Supplementary Information (SI) for Chemical Communications.

Electronic Supplementary Information

Photomechanical Responses of Coordination Polymers Regulated by Precise Organization of the Photoactive Centers

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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_3** showing bending behavior

Video SV5: photosalient effects of **CP_1-CP_3**

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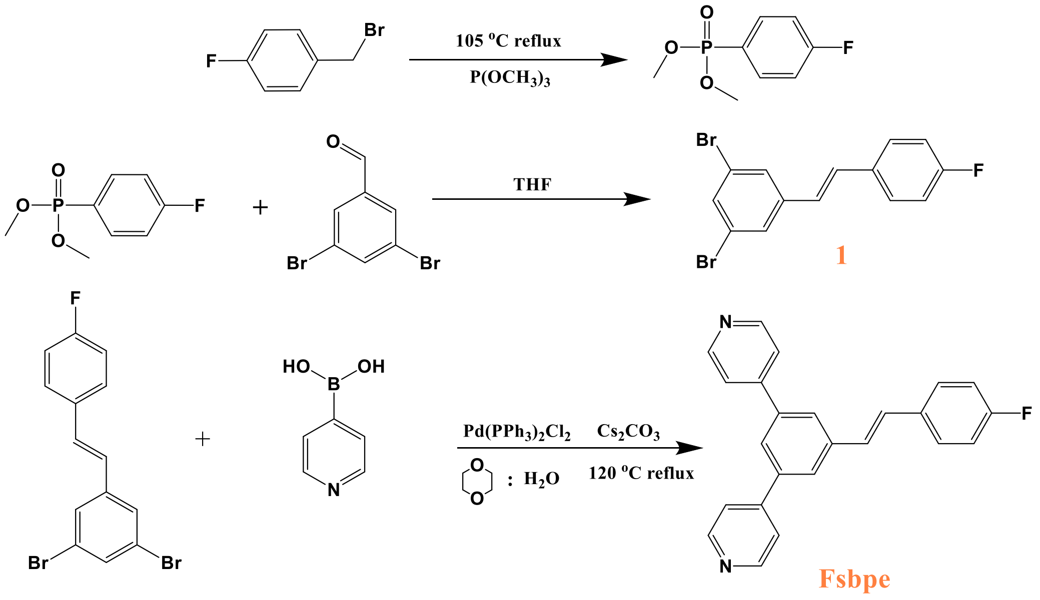
General procedures

The ligands 4-(3-(4-fluorostyryl)-5-(pyridin-4-yl)phenyl)pyridine (Fsbpe), 4,4'-(5-((4-fluorophenyl)ethynyl)-1,3-phenylene)dipyridine (Fepbpe) and 4-(3-(4-fluorostyryl)-5-((E)-2-(pyridin-4-yl)vinyl)styryl)pyridine) (Fsbpeb) were prepared according to literature methods.[S1] Other reagents were obtained commercially and used without further purification. Powder X-ray diffraction (PXRD) patterns were acquired on a Bruker D8 advance using Cu Kα radiation ($\lambda = 1.5406$ Å) from 5° to 50° with a scanning step size of 0.02°. Single-crystal X-ray diffraction data for **CP_1**, **CP_2**, **CP_3** and **CP_3'** were recorded on a Bruker Smart CCD diffractometer. ^1H 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 Fsbpe. A 50 mL round-bottom flask was charged with 1-(bromomethyl)-4-fluorobenzene (1.89 g, 10 mmol) and trimethyl phosphite (2.15 mL). The mixture was heated at 120 °C for a period of 8 h and then cooled to room temperature. A solution of 3,5-dibromo-4-methylbenzaldehyde (2.64 g, 11 mmol) in dry tetrahydrofuran was added under ice-water bath conditions, followed by dropwise addition of a solution of potassium tert-butoxide (2 g, 21 mmol) in tetrahydrofuran. The reaction was kept in an ice-water bath for 14 h and then diluted with H_2O (200 mL). The mixture was extracted with CH_2Cl_2 (3×50 mL). The organic phase was collected and concentrated to give the crude compound **1**. Yield: 1.99 g (56 %). ^{1}H NMR (400 MHz, DMSO-d_6, TMS, Figure. S1): δ7.55 (s, 2H, Ph-H), 7.53 (d, 1H, Ph-H), 7.48 (m, 2H, F-Ph-H), 7.09 (m, 2H, F-Ph-H), 7.07 and 7.03 (d, 1H, C=C), 6.86 and 6.82 (d, 1H, C=C). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): *δ* 163.00, 160.52, 139.81, 131.65, 129.29, 126.99, 124.39, 122.21, 114.90, 114.71 (Figure S1).

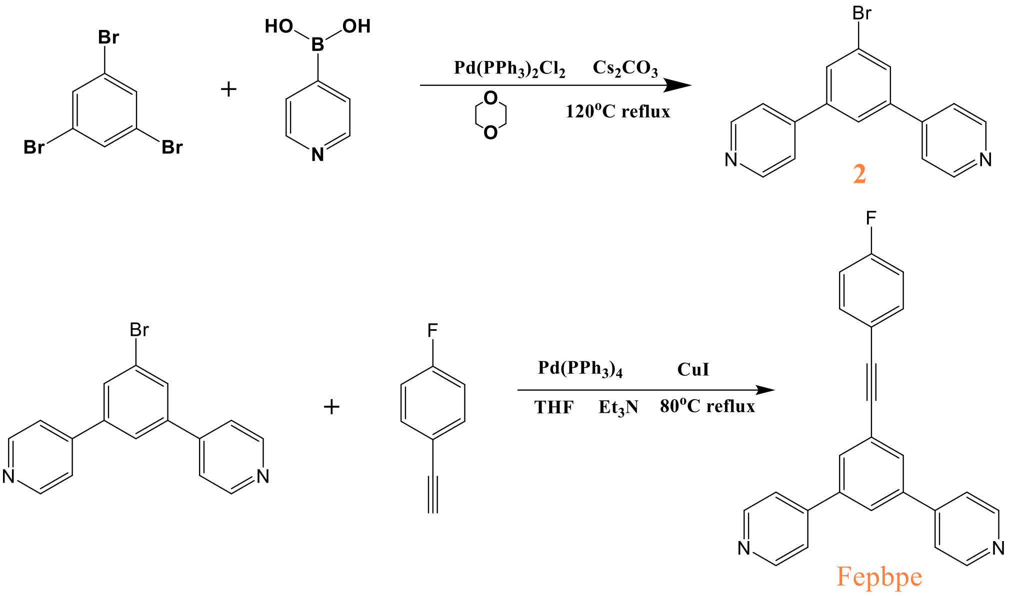
A 50 mL round-bottom flask was charged with **1** (1.78 g, 5 mmol), pyridine-4-boronic acid (1.84 g, 15 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.2 mmol) and a solution of anhydrous caesium carbonate (1.36 g, 10 mmol) in 20 mL of 1,4-dioxane and H_2O (v:v=1:1). The mixture was heated at 120 °C for a period of 48 h and then diluted with H_2O (200 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was collected and concentrated to give the crude product. Purification of the residue by flash chromatography (hexanes/EtOAc = 1:1 to 1:2) afforded Fsbpe as a pale yellow powder, Yield: 1.05 g (60 %). ^{1}H NMR (400 MHz, DMSO-d_6, TMS, Figure. S2): δ 8.73 (m, 4H, Py-H), 7.80 (d, 2H, Ph-H), 7.73 (s, 1H, Ph-H), 7.60 (m, 4H, Py-H), 7.55 (m, 2H, Ph-H), 7.25 and 7.21 (d, 1H, C=C), 7.16 and 7.12 (d, 1H, C=C), 7.11 (t, 2H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): *δ* 149.40, 146.72, 138.73, 138.04, 128.37, 127.19, 126.12, 124.51, 123.86, 120.75 (Figure S2).



Scheme S1. Synthesis of Fsbpe.

Synthesis of ligand Fepbpe. A 50 mL round-bottom flask was charged with 1,3,5-tribromobenzene (2.00 g, 6.4 mmol), pyridine-4-boronic acid hydrochloride (2.90 g, 12.8 mmol), $Pd(PPh_3)_2Cl_2$ (0.25 g, 0.35 mmol) and anhydrous caesium carbonate (4.17 g, 12.8 mmol) in 20 mL of 1,4-dioxane and H_2O (v:v=1:1). The mixture was heated at 120 °C for a period of 48 h and then diluted with H_2O (200 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was collected and concentrated to give the crude product of **2**, which was then recrystallized from MeOH and collected as a yellow powder. Yield: 1.83 g (92 %). ^1H NMR (400 MHz, DMSO-*d*$_6$, TMS): δ 8.72-8.73 (m, 4H, Py-H), 7.83-7.84 (d, 4H, C=C), 7.77 (s, 1H, Ph-H), 7.52-7.53 (m, 2H, Py-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): *δ* 149.47, 145.47, 140.6, 129.49, 123.49, 122.99, 122.65 (Figure S3).

A 50 mL round-bottom flask was charged with **2** (2.00 g, 6.4 mmol), 4-fluorophenylacetylene (1.10 g, 9.12 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.095 mmol) and cuprous iodide (0.28 g, 1.5 mmol) in 20 mL of THF and Et_3N (v:v=1:1). The mixture was heated at 80 °C for a period of 24 h and then diluted with H_2O (200 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the organic layers combined, dried with anhydrous Na_2SO_4 and evaporated *in vacuo*. The crude product was purified by silica gel column chromatography (hexanes/EtOAc = 1:1 to 1:2) to give a yellow powder of Fepbpe. Yield: 2.06 g (92 %). ^1H NMR (400 MHz, DMSO-*d*$_6$, TMS, Figure. S3): δ 8.48(m, 4H, Py-H), 7.58 (m, 3H, Py-H), 7.28-7.29 (d, 6H, Py-H and Ph-H), 6.80-6.82 (d, 2H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): *δ* 163.03, 160.54, 149.41, 146.05, 138.54, 132.68, 129.45, 124.49, 124.12, 114.95, 114.73, 88.86, 86.83 (Figure S4).

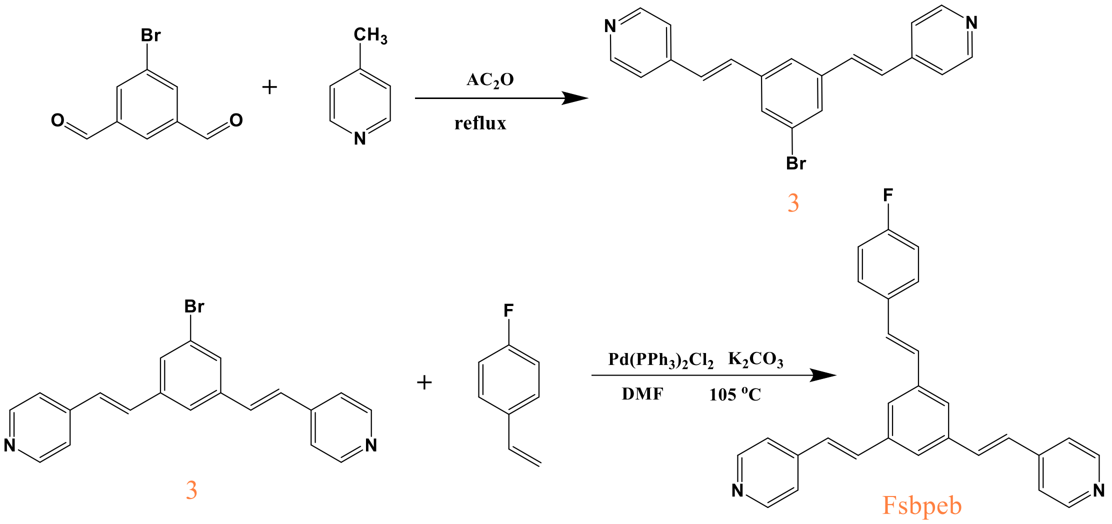


Scheme S2. The synthesis of Fepbpe.

Synthesis of ligand Fsbpeb. A 50 mL round-bottom flask was charged with 5-bromobenzene-1,3-dialdehyde (1.00 g, 4.7 mmol) and 4-methylpyridine (0.93 g, 10 mmol), in 2 mL of acetic anhydride. The mixture was heated at 130 °C for a period of 24 h and then diluted with H_2O (200 mL) to form compound **3**, yield: 0.85 g (50 %). ^1H NMR (400 MHz, DMSO-d_6, TMS): δ8.60 (m, 4H, Py-H), 7.61(d, 2H, Ph-H), 7.54 (s, 1H, Ph-H), 7.36 (m, 4H, Py-H), 7.23 and 7.19 (d, 4H, C=C), 7.05 and 7.01 (d, 4H, C=C). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.30, 142.83, 137.60, 130.09, 128.47, 127.03, 123.52, 122.48, 119.93 (Figure S5).

A 50 mL round-bottom flask was charged with 4-Fluorostyrene (2.68 g, 22 mmol), compound 3 (2.61 g, 7.2 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.2 mmol) and anhydrous potassium carbonate (2.07 g, 15 mmol) in 20 mL of DMF. The mixture was heated at 105 °C for a period of 2 h and then diluted with H_2O (200 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and concentrated at reduced pressure. Purification of the residue by flash chromatography (hexanes/EtOAc = 1:1 to 1:2) afforded Fsbpeb as a pale yellow powder. Yield: 1.63 g (56 %). ^1H NMR (400 MHz, DMSO-d_6, TMS, Figure. S1): δ8.62 (m, 4H, Py-H), 7.64 (s, 2H, Ph-H), 7.60 (s, 1H, Ph-H), 7.57 and 7.55

(d, 2H, Ph-H), 7.42 (m, 4H, Py-H), 7.38 (d, 2H, Ph-H), 7.37 and 7.33 (d, 4H, C=C), 7.21 (s, 1H, C=C), 7.17 (s, 1H, C=C), 7.14 and 7.10 (d, 2H, C=C). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.22, 143.38, 137.50, 136.11, 135.87, 131.57, 129.05, 127.80, 125.95, 125.63, 124.28, 123.65, 119.92 (Figure S6).



Scheme S3. The synthesis of Fsbpeb.

Preparation of [Cd(Fsbpe)(DBBA)$_2$]·2DMF (CP$_1$). A mixture containing 3,5-Dibromobenzoic acid (**DBBA**) (14.0 mg, 0.05 mmol), Fsbpe (17.6 mg, 0.05 mmol) and $CdSO_4\cdot 8/3H_2O$ (250 mg, 0.05 mmol) in DMF-H_2O-MeCN-HNO_3 (2 mL, 3:25:1:2 in volume ratio) was sealed in a Pyrex tube and heated at 140 °C for 10 h to yield pale yellowish block crystals of **CP$_1$** (38.0 mg, 65%, based on Fsbpe). Anal. Calcd for $C_{44}H_{37}N_4O_6CdFBr_4$: C, 45.21; H, 3.19; N, 4.79. found: C, 44.64; H, 3.07; N, 4.76. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, ppm): δ8.72 and 7.94(m, 8H, Py-H), 8.13 (d, 2H, Ph-H), 8.09 (s, 1H, Ph-H), 8.04 (d, 2H, Ph-H of HL$_1$), 7.99 (s, 1H, Ph-H of HL$_1$), 7.72 (m, 2H, F-Ph-H), 7.63 and 7.59 (d, 1H, CH=CH), 7.41 and 7.37 (d, 1H, CH=CH), 7.29 (t, 2H, F-Ph-H). IR (KBr disk, cm^{-1}): 3075(w), 1611(s), 1595(s), 1541(s), 1506(s), 1435(s), 1379(s), 1069 (w), 1019(m), 958(m), 822(m), 787(s), 739(s), 727(s), 628(s).

Preparation of [Cd(Fepbpe)(DBBA)$_2$]·2DMF (CP$_2$). A mixture containing DBBA (14.0 mg, 0.05 mmol), Fepbpe (17.5 mg, 0.05 mmol) and $CdSO_4\cdot 8/3H_2O$ (250 mg, 0.05

mmol) in DMF-H_2O-CH_3CN-HNO_3 (2 mL, 4:25:3:2 in volume ratio) was sealed in a Pyrex tube and heated at 140 °C for 10 h to yield yellowish-brown block crystals of **CP₂** (43.6 mg, 75 % based on Fepbpe). Anal. Calcd for $C_{44}H_{34}N_4O_6CdFBr_4$: C, 44.33; H, 2.94; N, 4.81. found: C, 44.23; H, 2.90; N, 4.77. ^1H NMR (400 MHz, DMSO-*d*$_6$, ppm): δ8.71 and 7.94 (m, 8H, Py-H), 8.23 (s, 1H, Ph-H), 8.02 (d, 2H, Ph-H of HL), 8.10 (s, 2H, Ph-H), 7.98 (s, 2H, Ph-H of HL), 7.70 (m, 2H, F-Ph-H), 7.35 (t, 2H, F-Ph-H). IR (KBr disk, cm^{-1}): 3074(w), 1716(s), 1612(s), 1541(s), 1506(s), 1434(s), 1411(s), 1378(s), 1223(s), 1153(w), 1070(s), 1019(m), 871(m), 830(s), 821(s), 781(s), 740(s), 717(s), 630(s).

Preparation of [Cd(Fsbpeb)(DBBA)$_2$] (CP$_3$). A mixture containing DBBA (14.0 mg, 0.05 mmol), $CdSO_4 \cdot 8/3H_2O$ (250 mg, 0.05 mmol) and Fsbpeb (20.2 mg, 0.05 mmol) in DMF-H_2O-HNO_3 (2 mL, 3:5:2 in volume ratio) was sealed in a Pyrex tube and heated at 140 °C for 10 h to yield yellow leaf-shaped crystals of **CP$_3$** (42.9mg, 80 %, based on Fsbpeb). Anal. Calcd for $C_{42}H_{27}N_2O_4CdFBr_4$: C, 46.94; H, 2.53; N, 2.61. found: C, 46.90; H, 2.51; N, 2.59.^1H NMR (400 MHz, DMSO-*d*$_6$, ppm, Fig. S9b): δ 8.60 and 7.61 (m, 8H, Py-H), 8.03 (d, 2H, Ph-H of HL_1), 7.95 (m, 1H, Ph-H of HL_1), 7.87 (d, 3H, Ph-H), 7.71 (m, 2H, F-Ph-H), 7.63 and 7.59 (d, 2H, CH=CH), 7.43 and 7.39 (d, 2H, CH=CH), 7.41 (s, 1H, CH=CH), 7.30 (s, 1H, CH=CH), 7.28 (t, 2H, F-Ph-H). IR (KBr disk, cm^{-1}):3071(w),1606(s), 1589(s), 1544(s), 1507(s), 1430(s), 1374(s), 1224(s), 1156(m), 1014(m), 977(m), 961(s), 867(m), 845(s), 785(s), 739(s), 726(s).

Photo-irradiation experiments

Crystals (*ca.* 0.5 g) of **CP$_1$**, **CP$_2$** and **CP$_3$** were placed between glass plates and exposed to a 100W high-pressure mercury lamp (λ = 365 nm) for 13h to form the corresponding photoproducts **CP$_1$'**, **CP$_2$'** and **CP$_3$'**, respectively.

Single crystal structure determination. Structures of **CP$_1$-CP$_3$** and **CP$_3$'** were solved by direct methods and refined by full-matrix least-squares techniques using the *SHELXL*-2019, Olex 2 programs.[S2] 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 crystal of CP3' was cracked after ultraviolet light irradiation, which caused the low diffraction quality and resulted in higher wR$_2$ value. A summary of key crystallographic information for **CP$_1$-CP$_3$** and **CP$_3$'** is given in Table S1. The CCDC codes for these compounds are 2362977-2362980.

Table. S1 Summary of crystal data and structure refinement parameters for **CP$_1$-CP$_3$** and **CP$_3$'**.

	CP$_1$	**CP$_2$**	**CP$_3$**	**CP$_3$'**
Emperical formula	$C_{44}H_{37}Br_4CdFN_4O_6$	$C_{44}H_{34}Br_4CdFN_4O_6$	$C_{42}H_{27}Br_4CdFN_2O_4$	$C_{42}H_{27}Br_4CdFN_2O_4$
Formula weight	1168.81	1165.79	1074.69	1074.69
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	*Pbcm*	*Pbcm*	*C*2/*c*	*C*2/*c*
a/Å	13.8988(5)	14.0326(3)	32.9042(2)	31.7904(7)
b/Å	21.9666(6)	22.0287(5)	13.83950(10)	13.9507(3)
c/Å	27.6464(13)	27.5640(8)	16.81450(10)	17.6164(4)
α/°	90	90	90	90
β/°	90	90	94.8430(10)	96.614(2)
γ/°	90	90	90	90
V/Å^3	8440.7(6)	8520.6(4)	7629.61(9)	7760.8(3)
D_c/g cm^{-3}	1.840	1.818	1.871	1.840
Z	8	8	8	8
μ (Mo-Kα)/mm^{-1}	9.070	8.985	9.914	9.747
Total reflections	23314	22184	30235	26895
No. observations	8512	8577	7954	7054
No. parameters	513	484	520	581
F (000)	4592	4568	4176	4176
R_1[a]	0.0601	0.0635	0.0516	0.1154
wR_2[b]	0.1664	0.1902	0.1428	0.3257
GOF[c]	1.032	1.025	1.056	1.167

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

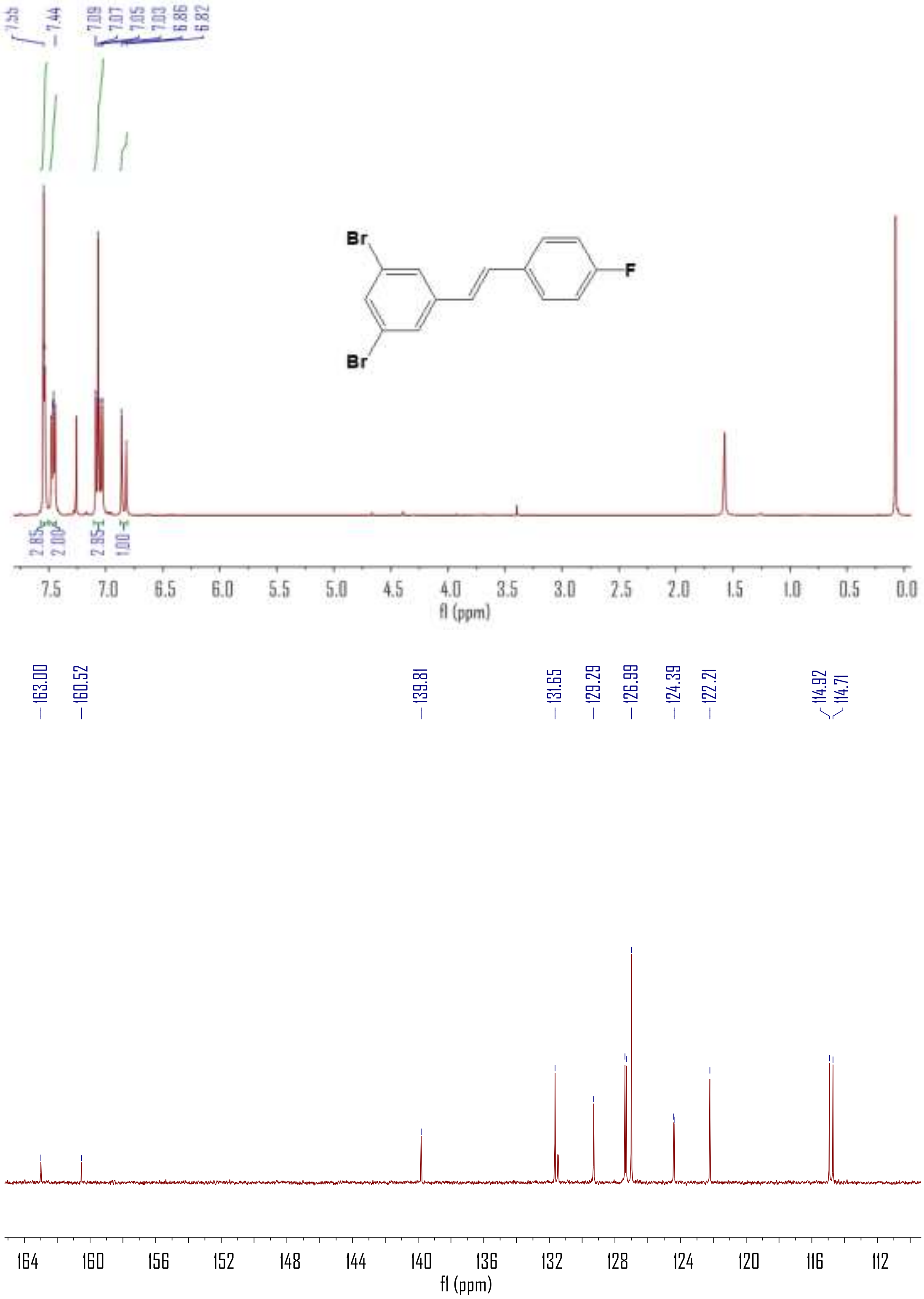


Figure. S1 The ^{1}H (a) and ^{13}C (b) NMR spectra of **compound 1** in $CDCl_3$.

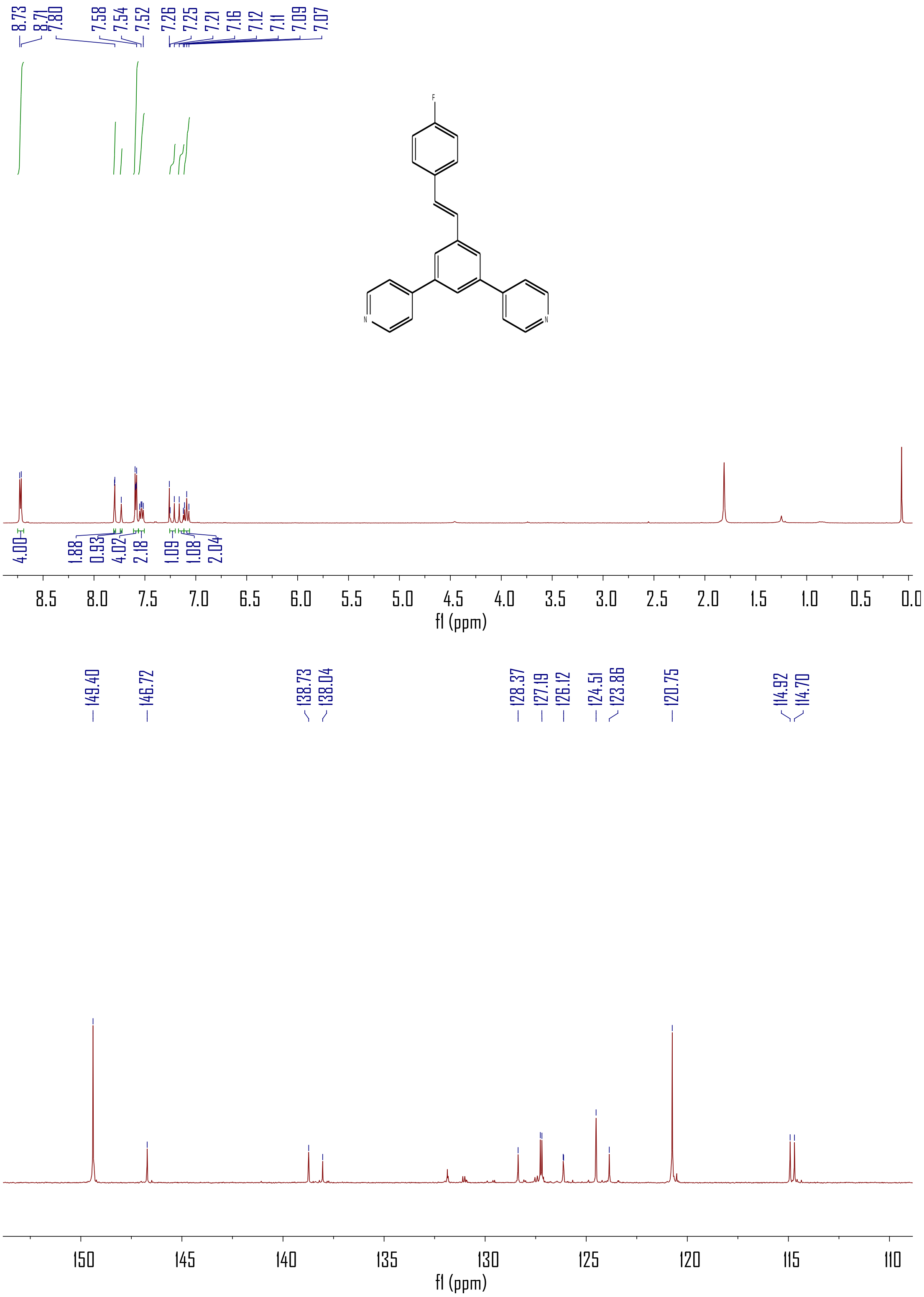


Figure. S2 The ^1H (a) and ^{13}C (b) NMR spectra of **Fsbpe** in $CDCl_3$.

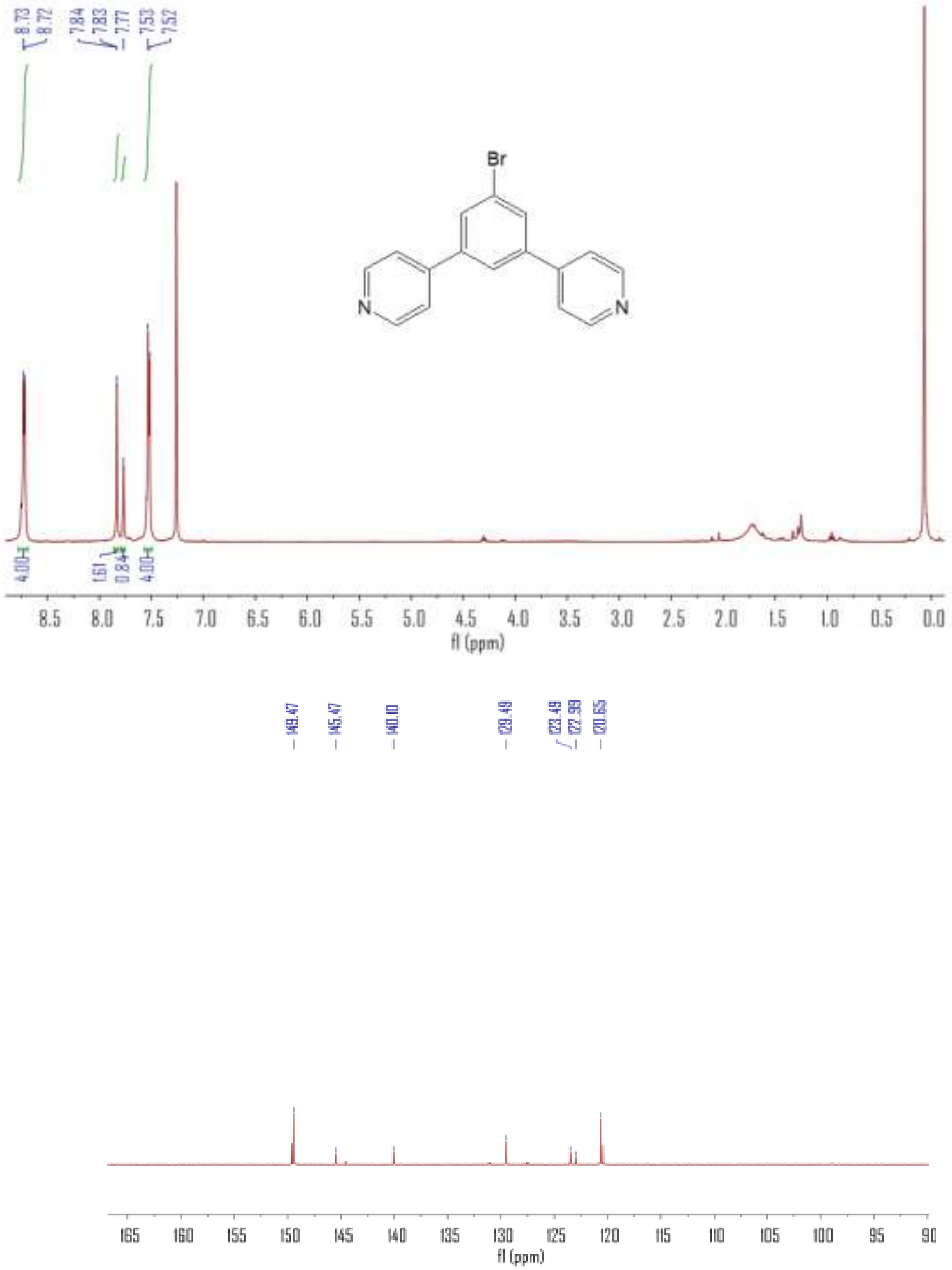


Figure. S3 The ^{1}H (a) and ^{13}C (b) NMR spectra of compound **2** in CDCl$_3$.

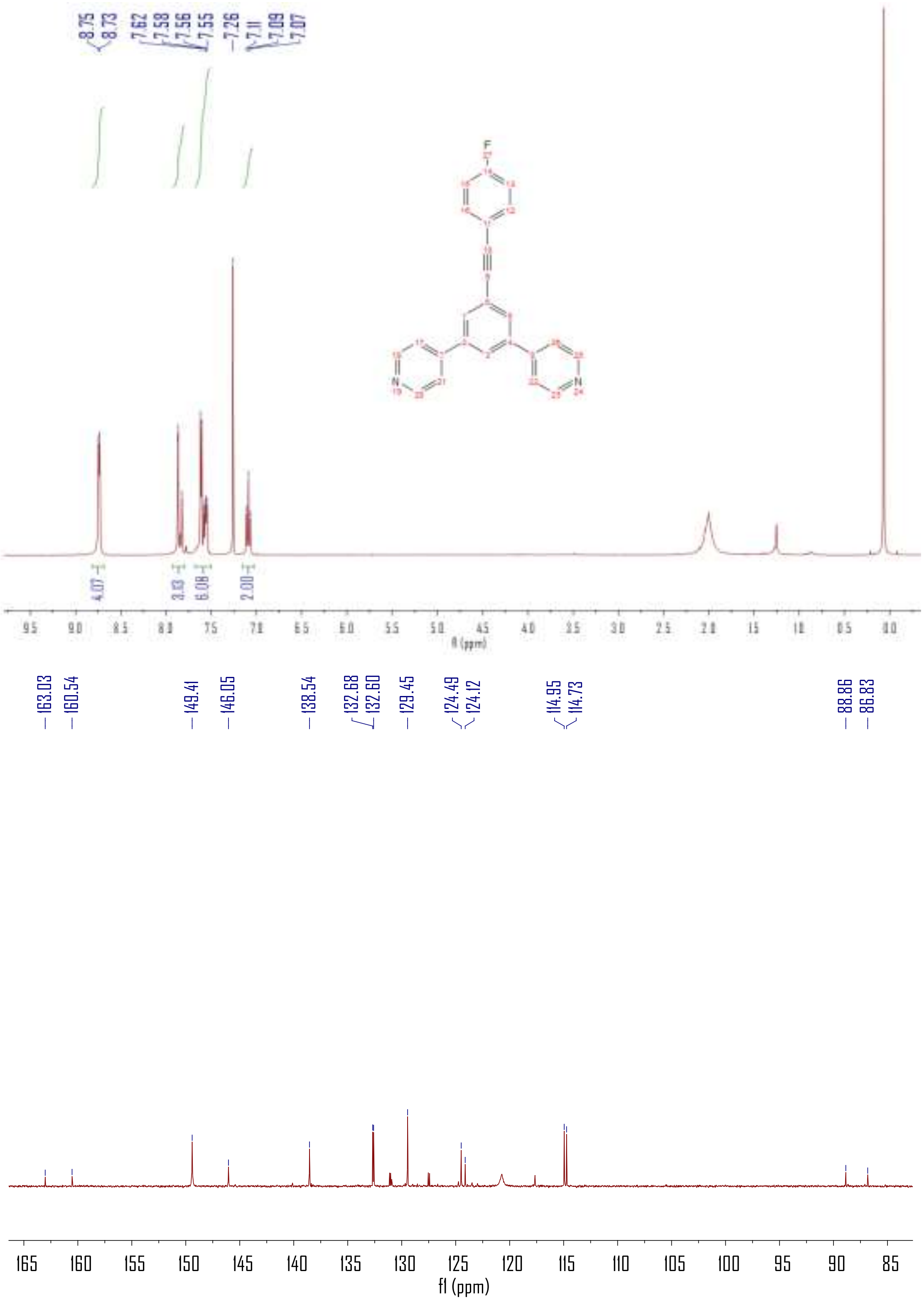


Figure. S4 The ^{1}H (a) and ^{13}C (b) NMR spectra of **Fepbpe** in $CDCl_3$.

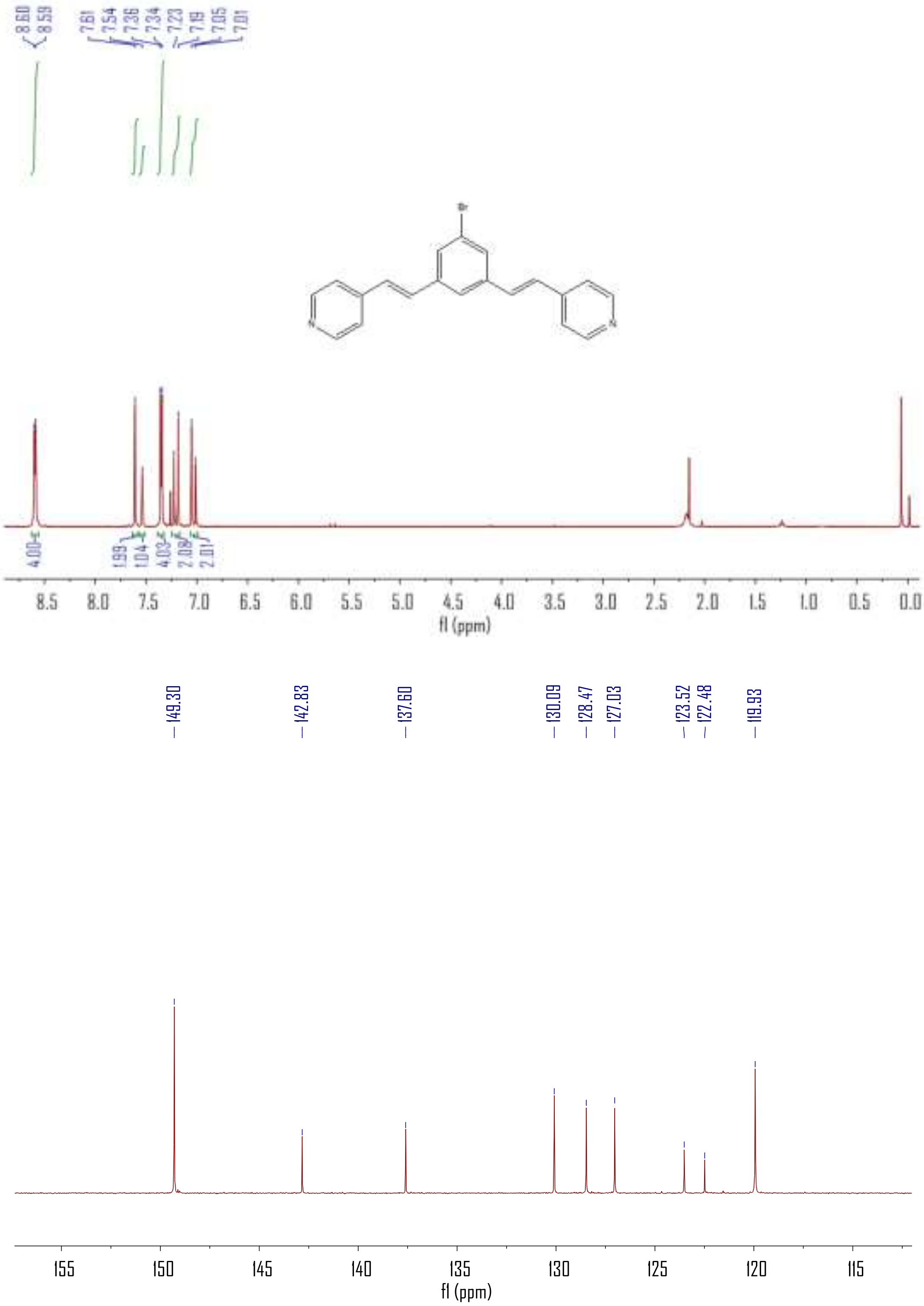


Figure. S5 The ^{1}H (a) and ^{13}C (b) NMR spectra of compound **3** in $CDCl_3$.

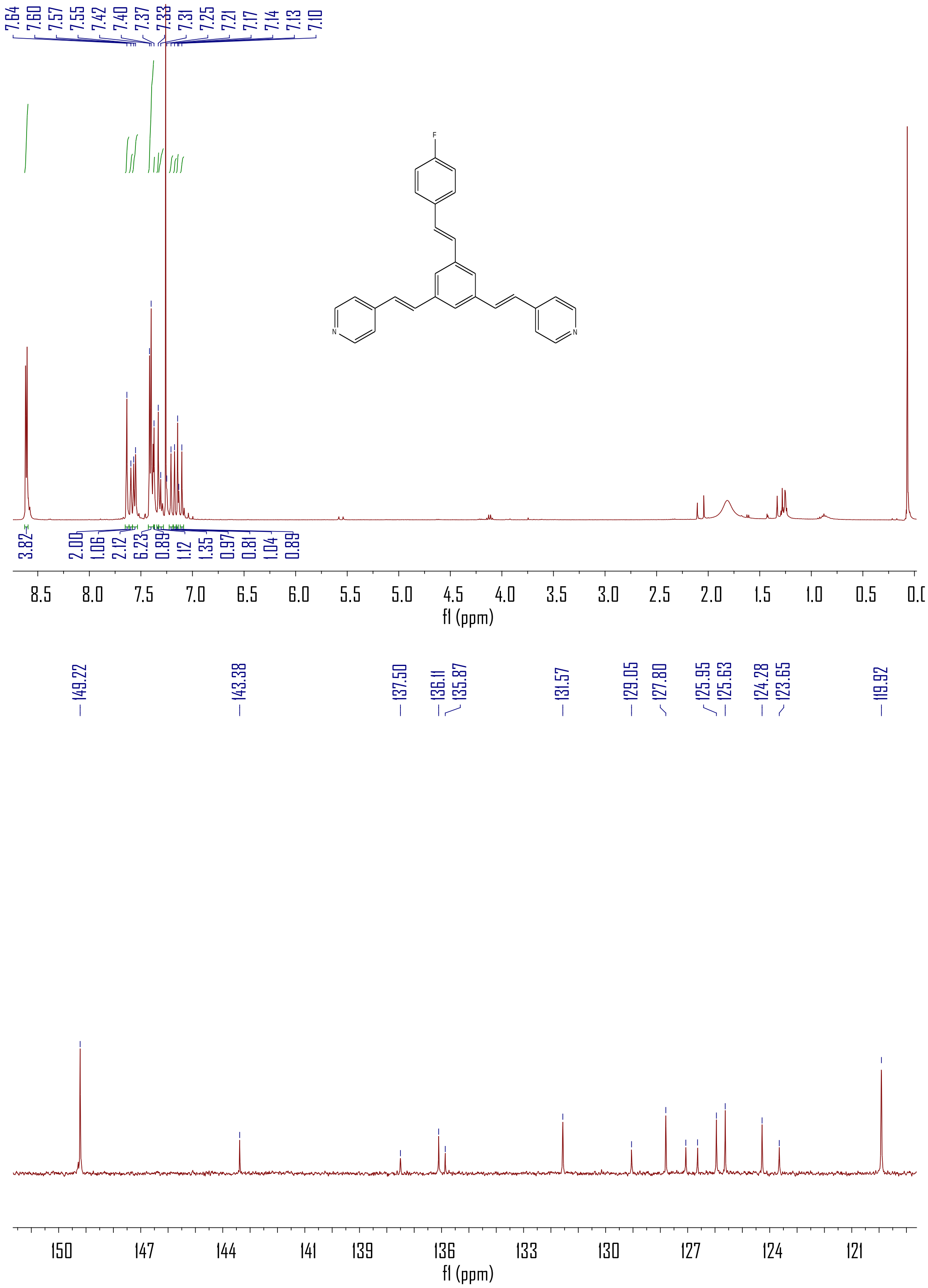
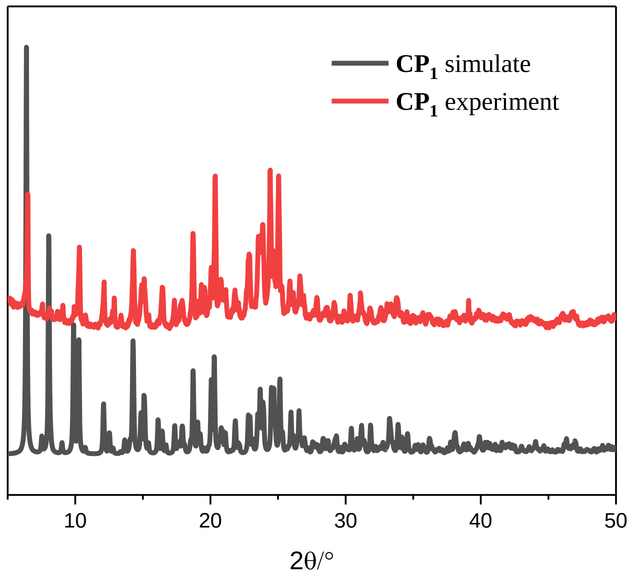


Figure. S6 The ^{1}H (a) and ^{13}C (b) NMR spectra of **Fsbpeb** in $CDCl_3$.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CP1 experiment
10
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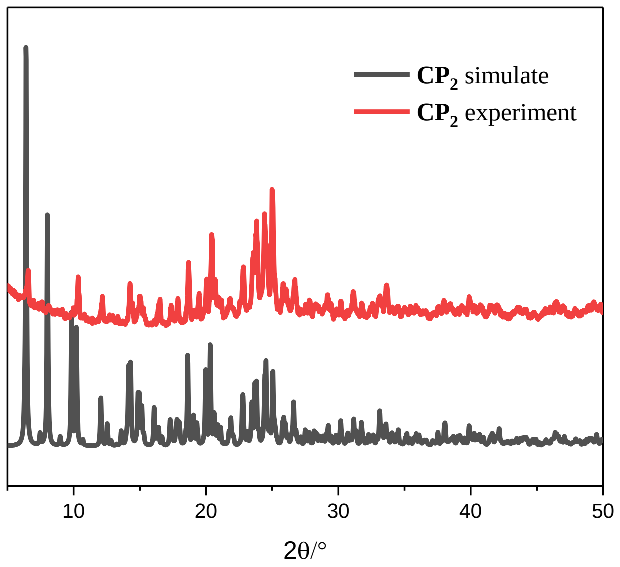
(a)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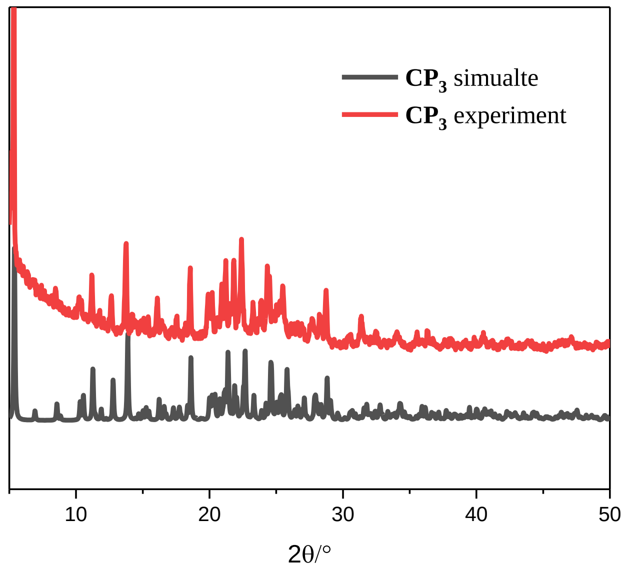
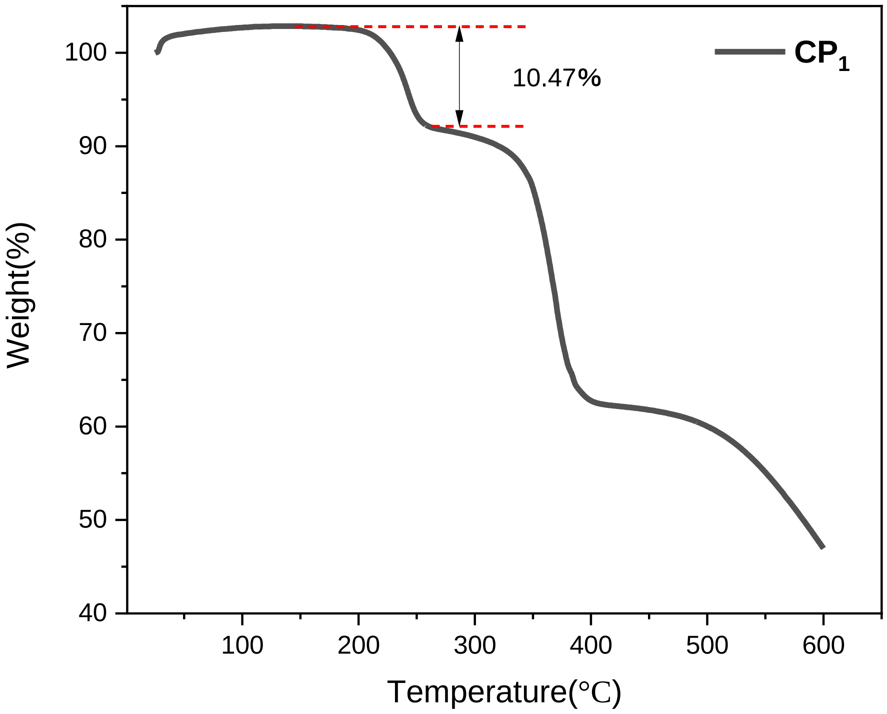
(b)

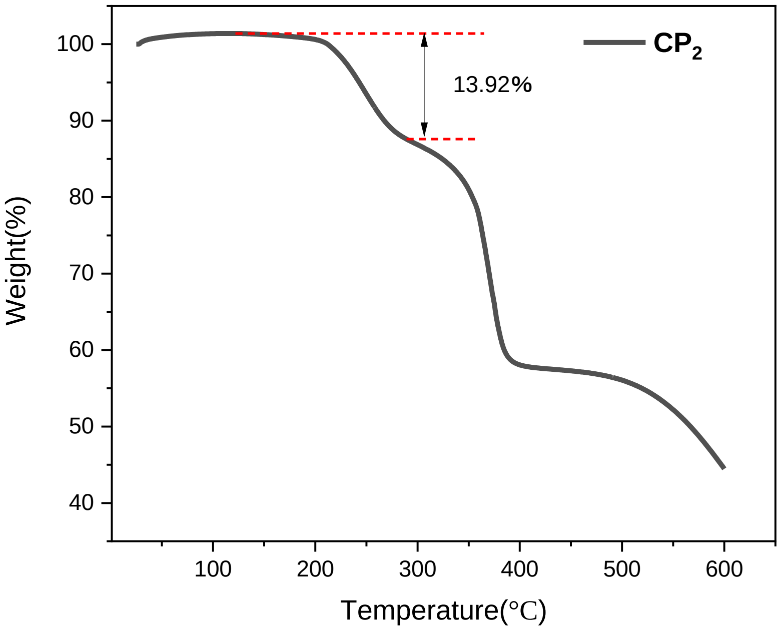


(c)

Figure. S7 PXRD patterns of **CP$_1$** (a), **CP$_2$** (b) and **CP$_3$** (c).



(a)



(b)

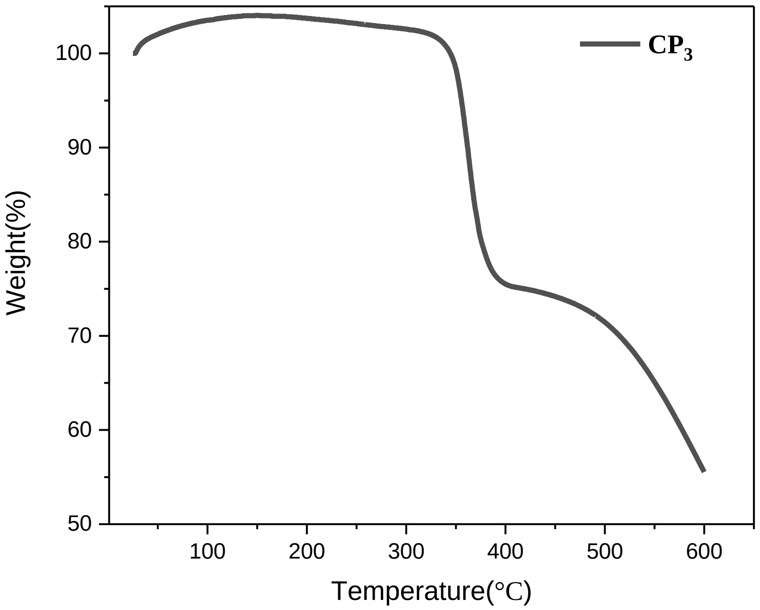


Figure. S8 Thermogravimetric plots of **CP$_1$** (a), **CP$_2$** (b) and **CP$_3$** (c).

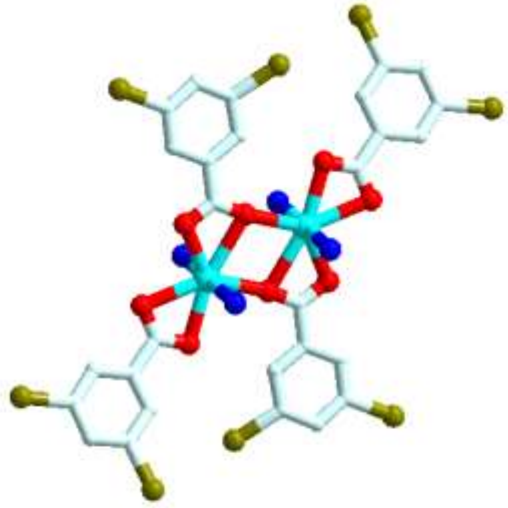


Figure. S9 View of the coordination environments of Cd (II) centers in **CP$_1$.**

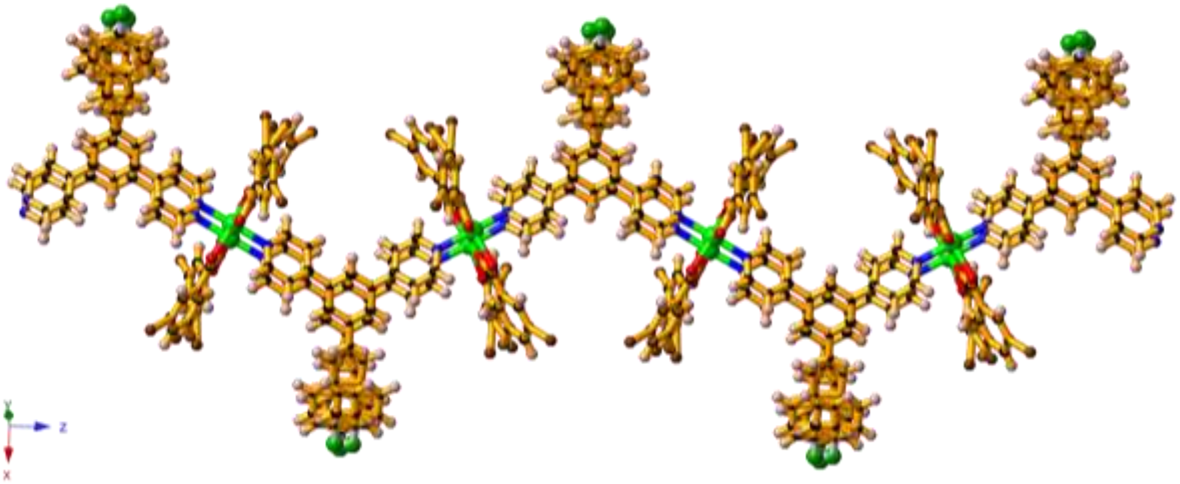


Figure. S10 1D chain like motif in **CP$_1$.**

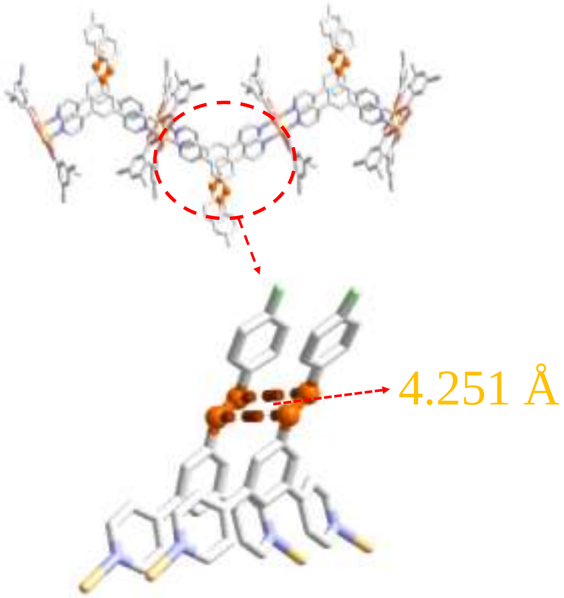
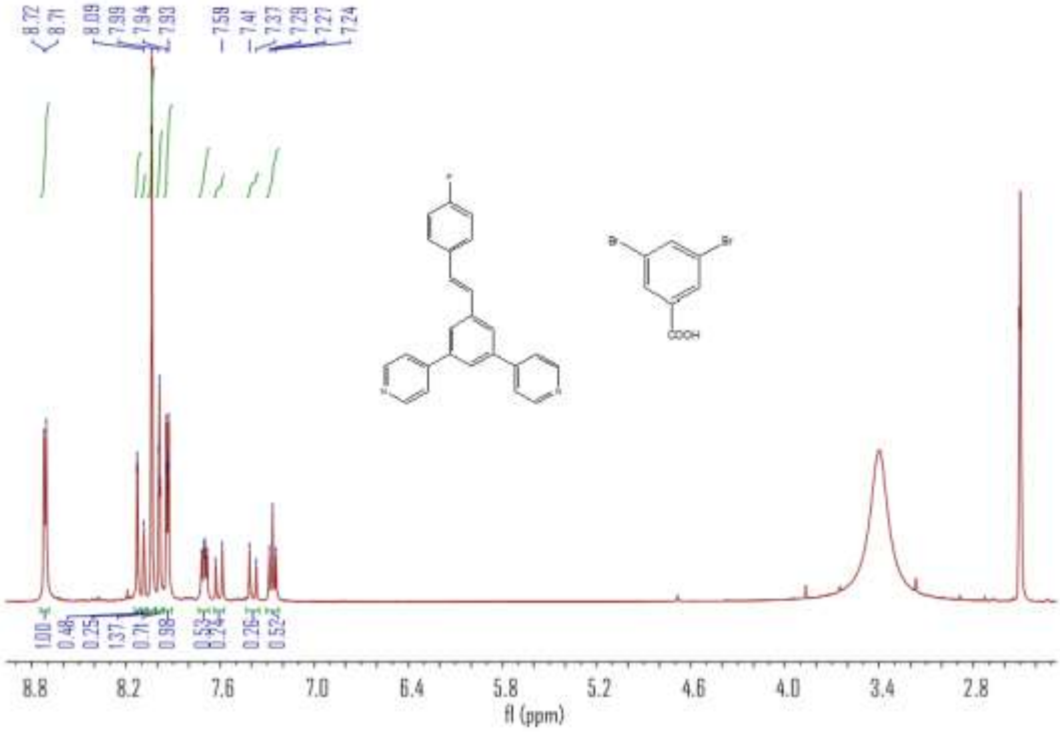
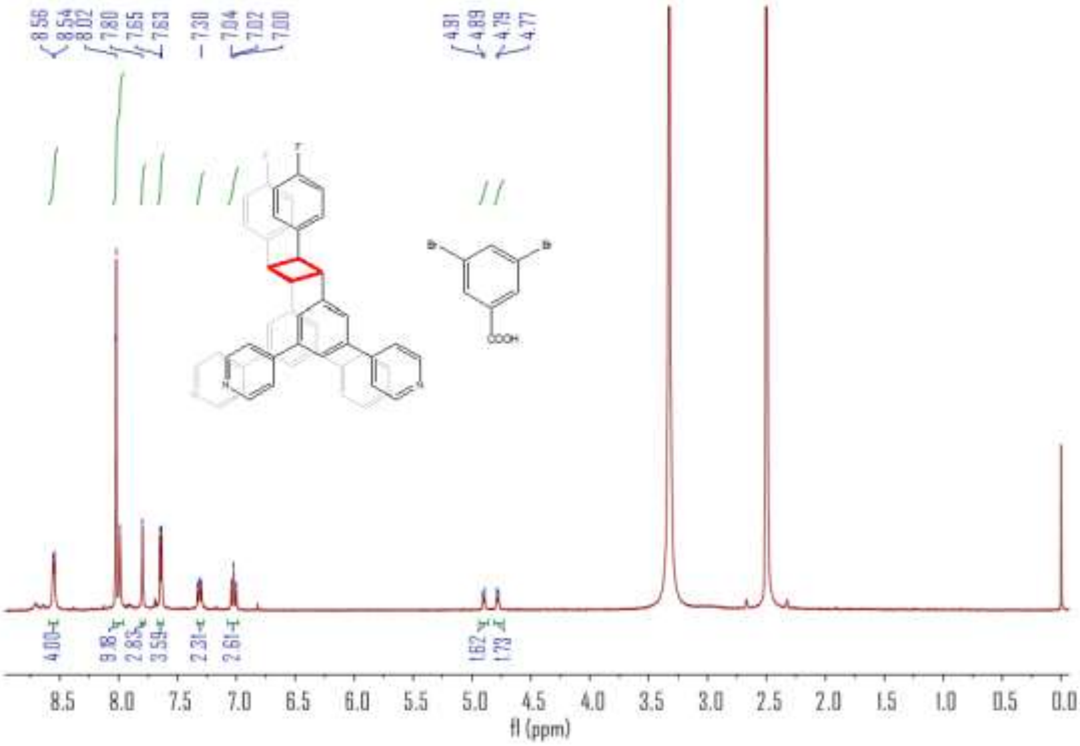


Figure. S11 The detailed structure of **CP$_1$** showing the C=C distance of 4.251Å.



(a)



(b)

Figure. S12 The ^{1}H NMR spectra of **CP_1** (a) and **CP_1'** (b) in DMSO-d_6.

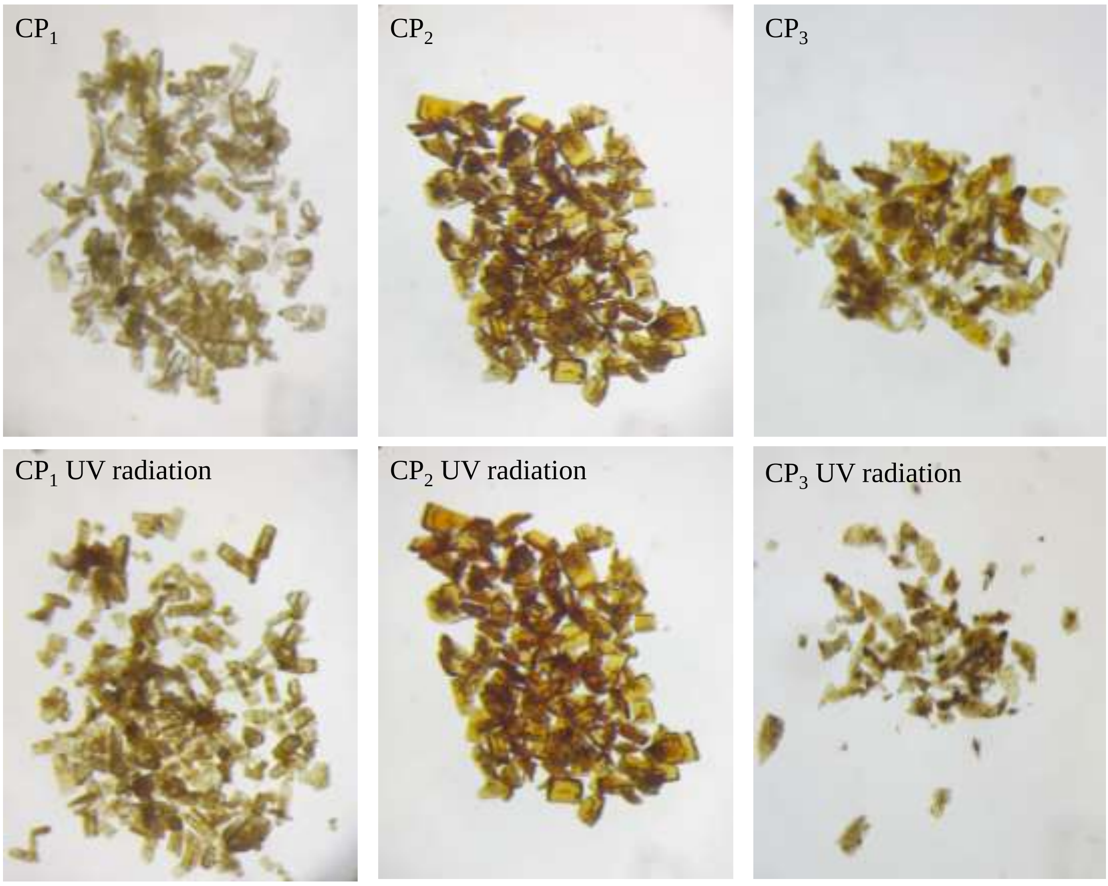


Figure. S13 Photographs of **CP_1-CP_3** before and after UV light irradiation.

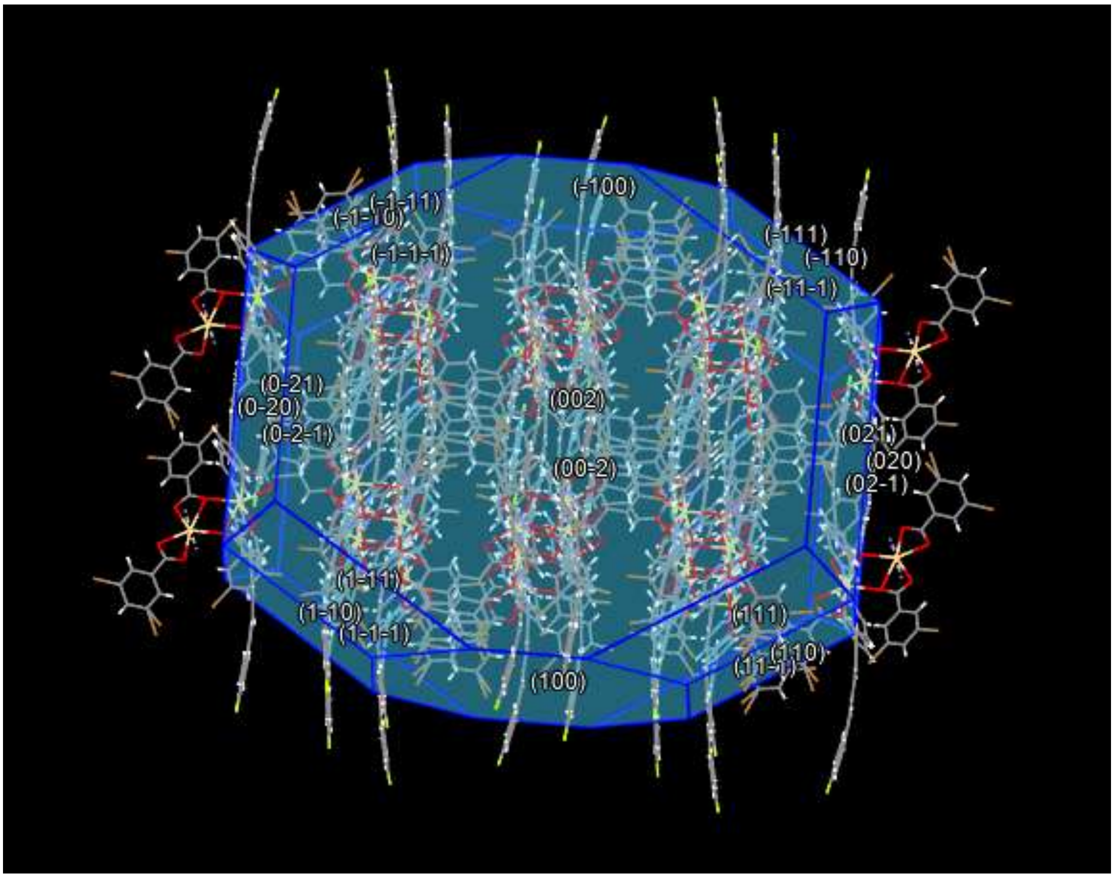


Figure. S14 PS behavior of **CP₁**.

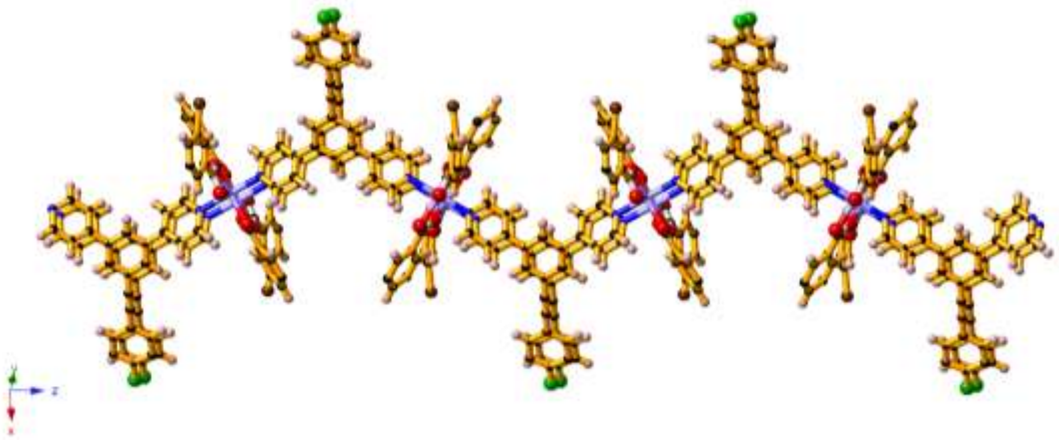


Figure. S15 1D chain motif of **CP₂**.

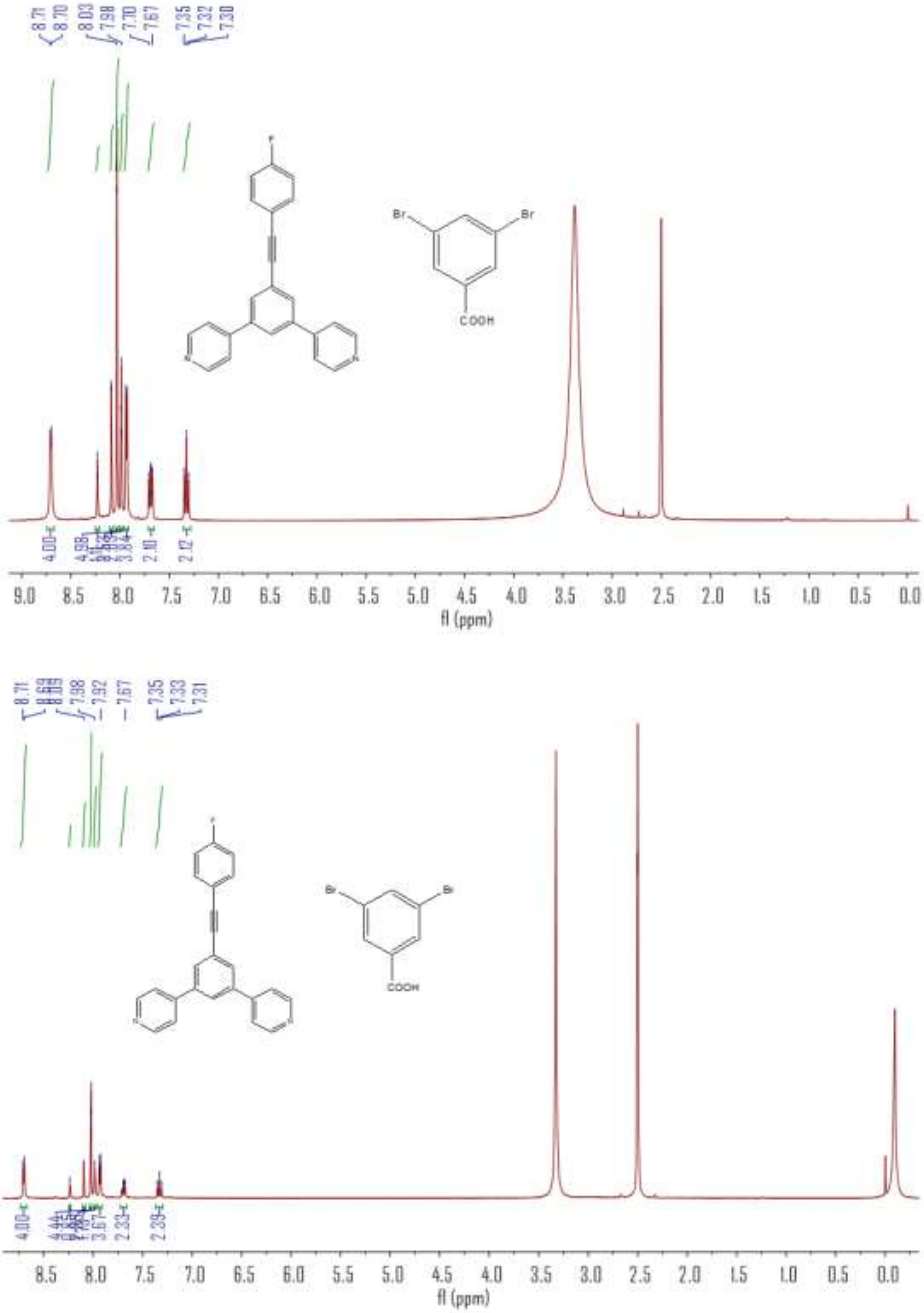


Figure. S16 The ^{1}HNMR spectra of **CP$_2$** before and after UV light irradiation.

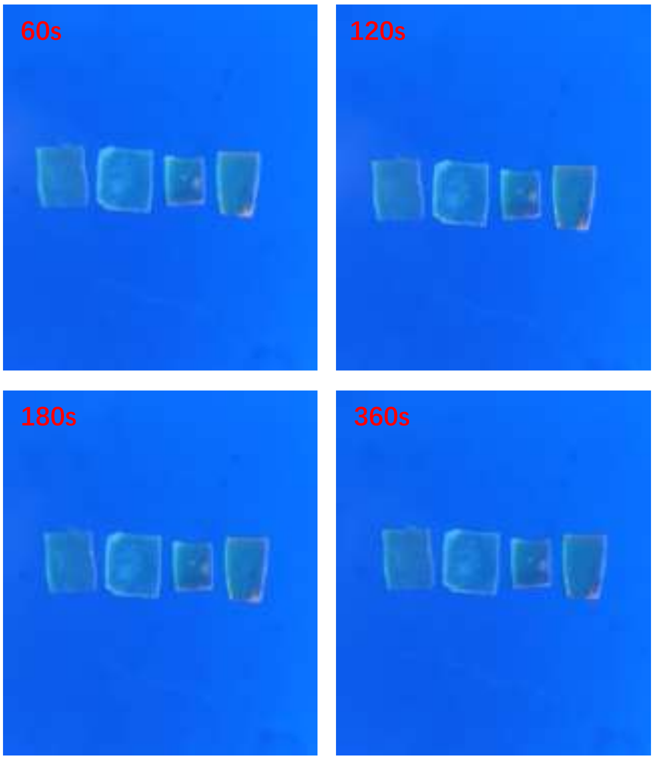


Figure. S17 PS behavior of **CP$_2$**.

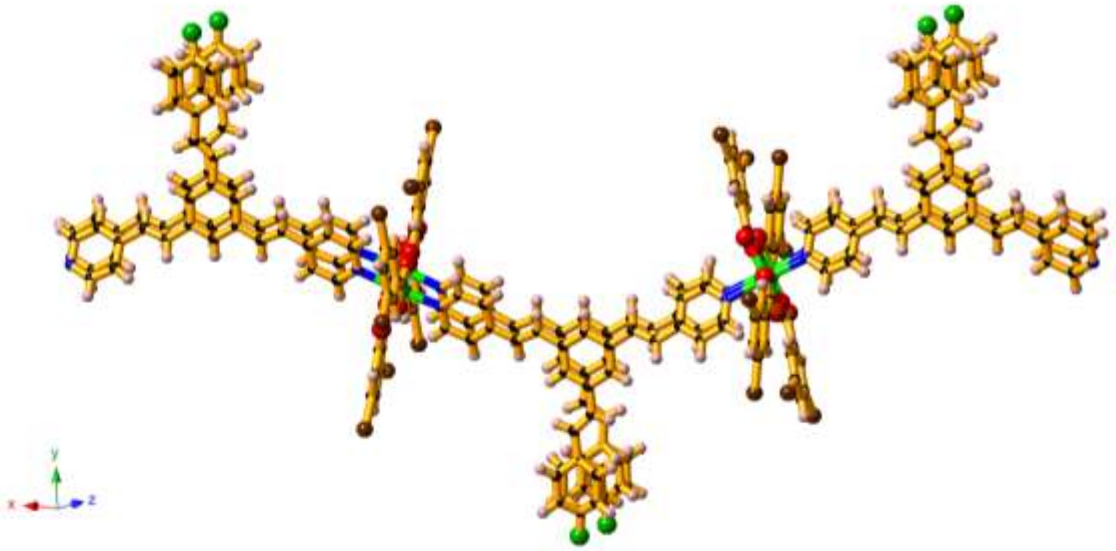
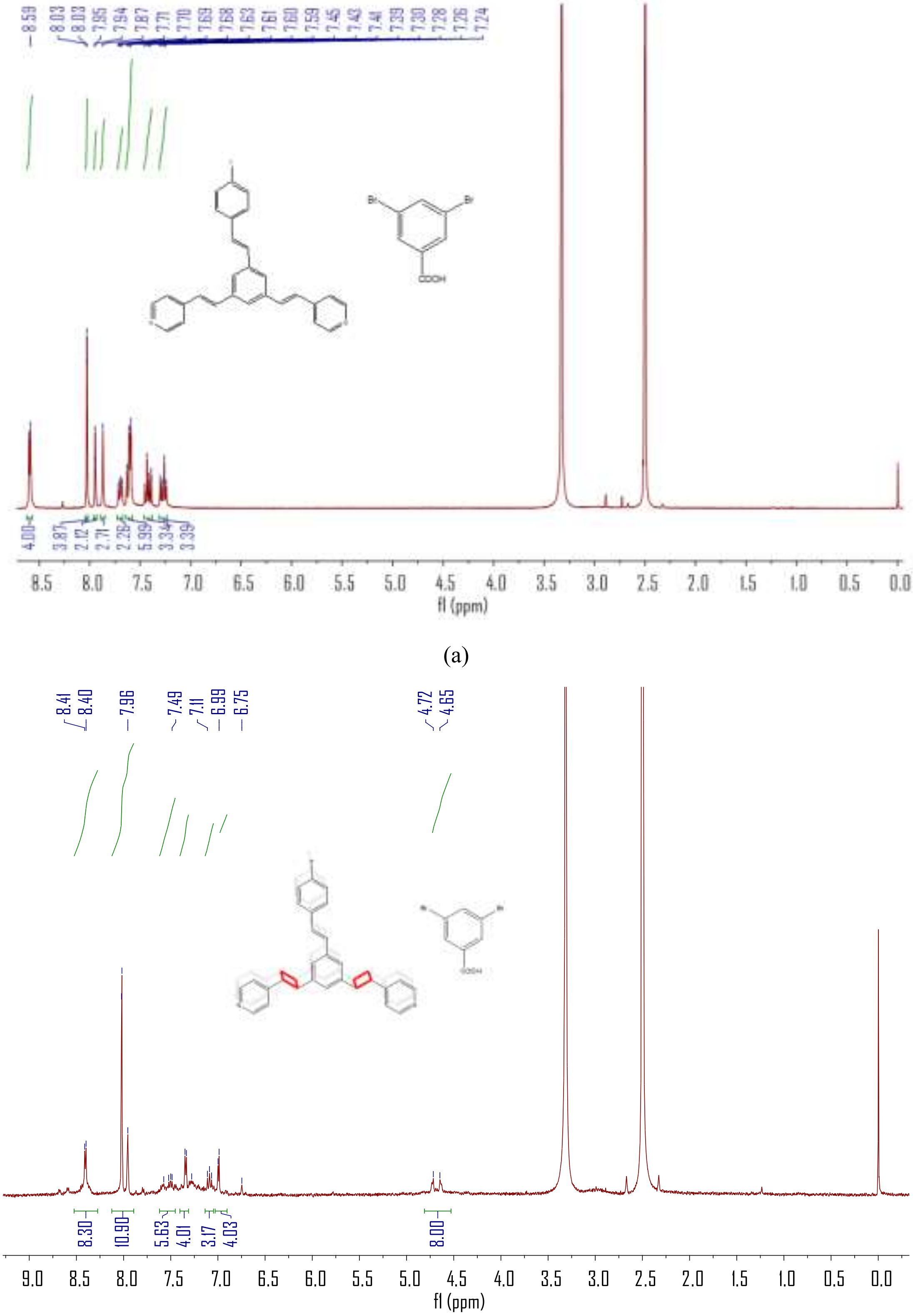


Figure. S18 1D chain like motif of **CP$_3$**.



(a)

(b)

Figure. S19 The ^{1}H NMR spectra of **CP$_3$** before and after UV light irradiation.

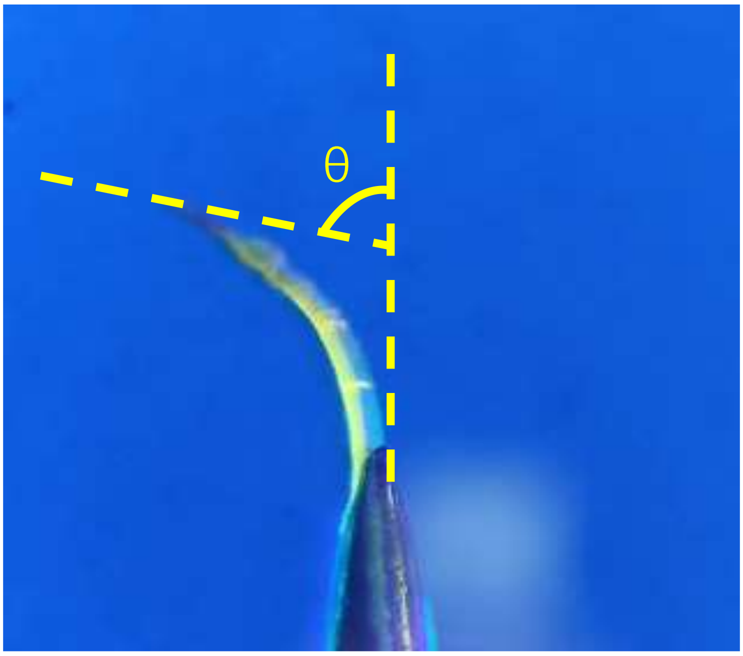


Figure. S20 The tip displacement angle for **CP**$_3$ upon UV light irradiation.

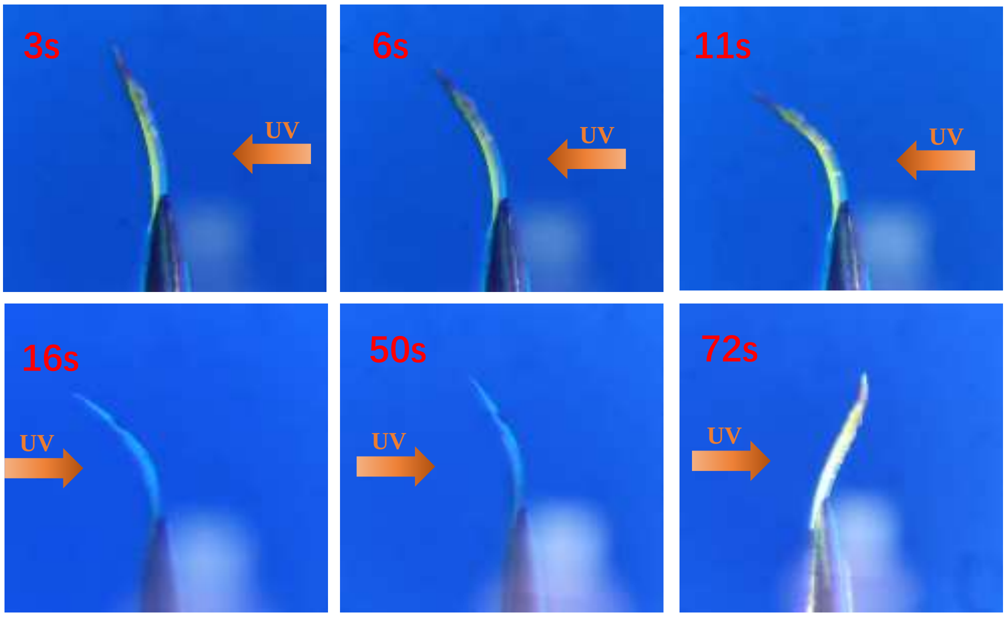


Figure. S21 **CP**$_3$ showed reversible bending behavior against UV light irradiation.

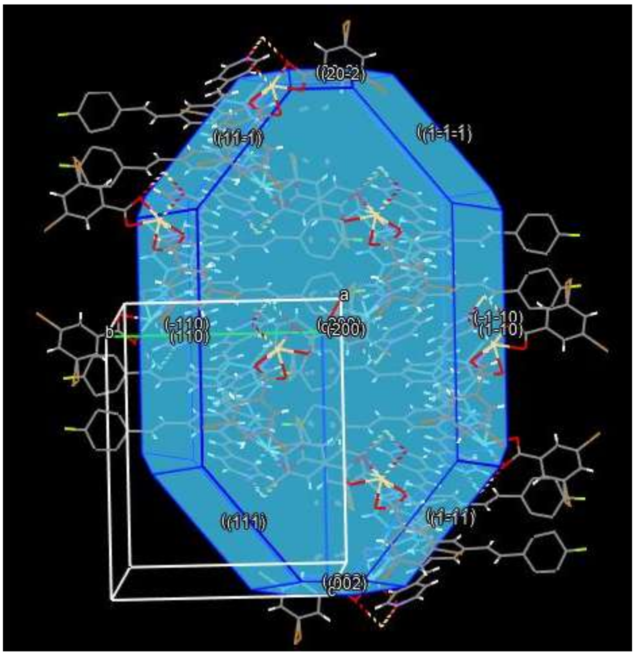


Figure. S22 Calculated growth morphology of **CP₃** from single crystal data (Mercury)[S3].

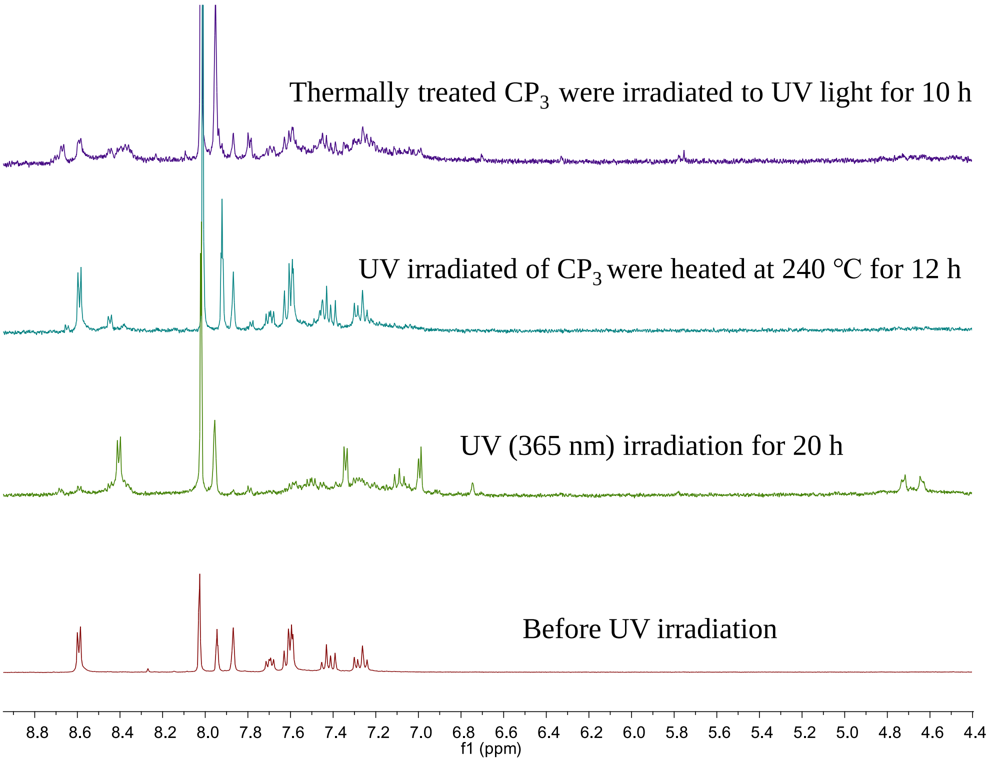


Figure. S23 The ^{1}H NMR spectra of **CP₃** treated by UV light and heating.

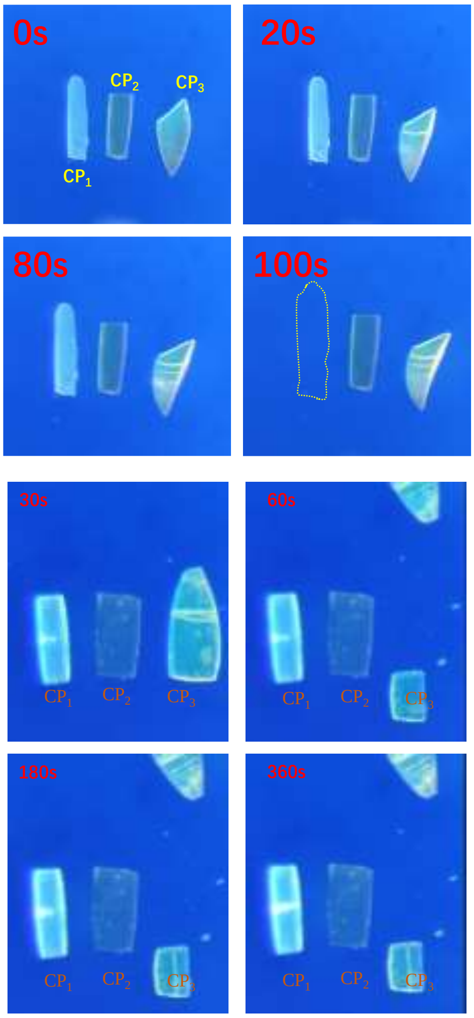


Figure. S24 The PS behaviors of **CP$_1$-CP$_3$** under UV light irradiation.

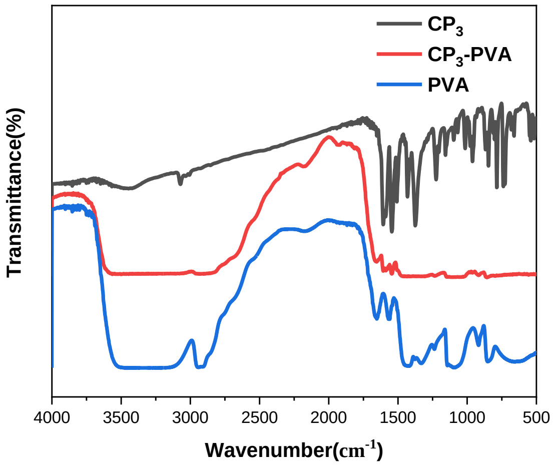


Figure. S25 IR spectra of **CP$_3$**, PVA and CP$_3$-PVA membrane.

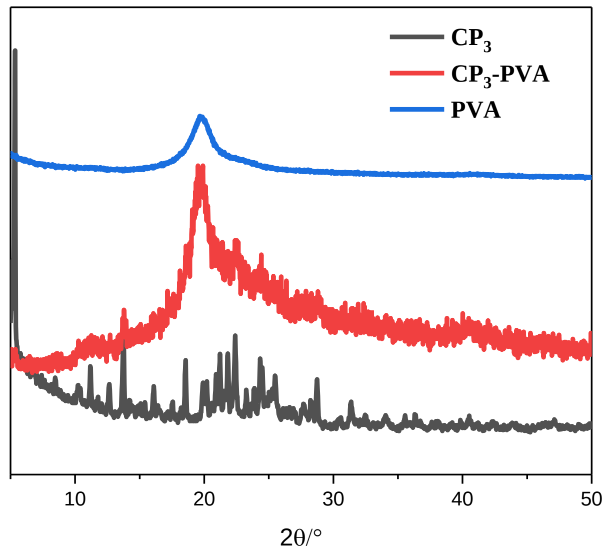


Figure. S26 PXRD profile of **CP_3-PVA** membrane.

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