Supplementary Information Section

Photoactive *meso*-tetra(4-pyridyl)porphyrin-tetrakis-[chloro(2,2´bipyridine)platinum(II) derivatives recognize and cleave DNA upon irradiation

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1. 4-TPyP Electronic absorption spectra

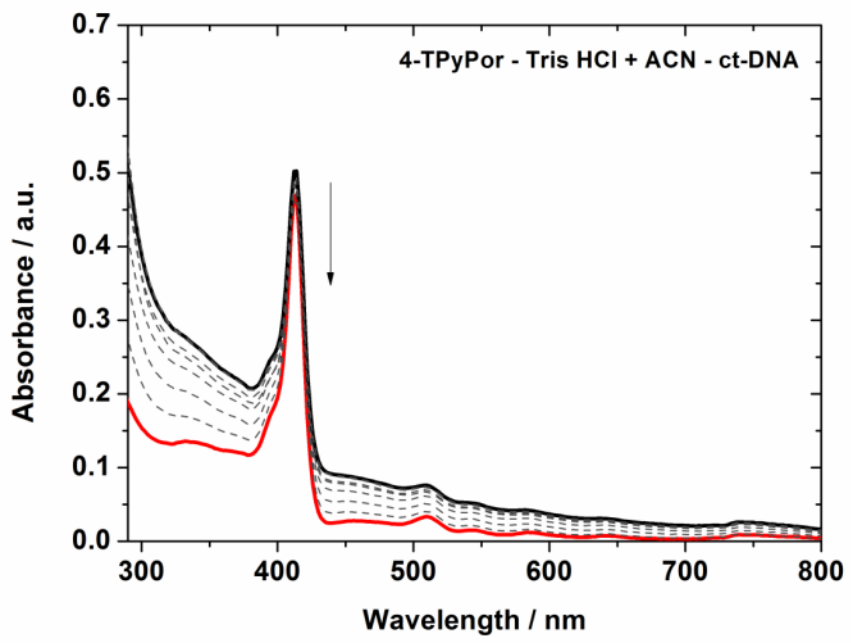

Figure S1. Electronic UV-vis absorption spectra of **4-TPyPor** (1.0 µM) with increasing CT-DNA concentrations (0.0 - 10.0 µM bp) in Tris-HCl buffer solution.

2. Circular dichroism assays

Table S1. Circular dichroism titrations

Titration (µL)	% CH3CN (v/v)	[Complex] (µM)	[CT-DNA] (µM)	r [complex]/[CT-DNA]
0*	2.0%	0.00	200.00	0.00
06	3.5%	7.39	197.04	0.04
16	6.0%	19.23	192.31	0.10
26	8.5%	30.52	187.79	0.16
36	11.0%	41.28	183.49	0.23
46	13.5%	51.57	179.37	0.29
56	16.0%	61.40	175.44	0.35
66	18.5%	70.82	171.67	0.41

*Initial reaction: CT-DNA (200.0 µM bp) in Tris-HCl (10.0 mM pH 7.4) and 2.0% (v/v) acetonitrile solution.

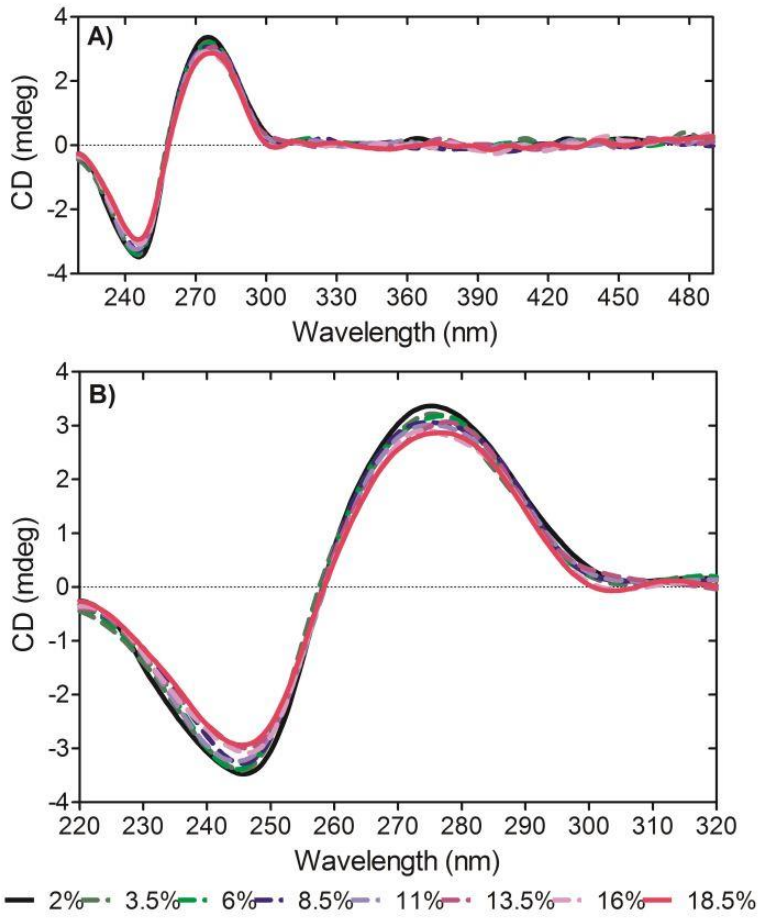

Figura S2. Acetonitrile dilution CD spectra. Initial reaction: CT-DNA (200.0 µM bp) in Tris-HCl (10.0 mM pH 7.4) and 2.0% (v/v) acetonitrile solution. The initial reaction was titrated with increased volumes of acetonitrile as demonstrated in Table S1.

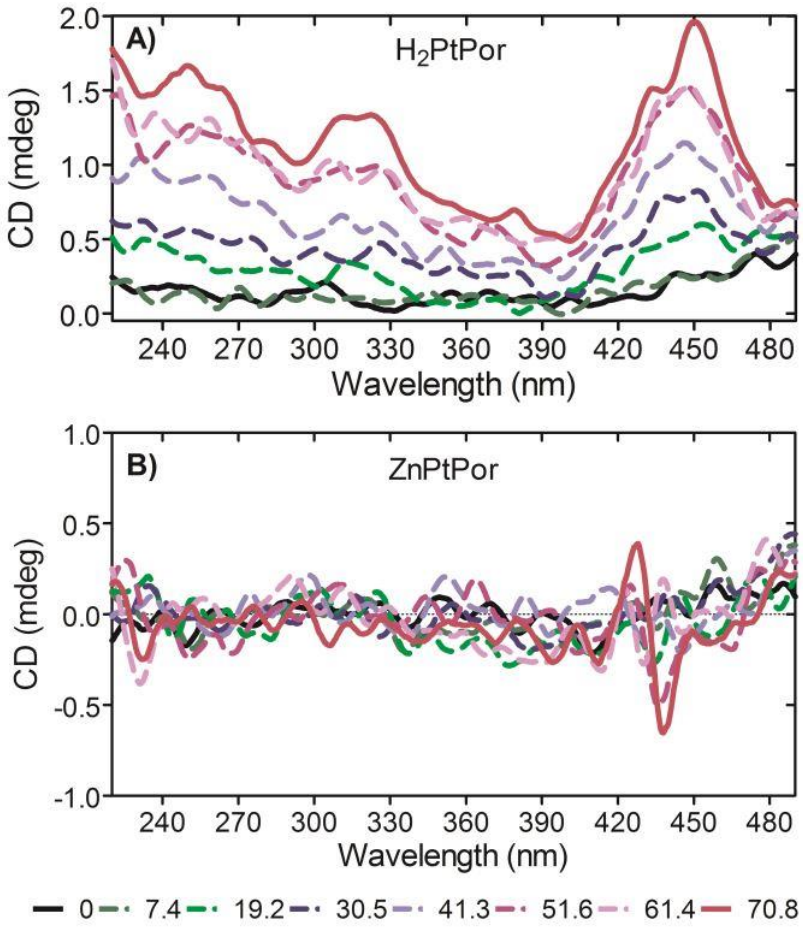

Figure S3. CD spectra of A) **H_2PtPor** and B) **ZnPtPor** titration into buffer. Initial reaction: Tris-HCl (10.0 mM pH 7.4) and 2.0% (v/v) acetonitrile solution. The initial reaction was titrated with increased amounts of complexes as indicated in Table S1.

3. 4-TPyP Emission spectra

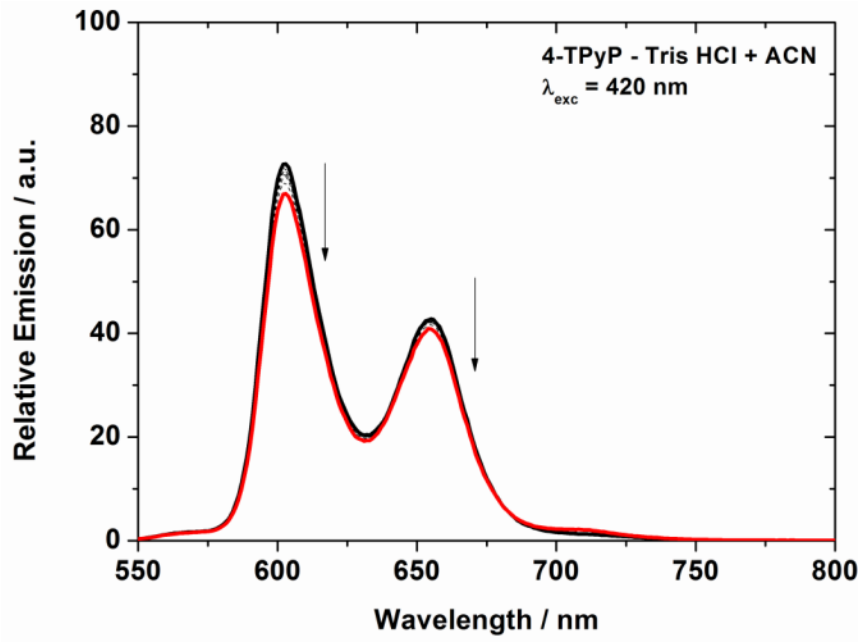

Figure S4. Emission spectra of **4-TPyPor** (1.0 µM) with increasing CT-DNA concentrations (0.0 - 10.0 µM bp) in Tris-HCl buffer solution. (λ_{exc} = 420 nm).

4. Plasmidial DNA cleavage by 4-TPyP

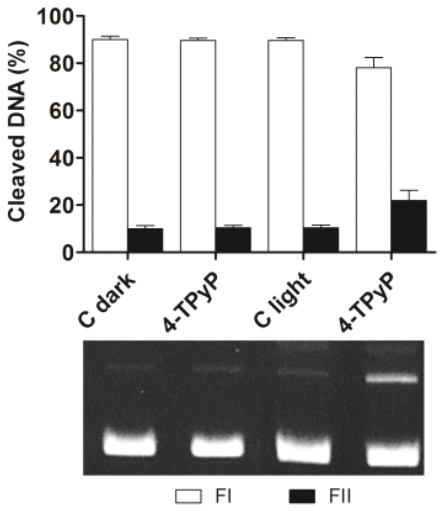

Figure S5. DNA cleavage by the precursor **4-TPyP**. Standard reactions: plasmid DNA (~25 µM bp), Tris-HCl (10 mM pH 7.4), 25 % (v/v) acetonitrile at 37°C. **4-TPyP** was added (3 µM final concentration). The dark reactions were incubated for 24 hours in absence of light while the irradiated trials were incubated for 90 minutes under visible light. Data represent mean and SD.

5. DNA groove binders

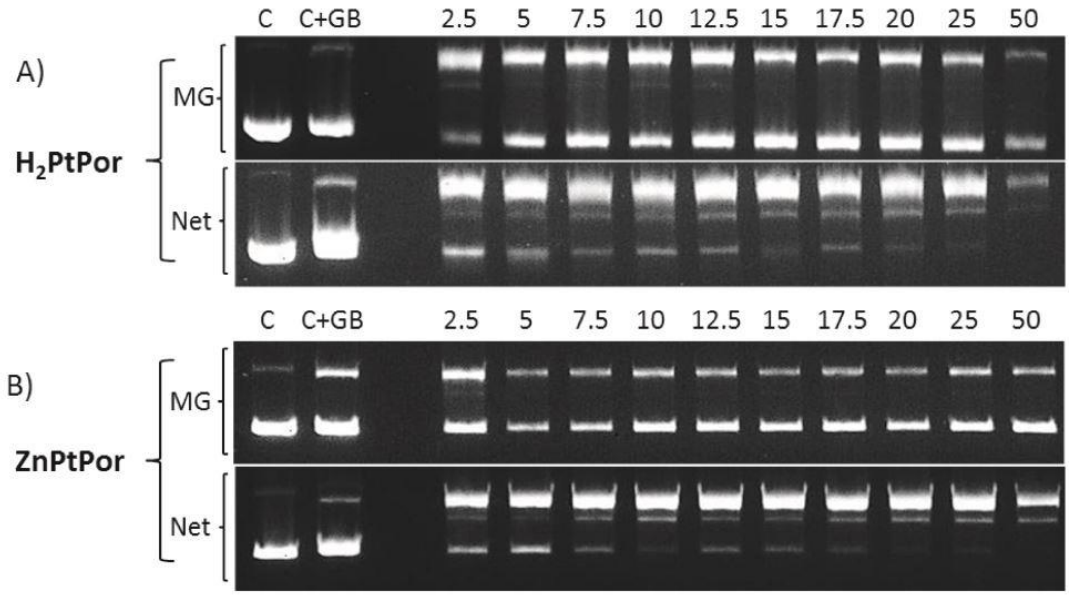

Figure S6. Influence of DNA groove binders in the DNA cleavage reaction. Standard reactions carried out in the presence of groove binders. *Standard reactions:* plasmid DNA (~25.0 µM bp), Tris-HCl (10.0 mM pH 7.4), 25% (v/v) acetonitrile solution. Pt(II)-porphyrins: A) **H_2PtPor** and B) **ZnPtPor** (4.0 µM final concentration). Groove binders: methyl green (MG) or netropsin (Net) were added to reactions. C – control without porphyrin; C+GB – control + corresponding groove binder. Groove binder concentration curve: 2.5 – 50 µM. All samples were incubated for 90 minutes at 37°C under visible light.

6. ROS scavengers

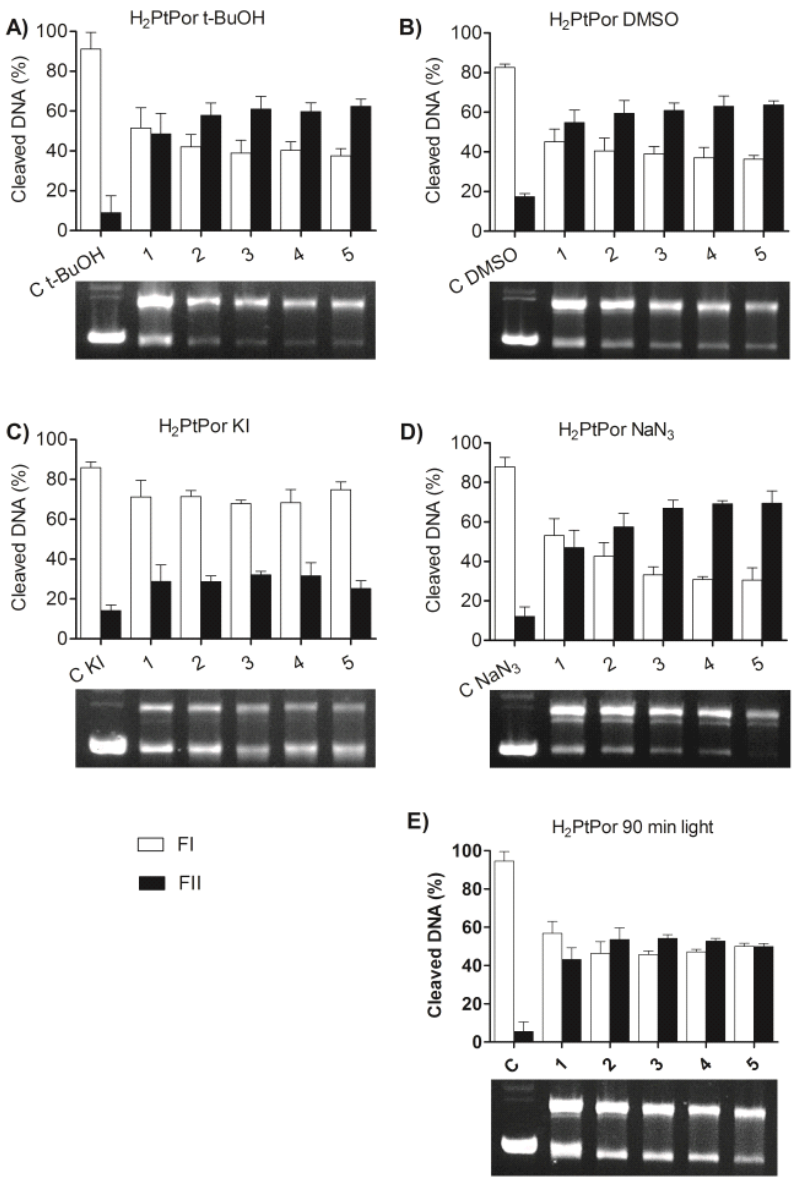

Figure S7. Plasmid-**H_2PtPor** reactions carried out in the presence of ROS scavengers. *Standard reactions:* **H_2PtPor** concentration curve (0.0-5.0 µM), plasmid DNA (~25.0 µM bp), Tris-HCl (10.0 mM pH 7.4), 25% (v/v) acetonitrile. *Scavengers added:* A) *t*-BuOH (0.8 mM), B) KI (8.0 mM), C) NaN_3 (8.0 Mm) and D) DMSO (0.8 mM). E) Control reactions without scavengers (from Figure 7, our manuscript). C – control + corresponding scavenger. All samples were incubated for 90 minutes at 37°C under visible light. Data represent mean and SD.

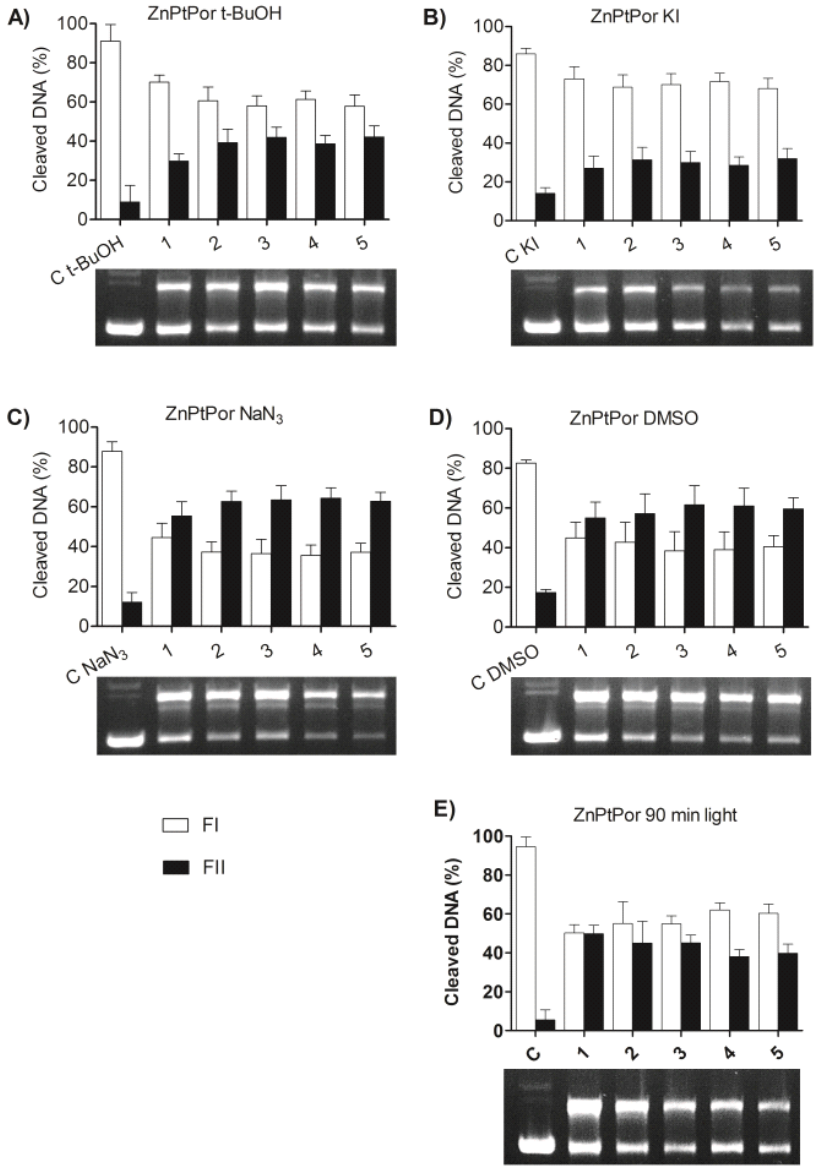

Figure S8. Plasmid-**ZnPtPor** reactions carried out in the presence of ROS scavengers. *Standard reactions:* **ZnPtPor** concentration curve (0.0-5.0 μM), plasmid DNA (~25.0 μM bp), Tris-HCl (10.0 mM pH 7.4), 25% (v/v) acetonitrile. *Scavengers added:* A) *t*-BuOH (0.8 mM), B) KI (8.0 mM), C) NaN_3 (8.0 mM) and D) DMSO (0.8 mM). E) control reactions without scavengers (from Figure 7, our manuscript). C – control + corresponding scavenger. All samples were incubated for 90 minutes at 37°C under visible light. Data represent mean and SD.

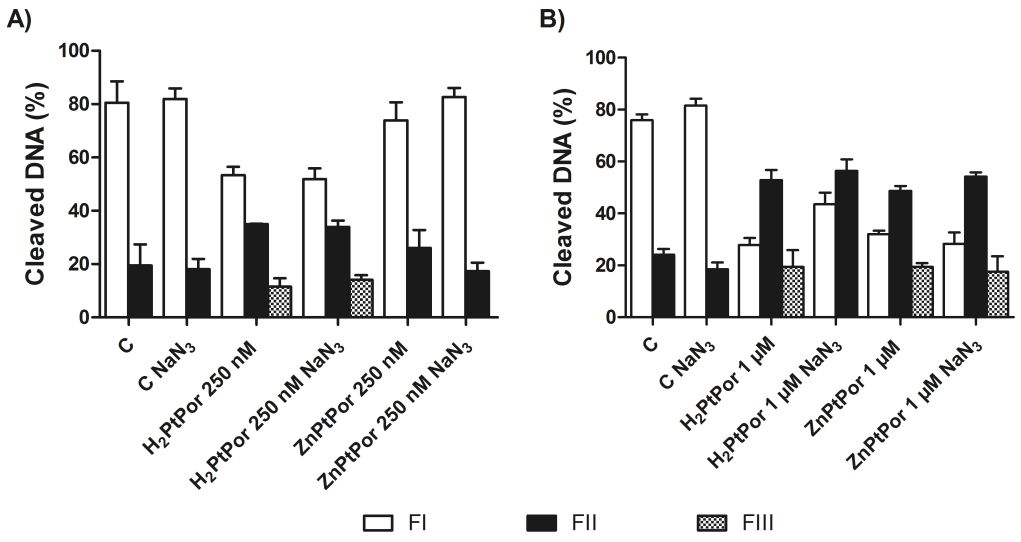

Figure S9. Plasmid-**H_2PtPor** and **ZnPtPor** reactions carried out in the presence of NaN_3 (8.0 mM). *Standard reactions:* **H_2PtPor** or **ZnPtPor** (250 nM (A) and 1 µM (B)), plasmid DNA (~25.0 µM bp), Tris-HCl (10.0 mM pH 7.4), 25% (v/v) acetonitrile. *Scavenger added:* NaN_3 (8.0 mM). C – control + NaN_3 (8.0 mM). All samples were incubated for 90 minutes at 37°C under visible light. Data represent mean and SD.

7. TEMPO

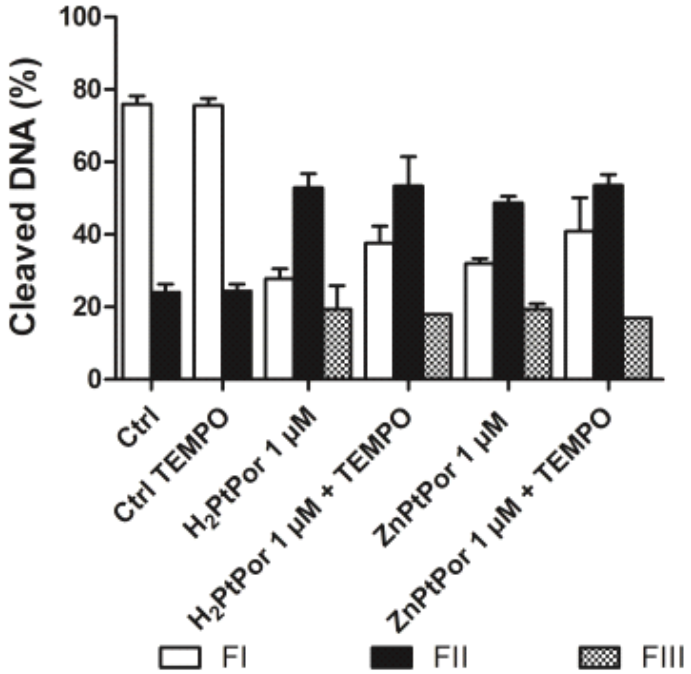

Figure S10. Plasmid-**H_2PtPor** and **ZnPtPor** reactions carried out in the presence of TEMPO. *Standard reactions:* **H_2PtPor** or **ZnPtPor** (1 µM), plasmid DNA (~25.0 µM bp), Tris-HCl (10.0 mM pH 7.4), 25% (v/v) acetonitrile. *Scavenger added:* TEMPO (2,2,6,6-tetramethyl-1-piperidine- 1-oxyl) (0.5 mM). Ctrl – control without porphyrin Ctrl + TEMPO – control + TEMPO (0.5 mM). All samples were incubated for 90 minutes at 37°C under visible light. Data represent mean and SD.

8. Anaerobic Atmosphere

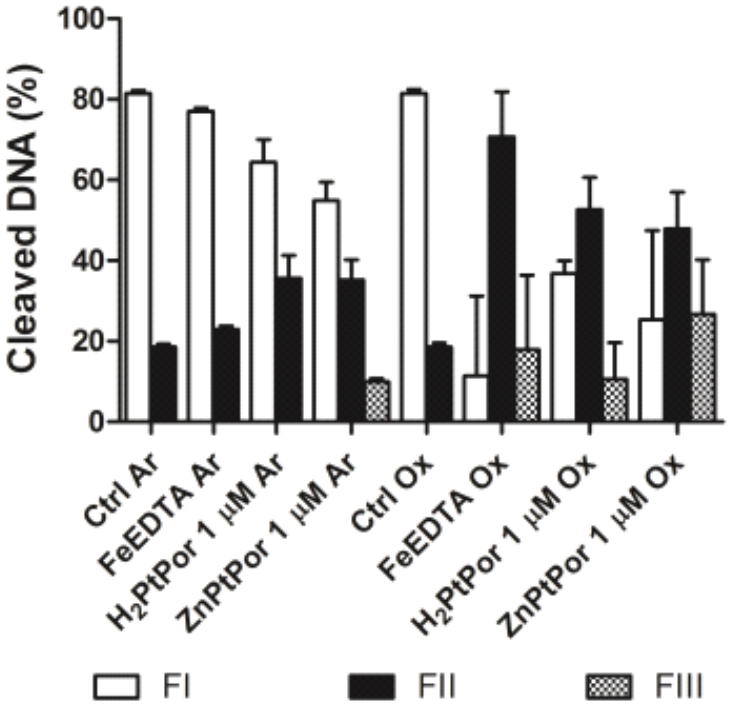

Figure S11. Argon atmosphere trials. Plasmid-**H_2PtPor** and **ZnPtPor** reactions carried out in argon (Ar) and oxygen (Ox) atmosphere. *Standard reactions:* **H_2PtPor** or **ZnPtPor** (1 μM), plasmid DNA (~25.0 μM bp), Tris-HCl (10.0 mM pH 7.4), 25% (v/v) acetonitrile. Ctrl – control without porphyrin. FeEDTA – control + FeEDTA (100 μM) + DTT (1,4 – dithiothreitol; 10 mM). All samples were incubated for 90 minutes at 37°C under visible light. Data represent mean and SD.

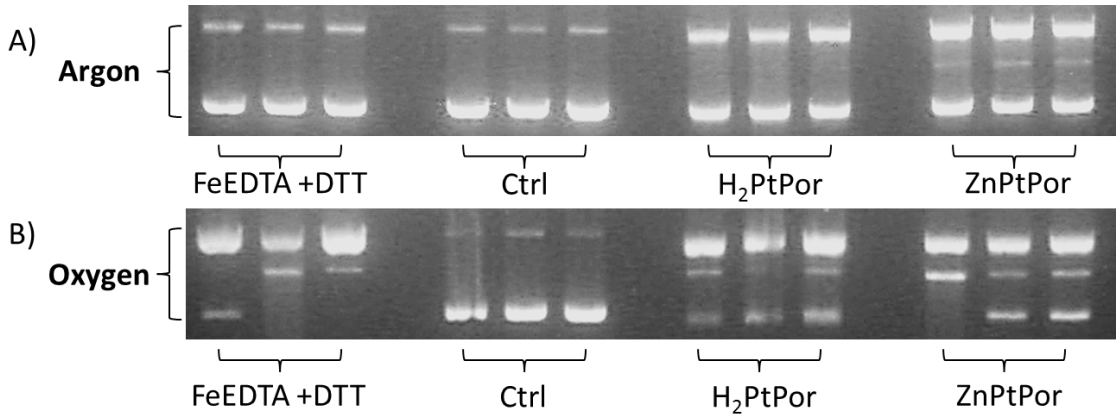

Figure S12. Agarose gel electrophoresis images of argon atmosphere trials. Plasmid-**H_2PtPor** and **ZnPtPor** reactions carried out in argon (Ar) and oxygen (Ox) atmosphere. *Standard reactions:* **H_2PtPor** or **ZnPtPor** (1 µM), plasmid DNA (~25.0 µM bp), Tris-HCl (10.0 mM pH 7.4), 25% (v/v) acetonitrile. Ctrl – control without porphyrin. FeEDTA – control + FeEDTA (100 µM) + DTT (1,4 – dithiothreitol; 10 mM). All samples were incubated for 90 minutes at 37°C under visible light.