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Polyoxometalates as artificial nucleases: hydrolytic cleavage of DNA promoted by a highly negatively charged Zr^{IV}-substituted Keggin polyanion

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Supporting Information

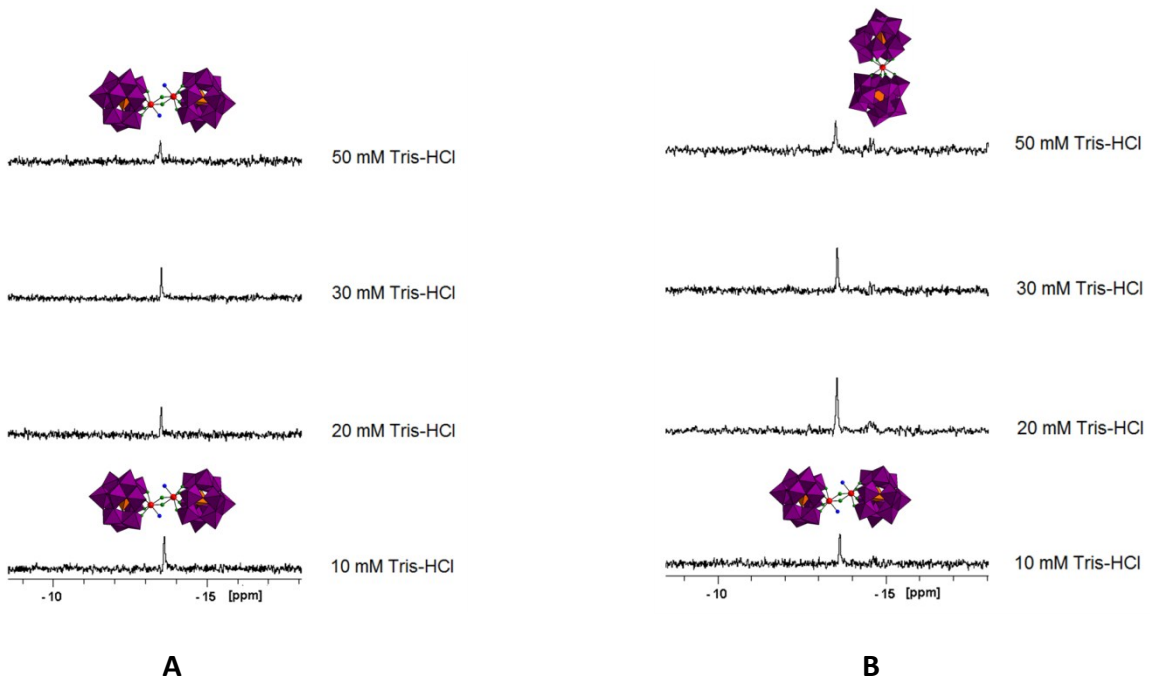

Fig. S1 ^{31}P NMR spectra of 2.0 mM of ZrK 2:2 in different concentrations (10.0 mM to 50.0 mM) of Tris-HCl buffer pH 7.0 after mixing (A) and after 3 days at 50 °C (B). (600 MHz, D_2O, 293K, NS = 256, 25% H_3PO_4)

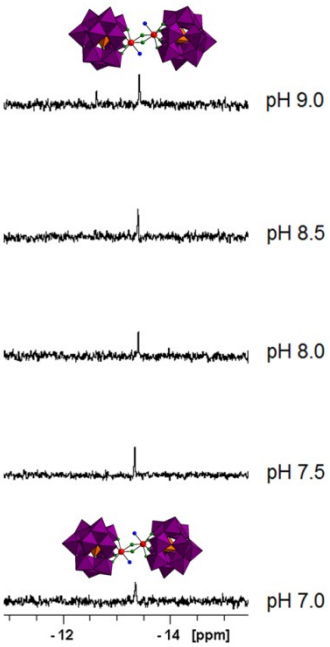

Fig. S2 ^{31}P NMR spectra of 0.25 mM of ZrK 2:2 in 10 mM Tris-HCl buffer pH 7.0 - 9.0 after mixing. (600 MHz, D_2O, 293K, NS = 256, 25% H_3PO_4)

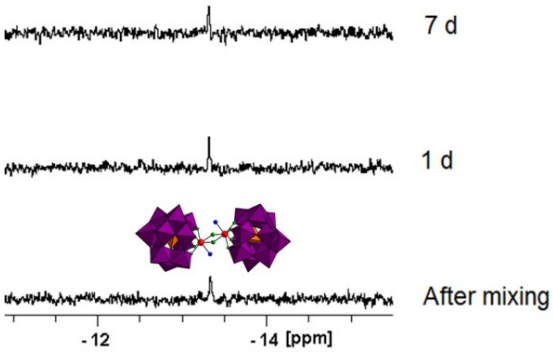

Fig. S3 ^{31}P NMR spectra of 0.25 mM of ZrK 2:2 in 10 mM Tris-HCl pH 7.0 at different time intervals at 50 °C. (600 MHz, D_2O, 293K, NS = 256, 25% H_3PO_4)

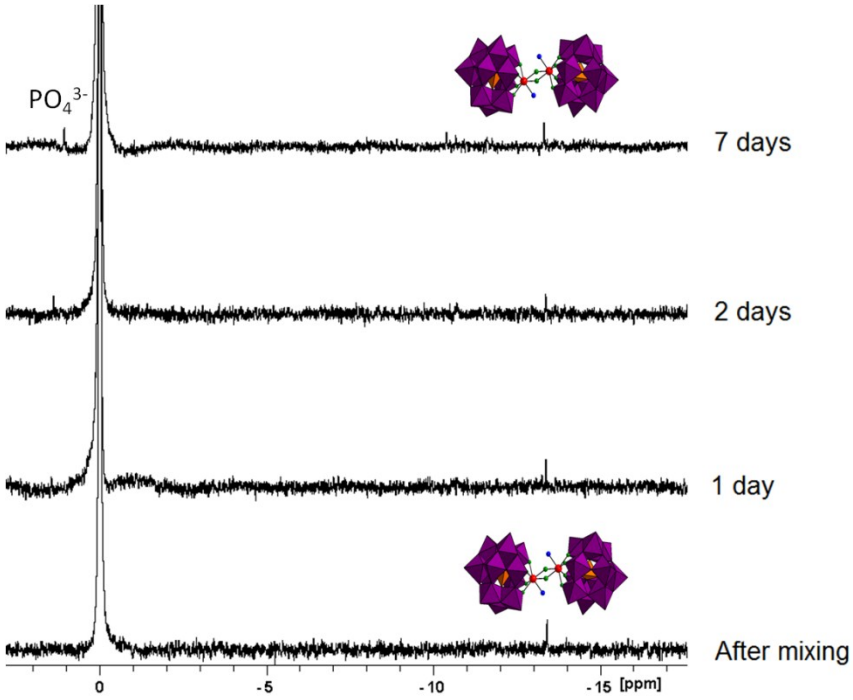

Fig. S4 ^{31}P NMR spectra of 0.25 mM of ZrK 2:2 in 10 mM Tris-HCl pH 8.0 at different time intervals at 50 °C. (600 MHz, D_2O, 293K, NS = 256, 25% H_3PO_4)

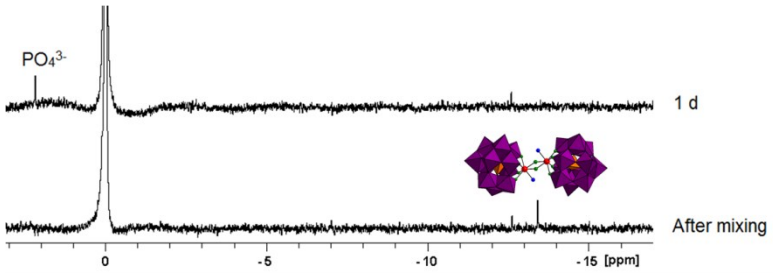

Fig. S5 ^{31}P NMR spectra of 0.25 mM of ZrK 2:2 in 10 mM Tris-HCl pH 9.0 at different time intervals at 50 °C. (600 MHz, D_2O, 293 K, NS = 256, 25% H_3PO_4)

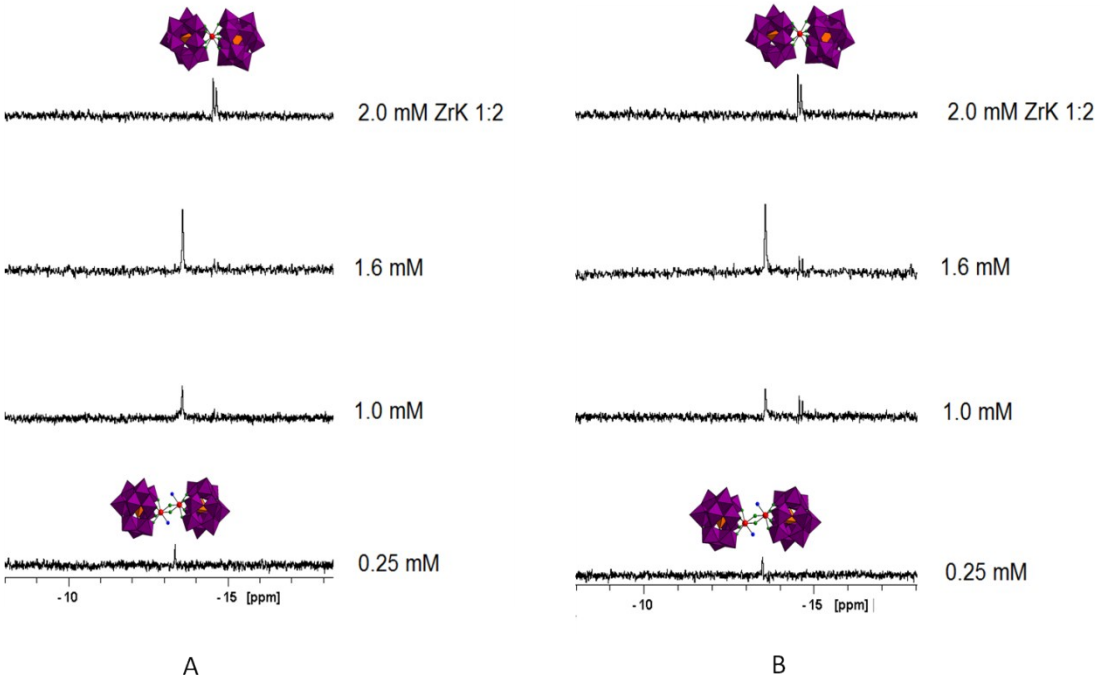

Fig. S6 ^{31}P NMR spectra of 0.25 - 1.6 mM of ZrK 2:2 in 10 mM Tris-HCl pH 7.0 after sample preparation (A) and 3 days (B) at 50 °C. ^{31}P NMR spectra of 2.0 mM of ZrK 2:2 in 10 mM Tris-HCl pH 7.0 was added for comparison. (600 MHz, D_2O, 293 K, NS = 256, 25% H_3PO_4)

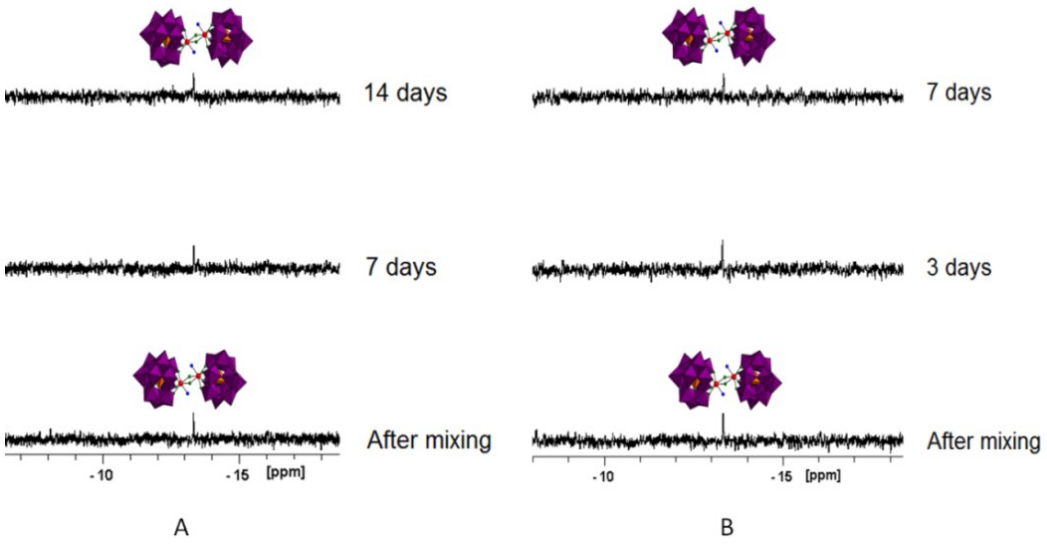

Fig. S7 ^{31}P NMR spectra of 0.25 mM of ZrK 2:2 in 10 mM Tris-HCl pH 7.0 at different time intervals at 37 °C (A) and 50 °C (B). (600 MHz, D_2O, 293 K, NS = 256, 25% H_3PO_4)

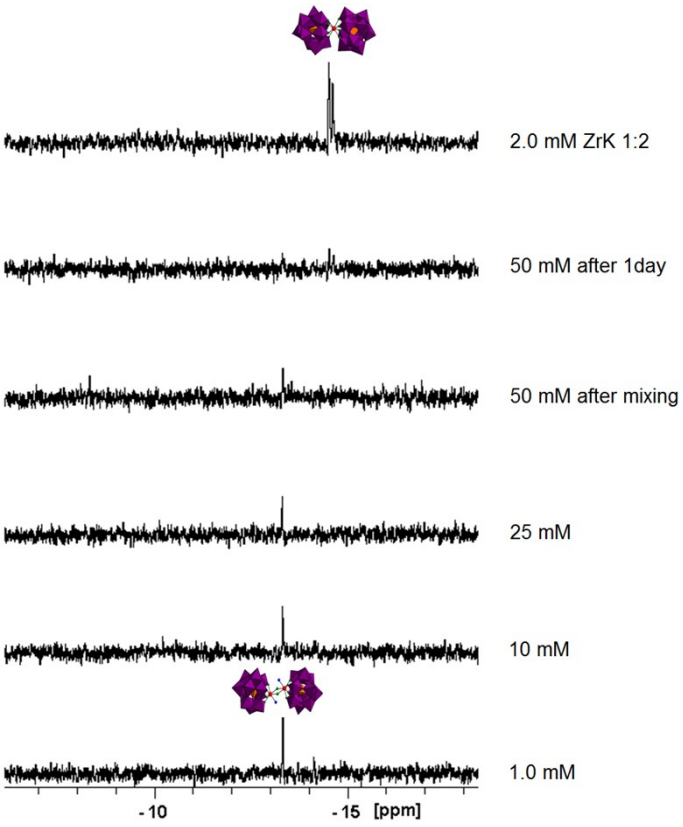

Fig. S8 ^{31}P NMR spectra of 0.25 mM of ZrK 2:2 in the presence of different $NaClO_4$ concentrations in 10 mM Tris-HCl pH 7.0. ^{31}P NMR spectra of 2.0 mM of ZrK 1:2 in 10 mM Tris-HCl pH 7.0 was added for comparison. (600 MHz, D_2O, 293 K, NS = 256, 25% H_3PO_4)

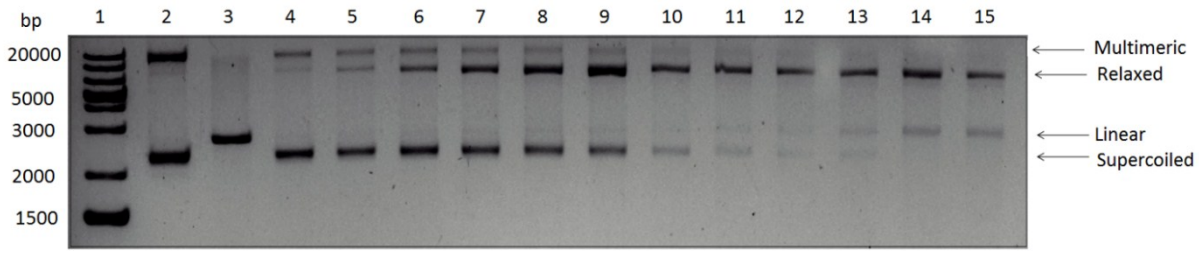

Fig. S9 Electrophoresis gel of the hydrolysis of 20 ng/μL plasmid pUC19 DNA in the presence of 0.25 mM ZrK 2:2 in 10 mM Tris-HCl at pH 7.0 and 37 °C. Lane 1: 1 kb plus DNA ladder, lane 2: pUC19 alone after sample preparation and without heating, lane 3: linear pUC19 alone, lane 4: after mixing, lane 5-lane 15: after 24h, 48h, 72h, 97h, 121h, 145h, 167.5h, 192.5h, 216.5h and 240.5h incubation respectively.

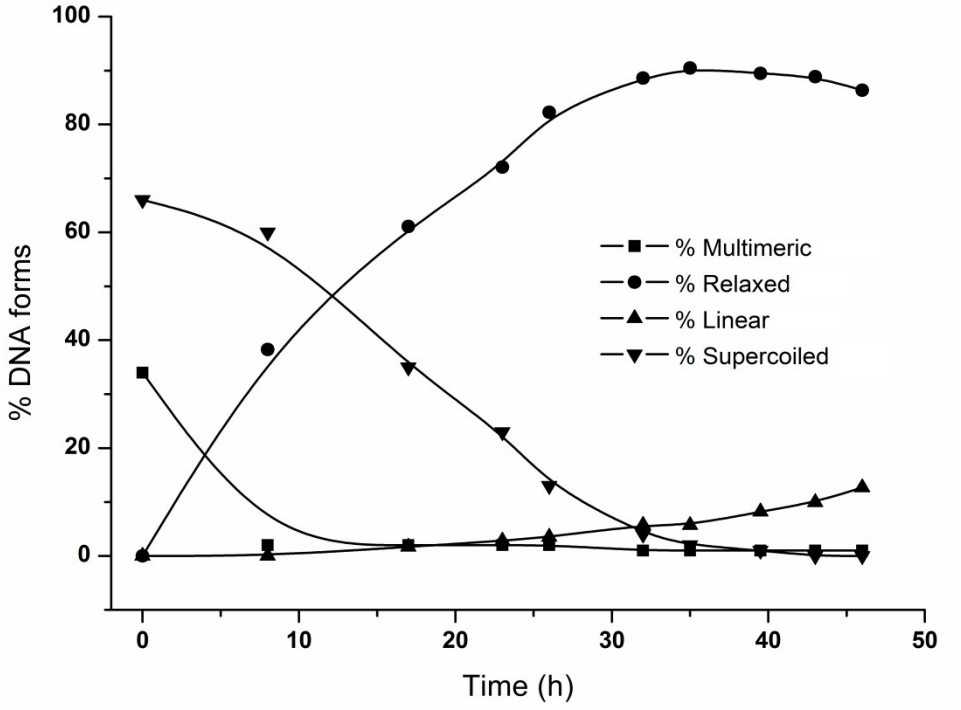

Fig. S10 Percentage of multimeric, relaxed, linear and supercoiled forms as a function of reaction time for the reaction between 20 ng/μL plasmid DNA pUC19 in the presence of 0.25 mM ZrK 2:2 in 10 mM Tris-HCl at pH 7.0 and 50 °C.

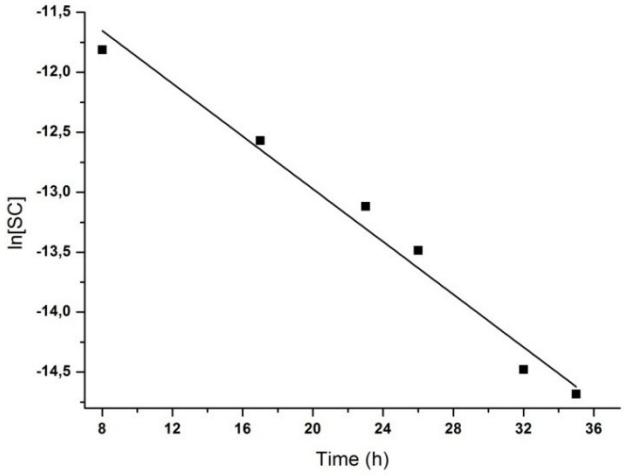

Fig. S11 ln[SC pUC19] as a function of time (linear fit with R^2 = 0.97) for the reaction between 20 ng/μl plasmid DNA pUC19 in the presence of 0.25 mM ZrK 2:2 in 10 mM Tris-HCl at pH 7.0 and 50 °C.

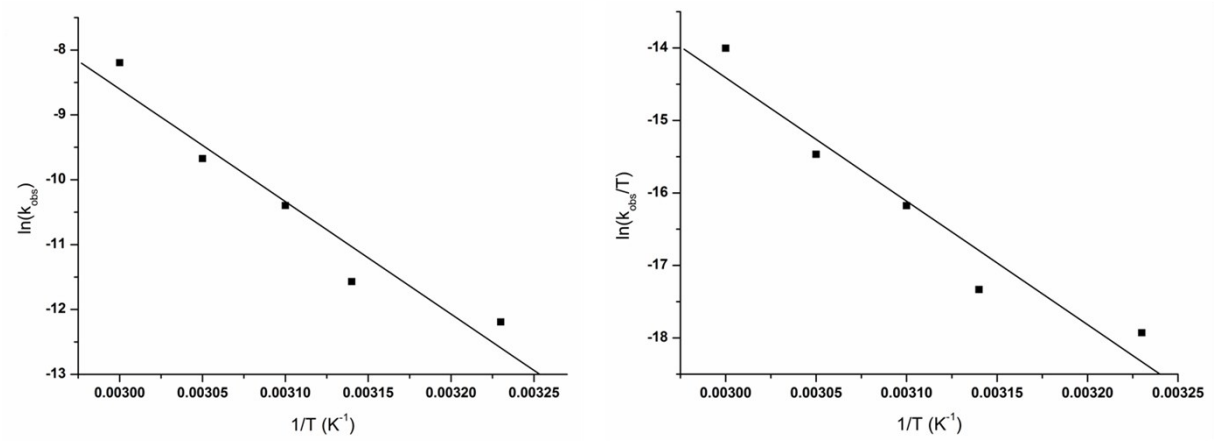

Fig. S12 A: Arrhenius plot of ln(k_{obs}) as a function of 1/T (Arrhenius equation: $lnk_{obs} = lnA - \frac{E_a 1}{R\,T}$) and B: Eyring plot of ln(k_{obs}/T) as a function of 1/T (Eyring equation: $ln\frac{k_{obs}}{T} = \frac{-\,\Delta H^{\ddagger}\ 1}{R\quad T} + ln\frac{k_b}{h} + \frac{\Delta S^{\ddagger}}{R}$) for the hydrolysis of 20 ng/μLpUC19 in the presence of 0.25 mM ZrK 2:2 in 10 mM Tris-HCl pH 7.0.

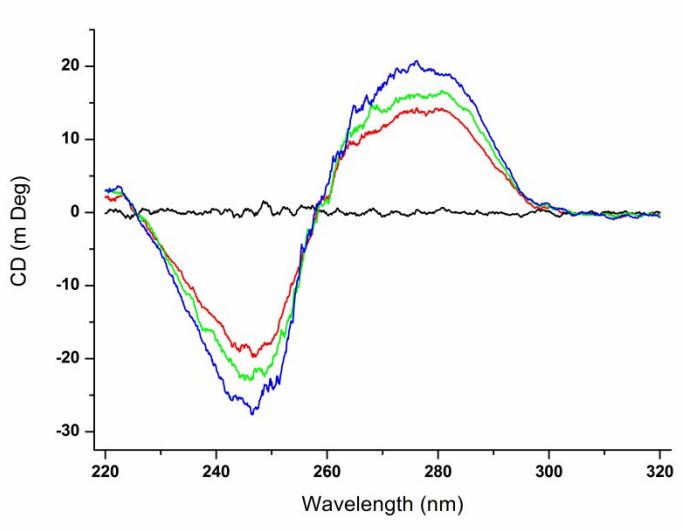

Fig. S13 CD spectra of 160 µM ZrK 2:2 (black), 0.2 µM ctDNA (red), 0.2 µM ctDNA in the presence of 2.5 µM ZrK 2:2 (green) and 0.2 µM ctDNA in the presence of 5 µM ZrK 2:2 (blue). All of the spectra were recorded in 10 mM Tris-HCl buffer pH 7.0 at room temperature.

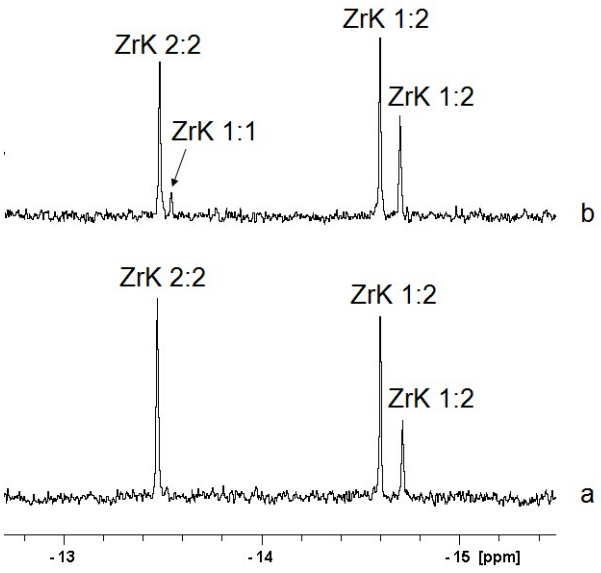

Fig. S14 ^{31}P spectra of (a) 3.0 mM ZrK 2:2 and (b) a mixture of 3.0 mM ZrK 2:2 and 0.32 mM ctDNA (b) in D_2O at pH 7.0 and 293K.

Table S1. The diffusion coefficient of 3.0 mM ZrK 2:2 in the absence and in the presence of 0.32 mM ctDNA at 298K and 280K.

Sample	Species	Chemical shift (ppm)	Diffusion coefficient (m^2/s)
ZrK 2:2 (298K)	ZrK 2:2 ZrK 1:2	-13.49 -14.67 and -14.77	2.82×10^{-10} 1.74×10^{-10} } Difference: 1.08×10^{-10} — Difference: 1.04×10^{-10}
ZrK 2:2 + ctDNA (298K)	ZrK 2:2 ZrK 1:2	-13.49 -14.67 and -14.77	1.78×10^{-10} 1.66×10^{-10}
ZrK 2:2 (280K)	ZrK 2:2 ZrK 1:2	-13.49 -14.67 and -14.77	1.06×10^{-10} 0.95×10^{-10} } Difference: 0.11×10^{-10} — Difference: 0.02×10^{-10}
ZrK 2:2 + ctDNA (280K)	ZrK 2:2 ZrK 1:2	-13.49 -14.67 and -14.77	1.04×10^{-10} 0.87×10^{-10}

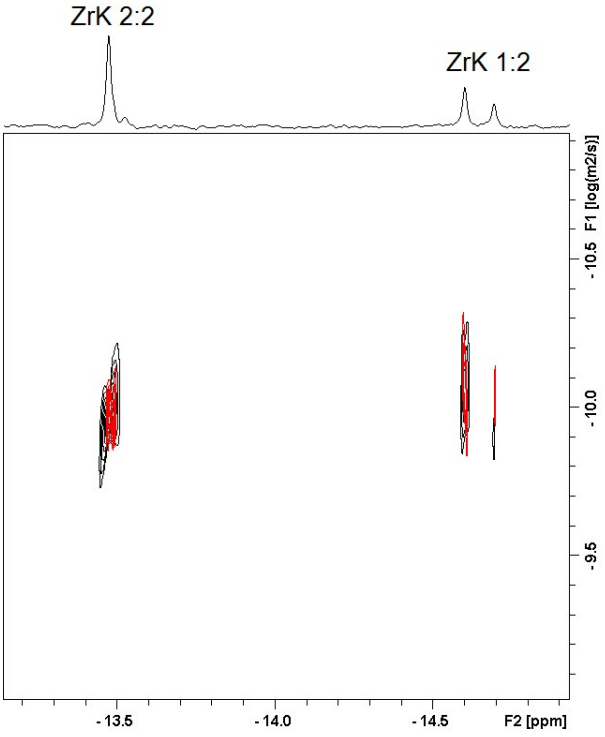

Fig. S15 ^{31}P DOSY spectra of 3.0 mM ZrK 2:2 (black) and of a mixture of 3.0 mM ZrK 2:2 and 0.32 mM ctDNA in D_2O at pH 7.0 and 280K (red).