Supporting Information

Light-driven structural transformations in isotypical Cd(II) complexes: stereoselectivity and photosalient motion

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Experimental section

Materials and physical method

All chemicals purchased were reagent grade and were used without further purification. Elemental analysis (carbon, hydrogen and nitrogen) was performed on a Perkin–Elmer 240C elemental analyzer. Infrared spectrum in KBr (4000–500 cm⁻¹) was recorded using a Perkin–Elmer FT-IR spectrum RX1 spectrometer. ¹H NMR spectra were recorded on a 400 MHz Bruker Avance 400 FT NMR spectrometer with TMS as an internal reference in DMSO- d_6 solution. CARL ZEISS UHR Field Emission Scanning Electron Microscope (FESEM) was used for SEM images. Photodimerization reaction was carried out using Luzchem photoreactor (8 W UVA lamps) at ~350 nm at room temperature. Crystalline ground powder was packed between the glass slides and irradiated under UV light. Glass slides were flipped at regular intervals of time to maintain uniform exposure of UV radiation. Leica DM2700M fluorescence microscope attached with high-resolution camera is used to observe the photomechanical motion of single crystals.

Syntheses of Compounds

Synthesis of 1: A solution of 4-nvp ligands (0.046 g, 0.2 mmol) in MeOH (2 ml) was slowly and carefully layered to Cd(NO₃)₂·4H₂O (0.061 g, 0.2 mmol), in H₂O (2 ml) using 2 ml 1:1 (= v/v) buffer solution of MeOH and H₂O. Afterward, a solution of Hbz (0.024 g, 0.2 mmol) neutralized with Et₃N (0.021 g, 0.2 mmol) in 2 mL EtOH was layered upon it. After few days, light yellow colored needle-shaped crystals of $[Cd(bz)_2(4-nvp)_2]$ (1) were obtained (0.09 g, yield 60%). Elemental analysis (%) calcd for C₉₆H₇₂Cd₂N₄O₈: C, 70.55; H, 4.44; N, 3.43; found: C, 70.2; H, 4.46; N, 3.2. IR (KBr pellet, cm-1): 1538 v_{as} (COO⁻), 1396 v_{sys} (COO⁻). IR (KBr pellet, cm-1): 1538

Synthesis of 1': The complex **1'** was synthesized by UV irradiation of **1**. Yellow colored needle single crystals of **1** were irradiated using a UV-lamp (LZC-UVA; Luzchem) centred at ~350 nm wavelength for 30 min to obtain photodimerized product in almost quantitative yield.

Synthesis of 2 and 3: Complexes 2 and 3 were prepared concomitantly in similar way as complex 1 by replacing H-4clbz (0.031 g, 0.2 mmol) with Hbz and 2 ml buffer solution of MeOH and H₂O. After few days, the crystals of two complexes separated visually as block shaped crystals of $[Cd(4-clbz)_2(4-nvp)_2]$ (2) and needle shaped crystals of $[Cd(4-clbz)_2(4-nvp)_2]$ (3) (0.13 g, total yield 75%). Elemental analysis (%) calcd for complex 2: C₉₆H₆₈Cd₂Cl₄N₄O₈: C, 65.06; H, 3.87; N, 3.16; found: C, 65.03; H, 3.7; N, 3.18. IR (KBr pellet, cm⁻¹): 1589 v_{as} (COO⁻), 1401 v_{sys} (COO⁻) and for 3: C, 65.06; H, 3.87; N, 3.16; found: C, 65.04; H, 3.9; N, 3.02. IR (KBr pellet, cm⁻¹): 1588 v_{as} (COO⁻), 1398 v_{sys} (COO⁻).

Synthesis of 2': The complex **2'** was synthesized by UV irradiation of **2**. Yellow colored block shape single crystals of **2** were irradiated using a UV-lamp (LZC-UVA; Luzchem) centered at ~350nm wavelength for 30min to obtain photodimerized product in almost quantitative yield.

Synthesis of 3': The complex **3'** was synthesized by UV irradiation of **3**. Yellow colored needle single crystals of **3** were irradiated using a UV-lamp (LZC-UVA; Luzchem) centered at ~350nm wavelength for 30 min to obtain photodimerized product in almost quantitative yield.

Synthesis of 4 and 5: Complex 4 and 5 were prepared concomitantly in similar way as complex 1 by replacing H-4brbz (0.042 g, 0.2 mmol) with Hbz and 2 mL buffer solution of MeOH and H₂O. After few days, the two compounds separated visually as block shaped crystals of $[Cd(4-brbz)_2(4-nvp)_2]$ (4) and needle shaped crystals of $[Cd(4-brbz)_2(4-nvp)_2]$ (5) (0.15 g, total yield 80%). Elemental analysis (%) calcd for complex 4: C₉₆H₆₈Br₄Cd₂N₄O₈: C, 65.06; H, 3.87; N, 3.16; found: C, 65.04; H, 3.75; N, 3.21. IR (KBr pellet, cm⁻¹): 1538 v_{as} (COO⁻), 1399 v_{sys} (COO⁻) and for 5: C₉₆H₆₈Br₄Cd₂N₄O₈: C, 65.06; H, 3.87; N, 3.6; N, 3.04. IR (KBr pellet, cm⁻¹): 1585 v_{as} (COO⁻).

Synthesis of 4': The complex **4'** was synthesized by UV irradiation of **4**. Yellow colored block shape single crystals of **4** were irradiated using a UV-lamp (LZC-UVA; Luzchem) centered at ~350 nm wavelength for 30 min to obtain photodimerized product in almost quantitative yield.

Synthesis of 5': The complex **5'** was synthesized by UV irradiation of **5**. Yellow colored needle single crystals of **5** were irradiated using a UV-lamp (LZC-UVA; Luzchem) centered at ~350 nm wavelength for 30 min to obtain photodimerized product in almost quantitative yield.

General X-ray Crystallography

Single crystals of the all the compounds having suitable dimension were used for data collection using a Kappa Four Circle diffractometer equipped with graphite-monochromated MoK_a radiation ($\lambda = 0.71073$ Å). The crystal structure was solved using the SHELXT 2018/6 structure solution program.^{S1} Least squares refinements of all reflections within the hkl range $-12 \le h \le 12, -17 \le k \le 17, -21 \le l \le 21$ for 1; $-15 \le h \le 15, -16 \le k \le 16, -21 \le l \le 21$ for 2; $-13 \le h \le 13, -17 \le k \le 17, -20 \le l \le 20$ for 3; $-15 \le h \le 15, -16 \le k \le 16, -21 \le l \le 21$ for 4; $-14 \le h \le 14, -19 \le k \le 19, -22 \le l \le 22$ for 5; $-12 \le h \le 12, -17 \le k \le 17, -21 \le l \le 21$ for 1'; $-12 \le h \le 12, -17 \le k \le 17, -19 \le l \le 19$ for 3' and $-13 \le h \le 13, -17 \le k \le 17, -20 \le l \le 20$ for 5' were used to figure out the unit cell parameters and crystal-orientation matrices. The collected data ($I > 2\sigma(I)$) was integrated by using SAINT^{S2} program, and the absorption correction was done by SADABS.^{S3} Non-hydrogen atoms were refined by the help of anisotropic displacement parameters. All the hydrogen atoms were placed in their geometrically perfect positions and constrained to ride on their parent atoms. Crystallographic data for all compounds are summarized in Table S1-S2 (ESI[†]) and selected bond lengths and bond angles are given in Table S3–S6 (ESI[†]).

Formula	$ \begin{array}{ c c c c c } C_{96}H_{72}Cd_2N_4 \\ O_8 \end{array} $	$\begin{array}{c} C_{96}H_{68}Cd_{2}Cl_{4}N_{4}\\ O_{8} \end{array}$	C ₄₈ H ₃₄ CdCl ₂ N 2 O ₄	$\begin{array}{ c c }\hline C_{96}H_{68}Br_4Cd_2\\ N_4O_8\end{array}$	$\begin{array}{c c} C_{48}H_{34}Br_2Cd\\ N_2 \ O_4 \end{array}$
	(1)	(2)	(3)	(4)	(5)
Fwt	1634.37	1772.14	886.07	1949.98	974.99
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
space group	ΡĪ	рĪ	PĪ	Pl	PĪ
<i>a</i> (Å)	9.4671	11.1501	10.0272	11.1738	9.9999
<i>b</i> (Å)	13.1364	11.4178	13.3466	11.5824	13.5052
<i>c</i> (Å)	15.9602	15.5836	15.3424	15.6194	15.3052
α (deg)	75.787	104.359	82.544	105.000	81.589
β (deg)	89.627	97.790	79.682	97.655	80.261
γ (deg)	75.979	93.708	86.948	93.633	86.058
$V(Å^3)$	1863.8	1894.22	2002.1	1925.0	2013.2
Ζ	1	1	2	1	2
Temp (K)	120	120	127	120	100
$D_{\rm calcd}$ (g/cm ³)	1.456	1.554	1.47	1.682	1.608
μ (mm ⁻¹)	0.636	0.768	0.727	2.693	2.575
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
GOF on F^2	1.054	1.047	1.026	1.043	1.042
final <i>R</i> indices	R1 = 0.0275	R1 = 0.0238	R1 = 0.0297	R1 = 0.0242	R1 = 0.0307
$[I > 2\sigma(I)]^{a,b}$	wR2 = 0.0699	wR2 = 0.0602	wR2 = 0.0647	wR2 = 0.0610	wR2 = 0.0680
$-\mathrm{ve} \leq h \leq +\mathrm{ve}$	$-12 \le h \le +12$	$-15 \le h \le +15$	$-12 \le h \le +12$	$-15 \le h \le +15$	$-14 \le h \le +14$
$-\mathrm{ve} \leq k \leq +\mathrm{ve}$	$ -17 \le k \le +17$	$-16 \le k \le +16$	$-16 \le k \le +16$	$ -16 \le k \le +16$	$ -19 \le k \le +19$
$-\mathrm{ve} \leq l \leq +\mathrm{ve}$	$ -21 \le l \le +21$	$-21 \le l \le +21$	-18 ≤ <i>l</i> ≤ +18	$ -21 \le l \le +21$	$ -22 \le l \le +22$

Table S1. Crystal data and refinement parameters of complexes 1-5

 ${}^{a}R1 = \Sigma ||F_{o}| ||\Sigma|F_{o}|, {}^{b}wR2 = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w (F_{o}^{2})^{2}]^{1/2}$

Formula	$C_{96}H_{72}Cd_2N_4O_8$	$C_{48}H_{34}CdCl_2N_2O_4$	$C_{48}H_{34}Br_2CdN_2O_4$
		(3)	(5)
Fw	1634.37	886.07	974.99
Crystsyst	Triclinic	Triclinic	Triclinic
space group	PĪ	Pl	PÌ
<i>a</i> (Å)	9.4813	9.9972	9.9893
<i>b</i> (Å)	12.7868	13.3335	13.4359
<i>c</i> (Å)	16.4751	15.2941	15.3143
a(deg)	108.737	82.257	81.433
β (deg)	90.680	83.648	84.652
γ (deg)	101.439	87.075	86.378
$V(Å^3)$	1847.8	2006.3	2021.1
Ζ	1	2	2
Temp (K)	120	123	125
$D_{\text{calcd}}(\text{g/cm}^3)$	1.469	1.467	1.602
μ (mm ⁻¹)	0.641	0.726	2.565
$\lambda(\text{\AA})$	0.71073	0.71073	0.71073
GOF on F^2	1.091	1.017	1.034
final <i>R</i> indices $[I > 2\sigma(I)]^{a,b}$	R1= 0.0439	R1 = 0.0388	R1 = 0.0396
	wR2 = 0.1050	wR2 = 0.0754	wR2 = 0.0798
$-\mathrm{ve} \leq h \leq +\mathrm{ve}$	$-12 \le h \le +12$	$-12 \le h \le +12$	$-13 \le h \le +13$
$\begin{vmatrix} -\text{ve} \le k \le +\text{ve} \\ -\text{ve} \le l \le +\text{ve} \end{vmatrix}$	$-17 \le k \le +17$ $-21 \le l \le +21$	$-16 \le k \le +16$ $-18 \le l \le +18$	$\begin{vmatrix} -17 \le k \le +17 \\ -20 \le l \le +20 \end{vmatrix}$

Table S2. Crystal data and refinement parameters of complexes 1', 3' and 5'

 ${}^{a}R1 = \Sigma ||F_{o}| \quad |F_{c}|| / \Sigma |F_{o}|, {}^{b}wR2 = [\Sigma w (F_{o}{}^{2} - F_{c}{}^{2})^{2} / \Sigma w (F_{o}{}^{2})^{2}]^{1/2}$

Bond length (Å) of 1		Bond length (Å) of 2		Bond length (Å) of 3		Bond length (Å) of 4		Bond length (Å) of 5	
Cd(1)-O(1)	2.2919(14)	Cd(1)-O(1)	2.3339(11)	Cd(1)-O(1)	2.3154(16)	Cd(1)-O(1)	2.3357(14)	Cd(1)-O(1)	2.3261(14)
Cd(1)-O(3)	2.3787(13)	Cd(1)-O(2)	2.5490(11)	Cd(1)-O(2)	2.6414(16)	Cd(1)-O(2)	2.3716(14)	Cd(1)-O(2)	2.6129(14)
Cd(1)-O(4)	2.3697(13)	Cd(1)-O(3)	2.3871(11)	Cd(1)-O(3)	2.3823(17)	Cd(1)-O(3)	2.5359(13)	Cd(1)-O(3)	2.3899(15)
Cd(1)-N(1)	2.3194(15)	(Cd1)-O(4)	2.3798(11)	Cd(1)-O(4)	2.3983(17)	Cd(1)-O(4)	2.3971(13)	Cd(1)-O(4)	2.4003(14)
Cd(1)-N(2)	2.3069(15)	Cd(1)-N(1)	2.3109(12)	Cd(1)-N(1)	2.2919(19)	Cd(1)-N(1)	2.3134(15)	Cd(1)-N(1)	2.2940(15)
Cd(1)-O(1)_a	2.7246(14)	Cd(1)-N(2)	2.3125(11)	Cd(1)-N(2)	2.3022(19)	Cd(1)-N(2)	2.3144(14)	Cd(1)-N(2)	2.2985(15)
Cd(1)-O(2)_a	2.3041(12)	Cd(1)-O(2)_a	2.3752(10)	Cd(1)-O(2)_b	2.3646(17)	Cd(1)-O(3)_a	2.3827(13)	Cd(1)-O(2)_c	2.3699(14)

 Table S3. Selected bond lengths in complexes 1-5

Table S4. Selected bond angles in complexes 1- 5

Bond angle (°) of	1	Bond angle (°) of	f 2	Bond angle (°) of	3	Bond angle (°) or	f 4	Bond angle (°) of	f 5
O(1)-Cd(1)-O(3)	144.28(5)	O(1)-Cd(1)-O(2)	53.46(3)	O(1)-Cd(1)-O(2)	52.37(6)	O(1)-Cd(1)-O(2)	140.37(5)	O(1)-Cd(1)-O(2)	52.77(4)
O(1)-Cd(01)-O(4)	88.78(5)	O(1)-Cd(1)-O(3)	85.24(4)	O(1)-Cd(1)-O(3)	86.24(6)	O(1)-Cd(1)-O(3)	53.62(4)	O(1)-Cd(1)-O(3)	85.70(5)
O(1)-Cd(01)-N(1)	84.63(5)	O(1)-Cd(1)-O(4)	140.27(4)	O(1)-Cd(1)-O(4)	141.34(6)	O(1)-Cd(1)-O(4)	85.46(5)	O(1)-Cd(1)-O(4)	140.71(5)
O(1)-Cd(01)-N(2)	90.01(5)	O(1)-Cd(1)-N(1)	92.02(4)	O(1)-Cd(1)-N(1)	94.40(6)	O(1)-Cd(1)-N(1)	92.19(5)	N(1)-Cd(1)-O(1)	94.18(5)
O(1)-Cd(01)-O(1)_a	76.96(5)	O(1)-Cd(1)-N(2)	93.63(4)	O(1)-Cd(1)-N(2)	90.59(6)	O(1)-Cd(1)-N(2)	93.43(5)	N(2)-Cd(1)-O(1)	90.90(5)
O(1)-Cd(01)-O(2)_a	127.88(5)	O(1)-Cd(1)-O(2)_a	120.10(4)	O(1)-Cd(1)-O(2)_b	125.84(6)	O(1)-Cd(1)-O(3)_a	129.15(5)	O(1)-Cd(1)-O(2)_c	125.63(5)
O(3)-Cd(01)-O(4)	55.53(4)	O(2)-Cd(1)-O(3)	138.65(4)	O(2)-Cd(1)-O(3)	138.45(5)	O(2)-Cd(1)-O(3)	165.57(4)	O(2)-Cd(1)-O(3)	138.36(5)
O(3)-Cd(01)-N(1)	92.78(5)	O(2)-Cd(1)-O(4)	165.92(4)	O(2)-Cd(1)-O(4)	166.28(6)	O(2)-Cd(1)-O(4)	55.28(4)	O(2)-Cd(1)-O(4)	166.52(4)
O(3)-Cd(01)-N(2)	93.31(5)	O(2)-Cd(1)-N(1)	91.78(4)	O(2)-Cd(1)-N(1)	81.97(6)	O(2)-Cd(1)-N(1)	91.11(5)	O(2)-Cd(1)-N(1)	82.47(5)
O(3)-Cd(01)-O(1)_a	87.62(4)	O(2)-Cd(1)-N(2)	86.86(4)	O(2)-Cd(1)-N(2)	94.70(6)	O(2)-Cd(1)-N(2)	88.44(5)	O(2)-Cd(1)-N(2)	94.17(5)
O(3)-Cd(01)-O(2)_a	137.53(4)	O(2)-Cd(1)-O(2)_a	75.78(3)	O(2)-Cd(1)-O(2)_b	73.95(5)	O(2)-Cd(1)-O(3)_a	90.48(5)	O(2)-Cd(1)-O(2)_c	73.25(4)
O(4)-Cd(01)-N(1)	89.58(5)	O(3)-Cd(1)-O(4)	55.31(4)	O(3)-Cd(1)-O(4)	55.61(6)	O(3)-Cd(1)-O(4)	139.01(4)	O(3)-Cd(1)-O(4)	55.07(5)
O(4)-Cd(01)-N(2)	93.29(5)	O(3)-Cd(1)-N(1)	87.34(4)	O(3)-Cd(1)-N(1)	100.01(6)	O(3)-Cd(1)-N(1)	91.73(5)	O(3)-Cd(1)-N(1)	99.88(5)
O(4)-Cd(01)-O(1)_a	163.41(5)	O(3)-Cd(1)-N(2)	88.68(11)	O(3)-Cd(1)-N(2)	88.46(6)	O(3)-Cd(1)-N(2)	86.72(5)	O(3)-Cd(1)-N(2)	88.65(5)
O(4)- Cd(01)-O(2)_a	143.05(4)	O(3)-Cd(1)-O(2)_a	145.05(4)	O(3)-Cd(1)-O(2)_b	147.57(5)	O(3)-Cd(1)-O(3)_a	75.66(4)	O(3)-Cd(1)-O(2)_c	148.34(5)
N(1)-Cd(01)-N(2)	173.87(5)	O(4)-Cd(1)-N(1)	90.76(4)	O(4)-Cd(1)-N(1)	94.43(6)	O(4)-Cd(1)-N(1)	87.18(5)	O(4)-Cd(1)-N(1)	94.50(5)
N(1)-Cd(01)-O(1)_a	78.98(5)	O(4)-Cd(1)-N(2)	88.67(4)	O(4)-Cd(1)-N(2)	86.72(6)	O(4)-Cd(1)-N(2)	99.33(5)	O(4)-Cd(1)-N(2)	86.68(5)
N(1)-Cd(01)-O(2)_a	89.59(5)	O(4)-Cd(1)-O(2)_a	90.63(4)	O(2)_b-Cd(1)-O(4)	92.53(5)	O(4)-Cd(1)-O(3)_a	144.76(4)	O(4)-Cd(1)-O(2)_c	93.39(5)
N(2)-Cd(01)-O(1)_a	96.92(5)	N(1)-Cd(1)-N(2)	171.80(4)	N(1)-Cd(1)-N(2)	170.42(7)	N(1)-Cd(1)-N(2)	171.71(5)	N(1)-Cd(1)-N(2)	170.36(5)
N(2)-Cd(01)-O(2)_a	91.35(5)	N(1)-Cd(1)-O(2)_a	85.32(4)	O(2)_b-Cd(1)-N(1)	83.66(6)	N(1)-Cd(1)-O(3)_a	85.28(5)	N(1)-Cd(1)-O(2)_c	83.82(5)
O(1)a-Cd(01)-O(2)_a	51.17(4)	N(2)-Cd(1)-O(2)_a	86.51(4)	O(2)_b-Cd(1)-N(2)	86.79(6)	N(2)-Cd(1)-O(3)_a	86.45(5)	N(2)-Cd(1)-O(2)_c	86.56(5)

Bond length (Å) of 1'		Bond length (Å) of 3'		Bond length (Å) of 5'	
Cd(1)-O(2)	2.259(2)	Cd(1)-O(1)	2.340(2)	Cd(01)-O(1)	2.338(2)
Cd(1)-O(3)	2.325(2)	Cd(1)-O(2)	2.574(2)	Cd(01)-O(2)	2.562(2)
Cd(1)-O(4)	2.432(2)	Cd(1)-O(3)	2.373(2)	Cd(01)-O(3)	2.385(2)
Cd(1)-N(1)	2.292(3)	Cd(1)-O(4)	2.389(2)	Cd(01)-O(4)	2.374(2)
Cd(1)-O(1)_d	2.308(3)	Cd(1)-N(1)	2.313(3)	Cd(01)-N(1)	2.309(3)
Cd(1)-N(2)_d	2.330(3)	Cd(1)-N(2)	2.305(3)	Cd(01)-N(2)	2.303(2)
		Cd(1)-O(1)_c	2.352(2)	Cd(01)-O(2)_b	2.354(2)

Table S5. Selected bond lengths in complexes 1', 3 'and 5 '

Table S6. Selected bond angles in complexes 1', 3 'and 5 '

Bond angle (°) of 1'		Bond angle (°) of 3'		Bond angle (°) of 5'	
O(2)-Cd(1)-O(3)	149.83(7)	O(1)-Cd(1)-O(2)	53.26(7)	O(1)-Cd(01)-O(2)	53.23(7)
O(2)-Cd(1)-O(4)	94.72(7)	O(1)-Cd(1)-O(3)	139.09(7)	O(1)-Cd(01)-O(3)	83.52(7)
O(2)-Cd(1)-N(1)	91.94(8)	O(1)-Cd(1)-O(4)	83.71(7)	O(1)-Cd(01)-O(4)	138.79(7)
O(2)-Cd(1)- O(1)_d	117.10(8)	O(1)-Cd(1)-N(1)	92.82(9)	O(1)-Cd(01)-N(1)	92.14(8)
O(2)-Cd(1)-N(2)_d	86.86(8)	O(1)-Cd(1)-N(2)	90.39(9)	O(1)-Cd(01)-N(2)	90.66(8)
O(3)-Cd(1)-O(4)	55.56(7)	O(1)-Cd(1)-O(2)_c	128.39(7)	O(1)-Cd(01)- O(1)_b	128.14(7)
O(3)-Cd(1)-N(1)	93.32(8)	O(2)-Cd(1)-O(3)	167.53(7)	O(2)-Cd(01)-O(3)	136.71(7)
O(3)-Cd(1)-O(1)_d	92.30(8)	O(2)-Cd(1)-O(4)	136.93(7)	O(2)-Cd(01)-O(4)	167.90(7)
O(3)-Cd(1)-N(2)_d	90.62(8)	O(2)-Cd(1)-N(1)	86.02(8)	O(2)-Cd(01)-N(1)	86.29(8)
O(4)-Cd(1)-N(1)	90.68(8)	O(2)-Cd(1)-N(2)	90.16(8)	O(2)-Cd(01)-N(2)	90.09(8)
O(4)-Cd(1)-O(1)_d	147.84(8	O(2)-Cd(1)-O(2)_c	75.16(7)	O(2)-Cd(01)-O(2)_b	74.93(7)
O(4)-Cd(1)-N(2)_d	95.21(8)	O(3)-Cd(1)-O(4)	55.38(7)	O(3)-Cd(01)-O(4)	55.27(7)
N(1)-Cd(1)-O(1)_d	92.68(10)	O(3)-Cd(1)-N(1)	94.11(9)	O(3)-Cd(01)-N(1)	98.36(9)
N(1)-Cd(1)-N(2)_d	174.07(9)	O(3)-Cd(1)-N(2)	88.14(9)	O(3)-Cd(01)-N(2)	88.54(8)
O(1)_d-Cd(1)-N(2)_d	82.73(10)	O(3)-Cd(1)-O(2)_c	92.43(7)	O(3)-Cd(01)-O(2)_b	148.17(7)
		O(4)-Cd(1)-N(1)	99.33(9)	O(4)-Cd(01)-N(1)	93.77(8)

O(4)-Cd(1)-N(2)	88.15(9)	O(4)-Cd(01)-N(2)	88.47(8)
O(4)-Cd(1)-O(2)_c	147.68(7)	O(4)-Cd(01)-O(2)_b	93.01(7)
N(1)-Cd(1)-N(2)	172.14(10)	N(1)-Cd(01)-N(2)	172.81(9)
O(2)_b-Cd(1)-N(1)	84.00(9)	N(1)-Cd(01)-O(2)_b	85.16(9
O(1)_b-Cd(1)-N(2)	88.00(9)	N(2)-Cd(01)-O(2)_b	87.91(7)

Symmetric transformation: a =1-x, 1-y, 1-z, b = 2-x, 1-y, 1-z, c = -x, 1-y, 1-z, d = 2-x, 2-y, 1-z



Fig. S1 a) 1D supramolecular chain of 2 formed via $\pi^{\dots}\pi$ interaction. b) 1D supramolecular chain of 4 formed via $\pi^{\dots}\pi$ interaction.



Fig. S2 ¹H NMR spectrum (400 MHz, DMSO-d₆) of complex 1.



Fig. S3 ¹H NMR spectrum (400 MHz, DMSO-d₆) of complex 1'.



Fig. S4 ¹H NMR spectrum (400 MHz, DMSO-d₆) of complex 2.



Fig. S5 ¹H NMR spectrum (400 MHz, DMSO-d₆) of complex 2'.



Fig. S7 ¹H NMR spectrum (400 MHz, DMSO-d₆) of complex 3'.



Fig. S8 ¹H NMR spectrum (400 MHz, DMSO-d₆) of complex 4.



Fig. S9 ¹H NMR spectrum (400 MHz, DMSO-d₆) of complex 4'.



Fig. S10 ¹H NMR spectrum (400 MHz, DMSO-d₆) of complex 5.



Fig. S11 ¹H NMR spectrum (400 MHz, DMSO-d₆) of complex 5'.



Fig. S12 Optical images of 1-5.



Fig. S13 SEM images of **1**: a) before and b) after UV irradiation; **2**: c) before and d) after UV irradiation; **3**: e) before and f) after UV irradiation; **4**: g) before and h) after UV irradiation and **5**: i) before and j) after UV irradiation.



Fig. S14 1D supramolecular chain of **5** formed via $\pi^{\dots}\pi$ interaction and the 1D chain polymer of **5'** upon UV irradiation of **5** via SCSC transformation(hydrogen atoms are removed for the clarity).

Non-covalent Interactions

The differences in molecular packing within the crystal system mainly driven by various non-covalent interactions present in the crystal lattice. To better understand this phenomenon, we have examined the intermolecular interactions responsible for the varying molecular packing in the crystal system.

In group I, which contains an isostructural compound (1), naphthyl hydrogens of the pair of 4-nvp molecules exhibit non-covalent interactions with the benzoic acids of neighboring units. Specifically, one hydrogen from the 4-nvp interacts with the carboxylic carbon of the benzoic acid (np-H...C-O at 2.78 Å), while the other hydrogen interacts with three carbons of the benzoic group (np-H...C, np-H...C, np-H...C at distances of 2.85 Å, 2.72 Å, and 2.85 Å, respectively). Additionally, the two benzoic acid groups from neighboring units exhibit interactions such as H...C-H and H...H-C (with distances of 2.86 Å and 2.39 Å, respectively). These interactions likely cause the 4-nvp ligands to align in an HH fashion.

Despite these interactions, group I compounds are not an isostructural with the remaining compounds, even though the photoreactive ligands are aligned in an HH fashion as in 2 and 4. In contrast, groups II and III demonstrate interactions involving one of the oxygens in the benzoic acids with the hydrogens of pyridine, olefin, and naphthalene (e.g., bz-O...H-py at 2.37 Å, bz-O...H-C=C at 2.54 Å, and bz-O...H-np at 2.60 Å) in Fig. S16 (ESI⁺). Among these interactions, the one between the benzoic acid's oxygen and the naphthalene's hydrogen enables the 4-nvp to exhibit a torsion angle of 33.2 degrees (Fig. S15a, ESI⁺). In group II isostructural compounds, one of the oxygens of the halobenzoic acid (xbz) interact only with the hydrogens from pyridine and olefin of the 4-nvp ligands (clbz-O...H-py at 2.49 Å, brbz-O...H-py at 2.47 Å, clbz-O...H-C=C at 2.43 Å, and brbz-O...H-C=C at 2.45 Å) in Fig S16, and not with the hydrogen of naphthalene. This results in the 4-nvp ligands being parallel to each other with a negligible torsion angle of 7.32° and 9.17° (Fig. S15b and S15d, ESI⁺). Furthermore, the pair of 4-nvp ligands interacts with the carbon atoms of the same halobenzoic acids in the 2 and 4 compounds, leading to their HH alignment similar to that seen in group I isostructural compounds.

In contrast, group III isostructural compounds feature two oxygens from halobenzoic acids (one from each) that engage in non-covalent interactions with the hydrogen of pyridine, resulting in interactions like clbz-O...H-py and clbz-O...H-py at distances of 2.60 Å and 2.61 Å. Additionally, the naphthyl hydrogen interacts with the carbon atoms of the adjacent halobenzoic acid (np-H...C-clbz at 2.94 Å and 2.83 Å, and np-H...C-brbz at 2.92 Å and 2.86 Å in compounds **3** and **5**, respectively) further the non-planar 4-nvp carbon atoms having an non-covalent interactions with the hydrogens of planar 4-nvp (np-H...C-np 2.94 Å, 2.83 Å in **3** and 2.92 Å,2.86 Å) seen in Fig. S16. Notably, there is a lack of non-covalent interactions between the oxygen of the halobenzoic group and the olefin hydrogens. These major non-covalent interactions likely lead to a non-planar orientation of the ligands, resulting in torsion angles of 60.56° and 60.70° (Fig. S15c

and S15e, ESI[†]) in compounds **3** and **5**, respectively, causing misalignment with the neighboring ligands.

Conversely, the planar 4-nvp is aligned HT with the neighboring unit's 4-nvp. This alignment may be attributed to the presence of non-covalent interactions between two halo groups (bz-x...H is 2.95 Å and 3.02 Å in **3** and **5** respectively) the interaction of halogen with the pyridyl carbon atom of the no-planar 4-nvp (bz-x...C-py is 3.29 Å and 3.27 Å in **3** and **5** respectively) as illustrated in Fig. S16 (ESI[†]).



Fig. S15 a)-e) Torsion angle of 1-5 respectively.







[Cd(4-brbz)₂(4-nvp)₂] (5) HT

Fig. S16 Non-covalent interactions in Group I (1), Group II (2 and 4), and Group III (3 and 5).

Isostructural Analysis

The differing photomechanical properties of compounds **1-5** can be attributed to variations in their molecular arrangement and packing behavior within the crystal lattices. It is expected that replacing Cl with Br often can result in isostructural compounds. To confirm this, we systematically compared the single-crystal structures and cell parameters of these compounds.

Preliminary studies revealed that compounds 1-5 crystallize in the *P*-1 space group; however, their unit cell parameters differ. Notably, compound 1 has a distinct set of unit cell parameters, whereas compounds 2 and 4 share a similar set, as do compounds 3 and 5. Based on these observations, the five compounds can be categorized into three groups: Group I (compound 1), Group II (compounds 2 and 4), and Group III (compounds 3 and 5).

To quantitatively assess isostructurality, we utilized the CrystalCMP software to analyze molecular packing similarities. The similarity matrix and CMP dendrogram indicated that not all compounds are isostructural.⁴⁻⁶ A close examination of the PS_{ab} values showed that compound 1 is not isostructural with any of the other compounds, as its PS_{ab} value is significantly greater than zero. However, it does exhibit a slightly lower degree of similarity with compounds 2 and 4, which share a similar alignment of their photoreactive ligands, 4-nvp, in a HH configuration. Conversely, 1 has a higher PS_{ab} value when compared to 3 and 5, also in the structure overlay is clearly observed [1 (red) which not overlap with the rest of the compounds] leading us to classify it as a Group I isostructural compound.

Compounds 2 and 4 show lower PS_{ab} values, indicating a higher degree of similarity between them. In contrast, the higher PS_{ab} values are observed with compound 3 and 5 and this demonstrate their non-isostructurality, further supported by the structural overlay. As expected, compounds 3 and 5 are isostructural to one another and they exhibited lower PS_{ab} values, showcasing good structural overlap (Fig. S17-18, ESI[†]). Compounds 2 and 4 are categorized as Group II isostructural compounds, whereas 3 and 5 are classified as Group III (Fig S15-18, ESI[†]).



Fig. S17 a) Structure overlay of group I (compound 1 red). b) Structural overlay of group II isostructural compounds (compound 2 yellow, and compound 4 blue) c) Structural overlay of group III isostructural compounds (compound 3 green and compound 5 sky blue).



Fig. 18 a) Similarity matrix of 1-5. b) Structural overlay of 1-5. c) Dendrogram calculated from similarity matrix.



Fig. S19 PXRD patterns of simulated (pink) and before UV irradiation (blue) of complex 1.



Fig. S20 PXRD patterns of simulated (pink) and after UV irradiation (blue)of complex 1'.



Fig. S21 PXRD patterns of simulated (pink), before UV (blue) and after UVirradiation (olive) of complex 2.



Fig. S22 PXRD patterns of simulated (pink) and before UV irradiation (blue)of complex 3.



Fig. S23 PXRD patterns of simulated (pink) and after UV irradiation (blue) of complex 3'.



Fig. S24 PXRD patterns of simulated (pink), before UV irradiation (blue) and after UV irradiation (olive) of complex 4.



Fig. S25 PXRD patterns of simulated (pink) and before UV irradiation (blue) of complex 5.



Fig. S26 PXRD patterns of simulated (pink) and after UV irradiation (blue) of complex 5'.



Fig. S27 IR Spectrum of complex 1.



Fig. S28 IR Spectrum of complex 2.



Fig. S29 IR Spectrum of complex 3.



Fig. S30 IR Spectrum of complex 4.



Fig. S31 IR Spectrum of complex 5.

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