Electronic Supplementary Information

Carboxylic acids and metal ions co-driven assembly of triene coordination polymers for [2+2] photocycloaddition

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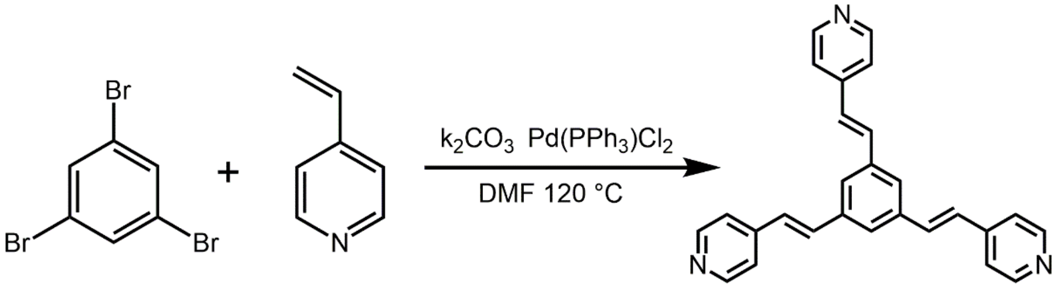
Experimental

1. General methods and procedures

Ligand 1,3,5-tri-4-pyridyl-1,2-ethenylbenzene (tpeb) were prepared according to the literature methods.[S1] Other chemical reagents were directly available from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were acquired on a PANalytical X'Pert PRO MPD system (PW3040/60) using Cu Kα radiation (λ = 1.5406 Å) from 3° to 50° with a scanning step size of 0.02°. NMR spectra were recorded on BRUKER AVANCE III HD (400 MHz) at room temperature and referenced to the residual protonated solvent for NMR spectra. Proton chemical shift δ H = 7.26 ($CDCl_3$) and δ H = 2.50 (d_6-DMSO) ppm are reported relative to the solvent residual peak. Elemental analyses (C, H and N) were performed on a Carlo-Erba CHNO-S microanalyzer. Fourier-transform infrared (IR) spectra of the solid samples in the range 400-4000 cm^{-1} were recorded on a Specode 75. Thermogravimetric analyses (TGA) were performed on a PerkinElmer TGA 4000 under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. UV−vis spectra were recorded on a Varian Cary-50 UV−Vis spectrophotometer.

2. Synthesis

2.1 Synthesis of 1,3,5-tri-4-pyridyl-1,2-ethenylbenzene (tpeb)



Adapted from a literature procedure,[S1] ligand tpeb was synthesized as follows. *N*,*N*-Dimethylformamide (25 mL) was added to a mixture of 1,3,5-tribromobenzene (5.666 g, 18 mmol), 4-vinylpyridine (6.750 g, 60 mmol), K_2CO_3 (7.463 g, 54 mmol), bis(triphenylphosphine)palladium(II)dichloride (0.384 g, 0.54 mmol) in a 100 mL round-bottom flask at room temperature. The reaction mixture was heated to 120 °C (external temperature of oil bath) under N_2 atmosphere and stirred for 48 h. After cooling to ambient temperature, *N*,*N*-Dimethylformamide was removed under reduced pressure by evaporation and the solid after evaporation was extracted with CH_2Cl_2. The organic layer was separated and the aqueous layer was washed with CH_2Cl_2. The combined organic layers were dried over Mg_2SO_4 and concentrated in vacuo. The resulting brown-yellow powder was recrystallized with anhydrous diethyl ether and filtered to give the yellow powder as the pure tpeb ligand with a yield of 82%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.62 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.66 (s, 3H), 7.40 (dd, *J* = 4.6, 1.6 Hz, 6H), 7.34 (d, *J* = 16.0 Hz, 3H), 7.12 (d, *J* = 16.0 Hz, 3H) (Fig. S1).

2.2 Synthesis of $\{[Zn(1,2\text{-chdc})(tpeb)]\cdot H_2O\}_n$ (**CP1**)

To a Pyrex glass tube was loaded $Zn(NO_3)_2\cdot 6H_2O$ (6.0 mg, 0.02 mmol), tpeb (7.7 mg, 0.02 mmol), 1,2-chdc (3.4 mg, 0.02 mmol), MeCN (0.5 mL) and H_2O (1 mL). The tube was sealed and heated in an oven at 150 °C for 24 h, and then cooled to ambient temperature to form orange rhomboid crystals of **CP1**, which were washed with ethanol and H_2O and dried in air (63% yield based on Zn). Anal. calcd. (%) for $C_{35}H_{33}N_3O_5Zn$: C, 65.52, H, 5.14, N, 6.55; found: C, 65.68, H, 5.07, N, 6.71. FT-IR (cm^{-1}): 3034 (m), 1737 (m), 1597 (s), 1502 (w), 1429 (m), 1379 (m), 1278 (w), 1224 (m), 1024 (m), 966 (m), 846 (m), 731 (w), 680 (m).

2.3 Synthesis of {[Zn(1,3-chdc)(tpeb)]·H_2O}*n* (**CP2**)

After a Pyrex glass tube was charged with a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (6.0 mg, 0.02 mmol), tpeb (3.9 mg, 0.01 mmol) and 1,3-chdc (3.4 mg, 0.02 mmol) in H_2O (1 mL) and DMF (0.5 mL), 0.1 mL of 0.1 M HNO_3 solution was injected. The tube was then sealed and heated in an oven to 120 ºC at the rate of 1 ºC min^{-1} and then reacted for 24 h. After it was cooled to ambient temperature at the rate of 10 ºC h^{-1}, yellow rod-shaped crystals of **CP2** were formed and collected by filtration, washed with H_2O, and dried in air (78% based on tpeb). Anal. calcd. (%) for $C_{35}H_{33}N_3O_5Zn$: C, 65.52, H, 5.14, N, 6.55; found: C, 65.39, H, 5.19, N, 6.58. FT-IR (cm^{-1}): 3030 (m), 1737 (m), 1635 (w), 1595 (s), 1502 (w), 1410 (m), 1217 (m), 1018 (w), 962 (m), 842 (m), 798 (m), 732 (w), 677 (m).

2.4 Synthesis of [Zn (1,4-chdc)(tpeb)]*n* (**CP3**)

$Zn(NO_3)_2 \cdot 6H_2O$ (59.5 mg, 0.2 mmol), 1,4-chdc (34.4 mg, 0.2 mmol) and tpeb (38.7 mg, 0.1 mmol) were mixed into a 35 ml Teflon-sealed autoclave, then DMA (5 mL), H_2O (10 mL) and 0.25 mL of 0.1 M HNO_3 solution were added. The autoclave was sealed and heated in an oven to 120 ºC at the rate of 1 ºC min^{-1} and then reacted for 24 h. After it was cooled to ambient temperature at the rate of 10ºC h^{-1}, the yellow flake crystals of **CP3** were isolated and washed with DMA and dried in air (84% based on tpeb). Anal. calcd. (%) for $C_{35}H_{31}N_3O_4Zn$: C, 67.40, H, 4.98, N, 6.74; found: C, 67.36, H, 5.09, N, 6.93. FT-IR (cm^{-1}): 3026 (m), 1741 (m), 1631 (w), 1593 (s), 1502 (w), 1442 (w), 1429 (m), 1340 (m), 1300 (m), 1203 (m), 1068 (w), 1016 (m), 950 (s), 842 (s), 800 (m), 677 (m).

2.5 Synthesis of {[Cd_2(1,2-chdc)(1,2-Hchdc)(H_2O)(tpeb)$_2$]·(NO_3)(H_2O)}*n* (**CP4**)

Yellow rod-shaped of **CP4** were obtained in a similar manner to that used for the isolation of **CP2**, using $Cd(NO_3)_2 \cdot 4H_2O$ (6.2 mg, 0.02 mmol), 1,2-chdc (3.4 mg, 0.02 mmol), tpeb (7.7 mg, 0.02 mmol) as starting materials in H_2O/DMF without HNO_3 solution (72% based on Cd). Anal. calcd. (%) for $C_{70}H_{67}N_7O_{13}Cd_2$: C, 58.37, H, 4.66, N, 6.81; found: C, 58.51, H, 4.59, N, 6.49. FT-IR (cm^{-1}): 3300 (b), 3030 (m), 1739 (m), 1635 (w), 1606 (s), 1575 (s), 1502 (m), 1413 (m), 1300 (m), 1226 (m), 1068 (w), 1012 (m), 968 (s), 846 (s), 802 (s), 763 (m), 711 (m), 678 (s).

2.6 Synthesis of [Cd(1,3-chdc)(tpeb)]*n* (**CP5**)

Yellow flake of **CP5** were obtained in a similar manner to that used for the isolation of **CP3**, using $Cd(NO_3)_2 \cdot 4H_2O$ (24.7 mg, 0.08 mmol), 1,3-chdc (13.8 mg, 0.08 mmol), tpeb (15.5 mg, 0.04 mmol) as starting materials in H_2O (5 mL) and DMF (3.5 mL) with 0.2 mL HNO_3 solution (88% based on tpeb). Anal. calcd. (%) for $C_{35}H_{31}N_3O_4Cd$: C, 62.68, H, 4.62, N, 6.26; found: C, 62.25, H, 4.79, N, 6.39. FT-IR (cm^{-1}): 3036 (m), 1732 (m), 1633 (w), 1593 (s), 1500 (m), 1402 (s), 1224 (m), 1066 (m), 1014 (s), 966 (s), 842 (s), 798 (s), 742 (m), 677 (s).

2.7 Synthesis of [Cd(1,4-chdc)(tpeb)]*n* (**CP6**)

Yellow flake of **CP6** were obtained in a similar manner to that used for the isolation of **CP2**, using $Cd(NO_3)_2 \cdot 4H_2O$ (6.2 mg, 0.02 mmol), 1,4-chdc (3.4 mg, 0.02 mmol), tpeb (3.9 mg, 0.01 mmol) as starting materials in H_2O (1.2 mL) and DMA (0.3 mL) with 0.1 mL HNO_3 solution (82% based on tpeb). Anal. calcd. (%) for $C_{35}H_{31}N_3O_4Cd$: C, 62.68, H, 4.62, N, 6.26; found: C, 62.36, H, 4.39, N, 6.53. FT-IR (cm^{-1}): 3028 (m), 1741 (m), 1618 (m), 1608 (s), 1570 (s), 1502 (m), 1446 (m), 1402 (s), 1342 (m), 1303 (m), 1205 (m), 1068 (w), 1016 (m), 952 (m), 842 (s), 798 (m), 677 (s).

2.8 Synthesis of **CP2a**-**CP6a**

Irradiation of single crystals of **CP2**-**CP6** (100 mg) by using a high power LED lamp source (Beijing Perfectlight: PLSLED 100C) of 365 nm wavelength with 50 W power at 298 K for 6 h, 28 h, 10 h, 20 h and 24 h afforded its photoproduct **CP2a**-**CP6a**.

2.9 Photocurrent response measurements

Photocurrent response measurements were performed on a CHI 660E electrochemical analyzer (Chenhua, Shanghai) with a conventional three electrode arrangement consisting of glassy carbon electrode as working electrode, platinum as the counter electrode, and Ag/AgCl as the reference electrode. The aqueous solution of 0.1 mol L^{-1} Na_2SO_4 was used as the electrolyte. For the preparation of the working electrode, 2.5 mg of the crystalline powder and 2.5 mg carbon black was dispersed in 485 μL of isopropanol solvent followed by adding 15 μL of Nafion (5 wt%). After sonication for 1 h to form a homogeneous ink, a 20 μL drop was cast on a freshly polished GCE (Effective area 0.196 cm^2) and dried under ambient conditions. High power LED lamp source of 475 nm wavelength with an output power of 90 W was used for the electrochemical test, which was fixed 10 cm from the electrode. The electrode excitation time was 0-500 s with 20 s interval, and the test voltage was 0.5 V.

3. X-ray data collection and structure determination

Single crystals of CP1-CP6 suitable for X-ray diffraction were obtained directly from the above preparations. Single crystals coated with Paratone oil on a Cryoloop pin were mounted on a Bruker Smart CCD diffractometer with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) (**CP2**, **CP6**) and a graphite monochromated Ga Kα radiation (λ = 1.34138 Å) (**CP1**, **CP3**, **CP4**, **CP5**) at 120 K (**CP2**), 273 K (**CP3**), 137 K (**CP1**, **CP4**, **CP5**) and 296 K (**CP6**). Bruker SAINT was employed for the refinement of cell parameters and the reduction of collected data and absorption corrections (multi-scan) were applied. The crystal structures of all compounds were solved by Direct methods and refined by full-matrix least-squares techniques using the *SHELXL-2018* program.[S2] The non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms bonded to C and N atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. There are highly disordered water molecules in **CP5** and it is not possible to identify the position of their hydrogen atoms based on the residual peaks on the Fourier diagram. We removed the diffraction electron data for these highly disordered water molecules using the SQUEEZE command of the PLATON package[S3] and used the resulting data for further refinement to produce the final cif file. A summary of the pertinent crystallographic data for these compounds is provided in Table S1. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge

Crystallographic Data Centre (CCDC), under deposition numbers 2251590 (**CP1**), 2251591 (**CP2**), 2251592 (**CP3**), 2251593 (**CP4**), 2251594 (**CP5**) and 2251595 (**CP6**), respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

Table S1 Summary of crystal data and structure refinement parameters for **CP1**, **CP2**, **CP3**, **CP4**, **CP5** and **CP6**.

Compounds	**CP1**	**CP2**	**CP3**
Empirical formula	$C_{35}H_{33}N_3O_5Zn$	$C_{35}H_{33}N_3O_5Zn$	$C_{35}H_{31}N_3O_4Zn$
Formula weight	641.01	641.01	623.00
Temperature (K)	137.0	120(2)	273(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbcm* (57)	$P2_1/n$ (14)	*C*2/*c* (15)
a (Å)	12.4054(11)	7.9429(3)	30.222(7)
b (Å)	10.6944(10)	27.8055(9)	13.045(2)
c (Å)	24.935(2)	12.8882(5)	15.589(3)
β (°)	90	96.7670(10)	91.586(12)
Volume (Å^3)	3308.1(5)	2826.61(18)	6144(2)
Z	4	4	8
μ (mm^{-1})	0.907	0.920	0.955
ρ_{calc} (g cm^{-3})	1.287	1.506	1.347
F(000)	1336	1336	2592
Reflections collected	41500	44579	141630
Independent reflections	3295	6486	7047
R_{int}	0.0613	0.0650	0.0616
R_1[a]	0.1398	0.0569	0.0533
wR_2[b]	0.2727	0.1650	0.1748
GOF[c]	1.124	1.049	1.061

to be continued for **Table S1**

Compounds	**CP4**	**CP5**	**CP6**
Empirical formula	$C_{70}H_{67}N_7O_{13}Cd_2$	$C_{35}H_{32}N_3O_4Cd$	$C_{35}H_{31}N_3O_4Cd$
Formula weight	1439.10	671.03	670.03
Temperature (K)	137	136(2)	296.15
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca* (61)	*C*2/*c* (15)	*C*2/*c* (15)
a (Å)	14.6634(13)	29.288(4)	29.558(6)
b (Å)	24.805(2)	13.0795(16)	13.226(3)
c (Å)	34.107(3)	16.931(2)	16.250(4)
β (°)	90	94.192(5)	93.107(7)
Volume (Å^3)	12405.6(18)	6468.5(14)	6343(2)
Z	8	8	8
μ (mm^{-1})	4.063	3.829	0.730
ρ_{calc} (g cm^{-3})	1.541	1.378	1.403
F(000)	5888	2744	2736
Reflections collected	184940	73708	68662
Independent reflections	14183	7395	7298
R_{int}	0.0624	0.0677	0.0721
$R_1{}^a$	0.0402	0.0884	0.0806
$wR_2{}^b$	0.0997	0.2681	0.2568
GOF^c	1.084	1.068	1.027

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR_2 = \{\Sigma w(F_o{}^2-F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$. ^{c}GOF $= \{\Sigma w((F_o{}^2-F_c{}^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total numbers of parameters refined.

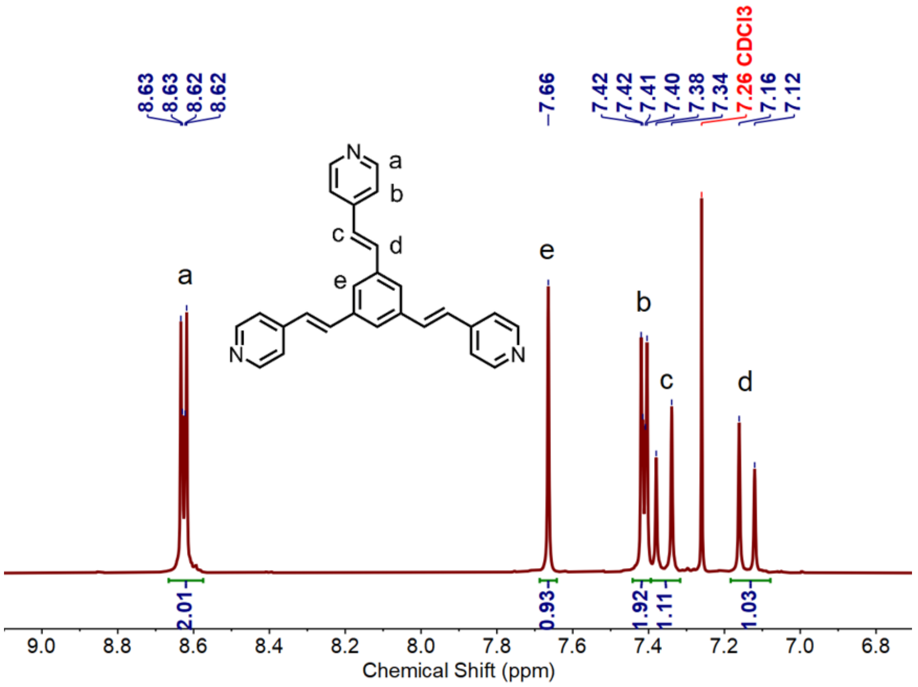


Fig. S1 ^{1}H NMR data of tpeb ligand (400 MHz, $CDCl_3$).

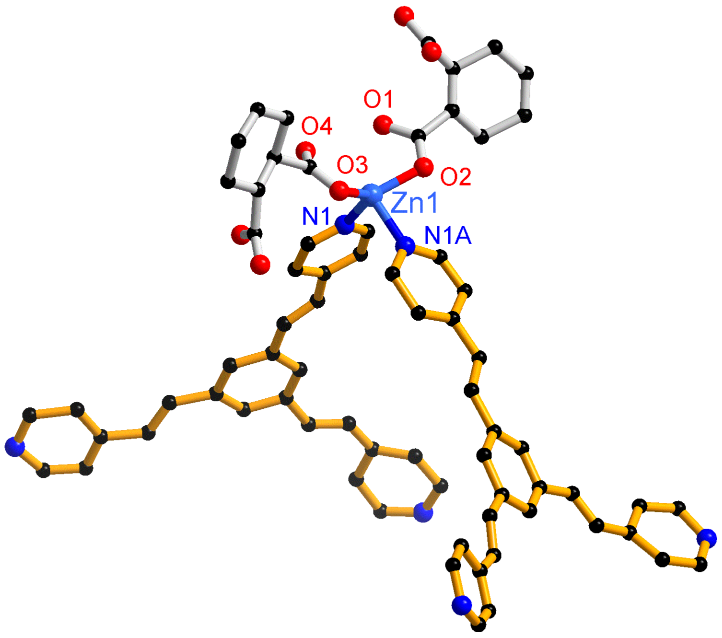


Fig. S2 View of the coordination environment of the Zn1 in **CP1** with a labelling scheme. Hydrogen atoms were omitted for clarity.

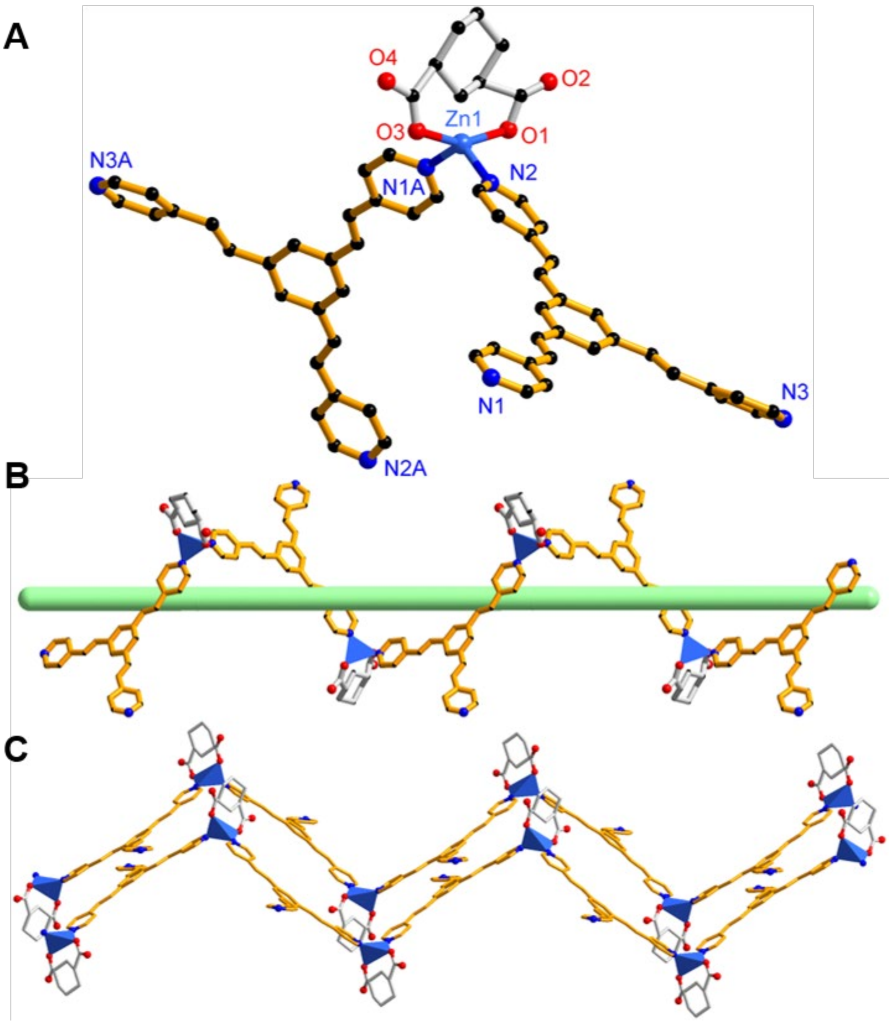


Fig. S3 (A) View of the coordination environment of the Zn1 in **CP2** with a labelling scheme. (B) A section of the 1D helix chain extending along the *b* axis of **CP2**. (C) Two adjacent 1D chains in the structure of **CP2**. Hydrogen atoms were omitted for clarity.

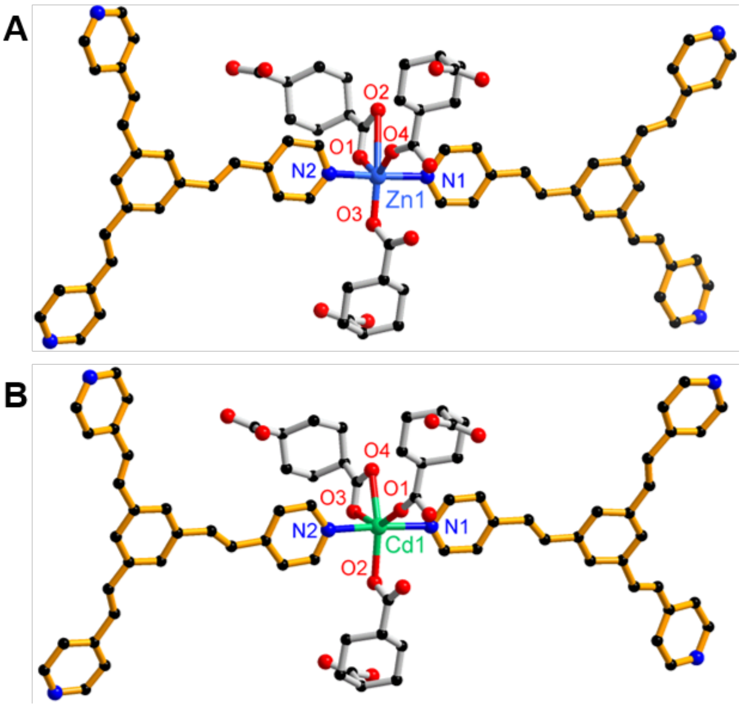


Fig. S4 View of the coordination environment of the Zn1 in **CP3** (A) with a labelling scheme, same as Cd1 in **CP6** (B). Hydrogen atoms were omitted for clarity.

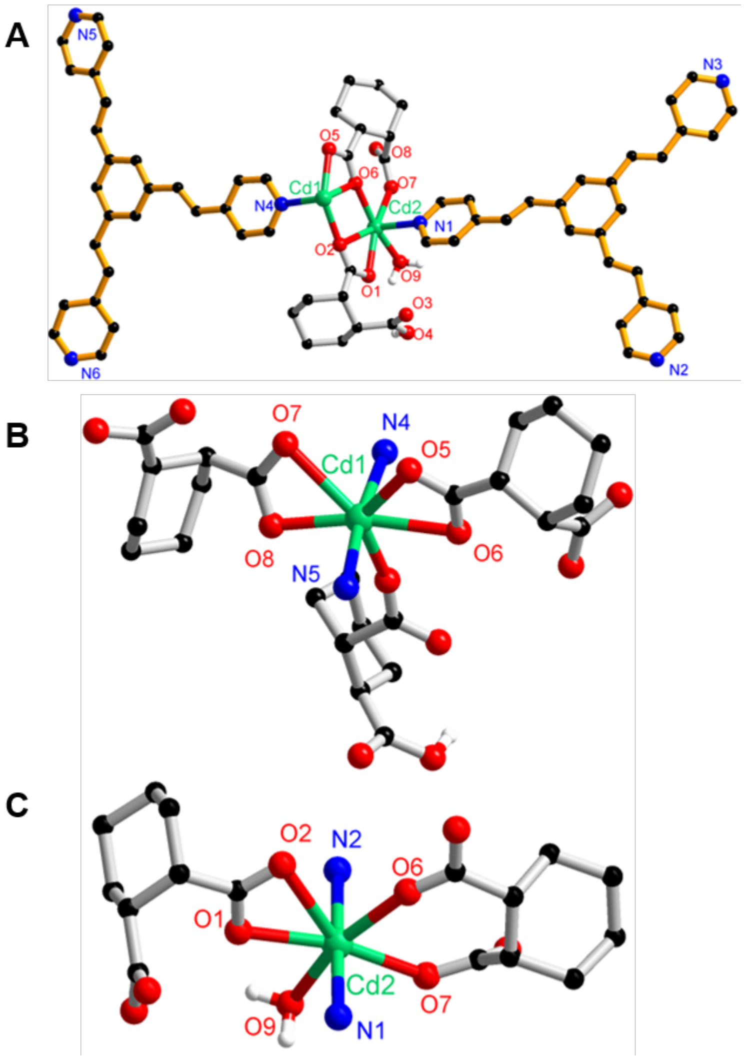


Fig. S5 View of the asymmetric unit of **CP4** with a labelling scheme (A) and the different coordination environments of Cd1 (B) and Cd2 (C) in **CP4**. Hydrogen atoms were omitted for clarity.

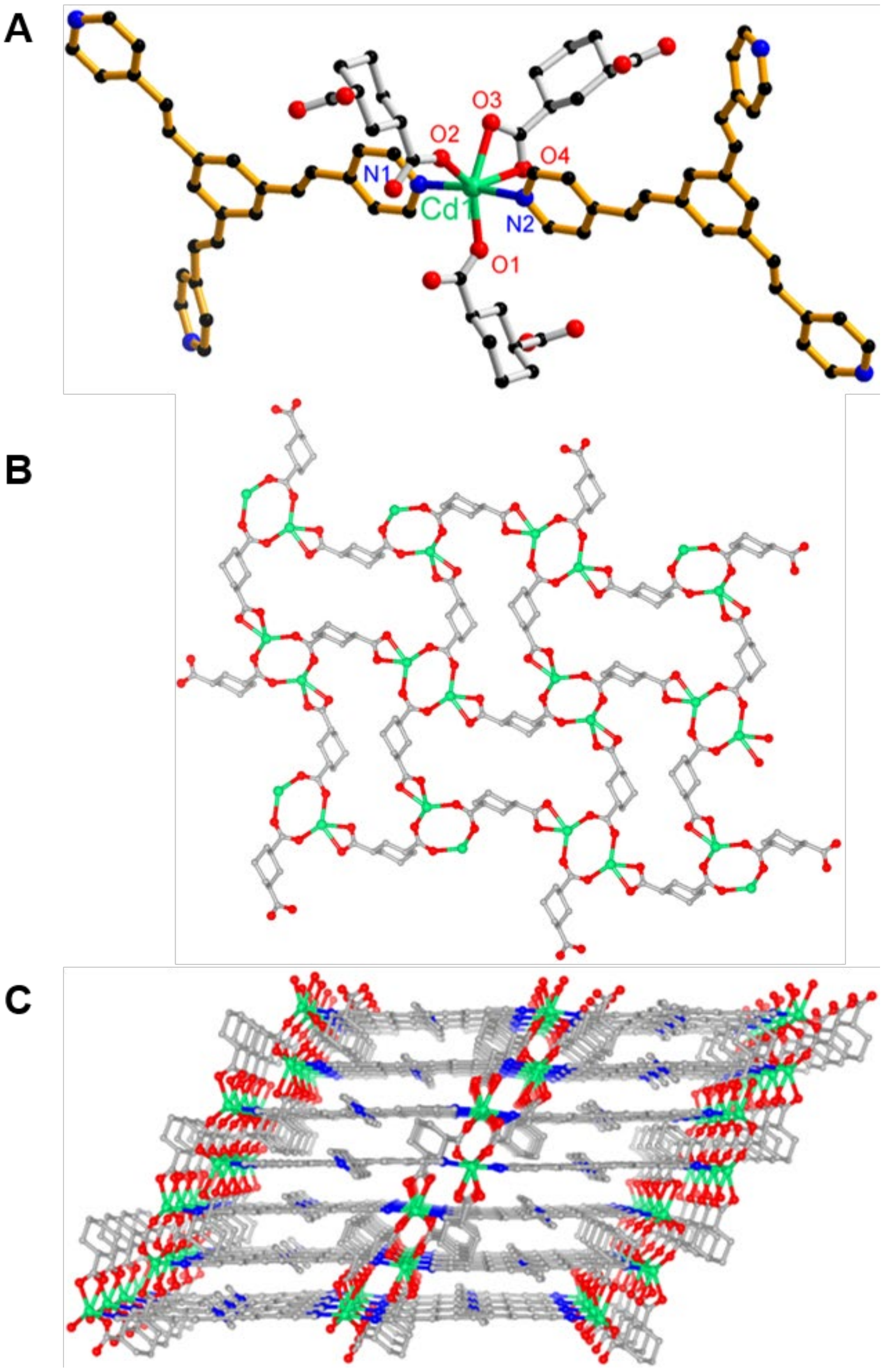


Fig. S6 (A) View of the coordination environment of the Cd1 in **CP5**. (B) A 2D layer composed of 1,3-chdc linkers and Cd^{2+} in **CP5**. (C) The 3D pillar-layer framework of **CP5**. Hydrogen atoms were omitted for clarity.

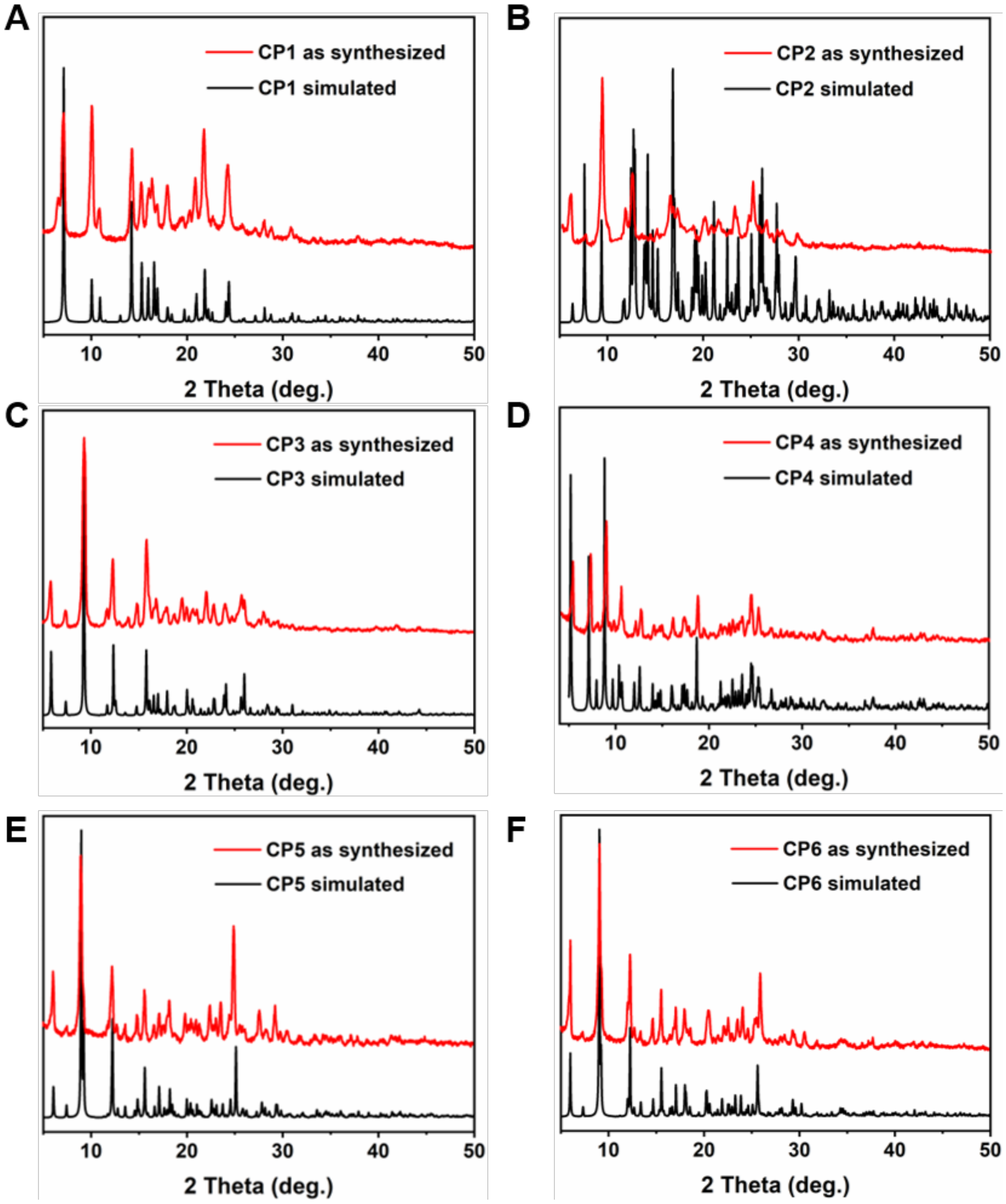


Fig. S7 The PXRD patterns of **CP1-CP6**.

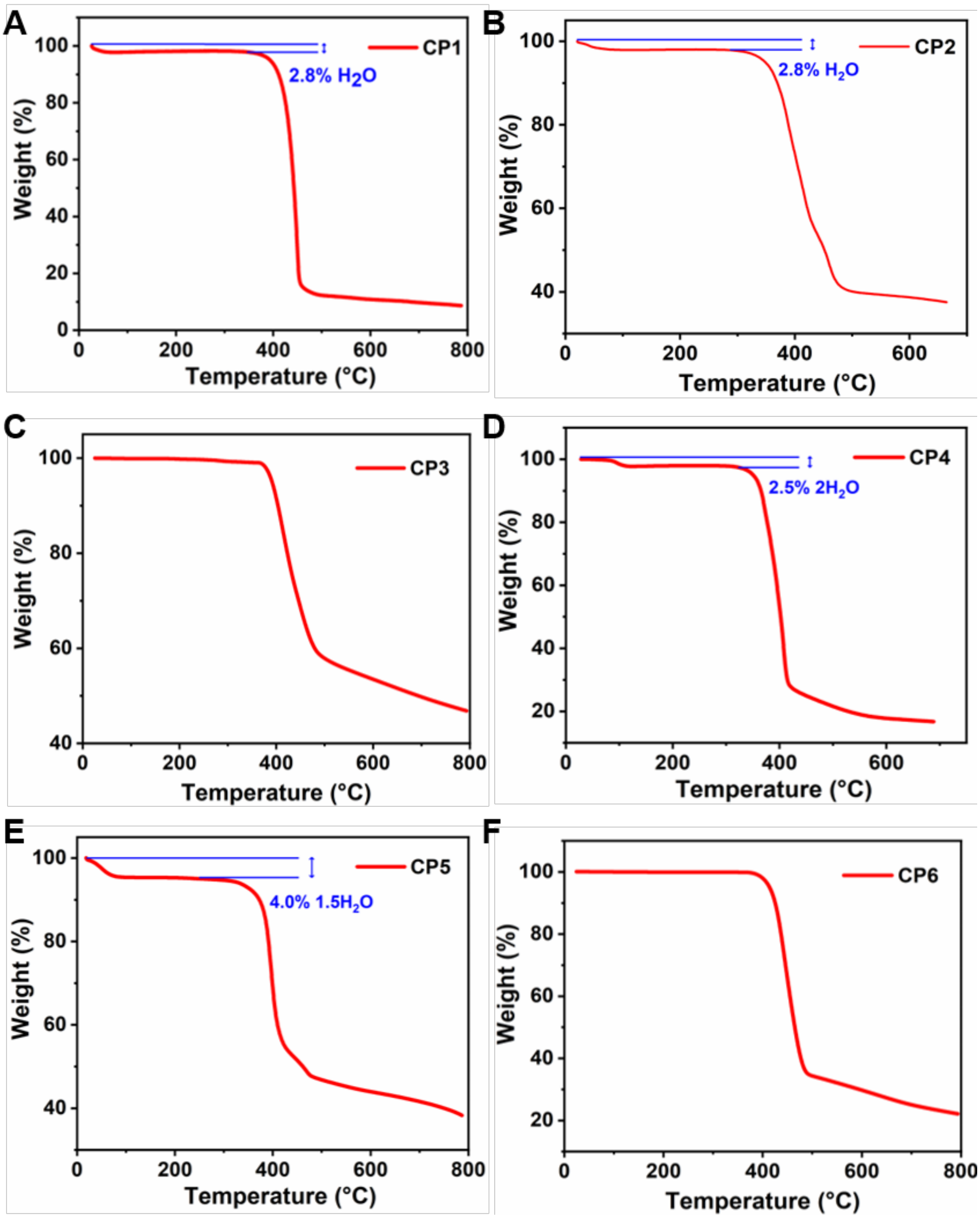


Fig. S8 The TGA curves of **CP1-CP6** in a N_2 atmosphere from room temperature to 800 °C.

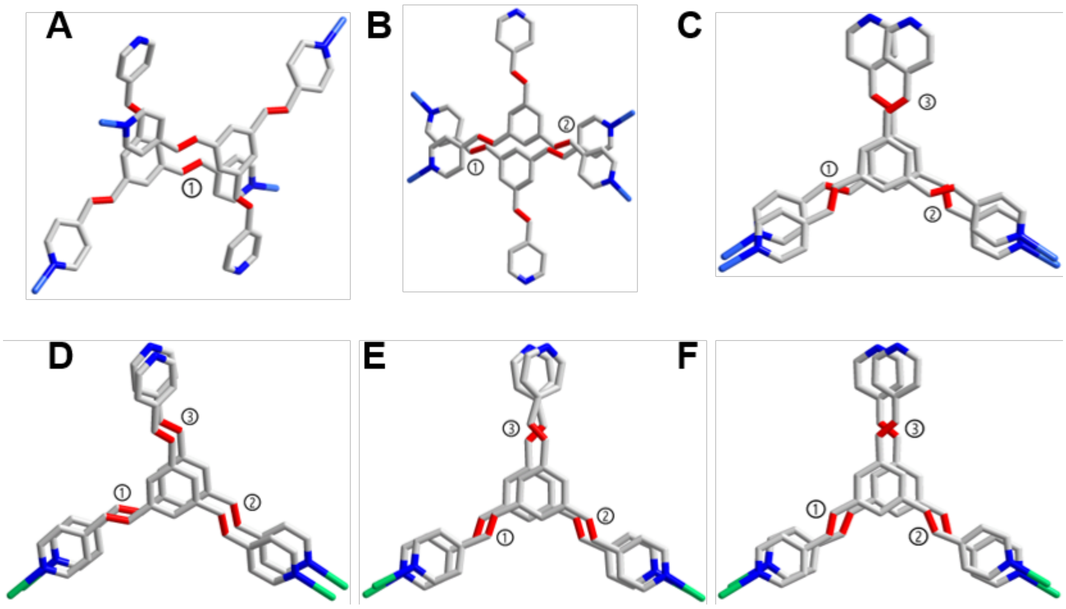


Fig. S9 View of the alignment of the tpeb ligands in **CP1-CP6**.

Table S2 The distances of C=C bonds in **CP1-CP6**.

C=C	①	②	③
CP1	4.898 Å/4.898 Å (parallel)	-	-
CP2	3.927 Å/4.207 Å (crisscross)	3.927 Å/4.207 Å (crisscross)	-
CP3	3.662 Å/3.788 Å (crisscross)	3.662 Å/3.788 Å (crisscross)	3.850 Å/4.543 Å (crisscross)
CP4	3.683 Å/3.820 Å (parallel)	3.811 Å/3.821 Å (parallel)	3.852 Å/4.017 Å (parallel)
CP5	3.670 Å/3.684 Å (parallel)	3.670 Å/3.684 Å (parallel)	4.012 Å/4.070 Å (crisscross)
CP6	3.623 Å/3.638 Å (parallel)	3.623 Å/3.638 Å (parallel)	3.954 Å/4.501 Å (crisscross)

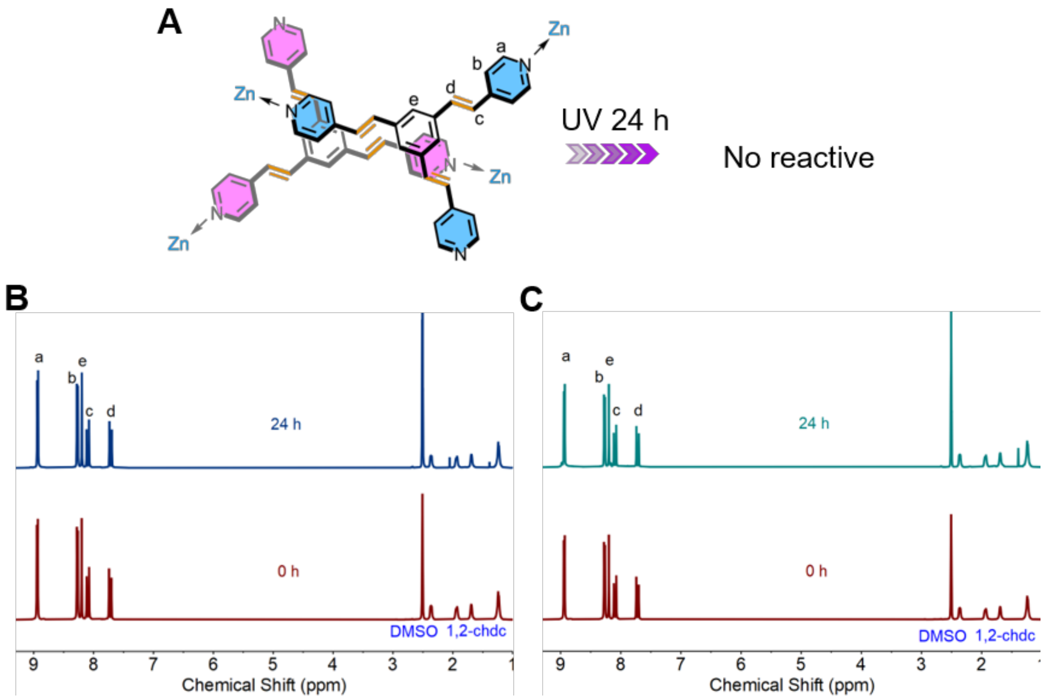


Fig. S10 The ^{1}H NMR spectra of **CP1** after UV light ($\lambda = 365$ nm) irradiation at 298 K (B) and 263 K (C) for 24 h (400 MHz, DMSO-d_6) and the alignment of tpeb ligands in **CP1** (A).

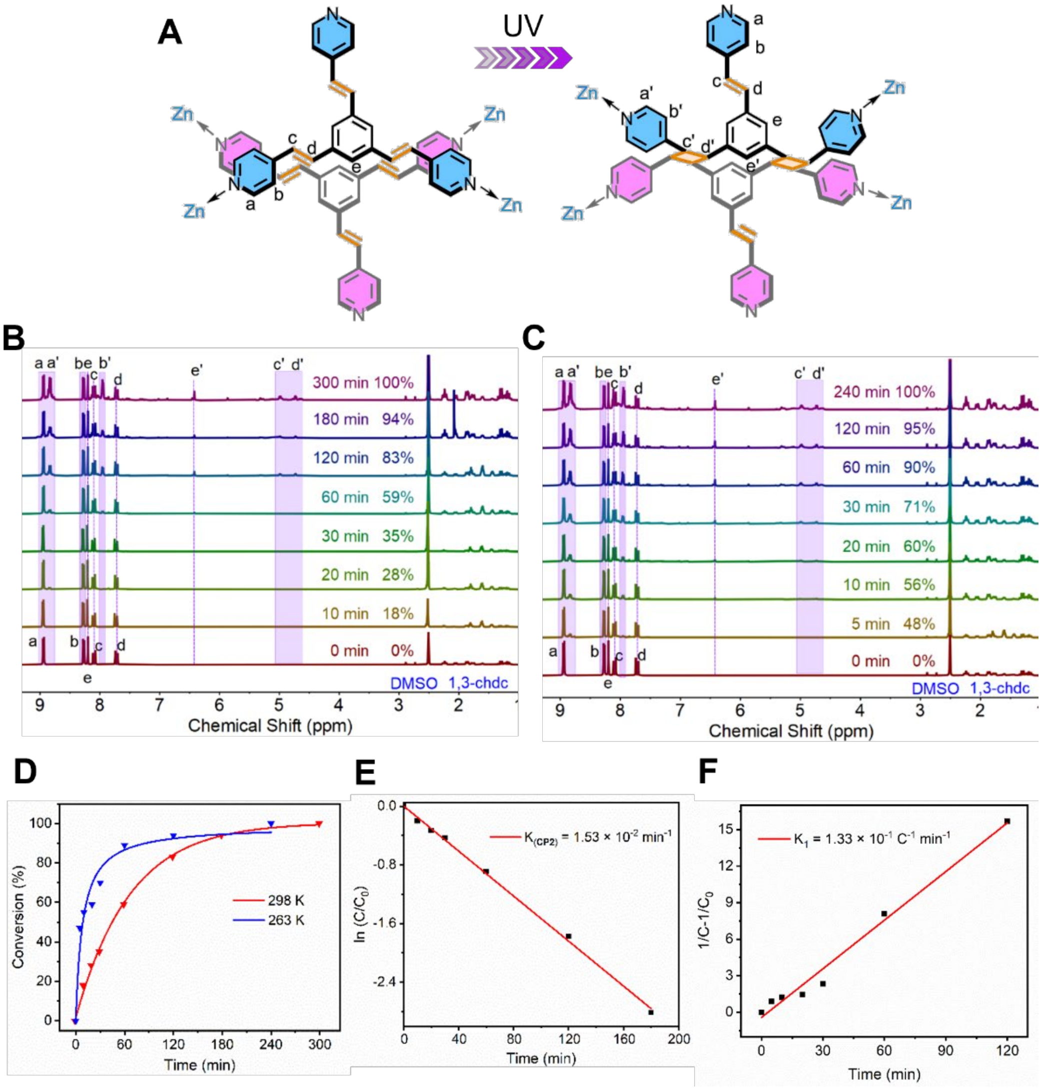


Fig. S11 The ^{1}H NMR spectra of **CP2** after UV light ($\lambda = 365$ nm) irradiation at 298 K (B) and 263 K (C) for different time (400 MHz, DMSO-d_6) and the alignment of tpeb ligands before and after the photocycloaddition reaction (A). Plots of conversion of tpeb in **CP2** versus irradiation time based on ^{1}H NMR result (D) and corresponding fitting of kinetic rate at 298 K (E) and 263 K (F) of **CP2**.

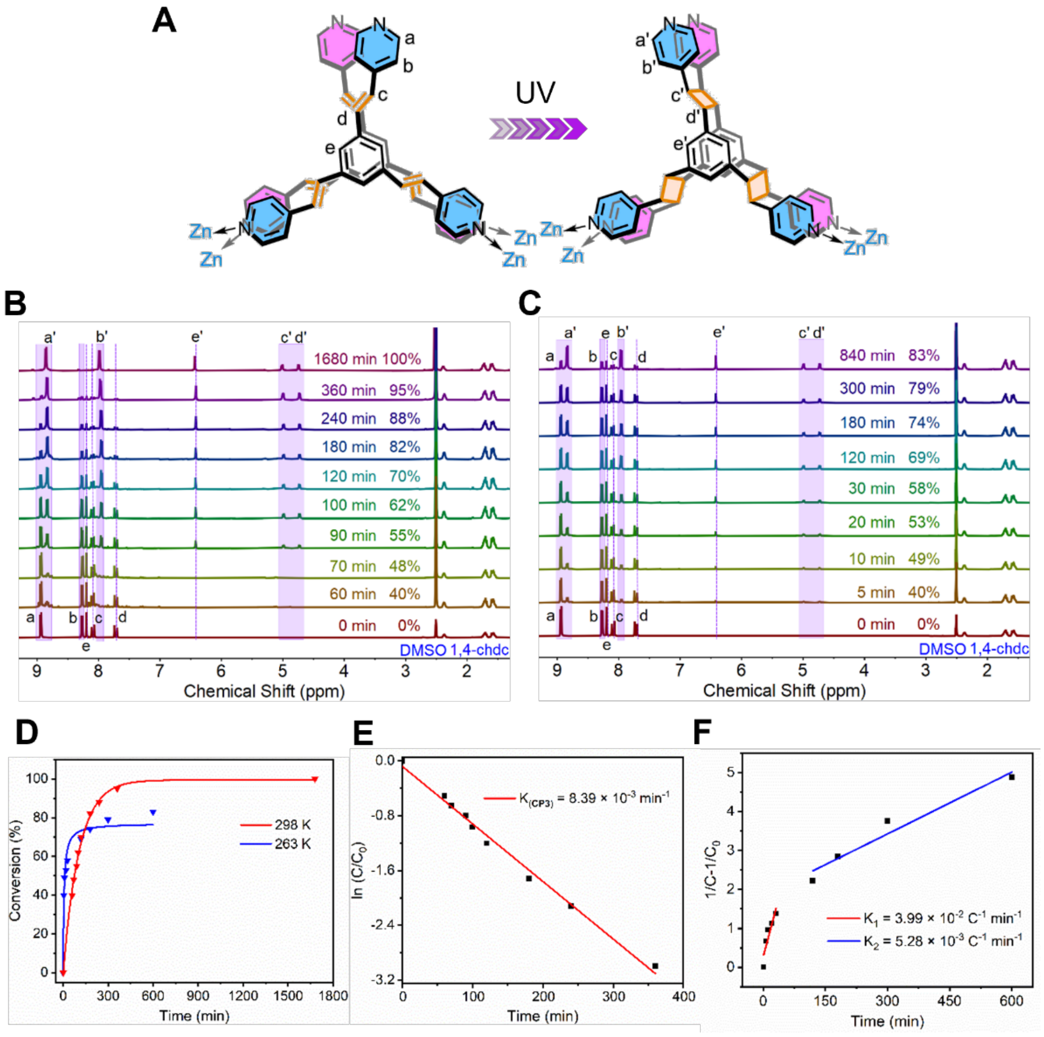


Fig. S12 The ^{1}H NMR spectra of **CP3** after UV light (λ = 365 nm) irradiation at 298 K (B) and 263 K (C) for different time (400 MHz, DMSO-d_6) and the alignment of tpeb ligands before and after the photocycloaddition reaction (A). Plots of conversion of tpeb in **CP3** versus irradiation time based on ^{1}H NMR result (D) and corresponding fitting of kinetic rate at 298 K (E) and 263 K (F) of **CP3**.

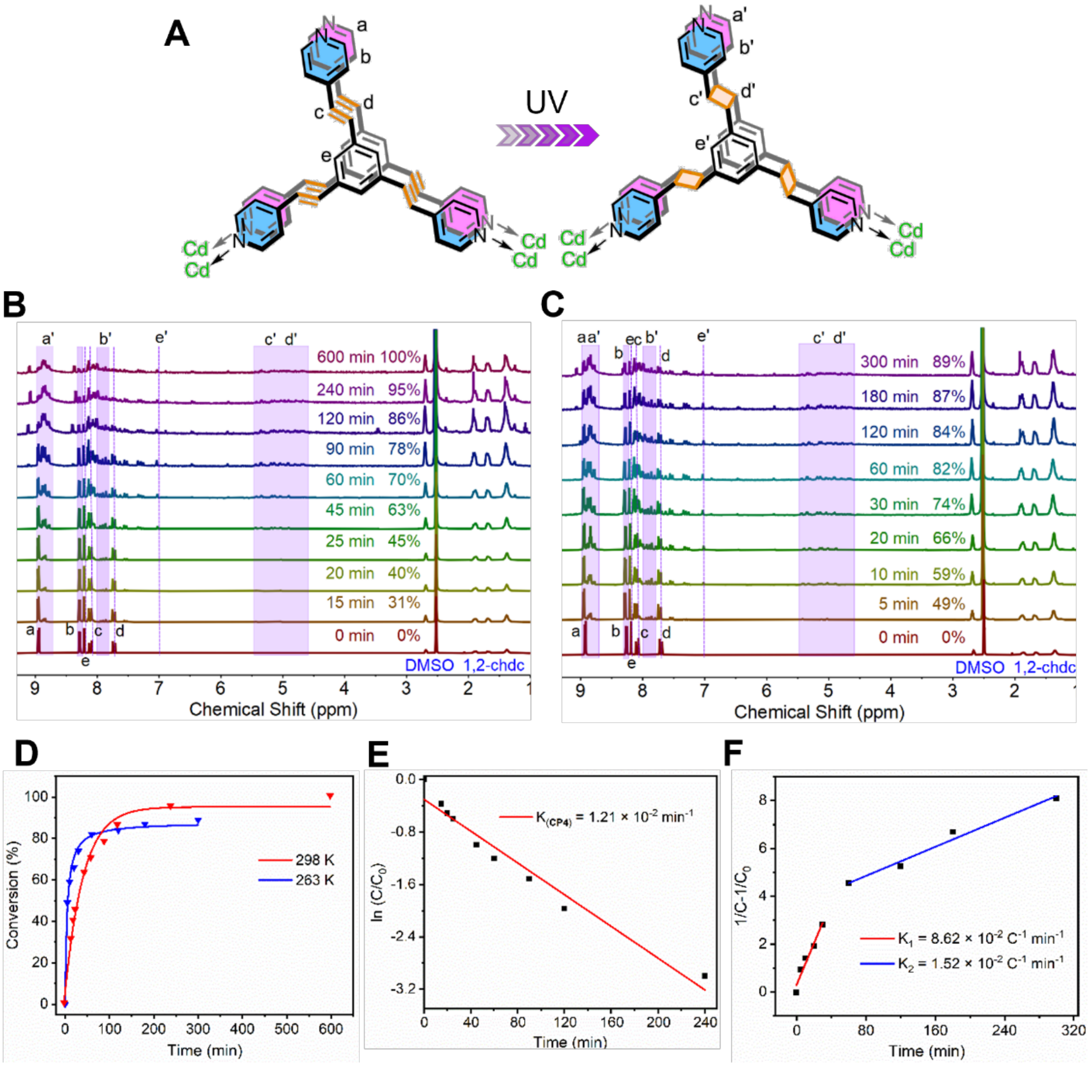


Fig. S13 The ^{1}H NMR spectra of **CP4** after UV light (λ = 365 nm) irradiation at 298 K (B) and 263 K (C) for different time (400 MHz, DMSO-d_6) and the alignment of tpeb ligands before and after the photocycloaddition reaction (A). Plots of conversion of tpeb in **CP4** versus irradiation time based on ^{1}H NMR result (D) and corresponding fitting of kinetic rate at 298 K (E) and 263 K (F) of **CP4**.

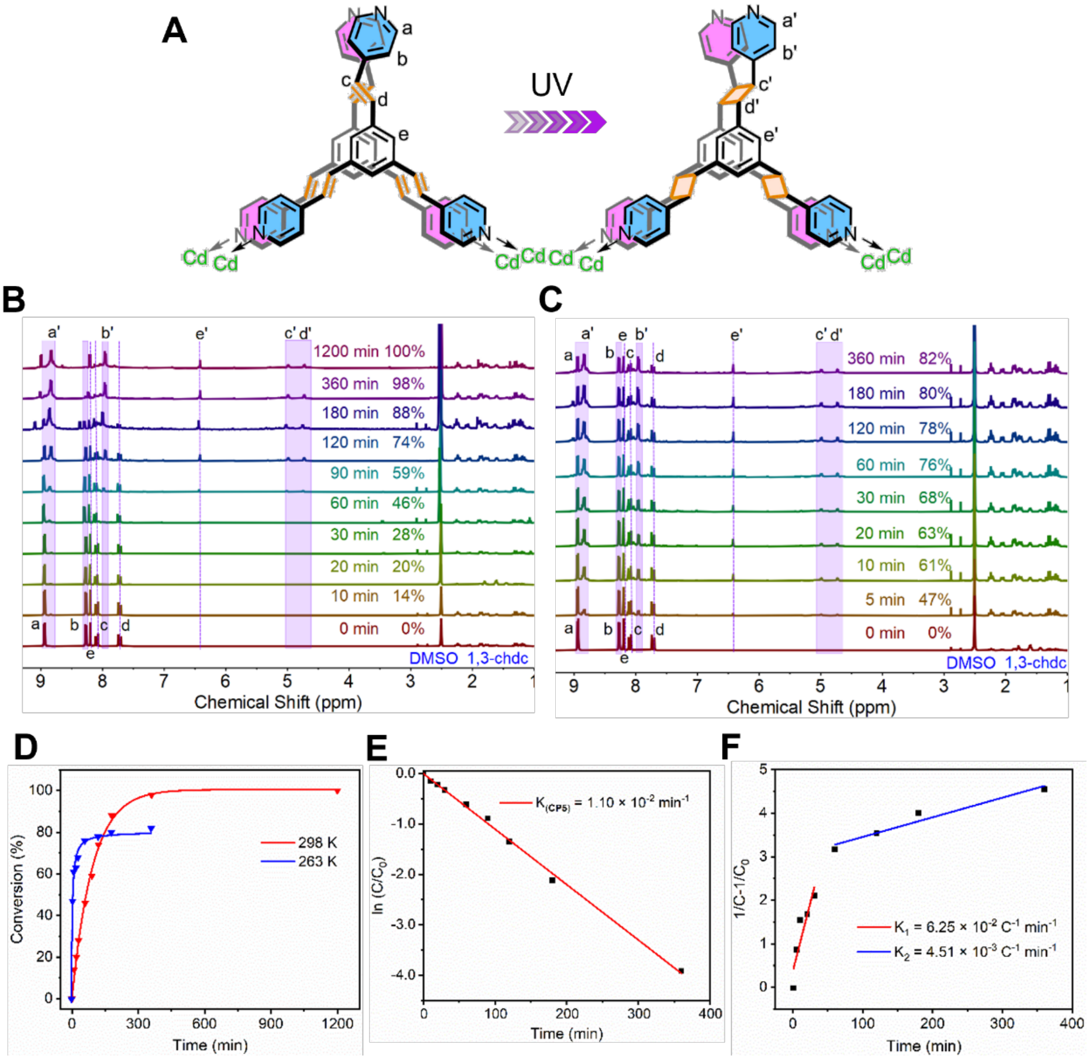


Fig. S14 The ^{1}H NMR spectra of **CP5** after UV light ($\lambda = 365$ nm) irradiation at 298 K (B) and 263 K (C) for different time (400 MHz, DMSO-d_6) and the alignment of tpeb ligands before and after the photocycloaddition reaction (A). Plots of conversion of tpeb in **CP5** versus irradiation time based on ^{1}H NMR result (D) and corresponding fitting of kinetic rate at 298 K (E) and 263 K (F) of **CP5**.

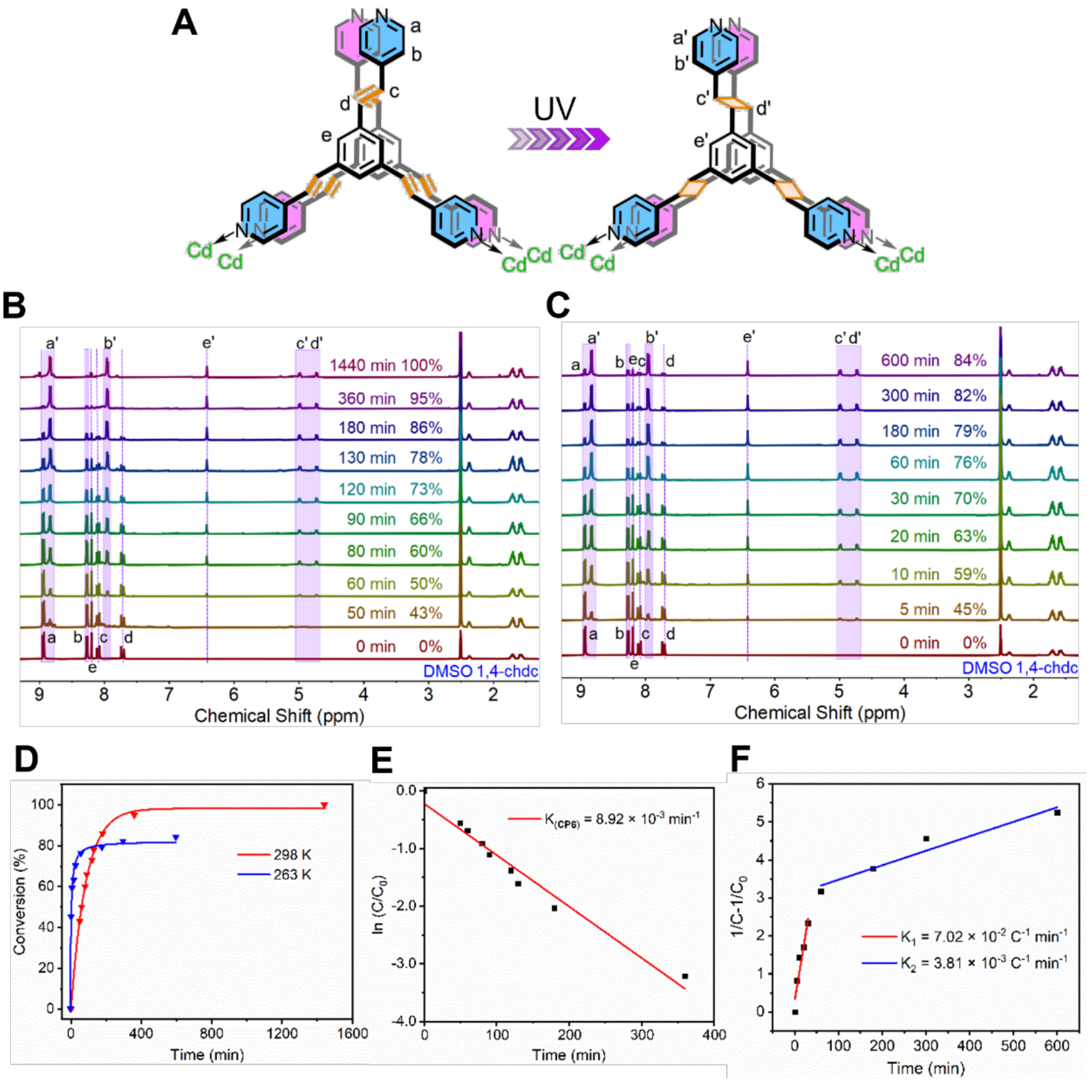


Fig. S15 The ^{1}H NMR spectra of **CP6** after UV light (λ = 365 nm) irradiation at 298 K (B) and 263 K (C) for different time (400 MHz, DMSO-d_6) and the alignment of tpeb ligands before and after the photocycloaddition reaction (A). Plots of conversion of tpeb in **CP6** versus irradiation time based on ^{1}H NMR result (D) and corresponding fitting of kinetic rate at 298 K (E) and 263 K (F) of **CP6**.

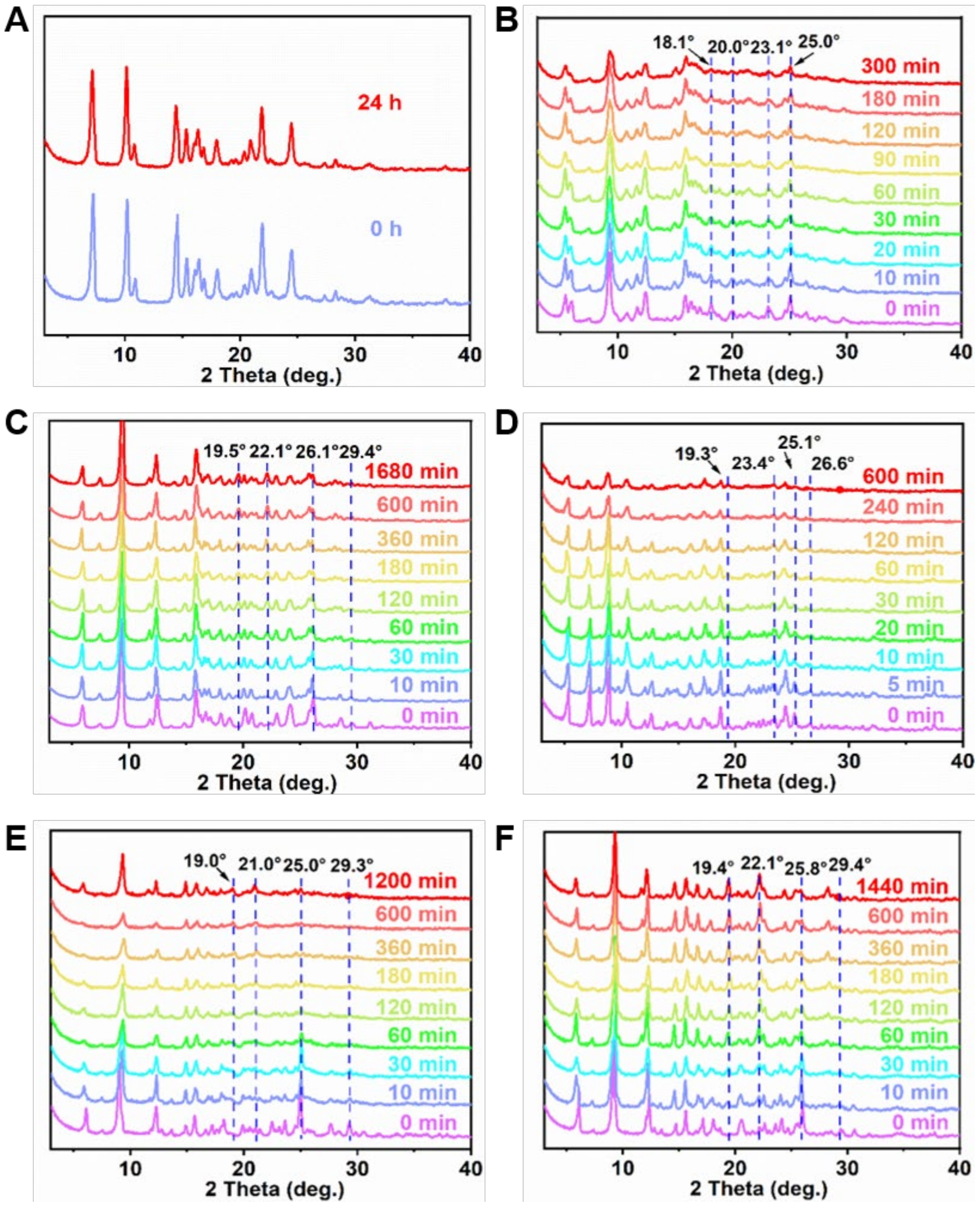


Fig. S16 The PXRD patterns of **CP1**-**CP6** after UV irradiation for different time at 298 K.

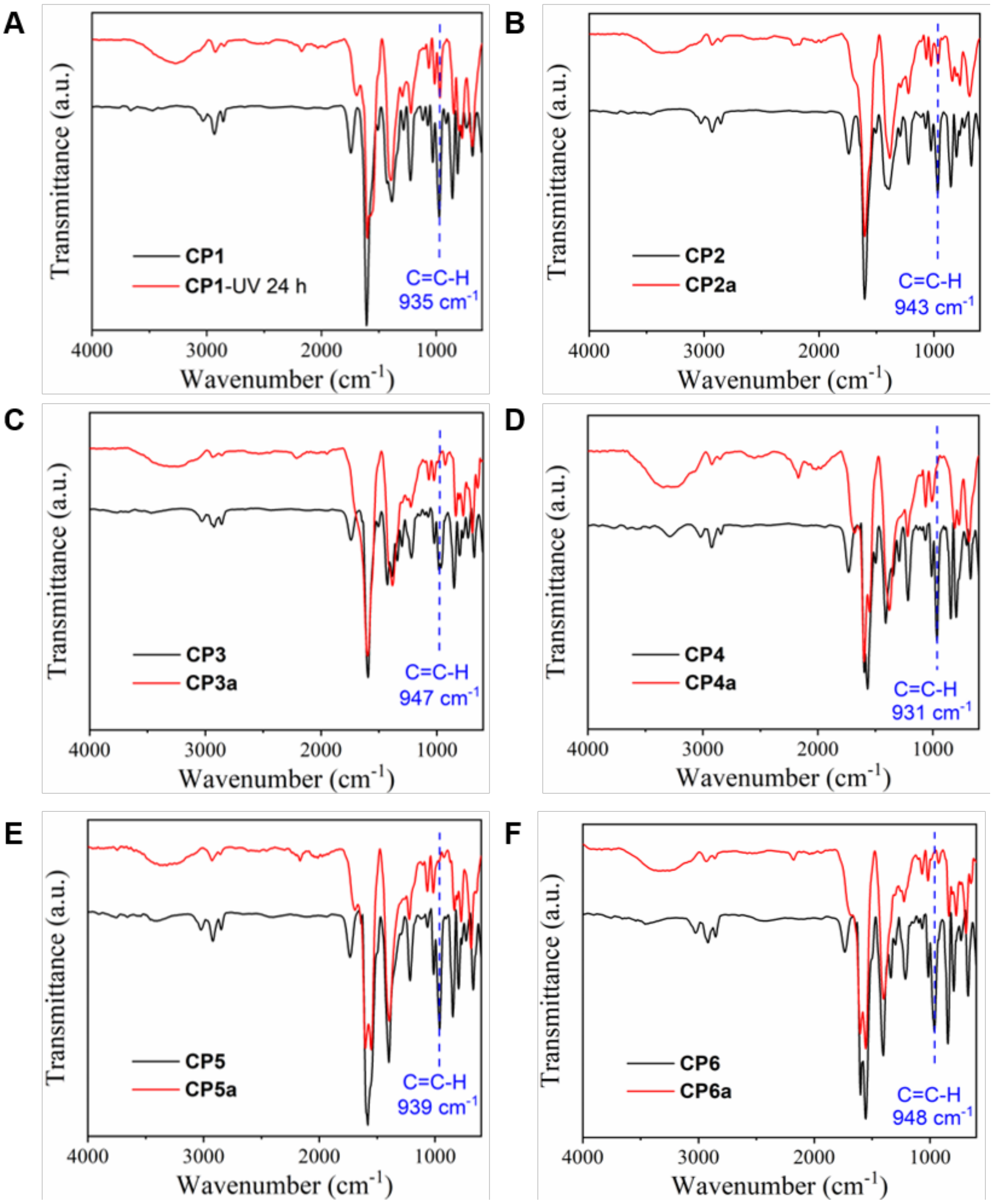


Fig. S17 Infrared spectra of **CP1-CP6** before and after the photoreaction at 298 K.

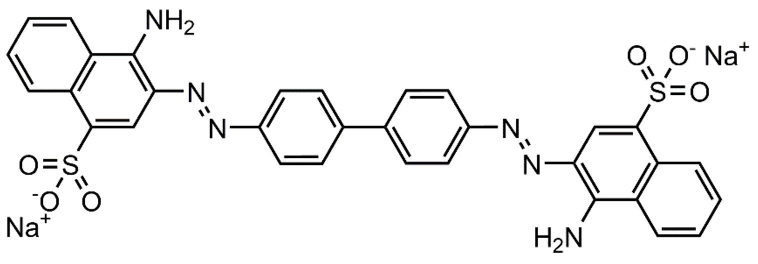


Fig. S18 The structure of Congo Red (CR).

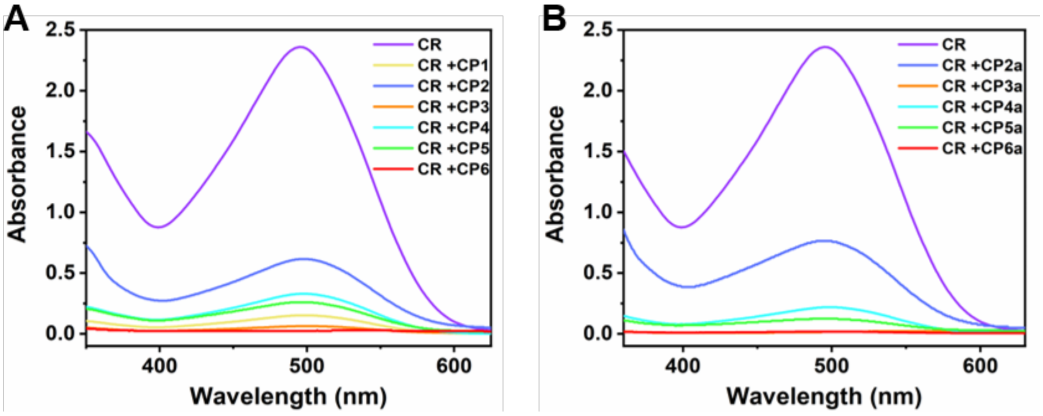


Fig. S19 UV-vis spectra of the adsorption of **CP1-CP6** (A) and **CP2a-CP6a** (B) to CR in aqueous solution.

Table S3 Adsorption capacity of **CP1-CP6** on CR in aqueous solution.

	CP1	**CP2**	**CP3**	**CP4**	**CP5**	**CP6**
CR (mg·g^{-1})	748.48	591.20	778.31	688.14	711.88	789.83

Table S4 Adsorption capacity of **CP2a-CP6a** on CR in aqueous solution.

	CP2a	**CP3a**	**CP4a**	**CP5a**	**CP6a**
CR (mg·g^{-1})	540.9	792.37	725.77	757.30	793.90

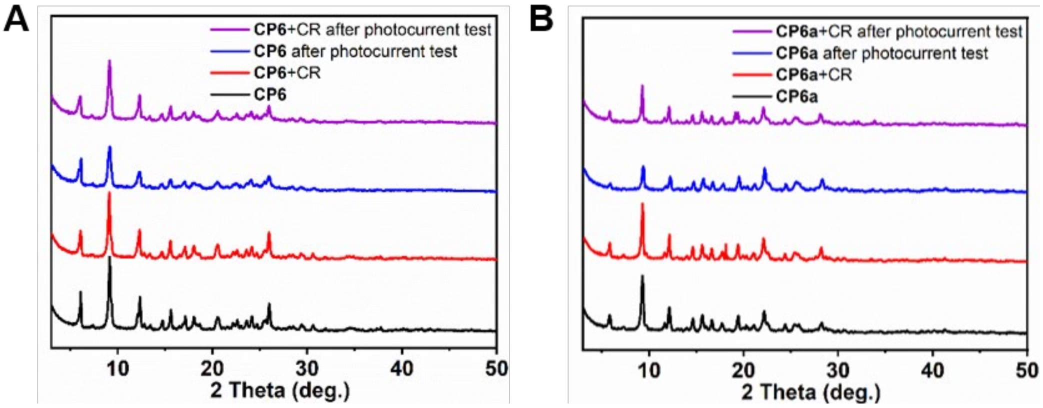


Fig. S20 The PXRD patterns of **CP6** and **CP6**+CR, **CP6a** and **CP6a**+CR before and after photocurrent test.

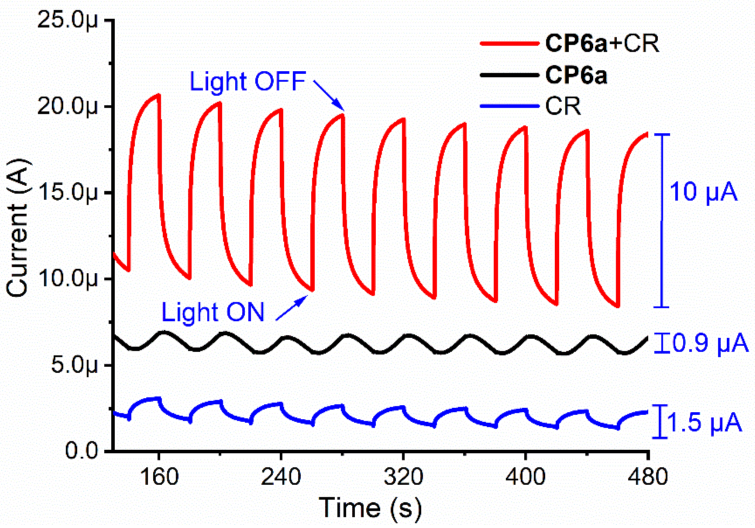


Fig. S21 Photocurrent responses of CR, **CP6a** and **CP6a**+CR coated on glassy carbon electrodes.

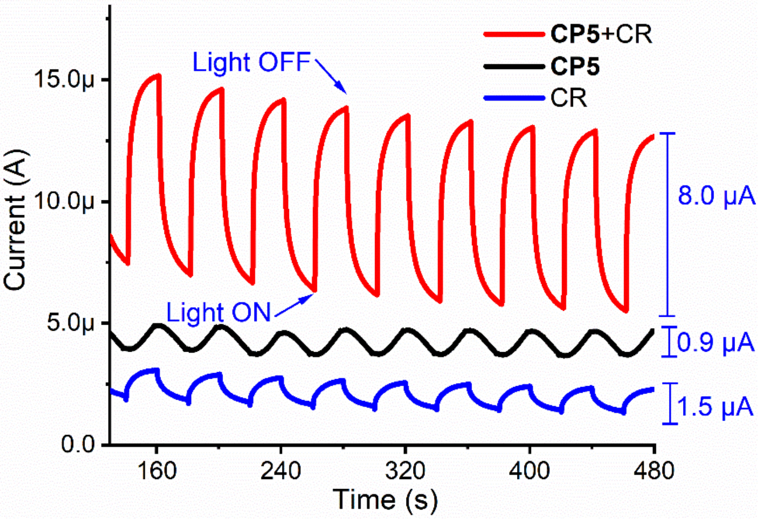


Fig. S22 Photocurrent responses of CR, **CP5** and **CP5**+CR coated on glassy carbon electrodes.

References

1 A. J. Amoroso, A. Thompson, J. P. Maher, J. A. McCleverty and M. D. Ward, Dinucleating, trinucleating, and tetranucleating pyridyl ligands which facilitate multicenter magnetic exchange between paramagnetic molybdenum centers, *Inorg. Chem.*, 1995, **34**, 4828-4835.

2 G. M. Sheldrick, Crystal structure refinement with Shelxl, *Acta. Cryst. C.*, 2015, **71**, 3-8.

3 A. L. Spek, Single-crystal structure validation with the program PLATON, *J. Appl. Cryst.*, 2003, **36**, 7-13.