Electronic Supplementary Information

A simple, efficient, and environmentally friendly strategy for preparing P(VDF-TrFE) with double bonds

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Experimental section

Material

The copolymer P(VDF-TrFE) 70/30 mol% was obtained from Arkema Piezotech. Sodium hydroxide and acetone were obtained from National Medicines Group Chemical Reagent Co., Ltd. Hexane, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and *N*-methyl-2-pyrrolidone (NMP) were obtained from Aladdin.

Synthesis of Unsaturated P(VDF-TrFE)

A series of P(VDF-TrFE-DB) copolymers were directly synthesized from P(VDF-TrFE) and NaOH under diverse conditions, including variations in solvent type, reaction temperature, reaction time, alkaline amount, and solution concentrations, as outlined in **Table S3**. For instance, entry 3 was selected as an example. In a 25 mL round-bottom flask, 200 mg of P(VDF-TrFE) 70/30 and 4 mL of DMF were added and stirred at 70 ℃ until complete dissolution. Subsequently, 100 mg of solid NaOH was dissolved in 0.2 mL of deionized water, and then diluted with 1 mL of DMF. The diluted NaOH solution was then dropwise added to the P(VDF-TrFE) solution, and the mixtures were heated to 70 ℃ for 4 h. The reaction was halted upon reaching the designated reaction time, and the mixture was subsequently cooled to room temperature. The reaction mixture was precipitated in deionized water. The crude product was dissolved in acetone and precipitated in hexane. After three washes with hexane, the product was dried overnight in a vacuum oven at 60 ℃, yielding brownish solid agglomerates.

Preparation of rigid device for ferroelectric response test

A solution consisting of 100 mg P(VDF-TrFE-DB) in 2 mL cyclohexanone was prepared. This solution was deposited onto an Au(111)/Ti/SiO2/Si wafer (10 mm × 10 mm) using spin-coating at 500 rpm for 5 s and 2500 rpm for 35 s to achieve a uniform film. Subsequently, the film was naturally dried in a ventilation cabinet for 24 hours and then subjected to vacuum oven treatment at 60 ℃ for 8 hours. This process yielded a film with a thickness of approximately 250 nm. Finally, a gold (Au) electrode with a diameter of 200 μm and thickness of 100 nm was deposited via magnetron sputtering to create the Au/P(VDF-TrFE-DB)/Au/Ti/SiO_2/Si structure. *P–E* loops at room temperature were acquired using a Premiere II ferroelectric tester from Radiant Technologies, Inc., USA.

Characterization

^{1}H NMR spectra were recorded using a Bruker (Advance III) 600 MHz spectrometer with acetone-d_6 as the solvent and tetramethylsilane as an internal standard. The chemical structures were determined via the FTIR and X-ray Photoelectron Spectroscopy (XPS) spectra. FTIR spectra were obtained using an Agilent CARY 660 FTIR spectrometer, and the XPS spectrums were acquired using a Kratos AXIS SUPRA X-ray photoelectron spectrometer with a monochromatic Al Ka source.

Calculation of Double Bond Content in P(VDF-TrFE-DB)

The content of VDF can be represented by the sum of the unreacted VDF content "a/2", the content of -CF=CH- "b", and the content of -CH=CH- "c/2", i.e., (a/2 + b + c/2). Similarly, the content of TrFE can be represented by the sum of the unreacted TrFE content "1", the content of -CH=CH- "c/2", and the content of -CF=CF- "x", i.e., (x + 1 + c/2). This relationship, with a VDF to TrFE ratio of 68.43:31.57, calculated based on the ^{1}H NMR (**Fig. S5**), is mathematically expressed by equation (1). The content of all double bonds in the reaction product can be represented as (x + c/2 + b), and the content of all chemical structures can be represented as (a/2 + 1 + b + c/2 + x). Therefore, the double bond content can be expressed by equation (2). By combining equations (1) and (2), the total double bond content in the product can be calculated.

$$\frac{31.57}{68.43}=\frac{x+1+\frac{c}{2}}{\frac{a}{2}+b+\frac{c}{2}}\#\ (1)$$

$$Content(DB)=\frac{x+b+\frac{c}{2}}{\frac{a}{2}+1+x+b+\frac{c}{2}}=\frac{31.57a+200b+31.57c-136.86}{100a+200b+31.57c}\#\ (2)$$

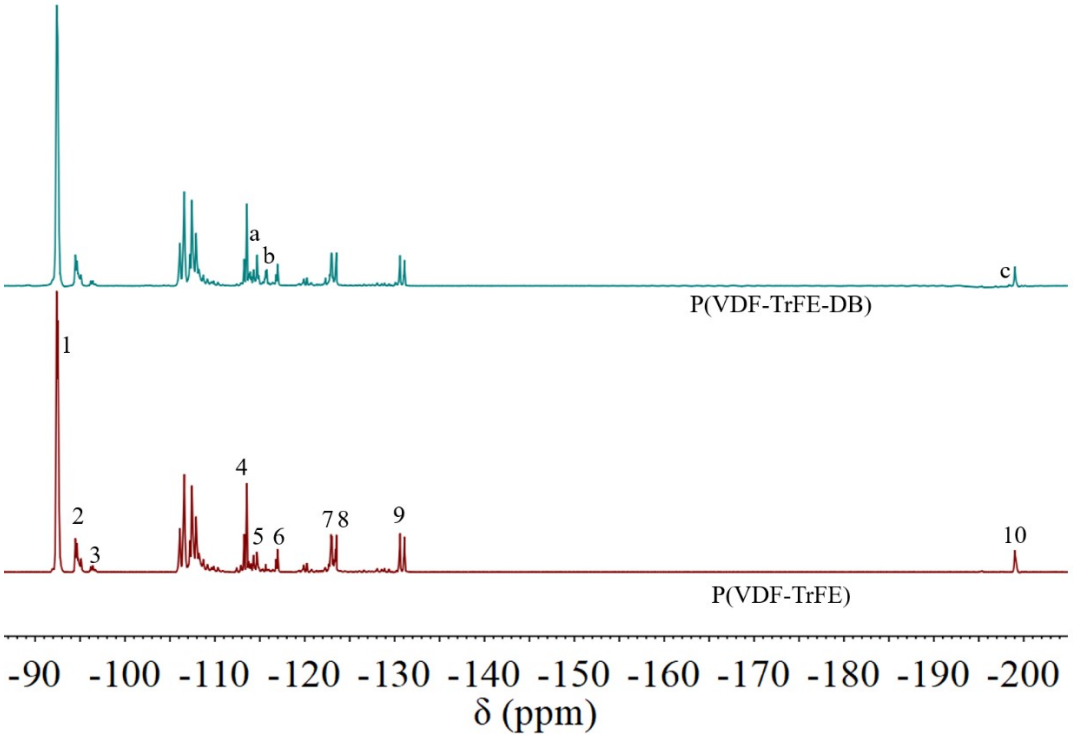

Fig. S1 ^{19}F NMR spectra of P(VDF-TrFE) and P(VDF-TrFE-DB), with detailed chemical structures denoted by corresponding numbers and characters, as illustrated in **Table S1**.

Table S1 ^{19}F NMR chemical shifts and assignments of P(VDF-TrFE-DB)s and P(VDF-TrFE-DB)s

Signal	Chemical composition	Chemical shift/ppm
1	–$CF_2CH_2C\boldsymbol{F}_2CH_2CF_2$–	-92.4
2	–$CHFCH_2C\boldsymbol{F}_2CH_2CF_2$–	-94.4 to -95.0
3	–$CH_2CH_2C\boldsymbol{F}_2CH_2CF_2$–	-95.0 to -96.5
4-6	–$CHFC\boldsymbol{F}_2CF_2CH_2CF_2$–	-112.0 to -117.0
a	$CH{=}C\boldsymbol{F}$	-113.9
b	$C\boldsymbol{F}{=}C\boldsymbol{F}$	-115.8
7-8	-$CH_2CHFC\boldsymbol{F}_2CHFCF$–	-123.0
9	–$CH_2CF_2C\boldsymbol{F}_2CHFCH_2$–	-130.3
c	–$C\boldsymbol{F}HCF_2CF_2CH{=}CHCF_2$–	-198.4
10	–$CF_2CF_2CH\boldsymbol{F}CH_2CF_2$–	-199.0

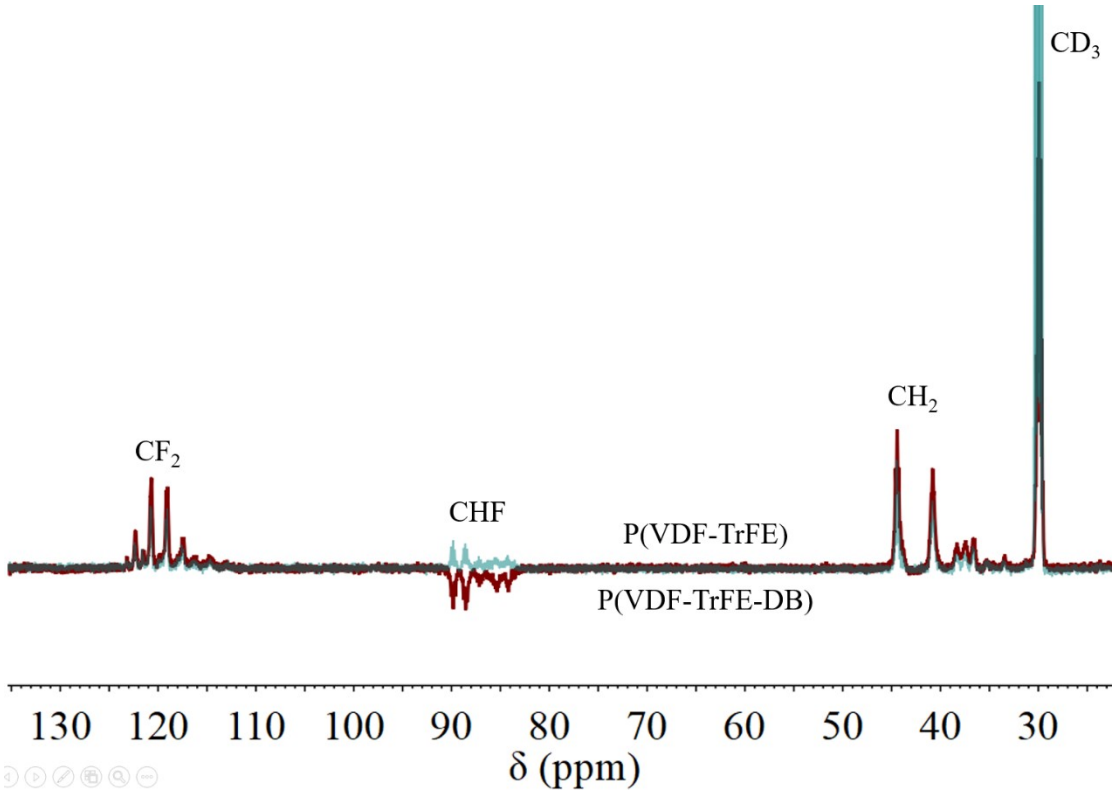

Fig. S2 ^{13}C NMR spectra of P(VDF-TrFE) and P(VDF-TrFE-DB)s

A series of P(VDF-TrFE-DB) copolymers were directly synthesized from P(VDF-TrFE) under various conditions, as detailed in **Table S2**. The chemical composition of the resulting P(VDF-TrFE-DB) was identified through ^{1}H NMR analysis, and the ^{1}H NMR spectra for all reactions are shown in **Fig. S3-S18**.

Table S2 Chemical compositions of P(VDF-TrFE-DB)s synthesized under various reaction conditions

Entry	Temperature (℃)	Time (h)	Solvent (mL)	P(VDF-TrFE) (mg)	NaOH (mg)	Double Bonds (%)	Yield (%)
1	70	4	DMSO (5)	200	100	0.92	35.06
2	70	4	NMP (5)	200	100	1.97	9.13
3	70	4	DMF (5)	200	100	5.68	64.17
4	70	0.25	DMF (5)	200	100	1.85	66.97
5	70	1	DMF (5)	200	100	4.64	64.29
6	70	12	DMF (5)	200	100	5.74	50.90
7	70	24	DMF (5)	200	100	7.01	28.73
8	50	4	DMF (5)	200	100	2.22	66.22
9	90	4	DMF (5)	200	100	6.97	24.87
10	110	4	DMF (5)	200	100	8.69	15.09
11	70	4	DMF (5)	200	50	2.56	67.08
12	70	4	DMF (5)	200	75	3.84	64.82
13	70	4	DMF (5)	200	125	7.06	46.81
14	70	4	DMF (3.3)	200	100	5.47	57.43
15	70	4	DMF (2.5)	200	100	4.59	64.26
16	70	4	DMF (2)	200	100	4.49	55.06

*Yield = m_p/m_r, where m_p represents the mass of the resulting P(VDF-TrFE-DB) product, and m_r denotes the mass of the raw material P(VDF-TrFE).

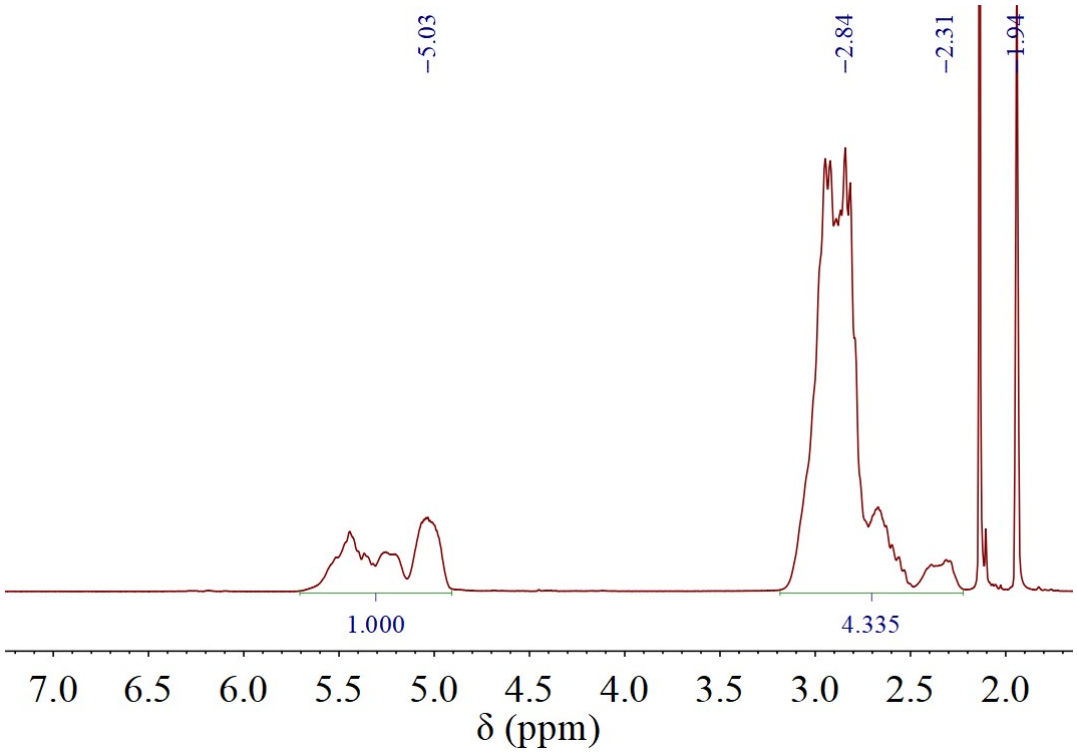

Fig. S3 [1]H NMR spectrum of pristine P(VDF-TrFE) 70/30 mol%. (The calculated VDF to TrFE ratio was 68.43:31.57)

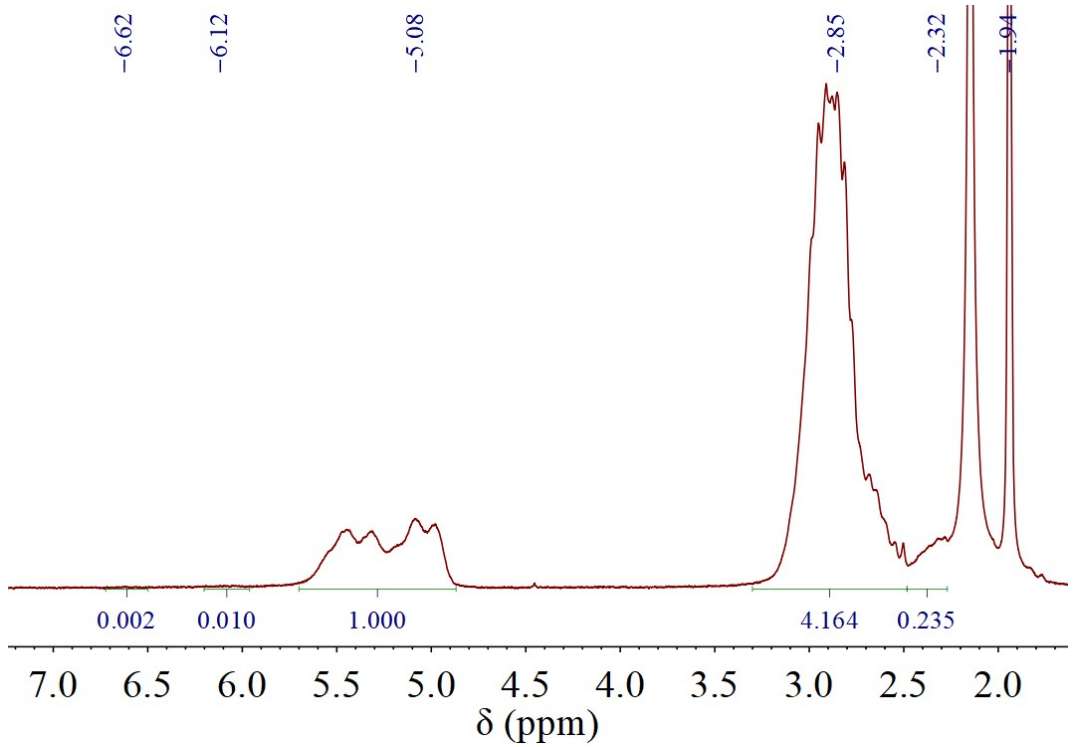

Fig. S4 [1]H NMR spectrum of the P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 1 of **Table S3**

Fig. S5 ^{1}H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 2 of **Table S3**

Fig. S6 ^{1}H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 3 of **Table S3**

Fig. S7 ^{1}H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 4 of **Table S3**

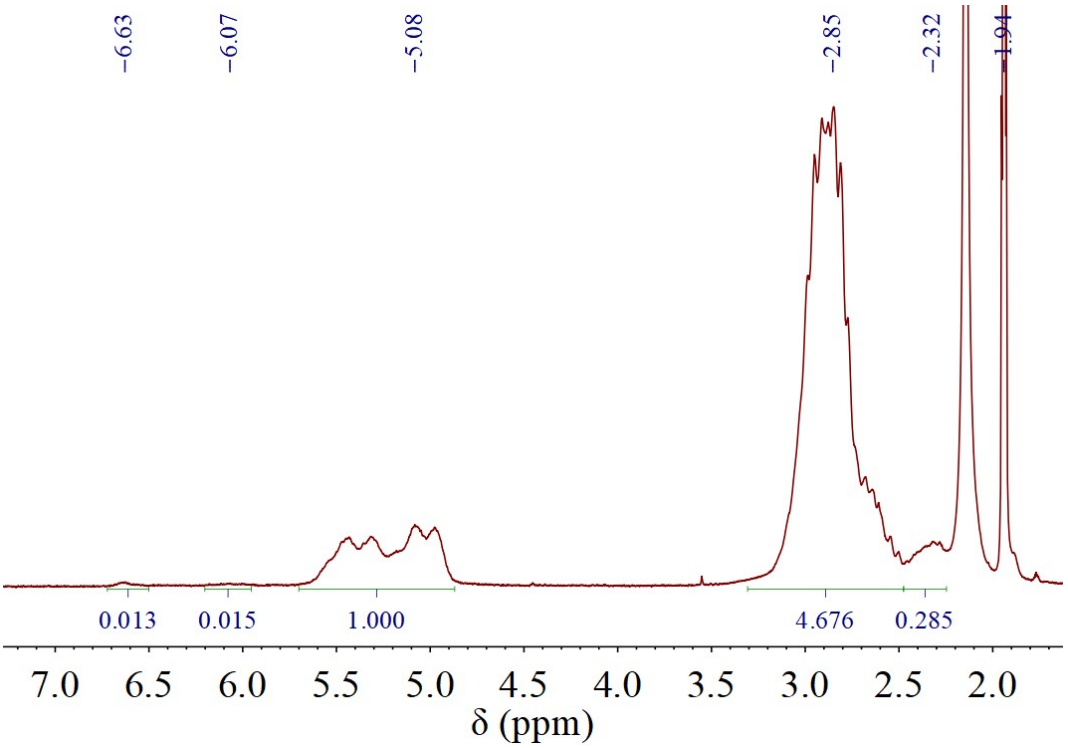

Fig. S8 [1]H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 5 of **Table S3**

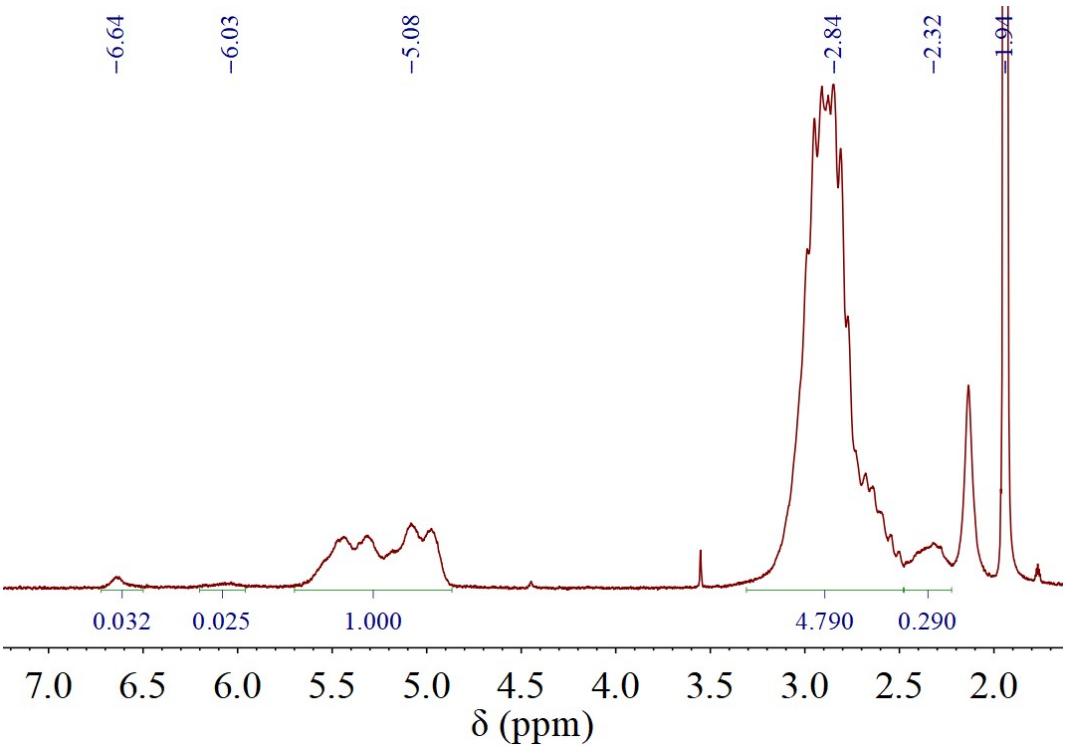

Fig. S9 [1]H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 6 of **Table S3**

Fig. S10 ^{1}H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 7 of **Table S3**

Fig. S11 ^{1}H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 8 of **Table S3**

Fig. S12 ^{1}H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 9 of **Table S3**

Fig. S13 ^{1}H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 10 of **Table S3**

Fig. S14 ^{1}H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 11 of **Table S3**

Fig. S15 ^{1}H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 12 of **Table S3**

Fig. S16 ^{1}H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 13 of **Table S3**

Fig. S17 ^{1}H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 14 of **Table S3**

Fig. S18 [1]H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 15 of **Table S3**

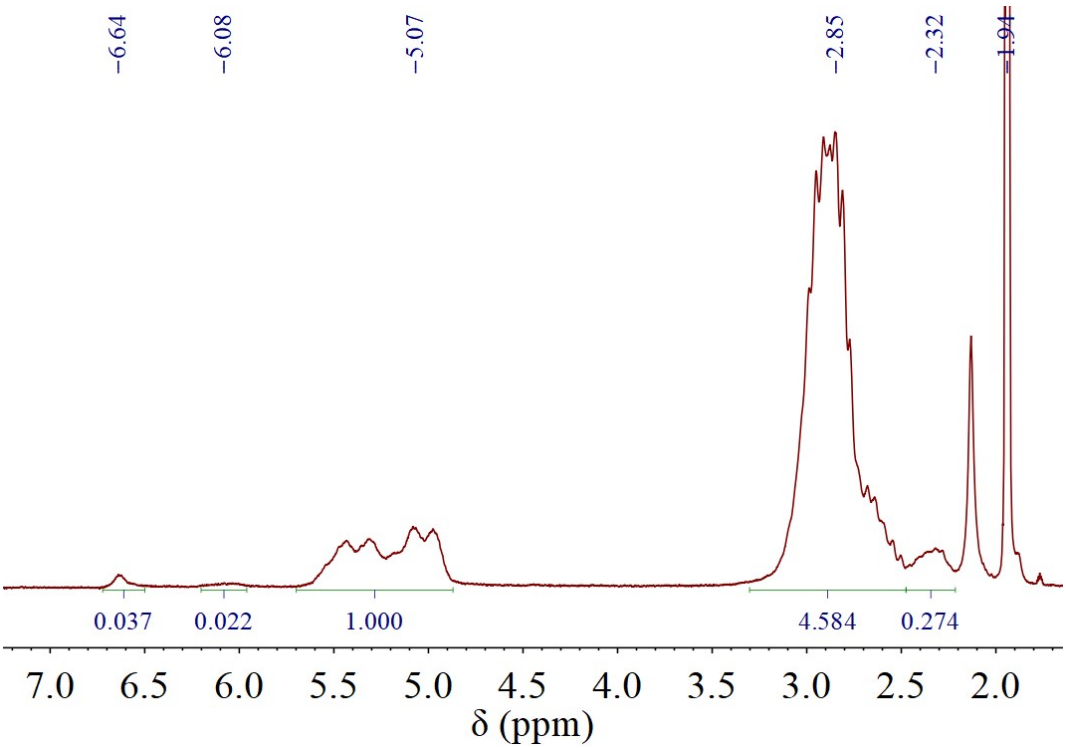

Fig. S19 [1]H NMR spectrum of P(VDF-TrFE-DB) as synthesized from the reaction as depicted in entry 16 of **Table S3**

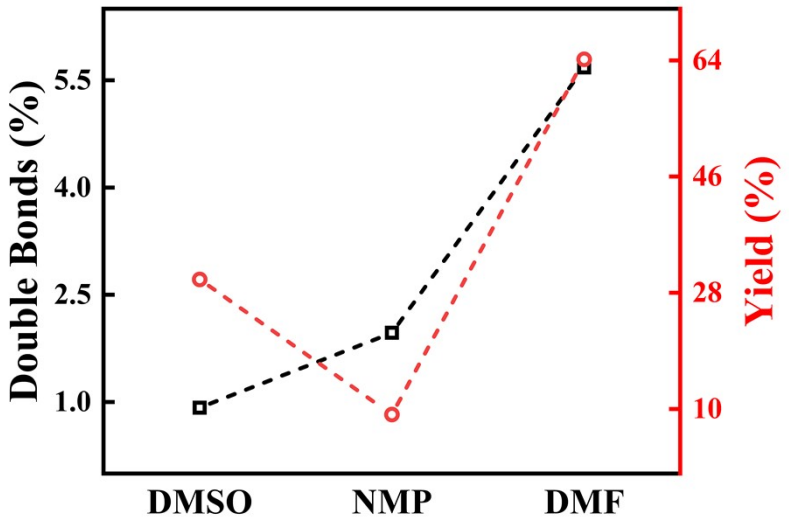

Fig. S20 Dependence of double bond content and reaction yield on different solvents

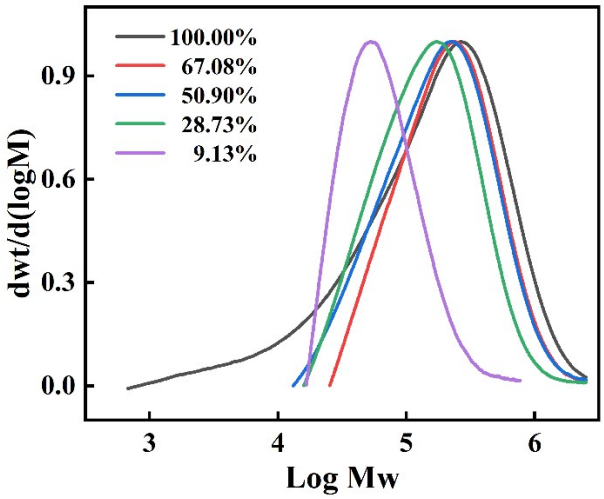

Fig. S21 Molecular weight distribution of P(VDF-TrFE) and P(VDF-TrFE-DB)s

Table S3 Molecular weights of P(VDF-TrFE-DB)s with different yields and P(VDF-TrFE)

Yield (%)	Temperature (℃)	Time (h)	Solvent (mL)	P(VDF-TrFE) (mg)	NaOH (mg)	Mw (g/mol)	Mn (g/mol)	PDI
100	/	/	/	/	/	311146	75366	4.13
67.08	70	4	DMF (5)	200	50	295316	152758	1.93
50.90	70	12	DMF (5)	200	100	268169	119976	2.24
28.73	70	24	DMF (5)	200	100	207031	102948	2.01
9.13	70	4	NMP (5)	200	100	78660	52874	1.49

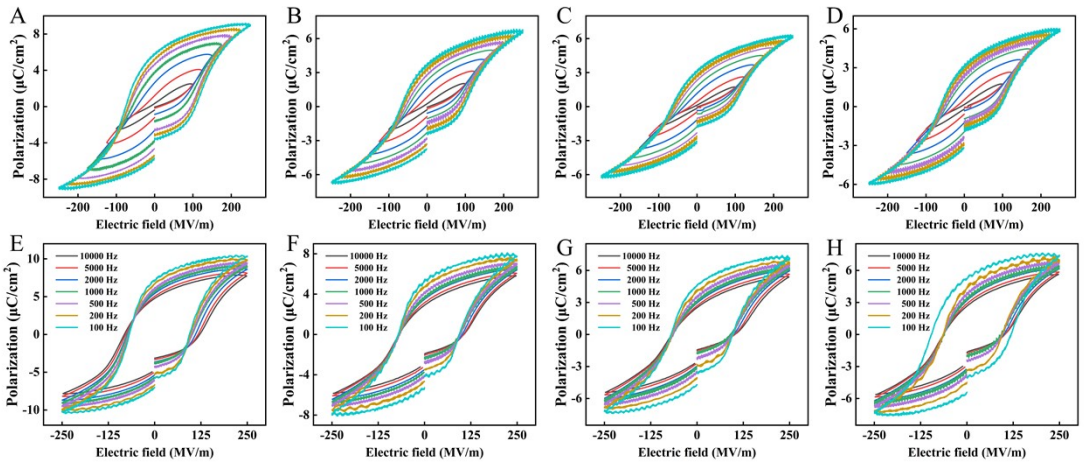

Fig. S22 *P–E* loops of P(VDF-TrFE-DB) films with different double bond contents. (A, B, C, D) *P–E* loops of P(VDF-TrFE-DB) films with double bond content of 2.5%, 3.3%, 3.9% and 4.8% at 1000 Hz, respectively; (E, F, G, H) *P–E* loops of P(VDF-TrFE-DB) films with double bond content of 2.5%, 3.3%, 3.9% and 4.8% at 250 MV/m, respectively.

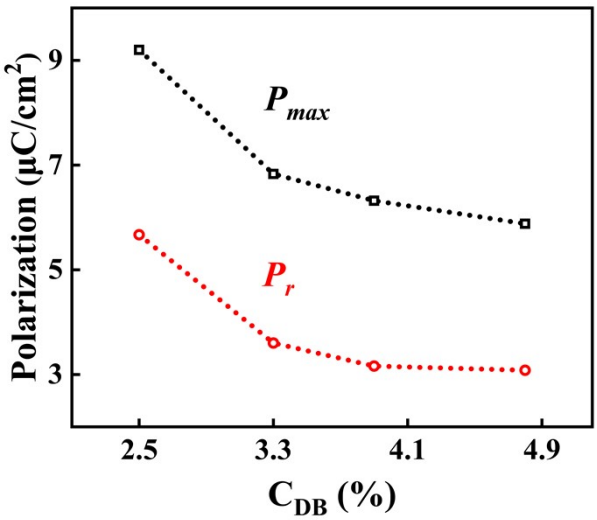

Fig. S23 P_{max} and P_r of P(VDF-TrFE-DB) films with different double bond contents