Electronic Supplementary Information

Fuel from Waste: Electrosynthesizing Ammonia Directly from Agricultural Digestate through Ligand Isomerization

Rahul Mahadeo Mendhe, Ritwik Mondal, Alagar Raja Kottaichamy, Akshay Haridas, Harish Makri Nimbegondi Kotresh, Chathakudath Prabhakaran Vinod, Ravikumar Thimmappa, Musthafa Ottakam Thotiyl*

*Department of Chemistry and Centre for Energy Science, Indian Institute of Science Education and Research, Pune, Dr. Homi Bhabha Road, Pune, 411008, India.

Department of Chemistry, Acharya Institute of Technology, Bangalore 560107, India.

Catalysis and Inorganic Chemistry Division, CSIR-NCL, Pune 411008, India.

Department of Chemistry, Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva 8410501, Israel

*Correspondence: musthafa@iiserpune.ac.in

Electronic Supplementary Material (ESI) for Green Chemistry. This journal is © The Royal Society of Chemistry 2024.
1. Materials and Methods

1.1 Chemicals:

The chemicals such as N, N-dimethylformamide (DMF) (99%), hexane (95%), isopropyl alcohol (99%), nickel (II) chloride hexahydrate (≥98%), ammonium molybdate (99.99%), 4-nitrophthalimide (98%), 3-nitrophthalimide (98%), sodium sulfide nonahydrate (≥98%), ammonium chloride (≥98%), methanol (99%), sulfuric acid (96%), and nitrobenzene (99%) were purchased from Alfa Aesar, India. Dimethyl sulfoxide-d6 (DMSO-d6) (99.9 atom % D), hydrochloric acid (37.0%), carbon nanotubes (CNT), and Nafion solutions (5 wt%) were obtained from Sigma Aldrich, India.

1.2 Synthesis:

1.2.1 Synthesis of 1,8,15,22-tetranitronickel phthalocyanine (α-TNNiPc) and 2,9,16,23-tetranitronickel phthalocyanine (β-TNNiPc):

The synthesis of 1,8,15,22-tetranitronickel phthalocyanine (α-TNNiPc) and 2,9,16,23-tetranitronickel phthalocyanine (β-TNNiPc) was carried out according to the procedures described in the literature previously.\textsuperscript{1-5} In a 250 ml round-bottomed flask, a finely ground mixture of 3-nitrophthalimide/4-nitrophthalimide (3.86 gm), urea (6.0 gm), ammonium molybdate (0.05 gm), ammonium chloride (0.5 gm), and 30 mL of nitrobenzene were added slowly with continuous stirring. Afterwards, the reaction mixture was stirred for 10 minutes to achieve homogeneity, followed by the addition of nickel (II) chloride as the metal salt (1.2 gm). Subsequently, vigorous stirring was carried out at 100 °C for approximately 30 minutes. The temperature was then increased at a rate of 10 °C/30 minutes to 180 °C, and the reaction mixture was refluxed at this temperature for about 4 hours. Afterwards, the mixture was
diluted with toluene (50 mL), and the resulting precipitate was filtered and thoroughly washed with hot water and methanol. Additional washing with hexane was performed, and the precipitate was finally dried in an oven at 80 °C.

1.2.2. Synthesis of 1,8,15,22-tetraaminonickel phthalocyanine (α-TANiPc) / 2,9,16,23-tetraaminonickel phthalocyanine (β-TANiPc)

In a 250 ml round-bottomed flask, 0.75 g of 1,8,15,22-tetranitronickel phthalocyanine (α-TNNiPc)/2,9,16,23-tetranitronickel phthalocyanine (β-TNNiPc), 3.0 gm of sodium sulfide nonahydrate, and 30 mL of N, N-dimethylformamide were added. The reaction mixture was heated to 80 °C for about 2 hours with constant stirring. It was then cooled to room temperature and diluted with ice water (200 mL). The resulting precipitate was filtered off and washed thoroughly with hot water, followed by methanol and finally with hexane. The obtained precipitate was dried in a vacuum oven at 65°C, resulting in the formation of 1,8,15,22-tetraaminonickel phthalocyanine (α-TANiPc)/2,9,16,23-tetraaminonickel phthalocyanine (β-TANiPc).6,7

1.2.3. Synthesis of NiPc, α-TANiPc and β-TANiPc incorporated over CNT:

NiPc, α-TANiPc and β-TANiPc were mixed separately with carbon nanotubes (CNT) in a stoichiometric ratio of 3:7 (w/w) in DMF. Then, the mixture was sonicated for 30 minutes. After sonication, the suspension was stirred at 80°C for 24 hours. The resulting mixture was subjected to centrifugation to obtain the final precipitate, which was carefully washed with DMF and subsequently with ethanol. To obtain the final composite, the washed precipitate was dried overnight in the vacuum oven at 65°C.8-10

1.3. Methodologies:
1.3.1. Characterization:

A comprehensive set of characterization techniques were employed to analyze NiPc, α-TANiPc and β-TANiPc. UV-visible measurements were conducted using a Perkin Elmer Lambda 950 instrument in a quartz cuvette, providing detailed information about the absorption and electronic transitions of the compounds. To further investigate the molecular structure, FTIR spectra of NiPc, α-TANiPc and β-TANiPc were collected using a Bruker Alpha ATR-FTIR. Raman spectra, which provide insight into the vibrational modes of the compounds, were recorded using a Raman microscope (LabRAM HR, Horiba Jobin Yvon). Scanning electron microscopy and energy dispersive X-ray spectroscopy were performed using a Zeiss Ultraplus-4095 instrument, allowing high-resolution imaging and elemental analysis. Nuclear magnetic resonance (NMR) spectra of NiPc, α-TANiPc and β-TANiPc were obtained using a Bruker 400 MHz spectrometer, revealing valuable information about the chemical environments and interactions in the molecules. Transmission electron microscopy (TEM) was performed using a Jeol JEM-2200FS instrument, enabling the visualization of the samples at the nanoscale. X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Scientific Kalpha+ spectrometer, with a monochromated Al Kα (1486.6 eV) X-ray source having a power of 72 W. A 180° double focusing hemispherical analyzer was employed for XPS analysis along with a 128-channel detector for electron energy analysis. An ultra-low energy co-axial electron beam and Ar⁺ ion beam were used for charge compensation, and the charge compensation gun was activated during spectral acquisition. The spectra were referenced for charge accumulation with a C1s standard value at 284.6 eV. A base pressure of better than approximately 5x10⁻⁹ mbar (gun vacuum) and 1x10⁻⁷ mbar (system vacuum) was maintained during data acquisition with the flood gun on. The individual core levels were analyzed at 50 eV, and a survey scan was conducted at 200 eV pass energy. Peak fitting of the N1s spectra was performed using
CasaXPS software, utilizing a smart background algorithm to enhance accuracy and reliability. Zeta potential measurements were conducted using the Zetasizer Nano ZS90 Analyser (Malvern) instrument.

1.3.2. Electrochemical Measurements:

The electrochemical experiments were conducted using a Biologic VMP 300 potentiostat. For the electrochemical measurements, a double-jacketed three-electrode cell with a 10 ml volume was utilized. The working electrode was a 3 mm diameter glassy carbon disk electrode (0.071 cm²), while a platinum disc electrode was used as the counter electrode, and an Ag/AgCl (sat. KCl) electrode was used as the reference electrode. To ensure consistency, all potentials were converted to the reversible hydrogen scale (RHE scale) by referencing the redox potentials of hydrogen redox reactions in the respective electrolytes using a Pt disc working electrode. Millipore water (18.2 MΩ.cm) was used to prepare all solutions. The electrolyte for product analysis having 1.75 mg/mL of NO₃⁻ concentration for all applied potential analysis. The electrode surface was polished using 0.05 μM alumina powder to ensure cleanliness. Prior to each measurement, the electrode underwent electrochemical cycling in the respective electrolytes to clean the surface. Impedance measurements were performed in the 100 kHz to 1 mHz frequency range with an AC amplitude of 10 mV (peak to peak) in Ar saturated solutions. The composite electrode (NiPc@CNT, α-TANiPc@CNT and β-TANiPc@CNT) modified glassy carbon electrodes were prepared using drop-casting. A homogeneous dispersion was created by sonicating a known amount of catalysts (NiPc@CNT, α-TANiPc@CNT and β-TANiPc@CNT) in isopropyl alcohol (IPA) with 5 wt% PVDF as the binder, resulting in a composite ink. This ink was then drop casted on a glassy carbon electrode.
Agricultural waste water recycling was performed in a three electrode two compartment cell (Fig. 5a, main manuscript) with the β-TANiPc@CNT (2.5 mg cm$^{-2}$) drop-casted over Toray carbon sheet (area = 4 cm$^2$) as the electrocatalyst for NO$_3$RR. A large area Pt foil (~7 cm$^2$) as the counter electrode. The reference and working electrodes were housed in the same compartment. The two half cells were separated by Nafion 117 membrane. The electrolyte of agricultural waste water collected from Bhandara, Maharashtra, India was continuously pumped into the device at a flow rate of 20 mL min$^{-1}$ from a two-litre reservoir for almost 100 hours. Before and after electrolysis, nitrate concentration was monitored by UV-visible spectroscopy. Before and after electrolysis, ammonia concentration was monitored by UV-visible spectroscopy and NMR spectroscopy. The potentials are converted to RHE scale by experimentally calibrating the potential with respect to hydrogen redox at that pH.

1.2.3.1 In-situ electrochemical mass spectrometry

In-situ electrochemical mass spectrometry were performed using a HPR-40 quadrupole mass analyser from Hiden Analytical, employing a standard QIC inlet. The setup involved a 'T' shaped connector with the mass spectrometer inlet, cell outlet, and an exhaust to the surroundings. Argon (Ar) was employed as the carrier gas for the cathodic half-cell experiments.

1.3.2.1 Self-assembled monolayer deposition over glassy carbon electrode

Monolayer assembly of α-TANiPc and β-TANiPc and unsubstituted NiPc molecules were achieved by the self-assembly process. 2 mg/mL NiPc, α-TANiPc and β-TANiPc solutions were prepared in dimethyl formamide (DMF) by ultrasonication. GC electrodes were first polished by alumina polishing powder and then cleaned electrochemically. The polished GC electrode electrochemically cleaned between the potential 0 V to 1.1 V vs Ag/AgCl (Sat. KCl).
The electrodes were washed with distilled water and finally with DMF. These electrodes were then incubated in $\alpha$-TANiPc and $\beta$-TANiPc solution for 24 hours without disturbing it. The modified electrodes were washed with fresh DMF to remove physiosorbed molecules and finally washed with distilled water.

The Sauerbrey equation was then used to find the mass of adsorbed molecules on the crystal by correlating the frequency shift ($\Delta f$) to mass change ($\Delta m$) (equation 1).

$$\Delta m = - C (\Delta f/n) \ldots \text{ (equation S1)}$$

where, $\Delta f$ is the net resonance frequency shift due to adsorption of molecules and $n$ is the overtone number (QCM analysis were measured at the third overtone ($n=3$)). The sensitivity ($C$) of the QCM crystal was 5.608 ng cm$^{-2}$ Hz$^{-1}$.

The surface coverage ($\Gamma$, mol cm$^{-2}$) was calculated using equation 2,$^{11}$

$$\Gamma = \frac{\Delta m}{\text{Molecular mass}} \ldots \text{ (equation S2)}$$

1.3.3. Determination of ion concentration:

To determine the ion concentration of $\text{NO}_2^-$ and $\text{NO}_3^-$ in the electrolytes, ultraviolet-visible (UV-Vis) spectrophotometry was employed. An NMR technique was used to determine the concentration of $\text{NH}_3$. Electrolytes were diluted to suitable concentrations to match the calibration curve range for accurate analysis. The specific detection methods for different ions are outlined below:

1.3.3.1. Determination of ammonia:

The concentration of $\text{NH}_3$ was quantitatively determined using a 400 MHz $^1\text{H}$ nuclear magnetic resonance (NMR) spectroscopy. $\text{D}_2\text{O}$ was used as the solvent, and maleic acid
(C₄H₄O₄) served as the internal standard. To create the calibration curve, the following steps were followed.:¹²

Firstly, a series of ammonium chloride (NH₄Cl) solutions with known concentrations were prepared in an aqueous solution. After that, 0.5 mL of the standard solution was mixed with 50 μL of 0.5 M H₂SO₄, 50 μL of D₂O and 25μL of 12.5 mM C₄H₄O₄. Then, the mixture was analyzed using a 400 MHz Bruker NMR spectrometer at room temperature. Finally, the calibration curve was established by determining the peak area ratio between NH₄⁺ and C₄H₄O₄.

To test the production of NH₄⁺ resulting from NO₃⁻ reduction, the pH of the obtained electrolyte needed to be adjusted to 2.0 before conducting the test. The testing process for the produced NH₄⁺ was similar to that used for creating the calibration curve. The amount of produced NH₄⁺ was calculated based on the calibration curve obtained previously.¹²

1.3.3.2. Determination of nitrate:

A certain volume of electrolyte was extracted from the electrolytic cell, which was further diluted to 5 mL. To this solution, 0.1 mL of 1 M HCl and 0.01 mL of a 0.8 wt% sulfamic acid solution were added. The resulting solution was subjected to UV-Vis spectrophotometry, and the absorption intensities at wavelengths of 220 nm and 275 nm were recorded. The final absorbance value was calculated using the equation: \( A = A_{220\text{ nm}} - 2A_{275\text{ nm}} \). To establish a concentration-absorbance curve, a series of standard sodium nitrate solutions were used, using pre-dried sodium nitrate crystals (NaNO₃) dried at 105-110 °C (for 4 hours).¹²-¹⁴

1.3.3.3. Determination of nitrite:
For this analysis, a colour reagent comprising p-aminobenzenesulfonamide (4 g), N-(1-Naphthyl) ethylenediamine dihydrochloride (0.2 g), ultrapure water (50 mL), and phosphoric acid (10 mL, ρ=1.70 g/mL) was prepared. Similarly, a specific volume of electrolyte was taken from the electrolytic cell and diluted to 5 mL. Then, 0.1 mL of the colour reagent was added to the 5 mL solution and mixed thoroughly. After about 20 minutes, the absorption intensity at a wavelength of 520 nm was measured using UV-Vis spectrophotometry. A calibration curve relating concentration to absorbance was established using a series of standard sodium nitrite solutions.\textsuperscript{12-14}

1.3.3.4. Determination of hydrazine:

For the determination of N\textsubscript{2}H\textsubscript{4} (hydrazine) formation during the NO\textsubscript{3}RR (nitrate reduction reaction), a detection method was carried out using Watt and Chrisp’s method. This method involves the use of a chromogenic reagent to detect and quantify N\textsubscript{2}H\textsubscript{4}. The chromogenic reagent was prepared by combining 5.99 g of p-dimethylaminobenzaldehyde and 30 mL of concentrated HCl in the presence of 300 mL of ethanol.

To quantify the N\textsubscript{2}H\textsubscript{4} concentration, the absorbance of the resulting solution was measured at a wavelength of 460 nm. This measurement was performed using standard N\textsubscript{2}H\textsubscript{4} solutions of known concentrations, which served as a calibration curve for the analysis.\textsuperscript{12}

1.3.3.5. Detection of nitrate by brown ring test:

Take 2 mL of a nitrate-containing solution into a test tube and introduce an equal volume of ferrous sulfate (FeSO\textsubscript{4}). Gradually add concentrated H\textsubscript{2}SO\textsubscript{4} along the inner wall of the test tube. Observe the formation of a distinctive brown ring at the interface of the two layers.\textsuperscript{15}
1.3.3.5. Detection of ammonia by Nessler’s reagent test:

2 mL of the ammonia-containing solution was added to an aqueous potassium sodium tartrate solution (KNaC₄H₆O₆, 100 µL, 500 g L⁻¹). Then, Nessler’s reagent (100 µL) was added to the above solution, which was mixed thoroughly. After 10 minutes, the solution turned to a yellow colour.¹⁶

1.3.4. Isotope Labelling Experiments:

An isotope-labelled tracer experiment was conducted using ten mM K₁⁵NO₃ as the nitrogen source. Following 3 hours of electroreduction at 0.8 V, the electrolyte (2 mL) in the cathodic chamber was treated using a 0.5 M H₂SO₄ (50 µL) aqueous solution. Subsequently, the neutralized electrolyte (525 µL) was combined with 50 µL of deuterium oxide (D₂O). The resulting mixture was then analyzed by a 400 MHz ¹H NMR spectrometer.¹²,¹⁴

1.3.5. Calculations of the nitrate removal, selectivity, Faradaic efficiency

The following calculations are performed to assess the NH₃ yield rate, conversion efficiency rate, selectivity, and Faradaic efficiency for the electroreduction of nitrate:

Calculation S1

Faradaic Efficiency Calculation

The Faradaic efficiency (Faradaic efficiency) is defined based on the electric charge consumed for synthesizing ammonia and the total charge passed through the electrode, as shown in Equation 1:

Faradaic efficiency = \((8F \times c\text{NH}_3 \times V) / (M_{\text{NH}_3} \times Q)\)  \hspace{1cm} (equation 1)
F represents the Faraday constant (96485.33 C mol\(^{-1}\)), Q is the total charge consumed (Q=I × t, where I is current and t is time in seconds).

**Calculation for β-TANiPc at -1 V vs. RHE**

Faradaic efficiency = \(\frac{8 \times 96485.33 \times 0.41 \times 25}{17 \times 565.41}\) \(\approx 82\)%

**Calculation S2**

**Conversion Efficiency/Rate Calculation**

The conversion rate (Conversion) is calculated using Equation 2:

\[
\text{Conversion of NO}_3^- \text{ to NH}_3 = \frac{C_{\text{NH}_3}}{C_{\text{NO}_3^-}} \times 100 \quad \text{(equation 2)}
\]

\(C_{\text{NH}_3}\) = Amount of NH\(_3\) formed in mmol

\(C_{\text{NO}_3^-}\) = Initial concentration of NO\(_3^-\) in mmol

**Calculation for β-TANiPc at -1 V vs. RHE**

Overall conversion of NO\(_3^-\) = NO\(_3^-\) consumed (\(\Delta C_{\text{NO}_3^-}\)) \(\times 100\) / initial nitrate (\(C_{\text{NO}_3^-}\))

\(\Delta C_{\text{NO}_3^-}\) = 0.67 mmol

\(C_{\text{NO}_3^-}\) = 0.70 mmol

Overall conversion of NO\(_3^-\) = \(0.67 \times 100\) / 0.70 = 95%

**Calculation S3**

**Selectivity Calculation**

The selectivity of ammonia or nitrite is determined using Equation 3

\[
\text{Selectivity towards NH}_3 \text{ formation} = \frac{C_{\text{NH}_3}}{\Delta C_{\text{NO}_3^-}} \times 100 \quad \text{(equation 3)}
\]

\(C_{\text{NH}_3}\) = amount of NH\(_3\) formed in mmol

\(\Delta C_{\text{NO}_3^-}\) = change in concentration of nitrate during NO\(_3^-\)RR in mmol (amount of nitrate utilized)

**Calculation For β-TANiPc at -1 V vs. RHE**

\(C_{\text{NH}_3}\) = 0.60 mmol

\(\Delta C_{\text{NO}_3^-}\) = 0.67 mmol
Selectivity to NH$_3$ = C$_{NH3}$*$100/\Delta C_{NO3-}$ = 0.60*100/ 0.67 = 89%

Calculation S4

NH$_3$ Yield Calculation

The yield of ammonia (Yield NH$_3$) is determined using Equation 4

\[ \text{Yield rate (NH}_3) = \frac{c_{NH3} \cdot V}{t \cdot S} \] (equation 4)

c$_{NH3}$ = mass concentration of NH$_3$ (mg/mL)
V = Total volume (mL)
t = Time (h)
S = Surface area of electrode (cm$^2$)

Calculation For $\beta$-TANiPc at -1 V vs. RHE

c$_{NH3}$ = 0.41 mg/mL
V = 25 mL
t = 3 h
S = 4 cm$^2$

Yield rate (NH$_3$) = (0.41 mg/mL*25 mL)/(3 h*4 cm$^2$) = 0.85 mg h$^{-1}$ cm$^{-2}$
**Fig. S1.** Matrix Assisted Laser Desorption Ionization – Time of Flight (MALDI-TOF) spectra of a) NiPc, b) α-TANiPc and c) β-TANiPc.
**Fig. S2.** Raman spectra of unsubstituted NiPc, α-TANiPc and β-TANiPc.
Fig. S3. FESEM images of a) NiPc, b) α-TANiPc and c) β-TANiPc.
**Fig. S4.** FESEM EDX mapping images and elemental analysis of a) NiPc, b) α-TANiPc and c) β-TANiPc.
Fig. S5. TEM images of a) NiPc, b) α-TANiPc and c) β-TANiPc.
Fig. S6. Characterization of Composite molecules. a) UV-Vis spectra, b) ATR-FTIR spectra and c) Raman spectra.
Fig. S7. FESEM image of a) NiPc/CNT, b) α-TANiPc/CNT and c) β-TANiPc/CNT.
Fig. S8. FESEM EDX mapping images along with elemental analysis of a) NiPc/CNT, b) α-TANiPc/CNT and c) β-TANiPc/CNT.

Table S1. Parameters extracted from the electrochemical impedance spectra.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>NiPc</th>
<th>α-TANiPc</th>
<th>β-TANiPc</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_s (Ohm cm²)</td>
<td>0.41</td>
<td>0.55</td>
<td>0.58</td>
</tr>
<tr>
<td>C_dl (F cm²)</td>
<td>2.34E-6</td>
<td>1.70E-4</td>
<td>8.17E-4</td>
</tr>
<tr>
<td>R_ct (Ohm cm²)</td>
<td>23.32</td>
<td>8.99</td>
<td>3.08</td>
</tr>
<tr>
<td>W (Ohm cm²)</td>
<td>0.00057</td>
<td>0.00066</td>
<td>0.00032</td>
</tr>
</tbody>
</table>
Fig. S9. Cyclic voltammograms at scan rate of 20 mV s$^{-1}$ in Ar saturated 20 mM HClO$_4$ with and without 10 mM NaNO$_3$ electrolyte for a) NiPc/CNT, b) $\alpha$-TANiPc/CNT and c) $\beta$-TANiPc/CNT.
Fig. S10. Quartz crystal microbalance response during the adsorption of isomeric molecules on a carbon-coated quartz resonator from a 0.2 mM solution of (a) α-TANiPc and (b) β-TANiPc in dimethylformamide (DMF). The wine trace shows the frequency change during the adsorption and the violet trace shows the corresponding mass change (using Sauerbrey equation). Surface coverage (Γ) values of the molecules are provided in respective plots.

Fig. S11. Cyclic voltammograms of glassy carbon electrodes modified with a monolayer of all molecular catalysts in Ar-saturated 20 mM HClO₄ containing 10 mM NaNO₃ at a scan rate of 20 mV s⁻¹.
Fig. S12. UV-Vis spectra for hydrazine detection.

Fig. S13. The concentration-dependent calibration curves for NH$_4^+$. (a) NMR spectra of NH$_4^+$ at different concentrations and (b) standard calibration curve for ammonia. The calibration curves demonstrate good linearity.
Fig. S14. The concentration-absorption calibration curves for nitrite detection. (a) UV-Vis absorption spectra for nitrite at different concentrations and (b) standard calibration curve for various nitrite concentrations.

Fig. S15. The concentration-absorption calibration curves for nitrate detection. (a) UV-Vis absorption spectra for nitrite at different concentrations and (b) standard calibration curve for various nitrate concentrations.
Fig. S16. (a) \( \text{H}_2 \) detection by in-situ differential electrochemical mass spectrometry at -0.8 V vs. RHE. When the cell is ON, the partial pressure of \( \text{H}_2 \) increases and it decays to the base line when the cell is OFF. (b) The Faradaic efficiency towards \( \text{H}_2 \) formation.
Fig. S17. a) $^1$H NMR spectra demonstrating NH$_3$ formation ($I = \text{NH}_4^+$ peak integration value with respect to maleic acid peak), b) UV-Visible spectra for NO$_2^-$ formation and c) UV-Visible spectra for NO$_3^-$ consumption at different applied potentials from -0.6 V to -1.0 V vs. RHE for unsubstituted NiPc/CNT system.
Fig. S1. a) $^3$H NMR spectra demonstrating NH$_3$ formation ($I = $ NH$_4^+$ peak integration value with respect to maleic acid peak), b) UV-Visible spectra for NO$_2^-$ formation and c) UV-Visible spectra for NO$_3^-$ consumption at different applied potentials from -0.6 V to -1.0 V vs. RHE for $\alpha$-TANiPc/CNT.
Fig. S19. a) $^1$H NMR spectra demonstrating NH$_3$ formation (I = NH$_4^+$ peak integration value with respect to maleic acid peak), b) UV-Visible spectra for NO$_2^-$ formation and c) UV-Visible spectra for NO$_3^-$ consumption at different applied potentials from -0.6 V to -1.0 V vs. RHE for β-TANiPc/CNT.
**Fig. S20.** (a) Conversion % of NO$_3^-$ to NH$_3$ and (b) NH$_3$ selectivity with unsubstituted NiPc, α-TANiPc and β-TANiPc at different applied potentials.

**Fig. S21.** Comparison of nitrite (NO$_2^-$) formation during NO$_3$RR on NiPc, α-TANiPc and β-TANiPc at different applied potentials.
Fig. S22. Potential dependent post electrolytic concentration of $\text{NO}_3^-$, $\text{NH}_3$ and $\text{NO}_2^-$ for (a) NiPc, (b) $\alpha$-TANiPc and (c) $\beta$-TANiPc.
Fig. S23. Chronoamperometry at a constant applied potential of -1.0 V vs. RHE for 100 hours.

Fig. S24. Ni 2p XPS spectra of electrolyte treated isomeric molecules in comparison to unsubstituted NiPc.
**Fig. S25.** C1s XPS spectra of electrolyte-treated $\alpha$-TANiPc and $\beta$-TANiPc isomeric molecules in comparison to unsubstituted NiPc.

**Fig. S26.** Cyclic voltammogram for 10 mM ruthenium hexamine chloride solution in 0.1 M HClO$_4$ medium at a scan rate of 20 mV/s with NiPc, $\alpha$-TANiPc, and $\beta$-TANiPc isomeric molecules.
Scheme S1. Protonated structures of unsubstituted NiPc, α-TANiPc and β-TANiPc isomeric molecules.

Fig. S27. BET surface area measurements (a) The N₂ adsorption-desorption isotherms for NiPc, α-TANiPc and β-TANiPc isomeric molecules and (b) surface area, total pore volume and average pore diameter derived from the BET measurements.
Fig. S28. Contact angle images for (a) CNT, (b) NiPc, (c) α-TANiPc and (d) β-TANiPc composite electrodes along with the corresponding contact angles.
Fig. S29. (a) UV-Vis absorption spectra for nitrate detection before and after electrolysis at 20 mA/cm² for 100 hours. The electrolysis was carried out with β-TANiPc isomer molecule using agricultural waste water. (b) The corresponding concentrations of nitrate before and after electrolysis.

Fig. S30. UV-Visible spectra for (a) NO₂⁻ and (b) hydrazine after 100 hours of continuous electrolysis of agro waste water.
Fig. S31. (a) XPS spectra and (b) FTIR spectra of β-TANiPc isomer molecule before and after 100 h of electrochemical recycling of agricultural waste water to ammonia.
Table S2. Comparison of Faradaic efficiency and ammonia yield by electrocatalytic nitrate reduction reaction on various molecular catalysts.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Electrolyte</th>
<th>Faradaic efficiency</th>
<th>Applied potential</th>
<th>Yield</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-TANiPc/CNT</td>
<td>Actual agro-waste water (420 mg/L of nitrate)</td>
<td>84%</td>
<td>5 mA cm⁻²</td>
<td>0.35 mg h⁻¹ cm⁻² (at an average voltage of -0.53 V vs RHE)</td>
<td>This work</td>
</tr>
<tr>
<td>NiPc-CNT Sponge</td>
<td>0.5 M Na₂SO₄ + NO₃⁻</td>
<td>86.8%</td>
<td>-1.2 vs. Ag/AgCl</td>
<td>33 N·mg L⁻¹</td>
<td>12</td>
</tr>
<tr>
<td>FePc-pz</td>
<td>1 M H₂SO₄ + NO₃⁻</td>
<td>31.9%</td>
<td>-1 V vs. RHE</td>
<td>33.6 μg h⁻¹ mg⁻¹</td>
<td>17</td>
</tr>
<tr>
<td>FePc</td>
<td>0.1 N HCl + KNO₃</td>
<td>100%</td>
<td>-1.5 V vs. RHE</td>
<td>35067.09 μg h⁻¹ mg⁻¹</td>
<td>18</td>
</tr>
<tr>
<td>CoPc-RGO</td>
<td>0.1 M K₂SO₄ + KNO₃</td>
<td>95.1%</td>
<td>-0.2 V vs. RHE</td>
<td>58.82 μg h⁻¹ mg⁻¹</td>
<td>19</td>
</tr>
<tr>
<td>MOF@CuPc</td>
<td>0.5 M Na₂SO₄ and NaNO₃</td>
<td>94.3%</td>
<td>-0.75 V vs. RHE</td>
<td>0.044 mmol h⁻¹ cm⁻² (0.75 mg h⁻¹ cm⁻²)*</td>
<td>20</td>
</tr>
<tr>
<td>CuPc@MXene</td>
<td>0.5 M Na₂SO₄ + NO₃⁻</td>
<td>(85.7% Selectivity)</td>
<td>-1.06 V vs. RHE</td>
<td>0.27 mg h⁻¹ cm⁻²</td>
<td>21</td>
</tr>
</tbody>
</table>

*Values are converted based on the available data.
References: