ESI

Two Host-Guest Grown Ether Supramolecules Show Switchable Phase Transition, Dielectric and Second-Harmonic Generation Effect

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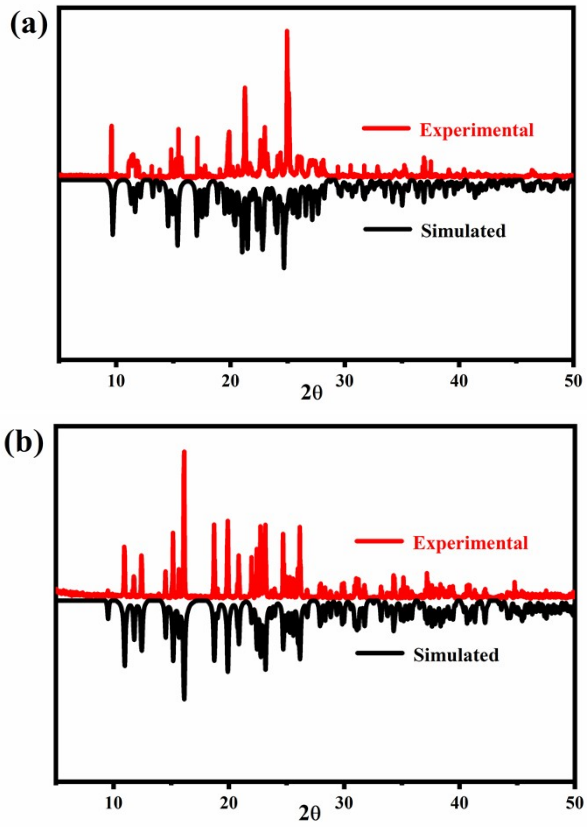


Figure S1. The powder X-ray diffraction patterns of compounds **1** (a) and **2** (b) with the simulated one in black and the experimental one in red.

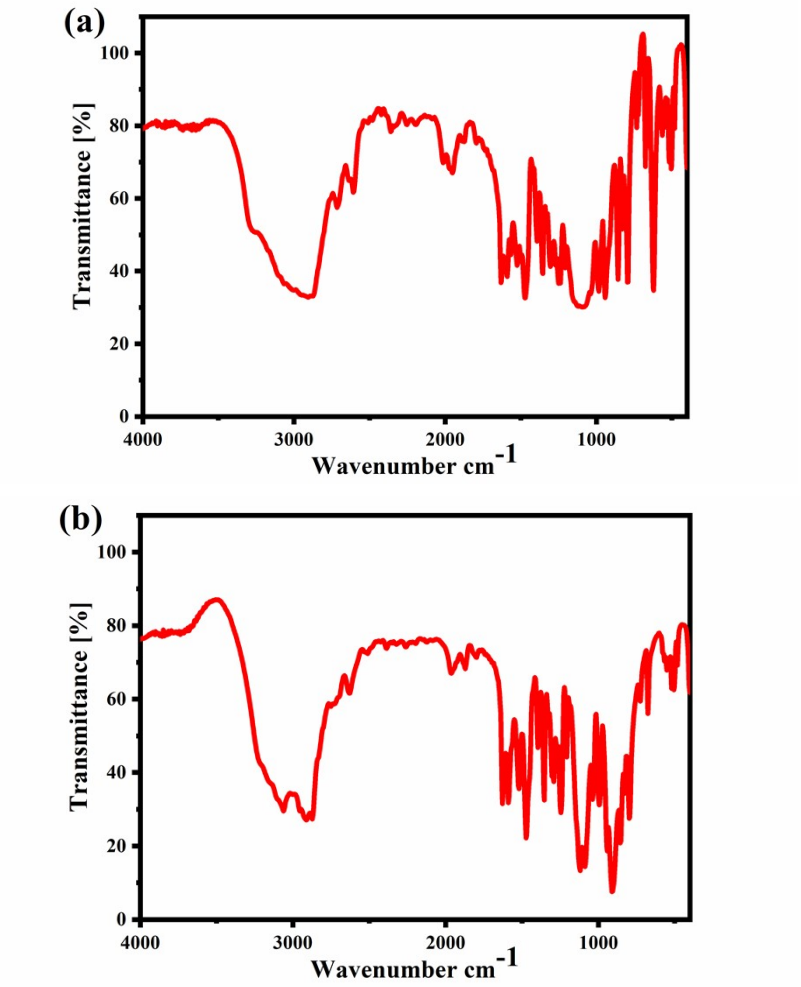
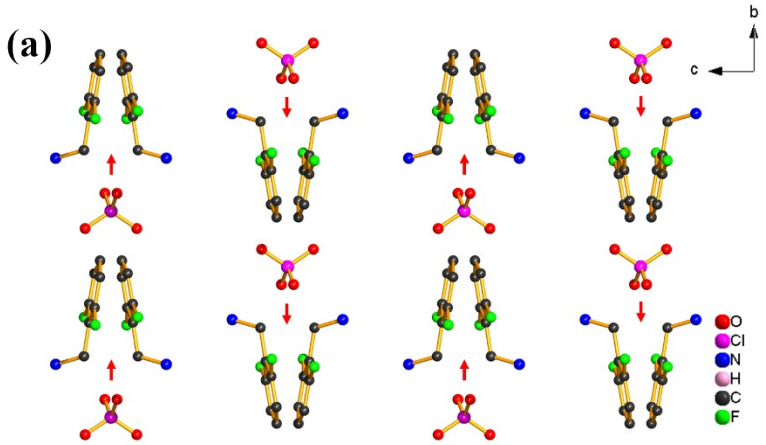


Figure S2. Infrared (IR) spectra of solid compounds **1** (a) and **2** (b) in KBr pellet recorded at room temperature.



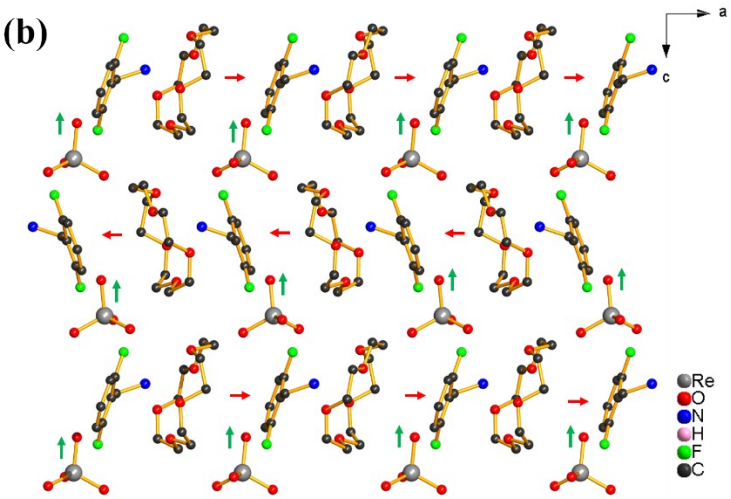


Figure S3. (a) the stacking packing of **1** viewed along the *a*-axis of compound **1**, (b) the stacking packing of **2** viewed along the *b*-axis of compound **2**.

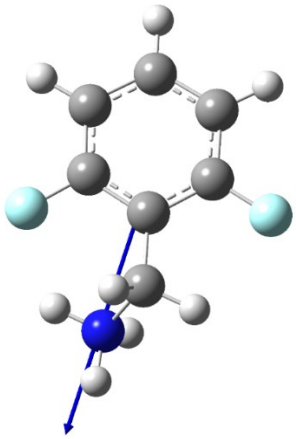


Figure S4. Schematic diagram of the dipole moment of the organic ammonium, the blue arrow indicates the direction of the dipole.

Calculation condition:

The geometry optimization and dipole moment were calculated at b3lyp/6-31G(d) level with Gaussian 16 software. DFT-D dispersion correction was treated with DFT-D3 method with Becke-Jonson damping.[1] We constructed molecular conformation based on the experimentally measured single crystal X-ray diffraction structure.

1. Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J Comput Chem* **2011,** *32* (7), 1456-1465.

Table S1. Bond lengths (Å) and angles (°) of **1** at 293 K.

1			
O8-Cl2	1.283(6)	O4-C9	1.431(4)
O10-Cl2	1.263(6)	O4-C8	1.448(5)
Cl1-O7	1.373(4)	C11-C12	1.378(5)
Cl1-O7[1]	1.373(4)	C11-C16	1.389(5)
Cl1-O6[1]	1.399(3)	C11-C17	1.505(5)
Cl1-O6	1.399(3)	F2-C12	1.351(4)
Cl2-O10[2]	1.263(6)	C5-C6	1.501(5)
Cl2-O8[2]	1.283(6)	C4-C3	1.501(5)
O2-C5	1.424(4)	C12-C13	1.362(6)
O2-C4	1.423(4)	C16-F1	1.348(5)
O3-C6	1.414(5)	C16-C15	1.371(7)
O3-C7	1.415(4)	C1-C2	1.505(5)
O5-C1	1.408(4)	C10-C9	1.497(5)
O5-C10	1.407(5)	C8-C7	1.478(6)
O1-C2	1.411(4)	C15-C14	1.366(8)
O1-C3	1.412(4)	C14-C13	1.324(8)
N1-C17	1.472(4)		
O7-Cl1-O7[1]	110.3(6)	O2-C5-C6	112.7(3)
O7-Cl1-O6[1]	110.0(3)	O2-C4-C3	106.7(3)

O7[1]-Cl1-O6[1]	106.8(3)	F2-C12-C11	116.3(3)
O7-Cl1-O6	106.8(3)	F2-C12-C13	119.4(4)
O7[1]-Cl1-O6	110.0(3)	C11-C12-C13	124.3(4)
O6[1]-Cl1-O6	113.0(4)	F1-C16-C15	120.7(4)
O10[2]-Cl2-O10	112.3(10)	F1-C16-C11	116.3(4)
O10[2]-Cl2-O8	115.5(8)	C15-C16-C11	123.0(4)
O10-Cl2-O8	101.0(5)	O1-C3-C4	112.5(3)
O10[2]-Cl2-O8[2]	101.0(5)	N1-C17-C11	112.7(3)
O10-Cl2-O8[2]	115.5(8)	O5-C1-C2	108.2(3)
O8-Cl2-O8[2]	112.2(8)	O5-C10-C9	106.5(3)
C5-O2-C4	114.9(3)	O4-C8-C7	112.4(3)
C6-O3-C7	112.6(3)	O3-C6-C5	108.8(3)
C1-O5-C10	113.0(3)	O1-C2-C1	109.8(3)
C2-O1-C3	113.1(3)	O3-C7-C8	108.7(3)
C9-O4-C8	113.1(3)	O4-C9-C10	108.8(3)
C12-C11-C16	113.7(3)	C14-C15-C16	118.7(5)
C12-C11-C17	124.5(3)	C13-C14-C15	121.1(5)
C16-C11-C17	121.8(3)	C14-C13-C12	119.1(5)

Table S2. Bond lengths (Å) and angles (°) of **2** at 293 K

2			
Re1-O2	1.685(8)	O5-C18	1.433(12)
Re1-O4	1.688(7)	C8-C30	1.364(12)

Re1-O3	1.703(7)	C8-C33	1.380(12)
Re1-O1	1.731(8)	C8-C12	1.503(9)
N1-C12	1.497(10)	C10-C13	1.479(14)
O6-C13	1.400(12)	C11-C22	1.52(2)
O6-C19	1.409(11)	C14-C24	1.495(17)
O7-C10	1.416(12)	C17-C21	1.336(17)
O7-C14	1.413(12)	C17-C33	1.374(14)
O8-C24	1.404(13)	C18-C19	1.471(18)
O8-C34	1.409(14)	C21-C35	1.396(18)
O9-C11	1.402(13)	C26-C34	1.476(17)
O9-C26	1.418(13)	C30-F2	1.351(11)
F1-C33	1.355(11)	C30-C35	1.371(12)
O5-C22	1.399(17)		
O2-Re1-O4	108.4(6)	O6-C13-C10	109.0(9)
O2-Re1-O3	109.8(5)	O7-C14-C24	112.3(8)
O4-Re1-O3	110.4(5)	C21-C17-C33	118.5(10)
O2-Re1-O1	111.2(6)	C19-C18-O5	109.1(8)
O4-Re1-O1	107.4(6)	C18-C19-O6	107.8(10)
O3-Re1-O1	109.6(4)	C17-C21-C35	121.9(10)
C13-O6-C19	115.7(9)	O5-C22-C11	113.4(9)
C10-O7-C14	113.1(9)	O8-C24-C14	106.0(9)
C24-O8-C34	113.5(8)	O9-C26-C34	109.1(9)
C11-O9-C26	112.8(10)	O8-C34-C26	113.0(9)
C22-O5-C18	113.8(10)	F2-C30-C8	115.9(7)

C30-C8-C33	114.9(8)	F2-C30-C35	119.2(9)
C30-C8-C12	123.8(8)	C8-C30-C35	124.8(10)
C33-C8-C12	121.3(8)	F1-C33-C8	118.4(8)
O7-C10-C13	109.8(9)	F1-C33-C17	118.2(9)
O9-C11-C22	110.2(10)	C8-C33-C17	123.5(10)
N1-C12-C8	112.1(6)	C30-C35-C21	116.4(10)

Table S3. 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--H1A···O2	0.89	2.02	2.871(3)	160
N1--H1A···O3	0.89	2.42	2.941(4)	118
N1−H1B···O4	0.89	1.97	2.830(3)	161
N1−H1B···O5	0.89	2.56	3.015(4)	113
N1−H1C···F2	0.89	2.36	2.887(4)	118
N1−H1C···O1	0.89	2.43	2.914(3)	115
N1−H1C···O8	0.89	2.38	2.989(9)	125

Table S4. 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−H1A···F2	0.89	2.54	2.887(8)	104
N1−H1A···O7	0.89	2.50	2.908(8)	108
N1−H1A···O3	0.89	2.13	2.889(10)	143
N1−H1B···O5	0.89	1.95	2.833(9)	169
N1−H1B···O6	0.89	2.50	2.994(8)	115

N1−H1C···O7	0.89	2.57	2.908(9)	103
N1−H1C···O8	0.89	2.01	2.895(8)	172
N1−H1C···O9	0.89	2.49	2.903(8)	109