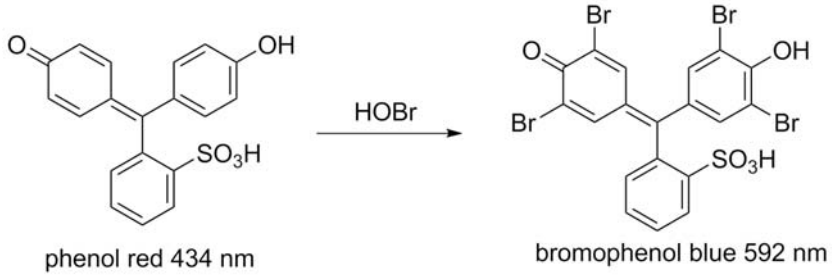
Supporting information

The *Aae*APO enzyme preparation was homogeneous by SDS/PAGE, and exhibited an $A_{418\ nm}/A_{280\ nm}$ ratio of 1.7. The specific activity of the peroxygenase was 59 Umg^{-1}, where 1 U represents the oxidation of 1 µmol of 3,4-dimethoxybenzyl alcohol to 3,4-dimethoxybenzaldehyde in 1 min at RT. Chloroperoxidase was purchased from Bio-Research Products, Inc. with RZ of $A_{400\ nm}/A_{280\ nm}$ > 1.3, 1,296 U mg^{-1}, where 1 unit represents the amount of CPO catalyzing the formation of 1 µmol of dichlorodimedone from monochlorodimedone in 1 min at 25 °C, pH 2.75, 0.02 M KCl, 2 mM H_2O_2. All chemicals were of the best available purity from Aldrich. Sodium hypochlorite solution was standardized spectrophoto-metrically (ε_{292nm}=350 $M^{-1}cm^{-1}$). Sodium hypobromite solution was freshly prepared by mixing sodium hypochlorite with sodium bromide under slightly basic conditions. A 5% excess of sodium bromide was used to ensure full conversion.[1] The final concentration of sodium hypobromite solution was determined spectrophotometrically (ε_{329nm}=332 $M^{-1}cm^{-1}$). Buffers were freshly prepared daily using either citric acid/sodium citrate (pH 3-5) or KH_2PO_4/K_2HPO_4 (pH 6 and 7). UV/Vis spectral measurements were performed on a Hewlett-Packard 8453 diode-array spectrophotometer at RT. Stopped-flow experiments were carried out on a Hi-Tech SF-61 DX2 double-mixing instrument with a 1 cm path length equipped with an ISOTEMP 3013 D thermostated bath.



Scheme S1. Phenol red conversion to bromophenol blue upon the addition of HOBr.

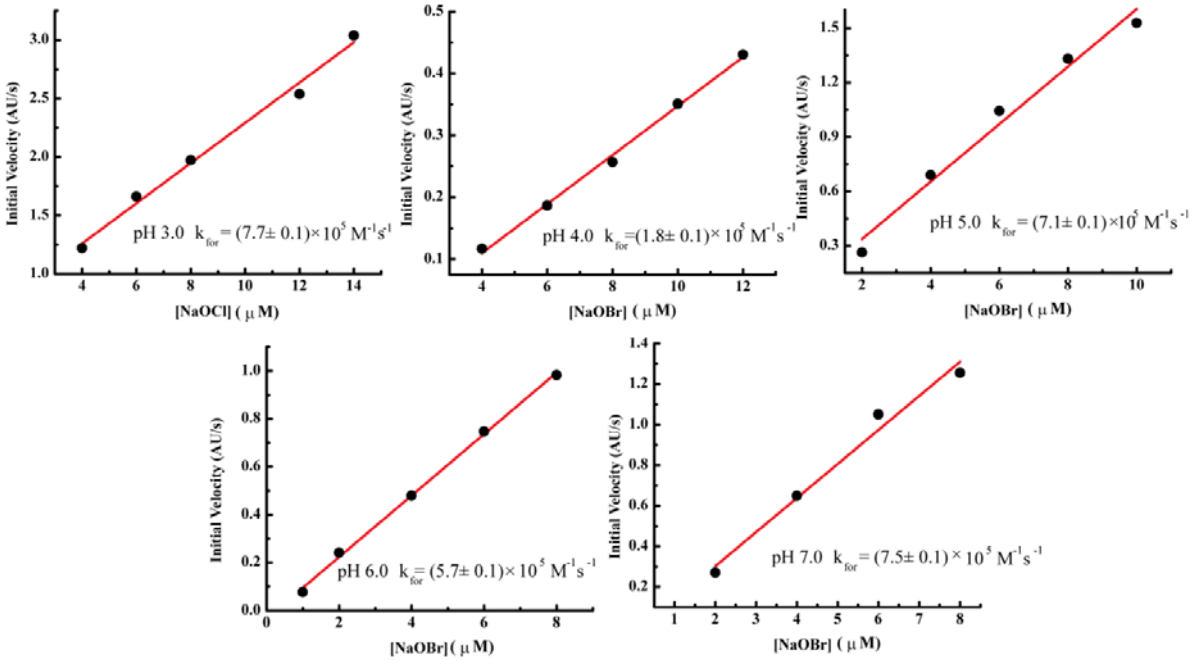


Figure S1. Initial velocity of ferric *Aae*APO oxidation as a function of [NaOX] for the reaction between 2 µM *Aae*APO with NaOX, pH 3-7.

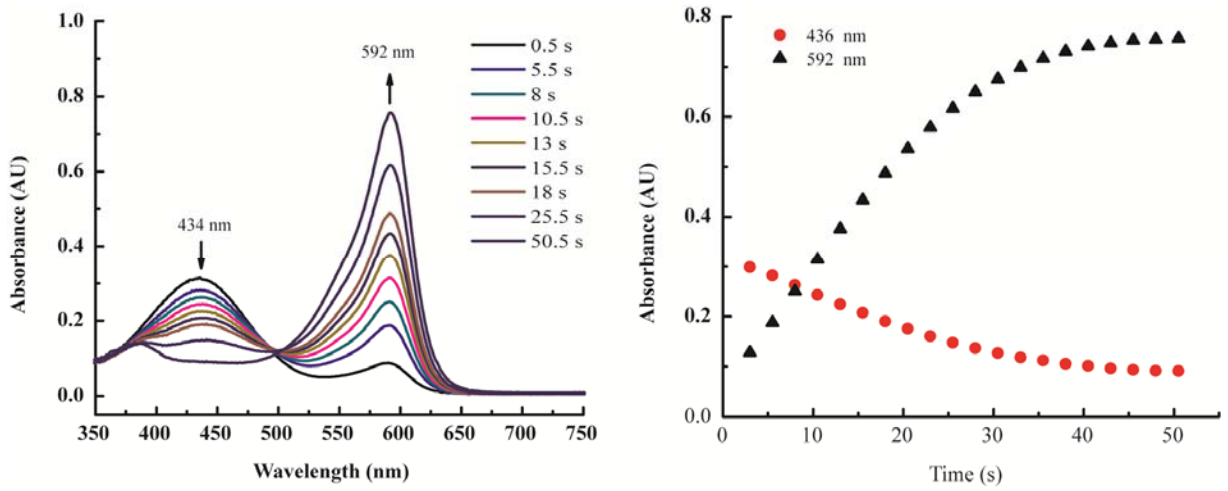


Figure S2. UV/Vis spectral changes observed for the bromination of phenol red (λ_{max}=434 nm) to form bromophenol blue (λ_{max}=592 nm) by 1 mM of H_2O_2, 10 μM NaBr and 20 nM of *Aae*APO at pH 5.0, RT.

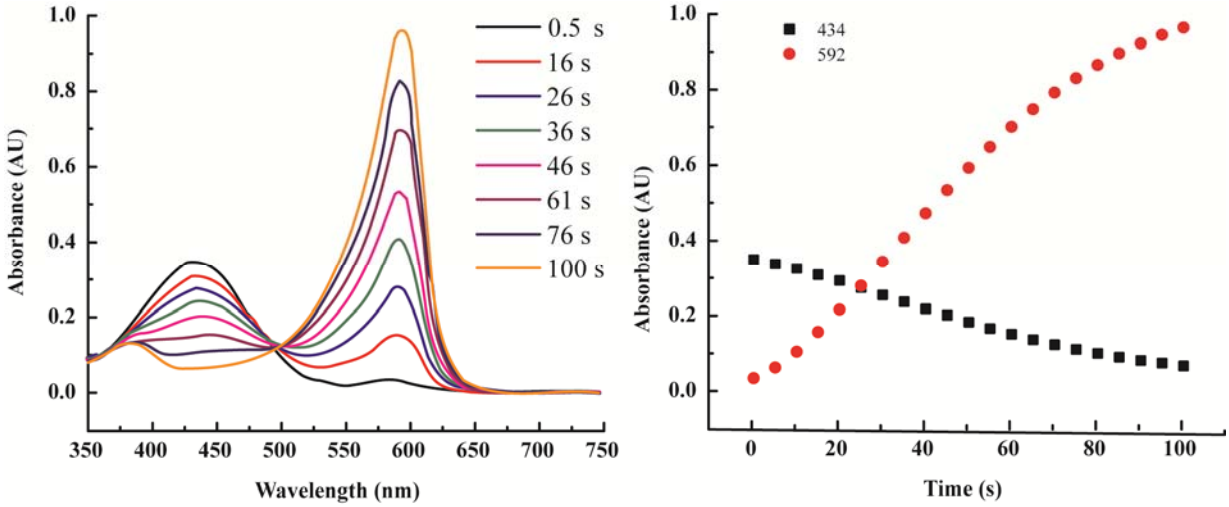


Figure S3. UV/Vis spectral changes observed for the bromination of phenol red (λ_{max}=434 nm) to bromophenol blue (λ_{max}=592 nm) by 1 mM of H_2O_2, 10 mM NaBr and 20 nM of CPO at pH 5.0, RT.

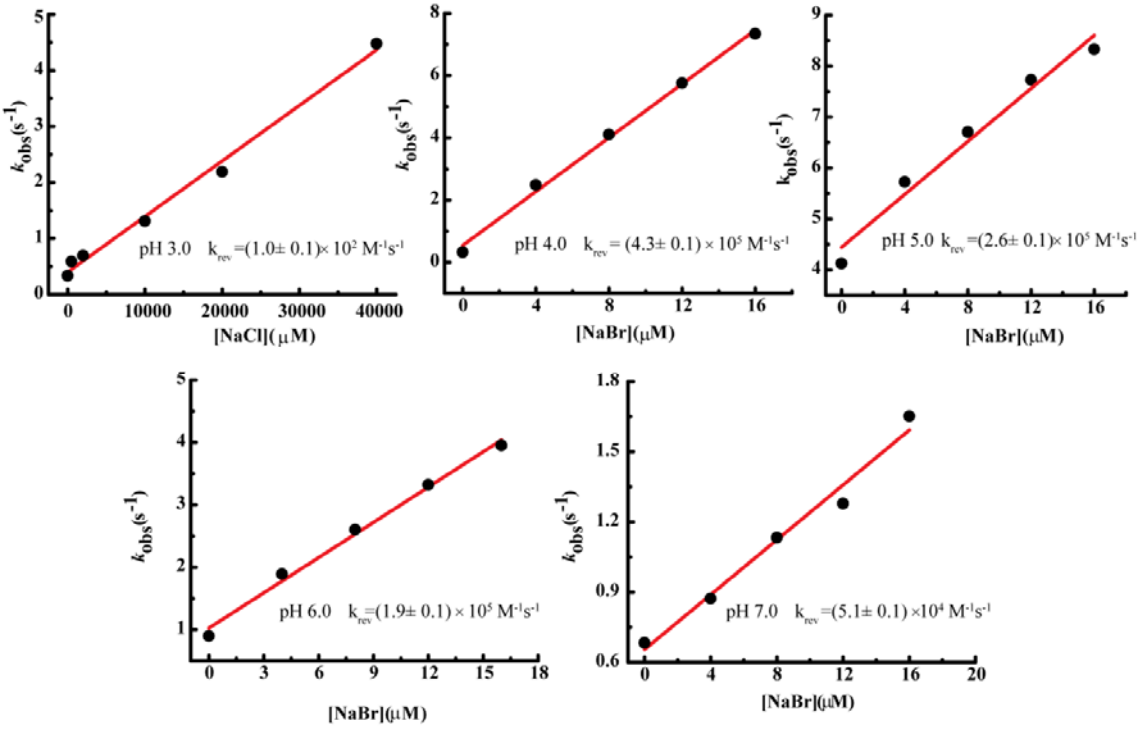


Figure S4. Pseudo-first order rate constants, k_{obs}, as a function of [NaX] for the reaction between *Aae*APO-I with halide ions at different pHs.

Table S1. Kinetic and thermodynamic data, k_{for}, k_{rev}, K_{equi} and $E'_{(cpd\text{-}I/ferric)}$, for oxygen atom transfer between halide ions and CPO-I.[a]

pH	k_{for} ($M^{-1}s^{-1}$)	k_{rev} ($M^{-1}s^{-1}$)	K_{equi}	$E'_{(cpd\text{-}I/ferric)}$ [b] [V, vs.NHE]
4.0	1.1×10^{6}	5.0×10^{5}	2.28	1.22
5.0	2.3×10^{6}	6.7×10^{4}	34.8	1.16
6.0	1.6×10^{6}	1.5×10^{3}	1067	1.10
7.0	1.6×10^{6}	7.4×10^{2}	2176	1.06

[a] Typical errors for the rate data are ~1% or less. [b] based on the $HOBr/Br^{-}$ couple at 4°C except as noted.[2]

[1] D. Lahaye, J. T. Groves, *J. Inorg. Biochem.* **2007**, *101*, 1786-1797.

[2] A. J. Bard, R. Parsons, J. Jordan, *Standard Potentials in Aqueous Solution*, Marcel Dekker, Inc., New York, **1985**, p. 67-92.