Supporting Information

Reductive and Oxidative DNA Damage by Photoactive Platinum(II) Intercalators

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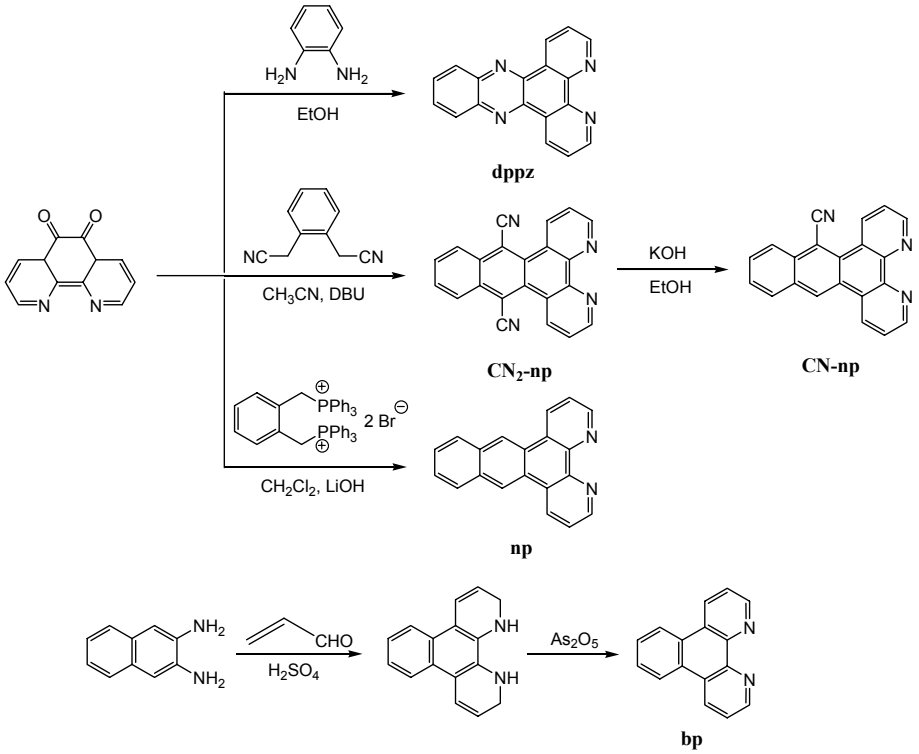
Supporting Information Available: Scheme depicting the synthesis of the ligand, glassy emission spectra, CIF file and structural parameters of crystal structure of **2**·$(DMF)_3$·$(H_2O)_2$, additional figures of the UV-vis traces of Pt(II) complexes upon DNA titration and HPLC traces for photoreactions with ^{Cp}C, $d^{Cp}G$ and DNAs. This material is available free of charge via the Internet at http://pubs.acs.org.



Scheme S1 Ligand Synthesis

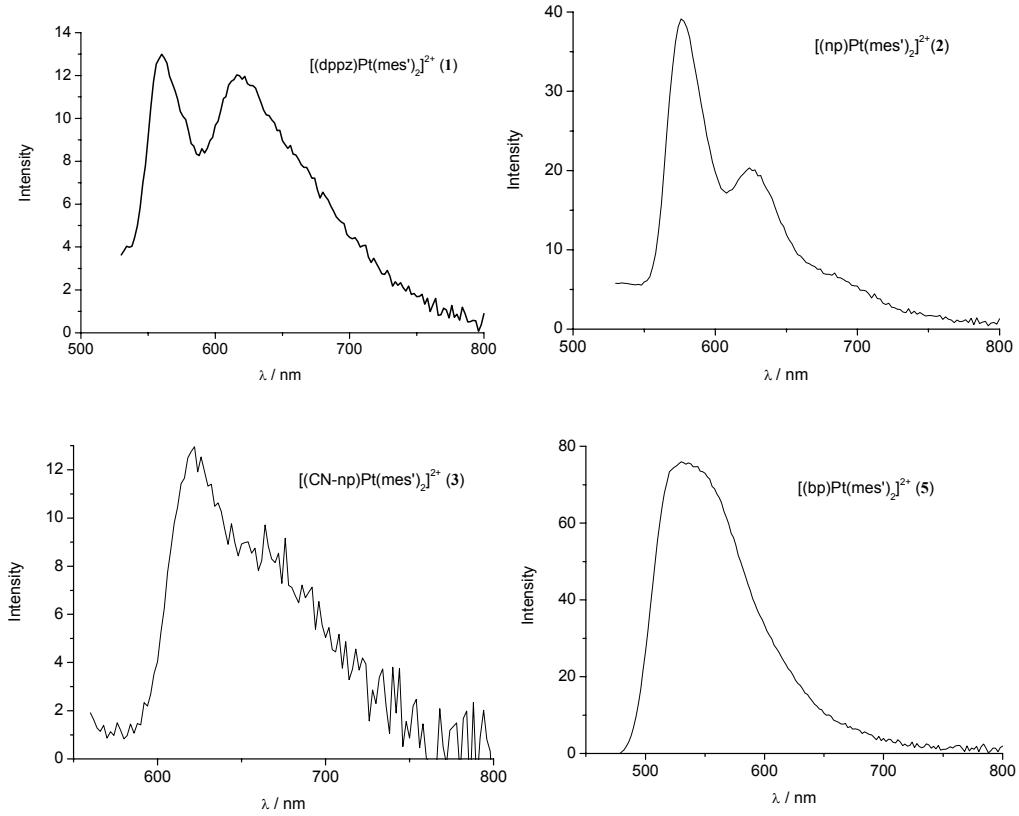


Figure S1 Emission spectra of complex **1**–**3** and **5** in 10 M LiCl at 77 K, λ_{ex} = 370 nm, concentration ~ 5×10^{-5} M.

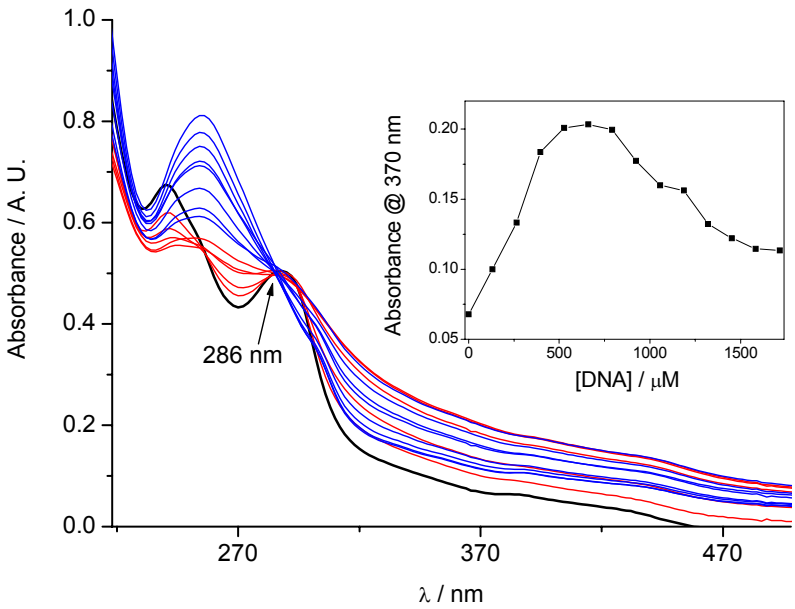


Figure S2 Absorption traces of the titration of a 20-mer DNA into a 20 μM [(np)Pt(mes')$_2$]Cl$_2$ (**2**) in a buffer of 20 mM sodium phosphate and 50 mM NaCl, pH 7.0. Inset: Plot of the absorbance at 370 nm against the amount of DNA added.

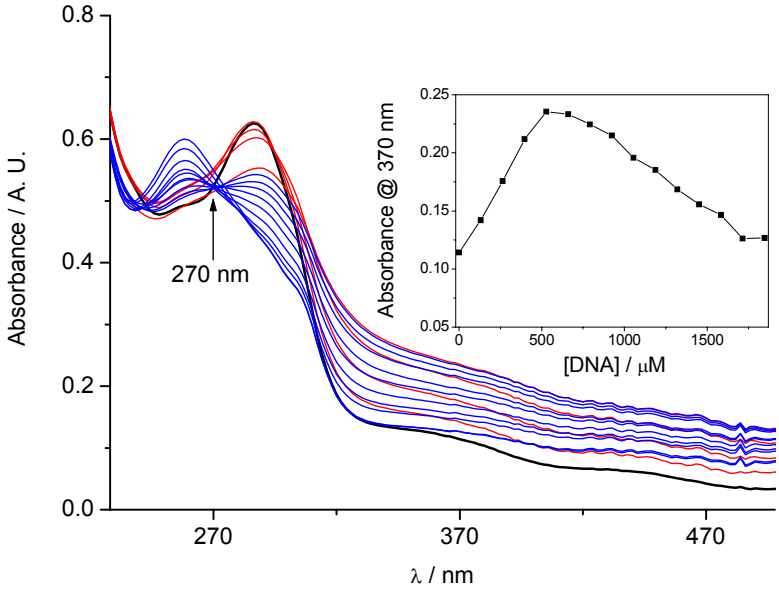


Figure S3 Absorption traces of the titration of a 20-mer DNA into a 20 μM [(CN-np)Pt(mes')$_2$]Cl$_2$ (**3**) in a buffer of 20 mM sodium phosphate and 50 mM NaCl, pH 7.0. Inset: Plot of the absorbance at 370 nm against the amount of DNA added.

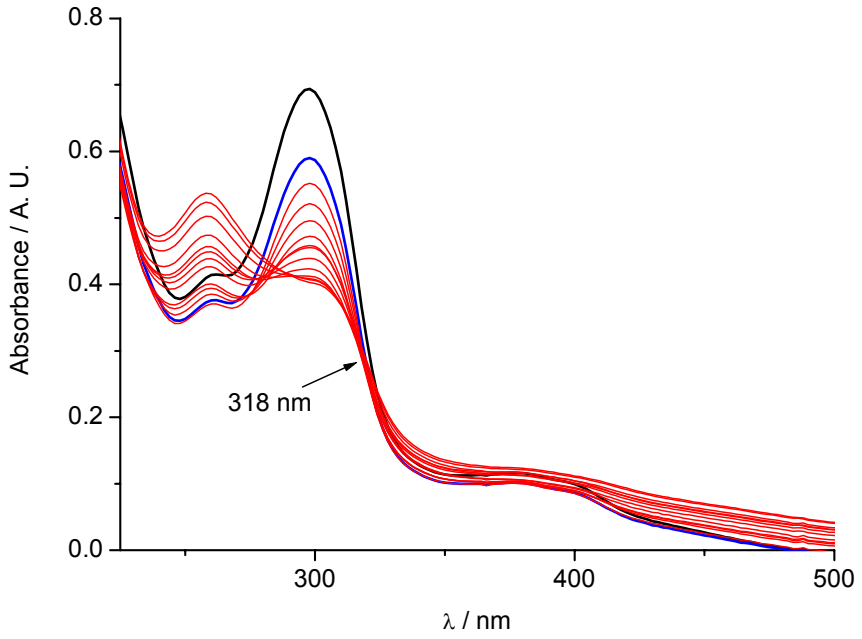


Figure S4 Absorption traces of the titration of a 20-mer DNA into a 20 μM $[(CN_2\text{-np})Pt(mes')_2]Cl_2$ (**4**) in a buffer of 20 mM sodium phosphate and 50 mM NaCl, pH 7.0.

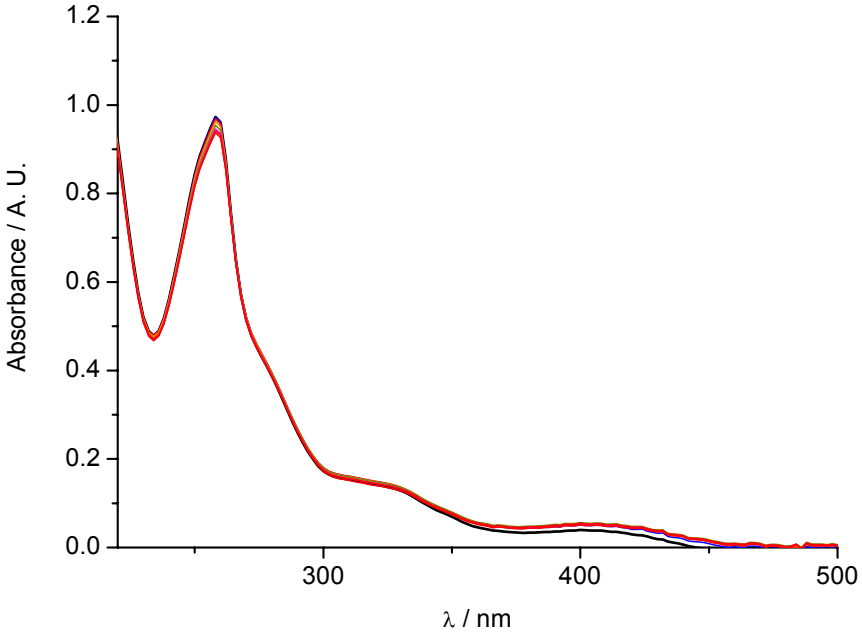


Figure S5 Absorption traces of the titration of a 20-mer DNA into a 20 μM $[(bp)Pt(mes')_2]Cl_2$ (**5**) in a buffer of 20 mM sodium phosphate and 50 mM NaCl, pH 7.0.

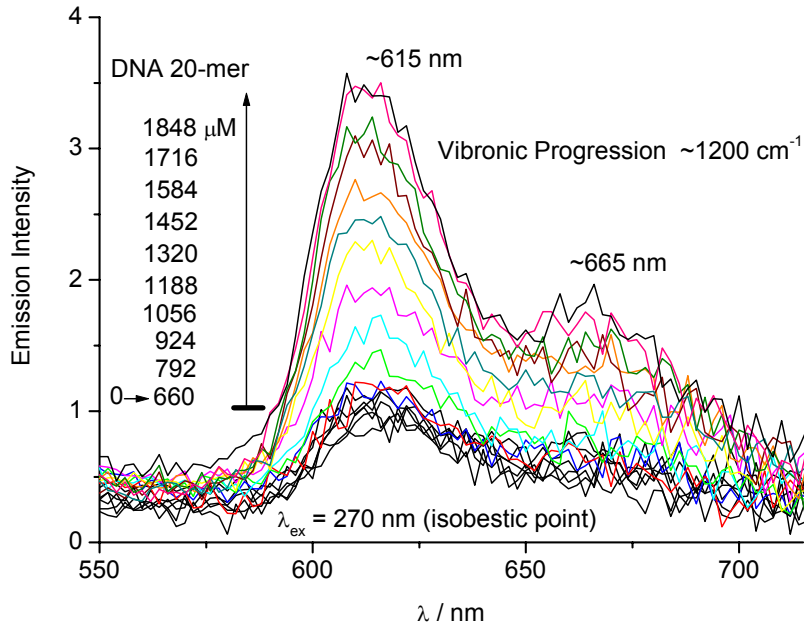


Figure S6 Emission traces of the titration of a 20-mer DNA into a 20 μM [(CN-np)Pt(mes')$_2$]Cl$_2$ (**3**) in a buffer of 20 mM sodium phosphate and 50 mM NaCl, pH 7.0.

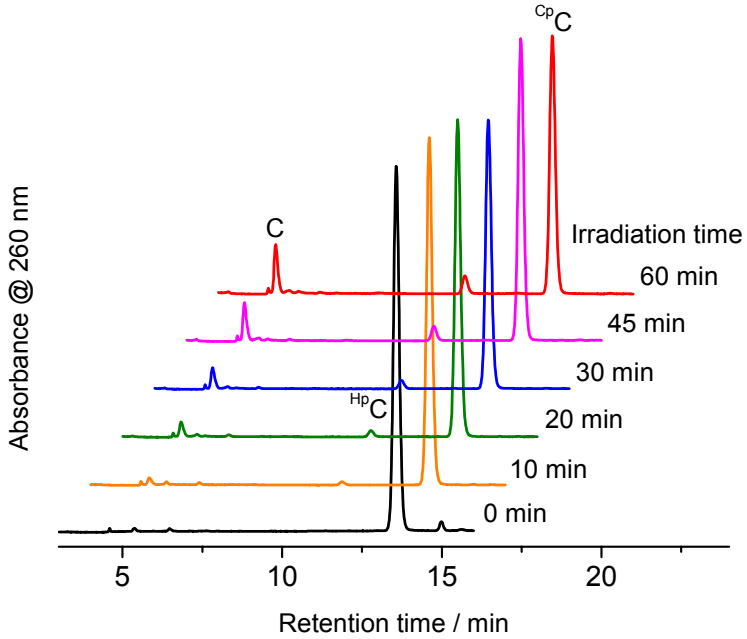


Figure S7 HPLC traces for photoreaction of ^{Cp}C nucleoside in the presence of [(CN-np)Pt(mes')2]$^{2+}$ complex. Conditions: 30 μL aliquot, 500 μM ^{Cp}C; 500 μM Pt(II) complex; 50 mM NaCl; 20 mM NaP buffer; pH 7.0; 370 nm (~12.5 mW).

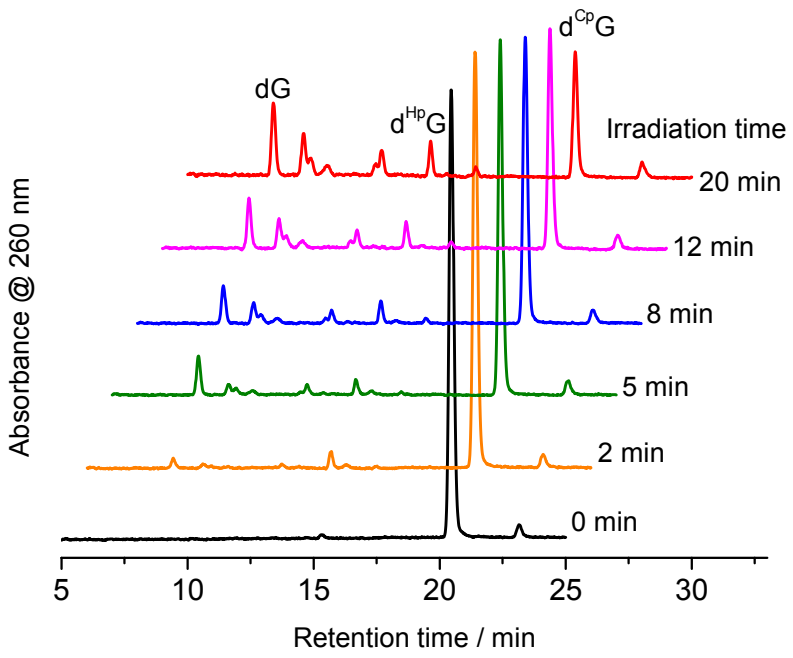


Figure S8 HPLC traces for photoreaction of ^{Cp}C nucleoside in the presence of [(np)Pt(mes')2]$^{2+}$ complex. Conditions: 30 µL aliquot, 20 µM ^{Cp}C; 20 µM Pt(II) complex; 50 mM NaCl; 20 mM NaP buffer; pH 7.0; 370 nm (~12.5 mW).

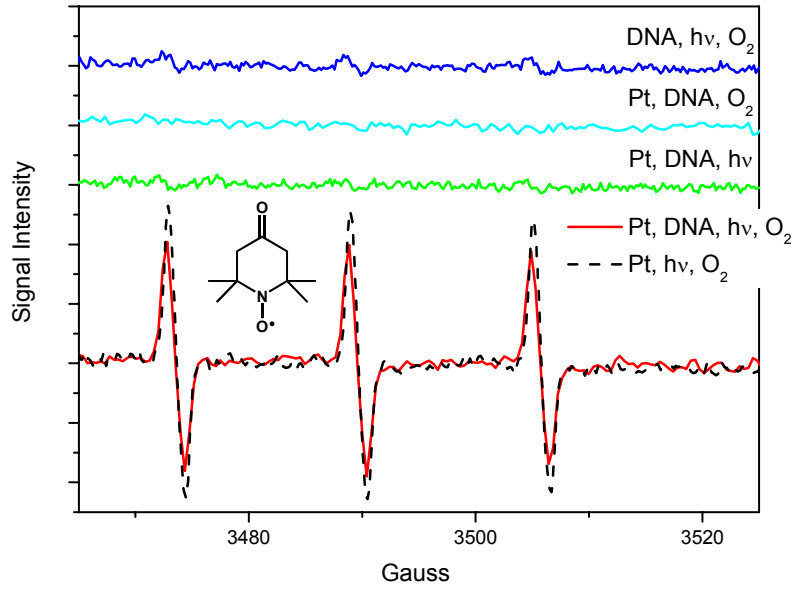
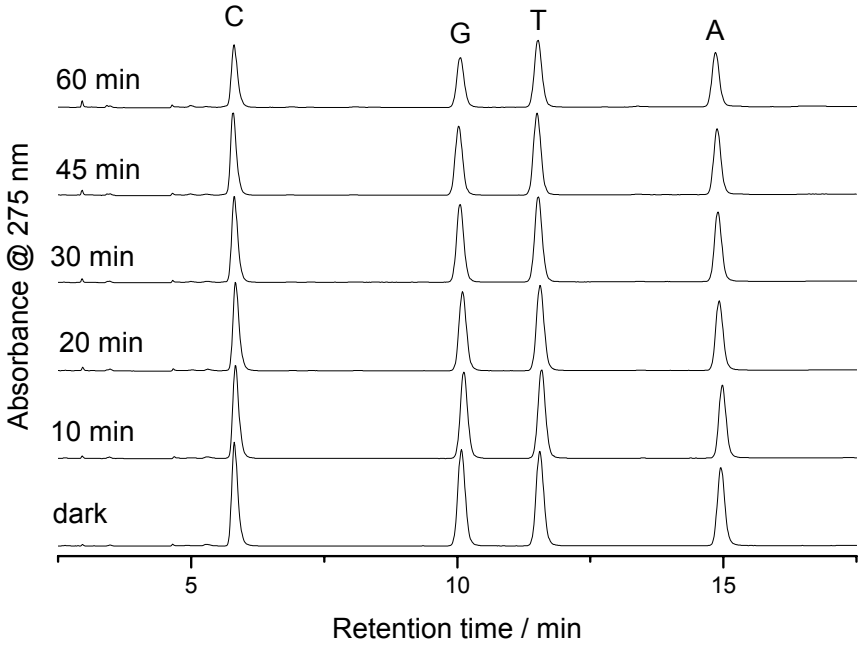


Figure S9 EPR spectra of the mixtures of complex **1** and TEMP. General conditions: 150 μL aliquot; 20 mM TEMP; 500 μM $[(dppz)Pt(Mes')_2]^{2+}$; 20 μM DNA where applicable; 50 mM NaCl; 20 mM NaP buffer; pH 6.99; room temperature; 370 nm (~8 mW) irradiation 10 min where applicable; three freeze-pump-thaw cycles where applicable; X-band EPR spectra were obtained on a Bruker EMX spectrometer equipped with a rectangular cavity working in the TE_{102} mode; EPR parameters: receiver gain = 1×10^4, modulation amplitude = 2 G, microwave power = 10 mW, 5 scans.



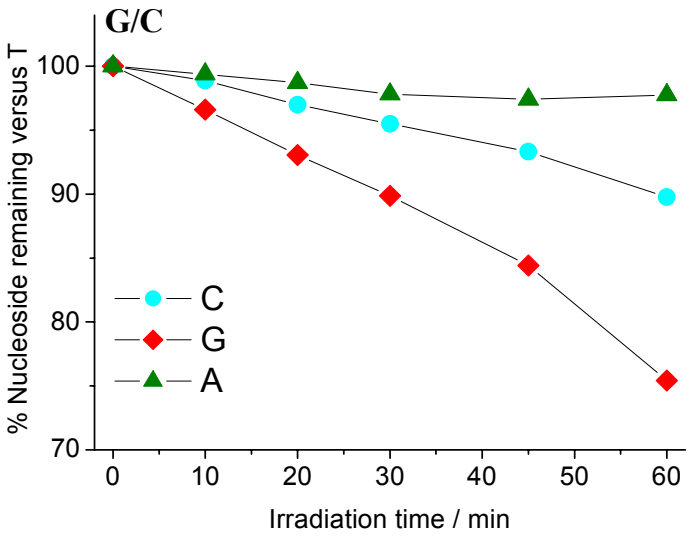
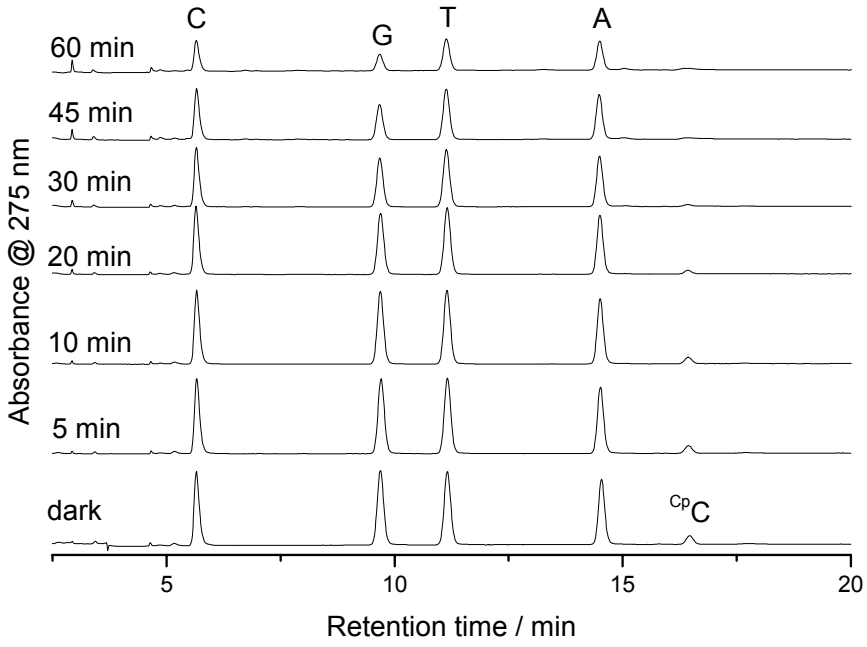


Figure S10 HPLC traces of DNA base damages during the photoreaction of 5 μM DNA duplex **G**/**C** and 50 μM $[(dppz)Pt(mes')_2]^{2+}$ complex in buffer in the presence of O_2.



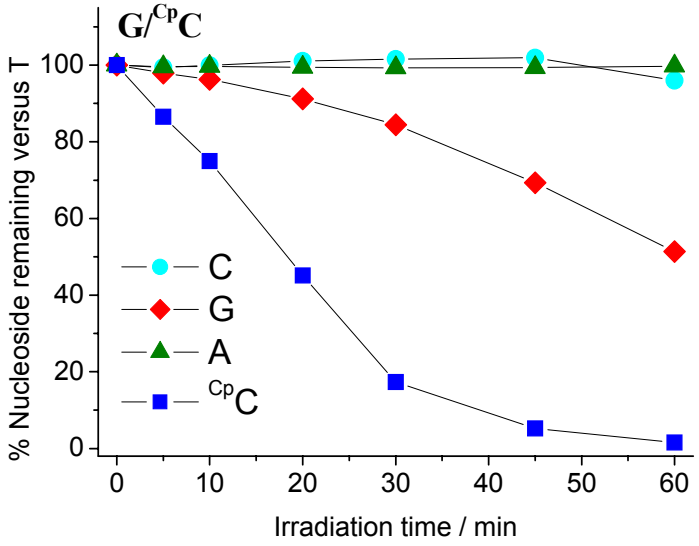


Figure S11 HPLC traces of DNA base damages during the photoreaction of 5 μM DNA duplex **G/^{Cp}C** and 50 μM $[(dppz)Pt(mes')_2]^{2+}$ complex in buffer in the presence of O_2.

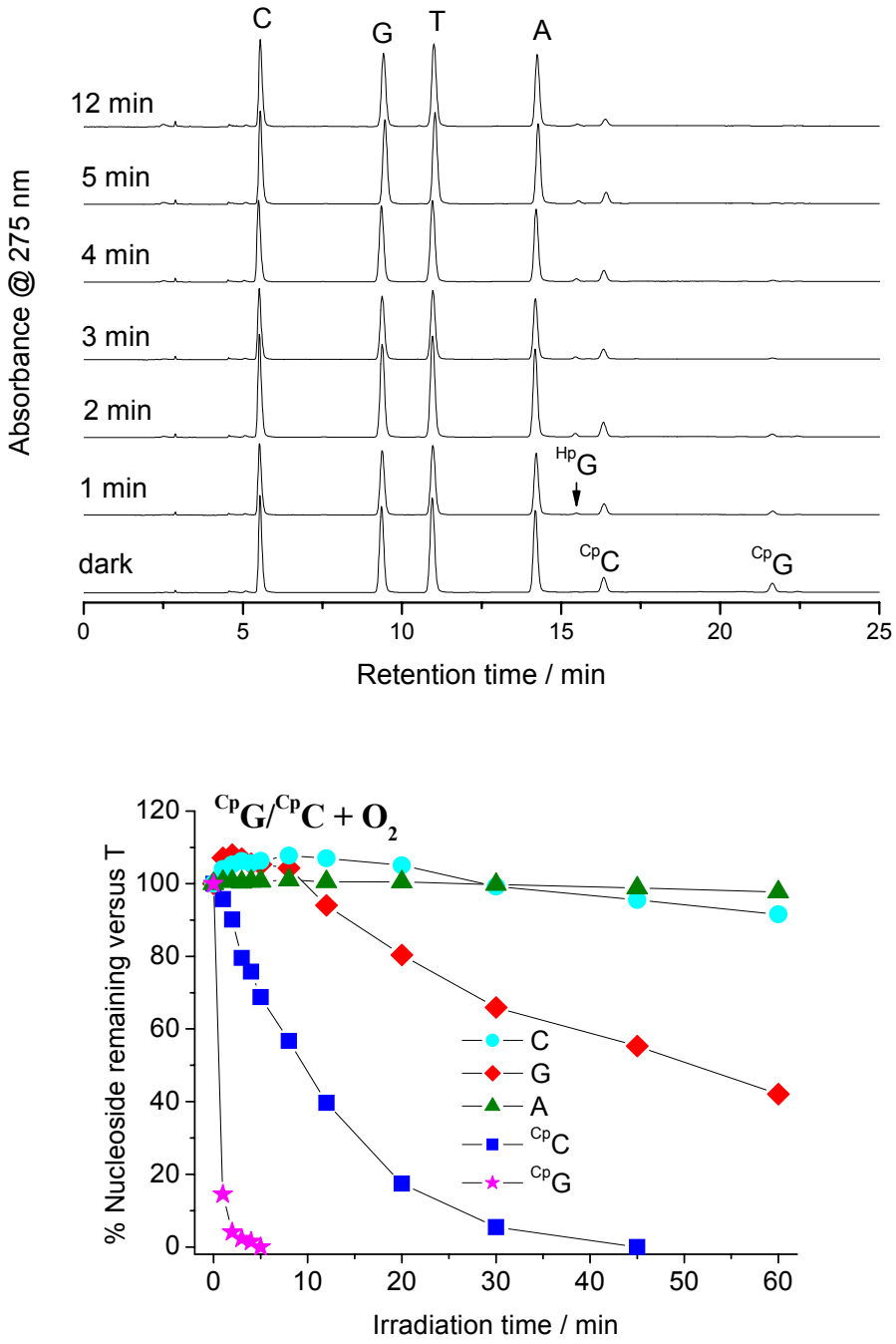


Figure S12 HPLC traces of DNA base damages during the photoreaction of 5 μM DNA duplex **^{Cp}G/^{Cp}C** and 50 μM $[(dppz)Pt(mes')_2]^{2+}$ complex in buffer in the presence of O_2.

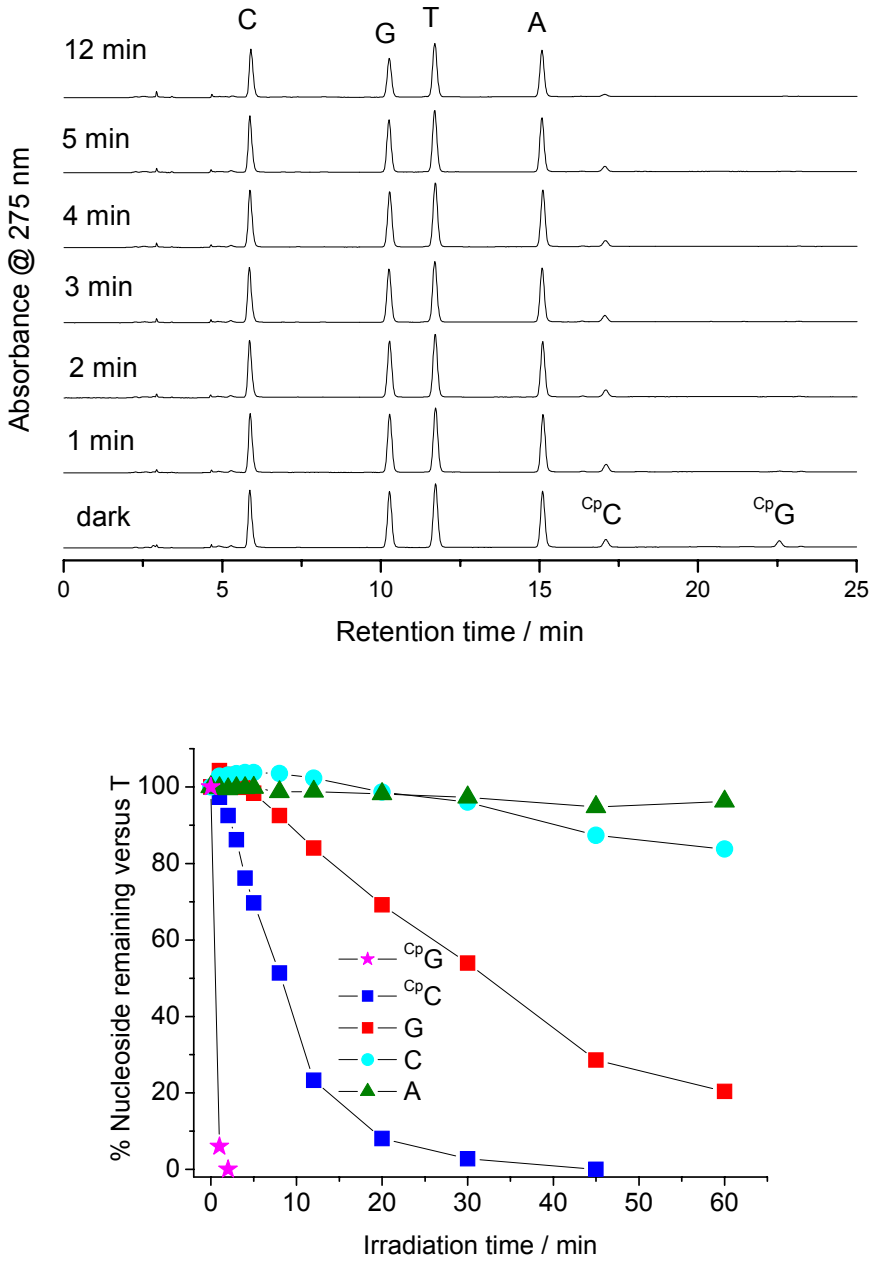
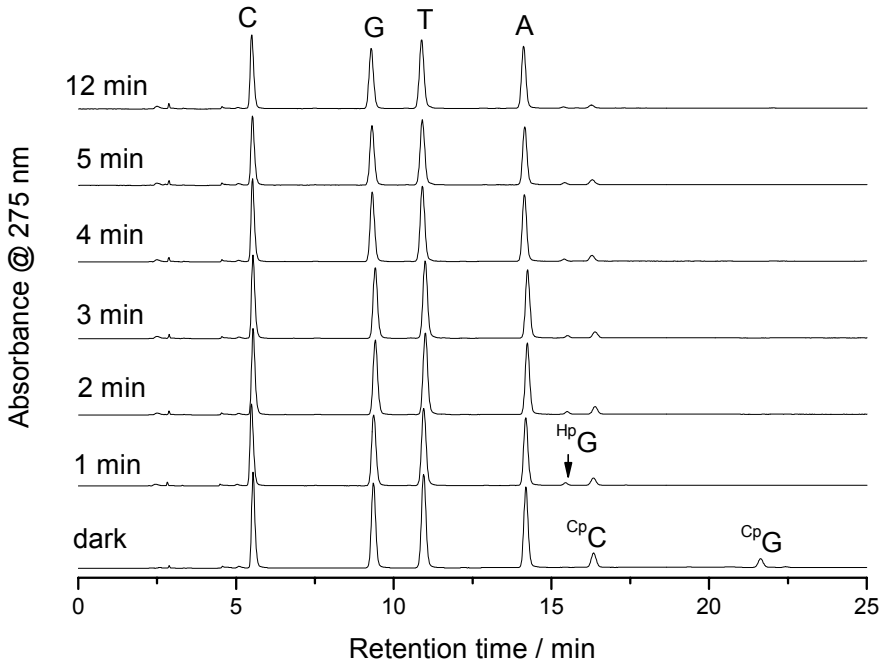


Figure S13 HPLC traces of DNA base damages during the photoreaction of 5 μM DNA duplex **^{Cp}G**/**^{Cp}C** and 50 μM $[(dppz)Pt(mes')_2]^{2+}$ complex in D_2O in the presence of O_2.



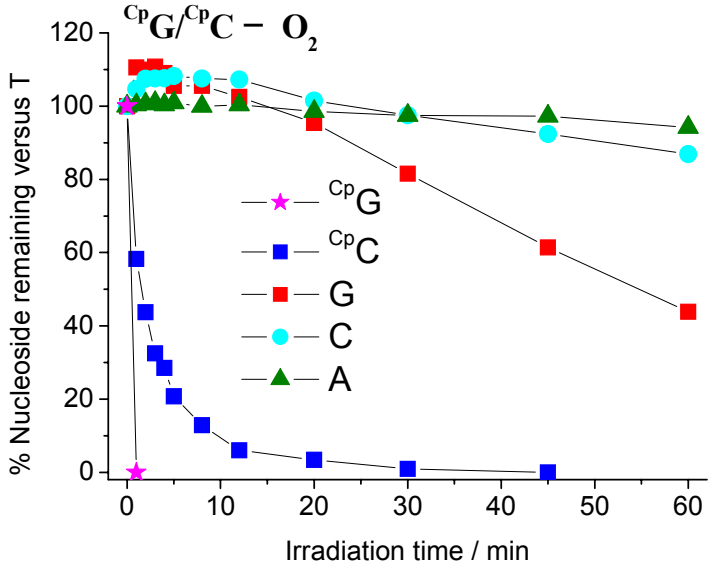


Figure S14 HPLC traces of DNA base damages during the photoreaction of 5 μM DNA duplex **^{Cp}G/^{Cp}C** and 50 μM $[(dppz)Pt(mes')_2]^{2+}$ complex in buffer in the absence of O_2.

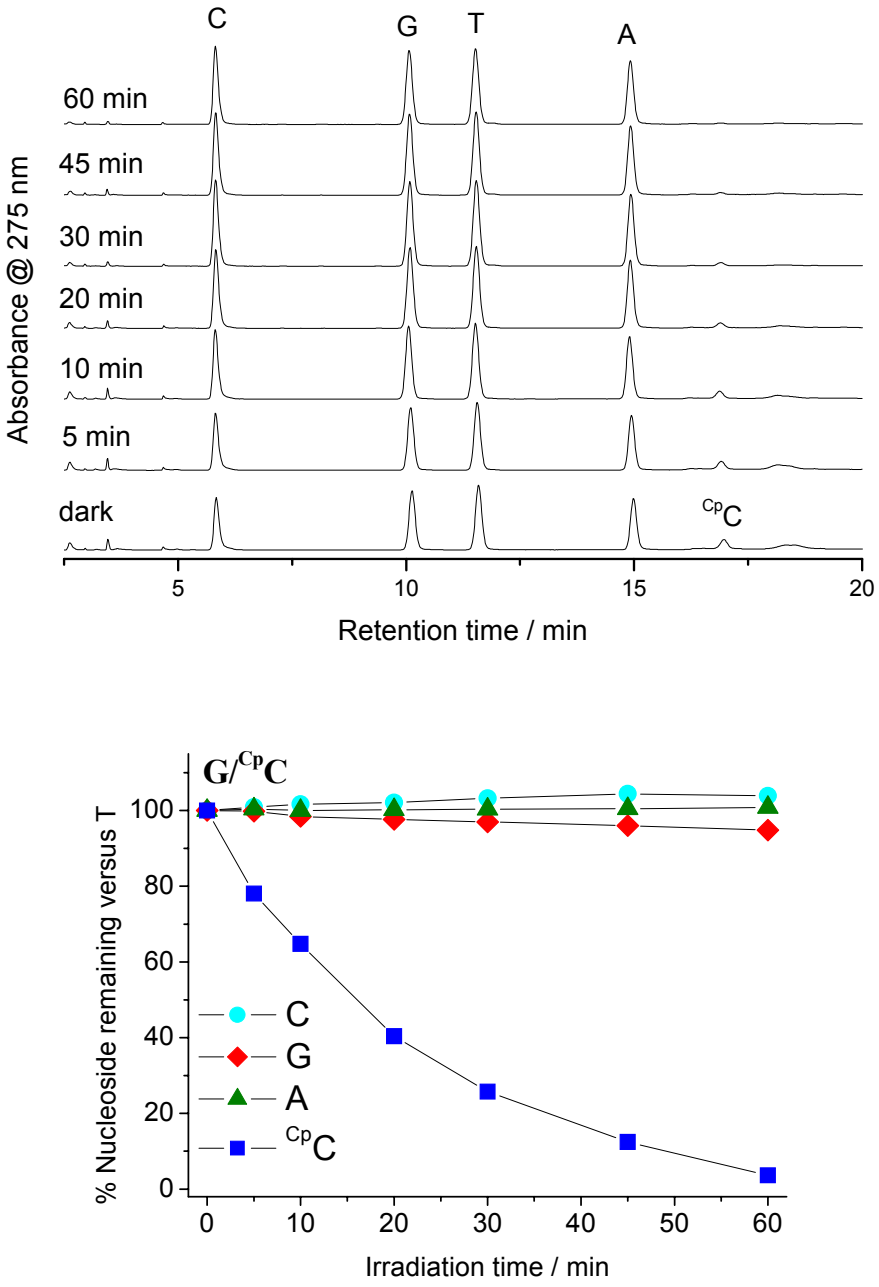


Figure S15 HPLC traces of DNA base damages during the photoreaction of 5 μM DNA duplex **G**/^{Cp}**C** and 5 μM $[(dppz)Pt(mes')_2]^{2+}$ complex in buffer in the presence of O_2.

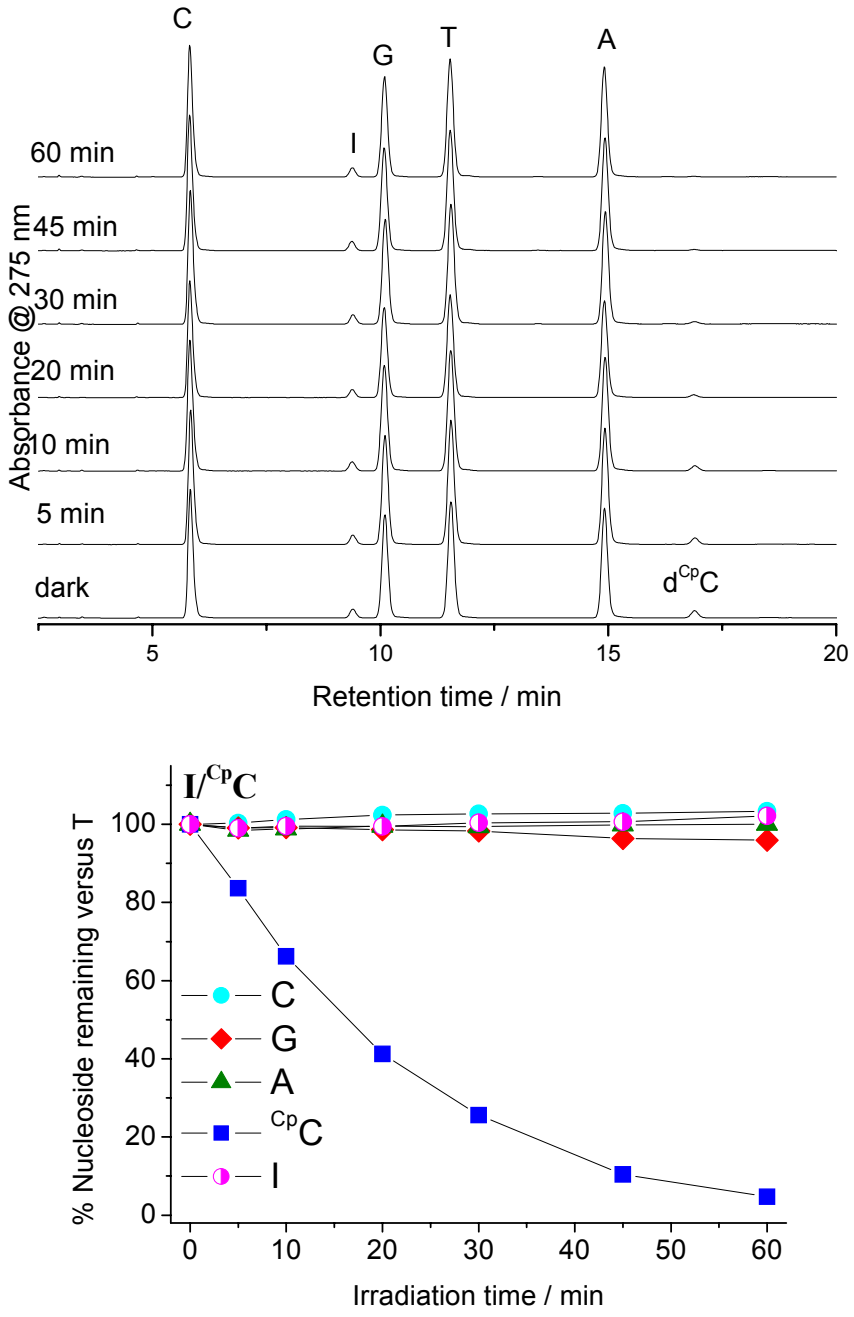


Figure S16 HPLC traces of DNA base damages during the photoreaction of 5 μM DNA duplex **I**/^{Cp}**C** and 5 μM $[(dppz)Pt(mes')_2]^{2+}$ complex in buffer in the presence of O_2.

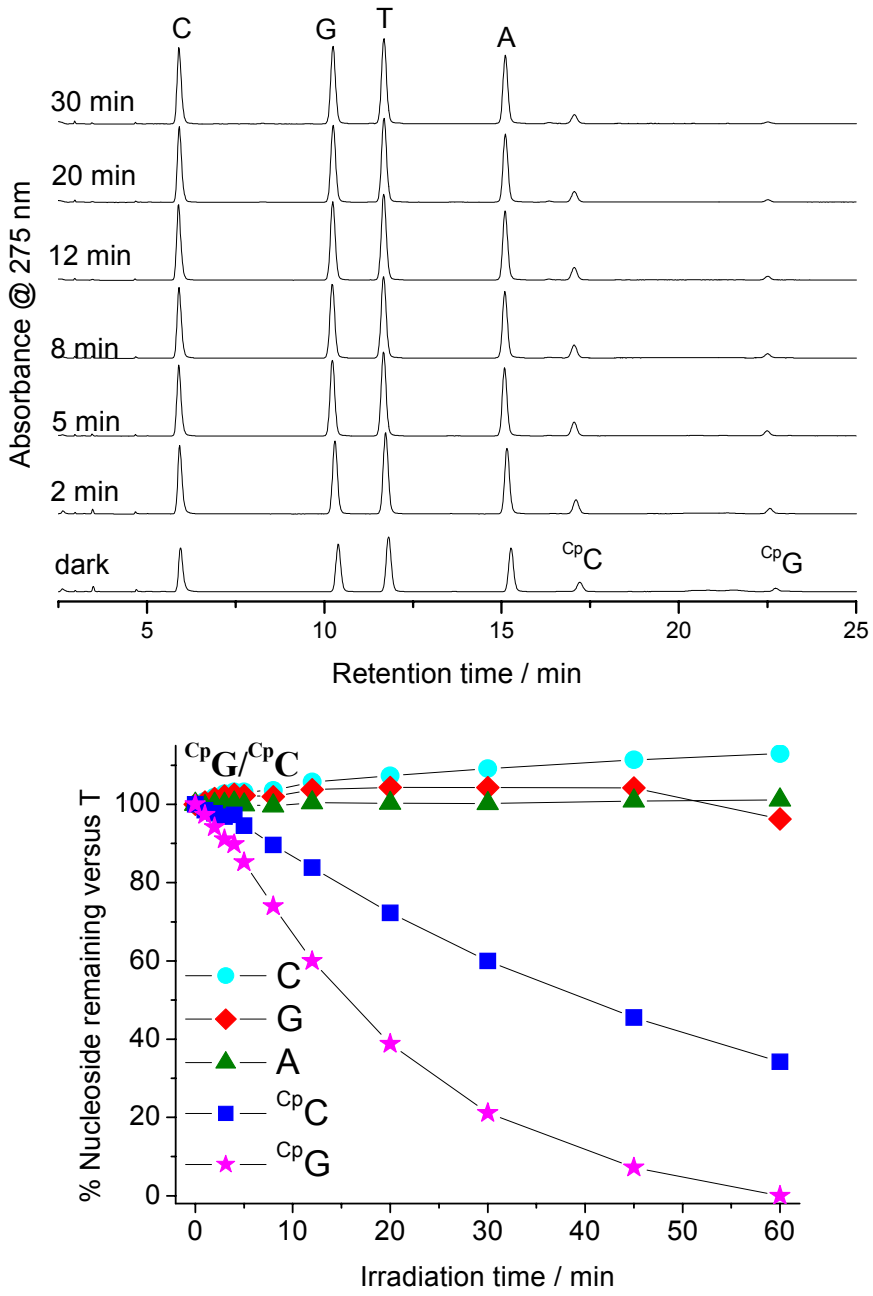


Figure S17 HPLC traces of DNA base damages during the photoreaction of 5 μM DNA duplex **^{Cp}G/^{Cp}C** and 5 μM $[(dppz)Pt(mes')_2]^{2+}$ complex in buffer in the presence of O_2.

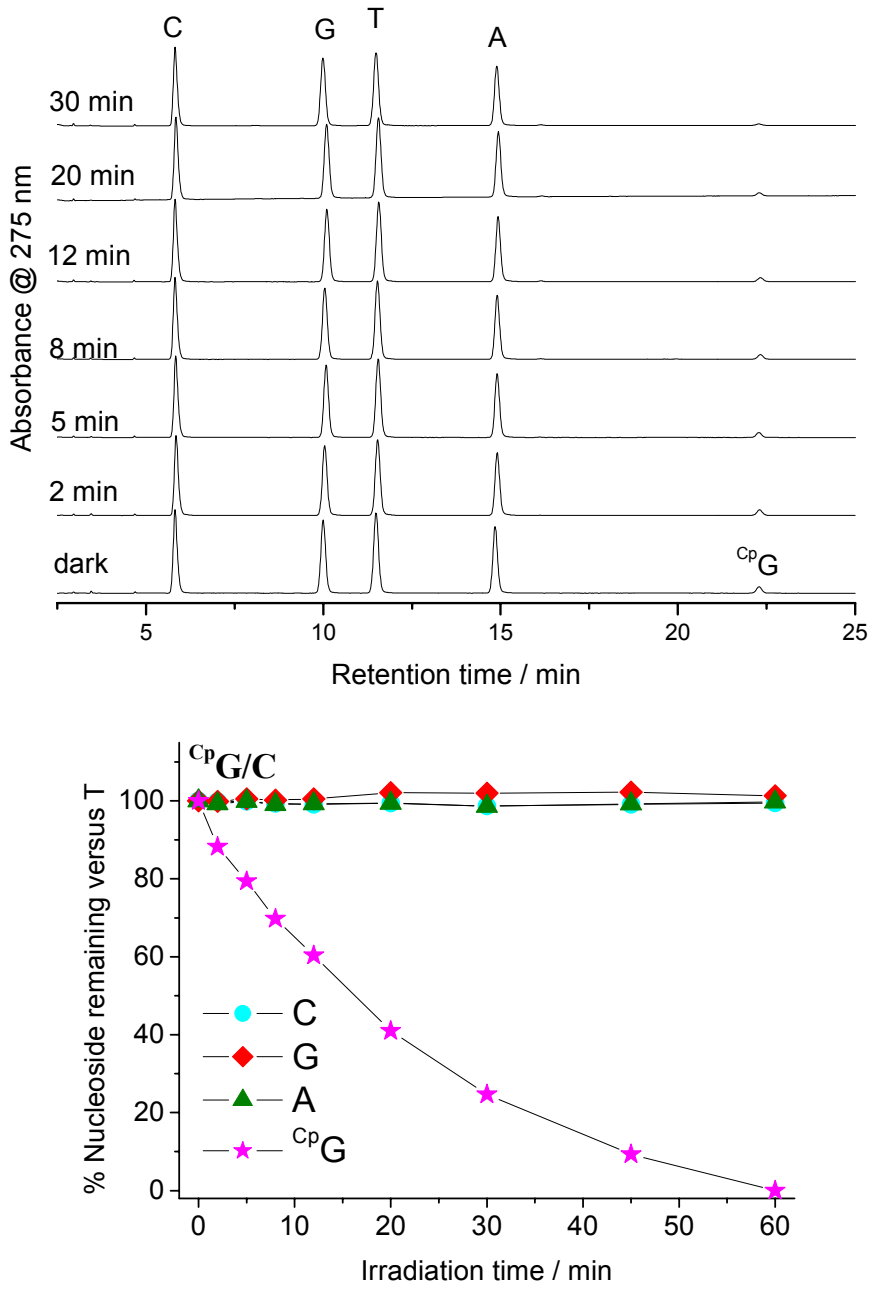


Figure S18 HPLC traces of DNA base damages during the photoreaction of 5 μM DNA duplex **^{Cp}G/C** and 5 μM $[(dppz)Pt(mes')_2]^{2+}$ complex in buffer in the presence of O_2.

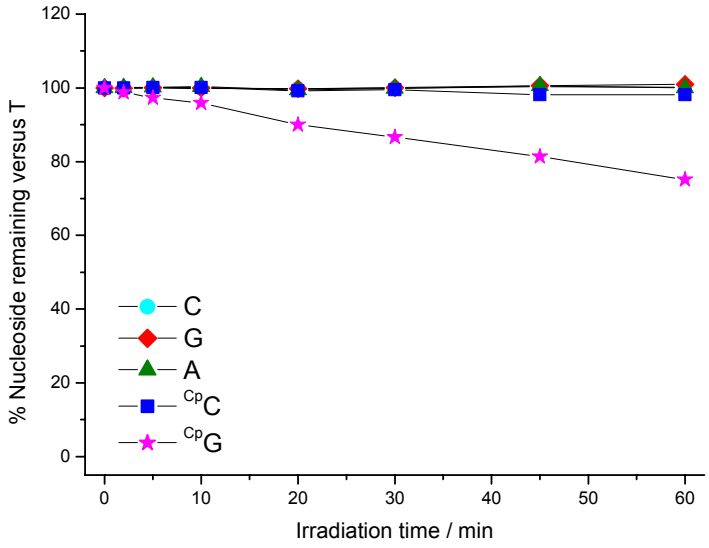


Figure S19 Percent nucleoside remaining after photoreaction of 5 μM [(bp)Pt(mes')$_2$]Cl$_2$ (**5**) and 5 μM duplex ^{Cp}**G**/^{Cp}**C** in the presence of O_2, and after nuclease digestion and HPLC analysis. For HPLC quantitation, T was used as internal standard.

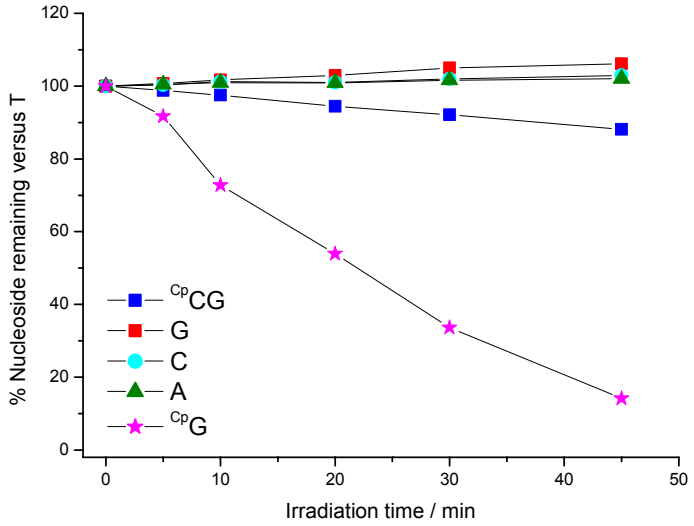


Figure S20 Percent nucleoside remaining after photoreaction of 50 μM [(bp)Pt(mes')$_2$]Cl$_2$ (**5**) and 5 μM duplex ^{Cp}**G**/^{Cp}**C** in the presence of O_2, and after nuclease digestion and HPLC analysis. For HPLC quantitation, T was used as internal standard.

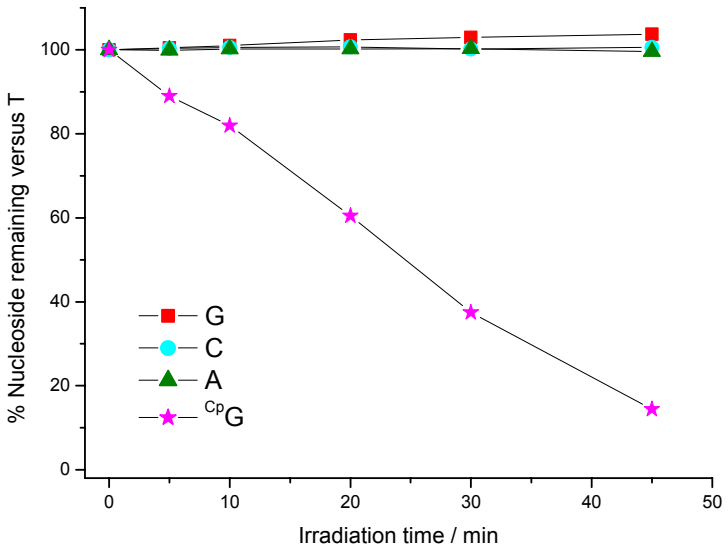


Figure S21 Percent nucleoside remaining after photoreaction of 50 μM $[(bp)Pt(mes')_2]Cl_2$ (**5**) and 5 μM duplex **^{Cp}G/C** in the presence of O_2, and after nuclease digestion and HPLC analysis. For HPLC quantitation, T was used as internal standard.

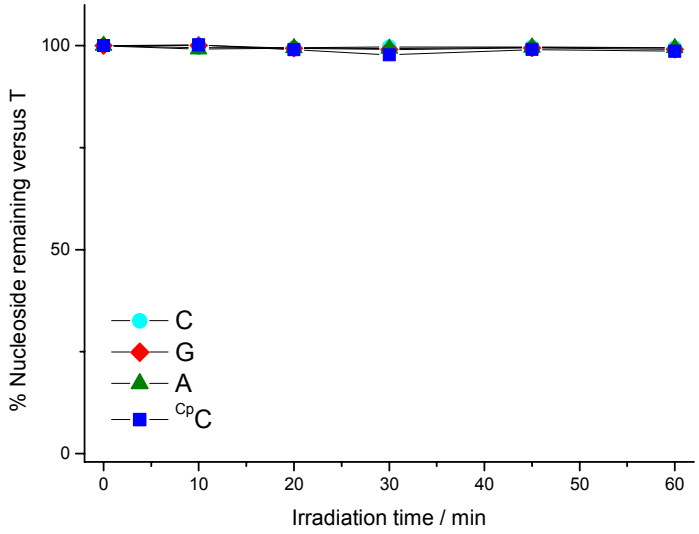


Figure S22 Percent nucleoside remaining after photoreaction of 50 μM $[(bp)Pt(mes')_2]Cl_2$ (**5**) and 5 μM duplex **G/^{Cp}C** in the presence of O_2, and after nuclease digestion and HPLC analysis. For HPLC quantitation, T was used as internal standard.