Electronic Supplementary Information

Tuning the configuration of the flexible metal-alkene-framework affords pure cycloisomers in solid state photodimerization†

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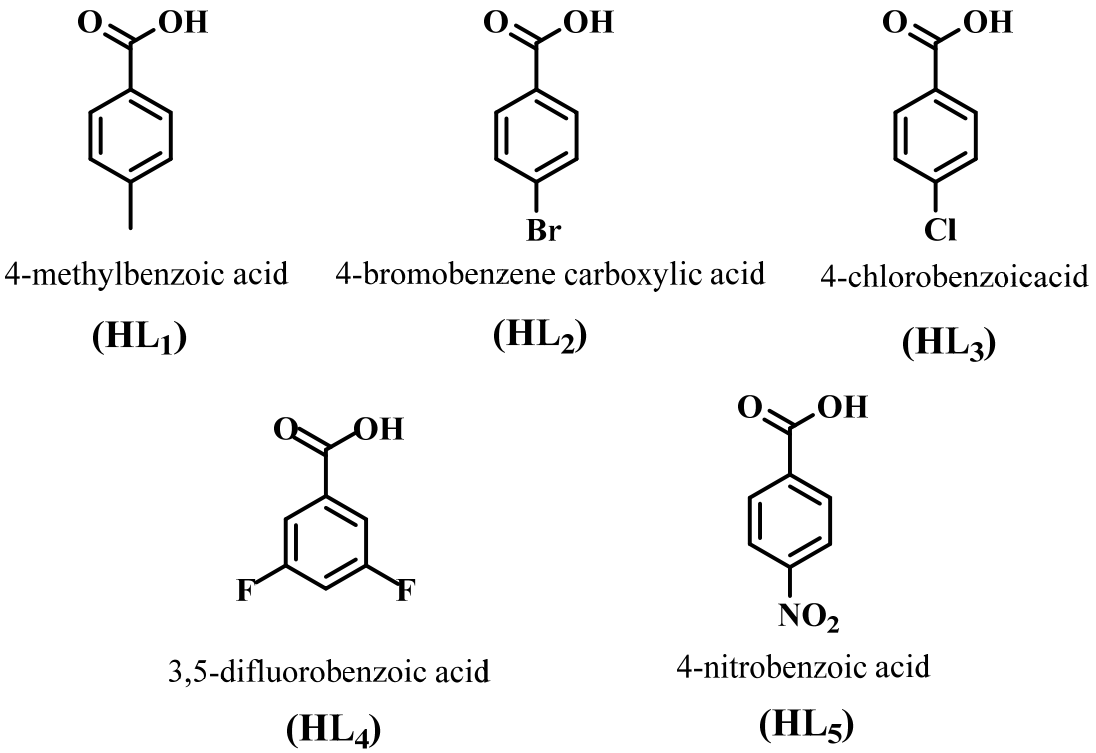
General Procedures.

The ligand 3,5-bis-(2-(pyridin-4-yl)vinyl)pyridine (bpvp) was prepared according to literature methods[1]. Other reagents were obtained commercially and used without further purification. Powder X-ray diffraction (PXRD) patterns were acquired on a PANalyticalX'Pert PRO MPD system (PW3040/60) using Cu Kα radiation (λ = 1.5406Å) from 5° to 50° with a scanning step size of 0.02°. Single-crystal X-ray diffraction data for **CP_1, CP_2, CP_3, CP_4** and **CP_5** were recorded on a Bruker Smart CCD diffractometer or Agilent Xcalibur E. ^{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. 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. 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. The mass spectra were recorded at Bruker micrOTOF-Q III mass spectrometer. 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. The fluorescence spectra were acquired on a JASCO FP-6500 fluorescence spectrophotometer with powdered samples.

Computational studies

All calculations were performed using Gaussian 09.[2] The geometry optimizations

were optimized using B3LYP functional[3] with the triple zeta basis set 6-311++G(d,p).[4] No symmetry constraints were imposed. Analytical frequencies were calculated to verify the nature of all stationary points as minima.



4-methylbenzoic acid **(HL_1)** | 4-bromobenzene carboxylic acid **(HL_2)** | 4-chlorobenzoicacid **(HL_3)**

3,5-difluorobenzoic acid **(HL_4)** | 4-nitrobenzoic acid **(HL_5)**

Scheme S1 The carboxylic acids used in this work.

Experimental

Synthesis

Synthesis of ligand bpvp: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.69 (d, 2H, Ph-H), 8.63 (d, 4H, Py-H), 8.00 (s, 1H, Ph-H), 7.41 (d, 4H, Py-H), 7.33 and 7.17 (d, 4H, CH=CH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 150.50, 148.59, 143.77, 132.04, 130.44, 129.08, 128.89, 121.05 (**Fig. S1**).

Synthesis of CP_1-CP_5

Preparation of $[Cd_3(bpvp)_2(L_1)_6]\cdot 0.5HL_1\cdot H_2O$ (CP_1): Bpvp (6 mg, 0.021 mmol), $CdSO_4\cdot 8/3H_2O$ (26.0 mg, 0.101 mmol) and HL_1 (13.6 mg, 0.010 mmol) were placed

in a thick Pyrex test tube. To this mixture was added 2 mL of solvent (DMF / H_2O = 1:2) and one drop of concentrated nitric acid. The tube was then sealed and heated at 140 °C for 10 hours. Cooling to room temperature resulted in yellow crystals of **CP_1**, that were washed with EtOH and H_2O and dried in air. Yield: 80% based on bpvp. mp. 299.1℃ - 302.2℃. Anal. calcd for $C_{90}H_{78}Cd_3N_6O_{14}$: C, 59.89; H, 4.36; N, 4.66; found: C, 59.72; H, 4.39; N, 4.71. IR (KBr, cm^{-1}): 3436m, 30354m, 2919m, 1932w, 1704w, 1608s, 1531s, 1400s, 1288w, 1222w, 1176s, 1106w, 1068w, 1018s, 767s, 620m, 555m, 420m. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ (bpvp) 8.76 (d, 4H, Ph-H), 8.63 (d, 8H, Py-H), 8.47 (s, 2H, Ph-H), 7.62 (d, 8H, Py-H), 7.66 and 7.53 (d, 8H, CH=CH);δ (L_1) 7.87 (d, 8H, Ph-H), 7.23 (d, 8H, Ph-H), 2.34 (s, 12, CH_3) (**Fig. S12a**).

Preparation of $[Cd_3(bpvp)_2(L_2)_6]\cdot HL_2\cdot 2H_2O$ (CP_2): CP_2 (yellow) was prepared in a similar manner to that of **CP_1**, but HL_2 (12.0 mg, 0.060 mmol) was used instead of HL_1. Yield: 75% based on bpvp. mp. 313.1℃-314.5℃. Anal. calcd for $C_{87}H_{59}Br_7Cd_3N_6O_{16}$: C, 44.64; H, 2.54; N, 3.59; found: C, 44.60; H, 2.43; N, 3.61. IR (KBr, cm^{-1}): 3428m, 3054w, 1928w, 1704w, 1670w, 1596s, 1535s, 1403s,1276w, 1226w, 1168m, 1141s, 1068s, 1010s, 971m, 852s, 802m, 771s, 690m, 663w, 560m, 532m. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ (bpvp) 8.76 (d, 4H, Ph-H), 8.62 (d, 8H, Py-H), 8.46 (s, 2H, Ph-H), 7.62 (d, 8H, Py-H), 7.66 and 7.53 (d, 8H, CH=CH); δ (L_2) 7.96 (d, 8H, Ph-H), 7.49 (d, 8H, Ph-H) (**Fig. S13a**).

Preparation of $[Cd_3(bpvp)_2(L_3)_6]\cdot HL_3\cdot CH_3OH$ (CP_3): CP_3 (yellow) was obtained in a similar manner to that of **CP_1**, but HL_3 (11.0 mg, 0.071 mmol) was used instead

of HL_1.Yield: 90% based on bpvp. mp. 313.5℃-316.1℃. Anal. calcd for $C_{88}H_{63}Cd_3C_{17}N_6O_{15}$: C, 52.07; H, 3.13; N, 4.14; found: C, 52.12; H, 3.06; N, 4.21. IR (KBr, cm^{-1}): 3440m, 3066w, 1589s, 1542s, 1396s, 1276w, 1222w, 1168w, 1095s, 1014s, 968m, 852s, 775s, 690m, 536s, 470w. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ (bpvp) 8.76 (d, 4H, Ph-H), 8.62 (d, 8H, Py-H), 8.46 (s, 2H, Ph-H), 7.62 (d, 8H, Py-H), 7.66 and 7.53 (d, 8H, CH=CH); δ (HL_3) 7.96 (d, 8H, Ph-H), 7.49 (d, 8H, Ph-H) (**Fig. S14a**).

Preparation of $[Cd_2(bpvp)_2(L_4)_4]$ (CP_4): CP_4 (yellow) was obtained in a similar manner to that of **CP_1**, but HL_4 (13.4 mg, 0.085 mmol) was used to instead of HL_1. Yield: 75.3% based on bpvp. mp. 318.3℃-321.7℃. Anal. calcd for $C_{66}H_{42}Cd_2F_8N_6O_8$: C, 55.67; H, 2.97; N, 5.90; found: C, 55.61; H, 3.02; N, 5.95. IR (KBr, cm^{-1}): 3434m, 1612s, 1558s, 1469m, 1434s, 1388s, 1295m, 1222m, 1118s, 894m, 859s, 806m, 775s, 698m, 667m, 559m, 532m. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ (bpvp) 8.76 (d, 4H, Ph-H), 8.62 (d, 8H, Py-H), 8.46 (s, 2H, Ph-H), 7.61 (d, 8H, Py-H), 7.66 and 7.52 (d, 8H, CH=CH); δ (HL_4) 7.54 (m, 8H, Ph-H), 7.37 (m, 4H, Ph-H) (**Fig. S15a**).

Preparation of $[Cd_3(bpvp)_3(L_5)_6(H_2O)]$ (CP_5): CP_5 (red) was obtained in a similar manner to that of **CP_1**, but HL_5 (12.0 mg, 0.072 mmol) was used instead of HL_1. Yield: 85% based on bpvp. mp. 311.4℃-313.2 ℃. Anal. calcd for $C_{99}H_{71}Cd_3N_{15}O_{25}$: C, 53.85; H, 3.24; N, 9.52; found: C, 53.94; H, 3.18; N, 9.48. IR (KBr, cm^{-1}): 3452w, 3074w, 1614s, 1515s, 1403s, 1346s, 1222w, 1106m, 1014s, 971s, 836s, 725s, 618m, 559m, 520s. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ (bpvp) 8.76 (d, 4H, Ph-H), 8.62 (d, 8H, Py-H), 8.45 (s, 2H, Ph-H), 7.61 (d, 8H, Py-H), 7.65 and 7.52 (d, 8H, CH=CH);

δ (HL_5) 8.27 (d, 8H, Ph-H), 8.19 (d, 8H, Ph-H) (**Fig. S16a**).

Photo-irradiation experiment

Crystals (*ca* 0.5 g) of **CP_1**, **CP_2**, **CP_3**, **CP_4** or **CP_5** were placed between glass plates and exposed to a 100W high-pressure mercury lamp (λ = 365 nm) for 2h to form the corresponding photoproducts of **CP_1'**, **CP_2'**, **CP_3'**, **CP_4'** or **CP_5'**, respectively.

Separation of Isomer α and Isomer β

Isomer α: CP_4' (500 mg) was mixed with 30 mL of NaOH solution (4 M) and stirred at room temperature for 2 h. The solution was extracted with $CHCl_3$ (3×30 mL) and the combined organic extracts were concentrated *in vacuo* to produce **Isomer α** as a white powder. Yield: 94% based on **CP_4'**. mp. 225.6℃-226.0℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ (Isomer α) 8.49 (d, 8H, Py-H), 7.87 (m, 4H,Py-H), 7.66 (s, 2H, Py-H), 7.10 (d, 8H, Py-H), 4.73~4.60 (d, 8H, -C_4H_4-); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.21, 147.27, 147.17, 134.58, 131.55, 122.18, 49.01, 42.05 (**Fig. S19**).

Isomer β: Isomer β (white powder) was obtained in a similar manner to that of Isomer α but **CP_1'** (500 mg) was used instead of **CP_4'**.Yield: 97% based on **CP_1'**. mp. 244.5℃-245.1℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ (**Isomer β**) 8.50~8.46 (m, 8H, Py-H), 8.07 and 7.85 (s, 4H,Py-H), 7.30 (s, 2H, Py-H), 7.14~7.05 (m, 8H, Py-H), 4.77~4.75 (m, 8H, -C_4H_4-); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.23, 149.12, 147.01, 146.79, 144.18, 137.94, 131.78, 131.67, 122.17, 122.03, 48.82, 48.14, 41.92, 41.88 (**Fig. S22**).

Single crystal structure determination: Structures were solved by Direct methods and refined by full-matrix least-squares techniques using the *SHELXL*-2014,

SHELXL-2017 or *SHELXL*-2018 programs. 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. The SQUEEZE program was used to remove the contribution of the highly disordered lattice solvent (for **CP1**). A summary of key crystallographic information for **CP1-CP5**, Isomer α and Isomer β is given in Table 1. The CCDC codes for these compounds are 2033936-2033942.

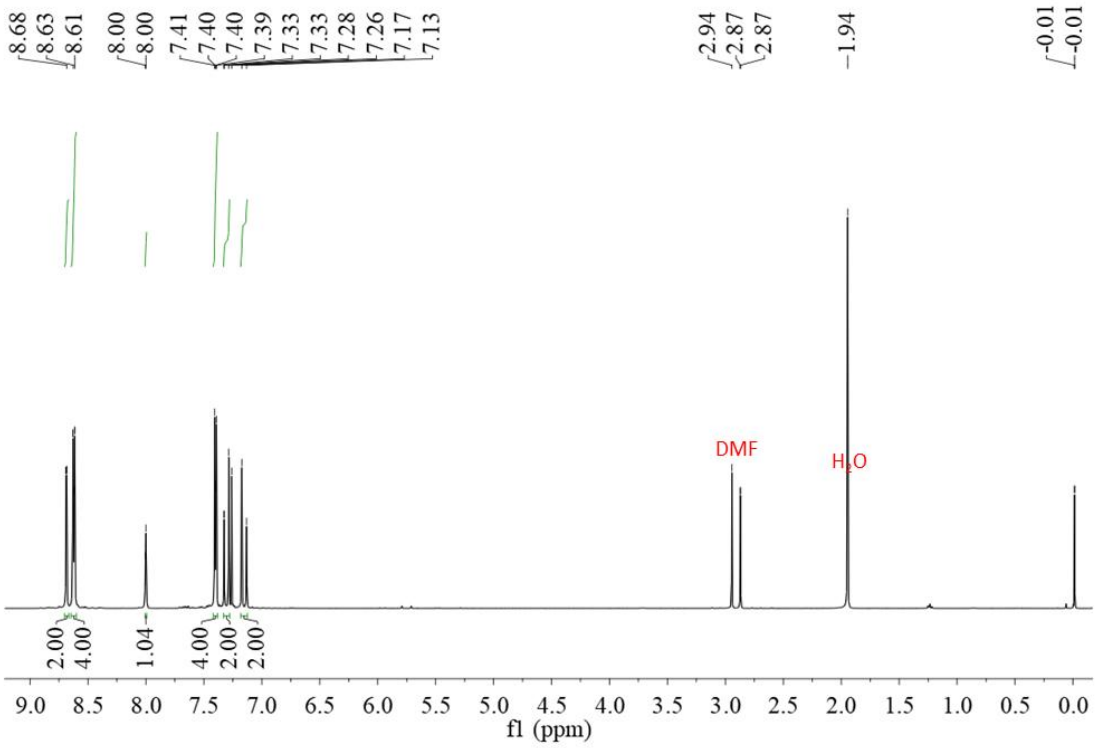
Table S1 Summary of Crystal Data and Structure Refinement Parameters for **CP1-CP5**, **Isomer α** and **Isomer β**

	CP1 (2033939)	**CP2** (2033938)	**CP3** (2033937)	**CP4** (2033936)
Empirical formula	$C_{90}H_{78}Cd_3N_6O_{14}$	$C_{87}H_{59}Br_7Cd_3N_6O_{16}$	$C_{88}H_{63}Cd_3C_{l7}N_6O_{15}$	$C_{66}H_{42}Cd_2F_8N_6O_8$
Formula weight	1804.78	2340.97	2029.79	1423.85
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P-1*	*P-1*	*P-1*	*P-1*
a/Å	11.308(5)	11.2823(7)	11.3948(13)	11.5990(6)
b/Å	20.365(8)	19.7270(13)	19.656(2)	12.8851(9)
c/Å	20.908(9)	21.7507(15)	21.412(3)	21.3522(12)
α/°	110.484(5)	67.5530(10)	67.534(2)	101.600(5)
β/°	100.264(6)	90.2020(10)	90.301(3)	103.465(4)
γ/°	96.098(6)	73.3800	73.1500	94.762(5)
V/Å^3	4364(3)	4252.5(5)	4204.8(9)	3011.7(3)
D_c/g cm^{-3}	1.374	1.828	1.603	1.570
Z	2	2	2	2
μ (Mo-Ka)/mm^{-1}	0.788	4.102	1.044	0.793
Total reflections	23755	42492	36877	24099
Unique reflections	15144	14898	14361	10598
No. observations	10888	10698	8718	6289
No. parameters	1058	1087	1074	811
F(000)	1832	2280	2032	1424
R_1[a]	0.0432 (10888)	0.0674 (10698)	0.0783 (8718)	0.0554 (6289)
wR_2[b]	0.1321 (15144)	0.2160 (14898)	0.2481 (14361)	0.1361 (10598)
GOF[c]	1.014	1.043	1.047	1.031

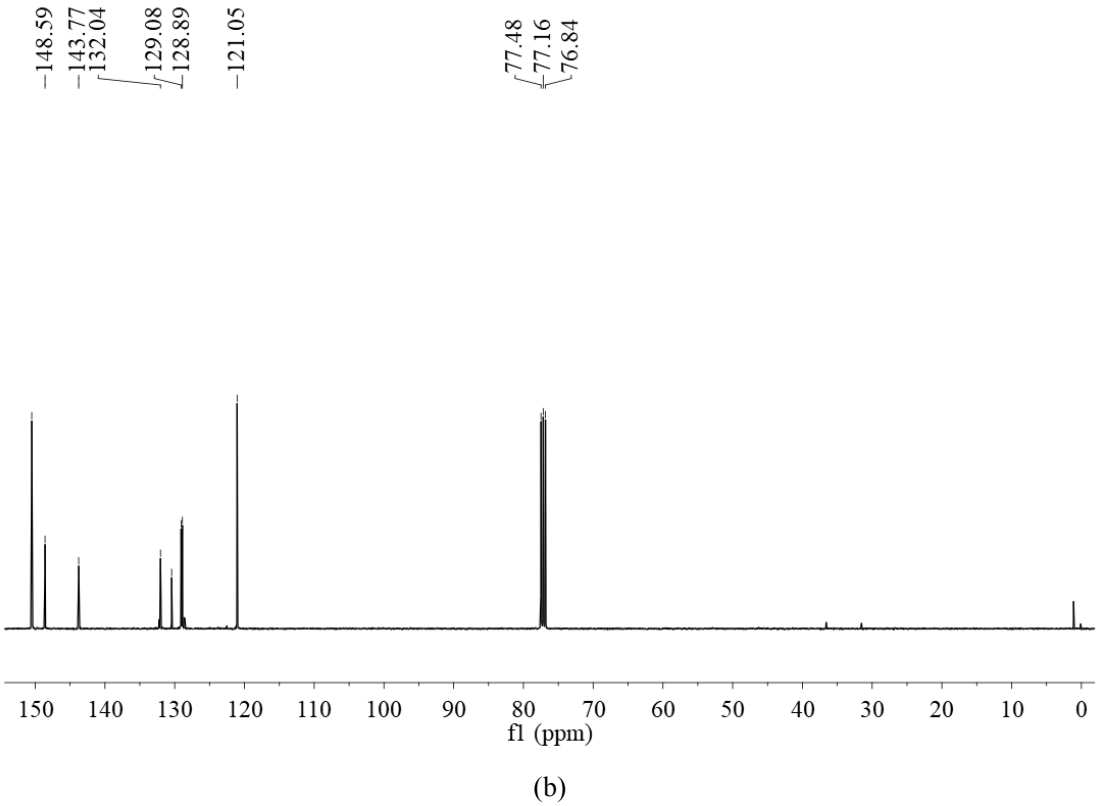
to be continued for **Table S1**

	CP$_5$ (2033940)	**Isomer α** (2033941)	**Isomer β** (2033942)
Empirical formula	$C_{99}H_{71}Cd_3N_{15}O_{25}$	$C_{39}H_{35}Cl_3N_6O_2$	$C_{38}H_{36}N_6O_3$
Formula weight	2201.89	726.08	624.73
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*P-1*	$P2_1/c$
a/Å	41.888(16)	12.2763(11)	10.8951(5)
b/Å	13.237(5)	12.7413(12)	18.6016(8)
c/Å	37.521(13)	13.7157(13)	19.3051(9)
α/°	90	76.210(8)	90
β/°	102.236(13)	67.384(9)	90.318(6)
γ/°	90	63.288(9)	90
V/Å^3	20332(13)	1763.4(3)	3912.4(3)
D_c/g cm^{-3}	1.439	1.367	10.61
Z	8	2	4
μ/mm^{-1}	0.701	0.305	0.551
Total reflections	66726	12673	43859
Unique reflections	17740	6219	7129
No. observations	14996	4097	4490
No. parameters	1288	451	478
F(000)	8880	756	1320.0
R_1[a]	0.0500(14996)	0.0788(4097)	0.0378(4490)
wR_2[b]	0.1440(17740)	0.2138(6219)	0.1032(7129)
GOF[c]	1.107	1.064	1.047

[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]$\text{GOF} = \{\Sigma w((F_0^2 - F_c^2)^2)/(n - p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

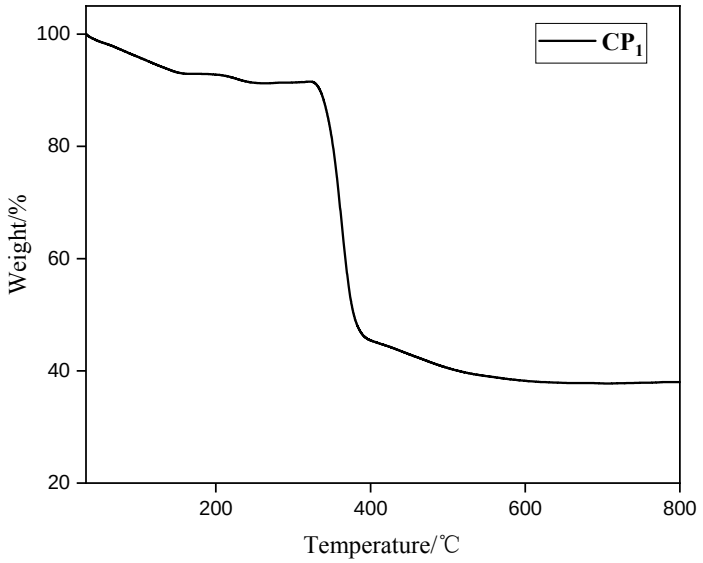


(a)

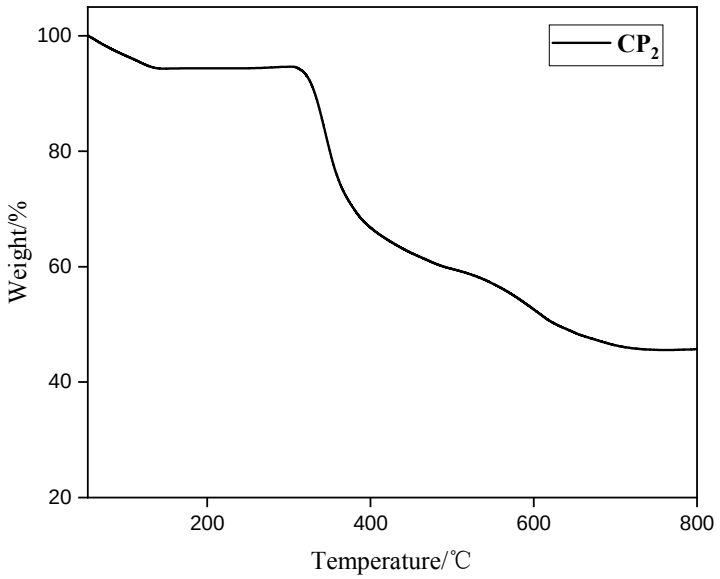


(b)

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


CP1
100
80
60
40
20
Weight/%
200
400
600
800
Temperature/℃

(a)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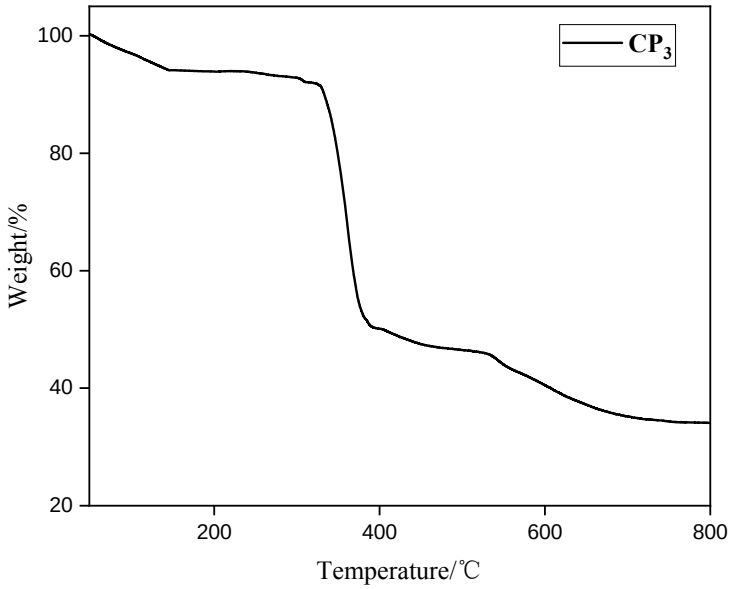
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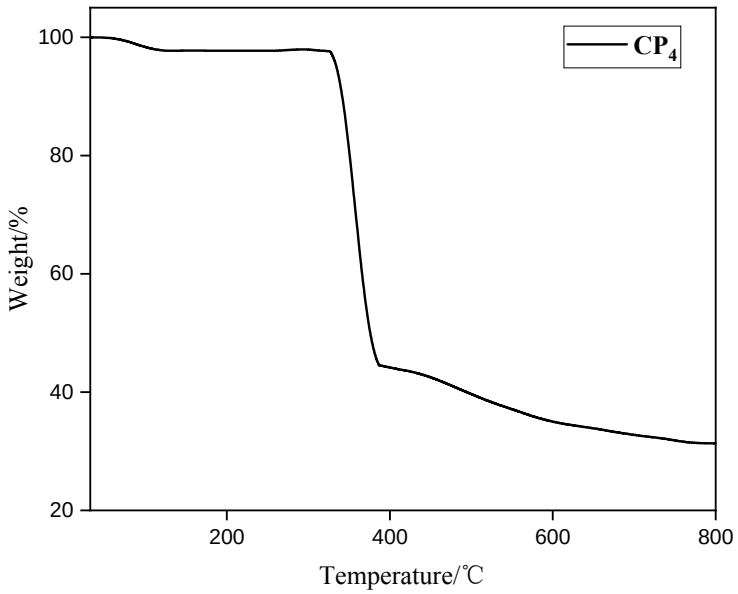
600
800
Temperature/℃

(c)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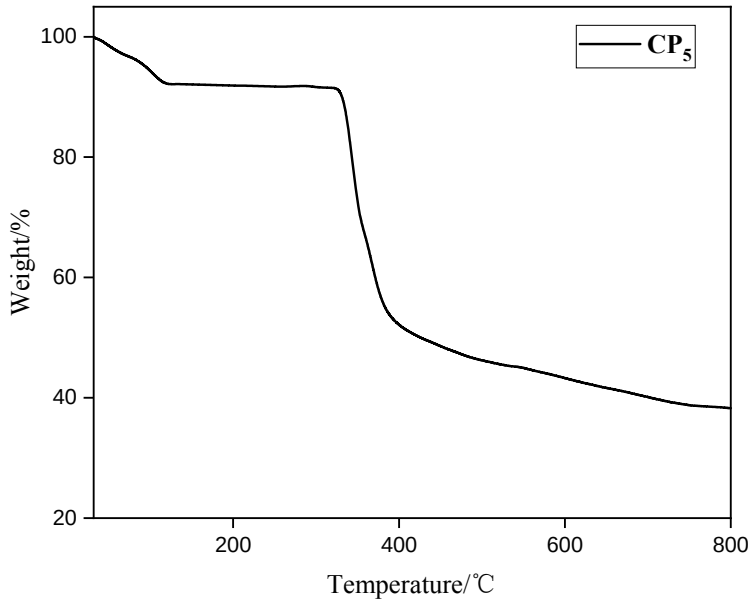
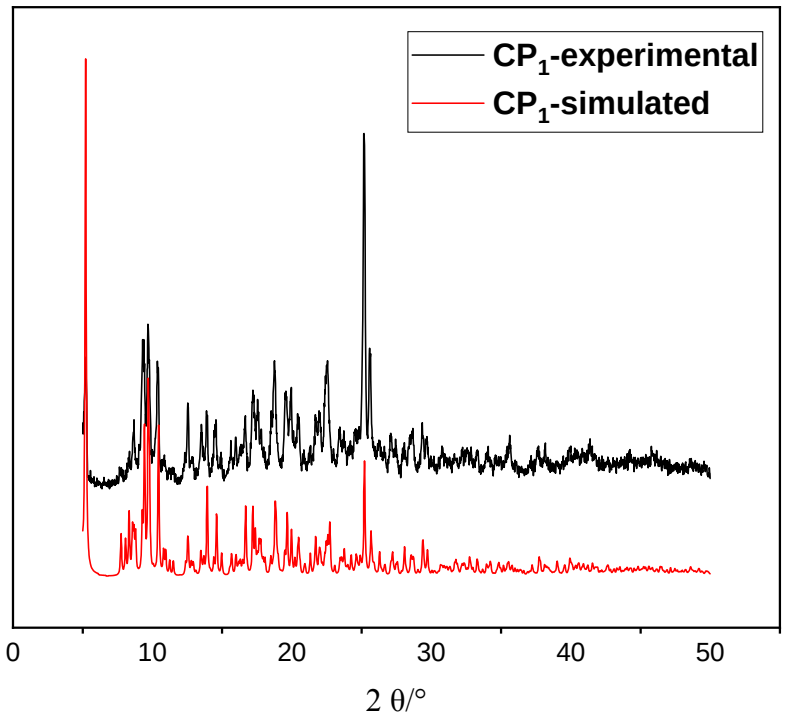
40
20
Weight/%
200
400
600
800
Temperature/℃

(d)

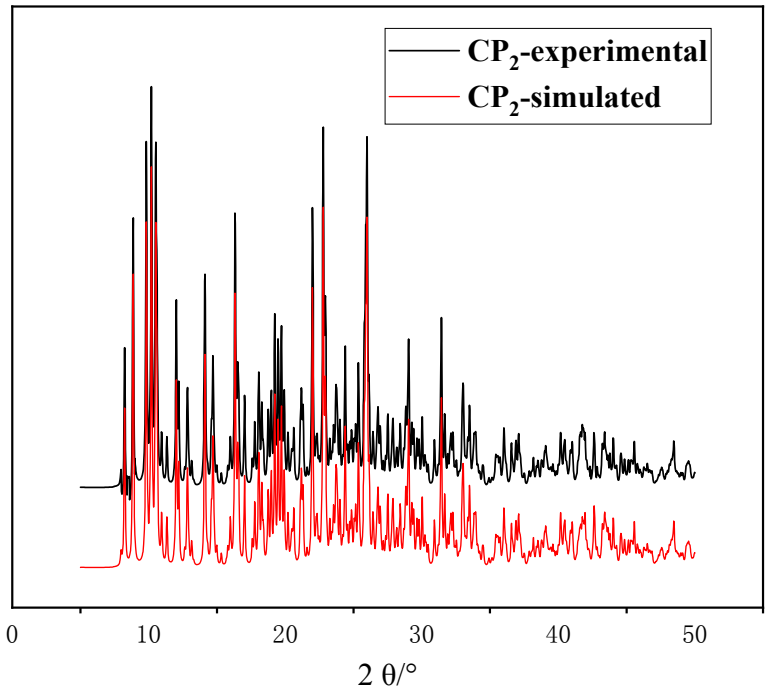


(e)

Fig. S2 Thermogravimetric analysis plots of (**CP1** (a), **CP2** (b), **CP3** (c), **CP4** (d), **CP5** (e).



(a)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CP2-simulated
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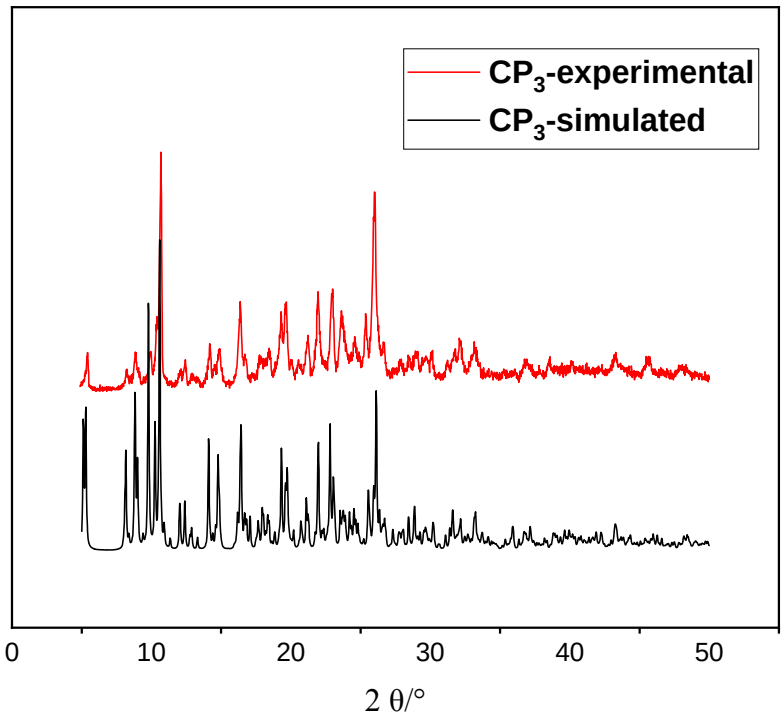
10
20
30
40
50
2 θ/°

(b)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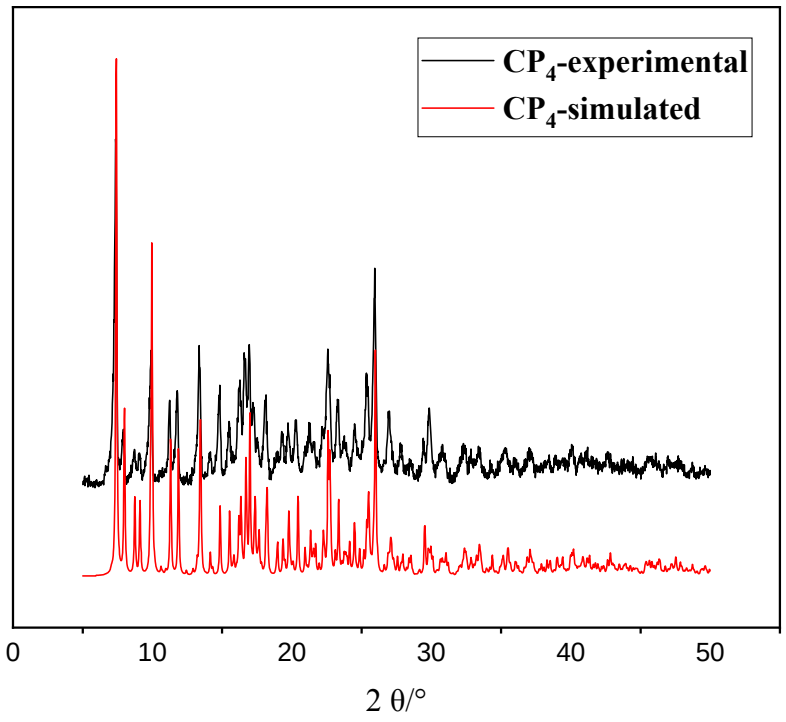
CP3-simulated
0
10
20
30
40
50
2 θ/°

(c)



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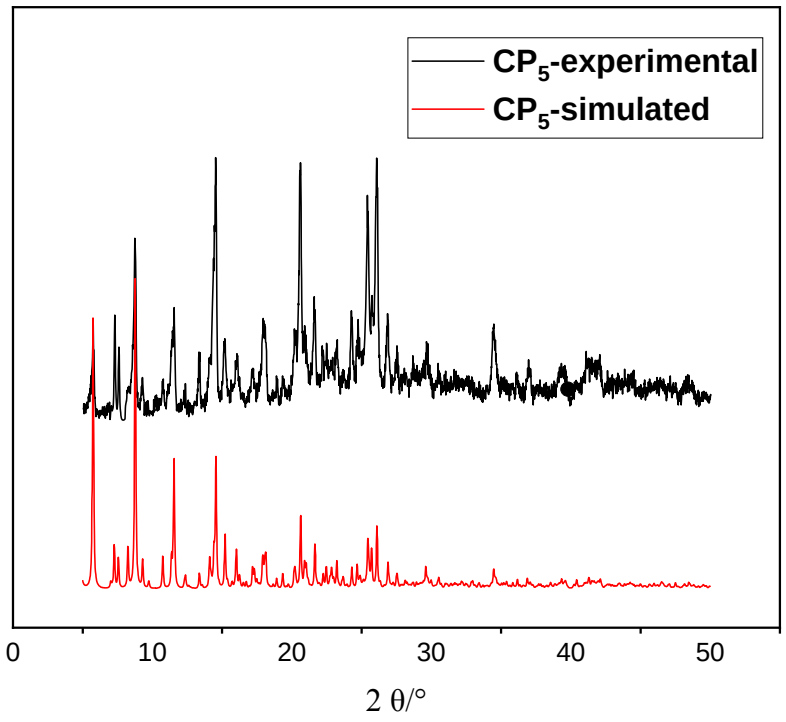


(e)

Fig. S3 PXRD patterns of **CP1** (a), **CP2** (b), **CP3** (c), **CP4** (d), **CP5** (e).

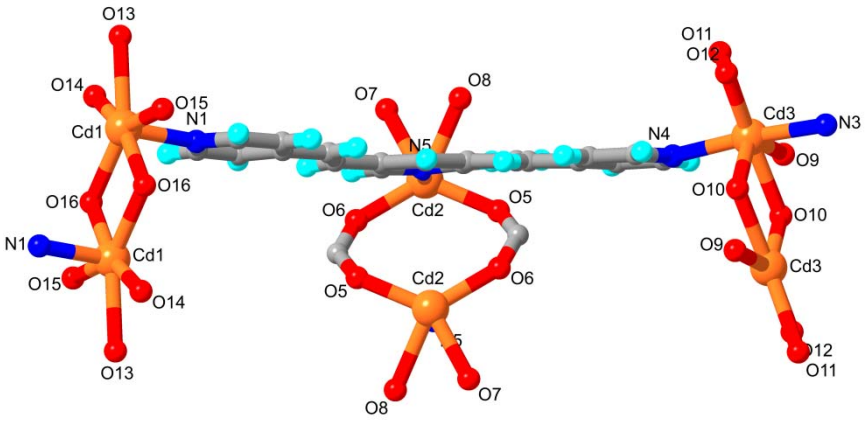


Fig. S4 View of the coordination environments of Cd(II) centers in **CP_1**.

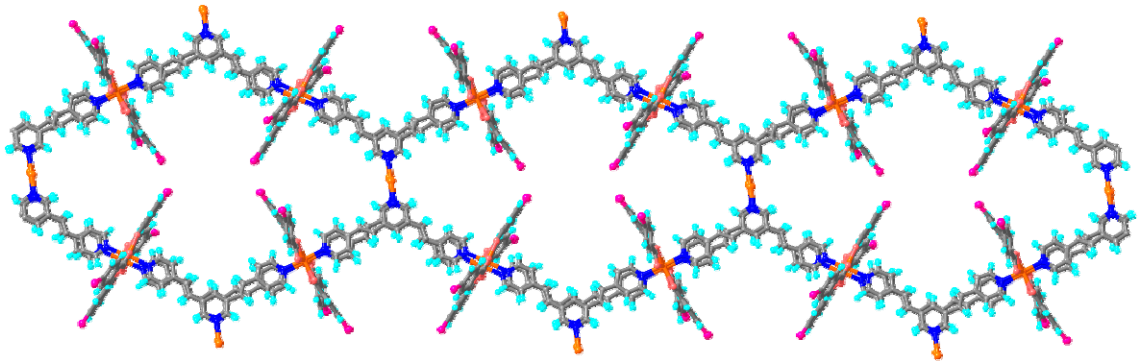


Fig. S5 The adjacent zigzag chains are connected to form a 2D network.

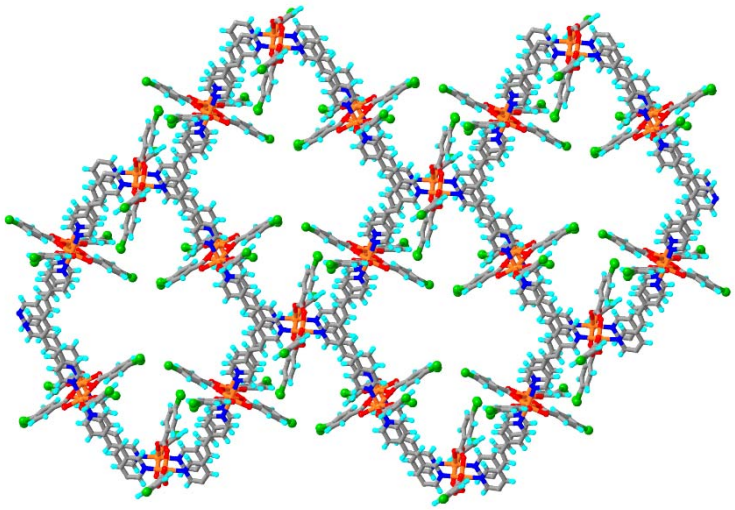


Fig. S6 View of the 2D network showing hexagonal windows.

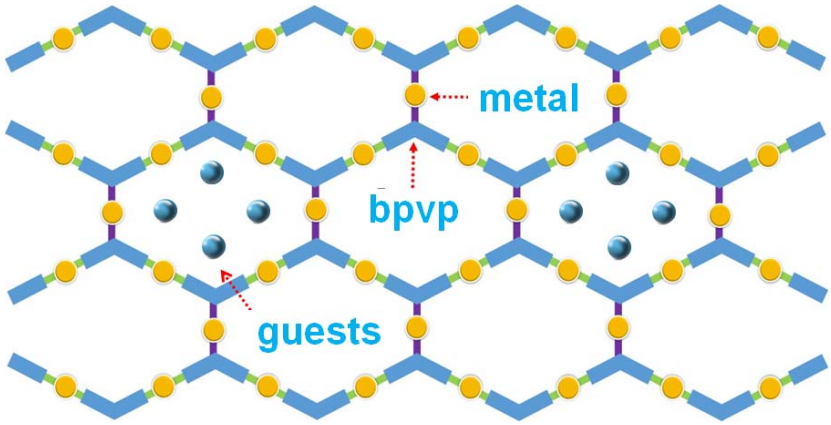
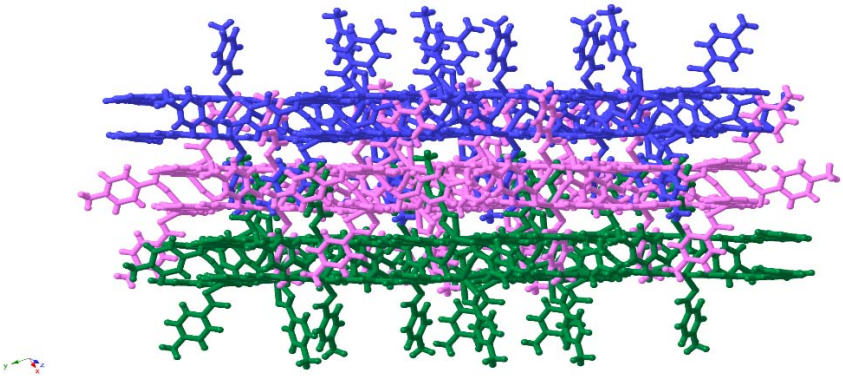
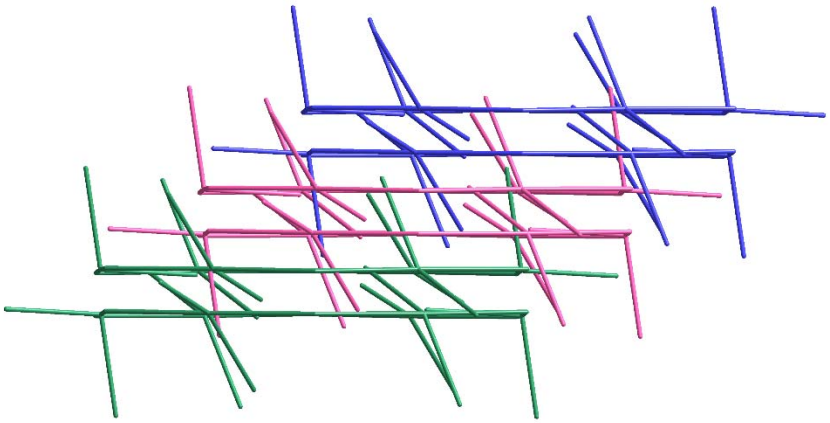


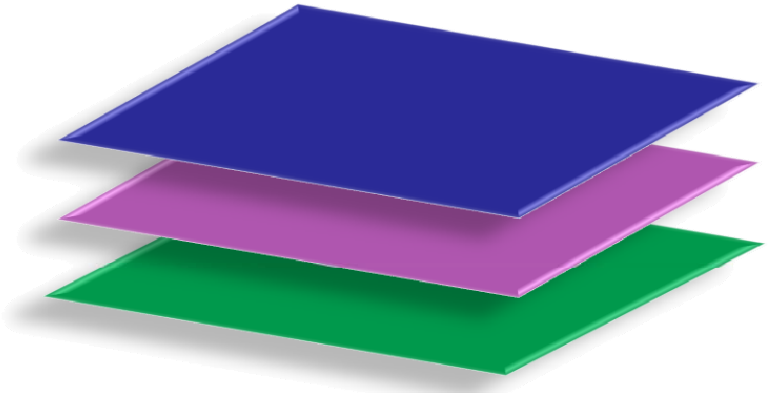
Fig. S7 Cartoon showing the 2D network in **CP_1-CP_3**.



(a)



(b)



(c)

Fig. S8 (a) 3D polypseudo-threading network; (b) A schematic illustration of three adjacent 2D layers; (c) A schematic illustration of the mutual polypseudo-threading of three layers.

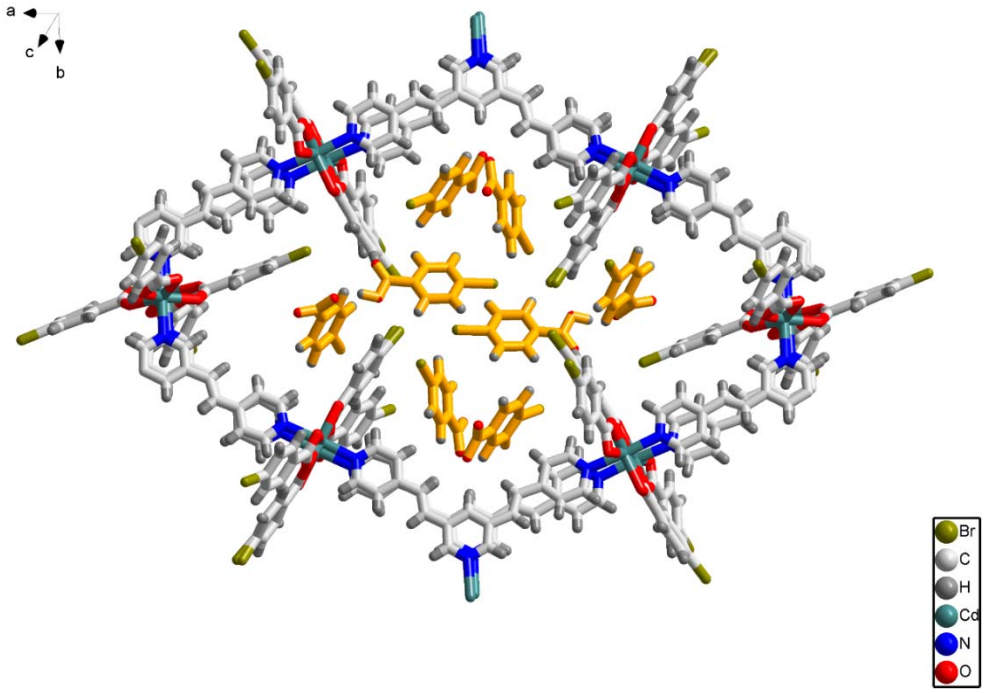
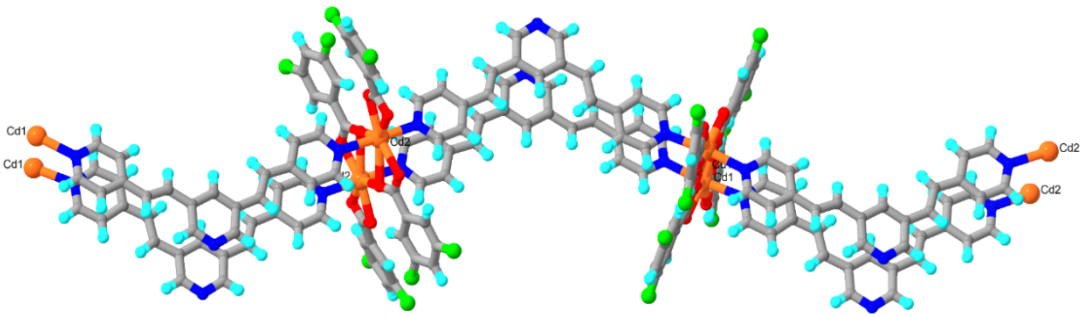
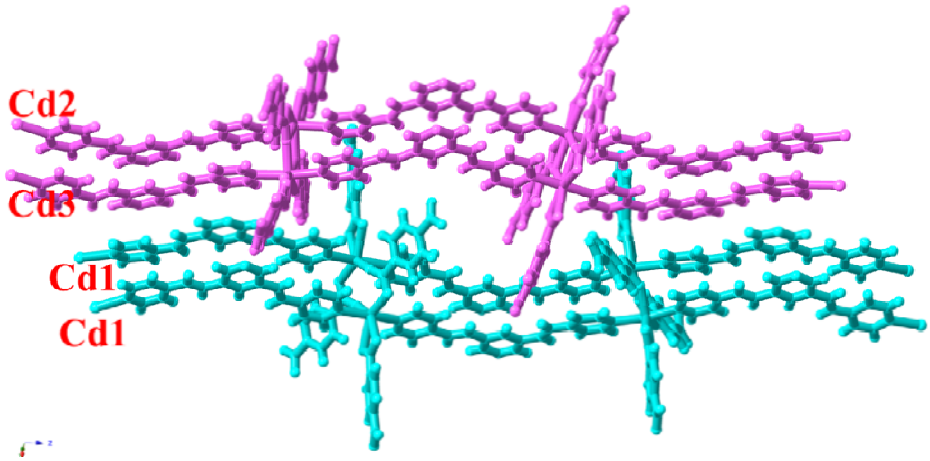


Fig. S9 Fourteen L_2 (or HL_2) molecules were embedded in the hexagonal window in **CP_2**.

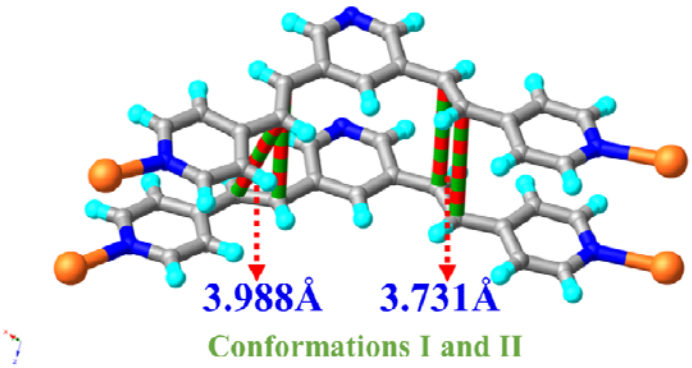


(a)

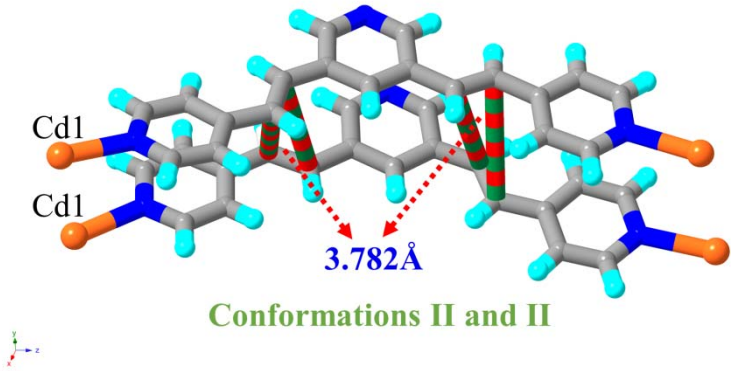


(b)

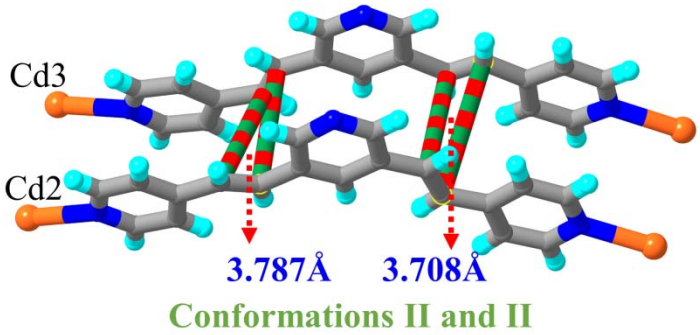
Fig. S10 View of the 1D chain structures of **CP$_4$** (a) and **CP$_5$** (b).



(a)

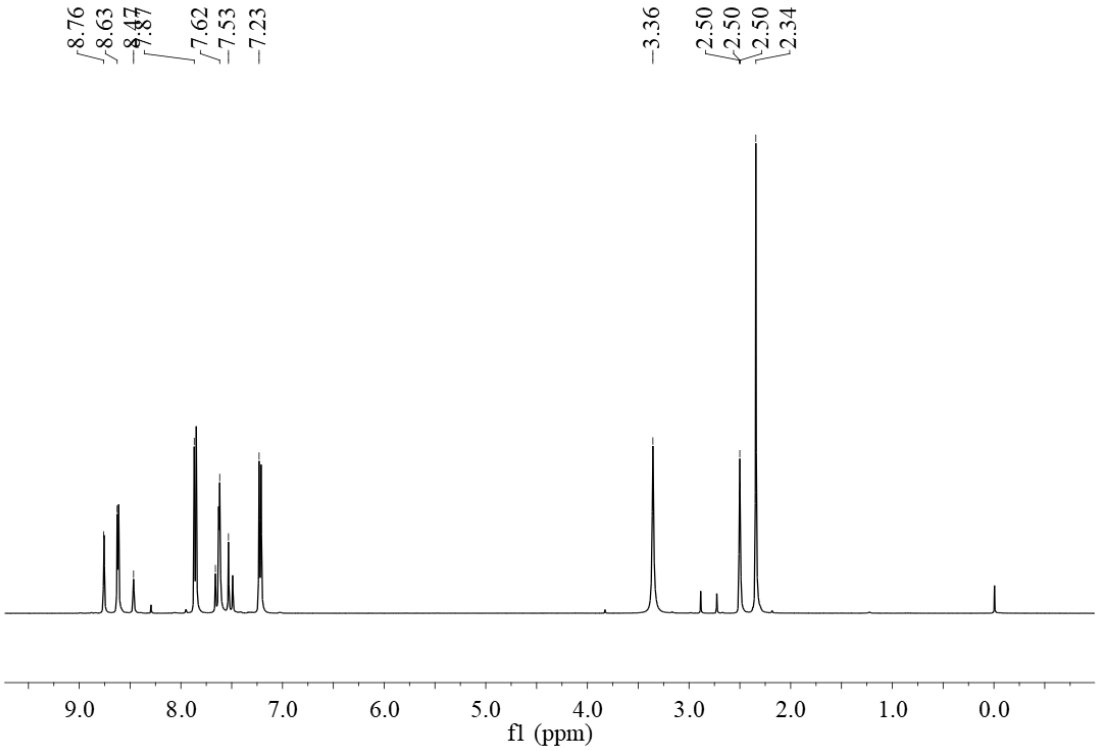


(b)

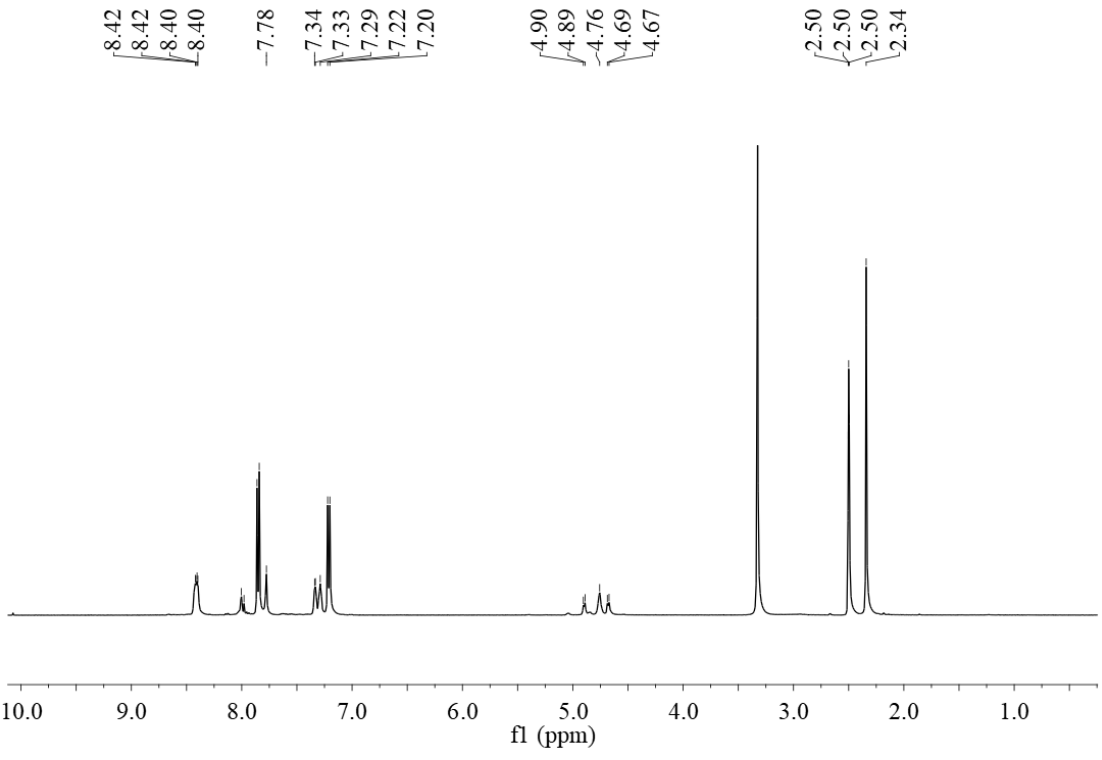


(c)

Fig. S11 View of the distances between each pair of C=C in **CP$_4$** (a) and **CP$_5$** (b), showing the face-to-face alignment of each bpvp pair in **CP$_4$** and **CP$_5$**.

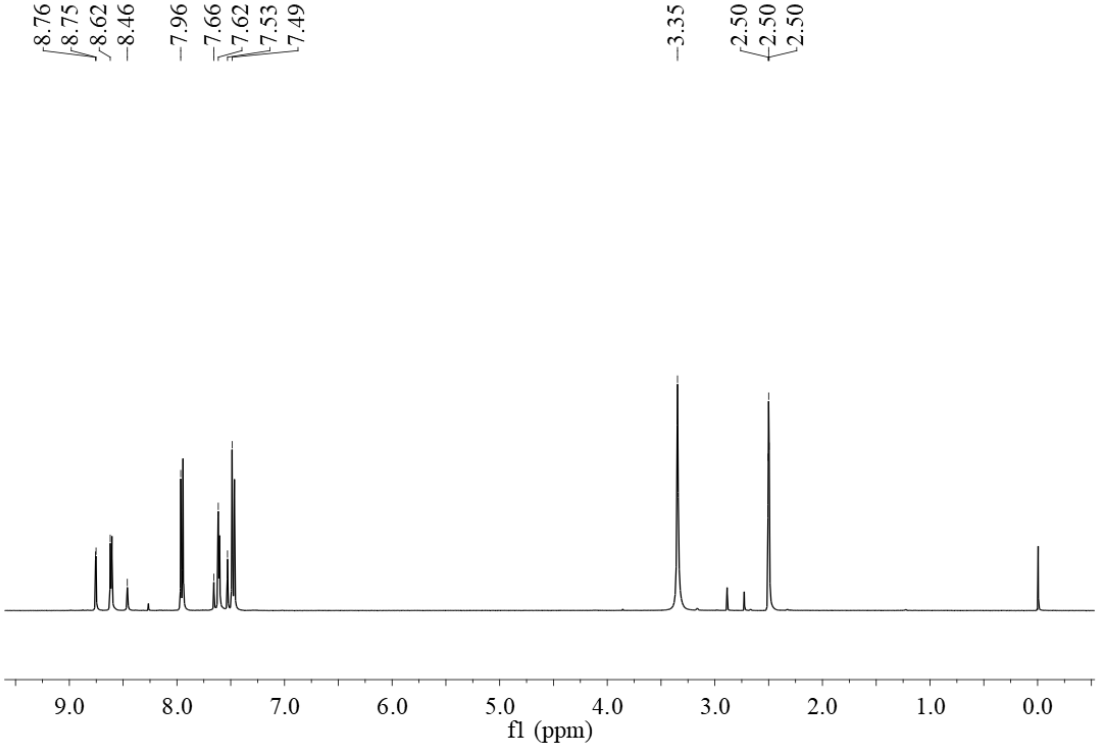


(a)

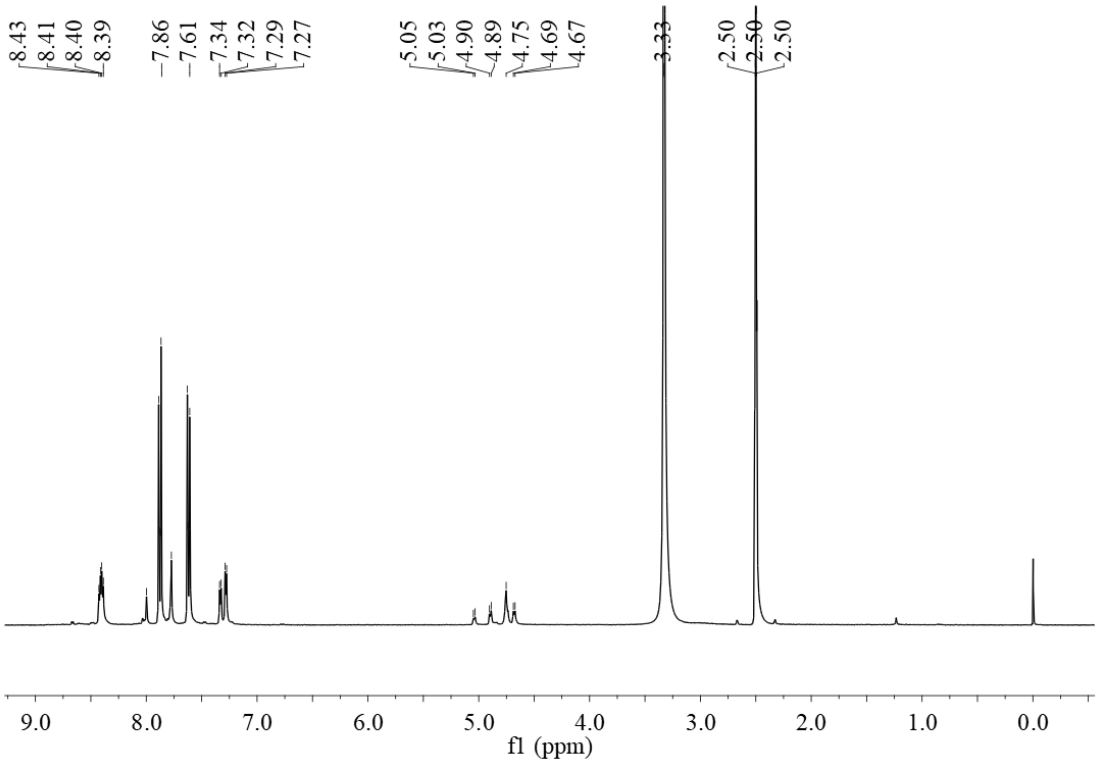


(b)

Fig. S12 (a) The ^{1}H NMR spectrum of **CP$_1$**; (b) The ^{1}H NMR spectrum of **CP$_1$'** (DMSO-d_6).

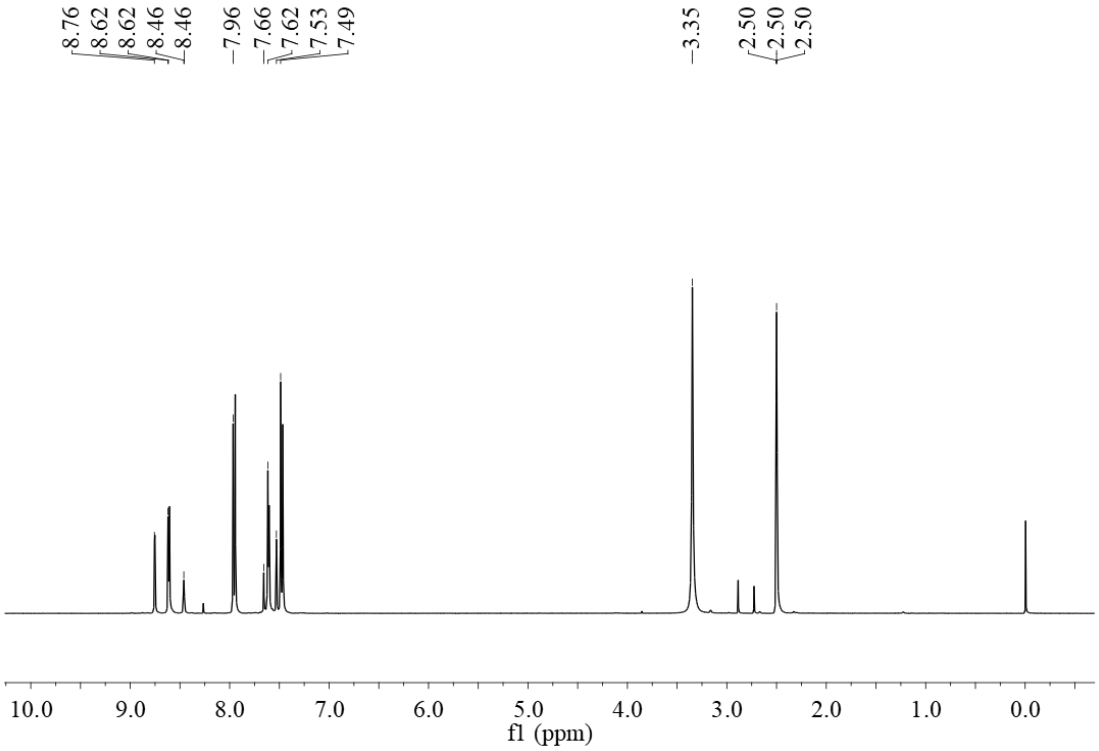


(a)

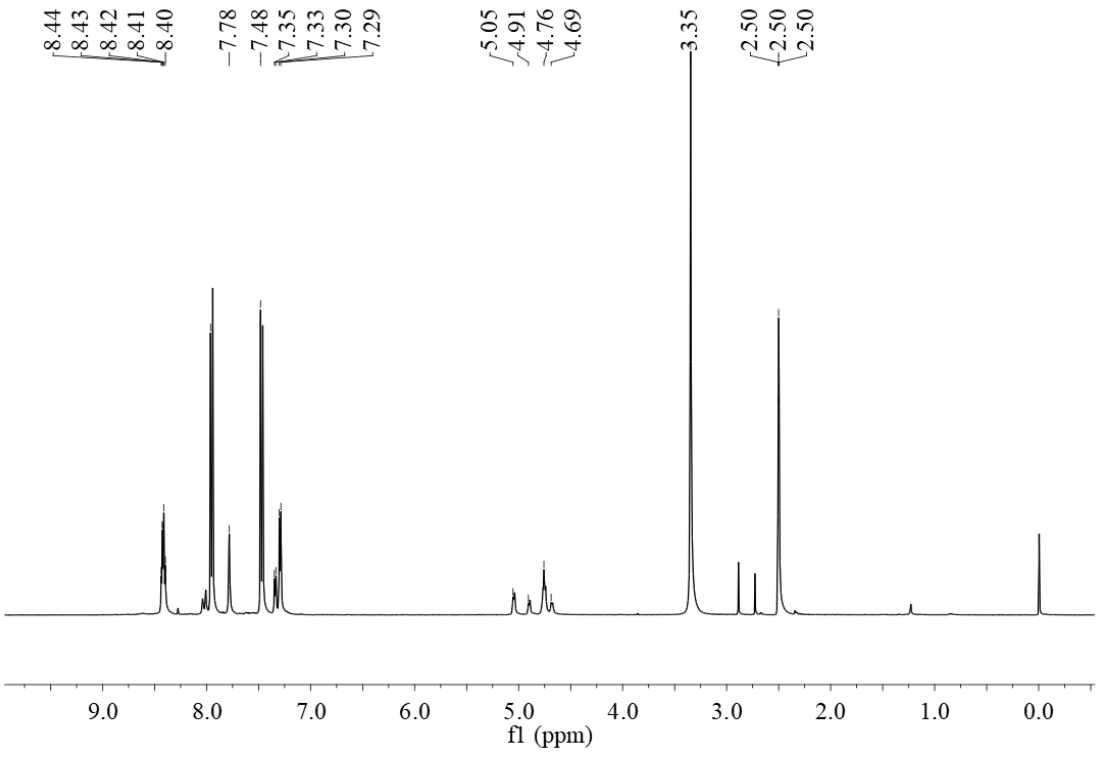


(b)

Fig. S13 (a) The ^{1}H NMR spectrum of **CP$_2$**; (b) The ^{1}H NMR spectrum of **CP$_2$'** (DMSO-*d*$_6$).

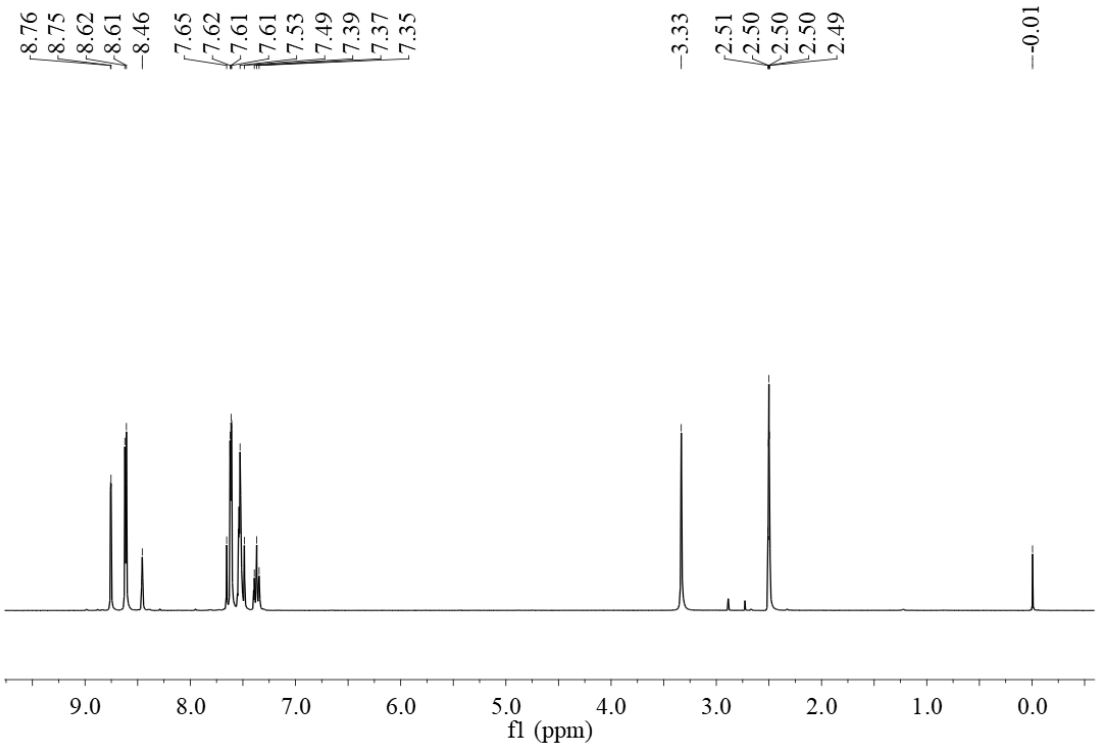


(a)

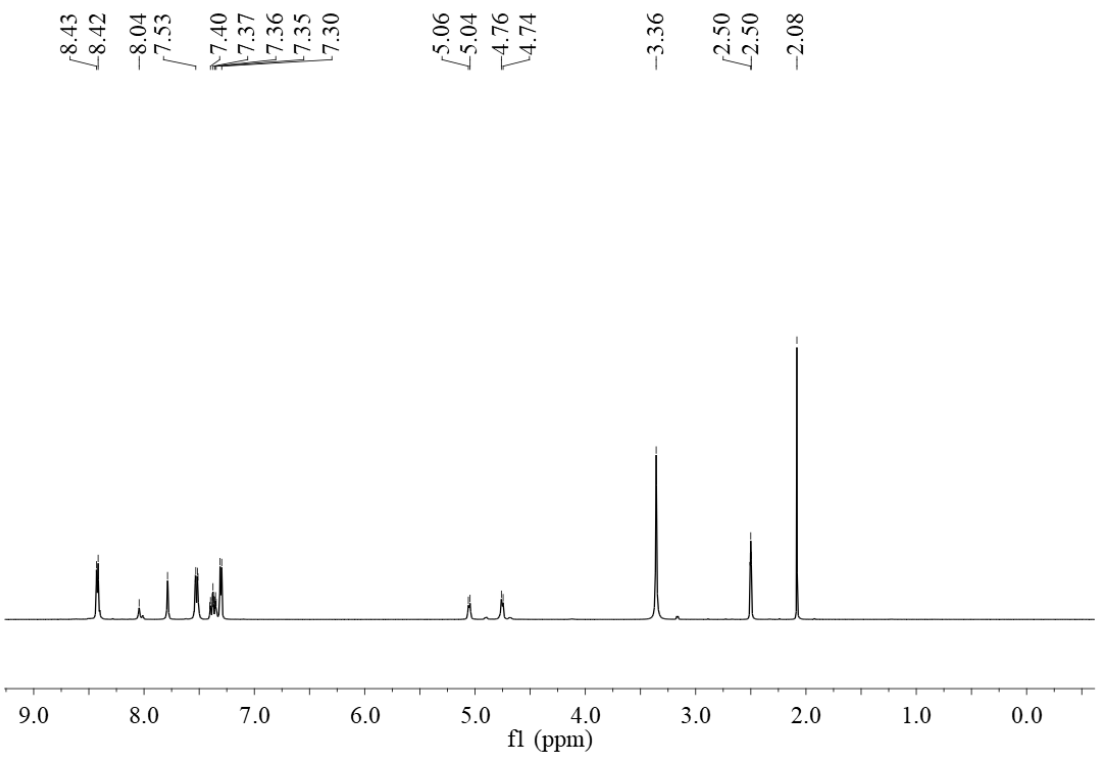


(b)

Fig. S14 (a) The ^{1}H NMR spectrum of **CP$_3$**; (b) The ^{1}H NMR spectrum of **CP$_3$'** (DMSO-d_6).

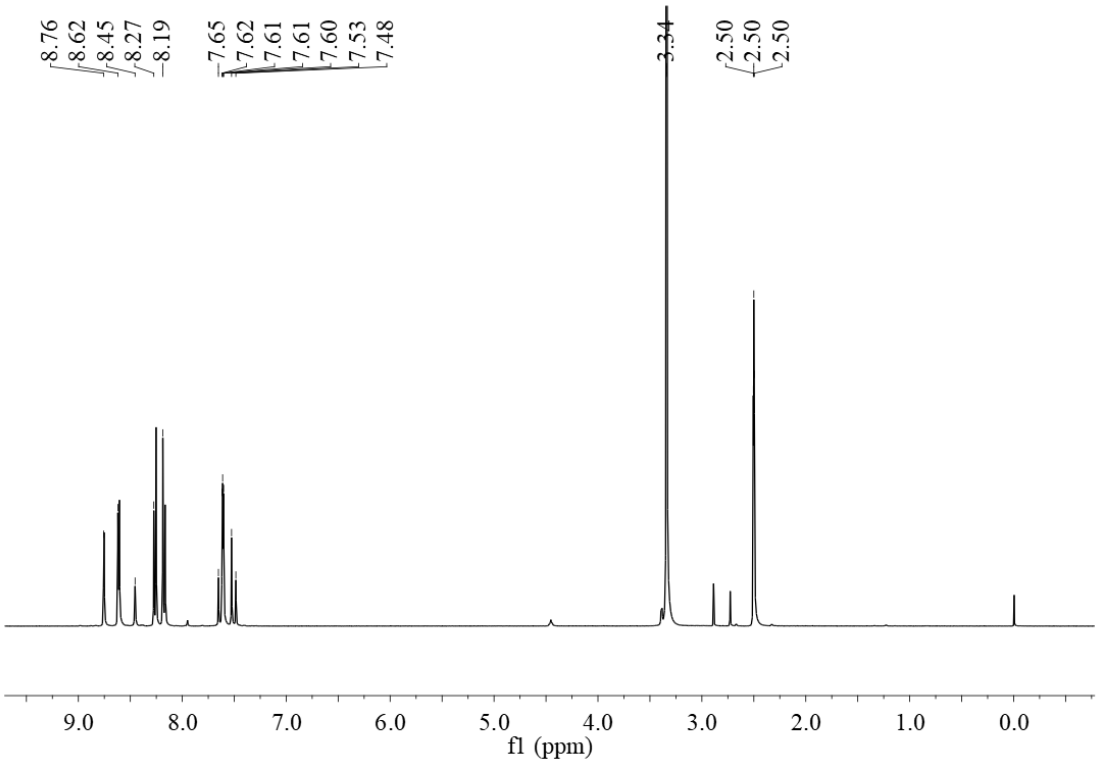


(a)

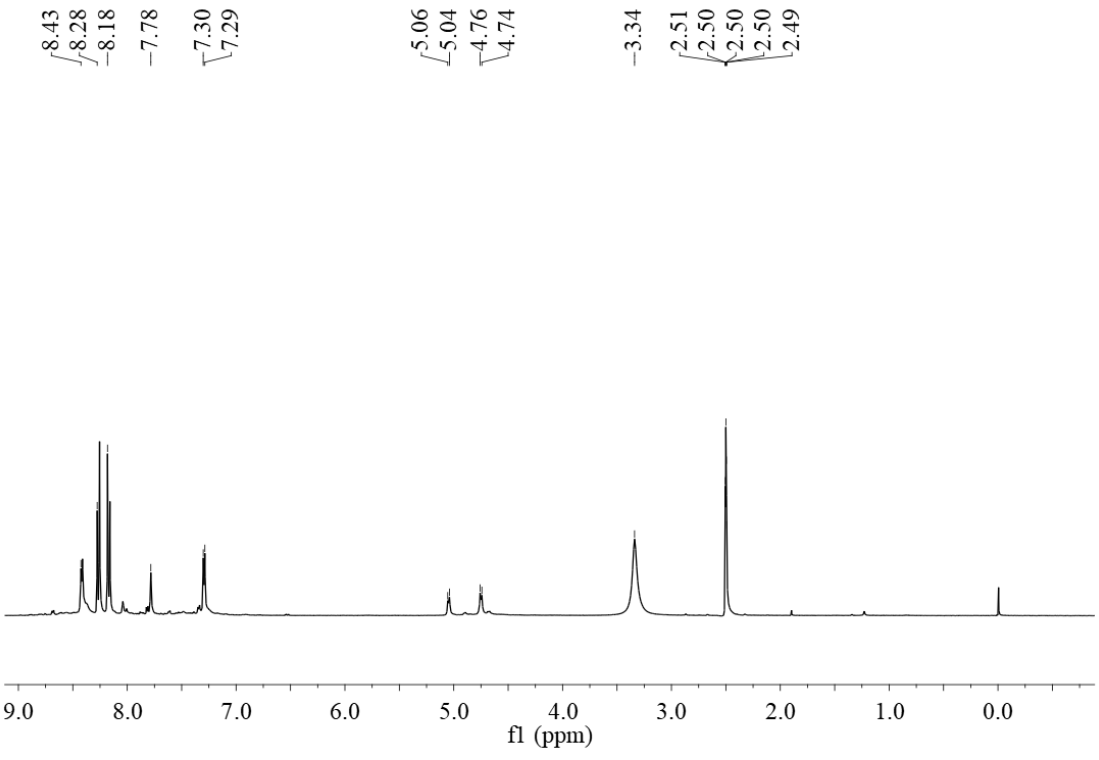


(b)

Fig. S15 (a) The ^{1}H NMR spectrum of **CP$_4$**; (b) The ^{1}H NMR spectrum of **CP$_4$'** (DMSO-d_6).

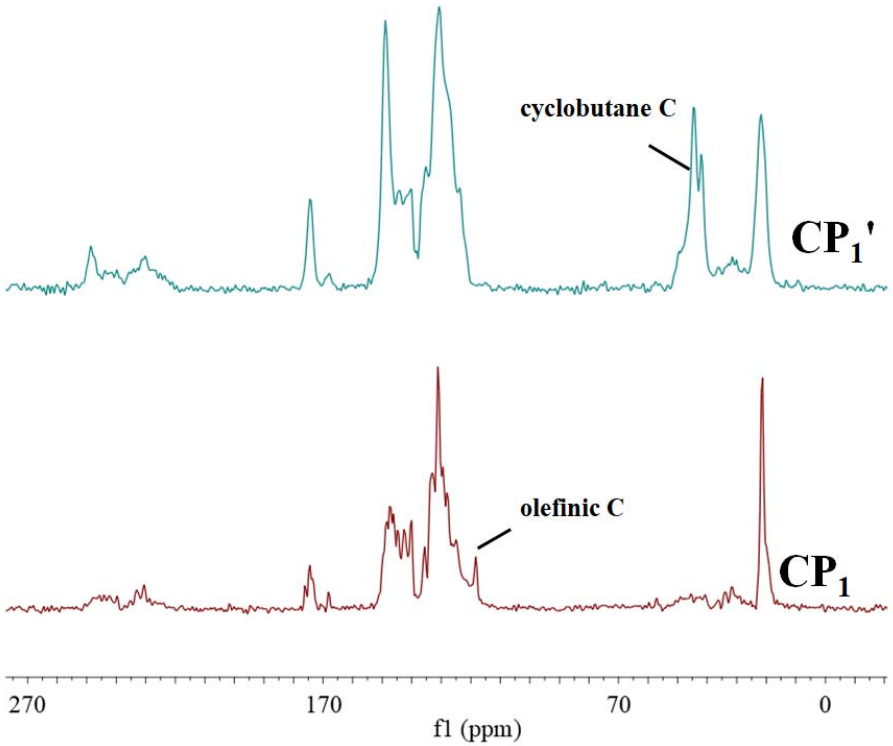


(a)

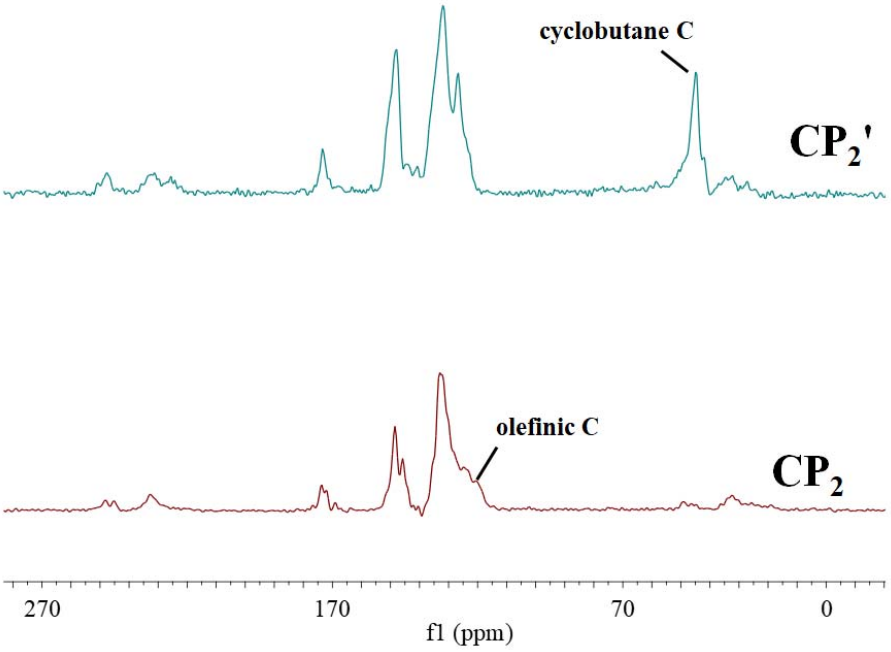


(b)

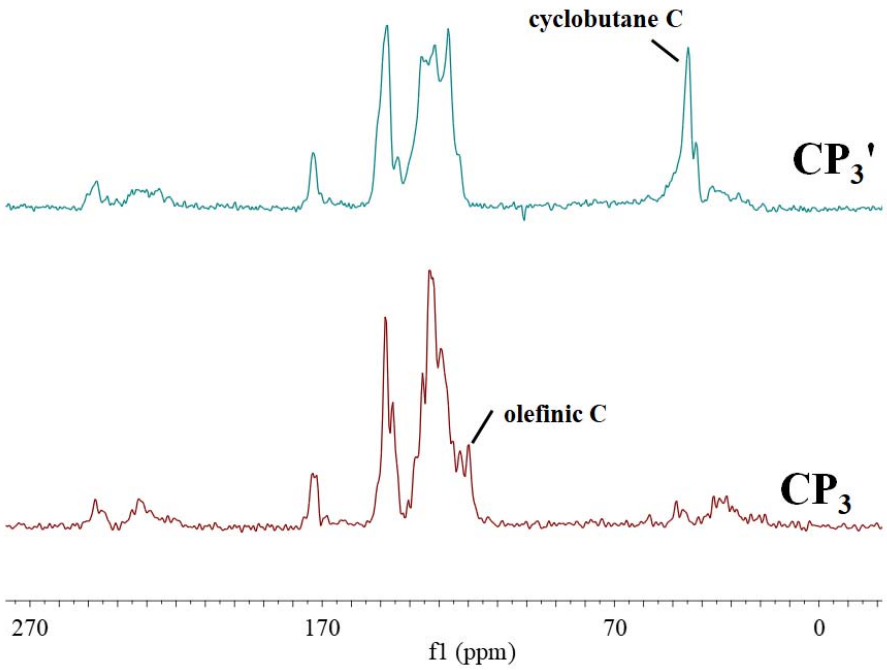
Fig. S16 (a) The ^{1}H NMR spectrum of **CP$_5$**; (b) The ^{1}H NMR spectrum of **CP$_5$'** (DMSO-d_6).


cyclobutane C
CP1'
olefinic C
CP1
270
170
70
0
f1 (ppm)

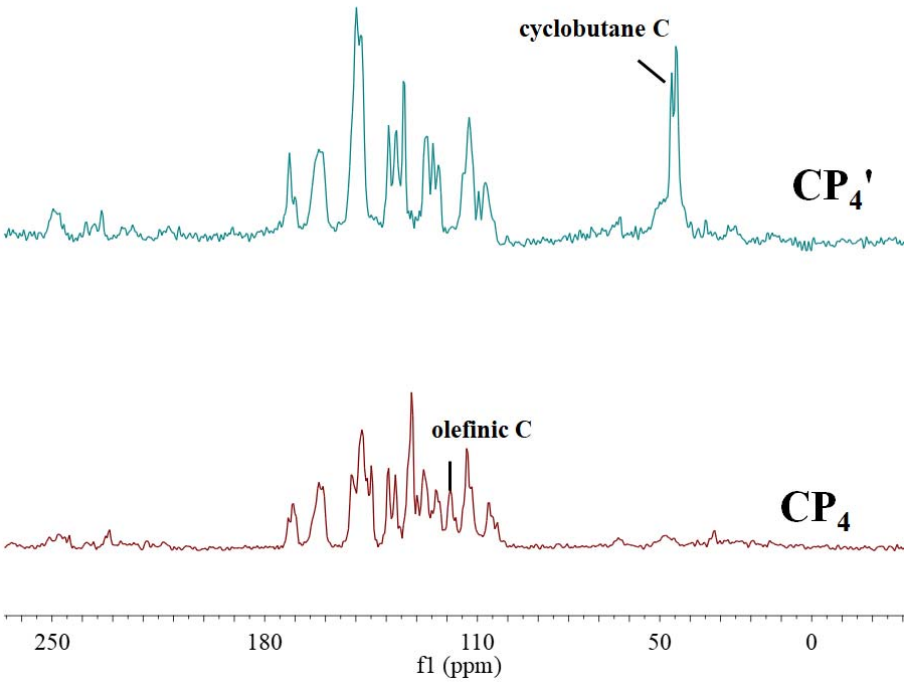
(a)


cyclobutane C
CP2'
olefinic C
CP2
270
170
70
0
f1 (ppm)

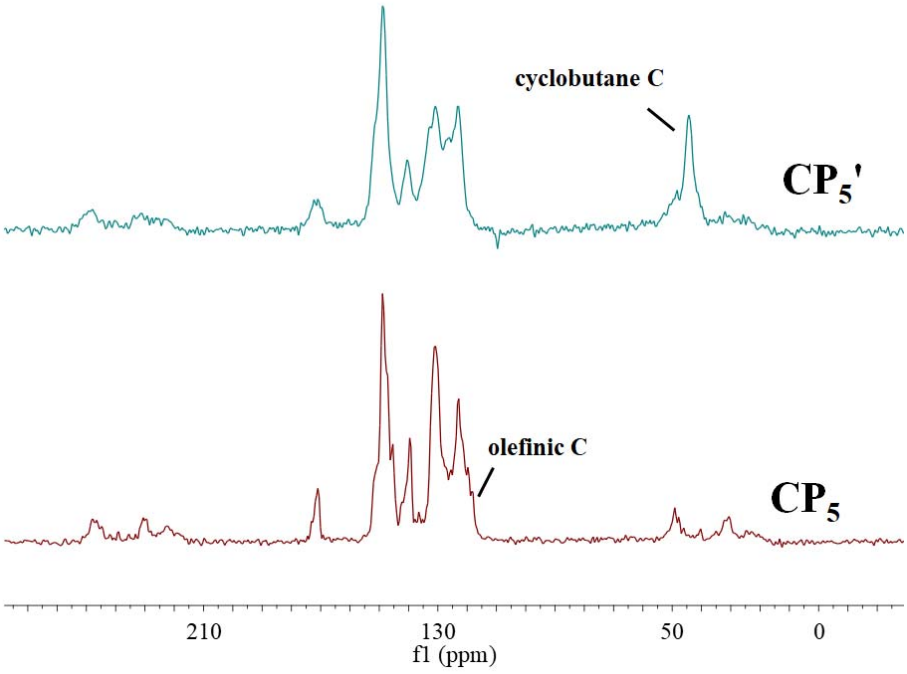
(b)


cyclobutane C
CP3'
olefinic C
CP3
270
170
70
0
f1 (ppm)

(c)


cyclobutane C
CP4'
olefinic C
CP4
250
180
110
50
0
f1 (ppm)

(d)



(e)

Fig. S17 The CPMAS ^{13}C NMR spectra of **CP$_1$** to **CP$_1$'** (a), **CP$_2$** to **CP$_2$'** (b), **CP$_3$** to **CP$_3$'** (c), **CP$_4$** to **CP$_4$'** (d), **CP$_5$** to **CP$_5$'** (e).

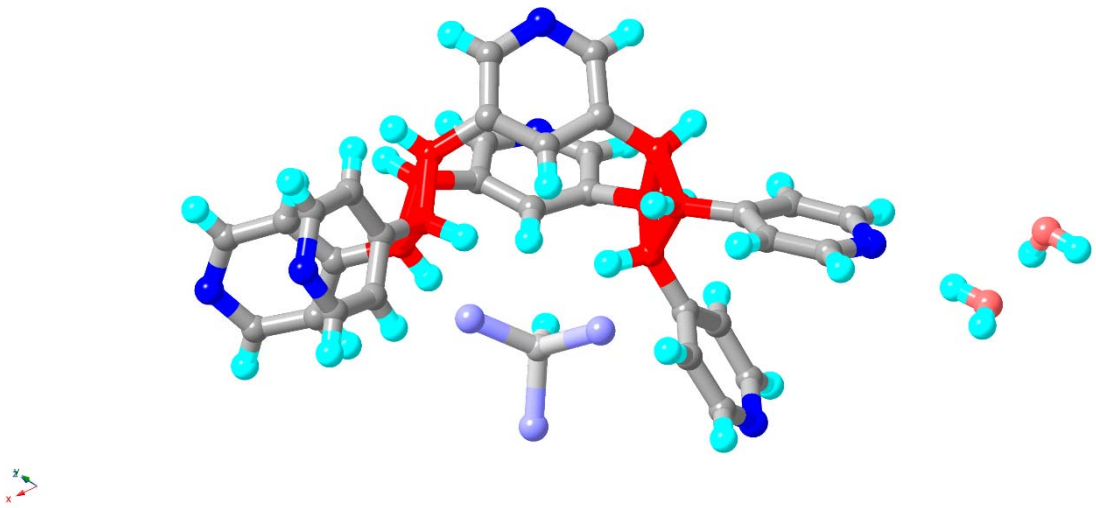
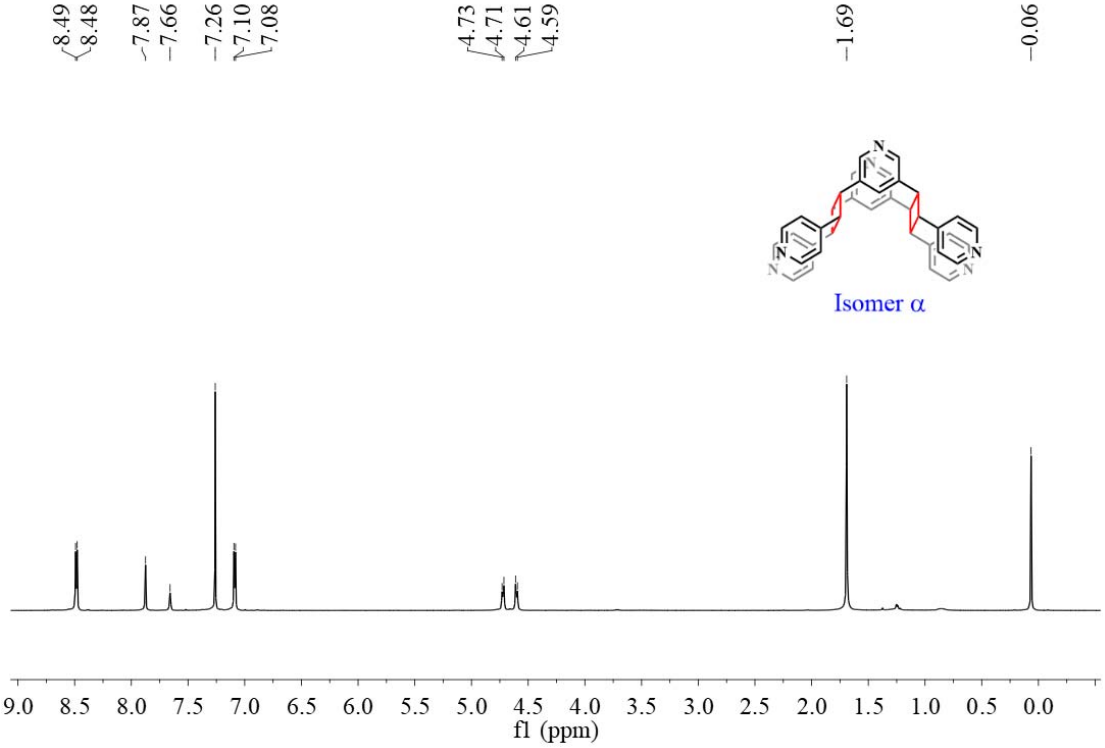
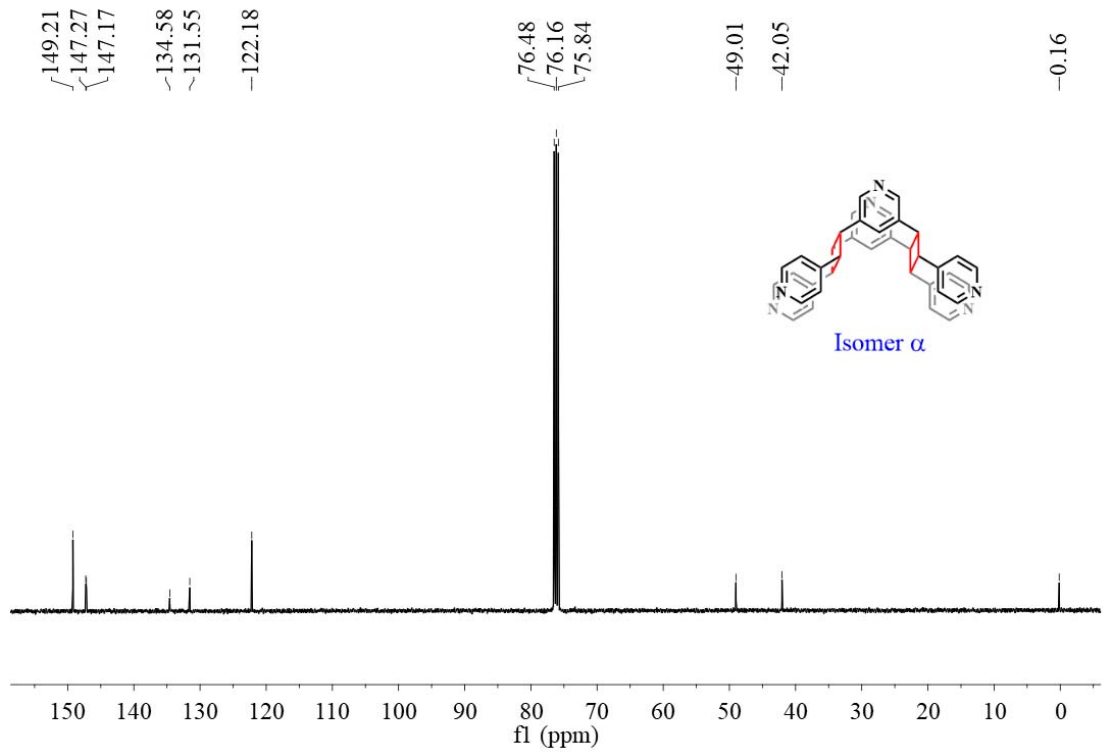


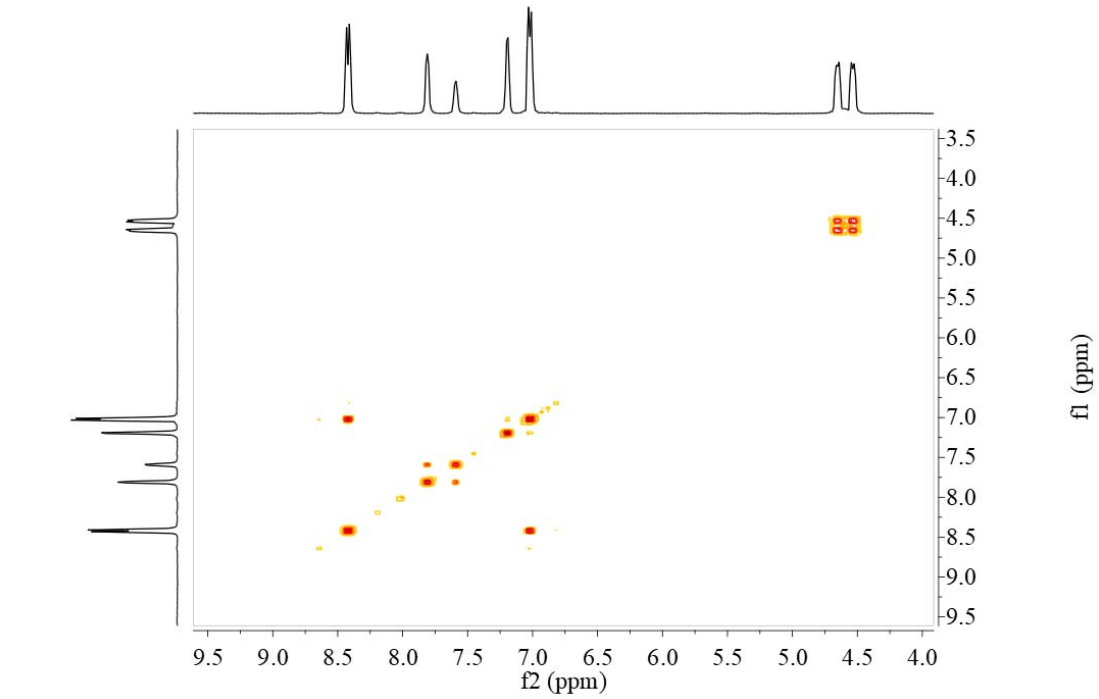
Fig. S18 The crystal structure of **Isomer α.**


8.49
8.48
7.87
7.66
7.26
7.10
7.08
4.73
4.71
4.61
4.59
1.69
0.06
Isomer α
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

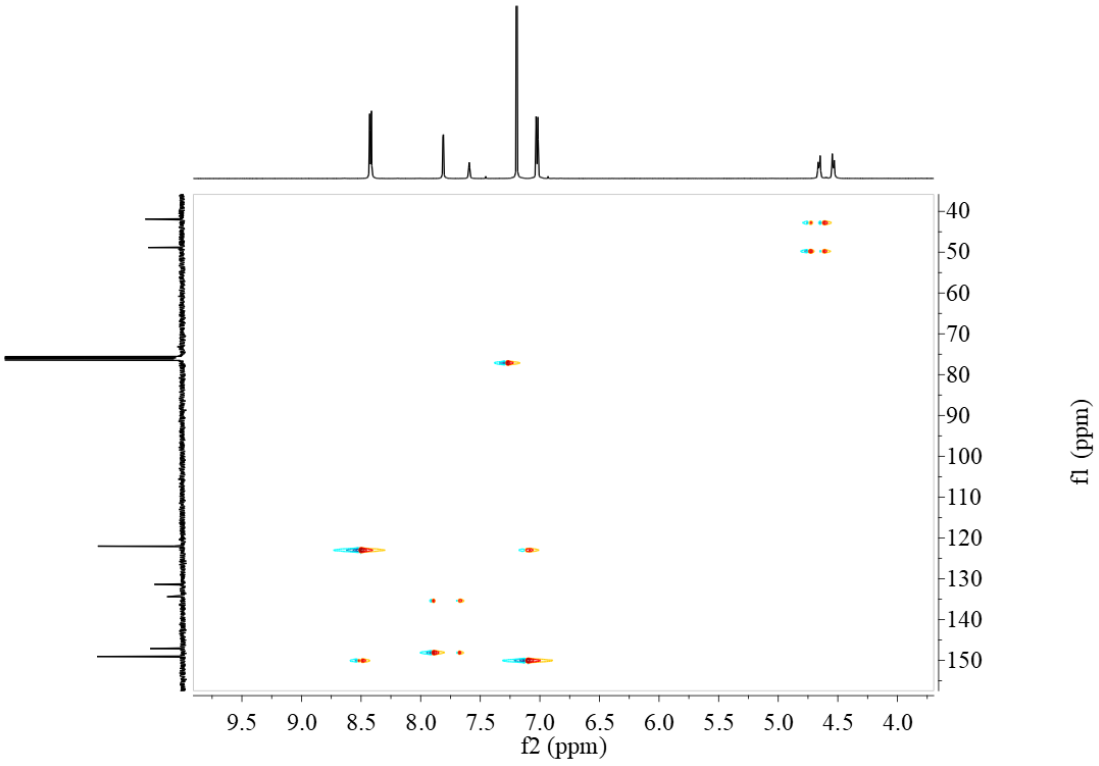
(a)


149.21
147.27
147.17
134.58
131.55
122.18
76.48
76.16
75.84
49.01
42.05
0.16
Isomer α
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

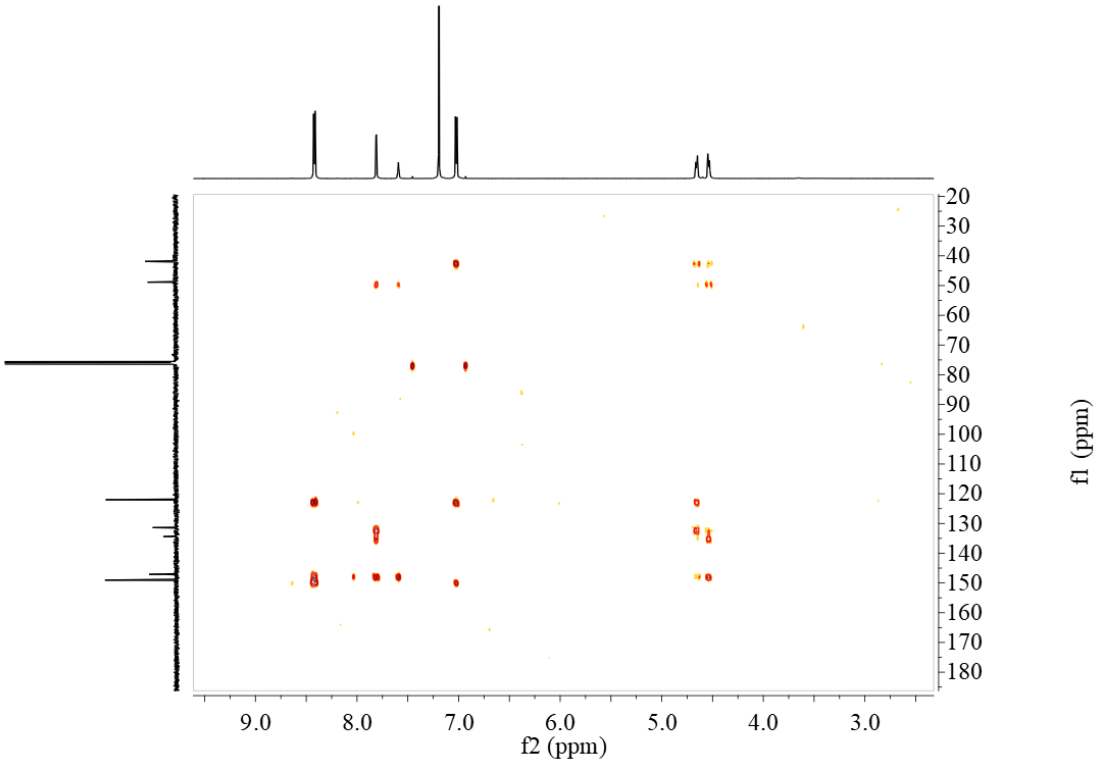
(b)


3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0
f2 (ppm)

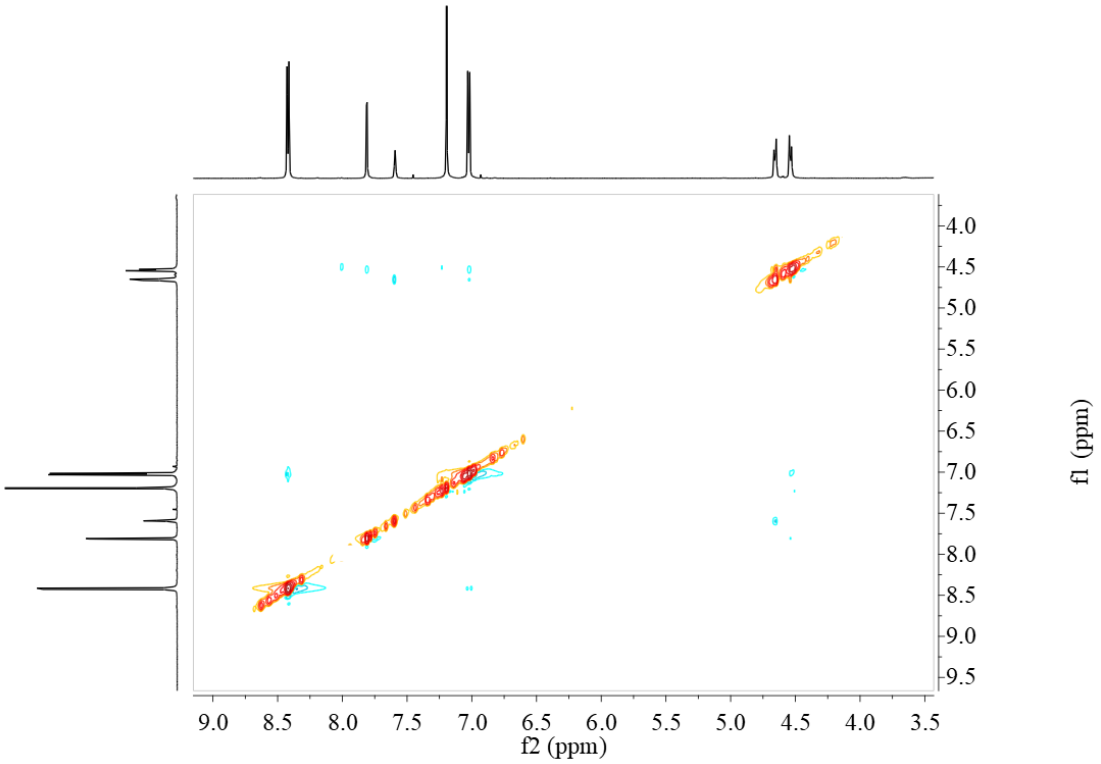
(c)


40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0
f2 (ppm)

(d)



(e)



(f)

Fig. S19 The ^{1}H (a), ^{13}C (b), H-H COSY (c), HSQC (d), HMBC (e), NOESY (f) NMR spectra of **Isomer α** in $CDCl_3$.

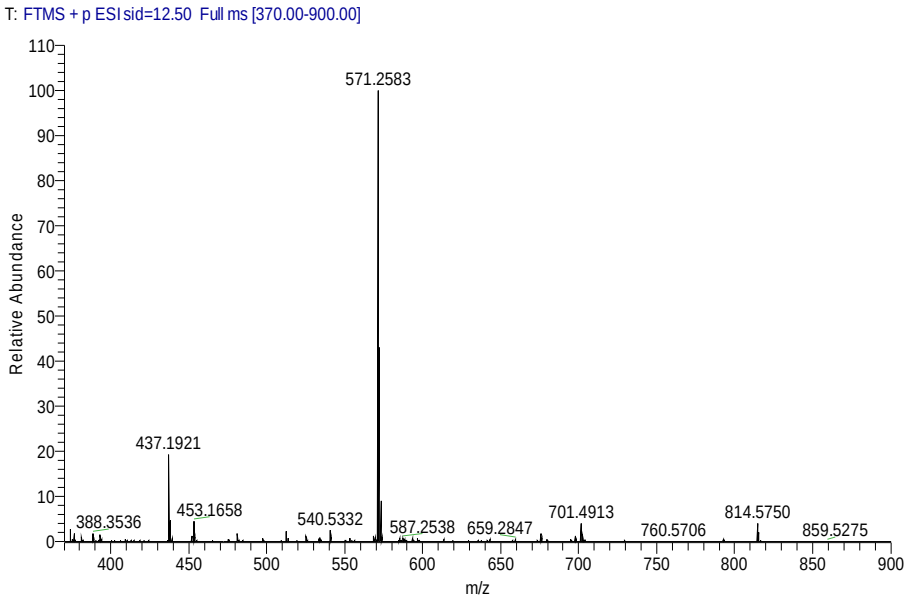


Fig. S20 The mass spectrum of **Isomer α**.

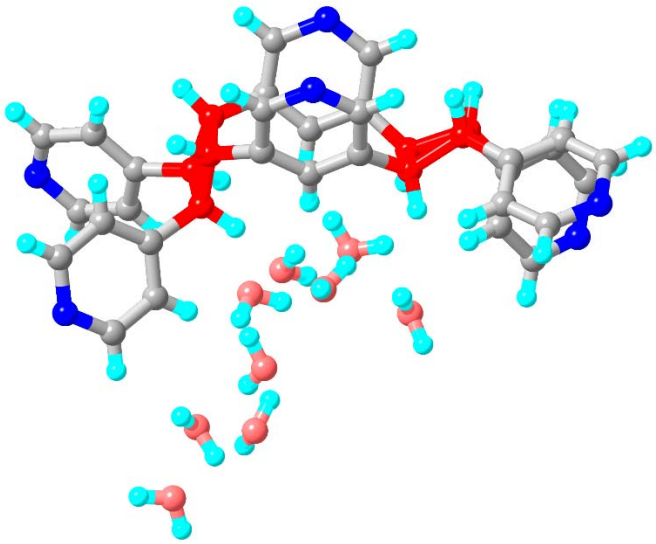
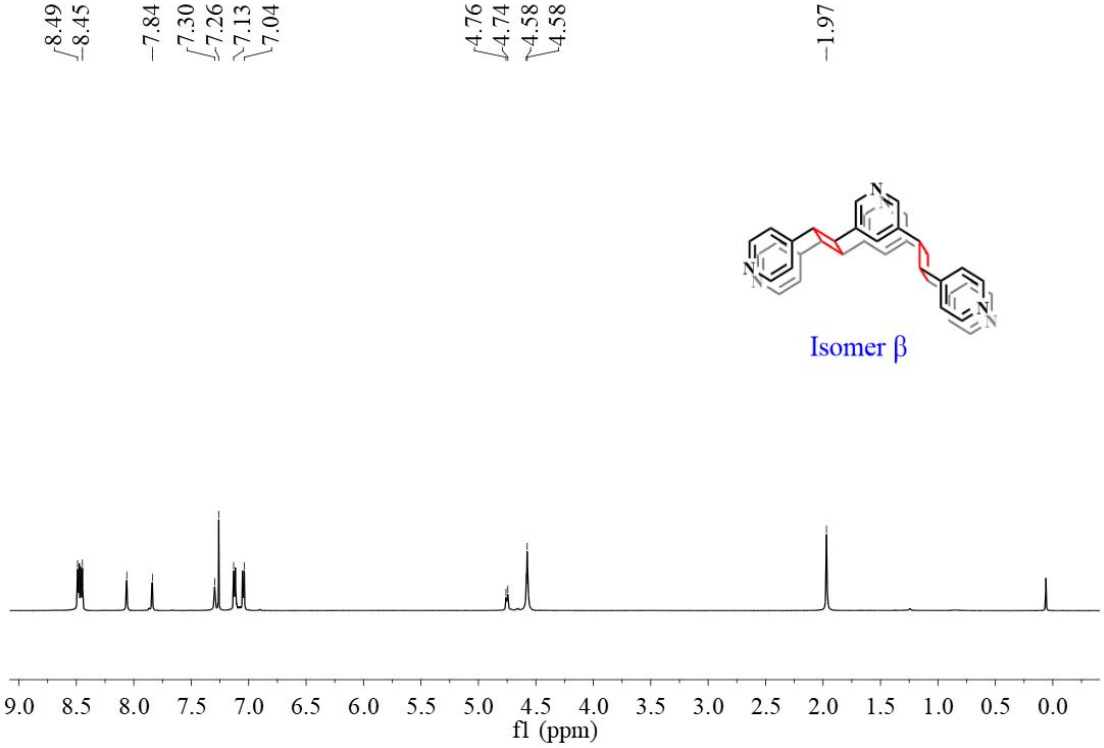
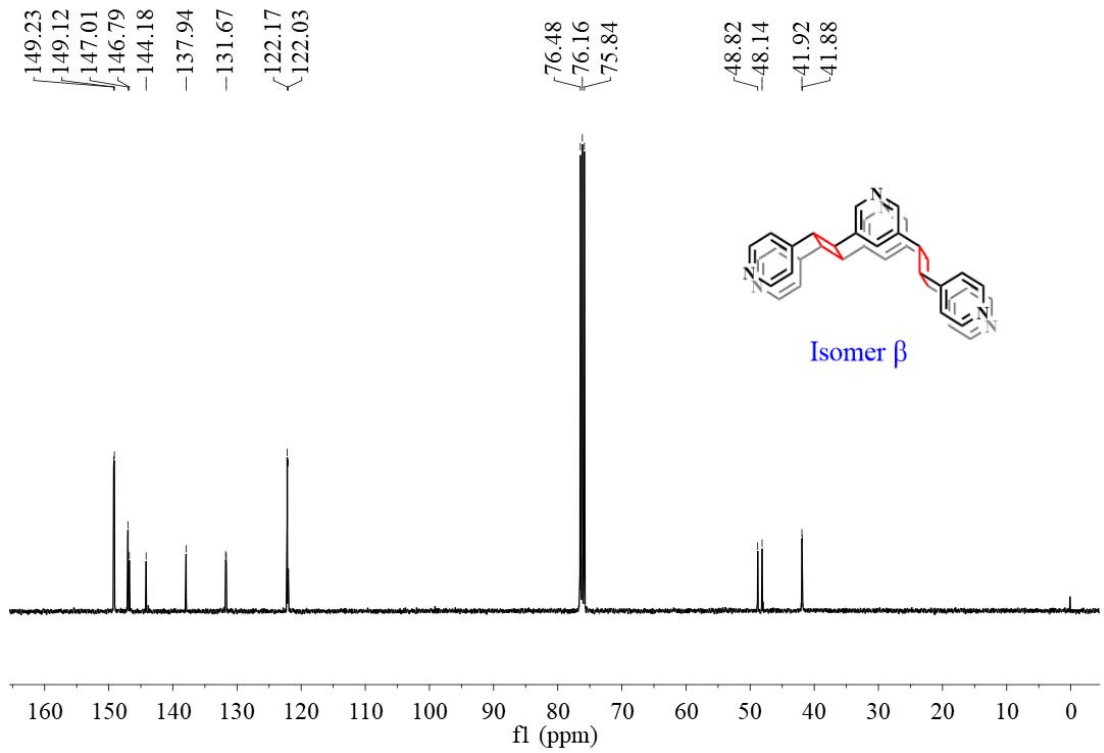


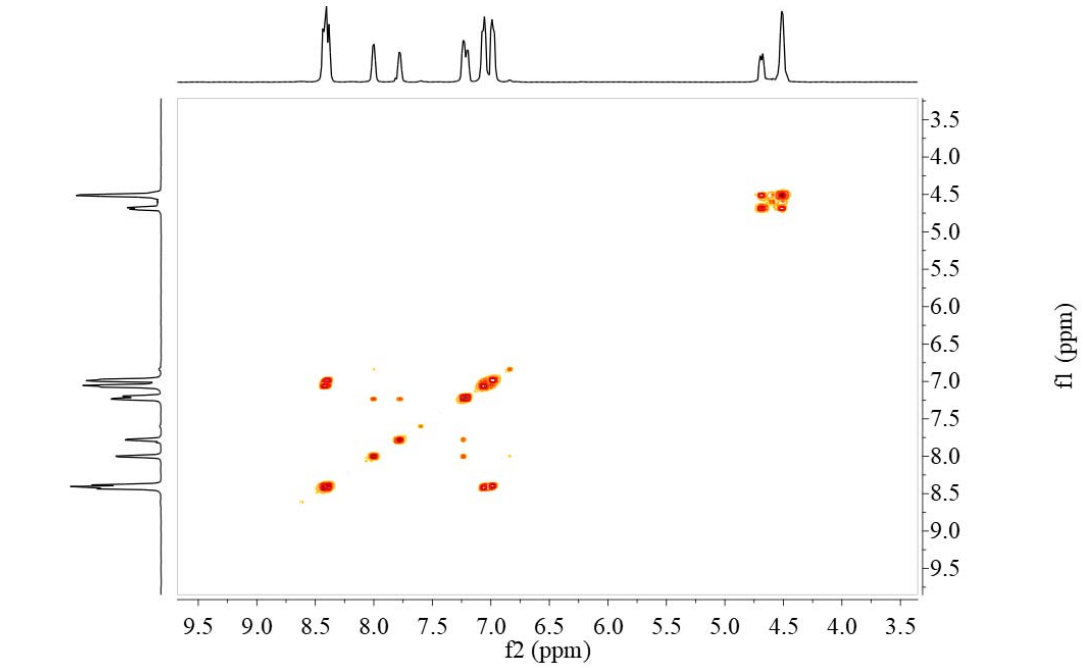
Fig. S21 The crystal structure of **Isomer β.**


8.49
8.45
7.84
7.30
7.26
7.13
7.04
4.76
4.74
4.58
4.58
1.97
Isomer β
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

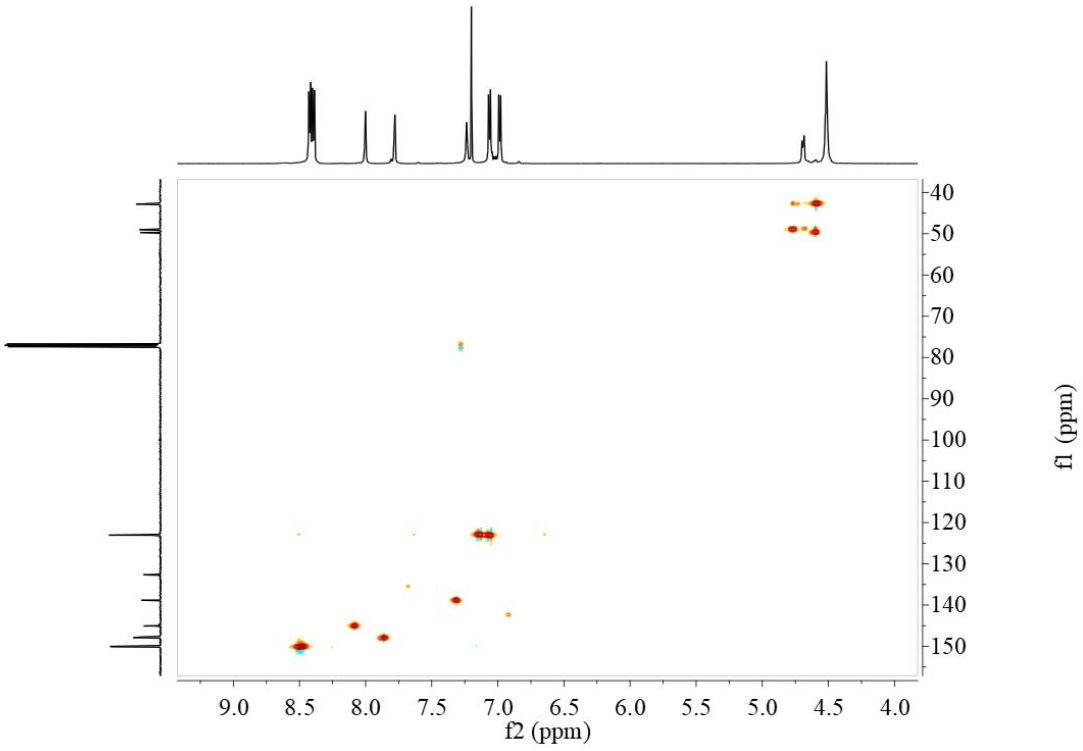
(a)


149.23
149.12
147.01
146.79
144.18
137.94
131.67
122.17
122.03
76.48
76.16
75.84
48.82
48.14
41.92
41.88
Isomer β
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

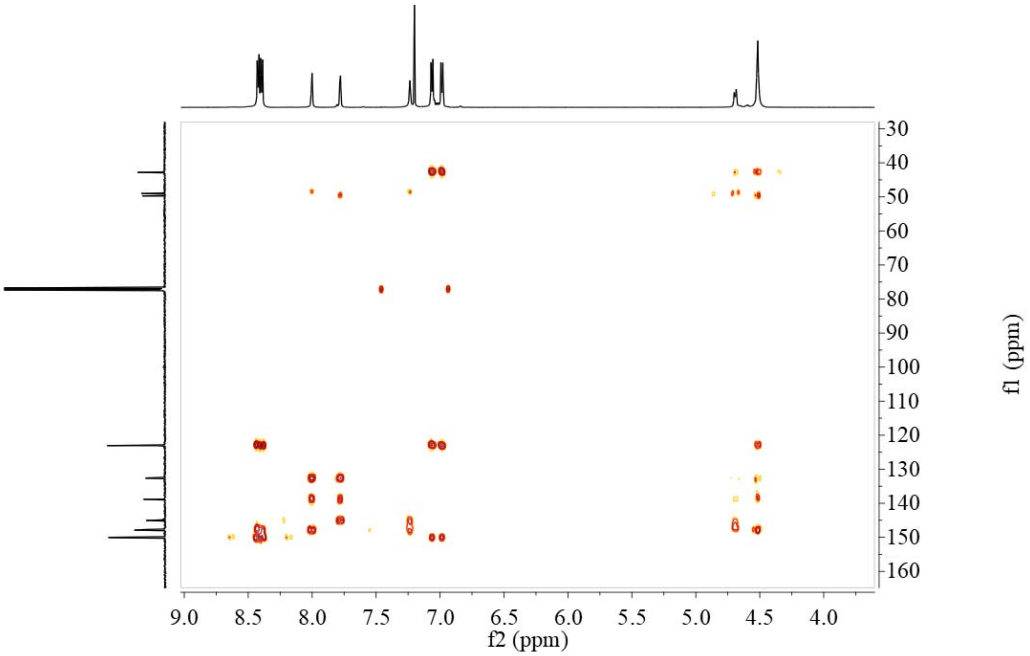
(b)


3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5
f2 (ppm)

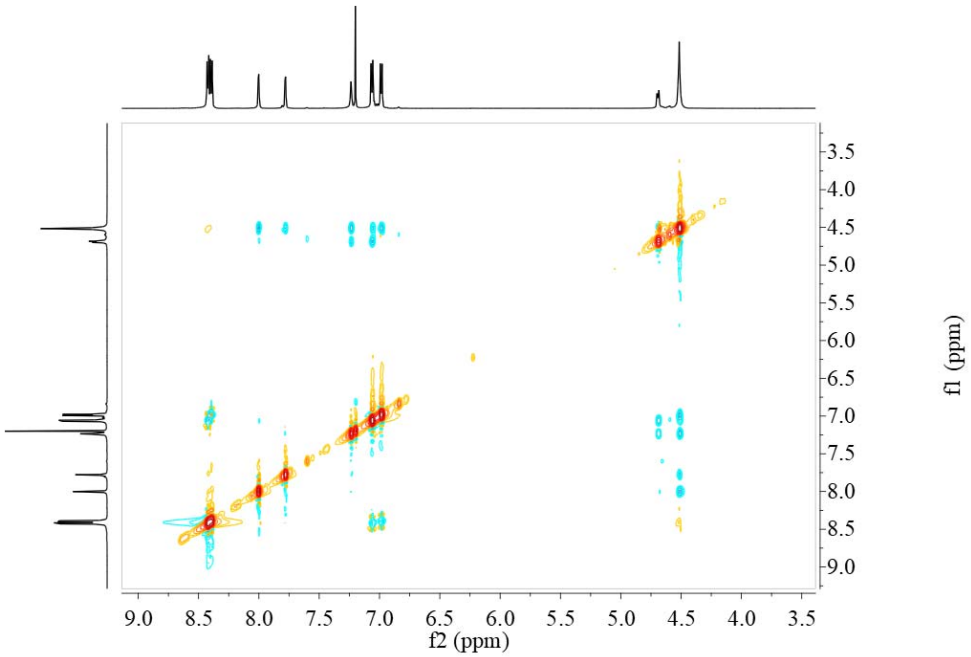
(c)


40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0
f2 (ppm)

(d)



(e)



(f)

Fig. S22 The ^{1}H (a), ^{13}C (b), H-H COSY (c), HSQC (d), HMBC (e), NOESY (f) NMR spectra of **Isomer β** in $CDCl_3$.

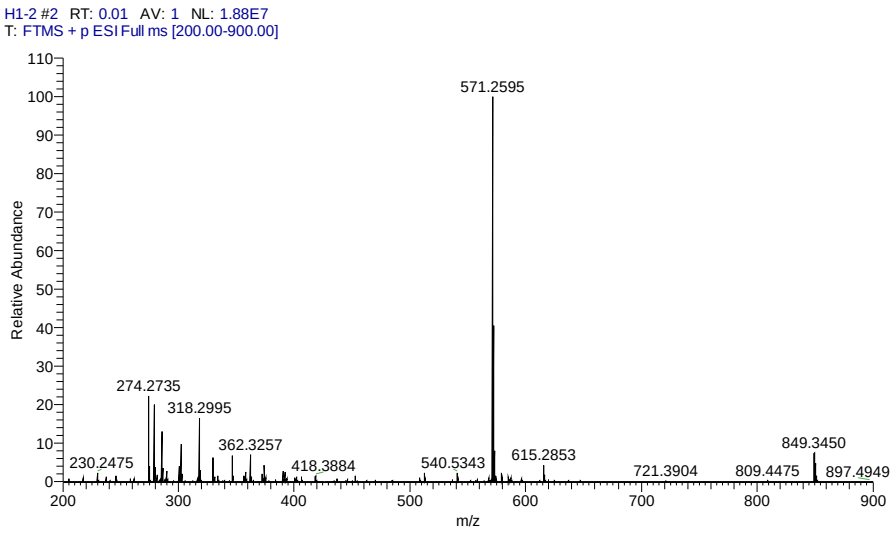


Fig. S23 The mass spectrum of **Isomer β**.

Table S2 A summary of isomer ratios, number of guest molecules, dimensions of framework structures and dimensions of guest molecules in **CP_1-CP_3**

	Number of guest molecules	Dimensions of guest molecules[5]	Dimensions of framework structures	Ratios of **Isomer α** to **Isomer β** from irradiation of **CP_1** and **CP_3**
CP_1	14	6.57 Å × 4.02 Å × 10.07 Å	36.493 Å × 33.910 Å	**Isomer α : Isomer β = 0 : 1**
CP_2	14	6.55 Å × 3.66 Å × 10.57 Å	36.157 Å × 34.154 Å	**Isomer α : Isomer β = 3 : 7**
CP_3	14	6.55 Å × 3.50 Å × 10.33 Å	35.959 Å × 35.520 Å	**Isomer α : Isomer β = 1 : 1**

Table S3 The relative Gibbs free energies (kcal/mol) for **Isomer α** and **Isomer β**

Compound	**Isomer α**	**Isomer β**
Relative Gibbs free energies (kcal/mol)	0	0.94

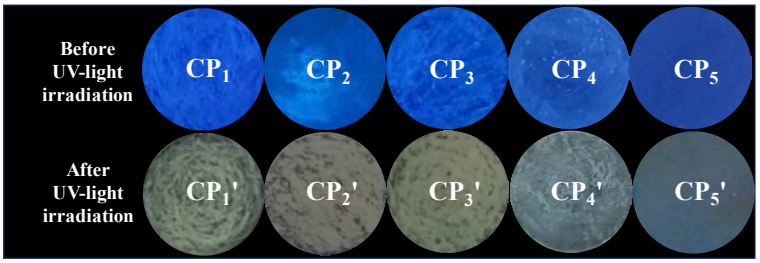


Fig. S24 Photograph of filter papers impregnated with solution of CP_1-CP_5 and CP_1'-CP_5' in DMF (365 nm).

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