Electronic Supporting Information

Inducing Configurational Stability in Inherently Flexible Expanded Heterohelicenes and Unlocking Stimuli-Responsive Chiroptical Switching

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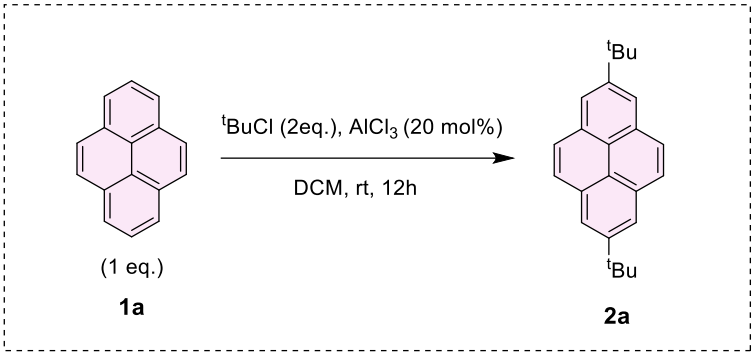
S1. Materials, Methods, and Instrumentation

Dry solvents and reagents were purchased from commercial suppliers and used without further purification. Deuterated solvents, $RhCl_3.xH_2O$ were purchased from Aldrich. $[Cp^*RhCl_2]_2$ was synthesized according to the reported procedure.[S1] ^1H, $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AVANCE III 400, 500, and 700 MHz NMR spectrometers at room temperature unless mentioned otherwise. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard ($CHCl_3$: δ = 7.26 ppm for ^1H spectra, 77.2 ppm for $^{13}C\{^1H\}$ spectra; DMSO: δ = 2.50 ppm for ^1H spectra, 39.5 ppm for $^{13}C\{^1H\}$ spectra). All coupling constants (J) are expressed in hertz (Hz) and are only given for ^1H– ^1H couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublets of doublets), and m (multiplet). ESI mass spectrometry was performed on a Bruker microTOF QII spectrometer. Steady-state absorption spectra were recorded on Cary 100 UV-vis spectrophotometer.

Single-crystal X-ray diffraction data were collected at low temperatures using a Bruker D8 QUEST PHOTON 100 diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data reduction was performed using the Bruker Apex V software suite, and the crystal structures were solved via Intrinsic Phasing using the ShelXT program. Steady-state absorption spectra were recorded on a Cary 100 UV-Vis spectrophotometer, while steady-state fluorescence measurements were conducted using a HORIBA Fluoromax spectrofluorometer. Time-resolved fluorescence spectroscopy was performed with a FLS1000 spectrometer, Edinburgh Instruments, and Delta Flex-01 DD/HORIBA .Chiral separation was performed using Agilent 1260 Infinity II HPLC system. CD spectra were recorded in a JASCO J-815 CD spectrometer with a Peltier MCB-100 and JASCO J-1500 with a Peltier CTU-100. Circularly polarized luminescence (CPL) measurements were carried out with a Jasco CPL-300 spectrometer equipped with a Peltier PTC-510. DLS measurements were performed in Zetasizer ULTRA Malvern with a 633 nm laser at a back scattering angle of 173°.

S2. Synthesis of Expanded Poly-aza[9]helicenes Precursors

Synthesis of 2,7-di-tert-butylpyrene (2a)[S2]

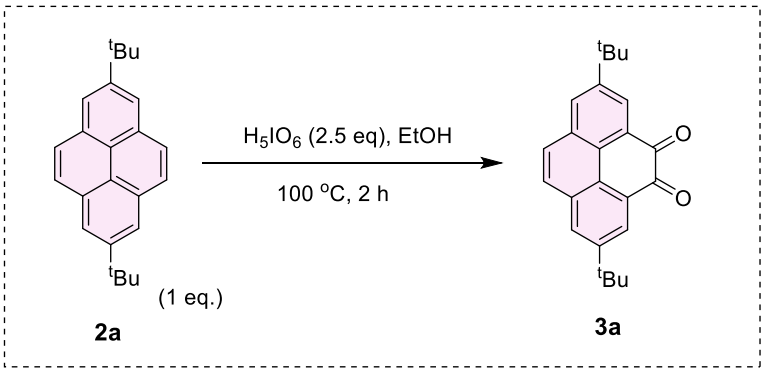


Scheme S1. Synthesis of **2a**.

Pyrene (**1a**) (2.042 g, 10 mmol) was taken in a 100 mL two-neck RB, dissolved in 40 mL of dichloromethane. While being stirred and maintaining the temperature of 5 ^{o}C, $AlCl_3$ (0.266 g, 20 mol%) was added to the mixture. The Ar atmosphere was maintained during the whole process. Then, ^{t}BuCl (1.849 g, 20 mmol) dissolved in 6 mL of CH_2Cl_2 was added to the mixture, maintaining the Ar atmosphere. Further, the mixture was stirred at room temperature for 12 h. The organic part was separated by extraction with $CHCl_3$ and dried under reduced pressure. Yield: 2.808 g, 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 4H), 8.02 (s, 4H), 1.58 (s, 18H). The NMR data were compared with those of a previously reported compound in the literature.[S2]

Synthesis of 2,7-di-tert-butylpyrene-4,5-dione (3a)[S2]

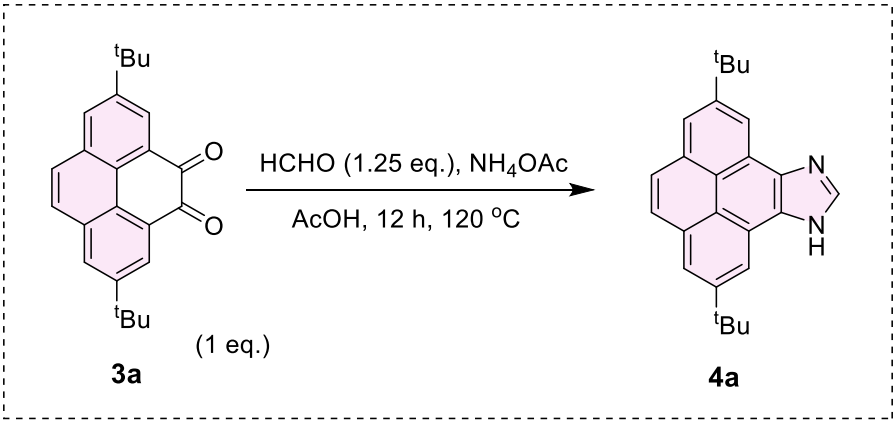


Scheme S2. Synthesis of **3a**.

2,7-di-tert-butylpyrene **(2a)** (2.040 g, 6.48 mmol) and periodic acid (3.700 g, 16.23 mmol) were dissolved in 90 mL of ethanol. The mixture was refluxed for 2 hours at 100 °C under an N_2 atmosphere. After that red-colored reaction mixture was cooled to room temperature, and 70 mL of water and 50 mL, 20% $Na_2S_2O_3$ were added successively. The mixture was stirred for 30 minutes below 5 °C. The organic part was extracted with $CHCl_3$ and dried using a rotavapor. Then the crude mixture was purified using silica gel column chromatography with a $CHCl_3$/hexane (40%–100%) solvent system. Yield = 1.445 g, 64%.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.55 (d, *J* = 2.0 Hz, 2H), 8.12 (d, *J* = 2.0 Hz, 2H), 7.80 (s, 2H), 1.49 (s, 18H).

Synthesis of 2,7-di-tert-butylpyrene-[4,5-*d*]-imidazole (4a)[S3]

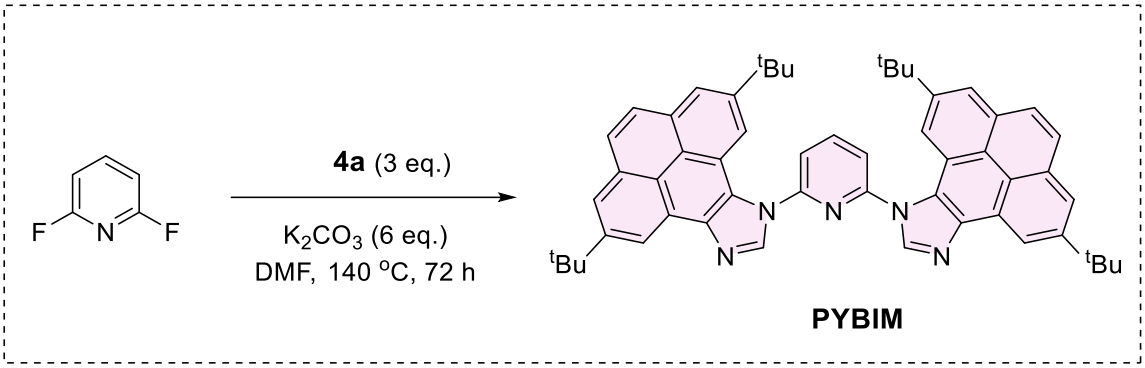


Scheme S3. Synthesis of **4a**.

A mixture of **3a** (1.500 g, 4.35 mmol), NH_4OAc (7.200 g, 91.2 mmol), HCHO (408 µL of a 37% aq. solution, 5.4 mmol), and AcOH (40 mL) was refluxed under aerobic conditions for 12 hours at 120 °C. Distilled water (60 mL) was added to the mixture after cooling it to room temperature, which produced a brown precipitate. The mixture was then neutralized with a 25% aqueous ammonia solution. The precipitate was filtered, washed with sufficient water, and dried in the oven at 90 °C for 5 hours. Yield: 1.236 g, 80%.

^{1}H NMR (400 MHz, DMSO-d_6) *δ* 13.64 (s, broad, 1H), 8.76 (s, 2H), 8.42 (s, 1H), 8.21 (s, 2H), 8.11 (s, 2H), 1.57 (s, 18H).

Synthesis of 2,6-bis(2,7-di-tert-butyl-9H-pyreno[4,5-*d*]-imidazol-9-yl) pyridine (PYBIM)



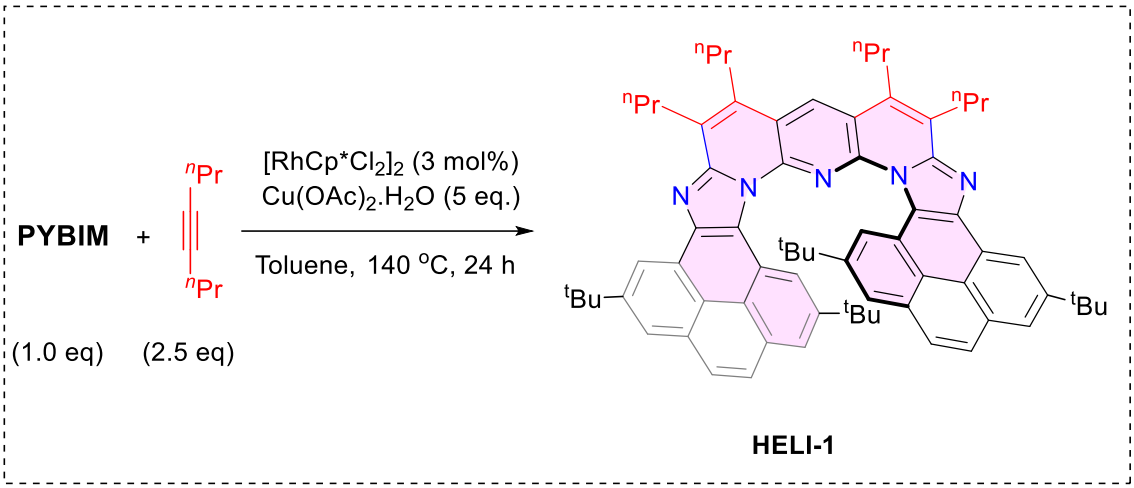
Scheme S4. Synthesis of **PYBIM**.

The mixture of **4a** (1.000 g, 2.82 mmol), 2,7-difluoropyridine (85.2 µL, 0.94 mmol), K_2CO_3 (0.779 g, 5.64 mmol), and DMF (5 mL) was taken in a pressure tube. The mixture was refluxed at 140 °C for 72 hours. The mixture was cooled to room temperature, and water (40 mL) was added and extracted with DCM (40 mL x 2). The organic part was further extracted twice with water (50 mL) to get rid of DMF. The organic part was dried and purified using a silica gel column chromatography with a MeOH/$CHCl_3$ (1-5%) solvent system. Yield: 0.492 g, 68%.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.06 (s, 2H), 8.53 (s, 2H), 8.36 (t, *J* = 7.2 Hz, 1H), 8.25 (d, *J* = 12.1 Hz, 4H), 8.14 - 8.07 (m, 4H), 8.03 (d, *J* = 11.8 Hz, 2H), 7.94 (d, *J* = 7.5 Hz, 2H), 1.65 (s, 18H), 1.34 (s, 18H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 150.7, 149.7, 147.9, 142.1, 141.2, 140.4, 132.1, 131.5, 128.3, 127.8, 126.0, 125.9, 122.2, 122.1, 122.0, 121.4, 119.7, 117.5, 117.2, 35.6, 35.4, 32.1, 32.0. **HRMS** (ESI, positive ion) *m/z*: $[M + H]^+$ Calculated, 784.4301; Found, 784.4371.

Note: The pyridine ring protons appeared as triplet at 8.36 ppm, with 1H integration, and doublet at 7.94 ppm, with 2H integration. and the imidazole ring protons appeared at singlet at 9.06 ppm, with 2H integration.

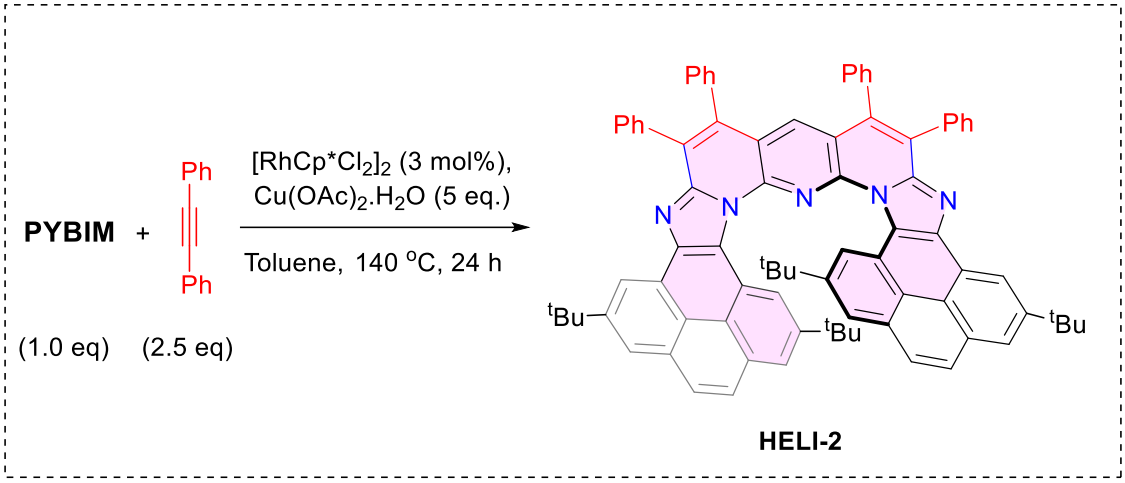
S3. Synthesis of Expanded Poly-aza[9]helicenes HELI-1 and HELI-2



Scheme S5. Synthesis of **HELI-1** using catalytic double rollover π-expansion strategy.

A mixture of **PYBIM** (40 mg, 0.05 mmol), $[RhCp^*Cl_2]_2$ (3 mol%), and $Cu(OAc)_2.H_2O$, (50 mg, 0.25 mmol) was taken in an oven-dried pressure tube and 2 mL of dried toluene to it. Further, 4-octyne (19 µL, 2.5 eq.) was added to the mixture. Next, the mixture was refluxed at 140 °C for 24 hours. After cooling the reaction mixture to room temperature, 8 mL of saturated aqueous K_2CO_3 solution was added to remove Cu-salts. The organic part was extracted twice using $CHCl_3$ and dried under reduced pressure. The crude mixture was subjected to column chromatography using a $CHCl_3$/hexane 30 – 80 % solvent system to get the yellow-colored product. Yield: 31 mg, 62%.

^{1}H NMR (400 MHz, $CDCl_3$) *δ*.9.23 (s, 2H), 9.02 (s, 1H), 8.94 (s, 2H), 8.19 (s, 2H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.38 (s, 2H), 3.62 – 3.47 (m, 4H), 3.40 – 3.26 (m, 4H), 1.72 (s, 18H), 1.01 – 0.80 (m, 20H), 0 25 (s, 18H). **^{13}C NMR** (176 MHz, $CDCl_3$) *δ* 149.4, 148.5, 146.2, 141.9, 140.0, 130.8, 130.5, 129.5, 129.0, 127.6, 126.3, 126.2, 125.9, 125.8, 125.5, 122.2, 122.2, 121.9, 121.0, 118.9, 117.4, 117.3, 35.3, 33.9, 31.9, 30.2, 29.9, 29.5, 23.8, 23.4, 14.6, 14.4, 0.8. **HRMS** (APCI, positive ion) *m/z*: $[M + H]^+$ Calculated, 1000.6252; Found, 1000.6234.



Scheme S6. Synthesis of **HELI-2** via catalytic double rollover π-expansion strategy.

A mixture of **PYBIM** (40 mg, 0.05 mmol), $[RhCp^*Cl_2]_2$ (3 mol%), $Cu(OAc)_2.H_2O$, (50 mg, 0.25 mmol), and diphenylacetylene (22 mg, 2.5 eq.) was taken in a pressure tube and dissolved in 2 mL of dried toluene. Next, the mixture was refluxed at 140 °C for 24 hours. After cooling the reaction mixture to room temperature, 8 mL of saturated aqueous K_2CO_3 solution was added to remove Cu-salts. The organic part was extracted twice using $CHCl_3$ and dried under reduced pressure. The crude mixture was subjected to column chromatography using a $CHCl_3$/hexane 40 - 70% solvent system to get a pure product. Yield: 41 mg, 73%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, J = 1.3 Hz, 2H), 9.03 (s, 2H), 8.46 (s, 1H), 8.20 (d, J = 1.4 Hz, 2H), 7.94 (d, J = 8.9 Hz, 2H), 7.76 (d, J = 8.9 Hz, 2H), 7.66 (d, J = 7.0 Hz, 4H), 7.42 (s, 2H), 7.42 – 7.26 (m, 16H), 1.64 (s, 18H), 0.32 (s, 18H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 149.1, 148.8, 146.5, 143.2, 141.1, 137.2, 136.3, 135.7, 135.2, 132.0, 131.2, 131.1, 130.9, 130.8, 129.9, 128.4, 128.1, 127.9, 127.9, 127.8, 127.7, 126.8, 126.3, 125.7, 122.8, 122.8, 122.5, 122.4, 121.7, 119.6, 118.7, 118.3, 35.6, 34.3, 32.1, 30.4. **HRMS** (APCI, positive ion) *m/z*: $[M + H]^+$ Calculated, 1136.5600; Found, 1136.5626.

Note: The absence of the pyridine doublet peak at 7.94 ppm (for 2 protons) and the imidazole singlet peak at 9.06 ppm (for 2 protons), along with the appearance of a new singlet peak at 9.02 ppm (for **HELI-1**) and at 8.46 ppm (for **HELI-2**) for the central pyridine unique proton, in the ^{1}H NMR spectra of **HELI-1** and **HELI-2** in $CDCl_3$ indicated the formation of the desired rollover-annulated compounds. Interestingly, the signal at 0.25 ppm (for **HELI-1**) and at 0.32 ppm (for **HELI-2**) were expected for the inner ^{t}Bu groups, as

the chemical shifts were highly shielded by the ring current of the two terminal overlapping rings of the azahelicene backbone. In contrast, the protons of the corresponding outer ^{t}Bu groups appeared at 1.72 ppm (for **HELI-1**) and 1.64 ppm (for **HELI-2**).

S4. Single Crystal X-Ray Diffraction Analysis

Table S1: Crystal data and structure refinement for HELI-1.

Identification code	HELI-1
Empirical formula	$C_{71}H_{77}N_5O_{0.5}Cl_{0.5}$
Formula weight	1026.10
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	13.162(3)
b/Å	14.991(4)
c/Å	16.491(4)
α/°	79.736(12)
β/°	78.645(9)
γ/°	66.662(10)
Volume/Å^3	2911.0(13)
Z	2
ρ_{calc}g/cm^3	1.171
μ/mm^{-1}	0.091
F(000)	1101.0
Crystal size/mm^3	0.028 × 0.019 × 0.009
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.95 to 60.254
Index ranges	-18 ≤ h ≤ 18, -21 ≤ k ≤ 21, -23 ≤ l ≤ 23
Reflections collected	158115
Independent reflections	17080 [R_{int} = 0.0812, R_{sigma} = 0.0462]
Data/restraints/parameters	17080/24/719
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.1120, wR_2 = 0.3035
Final R indexes [all data]	R_1 = 0.1342, wR_2 = 0.3218

Structural analysis of HELI-1

d_{AI} = The vertical distance between the centroid of the ring A and ring I.

$\theta_{A\text{-}I}$ = The intersecting angle between two terminal ring A and I

$<\phi_{AE}>$ = Mean torsion angle from ring A to ring E

$<\phi_{IE}>$ = Mean torsion angle from ring I to ring E

$d_{A\text{-}E}$ = Distance from the centroid of ring A to plane E

$d_{I\text{-}E}$ = Distance from the centroid of ring I to the plane of ring E

$\theta_{A\text{-}E}$ / $\theta_{K\text{-}E}$ = The intersecting angle between two terminal ring and the central plane along ring F

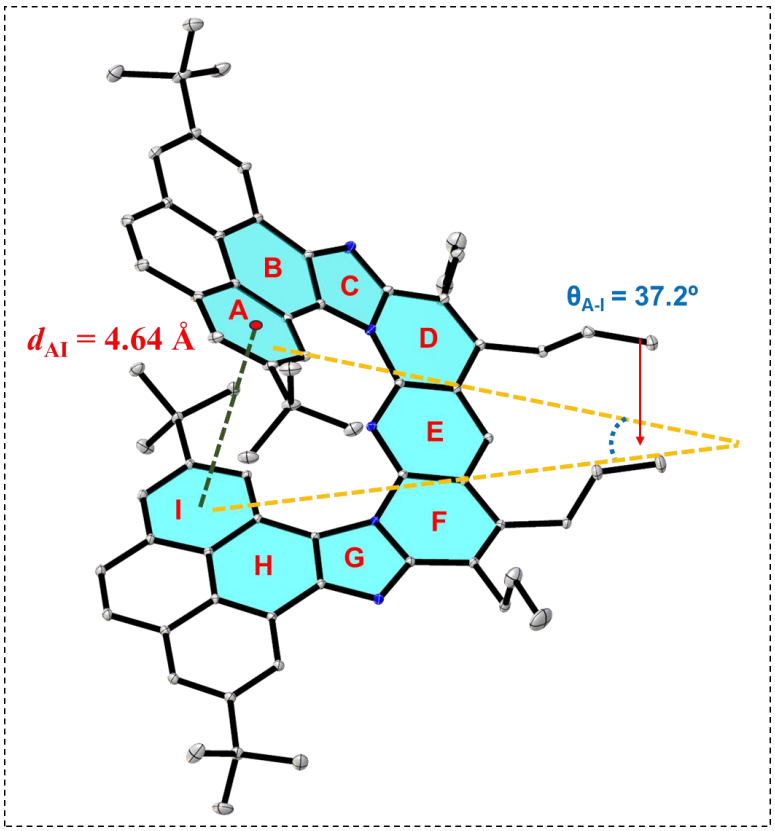


Figure S1a. Crystal structure of **HELI-1** (top view, H-atoms and free solvents are omitted for clarity). *P*-isomer is shown.

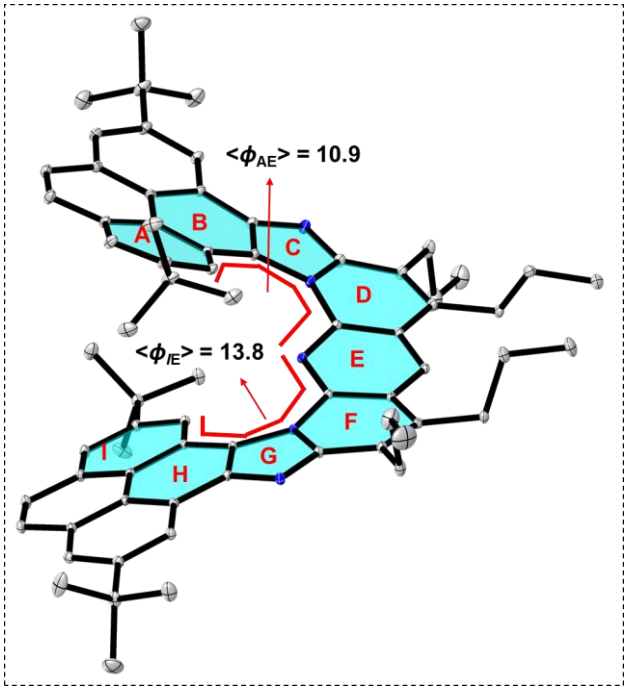


Figure S1b. Crystal structure of **HELI-1** (top view, H-atoms and free solvents are omitted for clarity). *P*-isomer is shown.

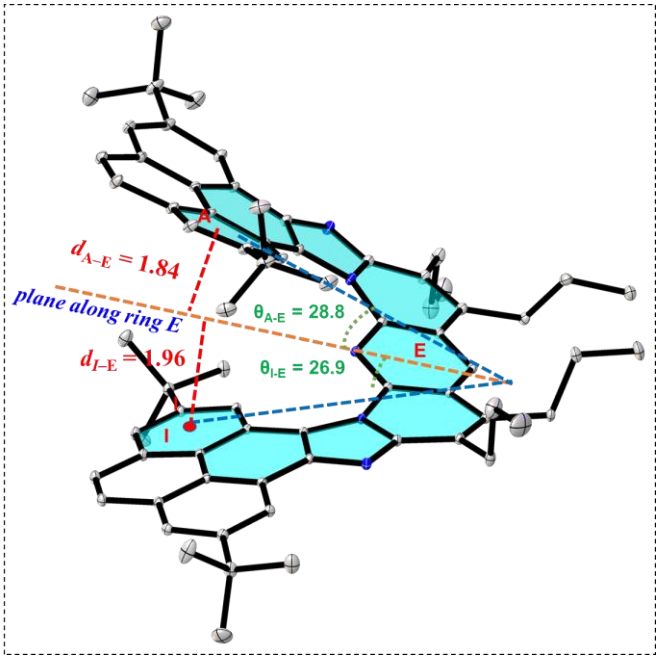


Figure S1c. Crystal structure of **HELI-1** (top view, H-atoms and free solvents are omitted for clarity). *P*-isomer is shown.

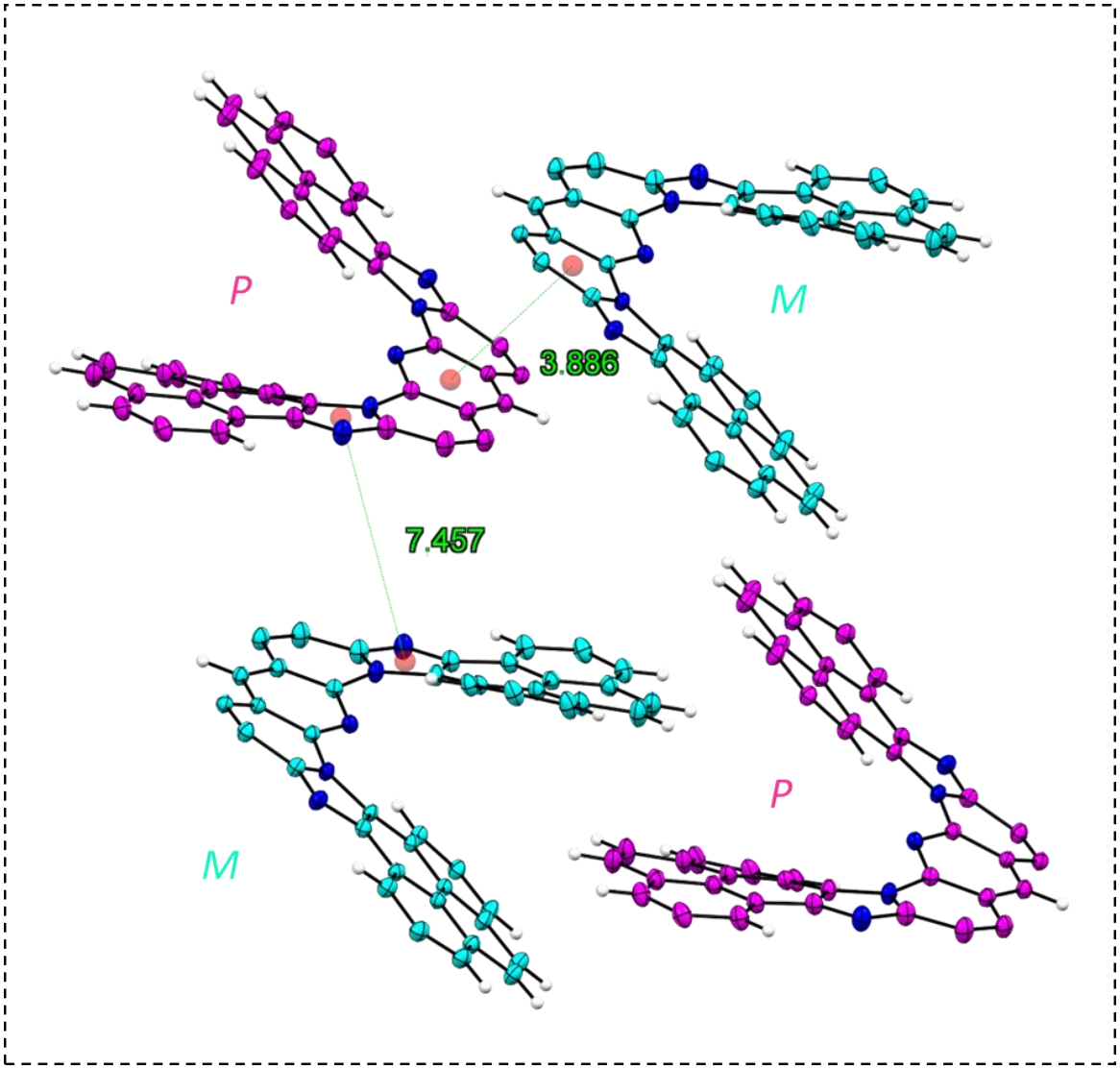


Figure S1d. Crystal packing structure of **HELI-1** (top view, H-atoms, ^{t}Bu groups, and free solvents are omitted for clarity; the distances shown are centroid to centroid distance).

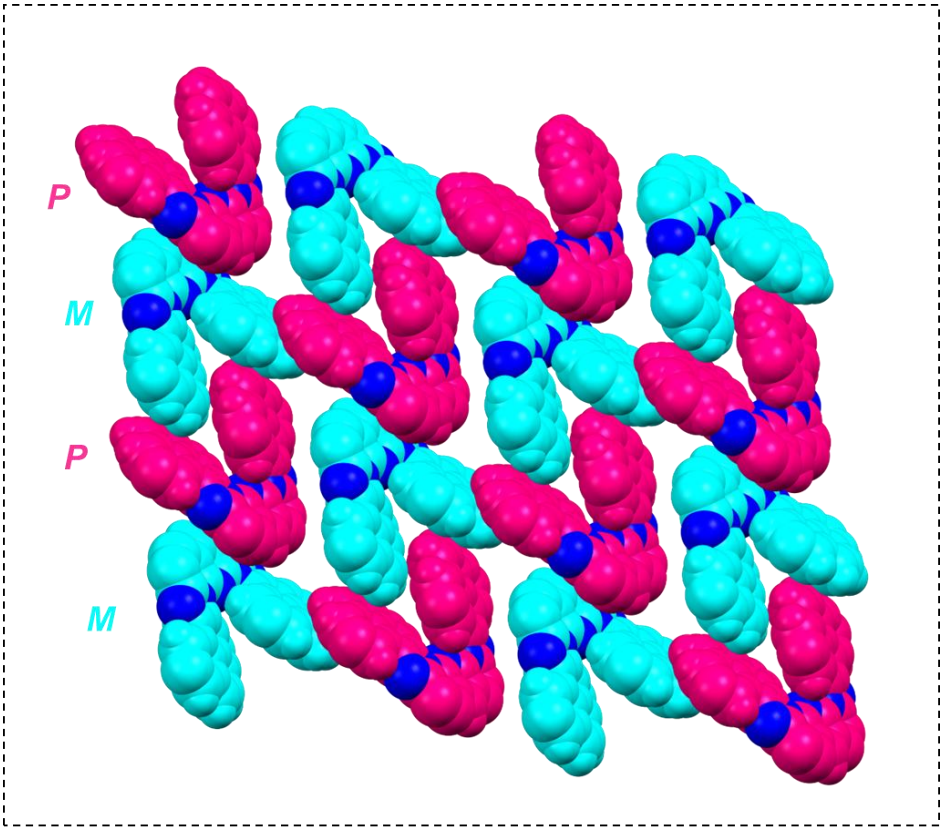


Figure S1e. Crystal packing structure of **HELI-1** (top view, H-atoms, ^{t}Bu groups, and free solvents are omitted for clarity; the distances shown are centroid to centroid distance).

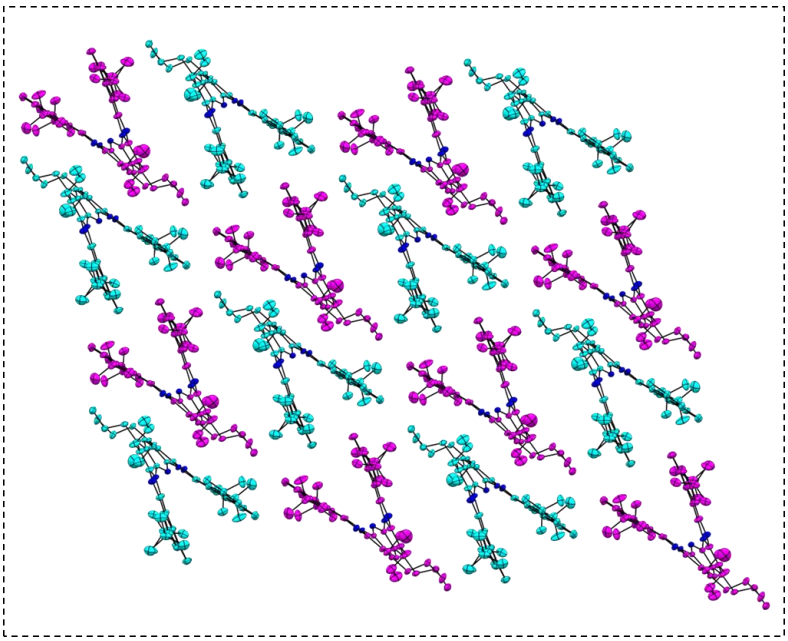


Figure S1f. Crystal packing structure of **HELI-1** (top view, H-atoms and free solvents are omitted for clarity).

Structural analysis of HELI-2

We attempted single-crystal X-ray diffraction analysis of HELI-2 many times. Several crystallization methods (diffusion, evaporation, solvent layering) and solvent screening have been tried. Among them the best data were obtained by diffusion method with hexane as outer solvent, and 1% MeOH + DCM as inner solvent. However, the quality of the crystal data is still poor. A couple of side-chain carbon atoms have been modelled as disordered. There are a few A- and B-level alerts due to poor diffraction quality. The structure has been shown below.

d_{AI} = The vertical distance between the centroid of the ring A and ring I.

$\theta_{A\text{-}I}$ = The intersecting angle between two terminal ring A and I

$\langle \phi_{AE} \rangle$ = Mean torsion angle from ring A to ring E

$\langle \phi_{IE} \rangle$ = Mean torsion angle from ring I to ring E

$d_{A\text{-}E}$ = Distance from the centroid of ring A to plane E

$d_{I\text{-}E}$ = Distance from the centroid of ring I to the plane of ring E

$\theta_{A\text{-}E}$ / $\theta_{K\text{-}E}$ = The intersecting angle between two terminal ring and the central plane along ring F

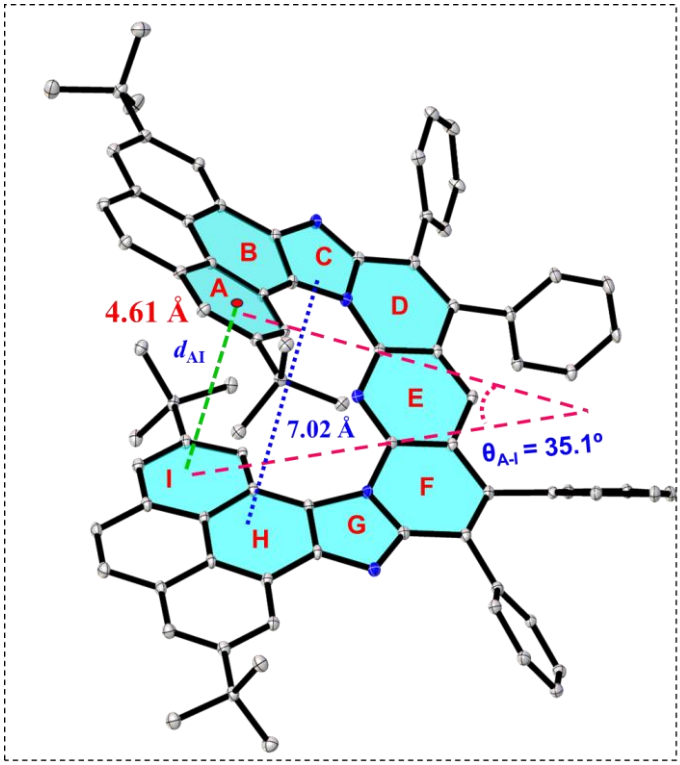


Figure S2a. Crystal structure of HELI-2 (top view, H-atoms and free solvents are omitted for clarity). *P*-isomer is shown.

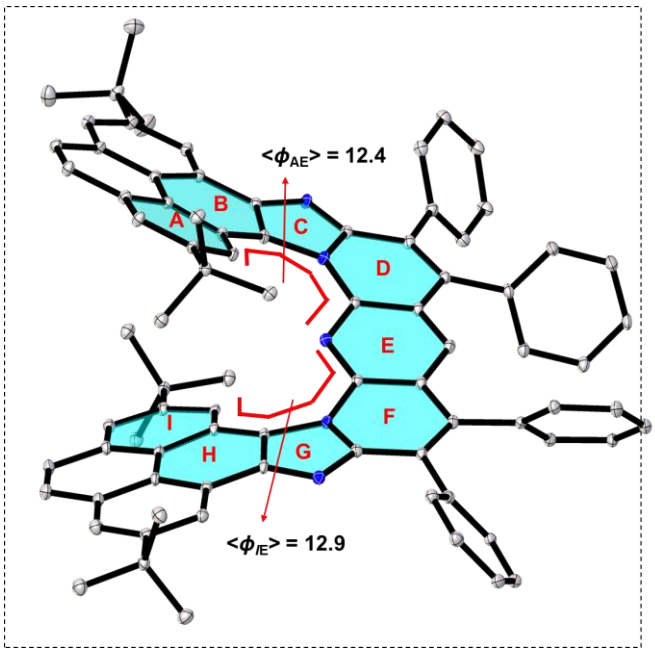


Figure S2b. Crystal structure of HELI-2 (top view, H-atoms and free solvents are omitted for clarity). *P*-isomer is shown.

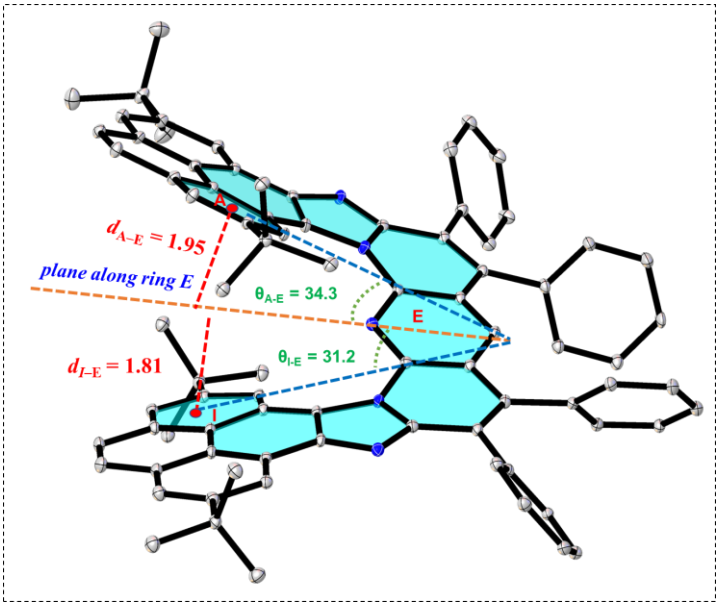


Figure S2c. Crystal structure of **HELI-2** (top view, H-atoms and free solvents are omitted for clarity). *P*-isomer is shown.

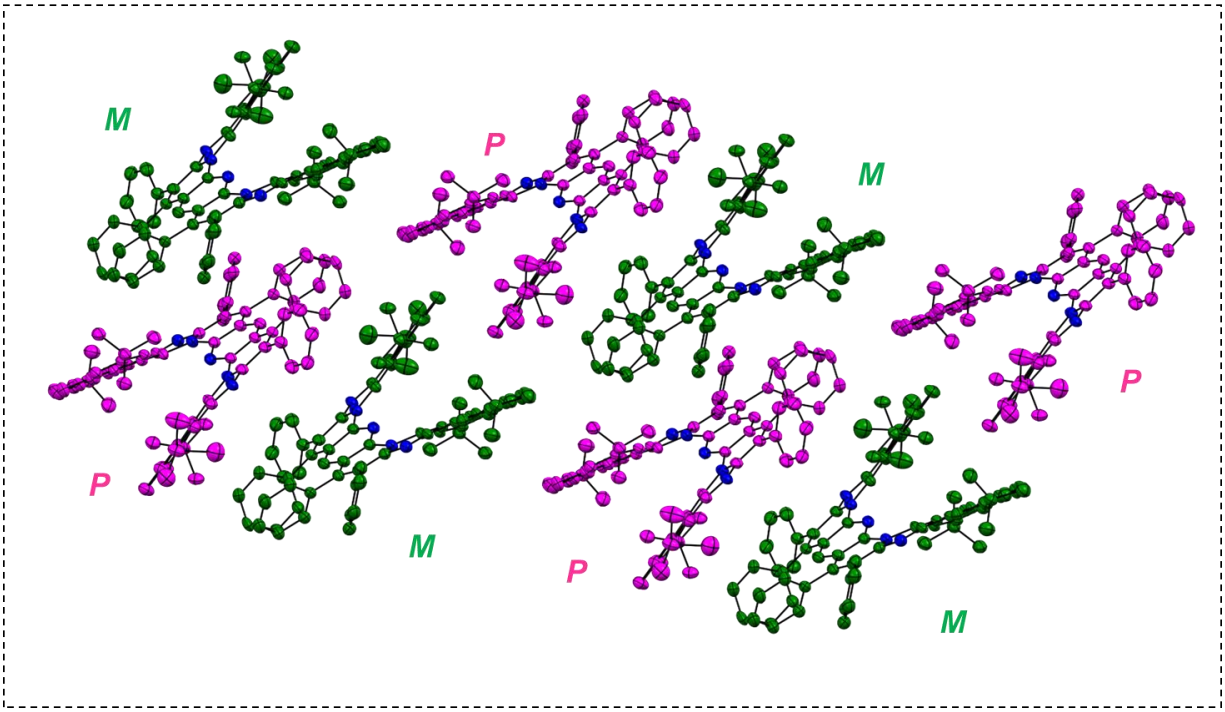


Figure S2d. Crystal packing structure of **HELI-2** (top view, H-atoms and free solvents are omitted for clarity).

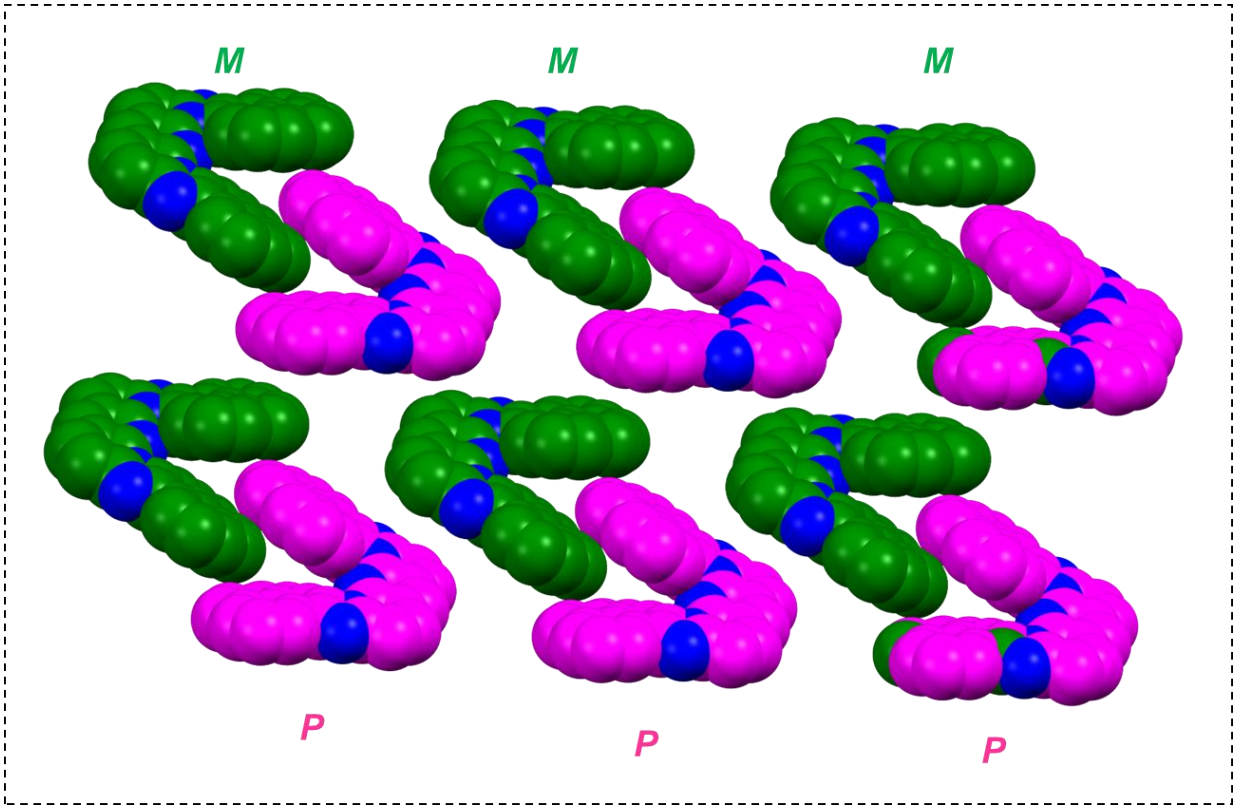


Figure S2e. Crystal packing structure of **HELI-2** (top view, H-atoms and free solvents are omitted for clarity).

S5. Enantiomerization Barrier Calculation

Gaussian 09 software was used to carry out all the computational studies.[S4] Transition state (TS) for the racemization process in the ground state (S_0) was calculated at the B3LYP/6-31g(d,p) level of theory. CPCM-CH_2Cl_2. The rate constant (k) was estimated using Eyring equation as follows: $k = (k_B T/h)\cdot\exp(-\Delta H^{\ddagger}/RT)\cdot\exp(\Delta S^{\ddagger}/R)$, where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the activation enthalpy and entropy for the racemization process, respectively, T is temperature, and k_B, h, and R are the Boltzman constant, Planck constant, and molar gas constant, respectively.

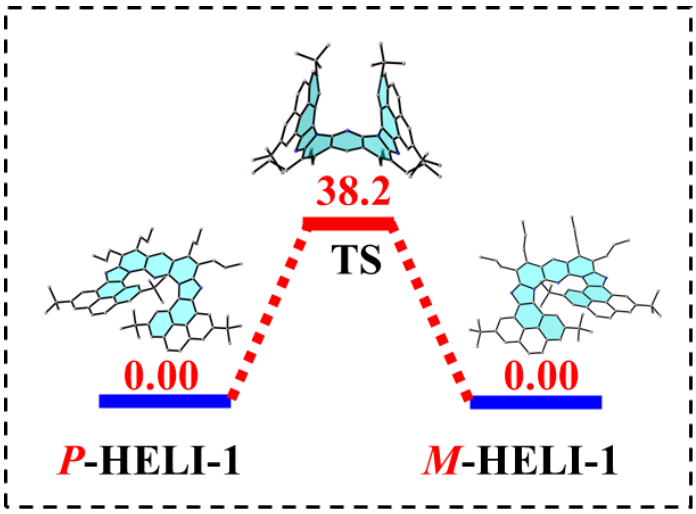


Figure S3. Enantiomerization process between (*P*)-**HELI-1** and (*M*)-**HELI-1** and the relative Gibbs free energy (kcal·mol^{-1}) calculated at the B3LYP/6-31g(d,p) level of theory. CPCM-CH_2Cl_2.

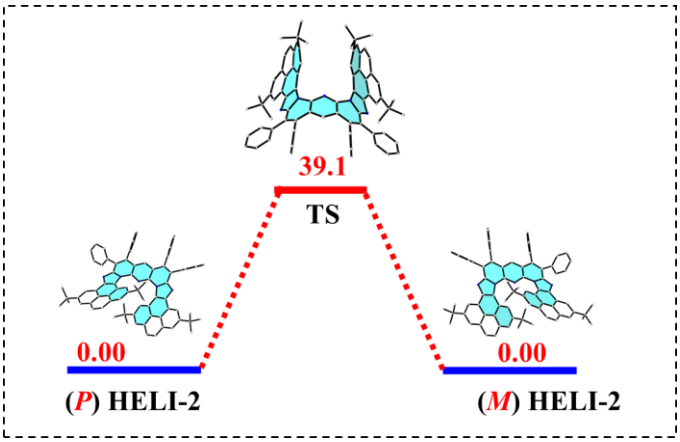


Figure S4. Enantiomerization process between (*P*)-**HELI-2** and (*M*)-**HELI-2** and the relative Gibbs free energy (kcal·mol^{-1}) calculated at the B3LYP/6-31g(d,p) level of theory. CPCM-CH_2Cl_2.

Table S2. Thermodynamic parameters of the helicene inversion process at different temperatures for **HELI-2**

Temperature (K)	$\Delta H^{\ddagger}$ (kcal·mol^{-1})	$\Delta S^{\ddagger}$ (kcal·mol^{-1}.K^{-1})	$\Delta G^{\ddagger}$ (kcal·mol^{-1})	k (s^{-1})	$t_{1/2}$
298.15	36.9	-7.28×10^{-3}	39.1	1.31×10^{-16}	1.68×10^{8} years
373.15	36.8	-7.66×10^{-3}	39.6	4.54×10^{-11}	4.84×10^{2} years

473.15	36.6	-8.03×10^{-3}	40.4	2.13×10^{-6}	3.76 days
573.15	36.5	-8.33×10^{-3}	41.3	2.16×10^{-3}	5.34 minutes

The $t_{1/2}$ value at various temperatures has been calculated by the Eyring equation as shown below:

$$k = \left(\frac{k_B T}{h}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)$$

The activation parameters,

$\Delta G^{\ddagger}$ = 0.062328 Ha = 39.11 kcal·mol^{-1}

$\Delta H^{\ddagger}$ = 0.058866 Ha = 36.938415 kcal·mol^{-1}

$\Delta S^{\ddagger}$ = -7.283×10^{-3} kcal·mol^{-1}K^{-1}

Given (298.15 K)

- R = 0.001987 kcal·mol^{-1}K^{-1}
- $k_B = 1.380649 \times 10^{-23}$JK^{-1}
- $h = 6.62607015 \times 10^{-34}$J·s

According to equation (1)

$$\frac{k_B T}{h} = \frac{(1.380649 \times 10^{-23}) J.K^{-1}(298.15)K}{6.62607015 \times 10^{-34} J.s} = 6.21 \times 10^{12}\ s^{-1}$$

$$RT = (0.001987) kcal.K^{-1}.mol^{-1}(298.15)\text{K} = 0.5924\ kcal/mol$$

$$\frac{\Delta H^{\ddagger}}{RT} = \frac{36.938415\ kcal/mol}{0.5924\ kcal/mol} = 62.35$$

$$\frac{\Delta S^{\ddagger}}{R} = \frac{-7.283 \times 10^{-3}\ kcal.K^{-1}.mol^{-1}}{0.001987\ kcal.K^{-1}.mol^{-1}} = -3.665$$

$$k = \left(\frac{k_B T}{h}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)$$

$$k = (6.21 \times 10^{12}) \exp(-62.35) \exp(-3.665)$$

$$= (6.21 \times 10^{12})(8.35 \times 10^{-28})(0.0256)$$

$$\boxed{k = 1.31 \times 10^{-16}\ s^{-1}}$$

Half-life (first-order racemization)

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.31 \times 10^{-16}}$$

$$\boxed{t_{1/2} = 5.29 \times 10^{15}\ s}$$

Convert to years:

$$\frac{5.25 \times 10^{15}}{3.154 \times 10^{7}} = \boxed{1.68 \times 10^{8}\ \textit{years}}$$

$$\boxed{k = 1.31 \times 10^{-16}\ s^{-1}}$$

$$\boxed{t_{1/2} \approx 1.7 \times 10^{8}\ \textit{years}}$$

S6. Molecular Spring Constant Calculation

Gaussian 09 software was used to carry out all the theoretical studies.[S4-S5] DFT calculations were performed with the B3LYP exchange-correlation functional by using 6-311g(2d,p) basis set for H, C, and N atoms.[S5] Initially, ground state geometry optimizations were carried out at B3LYP/6-31g(2d,p) for **HELI-1** and **HELI-3** in the gas phase to reduce the computational cost. The distance between the two carbon atoms at the end of the molecule was r = 5.24 Å and 4.47 Å for **HELI-1** and **HELI-3,** respectively. A relaxed potential energy surface was scanned with 10 steps in 0.2 Å increments at B3LYP/6-311g(2d,p) for both molecules. Molecular geometry was optimized in each step with a fixed distance between the two carbon atoms (r). The change of potential energy upon elongation of the distance between two carbon atoms is plotted and fitted based on the following equation:

$$y = Ax^2$$

where the coefficient A has the unit of kJ·mol^{-1}·Å^{-2}. By comparing the equation 1 with ΔE=(1/2)·k·(Δr^2), where E = relative energy, k = force constant, and r = the elongation of the distance between the two carbon atoms at the edge of the molecule, the force constant k (N·m^{-1}) was calculated from A (kJ·mol^{-1}·Å^{-2}) as follows: k=(2×10^{23}·N_A^{-1})·A, where N_A is the Avogadro constant. From this result, the force constant of the molecular spring was determined.

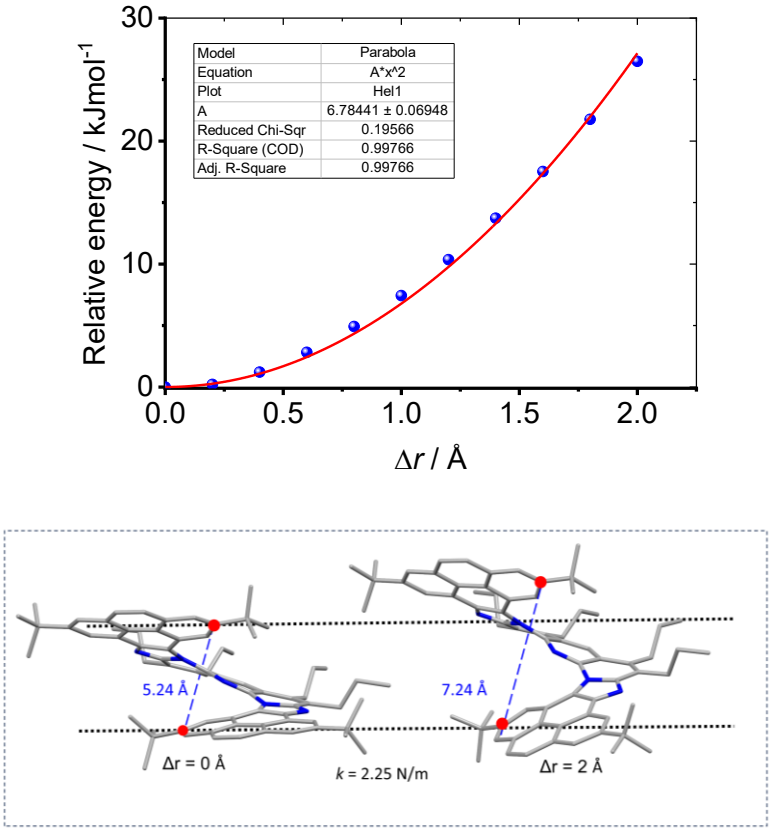


Figure S5a. Spring constant at B3LYP/6-311g (2d,p) level of theory for **HELI-1**.

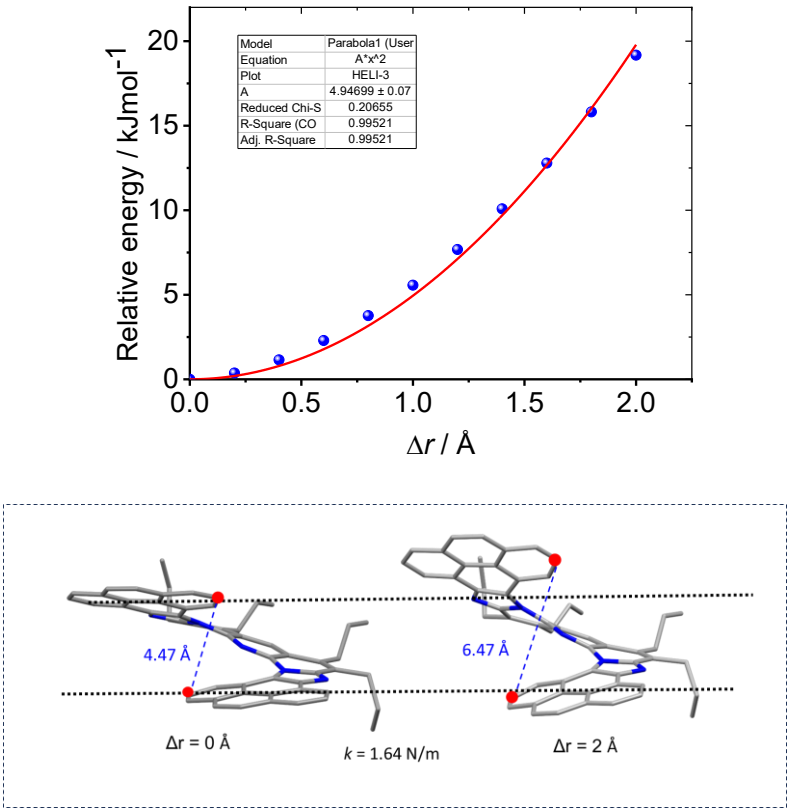


Figure S5b. Spring constant at B3LYP/6-311g (2d,p) level of theory for **HELI-3**.

S7. Resolution of HELI-1 and HELI-2 by Chiral HPLC

The *P*/*M* enantiomers of the poly-aza[9]-helicenes **HELI-1** were separated using an Agilent 1260 Infinity II HPLC system equipped with the CHIRALPAK-IB (250 mm × 4.6 mm) column, and for **HELI-2**, the CHIRALPAK IA-3 (250 mm × 4.6 mm) column. The eluent was n-hexane/isopropanol (90:10) with a 1 mL/min flow rate at 25 °C. The amount of sample injection was 10 μL of an approximate 0.33 mg/mL solution in the corresponding eluent. The chromatograms below were obtained using a detection wavelength of 260 nm.

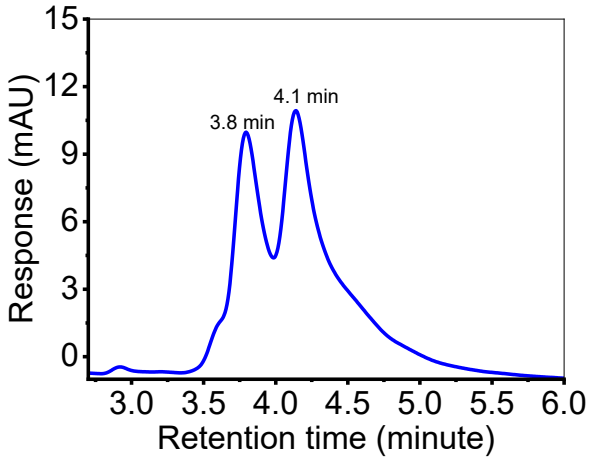


Figure S6. HPLC chromatogram of (*P*)/(*M*)- **HELI-1.**

Peak Analysis Data:

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%
1	(M)-**HELI-1**	VWD1B Wavelength = 260 nm	3.798	126.708	42.828	7.443	48.18
2	(P)-**HELI-1**	VWD1B Wavelength = 260 nm	4.139	169.145	57.172	8.004	51.82

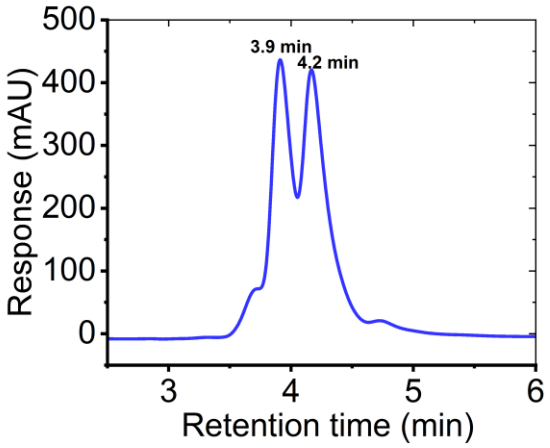


Figure S7. HPLC chromatogram of (*P*)/(*M*)- **HELI-2.**

Peak Analysis Data:

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%
1	(M)-**HELI-2**	VWD1B Wavelength = 260 nm	3.911	4266.48	49.68	318.84	51
2	(P)-**HELI-2**	VWD1B Wavelength = 260 nm	4.167	4320.54	50.31	306.35	49

S8. Spectroscopic Measurements

Steady-state absorption spectra were recorded on Cary 100 UV-Vis spectrophotometer. Conventional quartz cells of 1 cm path length were used for all the measurements. All steady-state fluorescence measurements were carried out on the HORIBA Fluoromax spectrofluorimeter. The fluorescence and UV-Vis spectra were recorded by using a 1.0 cm path-length quartz cuvette. Both excitation and emission slit were kept at 1 nm while recording the fluorescence spectra. All the experiments were carried out at ambient temperature (298K). Fluorescence quantum yields were determined by comparison with Coumarin 30 dye in CH_3CN (Φ_f = 0.67) for **HELI-2** and Rhodamine B in EtOH (Φ_f = 0.49) for the protonated **HELI-2** using the following equation:

$$\Phi_{f,i} = \Phi_{f,s} * \frac{F_i}{F_s} * \frac{f_s}{f_i} * \frac{n_i^2}{n_s^2}$$

where Φ_f = fluorescence quantum yield, subscript *i* denotes sample, and the subscript *s* refers to the standard dye, F = fluorescence integral, *n* = refractive index of the solvent, *f*

is the absorption factor at the excitation wavelength given by the following equation $f = 1 - 10^{-Abs}$, where Abs is the absorbance at the excitation wavelength. The excitation wavelength for the **HELI-2** compound was 420 nm.

Time-resolved fluorescence spectroscopy: Fluorescence lifetimes were measured on a FLS1000 spectrometer, Edinburgh Instruments, by the time-correlated single-photon-counting 2 (TCSPC) method. A 405 nm LED with a pulse repetition rate of 1 MHz was used as the light source. The instrument response function (IRF) was collected by using a scatterer (Ludox AS40 colloidal silica, Sigma-Aldrich).

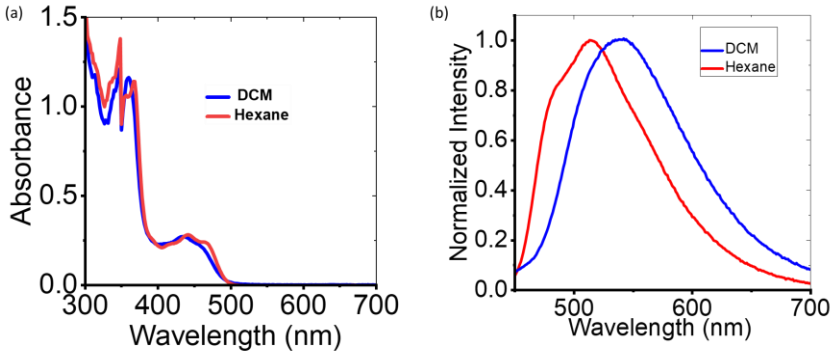


Figure S8. (a) Absorption and (b) emission spectra of **HELI-1** in hexane and in dichloromethane (DCM) (λ_{ex} = 435 nm). Concentration = 16 μM.

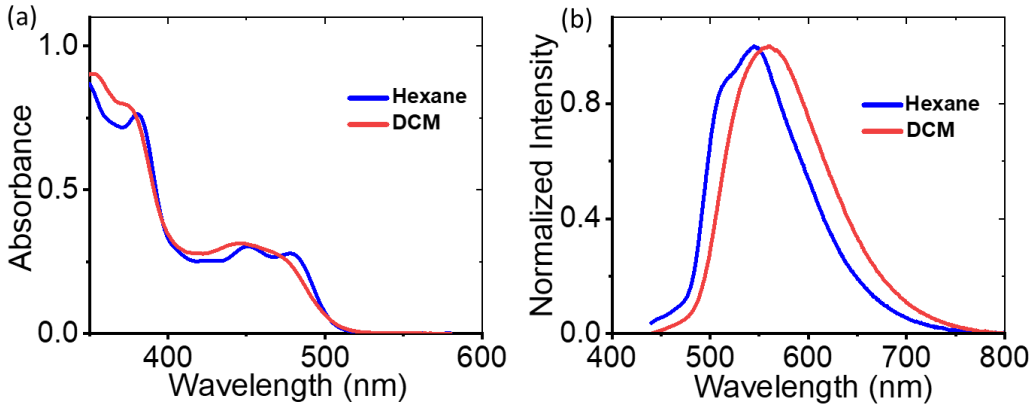


Figure S9. (a) Absorption and (b) emission spectra of **HELI-2** in hexane, and in dichloromethane (DCM) (λ_{ex} = 435 nm). Concentration = 15 mM.

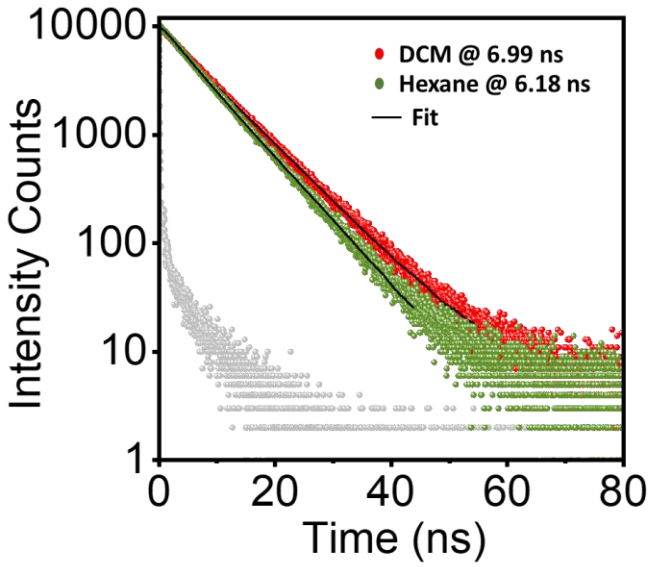


Figure S10. Fluorescence lifetime of **HELI-1** (16 mM) in dichloromethane

Table S3. Solvent-dependent photophysical properties of **HELI-1**

#	Solvent	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ (%)	τ (ns)
1	Hexane	435	513	28	6.18
2	Dichloromethane	431	540	32	6.99

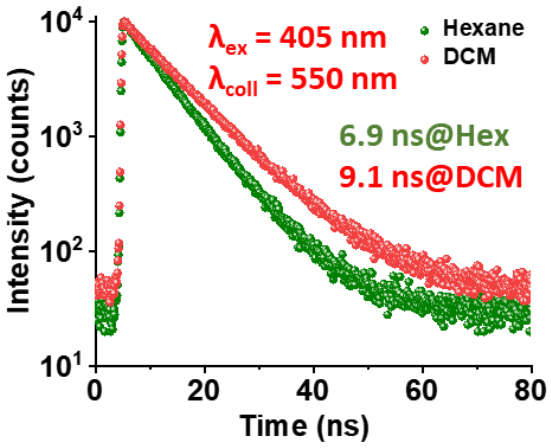


Figure S11. Fluorescence lifetime of **HELI-2** (15 μM) in dichloromethane.

Table S4. Solvent-dependent photophysical properties of **HELI-2**

#	Solvent	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ (%)	τ (ns)
1	Hexane	450	555	30	6.9
2	Dichloromethane	446	560	38	9.1

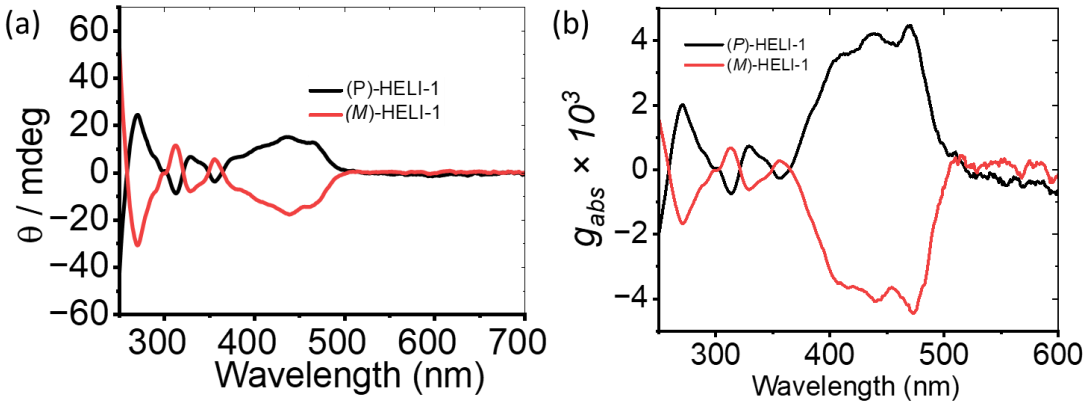


Figure S12. (a) CD spectra of (*P*)-**HELI-1** (black) and (*M*)-**HELI-1** (red) in DCM. (b) Absorption dissymmetry factors of (*P*)-**HELI-**1 (black) and (*M*)-**HELI-1** (red) in DCM. Concentration = 15 μM.

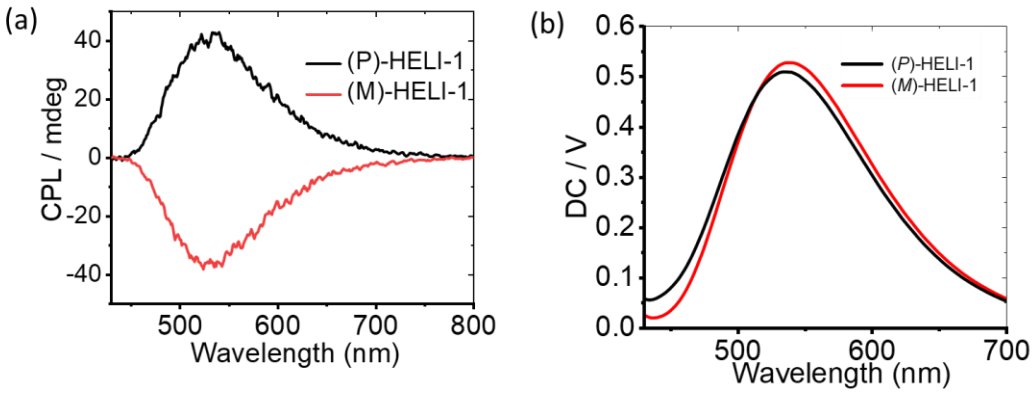


Figure S13. (a) CPL spectra and (b) corresponding DC volt spectra of (*P*)-**HELI-1** and (*M*)-**HELI-1** (15 μM) in DCM (λ_{ex} = 330 nm).

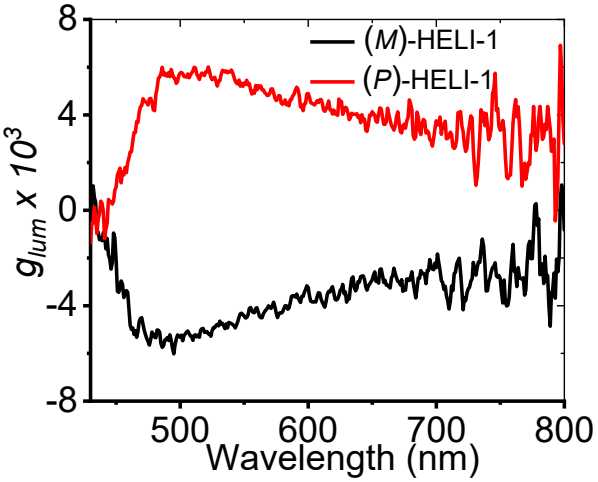


Figure S14. Luminescence dissymmetry factors of (*P*)-**HELI-1** and (*M*)-**HELI-1** in DCM (λ_{ex} = 330 nm).

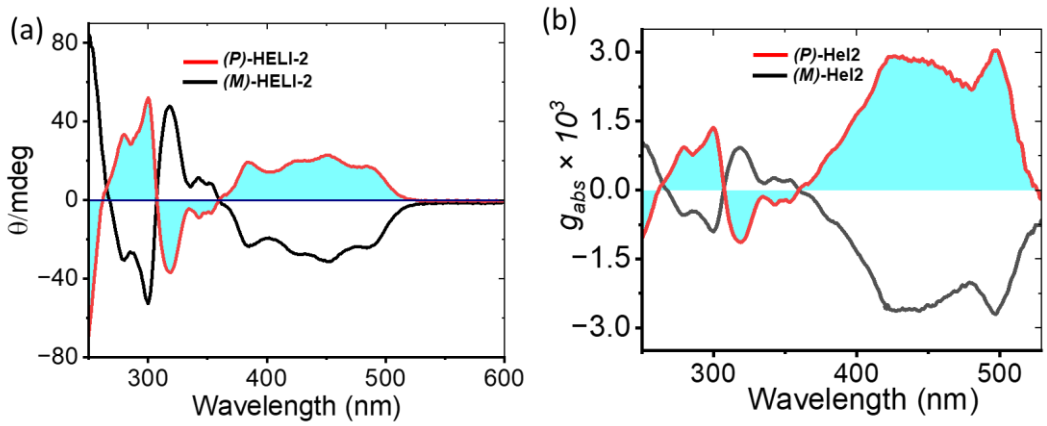


Figure S15. (a) CD spectra of *(P)*-**HELI-2** (red) and (*M*)-**HELI-2** (black) in hexane. (b) Absorption dissymmetry factors of (*P*)-**HELI-2** (red) and (*M*)-**HELI-2** (black) in hexane. Concentration = 18 μM.

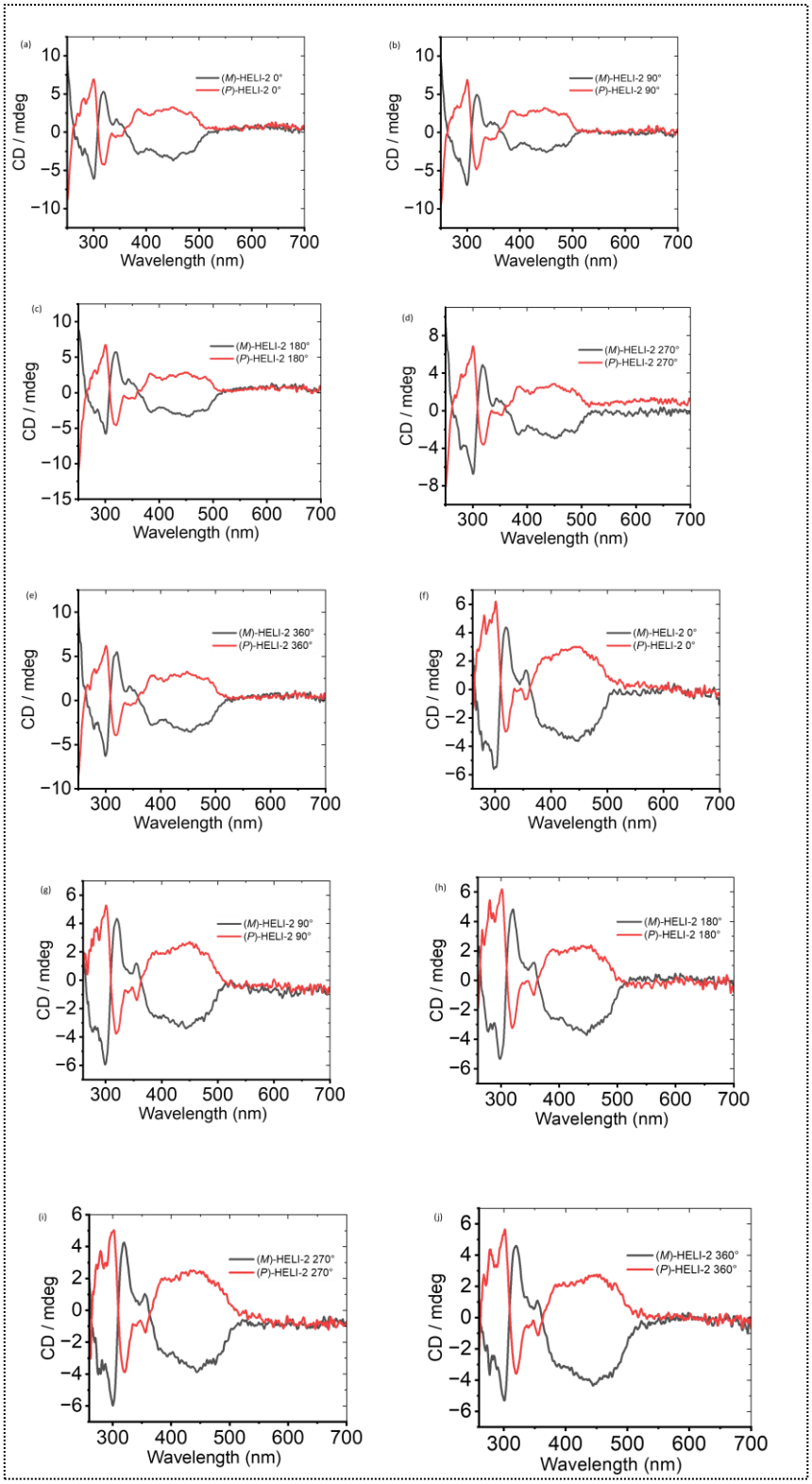


Figure S16. (a)–(e) CD spectra of *(P)*-**HELI-2** (red) and (*M*)-**HELI-2** (black) in hexane after rotation of the cuvette 0° to 360°. Concentration = 2.5 μM. (f)–(j) CD spectra of *(P)*-**HELI-2** (red) and (*M*)-**HELI-2** (black) in dichloromethane after rotation of the cuvette 0° to 360°. Concentration = 2.5 μM.

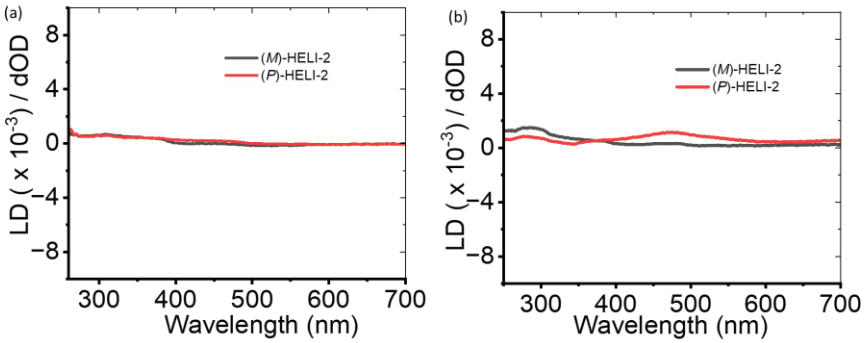


Figure S17. (a) LD spectra of *(P)*-**HELI-2** (red) and (*M*)-**HELI-2** (black) in dichloromethane, (b) LD spectra of *(P)*-**HELI-2** (red) and (*M*)-**HELI-2** (black) in hexane. Concentration = 2.5 μM.

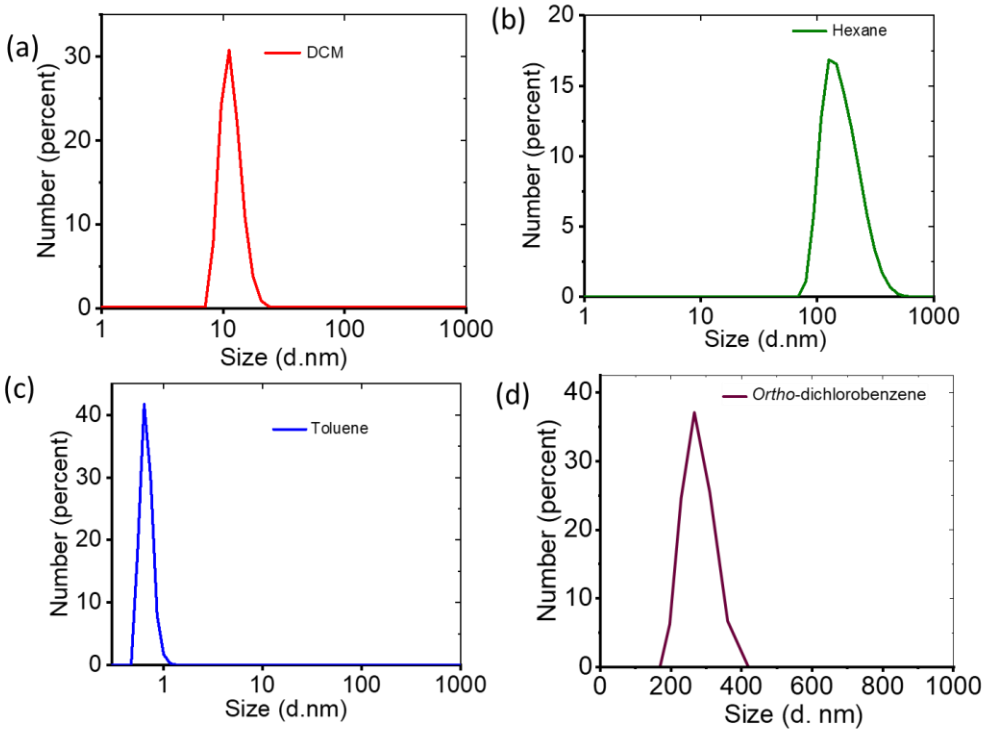


Figure S18. DLS of **HELI-2** at different solvents (DCM, hexane, toluene, and *ortho*-dichlorobenzene) with 18 μM concentration.

Inference: **HELI-2** is monomeric in DCM and toluene, and it is in an aggregated state in hexane and *ortho*-dichlorobenzene.

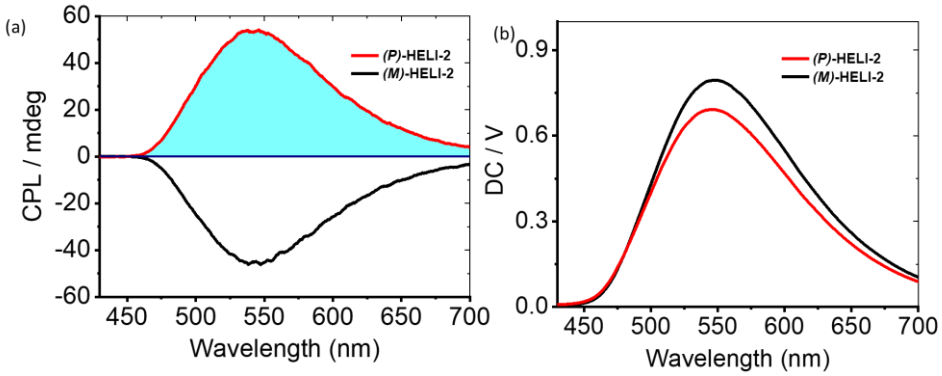


Figure S19. (a) CPL spectra and (b) corresponding DC spectra of (*P*)-**HELI-2** and (*M*)-**HELI-2** (18 μM) in hexane (λ_{ex} = 330 nm).

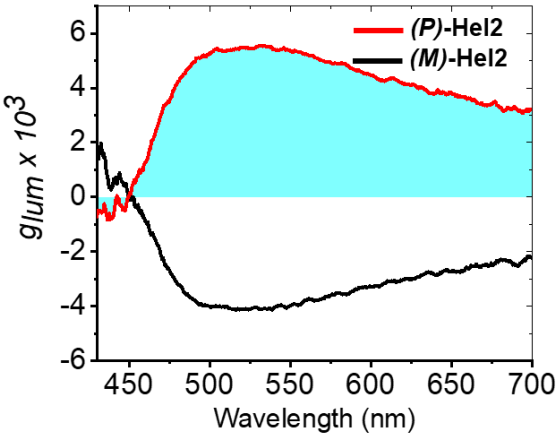


Figure S20. Luminescence dissymmetry factors of (*P*)-**HELI-2** and (*M*)-**HELI-2** in hexane (λ_{ex} = 330 nm).

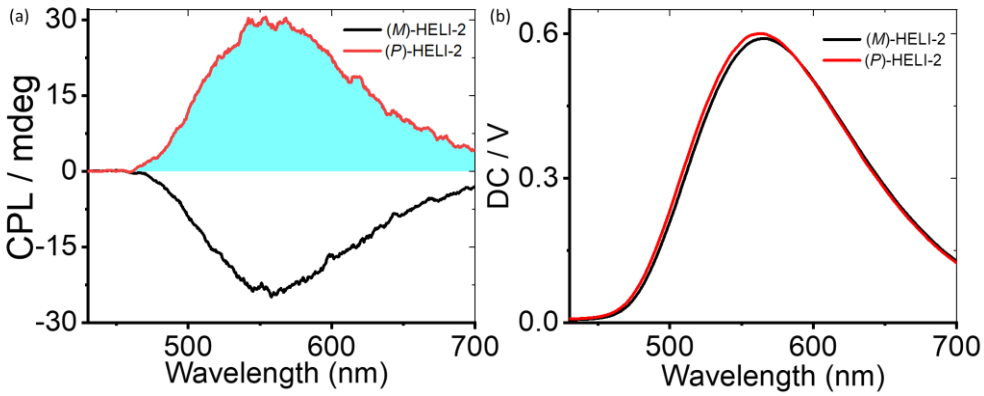


Figure S21. (a) CPL spectra and (b) corresponding DC volt spectra of (*P*)-**HELI-2** and (*M*)-**HELI-2** (18 μM) in DCM (λ_{ex} = 330 nm).

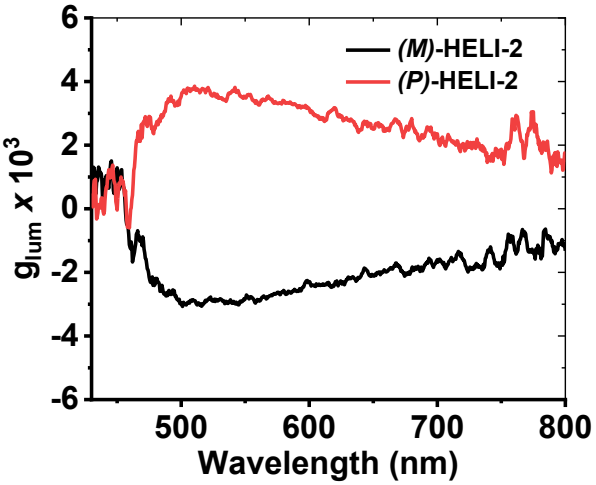


Figure S22. Luminescence dissymmetry factors of (*P*)-**HELI-2** and (*M*)-**HELI-2** in DCM (λ_{ex} = 330 nm).

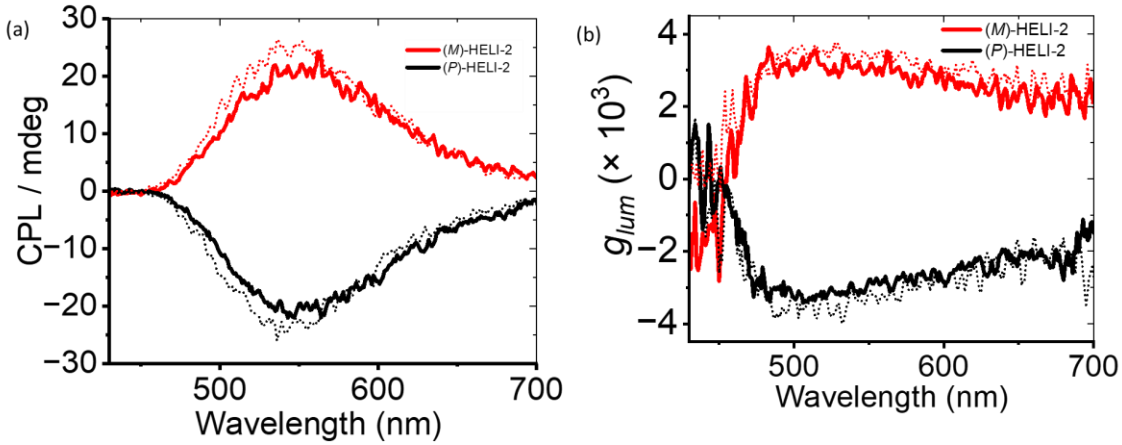


Figure S23. (a) CPL spectra of (*P*)-**HELI-2** and (*M*)-**HELI-2** (8 μM) in DCM (solid line) and toluene (dotted line) (λ_{ex} = 330 nm). (b) Luminescence dissymmetry factors of (*P*)-**HELI-2** and (*M*)-**HELI-2** (8 μM) in DCM (solid line) and toluene (dotted line) (λ_{ex} = 330 nm).

S9. Variable Temperature CD and CPL Studies

S9.1. CD Study in Toluene

Variable temperature CD measurements were performed in JASCO J-815 CD spectrometer equipped with a Peltier MCB-100. For both the enantiomers *P* and *M,* the sample preparation was done in toluene, and the concentration was maintained at 8 μM. After reaching the desired temperature, 6 CD measurements were done with a 10-minute interval.

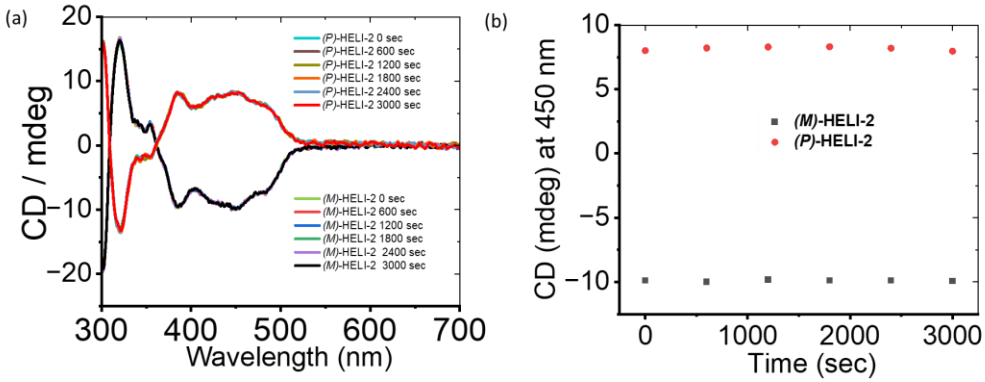


Figure S24. (a) CD spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 25 °C. (b) Variation of the CD signal of (*P*)/(*M*)-**HELI-2** in toluene at 450 nm with time.

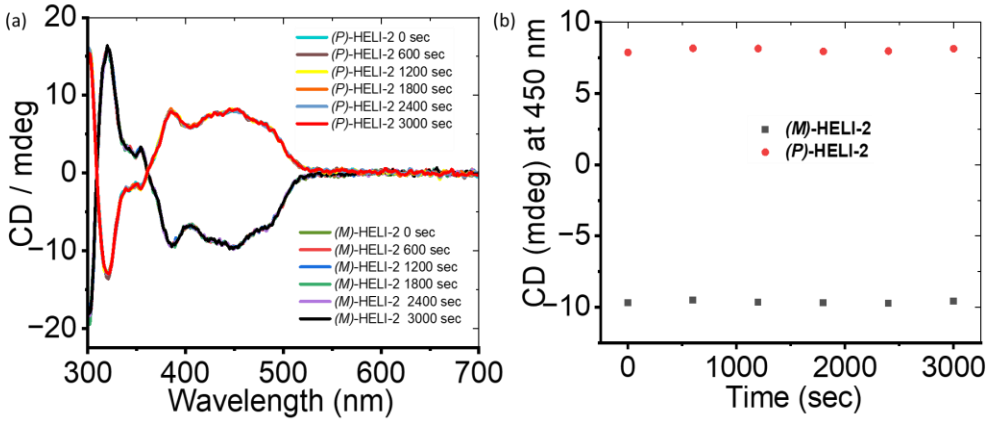


Figure S25. (a) CD spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 35 °C. (b) Variation of the CD signal of (*P*)/(*M*)-**HELI-2** in toluene at 450 nm with time.

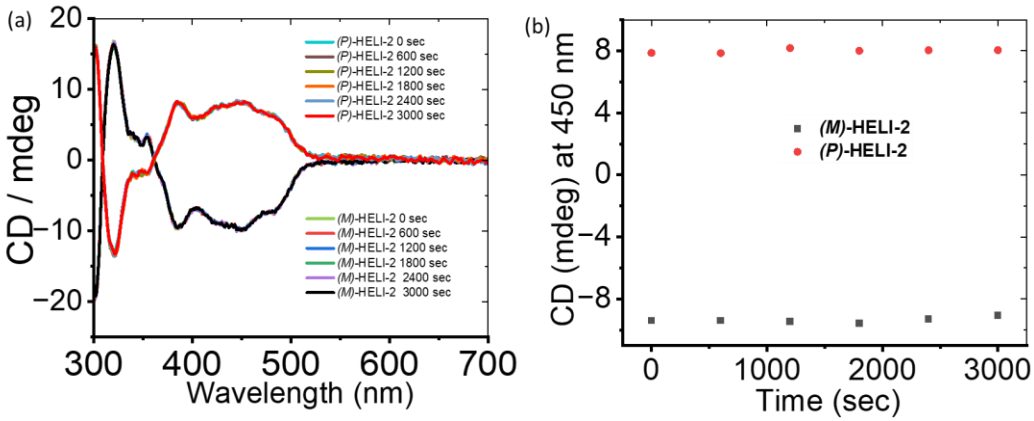


Figure S26. (a) CD spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 45 °C. (b) Variation of the CD signal of (*P*)/(*M*)-**HELI-2** in toluene at 450 nm with time.

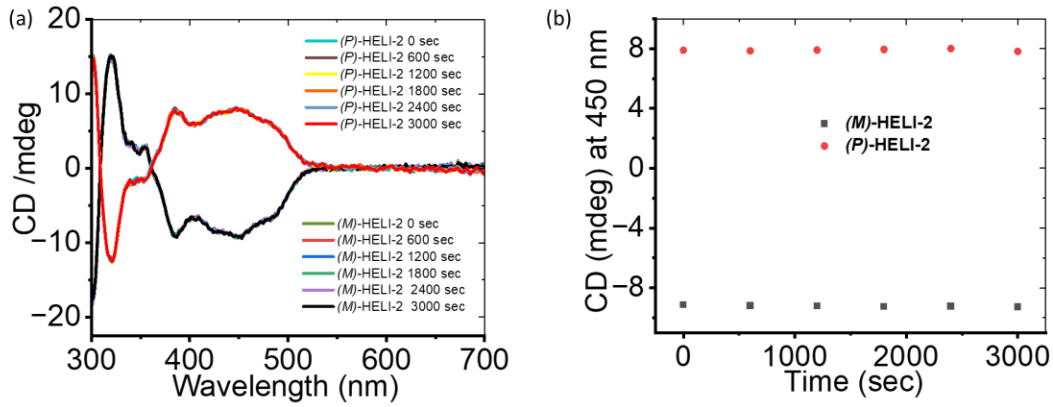


Figure S27. (a) CD spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 55 °C. (b) Variation of the CD signal of (*P*)/(*M*)-**HELI-2** in toluene at 450 nm with time.

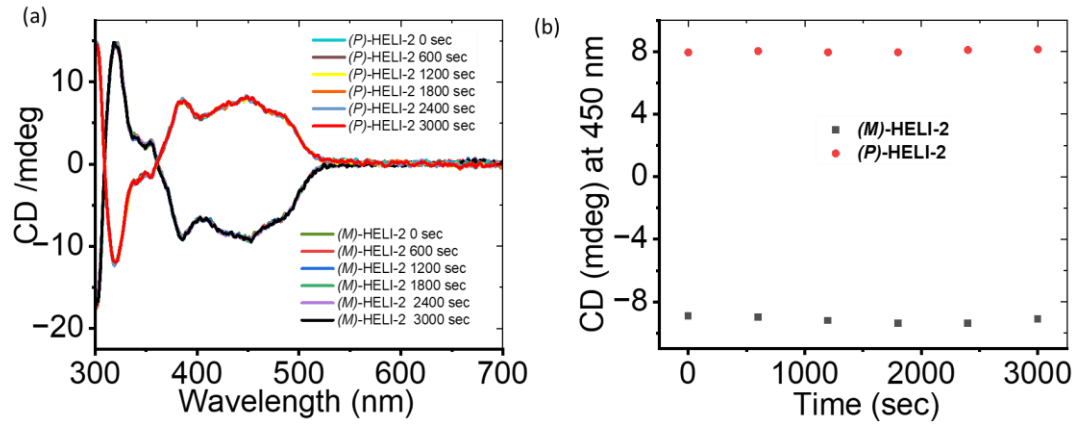


Figure S28. (a) CD spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 65 °C. (b) Variation of the CD signal of (*P*)/(*M*)-**HELI-2** in toluene at 450 nm with time.

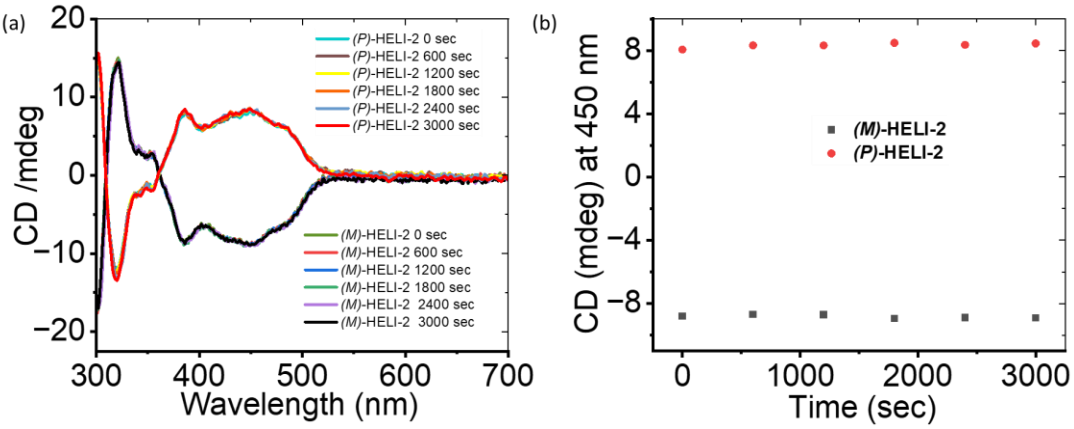


Figure S29. (a) CD spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 75 °C. (b) Variation of the CD signal of (*P*)/(*M*)-**HELI-2** in toluene at 450 nm with time.

S9.2. CD Study in *Ortho*-dichlorobenzene

Variable temperature CD measurements were performed in JASCO J-1500 spectrometer with a Peltier CTU-100. For both the enantiomers *P* and *M,* the sample preparation was done in *ortho*-dichlorobenzene, and the concentration was maintained at 8 μM. After reaching the desired temperature, 4 CD measurements were done with a 10-minute interval.

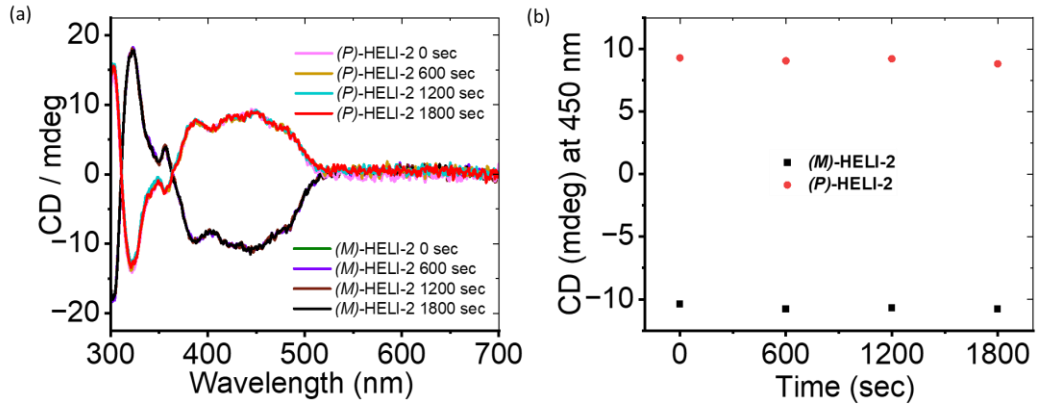


Figure S30. (a) CD spectra of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene (8 μM) at 20 °C. (b) Variation of the CD signal of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene at 450 nm with time.

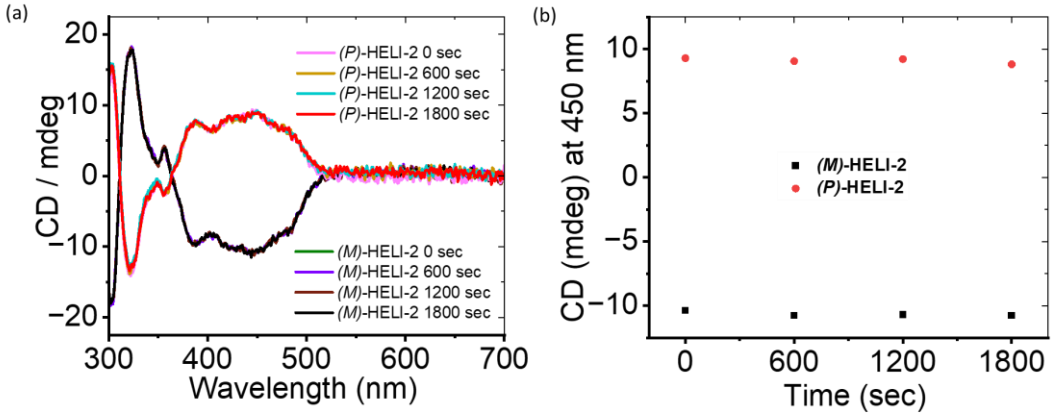


Figure S31. (a) CD spectra of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene (8 μM) at 30 °C. (b) Variation of the CD signal of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene at 450 nm with time.

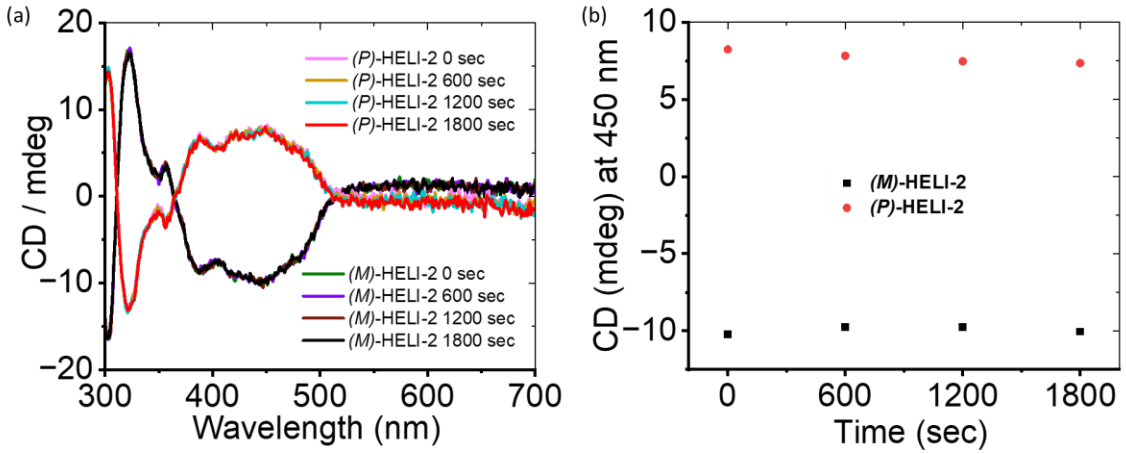


Figure S32. (a) CD spectra of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene (8 μM) at 40 °C. (b) Variation of the CD signal of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene at 450 nm with time.

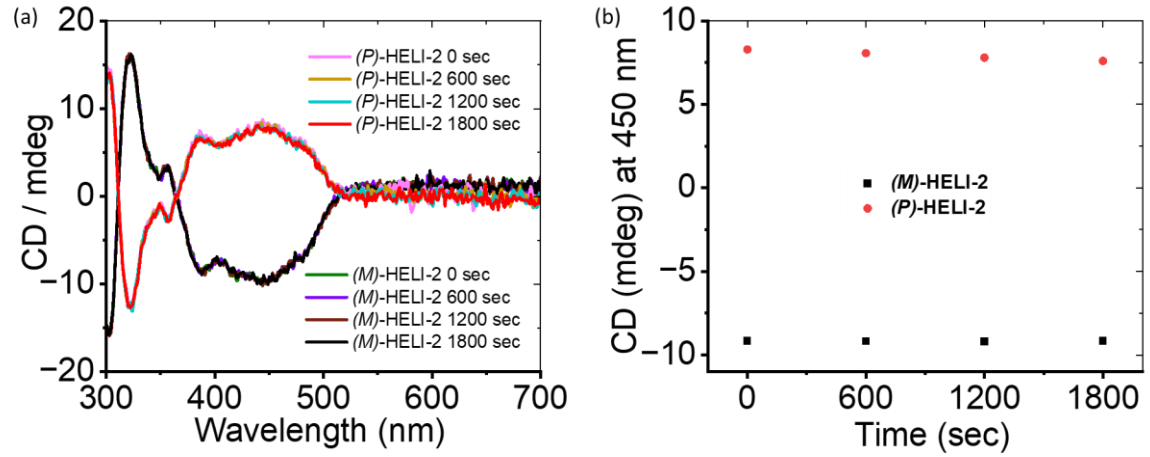


Figure S33. (a) CD spectra of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene (8 μM) at 50 °C. (b) Variation of the CD signal of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene at 450 nm with time.

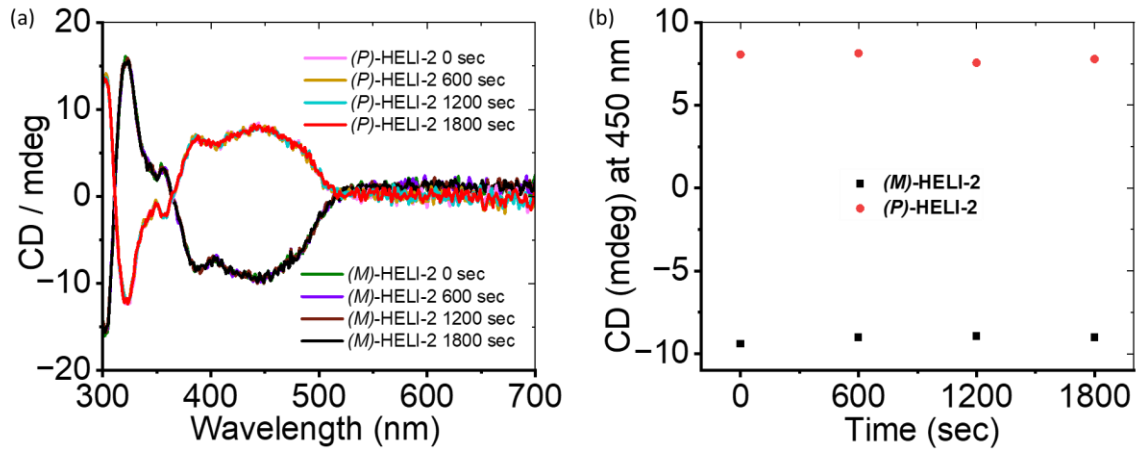


Figure S34. (a) CD spectra of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene (8 μM) at 60 °C. (b) Variation of the CD signal of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene at 450 nm with time.

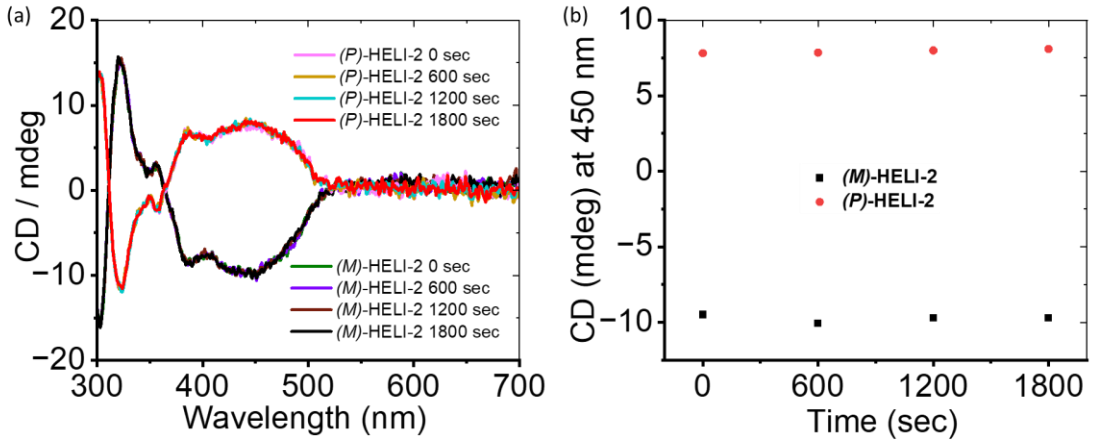


Figure S35. (a) CD spectra of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene (8 μM) at 70 °C. (b) Variation of the CD signal of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene at 450 nm with time.

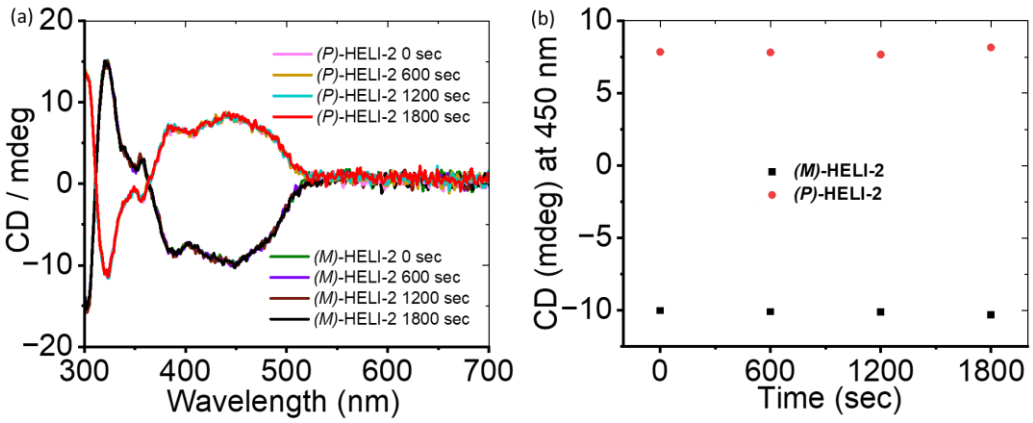


Figure S36. (a) CD spectra of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene (8 μM) at 80 °C. (b) Variation of the CD signal of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene at 450 nm with time.

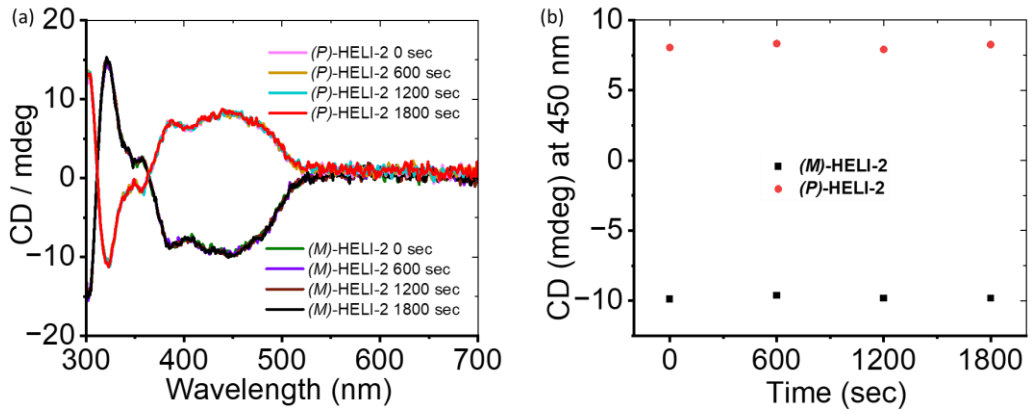


Figure S37. (a) CD spectra of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene (8 μM) at 90 °C. (b) Variation of the CD signal of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene at 450 nm with time.

S9.3. CPL Study in Toluene

For variable temperature CPL measurements, the JASCO CPL-300 equipped with PTC-510 Peltier has been used. For both the enantiomers *P* and *M,* the sample preparation was done in toluene, and the concentration was maintained at 8 μM. Measurement was started at 25 °C and carried out up to 75 °C with a 10 °C increment. After reaching the desired temperature, 6 CPL measurements were taken at 10-minute intervals.

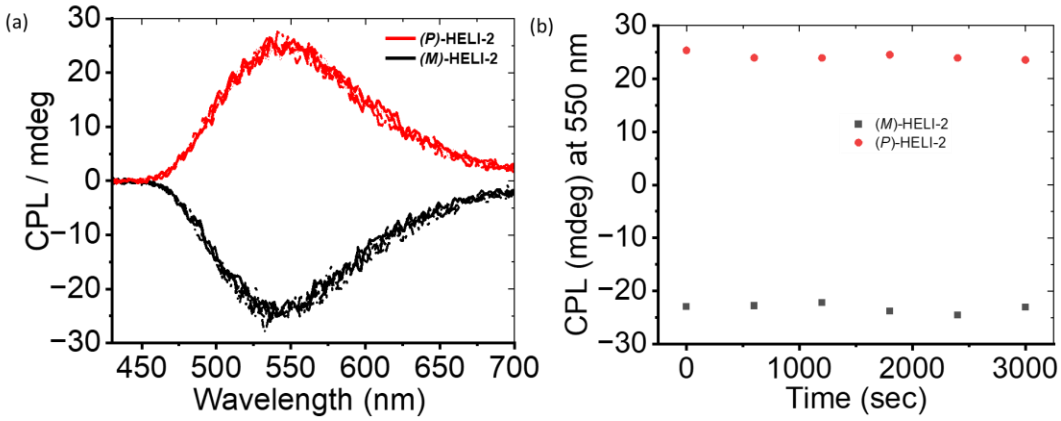


Figure S38. (a) CPL spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 25 °C at time 0 sec (solid red and black lines), and at time 600 sec to 3000 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-**HELI-2** in toluene at 550 nm with time (λ_{ex} = 330 nm).

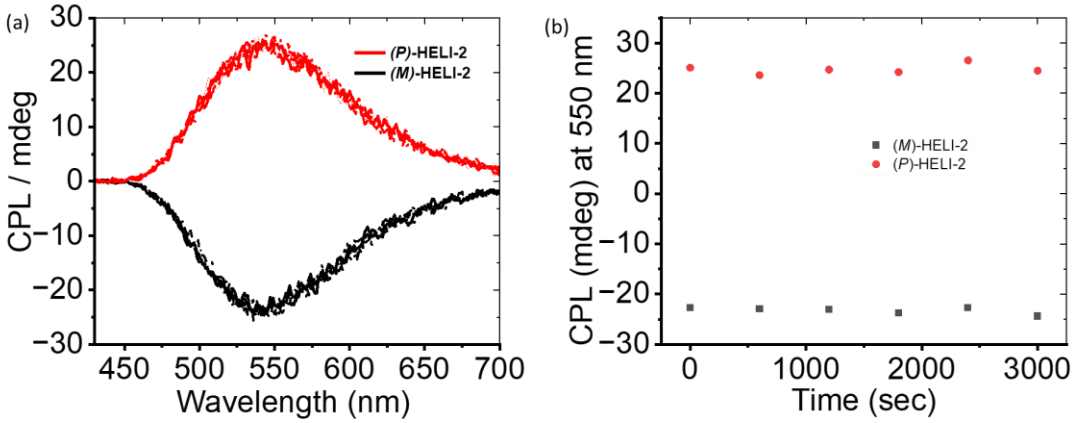


Figure S39. (a) CPL spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 35 °C at time 0 sec (solid red and black lines), and at time 600 sec to 3000 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-**HELI-2** in toluene at 550 nm with time (λ_{ex} = 330 nm).

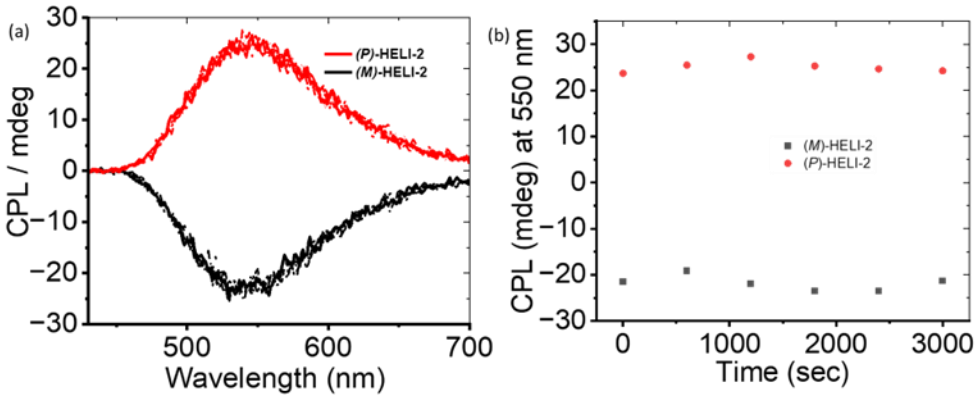


Figure S40. (a) CPL spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 45 °C at time 0 sec (solid red and black lines), and at time 600 sec to 3000 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-**HELI-2** in toluene at 550 nm with time (λ_{ex} = 330 nm).

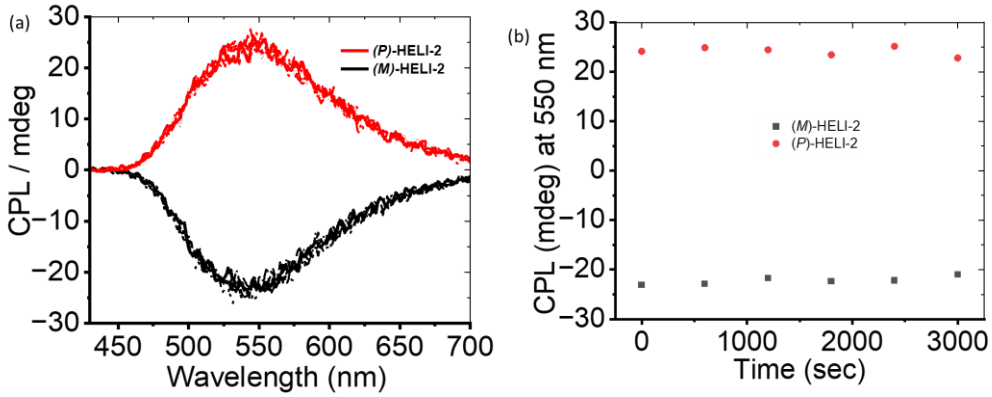


Figure S41. (a) CPL spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 55 °C at time 0 sec (solid red and black lines), and at time 600 sec to 3000 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-**HELI-2** in toluene at 550 nm with time (λ_{ex} = 330 nm).

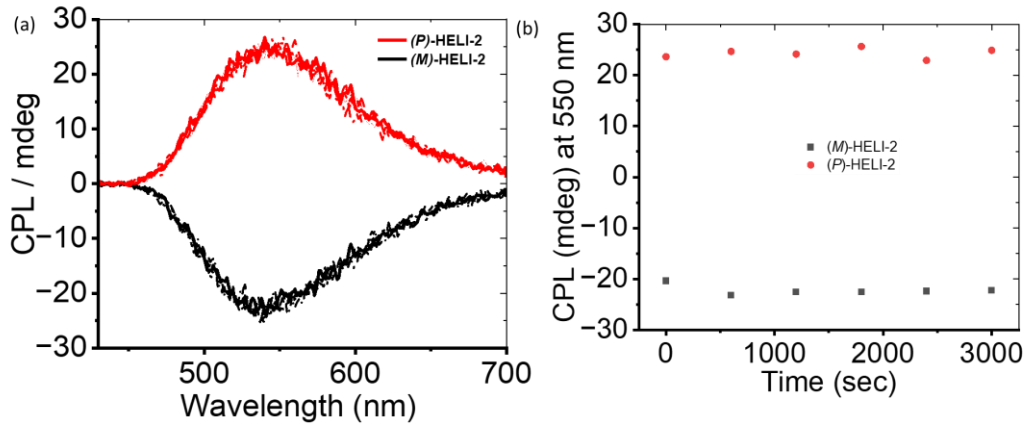


Figure S42. (a) CPL spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 65 °C at time 0 sec (solid red and black lines), and at time 600 sec to 3000 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-**HELI-2** in toluene at 550 nm with time (λ_{ex} = 330 nm).

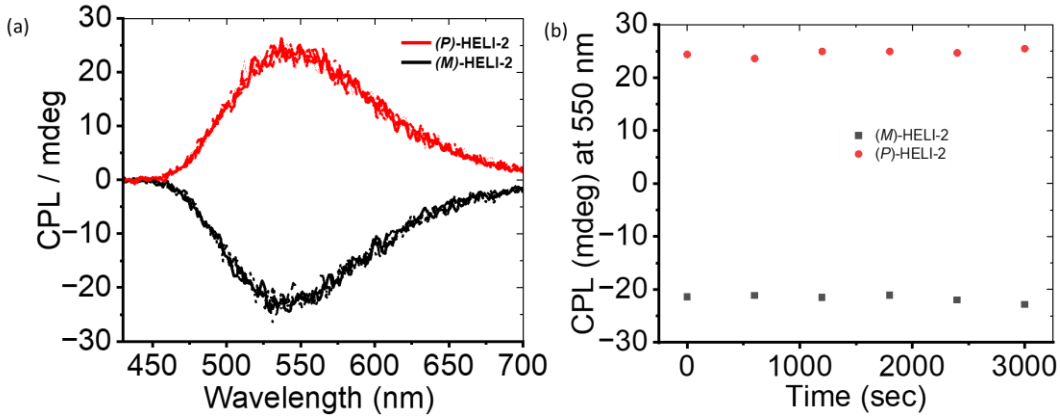


Figure S43. (a) CPL spectra of (*P*)/(*M*)-**HELI-2** in toluene (8 μM) at 75 °C at time 0 sec (solid red and black lines), and at time 600 sec to 3000 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-**HELI-2** in toluene at 550 nm with time (λ_{ex} = 330 nm).

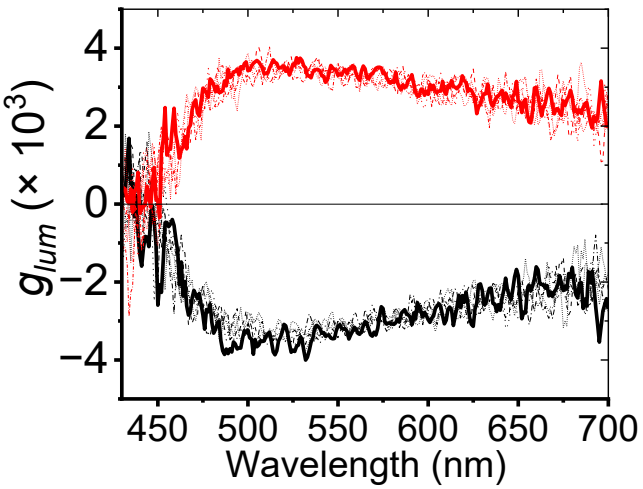


Figure S44. g_{lum} of (*P*)/(*M*)-HELI-2 in toluene at 25 °C (solid red and black lines), and at 35 °C to 75 °C (all dotted red and black lines) (λ_{ex} = 330 nm).

S9.4. CPL Study in *Ortho*-dichlorobenzene

For variable temperature CPL measurements, the JASCO CPL-300 equipped with PTC-510 Peltier has been used. For both the enantiomers *P* and *M,* the sample preparation was done in *ortho*-dichlorobenzene, and the concentration was maintained at 8 μM. Measurement was started at 20 °C and carried out up to 90 °C with a 10 °C increment. After reaching the desired temperature, 4 CPL measurements were taken at 10-minute intervals.

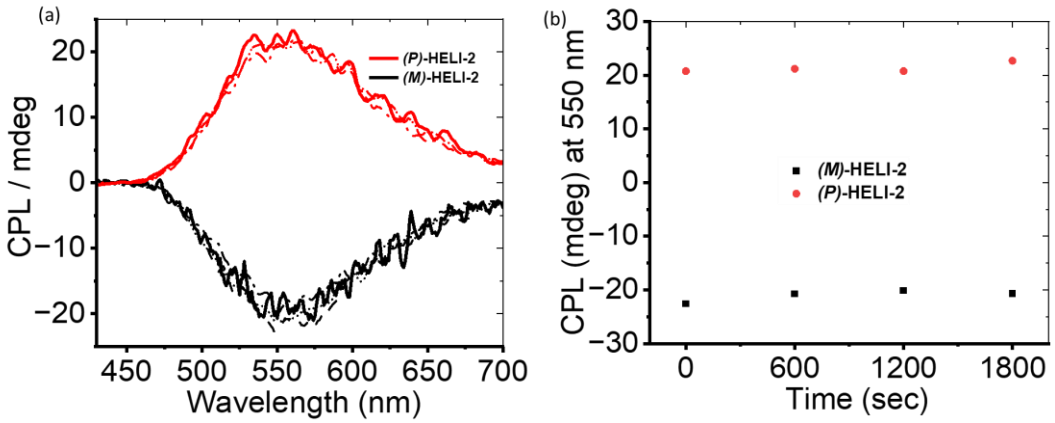


Figure S45. (a) CPL spectra of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene (8 μM) at 20 °C at time 0 sec (solid red and black lines), and at time 600 sec to 1800 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene at 550 nm with time (λ_{ex} = 330 nm).

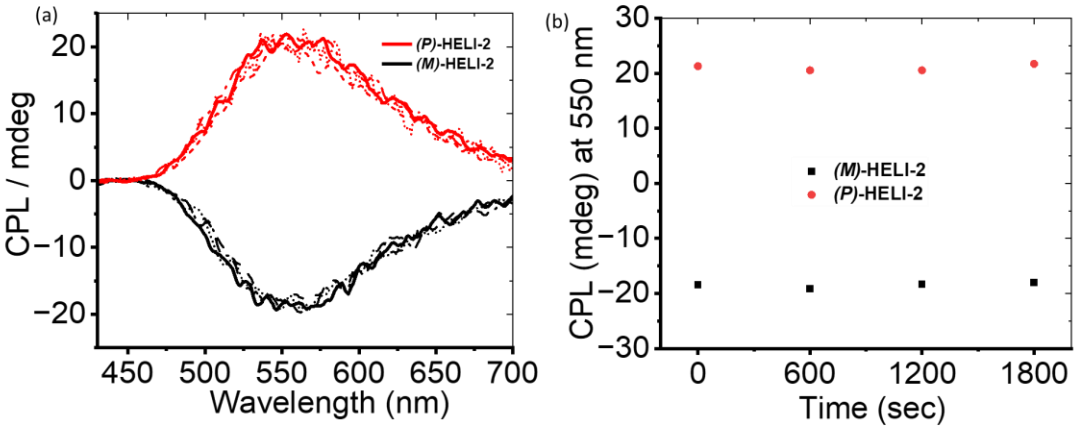


Figure S46. (a) CPL spectra of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene (8 μM) at 30 °C at time 0 sec (solid red and black lines), and at time 600 sec to 1800 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene at 550 nm with time (λ_{ex} = 330 nm).

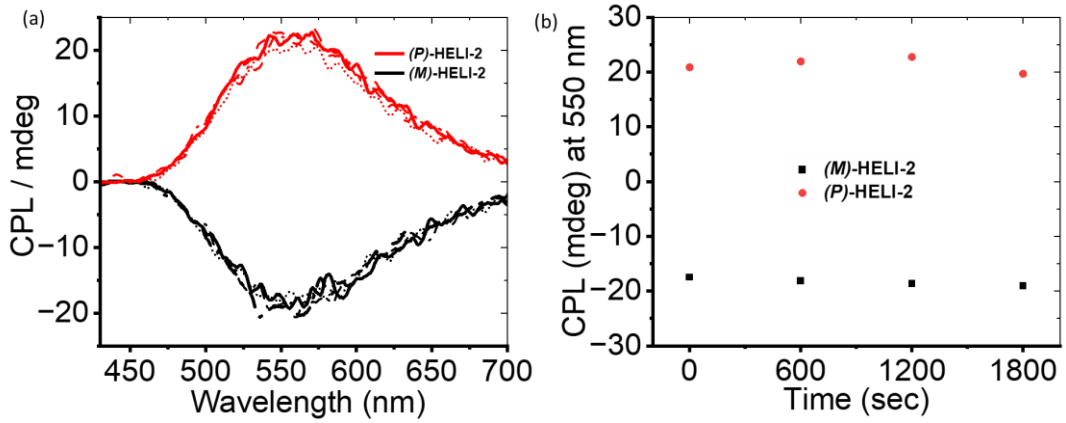


Figure S47. (a) CPL spectra of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene (8 μM) at 40 °C at time 0 sec (solid red and black lines), and at time 600 sec to 1800 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene at 550 nm with time (λ_{ex} = 330 nm).

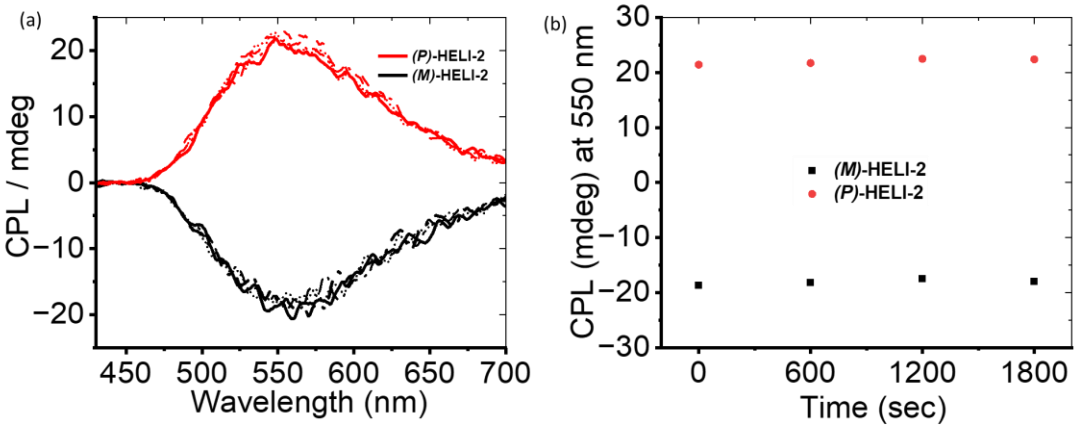


Figure S48. (a) CPL spectra of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene (8 μM) at 50 °C at time 0 sec (solid red and black lines), and at time 600 sec to 1800 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene at 550 nm with time (λ_{ex} = 330 nm).

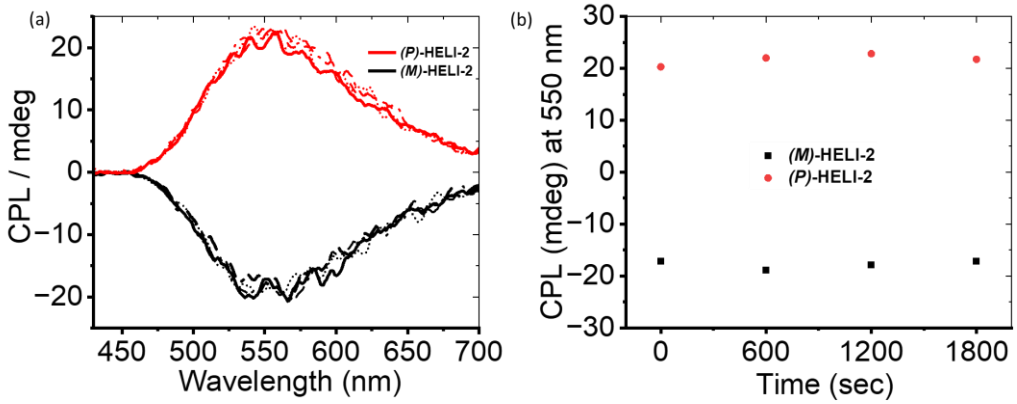


Figure S49. (a) CPL spectra of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene (8 μM) at 60 °C at time 0 sec (solid red and black lines), and at time 600 sec to 1800 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene at 550 nm with time (λ_{ex} = 330 nm).

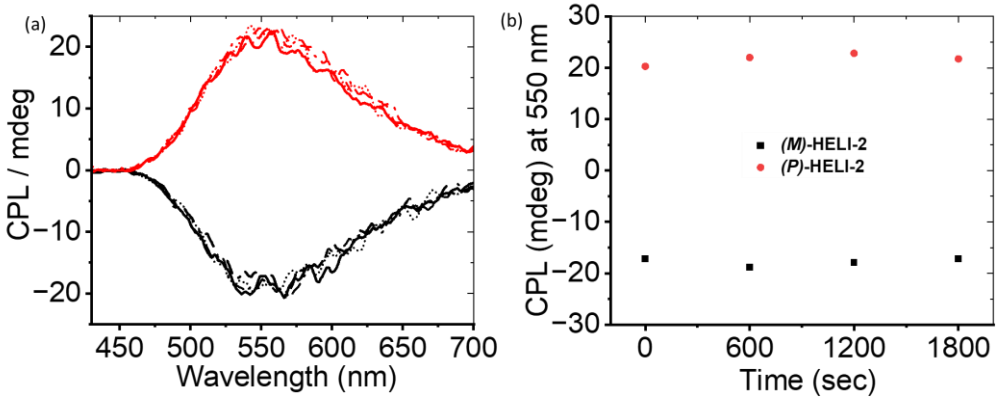


Figure S50. (a) CPL spectra of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene (8 μM) at 70 °C at time 0 sec (solid red and black lines), and at time 600 sec to 1800 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene at 550 nm with time (λ_{ex} = 330 nm).

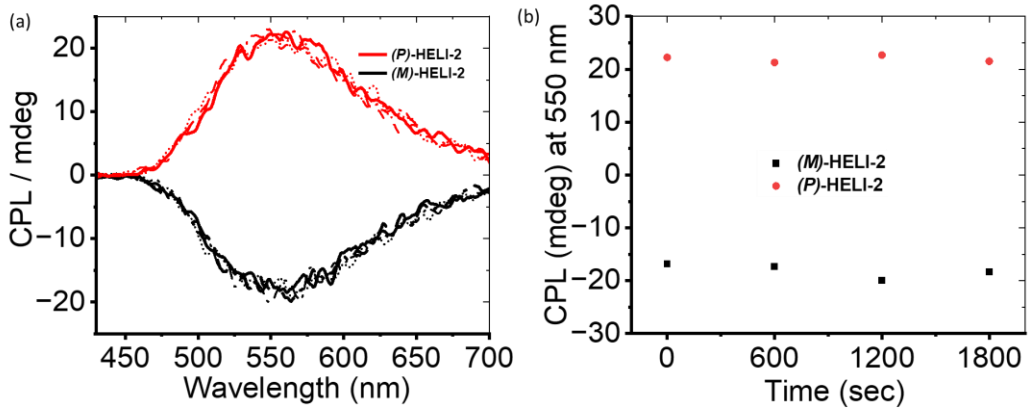


Figure S51. (a) CPL spectra of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene (8 μM) at 80 °C at time 0 sec (solid red and black lines), and at time 600 sec to 1800 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene at 550 nm with time (λ_{ex} = 330 nm).

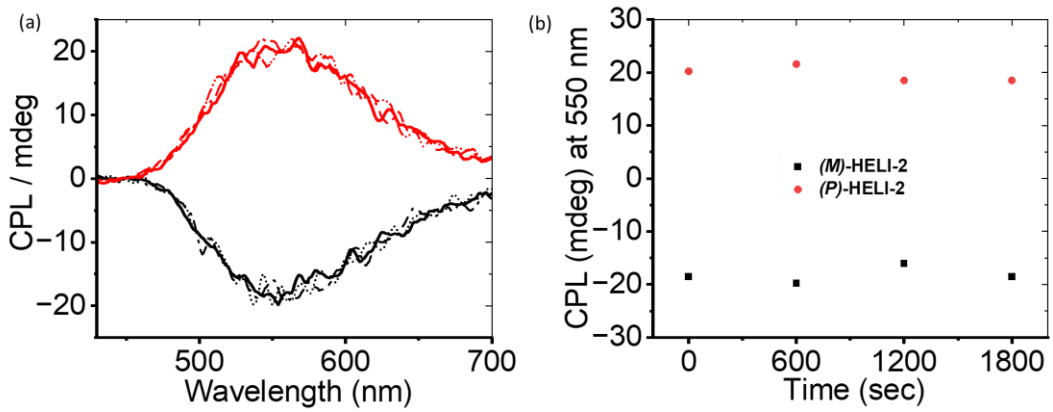


Figure S52. (a) CPL spectra of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene (8 μM) at 90 °C at time 0 sec (solid red and black lines), and at time 600 sec to 1800 sec (all dotted red and black lines). (b) Variation of the CPL signal of (*P*)/(*M*)-**HELI-2** in *ortho*-dichlorobenzene at 550 nm with time (λ_{ex} = 330 nm).

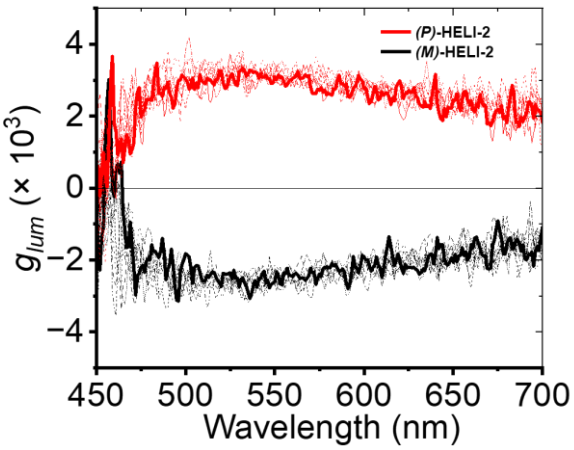


Figure S53. g_{lum} of (*P*)/(*M*)-HELI-2 in *ortho*-dichlorobenzene at 20 °C (solid red and black lines), and at 30 °C to 90 °C (all dotted red and black lines) (λ_{ex} = 330 nm).

S9.5. Thermal Stability Study of *(M)*-HELI-2 at 160 °C

For the thermal stability study, the enantiopure sample was dissolved in *ortho*-dichlorobenzene and heated at 160 °C in an oil bath. At 2 h intervals, the heating was paused, and the solution was allowed to cool to room temperature to record the CD spectrum. After measurement, the sample was reheated to 160 °C to continue the experiment. This procedure was repeated until a total heating duration of 12 h was reached.

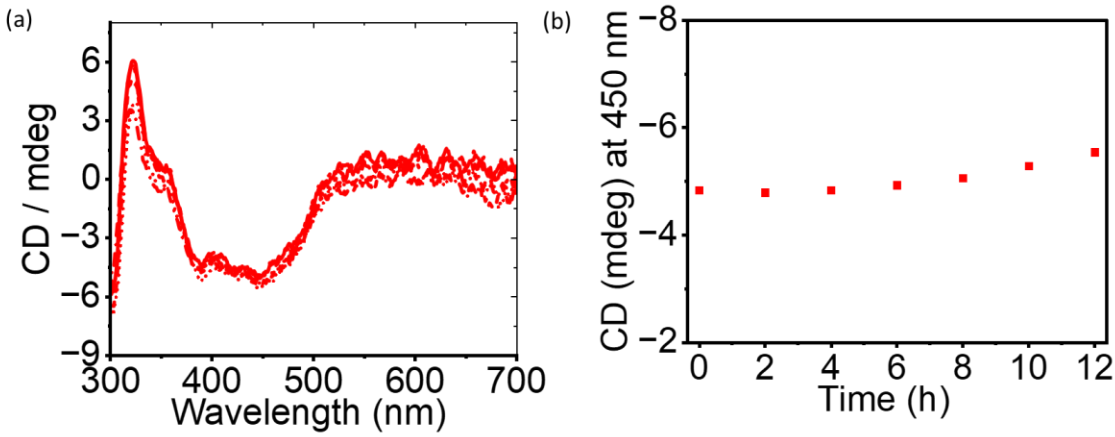


Figure S54. (a) CD spectra of (*M*)-HELI-2 in *ortho*-dichlorobenzene (4 μM) at 160 °C. (b) Variation of the CD signal of (*M*)-HELI-2 in *ortho*-dichlorobenzene at 450 nm with time.

S10. Acid-Base Responsive Reversible Behaviour in the Solution State

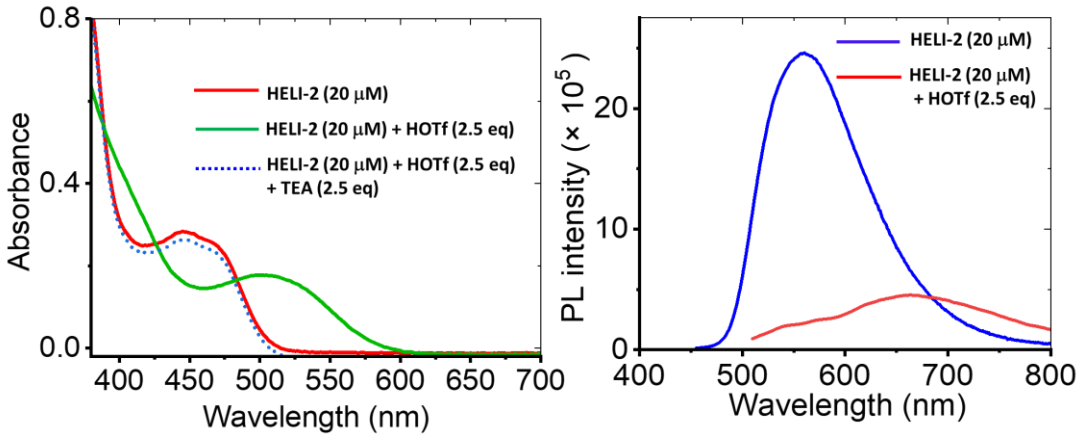


Figure S55. Absorption (left) and emission (right) spectra of **HELI-2** in DCM (20 μM) upon addition of 2.5 equiv. of triflic acid (HOTf), followed by 2.5 equiv. of triethylamine (Et_3N).

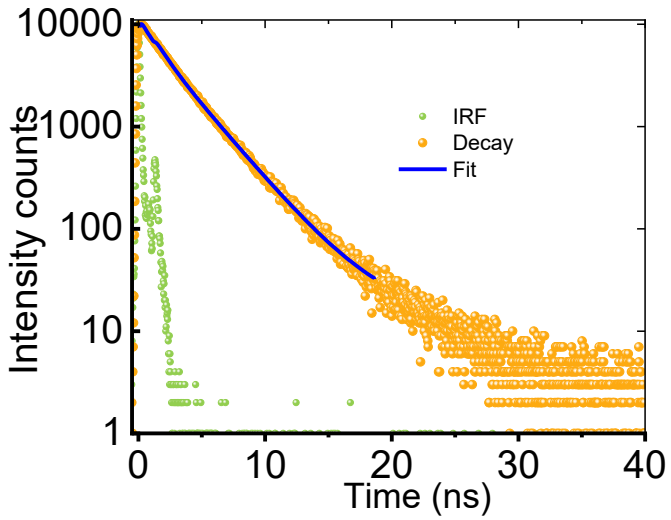


Figure S56. Fluorescence lifetime of protonated **HELI-2** (15 μM) in dichloromethane.

Table S5. Photophysical properties of protonated **HELI-2** in DCM

λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ (%)	τ (ns)
550	660	2	2.34

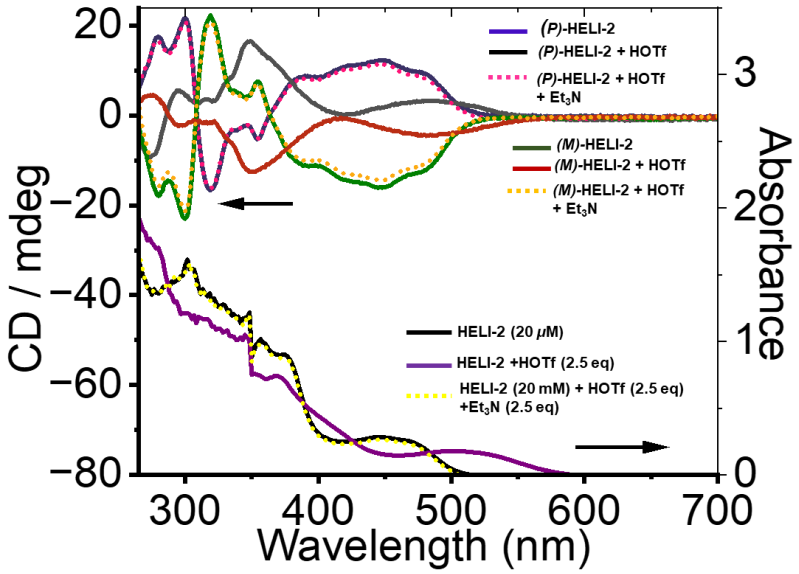


Figure S57. Absorption (bottom; with right-hand-side Y-axis) and CD (top; with left-hand-side Y-axis) spectra of (*P/M*)-**HELI-2** in DCM (8 μM) upon addition of 2.5 equiv. (for absorption) or 50 equiv. (for CD) of triflic acid (HOTf), followed by 2.5 equiv. (for absorption) or 50 equiv. (for CD) of triethylamine (Et_3N).

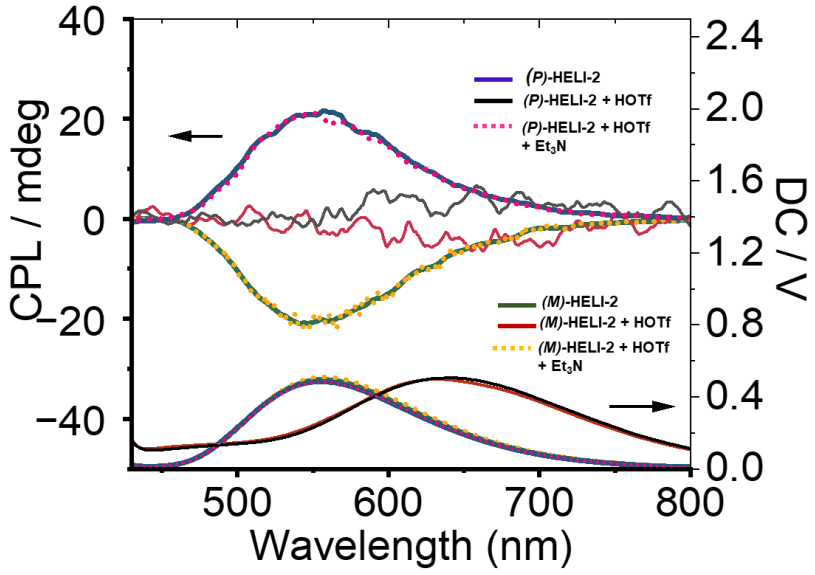


Figure S58. CPL (top; with left-hand-side Y-axis) and corresponding DC volt (bottom; with right-hand-side Y-axis) spectra of (*P/M*)-**HELI-2** in DCM (8 μM) upon addition of 50 equiv. of triflic acid (HOTf), followed by 50 equiv. of triethylamine (Et_3N) (λ_{ex} = 330 nm).

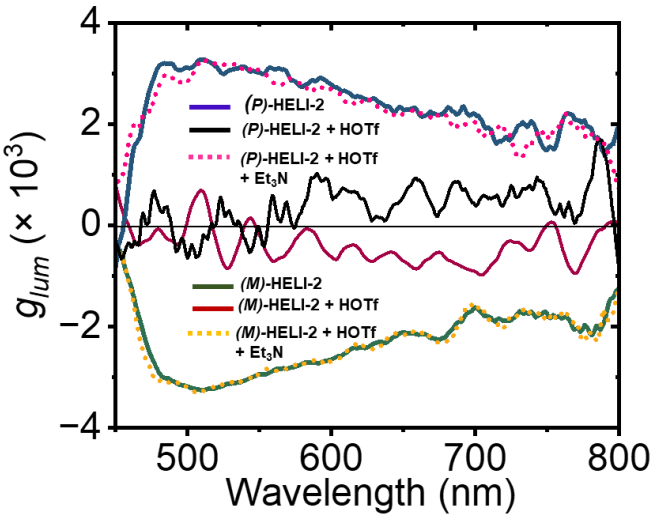


Figure S59. Luminescence dissymmetry factors of (*P*/*M*)-**HELI-2** in DCM upon addition of 50 equiv. of triflic acid (HOTf), followed by 50 equiv. of triethylamine (Et_3N) (λ_{ex} = 330 nm).

S11. Monitoring Stepwise Protonation Process by ^{1}H NMR Spectroscopy

A controlled stepwise protonation process was monitored by NMR titration experiment with **HELI-2** by addition of triflic acid in $CDCl_3$. As typically imidazole ring nitrogen is used to be more basic (pKa of the conjugate acid ~7.0) compared to pyridine ring nitrogen (pKa of the conjugate acid ~5.2), it is expected that the imidazole rings will be protonated first upon addition of triflic acid. It was observed that the H_a, H_e, and H_g protons were affected significantly upon acid addition (**Fig. S60**). In case of the H_e protons, the peak is shifted downfield to 8.29 ppm from 8.20 ppm and finally to 8.38 ppm at the saturation point. Similarly, the H_g proton is also shifted downfield to 8.60 ppm from 8.46 ppm and finally to 8.82 ppm, reaching a saturation point. These downfield shifts should be due to the protonation of the imidazole rings as well as the pyridine ring, making the fused pyrene and pyridine rings electron-deficient, and the effect was dominant on the H_e and H_g protons. However, the pyrene ring protons H_a showed an upfield shift from 9.03 ppm to 8.79 ppm and finally shifted to 8.65 ppm. This upfield shift might be due the interaction of the H_a protons with the OTf^- counter-anions which are introduced after the imidazole-ring protonation with HOTf and might be placed near to these protons. Finally, it was also oberved that the singlet peak due to the H_f protons of the pyrene rings experienced a negligible change (shifted downfield from 7.42 ppm to 7.44 ppm).

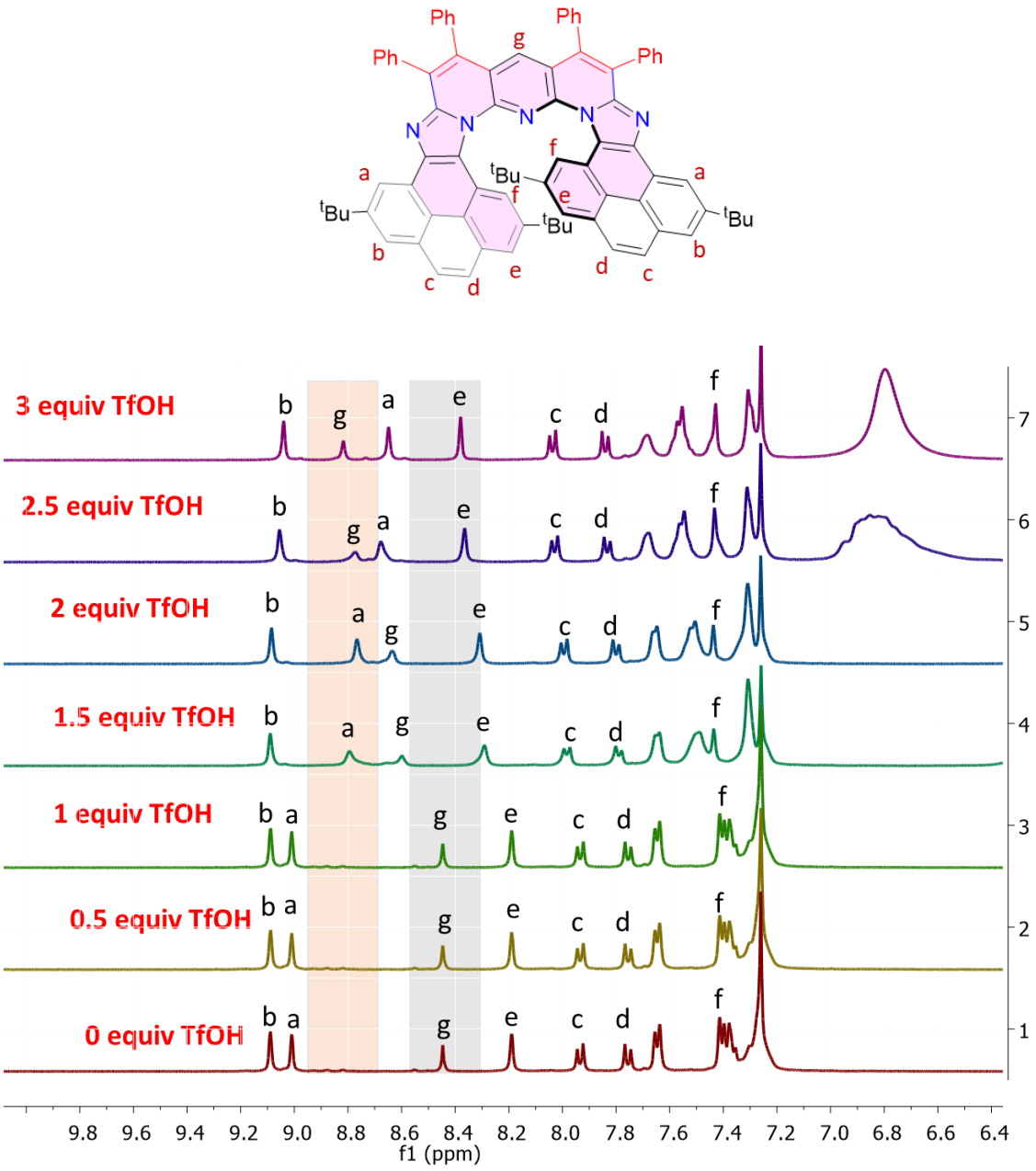


Figure S60. ^{1}H NMR spectra of **HELI-2** (10 mM) in $CDCl_3$ (500 MHz, 298 K) upon stepwise addition of triflic acid (HOTf).

S12. Acid-Base Responsive Reversible Behaviour in the Solid State

For studying the acid-base responsive behaviour in the solid state, thin films of the compounds were made on a quartz slide. At first, enantiomerically pure (*P*) and (*M*) **HELI-2** were dissolved in 50 μL of hexane. Then the solution (6 μM) was dropcast on the quartz slides and left to slow evaporation for 1 hour. CPL was recorded with the dropcast thin

films. After that, the dropcast films were left in triflic acid (HOTf) vapour chamber for 1 hour; a distinct colour change was observed from yellow to reddish orange, and the CPL activity was checked. After that, to regain the CPL activity, the protonated thin film was placed in a triethylamine (NEt_3) vapour chamber, and within 15 minutes, it retained its original yellow color, and the CPL activity was also restored.

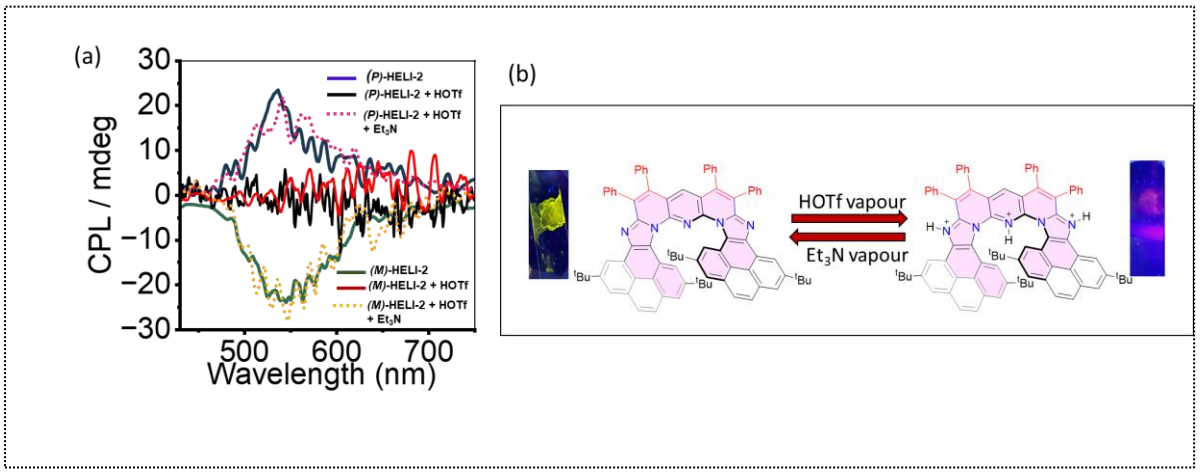
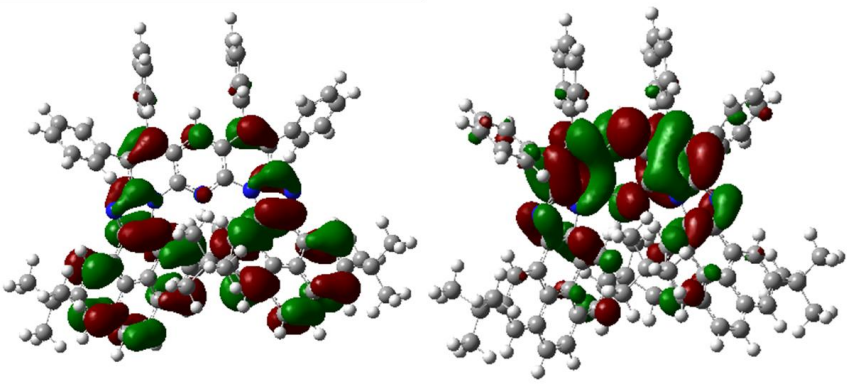


Figure S61. (a) CPL spectra of (*P*/*M*)-**HELI-2** thin film upon exposure to triflic acid (HOTf), vapour and triethylamine (Et_3N) vapour (λ_{ex} = 330 nm). (b) Colour change of drop-cast thin film upon exposure to triflic acid and triethylamine vapours.

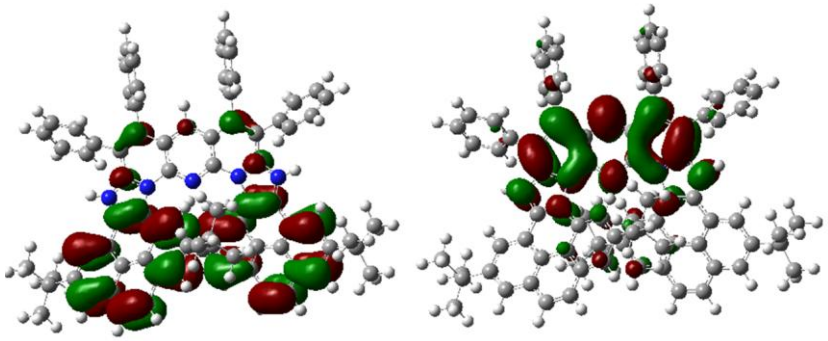
S13. Calculated HOMO and LUMO for HELI-2 and Protonated HELI-2

Gaussian 09 software was used to carry out all the computational studies.[S4] For FMO calculations, the geometry optimizations were performed at the 6-31G (d,p) level of theory in DCM using the CPCM model at 298.15 K and 1 atm. Frequency calculations were carried out to check the true minima of the optimized structures. For ground-state optimized geometries, it showed zero imaginary frequency. The effect of the counter anion was not considered during geometry optimizations of protonated helicene. Later, images of HOMO and LUMO were obtained from optimized geometry to check electronic distributions and the energy gap in between. Time-dependent (TD)-DFT calculations were carried out on the optimized structure using B3LYP/6-31g(d,p) as a basis set, and DCM was used as a solvent for calculations (CPCM model). The excited state energies along with the corresponding oscillator strengths (*f*) are listed in Tables S6a-3b. The UV/Vis spectra (Figure 52) were simulated using the GaussView6 visualization software package.



HOMO (– 5.17 eV) LUMO (– 2.25 eV)

Figure S62a. Kohn-Sham frontier orbital representation and MO energies of **HELI-2.**



HOMO (–6.19 eV) LUMO (–3.70 eV)

Figure S62b. Kohn-Sham frontier orbital representation and MO energies of protonated **HELI-2.**

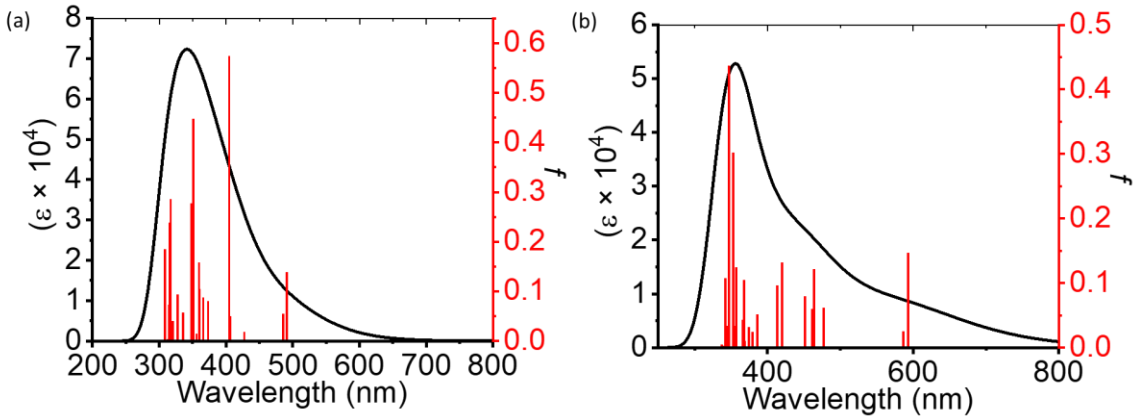


Figure S63. TD-DFT-calculated UV/Vis absorption spectra of (a) **HELI-2** and (b) protonated **HELI-2** calculated at B3LYP/6-31g(d,p), CPCM-CH_2Cl_2 level of theory.

Table S6a: TD-DFT-calculated UV/Vis absorption data for **HELI-2** at the B3LYP/6-31g(d,p) (solvent CPCM-CH_2Cl_2) level of theory.

Calcd. λ [nm]	*f*	Composition	Coefficient	Contribution (%)
491.22	0.1384	HOMO –> LUMO	0.70091	98.25
485.52	0.0553	HOMO-1–> LUMO	0.70081	98.22
427.28	0.0189	HOMO-2 –> LUMO HOMO –> LUMO+1	0.32215 0.61652	20.75 76.01
406.38	0.0496	HOMO-3 –> LUMO HOMO-1 –> LUMO+1	0.14410 0.67909	4.15 92.23
404.65	0.5746	HOMO-2 –> LUMO HOMO –> LUMO+1 HOMO –> LUMO+2	0.60621 0.31560 -0.14007	73.49 19.92 3.92
373.16	0.0809	HOMO-3 –> LUMO HOMO-1 –> LUMO+1 HOMO –> LUMO+3	0.63400 -0.14342 -0.21509	80.39 4.11 9.25
366.10	0.0872	HOMO-5 –> LUMO HOMO-1 –> LUMO+3 HOMO –> LUMO+2	0.15553 0.25266 0.61734	4.84 12.76 76.22
363.57	0	HOMO-4 –> LUMO HOMO-2 –> LUMO+1	0.65067 0.22847	84.67 10.43
360.54	0.105	HOMO-3 –> LUMO HOMO-2 –> LUMO+1 HOMO-1 –> LUMO+2 HOMO –> LUMO+3	0.11515 -0.14252 0.47361 0.48710	2.65 4.06 44.86 47.45
359.44	0.1579	HOMO-5 –> LUMO HOMO –> LUMO+2	0.65980 -0.17123	87.06 5.86
355.95	0.0146	HOMO-4 –> LUMO HOMO-3 –> LUMO	-0.16230 0.20130	5.26 8.10

		HOMO-2 –> LUMO+1	0.20540	8.43
		HOMO-2 –> LUMO+2	-0.11484	2.63
		HOMO-1 –> LUMO+2	-0.41402	34.28
		HOMO –> LUMO+3	0.42057	35.37
350.87	0.4472	HOMO-1 –> LUMO+3	0.61884	76.59
		HOMO –> LUMO+2	-0.21289	9.06
348.17	0.2779	HOMO-4 –> LUMO	-0.17562	6.16
		HOMO-2 –> LUMO+1	0.59875	71.70
		HOMO-1 –> LUMO+2	0.27110	14.69
335.75	0.0066	HOMO-5 –> LUMO	-0.12070	2.91
		HOMO-5 –> LUMO+3	0.13727	3.76
		HOMO-4 –> LUMO+1	0.16973	5.76
		HOMO-3 –> LUMO+1	0.30209	18.25
		HOMO-3 –> LUMO+2	0.21287	9.06
		HOMO-2 –> LUMO+3	0.28783	16.56
		HOMO-1 –> LUMO+4	0.28355	16.08
		HOMO-1 –> LUMO+7	0.12562	3.156
		HOMO –> LUMO+5	0.28162	15.86
335.66	0.0577	HOMO-5 –> LUMO+1	-0.15416	4.75
		HOMO-5 –> LUMO+2	-0.12721	3.23
		HOMO-3 –> LUMO	0.12027	2.89
		HOMO-3 –> LUMO+3	-0.19850	7.88
		HOMO-2 –> LUMO+1	0.10843	2.35
		HOMO-2 –> LUMO+2	-0.34010	23.13
		HOMO-1 –> LUMO+5	0.22443	10.07
		HOMO-1 –> LUMO+6	-0.10774	2.32
		HOMO –> LUMO+4	0.40906	33.46
		HOMO –> LUMO+7	0.14709	4.32
327.5	0.0938	HOMO-8 –> LUMO	-0.28863	16.66
		HOMO-7 –> LUMO	-0.14378	4.13
		HOMO-4 –> LUMO+1	-0.30840	19.02

		HOMO-3 –> LUMO+1	0.50756	51.52
320.34	0.0407	HOMO-8 –> LUMO	0.20373	8.30
		HOMO-4 –> LUMO+1	0.46579	43.39
		HOMO-3 –> LUMO+1	0.32521	21.15
		HOMO-2 –> LUMO+3	-0.11627	2.70
		HOMO-1 –> LUMO+4	-0.25432	12.93
		HOMO –> LUMO+5	-0.12406	3.07
317.35	0.2864	HOMO-8 –> LUMO	0.53999	58.31
		HOMO-4 –> LUMO+1	-0.31258	19.54
		HOMO-3 –> LUMO+1	0.13136	3.45
		HOMO-2 –> LUMO+3	-0.17282	5.97
		HOMO-1 –> LUMO+4	0.13098	3.43
316.93	0.13	HOMO-6 –> LUMO	0.63203	79.89
		HOMO-5 –> LUMO+1	0.14419	4.15
		HOMO-2 –> LUMO+2	-0.15943	5.08
		HOMO –> LUMO+4	-0.14657	4.29
315.41	0.2389	HOMO-6 –> LUMO	0.20825	8.67
		HOMO-2 –> LUMO+2	0.37254	27.75
		HOMO-1 –> LUMO+5	-0.16910	5.71
		HOMO –> LUMO+4	0.49254	48.51
		HOMO –> LUMO+7	-0.13191	3.48
314.64	0.0733	HOMO-8 –> LUMO	-0.12524	3.13
		HOMO-7 –> LUMO	0.64001	81.92
		HOMO-1 –> LUMO+4	-0.13871	3.84
		HOMO –> LUMO+6	0.11841	2.80
313.01	0.0038	HOMO-6 –> LUMO	-0.15178	4.60
		HOMO-5 –> LUMO+1	0.51908	53.88
		HOMO-2 –> LUMO+2	-0.29682	17.62
		HOMO-1 –> LUMO+5	-0.17914	6.418
		HOMO –> LUMO+4	0.16641	5.53
311.35	0.0022	HOMO-7 –> LUMO	0.12986	3.37

		HOMO-4 –> LUMO+1	0.16009	5.12
		HOMO-2 –> LUMO+3	-0.16515	5.45
		HOMO-1 –> LUMO+4	0.50075	50.15
		HOMO –> LUMO+5	-0.39199	30.73
309.04	0.0034	HOMO-8 –> LUMO	0.13633	3.71
		HOMO-4 –> LUMO+2	-0.10488	2.20
		HOMO-3 –> LUMO+2	-0.23074	10.64
		HOMO-2 –> LUMO+3	0.56424	63.67
		HOMO –> LUMO+5	-0.25500	13.00
308.35	0.1857	HOMO-5 –> LUMO+1	0.40154	32.24
		HOMO-5 –> LUMO+2	-0.16497	5.44
		HOMO-3 –> LUMO+3	-0.14904	4.44
		HOMO-2 –> LUMO+2	0.26740	14.30
		HOMO-1 –> LUMO+5	0.39450	31.12
		HOMO –> LUMO+7	0.13685	3.74

Table S6b: TD-DFT-calculated UV/Vis absorption data for the protonated **HELI-2** at the B3LYP/6-31g(d,p) (solvent CPCM-CH_2Cl_2) level of theory.

Calcd. λ [nm]	*f*	Composition	Coefficient	Contribution (%)
593.24	0.1466	HOMO –> LUMO	0.70547	99.53
586.06	0.0256	HOMO-1 –> LUMO	0.70463	99.30
477.44	0.0615	HOMO-2 –> LUMO	0.20088	8.07
		HOMO –> LUMO+1	0.67251	90.45
464.09	0.122	HOMO-2 –> LUMO	0.67400	90.85
		HOMO –> LUMO+1	-0.20133	8.10
461.32	0.0599	HOMO-3 –> LUMO	-0.35131	24.68
		HOMO-1 –> LUMO+1	0.60833	74.01
451.3	0.08	HOMO-3 –> LUMO	0.60758	73.83
		HOMO-1 –> LUMO+1	0.34781	24.19

419.58	0.132	HOMO-4 –> LUMO	0.69140	95.60
413.14	0.0961	HOMO-5 –> LUMO	0.69604	96.89
385.98	0.0517	HOMO-2 –> LUMO+1	0.68641	94.23
379.13	0.0242	HOMO-3 –> LUMO+1	0.68234	93.11
		HOMO –> LUMO+3	0.13573	3.86
374.6	0.0323	HOMO-9 –> LUMO	0.14877	4.42
		HOMO-6 –> LUMO	0.67500	91.12
371.44	0.0001	HOMO-8 –> LUMO	0.18449	6.80
		HOMO-7 –> LUMO	0.66189	87.62
368.39	0.01	HOMO-8 –> LUMO	0.24424	11.93
		HOMO-1 –> LUMO+2	-0.35795	25.62
		HOMO –> LUMO+3	0.52482	55.08
367.86	0.105	HOMO-1–> LUMO+3	-0.32012	20.49
		HOMO –> LUMO+2	0.61583	75.85
366.28	0.0429	HOMO-12 –> LUMO	-0.17691	6.26
		HOMO-8 –> LUMO	0.55705	62.06
		HOMO-7 –> LUMO	-0.11653	2.71
		HOMO-4 –> LUMO+1	0.21589	9.32
		HOMO-1 –> LUMO+2	0.20773	8.63
		HOMO –> LUMO+3	-0.17563	6.16
358.44	0	HOMO-9 –> LUMO	0.61854	76.51
		HOMO-6 –> LUMO	-0.11334	2.56
		HOMO-1 –> LUMO+3	-0.20600	8.48
		HOMO –> LUMO+2	-0.16777	5.63
357.18	0.1247	HOMO-10 –> LUMO	0.10085	2.03
		HOMO-4 –> LUMO+1	-0.36693	26.92
		HOMO-1 –> LUMO+2	0.47737	45.57
		HOMO –> LUMO+3	0.29054	16.88
354.89	0.0342	HOMO-11 –> LUMO	-0.15663	4.90
		HOMO-9 –> LUMO	0.26079	13.60

		HOMO-2 –> LUMO+1	0.11249	2.53
		HOMO-1 –> LUMO+3	0.54323	59.02
		HOMO –> LUMO+2	0.24084	11.60
353.07	0.3019	HOMO-12 –> LUMO	-0.21612	9.34
		HOMO-10 –> LUMO	0.13653	3.72
		HOMO-8 –> LUMO	-0.26052	13.57
		HOMO-7 –> LUMO	0.16912	5.72
		HOMO-4 –> LUMO+1	0.46487	43.22
		HOMO-1 –> LUMO+2	0.23294	10.85
		HOMO –> LUMO+3	0.17895	6.40
347.34	0.437	HOMO-12 –> LUMO	0.45189	40.84
		HOMO-10 –> LUMO	-0.39358	30.98
		HOMO-4 –> LUMO+1	0.24782	12.28
		HOMO-1 –> LUMO+2	0.12891	3.32
		HOMO –> LUMO+3	0.15750	4.96
345.51	0.0339	HOMO-13 –> LUMO	0.10758	2.31
		HOMO-11 –> LUMO	0.58398	68.20
		HOMO-5 –> LUMO+1	-0.31214	19.49
		HOMO-1 –> LUMO+3	0.14328	4.10
343.6	0.0202	HOMO-12 –> LUMO	0.43022	37.01
		HOMO-10 –> LUMO	0.51700	53.46
342.19	0.1082	HOMO-13 –> LUMO	0.12361	3.06
		HOMO-11 –> LUMO	0.28509	16.25
		HOMO-5 –> LUMO+1	0.59754	71.41
339.8	0.0029	HOMO-13 –> LUMO	0.66676	88.91
		HOMO-11 –> LUMO	-0.13618	3.70
336.94	0.0046	HOMO-10 –> LUMO	-0.10847	2.35
		HOMO-3 –> LUMO+3	-0.24607	12.11
		HOMO-2 –> LUMO+2	0.353096	24.94
		HOMO-1 –> LUMO+5	-0.22213	9.87
		HOMO-1 –> LUMO+7	-0.15540	4.83

		HOMO –> LUMO+4 HOMO –> LUMO+6	0.38733 0.20874	30.00 8.71

S14. Computational ECD Spectra

Gaussian 09 software was used for DFT calculations.[S4] TD-DFT has been performed using the B3LYP/6-31g(d,p) level of theory in dichloromethane using the CPCM model at 298.15 K and 1 atm.

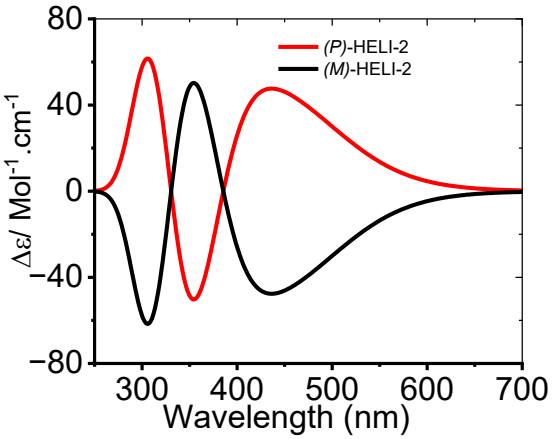


Figure S64. Computed ECD spectra of (*P*)-**HELI-2** and (*M*)-**HELI-2** in DCM.

S15. Cartesian Coordinates of the DFT Computed Molecules

HELI-1

N	2.333032000	1.334814000	0.078572000
N	0.016211000	1.369901000	-0.312392000
N	-4.526493000	1.165311000	-0.357450000
N	4.541389000	0.969853000	-0.231339000
N	-2.300652000	1.351129000	-0.700889000
C	1.165579000	2.033731000	-0.236981000
C	-1.103015000	2.050662000	-0.538639000
C	2.591763000	0.034131000	0.549061000
C	-1.902004000	-1.135041000	-1.438795000

C	3.954540000	-0.150636000	0.293513000
C	-2.619491000	-0.007743000	-0.881852000
C	1.291235000	3.424261000	-0.522514000
C	-1.165514000	3.474260000	-0.572231000
C	2.501201000	-2.145599000	1.631077000
C	-3.991615000	-0.068527000	-0.615232000
C	4.626860000	-1.389433000	0.583182000
C	5.117597000	3.686162000	-1.043625000
H	5.630211000	2.858589000	-1.543858000
H	5.101431000	4.521177000	-1.749810000
C	0.078031000	4.116977000	-0.621836000
H	0.102230000	5.190721000	-0.740454000
C	1.828138000	-0.911562000	1.334025000
C	-3.512811000	2.010989000	-0.435772000
C	2.592663000	4.041188000	-0.740830000
C	-2.437451000	4.181638000	-0.514493000
C	3.857374000	-2.393595000	1.235011000
C	-3.588182000	3.445633000	-0.361304000
C	3.569530000	1.861159000	-0.332167000
C	3.707800000	3.238072000	-0.726063000
C	-0.624808000	-1.090048000	-2.022894000
H	-0.098902000	-0.149407000	-2.015154000
C	2.659568000	5.528096000	-1.013656000
H	3.587623000	5.768412000	-1.537742000
H	1.852386000	5.819348000	-1.696444000
C	-4.723487000	-1.306988000	-0.642811000
C	-2.636825000	-2.369023000	-1.481490000
C	5.962241000	-1.626240000	0.250297000
H	6.508451000	-0.827314000	-0.239497000

C	-4.970368000	4.015238000	-0.135781000
H	-5.681889000	3.450261000	-0.747608000
H	-5.014273000	5.054534000	-0.471283000
C	0.563158000	-0.679931000	1.899992000
H	0.085973000	0.266242000	1.702963000
C	1.811632000	-3.138887000	2.389452000
C	-0.089811000	-1.628780000	2.700365000
C	-4.004488000	-2.462127000	-1.059012000
C	4.487779000	-3.635608000	1.534904000
C	0.534743000	-2.863642000	2.898891000
H	0.045577000	-3.635805000	3.485463000
C	7.376492000	4.478825000	-0.156208000
H	7.396992000	5.329958000	-0.846346000
H	7.941825000	4.760872000	0.737789000
H	7.905308000	3.648623000	-0.637753000
C	2.580863000	6.397399000	0.261516000
H	3.411721000	6.130673000	0.925099000
H	1.664342000	6.162452000	0.816107000
C	-0.022648000	-2.214278000	-2.606500000
C	-2.432753000	5.695621000	-0.545730000
H	-1.681405000	6.043208000	-1.264283000
H	-3.388861000	6.059044000	-0.931316000
C	5.940093000	4.086180000	0.199254000
H	5.947417000	3.245969000	0.902474000
H	5.444855000	4.919536000	0.712119000
C	6.587445000	-2.854873000	0.525423000
C	5.830424000	-3.840572000	1.164879000
H	6.272947000	-4.800889000	1.404695000
C	-6.069297000	-1.402949000	-0.282813000

H	-6.574875000	-0.493273000	0.022156000
C	-1.998241000	-3.530945000	-2.010074000
C	-2.167204000	6.360715000	0.822373000
H	-2.951294000	6.055722000	1.525081000
H	-1.224347000	5.985437000	1.238174000
C	-6.842994000	4.505739000	1.528094000
H	-6.896220000	5.557531000	1.224484000
H	-7.575156000	3.950743000	0.930821000
H	-7.153023000	4.445139000	2.576248000
C	-2.120525000	7.888080000	0.729191000
H	-1.319328000	8.220548000	0.059371000
H	-3.063790000	8.290623000	0.343378000
H	-1.942485000	8.337687000	1.711065000
C	-6.754281000	-2.630341000	-0.298534000
C	-0.709688000	-3.430383000	-2.553377000
H	-0.260778000	-4.329848000	-2.964468000
C	-4.695901000	-3.707145000	-1.099246000
C	2.625065000	7.895446000	-0.050750000
H	3.549349000	8.164181000	-0.574225000
H	1.784462000	8.193064000	-0.687837000
H	2.575650000	8.490490000	0.866507000
C	-5.432739000	3.942310000	1.335801000
H	-4.724040000	4.491443000	1.967711000
H	-5.400922000	2.897726000	1.663303000
C	-6.047145000	-3.764171000	-0.708436000
H	-6.536953000	-4.730780000	-0.745224000
C	-8.233458000	-2.680169000	0.128835000
C	-8.821557000	-4.101185000	0.044035000
H	-9.869691000	-4.082972000	0.358704000

H	-8.790366000	-4.495902000	-0.976799000
H	-8.292226000	-4.801385000	0.698419000
C	-8.360167000	-2.191760000	1.591669000
H	-7.788056000	-2.833986000	2.269494000
H	-7.996443000	-1.167137000	1.712510000
H	-9.408786000	-2.213093000	1.908429000
C	-9.066348000	-1.756935000	-0.792022000
H	-8.726013000	-0.718453000	-0.744209000
H	-9.002889000	-2.084325000	-1.835097000
H	-10.120431000	-1.776453000	-0.493705000
C	1.347653000	-2.149608000	-3.310348000
C	1.182265000	-2.592918000	-4.784158000
H	2.147422000	-2.550537000	-5.301089000
H	0.806400000	-3.617000000	-4.863405000
H	0.484411000	-1.936385000	-5.314555000
C	2.338922000	-3.101161000	-2.600015000
H	3.316059000	-3.067982000	-3.094584000
H	2.478323000	-2.813140000	-1.553531000
H	1.991587000	-4.138535000	-2.619813000
C	1.947581000	-0.731746000	-3.306267000
H	2.125490000	-0.368504000	-2.290339000
H	2.910371000	-0.741371000	-3.827134000
H	1.300064000	-0.014140000	-3.820760000
C	8.058536000	-3.066809000	0.120602000
C	8.577441000	-4.465333000	0.503830000
H	9.622596000	-4.565477000	0.194234000
H	8.535587000	-4.634220000	1.584813000
H	8.009200000	-5.260845000	0.010862000
C	8.196557000	-2.903766000	-1.411907000

H	7.587580000	-3.644651000	-1.940523000
H	7.883140000	-1.910369000	-1.746048000
H	9.240122000	-3.043977000	-1.715017000
C	8.943162000	-2.012634000	0.827910000
H	8.656903000	-0.992324000	0.556683000
H	8.868198000	-2.105171000	1.916479000
H	9.993196000	-2.150308000	0.547031000
C	-1.451238000	-1.351647000	3.368774000
C	-1.303589000	-1.497912000	4.902778000
H	-2.263336000	-1.304439000	5.394585000
H	-0.979834000	-2.502945000	5.188209000
H	-0.571324000	-0.784472000	5.295476000
C	-2.495375000	-2.372277000	2.858106000
H	-3.464373000	-2.193795000	3.337300000
H	-2.631613000	-2.286745000	1.775680000
H	-2.199395000	-3.401930000	3.079817000
C	-1.974925000	0.065987000	3.074599000
H	-1.289158000	0.837565000	3.439832000
H	-2.134425000	0.225483000	2.004463000
H	-2.936192000	0.212945000	3.577279000
C	-3.993346000	-4.871149000	-1.565140000
C	-2.710157000	-4.782040000	-2.008846000
C	2.461426000	-4.397048000	2.648599000
C	3.734154000	-4.640259000	2.233571000
H	1.909452000	-5.152786000	3.200951000
H	4.211184000	-5.593310000	2.445409000
H	-4.517356000	-5.823014000	-1.578507000
H	-2.196393000	-5.662053000	-2.386327000

HELI-1-TS:

C	-1.185931000	3.463740000	-0.670768000
C	-1.122376000	2.121903000	-0.201849000
C	0.039918000	4.123739000	-0.792733000
C	-2.402448000	4.005375000	-1.280292000
N	0.013320000	1.479570000	0.092810000
N	-2.324129000	1.387855000	-0.281764000
C	1.252480000	3.440911000	-0.665507000
H	0.049795000	5.139523000	-1.163236000
C	-3.332052000	3.106571000	-1.735236000
C	-2.522558000	5.496704000	-1.495074000
C	1.161704000	2.099066000	-0.200917000
C	-3.192972000	1.727336000	-1.340192000
C	-2.611953000	0.050331000	0.025143000
C	-4.531718000	3.438797000	-2.595000000
H	-1.668495000	5.872129000	-2.074734000
H	-3.406249000	5.711821000	-2.099645000
C	-2.622701000	6.294967000	-0.177180000
N	2.347976000	1.339710000	-0.286411000
N	-3.874176000	0.684429000	-1.779662000
C	-3.497983000	-0.362350000	-0.968698000
C	-2.504111000	-0.674255000	1.265420000
C	3.389052000	3.044229000	-1.733185000
H	-4.301129000	4.275413000	-3.261587000
H	-4.737100000	2.573882000	-3.233264000
C	-5.801303000	3.763711000	-1.781091000
H	-1.743608000	6.091626000	0.445708000
H	-3.489384000	5.934245000	0.390223000
C	-2.747831000	7.801582000	-0.417648000

C	2.602515000	-0.008360000	0.005523000
C	3.216574000	1.665163000	-1.349827000
C	-3.952314000	-1.727125000	-1.044156000
C	-3.005482000	-2.013641000	1.236414000
C	-2.218385000	-0.075905000	2.503699000
C	4.595774000	3.354559000	-2.591266000
H	-6.024538000	2.918369000	-1.119390000
H	-5.604815000	4.624015000	-1.129142000
C	-7.009019000	4.056840000	-2.675122000
H	-2.822985000	8.346848000	0.528372000
H	-1.877767000	8.189774000	-0.959185000
H	-3.639126000	8.036018000	-1.010262000
C	3.466325000	-0.435646000	-1.001243000
C	2.493012000	-0.741166000	1.242103000
N	3.864508000	0.608463000	-1.805486000
C	-3.637488000	-2.557854000	0.071260000
C	-4.663171000	-2.247274000	-2.127263000
C	-2.989673000	-2.776558000	2.439493000
C	-2.426474000	-0.758713000	3.712820000
H	-1.940684000	0.970740000	2.512142000
H	4.774834000	2.492971000	-3.241953000
H	4.387285000	4.206448000	-3.245602000
C	5.876010000	3.632035000	-1.776575000
H	-7.898065000	4.282177000	-2.077522000
H	-6.819417000	4.915956000	-3.328590000
H	-7.244845000	3.199116000	-3.314972000
C	3.878322000	-1.812816000	-1.098079000
C	2.951102000	-2.096863000	1.190225000
C	2.248682000	-0.149739000	2.490164000

C	-4.080864000	-3.909707000	0.058299000
C	-5.057913000	-3.596823000	-2.174297000
H	-4.893290000	-1.577950000	-2.949461000
C	-2.707465000	-2.130271000	3.652721000
H	6.076764000	2.771764000	-1.127000000
H	5.705828000	4.488570000	-1.112386000
C	7.089687000	3.902873000	-2.669544000
C	3.549827000	-2.647063000	0.010760000
C	4.560577000	-2.341177000	-2.194816000
C	2.927718000	-2.871420000	2.383708000
C	2.459210000	-0.851938000	3.691730000
H	2.007209000	0.906252000	2.515691000
C	-4.755771000	-4.404905000	-1.073847000
H	-2.803137000	-2.706984000	4.567782000
H	7.985988000	4.094405000	-2.070983000
H	7.299728000	3.047709000	-3.321700000
H	6.923554000	4.776066000	-3.310625000
C	3.949463000	-4.012040000	-0.023550000
C	4.912044000	-3.702320000	-2.262817000
H	4.803482000	-1.669251000	-3.011134000
C	2.690485000	-2.229803000	3.611801000
H	-5.064690000	-5.444098000	-1.057563000
C	4.595857000	-4.514298000	-1.169851000
H	2.780094000	-2.824074000	4.514330000
H	4.871646000	-5.562913000	-1.169891000
C	2.481625000	3.960678000	-1.269554000
C	2.638012000	5.450793000	-1.466638000
H	1.791287000	5.855764000	-2.036880000
H	3.524486000	5.651675000	-2.072099000

C	2.763406000	6.227901000	-0.138169000
H	1.881767000	6.037337000	0.485177000
H	3.622978000	5.837576000	0.420352000
C	2.925076000	7.734120000	-0.358276000
H	3.819621000	7.954438000	-0.951415000
H	2.062877000	8.151267000	-0.890792000
H	3.017438000	8.264255000	0.594801000
C	-2.515638000	-0.028019000	5.068477000
C	-5.806756000	-4.124478000	-3.412968000
C	2.643429000	-0.100817000	5.026441000
C	5.632591000	-4.236399000	-3.515440000
C	2.353049000	-0.997913000	6.248809000
H	3.080488000	-1.809527000	6.342433000
H	2.416327000	-0.403322000	7.165630000
H	1.356397000	-1.445378000	6.204776000
C	4.131865000	0.333099000	5.095755000
H	4.328182000	0.865691000	6.033500000
H	4.797694000	-0.534489000	5.050014000
H	4.386763000	0.999944000	4.265907000
C	1.772850000	1.166823000	5.114252000
H	2.051487000	1.911675000	4.363339000
H	0.714976000	0.935081000	4.983578000
H	1.897449000	1.636844000	6.095014000
C	-3.981946000	-0.129512000	5.563431000
H	-4.284419000	-1.169489000	5.716654000
H	-4.095015000	0.399150000	6.516640000
H	-4.671730000	0.319795000	4.841522000
C	-1.597479000	-0.688234000	6.117778000
H	-0.553881000	-0.661579000	5.800195000

H	-1.675129000	-0.161184000	7.074804000
H	-1.866079000	-1.733609000	6.295967000
C	-2.170271000	1.468807000	4.955094000
H	-2.216934000	1.933276000	5.945122000
H	-1.166710000	1.638293000	4.556523000
H	-2.880686000	1.995839000	4.310216000
C	5.941685000	-5.742026000	-3.417981000
H	6.445790000	-6.071873000	-4.331882000
H	6.603280000	-5.969185000	-2.575693000
H	5.030536000	-6.339248000	-3.309202000
C	6.969815000	-3.480346000	-3.701357000
H	6.816787000	-2.404028000	-3.822265000
H	7.628031000	-3.632231000	-2.839451000
H	7.489546000	-3.845755000	-4.593909000
C	4.738686000	-4.007203000	-4.757572000
H	3.788343000	-4.542634000	-4.660136000
H	4.513243000	-2.947429000	-4.907935000
H	5.242956000	-4.372443000	-5.659123000
C	-6.162740000	-5.618007000	-3.291904000
H	-6.823866000	-5.812275000	-2.441038000
H	-6.684996000	-5.944110000	-4.196885000
H	-5.270307000	-6.242666000	-3.182074000
C	-4.917587000	-3.940672000	-4.665965000
H	-4.662697000	-2.890354000	-4.834420000
H	-3.982381000	-4.502080000	-4.568361000
H	-5.440263000	-4.304572000	-5.557538000
C	-7.120931000	-3.328803000	-3.597775000
H	-7.775590000	-3.447448000	-2.727985000
H	-6.934572000	-2.259793000	-3.735404000

H	-7.660505000	-3.689601000	-4.480409000
C	-3.382287000	-4.161278000	2.381715000
C	-3.877062000	-4.709795000	1.237353000
C	3.734091000	-4.818827000	1.148107000
C	3.272212000	-4.267204000	2.305279000
H	-3.300557000	-4.757268000	3.286695000
H	-4.182340000	-5.752495000	1.214892000
H	4.004785000	-5.870594000	1.110271000
H	3.183294000	-4.870513000	3.204735000

(*P*)-HELI-2:

N	2.308576000	0.688158000	-0.438616000
N	0.000019000	0.718087000	0.000031000
N	-4.534755000	0.413912000	0.148405000
N	4.534768000	0.413938000	-0.148436000
N	-2.308551000	0.688129000	0.438633000
C	1.130618000	1.392817000	-0.185360000
C	-1.130598000	1.392797000	0.185402000
C	2.589526000	-0.653225000	-0.754669000
C	-1.834473000	-1.708032000	1.397749000
C	3.963736000	-0.772424000	-0.516450000
C	-2.589515000	-0.653249000	0.754678000
C	1.223226000	2.811730000	-0.081574000
C	-1.223211000	2.811714000	0.081661000
C	2.541879000	-2.945906000	-1.574272000
C	-3.963724000	-0.772444000	0.516440000
C	4.666721000	-2.015895000	-0.680154000
C	0.000006000	3.487300000	0.000053000
H	-0.000013000	4.568757000	0.000068000
C	1.834463000	-1.708008000	-1.397715000
C	-3.548011000	1.287312000	0.125860000

C	2.513506000	3.478252000	0.012338000
C	-2.513497000	3.478237000	-0.012260000
C	3.914673000	-3.108391000	-1.191870000
C	-3.655231000	2.710821000	-0.069989000
C	3.548028000	1.287335000	-0.125836000
C	3.655244000	2.710847000	0.070010000
C	-0.546696000	-1.582727000	1.943229000
H	-0.038608000	-0.639284000	1.830574000
C	-4.666716000	-2.015906000	0.680142000
C	-2.541893000	-2.945926000	1.574296000
C	6.016696000	-2.168701000	-0.362433000
H	6.543316000	-1.297994000	0.012813000
C	0.546683000	-1.582694000	-1.943185000
H	0.038607000	-0.639244000	-1.830541000
C	1.868780000	-4.037497000	-2.199124000
C	-0.089484000	-2.631750000	-2.621705000
C	-3.914681000	-3.108406000	1.191871000
C	4.578067000	-4.356131000	-1.368304000
C	0.573721000	-3.858232000	-2.703162000
H	0.098129000	-4.703841000	-3.191708000
C	0.089449000	-2.631774000	2.621780000
C	6.674645000	-3.400759000	-0.514969000
C	5.935148000	-4.475335000	-1.015310000
H	6.404296000	-5.442631000	-1.157828000
C	-6.016690000	-2.168702000	0.362407000
H	-6.543302000	-1.297991000	-0.012842000
C	-1.868806000	-4.037523000	2.199147000
C	-6.674649000	-3.400757000	0.514931000
C	-0.573752000	-3.858263000	2.703204000
H	-0.098156000	-4.703885000	3.191724000
C	-4.578086000	-4.356143000	1.368287000
C	-5.935162000	-4.475339000	1.015275000

H	-6.404317000	-5.442633000	1.157784000
C	-8.162982000	-3.517178000	0.136178000
C	-8.718728000	-4.935364000	0.363944000
H	-9.775184000	-4.967009000	0.078558000
H	-8.652441000	-5.235485000	1.414828000
H	-8.191762000	-5.681808000	-0.239458000
C	-8.340239000	-3.164728000	-1.359844000
H	-7.771044000	-3.852514000	-1.993839000
H	-8.001085000	-2.148711000	-1.580729000
H	-9.396125000	-3.234177000	-1.645153000
C	-8.989250000	-2.530898000	0.995376000
H	-8.668680000	-1.495738000	0.848217000
H	-8.889786000	-2.762695000	2.060815000
H	-10.051165000	-2.593164000	0.731462000
C	1.469986000	-2.472473000	3.288784000
C	1.336304000	-2.762337000	4.803446000
H	2.308885000	-2.655817000	5.297179000
H	0.975626000	-3.777034000	4.995230000
H	0.636904000	-2.064949000	5.276377000
C	2.468668000	-3.473840000	2.663127000
H	3.453590000	-3.371788000	3.132445000
H	2.584447000	-3.296650000	1.590335000
H	2.143189000	-4.509743000	2.797389000
C	2.042651000	-1.052523000	3.127335000
H	2.197096000	-0.795979000	2.075879000
H	3.014409000	-0.989918000	3.627576000
H	1.389635000	-0.297177000	3.577409000
C	8.162982000	-3.517193000	-0.136235000
C	8.718704000	-4.935386000	-0.364012000
H	9.775161000	-4.967050000	-0.078631000
H	8.652406000	-5.235499000	-1.414898000
H	8.191728000	-5.681825000	0.239388000

C	8.340265000	-3.164749000	1.359785000
H	7.771071000	-3.852530000	1.993786000
H	8.001127000	-2.148729000	1.580677000
H	9.396155000	-3.234212000	1.645079000
C	8.989253000	-2.530923000	-0.995444000
H	8.668695000	-1.495760000	-0.848288000
H	8.889777000	-2.762725000	-2.060881000
H	10.051169000	-2.593198000	-0.731538000
C	-1.470002000	-2.472437000	-3.288740000
C	-1.336302000	-2.762487000	-4.803367000
H	-2.308879000	-2.656034000	-5.297119000
H	-0.975618000	-3.777210000	-4.995013000
H	-0.636899000	-2.065157000	-5.276380000
C	-2.468758000	-3.473665000	-2.662985000
H	-3.453691000	-3.371549000	-3.132267000
H	-2.584480000	-3.296398000	-1.590199000
H	-2.143392000	-4.509610000	-2.797188000
C	-2.042579000	-1.052432000	-3.127465000
H	-1.389581000	-0.297186000	-3.577732000
H	-2.196899000	-0.795713000	-2.076033000
H	-3.014389000	-0.989871000	-3.627611000
C	-3.841525000	-5.453724000	1.929930000
C	-2.553007000	-5.295658000	2.335049000
C	2.552976000	-5.295632000	-2.335049000
C	3.841496000	-5.453705000	-1.929946000
H	2.012217000	-6.123880000	-2.785435000
H	4.344277000	-6.410037000	-2.047854000
H	-4.344311000	-6.410054000	2.047825000
H	-2.012256000	-6.123909000	2.785438000
C	5.026260000	3.265044000	0.261105000
C	5.846263000	2.789251000	1.296018000
C	5.528824000	4.256285000	-0.594501000

C	7.125547000	3.309382000	1.482933000
H	5.478118000	2.006033000	1.949249000
C	6.812519000	4.768415000	-0.412430000
H	4.912339000	4.623024000	-1.408141000
C	7.613595000	4.300537000	0.629765000
H	7.744042000	2.934919000	2.293504000
H	7.186538000	5.532158000	-1.088030000
H	8.612879000	4.701333000	0.773036000
C	2.540813000	4.965012000	0.159769000
C	2.954602000	5.558281000	1.361630000
C	2.135271000	5.796779000	-0.895993000
C	2.969958000	6.945435000	1.501128000
H	3.272106000	4.925800000	2.184494000
C	2.151546000	7.184736000	-0.756217000
H	1.813269000	5.351442000	-1.833213000
C	2.569383000	7.763040000	0.443100000
H	3.295766000	7.387416000	2.438205000
H	1.838633000	7.812455000	-1.585317000
H	2.582847000	8.843436000	0.552430000
C	-2.540821000	4.964987000	-0.159709000
C	-2.135244000	5.796755000	0.896036000
C	-2.954676000	5.558235000	-1.361557000
C	-2.151544000	7.184712000	0.756252000
H	-1.813194000	5.351424000	1.833243000
C	-2.970046000	6.945388000	-1.501063000
H	-3.272200000	4.925744000	-2.184404000
C	-2.569439000	7.763001000	-0.443051000
H	-1.838609000	7.812442000	1.585335000
H	-3.295880000	7.387361000	-2.438134000
H	-2.582917000	8.843396000	-0.552385000
C	-5.026245000	3.265026000	-0.261112000
C	-5.846091000	2.789434000	-1.296244000

C	-5.528911000	4.256115000	0.594608000
C	-7.125360000	3.309582000	-1.483220000
H	-5.477856000	2.006348000	-1.949573000
C	-6.812591000	4.768261000	0.412468000
H	-4.912534000	4.622704000	1.408395000
C	-7.613522000	4.300566000	-0.629918000
H	-7.743750000	2.935280000	-2.293943000
H	-7.186715000	5.531864000	1.088166000
H	-8.612792000	4.701382000	-0.773246000

(*M*)-HELI-2:

N	-2.308531000	0.688143000	-0.438686000
N	0.000002000	0.718124000	0.000093000
N	4.534723000	0.413950000	0.148486000
N	-4.534711000	0.413875000	-0.148406000
N	2.308541000	0.688201000	0.438827000
C	-1.130595000	1.392835000	-0.185402000
C	1.130587000	1.392858000	0.185561000
C	-2.589452000	-0.653268000	-0.754621000
C	1.834434000	-1.707988000	1.397805000
C	-3.963641000	-0.772497000	-0.516347000
C	2.589484000	-0.653213000	0.754736000
C	-1.223234000	2.811747000	-0.081673000
C	1.223200000	2.811774000	0.081782000
C	-2.541805000	-2.945932000	-1.574264000
C	3.963670000	-0.772429000	0.516422000
C	-4.666611000	-2.015978000	-0.680002000
C	-0.000023000	3.487334000	0.000055000
H	-0.000029000	4.568790000	0.000068000
C	-1.834389000	-1.708040000	-1.397693000
C	3.548008000	1.287368000	0.126015000
C	-2.513532000	3.478268000	0.012126000

C	2.513490000	3.478302000	-0.012057000
C	-3.914576000	-3.108447000	-1.191795000
C	3.655230000	2.710890000	-0.069769000
C	-3.548006000	1.287302000	-0.125906000
C	-3.655264000	2.710835000	0.069840000
C	0.546690000	-1.582646000	1.943356000
H	0.038627000	-0.639185000	1.830731000
C	4.666625000	-2.015928000	0.680007000
C	2.541832000	-2.945905000	1.574283000
C	-6.016568000	-2.168809000	-0.362216000
H	-6.543185000	-1.298116000	0.013068000
C	-0.546596000	-1.582716000	-1.943138000
H	-0.038512000	-0.639277000	-1.830428000
C	-1.868726000	-4.037498000	-2.199183000
C	0.089529000	-2.631728000	-2.621768000
C	3.914585000	-3.108415000	1.191754000
C	-4.577968000	-4.356185000	-1.368240000
C	-0.573691000	-3.858203000	-2.703270000
H	-0.098106000	-4.703797000	-3.191847000
C	-0.089432000	-2.631680000	2.621957000
C	-6.674513000	-3.400868000	-0.514762000
C	-5.935030000	-4.475418000	-1.015178000
H	-6.404173000	-5.442714000	-1.157706000
C	6.016571000	-2.168768000	0.362171000
H	6.543196000	-1.298061000	-0.013070000
C	1.868753000	-4.037489000	2.199169000
C	6.674495000	-3.400848000	0.514617000
C	0.573748000	-3.858184000	2.703334000
H	0.098162000	-4.703793000	3.191885000
C	4.577959000	-4.356178000	1.368101000
C	5.935006000	-4.475417000	1.014990000
H	6.404134000	-5.442731000	1.157446000

C	8.162804000	-3.517307000	0.135776000
C	8.718535000	-4.935499000	0.363540000
H	9.774946000	-4.967198000	0.077994000
H	8.652403000	-5.235556000	1.414452000
H	8.191445000	-5.681958000	-0.239736000
C	8.339988000	-3.164897000	-1.360263000
H	7.770725000	-3.852671000	-1.994210000
H	8.000873000	-2.148869000	-1.581153000
H	9.395855000	-3.234402000	-1.645629000
C	8.989135000	-2.531021000	0.994907000
H	8.668560000	-1.495862000	0.847750000
H	8.889731000	-2.762798000	2.060356000
H	10.051034000	-2.593299000	0.730931000
C	-1.469932000	-2.472373000	3.289049000
C	-1.336179000	-2.762321000	4.803691000
H	-2.308749000	-2.655870000	5.297462000
H	-0.975454000	-3.777016000	4.995398000
H	-0.636793000	-2.064928000	5.276634000
C	-2.468677000	-3.473671000	2.663393000
H	-3.453583000	-3.371601000	3.132741000
H	-2.584482000	-3.296442000	1.590608000
H	-2.143240000	-4.509592000	2.797604000
C	-2.042574000	-1.052398000	3.127726000
H	-2.197005000	-0.795757000	2.076291000
H	-3.014340000	-0.989830000	3.627958000
H	-1.389552000	-0.297105000	3.577876000
C	-8.162835000	-3.517321000	-0.135970000
C	-8.718566000	-4.935509000	-0.363758000
H	-9.774992000	-4.967198000	-0.078266000
H	-8.652382000	-5.235569000	-1.414666000
H	-8.191515000	-5.681973000	0.239547000
C	-8.340062000	-3.164919000	1.360066000

H	-7.770823000	-3.852701000	1.994026000
H	-8.000944000	-2.148895000	1.580971000
H	-9.395938000	-3.234417000	1.645402000
C	-8.989138000	-2.531028000	-0.995120000
H	-8.668567000	-1.495870000	-0.847948000
H	-8.889701000	-2.762800000	-2.060568000
H	-10.051045000	-2.593307000	-0.731179000
C	1.470079000	-2.472446000	-3.288762000
C	1.336371000	-2.762138000	-4.803458000
H	2.308977000	-2.655730000	-5.297166000
H	0.975528000	-3.776758000	-4.995338000
H	0.637093000	-2.064587000	-5.276327000
C	2.468689000	-3.473951000	-2.663222000
H	3.453628000	-3.371894000	-3.132500000
H	2.584453000	-3.296918000	-1.590401000
H	2.143161000	-4.509819000	-2.797631000
C	2.042861000	-1.052559000	-3.127172000
H	1.389948000	-0.297118000	-3.577233000
H	2.197259000	-0.796116000	-2.075687000
H	3.014661000	-0.990009000	-3.627341000
C	3.841405000	-5.453741000	1.929786000
C	2.552927000	-5.295643000	2.335008000
C	-2.552923000	-5.295630000	-2.335130000
C	-3.841420000	-5.453729000	-1.929969000
H	-2.012184000	-6.123853000	-2.785585000
H	-4.344204000	-6.410055000	-2.047903000
H	4.344172000	-6.410086000	2.047640000
H	2.012191000	-6.123885000	2.785430000
C	-5.026311000	3.265034000	0.260750000
C	-5.846431000	2.789260000	1.295599000
C	-5.528774000	4.256266000	-0.594919000
C	-7.125727000	3.309404000	1.482365000

H	-5.478363000	2.006048000	1.948867000
C	-6.812494000	4.768392000	-0.413002000
H	-4.912195000	4.623012000	-1.408484000
C	-7.613681000	4.300536000	0.629109000
H	-7.744316000	2.934972000	2.292876000
H	-7.186442000	5.532114000	-1.088665000
H	-8.612981000	4.701338000	0.772260000
C	-2.540876000	4.965025000	0.159478000
C	-2.954799000	5.558338000	1.361272000
C	-2.135201000	5.796758000	-0.896267000
C	-2.970170000	6.945497000	1.500716000
H	-3.272393000	4.925889000	2.184124000
C	-2.151499000	7.184716000	-0.756544000
H	-1.813076000	5.351387000	-1.833428000
C	-2.569485000	7.763065000	0.442702000
H	-3.296073000	7.387508000	2.437745000
H	-1.838486000	7.812406000	-1.585627000
H	-2.582959000	8.843464000	0.551989000
C	2.540818000	4.965059000	-0.159466000
C	2.135117000	5.796819000	0.896242000
C	2.954784000	5.558323000	-1.361267000
C	2.151410000	7.184774000	0.756467000
H	1.812965000	5.351476000	1.833408000
C	2.970153000	6.945479000	-1.500761000
H	3.272420000	4.925842000	-2.184079000
C	2.569426000	7.763080000	-0.442789000
H	1.838376000	7.812493000	1.585520000
H	3.296090000	7.387459000	-2.437793000
H	2.582902000	8.843476000	-0.552113000
C	5.026255000	3.265110000	-0.260797000
C	5.846279000	2.789352000	-1.295720000
C	5.528773000	4.256347000	0.594835000

C	7.125552000	3.309516000	-1.482602000
H	5.478165000	2.006134000	-1.948958000
C	6.812467000	4.768500000	0.412797000
H	4.912261000	4.623071000	1.408460000
C	7.613563000	4.300657000	-0.629390000
H	7.744075000	2.935095000	-2.293168000
H	7.186467000	5.532225000	1.088427000
H	8.612845000	4.701472000	-0.772632000

HELI-3:

N	0.024052000	0.706194000	0.158360000
N	-4.493996000	0.754395000	-0.448208000
N	-2.320605000	0.817835000	0.172656000
N	4.492504000	0.071751000	0.761708000
N	2.362445000	0.503997000	0.142401000
C	-4.275656000	-2.902584000	0.275203000
C	-4.065732000	-0.505315000	-0.126779000
C	-1.074868000	1.451416000	0.170295000
C	1.212920000	1.295047000	0.212190000
C	1.384267000	2.696656000	0.399430000
C	-2.151647000	-1.702876000	0.903397000
C	2.595505000	-0.855228000	-0.146264000
C	-2.955480000	-2.899634000	0.842114000
C	-4.867222000	-1.696276000	-0.199031000
C	-3.452596000	1.541895000	-0.243164000
C	3.905204000	-1.070551000	0.290297000
C	2.499920000	-3.156963000	-0.966914000
C	3.572780000	1.014844000	0.646204000
C	-1.054433000	2.876195000	0.128952000

C	-6.169342000	-1.699882000	-0.711904000
H	-6.597983000	-0.767146000	-1.062014000
C	-2.736978000	-0.523012000	0.305051000
C	1.866968000	-1.863243000	-0.884126000
C	-2.444008000	-4.116854000	1.392883000
C	4.536473000	-2.360177000	0.219532000
C	3.796603000	-3.408089000	-0.401087000
C	0.210111000	3.453734000	0.300011000
H	0.283189000	4.529967000	0.358863000
C	1.838404000	-4.217251000	-1.662920000
C	0.661556000	-1.666648000	-1.575068000
H	0.187686000	-0.698022000	-1.546889000
C	-6.338182000	-4.080496000	-0.321027000
H	-6.908874000	-5.003927000	-0.366078000
C	-2.264097000	3.649659000	-0.110712000
C	-3.435119000	2.975862000	-0.355717000
C	3.745209000	2.417949000	0.916718000
C	0.612357000	-3.973523000	-2.305109000
H	0.121386000	-4.784978000	-2.834818000
C	-6.895712000	-2.889806000	-0.777311000
H	-7.902549000	-2.885026000	-1.183981000
C	-4.752808000	3.623168000	-0.729469000
H	-4.581174000	4.634194000	-1.106873000
H	-5.180917000	3.048105000	-1.556883000
C	-2.170034000	5.159855000	-0.180640000
H	-3.137375000	5.601333000	0.067594000
H	-1.481277000	5.525067000	0.589596000
C	4.387454000	-4.707264000	-0.488992000

C	-5.038375000	-4.110729000	0.216238000
C	5.668794000	-4.920115000	0.051472000
H	6.108704000	-5.911360000	-0.014965000
C	-1.195442000	-4.121858000	2.037666000
H	-0.819142000	-5.050828000	2.456554000
C	-4.461875000	-5.321971000	0.727925000
H	-5.042379000	-6.238393000	0.668094000
C	-3.226990000	-5.319314000	1.297243000
H	-2.805462000	-6.235045000	1.702710000
C	5.815885000	-2.603826000	0.731596000
H	6.360001000	-1.787748000	1.194578000
C	2.682428000	3.267741000	0.725475000
C	-0.464563000	-2.947730000	2.152058000
H	0.487657000	-2.949225000	2.673909000
C	-0.930042000	-1.757779000	1.591622000
H	-0.328205000	-0.866252000	1.672452000
C	0.049310000	-2.705409000	-2.276913000
H	-0.884941000	-2.514401000	-2.796281000
C	6.373208000	-3.880940000	0.652086000
H	7.363357000	-4.063195000	1.058948000
C	-1.719828000	5.691144000	-1.559331000
H	-2.439173000	5.361105000	-2.318694000
H	-0.760116000	5.237160000	-1.833821000
C	-5.798318000	3.667096000	0.410048000
H	-5.989495000	2.643121000	0.746538000
H	-6.739113000	4.034139000	-0.018278000
C	5.119944000	2.844707000	1.395243000
H	5.008569000	3.552622000	2.223628000

H	5.618514000	1.961269000	1.801240000
C	3.662146000	-5.757571000	-1.146559000
H	4.112075000	-6.745151000	-1.198061000
C	2.449587000	-5.517874000	-1.713532000
H	1.915906000	-6.311639000	-2.229032000
C	6.037958000	3.479358000	0.325388000
H	6.979886000	3.745392000	0.821092000
H	5.602290000	4.423162000	-0.022227000
C	6.333262000	2.580422000	-0.878249000
H	5.420827000	2.345663000	-1.436191000
H	7.026942000	3.072564000	-1.567762000
H	6.780411000	1.632002000	-0.564807000
C	2.801265000	4.766924000	0.892836000
H	1.962265000	5.141363000	1.492747000
H	3.701465000	5.003906000	1.465216000
C	-1.599243000	7.217031000	-1.585834000
H	-2.554399000	7.693520000	-1.338244000
H	-0.855589000	7.569021000	-0.861902000
H	-1.295570000	7.571917000	-2.575651000
C	2.850768000	5.545509000	-0.441573000
H	1.957812000	5.322268000	-1.037145000
H	3.702055000	5.187456000	-1.032029000
C	-5.409214000	4.543954000	1.603364000
H	-6.183079000	4.511947000	2.377236000
H	-4.471454000	4.209604000	2.059654000
H	-5.282967000	5.591672000	1.307281000
C	2.963067000	7.057282000	-0.228472000
H	2.105810000	7.443125000	0.334808000

H	3.869724000	7.312503000	0.331317000
H	3.000601000	7.587975000	-1.184901000

Protonated HELI-2

7	2.312707000	0.702911000	-0.400574000
7	0.000000000	0.742838000	0.000002000
7	-4.467189000	0.410800000	0.129130000
7	4.467188000	0.410803000	-0.129127000
7	-2.312708000	0.702911000	0.400575000
6	1.125416000	1.419984000	-0.176676000
6	-1.125417000	1.419984000	0.176674000
6	2.590907000	-0.647557000	-0.751140000
6	-1.823780000	-1.682856000	1.408451000
6	3.953438000	-0.811299000	-0.515616000
6	-2.590907000	-0.647555000	0.751148000
6	1.222399000	2.840772000	-0.083039000
6	-1.222401000	2.840772000	0.083022000
6	2.522856000	-2.925347000	-1.588772000
6	-3.953438000	-0.811299000	0.515629000
6	4.663880000	-2.039281000	-0.674375000
6	-0.000002000	3.519600000	-0.000012000
1	-0.000002000	4.601491000	-0.000019000
6	1.823783000	-1.682862000	-1.408438000
6	-3.495509000	1.337091000	0.091136000
6	2.506274000	3.517571000	0.013447000
6	-2.506278000	3.517569000	-0.013471000
6	3.888934000	-3.111405000	-1.202083000
6	-3.644305000	2.738518000	-0.108803000
6	3.495508000	1.337094000	-0.091142000

6	3.644303000	2.738523000	0.108785000
6	-0.547328000	-1.527776000	1.971618000
1	-0.054883000	-0.574800000	1.873753000
6	-4.663879000	-2.039279000	0.674397000
6	-2.522853000	-2.925340000	1.588794000
6	6.011216000	-2.217719000	-0.347607000
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HELI-2 TS

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S16. ^{1}H, $^{13}C\{^{1}H\}$ NMR and ESI Mass Spectra

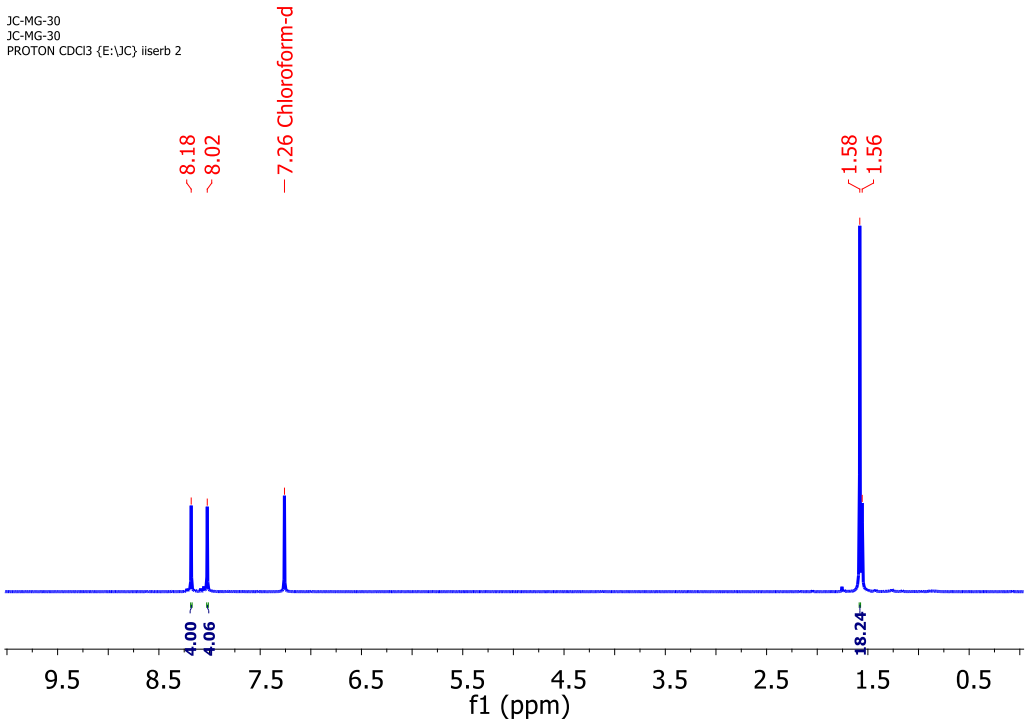

Figure S65. ^{1}H NMR spectrum of **2a** in $CDCl_3$ (400 MHz, 298 K)

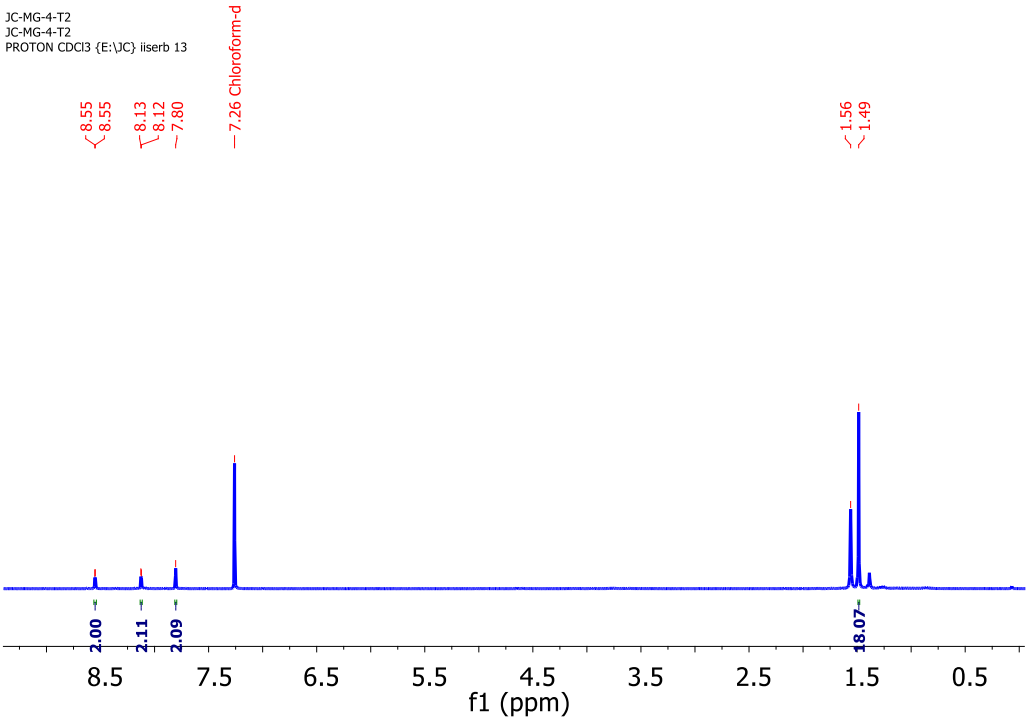

Figure S66. ^{1}H NMR spectrum of **3a** in $CDCl_3$ (400 MHz, 298 K)

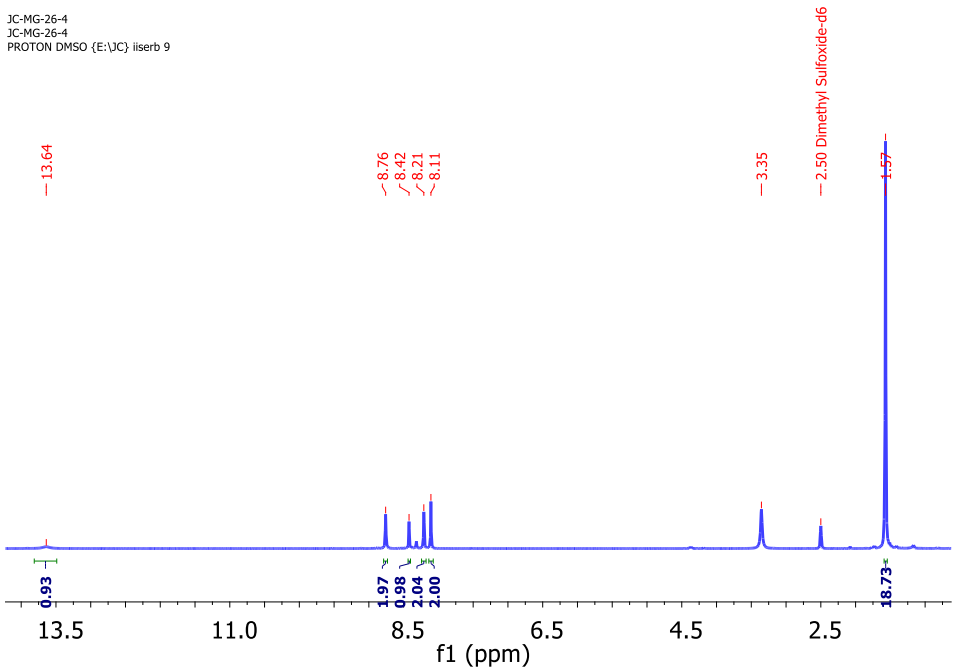

Figure S67. ^{1}H NMR spectrum of **4a** in DMSO-d_6 (400 MHz, 298 K)

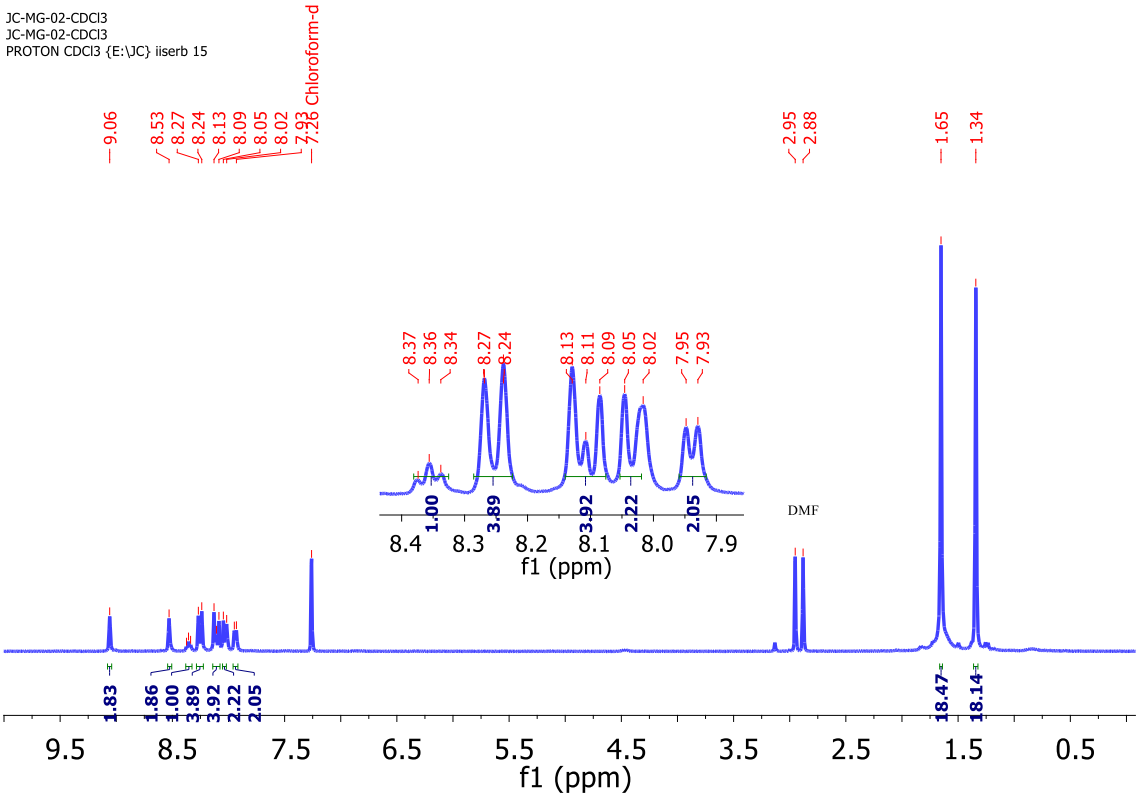

Figure S68. ^{1}H NMR spectrum of **PYBIM** in $CDCl_3$ (400 MHz, 298 K)

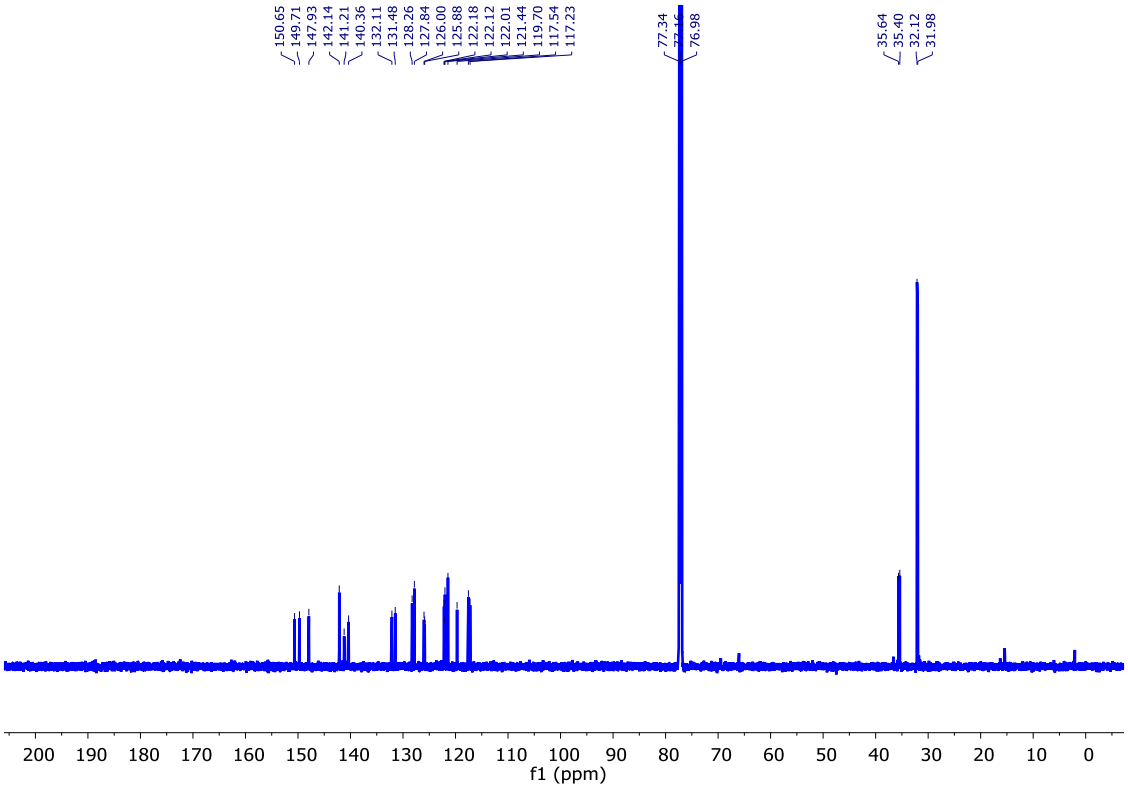

Figure S69. ^{13}C NMR spectrum of **PYBIM** in $CDCl_3$ (176 MHz, 298 K)

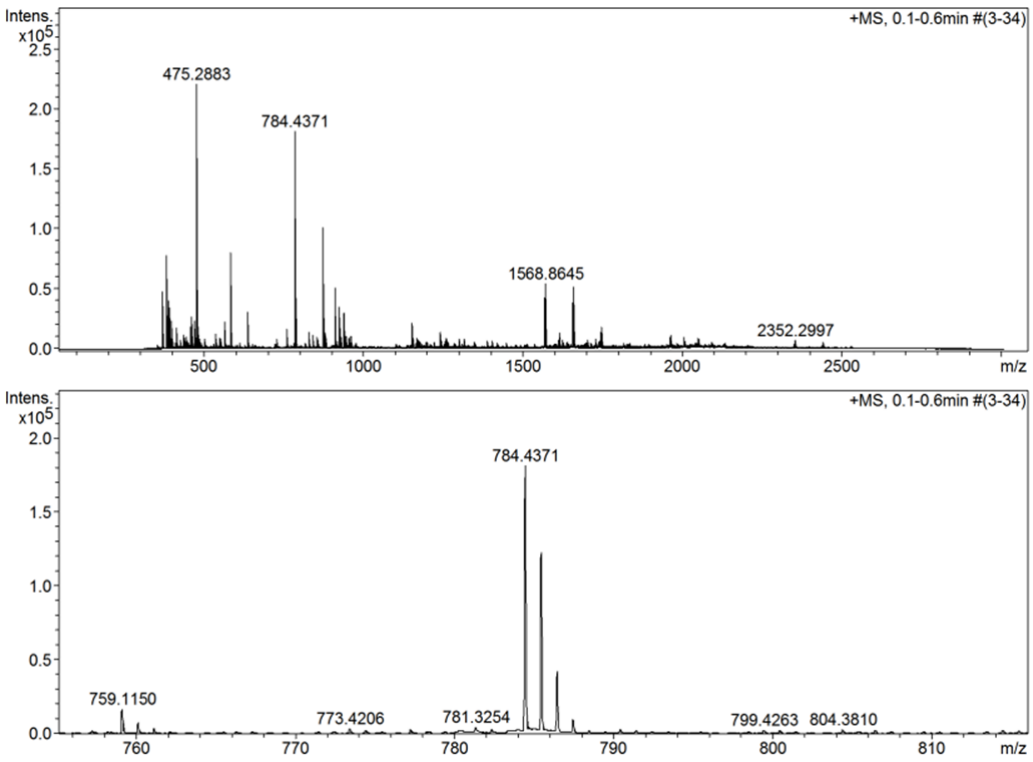

Figure S70. ESI-HRMS of **PYBIM** (positive ion mode)

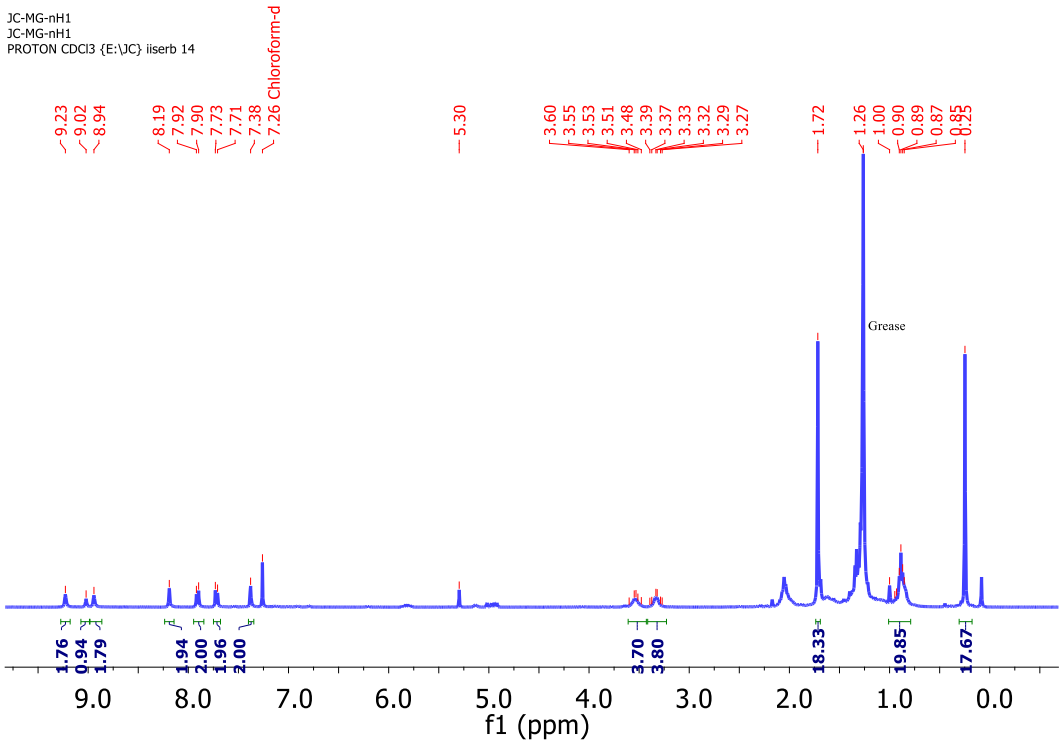

Figure S71. ^{1}H NMR spectrum of **HELI-1** in $CDCl_3$ (400 MHz, 298 K)

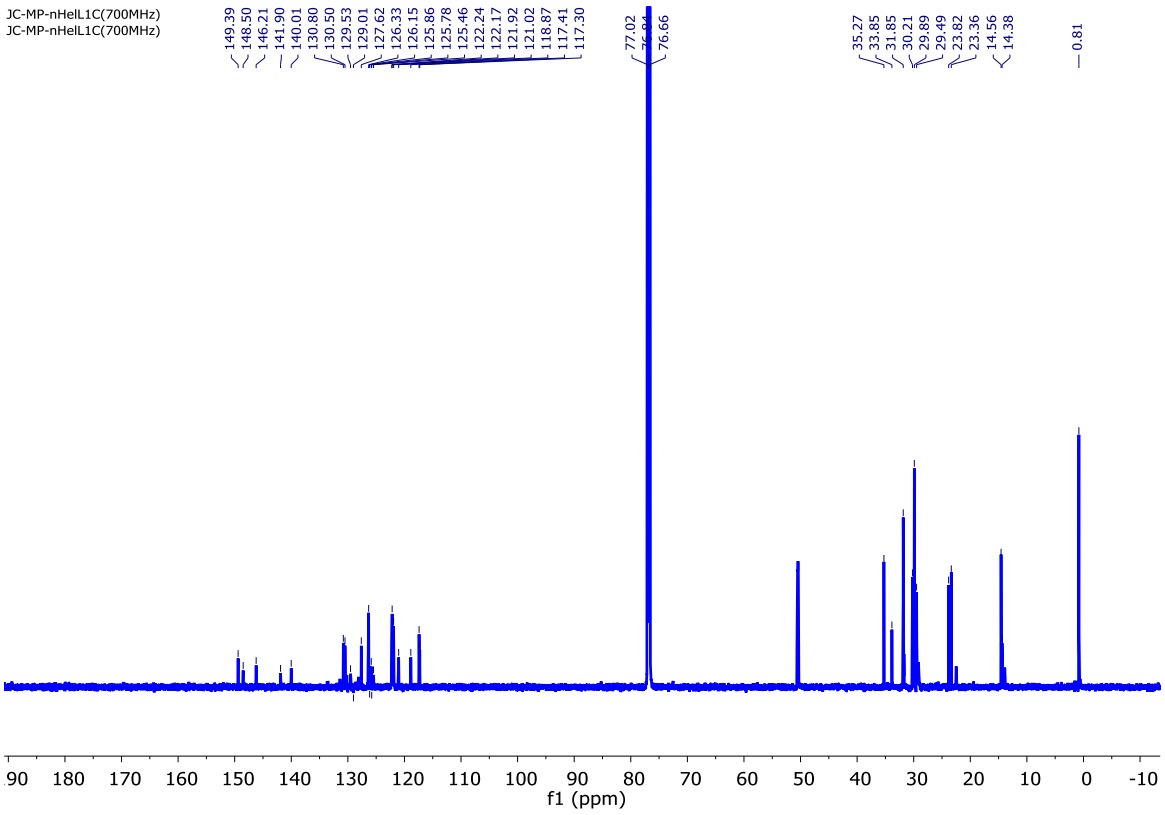

Figure S72. ^{13}C NMR spectrum of **HELI-1** in $CDCl_3$ (176 MHz, 298 K)

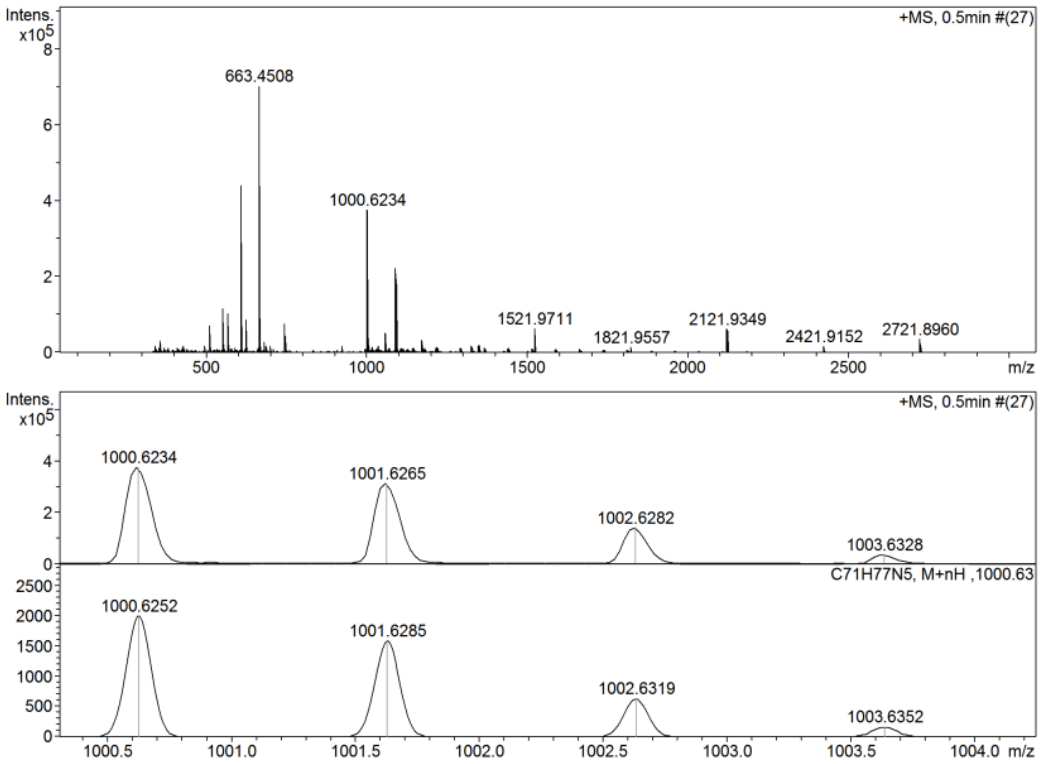

Figure S73. APCI-HRMS of **HELI-1** (positive ion mode)

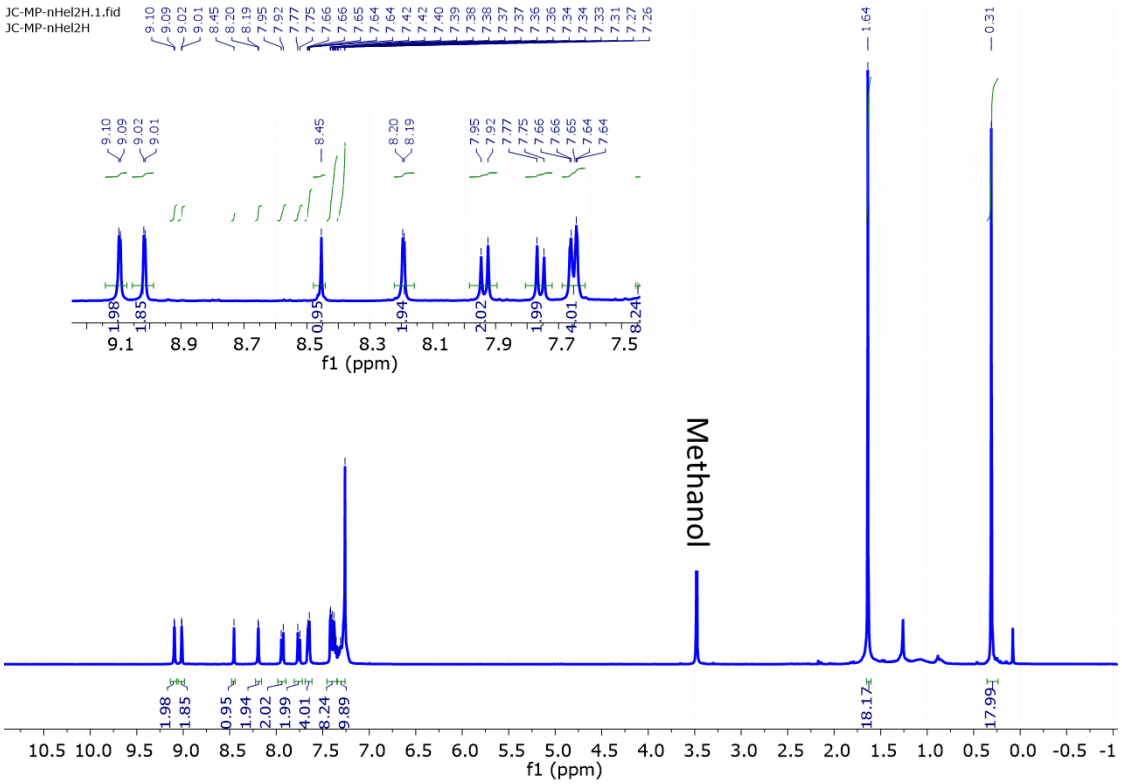

Figure S74. ^{1}H NMR spectrum of **HELI-2** in $CDCl_3$ (400 MHz, 298 K)

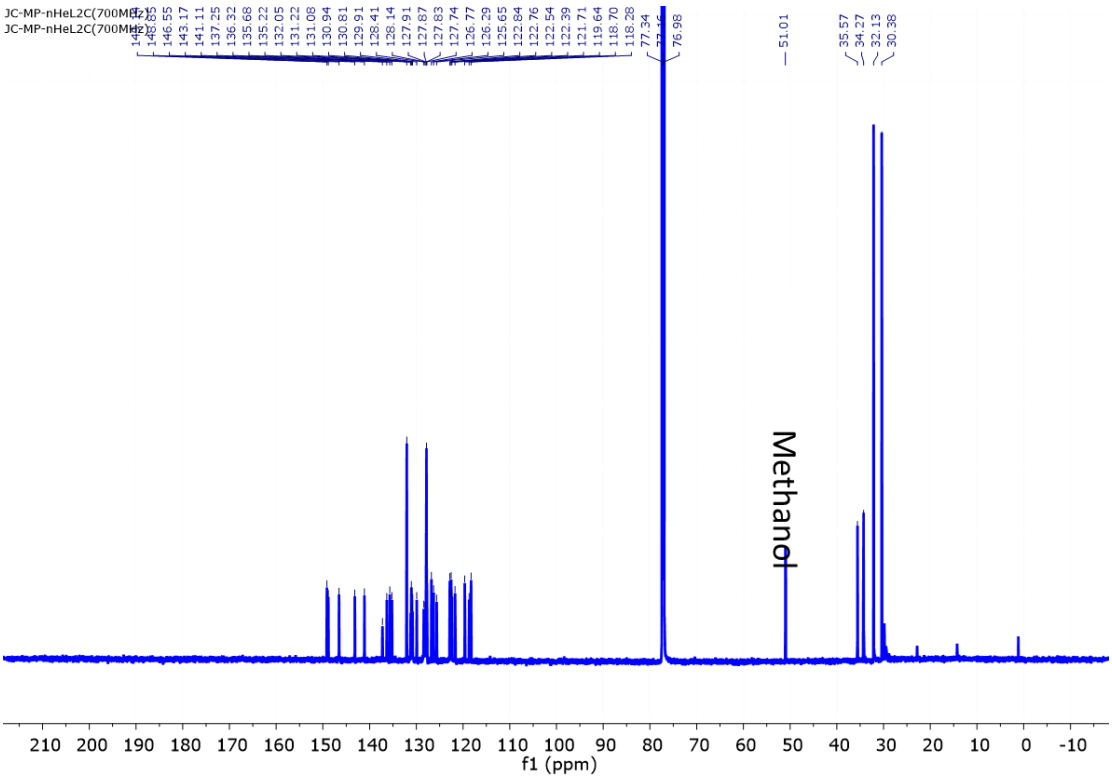

Figure S75. ^{13}C NMR spectrum of **HELI-2** in $CDCl_3$ (176 MHz, 298 K)

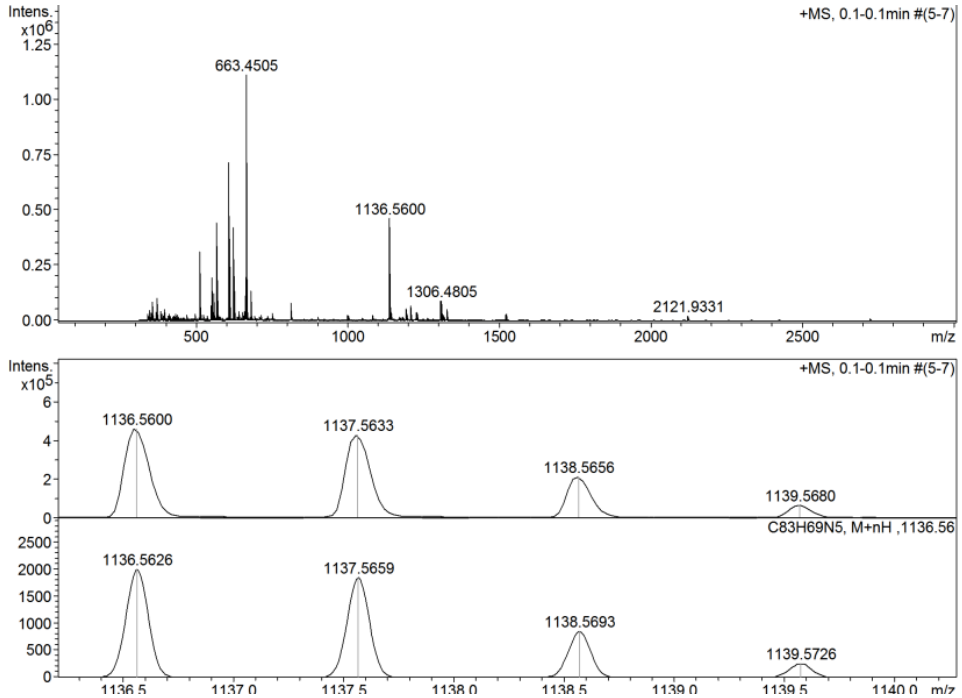

Figure S76. APCI-HRMS of **HELI-2** (positive ion mode)

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