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Electronic Supporting Information for

Ground and excited state interactions of metalloporphyrin PtTMPyP4 with polynucleotides [poly(dG-dC)]$_2$ and [poly(dA-dT)]$_2$

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Figures

Fig. S1: McGhee-von Hippel binding plot for PtTMPyP4 in [poly(dG-dC)]$_2$

Fig. S2: CD spectra of [poly(dG-dC)]$_2$ in absence and presence of PtTMPyP4

Fig. S3: CD spectra of PtTMPyP4-[poly(dG-dC)]$_2$ complexes minus initial GC signal

Fig. S4: Biexponential kinetic fit for PtTMPyP4-[poly(dG-dC)]$_2$ at [Nucl]/[Por] = 2.8

Fig. S5: Biexponential kinetic fit for PtTMPyP4 in the presence of [poly(dA-dT)]$_2$

Fig. S6: Triexponential kinetic fit for PtTMPyP4 in the presence of [poly(dA-dT)]$_2$

Fig. S7: Triexponential kinetic fit for PtTMPyP4 in the presence of [poly(dA-dT)]$_2$ (τ_1 fixed)

Fig. S8: UV/vis absorption spectra of PtTMPyP4 in presence of increasing concentrations of salmon testes DNA

Fig. S9: UV/vis and emission spectra of PtTMPyP4 in presence of poly(rA)

Fig. S10: Change in emission intensity of PtTMPyP4 in presence of poly(rA) in N_2-purged solution

Tables

Table S1: Biexponential fit parameters for PtTMPyP4 in [poly(dG-dC)]$_2$

Table S2: Biexponential fit parameters for PtTMPyP4 in [poly(dG-dC)]$_2$, τ_1 fixed.

Table S3: Biexponential fit parameters for PtTMPyP4 in [poly(dA-dT)]$_2$

Table S4: Biexponential fit parameters for PtTMPyP4 in [poly(dA-dT)]$_2$, τ_1 fixed.

Table S5: Triexponential fit parameters for PtTMPyP4 in [poly(dA-dT)]$_2$, τ_1 fixed.

Table S6: Triexponential fit parameters for PtTMPyP4 in [poly(dA-dT)]$_2$, τ_1 free

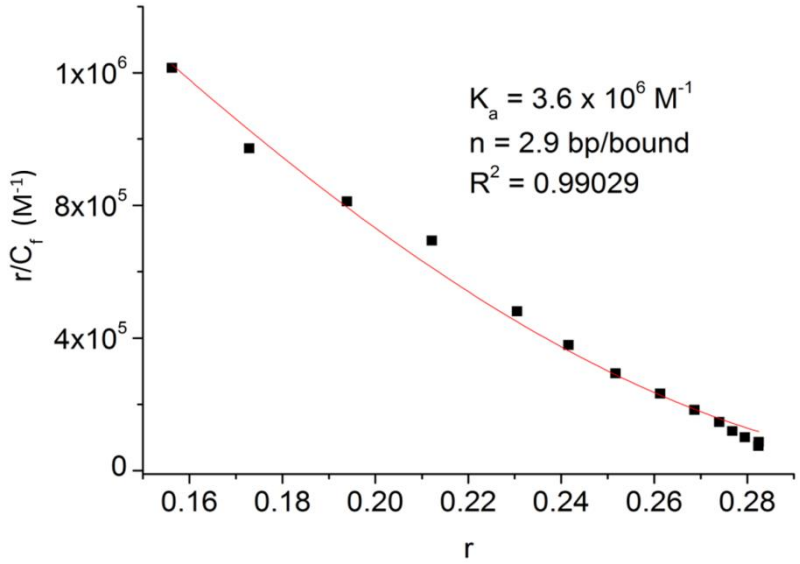

Fig. S1 Binding plot for PtTMPyP4 in $[poly(dG\text{-}dC)]_2$ fit by method of McGhee and von Hippel. In 50 mM phosphate buffer pH 6.8

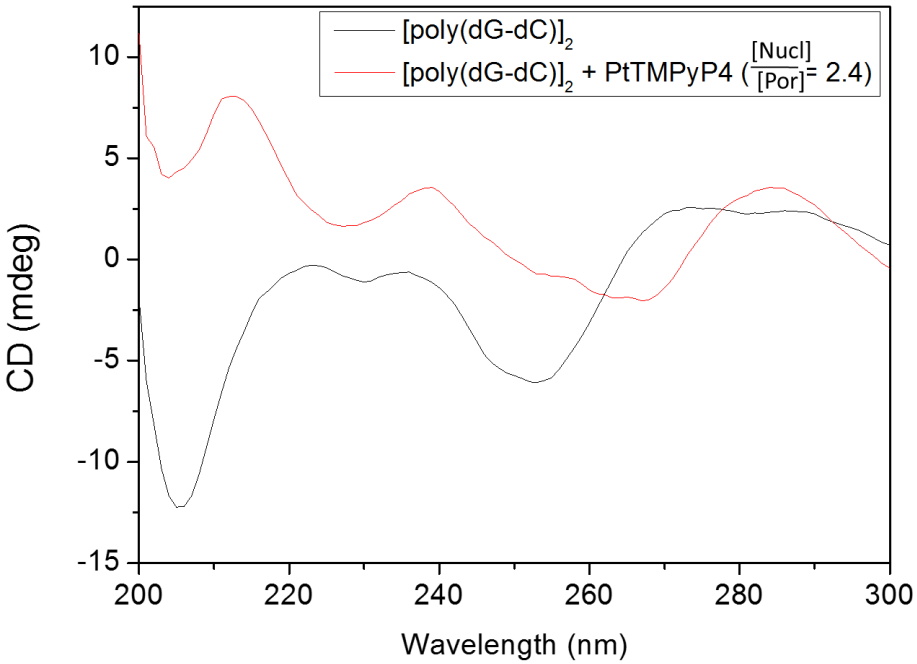

Fig. S2 CD spectra of DNA region for titration of PtTMPyP4 into $[poly(dG\text{-}dC)]_2$ showing first and last spectra. In 50 mM phosphate buffer pH 6.8.

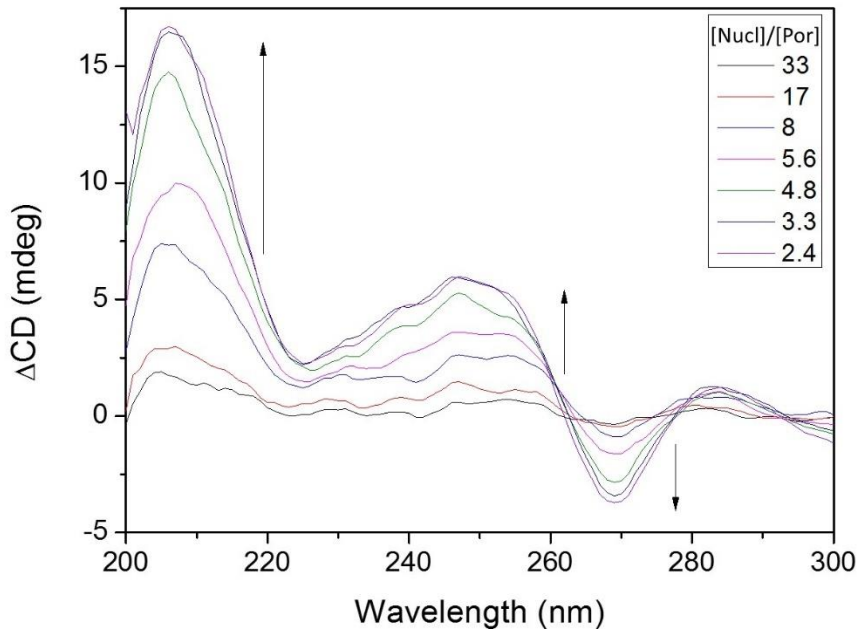

Fig. S3 CD spectra of DNA region for titration of PtTMPyP4 into $[poly(dG\text{-}dC)]_2$ with subtraction of the initial $[poly(dG\text{-}dC)]_2$ signal from each spectrum. In 50 mM phosphate buffer pH 6.8.

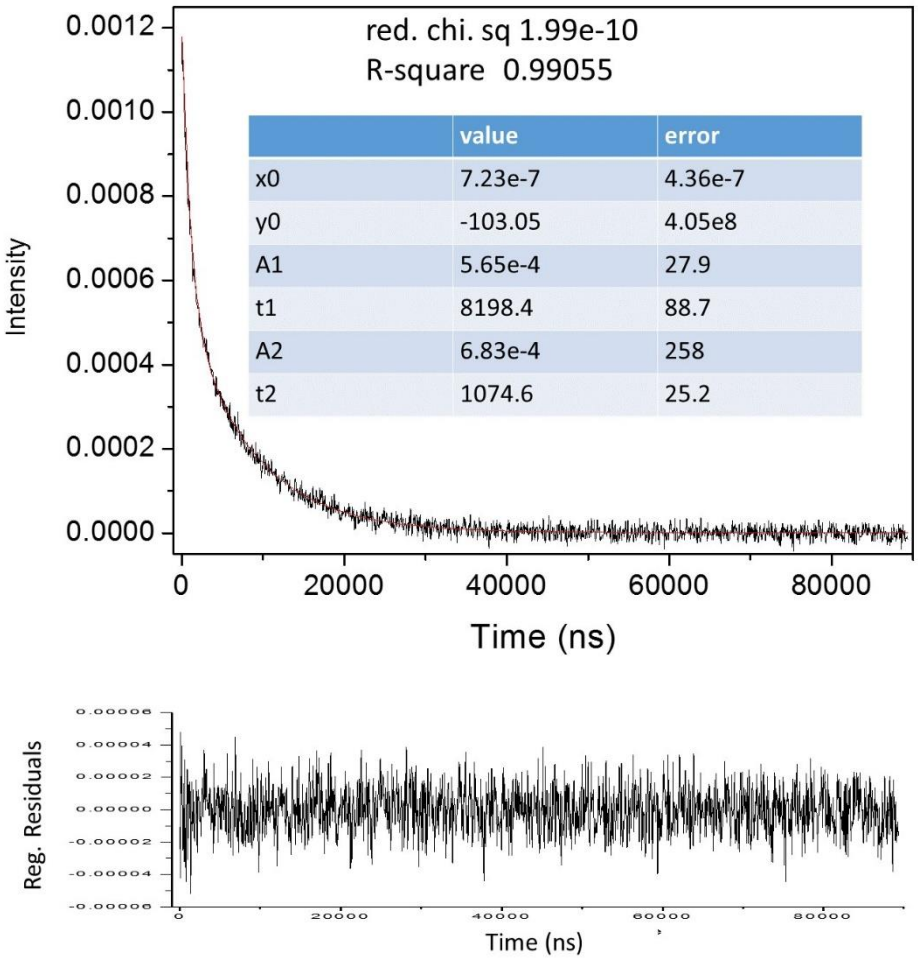

Fig. S4 Biexponential fit and residuals for PtTMPyP4-$[poly(dG\text{-}dC)]_2$ at [Nucl]/[Por] = 2.8. In 50 mM phosphate buffer pH 6.8. λ_{exc} = 355 nm, λ_{em} = 670 nm

Table S1 Biexponential fit parameters for PtTMPyP4 in [poly(dG-dC)]$_2$. In 50 mM phosphate buffer pH 6.8. λ_{exc} = 355 nm, λ_{em} = 670 nm

[Nucl]/[Por]	τ_1 (ns)	% (a)[a]	% (aτ)[b]	τ_2 (ns)	% (a)[a]	% (aτ)[b]	$\langle\tau\rangle/\tau_0$[c]
0	930	100	100	-	0	0	1
0.7	930	96	77	6920	4	23	1.26
1.4	970	90	54	7640	10	46	1.76
2.1	970	77	30	7740	23	70	2.71
2.8	1070	54	13	8200	46	87	4.68
3.6	820	36	6	7700	64	94	5.61
4.3	680	38	5	8400	62	95	5.88
5.0	640	39	5	8340	61	95	5.74
5.7	660	39	5	8600	61	95	5.91

[a] $a(\%) = a_i/\Sigma a_i$. [b] $a\tau(\%) = a_i\tau_i/\Sigma a_i\tau_i$. [c] $\langle\tau\rangle = \Sigma a_i\tau_i/\Sigma a_i$

Table S2 Biexponential fit parameters for PtTMPyP4 in [poly(dG-dC)]$_2$ with τ_1 fixed. In 50 mM phosphate buffer pH 6.8. λ_{exc} = 355 nm, λ_{em} = 670 nm

[Nucl]/[Por]	τ_1 (ns)	% (a)[a]	% (aτ)[b]	τ_2 (ns)	% (a)[a]	% (aτ)[b]	$\langle\tau\rangle/\tau_0$[c]
0	1000	100	1	-	0	0	1
1.4	1000	90	52	8920	10	48	1.75
2.1	1000	77	30	7910	23	70	2.59
2.8	1000	52	12	8030	48	88	4.39
3.6	1000	35	6	7910	65	94	5.46
4.3	1000	36	6	8390	64	94	5.76
5.0	1000	38	7	8820	62	93	5.83
5.7	1000	40	7	9010	60	93	5.84

[a] $a(\%) = a_i/\Sigma a_i$. [b] $a\tau(\%) = a_i\tau_i/\Sigma a_i\tau_i$. [c] $\langle\tau\rangle = \Sigma a_i\tau_i/\Sigma a_i$

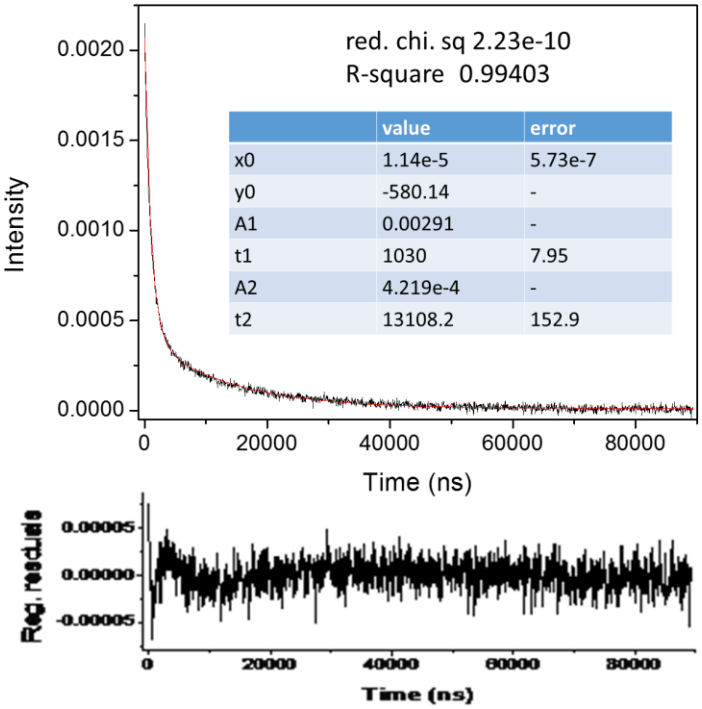

Fig. S5 Biexponential fit and residuals for PtTMPyP4-[poly(dA-dT)]$_2$ at [Nucl]/[Por] = 2.5. In 50 mM phosphate buffer pH 6.8. λ_{exc} = 355 nm, λ_{em} = 670 nm

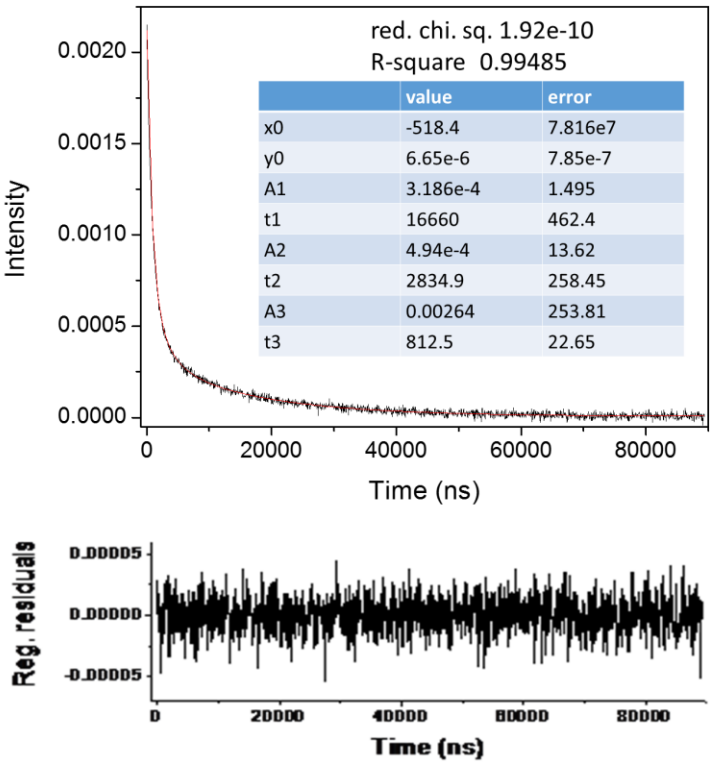

Fig. S6 Triexponential fit and residuals for PtTMPyP4-[poly(dA-dT)]$_2$ at [Nucl]/[Por] = 2.5. In 50 mM phosphate buffer pH 6.8. λ_{exc} = 355 nm, λ_{em} = 670 nm

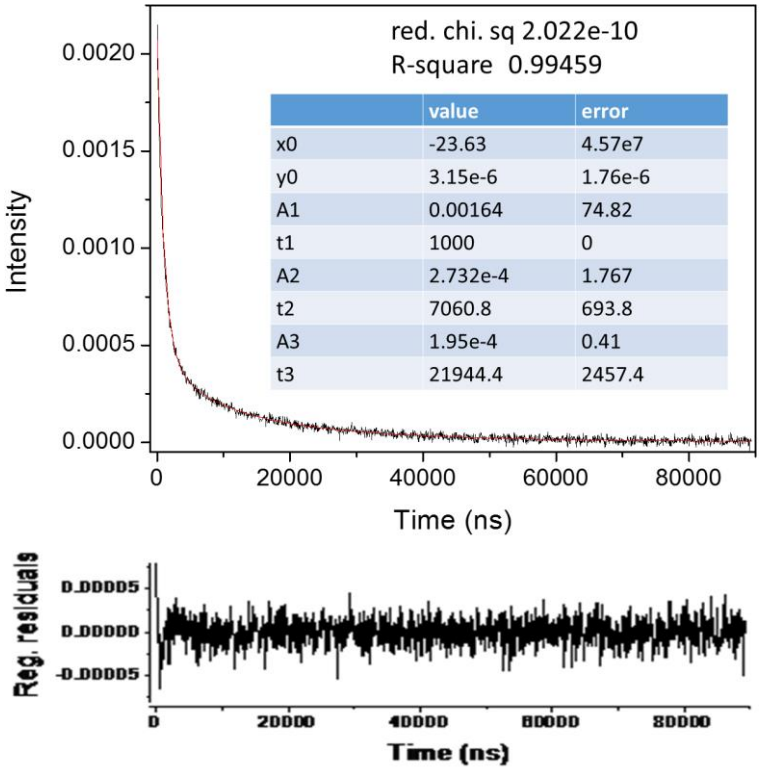

Fig. S7 Triexponential fit and residuals for PtTMPyP4-[poly(dA-dT)]$_2$ at [Nucl]/[Por] = 2.5. τ_1 fixed. In 50 mM phosphate buffer pH 6.8. λ_{exc} = 355 nm, λ_{em} = 670 nm

Table S3 Fitted parameters for biexponential emission decay of PtTMPyP4-[poly(dA-dT)]$_2$. In 50 mM phosphate buffer pH 6.8. λ_{exc} = 355 nm, λ_{em} = 670 nm

[Nucl]/[Por]	τ_1 (ns)	% (a)[a]	% (aτ)[b]	τ_2 (ns)	% (a)[a]	% (aτ)[b]
0.83	980	95	61	13500	5	39
1.7	1080	88	33	15400	12	67
2.5	1060	74	18	14000	26	83
3.3	1460	50	8	15700	50	92
4.9	1400	46	8	13000	54	92
6.5	1140	51	7	17000	49	93
8.1	1040	37	6	10100	63	94
9.7	920	34	5	9520	66	95

[a] $a(\%) = a_i/\Sigma a_i$. [b] $a\tau(\%) = a_i\tau_i/\Sigma a_i\tau_i$

Table S4 Fitted parameters for biexponential emission decay of PtTMPyP4-[poly(dA-dT)]$_2$ with τ_1 fixed. In 50 mM phosphate buffer pH 6.8. λ_{exc} = 355 nm, λ_{em} = 670 nm

[Nucl]/[Por]	τ_1 (ns)	% (a)[a]	% (aτ)[b]	τ_2 (ns)	% (a)[a]	% (aτ)[b]
0.83	1000	95	60	14300	5	40
1.7	1000	86	31	13800	14	69
2.5	1000	73	17	13500	27	83
3.3	1000	49	6	14400	51	94
4.9	1000	45	6	12200	55	94
6.5	1000	41	6	10700	60	94
8.1	1000	38	6	10100	63	94
9.7	1000	34	5	9600	66	95

[a] $a(\%) = a_i/\Sigma a_i$. [b] $a\tau(\%) = a_i\tau_i/\Sigma a_i\tau_i$

Table S5 Fitted parameters for triexponential emission decay of PtTMPyP4-[poly(dA-dT)]$_2$ with τ_1 fixed. In 50 mM phosphate buffer pH 6.8. λ_{exc} = 355 nm, λ_{em} = 670 nm

[Nucl]/[Por]	τ_1 (ns)	% (a)[a]	% (aτ)[b]	τ_2 (ns)	% (a)[a]	% (aτ)[b]	τ_3 (ns)	% (a)[a]	% (aτ)[b]
0.83	1000	95	60	14300	2	20	14300	2	20
1.7	1000	82	27	4110	8	11	19700	10	62
2.5	1000	70	14	6770	16	21	21100	15	64
3.3	1000	41	5	6600	29	21	22200	31	75
3.7	1000	46	6	6560	29	26	20300	24	67
4.2	1000	46	6	7800	36	35	25100	19	59
4.9	1000	38	5	7410	40	36	22800	22	60
6.5	1000	34	4	8500	56	56	32500	11	40
8.1	1000	32	4	7850	53	56	18900	16	40

[a] $a(\%) = a_i/\Sigma a_i$. [b] $a\tau(\%) = a_i\tau_i/\Sigma a_i\tau_i$

Table S6 Fitted parameters for triexponential emission decay of PtTMPyP4-[poly(dA-dT)]$_2$ with τ_1 free. In 50 mM phosphate buffer pH 6.8. λ_{exc} = 355 nm, λ_{em} = 670 nm

[Nucl]/[Por]	τ_1 (ns)	% (a)[a]	% (aτ)[b]	τ_2 (ns)	% (a)[a]	% (aτ)[b]	τ_3 (ns)	% (a)[a]	% (aτ)[b]
0.83	970	95	58	4850	1	31	15400	4	39
1.7	1010	90	42	4810	5	11	20500	5	47
2.5	750	75	21	2780	14	15	17100	10	64
3.3	410	39	2.3	3160	29	13	18200	33	85
3.7	320	33	1.7	2810	34	15	15900	33	84
4.2	390	35	2	3490	33	17	17000	32	81
4.9	420	40	2.7	3900	30	19	16500	30	79
6.5	460	44	3.5	5080	32	28	15900	25	68
8.1	340	40	2.6	3480	24	16	12100	36	82
9.7	280	30	1.5	2670	21	10	10500	48	89

[a] $a(\%) = a_i/\Sigma a_i$. [b] $a\tau(\%) = a_i\tau_i/\Sigma a_i\tau_i$

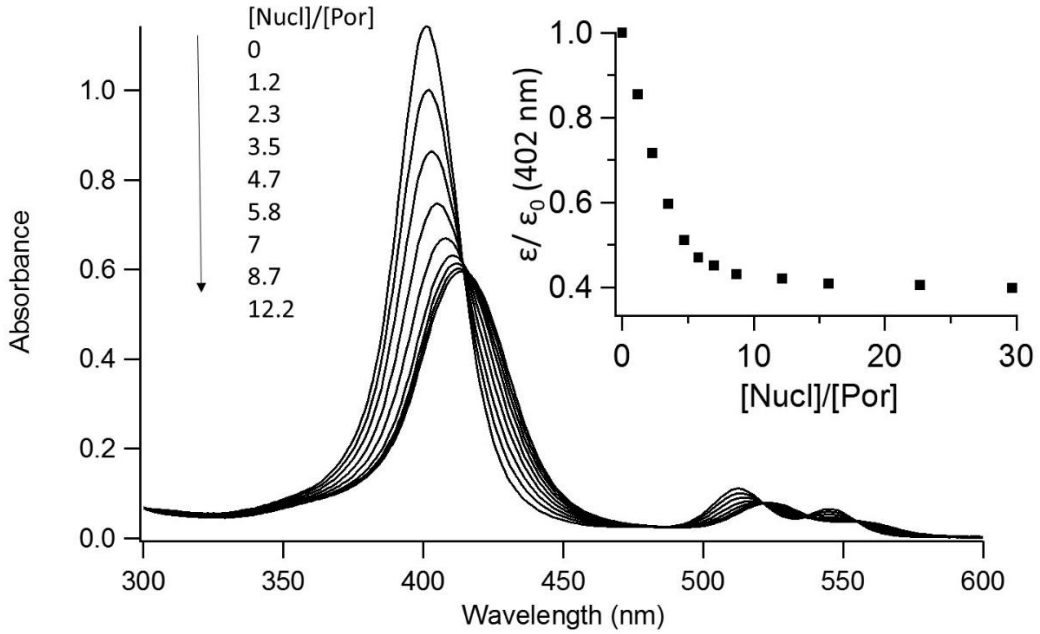

Fig. S8 UV/vis absorption spectra of 6 µM PtTMPyP4 in presence of increasing concentrations of salmon testes DNA. Inset: change in absorbance at 402 nm. In 50 mM phosphate buffer pH 6.8

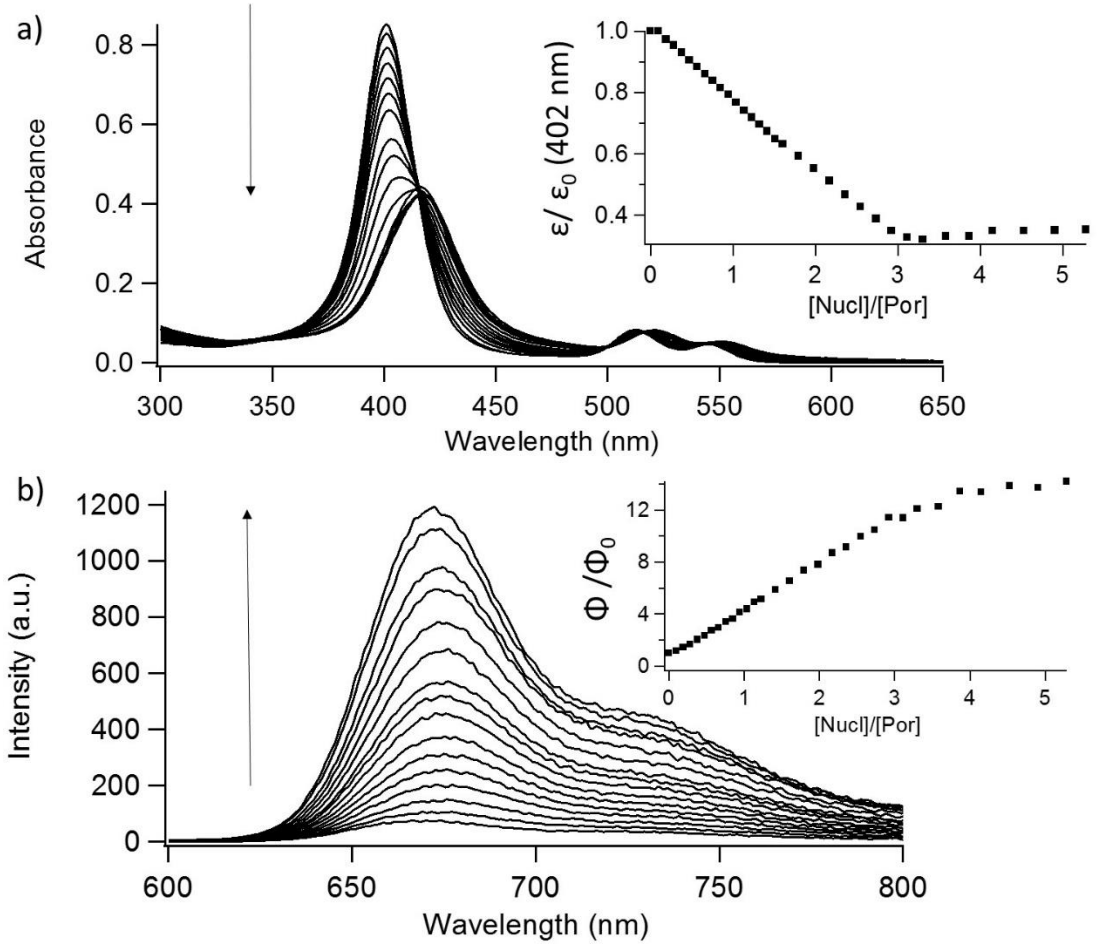

Fig. S9 (a) UV/vis titration of 5 µM PtTMPyP4 in presence of increasing poly(rA) concentrations. Inset shows change in absorption at 402 nm (b) change in emission with increasing concentrations of poly(rA). λ_{exc} = 523 nm. In 50 mM phosphate buffer pH 6.8

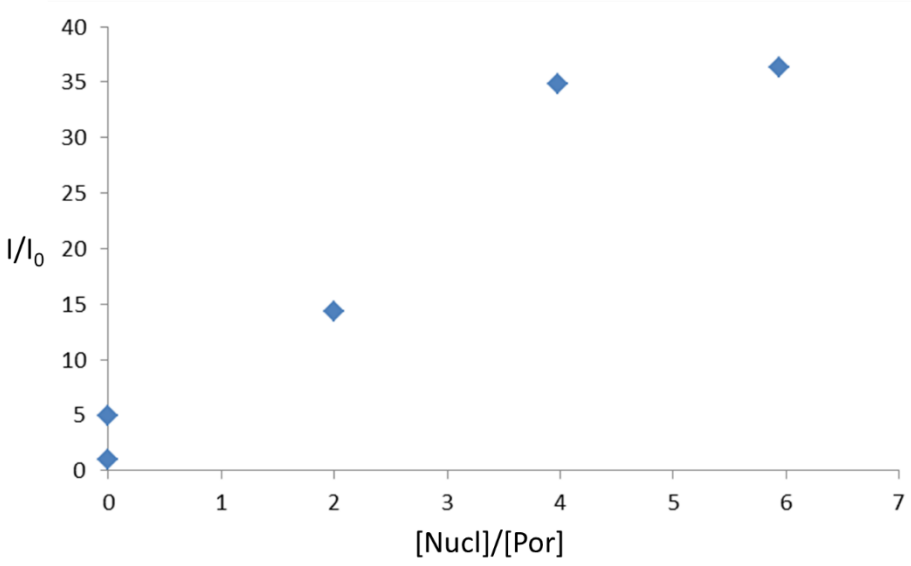

Fig. S10 Emission enhancement in N_2-purged PtTMPyP4 (5 µM) and PtTMPyP4-poly(rA) relative to aerated PtTMPyP4. In 50 mM phosphate buffer pH 6.8