Electronic Supplementary Information

Computational Microscopy Study of Granular Structure and pH Dependence of PEDOT:PSS

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S1: Appropriate Martini bead for hydrogenated PSS (PSS-H)

The present Martini CG model for PSS includes one negative charge on sulfonate group as a Qa bead (REF). To model the hydrogenation and PSS-H, we replace the Qa bead with a polar Martini bead. To find the most appropriate bead, we compare the radius of gyration and end-to-end distance from AA and CG models.

Calcualtion	Radius of Gyration (nm)	End-to-End (nm)
AA	1.5± 0.1	2.9±0.8
CG (with P1)	1.16±0.01	1.21±0.03
CG (with P3)	1.21±0.01	2.31±0.11
CG (with P5)	1.37±0.02	2.53±0.19

Table S1: The radius of gyration and end-to-end distance for PSS-H in the AA and CG models. PSS chain length is 50 monomer units.

From the present result in table SI-1 we conclude that the P5 (the most polar Martini bead) is the best choice to model PSS-H.

S2: RMSD and Energy of homogeneous and dispersion solution for 300 ns

To ensure that the equilibrium is reached we control that the Root-Mean-Square Deviation (RMSD) of PEDOT and PSS backbone and total energy reach saturation (see Figs. S1, S2).



Figure S1. The RMSD of PEDOT and PSS backbone in homogeneous and dispersive solutions.



Figure S2. The total energy for α =0.0, 0.2 and 1.0 in the (a) homogeneous and (b) Dispersive solutions.

To further confirm that the equilibrium in the system is achieved and the morphology does not change we performed the stimulated annealing calculations for the case of α =1.0 (corresponding to the highest concentration of ions). To this end we first extended the MD simulation time from 300 ns to 900 ns at 300K. After this, 600 ns of the simulated annealing was applied to the final solution. For the simulated annealing, the temperature was gradually increased from 300K to 700K in 300 ns and then reduced back to 300K during next 300 ns. After that the water molecules were evaporated during nearly 400 ns. The new simulation then takes totally 900+600+400=1900ns, i.e. nearly 2 microseconds. It should be also

stressed that due to a significant truncation of the phase space and the molecular degrees of freedom the Martini CG dynamics is 3-6 times faster as compared to the atomistic one, and the effective computational time is correspondingly longer.

Figure S3 shows the snapshots of the morphology after 300ns and 900ns of MD simulations at 300K and then after additional 600 ns of annealing followed by the drying. The granular structure remains apparently unchanged during whole simulation interval including the annealing and the subsequent drying, and is practically the same as reported in Fig. 4u (i.e. without the extended MD run and subsequent annealing).



Figure S3. Snapshots of PEDOT:PSS films at different stages of production runs. (a) after 300ns, (b) after 900 ns, (c) after 900 ns followed by 600 ns stimulated annealing, (d) a dry film after 900 ns and annealing. (e) a dry film without the additional MD run and annealing (the same as in Fig. 4u). In (a)-(d) temperature T=300K, hydration level Hy=70%. Dry films in (d), (e) correspond to the hydration level Hy=10%.

Note that we also confirmed that the micellar structure remained intact even after many annealing cycles. Having completed the first annealing, we further performed 10 additional cycles of the simulated annealing as described above (i.e. between 300 K and 700 K for totally 600 ns). The simulations show that the micellar shape of the PEDOT core and the PSS shell remains the same in the final PEDOT:PSS configuration.

S3: The PEDOT:PSS morphology for different deprotonation levels α



Figure S4. Snapshots of PEDOT:PSS morphology for different deprotonation levels α for dispersive initial distribution, (a,g) $\alpha = 0.0$, (b,h) $\alpha = 0.1$, (c,i) $\alpha = 0.2$, (d,j) $\alpha = 0.5$, (e,k) $\alpha = 0.8$, (f,l) $\alpha = 1.0$ at Hy=10%. The PEDOT chains are in blue color and green color is for PSS backbones.

S4: PEDOT stacking during water evaporation



Figure S5. The distribution of distance between PEDOT planes at different hydration level for starting from (a-c) homogeneous (d-f) dispersion solutions. The stacking between PEDOT planes occurs during initial solution stage, and the number of chains in the stacks do not change during water evaporation.