Supplementary Material (ESI) for Chemical Communications

Supporting Information

Direct Evidence for an Iron(IV)-Oxo Porphyrin π-Cation Radical as an Active Oxidant in Catalytic Oxygenation Reactions

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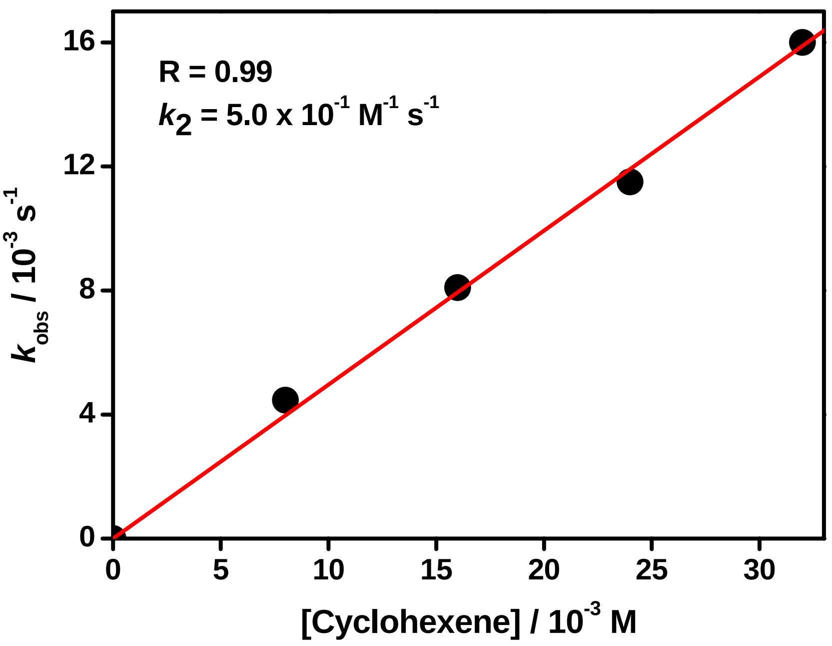
General Experimental Section

All chemicals obtained from Aldrich Chemical Co. were the best available purity and were used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under Ar prior to use (*Purification of Laboratory Chemicals*; Armarego, W. L. F.; Perrin, D. D., Eds.; Pergamon Press: Oxford, 1997.). *m*-CPBA was purified by washing with phosphate buffer (pH 7.4) followed by water and then dried under reduced pressure. $H_2{}^{18}O$ (95% ^{18}O-inriched) was purchased from ICON Services Inc. (Summit, NJ, USA). Fe(TMP)Cl was obtained from Mid-Century Chemicals (Posen, IL., USA).

All reactions were followed by monitoring UV-vis spectral changes of reaction solutions with a Hewlett Packard 8453 spectrophotometer equipped with an Optostat^{DN} variable-temperature liquid-nitrogen cryostat (Oxford instruments) at -40 ^{o}C or with a Hi-Tech Scientific SF-61 multimixing cryogenic stopped-flow instrument equipped with a Hi-Tech Scientific KinetaScan diode array rapid scanning unit at 25 ^{o}C. Product analysis was performed by injecting reaction solutions directly into GC (Agilent Technologies 6890N gas chromatograph equipped with a FID detector) and/or GC-MS (Thermo Finnigan FOCUS DSQ mass spectrometer interfaced with Finnigan FOCUS gass chromatograph).

Labeled water, $H_2{}^{18}O$, experiments were carried out by adding 4 equiv of *m*-CPBA to a reaction solution containing Fe(TMP)(Cl) (1 mM), substrates (50 mM), and $H_2{}^{18}O$ (0.5 M, 95% ^{18}O-enriched) in a solvent mixture of CH_3CN and CH_2Cl_2 (1:1) or in a solvent mixture of CH_3OH, CH_3CN, and CH_2Cl_2 (2:1.5:1.5) at 10 ^{o}C. The reaction mixture was stirred for 0.5 h and directly analyzed by GC-MS. In the epoxidation of cyclohexene,[16] ^{16}O and ^{18}O compositions in cyclohexene oxide (~60% yield based on the oxidant added) were determined by the relative abundances of the mass peaks at $m/z = 83$ for ^{16}O and $m/z = 85$ for ^{18}O.

(a)



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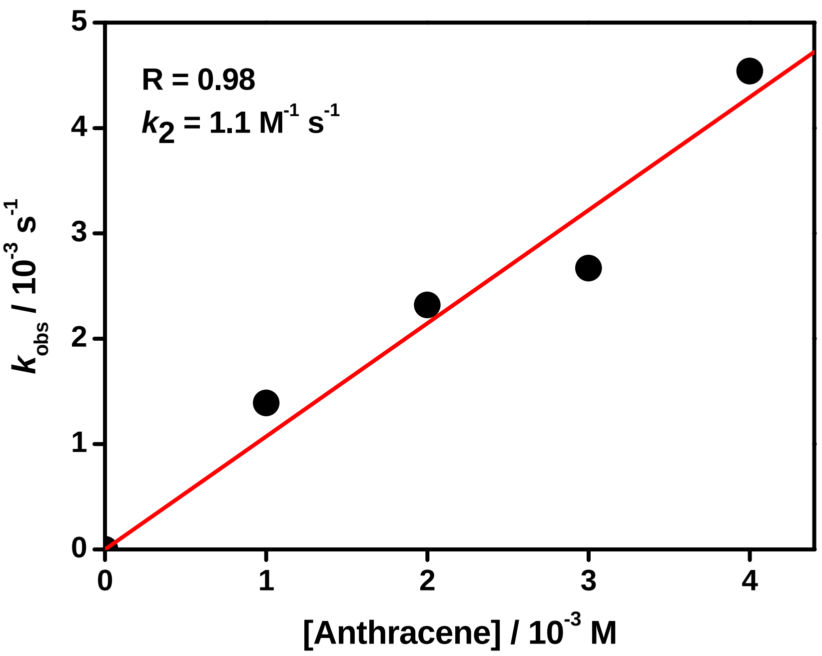
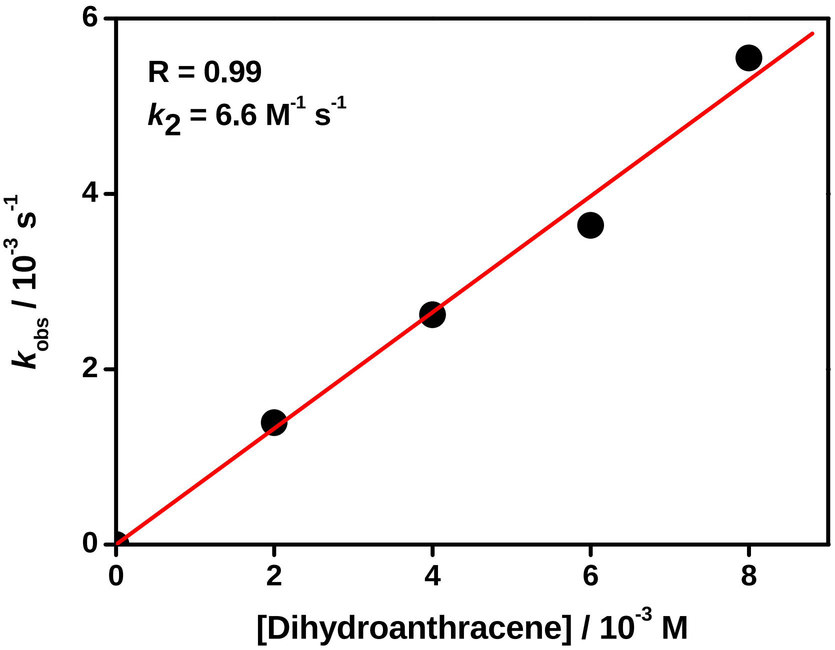


Figure S1 continued

(c)



(d)

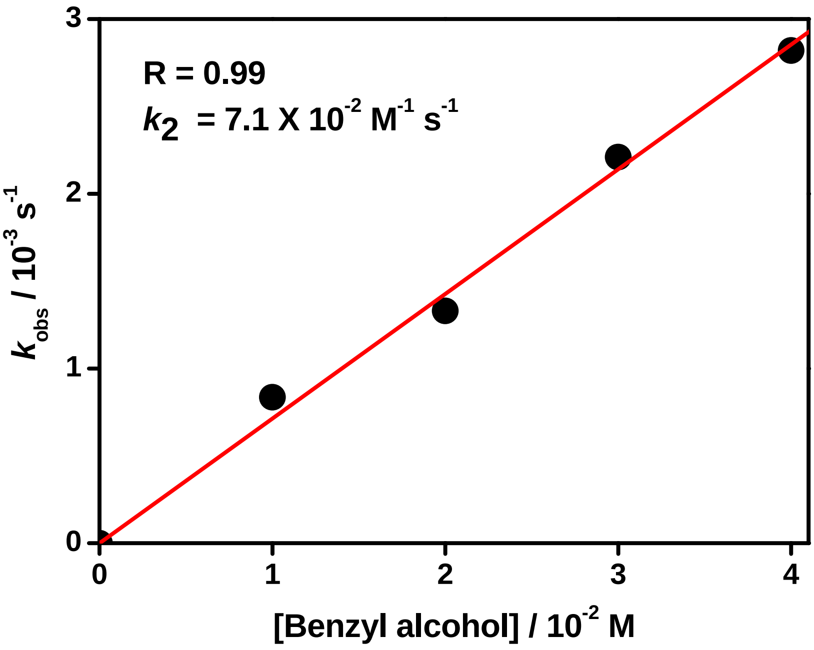
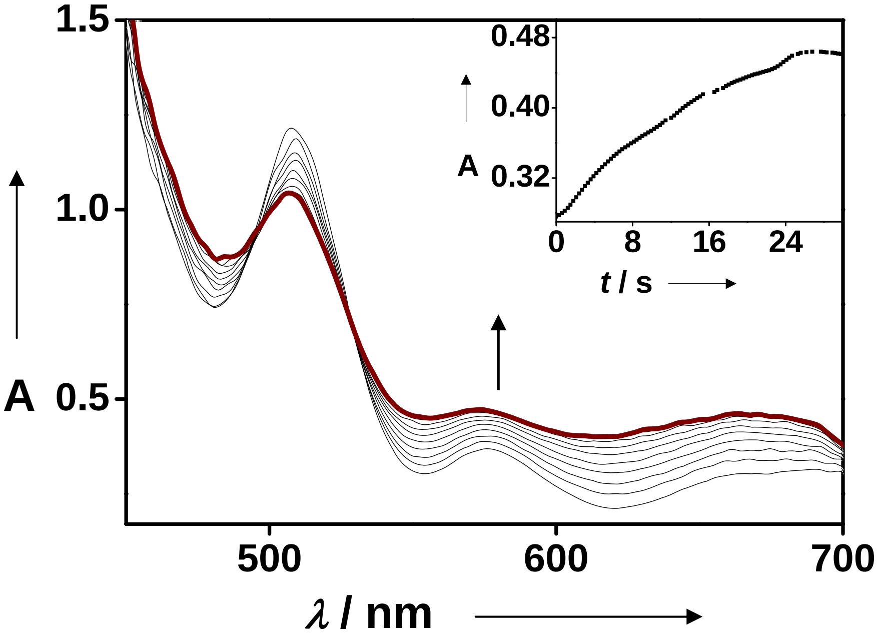


Figure S1. Plot of k_{obs} of $[(TMP)^{+\bullet}Fe^{IV}=O]^+$ (**1**) (2 mM) against substrate concentrations to determine second-order rate constants in a solvent mixture of CH_3CN and CH_2Cl_2 (1:1) at -40 °C; (a) cyclohexene, (b) anthracene, (c) dihydroanthracene, and (d) benzyl alcohol.

(a)



(b)

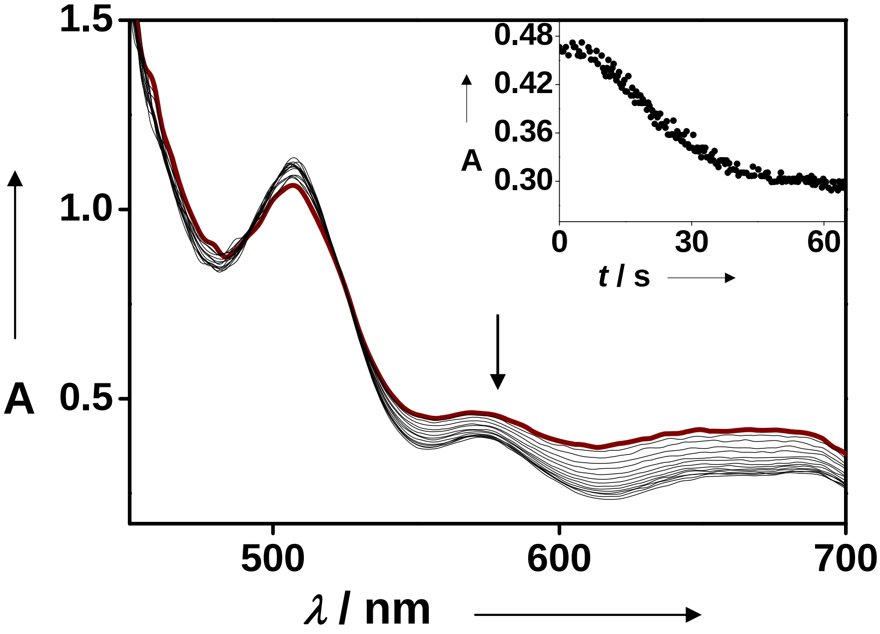
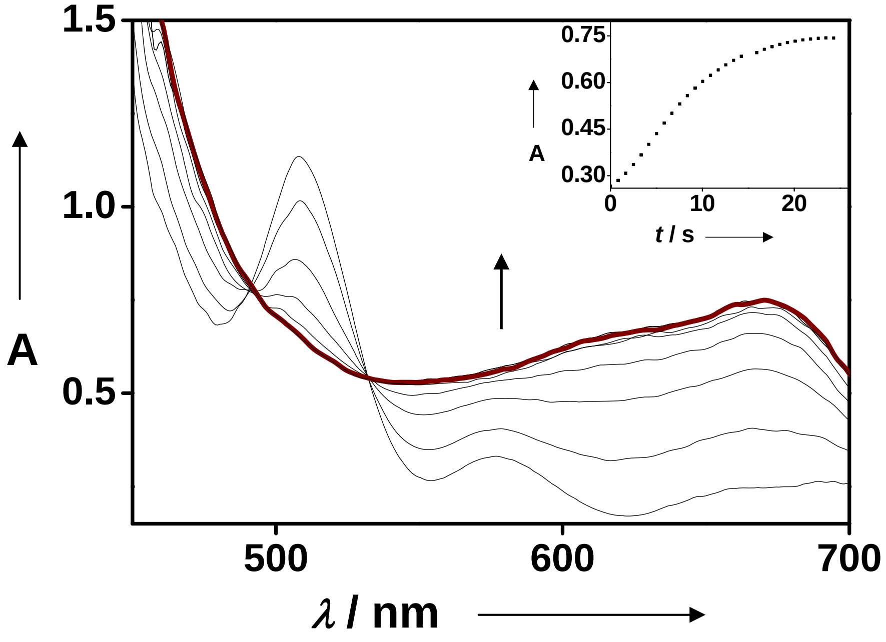


Figure S2 continued

(c)



(d)

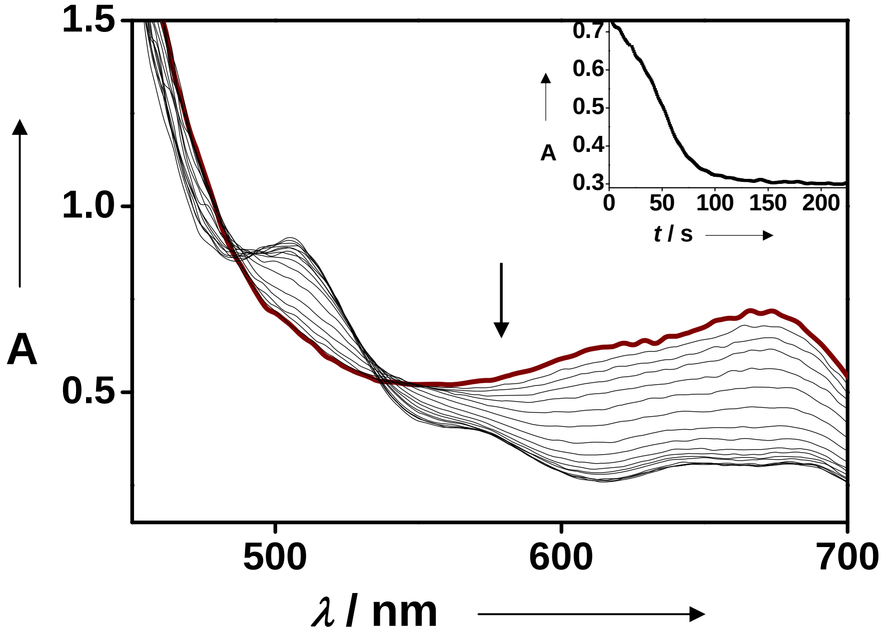


Figure S2. UV-vis spectral changes showing (a) the formation of **1** and (b) the disappearance of **1** in the catalytic oxygenation of dihydroanthracene (0.8 mM) and (c) the formation of **1** and (d) the disappearance of **1** in the catalytic oxidation of benzyl alcohol (0.8 mM) by Fe(TMP)Cl (0.08 mM) and *m*-CPBA (0.32 mM) in a solvent mixture of CH_3CN and CH_2Cl_2 (1:1) at 25 °C. Inset shows absorbance traces monitored at 666 nm.