Electronic Supplementary Information

for

A confinement-regulated $(H_3C–NH_3)^+$ ion as a smallest dual-wheel rotator showing bisected rotation dynamics

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Table S1 Summary of crystal data and structural refinements for **1** at 150 and 293 K

Temperature (K)	150(2)	293(2)
Empirical formula	$C_{13}H_{30}N_1O_6Cl_3Cu_1$	
Formula weight	466.27	
Space group	*P*-1	
a (Å)	8.5399(4)	8.646(1)
b (Å)	10.3775(3)	10.446(2)
c (Å)	12.2132(6)	12.352(2)
α (deg)	82.772(3)	82.605(2)
β (deg)	80.178(4)	79.325(2)
γ (deg)	82.737(3)	82.289(2)
Z	2	
D_{calcd} / g cm^{-3}	1.472	1.434
μ / mm^{-1}	1.444	1.407
GOF on F^2	1.006	1.028
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0659, 0.2148	0.0385, 0.1016
R_1, wR_2 (all data)	0.0726, 0.2176	0.0520, 0.1148

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Table S2 Selected bond lengths (Å) for **1** at 150 and 293 K

153 K			
Cu1–Cl2	2.209(2)	Cu1–Cl1	2.212(2)
Cu1–Cl3	2.302(2)	Cu1–Cl3#1	2.316(2)
293 K			
Cu1–Cl2	2.1972(9)	Cu1–Cl1	2.2037(9)
Cu1–Cl3	2.306(1)	Cu1–Cl3#1	2.323(1)

Symmetry code: #1. $-x + 1, -y, -z + 2$.

Table S3 The hydrogen-bond geometries (Å, °) for **2** at 150 and 293 K

	D–H···A	D–H	H···A	D···A	Angle
150 K	N1–H1C···O5	0.900(6)	2.05(1)	2.921(1)	162.0(5)
	N1–H1D···O1	0.900(6)	1.874(1)	2.720(1)	155.8(5)
	N1–H1E···O3	0.900(6)	2.192(2)	3.018(2)	152.3(6)
293 K	N1–H1C···O5	0.907(2)	2.027(7)	2.901(7)	161.5(2)
	N1–H1D···O1	0.904(2)	1.959(8)	2.819(8)	158.6(3)
	N1–H1E···O3	0.906(2)	2.124(9)	2.965(9)	154.2(3)

Table S4 Fitting parameters of the Havriliak–Negami equation for **1** at a series of temperatures from 160 to 230 K

T (K)	τ_0 (s)	ε_0	ε_∞	α	β
160	9.7×10^{-5}	3.10	3.02	0.13	0.54
170	2.6×10^{-5}	3.11	3.02	0.24	0.73
180	9.7×10^{-6}	3.13	3.03	0.24	0.83
190	3.6×10^{-6}	3.14	3.05	0.23	0.93
200	1.4×10^{-6}	3.17	3.06	0.22	1.0
210	7.0×10^{-7}	3.20	3.08	0.21	1.0
220	4.0×10^{-7}	3.22	3.09	0.21	1.0
230	2.4×10^{-7}	3.23	3.10	0.21	1.0

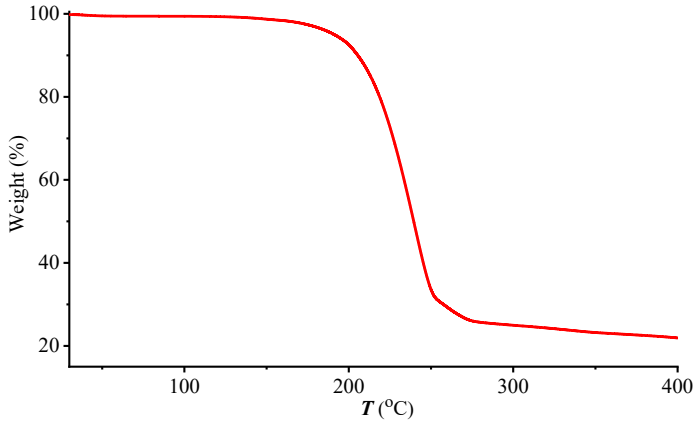

Fig. S1 Thermogravimetric curve for **1**.

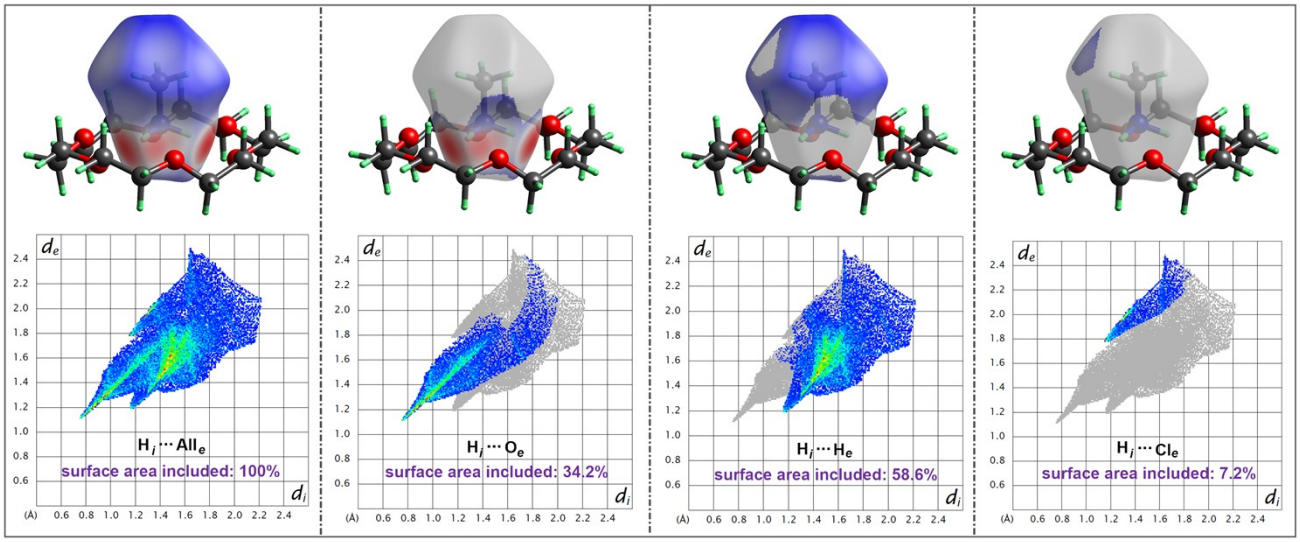

Fig. S2 Above: Views of the Hirshfeld surface (mapped with d_{norm}) of one $(CH_3NH_3)^+$ ion in **1** at 293 K, indicating the relative strength of the intermolecular interactions surrounding the $(CH_3NH_3)^+$ ion. The red, white, and blue regions represent molecular contacts shorter than, equal to, and longer than the van der Waals distance, respectively. Below: 2D fingerprint plots showing atomic contacts to the Hirshfeld surface of one $(CH_3NH_3)^+$ ion in **1** at 293 K, where d_i and d_e denote the distances from the surface to the nearest atom interior and exterior to the surface, respectively. The 2D plots were created by binning (d_e, d_i) pairs and coloring each bin of the resulting 2D histogram as a function of the fraction of surface points in that bin, ranging from blue (few points) through green to red (many points).

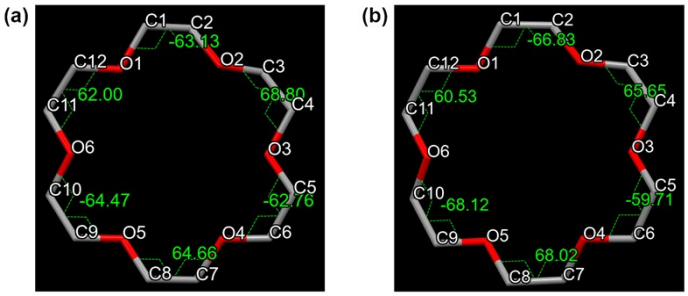

Fig. S3 Comparison of the conformations of the O1-containing 18-crown-6 molecule in **1** at 150 K (a) and 293 K (b), respectively, with slight change of their torsions.

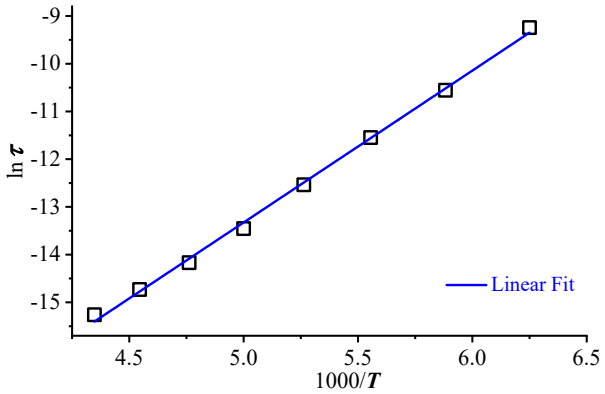

Fig. S4 Arrhenius plots of the relaxation time τ as a function of inverse temperature for **1**.

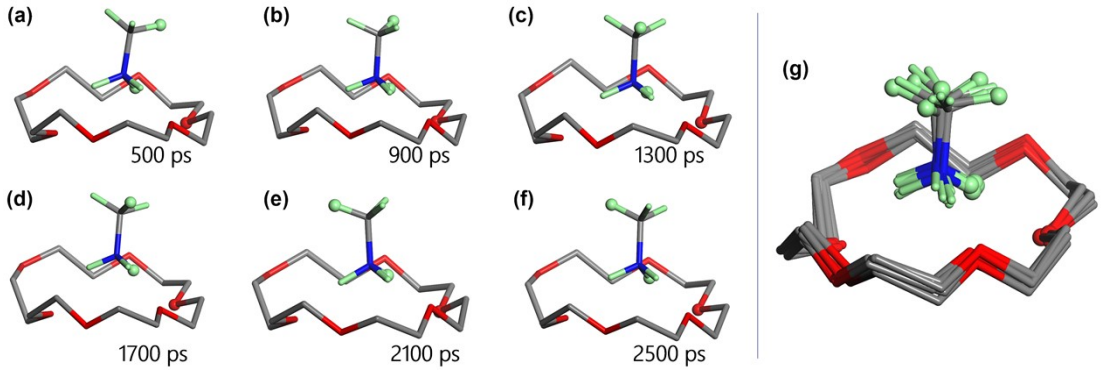

Fig. S5 Snapshots of NVT dynamic simulation for the $[(CH_3NH_3)(18\text{-crown-}6)]^+$ complex in **1** at T_S of 150 K (a-f), and the overlapping maps of these snapshots (g), to display their dynamics. The specified H and O atoms are highlighted by balls to guide the eye.

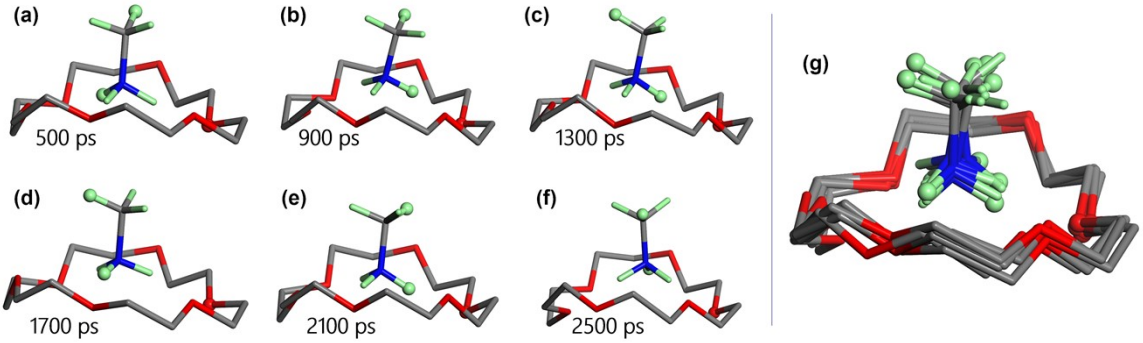

Fig. S6 Snapshots of NVT dynamic simulation for the $[(CH_3NH_3)(18\text{-crown-}6)]^+$ complex in **1** at T_S of 330 K (a-f), and the overlapping maps of these snapshots (g), to display their dynamics. The specified H and O atoms are highlighted by balls to guide the eye.

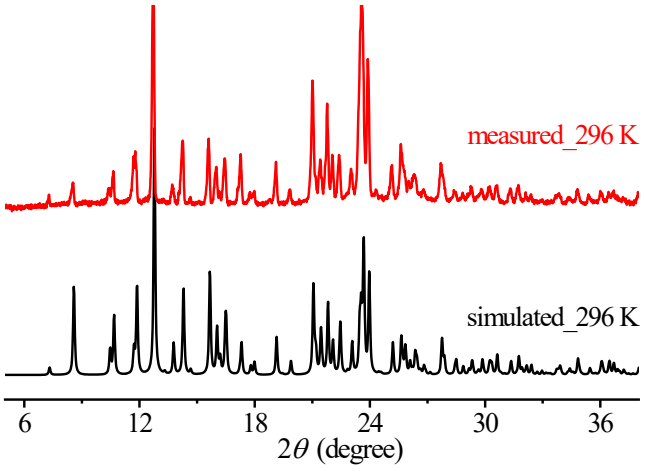

Fig. S7 Simulated and experimental PXRD patterns for **1** at room temperature.