Supplementary Information

Highly Transparent Tetraaminophthalocyanine Polymer Films for DSSC Cathodes

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Synthesis of nickel tetranitrophthalocyanine (NiTNPc)
To a 25 mL round bottom flask fitted with a condenser, 10 mL (129 mmol) of DMF was added and heated to 110 °C, while being degassed (N₂) with stirring. 1.307g (5.5 mmol) of NiCl₂ *6H₂O was then added, followed by 4.15 g (24 mmol) of 4-nitrophthalonitrile. The whole mixture was then brought up to 140 °C, the reaction was blue in color. Then 0.8 mL (5.25 mmol) of 1,8 diazabicyclo(5,4)undecene (DBU) was added and the reaction turned a maroon color. The reaction temperature is above the boiling point of DBU, however, the reaction is under mild reflux. Roughly 20 min later the reaction mixture appears to be heterogeneous black/dark blue in color. 40 min after reaching 140°C, another 0.3 mL (1.97 mmol) of DBU was added, the reaction seemed to fume slightly. An oil bath is recommended for heat control, as to not char any precipitated reaction products from heat gradients.

The reaction was stopped 5 hrs after the last addition of DBU and was poured into 50 mL of water, and was left to sit overnight. The suspension was filtered and washed with 200 mL of water. The material formed a thick cake, which appears to be slightly soluble in acetone. The solid was then stirred in a 0.5 M HCl solution then filtered and washed with copious water. The cake was then stirred in 0.5 M NaOH, then vacuum filtered. The filtrate was light brown in color. Again, the solid was stirred in 0.5 M HCl filter and then treated again with 0.5 M NaOH, filtered, and finally washed with copious water. At this point, the consistency of the solid was quite fine, and was similar to wet clay. Some of the solid was pulling though the filter paper, given the small particle size, a fine pore size frit is recommended. Chunky solids can trap impurities and the phthalocyanine should be ground up if they are present. The wet solid was then brought to a pH of ~7, then dried in a vacuum oven over night at ~70 °C. Total mass of the recovered solid was 2.39 grams (3.18 mmol), 57.8 % yield.

Synthesis of nickel tetraaminophthalocyanine (NiTAPc)
1.72 g (2.29 mmol) NiTNPc was added to ~50 mL of water, then 10.1 g (42 mmol) of sodium sulfide was added. The RBF (100 mL) fitted with a condenser was then placed in an oil bath. The reaction was held at ~70 °C with stirring for ~ 8 hrs.

The mixture was then vacuum filtered, and washed with copious amounts of water, then washed with 100 mL of acetone. The solid was stirred in 0.5 M HCl, vacuum filtered, then washed with water. This procedure was repeated with a 0.5 M NaOH solution. The solid was then neutralized (pH ~7) and washed with copious water, followed by ~50 mL of methanol in aliquots. The cake was then placed in vacuum oven and dried at 80 °C for 18 hrs. The recovered mass was 1.1 g (1.64 mmol), 71.6% yield.
Fig. S1. Reaction scheme for the synthesis and a proposed structure for the oxidative polymerization of nickel tetraaminophthalocyanine. Four isomers of the monomer are possible.
Fig. S2. $^1$H-NMR spectra of NiTAPc monomer in DMSO-d$_6$.

Fig. S3. FTIR spectra of monomeric NiTAPc powder.
Mass determination with EQCM

The added mass onto the electrode was related to the change in frequency using a reduced form of the Sauerbrey equation. \( \Delta f \) is the change in frequency, \( C_f \) is the calibration constant (226 Hz cm\(^2\) µg\(^{-1}\)) for a 10 MHz quartz crystal. NiTAPc film formation typically caused a change in frequency no greater than 0.3 \%, well under a 2 \% change in frequency, which is the general acceptable limit to use equation S1.

\[
\Delta f = C_f (\Delta \text{mass (µg cm}^{-2}\text{)})
\]

Equation [S1]
Analysis of NiTAPc films and Co(Bipy) by cyclic voltammetry

Fig. S5 (A) Cyclic voltammetry of bare glassy carbon as well as electrodes coated with NiTAPc formed through increasing cycle numbers. (B) Tafel plots derived from Fig. S5A. The data was collected with a scan rate of 10 mV s\(^{-1}\) in propylene carbonate based mediator.
Calculation of diffusion coefficients of Co(Bipy)

Using Nyquist plots obtained from symmetric cell impedance, diffusion coefficients were calculated with the CH instruments software with an Open Finite Diffusion circuit element. Fitting is shown in the Fig. S6. The circuit element is described by Hauch for diffusion within a symmetric cell, $i \omega$ are variables determined from fitting the spectra, $W$ is the Warburg parameter, $D$ is diffusion coefficient, $\delta$ is the diffusion layer thickness ($l$), for symmetric cell $\delta=0.5*l$.

\[
K_N = \frac{D}{\delta^2} \quad \quad Z_{\text{Open Finite}} = \frac{W}{\sqrt{i \omega}} \tanh\left(\sqrt{K_N}i \omega\right)
\]

Equation [S2]

Fig. S6. Typical 2-electrode symmetric cell impedance spectra (Nyquist) for a 2-cycle NiTAPc film on a glassy carbon electrode. The circuit elements present in the circuit diagram shown in the main text in Fig. 2 are pointed out relative to their respective location on the Nyquist plot. Typical experimental fit is also shown as a black line.

By measuring the limiting current in symmetric cell slow scan cyclic voltammetry experiments, the diffusion coefficients for Co(Bipy) were calculated using Equation S3, were $\delta$ is the diffusion layer thickness, $n$ is the number of electrons, $F$ is Faraday’s constant. $c$ is the concentration of the limiting species $[\text{Co}^{3+}(\text{Bipy})_3]$.
\[ D = \frac{J_{\text{limiting}}(\delta)}{nF \epsilon} \]  

Equation

**Synthetic Cost analysis of NiTAPc**

<table>
<thead>
<tr>
<th>Source</th>
<th>Purity (%)</th>
<th>Purchase amount (g)</th>
<th>Cost (dollar)</th>
<th>Dollar/g</th>
<th>g/mol</th>
<th>Mole equiv.</th>
<th>Dollar/g of chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-nitrophthalonitrile (TCI America) accessed 11-11-2017</td>
<td>&gt;98</td>
<td>100</td>
<td>192</td>
<td>1.92</td>
<td>173.13</td>
<td>4</td>
<td>1.76</td>
</tr>
<tr>
<td>DBU (Sigma) accessed 11-11-2017</td>
<td>&gt;98</td>
<td>2500</td>
<td>855</td>
<td>0.342</td>
<td>152.2</td>
<td>0.1</td>
<td>0.00689</td>
</tr>
<tr>
<td>NiCl*6H2O (Acros Organics) accessed 11-11-2017</td>
<td>&gt;98</td>
<td>1000</td>
<td>202</td>
<td>0.202</td>
<td>237.7</td>
<td>1</td>
<td>0.0636</td>
</tr>
<tr>
<td>DMF (Sigma) accessed 11-11-2017</td>
<td>&gt;99.5</td>
<td>42480</td>
<td>1405</td>
<td>0.0331</td>
<td>73.09</td>
<td>23.5</td>
<td>0.0752</td>
</tr>
<tr>
<td>NiTNPc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>755.2</td>
</tr>
</tbody>
</table>

**Step-2**

| sodium sulphide (9H2O) (Acros Organics) 11-11-2017                   | >98        | 500                 | 92            | 0.184    | 240.18 | 20          | 1.39                |
| NiTAPc 100% yield cost                                               |            |                     |               |          |        |             | 635.2               |
| NiTAPc 50 % yield cost                                               |            |                     |               |          |        |             | 635.2               |

**Estimated cost of electrode coated with 2-cycle NiTAPc film**

<table>
<thead>
<tr>
<th>$ Dollar/µg</th>
<th>Film mass µg/m²</th>
<th>Cost per $/m²</th>
</tr>
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<tbody>
<tr>
<td>0.00000652</td>
<td>100000</td>
<td>0.652</td>
</tr>
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</table>


Table S1. Estimated costs for synthesis and coating electrodes with poly-NiTAPc. Film mass is taken from 2-cycle EQCM experiments in the main text. 0.5 M solutions of NaOH and HCl used for NiTAPc purification were left out as they contributed a negligible amount to the cost.