Electronic Supplementary Information

Bulkiness effect dependent photosalient behavious of photoactive cadmium coordination polymers

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Video SV1: photosalient effects of **CP_1**

Video SV2: photosalient effects of **CP_2**

Video SV3: photosalient effects of **CP_3**

Video SV4: photosalient effects of **CP_1** showing bending behavior

Video SV5: photosalient effects of **CP_2** showing bending behavior

Video SV6: photosalient effects of **CP_3** showing jumping behavior

Video SV7: photosalient effects of **CP_1-PVA** membrane

Video SV8: photosalient effects of **CP_1-PVA** membrane

Video SV9: photosalient effects of the robot gripper

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General procedures

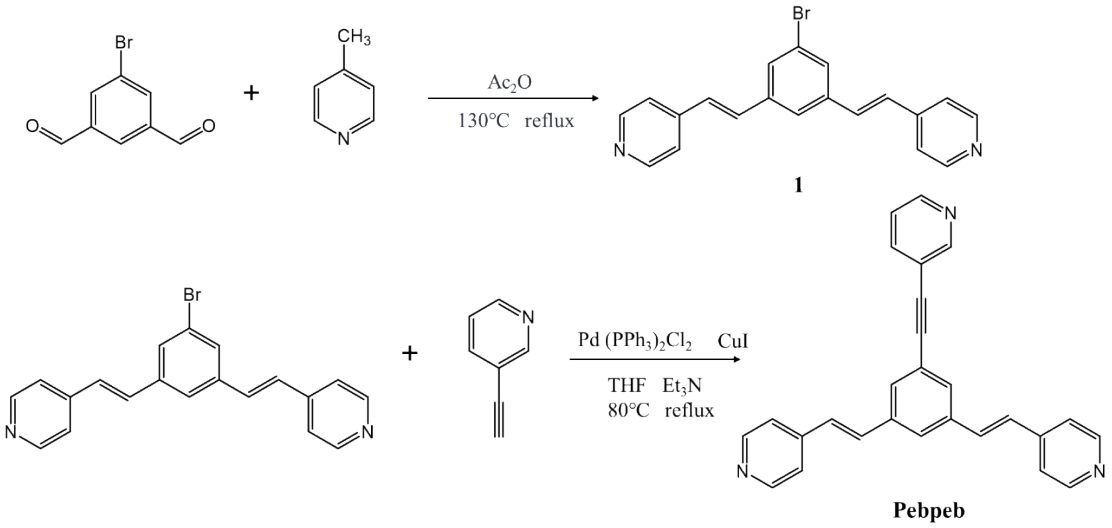
All chemicals were commercially accessible and used as received without further purification. Powder X-ray diffraction (PXRD) patterns were acquired on a Bruker D8 advance using Cu Kα radiation (λ = 1.5406 Å) from 5° to 50° with a scanning step size of 0.02°. Single-crystal X-ray diffraction data for **CP_1**, **CP_2** and **CP_3** were recorded on a Bruker Smart CCD diffractometer. ^{1}H NMR chemical shifts were referenced to the solvent signal in $CDCl_3$ or DMSO-d_6. ^{13}C-NMR spectra were recorded at a resonance frequency of 101.6 MHz on a Bruker AVANCE 400M spectrometer. IR spectra were recorded on a Varian 1000 FT-IR spectrometer (4000-400 cm^{-1}). Elemental analyses (C, H, N) were performed using a PE 2400 II elemental analyzer. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo Star System under a nitrogen atmosphere at a heating rate of 10 °C/min. Photo-irradiation experiments were conducted with a high-pressure mercury lamp at a wavelength of 365 nm.

Experimental

Synthesis of ligand Pebpeb. A 50 mL round-bottom flask was located with 5-bromobenzene-1, 3-dialdehyde (1.00 g, 5 mmol), 4-methylpyridine (1.13 g, 10 mmol) in 2 mL of acetic anhydride solvent. The mixture was heated at 130 °C for a period of 24 h and then diluted with H_2O (200 mL). The mixture was extracted by CH_2Cl_2 (3 × 50 mL). A brown powdery **1** was obtained. Yield: 1.75 g (82 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.58 (d, 4H, Ph-H), 7.81 (s, 1H, Ph-H), 7.57-7.53 (m, 2H, C=C), 7.50 (s, 2H, Ph-H), 7.39-7.34 (d, 2H, C=C). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.30, 146.01, 139.47, 131.64, 129.80, 128.10, 124.96, 123.25, 121.51 (Figure S1).

A 50 mL round-bottom flask was located with 4-(3-bromo-5-((E)-2-(pyridine-4-yl) vinyl) styrenyl) pyridine (1.00 g, 2.8 mmol), 3-alkynylpyridine (0.35 g, 3 mmol), $Pd(PPh_3)_2Cl_2$ (0.04 g, 0.0057 mmol) and CuI (0.08 g, 0.4 mmol) in 15 mL of

tetrahydrofuran and triethylamine solvent (3:1). The mixture was heated at 80 °C for a period of 48 h and then diluted with H_2O (200 mL). The mixture was extracted by CH_2Cl_2 (3 × 50 mL). The light-yellow product was isolated by column chromatography (ethyl acetate: methanol = 3:1). Yield: 1.17 g (87 %). ^{1}H NMR (400 MHz, DMSO-d_6, TMS, Figure. S2) δ 8.81 (s, 1H, Ph-H), 8.63-8.61 (d, 4H, Ph-H), 8.60 (d, 2H, Ph-H), 7.86-7.84 (d, 2H, Ph-H), 7.70-7.67 (s, 4H, Ph-H), 7.41 (d, 5H, Ph-H), 7.39 and 7.35 (s, 2H, C=C), 7.21 and 7.17 (s, 2H, C=C). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 151.77, 149.15, 147.10, 143.21, 138.16, 136.56, 132.29, 129.37, 127.12, 125.48, 119.97, 94.97, 87.29. M+1=386.1 (Figure S2).



Scheme S1. Synthesis of Pebpeb.

Preparation of [Cd_3(Pebpeb)$_2$(L_1)$_6$] (CP_1). A mixture containing 3-chlorobenzoic acid (HL_1) (9.5 mg, 0.05 mmol), $CdSO_4$·8/3H_2O (25 mg, 0.05 mmol) and Pebpeb (6.5 mg, 0.05 mmol) in DMAC-H_2O-HNO_3 (2 mL, 5:20:1 in volume ratio) was sealed in a Pyrex tube and heated at 140 ℃ for 10 h to yield yellow rod-shaped crystals of **CP_1** (5.35 mg, 82 %, based on Pebpeb). Anal. Calcd for C92H66Cd3Cl5N6O14: C, 57.77; H, 3.11; N, 4.21. found: C, 57.78; H, 3.13; N, 4.21. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, Fig. S15): δ 8.81 (s, 1H, Py-H), 8.63 (d, 1H, Py-H), 8.59 (d, 4H, Py-H), 8.03 (d,

2H, Ph-H of Pebpeb), 7.90 (s, 4H, Ph-H of HL_1), 7.87 (d, 4H, Ph-H of HL_1), 7.63 (s, 1H, Py-H), 7.59 (d, 2H, CH=CH), 7.55 (d, 4H, Py-H), 7.48 (d, 4H, Ph-H of HL_1), 7.44 (d, 4H, Ph-H of HL_1), 7.43 (s, 2H, CH=CH). IR (KBr disk, cm^{-1}): 3064(w), 1609(s), 1549(s), 1500(s), 1481(s), 1417(s), 1303(s), 1265(s), 1218(s), 1145(s), 1066 (w), 1013(m), 964(m), 874(m), 805(s), 765(s), 696(s), 543(s).

Preparation of $[Cd_3(Pebpeb)_2(L_2)_6]$ (CP_2). A mixture containing 3-nitrobenzoic acid (HL_2) (9.5 mg, 0.05 mmol), Pebpeb (6.5 mg, 0.05 mmol) and $CdSO_4 \cdot 8/3H_2O$ (25 mg, 0.05 mmol) in DMAC-H_2O-HNO_3 (2 mL, 5:20:1 in volume ratio) was sealed in a Pyrex tube and heated at 140 ℃ for 10 h to yield yellow rod-shaped crystals of **CP_2** (5.53 mg

, 85 %, based on Pebpeb). Anal. Calcd for C96H62N12O24Cd3: C, 54.73; H, 2.95; N, 7.98. Found: C, 54.74; H, 2.94; N, 7.99. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, Fig. S16): δ 8.82 (d, 1H, Py-H), 8.68(s, 3H, Ph-H of HL_2), 8.64 (d, 1H, Py-H), 8.62 and 8.59(m, 4H, Py-H),8.34 (t, 6H, Ph-H of HL_2), 8.04 (d, 2H, Ph-H of Pebpeb),7.88 (s, 1H, Py-H), 7.72 (t, 3H, Ph-H of HL_2), 7.64 (s, 1H, Py-H), 7.61 (s, 2H, CH=CH),7.60 (s, 4H, Py-H), 7.54 and 7.52 (m, 1H, Py-H), 7.50 (d, 2H, CH=CH), 7.46 (s, 1H, Ph-H of Pebpeb). IR (KBr disk, cm^{-1}): 3074(w), 1607(s), 1551(s), 1523(s), 1472(s), 1391(s), 1350(s), 1221(s), 1155(w), 1157(s), 1068(m), 1073(m), 1017(m), 1014(m), 963(m), 907(s), 830(s), 786(s), 723(s), 541(s).

Preparation of $[Cd_6(Pebpeb)_4(L_3)_{12}] \cdot HL_3$ (CP_3). A mixture containing 3-isopropyl benzoic acid (HL_3) (9.5 mg, 0.05 mmol), Pebpeb (6.5 mg, 0.05 mmol) and $CdSO_4 \cdot 8/3H_2O$ (25 mg, 0.05 mmol) in DMAC-H_2O-HNO_3 (2 mL, 3:20:1 in volume ratio) was sealed in a Pyrex tube and heated at 140 ℃ for 10 h to yield yellow block crystals of **CP_3** (5.66 mg, 87 % based on Pebpeb). Anal. Calcd for $C_{238}H_{220}Cd_6N_{12}O_{26}$: C, 65.88; H, 5.11; N, 3.87. found: C, 65.86; H, 5.09; N, 3.85. ^{1}H NMR (400 MHz, DMSO-d_6, ppm, Fig. S17): δ 8.81 (s, 1H, Py-H), 8.63 (d, 1H, Py-H), 8.59 (d, 4H, Py-

H), 8.03 (d, 2H, Ph-H of Pebpeb), 7.87 (s, 1H, Py-H), 7.84 (s, 4H, Ph-H of HL_3), 7.77 (d, 4H, Ph-H of HL_3), 7.63 (s, 1H, Py-H), 7.60 (s, 2H, CH=CH), 7.59 (s, 4H, Py-H), 7.48 (s, 2H, CH=CH), 7.44 (s, 1H, Ph-H of Pebpeb), 7.39 (d, 4H, Ph-H of HL_3), 7.34 (t, 4H, Ph-H of HL_3). IR (KBr disk, cm^{-1}):3051(w), 2955(s), 1713(s), 1607(s), 1540(s), 1459(s), 1389(s), 1331(s), 1218(m), 1120(m), 1045(m), 1015(m), 966(m), 923(s), 861(m), 805(s), 765(s), 699(s), 545(s).

Photo-irradiation experiment

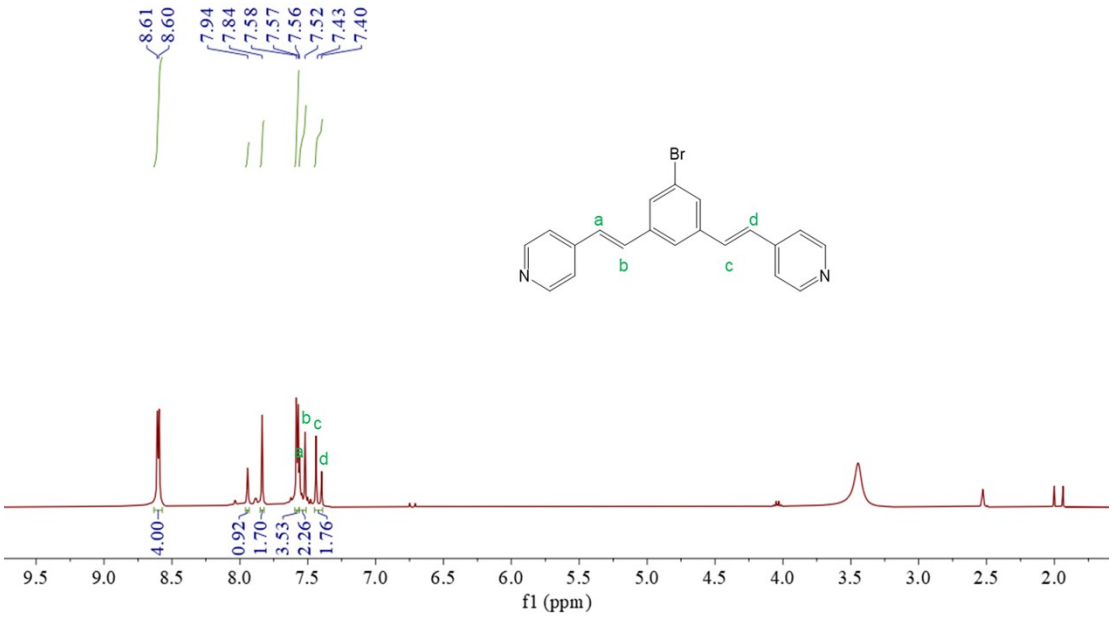
Crystals (ca 0.5 g) of **CP_1**, **CP_2** and **CP_3** were placed between glass plates and exposed to a 100 W high-pressure mercury lamp (λ = 365 nm) for 2 h to form the corresponding photoproducts of **CPs'**, respectively.

Single crystal structure determination. Structures of **CP_1-CP_3** were solved by direct methods and refined by full-matrix least-squares techniques using the *SHELXL*-2019, Olex 2 programs.[S1] Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were introduced at the calculated positions and included in the structure-factor calculations.[S2] A summary of key crystallographic information for **CP_1-CP_3** is given in Table S1. The CCDC codes for these compounds are 2405226-2405228.

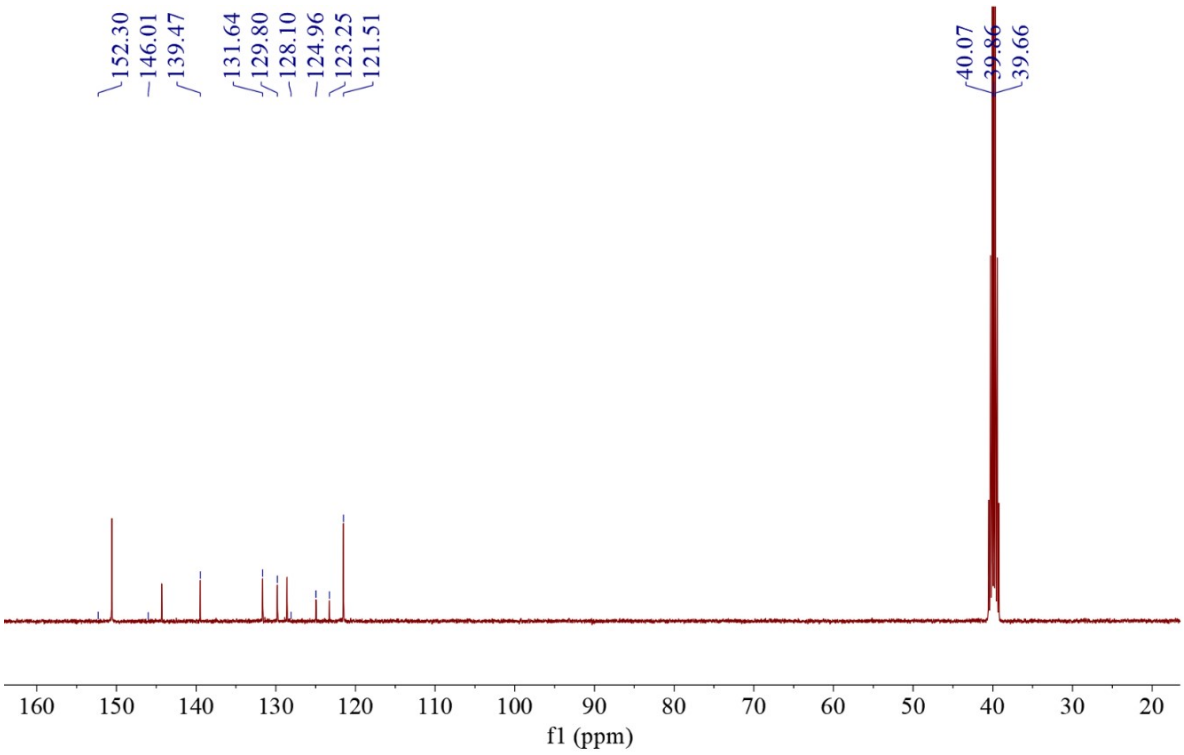
Table. S1 Summary of crystal data and structure refinement parameters for **CP_1-CP_3**.

	CP_1	**CP_2**	**CP_3**
Emperical formula	$C_{96}H_{62}Cd_3Cl_6N_6O_{12}$	$C_{96}H_{62}Cd_3N_{12}O_{24}$	$C_{238}H_{220}Cd_6N_{12}O_{26}$
Formula weight	2041.41	2104.86	4338.65
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	14.4964(11)	14.4569(8)	17.803(3)
b/Å	16.5414(13)	16.5945(9)	21.233(5)
c/Å	18.6341(13)	18.5996(10)	30.75(3)
α/°	87.128(6)	88.336(2)	82.149(12)
β/°	77.188(6)	78.624(2)	87.549(14)
γ/°	85.054(7)	85.858(2)	88.691(8)
V/Å^3	4338.6(6)	4362.5(4)	11503(13)
Dc/g cm^{-3}	1.563	1.602	1.253
Z	2	2	2
μ(Mo-Kα)/mm^{-1}	0.711	0.811	0.710
Total reflections	39131	82668	126910
Unique reflections	18674	20011	51941
No. observations	0	0	0
No. parameters	1108	1216	2529
F (000)	2044	2112.32	4456
R_1[a]	0.0735	0.0812	0.0508
wR_2[b]	0.1098	0.1135	0.1306
GOF[c]	1.079	1.027	1.079

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_0|$. [b]$wR_2 = \{\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2\}^{1/2}$. [c]GOF $= \{\Sigma w((F_0^2 - F_c^2)^2)/(n - p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

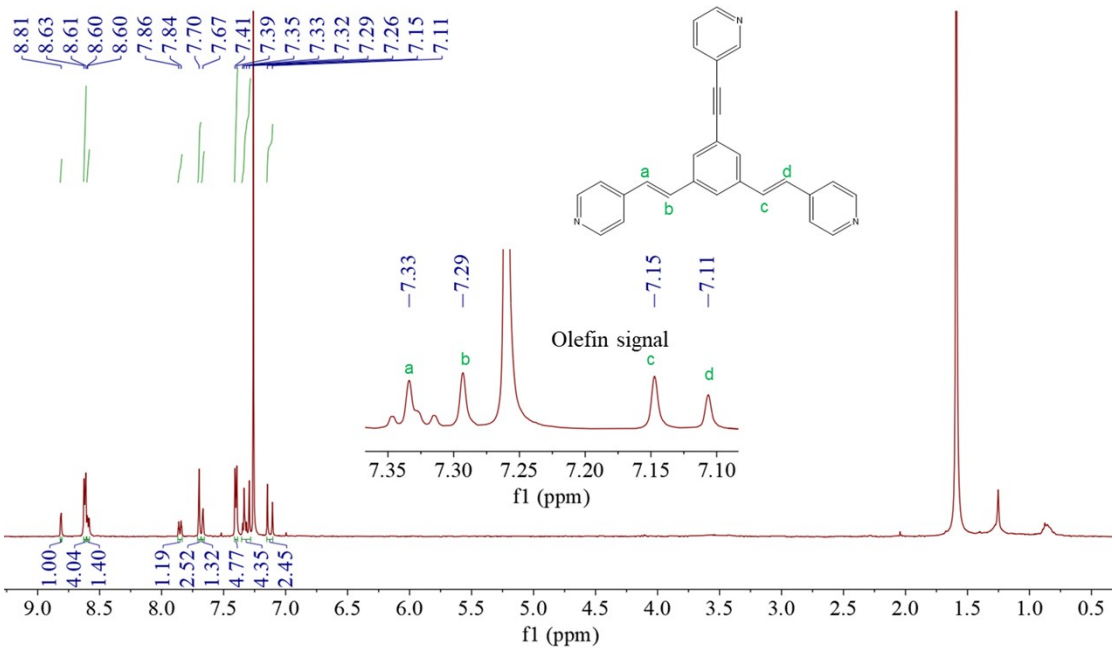


(a)

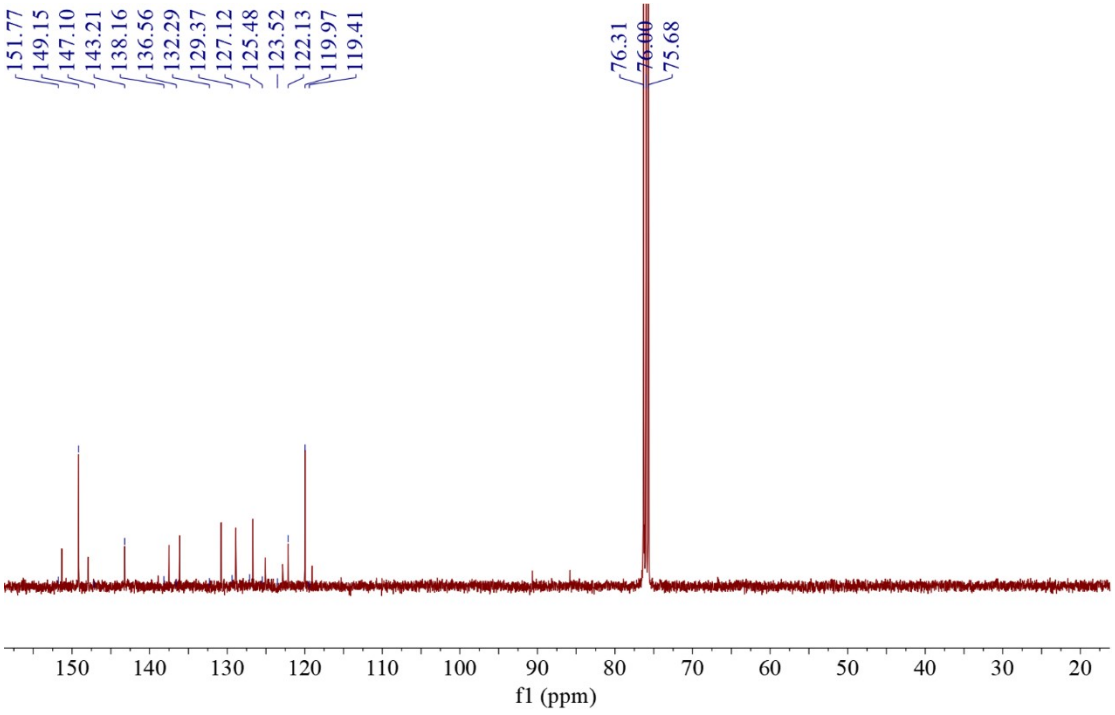


(b)

Figure. S1 The ^{1}H (a) and ^{13}C (b) NMR spectra of **1** in $CDCl_3$.

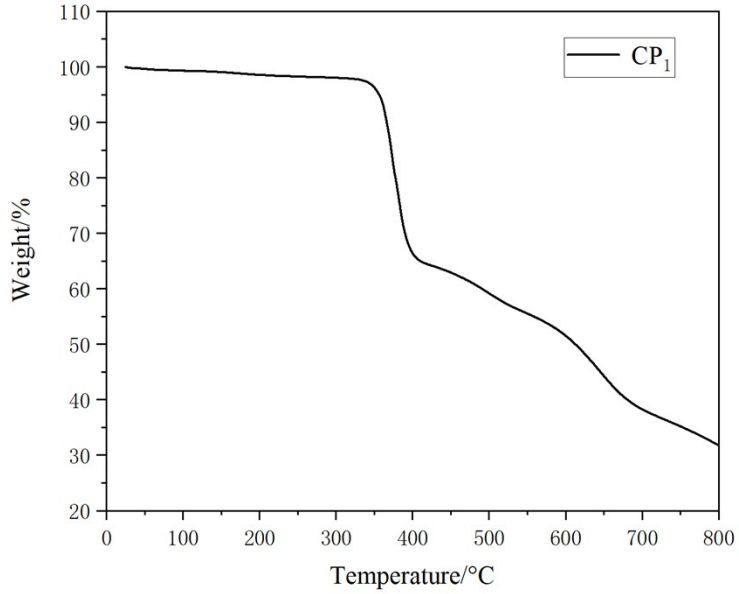


(a)

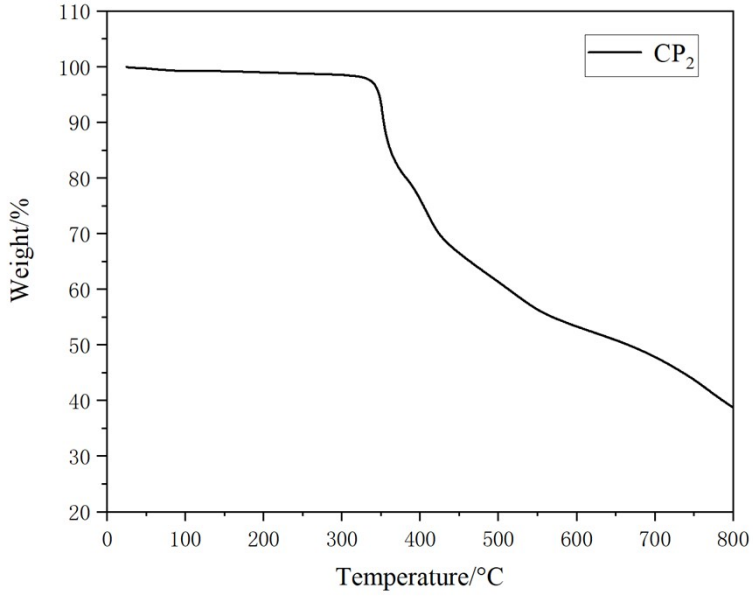


(b)

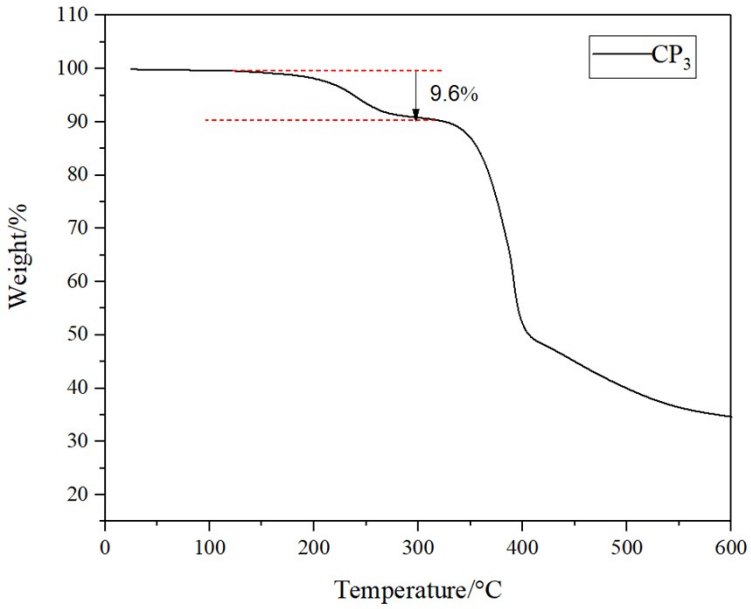
Figure. S2 The ^{1}H (a) and ^{13}C (b) NMR spectra of **Pebpeb** in $CDCl_3$.


CP1
Weight/%
Temperature/°C
110
100
90
80
70
60
50
40
30
20
0
100
200
300
400
500
600
700
800

(a)

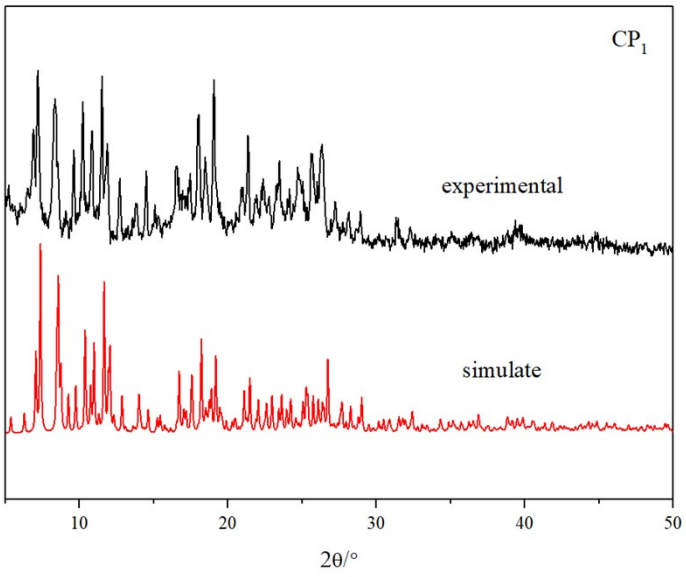

CP2
Weight/%
Temperature/°C
110
100
90
80
70
60
50
40
30
20
0
100
200
300
400
500
600
700
800

(b)

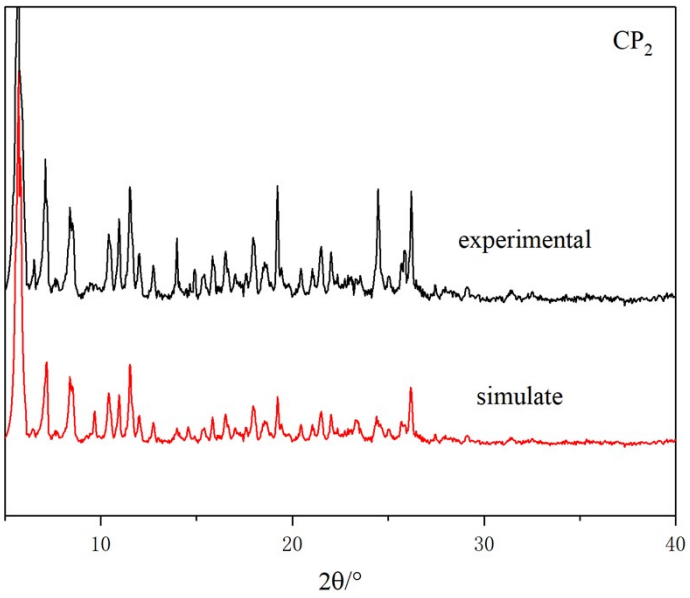


(c)

Figure. S3 Thermogravimetric plots of $\mathbf{CP_1}$ (a), $\mathbf{CP_2}$ (b) and $\mathbf{CP_3}$ (c).



(a)



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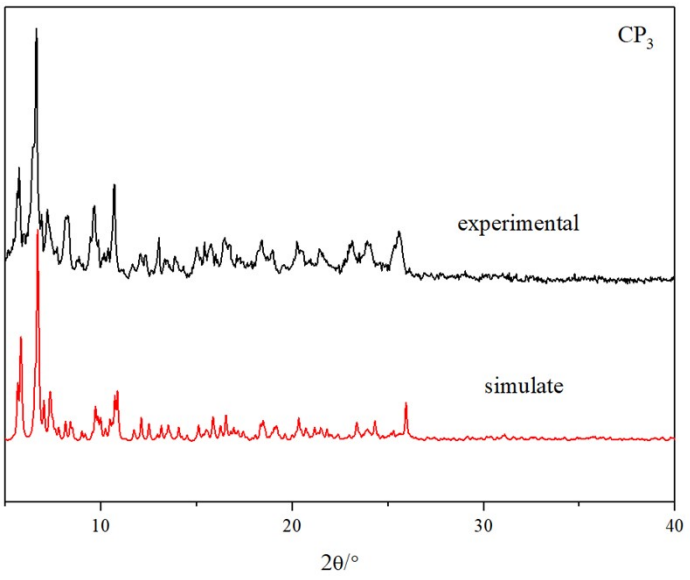
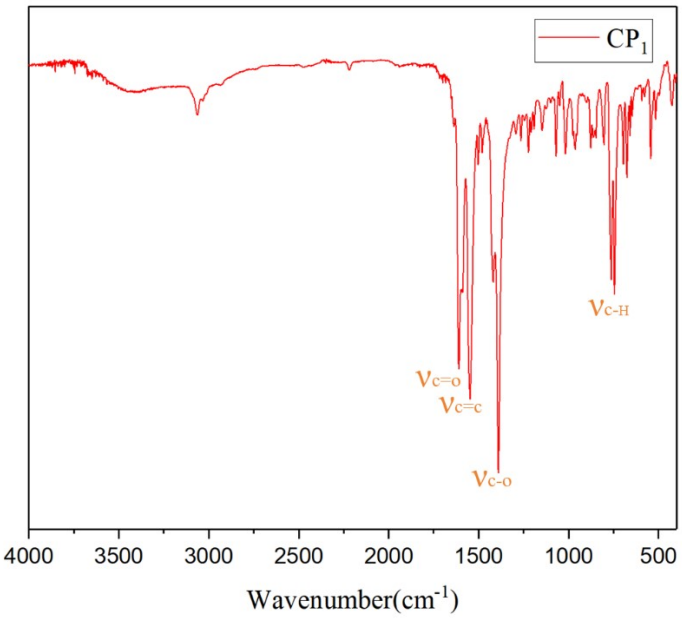
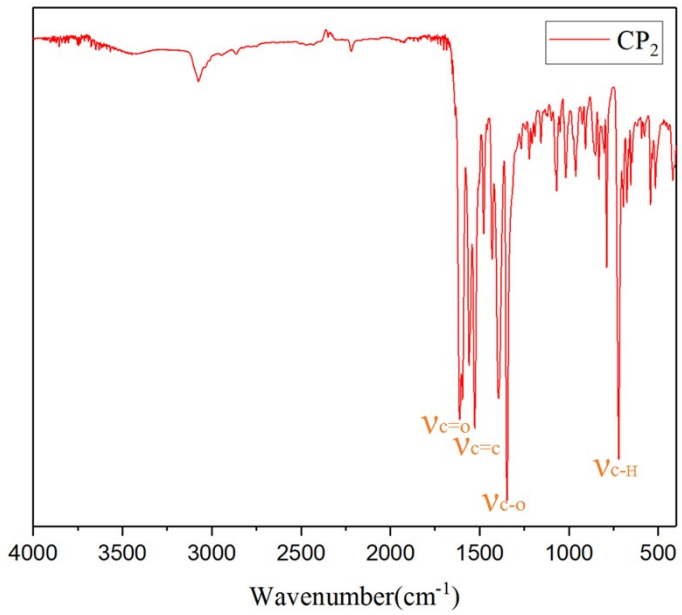


(c)

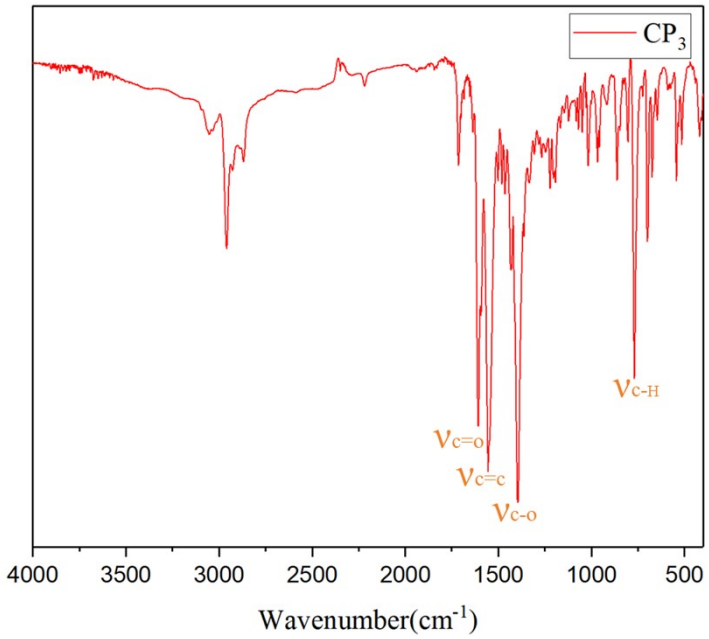
Figure. S4 PXRD patterns of **CP$_1$** (a), **CP$_2$** (b) and **CP$_3$** (c).


CP1
νc-H
νc=o
νc=c
νc-o
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)

(a)

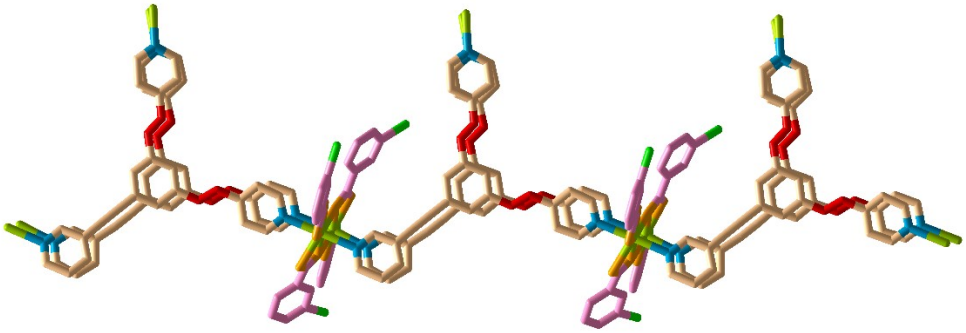

CP2
νc=o
νc=c
νc-o
νc-H
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)

(b)

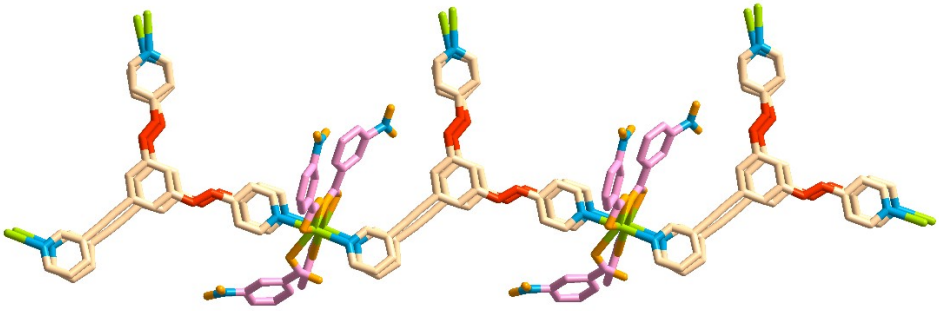


(c)

Figure. S5 IR spectra of **CP_1** (a), **CP_2** (b), **CP_3** (c).



(a)



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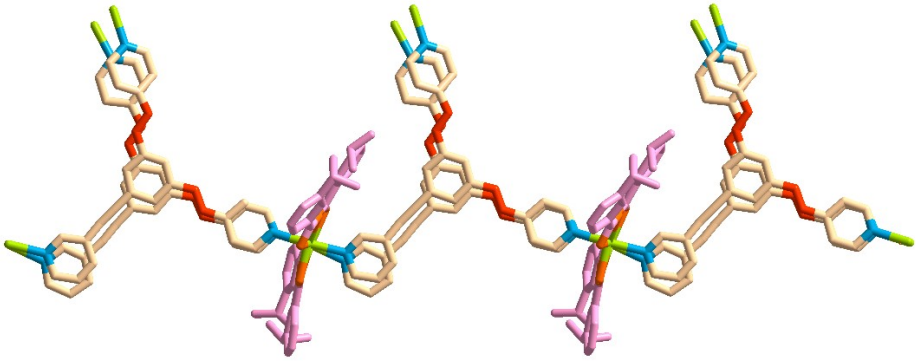
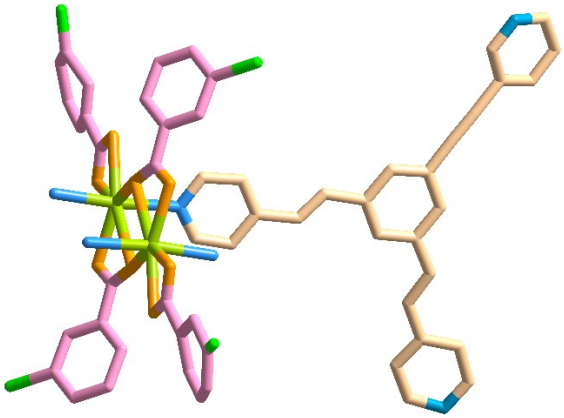
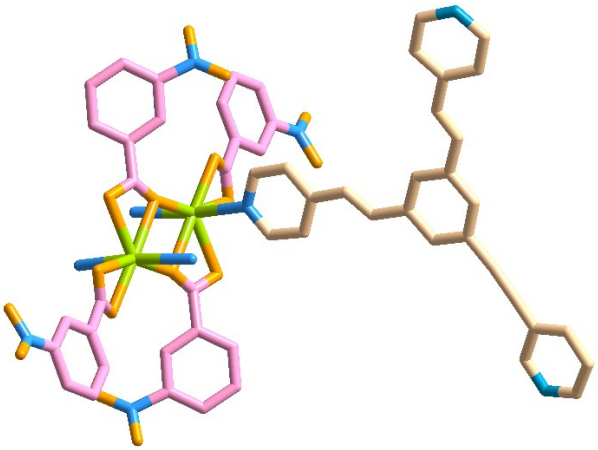


(c)

Figure. S6 View of the 1D chain structure of **CP_1-CP_3**.



(a)



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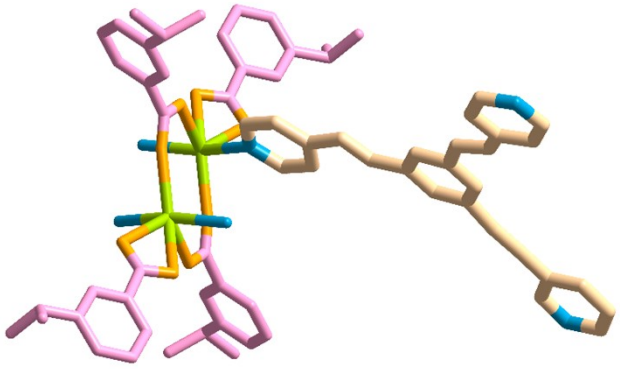


(c)

Figure. S7 View of the coordination environments of Cd (II) centers in **CP_1-CP_3**.

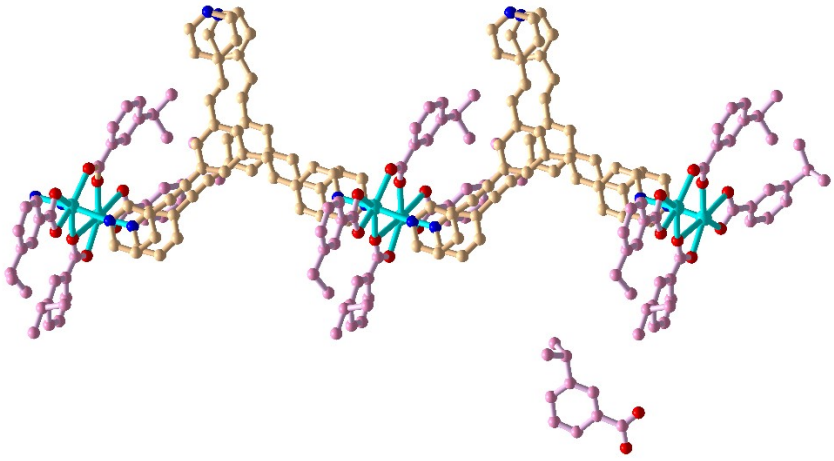


Figure. S8 The structural unit of **CP_3**.

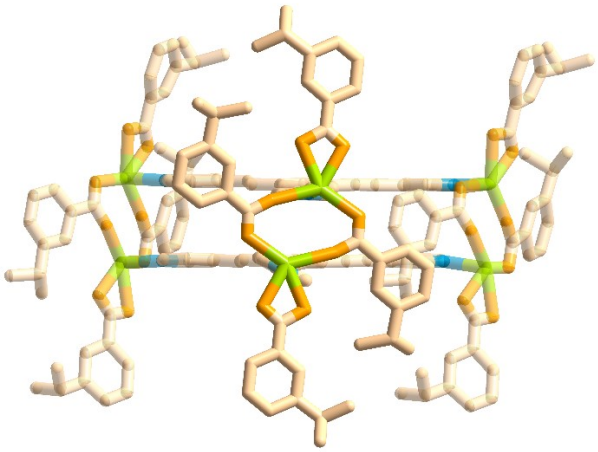
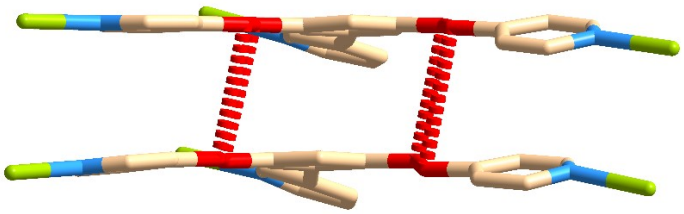
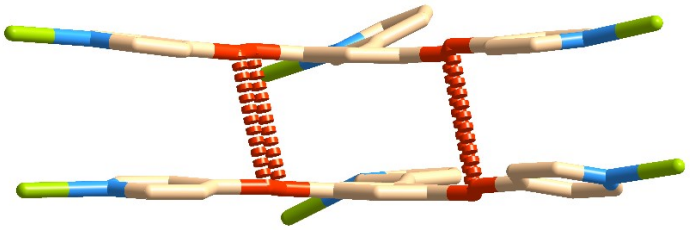


Figure. S9 Diagram of the coordination mode of carboxylic acid ligands with Pebpeb.



(a)



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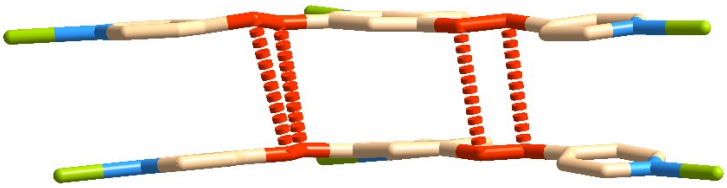
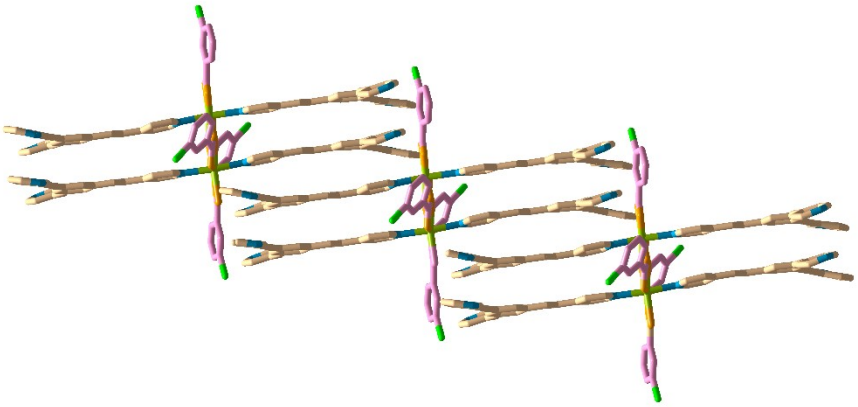
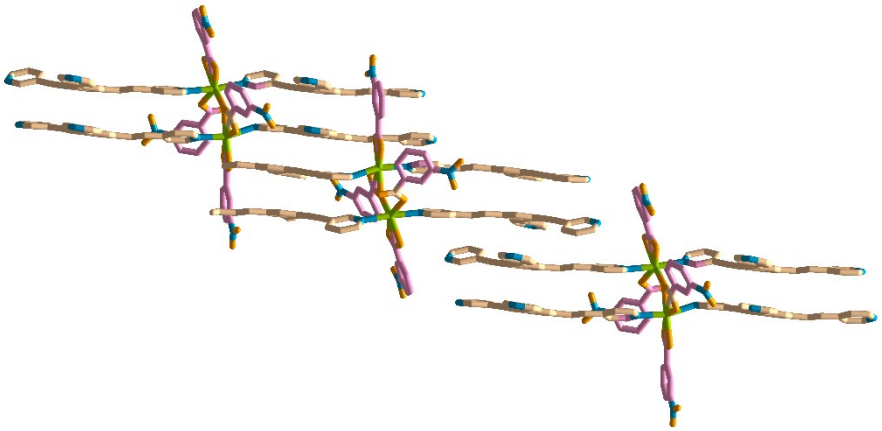


(c)

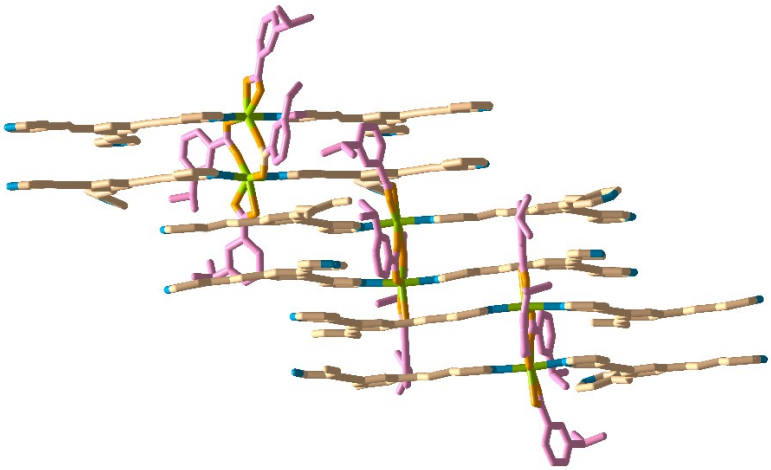
Figure. S10 View of the face-to-face alignment of Pebpeb pair in **CP_1-CP_3**.



(a)

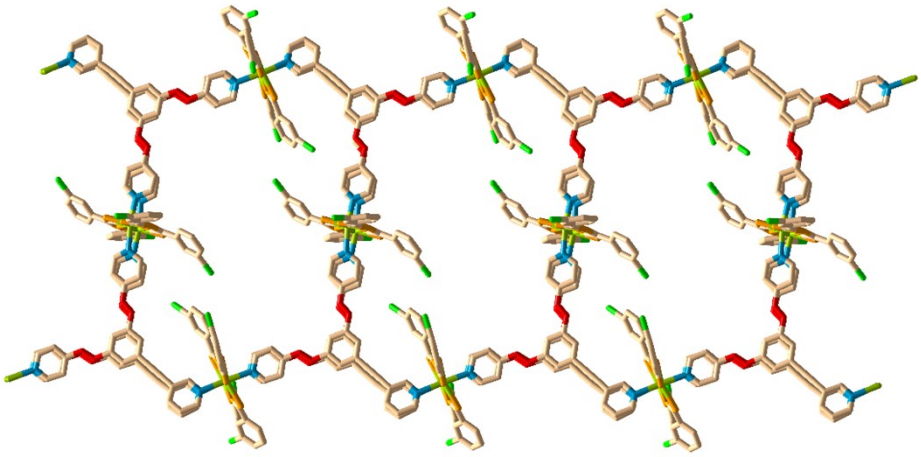


(b)

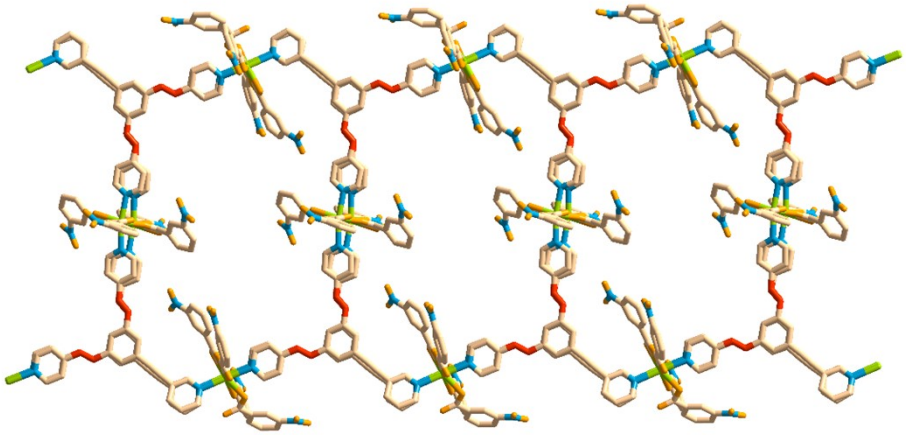


(c)

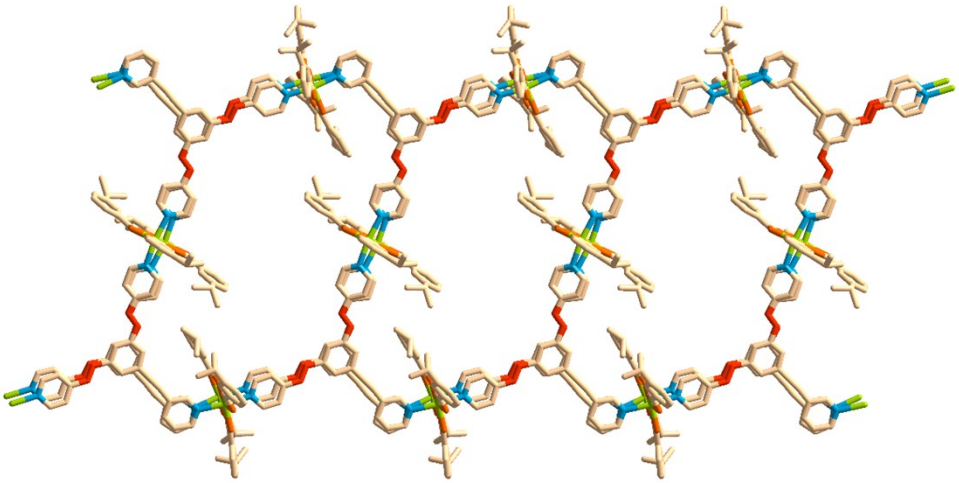
Figure. S11 The stacking ways of adjacent 1D chains in $\mathbf{CP_1}$ (a), $\mathbf{CP_2}$ (b), $\mathbf{CP_3}$ (c).



(a)

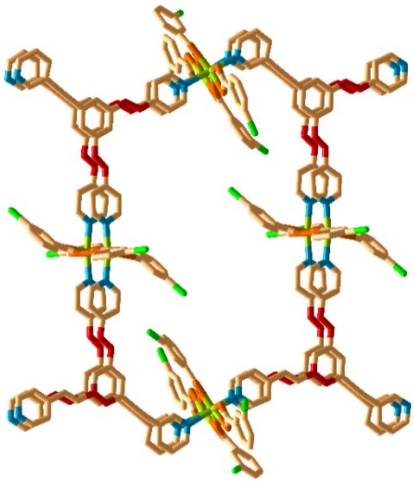


(b)

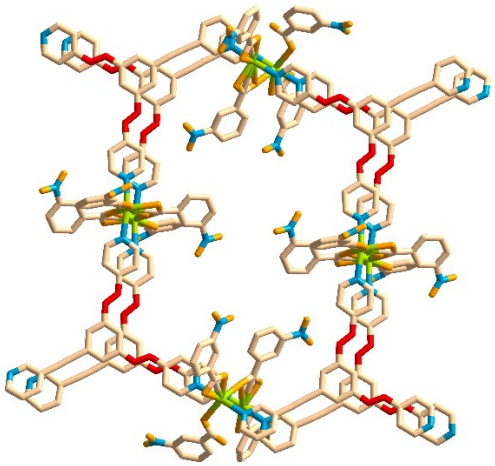


(c)

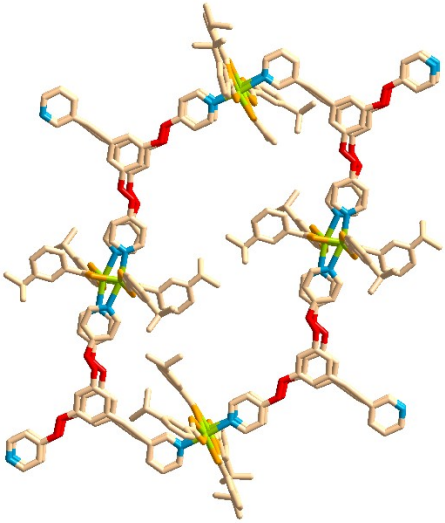
Figure. S12 The adjacent zigzag chains are connected to form a 1D tape motif.



(a)



(b)



(c)

Figure. S13 Diagram of the coordination mode of carboxylic acid ligands with Pebpeb.

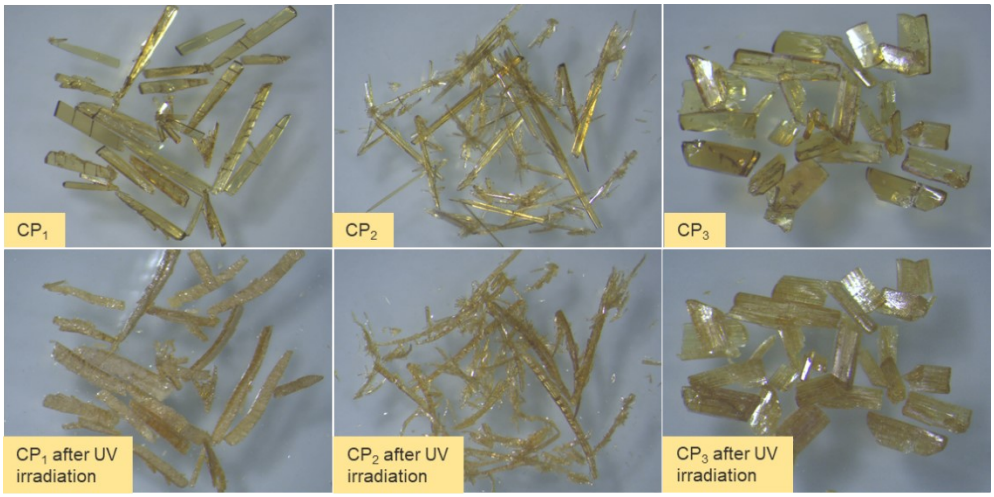


Figure. S14 PS behavior of **CP_1-CP_3**.

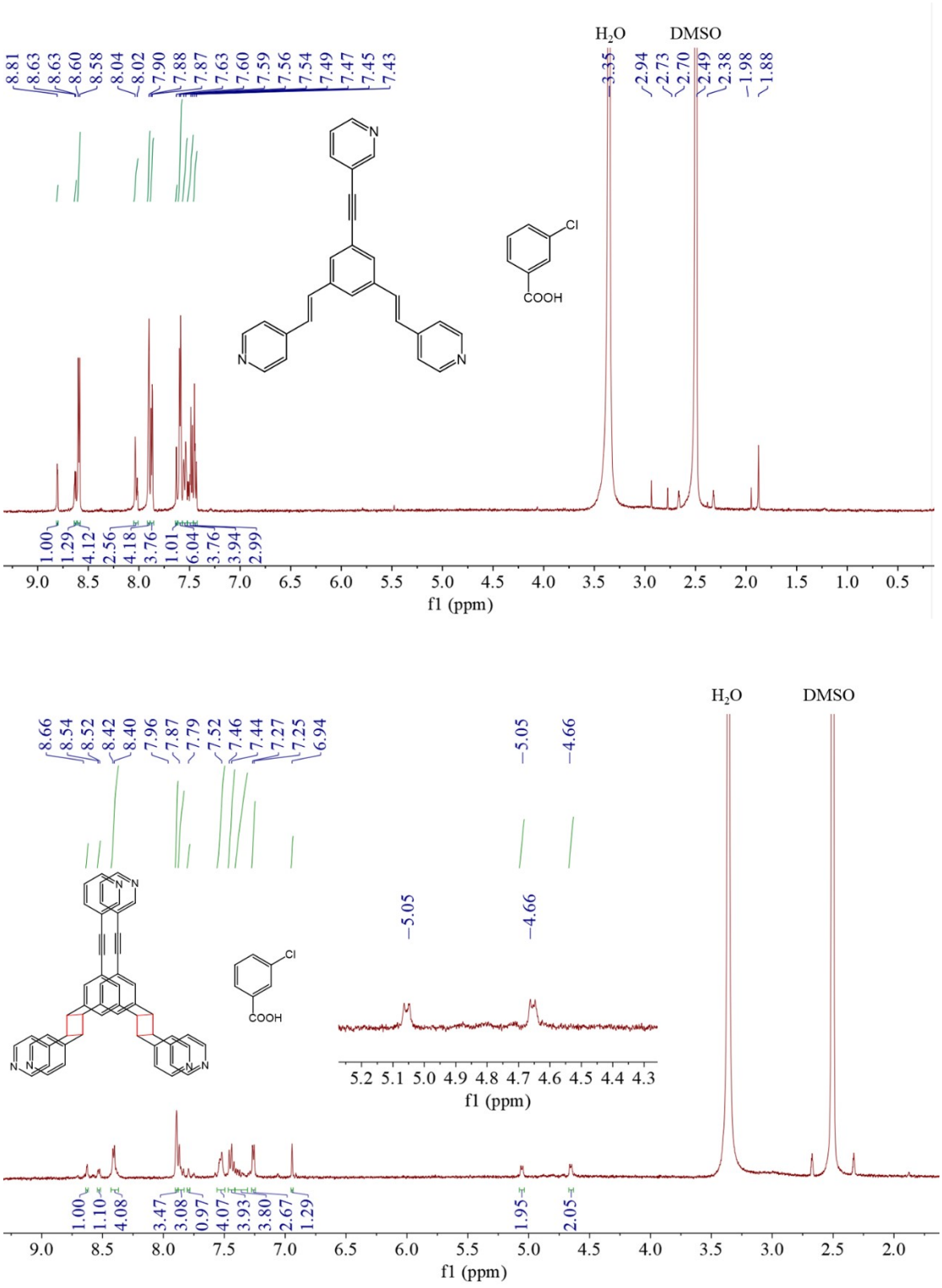


Figure. S15 The ^{1}H NMR spectra of $\mathbf{CP_1}$ before and after UV light irradiation.

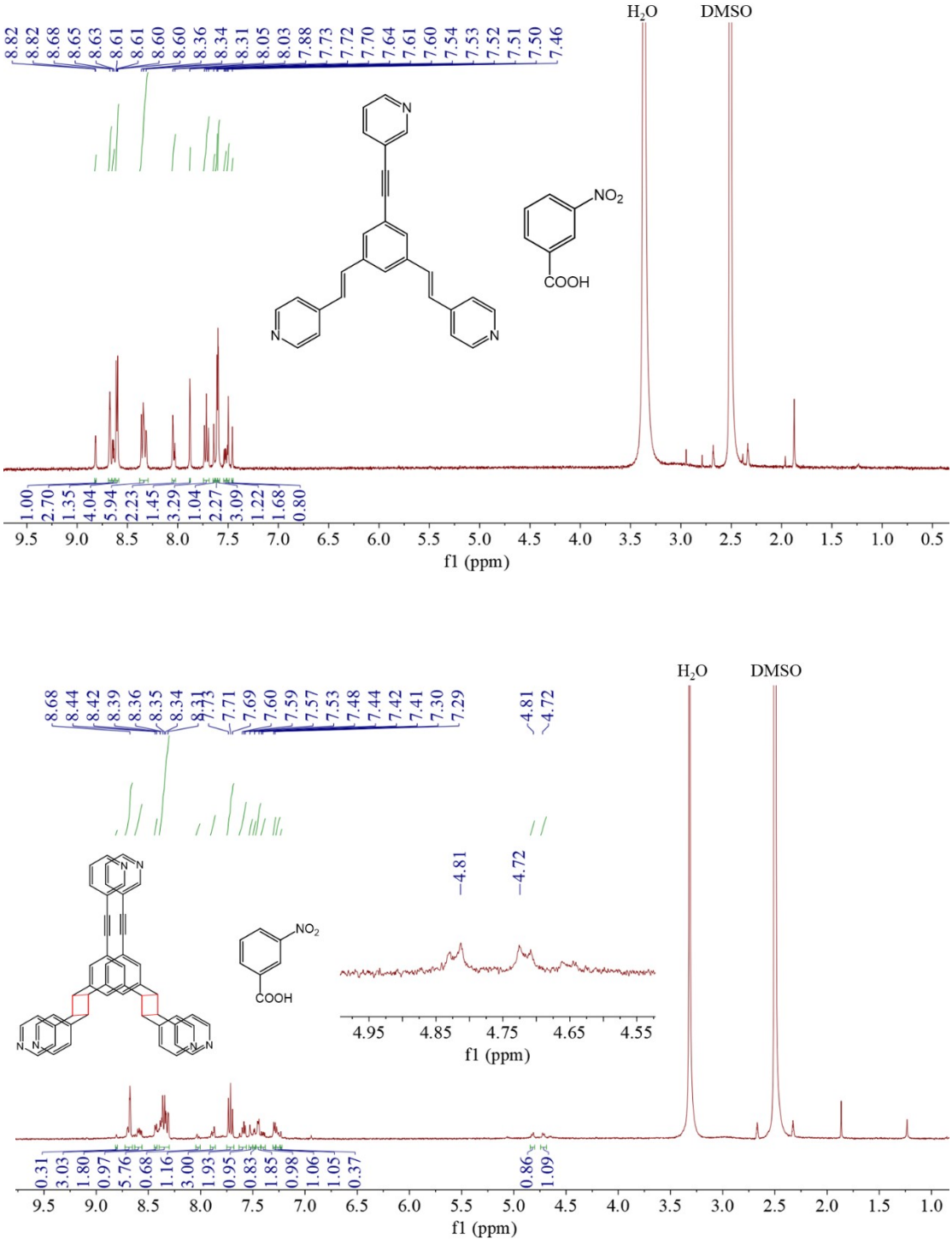


Figure. S16 The ^{1}H NMR spectra of **CP_2** before and after UV light irradiation.

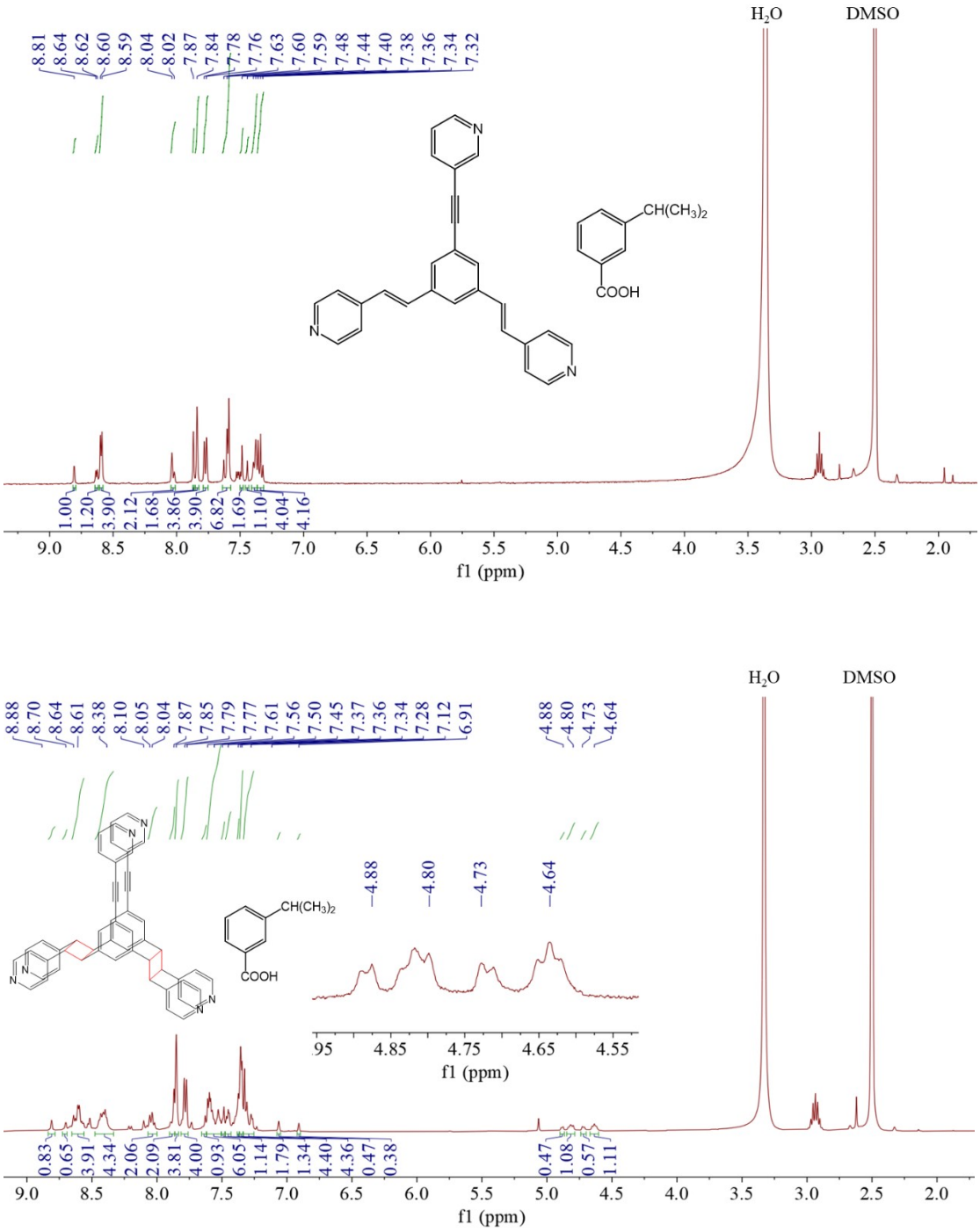


Figure. S17 The ^{1}H NMR spectra of **CP_3** before and after UV light irradiation.

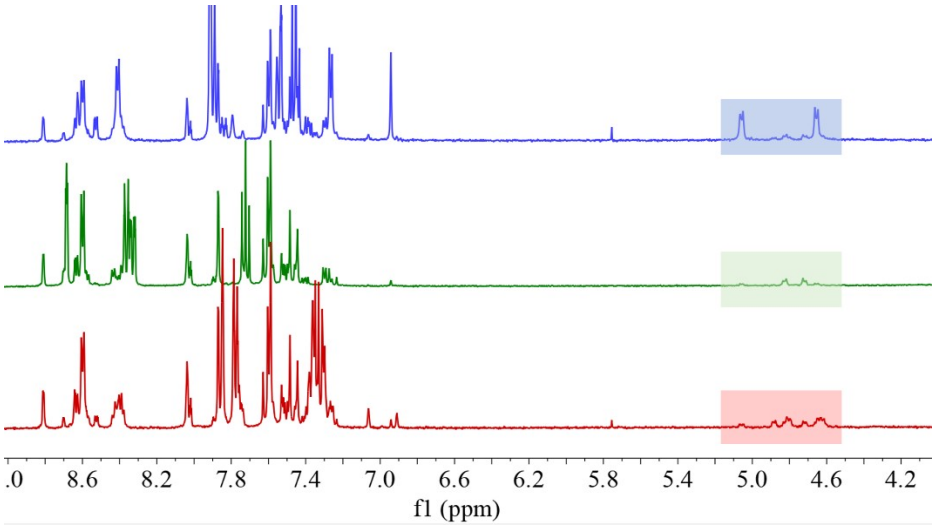


Figure. S18 ^{1}H NMR spectra of **CPs'**.

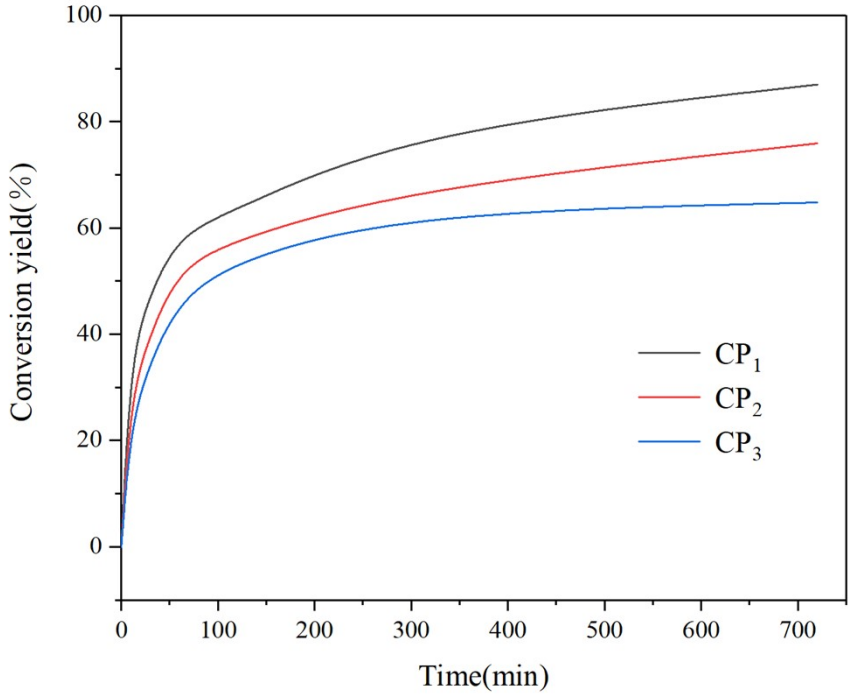


Figure. S19 Time versus percentage conversion plots for **CP_1-CP_3**.

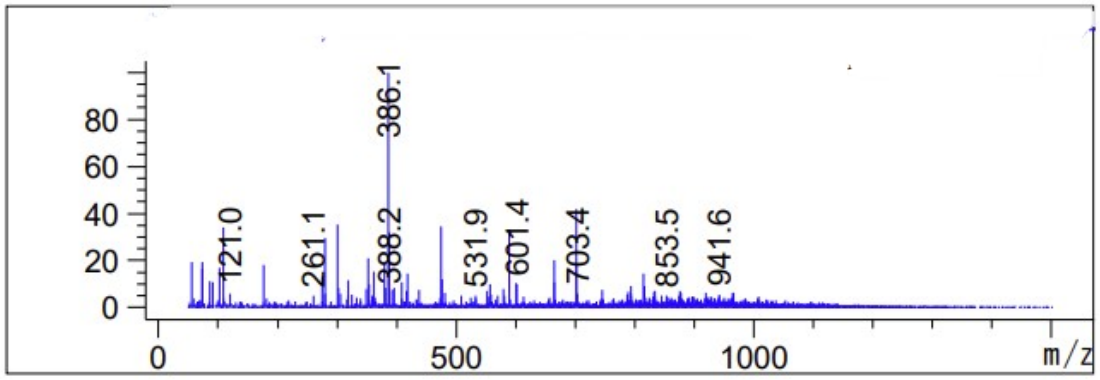


Figure. S20 Mass spectra of Pebpeb.

References

S1. F. Haque, A. Halder and D. Ghoshal, *Cryst. Growth Des.*, 2018, **18**, 5231-5244.

S2. J.-W. Wu, B.-F. Long, M.-F. Wang, D. J. Young, F.-L. Hu, Y. Mi and J.-P. Lang, Chemical Communications, 2022, 58, 2674-2677