Alicyclic Polyimides with Large Bandgap Exhibiting Superior High-Temperature Capacitive Energy Storage

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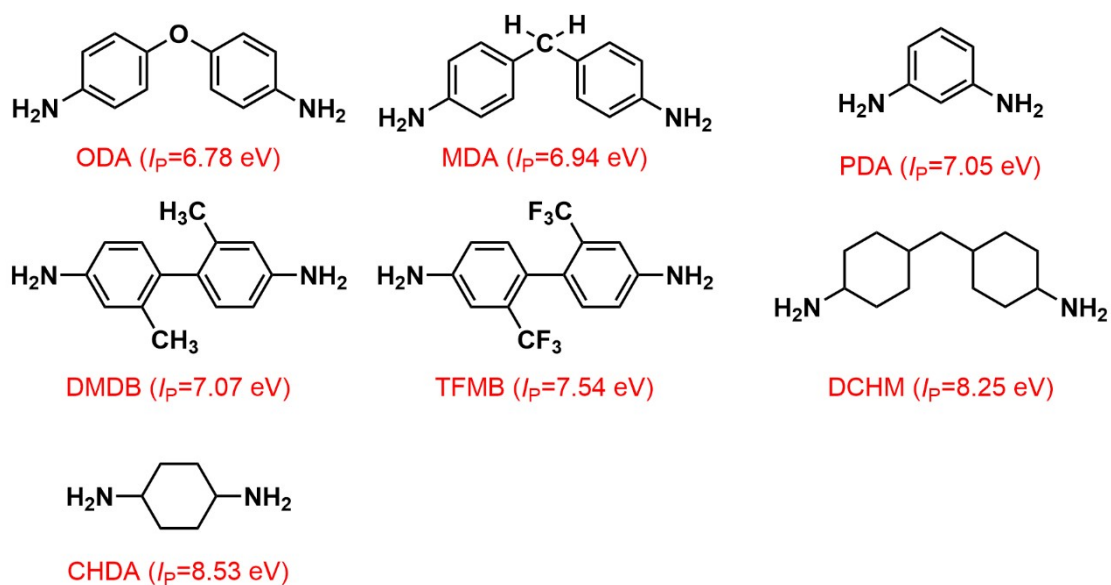
1. DFT calculation

Figure S1. Structures of diamines and their ionization potentials (I_P) calculated by the density functional theory at the B3LYP/6-311G(d,p) level.
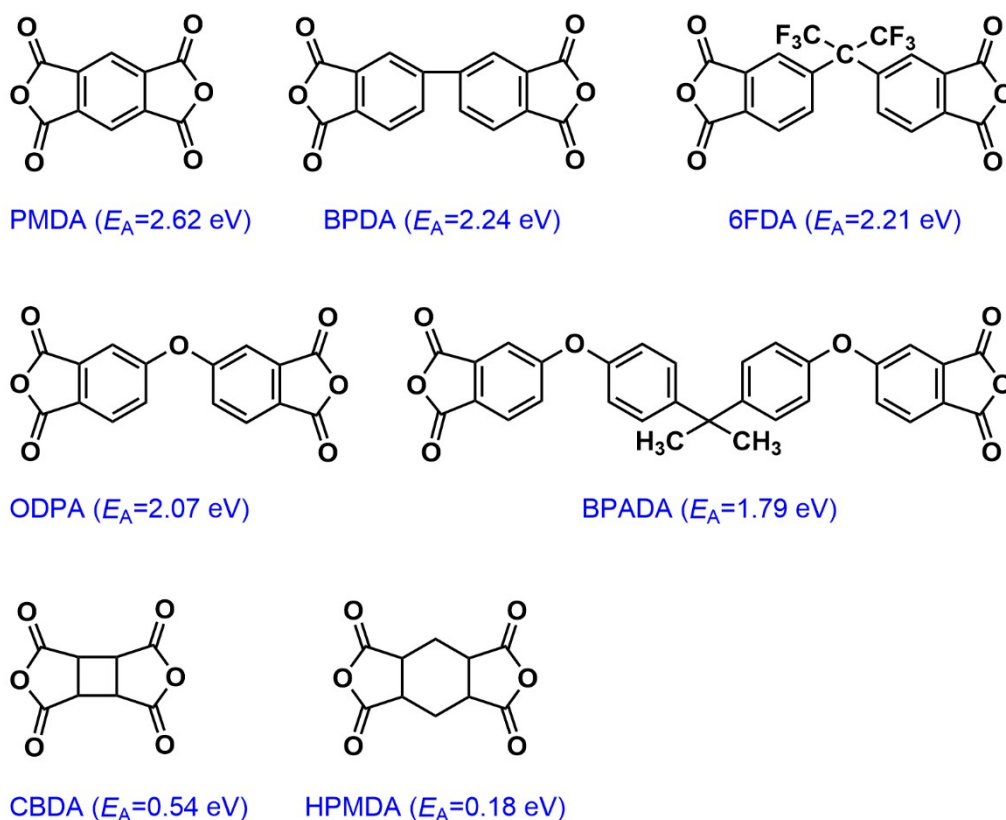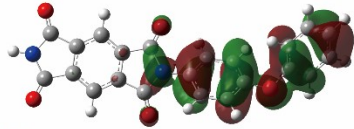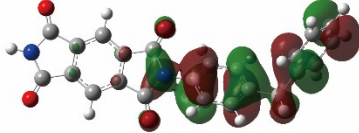

Figure S2. Structures of dianhydrides and their electron affinities (E_A) calculated by the density functional theory at the B3LYP/6-311G(d,p) level.
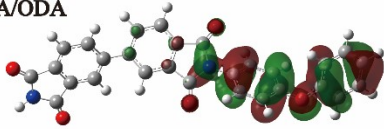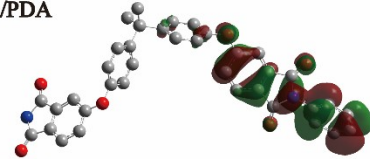
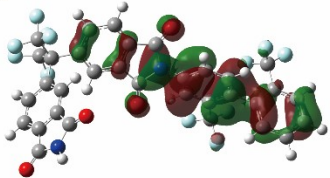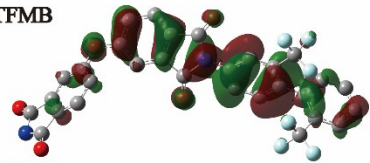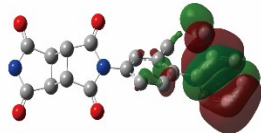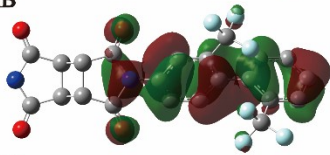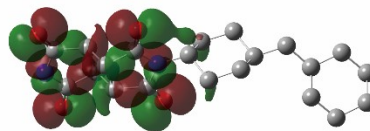PMDA/ODA   HOMO   LUMO
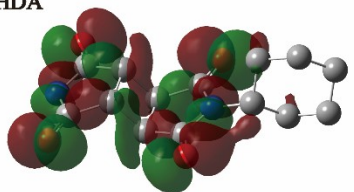
PMDA/MDA

BPDA/ODA

BPADA/PDA

6FDA/TFMB

ODPA/TFMB

CBDA/DMDB

CBDA/TFMB
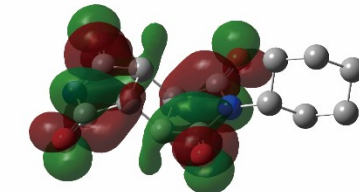
CBDA/DCHM

CBDA/CHDA
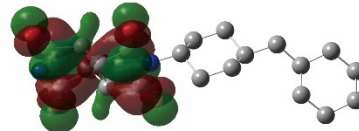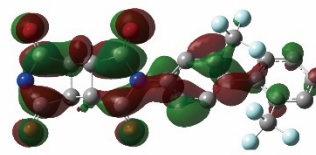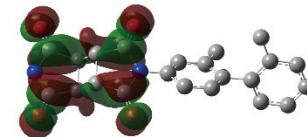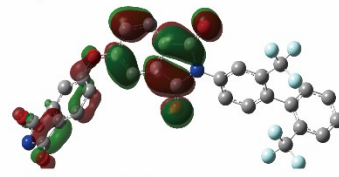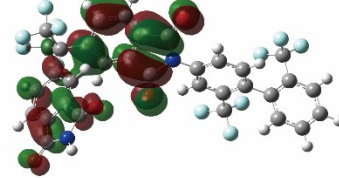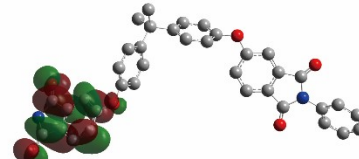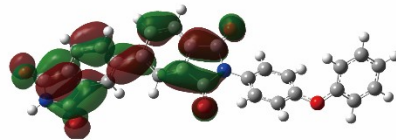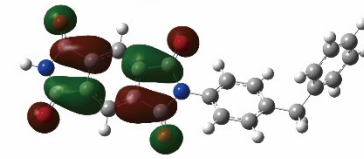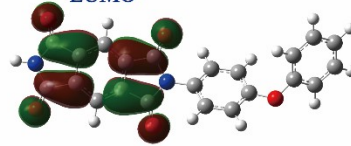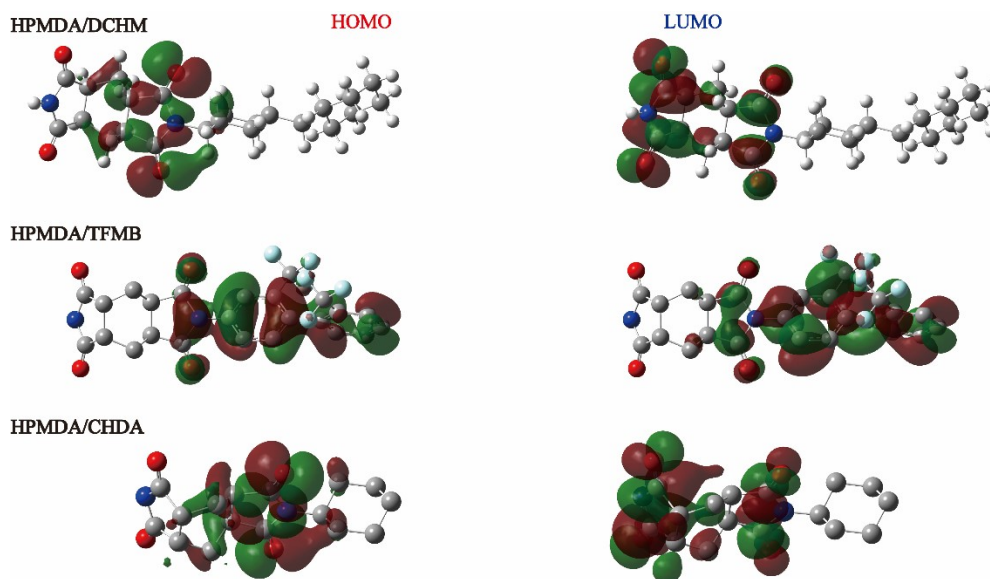
Figure S3. Spatial distributions of the HOMO (left-hand side) and LUMO (right-hand side) of PI model compounds.

Table S1. Summarization of the HOMO (E_{HOMO}) and LUMO (E_{LUMO}) energy levels of PI model compounds, and the ionization potential (I_{P}) and electron affinity (E_{A}) of the diamine and dianhydride monomers, respectively.

PI model	E_{HOMO}/eV	E_{LUMO}/eV	I_{P}/eV	E_{A}/eV
PMDA/ODA	-6.29	-3.48	6.78	2.62
PMDA/MDA	-6.64	-3.42	6.94	2.62
BPDA/ODA	-6.16	-2.95	6.78	2.24
ODPA/TFMB	-6.96	-2.83	7.54	2.07
BPADA/PDA	-6.52	-2.44	7.05	1.79
6FDA/TFMB	-7.08	-3.08	7.54	2.21
CBDA/DMDB	-6.79	-1.45	7.07	0.54
CBDA/TFMB	-7.29	-1.76	7.54	0.54
CBDA/DCHM	-7.46	-1.46	8.25	0.54
CBDA/CHDA	-7.48	-1.47	8.53	0.54
HPMDA/DCHM	-7.33	-1.16	8.25	0.18
HPMDA/TFMB	-7.17	-1.60	7.54	0.18
HPMDA/CHDA	-7.34	-1.16	8.53	0.18

2. Inherent viscosity

The molecular weights of the CBDA/TFMB and CBDA/DCMH were indirectly characterized by measuring the inherent viscosity of their corresponding PAA solution, since they are insoluble in common solvents. The inherent viscosity of the as-prepared PAA solutions (0.5 g/dL) was measured by using a Ubbelohde viscometer at 30 °C and calculated as:

$$\eta_{inh} = \ln(t/t_0)/C$$

where t_0 and t are the outflow time of the pure solvent and PAA solution with a concentration of 0.5 g/dL, respectively.[1]

Table S2. Inherent viscosity of various PAA solutions

PAA type	η_{inh}	Film-forming properties
CBDA/TFMB	2.02 dL g^{-1}	Good
CBDA/DCHM	1.54 dL g^{-1}	Good
CBDA/CHDA	0.36 dL g-1	Brittle
HPMDA/DCHM	0.40 dL g-1	Brittle
HPMDA/TFMB	0.40 dL g-1	Brittle
HPMDA/CHDA	0.39 dL g-1	Brittle

The inherent viscosities of the prepared CBDA/TFMB and CBDA/DCHM are larger than 1 dL g^{-1}, indicating that flexible PI films can be successfully obtained according to previous literature.[2]
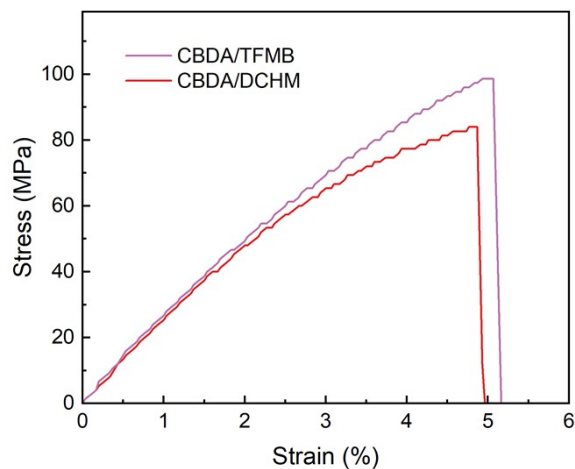
3. Mechanical properties

Figure S4. Stress-strain curves of CBDA/TFMB and CBDA/DCHM films.
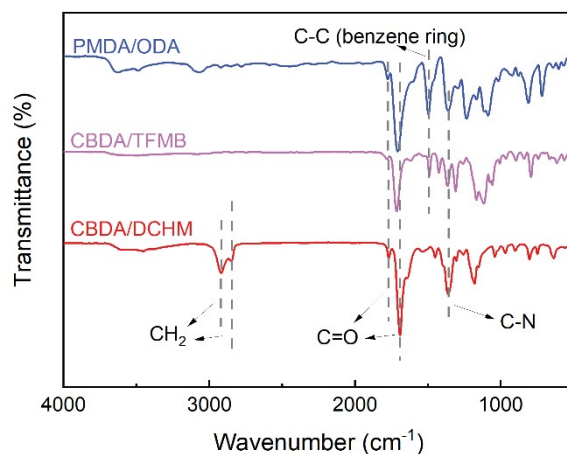
4. FT-IR and UV-Vis spectroscopy

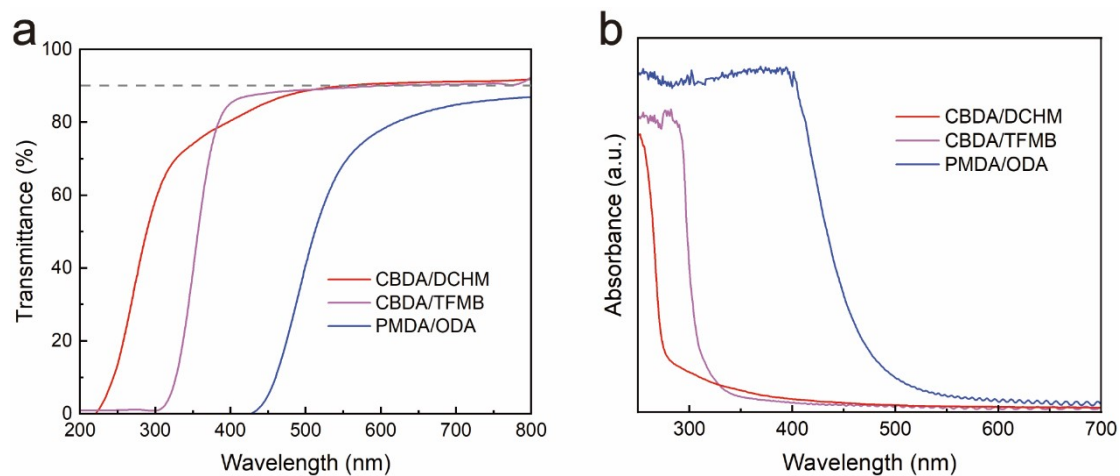**Figure S5.** FT-IR spectra of PMDA/ODA, CBDA/TFMB, and CBDA/DCHM films.

Figure S6. (a) UV-Vis transmission and (b) absorption spectra of PMDA/ODA,

CBDA/TFMB, and CBDA/DCHM films.
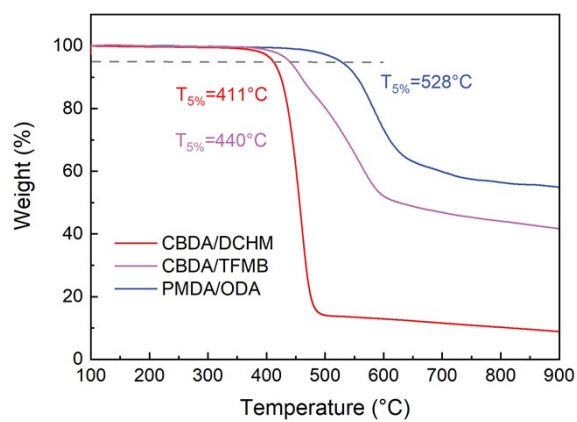
5. Thermal properties

Figure S7. TGA curves of PMDA/ODA, CBDA/TFMB and CBDA/DCHM measured in a nitrogen atomosphere at a heating rate of 10 ℃/min.
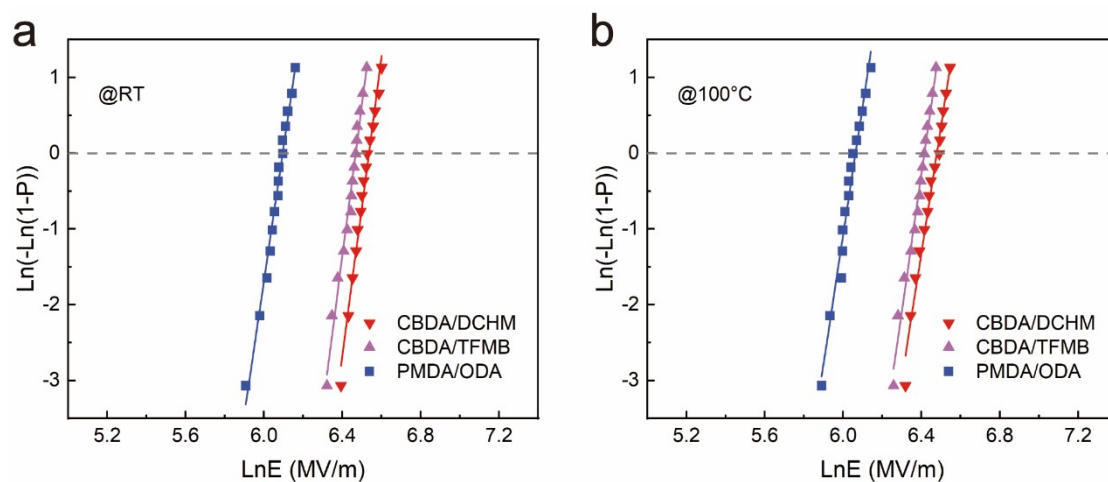
6. Electrical properties

Figure S8. Weibull statistic of dielectric breakdown strength of CBDA/DCHM, CBDA/TFMB, and PMDA/ODA at (a) room temperature and (b) 100 ℃.

Table S3. Weibull statistic parameters of CBDA/DCHM, CBDA/TFMB, and PMDA/ODA

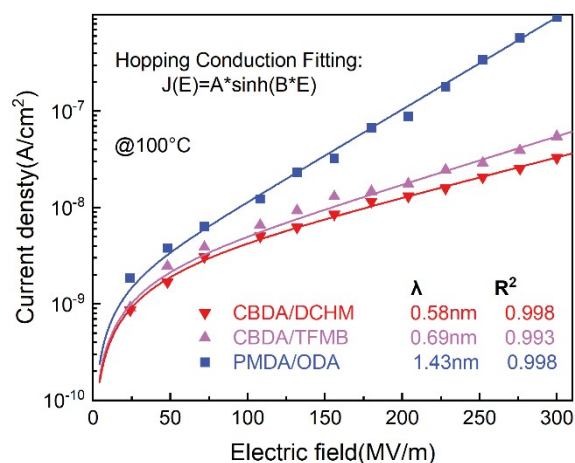| Temperature (°C)	Polyimide film	E_b (MV/m)	β
RT	PMDA/ODA	446	18
	CBDA/TFMB	645	20
	CBDA/DCHM	692	20
100 ℃	PMDA/ODA	428	17
	CBDA/TFMB	608	18
	CBDA/DCHM	652	17
150 ℃	PMDA/ODA	307	9
	CBDA/TFMB	556	13
	CBDA/DCHM	620	12
200 ℃	PMDA/ODA	270	6
	CBDA/TFMB	497	9
	CBDA/DCHM	605	10

Figure S9. Leakage current density of CBDA/DCHM, CBDA/TFMB, and PMDA/ODA as a function of electric field at 100 °C. Solid lines are the fitting of the hopping conduction model.
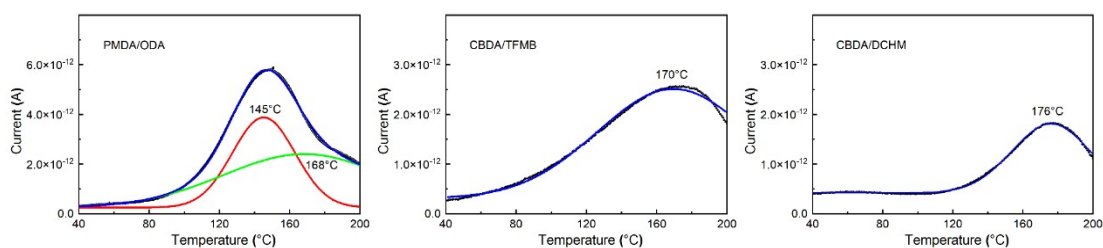

Figure S10. Gaussian fitting of the TSDC spectra of PMDA/ODA, CBDA/TFMB, and CBDA/DCHM.

Table S4. Charge trap parameters of PMDA/ODA, CBDA/TFMB, and CBDA/DCHM derived from the TSDC spectra

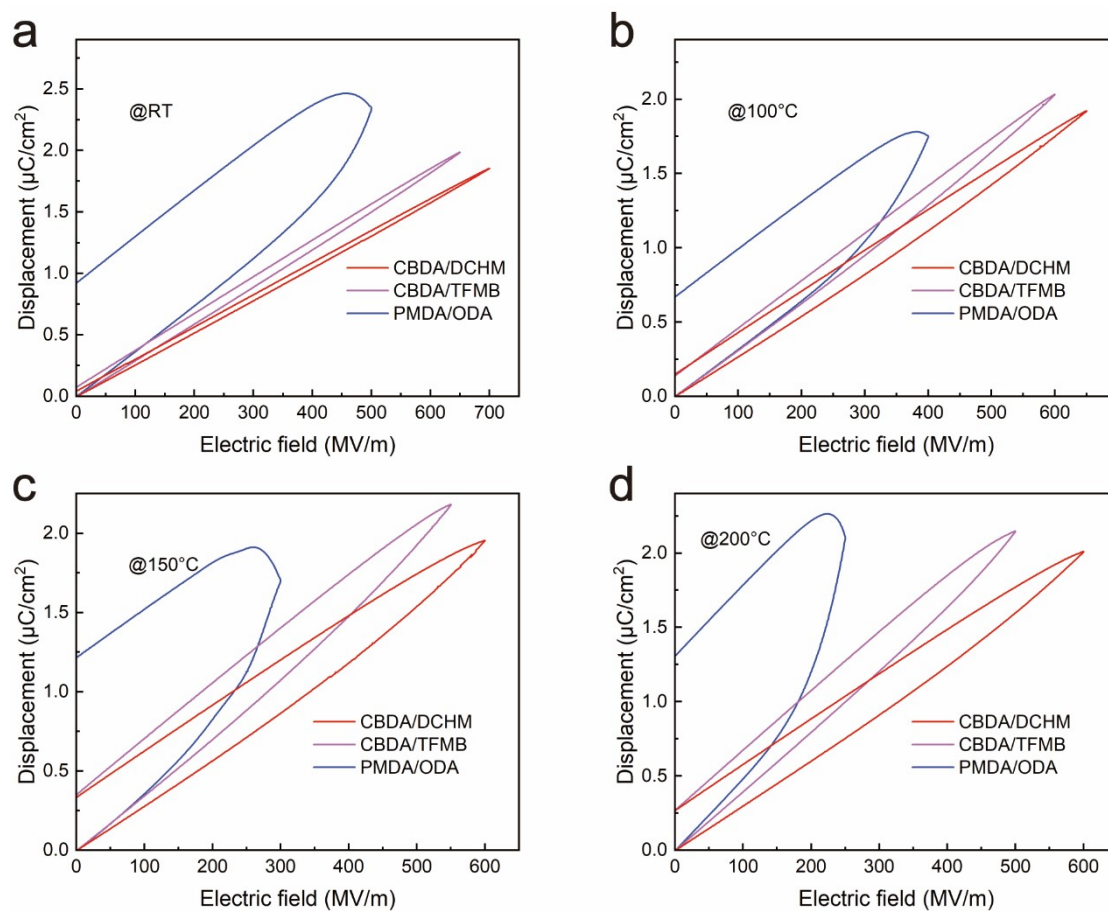| Sample	Temperature of Peak (°C)	Activation energy (eV)
PMDA/ODA	145	1.30
	168	1.36
CBDA/TFMB	170	1.37
CBDA/DCHM	176	1.39

Figure S11. Electric displacement-electric field (*D-E*) loops of CBDA/DCHM, CBDA/TFMB, and PMDA/ODA measured at (a) room temperature, (b) 100 °C, (c) 150 °C, and (b) 200 °C, at their respective maximum field strength.
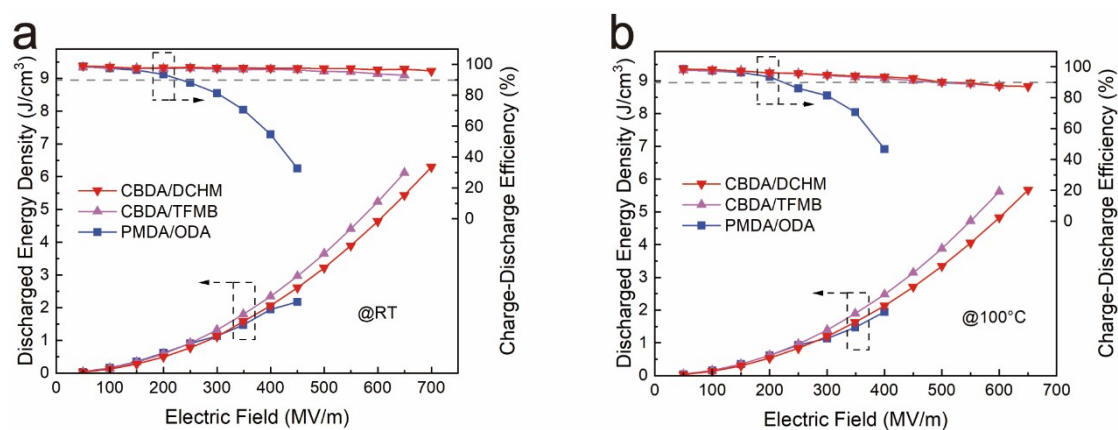

Figure S12. Discharged energy density and charge-discharge efficiency of CBDA/DCHM, CBDA/TFMB, and PMDA/ODA at (a) room temperature and (b) 100 °C.

Reference

1 J. Yi, C. Liu, Y. Tian, K. Wang, X. Liu and L. Luo, Polymer, 2021, 218, 123488.
2 M. Hasegawa, M. Horiuchi, K. Kumakura and J. Koyama, Polymer international, 2014, 63, 486-500.