Supporting Information

Anionic modulation induces molecular polarity in a three-component crown ethers system

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Measurement Methods

Thermal analyses.

Differential scanning calorimetry (DSC) measurements were performed with a NETZSCH DSC 200F3 instrument. Crystalline samples underwent both heating and cooling processes at a consistent rate of 20 K min^{-1} under aluminum crucibles and nitrogen atmosphere.

SHG and dielectric measurements.

The second harmonic generation (SHG) was examined using INSTEC instruments. Complex dielectric permittivities were assessed utilizing the DMS-1000 dielectric temperature spectrum measuring system. Silver conductive paste was utilized to coat the surfaces of the samples, serving dual roles as the top and bottom electrodes.

Single-crystal and powder X-ray crystallography.

X-ray single-crystal diffraction experiments were performed utilizing a Rigaku Saturn 924 diffractometer, outfitted with Mo-Kα radiation (λ = 0.71073 Å). X-ray diffraction (XRD) analyses were executed employing a PANalytical X'Pert3 diffractometer, equipped with a Cu Kα X-ray source (λ = 1.5418 Å, 40 kV, 150 mA), with a scan rate set at 10° min^{-1} for the measurements.

IR measurements.

The Fourier transform infrared (FTIR) spectra were acquired employing the Bruker Alpha II instrument.

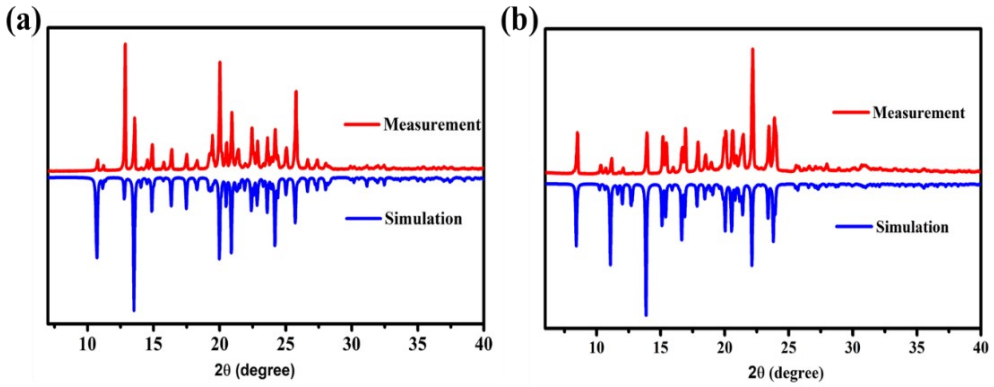

Figure S1. The X-ray powder diffractogram of compounds **1** (a) and **2** (b).

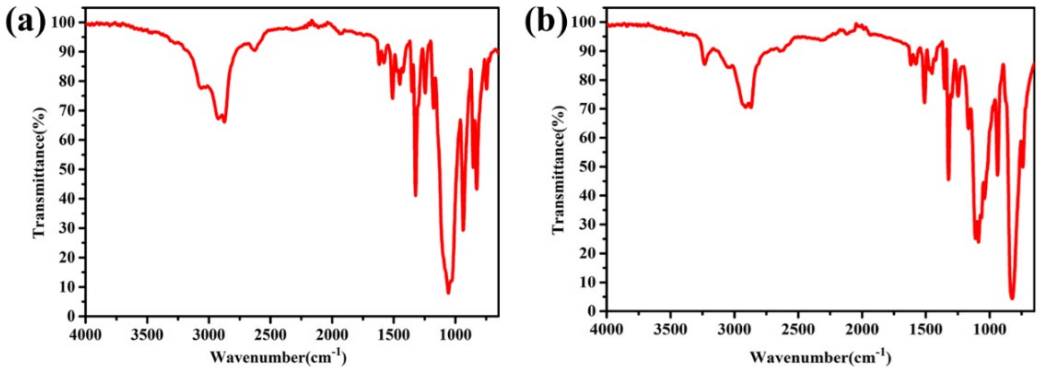

Figure S2. The infrared spectra of compounds **1**(a) and **2**(b).

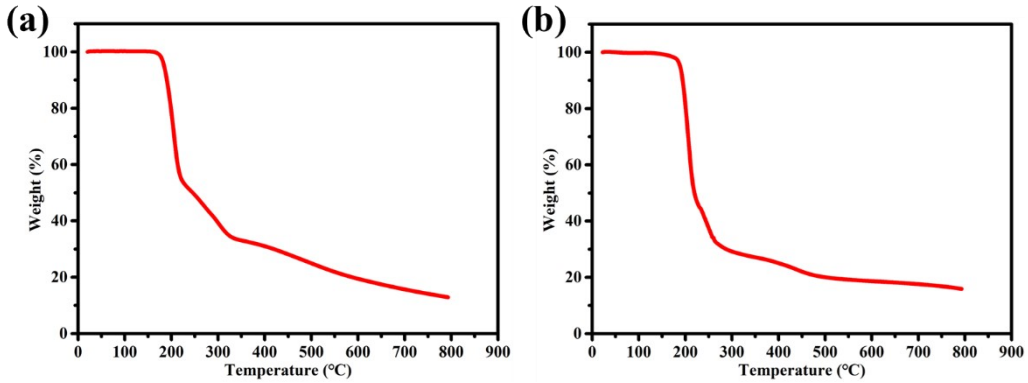

Figure S3. The TG analysis of compounds **1**(a) and **2**(b).

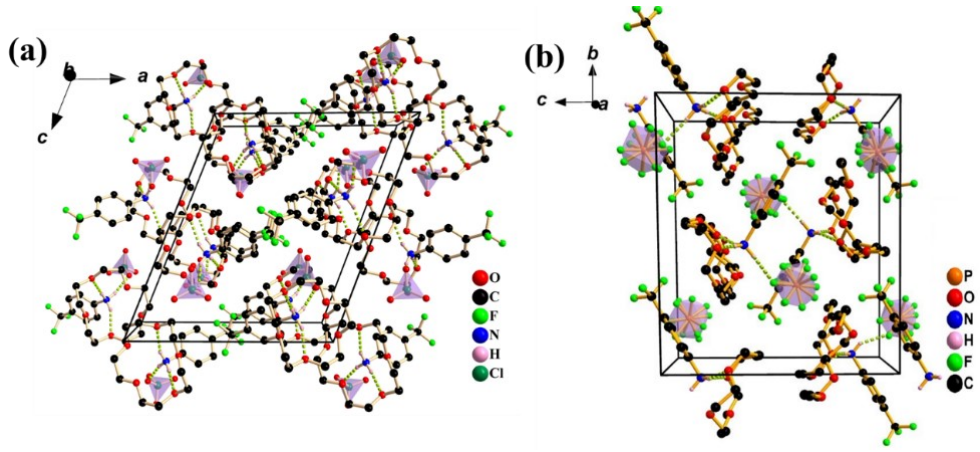

Figure S4. Stacking diagram of compounds **1**(a) and **2** (b) at LTP.

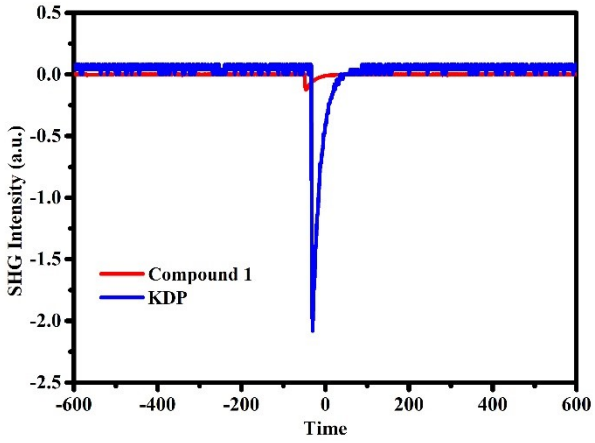

Figure S5. Comparison of SHG signaling of compound **1** with KDP.

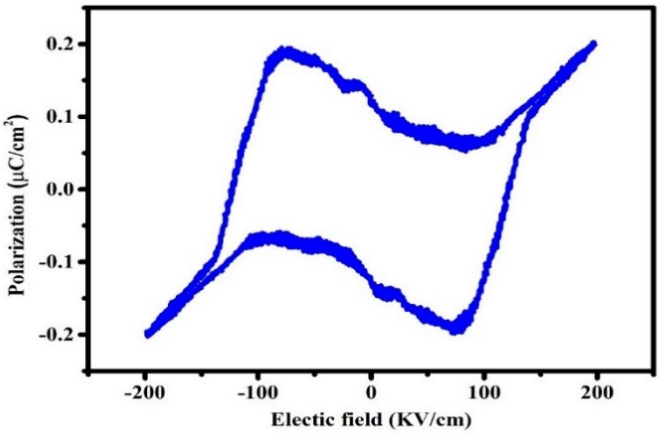

Figure S6. Electric hysteresis loop of **1.**

Table S1. Crystal data and structure refinement for crystals **1**.

Identification code	**1**	**1**
Temperature (K)	200 K	293 K
Formula	$C_{34}H_{52}Cl_2F_6N_2O_{18}$	$C_{17}H_{27}ClF_3NO_9$
Formula weight	961.68	481.85
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/c$
a/Å	14.5944(5)	14.9120(11)
b/Å	9.4697(2)	9.6790(5)
c/Å	17.1687(5)	16.9652(12)
α/°	90	90
β/°	111.882(4)	111.895(9)
γ/°	90	90
Volume/Å^3	2201.84(13)	2272.0(3)
Z	2	4
D_{calc} g/cm^3	1.451	1.409
μ/mm^{-1}	0.246	0.239
F (000)	1004.0	1008.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected	37369	35422
Independent reflections	11270 [R_{int} = 0.0323, R_{sigma} = 0.0332]	7200 [R_{int} = 0.0361, R_{sigma} = 0.0316]
Goodness-of-fit	1.085	1.924
Final R indexes [I≥2σ (I)]	R_1 = 0.0546, wR_2 = 0.1581	R_1 = 0.1972, wR_2 = 0.4990
Final R indexes [all data]	R_1 = 0.0683, wR_2 = 0.1684	R_1 = 0.2612, wR_2 = 0.5429
Flack parameter	0.23(2)	/

Table S2. The hydrogen bond length [Å] and bond angle [°] in compound **1**.

	D-H···A	D−H [Å]	H−A [Å]	D−A [Å]	D-H···A [°]
	N1-H1C···O6	0.91	2.54	3.134 (5)	124
	N1-H1C···O9	0.91	2.04	2.916 (4)	161
	N1-H1D···O2	0.91	1.93	2.819 (4)	165
	N1-H1D···O3	0.91	2.45	2.972 (4)	117
	N1-H1E···O4	0.91	2.13	2.983 (4)	156
200K	N1-H1E···O5	0.91	2.30	2.927 (4)	126
	N1-H2C···O11	0.91	2.05	2.901 (4)	154
	N2-H2C···O12	0.91	2.43	3.085 (4)	129
	N2-H2D···O10	0.91	2.43	2.888 (4)	112
	N2-H2D···O13	0.91	2.57	2.894 (5)	102
	N2-H2D···O14	0.91	1.94	2.842 (4)	170
	N2-H2E···O17	0.91	1.99	2.889 (6)	171
	N1-H1A···O7	0.89	2.48	2.963 (11)	114
	N1-H1A···O8	0.89	1.95	2.805(8)	161
	N1-H1B···O5	0.89	2.18	2.913 (9)	140
293K	N1-H1B···O6	0.89	2.27	3.031 (9)	144
	N1-H1E···O3	0.89	2.05	2.937(12)	172
	N1-H1E···O3A	0.89	2.19	2.990 (13)	149

Table S3. Selected bond lengths [Å] and bond angles [°] for **1**.

1 at 200K			
Cl2—O15	1.384(4)	Cl2—O16	1.446(4)
Cl2—O17	1.449(4)	Cl2—O18	1.408(4)
Cl1—O6	1.412(4)	Cl1—O7	1.382(6)
Cl1—O8	1.420(6)	Cl1—O9	1.431(3)
O6—Cl1—O8	107.7(4)	O6—Cl1—O9	110.4(2)
O7—Cl1—O6	111.3(4)	O7—Cl1—O8	107.6(5)
O7—Cl1—O9	111.8(4)	O8—Cl1—O9	108.0(3)
O15—Cl2—O16	104.5(4)	O15—Cl2—O17	110.6(3)
O15—Cl2—O18	112.4(3)	O16—Cl2—O17	105.7(3)
O18—Cl2—O16	109.5(3)	O18—Cl2—O17	113.5(3)
1 at 296K			
Cl1—O1	1.307(10)	Cl1—O2	1.405(10)
Cl1—O3	1.338(9)	Cl1—O4	1.413(10)
Cl1—O1A	1.380(12)	Cl1—O2A	1.317(11)
Cl1—O3A	1.467(10)	Cl1—O4A	1.362(12)
N1—C7	1.455(6)	O1—Cl1—O2	111.6(6)
O1—Cl1—O3	115.1(6)	O1—Cl1—O4	109.8(6)
O2—Cl1—O4	102.9(6)	O3—Cl1—O2	108.8(6)
O3—Cl1—O4	107.9(5)	O1A—Cl1—O3A	103.6(6)
O2A—Cl1—O1A	113.9(6)	O2A—Cl1—O3A	108.0(6)
O2A—Cl1—O4A	115.0(6)	O4A—Cl1—O1A	111.2(7)
O4A—Cl1—O3A	104.0(6)		

Table S4. Crystal data and structure refinement for crystals **2**.

Identification code	**2**
Temperature (K)	200 K

Formula	$C_{17}H_{27}F_9NO_5P$
Formula weight	527.37
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.5818(4)
b/Å	15.9181(6)
c/Å	13.8015(5)
α/°	90
β/°	93.642(3)
γ/°	90
Volume/Å^3	2320.06(15)
Z	4
D_{calc} g/cm^3	1.510
μ/mm^{-1}	0.219
F (000)	1088.0
Radiation	MoKα (λ = 0.71073)
Reflections collected	28272
Independent reflections	6169 [R_{int} = 0.0419, R_{sigma} = 0.0390]
Goodness-of-fit	1.071
Final R indexes [I≥2σ (I)]	R_1 = 0.0724, wR_2 = 0.1939
Final R indexes [all data]	R_1 = 0.1027, wR_2 = 0.2116

Table S5. The hydrogen bond length [Å] and bond angle [°] in compound **2**.

D-H···A	D−H [Å]	H−A [Å]	D−A [Å]	D−H···A [°]
N1-H1C···O2	0.91	2.49	2.910 (3)	108

	N1-H1C···O3	0.91	1.93	2.836 (3)	173
	N1-H1C···O4	0.91	2.56	2.963 (3)	107
	N1-H1D···F3A	0.91	2.37	3.130 (6)	142
200K	N1-H1D···F4A	0.91	2.16	2.959 (6)	146
	N1- H1D···F2	0.91	2.08	2.983 (11)	174
	N1- H1D···F3	0.91	2.44	3.073 (9)	127
	N1- H1E···O1	0.91	2.36	2.894 (3)	118
	N1- H1E···O5	0.91	2.02	2.886 (3)	163

Table S6. Selected bond lengths [Å] and bond angles [°] for **2**.

2 at 200K			
P1—F1	1.521(7)	P1—F2	1.509(6)
P1—F3	1.714(6)	P1—F4	1.648(9)
P1—F5	1.475(9)	P1—F6	1.482(9)
P1—F1A	1.590(4)	P1—F2A	1.696(3)
P1—F3A	1.585(3)	P1—F4A	1.572(4)
P1—F5A	1.568(4)	P1—F6A	1.559(6)
F1—P1—F4	162.3(6)	F1—P1—F3	81.4(5)
F2—P1—F1	95.5(6)	F2—P1—F3	84.3(5)
F2—P1—F4	83.3(6)	F4—P1—F3	80.9(5)
F5—P1—F1	105.4(7)	F5—P1—F2	112.0(7)
F5—P1—F3	161.1(7)	F5—P1—F4	91.3(6)
F5—P1—F6	109.1(7)	F6—P1—F1	104.2(6)
F6—P1—F2	127.1(6)	F6—P1—F3	52.0(6)
F6—P1—F4	63.8(7)	F6A—P1—F1A	74.9(4)
F6A—P1—F2A	157.2(3)	F6A—P1—F3A	100.9(4)
F6A—P1—F4A	115.6(4)	F6A—P1—F5A	89.3(4)
F5A—P1—F1A	98.4(3)	F5A—P1—F2A	84.8(3)
F5A—P1—F3A	168.9(3)	F5A—P1—F4A	85.5(3)
F4A—P1—F1A	169.0(3)	F4A—P1—F2A	86.0(2)
F4A—P1—F3A	86.1(3)	F3A—P1—F1A	88.7(3)
F3A—P1—F2A	87.4(2)	F1A—P1—F2A	84.1(2)