Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for

High Catalytic Methane Oxidation Activity of Monocationic μ–Nitrido-Bridged Iron Phthalocyanine Dimer with Sixteen Peripheral Methyl Groups

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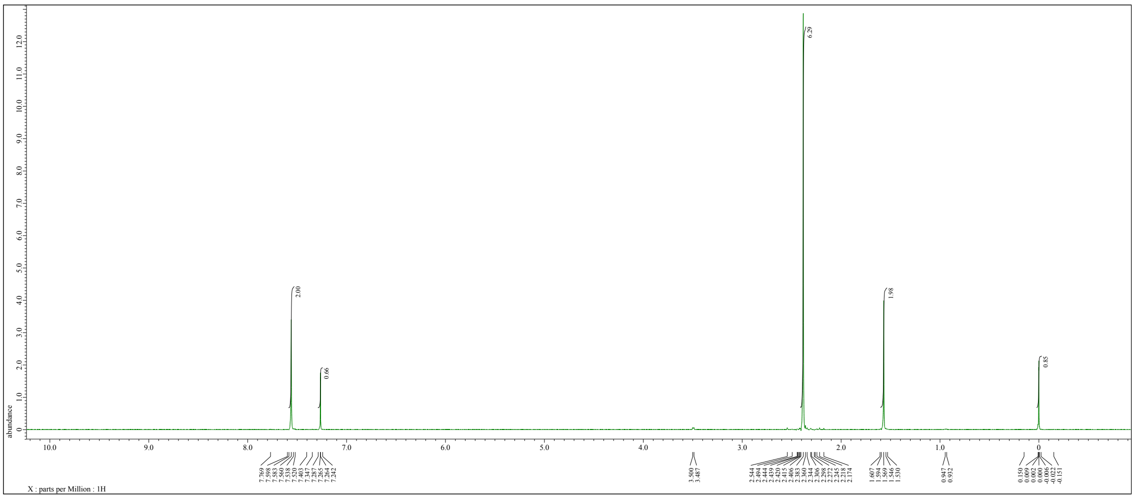


Figure S1. ^{1}H-NMR spectrum of 1,2-dicyano-4,5-dimethylbenzene **5** in $CDCl_3$.

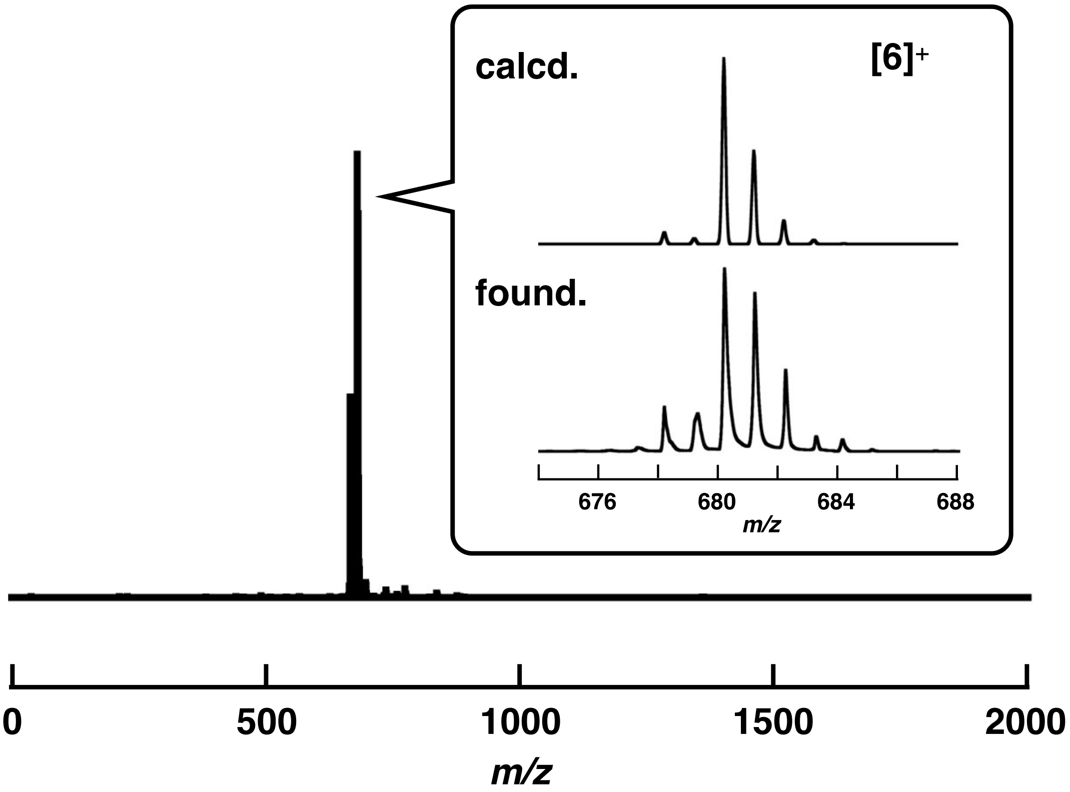


Figure S2. MALDI-TOF spectrum of **6**. Inset: Comparison of the calculated and observed isotopic distribution patterns of **[6]$^+$.**

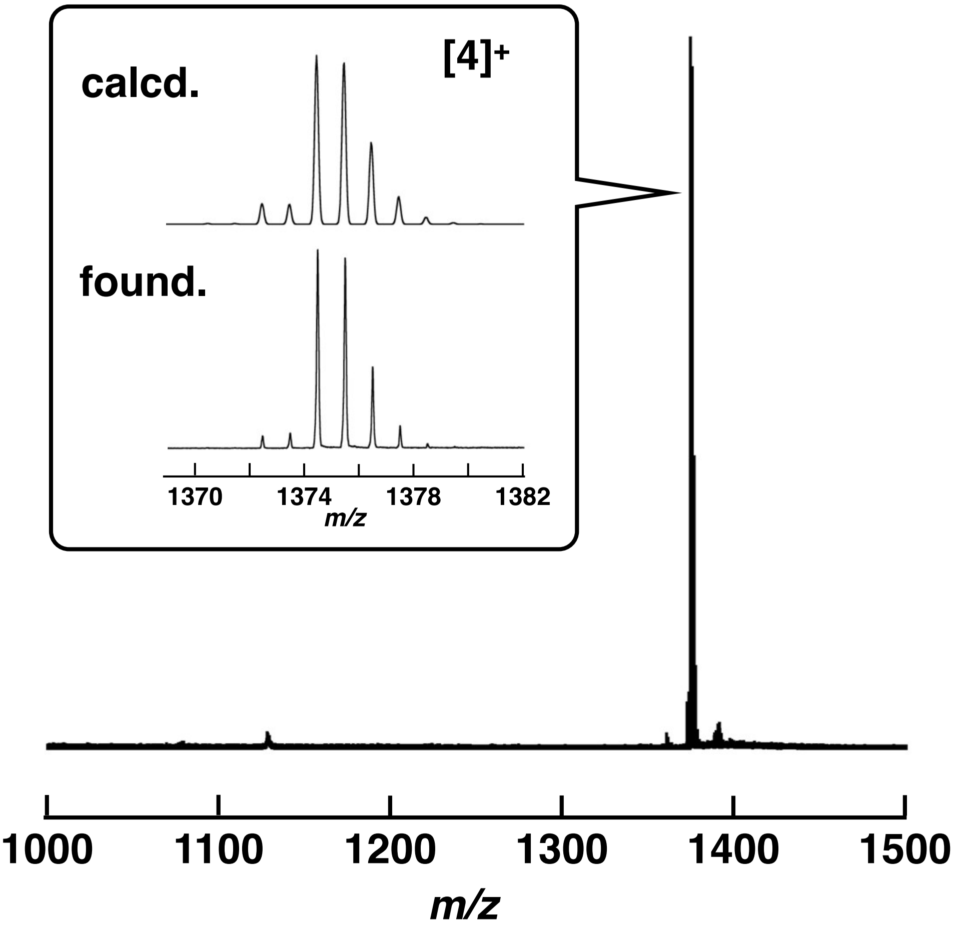
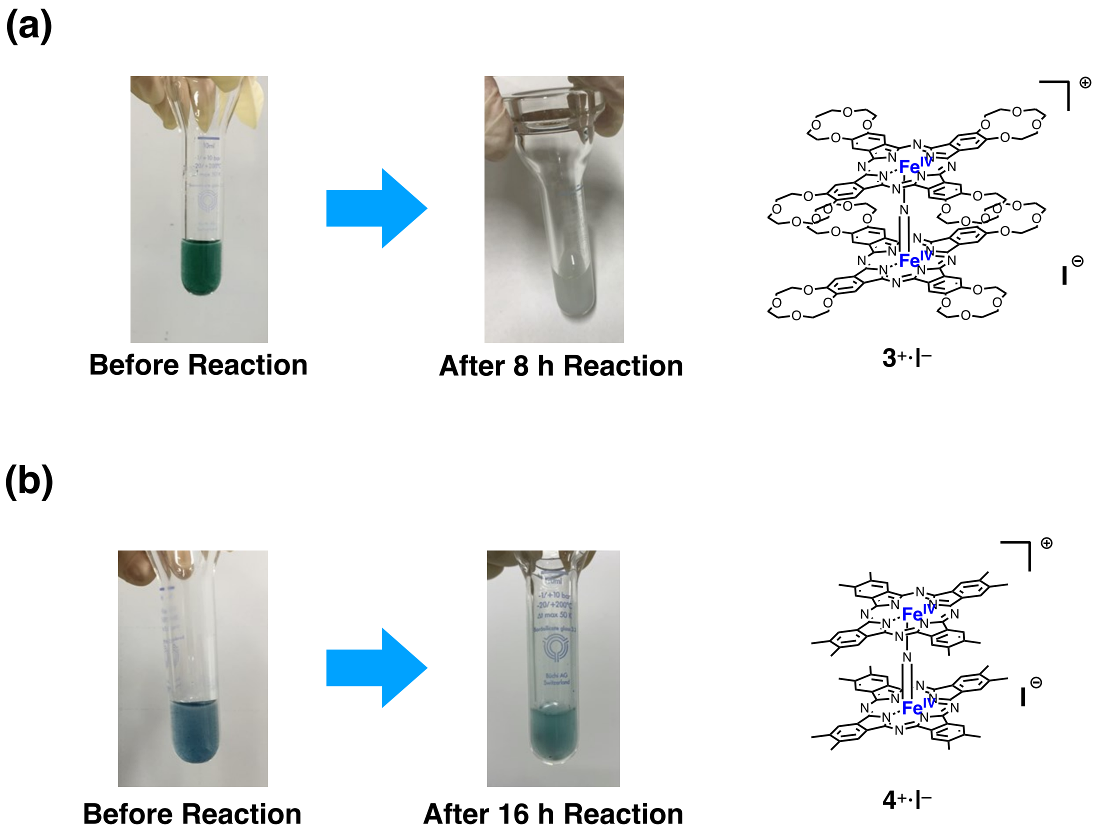


Figure S3. MALDI-TOF spectrum of **$4^{+}\cdot I^{-}$**. Inset: Comparison of the calculated and observed isotopic distribution patterns of **$[4]^{+}$**.

Table S1. Amounts of the oxidized products observed in the reactions under methane (1.0 MPa) or N_2 (1.0 MPa) atmosphere using μ-nitrido-bridged iron phthalocyanine dimer-based catalysts on silica supports.

Entry	Catalyst	Reaction Time / h	Gas	Additive	$[CH_3OH]$ / mM	[HCHO] / mM	[HCOOH] / mM	TTN(CH_4) or TTN(N_2)	TTN_{eff}	MCN_{eff}
1	$\mathbf{4}^+\cdot I^-/SiO_2$	4	CH_4 (1.0 MPa)	•••	0.19	0.36	0.50	44	36	16
2	$\mathbf{4}^+\cdot I^-/SiO_2$	8	CH_4 (1.0 MPa)	•••	0.21	0.68	1.41	104	86	32
3	$\mathbf{4}^+\cdot I^-/SiO_2$	12	CH_4 (1.0 MPa)	•••	0.19	0.75	2.15	147	135	51
4	$\mathbf{4}^+\cdot I^-/SiO_2$	16	CH_4 (1.0 MPa)	•••	0.21	0.72	2.25	151	147	55
5	$\mathbf{4}^+\cdot I^-/SiO_2$	4	N_2 (1.0 MPa)	•••	0.02	0.06	0.10	8	•••	•••
6	$\mathbf{4}^+\cdot I^-/SiO_2$	8	N_2 (1.0 MPa)	•••	0.05	0.36	0.09	19	•••	•••
7	$\mathbf{4}^+\cdot I^-/SiO_2$	12	N_2 (1.0 MPa)	•••	0	0.07	0.19	12	•••	•••
8	$\mathbf{4}^+\cdot I^-/SiO_2$	16	N_2 (1.0 MPa)	•••	0	0.06	0.04	5	•••	•••
9	$\mathbf{4}^+\cdot I^-/SiO_2$	4	CH_4 (1.0 MPa)	10 mM Na_2SO_3	0.27	0.82	0.31	51	27	14
10	$\mathbf{4}^+\cdot I^-/SiO_2$	4	N_2 (1.0 MPa)	10 mM Na_2SO_3	0.10	0.34	0.19	24	•••	•••
11	$\mathbf{1}^+\cdot I^-/SiO_2$	4	CH_4 (1.0 MPa)	•••	0.51	0.29	0.67	57	5	2
12	$\mathbf{1}^+\cdot I^-/SiO_2$	4	N_2 (1.0 MPa)	•••	0.47	0.30	0.60	52	•••	•••

All reactions were performed in the absence of methane (under N_2 (1.0 MPa)), H_2O_2 (189 mM), and TFA (51 mM) in H_2O (3.0 mL) containing a silica-supported catalyst (55 μM as $\mathbf{4}^+$ or $\mathbf{1}^+$). Concentrations of the oxidized products observed in the presence of methane are the mean values of three different reactions. The TTN_{eff}, TTN, and MCN_{eff} values were calculated using equations (i) - (iv) in the main text.



(a) Before Reaction — After 8 h Reaction — $3^{+}\cdot I^{-}$

(b) Before Reaction — After 16 h Reaction — $4^{+}\cdot I^{-}$

Figure S4. Comparison of the pictures of the reaction mixtures before and after methane oxidation reaction by (a) $\mathbf{3}^{+}\cdot I^{-}/SiO_2$ or (b) $\mathbf{4}^{+}\cdot I^{-}/SiO_2$.

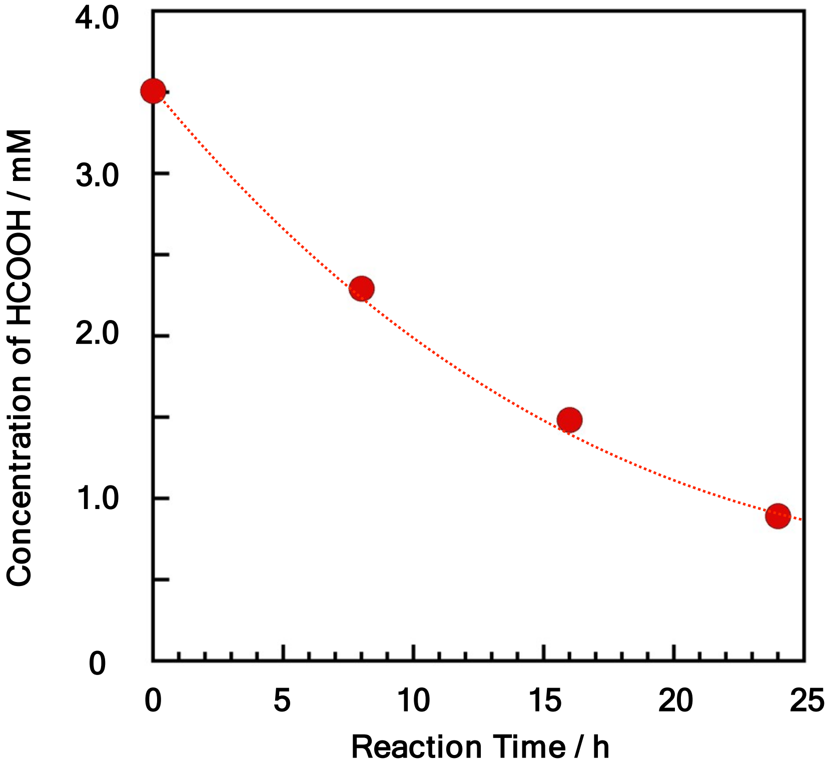


Figure S5. Time dependence of the concentration of HCOOH during the oxidation reaction of HCOOH (3.51 mM (initial concentration) in 3.0 mL of H_2O) by $\mathbf{4}^+\cdot I^-/SiO_2$ in the presence of 51 mM TFA and 189 mM H_2O_2 under N_2 atmosphere at 60 °C.