Supporting Materials

Reversible Phase Transition and Switchable Dielectric Behaviors Triggered by Rotation and Order-Disorder Motions of Crowns

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1. Figure S1 to S4

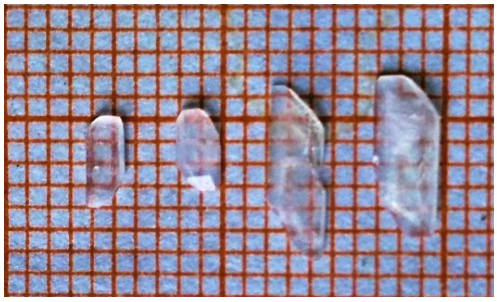


Figure S1 The block crystal of compound **1**.

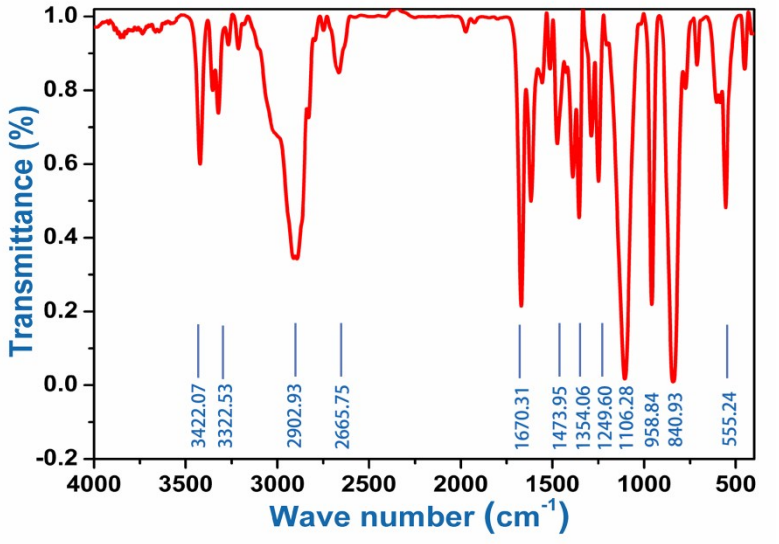


Figure S2 the IR spectrum of compound **1** at room temperature.

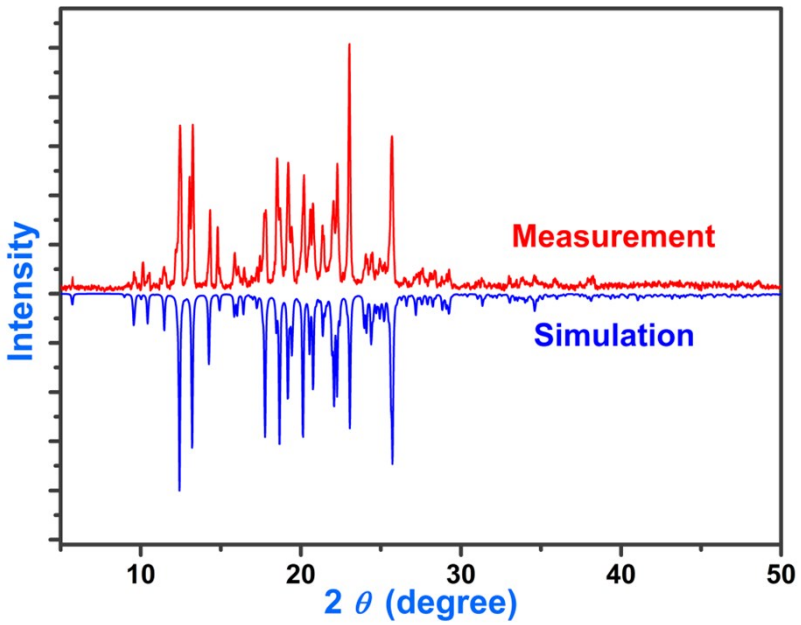
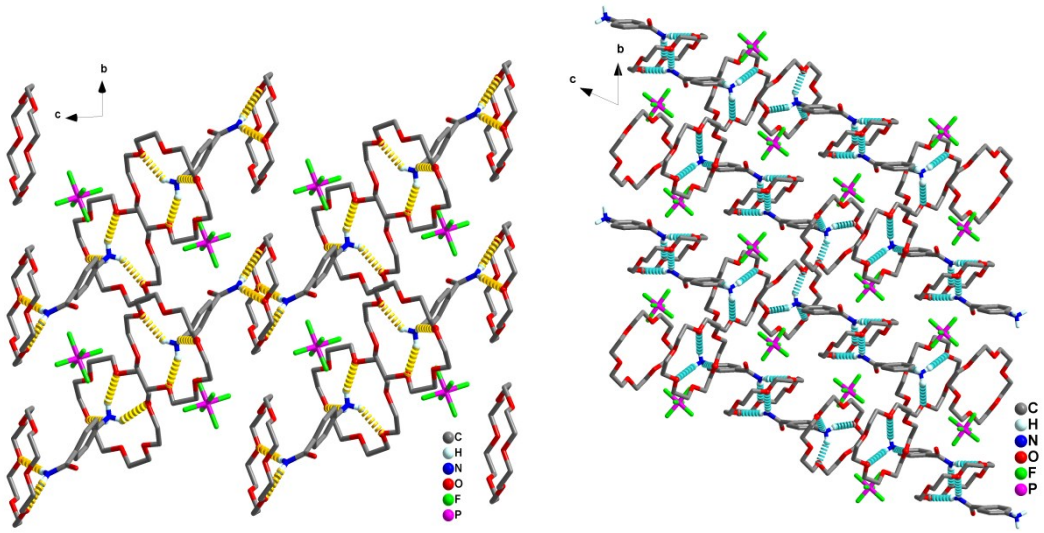


Figure S3 the experimental PXRD patterns and the simulation based on the single-crystal analysis of **1**.



(a) (b)

Figure S4 Viewed from the *a*-axis direction shows (a) the parallel crown cycles in the packing diagram of **1-RTP** and (b) the interlaced crown cycles in the packing diagram of **1-LTP**.

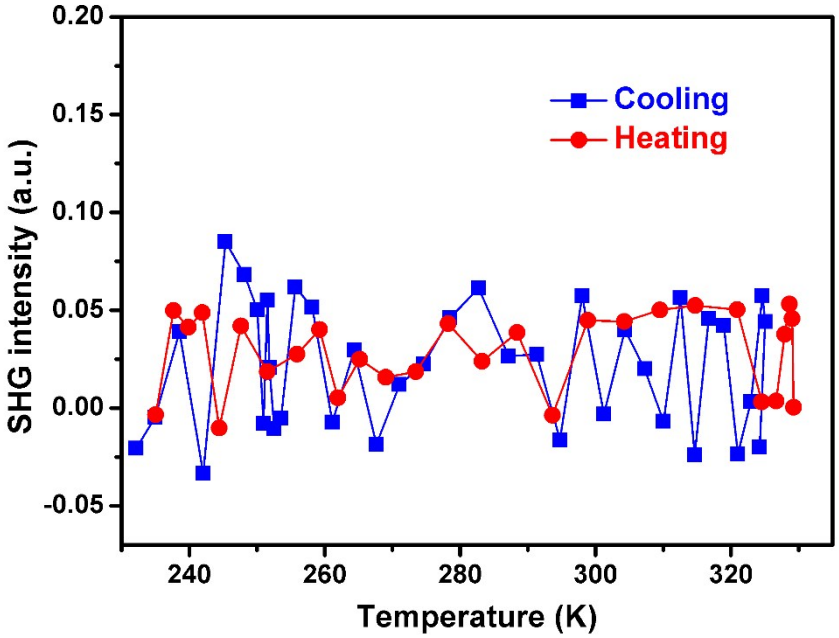


Figure S5 The SHG intensity dependence on temperature during the cooling and heating processes.

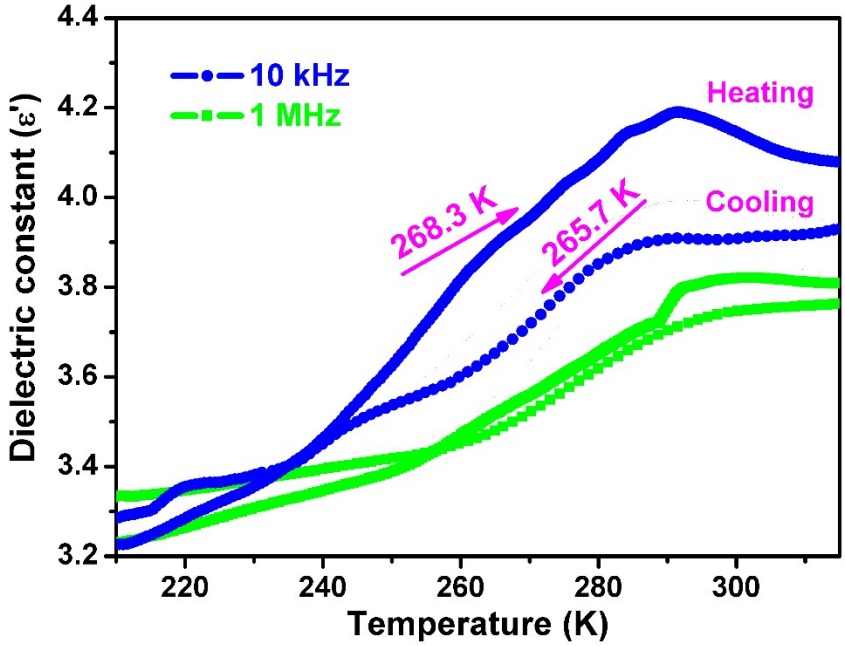


Figure S6 The dielectric constant dependence on the temperature under 10 kHz, and 1 MHz.

2. Table S1

Table S1 Intermolecular Hydrogen Bond Lengths (Å) and Angles (Degrees) for **1-RTP** and **1-LTP**.

D-H···A	D-H	H···A	D···A	∠D-H···A
1-RTP				
N2-H2C···O2	0.89	2.01	2.862(5)	159.1
N2-H2A···O4	0.89	2.05	2.840(6)	146.6
N2-H2B···O6	0.89	2.01	2.814(6)	150.4
N1-H1B···O8	0.86	2.23	3.064(5)	165.0
N1-H1A···O9#1	0.86	2.16	2.991(5)	161.9
1-LTP				
N2-H2C···O2#2	0.91	2.00	2.891(4)	167.3
N2-H2B···O6#2	0.91	1.90	2.803(4)	173.8
N2-H2A···O4#2	0.91	1.96	2.820(4)	156.9
N4-H4C···O10#3	0.91	2.04	2.874(4)	151.0
N4-H4B···O14#3	0.91	1.99	2.855(4)	157.9
N4-H4A···O12#3	0.91	1.99	2.882(4)	165.6
N3-H3B···O16	0.88	2.20	3.053(4)	164.6
N3-H3A···O18	0.88	2.09	2.943(4)	164.5
N1-H1B···O19	0.88	2.19	3.044(4)	165.1
N1-H1A···O15	0.88	2.12	2.973(4)	163.5

Symmertry codes: #1: -x+1, -y, -z+1; #2: -x+1,-y+1,-z; #3: x-1, y, z.

3. Calculation of the Δ*S* and *N* for the cooling and heating cycles

3.1 In the cooling cycle mode

$$\begin{aligned}
\Delta S &= \int_{T_1}^{T_2} \frac{Q}{T}\, dT \\
&\approx \frac{\Delta H}{T_C} \\
&= \frac{1.107\ J \cdot g^{-1} \times 1357.2\ g \cdot mol^{-1}}{263.5\ K} \\
&= 5.702\ J \cdot mol^{-1} \cdot K^{-1} \\
\Delta S &= R \ln N \\
N &= \exp\left(\frac{\Delta S}{R}\right) = \exp\left(\frac{5.702\ J \cdot mol^{-1} \cdot K^{-1}}{8.314\ J \cdot mol^{-1} \cdot K^{-1}}\right) \\
&= 1.985 \\
\Delta H &= T\Delta S \\
&= 263.5\,K \times 5.702\ J \cdot mol^{-1} \cdot K^{-1} \\
&= 1502.5\ J \cdot mol^{-1}
\end{aligned}$$

3.2 In the heating cycle mode

$$
\begin{aligned}
\Delta S &= \int_{T_1}^{T_2} \frac{Q}{T}\, dT \\
&\approx \frac{\Delta H}{T_C} \\
&= \frac{0.9713\ J \cdot g^{-1} \times 1357.2\ g \cdot mol^{-1}}{264.0\ K} \\
&= 4.993\ J \cdot mol^{-1} \cdot K^{-1} \\
\Delta S &= R \ln N \\
N &= \exp\left(\frac{\Delta S}{R}\right) = \exp\left(\frac{4.993\ J \cdot mol^{-1} \cdot K^{-1}}{8.314\ J \cdot mol^{-1} \cdot K^{-1}}\right) \\
&= 1.823 \\
\Delta H &= T\Delta S \\
&= 264.0\,K \times 4.993\ J \cdot mol^{-1} \cdot K^{-1} \\
&= 1318.2\ J \cdot mol^{-1}
\end{aligned}
$$