

**Supplementary Information** for

**Catalytic Methane Oxidation by Supramolecular Conjugate Based on  
 $\mu$ -Nitrido-Bridged Iron Porphyrinoid Dimer**

Yasuyuki Yamada,<sup>1,2,3\*</sup> Kentaro Morita, Nozomi Mihara,<sup>1</sup> Kazunobu Igawa,<sup>4</sup> Katsuhiko Tomooka,<sup>4</sup> and Kentaro Tanaka<sup>1\*</sup>

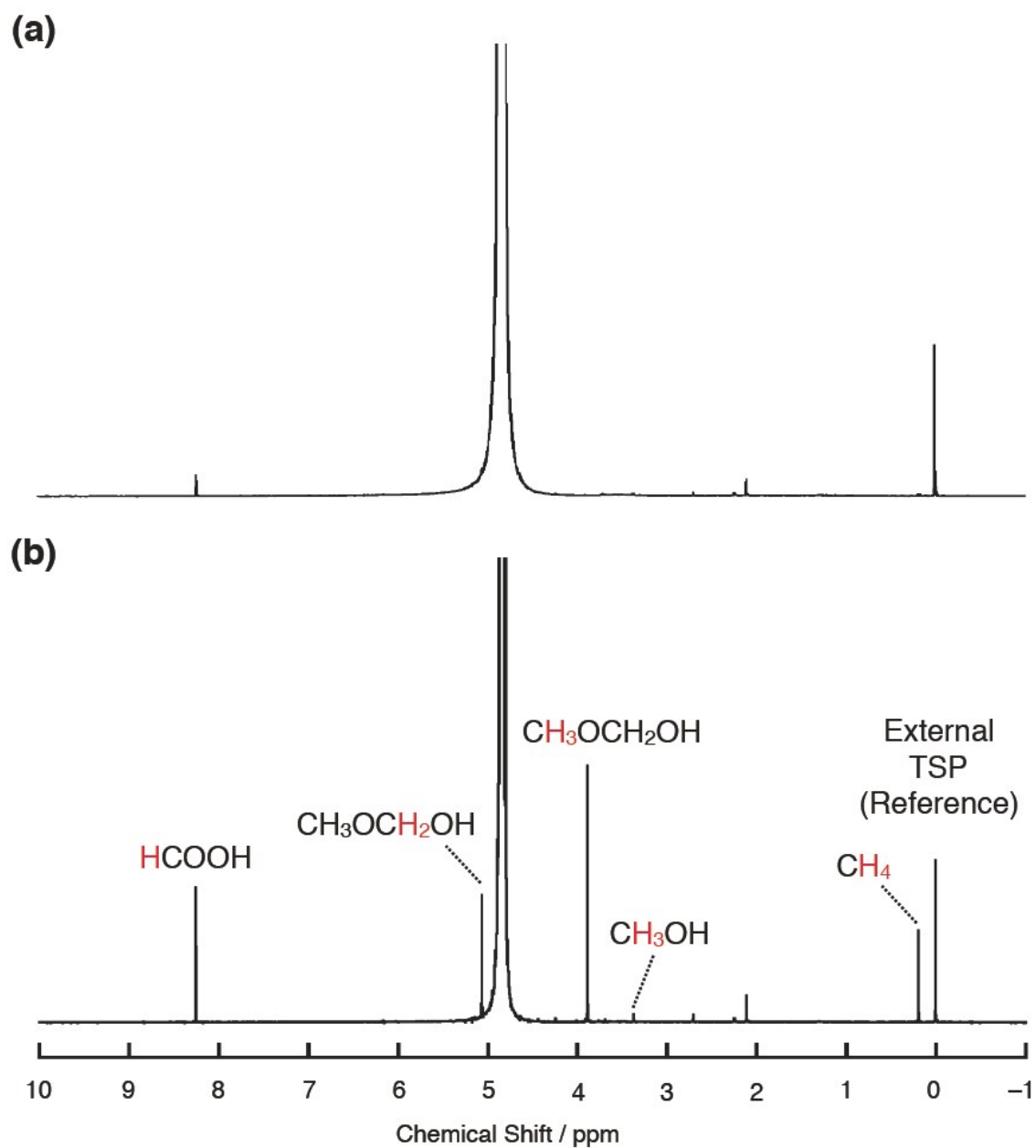
<sup>1</sup>*Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan*

<sup>2</sup>*Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan*

<sup>3</sup>*JST, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan*

<sup>4</sup>*Institute for Materials Chemistry and Engineering, and Department of Material and Molecular Sciences, Kyushu University, Kasuga-Koen, Kasuga, Fukuoka, 816-8580, Japan*

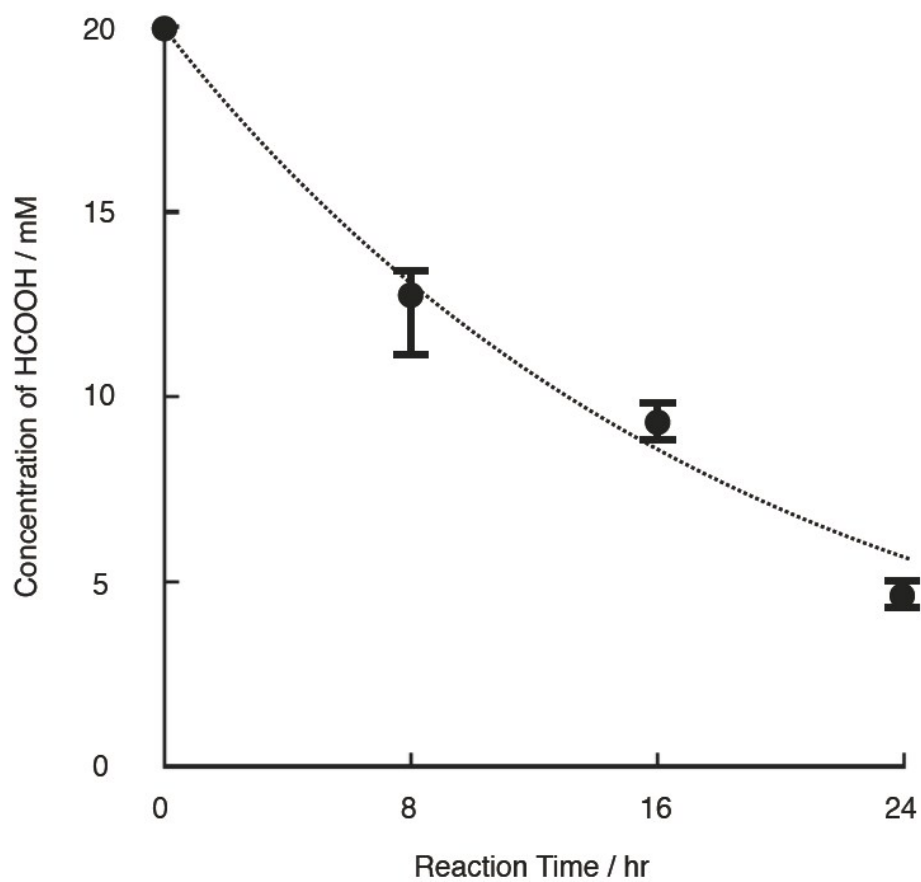
\*E-mail: [yamada.yasuyuki@h.mbox.nagoya-u.ac.jp](mailto:yamada.yasuyuki@h.mbox.nagoya-u.ac.jp), [kentaro@chem.nagoya-u.ac.jp](mailto:kentaro@chem.nagoya-u.ac.jp)



**Figure S1.** Comparison of  $^1\text{H}$ -NMR spectra of the reaction mixture in the (a) presence and (b) absence of methane. The reaction was carried out in  $\text{D}_2\text{O}$  (1.5 mL) in the presence of  $\mathbf{1}^{5+}\cdot 5\text{Cl}^-/\text{SiO}_2$  (141  $\mu\text{M}$  as  $\mathbf{1}^{5+}\cdot 5\text{Cl}^-$ ),  $\text{H}_2\text{O}_2$  (160 mM) and TFA (51 mM) under (a)  $\text{N}_2$  (1.0 MPa) or (b) methane (1.0 MPa) atmosphere at 60  $^\circ\text{C}$  for 8 hours.

**Table S1.** Oxidations of methane or ethane by  $\mu$ -nitrido-bridged iron porphyrinoid dimer-based catalysts on silica supports in the presence of  $\text{H}_2\text{O}_2$  in an acidic aqueous solution. Each reaction was carried out in the presence of a silica-supported catalyst (71  $\mu\text{M}$ ),  $\text{H}_2\text{O}_2$  (160 mM) and TFA (51 mM) in  $\text{H}_2\text{O}$  (1.5 mL) under methane or ethane (1.0 MPa) atmosphere at 60 °C.  $\text{TTN}_{\text{eff}}$ 's and  $\text{MCN}_{\text{eff}}$ 's were calculated according to the equations (i) - (iv) shown in the main text. \*Effective ethane conversion number ( $\text{ECN}_{\text{eff}}$ ) defined as the number of converted ethane into ethanol by one catalyst during the reaction.

No.	Catalyst	Substrate	$T / ^\circ\text{C}$	Reaction Time / hr	$\text{TTN}_{\text{eff}}$	$\text{MCN}_{\text{eff}}$
1	$\text{I}^{5+}\text{-5Cl}^-$	$\text{CH}_4$	60	1	2	3
2	$\text{I}^{5+}\text{-5Cl}^-$	$\text{CH}_4$	60	2	5	4
3	$\text{I}^{5+}\text{-5Cl}^-$	$\text{CH}_4$	60	3	9	5
4	$\text{I}^{5+}\text{-5Cl}^-$	$\text{CH}_4$	60	4	11	6
5	$\text{I}^{5+}\text{-5Cl}^-$	$\text{CH}_4$	60	5	14	7
6	$\text{I}^{5+}\text{-5Cl}^-$	$\text{CH}_4$	60	6	17	9
7	$\text{I}^{5+}\text{-5Cl}^-$	$\text{CH}_4$	60	7	23	11
8	$\text{I}^{5+}\text{-5Cl}^-$	$\text{CH}_4$	60	8	30	13
9	$\text{I}^{5+}\text{-5Cl}^-$	$\text{CH}_4$	60	16	51	21
10	$\text{I}^{5+}\text{-5Cl}^-$	$\text{CH}_4$	60	24	59	23
11	$\text{I}^{5+}\text{-5Cl}^-$	$\text{CH}_3\text{CH}_3$	60	24	241	*117
12	$\text{I}^{5+}\text{-Cu(II)-TPPS}^+\text{-Cl}^-$	$\text{CH}_4$	60	8	44	18
13	$\text{I}^{5+}\text{-Ni(II)-TPPS}^+\text{-Cl}^-$	$\text{CH}_4$	60	8	47	19



**Figure S2.** Changes in the concentration of HCOOH during the oxidation reaction of 20 mM (initial concentration) of HCOOH by  $\mathbf{1}^{5+} \cdot 5\text{Cl}^-/\text{SiO}_2$  in the presence of  $\text{H}_2\text{O}_2$  (160 mM) and TFA (51 mM) in  $\text{H}_2\text{O}$  (1.5 mL) at  $60^\circ\text{C}$ .