Supporting Information

Controllable Fluorescence Switching of a Coordination Chain Based on the Photo-Induced Single-Crystal-to-Single-Crystal Reversible Transformation of a *syn*-[2.2]Metacyclophane

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Table of Contents

Table S1. Selected Bond Lengths (Å) and Angles (deg) for related coordination compounds

Complex **1**

Cd(1)-O(1)	2.287(3)	Cd(1)-O(4)	2.287(3)
Cd(1)-N(3)	2.308(4)	Cd(1)-N(2)	2.318(4)
Cd(1)-O(3A)	2.411(3)	Cd(1)-O(3)	2.565(3)
Cd(1)-O(2)	2.573(3)	Cd(2)-O(5)	2.297(4)
Cd(2)-N(4)	2.305(4)	Cd(2)-N(1B)	2.314(4)
Cd(2)-O(8C)	2.320(3)	Cd(2)-O(7)	2.470(4)
Cd(2)-O(6)	2.492(4)	Cd(2)-O(7C)	2.565(3)
O(1)-Cd(1)-O(4)	143.26(12)	O(1)-Cd(1)-N(3)	90.10(13)
O(4)-Cd(1)-N(3)	93.92(13)	O(1)-Cd(1)-N(2)	87.40(13)
O(4)-Cd(1)-N(2)	90.73(13)	N(3)-Cd(1)-N(2)	174.92(13)
O(1)-Cd(1)-O(3A)	85.66(11)	O(4)-Cd(1)-O(3A)	130.46(11)
N(3)-Cd(1)-O(3A)	92.82(12)	N(2)-Cd(1)-O(3A)	82.58(12)
O(1)-Cd(1)-O(3)	161.00(11)	O(4)-Cd(1)-O(3)	53.32(10)
N(3)-Cd(1)-O(3)	98.68(12)	N(2)-Cd(1)-O(3)	82.47(12)
O(3A)-Cd(1)-O(3)	77.15(10)	O(1)-Cd(1)-O(2)	53.05(10)
O(4)-Cd(1)-O(2)	90.49(11)	N(3)-Cd(1)-O(2)	88.81(12)
N(2)-Cd(1)-O(2)	93.21(12)	O(3A)-Cd(1)-O(2)	138.70(10)
O(3)-Cd(1)-O(2)	143.27(9)	O(5)-Cd(2)-N(4)	92.54(14)
O(5)-Cd(2)-N(1B)	91.37(14)	N(4)-Cd(2)-N(1B)	175.06(13)
O(5)-Cd(2)-O(8C)	146.02(14)	N(4)-Cd(2)-O(8C)	90.83(13)
N(1B)-Cd(2)-O(8C)	87.61(14)	O(5)-Cd(2)-O(7)	83.47(12)
N(4)-Cd(2)-O(7)	91.65(13)	N(1B)-Cd(2)-O(7)	85.79(13)
O(8C)-Cd(2)-O(7)	130.22(12)	O(5)-Cd(2)-O(6)	54.23(12)
N(4)-Cd(2)-O(6)	88.59(13)	N(1B)-Cd(2)-O(6)	96.15(13)
O(8C)-Cd(2)-O(6)	92.10(13)	O(7)-Cd(2)-O(6)	137.65(11)
O(5)-Cd(2)-O(7C)	160.11(12)	N(4)-Cd(2)-O(7C)	92.60(12)
N(1B)-Cd(2)-O(7C)	82.71(13)	O(8C)-Cd(2)-O(7C)	53.04(12)

O(7)-Cd(2)-O(7C)	77.19(12)	O(6)-Cd(2)-O(7C)	145.12(11)

Complex **3**

Cd(1)-O(3)	2.282(3)	Cd(1)-O(2)	2.303(3)
Cd(1)-N(2A)	2.327(4)	Cd(1)-N(1)	2.333(4)
Cd(1)-O(1B)	2.358(3)	Cd(1)-O(1)	2.623(3)
Cd(1)-O(4)	2.628(3)		
O(3)-Cd(1)-O(2)	143.73(12)	O(3)-Cd(1)-N(2A)	92.76(15)
O(2)-Cd(1)-N(2A)	90.66(13)	O(3)-Cd(1)-N(1)	90.72(14)
O(2)-Cd(1)-N(1)	88.47(12)	N(2A)-Cd(1)-N(1)	175.22(12)
O(3)-Cd(1)-O(1B)	88.39(12)	O(2)-Cd(1)-O(1B)	127.68(10)
N(2A)-Cd(1)-O(1B)	90.63(13)	N(1)-Cd(1)-O(1B)	86.19(12)
O(3)-Cd(1)-O(1)	163.56(11)	O(2)-Cd(1)-O(1)	52.25(10)
N(2A)-Cd(1)-O(1)	90.44(12)	N(1)-Cd(1)-O(1)	85.30(11)
O(1B)-Cd(1)-O(1)	75.44(11)	O(3)-Cd(1)-O(4)	52.11(11)
O(2)-Cd(1)-O(4)	91.66(11)	N(2A)-Cd(1)-O(4)	93.01(12)
N(1)-Cd(1)-O(4)	91.72(12)	O(1B)-Cd(1)-O(4)	140.45(11)
O(1)-Cd(1)-O(4)	143.80(10)		

Complex **4**

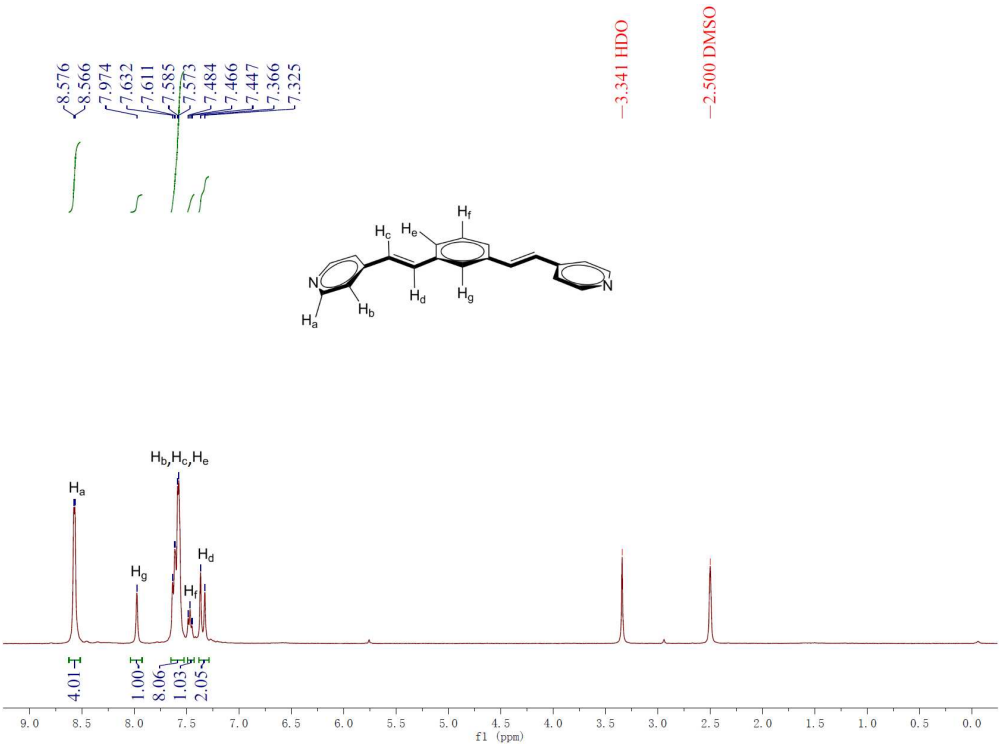
Cd(1)-O(4)	2.296(10)	Cd(1)-O(1)	2.305(10)
Cd(1)-N(2A)	2.306(11)	Cd(1)-N(1)	2.328(10)
Cd(1)-O(3A)	2.366(10)	Cd(1)-O(2)	2.535(9)
Cd(1)-O(3)	2.664(10)	Cd(2)-O(8B)	2.301(10)
Cd(2)-O(5)	2.317(11)	Cd(2)-N(4B)	2.319(11)
Cd(2)-N(3)	2.331(10)	Cd(2)-O(7)	2.351(9)
Cd(2)-O(6)	2.522(9)	Cd(2)-O(7B)	2.689(9)
O(4)-Cd(1)-O(1)	149.0(4)	O(4)-Cd(1)-N(2A)	90.9(4)
O(1)-Cd(1)-N(2A)	93.4(4)	O(4)-Cd(1)-N(1)	87.6(4)

O(1)-Cd(1)-N(1)	88.6(4)	N(2A)-Cd(1)-N(1)	178.0(4)
O(4)-Cd(1)-O(3A)	123.1(3)	O(1)-Cd(1)-O(3A)	87.7(4)
N(2A)-Cd(1)-O(3A)	89.1(4)	N(1)-Cd(1)-O(3A)	90.6(4)
O(4)-Cd(1)-O(2)	96.2(3)	O(1)-Cd(1)-O(2)	52.9(3)
N(2A)-Cd(1)-O(2)	93.1(3)	N(1)-Cd(1)-O(2)	88.4(3)
O(3A)-Cd(1)-O(2)	140.6(3)	O(4)-Cd(1)-O(3)	52.0(3)
O(1)-Cd(1)-O(3)	158.5(3)	N(2A)-Cd(1)-O(3)	89.8(3)
N(1)-Cd(1)-O(3)	88.2(3)	O(3A)-Cd(1)-O(3)	71.1(3)
O(2)-Cd(1)-O(3)	148.1(3)	O(8B)-Cd(2)-O(5)	148.7(4)
O(8B)-Cd(2)-N(4B)	90.9(4)	O(5)-Cd(2)-N(4B)	93.5(4)
O(8B)-Cd(2)-N(3)	87.4(3)	O(5)-Cd(2)-N(3)	88.8(4)
N(4B)-Cd(2)-N(3)	177.6(4)	O(8B)-Cd(2)-O(7)	123.1(3)
O(5)-Cd(2)-O(7)	87.9(3)	N(4B)-Cd(2)-O(7)	89.5(3)
N(3)-Cd(2)-O(7)	90.1(3)	O(8B)-Cd(2)-O(6)	96.3(3)
O(5)-Cd(2)-O(6)	52.6(3)	N(4B)-Cd(2)-O(6)	92.7(3)
N(3)-Cd(2)-O(6)	89.1(3)	O(7)-Cd(2)-O(6)	140.6(3)
O(8B)-Cd(2)-O(7B)	51.8(3)	O(5)-Cd(2)-O(7B)	158.9(3)
N(4B)-Cd(2)-O(7B)	90.3(3)	N(3)-Cd(2)-O(7B)	87.3(3)
O(7)-Cd(2)-O(7B)	71.3(3)	O(6)-Cd(2)-O(7B)	148.0(3)

Symmetry codes: (**1**) A: - *x*, - *y* + 1, - *z* + 1; B: *x* + 3, *y* + 1, *z* + 1; C: - *x* + 3, - *y* + 2, - *z* + 2. (**3**) A: *x* + 1, - *y* + 1, *z* - 1/2; B: - *x* + 1, - *y* + 1, - *z* + 1. (**4**) A: - *x* + 1, - *y* + 2, - *z* + 1; B: - *x* + 3, - *y* + 2, - *z*.

Crystal data for the re-irradiated sample from **4** upon irradiation with 254 nm UV light: $C_{68}H_{50}Cd_2F_4N_4O_9$, M_r = 1367.94, monoclinic, space group P_2/c, a = 11.282(2), b = 13.004(3), c = 21.054(4) Å, β = 102.42(3)°, V = 3016.8(11) Å^3, Z = 2, D_c = 1.506 g/cm^3, R_1 = 0.0888 ($I > 2\sigma$), wR_2 = 0.2070, GOF = 1.029. The cell parameters of this sample confirmed the reversible SCSC transformation from **4** to **3**.

(a)



(b)

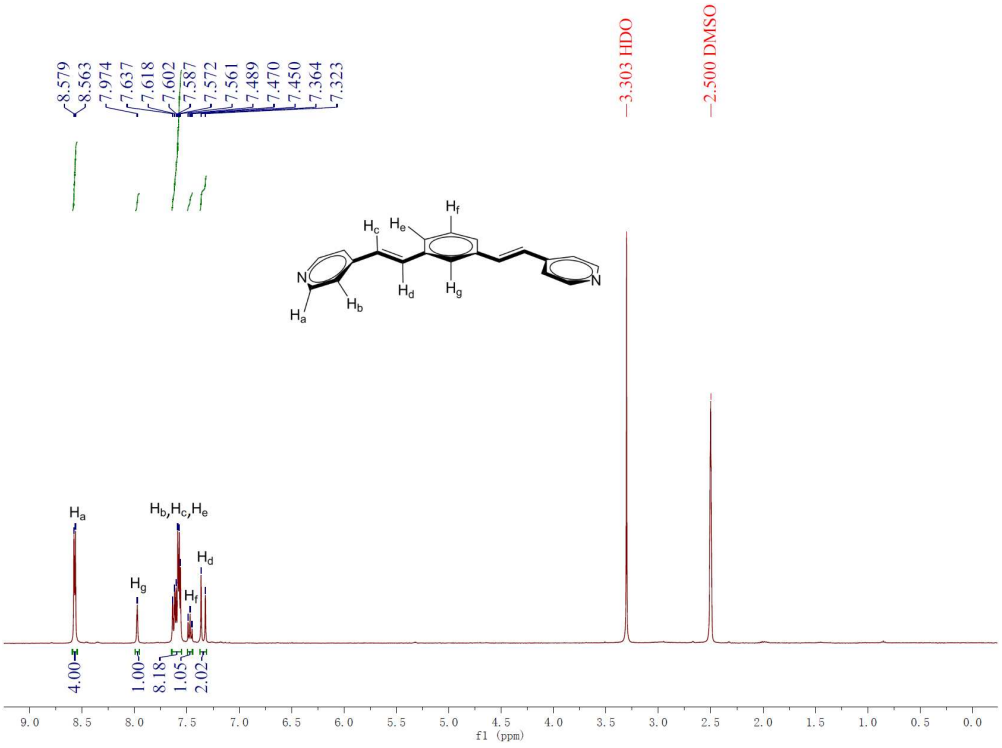
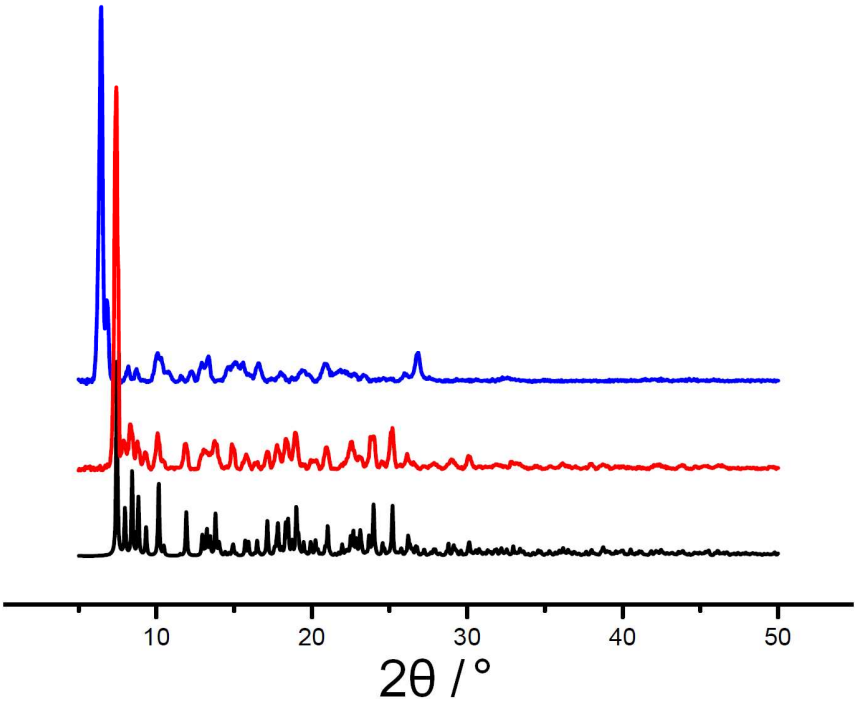
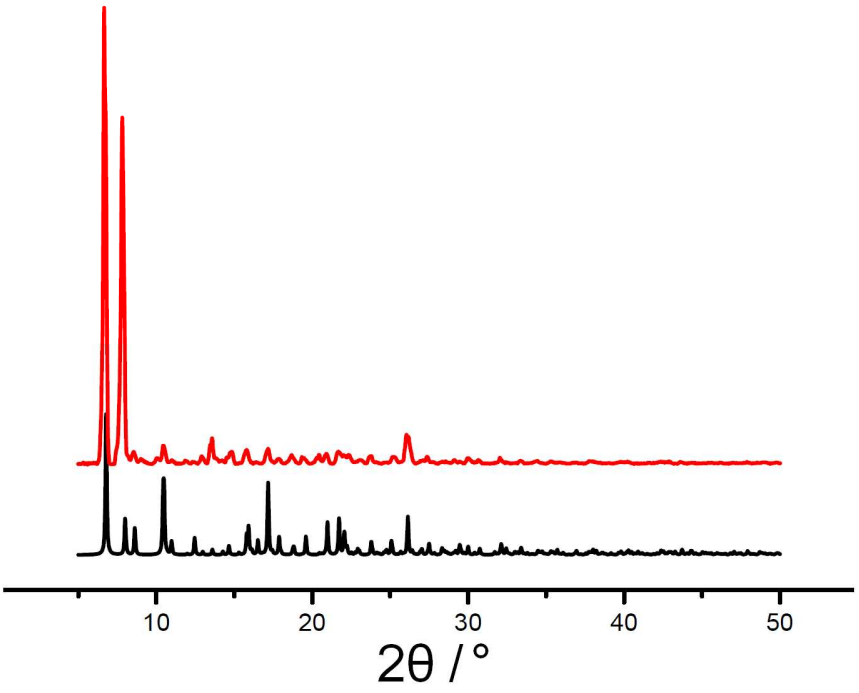


Figure S1. The ^{1}H NMR spectra of powdered **1,3-bpeb** before (a) and after (b) UV irradiation in d_6-DMSO at ambient temperature.

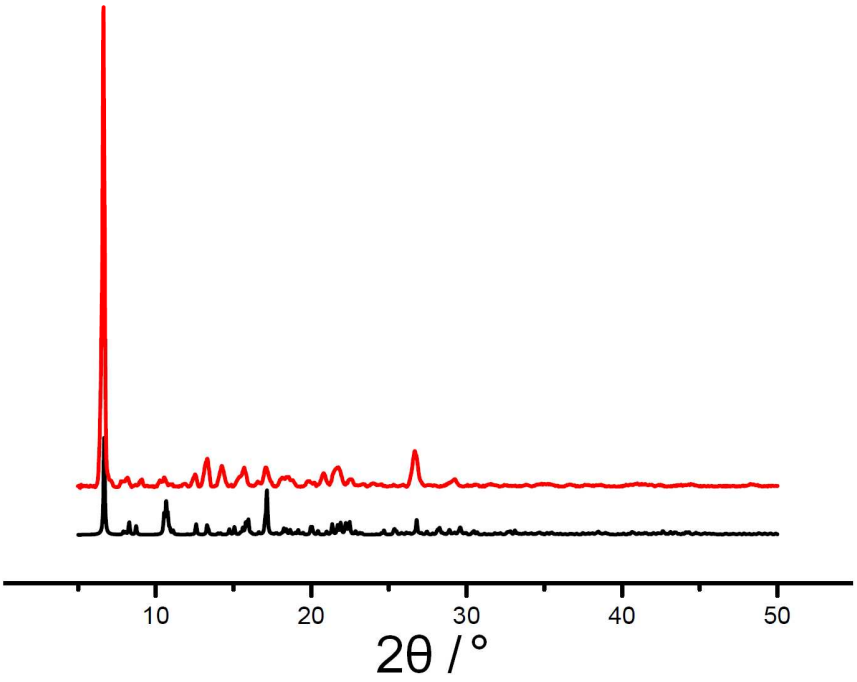
(a)



(b)



(c)



(d)

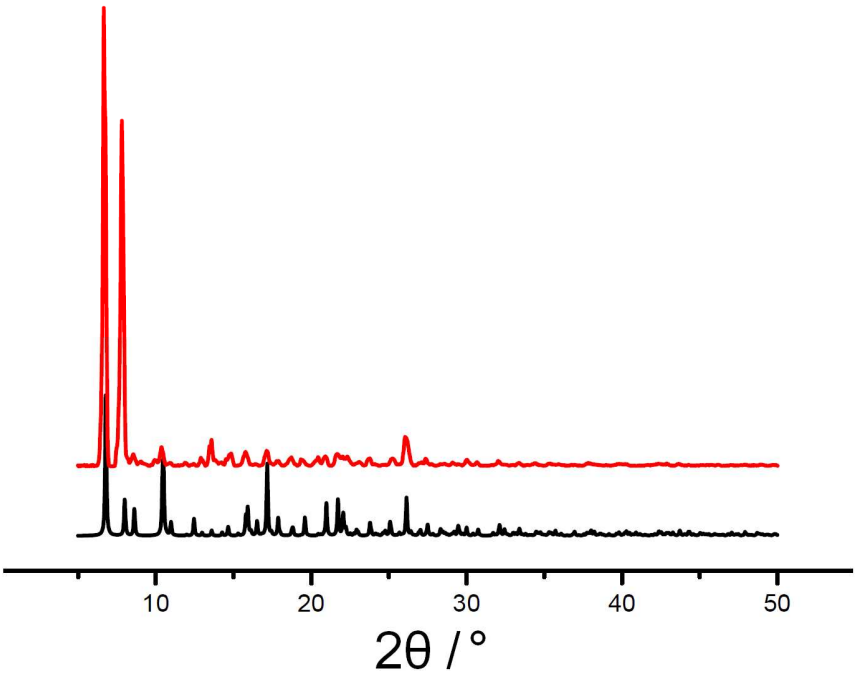


Figure S2. (a) PXRD pattern of **1** (from single crystal data: black; as-synthesis: red) and its photoproduct **1b** (blue). (b) PXRD patterns of **3** (from single crystal data: black; as-synthesis: red). (c) PXRD patterns of **4** (from single crystal data: black; as-synthesis: red). (d) PXRD patterns of **3** (from single crystal data: black) and the re-irradiated sample of **4** upon irradiation with 254 nm UV light (red). Figure S2d confirmed the reversible structural transformation from **4** to **3**.

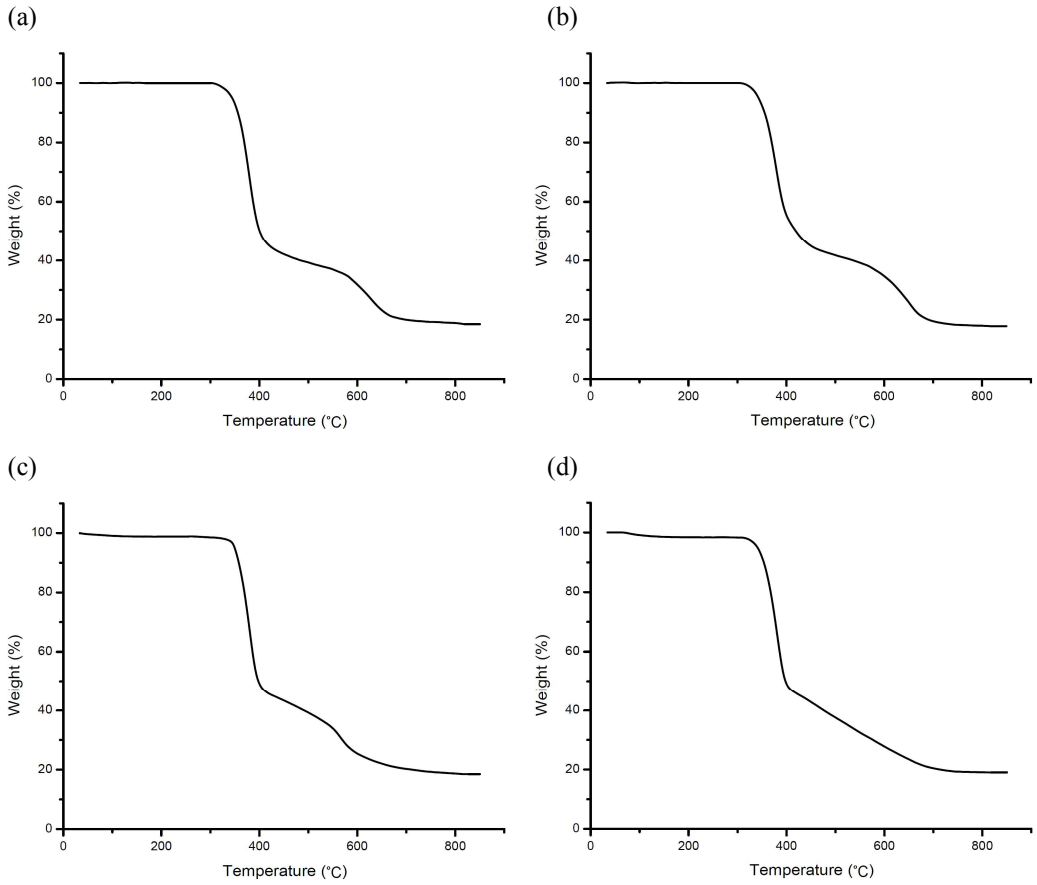
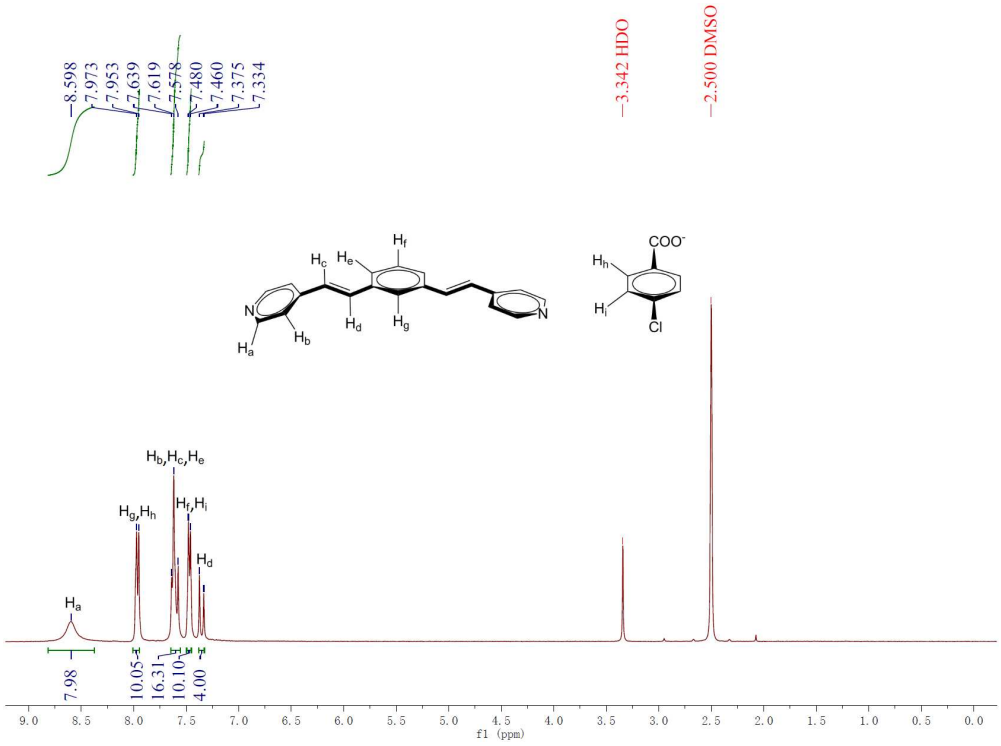
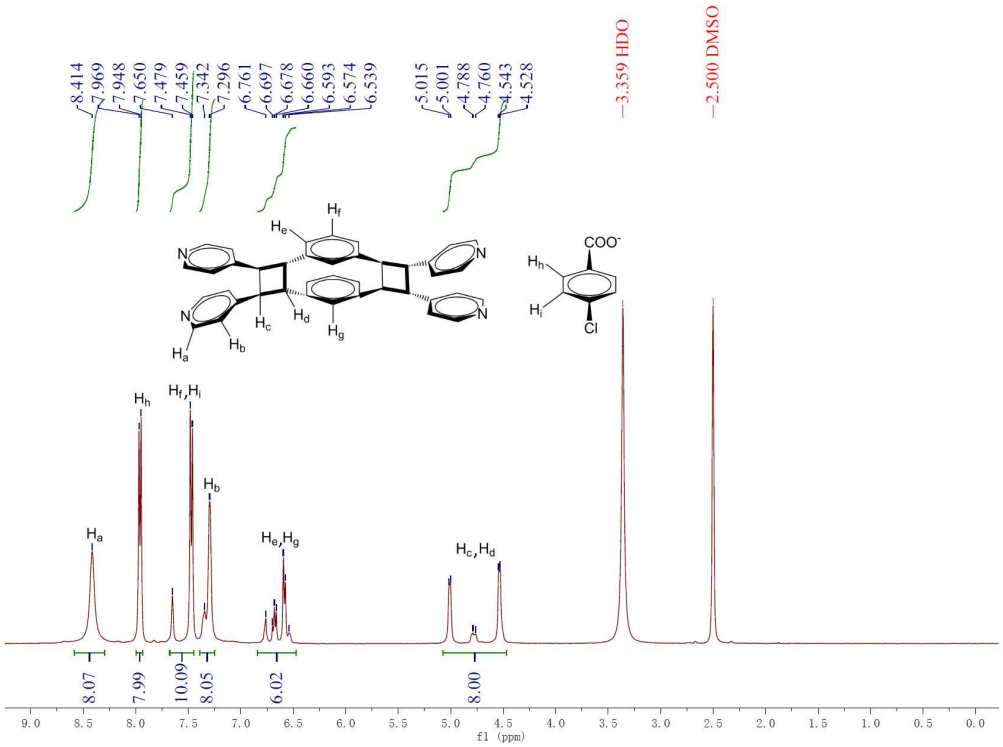


Figure S3. The TGA curves for **1** (a), **1a** (b), **3** (c) and **4** (d).

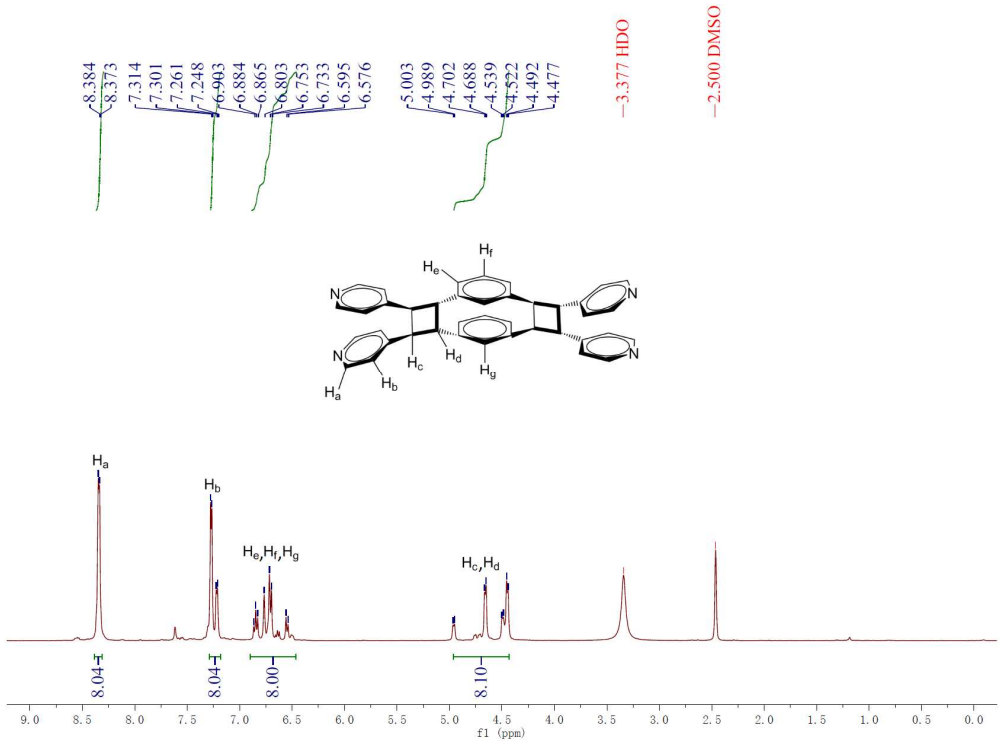
(a)


8.598
7.973
7.953
7.639
7.619
7.578
7.480
7.460
7.375
7.334
3.342 HDO
2.500 DMSO
Hb,Hc,He
Hg,Hh
Hf,Hi
Hd
Ha
7.98
10.05
16.31
10.10
4.00
f1 (ppm)

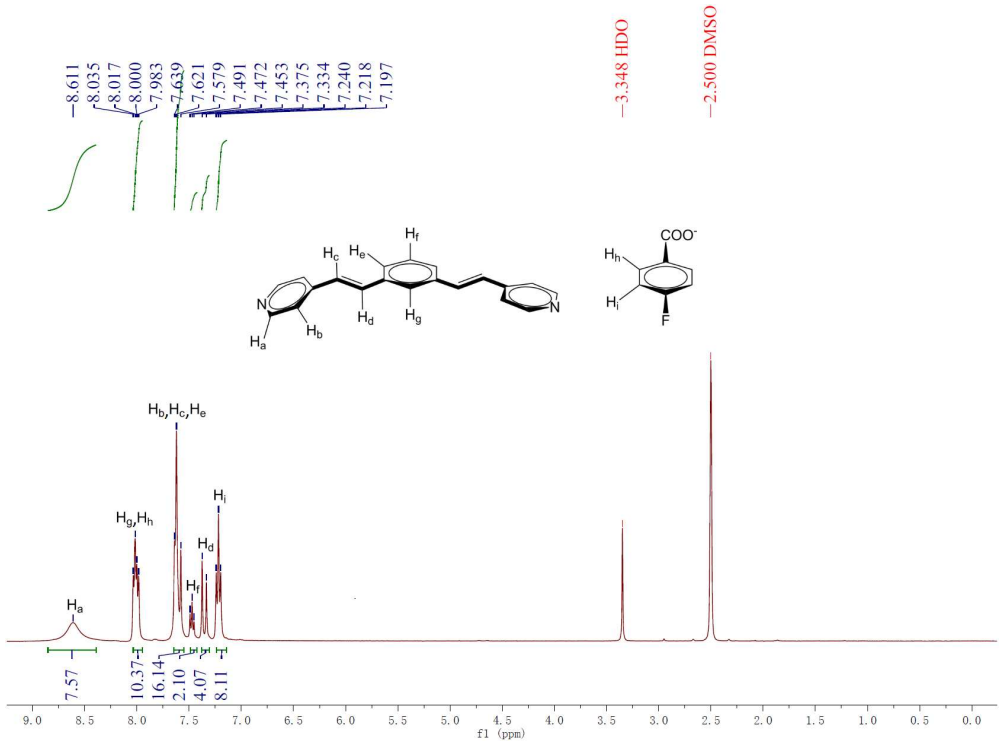
(b)


8.414
7.969
7.948
7.650
7.479
7.459
7.342
7.296
6.761
6.697
6.678
6.660
6.593
6.574
6.539
5.015
5.001
4.788
4.760
4.543
4.528
3.359 HDO
2.500 DMSO
Hh
Hf,Hi
Hb
Ha
He,Hg
Hc,Hd
8.07
7.99
10.09
8.05
6.02
8.00
f1 (ppm)

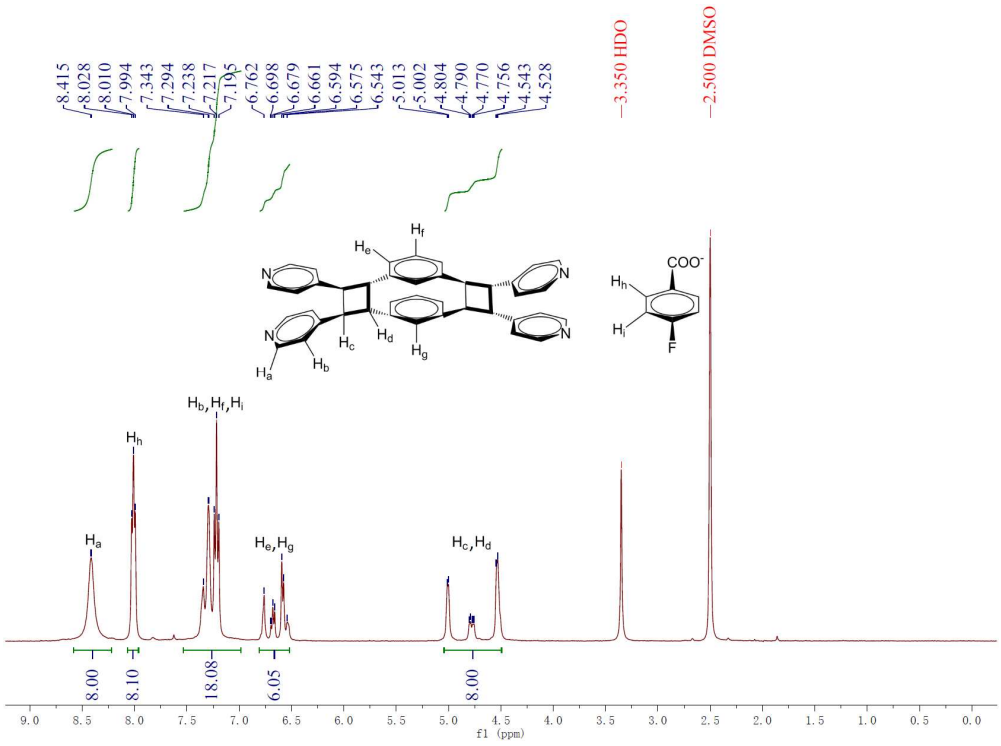
(c)


8.384
8.373
7.314
7.301
7.261
7.248
6.903
6.884
6.865
6.803
6.753
6.733
6.595
6.576
5.003
4.989
4.702
4.688
4.539
4.522
4.492
4.477
3.377 HDO
2.500 DMSO
Ha
Hb
He,Hf,Hg
Hc,Hd
8.04
8.04
8.00
8.10
f1 (ppm)

(d)


8.611
8.035
8.017
8.000
7.983
7.639
7.621
7.579
7.491
7.472
7.453
7.375
7.334
7.240
7.218
7.197
3.348 HDO
2.500 DMSO
Hb,Hc,He
Hg,Hh
Hi
Hd
Hf
Ha
7.57
10.37
16.14
2.10
4.07
8.11
f1 (ppm)

(e)



(f)

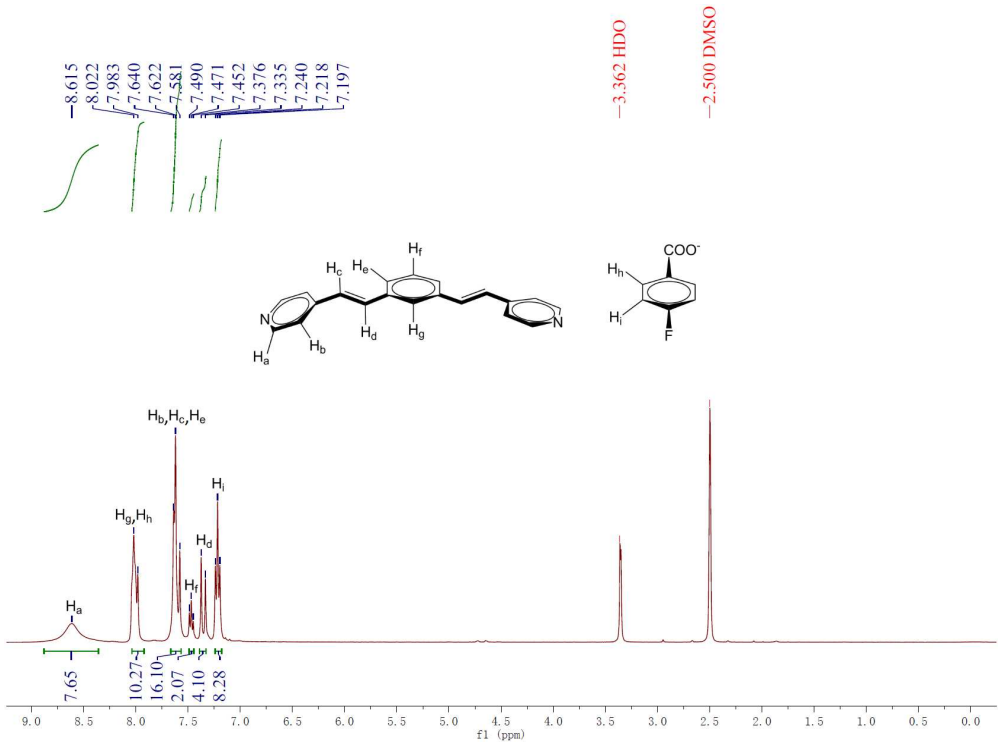


Figure S4. The ^{1}H NMR spectra of **1** (a), **1a** (b), dehydrated **2** (c), **3** (d), **4** (e) and short-wave UV irradiated sample from **4** (f) in d_6-DMSO at ambient temperature.

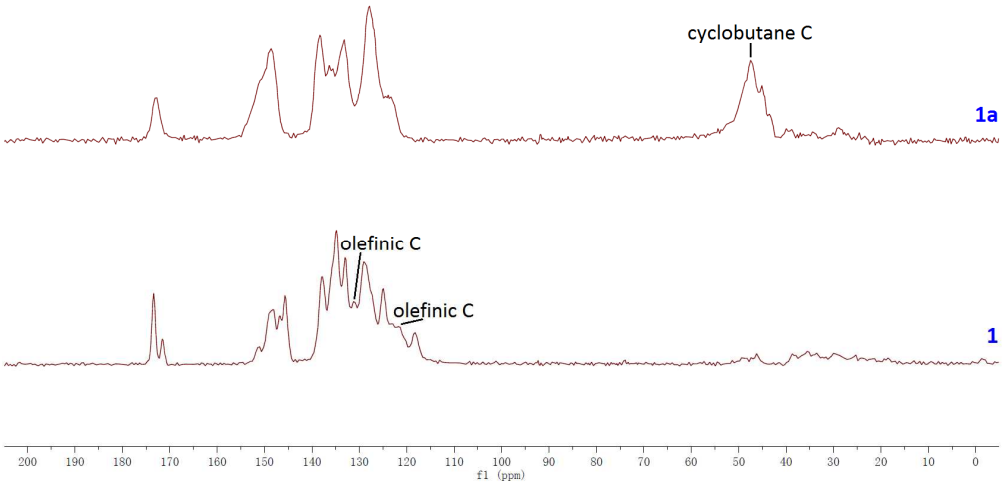
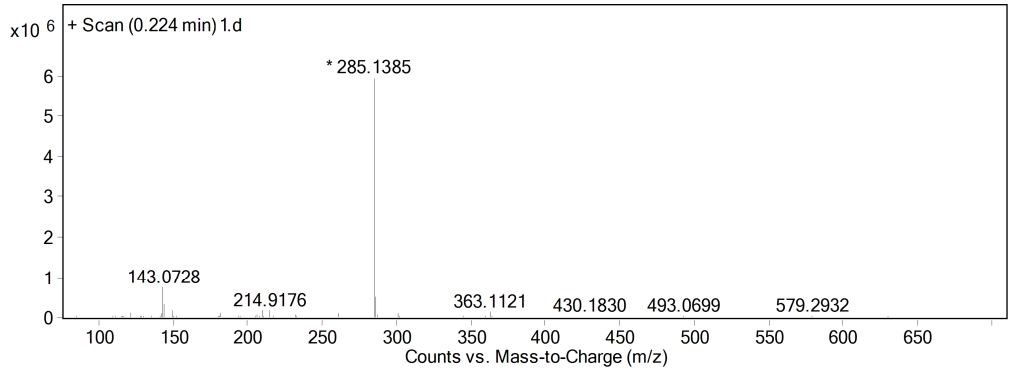


Figure S5. The ^{13}C-CPMAS NMR spectra of **1** and **1a**.

(a)



(b)

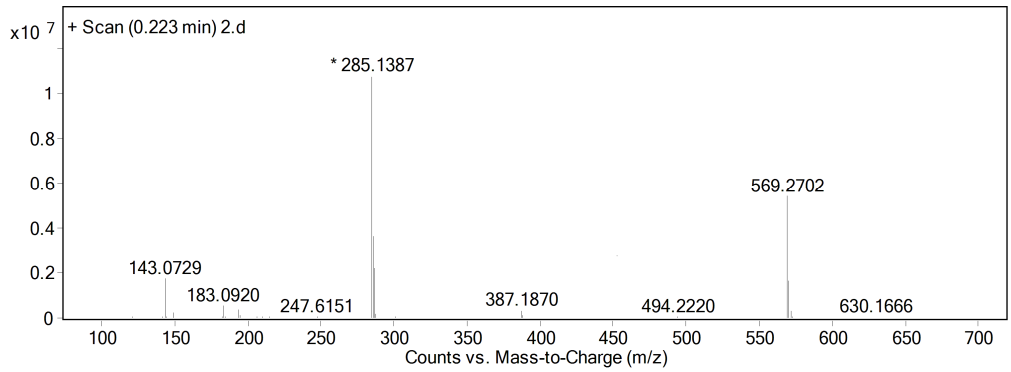
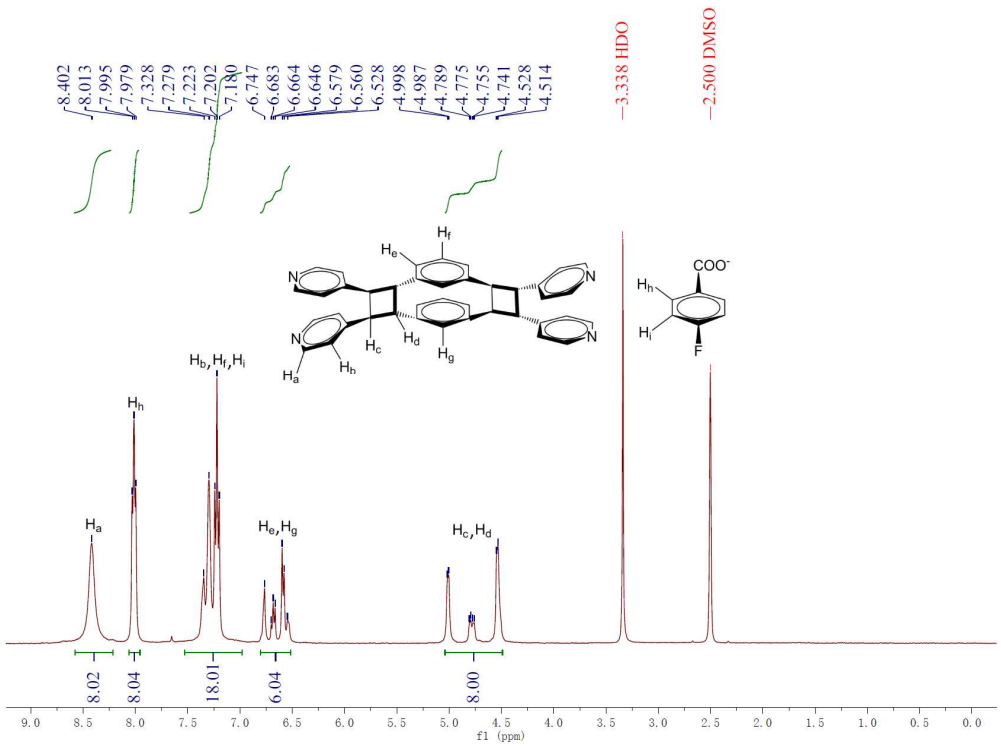


Figure S6. HRMS Spectra of **1,3-bpeb** (a) and ***syn*-tpmcp** (b).

(a)



(b)

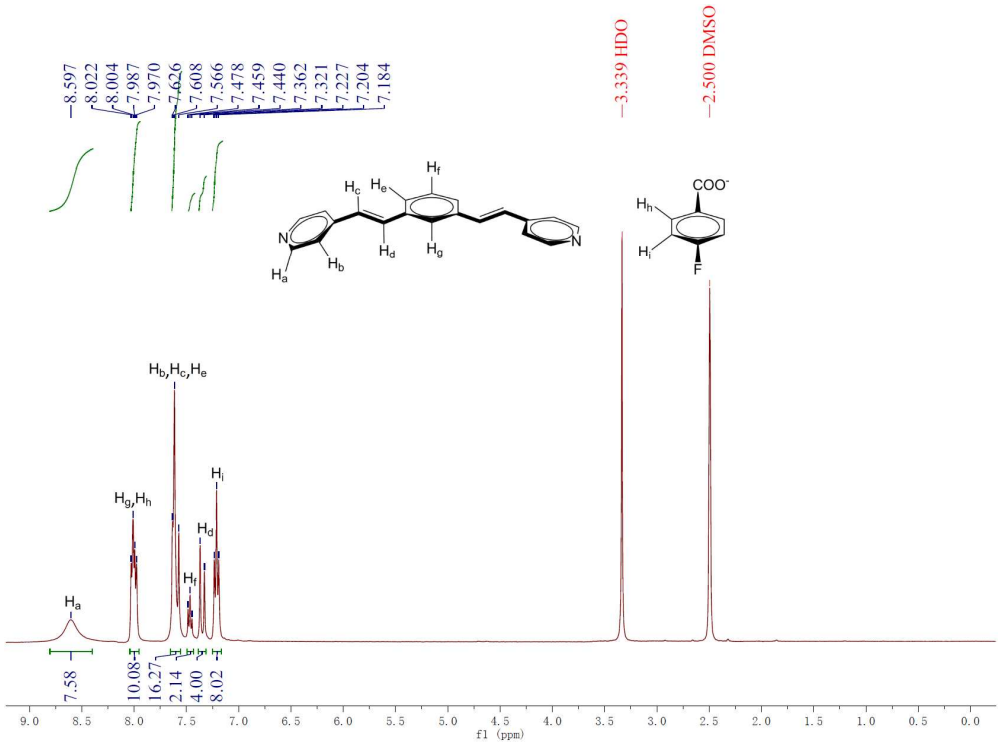


Figure S7. The ^{1}H NMR spectra of tiny particles of **3** with irradiation of 365 nm UV light for 2 min (a), and re-irradiation of 254 nm UV light for 2 min (b) (deuterated solvent: d_6-DMSO).