Supplementary Materials

Titanium-Anthraquinone Material as a New Design Approach for Electrodes in Aqueous Rechargeable Batteries

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Contents

Overview of Characterization Methods

Powder X-ray diffraction (PXRD) spectra were obtained with an Inel CPS 120 diffraction system using Cu K_α radiation. PXRD measurements on samples were all performed at ambient temperature (21 ± 1 °C). Field emission scanning electron microscopy (FESEM) and energy dispersive x-ray spectroscopy (EDS) was performed on a JEOL JSM-7401F. Samples were mounted on carb on tape and sputter coated with platinum before placement in the sample chamber of the instrument. Attenuated total reflectance (ATR) infrared spectroscopy (IR) spectroscopy was performed using a Cary 630 FTIR Spectrometer to provide evidence of the coordination of the metal directly to the anthraquinone.

Powder X-ray Diffraction of $Ti(1,8\text{-}DHAQ)_2$

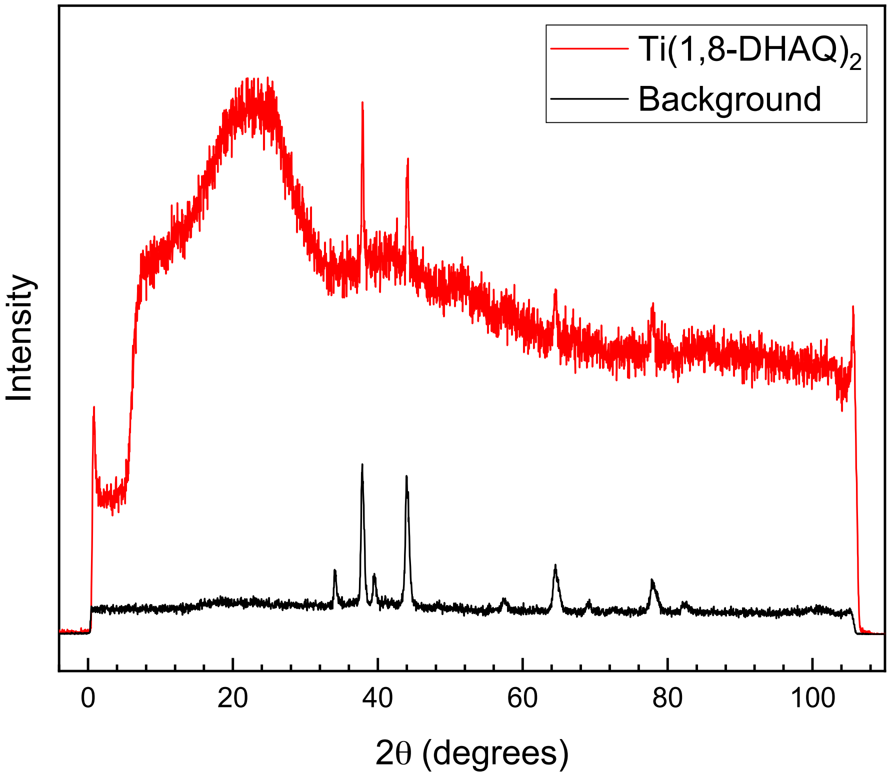

Figure S1: Powder XRD of the $Ti(1,8\text{-}DHAQ)_2$ material. The peaks at 38, 44, 65, and 78 degrees correspond with the aluminum sample holder pan, as shown by the background scan in black. The large broad region between 10 and 35 degrees is indicative of an amorphous compound.

Field-emission Scanning Electron Microscopy (FESEM)

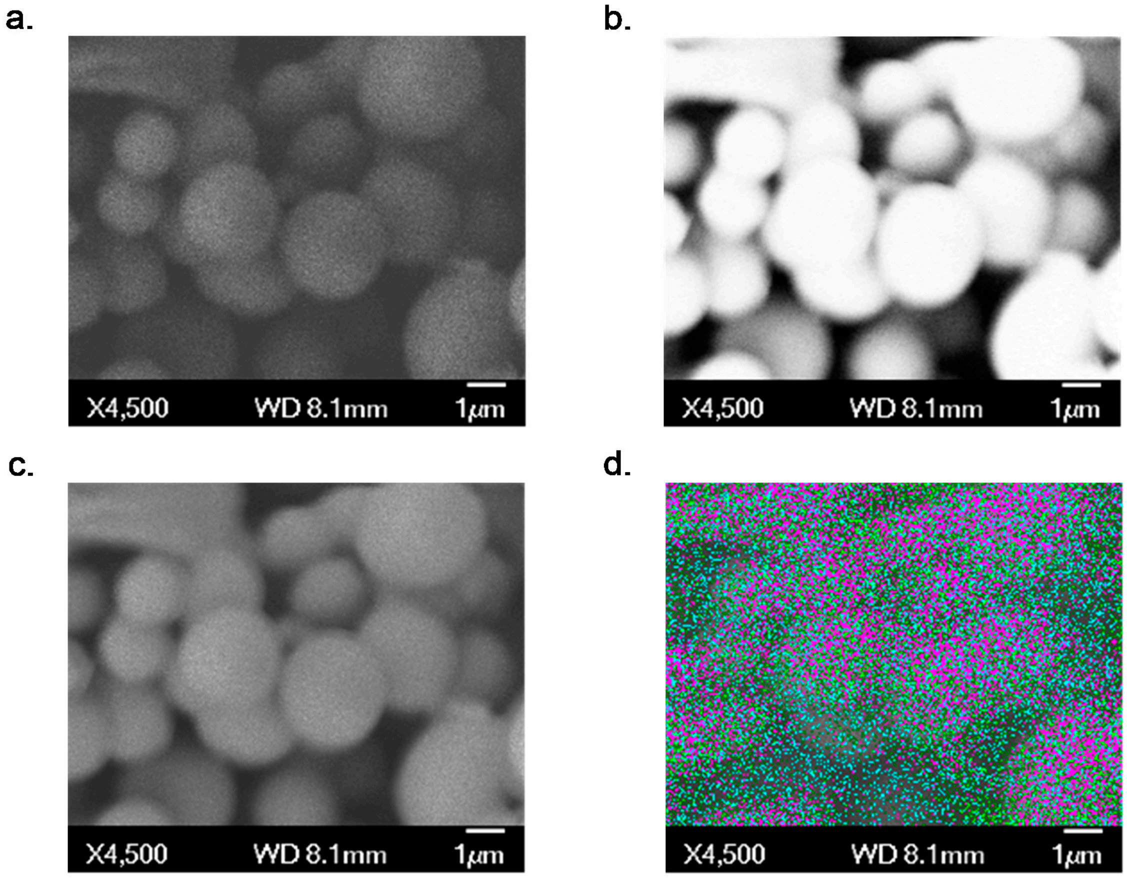

Figure S2: FESEM images with EDS mapping of Ti(1,8-DHAQ)$_2$ microparticles. Image (**a)** was taken only with the FESEM. Image (**b)** is the grey background for the EDS mapping. Image **(c)** is a composite of **(a)** superimposed on **(b)**, indicating that the two images align. Image **(d)** is the EDS mapping on image **(a)**.

Quantitative EDS Analysis

FESEM images of points taken

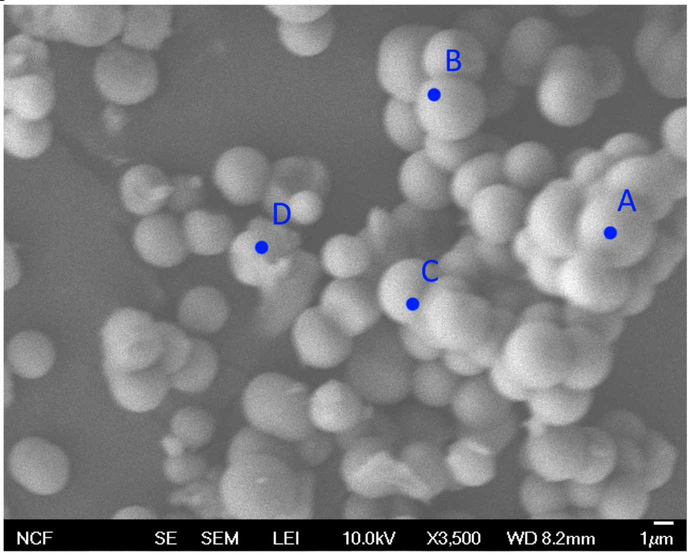

Figure S3: FESEM image of Ti(1,8-DHAQ)$_2$. The labeled blue points indicate where quantitative EDS spectra were measured.

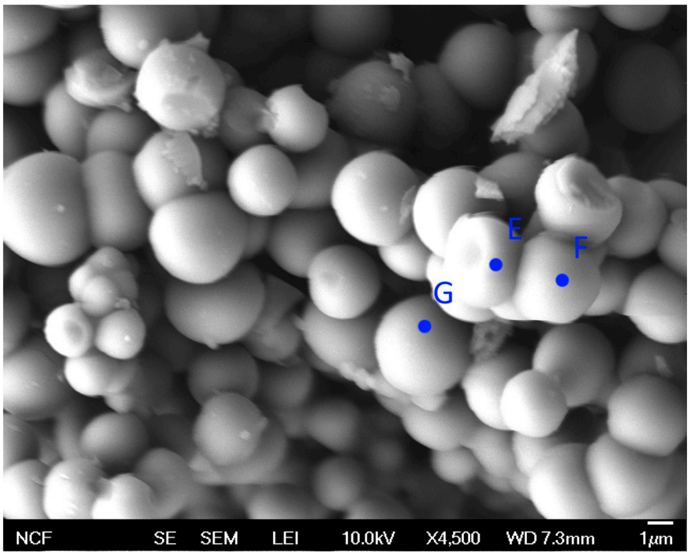

Figure S4: FESEM image of second sample of Ti(1,8-DHAQ)$_2$. The labeled blue points indicate where quantitative EDS spectra were measured.

EDS point spectra

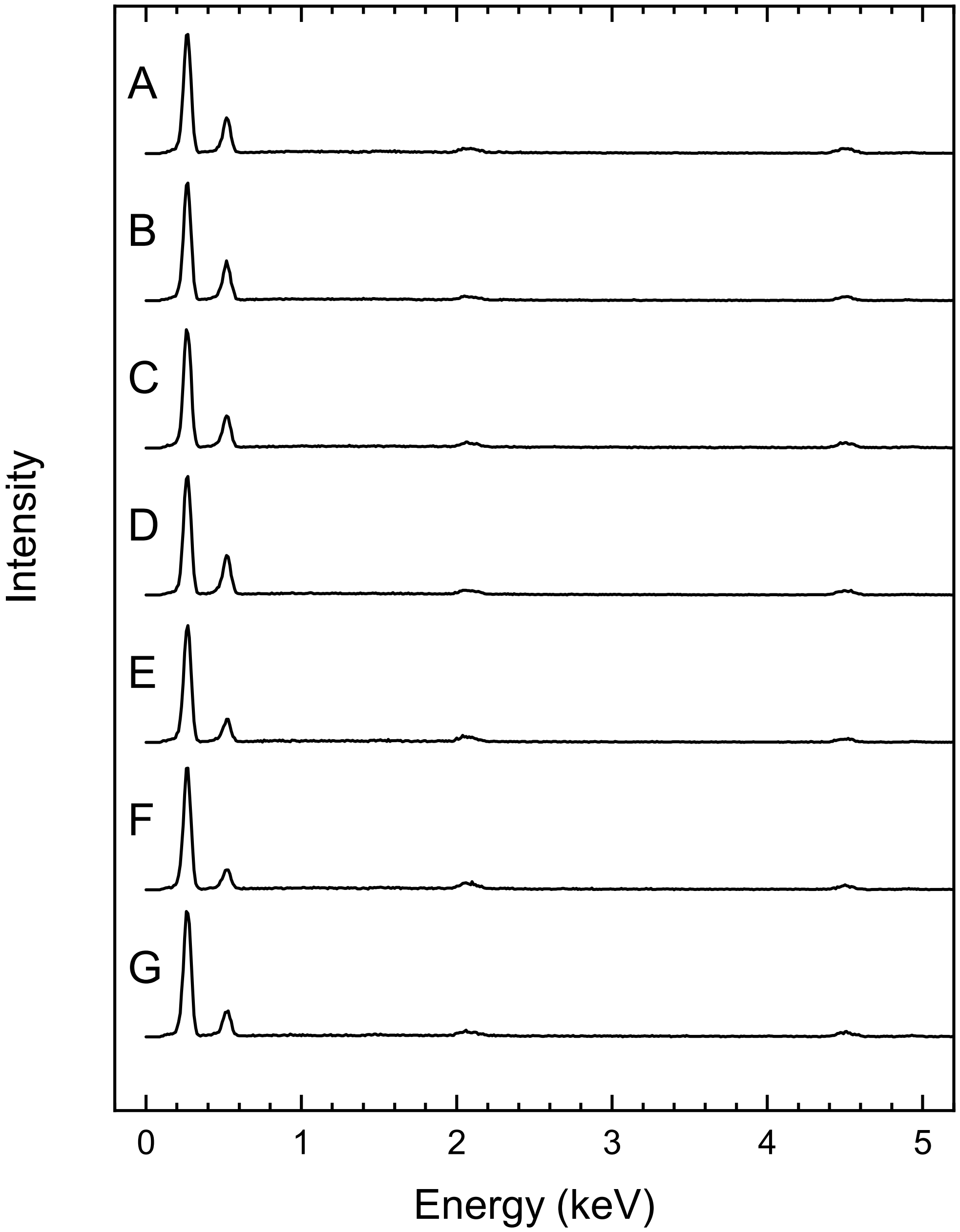

Figure S5: The small feature at 2 keV corresponds to the platinum coating applied to the sample. Peak at 4.51 keV is titanium, peak at 0.525 keV is oxygen, and peak at 0.277 keV is carbon.

Table of ratios from EDS

Atom percent	O	Ti
A	89%	11%
B	92%	8%
C	89%	11%
D	91%	9%
E	89%	11%
F	86%	14%
G	87%	13%
Average	89%	11%

Table S1: Relative atom percentages of the oxygen and titanium features of the EDS spectra in Figure S5. The average percentage of oxygen atoms contained in all samples is eight times larger than the titanium atom percentage, indicating that the molecule contains a ratio of titanium to oxygen of 1:8. Carbon was not shown due to the lower molecular weight and presence of carbon-rich mounting tape on the sample.

FESEM of Ti(1,8-DHAQ)$_2$ After Charging

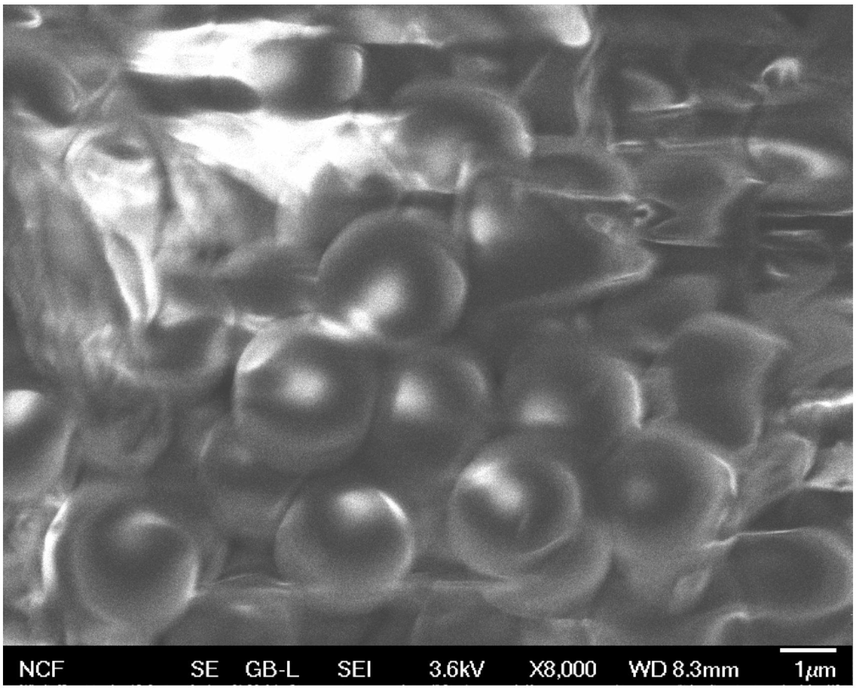

Figure S6: FESEM of Ti(1,8-DHAQ)$_2$ after charging. Material was deposited on a stainless steel mesh and charged by chronopotentiometry in a three-electrode cell. The mesh was removed, dried, and analyzed by FESEM.

Computational Procedure

Frequency calculations were performed to confirm the geometry optimizations were at a minimum energy and to provide the identification of the energies of vibrational modes relating to the carbonyl stretch of the anthraquinone starting material. Cartesian coordinates in Ångströms of the 1,8-DHAQ optimized geometry are given below.

C	-4.268564	0.423058	-0.005160
C	-3.048297	1.127413	-0.005298
C	-1.820640	0.403395	-0.007061
C	-1.854477	-1.016683	-0.008797
C	-3.072352	-1.691245	-0.008598
C	-4.272668	-0.965289	-0.006762
C	-0.552908	1.117604	-0.007045
C	0.697415	0.373350	-0.008493
C	0.697194	-1.047131	-0.010415
C	-0.587910	-1.807856	-0.011109
C	1.942046	1.067750	-0.008001
C	3.145086	0.334355	-0.009633
C	3.115922	-1.053692	-0.011518
C	1.898563	-1.750675	-0.011860
H	1.863117	-2.839759	-0.013354
H	4.055766	-1.608294	-0.012694
H	4.084835	0.887367	-0.009210
H	-3.063042	-2.780870	-0.009971
H	-5.194797	0.998418	-0.003771
H	-5.225525	-1.497224	-0.006648
O	-0.537682	2.396634	-0.005810
O	-0.602591	-3.038681	-0.011628
O	2.011632	2.406078	-0.005706
H	1.054127	2.726852	-0.004240
O	-3.085653	2.467021	-0.003756
H	-2.120577	2.764409	-0.004221

Table S2: Cartesian coordinates for the optimized geometry of 1,8-dihydroxyanthraquinone

Identification of 1,8-DHAQ Vibrational Modes

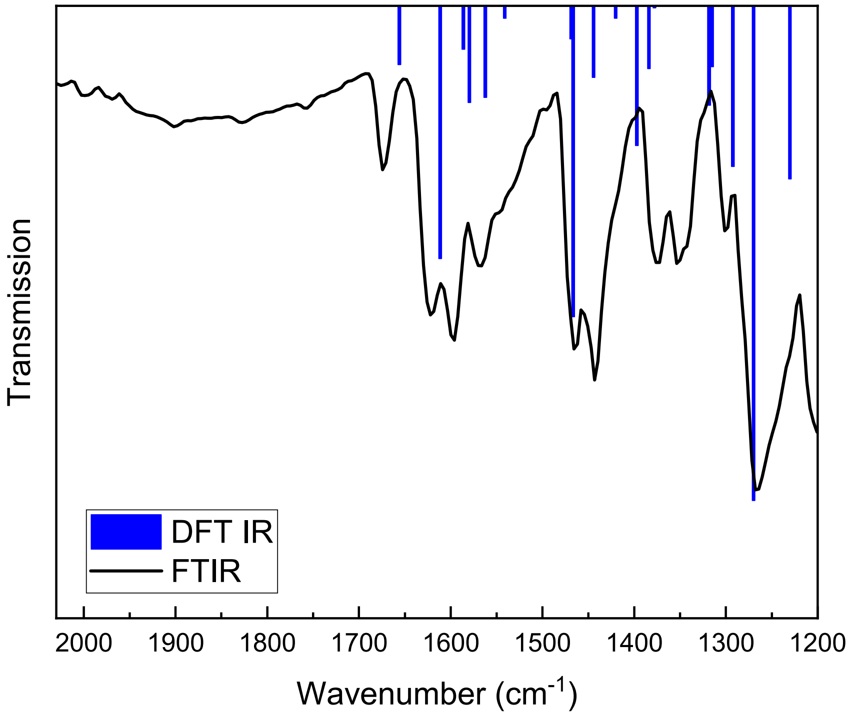

Figure S7: The experimental IR is shown in black, with the theoretical vibrational modes obtained by DFT shown in blue. The peaks at 1670 and 1620 cm-1 were visualized by Avogadro as stretches. The peak at 1670 cm-1 was largely produced by the lone carbonyl in the 10 position, while the peak at 1620 cm-1 corresponds to the movement of the bridging hydrogen atoms between the two hydroxy groups and the carbonyl in the 9 position.

Electrical Impedance Spectroscopy

Potentiostatic electrical impedance spectroscopy (EIS) was obtained of sample of active material mixed with PTFE binder and conductive powder as described in this paper's methods. The sample was deposited on GDL 39 AA carbon paper (SGL) and brought to 48%±3% state of charge in a 3 electrode cell vs. an Ag/AgCl reference electrode. The applied alternating current ranged from 100 kHz to 5 mHz with an amplitude of 10 mV rms and -50 mV applied voltage.

The resulting data was fit to the equivalent circuit shown below in Figure S7. The capacitance of the constant phase element (CPE) was calculated by the following relationship.

$$C = Y_0(\omega_{max})^{(a-1)}$$

Where C is calculated capacitance, Y_o is the CPE parameter for capacitance in units of $S{\cdot}s^a$, a represents the exponential non-ideal behavior parameter, and ω_{max} is the frequency at which the imaginary part of the impedance is at a maximum for this feature.

Schematic of EIS equivalent circuit components

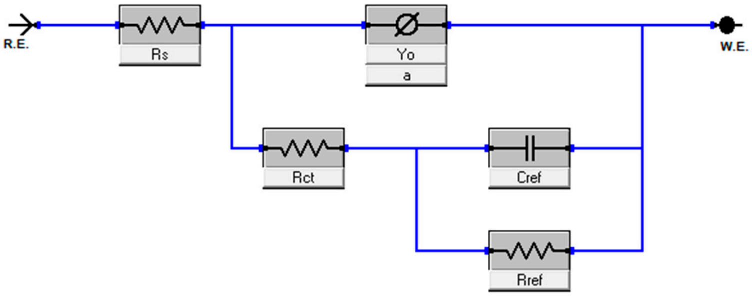

Figure S8: Equivalent circuit used to model Ti(1,8-DHAQ)$_2$ in a three-electrode system vs Ag/AgCl

Table of EIS equivalent circuit component parameters

Component	Fit Parameter	Unit
Rct	8.797E+00	ohm
Rsol	1.422E+01	ohm
Rref	5.536E+04	ohm
Yo	2.107E-04	S*s^a
a	8.848E-01	
Cref	1.065E-04	F

Table S3: Fit parameters when circuit components were analytically determined by the Nedler-Mead method.

Bode plot of experimental EIS with equivalent circuit fit

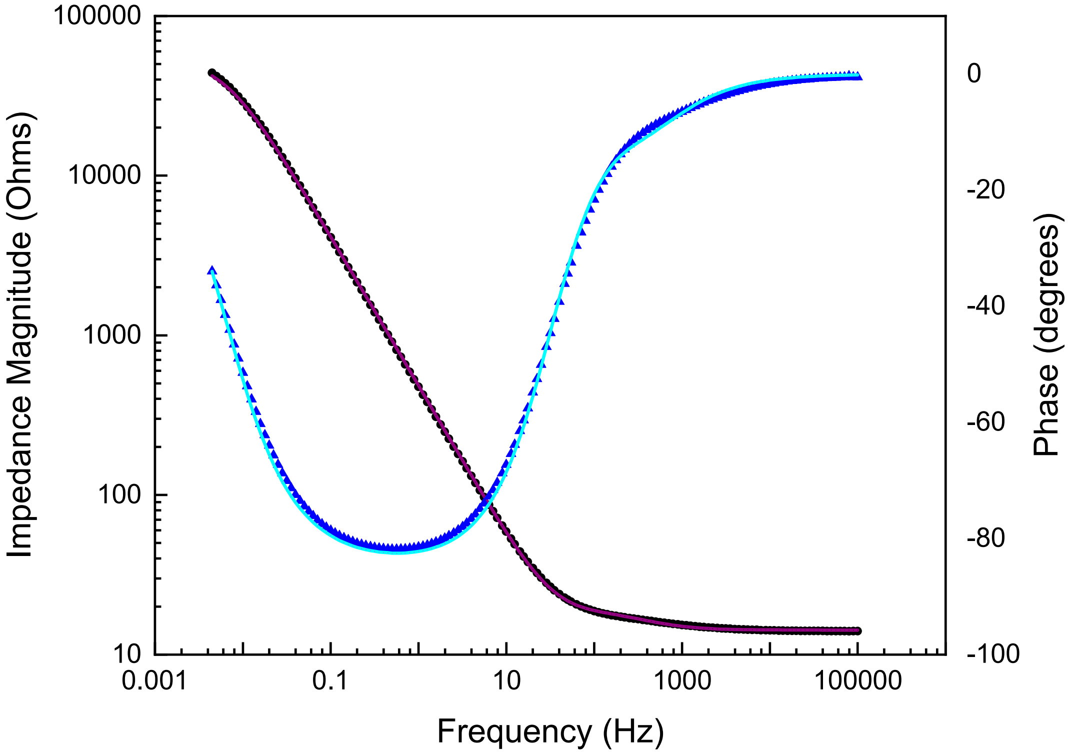

Figure S9: Bode plot of Ti(1,8-DHAQ)$_2$ vs. Ag/AgCl. Experimental impedance magnitude, as determined by EIS, is shown in the black circles, while the experimental phase angle is shown by the blue triangles. The fits for the impedance magnitude and phase are given by the purple and cyan lines, respectively.