

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

A Theoretical Mechanistic Study on Electrical Conductivity Enhancement of DMSO Treated PEDOT:PSS

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Initial Structures generated for DFT Calculations

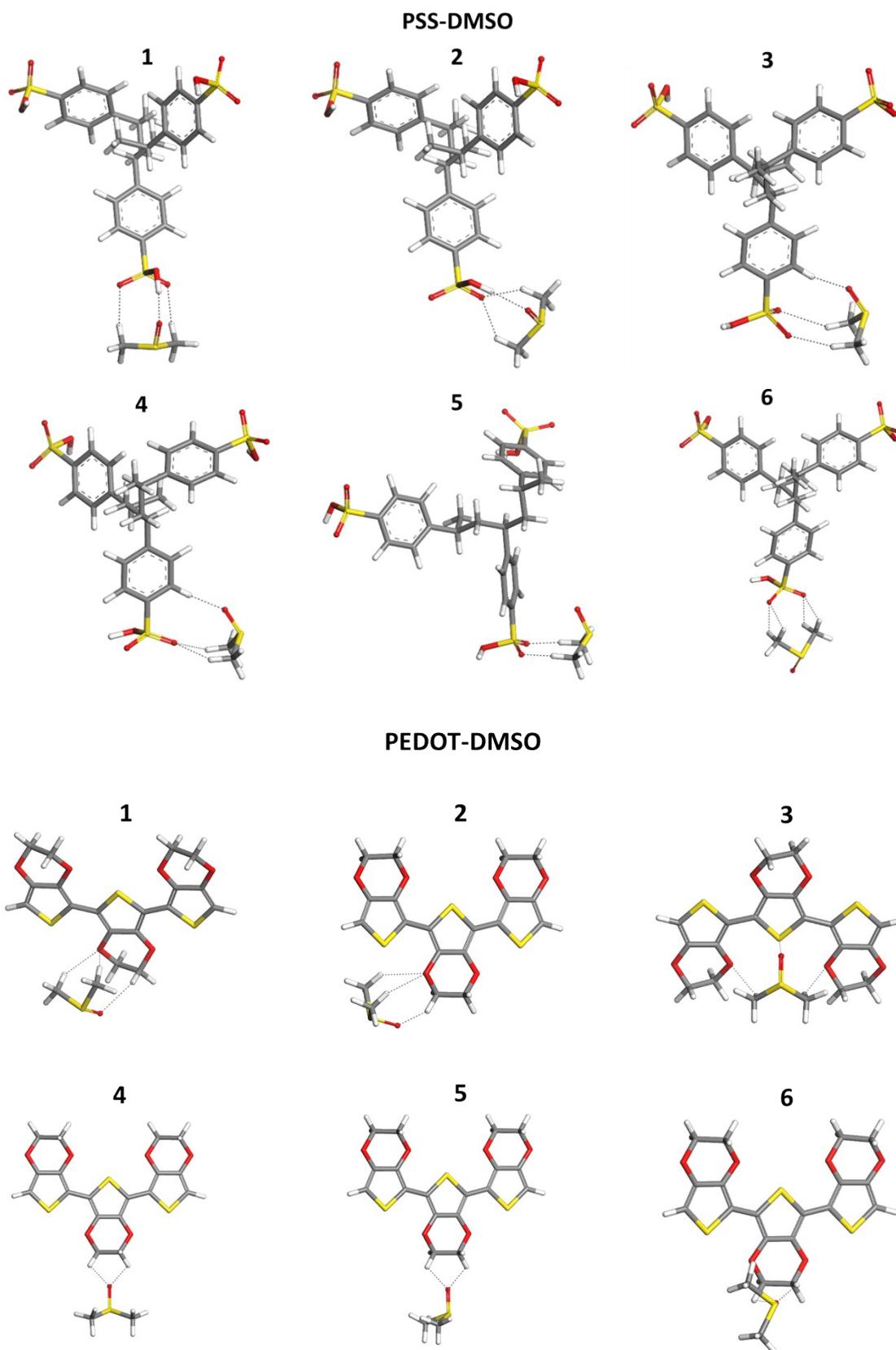


Figure S1. Six initial structures for DFT calculations for PSSH-DMSO and PEDOT-DMSO.

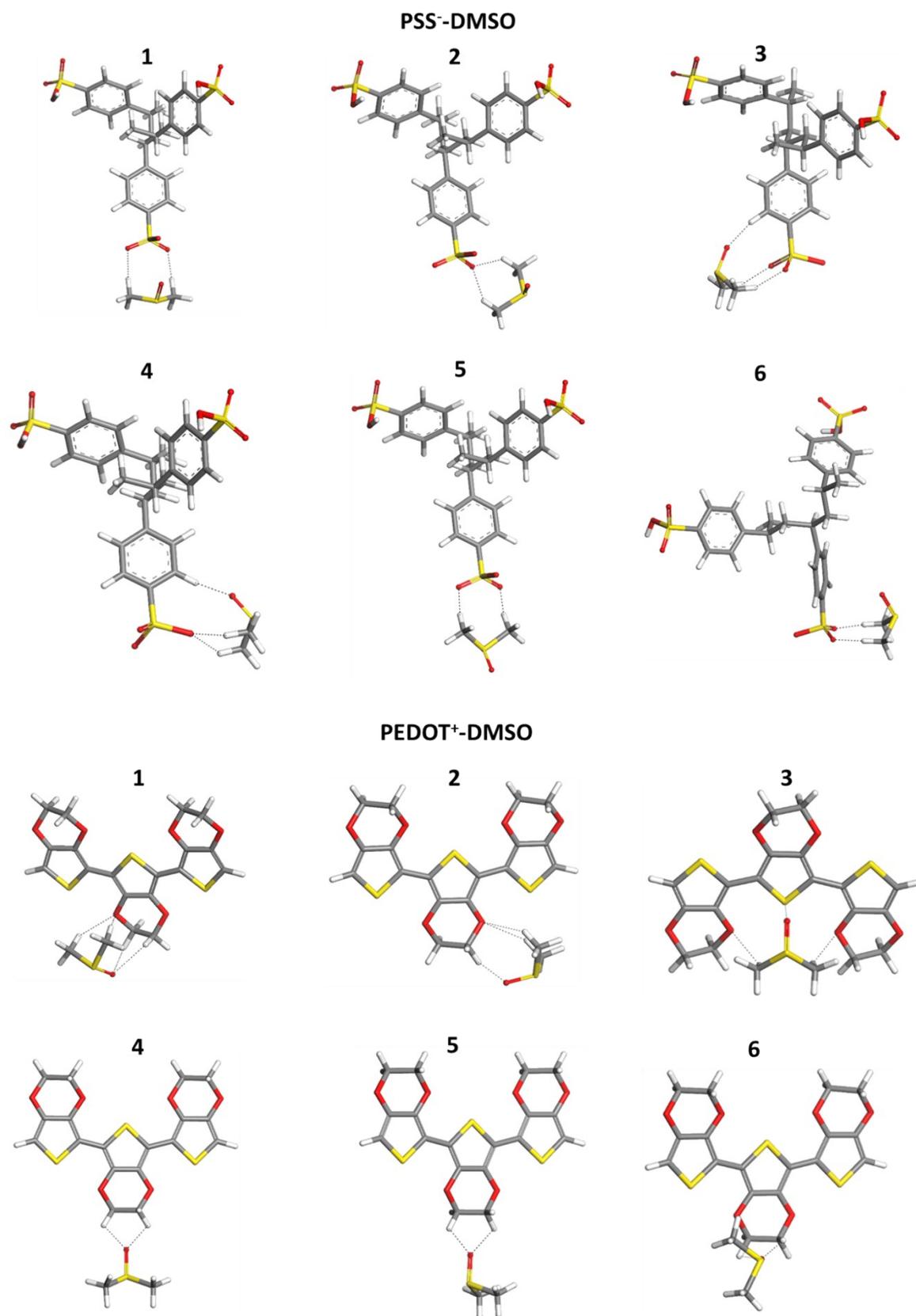


Figure S1-cont. Six initial structures for DFT calculations for PSS⁻-DMSO and PEDOT⁺-DMSO.

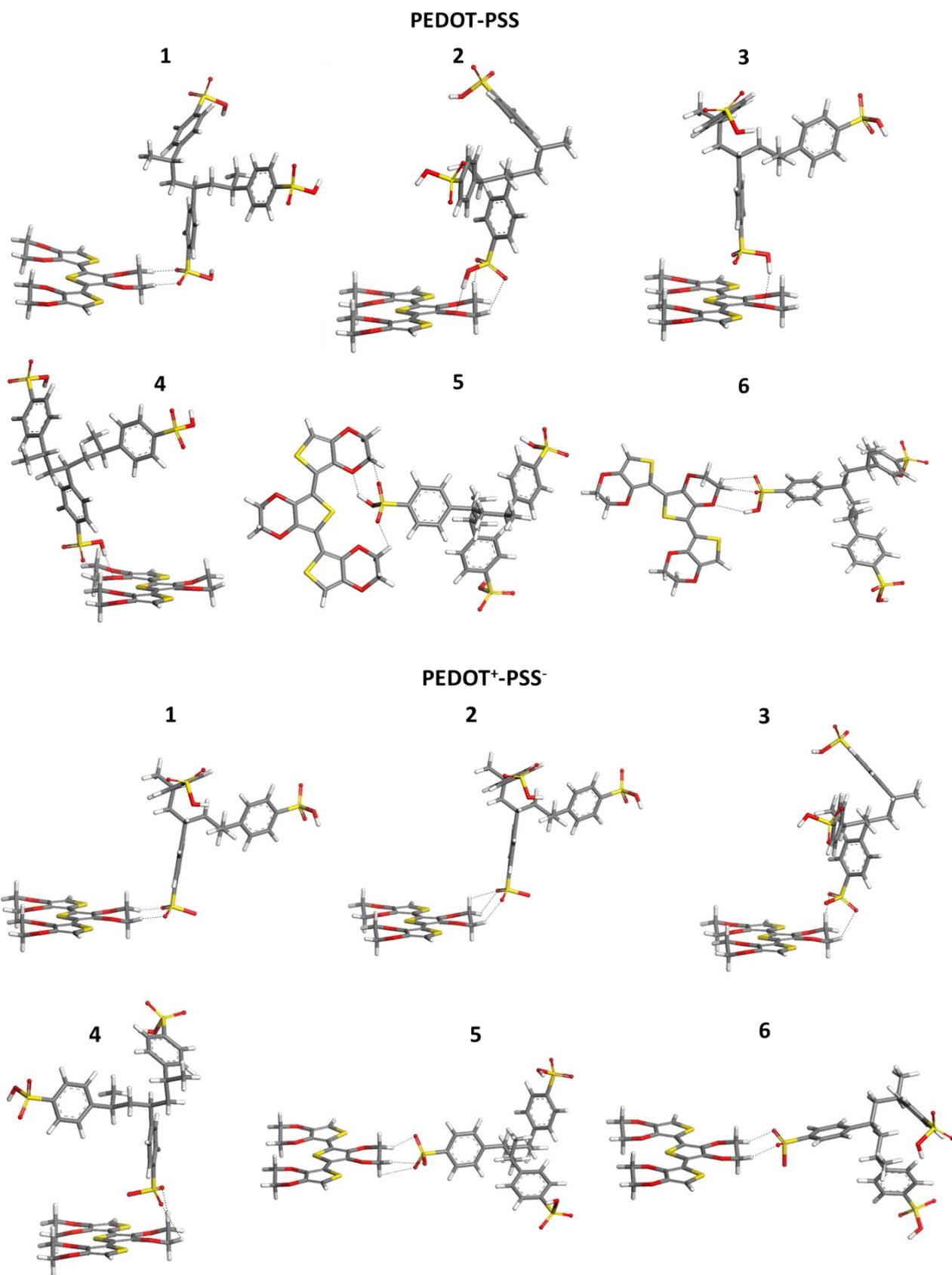


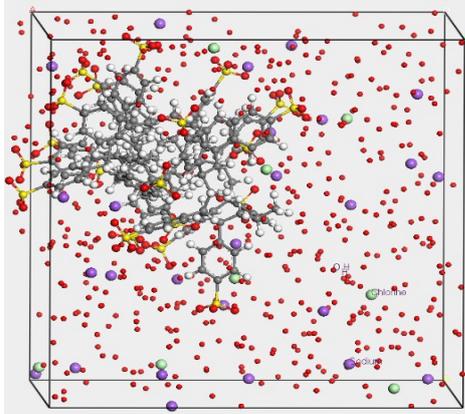
Figure S1-cont. Six initial structures for DFT calculations for PSSH-PEDOT and PSS⁻-PEDOT⁺.

Force Field Validation for PSS

400 cells were prepared for PSS₁₀ and PSS₂₀.

Cell structures are PSS₁₀, 12 Na⁺, 2 Cl⁻, 250 H₂O and PSS₂₀, 24 Na⁺, 4 Cl⁻, 1000 H₂O

a)



b)

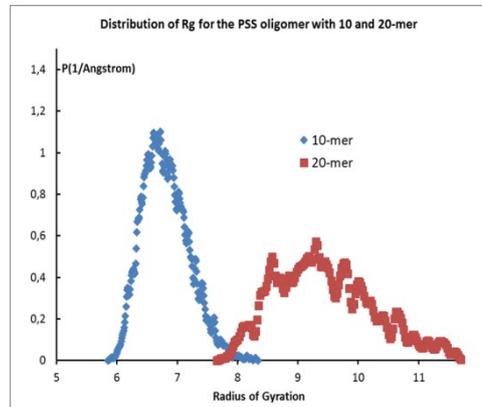
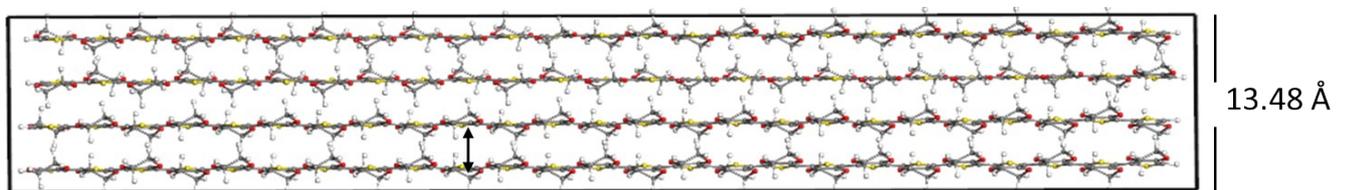


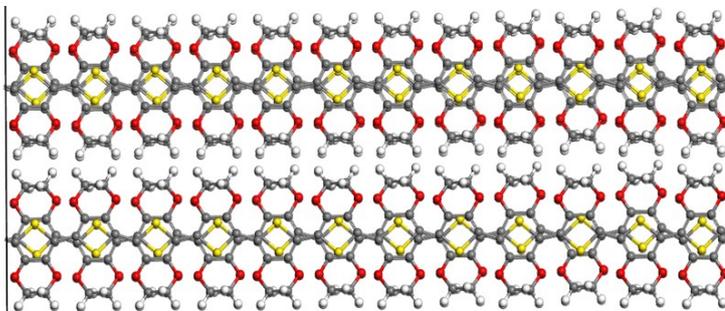
Figure S2a. Average Radius of Gyration for PSS oligomers are calculated for Force Field validation for PSS chains. A) One of the cell for PSS₂₀, 24 Na⁺, 4 Cl⁻, 1000 H₂O, B) Distribution of radius of gyration for 400 cells.

Force Field Validation for PEDOT



3.37 Å calculated
3.40 Å experimental*

*Condensed-phase Optimized Molecular Potential
for Atomistic Simulation Studies
(COMPASS)*



Fishbone structure
of PEDOT confirmed

Figure S2b. Force Field Validation for PEDOT chains by comparing PEDOT-PEDOT distance with experimental value⁴.

Table S1. Comparison of average Radius of Gyration for PSS10 and PSS20 with previous studies

	Rg for 10-mer PSS	Rg for 20-mer PSS
This study	0.68 nm	0.97 nm
Hoda ¹	0.74 nm	1.11 nm
Holm ²	0.72 nm	
Experimental ³	0.66 nm	1.09 nm

Molecular Dynamics Simulations Details

- (A) The first system represents high density PEDOT:PSS film structures. 8 chains $(PSS_{12})^{2-}$ and 8 chains $(PEDOT_6)^{2+}$ are constructed with and without 80 DMSO molecules which corresponds to 20% weight ratio. PSS to PEDOT molar ratio for the cell is 2 which was experimentally determined as 1.8.⁵ One of every three monomer of PEDOT and one of every six PSS monomer are charged according to experimental results. PEDOT chains shown by blue in color are kept as π -stack as two chains and PSS chains shown by red in color packed around PEDOT stacks as amorphous structures (Fig. 2a). Molecular mechanics minimization for 5000 steps are performed. Since the system is very dense and we could not observe any phase changes at room temperature simulation methods, simulated annealing method is applied. The temperature increased from 300 K to 1000 K and decreased again for ten times. Each heating and cooling in annealing step is 500 ps and total simulation time is 10 ns. NPT ensemble are applied with Nose' thermostat and Parrinello Barostat that let the cell size change in three dimensions as well as cell angles.
- (B) Two chains of $(PSS_{36})^{6-}$ and two chains of $(PEDOT_{18})^{6+}$ are used in the second model which prepared to understand charge screening, effect of DMSO concentration on the microphase separation between PSS and PEDOT. The PSS chains kept parallel and each PSS monomers are kept perpendicular to the PEDOT chains as determined by our DFT calculations as well as previous studies (Figure 2b). 20%, 55%, 67%, 75% weight ratio of DMSO which corresponds to 59, 286, 475 and 686 DMSO molecules. The chains are infinitely long in periodic cell and cell size is kept constant at $6 \times 5 \times 3$ nm³. NVT simulation at 500 K with Nose

thermostat are performed after minimization with the same non-bond summation methods for 6 ns for different DMSO concentrations. Structures and RDFs are calculated.

- (C) Third model studied by molecular dynamics simulation method is the core-shell structure of PEDOT:PSS where six chains of neutral PSS_{24} with two chains of $(\text{PSS}_{24})^{4-}$ formed shell and two chains of $(\text{PEDOT}_{12})^{4+}$ formed the conducting core. The cell without DMSO and the cell with 464 DMSO molecules which corresponds to 55% weight ratio are packed around PEDOT:PSS are constructed. 10 ns MD simulation are performed at NVT ensemble with Nose thermostat in $5.6 \times 5.6 \times 5.0 \text{ nm}^3$ cell to elucidate effect of DMSO on the PEDOT:PSS core shell morphology. It should be noted that DMSO packed around a central molecules of interest in Monte Carlo fashion in second and third system by checking that no unintentional bonds form across rings which is called spearing of ring, while ensuring realistic torsion angles and minimizing close atomic contacts until the box density reaches the target density.

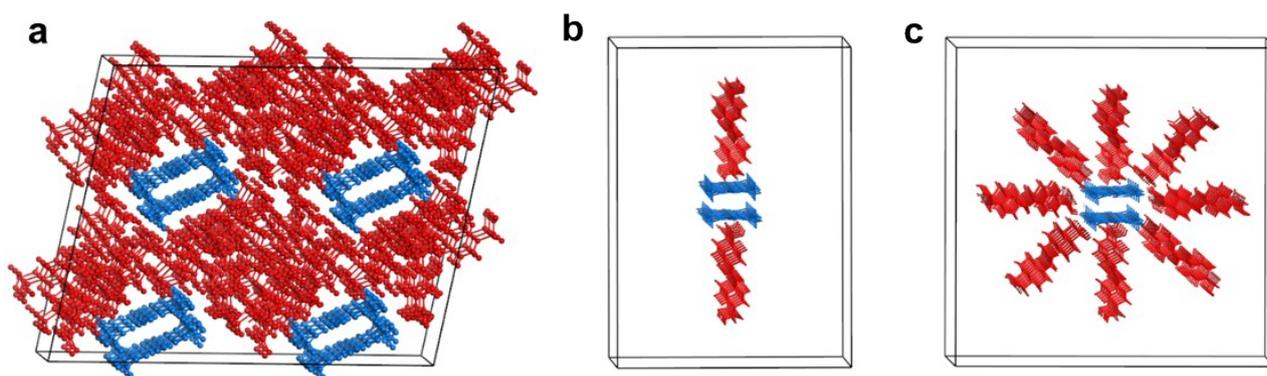


Figure S3. Initial structures constructed for MD simulations to pack DMSO into A) 8 amorphous chains $(\text{PSS}_{12})^{-2}$ and 8 chains $(\text{PEDOT}_6)^{+2}$ separated to four PEDOT-PEDOT B) 2 chains of $(\text{PSS}_{36})^{-6}$ and two chains of $(\text{PEDOT}_{18})^{+6}$ in the center C) 8 chains of $(\text{PSS}_{24})^{-6}$ formed shell and two chains of $(\text{PEDOT}_{12})^{+4}$ formed the conducting core.

Lowest Energy Structures and Interaction Energies calculated by DFT Calculations

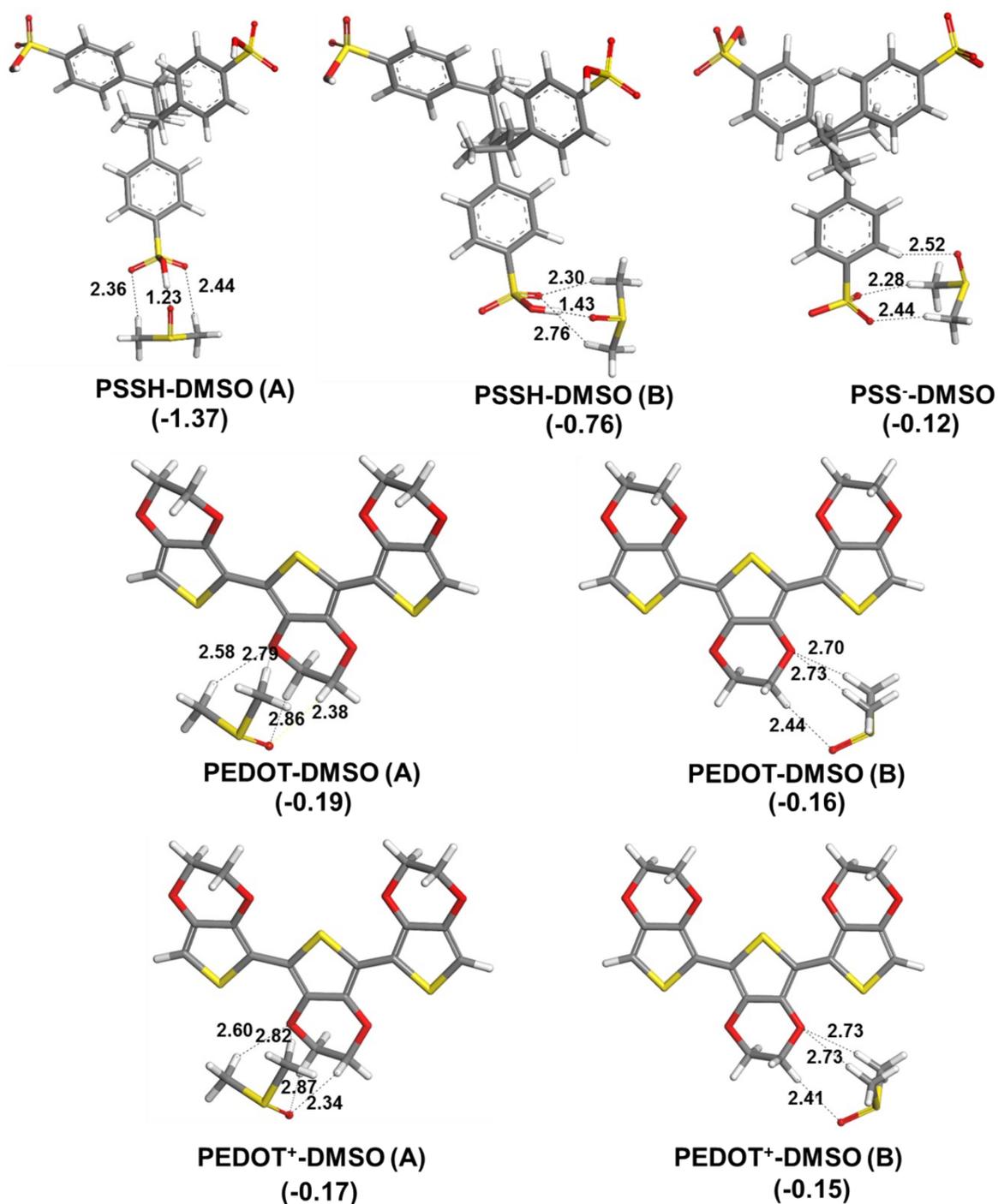


Figure S4a. Lowest energy optimized structures for PSSH-DMSO (2), PSS⁻-DMSO, PEDOT-DMSO (2), PEDOT⁺-DMSO (2). Interaction energies (eV) are given in paranthesis.

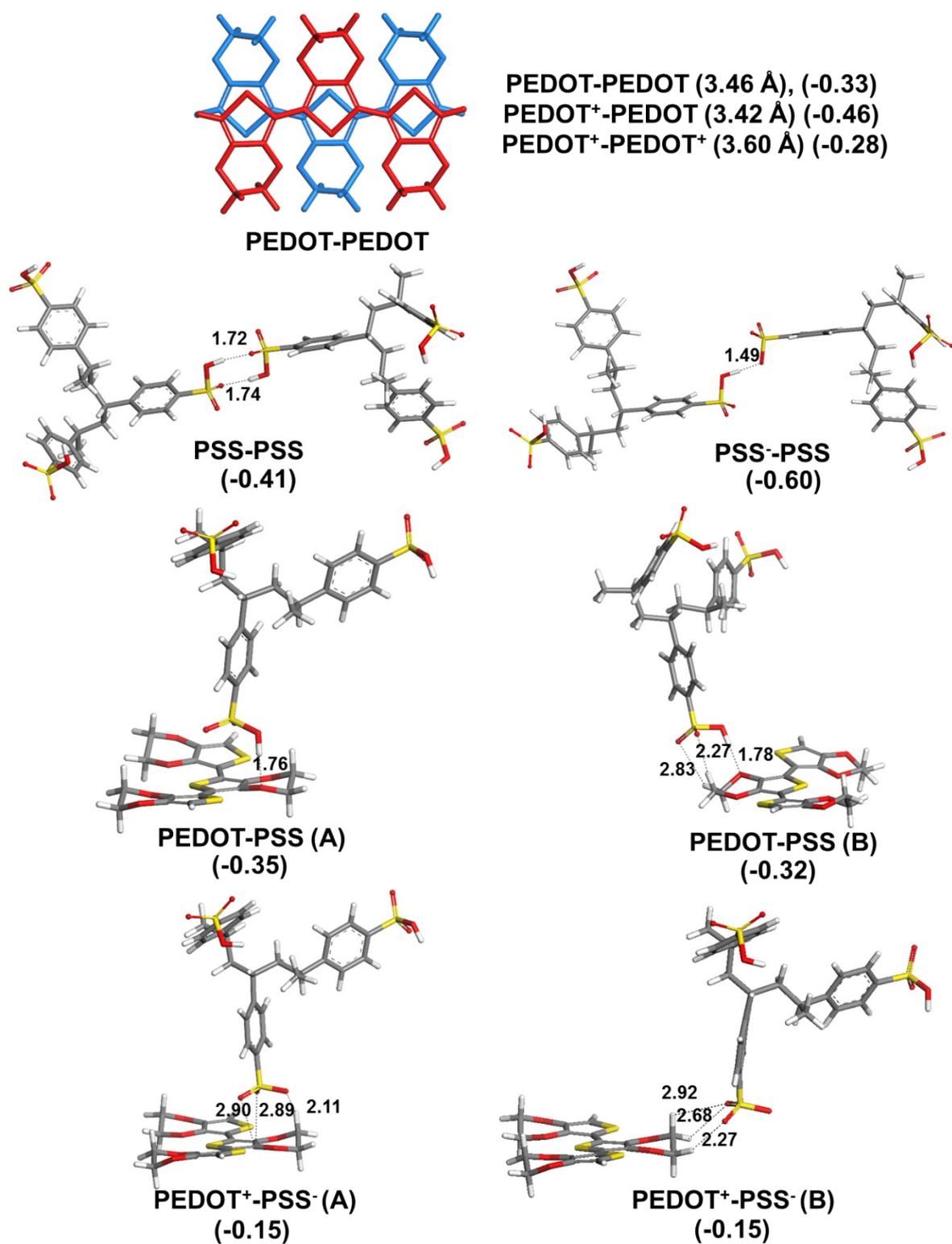


Figure S4b-Cont. Lowest energy optimized structures for PEDOT-PEDOT, PSSH-PSSH (2), PSS⁻-PSSH, PEDOT-PSSH (2), PEDOT⁺-PSS⁻ (2). Interaction energies (eV) are given in paranthesis.

PSS:PEDOT-water interactions

All components can form hydrogen bonds with water molecules with different strength and distances. Calculations showed that PSSH sulfonic acid groups have the lowest hydrogen bonding distance and strongest interaction with water molecules, which makes PSS a perfect water dispersant to dissolve PEDOT:PSS. However, hydrophobic PEDOT and PEDOT⁺ have relatively higher hydrogen bond distances. PSS⁻ and DMSO have average hydrogen bond distance with water. The number of molecules coordinated around a chain or molecule is also important as shown for DMSO interaction with two water molecules in ternary interaction as an example. PSS, especially neutral PSSH, monomers not only have stronger interaction with DMSO and water molecules but they also can coordinate higher number of them compared to PEDOT, due to their excess amount in PEDOT:PSS, larger molar volume, structure of polar sulfonate and sulfonic acid groups and 3D structure compared to 2D planar structure of PEDOT.

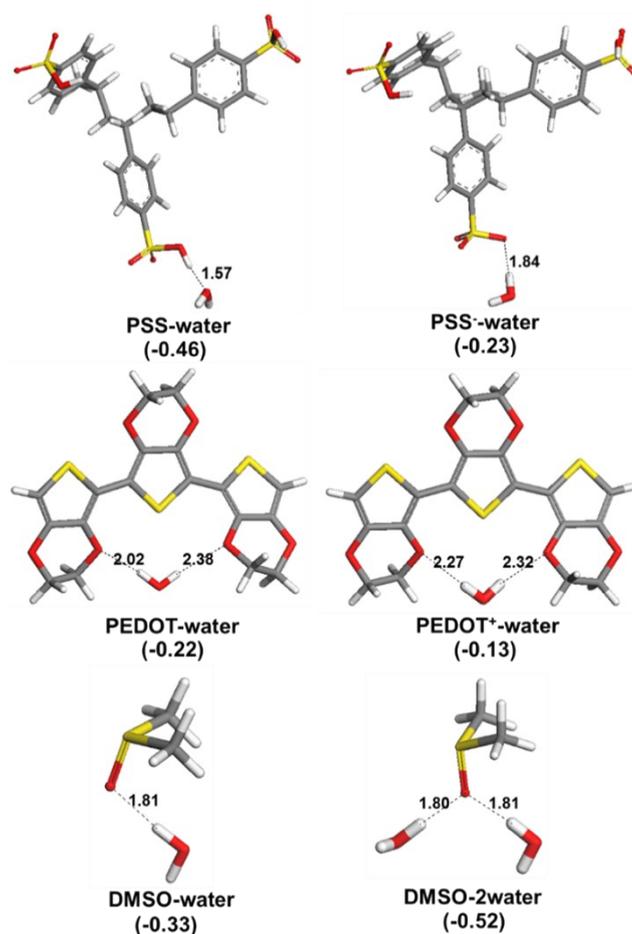


Figure S4c-Cont. Lowest-energy optimized structures for PSSH- H₂O, PSS⁻- H₂O, PEDOT- H₂O, PEDOT⁺- H₂O, DMSO-H₂O, DMSO-2H₂O

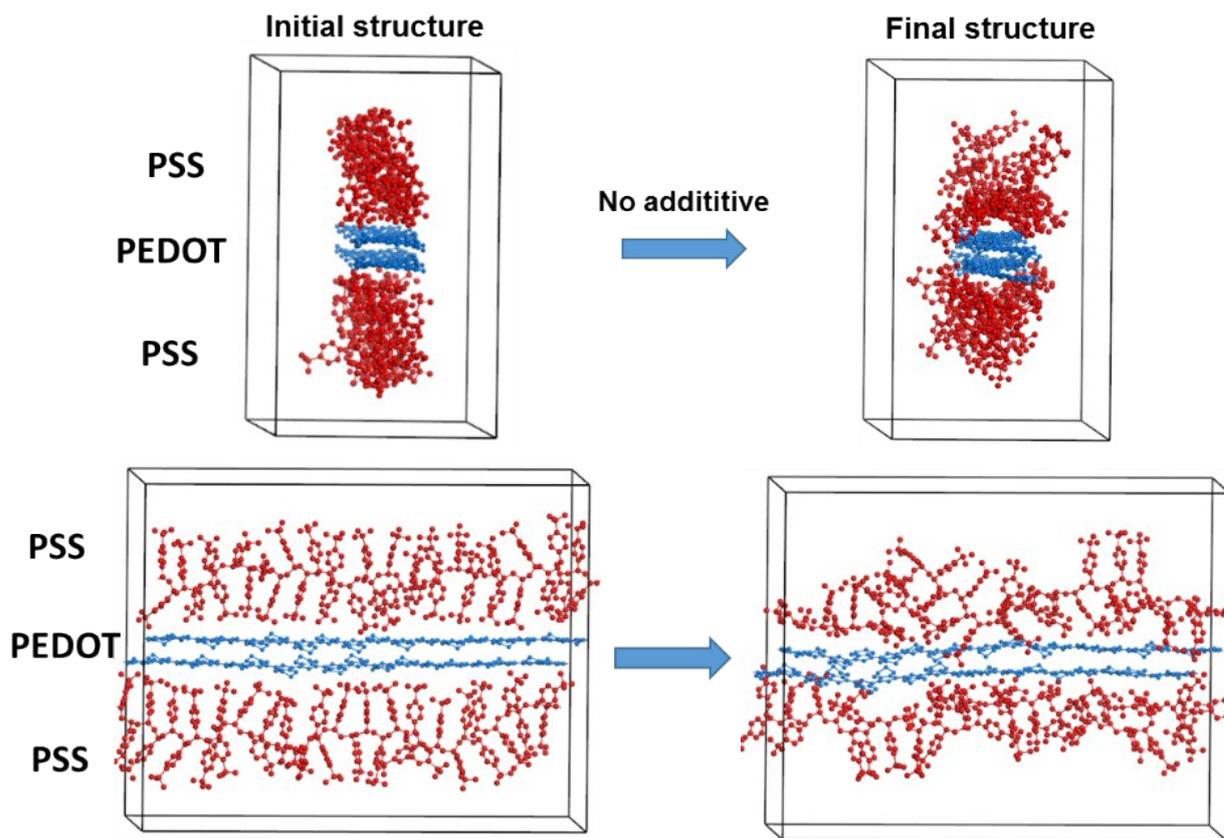


Figure S5. Initial and final structure after 6 ns for two chains of $(\text{PSS}_{36})^{6-}$ (red) and two chains of $(\text{PEDOT}_{18})^{6+}$ (blue) from -yz and -xy direction.

Hydrophobicity Calculations

Table S1 shows the results for hydrophobicity calculations by different approximations. Results in 1st column are obtained from ACD-ChemSketch. The 2nd calculation method is ChemAxon's own logP model based on the studies of Viswanadhan⁶, where the LogP of a molecule is composed of the increment of its atoms similar to the Ghose and Crippen method. Results in 3rd column is based on a training set named Consensus, which is based on three different approximation for LogP where Viswanadhan, Klopman and PhysProp studies were incorporated and dynamic adaptive coefficients were used according to the quality of predictions by each method.^{7,8}

Table S2. Hydrophobicity results for PEDOT:PSS-DMSO and water system components by from different softwares.

	ACD-ChemSketch	ChemAxon	Consensus
DMSO	-1.35	-1.43	-1.41
PEDOT ₃	2.96	1.36	3.14
PSS ₃	2.41	4	5.09
PSS ₃ ⁻	2.41	1.73	2.72
PEDOT	1.56	1.03	1.27
PSS	1.46	1.71	2.11
PSS ⁻	1.46	-0.55	-0.26
CSO ₃ H	-1.89	-1.21	-0.96
CSO ₃ ⁻	-1.89	-3.47	-3.34
water	-1.38	-0.65	-0.65

References

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