Electronic Supplementary Material (ESI) for ChemComm.

A chiral open-framework fluorinated cobalt phosphate consists of distorted F-encapsulated double 4-ring units with bulk homochirality

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Synthesis

The reagents employed were commercially available and used without further purification. Typically, a Teflon lined autoclave (volume 25 mL) was charged with a mixture of $CoCl_2.6H_2O$(0.238g), orthophosphoric acid (0.345g, 85 wt.% in water), diethylentriamine(DETA) (430μL, 99 wt.%), hydrofluoric acid(22μL, 40 wt.% in water) and 1-ethyl-3-methyl imidazolium bromide(1.91g, 99 wt.%). After 3 days of crystallization at 180 °C, the crystalline purple solid was obtained, further washed thoroughly with water several times, and then dried in the air. Purple crystals were obtained in 73% yield (based on $CoCl_2.6H_2O$). Calcd. for CAU-1: F: 1.79%; C: 9.05; H: 3.68; N: 7.92 wt.%; P:Co = 3:2; Found: F: 1.80%; C: 9.09; H: 3.69; N: 7.91 wt.%; P:Co = 1.493, which give a relative error within ±0.5%.

Characterization

X-ray powder diffraction(XRD) data were collected on a DX-2700BH diffractometer with Cu-Ka radiation (λ= 1.5418 Å). The crystal morphology was studied by field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010) using conventional sample preparation and imaging techniques. Fluoride contents in CAU-1 were determined on a fluoride ion-selective electrode with a saturated calomel electrode as reference (PXSJ-216F Ion Meter). X-ray photoelectron spectroscopy(XPS) measurements were taken on a Thermo Escalab 250Xi spectrometer equipped with an Al Ka X-ray source. Inductively Coupled Plasma(ICP) analysis was carried out on Agilent 720 ICP-OES apparatus. The elemental analysis was conducted on an elementary analytical instrument (Vario EL CUBE). Thermo

gravimetric analysis (TGA) was carried out in a thermobalance (TA Instruments, SDT-Q600) under dynamic air with a heating rate of 5°C min^{-1}. CD spectra were measured on the JASCO J-815 spectrometer (range: 200-800nm; path length: 1mm).

Crystallographic Analyses

The intensity data were collected on a Bruker AXS SMART APEX II diffractometer using graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å) at room temperature. The structure was solved by direct methods and refined by full-matrix least squares on F^2 with the SHELXTL-97 program. CCDC 1834442 contains the supplementary crystallographic data for this paper, these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

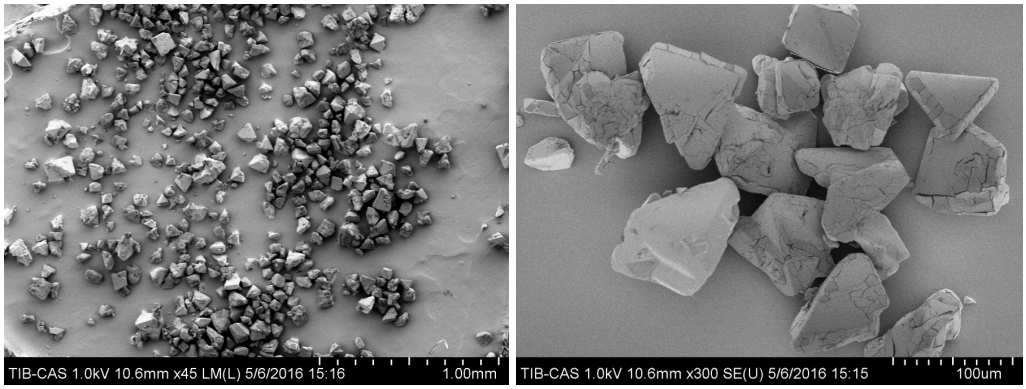

Fig. S1 The SEM images of CAU-1: (left) low magnification image (right) high magnification image.

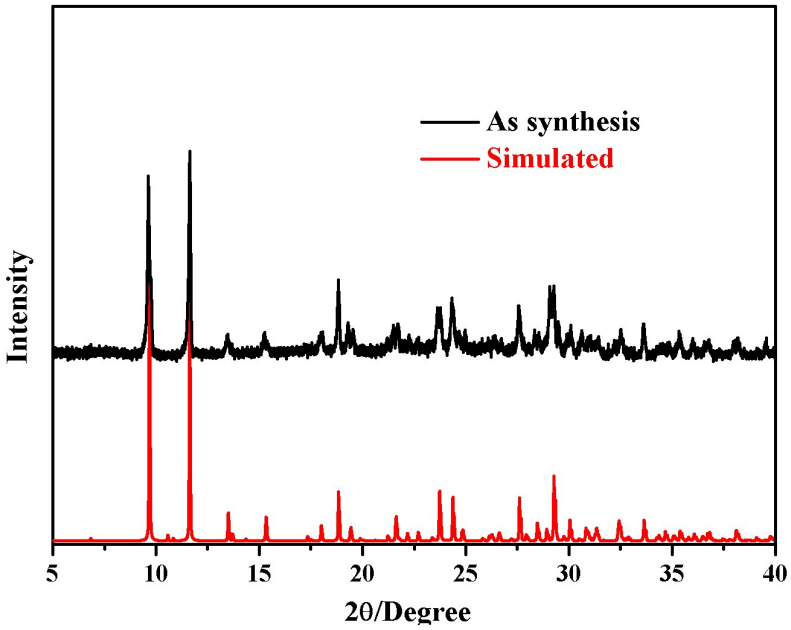

Fig. S2 Experimental and simulated powder X-ray diffraction patterns of CAU-1

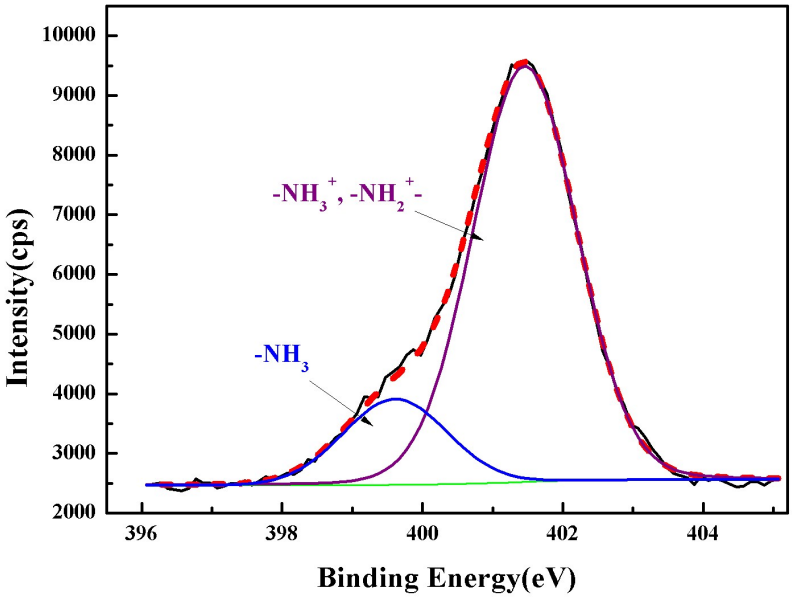

Fig. S3 N 1s peak in high resolution XPS spectra of CAU-1

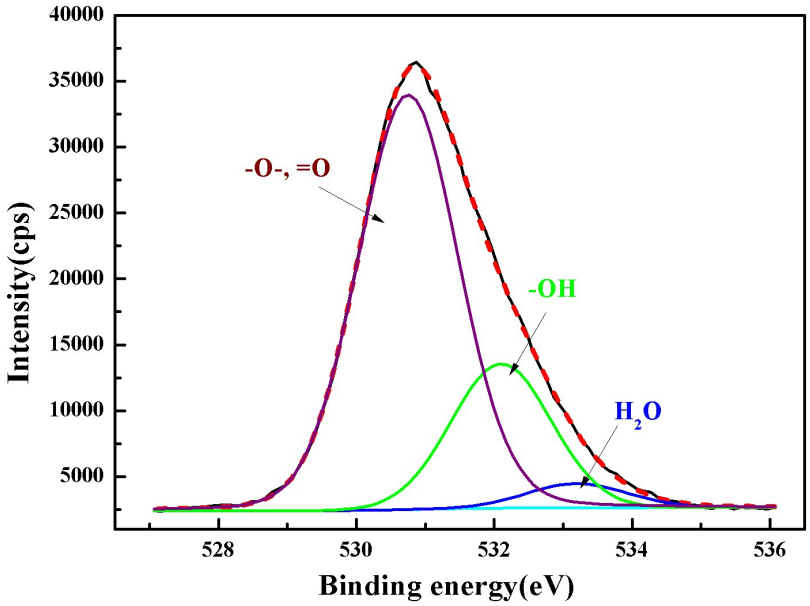

Fig. S4 O 1s peak in high resolution XPS spectra of CAU-1

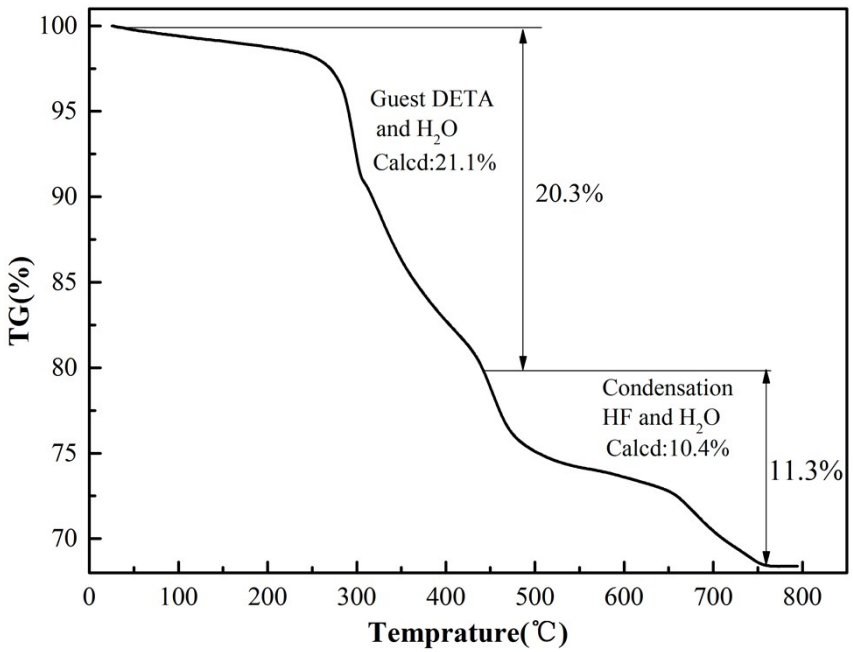

Fig. S5 TG curve for CAU-1

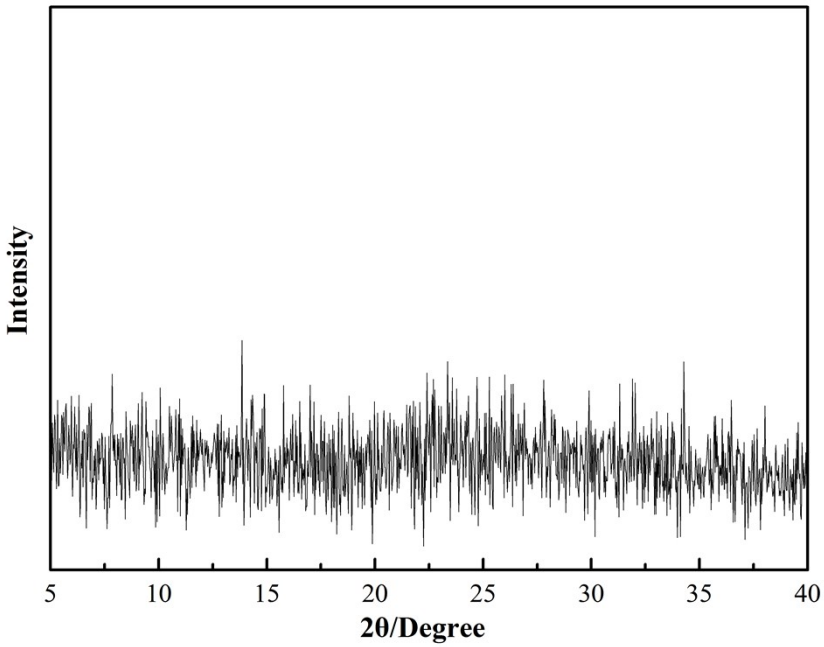

Fig. S6 XRD pattern of CAU-1 after calcination at 350℃ in air

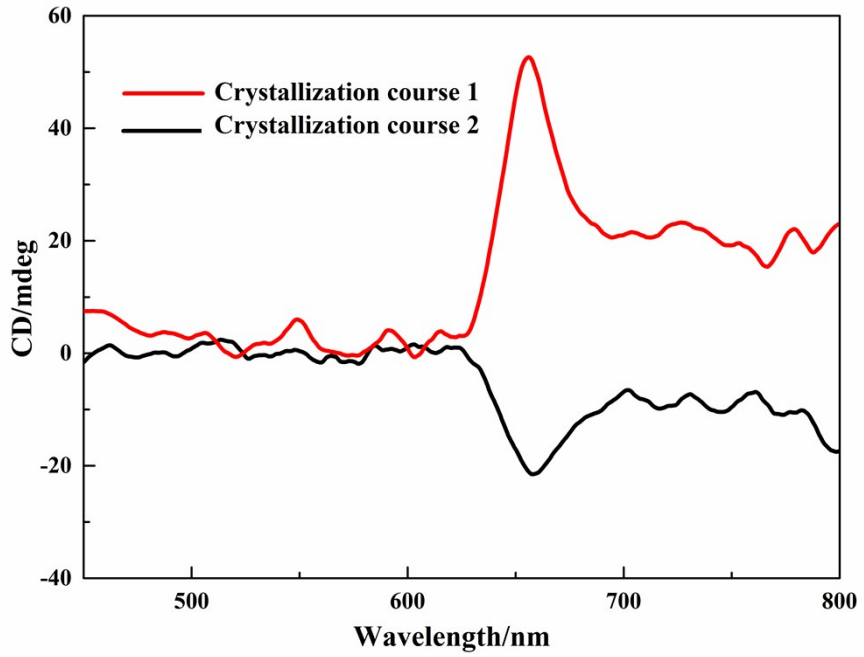

Fig. S7 Solid state CD spectra of bulk crystals corresponding to two different crystallization courses

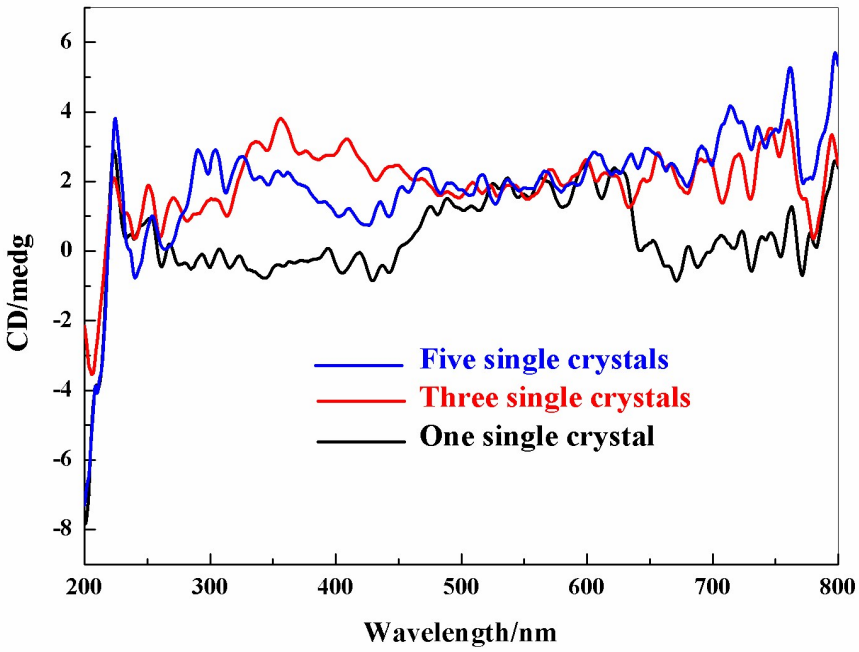

Fig. S8 Solid state CD spectra of one, three and five CAU-1 single crystals of the same crystallization course

Table S1 N1s peak and O1s fitting parameters for CAU-1

	N1s		O1s		
Chemical Speciation	$-NH_2$	$-NH_3^+$, $-NH_2^+-$	-O-, =O	-OH	H_2O
BE Position [a](eV)	399.45	401.29	530.60	531.93	533.04
Atomic Ratio (%)	16.7%	83.3%	4.0%	24%	72%
FWHM [b]	1.75	1.74	1.71	1.71	1.72

[a]:Bonding Energy(BE), [b]: Full Width Half Maximum(FWHM)

Table S2 Crystal data and structure refinement parameters of CAU-1

Identification code	CAU-1
Empirical formula	$C_8H_{39}Co_4FN_6O_{25}P_6$
Formula weight	1059.96
Temperature(K)	293(2) K
Wavelength(Å)	0.71073
Crystal system, space group	Orthorhombic, $P2_12_12$
a(Å)	18.247(3)
b(Å)	18.247(3)
c(Å)	9.4115(17)
α(˚)	90
β(˚)	90
γ(˚)	90
Volume(Å^3)	3139.4(9)
Z	4
Calculated density(g/cm^3)	2.234
Absorption coefficient(mm^{-1})	2.497
F(000)	2128
Limiting indices	-22<=h<=24, -24<=k<=14, -12<=l<=12
Reflections collected/ unique	22873/7794 [R(int) = 0.0856]
Goodness-of-fit on F^2	0.909
Final R indices[I>2σ(I)][a]	$R1$=0.0444, $wR2$=0.0736
R indices(all data)	$R1$= 0.0624, $wR2$=0.0785
Absolute structure parameter	0.00

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

Table S3 Select Bond lengths [Å] and angles [°] for CAU-1[a]

Co(1)-O(20)	1.938(2)	P(1)-O(9)	1.533(3)
Co(1)-O(16)	1.961(2)	P(1)-O(7)	1.557(2)
Co(1)-O(2)	1.994(2)	P(2)-O(5)	1.508(2)
Co(1)-O(17)#1	2.030(2)	P(2)-O(23)	1.529(2)
Co(1)-F(1)	2.361(2)	P(2)-O(17)	1.530(3)
Co(2)-O(9)	1.928(2)	P(2)-O(22)	1.619(2)
Co(2)-O(10)	1.956(2)	P(3)-O(4)	1.512(2)
Co(2)-O(3)	1.982(2)	P(3)-O(2)	1.523(2)
Co(2)-O(8)	2.086(2)	P(3)-O(3)	1.542(2)
Co(2)-F(1)	2.2348(19)	P(3)-O(1)	1.553(2)
Co(3)-O(7)	1.942(2)	P(4)-O(16)	1.513(3)
Co(3)-O(4)	1.944(2)	P(4)-O(6)	1.534(2)
Co(3)-O(6)	1.961(2)	P(4)-O(15)	1.535(2)
Co(3)-O(5)	2.099(2)	P(4)-O(14)	1.541(2)
Co(3)-F(1)	2.297(2)	P(5)-O(20)	1.503(2)
Co(4)-O(18)	1.947(2)	P(5)-O(19)	1.528(2)
Co(4)-O(12)	1.961(2)	P(5)-O(18)	1.535(2)
Co(4)-O(14)	1.968(2)	P(5)-O(10)	1.557(2)
Co(4)-O(13)#2	2.088(2)	P(6)-O(8)	1.481(2)
Co(4)-F(1)	2.2450(19)	P(6)-O(13)	1.495(3)
P(1)-O(11)	1.506(2)	P(6)-O(24)	1.523(3)
P(1)-O(12)	1.525(2)	P(6)-O(21)	1.569(3)
O(20)-Co(1)-O(16)	126.37(10)	O(14)-Co(4)-F(1)	90.31(8)
O(20)-Co(1)-O(2)	120.70(10)	O(13)#2-Co(4)-F(1)	173.77(9)
O(16)-Co(1)-O(2)	111.59(9)	O(11)-P(1)-O(12)	109.07(13)
O(20)-Co(1)-O(17)#1	93.75(10)	O(11)-P(1)-O(9)	108.41(13)
O(16)-Co(1)-O(17)#1	97.31(10)	O(12)-P(1)-O(9)	109.89(13)
O(2)-Co(1)-O(17)#1	90.19(9)	O(11)-P(1)-O(7)	109.56(13)
O(20)-Co(1)-F(1)	85.74(9)	O(12)-P(1)-O(7)	109.23(13)
O(16)-Co(1)-F(1)	86.40(8)	O(9)-P(1)-O(7)	110.66(13)
O(2)-Co(1)-F(1)	86.41(8)	O(5)-P(2)-O(23)	112.68(14)
O(17)#1-Co(1)-F(1)	175.70(8)	O(5)-P(2)-O(17)	110.52(14)
O(9)-Co(2)-O(10)	116.20(10)	O(23)-P(2)-O(17)	113.37(14)
O(9)-Co(2)-O(3)	126.87(10)	O(5)-P(2)-O(22)	108.03(14)
O(10)-Co(2)-O(3)	116.93(10)	O(23)-P(2)-O(22)	104.82(13)
O(9)-Co(2)-O(8)	85.92(10)	O(17)-P(2)-O(22)	106.96(13)
O(10)-Co(2)-O(8)	91.61(10)	O(4)-P(3)-O(2)	110.94(13)
O(3)-Co(2)-O(8)	93.43(9)	O(4)-P(3)-O(3)	110.10(14)
O(9)-Co(2)-F(1)	89.78(9)	O(2)-P(3)-O(3)	111.37(13)
O(10)-Co(2)-F(1)	91.65(8)	O(4)-P(3)-O(1)	109.07(14)
O(3)-Co(2)-F(1)	87.92(9)	O(2)-P(3)-O(1)	107.70(13)

O(8)-Co(2)-F(1)	175.44(9)	O(3)-P(3)-O(1)	107.55(13)
O(7)-Co(3)-O(4)	124.15(10)	O(16)-P(4)-O(6)	109.86(13)
O(7)-Co(3)-O(6)	115.91(10)	O(16)-P(4)-O(15)	109.48(13)
O(4)-Co(3)-O(6)	119.44(10)	O(6)-P(4)-O(15)	106.65(12)
O(7)-Co(3)-O(5)	92.10(9)	O(16)-P(4)-O(14)	111.41(13)
O(4)-Co(3)-O(5)	92.22(9)	O(6)-P(4)-O(14)	110.40(13)
O(6)-Co(3)-O(5)	92.78(9)	O(15)-P(4)-O(14)	108.92(12)
O(7)-Co(3)-F(1)	88.50(9)	O(20)-P(5)-O(19)	110.61(14)
O(4)-Co(3)-F(1)	88.65(8)	O(20)-P(5)-O(18)	110.56(14)
O(6)-Co(3)-F(1)	85.64(8)	O(19)-P(5)-O(18)	106.61(13)
O(5)-Co(3)-F(1)	178.42(8)	O(20)-P(5)-O(10)	112.32(14)
O(18)-Co(4)-O(12)	119.07(9)	O(19)-P(5)-O(10)	106.79(13)
O(18)-Co(4)-O(14)	122.97(10)	O(18)-P(5)-O(10)	109.73(13)
O(12)-Co(4)-O(14)	117.95(10)	O(8)-P(6)-O(13)	113.80(16)
O(18)-Co(4)-O(13)#2	83.46(10)	O(8)-P(6)-O(24)	109.35(15)
O(12)-Co(4)-O(13)#2	94.36(9)	O(13)-P(6)-O(24)	110.60(15)
O(14)-Co(4)-O(13)#2	93.37(9)	O(8)-P(6)-O(21)	108.84(14)
O(18)-Co(4)-F(1)	90.32(8)	O(13)-P(6)-O(21)	107.53(14)
O(12)-Co(4)-F(1)	88.34(8)	O(24)-P(6)-O(21)	106.43(16)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,y-1/2,-z+1, #2 x-1/2, -y+3/2,-z, #3 x+1/2,-y+3/2,-z, #4 -x+3/2,y+1/2,-z+1.