Electronic Supplementary Material (ESI) for Dalton Transactions.

Controlling with light the interaction between *trans* tetrapyridyl ruthenium complexes and an oligonucleotide

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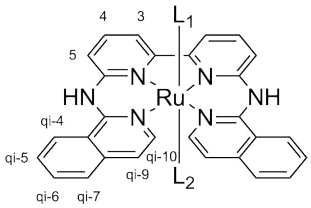
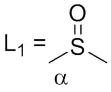
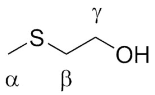
Supporting Information

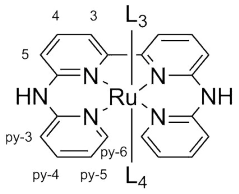
Proton numbering scheme for NMR assignment



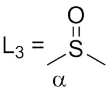
[**1**]$^{+}$
[**3**]$^{2+}$

[**1**]Cl: L_1 =  L_2 = Cl

[**3**]$(PF_6)_2$: $L_1 = L_2$ = 



[**2**]$^{+}$
[**4**]$^{2+}$

[**2**]Cl: L_3 =  L_4 = Cl

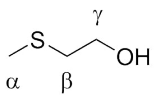
[**4**]$(PF_6)_2$: $L_3 = L_4$ = 

Figure S1. Chemical structure of [Ru(bapbpy)L_2] and of [Ru(biqbpy)L_2] and atom numbering used in NMR attribution.

Mass and UV-vis spectra for the photoreactivity studies

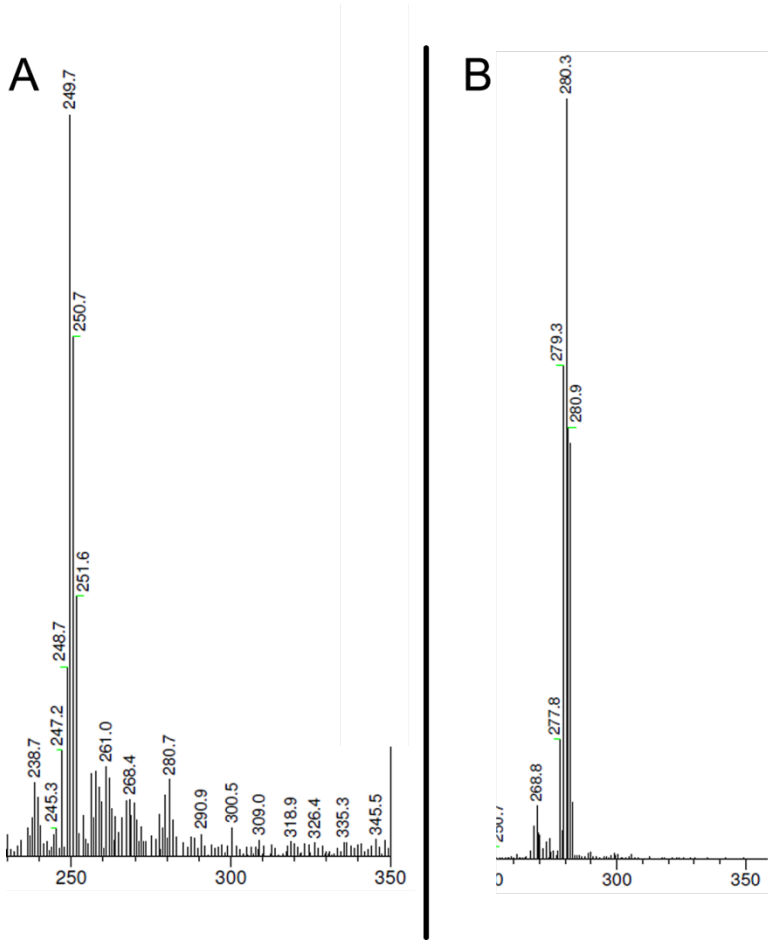


Figure S2. Mass spectra of complex [2]Cl in the dark (A) with calc. m/z = 280.0 for $[1 - Cl + CD_3OD]^{2+}$ and after blue light irradiation (B) with calc. m/z = 250.0 for $[Ru(biqbpy) + H_2O + CD_3OD]^{2+}$ and measured in MeOH. λ_{irr} = 445 nm, $\Delta\lambda_{1/2}$ = 22 nm, photon flux photon flux $\Phi = 1.81 \times 10^{-7}$ mol.s^{-1}, t_{irr} = 10 min.

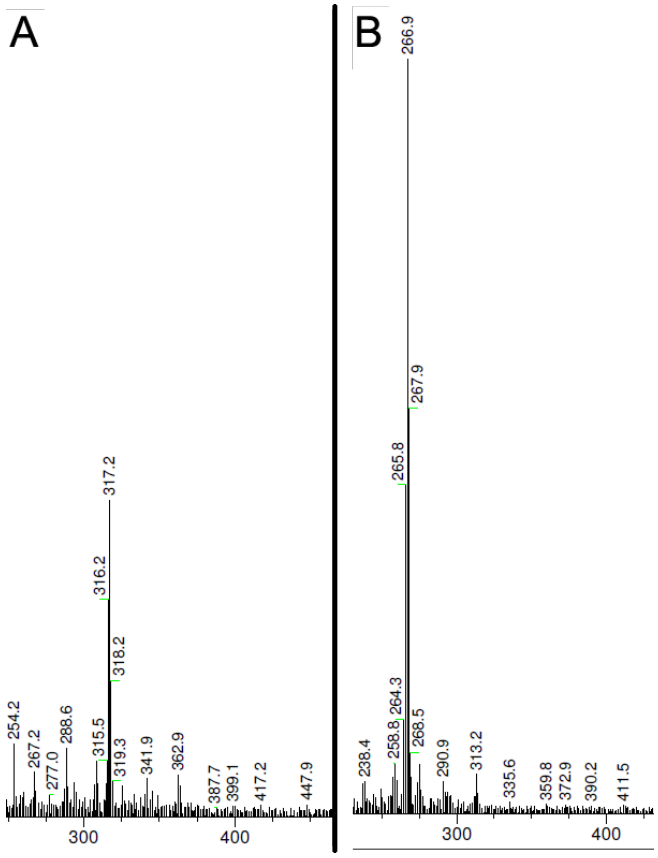


Figure S3. Mass spectra of complex [3](PF$_6$)$_2$ (A) And [4](PF$_6$)$_2$ (B) with calc. m/z = 317.1 for [Ru(biqbpy)(Hmte) – Hmte]$^{2+}$ and calc. m/z = 267.0 for [Ru(bapbpy)(Hmte) – Hmte]$^{2+}$after light-activation (λ_{irr} = 445 nm, $\Delta\lambda_{1/2}$ = 22 nm, photon flux photon flux Φ = 1.81 × 10^{-7} mol.s^{-1}, t_{irr} = 10 min) measured in MeOH.

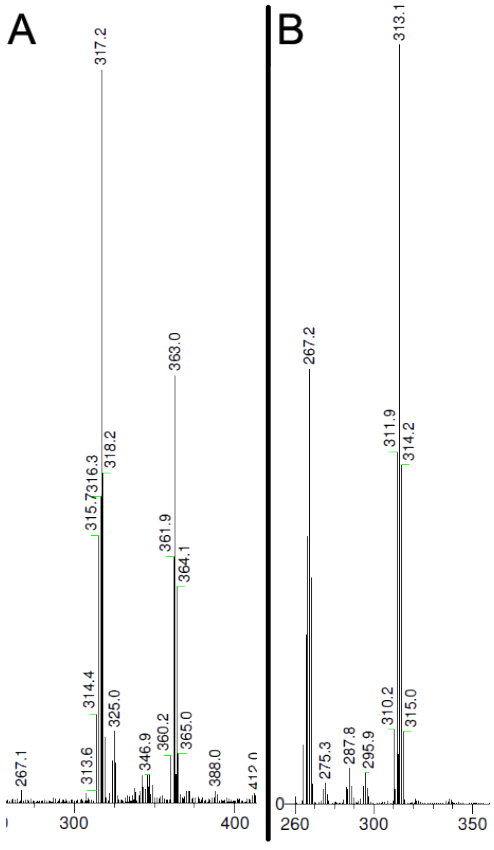


Figure S4. Mass spectra of complex [3](PF$_6$)$_2$ (A) and [4](PF$_6$)$_2$ (B) with calc. m/z = 267.0 for [Ru(biqbpy)(Hmte) – Hmte]$^{2+}$, calc. m/z = 313.1 for [Ru(biqbpy)(Hmte)$_2$]$^{2+}$, calc. m/z = 326.1 for [Ru(bapbpy)(Hmte) – Hmte]$^{2+}$, and calc. m/z =363.1 for [Ru(biqbpy)(Hmte)$_2$]$^{2+}$ measured in MeOH.

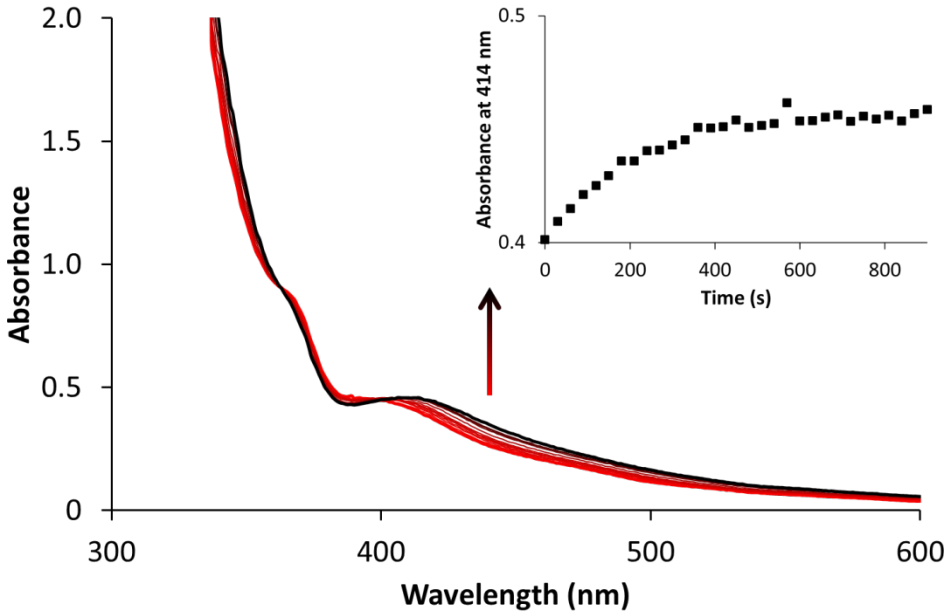


Figure S5. Evolution of the electronic absorption spectra of a solution of [4](PF$_6$)$_2$ in demineralized water (5 v/v% Acetone-d6) upon blue light irradiation (λ_{irr} = 445 nm, $\Delta\lambda_{1/2}$ = 22 nm, photon flux Φ = 1.81 × 10^{-7} mol.s^{-1}, t_{irr} = 15 min). Time: 0 min (red curve) to 15 min (black curve). Conditions [Ru]$_0$= 0.05 mM, irradiated volume was 3.0 mL at 298 K. Inset: Plot of the absorbance at 414 nm as a function of irradiation time.

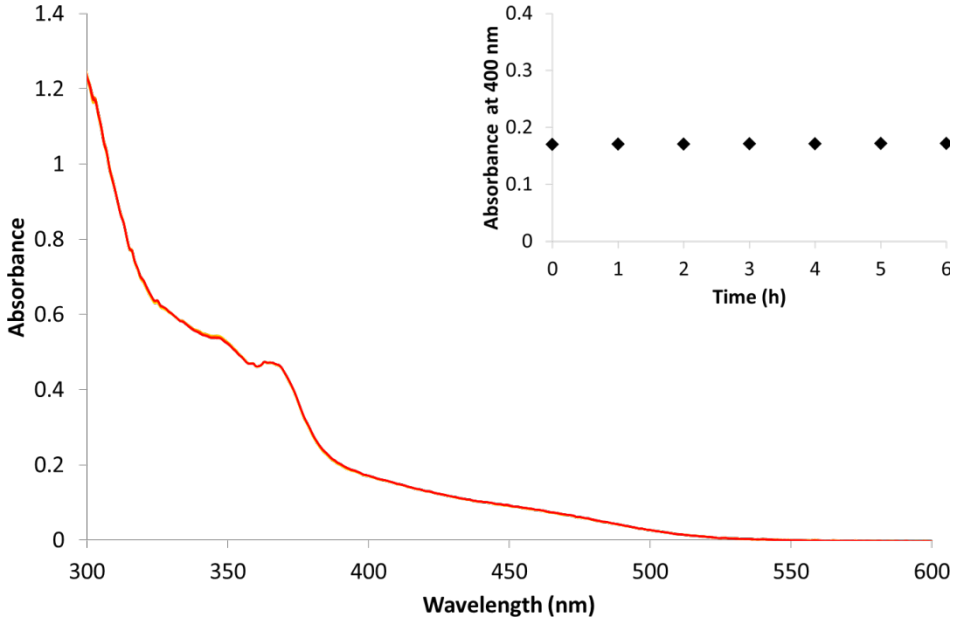


Figure S6. Stability of the UV-vis absorption spectrum of a solution of [2]Cl in demineralized water over 6 hours in the dark. Inset: evolution of absorbance at 400 nm. Conditions: [Ru] = 0.05 mM, T = 298 K.

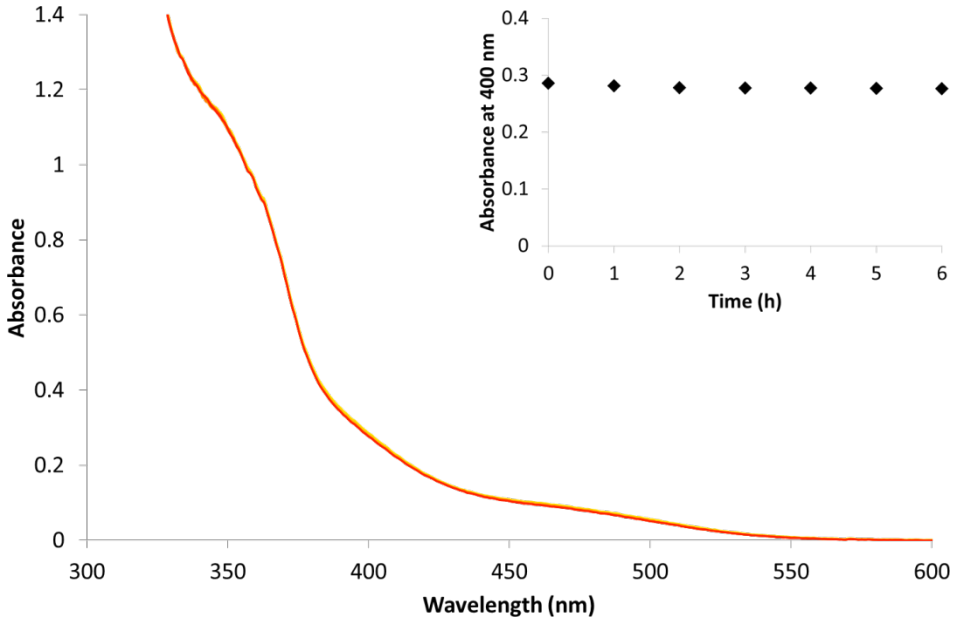


Figure S7. Stability of the UV-vis absorption spectrum of a solution of [1]Cl in demineralized water over 6 hours in the dark. Inset: evolution of absorbance at 400 nm. Conditions: [Ru] = 0.05 mM, T = 298 K.

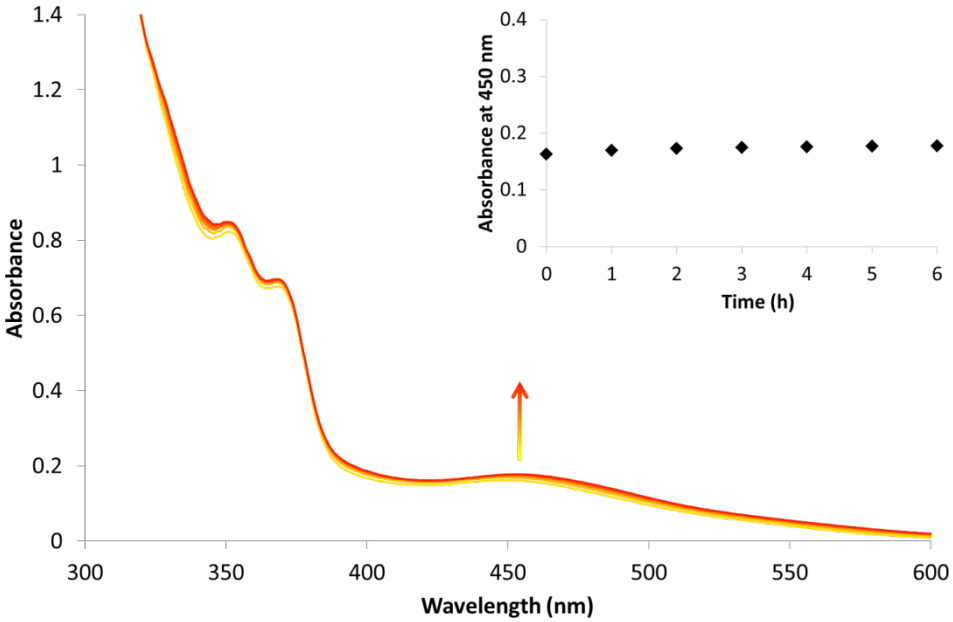


Figure S8. Evolution of UV-vis spectrum of [3](PF$_6$)$_2$ over 6 hours in demineralized water in the dark. Inset: evolution of absorbance at 400 nm. Conditions: [Ru] = 0.05 mM, T = 298 K.

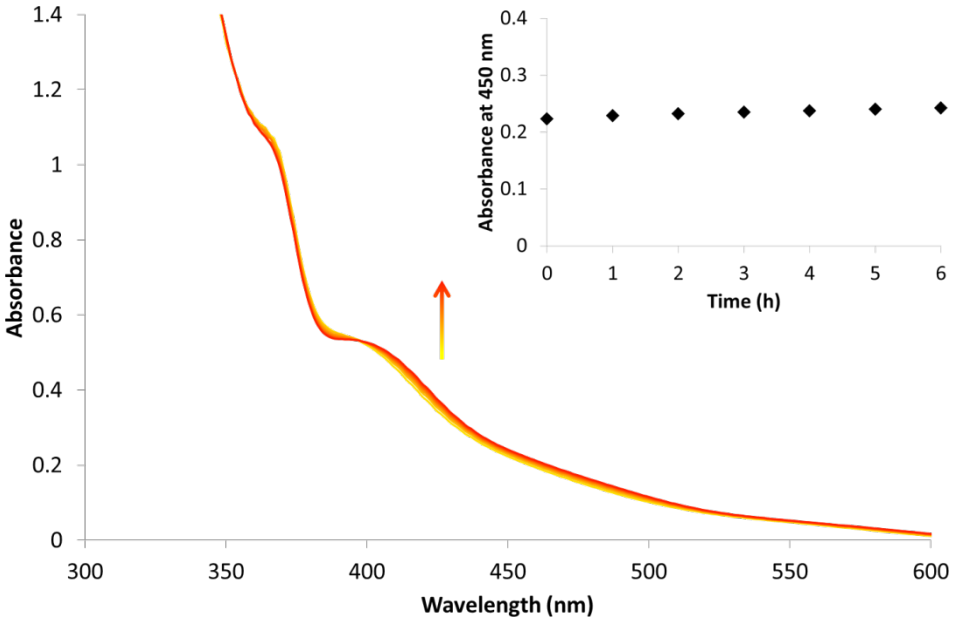


Figure S9. Evolution of UV-vis spectrum of [4](PF$_6$)$_2$ over 6 hours in demineralized water in the dark. Inset: evolution of absorbance at 400 nm. Conditions: [Ru] = 0.05 mM, T = 298 K

Gel studies

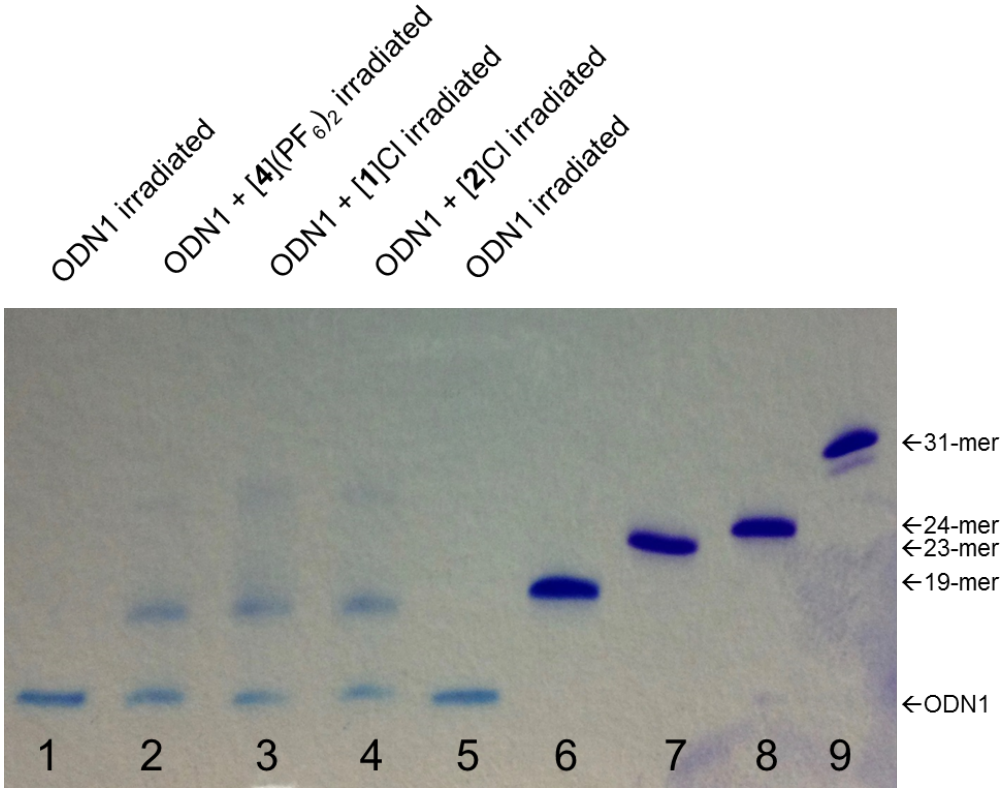


Figure S10. Light-induced binding of [1]Cl, [2]Cl, or [4]$(PF_6)_2$ (lane 2, 3, and 4) analyzed by polycramide gel including ODN1 (dark, lane 1), ODN1 (irradiated, lane 5), 19, 23, 24, 31-mer control. Conditions: T = 25 °C, [Ru] = 0.75 mM, [ODN] = 0.25 mM, Staining agent: Toluidine blue, λ_{irr} = 445 nm, $\Delta\lambda_{1/2}$ = 22 nm, photon flux $\Phi = 2.2 \times 10^{-7}$ mol.s^{-1}, t_{irr} = 10 min.

Data for the ESI-HRMS experiments with the ODN

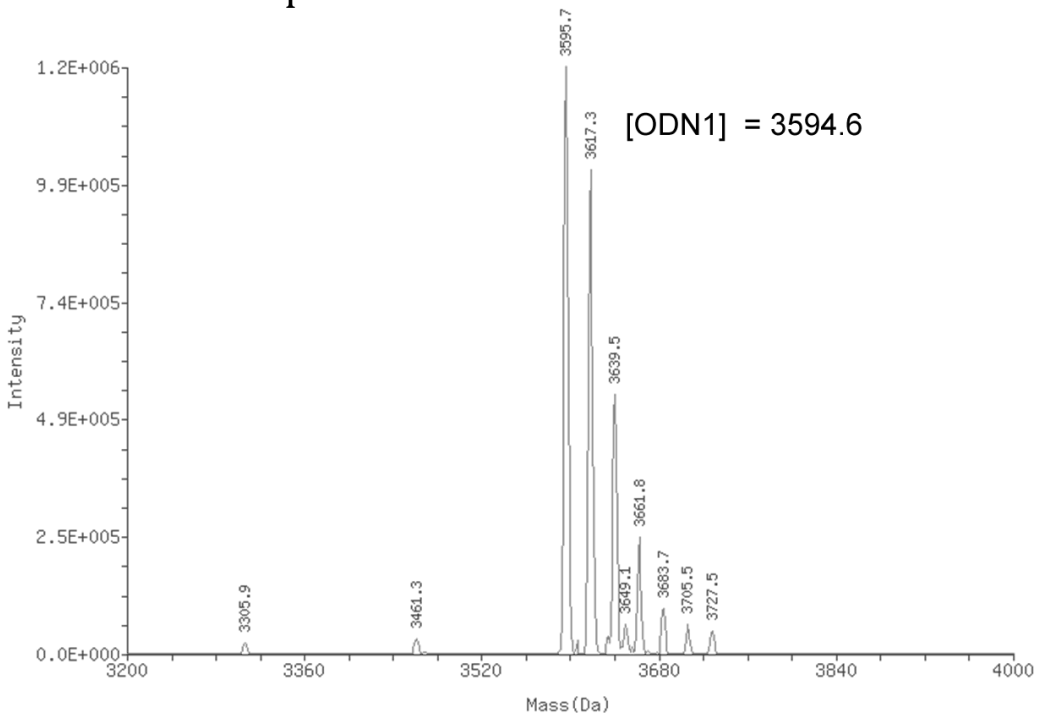


Figure S11. Deconvoluted mass spectrometry data of ODN1 (s($^{5'}$CTACGGTTTCAC$^{3'}$), see Scheme S12, or $C_{116}H_{149}N_{40}O_{72}P_{11}$). Conditions: [ODN] = 0.03 mM, incubation time 6 h, T = 298 K.

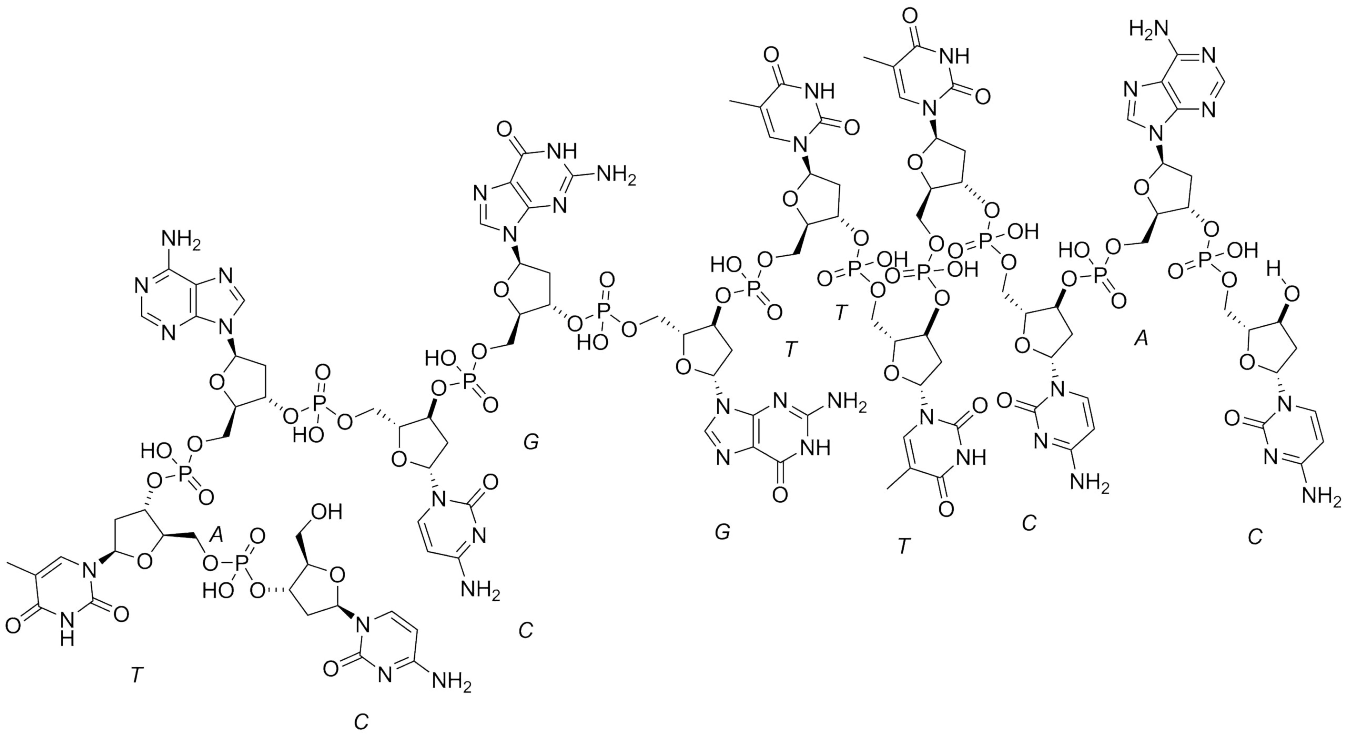


Figure S12. Chemical structure of ODN1 (s($^{5'}$CTACGGTTTCAC$^{3'}$). Molecular formula is $C_{116}H_{149}N_{40}O_{72}P_{11}$, m/z = 3595.64.

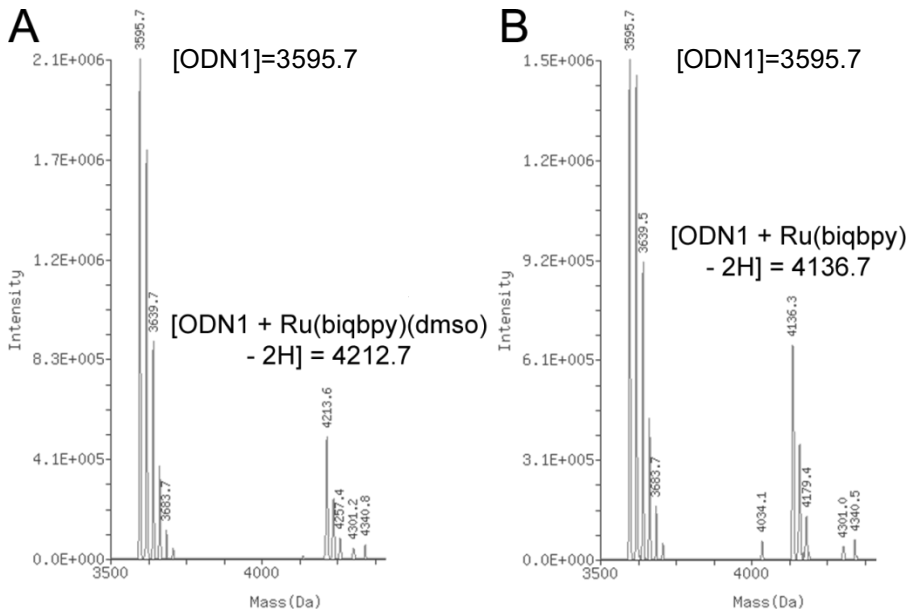


Figure S13. Deconvoluted mass spectrometry data of ODN1 and [1]Cl incubated in the dark (A) or after light-activation (B). Conditions: [ODN] = 0.03 mM, [Ru] = 0.09 mM, $t_{incubation}$ = 6 h, T = 298 K, λ_{irr} = 445 nm, $\Delta\lambda_{1/2}$ = 22 nm, photon flux Φ = 2.17 × 10^{-7} mol.s^{-1}.

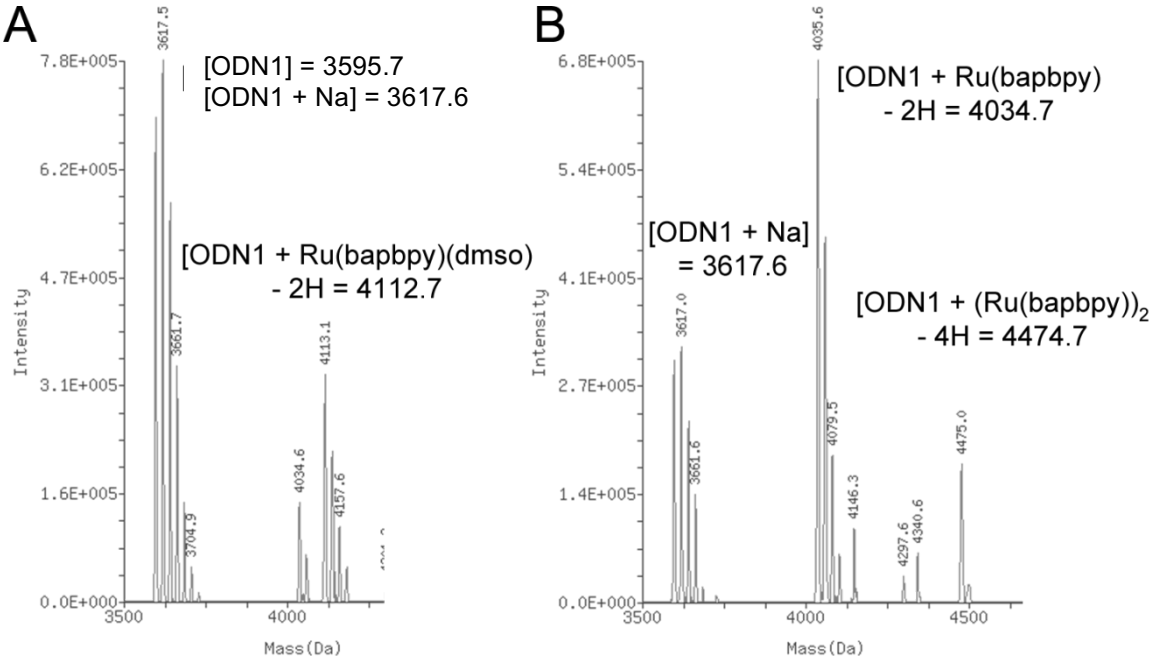


Figure S14. Deconvoluted mass spectrometry data of ODN1 and [2]Cl incubated in the dark (A) or after light-activation (B). Conditions: [ODN] = 0.03 mM, [Ru] = 0.09 mM, $t_{incubation}$ = 6 h, T = 298 K, λ_{irr} = 445 nm, $\Delta\lambda_{1/2}$ = 22 nm, photon flux Φ = 2.17 × 10^{-7} mol.s^{-1}.

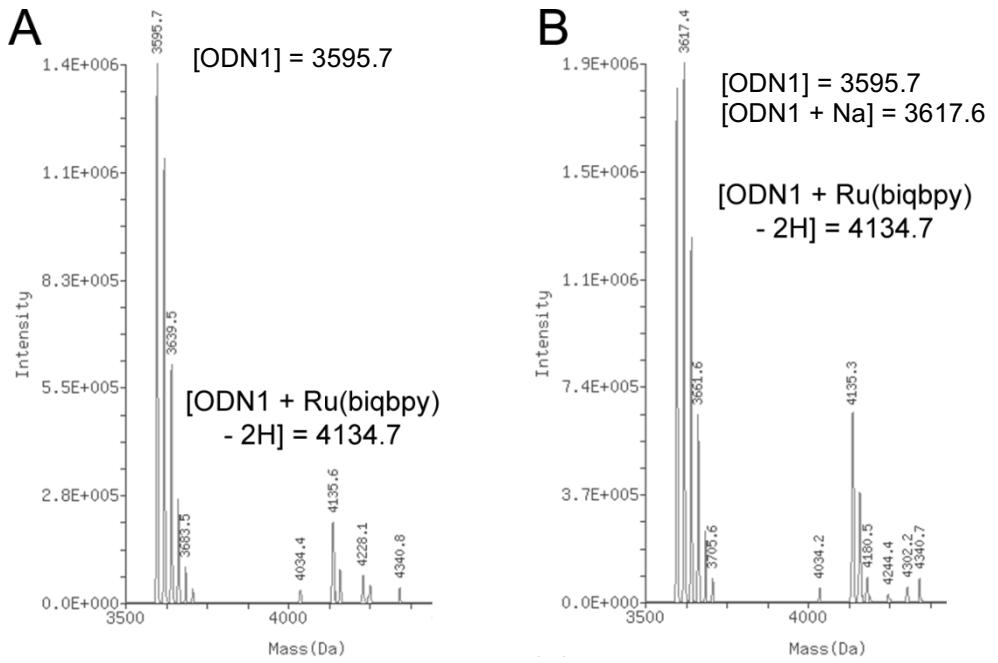


Figure S15. Deconvoluted mass spectrometry data of ODN1 and [3](PF6)$_2$ incubated in the dark (A) or after light-activation (B). Conditions: [ODN] = 0.03 mM, [Ru] = 0.09 mM, $t_{incubation}$ = 6 h, T = 298 K λ_{irr} = 445 nm, $\Delta\lambda_{1/2}$ = 22 nm, photon flux $\Phi = 2.17 \times 10^{-7}$ mol.s^{-1}.

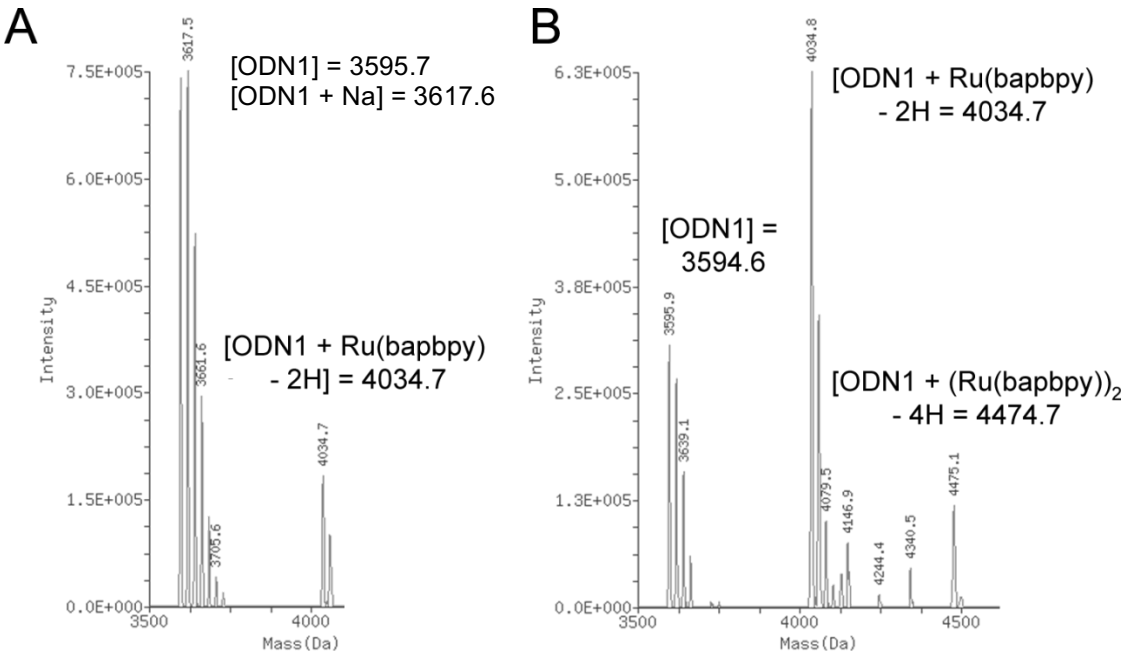


Figure S16. Deconvoluted mass spectrometry data of ODN1 and [4](PF6)$_2$ incubated in the dark (A) or after light-activation (B). Conditions: [ODN] = 0.03 mM, [Ru] = 0.09 mM, $t_{incubation}$ = 6 h, T = 298 K, λ_{irr} = 445 nm, $\Delta\lambda_{1/2}$ = 22 nm, photon flux $\Phi = 2.17 \times 10^{-7}$ mol.s^{-1}.