Electronic Supplementary Information (ESI†)

UV-induced single-crystal-to-single-crystal conversion from a coordination ladder to a two-dimensional network through intermolecular carbon-carbon coupling reaction

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Table of Contents

Experimental Section

General procedure. The ligand 1-(2-pyridyl)-2-(3-pyridyl)-ethylene (2,3'-bpe) was prepared as reported previously.[1] Other reagents were purchased from TCI Co., Ltd., and Sigma-Aldrich Co. All the chemicals were used without any further purification. Infrared (IR) samples were prepared as KBr pellets, and spectrum was obtained in the 4000–400 cm^{-1} range using a Nicolet Avatar 360 FT-IR spectrophotometer. The elemental analyses for C, H and N were performed on an EA1110 CHNS elemental analyzer. PXRD patterns were obtained using a PANalytical X'Pert PRO MPD system (PW3040/60). Thermal analysis were performed with a Perkin_Elmer TGA-7 thermogravimetric analyser at a heating rate of 10 °C/min and a flow rate of 100 cm^3/min (N_2). ^1H NMR spectra were recorded at ambient temperature on a Bruker ADVANCE III (400MHz) spectrometer. UV-vis absorption spectra were obtained with a Shimadzu UV-3600 spectrophotometer. The fluorescence spectra were obtained on a JASCO FP-8600 spectrofluorometer.

Preparation of $[Cd_2(\mu\text{-}OH_2)_2(2,5\text{-}fdc)_2(2,3'\text{-}bpe)_2]_n$ (1). To a 50 mL Teflon-lined autoclave was loaded $Cd(NO_3)_2{\cdot}4H_2O$ (0.308 g, 1 mmol), 2,5-H_2fdc (0.156 g, 1 mmol), 2,3'-bpe (0.182 g, 1 mmol), NaOH solution (2 mL, 1 $mol{\cdot}L^{-1}$) and H_2O (25 mL). The Teflon-lined autoclave was sealed and heated in an oven to 150°C for two days, and then cooled to ambient temperature at a rate of 5°C h^{-1} to form colorless block crystals of **1**. Yield: 0.383 g (82% yield based on Cd). Anal. calcd. for $C_{36}H_{28}Cd_2N_4O_{12}$: C, 46.32; H, 3.02; N, 6.00. Found: C, 46.04; H, 2.87; N, 5.91. IR (KBr, cm^{-1}): 3431m, 1602s, 1558s, 1509w, 1411s, 1328s, 1294m, 1261m, 1220m, 1124w, 1025m, 964s, 870m, 820s, 696s, 545s, 458m. ^1H NMR (400 MHz, DMSO-d_6) δ 8.85 (s, 2H), 8.61 (d, J = 4.0 Hz, 2H), 8.51 (d, J = 4.4 Hz, 2H), 8.13 (d, J = 8.0 Hz, 2H), 7.83 (t, 2H), 7.71 (d, J = 16.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.45 (t, 4H), 7.30 (s, 6H).

Preparation of $[Cd_2(\mu\text{-}OH_2)_2(2,5\text{-}fdc)_2(bpbpcb)]_n$ (2): Single crystals of **1** (0.187 g) were irradiated by a 20W LED lamp (λ_{em} = 365 nm) for approximately 4 h to form crystals of **2** in quantitative yield (based on **1**). Anal. calcd. for $C_{36}H_{28}Cd_2N_4O_{12}$: C, 46.32; H, 3.02; N, 6.00. Found: C, 46.58; H, 3.11; N, 6.22. IR (KBr, cm^{-1}): 3430m, 1599s, 1559s, 1507w, 1410s, 1325s, 1296m, 1262m, 1221m, 1126w, 1026m, 966s, 868m, 818s, 695s, 547s, 455m. ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.42 (t, 4H), 8.21 (d, J = 4.4 Hz, 2H), 7.55 (m, 4H), 7.14 (m, 4H), 7.05 (t, 2H), 4.91 (t, 2H), 4,75 (t, 2H).

Isolation of 1,3-bis(2-pyridyl)-2,4-bis(3-pyridyl)cyclobutane (bpbpcb): A mixture of disodium ethylenediaminetetraacetate dihydrate ($Na_2H_2edta·2H_2O$, 0.186 g, 0.5 mmol), NaOH (0.040 g, 1 mmol), H_2O (15 mL), CH_2Cl_2 (15 mL) and **2** (0.141 g, 0.15 mmol) were placed in a 100 mL flask and stirred for 2 h. The organic phase was separated from the reaction mixture and the aqueous layers were extracted with CH_2Cl_2 (3 x 15 mL). The combined organic phase was washed with NaOH solution and H_2O, and dried with anhydrous Na_2SO_4. Finally, the organic phase was concentrated to dryness in vacuo to give bpbpcb as colorless powder. Yield: 0.049 g (90% yield based on **2**). IR (KBr, cm^{-1}): 3179m, 1586s, 1569s, 1472s, 1424s, 1293m, 1212m, 1023m, 992m, 961m, 818m, 753s, 532m. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.42 (t, 4H), 8.21 (d, J = 3.6 Hz, 2H), 7.55 (m, 4H), 7.14 (m, 4H), 7.05 (t, 2H), 4.91 (t, 2H), 4,76 (t, 2H).

X-ray diffraction crystallography: All measurements were collected on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo-Kα (λ = 0.71073 Å) by using the Φ/ω scan technique. Absorption correction was based on symmetry equivalent reflections using the SADABS program. Single crystals of **1** and **2** suitable for X-ray analysis were obtained directly from the above preparations. The crystal structures of **1** and **2** were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the *SHELXL-2014* program.[2] All non-hydrogen atoms refined anisotropically. The H atoms of the water molecules in **1** and **2** were located from the Fourier map and included in the final refinement by use of geometrical restraints with the O–H distances being fixed at 0.85 Å and U_{iso}(H) equivalent to 1.5 times of U_{eq}(O). All other H atoms were introduced at the calculated positions and included in the structure-factor calculations.

Table S1 Summary of Crystallographic Data for **1** and **2**.

Compound	**1**	**2**
chemical formula	$C_{36}H_{28}Cd_2N_4O_{12}$	$C_{36}H_{28}Cd_2N_4O_{12}$
formula weight	933.44	933.44
crystal system	triclinic	triclinic
space group	*P***Error!**	*P***Error!**
a (Å)	9.1726(18)	8.8826(18)
b (Å)	13.801(3)	14.431(3)
c (Å)	14.975(3)	14.620(3)
α (°)	96.69(3)	96.59(3)
β (°)	92.67(3)	93.46(3)
γ (°)	98.02(3)	99.33(3)
V (Å^3)	1860.6(7)	1831.1(7)
Z	2	2
D_c (g/cm^3)	1.666	1.693
F(000)	928	928
μ (MoKα,cm^{-1})	1.210	1.230
total no. of reflns	29965	30316
no. of unique reflns	8450	8340
no. of obsd. reflns	487	487
R_{int}	0.0374	0.0269
$R_1{}^a$	0.0543	0.0464
$wR_2{}^b$	0.1403	0.1160
GOF^c	1.079	1.131

^{a} $R = \sum||F_o|-|F_c||/\sum|F_o|$. ^{b} $wR = \{\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. ^{c} $GOF = \{\sum w[(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is total number of parameters refined.

Table S2 Selected Bond Lengths (Å) and Angles (º) for **1** and **2**.

1

Cd(1)-O(8A)	2.219(4)	Cd(1)-O(11)	2.273(4)
Cd(1)-O(1)	2.326(4)	Cd(1)-N(1)	2.379(5)
Cd(1)-N(2B)	2.389(4)	Cd(1)-O(2)	2.570(4)
Cd(2)-O(3)	2.242(4)	Cd(2)-O(12)	2.262(4)
Cd(2)-O(7)	2.287(4)	Cd(2)-N(3)	2.367(5)
Cd(2)-N(4C)	2.382(5)		
O(8A)-Cd(1)-O(11)	126.07(15)	O(8A)-Cd(1)-O(1)	96.33(14)
O(11)-Cd(1)-O(1)	137.55(15)	O(8A)-Cd(1)-N(1)	93.04(17)
O(11)-Cd(1)-N(1)	94.96(18)	O(1)-Cd(1)-N(1)	83.52(17)
O(8A)-Cd(1)-N(2B)	86.82(16)	O(11)-Cd(1)-N(2B)	89.93(17)
O(1)-Cd(1)-N(2B)	90.56(17)	N(1)-Cd(1)-N(2B)	174.02(18)
O(8A)-Cd(1)-O(2)	146.38(14)	O(11)-Cd(1)-O(2)	84.76(14)
O(1)-Cd(1)-O(2)	53.73(13)	N(1)-Cd(1)-O(2)	97.58(15)
N(2B)-Cd(1)-O(2)	79.42(15)	O(3)-Cd(2)-O(12)	124.39(15)
O(3)-Cd(2)-O(7)	97.83(15)	O(12)-Cd(2)-O(7)	137.62(16)
O(3)-Cd(2)-N(3)	94.46(17)	O(12)-Cd(2)-N(3)	93.40(18)
O(7)-Cd(2)-N(3)	85.99(16)	O(3)-Cd(2)-N(4C)	85.77(17)
O(12)-Cd(2)-N(4C)	90.87(18)	O(7)-Cd(2)-N(4C)	88.69(17)
N(3)-Cd(2)-N(4C)	174.66(17)		

2

Cd(1)-O(6)	2.241(3)	Cd(1)-O(11)	2.251(4)

Cd(1)-O(2)	2.304(4)	Cd(1)-N(1)	2.376(4)
Cd(1)-N(2A)	2.381(4)	Cd(1)-O(1)	2.597(4)
Cd(2)-O(4B)	2.262(4)	Cd(2)-O(12)	2.264(4)
Cd(2)-N(3)	2.367(4)	Cd(2)-O(8)	2.381(4)
Cd(2)-N(4C)	2.386(4)	Cd(2)-O(9)	2.493(4)
O(6)-Cd(1)-O(11)	120.07(15)	O(6)-Cd(1)-O(2)	98.26(13)
O(11)-Cd(1)-O(2)	141.51(14)	O(6)-Cd(1)-N(1)	95.51(14)
O(11)-Cd(1)-N(1)	89.28(16)	O(2)-Cd(1)-N(1)	90.44(14)
O(6)-Cd(1)-N(2A)	84.42(14)	O(11)-Cd(1)-N(2A)	93.69(16)
O(2)-Cd(1)-N(2A)	86.23(14)	N(1)-Cd(1)-N(2A)	176.61(14)
O(6)-Cd(1)-O(1)	145.64(13)	O(11)-Cd(1)-O(1)	89.19(13)
O(2)-Cd(1)-O(1)	53.49(12)	N(1)-Cd(1)-O(1)	102.97(13)
N(2A)-Cd(1)-O(1)	75.47(13)	O(4B)-Cd(2)-O(12)	124.39(14)
O(4B)-Cd(2)-N(3)	92.92(15)	O(12)-Cd(2)-N(3)	98.75(15)
O(4B)-Cd(2)-O(8)	93.11(13)	O(12)-Cd(2)-O(8)	142.37(13)
N(3)-Cd(2)-O(8)	80.54(14)	O(4B)-Cd(2)-N(4C)	86.49(14)
O(12)-Cd(2)-N(4C)	86.66(15)	N(3)-Cd(2)-N(4C)	173.77(15)
O(8)-Cd(2)-N(4C)	93.29(15)	(4B)-Cd(2)-O(9)	145.49(13)
O(12)-Cd(2)-O(9)	88.61(13)	N(3)-Cd(2)-O(9)	91.34(14)
O(8)-Cd(2)-O(9)	53.95(12)	N(4C)-Cd(2)-O(9)	85.69(14)

Symmetry codes: (**1**) A: $x + 1, y + 1, z + 1$; B: $- x + 1, - y + 1, - z + 1$; C: $- x, - y, - z$. (**2**) A: $x + 1, y, z$; B: $x + 1, y + 1, z + 1$; C: $x - 1, y, z$.

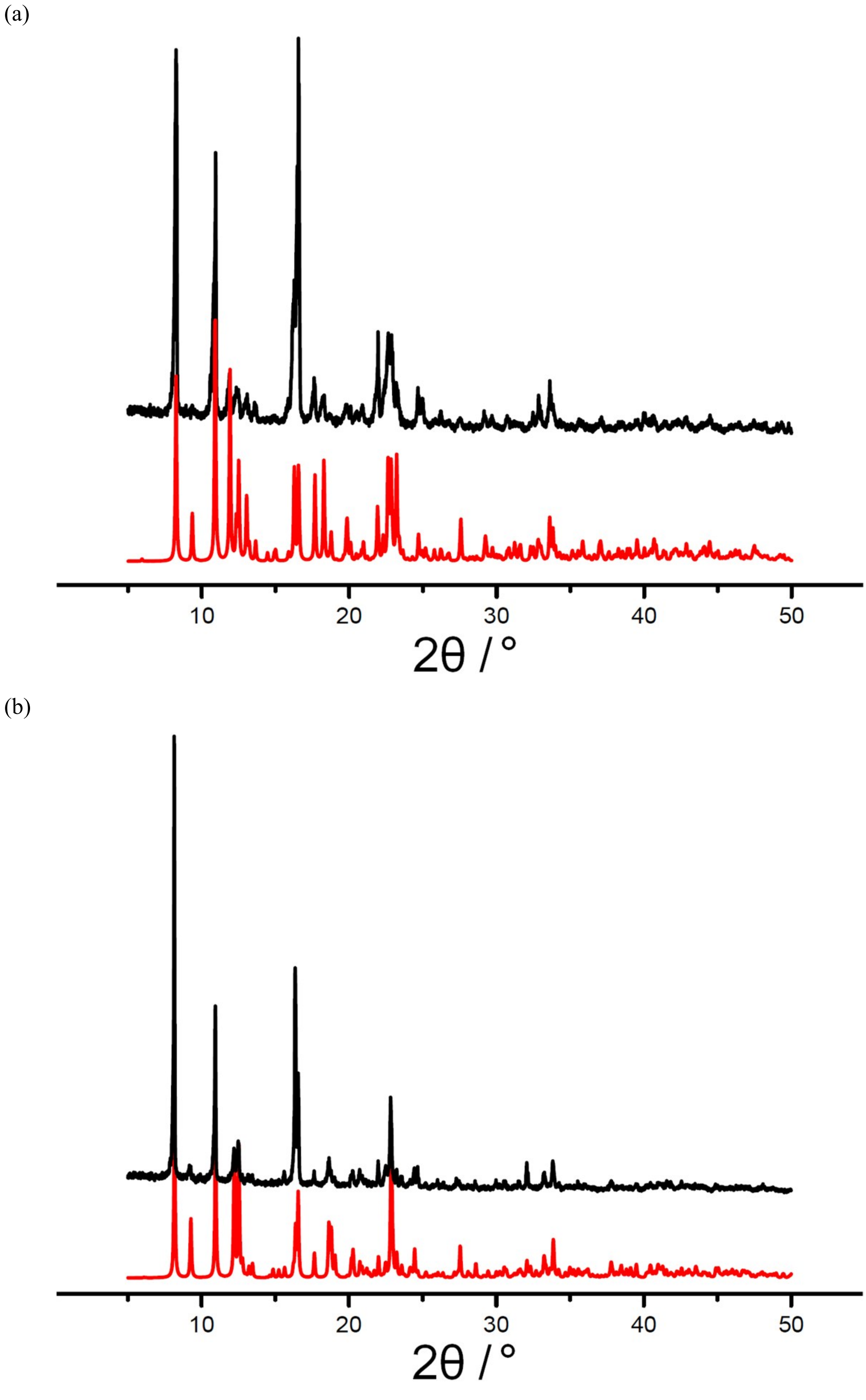

Fig. S1 (a) PXRD pattern of **1** (from single crystal data: red; as-synthesis: black). (b) PXRD pattern of **2** (from single crystal data: red; as-synthesis: black).

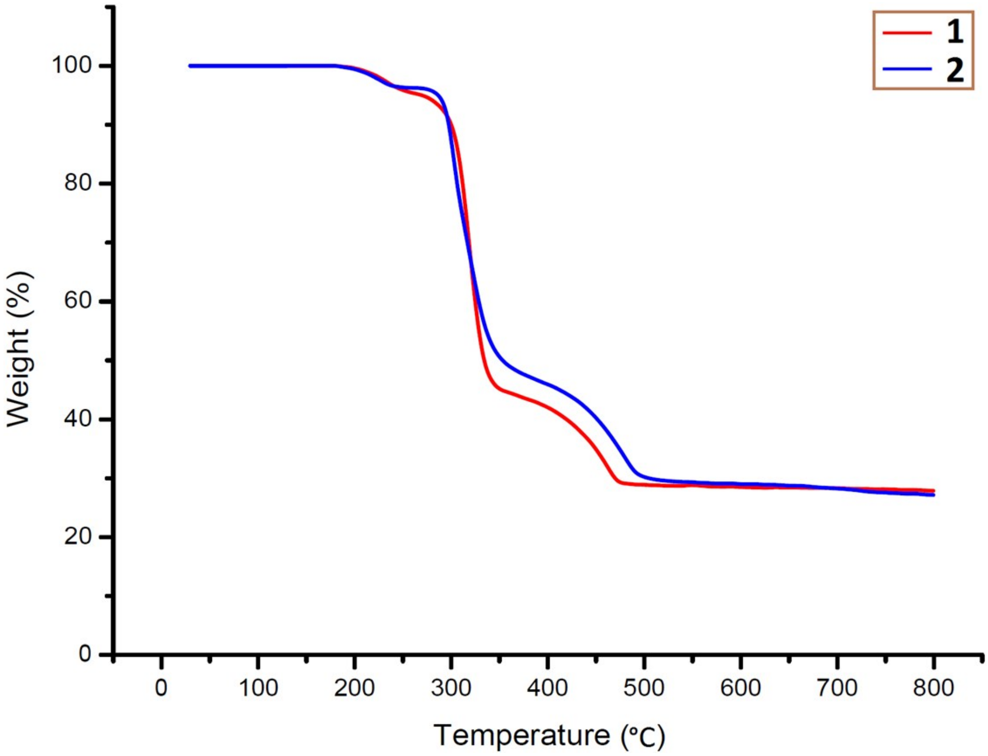

Fig. S2 The TGA curves for **1** and **2**. For **1**, a minor weight loss of two coordinated water molecules per formula unit (obsd, 4.12%; calcd, 3.86%) occurred from 181 to 250 °C. Then the framework gradually collapsed. The remaining weight of the CdO residue is 27.86% (calcd. 27.51%). The TGA curve of **2** displays a first weight loss of 3.68% at 182-248 °C, corresponding to the loss of two coordinated water molecules per formula unit (calcd. 3.86%). Then the framework began to decompose, accompanied by the release of organic ligands. Finally, the remaining weight (obsd, 27.16%) indicated the CdO residue (calcd. 27.51%).

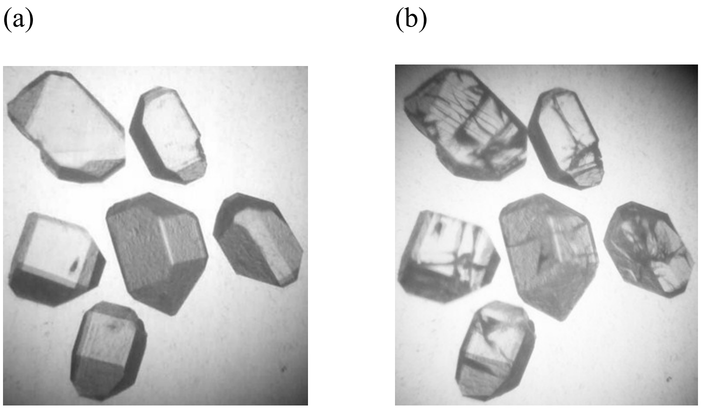

Fig. S3 Optical micrographs of single crystals before (a) and after (b) photoreaction.

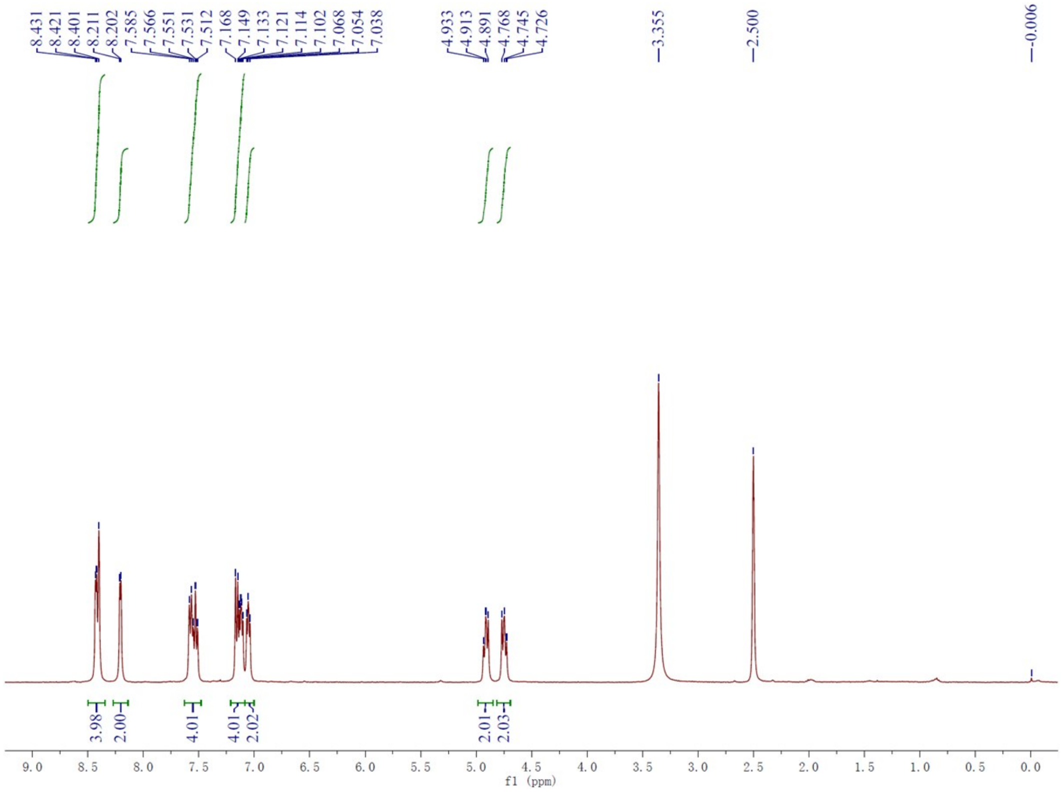

Fig. S4 The ^{1}H NMR spectrum of bpbpcb.

References:

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2 (a) G. M. Sheldrick, *SHELXL-2014*, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 2014; (b) A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr*. 2009, **65**, 148.