SUPPORTING INFORMATION

DNA binding selectivity of oligopyridine-Ruthenium(II)-Lysine conjugate.

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Table S1. ¹H chemical shifts (ppm) of the free oligonucleotide sequences $d(CGCGCG)_2$ and $d(GTCGAC)_2$ at H_2O/D_2O (9:1), 50 mM phosphates buffer (pH = 7.0) at 298 K. Chemical shifts are referenced to HOD signal (4.75 ppm).

Sequence	H8/H6	H5/H2/CH3	H1′	H2′	H2′′	H3′	NH*	NH ₂ *
C1	7.46	5.74	5.60	1.79	2.27	4.56		
G2	7.82		5.75	2.54	2.65	4.83	12.98	8.32
C3	7.23	5.76	5.61	1.85	2.15	4.69		8.23
G4	7.77		5.92	2.51	2.59	4.84	13.01	8.23
C5	7.19	5.32	5.74	2.51	2.59	4.84		8.32
G6	7.77		6.00	2.51	2.49	4.52		
Sequence								
G1	7.85		5.56	2.28	2.44	4.94		
T2	7.39	1.20	6.07	2.10	2.44	4.82	13.80	
C3	7.39	5.56	5.87	2.57	2.66	4.70		8.49
G4	7.84		5.48	1.92	2.10	4.83	12.76	8.49
A5	8.06	7.87	6.17	2.52	2.79	4.94		8.02
C6	7.15	5.50	5.91	2.00	2.04	4.39		

* hydrogen bonding protons.

Table S2. Complex (2) protons chemical shifts (ppm) in the absence and presence of the oligonucleotide sequences $d(CGCGCG)_2$ and $d(GTCGAC)_2$ at H_2O/D_2O (9:1), 50 mM phosphates buffer (pH = 7.0) at 298 K. Chemical shifts are referenced to HOD signal (4.75 ppm).

Protons	Free (2)	d(CGCGCG) ₂	d(GTCGAC) ₂
bpy H5	7.58	8.28	8.27
bpy H6	9.73	9.67	9.66
bpy H3	9.12	9.27	9.02
bpy H5′	6.97	6.89	n.a.
bpy H6′	8.37	8.58	8.46
bpy H3′	8.77	n.a.	8.58
terpy H3H3'	7.72	7.82	7.82
terpy H4H4'	7.32	7.25	7.21
terpy H5H5'	7.98	7.71	7.89
terpy H6H6'	8.46	n.a.	8.33
terpy H5''H3''	8.60	8.57	8.58
terpy H4''	8.29	8.39	8.33
Lys'Ha	4.42	4.29	4.29
Lys′Hβ	1.85	1.77	1.78
Lys′Hγ	1.43	n.a.	1.45
Lys′Hδ	1.73	1.39	1.43
Lys′Hε	3.04	3.10	3.10
Lys Ha	4.63	4.60	4.55
Lys Hβ	2.06	1.98	1.99
Lys Hγ	1.43	n.a.	1.45
Lys Hδ	1.59	1.52	1.50
Lys Hε	3.17	3.12	3.09

n.a. = not assigned.

DS1. Determination of K_b

The binding constant of complex (2) was determined from the absorption titration of (2) $(2 \times 10^{-4} \text{ M}, 50 \text{ mM} \text{ buffer phosphates}, \text{pH} = 7.0, 298 \text{ K})$ with a solution of ct-DNA in the same conditions as (2). During the titration the intensity of the absorbance at 480 nm was increased with a negligible red shift (~ 1 nm) and the intrinsic binding constant Kb was calculated according to the following equations [1]:

(1) $(e_a - e_f)/(e_b - e_f) = [b - (b^2 - (2K_b^2 C_t C_{DNA})/s)^{1/2}]/2K_b C_t,$

(2)
$$b = l + K_b C_t + K_b C_{DNA})/2s$$

where e_a , e_f and e_b are the extinction coefficients for, (e_a) the MLCT absorption band (480 nm) at any DNA concentration, (e_f) the MLCT absorption band for the free complex and (e_b) the MLCT absorption band at the DNA concentration when the complex is completely bound; K_b is the binding constant in M⁻¹; C_t is the initial complex concentration in M; C_{DNA} is the concentration of DNA (phosphate nucleotide) in M; s is the average number of DNA bases interacting with the complex. Since the complex interacts rather selectively with guanine bases of ct-DNA, a value of s between 3 and 10 was assumed. From the ($e_a - e_f$)/($e_b - e_f$) vs. C_{DNA} plot and the non-linear fitting of the titration curve, the K_b and s values were calculated as 55.0 ± 1.5×10^4 M⁻¹ and 8 ± 0.5 respectively.

[1] G. A. Neyhart, N. Grover, S. R. Smith, W. A. Kalsbeck, T. A. Fairley, M. Cory,H. H. Thorp., J. Am. Chem. Soc. (1993), 115, 4423-4428.





Figure S1. 500 MHz time-dependent ¹H NMR spectra of the hydrolysis of $[Ru(terpy)(4,4'-(COLysCONH_2)_2bpy)Cl]Cl_3$ in D₂O (50 mM phosphate buffer, *p*H = 7.0, 310 K).



Figure S2. LD spectra of ct-DNA upon gradual addition of $[Ru(terpy)(4,4'-(COLysCONH_2)_2 bpy)(H_2O)]Cl_4$ at ratios r = 0, 0.025, 0.050, 0.075, 0.100 and 0.125.



Figure S3. ¹H ¹H COSY (500 MHz, H₂O/D₂O 9:1, 50 mM phosphate buffer, *p*H 7.0, 298 K) spectra, (A) of the oligonucleotide $d(CGCGCG)_2$ treated with complex (2) at ratio 1:1 and (B) of free complex (2), showing the H δ -H ϵ coupling of Lysine aliphatic protons.



Figure S4. ICD plot versus r of ct-DNA upon addition of $[Ru(terpy)(4,4'-(COLysCONH_2)_2 bpy)(H_2O)]Cl_4$ at ratios r = 0, 0.025, 0.050, 0.075, 0.100 and 0.125.

DS2. CD and LD information.

<u>CD parameters:</u> Temperature 25 °C, speed 200 nm/min, bandwidth 2nm, step 0.5nm, averaging time 1s, accumulations 3; CD was calibrated by standard procedure using ACS (0.06% aqueous solution in 1cm couette).

<u>LD parameters:</u> Temperature 25 °C, speed 500 nm/min, bandwidth 2nm, step 0.5nm, averaging time 0.25s, accumulations 2. Flow LD spectra were collected by using a flow Couette cell in a Jasco J-720 spectropolarimeter adapted for LD measurements. The flow cell consists of a fixed outer cylinder and a rotating solid quartz inner cylinder, separated by a gap of 0.5 mm, giving a total pathlength of 1 mm. The rotational speed of the inner cylinder was 1200RPM.