

Supplementary Information for

**μ -Nitrido-Bridged Iron Phthalocyanine Dimer
Bearing Eight Peripheral 12-Crown-4 Units
and Its Methane Oxidation Activity**

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Synthesis of 4,5-dicyano-benzo-12-crown-4 (**3**).^[1]

4,5-dibromo-benzo-12-crown-4 (2.51 g, 6.57 mmol), CuCN (2.51 g, 28.0 mmol), and dry DMF (80 mL) were added to a 100 mL schlenk flask. Oxygen was removed by freezing-thaw method by 4 times. The suspension was stirred at 160 °C for 87 hrs, and then poured into 28% aqueous NH₃ (200 mL). After stirring under air for 3 hrs, the resulting blue mixture was extracted with AcOEt (300 mL × 3). The combined organic layer was washed with water (200 mL × 2) and brine (100 mL × 2), dried over anhydrous Na₂SO₄, filtered, and evaporated to give colorless solid (1.72 g). The crude product was purified by recrystallization from MeOH (100 mL) to afford the title compound **3** as a colorless solid (1.47 g, 5.36 mmol, 82 %). ¹H NMR (400 MHz, CDCl₃/TMS) : δ = 7.29 (s, 2H), 4.29-4.27 (m, 4H), 3.88-3.86 (m, 4H), 3.74 (s, 4H).

Synthesis of an iron phthalocyanine bearing four 12-crown-4 units (**4**).

3 (1.00 g, 3.65 mmol), Fe(II)(OAc)₂ (0.162 g, 0.931 mmol), and *N,N*-dimethylaminoethanol (10 mL) were added to a 100 mL schlenk flask. Oxygen was removed by freezing-thaw method by 4 times. The solution was heated for 39 hrs at the bath temperature of 180 °C under 300 W Hg lamp irradiation. The crude product was purified by reprecipitation from CHCl₃/MeOH. After the residue was dissolved in CHCl₃ (400 mL), the organic layer was washed with water (300 mL × 3) and dried over anhydrous Na₂SO₄, filtered, and evaporated to give the title compound **4** was obtained as a dark green solid (0.667 g, 0.579 mmol, 63%). This compound was used for the next reaction without further purification. MALDI-TOF MS : m/z = 1152.32: calcd for C₅₆H₅₆FeN₈O₁₆ ([M]⁺) found: 1152.32.

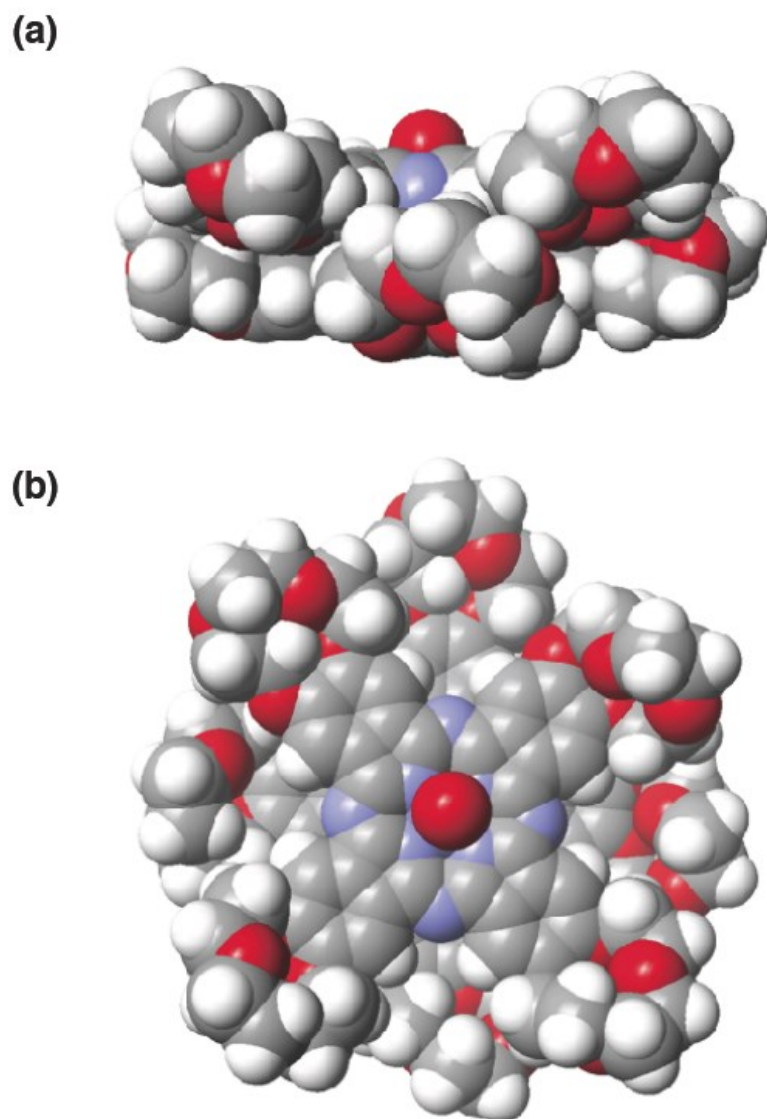


Figure S1. Molecular modeling of **2_{oxo}** using MM3 force field in SIGRESS software. (a) side view, (b) top view.

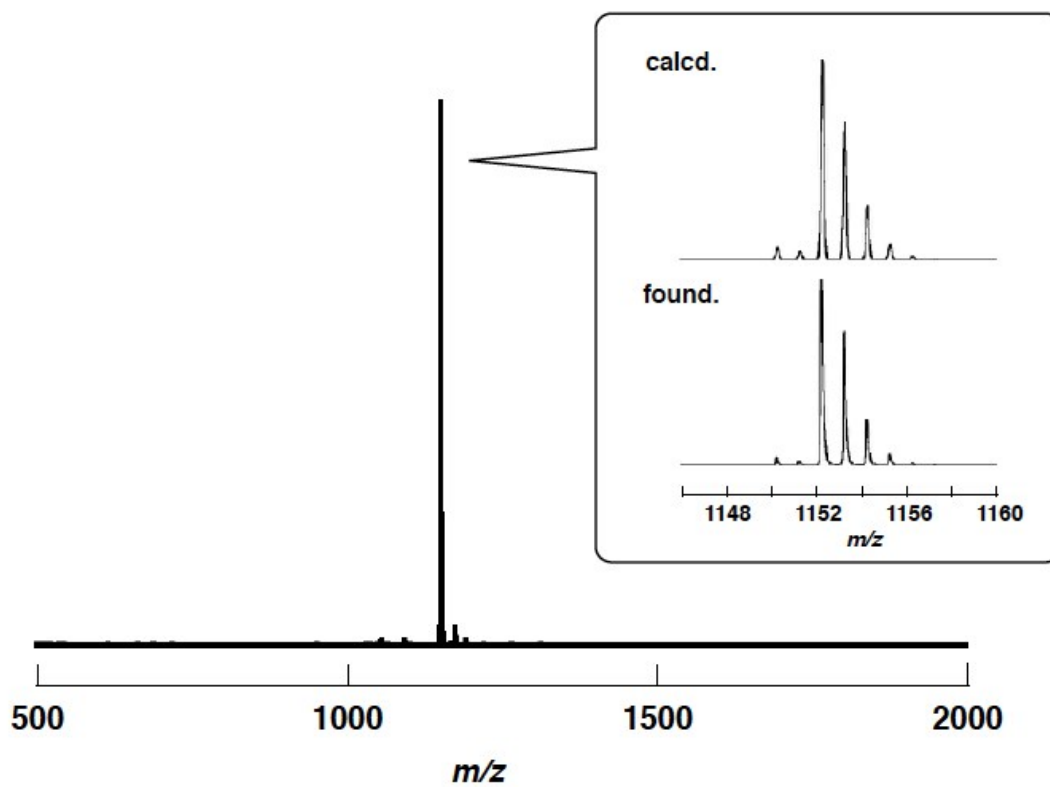


Figure S2. MALDI-TOF spectrum of **4**. Inset: Comparison of the calculated and observed isotopic distribution patterns of [**4**⁺].

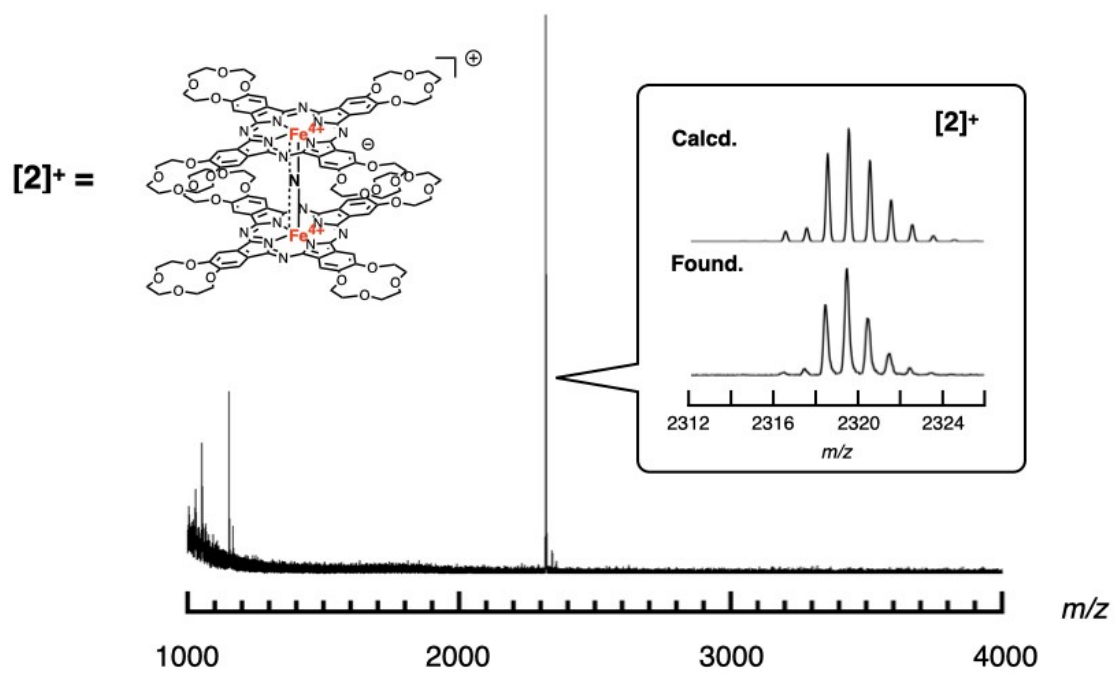


Figure S3. MALDI-TOF spectrum of $2^+ \cdot I^-$. Inset: Comparison of the calculated and observed isotopic distribution patterns of $[2]^+$.

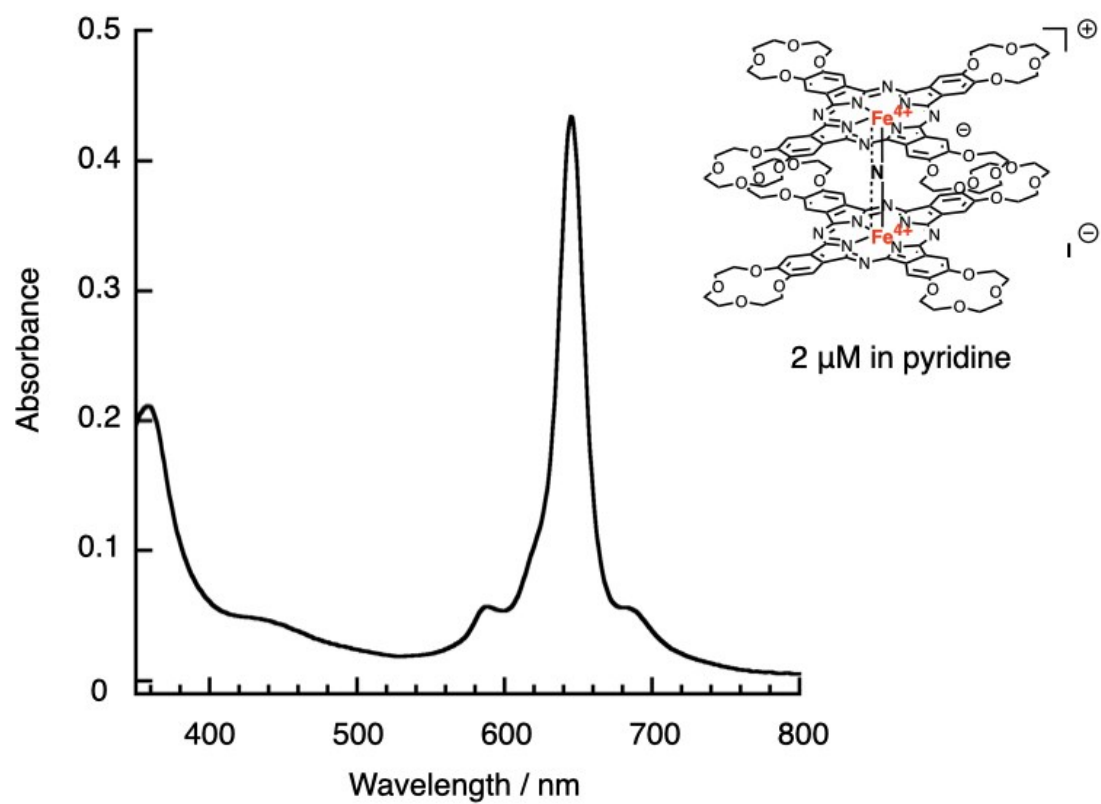


Figure S4. UV-Vis spectrum of $\mathbf{2}^+\cdot\text{I}^-$ (2.0 μM) in pyridine at 293 K.

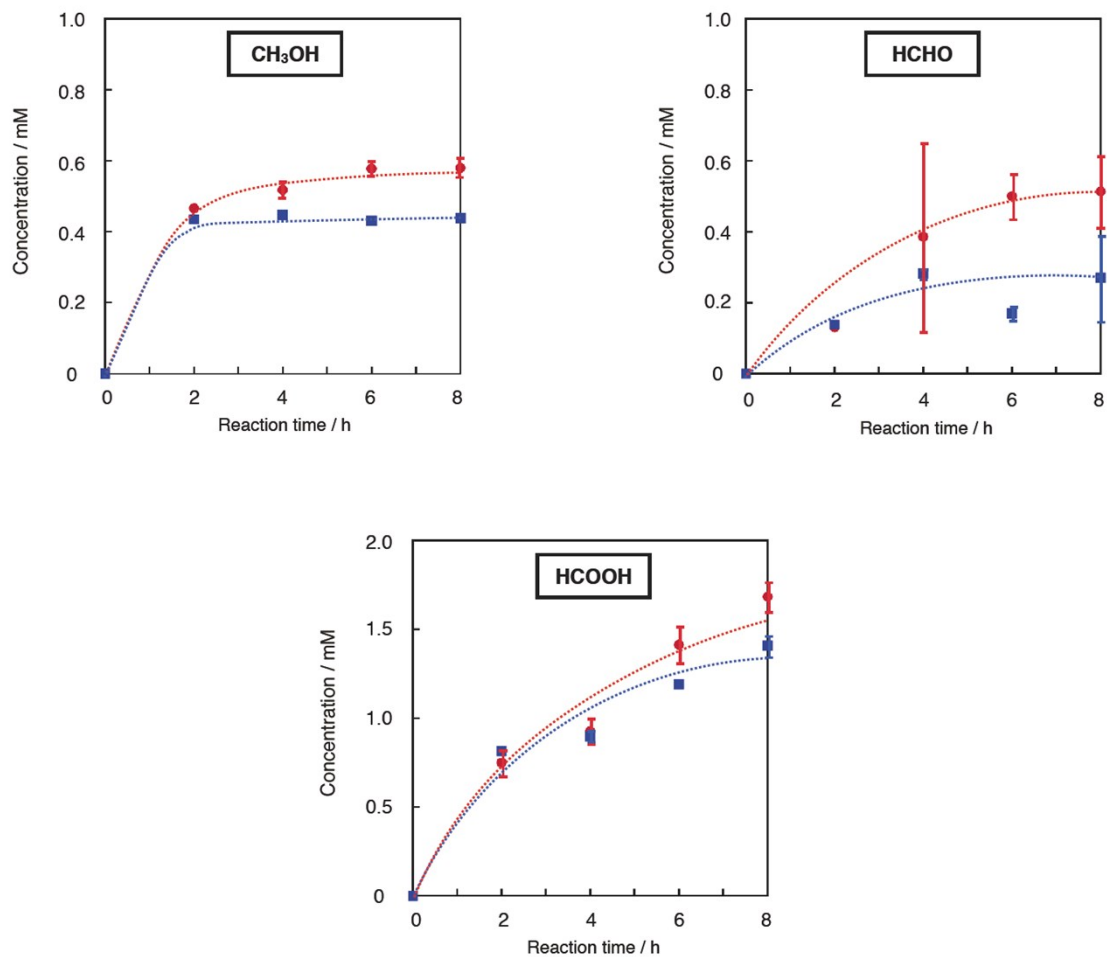


Figure S5. Time dependences of the concentrations of CH₃OH, HCHO, and HCOOH observed in the catalytic reactions using **2**⁺·I-/SiO₂ (red filled circle: under CH₄ atmosphere, blue filled square: under N₂ atmosphere). Error bars represent the S.D. of three independent reactions.

Table S1. Amounts of the oxidized products observed in the reactions under N₂ atmosphere using μ -nitrido-bridged iron phthalocyanine dimer-based catalysts on silica supports.

| Entry | Catalyst | Reaction Time / h | Gas | Additive | [CH ₃ OH] / mM | [HCHO] / mM | [HCOOH] / mM | TTN(N ₂) |
|-------|--|-------------------|--------------------------|---|---------------------------|-------------|--------------|----------------------|
| 1 | 2⁺ -I/SiO ₂ | 2 | N ₂ (1.0 MPa) | ••• | 0.44 | 0.14 | 0.82 | 58 |
| 2 | 2⁺ -I/SiO ₂ | 4 | N ₂ (1.0 MPa) | ••• | 0.45 | 0.28 | 0.90 | 68 |
| 3 | 2⁺ -I/SiO ₂ | 6 | N ₂ (1.0 MPa) | ••• | 0.43 | 0.17 | 1.19 | 79 |
| 4 | 2⁺ -I/SiO ₂ | 8 | N ₂ (1.0 MPa) | ••• | 0.44 | 0.27 | 1.41 | 95 |
| 5 | 2⁺ -I/SiO ₂ | 6 | N ₂ (1.0 MPa) | 100 mM Na ₂ SO ₃ | 0.42 | 0.43 | 1.06 | 81 |
| 6 | 1⁺ -I/SiO ₂ | 4 | N ₂ (1.0 MPa) | ••• | 0.47 | 0.30 | 0.60 | 52 |

All reactions were performed under N₂ (1.0 MPa) in the presence of H₂O₂ (189 mM), and TFA (51 mM) in H₂O (3.0 mL) containing a silica-supported catalyst (55 μ M as **2⁺** or **1⁺**). Concentrations of the oxidized products are the mean values of three different reactions. The TTN_{eff} values were calculated using equations (i) and (ii) in the main text.

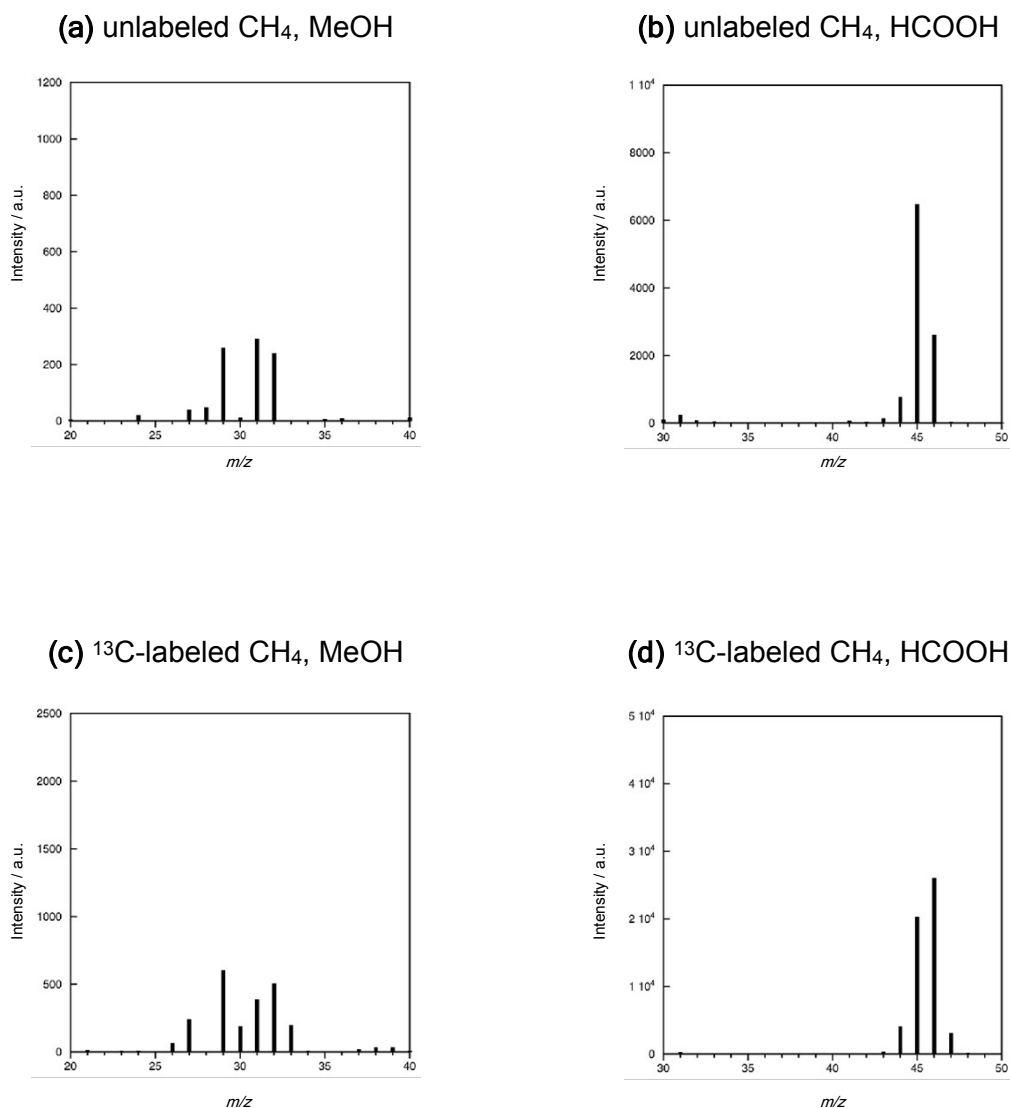


Figure S6. Comparison of Mass spectra of the oxidized products of methane (MeOH and HCOOH) obtained in the reactions of unlabeled CH₄ and ¹³C-labeled CH₄. (a) a Mass spectrum of MeOH obtained in the oxidation reaction of unlabeled CH₄. (b) a Mass spectrum of HCOOH obtained in the oxidation reaction of unlabeled CH₄. (c) a Mass spectrum of MeOH obtained in the oxidation reaction of ¹³C-labeled CH₄. (d) a Mass spectrum of HCOOH obtained in the oxidation reaction of ¹³C-labeled CH₄. Oxidation reactions were performed using the same reaction condition that described in the main text. As for the Mass spectra of HCHO, comparison was difficult because the parent peaks of the derivatized HCHO including formaldehyde's CH₂ were not observed (only the fragments originated from PFBHA moiety were clearly identified).

Reference

- [1] Y. Gao, P. Ma, Y. Chen, Y. Zhang, Y. Bian, X. Li, J. Jiang, C. Ma, *Inorg. Chem.*, **48**, 45–54 (2009).