

## Dimethylphosphite Electrosynthesis from Inorganic Phosphorus Building Blocks via Oxidative Coupling

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## 1. Material and Methods:

### Chemical Reagents:

Palladium foil (Pd, 0.025 mm, 99.9%), dimethylformamide (DMF,  $\geq 99.8\%$ ), methanol ( $\geq 99.8\%$ ) were purchased from Fisher Scientific. Palladium chloride ( $\text{PdCl}_2$ , 99.9%) was obtained from VWR. Hydrochloride (0.5M, HCl), sulfuric acid were acquired from Anachemia. Hypophosphorous acid (50 wt% in  $\text{H}_2\text{O}$ ), dimethyl sulfoxide-d6 (d-DMSO, 99.9 atom % D), tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ , 98%) were obtained from Sigma-Aldrich. All chemicals were used without further purification.

### Catalyst Preparation:

Pd synthesis: Rough Pd foil was synthesized by an electrochemical deposition method. Commercial Pd foil was cut and polished by alumina powder. After washing with DI water, the Pd foil was used as the working electrode in the electrochemical roughening procedure. Here, Pd was electrodeposited on the foil surface (approx.  $1\text{ cm}^2$ ) at  $-0.2\text{ V}$  vs. Ag/AgCl until 13 C of charge was passed, using an aqueous electrodeposition precursor solution of 15.9 mM  $\text{PdCl}_2$  with 0.5 M HCl.

### Physical characterization:

Scanning electron microscope characterization was conducted on FEI Quanta 450 Environmental Scanning Electron Microscope (FE-ESEM).

### Electrochemistry and product qualification:

Cyclic voltammetry (CV) and other electrochemical measurements were conducted by a Bio-Logic SP-200 Potentiostat (BioLogic Science Instruments, France). A standard three-electrode configuration was employed, and a batch cell was used for the measurements. Two rough Pd foils were used as working and counter electrode, and an Ag wire was used as a quasi-reference electrode. The mixture of methanol, 20 mM  $\text{TBAPF}_6$  supporting electrolyte, and different concentrations of  $\text{H}_3\text{PO}_2$  was used as electrolyte. The CVs were measured in the range of  $0 \sim 1.8\text{ V}$  (vs. Ag) with a sweep rate of  $10\text{ mV s}^{-1}$ . Before each experiment, the electrolyte was purged with  $\text{N}_2$  for 20 minutes to remove dissolved reactive gases like  $\text{O}_2$ . Prior to controlled potential electrolysis, the reactor was sealed and the electrolyte was stirred at 500 rpm throughout the reaction. All reactions were carried out at room temperature.

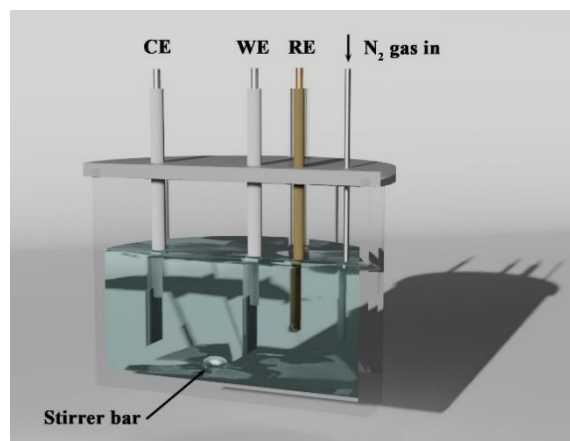
To analyze products after electrolysis, 1H NMR (Bruker AVANCE III 400), 2D NMR (1H-31P HMBC, Bruker AVANCE II 700) and mass spectrometry were performed to reveal the composition of the species formed. After 6h reaction, 400  $\mu\text{L}$  liquid was extracted from the reactor and mixed with 400  $\mu\text{L}$  d-DMSO.  $\text{TBAPF}_6$  was used as an internal standard. The quantity of the products was calculated based on the calibration curve of the standard samples. The Faradaic efficiency (FE) was calculated by the following formula:

$$\epsilon_{\text{FE}} = \frac{\alpha n F}{Q}$$

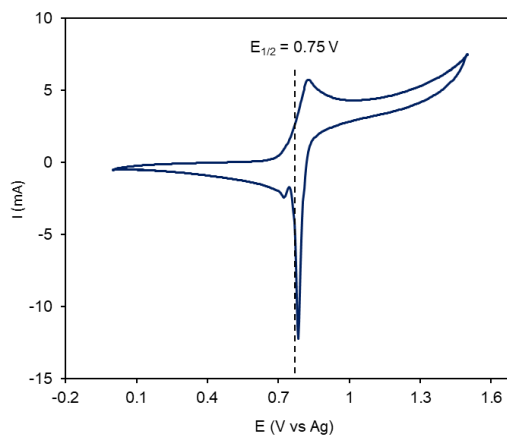
where  $\alpha$  is electron transfer number (for the formation of dimethyl phosphite (DMP)  $\alpha$  is 2),  $n$  is the moles of the products,  $F$  is the Faraday constant ( $96485\text{ C mol}^{-1}$ ), and  $Q$  is the sum of the charge passed during the reaction. For the curves of FE and partial current density, error bars are added from three independent experiments. Partial current density is given using the geometric surface area of the electrode.

Thermochemical DMP generation was carried out using 50 mM  $\text{H}_3\text{PO}_2$  and 20 mM  $\text{TBAPF}_6$  in methanol with 50 mM sodium phosphite at 70°C for 24 hrs.

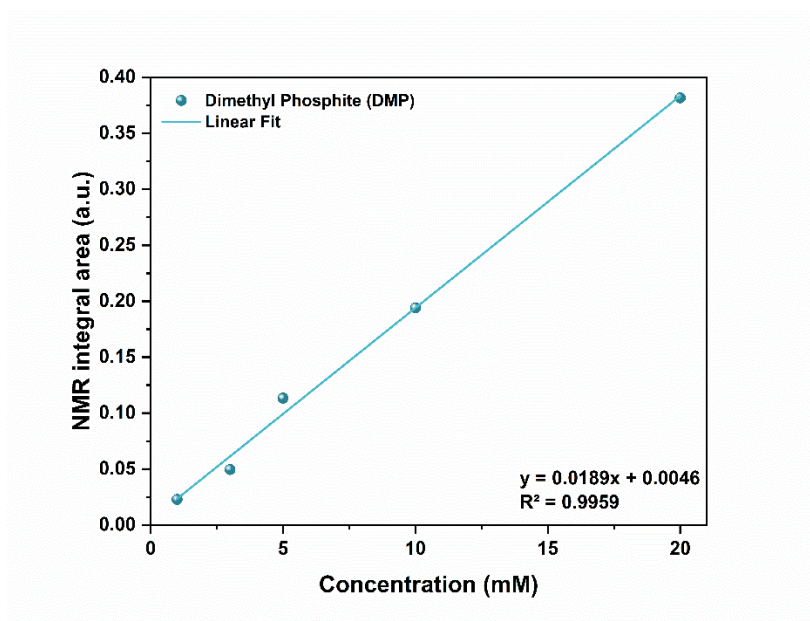
2. Supplementary figures:



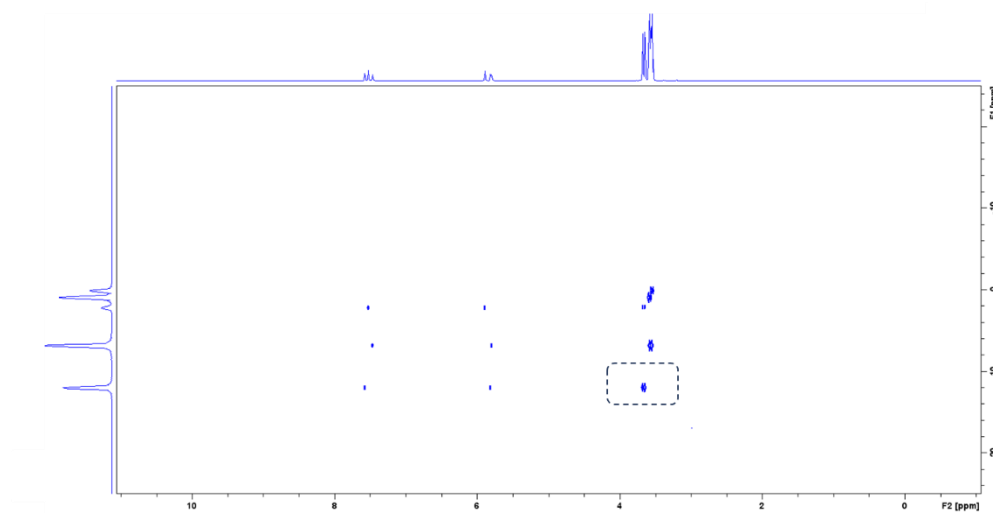
**Figure S1.** Illustration of the batch reactor used in this work.



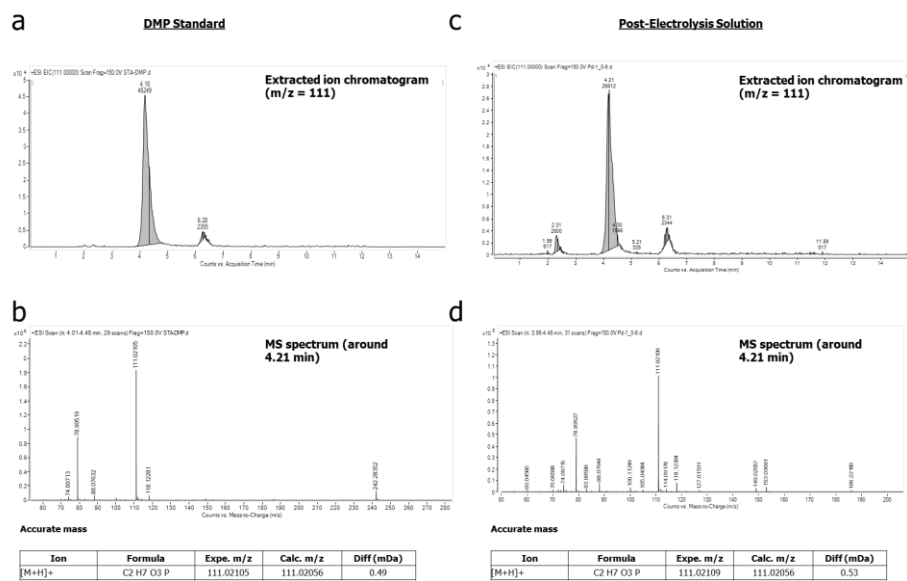
**Figure S2.** CV of ferrocene using Ag as a quasi-reference electrode in DMF electrolyte with 20 mM TBA  $\text{PF}_6$  supporting electrolyte.



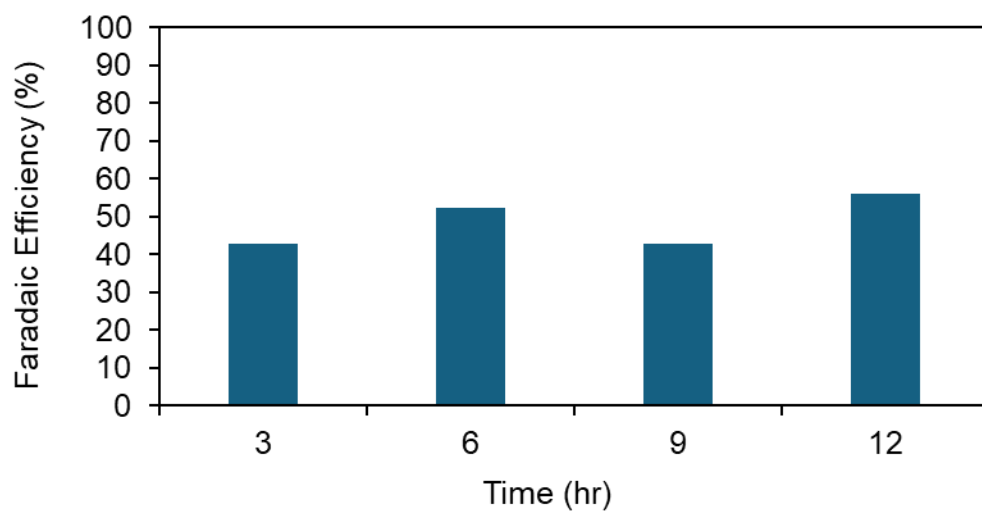
**Figure S3.** NMR calibration curve of DMP using TBAPF<sub>6</sub> as an internal standard.



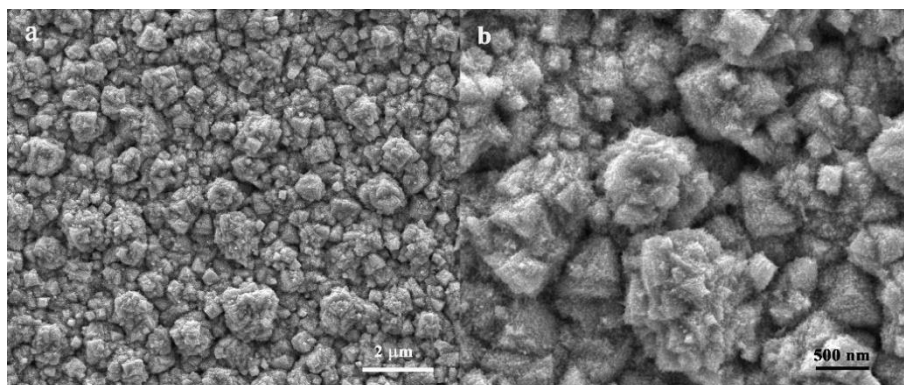
**Figure S4.** HMBC (Heteronuclear Multiple Bond Correlation) NMR of <sup>31</sup>P and <sup>1</sup>H nuclei showing the expected correlation of the DMP <sup>31</sup>P signal around 12 ppm and <sup>1</sup>H signal at 3.7 ppm



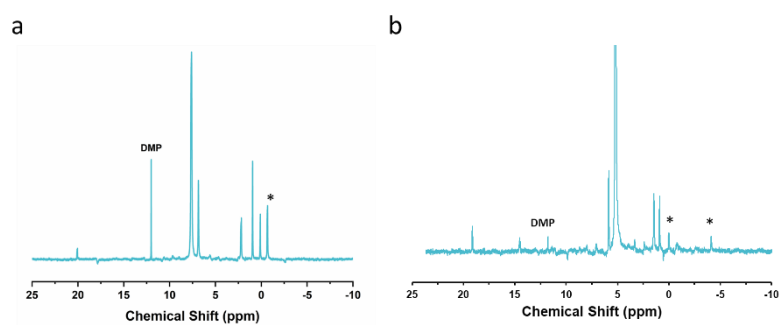
**Figure S5.** Chromatogram signals and mass spectra of a DMP standard solution (a, b) and our post-electrolysis solution (c, d).



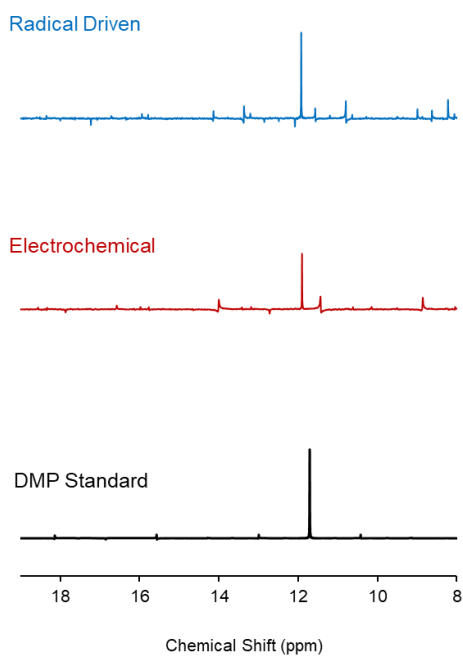
**Figure S6.** Selectivity of the reaction over extended times using a rough Pd electrode at -1 V in methanol electrolyte with 0.1 M  $\text{H}_3\text{PO}_2$



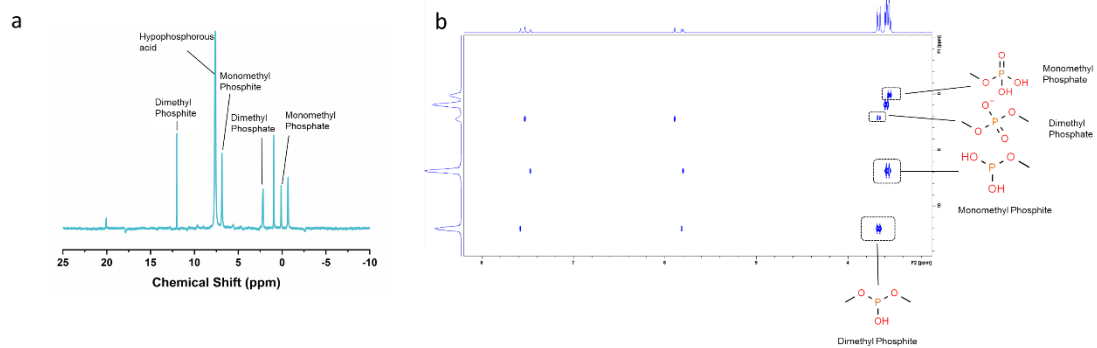
**Figure S7.** SEM images of the working electrode (roughed Pd foil) after 6 hrs of reaction at -1 V vs. Ag at low (a) and high (b) magnifications.



**Figure S8.**  $^{31}\text{P}$  NMR spectra of a post reaction solution using 100% methanol (a) and 25% methanol (b) showing potential phosphate and/or pyrophosphate byproducts in the 2 to -5 ppm range indicated by a \*.

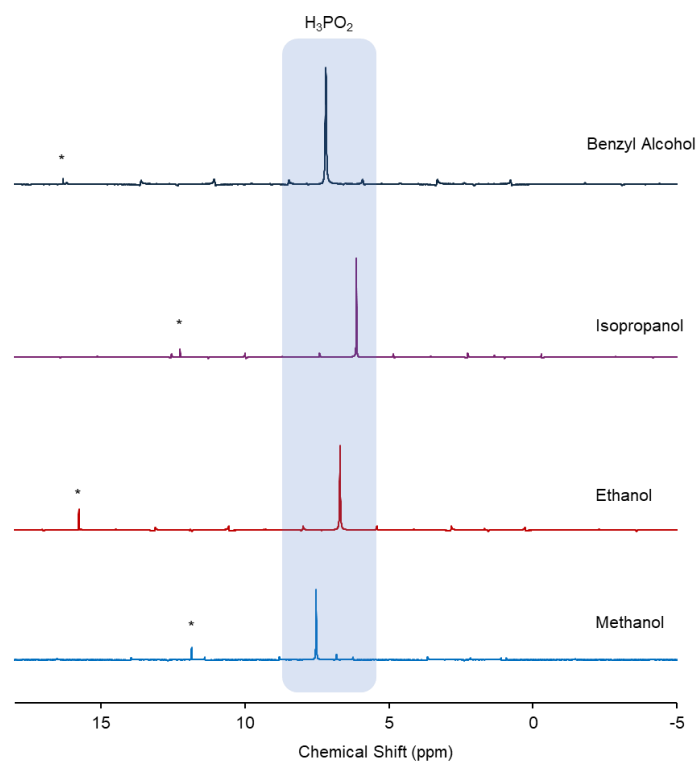


**Figure S9.**  $^{31}\text{P}$  NMR spectra of a DMP standard, electrochemically generated DMP, and DMP generated via a radical initiator, sodium thiosulfate, at  $70^\circ\text{C}$  in the same reaction solution but in the absence of electrodes or electrochemical steps.



**Figure S10.**  $^{31}\text{P}$  NMR (a) and HMBC P-H NMR (b) illustrating additional peaks that are tentatively attributed to phosphite and phosphate esters found in our post electrolysis solution.





**Figure S11.**  $^{31}\text{P}$  NMR spectra of the post electrolysis solution when using other alcohols as the solvent besides methanol. The  $\text{H}_3\text{PO}_2$  peak shifts due to the different solvents and the peaks indicated with a \* are tentatively attributed to coupling products.