Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPLEMENTARY INFORMATION FOR

Photosensitized H_2 Generation from "One-Pot" and "Two-Pot" Assemblies of a Zinc-Porphyrin/Platinum Nanoparticle/Protein Scaffold

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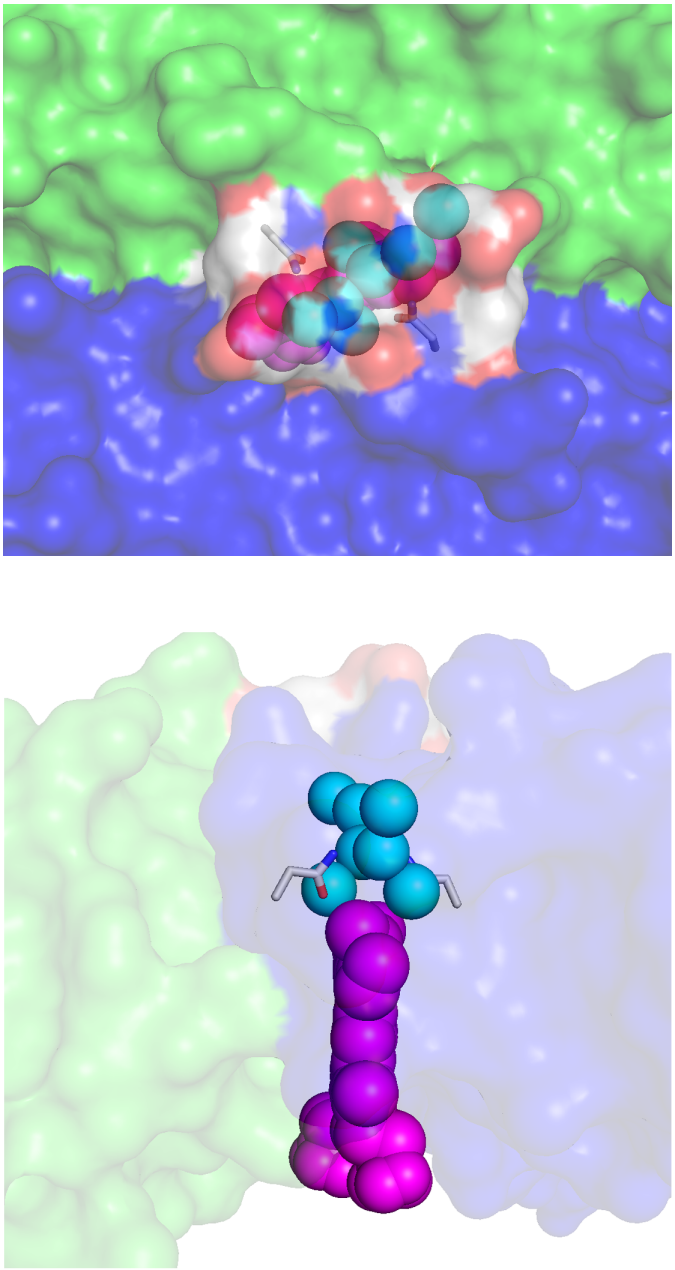

Figure S1. Hydrogen bonded water network (cyan-colored spheres) within the pocket between the vinyl side of the heme and Bfr surface in the 3e2c crystal structure. Viewing directions are equivalent to those in Figure 2. The two symmetrically disposed N23 side chains (sticks) are hydrogen bonded to the water network and were substituted with G in the 5gly-dimer.

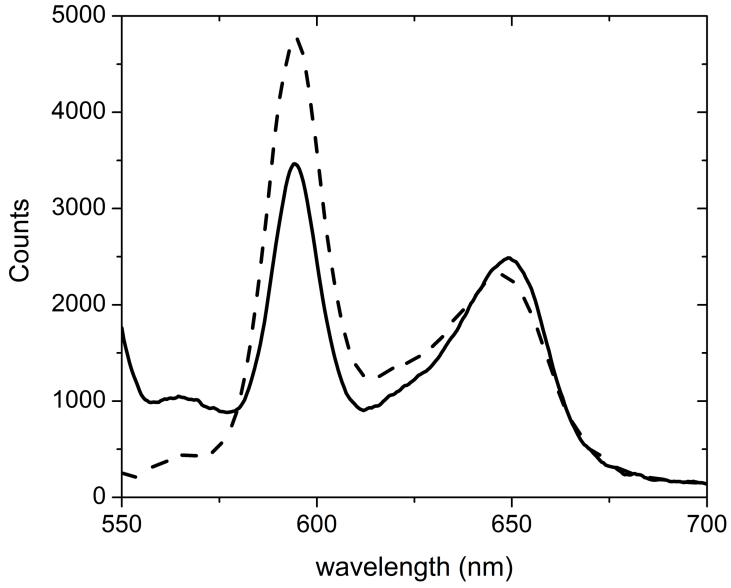

Figure S2. Fluorescence emission spectra of 60 uM ZnPP-Bfr dimer (solid line) and 60 uM ZnPP-5gly-Bfr (dashed line). 60 uM 5gly-ZnPP-Bfr dimer and 60 uM ZnPP-Bfr dimer in 50 mM MES 0.5 M NaCl, pH 6 at 390 nm using a StellarNet Miniature Fiber Optic Spectrometer equipped with GREEN-Wave LED, excitation at 502 nm.

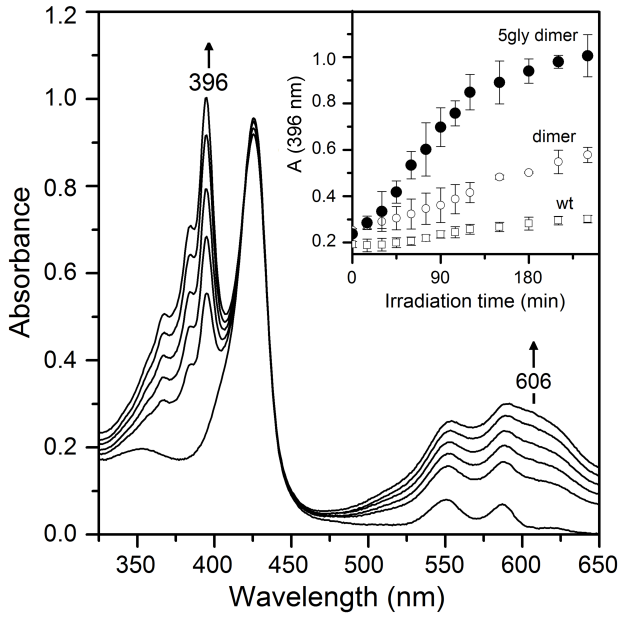

Figure S3. UV-vis absorption spectral time course of MV^{2+} reduction to $MV^{\bullet+}$ induced by irradiation with white light from a 300 W halogen lamp (3.8 mW/cm^2) of an anaerobic solution containing 10 μM ZnPP-5gly Bfr dimer, 2 mM MV, and 0.1 M TEOA in 50 mM MES pH 6. The positions of MV^+ absorption maxima at 396 nm and 606 nm are indicated with arrows indicating absorbance increased with time. The absorption features at ~430, 550 and 590 nm are due to the ZnPPIX. Inset: $A_{396\ nm}$ time courses for MV^{2+} reduction using 10 μM ZnPP-5gly-Bfr-dimer (closed circles), ZnPP-Bfr dimer (open circles), or ZnPP-wtBfr (open squares). Data points are the average from at least three experiments with standard deviations indicated by vertical bars.

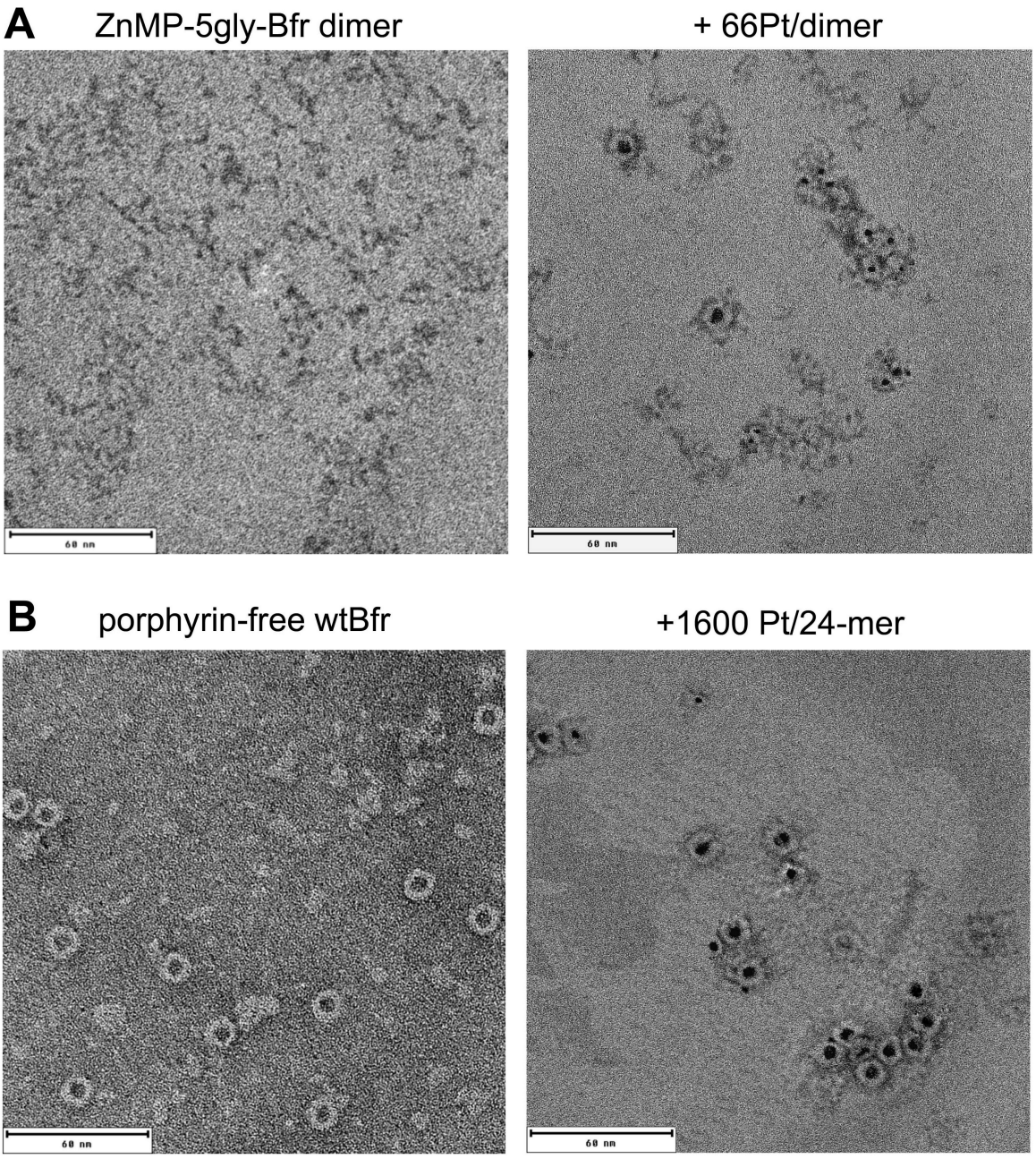

Figure S4. (A) Uranyl acetate negatively stained TEM image pairs of as-isolated proteins (left panels) or post-workup samples of Pt salt/borohydride reactions (right panels) using **(A)** 66 molPt/mol ZnMP-5gly-Bfr dimer or **(B)** 1600 Pt/porphyrin-free wtBfr. Scale bars for TEM images represent 60 nm.

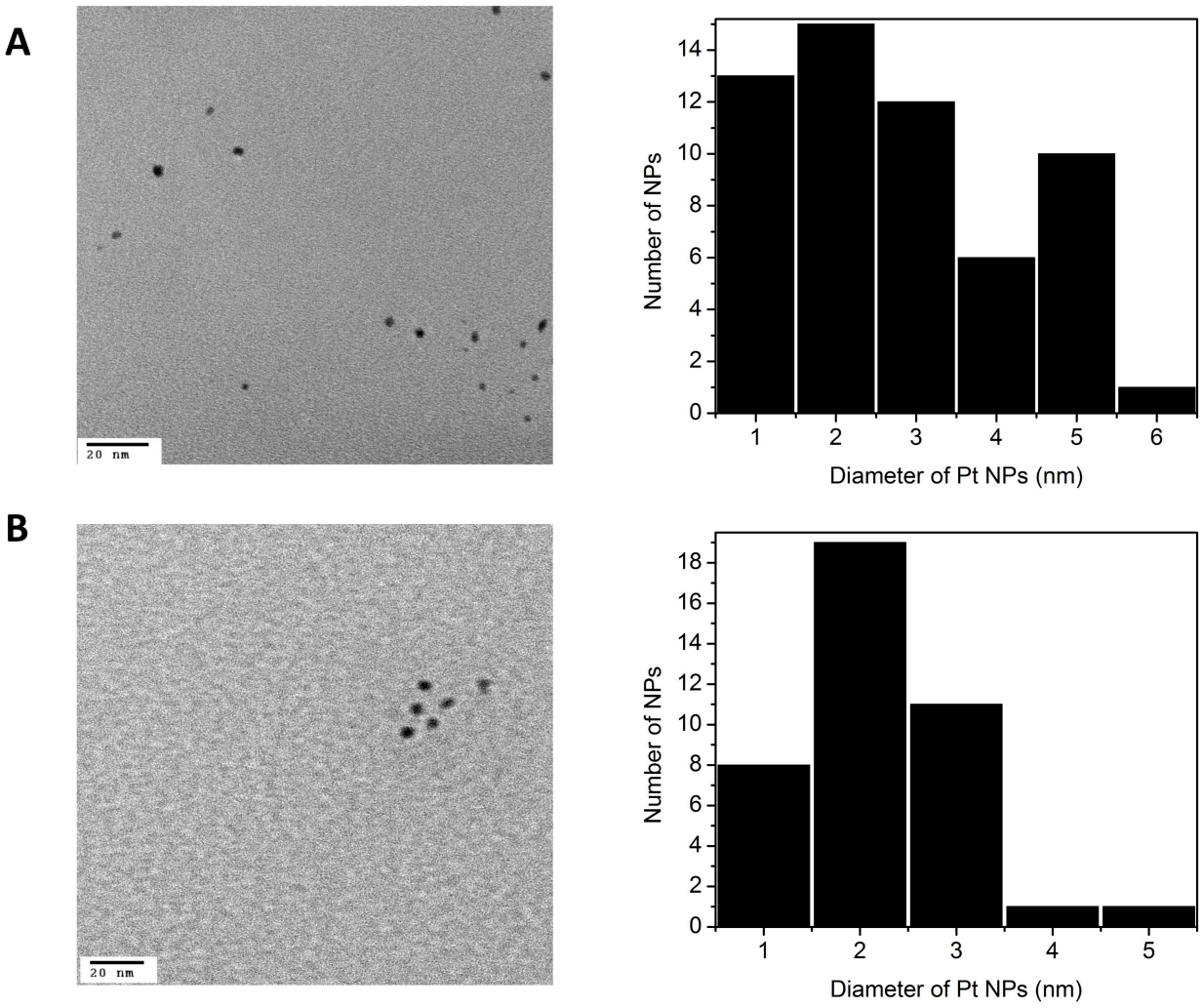

Figure S5. Unstained TEM images used for Pt nanoparticle sizing. 10 uL of 40 ug/mL of Pt-loaded protein was dropped on carbon-coated Cu grids. After 2 minutes, excess sample was wicked with filter paper and grids were left to dry at room temperature. **(A)** TEM of post-work up sample from Pt salt/borohydride reactions using 66Pt/ZnMP-5gly-Bfr dimer (right panel) and corresponding Pt NP size distribution (left panel). **(B)** TEM of post-work up sample from Pt salt/borohydride reactions using 1600 Pt^{IV}/porphyrin-free wtBfr 24-mer (right panel) and corresponding Pt NP size distribution (left panel). More than 50 measurements of unstained Pt NPs were taken from multiple locations on the grid to determine average diameter range. Scale bars in TEM images represent 20 nm.

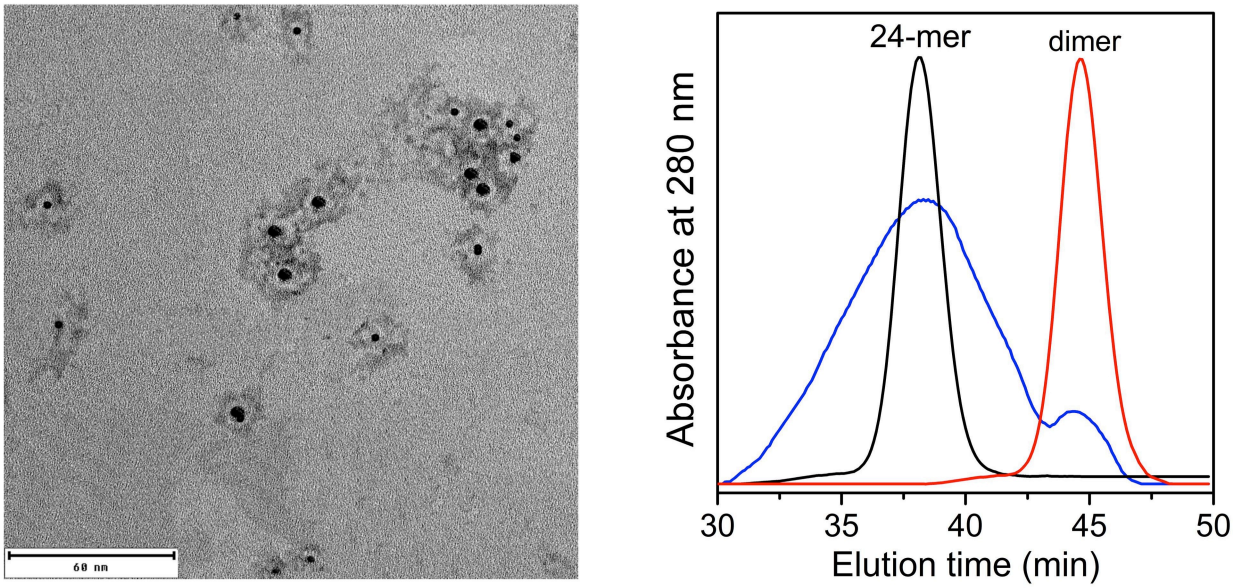

Figure S6. (left panel) negatively stained TEM image or (right panel) SEC of post-workup samples from with $K_2PtCl_4/NaBH_4$ reactions using 133 Pt/ZnMP-5gly-Bfr dimer (blue). The post-workup protein contained 73 Pt/Bfr dimer (~880/effective 24-mer). 24-mer (black) and dimer (red SECs are of unreacted wtBfr 24-mer and Bfr dimer, respectively.

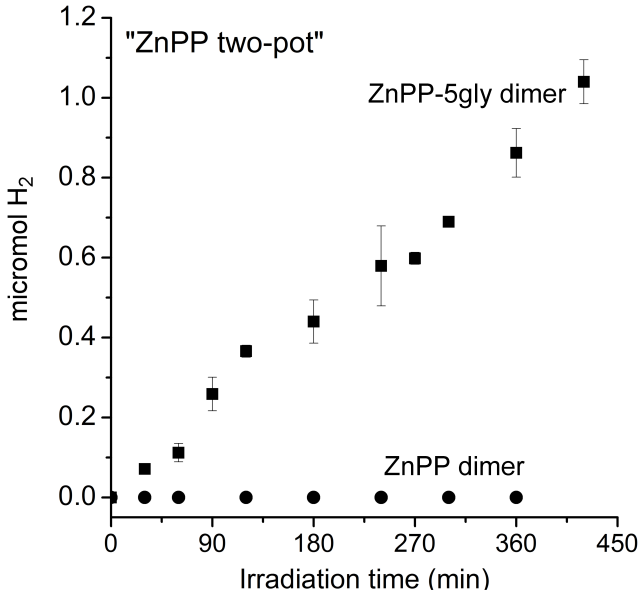

Figure S7. Time dependence of photosensitized H_2 production using "ZnPP two-pot" mixtures. Solutions contained porphyrin-free Pt NP@ wtBfr at 20 μM Pt, 0.1 M TEOA, 2 mM MV, and 10 μM of either ZnPP-Bfr dimer (filled circles) or ZnPP-5gly-Bfr dimer (filled squares) in 50 mM MES pH 6, 0.5 M NaCl. Samples were continuously irradiated with a 300 W halogen lamp (3.8 mW/cm^2) at room temperature. Data points are the average from six experiments with standard deviations indicated by vertical bars.