Electronic Supporting Information

Countercation-directed chiral resolution of $[Mo_2O_4(H_2dtpa)]^-$, syntheses, crystal structures and CD spectra of (λ)-$[NEt_4][Mo_2O_4(H_2dtpa)]$ and (δ)-$Na[Mo_2O_4(H_2dtpa)]$

Fengcai Li Li Xu*

Email: xli@fjirsm.ac.cn

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

Experimental Section

Materials. All chemicals were obtained from commercial sources and used without further purification. the $[Mo_2O_4(H_2O)_6]^{2+}$ ion was obtained by reduction of an acidic solution of the molybdate precursor $[(NH_4)_6Mo^{VI}{}_7O_{24}]$, $[Na_2Mo^{VI}O_4]$ or $[Li_2Mo^{VI}O_4]$ with hydrazine hydrate and the pH value was raised with NH3, NaOH, or LiOH respectively.[17] The preparation of a 0.10 M Solution of $[Mo_2O_4(H_2O)_6]^{2+}$ ion in 4 M HCl was synthesized according to published procedures[17]. The procedure is identical starting from $(NH_4)_6Mo^{VI}{}_7O_{24}\cdot 4H_2O$ (2.91 g,2.35 mmol) and $Na_2MoO_4.2H_2O$ (4 g, 16.53 mmol), repectively.

Synthesis of (λ)-$[N(C_2H_5)_4][Mo_2O_4(H_2dtpa)]\cdot 3H_2O$ ((λ)-1)

A total of H_5DTPA (0.393g , 1 mmol) was added to 10mL (1 mmol) of a solution of $[Mo_2O_4(H_2O)_6]^{2+}$ obtained from the reduction of $(NH_4)_6Mo^{VI}{}_7O_{24}\cdot 4H_2O$ as described above. A solution of $(C_2H_5)_4NCl$ (0.3314g, 1mmol) was then added, and the pH was increased to 4 by the addition of $NH_3\cdot H_2O$ aqueous. The deep red solution was then left to evaporate at room temperature. Red parallelepipedic crystals **(λ)-1** were isolated by filtration after 2 days.Yield: 0.50 g (70% based on Mo). Calcd for $C_{22}H_{46}Mo_2N_4O_{17}$ (830.49): N,6.746; C, 31.81; H, 5.58. Found: N, 6.72; C,31.35; H, 5.29. FTIR (KBr pellets, cm-1): 3441(m). 2924(w), 1744(m.sh) , 1634(s.sh) , 1391(s,sh) , 1215(m,sh) ,1166 (w,sh) ,1084(m.sh) 964(s,sh) ,752(m,sh) , 670(w) ,482(m,sh).

Synthesis of (δ)- $Na(H_2O)[Mo_2O_4(H2DTPA)]\cdot 2H_2O$ ((δ)-2)

A total of H_5DTPA (0.393g, 1 mmol) was added to 10mL (1 mmol) of a solution of $[Mo_2O_4(H_2O)_6]^{2+}$ obtained from the reduction of $Na_2MoO_4.2H_2O$ as described above. A solution of $(C_2H_5)_4NCl$ (0.1657g, 1mmol) was then added, and the pH was increased to 3 by the addition of 1 mol/L NaOH aqueous. The orange precipitates generated immediately and were filtrated , The orange precipitates were dissolved in water and the solution was then left to evaporate at room temperature, Red prismatical crystals **(δ)-2** were collected by filtration after 2 days., washed with C_2H_5OH, and dried in air. Yield: 0.66 g (80% based on Mo). Calcd for C_{14} $H_{262}Mo_2N_3NaO_{17}$ (723.25): N,5.81; C, 23.25; H, 3.62. Found: N, 5.84;C, 23.34; H, 3.48. FTIR (KBr pellets, cm-1): 3532(w) , 3364(m) , 2524(vw) ,2056(vw) , 1728(w ,sh) 1634(s,sh) ,1431.57(w) ,1394(w) , 1335(w), 1295(w), 1231(m,sh), 1078(w,sh), 939(s,sh), 854(w,sh), 797(w,sh), 758(m,sh), 726(w), 598(vw), 511(m,sh), 477(w).

Physical Techniques

Elemental analyses (C, H, N) were performed on a Vario EL III elemental analyzer. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the range 4000–400$cm^{-1.}$. The solid UV–vis spectra were recorded on Lambda35 spectrophotometer. The solution UV–vis spectra were recorded on Lambda 900 spectrophotometer.The thermogravimetric measurements were performed on a Netzsch STA449C apparatus in nitrogen atmosphere with a heating rate of 10 □/min from 38 to 800 □. the solid-state circular dichroism (CD) were recorded on a MOS-450 spectropolarimeter with the ratio100/1 of dried KCl and sample from 200 to 600 nm. the solid-state circular dichroism (CD) were recorded on a MOS-450 spectropolarimeter with the ratio 100/1 of dried KCl and sample from 200 to 600 nm. The liquid Circular dichroism were measured at room temperature in a 1.0 cm path length quartz cell. CD data were collected at 1 nm intervals using averaging times of 0.5 s/nm. The spectral bandwidth was 1 nm. Sample concentrations were 50μM..

Crystal structure refinement

Suitable single crystals of compounds **(λ)-1** and **(δ)-2** were mounted on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo Ka radiation (λ= 0.71073 Å). The CrystalClear software was used for data reduction and empirical absorption correction[1]. The structures were solved by the direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on F2 (SHELXTL Version 5.1)[2]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C atoms and carboxyl O atoms were located at geometrically calculated positions and treated by constrained refinement. Coordination water hydrogen atoms for compound **(λ)-1** and **(δ)-2** were located from difference maps and refined by a mixture of independent and constrained refinement. Hydrogen bonds for **(λ)-1** and **(δ)-2** are summarized in Table S1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge

Crystallographic Data Centre as supplementary publication no. CCDC-867337 ((**λ**)**-1**) and CCDC-867338 ((**δ**)**-2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK(fax:+44(0)1223762911;e-mail: deposit@ccdc.cam.ac.uk).

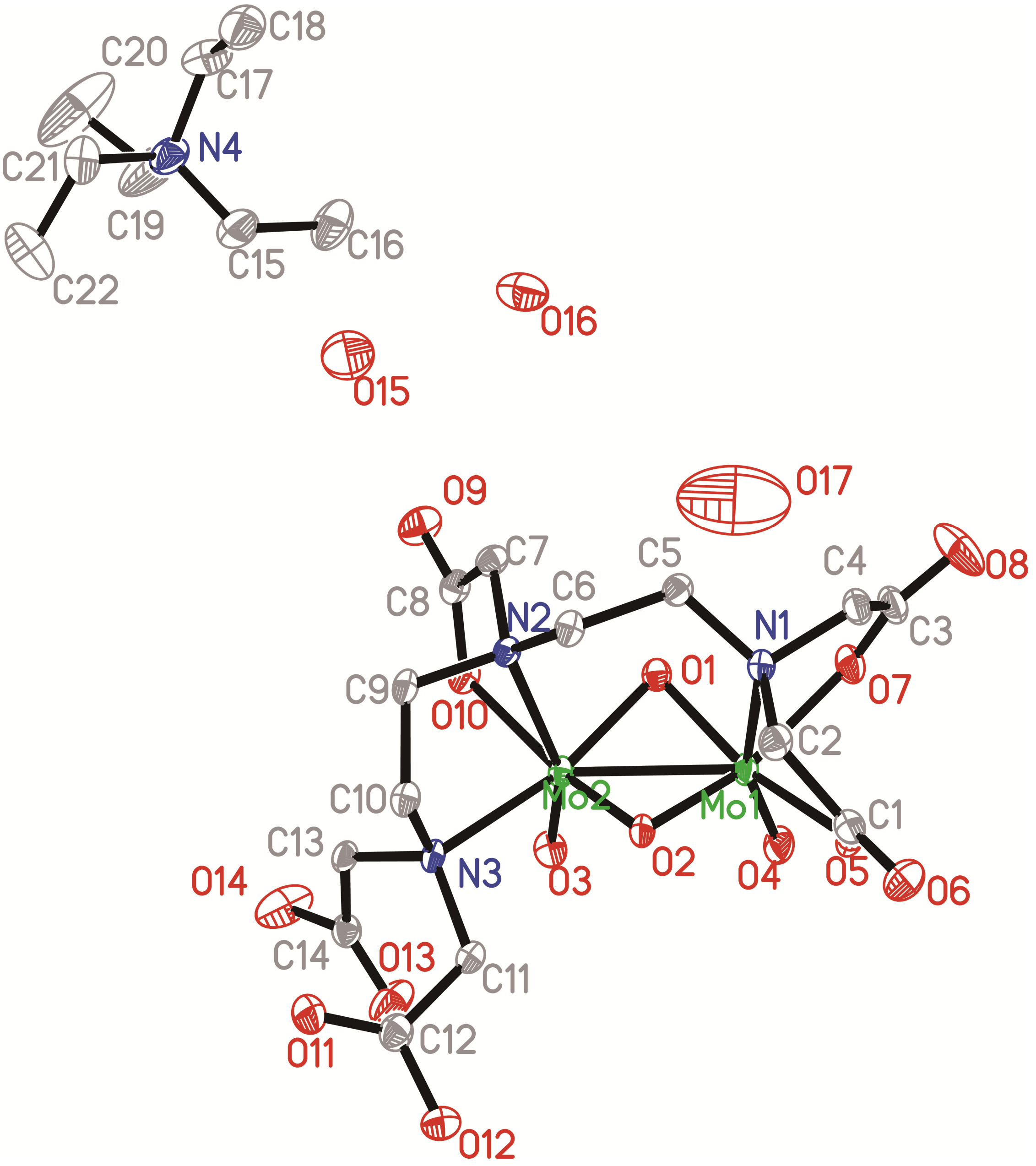


Fig. S1. Structure of complex **(λ)-1** with 30% displacement ellipsoids probability level. Hydrogen atoms are omitted for clarity.

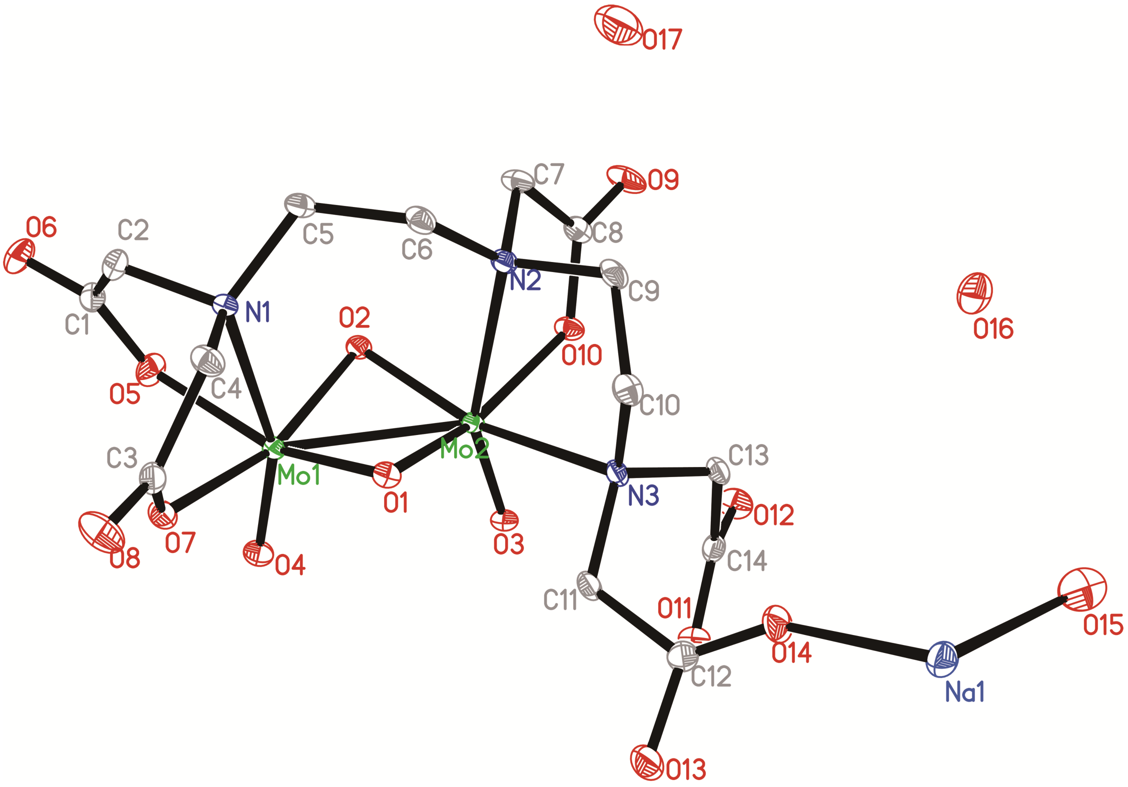


Fig. S2. The Structure of **(δ)-2** with atomic numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

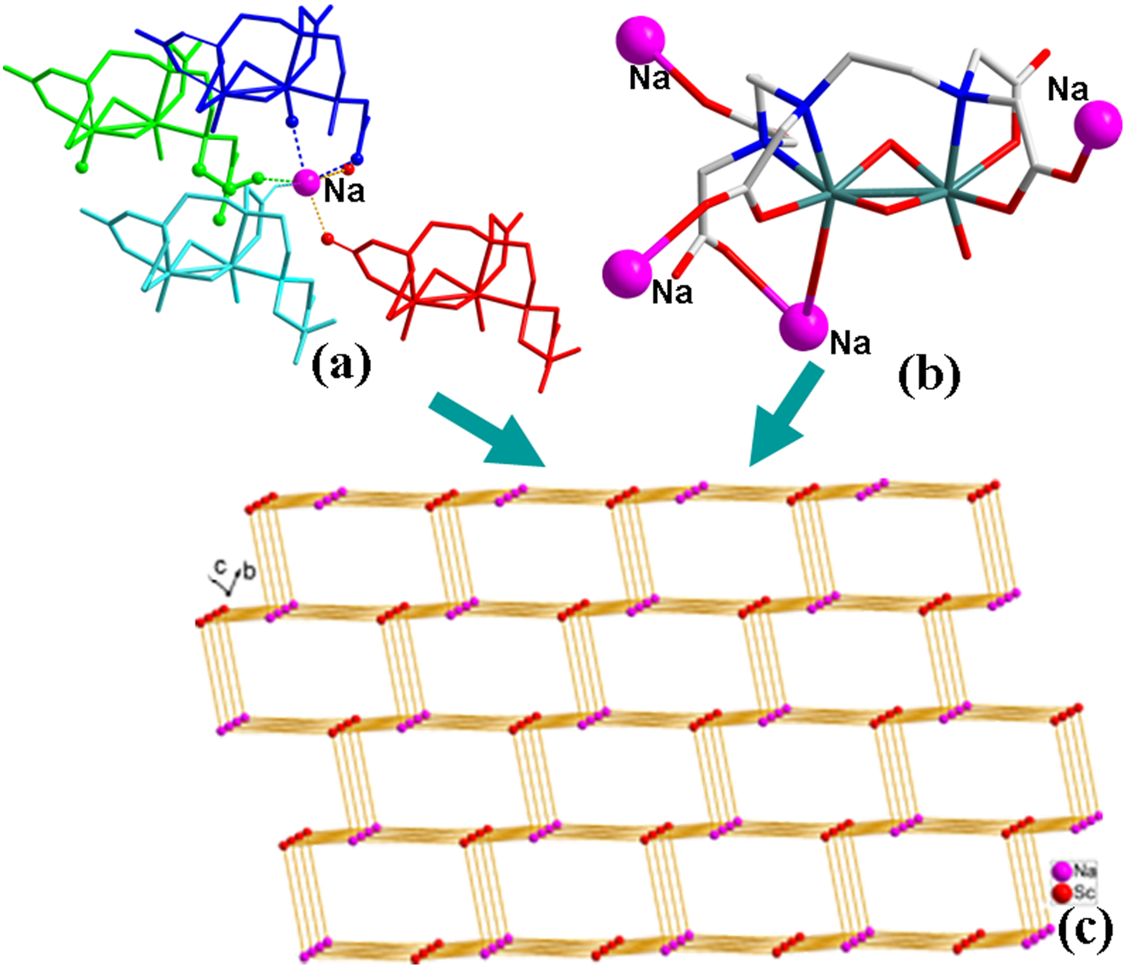
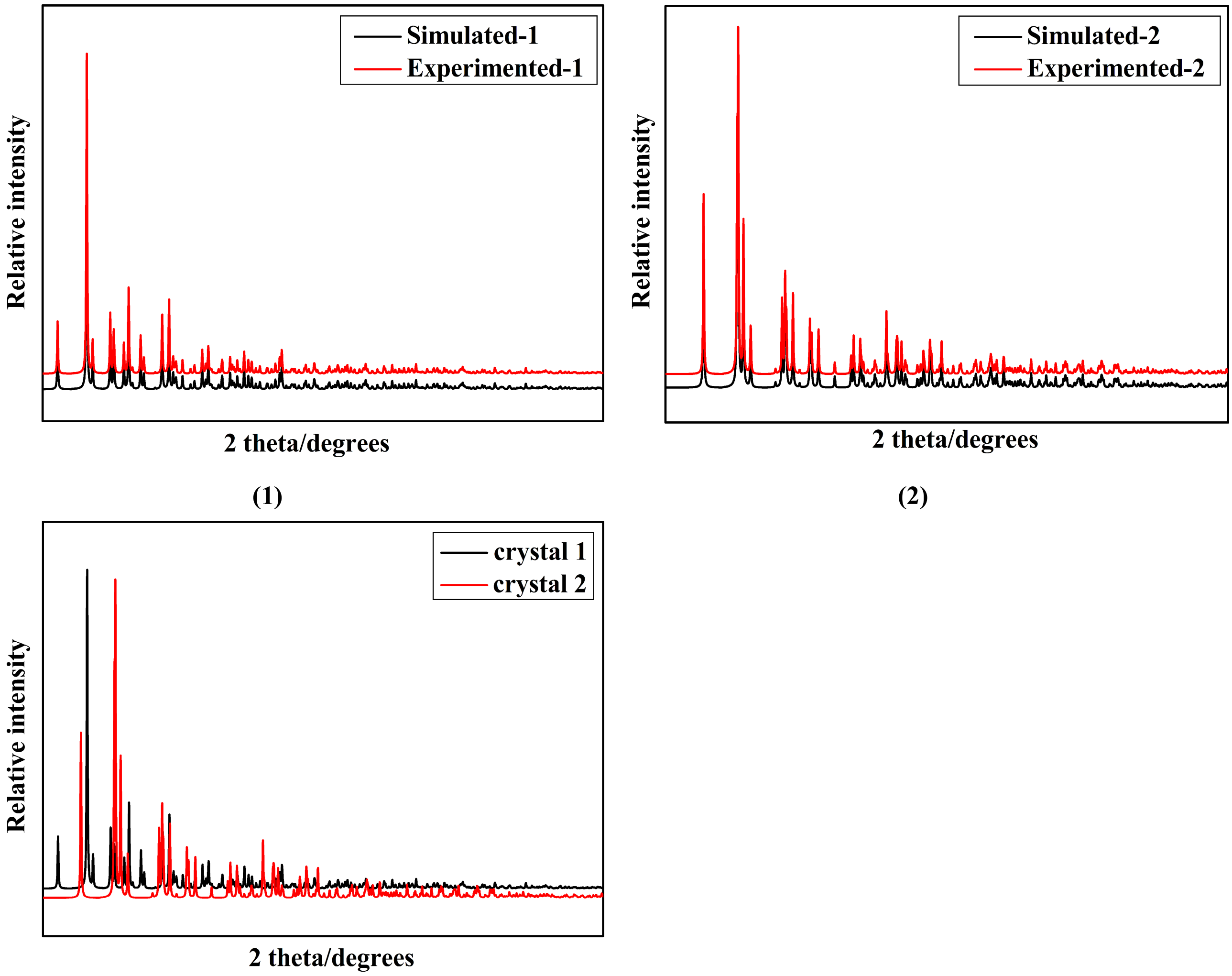


Fig. S3. Crystallography of **(δ)-2**: (a) local coordination environment of Na^+ ion (b) coordination modes of $[Mo_2O_4(H_2dtpa)]^-$ unit (c) (4,4)-connected net with **dia** topology of and **(δ)-2.**



(1)

(2)

(3)

Fig. S4. (1)X-Ray powder spectrums of complex **(λ)-1** by simulated and experimented with single crystal data; (2) X-Ray powder spectrums of complex and **(δ)-2** by simulated and experimented with single crystal data; (3) Comparison of X-Ray powder spectrums of complex **(λ)-1** and **(δ)-2** by experimented with single crystal data.

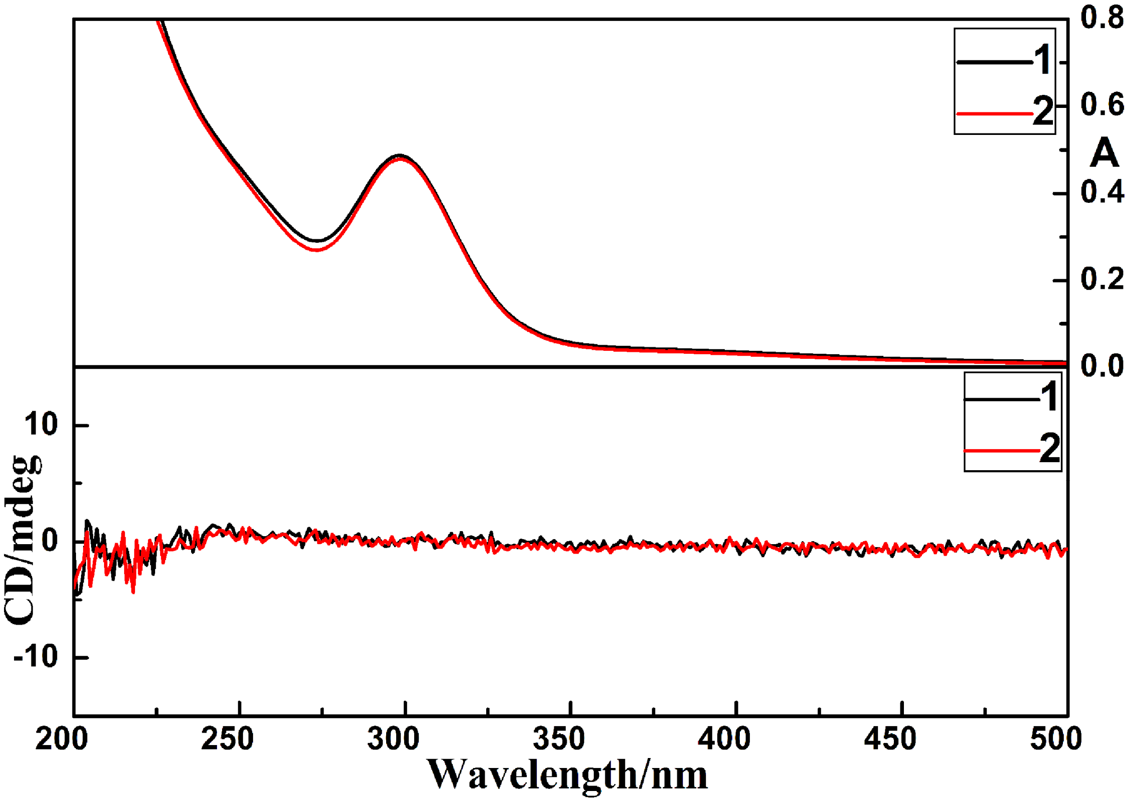


Fig. S5. Absorbtion(AB) and CD spectras of compound **(λ)-1** and **(δ)-2** in water . **uper** :Absorbtion spectras , black curver for **(λ)-1** and red curver for **(δ)-2**, respectively**; lower:** CD spectras, black curver for **(λ)-1** and red curver for **(δ)-2**, respectively.

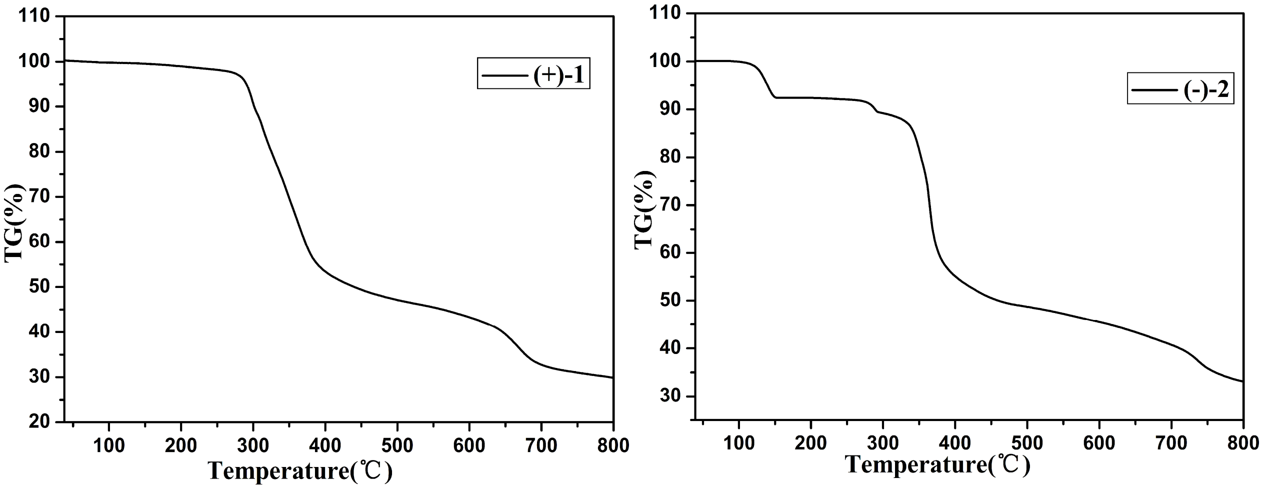


Fig. S6. The TG curves of compounds **(λ)-1 (left)** and **(δ)-2 (right).**

Table S1. Hydrogen bonds for **(λ)-1** and **(δ)-2** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
(+)-1				
O(12)-H(12)...O(16)#1	0.82	1.75	2.543(5)	163.6
O(14)-H(14)...O(9)#2	0.82	1.87	2.667(4)	164.2
(-)-2				
O(12)-H(12)...O(15)#1	0.82	1.77	2.575(7)	165.0
O(13)-H(13)...O(16)#7	0.82	1.75	2.544(7)	163.6
O(15)-H(15A)...O(8)#8	0.85	1.89	2.705(8)	159.8
O(15)-H(15B)...O(17)#9	0.85	2.02	2.804(7)	152.7
O(16)-H(16A)...O(6)#10	0.85	1.94	2.759(7)	162.6
O(16)-H(16B)...O(10)#4	0.85	2.09	2.808(7)	141.2
O(17)-H(17A)...O(2)#4	0.85	2.04	2.881(7)	168.9
O(17)-H(17B)...O(4)#11	0.85	2.17	3.013(7)	172.6

Symmetry transformations used to generate equivalent atoms:

(+)-1: #1 x,y-1,z #2 -x+1,y-1/2,-z

(-)-2: #1 x+1,y,z #2 x-1,y+1,z #3 x-1,y+1,z-1 #4 x-1,y,z
#5 x+1,y-1,z+1 #6 x+1,y-1,z #7 x,y+1,z #8 x,y,z-1
#9 x,y+1,z-1 #10 x-1,y,z-1 #11 x-1,y-1,z

References

1 CrystalClear version 1.3, Rigaku Corp, 2000.

2 G. M. Sheldrick, SHELXS-97, Program for solution of crystal structures, University of Göttingen, Germany, 1997.