Electronic Supplementary Material (ESI) for New Journal of Chemistry

A heterogeneous water oxidation catalyst from dicobalt octacarbonyl and 1,2-bis(diphenylphosphino)ethane

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New Journal of Chemistry

Supporting Information

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Materials

Commercially available xylenes (J. T. Baker, ACS Reagent Grade), 1,2-bis(diphenylphosphino)ethane (Aldrich, 97%) , Xantphos (Strem), 2,2'-bis(diphenylphosphino)diphenyl ether (Aldrich), nitric acid (BDH, 67–70%, trace metals analysis grade), sulfuric acid (J. T. Baker, 96%, ACS Reagent Grade), potassium phosphate monobasic (Sigma Life Science, >99.0%), hydrogen peroxide (J. T. Baker, 30%, ACS Reagent Grade), potassium nitrate (Acros Organics, ACS Reagent Grade), sodium sulfate (Aldrich, ACS Reagent Grade), sodium acetate (Aldrich, ACS Reagent Grade), sodium tetraborate decahydrate ("borax," Mallinckrodt, ACS Reagent Grade), boric acid (J. T. Baker, ACS Reagent Grade), and potassium hydroxide (J. T. Baker, ACS Reagent Grade) were used as received. Dicobalt octacarbonyl (Strem, stabilized with 1-5% hexane) could be used as received, but required recrystallization from pentane after long periods (acceptable if bright orange or red, but no darker). Potassium bromide (Acros Organics, 99+%, spectroscopic grade), was dried over an open flame in a Schlenck flask under vacuum immediately prior to use.

Synthetic Procedures

Mass balance Studies

Trials were conducted in triplicate (precise data in table below). Small Teflon-coated stirbars were placed in glass vials (9×85 mm, Exetainer® by Labco Limited), and their combined mass recorded (open to air). The vials were brought into a nitrogen-filled glovebox and were charged with *ca.* 100 μmol each of $Co_2(CO)_8$ (freshly recrystallized from pentane) and dppe. The vials were then each sealed with a threaded cap with a Teflon/rubber layered septum, and removed from the glovebox. Xylenes (800 μL, freshly sparged with dry nitrogen for 30 minutes) was added by syringe, and the resulting mixture was stirred at ambient temperature for 5 minutes, before being inserted into a 2 cm deep aluminum heating block, and stirred for 1.5 hours at 160 °C. The vials were then removed and allowed to cool to ambient temperature. Volatiles were removed by vacuum, and the contents were dried for 15 hours at ambient temperature and < 1 torr. The caps were removed, and the precise mass of each vial, including stirbar and solid products, was determined (open to air). Xylenes (800 μL) was added to each vial by syringe, and the resulting mixtures were stirred open to the atmosphere for 72 hours at ambient temperature. Volatiles were removed by vacuum, and the contents were dried for 15 hours at ambient temperature and < 1 torr. The caps were removed, and the precise mass of each vial, including stirbar and solid products, was determined (open to air).

Trial	A	B	C
Mass of vial + stirbar	11.446 g	11.7645 g	11.8234 g
Mass of $Co_2(CO)_8$	34.0 mg 99.4 μmol	36.7 mg 107.3 μmol	34.5 mg 100.9 μmol
Mass of dppe	39.6 mg 99.4 μmol	42.5 mg 106.7 μmol	40.5 mg 101.7 μmol
Δ Mass for thermolysis	−15.1 mg −20.5 %[a] 539 μmol CO[b] 5.4 equiv. CO[c]	−17.7 mg −22.3 %[a] 632 μmol CO[b] 5.9 equiv. CO[c]	−21.4 mg −28.5 %[a] 764 μmol CO[b] 7.6 equiv. CO[c]
Δ Mass for aeration	+2.7 mg +3.7 %	+3.3 mg +4.2 %	+6.6 mg +8.8 %
Δ Mass total	−12.4 mg −18.8 %	−14.4 mg −18.2 %	−14.8 mg −19.7 %

[a] % = 100 × (Δ Mass) / ([mass $Co_2(CO)_8$] + [mass dppe]). [b] Assuming all mass lost is released CO. [c] Making previous assumption, and calculating based on moles of $Co_2(CO)_8$.

Characterization of 1

Microscopy/EDX

High resolution transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy in the TEM (TEM-EDX) were used to determine particle size, crystallinity, and elemental composition with an FEI Tecnai Osiris TEM operating at 200 kV. TEM images and TEM-EDX spectra were taken using silicon monoxide coated TEM grids (Ted Pella, Product #01829) in order to monitor carbon content in the as-synthesized material. For studies of sample alteration after prolonged electrolysis in different electrolytes, scanning electron microscope (SEM) images and SEM-EDX spectra of the as-deposited (below) and post-electrolysis (page S18) electrodes were taken using the electrode preparation procedure described below and a Hitachi SU-70 SEM.

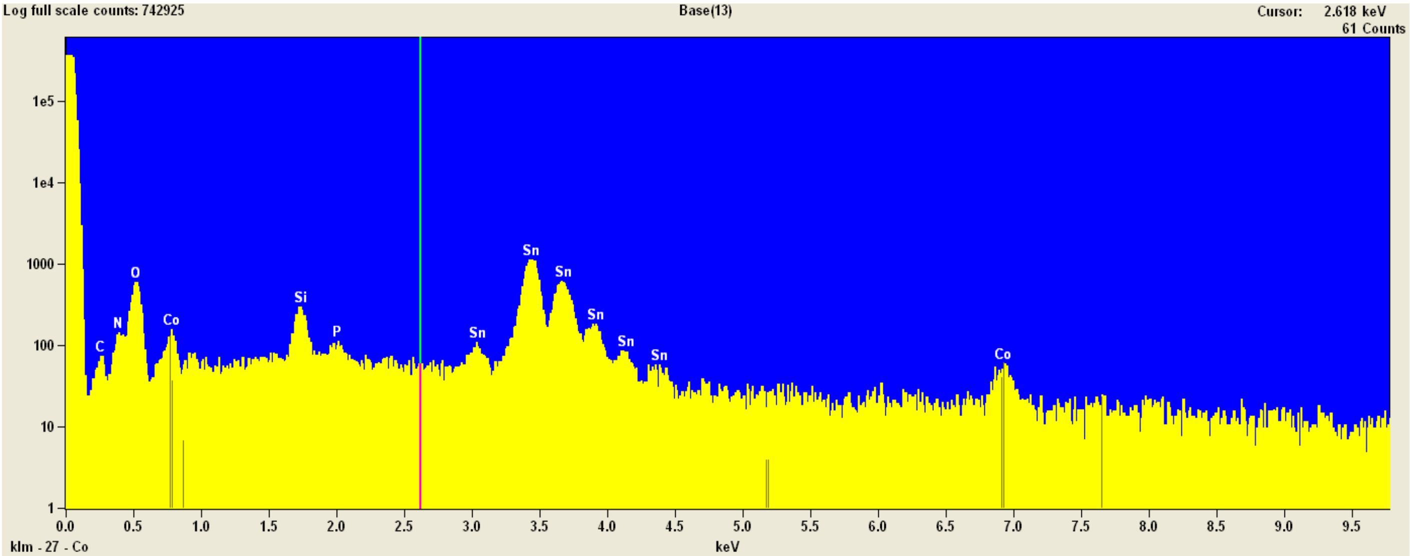


Figure S1. SEM-EDX spectrum showing C, Co, and P from **1** with the remaining signals arising from the substrate and sample holder.

X-Ray Diffraction

Powder samples of **1**, dppe and dppeO$_2$ were subjected to 1.5418 Å radiation using a Bruker aXS D8 Focus spectrometer with a Cu source (40 mA, 40 kV), with a stationary sample holder. The spectra below were recorded using a 0.02° increment and 5 or 10 second exposure time per data point (see graph footnote for details).

As can be seen in the spectra and lists below, the diffraction pattern of dppeO$_2$ and that observed in samples of Co-dppe are very similar, but not identical. The signal-to-noise apparent in the spectra of Co-dppe suggests that only a very small proportion of the sample is crystalline. These data could indicate minor contamination with crystallites of Co-dppe, which are a different crystalline phase than that observed for the pure compound. Or these data could indicate a small percentage of Co-dppe exists as a crystalline material, which is structurally similar to dppeO_2. Or there is a third, unidentified compound, which is structurally similar to dppeO_2. We are unable to distinguish these possibilities at this time.

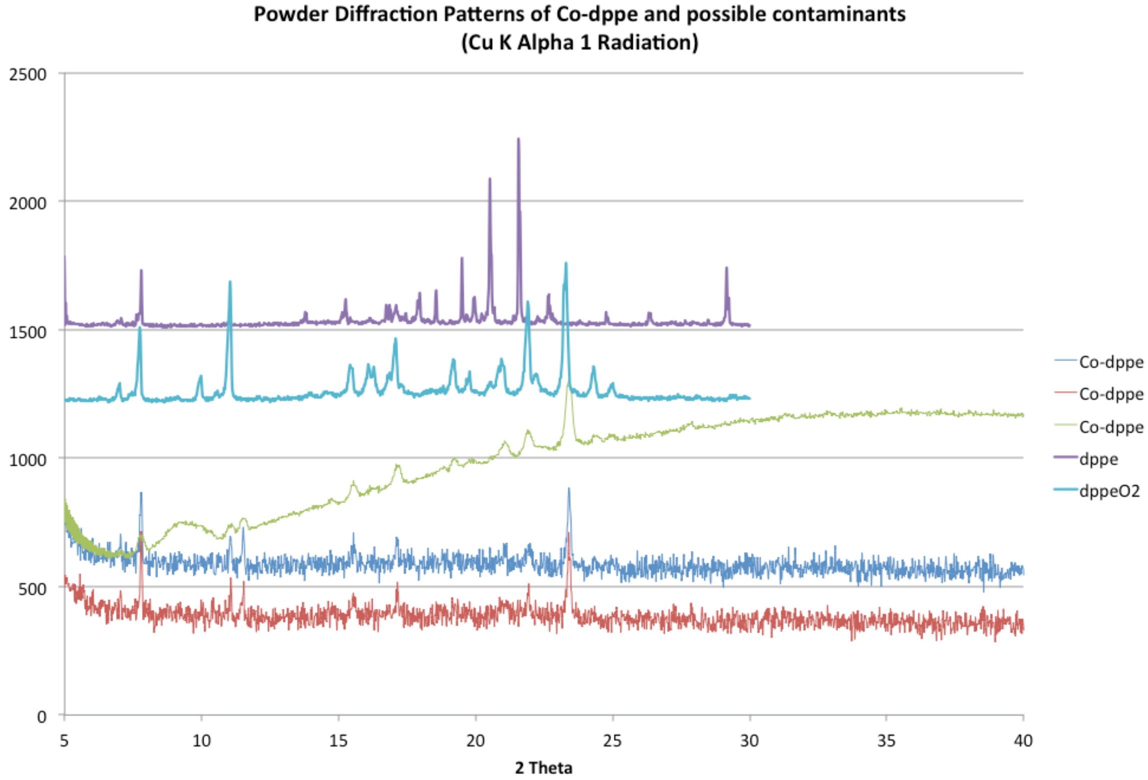


Figure S2. Full XRD spectra of **1** (Co-dppe), taken with different samples of **1** and different filters, and spectra of dppe and dppeO_2, taken on the same instrument. 5 seconds exposures used for red, teal and purple spectra; 10 seconds for green and blue spectra.

List of peaks (2 theta in °; * denotes peaks that definitely are not in both spectra.)

Co-dppe	dppeO$_2$	dppeO$_2$ (continued)
7.78	6.98	19.18
11.04	7.74	19.78
11.52*	9.94	20.94
15.54	11.04	21.90
17.10	15.40	22.18
23.40*	16.08*	23.30*
24.30	16.28*	24.30
	17.06	25.00

ICP-MS

Before analysis, the catalyst was digested according to a modification of a published procedure.[1] A sample of the catalyst (11.5 mg) was combined with 1.00 mL nitric acid (70%, trace metals analysis grade) in a vial, which was sealed with a plastic screw-cap containing a Teflon-lined septum. The mixture was heated in a 100 °C oil bath for 30 minutes, then allowed to cool to ambient temperature. Aqueous hydrogen peroxide (1.00 mL, 30%) was added to the mixture, and the mixture was heated in a 100 °C oil bath for 30 minutes (the vial was vented with a 20G needle for 3 seconds, to relieve excess pressure, after 3 minutes of heating). The mixture became turbid upon cooling to ambient temperature, so another portion of aqueous hydrogen peroxide (1.00 mL, 30% was added), and the mixture was heated in a 100 °C oil bath for an additional 30 minutes. The resulting solution remained homogeneous upon cooling to ambient temperature, and even when immersed in a 0 °C ice bath for 20 minutes.

The resulting solution was diluted to 25.00 mL with water (from a Thermo Scientific Barnstead Nanopure purifier) in a volumetric flask. A 500.0 µL aliquot was diluted to 50.00 mL with 2.0% nitric acid (trace metals analysis grade), and subjected to analysis on a Perkin-Elmer DRC-e ICP-MS, equipped with a Scott spray chamber and Cross Flow nebulizer. Internal standards (Sc-45, Y-89, In-115 and Ho-165) were continuously introduced at a fixed concentration with a mixing tee. This solution was found to contain 405 μg/L ^{31}P and 771 μg/L ^{59}Co, which indicates **1** is comprised of 8.710 % P, w/w, 16.797 % Co (1 : 0.987 P/Co molar ratio).

Sample	P-31 (ppb)	Co-59 (ppb)	Ru-101 (ppb)	Rh-103 (ppb)	Ir-191 (ppb)	Pt-194 (ppb)
1	405	771	0.00026	0.00070	0.00094	0.00000
2	405	787	0.00000	0.00062	0.00026	0.00000
3	392	760	0.00008	0.00043	0.00058	0.00000
Average	401	773	0.00028	0.00058	0.00059	0.00000

Elemental Analysis

Combustion elemental analyses were conducted in duplicate by Robertson Microlit, using an additional oxidant. The results are displayed in the table below:

Sample	C	H	N
1	45.39 %	3.94 %	<0.02 %
2	45.18 %	4.00 %	<0.02 %

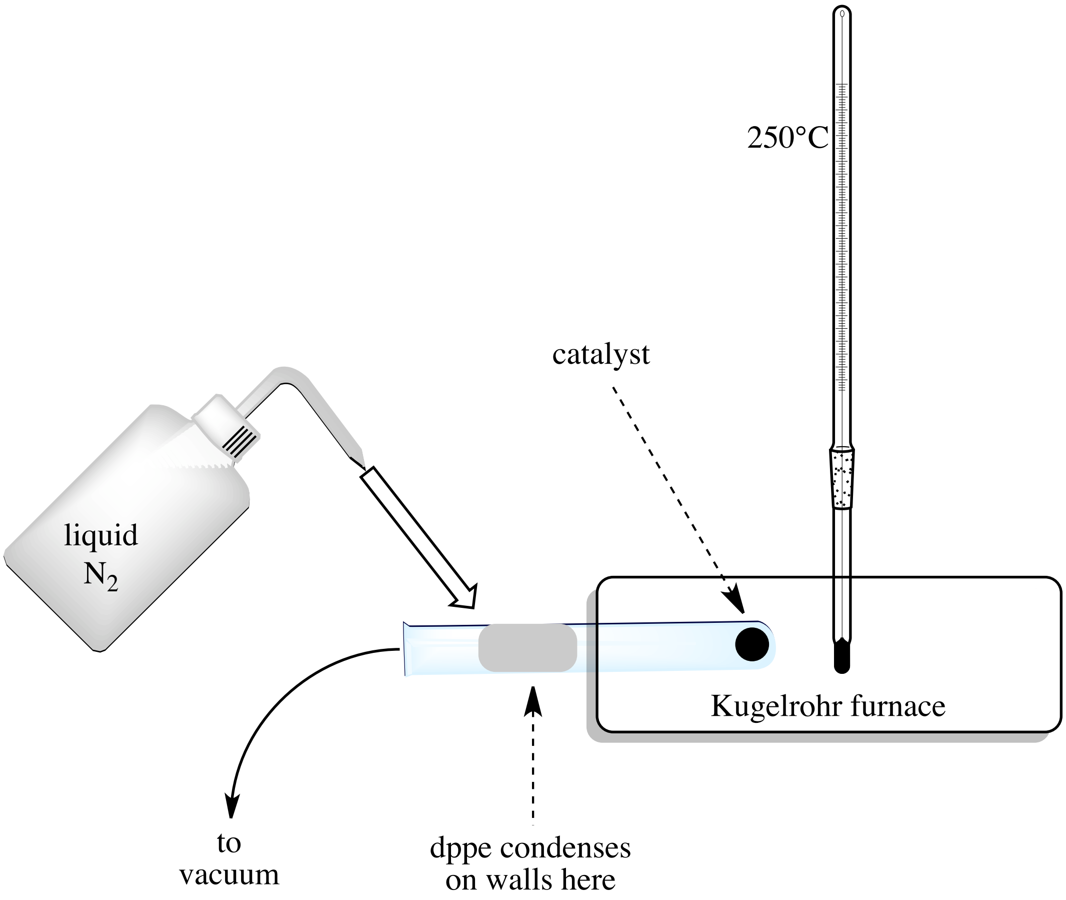
Temperature Programmed Desorption:

A U-shaped quartz tube (5×30 mm) was charged with **1** (2.8 mg). A constant flow of dry helium (50 mL/min) was used to purge the tube for 10 minutes, and maintained throughout the experiment. A small, but consistent percentage of the exhaust flow was diverted to a mass spectrometer (Stanford Research Systems RGA100, employing an electron-impact ionizer, a quadrupole mass filter and a Faraday cup ion detector) over the course of the experiment, and the masses of H_2O ($m/z = 18$), CO ($m/z = 28$), and CO_2 ($m/z = 44$) were monitored. After adequate purging, the quartz tube was inserted into a programmable heating chamber, heated at a rate of 10 °C/min. to 100 °C, held constant at 100 °C for 10 minutes, and then heated at a rate of 10 °C/min to 890 °C.

By the time the sample reached 300°C it had lost H_2O, CO, and CO_2 in a 3.19 : 1.91 : 1 molar ratio (calibrated with calcium oxalate monohydrate, which releases the gases in a strict 1 : 1 : 1 molar ratio; 3.73 μmol H_2O/mg **1** (6.7 % w/w), 2.23 μmol CO/mg **1** (6.2 %) and 1.17 μmol CO_2/mg **1** (5.2 %), respectively). It is assumed that the CO_2 is produced by oxidation of a portion of the CO by the Co oxide during thermolysis.

Destructive distillation

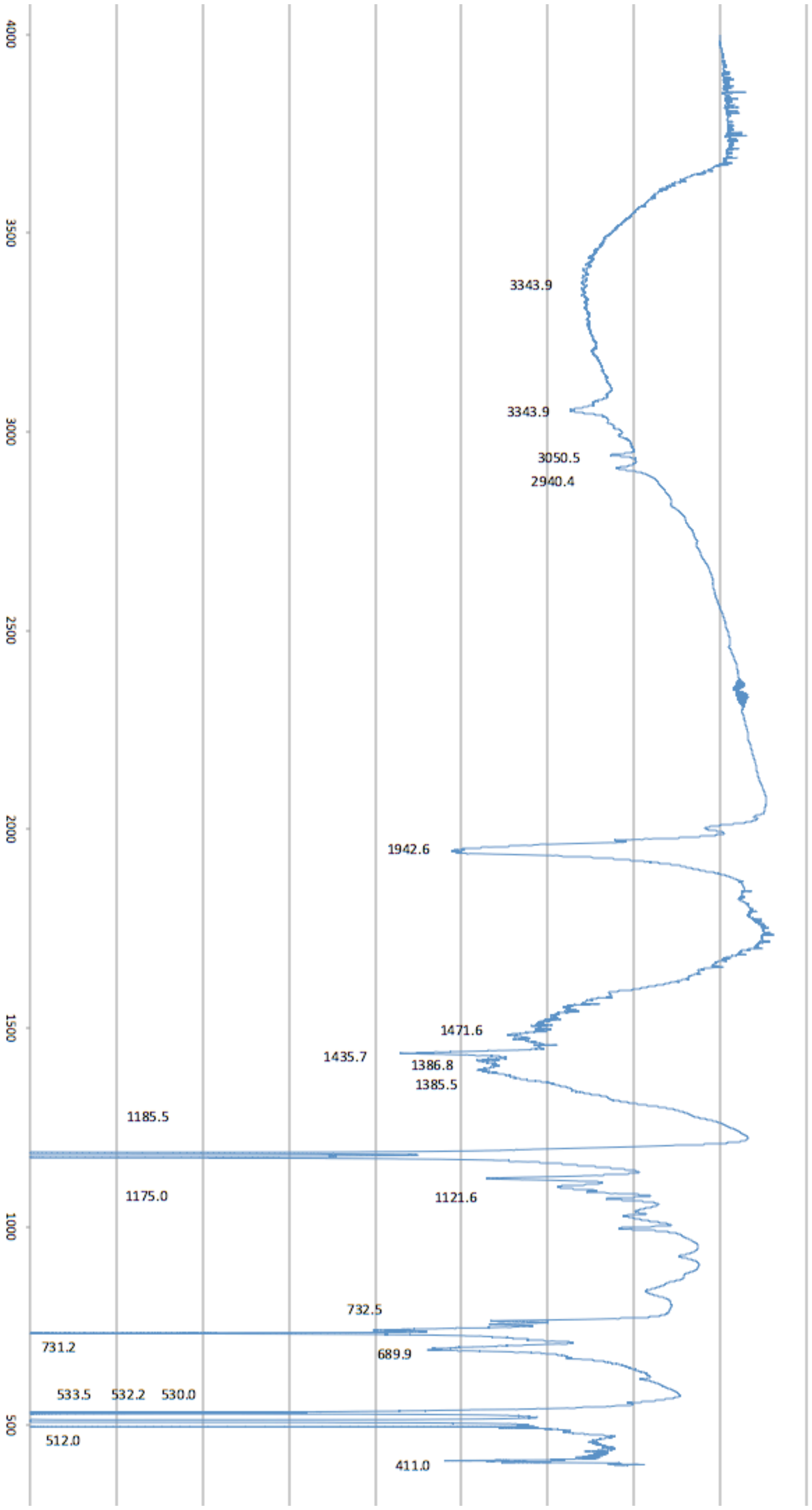
A 16×150 mm test tube was charged with 27.1 mg of **1** and sealed with a rubber septum. The septum was pierced with a 22G needle, and connected to a vacuum line (pressure < 1 torr throughout distillation). The base 75 mm of the tube was heated to 250 °C in a kugelrohr furnace (see diagram below.) The other half of the tube was cooled in a stream of liquid nitrogen, which was expelled from a plastic wash bottle. After 2 hours subjected to these conditions, the tube was brought into a nitrogen-filled glovebox. The lower portion of the tube, containing the residue was cut off. The portion of the tube containing the sublimate was washed into a flask using dichloromethane. After concentration under vacuum, the sublimate was dissolved in $CDCl_3$ and identified as dppe by ^1H NMR, ^{31}P NMR and LC-MS. The amount was determined to be 220.0 μmol by integration against an internal standard. This accounts for 32.4 % of the mass of added **1** (58 % of the ligand expected to be contained in 27.1 mg of **1.**)



Photograph of the test tube (16×150 mm) and contents just after distillation:

IR

Spectroscopy grade KBr (112 mg, anhydrous) and **1** (2.4 mg) were mixed together and cast into a pellet using a 10 mm die and a hydraulic press (2000 psi applied). The pellet was then analyzed with a Midac M1200 spectometer, purged with a constant flow of dry nitrogen gas (2 ml/min.).


4000
3500
3000
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1000
500
3343.9
3343.9
3050.5
2940.4
1942.6
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1435.7
1386.8
1385.5
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1121.6
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530.0
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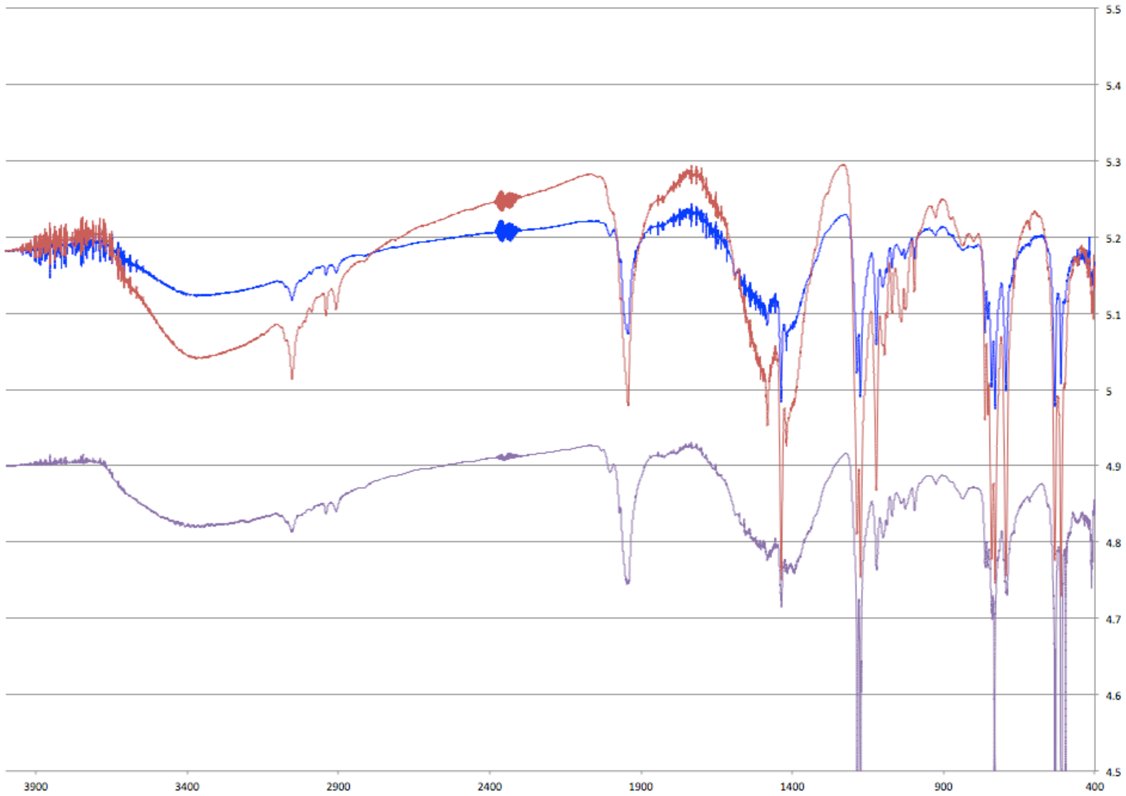


Figure S3. Three different batches of catalyst prepared on different days show nearly identical IR spectra.

Solubility Studies

Aliquots of the catalyst (3–8 mg) were combined with 1.0 mL quantities of the following solvents: acetonitrile, chloroform, dimethyl carbonate, dimethylformamide, dimethylsulfoxide, 1,2-dimethoxyethane, ethyl acetate, ethylene glycol, methanol, nitromethane, pyridine, triethylamine and water. Even after prolonged stirring and sonication, no detectable ^{31}P signal was found in any of the supernatants.

Solid State NMR

The MAS NMR was run on 500 MHz wide-bore Varian INOVA spectrometer with a 9.5 mm Chemagnetics MAS probe spinning at 3.5 kHz. The magic angle was adjusted with KBr, and the ^{31}P chemical shift was referenced to liquid phosphoric acid, taken as 0 PPM. The pulse width was 30 degrees, the relaxation delay was 60 seconds, and the number of scans was 1260. Total acquisition time was 21 hours.

As the MAS speed was low compared with the very broad ^{31}P chemical shift tensor, we observed a lot of rotational sidebands. Because of limited 1H decoupling power, the center line of the ^{31}P spectrum was also very broad, around 1.5 kHz. In order to determine the isotropic chemical shift, we ran another experiment with 3 kHz MAS. Comparing these two data sets, we assigned 32 ppm as the isotropic chemical shift position. As the center peak was very broad, we were not able determine how many isotropic peaks are present.

Electrochemistry of 1

CVs

Cyclic voltammograms in Figure 2a were used to determine performance of catalytic materials made using different organophosphine ligands. To ensure that the samples were stable throughout the CV, samples were equilibrated at 1.2 V vs. Ag/AgCl for 4 minutes beforehand and no major increase or decrease in current was observed. Figure 2a shows CVs for cobalt-phosphine materials made with four different organophosphines, with blue, purple, red, black and green denoting dppe, oxidized dppe, Xantphos, triphenylphosphine, and DPEphos, respectively. Scan rate: 10 mV/s, 0.1 M potassium phosphate, pH 6.8, no IR compensation, Pt wire counter electrode, Ag/AgCl reference, solution was gently stirred to assist mass transport of O_2 bubbles. Below are the analogous CVs performed in borate electrolyte.

Tafel Plots

Co-dppe samples were tested for current stability prior to collection of Tafel plot data. Samples in hydroxide, nitrate, and sulfate did not experience an increase or decrease in current over 10 minutes at 1.2 V vs. Ag/AgCl. Phosphate buffer caused a slight decrease in current, which we attribute to coordination of PO_4^{3-}. Samples in borate buffers showed a steady increase in current which lasted ~1 hour, and were allowed to stabilize before obtaining Tafel plot data. We attribute this to incorporation of borate into the catalyst. Unlike previously discovered Co-Bi catalysts, however, we still see spectroscopic evidence of phosphorus (from dppe) in EDX spectra after >2 hours of water oxidation at 1.4 V vs. Ag/AgCl suggesting that it plays a role in this catalyst's enhanced stability compared to other Co-Bi materials. Tafel plots were taken while the solution was stirred at 25 mV steps between 0.75 V vs. Ag/AgCl and 1.4 V vs. Ag/AgCl with a 10 second rest time between data points. After initial spikes in current caused from capacitance, steady-state values were attained within approximately 2 minutes and plotted in Figure 2a.

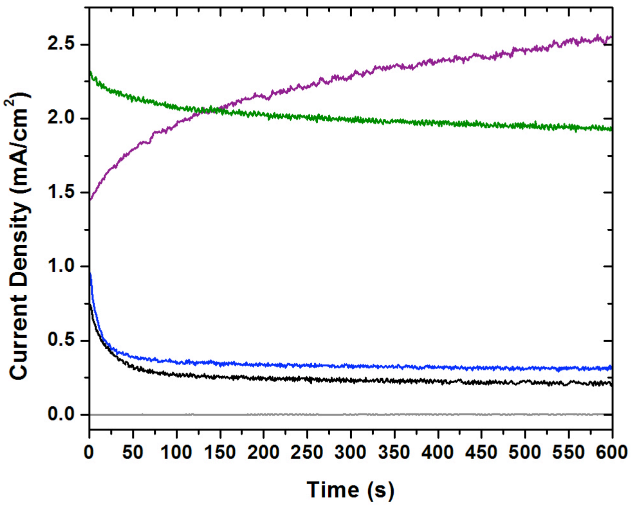


Figure S4. 10 minute chronoamperograms of samples at 1.2 V vs. Ag/AgCl taken prior to Tafel plots at pH 7 in 0.1 M nitrate (black), sulfate (blue), phosphate (green), and borate (purple) buffers. Control samples were taken in different buffers using an FTO/glass slide without any catalyst (grey).

Electrochemistry in basic conditions was performed using an FTO electrode with a catalyst surface loading of 0.42 mg/cm^2, and 0.10 M NaOH. After equilibration (10 minutes, 0.80 V vs Ag/AgCl), the Tafel plot was taken at 25 mV steps between 0.360 and 1.210 V vs Ag/AgCl with a 5 second rest time between data points. Amperometric data was recorded for 5 minutes at each potential, and values for the last 2.5 minutes were averaged to afford the value included in the Tafel plot.

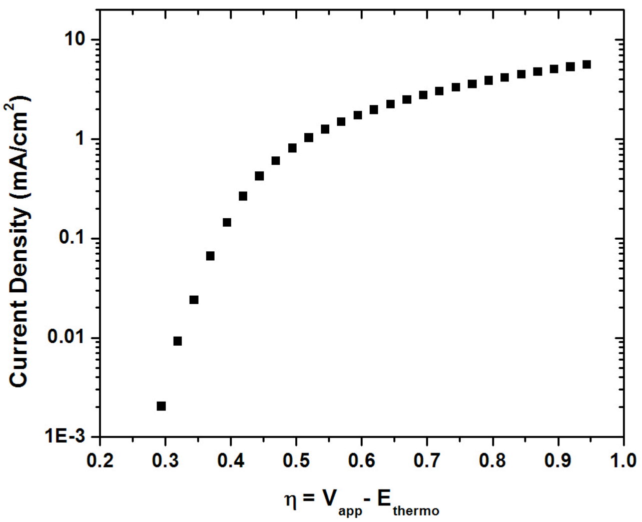


Figure S5. Tafel plot of Co-dppe in pH 13 NaOH, the linear region slope is 63 mV/decade.

Fluorescence Oxygen Detection

Oxygen detection was performed with a TauTheta MFPF-100KHz using phase fluorometry (calibrated with argon [Tech Air] and air). A 250 mL three-neck round bottom flask was charged with 0.1 M borate electrolyte (leaving *ca*. 60 mL headspace). A large, Teflon-coated stirbar was used to agitate the electrolyte gently. The flask was thermostated at 25 °C. A reference electrode (Ag/AgCl), the working electrode, and a Pt wire counter electrode were each inserted through large rubber septa, and the oxygen detector was inserted through the rubber septum with the anode. The septa were then inserted into the necks of the flask such that the electrodes were all submerged and tip of the fluorescence probe was *ca.* 3 cm above the surface of the electrolyte.

Once assembled, the septa were secured with Parafilm® and electrical tape. The flask was purged with argon (which was bubbled through the electrolyte, not just the headspace) until the oxygen level reached a stable minimum. The purge was ceased, and the oxygen level monitored for 30 minutes to be sure that there was no leakage. A constant potential of 1.4 V vs the Ag/AgCl reference electrode was then applied for 60 minutes, and oxygen detection was maintained until oxygen levels reached a stable maximum. The headspace volume was determined to be 55.0 mL at the end of the experiment.

Stability Studies and Post-Electrolysis Analyses

Chronoamperograms at varied potentials for one hour in sulfate, borate, and phosphate buffers were performed using the conditions outlined above, and the best of four samples are shown in Figure 2b and Figure 2c. No decay in current or of the catalyst deposited on the FTO electrode was seen for any applied potential in a borate buffer. In sulfate, no decrease in current or degradation of catalyst was seen at 1.1 V vs. Ag/AgCl (1.3 V vs. NHE) or 1.2 V vs. Ag/AgCl (1.4 V vs. NHE), while a slight decrease in current can be seen at 1.3 V vs. Ag/AgCl (1.5 V vs. NHE) and finally a significant decrease in current and degradation of catalyst at 1.4 V vs. Ag/AgCl (1.6 V vs. NHE). In phosphate, chronoamperograms show stable current at 1.1 V vs. Ag/AgCl (1.3 V vs. NHE), however at all higher potentials there is a slow degradation of current observed as shown below.

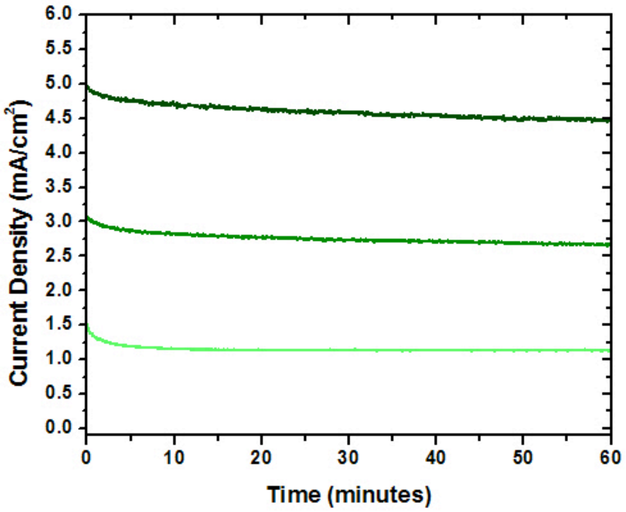


Figure S6. Hour long chronoamperograms of Co-dppe in phosphate buffer at pH 7 at 1.1 V vs. Ag/AgCl (bottom), 1.2 V vs. Ag/AgCl (middle), and 1.3 V vs. Ag/AgCl (top).

After 2 hours of electrolysis at 1.4 V vs Ag/AgCl (1.6 V vs. NHE), the Co-dppe retains phosphorus as shown by SEM-EDX. Similar retention of phosphorus is seen in sulfate buffered samples after 2 hours of electrolysis.

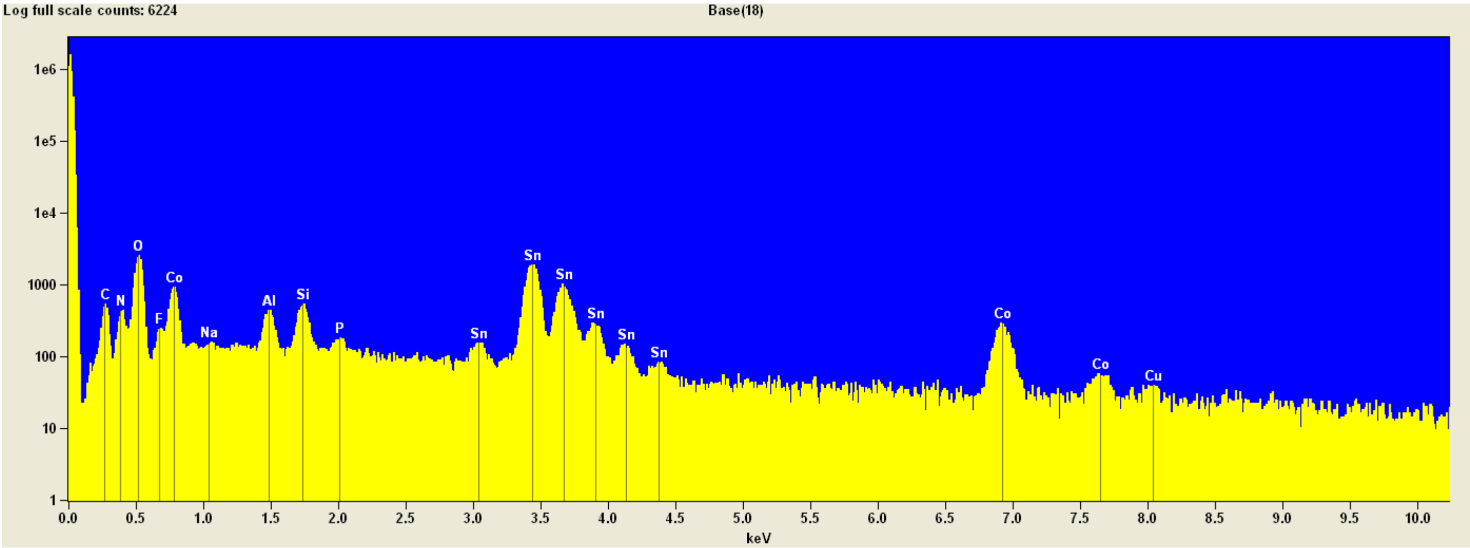


Figure S7. SEM-EDX spectrum of elements in the Co-dppe catalyst on an FTO/glass slide showing presence of P after 2h of electrolysis in a borate buffered solution. Sn, Cu, Si, Al, and F peaks arise from the sample holder and substrate.

Long-term stability studies were performed in a two-compartment electrochemical cell with each compartment separated by a glass frit. We investigated 12 hour uninterrupted stability at 1.4 V vs. Ag/AgCl, and also show that after over 40 hours of intermittent use at varied potentials between 1.1 V vs. Ag/AgCl and 1.4 V vs. Ag/AgCl high activity is still retained.

While the samples in borate seem to cause a change in the catalyst, it is reversible. Upon immersing a sample in a sulfate buffered solution after 12h of electrolysis in a borate buffered solution, it regains the lesser activity observed prior to exposure to borate.

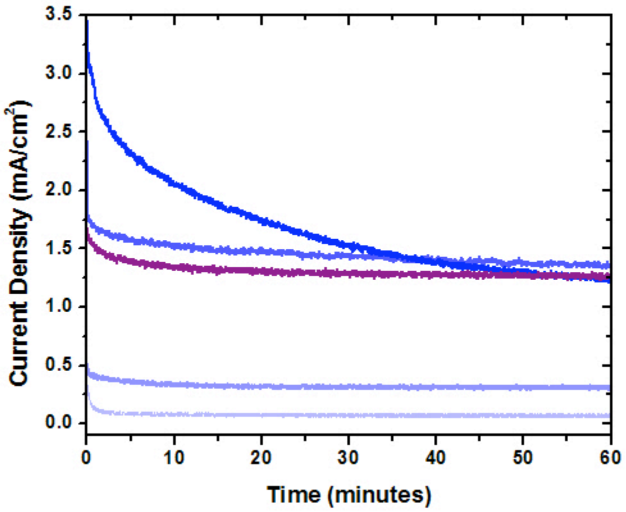
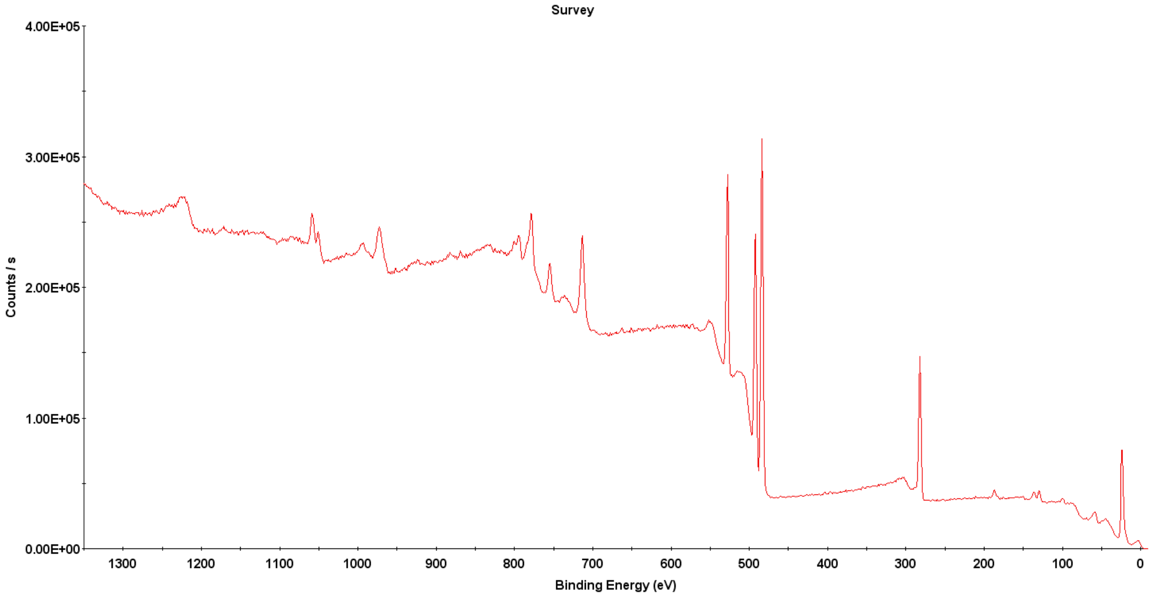


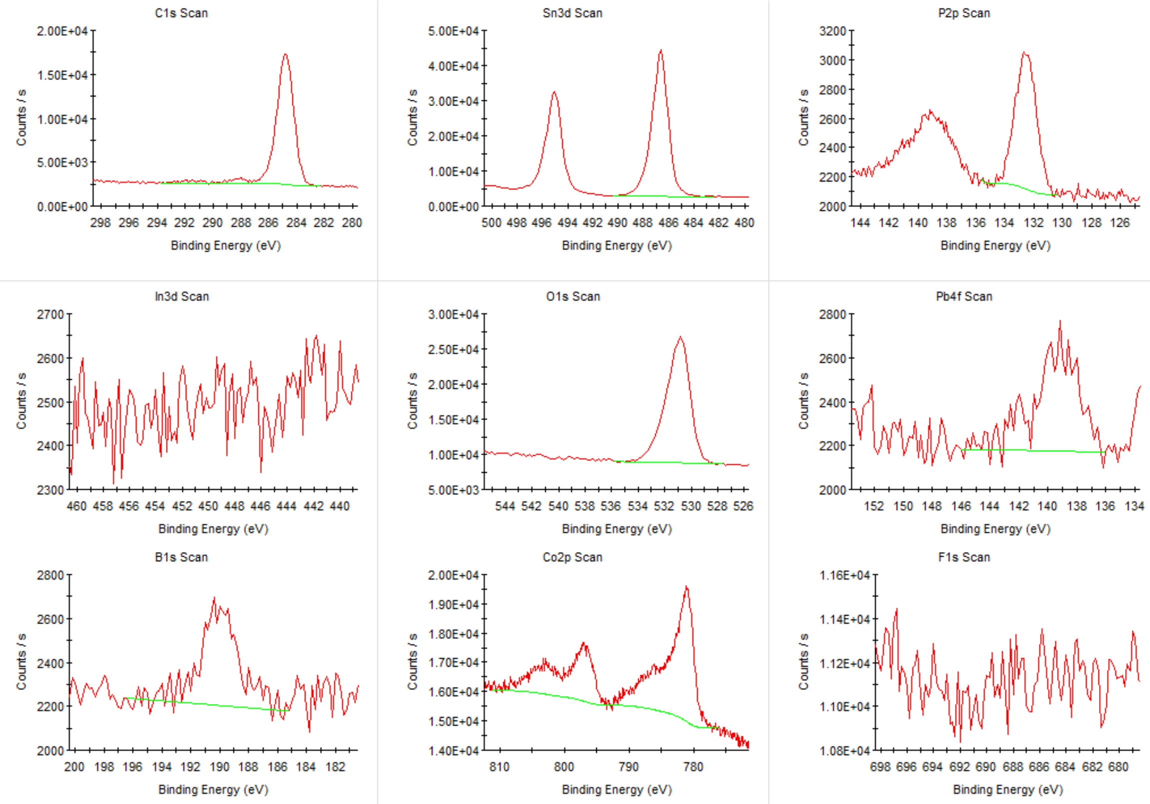
Figure S8. Blue traces show 1h chronoamperograms in pH 7 sulfate solution at potentials of 1.1, 1.2, 1.3 and 1.4 V vs Ag/AgCl. The purple trace shows a 1h chronoamperogram in the same sulfate solution (at 1.3 V vs. Ag/AgCl) using a sample previously used for 12h of water oxidation in borate at 1.4 V vs. Ag/AgCl. No degradation is observed at potentials below 1.4 V, and the two chronoamperograms run at 1.3 are within experimental error, indicating irrelevance of sample history.

XPS Analysis:

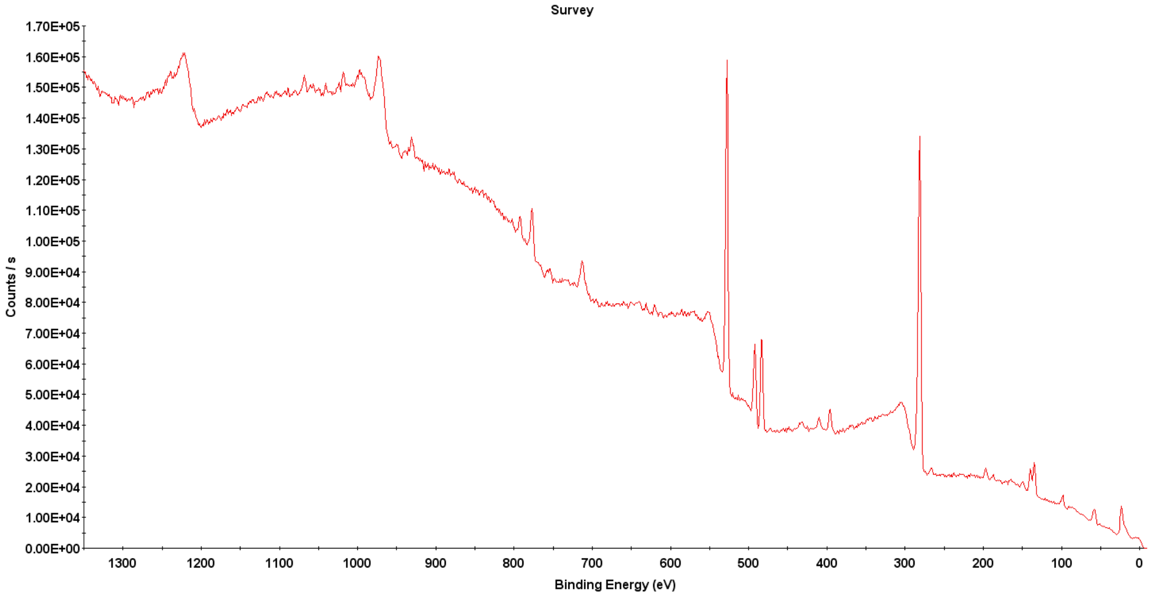
FTO electrodes (one blank [A], one with fresh catalyst deposited on it [B], one with catalyst that had undergone >40h electrolysis in borate [C], and one with catalyst that had undergone electrolysis in sulfate [D]) were sent to CAMCOR (at the University of Oregon) for XPS analysis. Spectra were taken on a ThermoScientific ESCALAB 250 instrument, employing monochromatized X-rays from an aluminum source. Pass energies of 150 eV and 20 eV were used for survey and composition scans, respectively. In both cases a beam-width of 500 μm was used.

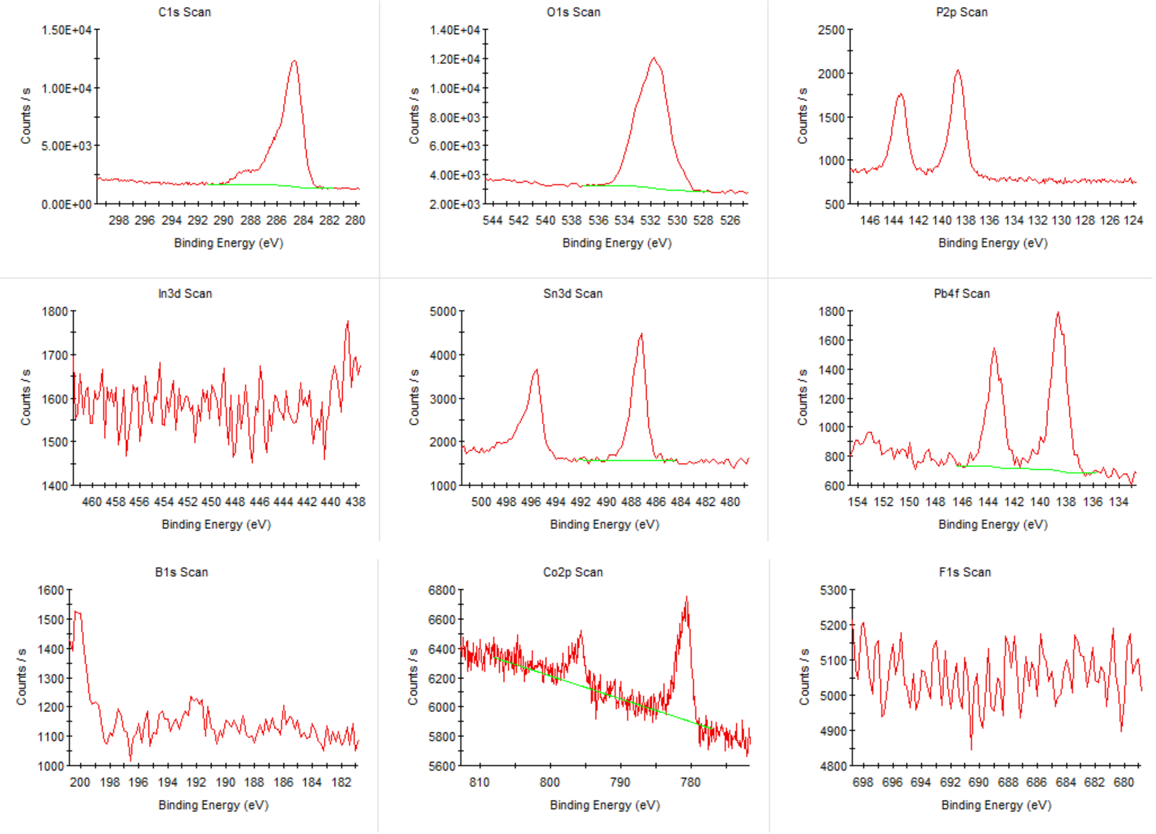
Fresh Catalyst Survey and regional scans:



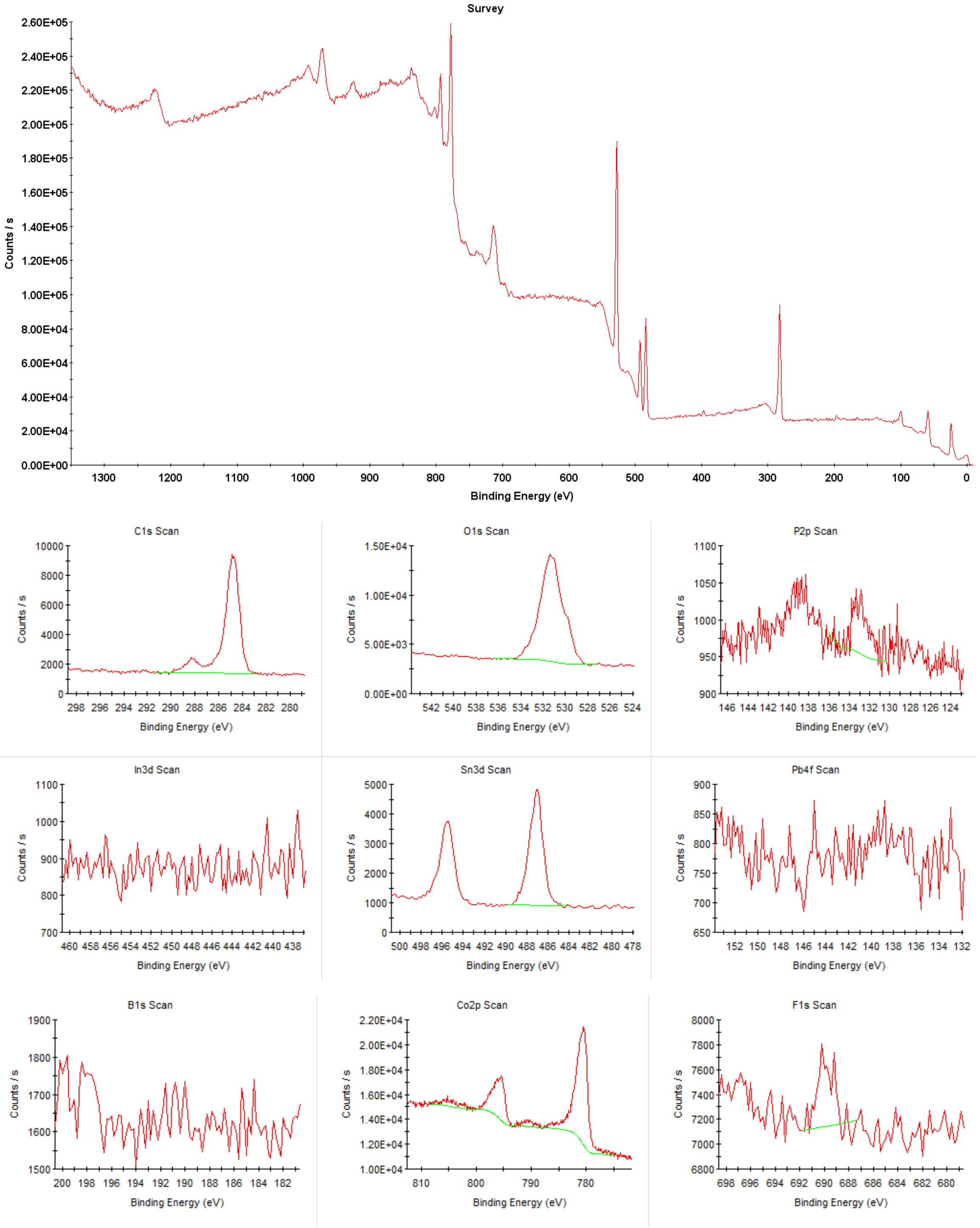


Catalyst used in borate survey and regional scans:





Catalyst used in sulfate survey and regional scans:



Loading studies:

Suspensions of **1** in ethyl acetate were prepared in the following manner: A 20 mL scintillation vial (A) was charged with **1** (2.4 mg) and ethyl acetate (12.0 mL). Another vial (B) was charged with ethyl acetate (12.0 mL). Vial A was sonicated briefly and well mixed just before a portion (1.00 mL) of the suspension was transferred to vial B. Portions of each suspension (500 μL) were thoroughly applied to FTO-electrodes (A and B), while a third electrode was treated with 500 μL of ethyl acetate only. After drying for 30 minutes, the electrodes were assessed by chronoamperometry at 1.6 V vs NHE in pH 7.0 0.1 M borate electrolyte. Current densities reported in the table below are averages of the current density over the last five minutes of a 20-minute CA.

Electrode	A	B	blank
μg **1**/cm^2	15.5	1.29	0
mA/cm^2	0.540	0.538	0.018
Calculated Molecules of (O_2)/Co atom•h	93	1120	NA

Differentiation from Co-Pi and Co_3O_4

Electrolysis was conducted in either 0.1 M borax at pH 7 or in 0.1 M phosphate at pH 7. The working electrode was either: an FTO electrode activated with Co-Pi by the method published,[2] an FTO electrode with Co_3O_4 deposited on it, an FTO electrode with **1** deposited on it, or an FTO electrode with **1** deposited on it which had been run at 1.4 V vs Ag/AgCl in 0.1 M borate for 12h before beginning the experiment. Platinum mesh was used for the counterelectrode, and Ag/AgCl as the reference. Each of the plates was subjected to 6 consecutive 1 h chronoamperometry experiments at 1.40 V vs Ag/AgCl in alternating fresh 20 mL electrolyte solutions (borate, then phosphate, then borate, then phosphate etc.). All electrodes were rinsed with 18 MΩ deionized water before introduction to the new electrolyte. The setup was such that the three electrodes were always in the same position relative to each other, to ensure minimal change in current due to resistivity. The currents in the chart below are average values for the last 10 minutes of each hour-long run, which clearly demonstrate three different behaviors: Co-Pi, which is better in phosphate than in borate; Co_3O_4 which is worse in each successive run; and **1** which is better in borate than in phosphate.

	Co-Pi	Co_3O_4	**1**	**1** after 12h
Borate	1.6 mA	0.9 mA	1.7 mA	0.8 mA
Phosphate	3.4 mA	0.7 mA	0.4 mA	0.5 mA
Borate	1.6 mA	0.6 mA	0.8 mA	0.7 mA
Phosphate	3.2 mA	0.3 mA	0.3 mA	0.3 mA
Borate	1.5 mA	0.3 mA	0.7 mA	1.0 mA
Phosphate	3.0 mA	0.3 mA	0.3 mA	0.2 mA

Synthesis and Limited Characterization of Other Related Catalysts

Inside a N_2 atmosphere glovebox, a stock solution of $Co_2(CO)_8$ was prepared by weighing 975 mg into a Schlenk bomb and adding 39 mL of N_2 sparged xylenes. The ligands 1,2-ethanediylbis[diphenylphosphine oxide], DPEphos, triphenylphosphine, 1,2-Bis(1-piperidinyl)ethane, TMEDA, EDTA, 4,4'-bipyridine, 2, 2'-bipyridine, dppm, dppe, dppb, and dppp were weighed out into reaction tubes in an equimolar ratio to the $Co_2(CO)_8$ (except PPh_3 2 mol eq). The tubes were sealed, evacuated and refilled with N_2 three times. Under nitrogen, 3 mL of the cobalt solution was added to each tube. The reactions were allowed to stir for 30 min under nitrogen purge. They were then heated to 160 °C for 90 min. The reactions were cooled to room temperature and allowed to stir open to air for 36 hrs. They were then centrifuged down and decanted. The solids were washed with ethyl acetate, centrifuged, and decanted until the solution was still clear after separation. The resulting solids were dried on high vacuum. IR spectra were recorded for each material. Approximately 1 mg of each material was suspended in 250 µL of ethyl acetate by sonicating and then drop casting onto fresh FTO electrodes. The electrodes were allowed to dry overnight before electrochemical measurements were made. The electrochemical measurements were carried out in a small beaker with 40 mL 0.1 M borate electrolyte pH 7. An Ag/AgCl reference electrode was used along with platinum mesh as the counter electrode. Each sample underwent a 1.2 V (vs Ag/AgCl) applied potential for 4 min prior to recording a CV for the material. A CV was recorded from 0.2 to 1.4 V at a scan rate of 10 mV/sec.

Figure S9. Cyclic Voltammograms (3 cycles each) in pH 7.0 borate of cobalt catalysts with different ligands incorporated.

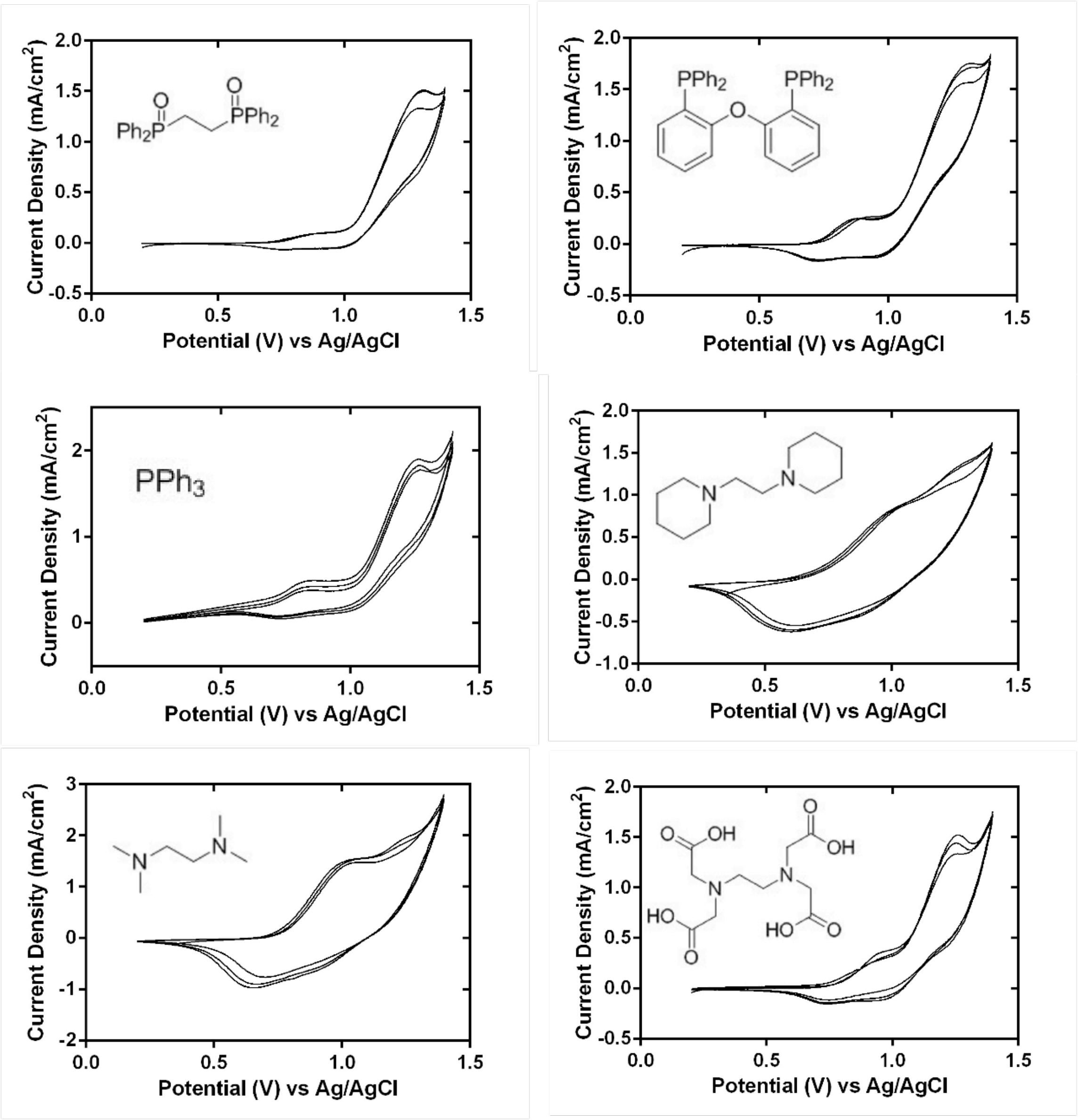
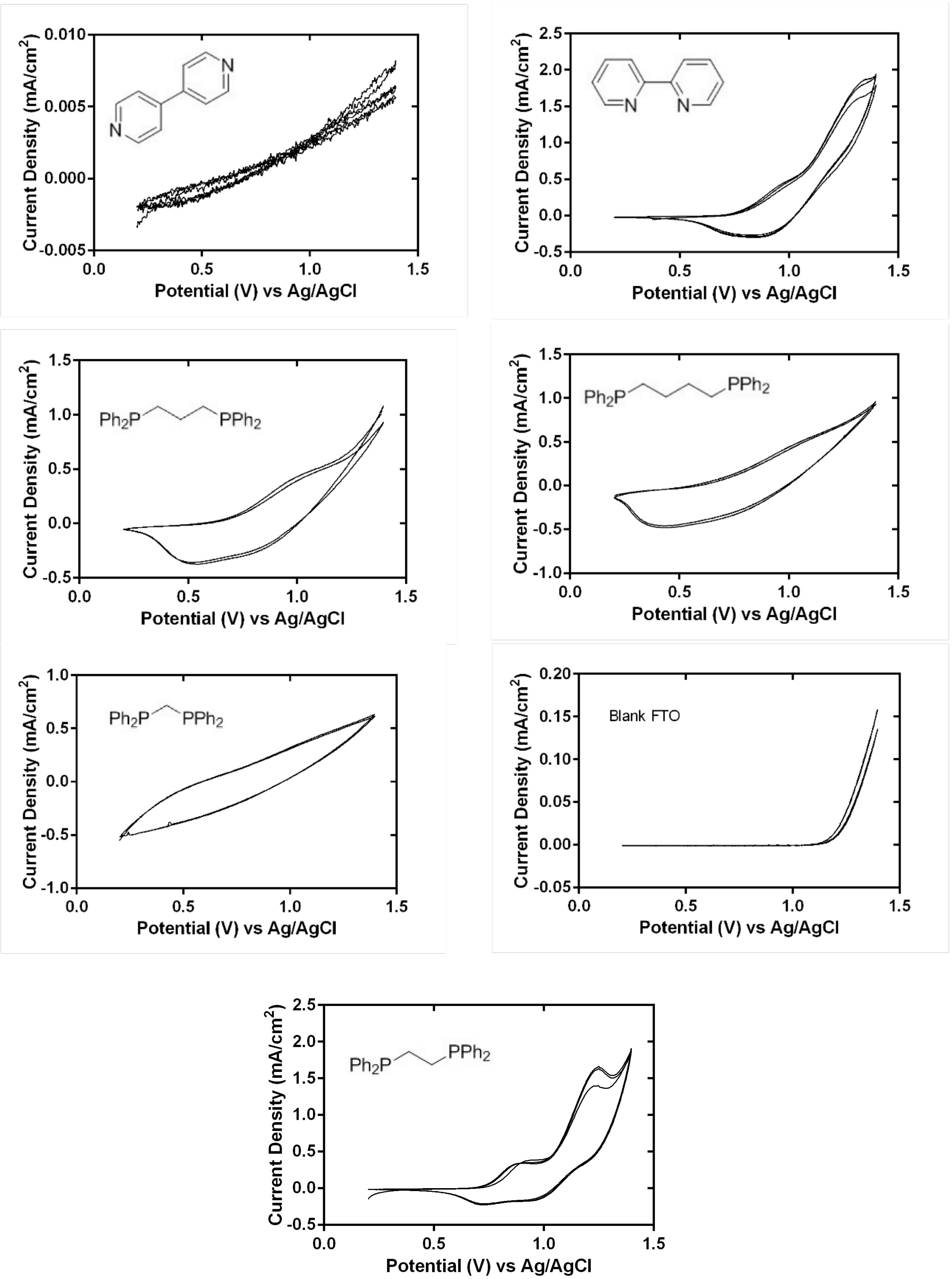
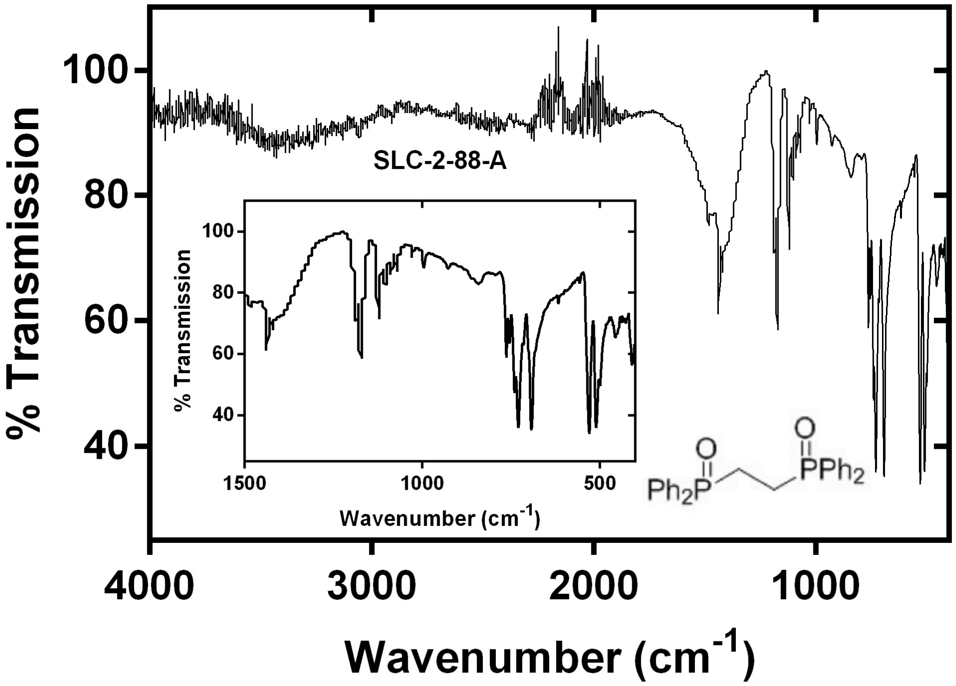


Figure S9 continued.

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40
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4000
3000
2000
1000
Wavenumber (cm^{-1})
% Transmission
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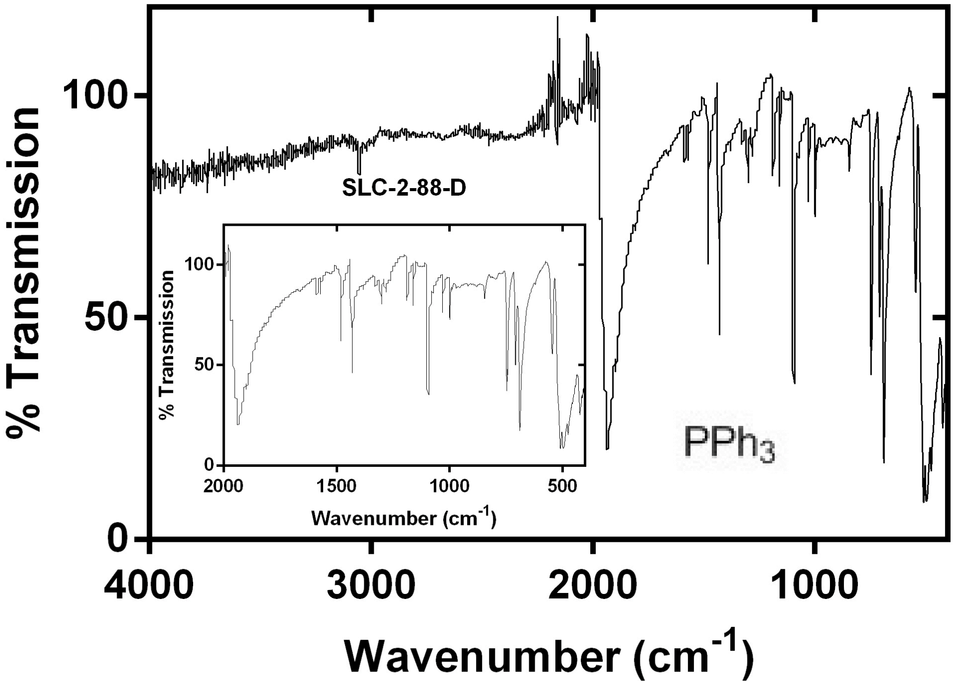
60
40
1500
1000
500
Wavenumber (cm^{-1})
$Ph_2P(O)CH_2CH_2P(O)Ph_2$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% Transmission
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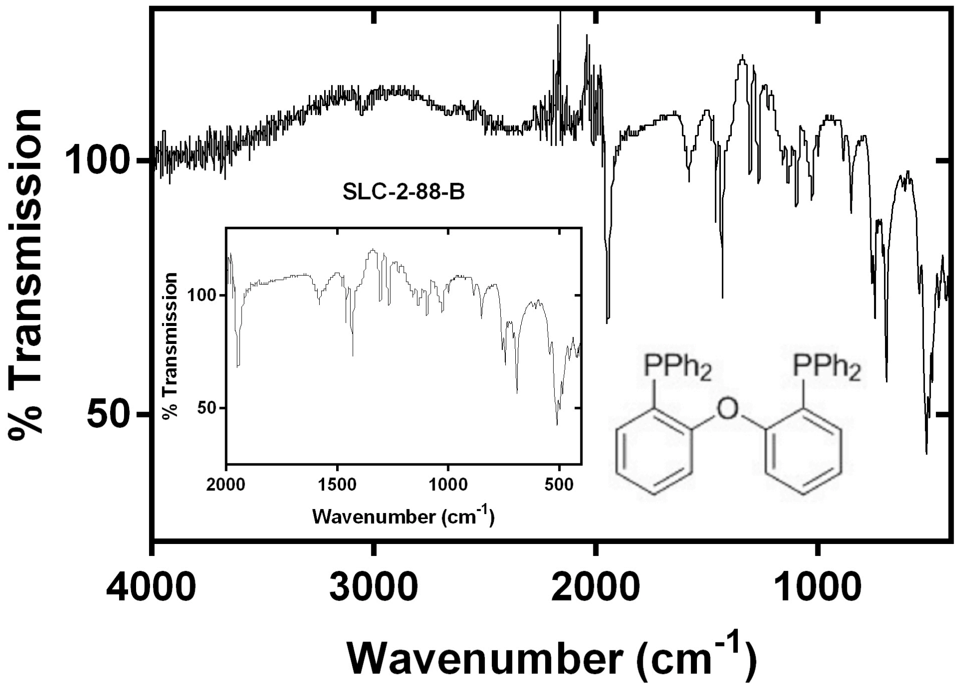
500
Wavenumber (cm^{-1})
PPh_3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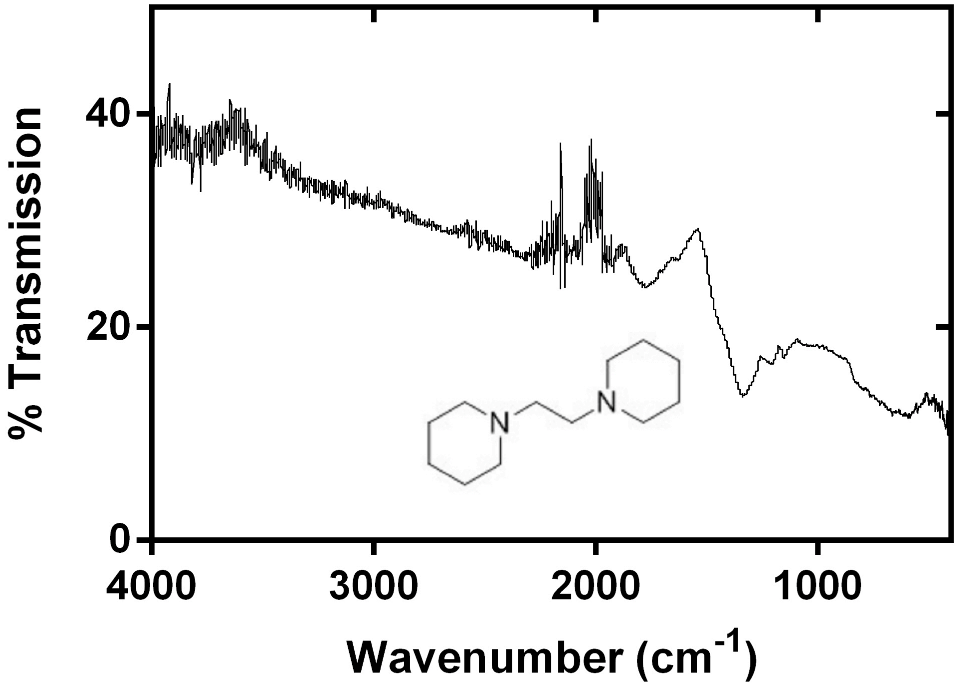
PPh$_2$
O
PPh$_2$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Wavenumber (cm^{-1})
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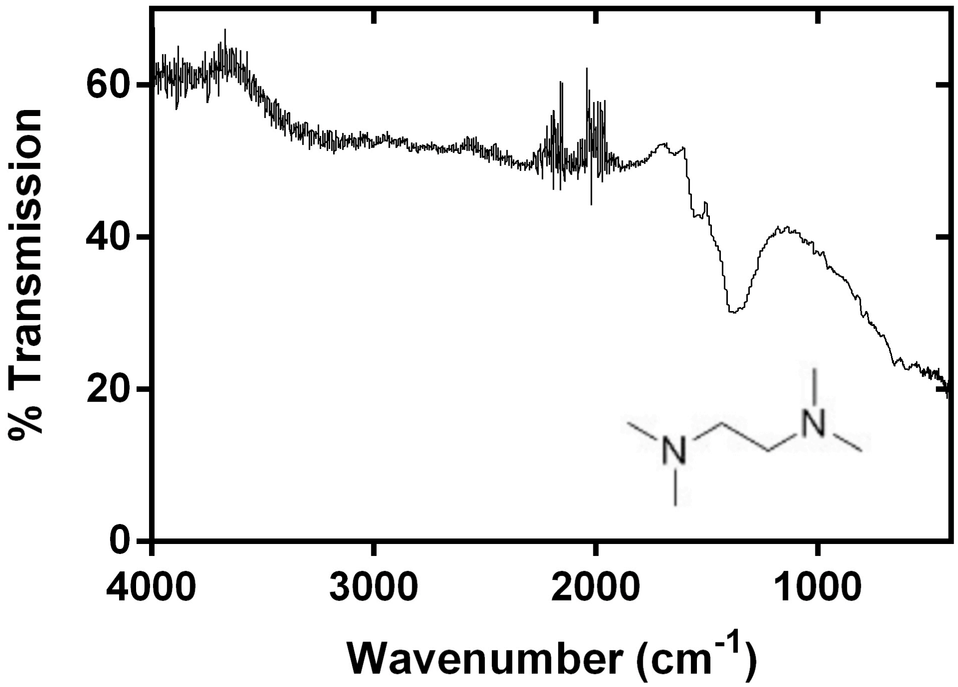
N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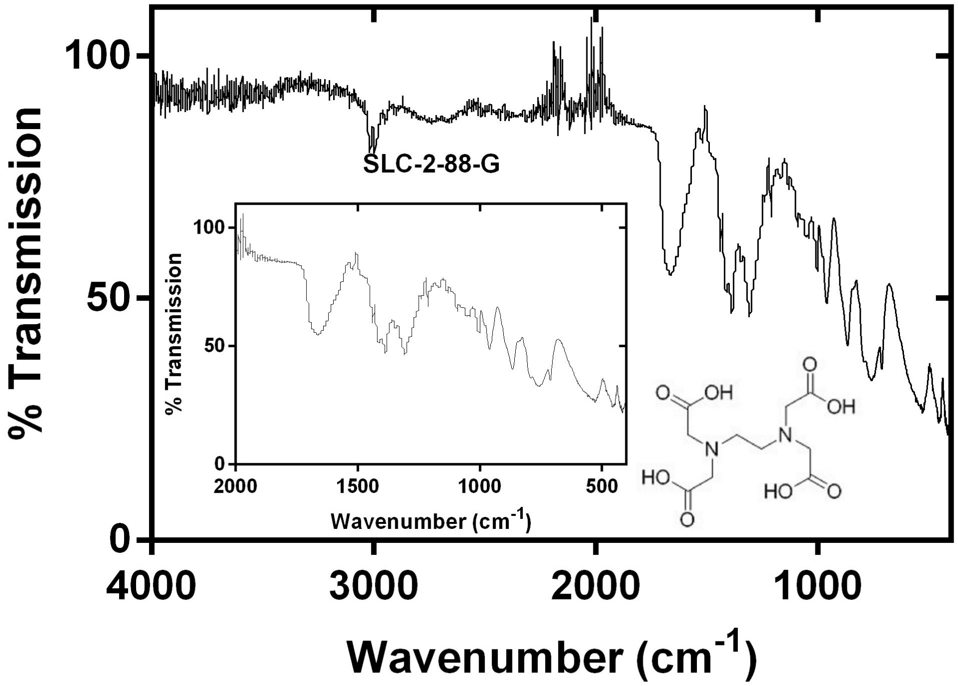
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1000
500
Wavenumber (cm-1)
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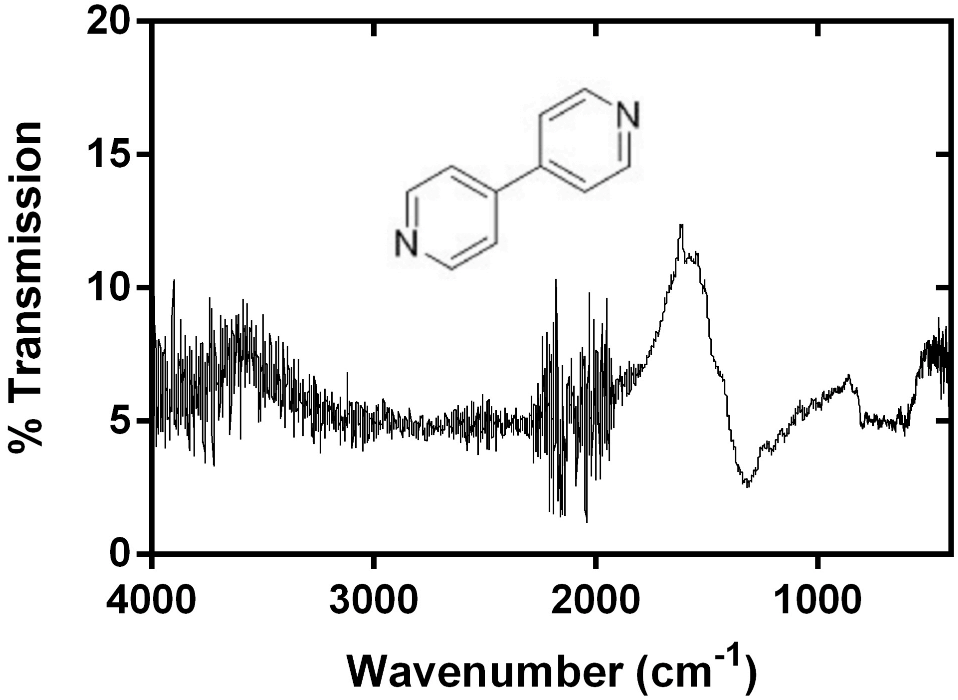
OH
O
OH
N
N
HO
O
HO
O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15
10
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Wavenumber (cm^{-1})
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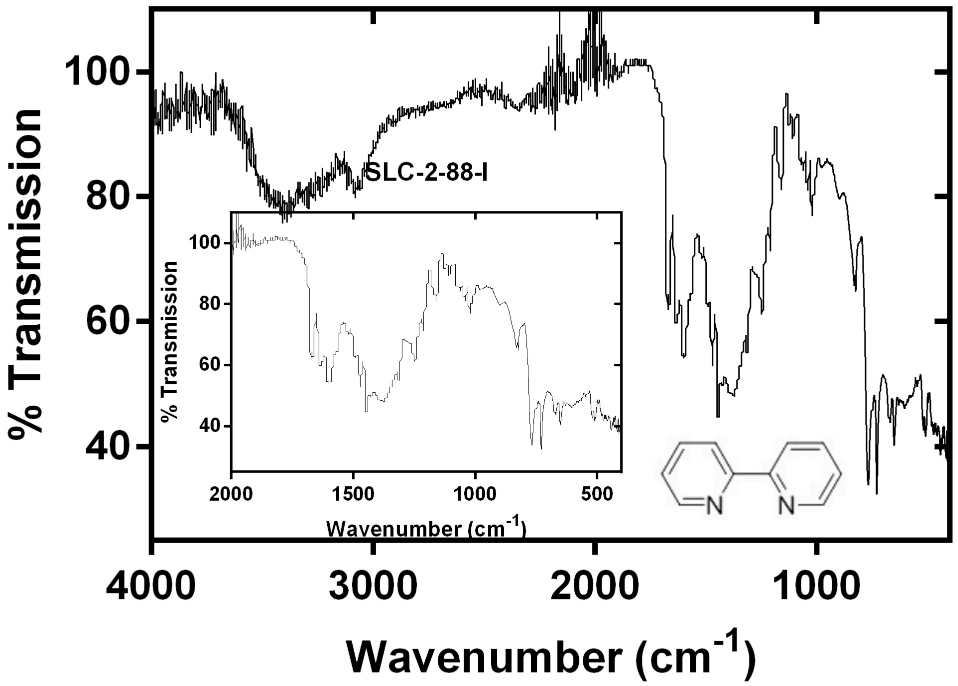
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Wavenumber (cm^{-1})
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% Transmission
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1500
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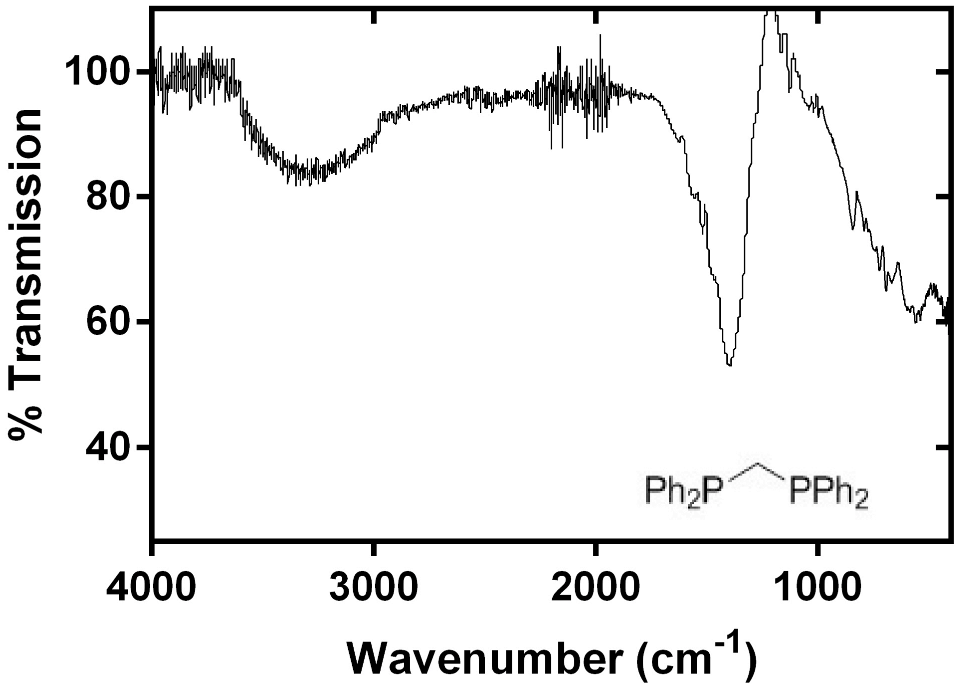
500
Wavenumber (cm^{-1})
N
N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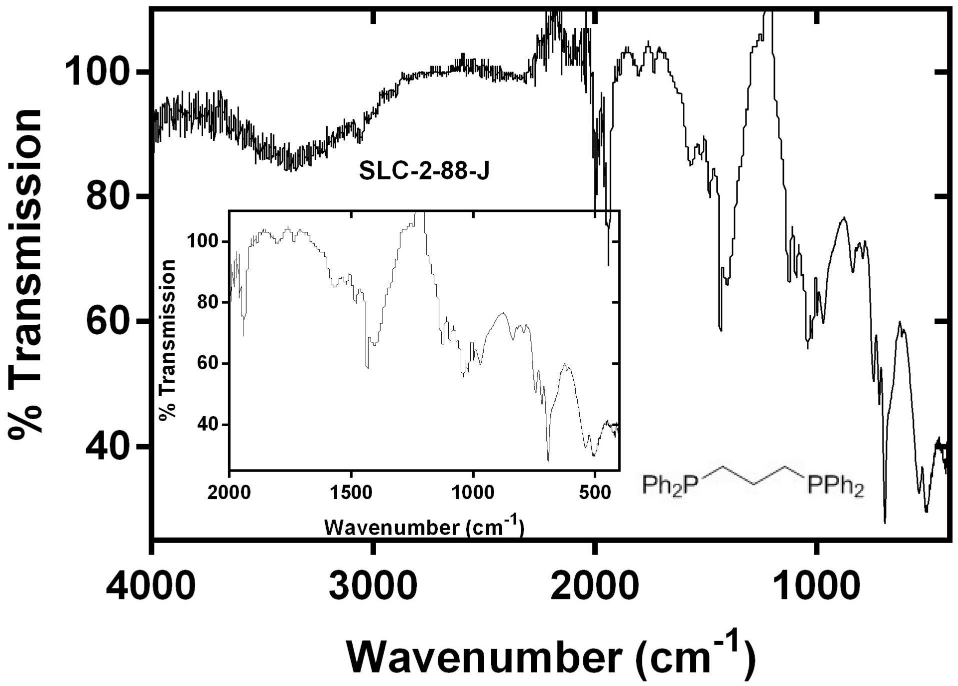
Wavenumber (cm^{-1})
Ph$_2$P PPh$_2$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% Transmission
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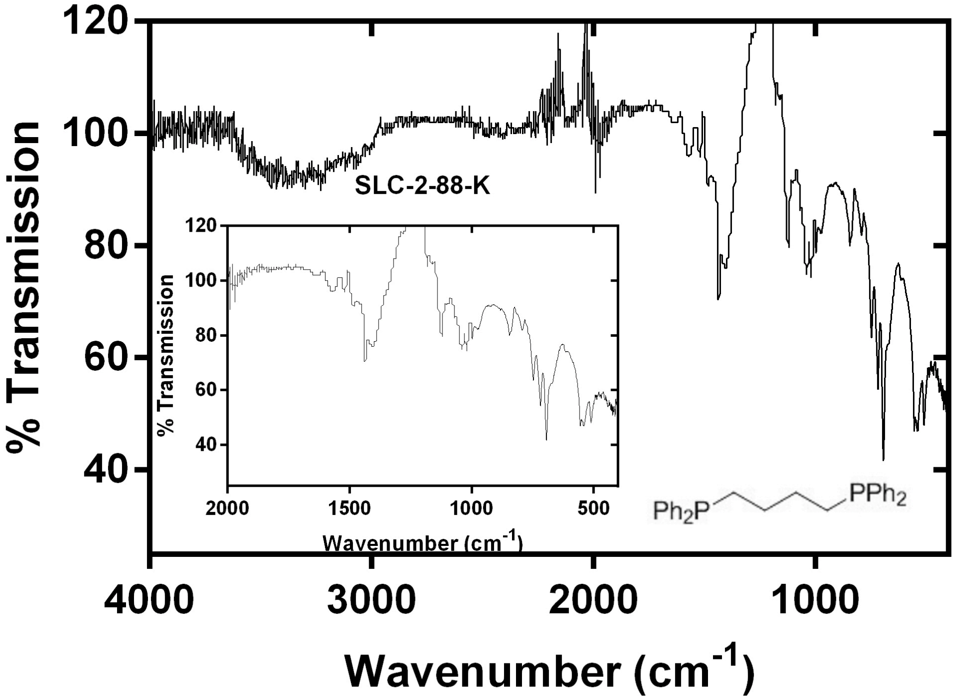
1500
1000
500
Wavenumber (cm^{-1})
Ph$_2$P PPh$_2$



References:

1. R. Patrik Pettersson and M. Olsson, *Journal of Analytical Atomic Spectrometry, 1998,* ***13****, 609.*

2. Y. Surendranath, M. Dincă and D. G. Nocera, *J. Am. Chem. Soc.*, 2009, **131**, 2615.