Electronic Supplementary Material (ESI) for Dalton Transactions

Sensitivity of [Ru(phen)$_2$dppz]$^{2+}$ Light Switch Emission to Ionic Strength, Temperature, and DNA Sequence and Conformation

Andrew W. McKinley, Per Lincoln and Eimer M. Tuite*

SUPPLEMENTARY INFORMATION

Δ		τ_L = 773 (±29) ns		τ_S = 132 (±9) ns	
[Ru]/[Nu]	**[Nu]/[Ru]**	***α*$_L$ / %**	***f*$_L$ / %**	***α*$_S$ / %**	***f*$_S$ / %**
0.24	4	*86*	97	*14*	3
0.20	5	*80*	96	*20*	4
0.16	6	*76*	95	*24*	5
0.12	8	*60*	90	*40*	10
0.06	17	*57*	89	*43*	11
0.03	33	*41*	80	*59*	20
0.01	100	*21*	61	*79*	39

TABLE S1. Global SPC analysis for Δ-[Ru(phen)$_2$dppz]$^{2+}$ with [poly(dA-dT)]$_2$. [Ru] = 25 μM. 10 mM NaCl/1 mM sodium cacodylate (pH 7); 25 ^{o}C: λ_{ex} = 337 nm; λ_{em} = 620 nm. χ^2 = 1.20 for the global fit.

Λ		τ_L = 297 (±5) ns		τ_S = 37 (±2) ns	
[Ru]/[Nu]	**[Nu]/[Ru]**	***α*$_L$ / %**	***f*$_L$ / %**	***α*$_S$ / %**	***f*$_S$ / %**
0.24	4.2	*58*	92	*42*	8
0.20	5.0	*60*	92	*40*	8
0.16	6.3	*52*	90	*48*	10
0.12	8.0	*44*	86	*56*	14
0.06	16.7	*31*	78	*69*	22
0.03	33.3	*21*	68	*79*	32
0.01	100.0	*11*	50	*89*	50

TABLE S2. Global SPC analysis for Λ-[Ru(phen)$_2$dppz]$^{2+}$ with [poly(dA-dT)]$_2$. [Ru] = 25 μM. 10 mM NaCl/1 mM sodium cacodylate (pH 7); 25 ^{o}C: λ_{ex} = 337 nm; λ_{em} = 620 nm. χ^2 = 1.20 for the global fit.

Δ	[poly(dA-dT)]$_2$				[poly(dG-dC)]$_2$			
[Nu]/[Ru]	**τ_L / ns**	**α_L / %**	**τ_S / ns**	**α_S / %**	**τ_L / ns**	**α_L / %**	**τ_S / ns**	**α_S / %**
2	464	*57*	68	*43*	174	*35*	54	*65*
4	700	*67*	143	*33*	241	*39*	71	*61*
8	791	*62*	144	*38*	260	*67*	64	*33*
12.5	756	*56*	129	*44*	254	*73*	61	*27*
25	739	*42*	132	*58*	256	*77*	76	*23*
50	737	*26*	135	*74*	248	*78*	67	*22*
100	727	*18*	137	*82*	255	*80*	90	*20*
$\tau_{average}$ (SD)	742 (30)		137 (6)		252 (7)		72 (10)	

TABLE S3. Time-resolved emission of Δ-[Ru(phen)$_2$dppz]$^{2+}$ with alternating homo-polynucleotides. [Ru] = 20 μM; 5 mM phosphate (pH 6.9); 25 ^{o}C; λ_{ex} = 440 nm; λ_{em} >540 nm. τ_i = emission lifetime; α_i = pre-exponential factor.

Λ	[poly(dA-dT)]$_2$				[poly(dG-dC)]$_2$			
[Nu]/[Ru]	**τ_L / ns**	**α_L / %**	**τ_S / ns**	**α_S / %**	**τ_L / ns**	**α_L / %**	**τ_S / ns**	**α_S / %**
2	243	*47*	53	*53*	116	*29*	37	*71*
4	298	*57*	54	*43*	108	*45*	41	*55*
8	331	*35*	42	*65*	136	*13*	48	*87*
12.5	352	*25*	44	*75*	139	*9*	42	*91*
25	325	*18*	38	*82*	164	*5*	40	*95*
50	327	*10*	36	*90*	165	*4*	41	*96*
100	329	*9*	36	*91*	168	*3*	39	*97*
$\tau_{average}$ (SD)	327 (17)		42 (7)		147 (23)		42 (3)	

TABLE S4. Time-resolved emission of Λ-[Ru(phen)$_2$dppz]$^{2+}$ with alternating homo-polynucleotides. [Ru] = 20 μM; 5 mM phosphate (pH 6.9); 25 ^{o}C; λ_{ex} = 440 nm; λ_{em} >540 nm. τ_i = emission lifetime; α_i = pre-exponential factor.

P/D = 50

[NaCl]/mM	τ_1 / ns	α_1 / %	τ_2 / ns	α_2 / %	I/I_0	pred $I(\tau)/I_0$
0	776	*23*	138	*77*	1.00	1.00
7	825	*24*	143	*76*	1.01	1.06
13	791	*26*	133	*74*	1.10	1.07
27	809	*28*	138	*72*	1.16	1.15
50	801	*31*	136	*69*	1.22	1.21
82	837	*33*	143	*67*	1.30	1.29
146	829	*37*	143	*63*	1.37	1.38
208	827	*44*	134	*56*	1.27	1.54
549	814	*50*	135	*50*	1.06	1.67
1222	796	*58*	137	*42*	0.64	1.82
	811 (19)		138 (4)			

P/D = 6

[NaCl]/mM	τ_1 / ns	α_1 / %	τ_2 / ns	α_2 / %	I/I_0	pred $I(\tau)/I_0$
0	860	*64*	171	*36*	-	1.00
7	885	*64*	194	*36*	-	1.04
13	876	*65*	178	*35*	-	1.03
26	869	*67*	171	*33*	-	1.04
49	880	*68*	187	*32*	-	1.08
82	852	*71*	156	*29*	-	1.06
145	873	*69*	172	*31*	-	1.07
207	859	*73*	171	*27*	-	1.09
547	841	*72*	188	*28*	-	1.07
1219	832	*71*	175	*29*	-	1.04
	863 (17)		176 (11)			

TABLE S5: Effect of added NaCl on the emission lifetimes of Δ-$[Ru(phen)_2dppz]^{2+}$ with $[poly(dA\text{-}dT)]_2$. [Ru] = 20 µM; 5 mM phosphate (pH 6.9); 25 ^{o}C; λ_{ex} = 440 nm; λ_{em} >540 nm. τ_i = emission lifetime; α_i = pre-exponential factor.

P/D = 50

$[MgCl_2]$/mM	τ_1 / ns	α_1 / %	τ_2 / ns	α_2 / %	I/I_0	pred $I(\tau)/I_0$
0.000	799	*17*	141	*141*	1.00	1.00
0.005	693	*21*	126	*126*	1.00	0.97
0.013	751	*19*	140	*140*	0.95	1.03
0.024	694	*19*	124	*124*	0.95	0.93
0.05	749	*19*	124	*124*	0.94	0.96
0.07	712	*21*	122	*122*	0.95	0.99
0.14	718	*24*	122	*122*	0.96	1.06
1.35	742	*38*	136	*136*	1.25	1.46
2.32	758	*40*	112	*112*	1.34	1.49
4.70	824	*39*	146	*146*	1.36	1.63
9.86	743	*44*	113	*113*	1.39	1.56
22.6	753	*42*	106	*106*	1.39	1.52
	745 (39)		126 (13)			

P/D = 6

$[MgCl_2]$/mM	τ_1 / ns	α_1 / %	τ_2 / ns	α_2 / %	I/I_0	pred $I(\tau)/I_0$
0.0	831	*65*	155	*35*	-	1.00
0.3	851	*70*	176	*30*	-	1.09
0.5	846	*70*	152	*30*	-	1.07
1.1	896	*67*	198	*33*	-	1.11
1.8	878	*70*	181	*30*	-	1.12
3.1	883	*68*	186	*32*	-	1.11
5.2	876	*70*	177	*30*	-	1.12
10.4	915	*69*	200	*31*	-	1.16
20.5	884	*69*	196	*31*	-	1.13
49.7	878	*68*	207	*32*	-	1.11
94.7	917	*67*	181	*33*	-	1.12
173.0	821	*71*	151	*29*	-	1.05
294.9	802	*71*	146	*29*	-	1.02
404.6	817	*68*	197	*32*	-	1.04
	863 (17)		179 (20)			

TABLE S6: Effect of added $MgCl_2$ on the emission lifetimes of Δ-$[Ru(phen)_2dppz]^{2+}$ with $[poly(dA\text{-}dT)]_2$. [Ru] = 20 µM; 5 mM phosphate (pH 6.9); 25 °C; λ_{ex} = 440 nm; λ_{em} >540 nm. τ_i = emission lifetime; α_i = pre-exponential factor.

	Δ-[Ru(phen)$_2$dppz]$^{2+}$				Λ-[Ru(phen)$_2$dppz]$^{2+}$			
T / °C	**τ_1 / ns**	**α_1 / %**	**τ_2 / ns**	**α_2 / %**	**τ_1 / ns**	**α_1 / %**	**τ_2 / ns**	**α_2 / %**
14	274	*70*	80	*30*	483	*1*	41	*99*
26	241	*77*	61	*23*	145	*1*	42	*99*
32	243	*66*	82	*34*	138	*1*	41	*99*
42	223	*60*	79	*40*	155	*1*	45	*99*
52	178	*67*	63	*33*	144	*1*	41	*99*
65	130	*69*	29	*31*	111	*2*	37	*98*

TABLE S7: Effect of temperature on the emission lifetimes of Δ- and Λ-[Ru(phen)$_2$dppz]$^{2+}$ with [poly(dG-dC)]$_2$. [Nu]/[Ru] = 50; [Ru] = 5 μM; 5 mM phosphate (pH 6.9); λ_{ex} = 440 nm; λ_{em} >540 nm.

DNA Type	**Relative I_f (%)**
[poly(dT)]-[poly(dA)]•[poly(dT)]	197
[poly(dA)]•[poly(dT)]	147
[poly(dA-dT)]•[poly(dA-dT)]	100
C. perfringens (30% GC)	117
T4 DNA (35% GC)	76
calf thymus (42% GC)	72
E. coli (50% GC)	69
[poly(dA-dC)]•[poly(dG-dT)]	59
poly(dA-dG)]•[poly(dC-dT)]	38
M. lysodeikticus (72% GC)	46
[poly(dG-dC)]•[poly(dG-dC)]	17
[poly(dG)]•[poly(dC)]	14

TABLE S8. Emission intensity of Δ-[Ru(phen)$_2$dppz]$^{2+}$ with various nucleic acids at low binding ratio, relative to that with [poly(dA-dT)]$_2$. [Ru] = 20 μM; [Nu]/[Ru] = 50; 5 mM phosphate (pH 6.9); 25 °C; λ_{ex} = 440 nm; λ_{ex} = 615 nm.

Nucleic Acid	λ_{max}	Molar Extinction Coefficient per base (M^{-1} cm^{-1})
[poly(dA)]•[poly(dT)]	260	6,000
[poly(dA-dT)]•[poly(dA-dT)]	262	6,700
[poly(dG-dC)]•[poly(dG-dC)]	254	8,400
[poly(dG)]•[poly(dC)]	253	7,400
[poly(dI-dC)]•[poly(dI-dC)]	251	6,900
[poly(dI)]•[poly(dC)]	245	5,300
[poly(dA-dC)]•[poly(dG-dT)]	258	6,500
poly(dA-dG)]•[poly(dC-dT)]	260	5,700
[poly(dA)]	257	8,600
[poly(dT)]	264	8,520
[poly(rA)]•[poly(rU)]	254	6,300
[poly(rA)]	257	9,800
calf thymus (45% GC)	260	6,400
C. perfringens (27% GC)	260	6,200
E. coli (50% GC)	260	6,565
M. lysodeikticus (72% GC)	260	6,950
T2 DNA (35% GC)	260	6,600
T4 DNA (35% GC)	260	6,600

TABLE S9. Extinction Coefficients of Nucleic Acids.

REFERENCES: GE Healthcare Catalogue Edn 1 2008/2009, Technical Appendix; Wells, R. D. et al. J. Mol. Biol. 54, 465-497 (1970); G. Felsenfeld and S. Z. Hirschmann, J. Mol. Biol. 13, 407-427 (1965); R. C. Warner J. Biol. Chem. 229, 711-724 (1957); J. T. O. Kirk Biochem. J. 105,673 (1967); W. Muller and D. M. Crothers, Eur. J. Biochem. 54, 267-277 (1975).

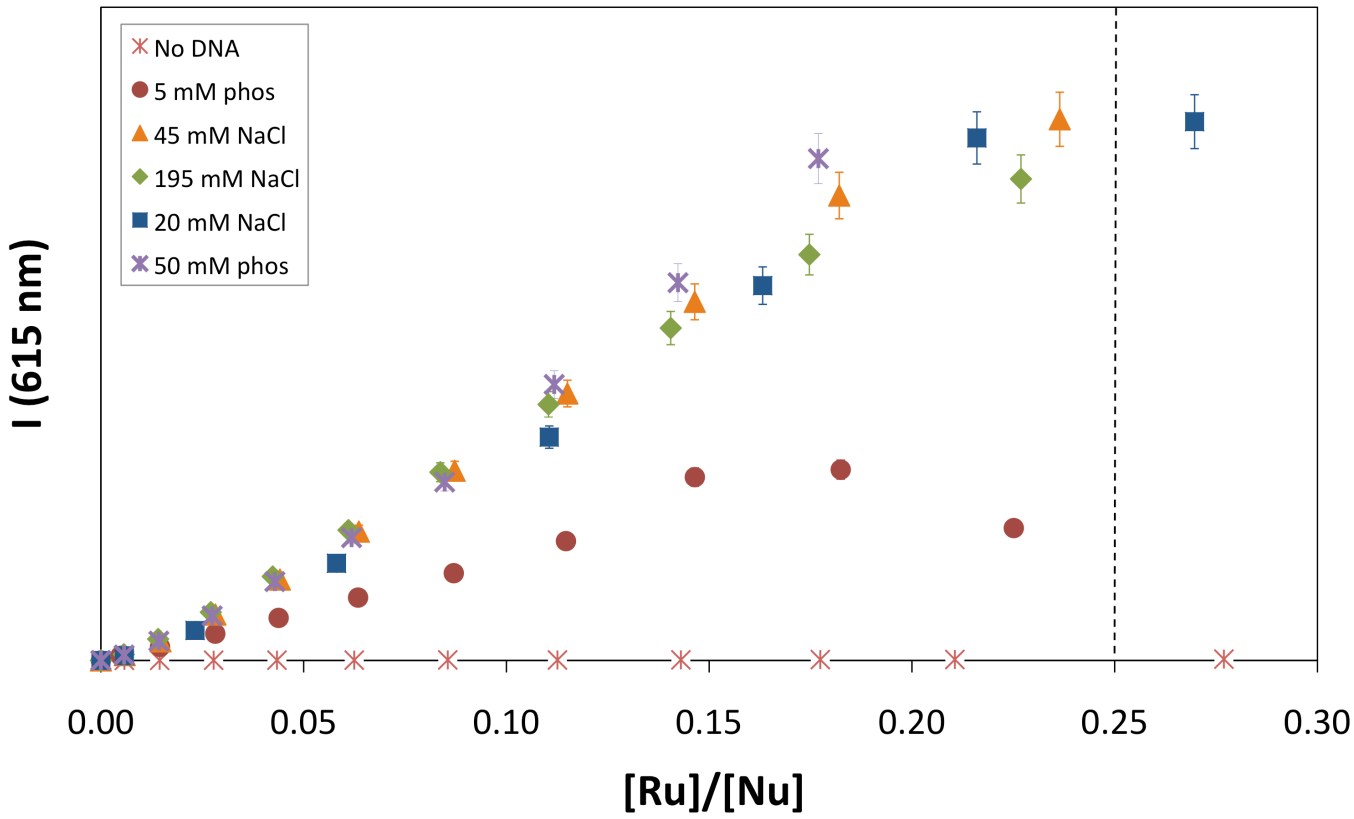

FIGURE S1. Effect of ionic strength on the emission intensity of Δ-$[Ru(phen)_2dppz]^{2+}$ bound to $[poly(dA\text{-}dT)]_2$. Aliquots of $[Ru(phen)_2dppz]^{2+}$ were added to $[poly(dA\text{-}dT)]_2$ (10 μM) in 5 mM phosphate (pH 6.9) buffer and equilibrated for 10 min before the emission intensity was recorded with λ_{ex} = 440 nm/λ_{em} = 615 nm (25 °C).

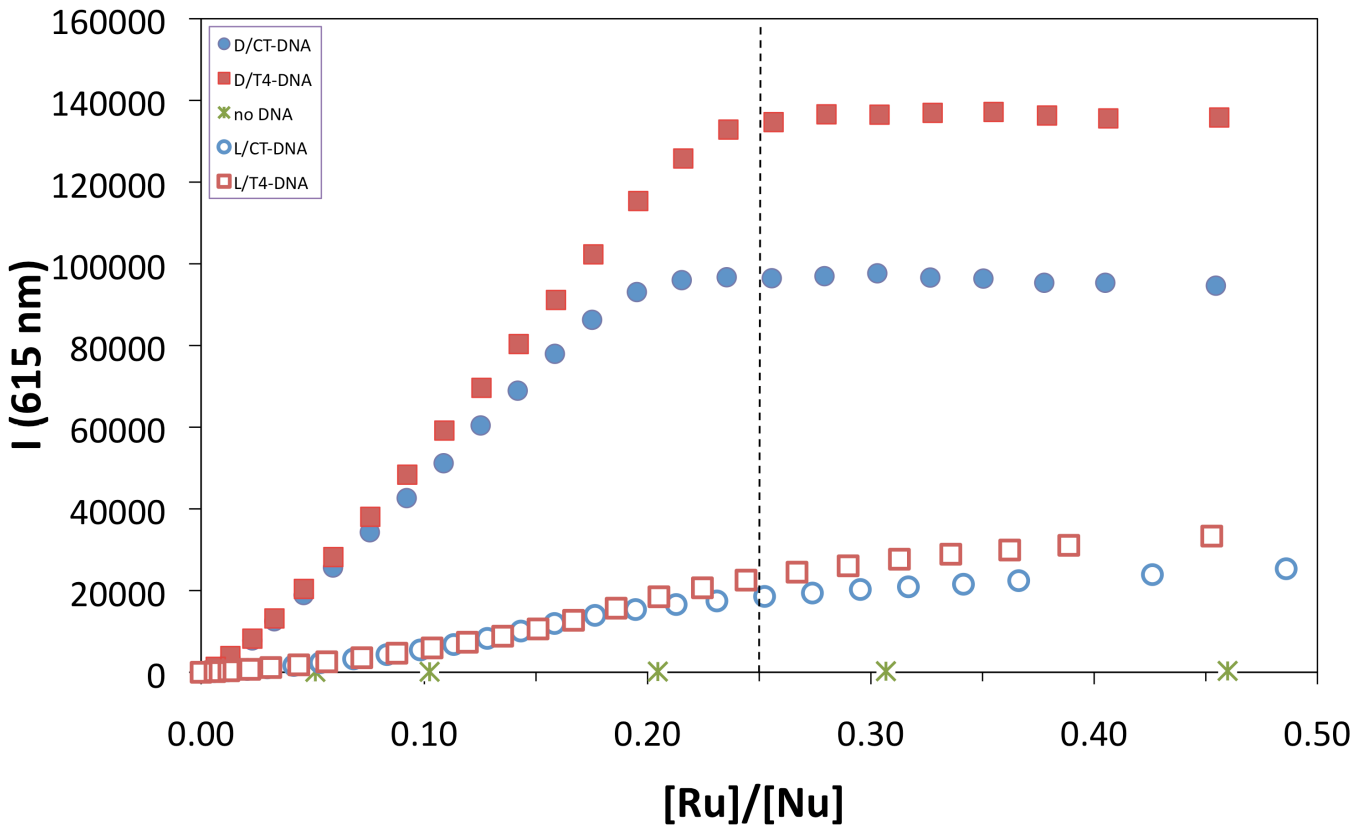

FIGURE S2: Steady-state emission of Δ- and Λ-$[Ru(phen)_2dppz]^{2+}$ with T4- and CT-DNA as a function of binding ratio. Aliquots of $[Ru(phen)_2dppz]^{2+}$ were added to DNA (7.5 µM) in 5 mM phosphate (pH 6.9) buffer and equilibrated for 10 min before the emission intensity was recorded with λ_{ex} =480 nm/λ_{em} = 618 nm (30 °C). Emission increases as the complex is added until it plateaus when binding sites saturate close to 0.20-0.25 ruthenium complexes per nucleotide.

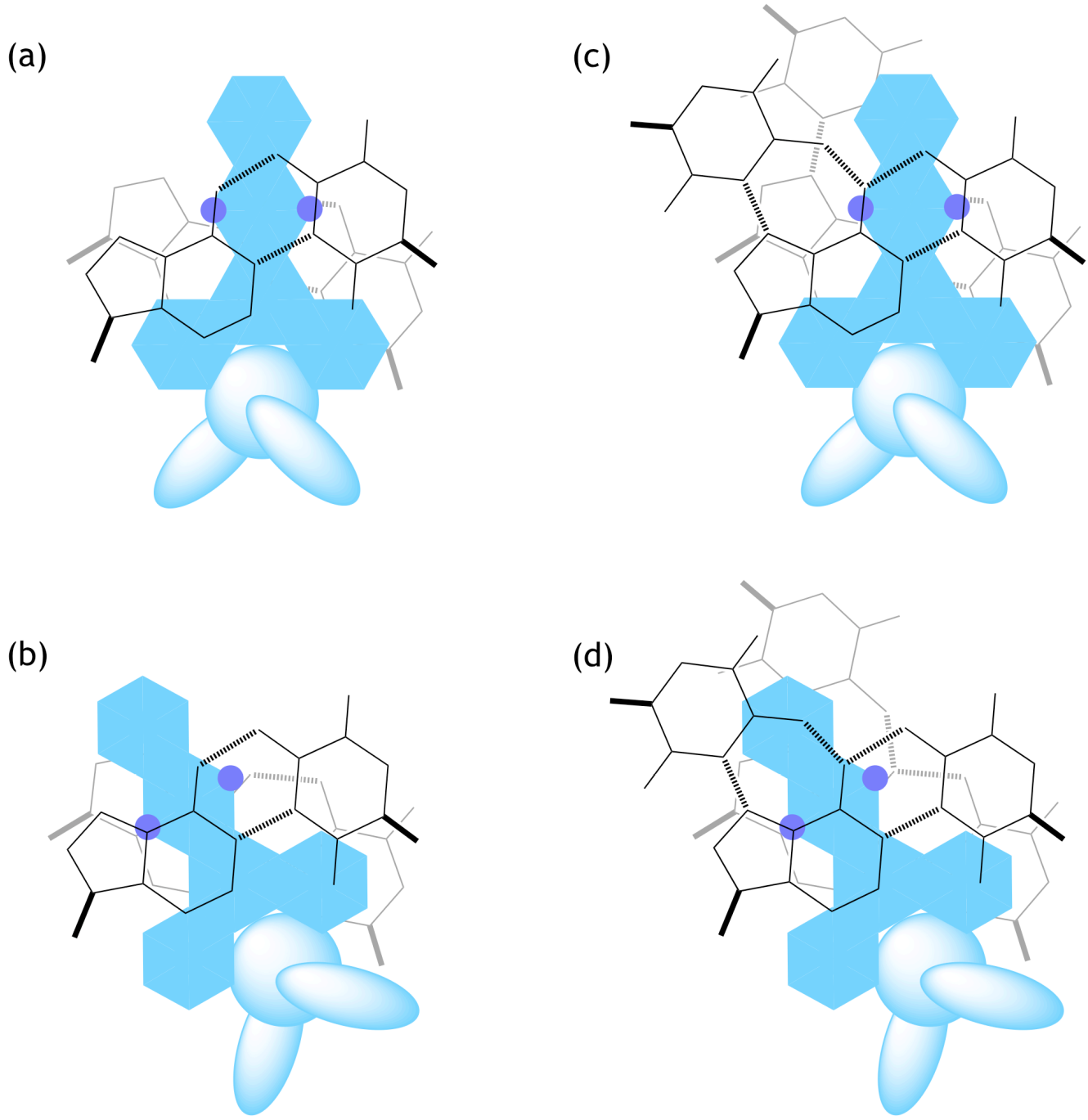

FIGURE S3: Cartoons depicting potential intercalation geometries for Δ-[Ru(phen)$_2$dppz]$^{2+}$ bound to duplex [poly(dA)]•[poly(dT)], and triplex [poly(dT)]∗[poly(dA)]•[poly(dT)]. (a) Symmetric and (b) canted intercalation with duplex, and (c) symmetric and (d) canted intercalation with triplex. The twist angle at the AT step is shown as 36 °C in all cases for simplicity.