### Supporting Information

# Pyrolysis-free Oxygen Reduction Reaction (ORR) Electrocatalysts Composed of Unimolecular Layer Metal Azaphthalocyanines Adsorbed onto Carbon Materials

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## Appendix

Supporting information, S1. Synthesis of metal AzPc-4N molecules	S-2
Supporting information, S2. MALDI-TOF-MS measurement of catalytic molecules	S-4
Supporting information, S3. TGA curves of catalysts	S-5
Supporting information, S4. EDS spectra of catalysts	S-6
Supporting information, S5. UPS measurement of catalytic molecules and catalysts	S-7
Supporting information, S6. UV-Vis spectra of catalyst molecules	S-8
Supporting information, S7. LSV curve of GC	S-9

#### Supporting information, S1. Synthesis of metal AzPc-4N molecules

#### Synthesis of FeAzPc-4N-iso

29H,31H-Tetrapyrido[3,4-b:3',4'-g:3",4"-l:3"',4"'-q]porphyrazine, iron complex (CAS Registry Number: 87321-02-6)



Scheme S1. Synthetic route of FeAzPc-4N-iso.

4.9 g (29.3 mmol) of 3,4-pyridinedicarboxylic acid, 13.6 g of urea and 260 mg of ammonium molybdate tetrahydrate were mixed in a three-neck glass bottle at 160 °C for 30 min with stirring. 4.0 g of iron (III) chloride hexahydrate and 8.0 g of urea was added into the mixture and then heated at 210 °C with stirring. After 2 hours, 60 mL of N-methylpyrrodlidone was added into the mixture and the mixture was stirred at 210 °C for 1 hour. After cooling to 80 °C, 100 mL of methanol and 150 mL of water was added into the solution. The precipitates were filtered and washed with water, methanol and acetone. The corrected precipitates were dried under vacuum. The final yielded amount was 3.0 g.

#### Synthesis of NiAzPc-4N

29H,31H-Tetrapyrido[2,3-b:2',3'-g:2",3"-l:2"',3"'-q]porphyrazine, nickel complex

(CAS Registry Number: 23272-68-6)



Scheme S2. Synthetic route of NiAzPc-4N.

5.0 g (30 mmol) of 2,3-pyridinedicarboxylic acid, 1.96 g of nickel (II) acetate tetrahydrate, 7.2 g of urea and 90 mg of ammonium molybdate tetrahydrate were mixed in a three-neck glass bottle at 190 °C for 1 hour with stirring. 30 mL of N-methylpyrrodlidone was added into the mixture and the mixture was stirred at 190 °C for 1.5 hour. After cooling to 90 °C, 70 mL of methanol and 70 mL of water was added into the solution. The precipitates were filtered and washed with water and methanol. The corrected precipitates were dried under vacuum. The final yielded amount was 2.2 g.

#### Synthesis of CuAzPc-4N

29H,31H-Tetrapyrido[2,3-b:2',3'-g:2",3"-l:2"',3"'-q]porphyrazine, copper complex

(CAS Registry Number: 1964496-05-6)



Scheme S3. Synthetic route of CuAzPc-4N.

5.0 g (30 mmol) of 2,3-pyridinedicarboxylic acid, 1.30 g of copper (II) chloride dihydrate, 7.2 g of urea and 90 mg of ammonium molybdate tetrahydrate were mixed in a three-neck glass bottle at 200 °C for 30 min with stirring. 10 mL of N-methylpyrrodlidone was added into the mixture and the mixture was stirred at 190 °C for 1.5 hour. After cooling to room temperature, 80 mL of methanol and 100 mL of water was added into the solution. The precipitates were filtered and washed with water and methanol. The corrected precipitates were dried under vacuum. The final yielded amount was 2.3 g.

# Supporting information, S2. MALDI-TOF-MS measurement of catalytic molecules

Matrix assisted laser deposition / ionization time of flight mass spectroscopy (MALDI-TOF-MS) measurement of catalytic molecules were performed by using REFLEXIII, Bruker Daltonics with using alpha-Cyano-4-hydroxycinnamic acid (CHCA) as a matrix.



Figure S1. MALDI-TOF-MS spectra of catalyst molecules used in the experiment.

# Supporting information, S3. TGA curves of catalysts

Thermogravimetric analysis (TGA) curves of catalysts were performed by DSC404F3-ST Pegasus, Netzsch, Co. Ltd. with  $N_2$  gas flow.



Figure S2. TGA curves of prepared catalysts.



Supporting information, S4. EDS spectra of catalysts

Figure S3. EDS spectra obtained from catalysts measured by STEM-EDS measurements. Signals of center metals of respective catalysts (Fe (a)-(c), Ni (d) and Cu (e)) were clearly observed.

## Supporting information, S5. UPS measurement of catalytic molecules and catalysts

Ultraviolet photoelectron spectroscopy (UPS) of KB, catalyst molecules and catalysts were performed by using AC-2, RIKEN Keiki, Co. Ltd. to evaluate working potential, which corresponds to the ionization potential of the material. Irradiation power, measurement time, and anode potential were 50.0 nW, 20 sec, and 2990 V, respectively. The ionization potential was measured ranging from 4.0 eV to 7.0 eV with 0.10 eV step. The ionization potential was estimated by the intersection of the baseline and the tangent to the spectrum.



Figure S4. UPS spectra of KB (a), catalyst molecules (b)-(f) and catalysts (g)-(k), respectively.

# Supporting information, S6. UV-Vis spectra of catalyst molecules

Ultraviolet-visible (UV-Vis) spectra of catalyst molecule solutions in DMSO were measured by V-570, Jasco, Co. Ltd.



Figure S5. UV-Vis spectra of catalyst molecule solution. (a) FeAzPc-4N, (b) FeAzPc-4N-iso, (c) FePc, (d) NiAzPc-4N, (e)CuAzPc-4N.

Supporting information, S7. LSV curve of GC



Figure S6. LSV curve of GC only.