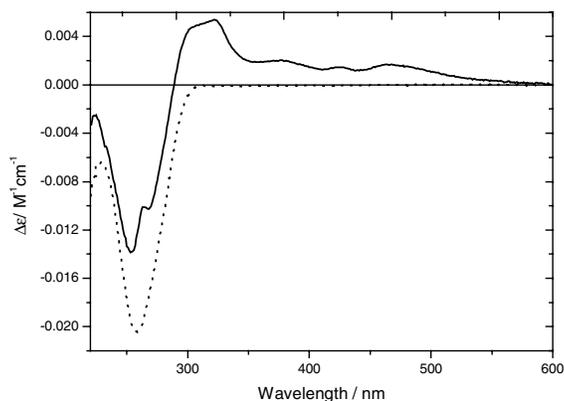
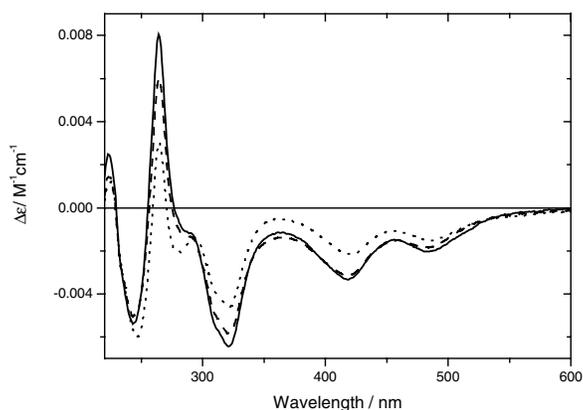


Supporting Information



A.



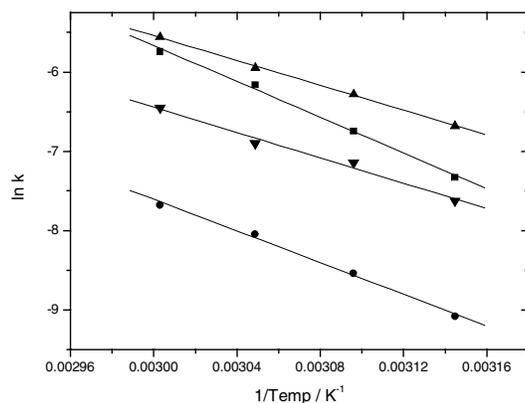
B.

S1. Dissociation from calf thymus DNA. A buffered solution (100 mM NaCl, 1 mM sodium cacodylate, pH 7) of 160 μM calf thymus DNA and 10 μM Δ,Δ -[μ -(11,11'-bidppz)(phen)₄Ru₂]Cl₄ (P/Ru=8) was used. In A. an LD spectrum of the solution was recorded immediately after mixing (solid line). Hereafter SDS was added to a final concentration of 0.6% and another LD spectrum was recorded (dotted line). From the figure it is obvious that the complex immediately dissociates to the SDS-micelles, indicating that the complex is bound to DNA in some of the grooves or externally bound. In B. the solution was first pre-equilibrated (overnight at 50°C) to reach the final binding mode and then an LD spectrum was recorded (solid line). As in A., SDS was added and the LD measured (dashed line) directly, but as an insignificant amount of complex dissociated the

solution was left at 45°C for 24 h and measured upon again (dotted line). It is evident that still after this treatment most of the complex is still bound to the DNA. As the dissociation is very slow, it is a clear indication that the complex is threaded through the DNA and sterically hindered to escape the DNA.

Temperature /°C	Rearrangement		Dissociation	
	$k_1 \times 10^3/s^{-1}$ (C ₁)	$k_2 \times 10^3/s^{-1}$ (C ₂)	$k_1 \times 10^3/s^{-1}$ (C ₁)	$k_2 \times 10^3/s^{-1}$ (C ₂)
45	0.66 (0.58)	0.11 (0.42)	1.3 (0.49)	0.49 (0.51)
50	1.2 (0.63)	0.20 (0.37)	1.9 (0.54)	0.79 (0.46)
55	2.1 (0.69)	0.32 (0.31)	2.6 (0.71)	1.0 (0.29)
60	3.2 (0.75)	0.46 (0.25)	3.8 (0.80)	1.6 (0.20)

A.



B.

S2. Rates of DNA binding mode rearrangement and DNA dissociation. A buffered solution (100 mM NaCl, 1 mM sodium cacodylate, pH 7) of 160 μ M calf thymus DNA and 10 μ M Δ,Δ -[μ -(11,11'-bidppz)(phen)₄Ru₂]Cl₄ (P/Ru=8) was used. For the dissociation, SDS was added to a final concentration of 0.6 %. The rearrangement of the bidppz complex bound to DNA was followed, at different temperatures (45, 50, 55 and 60°C), using the increase in emission intensity when going from the initial to the final intercalative binding mode. The SDS dissociation from the final DNA

binding mode are studied at the same temperatures using the decrease in emission intensity when the bidppz complex dissociates from DNA and binds to the SDS micelles. Both the rearrangement and dissociation are fitted by a double exponential function ($C_1 e^{-k_1 t} + C_2 e^{-k_2 t}$) in order to get a good fit. The results from the fitting can be seen in A. In B. the two rate constants for rearrangement (■ and ●) and the two rate constants for dissociation (▲ and ▼) are plotted against $1/T$ to get the activation energy and pre-exponential of the processes. The data gives $\ln A_1=28$, $E_{a1}=94$ kJ/mol and $\ln A_2=22$, $E_{a2}=83$ kJ/mol for the rearrangement and $\ln A_1=18$, $E_{a1}=65$ kJ/mol and $\ln A_2=18$, $E_{a2}=66$ kJ/mol for the dissociation.