

Electronic Supplementary Information

Proton coupled electron transfer from Co_3O_4 nanoparticles to photogenerated $\text{Ru}(\text{bpy})_3^{3+}$: base catalysis and buffer effect.

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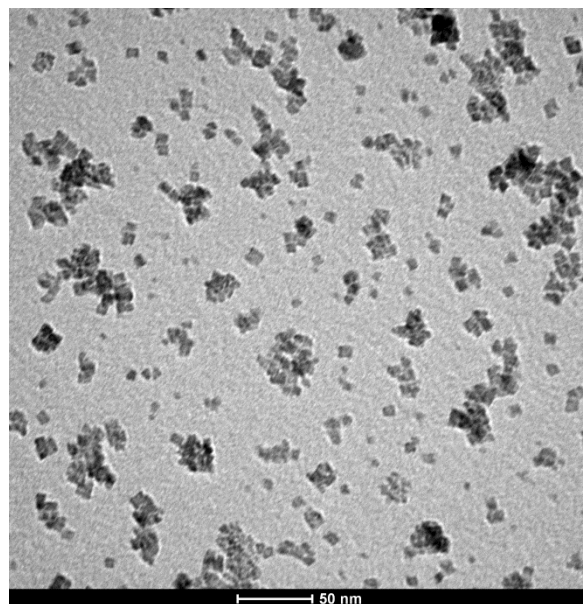


Figure S1. Transmission Electron Microscopy image of cubic Co_3O_4 NPs. Average NP size: 5 ± 1 nm.

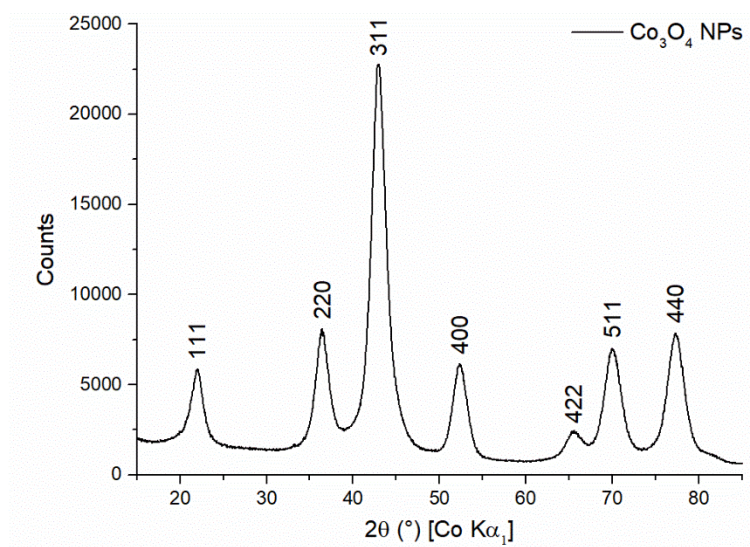


Figure S2. Powder X-ray diffraction pattern of Co_3O_4 NPs: cubic spinel structure, $Fd\bar{3}m$ space group. Source: $\text{Co K}\alpha_1$ ($\lambda = 1.788965 \text{ \AA}$).

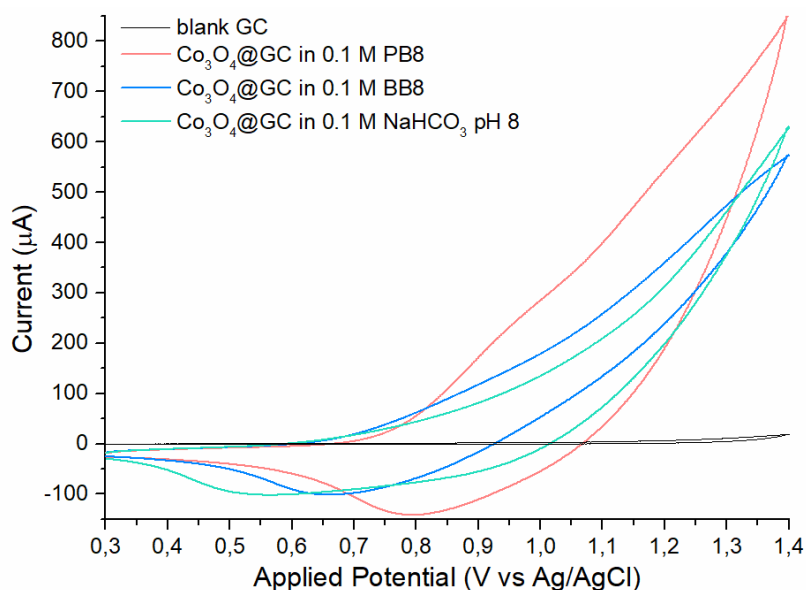


Figure S3. Cyclic voltammetry for Co₃O₄ NPs deposited onto glassy carbon, performed at pH 8 in different buffers. Working electrode: Glassy carbon (0.07 cm²); counter electrode: Pt (0.02 cm²); reference electrode: Ag/AgCl (3M NaCl); scan rate: 100 mV/s.

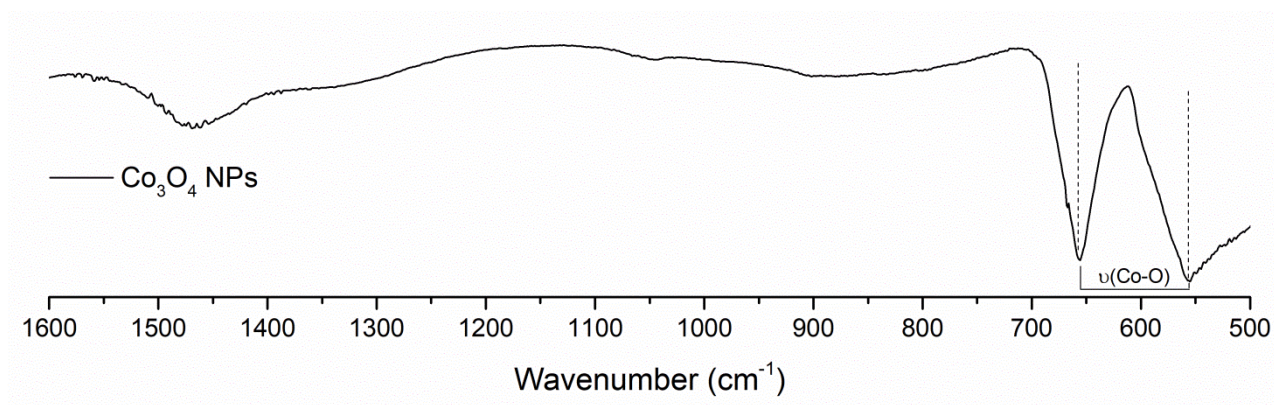


Figure S4. ATR-IR of Co₃O₄ NPs.

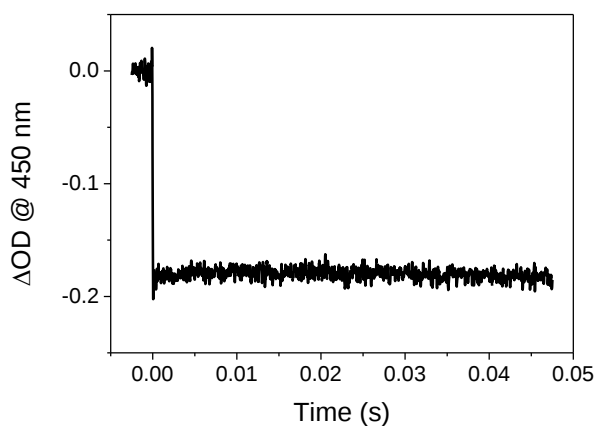


Figure S5. Laser flash photolysis ($\lambda_{\text{exc}} = 355 \text{ nm}$) of 50 μM Ru(bpy)₃²⁺ in the presence of 5 mM Na₂S₂O₈ and 100 μM CoFe₂O₄ NPs in 10 mM borate buffer at pH 8.

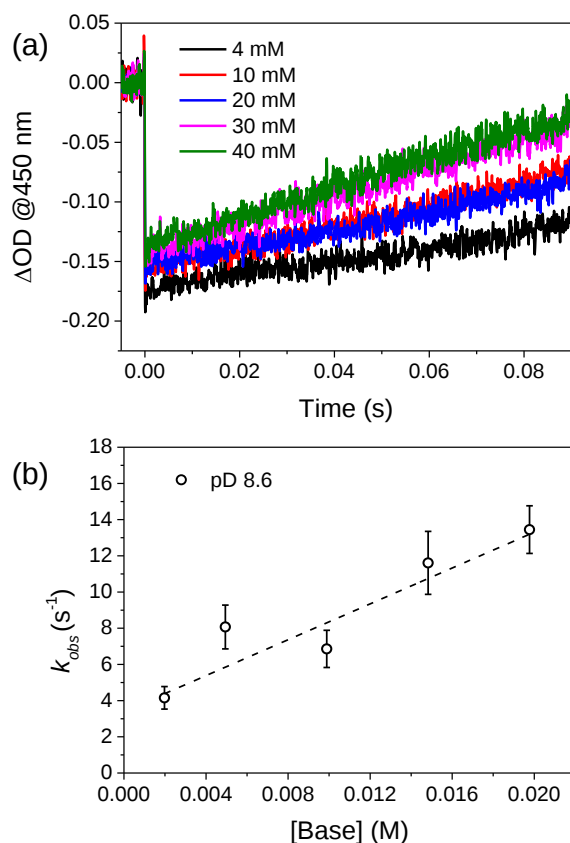


Figure S6. (a) Laser flash photolysis ($\lambda_{exc} = 355 \text{ nm}$) of $50 \mu\text{M Ru(bpy)}_3^{2+}$ in the presence of $5 \text{ mM Na}_2\text{S}_2\text{O}_8$ and $100 \mu\text{M Co}_3\text{O}_4$ NPs in 4-30 mM borate buffer at pD 8.6. (b) plot of k_{obs} vs [Base].

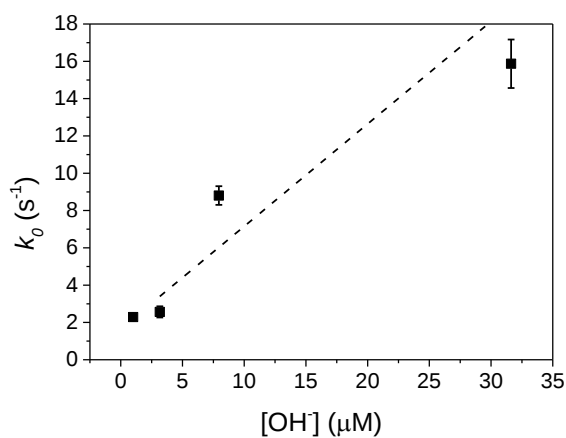


Figure S7. Plot of k_0 vs $[\text{OH}^-]$. See table 1 in the main text for k_0 values, determined from flash photolysis experiments in borate buffer, pH 8.0 – 9.5.

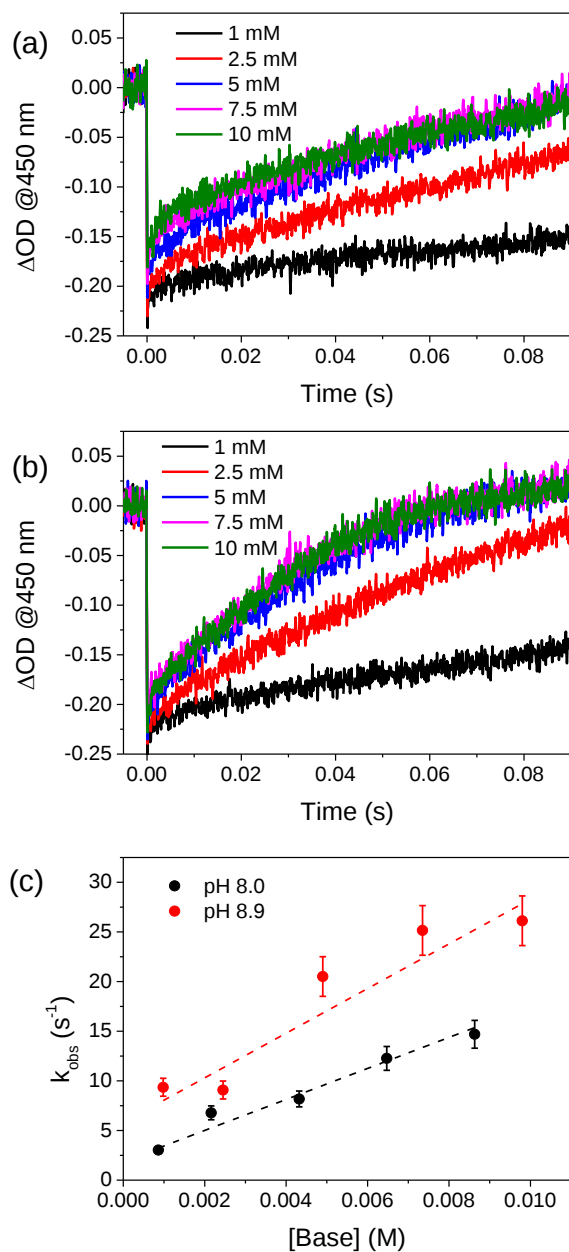


Figure S8. (a) laser flash photolysis ($\lambda_{\text{exc}} = 355 \text{ nm}$) of $50 \mu\text{M Ru}(\text{bpy})_3^{2+}$ in the presence of $5 \text{ mM Na}_2\text{S}_2\text{O}_8$ and $100 \mu\text{M Co}_3\text{O}_4$ NPs in $1\text{--}10 \text{ mM}$ phosphate buffer at pH 8.0. (b) Laser flash photolysis ($\lambda_{\text{exc}} = 355 \text{ nm}$) of $50 \mu\text{M Ru}(\text{bpy})_3^{2+}$ in the presence of $5 \text{ mM Na}_2\text{S}_2\text{O}_8$ and $100 \mu\text{M Co}_3\text{O}_4$ NPs in $1\text{--}10 \text{ mM}$ phosphate buffer at pH 8.9. (c) Plot of k_{obs} vs [Base].

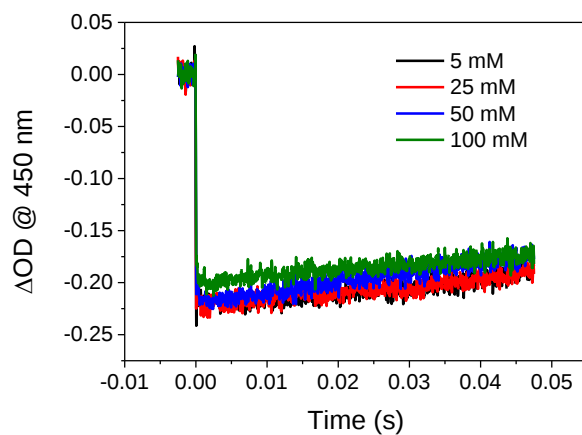


Figure S9. Laser flash photolysis ($\lambda_{\text{exc}} = 355 \text{ nm}$) of $50 \text{ } \mu\text{M}$ $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of 5 mM $\text{Na}_2\text{S}_2\text{O}_8$ and $100 \text{ } \mu\text{M}$ Co_3O_4 NPs at pH 8.0, in 5-100 mM carbonate buffer.

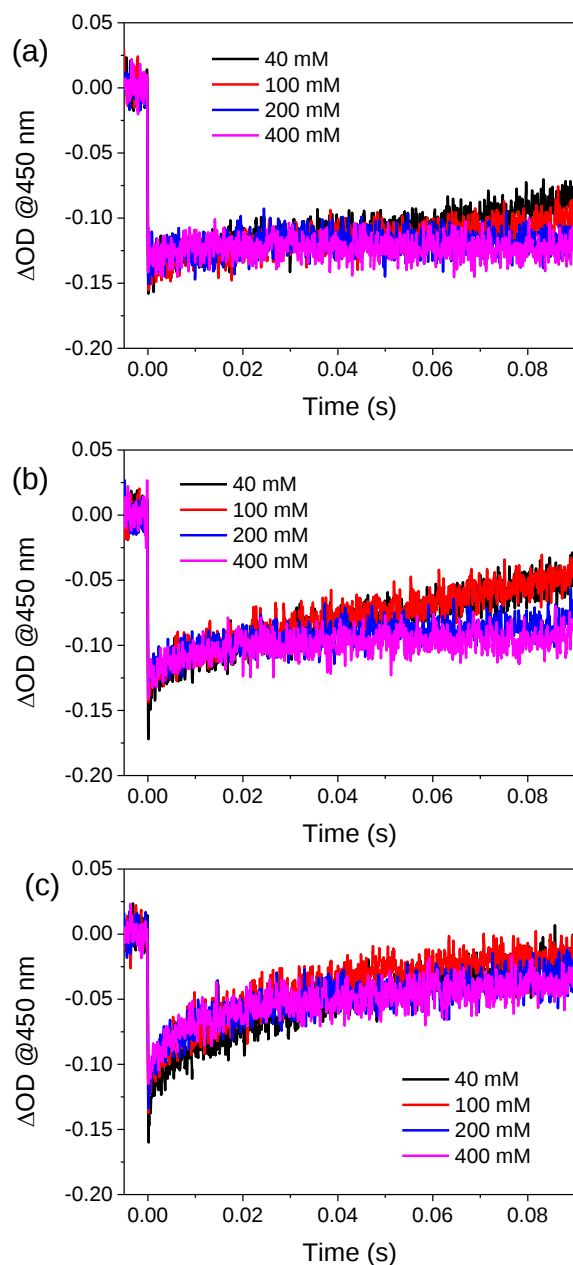


Figure S10. Laser flash photolysis ($\lambda_{\text{exc}} = 355 \text{ nm}$) of $50 \mu\text{M Ru(bpy)}_3^{2+}$ in the presence of $5 \text{ mM Na}_2\text{S}_2\text{O}_8$ and $100 \mu\text{M Co}_3\text{O}_4$ NPs at: (a) pH 8.0, in 40-400 mM borate buffer; (b) pH 8.5, in 40-400 mM borate buffer; (c) pH 8.9, in 40-400 mM borate buffer.

Table S1. Ru(III) lifetime (τ) and associated kinetic rate constants (k) for the flash photolysis experiments conducted at different pH and borate buffer concentration. For the sake of comparison, τ (and derived k values) are reported from: (i) experimentally determination at half recovery of the ΔOD^{450} in the experimental traces (values used in the discussion in the main text) and (ii) from mono or bi-exponential fittings. Bi-exponential fittings converged into a monoexponential fitting, unless in the cases indicated by footnote (b). Uncertainty in the τ values determined at the half recovery of the ΔOD traces is estimated as 10 or 15% of the value; uncertainty in the τ values determined by exponential fitting is provided by the fitting (see traces below).

buffer	Determined at the half recovery of the ΔOD traces		Determined from exponential fittings	
	τ (s)	k_{obs} (s^{-1})	τ (s)	k_{obs} (s^{-1})
Borate, pH 8				
4 mM	0.254±0.038 ^(a)	2.73±0.41	0.284±0.004	2.44±0.04
10 mM	0.186±0.028 ^(a)	3.72±0.56	0.217±0.003	3.19±0.04
20 mM	0.147±0.022 ^(a)	4.71±0.71	0.163±0.002	4.25±0.05
30 mM	0.160±0.024	4.33±0.65	0.183±0.003	3.79±0.06
40 mM	0.151±0.023	4.59±0.69	0.162±0.002	4.28±0.05
100 mM	0.218±0.033	3.18±0.48	0.244±0.004	2.84±0.05
200 mM	1.280±0.190	0.54±0.08	-	-
400 mM	-	-	-	-
Borate, pH 8.5				
4 mM	0.191±0.029 ^(a)	3.63±0.54	0.222±0.004	3.12±0.04
10 mM	0.121±0.018 ^(a)	5.73±0.86	0.131±0.002	5.29±0.05
20 mM	0.083±0.012	8.35±1.25	0.082±0.001	8.45±0.10
30 mM	0.066±0.010	10.5±1.6	0.073±0.001	9.49±0.13
40 mM	0.059±0.009	11.7±1.8	0.070±0.001	9.90±0.13
100 mM	0.065±0.009	10.7±1.6	0.072±0.001	9.63±0.13
200 mM	0.184±0.028	3.77±0.56	0.217±0.004	3.19±0.06
400 mM	0.326±0.049	2.12±0.32	0.372±0.006	1.86±0.03
Borate, pH 8.9				
4 mM	0.058±0.006	11.9±1.2	0.0621±0.0006	11.16±0.11
10 mM	0.053±0.005	13.1±1.3	0.0558±0.0005 ^(b)	12.42±0.11
20 mM	0.034±0.003	20.4±2.0	0.0390±0.0004 ^(b)	17.77±0.20
30 mM	0.026±0.003	26.7±2.7	0.0413±0.0004 ^(b)	16.78±0.17
40 mM	0.020±0.002	34.7±3.5	0.0341±0.0004 ^(b)	20.32±0.18
100 mM	0.016±0.002	43.3±4.3	0.0284±0.0003 ^(b)	24.41±0.23
200 mM	0.020±0.002	35.0±3.5	0.054±0.001 ^(b)	12.83±0.22
400 mM	0.023±0.002	30.1±3.0	0.074±0.001 ^(b)	9.37±0.13
Borate, pH 9.5				
4 mM	0.037±0.004	18.7±1.9	0.0295±0.0002	23.41±0.16
10 mM	0.033±0.003	21.0±2.1	0.0266±0.0002	26.06±0.20
20 mM	0.022±0.002	30.9±3.1	0.0192±0.0002	36.10±0.38
30 mM	0.020±0.002	33.6±3.4	0.0166±0.0002	41.76±0.51
40 mM	0.017±0.002	40.8±4.1	0.0133±0.0002	52.12±0.76
100 mM	0.012±0.001	58.8±5.9	0.0100±0.0001	69.31±0.69
200 mM	0.029±0.003	23.5±2.3	0.0333±0.0002	20.81±0.12
400 mM	0.040±0.004	17.3±1.7	0.0919±0.001	7.54±0.58

^(a)determined from a linear fitting of the traces; ^(b)determined from a weighted average of the two τ values from a bi-exponential fitting.

Table S2. Kinetic rate constants for PCET from Co_3O_4 NPs to $\text{Ru(III)(bpy)}_3^{3+}$ in flash photolysis experiments in borate buffer, determined from: (i) experimentally determination at half recovery of the ΔOD^{450} in the experimental traces (values used in the discussion in the main text) and (ii) from mono or bi-exponential fittings, see Table S1.

pH	Determined plotting k_{obs} (determined at the half recovery of the ΔOD traces)		Determined plotting k_{obs} (from exponential fittings)	
	k_0 (s^{-1})	$k_B/100$ ($\text{M}^{-1}\text{s}^{-1}$)	k_0 (s^{-1})	$k_B/100$ ($\text{M}^{-1}\text{s}^{-1}$)
8.0	2.3 ± 0.2	6.3 ± 0.9	2.0 ± 0.1	5.6 ± 0.3
8.5	2.6 ± 0.2	6.3 ± 0.5	2.6 ± 0.8	5.7 ± 0.9
8.9	8.8 ± 0.5	8.5 ± 1.2	10.4 ± 2.0	4.0 ± 1.8
9.5	15.9 ± 1.1	7.0 ± 0.7	19.0 ± 1.0	8.8 ± 0.4

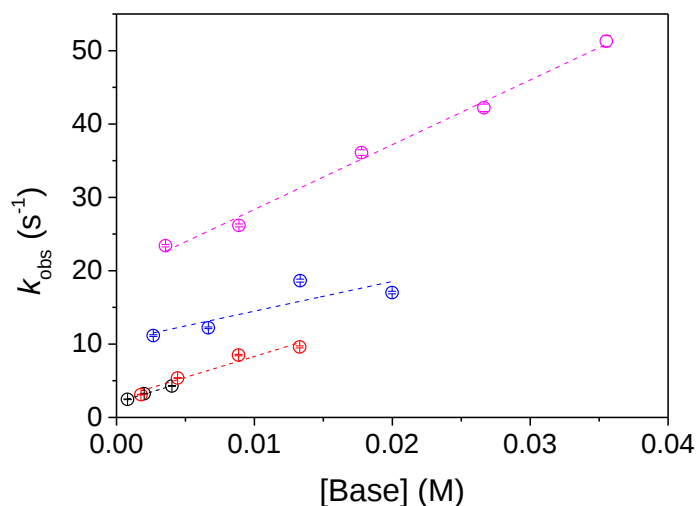


Figure S11. Plot of k_{obs} (from exponential fittings) vs. $[\text{Base}]$, where Base is B(OH)_4^- , and the concentrations are given by $[\text{Base}] = f_B \times [\text{buffer}]$, where f_B is the fraction of the basic form of the buffer in solution, and $[\text{buffer}]$ is the total buffer concentration; pK_a for the $\text{H}_3\text{BO}_3/\text{B(OH)}_4^-$ couple = 8.6.

