Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Why does solvent treatment increase conductivity of PEDOT:PSS? Insight from molecular dynamics simulations

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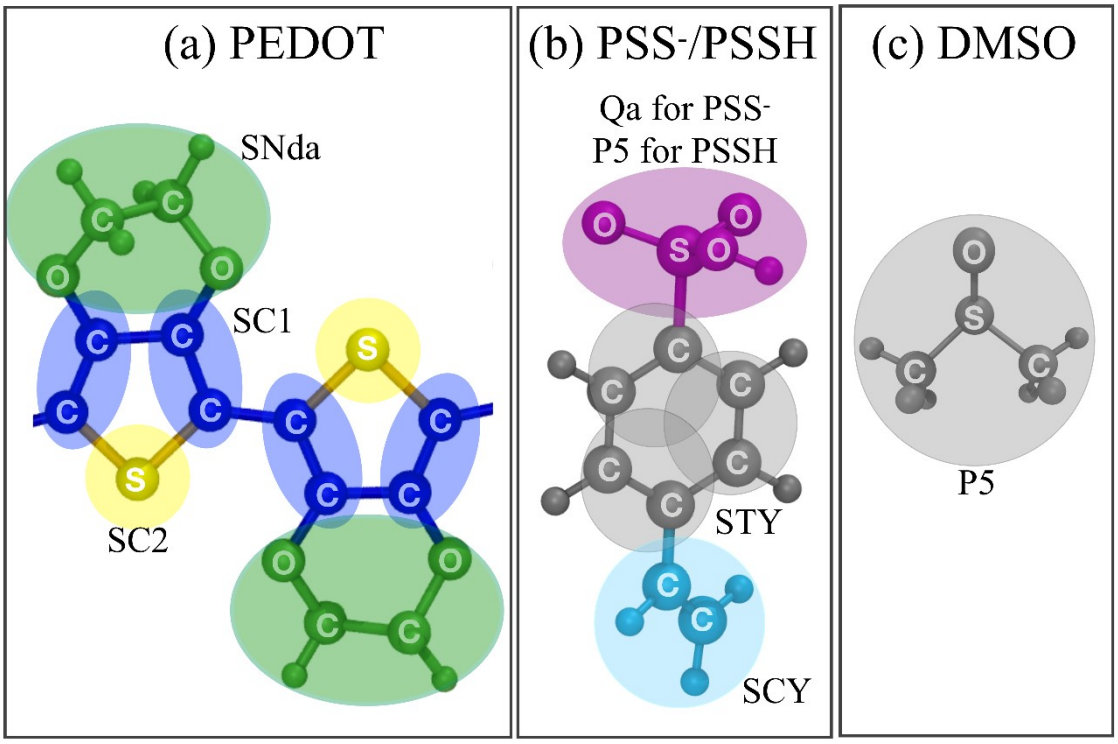

Figure S1: MARTINI coarse grained models for (a) PEDOT, (b) PSS^- and PSSH and (c) DSMO used in the present work, where Martini beads are indicated.

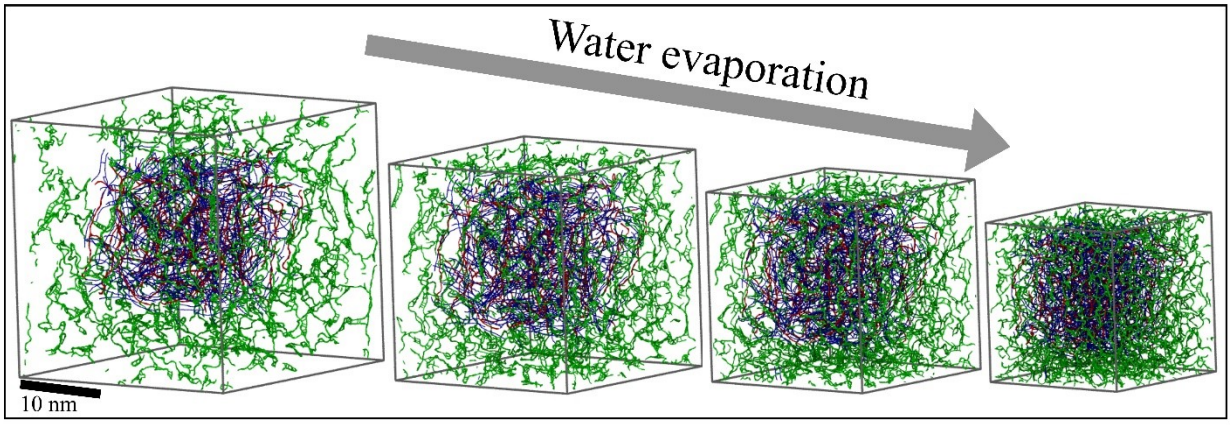

Figure S2: Illustration of the preparation of the dry PEDOT:PSS film from the initial water solution. Here PEDOT, PSS^- and PSSH are shown in blue, red and green, respectively.

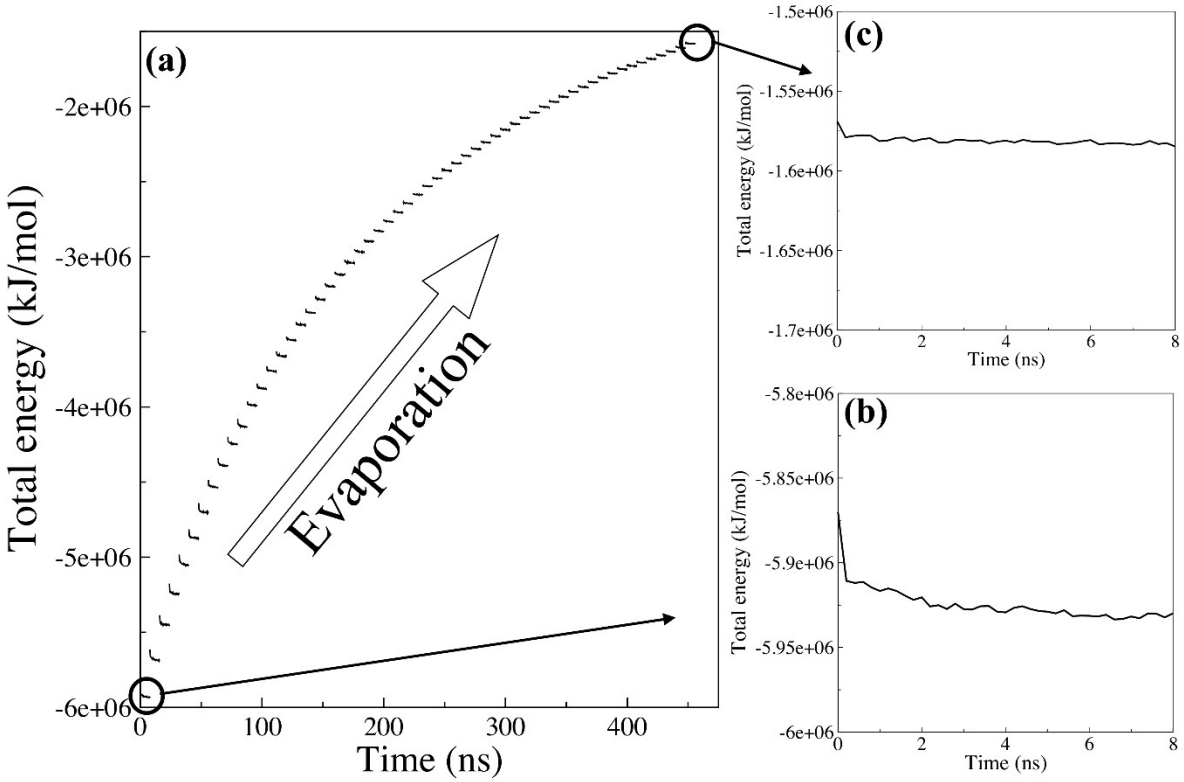

Figure S3: (a) Evolution of the total energy during water evaporation. (b),(c) zoom-in of the first and last steps respectively.

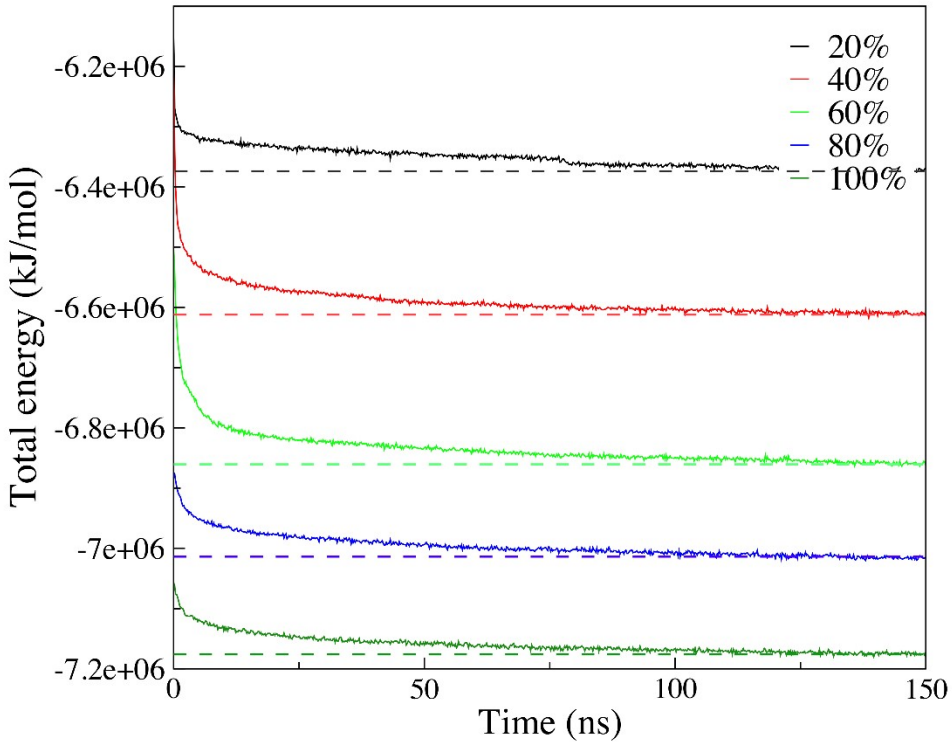

Figure S4: Evolution of the total energy during deprotonation.

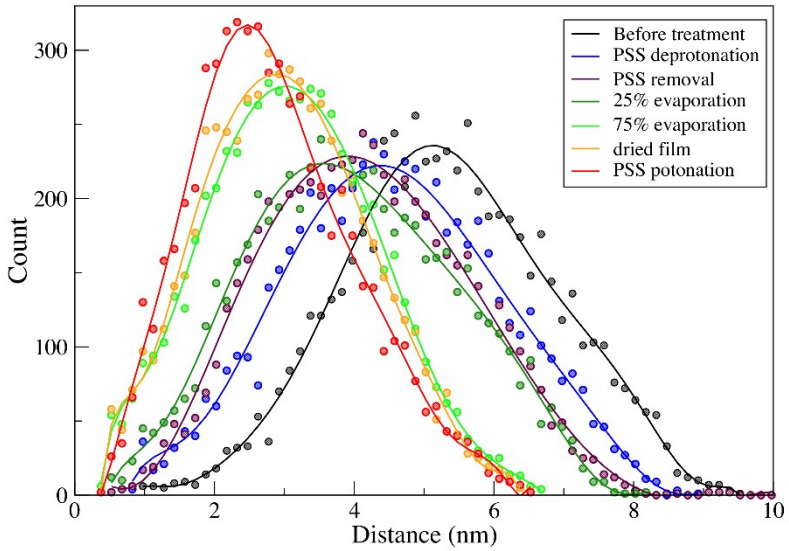

Figure S5: The statistical analysis of minimum distance between PEDOT chains belonging to two different cores during solvent treatment. Note that the black and red curves are the same as in Fig. 3b.

Table S1: Composition of the computational box for the preparation of the initial dry film.

Molecule	Number of chains	Chain length	Number of monomers/ sulfonate groups	charges	Total charge
PEDOT	500	12	500 ×12 = 6000	One charge per 3 monomers	+2000*e*
PSS (in PEDOT-rich region)	63	50	63 × 50 = 3150	-0.635*e* per sulfonate group, i.e. approximately 2/3 sulfonate groups of PSS are deprotonated	-2000*e*
PSSH (in PSS-rich region)	217	50	217 × 50 = 10850	0	0

Table S2: Content of the computational box during preparation of the thin film

Step	PEDOT chains/	protonated sulphonate groups		De-protonated sulphonate groups		water	Na+	Protocol key point NPT ensemble (T=300 K and P=1 atm)
		PEDOT-rich region	PSS-rich region	PEDOT-rich region	PSS-rich region			
Initial solution	500	1150	10850	2000	0	136060	0	50 ns equilibration with polymer position restraints, 150 ns MD simulation
Water evaporation	500	1150	10850	2000	0	136060 → 0	0	Water is evaporated gradually with 1.25 % step, 4 ns equilibration with polymer position restraints, 8 ns MD simulation

Table S3: Content of the computational box during solvent treatment

Step	PEDOT chains	protonated sulphonate groups		De-protonated sulphonate groups		DMSO	Na+	Protocol key point NPT ensemble (T=300 K and P=1 atm)
		PEDOT - rich region	PSS-rich region	PEDOT-rich region	PSS-rich region			
Immersing film into DMSO	500	1150	10850	2000	0	117665	0	50 ns equilibration with polymer position restraints, 250 ns MD simulation
PSS deprotona-tion	500	1150 → 0	10850 → 0	2000 →3150	0 → 10850	117665	0 → 12000	In 5 steps, 50 ns equilibration with polymer position restraints, 150 ns MD simulation
Removal of detached PSS	500	0	0	3150	10850 →5050	117665	12000→ 8200	In 3 steps, 50 ns equilibration with polymer position restraints, 150 ns MD simulation
DMSO evaporation	500	0	0	3150	5050	117665 → 0	8200	DMSO is evaporated gradually with 1.25 % step, 4 ns equilibration with polymer position restraints, 8 ns MD simulation
PSS protonation	500	0 → 1150	0 → 5050	3150 →2000	5050 → 0	0	8200 → 0	50 ns equilibration with polymer position restraints, 150 ns MD simulation

Table S4: Input files for the initial PEDOT:PSS solution

No	File name	File description
1	initial.gro	Initial geometry file
2	DMSO.itp	DMSO topology file
3	PEDOT12.itp	PEDOT topology file
4	PSSH.itp	PSSH chains topology file
5	PSSmix.itp	PSS-/PSSH chains topology file
6	martini_v2.0_ions.itp	Martini force field file for ions
7	martini_v2.2P_PS.itp	General Martini force field file
8	top.top	Topology file
9	posreP.itp	Position restraints file for PEDOT chains
10	posrePSS.itp	Position restraints file for PSS chains
11	eq.mdp	Equilibration input file with position restraints on polymer chains
12	md.mdp	Production run input file