SUPPORTING INFORMATION

Phthalocyanines as a Pi-Pi Adsorption Strategy to Immobilize Catalyst on Carbon for Electrochemical Synthesis

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Electrochemical measurements and reagents-

All reagents used were commercially available unless stated otherwise. All chemicals were used as received. Electrochemical measurements were conducted with either a Pine Wavenow potentiostat or a CH Instruments 660D. For prolonged experiments at pH 10, a double junction was used containing 0.1 M phosphate buffer. If experiments were only a few hours, then the saturated calomel electrode (SCE) reference was found to be suitably stable. The potential of the reference was checked daily versus an SCE standard. Counter electrodes were carbon composites or carbon rods for small scale experiments, and unless stated otherwise a platinum plate for bulk electrolysis.

Solutions for bulk electrolysis involving CoTPc were made to achieve concentrations of 0.3 M carbonate at a pH of 10 with 5 x 10^{-5} M CoTPc, and 1.2 x 10^{-3} M sodium dodecyl sulfate (SDS). An example solution is made by dissolving 1.26 mg of CoTPc in 300 µL of DMSO, and 2 mg (7 eq) of SDS. A separate solution of 0.3 M carbonate buffer was made with 5 mg of SDS in 20 mL of buffer. Both solutions were sonicated briefly to dissolve solids. This solution was quite stable and could be used over the course of days.

For bulk electrolysis using pyrene-TEMPO and CoPTc, the catalyst were dissolved in acetonitrile and acetone, respectively, at a concentration of 4 x 10^{-4} M and vitreous carbon cubes of dimension ~1 cm by 0.5 cm were saturated with the catalyst solution and then dried in a vacuum oven at 60 Celsius. Both pyrene and CoTPc bulk electrolysis experiments contained acetonitrile at a ratio of 1:10 acetonitrile to buffer to help aid in dissolving the substrates.
Electrochemical oxidation of alcohols and work-up-

Once the reaction had passed theoretical current needed for full conversion or had diminished to 100’s of µA, the reaction was stopped. The solution was poured into a separatory funnel and the electrolysis cell and the vitreous carbon was rinsed with diethyl ether (~ 10 mL). The aqueous phase was made acidic by the addition of 0.3 M HCl until a pH of ~ 4 was obtained. The ether was then added to the separatory funnel and the organics were extracted. The vitreous carbon was washed two more times with ~ 5 mL of ether, and this ether was used to extract from the aqueous phase as well. The organic phases were combined and dried with anhydrous magnesium sulfate. The ether was removed by rotary evaporation and the crude re-dissolved in a small amount of 1:3 ethylacetate to hexane mixture. The mixture was passed through a small pipette column filled with a small plug of silica gel. The pipette column served to remove any leftover catalyst or solids. The solid material was not exhaustively purified instead the products were analyzed with $^1$H-NMR to obtain a yield for the major identifiable product. 4-nitrophthalonitrile was used an internal standard which has three distinct aromatic peaks, these are shown in the spectra of 4-trifluoromethyl benzaldehyde. Products were identified with known $^1$H-NMR spectra.1

Synthesis of 4-TEMPO-phthalonitrile-

In one iteration, 50 mL of dry DMF was degassed vigorously by bubbling nitrogen for 20 minutes. Under nitrogen atmosphere the reagents of 4-nitrophthalonitrile (3.001 g) and 4-hydroxy-TEMPO (3.401 g) were added followed by 10 grams of K$_2$CO$_3$. TEMPO is easier to remove in the end of the reaction and is recommended to be in an excess. The mixture was continued to be degassed for an additional 40 minutes at room temperature and then held under positive nitrogen pressure and room temperature with stirring. The reaction proceeds slowly and was monitored over the course of 2 days via TLC using a 50:50 hexane:ethylacetate mixture until complete. Once finished, 100 mL of DI water was added to the DMF which caused the product to precipitate. The mixture was left to sit for 3 hours, and then vacuum filtered. The off-white solid was washed with 2 liters of DI water in aliquots to remove the DMF and potassium carbonate. The solid was then dissolved in chloroform and passed through a clean fritted filter and the solvent was removed with rotary evaporation. The recovered light reddish solid was dried in a vacuum oven for 24 hours at 35 Celsius. The recovered mass was 4.85 g.

Synthesis of cobalt-TEMPO-phthalocyanine (CoTPc)-

Synthesis was performed in a 3-neck flask with the round bottom flask fitted with a condenser. The flask was purged with nitrogen and 8 mL of hexanol was added along with 1.8 gram of 4-TEMPO-phthalonitrile and 0.34 g of CoCl*6H$_2$O and 50 µL of DBU. The reaction was then brought to 120 Celsius while under nitrogen and maintained for 5 hours. It is advantageous to use an oil or wax bath when preparing phthalocyanines, the products can precipitate and become over-heated on the walls of the flask. The reaction was slowly cooled and then ~20 mL of hexane was added, which caused a precipitation of the CoTPc. After 20 minutes, the mixture was vacuum filtered. The solid was then washed with copious amounts of hexane
followed by diethyl ether. The crude solid was then washed via filtration with 300 mL of DI water in aliquots. Finally, the solid was dissolved in acetone and passed through a fritted filter. The remaining acetone was removed with rotary evaporation and the solid was dried under vacuum in a 60 Celsius oven for 12 hours. Final recovered mass was 0.91 grams (64% yield).

**Synthesis of pyrene-TEMPO-**

The synthesis of TEMPO-pyrene was performed as previously reported. The product was purified using silica gel column chromatography with 50:50 hexane:ethylacetate. $^1$H-NMR spectra was obtained by using phenylhydrazine to reduce the complex. Phenylhydrazine has some apparent overlap with the chemical shifts of pyrene-TEMPO, however, the spectra matched previous reported spectra nearly identically.$^1$

**Composite electrode fabrication-**

Composite electrodes were fabricated analogues to previous reports.$^2$ Briefly, a pre-weighed amount poly-methylmethacrylate was dissolved in ethylacetate (~1g/13 mL). Graphite powder 7-11 µm (Alfa) was then added to the mixture in a ratio of 2:1 graphite, followed by addition of catalyst at a ratio of 4E-5 moles catalyst/ 1 gram graphite. The mixture was then vortex mixed for 1 minute. The slurry is then dried on a non-stick surface until it reaches a rubber-like consistency and it is then placed in premade PMMA templates and dried under mild pressure in a heat press at 50 Celsius.
Figure S1 Oxidation of 2 mM benzyl alcohol in pH ~10 carbonate 0.1 M at 100 mV/s scan rate. The CoTPc electrodes were the same used in Figure 2 of the main text. For carbon electrodes, the black solid trace is nearly identical to dotted black trace, which indicates that the carbon is nearly inert to alcohol oxidation within the aqueous potential window.

Figure S2 Cyclic voltammetry of CoTPc and pyrene-TEMPO modified electrodes in benzyl al in pH ~10 carbonate 0.3 M at 100 mV/s scan rate. The CoTPc and pyrene electrodes were the same used in Figure 2 of the main text. The reductive wave was used for integration to determine the molar coverage per unit area. Diameter of each electrode was 3 mm.
XPS Measurements-

Spectra were obtained using a Kratos Axis Ultra instrument, with 300x700 μm analysis area, using monochromatic Al K-α radiation (1486.6 eV kinetic energy). Both survey and region spectra for all elements observed were taken. Intensities were corrected using sensitivity factors for the Kratos instrument - Co = 3.59, N = 0.477, O = 0.780. Samples for XPS used carbon Toray paper as a substrate, and the same electrolysis conditions were used as those for the vitreous carbon bulk electrolysis experiments. A potential of 0.8 V vs. SCE was held for 1 hour in an undivided cell. After electrolysis the electrodes were washed with copious amounts of DI water, dried, and introduced to the XPS vacuum system and allowed to degas for several hours before analysis.

As shown in the survey spectra in Figure S3, the blank carbon sample shows a large peak for C 1s, and a small peak for O 1s, presumably due to interactions in air. The carbon sample loaded with CoTPc and simply dried before analysis showed peaks for N 1s, Co 2p, and a larger peak for O1, as expected from the molecular composition. Small peaks are also observed for Na and F. The sodium most likely originates from the buffer solution, and it is hypothesized that the small amount of fluorine is from the carbon paper. It is possible that trace fluorine is present from small amounts of binder used to hold the propriety carbon paper together, extracted to the XPS-sensitive surface region by the solvent used for drop casting the CoTPc.

Figure S4 shows a higher resolution scan over the Co 2p region, showing the expected 2p3/2 – 2p1/2 doublet. It can be seen that there is no significant Co intensity on the blank carbon paper. The maximum Co signal is seen for the sample prepared by drop casting CoTPc with no subsequent electrolysis. For the two examples exposed to electrolysis conditions, the amount of Co remaining on the surface is substantially reduced.
**Figure S3** Survey scan of carbon paper both with and without CoTPc adsorption, as well as after electrolysis with and without CoTPc/surfactant in the electrolysis solution.

**Figure S4** High resolution XPS spectra of Co 2p region from the catalyst CoTPc loaded on carbon paper.
Figure S5 UV-Vis spectra of CoTPc

Figure S6 ESI-mass spectra of CoTPc
$^1$H-NMR Spectra of pyrene-TEMPO (400 MHz CDCl$_3$)

$^1$H-NMR spectra of 4-TEMPO-phthalonitrile (400 MHz CDCl$_3$)
$^1$H-NMR Spectra of benzil (400 MHz CDCl$_3$)- 1 mmol undivided cell CoTPc

$^1$H-NMR Spectra of benzaldehyde (400 MHz CDCl$_3$)-1 mmol divided cell CoTPc
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$^1$H-NMR of 3-methyl benzaldehyde from divided cell with CoTPc (400 MHz CDCl$_3$)

$^1$H-NMR of 4-bromo benzaldehyde from divided cell with CoTPc (400 MHz CDCl$_3$)
\(^1\)H-NMR of piperonal from divided cell with CoTPc (400 MHz CDCl\textsubscript{3})
$^1$H-NMR of 4-chloro benzaldehyde I from divided cell with CoTPc (400 MHz CDCl$_3$)

$^1$H-NMR of the oxidation products from undivided cell with 3mM 4-methoxy-TEMO (400 MHz CDCl$_3$)
GC-MS spectra of the oxidative product from phenethyl alcohol and CoTPc based electrolysis
GC-MS spectra of the oxidative product from piperonyl alcohol and CoTPc based electrolysis in undivided cell
GC-MS spectra of the oxidative product(s) from 4-trifluoromethyl benzyl alcohol and CoTPc based electrolysis
GC-MS spectra of the oxidative product(s) from benzyl alcohol and CoTPc based electrolysis (undivided cell) which was stopped mid-reaction.
GC-MS spectra of the oxidative product from benzyl alcohol and CoTPc based electrolysis in a divided cell.
GC-MS of the oxidation products from undivided cell with 3mM 4-methoxy-TEMPO
GC-MS spectra of the oxidative product from benzyl alcohol and CoTPc based electrolysis in an undivided cell
References