

# ADVANCED FUNCTIONAL MATERIALS

## Supporting Information

for *Adv. Funct. Mater.*, DOI: 10.1002/adfm.201301328

Dependence of Dye Regeneration and Charge Collection on  
the Pore-Filling Fraction in Solid-State Dye-Sensitized Solar  
Cells

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## **Supporting Information for**

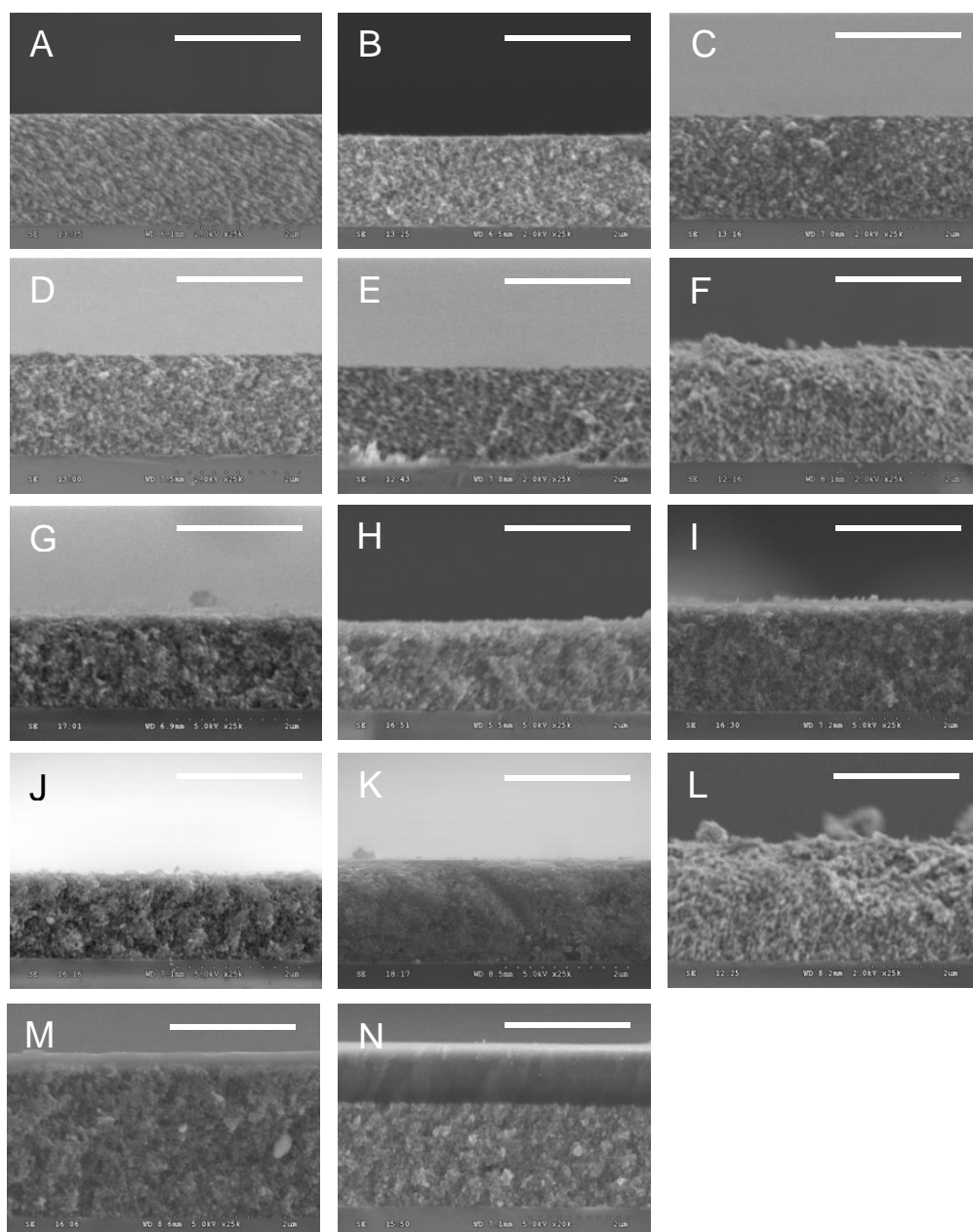
Dependence of Dye Regeneration and Charge Collection on the Pore-Filling Fraction in Solid-State Dye-Sensitized Solar Cells

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## Cross-Sectional SEM Images

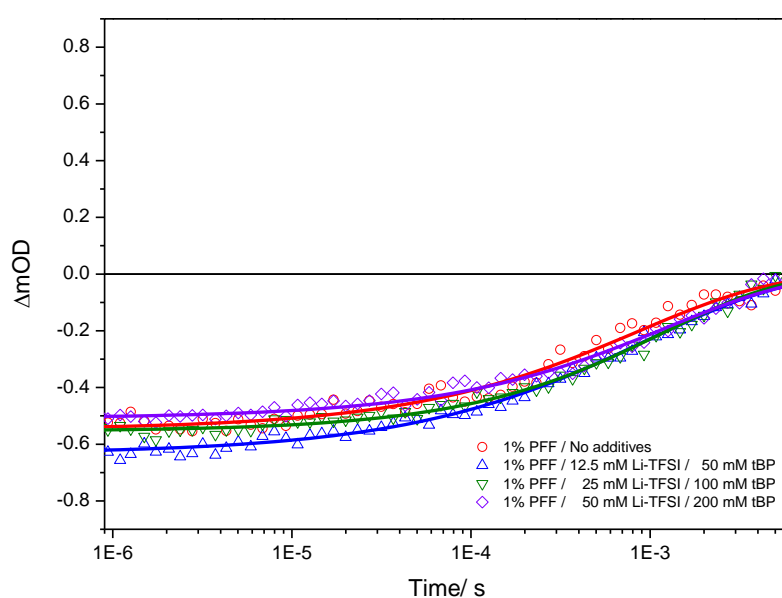
Cross-sectional Scanning Electron Microscopy (SEM) images were taken to allow determination of the thickness  $d$  of the TiO<sub>2</sub> layer as well as the thickness  $d_{cl}$  of the capping layer, which were both used for the calculation of the pore-filling fraction as described in the main text.



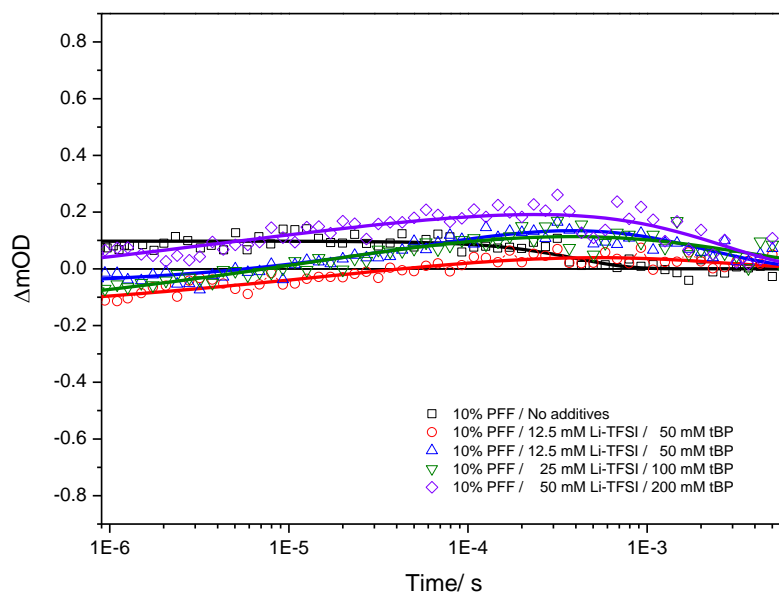
**Figure S1.** Cross-sectional SEM images of TiO<sub>2</sub>/C106/spiro-OMeTAD samples prepared with varying volume concentrations of spiro-OMeTAD in the initial solution: (A) 0%, (B) 0.5%, (C) 1.0%, (D) 1.5%, (E) 2.0%, (F) 2.5%, (G) 3.0%, (H) 3.5%, (I) 4.0%, (J) 4.5%, (K) 5%, (L) 7.5%, (M) 10%, (N) 20%. The scale bars are 2 μm long.

## Influence of Ionic Additives on Dye Regeneration

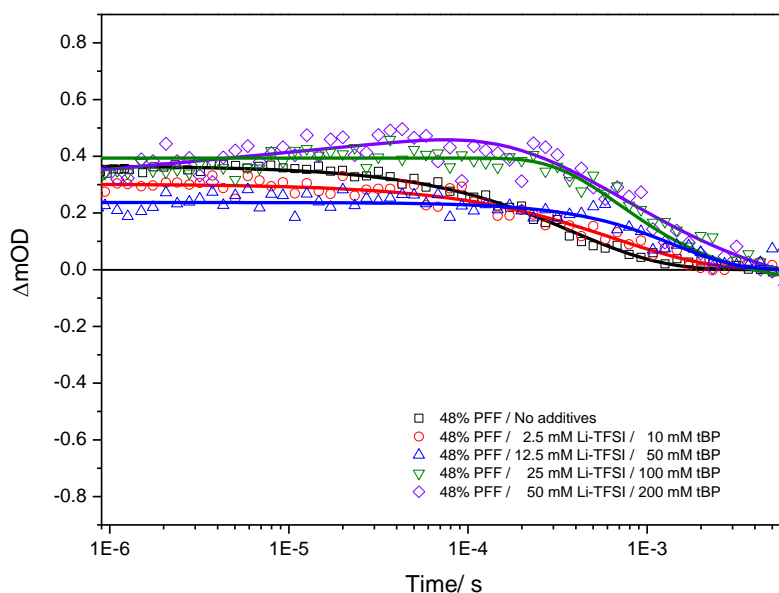
To determine the influence of ionic additives on the hole-transfer yield, we performed transient absorption measurements with an excitation wavelength of 550 nm and a probe wavelength of 520 nm with samples containing various concentrations of tBP and Li-TFSI. Results are shown in **Fig. S2-S4**. Within the experimental error, we observed no significant dependence of the hole-transfer yield on the concentration of tBP and Li-TFSI.



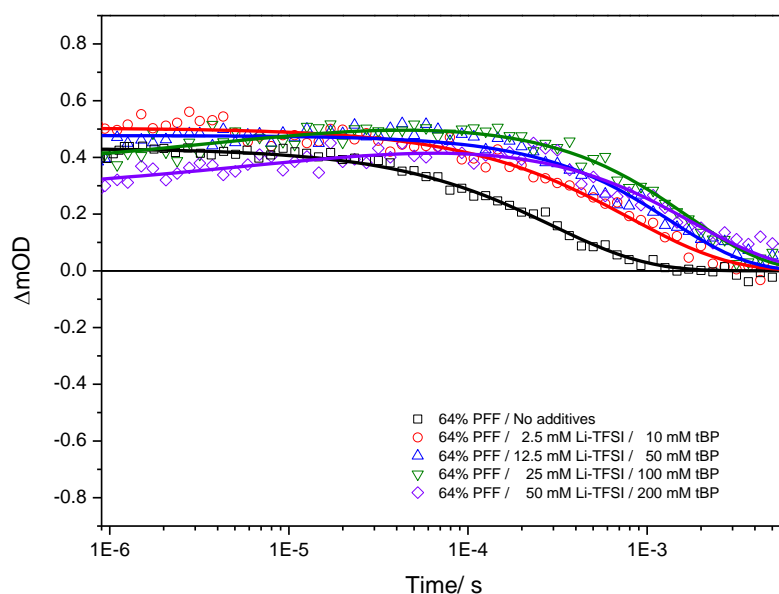
**Figure S2.** Microsecond transient absorption dynamics of TiO<sub>2</sub>/C106/spiro-OMeTAD samples with a pore-filling fraction of 1% and varying concentrations of the standard additives Li-TFSI and tBP. All samples were measured at a probe wavelength of 520 nm and were excited at 550 nm with a fluence of 50  $\mu\text{J cm}^{-2}$ . Results are averages over data obtained from two samples with identical pore-filling fraction. The solid lines are a guide to the eye.



**Figure S3.** Microsecond transient absorption dynamics of  $\text{TiO}_2\text{C106}/\text{spiro-OMeTAD}$  samples with a pore-filling fraction of 10% and varying concentrations of the standard additives Li-TFSI and tBP. All samples were measured at a probe wavelength of 520 nm and were excited at 550 nm with a fluence of  $50 \text{ uJ cm}^{-2}$ . Results are averages over data obtained from two samples with identical pore-filling fraction. The solid lines are a guide to the eye.



**Figure S4.** Microsecond transient absorption dynamics of  $\text{TiO}_2/\text{C106}/\text{spiro-OMeTAD}$  samples with a pore-filling fraction of 48% and varying concentrations of the standard additives Li-TFSI and tBP. All samples were measured at a probe wavelength of 520 nm and were excited at 550 nm with a fluence of  $50 \text{ uJ cm}^{-2}$ . Results are averages over data obtained from two samples with identical pore-filling fraction. The solid lines are a guide to the eye.

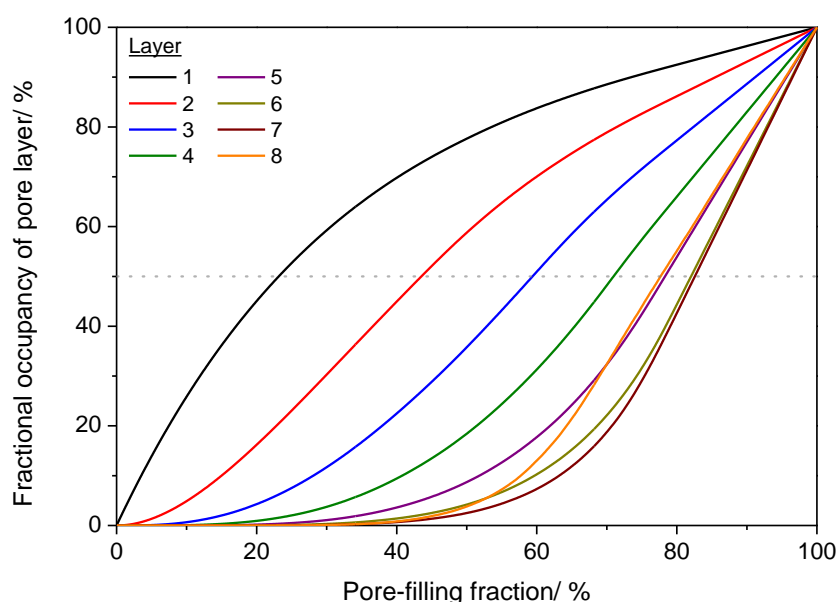


**Figure S5.** Microsecond transient absorption dynamics of  $\text{TiO}_2/\text{C106}/\text{spiro-OMeTAD}$  samples with a pore-filling fraction of 64% and varying concentrations of the standard additives Li-TFSI and tBP. All samples were measured at a probe wavelength of 520 nm and were excited at 550 nm with a fluence of  $50 \text{ uJ cm}^{-2}$ . Results are averages over data obtained from two samples with identical pore-filling fraction. The solid lines are a guide to the eye.

### Monte Carlo Simulation of Fractional Occupancy of Spiro-OMeTAD Layers

In the proposed simple model of random pore infiltration, a spiro-OMeTAD hole-transporter molecule settles inside the pore by assuming a randomly selected position at the inner surface sites. This position may be directly at the dye monolayer, or, in case that this specific surface position is already covered by a spiro-OMeTAD molecule, on top of the existing molecule to contribute to a second, third or subsequent layer. As each successive layer contains fewer positions than the previous one and a direct mapping between layers is thus not possible, it is assumed that the number of available surface sites in each layer above the first layer is given by the difference between the number of infiltrated molecules in the previous layer and the number of already infiltrated molecules in this layer. If the number of infiltrated molecules in the previous layer exceeds the maximum possible number of molecules in the current layer, it is given by the difference between the maximum possible number of molecules in the current layer and the number of already infiltrated molecules in this layer. A Monte Carlo simulation

based on these assumptions is run to fill successive sites up to the point where a certain fraction of total available sites in the pore is filled, which corresponds to the pore-filling fraction (PFF). For this given simulated distribution of spiro-OMeTAD, the fractional occupancy of each spiro-OMeTAD layer can then be directly calculated, as shown in **Fig. S6**. The fractional dye coverage in spiro-OMeTAD,  $p(PFF)$ , as used to describe the hole-transfer yield from dye to spiro-OMeTAD, here corresponds to the result obtained for Layer 1.

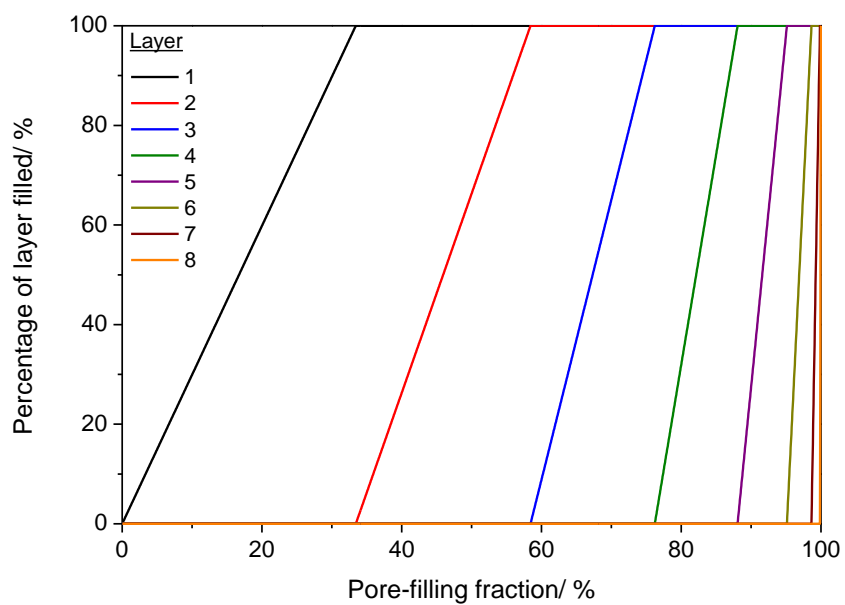


**Figure S6.** Simulated fractional occupancy of each spiro-OMeTAD layer in a pore with a 20 nm diameter for the random infiltration model. The dotted grey line indicates the pore-filling fraction (0.5) at which the onset of diffusion through the layer is expected to occur according to percolation theory based on a simple 2D lattice, as described in the main manuscript.

Similarly to the model of random pore infiltration, in the conformal coating model a spiro-OMeTAD hole-transporter molecule settles inside the pore by assuming a randomly selected position in the lowest layer which is not completely filled yet. If this position is already occupied with another spiro-OMeTAD molecule, the molecule diffuses to a random adjacent position until a free position is found and settles there. For this given simulated distribution of

spiro-OMeTAD, the fractional occupancy of each spiro-OMeTAD layer can be seen in **Fig.**

**S7.**



**Figure S7.** Simulated fractional occupancy of each spiro-OMeTAD layer in a pore with a 20 nm diameter assuming the conformal coating model.



### Derivation of Equation 3 in the main manuscript

Lateral hole-hopping is modeled by starting with placement of a hole on a random dye molecule. For the subsequent hole motion, it is then assumed that if no spiro-OMeTAD molecule is attached to the dye monolayer at this starting position, the hole transfers to a random adjacent dye molecule. If a spiro-OMeTAD molecule is attached to this dye molecule, hole transfer to that spiro-OMeTAD molecule occurs. If no spiro-OMeTAD molecule is present, the hole transfers to another random adjacent dye molecule. This process is continued until transfer to spiro-OMeTAD or recombination with an electron has occurred. If the probability of a spiro-OMeTAD molecule being attached to the specific dye molecule after  $i$  steps is defined as  $p_i$  and no recombination has occurred within a time interval  $t$ , the hole-transfer yield is given by

$$\eta_{ht}(t) = p_0 + \sum_{i=1}^{n(t)} \left[ p_i \prod_{k=0}^{i-1} (1 - p_k) \right]$$

The probability  $p_i$  can be calculated by dividing the number  $s$  of spiro-OMeTAD molecules in the surface layer by the number  $T-i$  of total positions in the surface layer the hole has not transferred to, i.e.

$$p_i = \frac{s}{T - i}$$

As  $p_0 = p(\text{PFF})$ , it follows that

$$p_i = \frac{T}{T - i} p(\text{PFF})$$

The hole-transfer yield is then given by

$$\eta_{ht}(t) = p(\text{PFF}) \left[ 1 + \sum_{i=1}^{n(t)} \frac{T}{T - i} \prod_{k=0}^{i-1} \left( 1 - \frac{T}{T - k} p(\text{PFF}) \right) \right]$$

If the number  $n(t)$  of dye molecules the hole transfers to within time interval  $t$  is much smaller than the number  $T$  of possible spiro-OMeTAD molecules in the surface layer, i.e.  $n(t) \ll T$ , then  $p_i \approx p(\text{PFF})$  and

$$\begin{aligned} \eta_{ht}(t) &\approx p(\text{PFF}) + \sum_{i=1}^{n(t)} \left[ p(\text{PFF}) \prod_{k=0}^{i-1} (1 - p(\text{PFF})) \right] \\ &= p(\text{PFF}) \sum_{i=0}^{n(t)} [1 - p(\text{PFF})]^i \\ &= 1 - [1 - p(\text{PFF})]^{n(t)+1} \end{aligned}$$

where the geometric series was applied in the last step.