A single-crystal platform for unveiling ultrafast and complex photochemical cascade reactions

Qiaoqiao Zhang[1,4], Yun-Hu Deng[1,4], Yong Wang[1,4], Ming-Hao Du[1]*, Qi Liu[1], Brendan F. Abrahams[2], Pierre Braunstein[3], Jian-Ping Lang[1]*

[1]College of Chemistry, Chemical Engineering and Materials, Soochow University, Suzhou 215123, P. R. China.

[2]School of Chemistry, University of Melbourne, Victoria 3010, Australia.

[3]Université de Strasbourg, Institut de Chimie (UMR 7177 CNRS), 4 rue Blaise Pascal-CS 90032, 67081 Strasbourg, France.

[4]These authors contributed equally: Qiaoqiao Zhang, Yun-Hu Deng, Yong Wang

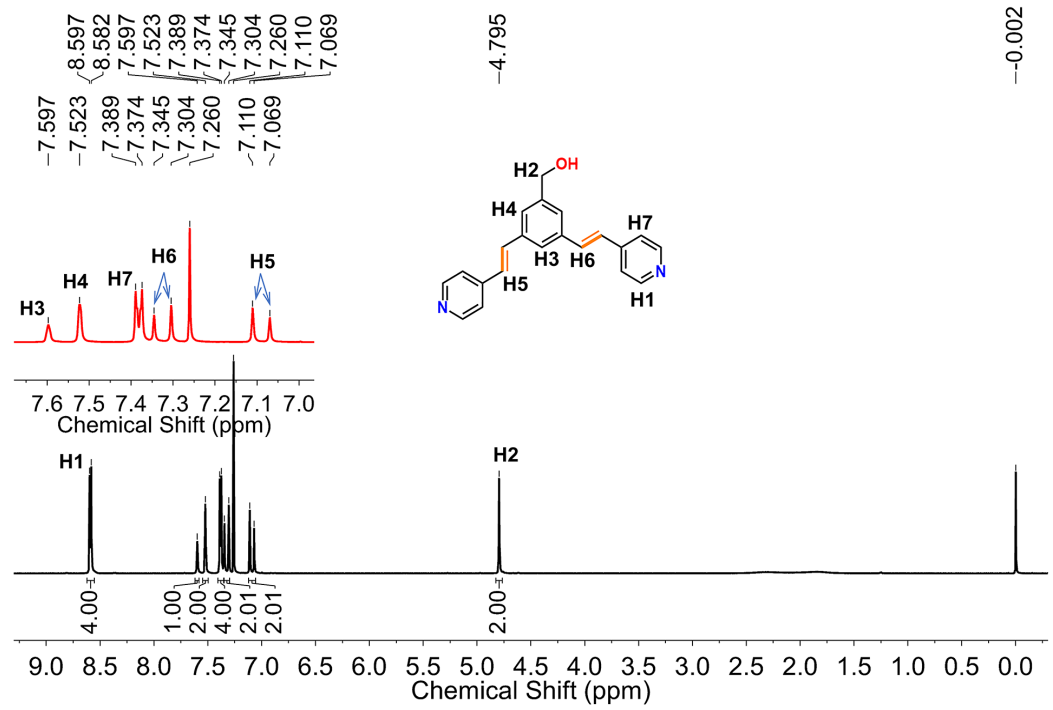
*email: jplang@suda.edu.cn; mhdu@suda.edu.cn

Table of Contents

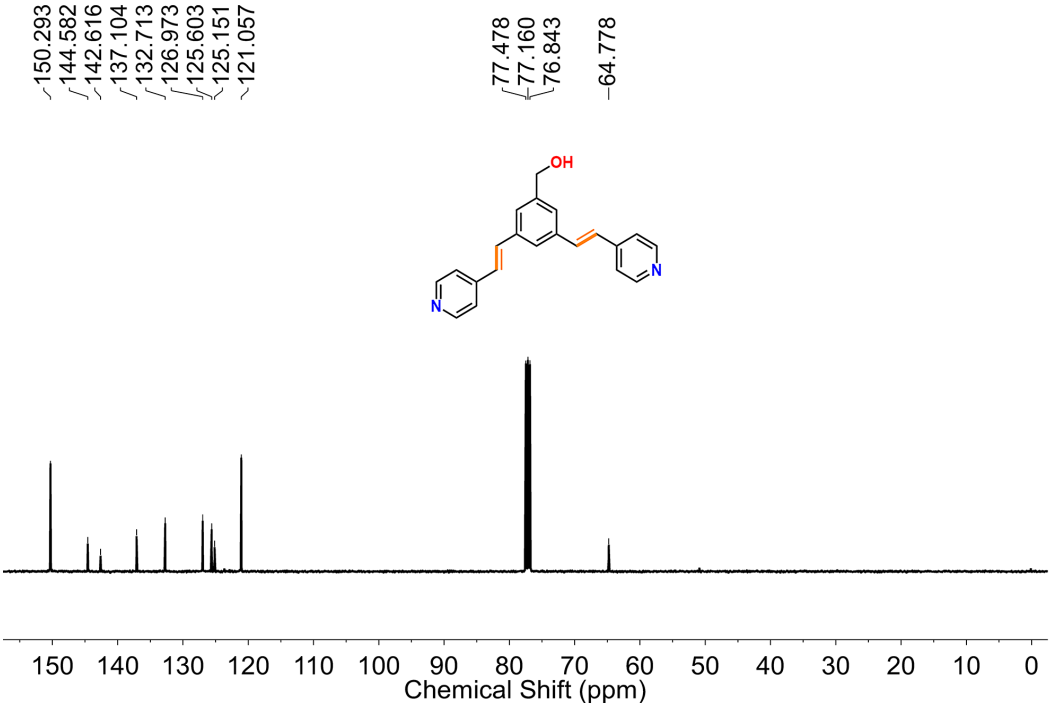
Supplementary figures for experiments and calculations S1

Supplementary tables for experiments and calculations S11

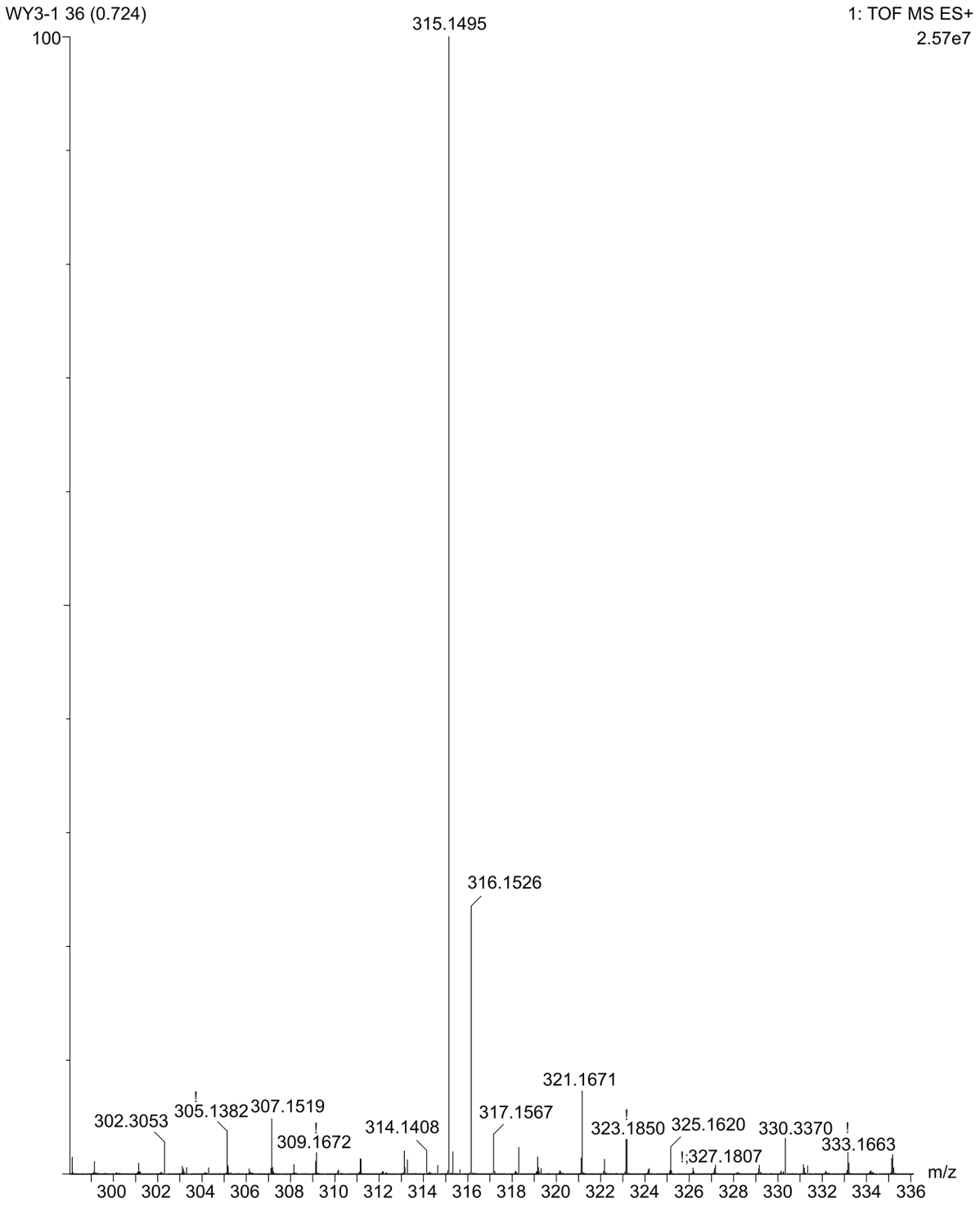
Supplementary references S18



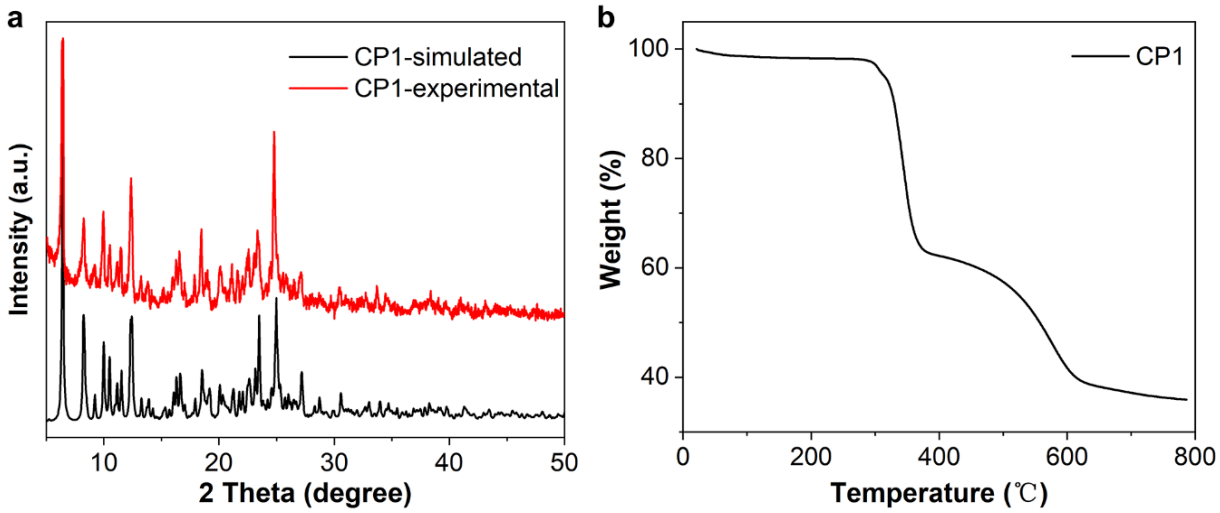
Supplementary Fig. 1 | ^{1}H NMR experiment of the olefinic ligand. The ^{1}H NMR (400 MHz, $CDCl_3$, ppm) spectrum of CH_2OH-1,3-bpeb.



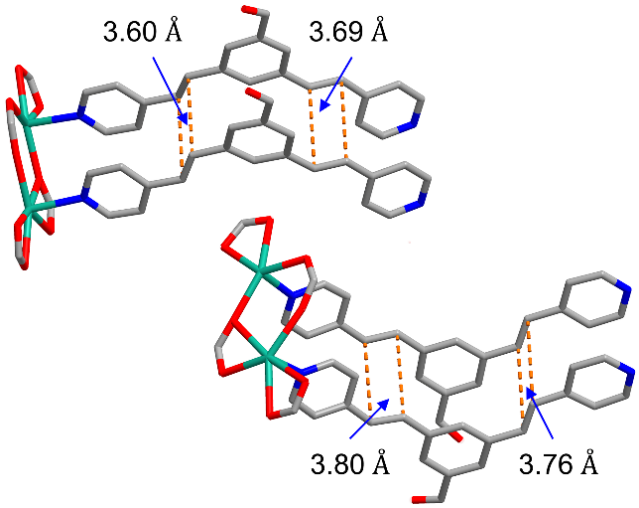
Supplementary Fig. 2 | ^{13}C NMR experiment of the olefinic ligand. The ^{13}C NMR (101 MHz, $CDCl_3$, ppm) spectrum of CH_2OH-1,3-bpeb.



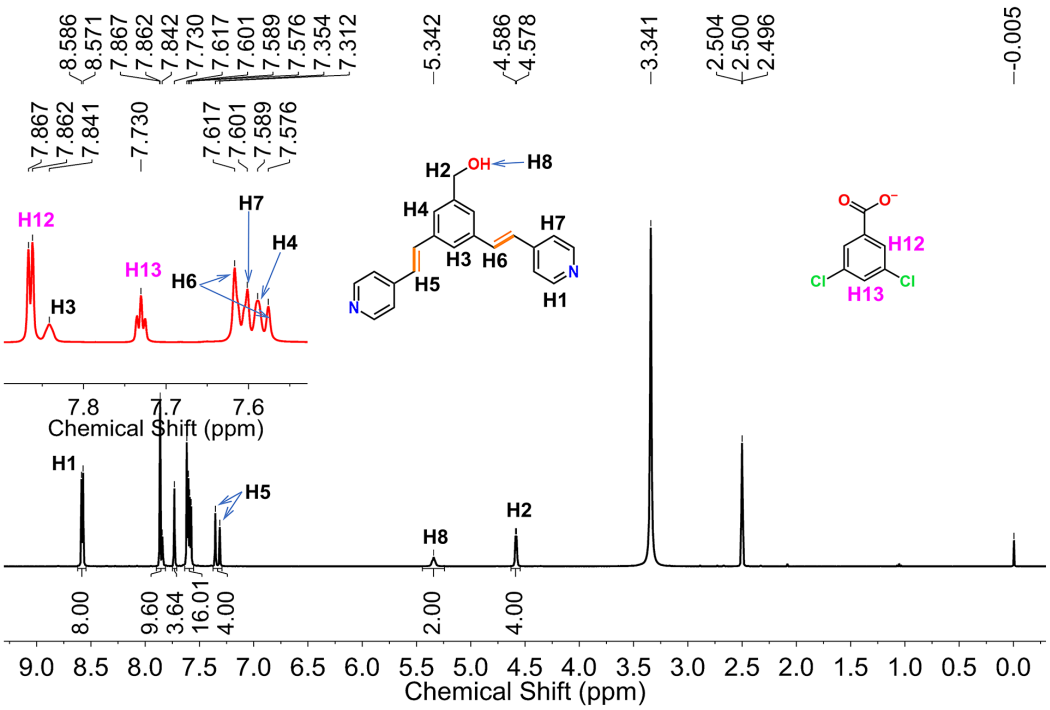
Supplementary Fig. 3 | MS experiment of the olefinic ligand. The MS of CH_2OH-1,3-bpeb.



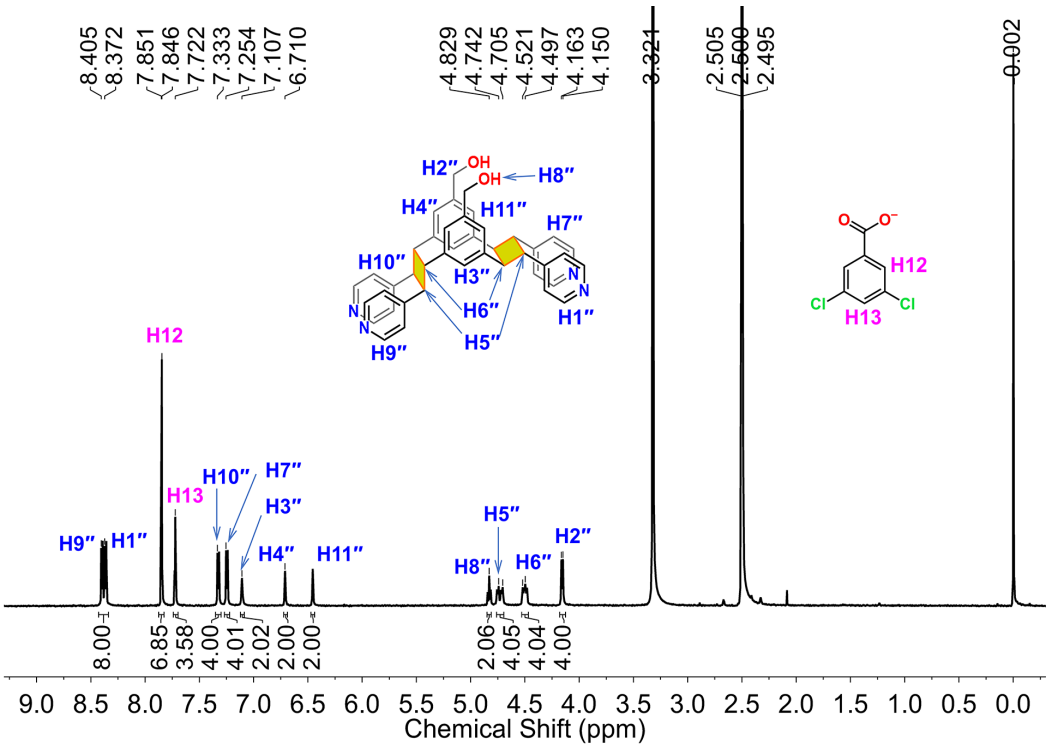
Supplementary Fig. 4 | PXRD and TG experiments of CP1. a, PXRD diffraction patterns and **b**, TG analysis curve of **CP1**.



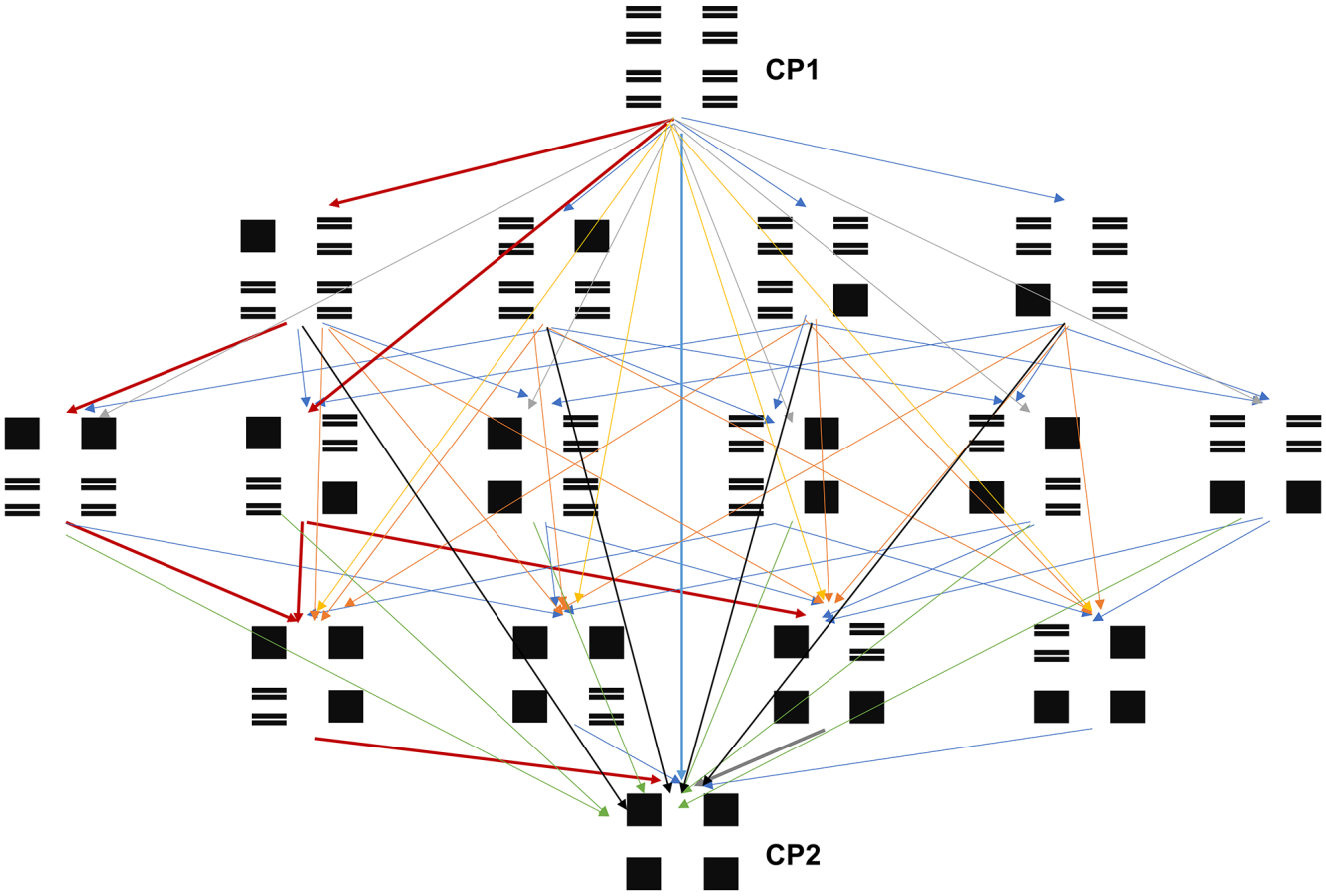
Supplementary Fig. 5 | View of the crystal structure of CP1. The smallest asymmetric unit of **CP1** displaying two pairs of face-to-face (parallel) CH_2OH-1,3-bpeb ligands, where lattice water molecules and hydrogen atoms have been omitted for clarity. Atom color codes: Cd, bluish green; C, gray; N, blue; O, red.



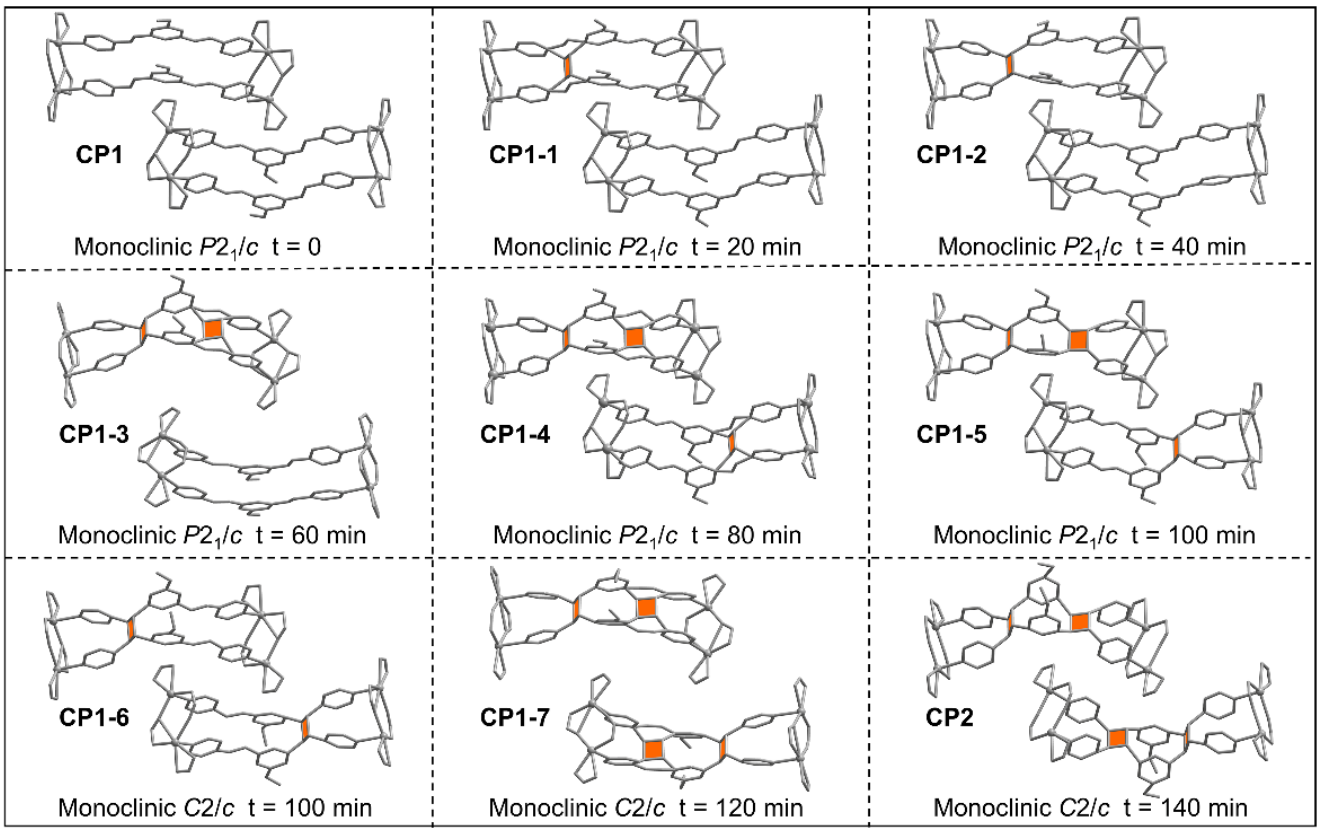
Supplementary Fig. 6 | NMR experiment of CP1. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) spectrum of **CP1**.



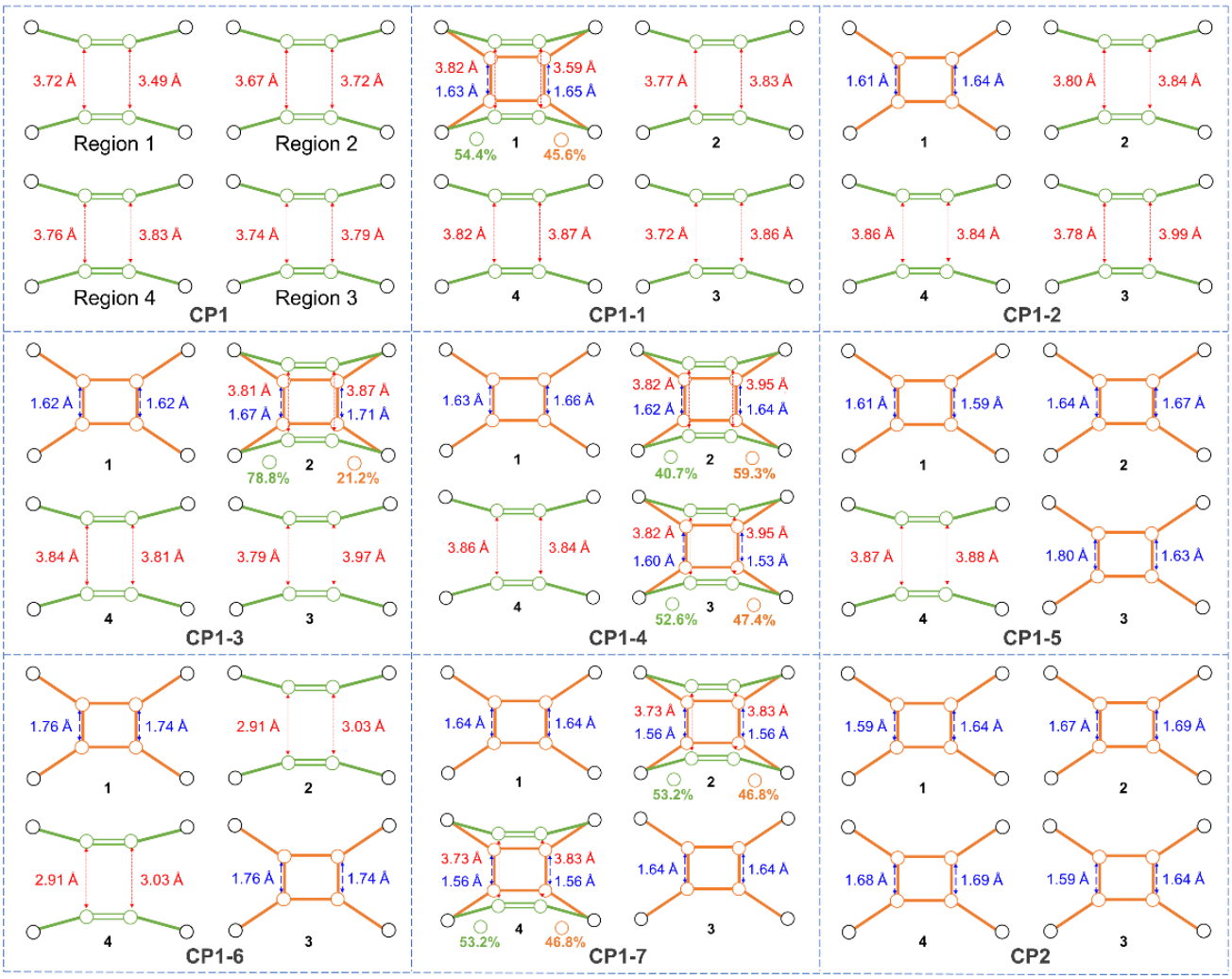
Supplementary Fig. 7 | NMR experiment of CP1 after photoirradiation. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) spectrum of **CP1** after irradiation with ultraviolet light for 25 s at 298 K.



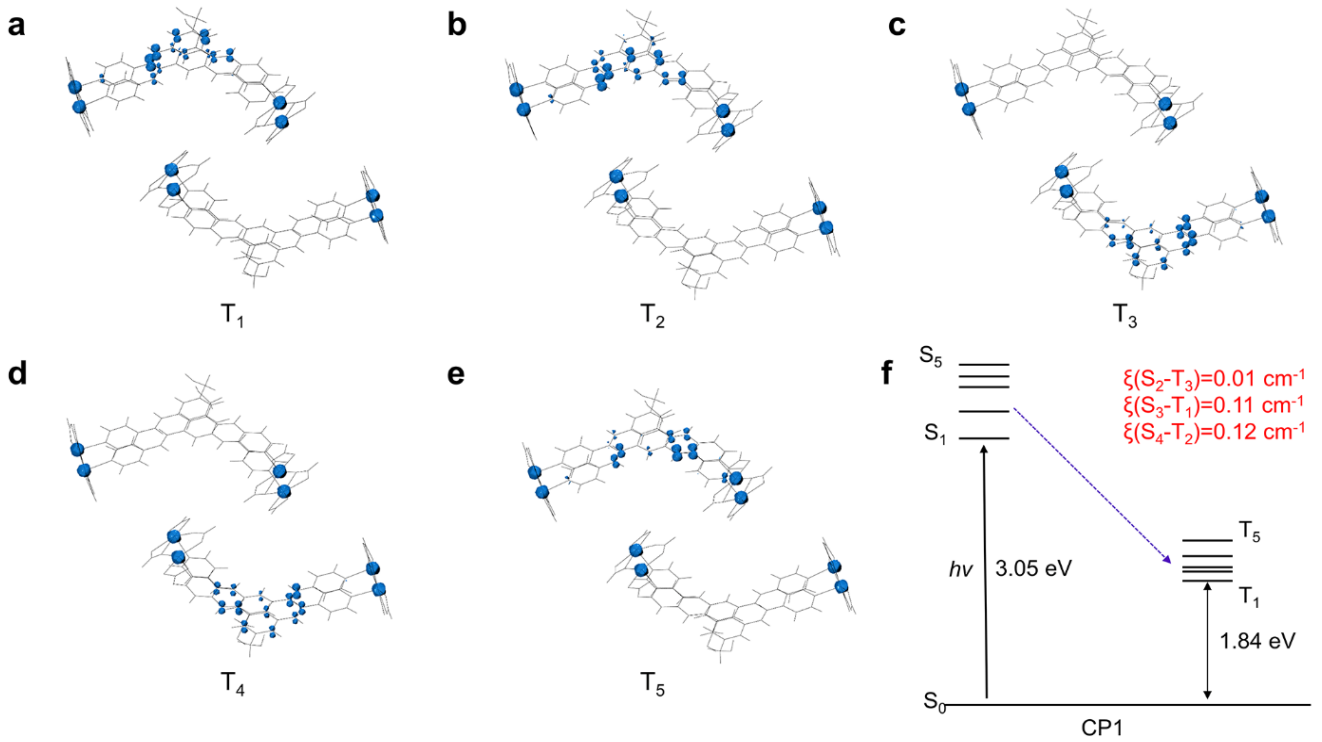
Supplementary Fig. 8 | All possible intermediates and reaction paths of CP1. The 14 possible intermediates and corresponding 75 reaction routes in the reaction process of **CP1** to **CP2**.



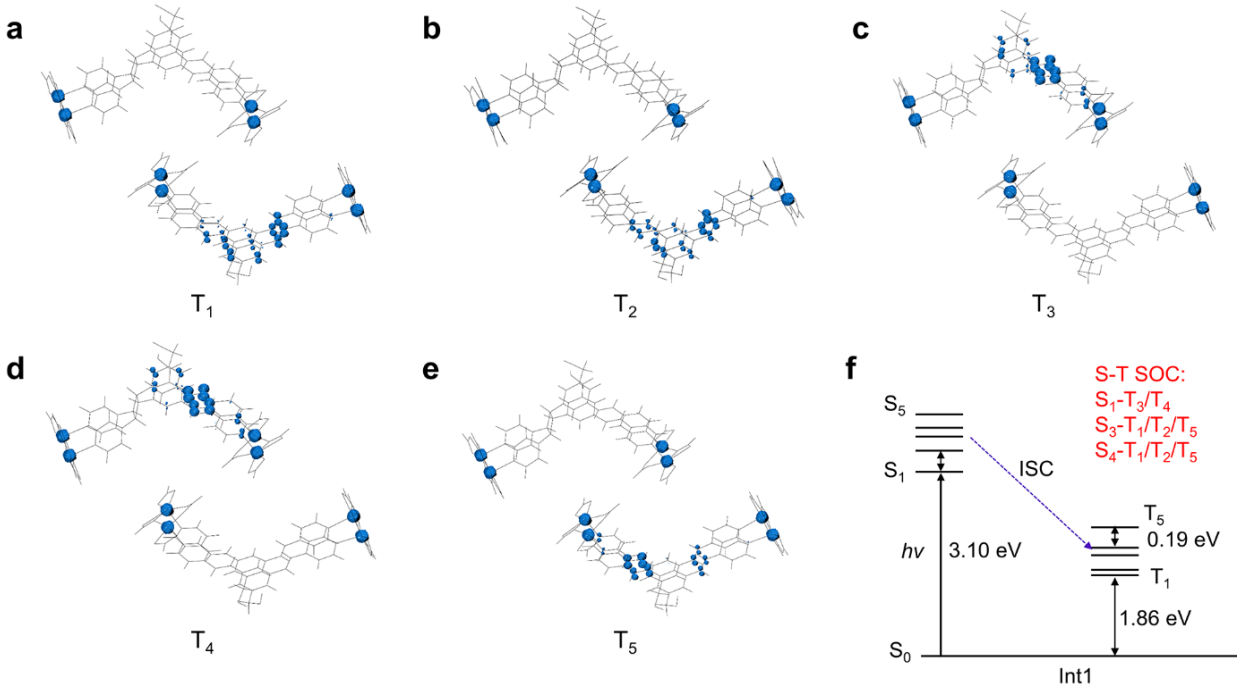
Supplementary Fig. 9 | Crystallographic snapshots of the photoreaction from CP1 to CP2. Snapshots of the crystal structures during low-temperature (173 K) reaction leading to direct observation of a series of intermediates.



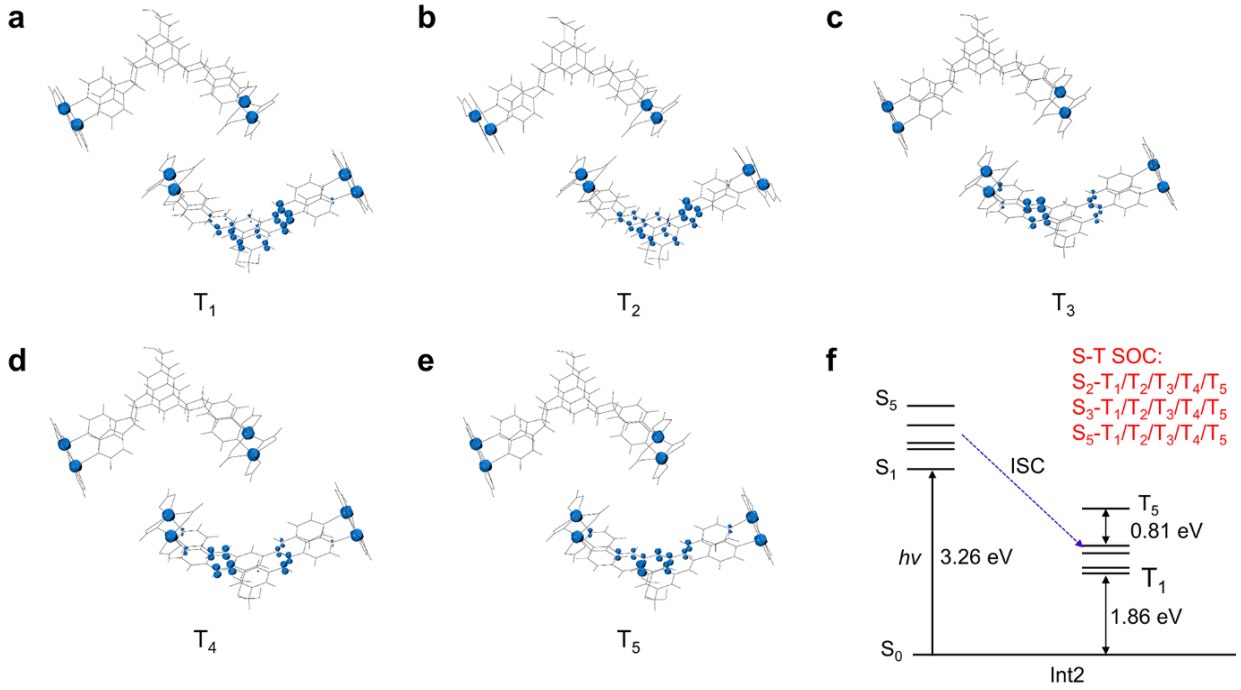
Supplementary Fig. 10 | The C-C distance changes during crystallographic snapshots. The changes of C-C distances in snapshot of the crystal structures during low-temperature (173 K) reaction.



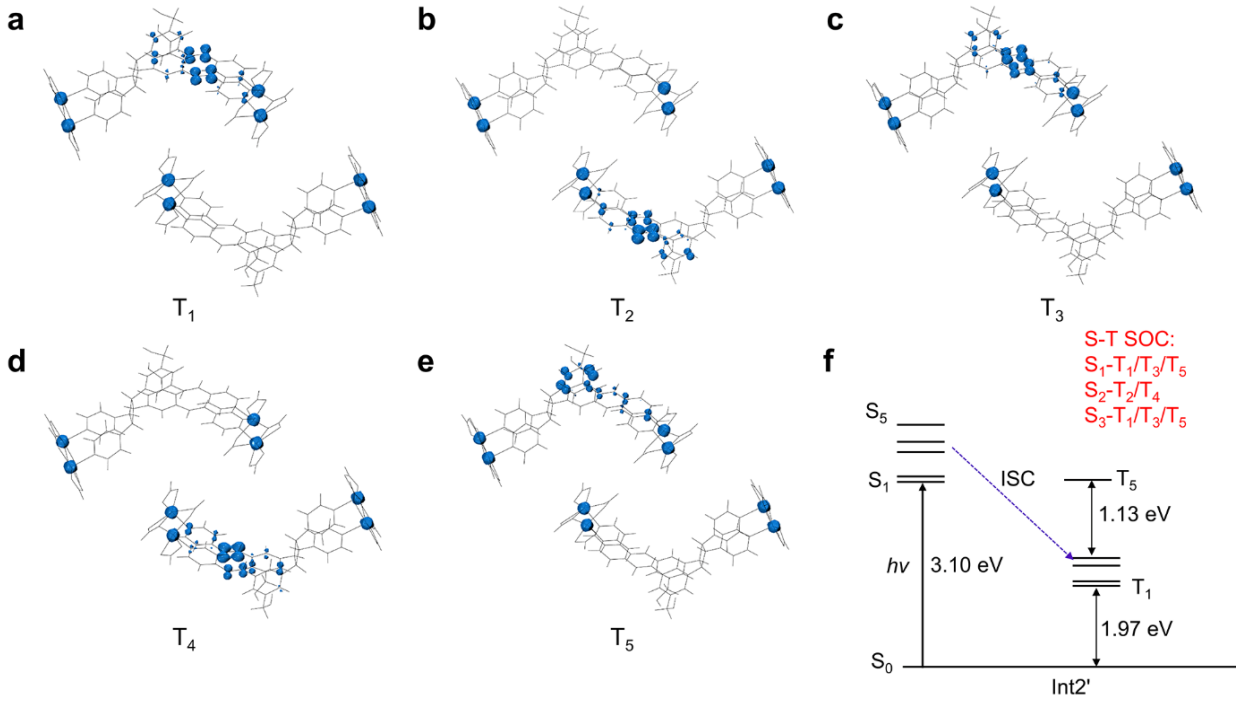
Supplementary Fig. 11 | Odd electron density (OED) and spin-orbit coupling (SOC) calculations of CP1. a-e, The OED distributions for T_1-T_5 states and **f**, SOC analysis of singlet-triplet (S-T) excited states (SOC constant, ξ) in **CP1**.



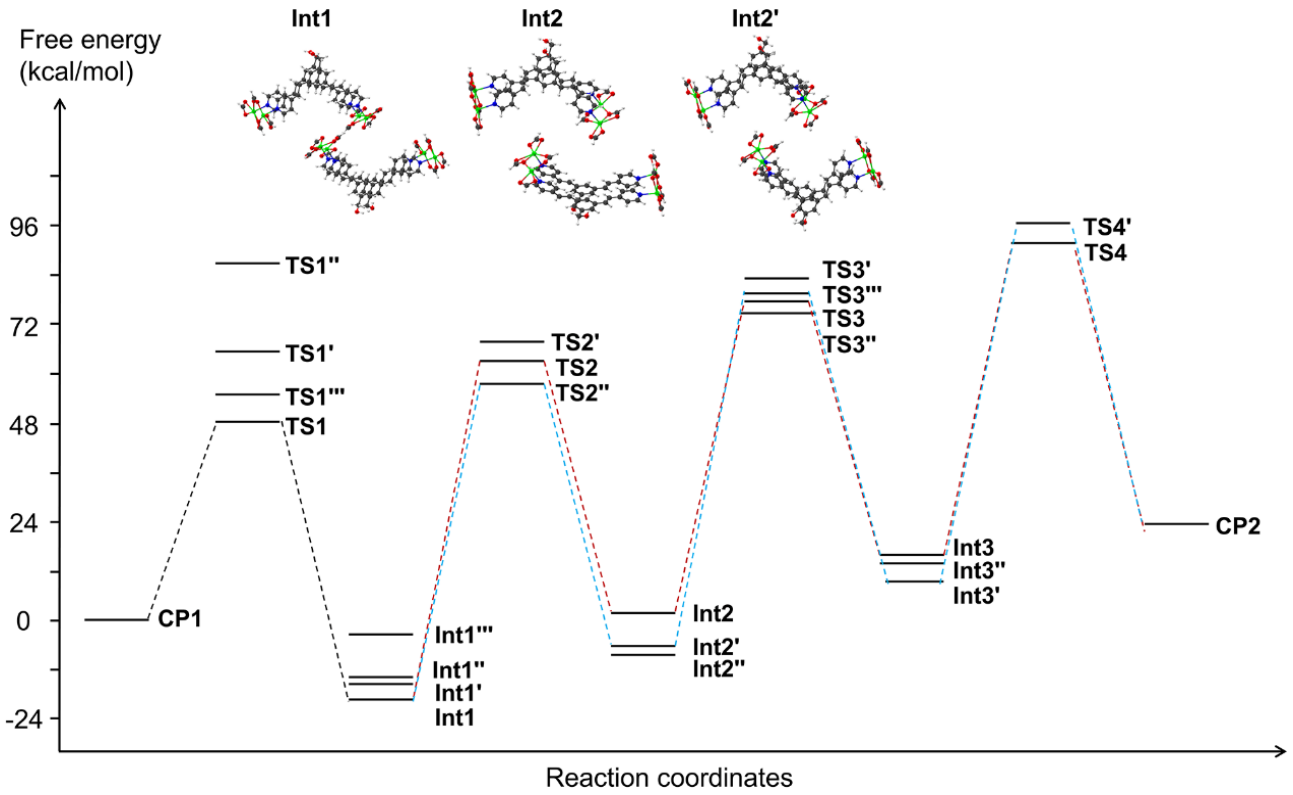
Supplementary Fig. 12 | OED and SOC calculations of Int1. **a-e**, OED distributions for T_1-T_5 states and **f**, SOC analysis of S-T excited states in **Int1**.



Supplementary Fig. 13 | OED and SOC calculations of Int2. **a-e**, OED distributions for T_1-T_5 states and **f**, SOC analysis of S-T excited states in **Int2**.



Supplementary Fig. 14 | OED and SOC calculations of Int2'. **a-e**, OED distributions for T_1-T_5 states and **f**, SOC analysis of S-T excited states in **Int2'**.



Supplementary Fig. 15 | Energy profiles (in kcal/mol) for the transformation process from CP1 to CP2. Reaction path and Gibbs free energy change involving transition states and intermediates during the photoreaction from **CP1** to **CP2**.

Supplementary Table 1 | Comparsion of some representive photochemical addition rates in single-crystal platforms.

Reactants	Irradiation condition	Yield	Total time	Ref.
CP1	365 nm (80 W)	100%	25 s	This work
1-Vinylnaphthalene; methyl acrylate	UiO-69-phen(binap)Cu photocatalyst; 4-dimethylaminopyridine; 1,2-dichloroethane; N_2; 440 nm (40 W)	73%	48 h	1
Chalcone derivatives	MOC-16 photocatalyst; DMSO; N_2; 450 nm (24 W)	41~97%	1~12 h	2
[Zn(bdc)(3-F-spy)]	365 nm with power density of 21.6 mW cm^{-2}	100%	1 min	3
$[Zn(4\text{-}Fb)_2(tkpvb)]_n$	365 nm (80 W)	100%	1 h	4
$[Zn_2(benzoate)_4(2F\text{-}4spy)_2]$	375 nm	100%	1 h	5
$[PbI_2(5\text{-}SPym)(DMF)]$	360 nm	100%	1.5 h	6
$[Zn_4L_2(OH)_2(4,4'\text{-}bpe)_2](ClO_4)_4 \cdot 4H_2O$	419 nm	100%	5 h	7
2(5-OMe-res)·2(4-pyr-poly-3-ene)	UV light (500 W Hg lamp)	100%	72 h	8
Monomer I and II	UV light (450 W Hg lamp)	100%	36 h	9

Supplementary Table 2 | Summary of crystal data and structure refinement parameters for **CP1**, **CP1-1**, **CP1-2**, **CP1-3**, **CP1-4**, **CP1-5**, **CP1-6**, **CP1-7**, **CP2**.

	CP1	**CP1-1**	**CP1-2**	**CP1-3**	**CP1-4**
Empirical formula	$C_{70}H_{52}Cd_2Cl_8N_4O_{12}$	$C_{70}H_{48}Cd_2Cl_8N_4O_{10}$	$C_{70}H_{48}Cd_2Cl_8N_4O_{10}$	$C_{70}H_{48}Cd_2Cl_8N_4O_{10}$	$C_{70}H_{48}Cd_2Cl_8N_4O_{10}$
Formula weight	1649.55	1613.52	1613.52	1613.52	1613.52
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	14.5978(6)	14.8185(15)	14.8687(7)	14.8801(12)	14.893(4)
b/Å	33.6931(15)	33.726(3)	33.5918(15)	33.650(3)	33.653(10)
c/Å	28.1944(13)	28.389(3)	28.2887(13)	28.297(3)	28.302(8)
α/°	90	90	90	90	90
β/°	102.5520(10)	103.239(3)	103.812(2)	103.897(3)	104.480(11)
γ/°	90	90	90	90	90
V/Å^3	13535.8(10)	13811(2)	13720.7(11)	13754(2)	13734(7)
D_c/g cm^{-3}	1.619	1.552	1.562	1.558	1.561
Z	8	8	8	8	8
μ/mm^{-1}	1.010	5.585	5.622	5.608	5.616
Total reflections	248565	105832	82136	163937	304887
Unique reflections	23907	23147	31050	24237	24104
F(000)	6624	6464	6464	6464	6464
R_1[a]	0.0690	0.1027	0.0829	0.0724	0.1016
wR_2[b]	0.1969	0.3294	0.2748	0.2145	0.3113
GOF[c]	1.065	1.066	1.070	1.028	1.075

to be continued for **Supplementary Table 2**

	CP1-5	**CP1-6**	**CP1-7**	**CP2**
Empirical formula	$C_{70}H_{48}Cd_2Cl_8N_4O_{10}$	$C_{70}H_{48}Cd_2Cl_8N_4O_{10}$	$C_{70}H_{48}Cd_2Cl_8N_4O_{10}$	$C_{70}H_{48}Cd_2Cl_8N_4O_{10}$
Formula weight	1613.52	1613.52	1613.52	1613.52
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$	$C2/c$
a/Å	14.9038(18)	28.210(8)	28.300(4)	28.0542(14)
b/Å	33.566(4)	33.582(9)	33.655(4)	33.5024(15)
c/Å	28.295(3)	14.918(4)	14.941(2)	14.7964(10)
α/°	90	90	90	90
β/°	104.988(4)	105.247(11)	105.277(6)	105.022(2)
γ/°	90	90	90	90
V/Å^3	13673(3)	13635(6)	13727(3)	13431.6(13)
D_c/g cm^{-3}	1.568	1.572	1.561	1.596
Z	8	8	8	8
μ/mm^{-1}	5.641	5.657	5.619	1.014
Total reflections	195792	100722	157426	188465
Unique reflections	24185	11919	12241	11028
F(000)	6464	6464	6464	6464
R_1[a]	0.0971	0.1268	0.1251	0.1839
wR_2[b]	0.3291	0.3288	0.3086	0.3821
GOF[c]	1.069	1.201	1.019	1.115

[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.

Supplementary Table 3 | The SOC constant ξ between singlet and triplet states for **CP1**.

Singlet	Triplet	ξ(cm^{-1})
S_2	T_3	0.01
S_3	T_1	0.11
S_4	T_2	0.12

Supplementary Table 4 | The SOC constant ξ between singlet and triplet states for **Int1**.

Singlet	Triplet	ξ(cm^{-1})
S_1	T_3	0.05
S_1	T_4	0.07
S_3	T_1	0.64
S_3	T_2	0.67
S_3	T_5	0.72
S_4	T_1	2.73
S_4	T_2	2.04
S_4	T_5	8.32

Supplementary Table 5 | The SOC constant ξ between singlet and triplet states for **Int2**.

Singlet	Triplet	ξ(cm^{-1})
S_2	T_1	1.66
S_2	T_2	1.41
S_2	T_3	1.61
S_2	T_4	1.60
S_2	T_5	0.75
S_3	T_1	6.08
S_3	T_2	1.67
S_3	T_3	2.01
S_3	T_4	1.98
S_3	T_5	0.94
S_5	T_1	0.72
S_5	T_2	1.43
S_5	T_3	0.59
S_5	T_4	1.50
S_5	T_5	1.41

Supplementary Table 6 | The SOC constant ξ between singlet and triplet states for **Int2'**.

Singlet	Triplet	ξ(cm^{-1})
S_1	T_1	0.05
S_1	T_3	0.07
S_1	T_5	0.14
S_2	T_2	0.08
S_2	T_4	0.08
S_3	T_1	0.23
S_3	T_3	0.14
S_3	T_5	0.09
S_4	T_2	0.31

Supplementary Table 7 | The single point energy (E, a.u.) and free energy (G, a.u.) of transition states and intermediates at M062X-D3/def2-TZVP level during the photoreaction process from **CP1** to **CP2**.

Compounds	E (a.u.)	G (a.u.)
CP1	-8352.02925665	-8352.33557524
TS1	-8351.94393767	-8352.25619621
Int1 **(CP1-2**)	-8352.04902094	-8352.36721943
TS2	-8351.91538098	-8352.23232761
Int2 (**CP1-3**)	-8352.02015287	-8352.33384765
TS2'	-8351.91581225	-8352.23128609
Int2"	-8352.03345891	-8352.34871181
TS3	-8351.89951053	-8352.21011996
Int3 (**CP1-5**)	-8352.00481651	-8352.31277550
TS3'	-8351.89552794	-8352.20387804
Int3"	-8352.00465602	-8352.31539025
TS2"	-8351.92766364	-8352.24304747
Int2'	-8352.03364267	-8352.34621182
TS3"'	-8351.90072500	-8352.20998908
TS3"	-8351.90764677	-8352.21442664
Int3'	-8352.01074219	-8352.31834293
TS4	-8351.88285679	-8352.18714301
TS4'	-8351.88127065714	-8352.18209324714
CP2	-8351.98195783	-8352.28492953
TS1'	-8351.93740667	-8352.25011667
Int1'	-8352.04200042	-8352.36310223
TS1"	-8351.88427982	-8352.19571145
Int1"'	-8352.02048805	-8352.33903271
TS1"'	-8351.94028606	-8352.25042806
Int1"	-8352.04618453	-8352.36214953

Supplementary Table 8 | Summary of the distances between non-reactive active centers during the photochemical reaction (the labels of d1-d8 are shown in Extended Data Fig. 2).

	CP1	**CP1-1**	**CP1-2**	**CP1-3**	**CP1-4**	**CP1-5**	**CP1-6**	**CP1-7**	**CP2**
d1	3.94 Å	4.02 Å	4.10 Å	4.10 Å	4.15 Å	4.18 Å	4.14	4.14 Å	4.16 Å
d2	3.93 Å	4.02 Å	4.04 Å	4.05 Å	4.09 Å	4.11 Å	4.14 Å	4.14 Å	4.16 Å
d3	3.72 Å	3.91 Å	4.07 Å	4.06 Å	4.07 Å	4.18 Å	4.14 Å	4.11 Å	4.20 Å
d4	3.64 Å	3.70 Å	3.72 Å	3.75 Å	3.86 Å	3.94 Å	3.80 Å	3.87 Å	3.93 Å
d5	3.73 Å	3.90 Å	3.97 Å	3.98 Å	4.05 Å	4.06 Å	3.80 Å	3.87 Å	3.93 Å
d6	3.61 Å	3.68 Å	3.69 Å	3.69 Å	3.75 Å	3.72 Å	4.14 Å	4.11 Å	4.20 Å
d7	11.05 Å	11.23 Å	11.35 Å	11.37 Å	11.40 Å	11.42 Å	11.45 Å	11.49 Å	11.39 Å
d8	11.72 Å	11.70 Å	11.62 Å	11.63 Å	11.58 Å	11.53 Å	11.45 Å	11.49 Å	11.39 Å

Supplementary references

1 Guo, J. et al. Visible light-mediated intermolecular crossed [2 + 2] cycloadditions using a MOF-supported copper triplet photosensitizer. *Nat. Catal.* **7**, 307-320, (2024).

2 Wang, J.-S. et al. Cage-confined photocatalysis for wide-scope unusually selective [2 + 2] cycloaddition through visible-light triplet sensitization. *Nat. Commun.* **11**, 4675, (2020).

3 Shi, Y.-X., Zhang, W.-H., Abrahams, B. F., Braunstein, P. & Lang, J.-P. Fabrication of photoactuators: macroscopic photomechanical responses of metal-organic frameworks to irradiation by UV light. *Angew. Chem. Int. Ed.* **58**, 9453-9458, (2019).

4. Yang, Z.-Y. et al. Photopolymerization-driven macroscopic mechanical motions of a composite film containing a vinyl coordination polymer. *Angew. Chem. Int. Ed.* **62**, e202302429 (2023).

5. Medishetty, R. et al. Single crystals popping under UV light: a photosalient effect triggered by a [2 + 2] cycloaddition reaction. *Angew. Chem. Int. Ed.* **53**, 5907-5911 (2014).

6 Rath, B. B. & Vittal, J. J. Single-crystal-to-single-crystal [2 + 2] photocycloaddition reaction in a photosalient one-dimensional coordination polymer of Pb(II). *J. Am. Chem. Soc.* **142**, 20117-20123, (2020).

7. Papaefstathiou, G. S., Zhong, Z., Geng, L. & MacGillivray, L. R. Coordination-driven self-assembly directs a single-crystal-to-single-crystal transformation that exhibits photocontrolled fluorescence. *J. Am. Chem. Soc.* **126**, 9158-9159 (2004).

8 Gao, X., Friščić, T. & MacGillivray, L. R. Supramolecular construction of molecular ladders in the solid state. *Angew. Chem. Int. Ed.* **43**, 232-236, (2004).

9 Wang, Z. et al. Polyladderane constructed from a gemini monomer through photoreaction. *Angew. Chem. Int. Ed.* **56**, 12155-12159, (2017).