Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information

For

Catalytic oxygenation of phenols by arthropod hemocyanin, an oxygen carrier protein, from *Portunus trituberculatus*

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Contents:

Fig. S1

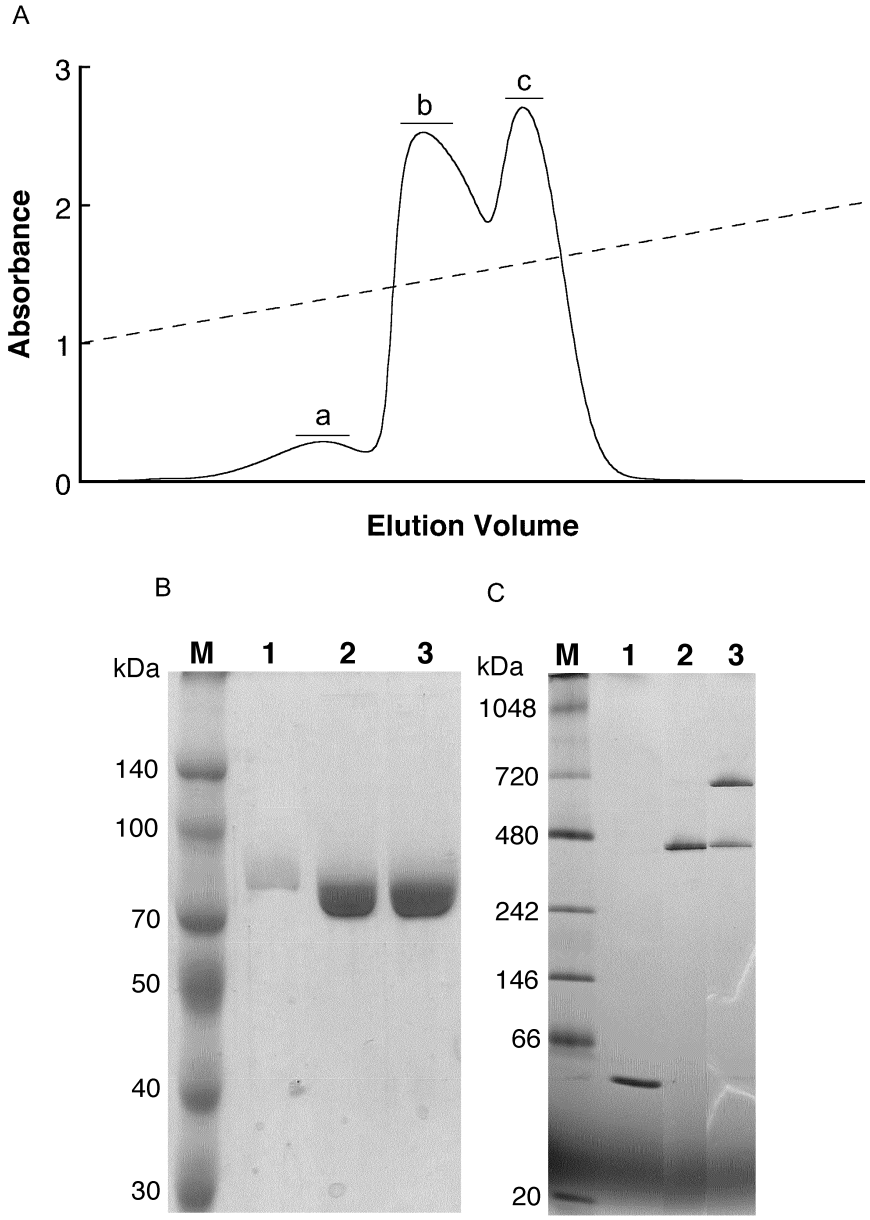

Fig. S1 (A) The elution diagram of multimeric and monomeric *Pt*-Hc after dialysis with 0.05 M Tris-HCl buffer, pH 8.9 containing 0.01 M EDTA with ion-exchange column chromatography on RESORCE Q (Vol. 6 mL, GE Healthcare) at 4 °C in a 0.05 M Tris-HCl buffer, pH 8.9, with 0.01 M EDTA. Elution was carried out in a 0-0.4 M NaCl gradient using a ÄKTA prime plus. (B) SDS/10 % polyacrylamide gel electrophoresis. M, maker protein; 1, fraction a (*Pt*-1Hc); 2, fraction b (*Pt*-6Hc); 3, fraction c (*Pt*-12Hc). (C) Blue native polyacrylamide gel electrophoresis. M, maker protein; 1, fraction a (*Pt*-1Hc); 2, fraction b (*Pt*-6Hc); 3, fraction c (*Pt*-12Hc).

Fig. S2

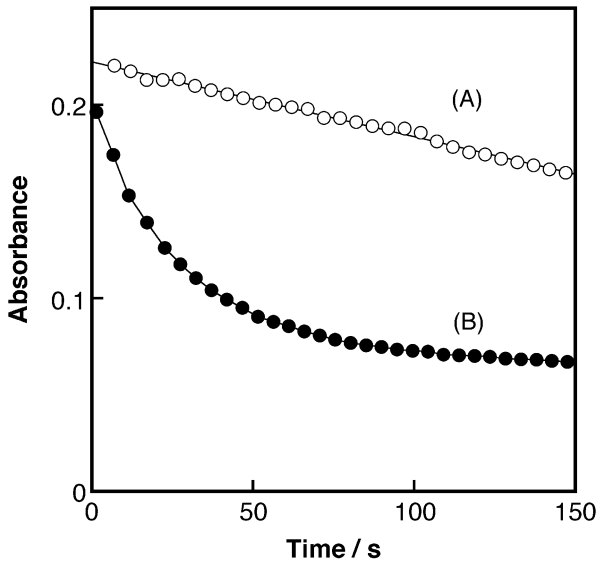

Fig. S2 Time courses of the absorbance change at 338 nm for the reactions of the oxy-form of monomeric *Pt*-1Hc (14 μM) and *p*-methylphenol (5 mM) (A) in the absence of urea and (B) in the presence of 3 M urea in 0.5 M borate buffer (pH 9.0) containing 10 % (v/v) methanol at 25 °C under anaerobic conditions.

Fig. S3

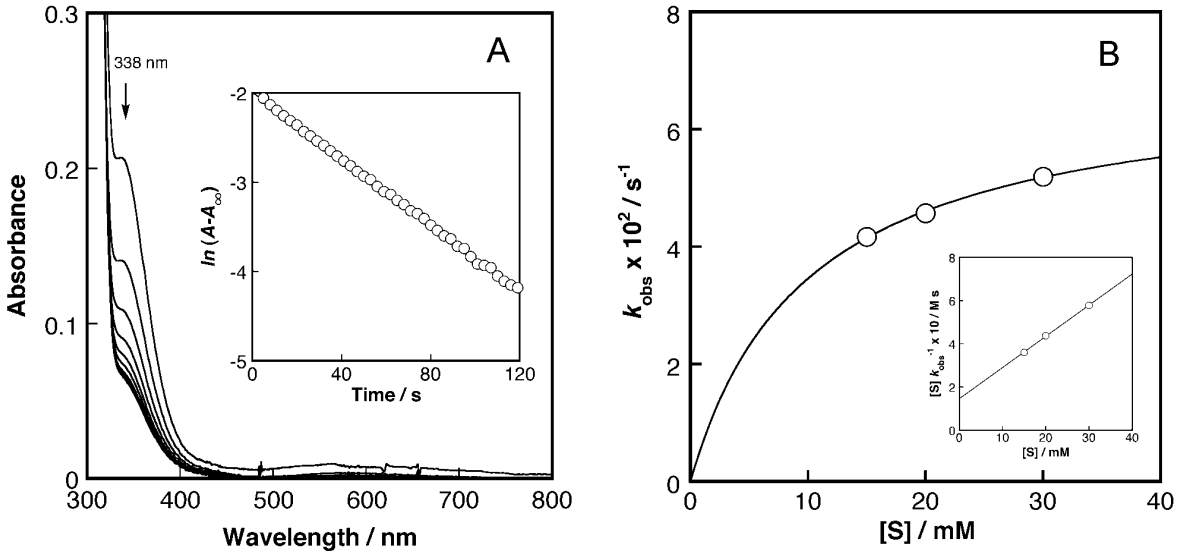

Fig. S3 (A) Spectral change observed upon addition of *p*-fluorophenol (10 mM) to the oxy-form of monomeric *Pt*-1Hc (13 μM) in 0.5 M borate buffer (pH 9.0) containing 10 % (v/v) methanol and 3 M urea at 25 °C under N_2: 15 s interval (Inset: First-order plot based on the absorption change at 338 nm). (B) Plot of k_{obs} vs. [Substrate] (Inset: Hanes-Woolf plot).

Fig. S4

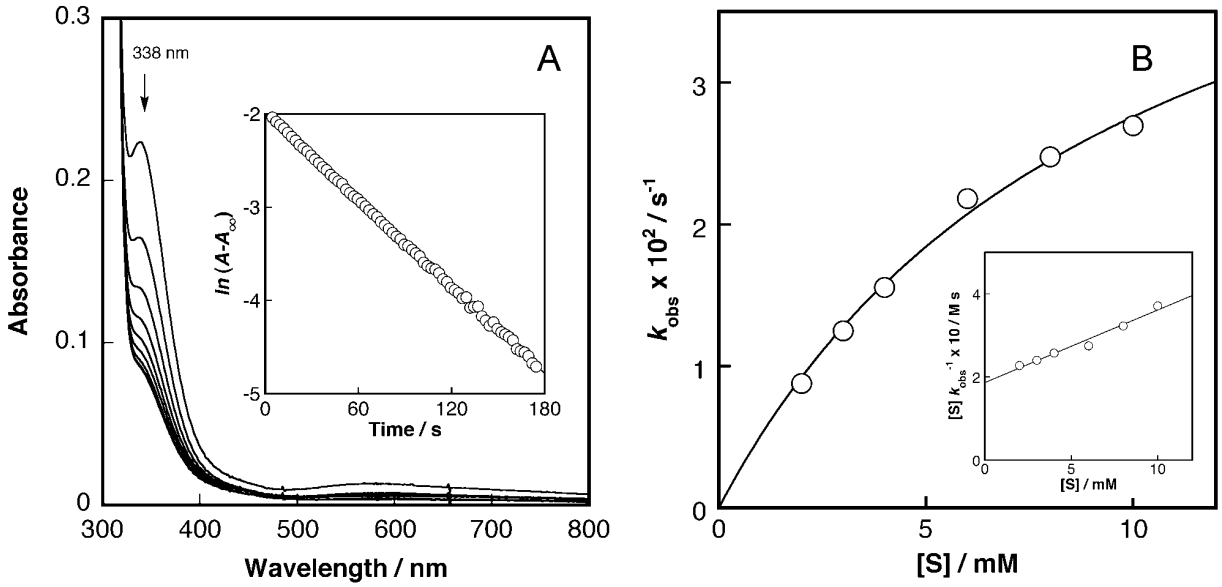

Fig. S4 (A) Spectral change observed upon addition of *p*-chlorophenol (4 mM) to the oxy-form of monomeric *Pt*-1Hc (13 μM) in 0.5 M borate buffer (pH 9.0) containing 10 % (v/v) methanol and 3 M urea at 25 °C under N_2: 15 s interval (Inset: First-order plot based on the absorption change at 338 nm). (B) Plot of k_{obs} vs. [Substrate] (Inset: Hanes-Woolf plot).

Fig. S5

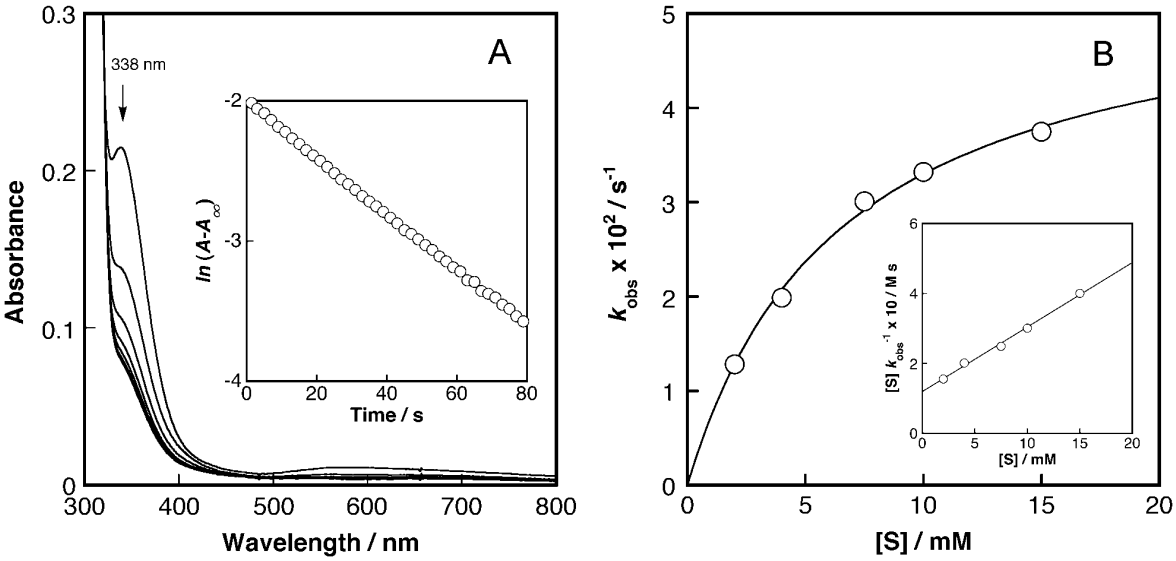

Fig. S5 (A) Spectral change observed upon addition of *p*-bromophenol (4 mM) to the oxy-form of monomeric *Pt*-1Hc (13 μM) in 0.5 M borate buffer (pH 9.0) containing 10 % (v/v) methanol and 3 M urea at 25 °C under N_2: 40 s interval (Inset: First-order plot based on the absorption change at 338 nm). (B) Plot of k_{obs} vs. [Substrate] (Inset: Hanes-Woolf plot).

Fig. S6

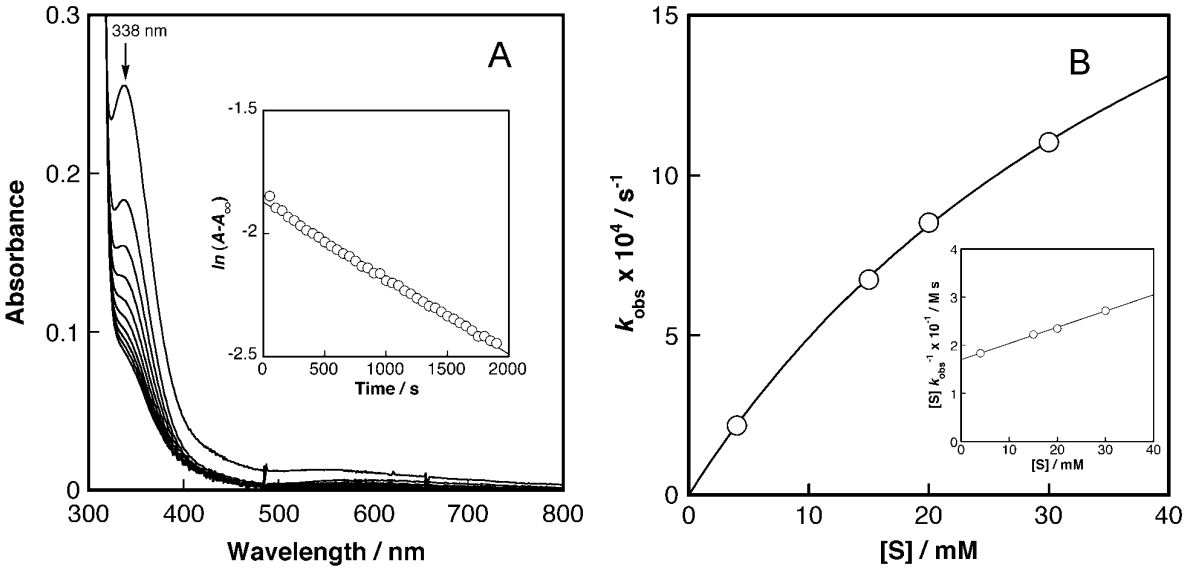

Fig. S6 (A) Spectral change observed upon addition of *p*-cyanophenol (10 mM) to the oxy-form of monomeric *Pt*-1Hc (13 μM) in 0.5 M borate buffer (pH 9.0) containing 10 % (v/v) methanol and 3 M urea at 25 °C under N_2: 1000 s interval (Inset: First-order plot based on the absorption change at 338 nm). (B) Plot of k_{obs} vs. [Substrate] (Inset: Hanes-Woolf plot).

Fig. S7

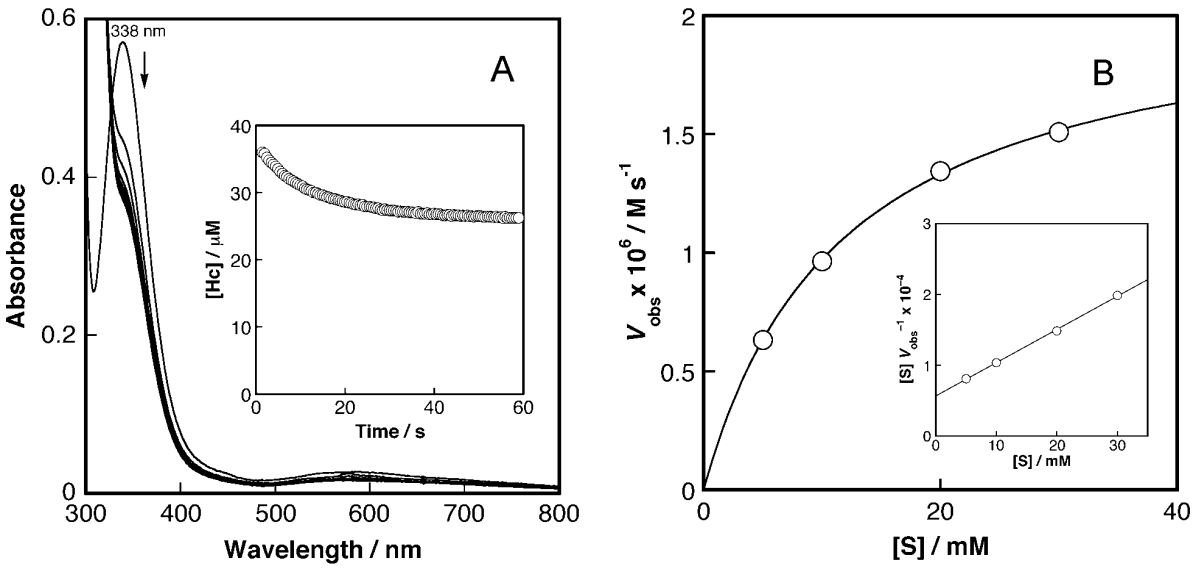

Fig. S7 (A) Spectral change of the fast phase observed upon addition of *p*-methoxyphenol (10 mM) to the oxy-form of hexameric *Pt*-6Hc (39 μM) in 0.5 M borate buffer (pH 9.0) containing 10 % (v/v) methanol and 3 M urea at 25 °C under N_2: 10 s interval (Time course of the absorption change at 338 nm). (B) Plot of k_{obs} vs. [Substrate] (Inset: Hanes-Woolf plot).

Fig. S8

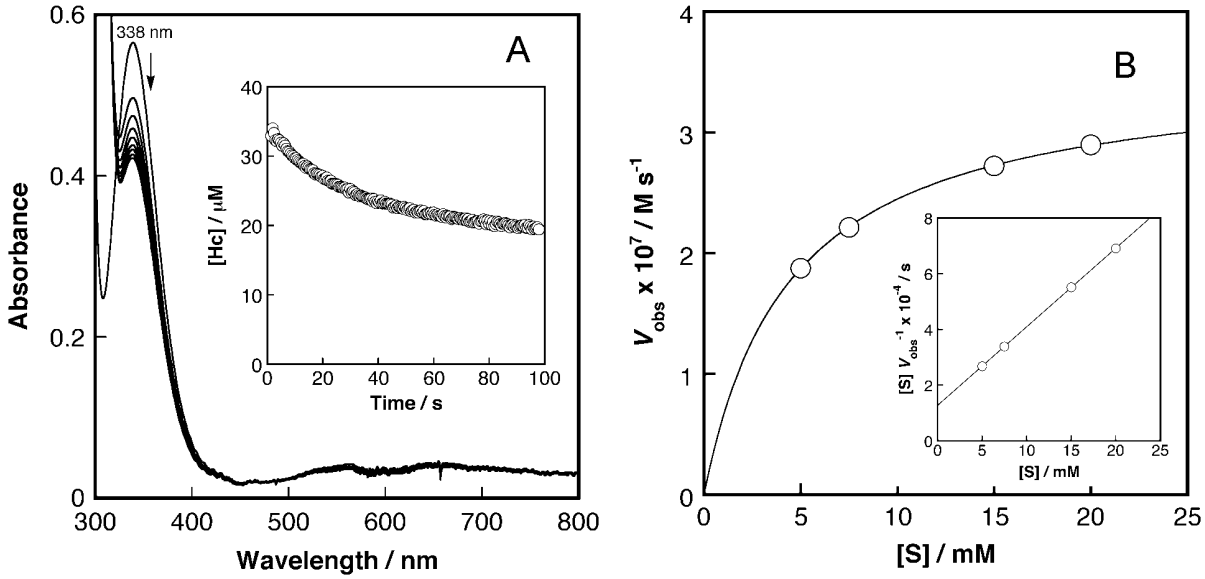

Fig. S8 (A) Spectral change of the fast phase observed upon addition of *p*-fluorophenol (10 mM) to the oxy-form of hexameric *Pt*-6Hc (39 μM) in 0.5 M borate buffer (pH 9.0) containing 10 % (v/v) methanol and 3 M urea at 25 °C under N_2: 10 s interval (Time course of the absorption change at 338 nm). (B) Plot of k_{obs} vs. [Substrate] (Inset: Hanes-Woolf plot).

Fig. S9

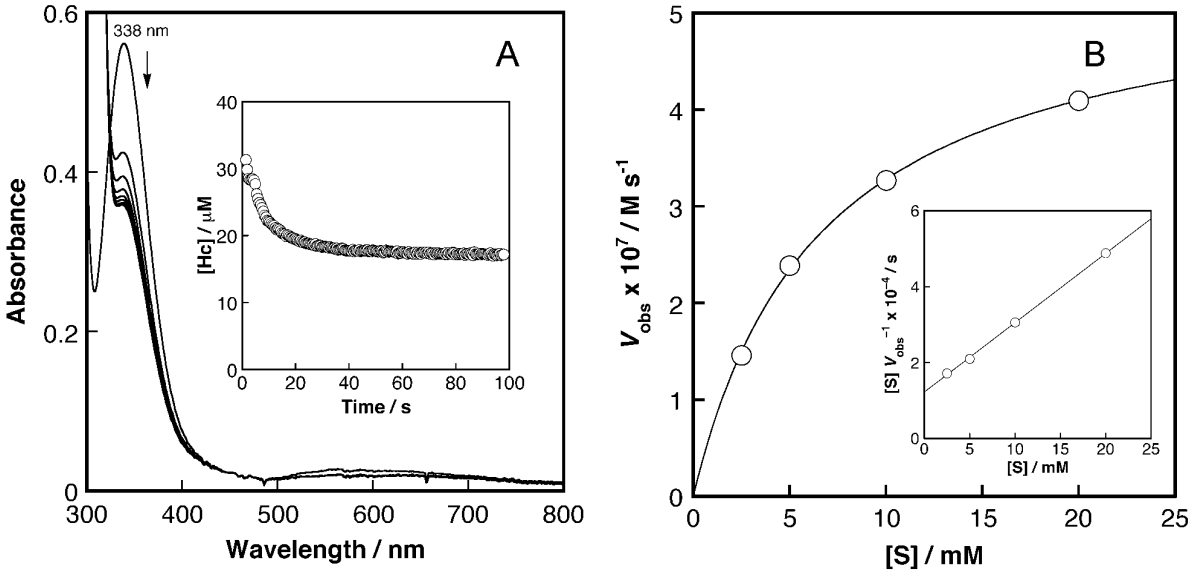

Fig. S9 (A) Spectral change of the fast phase observed upon addition of *p*-chlorophenol (10 mM) to the oxy-form of hexameric *Pt*-6Hc (39 μM) in 0.5 M borate buffer (pH 9.0) containing 10 % (v/v) methanol and 3 M urea at 25 °C under N_2: 10 s interval (Time course of the absorption change at 338 nm). (B) Plot of k_{obs} vs. [Substrate] (Inset: Hanes-Woolf plot).

Fig. S10

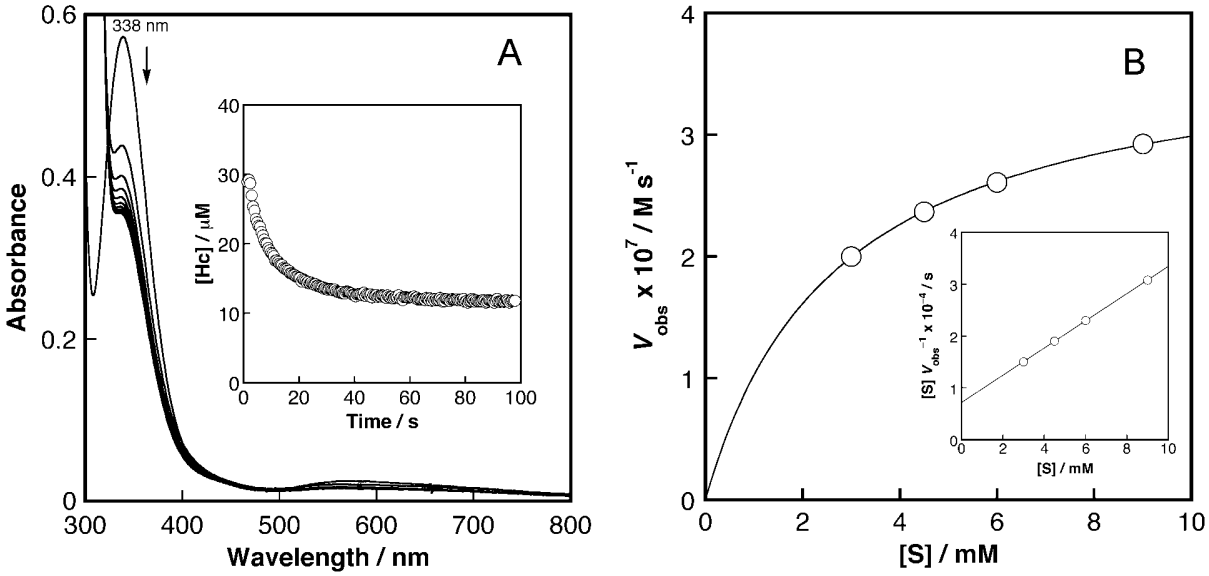

Fig. S10 (A) Spectral change of the fast phase observed upon addition of *p*-bromophenol (6 mM) to the oxy-form of hexameric *Pt*-6Hc (39 μM) in 0.5 M borate buffer (pH 9.0) containing 10 % (v/v) methanol and 3 M urea at 25 °C under N_2: 10 s interval (Time course of the absorption change at 338 nm). (B) Plot of k_{obs} vs. [Substrate] (Inset: Hanes-Woolf plot).

Fig. S11

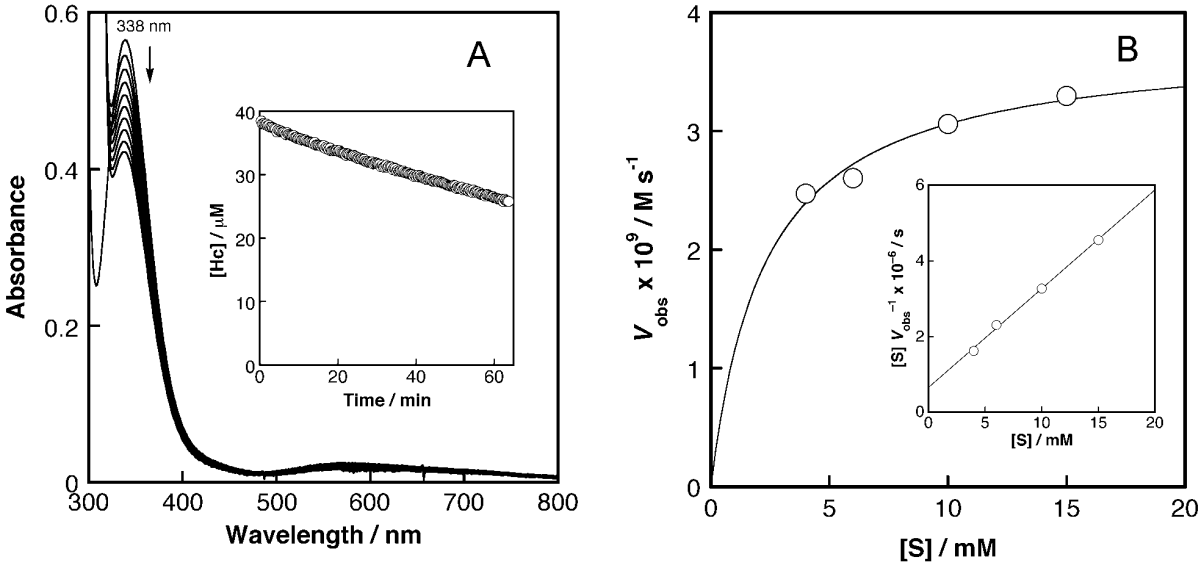

Fig. S11 (A) Spectral change of the fast phase observed upon addition of *p*-cyanophenol (10 mM) to the oxy-form of hexameric *Pt*-6Hc (39 μM) in 0.5 M borate buffer (pH 9.0) containing 10 % (v/v) methanol and 3 M urea at 25 °C under N_2: 400 s interval (Time course of the absorption change at 338 nm). (B) Plot of k_{obs} vs. [Substrate] (Inset: Hanes-Woolf plot).

Scheme S1