# Supporting information

# Terphenyl-based Colorless and Heat-resistant Polyimides with Controlled Molecular Structure by Methyl Side Groups

*Yunzhi Fang[a], Xiaojie He[b], Jun-Chen Kang[a], Le Wang[a], Tong-Mei Ding[a], Xuemin Lu[a], Shu-Yu Zhang[a]*, Qinghua Lu[a]*.*

[a]School of Chemistry and Chemical Engineering, Shanghai Key Laboratory of Electrical Insulation and Thermal Aging, Shanghai Jiao Tong University, Shanghai 200240, China.

[b]School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China.

*Corresponding author. E-mail address: qhlu@sjtu.edu.cn; zhangsy16@sjtu.edu.cn.

# Contents

## 1. Characterization

Figure S1. $^{1}H$ NMR and $^{13}C$ NMR spectra of DMTD.

Figure S2. $^{1}H$ NMR and $^{13}C$ NMR spectra of TMTD.

Figure S3. $^{1}H$ NMR and $^{13}C$ NMR spectra of 23TMTD.

Figure S4. $^{1}H$ NMR and $^{13}C$ NMR spectra of HMTD.

Figure S5. $^{1}H$ NMR and $^{13}C$ NMR spectra of 23HMTD.

Figure S6. DSC curves of polyimides.

Figure S7. The conformer search – energy curves at specific torsions of (a) $\varphi_a$, (b) $\varphi_b$ and (c) $\varphi_c$ of optimized repeating units by computer simulation.

Table S1. $T_g$ of Reported CPIs.

Table S2. The Molecular Weights of Polyimides.

Table S3. The Solubilities of Polyimides.

Table S4. The Mechanical Properties of Polyimides.

Table S5. Comparison of Typical Properties of Methyl-Substituted Biphenyl and Terphenyl Polyimides.

## 2. Theoretical Calculation Details

# 1. Characterization

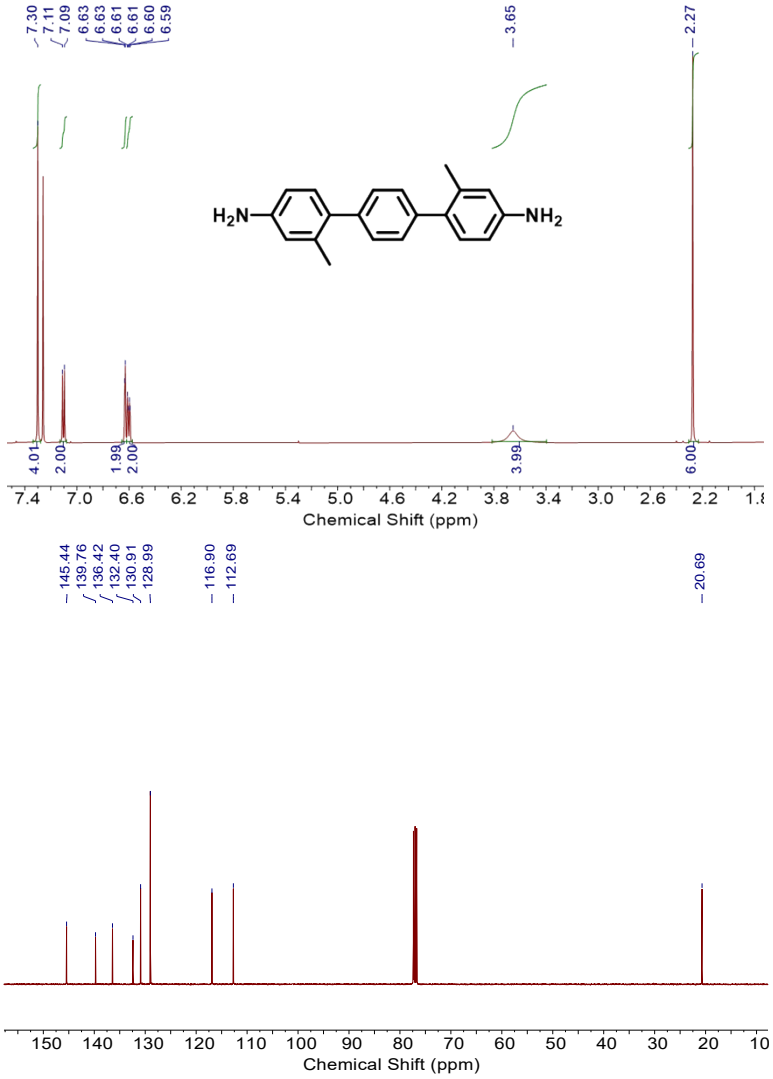



Figure S1. $^{1}H$ NMR and $^{13}C$ NMR spectra of DMTD.

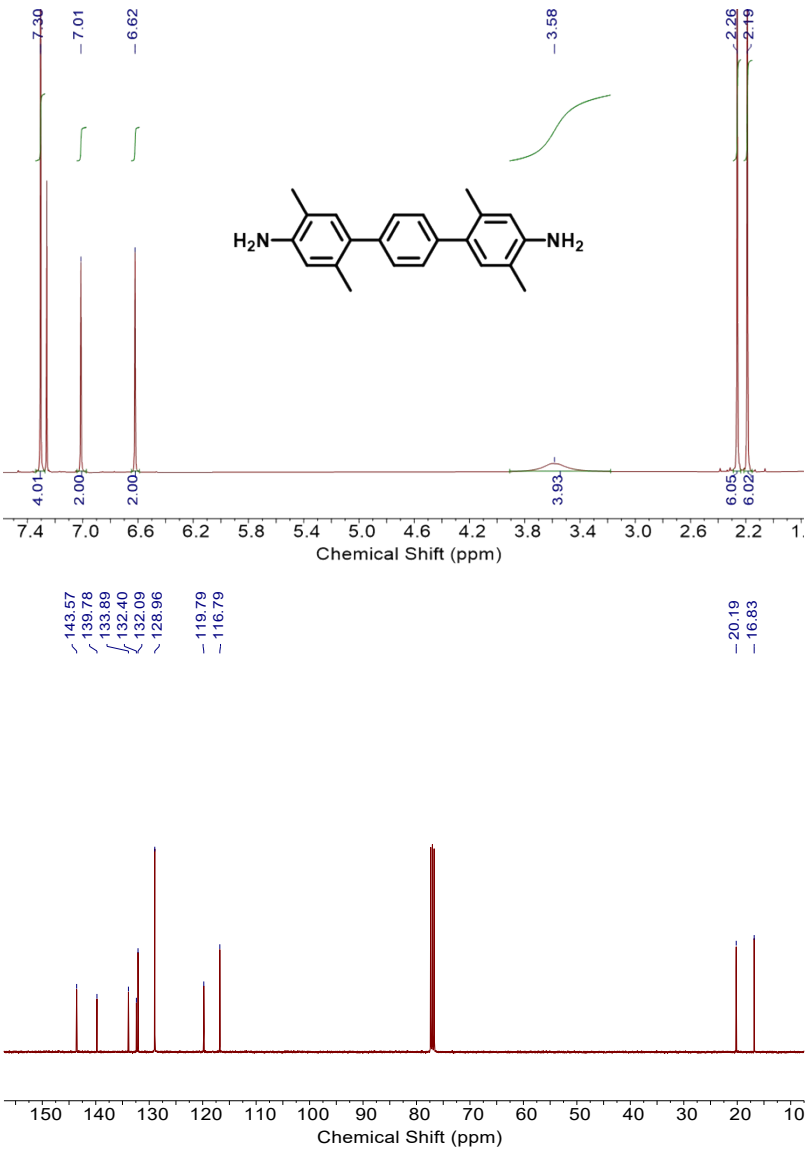



Figure S2. $^{1}H$ NMR and $^{13}C$ NMR spectra of TMTD.

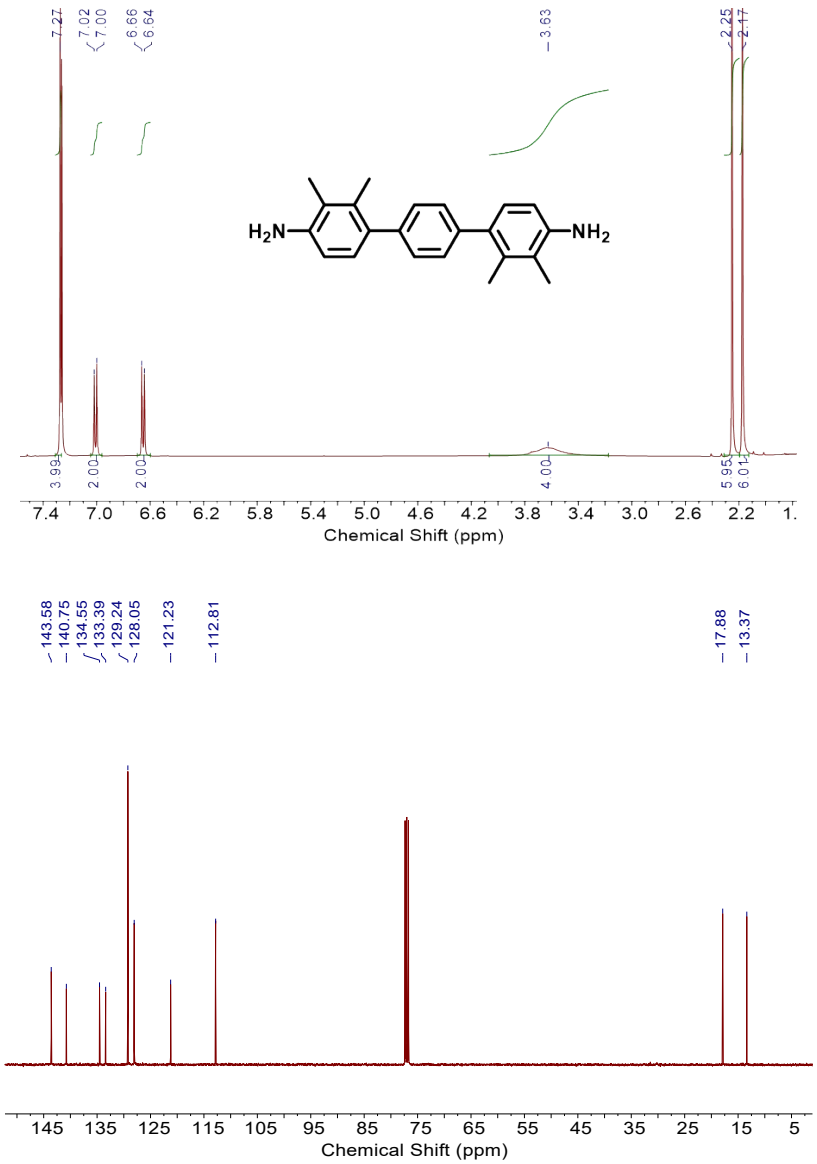



Figure S3. $^{1}H$ NMR and $^{13}C$ NMR spectra of 23TMTD.

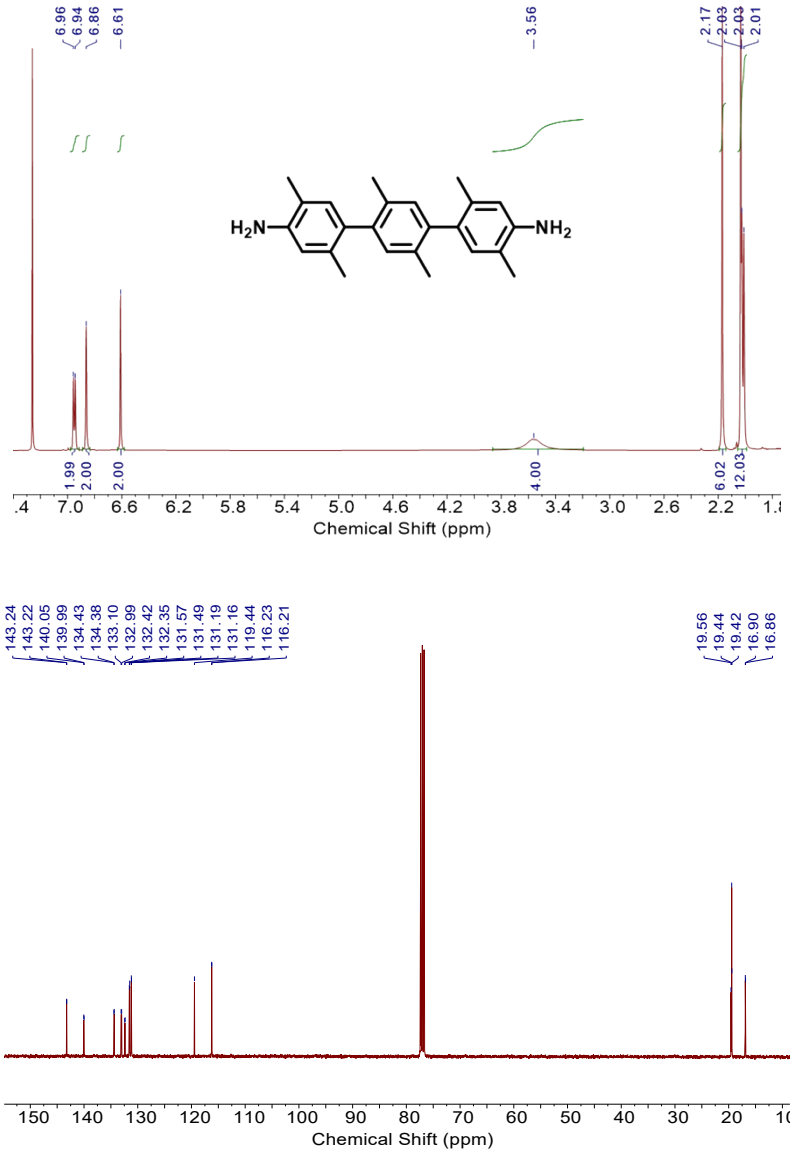



Figure S4. $^{1}H$ NMR and $^{13}C$ NMR spectra of HMTD.

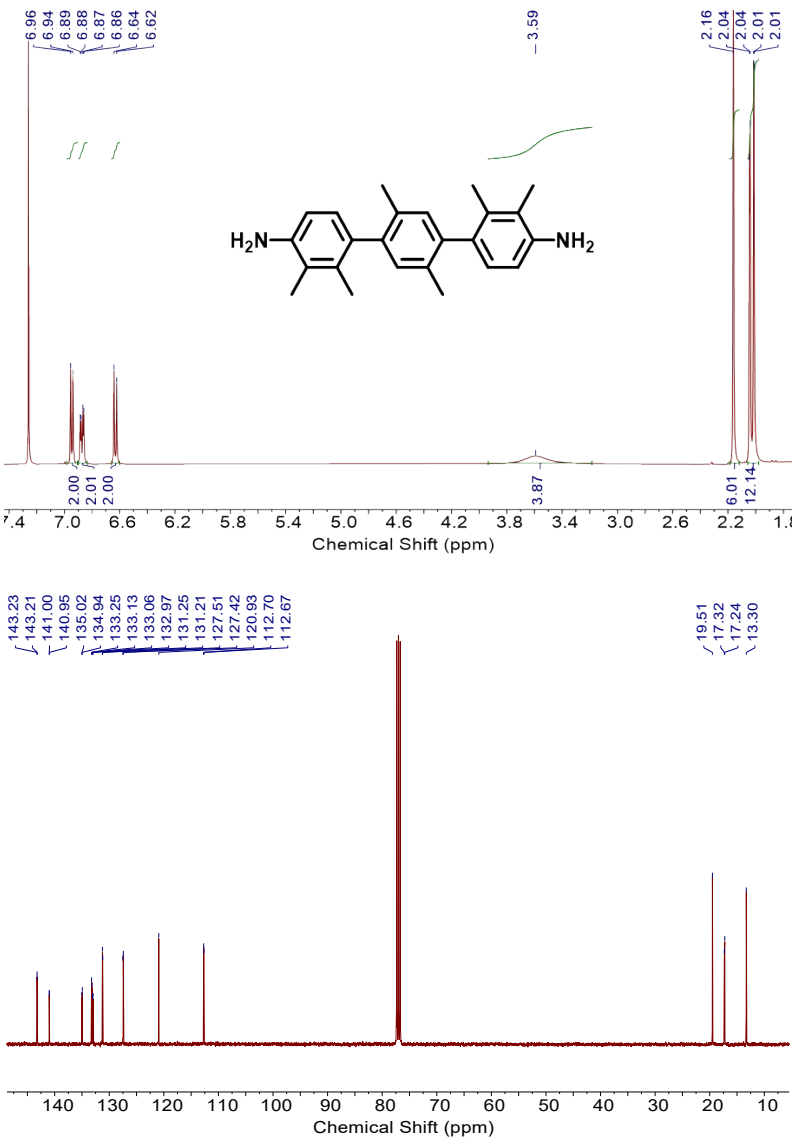



Figure S5. $^{1}$H NMR and $^{13}$C NMR spectra of 23HMTD.

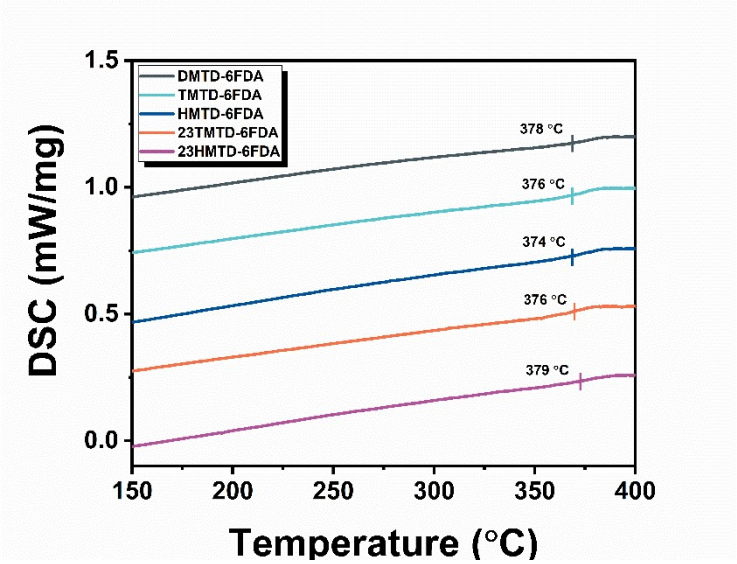



Figure S6. DSC curves of polyimides.

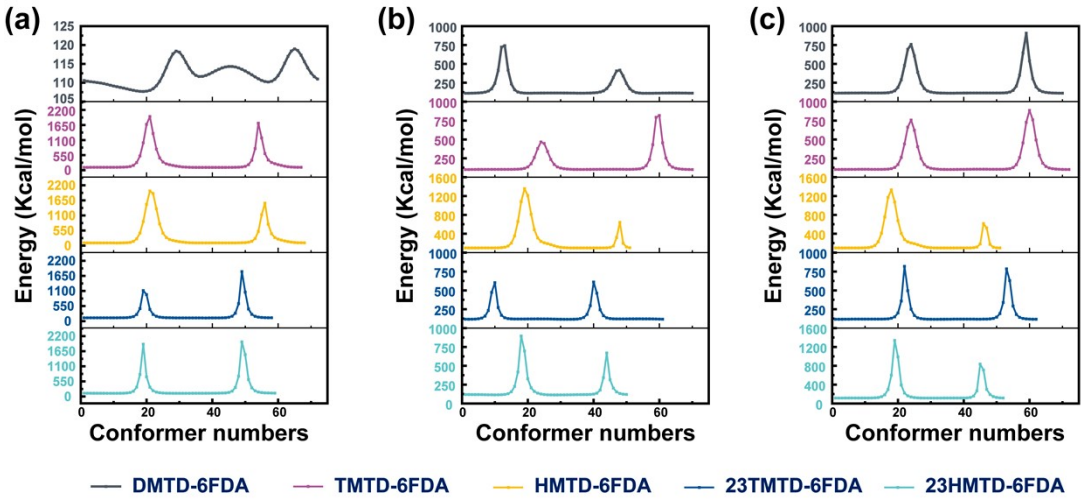



Figure S7. The conformer search – energy curves at specific torsions of (a) $\varphi_a$, (b) $\varphi_b$ and (c) $\varphi_c$ of optimized repeating units by computer simulation.

The conformer search based on the torsions of $\varphi_a$, $\varphi_b$ and $\varphi_c$ reflected the effect of the substitution position of the methyl-groups on their conformations, as shown in **Figure S7**. **DMTD-6FDA** exhibited the lowest energy of all of the searched conformers based on $\varphi_a$; thus, indicating more opportunities existed for conformational transition

when without restriction of methyl groups at the ortho-position of the amino. Furthermore, when two additional methyl groups were substituted to the 2' and 5' positions of the p-terphenyl, the conformer energy in **Figures S7b and 7c** exhibited a significant increase for **HMTD-6FDA** and **23HMTD-6FDA**, which again proved the structural manipulation in increasing the steric hindrance of molecular chain and to obtain a higher $T_g$.

**Table S1.** $T_g$ of Reported CPIs.

| Sample | $T_g$ by DSC (°C) | $T_g$ by DMA (°C) | Reference |
|---|---|---|---|
| **PAI-1** | 318 | / | 1 |
| **PAI-2** | 314 | / | 1 |
| **tert-butyl-PI** | 317 | 342 | 2 |
| **II-1** | 299 | / | 3 |
| **PI-TBS-1F** | 302 | 319 | 4 |
| **PI-TBS-1O** | 297 | 311 | 4 |
| **PI-5** | 333 | 343 | 5 |
| **6FDA-ADMDA** | / | 383 | 6 |
| **6FDA-DMADMDA** | / | 392 | 6 |
| **6FDA-TFMB** | 335 | / | 7 |

**Table S2.** The Molecular Weights of Polyimides.

| Sample | $M_n$ ($\times 10^3$) | $M_w$ ($\times 10^3$) |
|---|---|---|
| **DMTD-6FDA** | 98 | 265 |
| **TMTD-6FDA** | 49 | 141 |
| **HMTD-6FDA** | 44 | 118 |
| **23TMTD-6FDA** | 101 | 252 |
| **23HMTD-6FDA** | 104 | 278 |

**Table S3.** The Solubilities of Polyimides.

| Sample | Solvent | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **DMSO** | **DMAC** | **DMF** | **NMP** | **$CHCl_3$** | **THF** | **$CH_2Cl_2$** | **Acetone** |
| **TD-6FDA[a]** | - | - | - | - | - | - | - | - |
| **DMTD-6FDA** | ++ | ++ | ++ | ++ | ++ | ++ | ++ | - |
| **TMTD-6FDA** | ++ | ++ | ++ | ++ | ++ | ++ | ++ | + |
| **HMTD-6FDA** | ++ | ++ | ++ | ++ | ++ | ++ | ++ | + |
| **23TMTD-6FDA** | ++ | ++ | ++ | ++ | ++ | ++ | ++ | + |
| **23HMTD-6FDA** | ++ | ++ | ++ | ++ | ++ | ++ | ++ | + |

[a]TD-6FDA was synthesized from 4,4"-Diamino-p-terphenyl and 6FDA.

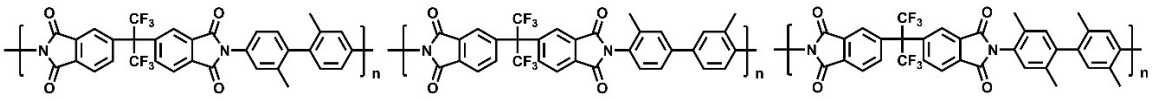
++: soluble at room temperature; +: partially soluble upon heating; –: insoluble at room temperature.

**Table S4.** The Mechanical Properties of Polyimides.

| Sample | $\delta_{max}$ (Mpa) | εb (%) | E (GPa) |
|---|---|---|---|
| **DMTD-6FDA** | 108±7 | 14.2±3.0 | 2.2±0.1 |
| **TMTD-6FDA** | 125±3 | 5.5±0.1 | 2.8±0.1 |
| **HMTD-6FDA** | 96±2 | 3.8±0.7 | 2.8±0.2 |
| **23TMTD-6FDA** | 147±5 | 4.9±0.6 | 3.2±0.3 |
| **23HMTD-6FDA** | 158±4 | 5.4±0.2 | 3.4±0.1 |

**Table S5.** Comparison of Typical Properties of Methyl-Substituted Biphenyl and Terphenyl Polyimides.

| Sample | d (um) | $T_g$ | YI | E (GPa) |
|---|---|---|---|---|
| **DMTD-6FDA** | 15 | 391 | 5.30 | 2.2±0.1 |
| **TMTD-6FDA** | 16 | 396 | 2.60 | 2.8±0.1 |
| **HMTD-6FDA** | 16 | 407 | 1.48 | 2.8±0.2 |
| **23TMTD-6FDA** | 18 | 402 | 2.17 | 3.2±0.3 |
| **23HMTD-6FDA** | 17 | 413 | 1.66 | 3.4±0.1 |
| **22DMB-PI** | 17 | 390 | 7.59 | 3.0 |
| **33DMB-PI** | 18 | 397 | 5.89 | 2.3 |
| **2255TMB-PI** | 15 | 407 | 4.60 | 1.8 |



**22DMB-PI** **33DMB-PI** **2255TMB-PI**

# 2. Theoretical Calculation Details

## 2.1 Calculation of molecular orbital energy, dihedral angle, FFV and CED

The repeating unit of polyimide was used as the model compound and was constructed by BIOVIA material studio 2019 software. The DFT theory was performed using DMol3 module where GGA/PW91 was applied. The condition in the electronic exchange was Double Numerical plus polarization DNP4.4. After the structures were optimized and the virtual frequency was removed, the structures of energy minimization were obtained. The Frontier molecular orbital energy was calculated by

choosing orbitals on the properties tab and the torsion was obtained by measure tool.

FFV and CED were calculated with the aid of Synthia module of BIOVIA material studio 2019 software. The repeating unit was constructed and then optimized by using Forcite. The homopolymer of polyimide was then defined by using Repeat Unit tool in the Polymer Builder functionality. On the Synthia Calculation dialog, calculating the van der Waals molar volume and Cohesive energy, and finally the FFV and CED values can be obtained through density and theoretical formula.

# Reference


1. H. Zuo, G. Qian, H.-B. Li, F. Gan, Y. Fang, X. Li, J. Dong, X. Zhao and Q. Zhang, *Polym.Chem.*, 2022, **13**, 2999-3008.
2. X. Wu, C. Shu, M. Zhong, X. Fan, Z. Yu, W. Huang and D. Yan, *Appl. Surf. Sci.*, 2022, **583**.
3. Z. Zheng, Y. Xu, Z. Ye, L. Yan, Y. Tao, W. Ma, J. Liu and C. Jian, *Polymer Science, Series B*, 2020, **62**, 756-764.
4. Y. C. Wu, Z. G. Chen, J. Q. Ji, Y. B. Zhou, H. H. Huang, S. M. Liu and J. Q. Zhao, *Eur. Polym. J.*, 2020, **132**.
5. Q. Wu, X. Ma, F. Zheng, X. Lu and Q. Lu, *Polym. Int.*, 2019, **68**, 1186-1193.
6. J. Miao, X. F. Hu, X. W. Wang, X. S. Meng, Z. Wang and J. L. Yan, *Polym.Chem.*, 2020, **11**, 6009-6016.
7. T. Matsuura, Y. Hasuda, S. Nishi and N. Yamada, *Macromolecules*, 1991, **24**, 5001-5005.