

Electronic Supplementary Information

Reversible dielectric switching behaviour of a 1D coordination polymer induced by photo and thermal irradiation

Jia-Yun Sima,^{ab} Hong-Xi Li,^{*a} David J. Young,^c Pierre Braunstein,^d and Jian-Ping Lang^{*ab}

^aCollege of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, Jiangsu, People's Republic of China.

^bState Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

^cCollege of Engineering, Information Technology and Environment, Charles Darwin University, Northern Territory 0909, Australia

^dInstitut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 rue Blaise Pascal - CS 90032, 67081 Strasbourg, France

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Experimental section

General procedures. All chemicals and reagents were obtained from commercial sources and used as received. Infrared spectra were recorded on a Varian Scamiter-1000 spectrometer (4000–400 cm^{-1}). Elemental analyses for C, H, and N were performed on a Carlo-Erba CHNO-S microanalyzer. The powder X-ray diffraction (PXRD) measurements were carried out on a PANalytical X'Pert PRO MPD system (PW3040/60). ^1H NMR spectra were recorded at ambient temperature on Varian UNITY plus-400 (400 MHz) spectrometer. ^1H NMR chemical shifts were referenced to the solvent signal in $\text{DMSO-}d_6$. Cross-polarization magic angle spinning (CP MAS) ^{13}C NMR spectra were recorded at a resonance frequency of 101.6 MHz on a BRUKER ADVANCE DSX 400 MHz spectrometer at ambient temperature. UV–vis absorption spectra were obtained with a Shimadzu UV-2600 spectrophotometer. Thermal analyses were performed with a PerkinElmer TGA-7 thermogravimetric analyzer at a heating rate of 10 $^\circ\text{C}/\text{min}$ and a flow rate of 100 cm^3/min (N_2).

Synthesis of 2,9-bis-(2-pyridin-3-yl-vinyl)-[1,10]phenanthroline (3-bpep). A mixture of 2,9-dimethyl-1,10-phenanthroline (2.08 g, 0.01 mol) and 3-pyridinecarboxaldehyde (25 ml) was added into a 100 ml round-bottomed flask. The round-bottom flask was evacuated and flushed with nitrogen three times. Deoxygenated acetic anhydride (20 ml) was added to the reactor. The reaction mixture was heated at 140 $^\circ\text{C}$ for 24 hours. After cooling to ambient temperature, water (50 mL) and CH_2Cl_2 (50 mL) was added into the mixture. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to give 3-bpep. Yield: 3.09 g (80% based on 2,9-dimethyl-1,10-phenanthroline). ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.99 (m, 2H), 8.57 (d, 2H), 8.51 (d, 2H), 8.29 (d, 2H), 8.08 (dd, 4H), 7.96 (s, 2H), 7.81 (d, 2H), 7.51 (dd, 2H). Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{N}_4$: C, 80.81; H 4.69; N 14.50%; found: C, 80.80; H 4.73; N 14.47%. IR (KBr disc): 3035(w), 1577(s), 1495(s), 1416(m), 1368(m), 1145(w), 1026(w), 967(s), 848(s), 811(w), 701(m), 636(w) cm^{-1} .

Synthesis of $\{[\text{Zn}_2(\text{3-bpep})_2(\text{2,5-FDC})_2] \cdot 1.5\text{H}_2\text{O}\}_n$ (1). To a Pyrex glass tube (15cm in length, 7 mm in inner diameter) was loaded $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (30 mg, 0.1 mmol), 2,5- H_2BDC (16 mg, 0.1 mmol), 3-bpep (19 mg, 0.05 mmol), 2 mL of H_2O and 1 mL of MeCN. The tube was sealed and

heated in an oven to 150 °C for 1 day and cooled to ambient temperature at a rate of 5 °C per 60 min. Light yellow crystals were formed, which were collected by filtration, washed with MeCN and Et₂O, and dried in vacuo. Yield: 26 mg (40% based on Zn). Anal. Calcd for C₁₂₈H₈₀N₁₆O₂₀Zn₄: C 63.43; H 3.33; N 9.25%; found: C 63.39; H 3.41; N 9.18%. IR (KBr disc): 3432(m), 3061(w), 1636(s), 1581(s), 1502(s), 1412(m), 1334(s), 1219(m), 1156(m), 1103(w), 1023(m), 964(m), 873(m), 806(m), 590(w) cm⁻¹.

Synthesis of {[Zn₂(3-bpep)(*trans,rctt*-3-bppbpycb)_{0.5}(2,5-FDC)₂]·H₂O}_n (2). Light yellow crystals of **1** (0.2 g) were irradiated with a high-pressure mercury lamp (365 nm) for 6 h to get brown crystals of **2**. Anal. Calcd for C₆₄H₄₀N₈O₁₀Zn₂: C 63.43; H 3.33; N 9.25%; found: C 63.46; H 3.34; N 9.28%. IR (KBr disc): 3035(w), 1613(w), 1577(s), 1497(s), 1415(m), 1365(w), 1219(m), 1145(m), 1101(w), 1025(m), 967(m), 877(m), 807(m), 588(w) cm⁻¹.

Single crystal X-ray crystallography. Crystals of **1** and **2** suitable for X-ray diffraction were mounted with Fomblin in a cryoloop. The collection of crystal data of **1** was performed on a Rigaku Saturn 724 + CCD X-ray diffractometer using graphite monochromated Mo K α (λ = 0.71073 Å) radiation at 153 K. The collection of crystal data of **2** was carried out on a Bruker APEX-II CCD X-ray diffractometer using graphite monochromated Mo K α (λ = 0.71073 Å) radiation at 223 K. The crystal structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with the *SHELXTL-2018* program.^{S1} In **1** and **2**, free solvent water molecules are disordered, and attempts to locate and refine all the solvent molecule peaks were unsuccessful. Diffused electron densities resulting from these solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.^{S2,S3} In **1**, a total of 36 electrons were found in a unit cell, corresponding to approximately one H₂O molecule per chemical formula. In **2**, a total of 41 electrons were found in a unit cell, corresponding to approximately two H₂O molecules per chemical formula. In **1**, the H₂O molecule was refined to one-half occupancy to give an acceptable thermal parameter. Except for the O atom of H₂O molecule in **1**, all non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. Selected bond lengths and angles of **1** and **2** are listed in Table S2 and Table S3. Crystallographic data have been deposited in Cambridge Crystallographic Data Center (CCDC) with the numbers of 1891747 and 1891748 for **1** and **2**.

Dielectric measurement. We examined the dielectric characteristics of **1** and **2** in powder discs using a Novocontrol Concept 80 instrument. Each pellet sample (*ca.* 1 g powder of dehydrated **1**, **2** and regenerated **1**) was prepared as a disc by a mini-type compressor. The disc size was approximately 0.5 cm in thickness and 2 cm in diameter. Temperature-invariable experiments at 298.3K and temperature-variable experiments in the range of 303.34-383.40 K were conducted with a coded heater employing an Agilent E4991A instrument. Two copper electrodes (0.25 cm thick, 1 cm in diameter) were used to sandwich the sample disc for the dielectric measurement.

References

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- S2 A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.
- S3 L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3.

Table S1 Crystal data and structure refinement parameters for **1** and **2**.

	1	2
empirical formula	C ₁₂₈ H ₈₀ N ₁₆ O ₂₁ Zn ₄	C ₆₄ H ₄₀ N ₈ O ₁₀ Zn ₂
formula weight	2439.65	1211.82
crystal system	Triclinic	Triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.303(2)	12.160(19)
<i>b</i> (Å)	16.818(3)	16.108(3)
<i>c</i> (Å)	17.303 (4)	16.784(3)
α (deg)	114.03(3)	63.358(5)
β (deg)	91.59(3)	71.354(5)
γ (deg)	103.58(3)	79.299(5)
<i>V</i> (Å ³)	2891.8(13)	2780.5(8)
ρ_{calc} (g cm ⁻³)	1.401	1.447
<i>Z</i>	1	2
μ (mm ⁻¹)	0.898	0.932
<i>F</i> (000)	1248	1240
<i>R</i> ₁ ^a	0.0730	0.0807
<i>wR</i> ₂ ^b	0.1963	0.2235
<i>GOF</i> ^c	1.100	1.056

^a $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^b $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2\}^{1/2}$. ^c $GOF = \{\Sigma w((F_o^2 - F_c^2)^2) / (n-p)\}^{1/2}$, where *n* = number of reflections and *p* = total number of parameters refined.

Table S2 Selected bond lengths (Å) and angles (°) for **1**.

Zn(1)-O(1)	1.923(3)	O(10)#1-Zn(1)-N(3)	98.10(13)
Zn(1)-O(10)#1	1.988(3)	N(2)-Zn(1)-N(3)	82.57(13)
Zn(1)-N(2)	2.054(3)	O(1)-Zn(1)-C(64)#1	101.36(12)
Zn(1)-N(3)	2.067(3)	O(10)#1-Zn(1)-C(64)#1	28.28(14)
Zn(1)-C(64)#1	2.593(4)	N(2)-Zn(1)-C(64)#1	104.87(13)
Zn(2)-O(6)	1.947(3)	N(3)-Zn(1)-C(64)#1	125.29(14)
Zn(2)-O(5)	1.974(3)	O(6)-Zn(2)-O(5)	109.46(11)
Zn(2)-N(6)	2.066(3)	O(6)-Zn(2)-N(6)	117.42(12)
Zn(2)-N(7)	2.082(3)	O(5)-Zn(2)-N(6)	118.47(12)
O(1)-Zn(1)-O(10)#1	111.60(13)	O(6)-Zn(2)-N(7)	129.65(13)
O(1)-Zn(1)-N(2)	129.01(13)	O(5)-Zn(2)-N(7)	96.97(11)
O(10)#1-Zn(1)-N(2)	112.20(14)	N(6)-Zn(2)-N(7)	82.46(12)
O(1)-Zn(1)-N(3)	115.44(12)		

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

Table S3 Selected bond lengths (Å) and angles (°) for **2**.

Zn(1)-O(5)	1.910(4)	O(6)-Zn(1)-N(6)	100.78(18)
Zn(1)-O(6)	1.924(4)	O(5)-Zn(1)-N(7)	111.93(17)
Zn(1)-N(6)	2.044(5)	O(6)-Zn(1)-N(7)	119.68(19)
Zn(1)-N(7)	2.048(5)	N(6)-Zn(1)-N(7)	82.74(19)
Zn(2)-O(10)#1	1.921(4)	O(10)#1-Zn(2)-O(1)	116.94(19)
Zn(2)-N(2)	2.048(5)	O(10)#1-Zn(2)-N(2)	118.85(19)
Zn(2)-N(3)	2.044(5)	O(1)-Zn(2)-N(2)	114.6(2)
O(1)-Zn(2)	1.926(4)	O(10)#1-Zn(2)-N(3)	116.43(17)
O(5)-Zn(1)-O(6)	112.34(19)	O(1)-Zn(2)-N(3)	100.87(18)
O(5)-Zn(1)-N(6)	127.13(19)	N(2)-Zn(2)-N(3)	82.72(18)

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

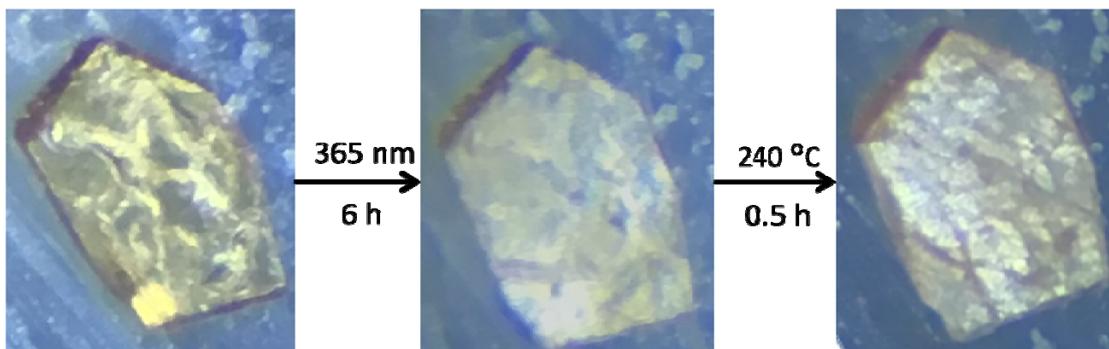


Fig. S1 Pictures of crystals of **1** (left), **2** (middle) and regenerated **1** (right).

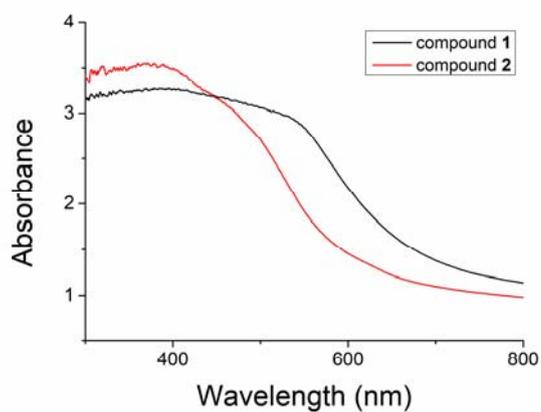


Fig. S2 Solid state UV-vis adsorption spectra of **1** and **2**.

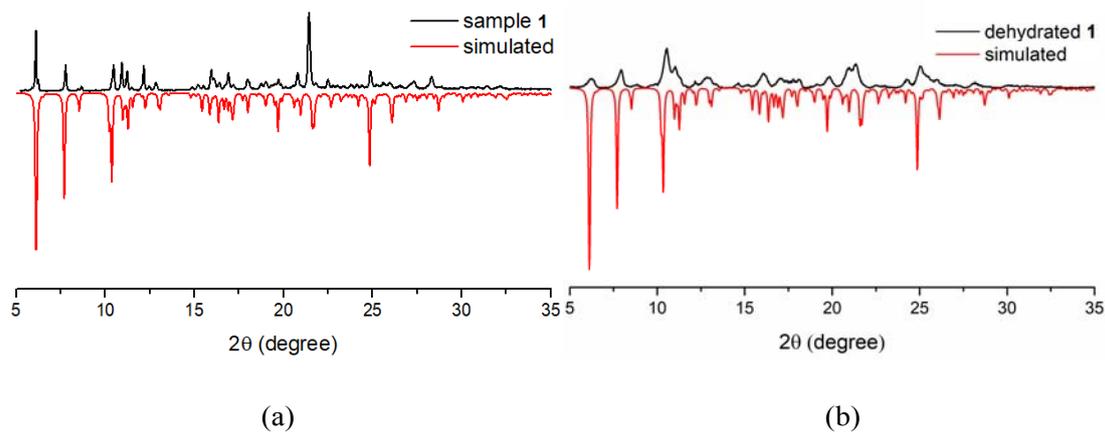


Fig. S3 (a) The observed PXRD patterns (black) and those (red) simulated from the single crystal data of **1**. (b) The observed PXRD patterns (black) of dehydrated **1** and those (red) simulated from the single crystal data of **1**.

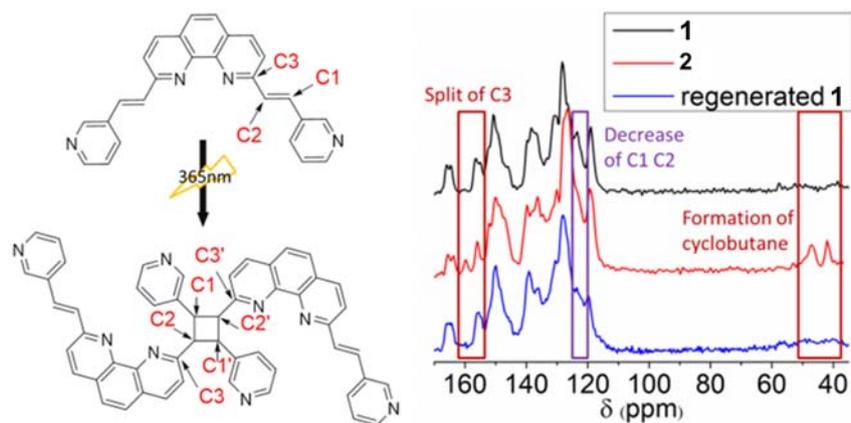


Fig. S4 (a) Carbon environments in 3-bpep and 3-bpbpycb. (b) ¹³C CP/MAS NMR spectra of **1**, **2** and **1** regenerated from **2**. Distinguishable sections are marked by dark red (main) and purple (minor) rectangles.

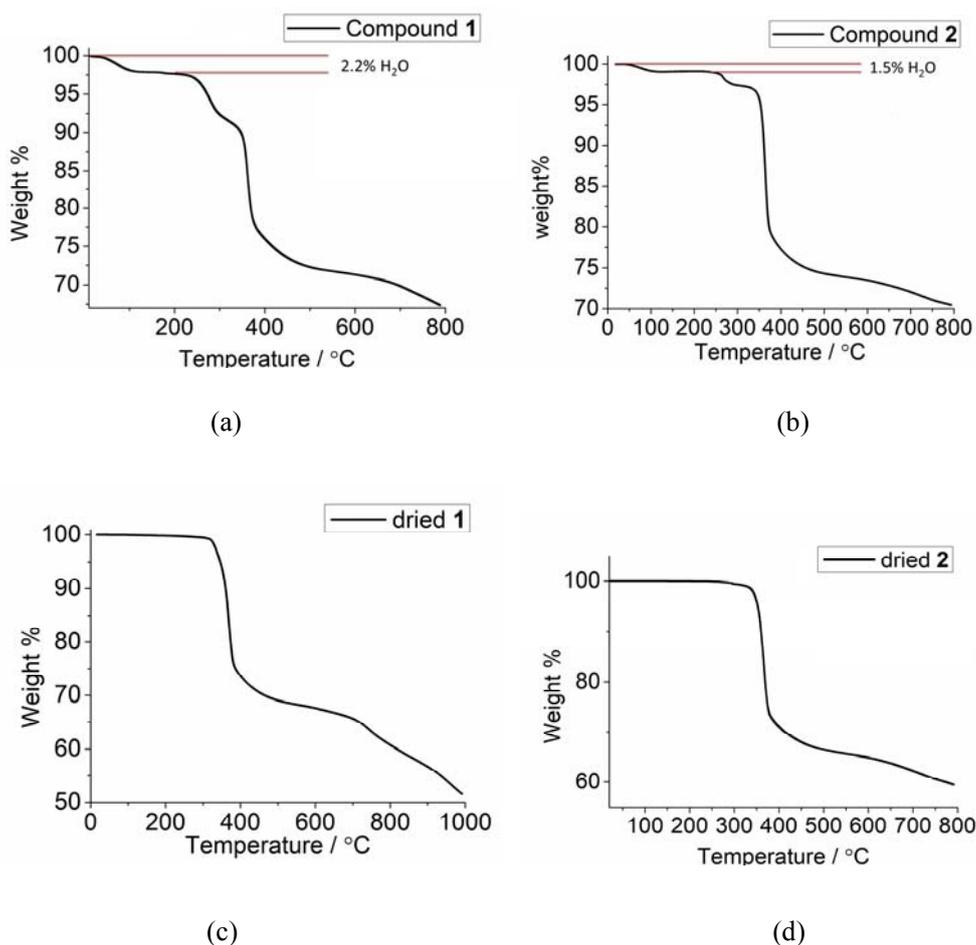
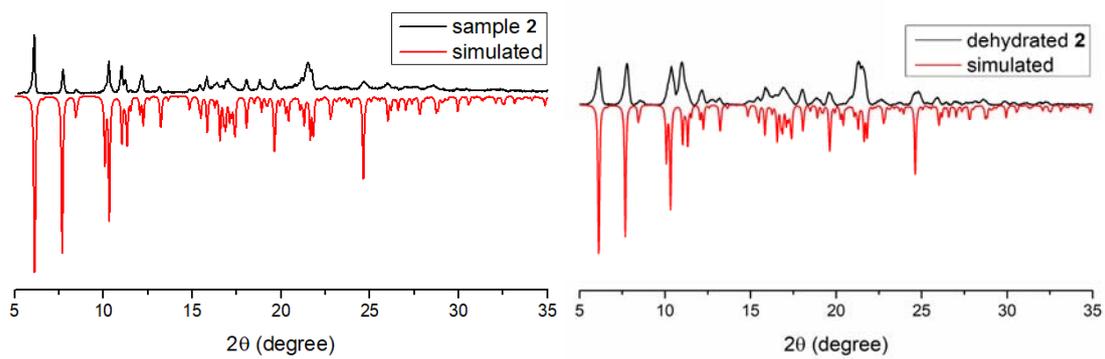


Fig. S5 TGA curves of hydrated **1** (a), hydrated **2** (b), dehydrated **1** (c) and dehydrated **2** (d).



(a)

(b)

Fig. S6 (a) The observed PXRD patterns (black) and those (red) simulated from the single crystal data of **2**. (b) The observed PXRD patterns (black) of dehydrated **2** and those (red) simulated from the single crystal data of **2**.

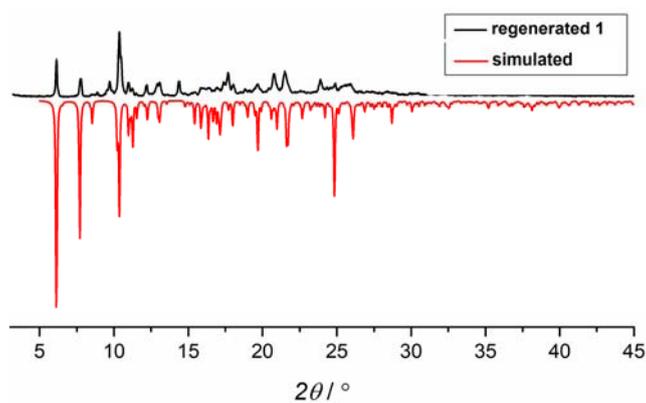


Fig. S7 The observed PXRD patterns of the regenerated sample **1** (black) and those simulated from the single crystal data of **1** (red).

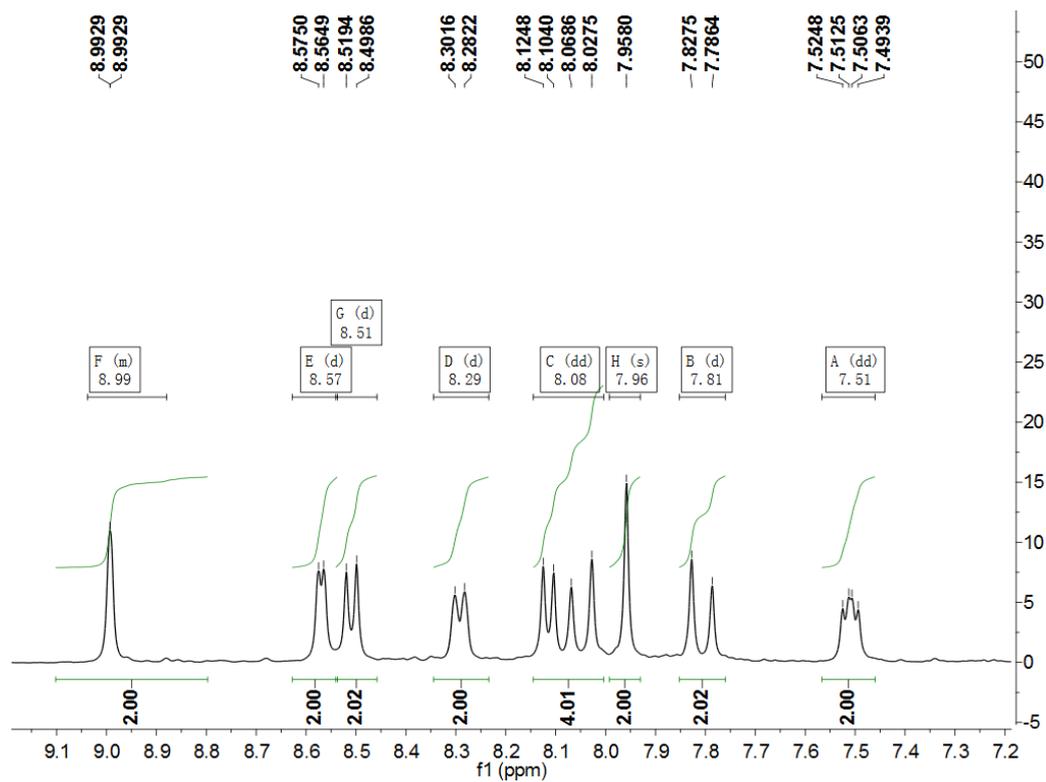


Fig. S8 The ^1H NMR spectrum of the 3-bpep ligand in $\text{DMSO-}d_6$.

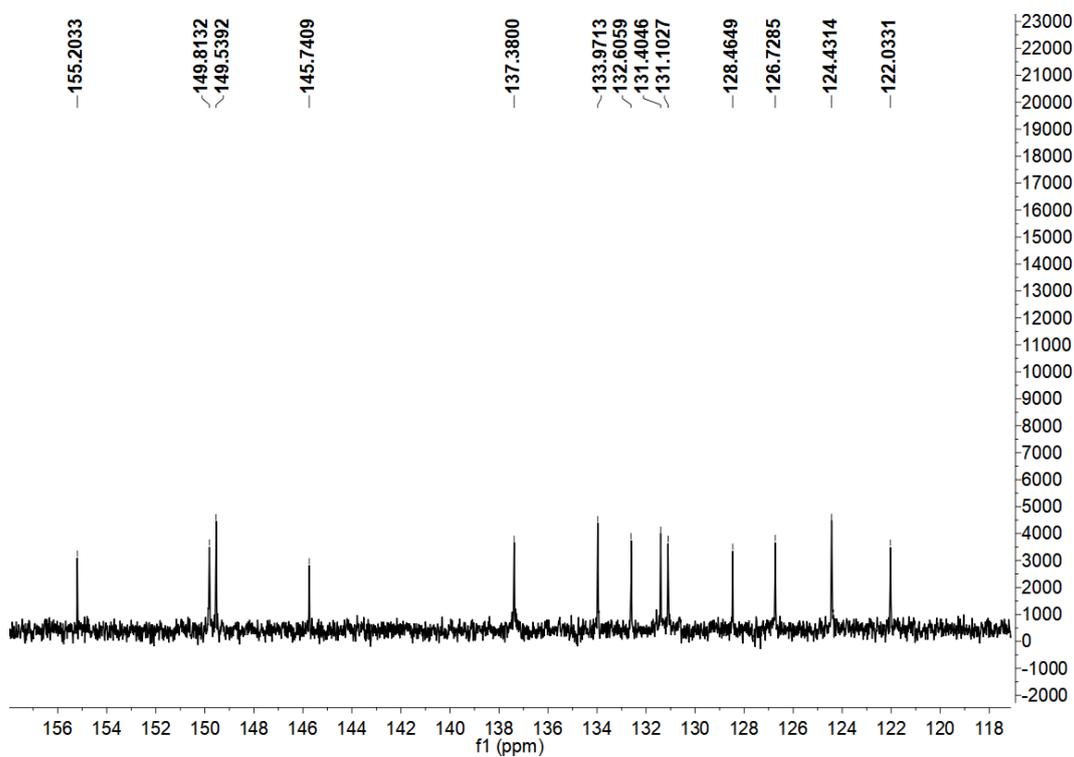


Fig. S9 The ^{13}C NMR spectrum of the 3-bpep ligand in $\text{DMSO-}d_6$.