Electronic Supplementary Information (ESI)

Molecular Design of High-Temperature Organic Dielectric Switches

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Experimental

Synthesis. All of the reagents were of analytical grade and used without further purification.

Tetramethylphosphonium picrate (1). An aqueous solution of tetramethylphosphonium chloride (0.6328g, 5mmol) was added to a stirred acetonitrile solution of equimolar picric acid (1.1455g, 5mmol) at room temperature. The resulting solution was filtered and allowed to stand in air at room temperature for several days, yielding yellow crystals of 1 (mp \sim 594 K).

Propyl-trimethyl-phosphonium picrate (2). Dehydrated dichloromethane (200 mL) was added into a dry flask under nitrogen at room temperature. Trimethylphosphine (8 mL, 77 mmol) and propyl bromide (6.41 mL, 50 mmol) then were added to this solution via syringe, respectively. The mixed solution was warmed to 40 °C and stirred for 3 d. The solvent was evaporated to yield the propyl-trimethyl-phosphonium bromide as white solid. Yellow crystals of **2** were obtained by the evaporation of a mixed acetonitrile aqueous solution containing equimolar propyl-trimethyl-phosphonium bromide (0.9954g, 5mmol) and picric acid (1.1455g, 5mmol) at room temperature. (**2**: mp ~ 466 K)

Methoxymethyl-trimethyl-phosphonium picrate (**3**). Dehydrated toluene (200 mL) was added into a dry flask under nitrogen at room temperature. Trimethylphosphine (6.22 mL, 60 mmol) and methoxymethyl bromide (4.06 mL, 50 mmol) then were added to this solution via syringe, respectively. The mixed solution was heated to 30 °C and refluxed for 6 h. The solvent was evaporated to yield the methoxymethyl-trimethyl-phosphonium bromide as white solid. Yellow crystals of **3** were obtained by the evaporation of a mixed acetonitrile aqueous solution containing equimolar methoxymethyl-trimethyl-phosphonium bromide (1.0051g, 5mmol) and picric acid (1.1455g, 5mmol) at room temperature. (**3**: mp ~ 443 K)

Allyl-trimethyl-phosphonium picrate (4). Dehydrated dichloromethane (200 mL) was added into a dry flask under nitrogen at 0 °C. Trimethylphosphine (8 mL, 77 mmol) and allyl bromide (6.41 mL, 50 mmol) then were added to this solution via syringe, respectively. The mixed solution was stirred for 12 h. The solvent was evaporated to yield the propyl-trimethyl-phosphonium bromide as white solid. Yellow crystals of **4** were obtained by the evaporation of a mixed acetonitrile aqueous solution containing equimolar allyl-trimethyl-phosphonium bromide (0.9854g, 5mmol) and picric acid (1.1455g, 5mmol) at room temperature. (**4**: mp ~ 496 K)

(2-Hydroxy-ethyl)-trimethyl-phosphonium picrate (5). Dehydrated toluene (200 mL) and 2-bromoethanol (10.6 mL, 150 mmol) were added into a dry flask under nitrogen at room temperature. Then, trimethylphosphine (14 mL, 135 mmol)

was added to this solution via syringe. The mixed solution was heated to 75 °C and refluxed for 24 h. The solvent was evaporated to yield the (2-Hydroxy-ethyl)-trimethyl-phosphonium bromide as white solid. Yellow crystals of **5** were obtained by the evaporation of a mixed acetonitrile aqueous solution containing equimolar (2-Hydroxy-ethyl)-trimethyl-phosphonium bromide (1.0051g, 5mmol) and picric acid (1.1455g, 5mmol) at room temperature. (**5**: mp \sim 528 K)

X-ray Crystallography. Variable-temperature X-ray diffraction data were collected using a Rigaku Saturn 724 diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). Data processing including empirical absorption correction was performed using the Crystalclear software package (Rigaku, 2005). The crystal structures were solved by direct methods and then refined by full-matrix least-squares refinements on F^2 using the SHELXLTL software package (SHELX-97). All non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were generated geometrically. The asymmetric units and the packing views were drawn with DIAMOND Visual Crystal Structure Information System Software. Crystallographic data and structure refinement are listed in Table S2. The bond lengths and angles are given in Table S4.

Powder X-ray Diffraction. Powder X-ray diffraction (PXRD) data were measured on a PANalytical X'Pert PRO X-ray diffractometer. Diffraction patterns were collected in the range of $2\theta = 5^{\circ}-50^{\circ}$ with a step size of 0.02°.

DSC Measurements. DSC measurements were performed on a Netzsch Model DSC 200 F3 instrument by heating and cooling the crystalline samples with a rate of 20 K/min. The sample was placed in aluminum crucible under nitrogen at atmospheric pressure.

Dielectric Constant Measurements. The powder-pressed pellets pasted with silver or carbon conducting glue were used in dielectric measurements. The temperature-dependent dielectric constants were measured on a Tonghui Model TH2828A impedance analyzer at the frequencies of 100 kHz and 1 MHz, with the applied AC field fixed at 1 V.

SHG Switching Measurement. SHG switching experiment was carried out on powder samples, using an unexpanded laser beam with low divergence (pulsed Nd:YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate). The instrument model is Ins 1210058, INSTEC Instruments, while the laser is Vibrant 355 II, OPOTEK

Compound	2	3	4	5
$T_{\rm tr}/{\rm K}$	367	393	352	347
$\Delta H/(kJ mol^{-1})$	17.09	17.48	14.03	25.22
$\Delta S/(J \text{ mol}^{-1} \text{ K}^{-1})$	46.55	44.47	39.86	72.69

Table S1. Summary of structural transition temperatures, enthalpy and entropy changes for **2-5** obtained from DSC analysis on heating.



Figure S1. IR spectrum, asymmetric unit, PXRD patterns of **1** at room temperature, and its DSC curve and the real part of the dielectric constant within 270-330 K. **1** crystallizes in the monoclinic space group C2/c (point group 2/m) at 293 K, with cell parameters of a = 19.532(7) Å, b = 11.187(2) Å, c = 27.511(5) Å, $\beta = 93.54(4)^\circ$, V = 6000(3) Å³.



Figure S2. IR spectrum of 2-5.



Figure S3. The asymmetric units of **2** (a), **3** (b), **4** (c), **5** (d) at 293 K and **5** (e) at 353 K. Symmetry codes in Figure S3e: (a) 1-x, y, 0.5-z; (b) -x, y, 1.5-z.

	2	3	4	5	5
Chemical Formula	$C_{12}H_{18}N_3O_7P$	$\begin{array}{c} C_{11}H_{16}N_3O_8\\ P\end{array}$	$C_{12}H_{16}N_{3}O_{7}P$	$C_{11}H_{16}N_3O_8$ P	$C_{11}H_{16}N_3O_8P$
Formula weight	347.26	349.24	345.25	349.24	349.24
Temperature (K)	293	293	293	293	353
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Orthorhombic
Space group	$P2_{1}/c$	$P2_{1}/c$	Pcab	<i>P</i> 1	Стст
<i>a</i> , Å	7.0034(14)	6.8885(14)	7.0408(14)	10.232(2)	11.5686(15)
b, Å	19.672(4)	19.726(4)	19.834(4)	9.883(2)	20.037(3)
<i>c</i> , Å	12.380(3)	12.287(4)	23.634(5)	8.5961(17)	7.0578(11)
α, deg	90	90	90	102.92(3)	90
β , deg	105.85(3)	107.24(3)	90	99.20(3)	90
γ, deg	90	90	90	68.34(3)	90
<i>V</i> , Å ³	1640.8(6)	1594.6(7)	3300.4(12)	784.6(3)	1636.0(4)
Ζ	4	4	8	2	4
	$-9 \le h \le 8$	$-8 \le h \le 8$	$-8 \le h \le 8$	$-10 \le h \le 13$	$-13 \le h \le 12$
Index ranges	$-20 \le k \le 25$	$-25 \le k \le 25$	$-20 \le k \le 24$	$-12 \le k \le 12$	$-21 \le k \le 23$
	$-16 \le l \le 15$	$-15 \le l \le 15$	$-29 \le l \le 28$	$-11 \le l \le 8$	$-7 \le l \le 8$
D_{calcd} , g•cm ⁻³	1.406	1.455	1.390	1.478	1.418
μ , mm ⁻¹	0.206	0.217	0.205	0.221	0.211
refns measured	10877	15454	18712	5491	3251
independent reflns	3730	3635	3242	5006	799
reflns used	2578	1997	2127	3313	394
Goodness-of-fit on F^2	1.198	1.135	1.108	1.042	1.012
Final R indices	$R_1 = 0.0781,$	$R_1 = 0.1002,$	$R_1 = 0.0995,$	$R_1 = 0.0769,$	$R_1 = 0.1223,$
$[I > 2 \operatorname{sigma}(I)]$	$wR_2 = 0.2043$	$wR_2 = 0.2064$	$wR_2 = 0.2374$	$wR_2 = 0.2254$	$wR_2 = 0.3895$

Table S2. Crystal data, data collection and reduction parameter of crystals of 2-5.



Figure S4. (a) Packing view of 2 along *a*-axis. (b) Picrate anion layers. (c) The π - π stacking interactions are 3.5977 Å

 (d_1) and 3.5025 Å (d_2) .



Figure S5. Packing view of **3** along *a*-axis (left) and picrate anion layers (right). The π - π stacking interactions are 3.5312 Å and 3.4345 Å.



Figure S6. Packing view of **4** along *b*-axis (left) and zig-zag anion sheets (right). The π - π stacking interactions are 3.5570 Å.



Figure S7. The packing views of the **5** in the β and α phase, showing the relationship between unit cells and the significant shifts of the cations. Only P atom and the C atoms bonded to the P atoms are shown for clarity. The unit cell with yellow edges in the β phase was chosen with the origin located on the P atom for convenience of comparison, while that in the α phase is the one corresponding to the unit cell chosen in the β phase. (a, b) The packing diagrams of the **5** in the β and α phases, viewed along the common *a*-axis. (c, d) The packing diagram of the **5** in the β and α phase, viewed along the common *c*-axis.



Figure S8. Variable-temperature PXRD patterns of **2-5**. The experimental PXRD patterns obtained at 293 K matches well with the respective simulated ones based on the crystal structures of the α phases, verifying the phase purities.

	Space group	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	α, deg	β , deg	γ, deg	V, Å ³
2β	Cmma	10.149	7.444	5.853	90	90	90	442.2
3β	Imma	20.786	11.648	5.217	90	90	90	1263.0
4β	<i>I</i> 4/ <i>m</i>	14.260	14.260	14.593	90	90	90	2967.2

Table S3. space groups and cell parameters of 2β , 3β and 4β phases.



Figure S9. The dielectric constant (ε') and dielectric loss (tan δ) of **2-5** at different frequencies in the heating process.



Figure S10. The ε '-switching of 5 without obvious fatigue after six switching cycles at 1 MHz.



Figure S11. The ε ' measured using the same thickness powder-pressed pellets (~ 0.7 mm) of 5 pasted with silver or carbon conducting glue with different areas.

	2	3	4	5
C1—C2	1.448 (4)	1.456 (5)	1.464(6)	1.458 (8); C12—C13 1.438 (9)
C2—C3	1.383 (4)	1.373 (5)	1.369(6)	1.379 (8); C13—C14 1.353 (8)
C3—C4	1.374 (4)	1.369 (5)	1.401(6)	1.439 (9); C14—C15 1.347 (8)
C4—C5	1.388 (4)	1.380 (5)	1.394(7)	1.403 (8); C15—C16 1.372 (9)
C5—C6	1.360 (4)	1.360 (5)	1.366(6)	1.402 (8); C16—C17 1.327 (8)
C6—C1	1.452 (4)	1.449 (5)	1.469(6)	1.408 (9); C17—C12 1.480 (9)
C1—O1	1.234 (4)	1.237 (4)	1.231(5)	1.258 (7); C12—O9 1.239 (8)
C2—N1	1.443 (4)	1.441 (5)	1.470(6)	1.405 (8); C13—N4 1.496 (9)
N1—O2	1.179 (4)	1.162 (4)	1.222(5)	1.212 (7); N4—O10 1.160 (8)
N1—O3	1.188 (4)	1.177 (4)	1.219(6)	1.159 (8); N4—O11 1.216 (7)
C4—N2	1.446 (4)	1.444 (5)	1.440(6)	1.434 (7); C15—N5 1.456 (8)
N2—O4	1.223 (4)	1.222 (5)	1.231(6)	1.219 (7); N5—O12 1.247 (8)
N2—O5	1.230 (4)	1.220 (5)	1.238(6)	1.186 (7); N5—O13 1.257 (8)
C6—N3	1.455 (4)	1.456 (5)	1.460(6)	1.465 (8); C17—N6 1.437 (9)
N3—O6	1.228 (4)	1.226 (5)	1.232(6)	1.194 (8); N6—O14 1.196 (10)
N3—O7	1.202 (4)	1.212 (5)	1.211(6)	1.131 (10); N6—O15 1.245 (10)
P1—C7	1.786 (4)	1.764 (5)	1.783(7)	1.716 (9); P2—C18 1.820 (7)
P1—C8	1.783 (4)	1.776 (5)	1.774(6)	1.797 (8); P2—C19 1.740 (6)
Р1—С9	1.772 (4)	1.771 (4)	1.786(6)	1.829 (7); P2—C20 1.780 (7)
P1—C10	1.790 (3)	1.800 (4)	1.805(5)	1.801 (6); P2—C21 1.771 (7)
C10—C11	1.515 (5)	C10—O8 1.410 (6)	1.427(7)	1.502 (11); C21—C22 1.522 (10)
C11—C12	1.512 (5)	O8—C11 1.366 (6)	1.200(7)	C11—O8 1.369 (10); C22—O16 1.466 (8)
C1—C2—C3	123.6 (3)	123.7 (4)	124.5(4)	123.7 (6); C12—C13—C14 126.2 (6)
C2—C3—C4	119.9 (3)	120.2 (4)	119.7(4)	118.3 (6); C13—C14—C15 119.0 (6)
C3—C4—C5	121.1 (3)	120.8 (4)	120.4(4)	121.2 (5); C14—C15—C16 120.7 (5)
C4—C5—C6	118.5 (3)	119.0 (4)	119.6(4)	117.3 (6); C15—C16—C17 121.0 (6)
C5—C6—C1	125.6 (3)	125.4 (4)	124.7(4)	125.7 (5); C16—C17—C12 123.7 (6)
C6—C1—C2	111.2 (3)	110.8 (4)	111.1(4)	113.7 (5); C17—C12—C13 109.3 (5)
O1—C1—C2	125.7 (3)	125.4 (4)	125.0(4)	125.7 (6); O9—C12—C13 125.5 (7)
O1—C1—C6	123.0 (3)	123.8 (4)	123.9(4)	120.6 (5); O9—C12—C17 125.2 (7)
N1-C2-C1	119.8 (3)	119.8 (4)	119.4(4)	119.7 (5); N4—C13—C12 118.6 (5)
N1—C2—C3	116.6 (3)	116.4 (4)	116.1(4)	116.5 (6); N4—C13—C14 126.2 (6)
N2—C4—C3	119.7 (3)	119.8 (4)	119.7(5)	117.9 (5); N5—C15—C14 121.4 (6)
N2-C4-C5	119.2 (3)	119.5 (4)	119.9(5)	120.7 (5); N5—C15—C16 118.0 (6)
N3—C6—C5	116.3 (3)	116.5 (4)	116.9(4)	111.8 (5); N6—C17—C16 121.3 (7)
N3—C6—C1	118.1 (3)	118.1 (4)	118.3(4)	122.4 (5); N6—C17—C12 114.9 (6)
O2—N1—C2	121.2 (3)	121.4 (4)	119.4(4)	120.6 (6); O10—N4—C13 118.8 (6)
O2—N1—O3	119.5 (3)	118.6 (4)	121.8(5)	115.0 (7); O10—N4—O11 121.2 (7)

Table S4. The bond lengths and angles of 2-5 at 293 K.

O3—N1—C2	119.3 (3)	120.0 (4)	118.8(5)	121.0 (6); O11—N4—C13 117.0 (6)
O4—N2—C4	119.2 (3)	118.5 (4)	118.9(5)	119.1 (5); O12—N5—C15 117.1 (6)
O4—N2—O5	122.2 (3)	122.8 (4)	122.3(5)	121.9 (5); O12—N5—O13 124.6 (6)
O5—N2—C4	118.6 (3)	118.6 (4)	118.8(5)	118.9 (5); O13—N5—C15 118.2 (6)
O6—N3—C6	117.7 (3)	117.7 (4)	116.8(5)	116.8 (6); O14—N6—C17 119.7 (7)
O6—N3—O7	123.4 (4)	118.7 (4)	123.6(5)	119.9 (7); O14—N6—O15 114.9 (8)
O7—N3—C6	118.8 (3)	123.7 (4)	119.6(5)	118.7 (6); O15—N6—C17 121.5 (8)
C7—P1—C8	108.9 (2)	110.6 (3)	111.6(4)	108.9 (4); C18—P2—C19 110.8 (3)
C7—P1—C9	109.8 (2)	110.5 (2)	108.3(4)	107.1 (4); C18—P2—C20 110.2 (4)
C7—P1—C10	109.48 (19)	108.8 (2)	108.2(3)	107.7 (3); C18—P2—C21 106.5 (3)
C8—P1—C9	109.8 (2)	111.2 (2)	110.0(3)	110.2 (4); C19—P2—C20 108.8 (3)
C8—P1—C10	110.14 (18)	107.3 (2)	109.7(3)	110.8 (3); C19—P2—C21 111.8 (3)
C9—P1—C10	108.75 (19)	108.3 (2)	109.0(3)	112.0 (3); C20—P2—C21 108.7 (3)
P1-C10-C11	114.6 (2)	P1—C10—O8 105.4 (3)	111.6(5)	115.4 (5); P2—C21—C22 119.4 (5)
C10—C11—C12	112.9 (3)	C10—O8—C11 115.1 (4)	145.4(13)	C10—C11—O8 115.8 (6);
				C21—C22—O16 109.6 (6)