Electronic Supporting Information

This PDF file includes:

1. Supplementary figures

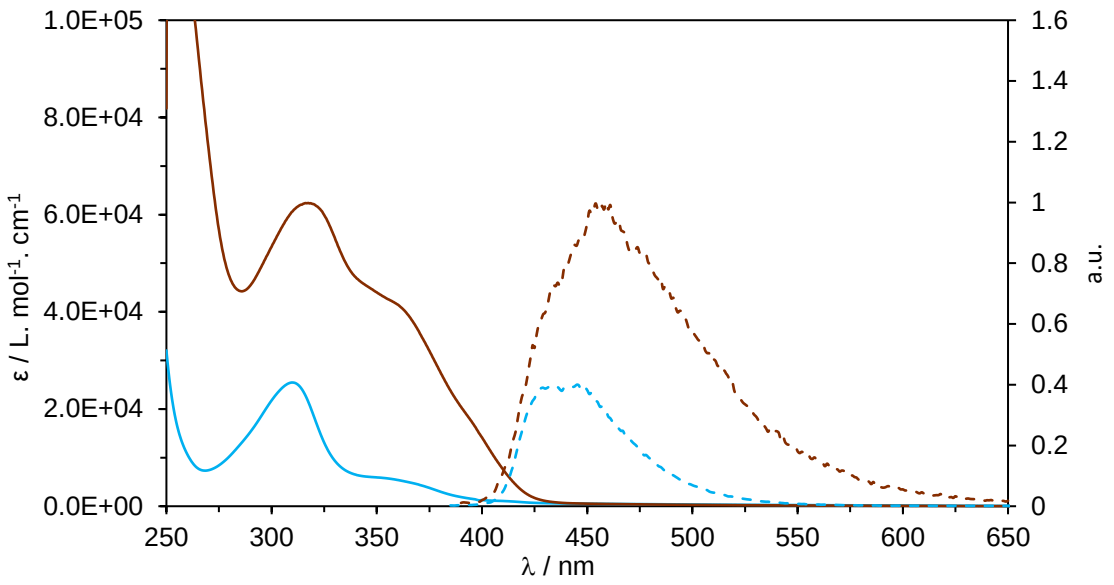


Figure S1. Absorption (solid) and fluorescence emission (dashed) spectra of **1** (brown) and **2** (cyan) in $CHCl_3$. (λ_{exc} = 370 nm).

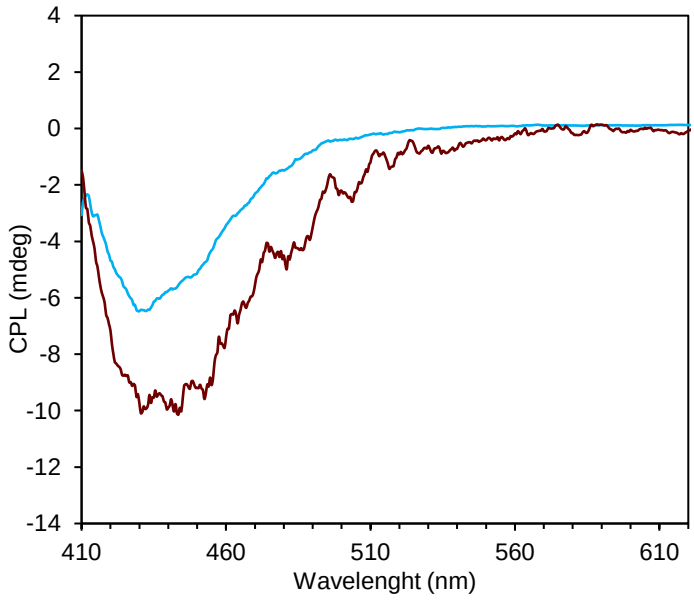


Figure S2. CPL spectra of *P*-**1** (brown) in $C_2H_2Cl_4$ and *P*-**2** (cyan) in $CHCl_3$.

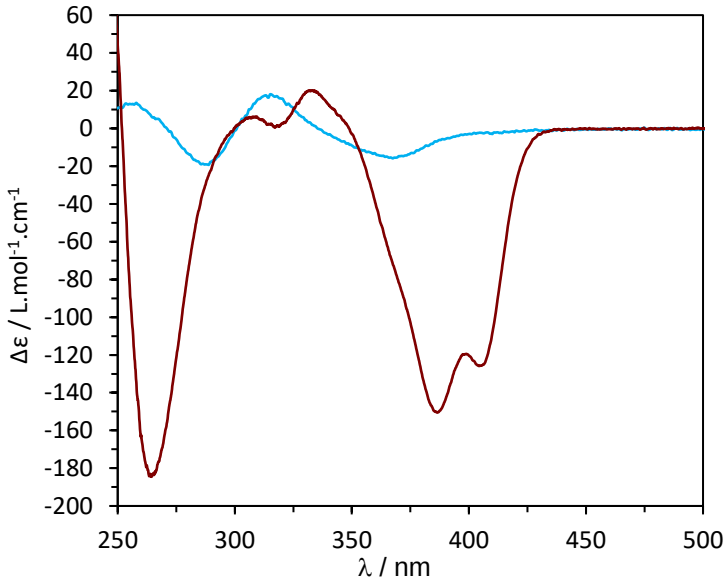


Figure S3. ECD spectra of *P*-**1** (brown) in $C_2H_2Cl_4$ and *P*-**2** (cyan) in $CHCl_3$.

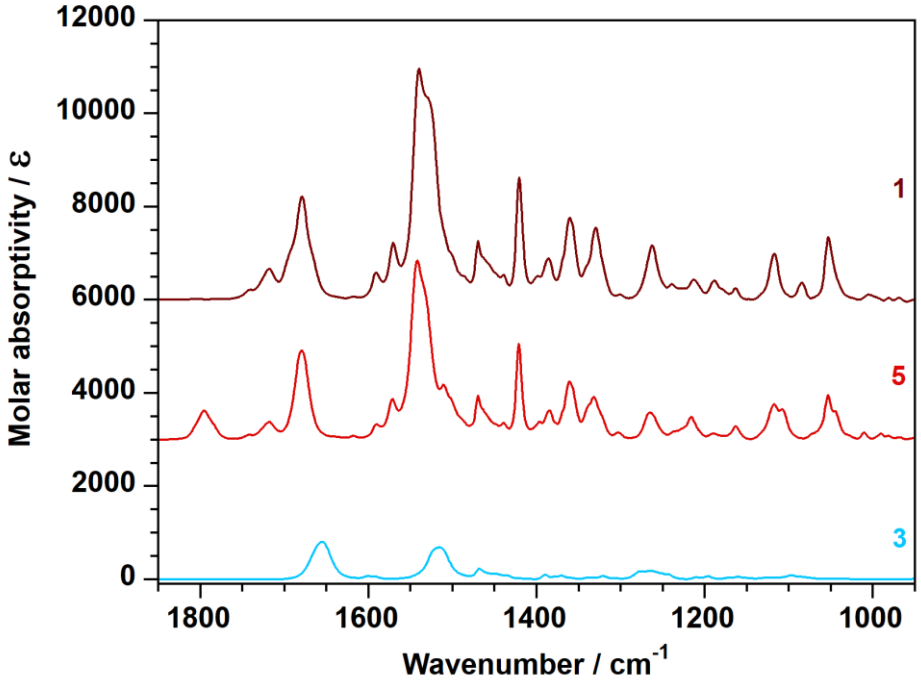


Figure S4. Infrared absorption spectra of **3** (cyan), **5** (red) and **1** (brown) in $CDCl_3$.

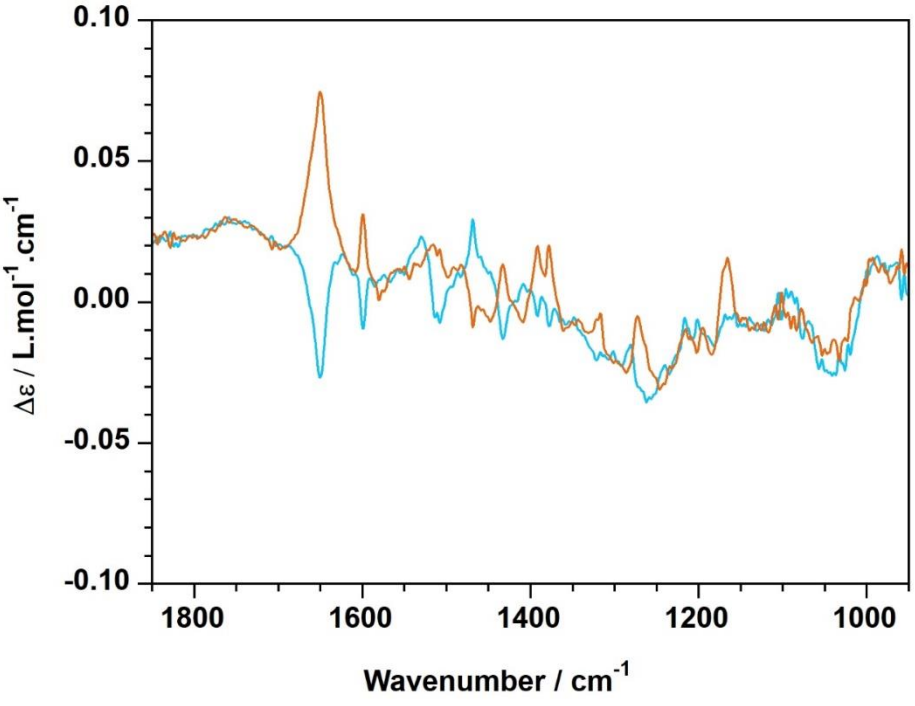


Figure S5. VCD spectra of *P*-**3** (cyan) and *M*-**3** (orange) in $CDCl_3$.

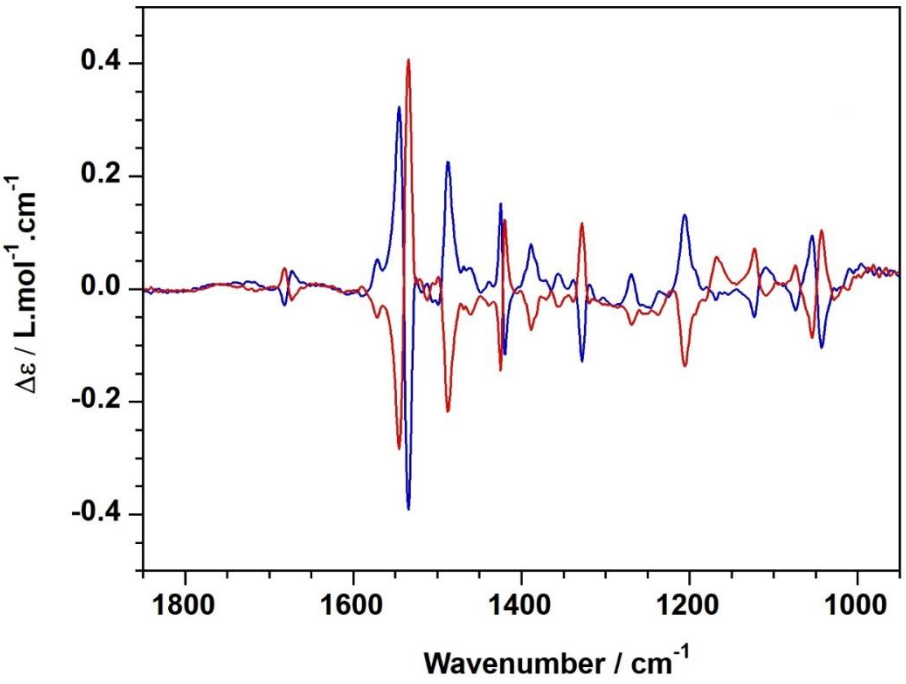


Figure S6. VCD spectra of *P*-**5** (blue) and *M*-**5** (red) in $CDCl_3$.

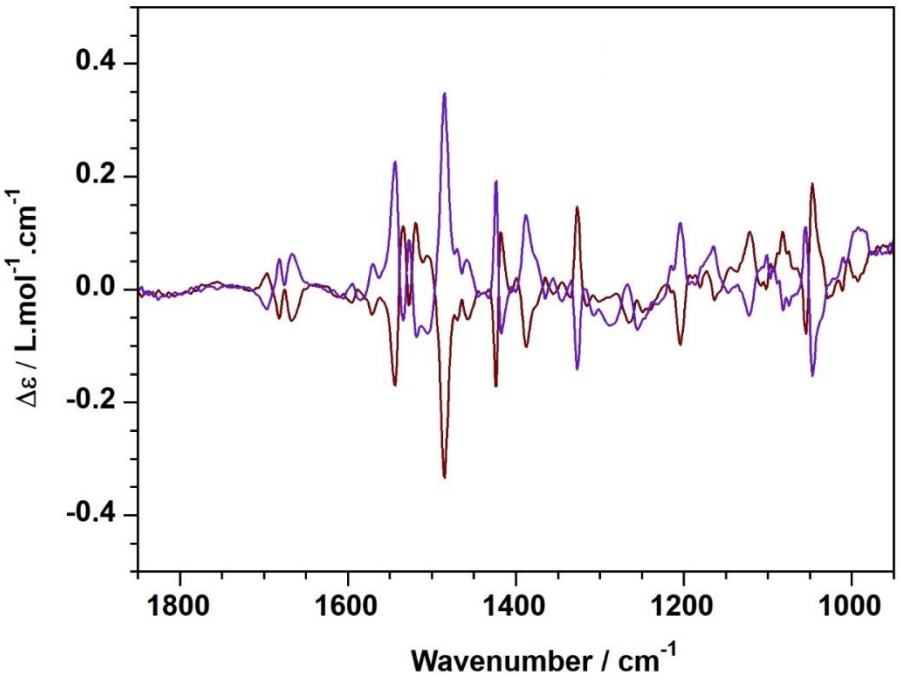


Figure S7. VCD spectra of *P*-**1** (brown) and *M*-**1** (purple) in $CDCl_3$.

2. Supplementary methods

2.1. Nuclear magnetic resonance spectroscopy

NMR spectra were recorded on two different NMR spectrometers: (1) an Avance I NMR spectrometer (Bruker Biospin) with a vertical 7.05T narrow-bore/ultrashield magnet operating at 300 MHz for ^{1}H observation, and 75 MHz for ^{13}C observation by means of a 5-mm direct BBO H/X probe with Z gradient capabilities; (2) an Avance NEO NMR spectrometer (Bruker BioSpin) with a vertical 16.45 T narrow-bore / ultrashield magnet operating at 700 MHz for ^{1}H observation by means of a 5-mm TXI ^{1}H / ^{13}C / ^{15}N probe with Z gradient capabilities. Chemical shifts are reported in parts per million (ppm, δ) with tetramethylsilane as an internal standard. ^{1}H NMR splitting patterns with observed first-order coupling are designated as singlet (s), doublet (d), triplet (t), or quartet (q). Coupling constants (J) are reported in hertz. Data processing was performed with Topspin 3.5 software. Samples were not degassed. Deuterated chlorinated solvents from Aldrich were used after filtration through an alumina pad.

2.2. High-resolution mass spectrometry

HR-MS spectra were performed by the CESAMO (ISM, University of Bordeaux, France) on a QExactive™ benchtop Orbitrap mass spectrometer coupled to a Vanquish UHPLC system (Thermo Scientific, San Jose, USA). The instrument is equipped with an ESI source and spectra were recorded in the positive mode. Samples were introduced by injection through a 20 µL sample loop into a 300 µL/min flow of methanol from the LC pump. XCalibur software version 4.1 was used for data acquisition and FreeStyle software version 1.5 for processing (Themo Scientific, San Jose, USA).

2.3. X-ray crystallography

The X-ray diffraction measurements were carried out on a Rigaku FRX rotating anode (2.9 kW) diffractometer at the IECB x-ray facility (UMS 3033 – UMS001). CuKα radiation monochromated with high flux Osmic Varimax mirrors was used for data collections. The X-ray source is equipped with a Dectris Pilatus 200K detector and partial chi goniometer.

2.4. UV-visible absorption, Fluorescence emission, Circular Dichroism (ECD), Circularly Polarized Luminescence (CPL), Infrared (IR) and Vibrational Circular Dichroism (VCD)

UV-visible absorption spectra were recorded on a UV-1650PC SHIMADZU spectrophotometer using a 1 cm pathlength quartz cuvette.

Steady-state emission spectra were recorded on a spectrofluorometer fitted with a PMT detector and exciting with a 450W Xe-lamp across a double monochromator, and were corrected for instrumental response. The fluorescence and reaction quantum yield were determined in degassed chloroform and air-equilibrated solutions as follows. The luminescence quantum yield (Φ) was calculated by using the equation $\Phi = \Phi_r(I/I_r)(A_r/A)(\eta^2/\eta_r^2)$ in which Φ_r refers to the quantum yield reference, I is the integrated

emission intensity, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent.[1] An optically dilute solution of quinine sulphate (λ_{exc} = 370 nm) in 1 N sulphuric acid was used as the standard, Φ_f = 0.54.

CD spectra were recorded on a JASCO J-815 spectropolarimeter using a 1 mm pathlength quartz cuvette. CPL spectra were recorded on a CPL-300 spectrophotometer using a 1 cm pathlength quartz cuvette.

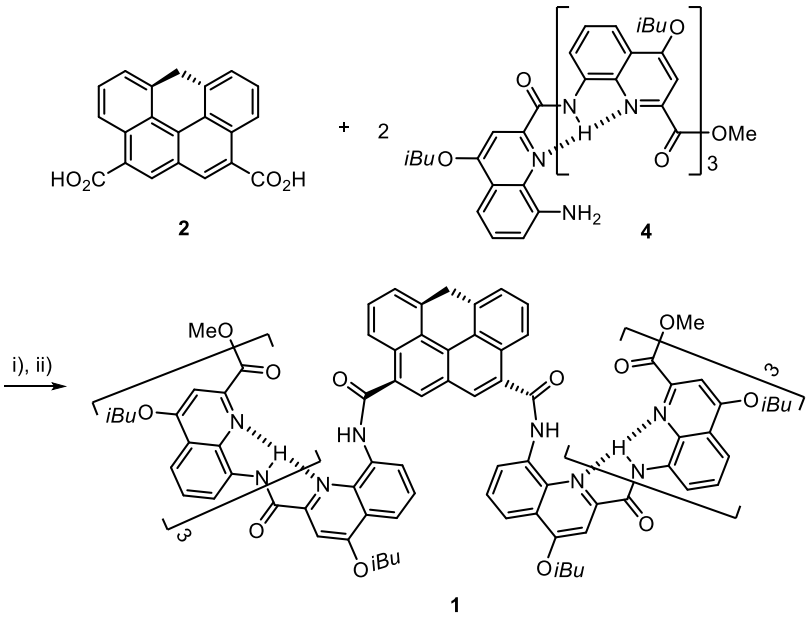
The IR and VCD spectra of the two enantiomers of **1**, **3** and **5** were recorded on a FTIR spectrometer equipped with a VCD optical bench.[2] IR absorption and VCD spectra were recorded at a resolution of 4 cm^{-1}, by coadding 50 and 48000 scans (16 h acquisition time), respectively. Samples were held in a 200 μm path length cell with BaF_2 windows. IR and VCD spectra were measured in $CDCl_3$ solvent at a concentration of 6 mM, 15 mM and 10 mM for **1**, **3** and **5**, respectively.

3. Synthetic schemes

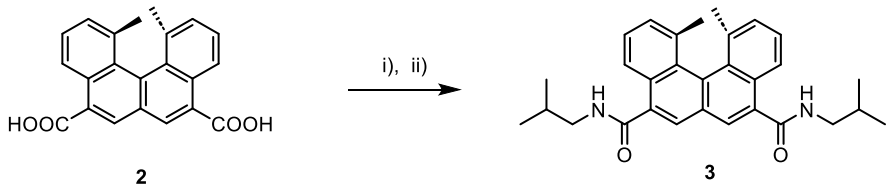
All reactions were carried out under a dry nitrogen atmosphere. Commercial reagents were purchased from Sigma-Aldrich, Alfa-Aesar or TCI and used without further purification unless otherwise specified. Chloroform ($CHCl_3$) and diisopropylethylamine (DIPEA) were dried over calcium hydride (CaH_2) and distilled prior to use.

Quinoline tetramers **4** and **5** were obtained as described by Huc et al.[3]

[4]carbohelicene **2** was prepared as described by Yamaguchi et al.[4]



Scheme S1. Synthesis of **1**: *i*) $SOCl_2$; *ii*) DIPEA, $CHCl_3$.



2 3

Scheme S2. Synthesis of **3** : *i*) $SOCl_2$; *ii*) Isobutylamine, DIPEA, $CHCl_3$.

4. References

[1] Eaton, D. E. Handbook of Organic Photochemistry, Vol 1; Scaiano, J. C., Ed.; CRC: Boca Raton, FL, 1989.

[2] T. Buffeteau, F. Lagugné-Labarthet and C. Sourisseau, *Appl. Spectrosc.* 2005, **59**, 732.

[3] T. Qi, T. Deschrijver and I. Huc, *Nature Protoc.*, 2013, **8**, 693.

[4] H. Okubo, M. Yamaguchi and C. Kabuto, *J. Org. Chem.*, 1998, **63**, 9500.

5. Experimental procedures for synthesis

Synthesis of *P*-1 : *(NB: the synthesis was performed with P-helicene precursor and repeated with the M-enantiomer)*

In a Schlenk tube under an inert atmosphere, [4]carbohelicene *P*-**2** (24 mg, 0.071 mmol) was dissolved in $SOCl_2$ (0.7 mL, [C] = 100 mM). The reaction was stirred under reflux for 4 h. The solvent was removed and the residue was dried under vacuum for 3 h, then solubilized in dry DCM and again dried under vacuum for 2 h to yield the corresponding di-acid chloride as a yellow solid. The latter was dissolved in dry $CHCl_3$ (1 mL), cooled down to 0 °C, and a freshly prepared solution of quinoline tetramer amine **4** (214 mg, 0.213 mmol) and distilled DIPEA (0.073 mL, 0.426 mmol) in dry $CHCl_3$ (1 mL) was added dropwise. The reaction was allowed to proceed overnight at RT. The volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and washed with a 5% NH_4Cl solution and pure water. The organics were dried over $MgSO_4$, filtered and the solvents were removed under reduced pressure. The residue was purified by chromatography (silica gel) eluting with (cyclohexane/ethyl acetate 8:2, v/v) to yield *P*-**1** as a pale yellow powder (27 mg, 16 %).

^{1}H NMR (*P*-1-*M*, $CDCl_3$, 700 MHz) δ 11.42 (s, 2H), 11.41 (s, 2H), 11.04 (s, 2H), 8.83 (s, 2H), 8.33 (dd, *J* = 8.2, 4.0 Hz, 4H), 8.11 (dd, *J* = 7.2, 0.9 Hz, 2H), 8.05 (dd, *J* = 7.9, 1.1 Hz, 2H), 7.79 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.73 – 7.71 (m, 2H), 7.70 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.68 (d, *J* = 6.5 Hz, 2H), 7.51 (s, 2H), 7.49 – 7.46 (m, 2H), 7.43 – 7.40 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.97 (dd, *J* = 7.1, 0.9 Hz, 2H), 6.72 (dd, *J* = 7.1, 0.7 Hz, 2H), 6.65 (s, 2H), 6.50 (dd, *J* = 8.0, 1.1 Hz, 2H), 6.45 (s, 2H), 6.27 (s, 2H), 6.21 (s, 2H), 5.45 (t, *J* = 7.6 Hz, 2H), 4.39 (t, *J* = 7.5, 6.5 Hz, 2H), 4.35 (t, *J* = 7.4 Hz, 2H), 3.77 (dd, *J* = 6.4, 3.5 Hz, 4H), 3.70 (t, *J* = 6.6 Hz, 2H), 3.60 (t, *J* = 6.6 Hz, 2H), 3.52 (t, *J* = 6.8 Hz, 2H), 3.49 (t, *J* = 6.8 Hz, 2H), 2.85 (s, 6H), 2.64 – 2.57 (m, 2H), 2.28 – 2.25 (m, 2H), 2.24 – 2.20 (m, 2H), 2.15 – 2.13 (m, 2H), 1.42 – 1.38 (m, 12H), 1.18 (dd, *J* = 22.1, 6.8 Hz, 12H), 1.10 (t, *J* = 6.5 Hz, 12H), 1.07 (dd, *J* = 6.7, 3.7 Hz, 12H).

^{1}H NMR (*P*-1-*P*, $CDCl_3$, 700 MHz) δ 11.48 (s, 4H), 11.28 (s, 2H), 9.06 (s, 2H), 9.03 (d, *J* = 8.3 Hz, 2H), 8.31 (d, *J* = 7.0 Hz, 2H), 7.97 (dd, *J* = 7.9, 1.1 Hz, 2H), 7.94 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.85 (dd, *J* = 7.3, 1.0 Hz, 2H), 7.83 (dd, *J* = 6.8, 0.6 Hz, 2H), 7.74 (d, *J* = 1.1 Hz, 2H), 7.73 (s, 2H), 7.58 (d, *J* = 7.0 Hz, 2H), 7.41 (s, 2H), 7.36 (s, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.11 (s, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.70 (s, 2H), 6.40 (d, *J* = 8.1 Hz, 2H), 6.32 (s, 2H), 6.15 (s, 2H), 5.64 (s, 2H), 5.43 – 5.38 (m, 2H), 4.41 – 4.37 (m, 2H), 4.35 (t, *J* = 7.4 Hz, 2H), 3.88 – 3.81 (m, 2H), 3.52 (t, *J* = 6.8 Hz, 2H), 3.42 (t, *J* = 6.8 Hz, 2H), 3.27 – 3.21 (m, 2H), 3.02 – 2.97 (m, 2H), 2.87 (s, 2H), 2.74 (t, *J* = 6.5 Hz, 2H), 2.35 – 2.30 (m, 2H), 2.13 – 2.10 (m, 2H), 2.10 – 2.05 (m, 2H), 1.41 – 1.40 (m, 12H), 1.21 (d, *J* = 6.8 Hz, 12H), 1.03 – 0.99 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 12H).

^{13}C NMR (*P*-1, 75 MHz, $CDCl_3$) δ 163.5, 163.4, 163.3, 163.3, 163.2, 163.2, 163.1, 163.0, 162.1, 162.0, 161.4, 161.0, 161.0, 160.9, 159.7, 159.5, 150.2, 150.0, 149.7, 149.7, 149.2, 149.0, 145.0, 144.9, 138.8, 138.8, 138.4, 138.1, 137.9, 137.8, 137.8, 137.5, 136.8, 136.7, 133.9, 133.8, 133.8, 133.7, 133.7, 133.1, 132.4, 132.1, 131.8, 131.1, 130.8, 130.4, 130.3, 130.1, 128.7, 128.3, 127.9, 127.6, 127.5, 127.3,

127.2, 126.9, 126.5, 126.4, 124.9, 124.7, 124.7, 124.3, 122.5, 122.2, 121.8, 121.6, 121.5, 121.3, 121.0, 120.9, 117.2, 117.0, 116.9, 116.7, 116.4, 116.3, 115.8, 115.4, 115.3, 115.0, 114.6, 114.3, 100.2, 100.1, 100.0, 99.8, 97.8, 97.7, 97.2, 77.4, 75.7, 75.6, 75.2, 74.9, 74.7, 74.4, 53.6, 51.9, 51.9, 31.1, 28.5, 28.4, 28.2, 28.2, 28.1, 28.1, 27.8, 24.0, 23.8, 19.7, 19.7, 19.6, 19.5, 19.5, 19.5, 19.4, 19.2, 19.2.

HRMS (ESI$^+$) m/z 2309.9918 $[M+H]^+$ (calc. 2309.9877 for $C_{113}H_{136}O_{20}N_{16}$).

Synthesis of 3 : The [4]carbohelicene **2** (47 mg, 0.14 mmol) was dissolved in $SOCl_2$ (1 mL) and refluxed for 4 h. The solvent was removed under vacuum for 1 h then solubilized in dry CH_2Cl_2 and dried again under vacuum for 2h, yielding the corresponding acid chloride as a yellow powder. Isobutylamine (41 µL, 0.41 mmol) was dissolved in dry $CHCl_3$ (1 mL) and DIPEA (0.12 mL, 0.7 mmol) was added. This solution was added dropwise at 0 ºC to a freshly prepared acid chloride solution in dry $CHCl_3$ (2 mL). The reaction was stirred at room temperature overnight. After reaction completion, the crude was dissolved in CH_2Cl_2 and washed with HCl 1 M and water. The organic phase was dried over $MgSO_4$, filtered, and the solvents removed under reduced pressure. The residue was subject to preparative GPC to yield pure helicene **3** as a light-yellow powder (27 mg, 44%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.1 Hz, 2H), 7.90 (s, 2H), 7.64 (t, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.1 Hz, 2H), 6.20 (t, *J* = 6.0 Hz, 2H), 3.46 (td, *J* = 6.5, 2.9 Hz, 4H), 2.02 (dt, *J* = 13.4, 6.7 Hz, 2H), 1.93 (s, 6H), 1.08 (dd, *J* = 6.7, 1.5 Hz, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 137.1, 134.9, 131.4, 129.9, 129.8, 129.3, 128.2, 127.3, 123.9, 123.0, 47.7, 28.9, 23.5, 20.4.

HRMS (ESI$^+$) m/z 477.2493 $[M+Na^+]$ (calc 477.2512 for $C_{30}H_{34}N_2O_2$).

6. Crystallography

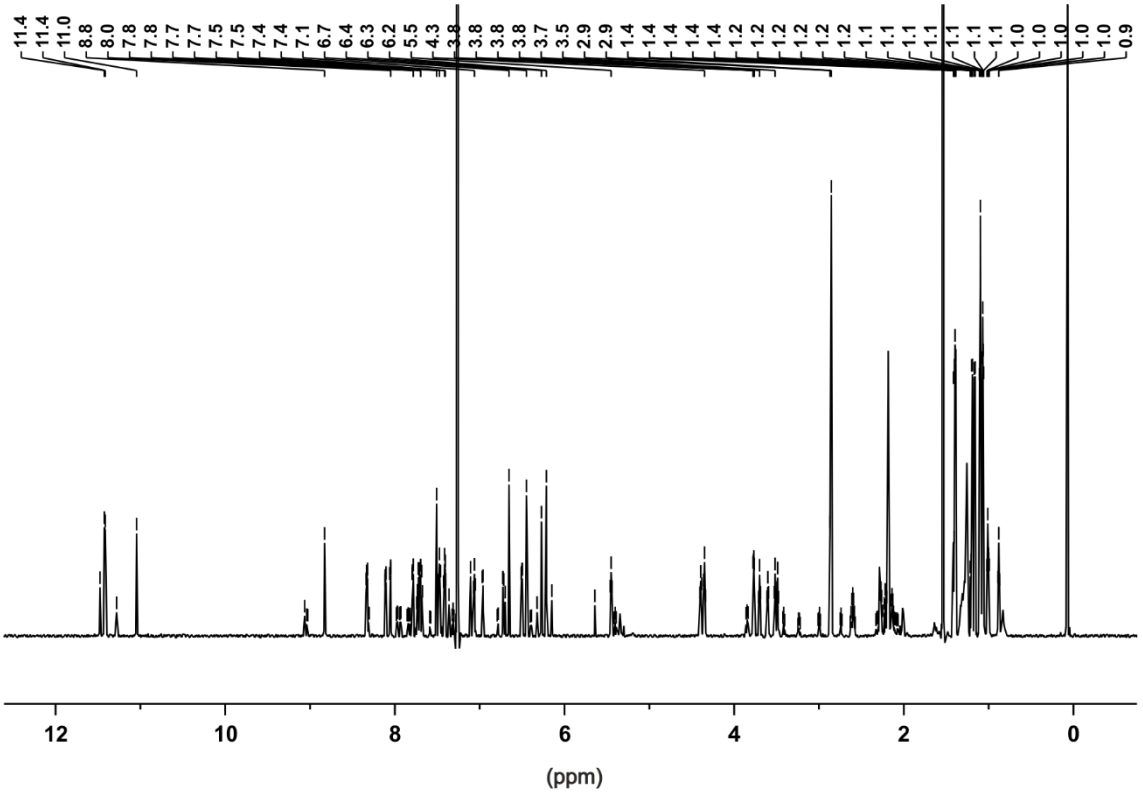
Table S1. Crystallographic data from crystals obtained from diffusion of hexane in chloroform solution of *P*-**1** (CCDC number: 2304953)

Compound	***P*-1** (from $CHCl_3$)
Chemical formula	$C_{136}H_{132}N_{16}O_{20}$
Formula weight, g/mol	2310.57
Temperature, K	120
Crystal system	monoclinic
Space group	$P2_1$
a, Å	14.1672(2)
b, Å	23.1965(4)
c, Å	19.4276(3)
α, °	90
β, °	90.664(2)
γ, °	90
V, $Å^3$	6384.05(17)
Z	2
$\rho_{calc,}$ g/cm^3	1.202
μ, mm^{-1}	0.663
F(000)	2440.0
Crystal size, mm^3	0.1 × 0.05 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection, °	6.238 to 140.114
Index ranges	$-17 \leq h \leq 14$, $-28 \leq k \leq 26$,
Reflections collected	33246
Independent reflections	17952 [R_{int} = 0.0288, R_{sigma} = 0.0595]
Data/restraints/parameters	17952/85/1521
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0902, wR_2 = 0.2498
Final R indexes [all data]	R_1 = 0.1021, wR_2 = 0.2657
Largest diff. peak/hole / e $Å^{-3}$	0.68/-0.79
CCDC #	2304953

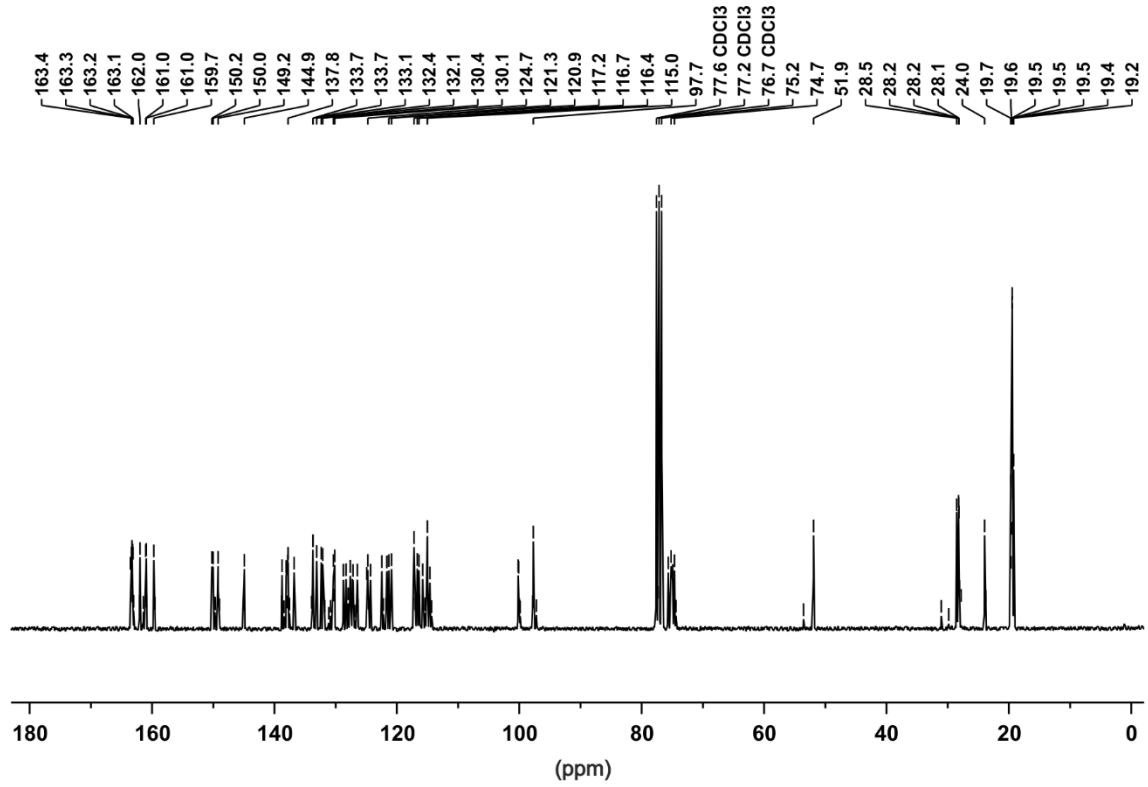
Table S2. Crystallographic data from crystals obtained from DMSO solution of *P*-**1** (CCDC number: 2333345)

Compound	***P*-1** (from DMSO)
Empirical formula	$C_{278}H_{282}N_{32}O_{43}S_3$
Formula weight	4855.52
Temperature/K	130
Crystal system	monoclinic
Space group	$P2_1$
a/Å	17.5282(6)
b/Å	21.4764(7)
c/Å	34.6216(11)
α/°	90
β/°	102.611(3)
γ/°	90
Volume/Å^3	12718.6(7)
Z	2
ρ_{calc}g/cm^3	1.268
μ/mm^{-1}	0.923
F(000)	5132.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.876 to 155.258
Index ranges	-22 ≤ h ≤ 22, -21 ≤ k
Reflections collected	93019
Independent reflections	39648 [R_{int} = 0.0570,
Data/restraints/parameters	39648/97/3251
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0656, wR_2 =
Final R indexes [all data]	R_1 = 0.0858, wR_2 =
CCDC #	2333345

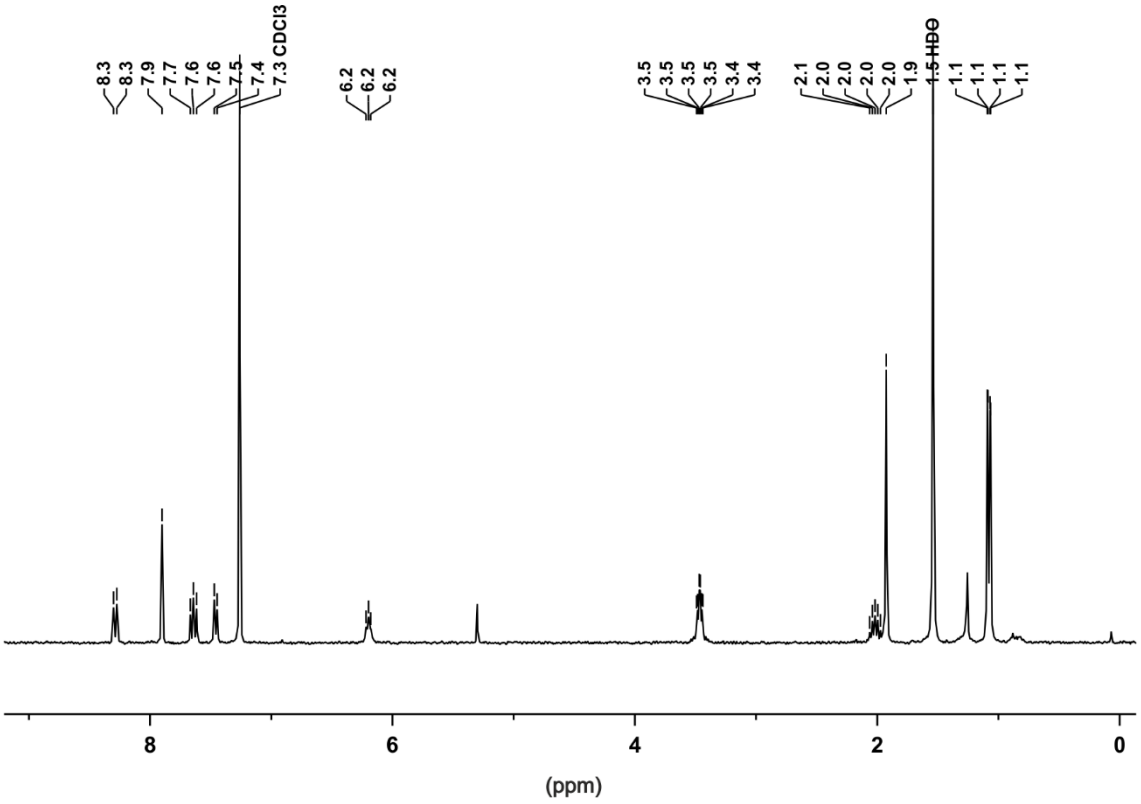
7. Characterization of new synthetic compounds



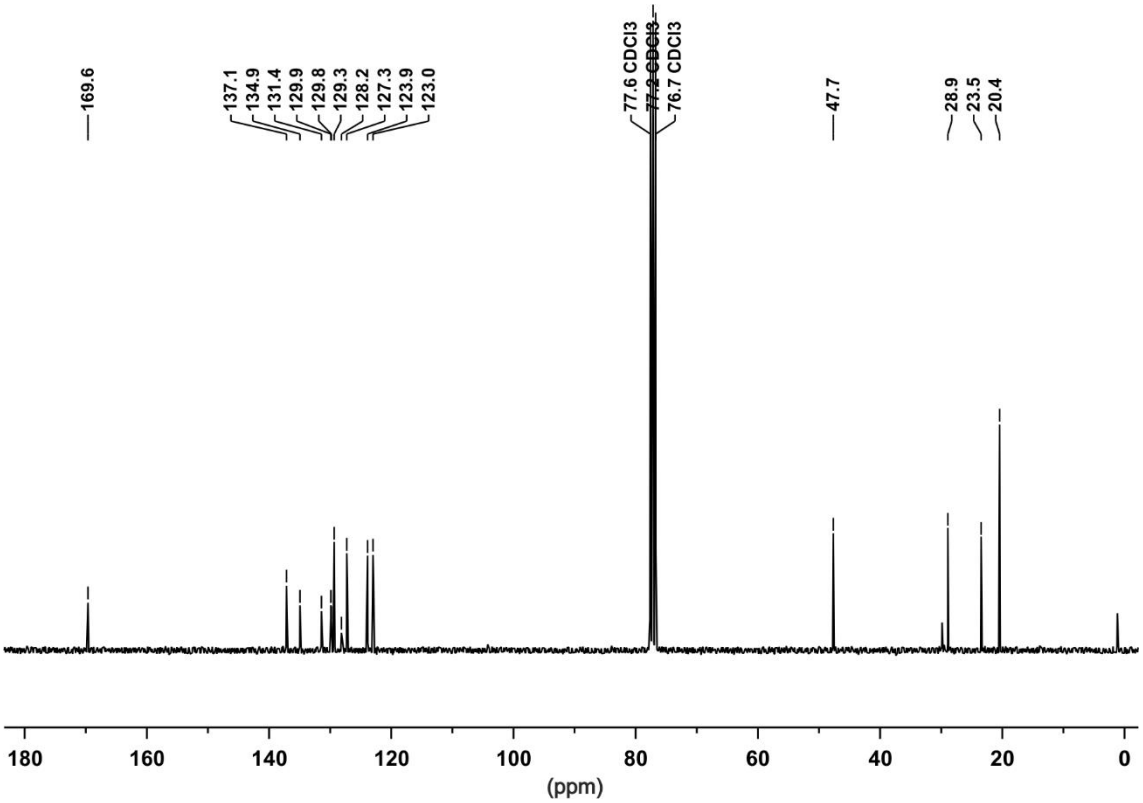
^{1}H NMR (700 MHz) spectrum of **1** in $CDCl_3$.



^{13}C NMR (300 MHz) spectrum of **1** in $CDCl_3$.



^{1}H NMR (300 MHz) spectrum of **3** in $CDCl_3$.



^{13}C NMR (300 MHz) spectrum of **3** in $CDCl_3$.