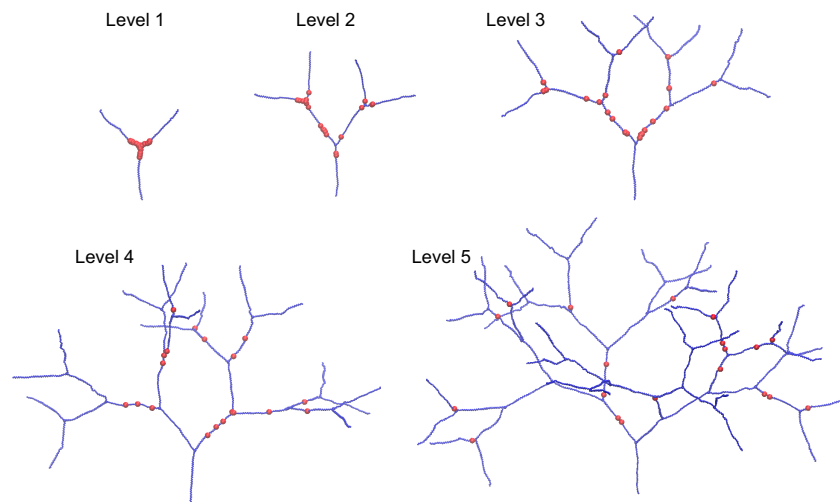
S-3   Additional Results

Figure S4: Positions of the 20 selected carbons on the PE trees.

References

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(3) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236, DOI: `10.1021/ja9621760`.

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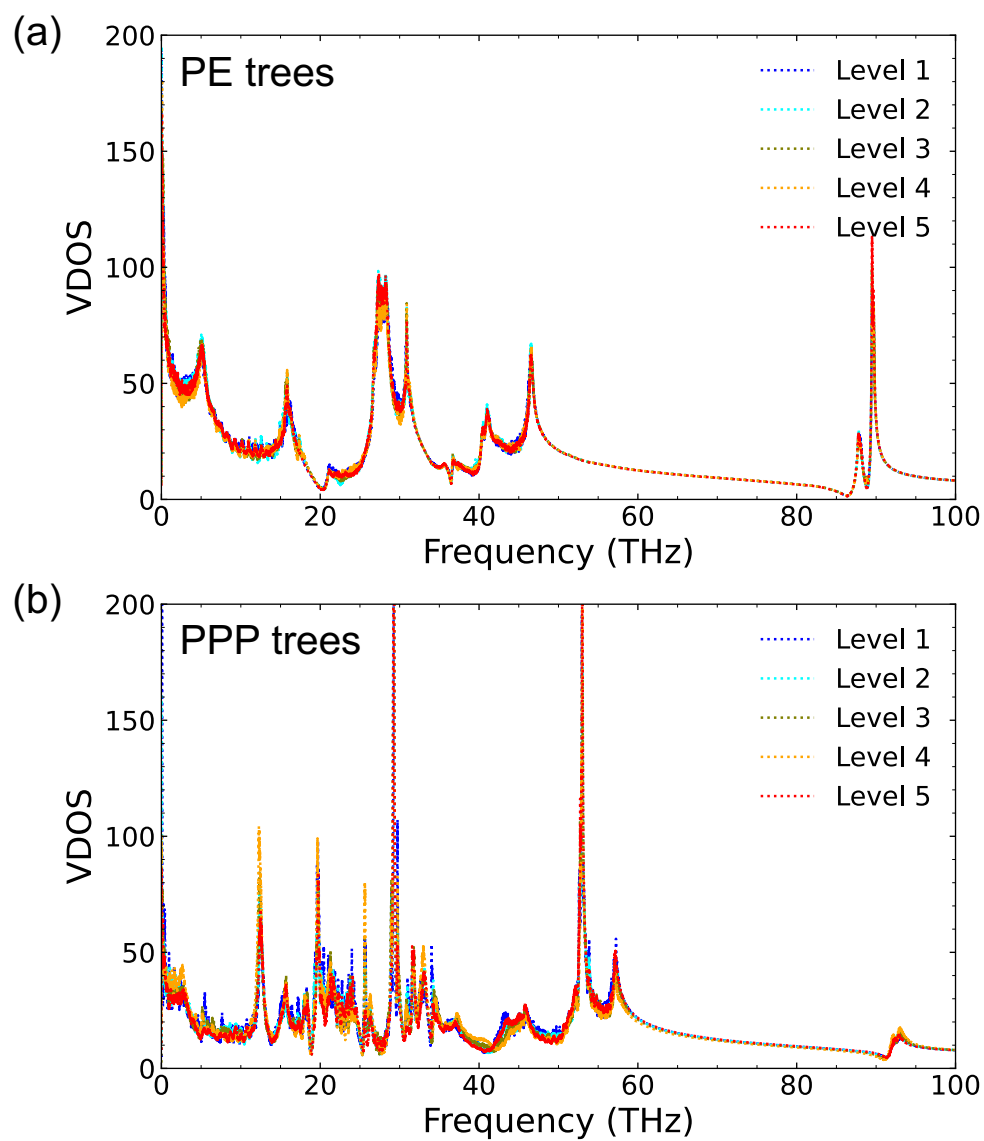
Figure S5: The extended VDOS spectrum comparisons for different trees, where the frequency is set to 100 THz, for both (a) PE C50 and (b) PPP C48 trees. (Arbitrary units in the y-axis.)
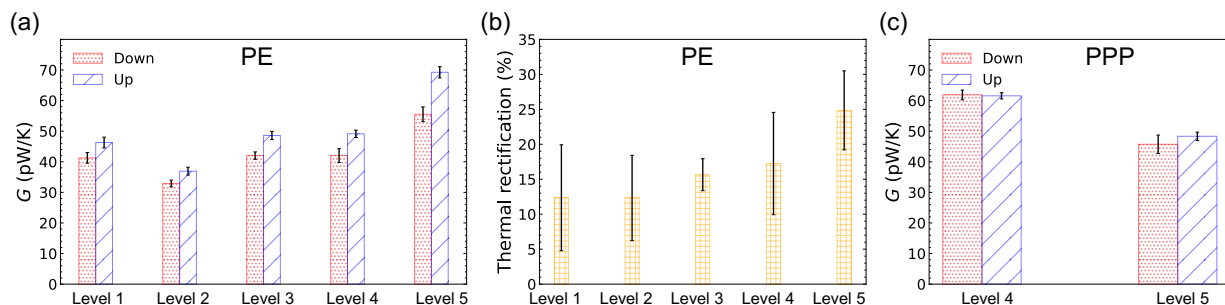
Figure S6: Thermal rectification effect in tree polymers, using temperature setup 100 K and 300 K. (a) up and down heat flux for PE C50 trees at levels 1 to 5. (b) Thermal rectification ratios for PE C50 trees at levels 1 to 5, which is calculated by $(G_{\mathrm{u}p} - G_{\mathrm{d}own})/G_{\mathrm{d}own}$, where ($G_{\mathrm{u}p}$ and $G_{\mathrm{d}own}$ are up and down direction heat flux values, respectively. (c) up and down heat flux for PPP C48 trees at levels 4 and 5 (no rectification).
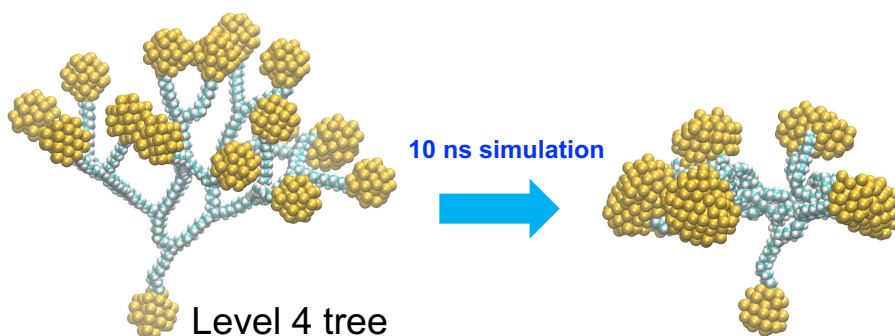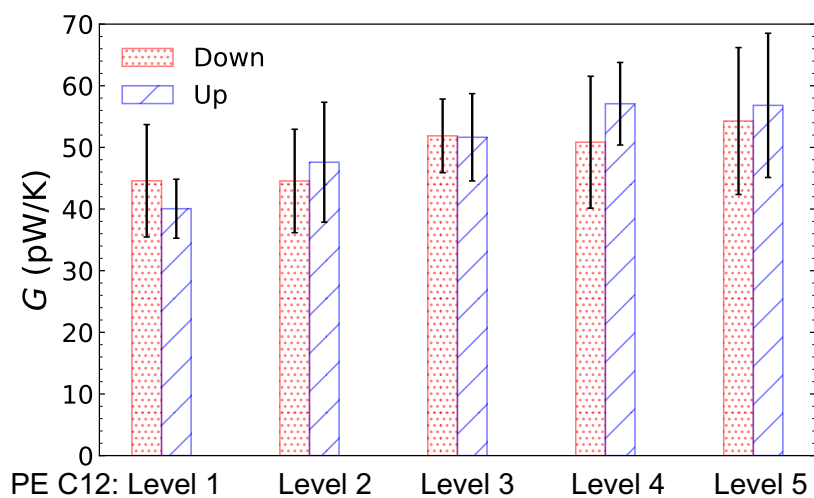

Figure S7: Top figure shows up and down heat conductances in PE C12 trees from level 1 to level 5. Bottom scheme shows the tree structure is unstable, and AuNPs are migrating during the simulation.
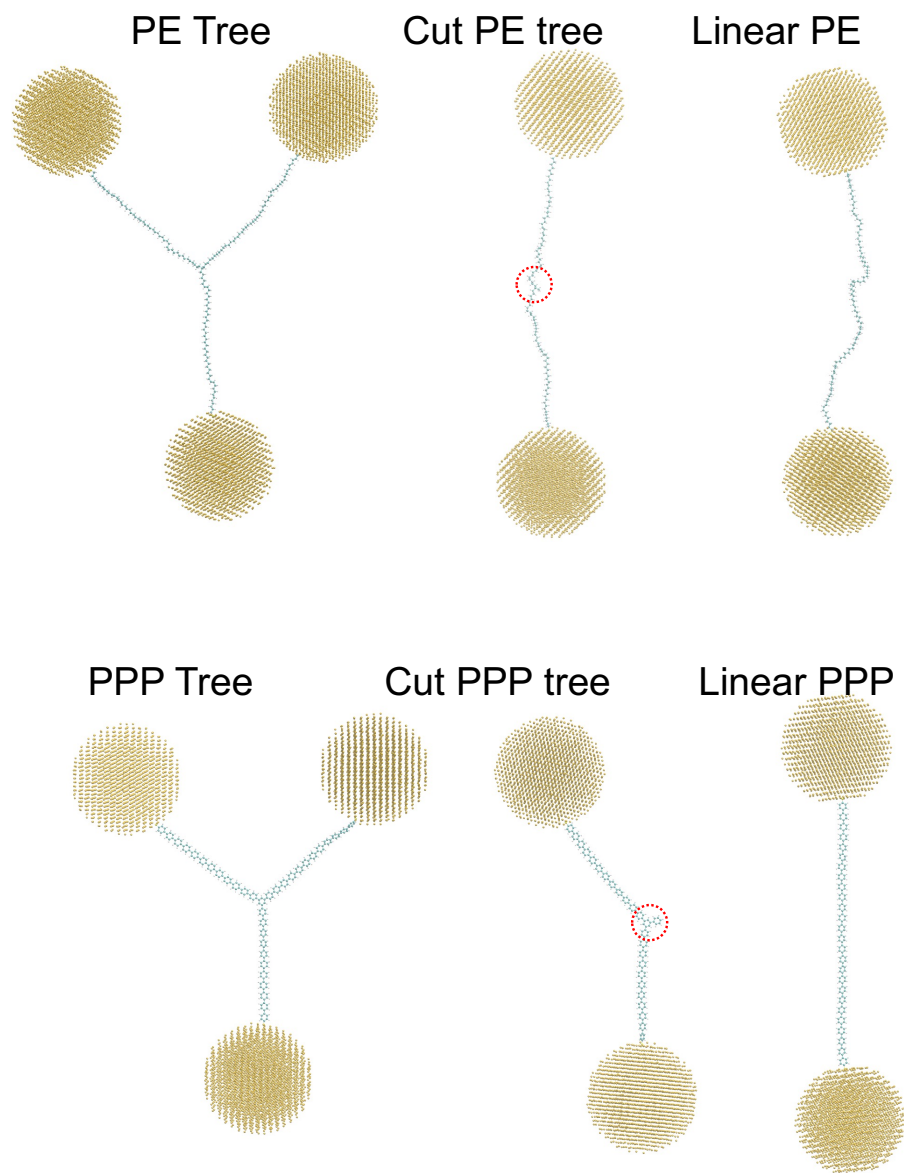
S9

Figure S8: Structures of PE and PPP tree, cut tree and linear chain networks. At the branching position, the PE cut tree has one CH_3 residue group and the PPP cut tree has one benzene ring residue group. The linear polymers has no branching groups.
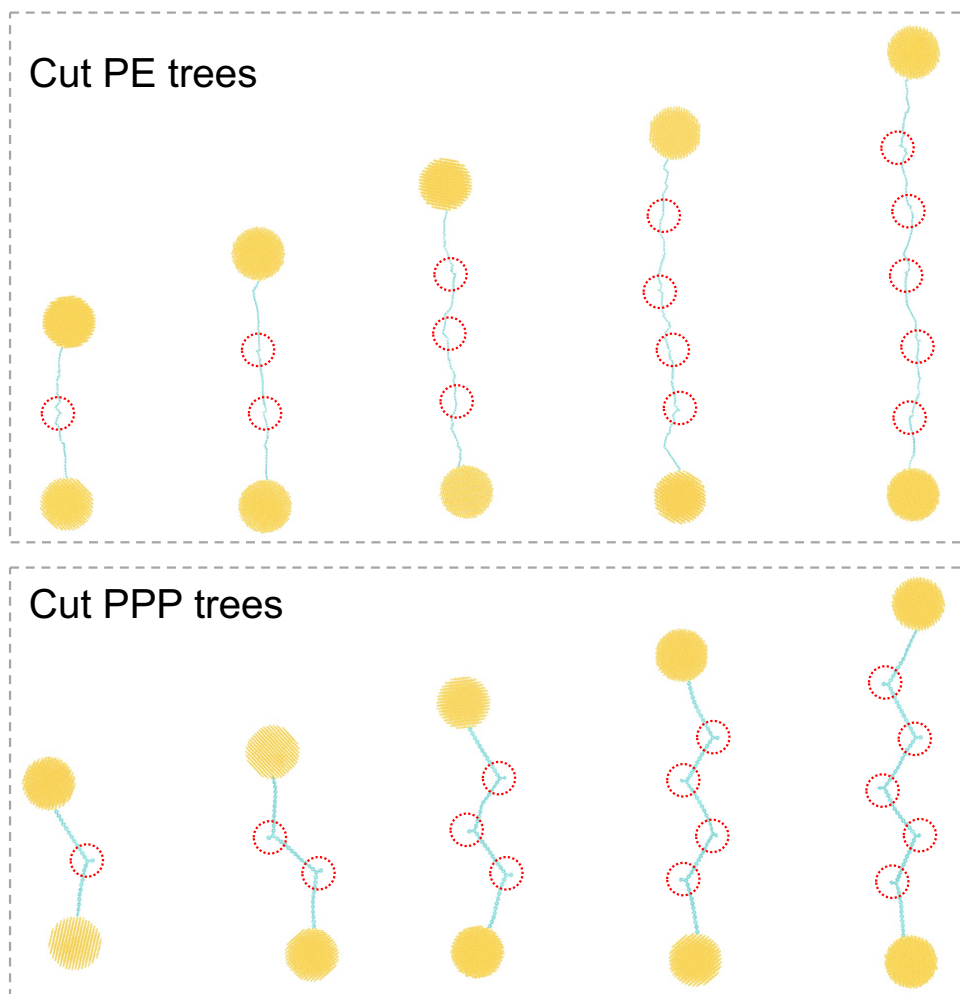
Figure S9: Structures of PE (top row) and PPP (bottom row) cut tree networks.

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