

Efficient Catalytic Epoxidation in Water by Axial N-Ligand-Free Mn-Porphyrins within a Micellar Capsule

Takumi Omagari, Akira Suzuki, Munetaka Akita, and Michito Yoshizawa*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

S Supporting Information

ABSTRACT: Epoxidation of styrenes is efficiently catalyzed by micelle-like molecular capsules providing Mn-porphyrins in water at room temperature. In contrast to usual Mn-porphyrin catalysts, the encapsulated Mn-porphyrin catalysts show higher reactivities (up to 1350 TON for 1 h) even without the addition of imidazole ligands. Spectroscopic studies and competitive-binding experiments demonstrate that the efficient catalytic cycle stems from the enforced proximity of the catalyst and substrates as well as the smooth replacement of the products by substrates in the hydrophobic cavity of the capsule.

Cytochrome P450, a group of enzymes known as monooxygenases, provides a metallo-porphyrin catalyst in the pocket surrounded by large protein assemblies.¹ The confined microspace of the pocket is of essential importance to enhance the selectivity and efficiency of the enzymatic reaction in water under very mild conditions. Inspired by such biological catalysts, a great deal of attention has been paid to the synthesis of various metallo-porphyrin compounds surrounded with covalently linked bulky substituents to explore the structure–reactivity relationships.² On the other hand, the encapsulation of metallo-porphyrin compounds in the cavity of synthetic cages through noncovalent interactions^{3,4} would be highly expected to develop novel bioinspired catalysts but remains uncommon^{5,6} due to the difficulty of binding the large polyaromatic framework (>1 nm in diameter) of the porphyrin ring.⁷ Although there are a few reports on encapsulated metallo-porphyrin catalysts utilized in organic media,⁵ efficient catalytic reactions in water have been seldom achieved by such supramolecular metallo-porphyrins.⁸ Here we report olefin epoxidation in water catalyzed by Mn-porphyrins encapsulated in a capsular polyaromatic assembly (Figure 1a).

As a new type of aqueous host, we recently reported that polyaromatic amphiphile **1** composed of a bent bis-anthracene framework with two hydrophilic groups (Figure 1b,c; left) forms micelle-like molecular capsule **2** with a polyaromatic shell.⁹ The polyaromatic capsule enables hydrophobic compounds (e.g., fluorescent dyes, fullerenes, and carbon nanotubes) to dissolve in water upon encapsulation, yet the potential utility of **2** as a reaction vessel has been unexplored so far.^{9,10} Thus, as an initial investigation, we focused on the well-studied epoxidation reaction of styrenes by Mn-porphyrin catalysts. In general, the addition of an excess amount of imidazole (10–80 equiv per the catalyst) as an axial ligand is

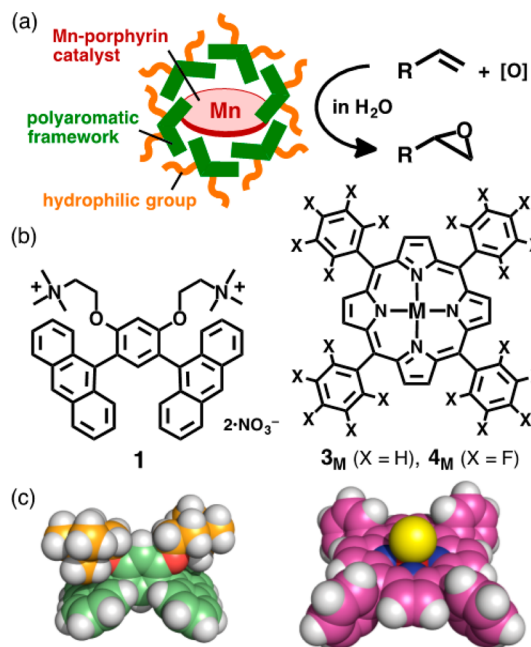


Figure 1. (a) Schematic representation of olefin epoxidation catalyzed by an encapsulated Mn-porphyrin catalyst in water. (b) Chemical structures of polyaromatic amphiphile **1** and metallo-tetraphenylporphyrins **3_M** and **4_M** and (c) space-filling representations of **1** (left) and **3_{Mn-Cl}** (right).

crucial for the reaction to activate the manganese center upon strong coordination.^{11,12} Herein, we describe (i) the encapsulation of metallo-porphyrins **3_M** (M = Mn-Cl, Zn, Ni, and Co) and fluorinated Mn-porphyrin **4_{Mn-Cl}** (Figure 1b,c) within aqueous polyaromatic capsule **2** and (ii) the efficient catalytic epoxidation of styrenes in water by the encapsulated Mn-porphyrins without axial imidazole ligands under ambient conditions. The keys of the efficient catalytic cycle are the enforced proximity of the manganese catalyst and substrates through hydrophobic effects and also the smooth replacement of the products by substrates in the hydrophobic cavity.

Manual grinding a mixture of polyaromatic amphiphile **1** and manganese(III) tetraphenylporphyrin chloride (**3_{Mn-Cl}**) readily furnished water-soluble host–guest complex **2**⊃**3_{Mn-Cl}**. When solids of **1** (1.5 mg, 2.0 μmol) and **3_{Mn-Cl}** (0.7 mg, 1.0 μmol) were gently ground for 5 min and then dissolved in H₂O (1.0 mL) at room temperature (r.t.), a clear green solution of

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polyaromatic capsule **2** containing one molecule of hydrophobic $3_{\text{Mn-Cl}}$ was obtained after removing the excess $3_{\text{Mn-Cl}}$ by filtration (Figure 2a).¹³ The Mn-porphyrin is highly hydro-

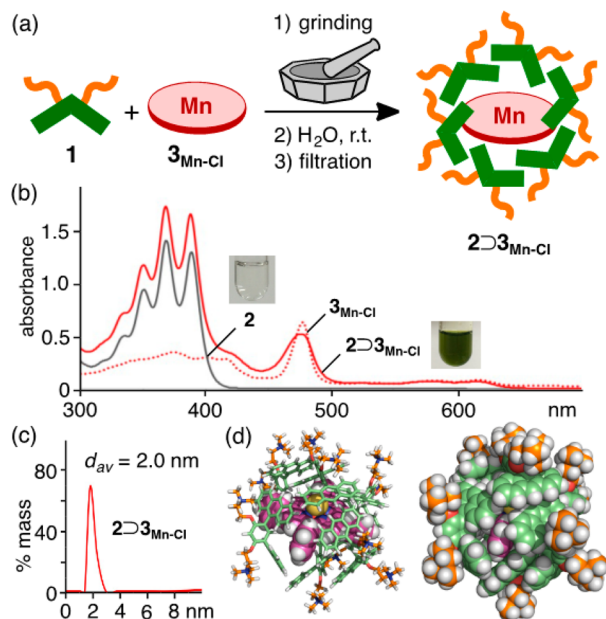


Figure 2. (a) Schematic representation of the preparation of $2@3_{\text{Mn-Cl}}$. (b) UV-vis spectra (r.t.) of **2** and $2@3_{\text{Mn-Cl}}$ in H_2O (1.0 mM based on **1**) with their photographs and $3_{\text{Mn-Cl}}$ in CH_2Cl_2 (0.05 mM). (c) Size distribution of $2@3_{\text{Mn-Cl}}$ by DLS measurement. (d) Optimized structure of $2@3_{\text{Mn-Cl}}$.

phobic, and thereby the grinding operation is essential for efficient solubilization in water.¹⁴ The yield and detailed structure of the product were confirmed by UV-vis absorption spectroscopy and dynamic light scattering (DLS) analysis. The UV-vis spectrum of the resultant solution showed new absorption bands at 476 nm and ~600 nm derived from the Soret band and Q-band of the encapsulated $3_{\text{Mn-Cl}}$, respectively (Figure 2b). The absorption maximum of the Soret band is quite similar to that of free $3_{\text{Mn-Cl}}$ (477 nm) dissolved in CH_2Cl_2 , indicating the accommodation of monomeric $3_{\text{Mn-Cl}}$. Based on the absorption bands of capsule **2** at 330–410 nm, the observed intensity of the guest absorption bands indicated that 63% of **2** encapsulates one molecule of $3_{\text{Mn-Cl}}$ in the cavity.¹⁵ Although the ^1H NMR spectrum displayed very broad peaks of **2** owing to the encapsulation of paramagnetic $3_{\text{Mn-Cl}}$ (Figure S3), the DLS analysis showed a sharp size-distribution peak, which indicates the presence of only small particles with an average diameter of 2.0 nm (Figure 2c). The observed size is comparable to the core diameter of an optimized structure composed of one molecule of $3_{\text{Mn-Cl}}$ fully encircled by capsule **2** composed of six molecules of **1** (Figure 2d). In sharp contrast to typical micelles, notably, polyaromatic capsule **2** strongly binds the Mn-catalyst in water through effective hydrophobic effect and π -stacking interactions so that the encapsulated $3_{\text{Mn-Cl}}$ could be scarcely extracted from the aqueous $2@3_{\text{Mn-Cl}}$ solution with CH_2Cl_2 even by vigorous stirring.

In a manner similar to the preparation of $2@3_{\text{Mn-Cl}}$, various water-soluble metallo-porphyrin composites $2@3_{\text{Zn}}$, $2@3_{\text{Ni}}$, $2@3_{\text{Co}}$, and $2@4_{\text{Mn-Cl}}$ were obtained from **1** and the corresponding metallo-tetraphenylporphyrins (M = Zn, Ni, and Co) and fluorinated Mn-tetraphenyl porphyrin through

grinding.¹⁶ In the absorption spectra, the Soret bands of the bound 3_{Zn} , 3_{Ni} and 3_{Co} were found at $\lambda_{\text{max}} = 430, 411,$ and 419 nm, respectively (Figure 3). A Soret band derived from

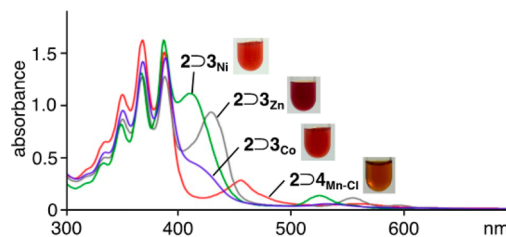


Figure 3. UV-vis spectra (H_2O , 1.0 mM based on **1**, r.t.) and their photographs of $2@3_{\text{Zn}}$, $2@3_{\text{Ni}}$, $2@3_{\text{Co}}$, and $2@4_{\text{Mn-Cl}}$.

fluorinated Mn-porphyrin $4_{\text{Mn-Cl}}$ within **2** appeared at 457 nm, which is largely shifted ($\Delta\lambda = -19$ nm) as compared with nonfluorinated $3_{\text{Mn-Cl}}$ within **2**. Although $3_{\text{Mn-Cl}}$ was solubilized in water upon encapsulation by conventional sodium dodecyl sulfate amphiphiles (namely, SDS micelle), the solubilizing ability is 20-times lower than that of **1** even using a large amount (10-times) of the SDS amphiphile (Figure S1).

Water-soluble Mn-porphyrin composite $2@3_{\text{Mn-Cl}}$ turned out to be effective as a catalyst for styrene epoxidation in aqueous solutions under ambient conditions. When 4-chlorostyrene (**5**; 100 μmol), iodossylbenzene (200 μmol), and imidazole (10 μmol) were agitated in a H_2O solution (1.0 mL) of catalyst $2@3_{\text{Mn-Cl}}$ (0.2 μmol based on $3_{\text{Mn-Cl}}$) at r.t. for 4 h, the corresponding epoxide **6** was formed in 69% yield with a turnover number (TON) of 345 (Table 1, entry 1), as

Table 1. Catalytic Epoxidation of Chlorostyrenes^a

entry	catalyst (μmol)	solvent	time (h)	imidazole (μmol)	yield (%)	TON
1	$2@3_{\text{Mn-Cl}}$ (0.2)	H_2O	4	10	69	345
2	$3_{\text{Mn-Cl}}$ (0.2)	CH_2Cl_2	4	10	62	310
3	$2@4_{\text{Mn-Cl}}$ (0.06)	H_2O	1	10	83	1383
4	$4_{\text{Mn-Cl}}$ (0.06)	CH_2Cl_2	1	10	99	1650
5	$2@3_{\text{Mn-Cl}}$ (0.2)	H_2O	4	0	56	280
6	$3_{\text{Mn-Cl}}$ (0.2)	CH_2Cl_2	4	0	2	10
7	$2@4_{\text{Mn-Cl}}$ (0.06)	H_2O	1	0	70	1167
8	$4_{\text{Mn-Cl}}$ (0.06)	CH_2Cl_2	1	0	12	200
9 ^b	$2@4_{\text{Mn-Cl}}$ (0.06)	CH_3OH	1	0	8	133
10 ^b	$2@4_{\text{Mn-Cl}}$ (0.06)	THF	1	0	2	33
11 ^c	$2@4_{\text{Mn-Cl}}$ (0.06)	H_2O	1	0	78	1300
12 ^d	$2@4_{\text{Mn-Cl}}$ (0.06)	H_2O	1	0	81	1350

^aConditions: catalyst (0.01–0.2 μmol), 4-chlorostyrene (100 μmol), imidazole (10 or 0 μmol), PhIO (200 μmol) in H_2O or CH_2Cl_2 at r.t. for 1 or 4 h. ^bCatalyst $2@4_{\text{Mn-Cl}}$ disassembled into **1** and $4_{\text{Mn-Cl}}$ in this solvent. ^c3-Chlorostyrene (100 μmol) was employed instead of **5**. ^d2-Chlorostyrene (100 μmol) was employed instead of **5**.

evaluated by ^1H NMR and GC analyses.^{13,17} Both the catalyst ($3_{\text{Mn-Cl}}$) and oxidant (iodosylbenzene) are essential for this reaction (Table S1). Epoxidation of **5** in an organic solvent (CH_2Cl_2) also yielded **6** in 62% yield (TON = 310) by using the $3_{\text{Mn-Cl}}$ catalyst with imidazole ligands (entry 2). A classical SDS micelle (10 mM) containing $3_{\text{Mn-Cl}}$ (0.01 μmol) showed a lower catalytic activity (2% yield; Table S2) for **5** in H_2O due to the lower host capability. Fluorinated Mn-porphyrin composite $2\text{D}4_{\text{Mn-Cl}}$ exhibited better catalytic activity (83% yield, TON = 1383 for 1 h; entry 3) than that of $2\text{D}3_{\text{Mn-Cl}}$ in water, because of the intrinsic high reactivity of $4_{\text{Mn-Cl}}$ (entry 4). These results demonstrated that the Mn-porphyrins display their high catalytic performance even within the polyaromatic shell of **2** in aqueous solutions.

To our surprise, without the addition of the axial imidazole ligand, epoxide **6** was also obtained from chlorostyrene **5** in moderate yield (56%) by the use of catalyst $2\text{D}3_{\text{Mn-Cl}}$ in H_2O at r.t. for 4 h (Table 1, entry 5). In marked contrast, the catalytic reaction hardly proceeded by $3_{\text{Mn-Cl}}$ in CH_2Cl_2 without imidazole (only 2% yield; entry 6). Thus, the catalytic efficiency of $2\text{D}3_{\text{Mn-Cl}}$ is 28-fold higher than that of $3_{\text{Mn-Cl}}$ in the absence of imidazole. Moreover, it is noteworthy that fluorinated Mn-porphyrin $4_{\text{Mn-Cl}}$ showed higher catalytic reactivity toward 4-chlorostyrene within capsule **2** in water (70% yield, TON = 1167) than that without **2** in CH_2Cl_2 (12% yield, TON = 200) under imidazole-free conditions (1 h; entries 7 and 8, respectively). The catalytic efficiency of $4_{\text{Mn-Cl}}$ was enhanced by 5.8-times by using capsule **2**. The possibility of the catalytic reaction outside the capsule in water is highly excluded because of the extreme hydrophobicity of $4_{\text{Mn-Cl}}$ and the lower reactivity of $2\text{D}4_{\text{Mn-Cl}}$ in organic solvents (<10%; entries 9 and 10), where the $2\text{D}4_{\text{Mn-Cl}}$ catalyst disassembles into monomeric **1** and $4_{\text{Mn-Cl}}$ owing to the lack of intermolecular interactions. Catalytic epoxidation of 3-chlorostyrene and 2-chlorostyrene gave rise to the corresponding epoxides in 78% (TON = 1300) and 81% (TON = 1350) yields, respectively, by $2\text{D}4_{\text{Mn-Cl}}$ under the same conditions (entries 11 and 12). These results are most probably due to the close proximity of the catalyst and the substrate (i.e., concentration effect) in the hydrophobic cavity.¹⁸ Both the inside space of the capsule and the Mn-catalyst are highly hydrophobic so that it is difficult for a water molecule to act as the axial ligand of the catalyst in the confined cavity.¹⁹ The formation of a Mn-porphyrin μ -oxo dimer as a deactivated catalyst was not observed in the UV-vis spectrum after the catalytic reaction within the capsule (Figure S8).

Finally, we studied the mechanism of the catalytic epoxidation reaction within polyaromatic capsule **2**. Metalloporphyrin compounds are spectroscopically sensitive to the state of the metal centers, and thereby UV-vis analysis clearly indicated (i) the formation of a high-valent Mn-oxo species ($3_{\text{Mn=O}}$), (ii) the co-encapsulation of substrate **5** and catalyst $3_{\text{Mn-Cl}}$, (iii) the effective oxidation of the encapsulated **5** by the Mn-oxo species, and (iv) the smooth replacement of product **6** by the substrate in the cavity of **2** (Figure 4a).

A green aqueous solution of $2\text{D}3_{\text{Mn-Cl}}$ (Figure 4b, A) turned reddish brown by adding a pale yellow solid of iodosylbenzene (50 equiv based on $3_{\text{Mn-Cl}}$) within 1 min at r.t. The UV-vis spectrum exhibited a new absorption band at $\lambda_{\text{max}} = 425$ nm, assignable to the Mn-oxo species $3_{\text{Mn=O}}$ (Figure 4b, C). The Soret band is greatly shifted toward the blue ($\Delta\lambda = -51$ nm) as compared with that of $3_{\text{Mn-Cl}}$ within **2**.^{20a} In contrast, the Soret band of the encapsulated $3_{\text{Mn-Cl}}$ was slightly shifted by $\Delta\lambda = +9$ nm only within the capsule by the treatment with 4-

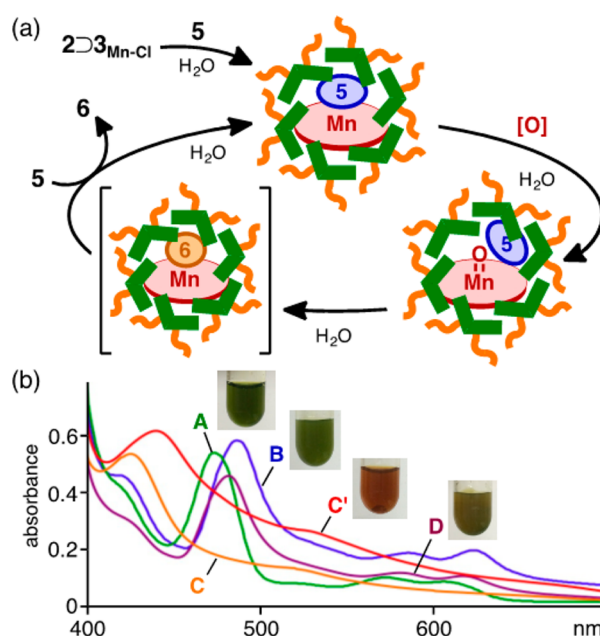


Figure 4. (a) Schematic representation of the catalytic epoxidation of styrenes in the presence of $2\text{D}3_{\text{Mn-Cl}}$ and (b) UV-vis spectra (H_2O , 1.0 mM based on **1**, r.t.) and their photographs of A: $2\text{D}3_{\text{Mn-Cl}}$, B: after the addition of **5** into solution A (= $2\text{D}3_{\text{Mn-Cl}}\cdot\text{5}$), C: $2\text{D}3_{\text{Mn=O}}$, C': after the addition of iodosylbenzene into solution B ($\approx 2\text{D}3_{\text{Mn=O}}\cdot\text{5}$), D: solution C' after 5 min at r.t. (= $2\text{D}3_{\text{Mn-Cl}}\cdot\text{5}$) + $2\text{D}3_{\text{Mn-Cl}}$.

chlorostyrene (50 equiv) at r.t. (Figure 4b, B), suggesting the co-encapsulation of hydrophobic **5** and $3_{\text{Mn-Cl}}$ in the cavity of **2**.^{20b} When iodosylbenzene (50 equiv) was added to the resultant H_2O solution including $2\text{D}3_{\text{Mn-Cl}}\cdot\text{5}$, the absorption band ($\lambda_{\text{max}} = 487$ nm) disappeared and a new absorption band derived from the Mn-oxo species appeared around 440 nm (Figure 3b, C').²¹ The obtained $3_{\text{Mn=O}}$ species efficiently reacted with **5** without imidazole due to the enforced proximity to generate $3_{\text{Mn-Cl}}$ within 5 min, as indicated by the disappearance of the Mn-oxo band (Figure 4b, D). In addition, the appearance of a new absorption band around 480 nm suggests the regeneration of $2\text{D}3_{\text{Mn-Cl}}\cdot\text{5}$ (and $2\text{D}3_{\text{Mn-Cl}}$) after the replacement of slightly hydrophilic product **6** by hydrophobic substrate **5** within the capsule. Competitive-binding experiment also revealed that the selective encapsulation of **5** by $2\text{D}3_{\text{Mn-Cl}}$ from a mixture of **5** and **6** (Figure S11) in water at r.t. Accordingly, the present epoxidation reaction catalyzed with efficient turnover in the microspace of the capsule. In previous reports, whereas the cavities of supramolecular cages and capsules can greatly accelerate various chemical reactions, high catalytic turnovers (>1000 TON for 1 h) in their cavities remain unusual in water.^{4,22}

In conclusion, we have achieved the efficient catalytic epoxidation of styrenes by using novel supramolecular metalloporphyrin catalysts in water. The aqueous catalysts are composed of simple Mn-porphyrins encapsulated strongly by a micellar polyaromatic capsule. The catalytic epoxidation of styrenes efficiently proceeds within the capsule (up to 1350 TON for 1 h) without the aid of axial imidazole ligands under ambient conditions. Spectroscopic analysis and competitive-binding experiments revealed the efficient catalytic cycles arise from the close proximity of the catalyst and substrates as well as the facile replacement of products by substrates in the cavity of the capsule. Further development of regio- and stereoselective

catalytic reactions in aqueous media by using transition-metal catalysts within the present capsule is now under investigation in our group.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11665.

Experimental details and characterization data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*yoshizawa.m.ac@m.titech.ac.jp

Notes

The authors declare no competing financial interest.

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(13) See the Supporting Information.

(14) Without grinding, when a suspended solution of **1** and $3_{\text{Mn-Cl}}$ in H_2O was vigorously stirred for 1 week at r.t., the $2\text{D}3_{\text{Mn-Cl}}$ composite was obtained in only 39% yield (Figure S4).

(15) NMR, DLS, and UV-vis analyses indicated that one molecule of nonplanar $3_{\text{Mn-Cl}}$ is encapsulated by six molecules of **1** in water. The host-guest ratio was estimated by UV-vis analysis in CH_2Cl_2 after the evaporation of the aqueous solution of $2\text{D}3_{\text{Mn-Cl}}$.

(16) The yields of the host-guest complexes were estimated by UV-vis analysis: $2\text{D}3_{\text{Zn}}$ (36%), $2\text{D}3_{\text{Ni}}$ (53%), $2\text{D}3_{\text{Co}}$ (38%), and $2\text{D}4_{\text{Mn-Cl}}$ (18%).

(17) The epoxidation reaction catalyzed by $2'\text{D}3_{\text{Mn-Cl}}$ bearing Cl^- counterions gave **6** in 58% yield (Table S2) under the same conditions. The catalytic reactivity is insensitive to the counterions of the capsule.

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(20) (a) UV-vis absorption band of the Mn-oxo species of $3_{\text{Mn-Cl}}$ in CH_2Cl_2 (without **2**) was found at $\lambda_{\text{max}} = 425 \text{ nm}$ (Figure S9). (b) The shift of the Soret band of $3_{\text{Mn-Cl}}$ was not observed in CH_2Cl_2 (without **2**) even by the addition of excess **5**. Thus, the observed shift (+9 nm) in **2** is most probably derived from coordinative interactions between the vinyl group of **5** and the Mn center.

(21) A similar absorption band appeared by the treatment of an aqueous $2\text{D}3_{\text{Mn=O}}$ solution with **5** at r.t.

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