Supporting Information

Materials and methods

Materials. Complex **1** was purchased from Sigma Aldrich, and complex **2** was prepared as reported previously.[1] GSH, Cys, DTNB, catalase, anthracene, and HEPES buffer were purchased from Sigma Aldrich. NADH from Bio Basic Canada. $AscH^-$, DMSO, and sodium dithionite ($Na_2S_2O_4$) were purchased from Fisher Scientific. All solutions were prepared in ultrapure water (ρ=18.2 $M\Omega cm^{-1}$). All reagents and solvents were used without further purification.

Stock Solutions. Complexes **1** and **2** stock solutions were prepared by dissolving **1** and **2** in DMSO. HEPES stock solution was prepared by dissolving the free acid powder in ultrapure water and adjusting the pH with a concentrated solution of NaOH. GHS, Cys, NADH, and $AscH^-$ solutions were prepared daily in ultrapure water.

UV-Vis Spectrophotometric Measurements. UV-Vis spectra were recorded at room temperature (thermo statted to 25 °C) in the 200–800 nm window with a Cary 60 UV Vis spectrophotometer (Agilent Technologies) using 1 mL quartz cells of 1 cm path length. The DTNB assay was monitored at 412 nm (TNB absorption peak), the oxidation of NADH at 340 nm, and the oxidation of $AscH^-$ at 265 nm.

DTNB assay. 5 µL aliquots were taken at different time points from the reaction mixture and added to a solution containing 85 µL Tris-EDTA solution (Tris buffer 250 mM pH 8.2, EDTA 1 µM) and 10 µL of DTNB 1 mM to monitor the consumption of free thiol groups spectrophotometrically at 412 nm.[2]

HPLC and LC-MS Spectrometry. The HPLC analysis of GSH and GSSG was performed using a Hitachi Primaide instrument on a C18 column (XBridge Peptide BEH C18 column from Waters, 4.6 mm 150 mm, pore size 300 Å, particle size 3.5 m) using 0.1% aqueous TFA (solvent A) and 90% CH_3CN/0.1% TFA in water (solvent B) with a linear gradient from 2 to 7% solvent B in 7 min. The attribution of the peaks was achieved by comparison with a solution containing GSH or GSSG only and via LC-MS spectra that were recorded using an LCQ Fleet ion trap mass spectrometer (Thermo Fischer) coupled to a Ultimate3000 RSLCnano system equipped with an ACQUITY UPLC BEH C18 column (130 Å, 1.7 m, 1.0 mm 150 mm).

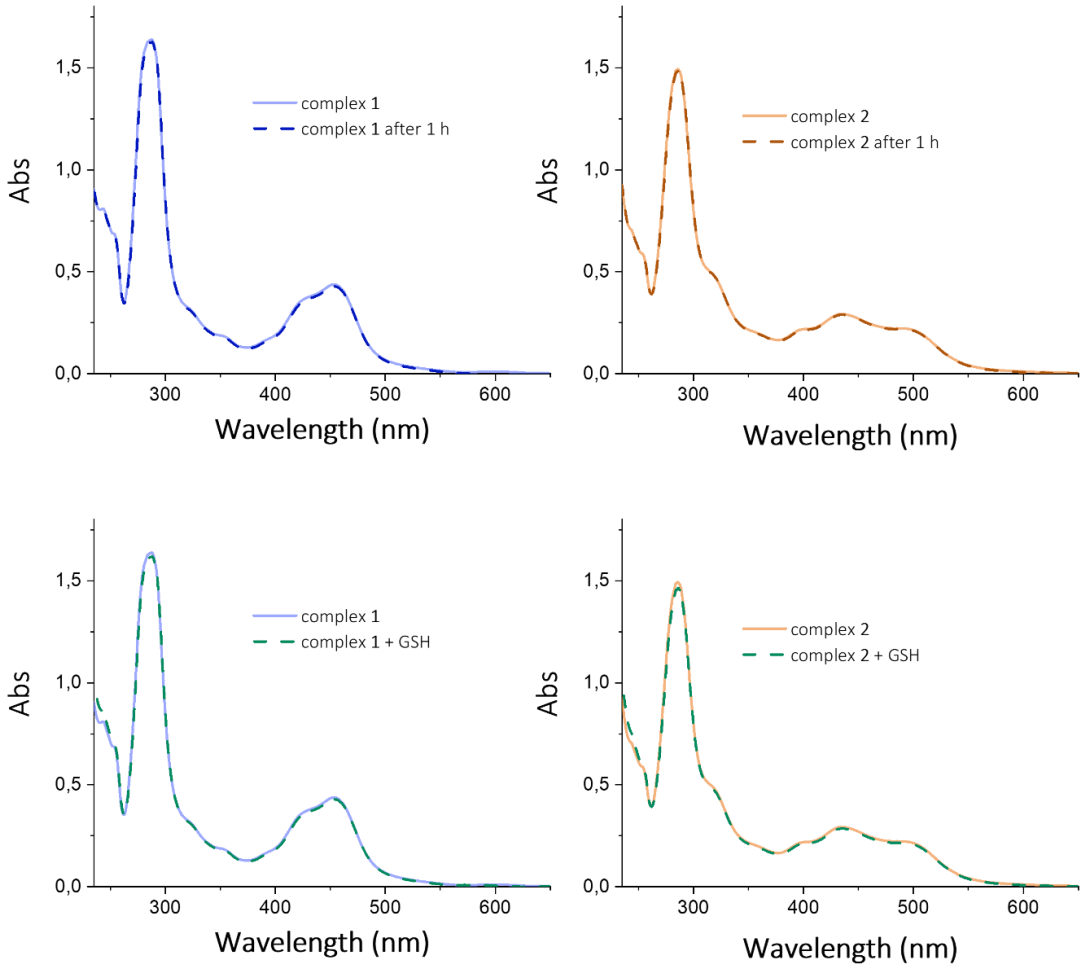

Figure S1. Stability of complex 1 and 2 over 1 h at pH 7.4 and upon addition of GSH. Conditions: [1] and [2] 30 µM, [GSH] 1 mM, HEPES 100 mM, pH 7.4, 25 °C.

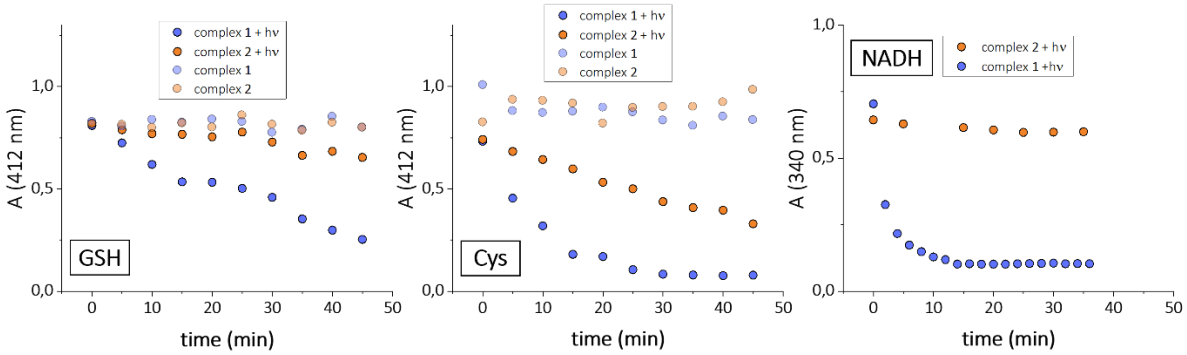

Figure S2. Oxidation of GSH and Cys with and without irradiation followed by DTNB assay (TNB^{2-} peak at 412 nm) and NADH oxidation (peak at 340 nm). Conditions: [GSH] 1 mM, [Cys] 1 mM, [NADH] 100 µM, [1] and [2] 30 µM for GSH and Cys, 10 µM for NADH experiment, HEPES 100 mM, pH 7.4, $\lambda_{exc}^{450\,nm}$, 25 °C.

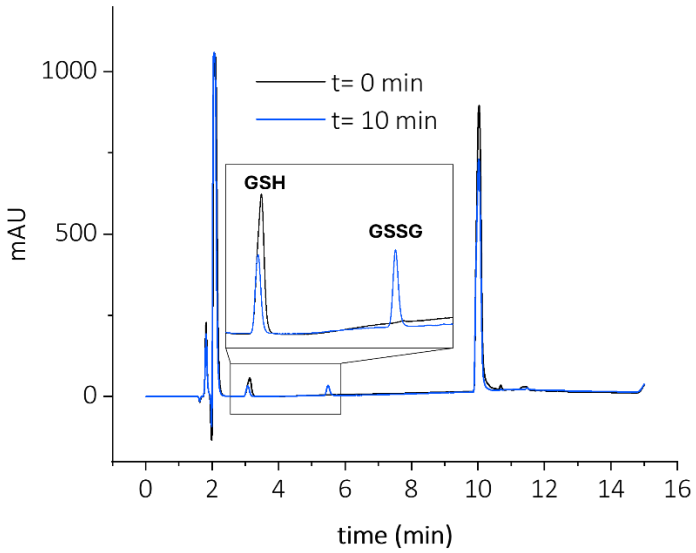

Figure S3. HPLC chromatograms showing GSH (Rt ~ 3.0 min) and GSSG (Rt ~ 5.5 min) peaks during the reaction of complex **1** with GSH at pH 7.4 under irradiation at 450 nm. No other species besides GSH and GSSG were detected. Conditions: [GSH] 1 mM, [**1**] 30 µM HEPES 100 mM, pH 7.4, $\lambda_{exc}^{450\,nm}$, 25 °C.

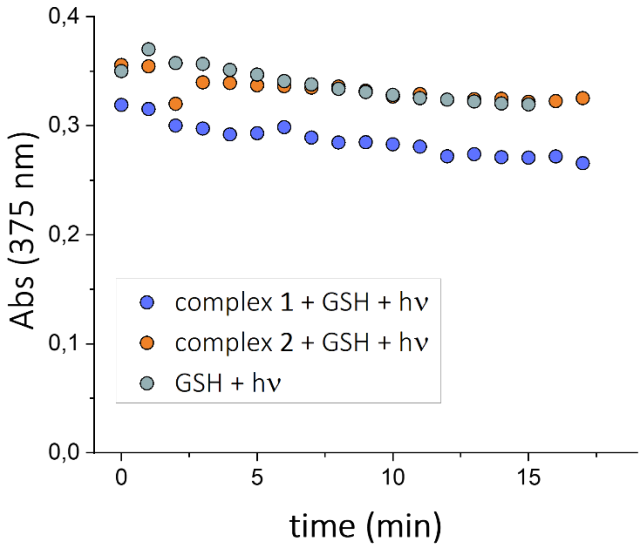

Figure S4. Anthracene consumption was followed by the decrease of its absorption peak at 375 nm during the oxidation of GSH by **1** and **2**. Conditions: [Anthracene] 60 µM, [1] and [2] 30 µM, [GSH] 1 mM, HEPES 100 mM, pH 7.4, $\lambda_{exc}^{450\,nm}$, 25 °C.

References

[1] S.-A. Hua, M. Cattaneo, M. Oelschlegel, M. Heindl, L. Schmid, S. Dechert, O. S. Wenger, I. Siewert, L. González, F. Meyer, *Inorg Chem* **2020**, *59*, 4972–4984.

[2] G. L. Ellman, Arch. Biochem Biophys. **1959**, *82*, 70–77.