Supplementary Information

Strong circularly polarized luminescence via intramolecular excited-state symmetry-breaking charge separation

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1. Experimental section

1.1. Material and methods

All chemicals and solvents were purchased from Sigma Aldrich (Merck), Fluorochem, or TCI and were used without further purification unless otherwise stated. Column chromatography was performed with SiO_2 (40-63 μm). NMR data (^1H and ^{13}C) were recorded at 25 °C with Bruker AC300 spectrometer. Mass spectrometry was performed by the CESAMO analytical center (University of Bordeaux, France) on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is equipped with an ESI source and spectra were recorded in the positive mode. The electrospray needle was maintained at 5000 V and operated at room temperature. Samples were introduced by injection through a 20 µL sample loop into a 4500 µL/min flow of methanol from the LC pump. FT-IR spectra were measured with a Nicolet Impact 400D spectrophotometer. UV-vis spectra were measured with a PerkinElmer UV/VIS/NIR Lamba 750 spectrometer and the extinction coefficients were calculated using the Lambert-Beer Law. Fluorescence spectra were measured on a Fluormax-4 spectrophotometer. Quantum yields were determined from corrected emission spectra using quinine sulfate (FQY = 0.55 in 0.5 M H_2SO_4) as a fluorescent standard. The CPL measurements were performed on a JASCO CPL-300 spectrometer in different solvents with an excitation wavelength of 365 nm for compound **1**, 340 nm for compound **2**, and 350 nm for **3**. All optical measurements were performed at room temperature. Lifetime spectra were performed on a PicoQuant PDL 800-D. The excitation originated from a diode laser at 310 nm operated in pulsed mode.

1.2. Synthesis

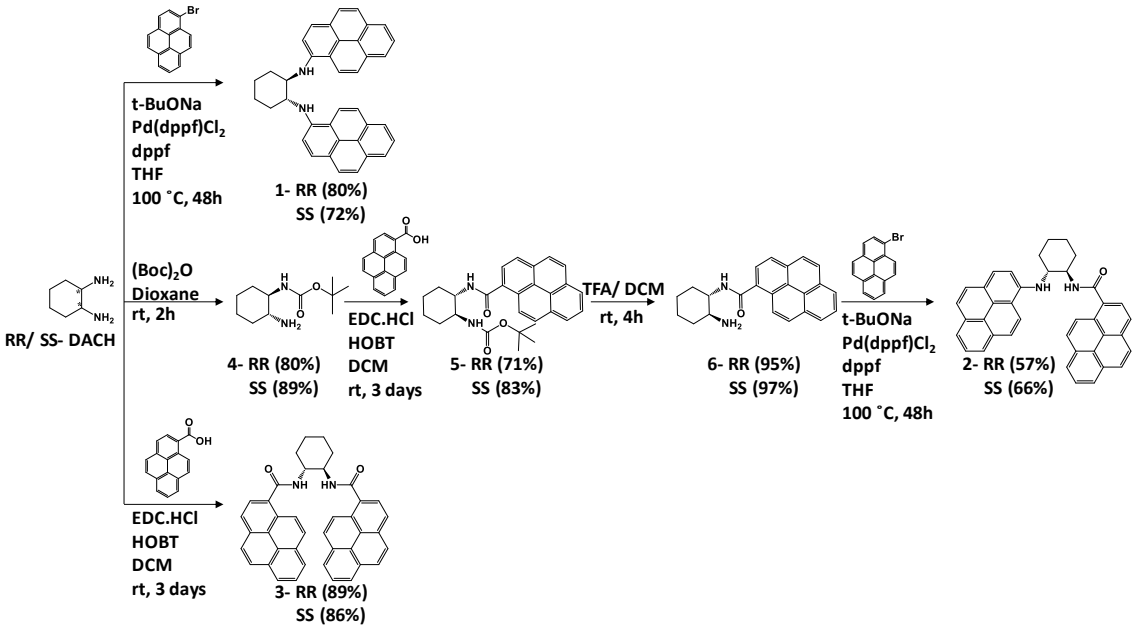
The synthesis of the derivatives **1**, **2,** and **3** is shown in **Scheme S*1***. Compounds **1** and **2** showed good solubility in organic solvents, while derivative **3** is poorly soluble due to a greater propensity towards aggregation.
Compounds **3**, **4**, and **5** were synthesized according to the procedures described in the literature[1],[2] and the structures were confirmed by ^1H NMR.

Synthesis of 1 (RR or SS): The compound was obtained by Buchawald-Hartwing coupling between 1-bromopyrene (200 mg, 7.06 mmol), the corresponding R,R or S,S 1,2-cyclohexanediamine (37 mg, 3.21 mmol), *t*-BuONa (68 mg, 7.06 mg), $Pd(dppf)Cl_2$ (40 mg, 0.55 mmol) and dppf (80 mg, 0.144 mmol) placed in a Schlenk tube under inert conditions. Then, 10 mL of dry THF was added and the reaction mixture was stirred for 48h at 100 ˚C. The solvent was removed under reduced pressure and the product was purified through a flash column using CH_2Cl_2 as the eluent followed by recrystallization from EtOH to afford **1** (RR or SS) as a light-yellow solid (yield: RR 80% and SS 72%) ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.11 (d, J=6 Hz, 2H), 8.05 (d, J=6 Hz, 2H), 7.93 (m, J=6 Hz, 2H), 7.85 (t, J=6 Hz, 2H), 7.79 (d, J= 6 Hz, 2H), 7.73 (q, J=12 Hz, J=6 Hz 4H), 7.54 (d, J=12 Hz, 2H), 5.01 (s, 2H), 3.88 (d, J= 6 Hz, 2H), 2.63 (d, J=12 Hz, 2H), 1.95-

1.92 (m, 2H), 1.67-1.49 (m,4H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 141.9, 132.4, 131.7, 127.7, 126.2, 126.1, 125.6, 124.0, 123.7, 123.6, 123.5, 119.5, 117.8, 110.2, 58.7, 32.8, 24.9. HR-MS: 514.24 [M+] (calc. 515.24 pour $C_{38}H_{30}N_2$]).

Synthesis of 2 (RR or SS): Were synthesized using the same procedure as derivative **1**. Where 1-bromopyrene (10.0 mg, 0.88 mmol), the respective RR or SS *N*-2-aminocyclohexyl)pyrene-1-carboxamide **6** (30 mg, 0.88 mmol), t-BuONa (12.6 mg, 1.31 mmol), Pd(dppf)Cl_2 (19 mg, 0.26 mmol) and dppf (19 mg, 0.35 mmol) were places in a Schleck under inert conditions. Then, 10 mL of dry THF was added to the mixture and the reaction was stirred for 48h at 100 ˚C. The crude reaction mixture was filtered through celite and the solvent was removed under reduced pressure. Then, the product was purified through a silica gel column using CH_2Cl_2 as the eluent to afford **2** (RR or SS) as a light-yellow solid (yield: RR 57% and SS 66%). ^{1}H NMR (300 MHz, THF-d8) δ (ppm) 8.52 (d, J= 12 Hz, 1H), 8.42 (d, 9 Hz, 1H), 8.13 (dd, J=1.5 Hz, J=6 Hz, 1H). 8.08- 7.78 (m, 13H), 7.66 (d, 9 Hz, 1H), 7.61 (d, 9 Hz, 1H), 7.35 (d, 6 Hz,1H), 6.77 (d, 6 Hz, 1H), 4.59-4.53 (m, 1H), 3.72-3.69 (m, 1H), 2.64- 2.61 (m, 1H), 2.36-2.32 (m, 1H), 1.98-1.89 (m, 2H), 1.67-1.51 (m, 4H). ^{13}C NMR (300 MHz, THF-d8) δ (ppm) 171.9, 144.1, 133.9, 133.5, 133.4, 133.2, 132.3, 131.8, 129.5, 129.1, 128.7, 128.6, 128.0, 127.4, 127.0, 126.6, 126.4, 126.3, 126.1, 126.0, 125.9, 125.4, 124.9, 124.0, 123.6,123.2, 123.1, 122.0, 118.4, 117.2, 108.8, 60.7, 54.4, 53.9, 33.7, 33.3, 26.6. FT-IR (KBr), ν (cm^{-1}): 3393, 3297, 3038, 2931, 2859, 1615, 1602, 1524. HR-MS: 543.2428 [M+] (calc. 543.2430 pour $C_{39}H_{31}ON_2$).

Synthesis of 6 (RR or SS): *N*-2-aminocyclohexyl)pyrene-1-carboxamide **5** (30 mg, 0.0678 mmol) was dissolved in DCM (4 ml) and then TFA (4 mL) was added at 0 ˚C. The reaction was then allowed to reach rt and stirred for 4h. After the deprotection reaction was complete 10 mL of water was added and the crude product was washed with DCM and neutralized with NaOH. The solvent was removed under reduced pressure to afford **6** in the form of a white solid (yield: RR 95% and SS 97%). ^{1}H NMR (300 MHz, DMSO) δ (ppm): 8.70 (d, 9 Hz, 1H), 8.62 (d, 9 Hz, 1H), 8.41-8.35 (m, 4H), 8.30-8.22 (m, 3H), 8.14 (t, 6H, 1H), 7.98 (s, 2H), 4.11-4.06 (m, 1H), 2.08 (t, 12 Hz, 1H), 2.18-2.08 (m, 2H), 1.79 (d, 9 HZ, 2H), 1.51-1.31 (m, 4H).



Scheme S1- Reaction scheme for the preparation of compounds **1**-**3**.

2. Spectroscopic characterization

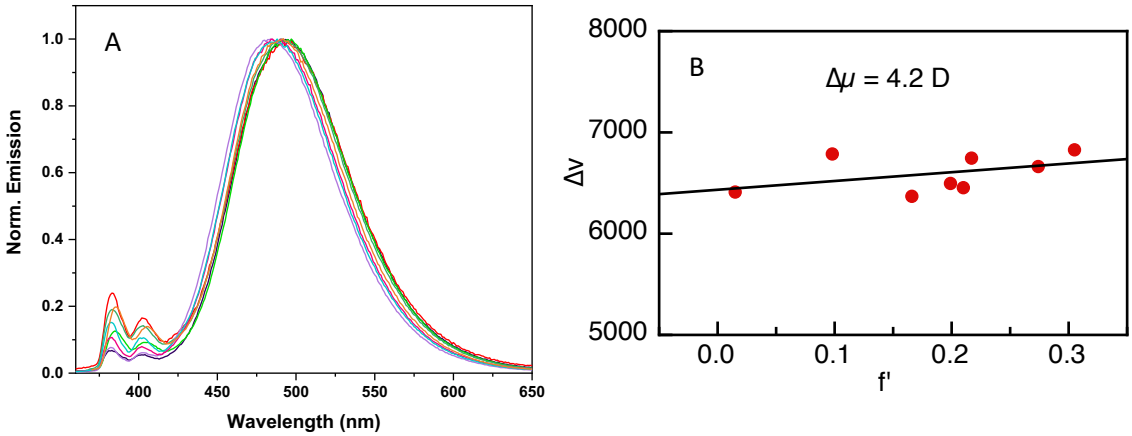


Figure S1. A: Excimer contribution to the emission of **3** in various solvents (λ_{ex} = 350 nm). From left to right: toluene, di-n-butylether, diethylether, ethylacetate, dichloromethane, tetrahydrofuran, acetonitrile, DMF. B: Lippert-Mataga plot and linear best fit is shown on the right.

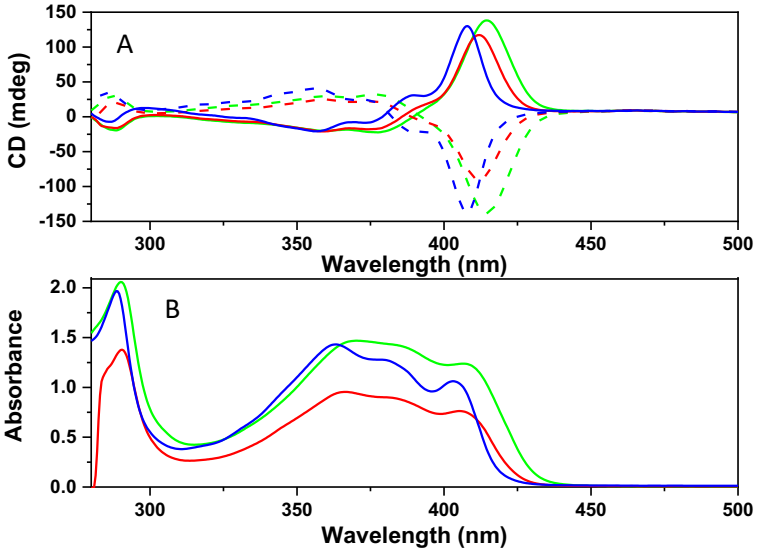


Figure S2. Circular dichroism (A) and electronic absorption spectra (B) of 1 in cyclohexane (blue) toluene (red) and dichloromethane (green).

Procedure for determining excimer (EX) and locally excited state (LE) contributions: The overall emission $I_T(\lambda)$ is given by:

$$I_T(\lambda) = \alpha I_{LE}(\lambda) + (1-\alpha) I_{EX}(\lambda)$$

Where $I_{LE}(\lambda)$ and $I_{EX}(\lambda)$ are the contributions from the LE and EX states and α is a constant ($0 \leq \alpha \leq 1$). Because the excimer lifetime is substantially longer than the residual LE emission (15 to 22 ns vs. 0.1 to 0.6 ns, respectively) and both excited states are quenched by oxygen, only LE emission is recorded in oxygen-saturated solutions ($\alpha \approx 1$). The LE emission is then subtracted from the spectra acquired under deoxygenated conditions by visual fitting so as to completely remove the LE contribution and not introduce negative absorption peaks. The value of α is then determined from the ratio of the integrated LE and EX emission. An example is given in Figure S3 for **1** in cyclohexane.

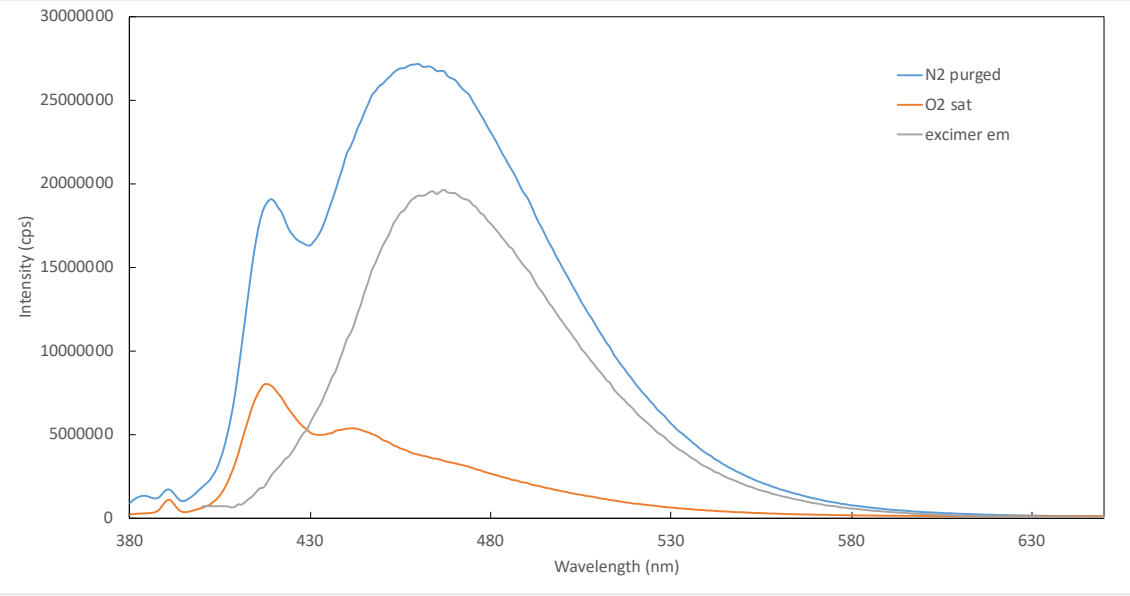


Figure S3. Emission of **1** in cyclohexane (λ_{ex} = 365 nm) recorded under nitrogen-purged conditions (blue line) and oxygen-saturated conditions (red line). The gray line is the emission attributed to the excimer obtained by subtracting the red spectra from the blue one after compensating for partial quenching by oxygen. The relative areas below the red and blue spectra give α = 0.39.

3. Structural Characterization

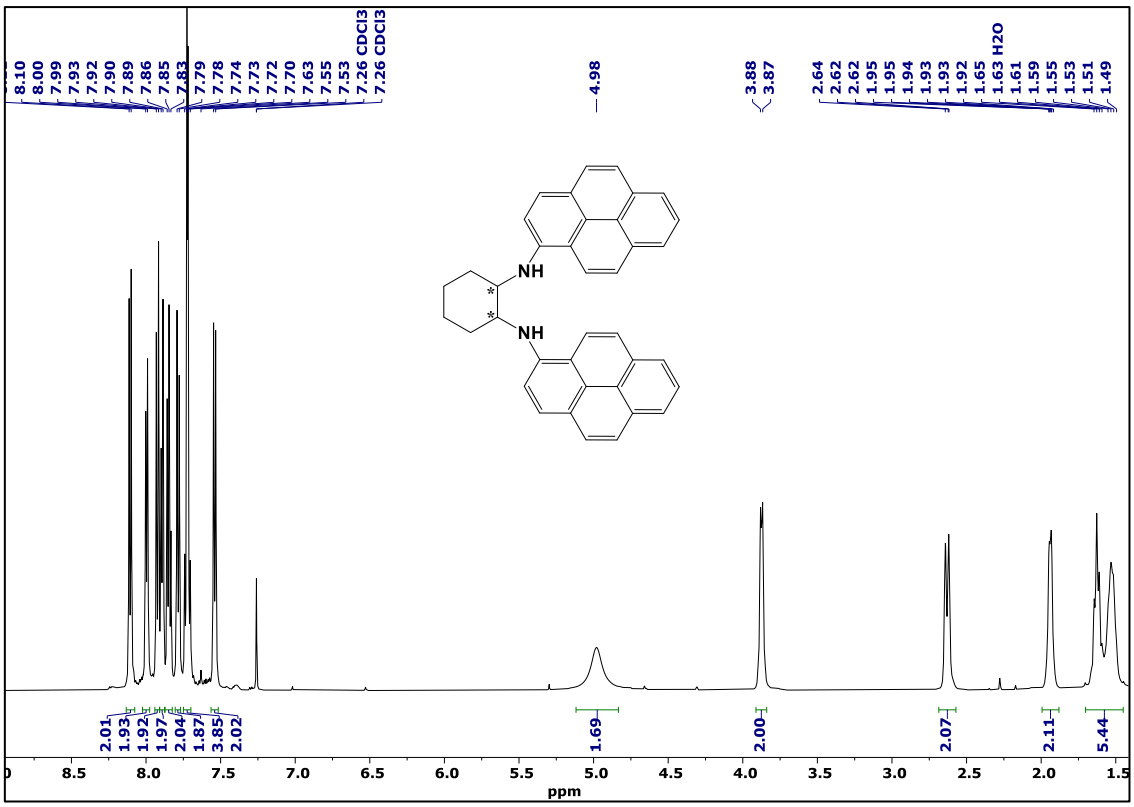


Figure S4- ^{1}H NMR of compound **1** ($CDCl_3$ at 25 °C).

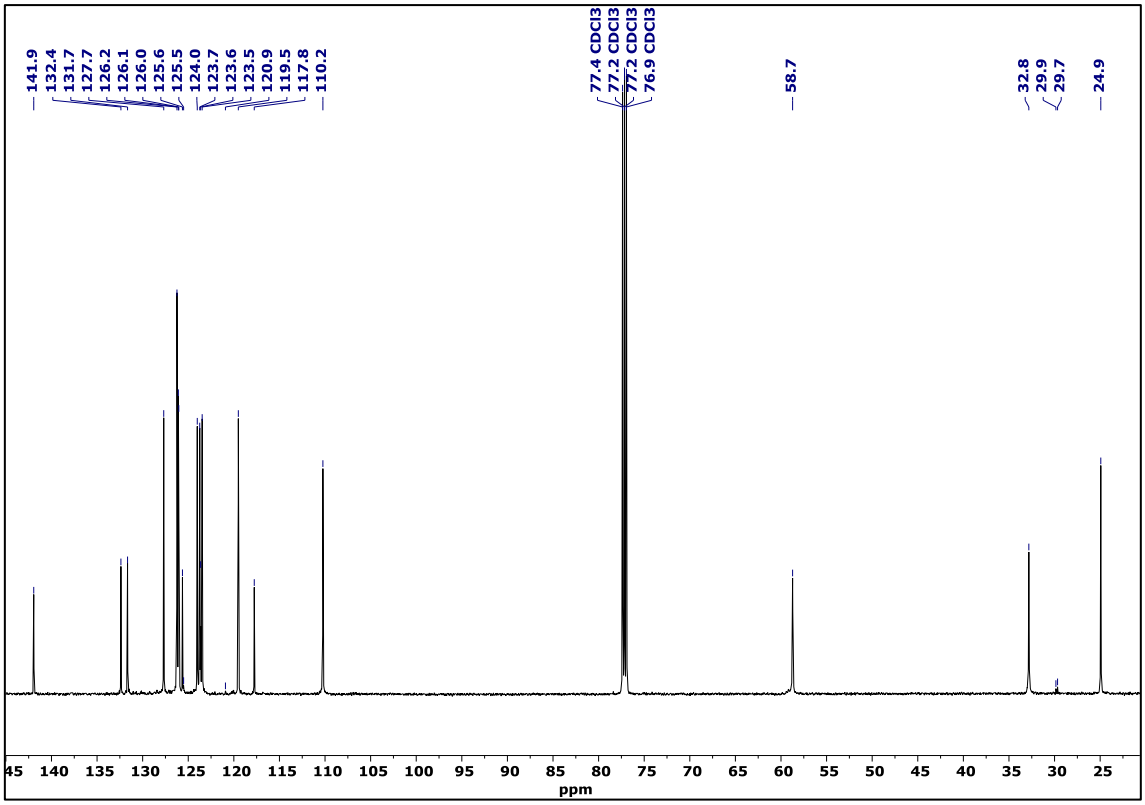


Figure S5- ^{13}C NMR of compound **1** ($CDCl_3$ at 25 °C).

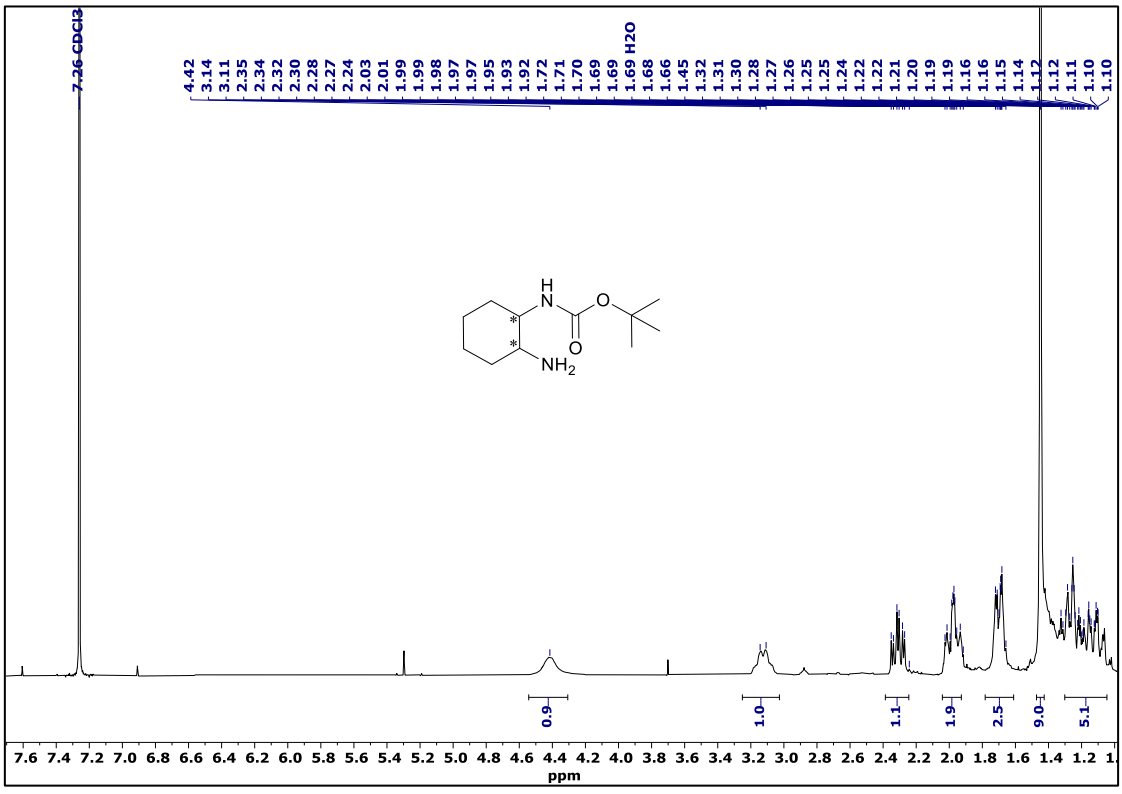


Figure S6- ^{1}H NMR of compound **4** ($CDCl_3$ at 25 °C).

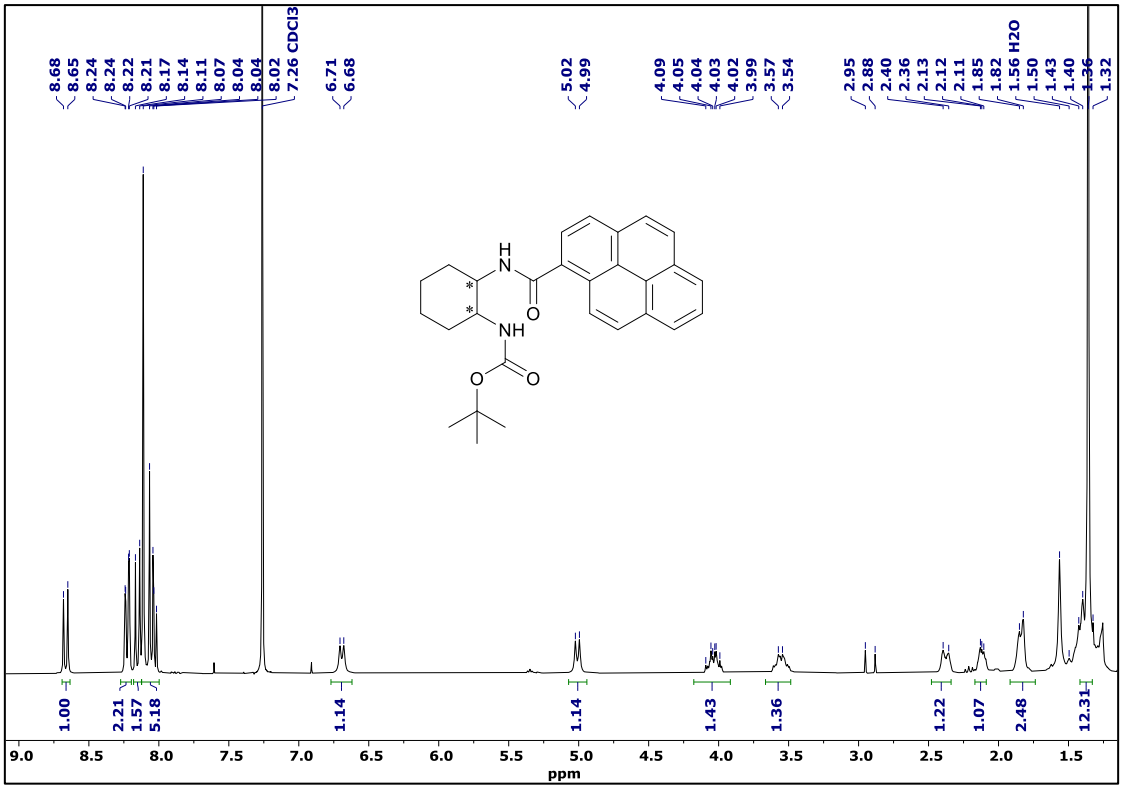


Figure S7- ^{1}H NMR of compound **5** ($CDCl_3$ at 25 °C).

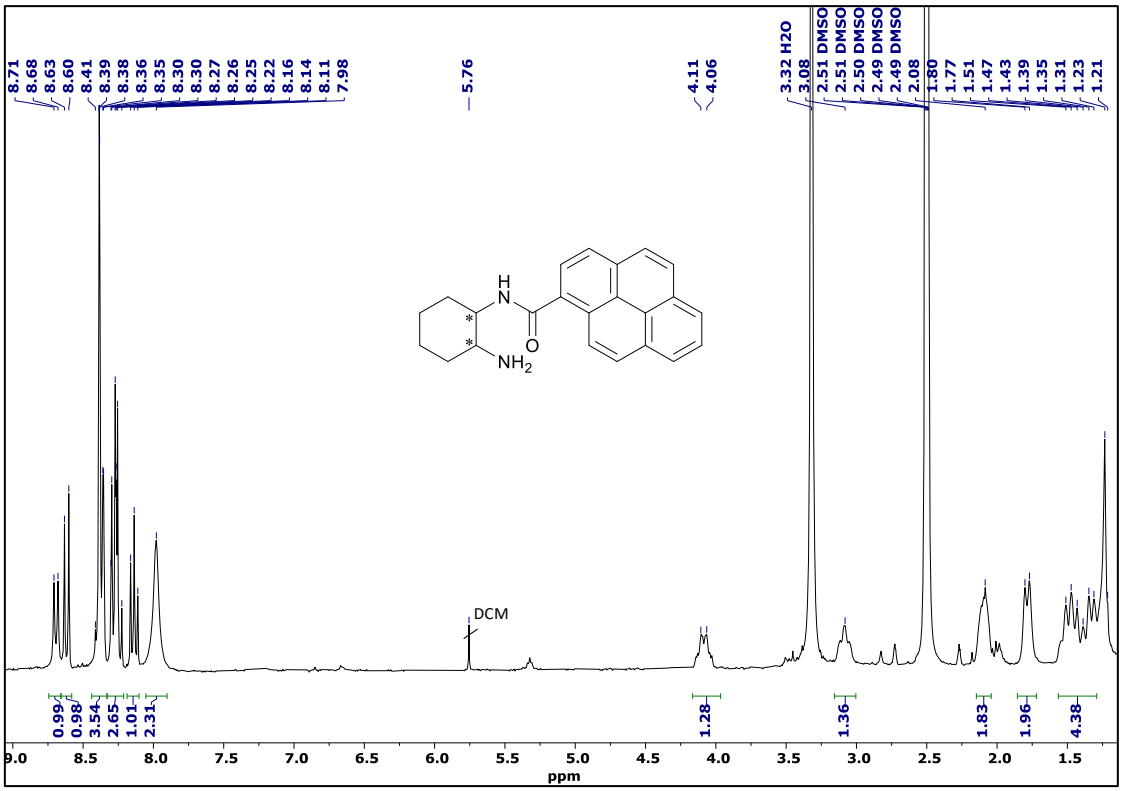


Figure S8- ^{1}H NMR of compound **6** (DMSO at 25 °C).

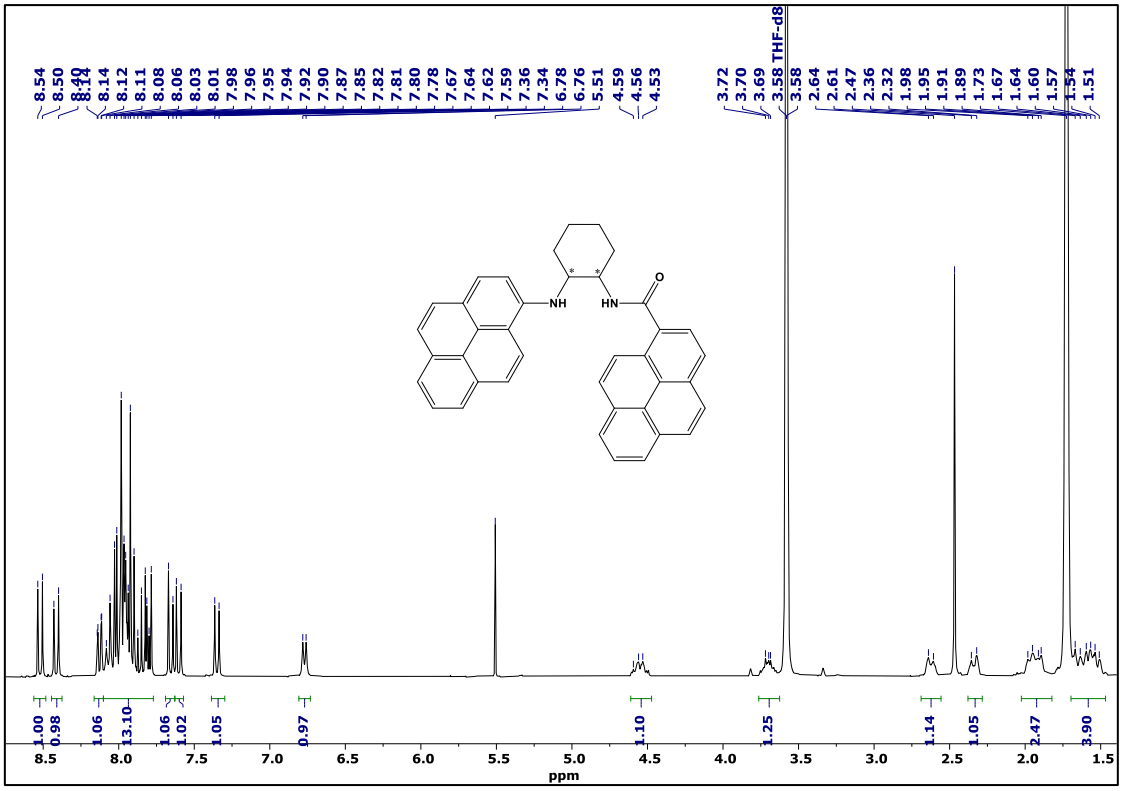


Figure S9- ^{1}H NMR of compound **2** (THF-d8 at 25 °C).

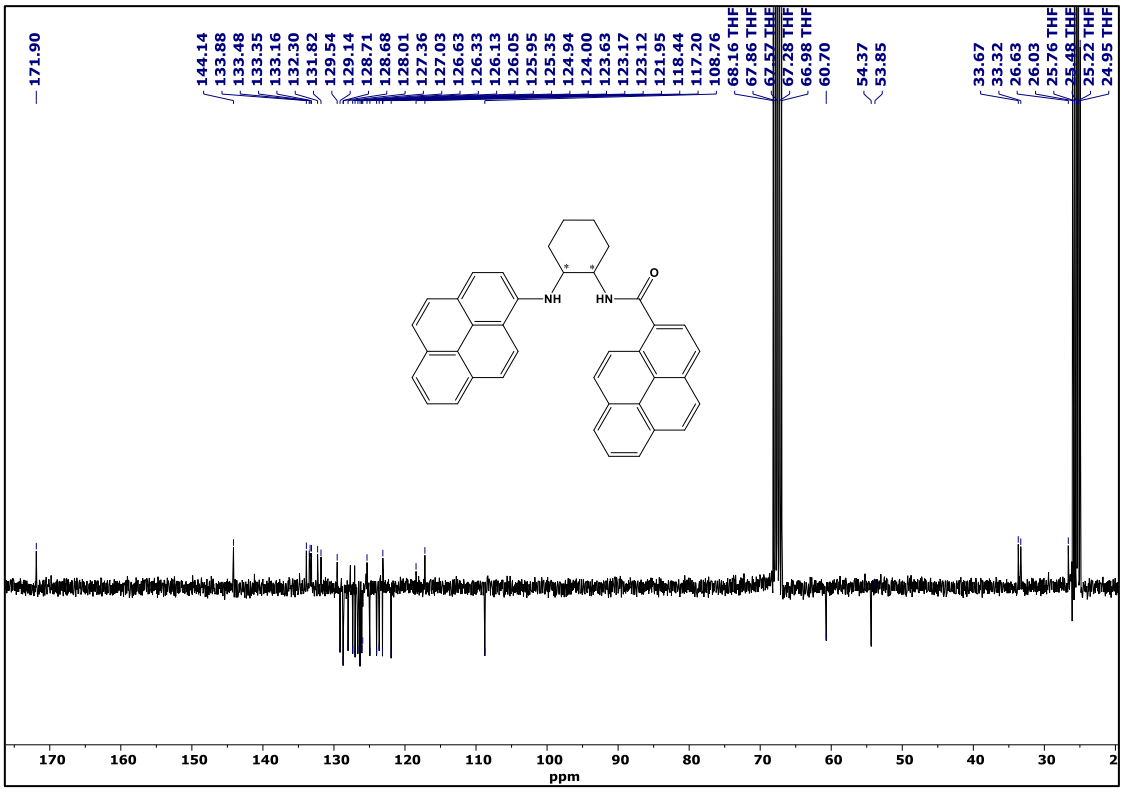


Figure S10- ^{13}C NMR of compound **2** (THF-d8 at 25 °C).

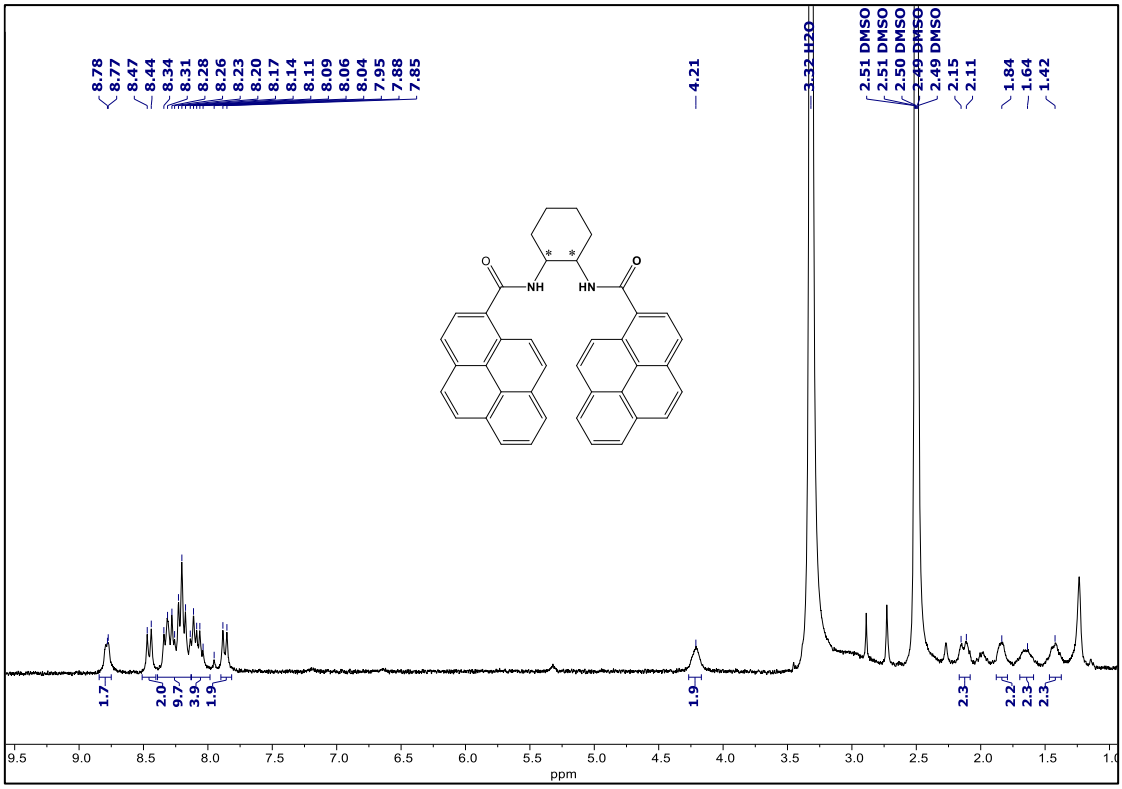


Figure S11- ^{1}H NMR of compound **3** (DMSO at 25 °C).

4. Cyclic voltammetry

Voltammograms were acquired on a AUTOLAB PGSTAT 302N station equipped with a Pt working and counter electrodes and an Ag/AgCl reference electrode referenced to ferrocene. Solutions were purged with Ar prior to measurements.

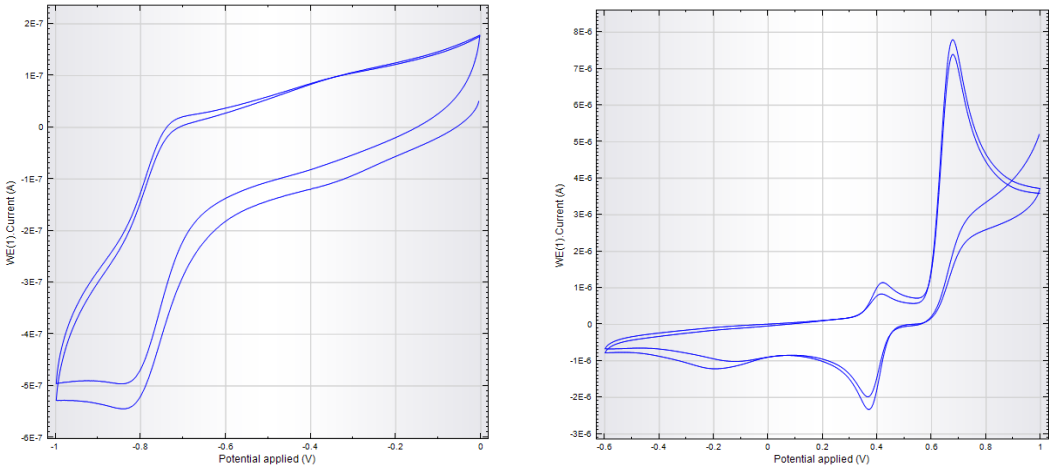


Figure S12- Cyclic voltammograms of 1 in DMF (1 mM) with $LiClO_4$ (0.1 M) as supporting electrolyte.

References

[1] Beena, S. Joshi, N. Kumar, S. Kidwai, R. Singh, D. S. Rawat, *Arch. Pharm.* **2012**, *345*, 896–901.

[2] S. Hu, L. Hu, X. Zhu, Y. Wang, M. Liu, *Angew. Chem. Int. Ed.* **2021**, *60*, 19451–19457.