Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supporting Information

Manipulation and Measurement of pH sensitive Metal-Ligand Binding Using Electrochemical Proton Generation and Metal Detection

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S1. Fabrication of the BDD Ring Disc Electrode

A 600 µm thick wafer of high quality (minimal sp^2 content) boron doped diamond (BDD) was laser micromachined (E-355H-3-ATHI-O system, Oxford Lasers) into a column of 500 µm radius and a hollow cylinder of inner radius 760 µm and outer radius 810 µm. The BDD was then acid cleaned in KNO_3 (Sigma Aldrich) saturated, concentrated H_2SO_4 (>95 %, Fisher Chemical) for 30 minutes at ~300 °C until brown fumes were no longer observed and then sonicated in Milli-Q water (resistivity 18.2 MΩ cm at 25 °C) for 10 mins. The front surface of the BDD column and hollow cylinder were adhered to a glass slide using a thin layer of super glue (Loctite) and the rear surface sputtered (Moorfield) with Ti/Au (10/300 nm), before removing the glue with acetone and then annealing at 400 °C for 5 hours. The front face of the cylinder and surrounding hollow cylinder were placed on adhesive Gel-Pak (Gel-Pak, Hayward CA), onto which a vacuum grease coated teflon mould (cylindrical, 1.5 cm inner diameter and 3 cm outer diameter, depth = 1 cm), was also placed, and sealed in place with a thin layer of non-conductive epoxy resin (Epoxy Resin RX771C/NC, Aradur Hardener HY1300GB, Robnor Resins), see **Figure S1**. Insulated copper wires were individually connected, using a dissection microscope (Motic) to aid alignment to the sputtered Au contact pads on each electrode using conductive silver epoxy (Circuitworks, ITW Chemtronics). Finally, the mould was filled with the same non-conductive epoxy. Once dry (after ~24 hrs) the electrode was removed and the excess epoxy on the front surface polished back with silicon carbide paper (Carbimet, Buehler) of decreasing roughness to reveal the co-planar ring disc electrodes. Before use the electrodes were polished with alumina polish (0.05 µm Micropolish, Buehler) and rinsed with Milli-Q water.

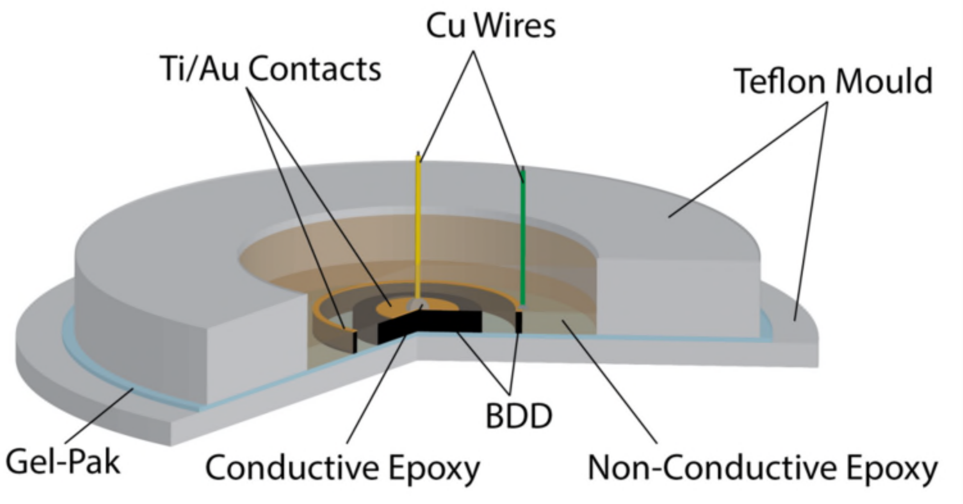

Figure S1: Schematic of BDD ring disc assembly in the teflon mould. Conductive silver epoxy is used to attach copper wires to the Ti/Au contacts on the rear of the electrodes, before sealing the arrangement with non-conductive epoxy.

S2. Electrochemical Set-Up and Instrumentation

For electrochemical detection of Cu^{2+} in solutions of 100 µM $Cu(NO_3)_2$ and 100 µM TETA with 0.1 M KNO_3 supporting electrolyte at bulk pH 2.5 - 5.01 (pH adjusted using 0.1 M HNO_3 and 0.1 M KOH), a simple three electrode arrangement was used; the BDD disc was connected as the working electrode *vs.* an SCE reference electrode and a Pt wire counter electrode. The BDD ring remained unconnected for these experiments. Cu was deposited on the electrode surface at -0.5 V for 60 s using an amperometric *i-t* method (CHI730A Potentiostat, CH Instruments Inc), ASV experiments were performed immediately following electrodeposition by scanning in a positive potential direction using linear sweep voltammetry from -0.25 V to +0.5 V at a potential scan rate of 0.1 V s^{-1}.

For Cu^{2+} detection with *in-situ* proton generation the detector electrode (disc) was set-up as described above. The generator (ring) electrode was connected as a working electrode, *vs.* a second Pt counter electrode, to a galvanostat (Keithley Source Meter). The electrodes were placed in a solution of 100 µM $Cu(NO_3)_2$ and 100 µM TETA with 0.1 M KNO_3 supporting electrolyte, adjusted to bulk pH 6.4 using KOH. To generate a local pH change, a constant current in the range 0.1 – 2 mA cm^{-2} was applied to the ring electrode using the galvanostat for a period of 300 s. After 300 s, with the current applied to the ring still being maintained, the potential at the detector electrode was switched on using the potentiostat (-0.5 V for 60 s vs. SCE as before) for electrodeposition of Cu^{2+}. The potential was then immediately swept from -0.25 V to +0.5 V at 0.1 V s^{-1} to strip electrodeposited Cu from the electrode surface.

S3. Normalised ASV Data Recorded under *In-situ* pH Generation Conditions

ASV data for Cu^{2+} stripping from the detector (disc) electrode in the presence of TETA at a range of constant generator (ring) currents (0.1 – 1.98 mA cm^{-2}) is shown in **Figure S3**, performed immediately following electrodeposition as described in **ESI S2.** The current data has been normalised with respect to $i_{p,\ max}$. Normalised peak current data is shown in **Table 1** in the main text, versus the applied ring current.

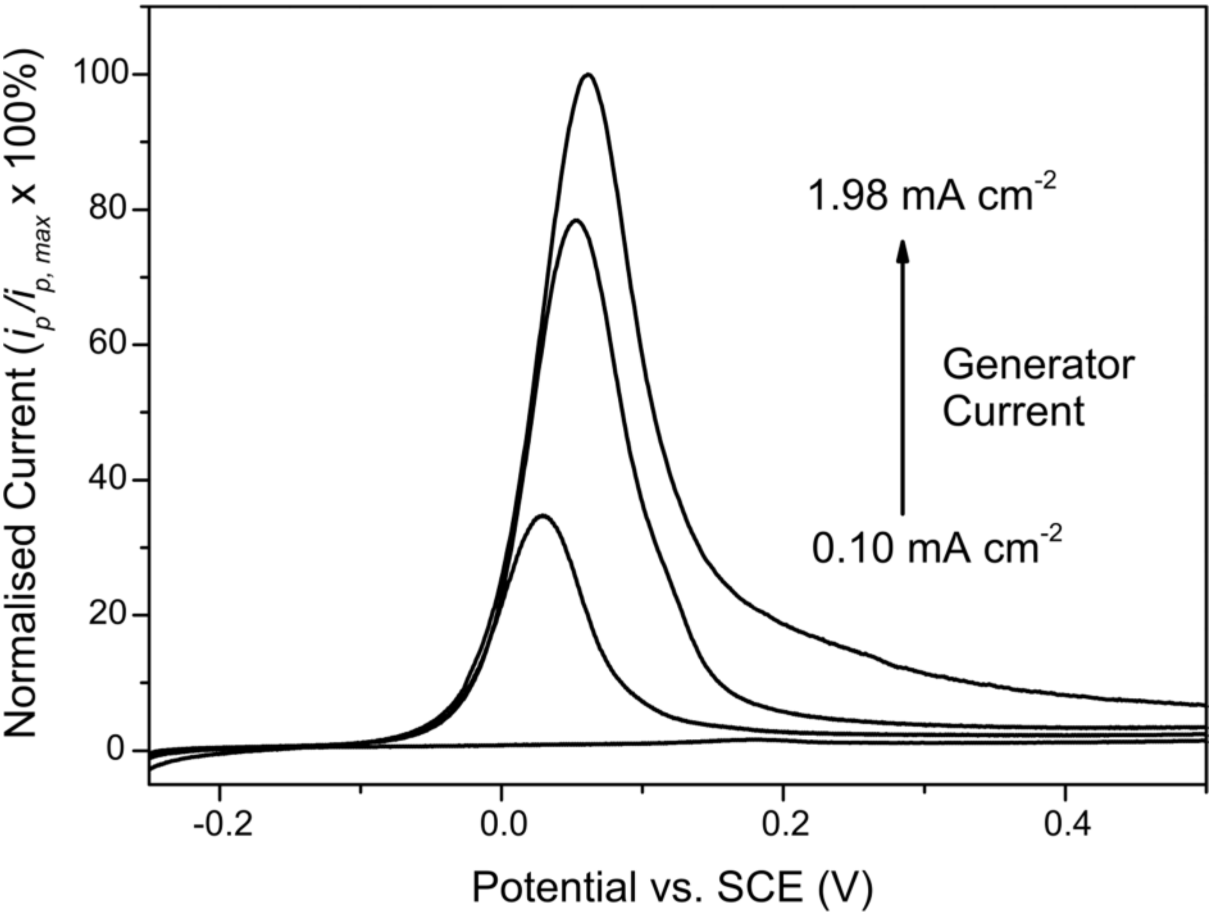

Figure S2. LSV data corresponding to **Table 1** in the main text, showing normalised stripping peaks ($i_p/i_{p,max}$ × 100%) of 100 µM Cu^{2+} in the presence of 100 µM TETA at the detector electrode, for a range of constant currents applied to the generator (0.1 – 1.98 mA cm^{-2}).