

Supplemental Materials for

Exploring high thermal conductivity polymers via interpretable machine learning with physical descriptors

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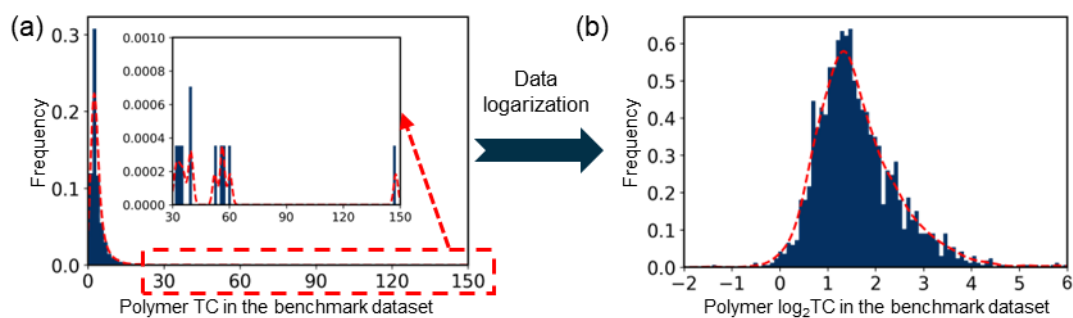
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Supplementary Note 1. Thermal conductivity distribution of the benchmark data

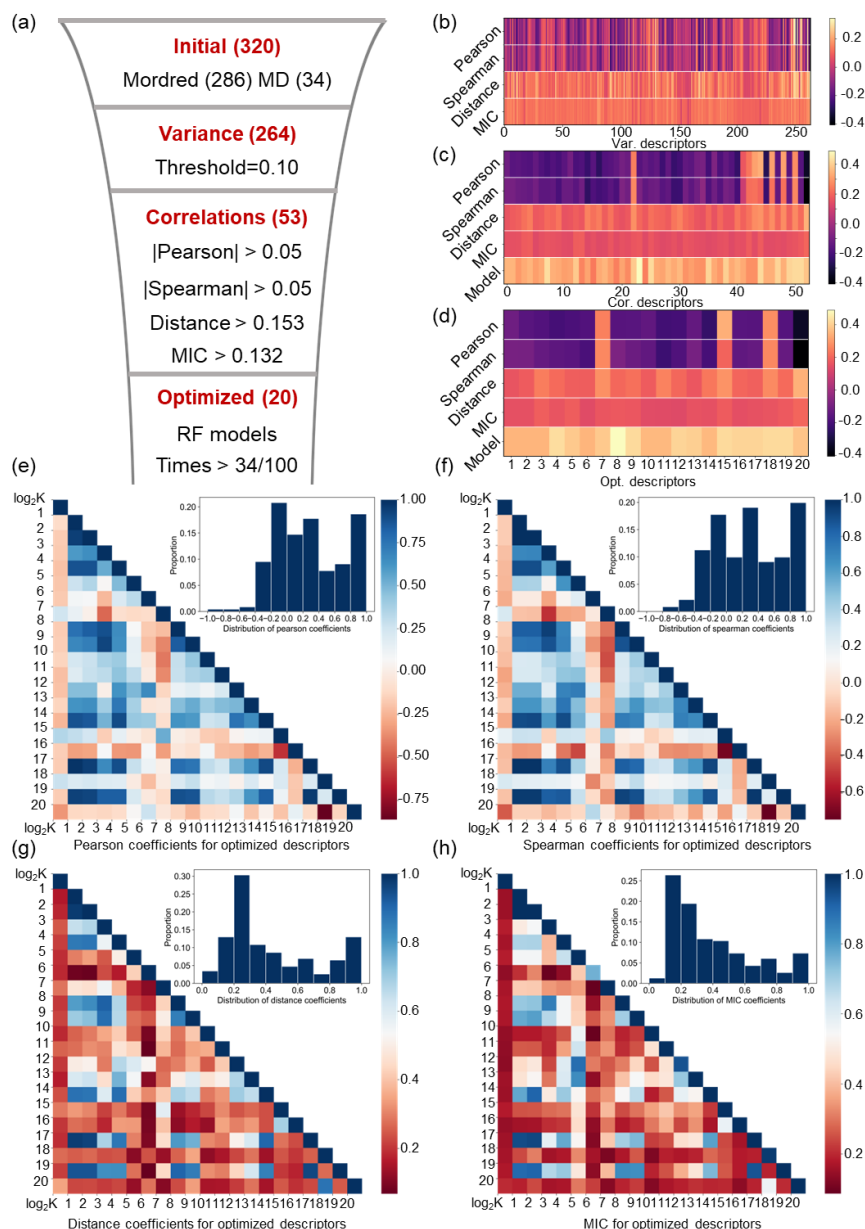
Supplementary Figure 1 illustrates the distributions of raw thermal conductivity (TC) and log-transformed thermal conductivity ($\log_2\text{TC}$) in the benchmark dataset. Given the wide TC distribution of the original data, the log-transformed TC of $\log_2\text{TC}$ is closer to the normal distribution, which contributes to the generalization ability of the machine learning model across the thermal conductivity range .



Supplementary Figure 1: Distribution of (a) TC and (b) $\log_2\text{TC}$ in the benchmark dataset

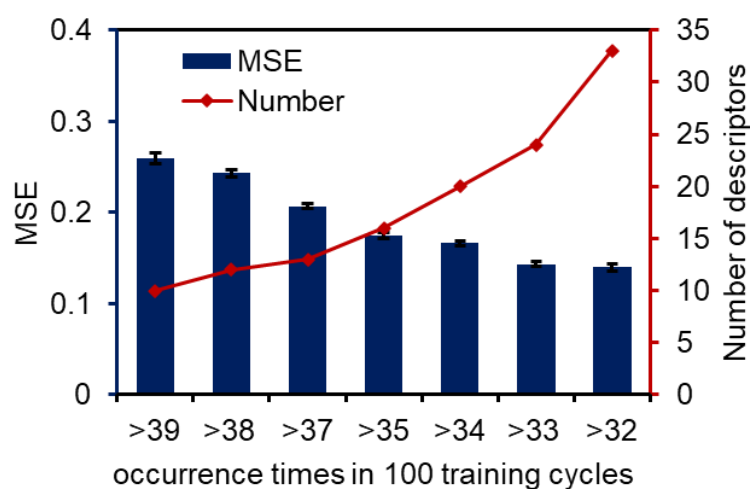
Supplementary Note 2. Downselection of polymer descriptors

Polymer descriptors were downselected in three stages: removing features with low variance (Var.), primary filtering referred to different correlation coefficients (Cor.), and final selection assisted with ML model (Opt.), as shown in Supplementary Figure 2.



Supplementary Figure 2: Downselection and analysis of descriptors. (a) Process of descriptors downselection. (b), (c) and (d) Relationship between descriptors at different stages (Var., Cor. and Opt.) and thermal conductivity based on various metrics or frequency of occurrence of descriptors through 100 Random Forest (RF) model selections. (e), (f), (g) and (h) Pearson, Spearman, Distance and MIC correlation matrices showing correlations among optimized descriptors and TC. The inset shows the distribution statistics of the corresponding correlation coefficient values respectively. The description of the 20 optimized descriptors is available in Supplementary Note S3.

We trained the RF model 100 cycles during the feature selection stage, and randomly disrupted the input descriptors before each running. The optimized descriptors were determined by a statistical threshold, whereby the occurrence of descriptors with a frequency greater than this threshold is retained. Supplementary Figure 3 shows the performance of the RF model with different physical descriptor ensembles determined by various thresholds from 0.39 to 0.32. Overall, as the threshold decreases, the number of reserved descriptors increases and its performance becomes better. Balancing the mean-square error (MSE) of the ML model and the number of descriptors, 20 optimized descriptors were retained with a threshold of 0.34.



Supplementary Figure 3: Performance of ML models trained with different ensembles of threshold-determined physical descriptors

Supplementary Note 3. List of MD-inspired and Mordred-based fingerprints

The MD-inspired descriptors include force field related (FF-related) descriptors and thermal conductivity related (TC-related) descriptors, listed in Supplementary Table 1.

Supplementary Table 1. Descriptions of all MD-inspired descriptors

Name	Description
Epsilon_max	Maximum value of the depth of the energy potential (Lennard–Jones parameter)
Epsilon_min	Minimum value of the depth of the energy potential (Lennard–Jones parameter)
Epsilon_average	Average value of the depth of the energy potential (Lennard–Jones parameter)
Sigma_max	Maximum value of the equilibrium distance (Lennard–Jones parameter)
Sigma_min	Minimum value of the equilibrium distance (Lennard–Jones parameter)
Sigma_average	Average value of the equilibrium distance (Lennard–Jones parameter)
Kb_max	Maximum value of force constants of the bond
Kb_min	Minimum value of force constants of the bond
Kb_average	Average value of force constants of the bond
R0_max	Maximum value of equilibration structural parameters of the bond
R0_min	Minimum value of equilibration structural parameters of the bond
R0_average	Average value of equilibration structural parameters of the bond
Ka_max	Maximum value of force constants of the bond angle
Ka_min	Minimum value of force constants of the bond angle
Ka_average	Average value of force constants of the bond angle
Theta0_max	Maximum value of equilibration structural parameters of the bond angle
Theta0_min	Minimum value of equilibration structural parameters of the bond angle
Theta0_average	Average value of equilibration structural parameters of the bond angle
Kd_max	Maximum value of force constants of the dihedral angle
Kd_min	Minimum value of force constants of the dihedral angle
Kd_average	Average value of force constants of the dihedral angle
Nd_max	Maximum value of multiplicity for the torsional angle parameters
Nd_min	Minimum value of multiplicity for the torsional angle parameters
Nd_average	Average value of multiplicity for the torsional angle parameters
Delta_max	Maximum value of phase angle for the torsional angle parameters
Delta_min	Minimum value of phase angle for the torsional angle parameters
Delta_average	Average value of phase angle for the torsional angle parameters
Ki_max	Maximum value of force constants of the improper angle
Ki_min	Minimum value of force constants of the improper angle
Ki_average	Average value of force constants of the improper angle
MW	Molecular weight of monomer
MW_ratio	The ratio of the molecular weight of the main chain to that of the monomer
Vdw	Van der Waals volume of the monomer
Cross-sectional	Equivalent cross-sectional area of polymer chain

The Mordred-based descriptors were calculated by Mordred software , the 286 Mordred-based descriptors in this work are listed in Supplementary Table 2, and the detailed meaning could be found at <https://mordred-descriptor.github.io/documentation/master/descriptors.html> (accessed Aug 10, 2022).

Supplementary Table 2. Descriptions of 286 Mordred-based descriptors

ABC	nAcid	nBase	SpMax_A	SpMAD_A
LogEE_A	VE1_A	VR1_A	VR3_A	nAromAtom
nAtom	nBridgehead	nHetero	nH	nN
nO	nS	nF	nCl	nBr
ATS0dv	ATS0Z	AATS0dv	AATS0d	AATS2d
AATS0Z	AATS1Z	AATS2Z	AATS3Z	ATSC0dv
ATSC1dv	ATSC2dv	ATSC3dv	ATSC4dv	ATSC5dv
ATSC6dv	ATSC7dv	ATSC8dv	ATSC1d	ATSC2d
ATSC3d	ATSC4d	ATSC5d	ATSC6d	ATSC7d
ATSC8d	ATSC0Z	ATSC1Z	ATSC2Z	ATSC3Z
ATSC4Z	ATSC5Z	ATSC6Z	ATSC7Z	ATSC8Z
AATSC0dv	AATSC1dv	AATSC2dv	AATSC3dv	AATSC0d
AATSC1d	AATSC2d	AATSC3d	AATSC0Z	AATSC1Z
AATSC2Z	AATSC3Z	MATS1dv	MATS2dv	MATS3dv
MATS1d	MATS2d	MATS3d	MATS1Z	MATS2Z
MATS3Z	GATS1dv	GATS2dv	GATS3dv	GATS1d
GATS2d	GATS3d	GATS1Z	GATS2Z	GATS3Z
BCUTdv-1h	BCUTdv-1l	BCUTd-1h	BCUTd-1l	BCUTZ-1h
BCUTZ-1l	BalabanJ	BertzCT	nBondsD	nBondsT
C1SP1	C2SP1	C1SP2	C3SP2	C1SP3
C2SP3	C3SP3	C4SP3	HybRatio	Xch-4d
Xch-5d	Xch-6d	Xch-4dv	Xc-3d	Xc-4d
Xc-5d	Xc-6d	Xpc-4d	AXp-0d	AXp-1d
AXp-2d	AXp-3d	NsCH3	NdCH2	NssCH2
NdsCH	NsssCH	NddC	NdssC	NaaaC
NssssC	NsNH2	NssNH	NaaNH	NdsN
NaaN	NsssN	NaasN	NsOH	NdO
NssO	NaaO	NdS	NssS	NaaS
NddssS	SsssCH	SdssC	SaasC	SaaaC
SsssN	SaasN	AETA_beta	AETA_beta_s	ETA_beta_ns_d
AETA_beta_ns_d	AETA_eta_RL	AETA_eta_BR	ETA_epsilon_3	ETA_dBeta
fragCpx	fMF	nHBAcc	IC0	IC1
IC2	IC3	SIC0	SIC1	SIC2
SIC3	SIC4	BIC5	CIC0	MIC0
MIC1	MIC2	Kier2	Kier3	FilterItLogS
PEOE_VSA1	PEOE_VSA2	PEOE_VSA3	PEOE_VSA4	PEOE_VSA6
PEOE_VSA7	PEOE_VSA8	PEOE_VSA9	PEOE_VSA10	PEOE_VSA11

PEOE_VSA12	PEOE_VSA13	SMR_VSA1	SMR_VSA3	SMR_VSA4
SMR_VSA6	SMR_VSA9	SlogP_VSA1	SlogP_VSA2	SlogP_VSA3
SlogP_VSA4	SlogP_VSA5	SlogP_VSA7	SlogP_VSA8	SlogP_VSA10
SlogP_VSA11	EState_VSA1	EState_VSA2	EState_VSA3	EState_VSA4
EState_VSA5	EState_VSA6	EState_VSA7	EState_VSA8	EState_VSA9
EState_VSA10	VSA_EState1	VSA_EState2	VSA_EState3	VSA_EState4
VSA_EState5	VSA_EState7	VSA_EState8	VSA_EState9	AMID_h
AMID_N	AMID_O	AMID_X	nRing	n5Ring
n6Ring	n7Ring	nHRing	n4HRing	n5HRing
n6HRing	n5aRing	naHRing	n6aHRing	nARing
n5ARing	n6ARing	nAHRing	n5AHRing	n6AHRing
nFRing	n7FRing	n8FRing	n9FRing	n10FRing
n11FRing	n12FRing	nG12FRing	nFHRing	n7FHRing
n8FHRing	n10FHRing	nG12FHRing	nFaRing	n8FaRing
n9FaRing	n10FaRing	nG12FaRing	nFaHRing	nFARing
n10FARing	n12FARing	nG12FARing	nFAHRing	nG12FAHRing
RotRatio	SLogP	TopoPSA(NO)	TopoPSA	GGI4
GGI5	GGI6	GGI7	JGI1	JGI2
JGI3	JGI4	JGI5	JGI6	JGI7
JGI8	JGI9	JGI10	JGT10	TopoShapeIndex
mZagreb1				

Supplementary Note 4. Descriptions of optimized descriptors for polymer thermal conductivity (TC) prediction

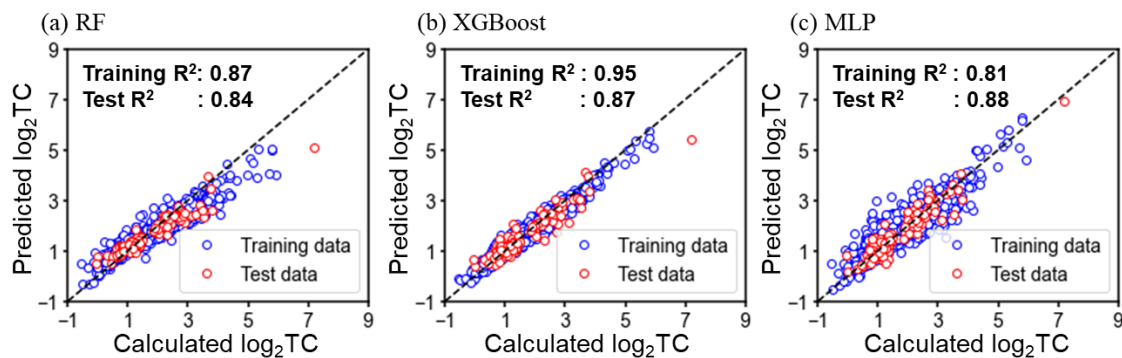
Polymer optimized descriptors were obtained by downselection, listed in Supplementary Table 3.

Supplementary Table 3. Descriptions of all Optimized descriptors

No.	Name	Description	Block
1	ABC	Atom-bond connectivity index	Atom-bond connectivity index descriptor
2	LogEE_A	LogEE of adjacency matrix	Adjacency matrix descriptor
3	Nh	Number of H atoms	Atom count descriptor
4	ATSC0dv	Centered moreau-broto autocorrelation of lag 0 weighted by valence electrons	Centered Autocorrelation of Topological Structure descriptor
5	BCUTdv-1h	First heighest eigenvalue of Burden matrix weighted by valence electrons	BCUT descriptor
6	Xc-4d	4-ordered Chi cluster weighted by sigma electrons	Chi descriptor
7	ETA_dBeta	ETA delta beta	ETA delta beta descriptor
8	CIC0	0-ordered complementary information content	Complementary information content descriptor
9	Kier2	kappa shape index 2	Kappa shape index 2 descriptor
10	SMR_VSA6	MOE MR VSA Descriptor 6 ($2.75 \leq x < 3.05$)	MOE type descriptors using Wildman-Crippen MR and surface area contribution
11	SlogP_VSA3	MOE logP VSA Descriptor 3 ($-0.20 \leq x < 0.00$)	MOE type descriptors using Wildman-Crippen LogP and surface area contribution
12	EState_VSA10	EState VSA Descriptor 10 ($9.17 \leq x < 15.00$)	MOE type descriptors using EState indices and surface area contribution
13	TopoPSA(NO)	Topological polar surface area (use only nitrogen and oxygen)	Topological polar surface area descriptor
14	mZagreb1	modified Zagreb index (version 1)	Zagreb index descriptor
15	Kd_average	Average value of force constants of the dihedral angle	FF-related descriptor
16	Nd_average	Average value of multiplicity for the torsional angle parameters	FF-related descriptor
17	MW	Molecular weight of monomer	TC- related descriptor
18	MW_ratio	The ratio of the molecular weight of the main chain to that of the monomer	TC- related descriptor
19	Vdw	Van der Waals volume of the monomer	TC- related descriptor
20	Cross-sectional	Equivalent cross-sectional area of polymer chain	TC- related descriptor

Supplementary Note 5. Construction of different ML models with optimized descriptors

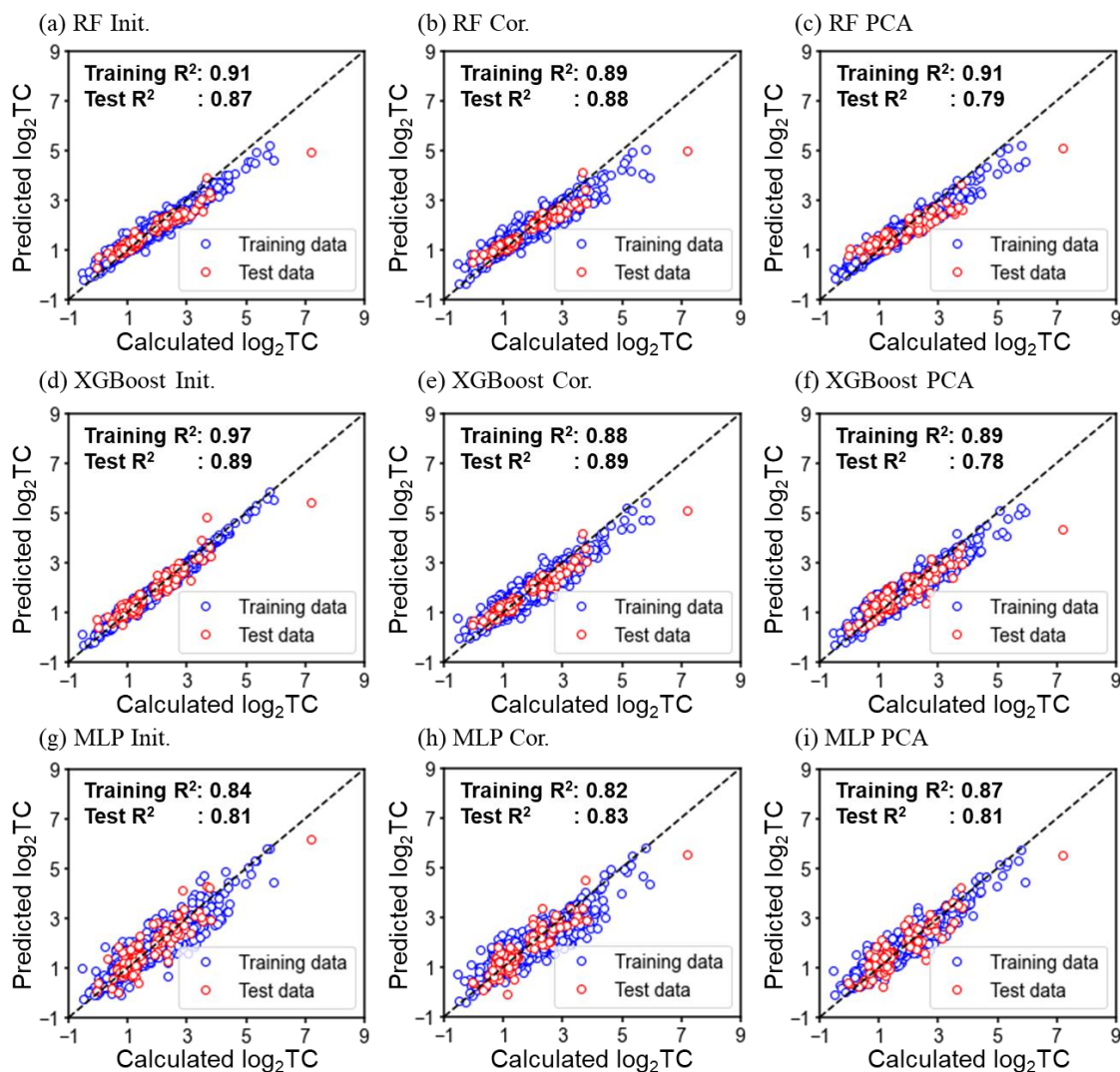
Supplementary Figure 4 shows the RF, XGBoost and MLP models trained with the optimized descriptors. The test set consisted of 100 randomly selected polymer structures from the benchmark dataset.



Supplementary Figure 4: Construction of different ML models with optimized descriptors

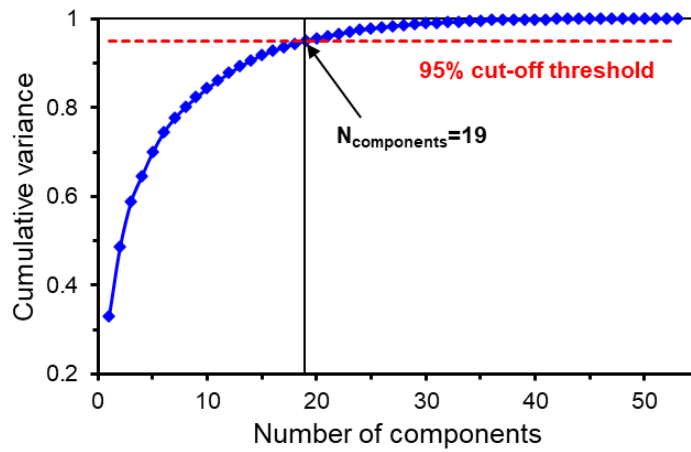
Supplementary Note 6. Accuracy of ML models trained by different sets of descriptors

Supplementary Figure 5 shows the accuracy of ML models at different descriptors down-selection stages. The extra principal component analysis (PCA)¹ technique with 95% variance was used to compare.



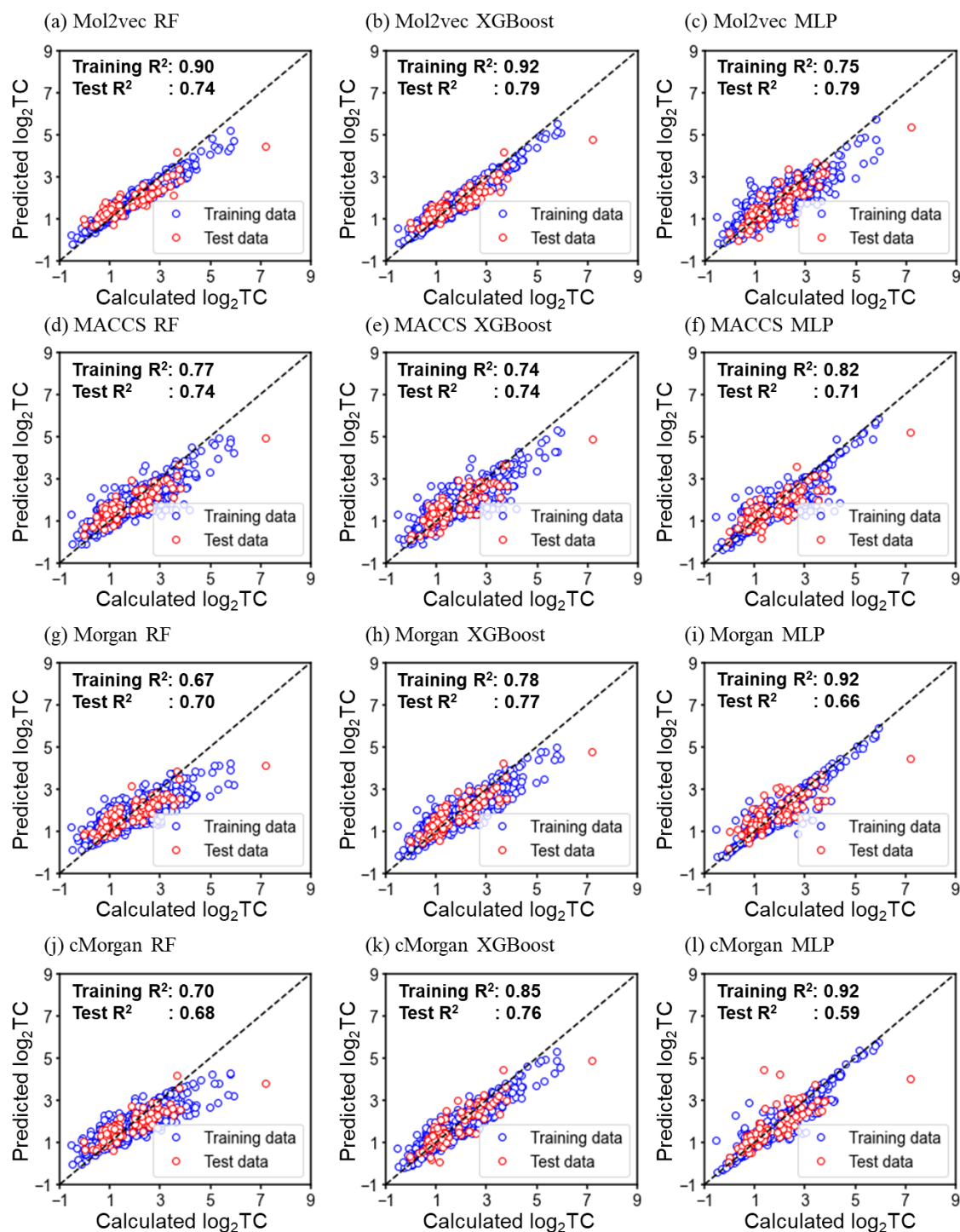
Supplementary Figure 5: Accuracy of ML models at different descriptors downselection stages

Supplementary Figure 6 represents the relationship between the number of principal components and cumulative variance. Here, the PCA with 19 principal components of 95% variance was performed.



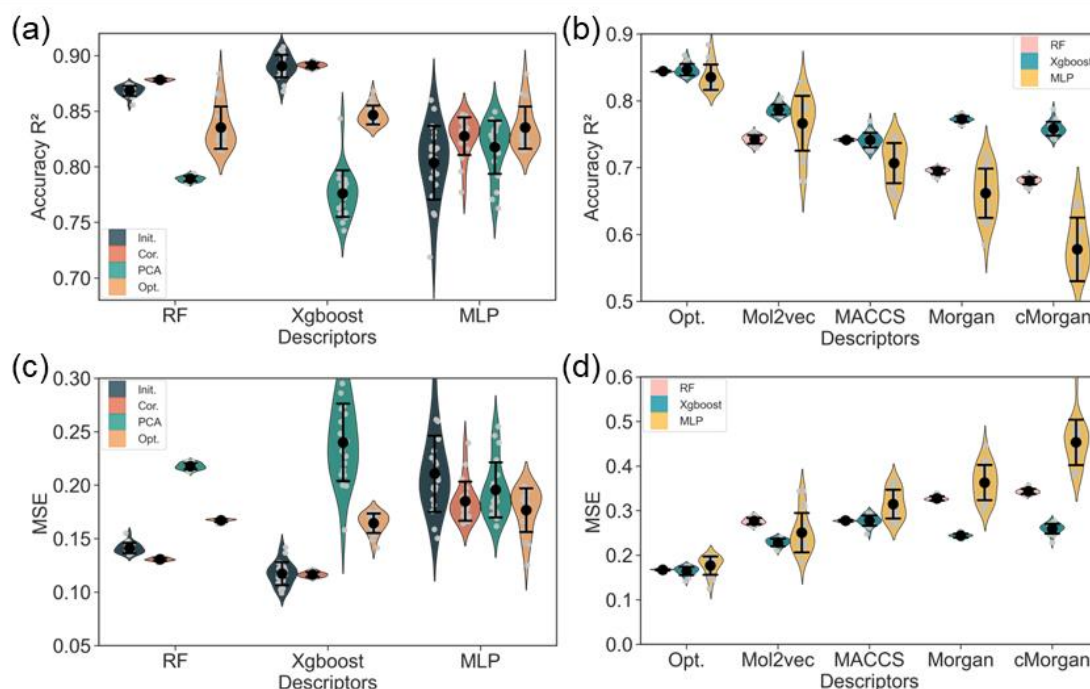
Supplementary Figure 6: Relationship between the number of principal components and cumulative variance

Supplementary Figure 7 shows the training and testing accuracy of ML models using Mol2vec , MACCS , Morgan and Morgan count (cMorgan) graph descriptors.



Supplementary Figure 7: Accuracy of ML models with various graph descriptors

Supplementary Figure 8 displays the accuracy of the trained ML models with physical descriptors at different down-selection stages or with graph descriptors. Combining the results of R^2 and mean-square error (MSE), the performance of machine learning has a slight reduction accompanied by a reduction in the dimensionality of the physical descriptors, but the ML models trained by optimized descriptors are always better than 95% PCA-derived descriptors (Supplementary Figure 8a and 8c). Further, optimized descriptors have significant advantages over the other graph descriptors (Supplementary Figure 8b and 8d).

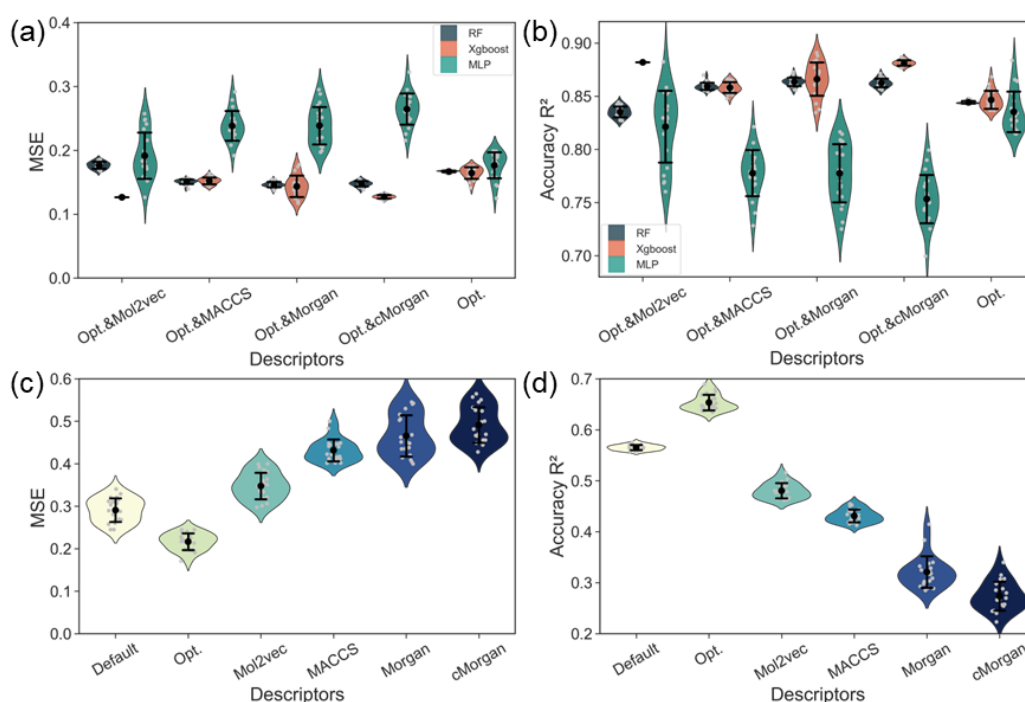


Supplementary Figure 8: Accuracy of the trained ML models with different types of descriptors. (a) and (c) Accuracy R^2 and mean-square error (MSE) of ML models at different down-selection stages. (b) and (d) Accuracy R^2 and MSE of ML models with different polymer representation approaches.

We additionally evaluated ML models with a hybrid descriptor set composed of the optimized descriptors and one of the graph descriptors in Supplementary Figure 9a and 9b. The performance of RF and XGBoost models trained with hybrid descriptors is only a small improvement or even comparable to that of trained with optimized descriptors, which reflects the fact that the optimized descriptors cover relatively complete information about the polymer structures. Meanwhile, due to the redundant information introduced by the hybrid descriptors, the trained MLP models are overfitted and the overall performance is worse than that of the model trained with the optimized descriptors.

Furthermore, we applied the optimized descriptors or graph descriptors to train the directed message passing neural network (DMPNN) models in Chemprop. The benchmark dataset containing

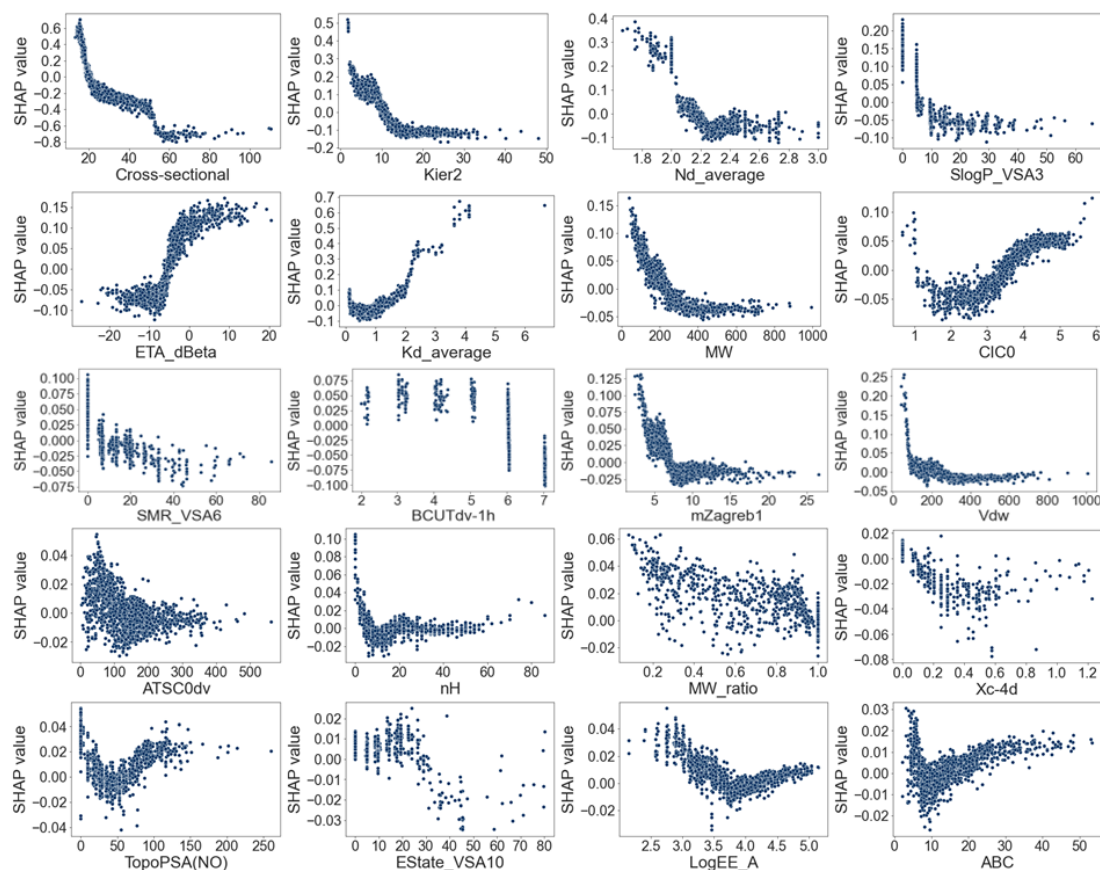
1735 polymer structures was randomly divided by training data, test data and validation data of 8:1:1, and the hyperparameters for the DMPNN models were optimized using the internal implementation of Chemprop, which relies on Bayesian optimization. The Chemprop toolkit has a built-in 2D molecular graph representation for training ML models, which we call the default descriptors. As shown in Supplementary Figure 9c and 9d, despite the limited amount of data in the available benchmark dataset makes it difficult to output a high-performance DMPNN model, the performance of the optimized descriptors is the best compared to other descriptors. This illustrates the potential of optimized descriptors for applications in diverse and complex ML models.



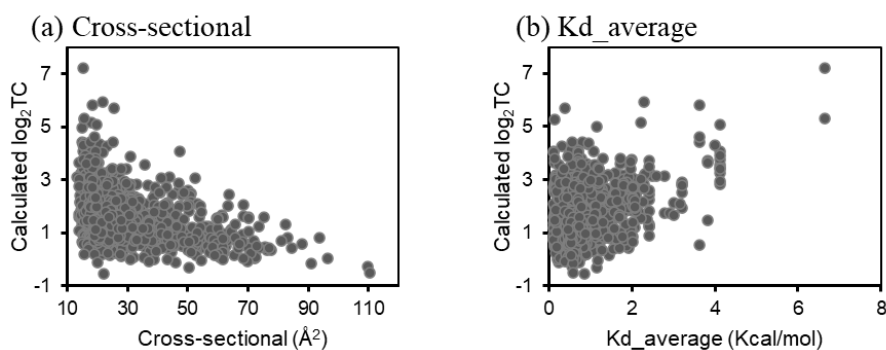
Supplementary Figure 9: Evaluation of ML models with various types of descriptors. (a) MSE and R² of ML models which trained by a hybrid descriptor set composed of the optimized descriptors and one of the graph descriptors. (b) MSE and R² of directed message passing neural network (DMPNN) models trained with different types of descriptors.

Supplementary Note 7. Analysis of the feature importance

Supplementary Figure 10 exhibits the SHAP values for each optimized descriptor of the training data set polymers as a function of the corresponding descriptor value. The subplots are sorted by the average SHAP value. The SHAP values of the top-ranked features corresponding to the training dataset polymers show a monotonic relationship with the feature values overall, while the lower-ranked features have difficulty in capturing this rule. Wherein, the relationships between two important MD-inspired descriptors and TC are shown in Supplementary Figure 11.



Supplementary Figure 10: Distribution of SHAP values for each optimized descriptor



Supplementary Figure 11: Relationships between two important MD-inspired descriptors and TC of 1735 benchmark polymers.

Supplementary Note 8 Discovery of polymers with high thermal conductivity (PHTC) by proposed ML workflow

We performed virtual screening of polymer data in PolyInfo and PIIM based on the trained RF, XGBoost and MLP machine learning models, respectively. In this work, a total of 107 polymer structures with thermal conductivity greater than $20 \text{ W m}^{-1}\text{K}^{-1}$ were identified and validated by molecular dynamics simulations, as listed in Supplementary Table 4, and the relevant monomer structure can be viewed in Supplementary Figure 12 by polymer ID (PID). The TC obtained from RF, XGBoost and MLP model predictions and MD simulations are $\log_2\text{TC}$ in $\text{W m}^{-1}\text{K}^{-1}$. The effective cross-sectional area of the polymer is given in $\text{\AA}^2$. In addition, we calculated the thermal conductivity of 58 of these structures in the amorphous state using nonequilibrium molecular dynamics. The TC of these amorphous polymers (ATC, $\text{W m}^{-1}\text{K}^{-1}$) easily results in a large value, owing to the large chain stiffness.

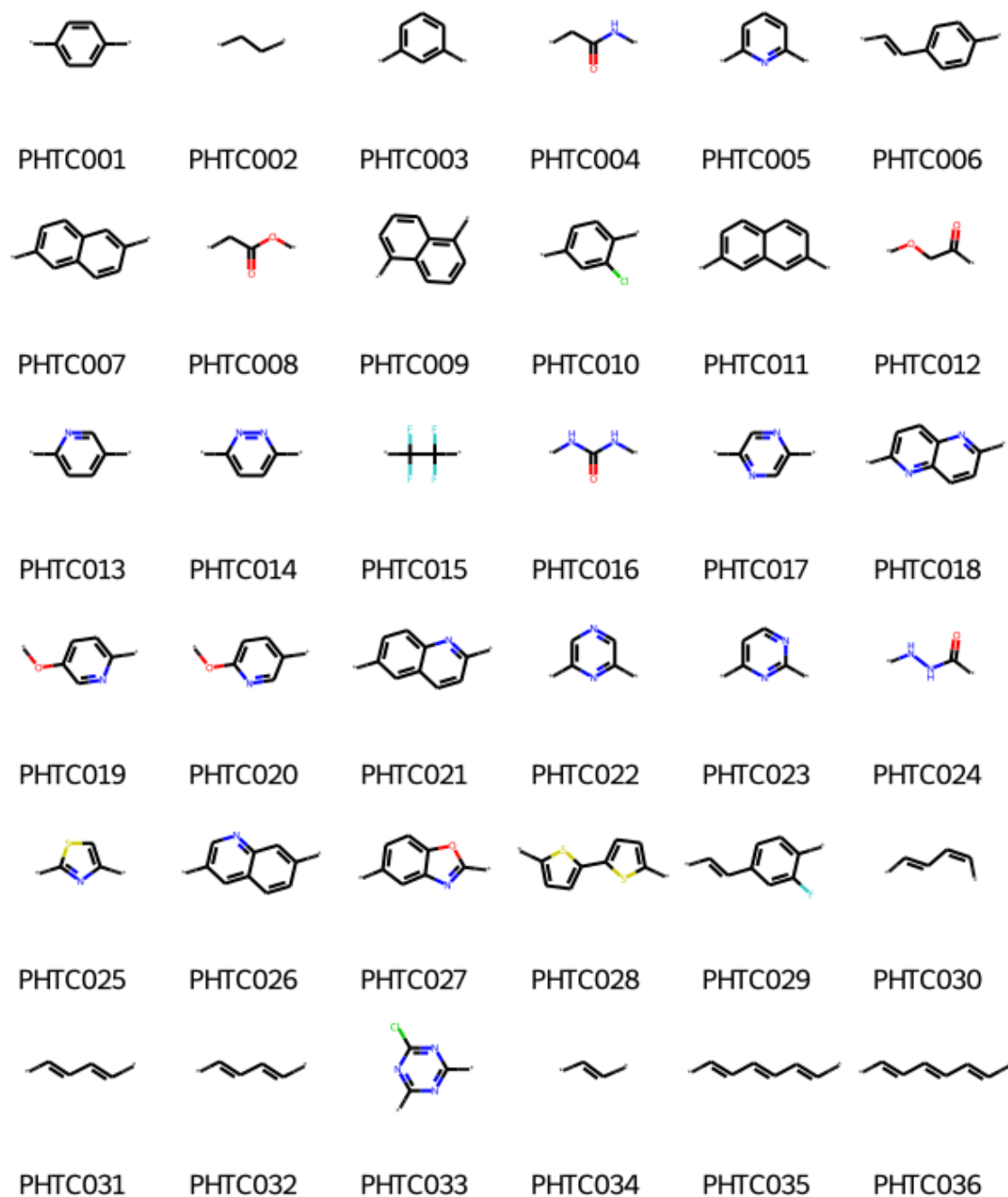
Supplementary Table 4. MD-validated polymers with thermal conductivity greater than $20 \text{ W m}^{-1}\text{K}^{-1}$

PID	SMILES	SA	Cross	RF	XGBoost	MLP	MD	ATC
PHTC001	[*]c1ccc([*])cc1	1.05	18.32	5.00	5.77	6.28	5.81	1.22
PHTC002	[*]CC[*]	1.12	15.69	3.91	4.66	5.30	5.28	0.46
PHTC003	[*]c1cccc([*])c1	1.50	20.74	4.02	5.21	5.86	4.59	0.28
PHTC004	[*]CC(=O)N[*]	2.07	15.13	4.00	4.34	4.05	4.41	0.38
PHTC005	[*]c1cccc([*])n1	2.15	19.72	4.65	4.98	5.65	5.06	0.38
PHTC006	[*]C=Cc1ccc([*])cc1	2.17	16.76	4.29	4.36	5.48	5.13	1.22
PHTC007	[*]c1ccc2cc([*])ccc2c1	2.17	18.28	3.55	4.37	5.01	5.12	1.20
PHTC008	[*]CC(=O)O[*]	2.21	15.09	4.01	4.45	4.36	4.98	0.23
PHTC009	[*]c1cccc2c([*])cccc12	2.22	23.86	3.17	3.81	4.36	4.35	
PHTC010	[*]c1ccc([*])c(Cl)c1	2.23	21.89	3.73	4.06	5.34	4.61	0.74
PHTC011	[*]c1ccc2ccc([*])cc2c1	2.28	19.21	3.81	4.49	5.05	4.62	0.35
PHTC012	[*]OCC([*])=O	2.28	20.86	3.31	4.17	3.70	4.33	0.27
PHTC013	[*]c1ccc([*])nc1	2.33	16.98	4.85	5.08	5.45	4.50	
PHTC014	[*]c1ccc([*])nn1	2.48	15.68	4.87	5.91	4.97	5.05	
PHTC015	[*]C(F)(F)C([*])(F)F	2.51	25.57	4.05	5.27	5.07	5.71	0.20
PHTC016	[*]NC(=O)N[*]	2.57	14.34	4.53	4.91	3.76	5.47	0.53
PHTC017	[*]c1cnc([*])cn1	2.62	15.75	5.11	6.08	5.85	6.62	
PHTC018	[*]c1ccc2nc([*])ccc2n1	2.64	16.79	3.96	4.00	5.62	5.93	
PHTC019	[*]Oc1ccc([*])nc1	2.65	14.79	4.16	4.46	4.17	4.43	
PHTC020	[*]Oc1ccc([*])cn1	2.65	14.74	4.16	4.52	4.17	4.76	0.23
PHTC021	[*]c1ccc2nc([*])ccc2c1	2.78	17.62	3.96	4.19	5.59	4.38	
PHTC022	[*]c1cncc([*])n1	2.80	18.06	5.08	5.84	5.53	4.34	
PHTC023	[*]c1ccnc([*])n1	2.82	18.06	5.08	5.82	5.52	5.00	0.25

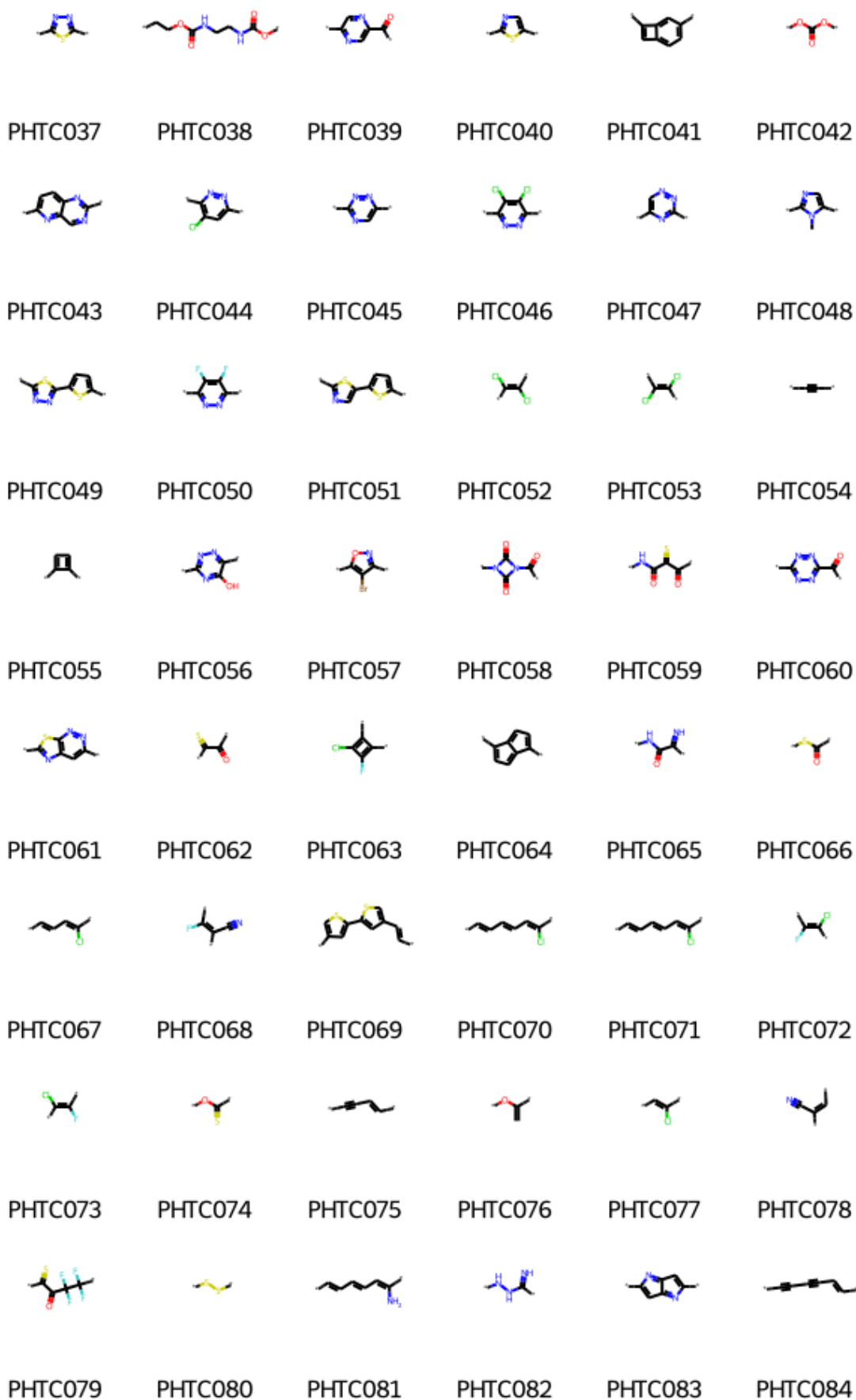
PID	SMILES	SA	Cross	RF	XGBoost	MLP	MD	ATC
PHTC024	[*]NNC([*])=O	2.86	14.28	4.19	4.56	3.32	4.83	0.46
PHTC025	[*]c1csc([*])n1	2.87	15.82	5.11	6.20	5.76	5.75	0.27
PHTC026	[*]c1cnc2cc([*])ccc2c1	2.91	17.29	3.99	4.24	5.63	4.82	0.72
PHTC027	[*]c1ccc2oc([*])nc2c1	2.97	15.17	3.91	3.55	3.59	4.34	0.44
PHTC028	[*]c1ccc(-c2ccc([*])s2)s1	3.00	15.98	4.06	4.26	4.22	5.64	0.42
PHTC029	[*]C=Cc1ccc([*])c(F)c1	3.04	17.60	3.89	4.34	4.80	4.41	
PHTC030	[*]C=C/C=C\[*]	3.07	15.68	5.06	5.35	5.79	5.33	
PHTC031	[*]C=C/C=C/[*]	3.07	14.06	5.05	5.10	5.97	7.55	1.13
PHTC032	[*]/C=C/C=C/[*]	3.07	14.26	5.05	5.10	5.95	6.91	0.89
PHTC033	[*]c1nc([*])nc(Cl)n1	3.09	13.85	4.53	5.64	5.63	6.51	0.15
PHTC034	[*]C=C[*]	3.12	15.35	5.08	5.44	6.92	7.21	0.83
PHTC035	[*]C=C/C=C/C=C/[*]	3.20	13.73	4.65	4.34	4.86	7.42	1.02
PHTC036	[*]/C=C/C=C/C=C/[*]	3.20	13.60	4.65	4.34	4.87	7.31	1.11
PHTC037	[*]c1nnc([*])s1	3.27	8.76	5.09	6.04	6.14	5.75	0.59
PHTC038	[*]CCOC(=O)NCCNC(=O)O[*]	3.33	15.55	3.20	4.10	3.65	4.38	
PHTC039	[*]C(=O)c1cnc([*])cn1	3.34	15.80	4.11	4.34	4.35	4.54	
PHTC040	[*]c1cnc([*])s1	3.35	15.34	4.86	5.77	5.40	4.95	
PHTC041	[*]C1=Cc2ccc([*])cc21	3.37	18.78	4.37	4.64	5.50	5.11	
PHTC042	[*]OC(=O)O[*]	3.38	11.93	3.97	4.05	3.96	5.61	0.21
PHTC043	[*]c1ccc2nc([*])ncc2n1	3.39	15.82	3.98	3.95	5.54	5.83	0.82
PHTC044	[*]c1cc(Cl)c([*])nn1	3.45	19.29	4.19	5.08	4.97	4.52	
PHTC045	[*]c1cnc([*])nn1	3.49	14.33	5.06	5.97	5.57	6.46	0.90
PHTC046	[*]c1nnc([*])c(Cl)c1Cl	3.51	15.39	4.11	5.12	5.41	4.60	
PHTC047	[*]c1cnnc([*])n1	3.53	16.38	5.04	5.92	5.33	5.60	0.17
PHTC048	[*]c1cnc([*])n1C	3.55	19.00	4.25	4.46	5.63	4.49	
PHTC049	[*]c1ccc(-c2nnc([*])s2)s1	3.63	14.53	4.15	4.39	4.83	5.39	0.33
PHTC050	[*]c1nnc([*])c(F)c1F	3.64	12.41	4.40	5.32	4.51	4.75	
PHTC051	[*]c1ccc(-c2cnc([*])s2)s1	3.76	15.25	4.17	4.44	4.85	5.51	0.59
PHTC052	[*]C(Cl)=C([*])Cl	3.86	20.41	4.17	4.38	4.81	5.13	0.29
PHTC053	[*]/C(Cl)=C(/[*)Cl	3.86	20.56	4.13	4.42	4.80	5.08	0.25
PHTC054	[*]C#C[*]	3.87	5.85	4.23	4.58	5.15	9.63	
PHTC055	[*]C1=CC=C1[*]	3.90	22.30	4.36	5.72	5.65	4.62	
PHTC056	[*]c1nnc([*])c(O)n1	3.90	16.45	4.50	5.18	4.20	4.96	0.76
PHTC057	[*]c1noc([*])c1Br	3.90	11.67	4.61	5.55	4.77	4.97	
PHTC058	[*]C(=O)N1C(=O)N([*])C1=O	4.04	16.85	3.66	4.36	5.49	5.37	0.36
PHTC059	[*]NC(=O)C(=S)C([*])=O	4.08	21.85	4.01	5.07	4.60	5.91	0.18
PHTC060	[*]C(=O)c1nnc([*])nn1	4.09	11.89	4.36	5.35	4.15	5.95	0.24
PHTC061	[*]c1cc2nc([*])sc2nn1	4.09	14.51	4.38	4.81	5.11	4.35	
PHTC062	[*]C(=O)C([*])=S	4.20	16.81	3.78	4.92	4.41	5.03	
PHTC063	[*]C1=C(F)C(Cl)=C1[*]	4.28	17.13	4.69	4.59	5.00	5.84	

PID	SMILES	SA	Cross	RF	XGBoost	MLP	MD	ATC
PHTC064	[*]C1=CC=C2C([*])=CC=C12	4.32	22.02	3.94	3.73	4.63	6.16	0.67
PHTC065	[*]NC(=O)C([*])=N	4.32	18.67	3.86	5.17	3.12	4.37	
PHTC066	[*]SC([*])=O	4.34	8.22	4.70	5.29	4.52	6.73	0.25
PHTC067	[*]/C=C/C=C([*])Cl	4.36	17.41	4.65	3.72	4.63	5.90	
PHTC068	[*]/C(F)=C(/[*])C#N	4.36	20.54	3.77	5.11	3.47	6.02	0.38
PHTC069	[*]C=Cc1csc(-c2cc([*])cs2)c1	4.45	15.88	3.69	3.61	3.08	4.33	
PHTC070	[*]/C=C/C=C/C=C([*])Cl	4.45	15.96	4.28	4.78	3.99	5.66	
PHTC071	[*]/C=C/C=C/C=C(/[*])Cl	4.45	15.96	4.28	4.78	3.99	5.66	
PHTC072	[*]/C(F)=C(/[*])Cl	4.46	18.39	4.44	5.10	4.90	6.18	0.30
PHTC073	[*]C(F)=C([*])Cl	4.46	17.50	4.69	5.25	4.94	5.83	0.36
PHTC074	[*]OC([*])=S	4.53	14.49	4.63	5.07	3.76	5.20	
PHTC075	[*]C#CC=C[*]	4.54	18.03	4.51	5.02	5.18	5.16	1.07
PHTC076	[*]OC([*])=C	4.54	19.19	4.07	4.36	3.57	4.55	
PHTC077	[*]/C=C(/[*])Cl	4.55	21.62	4.28	4.80	5.14	6.03	0.35
PHTC078	[*]C=C([*])C#N	4.58	24.93	3.53	4.00	2.70	4.88	
PHTC079	[*]C(=S)C(=O)C(F)(F)C([*])(F)F	4.59	25.30	3.19	4.28	3.92	4.41	
PHTC080	[*]SS[*]	4.66	13.04	3.77	3.91	0.95	4.93	
PHTC081	[*]/C=C/C=C/C=C([*])N	4.66	15.44	4.20	4.41	4.69	5.53	0.57
PHTC082	[*]NNC([*])=N	4.67	15.08	4.45	4.61	4.41	4.51	
PHTC083	[*]C1=CC2=NC([*])=CC2=N1	4.75	17.77	4.55	4.07	4.51	6.10	0.59
PHTC084	[*]C#CC#CC=C[*]	4.78	12.75	4.11	3.79	4.61	5.99	
PHTC085	[*]C=C([*])F	4.82	17.93	4.71	5.35	4.81	6.64	0.52
PHTC086	[*]/C=C/N[*]	4.83	15.68	5.02	5.28	6.52	5.44	0.53
PHTC087	[*]C#C/C(C#N)=C(/[*])C#N	4.88	15.14	3.46	5.00	4.71	5.37	0.49
PHTC088	[*]/N=C/C(=S)N[*]	4.88	18.77	4.37	4.29	5.00	5.06	0.24
PHTC089	[*]/N=N/C([*])=O	4.90	8.82	4.55	5.76	6.04	7.35	
PHTC090	[*]/C=C/O[*]	4.92	15.71	3.94	3.83	3.43	4.60	
PHTC091	[*]=CC=NN=[*]	4.98	5.95	4.69	4.92	7.53	4.71	
PHTC092	[*]NN[*]	5.00	11.88	4.79	5.37	6.33	4.60	
PHTC093	[*]/N=N/[*]	5.05	5.21	4.83	5.95	6.81	10.38	
PHTC094	[*]N=N[*]	5.05	5.93	4.83	5.95	6.76	10.01	
PHTC095	[*]/N=C(/[*])Cl	5.08	9.62	5.06	5.71	6.50	6.98	0.12
PHTC096	[*]C#C/C(C#N)=C(/[*])Cl	5.14	14.06	3.63	5.06	4.58	5.79	0.58
PHTC097	[*]/C=N/C=C(/[*])C	5.14	17.30	4.02	3.64	4.36	4.72	
PHTC098	[*]/C=C/C=CS[*]	5.17	14.14	4.14	3.28	4.13	4.36	
PHTC099	[*]C1=CC2=CC([*])=NC2=N1	5.28	17.50	4.62	4.10	4.55	5.79	
PHTC100	[*]/C=C/N=C([*])Cl	5.38	19.65	4.16	4.37	4.61	5.60	0.25
PHTC101	[*]/C=C/S[*]	5.44	14.40	4.57	4.20	5.74	4.35	
PHTC102	[*]/C=N/[*]	5.53	14.02	5.10	6.07	6.07	6.82	0.31
PHTC103	[*]/N=N/N=C(/[*])C#N	5.66	11.24	3.69	5.07	4.33	6.68	0.19

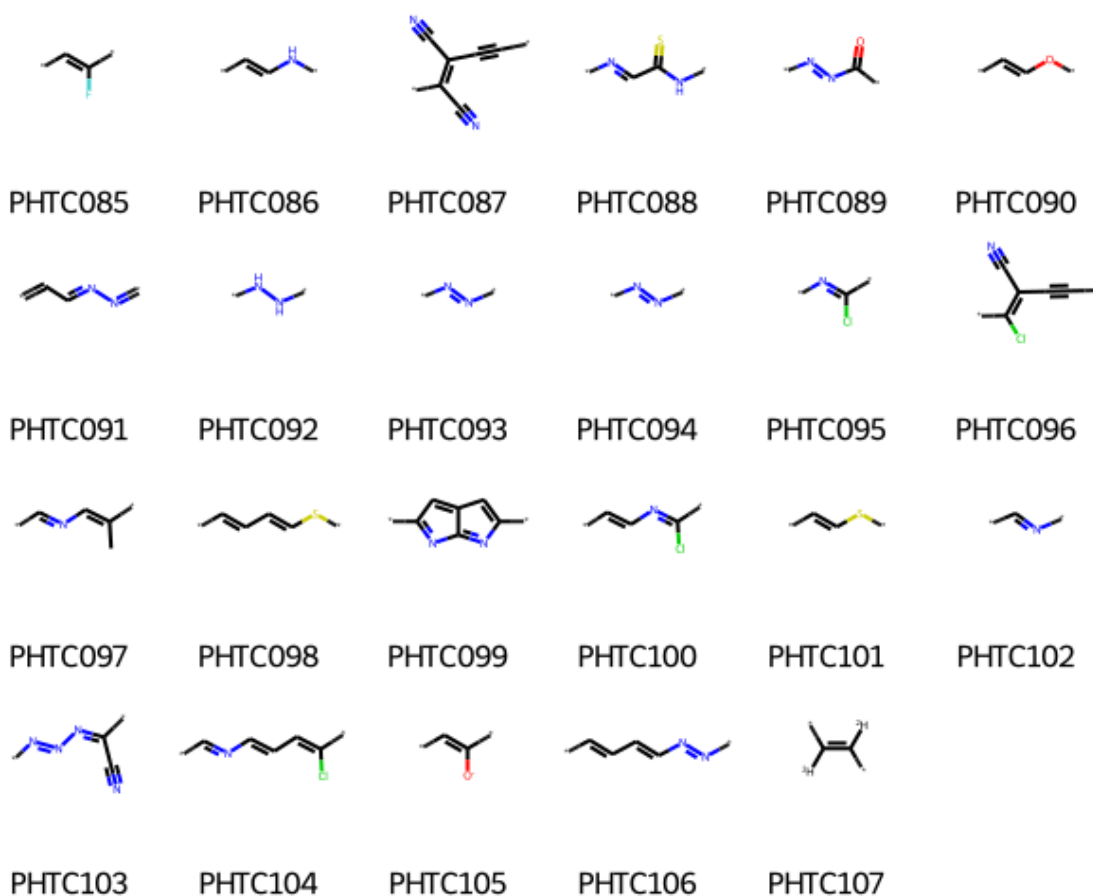
PID	SMILES	SA	Cross	RF	XGBoost	MLP	MD	ATC
PHTC104	<chem>[*]/C=N/C=C/C=C(/[*])Cl</chem>	5.70	15.50	4.33	4.46	4.07	5.70	
PHTC105	<chem>[*]/C=C(/[*])[O-]</chem>	5.73	18.54	4.07	4.66	2.87	6.10	
PHTC106	<chem>[*]/C=C/C=C/N=N/[*]</chem>	5.76	12.71	4.74	4.11	7.01	6.59	0.85
PHTC107	<chem>[*]C([2H])=C([*])[2H]</chem>	7.27	11.30	4.32	4.33	1.07	7.48	



Supplementary Figure 12: Continued



Supplementary Figure 12: Continued



Supplementary Figure 12: Polymer monomer structures with TC greater than $20 \text{ W m}^{-1}\text{K}^{-1}$ verified by MD simulations. Polymer properties can be found in Supplementary Table 4 using the PID.

Supplementary Note 9. Symbolic regression for characterizing the TC of promising polymers

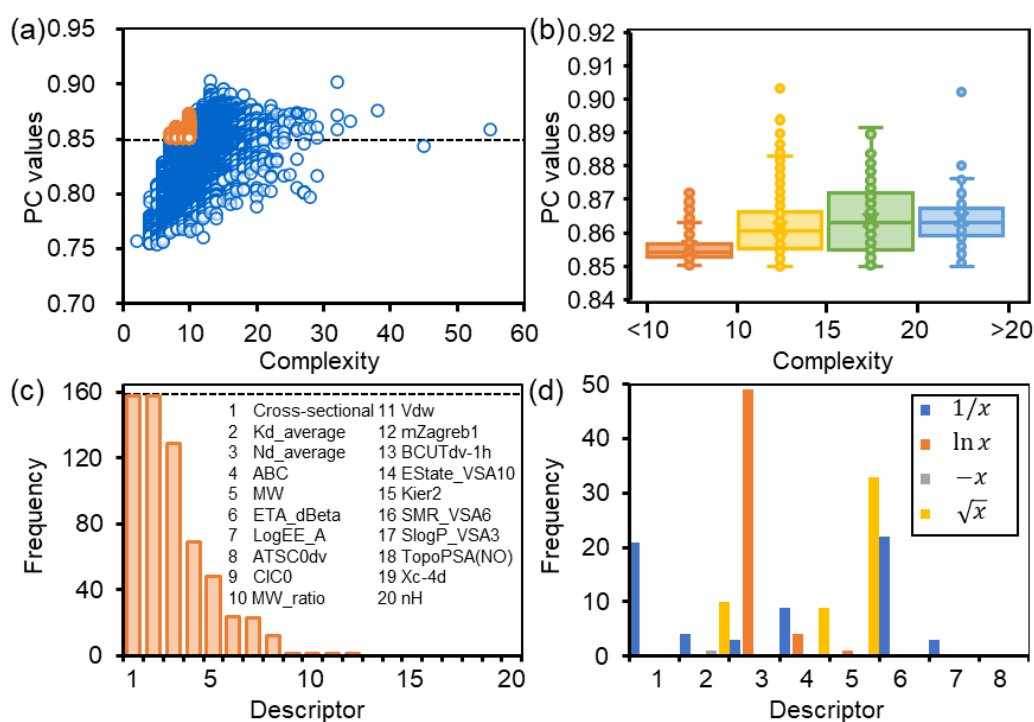
The 107 promising polymer structures ($TC > 20 \text{ W m}^{-1}\text{K}^{-1}$) with optimized descriptors were utilized for symbolic regression (SR), where 20% structures were randomly selected for testing set. The mathematical formulae were acquired and selected using an efficient stepwise strategy with SR based on a genetic programming (GPSR) as implemented in the `gplearn` code. At first, Pearson coefficients were used as evaluation metrics of training fitness to filter optimized descriptors and generate sub-descriptors, and the grid search strategy with the hyperparameters listed in Supplementary Table 5 was applied in GPSR. The hyperparametric combinations corresponding to the 22380 formulas are characterized by complexity and training fitness of Pearson coefficients (PC) as shown in Supplementary Figure 13a. The complexity is equivalent to the formula length in `gplearn`. Among these formulas, 4365 of them with PC values not less than 0.85 are statistically by complexity in Supplementary Figure 13b. Generally, the formulas with large complexity have a higher training fitness. But the formulas are also usually quite long and do not facilitate the calculation and analysis. Only formulas with large fitness and low complexity are appropriate, so we selected 158 formulas with the PC value not less than 0.85 and complexity within 10 for subsequent analysis. By counting the frequency of occurrence of the 20 optimized descriptors in 158 formulas, the first 8 descriptors were finally retained, as presented in Supplementary Figure 13c. It is worth emphasizing that the MD-inspired descriptors of cross-sectional area (cross-sectional) and dihedral force constants ($Kd_average$) appeared in each of the formulas. And, we additionally estimated the frequency of occurrence of sub-descriptors created by taking the inverse ($-x$), logarithm ($\ln x$), and so on, as shown in Supplementary Figure 13d. As a result, a new ensemble containing 22 descriptors which have a strong association with TC is listed in Supplementary Table 6 for retraining in `gplearn`.

Further, we reset the grid search hyperparameters listed in Supplementary Table 7, and utilized the accuracy R^2 as the evaluation metric. The 19580 formulas with fitting accuracy greater than 0.6 versus complexity are visualized in Supplementary Figure 14a. The effective accuracy is the average of the training and testing accuracy. Despite the fact that the effective accuracy of some formulas exceeds 0.8, and their complexity is greater than 50. The Pareto front of accuracy R^2 vs. complexity (no more than 30) of 9073 mathematical formulas shown via density plot in Supplementary Figure 14b, and the points of c, d, e and f were identified by Latin hypercube sampling approach². The formulas for the four points are listed in Supplementary Table 8, and their fitting results compared with MD calculated $\log_2 TC$ are

displayed in Supplementary Figure c-f. The definitions of the variables x_0 to x_{21} can be found in Supplementary Table 6.

Supplementary Table 5. Setup of hyperparameters in gplearn for filter and generate new sub-descriptors

Parameter	Value	Combination
Generations	300	1
Population size in every generation	1000,2000	2
Probability of crossover (pc)	[0.30,0.90], step=0.05	746
Subtree mutation (ps)	[(1-pc)/3,(1-pc)/2] (step= 0.01)	
Hoist mutation (ph)	[(1-pc)/3,(1-pc)/2] (step = 0.01)	
Point mutation (pp)	1-pc-ps-ph	
Function set	$\{+, -, \times, \div, \sqrt{x}, \ln x, x , -x, 1/x\}$	1
Parsimony coefficient	auto	1
Metric	Pearson coefficient	1
Stopping criteria	0.900	1
Random_state	0, 1, 2, 3, 4	5
Init_depth	[2, 6], [4, 8], [6, 10]	3



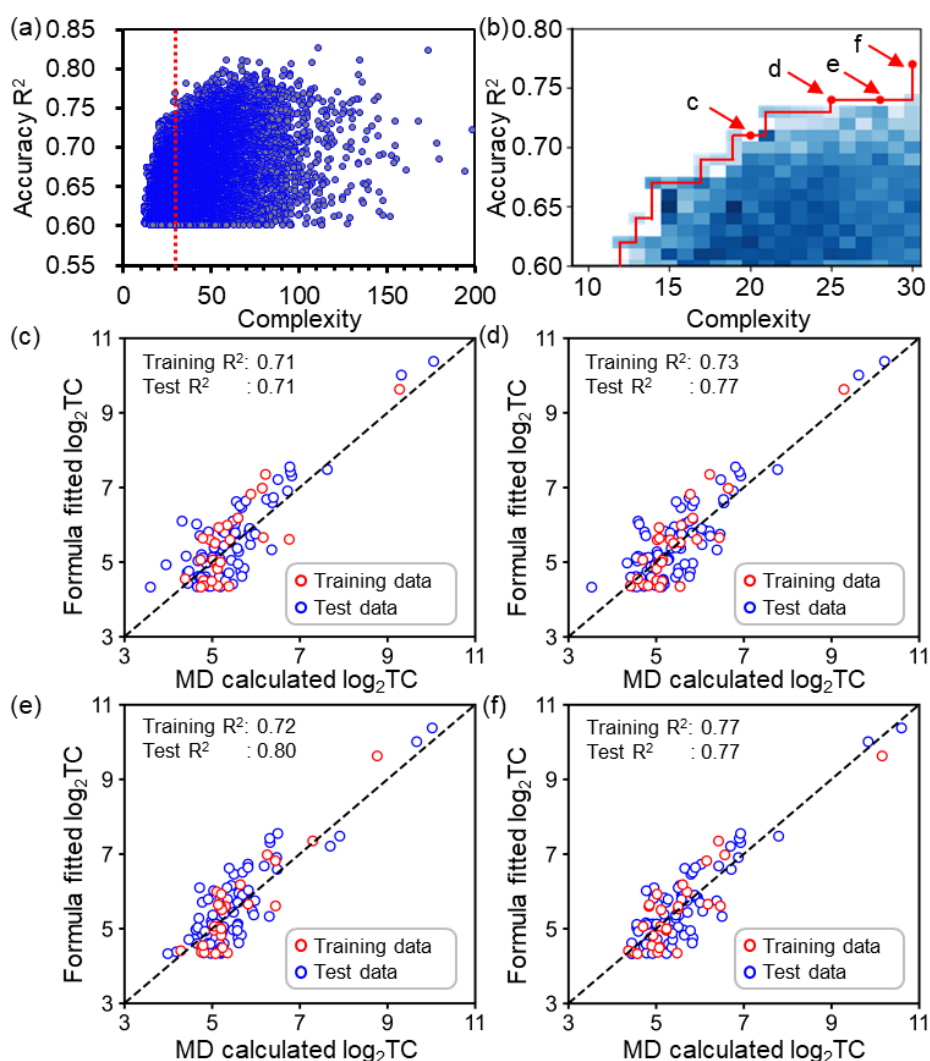
Supplementary Figure 13: Filtering optimized descriptors and creating sub-descriptors in gplearn through Pearson coefficient (PC) values. (a) Mathematical formula complexity versus PC values. (b) Statistics of formulas with Pearson coefficient not less than 0.85 by complexity. (c) and (d) Frequency of occurrence of optimized descriptors and sub-descriptors in 158 mathematical formulas (PC values ≥ 0.85 and complexity ≤ 10).

Supplementary Table 6. New descriptors ensemble for GPSR

Variable	Format	PC values	Variable	Format	PC values
x_0	ABC	-0.37	x_{11}	-ETA_dBeta	0.11
x_1	10/ABC	0.44	x_{12}	Kd_average	0.20
x_2	$\sqrt{ABC}$	-0.39	x_{13}	$\sqrt{Kd_average}$	0.12
x_3	ATSC0dv	-0.32	x_{14}	LogEE_A	-0.40
x_4	Cross-sectional	-0.52	x_{15}	MW	-0.39
x_5	10/Cross-sectional	0.63	x_{16}	MW/100	-0.39
x_6	1-10/Cross-sectional	0.59	x_{17}	100/MW	0.52
x_7	100/Cross-sectional	0.63	x_{18}	$\sqrt{MW}$	-0.43
x_8	$\sqrt{100/Cross - sectional}$	0.62	x_{19}	Nd_average	-0.31
x_9	-10/Cross-sectional	-0.63	x_{20}	log Nd_average	-0.35
x_{10}	ETA_dBeta	-0.11	x_{21}	- log Nd_average	0.44

Supplementary Table 7. Reset of hyperparameters in gplearn for GPSR

Parameter	Value	Combination
Generations	300	1
Population size in every generation	5000	1
Probability of crossover (pc)	[0.30,0.90], step=0.05	746
Subtree mutation (ps)	[(1-pc)/3,(1-pc)/2] (step= 0.01)	
Hoist mutation (ph)	[(1-pc)/3,(1-pc)/2] (step = 0.01)	
Point mutation (pp)	1-pc-ps-ph	
Function set	{+, −, ×, ÷, $\sqrt{x}$, $\ln x$, $ x $, $-x$, $1/x$ }	1
Parsimony coefficient	0.001, 0.003, 0.005	3
Metric	R^2	1
Stopping criterial	0.900	1
Random_state	0, 1, 2, 3, 4	5
Init_depth	[2, 6], [4, 8], [6, 10], [2, 10]	4



Supplementary Figure 14: GPSR for TC prediction of promising polymers. (a) 19580 formulas with fitting accuracy greater than 0.6 versus complexity. (b) Pareto front of accuracy R^2 vs. complexity of 9073 mathematical formulas shown via density plot. The four points of c, d, e and f represent the four formulas at the Pareto front, whose fitting results vs. MD calculated TC are plotted in (c), (d), (e) and (f) respectively.

Supplementary Table 8. The four mathematical formulas at the Pareto front in Supplementary Figure 14b

Point	Formulas	R ²	Complexity
c	$\log_2 TC = \sqrt{(x_{12} - x_8 - x_{16} + 0.49) \times x_9 \times (x_6 + x_{20})} + \sqrt{\ln(x_{12})}$ $+ x_{21}$	0.71	20
d	$\log_2 TC = \sqrt{x_{12} - \ln \left[(x_8 - x_{11}) \times \frac{x_8}{\ln(\sqrt{x_{19}})} \right] \times (x_6 + x_{20}) \times x_7}$ $+ x_{21} + \sqrt{\ln x_{12}}$	0.74	25
e	$\log_2 TC = \ln \left[\frac{1}{x_{10} \times (x_1 - x_2)} - x_{12} \right] \times (x_5 - 0.824)$ $+ \frac{x_{17}}{\sqrt{\frac{x_3}{(x_{12} - x_{11}) \times x_5}}} + x_{21} + x_{13}$	0.74	28
f	$\log_2 TC = \sqrt{x_8 + \left[\frac{x_{10}}{\ln(\ln x_{17} - \chi_{12}) + x_8} - x_{12} \right] \times (x_6 + x_{20}) \times \frac{x_8}{x_{20}}}$ $+ x_{21} + \sqrt{x_{19} - x_{16}}$	0.77	30

Supplementary Note 10. Investigation of thermal transport in different polymer hierarchical structures including polymer chains and amorphous polymers

An automated pipeline implemented in Radonpy toolkit for the modeling and simulation of amorphous polymers, as shown in Supplementary Figure 15. For each polymer simulation, the monomer was entered into the pipeline in the form of SMILES, and a polymer chain containing about 1000 atoms was generated by polymerization of the repeating unit using a self-avoiding random walk algorithm. Next, the GAFF2 force field with the information of bonds, angles, dihedrals, impropers and inter-chain interactions was assigned for the polymer chain. A simulation cell with 10 non-overlapping chains was formed by copying, arranging and rotating the individual chain. Then, the temperature of the simulation cell was increased from 300K to 700K, and maintained at 700K for 1ns in the NVT ensemble with a Nosé–Hoover thermostat for packing the system. After the packing simulation, the system was equalized following a 21-step equilibrium protocol³ at alternating temperatures of 300K and 600K for approximately 1.5 ns of each stage while the system was compressed to 50,000 atm and then decompression to 1 atm by combining the NVT and NPT simulations.

The equilibrium amorphous model contains approximately 10,000 atoms, and the NPT simulation was performed for 5ns with a timestep of 1fs to record the parameters for calculating properties of equilibrium systems such as radius of gyration, specific heat capacity and volumetric heat capacity. The radius of gyration R_g was calculated by:

$$R_g = \sqrt{\frac{1}{N} \sum_{i=1}^N (r_i - r_{mean})^2} \quad (1)$$

where N is the number of repeating units, r_{rep} is the position of repeating unit i , r_{mean} is the mean position of the repeating unit in a polymer chain.

The specific heat capacity C_p was calculated from the fluctuations in the enthalpy H :

$$C_p = \frac{\langle \delta H^2 \rangle}{mk_B T^2} \quad (2)$$

where $\langle \cdot \rangle$ represent time averaging, m is the mass of atoms in the system, k_B is the Boltzmann constant, and T is the temperature.

The volumetric thermal expansion coefficient α_V was calculated by the covariance of volume V of enthalpy H ⁴:

$$\alpha_V = \frac{\langle \delta V \delta H \rangle}{k_B T^2 \langle V \rangle} \quad (3)$$

The isothermal compressibility β_T and isothermal bulk modulus K_T were calculated based on the fluctuations in the volume ⁴:

$$\beta_T = \frac{\langle \delta V^2 \rangle}{k_B T \langle V \rangle} \quad (4)$$

$$K_T = \frac{1}{\beta_T} \quad (5)$$

Hence, the volumetric heat capacity may be expressed as ⁴:

$$C_V = C_P - \frac{\alpha_V^2 T \langle V \rangle}{\beta_T m} \quad (6)$$

Since the volumetric heat capacity is mainly dependent on the characteristics of the repeating units of the polymer, the C_V of polymer chains and amorphous polymers formed from the identical repeating unit is almost the same.

Applying the strain enables the de-entanglement of disordered chains in amorphous polymers to obtain oriented and ordered polymer chain segments. Moreover, the stretching process is available in the MD simulations. The pipeline provided the interface for applying various strains to the polymer system at constant temperature and strain rate. The stretched polymer model was required to relax in the NVT ensemble for 1 ns with a timestep of 0.2 fs to release the internal stress.

To the ATC of amorphous polymers, the reverse non-equilibrium molecular dynamics (NEMD) simulation was performed with the equilibrium model with 3x replication (~30,000 atoms) in thermal transport heat transform direction (x -direction). The system was divided into N ($N=20$ in this work) slabs along the x -direction, and the temperature gradients were generated by exchanging the velocity between the coldest atom in slab $N/2$ and the hottest atom in slab 0, as shown in the right part of Supplementary Figure 15. To prevent temperature shifts after cell replication, the system was initially run at 300K for 2ps. After that, the reverse NEMD simulation was run at 300K for 1 ns with 5000 cycles of velocity swaps. According to the exchanged energy obtained using the Müller-Plathe algorithm ΔE and the temperature gradient $\partial T / \partial x$ output by reverse NEMD simulation, the ATC λ can be expressed by:

$$\lambda = \frac{J_Q}{(\partial T / \partial x)} = \frac{\Delta E}{2A\Delta t(\partial T / \partial x)} \quad (7)$$

where J_Q is heat flux, A is the cross-sectional area of the amorphous system in the direction of heat flux, Δt is the simulation time.

Additional thermal conductivity decomposition analysis was employed to quantify the contribution of six components including of bond, angle, dihedral (dihed), convection (conv), nonbonded (non) and

improper, to the thermal conductivity. The energy flux along the direction of unit vectors J_u can be expressed as the contribution of convection (first term) and interatomic interactions (second term) ⁵:

$$J_u = \frac{1}{V} \left\{ \sum_{i \in V} e_i v_{i,u} + \sum_{i \in V} (S_i v_i)_u \right\} \quad (8)$$

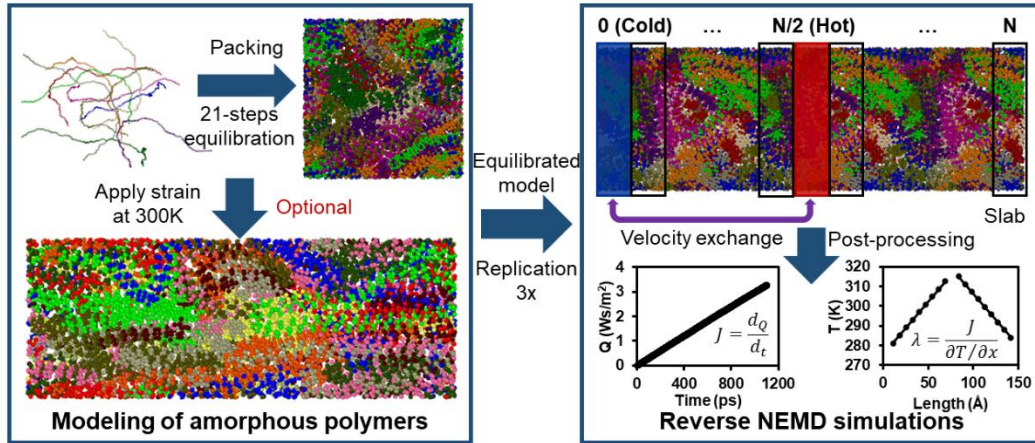
where e_i is potential and kinetic energy of each atom, $v_{i,u}$ is the velocity of the atom, S_i is the stress tensor and i is the index of atoms. The second term can be further divided into each component of the interactions. The stress tensor for component (a, b) is:

$$S_{ab} = \sum_{n=1}^{N_p} r_{i0,a} F_{i,b} + \sum_{n=1}^{N_b} r_{i0,a} F_{i,b} + \sum_{n=1}^{N_a} r_{i0,a} F_{i,b} + \sum_{n=1}^{N_d} r_{i,a} F_{i,b} + \sum_{n=1}^{N_i} r_{i0,a} F_{i,b} + Kspace(n_{i,a}, F_{i,b}) \quad (9)$$

The stress tensor was divided into six parts of the contributions pairwise, bond, angle, dihedral, improper and K-space, sequentially. where r_{i0} is the relative position of atom i to the geometric center of its interacting atoms, F_i is the force acting on atom i . Therefore, the thermal for each part λ_{par} can be written as:

$$\lambda_{par} = \frac{J_{par}}{J} \lambda \quad (10)$$

where J is the total heat flux calculated by Equation (8), and J_{par} is partial heat flux of each part in Equations (8) and (9), λ is the total thermal conductivity of polymers.



Supplementary Figure 15: Automated pipeline for the calculation of thermal conductivity of amorphous polymers (ATC) by reverse non-equilibrium molecular dynamics (NEMD) simulations.

To acquire a unified understanding of the effect of dihedral angle on the thermal conductivity of polymers with different hierarchical structures, we chose polyethylene (PE) as the object, due to its excellent mechanical properties and single backbone dihedral type of C-C-C-C (C denotes carbon atom).

Supplementary Figure 16a demonstrates the ATC of amorphous polymers under various strains ranging from 0 to 100%. The strain rate was unified as $1 \times 10^9 \text{ s}^{-1}$ and the temperature at 300K. It is noteworthy to mention that this work mainly focused on the relationships between polymer microstructures under different strains and ATC, rather than the length effect of the models. Therefore, we first estimated the ATC of the stretched amorphous polymer with finite length using equilibrium molecular dynamics (EMD) simulations. In EMD simulation, the ATC calculation was carried out under an NVT ensemble for 1 ns using the Green–Kubo formula:

$$\lambda = \frac{V}{k_B T^2} \int_0^\infty \langle J_x(0) J_x(t) \rangle dt \quad (11)$$

where J_x is the heat flux along the x -direction, which is consistent with the direction of stretching.

The orientational order parameter of the backbone was used for characterized the polymer chain alignment⁶:

$$P_{2b} = 1.5 \langle (e_i \cdot e_x)^2 \rangle - 0.5 \quad (12)$$

where e_x is the unit vector in the direction of applied strain, and the local chain orientation at atom i was computed from the chord connecting second neighbor atoms⁷: $e_i = (r_{i+1} - r_{i-1}) / |r_{i+1} - r_{i-1}|$.

In Supplementary Figure 16a, with the increased strain applied to the amorphous PE, the orientational order parameters are subsequently raised, resulting in a larger ATC. The two blue stars indicate the ATC of the amorphous polymers without strain and with 100% strain, which calculated by reverse NEMD simulations. This work was mainly concerned with the effect of dihedral energy on the thermal conductivity of the identical polymer structure, and the difference between the ATC calculated by reverse NEMD and EMD was acceptable, therefore the NEMD simulations were adopted in the subsequent research. The R_g calculated from amorphous polymers under different strains is displayed in Supplementary Figure 16b, with a close positive correlation with the persistent length ξ , namely⁸:

$$\xi = \frac{R_g^2 \times 6}{2(2N - 1) \times l} + \frac{l}{2} \quad (13)$$

where l is the bond length, $l=1.526 \text{ \AA}$ for PE. The large ξ suggests that the amorphous system has large rigid chain segments, which is conducive to intra-chain heat transport and generates high ATC. Evidently, the stretching effect is favorable for achieving large rigid chain segments.

Through GAFF2 force field, the dihedral energy $E_{dihedral}$ is computed using:

$$E_{dihedral} = \sum_{dihedrals} K_d [1 + \cos(n_d \varphi - \delta_d)] \quad (14)$$

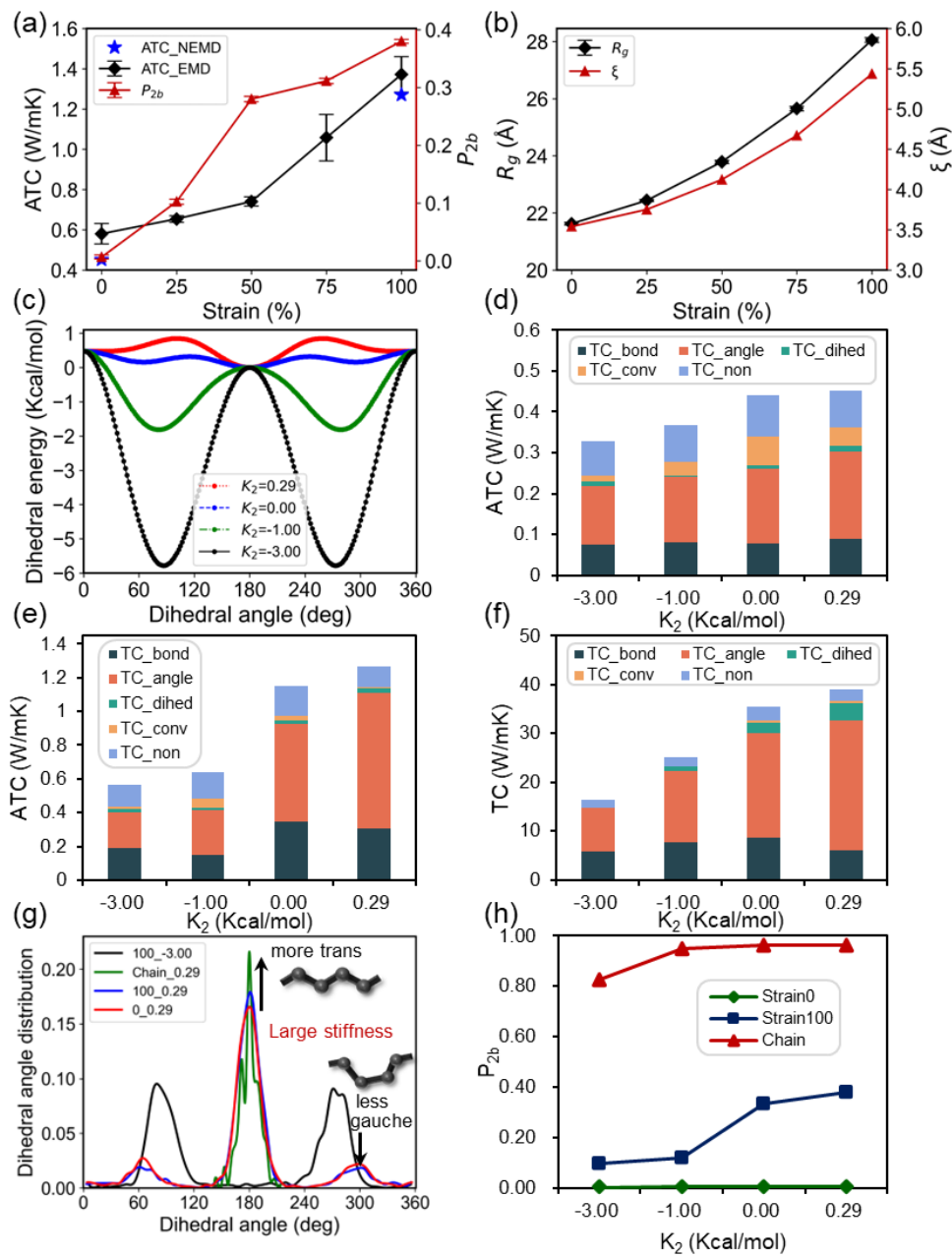
where K_d is the force constant of dihedral, δ is the phase angle for the torsional angle parameters, n is the multiplicity. For the C-C-C-C dihedral, there are three sets of parameters, as listed in

Supplementary Table 9. The dihedral energy curve can be adjusted by modifying the force constant so as to explore the effect of disorder on thermal conductivity. We increased the disorder of polymer systems by switching the force constant of K_2 from 0.29 to 0.00, -1.00 and -3.00 kcal/mol, respectively. The modified dihedral energy curves are demonstrated in Supplementary Figure 16c.

Supplementary Figure 16d-f illustrates the thermal conductivity of strain-free amorphous PE (0-strained PE), 100% strained amorphous PE (100%-strained PE), and PE chains, with different modified dihedral energy, respectively. Here, ATC was specifically defined as the thermal conductivity of the amorphous polymer to distinguish it from that of polymer chains. Each ATC or TC was quantified into five components of the contribution of bond, angle, dihedral, convection and nonbonded, since the contribution of improper was negligible. The intra-chain heat transport associated with bonds, angles and dihedrals is dominant for the contribution to thermal conductivity. Combined with Supplementary Figure 16h, we concluded that low dihedral energy leads to a decrease in the orientational order parameter and an increase in disorder for the PE with different hierarchical structures, which not only directly weakens the dihedral contribution, but also accounts for the lower angular contribution. For different hierarchical structures, the 0-strained PE model is relatively insensitive to the reduction in dihedral energy, because its orientational order parameter is close to 0. While the original chain orientation of 100% strained PE and individual PE chains are kept at a certain level separately, thereby the change of dihedral energy makes the reduction of ATC/TC more significant. When the K_2 shifts from 0.29 to -3.00 kcal/mol, the ATC of 100% strained PE decreases from 1.27 to 0.56 W m⁻¹K⁻¹, and the TC of PE chain decreases from 38.98 to 0.56 W m⁻¹K⁻¹. The impact of the dihedral term on thermal conductivity is more significant with increasing polymer orientational order parameters. In addition, we counted the dihedral distribution of different PE systems in Supplementary Figure 16g. The dihedral angle of 180 deg corresponds to trans conformation, while dihedral angles of 60 deg and 300 deg correspond to gauche transformation. Increasing the dihedral energy or applying the stain makes more gauche conformations transform to trans conformations, thus resulting in large chain stiffness and high thermal conductivity.

Table S9. List of parameters of the C-C-C-C dihedral

Dihedral	K_d (kcal/mol)	n_d	δ_d (deg)
C-C-C-C	$K_3=0.13$	$n_3=3$	$\delta_3=0$
	$K_2=0.29$	$n_2=2$	$\delta_2=180$
	$K_1=0.11$	$n_1=1$	$\delta_1=0$



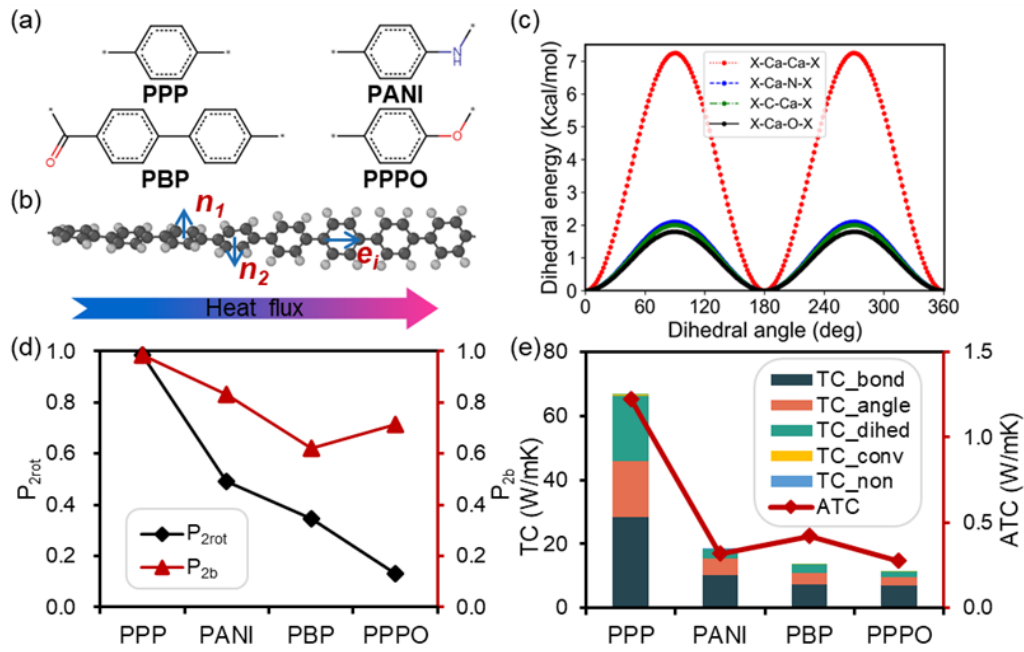
Supplementary Figure 16: Investigation of thermal conductivity of PE with different hierarchical structures by changing dihedral energy. (a) ATC and orientational order parameters (P_{2b}) of amorphous PE with varying strains. (b) Radius of gyration (R_g) and persistent length (ξ) of amorphous PE with varying strains. (c) dihedral energy curve. (d), (e) and (f) thermal conductivity of amorphous PE, 100% strained amorphous PE and PE chains with various dihedral energies, in which each thermal conductivity was quantified into five components of the contribution of bond, angle, dihedral (dihed), convection (conv) and nonbonded (non). (g) dihedral angle distribution. The legend depicts the pairs of polymer structure and dihedral energy force constant K_2 , e.g., 100_-3.00 means 100% strained amorphous polymer with modified K_2 of -3.00 kcal/mol. (h) orientational order parameters of different PE hierarchical structures.

The low dihedral energy increases the disorder of the polymer systems, which is mainly attributed to the severe chain rotation. For the study of the behavior of polymer chain rotation, a well-defined reference plane in the structure is required. This is facilitated by the coplanarity of the carbon atoms in the benzene ring of aromatic polymers, and the polymers of Poly(p-phenylene) (PPP), Polyaniline (PANI), Poly(benzophenone) (PBP) and Poly(p-phenylene oxide) (PPPO) were picked in this study, as shown in Supplementary Figure 17a. The orientational parameter P_{2rot} was defined as:

$$P_{2rot} = 1.5 \left\langle (n_j \cdot n_k)^2 \right\rangle - 0.5 \quad (15)$$

where n_j and n_k are the unit normal vectors of two planes of adjacent benzene rings along the heat flux transport direction in Supplementary Figure 17b.

The energy curves of critical dihedrals of four polymers are exhibited in Supplementary Figure 17c, where Ca indicates the carbon atom in the aromatic ring, C indicates the rest carbon atom, N indicates the nitrogen atom, O indicates the oxygen atom and X indicates any atom. Overall, the X-Ca-Ca-X has the largest dihedral energy, then X-Ca-N-X, X-C-Ca-X and X-Ca-O-X by decreasing order of dihedral energy. The large dihedral energy corresponds to a strong chain stiffness to suppress the chain rotation, allowing for a large rotational parameter. The ranking of the four polymers by orientational parameters (Supplementary Figure 17d) and chain TC (Supplementary Figure 17e) from largest to smallest is PPP, PANI, PBP and PPPO. however, the ranking by orientational order parameters is different, where PBP has the smallest value. As PBP has two dihedral angles X-Ca-Ca-X and X-C-Ca-X, and great dihedral energy differences may lead to poor stiffness matching of the chain. This does not determine the length of locally rigid chain segments, where the corresponding amorphous system has a larger ATC compared to that of PANI and PPPO in Supplementary Figure 17e.



Supplementary Figure 17: Four aromatic polymers for probing the effect of chain rotation phenomenon on thermal conductivity. (a) repeating units of aromatic polymers of Poly(p-phenylene) (PPP), Polyaniline (PANI), Poly(benzophenone) (PBP) and Poly(p-phenylene oxide) (PPPO). (b) schematic drawing of the plane normal vector n_1 and n_2 , and the backbone vector in e_i . (c) dihedral energy curve, where Ca indicates the carbon atom in the aromatic ring, C indicates the rest carbon atom, N indicates the nitrogen atom, O indicates the oxygen atom and X indicates any atom. (d) Rotational order parameters (P_{2rot}) and orientational order parameters (P_{2b}). (e) TC of polymers and ATC of amorphous polymers corresponding to four repeating units.

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