Supporting Information of

Tuning Catalytic Activity with Steric and Electron-Withdrawing Effects of Porphyrin Substituent.

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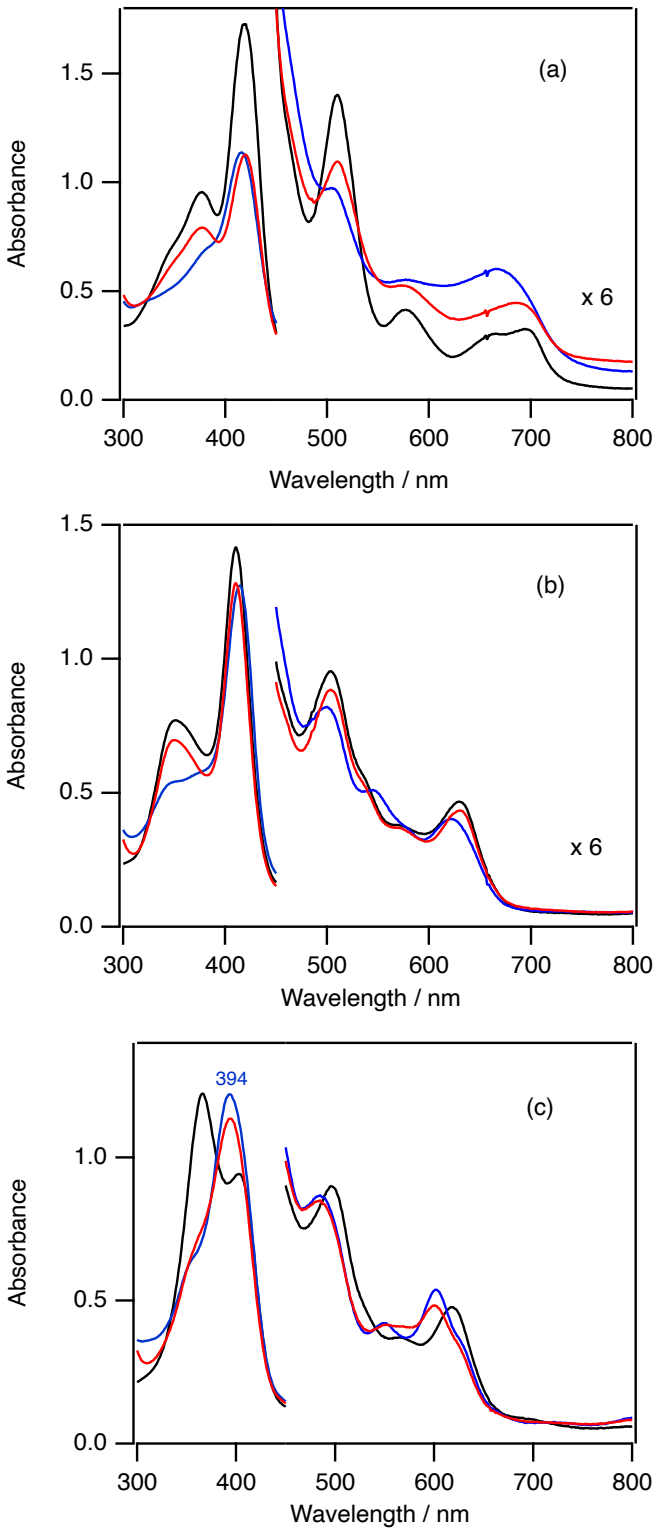

Figure S1. Absorption spectral changes in the catalytic cyclohexane oxidation reactions of **2-Cl** (a), **3-Cl** (b), and **5-Cl** (c) with ^{s}Ph-IO at 20 °C. The concentration of cyclohexane is 0.2 M. Black line: before addition of ^{s}Ph-IO, blue line: immediate after the addition of ^{s}Ph-IO, red line: after 300 s.

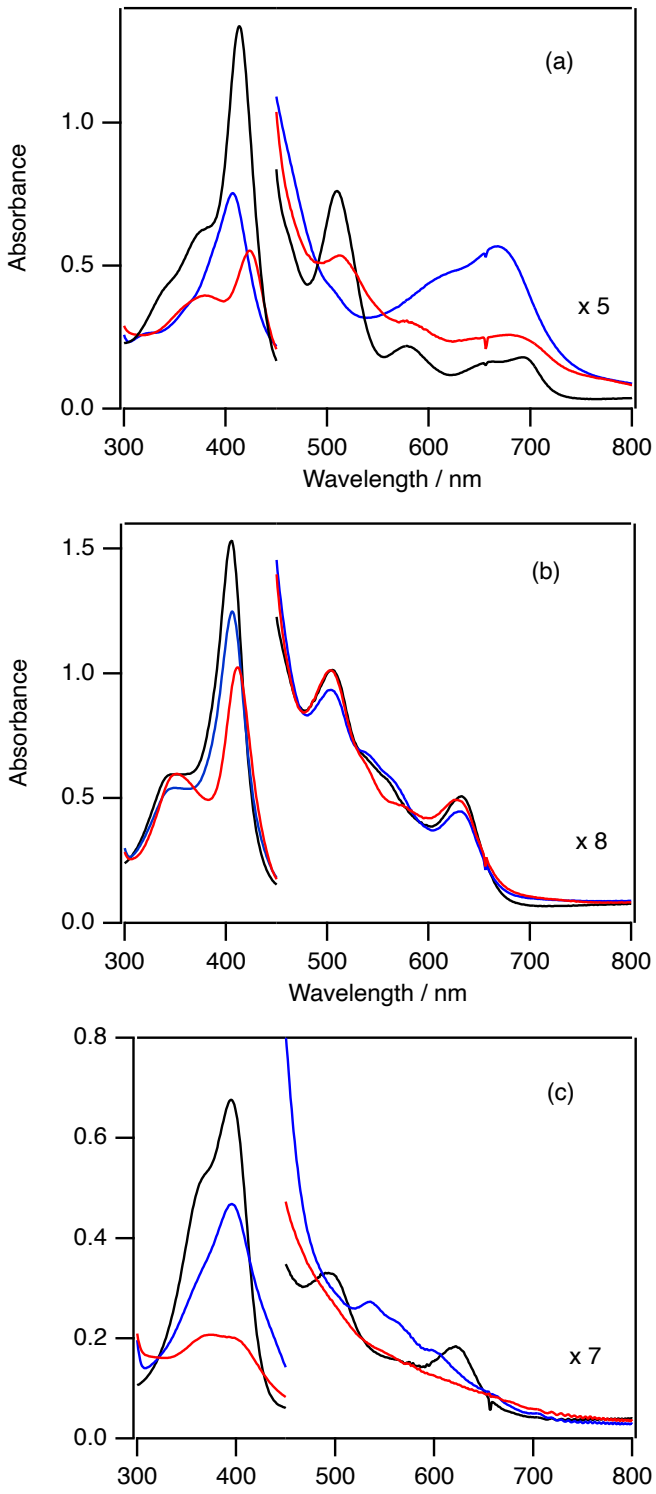

Figure S2. Absorption spectral changes in the catalytic cyclohexane oxidation reactions of **2-TFA** (a), **3-TFA** (b), and **5-TFA** (c) with mCPBA at 20 °C. The concentration of cyclohexane is 0.2 M. Black line: before addition of mCPBA, blue line: immediate after the addition of mCPBA, red line: after 300 s.

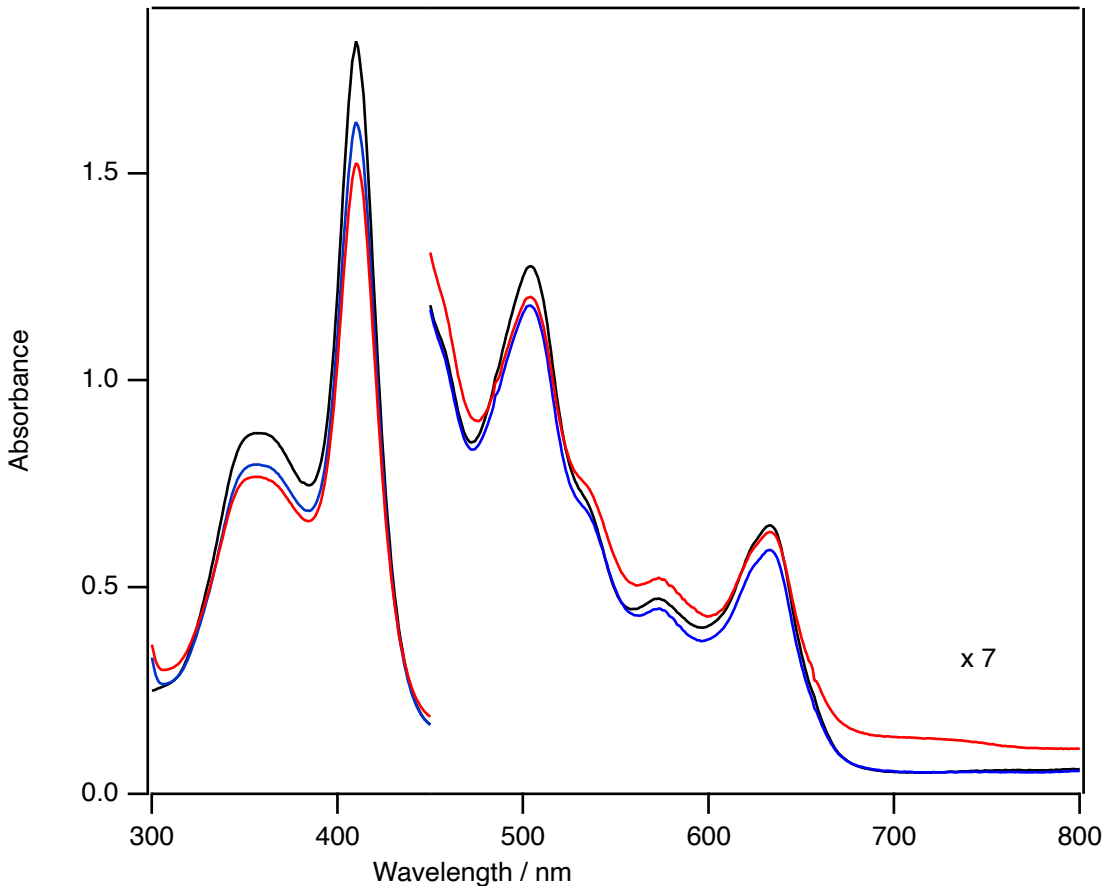

Figure S3. Absorption spectral changes in the catalytic reactions of **3-Cl** with cyclohexane (0.2 M) at –80 °C. Black line: before the addition of mCPBA (10 equiv), blue line: immediate after the addition of mCPBA, red line: after 300 s.

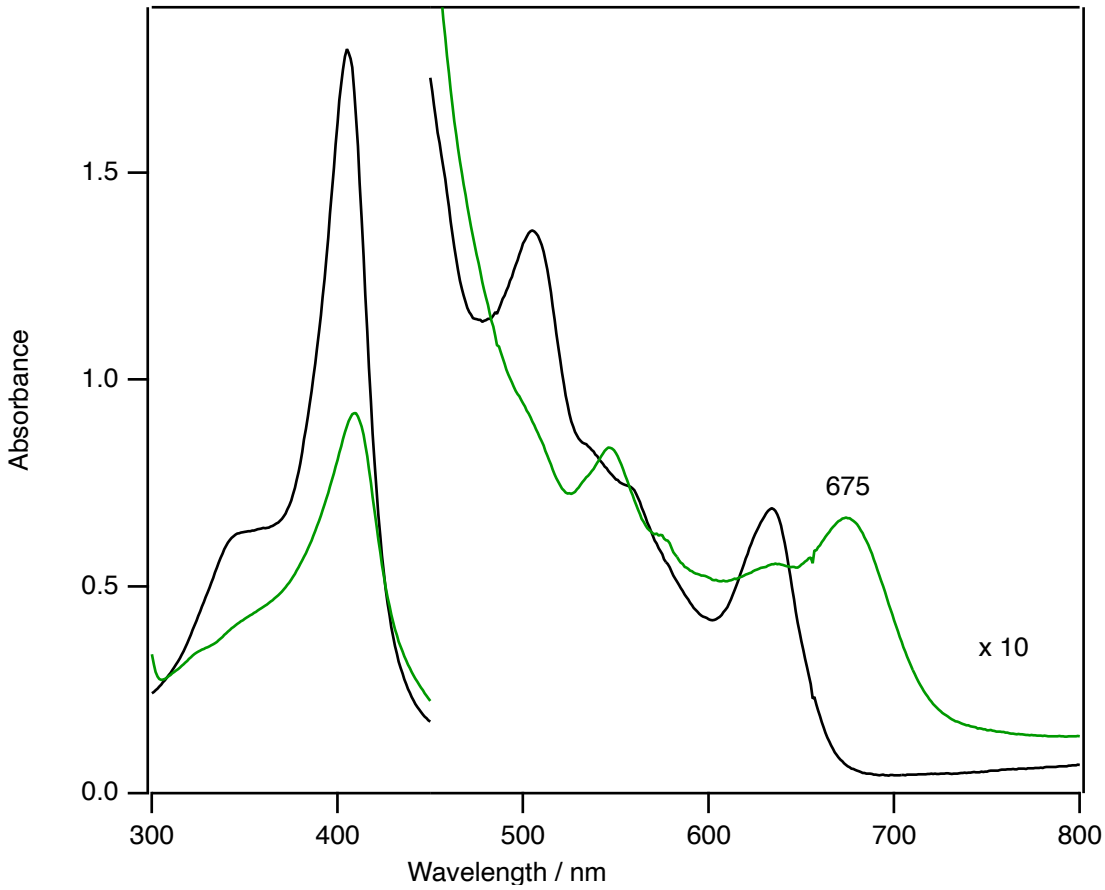

Figure S4. Absorption spectral change for the reaction of **3-TFA** with 10 equiv of mCPBA in the absence of cyclohexane at –80 °C. Black: 3-TFA, green: 20 s after addition of 10 equiv of mCPBA.

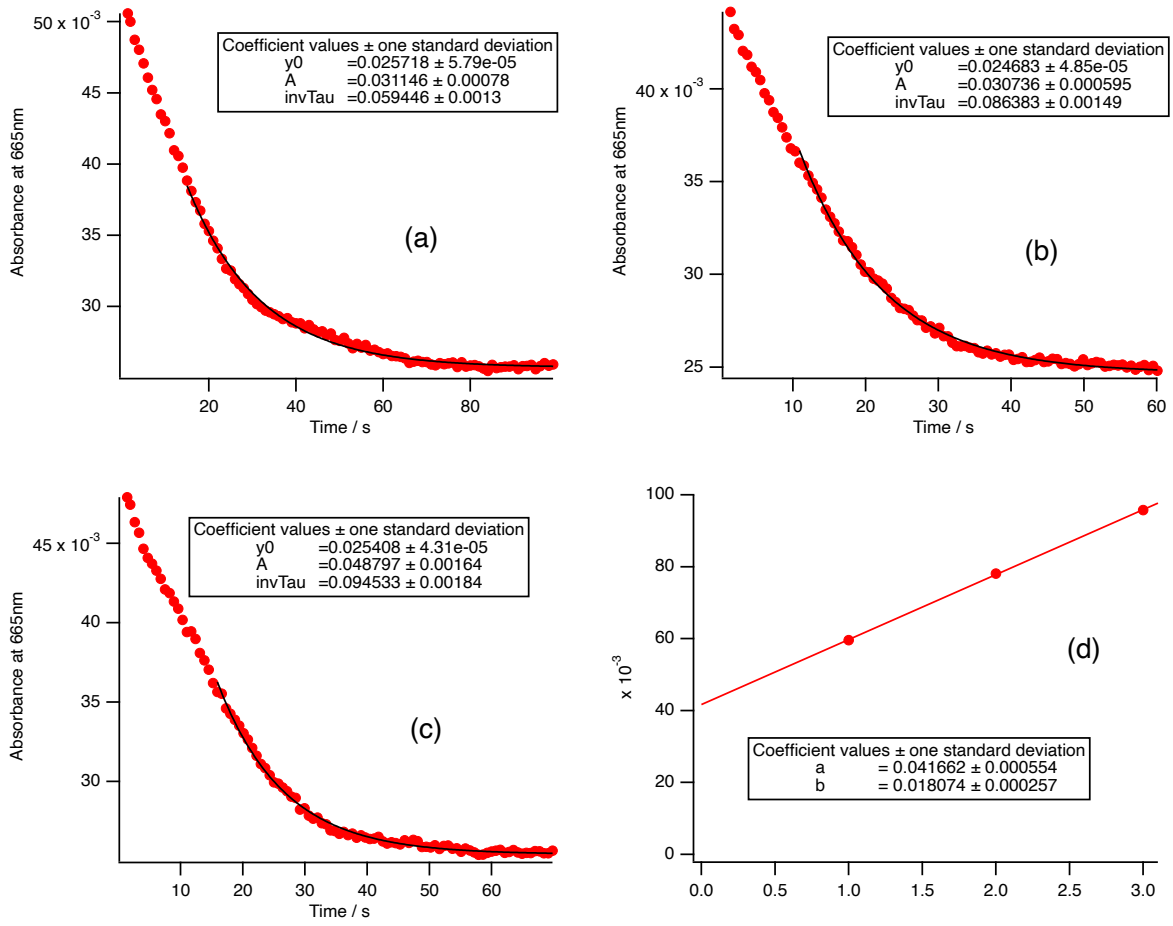

Figure S5. (a) ~ (c) Time courses of the absorbance at 665 nm in the reactions of **2-Cpd I** with cyclohexane at 20 °C. Concentration of cyclohexane, (a) 1.0 M, (b) 2.0 M, and (c) 3.0 M. (d) Dependence of the rate constant with the concentration of cyclohexane. The second-order rate constant can be estimated from the gradient of the simulation line, 1.8×10^{-2} $M^{-1}s^{-1}$.