

**Supporting information for:**

**Optimizing the Energy Offset Between Dye and  
Hole-Transporting Material in Solid-State  
Dye-Sensitized Solar Cells**

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# Chemical Oxidation of HTM Solution Through Titration with $\text{NOBF}_4$

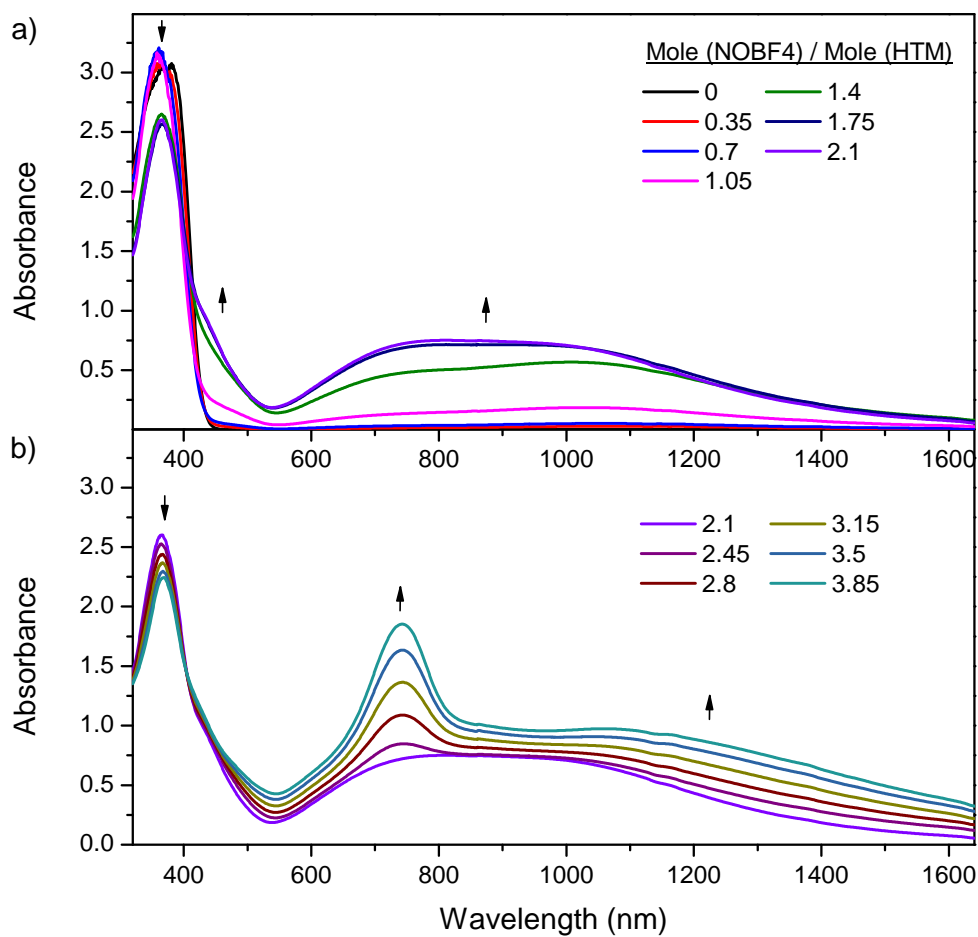


Figure S1: Stepwise chemical oxidation of  $4 \times 10^{-4}$  M HTM **1** in acetonitrile and chlorobenzene (1:1) with increasing amounts of  $\text{NOBF}_4$ : (a) From HTM  $1^0$  over HTM  $1^+$  to HTM  $1^{2+}$ , (b) from HTM  $1^{2+}$  towards higher oxidized states.

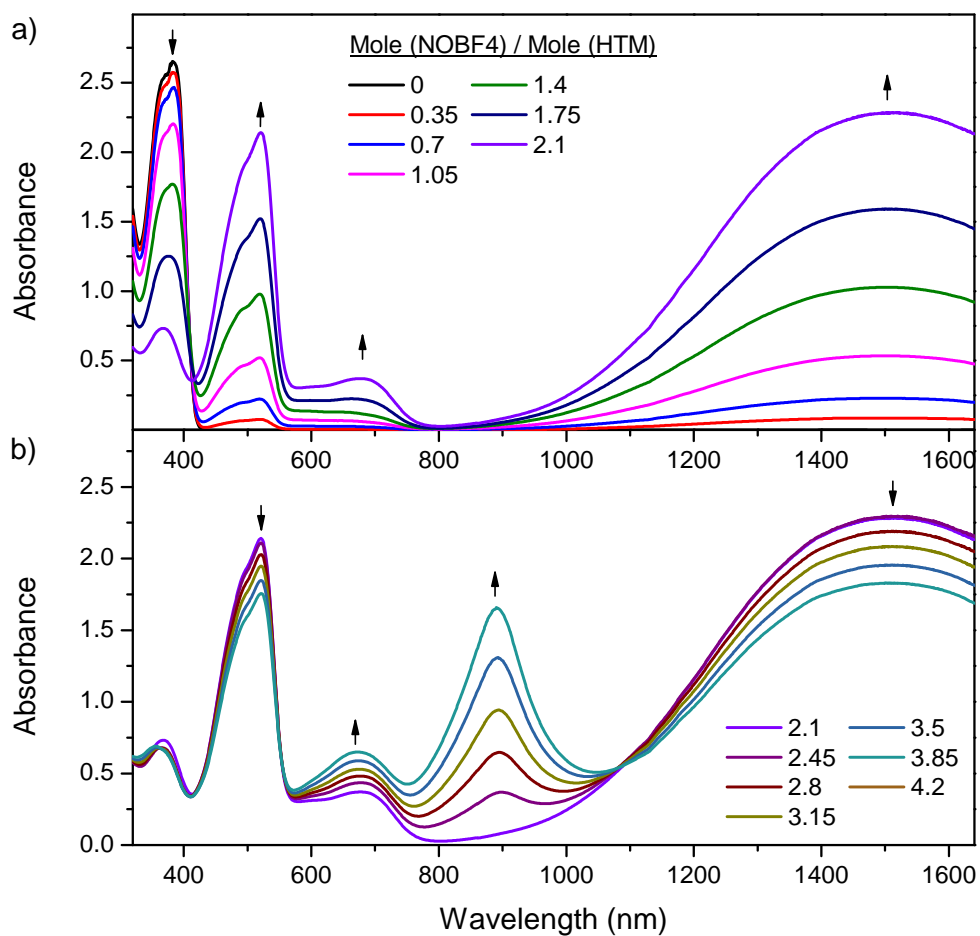


Figure S2: Stepwise chemical oxidation of  $4 \times 10^{-4}$  M spiro-OMeTAD in acetonitrile and chlorobenzene (1:1) with increasing amounts of NOBF<sub>4</sub>: (a) From spiro-OMeTAD<sup>0</sup> over spiro-OMeTAD<sup>+</sup> to spiro-OMeTAD<sup>2+</sup>, (b) from spiro-OMeTAD<sup>2+</sup> towards spiro-OMeTAD<sup>4+</sup>.

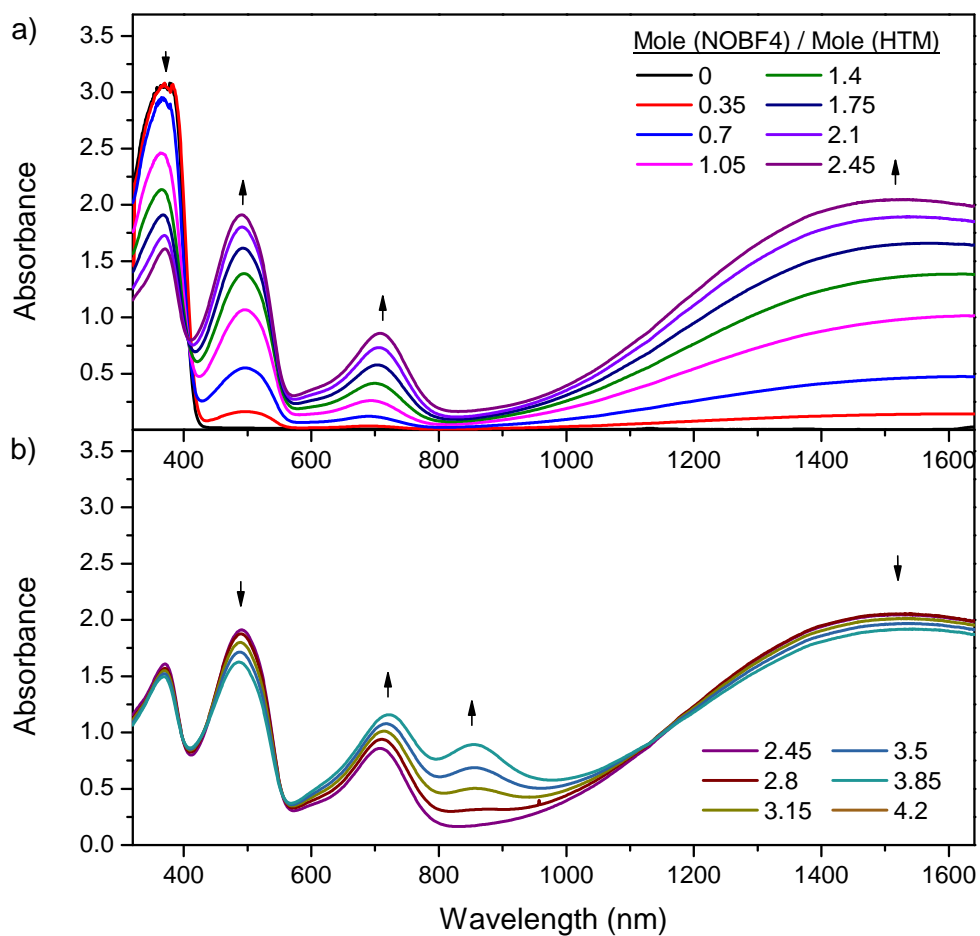


Figure S3: Stepwise chemical oxidation of  $4 \times 10^{-4}$  M HTM **2** in acetonitrile and chlorobenzene (1:1) with increasing amounts of NOBF<sub>4</sub>: (a) From HTM **2**<sup>0</sup> over HTM **2**<sup>+</sup> to HTM **2**<sup>2+</sup>, (b) from HTM **2**<sup>2+</sup> towards higher oxidized states.

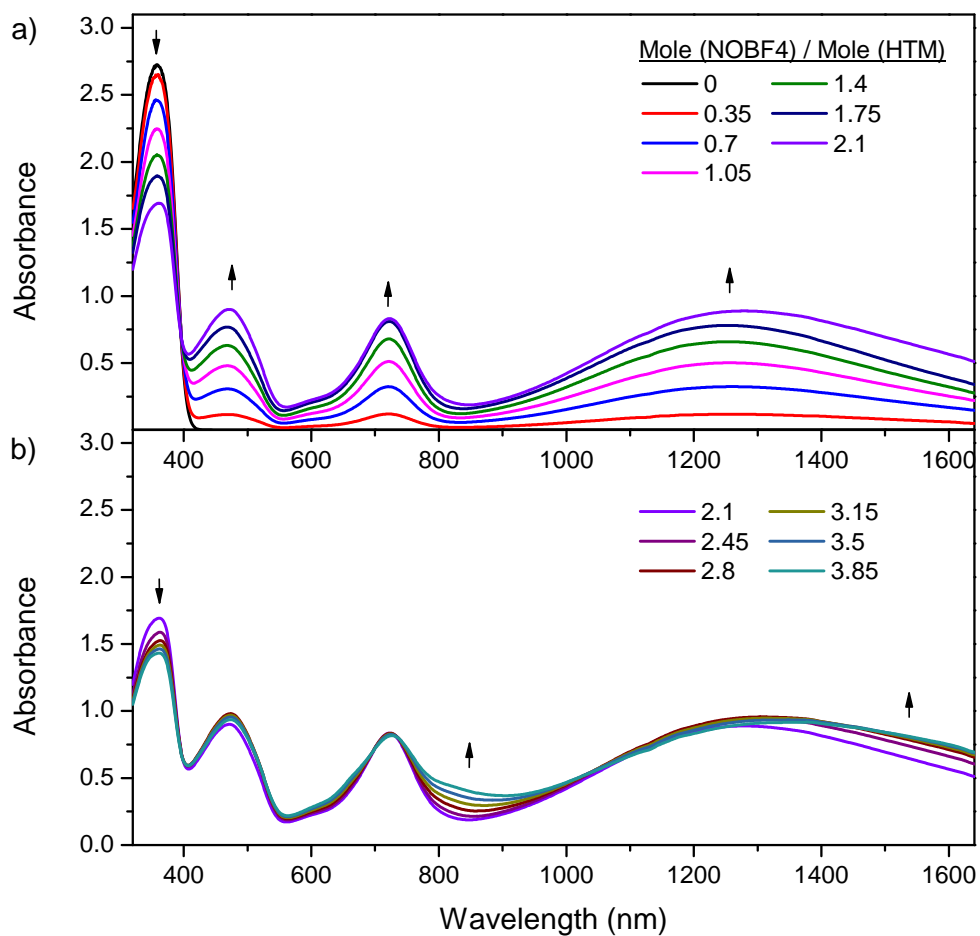


Figure S4: Stepwise chemical oxidation of  $4 \times 10^{-4}$  M HTM **3** in acetonitrile and chlorobenzene (1:1) with increasing amounts of NOBF<sub>4</sub>: (a) From HTM **3**<sup>0</sup> over HTM **3**<sup>+</sup> to HTM **3**<sup>2+</sup>, (b) from HTM **3**<sup>2+</sup> towards higher oxidized states.

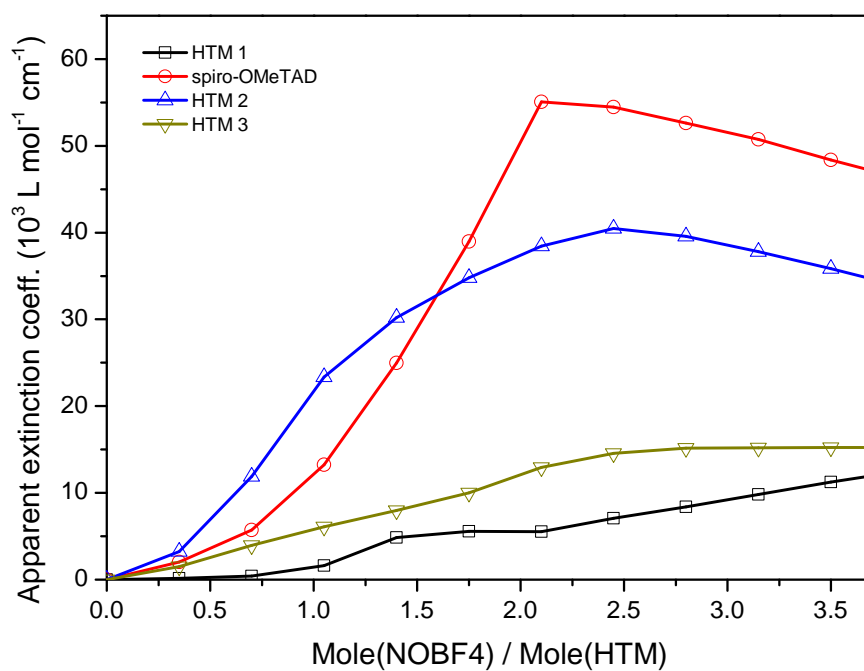


Figure S5: Stepwise chemical oxidation at 520 nm of the four different hole-transporting materials for varying concentrations of NOBF<sub>4</sub>.

## Cyclic Voltammetry of Hole-Transporting Materials

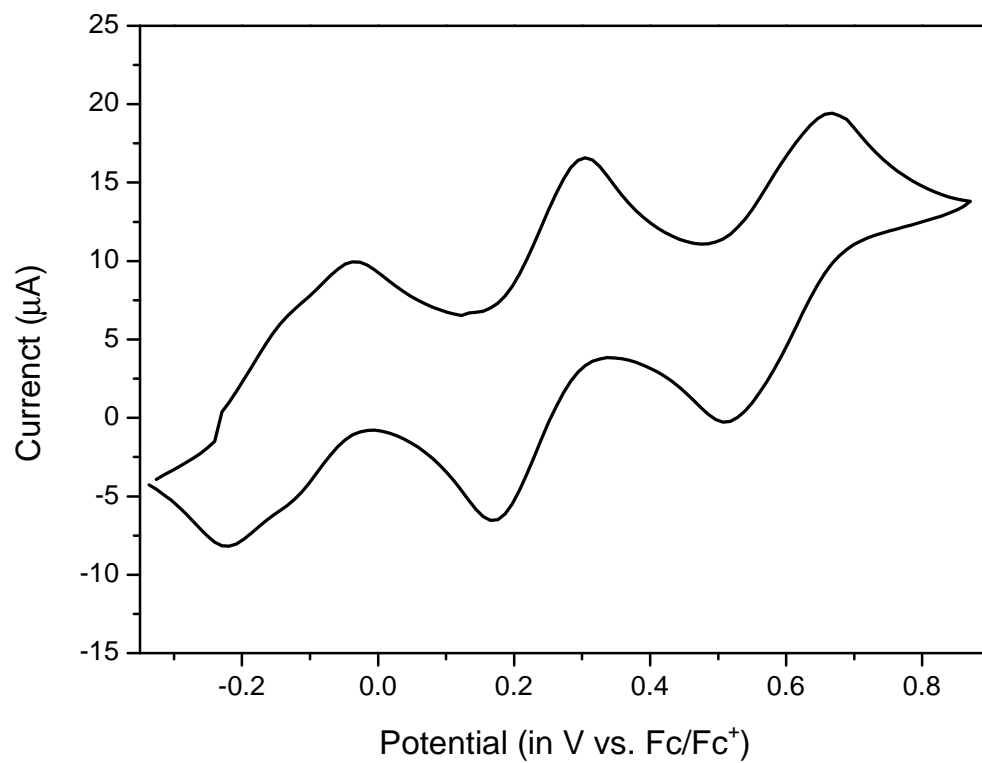


Figure S6: Cyclic voltammetry of dissolved HTM **1**  $1.7 \times 10^{-3}$  M in a solution of 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane. The scan rate was  $100 \text{ mVs}^{-1}$ .

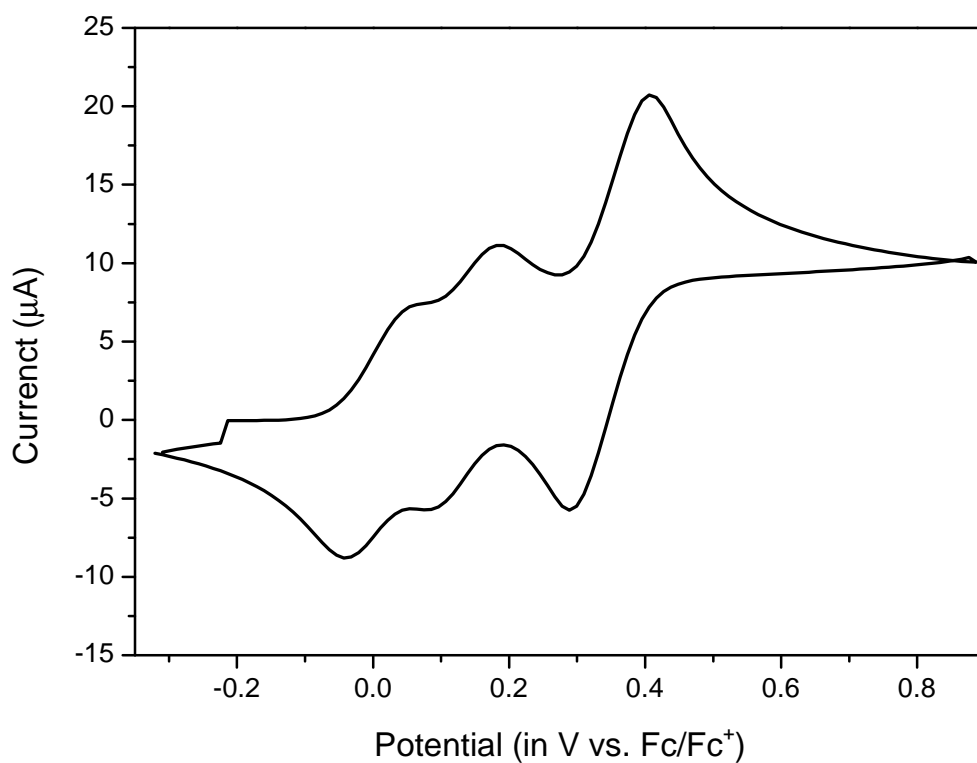


Figure S7: Cyclic voltammetry of dissolved spiro-OMeTAD  $1.7 \times 10^{-3}$  M in a solution of 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane. The scan rate was  $100 \text{ mVs}^{-1}$ .



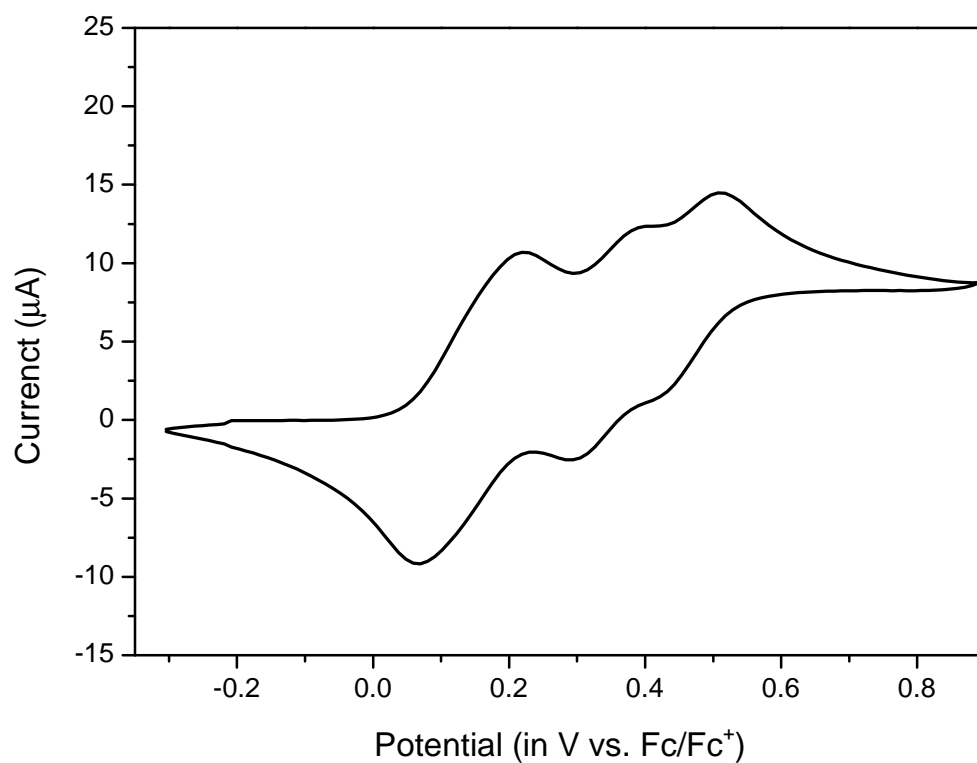


Figure S8: Cyclic voltammetry of dissolved HTM **2**  $1.8 \times 10^{-3}$  M in a solution of 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane. The scan rate was  $100 \text{ mVs}^{-1}$ .

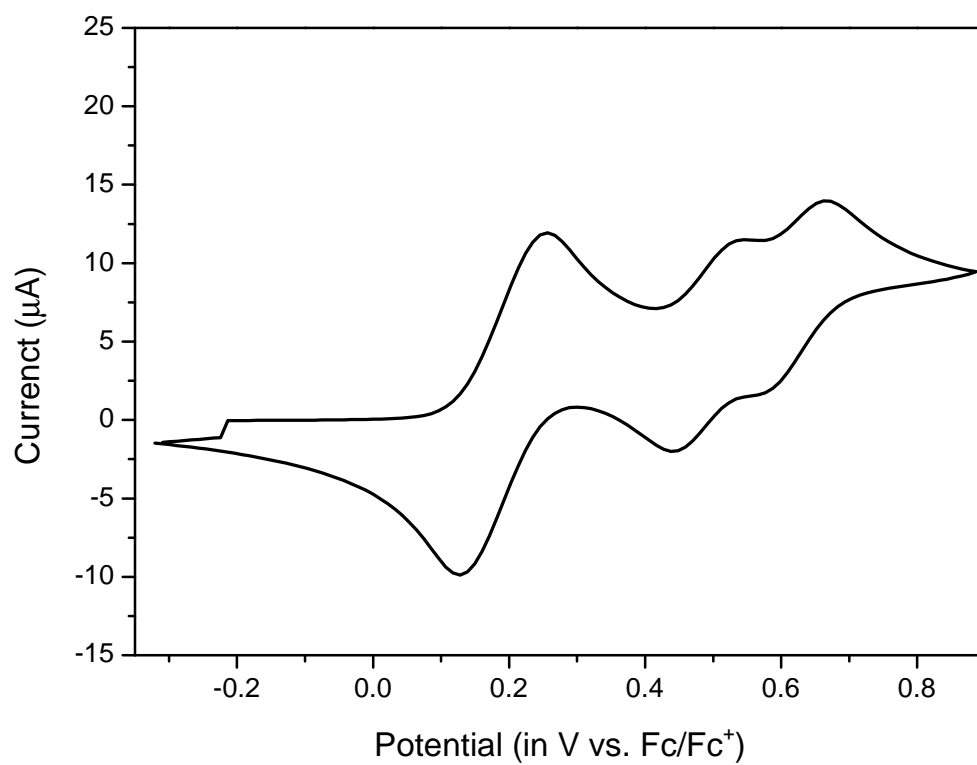


Figure S9: Cyclic voltammetry of dissolved HTM **3**  $1.5 \times 10^{-3}$  M in a solution of 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane. The scan rate was  $100 \text{ mVs}^{-1}$ .

## Charge-Collection Efficiency

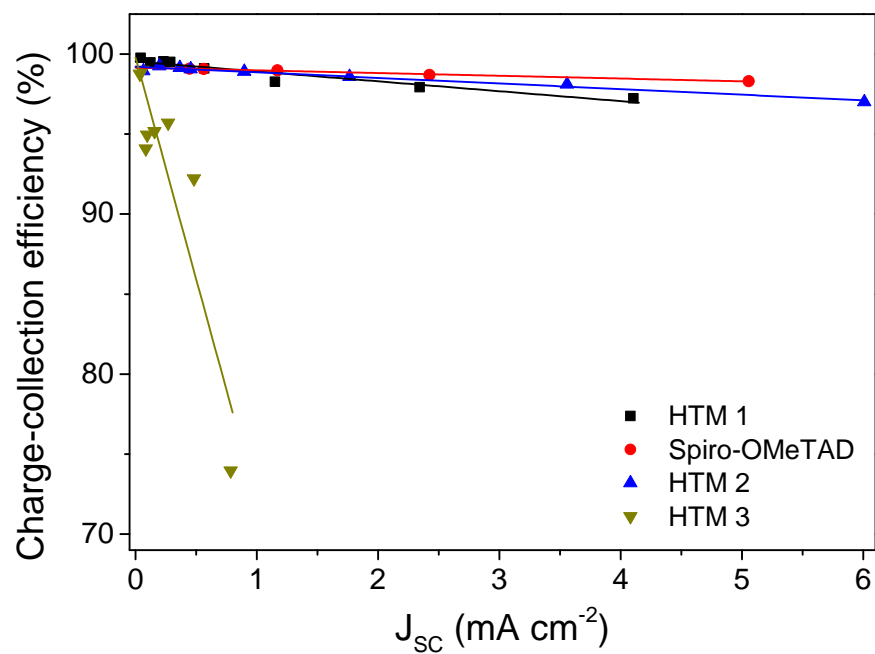


Figure S10: Charge-collection efficiency of each HTM for different short-circuit currents. The solid lines are a linear fit to the data.

## Capacitance Measurements

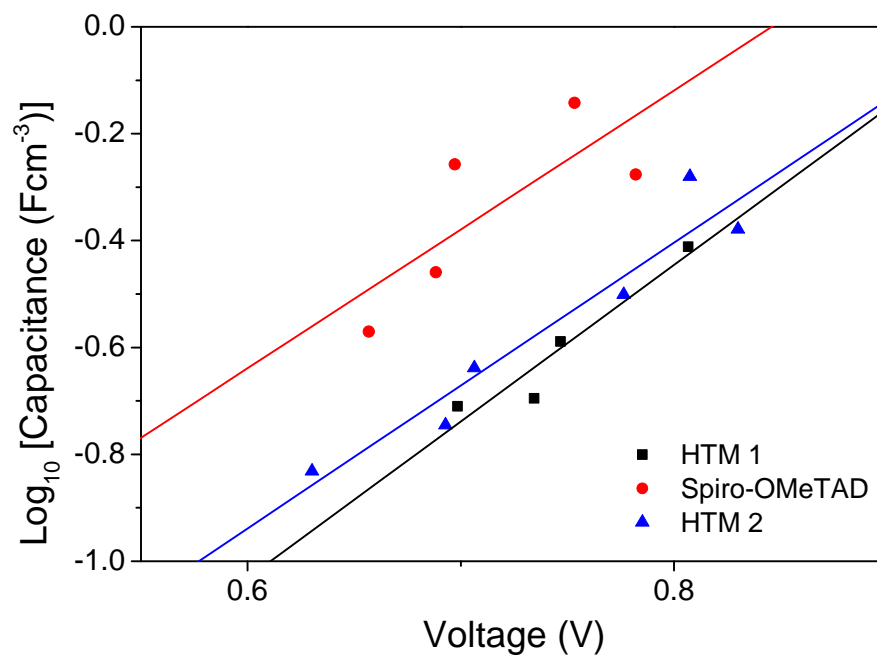


Figure S11: Capacitance measurements for HTM1, spiro-OMeTAD and HTM2. The solid lines are an exponential fit to the capacitance.