Electronic Supplementary Information

Single-crystal-to-single-crystal transformation of a coordination polymer from 2D to 3D by [2+2] photodimerization assisted with a coexisting flexible ligand

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Experimental section

All chemicals and solvents were of reagent grade and used without further purification. Elemental analyses were performed at the UNIST Central Research Facilities Center (UCRF) in Ulsan National Institute of Science and Technology (UNIST). IR spectra were recorded with a ThermoFisher Scientific Nicolet 6700 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) were performed under N_2(g) atmosphere at a scan rate of 1 ^oC min^{-1} using Q50 from TA instruments. X-ray powder diffraction data were recorded on a Bruker D2 phaser diffractometer at 30 kV and 10 mA for Cu Kα (λ = 1.541 Å), with a step size of 0.02° in 2θ. Nuclear magnetic resonance (NMR) spectra were recorded on a Agilent 400-MR DD2 spectrometer.

Synthesis of [Ni(adipate)(4-spy)$_2$(H_2O)] (1)

$Ni(NO_3)_2 \cdot 6H_2O$ (29.3 mg, 0.1 mmol) and the sodium adipate (19 mg, 0.1 mmol) were dissolved in a mixture of ethanol and water with volume ratio of 2 mL:1 mL and 1 mL:2 mL respectively. The solution of $Ni(NO_3)_2 \cdot 6H_2O$ was diffused onto the latter solution. Subsequently, a methanol solution (3 mL) of 4-styrylpyridine (4-spy) (18 mg, 0.1 mmol) was carefully added. The mixture solution allowed to stand at room temperature for 7 days until the green crystals were fully synthesized. Yield: 64%. Anal. Calcd for $Ni_1C_{32}H_{32}N_2O_5$: C, 65.83; H, 5.49; N, 4.80.; Found: C, 64.51; H, 5.50; N, 4.78.

Synthesis of single crystals of [Ni(adipate)(*rctt*-ppcb)(4-spy)$_2$(H_2O)$_2$] (2) from 1

After UV irradiation (365 nm, 0.7 klx by Hg lamp) of **1** for 24 h, green crystals of [Ni_2(4-ppcb)(4-spy)$_2$(H_2O)$_2$] (**2**) (*rctt*-ppcb = *regio*-*cis*, *trans*, *trans*-1,3-bis(4'-pyridyl)-2,4-bis(phenyl)cyclobutene) were obtained. Anal. Calcd for $Ni_1C_{32}H_{32}N_2O_5$: C, 65.83; H, 5.49; N, 4.80.; Found: C, 65.34; H, 5.35; N, 4.79.

Preparation of the bulk powder sample of 2

For preparation, the crystals of **1** were ground in powder form, and thinly spread onto the glass substrate. Upon the UV-irradiation (365 nm, 1.2 klx by Hg lamp), the bulk samples of **2** (6 h) and **1'** (1 h) was synthesized.

Single-crystal X-ray crystallography

Single crystals of **1, 2**, and **1'** were coated with paratone-*N* oil, and the diffraction data were measured at 100 K with synchrotron radiation (λ = 0.63000, 0.70000, and 0.70000 Å, respectively) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111)

double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Republic of Korea. The ADSC Q210 ADX program[S1] were used for data collection, and HKL3000sm (Ver. 730r)[S2] were used for cell refinement, reduction, and absorption correction. The crystal structures were solved by direct methods with SHELX-XS (Ver. 2014/5)[S3] and refined by full-matrix least-squares calculations with SHELX-XL (Ver. 2014/7)[S4]. All non-hydrogen atoms in whole structures were refined anisotropically. A summary of the crystals and some crystallographic data are given in Table S1-S6. CCDC 1524563 (**1**), CCDC 1524564 (**2**), and CCDC 1524565 (**1'**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 EX, UK.

References

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Table S1. Crystallographic data for [Ni(adipate)(spy)$_2$(H$_2$O)] (**1**).

Empirical formula	C32 H32 N2 O5 Ni
Formula weight	583.30
Temperature	100(2) K
Wavelength	0.63000 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 18.788(4) Å
	b = 8.3400(17) Å
	c = 18.868(4) Å
	α = 90°
	β = 115.53(3)°
	γ = 90°
Volume	2696.6(11) Å^3
Z	4
Density (calculated)	1.437 g cm^{-3}
Absorption coefficient (μ)	0.552 mm^{-1}
F(000)	1224
θ range for data collection	1.797 to 33.355°.
Index ranges	-32<=h<=32, -14<=k<=14, -32<=l<=32
Reflections collected	40553
Independent reflections	12624 [R(int) = 0.0660]
Completeness to θ = 28.00°	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12624 / 0 / 369
Goodness-of-fit on F^2	0.975
R_1[a], wR_2[b] [$I>2\sigma(I)$]	0.0406, 0.1008
R_1[a], wR_2[b] (all data)	0.0683, 0.1107
Largest diff. peak and hole	0.677 and -1.299 e.Å^{-3}

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + (0.00)P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table S2. Crystallographic data for $[Ni_2(adipate)_2(spy)_2(rctt\text{-ppcb})(H_2O)_2]$ (**2**).

Empirical formula	C64 H64 N4 O10 Ni2
Formula weight	1166.61
Temperature	100(2) K
Wavelength	0.70000 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 21.305(4) Å
	b = 8.5080(17) Å
	c = 30.830(6) Å
	α = 90°
	β = 94.27(3)°
	γ = 90°
Volume	5575(2) Å^3
Z	4
Density (calculated)	1.390 g cm^{-3}
Absorption coefficient (μ)	0.708 mm^{-1}
F(000)	2448
θ range for data collection	1.552 to 33.270°.
Index ranges	-33<=h<=33, -12<=k<=12, -47<=l<=47
Reflections collected	34671
Independent reflections	18478 [R(int) = 0.0431]
Completeness to θ = 28.00°	98.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18478 / 101 / 851
Goodness-of-fit on F^2	1.010
$R_1{}^a$, $wR_2{}^b$ [$I>2\sigma(I)$]	0.0774, 0.2061
$R_1{}^a$, $wR_2{}^b$ (all data)	0.1578, 0.2500
Largest diff. peak and hole	1.459 and -1.153 e.Å^{-3}

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.1424P)^2 + (0.00)P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table S3. Crystallographic data for [Ni(adipate)(spy)($spy_{0.6}$·½*rctt*-$ppcb_{0.4}$)(H_2O)] (**1'**).

Empirical formula	C32 H32 N2 O5 Ni
Formula weight	583.30
Temperature	100(2) K
Wavelength	0.65000 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 18.732(4) Å
	b = 8.4040(17) Å
	c = 18.827(4) Å
	α = 90°
	β = 115.03(3)°
	γ = 90°
Volume	2685.5(11) Å^3
Z	4
Density (calculated)	1.443 g cm^{-3}
Absorption coefficient (μ)	0.603 mm^{-1}
F(000)	1224
θ range for data collection	1.847 to 33.341°.
Index ranges	-31<=h<=31, -12<=k<=12, -24<=l<=24
Reflections collected	37046
Independent reflections	10138 [R(int) = 0.1010]
Completeness to θ = 28.00°	94.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10138 / 86 / 497
Goodness-of-fit on F^2	1.076
R_1[a], wR_2[b] [$I>2\sigma(I)$]	0.0629, 0.1620
R_1[a], wR_2[b] (all data)	0.1407, 0.1917
Largest diff. peak and hole	0.877 and -1.491 e.Å^{-3}

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0919P)^2 + (0.00)P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table S4. Selected bond lengths (Å) and angles (deg.) of **1**.

Ni(1)-O(1)	2.0438(10)	Ni(1)-O(2)	2.0664(10)
Ni(1)-O(3)$^{\#1}$	2.0779(12)	Ni(1)-O(4)$^{\#2}$	2.0923(12)
Ni(1)-N(1)	2.1017(11)	Ni(1)-N(2)	2.1103(11)
O(1)-Ni(1)-O(2)	175.57(4)	O(1)-Ni(1)-O(3)$^{\#1}$	96.83(4)
O(2)-Ni(1)-O(3)$^{\#1}$	80.82(4)	O(1)-Ni(1)-O(4)$^{\#2}$	87.31(4)
O(2)-Ni(1)-O(4)$^{\#2}$	94.92(4)	O(3)$^{\#1}$-Ni(1)-O(4)$^{\#2}$	175.44(4)
O(1)-Ni(1)-N(1)	88.75(4)	O(2)-Ni(1)-N(1)	87.37(4)
O(3)$^{\#1}$-Ni(1)-N(1)	86.81(5)	O(4)$^{\#2}$-Ni(1)-N(1)	91.40(5)
O(1)-Ni(1)-N(2)	94.74(4)	O(2)-Ni(1)-N(2)	89.06(4)
O(3)$^{\#1}$-Ni(1)-N(2)	90.62(5)	O(4)$^{\#2}$-Ni(1)-N(2)	90.93(5)
N(1)-Ni(1)-N(2)	175.89(4)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2 #2 -x+1,-y+1,-z+1 #3 -x+1/2,y-1/2,-z+1/2

Table S5. Selected bond lengths (Å) and angles (deg.) of **2**.

Ni(1)-O(7)	2.043(2)	Ni(1)-O(3)	2.055(3)
Ni(1)-O(1)	2.059(2)	Ni(1)-O(5)$^{\#1}$	2.062(2)
Ni(1)-N(3)	2.113(3)	Ni(1)-N(1)	2.137(3)
Ni(2)-O(2)	2.053(2)	Ni(2)-O(8)	2.056(2)
Ni(2)-O(6)$^{\#2}$	2.064(2)	Ni(2)-O(9)$^{\#3}$	2.071(3)
Ni(2)-N(2)$^{\#4}$	2.105(3)	Ni(2)-N(4)	2.110(3)
O(7)-Ni(1)-O(3)	175.61(9)	O(7)-Ni(1)-O(1)	95.88(10)
O(3)-Ni(1)-O(1)	88.43(10)	O(7)-Ni(1)-O(5)$^{\#1}$	80.22(9)
O(3)-Ni(1)-O(5)$^{\#1}$	95.50(9)	O(1)-Ni(1)-O(5)$^{\#1}$	175.30(10)
O(7)-Ni(1)-N(3)	92.55(11)	O(3)-Ni(1)-N(3)	86.46(11)
O(1)-Ni(1)-N(3)	92.44(10)	O(5)$^{\#1}$-Ni(1)-N(3)	90.37(9)
O(7)-Ni(1)-N(1)	93.45(11)	O(3)-Ni(1)-N(1)	87.44(11)
O(1)-Ni(1)-N(1)	88.49(10)	O(5)$^{\#1}$-Ni(1)-N(1)	89.12(10)
N(3)-Ni(1)-N(1)	173.80(12)	O(2)-Ni(2)-O(8)	174.01(10)
O(2)-Ni(2)-O(6)$^{\#2}$	95.04(10)	O(8)-Ni(2)-O(6)$^{\#2}$	80.79(9)
O(2)-Ni(2)-O(9)$^{\#3}$	88.51(10)	O(8)-Ni(2)-O(9)$^{\#3}$	95.68(9)
O(6)$^{\#2}$-Ni(2)-O(9)$^{\#3}$	176.44(9)	O(2)-Ni(2)-N(2)$^{\#4}$	88.62(10)
O(8)-Ni(2)-N(2)$^{\#4}$	87.12(10)	O(6)$^{\#2}$-Ni(2)-N(2)$^{\#4}$	90.62(11)
O(9)$^{\#3}$-Ni(2)-N(2)$^{\#4}$	89.68(12)	O(2)-Ni(2)-N(4)	94.41(10)
O(8)-Ni(2)-N(4)	89.95(9)	O(6)$^{\#2}$-Ni(2)-N(4)	90.47(11)
O(9)$^{\#3}$-Ni(2)-N(4)	89.04(11)	N(2)$^{\#4}$-Ni(2)-N(4)	176.67(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+2 #2 -x+1,-y+1,-z+2 #3 -x,-y+1,-z+2

#4 x,-y+3/2,z+1/2

Table S6 Selected bond lengths (Å) and angles (deg.) of **1'**.

Ni(1)-N(1A)	1.990(12)	Ni(1)-O(1)	2.047(2)
Ni(1)-O(2)	2.068(2)	Ni(1)-O(3)$^{\#1}$	2.0763(19)
Ni(1)-O(4)$^{\#2}$	2.084(2)	Ni(1)-N(2)	2.108(3)
Ni(1)-N(1B)	2.286(16)		
N(1A)-Ni(1)-O(1)	89.2(5)	N(1A)-Ni(1)-O(2)	85.7(3)
O(1)-Ni(1)-O(2)	95.52(8)	N(1A)-Ni(1)-O(3)$^{\#1}$	88.2(5)
O(1)-Ni(1)-O(3)$^{\#1}$	175.74(8)	O(2)-Ni(1)-O(3)$^{\#1}$	80.93(8)
N(1A)-Ni(1)-O(4)$^{\#2}$	92.9(3)	O(1)-Ni(1)-O(4)$^{\#2}$	87.46(8)
O(2)-Ni(1)-O(4)$^{\#2}$	176.69(8)	O(3)$^{\#1}$-Ni(1)-O(4)$^{\#2}$	96.02(8)
N(1A)-Ni(1)-N(2)	175.7(4)	O(1)-Ni(1)-N(2)	93.44(9)
O(2)-Ni(1)-N(2)	90.69(9)	O(3)$^{\#1}$-Ni(1)-N(2)	88.97(8)
O(4)$^{\#2}$-Ni(1)-N(2)	90.55(9)	O(1)-Ni(1)-N(1B)	89.7(6)
O(2)-Ni(1)-N(1B)	90.8(4)	O(3)$^{\#1}$-Ni(1)-N(1B)	88.0(6)
O(4)$^{\#2}$-Ni(1)-N(1B)	87.8(4)	N(2)-Ni(1)-N(1B)	176.3(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y-1/2,-z+1/2 #2 x+1/2,-y+1/2,z+1/2

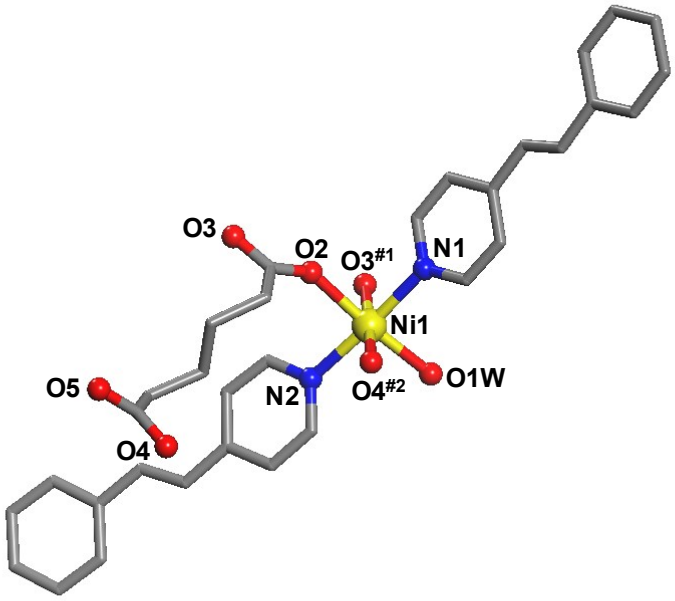

Fig. S1 An asymmetric unit of **1**. Symmetry operations: #1, -x+1/2, y+1/2, -z+1/2; #2, -x+1, -y+1, -z+1.

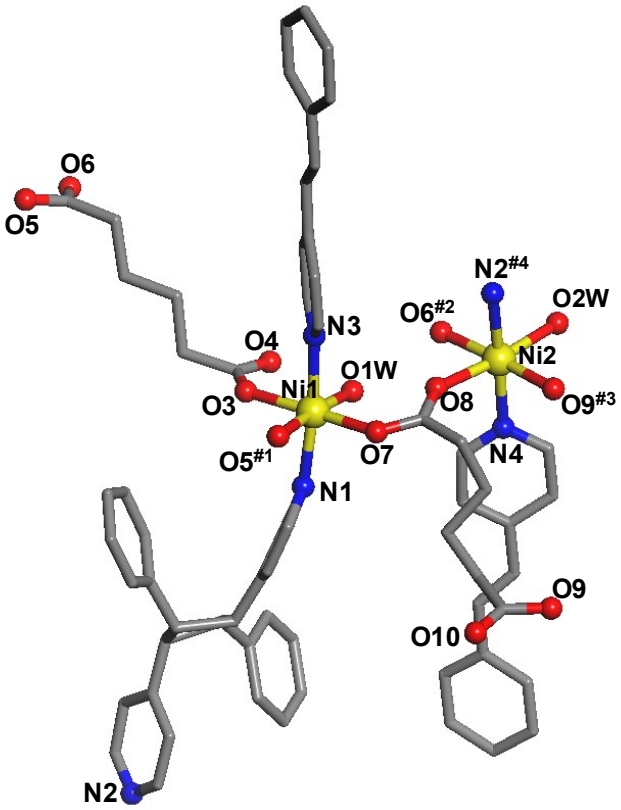

Fig. S2 An asymmetric unit of **2**. Disordered parts are omitted for clarity. Symmetry operations: #1, -x+1, -y+2, -z+2; #2, -x+1, -y+1, -z+2; #3, -x, -y+1, -z+2; #4, x, -y+3/2, z+1/2.

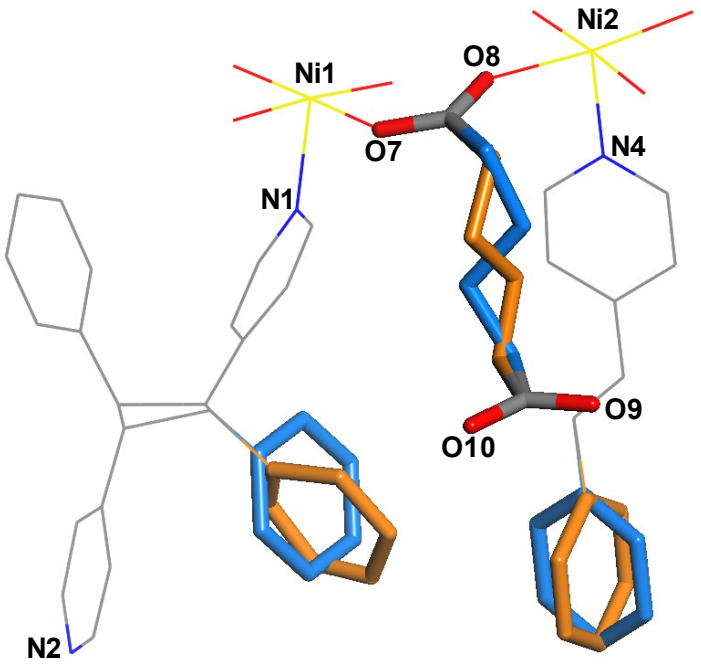

Fig. S3 Disorders observed in **2**: one adipate, a phenyl ring of a spy ligand, and a phenyl ring of *rctt*-ppcb.

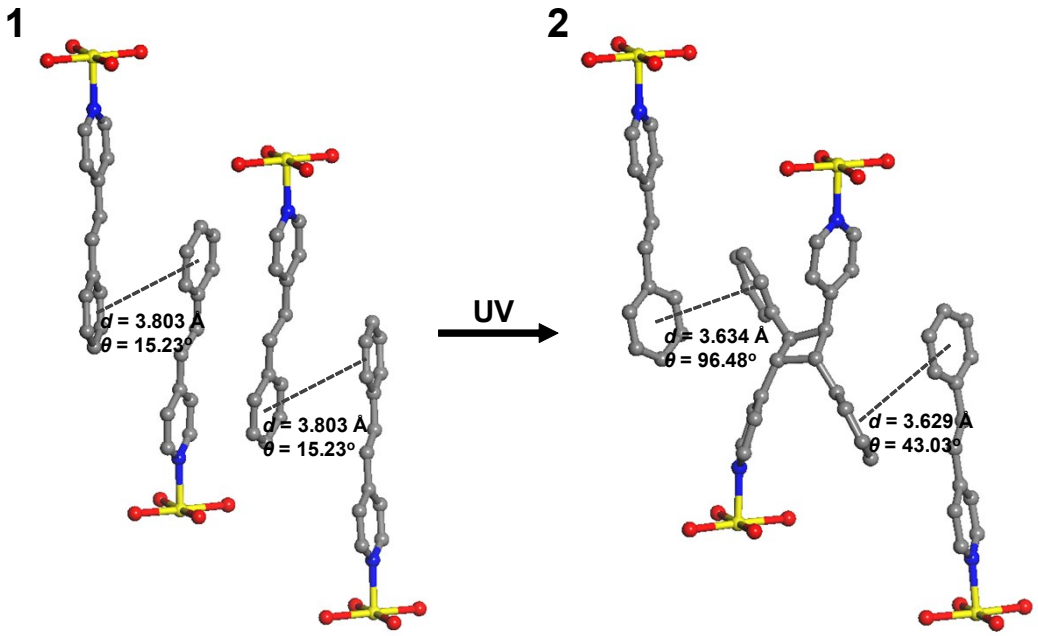

Fig. S4 The geometrical change of π-π interactions with the phenyl rings, from the offset face-to-face interaction in **1** to the edge-to-face interaction in **2**.

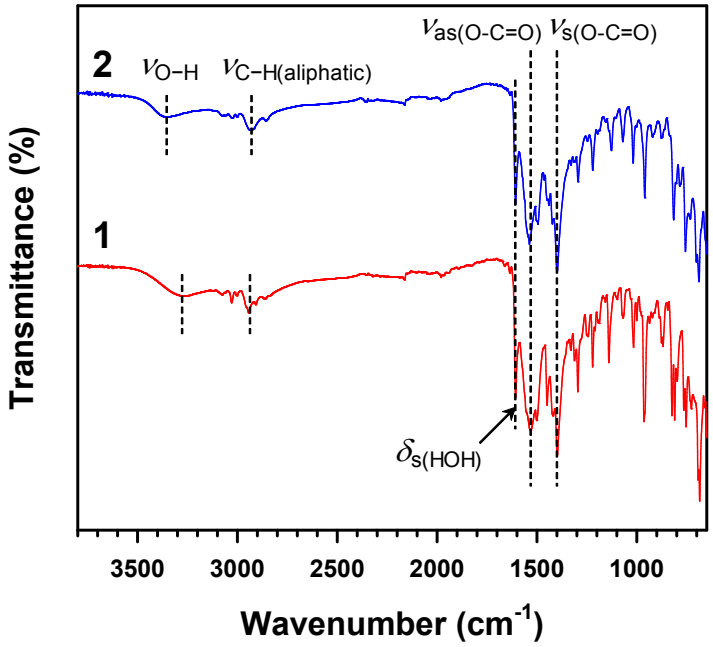

Fig. S5 FT-IR spectra of **1** and **2**. FT-IR for **1** (ATR): ν_{O-H}, 3272; $\nu_{C-H(aliphatic)}$, 2944; $\delta_{s(HOH)}$, 1607; $\nu_{as(O-C=O)}$, 1532; $\nu_{s(O-C=O)}$, 1398 cm^{-1}. FT-IR for **2** (ATR): ν_{O-H}, 3354; $\nu_{C-H(aliphatic)}$, 2930; $\delta_{s(HOH)}$, 1607; $\nu_{as(O-C=O)}$, 1538; $\nu_{s(O-C=O)}$, 1399 cm^{-1}.

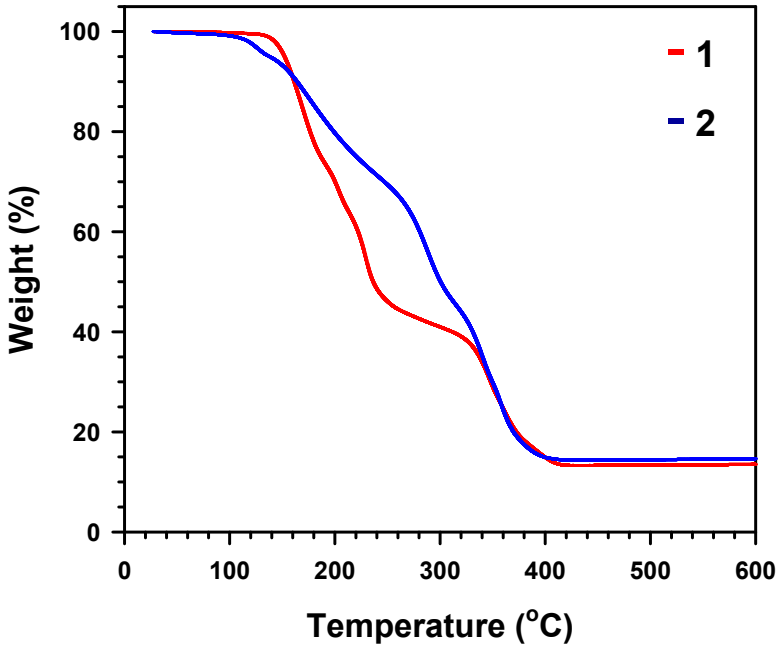

Fig. S6 TGA traces of **1** and **2**.