

Supporting Information for:

Iron porphyrins anchored to a thermosensitive polymeric core-shell nanosphere as a thermotropic catalyst

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Experimental Section

Materials.

N-isopropylacrylamide (NIPAAm) (Acros) was recrystallized from hexane. Styrene, methylene bisacrylamide (MBA), vinyl pyridine, 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V50), acetonitrile, dichloroethane and decane were used as received from Aldrich Chemical Co. Cyclohexene (Aldrich) was purified by filtration through silica gel prior to use. Sodium salt of 5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphinato iron(III) [Fe(TDFPPS)]³⁺ and sodium salt of 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinato iron(III) [Fe(TDCPPS)]³⁺ were used as received from Mid-Century Chemicals. Iodosylbenzene (PhIO) was prepared from iodobenzene diacetate by a literature method [1].

Instrumentations.

Scanning electron microscopy (SEM) (JEOL JSM-5200), dynamic light scattering (DLS) (ALV-5000/60X0) and UV-vis spectrophotometer (Hewlett Packard 8453) were used to characterize the nanosphere materials. Products for cyclohexene oxidation were analyzed by a gas chromatography (Agilent Technologies 6890N) equipped with a FID detector using a 25-m capillary column.

Preparation of the metalloporphyrin bound core-shell nanosphere.

The core was prepared by copolymerizing styrene (18.0 g, 1.7×10^{-1} mol) and *N*-isopropyl acryl amide (NIPAAm) (2.0 g, 1.8×10^{-2} mol) in water at 70 °C and using 2,2'-azobis(2-methylpropionamide) dihydrochloride (V50) (0.2 g, 7.2×10^{-1} mmol) as an initiator. The core particle was separated by ultrafiltration with a cut-off molecular weight of 100,000 membrane, and then freeze-dried. On the core particle (3.0 g), NIPAAm (1.83 g, 1.6×10 mmol), vinyl pyridine (0.032 g, 2.9×10^{-1} mmol) and methylene bisacrylamide (MBA) (0.09 g, 5.8×10^{-1} mmol) were copolymerized in water at 70 °C using V50 (0.0336 g, 1.2×10^{-1} mmol) as an initiator [2,3]. The core-shell nanospheres were separated by ultrafiltration and freeze-dried. To prepare the metalloporphyrin bound core-shell nanosphere, the core-shell nanospheres (0.5 g) was added to an iron porphyrin complex (1×10^{-2} mmol) in aqueous solution (100 mL). The metalloporphyrin bound core-shell nanosphere was washed three times with water (100 mL) followed by ultrafiltration. The filtered nanosphere was then freeze-dried.

Loading of iron porphyrins to the core-shell nanosphere.

The loading of iron porphyrins to the core-shell nanosphere was determined by monitoring the disappearance of Soret bands at 410 nm for [Fe(TDCPPS)]³⁺ or 385 nm for [Fe(TDFPPS)]³⁺. To the iron porphyrin aqueous solution (0.1 mM, 100 ml) was core-shell nanospheres (0.5 g) added. Then, the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was centrifuged at 13,000 rpm for 15 min and the supernatant was checked with UV-vis spectrophotometer. The UV-vis spectra of iron porphyrin solutions before and after the addition of core-shell nanosphere were compared (Fig. S1).

Catalytic oxidation of cyclohexene.

In a typical oxidation reaction, iodosylbenzene (PhIO, 2.5×10^{-2} mmol) and cyclohexene (2.5×10^{-2} mmol) were added to a reaction solution containing an iron porphyrin catalyst (2.5×10^{-4} mmol) or an iron porphyrin bound nanosphere (2.5×10^{-4} mmol) in water (2.0 mL). The reaction mixture was stirred for 7 h at room temperature. The products were extracted with dichloroethane (2.0 mL) and analyzed by gas chromatography using decane as an internal standard [4]. Product yields were determined by comparison against standard curves prepared with known authentic samples.

Partition coefficient determination.

The partition coefficient of cyclohexene was measured as a function of temperature in a range of 15 °C to 50 °C. The core-shell nanosphere (9.0 mg) was dispersed in water (1.0 mL) at a given temperature. The cyclohexene (1.3 microliter) was injected using a

microsyringe. The mixture was stirred for 20 minutes in a closed tube at a given temperature. Then, the suspension was centrifuged for 2 minutes and supernatant was filtered through membrane filter with 0.2 micron pores. Then, the filtrate (0.2 mL) was taken and extracted with the same amount of 1,2-dichloroethane, followed by analysis by gas chromatography.

Recycling experiment performed with the nanocatalyst.

Iodosylbenzene (2.5×10^{-2} mmol) and cyclohexene (2.5×10^{-2} mmol) were added to a reaction solution containing **1** (2.5×10^{-4} mmol) in a solvent mixture (2.0 mL) of acetonitrile and water ($v/v = 1 : 1$). The reaction mixture was stirred for 7 h at room temperature. An aliquot (0.2 mL) of the reaction mixture was then extracted with dichloroethane (0.2 mL) and analyzed by gas chromatography using decane as an internal standard [4]. Product yields were determined by comparison against standard curves prepared with known authentic samples. The remaining reaction mixture was centrifuged at 13,000 rpm for 30 min to separate the nanocatalyst and the supernatant decanted. The nanocatalyst was rinsed with acetonitrile/water ($v/v = 1 : 1$) three times and then vacuum dried overnight. The oxidation reaction was repeated three times by adding cyclohexene and PhIO under the identical conditions, and the product yields were analyzed by the same procedures described above.

References

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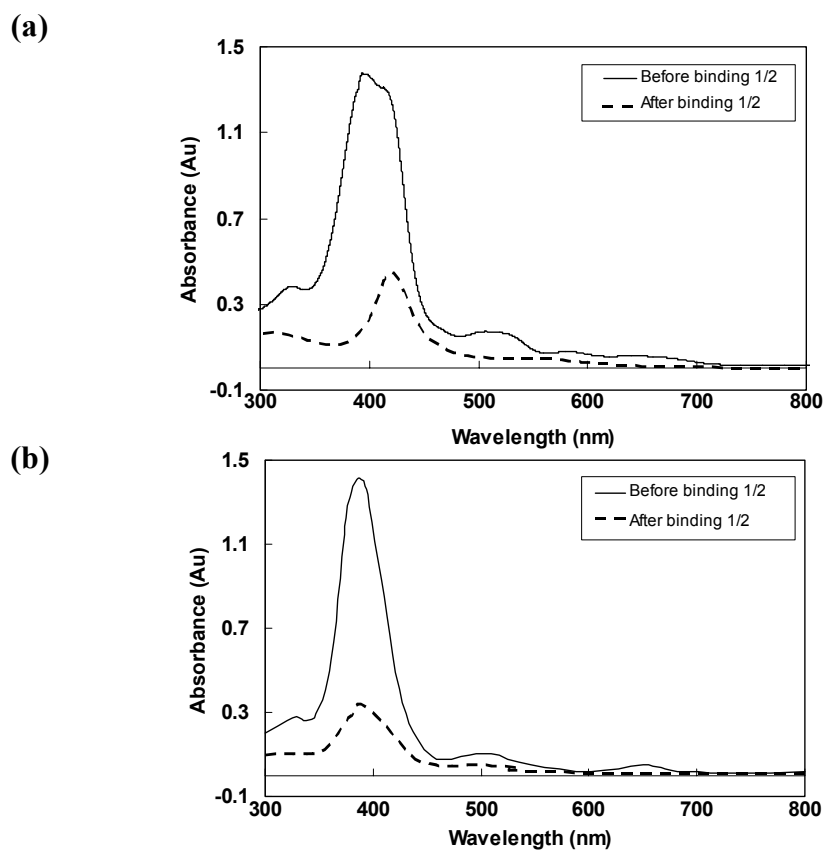


Figure S1. UV-vis spectral changes of (a) $[\text{Fe}(\text{TDCPPS})]^{3+}$ and (b) $[\text{Fe}(\text{TDFPPS})]^{3+}$ before and after the addition of core-shell nanosphere in aqueous solution.

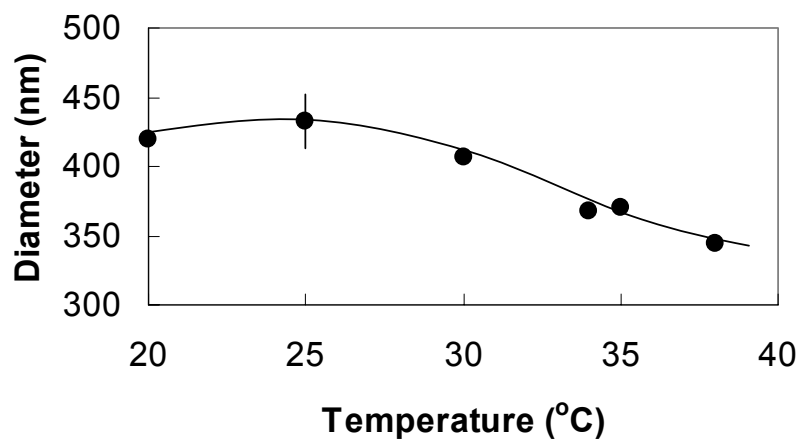


Figure S2. Diameter change of core-shell nanosphere as a function of temperature in aqueous solution.