Electronic Supplementary Information (ESI)

1. General

All reagents and starting materials were obtained from commercial suppliers and used without further purification. Anhydrous dichloromethane (DCM) were distilled under a nitrogen atmosphere over sodium and calcium hydride, respectively. Compound 3,10-dibromo-1,1-bis(4-tetradecylphenyl)-1H-cyclopenta[ghi]perylene (**1**) was synthesized according to the literature.[1] Column chromatography was performed on silica gel 60 (Merck 40-60 nm, 230-400 mesh). All NMR spectra were recorded on the Bruker AMX500 spectrometer. All chemical shifts are quoted in ppm, relative to tetramethylsilane, using the residual solvent peak as a reference standard. Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI MS) measurements were performed on a Finnigan TSQ 7000 triple stage quadrupole mass spectrometer. UV-vis-NIR absorption spectra was recorded on a Shimadzu UV-1700/UV-3600 spectrophotometer. Continuous wave X-band ESR spectra of **DA-Per** in solution were obtained with a JEOL (FA200) spectrometer using a variable temperature liquid nitrogen cryostat. The ESR data recorded in powder were fitted by the following equation:

$$IT = \frac{C}{K_B[3 + exp^{-2J/K_BT})]}$$

Where, I is the ESR intensity, C is the constant, K_B is Boltzam constant, and $-2J$ is correlated to the excatiaon energy from the singlet state to the triplet state.

2. Additional spectra

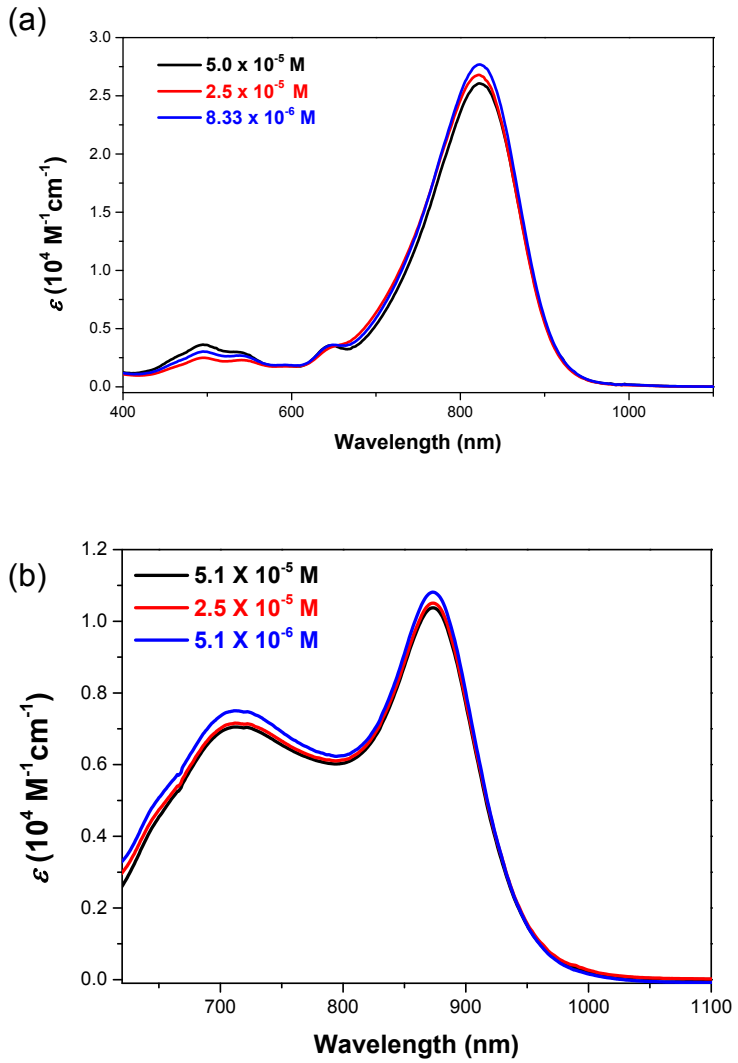

Figure S1. Concentration-dependent absorption spectra of **DA-Per** in (a) DCM and (b) $CHCl_3$.

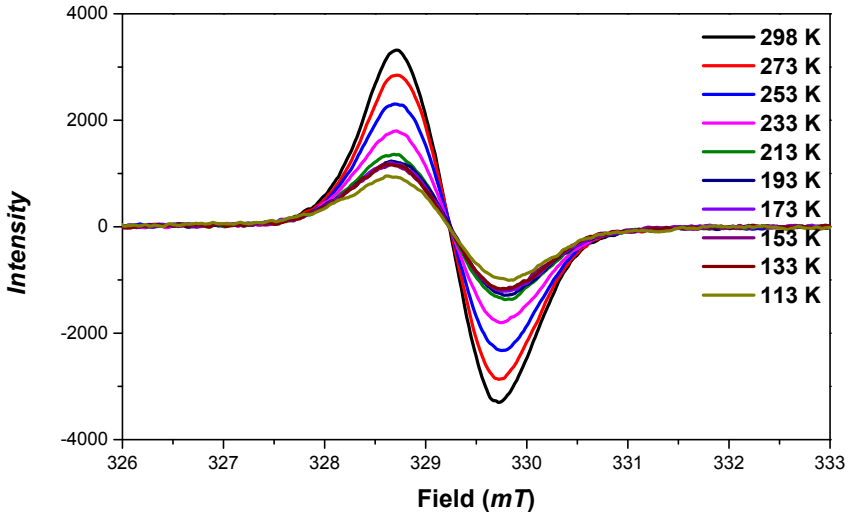

Figure S2. VT ESR spectra of the **DA-Per** recorded in powder.

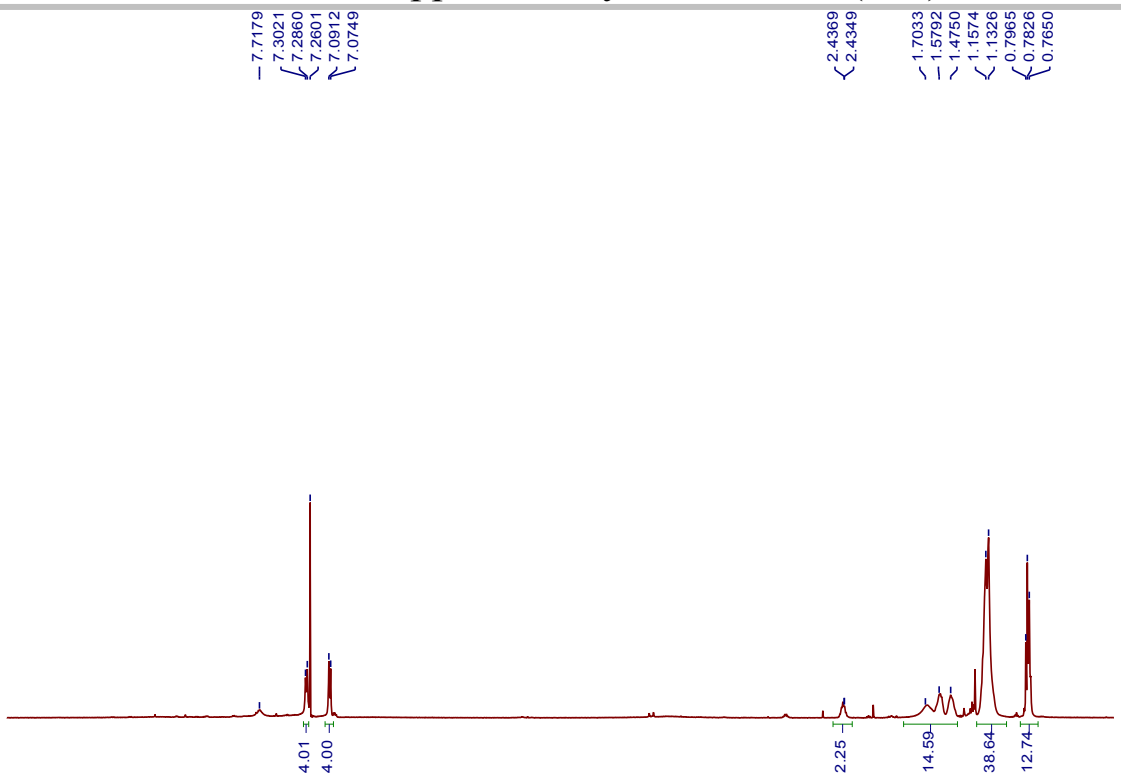

Figure S3. ^{1}H NMR (500 MHz) spectrum of compound **DA-Per** in $CDCl_3$ at room temperature.

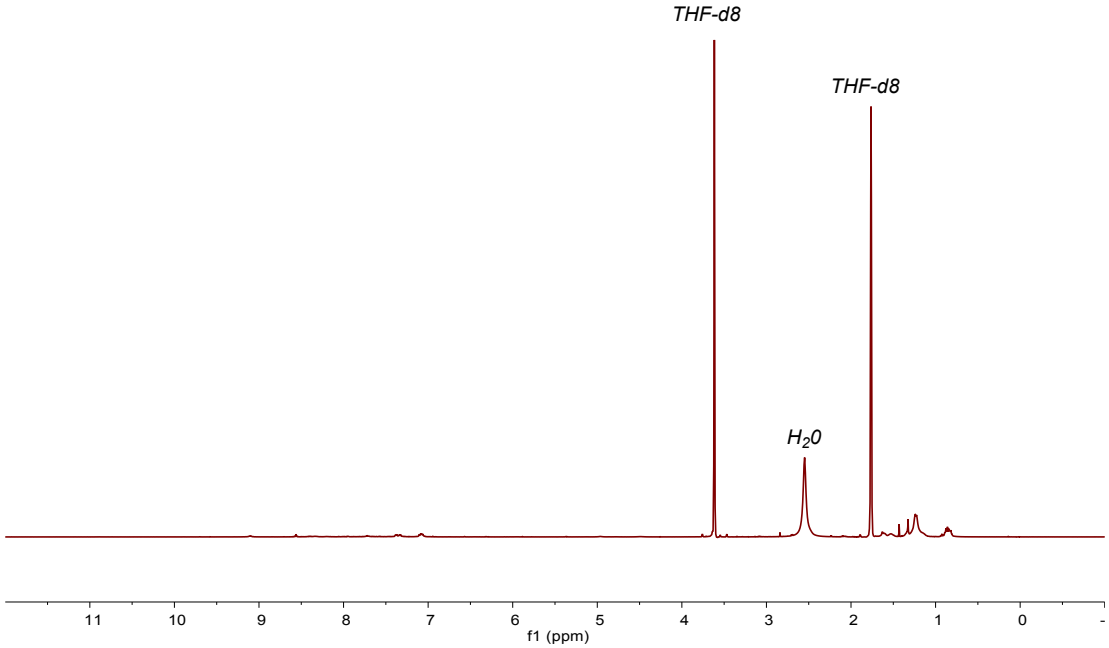

Figure S4. ^{1}H NMR (500 MHz) spectrum of compound **DA-Per** in THF-d_8 at room temperature.

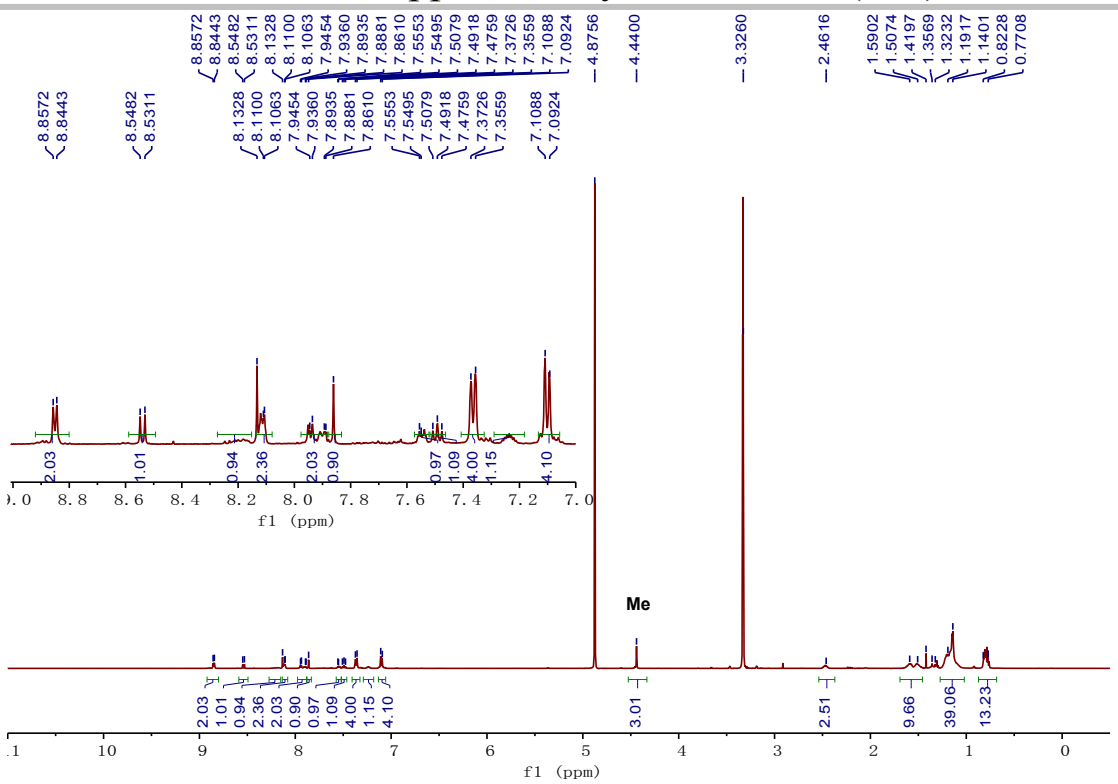

Figure S5. ^{1}H NMR (500 MHz) spectrum of compound **DA-Per** in CD_3OD-d_4 at room temperature.

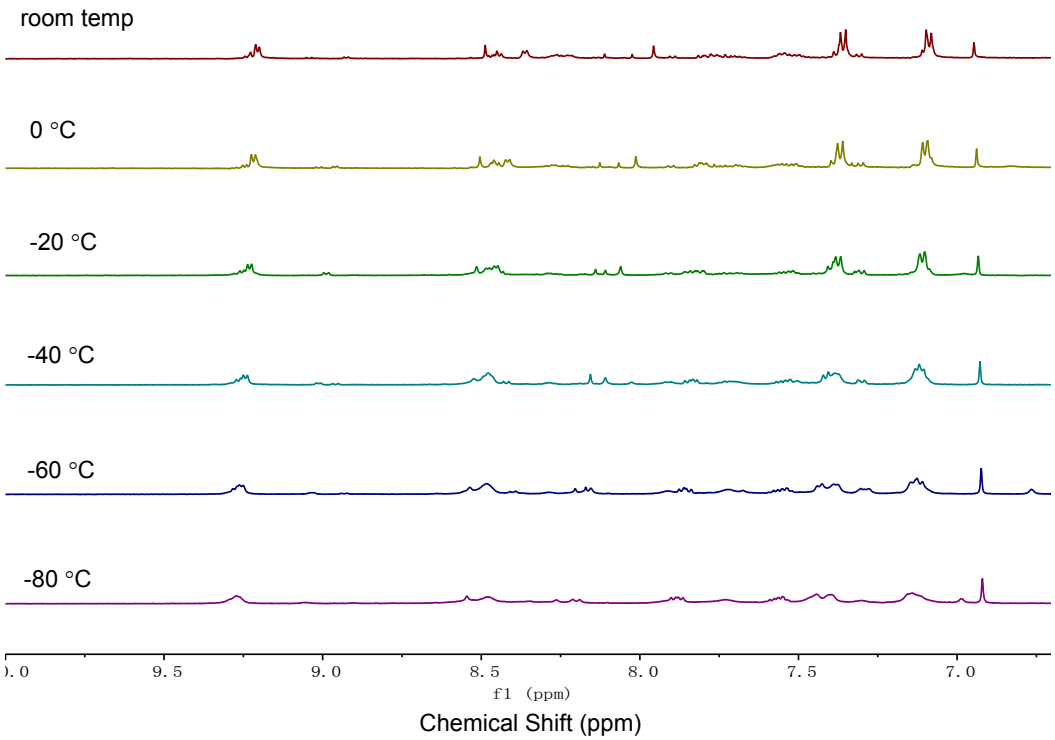

Figure S6. VT ^{1}H NMR spectra of **DA-Per** (500 MHz, aromatic region) in acetone-d_6.

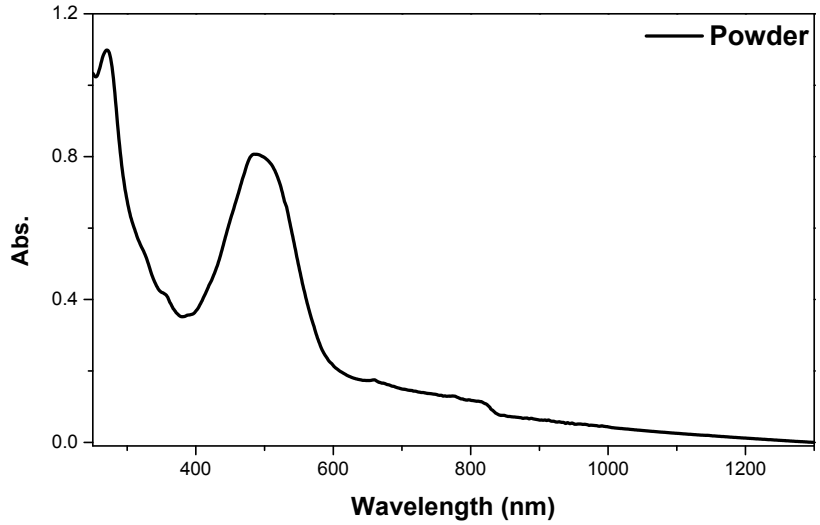

Figure S7. UV-vis absorption spectrum of the **DA-Per** recorded in powder.

3. Theoretical calculations

All results presented in this report have been obtained for a molecular model where the branched alkyl chains are replaced by methyl groups in **DA-Per**. Molecular geometries of molecule in the ground state and the singlet excited state have been obtained at both the B3LYP/6-311G(d,p) level with Gaussian 09 package[2] utilizing a high performance computing cluster facility of NUS. The environment effects geometries were included by using the polarizable continuum model (PCM). Therefore, the diradical radical character and vertical excitaion energies of **DA-Per** were calculated using the restricted active space spin flip method (RAS-SF)[3] with Q-Chem 4.3 package based on the optimsed triplet state geometies in different solvents.[4] The diradical character index (y_0) is defined as the occupation number of the lowest unoccupied natural orbital (LUNO). Time-dependent DFT calculalations were conducted at B3LYP/6-31G(d,p) level based on the ground geometries optimised at the B3LYP/6-31G(d,p) level in different solvents.

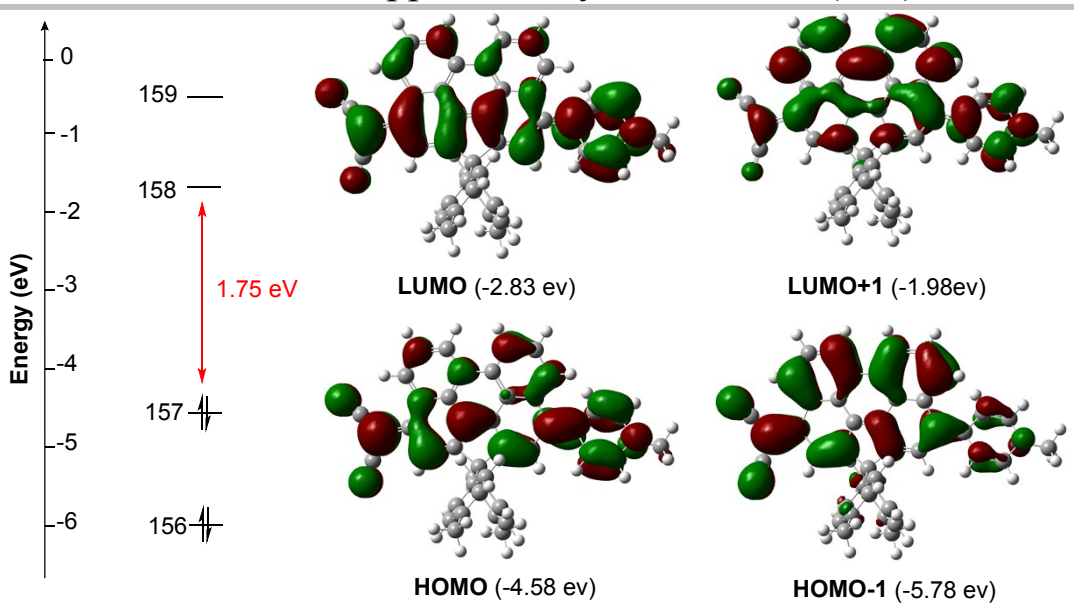

Figure S8. Frontier molecular orbital profiles and energy diagram of **DA-Per** obtained by B3LYP/6-31G(d,p) level calculation under gas phase.

Table S1. Selected TD-DFT (B3LYP/6-31G(d,p)) calculated energies, oscillator strength and compositions of major electronic transitions of **DA-Per** (in DMSO).

Calcd. (nm)	*f*	Composition (H=HOMO, L= LUMO, L+1 = LUMO+1, etc.)
700.4	1.068	HOMO->LUMO (101 %)
543.0	0.026	HOMO->LUMO+1 (97%)
448.5	0.0026	HOMO-1>LUMO (73%)

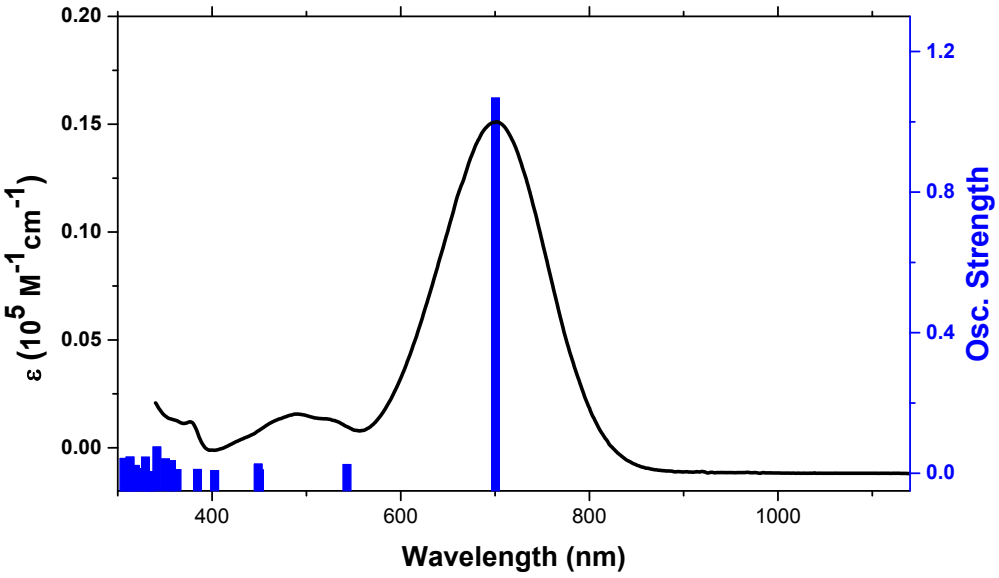

Figure S9. Calculated stick spectrum (B3LYP/6-31G(d,p)) of **DA-Per** along with the experimental spectrum in DMSO.

4. Additional NMR spectra and HR-Mass spectra

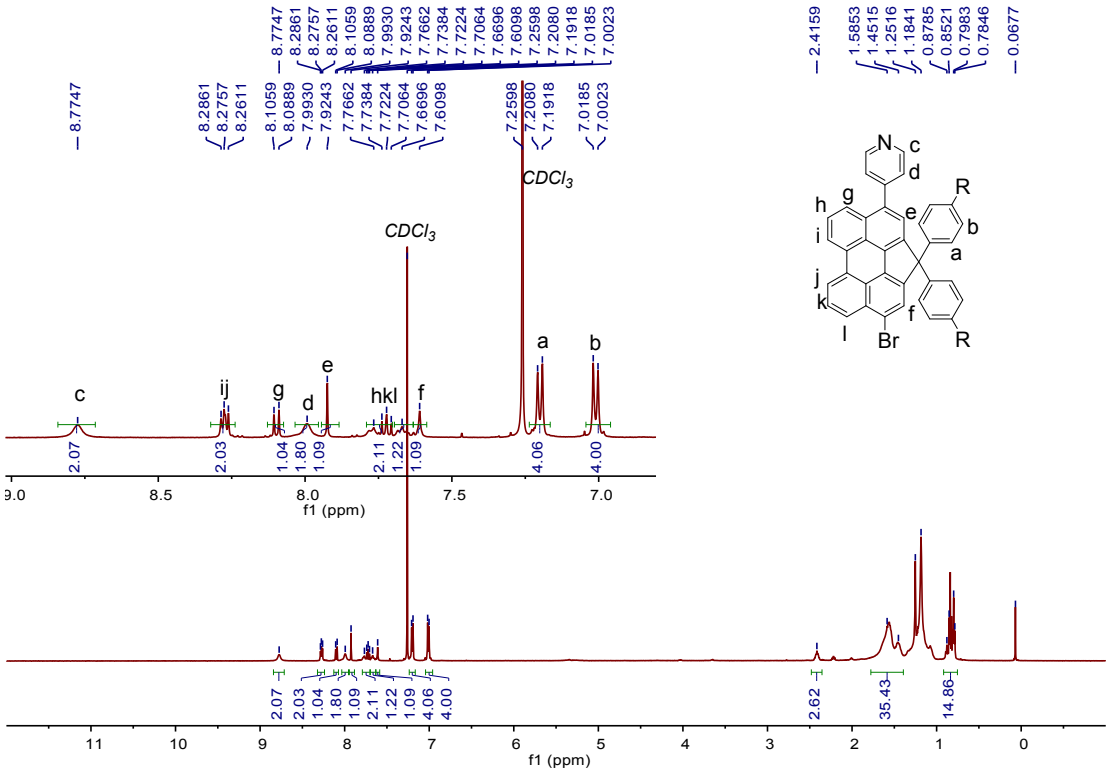

Figure S10. ^{1}H NMR spectrum of compound **2** (500 MHz, $CDCl_3$, rt).

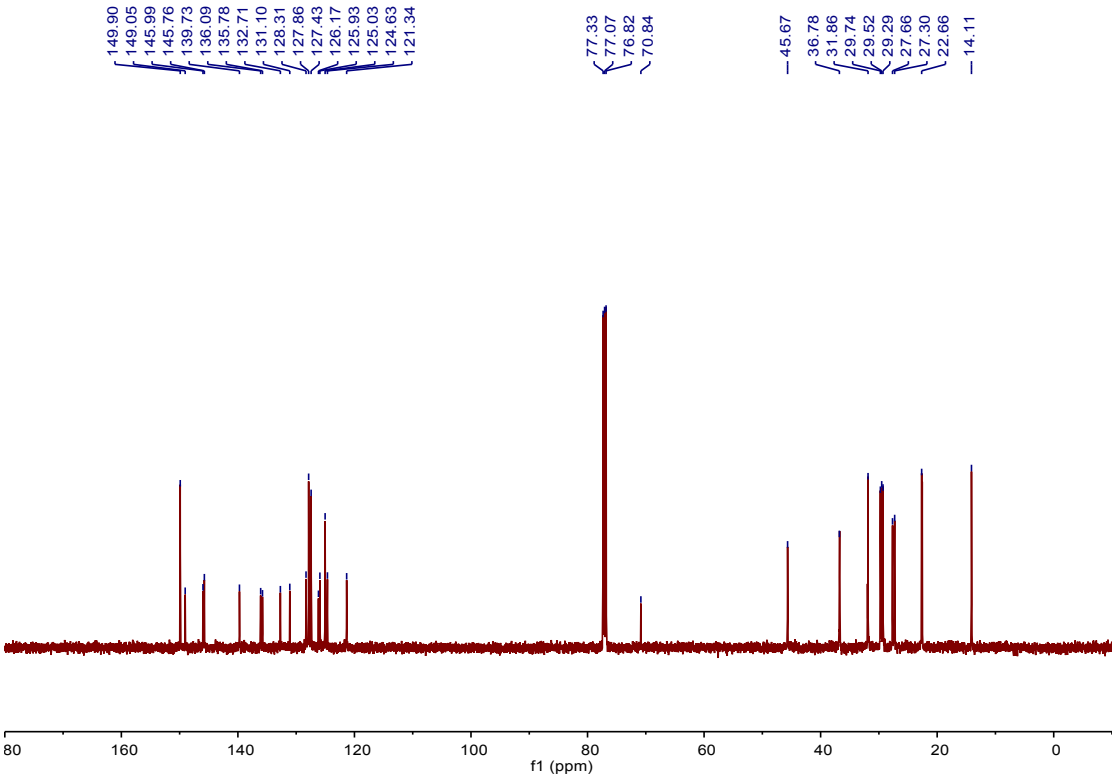

Figure S11. ^{13}C NMR spectrum of compound **2** (125 MHz, $CDCl_3$, rt).

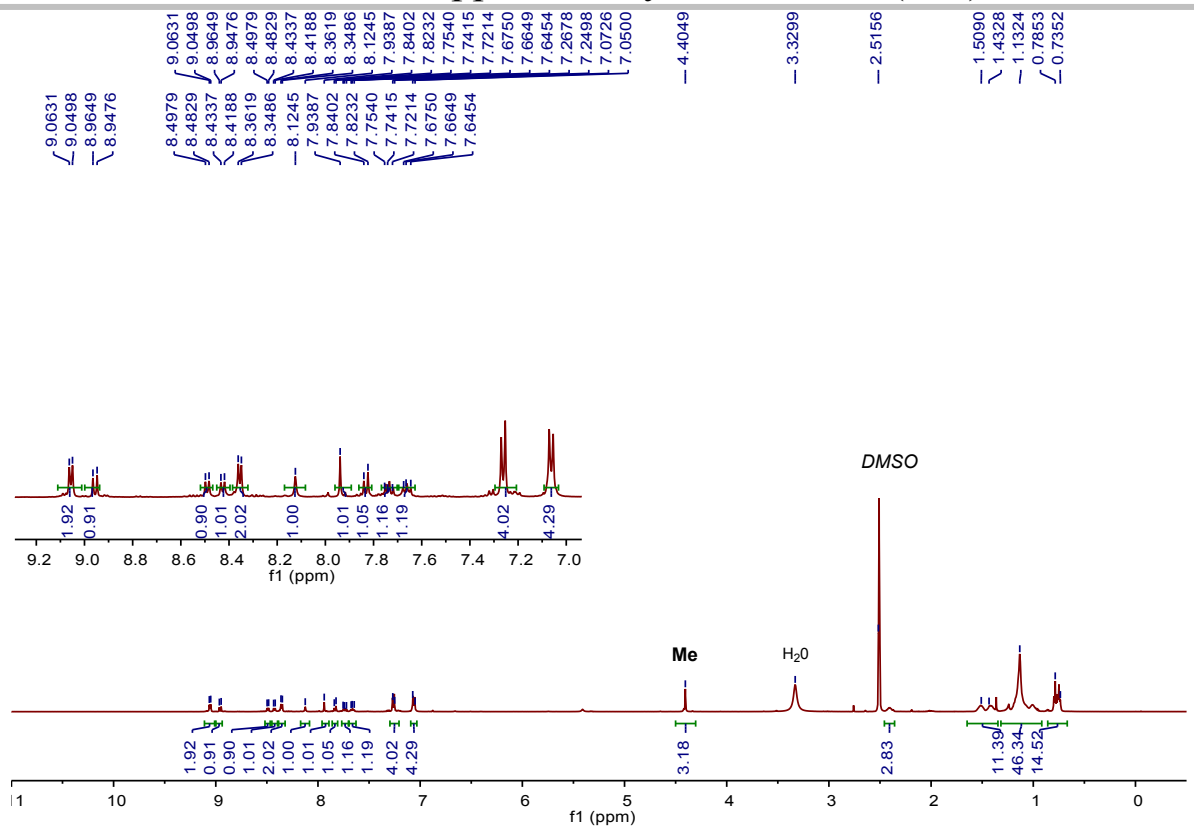

Figure S12. [1]H NMR spectrum of compound **DA-Per** (500 MHz, DMSO-d_6, rt).

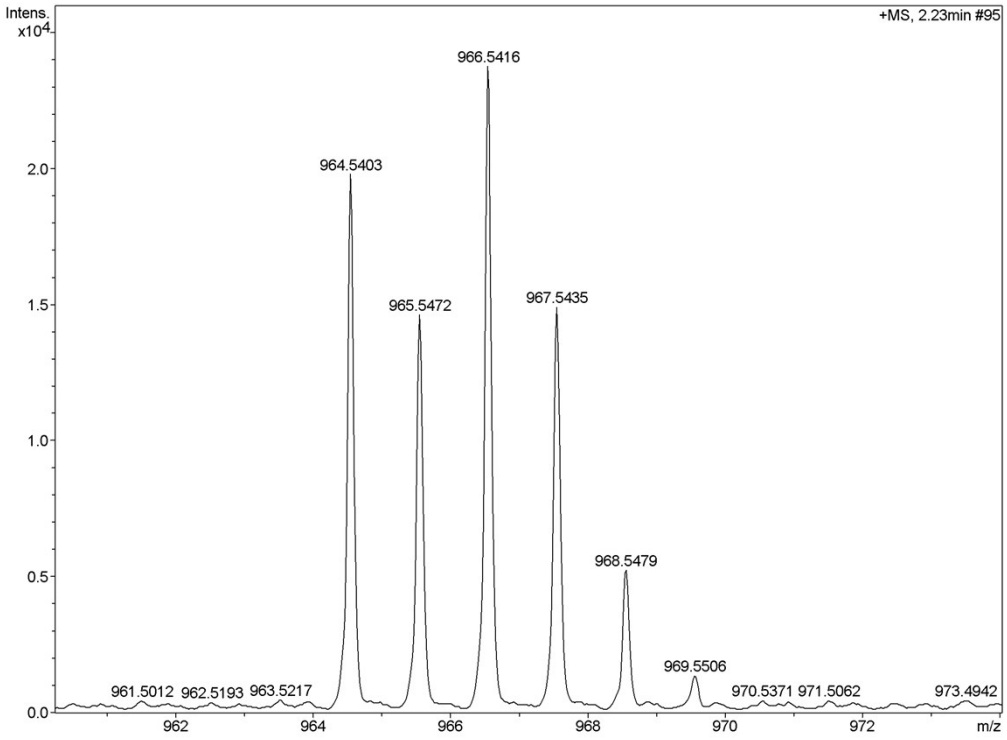

Figure S13. HR mass spectrum (APCI) of the compound **2**.

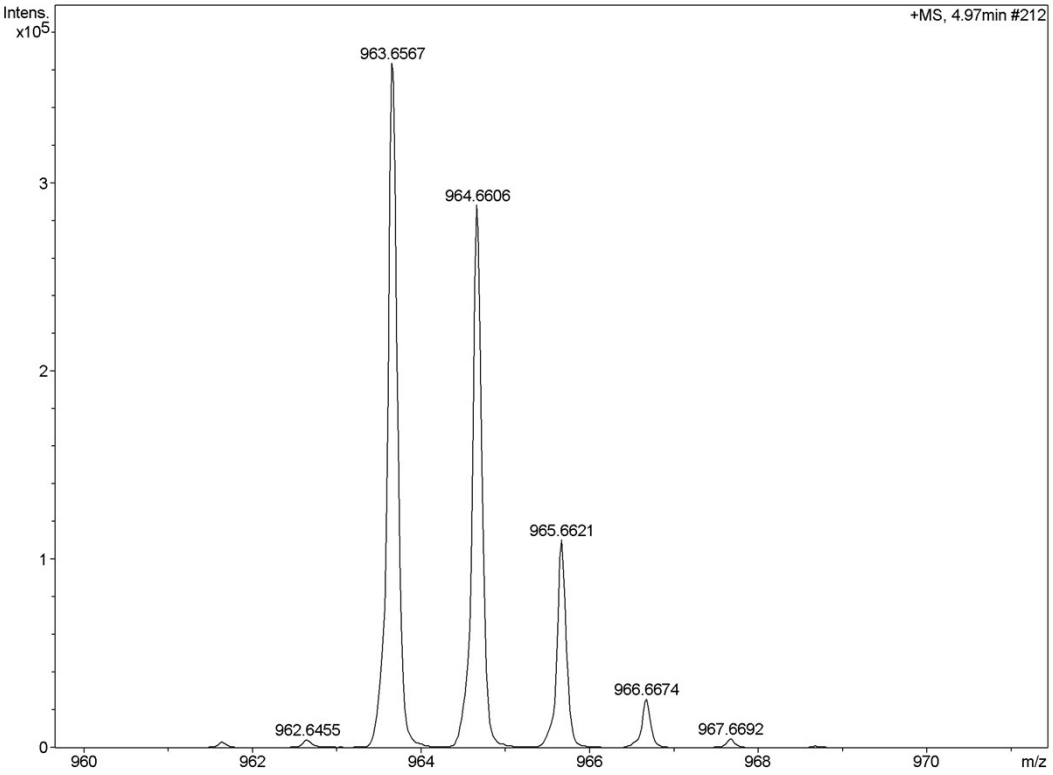

Figure S14. HR mass spectrum (APCI) of the compound **DA-Per**.

5. References

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