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Photoreduction of a Self-Assembled (Lipidporphyrinato)iron(III) Complex in Saline by LMCT Excitation: Co-Aggregated Hyaluronic Acid Allows an Irreversible Electron Transfer

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An amphiphilic (tetraphenylporphyrinato)iron(III) derivative with four alkylphosphocholine groups and a proximal imidazole [(lipidporphyrinato)iron(III); **1a**] was self-assembled in phosphate-buffered saline (pH 7.3, [NaCl] = 0.15 M) to form spherical micelles with a diameter of 10 nm. The obtained solution showed a distinct absorption band at 362 nm, which was assigned to the ligand-to-metal [Cl^- to iron(III)] charge transfer (LMCT) transition. Light irradiation into this CT band under an Ar atmosphere did not induce any changes in the UV-vis absorption spectrum. On the other hand, the addition of glucose (150 mM) to the solution led to complete photoreduction of the central iron(III) ion, giving a five-N-coordinated high-spin iron(II) complex. It has also been found that a small excess amount of hyaluronic acid ([units] = 100 μM) showed the same effect. The photoreduction was only seen by LMCT irradiation in the presence of the saccharide. It probably occurred via intramolecular electron transfer from Cl^- to iron(III), and the produced chlorine radical was scavenged by the saccharide, which prevented a back electron transfer reaction (the quantum yields; ca. 0.007). Interestingly, hyaluronic acid changed the morphology of the **1a** assembly from the micelle to a thin fiber. This co-aggregated structure with hyaluronic acid would be responsible for the effective photoreduction of **1a**. The viscosity of the fiber solution significantly decreased during the photoreduction, which suggests that radical trapping induces depolymerization of the hyaluronic acid. Laser flash photolysis experiments showed that the reduction and the imidazole association to the iron(II) center are completed within 50 ns after a laser pulse. The photoreduced (lipidporphyrinato)iron(II) fibers can reversibly bind and release O_2 similar to the same fibers which were prepared by chemical reduction using ascorbic acid.

The photochemistry of Fe(III) porphyrins, especially photoreduction of the central iron(III) ion, has been extensively investigated over the past two decades, because of considerable interest in the photomanipulation of the native hemoproteins' activities.[1–10] A counter anion generally coordinates the Fe(III) porphyrin and shows a ligand-to-metal charge transfer (LMCT) transition in the UV region, which is often responsible for photoinduced electron transfer from a ligand to a metal.[1–9] In contrast to the fact that many of the previous studies concerning the photoreduction of metalloporphyrins have required external sensitizers,[11–16] photoexcitation of the LMCT excitation provides a clean reduction through intramolecular electron transfer. For instance, the alcoholate complexes of the Fe(III) porphyrins in aqueous or nonaqueous alkaline alcohols undergo photocleavage of the Fe^{III}–O bond to give Fe(II) porphyrins and alkoxy radicals.[1–5] In a benzene solution, the chloro(tetraphenylporphyrinato)iron(III) [$Fe^{III}Cl(tpp)$] can be reduced to the iron(II) complex upon LMCT irradiation.[6,7] The mechanism of this photoreduction was postulated to be photolysis of the Fe^{III}–Cl^- bond. This basic photochemistry for the Fe(III) porphyrins has been expected to be adapted to control of functions of natural hemoproteins and the model hemes under physiological conditions. However, such a development has never been realized, because the produced radicals easily recombine with the Fe(II) porphyrin in water. Gilbert et al. only reported the irreversible photoreduction of the carboxy(porphyrinato)iron(III) complexes in aqueous solution containing a large excess amount of carboxylic acid or amino acid.[8,9]

We have recently found that the (tetraphenylporphyrinato)iron(II) derivative with four alkylphosphocholine groups and an axially coordinated imidazole [(lipidporphyrinato)iron(II); **1b**, Chart 1] formed tubular fibers in water, and can reversibly bind and release O_2 like hemoglobin and myoglobin.[17] The only drawback of this fiber as an O_2 transporter is its relatively short lifetime of the O_2-adduct complex. The O_2-biniding capability is slowly inactivated accompanying autooxidation of the central iron(II) ion by a proton-driven process.[18] If we can reduce the autooxidized iron(III) center by light irradiation, this method would become the simplest way to revive their O_2-binding abilities and to maintain their activity for a longer time. This paper describes the photoreduction of the self-assembled (lipidporphyrinato)iron(III) complex (**1a**, Chart 1) in phosphate-buffered saline by LMCT excitation. The co-aggregated saccharide prevents back electron transfer and allows the photoreduction to be irreversible. The resulting **1b** fiber permitted a reversible O_2 binding.

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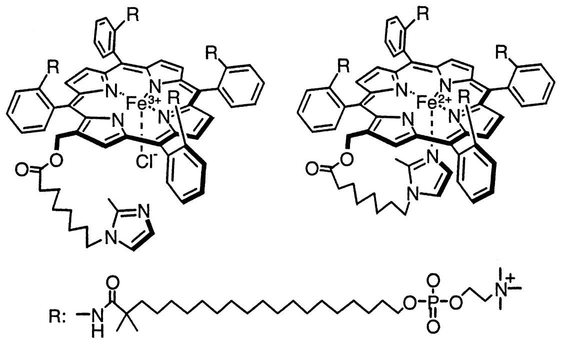

1a **1b**

Chart 1.

Experimental

Materials and General Methods. 2-[8-(2-Methylimidazole-1-yl)octanoyloxymethyl]-5,10,15,20-tetrakis{*α,α,α,α-o*-[2,2-dimethyl-20-({[2-trimethylammonio]ethoxy}phosphonatoxy)-icosanamide]phenyl}porphyrinatoiron(III) (**1a**) was prepared according to our previously reported procedures.[17] The hyaluronic acid sodium salt (from human umbilical cord) and amylose were purchased from Sigma Chem. Co. Glucose and other chemicals were obtained from the Kanto Chem. Co. and used without further purification. The water was deionized using an ADVANTEC GS-200 system.

Preparation of Aqueous (Lipidporphyrinato)iron(III) Solution. A methanol solution of **1a** (< 5 μL) was injected into phosphate buffered-saline (PBS; 1 mM, pH 7.3, [NaCl] = 150 mM, 2.5 mL) and the obtained homogeneous solution was incubated for 4 h at room temperature. The remaining methanol ($[CH_3OH] < 0.2$ vol%) was completely removed by dialysis with a cellulose tube in PBS for 1 h (2 times) and for another 15 h at 4 °C. The final concentration of **1a** was normally adjusted to 10 μM based on its molar extinction coefficient (ε_{424}: 5.8×10^4 M^{-1} cm^{-1}), and saccharides were directly added to this solution. The samples were held in a cuvette (optical path length 10 mm) and degassed by Ar bubbling for at least 30 min. Spectrophotometric measurements were performed using a JASCO UV-570 spectrophotometer.

Transmission Electron Microscopy (TEM). Negatively stained specimens for TEM were prepared according to our previously reported method.[19,20] The obtained grids were observed using a JEOL JEM-100CX electron microscope at an accelerating voltage of 100 kV.

Photoreduction of (Lipidporphyrinato)iron(III) Fibers. Continuous light irradiations were performed with a 250 W ultra-high-pressure Hg arc-lamp or a 150 W xenon arc-lamp under an Ar atmosphere in a dark room (25 °C). The light was filtered with cut-off filters (HOYA B-390, L-42, U-360, Y-50) to isolate the desired wavelength region. The filtered light was irradiated into a solution of **1a** contained in a 10-mm cuvette at a distance of 75 mm from the center of the light source. The UV-vis absorption spectra of the solution were measured at regular intervals. The quantum yield (Φ) was determined using the ferrioxalate actinometric procedure.[21]

Transient Absorption Spectroscopy. The transient absorption spectra after nano-second laser flash photolysis were measured using an ANDOR DH520-18F-WR ICCD detector with an ORIEL MS-257 imaging monochromator. The excitation laser pulse was generated from the THG (355 nm; pulse width, 5 ns) of a Spectron SL803G-10 Nd:YAG laser. A pulse xenon flash lamp (10 W, 10 Hz, 100 ns pulse width) was used as the monitor's light source. The path length of the cuvette was 10 mm, and all measurements were carried out using a two-channel simultaneous detection system (Tokyo Instruments, Ltd.) at 25 °C. The femto-second transient absorption spectra were measured by a Ti:sapphier laser system.[22] An excitation light pulse was obtained by amplifying a femtosecond Ti:sapphier laser (Mira 900 Basic, Coherent) pulse with a Q-switched YAG-pumped conventional regenerative amplifier (TR70-10, Continuum). The fundamental output from the regenerative amplifier (780 nm, 3–4 mJ/pulse, fwhm 170 fs,10 Hz) was frequency-doubled (390 nm) and used as an excitation light source. The residual of the fundamental output was focused into a quartz cuvette containing H_2O to generate a white-light continuum as the probe light.

Electron Spin Resonance (ESR) Spectroscopy. (a) (Lipidporphyrinato)iron(III) solution. The deaerated PBS solution of **1a** (0.2 mM) or **1a**/hyaluronic acid in a quartz sample tube was immersed in a Dewar flask filled with liquid nitrogen; they were applied to a JEOL JES-TE200 spectrometer equipped with a 100 kHz field modulator.

(b) (Lipidporphyrinato)iron(II) solution after photoirradiation. A deaerated PBS solution of **1a**/hyaluronic acid was irradiated with high-pressure Hg arc-light for 5 min. It was immediately transferred to a flattened quartz cell (width: 1 mm) under an argon atmosphere, and observed under the ambient condition.

Viscosity Measurements. The viscosity of a PBS solution of **1a**/hyaluronic acid was measured with a capillary viscometer (Oscillatory Capillary Rheometer and Density Meter, OCR-D, Anton Paar) at 25 °C with a shear rate range of 1–332 s^{-1} (capillary diameter and length of 0.9948 and 100.2 mm, respectively).

Results and Discussion

The phosphate buffered-saline solution (PBS; 1 mM, pH 7.3, [NaCl] = 150 mM) of the iron(III) **1a** complex was homogeneous and stable for more than 6 months without any precipitate. Transmission electron microscopy (TEM) of the obtained colloid showed spherical micelles with a diameter of 10 nm (the molecular length of **1a** is 4.6 nm) (Fig. 1a). This is in contrast to the corresponding iron(II) **1b** complex, which produces unique tubular fibers in water.[17] Most probably, the imidazolylalkyl arm of **1a** dissociates from the central iron(III)

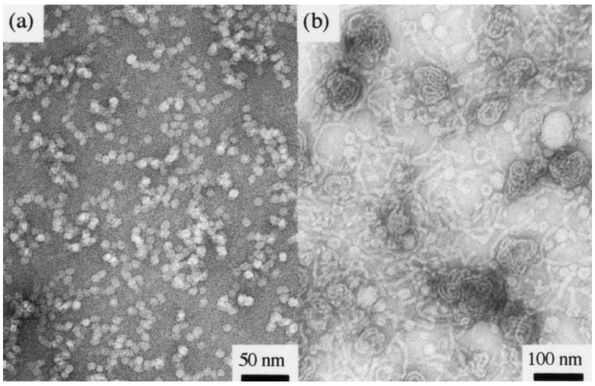

Fig. 1. Transmission electron micrographs of negatively stained samples of (a) iron(III) **1a** micelles and (b) iron(II) **1b** fibers with hyaluronic acid.

and acts as an amphiphilic chain at the porphyrin periphery. That is, the iron(III) **1a** is more hydrophilic than the iron(II) **1b**, which may prevent long fiber formation.

In the UV-vis absorption spectrum of the **1a** solution, a distinct band has appeared at 362 nm in the blue region of the Soret band (424 nm). Suslick et al. reported that $\mathrm{Fe^{III}Cl(tpp)}$ showed a similar absorption band in the UV region, which was a ligand-to-metal charge-transfer (LMCT) transition between the central iron(III) and a chloride anion ($\mathrm{Cl^-}$).[6,7] On the basis of the following three experimental results, we also assigned this peak (ε: 2.5×10^4 $\mathrm{M^{-1}\,cm^{-1}}$) as a LMCT band of $\mathrm{Fe^{III}}$–$\mathrm{Cl^-}$. (i) The absorption maximum significantly shifted to the lower energy region with a decrease in the electronegativity of the coordinated halide anions ($\mathrm{I^-} < \mathrm{Br^-} < \mathrm{Cl^-}$), while the Soret and Q bands, which are attributed to the π-π^* transitions, were not affected (Fig. 2). (ii) The absorption spectral pattern was dependent on the pH, due to a ligand exchange of the central iron(III) (Fig. 3). The spectrum of the five-coordinated iron(III) complex with a $\mathrm{Cl^-}$ at pH 4 (λ_{max}: 362, 424, 510, 577 nm) changed with an increase in the pH, and finally reached that of the five-coordinated complex with an $\mathrm{OH^-}$ at pH 10 (λ_{max}: 335, 422, 577 nm).[23,24] These spectral changes were reversibly observed (pK_a: 7.7). Under physiological pH (7.3), more than half of **1a** was the iron(III) high-spin complex with a $\mathrm{Cl^-}$. The probable six-coordinated Fe(III) complex with both an axially coordinated imidazole and a $\mathrm{Cl^-}$ was excluded, because the binding constant of 1,2-dimethylimidazole to the Fe(III) porphyrin was extremely low.[25,26] (iii) ESR spectroscopy also supported the five-coordinated structure of the micellar aggregated **1a**. The spectrum of the **1a** solution (0.2 mM) at 77 K exhibited the typical shape of the high-spin $\mathrm{Fe^{III}Cl(tpp)}$, and the obtained g values ($g_{\perp} = 5.3062$ and $g_{/\!/} = 1.9945$) were all in good agreement with those in a previous report.[27]

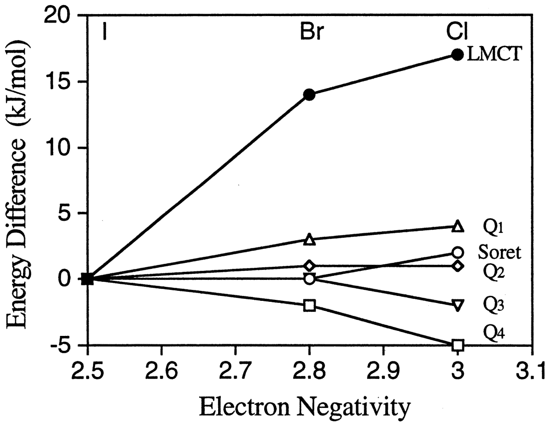

Fig. 2. Spectral changes of $\mathrm{Fe^{III}\text{-}X^-}$ (X: Cl, Br, I) as a function of electron negativity of the counter anion $\mathrm{X^-}$ (energy differences were calculated versus $\mathrm{Fe^{III}\text{-}I^-}$).

The photoirradiation of this **1a** micelle solution by the 365 nm-line of a high-pressure Hg arc-lamp under an Ar atmosphere did not induce any changes in the UV-vis absorption spectrum. On the other hand, the addition of glucose (150 mM) to the solution led to complete photoreduction of the central iron(III) ion. This absorption change was completed within 45 min, and the final spectrum suggested the formation of a five-N-coordinated iron(II) high-spin complex (λ_{max}: 443, 536, 566 nm) (Fig. 4). The well-defined isosbestic points (431, 462, 533, 589, 603, 625 nm) throughout the measurement reveal that no side reactions occurred. The reduction yield clearly depended on the amount of dissolved glucose, and a relatively high concentration (> 150 mM) was necessary for 100% reduction. Furthermore, it has been found that hyaluronic acid was much more effective compared to glucose. Only a small coexistence (21 μg$\mathrm{L^{-1}}$, [unit] = 100 μM) of hyaluronic acid achieved complete photoreduction, which also gave the spectrum of the five-N-coordinated iron(II) high-spin complex (λ_{max}: 443, 538, 565 nm) similar to that in Fig. 4.[28] The addition of glucose or hyaluronic acid in the dark led only negligibly small changes in the absorption and ESR spectra, which exhibited the typical shape of the high-spin iron(III) complex,

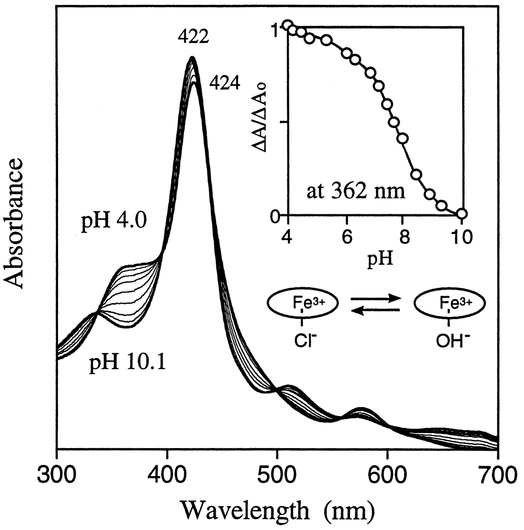

Fig. 3. Absorption spectral changes of the PBS solution of **1a** complex at various pH values (4.0, 5.0, 6.0, 7.0, 7.5, 8.0, 8.5, 9.0 and 10.1).

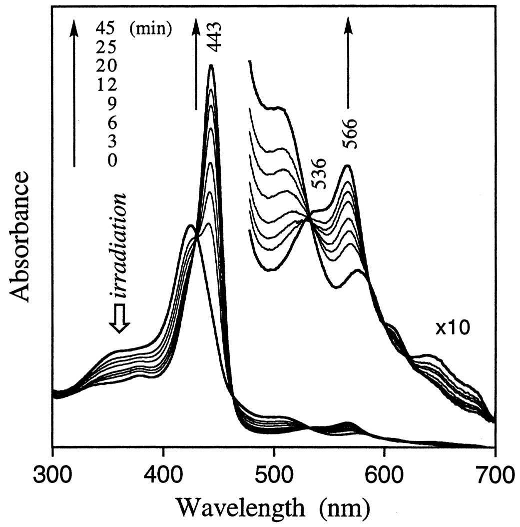

Fig. 4. UV-vis absorption spectral changes of the PBS solution of **1a** complex (10 μM) with glucose (150 mM) upon irradiation at 365 nm under an Ar atmosphere.

as seen in the homogeneous **1a** solution. These results suggest that the co-existence of saccharide neither affects the coordination structure of **1a** nor reduces the central iron(III) ion.

The photoactive region of the absorption spectrum of the **1a**/hyaluronic acid solution was then evaluated by light irradiation in the three wavelength regions: (a) < 400 nm, (b) 420–510 nm, and (c) > 500 nm. Irradiation of the CT band [region (a)] only led to an effective reduction of the iron(III) complex (Fig. 5). This wavelength dependence was quite similar to Hendrickson's result.[6] The obtained initial rates of the reduction for each case were 1.7×10^{-3}, 1.7×10^{-4} and 2.7×10^{-5} s^{-1}, respectively. Based on these findings, we can postulate that the irreversible photoreduction of **1a** is due to scavenging of the chlorine radicals ($Cl^{\bullet}$) produced by photocleavage of the Fe^{III}–Cl^{-} bond. It is also known that hydroxyl (porphyrinato)iron(III) can be photoreduced upon irradiation with light, $\lambda > 300$ nm.[29] Therefore, the other species, hydroxyl(lipidporphyrinato)iron(III), is also photoactive in the same manner as well. If the formed radical is trapped by hyaluronic acid, the disproportionation involving the oxygen atom of the glycoside group should be caused by the abstraction of hydrogen from the polysaccharide backbone.[30] Indeed, mucopolysaccharides are easily to be attacked by free radicals on the hydrogen at the carbon-5 adjacent to the carboxyl group.[31] Consequently, the mechanism of this irreversible photoreduction can be proposed as shown in Fig. 6. The LMCT excitated state (LMCT*) is located above the S_1 and S_2 states in energy, and the photoexcited species has two pathways for decay. The first is relaxation to the S_2 state, and the second affords Fe(II) porphyrin via intramolecular electron transfer. A part of the formed $Cl^{\bullet}$ that escapes from the solvent cage reacts with the active hydrogen of the neighboring hyaluronic acid, and then the iron(II) **1b** complex could accumulate. However, the charge recombination to $Fe^{III}Cl(Lp)$ is a facile reaction which returns to the ground state. The quantum yields (Φ) of this photoreduction for the **1a**/hyaluronic acid became 0.007, which is consistent with the former reported values of the photoreduction by LMCT excitation.[7] That is, the low quantum yield of this system is presumably due to the high probabilities of the deactivation of LMCT* to S_2, and back electron transfer from the iron(II) ion to the chlorine radical.

Interestingly, the TEM of the **1a**/hyaluronic acid solution showed the formation of unique thin fibers with a width of 5–10 nm (Fig. 1b). The co-existence of a small amount of hyaluronic acid obviously changed the morphology of the **1a** assembly from the micelle to the fiber, which is probably made of a polysaccharide coil combined the **1a** molecule. On the other hand, a larger excess amount of glucose should be necessary for complete photoreduction (vide supla), and no clear structure could be observed in the TEM of the **1a**/glucose solution. Gulcose is homogeneously dispersed in PBS in contrast to hyaluronic acid. Hence, the fibrous co-aggregate structure composed of **1a** and hyaluronic acid would be responsible for the radical trapping and the effective photoreduction.

Our attempt to detect the radicals by ESR spectroscopy unfortunately failed. No radicals were observed, probably due to their short lifetimes.[31] However, the ring opening and the cleavage of the glycosidic linkage should induce a decrease in viscosity.[29] Indeed, the viscosity of the PBS solution of **1a**/hyaluronic acid was simultaneously decreased as the photoreduction proceeded (Fig. 7).

The efficacy of other saccharides on the photoreduction of

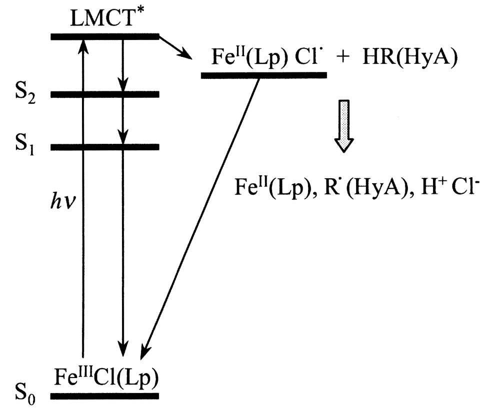

Fig. 6. Transient states and interconversion pathways for photoreduction of **1a**. Fe(Lp): (lipidporphyrinato)iron.

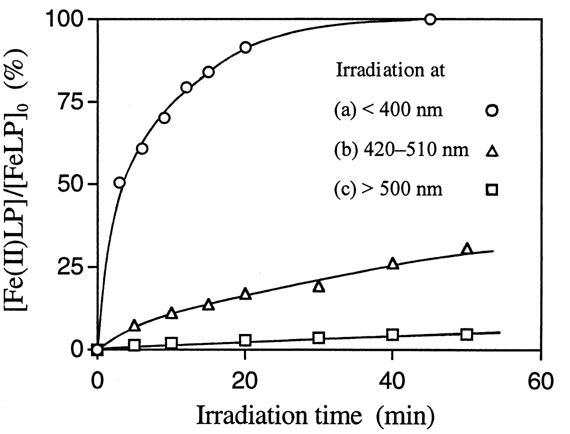

Fig. 5. Photoreduction of **1a** complex with hyaluronic acid ([unit] = 100 μM) in PBS solution by different wavelength light irradiation.

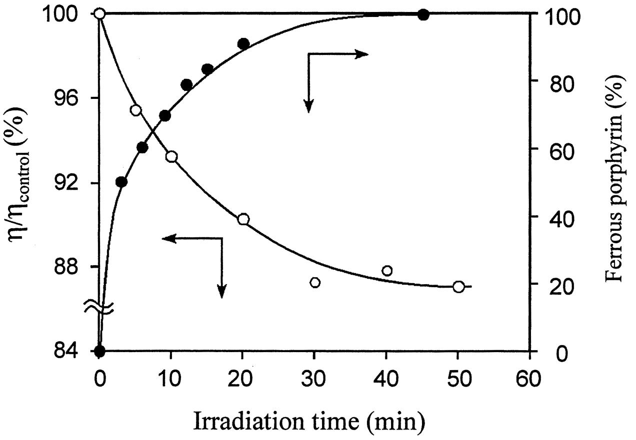

Fig. 7. The time dependence of viscosity and photoreduction ratio of the central iron(III) ion of the PBS solution of **1a**/hyaluronic acid.

the **1a** complex was compared (Fig. 8). The 100% reduction occurred only when hyaluronic acid or glucose coexisted. Amylose ([unit] = 100 μM), chondroitin 6-sulfate ([unit] = 100 μM), and glucronic acid (0.1 mM) did not contribute very much to the photoreduction of the central iron(III). These differences in the reduction behavior can be interpreted by the disparity in the rate of saccharide dehydrogenation, which competes with the recombination between the photolytically produced **1b** and the chlorine radical.

In order to analyze the photoreduction and imidazole binding to the reduced central iron(II), laser flash photolysis experiments were carried out. The deaerated **1a**/hyaluronic acid fiber solution showed that the reduction of the central iron(III) occurred within the duration time of the nano-second laser pulse. The transient absorption spectrum measured at 50 ns after the pulse was in good agreement with the difference spectrum of the five-N-coordinated iron(II) complex minus the iron(III) complex (λ_{max}: 443 nm, λ_{min}: 414 nm).[28] This result reveals that the axial base immediately associates with the photoreduced iron(II) ion, following the radical-scavenging by the saccharide. Femto-second laser flash photolysis was also performed (Fig. 9). We could not detect the LMCT* excitation of the **1a**/hyaluronic acid fiber, but bleaching of the ground state was seen in the Soret band region, and a broad band of the triplet state of the π-π* transition appeared around 455 nm. Within 100 ps, the bleaching of the ground state in the Soret region was recovered and the transient absorption disappeared with a slight delay. The lifetime of the excited state was calculated to be approximately 11 ps. These spectral changes are consistent with those of $Fe^{III}Cl(tpp)$, which shows a T–T lifetime of 50 ps and no fluorescence.[32] It can be concluded that fiber formation with hyaluronic acid does not influence the excited triplet lifetime of the **1a** complex, itself.

By bubbling O_2 gas through the photoreduced **1b** fiber solution, the UV-vis absorption spectrum changed to that of the O_2-adduct complex (λ_{max}: 425, 548 nm) in a fashion similar to the **1b** fiber, which was prepared by a previously reported procedure using chemical reduction of the central iron(III) with ascorbic acid.[16] The O_2 coordination was reversible at 25 °C depending on the O_2-partial pressure, and the O_2-binding abilities were identical to those of the **1b** fibers prepared with ascorbic acid.

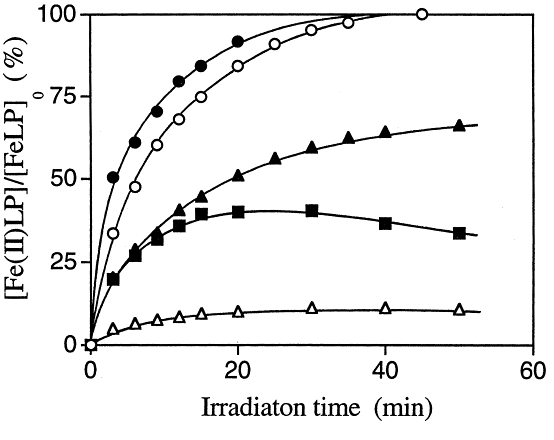

Fig. 8. Photoreduction of **1a** complex with several saccharaides in PBS solution by 365 nm-irradiation; ○: glucose 150 mM, ●: hyaluronic acid 21 mg/L ([unit] = 100 μM), ▲: amylose 25 mg/L ([unit] = 100 μM), ■: condroitin 6-sulfate 23 mg/L ([unit] = 100 μM), △: glucronic acid 0.1 mM.

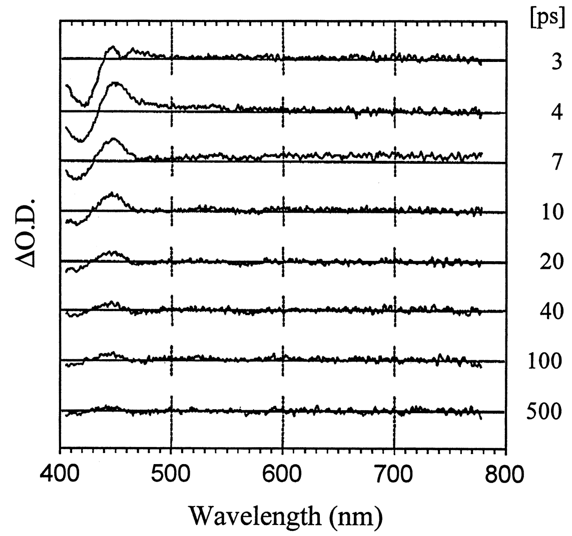

Fig. 9. Transient absorption spectra of the PBS solution of **1a**/hyaluronic acid. The sample was excited at 390 nm, and the shallow basin on the top of the 455 nm band at 3 ps is attributed to the Raman scattering of water.

Conclusion

Photoirradiation into the LMCT band of the self-assembled **1a** complex with hyaluronic acid led to a reduction of the central iron(III), providing a five-N-coordinated iron(II) **1b** complex, which could reversibly bind and release O_2. Hyaluronic acid plays a vital role as a radical scavenger. The abstraction of hydrogen atoms from the saccharides by the produced chlorine radical, following the photoinduced homolysis of the Fe^{III}–Cl^- bond, is a key step for accumulating the iron(II) complex. This is supported by a decrease in the viscosity of the **1a**/hyaluronic acid fiber solution during photoreduction, which means the depolymerization of hyaluronic acid by radical scavenging. The laser flash photolysis experiments revealed that the photoreduction of the central iron(III) ion and the imidazole association were completed within 50 ns. Further investigation and the application of this photoreduction for synthetic hemoproteins are now underway.

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