Electronic Supplementary Material for

Unprecedented Water-Controlled Rotator–Stator Conversion of Supramolecular Rotor in Crystals

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Experimental details.

Materials and General Methods. Reagents and solvents were commercially available and used without further purification. Thermogravimetric analysis was performed using a TA-Q50 system.

Synthesis of $[(\text{HPAA})(18\text{C6})]BF_4 \cdot 0.5H_2O(1\mathbf{w})$: 18C6 (18-Crown-6, 264 mg, 1 mmol) and PAA (4-phenylazoaniline, 197 mg, 1 mmol) was dissolved in the mixture of methanol and water (10 mL), then equivalent 50% HBF₄ aqueous solution was added to the mixture by drops. The mixed solution was evaporated in air at room temperature. After 1 week, red block-like crystals of $1\mathbf{w}$ were filtered and washed by ethanol, then dried in air (yield: *ca*. 85%).

Synthesis of $[(HPAA)(18C6)]BF_4$ (1): The crystal samples of 1 were obtained by heating 1w at 343 K for 3 h to remove the H₂O molecules in a single-crystal to single-crystal manner. It is worth noting that, the crystal sample of 1 can transfer back to 1w by exposing in humid air at room temperature after *ca*. 12 hours.

Crystal Structure Determination. Diffraction data of **1w**-RT, **1w**-LT, **1**-RT and **1**-LT were collected on a *Rigaku* XtaLAB P300DS single-crystal diffractometer equipped with a graphite-monochromated Cu K α radiation ($\lambda = 1.54178$ Å), respectively. The structures were solved with the direct methods and refined with a full-matrix least-squares technique with the *SHELX* program package. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were positioned geometrically and included in the refinement in the riding-model approximation. Crystal data as well as details of data collection and refinements for the complexes are summarized in **Table S2**. CCDC numbers: 1898785– 1898788 for **1**-RT, **1**-LT, **1w**-RT and **1w**-LT respectively.

Differential scanning calorimeter (DSC). The DSC measurements were performed by heating/cooling the powder sample sealed in aluminum crucibles at a rate of 10 K min⁻¹ on a TA DSC Q2000 instrument from 313 K to 193 K. The value of *N* is estimated by the Boltzmann equation, $\Delta S = R \ln N$, where *R* is the gas constant, *N* represent the ratio of the numbers of state. The value of ΔS calculated by its definition, $\Delta S = \Delta Q/T_c$, where the value of ΔQ is integrated from DSC results by TA Universal Analysis and the value of T_c is phase-transition temperature.

Dielectric measurement. The dielectric measurements were carried on a TH2828A impedance analyzer at 11 different frequencies from 1 kHz to 100 kHz, with an amplitude of 1.0 V, and a temperature sweeping rate of *ca*. 3 K min⁻¹ in a Mercury iTC cryogenic environment controller of Oxford Instrument. Pellets with 5 mm in diameter and 0.4–0.9 mm thick were prepared by pressing microcrystal samples at 780 MPa. Silver conduction paste deposited on the pressed-powder pellets surfaces was used as the

electrodes. The relaxation features of the imaginary part is characterized with the Arrhenius law, $\omega = \omega_0 \exp(E_a/k_BT)$ where ω_0 is a prefactor, E_a is a measure of average activation energy, and k_B is the Boltzmann constant.

Hirshfeld surfaces analysis. Hirshfeld surfaces and the related 2D-fingerprint plots were calculated with high resolution by selecting all disordered part of HPAA⁺ or 18C6 using *CrystalExplorer* with inputting structure file in CIF format (*Cryst. Growth Des.* **2010**, *10*, 4476). The Bond lengths related to hydrogen atoms were set to typical neutron values (C–H = 1.083 Å, N–H = 1.009 Å and O–H = 0.983 Å, respectively). Hirshfeld surfaces mapped with d_{norm} of HPAA⁺ and 18C6 are shown in **Fig. S5**. The surface areas (%) of Hirshfeld surface for 18C6 filtered by elements are listed in **Table S3**. The 2D-fingerprints of 18C6 filtered by elements are in **Fig. S6** and **Fig. S7**.

Ammonium	Role	Anion	Ref	Ammonium	Role	Anion	Ref
NH3	Stator	$\mathrm{BF_4}^-$	J. Am. Chem. Soc. 2014 , 136, 10033;	CN NH3 F	Rotator	Ni(dmit)2 ⁻	<i>CrystEngComm</i> , 2011 , 13, 6185.
NH3	Stator	ClO ₄ ⁻	Angew. Chem. Int. Ed. 2014 , 53, 2114.	F NH ₃	Rotator	ClO ₄ ⁻	Chem. Commun., 2018 , 54, 8076.
NH ₂	Stator	Ni(dmit)2 ⁻	Dalton Trans., 2010, 39, 8219.	NH ₃	Rotator	$\mathrm{BF_4}^-$	J. Am. Chem. Soc. 2011 , 133, 12780;
NH ₂ NH ₃	Stator	Ni(dmit)2 ⁻	Dalton Trans., 2010, 39, 8219.	NH ₃	Rotator	ClO4 ⁻	<i>Phys. Rev. Lett.</i> , 2013 , 110, 257601.
NH ₃	Stator	ClO ₄ -	<i>Chinese Chem.</i> <i>Lett.</i> , 2014 , 25, 723.	NH3	Rotator	Ni(dmit)2 ⁻	<i>Chem. Asian J.</i> 2007 , 2, 1083.
NH ₂	Stator	CuCl4 ⁻	Dalton Trans., 2017 , 46, 12760.	NH ₃	Rotator	BF ₄ ⁻ ClO ₄ ⁻	J. Am. Chem. Soc. 2015 , 137, 13345.
O NH3	Stator	Ni(dmit) ₂ -	<i>CrystEngComm</i> , 2013 , 15, 5307.	мн ₃	Rotator	BF ₄ ⁻ ClO ₄ ⁻	<i>Polyhedron</i> , 2014 , 69, 160.
NH ₃	Rotator	Ni(dmit)2 ⁻	<i>Inorg. Chem.</i> , 2007 , 46, 363.	OH NH ₃	Rotator	Cl⁻	private communication

Table S1. Roles of ammonium in the known ammonium–18C6 supramolecular rotors in crystals.

Compound	[(HPAA)(18C6)]BH	$F_4 \cdot 0.5 H_2 O(1 w)$	[(HPAA)(18C6)]BF ₄ (1)			
Formula	C ₂₄ H ₃₇ B	$F_4N_3O_{6.5}$	$C_{24}H_{36}BF_4N_3O_6$			
Formula weight	558	3.37	549.37			
Phase	1w-RT	1w-LT	1 -RT	1 -LT		
T / K	260(2)	103(2)	260(2)	170(2)		
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic		
Space group	$P2_{1}/n$	$P\overline{1}$	$P2_{1}/n$	$P2_{1}/n$		
<i>a</i> / Å	8.5409(2)	16.6990(5)	8.3295(1)	8.2583(1)		
<i>b</i> / Å	19.0473(4)	18.1887(7)	18.8925(4)	18.7293(2)		
<i>c</i> / Å	18.1701(3)	20.4536(6)	18.0731(3)	17.9111(2)		
lpha / °	90	85.905(3)	90	90		
eta / °	101.962(2)	66.150(3)	97.547(1)	96.2603(9)		
γ / °	90	79.132(4)	90	90		
V / Å ³	2891.7(1)	5579.9(5)	2819.44(8)	2753.85(6)		
Ζ	4	8	4	4		
$D_{\rm c}$ / g·cm ⁻³	1.283	1.329	1.294	1.325		
$R_{\rm int}$	0.0351	Merged	0.0367	0.0214		
$R_1[I>2\sigma(I)]^a$	0.0565	0.1115	0.0560	0.0305		
$wR_2\left[I>2\sigma(I)\right]^b$	0.1803	0.3258	0.1721	0.0818		
R_1 (all data)	0.0643	0.1219	0.0616	0.0322		
wR_2 (all data)	0.1899	0.3327	0.1801	0.0797		
GOF	1.104	1.071	1.057	1.031		
BASF	/	0.283(3)	/	/		

Table S2. Crystal data of 1w-RT, 1w-LT, 1-RT and 1-LT.

 ${}^{a}R_{1} = F_{o} - F_{c}/F_{o}, {}^{b}wR_{2} = \{w[(F_{o})^{2} - (F_{c})^{2}]^{2}/w[(F_{o})^{2}]^{2}\}^{1/2}$

Table S3a. Surface area (%) of Hirshfeld surface for 18C6 in **1w**-RT filtered by elements (blue: C– $H\cdots\pi$ interactions, green: C– $H\cdots$ F interactions, pink: O…H–N and black: multiple interactions).

Atom Outside Atom Inside	В	С	F	Н	Ν	0	sum
Н	0	5.2	14.3	63.9	2.4	3.0	88.8
О	0	0.5	0.0	10.7	0	0	11.2
sum	0	5.7	14.3	74.6	2.4	0	100

Table S3b. Surface area (%) of Hirshfeld surface for 18C6 in 1-RT filtered by elements.

Atom Outside Atom Inside	В	С	F	Н	N	0	sum
Н	0	4.9	16.4	63.6	1.8	0.4	87.1
О	0	0.3	0.1	12.5	0	0	12.9
sum	0	5.2	16.4	76.1	1.8	0	100



Fig. S1. TG result of **1w**. The loss of guest water gives only very small values for the weight loss before 60 $^{\circ}$ C as shown in the inset.



Fig. S2. The layer consisting of $[(HPAA)(18C6)]^+$ cations in **1w**-RT (a) and **1**-RT (b) viewed along the $[01\overline{1}]$ direction. Part of hydrogen atoms were omitted for clarity.



Fig. S3. The 2*2*2 super cells of 1w-RT (a) and 1-RT (b) viewed along the *a*-axis.



Fig. S4. Based on Deybe model of dielectric relaxation process, the activation energy (E_a) in **1** is evaluated by the linear fitting of $\ln \omega$ versus $1000/T_{peak}$ according the Arrhenius law.



Fig. S5. Hirshfeld surface mapped with d_{norm} for 18C6 molecules in **1w**-RT (a) and **1**-RT (b), HPAA⁺ cation in **1w**-RT (c) and **1**-RT (d), respectively. The interactions displayed in Hirshfeld surface are classified by different kinds of supramolecular interactions (pink: *van der Waals* interactions with 18C6, light blue: C–H··· π or π ··· π interactions with HPAA⁺, green: C–H···F interactions with BF₄⁻, black: *van der Waals* interactions with H₂O, and red: O···H–N interactions).



Fig. S6. The total (a) and decomposed (b-d) 2D-Fingerprint plots for 18C6 in **1**. Each point marks an individual pair (d_i , d_e), indicating distances to the nearest atom inside (d_i) and outside (d_e) of the Hirshfeld surface, and the colors of these points change with frequency of occurrence from blue (low), through green, to red (highest).



Fig. S7. The total (a) and decomposed (b-d) 2D-Fingerprint plots for 18C6 in **1w**. Each point marks an individual pair (d_i , d_e), indicating distances to the nearest atom inside (d_i) and outside (d_e) of the Hirshfeld surface, and the colors of these points change with frequency of occurrence from blue (low), through green, to red (highest).



Fig. S8. Temperature dependence of dielectric constant (ε ') for **1w** (a) and **1** (b) from 293 K to 420 K.



Fig. S9. Temperature dependence of dielectric constant (ϵ) for 1w (a) and 1 (b) from 180 K to 285 K