

Supplementary Information for Time-Resolved and Steady-State Irradiation of Hydrophilic Sulfonated Bis-triazinyl-(bi)pyridines – Modelling Radiolytic Degradation

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Reaction Kinetics Figures

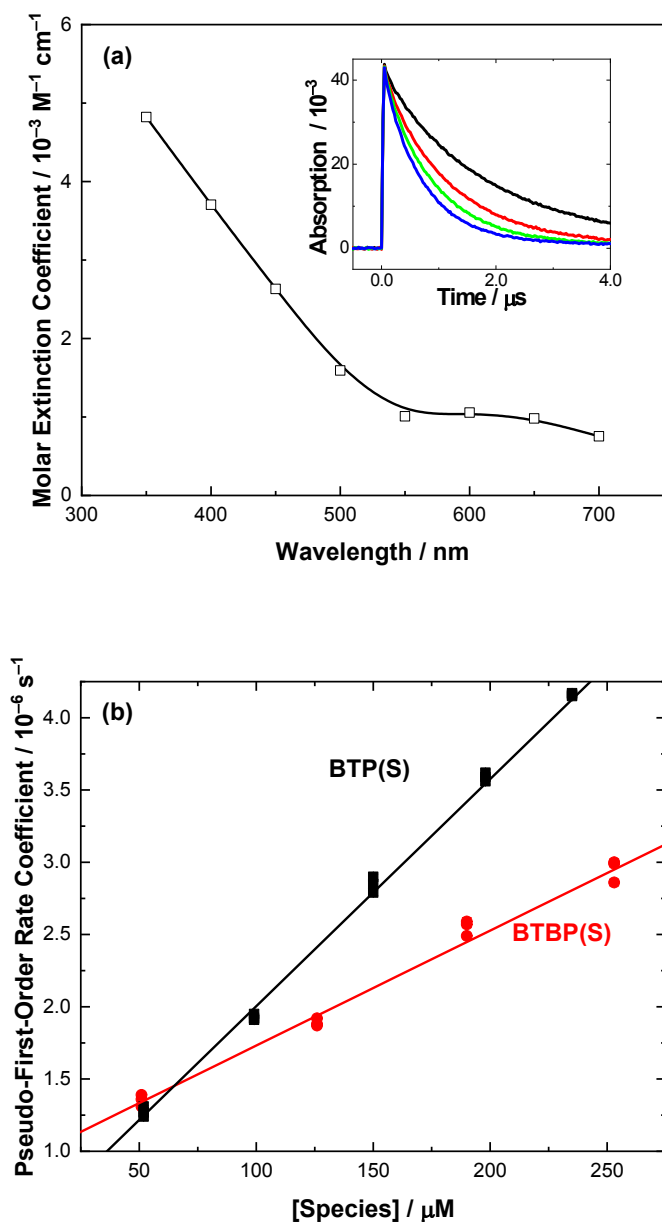


Figure 1. (a) Transient spectra for the reduction product of the hydrated electron reaction with BTBP(S) for 105.5 μM BTBP(S). Spectral intensity measured at end of hydrated electron decay ($\sim 5\text{-}6 \mu\text{s}$ after pulse, see *Inset*). *Inset*: Kinetic decay of the hydrated electron in pH 7.01, N_2 -saturated, aqueous solution containing 25.0 mM tertiary butanol at 22.4 $^\circ\text{C}$ in the presence of 21.4 (Black), 42.0 (Red), 61.2 (Green) and 105.5 (Blue) μM BTBP(S). (b) Second-order determination of the rate coefficient for the hydrated

electron reaction with BTP(S)(■) BTBP(S)(●). Solid line is a weighted linear fit, with slope corresponding to the second-order rate coefficient: $k_{\text{BTP(S)}} = (2.74 \pm 0.35) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{BTBP(S)}} = (7.98 \pm 0.26) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

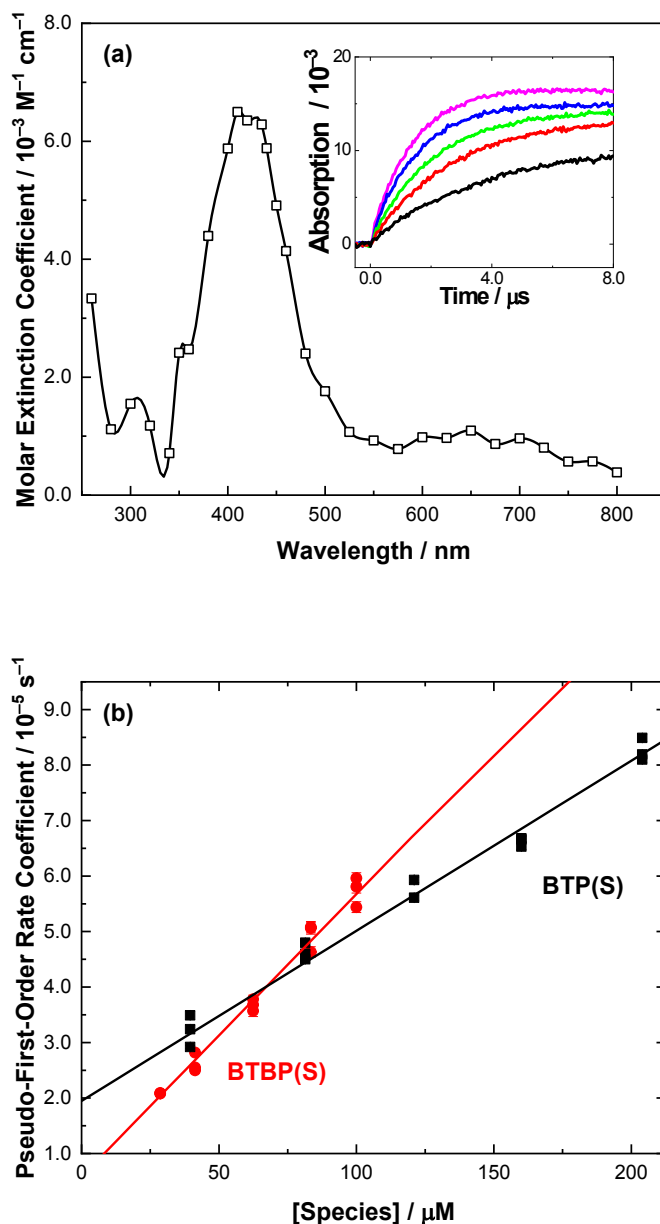


Figure 3. (a) Transient spectra for the reduction product of the hydrogen atom reaction with BTBP(S) for $146.0 \mu\text{M}$ BTBP(S). Spectral intensity measured at end of kinetic growth ($\sim 6\text{--}7 \mu\text{s}$ after pulse, see *Inset*). *Inset*: kinetic growth behavior in pH 2.00, N_2 -saturated aqueous solution containing 20.0 mM tertiary butanol at $22.3 \text{ }^\circ\text{C}$ in the presence of 30.7 (Black), 56.4 (Red), 85.9 (Green), 120.6 (Blue), and 146.0 (Magenta) μM BTBP(S). (b) Second-order determination of the rate coefficient for the hydrogen atom reaction with BTBP(S)(■) and BTP(S)(●), based upon pseudo-first-order exponential growth fits to raw kinetic data. Solid lines are weighted linear fits, with slopes corresponding to the second-order rate coefficient: $k_{\text{BTP(S)}} = (3.07 \pm 0.11) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{BTBP(S)}} = (5.20 \pm 0.18) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

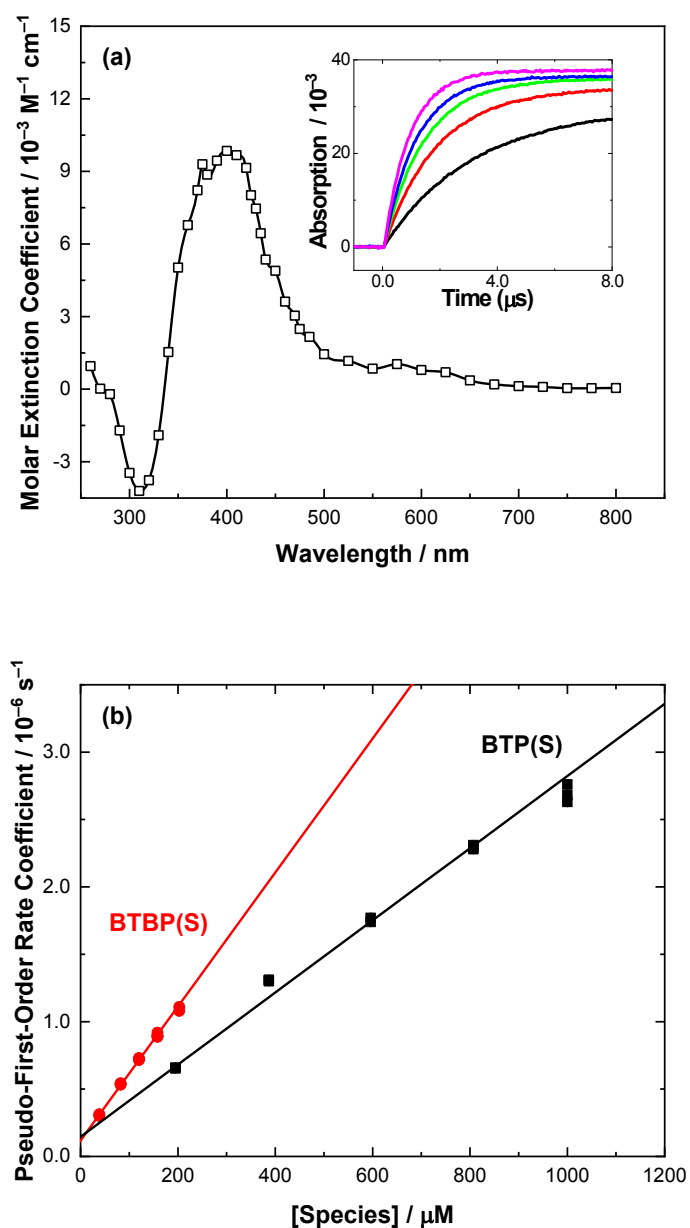


Figure 2. (a) Transient spectra for the oxidation product of the hydroxyl radical reaction with BTBP(S) for 202.6 μM BTBP(S). Spectral intensity measured at end of kinetic growth ($\sim 5\text{--}6$ μs after pulse, see *Inset*). *Inset*: kinetic growth behavior in pH 7.02, N_2O -saturated aqueous solution at 22.2 $^\circ\text{C}$ in the presence of 38.5 (Black), 82.3 (Red), 120.3 (Green), 158.1 (Blue), and 202.6 (Magenta) μM BTBP(S). (b) Second-order determination of the rate coefficient for the hydroxyl radical reaction with BTP(S) (■) and BTBP(S) (●), based upon pseudo-first-order exponential growth fits to raw kinetic data. Solid lines are weighted linear fits, with slopes corresponding to the second-order rate coefficient: $k_{\text{BTP(S)}} = (2.48 \pm 0.14) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{BTBP(S)}} = (4.24 \pm 0.05) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

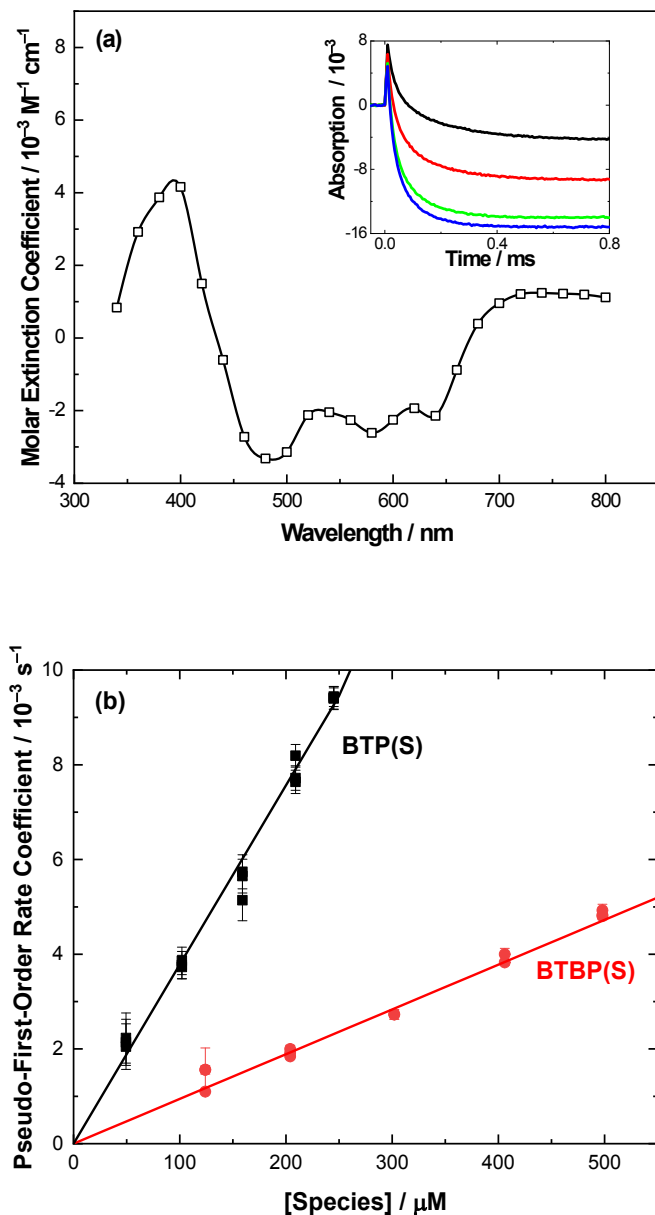


Figure 4. (a) Measured transient absorbance for the oxidation product of the nitrate radical reaction with BTBP(S) for 244.7 μM BTBP(S). Spectral intensity measured at end of kinetic growth ($\sim 600\text{--}700 \mu\text{s}$ after pulse, see *Inset*). *Inset*: Kinetic growth behavior in 6.0 M nitric acid at 22.0 $^{\circ}\text{C}$ in the presence of 49.4 (Black), 102.4 (Red), 208.7 (Green), and 244.7 (Blue) μM BTBP(S). (b) Second-order determination of the rate coefficient for the nitrate radical reaction with BTBP(S) (■) and BTBP(S) (●), based upon mixed first- and second-order decay fits to raw kinetic data. Solid lines are weighted linear fits, with slopes corresponding to the second-order rate coefficient: $k_{\text{BTBP(S)}} = (3.72 \pm 0.13) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{BTBP(S)}} = (1.04 \pm 0.07) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.