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·(H2O)2, additional figures of the UV-vis traces of Pt(II) complexes upon DNA titration and HPLC traces for photoreactions with CpC, dCpG 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, $\lambda_{\text{ex}} =$ 370 nm, concentration $\sim 5 \times 10^{-5}$ 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 [(CN₂-np)Pt(mes’)₂]Cl₂ (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]Cl₂ (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]Cl2 (3) in a buffer of 20 mM sodium phosphate and 50 mM NaCl, pH 7.0.

Figure S7  HPLC traces for photoreaction of CpC nucleoside in the presence of [(CN-np)Pt(mes')2]2⁺ complex. Conditions: 30 µL aliquot, 500 µM CpC; 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 C<sub>p</sub>C nucleoside in the presence of [(np)Pt(mes')<sub>2</sub>]<sup>2+</sup> complex. Conditions: 30 µL aliquot, 20 µM C<sub>p</sub>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+}; 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 $G^{\text{Cp}}C$ 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 \(^{\text{CpG/CpC}}\) and 50 µM \([\text{(dppz)Pt(mes')}_{2}]^{2+}\) complex in buffer in the presence of \(\text{O}_2\).
Figure S13  HPLC traces of DNA base damages during the photoreaction of 5 µM DNA duplex CpG/CpC and 50 µM [(dppz)Pt(mes’)2]2+ complex in D2O in the presence of O2.
Figure S14  HPLC traces of DNA base damages during the photoreaction of 5 µM DNA duplex $^{5p}$G/$^5p$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 $G^\text{CpC}$ 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°CpC and 5 μM [(dppz)Pt(mes')2]2+ complex in buffer in the presence of O₂.
Figure S17  HPLC traces of DNA base damages during the photoreaction of 5 μM DNA duplex $\text{CpG} / \text{CpC}$ and 5 μM $[(\text{dppz})\text{Pt(mes')}_2]^2+$ complex in buffer in the presence of $\text{O}_2$. 
Figure S18  HPLC traces of DNA base damages during the photoreaction of 5 µM DNA duplex \( \text{CpG/C} \) and 5 µM [(dppz)Pt(mes')]\(^2+\) complex in buffer in the presence of O\(_2\).
Figure S19  Percent nucleoside remaining after photoreaction of 5 μM [(bp)Pt(mes’)2]Cl2 (5) and 5 μM duplex \(^{\text{CpG}^{\text{CpC}}}\) in the presence of O2, 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]Cl2 (5) and 5 μM duplex \(^{\text{CpG}^{\text{CpC}}}\) in the presence of O2, 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]Cl2 (5) and 5 µM duplex CpG/C in the presence of O2, 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]Cl2 (5) and 5 µM duplex G/CpC in the presence of O2, and after nuclease digestion and HPLC analysis. For HPLC quantitation, T was used as internal standard.