Supporting Information

Modulating the regioselectively of solid-state photodimerization in coordination polymers crystals†

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Experimental

General methods

Synthesis

The ligand 1,4-bis[2-(4-pyridyl)ethenyl]benzene (1,4-bpeb) was prepared according to a literature method.[S1] Other reagents and chemicals were obtained commercially and used without further purification. Deionized water (distilled) was used throughout the experiments. Elemental analyses (C, H, and N) were performed using a PE 2400 II elemental analyzer. Mass spectra were recorded on a Bruker micr OTOF-Q III mass spectrometer. NMR spectra were recorded at ambient temperature on a Bruker AVANCE 400M spectrometer. ^{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 as KBr disks (4000-400 cm^{-1}). Photo-irradiation experiments were conducted with a high-pressure mercury lamp at a wavelength of 365 nm. Fluorescence spectra were collected on a JASCO FP-6500.

X-ray data collection and structure determination. Single-crystal X-ray diffraction data for **1, 2**, **3**, **1a**, **2a** and **3a** were recorded on a Bruker Smart CCD diffractometer or Agilent Xcalibur E with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293K. Structures were solved by Direct methods and refined by full-matrix least-squares techniques using the *SHELXL*-2014, *SHELXL*-2017 and *SHELXL*-2018 program.[S2] Non-hydrogen atoms were refined with anisotropic displacement parameters.

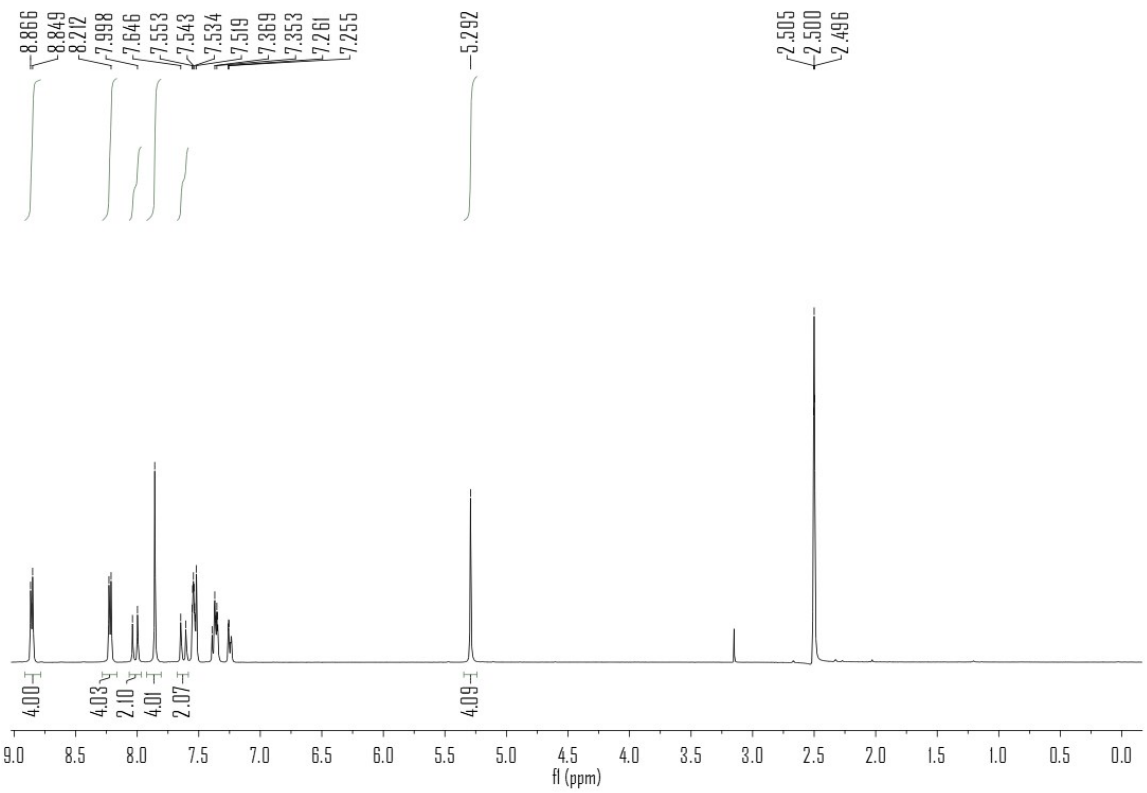


Figure S1. ^{1}H NMR spectrum of **1** (d_6-DMSO).

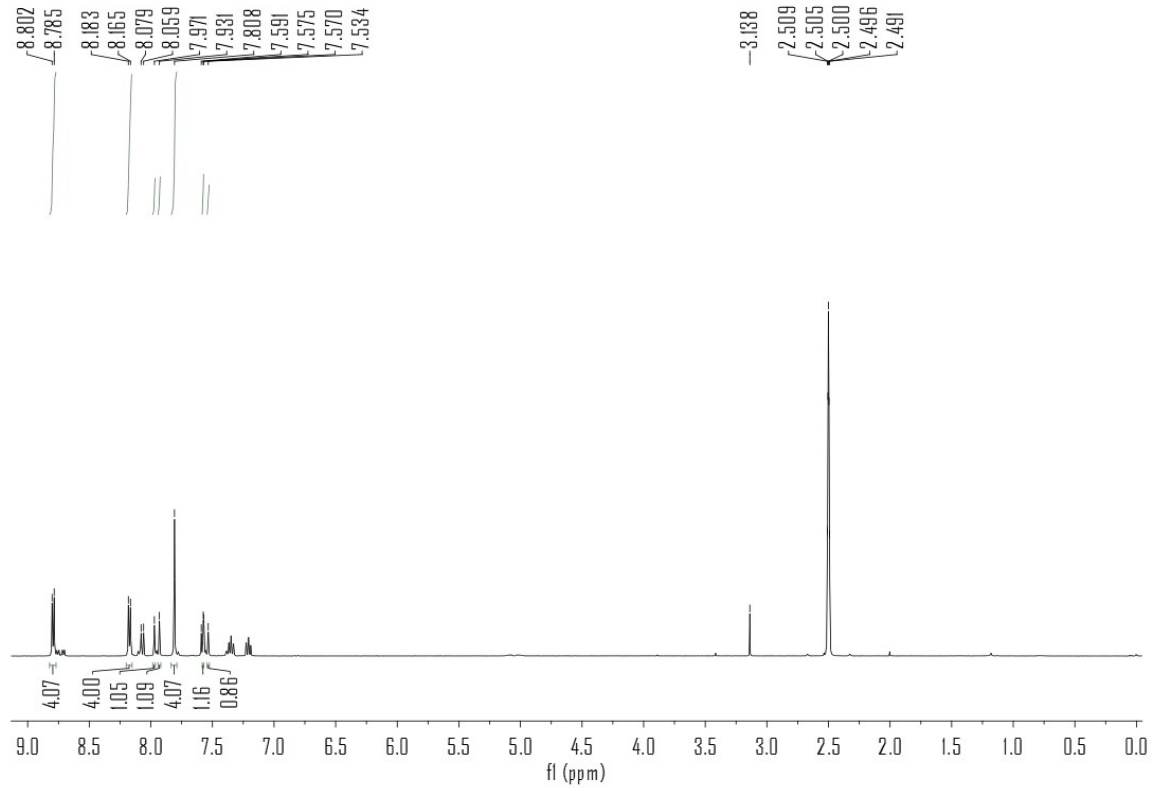


Figure S2. ^{1}H NMR spectrum of **2** (d_6-DMSO).

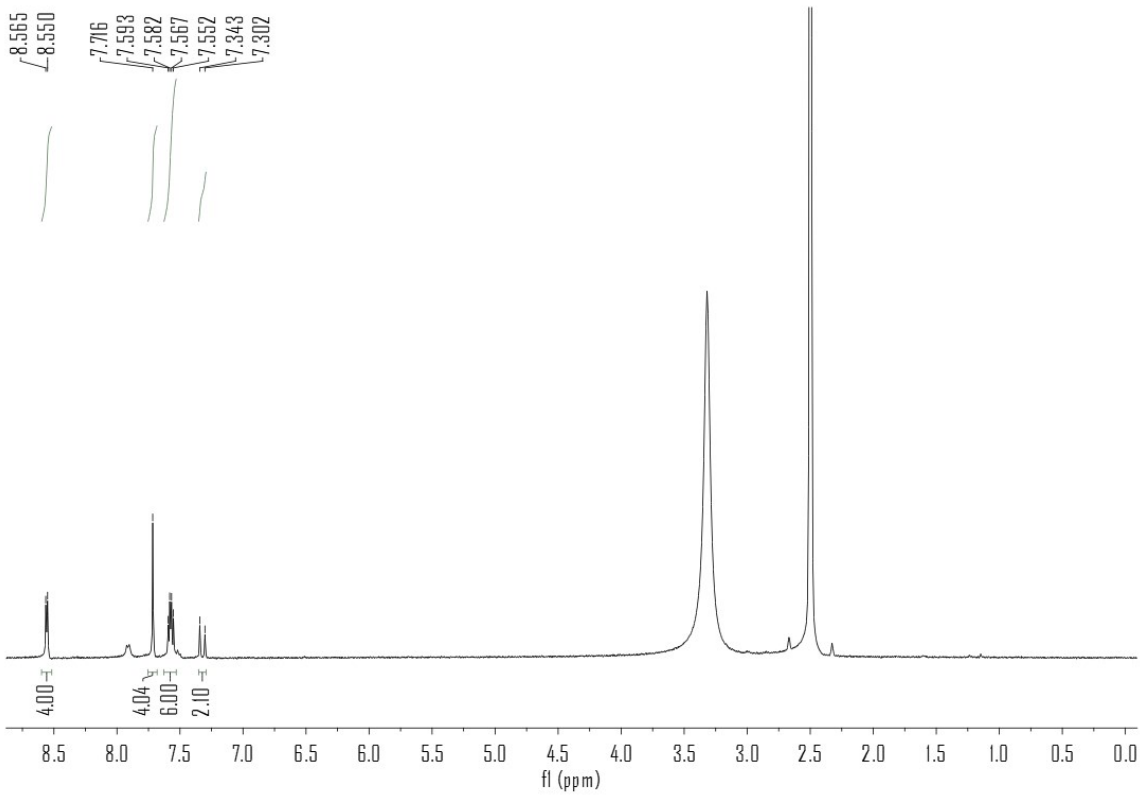
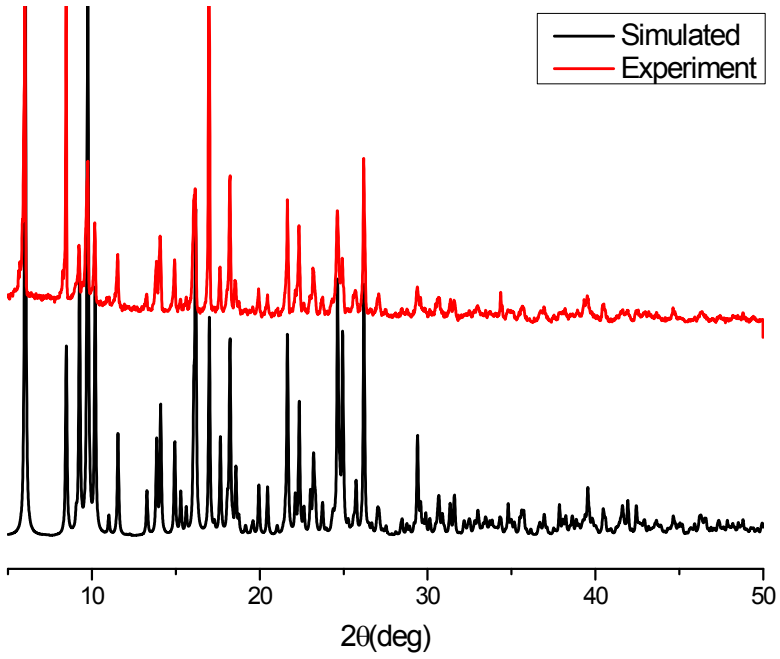
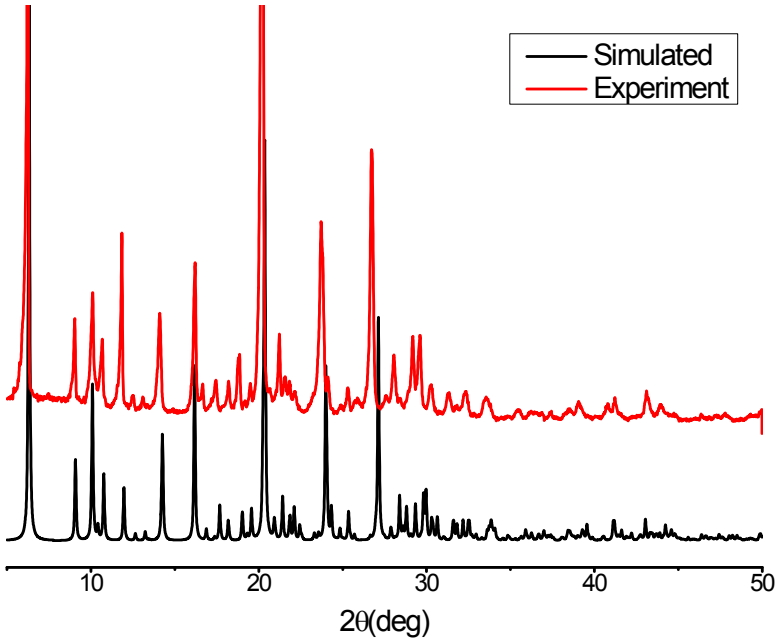


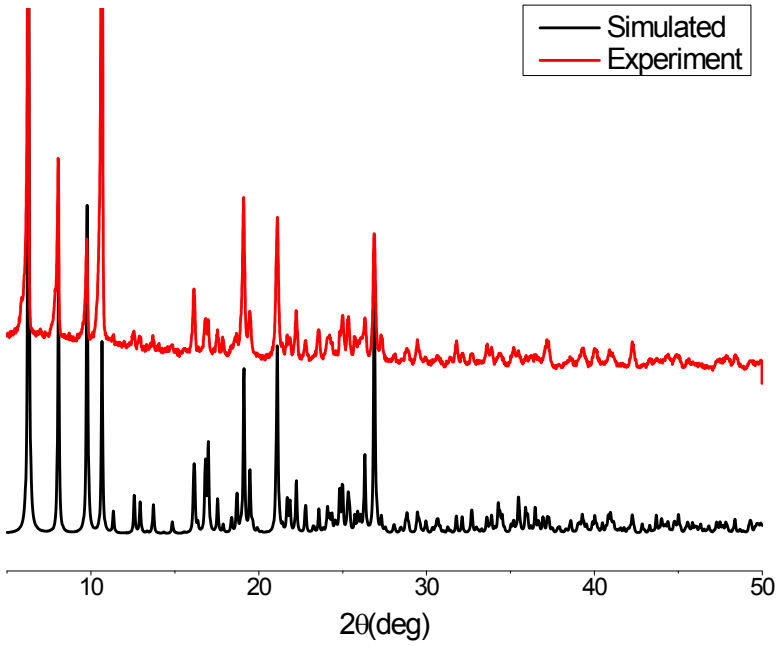
Figure S3. ^{1}H NMR spectrum of **3** (d_6-DMSO).



(*a*)


Simulated
Experiment
10
20
30
40
50
2θ(deg)

(*b*)


Simulated
Experiment
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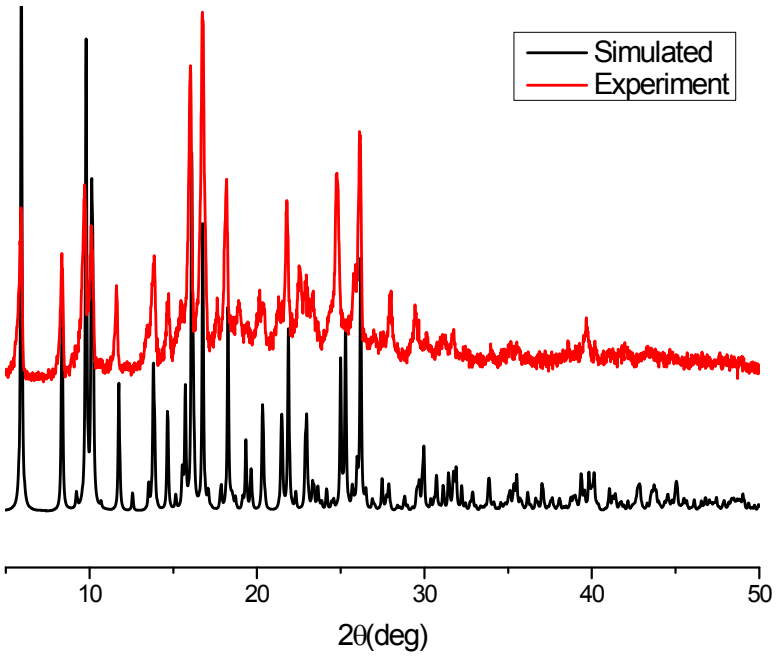
20
30
40
50
2θ(deg)

(*c*)


Simulated
Experiment
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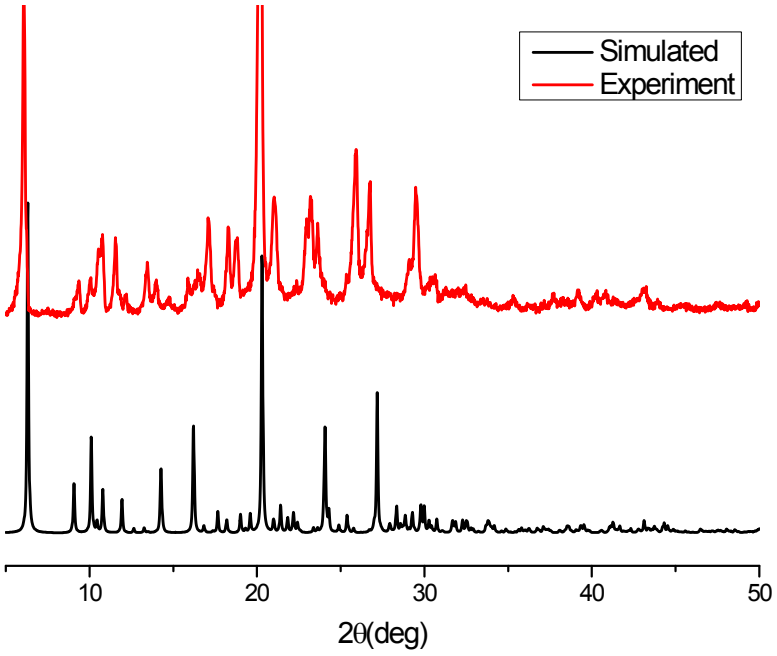
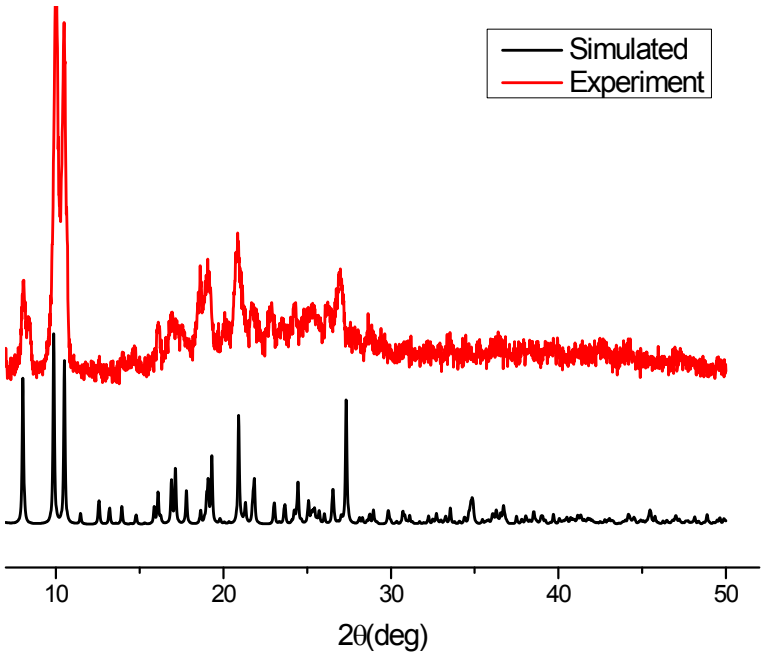
20
30
40
50
2θ(deg)

(d)

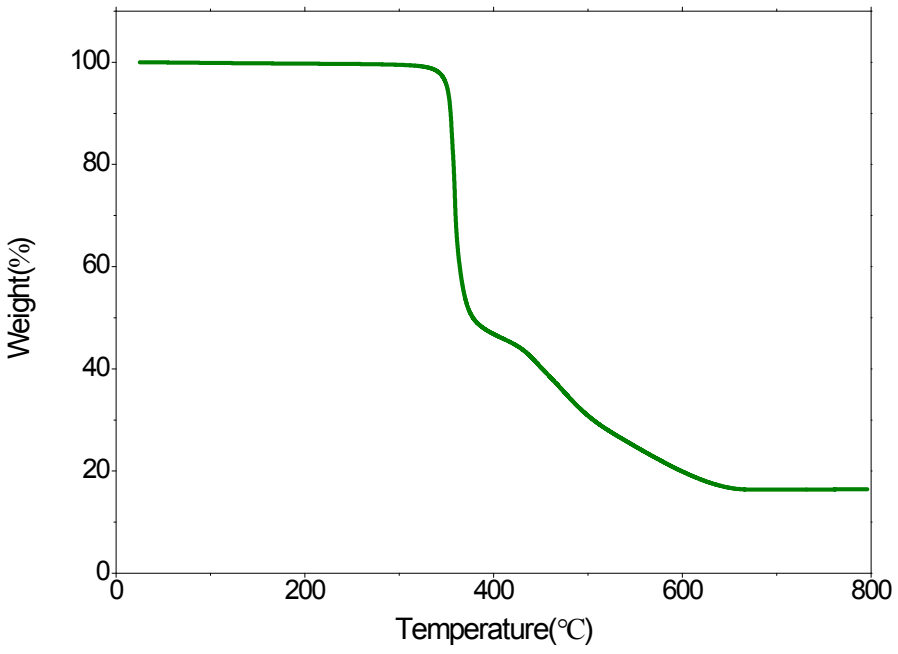

Simulated
Experiment
10
20
30
40
50
2θ(deg)

(*e*)

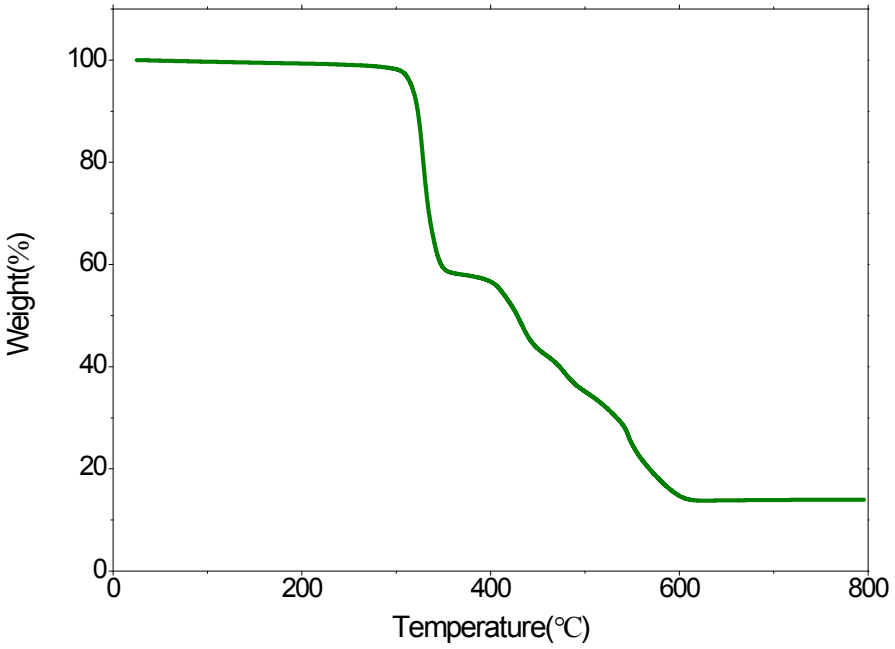


(*f*)

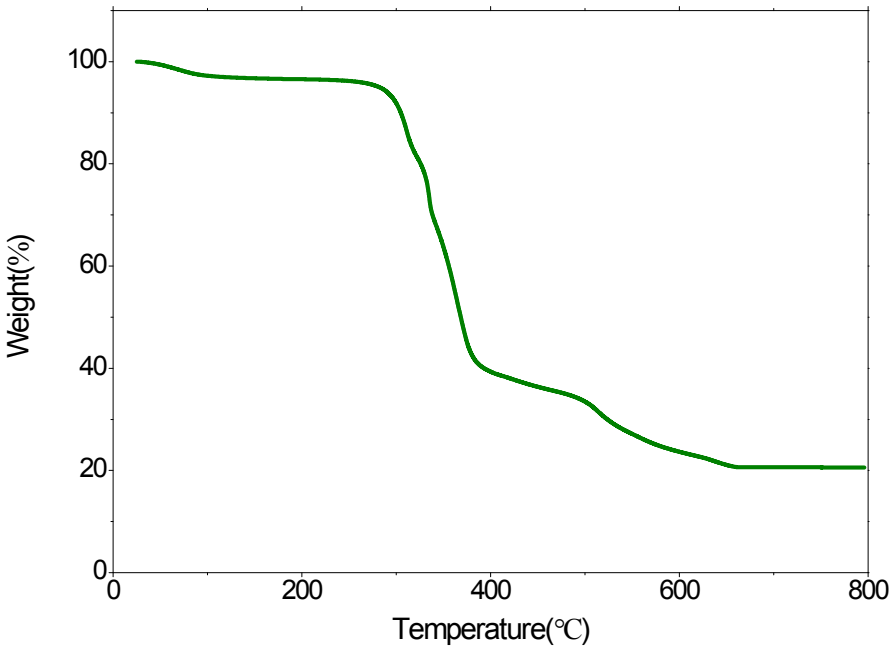
Figure. S4. PXRD spectra of (*a*)-**1,** (*b*)-**2,** (*c*)-**3,** (*d*)-**1a**, (*e*)-**2a**, (*f*)-**3a**.



(*a*)

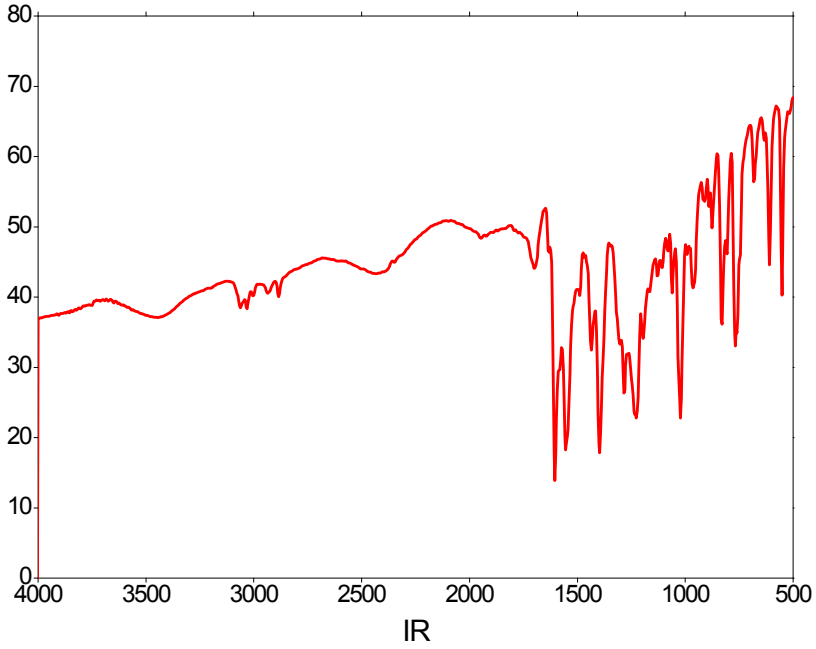


(*b*)

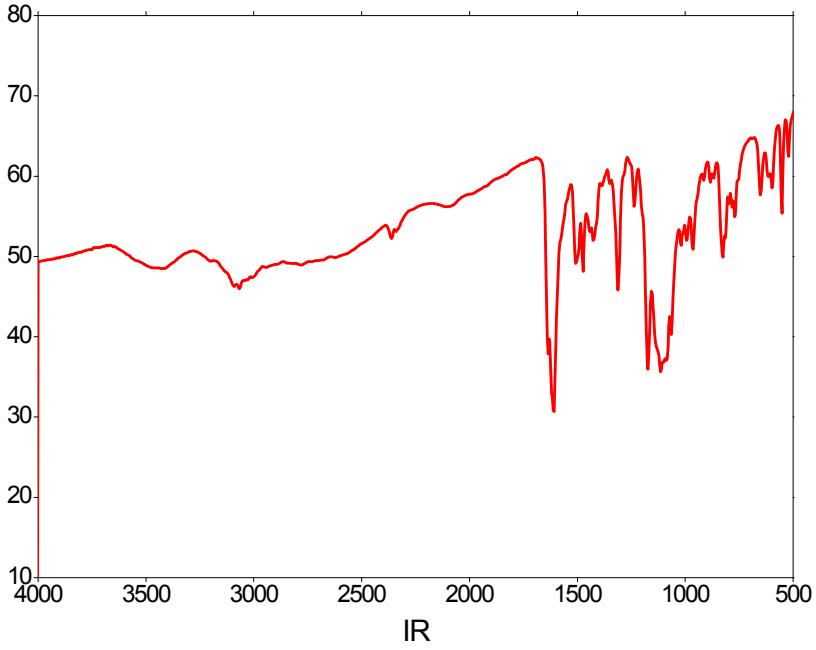


(*c*)

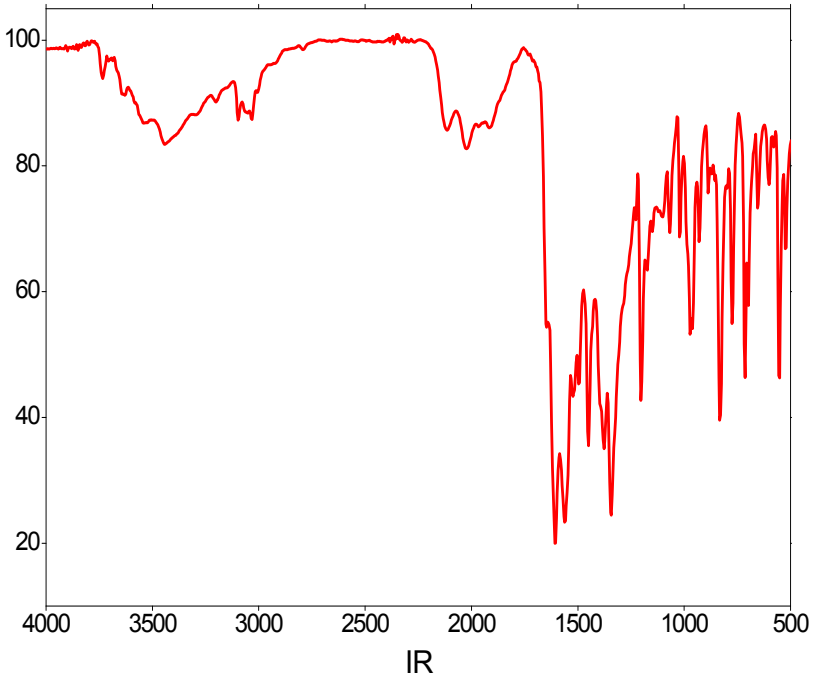
Figure S5. Thermogravimetric analyses of (*a*)-**1,** (*b*)-**2,** (*c*)-**3**.


80
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1500
1000
500
IR

(*a*)


80
70
60
50
40
30
20
10
4000
3500
3000
2500
2000
1500
1000
500
IR

(b)



(*c*)

Figure S6. Infrared spectroscopy of (*a*)-**1,** (*b*)-**2,** (*c*)-**3**.

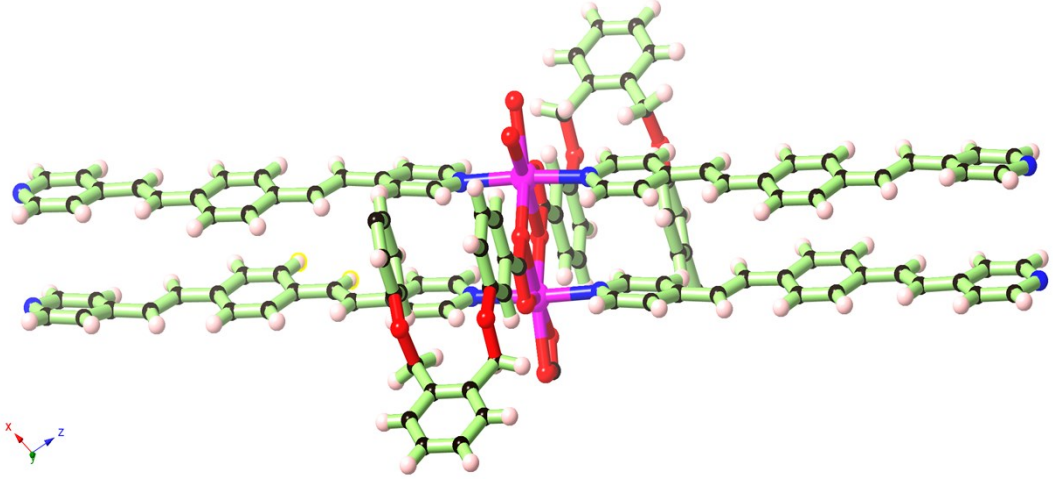


Figure S7. Crystal structure showing the arrangement of 1,4-bpeb in **1**.

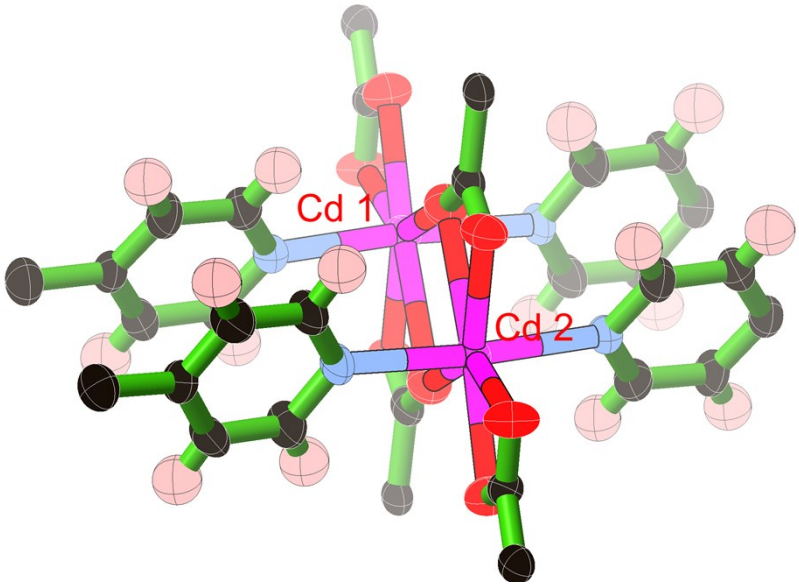
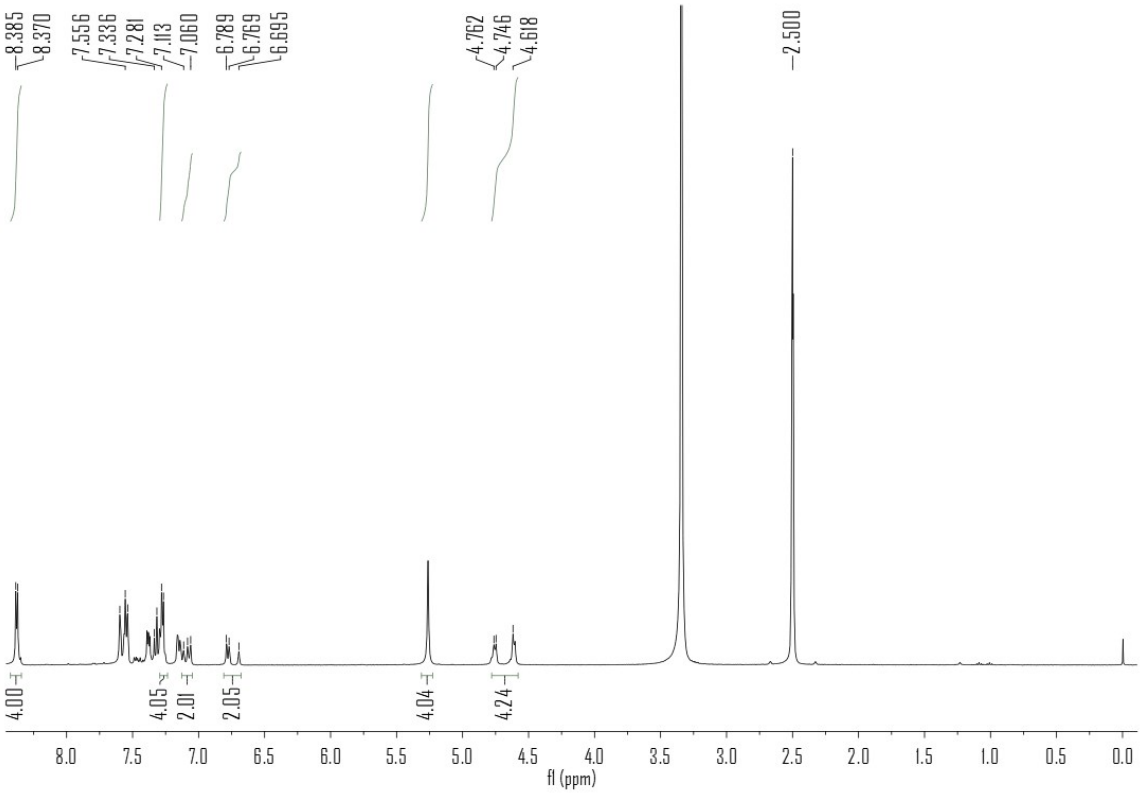
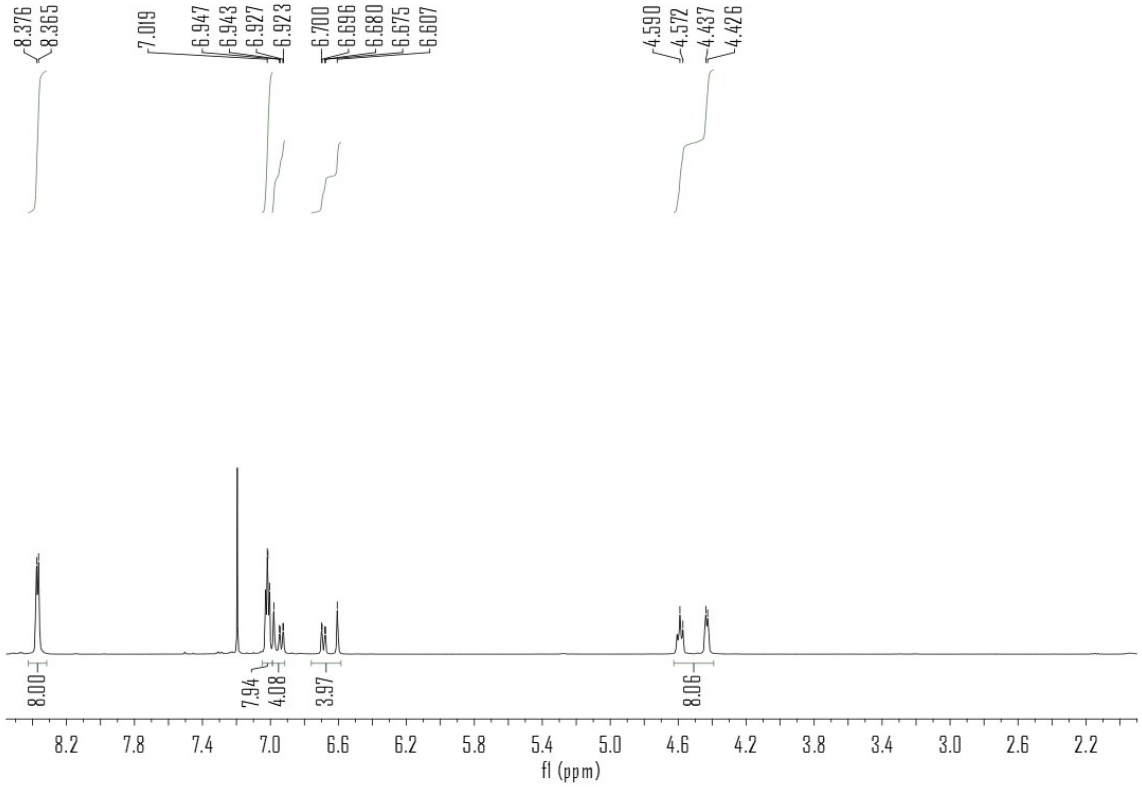


Figure S8. Coordination environment of Cd ions in compound **1**.

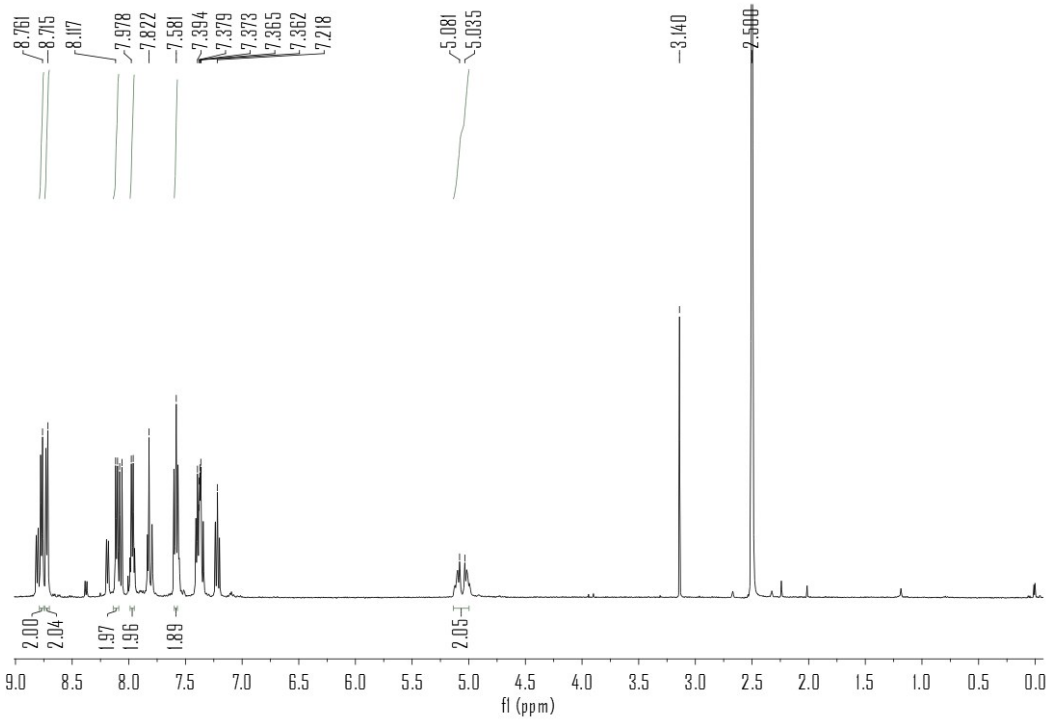


(*a*)

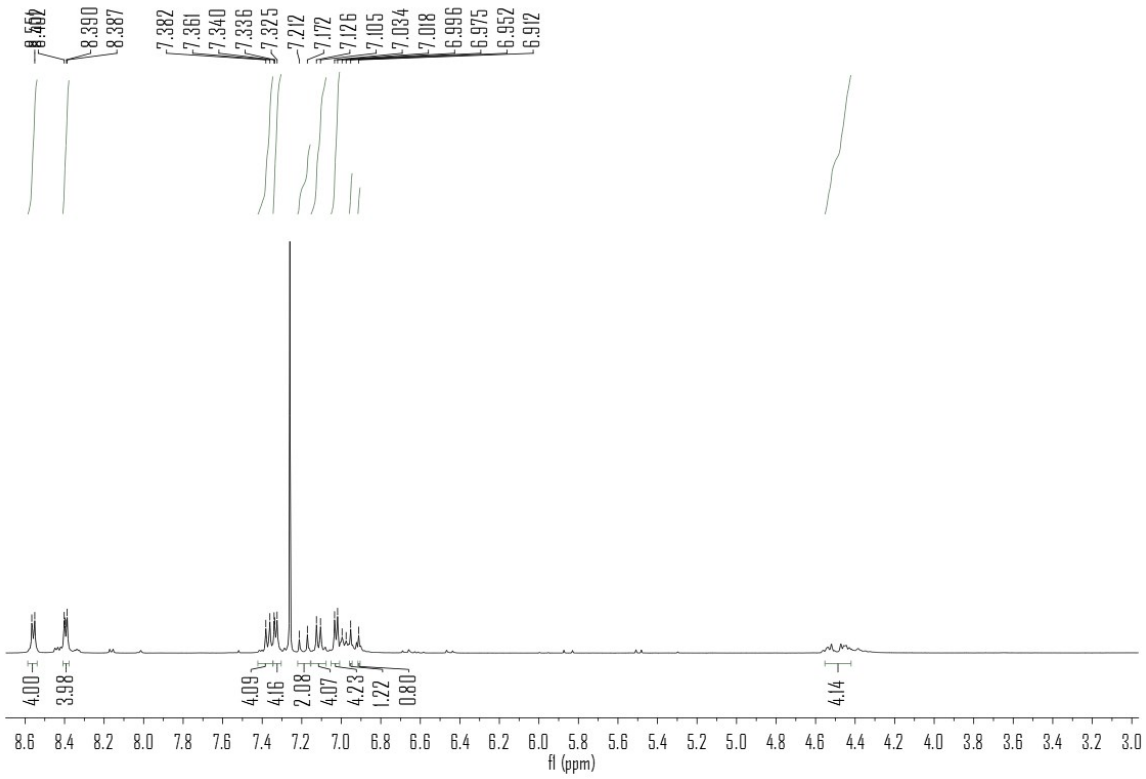


(*b*)

Figure S9. ^{1}H NMR spectrum of (*a*)-**1a,** (*b*)-***p*CP**.



(*a*)



(*b*)

Figure S10. [1]H NMR spectrum of (*a*)-**2a,** (*b*)- **bpbpvpcb**.

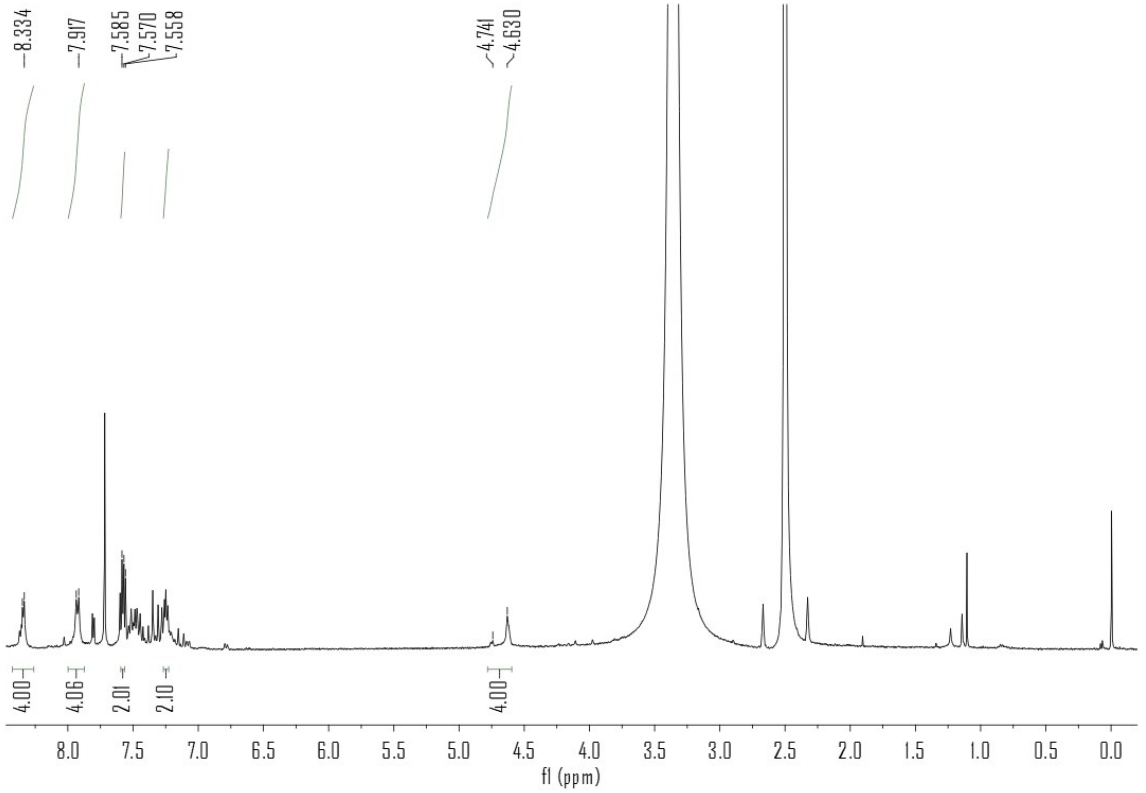
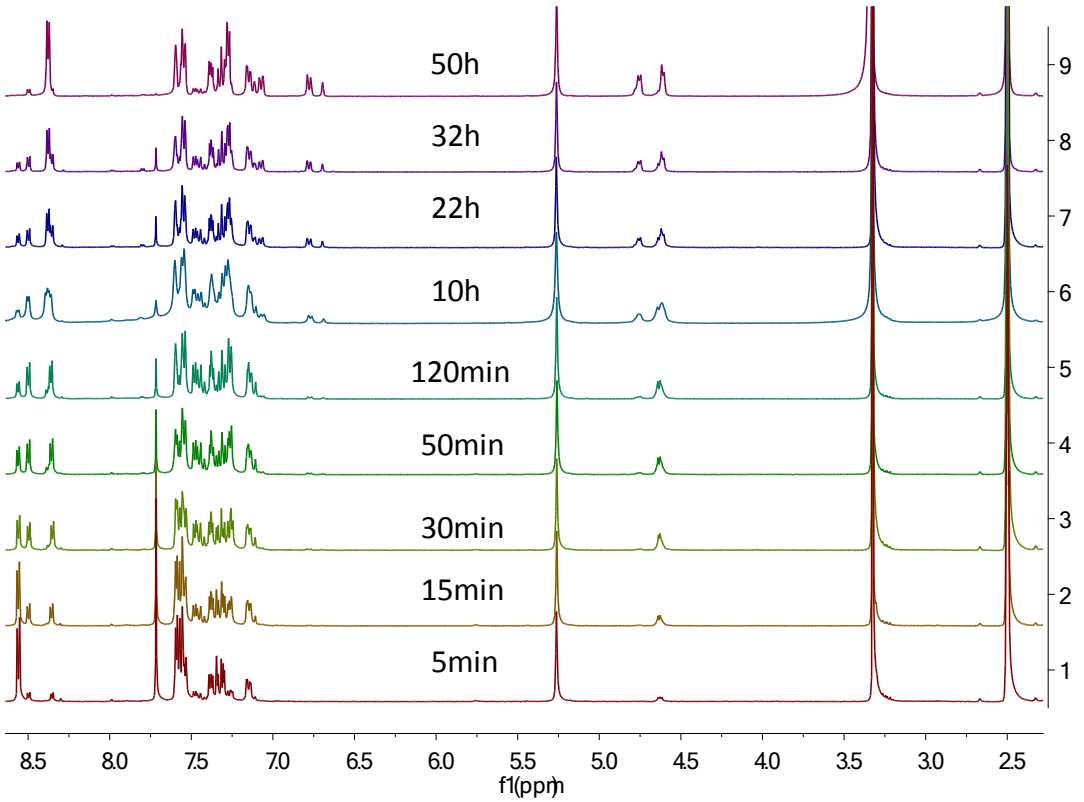
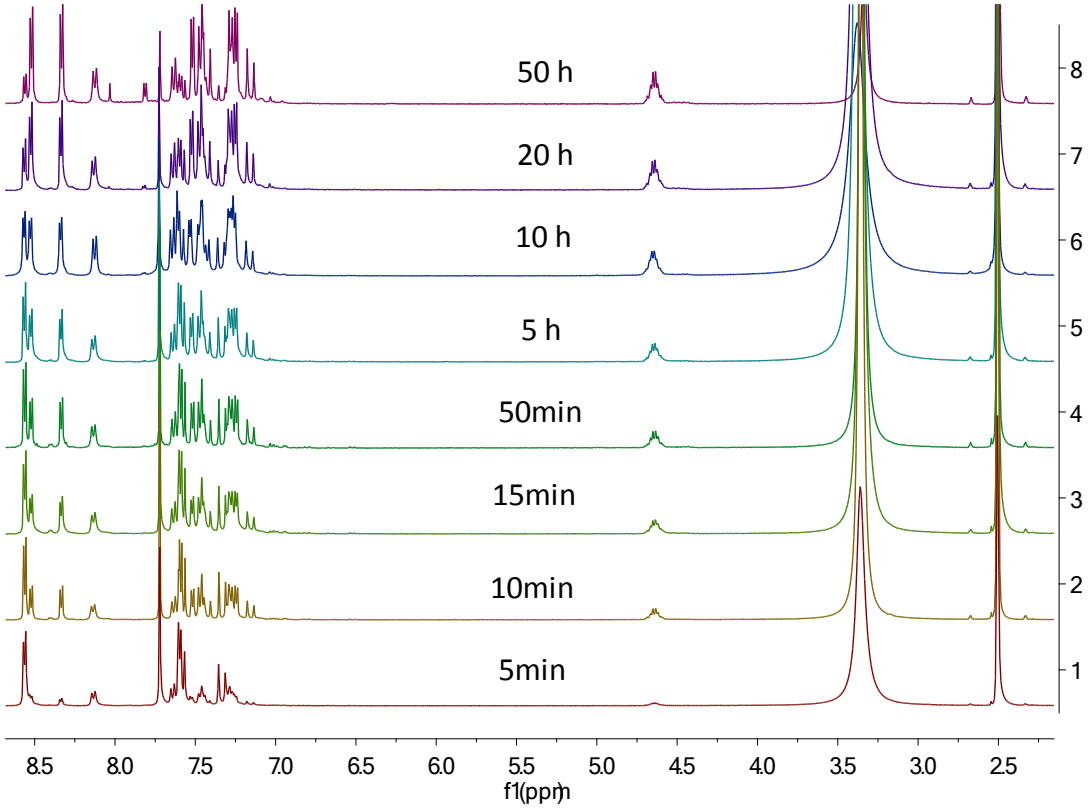


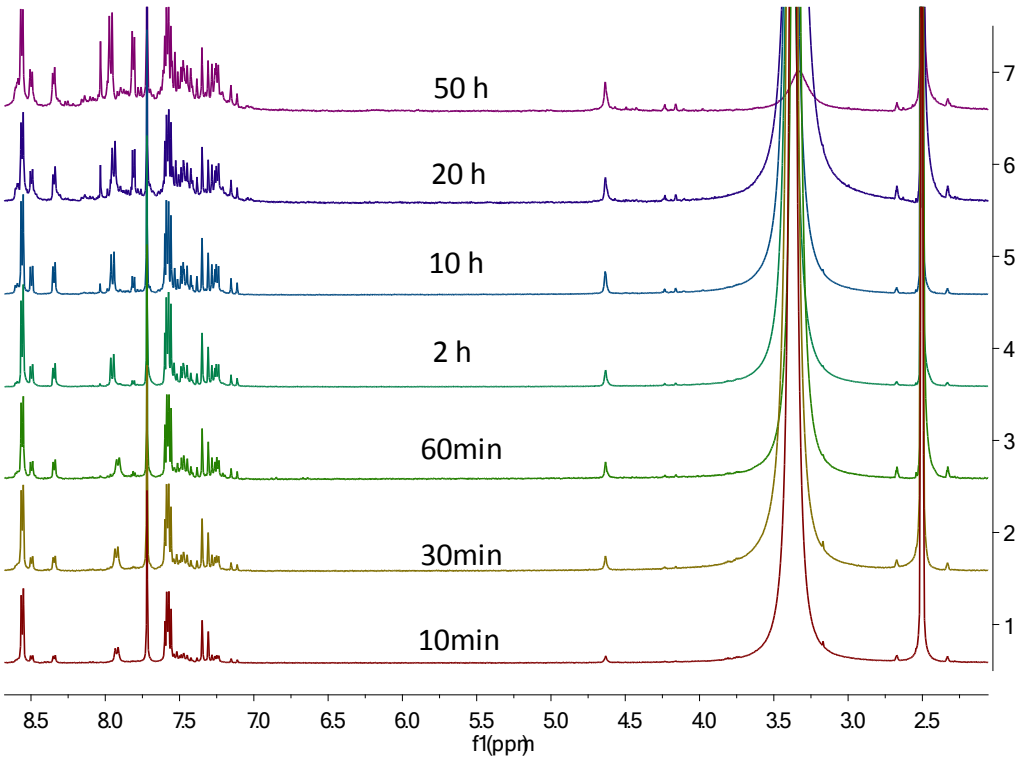
Figure S11. [1]H NMR spectrum of **3a**.


50h
32h
22h
10h
120min
50min
30min
15min
5min
9
8
7
6
5
4
3
2
1
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
f1(ppm)

(a)


50 h
20 h
10 h
5 h
50min
15min
10min
5min
8
7
6
5
4
3
2
1
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
f1(ppm)

(b)



(c)

Figure S12. ^{1}H-NMR spectra of (**a**)-**1,** (**b**)-**2,** (**c**)-**3** in DMSO-*d6* subjected to UV irradiation at different time intervals. The photodimerization was monitored by comparing ^{1}H-NMR cyclobuytl signals.