Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Super-heat resistant, transparent and low dielectric polyimides based on spirocyclic bisbenzoxazole diamines with T_g > 450°C

Peng Xiao[1], Xiaojie He[1], Feng Zheng[1], Qinghua Lu[1,2 *]

1. School of Chemical Science and Technology, Tongji University, Siping Road No. 1239, Shanghai, 200092 China

2. Shanghai Key Lab of Electrical & Thermal Aging, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Dongchuan Road No. 800, Shanghai, 200240 China

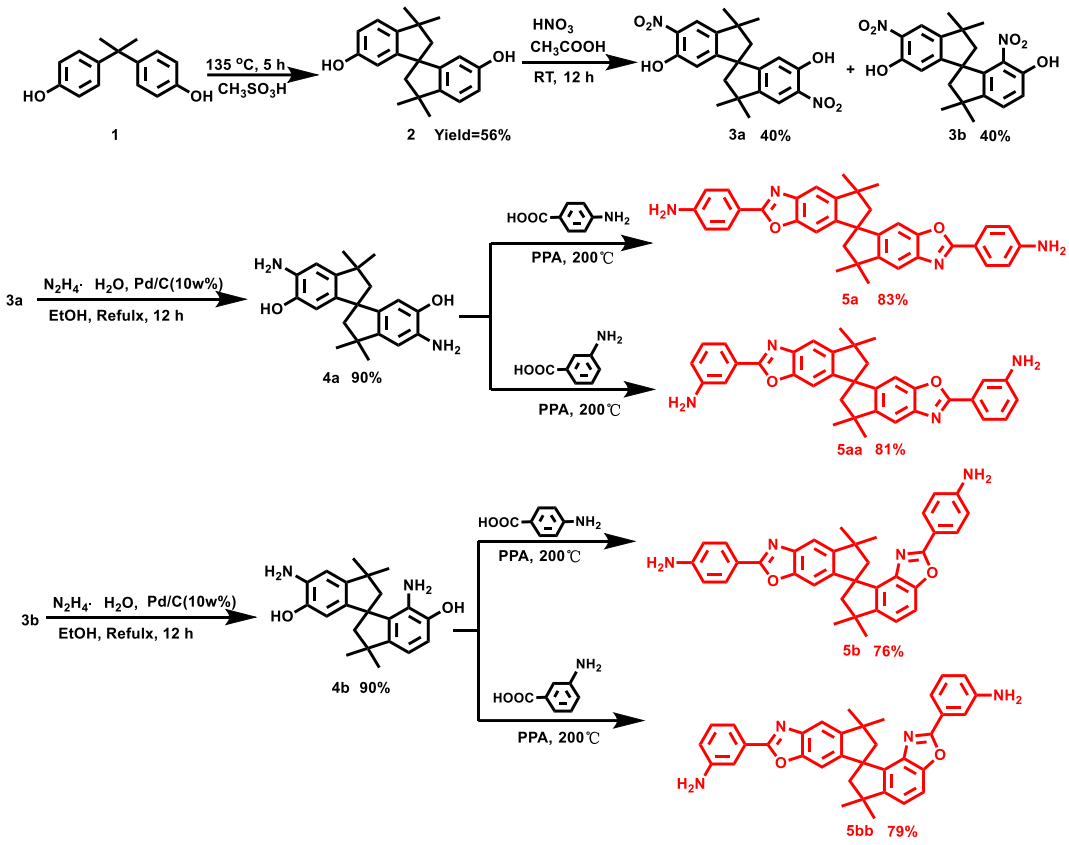
E-mail: qhlu@sjtu.edu.cn (Q.Lu). Tel. & Fax: (+86)021 54747535

Contents

1. Experimental details

1.1. Monomer synthesis

Four novel diamine monomers(**5a**, **5aa**, **5b** and **5bb)**, were synthesized via a four-step route, as shown in Scheme S1.



Scheme S1. Synthetic route of **5a**, **5aa, 5b,** and **5bb**.

Synthesis of 3,3,3′,3′-tetramethyl-1,1′-spirobisindane-6,6′-diol (2)

Bisphenol A (100 g, 0.439 mol) and methanesulfonic acid (10 mL) were mixed in a reaction flask by stirring and heated to 135°C for 4 h. The resulting brown sticky oil was poured into water (2000 mL) with vigorous stirring. Finally, white needle-like crystals 2 (25 g, yield: 56%) were obtained after recrystallization from ethanol/water (9/1). (TLC: dichloromethane/ligroin = 1/4, R_f = 0.25).

Synthesis of 3,3,3′,3′-tetramethyl-1,1′-spirobisindane-5,5′-dinitrol-6,6′-diol (3a) and 3,3,3',3'-tetramethyl-5,7'-dinitro-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diol (3b)

By reference[44-45], two isomeric nitro compounds (**3a** and **3b**) were synthesized : compound **2** (3.08 g, 10.0 mmol) was dissolved in acetic acid (100 mL), to which a mixed solution of HNO_3 (4 N, 2.1 equiv., 5.3 mL) and acetic acid (50.0 mL) was added dropwise over

15 min. The mixed slurry was stirred overnight and then cooled to room temperature before filtration. Light yellow solids **3a** (1.59 g, yield: 40.0%) (TLC: dichloromethane/ligroin = 1/1, R_f = 0.6) and **3b** (1.58 g, yield: 40.0%) (TLC: dichloromethane/ligroin = 1/1, R_f = 0.7) was obtained by column separation, eluting with dichloromethane/ligroin.

Synthesis of 3,3,3′,3′-tetramethyl-1,1′-spirobisindane-5,5′-diamino-6,6′-diol (4a) and 5,7'-diamino-3,3,3',3'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diol (4b)

The suspension of yellow solid **3a** or **3b** (10.0 g, 25.0 mmol) and Pd/C (0.8 g) in 200 mL ethanol was heated to reflux, and $N_2H_4 \cdot H_2O$ (80%, 20 mL) was added dropwise over 0.5 h. The mixture was stirred for 10 h, and the precipitate was collected by filtration and the solution was cooled to room temperature, the solution was poured into distilled water and the resulting white precipitate was collected. The solid was dried under vacuum at 80°C, and finally white powder **4a** or **4b** was obtained (8.1 g, 96%).

Synthesis of 4,4'-(5,5,5',5'-tetramethyl-5,5',6,6'-tetrahydro-7,7'-spirobi[indeno[5,6-d]oxazole]-2,2'-diyl)dianiline (5a)

PPA (70 g) and P_2O_5 (10 g) were placed in a thoroughly dried 500 mL three-necked flask equipped with a mechanical stirrer and a nitrogen inlet/outlet. The mixture was stirred and heated at 100°C until the P_2O_5 had completely dissolved. After cooling to room temperature, **4a** (6.76 g, 20.0 mmol) and 4-aminobenzoic acid (5.80 g, 42.3 mmol) were stirred into the mixture to produce a thick paste. The resulting mixture was slowly heated to 200°C and maintained at this temperature for 10 h. After cooling to 100°C, the reaction mixture was poured into ice-cold water with rapid stirring. The resulting reaction mixture was neutralized with 10% sodium carbonate solution, the precipitate was filtered off and rinsed several times with distilled water. The crude product was purified by chromatography on neutral alumina, eluting with ethyl acetate/ligroin (3:1, v/v, R_f = 0.6) to afford a white solid 5a (8.97 g, 83%). FTIR (KBr, cm^{-1}): 3458, 3375, 3322, 3192 (amine NH), 2950, 2925 (CH_3), 2860 (CH_2), 1605 (NH_2, C=N), 1173 (oxazole C-O-C). ^{1}H NMR (DMSO-d_6, 600 MHz): δ 7.79 (d, J =7.8 Hz, 4H, Ar-H), 7.48 (s, 2H, Ar-H), 6.89 (s, 2H, Ar-H), 6.67 (d, J =7.8 Hz, 4H, Ar-H), 5.94 (s, 4H, NH_2), 2.42 (s, 2H, CH_2), 2.42 (s, 2H, CH_2), 2.28 (s, 2H, CH_2), 1.42 (s, 6H, CH_3), 1.33 (s, 6H, CH_3) ppm. ^{13}C NMR (DMSO-d_6, 150 MHz): δ 164.1, 152.8, 150.2, 149.1, 147.8, 142.5, 129.2, 114.0, 113.6, 112.1, 105.7, 60.2, 60.0, 57.6, 43.3, 32.3, 30.7 ppm. HRMS (ESI): Calcd. for:

$C_{35}H_{32}N_4O_2$ $[M+H]^+$: 541.2525; Found: 541.2526.

Synthesis of 3,3'-(5,5,5',5'-tetramethyl-5,5',6,6'-tetrahydro-7,7'-spirobi[indeno[5,6-d]oxazole]-2,2'-diyl)dianiline (5aa)

Diamine **5aa** was synthesized according to a procedure similar to that described for **5a**, but using **4a** and 3-aminobenzoic acid as starting materials. The product was obtained as a white solid **5aa** (8.75 g, 81%). FTIR (KBr, cm^{-1}): 3406, 3317, 3207 (amine NH), 2950, 2925 (CH_3), 2860 (CH_2), 1605 (NH_2, C=N), 1173 (oxazole C-O-C). ^1H NMR (DMSO-d_6, 600 MHz): δ 7.63 (s, 2H, Ar-H), 7.36 (s, 2H, Ar-H), 7.25 (d, J =7.8 H_Z, 2H, Ar-H), 7.19 (dd, J =7.8 H_Z, 2H, Ar-H), 7.04 (s, 2H, Ar-H), 6.76 (d, J =7.8 H_Z, 2H, Ar-H), 5.47 (s, 4H, NH_2), 2.48 (d, J =12.6 H_Z, 2H, CH_2), 2.34 (d, J =13.2 H_Z, 2H, CH_2), 1.48 (s, 6H, CH_3), 1.39 (s, 6H, CH_3) ppm. ^{13}C NMR (DMSO-d_6, 150 MHz): δ 163.6, 150.5, 149.8, 149.6, 149.0, 142.1, 130.1, 127.61, 117.58, 114.9, 113.1, 112.3, 106.2, 60.23, 60.0, 57.7, 43.4, 32.3, 30.8 ppm. HRMS (ESI): Calcd. for: $C_{35}H_{32}N_4O_2$ $[M+H]^+$: 541.2525; Found: 541.2527. HRMS (ESI): Calcd. for: $C_{35}H_{32}N_4O_2$ $[M+H]^+$: 541.2525; Found: 541.2523.

Synthesis of 4,4'-(5',5',6,6-tetramethyl-5',6,6',7-tetrahydrospiro[indeno[4,5-d]oxazole-8,7'-indeno[5,6-d]oxazole]-2,2'-diyl)dianiline (5b)

Diamine **5b** was synthesized according to a procedure similar to that described for **5a**, but using **4b** and 4-aminobenzoic acid as starting materials. The product was obtained as a white solid **5b** (8.21 g, 76%). FTIR (KBr, cm^{-1}): 3468, 3342, 3223 (amine NH), 2950, 2925 (CH_3), 2860 (CH_2), 1605 (NH_2, C=N), 1173 (oxazole C-O-C). ^1H NMR (DMSO-d_6, 600 MHz): δ 7.74 (d, J = 9.0 Hz, 2H, Ar-H), 7.58 (d, J = 8.4 Hz, 2H, Ar-H), 7.54 (d, J = 8.4 Hz, 1H, Ar-H), 7.51 (s, 1H, Ar-H), 7.20 (d, J = 8.4 Hz, 1H, Ar-H), 6.78 (s, 1H, Ar-H), 6.64 (d, J = 9.0 Hz, 2H, Ar-H), 6.57 (d, J = 9.0 Hz, 2H, Ar-H), 5.90 (s, 2H, NH_2), 5.87 (s, 2H, NH_2), 2.98 (d, J = 12.6 Hz, 1H, CH_2), 2.47 (d, J = 13.2 Hz, 1H, CH_2), 2.32 (d, J = 13.2 Hz, 1H, CH_2), 2.80 (d, J = 13.2 Hz, 1H, CH_2), 1.57 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.34 (s, 3H, CH_3) ppm. ^{13}C NMR (DMSO-d_6, 150 MHz): δ 163.9, 163.6, 152.7, 150.7, 150.0, 148.8, 148.6, 148.0, 142.2, 138.5, 138.3, 129.2, 129.1, 118.0, 114.0, 113.7, 113.4, 112.3, 112.3, 109.8, 105.0, 61.0, 57.5, 56.9, 44.3, 43.4, 32.8, 32.3, 31.3, 30.7 ppm. HRMS (ESI): Calcd. for: $C_{35}H_{32}N_4O_2$ $[M+H]^+$: 541.2525; Found: 541.2524.

Synthesis of 3,3'-(5',5',6,6-tetramethyl-5',6,6',7-tetrahydrospiro[indeno[4,5-d]oxazole-

8,7'-indeno[5,6-d]oxazole]-2,2'-diyl)dianiline (5bb)

Diamine **5bb** was synthesized according to a procedure similar to that described for **5a**, but using **4b** and 3-aminobenzoic acid as starting materials. The product was obtained as a white solid (8.54 g, 79%). FTIR (KBr, cm^{-1}): 3448, 3334, 3224 (amine NH), 2950, 2925 (CH_3), 2860 (CH_2), 1605 (NH_2, C=N), 1173 (oxazole C-O-C). ^1H NMR (DMSO-d_6, 600 MHz): δ 7.19 (dd, J = 3.6 H_Z, 2H, Ar-H), 7.33 (s, 1H, Ar-H), 7.31 (d, J = 8.4 H_Z, 1H, Ar-H), 7.22 (d, J = 7.8 H_Z, 1H, Ar-H), 7.15-7.17 (m, 1H, Ar-H), 7.06-7.11 (m, 1H, Ar-H), 6.90 (s, 1H, Ar-H), 6.73 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H, Ar-H), 6.68 (d, J = 7.8 H_Z, 1H, Ar-H), 5.43 (s, 2H, NH_2), 5.39 (s, 2H, NH_2), 3.00 (d, J = 12.6 Hz, 1H, CH_2), 2.51 (d, J = 13.2 Hz, 1H, CH_2), 2.32-2.36 (m, 2H, CH_2), 1.60 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.35 (s, 3H, CH_3) ppm. ^{13}C NMR (DMSO-d_6, 150 MHz): δ 163.5, 163.2, 151.1, 149.9, 149.8, 149.4, 149.2, 141.1, 139.2, 138.0, 130.2, 127.8, 127.6, 119.5, 117.7, 117.6, 115.1, 115.0, 113.4, 112.4, 112.3, 110.5, 105.6, 61.1, 57.7, 57.2, 44.5, 43.6, 32.8, 32.4, 31.4, 30.9 ppm. HRMS (ESI): Calcd. for: $C_{35}H_{32}N_4O_2$ $[M+H]^+$: 541.2525; Found: 541.2528.

1.2．Computational Simulation

Net charges of nitrogen atoms in the amine groups of the diamines

The structures of **5a**, **5aa**, **5b**，and **5bb** were built using the Visualizer module. First, the different diamine structures were optimized, and the elimination of the imaginary frequency ensures that the structure is in the lowest energy state. Then check “Electron density” and “Electrostatics” in the properties of the $DMol^3$ calculation dialog box. After the calculation, select the “Analysis” of the $DMol^3$ module, select Electron density, Density field select Total density, and present the electron density on the molecule. On this basis, select potentials in the Analysis section, make sure that the View isosurface on import option is not checked, click the "Import" button, switch to the Isosurface tab, and select $DMol^3$ electrostatic potential in the Mapped field area. At this point the electrostatic potential is drawn on the electron isodensity surface, finally use the Color Map to change the color scheme of the pattern.

HOMO-LUMO gap energies of PIs

HOMO-LUMO gap energies were calculated by Material Studio 2019 software. The repeating units of the polyimide were first geometrically optimized to eliminate the imaginary

frequencies in the vibrational frequencies. Then check "Orbitals" in the Properties tab of the "Calculation" dialog box. After the calculation, select the Analysis section of the DMol^3 module, select "Orbitals", select "Available" for "Filter", and display the HOMO and LUMO tracks in turn.

Glass Transition Temperature (T_g) of PIs

Fox and Flory[1-3] proposed a free-volume theory to explain the glass transition: as the temperature increases, the change in the free volume or void volume of the polymer is very small under T_g, but there is a mutation in the glass transition. The transition temperature is the temperature at which the free volume reaches a certain critical value. Therefore, a common way to determine T_g is to plot the curve of density versus temperature. Five amorphous cells with 12 structurally optimized PI chains were established by the Amorphous Cell module. Geometry optimization of these models was carried out using the smart algorithm with maximum interactions of 50000 steps in the Forcite Module. 50 ps NPT dynamics was then performed to obtain a structure of reasonable density. Then, 400 ps molecular dynamics was performed under the NVT ensemble at 298 K to eliminate internal stress, Finally, 800 ps molecular dynamics under the NPT ensemble at 0.0001 GPa and 298 K was carried out at the initial speed of the previous step to obtain a stable equilibrium density. On this basis, to simulate T_g, temperature scanning was performed to reduce the temperature from 950 to 400 K at 20 K intervals. COMPASS II force field was utilized in the MD simulations.

References

1. T. G. Fox, T. G, Jr, P. J. Flory, *J. Appl. Phys.,* 1950, **21**, 581−591.
2. T. G. Fox, T. G, Jr, P. J. Flory, *J. Phys. Chem. A*, 1951, **55**, 221−234.
3. T. G. Fox, T. G, P. J. Flory, *J. Polym. Sci.*, 1954, **14**, 315−319.

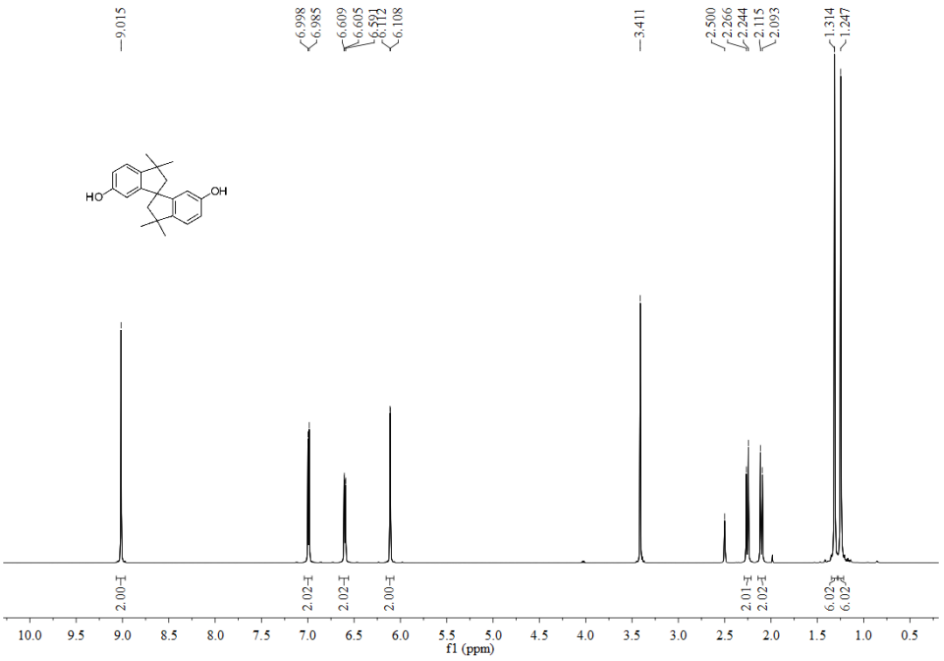


Fig. S1. ^{1}H NMR spectrum of **2** in DMSO-d_6.

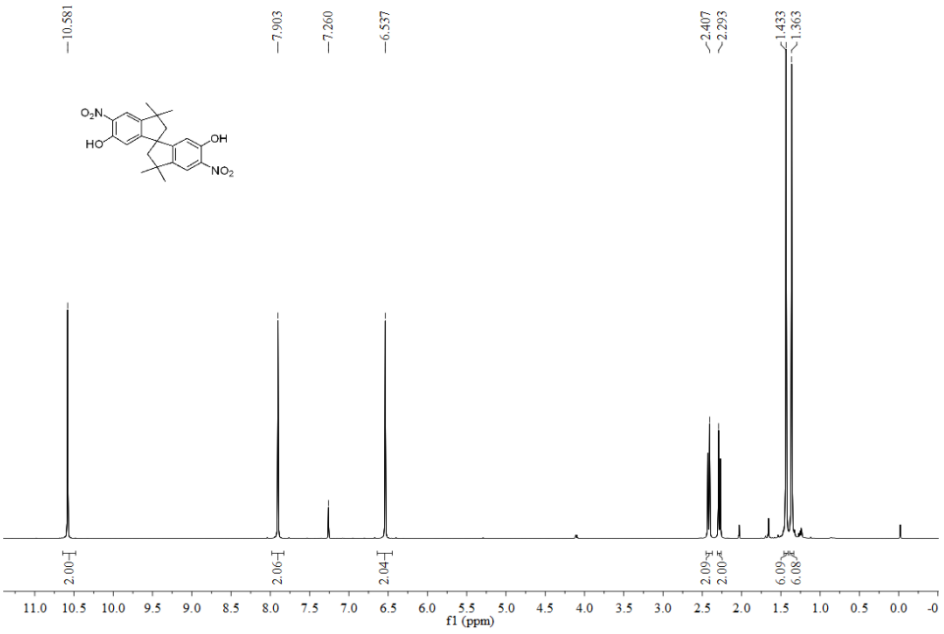


Fig. S2. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

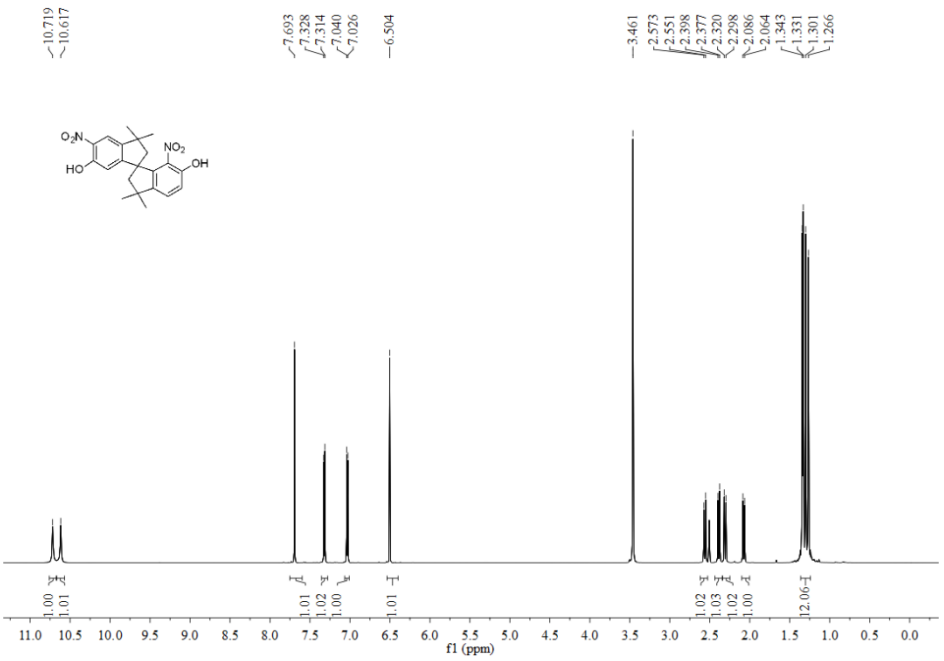


Fig. S3. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

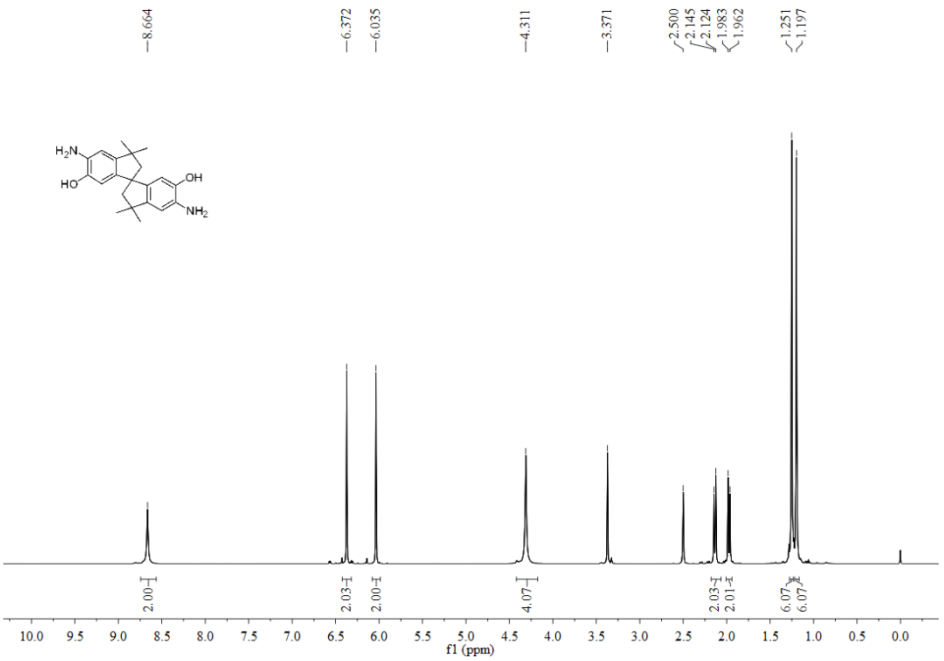


Fig. S4. ^{1}H NMR spectrum of **4a** in DMSO-d_6.

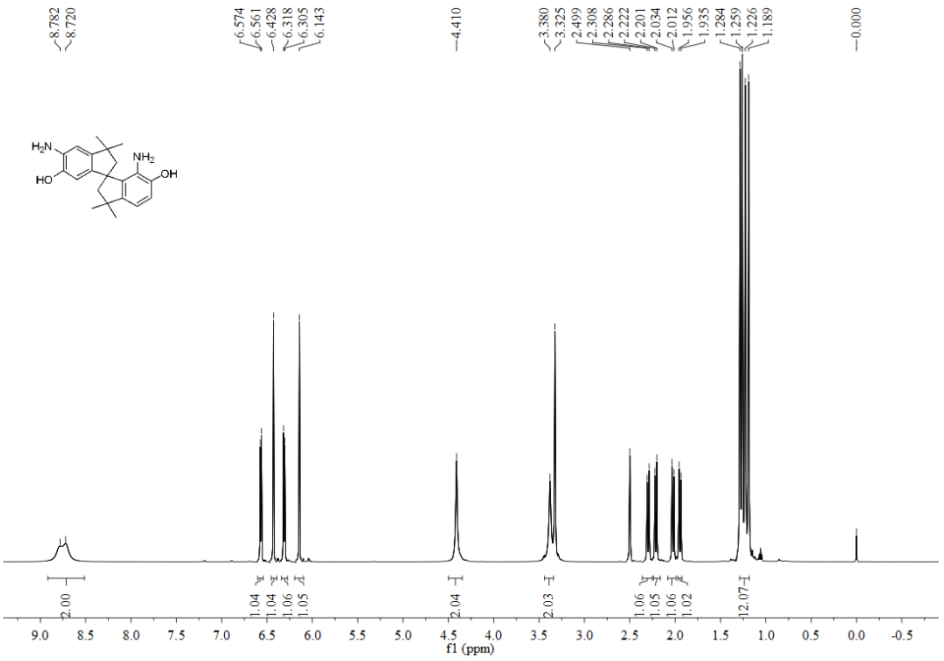


Fig. S5. ^{1}H NMR spectrum of **4b** in DMSO-d_6.

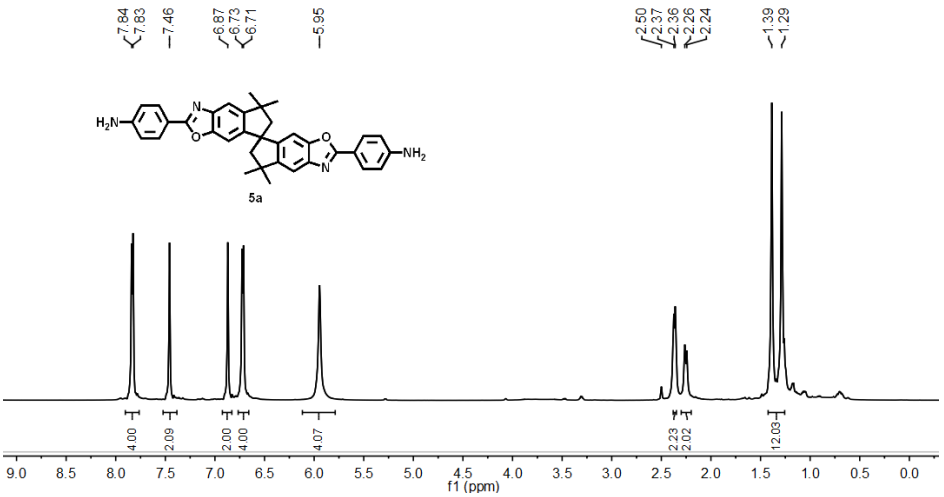


Fig. S6. ^{1}H NMR spectrum of **5a** in DMSO-d_6.

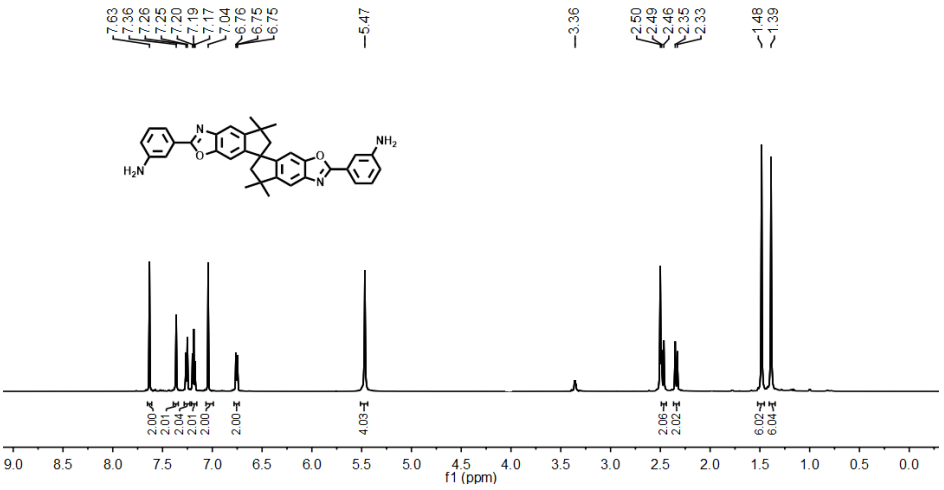


Fig. S7. ^{1}H NMR spectrum of **5aa** in DMSO-d$_6$.

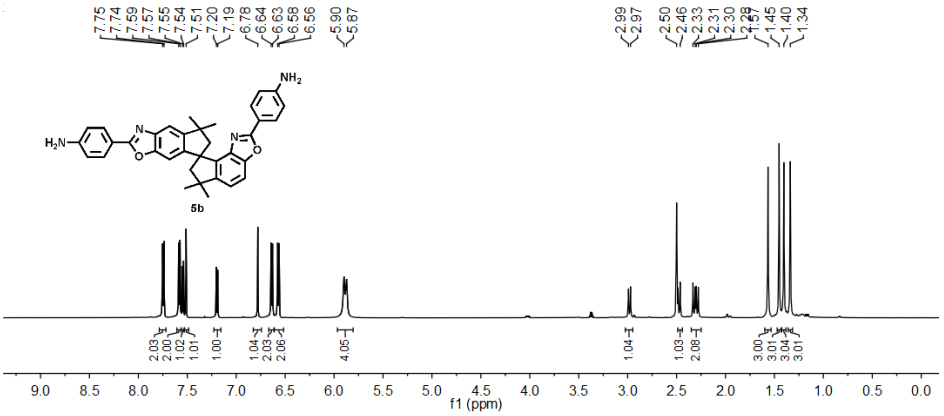


Fig. S8. ^{1}H NMR spectrum of **5b** in DMSO-d$_6$.

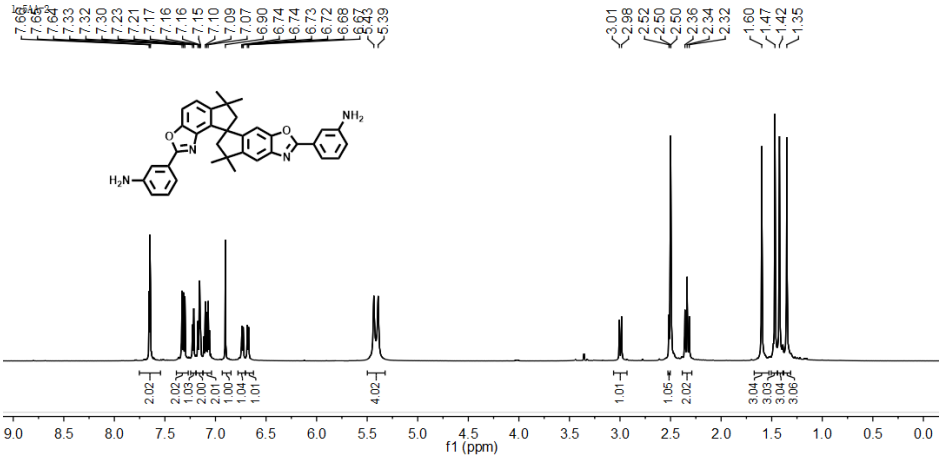


Fig. S9. ^{1}H NMR spectum of **5bb** in DMSO-d$_6$.

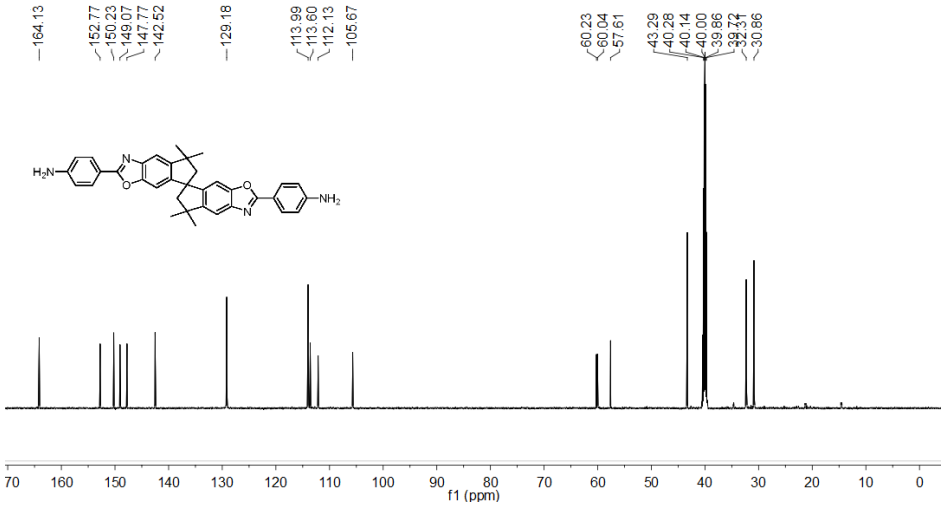


Fig. S10. ^{13}C NMR spectrum of **5a** in DMSO-d$_6$.

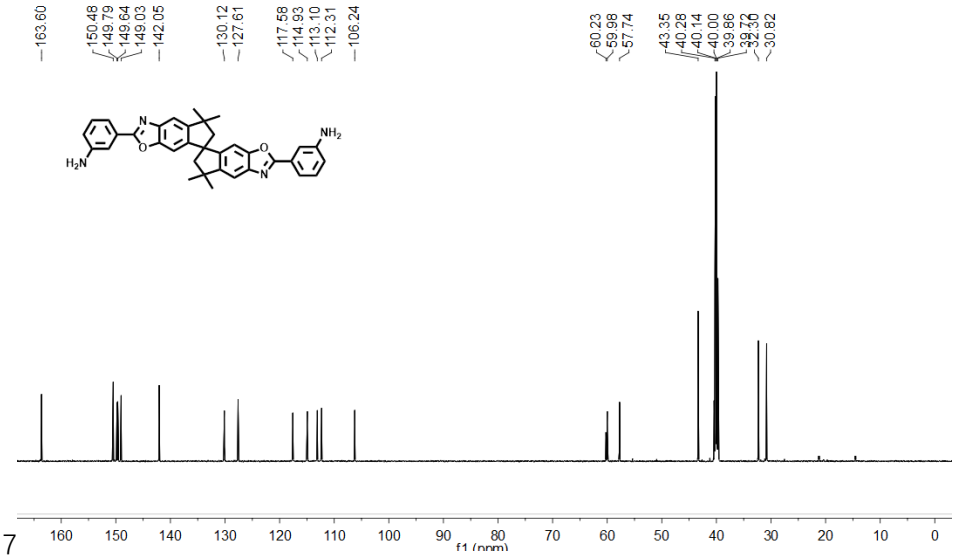


Fig. S11. ^{13}C NMR spectrum of **5aa** in DMSO-d$_6$.

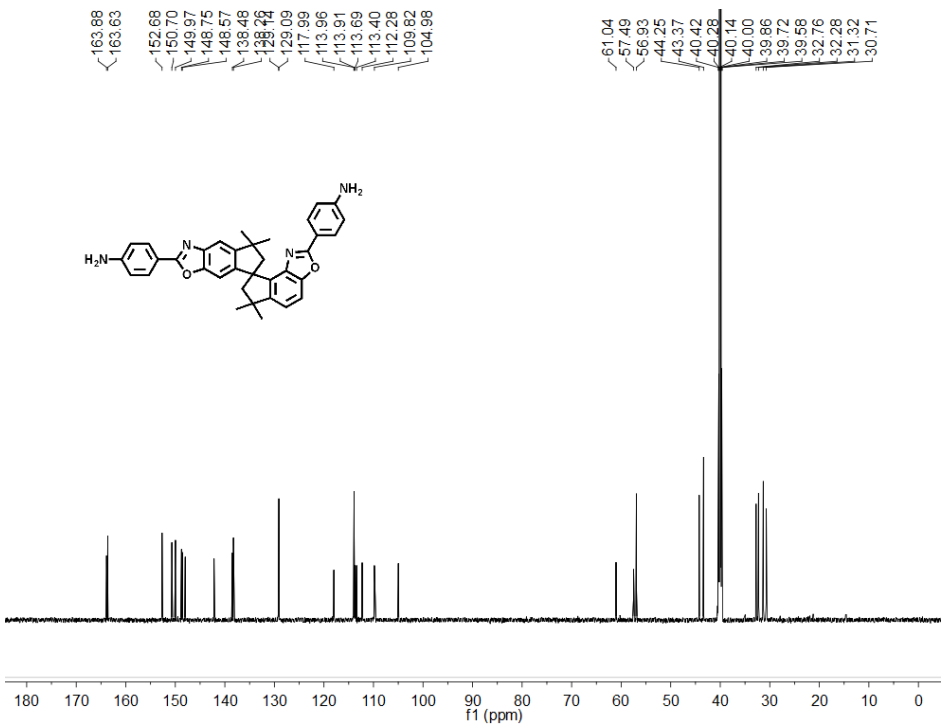


Fig. S12. ^{13}C NMR spectrum of **5b** in DMSO-d$_6$.

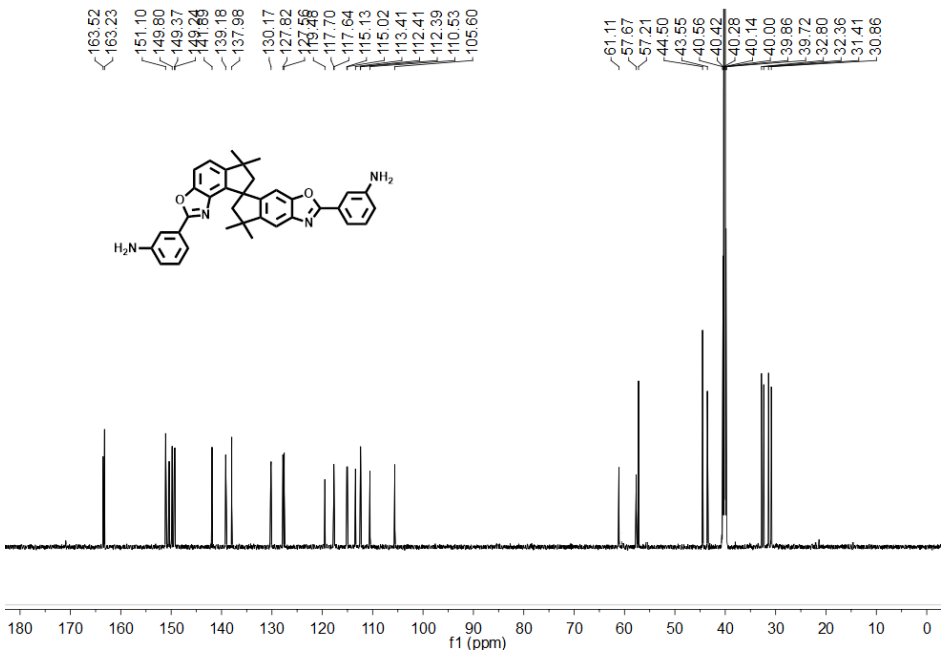


Fig. S13. ^{13}C NMR spectrum of **5bb** in DMSO-d$_6$.

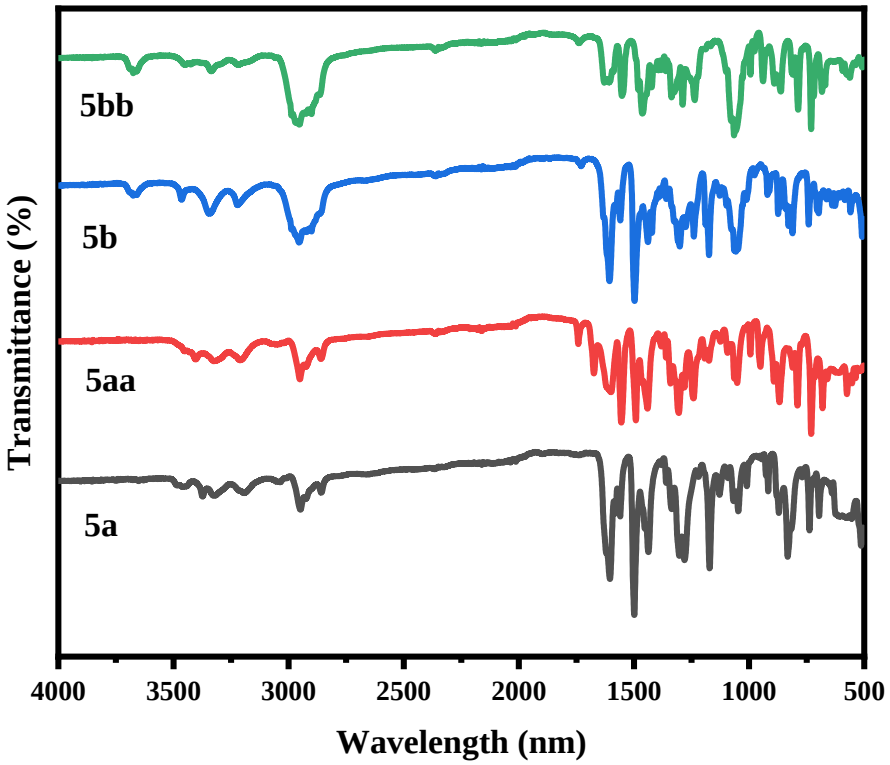


Fig. S14. FTIR spectra of **5a**, **5aa**, **5b** and **5bb**

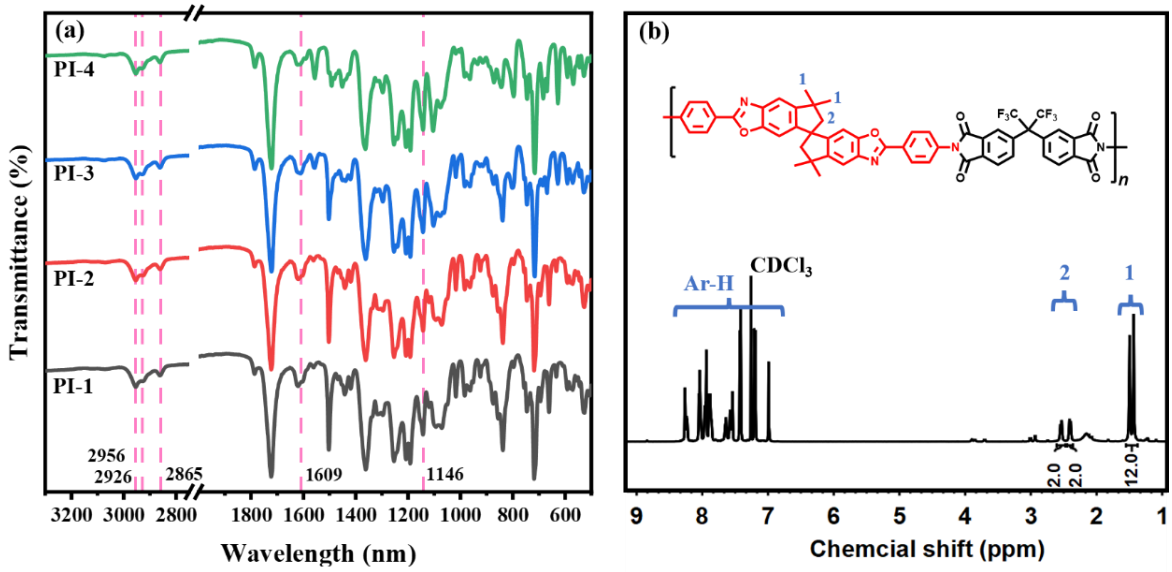


Figure. S15. (a) ATR-FTIR spectra of the PI-1 to PI-4; (b) ^{1}H NMR spectrum of PI-1 ($CDCl_3$).

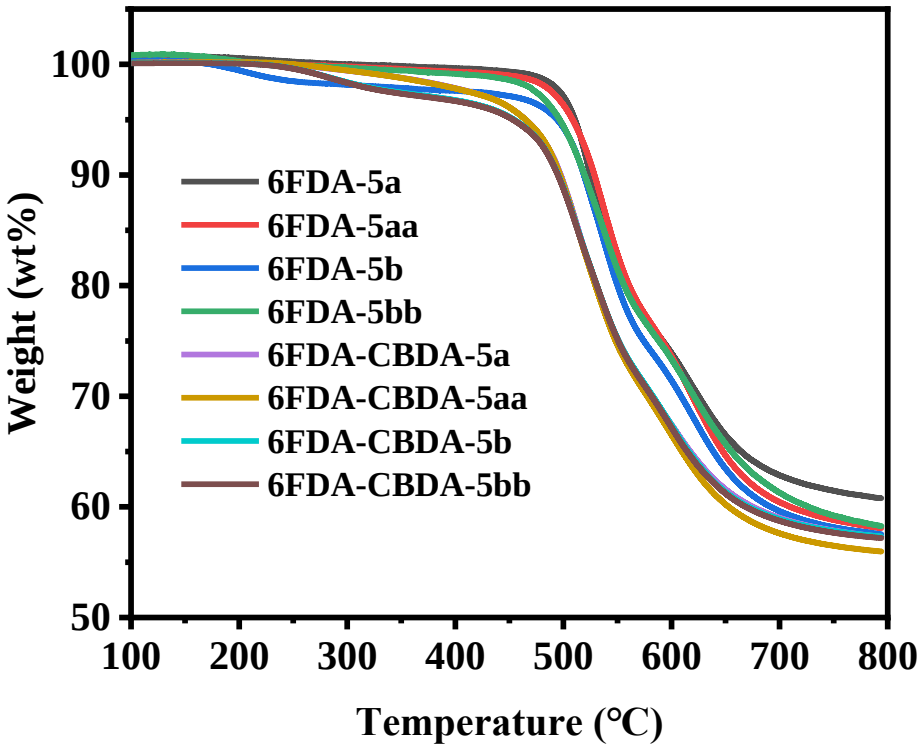


Fig. S16. TGA curves of **PI-1** to **PI-8** films

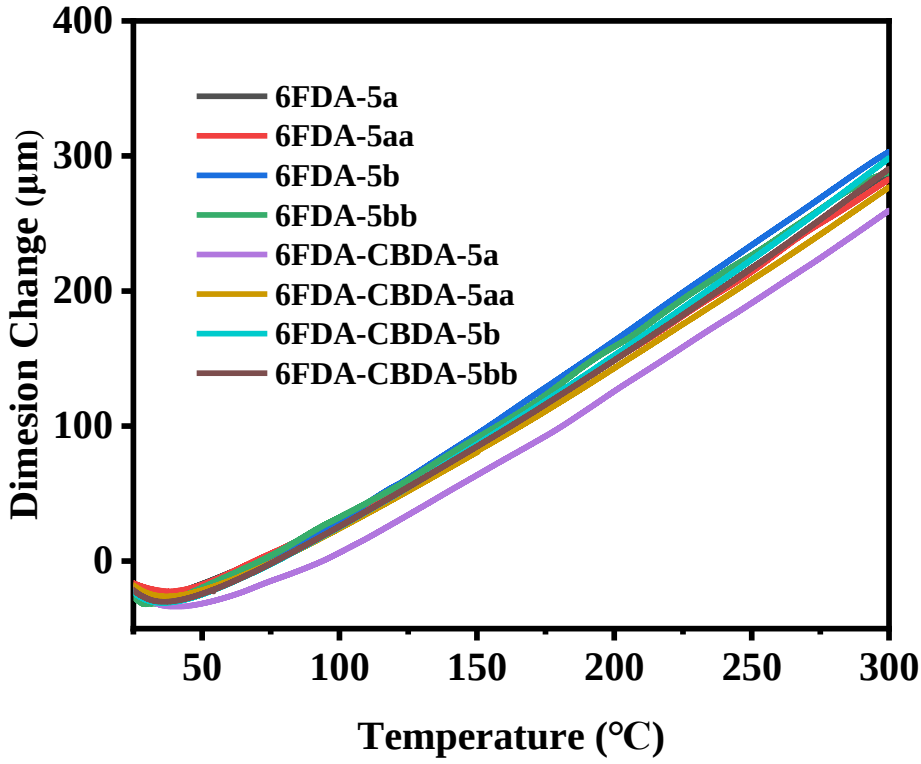


Fig. S17. TMA curves of **PI-1** to **PI-8** films

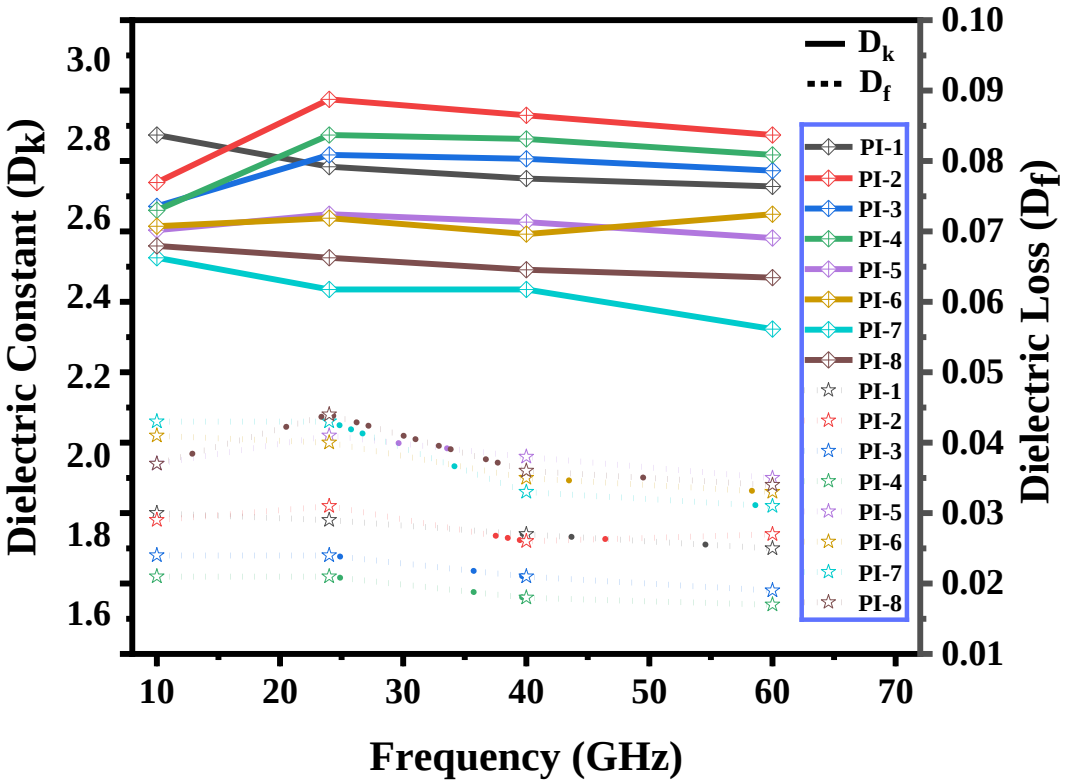


Figure 18. Dielectric constants and dielectric loss of PIs from 10/24/40/60 GHz.

Table. S1. Molecular Weights and PDIs of PAAs

code	polymer	M_n ($\times 10^4$)	M_w ($\times 10^4$)	PDI
PI-1	6FDA-5a	3.5	7.2	2.1
PI-2	6FDA-5aa	4.2	8.0	1.9
PI-3	6FDA-5b	4.2	9.8	2.3
PI-4	6FDA-5bb	5.1	11.4	2.5
PI-5	6FDA-CBDA-5a	4.5	8.7	1.9
PI-6	6FDA-CBDA-5aa	4.1	9.5	2.3
PI-7	6FDA-CBDA-5b	5.0	10.3	2.1
PI-8	6FDA-CBDA-5bb	5.3	10.9	2.0

Table S2. Solubility of poly(spirocyclic bisbenzoxazole-co-imide) fibrous powders[a]

Code	Solvent								
	DMAc	DMF	DMSO	NMP	DCM	$CHCl_3$	THF	Acetone	MeOH
PI-1	++	++	++	++	++	++	++	-	-
PI-2	++	++	++	++	++	++	++	-	-
PI-3	++	++	++	++	++	++	++	-	-
PI-4	++	++	++	++	++	++	++	-	-
PI-5	++	++	++	++	+	+	++	-	-
PI-6	++	++	++	++	+	+	+	-	-
PI-7	++	++	++	++	+	+	+	-	-
PI-8	++	++	++	++	+	+	+	-	-

[a]Key: at room temperature: ++, readily soluble; +, soluble; −, insoluble.