

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

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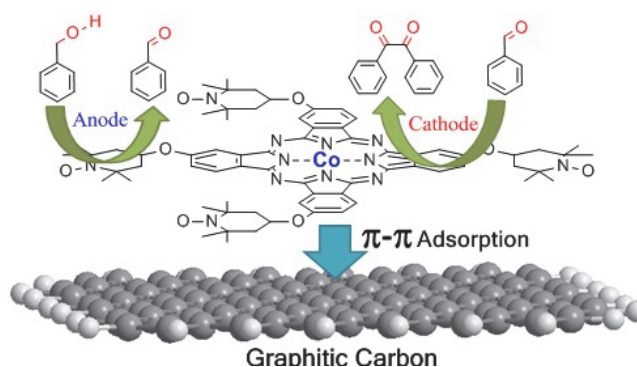
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Abstract In most electrochemical synthesis, reactions are happening at or near the electrode surface. For catalyzed reactions, ideally, the electrode surface would solely contain the catalyst, which then simplifies purification and lowers the amount of catalyst needed. Here, a new strategy involving phthalocyanines (Pc) to immobilize catalysts onto carbon electrode surfaces is presented. The large π structure of the Pc enables adsorption to the sp^2 structure of graphitic carbon. TEMPO modified Pc were chosen as a proof of concept to test the new immobilization strategy. It was found that the TEMPO-Pc derivatives functioned similarly or better than the widely used pyrene adsorption method. Interestingly, the new TEMPO-Pc catalyst appears to facilitate a cascade reaction involving both the anode and the cathode. The first step is the generation of an aryl aldehyde (anode) followed by the reduction of the aryl aldehyde in a pinacol type coupling reaction at the cathode. The last step is the oxidation of a hydrobenzoin to create benzil. This work demonstrates the unique ability of electrochemistry and bi-functional catalysts to enable multi-step chemical transformations, performing both reductive and oxidative transformations in one pot.

Keywords Electrochemistry, phthalocyanines, alcohol oxidation, electro-synthesis, pyrene.

Introduction-

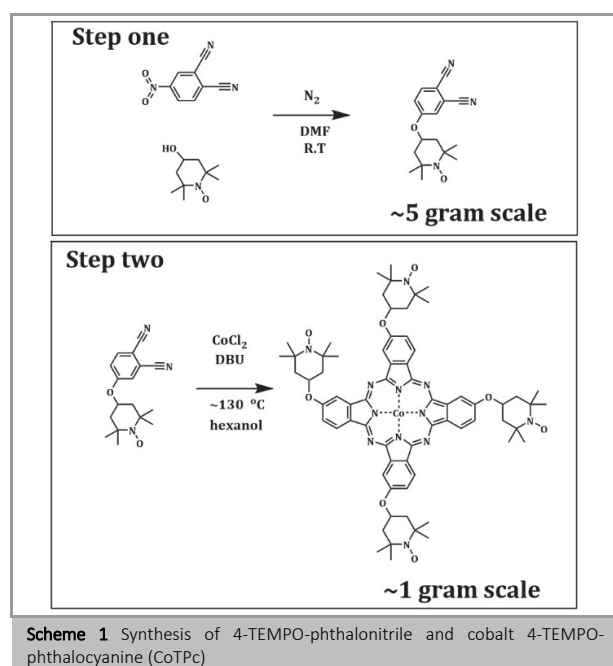
Immobilizing catalysts to electrode surfaces is of great importance for applied electrochemistry as a whole, including: sensors,¹ energy conversion,² electrofuels, solar fuels,³ and electrochemical synthesis.⁴ The attachment of catalysts to electrode surfaces can turn an inert electrode surface into one that is highly catalytic. In terms of electrochemical synthesis, surface-bound catalysts have a number of advantages, such as low catalyst loading, simplified product purification, lowered over-potentials which limit unfavorable side reactions, and reduced energy consumption. Surface bound catalysts also have the potential to be reused many times over, or possess the ability to be regenerated easily.

As a platform for modifying electrodes with surface bound catalysts, sp^2 carbon is arguably one of the most favorable supporting electrodes. Carbon is ubiquitous and inherently low cost. Carbon also has excellent chemical stability, is highly conductive, and kinetically fast. For these reasons, carbon has been a historically popular electrode material in the field of electrochemistry.⁵ Methods to immobilize catalytic moieties to carbon are numerous, which include covalent grafting, dropcasting, polymer coatings, electropolymerization, and adsorption.⁶ Of these methods, adsorption is popular and almost exclusively uses pyrene π - π interactions with a carbon surface. Modified electrodes using pyrene as an immobilization moiety have found utilization in a wide range of applications, with hundreds of articles now highlighting the advantage of the system.⁷ While quite popular, pyrene has been reported as having stability issues, even when 8 pyrene units are attached to a single redox center.⁸ To address these issues, we were motivated to find an alternative adsorptive functional group, since there is a lack of adsorptive functional groups other than pyrene in the literature. Ostensibly, a new pyrene alternative would simply consist of a large aromatic complex, that is low cost, easy to derivatize, and has favorable chemical stability.

Herein, we report phthalocyanines (Pc) as a low-cost pyrene substitute. Phthalocyanines are currently used in many industrial applications and are mass produced on the ton scale.⁹ Pcs also have a rich history in the field of electrochemical and chemical catalysis due to their stability and high activity.¹⁰ Typically phthalocyanines are used for their catalytic metal center,¹¹ for applications such as thiol oxidation,¹² CO_2 reduction,¹³ or oxygen reduction.¹⁴ In this work, it was hypothesized that the large aromatic Pc ring could be used to anchor catalytic moieties to a carbon surface. Indeed, phthalocyanines are well known to adsorb/interact with graphitic and metallic surfaces. Specifically,

phthalocyanines have a reported adsorption energy of a few 100 kJ/mole, while pyrene is reported as 42 kJ/mole.¹⁵

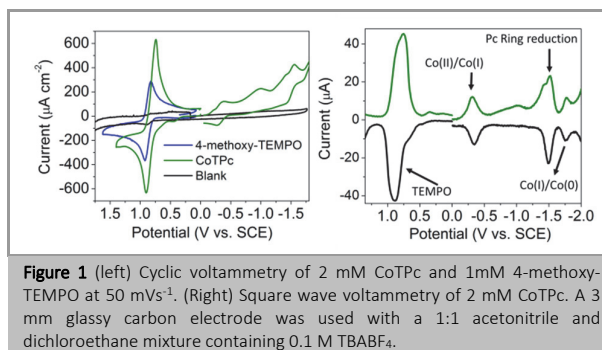
To test this hypothesis, TEMPO derivatized phthalocyanes were chosen. Currently, only two reports exist for the derivatization of a phthalocyanine with TEMPO, both are a demonstration for the detection of ascorbic acid.¹⁶ The Pc described in both reports contained a zinc metal center and was not used as an adsorbed catalyst on carbon. Our work herein presents the synthesis and characterization of cobalt phthalocyanine modified with TEMPO (CoTPc), which until now is an unknown compound. The catalyst was integrated into composite electrodes and tested for activity and catalytic stability. Finally, the TEMPO-Pc catalyst is compared to 4-methoxy-TEMPO in solution as well as with the already reported pyrene-TEMPO catalyst.



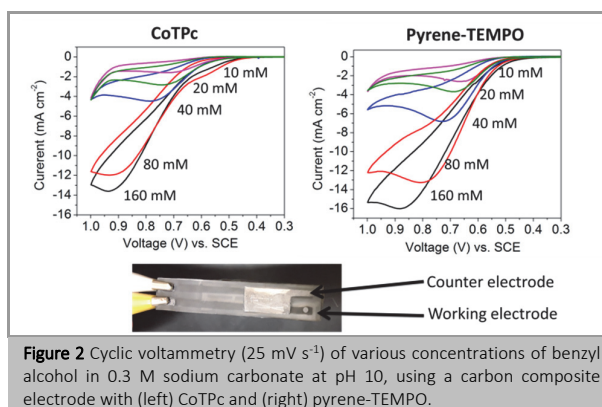
TEMPO was chosen as it has well known activity for the oxidation of alcohols. Historically alcohol oxidation typically utilized stoichiometric oxidants,¹⁷ such as chromium oxides, Dess-Martin periodinane,¹⁸ or activated DMSO (Swern), and more recently aerobic oxidations.¹⁹ In the past few years, TEMPO has gained significant attention for alcohol oxidation and a current review proposes their use for commercial applications.²⁰ TEMPO modified electrodes are well known; however, only a handful of reports are related to adsorption based immobilization.²¹

Scheme 1 shows the 2-step synthesis of the previously unreported CoTPc catalyst used in this work. The reaction starts with the synthesis of 4-TEMPO phthalonitrile. Here, yields of 4-TEMPO phthalonitrile were ~80 % with no optimization. The starting material 4-nitrophthalonitrile is relatively inexpensive (\$1.9 U.S dollar /gram) and available from many chemical retailers. Nitro-displacement reactions are popular within the field of derivatizing phthalocyanines.²² In general alcohols, thiols, or amines can be used in these

displacement reactions, which makes the scope of possible derivatives large.



The CoTPc synthesis was straight forward; however, yields were low initially. It was found to be advantageous to decrease solvent and base amounts relative to the dinitrile. Details on the synthesis can be found in the SI. While a full optimization of CoTPc synthesis was not undertaken, ~50% yields at gram-scale were realized. The dinitrile was characterized by ¹H-NMR and GC-MS. CoTPc was confirmed through UV-Vis and ESI-MS, as shown in Figure S5 & S6. The UV-Vis spectra of CoTPc had the typical Q and Soret features for Pcs, and the molar absorptivity was calculated to be 133,100 M⁻¹ cm⁻¹. Exceptionally high molar absorptivity is typical of Pcs.



Phthalocyanines can also be characterized through electrochemistry, given that they have characteristic redox properties. Figure 1 shows typical redox behavior reported for cobalt phthalocyanines with an apparent Co(^{II}/^I) couple near -0.25 V vs. SCE and a ring reduction at -1.5 V vs. SCE and Co(^I/⁰) near -1.7 V vs. SCE.²³ There is also a redox process which is presumably from TEMPO related formation of the oxoammonium cation species on TEMPO.²⁴ The generation of the oxoammonium species is critical for the oxidation of alcohols.

Figure 2 has cyclic voltammograms of CoTPc and pyrene-TEMPO composite electrodes for the oxidation of benzyl alcohol. As expected the current increases with increasing substrate concentration. The new CoTPc catalyst performs similar to the pyrene-TEMPO modified electrode.

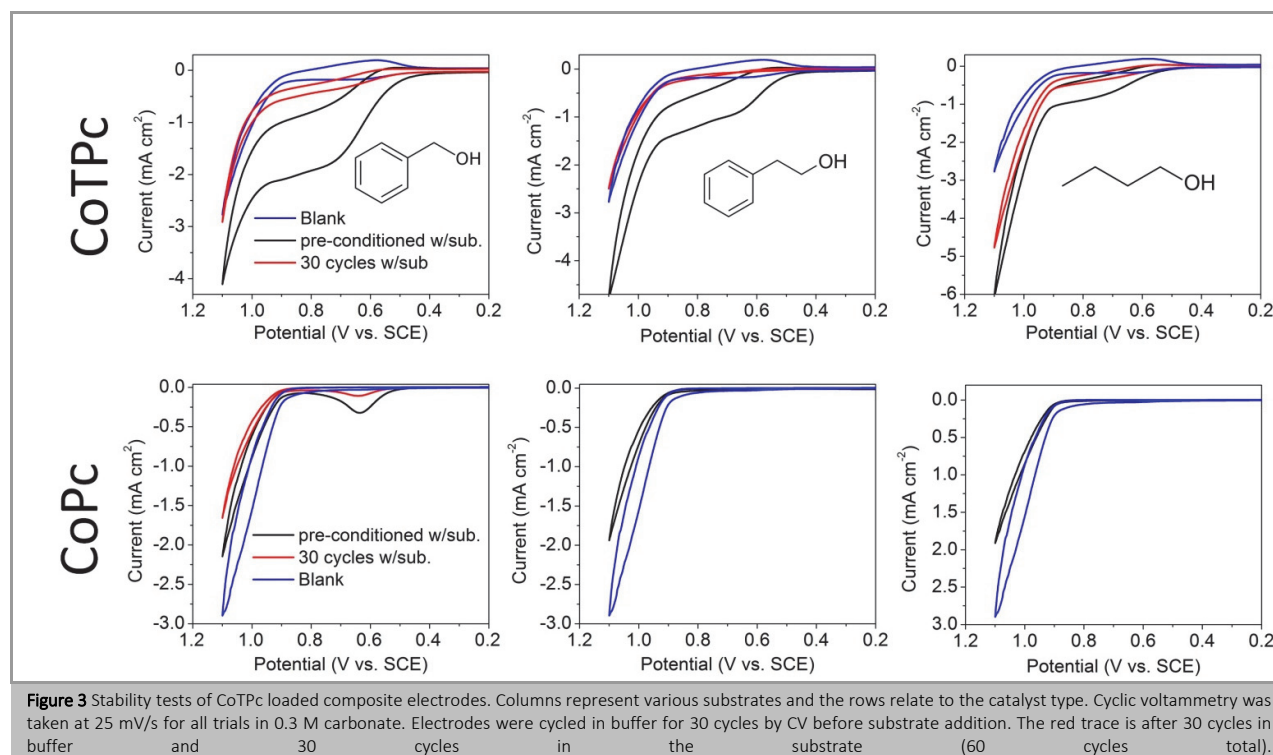


Figure 3 Stability tests of CoTPc loaded composite electrodes. Columns represent various substrates and the rows relate to the catalyst type. Cyclic voltammetry was taken at 25 mV/s for all trials in 0.3 M carbonate. Electrodes were cycled in buffer for 30 cycles by CV before substrate addition. The red trace is after 30 cycles in buffer and 30 cycles in the substrate (60 cycles total).

A somewhat unexpected result is that the pyrene-TEMPO catalyst is passing about 2 mA more current than the CoTPc electrodes at higher substrate concentrations. Differences in the coverage of the catalyst may explain the higher currents, where smaller pyrene molecules are better able to coat the graphite surface. However, Figure S2 shows that peaks relating to surface adsorbed catalyst are actually higher for the CoTPc modified electrode.

When the peaks from the cyclic voltammograms are integrated, a surface coverage of $4.0 \pm 0.3 \text{ nmol cm}^{-2}$ for CoTPc and $1.9 \pm 0.4 \text{ nmol cm}^{-2}$ for pyrene are observed. Error bars are from three separate measurements where the electrode was repeatedly sanded to expose a fresh surface. The integration results imply that there is $\sim 2\times$ the pyrene on the surface of the CoTPc electrode, which is reasonable considering each Pc contains four TEMPO molecules. This also implies that there is $\sim 2\times$ as much pyrene-TEMPO on the surface given that each pyrene only has one TEMPO moiety. Related to this, if any of the CoTPc is lost from the surface, it would have a significant detrimental impact on the overall current. This may explain why the pyrene TEMPO has somewhat higher currents at higher concentrations. Overall, Figure 2 is compelling evidence that Pc could be used as an alternative to pyrene as an adsorption moiety.

Cyclic voltammetry is a powerful tool to investigate stability and activity of a surface-bound catalyst. Figure 3 represents a stress test for the desorption of the catalyst from a graphite surface. The black traces are initial voltammograms in a solution containing the substrates of benzyl alcohol, phenethyl alcohol, and butanol. The black trace is generated after the electrode has undergone cycling in a 0.3 M carbonate buffer solution. Even after cycling in the buffer, large catalytic currents are still observed for all three substrates. The red

traces in Figure 3 indicated 30 cycles in the buffer solution containing substrate (60 total cycles on the electrode). Moving across the top row of Figure 3, the CoTPc modified electrodes see significant loss of catalysis as a function of the substrate. The loss of activity is amplified the most with the substrate phenethyl alcohol.

From Figure 3, it is also apparent that the cobalt metal center is active in an oxidative process with benzyl alcohol. Interestingly, it seems that CoPc is only active for the oxidation of benzylic alcohols and is completely inactive in the solvent window for phenethyl alcohol and butanol oxidation. The activity of the metal center is a potential major advantage of Pc over pyrene, in that the adsorption moiety can also have organometallic electrocatalytic properties. Bi-functional catalysts can enable cascade reactions. Cascade reactions are often found in biological systems²⁵ and have been proposed for total synthesis²⁶ and CO₂ conversion.²⁷ Discussed later is a cascade reaction that appears to be promoted by the CoTPc catalyst.

Given the lack of stability of CoTPc, it was hypothesized that CoTPc was becoming detached from the surface. X-ray photoelectron spectroscopy (XPS) was performed on carbon loaded with CoTPc to determine if the catalyst was being lost. Details on these measurements can be found in the SI. As shown in Figure S3 and S4, it was found that cobalt was still present on the surface even after an hour of electrolysis in the presence of substrate. However, there was a measurable loss of $\sim 30\%$ of cobalt and nitrogen from the surface over time. Nitrogen levels were lost at almost the exact same rate as the cobalt. Loss of catalysis could be related to both loss of CoTPc as well as TEMPO decomposition. Degradation of TEMPO at a similar pH has been reported under prolonged electrolysis.²⁸ At the present, it is unclear what the

culprit for diminished catalysis is, but a solution to the degradation problem is presented below.

After characterizing the stability of the catalyst as well as the activity towards differing substrates, bulk electrolysis was attempted. Initial attempts at bulk electrolysis of alcohols were not successful, as the reaction halted midway through the electrolysis. Possibly, it is for this reason that a seminal report of alcohol oxidation using pyrene-TEMPO had a small amount of the catalyst dissolved in solution during electrolysis.²⁴ If the catalyst is present in solution, even in very low concentration, the electrode can be regenerated in-situ over time.

The previous report used a 5×10^{-5} M concentration of pyrene-TEMPO catalyst in the electrolysis solution and this concentration was chosen here as the minimum concentration for CoTPc.²⁴ In order to make the CoTPc disperse in aqueous solutions, the surfactant sodium dodecylsulfate (SDS) was used in a low concentration. The dispersions were stable for weeks and details on the preparation can be found in the SI.

XPS analysis was performed on electrodes exposed to the surfactant/CoTPc solution (Figure S3 and S4) and it was found that there was a loss of ~70% of the Co signal from that of a fresh electrode. However, there was still significant Co present on the electrode surface. The surfactant is likely facilitating the release of CoTPc from the surface, but given that the electrolysis can maintain currents for hours, the CoTPc must be able to re-absorb to the surface.

The ability of the CoTPc catalyst to maintain activity for prolonged alcohol oxidation (bulk electrolysis) is shown in Figure 4. Instead of carbon composites, high surface area vitreous carbon was used, this helped to maintain a large active surface area and maintain higher currents. Figure 4 has a comparison of CoPc, CoTPc and pyrene-TEMPO catalysts. Surprisingly even at low concentrations of 0.0002 M, the dissolved catalyst of 4-methoxy-TEMPO was still measurably active. As an attempt to directly compare catalysts, the concentration of 4-methoxy-TEMPO was 4X the concentration of CoTPc, since CoTPc has 4 TEMPO molecules per Pc molecule. However, the currents with 4-methoxy-TEMPO were much lower than the adsorption-based catalyst, and electrolysis involving 4-methoxy TEMPO was stopped after ~8 hours, given that the time needed for full electrolysis would be impractical. Similar to 4-methoxy-TEMPO, the pyrene catalyst also deactivated before the full electrolysis was complete. Both of these catalyst deactivated near the midway point of the reaction and the results are shown in Table 1. As expected the major product for these reactions was benzaldehyde.

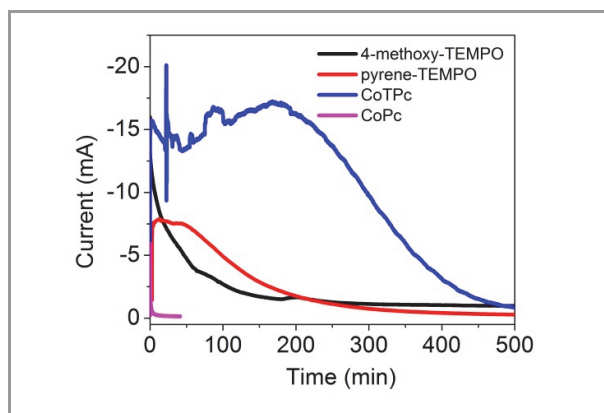
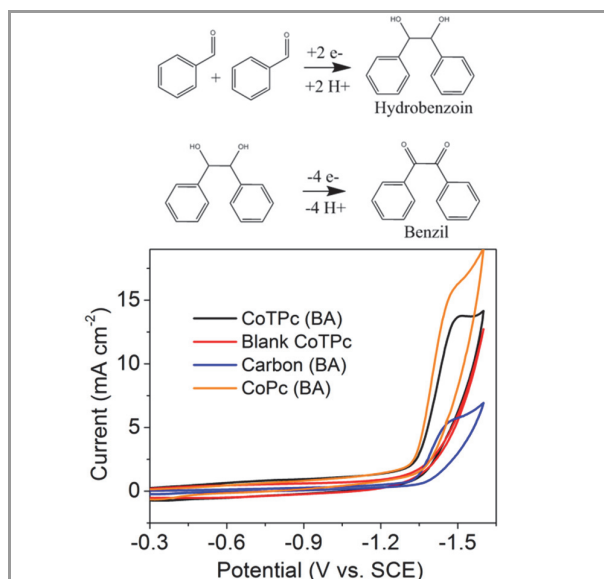


Figure 4 Bulk electrolysis of 1 mmol of benzyl alcohol with various TEMPO and Pc based catalyst. Applied potential was 0.8 V vs. SCE using a vitreous carbon working electrode in 15 mL of solution.

CoTPc had large sustained currents for multiple hours of electrolysis. Perhaps the increased and prolonged current over the pyrene catalyst was due to CoTPc having 4 times the TEMPO moieties. In fact the charge passed well exceeded what was expected for the reaction. Interestingly, when the product was isolated and characterized by ¹H-NMR and GC-MS, the nearly single product species was benzil. To the best of our knowledge, benzil is not a known oxidation product of benzyl alcohol, but it is likely formed from the oxidation of hydrobenzoin, which in theory could be formed through coupling at the cathode. Scheme 2 represents the hypothesized route for the formation of benzoin. For the coupling reaction to occur, the reduction of benzaldehyde (BA) would need to be favored over hydrogen evolution in order to create hydrobenzoin. At the bottom of Scheme 2 is evidence of catalyzed BA reduction when in the presence of CoTPc over that of a non-modified electrode. Drastic current increases are seen when the electrode is in the presence of CoTPc and CoPc. Logically, the main reaction at the cathode will involve the one occurring at the lowest overpotential which in the case of a CoTPc modified electrode would be benzaldehyde reduction.



Scheme 2 (Top) Scheme for the coupling reaction involving benzaldehyde to

form benzil. (Bottom) Cyclic voltammograms at 50 mV s⁻¹ in 0.3 M sodium carbonate pH 10 in the presence and absence of benzaldehyde (BA).

It is not entirely surprising that these coupling products are being formed. Electrochemical reduction of aldehydes to form hydrobenzoin has been reported at lead and mercury electrodes.²⁹ In fact, benzoin compounds are found as products in partial electrolysis experiments, as shown in the GC-MS in the SI. Typically, a suppression of side reactions (hydrogen evolution) is necessary to reduce benzaldehyde in alkaline solutions, related, phthalocyanines have been shown to be able to suppress side reactions in the selective reduction of CO₂, which occurs at potentials similar to what BA is reduced at in our system.³⁰ In Scheme 2 it is also shown that CoPc modified electrodes are also catalytic for BA reduction, giving some evidence that the metal center may be involved in the reaction.

To try and determine if CoTPc was fully responsible for the coupling reaction, experiments were performed with a higher concentration of 4-methoxy-TEMPO. The increased concentration (3 mM) allowed the reaction to maintain catalysis for a longer period of time. It was found that benzil could be created under this set of conditions, however, it was not the main product in the reaction (see table). Benzil by-product from a 4-acetamido-TEMPO based oxidation of benzyl alcohol has also been recently reported in similar amounts.³¹ It then appears that BA reduction is in competition with

hydrogen evolution for a variety of systems, and in the case of CoTPc, BA reduction is seemingly favoured.

The coupling products were not limited to benzyl alcohol. GC-MS and ¹H-NMR data for the oxidation of trifluoromethyl benzyl alcohol showed a significant amount of coupling products some of which were not fully oxidized to the diketone. The coupling is a potential major reason for the low yield of the aldehyde with this substrate. During the workup, it was the aim to isolate aldehydes and coupling products were most likely lost to the plug of silica used in purification.

Table 1 contains a brief summary for selected benzyl alcohol oxidations as well as a few sample benzylic and non-benzylic alcohol oxidations. When in a divided cell, the coupling products seen with CoTPc were completely absent, which is reasonable, since it is expected that benzoin is created at the cathode. The substrate piperonyl had no coupling products as well; however, this reaction was stopped at the theoretical charge needed for full electrolysis. The yield was also somewhat low with this reaction and it is possible that the coupling products were removed on the work-up.

Foreshadowing from Figure 3, the substrates of phenethyl ether and butanol were not successfully fully oxidized. In less than 30 minutes, these reactions had significant losses in current. Both of the reactions were made acidic and extracted with ethyl acetate and analyzed with GC-

Table 1 Results from the bulk electrolysis of various alcohol containing substrates. All conditions are for an undivided cell unless stated otherwise.

Substrate-Electrode	Scale (mmol)	Product	Conversion (%)	Yield (%)	Faradaic efficiency
Benzyl alcohol-CoTPc	1	benzil	91	48 ¹	85
Benzyl alcohol-CoTPc (Divided)	1	aldehyde	82	70 ¹	79
Benzyl alcohol-Pyrene TEMPO	1	aldehyde	35	28 ¹	70
Benzyl alcohol-4-methoxy-TEMPO	1	aldehyde	46	37 ¹	69
Phenethyl alcohol-CoTPc	2	aldehyde	< 5	na	na
Piperonyl alcohol-CoTPc	2	aldehyde	78	45 ¹	23
Butanol-CoTPc	2	carboxylic	< 5	na	na
4-trifluoromethyl-benzyl alcohol-CoTPc	1	aldehyde	100	12 ¹	8
4-trifluoromethyl-benzyl alcohol-CoTPc (Divided)	2	aldehyde	100	54 ²	46
Piperonyl alcohol-CoTPc (Divided)	1	aldehyde	100	88 ²	90
4-bromo-benzyl alcohol-CoTPc (Divided)	0.4	aldehyde	100	90 ²	90
4-chloro-benzyl alcohol-CoTPc (Divided)	0.4	aldehyde	100	74 ²	67
3-methyl-benzyl alcohol-CoTPc (Divided)	0.8	aldehyde	100	92 ²	81
-Benzyl alcohol-4-methoxy-TEMPO (3 mM)	1	aldehyde Benzil	>90	74 ¹ 4 ¹	69 11

¹Yields were calculated by ¹H-NMR using 4-nitrophthalonitrile as internal standard. ²Yields were calculated by mass. Phenethyl alcohol and butanol products were identified by GC-MS and the exact yield is unknown. The yield and faradaic efficiency are related to the identifiable products, the remaining percentage was either lost during work-up or are from side reactions which could not be quantified. Conversion percentage is the amount of substrate recovered after electrolysis compared with the initial substrate concentration.

MS. The major products appeared to be the aldehyde for phenethyl ether and the carboxylic acid for butanol. At the present time, it is unclear why these substrates deactivate the electrode so quickly. Related, the previous study with pyrene-TEMPO focused solely on benzylic alcohols.²⁴

In summary, phthalocyanines were tested as an adsorption moiety to immobilize molecular electrochemical catalyst. As a proof of concept, a new TEMPO modified cobalt phthalocyanine was synthesized and characterized extensively with electrochemistry. The catalyst showed excellent near term

stability for the oxidation of alcohols in aqueous systems and had initial small scale voltammetry similar to that of the pyrene-TEMPO catalyst. A strategy was developed to obtain longer term catalysis utilizing low concentrations of dissolved CoTPc catalyst. The CoTPc catalyst appeared to enable a cascade pinacol type coupling of aldehydes which demonstrates both the utility of electrochemical synthesis as well as the bi-functionality of the phthalocyanine catalyst. Overall, this initial study is motivating to explore the concept of phthalocyanine based adsorption for catalyst immobilization in more detail. Given that phthalocyanines are low-cost, easily derivatized, readily adsorb onto carbon, and shown here can enable unique chemistries.

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Acknowledgment

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

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