Electronic Supporting Information for:

Heme protein-mediated synthesis of PEDOT:PSS: Enhancing conductivity by inhibiting heme degradation

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Materials

EDOT (#483028), poly(styrenesulfonate) (MW = 70 kDa, #243051), hemoglobin (from bovine blood, #H2500), ABTS (#A1888) and 30% hydrogen peroxide (#95321) were purchased from Sigma-Aldrich. All solutions were prepared in 18 MΩ cm^{-1} water (Easy Pure II, Thermo Fisher Scientific).

Polymerization of PEDOT:PSS

PEDOT:PSS was polymerized by combining hemoglobin (4.8 µM by heme concentration), EDOT (50 mM) and PSS (25 mM) in an HCl-KCl buffer (pH 1.15) while stirring. The reaction was initiated by the addition of H_2O_2 (20 mM). Separate polymerizations were performed with ABTS (0.4 mM), EDTA (30 µM), or both ABTS and EDTA. The final reaction volume in all cases was 2.5 ml. The polymerizations were allowed to proceed for 3 hours followed by dialysis (cut-off MW = 1000 Da) against 3 L of 18 MΩ cm^{-1} water for 24 hours. Water was exchanged at 30 minutes, 3 hours and 18 hours.

Characterization of PEDOT:PSS

Visible and near IR spectra (Cary 17 spectrophotometer, OLIS) were collected on films of PEDOT:PSS. Conductivity of PEDOT:PSS films was determined by four point probe (SYS-301 probe station, Signatone). Film thickness was measured by profilometry (P15, Tencor). For near IR and conductivity measurements, films were prepared with dialyzed

PEDOT:PSS filtered through 2 µm syringe filters and drop cast onto glass substrates. The films were then heated in ambient atmosphere for 20 minutes at 60 ˚C before measurement.

Fluorescence investigations of hemoglobin degradation
Hemoglobin (50 µM) was combined with H_2O_2 (50 mM) and the emission spectra were collected (Excite: 320 nm, RF-5301 PC spectrofluorophotometer, Shimadzu). For kinetic fluorescence experiments, the emission at 445 nm was recorded every 10 minutes for 1 hour. The fluorescence measurements were repeated in the presence of ABTS (2 mM).

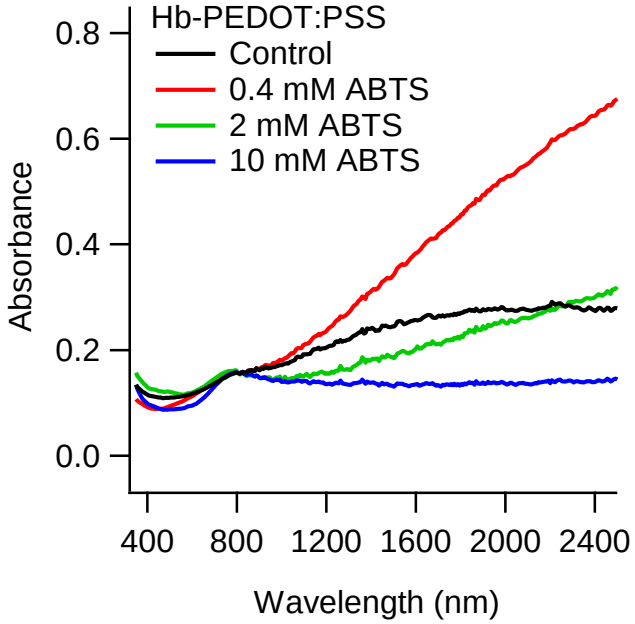

Fig. S1 Representative visible and near IR spectra of PEDOT:PSS synthesized with hemoglobin (Hb) in the absence of ABTS (black), 0.4 mM ABTS (red), 2 mM ABTS (green) and 10 mM ABTS (blue). Spectra are normalized by the absorbance at 800 nm for comparison. As ABTS concentration is increased above 0.4 mM, we observe a decrease in absorption at long wavelengths. This indicates a reduction in the bipolaron concentration. It is possible that ABTS is directly reducing PEDOT or that ABTS is reducing Hb preventing it from acting as an oxidant.

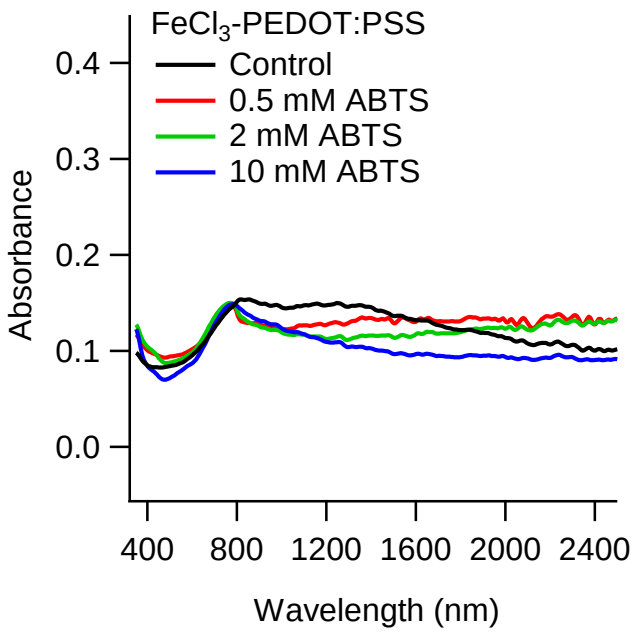

Fig. S2 Representative visible and near IR spectra of PEDOT:PSS synthesized with $FeCl_3$ in the absence of ABTS (black), 0.5 mM ABTS (red), 2 mM ABTS (green) and 10 mM ABTS (blue). Spectra are normalized by the absorbance at 800 nm for comparison. The stair step seen just above 800 nm is due to a detector change. No discernable trend is observed for PEDOT:PSS synthesized with iron chloride in the presence of ABTS.

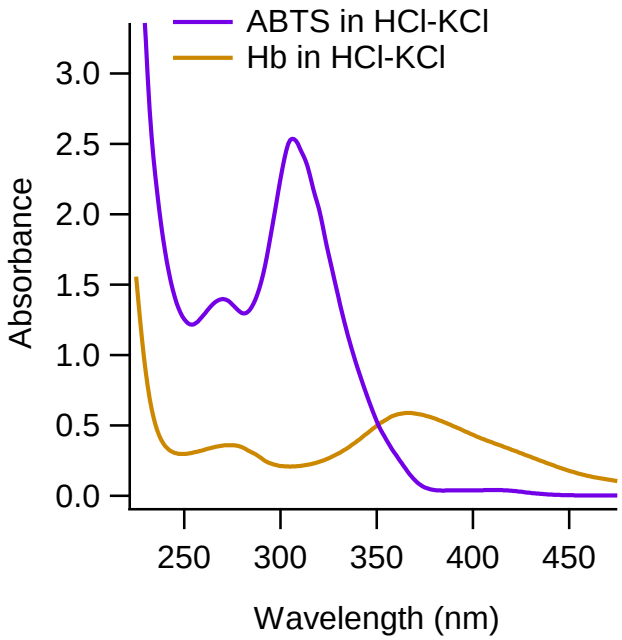

Fig. S3 Representative visible spectra of ABTS (purple) and Hb (orange) in an HCl-KCl buffer (pH 1.15). The spectral overlap of ABTS and Hb prevent unambiguous determination of heme degradation by monitoring the heme peak at 370 nm.

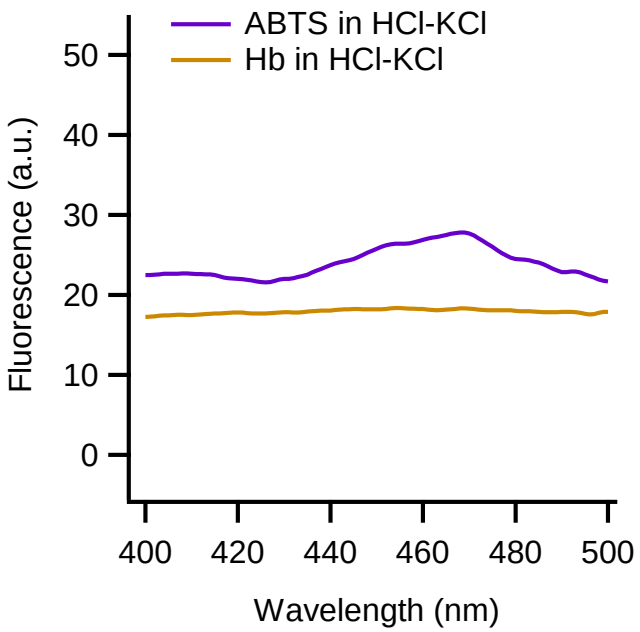

Fig. S4 Fluorescence emission spectra (ex: 320 nm) of ABTS (purple) and Hb (orange) in an HCl-KCl buffer (pH 1.15). There is no maximum at 445 nm from either ABTS or Hb before exposure to hydrogen peroxide. The peak at 470 nm is due to ABTS.[1] This peak is no longer significant after ten minutes of exposure to hydrogen peroxide (Figure S5).

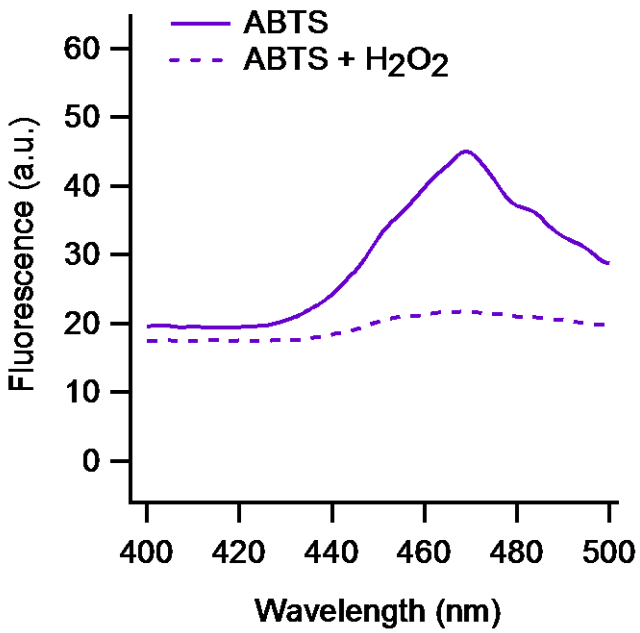

Fig. S5 Fluorescence emission spectra (ex: 320 nm) of ABTS before (purple, solid) and after (purple, dashed) exposure to hydrogen peroxide for ten minutes. The peak at 470 nm is due to ABTS.[1] This peak is no longer significant after ten minutes of exposure to hydrogen peroxide.

References

1. C. Lee and J. Yoon, *J. Photochem. Photobiol., A*, 2008, **197**, 232-238.