Supporting Information

Dynamics of excited-state conformational relaxation and electronic delocalization in conjugated porphyrin oligomers

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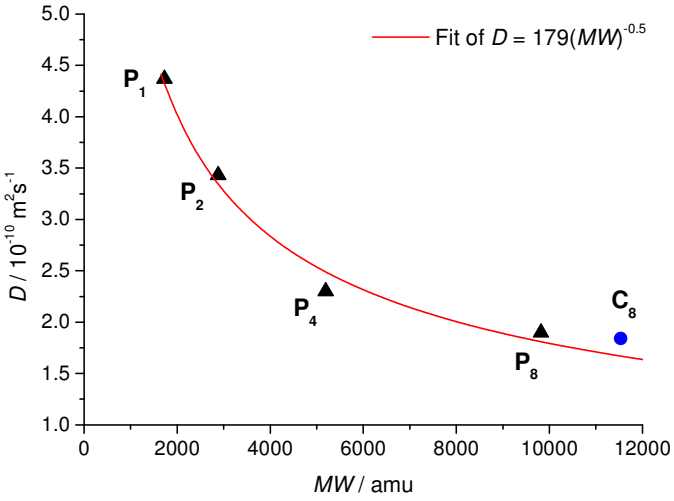

Figure S1. ^{1}H-NMR diffusion constant, D vs. formula molecular weight for single-stranded porphyrin oligomers, $\mathbf{P_n}$ (▲) and cyclic octamer, $\mathbf{C_8}$ (●) ($CDCl_3$ + 1% D_5-pyridine, 298 K, 500 MHz). The smooth curve shows a fit to $D \propto MW^{-0.5}$ which is expected for a spherical molecule. This is probably because the oligomers are relatively rigid, but have long flexible side-chains. The diffusion coefficient for $\mathbf{C_8}$ confirms that it is a 1:1 complex. The fit for $\mathbf{P_1}$ – $\mathbf{P_8}$ indicates the absence of aggregates.

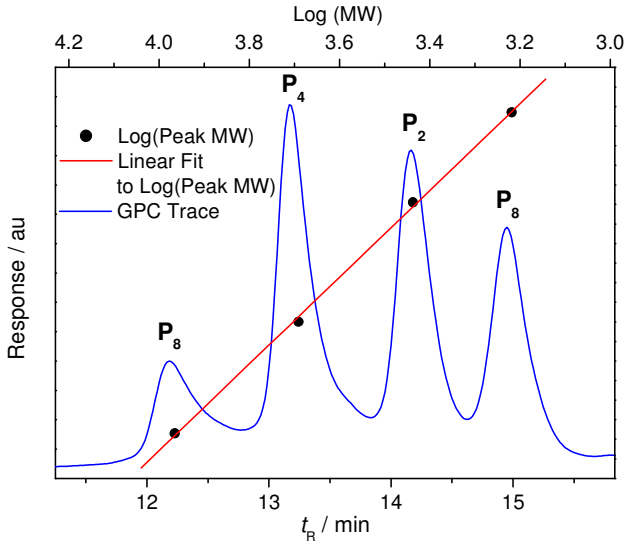

Figure S2. Analytical GPC traces of single-stranded porphyrin oligomers in THF (absorption signal at 255 nm; flow rate 1 mL min^{-1}; 298 K; 2 x 300 mm, 7.5 mm ID PLgel Mixed-E columns, Polymer Laboratories Ltd.). The good fit to $t_R \propto \log(MW)$ confirms the absence of aggregates.

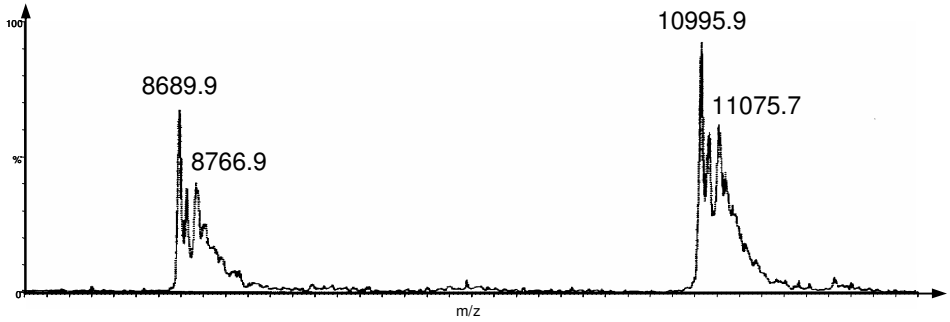

Figure S3. MALDI-ToF mass spectra of **C_8** (expected mass **C_8** 10985.2, found 10995.9; expected mass deprotected **P_8** 8680.4, found 8689.9), recorded in positive linear mode with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]- malononitrile (DCTB) as matrix.

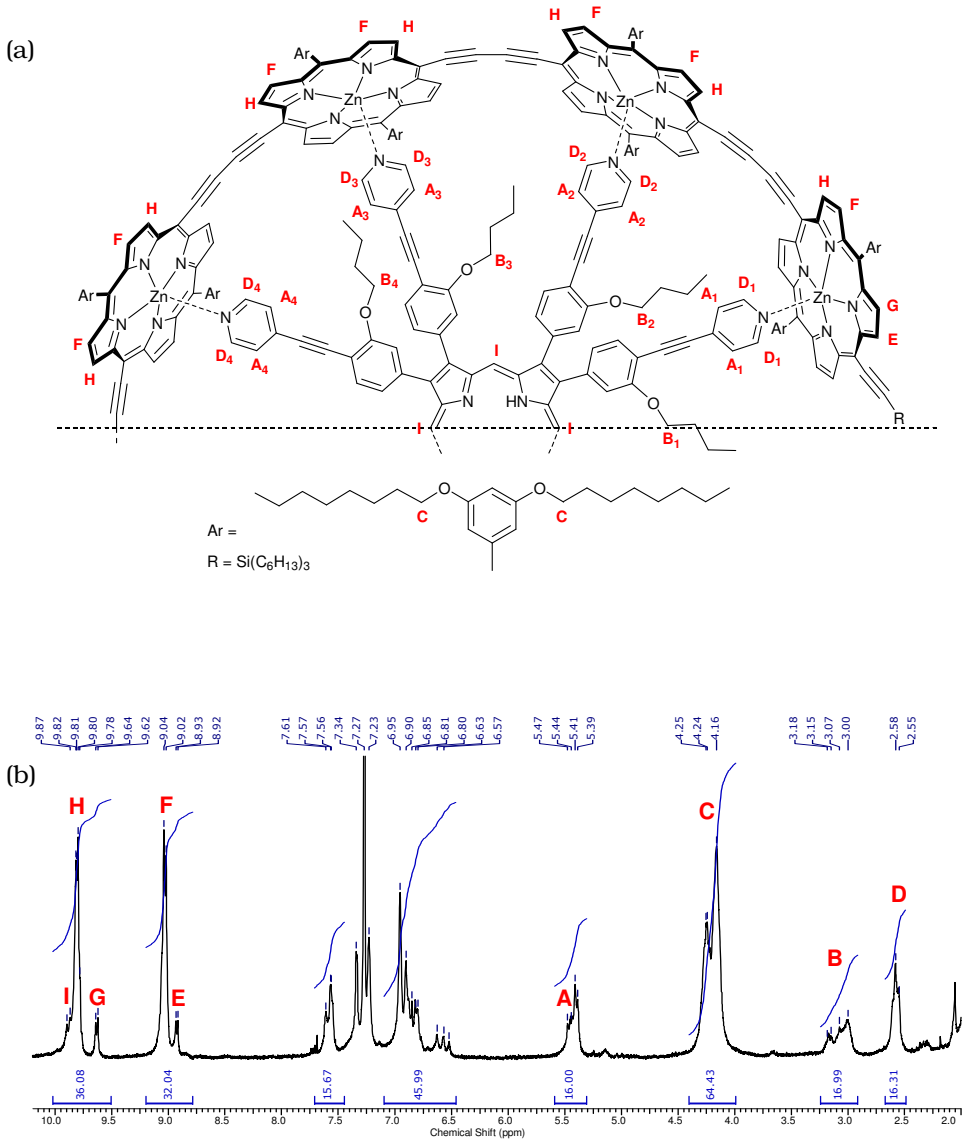

Figure S4. (a) Structure of template · trihexylsilyl-protected octamer complex $\mathbf{C_8}$. The dashed line represents a plane of symmetry. ***(b)*** ^{1}H-NMR spectrum of $\mathbf{C_8}$ (500 MHz, 298 K, $CDCl_3$, assigned by 2D-COSY and NOESY experiments). The low symmetry of the environment results in splitting of the template resonances, as expected. The integrations shown on these spectra confirm the 1:1 stoichiometry of the complex. The spectrum also confirms that all eight pyridyl sites are coordinated to zinc, e.g. through observation of the α-pyridyl resonances (D_1, D_2, D_3 and D_4) at 2.5 ppm.

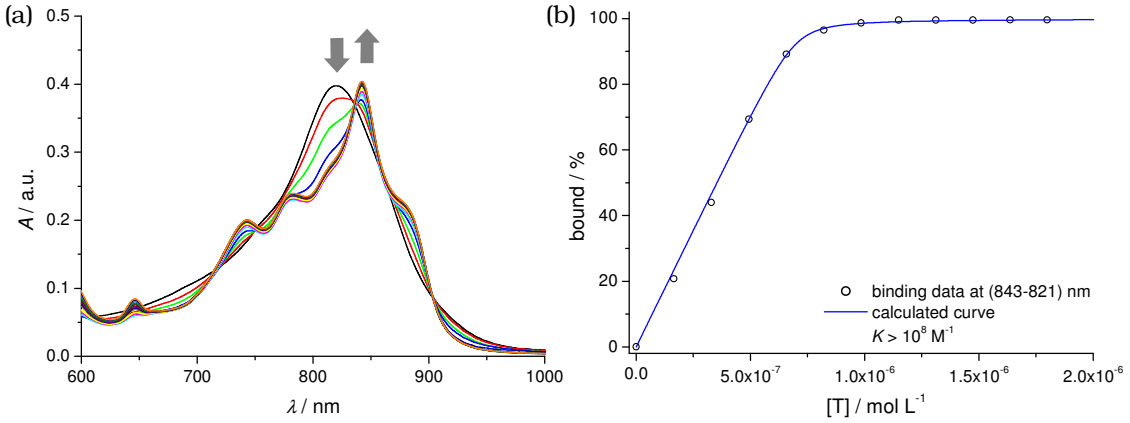

Figure S5. (a) UV-vis titration for the formation of $\mathbf{C_8}$ from template and pyridine-free linear porphyrin octamer, $\mathbf{P_8}$ ([$\mathbf{P_8}$] = 1.8 μM, 298 K, $CHCl_3$). ***(b)*** Binding isotherm obtained from the absorbance data at (843-821) nm. The data were fitted to a 1:1 binding isotherm to give a binding constant of $K > 10^8\ M^{-1}$. Arrows indicate areas of increasing and decreasing absorption during the titration. The isosbestic UV-vis spectra and sharp end-point indicate that it is essentially a two-state equilibrium, without significant concentrations of intermediates.

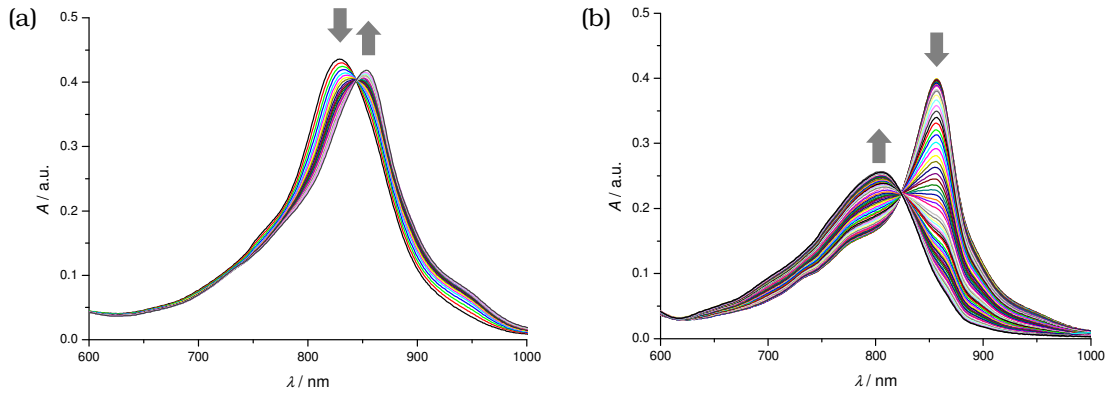

Figure S6. UV-vis titration for ***(a)*** the formation of $\mathbf{L_8}$ from BiPy and pyridine-free linear porphyrin octamer, $\mathbf{P_8}$ ([$\mathbf{P_8}$] = 0.54 μM, 298 K, $CHCl_3$) and ***(b)*** the break-up of the octamer ladder complex with excess BiPy ([$\mathbf{P_8}$] = 0.49 μM, 303 K, $CHCl_3$). Arrows indicate areas of increasing and decreasing absorption during the titration. The titration curves show simple isosbestic behaviour and sharp end-points. This indicates that both processes are essentially two-state equilibria, without significant concentrations of intermediates. The close similarities of the spectra of $\mathbf{L_8}$ with those of previously studied 4,4'-BiPy ladders[1] derived from closely related porphyrin oligomers supports the structured assignment of those assemblies.

[1] *J. Am. Chem. Soc.* **2006**, *128*, 12432; *J. Am. Chem. Soc.* **2007**, *129*, 13370; *J. Mater. Chem.* **2003**, *13*, 2796; *J. Am. Chem. Soc.* **2002**, *124*, 9712; *J. Am. Chem. Soc.* **1999**, *121*, 11538; *Inorg. Chem.* **1994**, *33*, 972.

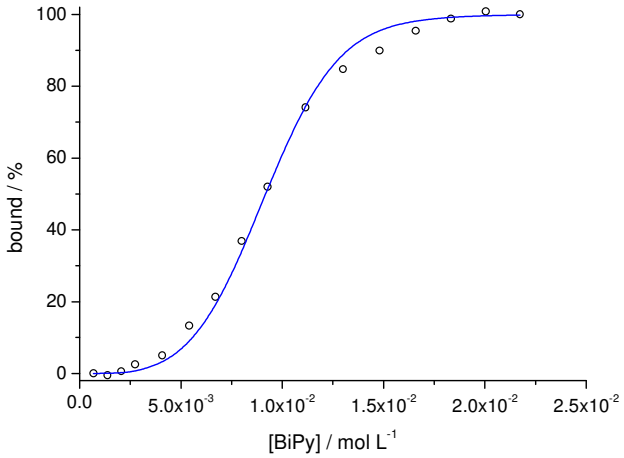

Figure S7. Binding isotherm obtained from the break-up titration of $\mathbf{L_8}$ with excess BiPy ([$\mathbf{P_8}$] = 0.49 μM, 303 K, $CHCl_3$). The cuvette was heated to 50 °C for 10 minutes between each aliquot addition to achieve equilibrium. The titration data for the ladder-breaking equilibrium at 825 nm were analyzed using eqs (S1)–(S7), where **O** is porphyrin octamer $\mathbf{P_8}$ and BiPy is 4,4'-bipyridine. This fitting equation approximates the total concentration of BiPy ([BiPy] = $[BiPy]_0$), This is valid since the concentration of bound BiPy is >1000 times less than the concentration of free BiPy. The binding isotherm fits well to the calculated curve for a two-state equilibrium. Fitting gives a binding constant of $K = 9.3 \times 10^9$ M^{-7}.

$$O_2BiPy_8 + 8BiPy \rightleftharpoons 2OBiPy_8 \tag{S1}$$

$$K = \frac{[OBiPy_8]^2}{[O_2BiPy_8][BiPy]^8} \tag{S2}$$

$$[O]_0 = 2[O_2BiPy_8] + [OBiPy_8] \tag{S3}$$

$$K[O_2BiPy_8][BiPy]_0^8 - \left([O]_0 - 2[O_2BiPy_8]\right)^2 = 0 \tag{S4}$$

$$[O_2BiPy_8] = \frac{[O]_0}{2} + \frac{K[BiPy]_0^8}{8} + \frac{\sqrt{K^2[BiPy]_0^{16} + 8K[BiPy]_0^8[O]_0}}{8} \tag{S5}$$

$$[OBiPy_8] = [O]_0 - 2[O_2BiPy_8] \tag{S6}$$

$$y = \frac{[OBiPy_8]}{[O]_0} = \frac{-\frac{K[BiPy]_0^8 + \sqrt{K^2[BiPy]_0^{16} + 8K[BiPy]_0^8[O]_0}}{4}}{[O]_0} \tag{S7}$$

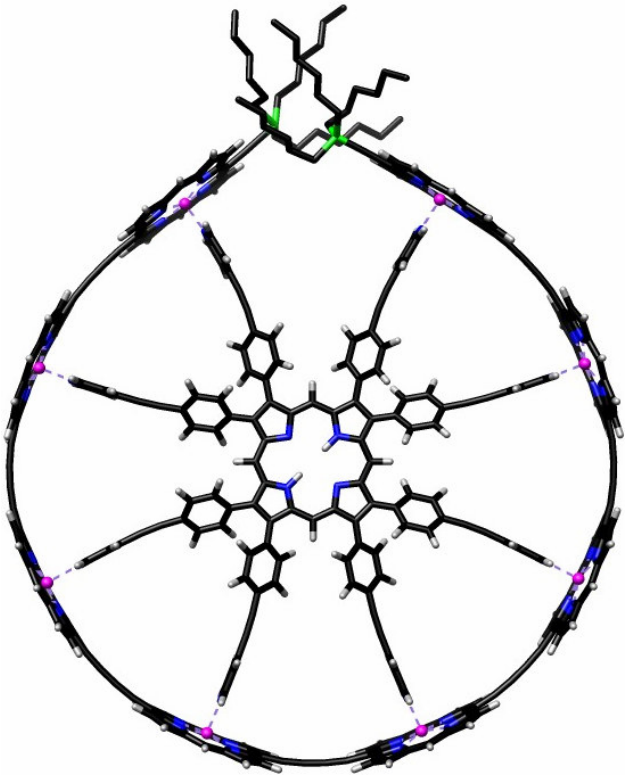

Figure S8. Geometry of $\mathbf{C_8}$ obtained by molecular mechanics geometry optimization (*meso*-aryl substituents omitted for clarity; calculated using the MM+ force-field, HyperChem 8.0, HyperCube, Inc., USA).

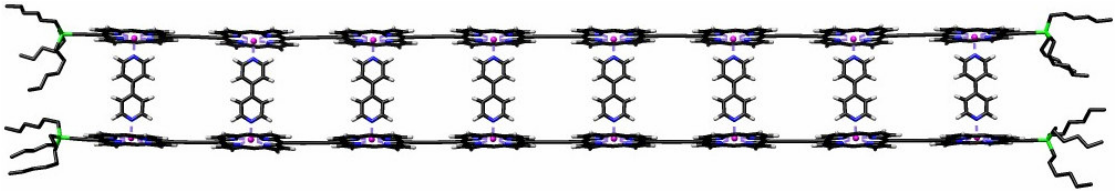

Figure S9. Geometry of $\mathbf{L_8}$ obtained by molecular mechanics geometry optimization (*meso*-aryl substituents omitted for clarity; calculated using the MM+ force-field, HyperChem 8.0, HyperCube, Inc., USA).

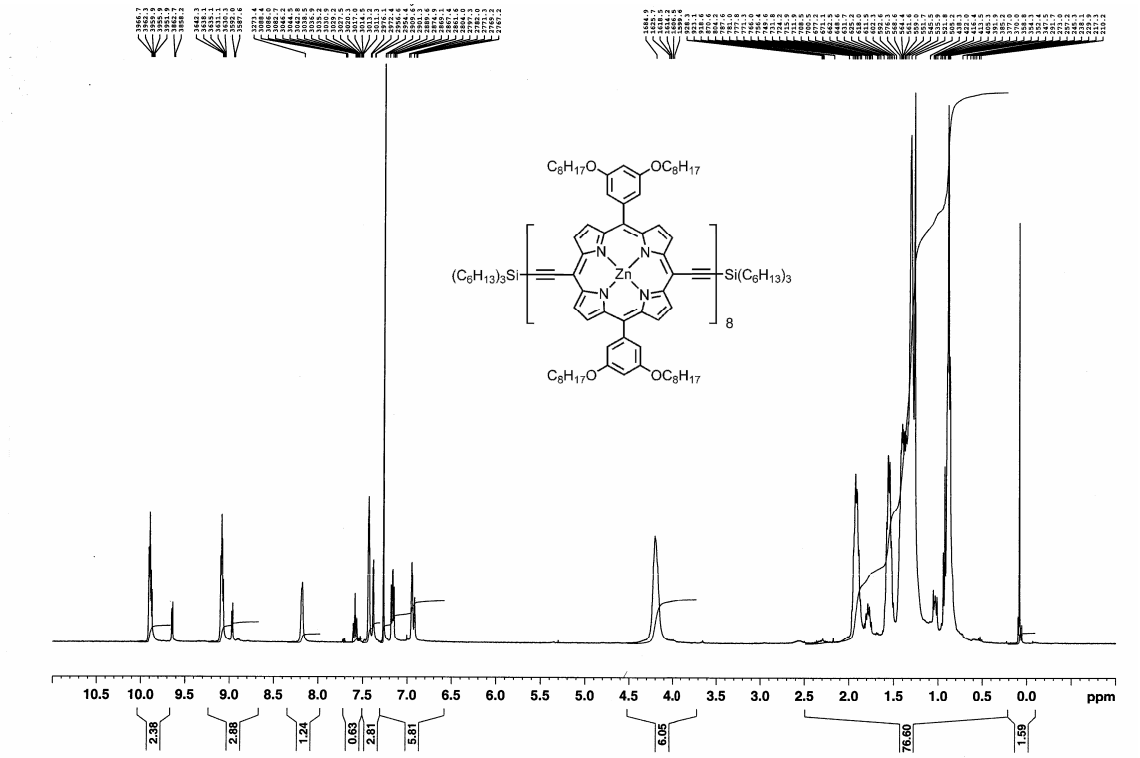

Figure S10. ^{1}H-NMR spectrum of $\mathbf{P_8}$ (400 MHz, 298 K, $CDCl_3$ / 1% D_5-pyridine).

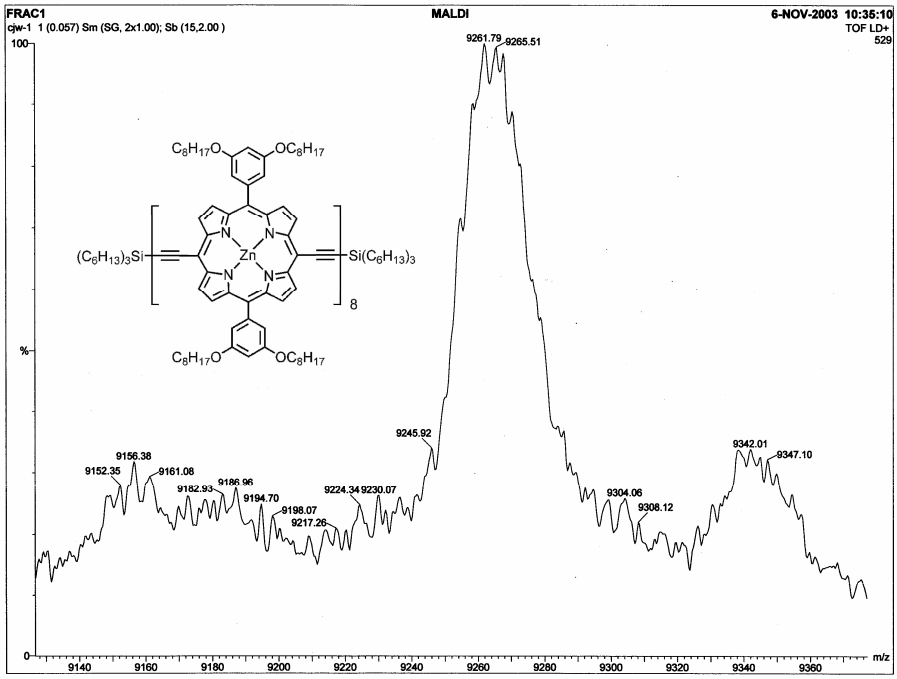

Figure S11. MALDI-ToF mass spectra of $\mathbf{P_8}$ (expected mass $\mathbf{P_8}$ 9245.5, found 9261.8), recorded in positive linear mode with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as matrix.