# **Electronic Supplementary Information**

# Molecular Catalysis at Polarized Interfaces Created by Ferroelectric BaTiO<sub>3</sub>

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### **Experimental Methods**

## General.

Unless otherwise specified, all solvents were obtained from Fisher Chemical (ACS grade) and used as received. PhCF<sub>3</sub> was purchased from Sigma-Aldrich and used as received.

### Preparation of reagents and catalysts.

1, 4a and 4b were synthesized and purified according to the literature.<sup>1</sup>

**Ball milling.** Bulk BaTiO<sub>3</sub> (2  $\mu$ m), LiNbO<sub>3</sub> (size not specified), TiO<sub>2</sub> (anatase phase, size not specified) and SrTiO<sub>3</sub> (<5  $\mu$ m) powders were purchased from Sigma-Aldrich. Bulk PbTiO<sub>3</sub> (325 mesh, 44  $\mu$ m) and CaTiO<sub>3</sub> powder (size not specified) was purchased from Strem Chemicals. (See below for unmilled particle sizes as determined by TEM.) Ball milling was performed with a Fritsch Pulverisette 7 Planetary Micro Mill Classic with 12 mL zirconium oxide grinding bowls. In a grinding bowl, 20 g of 2 mm diameter zirconium oxide grinding balls, 1.6000 g of heptane, and 80.0 mg of oleic acid were added, followed by either 80.0 mg of BaTiO<sub>3</sub>, 80.0 mg of PbTiO<sub>3</sub>, 80.0 mg of SrTiO<sub>3</sub>, 40.0 mg of CaTiO<sub>3</sub>, or 40.0 mg of TiO<sub>2</sub>. The bowl was sealed and spun in the ball mill for 16 cycles of 60 minutes at 500 rpm, then 30 minutes of rest. The direction of spinning was reversed after each cycle. The total time for the procedure was 24 hours.

Once ball milling was complete, the grinding bowl was opened and the nanoparticle suspension pipetted out into a glass vial for use in reactions. In order to remove residual oxide, grinding bowls and balls were thoroughly rinsed with hexane and sonicated several times in methanol, then briefly soaked in concentrated nitric acid for about 5 minutes and thoroughly washed with deionized water before being used again.

**TEM analysis of bulk and ball milled oxides.** TEM analysis was performed using an FEI Tecnai G2 F20 X-TWIN Transmission Electron Microscope operating at 200 kV. Samples were prepared by drop-casting dilute suspensions of the various oxides in methanol (for bulk powders) or heptane (for ball milled nanoparticles) onto copper TEM grids. Particle and nanoparticle sizes were estimated by measuring 100 different particles, from which the average size and standard deviation were calculated. Representative TEM images of the samples are shown in **Figures S1–S14**. Notably, bulk and ball milled LiNbO<sub>3</sub> particles had a flat, plate-like morphology, unlike the more granular appearance of the other oxides. The entry for LiNbO<sub>3</sub> reflects the particle width and not the thickness, which could not be measured by TEM.

Oxide	Size / nm		Oxide	Size / nm
Bulk BaTiO <sub>3</sub>	$900 \pm 250$		Bulk CaTiO <sub>3</sub>	$750\pm370$
Ball milled BaTiO <sub>3</sub> $8.5 \pm 3.0$			Ball milled CaTiO <sub>3</sub>	9.5 ± 3.7
Bulk PbTiO <sub>3</sub> $260 \pm 100$		Bulk SrTiO <sub>3</sub>	$920 \pm 320$	
Ball milled PbTiO <sub>3</sub> $7.4 \pm 3.0$		Ball milled SrTiO <sub>3</sub>	7.7 ± 2.5	
Bulk LiNbO <sub>3</sub>	$1800 \pm 1100$		Bulk TiO <sub>2</sub>	$120 \pm 40$
Ball milled LiNbO3 $45 \pm 2$			Ball milled TiO <sub>2</sub>	8.0 ± 2.4

Attachment of Rh porphyrin 4b to oxide surfaces. Bulk TiO<sub>2</sub>, CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, PbTiO<sub>3</sub>, or BaTiO<sub>3</sub> powder (~100 mg) was soaked overnight in a solution of 4b in CH<sub>2</sub>Cl<sub>2</sub> (~1 mM). Subsequently, the powder was allowed to settle overnight and the catalyst solution carefully pipetted off. The powder was then allowed to dry at room temperature and then baked at 150 °C under an atmosphere of N<sub>2</sub>. The resulting functionalized bulk powder was rinsed twice with CH<sub>2</sub>Cl<sub>2</sub> and sonicated in CH<sub>2</sub>Cl<sub>2</sub> (4 × 15 minutes) to remove unattached molecules of 4b. Particle suspensions were centrifuged (500 rpm) between each wash to facilitate this process. The functionalized powder was stored at room temperature, or subjected to ball milling (see above) before use.

**Spontaneous polarization measurements**. Spontaneous polarization of nanoparticles was measured through the electric response of cells filled with nanoparticles suspended in a heptane/oleic acid mixture,<sup>2</sup> an insulating non-polar fluid. An electric field applied across the cell aligns the ferroelectric (i.e. polar) nanoparticles such that their dipole moments become parallel to the field. A periodic *ac* electric field causes rotation of the polar nanoparticles, which gives rise to an *ac* displacement current. Integration of the positive (or negative) part of the displacement current density over half a period gives a displacement charge density proportional to the spontaneous polarization of the material,  $P_s$ , and the volume fraction of the material in the suspension.<sup>3</sup> The cells were made using approximately  $2\times3$  cm<sup>2</sup> glass plates, coated with a transparent conductive layer of indium tin oxide (ITO) on one side of each plate (the side adjacent to the suspension); a space of 8 microns between the ITO layers was achieved using non-polar glass spacer beads. Examples of the displacement current traces under a triangular voltage waveform are given in **Figure S15** for the ball milled BaTiO<sub>3</sub>, CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and TiO<sub>2</sub> nanoparticles. For clarity, the background from the cell filled with just heptane/oleic acid mixture (no nanoparticles) was subtracted from the original data.

The data in **Figure S1** show both the result of aggregation as a function of nanoparticle concentration (**Figure S15b**) and the differences between various titanium oxide-based materials (**Figure S15b,c**); **Figure S15a** shows half of the period of the *ac* symmetric triangular voltage

waveform used to measure the displacement currents. With a low enough concentration, where the nanoparticles do not interact with each other,<sup>4</sup> a single feature is observed. With higher concentrations side band structures (wings) form, which are the result of dynamic aggregation and disaggregation of nanoparticles.<sup>4</sup> When comparing the measured displacement current between BaTiO<sub>3</sub> (Figure S15b) and CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and TiO<sub>2</sub> nanoparticles (Figure S15c), one must note the concentrations used in each case. Because of the very weak signal in CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and TiO<sub>2</sub>, the concentrations used to get a measurable signal were far greater than the case of BaTiO<sub>3</sub>. For example, to get a similar displacement current in CaTiO<sub>3</sub>, 100 times more particles were required with respect to ferroelectric BaTiO<sub>3</sub>. The signals for SrTiO<sub>3</sub> and TiO<sub>2</sub> were noticeably smaller, where the displacement current in TiO<sub>2</sub> was about three orders of magnitude weaker than the measured current for BaTiO<sub>3</sub>. Despite the relatively large concentration of the particles used to obtain data for Figure S15c only a central peak was observed, this lack of aggregation would be expected for suspensions that had limited particle interactions, i.e. little Coulombic interaction,<sup>4</sup> in this case the particles are likely to be predominantly in a paraelectric phase. The spontaneous polarization values of the various titanium oxide-based nanoparticles in suspension were measured with a 5 mHz repetition rate with concentrations that did not result in aggregation. The spontaneous polarization values for each material tested (bulk powders and nanoparticles) are summarized in the table below.

Material	$P_{\rm s}$ / $\mu$ C cm <sup>-2</sup>
Unmilled BaTiO <sub>3</sub>	0
Unmilled BaTiO <sub>3</sub> annealed under N <sub>2</sub> at 150°C for 24 h	0
Ball milled BaTiO <sub>3</sub>	20
Unmilled CaTiO <sub>3</sub>	0
Ball milled CaTiO <sub>3</sub>	0.19
Unmilled SrTiO <sub>3</sub>	0
Ball milled SrTiO <sub>3</sub>	0.05
Unmilled TiO <sub>2</sub>	0
Ball milled TiO <sub>2</sub>	0.01

**Reaction setup.** Reactions were performed by diluting freshly ball milled 20:1:1 w/w/w heptane/oleic acid/nanoparticle suspensions to the appropriate nanoparticle concentration with a solution of Rh porphyrin catalyst 4a in CH<sub>2</sub>Cl<sub>2</sub>, followed by a solution of 1 in CH<sub>2</sub>Cl<sub>2</sub>. The reactions were allowed to proceed for 19 h, then analyzed using NMR and high-performance liquid chromatography (HPLC). 2 and 3 were the only major products observed. Results with other solvents besides CH<sub>2</sub>Cl<sub>2</sub> are summarized in Figure 5 in the main text.

**NMR analysis.** Nuclear magnetic resonance (NMR) data were obtained on a Varian Inova spectrometer at 600 MHz for <sup>1</sup>H nuclei. After the appropriate reaction time had elapsed, reactions or aliquots were quenched with at least 3 volumes of MeCN (Fisher Scientific) and filtered through a 0.22  $\mu$ m syringe filter to remove flocculated nanoparticles if necessary. The solvent was evaporated and the residue taken up into CD<sub>3</sub>CN (Cambridge Isotope Laboratories) to produce a sample for NMR analysis. Relative amounts of **1**, **2** and **3** were obtained through careful integration of the diagnostic peaks (1: 5.59 ppm, s, 1H; **2**: 2.31–2.30 ppm, m, 2H; **3**: 6.93–6.90 ppm, dt, 1H) of each substance on the <sup>1</sup>H NMR spectrum (600 MHz, CD<sub>3</sub>CN, nt = 200, at = 4 seconds, d1 = 6 seconds) of the solution, from which conversion and product ratio were calculated. The data was found to be consistent with the results from HPLC analysis (see below). Because of the small quantities of products and long acquisition time required per sample, most samples were analyzed only by HPLC. A sample NMR spectrum of the relevant regions for a reaction of **1** with **4a** is shown in **Figure S16**.

**HPLC analysis.** Reactions were analyzed on an Agilent 1200 HPLC equipped with a Diode Array Detector and an Agilent Eclipse-XDB-C18 reverse phase column. Analysis of **1**, **2** and **3** was carried out using the same method as the literature.<sup>1</sup> If the conversion was less than approximately 5%, two columns in series were used instead with a method of twice the length in order to improve peak separation. Peak areas were calculated after fitting to GaussMod curves in OriginPro 8.5.1, and adjusted for extinction coefficient (see below) to provide conversion and product ratios.

**Relative extinction coefficients of 1, 2 and 3.** The relative extinction coefficients of **1**, **2** and **3** at 210 nm were determined previously.<sup>1</sup>

Relative extinction coefficients at 210nm:

- 1: 1.15
- **2**: 1.62
- **3**: 1.00



**Figure S1.** Representative TEM image of bulk BaTiO<sub>3</sub> particles.



**Figure S2.** Representative TEM image of ball milled BaTiO<sub>3</sub> nanoparticles.



**Figure S3.** Representative TEM image of bulk PbTiO<sub>3</sub> particles.



**Figure S4.** Representative TEM image of ball milled PbTiO<sub>3</sub> nanoparticles.



**Figure S5.** Representative TEM image of bulk LiNbO<sub>3</sub> particles.



**Figure S6.** Representative TEM image of ball milled LiNbO<sub>3</sub> nanoparticles.



**Figure S7.** Representative TEM image of bulk CaTiO<sub>3</sub> particles.



**Figure S8.** Representative TEM image of ball milled CaTiO<sub>3</sub> nanoparticles.



**Figure S9.** Representative TEM image of bulk SrTiO<sub>3</sub> particles.



**Figure S10.** Representative TEM image of ball milled SrTiO<sub>3</sub> nanoparticles.



**Figure S11.** Representative TEM image of bulk TiO<sub>2</sub> particles.



Figure S12. Representative TEM image of ball milled  $TiO_2$  nanoparticles.



**Figure S13.** Examples of the displacement current traces under the symmetric triangular voltage waveform across the cells. (a) Half a period of *ac* waveform. (b) Measured displacement current in BaTiO<sub>3</sub> nanoparticle suspension, 0.0045 wt.% (solid red line, left y-axis) and 0.045 wt.% (dashed black line, right y-axis). (c) Measured displacement current in 0.45 wt.% CaTiO<sub>3</sub> (solid black line), 0.45 wt.% SrTiO<sub>3</sub> (dashed red line), and 0.225 wt.% TiO<sub>2</sub> (dotted blue line) nanoparticles.



**Figure S14.** Sample <sup>1</sup>H NMR spectrum of a typical reaction mixture quenched in CD<sub>3</sub>CN showing the diagnostic peaks for **1** (5.59 ppm, s, 1H), **2** (2.31–2.30 ppm, m, 2H), and **3** (6.93–6.90 ppm, dt, 1H). In this particular experiment, the ratio of **2**:**3** is determined to be 3.8:1.0 with 27.4% conversion. Oleic acid, which is present whenever BaTiO<sub>3</sub> nanoparticles are used, contributes a large number of other peaks elsewhere in the spectrum.

**Experimental data for Figure 2.** The observed ratios of 2:3 with various concentrations of 1, catalyst 4a and ball milled  $BaTiO_3$  (or other oxide) in  $CH_2Cl_2$  are summarized below. This data is presented in Figure 2 in the main text.

[1] / mM	[4a] / µM	[BaTiO₃] / mg mL <sup>−1</sup>	[oxide] / mg mL <sup>-1</sup>	2:3	% Conversion
2	20	0	0	$11.5 \pm 0.1$	98.3 ± 1.0
2	20	0.01	0	$12.0 \pm 0.3$	$97.4 \pm 0.3$
2	20	0.1	0	$11.8 \pm 0.5$	$97.5 \pm 0.2$
2	20	1	0	$10.0 \pm 1.6$	$97.2 \pm 0.2$
2	2	0	0	$11.0 \pm 0.2$	$94.3 \pm 0.3$
2	2	0.01	0	$7.9 \pm 0.1$	$61.9 \pm 3.1$
2	2	0.1	0	$7.1 \pm 0.1$	$54.3 \pm 0.6$
2	2	1	0	$6.3 \pm 0.2$	$45.2 \pm 0.6$
0.2	0.2	0	0	$10.7 \pm 0.3$	45.3 ± 1.8
0.2	0.2	0.01	0	$4.8 \pm 0.8$	$41.6 \pm 0.5$
0.2	0.2	0.1	0	3.7 ± 1.0	32.1 ± 4.7
0.2	0.2	1	0	$2.1 \pm 0.4$	$21.3 \pm 0.7$
0.2	0.2	0	1 (PbTiO <sub>3</sub> )	$2.1 \pm 0.1$	$8.4 \pm 0.3$
0.2	0.2	0	1 (LiNbO <sub>3</sub> )	$4.5 \pm 0.4$	$15.4 \pm 1.4$
0.2	0.2	0	1 (CaTiO <sub>3</sub> )	$11.1 \pm 1.3$	$13.5 \pm 0.1$
0.2	0.2	0	1 (SrTiO <sub>3</sub> )	$11.0 \pm 1.5$	$13.3 \pm 0.6$
0.2	0.2	0	1 (TiO <sub>2</sub> )	$9.5 \pm 0.3$	$80.2 \pm 2.9$

**Experimental data for Figure 3.** The observed ratios of **2**:**3** with 2 mM of **1** and 2  $\mu$ M **4a** in CH<sub>2</sub>Cl<sub>2</sub> at room temperature after various reaction times are summarized below. Ball milled oxide, if present, is used at a concentration of 1 mg mL<sup>-1</sup>. This data is presented in **Figure 3** in the main text.

<b>Reaction Time / h</b>	Ball Milled Oxide	2:3	% Conversion	
6	No oxide	$9.8 \pm 0.3$	$50.4\pm0.9$	
18	No oxide	$10.0 \pm 0.5$	$66.3 \pm 0.3$	
30	No oxide	$9.9 \pm 0.1$	$70.7 \pm 0.2$	
48	No oxide	$9.8 \pm 0.4$	73.4 ± 1.1	
72	No oxide	$9.9 \pm 0.3$	$75.5 \pm 0.6$	
96	No oxide	$9.9 \pm 0.3$	$76.9 \pm 0.4$	
6	BaTiO <sub>3</sub>	$4.6 \pm 0.3$	8.7 ± 0.4	
18	BaTiO <sub>3</sub>	5.7 ± 0.4	$13.9 \pm 1.0$	
30	BaTiO <sub>3</sub>	6.1 ± 0.5	$17.3 \pm 1.5$	
48	BaTiO <sub>3</sub>	6.1 ± 0.3	$20.2 \pm 1.1$	
72	BaTiO <sub>3</sub>	5.9 ± 0.3	23.1 ± 1.2	
96	BaTiO <sub>3</sub>	5.7 ± 0.1	26.3 ± 1.6	
6	PbTiO <sub>3</sub>	6.1 ± 0.4	8.2 ± 0.3	
18	PbTiO <sub>3</sub>	6.3 ± 0.2	$12.3 \pm 0.5$	
30	PbTiO <sub>3</sub>	7.6 ± 0.6	$15.1 \pm 0.3$	
48	PbTiO <sub>3</sub>	$7.0 \pm 0.2$	$20.0 \pm 0.9$	
72	PbTiO <sub>3</sub>	6.4 ± 0.3	21.3 ± 0.8	
96	PbTiO <sub>3</sub>	$7.2 \pm 0.2$	25.9 ± 1.3	
6	LiNbO <sub>3</sub>	5.5 ± 0.3	$14.0 \pm 0.6$	
18	LiNbO <sub>3</sub>	6.1 ± 0.5	$19.5 \pm 0.2$	

Reaction Time / h	Ball Milled Oxide	2:3	% Conversion	
30	LiNbO <sub>3</sub>	$6.6 \pm 0.1$	$25.3 \pm 1.0$	
48	LiNbO <sub>3</sub>	$6.7 \pm 0.2$	$30.4 \pm 1.0$	
72	LiNbO <sub>3</sub>	6.7 ± 0.1	$34.2 \pm 0.7$	
96	LiNbO <sub>3</sub>	$6.3 \pm 0.1$	39.9 ± 0.1	

Experimental data for **Figure 3**. (continued)

**Experimental data for Figure 4.** The effect of adding ball milled  $BaTiO_3$  on the observed ratios of 2:3 with 2 mM of 1 and 2  $\mu$ M of catalyst 4a in various solvents is summarized below. This data is presented in Figure 4 in the main text.

[1] / mM	[4a] / µM	[BaTiO3] / mg mL <sup>-1</sup>	Solvent	2:3	% Conversion	
2	2	0	PhCF <sub>3</sub>	$17.5 \pm 0.9$	71.5 ± 25.6	
2	2	1	PhCF <sub>3</sub>	$8.8 \pm 0.3$	$33.6 \pm 4.0$	
2	2	0	CH <sub>2</sub> Cl <sub>2</sub>	$11.0 \pm 0.2$	$94.3 \pm 0.3$	
2	2	1	CH <sub>2</sub> Cl <sub>2</sub>	6.3 ± 0.2	$45.2 \pm 0.6$	
2	2	0	THF	$17.9 \pm 0.5$	$32.8 \pm 23.7$	
2	2	1	THF	$2.7 \pm 0.7$	$7.7 \pm 0.7$	
2	2	0	EtOAc	9.4 ±1.5	88.3 ± 11.1	
2	2	1	EtOAc	$7.2 \pm 0.4$	$27.2 \pm 6.8$	
2	2	0	PhMe	$15.3 \pm 0.7$	98.0 ± 1.2	
2	2	1	PhMe	$10.2 \pm 0.9$	64.0 ± 11.7	

**Experimental data for Figure 5.** The observed ratios of 2:3 arising from the reaction of 1 with catalyst 4b unattached or attached to  $TiO_2$  or various titanates in  $CH_2Cl_2$  under various conditions are summarized below. This data is presented in Figure 5 in the main text.

[1] / mM	[4b] / µM	[BaTiO <sub>3</sub> ] / mg mL <sup>-1</sup>	BaTiO <sub>3</sub> treatment	Reaction Time / h	2:3	% Conversion
2	2	0		19	8.8 ± 0.6	89.3 ± 8.2
2	2	1	Ball milled, unfunctionalized	19	4.5 ± 1.3	30.8 ± 3.1
2	Attached to TiO <sub>2</sub>	1	Unmilled after functionalization	19	6.3 ± 0.1	2.9 ± 0.1
2	Attached to CaTiO <sub>3</sub>	1	Unmilled after functionalization	96	$6.2 \pm 0.1$	8.2 ± 0.4
2	Attached to SrTiO <sub>3</sub>	1	Unmilled after functionalization	96	$6.2 \pm 0.3$	3.1 ± 0.6
2	Attached to PbTiO <sub>3</sub>	1	Unmilled after functionalization	96	5.3 ± 0.1	2.1 ± 0.1
2	Attached to BaTiO <sub>3</sub>	1	Unmilled after functionalization	19	$2.2 \pm 0.1$	9.5 ± 0.5
2	Attached to BaTiO <sub>3</sub>	1	Ball milled after functionalization	19	$1.8 \pm 0.7$	5.1 ± 2.2

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