Supporting Information

Slippage of a porphyrin macrocycle over threads of varying bulkiness. Implications for the mechanism of threading polymers through a macrocyclic ring

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**Data analysis: determination of $k_{on}$ and $K_{assoc}$ values**

Threading kinetics were measured by using the time drive application of the fluorescence spectrometer software. The sample was excited at the wavelength corresponding to the maximum absorbance of the porphyrin Soret band and the emission at the wavelength corresponding to the maximum emission was recorded in time. Typically, to a weighed solution containing a known amount of porphyrin macrocycle, a weighed solution containing a known amount of viologen derivative was added and the solution mixed. After the mixing time (1.5 s) the measurement was started. The data were analyzed according to standard 1:1 kinetic isotherms that describe the kinetics involved in complex formation between A and B, forming C (Equations 1-4),[1] using the computer programs Excel or Grafit®. From the fit, both the rate constant $k_{on}$ and equilibrium association constant $K_{assoc}$ were obtained. All the experiments were performed in plural and at different concentrations of the viologen derivative to decrease the experimental error.

$$
A + B \xrightarrow{k_{on}} C \\
\frac{k_{on}}{k_{off}} \quad [C] = \frac{p}{q} \frac{\left(1 - \frac{q}{p} \frac{[C]_o}{q - [C]_o} e^{k_{on}(p-q)t}\right)}{\left(1 - \frac{p}{q} \frac{[C]_o}{q - [C]_o} e^{k_{on}(p-q)t}\right)}
$$

(1)
\[ p = [C]_{eq} = \frac{([A]_o + [B]_o + \frac{1}{K_{Assoc}}) - \sqrt{\left([A]_o + [B]_o + \frac{1}{K_{Assoc}}\right)^2 - 4 \cdot [A]_o \cdot [B]_o}}{2} \]  

\[ q = \frac{[A]_o [B]_o}{[C]_{eq}} \] 

\[ K_{assoc} = \frac{[C]_{eq}}{([A]_o - [C]_{eq})([B]_o - [C]_{eq})} = \frac{k_{on}}{k_{off}} \] 