

Concerted motions in supramolecular systems: metal-mediated assemblies of porphyrins that behave like nanometric step-machines

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Supplementary Information

1D and 2D NMR experiments were recorded at 500 MHz on a Varian 500. Proton peak positions were referenced to the peak of residual non deuterated solvent (set at δ 7.26 for CDCl₃, and δ 5.33 for CD₂Cl₂). UV-vis absorption spectra were recorded with a Jasco V-570 UV/Vis/NIR spectrophotometer. Emission spectra were taken on a Spex Fluoromax-2 spectrofluorimeter, equipped with Hamamatsu R3896 tubes. Solvents for spectroscopic measurements were of spectroscopic grade, all the other solvents were of reagent grade quality, and used as received. CDCl₃, used in NMR experiments, was treated with basic alumina prior to use.

Abbreviations: 4'*trans*DPyP = 5,15-bis(4'-pyridyl)-10,20-diphenylporphyrin, 4'*trans*DPyP-npm = 5,15-bis(4'-pyridyl)-2,8,12,18-tetra-*n*-propyl-3,7,13,17-tetramethylporphyrin.

Metallacycle **1** was synthesized as previously reported.³ 4'*trans*DPyP and 4'*trans*DPyP-npm were synthesized according to literature procedures.^{18,28}

Synthesis of **2** and **3**: metallacycle **1** (19 mg, 1.05×10^{-2} mmol) and 4'*trans*DPyP (6 mg, 1.05×10^{-2} mmol) were dissolved in CHCl₃ (20 mL) and the solution was stirred at room temperature for 15 min. Concentration in vacuo to ca. 5 mL followed by addition of *n*-hexane induced the precipitation of **2** as a dark-violet solid, that was isolated by filtration, washed with *n*-hexane and vacuum dried (23 mg, 93%). A similar procedure was followed for **3**: equimolar amounts of **1** (15 mg, 8.26×10^{-3} mmol) and 4'*trans*DPyP-npm (6 mg, 8.26×10^{-3} mmol) yielded **3** as a dark-violet solid (19 mg, 91%).

[**1**₂(μ -4'*trans*DPyP)₂] (**2**). δ_{H} (500 MHz; CDCl₃; 10 °C; see text for labels and colour code) -4.16 (4H, s, NH), 2.11 (4H, d, H_{2,6}, 4'*trans*DPyP), 2.87 (4H, d, H_{2,6}, 4'*trans*DPyP), 5.53 (4H, d, H_{3,5}, 4'*trans*DPyP), 6.68 (12H, m, H₅, **1** + β H_{13/17} + H_{3,5} 4'*trans*DPyP), 7.22 (4H, s, β H_{7/8}, **1**), 7.41 (4H, d, H₄, **1**), 7.46 (8H, m, mH, 4'*trans*DPyP), 7.53 (8H, m, H₅, **1** + pH, 4'*trans*DPyP), 7.59 (8H, m, mH + β H_{7/8}, **1**), 7.64 (8H, m, oH, 4'*trans*DPyP), 7.75 (20H, m, mH+pH, **1**), 7.83 (4H, d, β H_{12/18}, 4'*trans*DPyP), 7.87 (4H, br s, β H_{3/7}, 4'*trans*DPyP), 8.03 (4H, d, oH_b, **1**), 8.08 (4H, d, oH_b, **1**), 8.17 (4H, d, H₄, **1**), 8.24 (4H, d, oH_a, **1**), 8.39 (4H, d, oH_a, **1**), 8.49 (4H, br s, β H_{2/8}, 4'*trans*DPyP), 8.87 (4H, s, β H_{17/18}, **1**), 8.99 (4H, s, β H_{17/18}, **1**), 9.04 (12H, m, β H, **1**), 9.11 (4H, d, β H, **1**), 9.45 (4H, d, H₆, **1**), 9.49 (4H, d, H₆, **1**), 9.86 (8H, s, H₂, H₂, **1**).

[**1**₂(μ -4'*trans*DPyP-npm)₂] (**3**). δ_{H} (500 MHz; CD₂Cl₂; 0 °C; see text for labels and colour code): -3.93 (2H, s, NH), -3.53 (2H, s, NH), 0.67 (12H, t, -CH₂CH₂CH₃), 0.99 (12H, t, -CH₂CH₂CH₃), 1.46 (8H, m, -CH₂CH₂CH₃), 1.88 (8H, m, -CH₂CH₂CH₃), 2.17 (4H, br s, H_{2,6}, 4'*trans*DPyP-npm), 2.74 (4H, br s, H_{2,6}, 4'*trans*DPyP-npm), 3.15 (8H, br s, -CH₂CH₂CH₃), 3.89 (8H, br s, -CH₂CH₂CH₃), 5.28 (4H, br s, H_{3,5}, 4'*trans*DPyP-npm), 5.80 (4H, t, H₅, **1**), 6.55 (4H, d, H_{3,5}, 4'*trans*DPyP-npm), 7.27 (4H, d, H₄, **1**), 7.29 (4H, s, β H_{7/8}, **1**), 7.58 (4H, t, mH_b, **1**), 7.66 (4H, t, H₅, **1**), 7.75 (8H, m, mH+pH, **1**), 7.80 (12H, m, mH+pH, **1**), 7.92 (4H, s, β H_{7/8}, **1**), 8.01 (4H, d, oH_b, **1**), 8.27 (12H, m, oH,

1), 8.39 (4H, d, H4, 1), 8.92 (4H, d, β H_{17/18}, 1), 8.97 (8H, d, β H, 1), 9.09 (4H, s, β H_{17/18}, 1), 9.11 (4H, d, β H, 1), 9.19 (4H, d, β H, 1), 9.42 (H, d, H6, 1), 9.54 (4H, d, H6, 1), 9.64 (4H, s, H_{meso}), 9.81 (4H, s, H2, 1), 9.93 (4H, s, H2, 1). The resonances of the methyl groups of 4'*trans*DPyP-npm (two singlets expected), were not assigned as they fall in a very crowded region (see figure SI5).

Additional comments on the NMR spectra

In compound **2** (CDCl₃) the resonance of the internal NH protons is a singlet at 25 °C but, upon lowering the temperature, broadens and then splits into two equally intense singlets at $\delta = -4.13$ and -4.40 at -20 °C, as the exchange motion between the *purple* and *blue* positions within each macrocycle becomes slow on the NMR time-scale. In **3** (CD₂Cl₂) the resonance of the internal NH protons (see Figure 5) is already split in two equally intense singlets ($\delta = -3.83$ and -3.45) at 25 °C. This feature might be due to a slower exchange rate of the two internal protons compared to **2** and/or to the larger difference in chemical shift at the slow exchange limit between the two singlets in **3** ($\Delta\delta = 0.38$) compared to **2** ($\Delta\delta = 0.27$).

As said in the text, in **2** and **3** the rotation of the phenyl rings of **1** about the C_{meso}–C_{ring} bonds is slow on the NMR time scale at ambient temperature already. It is worth noting that in the less sterically congested sandwich **4** the rotation of the phenyl rings became slow – and the corresponding resonances resolved – only at -20 °C.

The *ortho* protons of **1** in **2** are actually exchanged by two different motions, both slow on the NMR time scale: rotation about the C_{meso}–C_{ring} bond, that exchanges *exo* (oH_a) and *endo* (oH_b) protons on each ring, and the more general step-like motion that exchanges *green* and *orange* protons. Accordingly, each resonance of the four *ortho* protons is connected to the other three in the ROESY spectrum by exchange cross-peaks and by exchange-NOE cross-peaks. Considering that, due to the unresolved resonances of *meta* and *para* protons, is not possible to distinguish through the H-H COSY spectrum which protons belong to the same ring, unambiguous attribution of the four *ortho* resonances is not possible. Based on the relative intensity of the exchange cross-peaks of all pairs of protons in **2**, we tentatively assign the most upfield doublets to the *endo* green (oH_b) and orange (oH_b) protons, respectively.

The coalescence of the resonances of H2 protons in **3** (¹H VT NMR, CDCl₃, see also Figure SI6) can be roughly estimated to be at 311 K, corresponding to a rate constant $k = 67$ s⁻¹ and a Gibbs free energy (ΔG^\ddagger) of 65.4 kJ mol⁻¹, that compares well with the value of 65.9 kJ mol⁻¹ found from the coalescence of the resonances of the H6 protons (see text).

Additional comments on the dynamic equilibrium in **2** and **3**

As an alternative explanation of the ROESY results, the two conformers of **2** and **3** might be in slow equilibrium through their components, i.e. through the dynamic association/dissociation of the Zn–N(pyridyl) bonds. This possible dynamic equilibrium – that would involve the symultaneous breaking/formation of multiple Zn–N(pyridyl) bonds – is totally shifted towards the sandwich assemblies, so that the components, at stoichiometric ratio, are at very low concentrations and thus undetectable in the NMR spectra. In fact, we showed that these sandwich assemblies have association constants higher than 10¹⁸ M⁻¹ and are fully assembled in chloroform at NMR concentrations.^{4,5}

With the aim of assessing this hypothesis we wanted to perform a ROESY experiment on a solution containing a 1:0.5 mixture of **3** and **1**. The sandwich assembly **3** was selected instead of **2** because its NMR spectrum in the aromatic region is less crowded. The alternative option, i.e. performing the ROESY experiment on a mixture containing an excess of the linker 4'*trans*DPyP-npm, is not feasible because the ¹H NMR resonances are known to broaden considerably.⁴

The detection of exchange cross-peaks between the resonances of the metallacycle **1** in its two states, i.e. free and bound in **3** (**1@3**), would establish the presence of such dynamic equilibrium. Unfortunately, the planned experiment proved to be unfeasible: the ¹H NMR spectrum of the mixture turned out to be too crowded, even at 500 MHz. The differences in chemical shifts between the resonances of **1** and those of **1@3** proved to be too small and no clearly resolved resonance was found in the investigated temperature range ($+25$ – -35 °C, CDCl₃). Thus the ROESY spectrum would not have allowed us to detect any cross-

peak that might be unambiguously assigned to an exchange between the sandwich assembly and the free metallacycle.

In conclusion, we have no experimental evidence of the existence this association/dissociation dynamic equilibrium in **2** and **3**.

UV-vis absorption and emission spectra of **2**

The UV-vis absorption spectrum of **2** is a very good superimposition of those of the molecular components **1** and 4'*trans*DPyP (Figure ESI1). This observation confirms the supramolecular nature of **2**, and is in good agreement with what already observed for its analogue **4**.⁵ The emission spectrum of **2** is very similar to that of the free-base component 4'*trans*DPyP (Figure ESI2). An analogous behavior was already observed for **4**.⁵

X-ray structure determination

Crystals of **2** suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into a chloroform solution of **2**. Data collection was carried out at the X-ray diffraction beamline of the Elettra Synchrotron, Trieste (Italy), using the rotating crystal method with the monochromatic wavelength of 1.0000 Å at 100(2) K. Data were collected on a MarResearch CCD detector. Data reduction and cell refinement carried out using the Denzo and Scalepack programs.^{3S} The structure was solved by direct methods followed by successive Fourier syntheses and refined on F^2 using SHELXL.^{4S} A ΔF map revealed a disordered chloroform molecule (occupancy factor 0.5, based on the electron density peaks). The hydrogen atoms are at fixed geometrically calculated positions. Only coordinating atoms were anisotropically refined. All the calculations were performed using the WinGX System, Version 1.80.05.^{5S}

The Zn and Ru ions have square pyramidal and octahedral geometry, respectively, with unexceptional coordination bond distances. The geometry of the staggered metallacycle is not particularly affected by axial coordination of the 4'*trans*DPyP linkers: the Zn(1)···Zn(2) and Ru(1)···Ru(2) distances are 10.121(3) and 14.057(2) Å, respectively, i.e. within the range measured for unbound **1**.³ However, some distortions are found in the geometry of the Zn-porphyrins, with max displacement of atoms out of the mean plane up to 0.35 Å. The 4'*trans*DPyP linkers form dihedral angles of 79.85(7) and 86.43(7)° with the Zn-porphyrins and, correspondingly, the Zn ions show a non linear coordination to the axial pyridyl rings, with the Zn–N(py)···C γ (py) angle of *ca.* 171°.

References

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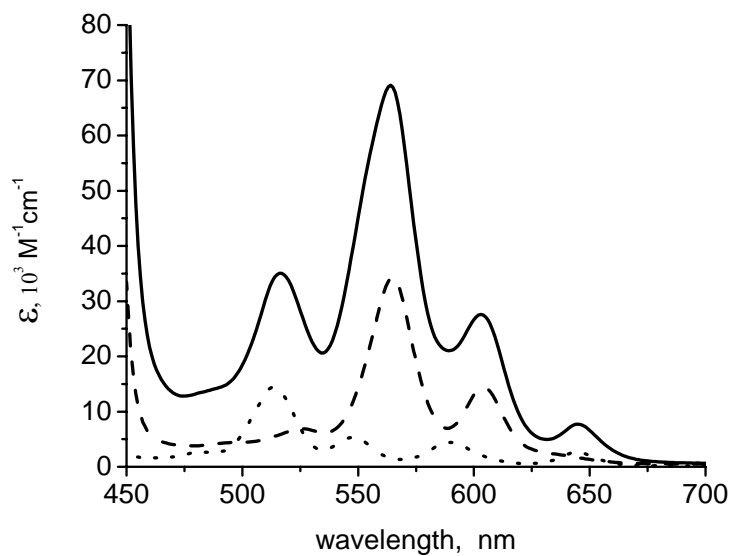


Figure ESI1. Absorption spectra of **2** (continuous line), **1** (dashed line) and 4'*trans*DPyP (dotted line).

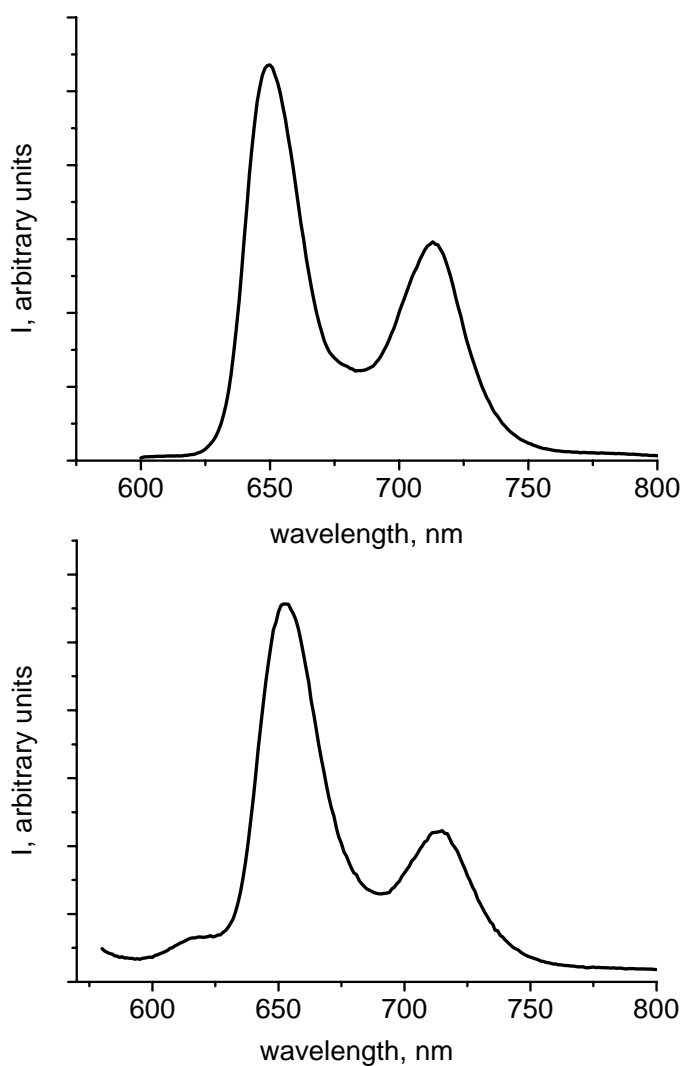


Figure ESI2. Emission spectra of 4'*trans*DPyP (top) and **2** (bottom) at room temperature in CH_2Cl_2 solution.

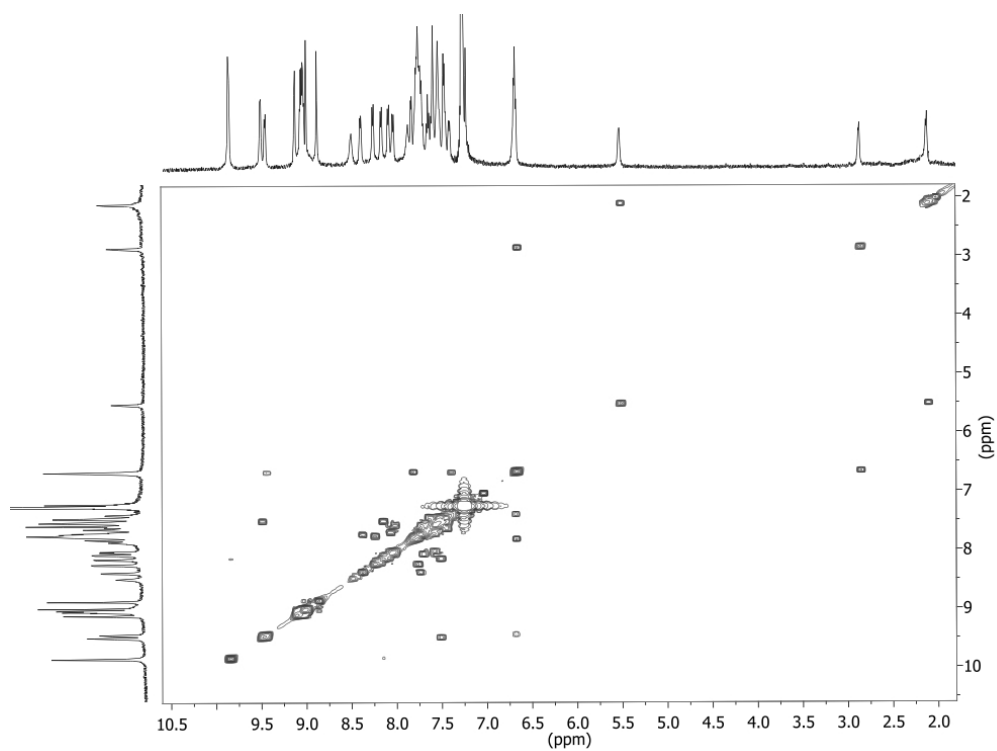


Figure ESI3. Selected region of the 2D H-H COSY NMR spectrum of **2** (CDCl₃, 10 °C). See text for labeling scheme.

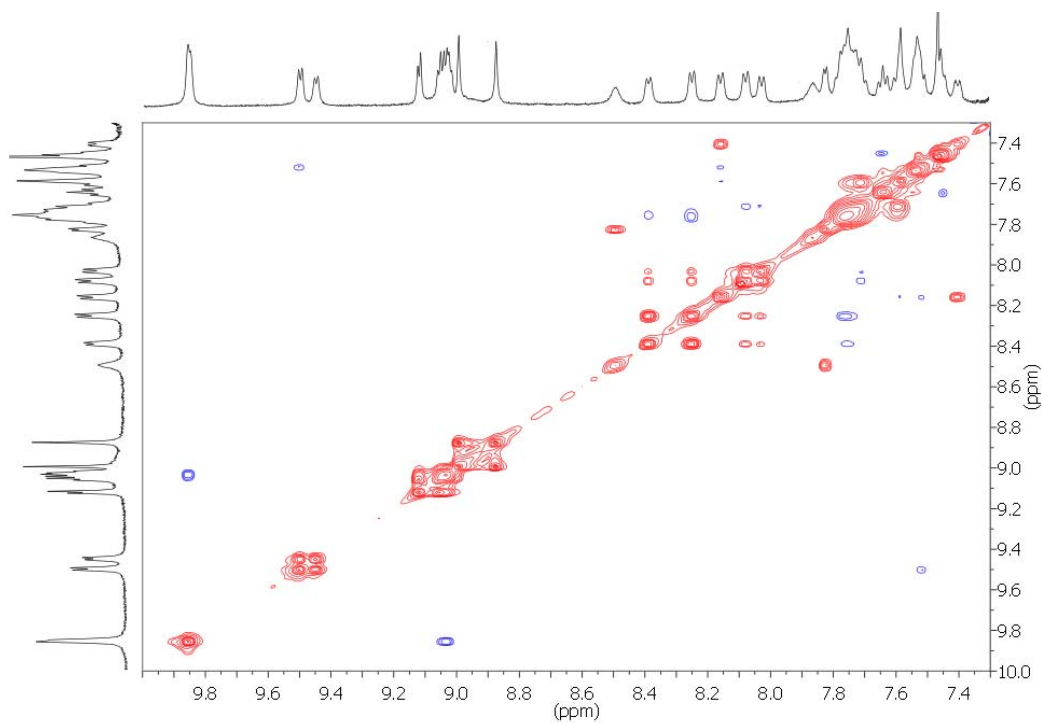


Figure ESI4. Selected region of the 2D ROESY NMR spectrum of **2** (CDCl₃, 10 °C, exchange peaks are in red). See text for labeling scheme.

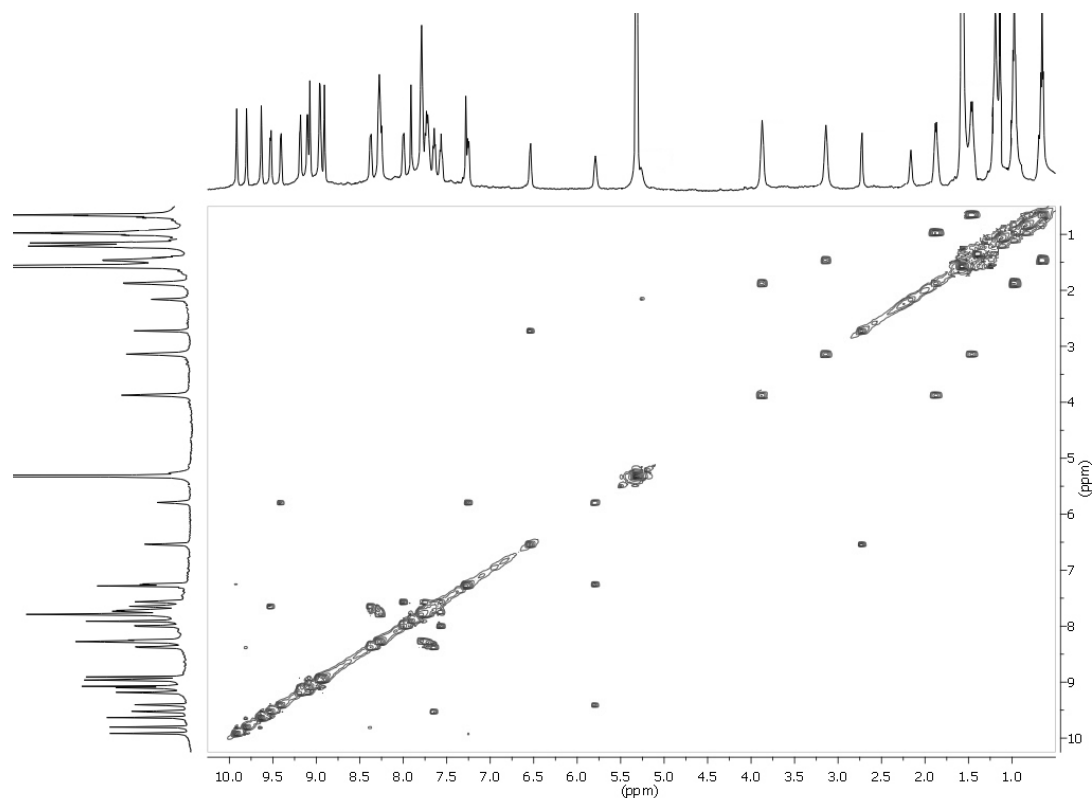


Figure ESI5. Selected region of the 2D H-H COSY NMR spectrum of **3** (CD_2Cl_2 , 0 °C). See text for labeling scheme.

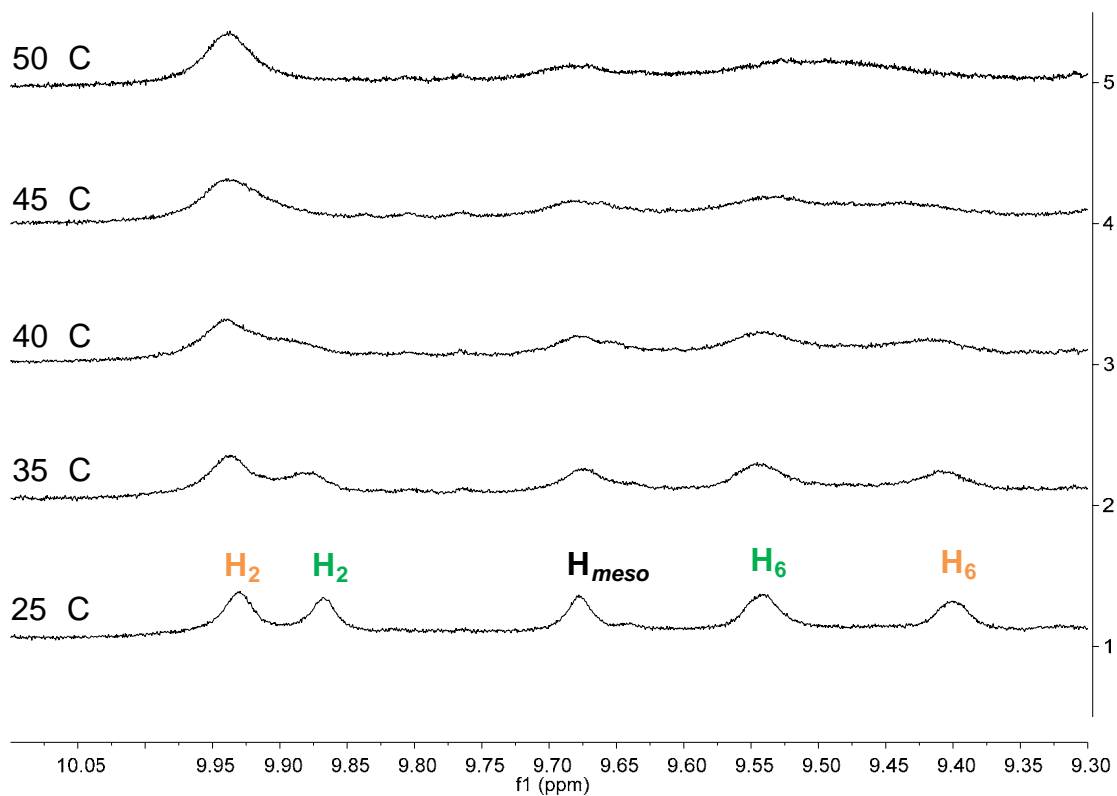


Figure ESI6. Selected region of the ^1H VT NMR of **3** (CDCl_3).