Supporting Information

Colorless Polyimides Derived from Norbornyl Bis-benzocyclobutene-containing Diamines

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Experimental

Materials

1*S*,2*R*,4*S*,5*R*-cyclohexanetetracarboxylic dianhydride (HPMDA) and *cis*-dicyclohexyl-3,3',4,4'-tetracarboxylic dianhydride (4,4'-HBPDA) were obtained from WeiHai Newera Kesense New Matertials Co.,Ltd (Weihai, China). CpODA was kindly provided by ENEOS Corporation (Tokyo, Japan). BTA and 6FDA were purchased from Tokyo Chemical Industry (Tokyo, Japan). All dianhydrides were dried at 150 °C in vacuum for 12 hour before polymerization. All other chemicals were obtained from Aladdin Industrial Corporation (Beijing, China) and used as received.

Monomer Syntheses

CANAL-4

To a flame-dried 100-mL glass tube were charged 3-bromo-2-methylaniline (1.8605 g, 10 mmol), $Pd(OAc)_2$ (0.0225 g, 0.1mmol), Ph_3P (0.0525 g, 0.2 mmol), Cs_2CO_3 (3.2582 g, 10 mmol), and 1,4-dioxane (35 mL). The tube was purged with nitrogen for 10 min, and then NBD (0.4607 g, 5 mmol) was added. Afterwards, the reaction was stirred at 150 °C for 24 h in nitrogen. After cooling to room temperature, the inorganic salts were removed by filtering through a thin Celite layer. The filtrate was concentrated by rotatory evaporation, and the resultant crude product was further purified by silica gel column using ethyl acetate/petroleum ether (1:2, *v*:*v*) as the eluent to afford CANAL-4 as a white solid (0.95 g, yield: 63%). CANAL-4 was a mixture of *syn* and *anti* regioisomers and used for most CPI synthesis without separation of the two isomers. M.P.: 176-185 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.52 (dd, *J* = 7.6, 3.2 Hz, 2H), 6.42 (d, *J* = 7.6 Hz, 2H), 4.57 (s, 4H), 3.10 (d, *J* = 3.5 Hz, 2H), 2.92 (d, *J* = 3.5 Hz, 2H), 2.16 (t, 2H), 1.88 (d, *J* = 7.4 Hz, 6H), 0.62 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.3, 145.1, 133.0, 120.1, 116.2, 114.2, 47.7, 47.6, 47.3, 47.2, 38.0, 36.9, 35.9, 26.4, 12.3, 12.2.

For comparison, *anti*-CANAL-4 and *syn*-CANAL-4 were isolated by column chromatography using a mixture of ethyl acetate and petroleum ether (1:5, *v*:*v*). *Anti*-CANAL-4: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (d, *J* = 7.6 Hz, 2H), 6.53 (d, *J* = 7.6 Hz, 2H), 3.50 (s, 4H), 3.16 (d, *J* = 4.0 Hz, 2H), 3.12 (d, *J* = 3.6 Hz, 2H), 2.29 (s, 2H), 2.01 (s, 6H), 0.77 (s, 2H).

Syn-CANAL-4: ^{1}H NMR (400 MHz, $CDCl_3$) δ6.69 (d, *J* = 7.6 Hz, 2H), 6.56 (d, *J* = 7.6 Hz, 2H), 3.50 (s, 4H), 3.20 (d, *J* = 4.0 Hz, 2H), 3.13 (d, *J* = 4 Hz, 2H), 2.34 (s, 1H), 2.26 (s, 1H), 2.05 (s, 6H), 0.80 (s, 2H).

CANAL-2

CANAL-2 was prepared using an analogous procedure to CANAL-4, using 3-bromo-2,6-dimethylaniline as the starting material instead of 3-bromo-2-methylaniline. A mixture of *syn* and *anti* regioisomers was also obtained with a yield of 73%. M.P.: 185-195 °C. ^{1}H NMR (400 MHz, DMSO-d6) δ 6.46 (s, 2H), 4.27 (s, 4H), 3.06 (d, *J* = 3.5 Hz, 2H), 2.97 (d, *J* = 3.5 Hz, 2H), 2.13 (s, 2H), 2.01 (s, 6H), 1.90 (s, 6H), 0.58 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 143.9, 142.9, 142.8, 132.9, 132.8, 121.4, 120.6, 115.6, 47.8, 47.7, 47.6, 47.5, 37.9, 37.0, 36.0, 26.4, 19.0, 12.6, 12.5.

CPI syntheses

The CPIs were prepared *via* a conventional one-step method in *m*-cresol with equal molar amounts of diamines and dianhydrides. A typical procedure is explained as follows: CANAL-4 (0.3024 g, 1 mmol), HPMDA (0.2242 g, 1 mmol), and *m*-cresol (3 mL) were charged into a 20-mL three-necked flask equipped with a mechanical stirrer. The mixture was stirred at 80 °C for 4 h and then at 180 °C for 13 h under nitrogen. The resulting solution was precipitated into ethanol (20 mL). The fibrous polymer was collected by filtration, Soxhlet extracted with ethanol for 24 h, and dried in vacuum at 120 °C for 12 h to afford HPMDA-CANAL-4 as an off-white solid (0.49 g, yield: 94%).

Film preparation

CPI films were cast from their *N*-methylpyrrolidone (NMP) or *m*-cresol solution (5 wt%). The solutions were filtered to remove impurities, and then cast onto glass substrates. The solvent was evaporated by heating in a conventional oven at 80 °C for 8 h, and then at 250 °C in vacuum for 2 h. The films were peeled off through immersing in warm water, and the film thickness was 20–30 μm.

Characterization

^{1}H and ^{13}C NMR spectra were obtained from a Bruker DPX 400 instrument using DMSO-d_6 or $CDCl_3$ as the solvents. Melting points were measured with a Q2000 differential scanning calorimetry (TA Instruments) from 23 to 250 °C with a heating rate of 5 °C min^{-1}. Fourier transform infrared (FTIR) spectra were obtained using an Agilent Cary 660 spectrometer. Gel permeation chromatography (GPC) was performed on a HLC-

8420 instrument (Tosoh Co.) equipped with a dynamic light scattering detector, using *N,N*-dimethylformamide (DMF) as the eluent at a flowrate of 0.3 mL min^{-1}. Tensile properties were measured using an Instron material testing system (Model 5982) with a constant displacement rate of 2.0 mm min^{-1}. Thermogravimetric analysis (TGA) was carried out using a TGA Q55 system (TA Instruments) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Dynamic mechanical thermal analysis (DMA) was performed on a Q850 DMA (TA Instruments) in tension mode with a frequency of 1 Hz and a heating rate of 5 °C min^{-1} from 40 to 490 °C. CTE was measured using a thermo-mechanical analyzer (Netzsch, TMA 402F1/F3) at a heating rate of 5 °C min^{-1} in the range 100 - 200 °C. Wide-angle X-ray diffraction (WAXD) was conducted on a Bruke D8 instrument utilized with Cu Kα radiation of wavelength (λ) 1.54 Å. The *d*-spacing values were calculated according to Brag's law ($d = n\lambda/2\sin\theta$). UV-vis spectra were recorded on a Perkin Elmer Lambda 950 spectrometer in transmittance mode in the wavelength range of 200–800 nm. Color intensity was evaluated using CHN Spec CS-820N spectrophotometer with an observational angle of 10° and CIE (Commission International del'Eclairage) standard D65 illuminant.

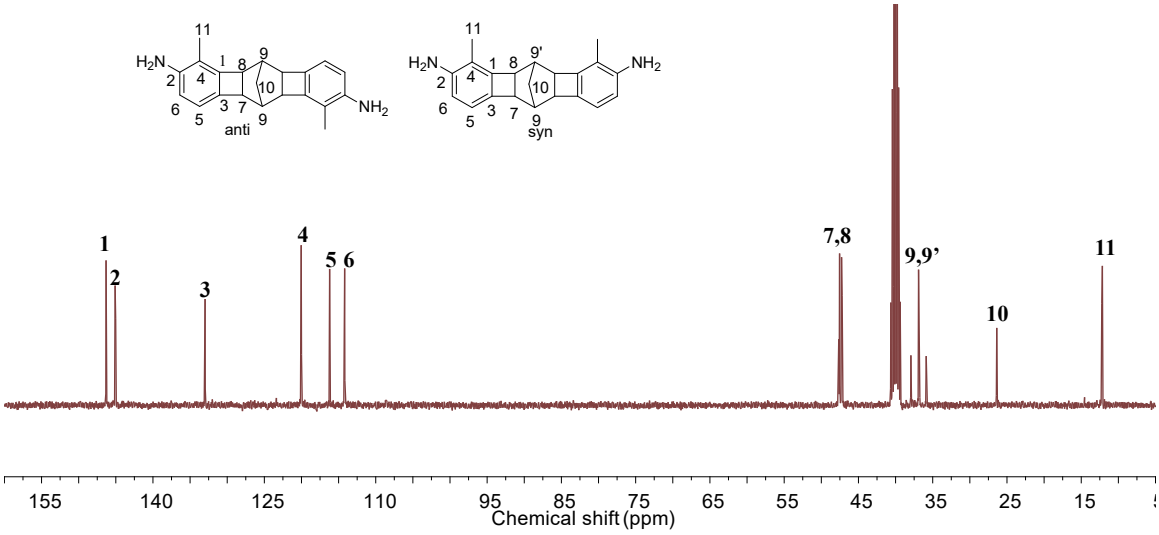


Figure S1. ^{13}C NMR spectrum of CANAL-4

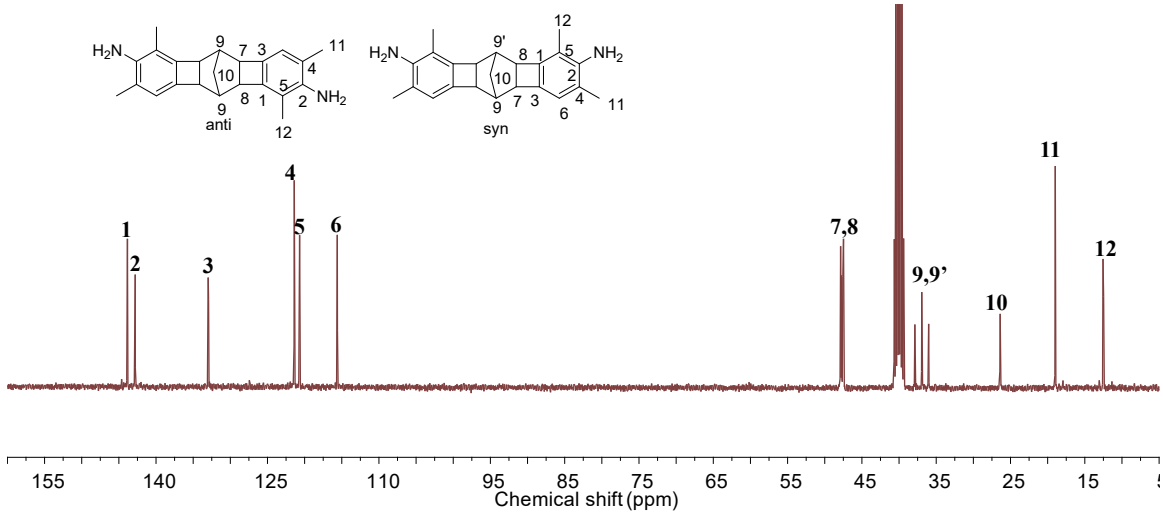


Figure S2. ^{13}C NMR spectrum of CANAL-2

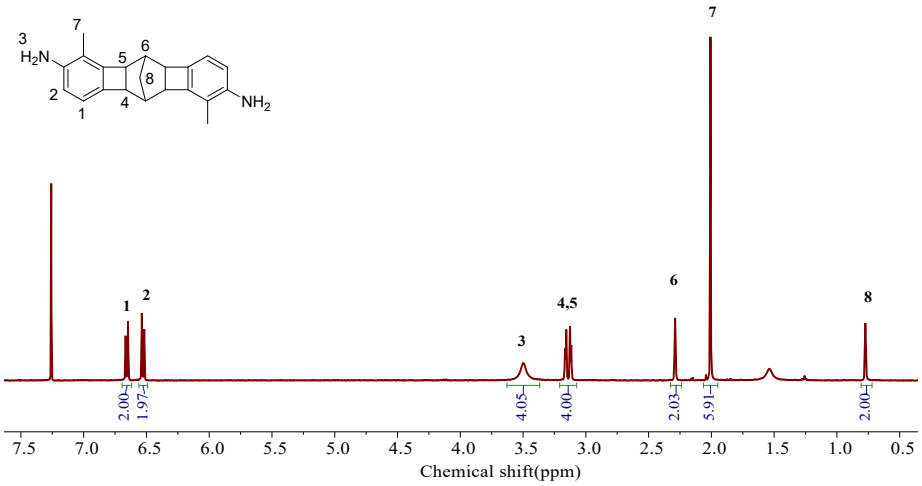


Figure S3. ^{1}H NMR spectrum of *anti*-CANAL-4

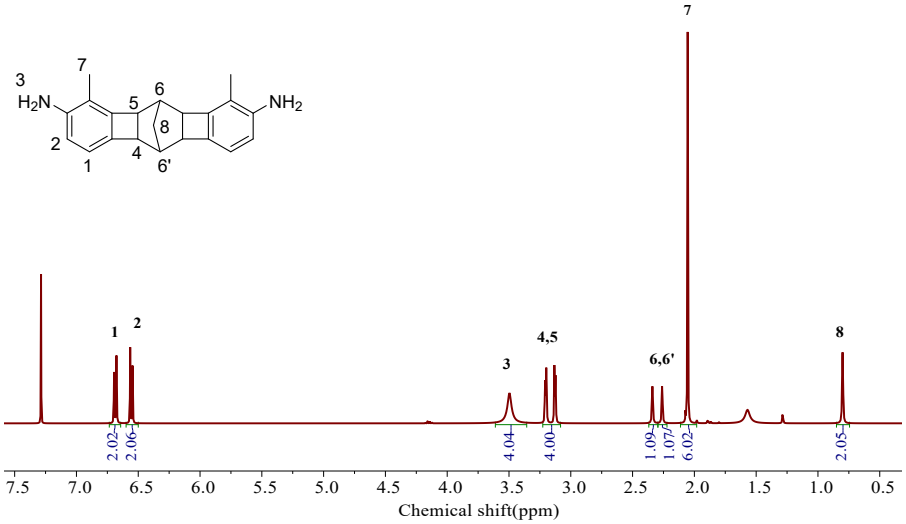


Figure S4. ^{1}H NMR spectrum of *syn*-CANAL-4

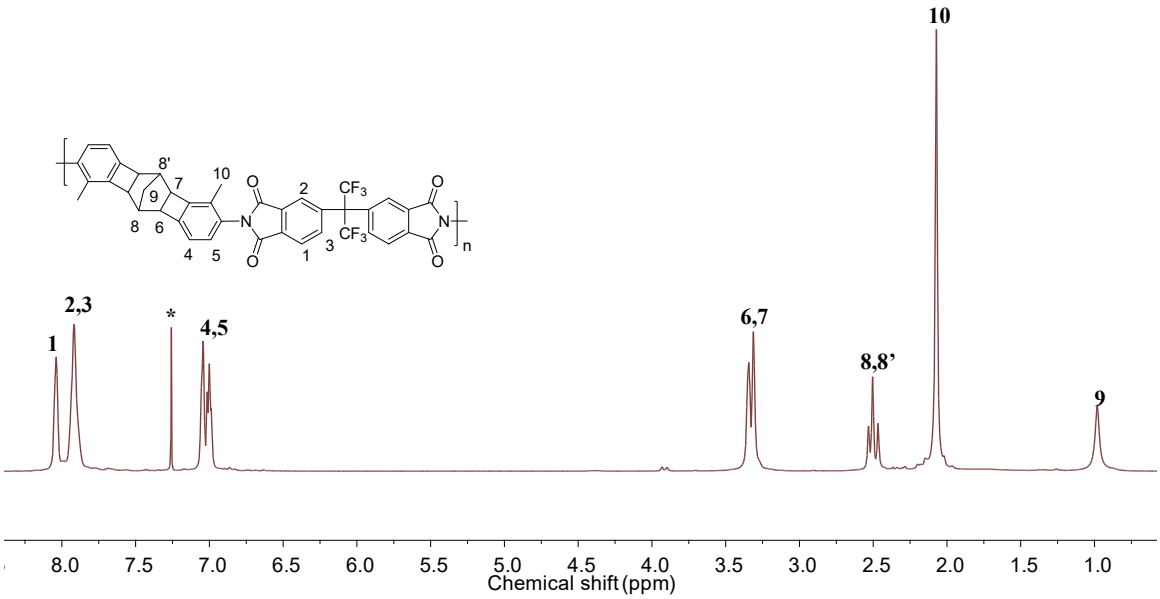


Figure S5. ^{1}H NMR spectrum of 6FDA-CANAL-4

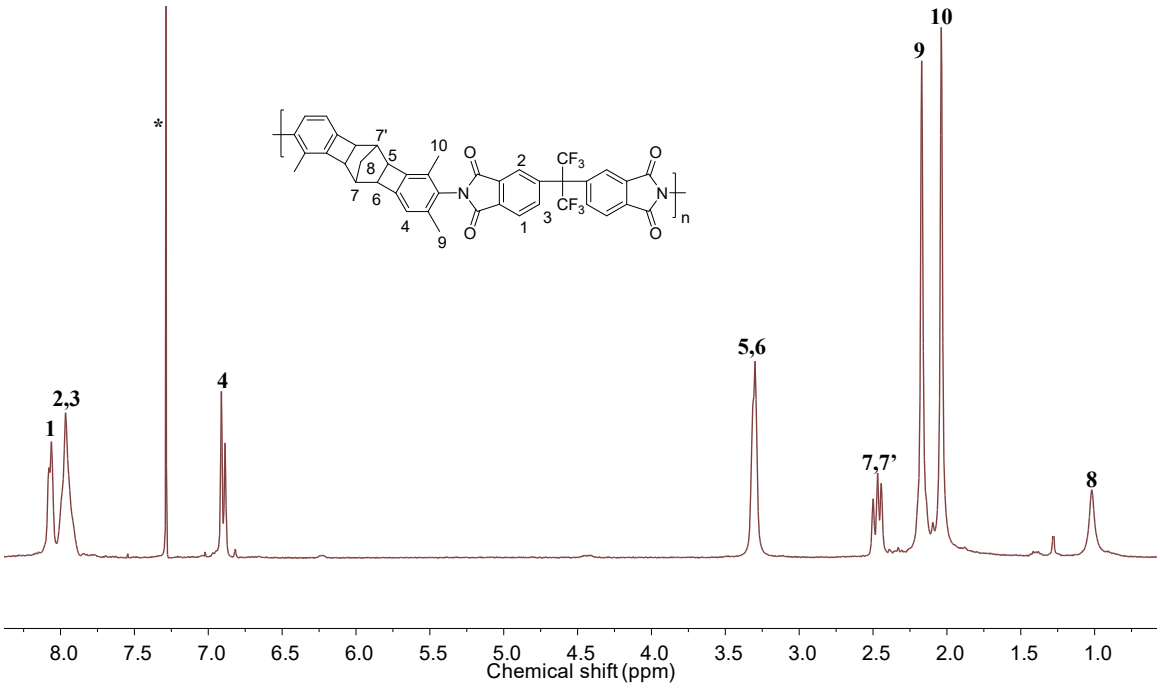


Figure S6. ^{1}H NMR spectrum of 6FDA-CANAL-2

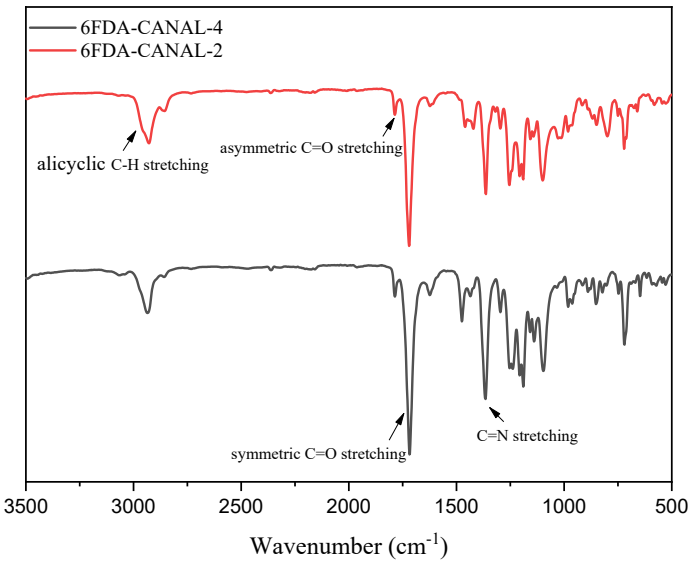


Figure S7. Representative FT-IR spectra of N2BC-containing CPIs

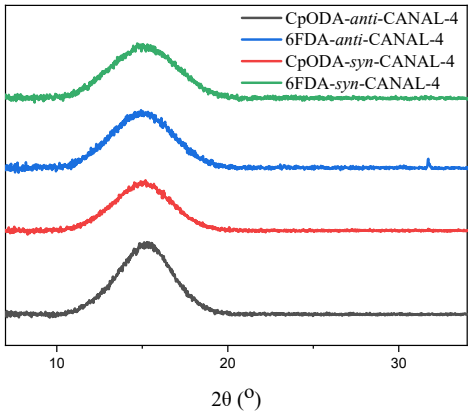


Figure S8. WAXD patterns of N2BC-containing CPIs from pure regioisomers

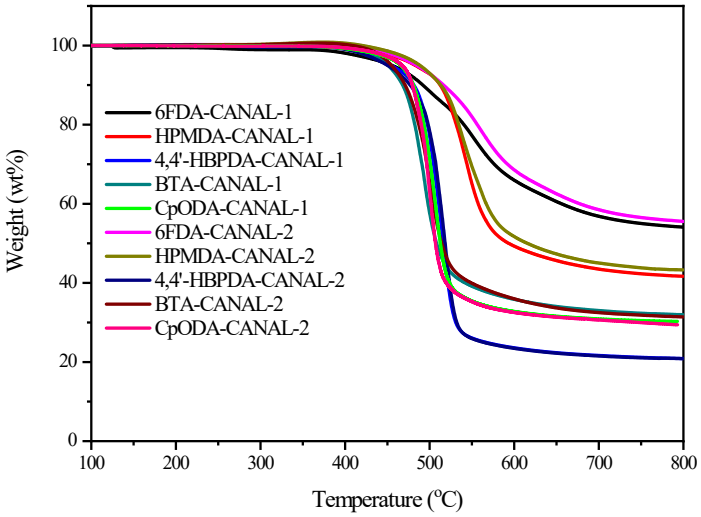


Figure S9. TGA curves of N2BC-containing CPIs

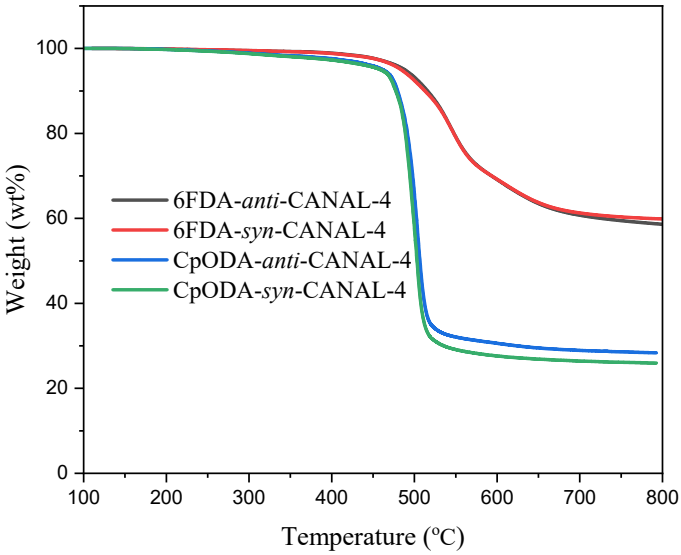


Figure S10. TGA curves of N2BC-containing CPIs from pure regioisomers

HPMDA-CANAL-4 HBPDA-CANAL-4

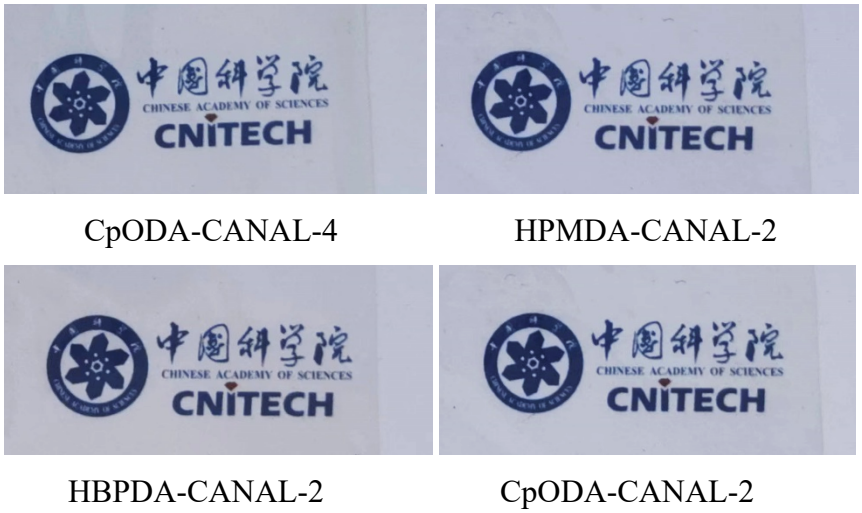
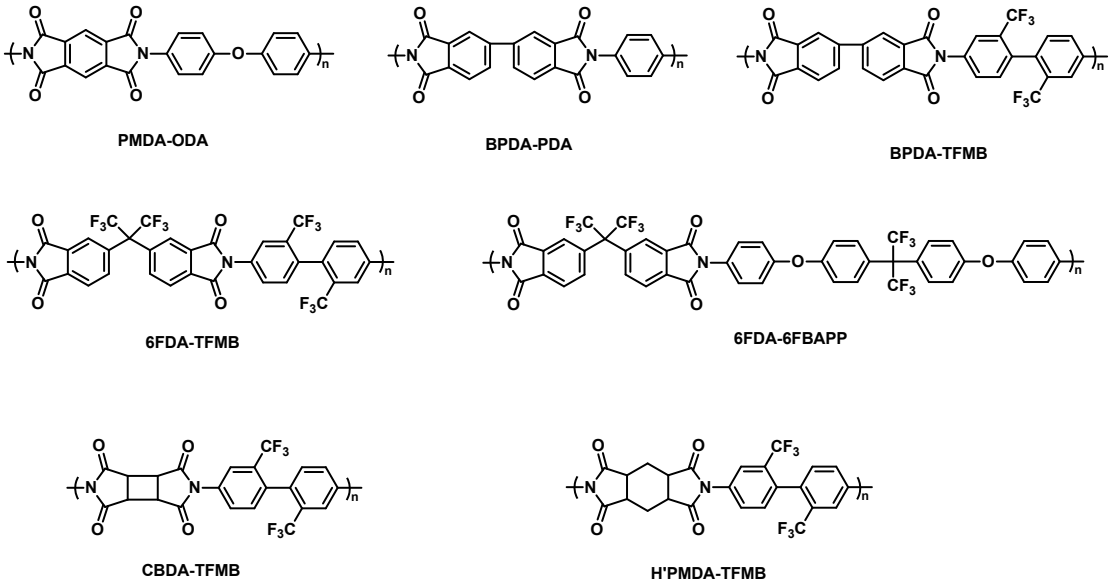


Figure S11. Images of representative N2BC-containing CPIs



Scheme S1. Structures of comparative polyimides (Yellow polyimides: PMDA-ODA and BPDA-PDA; Aromatic CPIs: 6FDA-TFMB, BPDA-TFMB, and 6FDA-6FBAPP; Semi-aromatic CPIs: CBDA-TFMB and H'PMDA-TFMB)

Table S1. Molecular weights and solubility of N2BC-containing CPIs

Polyimides	M_n (kg mol^{-1})	PDI	Solubility					
			m-Cresol	DMF	DMAc	NMP	$CHCl_3$	THF
6FDA-CANAL-4	28	2.88	+	+	+	+	+	+
6FDA-*anti*-CANAL-4	202	1.54	+	+	+	+	+	+
6FDA-*syn*-CANAL-4	157	1.48	+	+-	+	+	+	+-
HPMDA-CANAL-4	62	2.12	+	+	+	+	+	+-
HBPDA-CANAL-4	42	2.91	+	+	+	+	+	+-
BTA-CANAL-4	71	1.89	+	+	+	+	+-	+-

CpODA-CANAL-4	-[a]	-[a]	+	-	+-	+	+	-
CpODA-*anti*-CANAL-4	-[a]	-[a]	+	-	-	+	+	-
CpODA-*syn*-CANAL-4	-[a]	-[a]	+	-	+	+	+	-
6FDA-CANAL-2	63	2.17	+	+	+	+	+	+
HPMDA-CANAL-2	22	2.23	+	+	+	+	+	+-
HBPDA-CANAL-2	46	1.99	+	+	+	+	+	+-
BTA-CANAL-2	52	2.13	+	+	+	+	+-	+
CpODA-CANAL-2	42	2.03	+	+-	+-	+	+	+

[a]: Not measured due to poor solubility in DMF. +: Soluble at room temperature, +-: Partially soluble or swelling, -: Insoluble.