Supporting materials

The formation of a hydrated homochiral helix from an achiral zwitterionic salt, spontaneous chiral symmetry breaking and redox chromism of crystals

Qing-Xia Yao,[a] Wei-Min Xuan,[b] Hui Zhang,[b] Chao-Yang Tu [a] and Jie Zhang*[a]

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter and Graduate School of the Chinese Academy of Sciences, Fuzhou, Fujian 350002(China)*
[b]*Department of Chemistry College of Chemistry and Chemical Engineering Xiamen University, Xiamen 361005 (China)*

===

1. General Procedures

The IR spectrum was recorded as KBr pellets on a Spectrum One FT-IR spectrometer (PerkinElmer Instruments). The elemental analysis was determined using a Vario EL III CHNOS elemental analyzer. Thermogravimetric analysis was performed with a Mettler Toledo TGA/SDTA 851^e analyzer. Solid-state CD spectra were recorded using a J-810 spectropolarimeter. For each CD measurement ca.0.3 mg sample was taken to be mixed with 130 mg of a dried and well ground KCl powder. This mixture was then pressed into a disk for use. Diffuse spectral reflectance mesurements were made with a PerkinElmer Lambda900 UV/VIS/NIR Spectrometer. The spectrophotometer was calibrated against $BaSO_4$ surface for 100% reflectance over the wavelength range under consideration.

Data were collected on a Rigaku Mercury CCD diffractometer for Bpybc·5H_2O equipped with graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å) at room temperature. The CrystalClear program was used for the absorption correction. All structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXL-97 program package. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms bonded to C atoms were positioned geometrically (C–H = 0.95 or 0.99 Å). O_{1w} and O_{2w} were full-occupancy, O_{3w} was half-occupancy. Three hydrogen atoms (H_{1w}, H_{2w}, H_{3w}) on lattice water molecules were located while the other hydrogen atoms were not found by difference electron density maps. Selected bond lengths and angles are listed in Table S1. Due to the absence of heavy atom in Bpybc·5H_2O, the absolute configuration could not be established from the data obtained.

2. The synthesis of Bpybc·5H_2O:

1,1′-bis(4-carboxybenzyl)-4,4′-bipyridinium chloride ($H_2BpybcCl_2$) was synthesized based on the nucleophilic substitution reaction of 4,4′-bipyridine and 4-(chloromethyl)benzoic acid (refer to our paper published in Cryst. Growth Des. 2005, 5, 1939 for details). $H_2BpybcCl_2$ (0.245 g, 0.5 mmol) was dissolved in 8 mL of water and the pH value of the solution was adjusted to 7 with 0.5 mol/L NaOH solution. After filtration, 2 mL DMSO was then added to the above filtrate. Static solvent evaporation produces colorless prism crystals, yield > 35%. Anal. Calc. for $C_{26}H_{30}N_2O_9$: C, 60.69; H, 5.88; N, 5.44. Found: C, 60.71; H, 5.63; N, 5.29%.

Table S1. Some hydrogen bonding parameters in Bpybc·5H$_2$O.

D-H···A	D-H (Å)	H···A (Å)	D···A(Å)	D-H···A (°)	Symmetry codes
O1W-H1W···O1#C	0.86(5)	1.93(5)	2.788(4)	174.6(44)	2−x, 1−x+y, 2/3−z
O2W-H2W···O2	0.80(4)	1.97(4)	2.774(4)	173.8(48)	x, y, z
O3W-H3W···O1#C	0.88(2)	1.86(9)	2.655 (3)	151.3(83)	2−x, 1−x+y, 2/3−z

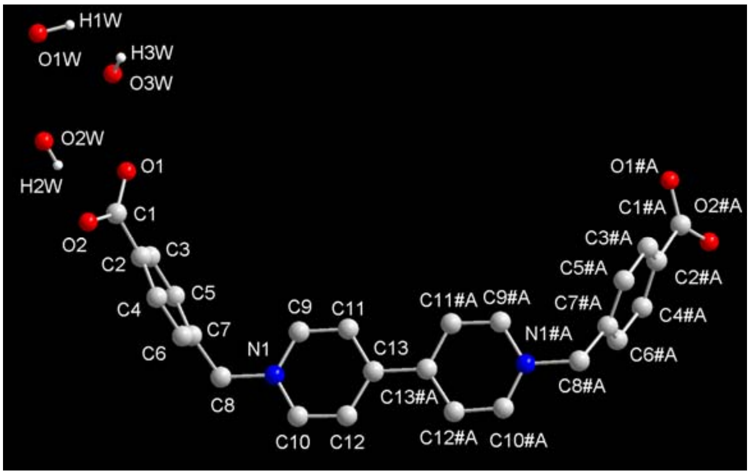


Fig. S1 An asymmetric unit in the crystal structure of Bpybc·5H$_2$O. Symmetry codes: '#A', (y, x, -z).

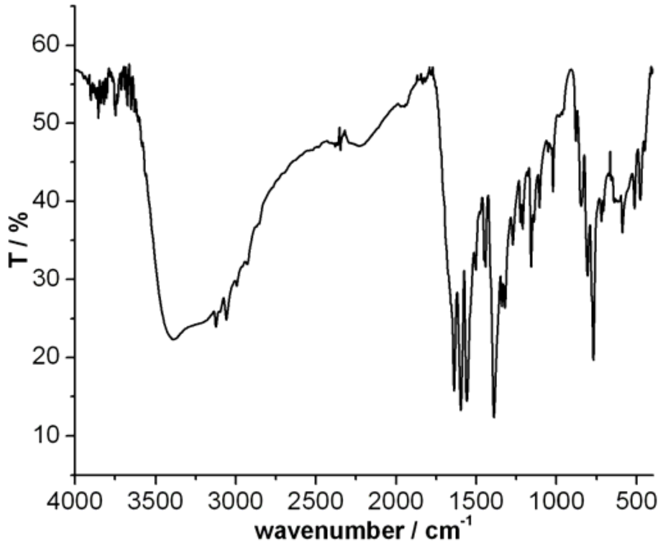


Fig. S2 IR spectrum of Bpybc·5H$_2$O.

IR (KBr pellet, cm^{-1}): 3390 (s), 3123 (m), 3058 (m), 2224 (w), 1637 (s), 1595 (s), 1557 (s), 1502 (m), 1441 (m), 1389 (s), 1340 (m), 1320 (m), 1271 (w), 1224 (w), 1209 (w), 1156 (m), 1104 (w), 1021 (w), 881 (w), 848 (w), 809 (m), 771 (s), 721 (w), 590 (w), 514 (w), 479 (w).

Band assignment: the IR spectrum of Bpybc·5H$_2$O exhibits broad bands around 2800-3600 cm^{-1} due to the stretching vibrations of the OH, CH$_2$, and CH groups. The strong band at 1637 cm^{-1} can be attributed to the typical C=N and C=C stretching vibrations of bipyridinium. The absence of any strong bands around 1700 cm^{-1} indicates that two carboxylic acid groups are deprotonated. Moreover, they show the asymmetric and symmetric stretching vibrations of the COO^{-} groups at 1595 and 1389 cm^{-1} separately.

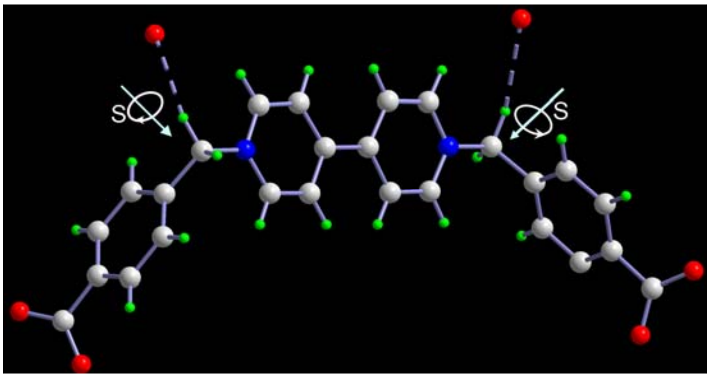


Fig. S3 *S*-enantiomers of the chiral organic structure unit in Bpybc·5H_2O containing left-handed helix (space group: $P3_221$). The hydrogen atom on the methylene carbon atom without C-H···O interaction is considered as the lowest priority group that is pointed away from the reader, the remaining three groups with the priority N1-C1-H(O) are arranged in counterclockwise fashion. The C-H···O hydrogen bonds are shown as dotted lines.

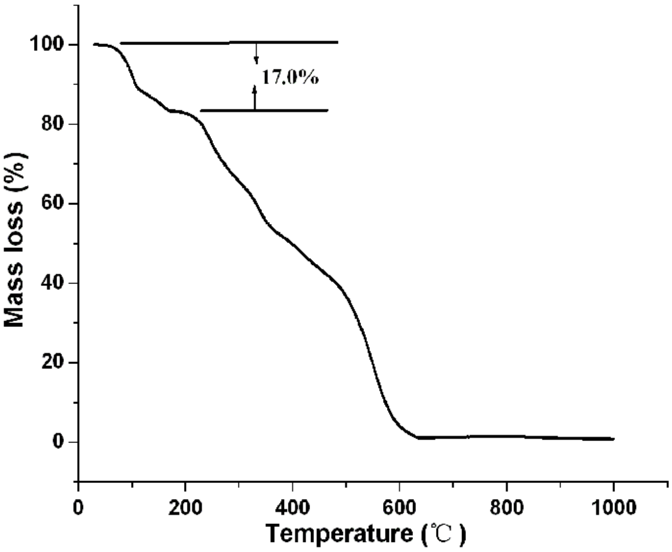
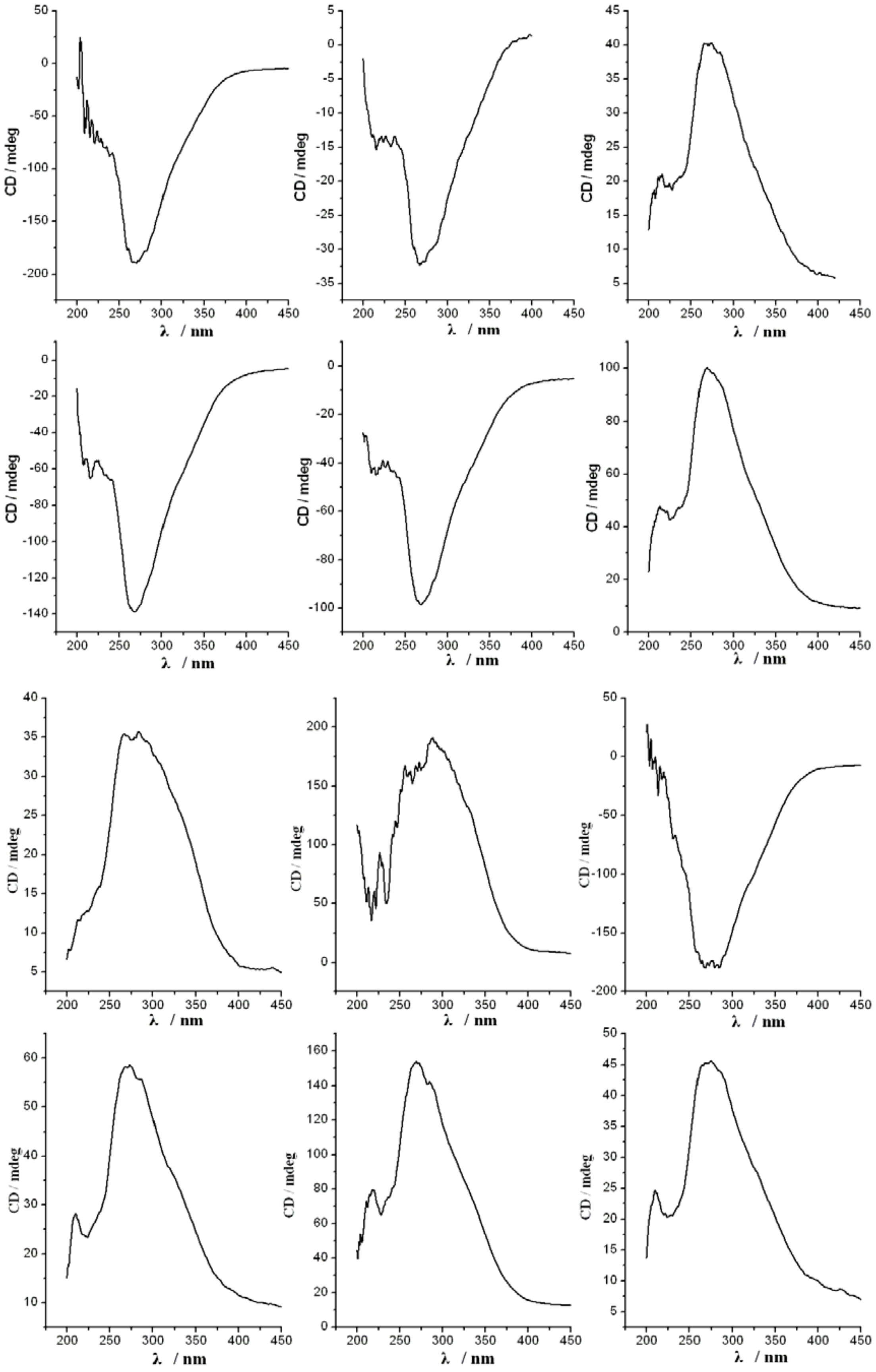
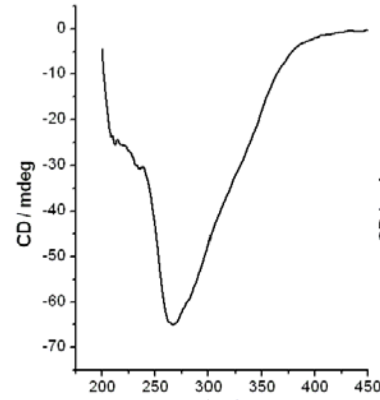
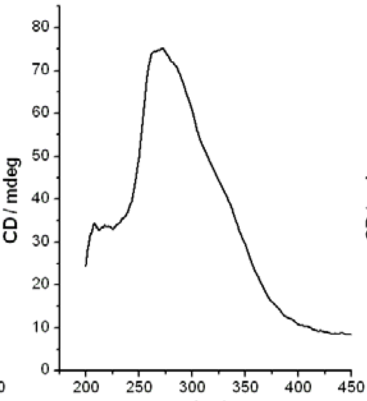


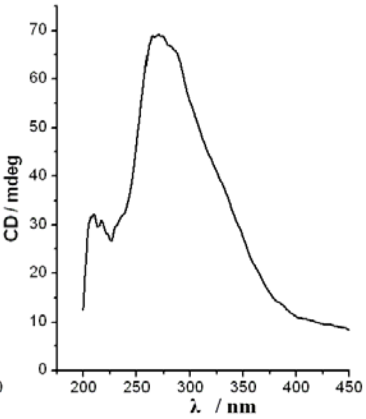
Fig. S4 TGA curve of Bpybc·5H_2O under air.

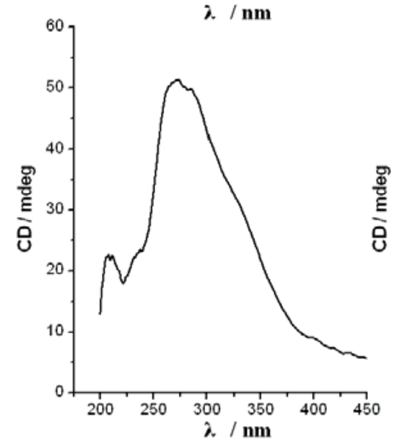
TGA of Bpybc·5H_2O shows that the compound can be stable up to 70 °C. Crystal lattice water molecules are gradually eliminated in the temperature range of 70-170 °C (observed mass loss, 17.0%; calcd, 17.5%). There exists a stage in the range 170-210 °C, showing almost unchanged mass loss. On heating up to 210 °C, the Bpybc molecule begins to decompose.

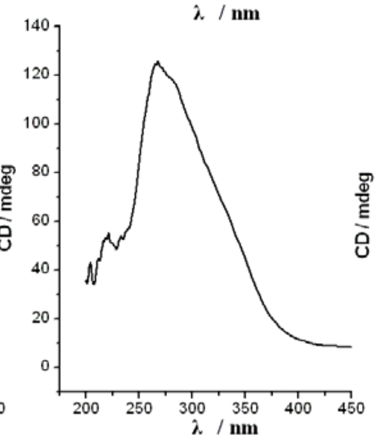

CD / mdeg
λ / nm
50
0
-50
-100
-150
-200
5
-5
-10
-15
-20
-25
-30
-35
45
40
35
30
25
20
15
10
-20
-40
-60
-80
-100
-120
-140
100
80
60
200
150
60
50
160
140
120
200
250
300
350
400
450

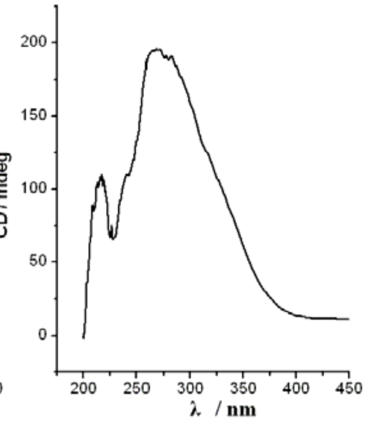

CD / mdeg
0
-10
-20
-30
-40
-50
-60
-70
200 250 300 350 400 450
λ / nm

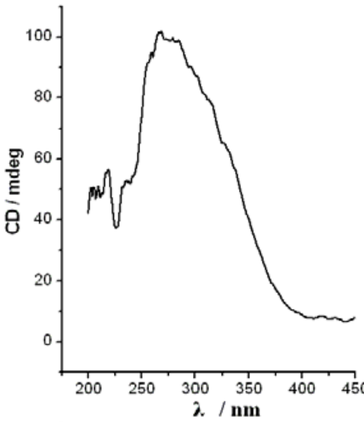

CD / mdeg
0
10
20
30
40
50
60
70
80
200 250 300 350 400 450
λ / nm

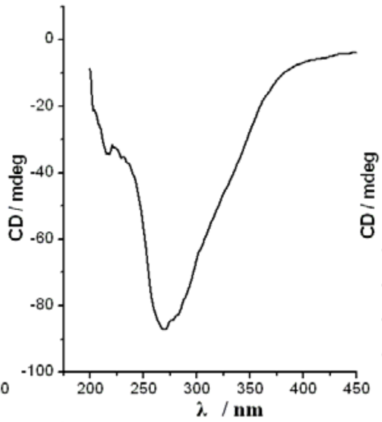

CD / mdeg
0
10
20
30
40
50
60
70
200 250 300 350 400 450
λ / nm

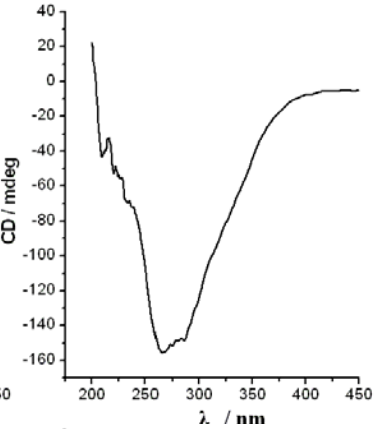

CD / mdeg
0
10
20
30
40
50
60
200 250 300 350 400 450
λ / nm

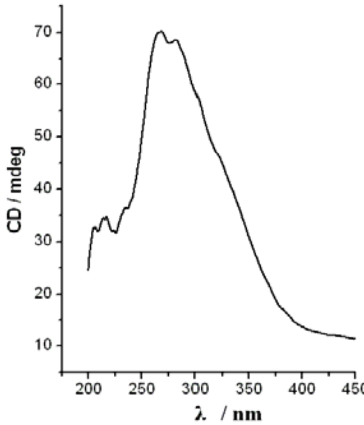

CD / mdeg
0
20
40
60
80
100
120
140
200 250 300 350 400 450
λ / nm

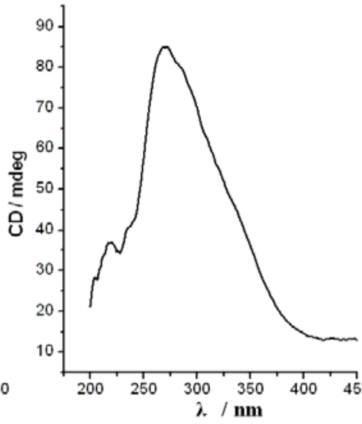

CD / mdeg
0
50
100
150
200
200 250 300 350 400 450
λ / nm

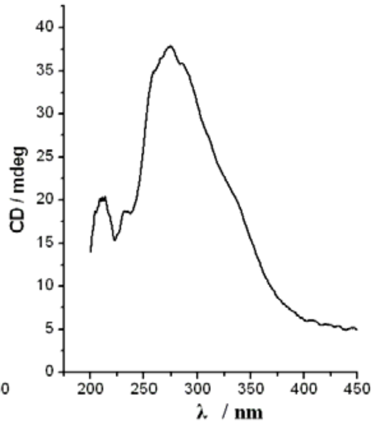

CD / mdeg
0
20
40
60
80
100
200 250 300 350 400 450
λ / nm


CD / mdeg
0
-20
-40
-60
-80
-100
200 250 300 350 400 450
λ / nm


CD / mdeg
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
200 250 300 350 400 450
λ / nm


CD / mdeg
10
20
30
40
50
60
70
200 250 300 350 400 450
λ / nm


CD / mdeg
10
20
30
40
50
60
70
80
90
200 250 300 350 400 450
λ / nm


CD / mdeg
0
5
10
15
20
25
30
35
40
200 250 300 350 400 450
λ / nm

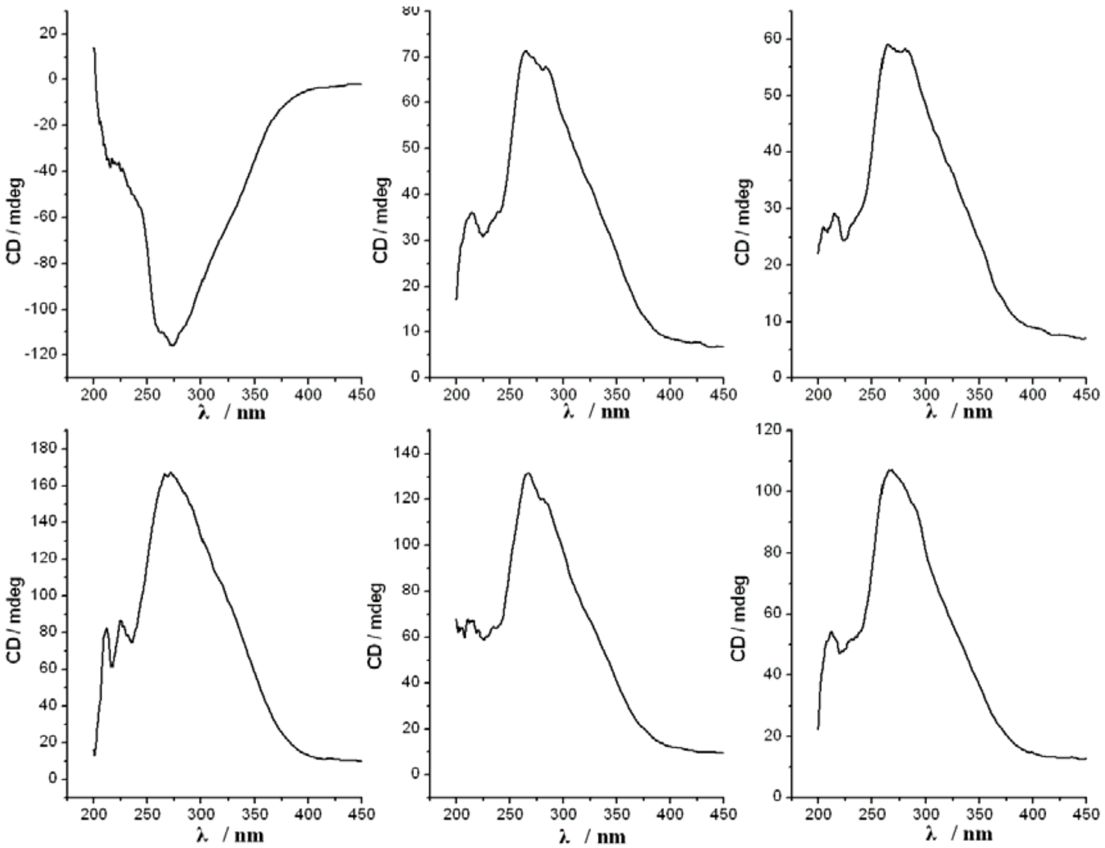
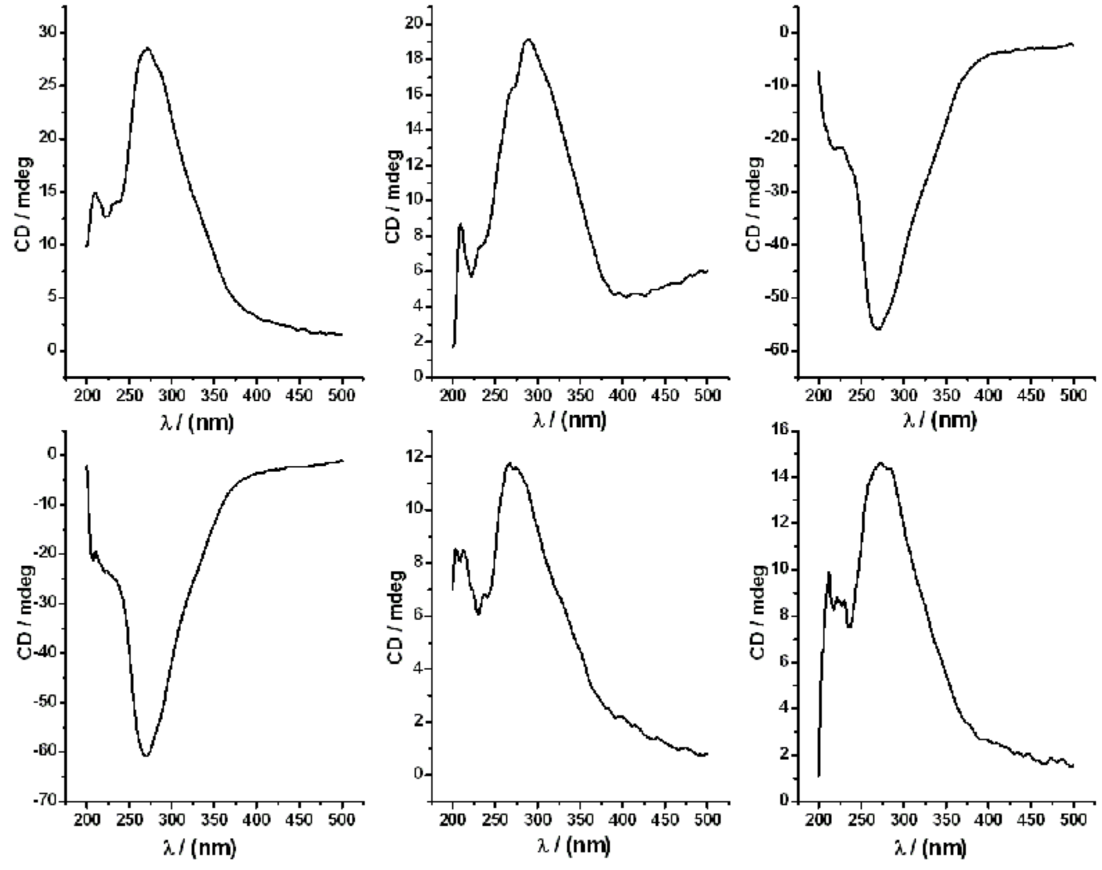


Fig. S5 Solid state CD spectra of Bpybc·5H_2O single crystal chosen from one crystallization randomly (30 crystals measured with *ee* = 40%).



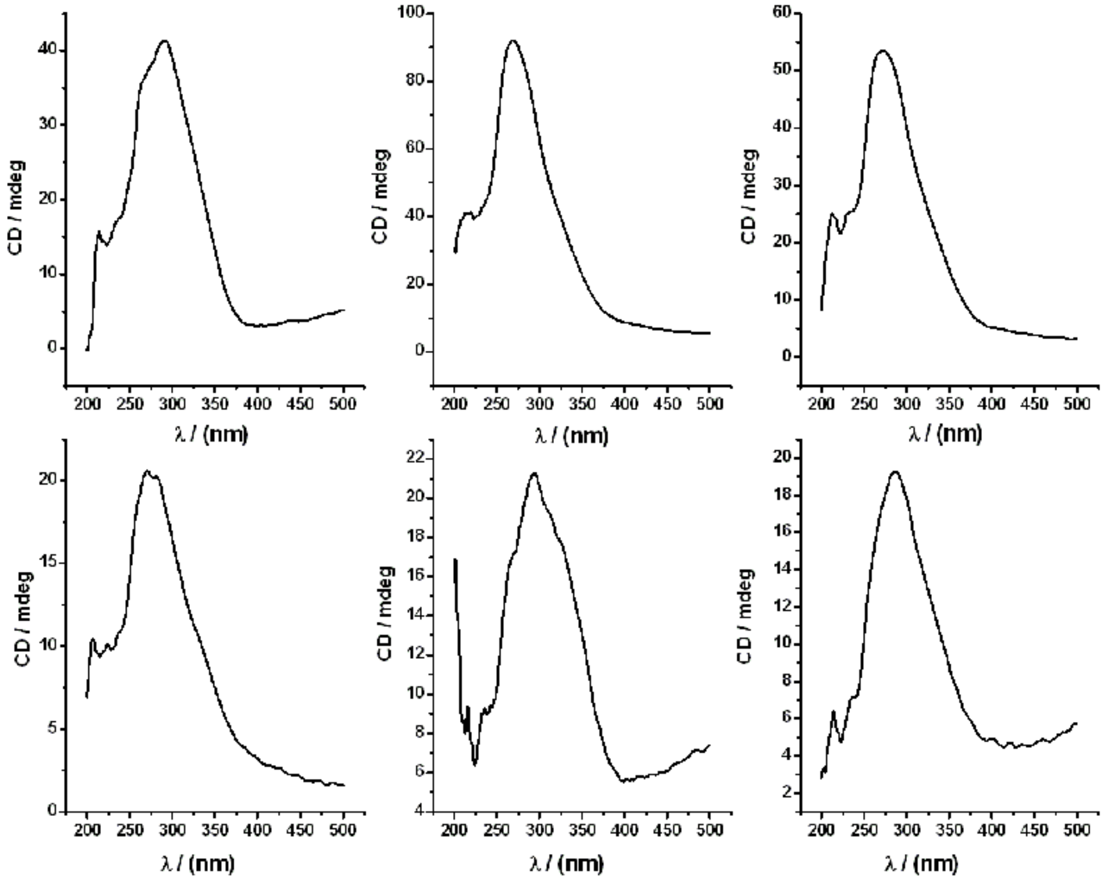


Fig. S6 Solid state CD spectra of twelve batches of powdered bulk samples showing that each crystallization is CD-active. All crystals obtained from one crystallization were well ground, and then took this powder sample of ca.0.3mg to mix with KCl powder for each measurement.