



Title	One-Step Preparation of Fe/N/C Single-Atom Catalysts Containing Fe-N-4 Sites from an Iron Complex Precursor with 5,6,7,8-Tetraphenyl-1,12-Diazatriphenylene Ligands
Author(s)	Matsumoto, Koki; Kato, Masaru; Yagi, Ichizo et al.
Citation	Chemistry-A European Journal, 28(5), e202103545 https://doi.org/10.1002/chem.202103545
Issue Date	2022-01-24
Doc URL	https://hdl.handle.net/2115/88153
Rights	This is the peer reviewed version of the following article: K. Matsumoto, M. Kato, I. Yagi, S. Xie, K. Asakura, S.-i. Noro, N. Tohnai, S. Campidelli, T. Hayashi, A. Onoda, Chem. Eur. J. 2022, 28(5), e202103545, which has been published in final form at https://doi.org/10.1002/chem.202103545 . This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley's version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited.
Type	journal article
File Information	Matsumoto_2022ChemAJ.pdf



One-step Preparation of Fe/N/C Single-atom Catalysts Containing Fe-N₄ Sites from an Iron Complex Precursor with 5,6,7,8-Tetraphenyl-1,12-diazatriphenylene Ligands

Koki Matsumoto,^[a,c] Masaru Kato,^[b,c] Ichizo Yagi,^[b,c] Siqi Xie,^[c] Kiyotaka Asakura,^[d] Shin-ichiro Noro,^[b,c] Norimitsu Tohnai,^[a] Stéphane Campidelli,^[e] Takashi Hayashi,^{*[a]} and Akira Onoda^{*[b,c]}

- [a] K. Matsumoto, Prof. N. Tohnai, Prof. T. Hayashi
Department of Applied Chemistry,
Graduate School of Engineering, Osaka University,
Suita 565-0871, Japan
E-mail: thayashi@chem.eng.osaka-u.ac.jp
- [b] Prof. A. Onoda, Dr. M. Kato, Prof. I. Yagi, Prof. S. Noro
Faculty of Environmental Earth Science, and Graduate School of Environmental Science,
Hokkaido University,
North 10 West 5, Kita-ku, Sapporo 060-0810, Japan
E-mail: akira.onoda@ees.hokudai.ac.jp, twitter: OnodaLab.Hokudai
- [c] K. Matsumoto, S. Xie
Graduate School of Environmental Science,
Hokkaido University,
North 10 West 5, Kita-ku, Sapporo 060-0810, Japan
- [d] Prof. K. Asakura
Institute for Catalysis,
Hokkaido University,
North 21 West 10, Kita-ku, Sapporo 001-0021, Japan
- [e] Dr. S. Campidelli
Université Paris-Saclay, CEA, CNRS, NIMBE, LICSEN
91191, Gif-sur-Yvette, France

Supporting information for this article is given via a link at the end of the document.

Abstract: Fe/N/C single-atom catalysts containing Fe-N_x sites prepared by pyrolysis are promising cathode materials for fuel cells and metal-air batteries due to their high oxygen reduction reaction (ORR) activities. We have developed iron complexes containing N2- or N3-chelating coordination structures with preorganized aromatic rings in a 1,12-diazatriphenylene framework tethering bromo substituents as precursors to precisely construct Fe-N₄ sites in an Fe/N/C catalyst. One-step pyrolysis of the iron complex with carbon black forms atomically dispersed Fe-N₄ sites without iron aggregates. X-ray absorption spectroscopy (XAS) and electrochemical measurements revealed that the iron complex with N3-coordination is more effectively converted to Fe-N₄ sites catalyzing ORR with a TOF value of 0.21 e-site⁻¹·s⁻¹ at 0.8 V vs RHE. This indicates that the formation of Fe-N₄ sites is controlled by precise tuning of the chemical structure of the iron complex precursor.

Development of platinum-free non-precious metal catalysts for the oxygen reduction reaction (ORR) is required for widespread use of environmentally friendly devices such as fuel cells and metal-air batteries.^[1] M/N/C single-atom catalysts have been investigated in this context. These catalysts contain atomically dispersed 3d-transition metal ion active sites with coordinating nitrogen atoms, M-N_x sites, in carbon materials.^[2] In particular, Fe/N/C catalysts are known to have superior characteristics in catalytic activity, durability, and metal atom utilization.^[3]

The Fe/N/C catalysts with atomically dispersed Fe-N_x sites have been prepared from a variety of precursors by pyrolytic

treatment.^[4] An ideal precursor is thus required to improve the conversion efficiency to construct Fe-N_x sites without forming metal aggregates. Precursors such as iron complexes mixed with support materials^[5] and nitrogen-containing polymers with iron ions^[6] have been reported to be graphitized during pyrolysis in the range of 700 °C–1100 °C, generating thermodynamically stable Fe-N_x sites in graphene layers. Concomitantly, iron atoms are also sintered and aggregated to form iron particles covered with carbon shells, iron oxides, and iron carbides as byproducts.^[7] These unfavorable and less active iron species were therefore removed by an acid washing process under harsh conditions, although this process damages the carbon structure of the catalysts. (Figure 1a).^[8] It has been recently reported that the Fe-N_x sites can be efficiently constructed using an iron co-doped zeolitic imidazolate framework (ZIF-8), which is capable of isolation of iron atoms within a 3D network of ZIF-8 and prevention of aggregation during pyrolysis.^[9] However, other successful examples have been limited.^[10]

We previously reported a method for preparing Fe/N/C catalysts using a polymer precursor with preorganized pyridine and phenyl rings in triphenylene units.^[11] The aromatic rings were then intramolecularly annulated during pyrolysis to construct Fe-N_x sites along the nanographene structure, although iron aggregates were formed to some extent. We thus envisioned the construction of the Fe-N₄ sites in the Fe/N/C catalysts in a highly efficient manner using new iron complex precursors containing 5,6,7,8-tetraphenyl-1,12-diazatriphenylene ligands with bromo

substituents (Figure 1b). In the newly designed ligands, the nitrogen atoms in the aromatic plane can strongly bind to the iron ion. Then, homolytic C–Br bond cleavage at the periphery of the ligands generates radical species, thereby assisting the graphitization of the precursors. In addition, the preorganized aromatic rings assist in formation of the thermodynamically stable nanographene containing hexabenzocoronene structures capable of N2-coordination which protects the iron center under pyrolytic conditions. Therefore, the iron complex precursors were converted to Fe–N₄ sites with perfect suppression of the aggregation of the iron atoms. Herein, we report that the Fe/N/C catalysts containing the Fe–N₄ sites catalyzing ORR can be efficiently prepared from the iron complex precursors with the 5,6,7,8-tetraphenyl-1,12-diazatriphenylene ligands in one-step pyrolysis without requiring an acid washing process.

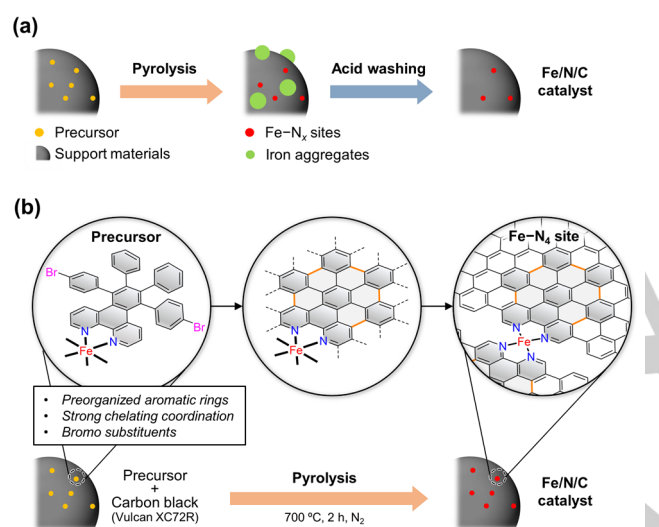


Figure 1. Schematic illustration of the preparation of Fe/N/C catalysts in (a) general methods and (b) our one-step pyrolysis method which does not include an acid washing process.

Firstly, we synthesized the 5,8-di(*p*-bromophenyl)-6,7-diphenyl-1,12-diazatriphenylene derivatives, **L1**, **L2**, and **L3**. (Figure 2a). **L1** and **L2** have an N2- and N3-chelating coordination structure, respectively. **L3**, which includes a phenyl ring at each of the 2 and 11 positions and does not form a stable iron complex, was prepared to verify the importance of strong Fe–N coordination in the precursor. Three ligands, 5,6,7,8-tetraphenyl-1,12-diazatriphenylene (**L4**), 3,8-dibromo-1,10-phenanthroline (**L5**), and 1,10-phenanthroline (**L6**), were used as reference derivatives to evaluate the contribution of preorganized aromatic rings and bromo substituents.

Thermal stabilities of **L1–L6** were determined by thermal decomposition temperatures (T_d) and mass loss values under pyrolysis condition (Figures 2a and S1). In fact, **L1–L4** have T_d values which are greater than those of **L5** and **L6**. Importantly, the mass loss values for **L1–L3** are significantly lower, whereas essentially 100% of the mass of **L4–L6** was decomposed or sublimed. The remaining masses of **L1–L3** were consistent with the mass of diazahexabenzocoronene without substituents. These results indicate that thermally durable nanographene structures are derived from the ligands **L1–L3** during pyrolysis under the assistance of the preorganized aromatic rings and C–C

coupling via the dissociation of the bromo substituents as planned by design.

Next, the iron complexes based on **L1–L6** were synthesized as the precursors. The obtained Fe(II) complexes, [Fe(**L1**)₃]²⁺, [Fe(**L2**)₂]²⁺, [Fe(**L4**)₃]²⁺, [Fe(**L5**)₃]²⁺, and [Fe(**L6**)₃]²⁺, were characterized by UV-vis absorption spectroscopy (Figures S2 and S3). X-ray crystal structures show that they have a typical octahedral geometry (Figures 2b, 2c, and S5).^[12] The ligand **L3**, in which the coordination site is sterically hindered by two adjacent phenyl groups, did not provide the corresponding iron complex (Figure S4).

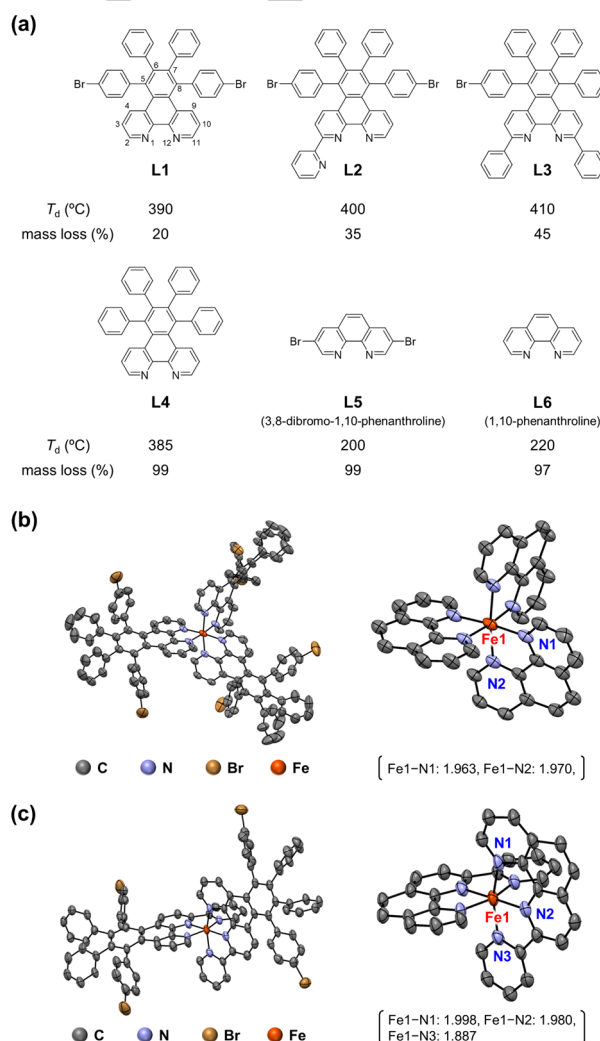


Figure 2. (a) Chemical structures of **L1–L6** ligands used to prepare the iron complex precursors. Thermal decomposition temperatures (T_d) and mass loss values near the decomposition temperature are described below each structure. (b) and (c) X-ray crystal structures of [Fe(**L1**)₃]²⁺ and [Fe(**L2**)₂]²⁺, respectively, with 50% thermal ellipsoid probability (hydrogen atoms, solvents and non-bonding counter anion ClO₄[−] are omitted for clarity.). Enlarged views of the iron complex are shown on the right side.

The Fe/N/C catalysts were prepared from these precursors (see Supporting Information). In brief, the precursor (0.05 mmol) was combined with carbon black (Vulcan® XC72R, VC) (100 mg), and the mixture was pyrolyzed at 700 °C for 2 h. After cooling to room temperature, the Fe/N/C catalysts, Fe/**L1**@VC–Fe/**L6**@VC, were obtained without acid washing treatment. The catalysts have similar carbon morphologies with a similar ratio of I_D/I_G , which was

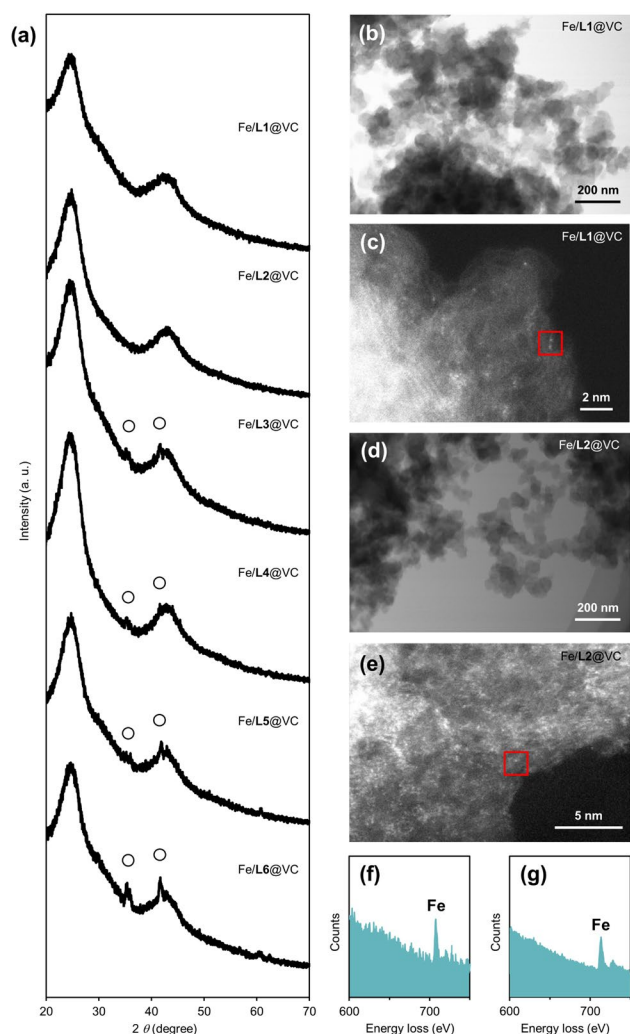


Figure 3. (a) XRD patterns of Fe/L1@VC–Fe/L6@VC. The XRD peaks of iron oxide are highlighted with open circles. (b) BF-STEM, and (c) HAADF-STEM images of Fe/L1@VC. (d) BF-STEM, and (e) HAADF-STEM images of Fe/L2@VC. EELS analysis of (f) Fe/L1@VC and (g) Fe/L2@VC in the HAADF-STEM images in the area highlighted with a red square.

confirmed by Raman measurements (Figure S6). Surprisingly, over 90% of iron atoms in the precursor, determined by ICP-OES, were found to be incorporated in Fe/L1@VC and Fe/L2@VC, while the 30–50% of iron atoms were lost in Fe/L3@VC–Fe/L6@VC after the pyrolysis. This result indicates that L1 and L2 suppress gasification of the catalyst precursor under pyrolytic conditions (Table S2). In addition, Fe/L1@VC and Fe/L2@VC have larger BET surface areas (328 m²·g^{−1} and 304 m²·g^{−1}, respectively) than the other catalysts (Table S3).

Importantly, X-ray diffraction (XRD) analysis reveals that the iron aggregates were not generated in Fe/L1@VC and Fe/L2@VC (Figure 3a), while broad peaks originating from amorphous carbon are observed.^[13] In contrast, sharp peaks at 35.5° and 42.6°, attributed to iron oxide, are observed with the broad peaks in Fe/L3@VC–Fe/L6@VC.^[14] Bright field scanning transition electron microscopy (BF-STEM) images support the absence of the iron aggregates in Fe/L1@VC and Fe/L2@VC (Figures 3b and 3d), whereas the iron aggregates exist in Fe/L3@VC–Fe/L6@VC (Figure S7). These findings are clearly supported by EDX mapping analysis (Figure S8). In addition,

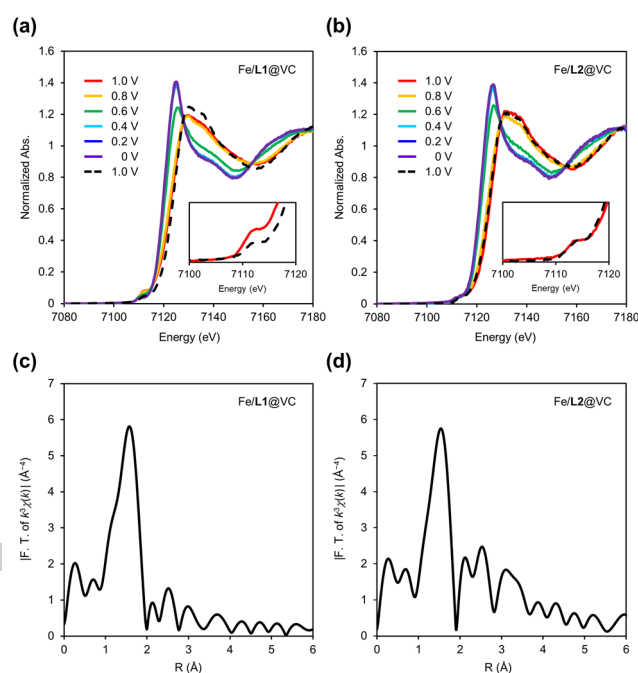


Figure 4. Potential-dependent Fe K-edge XANES spectra of (a) Fe/L1@VC and (b) Fe/L2@VC recorded in 0.1 M HClO₄ solution at 1.0 V (red line), 0.8 V (orange line), 0.6 V (green line), 0.4 V (light blue line), 0.2 V (blue line), and 0 V (purple line) vs RHE under N₂ atmosphere. The XANES spectra at 1.0 V vs RHE after sweeping voltage from 1.0 V to 0 V are shown in black dotted lines. The reduction potentials are 0.63 V vs RHE in Fe/L1@VC and 0.66 V vs RHE in Fe/L2@VC determined by linear combination fitting analysis. FT-EXAFS spectra of (c) Fe/L1@VC and (d) Fe/L2@VC at 1.0 V vs RHE.

atomical dispersion of iron atoms in Fe/L1@VC and Fe/L2@VC was confirmed by high-angle annular dark field STEM (HAADF-STEM) observations (Figures 3c and 3e) and electron energy loss spectroscopy (EELS) (Figures 3f and 3g). Taken together, [Fe(L1)₃]²⁺ and [Fe(L2)₂]²⁺ as precursors provide atomically dispersed iron atoms in the catalysts by one-step pyrolysis.

The iron atoms were found to be coordinated by nitrogen atoms in Fe/L1@VC and Fe/L2@VC by X-ray photoelectron spectroscopy (XPS) (Figure S9). The content of the nitrogen atoms in the Fe–N_x sites (Fe–N species) were calculated from the results of XPS and elemental analysis (Tables S2, S4 and S5). Fe/L1@VC (0.40 wt%) and Fe/L2@VC (0.63 wt%) have greater amounts of Fe–N species derived from nitrogen coordinating to iron atom, relative to Fe/L3@VC–Fe/L6@VC.^[15] Greater quantities of the Fe–N species in Fe/L2@VC are expected to originate from N3-chelating coordination structures in the [Fe(L2)₂]²⁺ precursor.

Encouraged by the evidence of the atomical dispersion of iron atoms in Fe/L1@VC and Fe/L2@VC, we set out to fully characterize the electronic states and environments around the Fe–N_x sites by *in-situ* electrochemical Fe K edge X-ray absorption spectroscopy (XAS) (Figures 4, S10 and S11). X-ray absorption near edge structure (XANES) profiles of Fe³⁺ species in Fe/N/C-type catalyst were observed at 1.0 V vs RHE (Figures 4a, 4b and S10).^[6b, 16] When the potential is decreased from 1.0 V to 0 V, the spectrum changes with isosbestic points and the absorption edge shifts to lower energy, suggesting a transition of the oxidation state from Fe³⁺ to Fe²⁺. It was also confirmed that the original XANES spectrum can be regenerated if a potential of 1.0 V is

applied again in Fe/L2@VC. This means that the iron active sites have a reversible $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple. Although the XANES spectrum of Fe/L1@VC at 1.0 V has pre-edge peak at about 7113 eV, the spectrum converts to match that of Fe/L2@VC when a potential of 1.0 V is applied again after reduction and oxidation in Fe/L1@VC.

The structures of the iron active sites in Fe/L1@VC and Fe/L2@VC were then analyzed by Fourier transform of extended X-ray absorption fine structure (FT-EXAFS) with the applied potential of 1.0 V (Figures 4c and 4d). Only one peak was observed in the R range between 1.0–2.0 Å corresponding to the first coordination sphere. The curve fitting analysis reveals that the coordination numbers of Fe–N are 4.3 ± 0.3 (Fe/L1@VC) and 4.1 ± 0.6 (Fe/L2@VC), and Fe–N bond lengths are 1.99 ± 0.02 Å (Fe/L1@VC) and 1.97 ± 0.02 Å (Fe/L2@VC) (Table S6). We thus concluded that the atomically dispersed active sites in Fe/L1@VC and Fe/L2@VC have an Fe–N₄ structure.

The ORR activities of the Fe/N/C catalysts containing the Fe–N₄ sites were determined by rotating ring-disk electrode (RRDE) measurements (Figure 5). Fe/L1@VC shows high catalytic activity with an onset potential of 0.90 V vs RHE. The onset potential of Fe/L2@VC is more positively shifted (0.93 V vs RHE). In contrast, Fe/L3@VC exhibits much lower ORR activity (0.69 V vs RHE), supporting the expectation that the precursor consisting of the stable iron–ligand complex is essential for producing the single-atom catalyst. Fe/L5@VC (0.82 V vs RHE) shows lower activity than Fe/L1@VC, because the diazatriphenylene framework will be better for the graphitization compared to phenanthroline. Moreover, Fe/L4@VC (0.86 V vs RHE) and Fe/L6@VC (0.79 V vs RHE) are less active than Fe/L1@VC and Fe/L5@VC. This suggests that the bromo substituents on the ligand frameworks induce controllable

polymerization. In addition, Fe/L2@VC shows the highest turnover frequency (TOF) at 0.8 V vs RHE with $0.21 \text{ e}^- \cdot \text{site}^{-1} \cdot \text{s}^{-1}$. This performance is better than that of Fe/L1@VC with $0.17 \text{ e}^- \cdot \text{site}^{-1} \cdot \text{s}^{-1}$ (Table S7). Fe/L2@VC further provides lower hydrogen peroxide yields of less than 5% in the range from 0 V to 0.8 V vs RHE relative to the other catalysts. Notably, these ORR activities are clearly correlated with the amounts of Fe–N species (Table S5) and the value of mass site density (MSD) of redox active iron species determined by cyclic voltammetry (Table S7).

In conclusion, the Fe/N/C single-atom catalysts prepared by one-step pyrolysis of the iron complexes are developed from the thermally durable 5,6,7,8-tetraphenyl-1,12-diazatriphenylene ligands L1 or L2, which have N2- or N3-chelating coordination, respectively, and preorganized aromatic rings with bromo substituents. The design of the ligand for the iron complex precursor is a key aspect for providing controlled graphitization of the precursor and constructing atomically dispersed Fe–N₄ sites. In particular, $[\text{Fe}(\text{L2})_2]^{2+}$ is more efficiently converted to a Fe–N₄ site than $[\text{Fe}(\text{L1})_3]^{2+}$. This indicates the significance of N3-coordination provided by the 5,6,7,8-tetraphenyl-1,12-diazatriphenylene ligand with an additional pyridine moiety for constructing the Fe–N₄ sites. Consequently, Fe/L2@VC contains a high quantity of Fe–N₄ sites and has high catalytic activity for ORR with positive-shifted onset potentials of 0.93 V vs RHE and a TOF value of $0.21 \text{ e}^- \cdot \text{site}^{-1} \cdot \text{s}^{-1}$. This work provides an attractive strategy for constructing atomically-defined metal active sites in a graphene layer by one-step pyrolysis, paving the way for the construction of on-demand metal active sites on the surface of carbon materials and other heterogeneous catalysts.

Experimental Section

Experimental procedures for the synthesis of precursors, X-ray crystallographic analysis, preparation of the Fe/N/C catalysts, characterizations, electrochemical measurements are described in the Supporting Information. Deposition numbers 2124179 (for $[\text{Fe}(\text{L1})_3]^{2+}$), 2124178 (for $[\text{Fe}(\text{L2})_2]^{2+}$), and 2124180 (for $[\text{Fe}(\text{L4})_3]^{2+}$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Numbers 25708031, JP15H03857, JP15H05804, and JP19K22202, JP19H04579, and the Iketani Science and Technology Foundation. K.M. acknowledges support from a Research Fellowship of JSPS. We acknowledge Prof. Nobuhito Imanaka and Dr. Shinji Tamura (Department of Applied Chemistry, Graduate School of Engineering, Osaka University) for Raman measurements, and Ms. Naomi Hirai (Research Institute for Electronic Science, Hokkaido University) for STEM-EELS analysis. XAS experiments were performed at the beamline BL12C in Photon Factory (Proposal No. 2021G083).

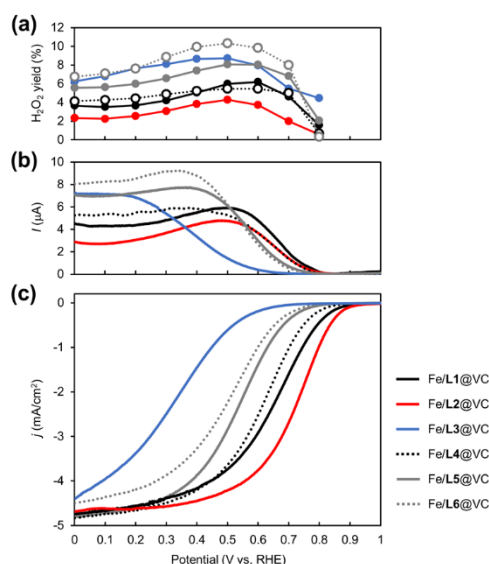
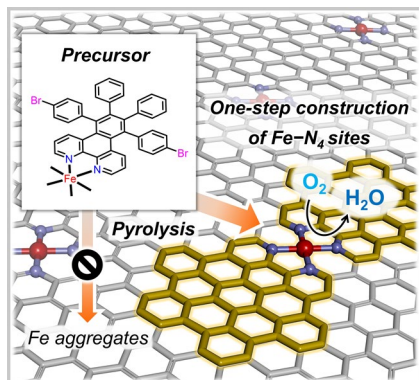


Figure 5. (a) H_2O_2 yield and (b) ring and (c) disk currents of Fe/N/C catalysts; Fe/L1@VC (black line), Fe/L2@VC (red line), Fe/L3@VC (blue line), Fe/L4@VC (black dotted line), Fe/L5@VC (gray line), Fe/L6@VC (gray dotted line). The linear sweep voltammograms were recorded during positive sweep with $5 \text{ mV} \cdot \text{s}^{-1}$ at 2000 rpm in an O_2 saturated $0.1 \text{ M HClO}_{4\text{aq}}$ solution. Catalyst loading: $0.41 \text{ mg}_{\text{cat}} \cdot \text{cm}^{-2}$. The onset potentials were determined for $j = -0.05 \text{ mA} \cdot \text{cm}^{-2}$. The electrocatalytic performance of commercially available Pt/C catalyst was evaluated by performing rotating disk electrode (RDE) measurements (Figure S12). The long-term durabilities of Fe/L1@VC and Fe/L2@VC were tested by the RDE measurements (Figure S13).

Keywords: Oxygen Reduction Reaction (ORR) • Fe/N/C single-atom catalyst • One-step preparation • Iron-diazatriphenylene complex • Fe–N₄ sites

- [1] a) S. Zaman, L. Huang, A. I. Douka, H. Yang, B. You, B. Y. Xia, *Angew. Chem. Int. Ed.* **2021**, *60*, 17832–17852; b) X. Zhao, L. Shao, Z. Wang, H. Chen, H. Yang, L. Zeng, *J. Mater. Chem. C* **2021**, *9*, 11252–11260.
- [2] a) C.-X. Zhao, B.-Q. Li, J.-N. Liu, Q. Zhang, *Angew. Chem. Int. Ed.* **2021**, *60*, 4448–4463; b) S. K. Kaiser, Z. Chen, D. F. Akl, S. Mitchell, J. Pérez-Ramírez, *Chem. Rev.* **2020**, *120*, 11703–11809.
- [3] a) M. Moriya, R. Takahama, K. Kamoi, J. Ohyama, S. Kawashima, R. Kojima, M. Okada, T. Hayakawa, Y. Nabae, *J. Phys. Chem. C* **2020**, *124*, 20730–20735; b) T. Marshall-Roth, N. J. Libretto, A. T. Wrobel, K. J. Anderton, M. L. Pegis, N. D. Ricke, T. V. Voorhis, J. T. Miller, Y. Surendranath, *Nat. Commun.* **2020**, *11*, 5283; c) U. Martinez, S. Komini Babu, E. F. Holby, H. T. Chung, X. Yin, P. Zelenay, *Adv. Mater.* **2019**, *31*, 1806545; d) A. Li, S. A. Nicolae, M. Qiao, K. Preuss, P. A. Szilágyi, A. Moores, M.-M. Titirici, *ChemCatChem* **2019**, *11*, 3602–3625.
- [4] a) H. Fei, J. Dong, D. Chen, T. Hu, X. Duan, I. Shakir, Y. Huang, X. Duan, *Chem. Soc. Rev.* **2019**, *48*, 5207–5241; b) R. Jasinski, *Nature* **1964**, *201*, 1212–1213.
- [5] a) Z. Chen, D. Higgins, A. Yu, L. Zhang, J. Zhang, *Energy Environ. Sci.* **2011**, *4*, 3167–3192; b) M. Kato, N. Fujibayashi, D. Abé, N. Matsubara, S. Yasuda, I. Yagi, *ACS Catal.* **2021**, *11*, 2356–2365; c) M. Lefèvre, E. Proietti, F. Jaouen, J.-P. Dodelet, *Science* **2009**, *324*, 71–74.
- [6] a) R. Bashyam, P. Zelenay, *Nature* **2006**, *443*, 63–66; b) M. Ferrandon, X. Wang, A. J. Kropf, D. J. Myers, G. Wu, C. M. Johnston, P. Zelenay, *Electrochim. Acta* **2013**, *110*, 282–291; c) G. Wu, K. L. More, C. M. Johnston, P. Zelenay, *Science* **2011**, *332*, 443–447.
- [7] a) A. L. Bouwkamp-Wijnoltz, W. Visscher, J. A. R. van Veen, E. Boellaard, A. M. van der Kraan, S. C. Tang, *J. Phys. Chem. B* **2002**, *106*, 12993–13001; b) U. I. Kramm, I. Herrmann-Geppert, J. Behrends, K. Lips, S. Fiechter, P. Bogdanoff, *J. Am. Chem. Soc.* **2016**, *138*, 635–640.
- [8] a) M.-X. Chen, M. Zhu, M. Zuo, S.-Q. Chu, J. Zhang, Y. Wu, H.-W. Liang, X. Feng, *Angew. Chem. Int. Ed.* **2020**, *59*, 1627–1633; b) W. Yang, T.-P. Feller, M. Antonietti, *J. Am. Chem. Soc.* **2011**, *133*, 206–209.
- [9] a) H. Zhang, H. T. Chung, D. A. Cullen, S. Wagner, U. I. Kramm, K. L. More, P. Zelenay, G. Wu, *Energy Environ. Sci.* **2019**, *12*, 2548–2558; b) C. H. Choi, C. Baldizzone, G. Polymeros, E. Pizzutillo, O. Kasian, A. K. Schuppert, N. Ranjbar Sahraie, M.-T. Sougrati, K. J. J. Mayrhofer, F. Jaouen, *ACS Catal.* **2016**, *6*, 3136–3146.
- [10] X. F. Lu, B. Y. Xia, S.-Q. Zang, X. W. Lou, *Angew. Chem. Int. Ed.* **2020**, *59*, 4634–4650.
- [11] K. Matsumoto, A. Onoda, T. Kitano, T. Sakata, H. Yasuda, S. Campidelli, T. Hayashi, *ACS Appl. Mater. Interfaces* **2021**, *13*, 15101–15112.
- [12] H. Petzold, P. Djomgoue, G. Hörner, S. Heider, C. Lochenie, B. Weber, T. Rüffer, D. Schaarschmidt, *Dalton Trans.* **2017**, *46*, 6218–6229.
- [13] J. Maruyama, I. Abe, *Chem. Mater.* **2006**, *18*, 1303–1311.
- [14] Z. Tian, C. Wang, Z. Si, L. Ma, L. Chen, Q. Liu, Q. Zhang, H. Huang, *Appl. Catal. A: Gen.* **2017**, *541*, 50–59.
- [15] L. Zhou, C. Yang, J. Wen, P. Fu, Y. Zhang, J. Sun, H. Wang, Y. Yuan, *J. Mater. Chem. A* **2017**, *5*, 19343–19350.
- [16] a) M. Ferrandon, A. J. Kropf, D. J. Myers, K. Artyushkova, U. Kramm, P. Bogdanoff, G. Wu, C. M. Johnston, P. Zelenay, *J. Phys. Chem. C* **2012**, *116*, 16001–16013; b) J. Li, M. T. Sougrati, A. Zitolo, J. M. Ablett, I. C. Oğuz, T. Mineva, I. Matanovic, P. Atanassov, Y. Huang, I. Zenyuk, A. Di Cicco, K. Kumar, L. Dubau, F. Maillard, G. Dražić, F. Jaouen, *Nat. Catal.* **2021**, *4*, 10–19.

Entry for the Table of Contents



Fe/N/C single-atom catalysts are prepared from iron complex precursors containing 5,6,7,8-tetraphenyl-1,12-diazatriphenylene ligands with two bromo substituents by one-step pyrolysis. The iron complex precursors were efficiently converted to atomically dispersed Fe-N₄ active sites without generating less active iron aggregates during pyrolysis. The Fe-N₄ active sites were identified by STEM-EELS observations and *in-situ* electrochemical Fe K edge X-ray absorption spectroscopic measurements. The Fe/N/C catalysts show high catalytic activity toward oxygen reduction reaction.