Electronic Supplementary Information (ESI†)

Single-Crystal to Single-Crystal Transformation of a Coordination Chain to a Two-Dimensional Coordination Network through a Photocycloaddition Reaction

Fan Yang,[a] Ni Ya Li,*[a,b] Ye Ge,*[a] and Dong Liu*[a,b]

[a] College of Chemistry and Materials Science, Huaibei Normal University, 100 DongShan Road, Huaibei 235000, Anhui, P. R. China
[b] Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials, School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huaian 223300, Jiangsu, P. R. China

Table of Contents

Experimental Section

General procedure. All chemicals and reagents were obtained from commercial sources and used as received. Infrared (IR) sample was prepared as a KBr pellet, and spectrum was obtained in the 4000–400 cm^{-1} range using a Nicolet Avatar 360 FT-IR spectrophotometer. The elemental analysis for C, H and N was performed on an EA1110 CHNS elemental analyzer. Powder XRD patterns were obtained using a PANalytical X'Pert PRO MPD system (PW3040/60). ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded in DMSO-d_6 at room temperature. Cross-polarization magic angle spinning (CPMAS) ^{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. Thermal analysis was performed with a Perkin_Elmer TGA-7 thermogravimetric analyser at a heating rate of 10 °C min^{-1} and a flow rate of 100 cm^{3} min^{-1} (N_2). The fluorescence spectra were obtained on a Perkin-Elmer LS55 spectrofluorometer.

Synthesis of [Cd(μ-OH$_2$)(2,5-fdc)(bpvb)]$_n$ (1): To a 25 mL Teflon-lined autoclave was loaded $Cd(NO_3)_2 \cdot 4H_2O$ (154 mg, 0.5 mmol), bpvb (142 mg, 0.5 mmol), 2,5-H$_2$tdc (86 mg, 0.5 mmol) and H_2O (15 mL). The Teflon-lined autoclave was sealed and heated in an oven to 175 °C for 2 d, and then cooled to ambient temperature at a rate of 5 °C h^{-1} to form light-yellow crystals of **1**. Yield: 236 mg (83% yield based on Cd). Anal. calcd. for $C_{26}H_{20}CdN_2O_6$: C, 54.90; H, 3.54; N, 4.92. Found: C, 55.26; H, 3.37; N, 5.09. IR (KBr disc, *v*, cm^{-1}): 3435 (*m*), 1599 (*s*), 1554 (*s*), 1495 (*s*), 1448 (*m*), 1413 (*s*), 1222 (*m*), 1139 (*m*), 1074(*s*), 971 (*m*), 818 (*s*), 781 (*m*), 699 (*s*), 546 (*m*).

***In-situ* synthesis of [Cd(μ-OH$_2$)(2,5-fdc)(bpbpvpcb)$_{0.5}$]$_n$ (2):** Single crystals of **1** (114 mg) were irradiated with a 20 W UV-LED lamp (λ = 365 nm) for approximately 5 h to form crystals of **2** in quantitative yield (based on **1**). Anal. calcd. for $C_{26}H_{20}CdN_2O_6$: C, 54.90; H, 3.54; N, 4.92. Found: C, 55.19; H, 3.71; N, 4.68. IR (KBr disc, *v*, cm^{-1}): 3437 (*m*), 1601 (*s*), 1555 (*s*), 1502 (*s*), 1440 (*m*), 1418 (*s*), 1223 (*m*), 1140 (*m*), 1071(*s*), 962 (*m*), 809 (*s*), 785 (*m*), 690 (*s*), 544 (*m*).

Isolation of bpbpvpcb: A mixture of $Na_2H_2edta \bullet 2H_2O$ (112 mg, 0.3 mmol), NaOH (24 mg, 0.6 mmol), H_2O (15 mL), CH_2Cl_2 (20 mL) and **2** (114 mg, 0.2 mmol) was 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 × 20 mL). The combined organic phase was washed with NaOH solution and H_2O and dried with anhydrous Na_2SO_4. The organic phase was concentrated to dryness in vacuo to give bpbpvpcb as light-yellow powder. Yield: 47 mg (83% yield based on **2**). ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.75 (d, 2H), 8.49 (d, 2H), 8.45 (dd, 2H), 8.25 (dd, 2H), 8.02 (d, 2H), 7.68 (d, 2H), 7.51 (s, 2H), 7.40 (dd, 2H), 7.31 (m, 4H), 7.18 (m, 8H), 4.69 (s, 4H).

X-ray diffraction crystallography: Single-crystal X-ray diffraction data for **1** and **2** were collected with 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.[1] Single crystals of **1** and **2** suitable for X-ray analysis were obtained directly from the above preparation procedure. And its structure was 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 hydrogen atoms of the water molecules in **1** and **2** were located from the Fourier map and included in the final refinement by the use of geometrical restraints with the O–H distances being fixed at 0.85 Å and U_{iso}(H) equivalent to 1.5 times U_{eq}(O). All other H atoms were introduced at the calculated positions and included in the structure-factor calculations.

References:

1 G. M. Sheldrick, *A program for the Siemens Area Detector Absorption correction*, University of Göttingen, Göttingen, Germany, 1997.

2 G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

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

Compound	**1**	**2**
chemical formula	$C_{26}H_{20}CdN_2O_6$	$C_{26}H_{20}CdN_2O_6$
formula weight	568.85	568.85
crystal system	triclinic	triclinic
space group	*P***Error!**	*P***Error!**
a (Å)	9.330(2)	9.353(6)
b (Å)	10.120(3)	10.076(6)
c (Å)	12.688(3)	12.911(8)
α (°)	101.561(8)	97.09(2)
β (°)	90.354(10)	96.377(19)
γ (°)	98.996(8)	100.882(16)
V ($Å^3$)	1158.4(5)	1174.4(13)
Z	2	2
D_c (g/cm^3)	1.631	1.609
F(000)	572	572
μ (MoKα,cm^{-1})	0.989	0.975
total no. of reflns	63141	61910
no. of unique reflns	5314	5339
no. of obsd. reflns	316	316
R_{int}	0.0270	0.0497
$R_1{}^a$	0.0202	0.0315
$wR_2{}^b$	0.0533	0.0652
GOF^c	1.064	1.122

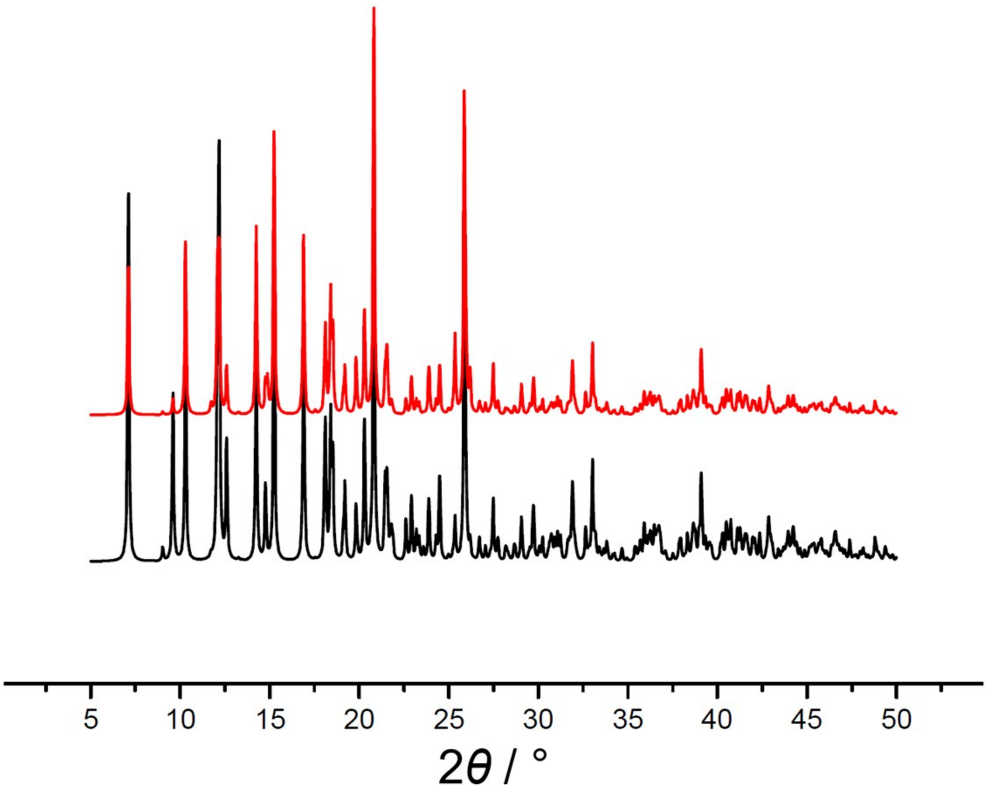
^{a} $R = \sum||F_o|-|F_c||/\sum|F_o|$. ^{b} $wR = \{\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. ^{c} $GOF = \{\sum w[(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$, where *n* is the number of reflections and *p* is total number of parameters refined.

Table S2. Selected bond lengths (Å) and angles (º) for **1** and **2**.

1			
Cd(1)-O(1)	2.2533(13)	Cd(1)-O(6)	2.2822(14)
Cd(1)-O(3A)	2.3214(13)	Cd(1)-N(1)	2.3260(15)
Cd(1)-N(2B)	2.3534(16)	Cd(1)-O(4A)	2.5666(14)
O(1)-Cd(1)-O(6)	126.49(5)	O(1)-Cd(1)-O(3A)	96.50(5)
O(6)-Cd(1)-O(3A)	136.64(5)	O(1)-Cd(1)-N(1)	90.03(5)
O(6)-Cd(1)-N(1)	91.67(5)	O(3A)-Cd(1)-N(1)	93.83(5)
O(1)-Cd(1)-N(2B)	87.42(5)	O(6)-Cd(1)-N(2B)	90.40(5)
O(3A)-Cd(1)-N(2B)	85.77(5)	N(1)-Cd(1)-N(2B)	177.36(5)
O(1)-Cd(1)-O(4A)	149.50(5)	O(6)-Cd(1)-O(4A)	83.86(5)
O(3A)-Cd(1)-O(4A)	53.84(4)	N(1)-Cd(1)-O(4A)	85.63(5)
N(2B)-Cd(1)-O(4A)	96.22(5)		
2			
Cd(1)-O(6)	2.265(2)	Cd(1)-O(1)	2.281(2)
Cd(1)-N(1)	2.322(3)	Cd(1)-N(2A)	2.341(3)
Cd(1)-O(4B)	2.371(2)	Cd(1)-O(3B)	2.478(2)
O(6)-Cd(1)-O(1)	127.38(8)	O(6)-Cd(1)-N(1)	93.34(8)
O(1)-Cd(1)-N(1)	91.67(8)	O(6)-Cd(1)-N(2A)	89.71(8)
O(1)-Cd(1)-N(2A)	87.52(8)	N(1)-Cd(1)-N(2A)	176.68(8)
O(6)-Cd(1)-O(4B)	142.26(7)	O(1)-Cd(1)-O(4B)	89.68(8)
N(1)-Cd(1)-O(4B)	92.31(8)	N(2A)-Cd(1)-O(4B)	84.47(8)
O(6)-Cd(1)-O(3B)	89.42(7)	O(1)-Cd(1)-O(3B)	143.05(7)
N(1)-Cd(1)-O(3B)	81.75(8)	N(2A)-Cd(1)-O(3B)	96.97(7)
O(4B)-Cd(1)-O(3B)	54.61(7)		

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

(a)



(b)

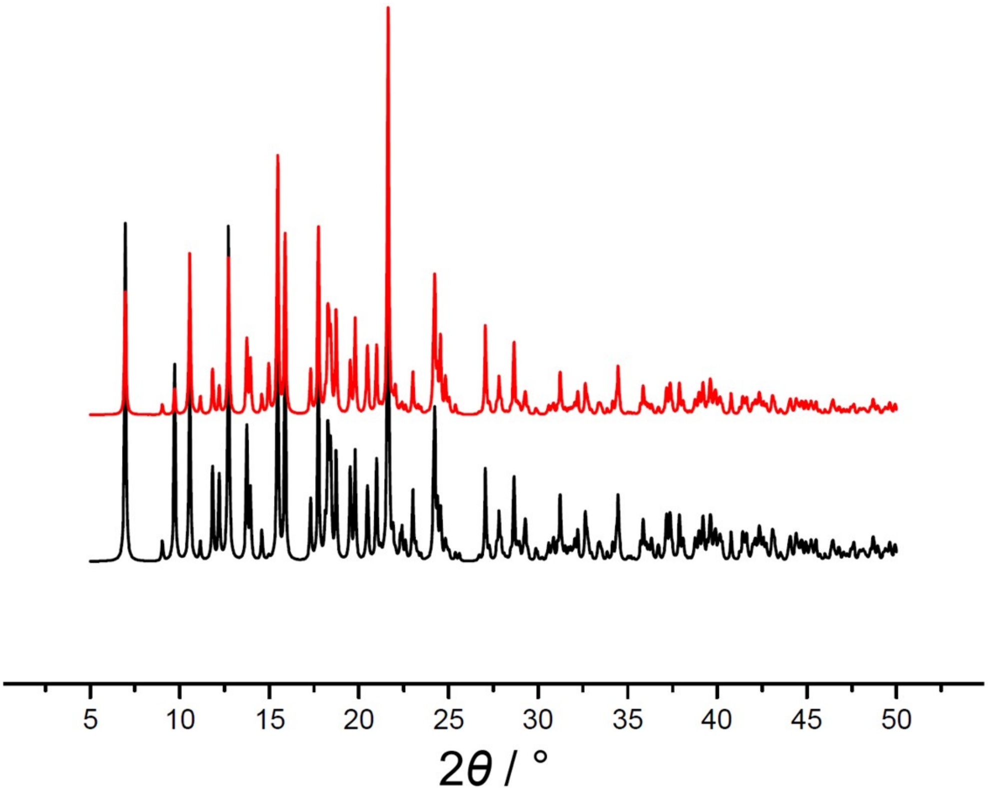


Fig. S1 PXRD patterns for **1** (a) and **2** (b). Simulated: black; Experimental: red.

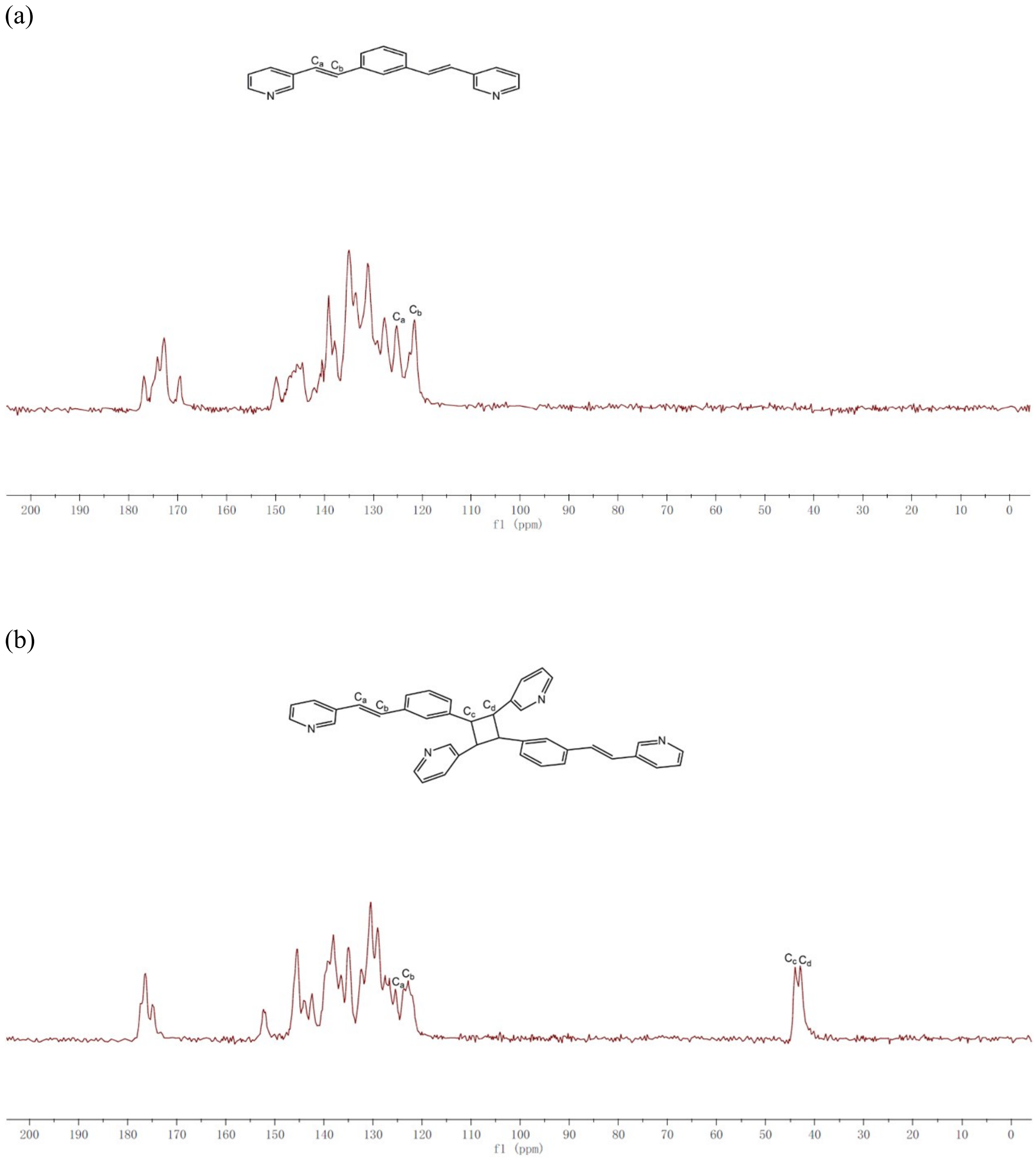


Fig. S2 The ^{13}C CPMAS NMR spectra of **1** (a) and **2** (b).

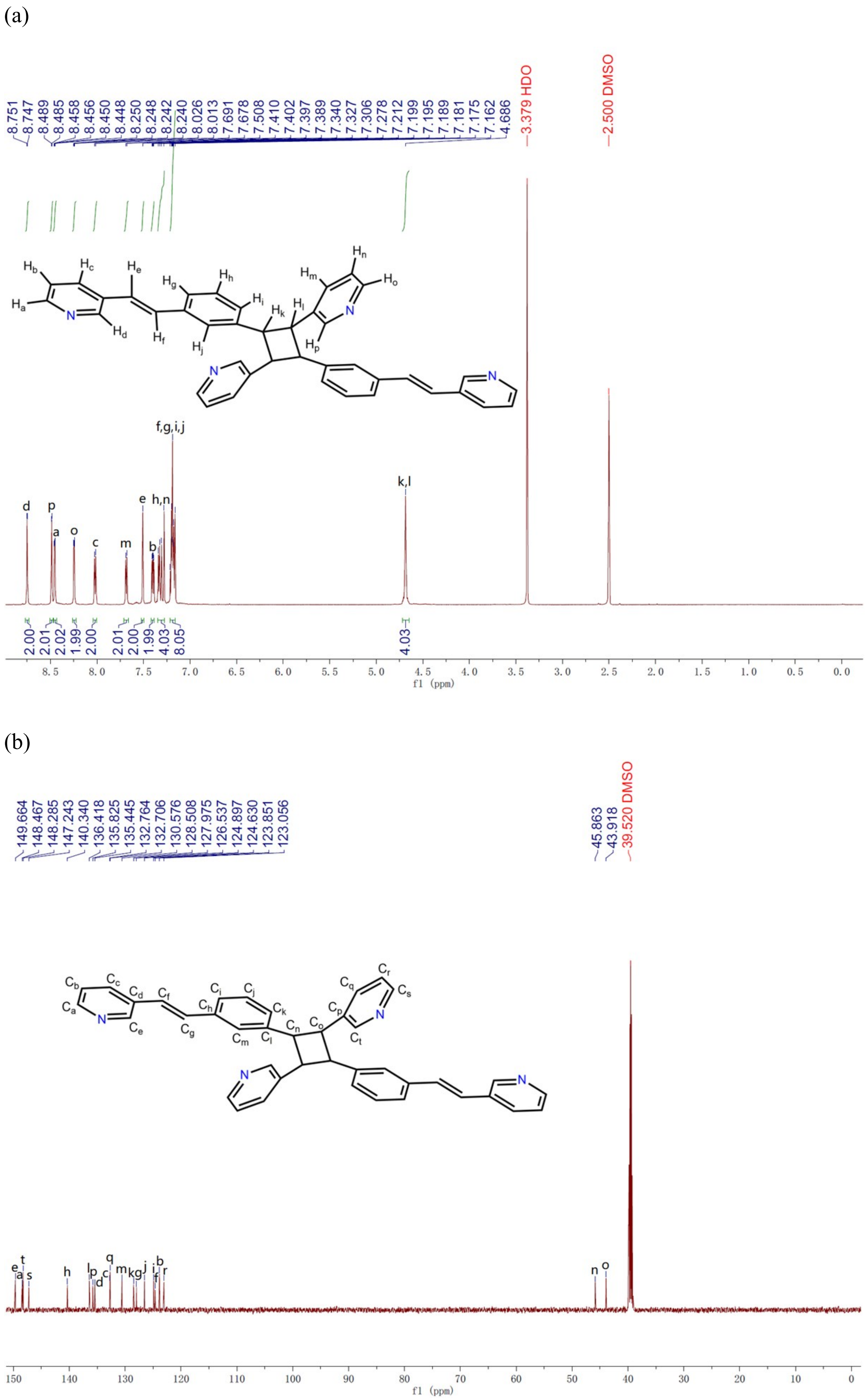


Fig. S3 (a) The ^{1}H NMR spectrum of bpbpvpcb in d_6-DMSO at ambient temperature. (b) The ^{13}C NMR spectrum of bpbpvpcb in d_6-DMSO at ambient temperature.

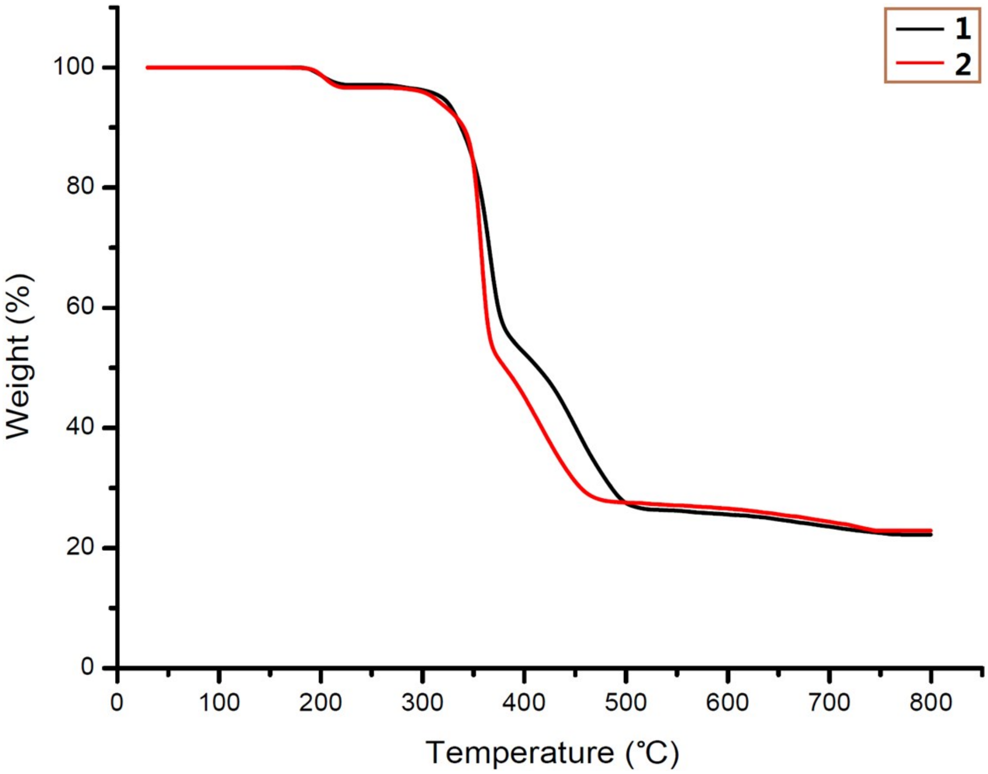


Fig. S4 The TGA curves for **1** and **2**.