Electronic Supplementary Information

A host-guest inclusion compound for reversible switching of quadratic nonlinear optical properties

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Experimental details

All the chemical reagents were purchased as high purity (AR grade) and used without any further purification. [(Dipropylammonium)(18-crown-6)]ClO_4 has been synthesized in aqueous solution of perchloric acid, dipropylamine and 18-crown-6 in a ratio of 1:1:1. XRPD patterns were recorded by an X-ray diffractometer (Rigaku Corporation SCXmini). Thermal properties including DSC and specific heat were respectively measured by a differential thermal analyzer of Netzsch DSC 200 F3 under nitrogen atmosphere in aluminum crucibles with the heating/cooling rate of 10 K/min. Dielectric experiments were carried out on polycrystalline powder specimen by TH2828 Precision LCR Meter at different frequency with an applied electric field of 0.5 V. The electrodes were made by sputtering silver onto both sides of samples and attaching copper leads with silver paste. Calibration of standard capacitor reveals that the experimental errors are within ± 1% accuracy. Variable-temperature SHG experiments were executed by Kurtz-Perry powder SHG test using an Nd:YAG laser (1064 nm) with input pulse of 350 mV under a programmable cryogenic cooling system.[1] The values of the nonlinear optical coefficients for SHG have been determined by comparison with a KDP reference.[2]

Variable-temperature X-ray single crystal diffraction experiments were performed on a Rigaku Saturn70 diffractometer with Mo/Cu-Kα radiation (λ = 0.71073/1.5406 Å). Absorption corrections were applied by using multi-scan program.[3] Crystal structures were solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXLTL software package using SHELXS-97.[4] All non-hydrogen atoms positions were located using difference Fourier methods as implemented in SHELXL-97. All of the non-hydrogen atoms were refined anisotropically and the positions of the hydrogen atoms were generated geometrically.

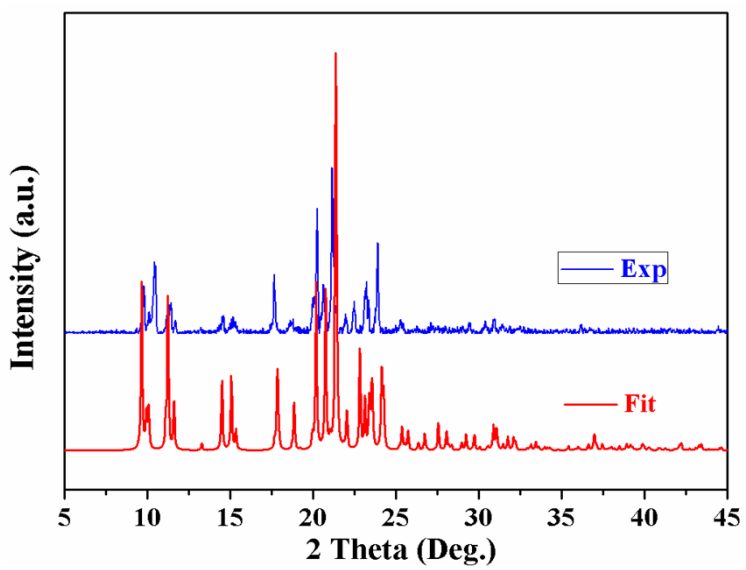


Figure S1. Simulated and experimental XRD powder patterns for [(DPA)(18-crown-6)]ClO_4

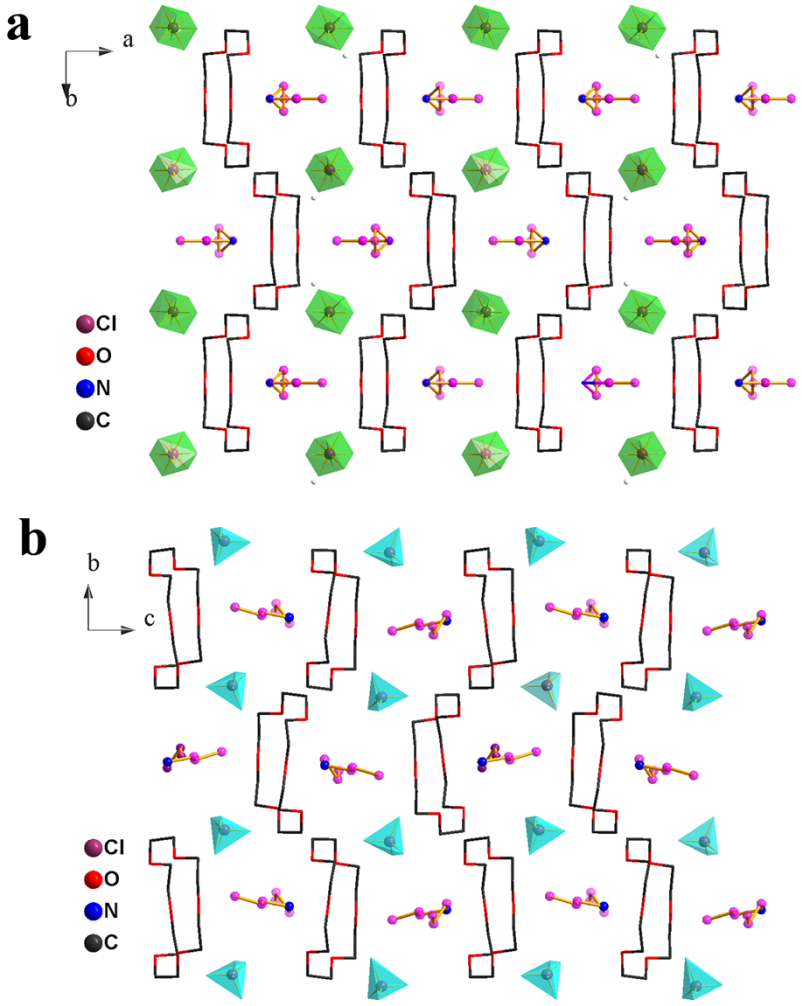
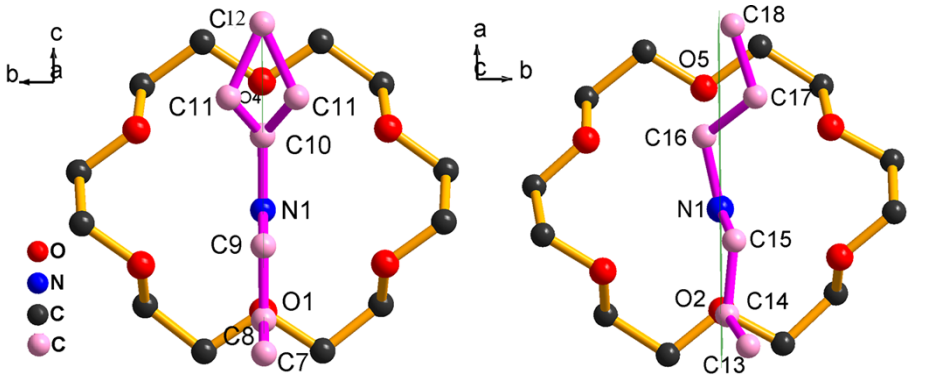


Figure S2. Packing views along the (a) *a*-axis (RTP) and (b) *c*-axis (LTP) for [(DPA)(18-crown-6)]ClO_4



ω_1 (C7 - C8 - C9 - N1) =180° **ω_3 (C13-C14-C15-N1)=174.45°**

ω_2 (C12-C11-C10-N1)=160.04° **ω_4 (C18-C17-C16-N1)=-174.88°**

Figure S3. The torsion angles for C–C–C–N of DPA cations at 100K and 293 K.

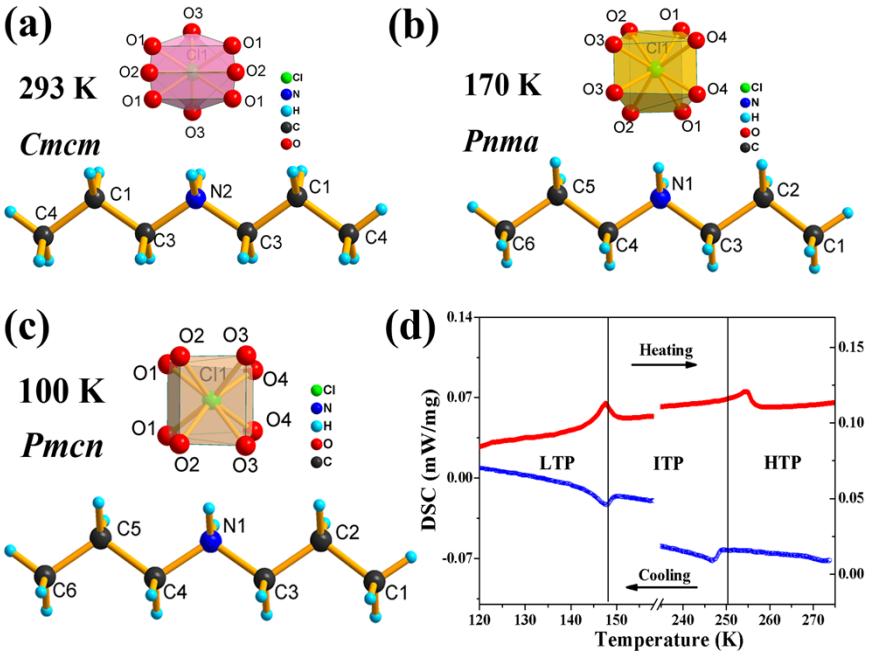


Figure S4. Asymmetric unit of (DPA)ClO_4 in (a) RTP, (b) ITP and (c) LTP. Hydrogen atoms are omitted for clarity. (d) DSC curves of 1 obtained on a heating–cooling cycle.

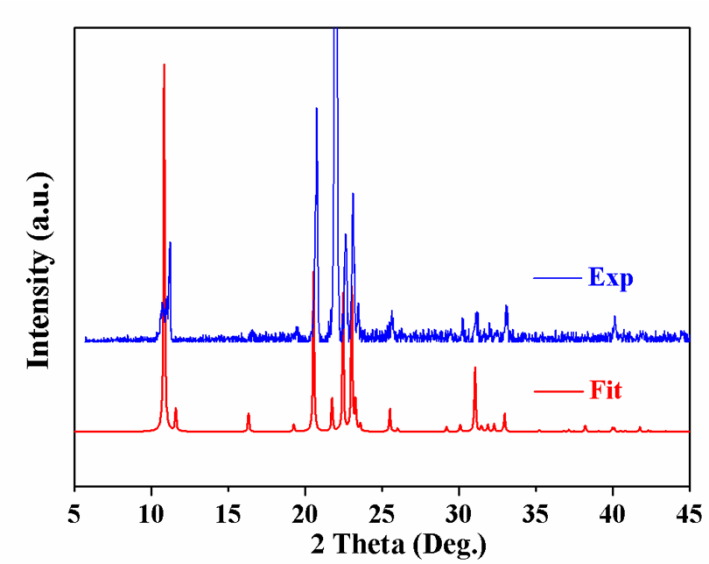


Figure S5. Simulated and experimental XRD powder patterns for $(DPA)ClO_4$

Table S1. Crystal data and structure refinement details for $[(DPA)(18\text{-crown-6})]ClO_4$ at 100K and 293 K.

Empirical formula		$C_{18}\ H_{40}\ Cl\ N\ O_{10}$
Formula weight	465.96	465.96
Temperature	100 K	293 K
Wavelength	0.71073	1.54184
Crystal system,	Orthorhombic,	Orthorhombic,
space group	$P2_12_12_1$	*Pnma*
a (Å)	10.031	16.577
c (Å)	15.109	15.142
c (Å)	16.199	10.091
V (Å^3)	2455	2532.78(9)
Z	4	4
Calculated density (mg/Å^3)	1.261	1.222
F(000)	1008	1008
Limiting indices	-13≤h≤13, -19≤k≤19, -21≤l≤19	-20≤h≤18, -18≤k≤18, -12≤l≤12
Reflections collected / unique	18956/5591 [R(int) = 0.0546]	8168/2620 [R(int) = 0.0162]
Completeness	99.6 %	97.3 %
Max. and min. transmission	0.9603 and 0.9603	0.7207 and 0.7207
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5591 / 0 / 273	2062 / 0 /182
Goodness-of-fit on F^2	1.077	1.044
Final R indices [I>2sigma(I)]	R_1 = 0.0376, wR_2 = 0.0903	R_1 = 0.0471, wR_2 = 0.1369
R indices (all data)	R_1 = 0.0482, wR_2 = 0.1329	R_1 = 0.0580, wR_2 = 0.1481

Table S2. Crystal data and structure refinement details for $(DPA)ClO_4$ at 100 K, 170K and 273K

Empirical formula		$C_6 H_{16} Cl N O_4$	
Formula weight	201.65	201.65	201.65
Temperature	100 K	170 K	273 K
Crystal system,	Orthorhombic,	Orthorhombic,	Orthorhombic,
space group	*Pmcn*	*Pnma*	*Cmcm*
a (Å)	7.4714(8)	8.5346(3)	16.354
b (Å)	16.0278(18)	7.5928(3)	8.649
c (Å)	8.4874(9)	16.1352(6)	7.727
V(Å^3)	1016.37(19)	1045.59(7)	1092.83
Z	4	4	4
Calculated density (mg/Å^3)	1.319	1.281	1.226
F(000)	432	432	432
Limiting indices	-8≤h≤8,	-10≤h≤10,	-19≤h≤20,
	-18≤k≤18,	-8≤k≤8,	-7≤k≤10,
	-10≤l≤9	-18≤l≤19	-6≤l≤9
Reflections collected/unique	5387 / 966 [R(int)= 0.0680]	5515 / 991 [R(int) = 0.0326]	1695 / 601 [R(int)= 0.0155]
Completeness	99.4 %	99.4 %	96.0 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints/parameters	966 / 1 / 98	991 / 1 / 103	601 / 19 / 53
Goodness-of-fit on F^2	1.265	1.078	1.116
Final R indices [I>2sigma(I)]	R_1 = 0.1108,	R_1 = 0.0346,	R_1 = 0.0723,
	wR_2 = 0.3618	wR_2 = 0.0830	wR_2 = 0.2089
R indices (all data)	R_1 = 0.1154,	R_1 = 0.0454,	R_1 = 0.0762,
	wR_2 = 0.3640	wR_2 = 0.0894	wR_2 = 0.2176

Table S3 Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 x 10^{-3}) for [(DPA)(18-crown-6)]ClO_4 at 293 K. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

ATOM	X	Y	Z	$U_{(eq)}$
Cl(1)	5000	0	5000	74(1)
O(4)	1012(1)	2500	6457(2)	67(1)
O(2)	2407(1)	905(1)	3050(1)	62(1)
O(3)	1689(1)	855(1)	5611(2)	68(1)

N(1)	3094(1)	2500	4210(2)	56(1)
C(1)	1846(2)	1725(2)	1279(2)	75(1)
C(6)	1032(2)	1726(2)	7241(2)	80(1)
C(3)	2385(2)	136(1)	3868(3)	80(1)
C(5)	978(1)	936(2)	6382(2)	81(1)
C(2)	1741(1)	960(2)	2173(2)	76(1)
C(9)	3930(2)	2500	3615(3)	79(1)
C(4)	1679(2)	101(1)	4785(3)	82(1)
C(10)	3098(2)	2500	5671(3)	109(2)
C(8)	3947(2)	2500	2167(3)	92(1)
C(7)	4766(3)	2500	1618(5)	154(3)
C(11)	3533(3)	2057(3)	6481(4)	70(1)
C(12)	3552(3)	2500	7922(4)	123(2)
O(1)	1843(1)	2500	2053(2)	58(1)
O(8)	5778(2)	29(3)	5416(4)	94(1)
O(6)	4644(3)	-802(3)	-4943(4)	104(1)
O(7)	4515(2)	532(3)	6049(6)	129(2)
O(5)	4896(3)	504(4)	3800(6)	147(2)

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^{-3}$) for [(DPA)(18-crown-6)]ClO_4 at 100 K. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

ATOM	X	Y	Z	$U_{(eq)}$
Cl(1)	9874(1)	7703(1)	2374(1)	23(1)
O(1)	16858(2)	3344(1)	168(1)	22(1)
O(2)	17982(2)	4934(1)	672(1)	22(1)
O(3)	17078(2)	6530(1)	19(1)	21(1)
O(5)	13582(2)	5146(1)	1561(1)	27(1)
O(6)	14317(2)	3447(1)	893(1)	28(1)
O(4)	14512(2)	6736(1)	790(1)	26(1)
N(1)	15764(2)	4943(1)	569(1)	20(1)
C(11)	18675(2)	4120(2)	756(2)	25(1)
C(2)	15011(3)	2628(2)	900(2)	26(1)
C(1)	15959(3)	2608(2)	186(2)	26(1)
C(10)	18853(2)	5667(2)	582(2)	24(1)
C(4)	12749(3)	4386(2)	1562(2)	33(1)
O(9)	9529(2)	7663(1)	3229(1)	33(1)
O(7)	10050(2)	6823(1)	2064(1)	39(1)
C(8)	16329(3)	7333(2)	25(2)	26(1)
C(9)	18043(2)	6498(2)	667(2)	22(1)
C(7)	15440(2)	7440(2)	767(2)	26(1)
C(12)	17681(2)	3401(2)	884(2)	26(1)
C(15)	16307(2)	4763(2)	-1409(2)	25(1)
C(14)	17806(3)	4866(2)	-1441(2)	28(1)

C(16)	14291(2)	5150(2)	-559(2)	24(1)
C(5)	12824(3)	5942(2)	1524(2)	31(1)
C(3)	13568(3)	3566(2)	1634(2)	32(1)
O(10)	8822(2)	8131(1)	1925(1)	39(1)
C(17)	13446(2)	4459(2)	-978(2)	28(1)
C(6)	13753(3)	6724(2)	1535(2)	30(1)
C(13)	18332(3)	4589(2)	-2286(2)	43(1)
O(8)	11096(2)	8190(2)	2280(2)	50(1)
C(18)	11993(3)	4755(2)	-1011(2)	40(1)

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement arameters ($Å^2 \times 10^{-3}$) for $(DPA)ClO_4$ at 273 K. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

ATOMS	X	Y	Z	$U_{(eq)}$
Cl(1)	0	7184(1)	2500	65(1)
N(2)	0	2889(4)	2500	54(1)
C(3)	-759(3)	1961(5)	2500	74(1)
C(1)	-1507(4)	2915(7)	2500	97(2)
O(2)	0	6160(20)	1080(20)	70(13)
O(3)	-617(7)	8152(8)	2500	249(5)
C(4)	-2272(6)	1904(17)	2500	159(5)
O(1)	-410(20)	6258(19)	1190(20)	107(6)

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement arameters ($Å^2 \times 10^{-3}$) for $(DPA)ClO_4$ at 170 K. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

ATOMS	X	Y	Z	$U_{(eq)}$
Cl(1)	2837(1)	2500	4892(1)	30(1)
N(1)	2863(2)	7500	4912(1)	24(1)
O(1)	2888(3)	3799(3)	4581(2)	51(1)
C(6)	1449(5)	7500	7160(2)	69(1)
C(2)	3190(3)	7500	3381(1)	38(1)
C(4)	1770(3)	7500	5631(1)	30(1)
O(2)	3744(3)	3809(3)	5342(2)	52(1)
C(5)	2611(3)	7500	6450(2)	41(1)
C(3)	2051(3)	7500	4095(1)	31(1)
O(3)	1712(3)	3272(3)	5425(2)	56(1)
C(1)	2324(5)	7500	2561(2)	63(1)
O(4)	2050(3)	1638(4)	4225(2)	60(1)

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement arameters ($Å^2 \times 10^{-3}$) for $(DPA)ClO_4$ at 100 K. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

ATOMS	X	Y	Z	$U_{(eq)}$

Cl(1)	7500	5114(2)	7096(3)	20(1)
N(1)	2500	5104(5)	7200(1)	18(2)
C(4)	2500	4373(7)	8316(14)	21(3)
C(2)	2500	6652(7)	6841(14)	24(3)
O(2)	6243(17)	5486(8)	6019(13)	29(4)
C(4)	6195(17)	4599(8)	6212(14)	33(4)
O(2)	6476(18)	5750(8)	7898(14)	30(4)
C(5)	2500	2832(9)	8266(19)	37(4)
C(3)	2500	3553(7)	7444(15)	27(3)
O(3)	2500	5929(7)	8017(14)	25(3)
C(1)	6625(19)	4601(8)	8204(14)	32(4)
O(4)	2500	7473(8)	7714(18)	33(3)

References

[1] S. K. Kurtz and T. T. Perry, *J. Appl. Phys,* 1968, 39, 3798.

[2] D. A. Robert, IEEE J, 1992, QE-28, 2057.

[3] *APEX2, SADABS* and *SAINT*. Bruker AXS Inc.: Madison, Wisconsin, USA.. 2008.

[4] G. M. Sheldrick, SHELXL *97*, *Program for Crystal Structure Solution;* University of GÖttingen: GÖttingen, Germany, 1997.