

Supporting Information File

Novel *meso*-substituted *trans*-A₂B₂ porphyrins: Synthesis and structure of their metal-mediated supramolecular assemblies

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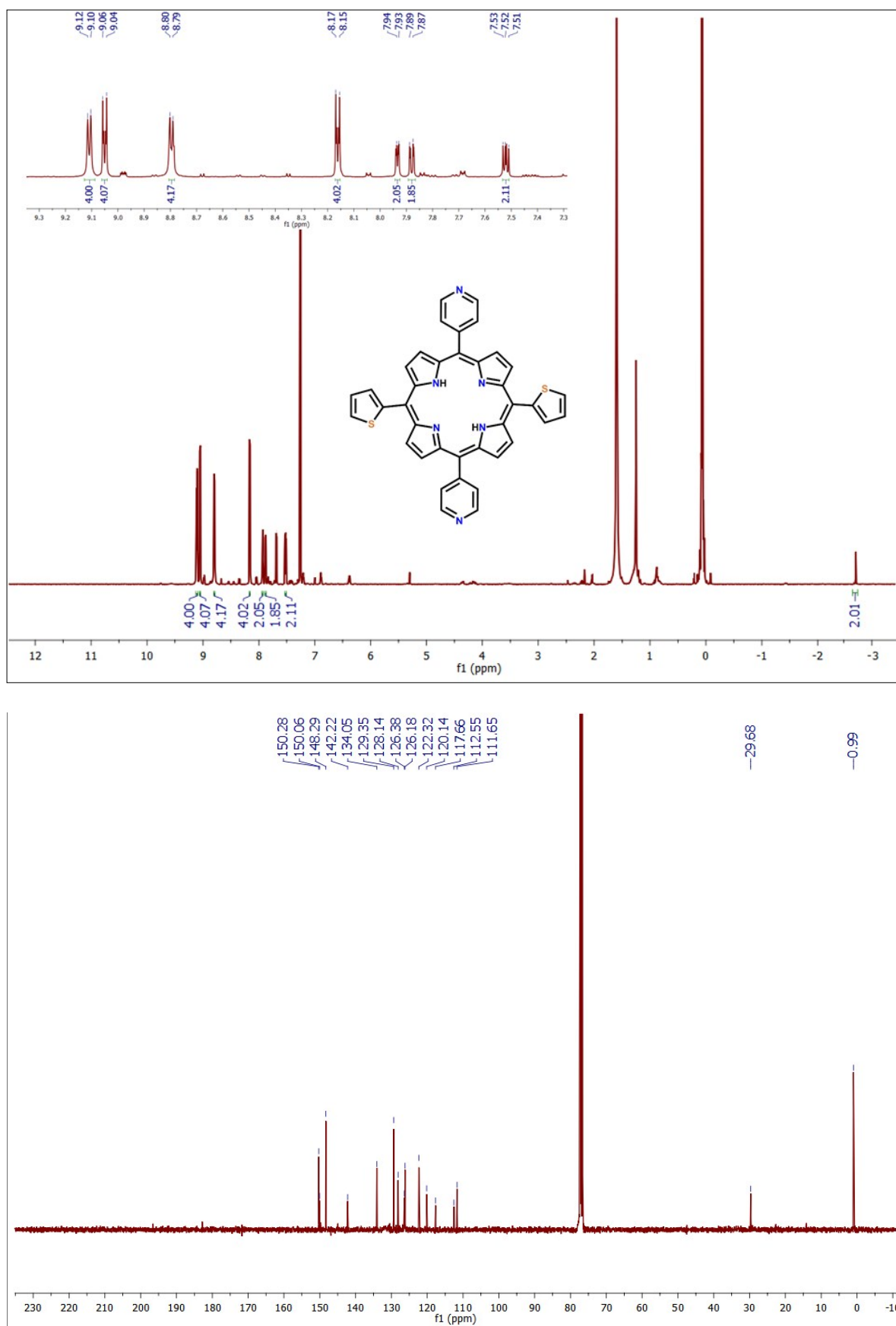


Fig. S1 ^1H NMR (400 MHz, CDCl_3 , 25 °C) and ^{13}C NMR (101 MHz, CDCl_3 , 25 °C) of **1** (DPyDThP).

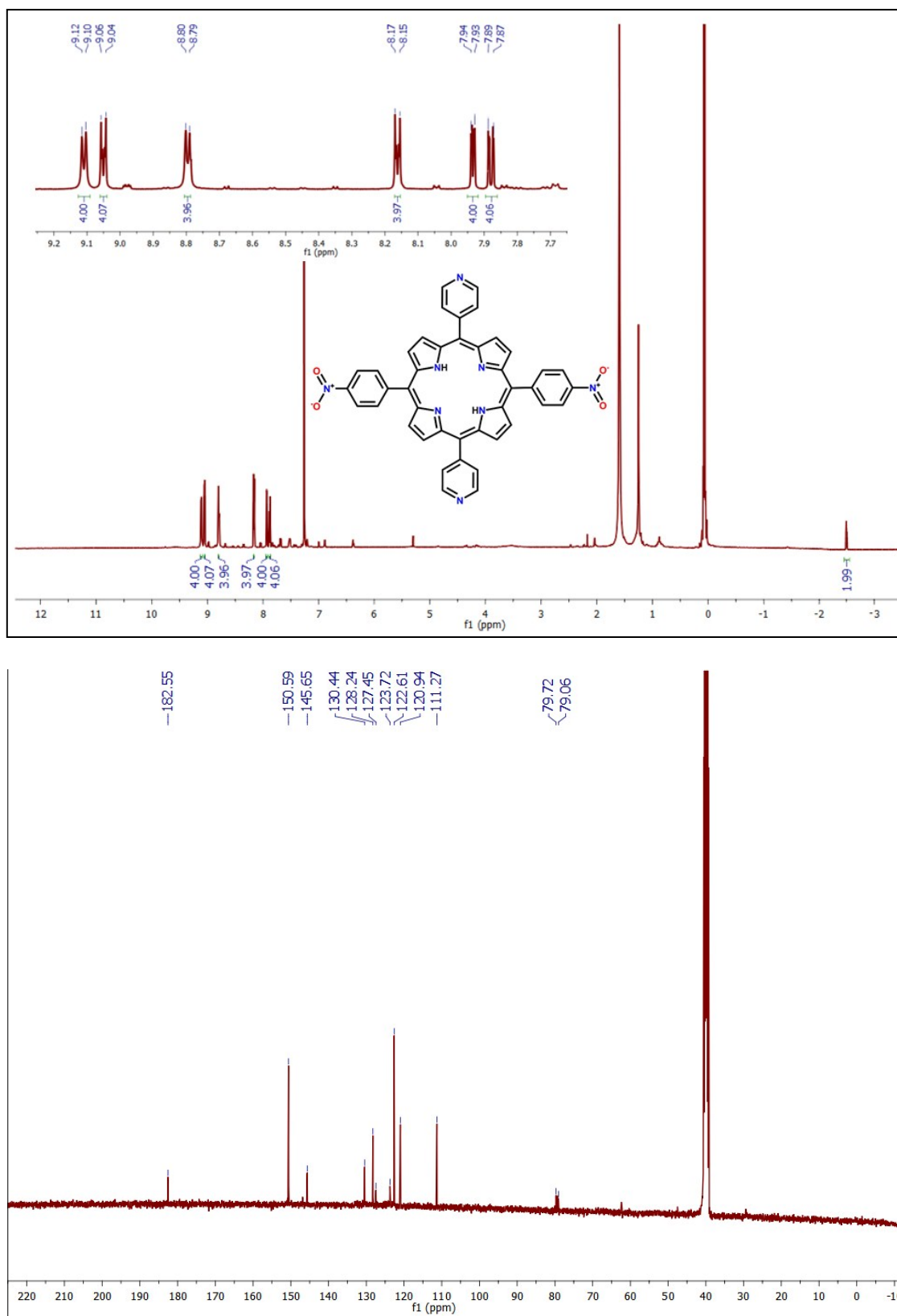


Fig. S2 ¹H NMR (400 MHz, CDCl₃, 25 °C) and ¹³C NMR (101 MHz, DMSO-*d*₆, 25 °C) of **2** (DPyDNO₂P).

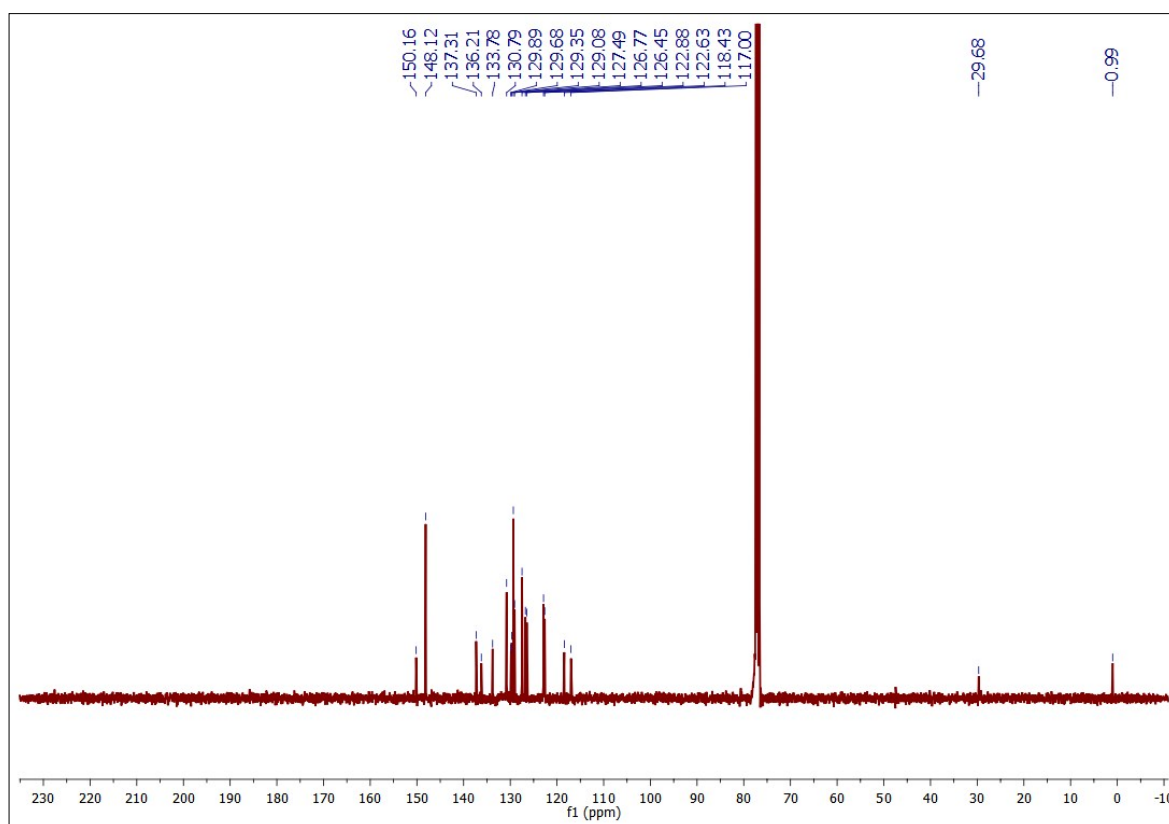
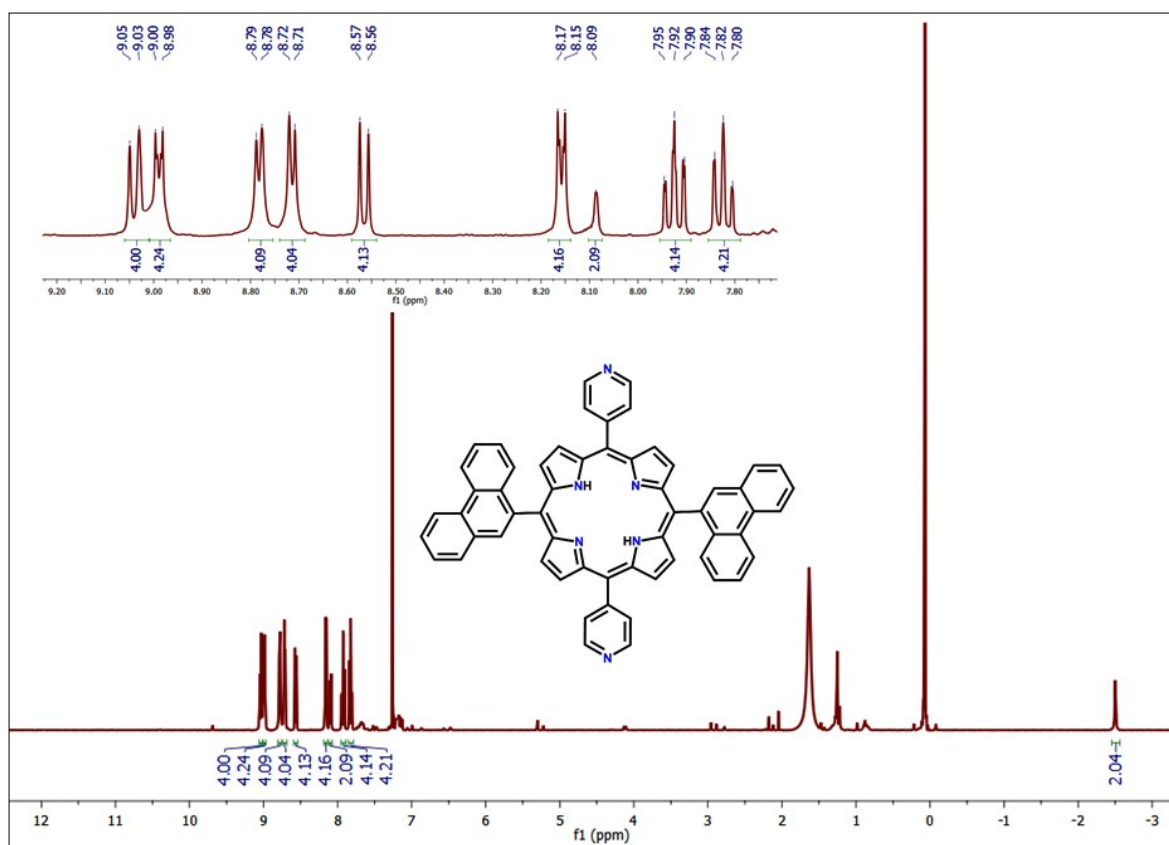


Fig. S3 ¹H NMR (400 MHz, CDCl₃, 25 °C) and ¹³C NMR (101 MHz, CDCl₃, 25 °C) of **3** (DPyDPhnP).

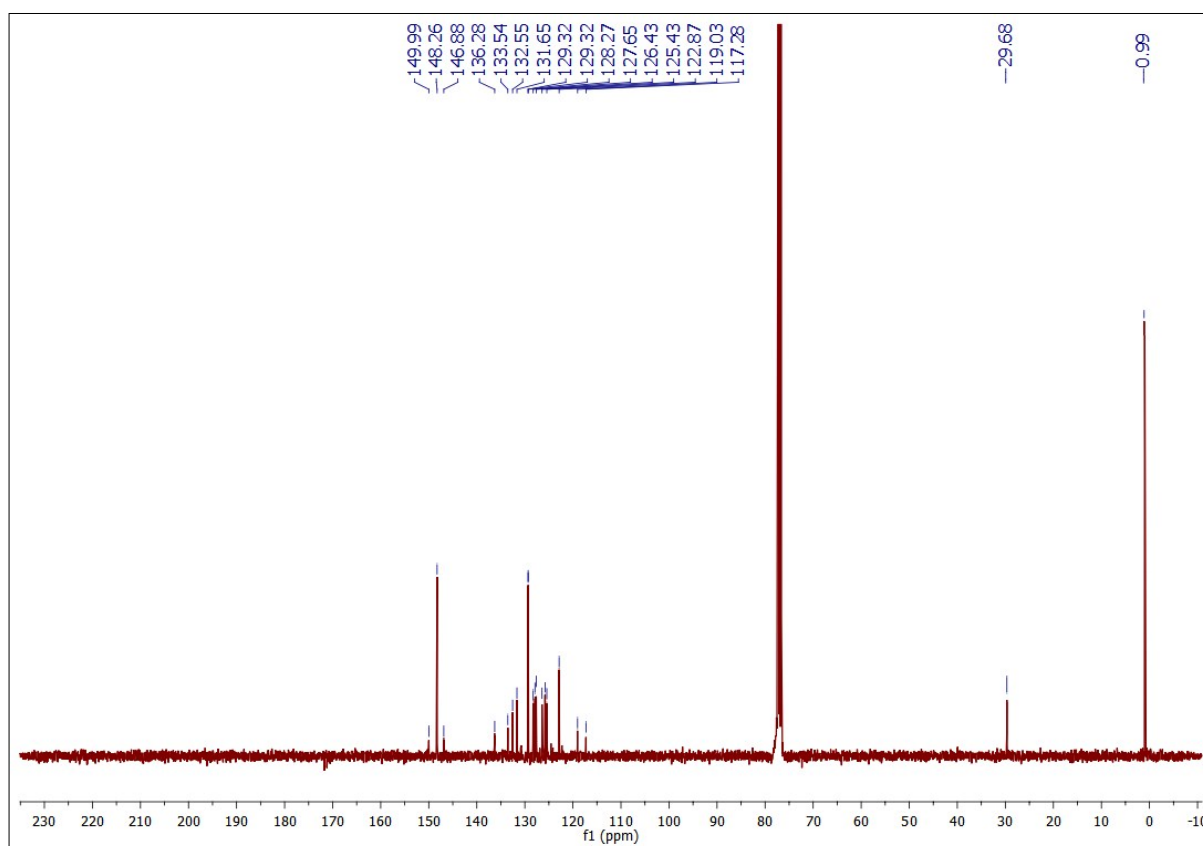
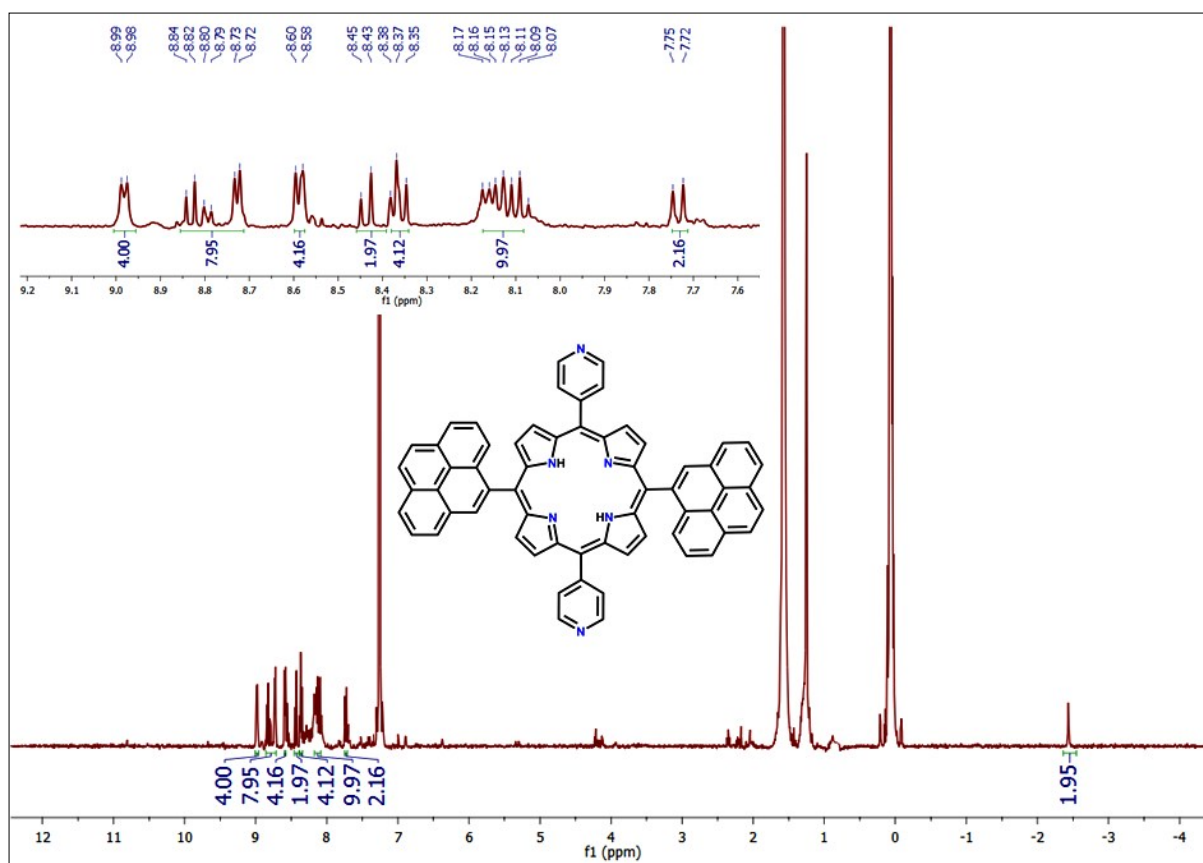


Fig. S4 ¹H NMR (400 MHz, CDCl₃, 25 °C) and ¹³C NMR (101 MHz, CDCl₃, 25 °C) of **4** (DPyDPyrP).

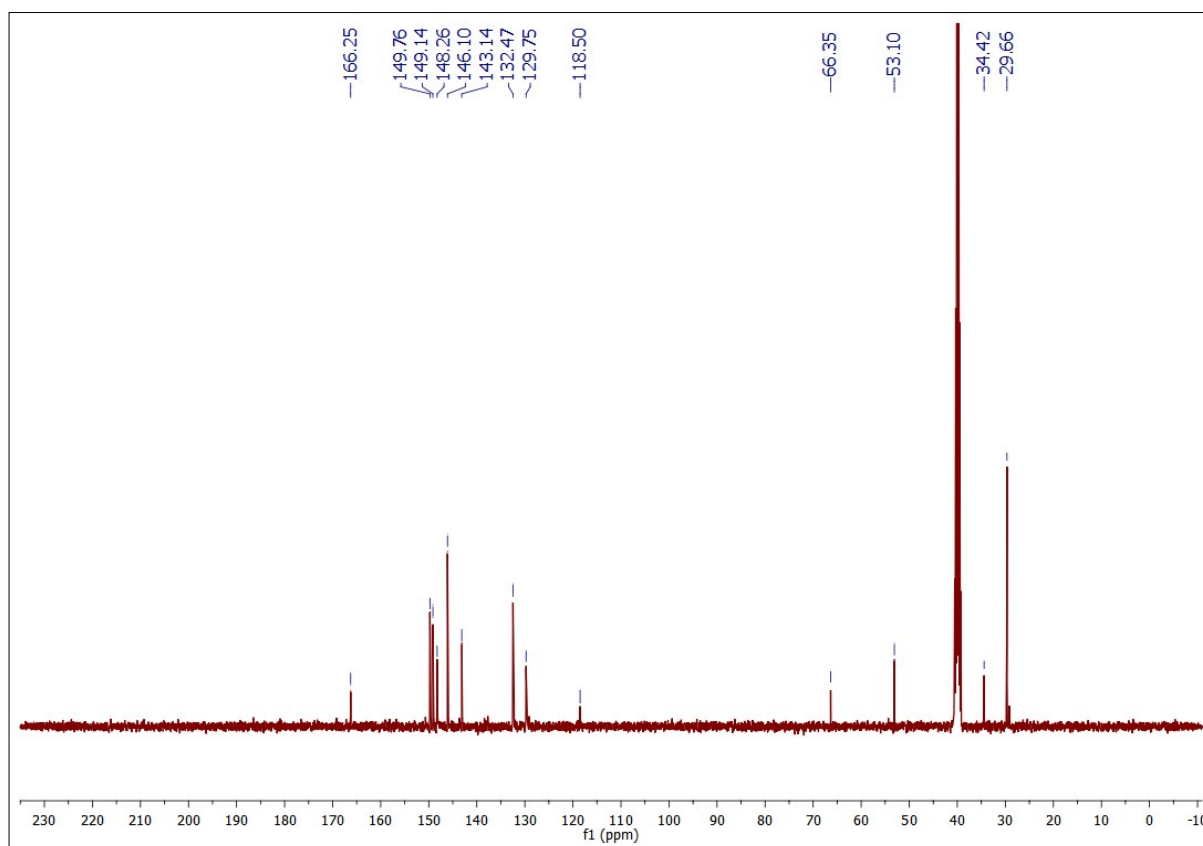
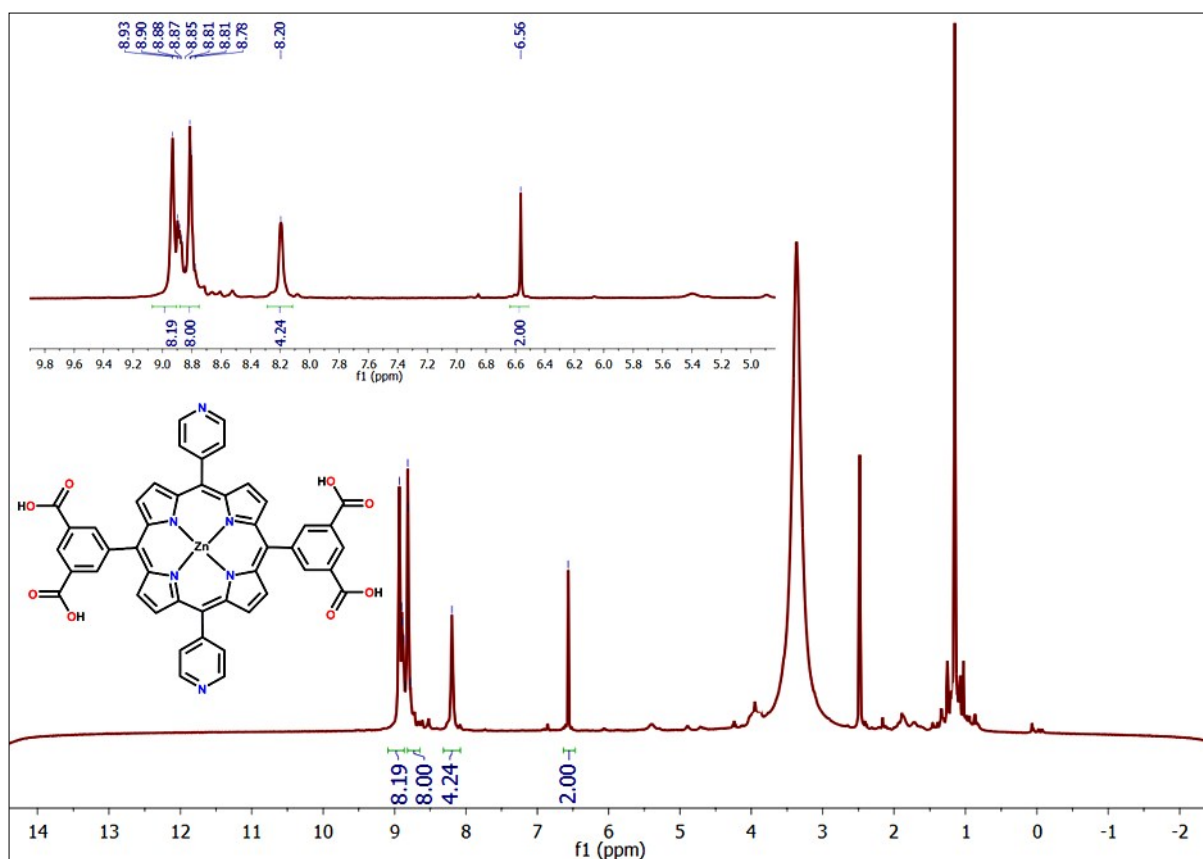


Fig. S5 ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C) and ¹³C NMR (101 MHz, DMSO-*d*₆, 25 °C) of **5a** (DPyDTcZP).

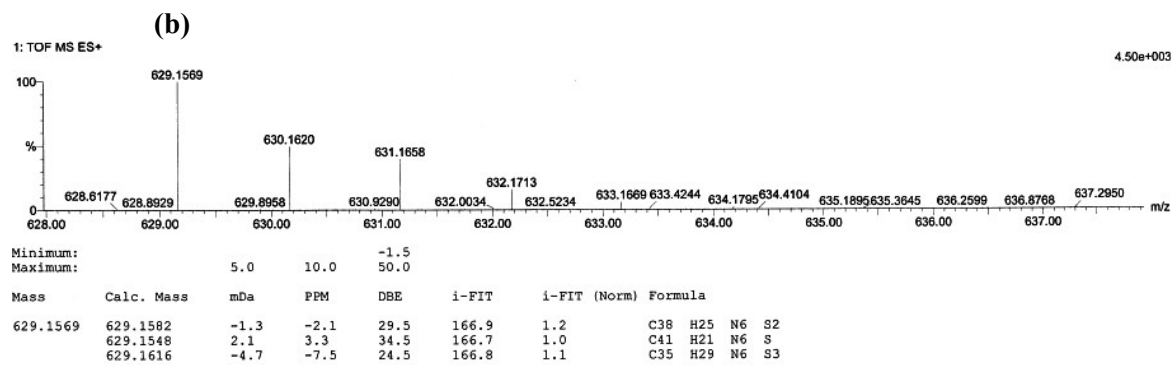
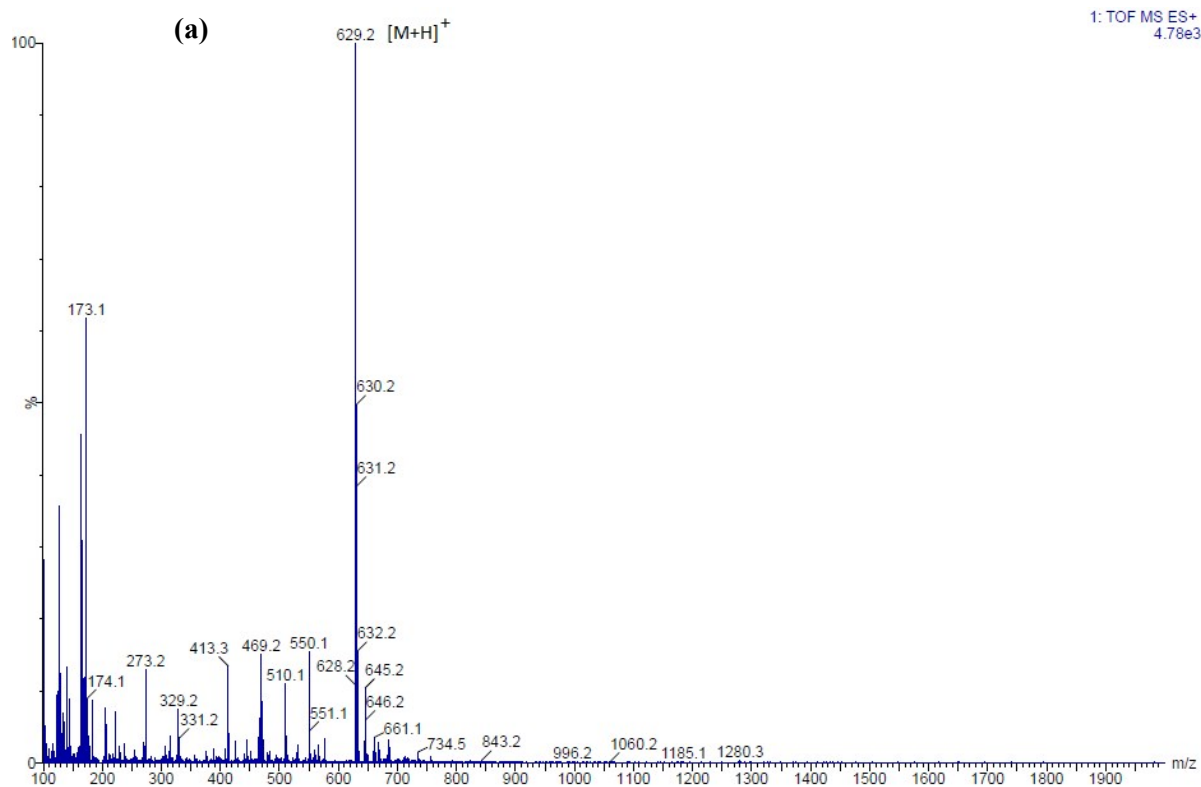


Fig. S6 (a) ESI-TOF-MS and (b) HRMS of 1.

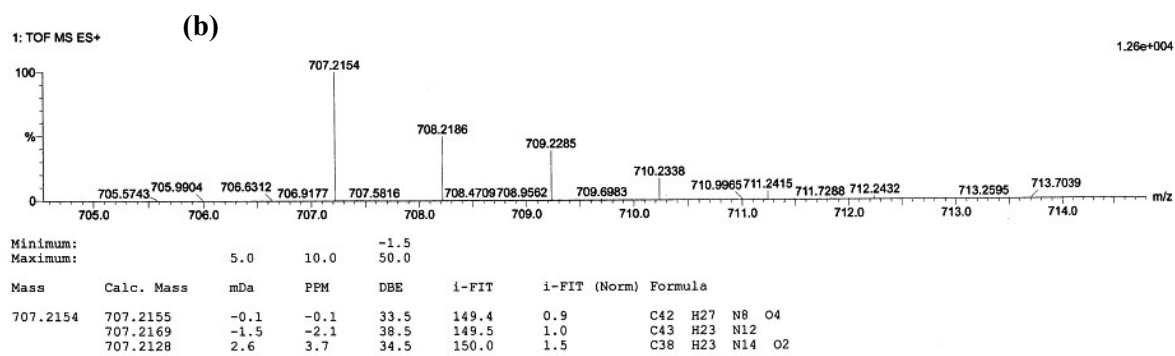
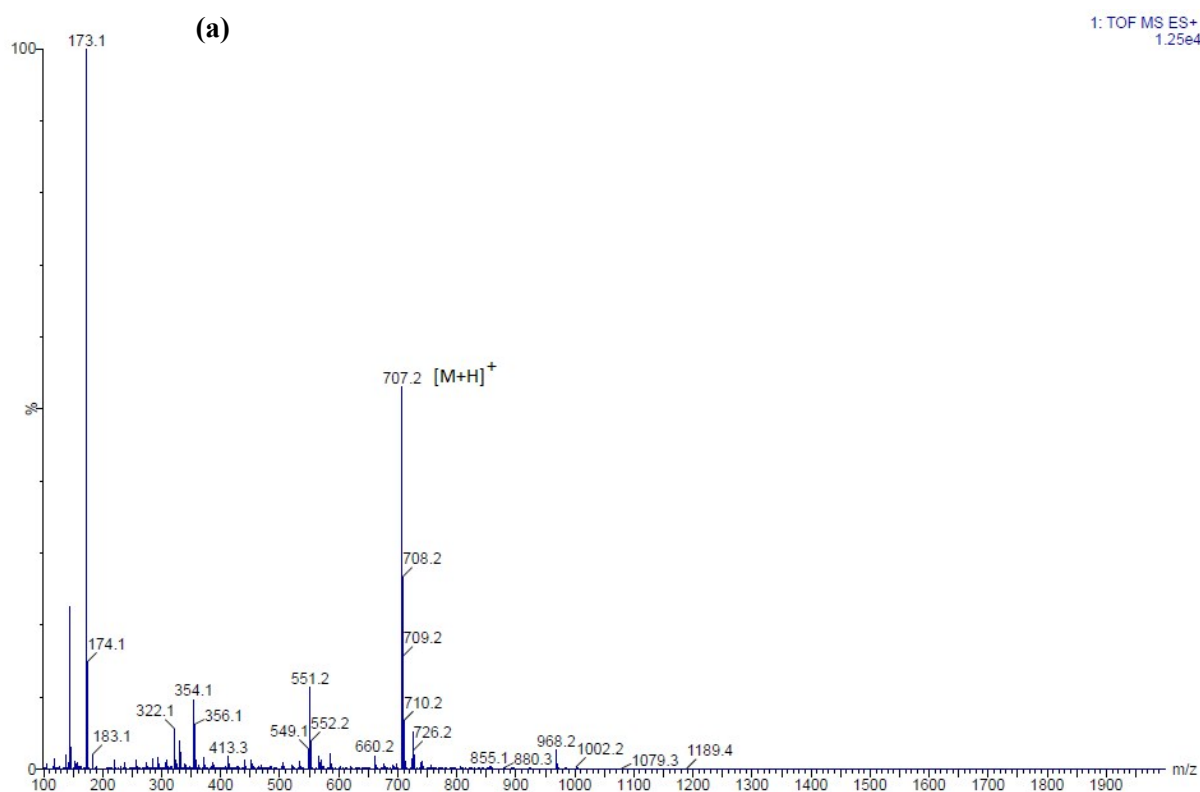


Fig. S7 (a) ESI-TOF-MS and (b) HRMS of 2.

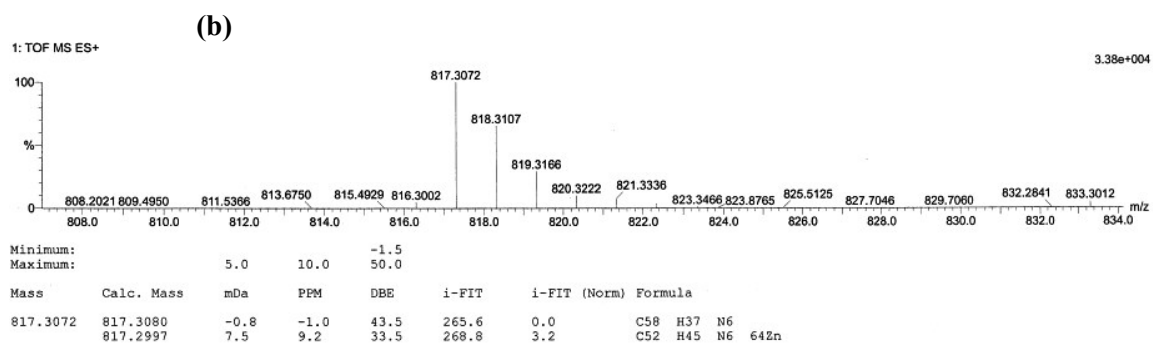
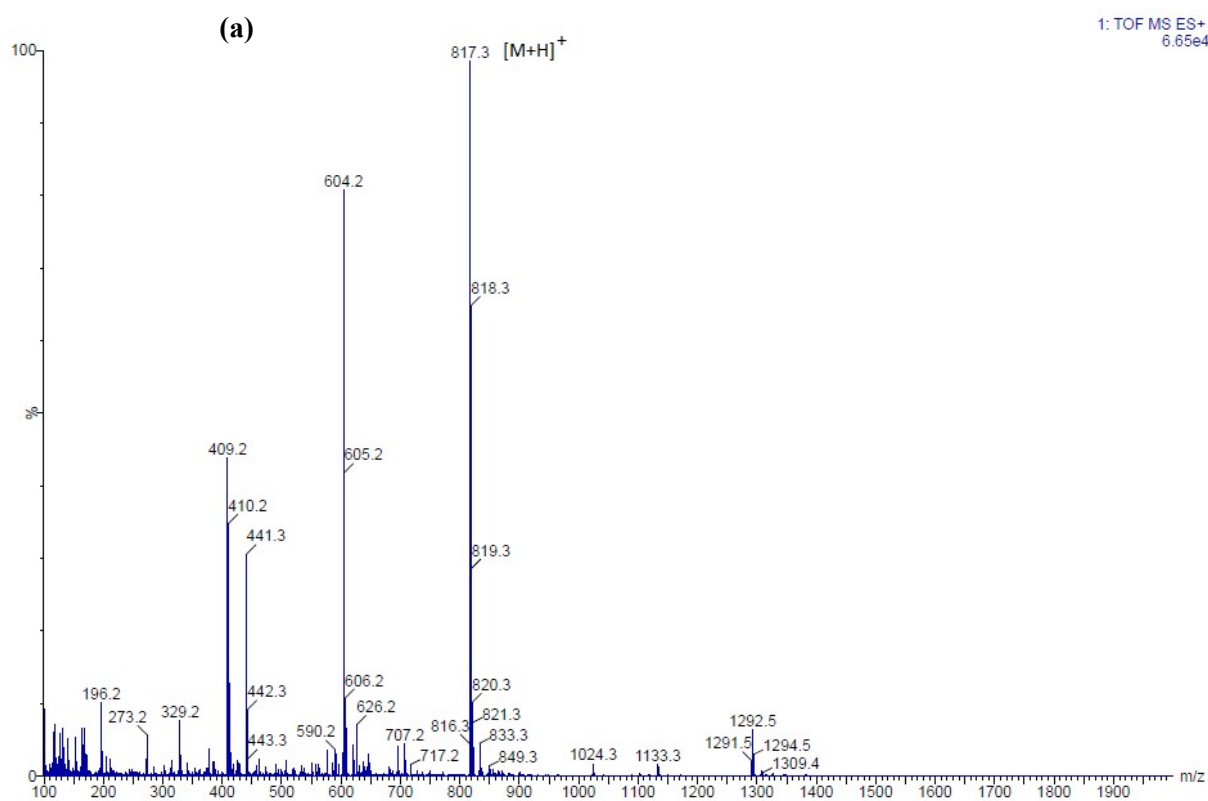


Fig. S8 (a) ESI-TOF-MS and (b) HRMS of **3**.

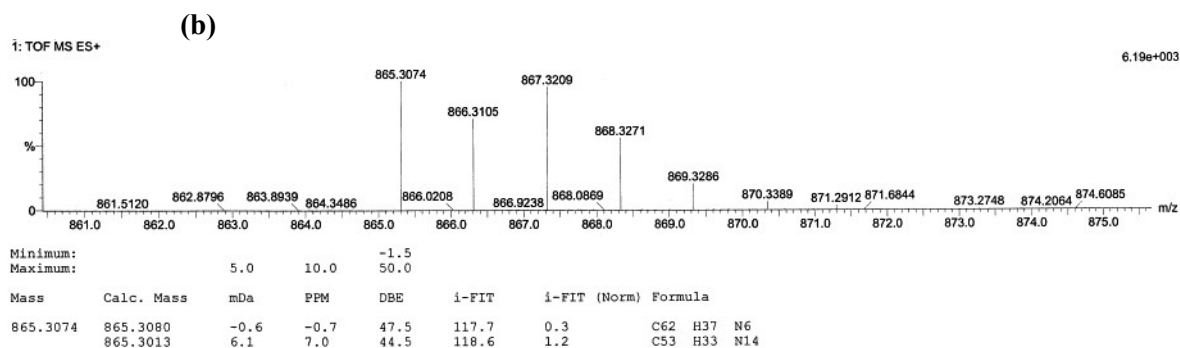
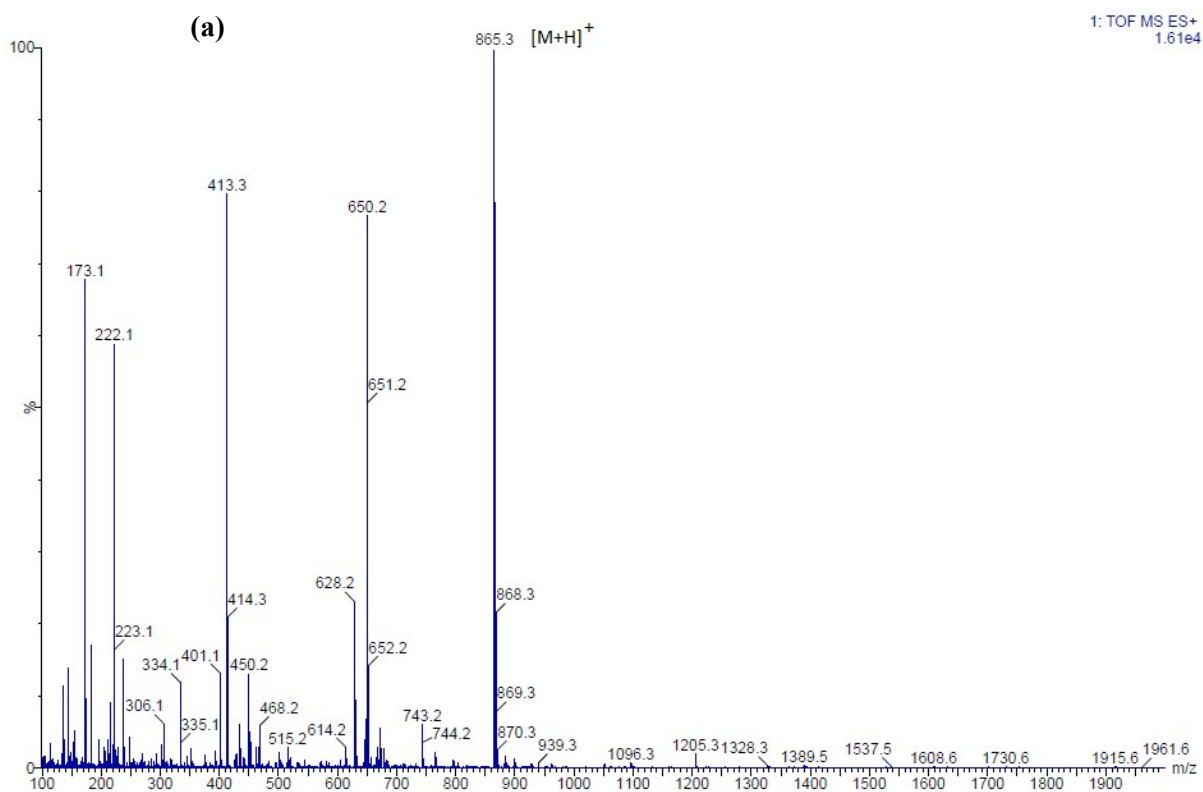


Fig. S9 (a) ESI-TOF-MS and (b) HRMS of 4.

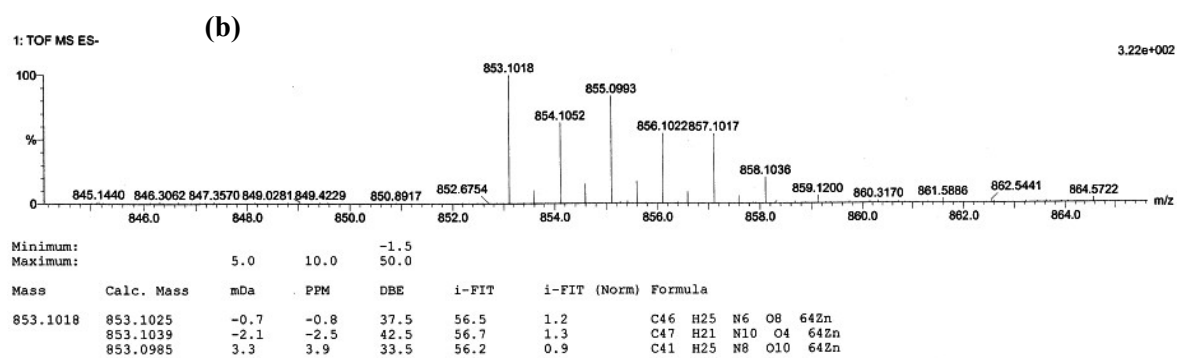
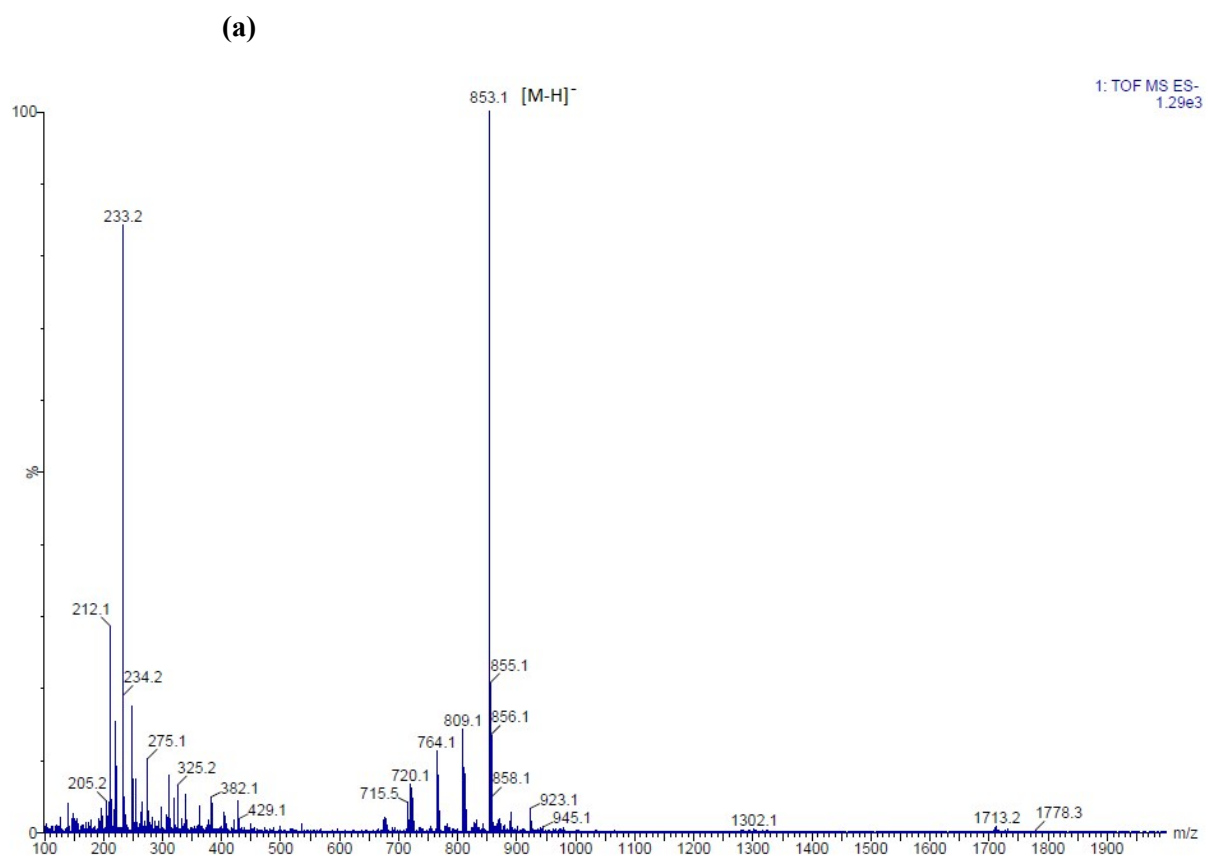


Fig. S10 (a) ESI-TOF-MS and (b) HRMS of 5.

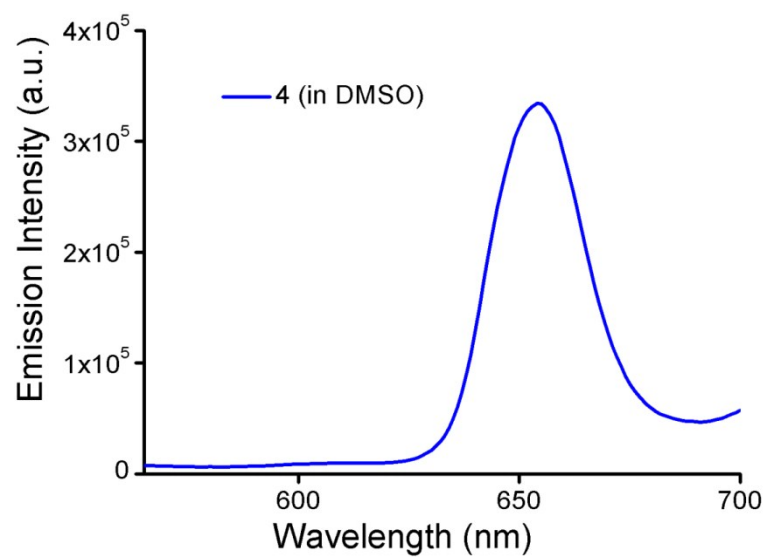


Fig. S11 Emission spectra of porphyrin **4** in DMSO excited at 420 nm wavelength.

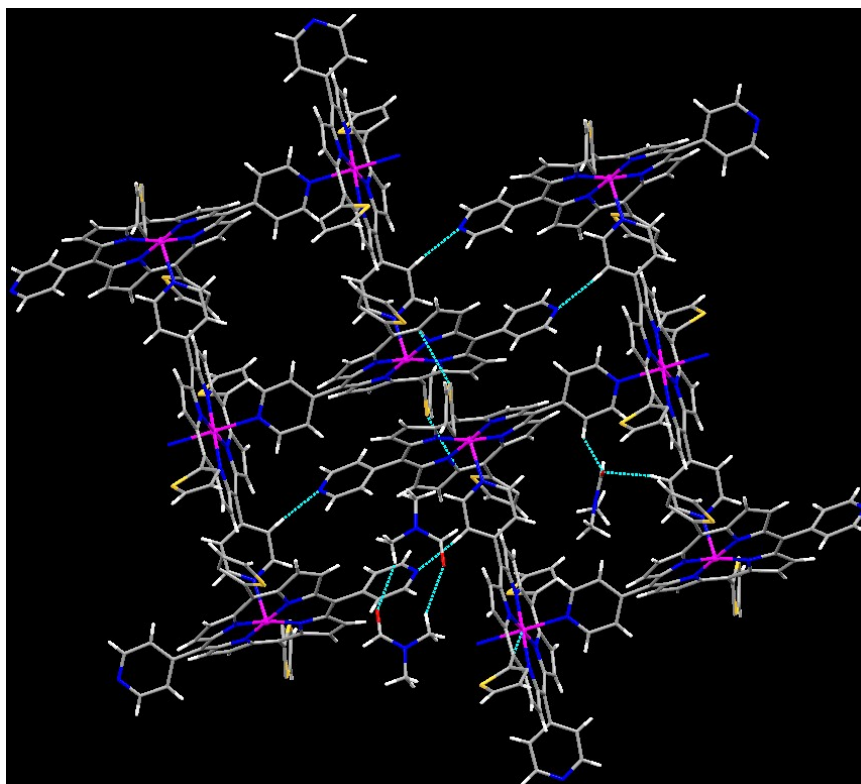


Fig. S12 H-bonding interactions (represented by cyan dotted lines) observed in **1a**.

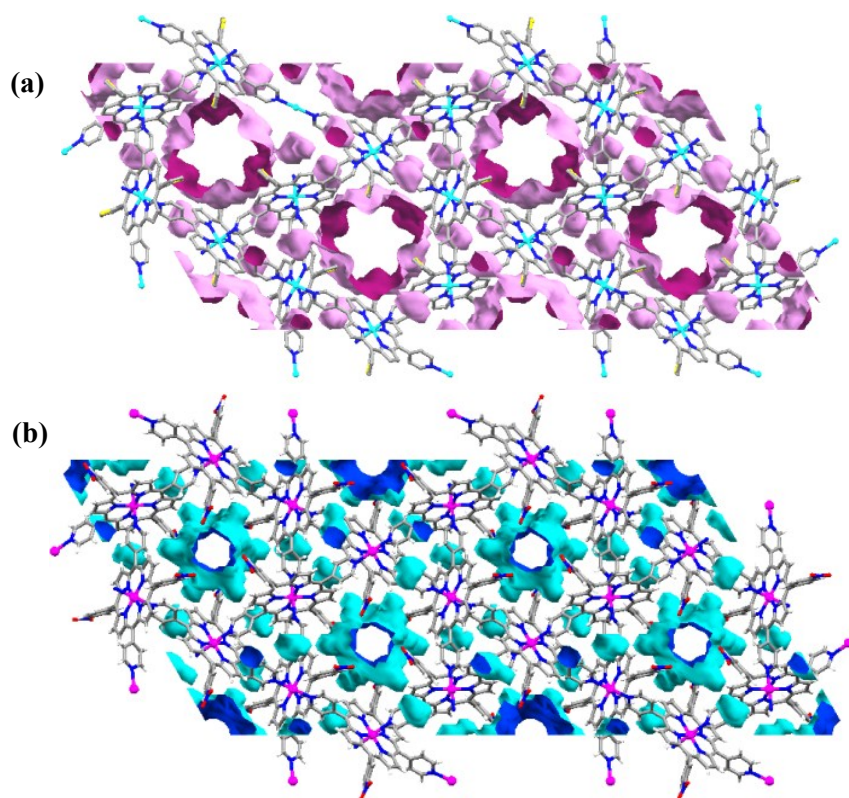


Fig. S13 The Connolly surfaces of **1b** (a) and **2a** (b) showing slightly more open space in **1b** than in **2a**.

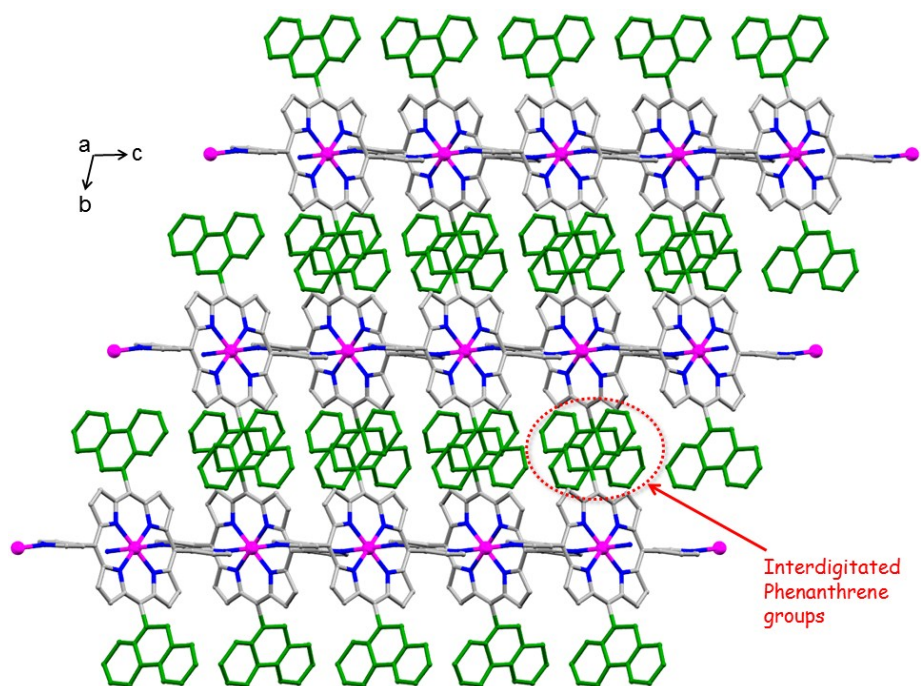


Fig. S14 Pendant phenanthrene groups lining the upper and lower surfaces of the 2D layers in complex **3a**. Phenanthrene groups of one layer are interdigitated between those of the adjacent layers.

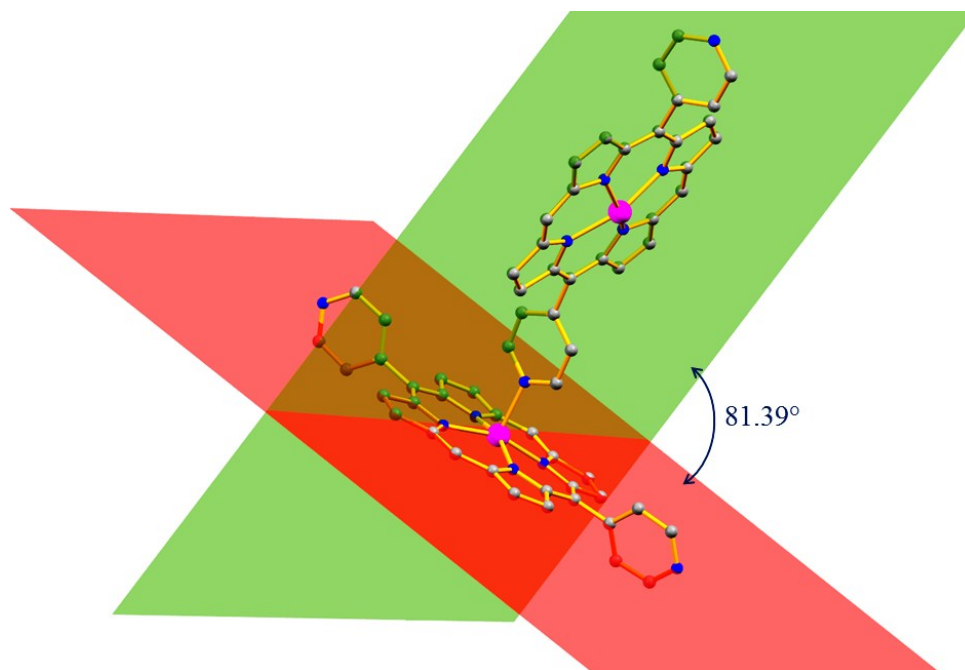


Fig. S15 Dihedral angle between two neighbouring porphyrin macrocycles for complex **4a**. Pyrene substituents are removed for clarity.

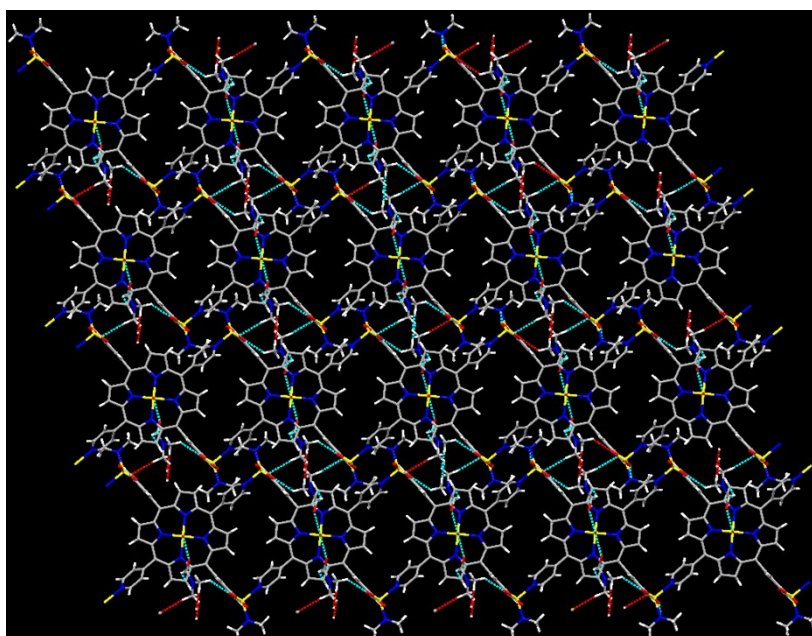


Fig. S16 H-bonding interactions (shown as cyan dotted lines) found in complex **5a**. Colour code: yellow - Zn (to distinguish from the H-bonding) and others same as mentioned before.

Table S1. Summary of SHAPE analysis for complex **5a**.

<i>Code</i>	<i>Entry</i>	<i>Symmetry</i>	<i>Geometry</i>
PP-5	1	D5h	Pentagon
vOC-5	2	C4v	Vacant octahedron
TBPY-5	3	D3h	Trigonal bipyramid
SPY-5	4	C4v	Spherical square pyramid
JTBPY-5	5	D3h	Johnson trigonal bipyramid J12

Structure [ML5]	PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5
Zn	,	31.992,	5.162,	4.276,	3.716, 5.094