Supplementary Information

Thermal-responsive luminescence/dielectric responses with reversibly shifted light emissions

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Experimental Section

Materials

All of the chemical reagents in the synthesis were of reagent grade and used without further purification. 4-Pyridinemethaneamine ($C_6H_8N_2$, 98%, Meryer), 18-Crown-6 ($C_{12}H_{24}O_6$, 98%, Meryer), and Hexafluorophosphoric acid (HPF_6, 70% in water, Mreda), *N*,*N*-Dimethylformamide (DMF, C_3H_7NO, Meryer)， Methanol (CH_4O, 98%, Mreda).

Synthesis and Crystal Growth

For [(4-Pyridinemethaneaminum)(18-Crown-6)][PF_6] (PCP-1), the colorless transparent block crystals were obtained by slow evaporation of methanol solutions containing 4-pyridinemethaneamine,18-crown-6 and HPF_6 with a molar ratio of 1 : 1: 1 at room temperature. For [4-Pyridinemethaneaminum][PF_6] (PP-1), the colorless transparent block crystals were obtained after one week by slow evaporation of DMF solutions containing 4-pyridinemethaneamine and HPF_6 with a molar ratio of 1 : 1 at room temperature.

Single-Crystal X-ray Diffraction (SC-XRD) Measurements

The crystallographic data of PP-1 and PCP-1 at different temperatures were collected by Bruker D8 VENTURE single crystal X-ray diffractometer with Cu-Kα radiation (λ = 1.54184 Å), and the structure of the samples was determined by APEX-III software. The crystal structure is further refined by SHELXT and OLEX2 1.5 software packages, and the positions of all non-hydrogen atoms are obtained according to the geometric method. Table S1 to Table S5 summarize the crystallographic data and structural refinement of PP-1 and PCP-1 at different temperatures.

Powder X-ray Diffraction (PXRD) Measurements

The powder X-ray diffraction data of PCP-1 and PP-1 were measured using a Bruker advanced powder X-ray diffractometer. The step size was set to 0.02°, and the diffraction pattern was recorded in the 2θ range of 5° to 40°. Additionally, the variable-temperature powder X-ray diffraction pattern was obtained within a

temperature range of 298-443 K.

Differential Scanning Calorimetry (DSC) Measurements

DSC measurements were performed on powder samples of PP-1 and PCP-1 with NETZSCH-214 instrument. About 10 mg of the sample was placed in an aluminum crucible, and the experiment was carried out under nitrogen atmosphere and atmospheric pressure with a programmed heating and cooling rate set at 20 K min^{-1}.

Dielectric Measurements

To determine the temperature-dependent dielectric constant, PCP-1 powder was compressed into sheets and subsequently cut into small squares. Afterwards, carbon glue was uniformly applied to the sample, and copper wires were affixed to both sides. The sample was then secured onto an electrode base for measurement. The variable dielectric constant of PCP-1 during heating and cooling cycles were measured using a TH2828A impedance analyzer within the frequency range of 500 Hz - 1 MHz.

Hirshfeld Surfaces Analysis

The Hirshfeld surface and the corresponding 2D fingerprint plots are obtained by separately importing the crystal data for PCP-1 and PP-1 in CIF file format into the Crystal Explorer software package for computation. The Hirshfeld surface provides information on intermolecular interactions, with the red, white, and blue color codes reflecting the distances between molecules: white areas correspond to distances close to the van der Waals radii, blue areas indicate longer distances, and red areas represent closer interactions (such as hydrogen bonds).

Fluorescence Measurements

The emission and excitation spectra of PP-1 and PCP-1 were determined by an Edinburgh FLS1000 fluorescence spectrophotometer, and the PL quantum efficiency and PL lifetime were characterized. The emission spectra of PP-1 and PCP-1 at 303-443 K were determined from the corresponding excitation spectra, and the CIE colorimetric coordinates were calculated from the emission spectra using the CIE

1931 software package.

UV-visible (UV-vis) Spectrophotometry Measurements

UV-vis absorption spectra of PP-1 and PCP-1 were characterized using an Agilent Cary5000 spectrophotometry at room temperature. The UV-vis spectrum was tested in the range of 200 nm-800 nm with a step of 1 nm.

Density Functional Theory (DFT) Calculations

The DFT calculations were performed by using Vienna Ab Initio Simulation Package (VASP).[1] The projector-augmented wave method (PAW)[2] and Perdew-Burke-Ernzerhof (PBE)[3] functional were used to describe the electron-ion and the exchange-correlation interactions respectively. Calculation was based on the crystal structures without structural relaxation and the energy convergence criteria was set to 10^{-6} eV. The cutoff energy of 550 eV and $3 \times 3 \times 2$ *k*-point meshed were used for all simulations.

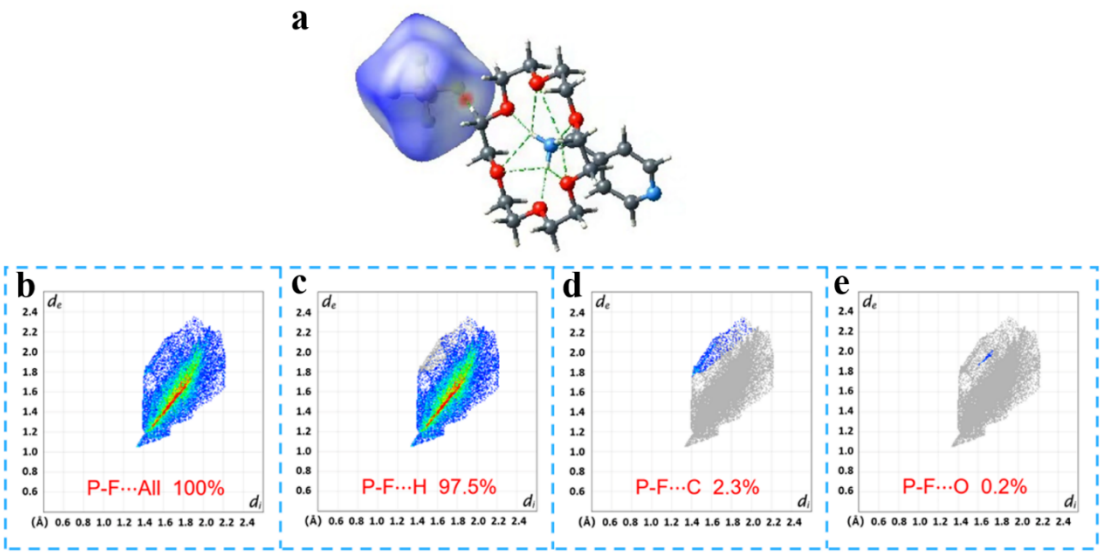

Fig. S1 (a) Hirshfeld d_{norm} surfaces of PCP-1. (b-e) 2D fingerprint plots of the PF_6^- in PCP-1 with all the interactions (b), P-F···H (c), P-F···C (d) and P-F···O (e) weak molecular interactions, respectively.

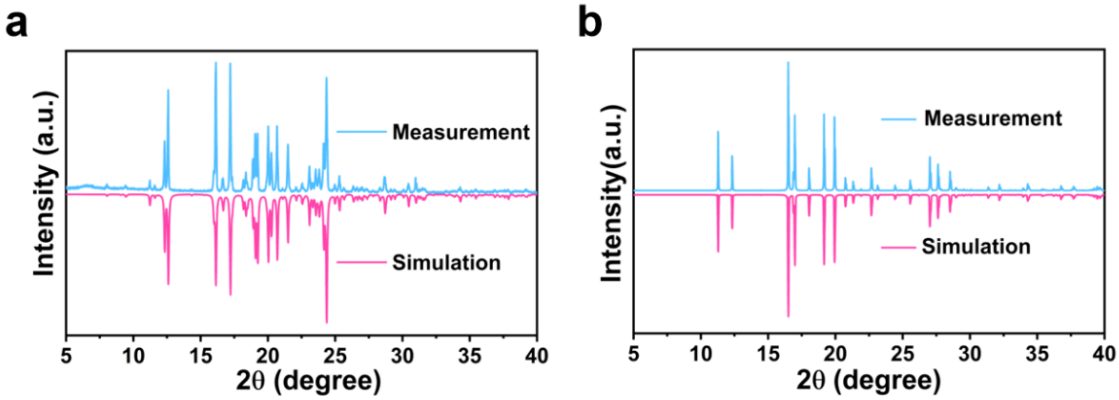

Fig. S2 (a-b) The measured and simulated PXRD patterns of PCP-1 (a) and PP-1 (b) at 303 K.

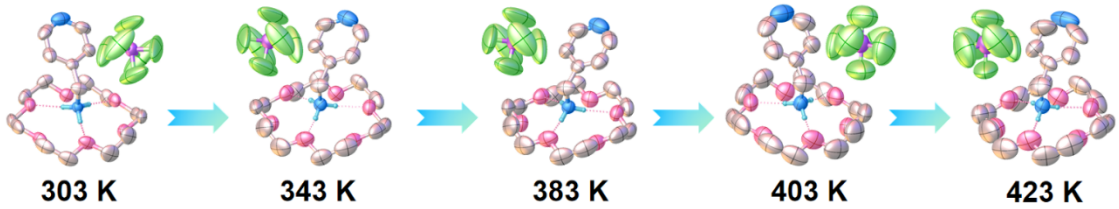

Fig. S3 Crystal structures of PCP-1 at different temperatures.

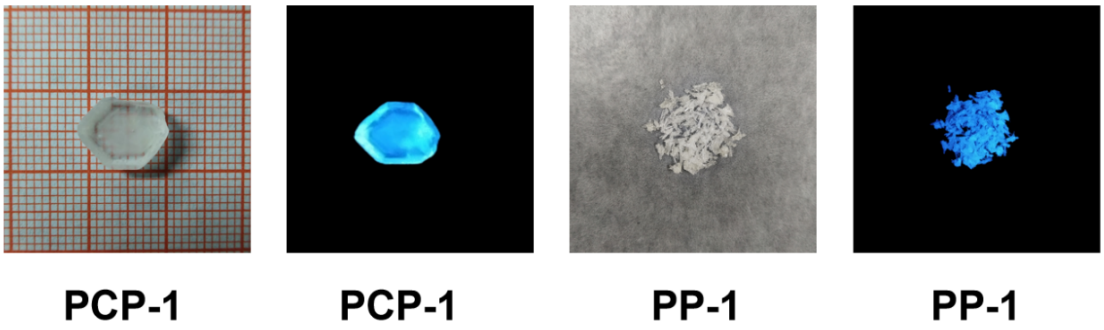

Fig. S4 Crystals of PCP-1 and PP-1 under natural light and 365 nm UV illumination.

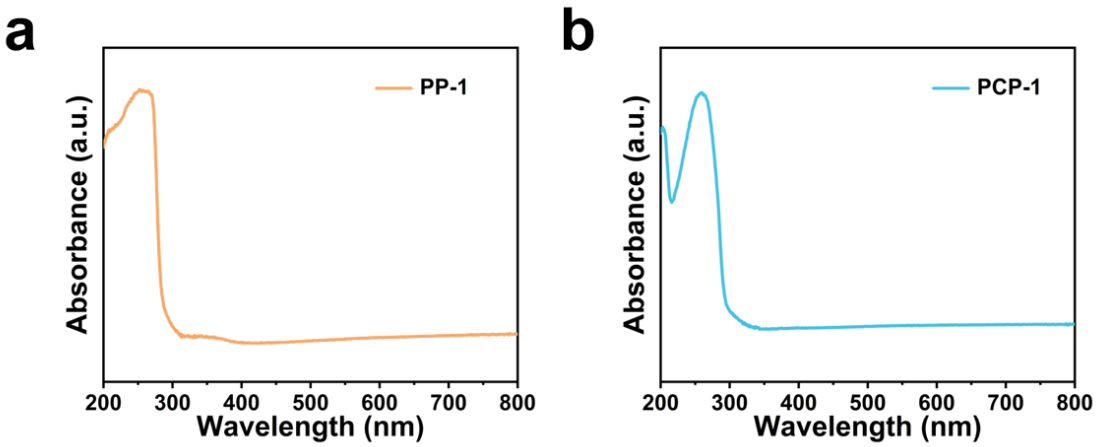

Fig. S5 (a-b) The UV-vis absorption of PP-1 (a) and PCP-1 (b).

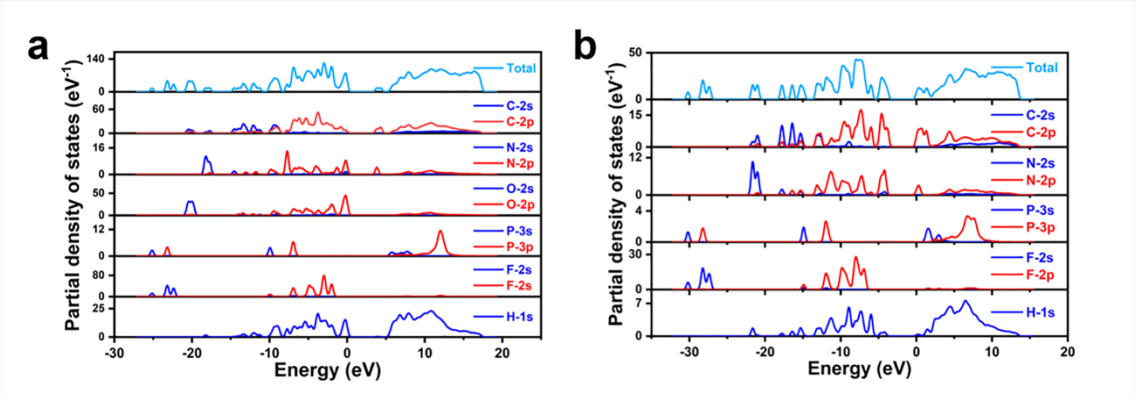

Fig. S6 The partial density of states (PDOS) of PCP-1 (a) and PP-1 (b).

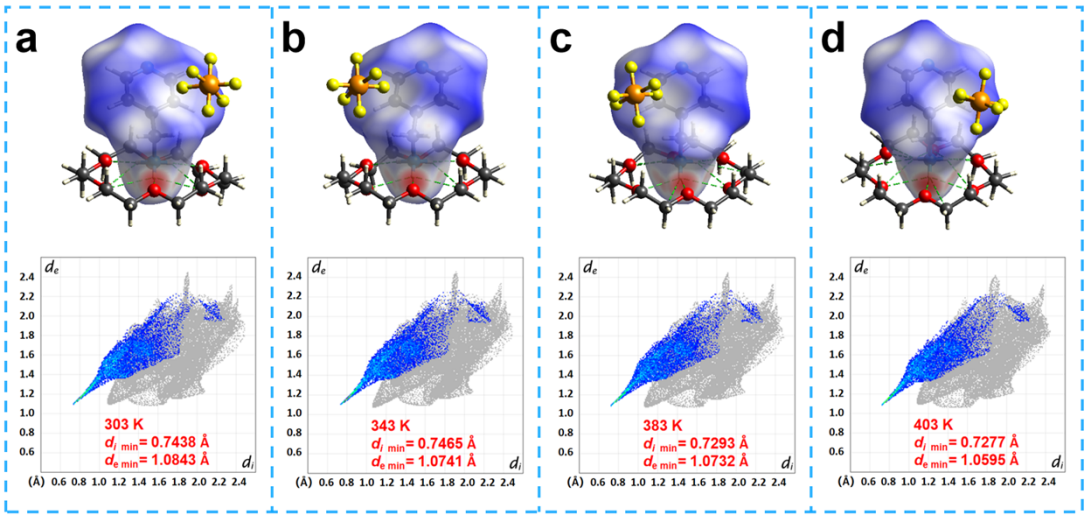

Fig. S7 (a-d) Hirshfeld surfaces and associated 2D fingerprint plots of the 4-PDMA cations in PCP-1 from 303 K to 403 K.

Table S1. Crystallographic data and structure refinement details of PP-1 and PCP-1 at 303 K.

Compound	PP-1	PCP-1
CCDC Code	2378756	2378751
Formula	$C_{12}H_{18}F_6N_4P$	$C_{18}H_{33}F_6N_2O_6P$
Fw	363.27	518.43
Temperature	303 K	303 K
Crystal Syst	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a(Å)	7.8459(16)	11.9665(15)
b(Å)	9.828(2)	10.5773(13)
c(Å)	10.5087(15)	19.8113(19)
α/°	90	90
β/°	92.439(11)	100.165(8)
γ/°	90	90
V(Å^3)	809.6(3)	2468.2(5)
Z	2	4
μ(mm^{-1})	2.137	1.730
GOF on F^2	1.125	0.999
R_1[[$I > 2\sigma(I)$]	0.0805(1088)	0.1246(2928)
wR_2 (all data)	0.2562(1592)	0.2549(4526)

Table S2. Hydrogen-bonding parameters of PP-1 at 303 K.

D*—H···*A	***D*—H(Å)**	**H···*A*(Å)**	***D*···*A*(Å)**	***D*—H···*A*(°)**
N2—H2*A*···F2^{ii}	0.89	2.01	2.824 (5)	152
N2—H2*A*···F1^{ii}	0.89	2.28	2.842 (5)	121
N2—H2*B*···F2^{i}	0.89	2.50	2.956 (5)	112
N2—H2*B*···F1	0.89	1.91	2.720 (5)	150
N2—H2*C*···N1^{iii}	0.89	1.96	2.846 (4)	175
C1—H1*A*···F1^{ii}	0.97	2.60	3.135 (6)	115
C1—H1*B*···F2^{i}	0.97	2.62	3.212 (6)	119
C3—H3···F3^{iv}	0.93	2.61	3.335 (9)	135
C5—H5···F2^{v}	0.93	2.63	3.397 (6)	140
C5—H5···F3^{v}	0.93	2.53	3.304 (7)	140

Symmetry code: (i) -X, -1/2+Y, 1/2-Z; (ii) -X, 1-Y, 1-Z; (iii) -1+X, +Y, +Z; (iv) +X, 1/2-Y, -1/2+Z; (v) 1-X,1-Y,1-Z

Table S3. Hydrogen-bonding parameters of PCP-1 at 303 K.

D*—H···*A	***D*—H(Å)**	**H···*A*(Å)**	***D*···*A*(Å)**	***D*—H···*A*(°)**
C18-H18*A*···F5^{i}	0.97	2.50	3.450 (8)	167
C18-H18*B*···O1^{ii}	0.97	2.57	3.508 (7)	164
N1-H1*C*···O1	0.89	2.50	2.938 (5)	111
N1-H1*C*···O6	0.89	2.00	2.886 (4)	171
N1-H1*E*···O5	0.89	1.95	2.834 (5)	174
N1-H1*D*···O2	0.89	2.03	2.839 (5)	150
N1-H1*D*···O4	0.89	2.45	2.913 (5)	113

Symmetry code: (i) 3/2-X, -1/2+Y, 3/2-Z; (ii) 1/2-X, -1/2+Y, 3/2-Z

Table S4. Crystallographic data and structure refinement details of PCP-1 at different temperatures.

Compound	**PCP-1**	**PCP-1**	**PCP-1**	**PCP-1**
CCDC Code	2378752	2378753	2378755	2378754
Formula	$C_{18}H_{33}F_6N_2O_6P$	$C_{18}H_{33}F_6N_2O_6P$	$C_{18}H_{33}F_6N_2O_6P$	$C_{18}H_{33}F_6N_2O_6P$
Fw	518.43	518.43	518.43	518.43
Temperature	343 K	383 K	403 K	423 K
Crystal Syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a(Å)	12.0220(15)	11.985(5)	11.994(5)	12.137(3)
b(Å)	10.629(2)	10.522(3)	10.463(3)	10.6827(16)
c(Å)	19.921(4)	19.813(7)	19.815(9)	20.015(6)
α/°	90	90	90	90
β/°	100.318(13)	100.634(18)	100.89(2)	100.751(15)
γ/°	90	90	90	90
V(Å^3)	2504.4(8)	2455.6(15)	2441.9(17)	2549.5(11)
Z	4	4	4	4
μ(mm^{-1})	1.705	1.739	1.749	1.675
GOF on F^2	1.043	0.986	0.998	1.173
R_1[[$I > 2\sigma(I)$]	0.1255(1834)	0.1179(2324)	0.1381(1710)	0.1446(1365)
wR_2 (all data)	0.2979(4423)	0.2606(4604)	0.3326(4250)	0.3477(4334)

Table S5. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for PCP-1 at different temperatures. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	303 K U_{eq}	Atom	343 K U_{eq}	Atom	383 K U_{eq}	Atom	403 K U_{eq}	Atom	423 K U_{eq}
O1	0.06235	O1	0.07913	O1	0.09239	O1	0.10533	O1	0.11813
O2	0.07596	O2	0.09309	O2	0.11498	O2	0.11682	O2	0.13591
O3	0.06774	O3	0.07839	O3	0.09551	O3	0.11801	O3	0.11925
O4	0.07464	O4	0.09662	O4	0.10739	O4	0.10253	O4	0.12091
O5	0.06329	O5	0.07665	O5	0.09284	O5	0.12609	O5	0.1494
O6	0.06376	O6	0.0867	O6	0.10318	O6	0.10651	O6	0.13713
C1	0.10242	C1	0.12541	C1	0.14398	C2	0.1496	C3	0.17271
C4	0.08103	C4	0.1045	C4	0.11793	C3	0.13217	C5	0.15743
C5	0.08597	C5	0.09618	C5	0.12506	C5	0.13295	C7	0.16732
C6	0.07731	C6	0.10739	C6	0.11448	C7	0.15613	C10	0.15873
C8	0.075	C8	0.10639	C8	0.12968	C9	0.13951	C11	0.16543
C9	0.07931	C9	0.09946	C9	0.14714	C10	0.12197	C12	0.13746
C10	0.09549	C10	0.10309	C10	0.11306	C11	0.1494	C13	0.18428
C11	0.09855	C11	0.12549	C11	0.12094	C12	0.13232	C14	0.13746
C12	0.08211	C12	0.10668	C12	0.12337	C13	0.13298	C15	0.14871
C14	0.08389	C14	0.09261	C14	0.12878	C16	0.13244	C16	0.16114
C16	0.08004	C16	0.10428	C16	0.13694	C17	0.1598	C17	0.19342
C18	0.08731	C18	0.12029	C18	0.10849	C18	0.1363	C18	0.1452
N1	0.04701	N1	0.06052	N1	0.06822	N1	0.07499	N1	0.08175
N2	0.09637	N2	0.118	N2	0.13674	N2	0.14782	N2	0.18978
C2	0.08975	C2	0.11146	C2	0.12434	C1	0.08345	C1	0.09085
C3	0.05442	C3	0.06614	C3	0.07447	C4	0.10459	C2	0.1846
C7	0.06759	C7	0.08352	C7	0.099	C6	0.10537	C4	0.11915
C13	0.0689	C13	0.08148	C13	0.09657	C8	0.13597	C6	0.11633
C15	0.07502	C15	0.08997	C15	0.10697	C14	0.12187	C8	0.1322
C17	0.08553	C17	0.10489	C17	0.1319	C15	0.1483	C9	0.16476

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3. J. P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.* 1996, **105**, 9982-9985.