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Electronic Supplementary Information

Controlled Formation of Chiral Networks and their Reversible Chiroptical Switching Behavior by UV/Microwave Irradiation

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Experimental

General methods

Ligands bpa and other metal salts were obtained commercially and used without further purification. The ligand 1,4-bis((E)-2-(pyridin -4-yl)vinyl)benzene (**L^2**) was prepared as reported previously.[1] Elemental analyses (C, H, and N) were performed using a PE 2400 II elemental analyzer. The FT-IR spectra were recorded with a Nicolet Mana-IR 550 spectrometer in dry KBr disks in the 400-4000 cm^{-1} range. The thermogravimetric analyses (TGA) were performed using a Mettler TGA/SDTA 851 thermal analyzer under an N_2 atmosphere with a heating rate of 10 ºC/min in the temperature region of 20-800 ºC. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 advance diffractometer using graphite monochromatized Cu Kα radiation (λ = 1.5406Å). The^{1}H NMR spectra were recorded at ambient temperature on a Varian UNITYplus-400 spectrometer. The ^{1}H NMR chemical shifts were referenced to the solvent signal in DMSO-d_6 or $CDCl_3$. The UV irradiation experiments were conducted with a high-pressure mercury lamp and a radiation with λ = 365nm.Solid state CD spectra were recorded with a JASCO J-810 spectropolarimeter. For the solid state CD spectra, and crystalline samples were ground to fine powders with potassium bromide and compressed into transparent disks and the concentration of each sample was 1.0 mg/200 mg KBr.

References

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Synthesis

{[Cd(L^1)(L^2)]$_2$}$_n$ (1). **Spontaneous**: To a thick Pyrex tube was loaded $CdSO_4$ (25 mg, 0.12 mmol), (E)-4,4'-(ethene-1,2-diyl)dibenzoic acid (**L^1**) (9.8 mg, 0.036 mmol), 1,4-bis((E)-2-(pyridin -4-yl)vinyl)benzene (**L^2**) (9 mg, 0.0317 mmol), 2 mL of DMF and H_2O (v/v = 4:6), and one drop of triethylamine. The tube was sealed and then heated at 145^{o}C for 48h. After it was cooled to room temperature at a rate of 5 ^{o}C /h, yellow crystals of **1** (19 mg) were formed, which were collected by filtration, washed with EtOH and Et_2O, and dried in air. Yield: 90% (based on bpeb). IR (KBr disk): 1620(s), 1581(m), 1502(m), 1401(m), 1228(w), 1179(m), 970(m), 880(w), 780(w), 570(m); Elemental analysis calcd. for $C_{36}H_{26}CdN_2O_4$: C, 65.22; H, 3.95; N, 4.23. Found: C, 65.11; H, 3.83; N, 4.19.

Inducing: To a thick Pyrex tube was loaded $CdSO_4$ (25 mg, 0.12 mmol), (E)-4,4'-(ethene-1,2-diyl)dibenzoic acid (**L^1**) (9.8 mg, 0.036 mmol), 1,4-bis((E)-2-(pyridin -4-yl)vinyl)benzene (**L^2**) (9 mg, 0.0317 mmol), 2 mL of DMF and H_2O (v/v = 4:6), (1R,2R) cyclohexane-1,2-diamine or (1S,2S) cyclohexane-1,2-diamine (0.25 mg, 0.0022 mmol, 1.8% w.r.t $CdSO_4$). The tube was sealed and then heated at 145 ^{o}C for 48h. After it was cooled to room temperature at a rate of 5^{o}C/h, yellow crystals of **1** were formed, which were collected by filtration, washed with EtOH and Et_2O, and dried in air.

UV irradiation

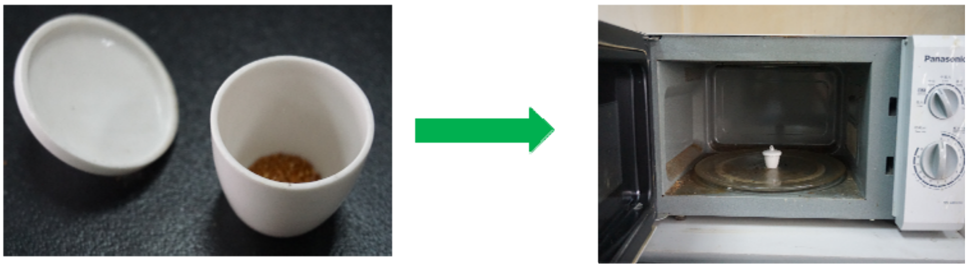
{[Cd(L^1)(L^3)]$_2$}$_n$ (2). Single crystals of **1** (500 mg) in between glass slides were irradiated with a Hg lamp for *ca*. 100 min to form **2** in 100% yield based on **1**. IR (KBr disk): 1620(s), 1581(m), 1502(m), 1401(m), 1228(w), 1179(m), 880(w), 780(w).

Conversion from 2 to 1 via heating

Single crystals of **2** (20 mg) were heating at 200 ^{o}C for 8h and the yellow of the crystals turn dark brown.

Conversion from 2 to 1 via microwave irradiation

As shown below, **s**ingle crystals of **2** (20 mg) in crucible were put into microwave oven (Panasonic NN-GM 331H) and then treated with microwave irradiation (moderate heat) in three time interval (3 min + 3 min + 4 min, 10 min in total, 420 w), yielding dark brown crystals of **1**.



Crucible **Microwave oven**

Microwave-assisted translation from 2 to 1

Isolation of L^{2} and L^{3}. Crystals of **2** or **1** were placed in a 150 mL flask and immersed in concentrated HNO_3 for one day. NaOH was added to adjust the solution to alkalinity before dichloromethanewas added. The organic phase was separated from the reaction mixture and the aqueous layers were also extracted using CH_2Cl_2 (4 × 30 mL). The combined organic extract was concentrated to dryness *in vacuo*. The resulting sample was then washed thoroughly with$H_2O$and dried with anhydrous Na_2SO_4 to give (**L^{2}**) or (**L^{3}**) as a yellow (**L^{2}**) or pale yellow (**L^{3}**) powder which was used for the ^{1}H NMR measurement.

X-ray data collection and structure determination. X-ray single-crystal diffraction data for **1** (**1P** and **1M**) and **2** (**2P** and **2M**) were collected on a Bruker Smart CCD diffractometer by using graphite monochromated Mo-Kα (λ = 0.71073Å). Cell parameters were refined and the data collected and reduced by using the program Apex II. The crystals structures of **1** (**1P** and **1M**) and **2** (**2P** and **2M**) were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the *SHELXL*-97 program.[2] All non-hydrogen atoms were refined anisotropically. All the H atoms were introduced at the calculated position and included in the structure-factor calculations. The atoms (C6 and C7) which belong to the C=C bonds are disordered with two occupancy. The “eadp” constraint was used to make the equal displacement parameters of C6 and C7.

References

2. G. M. Sheldrick, *SHELXS-97*and *SHELXL*-97. Program for the refinement of crystal structures, University of Göttingen, Germany. 1997.

Computational method. All calculations were performed using Gaussian 09, Revision A.02.[3] The geometry optimizations were optimized using B3LYP functional [4] with the triple zeta basis set

6-311++G(d,p).[5] analytical frequencies were calculated to verify the nature of all stationary points as minima.

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4. (a) A. D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648-5652; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.,* **1988**, *37*, 785-789.
5. M. P. Andersson, P. Uvdal, *J. Phys. Chem. A.,* **2005**, *109*, 2937-2941.

Table S1 Summary of crystal data and structure refinement parameters for samples **1M**, **1P**, **2M**, **2P**, **2M→1M**, and **2P→1P**.

	1M(1406667)	**1P(**1406668)	**2M**(1406672)	**2P**(1406670)	**2M→1M(**1406671)	**2P→1P(**1406669)
Emperical formula	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$
Formula weight	662.99	662.99	662.99	662.99	662.99	662.99
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	$P4_12_12$	$P4_32_12$	$P4_12_12$	$P4_32_12$	$P4_12_12$	$P4_32_12$
a/Å	14.5436(2)	14.573(3)	14.3664(7)	14.3555(3)	14.5029(3)	14.5230(2)
b/Å	14.5436(2)	14.573(3)	14.3664(7)	14.3555(3)	14.5029(3)	14.5230(2)
c/Å	29.1864(9)	28.941(11)	29.399(3)	29.4087(14)	29.2053(13)	29.1177(8)
α/°	90	90	90	90	90	90
β/°	90	90	90	90	90	90
γ/°	90	90	90	90	90	90
V/Å^3	6173.4(2)	6146(3)	6067.7(7)	6060.6(3)	6142.9(3)	6141.4(2)
D_c/g cm^{-3}	1.427	1.431	1.447	1.449	1.434	1.434
Z	8	8	8	8	8	8
μ (Mo-Kα)/mm^{-1}	0.749	0.752	0.762	0.763	0.753	0.753
Total reflections	16279	42086	47917	92400	94309	21193
Unique reflections	5445	5387	5336	5333	5420	5420
No. observations	4700	4114	4950	5015	5115	4835
No. parameters	403	403	406	407	395	395
Flack	0.00(3)	0.06(5)	0.03(4)	0.00(4)	0.00(3)	0.01(6)
F(000)	2688	2680	2672	2672	2688	2688
$R_1{}^a$	0.0359	0.0543	0.0402	0.0355	0.0324	0.0543
$wR_2{}^b$	0.0733	0.1276	0.1039	0.0907	0.0827	0.1264
GOF^c	1.042	1.106	1.084	1.018	1.095	1.149

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b\mathrm{w}R_2 = \{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$. ^{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.

Table S2 Summary of crystal data and structure refinement parameters for the six samples obtained in the presence of enantiopure (1*R*,2*R*) cyclohexane-1,2-diamine.

	(1406673)	**(1414979)**	**(1406674)**	**(1406675)**	**(1406676)**	**(1406677)**
Empericalformula	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$
Formula weight	662.99	662.99	662.99	662.99	662.99	662.99
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	$P4_32_12$	$P4_32_12$	$P4_32_12$	$P4_32_12$	$P4_32_12$	$P4_32_12$
a/Å	14.5318(4)	14.5294(3)	14.5128(14)	14.4791(5)	14.4739(3)	14.4958(3)
b/Å	14.5318(4)	14.5294(3)	14.5128(14)	14.4791(5)	14.4739(3)	14.4958(3)
c/Å	29.1429(15)	29.1842(16)	29.194(4)	29.069(2)	29.0695(12)	29.0361(15)
α/°	90	90	90	90	90	90
β/°	90	90	90	90	90	90
γ/°	90	90	90	90	90	90
V/Å^3	6154.2(4)	6160.9(4)	6149.0(12)	6094.2(5)	6089.9(3)	6101.3(4)
D_c/g cm^{-3}	1.431	1.430	1.432	1.445	1.446	1.444
Z	8	8	8	8	8	8
μ (Mo-Kα)/mm^{-1}	0.751	0.750	0.752	0.759	0.759	0.758
Total reflections	44194	44250	85258	39120	48397	27150
Unique reflections	5430	5435	5421	5376	5332	5384
No. observations	4839	4663	5041	4688	4641	4445
No. parameters	395	425	395	395	395	395
F(000)	2688	2688	2688	2688	2688	2688
Flack	0.02(4)	0.03(11)	-0.03(4)	0.01(4)	0.02(6)	0.08(10)
R_1[a]	0.0366	0.0956	0.0394	0.0402	0.0543	0.0933
wR_2[b]	0.0879	0.2303	0.1045	0.0950	0.1354	0.2252
GOF[c]	1.061	1.071	1.106	1.072	1.098	1.207

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [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.

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Table S3 Summary of crystal data and structure refinement parameters for the six samples obtained in the presence of enantiopure (1*S*,2*S*) cyclohexane-1,2-diamine.

	(1414980)	(1414981)	(1414982)	(1414983)	(1414984)	(1414985)
Emperical formula	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$
Formula weight	662.99	662.99	662.99	662.99	662.99	662.99
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	$P4_12_12$	$P4_12_12$	$P4_12_12$	$P4_12_12$	$P4_12_12$	$P4_12_12$
a/Å	14.4838(3)	14.4458(4)	14.4171(3)	14.5097(3)	14.5222(9)	14.5387(16)
b/Å	14.4838(3)	14.4458(4)	14.4171(3)	14.5097(3)	14.5222(9)	14.5387(16)
c/Å	29.2182(11)	29.3447(13)	29.1929(14)	28.8452(14)	29.245(3)	29.246(6)
α/°	90	90	90	90	90	90
β/°	90	90	90	90	90	90
γ/°	90	90	90	90	90	90
V/Å^3	6129.4(3)	6123.7(4)	6067.8(3)	6072.8(3)	6167.6(8)	6181.8(16)
D_c/g cm^{-3}	1.437	1.438	1.451	1.450	1.428	1.425
Z	8	8	8	8	8	8
μ (Mo-Kα)/mm^{-1}	0.754	6.051	0.762	0.761	0.750	0.748
Total reflections	19423	13673	24957	29129	55563	37936
Unique reflections	5406	6004	5349	5351	7507	5372
No. observations	4182	2801	4011	4412	4351	3453
No. parameters	395	395	395	400	388	407
F(000)	2688	2688	2688	2688	2688	2688
Flack	0.03(7)	-0.022(17)	0.04(7)	0.05(6)	0.08(6)	-0.01(9)
$R_1{}^a$	0.0694	0.0690	0.0689	0.0649	0.0771	0.0913
$wR_2{}^b$	0.1740	0.1765	0.1653	0.1590	0.1865	0.2052
GOF^c	1.094	1.026	1.057	1.035	1.082	1.153

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^b\mathrm{w}R_2 = \{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. ^{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.

Table S4 Summary of crystal data and structure refinement parameters for the ten randomly-taken crystals of **1** obtained in the absence of cyclohexane-1,2-diamine (to be continued).

	1(1424577)	**2**(1424578)	**3**(1424579)	**4**(1424580)	**5**(1424581)	**6**(1424582)
Empericalformula	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$
Formula weight	662.99	662.99	662.99	662.99	662.99	662.99
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	$P4_32_12$	$P4_32_12$	$P4_12_12$	$P4_32_12$	$P4_12_12$	$P4_12_12$
a/Å	14.5486(2)	14.4860(8)	14.4896(3)	14.4789(4)	14.5067(3)	14.4975(2)
b/Å	14.5486(2)	14.4860(8)	14.4896(3)	14.4789(4)	14.5067(3)	14.4975(2)
c/Å	29.1966(11)	28.911(3)	29.1167(10)	29.007(2)	28.8880(16)	29.1189(11)
α/°	90	90	90	90	90	90
β/°	90	90	90	90	90	90
γ/°	90	90	90	90	90	90
V/Å^3	6179.8(3)	6066.8(8)	6113.0(3)	6080.9(5)	6079.3(4)	6120.1(3)
D_c/g cm^{-3}	1.425	1.452	1.441	1.448	1.449	1.439
Z	8	8	8	8	8	8
μ (Mo-Kα)/mm^{-1}	0.748	0.762	0.756	0.760	0.761	0.755
Total reflections	23775	10408	13575	24969	17458	16218
Unique reflections	5453	5252	5388	5358	5338	5267
No. observations	4829	3129	4226	4082	3803	4264
No. parameters	406	394	394	394	400	394
F(000)	2688	2688	2688	2688	2688	2688
Flack	0.05(8)	-0.01(8)	-0.05(8)	0.11(7)	0.07(9)	0.00(8)
$R_1{}^a$	0.0862	0.0746	0.0780	0.0682	0.0824	0.0791
$wR_2{}^b$	0.1943	0.1821	0.1939	0.1664	0.2165	0.1967
GOF^c	1.142	1.018	1.102	1.108	1.069	1.100

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^b\mathrm{w}R_2 = \{\Sigma w(F_o{}^2-F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$. ^{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.

Table S4 Summary of crystal data and structure refinement parameters for the ten randomly-taken crystals of **1** obtained in the absence of cyclohexane-1,2-diamine.

	7(1429404)	**8**(1424583)	**9**(1424584)	**10**(1424585)
Empericalformula	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$	$C_{36}H_{26}CdN_2O_4$
Formula weight	662.99	662.99	662.99	662.99
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	$P4_12_12$	$P4_32_12$	$P4_12_12$	$P4_32_12$
a/Å	14.4906(3)	14.5803(4)	14.5474(2)	14.5616(3)
b/Å	14.4906(3)	14.5803(4)	14.5474(2)	14.5616(3)
c/Å	29.1148(11)	29.181(2)	29.2215(9)	29.1530(8)
α/°	90	90	90	90
β/°	90	90	90	90
γ/°	90	90	90	90
V/Å^3	6113.5(3)	6203.3(5)	6184.1(2)	6181.6(2)
D_c/g cm^{-3}	1.438	1.420	1.424	1.425
Z	8	8	8	8
μ (Mo-Kα)/mm^{-1}	0.756	0.745	0.748	0.748
Total reflections	13777	18752	20134	21429
Unique reflections	5395	5451	5454	5450
No. observations	3995	4500	4798	4810
No. parameters	394	394	406	394
F(000)	2688	2688	2688	2688
Flack	0.03(8)	-0.01(4)	0.02(5)	0.12(10)
$R_1{}^a$	0.0792	0.0465	0.0500	0.0983
$wR_2{}^b$	0.1930	0.0965	0.1156	0.2214
GOF^c	1.094	1.067	1.097	1.154

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. ^{b}w$R_2 = \{\Sigma w(F_o{}^2-F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$. ^{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.

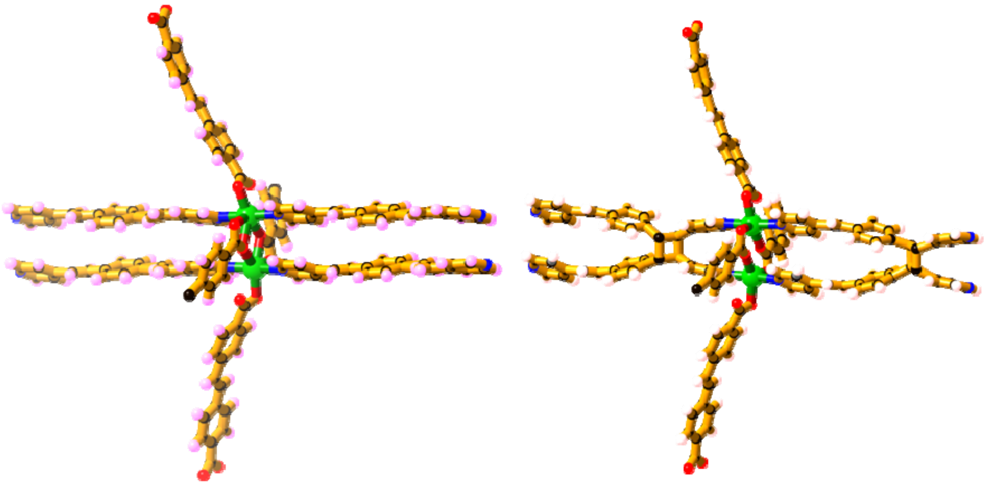


Fig. S1 View of the coordination environments of Zn(II) centers in **1P** (left) or **2P** (right).

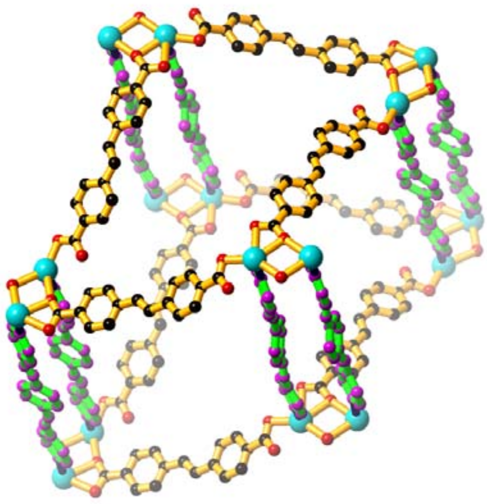


Fig. S2 View of the structure of [Cd_{16}(**L**^{1})$_8$(**L**^{2})$_8$].

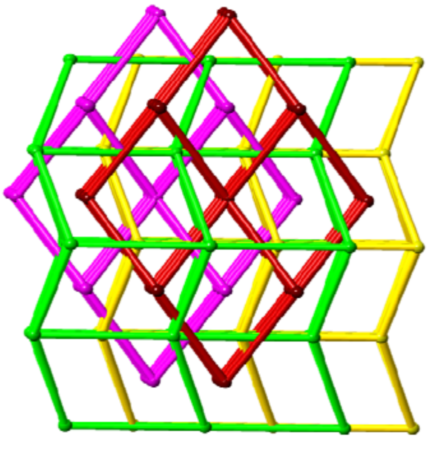


Fig. S3 Schematic representation of the 4-fold interpenetrating network.

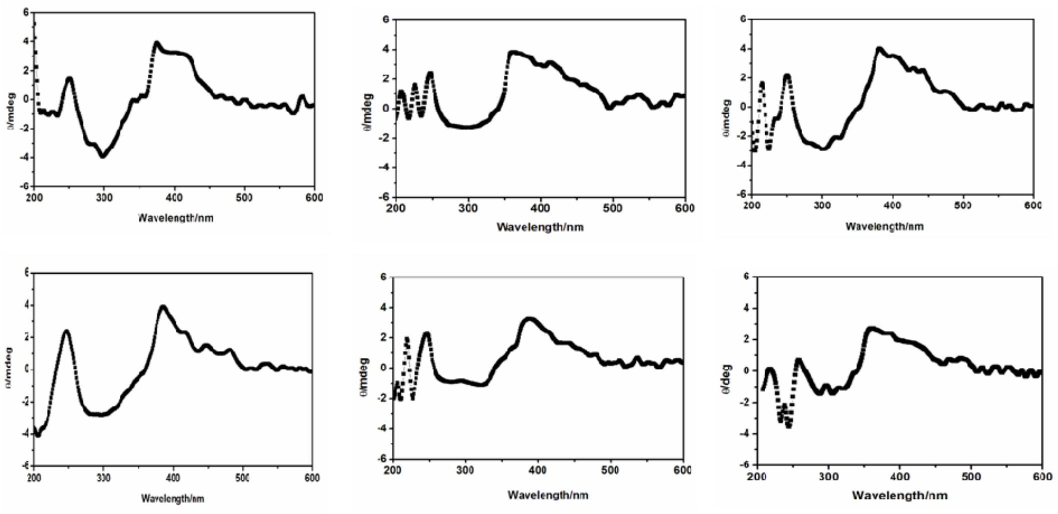


Fig. S4 Solid state CD spectra recorded for six crystals of **1** obtained in the presence of (1*S*,2*S*) cyclohexane-1,2-diamine.

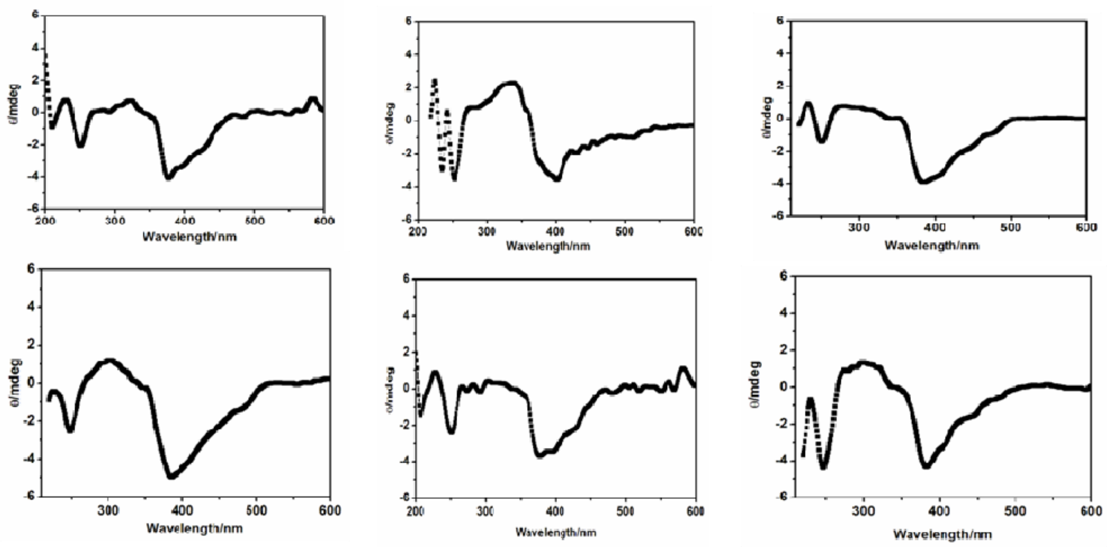


Fig. S5 Solid state CD spectra recorded for six crystals of **1** obtained in the presence of (R,R) cyclohexane-1,2-diamine.

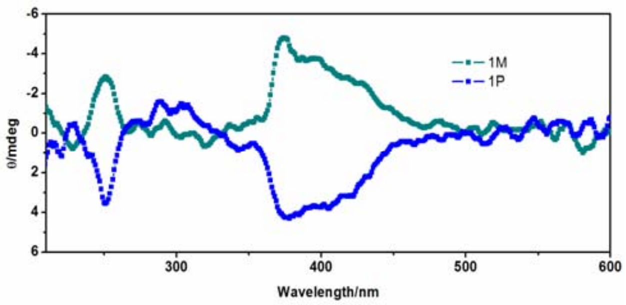


Fig. S6 CD spectra of the bulk samples of crystals in the presence of enantiopure cyclohexane-1,2-diamine.

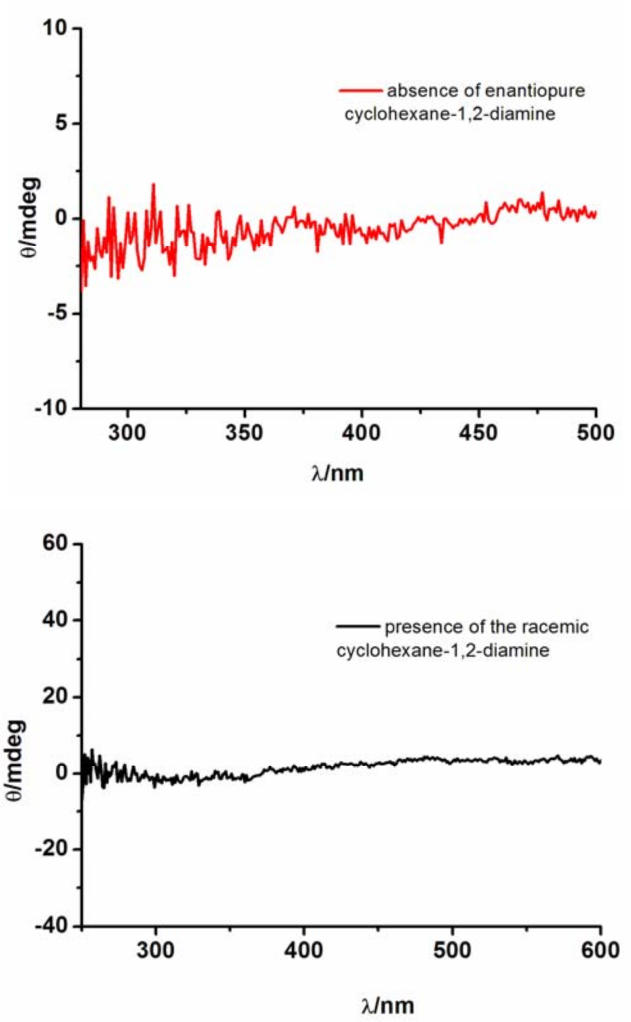


Fig. S7 CD spectra from the bulk samples in the absence of enantiopure cyclohexane-1,2-diamineor in the presence of the racemic cyclohexane-1,2-diamine.

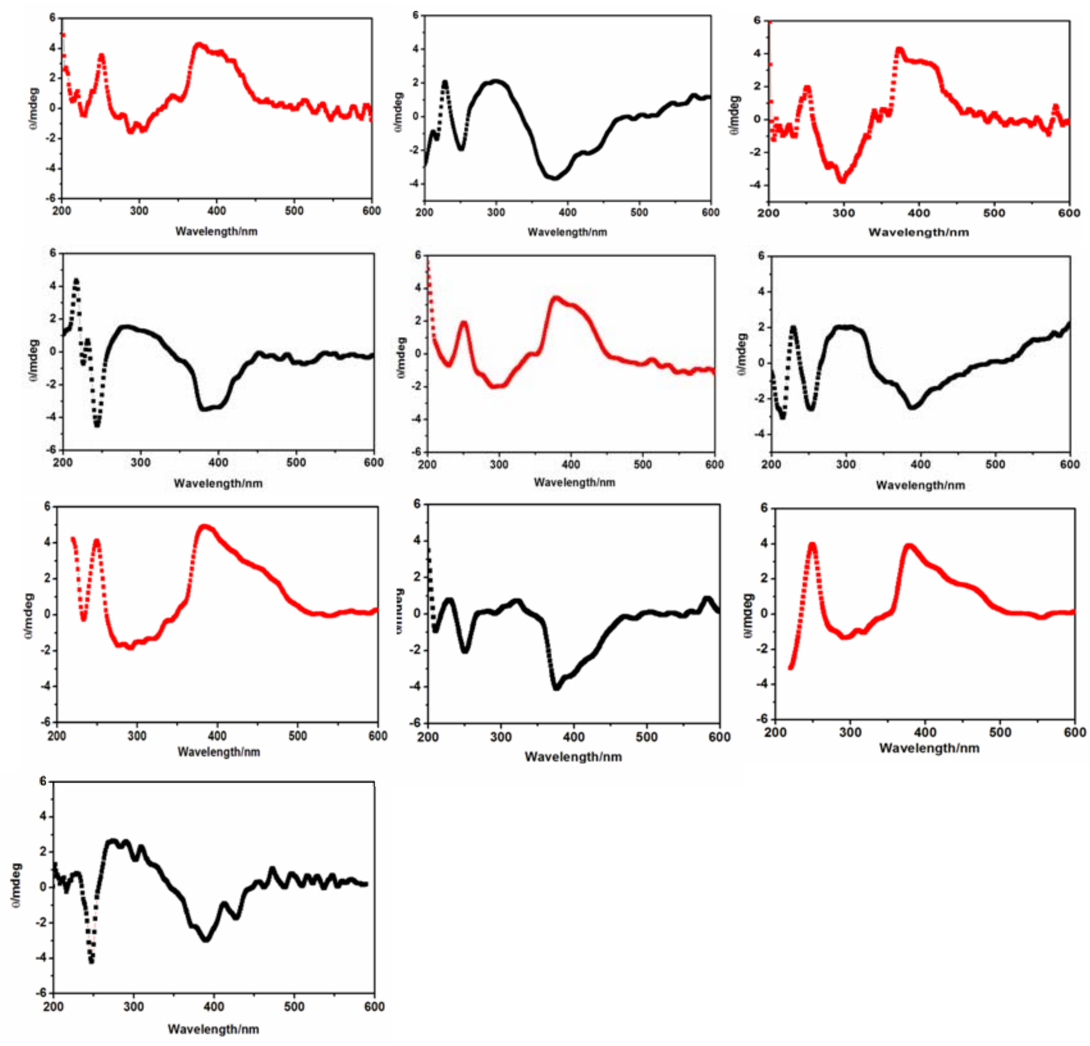
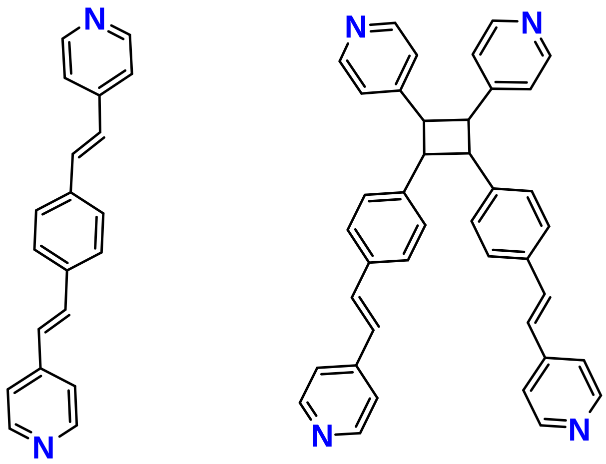


Fig. S8 Solid state CD spectra recorded for the six randomly-taken crystals of **1** obtained in the absence of cyclohexane-1,2-diamine.



$\mathbf{L^2}$ $\mathbf{L^3}$

Scheme S3 Conformations of $\mathbf{L}^2$ and $\mathbf{L}^3$ ligands.

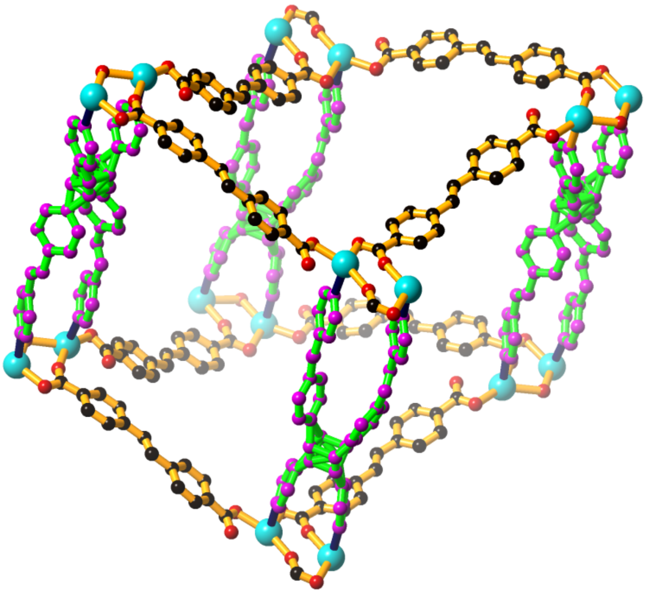


Fig. S9 View of the structure of [Cd$_{16}$(**L**^{1})$_8$(**L**^{3})$_4$].

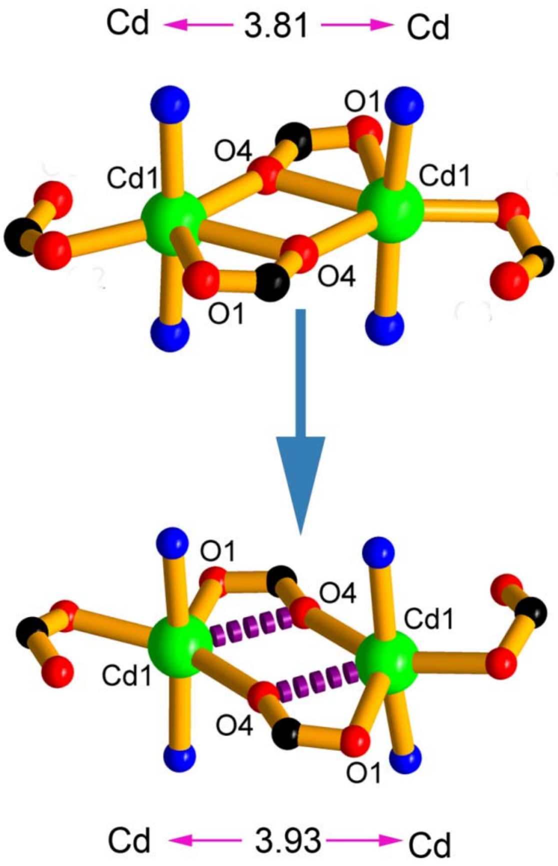


Fig. S10 The Cd···Cd distances before and after the UV irradiation (bottom showing the irradiated one).

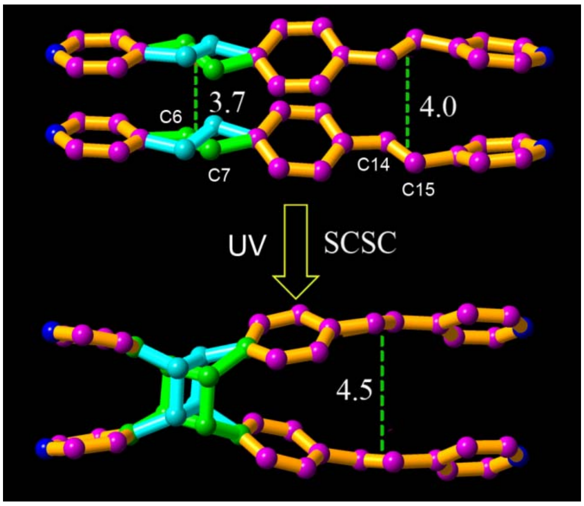


Fig. S11 Single crystal structure showing different distances (3.7 and 4.0 Å) between the olefinic bonds C6=C7 and C14=C15 before cycloaddition reaction. The pair (C6, C7) was disordered into two parallel C=C pairs and a disordered single cyclobutane ring is formed under UV irradiation.

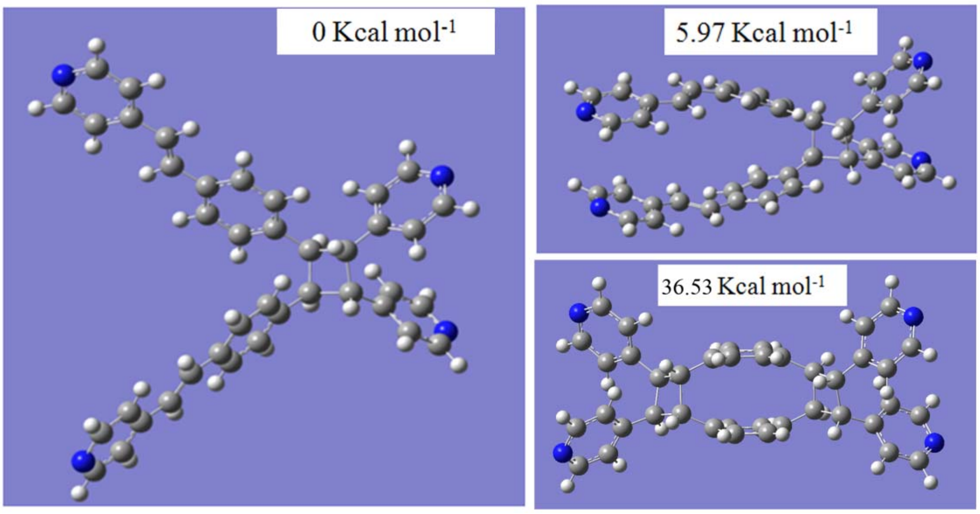
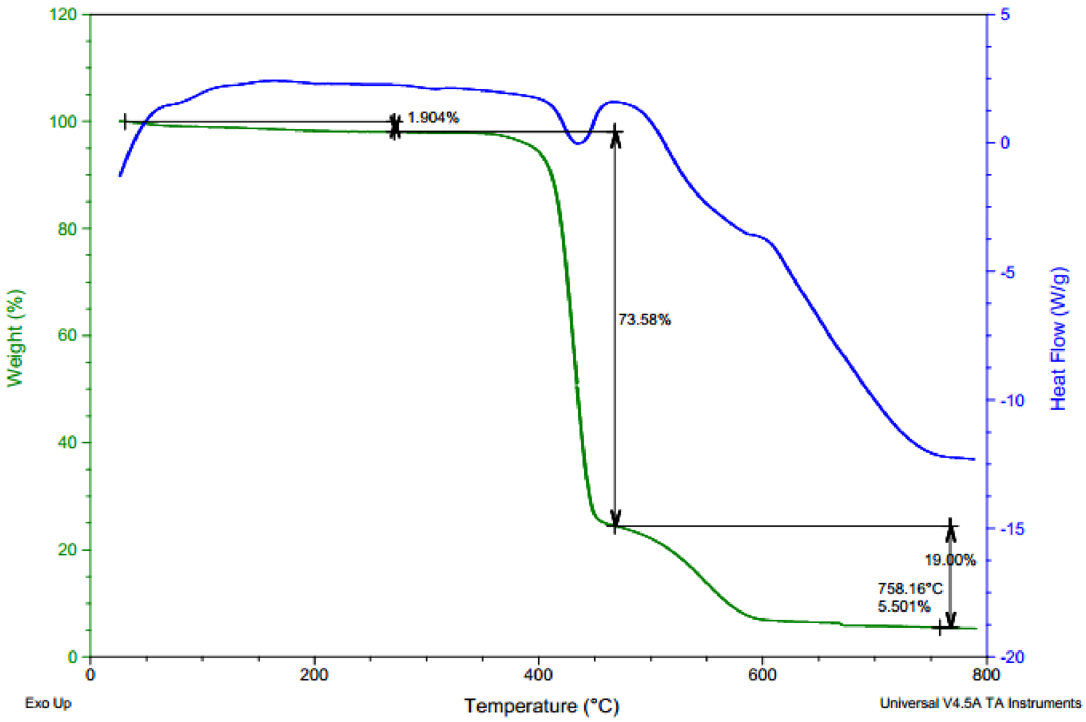


Fig. S12 Structural models of two possible photoproducts of **L^2**. The relative free energies (at 298.15K) compared to that product **a** are listed in insets. For simplicity, the Cd atoms and other auxiliary fragments in the X-ray crystal structures were not taken into consideration.



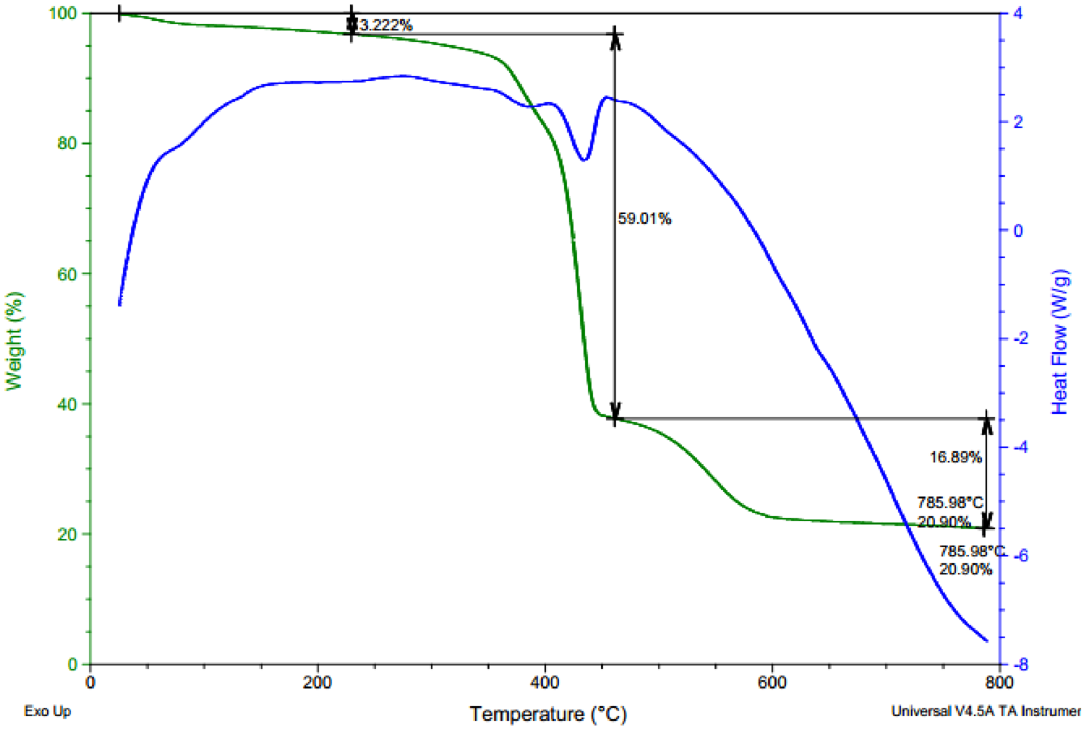


Fig. S13 The TG curves of **1** (upper) and **2** (down).

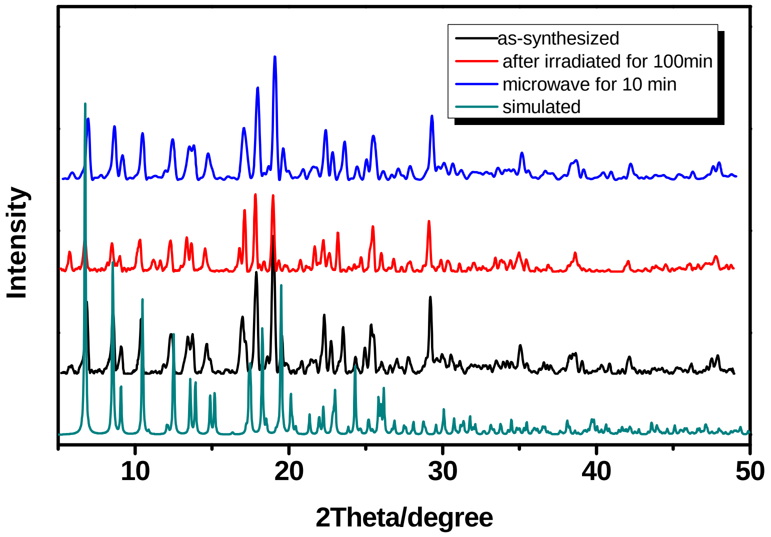


Fig. S14 Experimental and simulated PXRD patterns for **1**, **2** and **2** under microwave irradiation for 10min.

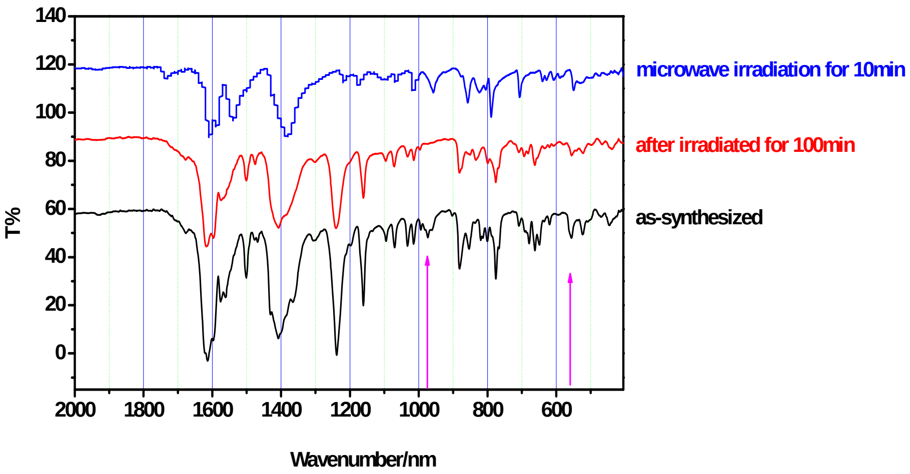


Fig. S15 The IR spectra of the samples **1**, **2**, and **2** under microwave irradiation for 10min.

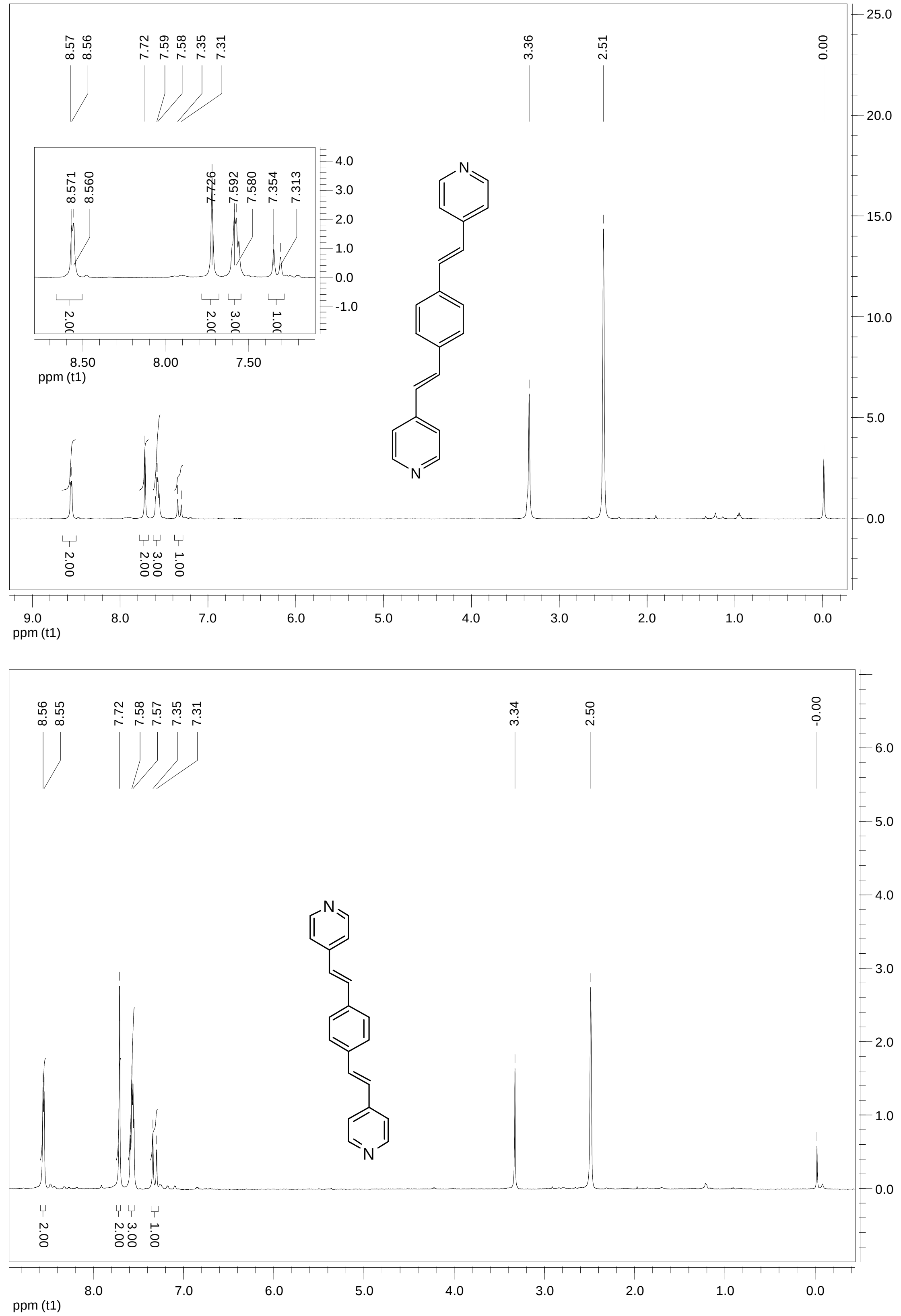


Fig. S16 The ^{1}H NMR spectra of the starting material $\mathbf{L^2}$ (up) and the ligand (down) extracted from **2** under microwave irradiation for 10 min (d_6-DMSO).

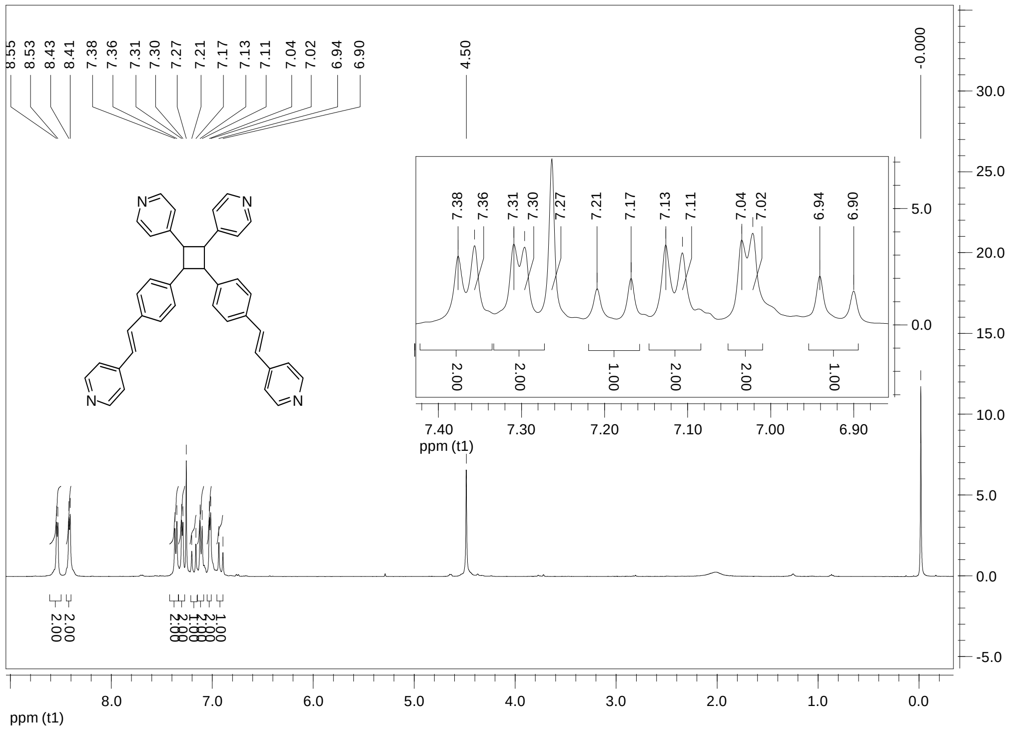
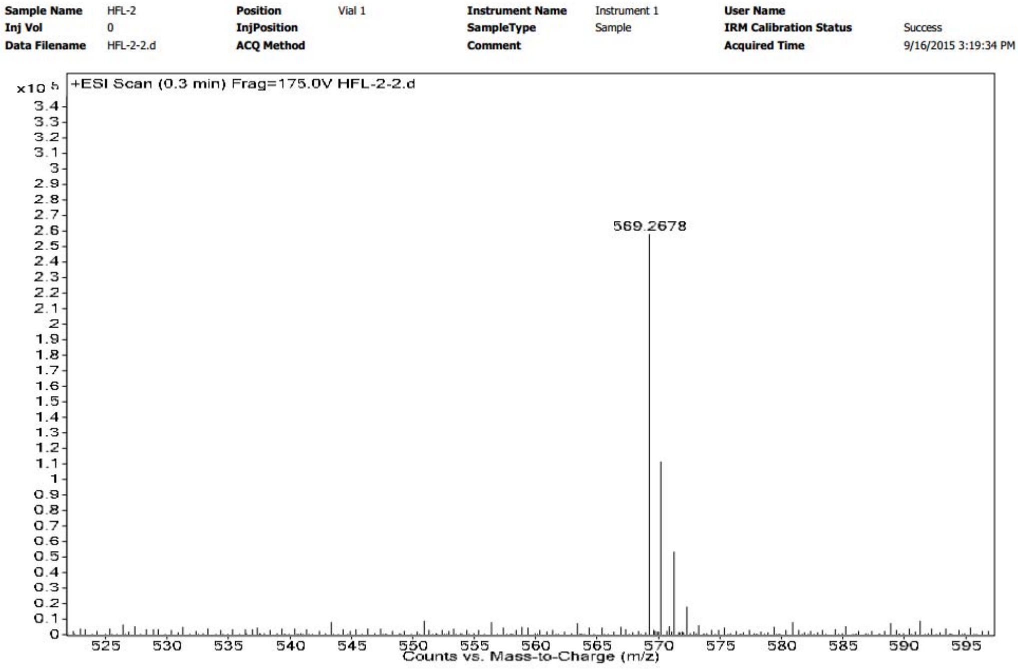


Fig. S17 The ^{1}H NMR spectrum of **L^3** extracted from **2** ($CDCl_3$).



Sample Name	HFL-2	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	HFL-2-2.d	**ACQ Method**		**Comment**		**Acquired Time**	9/16/2015 3:19:34 PM

Fig. S18 The positive-ion ESI mass spectrum of **L^3** in acetonitrile.

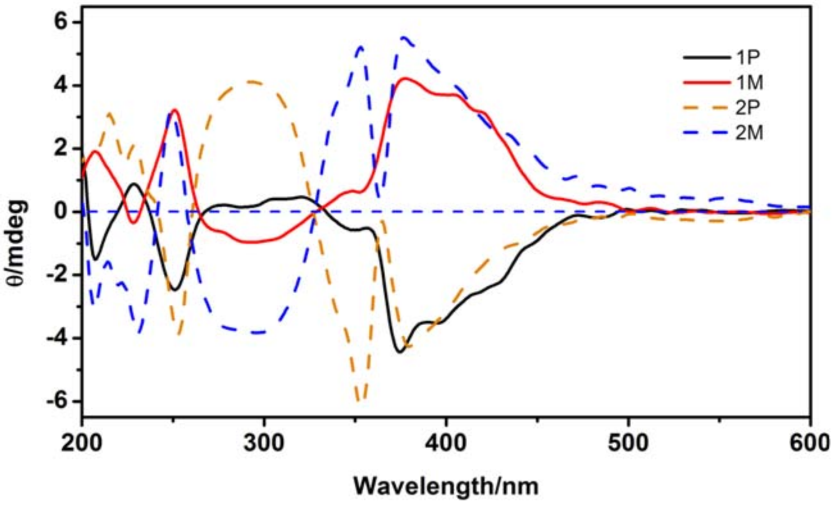


Fig. S19 The CD spectra for **1P**/**1M** and **2P**/**2M**.