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Design and synthesis of metal-based chemotherapeutic agents for targeted DNA interactions or DNA repair pathway modulation

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Appendix I: supporting information for chapter 2

pK_a determination

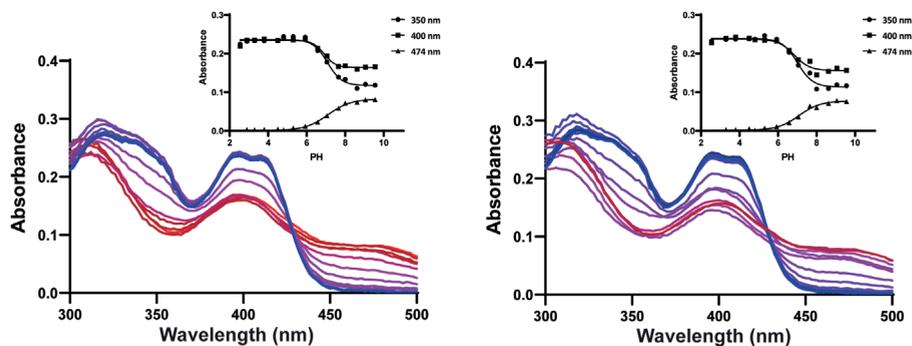


Figure Si.1. Absorption spectra at variable pH for [Pt(H₂L1)](Cl)₂. The blue/red gradient represents the range from acidic to basic conditions, respectively.

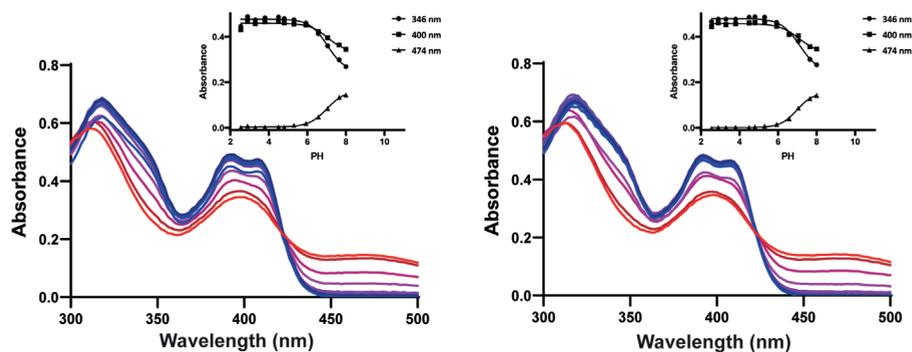


Figure Si.2. Absorption spectra at variable pH for [Pt(H₂L2)](Cl)₂. The blue/red gradient represents the range from acidic to basic conditions, respectively.

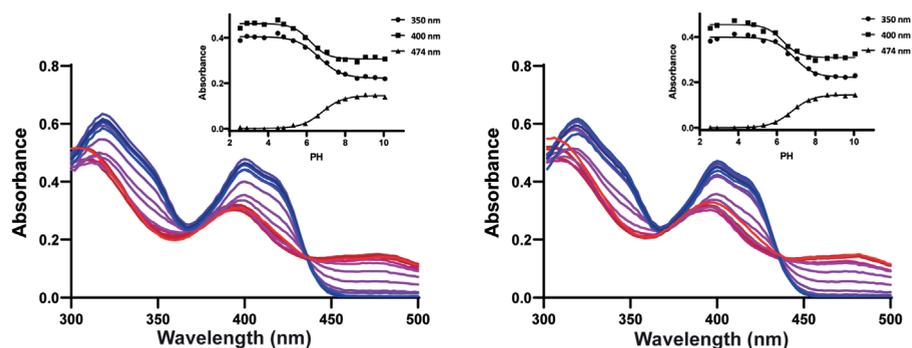


Figure Si.3. Absorption spectra at variable pH for [Pt(H₂L3)](Cl)₂. The blue/red gradient represents the range from acidic to basic conditions, respectively.

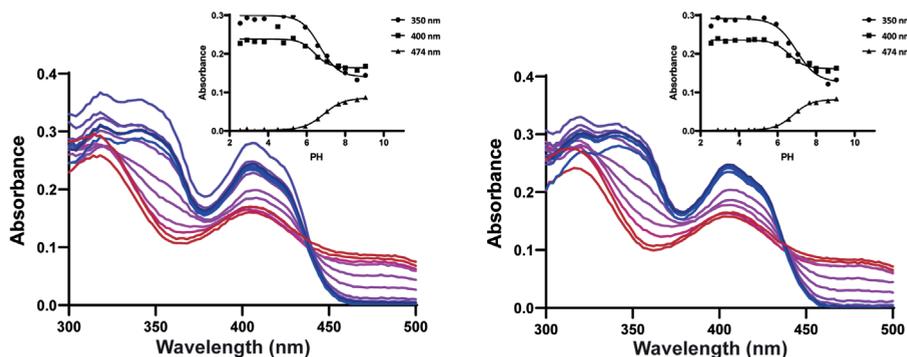


Figure Si.4. Absorption spectra at variable pH for $[\text{Pt}(\text{H}_2\text{L}_4)](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

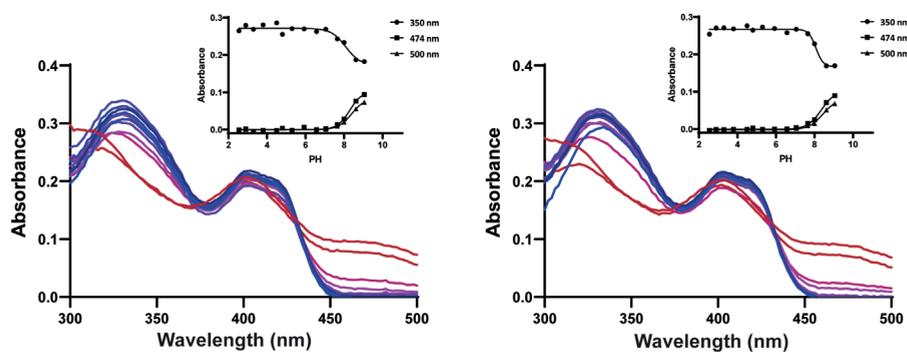


Figure Si.5. Absorption spectra at variable pH for $[\text{Pt}(\text{H}_2\text{L}_5)](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

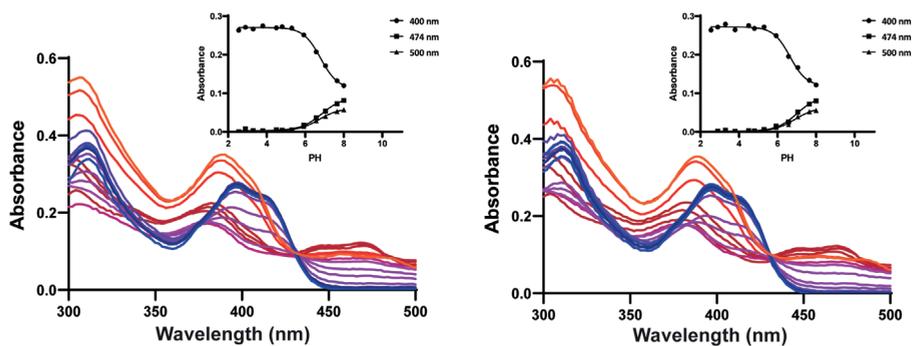


Figure Si.6. Absorption spectra at variable pH for $[\text{Pt}(\text{H}_2\text{L}_6)](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

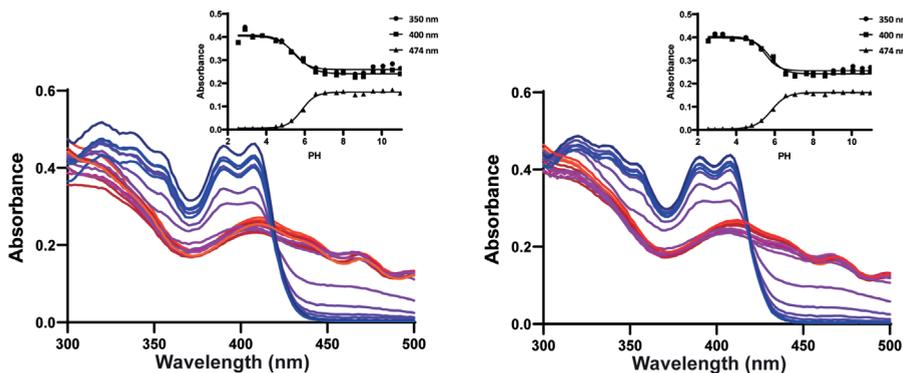


Figure SI.7. Absorption spectra at variable pH for $[\text{Pt}(\text{H}_2\text{L}_7)](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

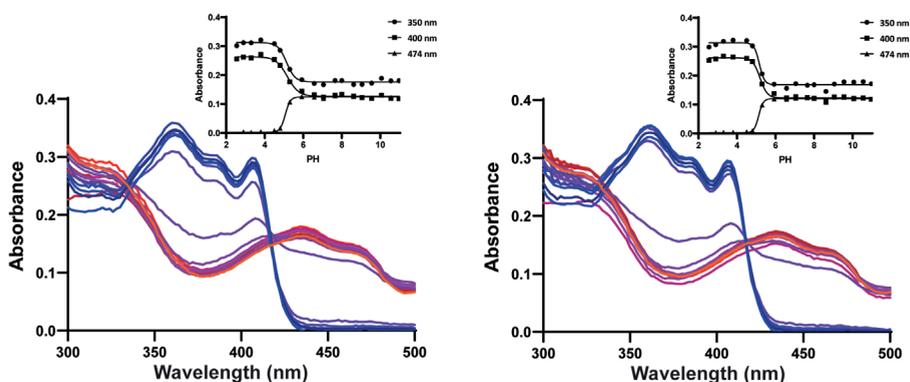


Figure SI.8. Absorption spectra at variable pH for $[\text{Pt}(\text{H}_2\text{L}_8)](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

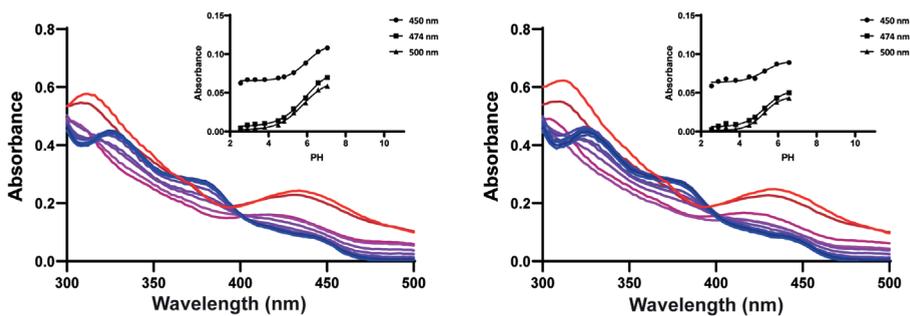


Figure SI.9. Absorption spectra at variable pH for $[\text{Pt}(\text{H}_2\text{L}_9)](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

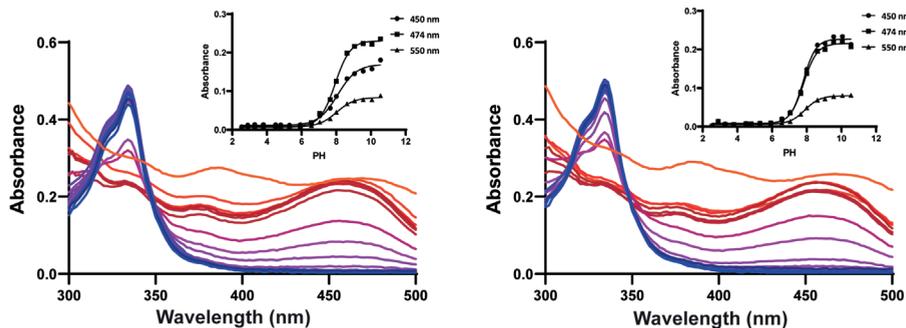


Figure SI.10. Absorption spectra at variable pH for $[\text{Pt}(\text{H}_2\text{L13})](\text{PF}_6)_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

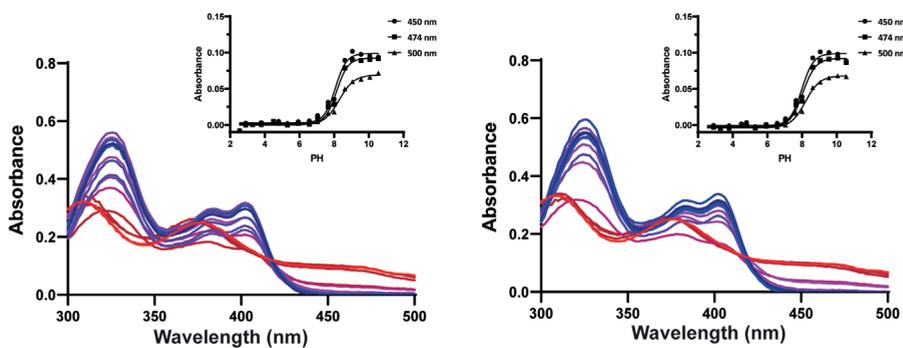


Figure SI.11. Absorption spectra at variable pH for $[\text{Pd}(\text{H}_2\text{L1})](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

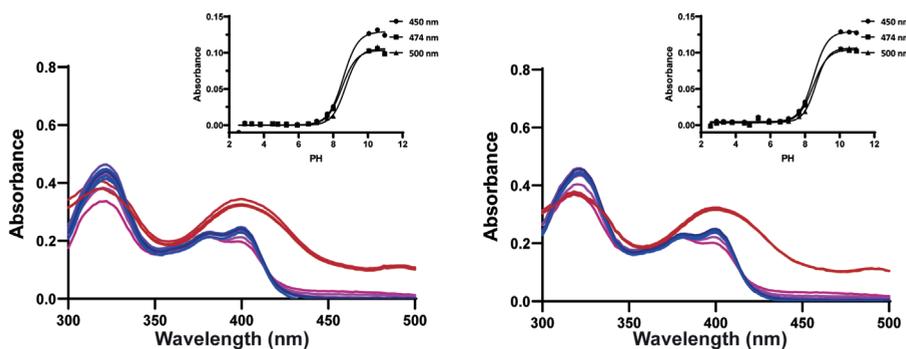


Figure SI.12. Absorption spectra at variable pH for $[\text{Pd}(\text{H}_2\text{L2})](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

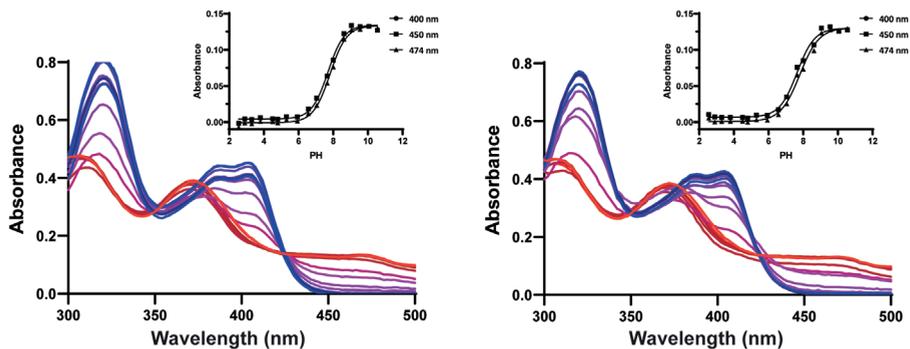


Figure SI.13. Absorption spectra at variable pH for $[\text{Pd}(\text{H}_2\text{L3})](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

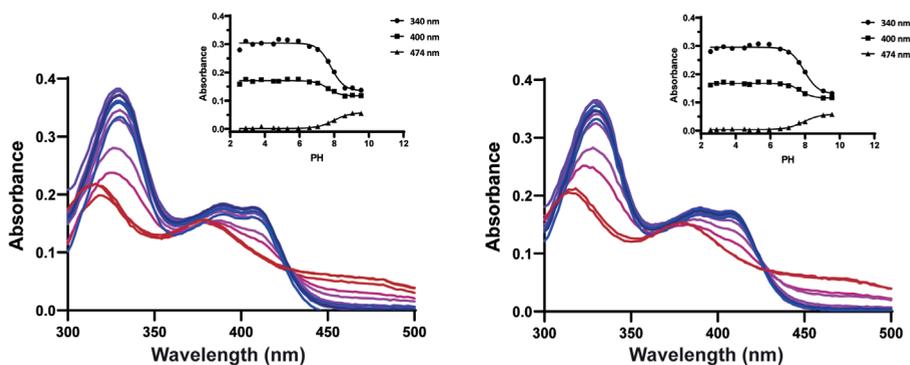


Figure SI.14. Absorption spectra at variable pH for $[\text{Pd}(\text{H}_2\text{L4})](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

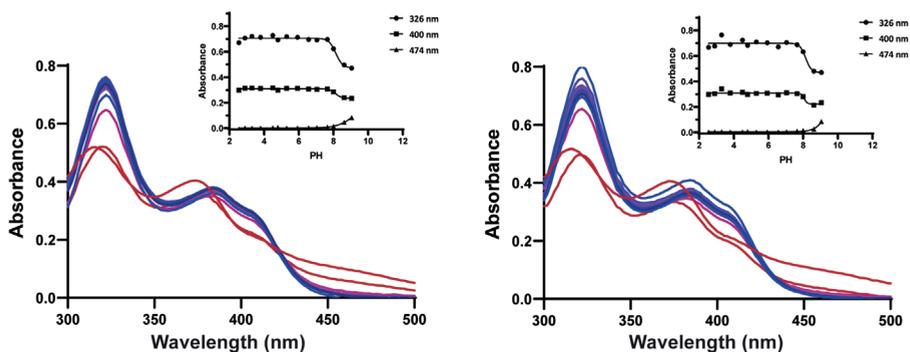


Figure SI.15. Absorption spectra at variable pH for $[\text{Pd}(\text{H}_2\text{L5})](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

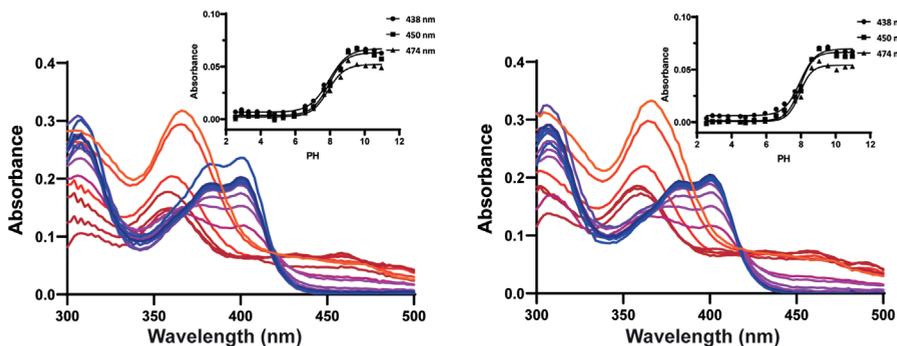


Figure SI.16. Absorption spectra at variable pH for $[\text{Pd}(\text{H}_2\text{L6})](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

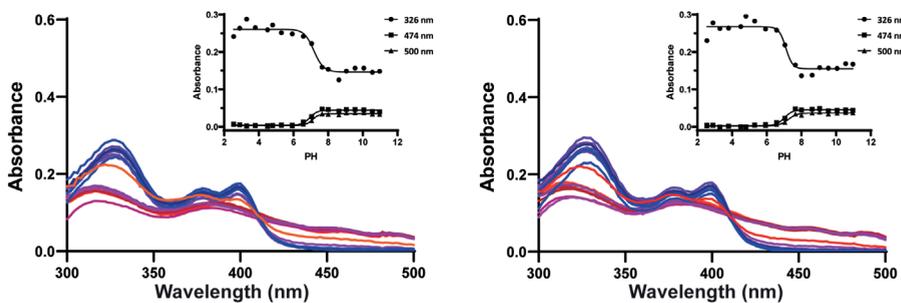


Figure SI.17. Absorption spectra at variable pH for $[\text{Pd}(\text{H}_2\text{L7})](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

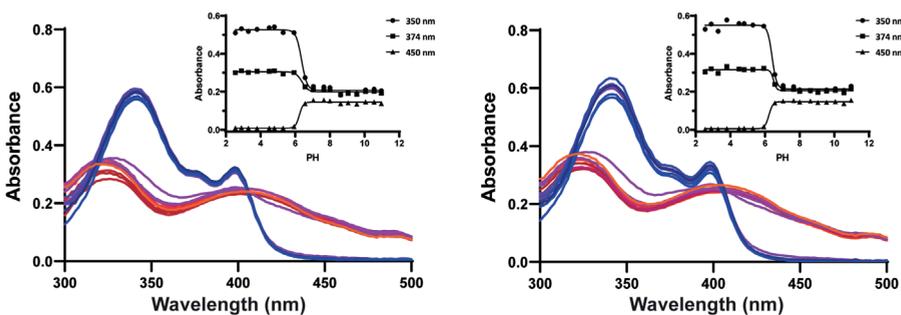


Figure SI.18. Absorption spectra at variable pH for $[\text{Pd}(\text{H}_2\text{L8})](\text{Cl})_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

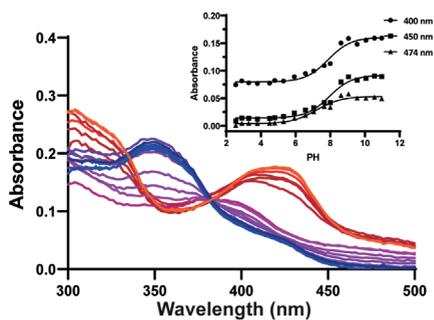
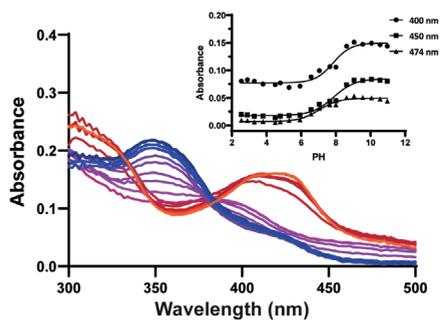


Figure SI.19. Absorption spectra at variable pH for $[Pd(H_2L9)](Cl)_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

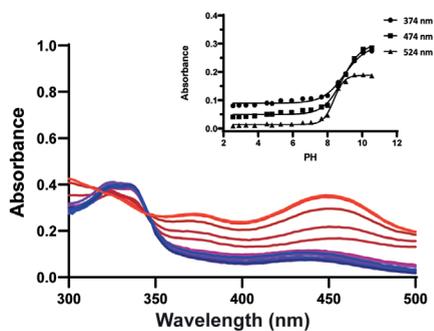
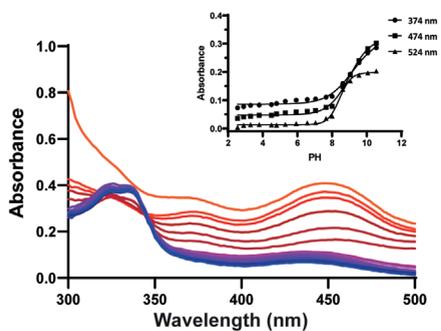


Figure SI.20. Absorption spectra at variable pH for $[Pd(H_2L13)](Cl)_2$. The blue/red gradient represents the range from acidic to basic conditions, respectively.

pUC19 Agarose gel electrophoresis

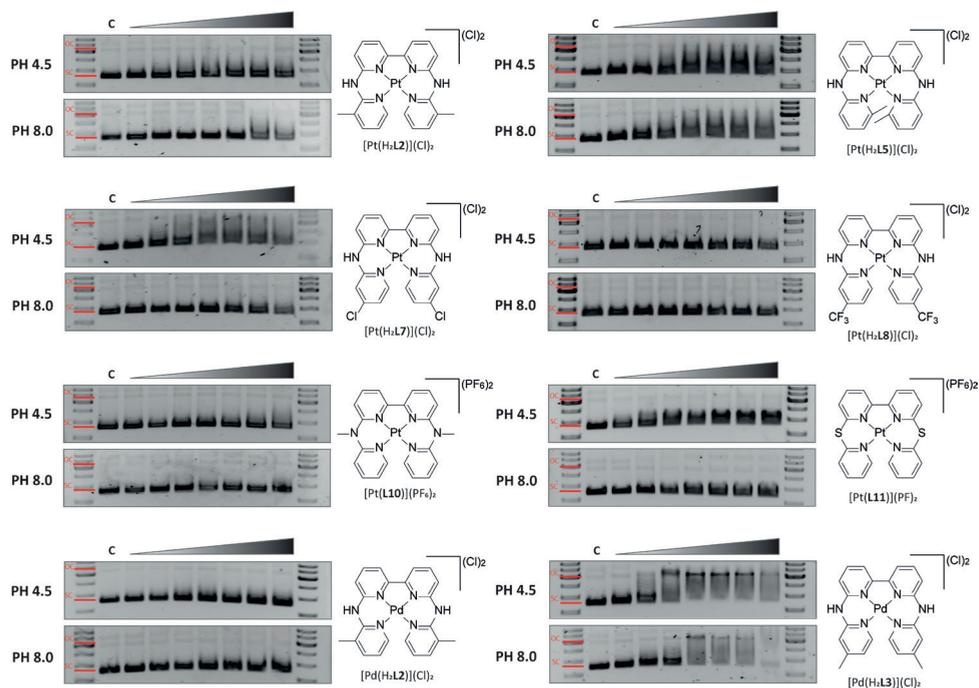


Figure S1.21. Agarose gel electrophoresis analysis of the interactions of pUC19 plasmid DNA and metal complexes at pH 4.5 and 8. Lane 1 and 10 contain the molecular ladders, lane 2 is the pUC19 DNA plasmid only control and lane 3-9 contained increasing metal complex (MC) to base pair (BP) concentration ratios (0.05, 0.1, 0.2, 0.5, 1, 2, 5).

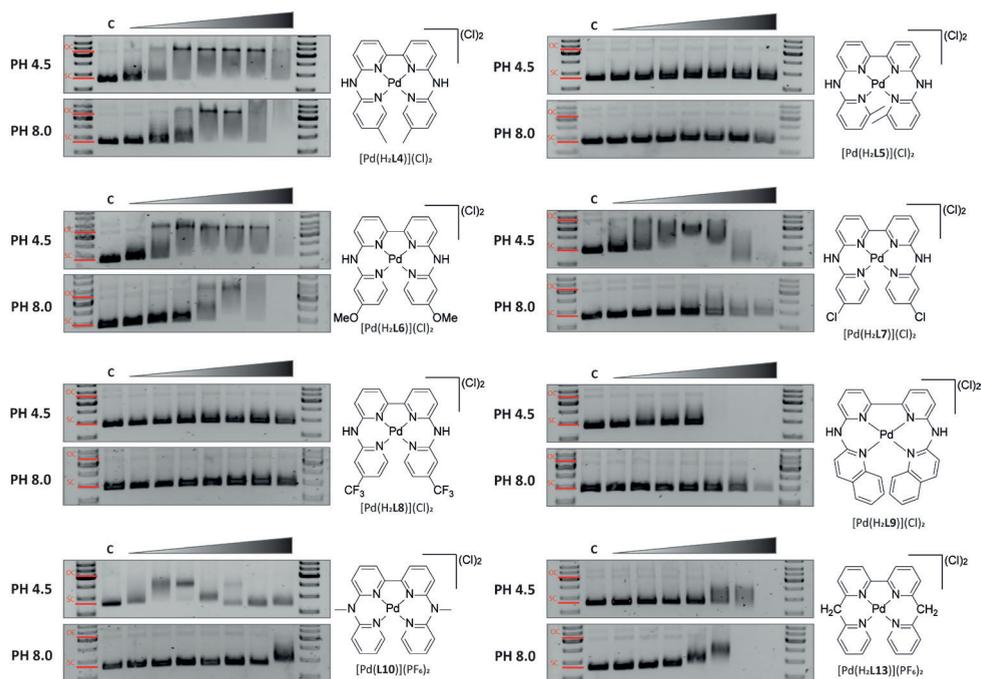


Figure SI.22. Agarose gel electrophoresis analysis of the interactions of pUC19 plasmid DNA and metal complexes at pH 4.5 and 8. Lane 1 and 10 contain the molecular ladders, lane 2 is the pUC19 DNA plasmid only control and lane 3-9 contained increasing metal complex (MC) to base pair (BP) concentration ratios (0.05, 0.1, 0.2, 0.5, 1, 2, 5).

Titration of $[M(H_2LX)]^{2+}$ complexes with calf thymus DNA analyzed by plate reader.

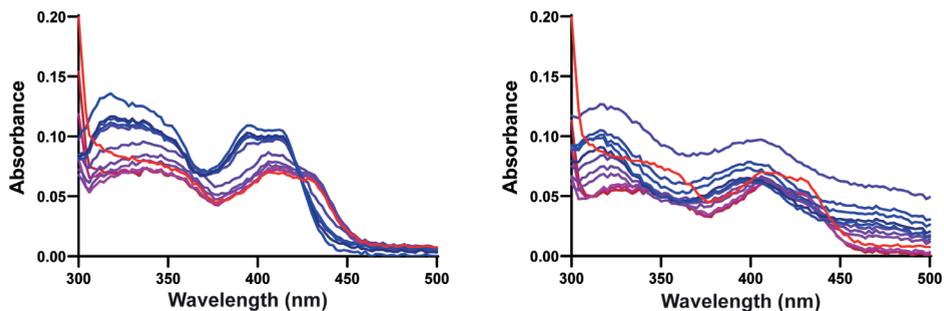


Figure SI.23. Calf thymus titration absorbance spectra of $[Pt(H_2L1)](Cl)_2$ ($33 \mu M$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu M$ basepairs, respectively.

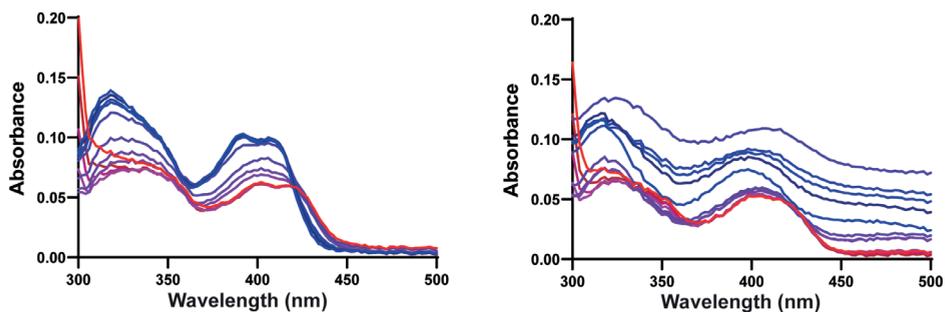


Figure SI.24. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{H}_2\text{L}_2)](\text{Cl})_2$ ($33 \mu\text{m}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to 666 μm basepairs, respectively.

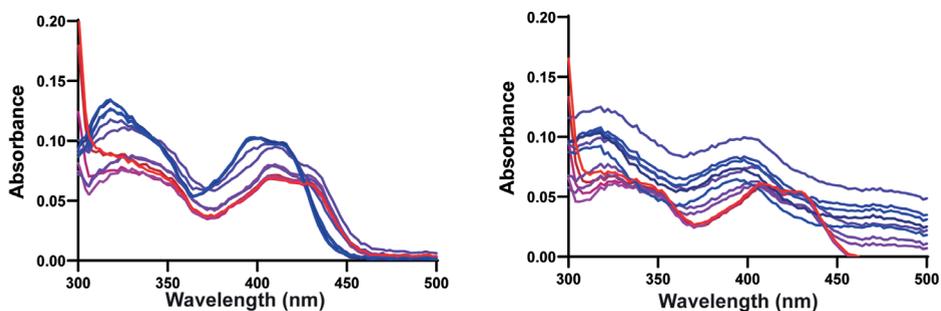


Figure SI.25. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{H}_2\text{L}_3)](\text{Cl})_2$ ($33 \mu\text{m}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to 666 μm basepairs, respectively.

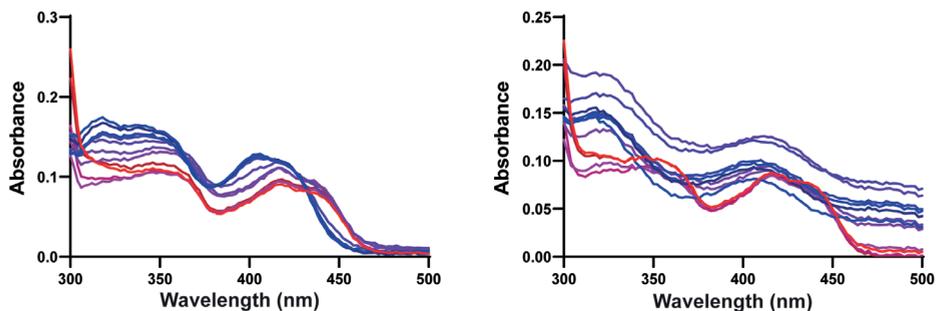


Figure SI.26. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{H}_2\text{L}_4)](\text{Cl})_2$ ($33 \mu\text{m}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to 666 μm basepairs, respectively.

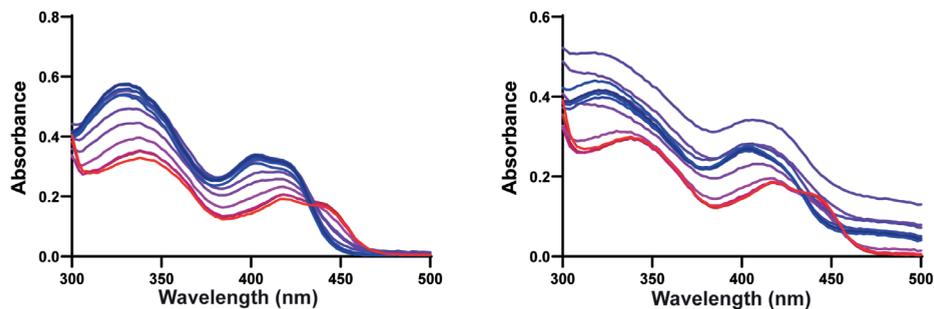


Figure SI.27. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{H}_2\text{L}_5)](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

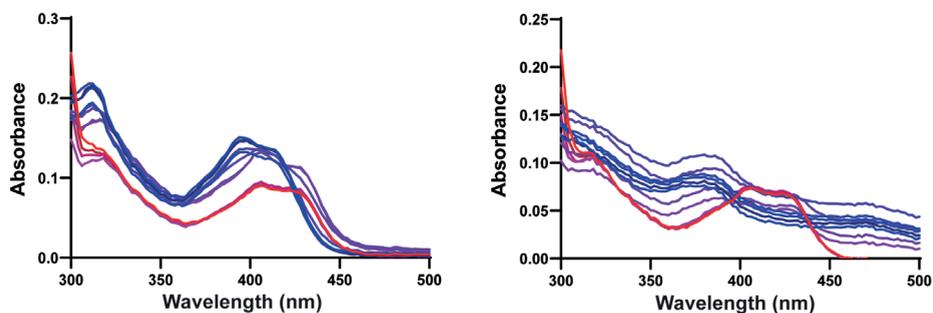


Figure SI.28. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{H}_2\text{L}_6)](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

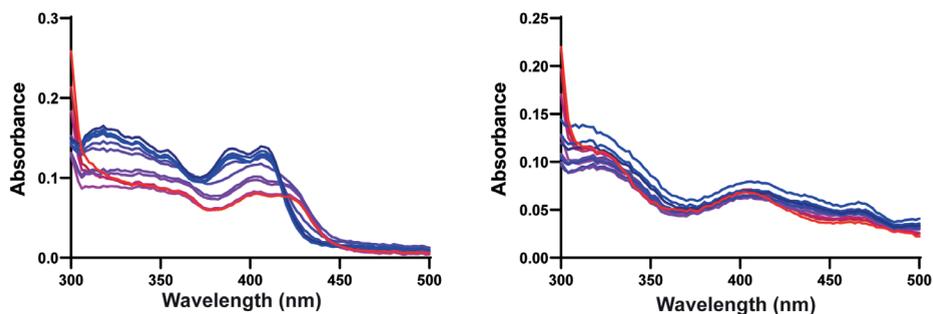


Figure SI.29. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{H}_2\text{L}_7)](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

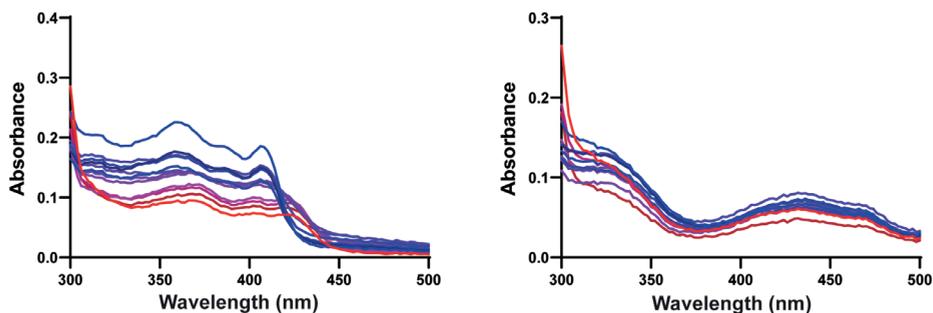


Figure SI.30. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{H}_2\text{L8})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

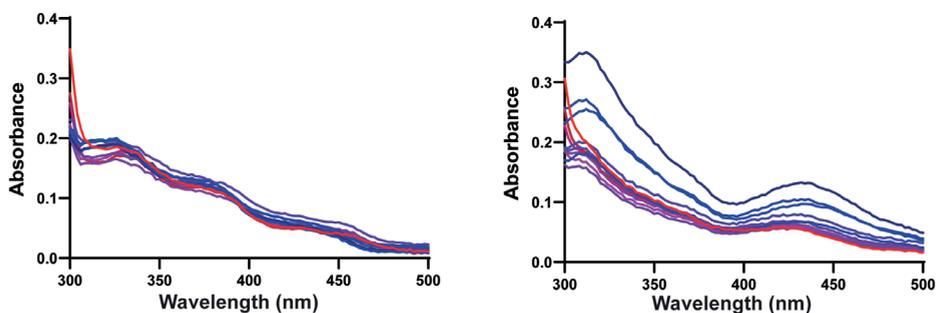


Figure SI.31. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{L9})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

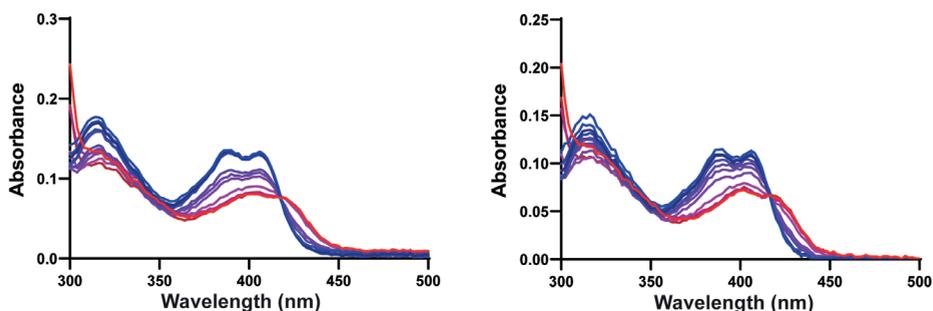


Figure SI.32. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{L10})](\text{PF}_6)_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

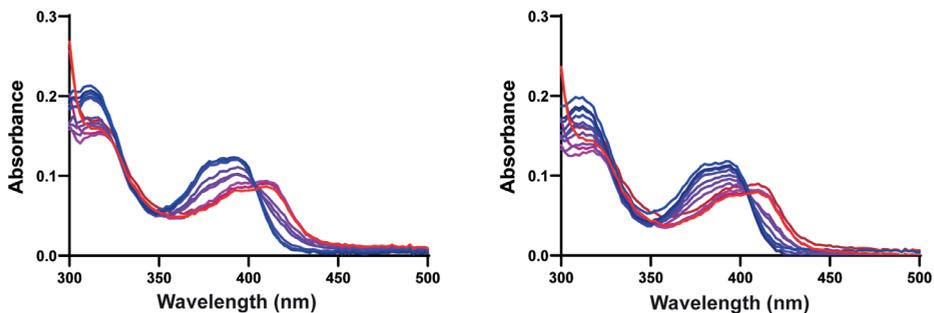


Figure SI.33. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{L11})](\text{PF}_6)_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

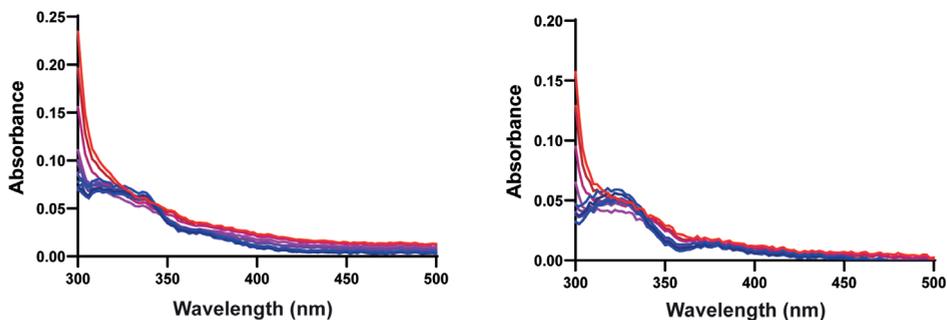


Figure SI.34. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{L12})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

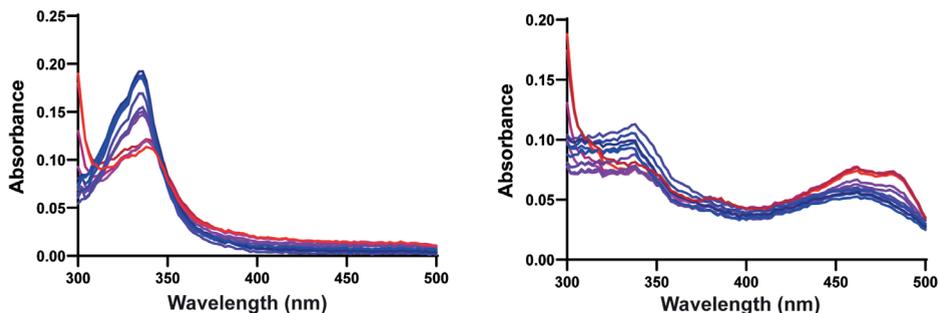


Figure SI.35. Calf thymus titration absorbance spectra of $[\text{Pt}(\text{H}_2\text{L13})](\text{PF}_6)_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

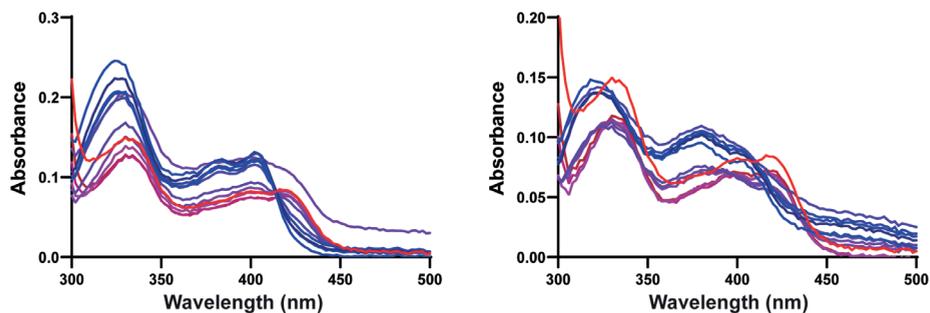


Figure SI.36. Calf thymus titration absorbance spectra of $[\text{Pd}(\text{H}_2\text{L1})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

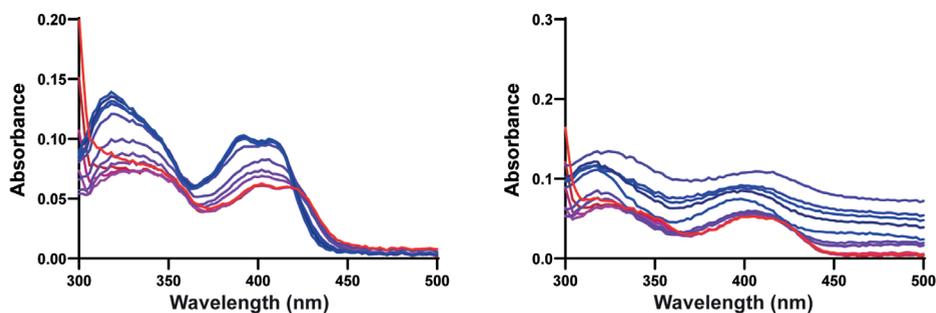


Figure SI.37. Calf thymus titration absorbance spectra of $[\text{Pd}(\text{H}_2\text{L2})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

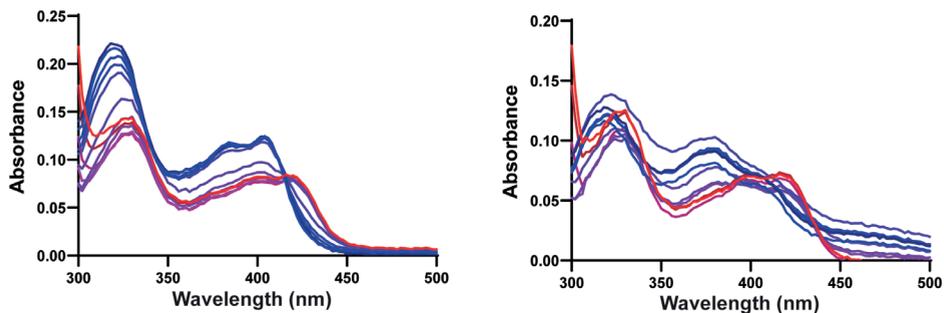


Figure SI.38. Calf thymus titration absorbance spectra of $[\text{Pd}(\text{H}_2\text{L3})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

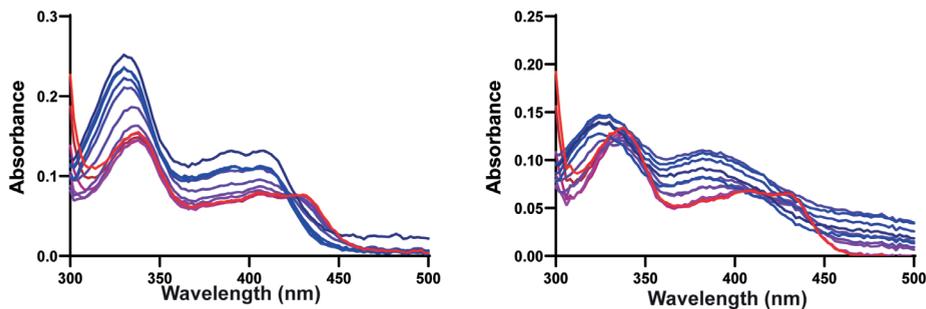


Figure SI.39. Calf thymus titration absorbance spectra of $[\text{Pd}(\text{H}_2\text{L4})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

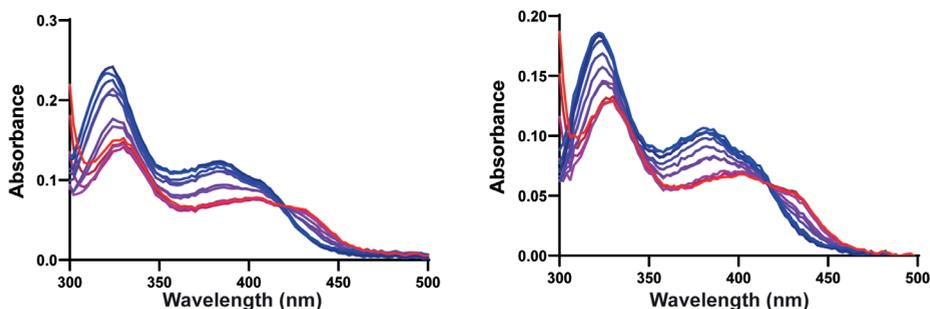


Figure SI.40. Calf thymus titration absorbance spectra of $[\text{Pd}(\text{H}_2\text{L5})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

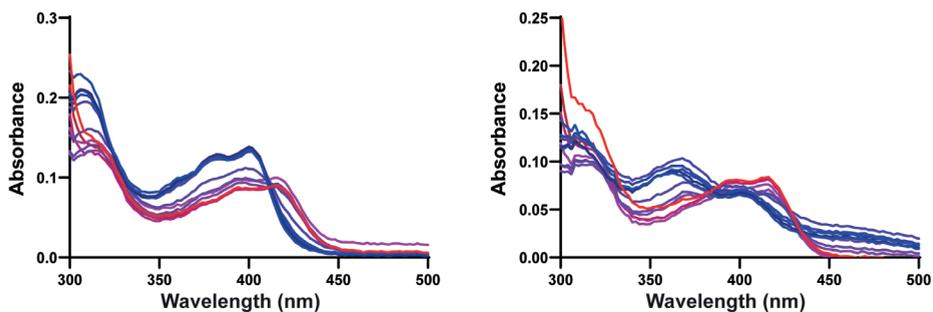


Figure SI.41. Calf thymus titration absorbance spectra of $[\text{Pd}(\text{H}_2\text{L6})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

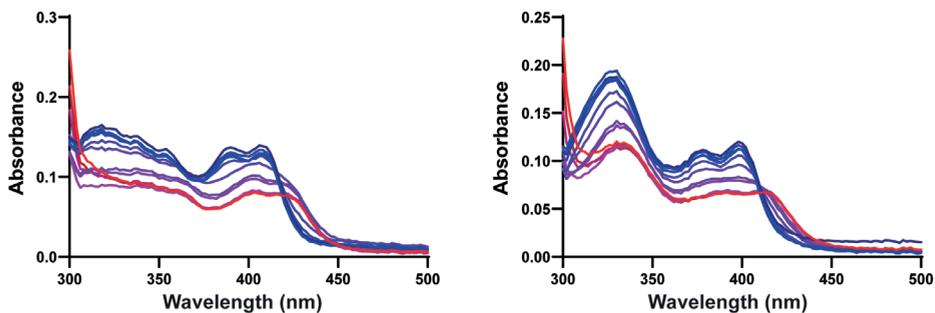


Figure SI.42. Calf thymus titration absorbance spectra of $[\text{Pd}(\text{H}_2\text{L7})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

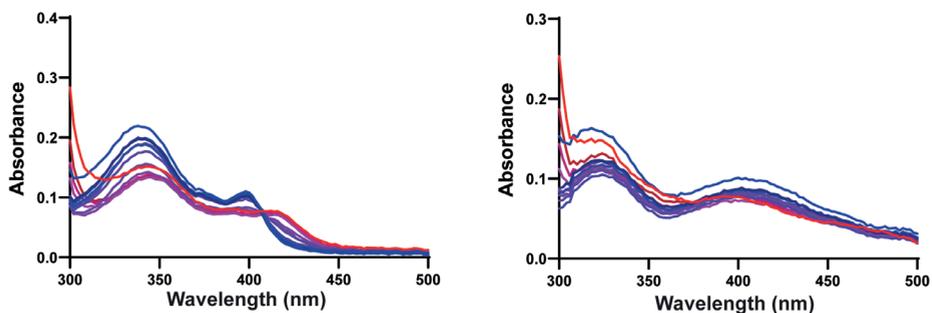


Figure SI.43. Calf thymus titration absorbance spectra of $[\text{Pd}(\text{H}_2\text{L8})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

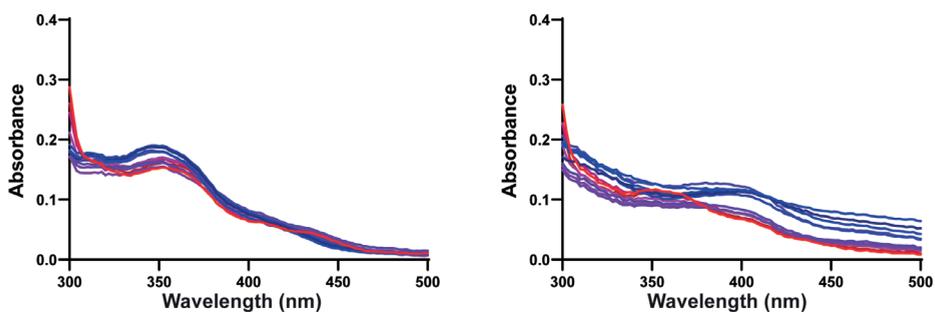


Figure SI.44. Calf thymus titration absorbance spectra of $[\text{Pd}(\text{H}_2\text{L9})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

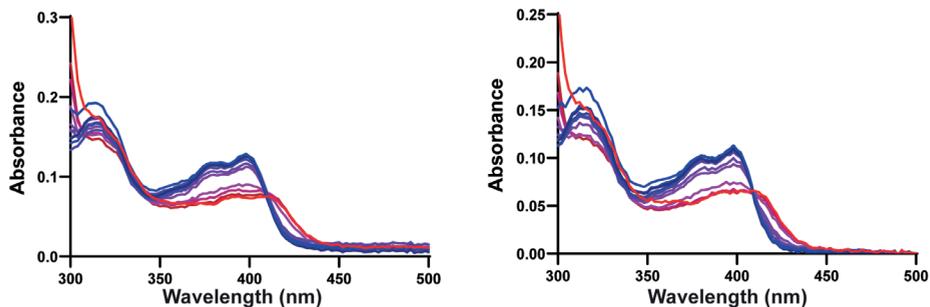


Figure SI.45. Calf thymus titration absorbance spectra of $[\text{Pd}(\text{L10})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

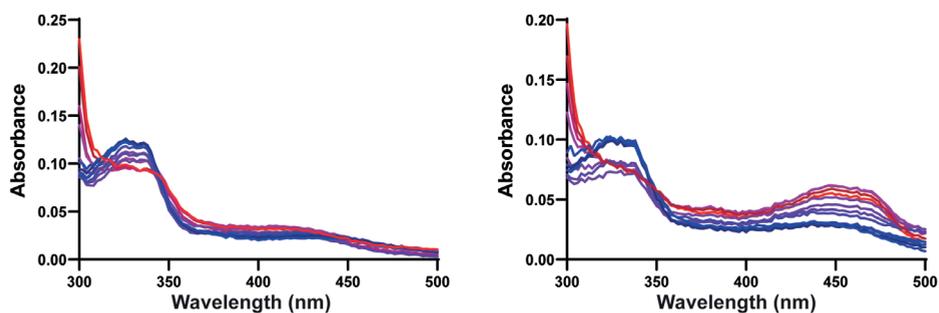


Figure SI.46. Calf thymus titration absorbance spectra of $[\text{Pd}(\text{H}_2\text{L13})](\text{Cl})_2$ ($33 \mu\text{M}$) at pH 5 (left) and pH 8 (right). The blue to red gradient represents increasing DNA concentration range from 0 to $666 \mu\text{M}$ basepairs, respectively.

Binding constant determination of $[\text{M}(\text{H}_2\text{LX})]^{2+}$ complexes to calf thymus DNA

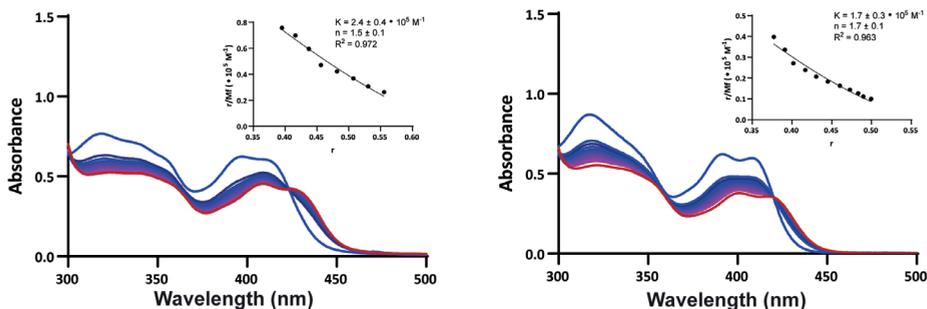


Figure SI.47. Calf thymus titration absorbance spectra of $100 \mu\text{M}$ $[\text{Pt}(\text{H}_2\text{L1})](\text{Cl})_2$ (left) and $[\text{Pt}(\text{H}_2\text{L2})](\text{Cl})_2$ (right) at pH 4.5. The blue to red gradient represents increasing DNA concentration from 0 to $360 \mu\text{M}$ basepairs, respectively. The inlays are Scatchard plots fitted to the McGhee-von Hippel model.

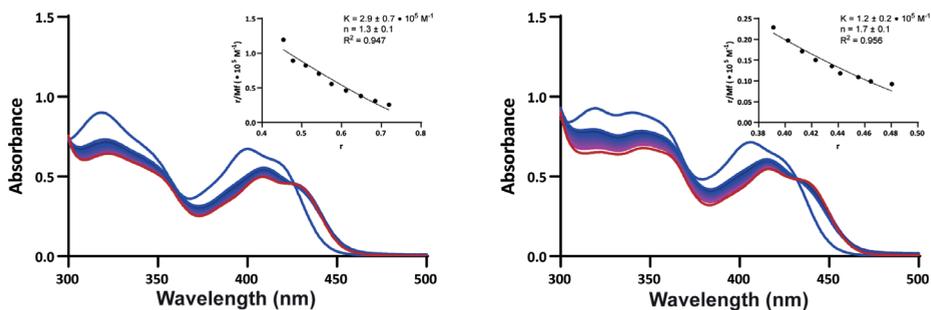


Figure SI.48. Calf thymus titration absorbance spectra of 100 μm $[\text{Pt}(\text{H}_2\text{L}_3)](\text{Cl})_2$ (left) and $[\text{Pt}(\text{H}_2\text{L}_4)](\text{Cl})_2$ (right) at pH 4.5. The blue to red gradient represents increasing DNA concentration from 0 to 360 μm base-pairs, respectively. The inlays are Scatchard plots fitted to the McGhee–von Hippel model.

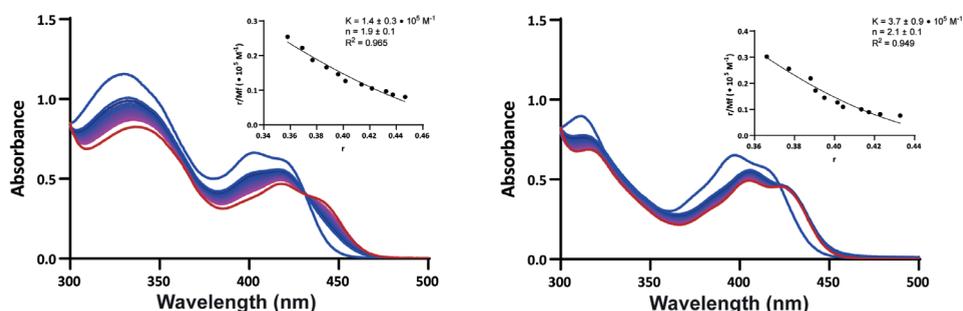


Figure SI.49. Calf thymus titration absorbance spectra of 100 μm $[\text{Pt}(\text{H}_2\text{L}_5)](\text{Cl})_2$ (left) and $[\text{Pt}(\text{H}_2\text{L}_6)](\text{Cl})_2$ (right) at pH 4.5. The blue to red gradient represents increasing DNA concentration from 0 to 360 μm base-pairs, respectively. The inlays are Scatchard plots fitted to the McGhee–von Hippel model.

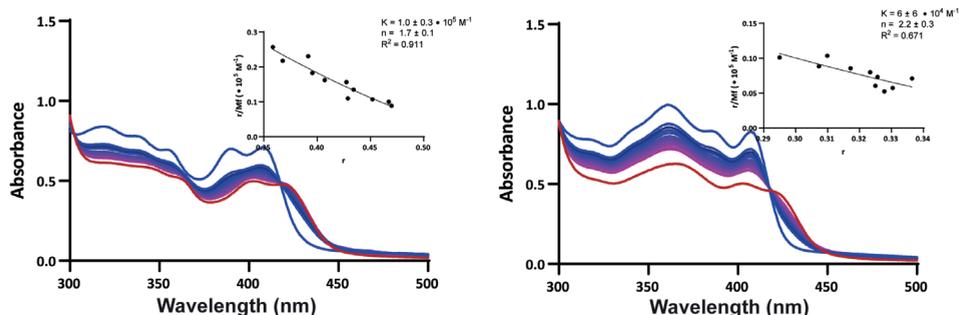


Figure SI.50. Calf thymus titration absorbance spectra of 100 μm $[\text{Pt}(\text{H}_2\text{L}_7)](\text{Cl})_2$ (left) and $[\text{Pt}(\text{H}_2\text{L}_8)](\text{Cl})_2$ (right) at pH 4.5. The blue to red gradient represents increasing DNA concentration from 0 to 360 μm base-pairs, respectively. The inlays are Scatchard plots fitted to the McGhee–von Hippel model.

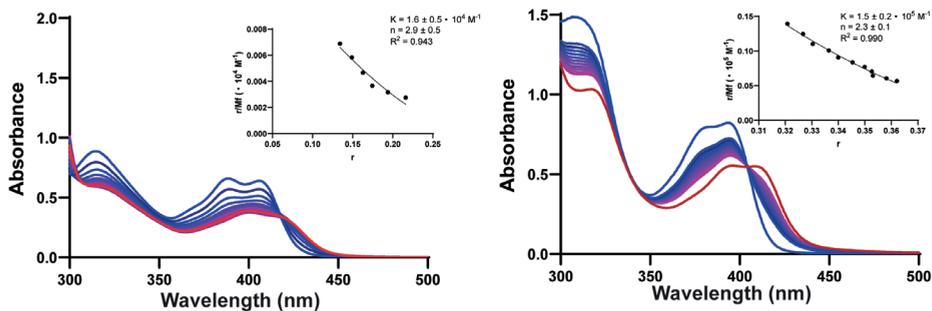


Figure SI.51. Calf thymus titration absorbance spectra of 100 μM $[\text{Pt}(\text{L10})](\text{PF}_6)_2$ (left) and $[\text{Pt}(\text{L11})](\text{PF}_6)_2$ (right) at pH 4.5. The blue to red gradient represents increasing DNA concentration from 0 to 1000 μM base-pairs for $[\text{Pt}(\text{L10})](\text{PF}_6)_2$ and 0 to 360 μM basepairs for $[\text{Pt}(\text{L11})](\text{PF}_6)_2$, respectively. The inlays are Scatchard plots fitted to the McGhee–von Hippel model.

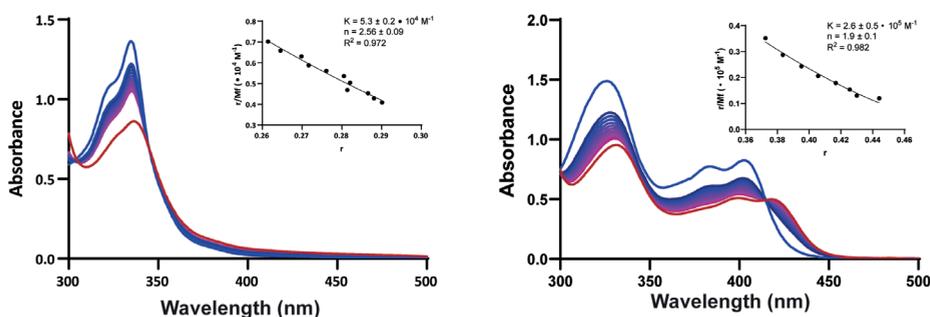


Figure SI.52. Calf thymus titration absorbance spectra of 100 μM $[\text{Pt}(\text{H}_2\text{L13})](\text{PF}_6)_2$ (left) and $[\text{Pd}(\text{H}_2\text{L1})](\text{Cl})_2$ (right) at pH 4.5. The blue to red gradient represents increasing DNA concentration from 0 to 360 μM base-pairs, respectively. The inlays are Scatchard plots fitted to the McGhee–von Hippel model.

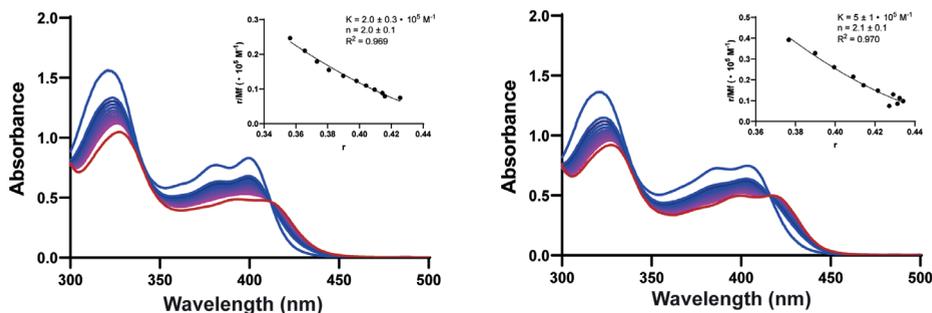


Figure SI.53. Calf thymus titration absorbance spectra of 100 μM $[\text{Pd}(\text{H}_2\text{L2})](\text{PF}_6)_2$ (left) and $[\text{Pd}(\text{H}_2\text{L3})](\text{Cl})_2$ (right) at pH 4.5. The blue to red gradient represents increasing DNA concentration from 0 to 360 μM base-pairs, respectively. The inlays are Scatchard plots fitted to the McGhee–von Hippel model.

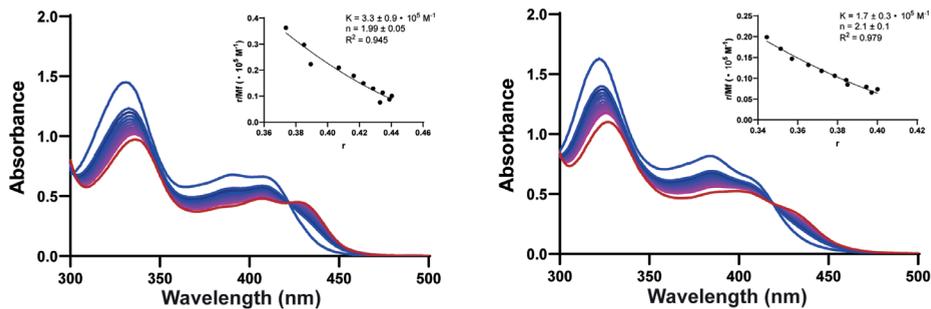


Figure SI.54. Calf thymus titration absorbance spectra of 100 μM $[\text{Pd}(\text{H}_2\text{L}_4)](\text{PF}_6)_2$ (left) and $[\text{Pd}(\text{H}_2\text{L}_5)](\text{Cl})_2$ (right) at pH 4.5. The blue to red gradient represents increasing DNA concentration from 0 to 360 μM basepairs, respectively. The inlays are Scatchard plots fitted to the McGhee-von Hippel model.

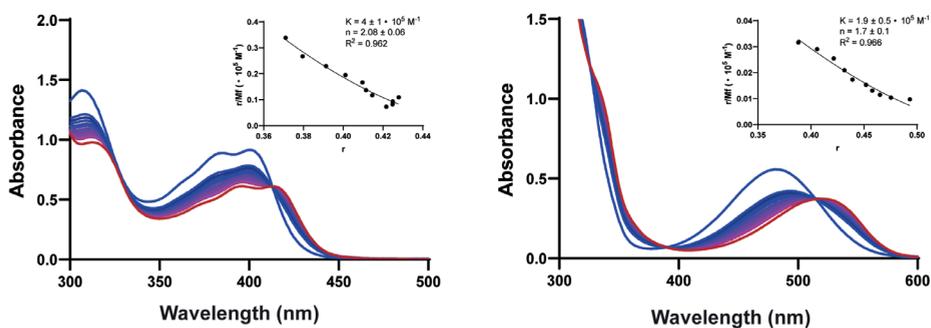


Figure SI.55. Calf thymus titration absorbance spectra of 100 μM $[\text{Pd}(\text{H}_2\text{L}_6)](\text{PF}_6)_2$ (left) and ethidium bromide (right) at pH 4.5. The blue to red gradient represents increasing DNA concentration from 0 to 360 μM basepairs, respectively. The inlay is a Scatchard plots fitted to the McGhee-von Hippel model.

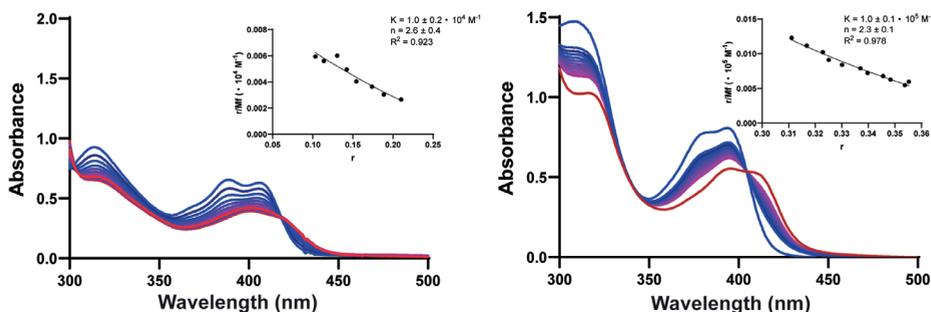


Figure SI.56. Calf thymus titration absorbance spectra of 100 μM $[\text{Pt}(\text{L}_{10})](\text{PF}_6)_2$ (left) and $[\text{Pt}(\text{L}_{11})](\text{PF}_6)_2$ (right) at pH 8. The blue to red gradient represents increasing DNA concentration from 0 to 360 μM basepairs, respectively. The inlay is a Scatchard plots fitted to the McGhee-von Hippel model.

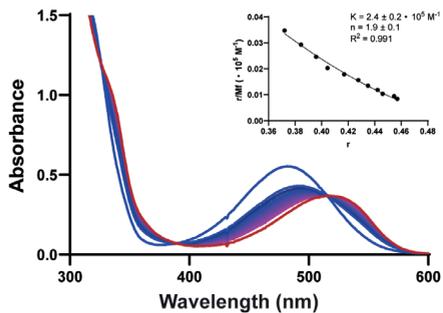


Figure SI.57. Calf thymus titration absorbance spectra of 100 μM ethidium bromide at pH 8. The blue to red gradient represents increasing DNA concentration from 0 to 360 μM basepairs, respectively. The inlay is a Scatchard plots fitted to the McGhee–von Hippel model.



Appendix II: supporting information for chapter 3

Crystal structures of diastereomers and epimers

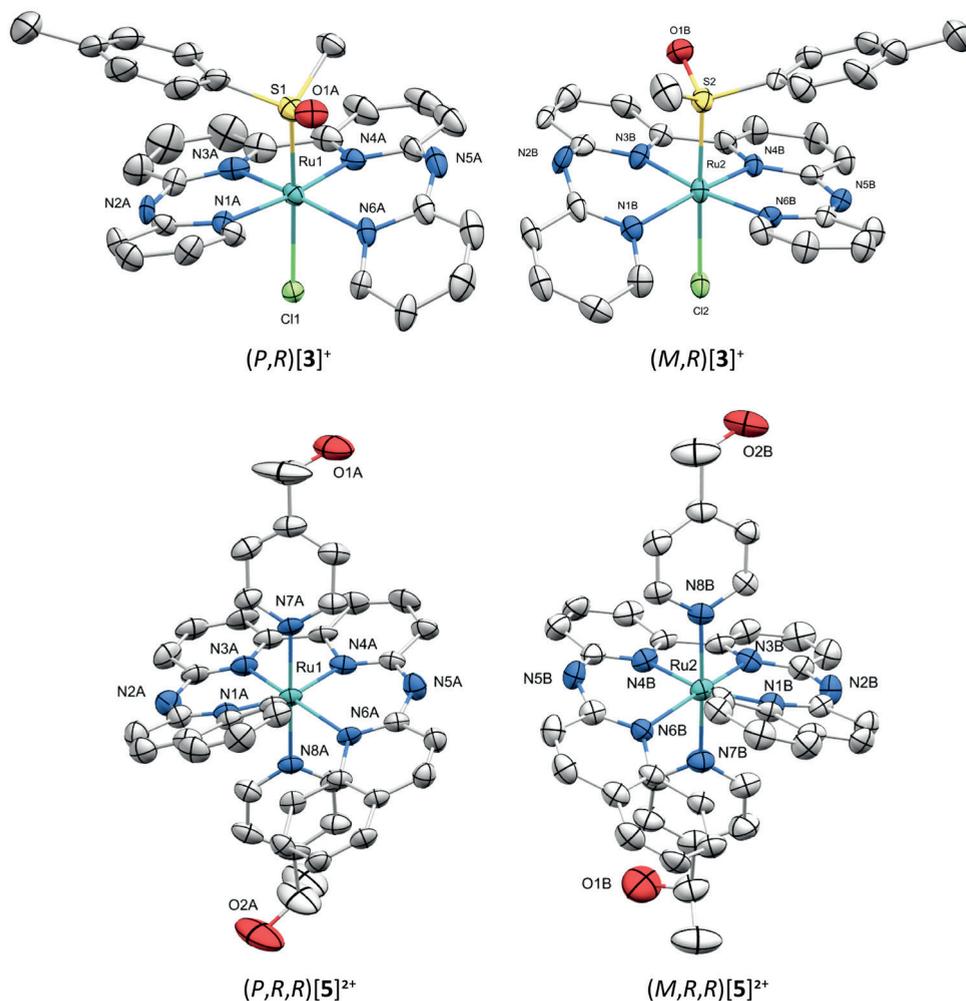


Figure SII.1. Displacement ellipsoid plots (50% probability level) for (P,R) and (M,R) diastereomers of $[3]PF_6$ and (P,R,R) and (M,R,R) epimers of $[5](PF_6)_2$ at 110(2) K. Counter ions and hydrogens have been omitted for clarity.

HPLC

Sample Name:	CG-85	Inj. Vol.:	25.0
Sample Type:	unknown	Dilution Factor:	1.0000
Program:	CJ-Chiral-prep-seperation-2ml/min	Operator:	n.a.
Inj. Date/Time:	16.11.21 15:06	Run Time:	20.09

No.	Time min	Peak Name	Type	Area mAU*min	Height mAU	Amount n.a.
TOTAL:				0.00	0.00	0.00

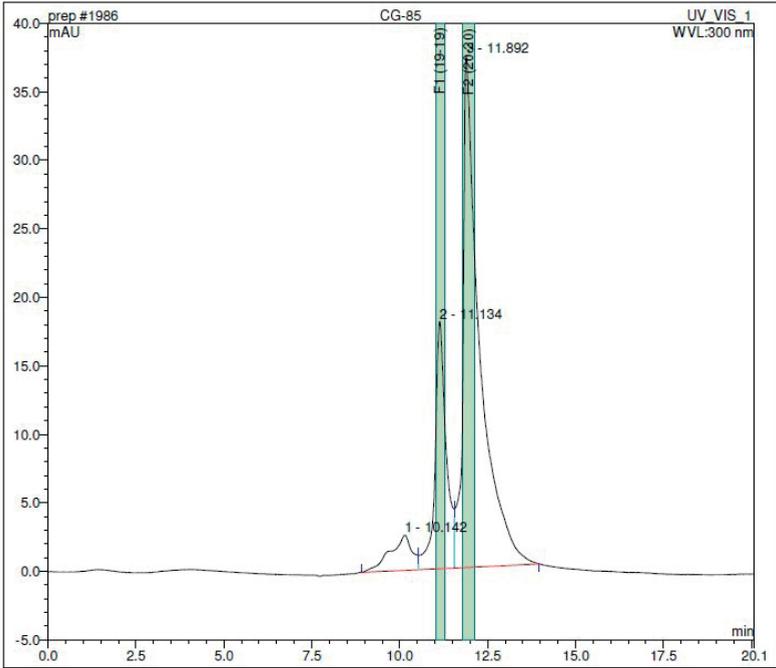


Figure SII.2. HPLC traces of [4]Cl with 0.1 M NH4Cl in MeOH eluent on the cyclobond I 2000 DMP column.



Appendix III: supporting information for chapter 4

Crystal structure

Table SIII.1. Selected distances and angles found for crystal structures of [6]²⁺

Compound	[6] ^{2+,a}
Ru1-N1	2.060(5)
Ru1-N2	1.968(5)
Ru1-N3	2.089(5)
Ru1-N4	2.118(5)
Ru1-N7	2.103(5)
Ru1-N8	2.065(5)
N1- Ru1-N3	158.7(2)
N7- Ru1-N8	79.0(2)

^a Consists of two crystallographically independent formular units for the structure. The bond distance and angles are given for molecule A.

Photochemical characterization

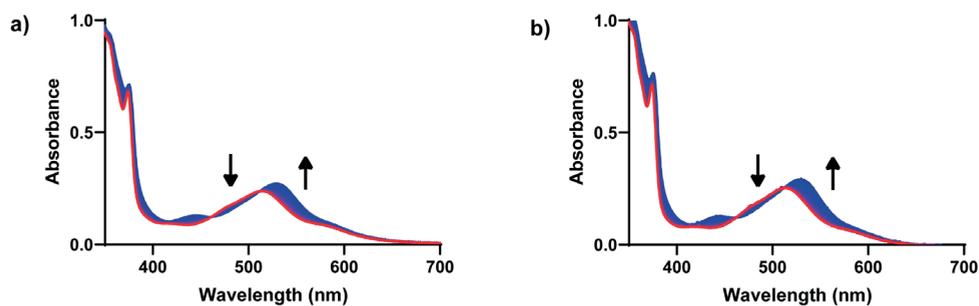
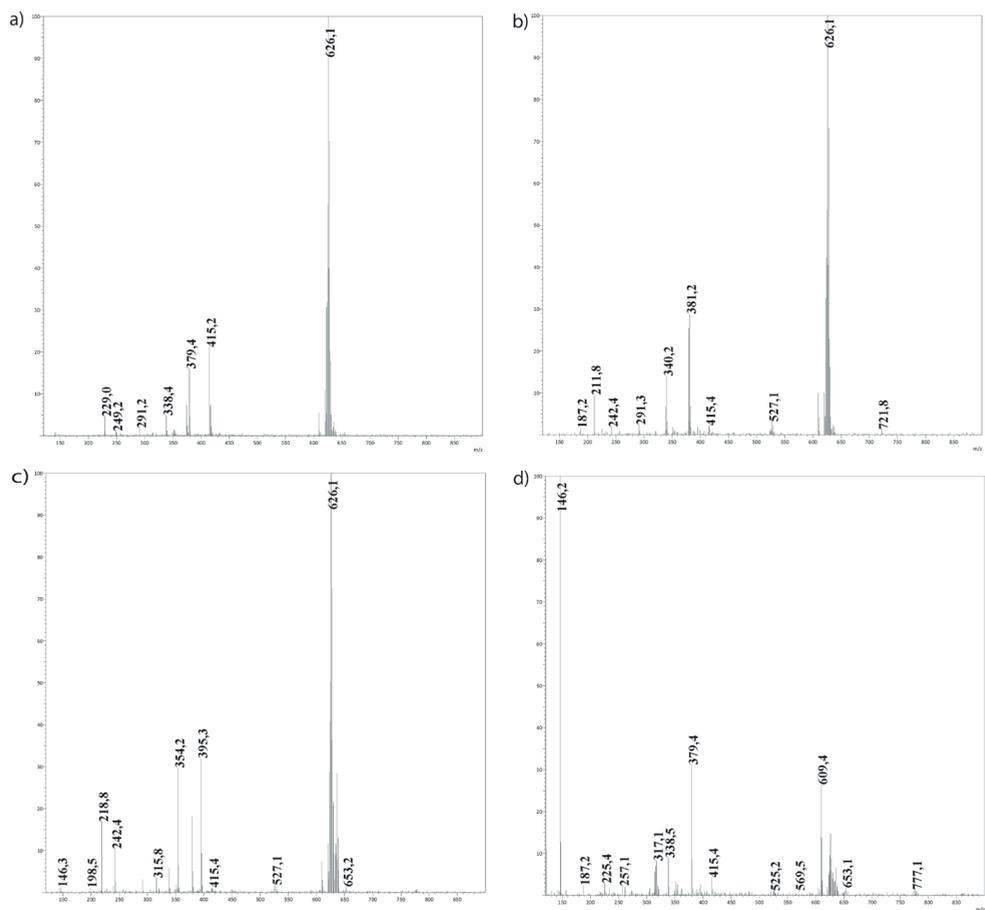


Figure SIII.1. a) Time evolution of the absorbance spectrum of compound [2]Cl₂ in MeCN (32 μM) upon green light (520 nm) irradiation, photon flux 5.7 · 10⁻⁹ mol s⁻¹, T = 295 K. b) Time evolution of the absorbance spectrum of compound [3]Cl₂ in MeCN (34 μM) upon green light (520 nm) irradiation, photon flux 5.7 · 10⁻⁹ mol s⁻¹, T = 295 K.



Facs

OMM2.5

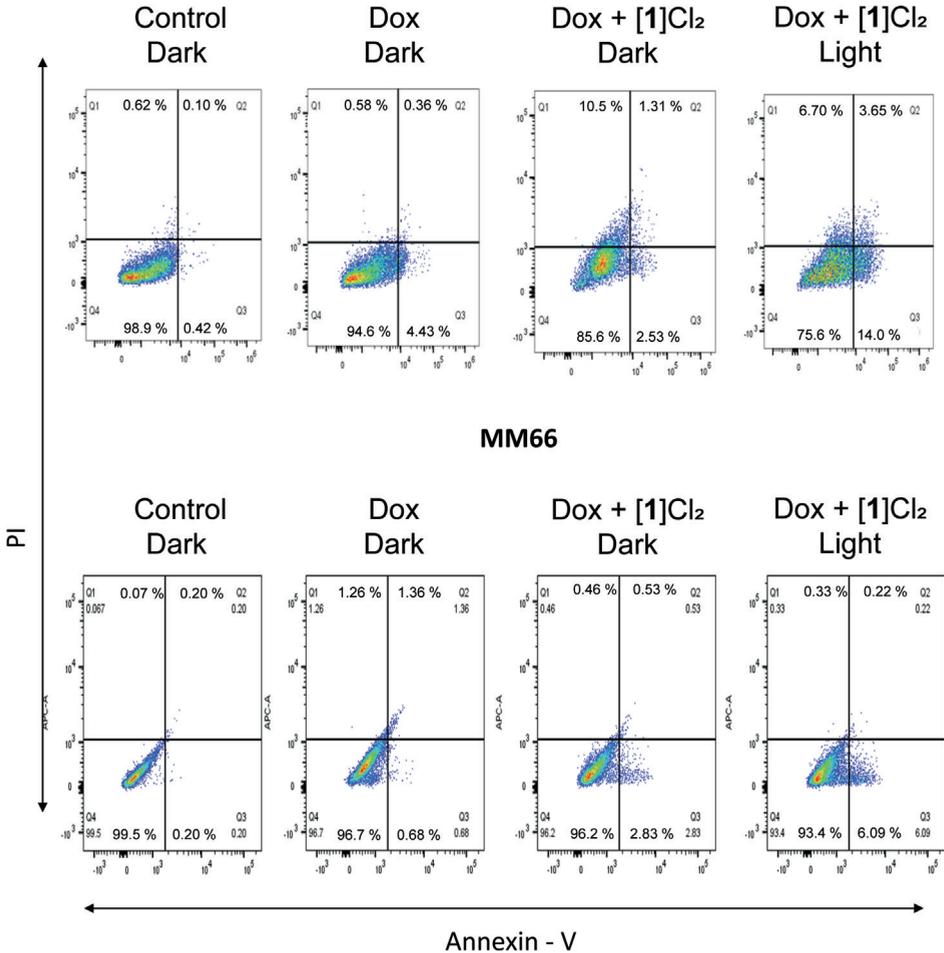


Figure SIII.3. Quantification of apoptosis by FACS in OMM2.5 and MM66 cells co-treated with [1]Cl₂ (50 μm) and Dox (500 nm) using Annexin V and Propidium Iodide (PI) staining. The cells were treated at t = 24 h with compound [1]Cl₂, followed by the addition of Dox (500 nM) at t = 48 h and light irradiation of 15 min green light (13.1 J/cm²). At t = 72 h the cells were prepared for FACS analysis.



Appendix IV: supporting information for chapter 5

NMR experiments

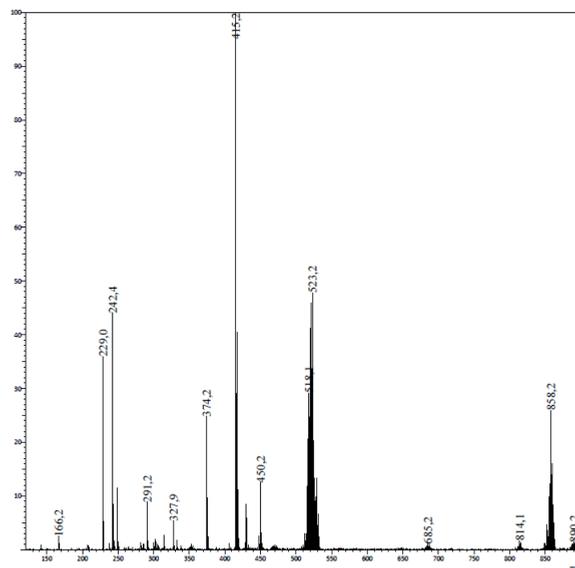


Figure SIV.1. ESI-MS measurement of the reaction product time evolution $^1\text{H-NMR}$ experiment of compound $[1]\text{Cl}_2$

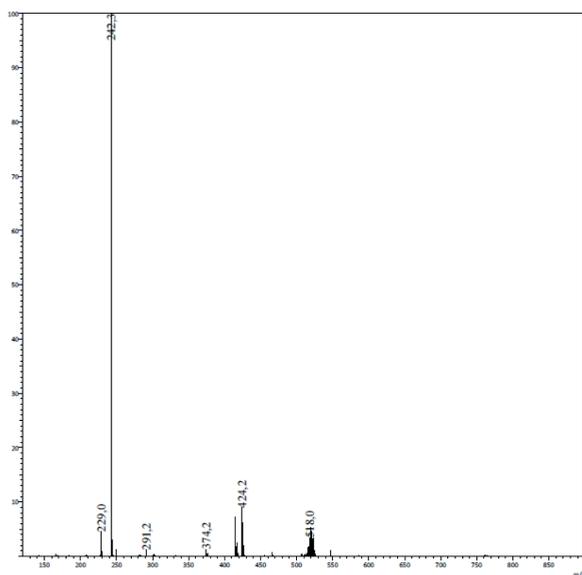


Figure SIV.2. ESI-MS measurement of the reaction product time evolution $^1\text{H-NMR}$ experiment of compound $[6]\text{Cl}_2$

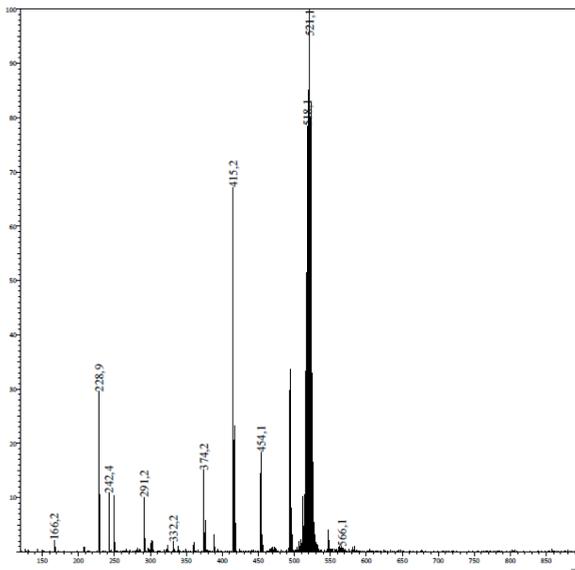


Figure SIV.3. ESI-MS measurement of the reaction product time evolution $^1\text{H-NMR}$ experiment of compound $[\mathbf{7}]\text{Cl}_2$

Quantum yield experiments

$[\text{Ru}(\text{bapbpy})(\text{B02})_2]\text{Cl}_2$ $[\mathbf{2}]\text{Cl}_2$

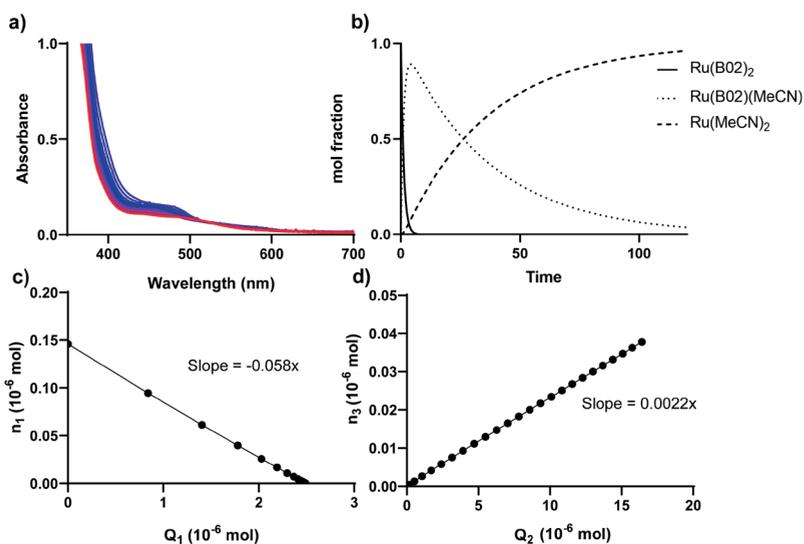


Figure SIV.4. a) Time evolution spectra of $[\mathbf{2}]\text{Cl}_2$ upon blue light irradiation (435 nm), b) reaction profile calculated by glotran for $[\mathbf{2}]\text{Cl}_2$, c) Amount of $\text{Ru}(\text{B02})_2$ (n_1) in mol vs absorbed photons by $\text{Ru}(\text{B02})_2$ (Q_1) in mol, where the slope is the quantum yield of the first substitution reaction. d) Amount of $\text{Ru}(\text{MeCN})_2$ (n_2) in mol vs absorbed photons by $\text{Ru}(\text{B02})(\text{MeCN})$ (Q_2) in mol, where the slope is the quantum yield of the second substitution reaction.

[Ru(bapbpy)(B0Ref)₂]Cl₂ [3]Cl₂

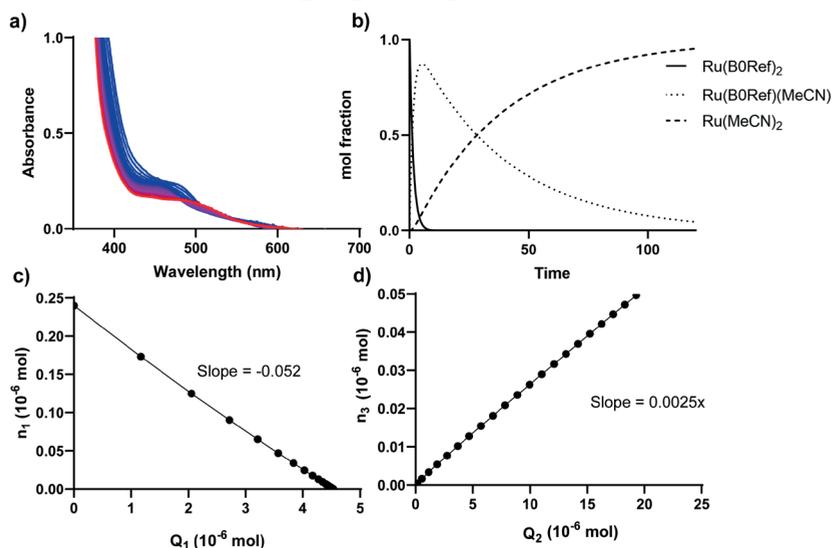


Figure SIV.5. a) Time evolution spectra of [3]Cl₂ upon blue light irradiation (435 nm), b) reaction profile calculated by gloteran for [3]Cl₂, c) Amount of Ru(B0Ref)₂ (n₁) in mol vs absorbed photons by Ru(B0Ref)₂ (Q₁) in mol, where the slope is the quantum yield of the first substitution reaction. d) Amount of Ru(MeCN)₂ (n₃) in mol vs absorbed photons by Ru(B0Ref)(MeCN) (Q₂) in mol, where the slope is the quantum yield of the second substitution reaction.

[Ru(bapbpy)(Py)₂]Cl₂ [4]Cl₂

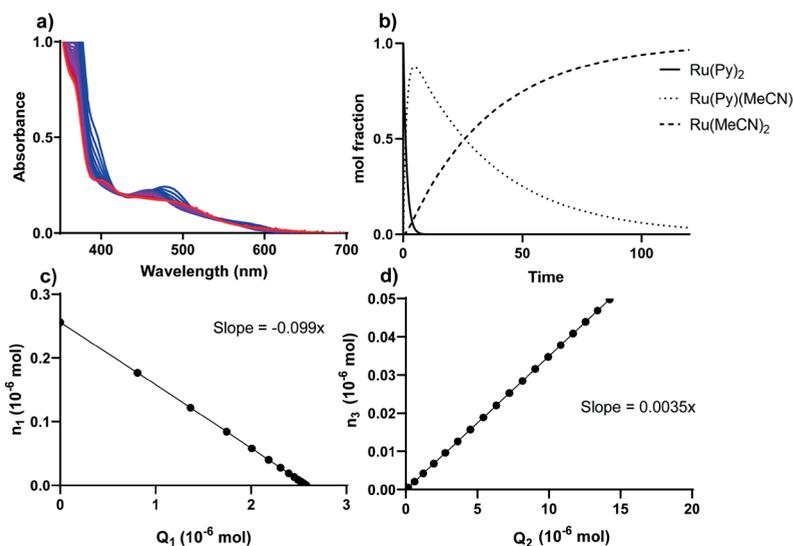


Figure SIV.6. a) Time evolution spectra of [4]Cl₂ upon blue light irradiation (435 nm), b) reaction profile calculated by gloteran for [4]Cl₂, c) Amount of Ru(Py)₂ (n₁) in mol vs absorbed photons by Ru(Py)₂ (Q₁) in mol, where the slope is the quantum yield of the first substitution reaction. d) Amount of Ru(MeCN)₂ (n₃) in mol vs absorbed photons by Ru(Py)(MeCN) (Q₂) in mol, where the slope is the quantum yield of the second substitution reaction.

[Ru(bapbpy)(BOCI)(STF31)]Cl₂ [6]Cl₂

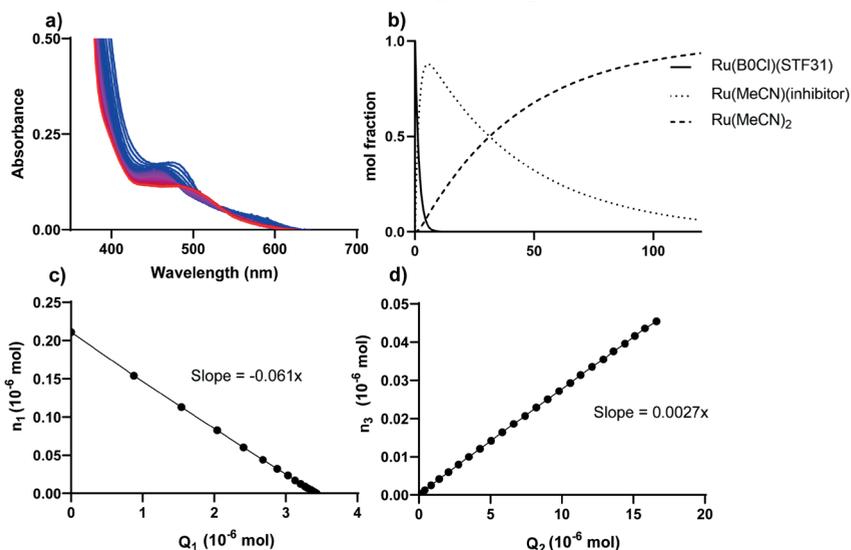


Figure SIV.7. a) Time evolution spectra of [1]Cl₂ upon blue light irradiation (435 nm), b) reaction profile calculated by gloteran for [1]Cl₂, c) Amount of Ru(BOCI)(STF31) (n₁) in mol vs absorbed photons by (BOCI)(STF31) (Q₁) in mol, where the slope is the quantum yield of the first substitution reaction. d) Amount of Ru(MeCN)₂ (n₃) in mol vs absorbed photons by (MeCN)(inhibitor) (Q₂) in mol, where the slope is the quantum yield of the second substitution reaction.

[Ru(bapbpy)(BOCI)(PIK71)]Cl₂ [7]Cl₂

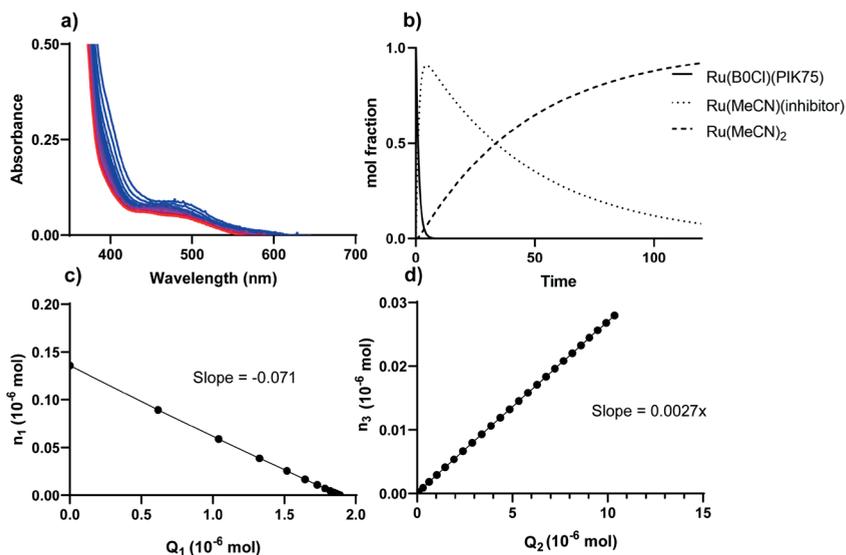


Figure 8. a) Time evolution spectra of [7]Cl₂ upon blue light irradiation (435 nm), b) reaction profile calculated by gloteran for [7]Cl₂, c) Amount of Ru(BOCI)(PIK75) (n₁) in mol vs absorbed photons by (BOCI)(PIK75) (Q₁) in mol, where the slope is the quantum yield of the first substitution reaction. d) Amount of Ru(MeCN)₂ (n₃) in mol vs absorbed photons by (MeCN)(inhibitor) (Q₂) in mol, where the slope is the quantum yield of the second substitution reaction.