

## Supporting Information

**Table 1.** Electrical characteristics for ssDSCs of various filling fractions.

| Sample name | Spiro-MeOTAD concentration<br>[mg mL <sup>-1</sup> ] | Overlayer thickness<br>[μm] | TiO <sub>2</sub> thickness<br>[μm] | Filling fraction<br>[%] | Voc<br>[mV] | Jsc<br>[mA/cm <sup>2</sup> ] | FF<br>[%] | η<br>[%] |
|-------------|--|-----------------------------|------------------------------------|-------------------------|-------------|------------------------------|-----------|----------|
| 12          | 200  | 0.58                        | 2                                  | 89.4                    | 745.2       | 6.3                          | 46.8      | 2.2      |
| 16          | 200  | 0.52                        | 2                                  | 89.5                    | 741.4       | 3.7                          | 61.2      | 1.7      |
| 35          | 200  | 0.32                        | 3.1                                | 65.5                    | 734.9       | 5.7                          | 54.0      | 2.3      |
| 13          | 100  | 0.19                        | 2                                  | 37.8                    | 731.3       | 5.2                          | 58.7      | 2.2      |
| 32          | 100  | 0.01                        | 3                                  | 28.6                    | 718.8       | 5.2                          | 57.0      | 2.1      |
| 15          | 25   | 0.00                        | 2.3                                | 8.3                     | 356.3       | 0.4                          | 32.9      | 0.0      |
| 34          | 25   | 0.00                        | 3.7                                | 6.1                     | 316.9       | 0.3                          | 29.9      | 0.0      |

**Table 2.** Comparison of characteristic penetration length (CPL), desorbed mass, and mass in pores for ssDSC samples

| Sample name               | TiO <sub>2</sub> thickness<br>[μm] | Spiro-MeOTAD concentration<br>[mg mL <sup>-1</sup> ] | Filling fraction<br>[%] | Calculated mass in pores<br>[μg/mm <sup>2</sup> ] | Calculated mass<br>[μg/mm <sup>2</sup> ] | Desorbed mass<br>[μg/mm <sup>2</sup> ] | CPL<br>[μm]    | CPL with viscosity correction<br>[μm] |
|---------------------------|------------------------------------|--|-------------------------|---|--|--|----------------|---------------------------------------|
| 12                        | 2                                  | 200  | 89.4                    | 1.22  | 1.80                                     | 1.17                                   | 1.79           | 1.32                                  |
| 16                        | 2                                  | 200  | 89.5                    | 1.22  | 1.73                                     | 1.11                                   | 1.79           | 1.32                                  |
| 13                        | 2                                  | 100  | 37.8                    | 0.51  | 0.70                                     | 0.57                                   | 0.76           | 0.70                                  |
| 32                        | 3                                  | 100  | 28.6                    | 0.58  | 0.59                                     | 0.53                                   | 0.86           | 0.79                                  |
| 15                        | 2.3                                | 25   | 8.3                     | 0.13  | 0.13                                     | 0.12                                   | 0.19           | 0.18                                  |
| 34                        | 3.7                                | 25   | 6.1                     | 0.15  | 0.15                                     | 0.14                                   | 0.22           | 0.22                                  |
| Average [a]<br>(std dev.) | 2.4<br>(0.6)                       | 200  | 80.9<br>(13.2)          | 1.25<br>(0.1)                                     | 1.78<br>(0.15)                           | 1.14◊<br>(0.04)                        | 1.86<br>(0.1)  | 1.36<br>(0.1)                         |
| Average [b]<br>(std dev.) | 3.7<br>(1.2)                       | 180  | 80.9<br>(13.2)          | 1.25<br>(0.1)                                     | 1.78<br>(0.15)                           | 1.14◊<br>(0.04)                        | 1.86<br>(0.1)  | 1.36<br>(0.1)                         |
| Average [c]<br>(std dev.) | 2.31<br>(0.6)                      | 100  | 35.9<br>(11.6)          | 0.53<br>(0.05)                                    | 0.69<br>(0.15)                           | 0.62◊<br>(0.12)                        | 0.78<br>(0.1)  | 0.72<br>(0.1)                         |
| Average [d]<br>(std dev.) | 2.25<br>(0.8)                      | 25   | 8.9<br>(2.0)            | 0.13<br>(0.01)                                    | 0.21<br>(0.07)                           | 0.13◊<br>(0.01)                        | 0.19<br>(0.02) | 0.18<br>(0.02)                        |

[a] Average of 6 samples with thicknesses between 2 and 3.3 μm; [b] Average of 3 samples with thicknesses between 2.6 and 5 μm; [c] Average of 7 samples with thicknesses between 1.4 and 3.1 μm; [d] Average of 6 samples with thicknesses between 1.4 and 3.7 μm.