Electronic Supplementary Material for

Enhancing switchable dielectric property for crystalline supramolecular rotor compounds by adding polar component

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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 [(HMNA)(18C6)]PF_6 (**1P**): Equivalent 68% HPF_6 aqueous solution was added to the mixed ethanol solution of 18C6 and MNA by drops. The mixed solution was evaporated in air. After 1 week, colourless block-like crystals of **1P** were filtered and washed by ethanol, then dried in air (yield: *ca.* 65%).

Synthesis of [(HMNA)(18C6)]SO_3CF_3 (**1S**): Equivalent HSO_3CF_3 was added to the mixed ethanol solution of 18C6 and MNA by drops. The mixed solution was evaporated in air. After 3 days, colourless block-like crystals of **1S** were filtered and washed by ethanol, then dried in air (yield: *ca.* 80%).

Crystal Structure Determination. Single-crystal diffraction data of **1P**-RT, **1P**-LT, **1S**-RT and **1S**-LT were collected on a Rigaku XtaLAB P300DS single-crystal diffractometer equipped with a graphite-monochromated Cu Kα radiation (λ = 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. Crystallographic data and refinements for the complexes are summarized in **Table S1**. CCDC numbers: 1982636-1982639 for **1P**-RT, **1P**-LT, **1S**-RT and **1S**-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. The value of N is estimated by the Boltzmann equation, $\Delta S = R\ln N$, where R is the gas constant, N represents 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 the phase-transition temperature.

Dielectric measurement. The dielectric measurements were carried on a TH2838 impedance analyzer at 10 different frequencies from 5 kHz to 200 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 0.2–0.9 mm thick were prepared by pressing microcrystal samples at 780 MPa. Silver conduction paste deposited on the surface of pressed-powder pellets was used as the electrodes.

Hirshfeld surfaces analysis. Hirshfeld surfaces and the related 2D-fingerprint plots were calculated with high resolution by *CrystalExplorer* with inputting structure file in CIF format. 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).

Table S1. Crystallographic parameters for **1P**-RT, **1P**-LT, **1S**-RT and **1S**-LT.

Compound	[(MNA)(18C6)]PF_6 (**1P**)		[(MNA)(18C6)]SO_3CF_3 (**1S**)	
Formula	$C_{19}H_{33}F_6N_2O_9P$		$C_{20}H_{33}F_3N_2O_{12}S$	
Formula weight	578.44		582.54	
Phase	**1P**-RT	**1P**-LT	**1S**-RT	**1S**-LT
T / K	298(2)	213(2)	298(2)	213(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	Pccn	Pccn	$P2_1/c$	$P2_1/c$
a / Å	17.7788(4)	16.774(3)	10.0129(3)	20.31807(19)
b / Å	19.7210(3)	20.000(3)	18.4433(5)	17.85897(16)
c / Å	15.0786(2)	15.122(3)	14.9448(3)	14.64020(12)
β / °	90	90	98.440(2)	96.2560(10)
V / Å^3	5286.79(16)	5073.0(15)	2729.98(13)	5280.70(8)
Z	8	8	4	8
D_c / g·cm^{-3}	1.453	1.515	1.417	1.465
R_{int}	0.0858	0.0422	0.0531	0.0228
R_1 [$I > 2\sigma(I)$] [a]	0.0867	0.0536	0.0685	0.0448
wR_2 [$I > 2\sigma(I)$] [b]	0.2941	0.1531	0.2038	0.1223
R_1 (all data)	0.0988	0.0560	0.0741	0.0496
wR_2 (all data)	0.3198	0.1568	0.2110	0.1282
GOF	1.009	1.098	1.081	1.032

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

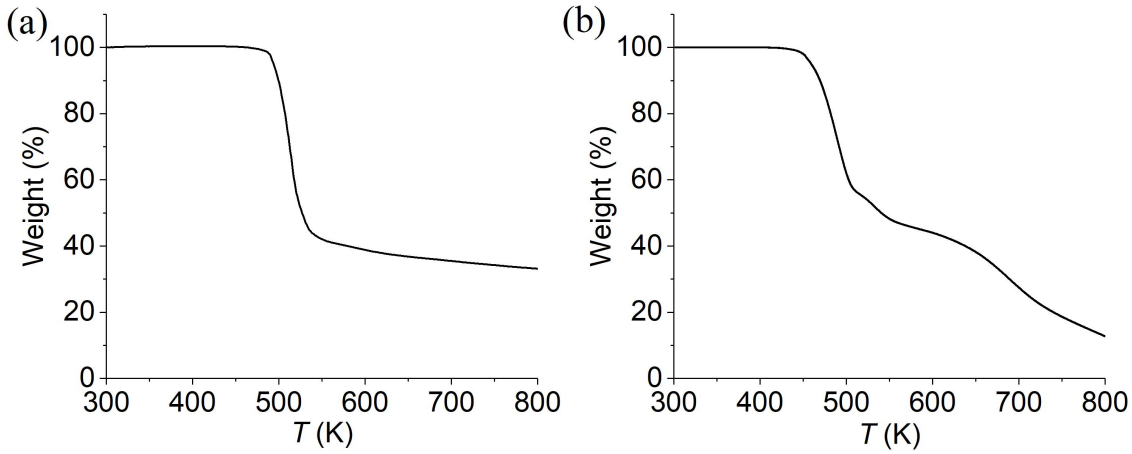

Figure S1. TG curves of **1P** (a) and **1S** (b).

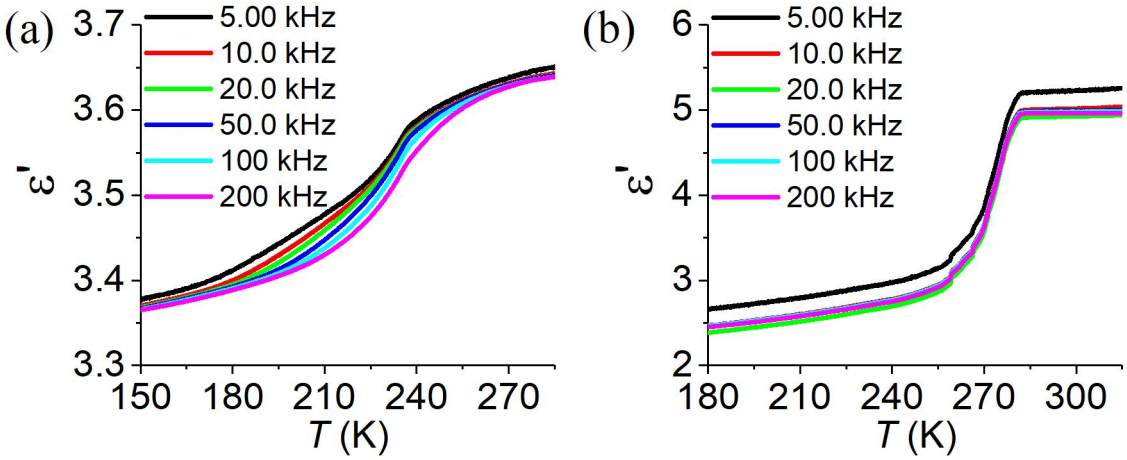

Figure S2. Temperature dependence of dielectric constant (ε') for **1P** (a) and **1S** (b).

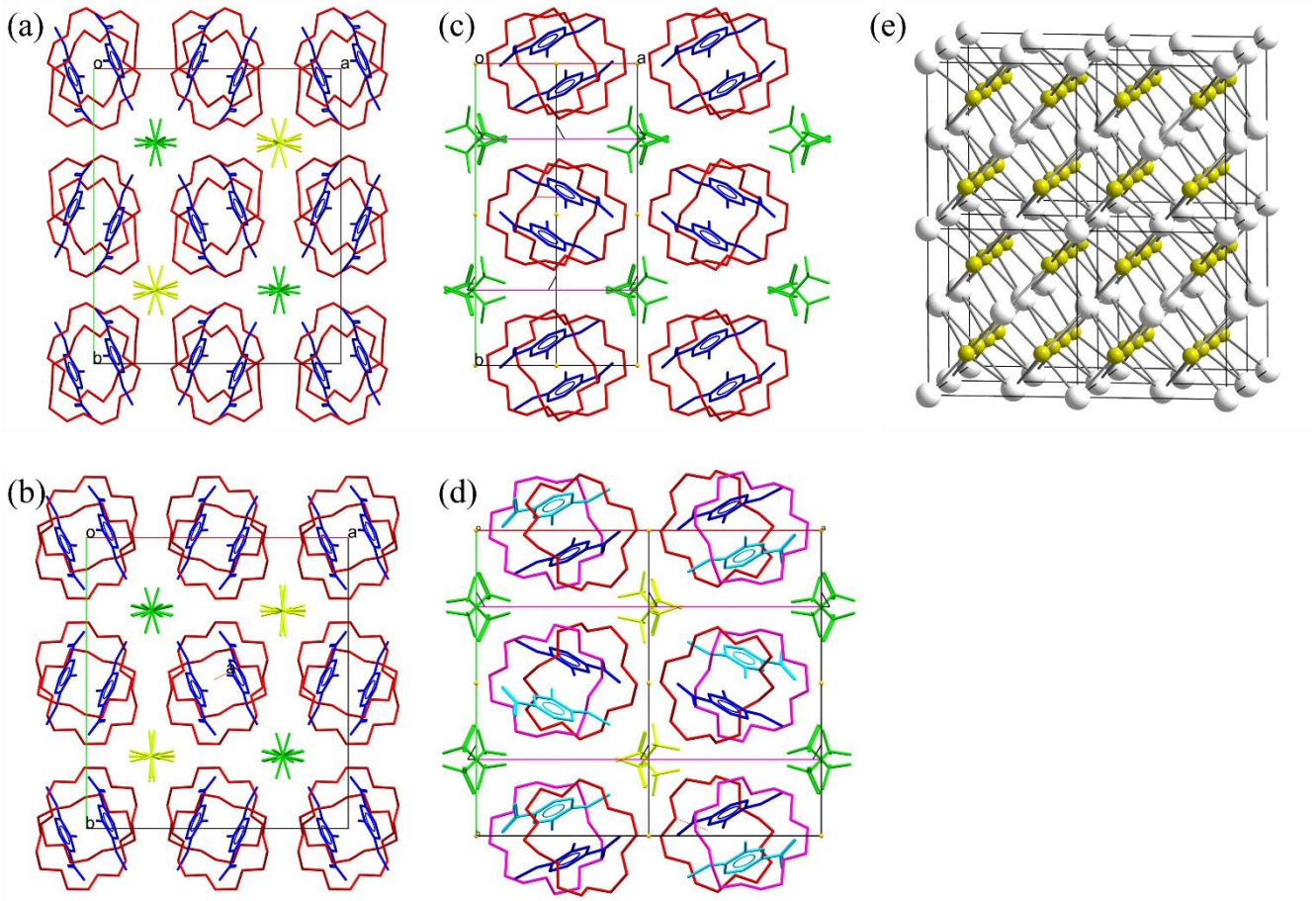

Figure S3. The packing modes of **1P**-RT (a), **1P**-LT (b), **1S**-RT (c) and **1S**-LT (d), and the topological connectivity (e) of dimer units (white spheres) and PF_6^- anions (yellow spheres). Different symmetry equivalences are distinguished with different colour: $HMNA^+$ mapped with blue or cyan, 18C6 mapped with red or pink, counter anion mapped with green or yellow.

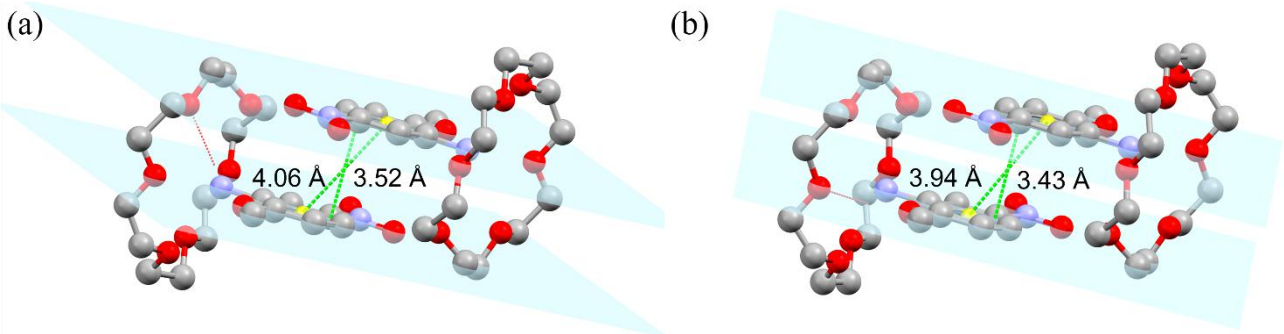

Figure S4. The supramolecular interactions between two $[(HMNA)(18C6)]^+$ cations in **1P**-RT (a) and **1S**-RT (b).

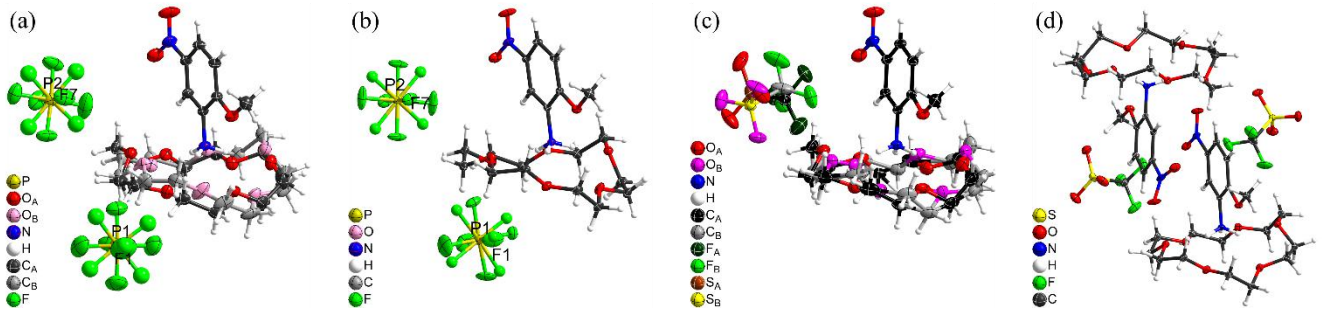

Figure S5. The asymmetry units of **1P**-RT (a), **1S**-RT (b), **1P**-LT (c), and **1S**-LT (d).

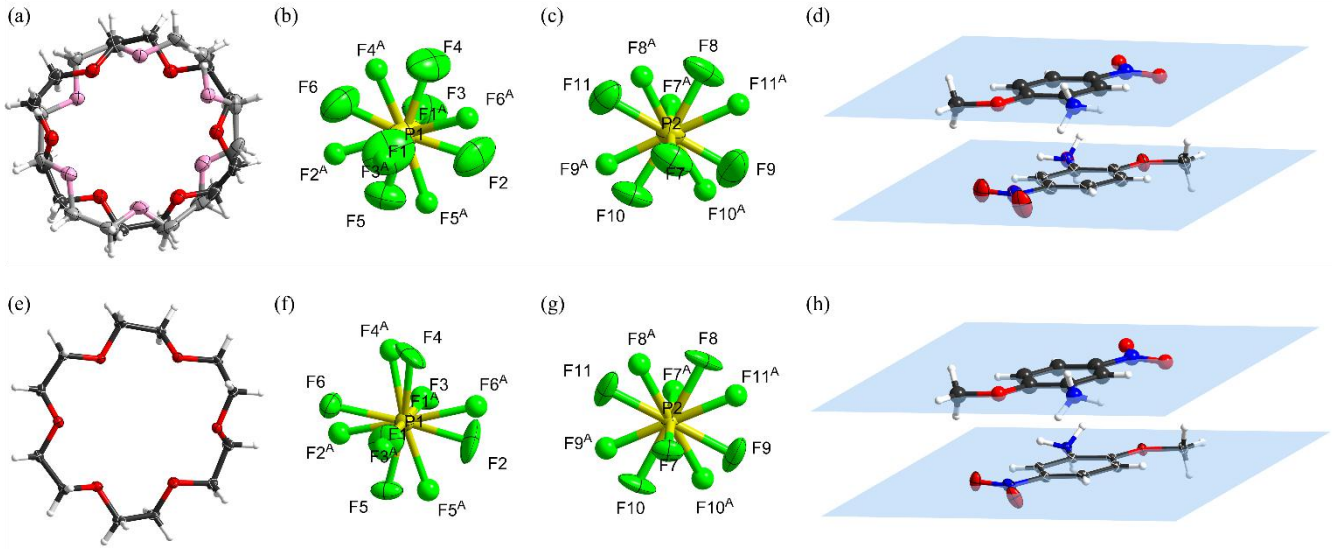

Figure S6. The structure details of 18C6 (a, e), PF_6^- anion (b, c, f and g), and $HMNA^+$ cation (d, h) in **1P**-RT (up row) and **1P**-LT (down row).

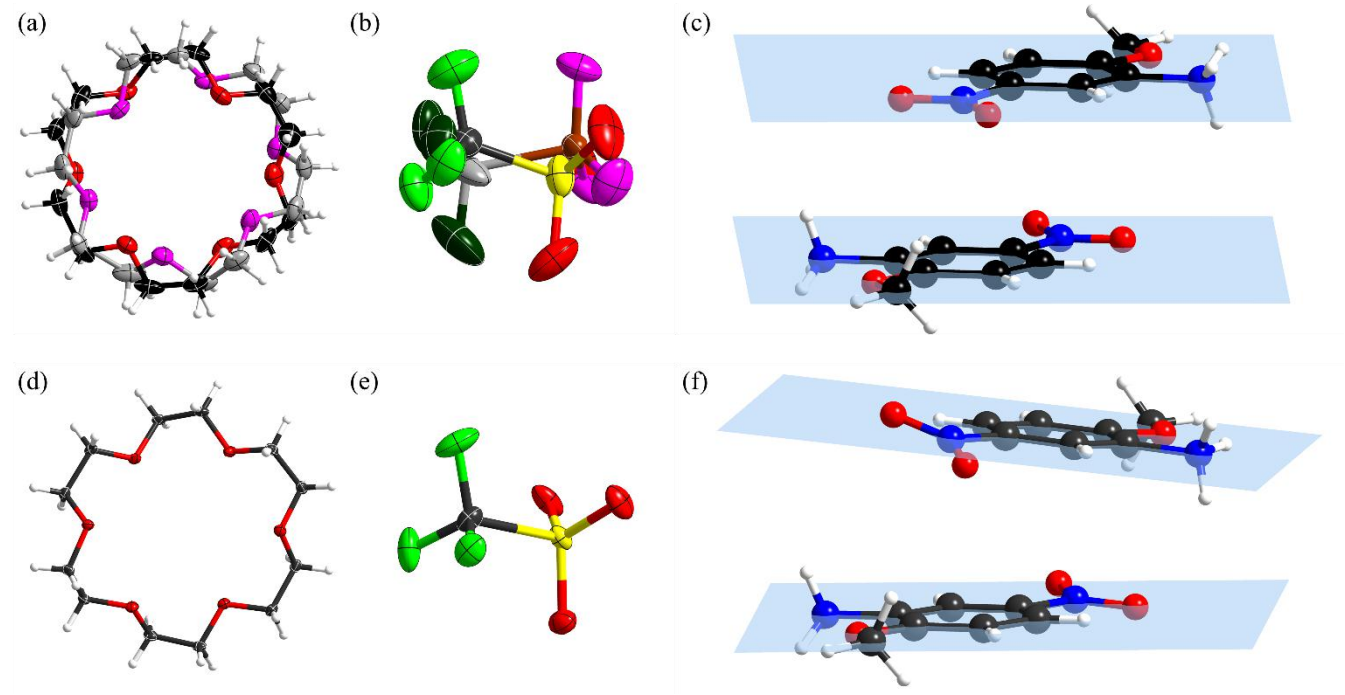

Figure S7. The structure details of 18C6 molecule (a, d), $SO_3CF_3^-$ anion (b, e), and $HMNA^+$ cation (c, f) in **1S**-RT (up row) and **1S**-LT (down row).

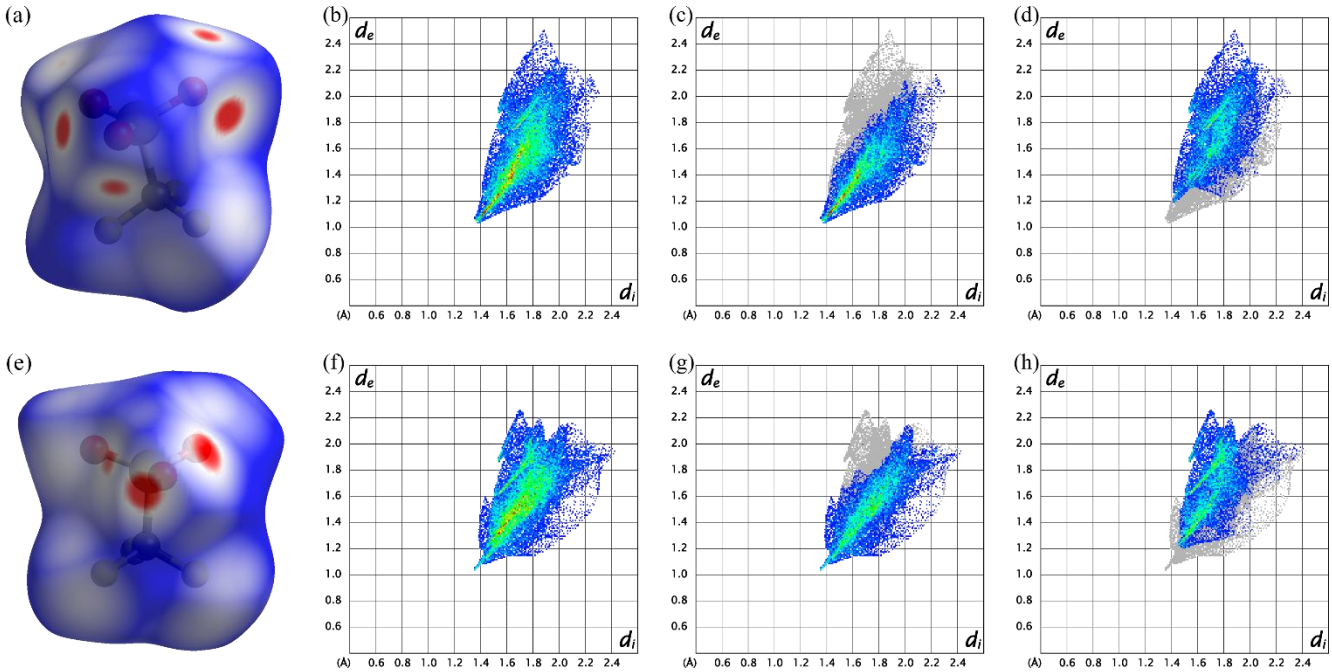

Figure S8. The Hirshfeld surfaces of $SO_3CF_3^-$ anions (a, e). The 2D-fingerprint plots of $SO_3CF_3^-$ anions for contacts between all interior atoms (b, f), O atoms (c, g) and F atoms (d, h) to all exterior atoms of the Hirshfeld surfaces.

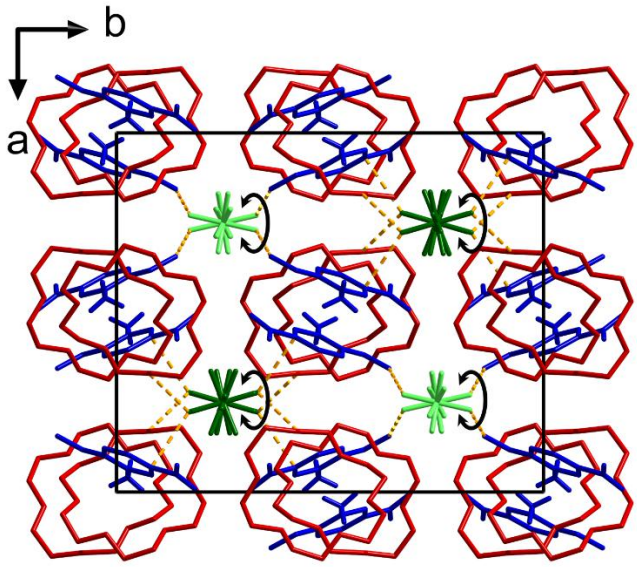

Figure S9. The supramolecular interactions between rotate axis of the PF_6^- anion and the dimer unit.

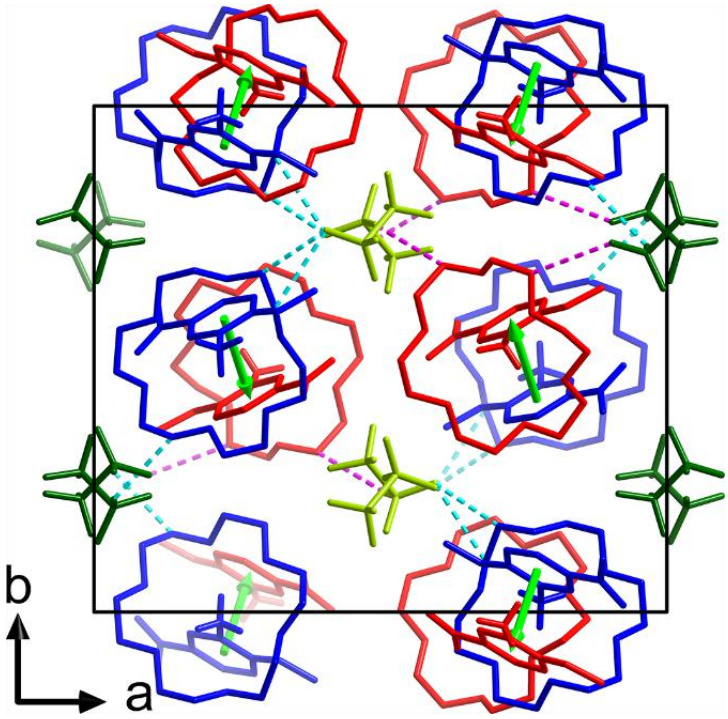

Figure S10. The direction and packing of asymmetry dimer unit.