

Supporting Information

Graphite-conjugated acids reveal a molecular framework for proton-coupled electron transfer at electrode surfaces

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Experimental Methods

Chemicals and materials. Sodium hydroxide (99.99%, semiconductor grade), perchloric acid (70%, 99.999% trace metals basis), sodium acetate, sodium phosphate dibasic (TraceSELECT, anhydrous, 99.999% trace metals basis), *o*-phenylenediamine (99.5%), and 3,4-diaminobenzoic acid (97%) were obtained from Sigma Aldrich and were used as received. 1,2,4-triaminobenzene dihydrochloride (>95.0%) was obtained from TCI America and used as received. 2,3-diaminophenol was obtained from Acros Organics and used as received. 4-ethoxybenzene-1,2,-diamine was purchased from Sigma Aldrich and used as received. 3,ethoxybenzene-1,2-diamine (95%) was obtained from AstaTech Inc. and used as received. 3,4-diaminophenol dihydrochloride (95%) was purchased from Enamine and used as received. Boric acid (Puratronic, 99.9995% trace metals basis) was purchased from Alfa Aesar and sulfuric acid (95.5-96.5%, OmniTrace) was obtained from EMD Millipore and used as received. All aqueous electrolyte solutions were prepared with reagent grade water (Millipore Type 1, 18.2 M Ω -cm resistivity). Dimethylformamide (EMD Chemicals), dimethyl sulfoxide (EMD Chemicals), and methanol (EMD Chemicals) were purified and dried prior to use by passing through a Glass Contour Solvent Purification System (SG Water USA, LLC). Ethanol (absolute, dried, Seccosolv) was supplied by MilliPore Sigma and was stored and used in an N₂ glovebox. Vitreous carbon plates were obtained from Goodfellow (VC000400). Ag/AgCl reference electrodes were obtained from eDAQ. Platinum wire (99.9%) and Platinum mesh (99.9%) were obtained from Alfa Aesar.

General electrochemical methods. All electrochemical experiments were conducted at ambient temperature (21 \pm 1 $^{\circ}$ C) using a Gamry REF 600 potentiostat or Biologic VSP potentiostat. All electrochemical experiments were conducted in a two-compartment electrochemical cell with a fine frit separating the working and auxiliary compartments. A platinum mesh was used as the counter electrode in the separated auxiliary compartment. Leakless aqueous Ag/AgCl (eDAQ) and were used as the reference electrode. Ag/AgCl electrodes were stored in reagent-grade water and were periodically checked relative to pristine reference electrodes to ensure against potential drift. All electrode potentials are plotted vs the normal hydrogen electrode (NHE, $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.198 \text{ V}$).

Preparation of GCCs.

GCCs were prepared on glassy carbon plates that were used as received. Ti wire was used to make electrical contact between the electrode and the potentiostat. The wire was secured either by coiling the end of the wire and clipping it to the plate or by securing it to the plate with tightly wrapped parafilm.

Preparation of GCC-phenazine

Glassy carbon plates were immersed in \sim 10 mL of 2 mM *o*-phenylenediamine in dry ethanol in an N₂ glovebox. The reaction vessel was subsequently sealed under inert atmosphere, removed from the glovebox, and heated under N₂ for 10 hours at 60 $^{\circ}$ C. Upon cooling, electrodes were washed with copious amounts of pure ethanol and subsequently treated with 0.1 M HClO₄ for 1 hour to hydrolyze adventitious imine linkages formed on the surface. Following acid treatment, electrodes were rinsed with water and dried in a 60 $^{\circ}$ C oven.

Preparation of GCC-phen-COOH

Glassy carbon plates were immersed in ~10 mL of 2 mM 3,4-diaminobenzoic acid in dry ethanol in an N₂ glovebox. The reaction vessel was subsequently sealed under inert atmosphere, removed from the glovebox, and heated under N₂ for 10 hours at 60°C. Upon cooling, electrodes were washed with copious amounts of pure ethanol and subsequently treated with 0.1 M HClO₄ for 1 hour to hydrolyze adventitious imine linkages formed on the surface. Following acid treatment, electrodes were rinsed with water and dried in a 60°C oven.

Preparation of GCC-phen-NH₂

Glassy carbon plates were immersed in ~10 mL of 2 mM 1,2,4-triaminobenzene dihydrochloride in dimethyl sulfoxide in an N₂ glovebox. The reaction vessel was subsequently sealed under inert atmosphere, removed from the glovebox, and heated under N₂ for 10 hours at 110°C. Upon cooling, electrodes were washed with copious amounts of pure ethanol and subsequently treated with 0.1 M HClO₄ for 1 hour to hydrolyze adventitious imine linkages formed on the surface. Following acid treatment, electrodes were rinsed with water and dried in a 60°C oven.

Preparation of GCC-phen-o-OH

Glassy carbon plates were immersed in ~10 mL of 2 mM 2,3-diaminophenol dihydrochloride in dry methanol in an N₂ glovebox. The reaction vessel was subsequently sealed under inert atmosphere, removed from the glovebox, and heated under N₂ for 10 hours at 60°C. Upon cooling, electrodes were washed with copious amounts of pure ethanol and subsequently treated with 0.1 M HClO₄ for 1 hour to hydrolyze adventitious imine linkages formed on the surface. Following acid treatment, electrodes were rinsed with water and dried in a 60°C oven.

Preparation of GCC-phen-m-OH

Glassy carbon plates were immersed in ~10 mL of 2 mM 3,4-diaminophenol dihydrochloride and 5 mM sodium ethoxide in dry ethanol in an N₂ glovebox. The reaction vessel was sealed under inert atmosphere, removed from the glovebox, and heated under N₂ for 10 hours at 60°C. Upon cooling, electrodes were washed with copious amounts of pure ethanol and subsequently treated with 0.1 M HClO₄ for 1 hour to hydrolyze adventitious imine linkages formed on the surface. Following acid treatment, electrodes were rinsed with water and dried in a 60°C oven.

Preparation of GCC-phen-o-OEt

Glassy carbon plates were immersed in ~10 mL of 2 mM 3-ethoxybenzene-1,2-diamine and 5 mM sodium ethoxide in dry ethanol in an N₂ glovebox. The reaction vessel was subsequently sealed under inert atmosphere, removed from the glovebox, and heated under N₂ for 10 hours at 100°C. Upon cooling, electrodes were washed with copious amounts of pure ethanol and subsequently treated with 0.1 M HClO₄ for 1 hour to hydrolyze adventitious imine linkages formed on the surface. Following acid treatment, electrodes were rinsed with water and dried in a 60°C oven.

Preparation of GCC-phen-m-OEt

Glassy carbon plates were immersed in ~10 mL of 1 mM 3-ethoxybenzene-1,2-diamine in dry ethanol in an N₂ glovebox. The reaction vessel was subsequently sealed under inert atmosphere, removed from the glovebox, and heated under N₂ for 10 hours at 60°C. Upon cooling, electrodes were washed with copious amounts of pure ethanol and subsequently treated with 0.1 M HClO₄ for 1 hour to hydrolyze adventitious imine linkages formed on the surface. Following acid treatment, electrodes were rinsed with water and dried in a 60°C oven.

XPS measurements and curve fitting. X-ray photoelectron spectra were recorded using a Physical Electronics PHI Versaprobe II with a monochromatic aluminum K α X-ray source (1486.6 eV) and a hemispherical energy analyzer. Data were collected at a base pressure of 5×10^{-9} torr using a 200 μm , 50 W focused beam at a take-off angle of 45°. Survey spectra were collected using a pass energy of 187.85 eV and a step size of 0.8 eV. High-resolution scans were collected with a pass energy of 23.50 eV and a step size of 0.1 eV. Survey spectra were analyzed using MultiPak software. The survey and high-resolution scans referenced to the graphitic C 1s peak (284.3 eV) of glassy carbon. High-resolution scans were fit with a Shirley-type background and Gaussian/Lorentzian line-shapes of 50% Gaussian shape.

The XPS data together indicate that the pyrazine moieties are on the surface with high uniformity. Survey spectra indicate incorporation of N into the graphitic electrodes (**Figures S13-19**). High-resolution N 1s XPS spectrum for GCC-phenazine was fit to one peak, and GCC-phen-COOH, GCC-phen-GCC-*o*-OH, GCC-phen-*m*-OH, GCC-phen-*o*-OEt, and GCC-phen-*m*-OEt were fit to two N peaks, one for each pyrazinic N, with 1:1 ratios at binding energies. GCC-phen-NH₂ was fit to two N peaks with a 2:1 ratio, corresponding to the pyrazinic N and the amine N. Peak positions are listed in the caption for each high-resolution XPS spectrum (**Figures S20-26**). The peak positions are in line with expected values for pyrazinic^{1,2} and/or amino nitrogen moieties² on N-containing carbons.

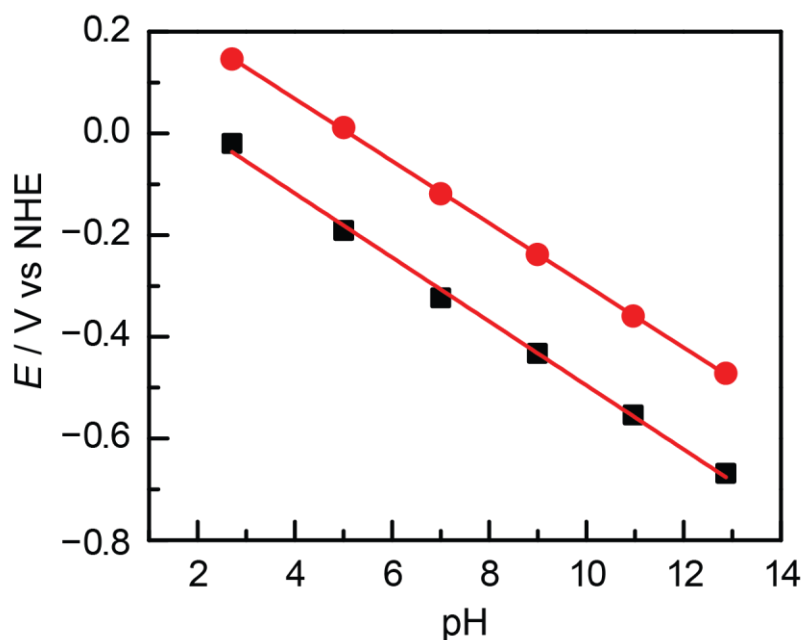


Figure S1. pH-dependence of GCC-phen-COOH. The red dots represent $E_{1/2}$ for the COOH wave, and the black squares represent $E_{1/2}$ for the pyrazine wave. The slopes of the best fit lines are -61 mV per pH unit and -63 mV per pH unit, respectively. The electrolyte was composed of 0.1 M sodium acetate, 0.1 M sodium phosphate, and 0.1 M sodium borate and was adjusted with 1 M HClO_4 and 1 M NaOH .

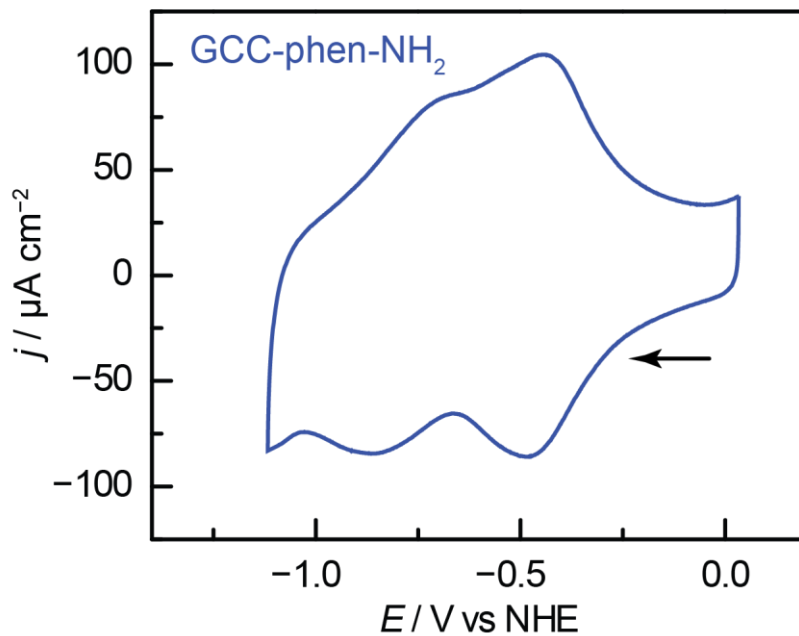


Figure S2. Cyclic voltammogram (100 mV s^{-1}) of GCC-phen- NH_2 in 0.1 M NaOH .

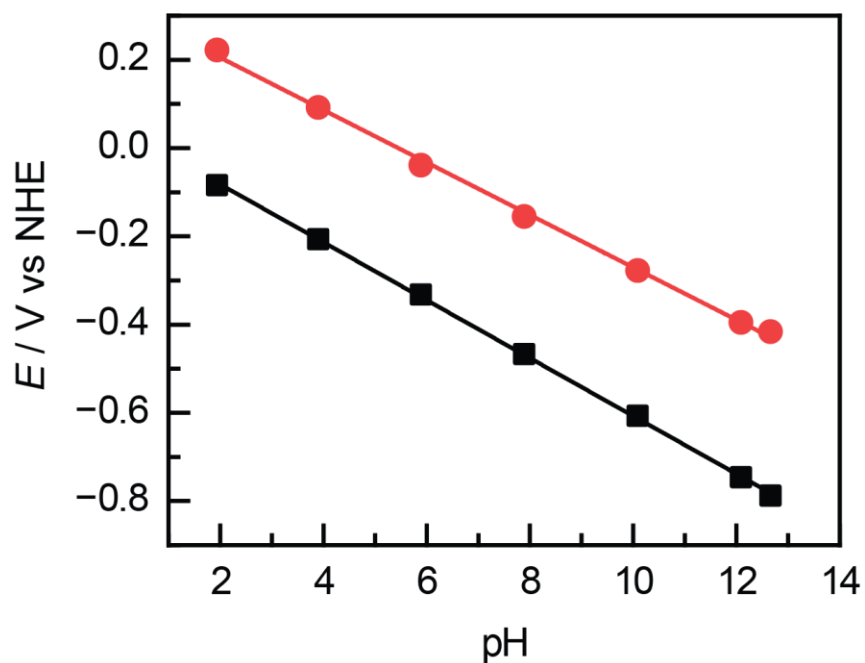


Figure S3. pH-dependence of GCC-phen-NH₂. The red dots represent $E_{1/2}$ for the NH₂ wave, and the black squares represent $E_{1/2}$ for the pyrazine wave. The slopes of the best fit lines are -59 mV per pH unit and -65 mV per pH unit, respectively. The electrolyte was composed of 0.1 M sodium acetate, 0.1 M sodium phosphate, and 0.1 M sodium borate and was adjusted with 1 M HClO₄ and 1 M NaOH.

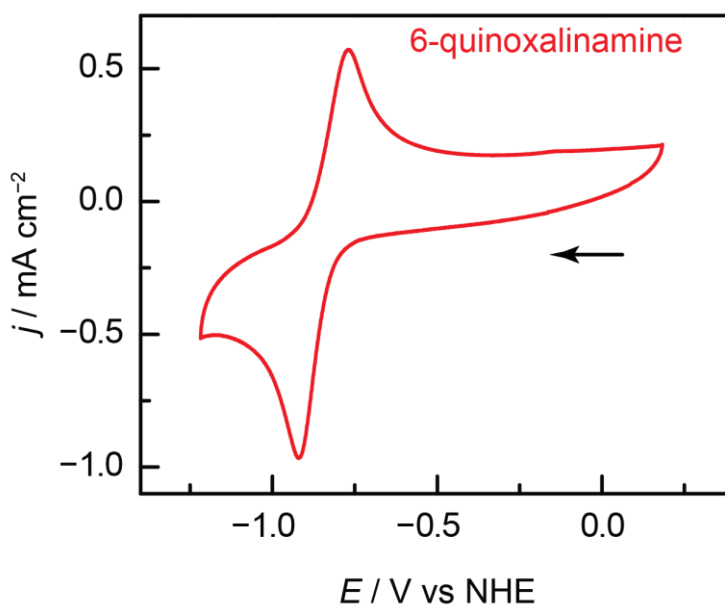


Figure S4. Cyclic voltammogram (100 mV s⁻¹) of 6-quinoxalinamine in 0.1 M NaOH.

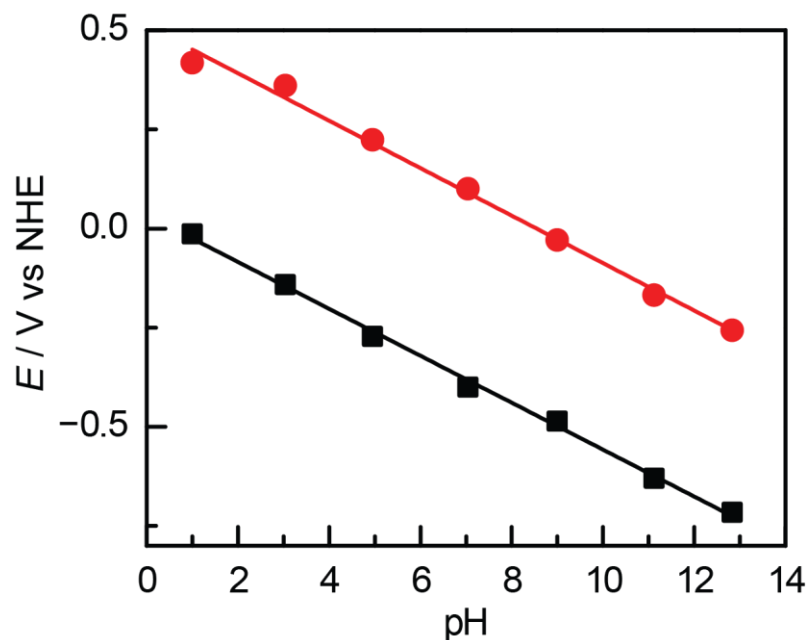


Figure S5. pH-dependence of GCC-phen-*m*-OH. The red dots represent $E_{1/2}$ for the OH wave, and the black squares represent $E_{1/2}$ for the pyrazine wave. The slopes of the best fit lines are -60 mV per pH unit and -59 mV per pH unit, respectively. The electrolyte was composed of 0.1 M sodium acetate, 0.1 sodium phosphate, and 0.1 M sodium borate and was adjusted with 1 M HClO₄ and 1 M NaOH.

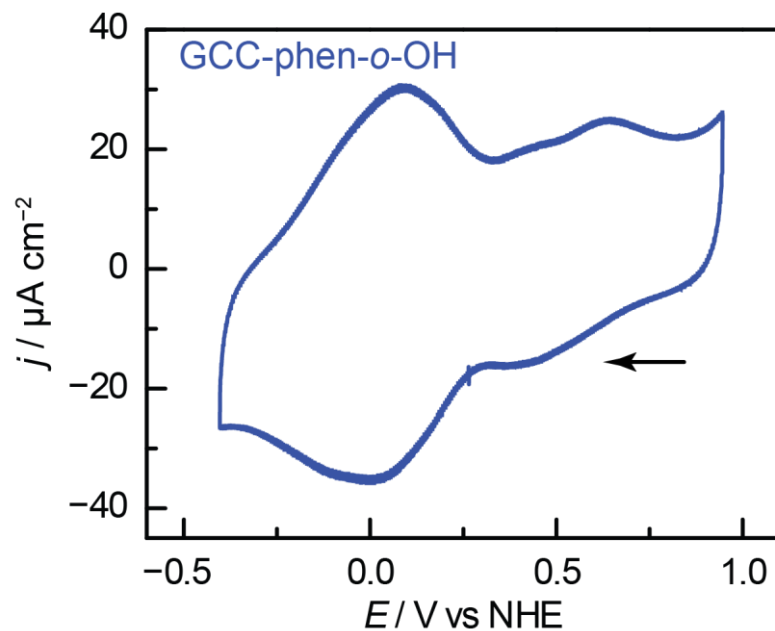


Figure S6. Cyclic voltammogram (100 mV s⁻¹) of GCC-phen-*o*-OH in 0.1 M HClO₄.

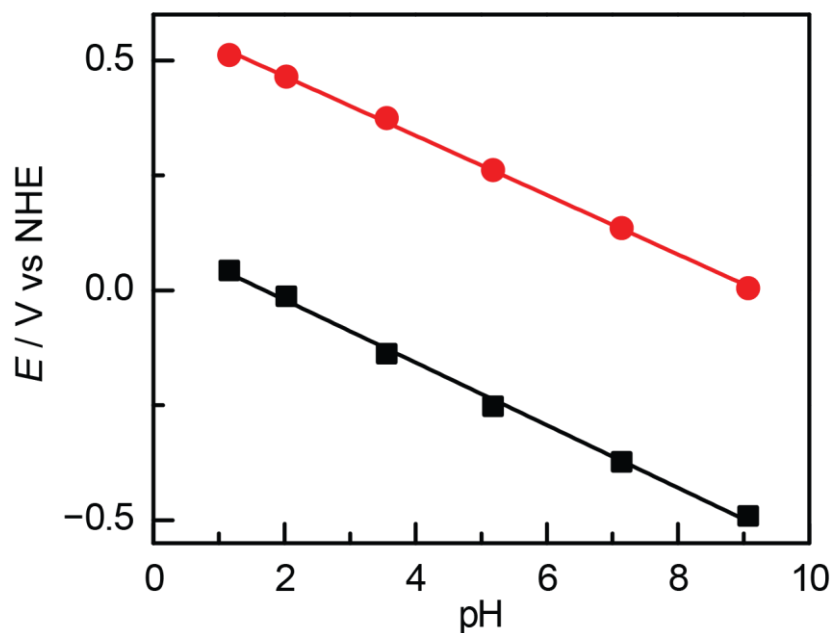


Figure S7. pH-dependence of GCC-phen-*o*-OH. The red dots represent $E_{1/2}$ for the OH wave, and the black squares represent $E_{1/2}$ for the pyrazine wave. The slopes of the best fit lines are -65 mV per pH unit and -71 mV per pH unit, respectively. The electrolyte was composed of 0.1 M sodium acetate, 0.1 sodium phosphate, and 0.1 M sodium borate and was adjusted with 1 M HClO₄ and 1 M NaOH.

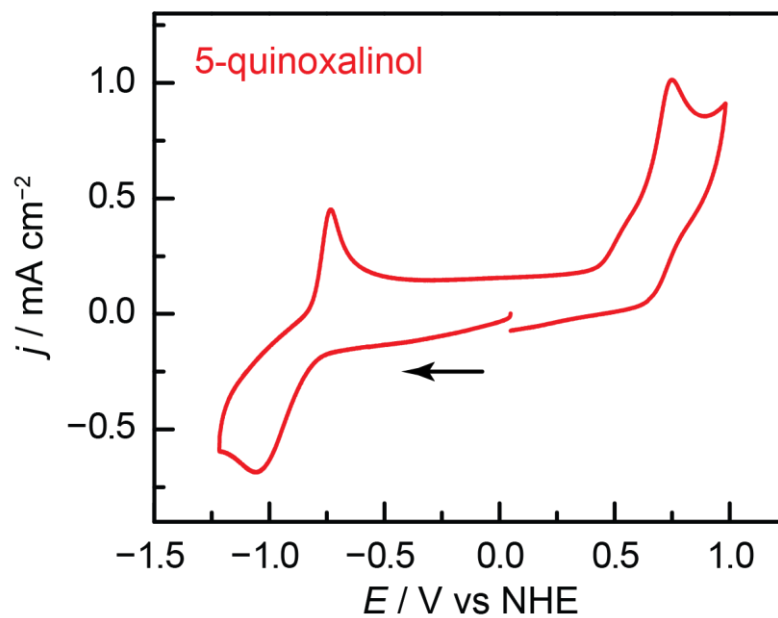


Figure S8. Cyclic voltammogram (100 mV s⁻¹) of 5-quinoxalinol in 0.1 M NaOH.

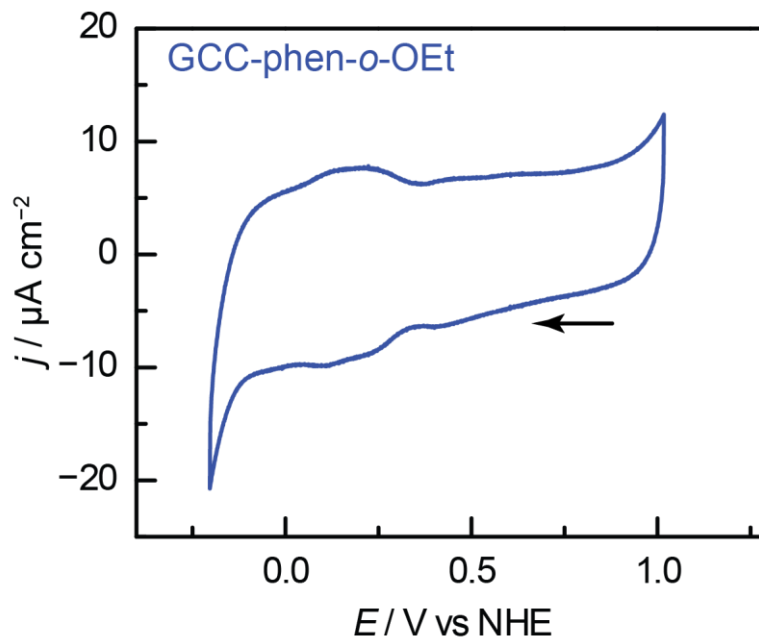


Figure S9. Cyclic voltammogram (100 mV s^{-1}) of GCC-phen-*o*-OEt in 0.1 M HClO_4 .

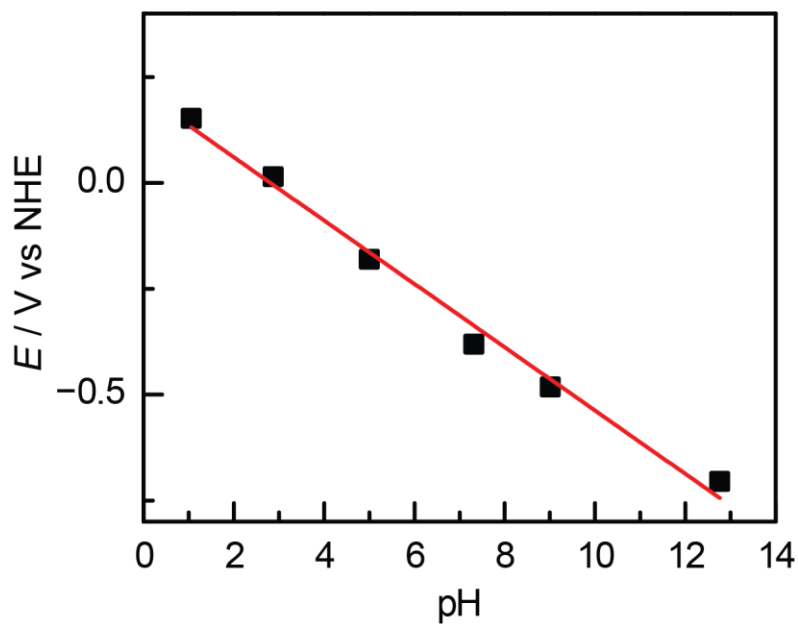


Figure S10. pH-dependence of GCC-phen-*o*-OEt. The black squares represent $E_{1/2}$ for the pyrazine wave. The slope of the best fit line is $-75 \text{ mV per pH unit}$. The electrolyte was composed of 0.1 M sodium acetate, 0.1 M sodium phosphate, and 0.1 M sodium borate and was adjusted with 1 M HClO_4 and 1 M NaOH .

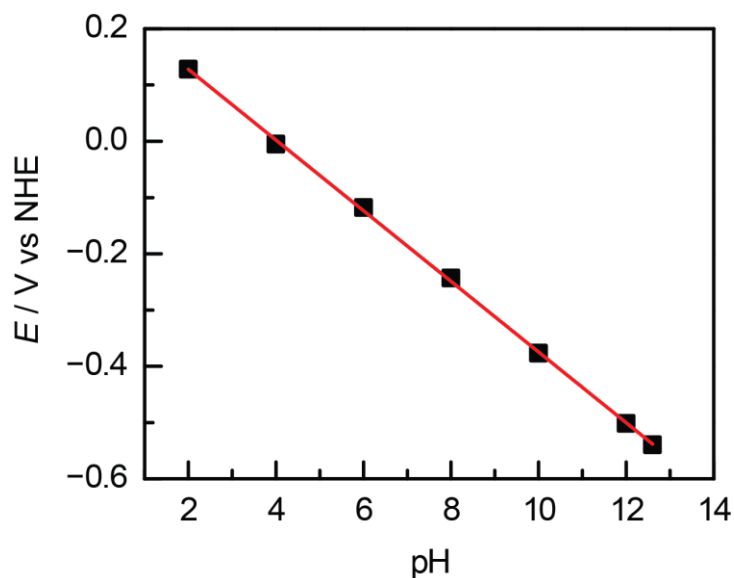


Figure S11. pH-dependence of GCC-phen-m-OEt. The black squares represent $E_{1/2}$ for the pyrazine wave. The slope of the best fit line is -63 mV per pH unit. The electrolyte was composed of 0.1 M sodium acetate, 0.1 M sodium phosphate, and 0.1 M sodium borate and was adjusted with 1 M HClO₄ and 1 M NaOH.

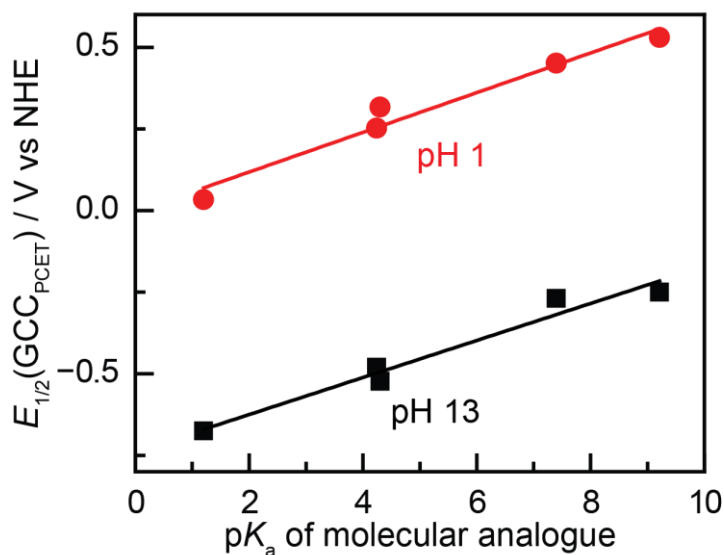


Figure S12. Plot of the potential of the proton-coupled electron transfer wave for each GCC extrapolated to pH 1 (red) and pH 13 (black) from the data in **Figure 4a** vs the pK_a of the acidic site of the corresponding molecular analogue. Values of the pK_a for molecular analogues were taken from the literature for phenazine,³ phenazine-2-carboxylic acid,⁴ phenazin-2-amine,⁵ phenazin-2-ol,⁵ and phenazin-1-ol.⁶ The slopes of the best fit lines are 61 mV/ pK_a unit at pH 1 and 57 mV/ pK_a at pH 13, and the computed E_{PZFC} values using **Eq. 10** are 0.02 for pH 1 and 0.00 for pH 13.

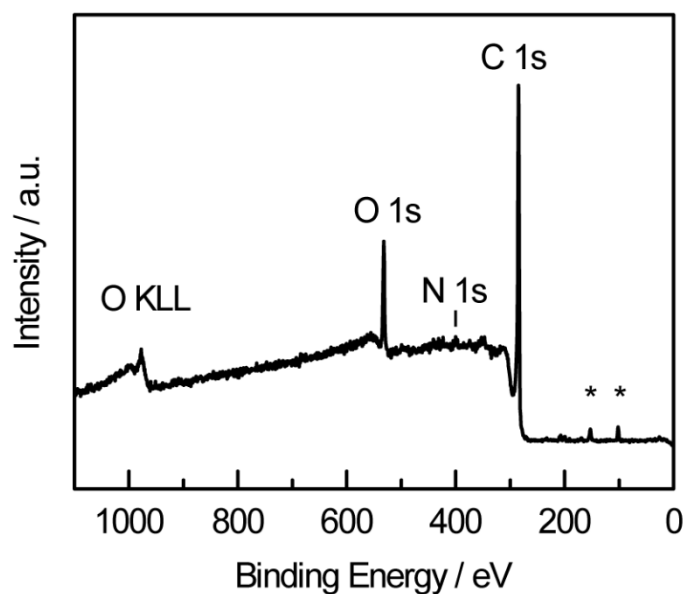


Figure S13. XPS survey spectrum of GCC-phenazine. *Indicates adventitious silicon introduced from glassware during electrode functionalization.

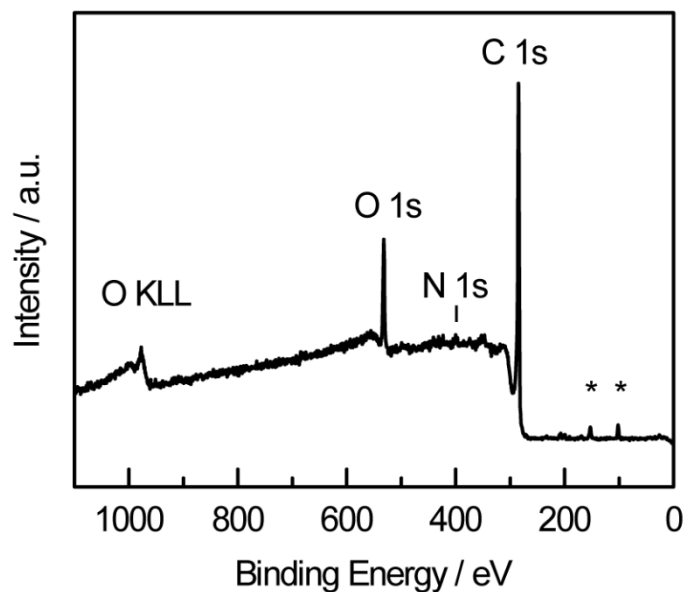


Figure S14. XPS survey spectrum of GCC-phen-COOH. *Indicates adventitious silicon introduced from glassware during electrode functionalization.

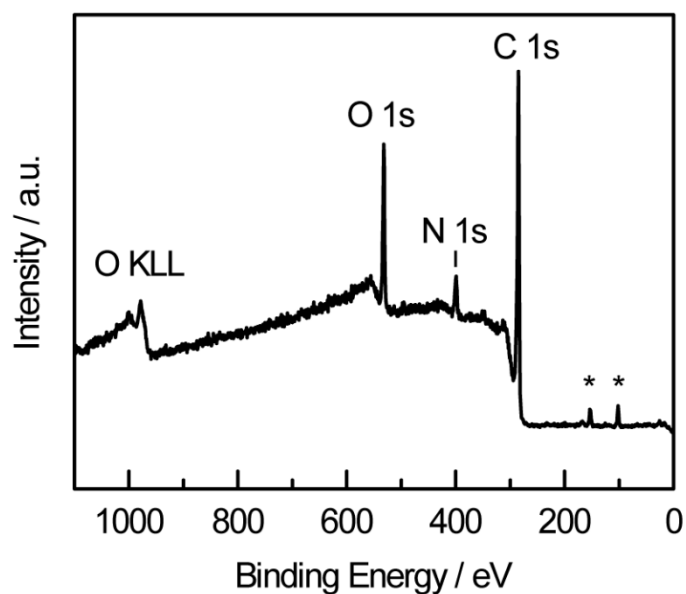


Figure S15. XPS survey spectrum of GCC-phen-NH₂. *Indicates adventitious silicon introduced from glassware during electrode functionalization.

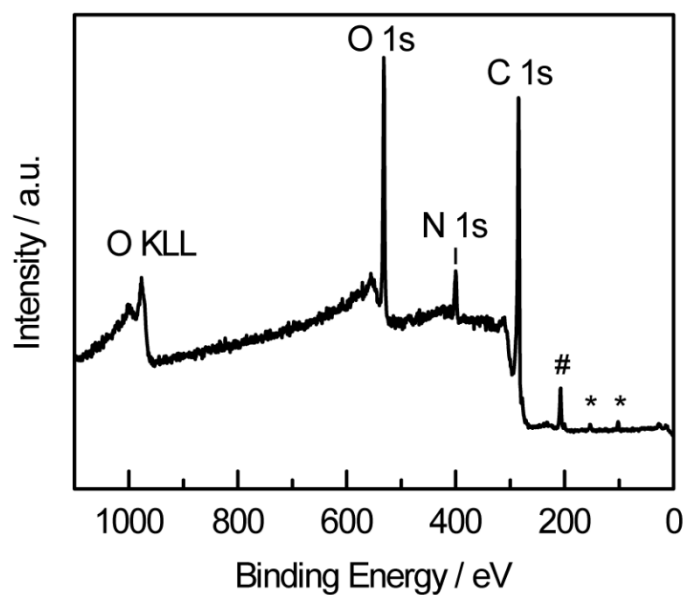


Figure S16. XPS survey spectrum of GCC-phen-*o*-OH *Indicates adventitious silicon introduced from glassware during electrode functionalization. #Indicates adventitious chloride.

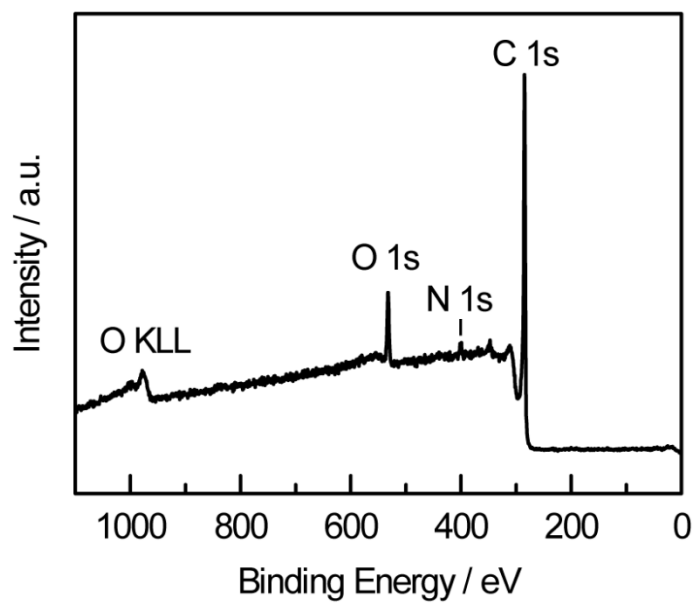


Figure S17. XPS survey spectrum of GCC-phen-*m*-OH.

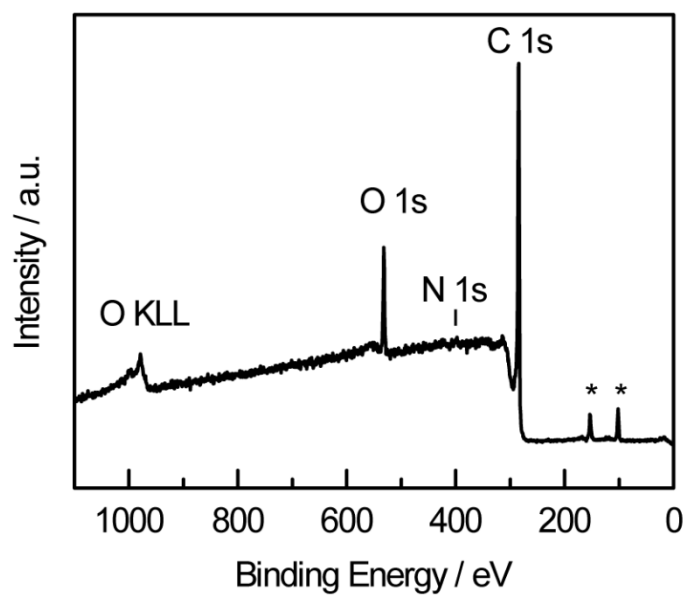


Figure S18. XPS survey spectrum of GCC-phen-*o*-OEt. *Indicates adventitious silicon introduced from glassware during electrode functionalization.

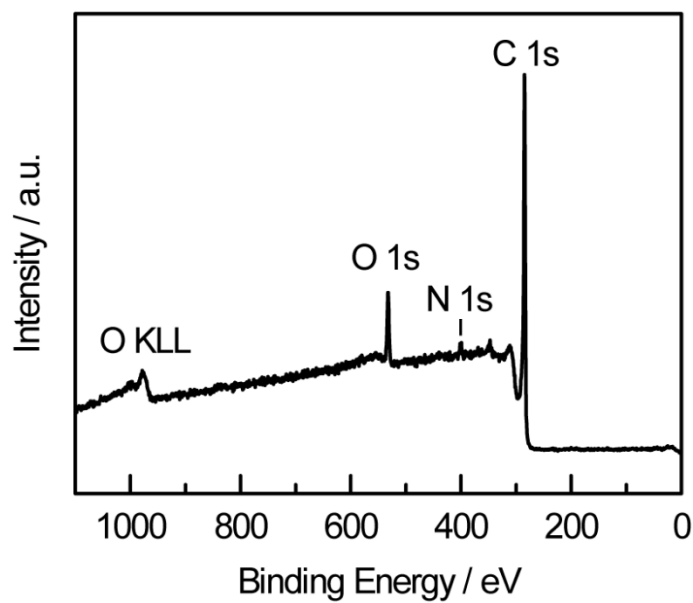


Figure S19. XPS survey spectrum of GCC-phen-*m*-OEt.

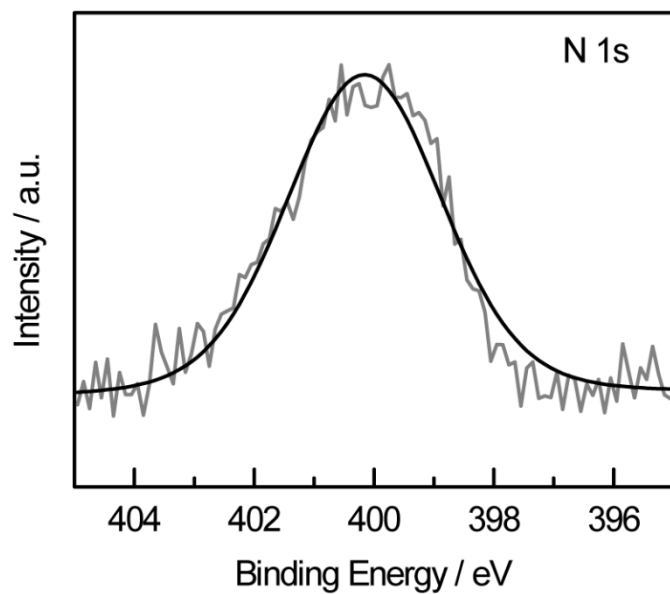


Figure S20. High-resolution N 1s XPS spectrum of GCC-phenazine. The peak is centered at 400.2 eV.

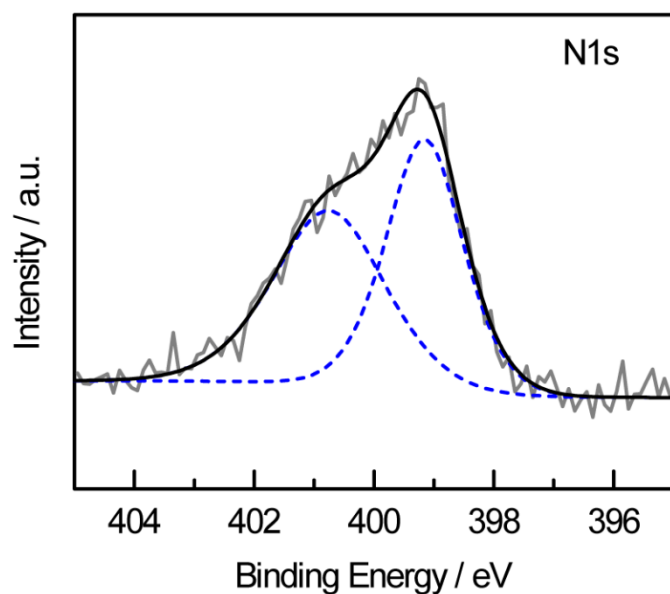


Figure S21. High-resolution N 1s XPS spectrum of GCC-phen-COOH. The peaks are centered at 400.7 eV (left) and 399.2 eV (right) in a 1:1 ratio.

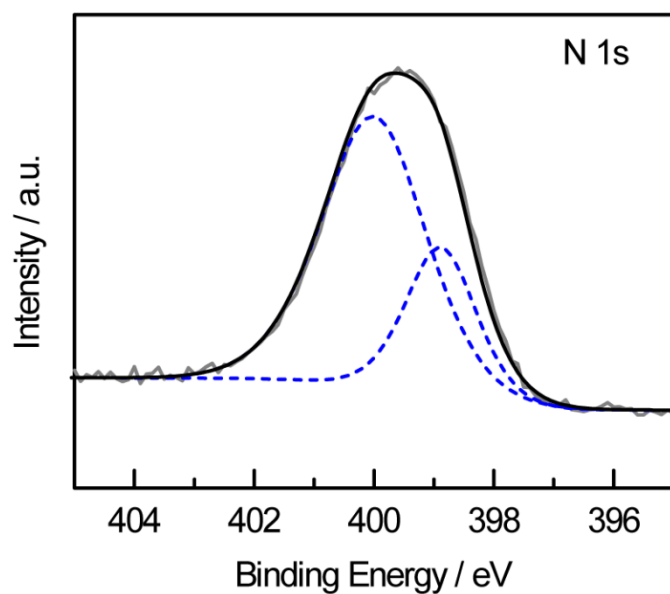


Figure S22. High-resolution N 1s XPS spectrum of GCC-phen-NH₂. The peaks are centered at 400.0 eV (left) and 398.9 eV (right) in a 2:1 ratio.

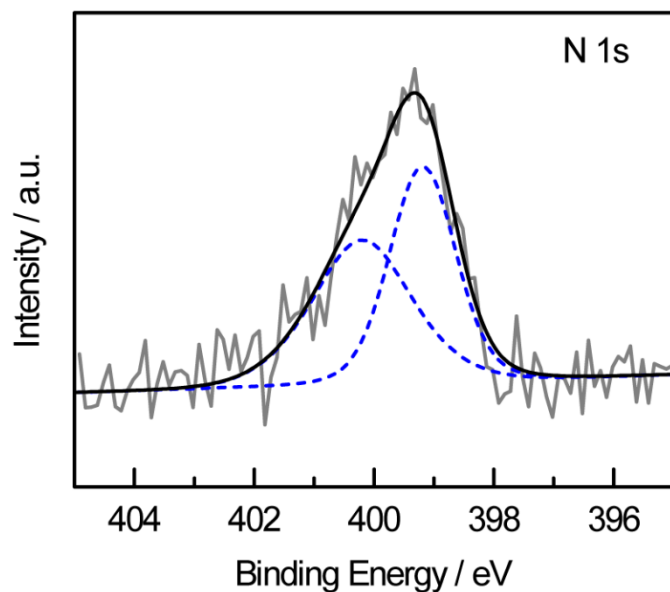


Figure S23. High-resolution N 1s XPS spectrum of GCC-phen-*o*-OH. The peaks are centered at 400.2 eV (left) and 399.2 eV (right) in a 1:1 ratio.

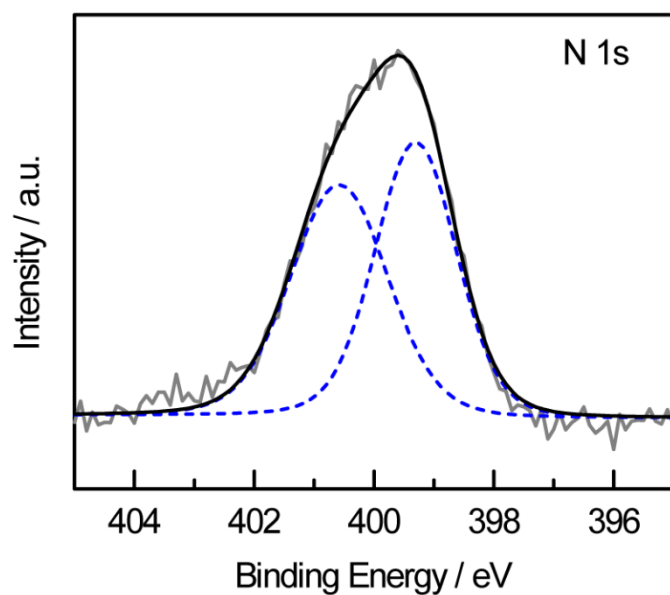


Figure S24. High-resolution N 1s XPS spectrum of GCC-phen-*m*-OH. The peaks are centered at 400.4 eV (left) and 399.2 eV (right) in a 1:1 ratio.

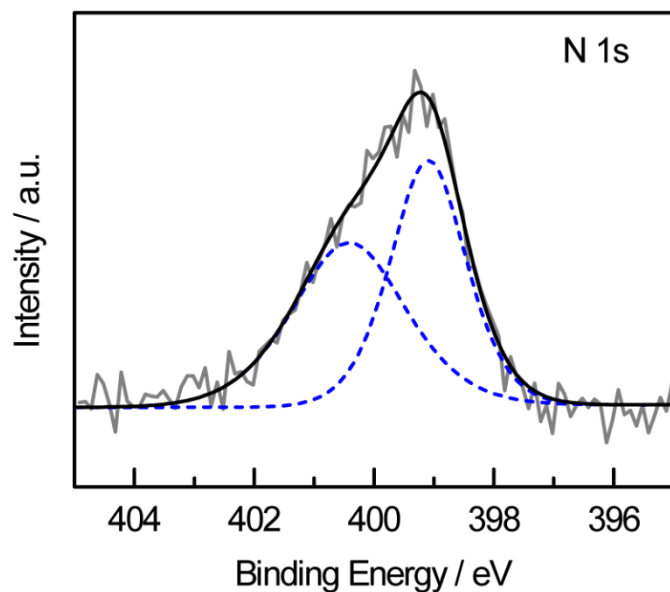


Figure S25. High-resolution N 1s XPS spectrum of GCC-phen-*o*-OEt. The peaks are centered at 400.4 eV (left) and 399.1 eV (right) in a 1:1 ratio.

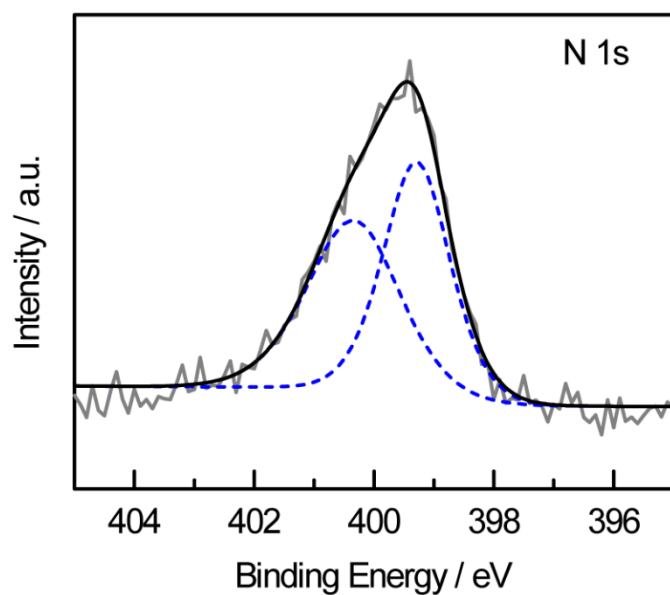


Figure S26. High-resolution N 1s XPS spectrum of GCC-phen-*m*-OEt. The peaks are centered at 400.3 eV (left) and 399.3 eV (right) in a 1:1 ratio.

References:

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