Molecular Design and Property Prediction of Sterically Confined Polyimides for Thermally Stable and Transparent Materials

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Table S1. Thermal properties of fluorinated PIs

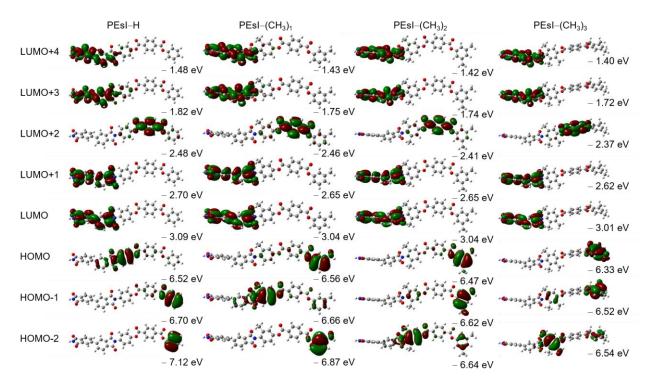


Figure S1. Calculated molecular orbitals and the corresponding energy levels of the basic units of PEsI–H and PEsI–(CH₃)_x model compounds (B3LYP/6–31G).

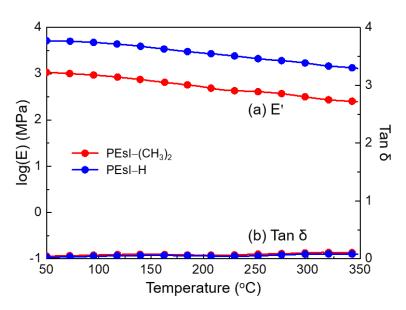


Figure S2. DMA thermograms of the PEsI–H and PEsI–(CH₃)₂ films (1 Hz, 3 °C min⁻¹). (a) storage modulus and (b) tan δ .

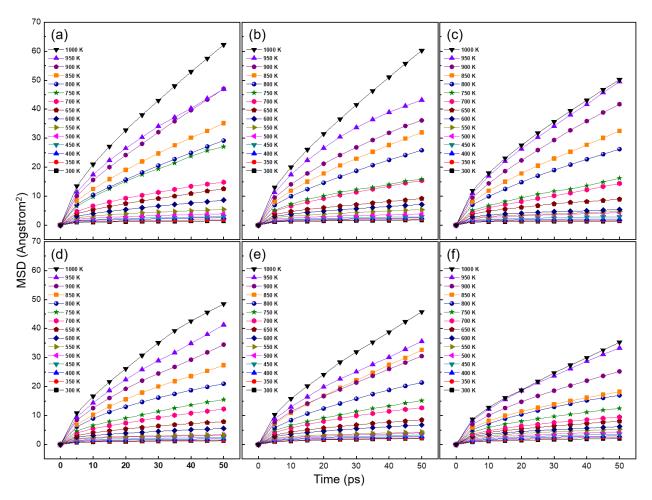


Figure S3. MSD of the structures as a function of time for the PEI systems. (a) PEI–(CH₃)₁, (b) PEI–(CH₃)₂, (c) PEI–(CH₃)₃, (d) PEI–(CF₃)₁, (e) PEI–(CF₃)₂, and (f) PEI–(CF₃)₃.

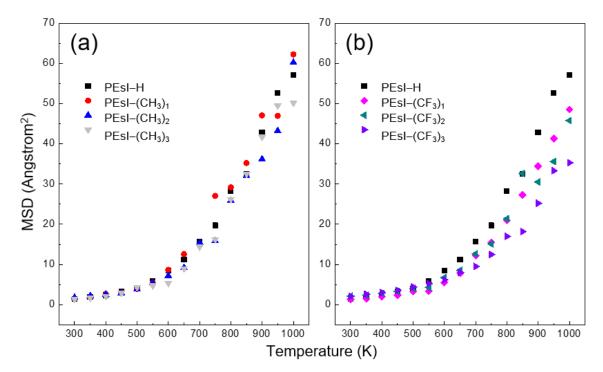


Figure S4. MSD curves as a function of temperature at 50 ps long time for the unit cell of PEsI systems.

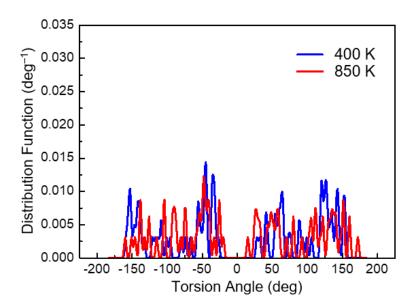


Figure S5. Torsion angle distributions of the PEsI–H systems by constant-NVT MD simulation at 400 and 850 K.

PI type	Molecular structure	Т _в (К)	CTE (ppm K ⁻¹)	Reference
Fluorinated ester-bridged PI	$ + \underbrace{ \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0$	651	8.3	Yang, S. et al. ¹
	$x = 5$ F_{3G} y y y y y $x = 30$	587	18.3	
PI containing pyridine and fluorinated units	$\begin{bmatrix} 0 & F_3 \\ -N & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1 \\ 0 & -1$	535	68	
	$\begin{bmatrix} \mathbf{r}_{3} \mathbf{C} & \mathbf{CF}_{3} \\ \mathbf{r}_{3} \mathbf{C} & \mathbf{CF}_{3} \end{bmatrix} \xrightarrow{\mathbf{r}_{3}} \mathbf{O} \xrightarrow{\mathbf{r}_{3}} \mathbf{O} \xrightarrow{\mathbf{CF}_{3}} \mathbf{O} \xrightarrow{\mathbf{CF}_$	548	64	Shang, D. et al. ²
		538	67	
PI derived from fluorinated tetracarboxylic dianhydride	F_3C HN O CF_3 CF_3 F_3C F_3C F_3C F_3C F_3C F_3C F_3C CF_3 F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C F_3C	543	8.3	Hasegawa , M. et al. ³
	$F_{3}C$ O $F_{3}C$ $F_{3}C$ $F_{3}C$ $F_{3}C$	505	26.5	
PI containing ether and fluorinated units	$\left[\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \end{array} \right]$	544	NA	Hsiao, S. et al.4
PI derived from multi- trifluoromethyl- substituted aromatic diamine	$\begin{bmatrix} 0 \\ N \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$	512	62.1	Yang, S. et al.⁵
Our model compounds	$rac{1}{1}$	731	12.8	This work

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