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'transDPyP = 5,15-bis(4'-pyridyl)-10,20-diphenylporphyrin, 4'transDPyP-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'transDPyP and 4'transDPyP-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'transDPyP (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'transDPyP-npm (6 mg, 8.26 × 10⁻³ mmol) yielded 3 as a dark-violet solid (19 mg, 91%).

[12(µ-4'transDPyP)2] (2). δH (500 MHz; CDCl3; 10 °C; see text for labels and colour code): -4.16 (4H, s, NH), 2.11 (4H, d, H2,6, 4'transDPyP), 2.87 (4H, d, H2,6, 4'transDPyP), 5.53 (4H, d, H3,5, 4'transDPyP), 6.68 (12H, m, H5, 1 + βH13/17 + H3,5 4'transDPyP), 7.22 (4H, s, βH7/8, 1), 7.41 (4H, d, H4, 1), 7.46 (8H, m, mH, 4'transDPyP), 7.53 (8H, m, H5, 1 + pH, 4'transDPyP), 7.59 (8H, m, mH + βH7/8, 1), 7.64 (8H, m, oH, 4'transDPyP), 7.75 (20H, m, mH+pH, 1), 7.83 (4H, d, βH12/18, 4'transDPyP), 7.87 (4H, br s, βH13/17, 4'transDPyP), 8.03 (4H, d, oHb 1), 8.08 (4H, d, oHb, 1), 8.17 (4H, d, H4, 1), 8.24 (4H, d, oHb, 1), 8.39 (4H, d, oHb, 1), 8.49 (4H, br s, βH12/18, 4'transDPyP), 8.87 (4H, s, βH17/18, 1), 8.99 (4H, s, βH17/18, 1), 9.04 (12H, m, βH, 1), 9.11 (4H, d, βH, 1), 9.45 (4H, d, H6, 1), 9.49 (4H, d, H6, 1), 9.86 (8H, s, H2, H2, 1).

[12(µ-4'transDPyP-npm)2] (3). δH (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, -CH2CH2CH2), 0.99 (12H, t, -CH2CH2CH2), 1.46 (8H, m, -CH2CH2CH3), 1.88 (8H, m, -CH2CH2CH3), 2.17 (4H, br s, H2,6, 4'transDPyP-npm), 2.74 (4H, br s, H2,6, 4'transDPyP-npm), 3.15 (8H, br s, -CH2CH2CH3), 3.89 (8H, br s, -CH2CH2CH3), 5.28 (4H, br s, H3,5, 4'-transDPyP-npm), 5.80 (4H, t, H5, 1), 6.55 (4H, d, H3,5, 4'transDPyP-npm), 7.27 (4H, d, H4, 1), 7.29 (4H, s, βH7/8, 1), 7.58 (4H, t, mHb, 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, βH7/8, 1), 8.01 (4H, d, oHb, 1), 8.27 (12H, m, oH,
1), 8.39 (4H, d, H4, 1), 8.92 (4H, d, βH17/18, 1), 8.97 (8H, d, βH, 1), 9.09 (4H, s, βH17/18, 1), 9.11 (4H, d, βH, 1), 9.19 (4H, d, βH, 1), 9.42 (H, d, H6, 1), 9.54 (4H, d, H6, 1), 9.64 (4H, s, Hmeso), 9.81 (4H, s, H2, 1), 9.93 (4H, s, H2, 1). The resonances of the methyl groups of 4transDPyP-npm (two singlets expected), were not assigned as they fall in a very crowded region (see figure S15).

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 simultaneous 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 so that the components, through the dynamic association/dissociation of the components, i.e. through the slow exchange between the two singlets in 3 (Δδ = 0.38) compared to 2 (Δδ = 0.27). As said in the text, in 2 and 3 the rotation of the phenyl rings of 1 about the Cmeso−Cring bond 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 Cmeso−Cring bond, that exchanges exo (oHa) and endo (oHb) 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 (oHb) and orange (oHb) 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°) 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 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 δ = -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 into two equally intense singlets (δ = -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 (Δδ = 0.38) compared to 2 (Δδ = 0.27).

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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’tansDPyP (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’tansDPyP (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.35 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’tansDPyP 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’tansDPyP 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
**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$_2$Cl$_2$ 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$_2$Cl$_2$, 0 °C). See text for labeling scheme.

Figure ESI6. Selected region of the $^1$H VT NMR of 3 (CDCl$_3$).