Electronic Supplementary Material (ESI) for Soft Matter

Resolving subnanometric structure of ultrathin films poly(3,4-ethylenedioxythiophene) on steel surfaces: a molecular modeling approach

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Constructing reliable molecular models based on experimental data

Our models were built based on the currenly available experimental information. The density of films constituted by PEDOT doped with ClO_4^- was determined to be 1.665 g·cm^{-1}.[1s] This density corresponds to EDOT segments and the counterions present in a film grown over a steel surface. The doping level of doped PEDOT was obtained by determining the amount of ClO_4^- ions in polymer samples using standard ion chromatography. [1s-2s] Results indicated that the number of positive charges supported by each repeat unit of PEDOT that had been obtained by anodic polymerization is +0.5. [1s, 3s] We assumed an average width of PEDOT films between 100 to 120 Å,[4s] which corresponds to the polymer growth on stainless steel considering a very small polymerization time (i.e. smaller than 5 s). Imposing such structural restrictions on any given orthorhombic volume unit:

$$d = \frac{\left(\frac{1}{2}y \times Mw_{ClO_4^-} + yMw_{EDOT}\right)}{A \times h} \qquad (1)$$

Where d is the density of PEDOT films doped with ClO_4^-, A and h are the area of the metal surface and the width of the polymer layer, respectively, y corresponds to the number of EDOT repeat units, $y/2$ the number of counter ions and M_W(EDOT) and $M_W(ClO_4^-)$ are the molecular of weight of the EDOT repeat unit and the perchlorate ion, respectively.

If the number of EDOT units is isolated from equation (1), leaving this value as function of the surface extension, the number of needed repeat units is 0.528 times the total area of the metal surface. Considering a surface with an edge of 102.2 Å and, therefore, a total surface of 10,444.84 Å^2, the required number of EDOT units will be 541, distributed over the whole considered volume (i.e. 100 Å × Area). Further, a thickness of 100 Å implies that each chain will present ~40 EDOT units, resulting in a system with 138 $(EDOT)_{40}$ chains. As each chain of 40 repeat units supports 20 positive charges, the number of ClO_4^- ions added to reach charge neutrality was 20×138= 2760.

In order to maintain periodic boundary conditions over the crystallographic *c*-direction, from now on referred as *z-axis*, two more considerations were to be applied. First, the width of the iron layer had to be large enough to ensure that the atoms of the polymer chains anchored on the top of the surface interacted with an infinite layer of iron atoms beneath them. Second, along the *z*-axis all atoms belonging to PEDOT chains or to ClO_4^- ions should be interacting with an infinite continuation of solvent molecules. If a cutoff of 14.0 Å was to be used, and without accounting for the iron layer, the minimal *z*-axis length should be 21.0 Å (1.5 time that cutoff). Applying the same reasoning, the iron layer should present at least that same length, which roughly accounts for 11 layers of iron atoms properly arranged in the fcc packing. Accordingly, the smallest length of *z*-axis should be 142 Å. However such configuration would only allow the presence of 21 Å of solvent phase on *c* direction, in front of 121 Å of solid phase. Thus, an extra solvent volume was added by increasing the total *z*-axis length up to 240 Å, which almost equalized the initial dimensions of both phases, solid and liquid.

Several initial assumptions were adopted to facilitate building initial arrangement of PEDOT chain on the steel surface. As we previously mentioned, iron atoms will be considered frozen spheres, since detailed crystal information for the steel substrate has not been reported. However, its force field parameters were extrapolated to be fully consistent with AMBER force field frame.[5s] The conformation adopted by the polymer main chain was considered totally extended, even though the molecules were not considered rigid. The charge of the polymer chains was not used to compute the total energy during the building phase and the generated arrangements were fit to minimize the van der Waals energy. This contribution was computed with the Lennard-Jones potential adapted to AMBER force field. Van der Waals parameters for EDOT repeat units were obtained from previous investigations in which fully compatible parameters with the AMBER framework were obtained.[2S, 6S]

We first tried to distribute regularly the 138 chains on the steel surface. Under such conditions there was not any arrangement that kept all the chains in phase with respect to the orientation of their projection over *z*-axis, i.e. setting angle. Hence, constant steric hindrances were obtained when all PEDOT chains were organized in layers with identical setting angle. Under such restrains the aim was focused on packing the PEDOT chains in layers organized with different setting angle. Five different packing arrangements were generated by independently moving the setting angle of two contiguous layers of chains.

Models displayed in **Figure S1a** only represent chain growing patterns that would lead to totally ordered distribution of chains over the alloy surface. In order to generate uncorrelated disordered arrangements, each generated model was modified using a metropolis based algorithm (in house program) that would randomly modify single chain positions off their ordered layer. Thus, a chain is randomly chosen and a translation and/or a rotation over z-axis is performed. If the new chain position does not imply overlaps with atoms from other chains that had not been moved in this step, a Metropolis criterion was applied to accept or reject the new movement. After approximately 3000 accepted single movements, the new structure was sufficiently dissimilar to the starting arrangement. From each generated ordered arrangement we obtained a new disordered structure (**Figure S1b**), understanding disorder as loss of regularity among the regular distribution of chains over the metal surface, reminding that the initial built models present rigid geometry.

Despite the success of such strategy, this approach did not allow generating structures in which there were zones of the metal surface significantly free of polymer chains. In other words, is such structures there were not patches on the metal surface that were free of polymer presence. To obtain models that could take into account such circumstance, a modification of the previous strategy was applied. New restrictions were introduced regarding the previous movements of individual chains. In this generation cycle, single positions over the surface would be randomly selected every *n* steps and such position would then be considered banned to sustain PEDOT growth. Thus, if during the following generation steps a newly selected chain were to be randomly moved to that particular position, the movement would automatically be rejected, ensuring the presence of positions over the surface that never bear a PEDOT chain. Moreover, such prohibited positions were not single metal atom positions but a cluster of the metallic crystal positions around the banned position. In other words, the random selection affects a whole patch of neighboring points over the steel surface. After 4500 movements (starting from any ordered arrangement), the PEDOT chains distribution was sufficiently disordered, whereas several patches free of polymer chains were generated (patches reaching few squared Angstroms). As **Figure S1c** shows, each generated model presented surface patches free of polymer chains that can easily be located for the presence of perchlorate ions filling the generated void (green spheres).

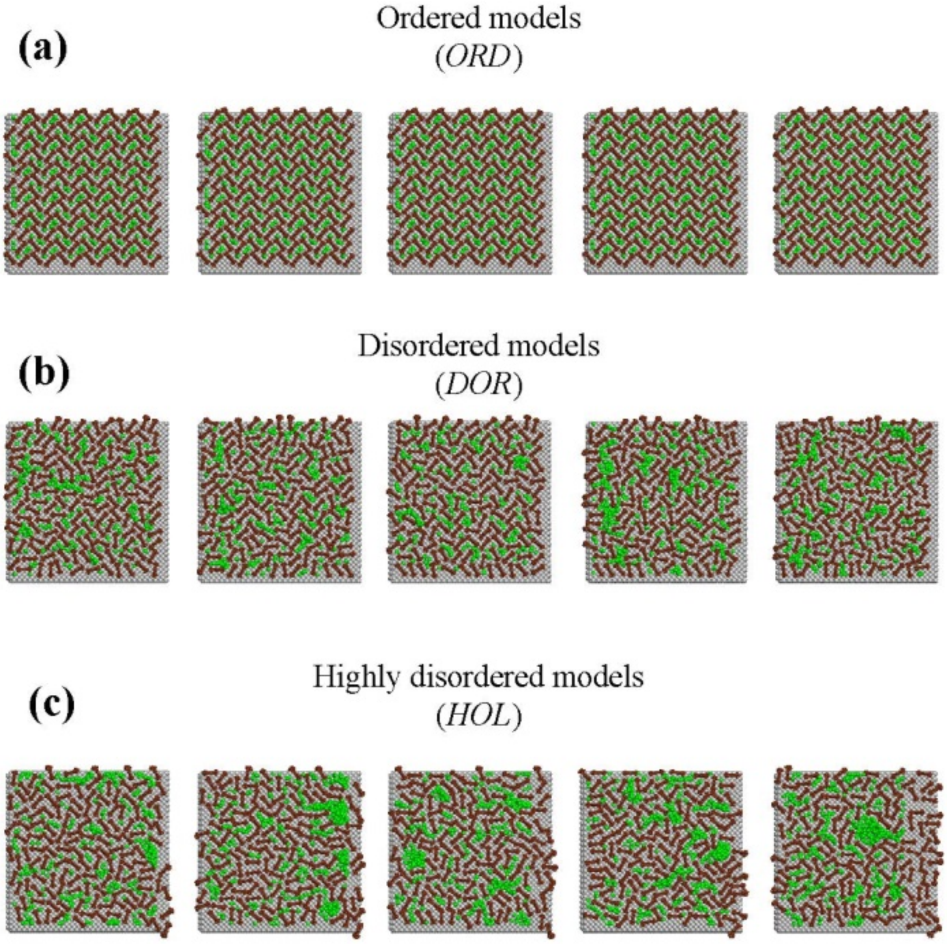

Figure S1.- Schematic equatorial projection of all the built molecular models: metal surface and perchlorate ions are represented by grey and green spheres, respectively; PEDOT chains are depicted as brown solid lines. From top to bottom: **(a)** the five initial models representing highly ordered chains distribution, **(b)** the five initial models representing moderately disordered chains distributions and **(c)** highly disordered chains distributions.

Using an early strategy envisaged to estimate the unoccupied space of any polymeric solid,[7S] the maximum amount of the 2760 Perchlorate ions were placed in free space left by the PEDOT chains, i.e. interstitial zones between polymer chains. Despite the apparent contradiction, the higher was the initial order in the chains disposition over the two directions of the iron surface the higher was the amount of perchlorate ions that fit in such interstitial zones. It is obvious that the presence of surface patches without polymer chains helped positioning ions there. However, the reduction in free space consequence of approaching polymer chains when breaking the symmetrical distribution was higher than the free space generated in the empty patches. Thus, ordered models allowed placing from 2725 to 2742 perchlorate ions, the disordered models only allowed inserting from 2690 to 2708, and the models with empty patches from 2638 to 2656, respectively. The remaining anions were place above the PEDOT layer, separating each perchlorate molecule by a minimum radial distance of 5.5 Å to ensure its solvation when the solvent is added.

Finally, each built model was placed in a orthorhombic cell of 104.1 × 104.1 × 240 Å. All the remaining free space of this simulation box was filled with acetonitrile molecules from a previously equilibrated simulated solvent box. This solvent system consisted in an orthorhombic box of 104.1 × 104.1 × 250 Å with a total amount of 30936 CH_3CN molecules, which reproduced the experimental density of this liquid (0.777 $g\cdot cm^{-3}$). Before starting the relaxation and equilibration of each of the initial models, the number of acetonitrile molecules was equalized for all the models, with a total of 21627 solvent molecules.

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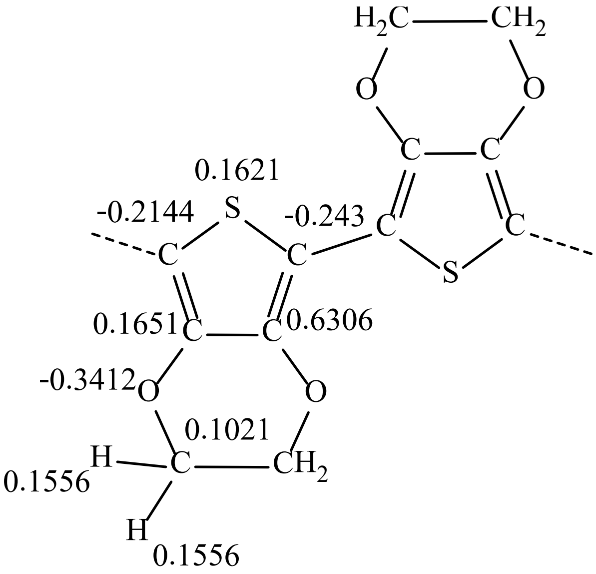


Scheme I

Schematic representation of a diEDOT unit. The partial charges previously obtained for studying oxidized PEDOT chains (reference 22 of the manuscript) and used in this work to compute the electrostatic component of the potential energy have been included, as well.

RESULTS

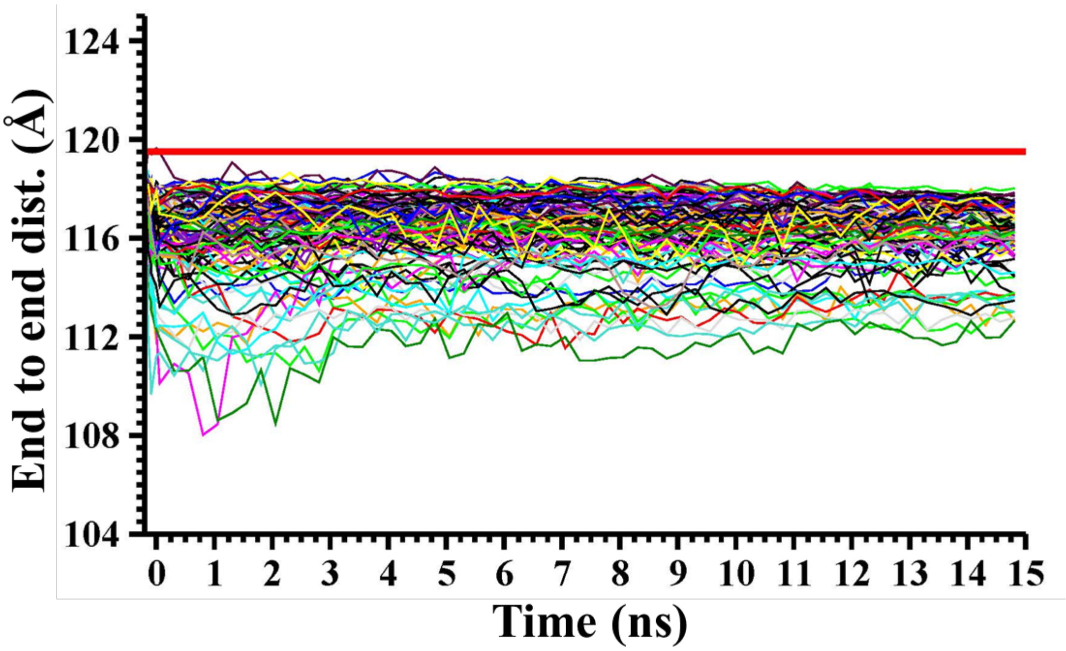


Figure S2.- Temporal evolution of the end to end distances of all present PEDOT chains for DOR models. A red horizontal line indicates the initial value of such magnitude at the beginning of the equilibration runs (.i.e. right after the energy minimization has been performed).

Table S1. Averaged mean end to end distance of PEDOT chains for each studied model using different time frames. Distances are provided in Angstroms and the respective standard deviations for every average are provided.

Δt[a]	ORD	DOR	HOL
0-0.050	117.4 ± 0.3	117.6± 0.3	117.3 ± 0.3
0-0.150	116.9 ± 0.2	117.1± 0.3	116.8± 0.2
14.5-15	116.4 ± 0.1	116.3± 0.1	116.4± 0.1
0.0-15	116.4 ± 0.1	116.4± 0.1	116.4± 0.1

[a] Period of time used to average each temporal mean end to end distance.

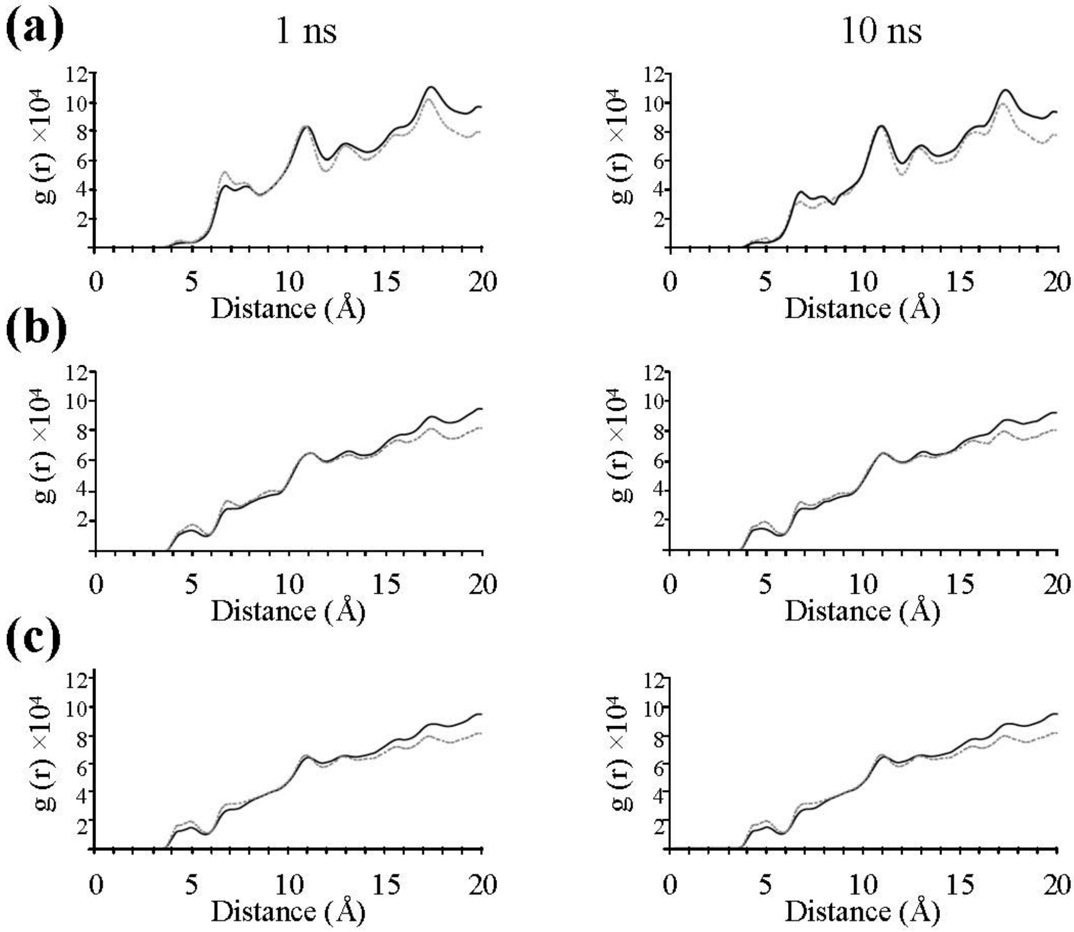
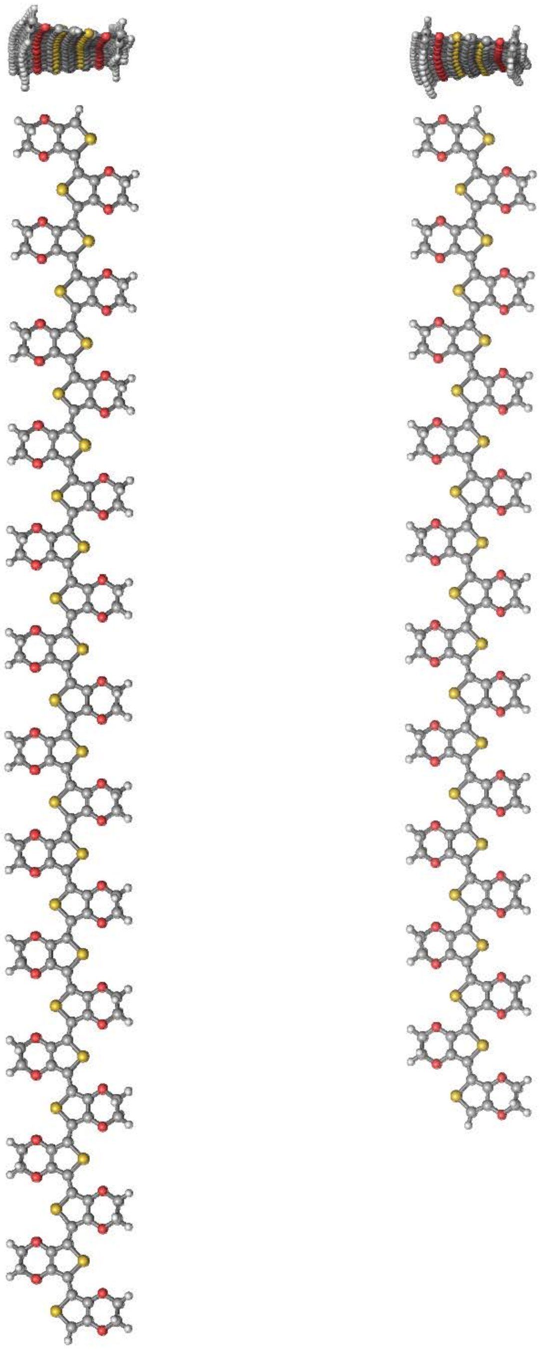
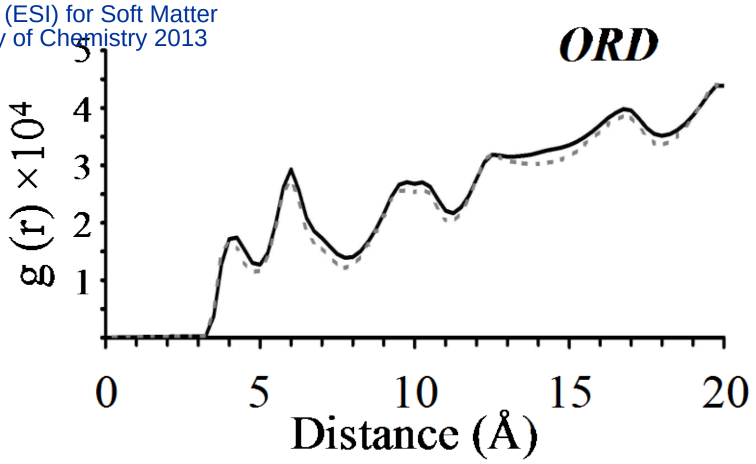


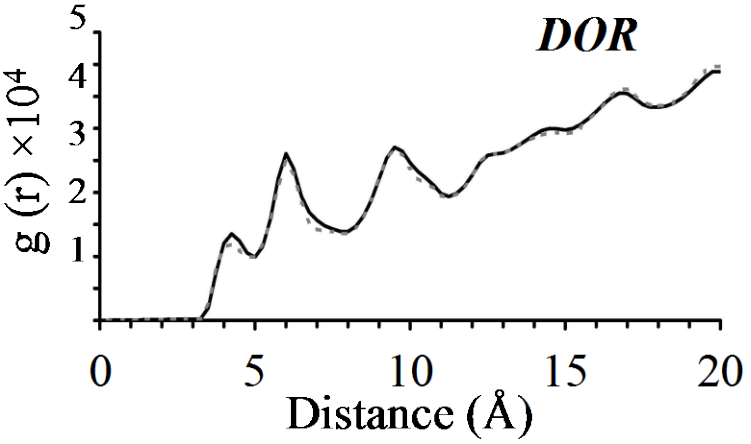
Figure S3.- Accumulated radial distribution of inter chain EDOT–EDOT distances, measured from the centers of mass, at two different time frames (left panel for the first ns of the simulation, right side for the last ns). Solid lines depict the results obtained for all polymer chains while dashed grey lines correspond to the central residues of each PEDOT chain. From to top to bottom: **(a)** *ORD,* **(b)** *DOR* and **(c)** *HOL* models.



$(EDOT)_{24}^{4+}$ $(EDOT)_{20}^{2+}$

Figure S4.- Equatorial (top) and Axial projection (bottom) of two PEDOT oligomers studied by Quantum Mechanics methodologies: all calculation have been performed using the unrestricted DFT formalism UB3LYP/6-31G(d) and all possible electronic states have been computed for each ionization state. In this figure, the electronic states of $(EDOT)_{24}^{4+}$ (left panel) corresponds to quintuplet state and the studied $(EDOT)_{20}^{2+}$ (right panel) is triplet state.





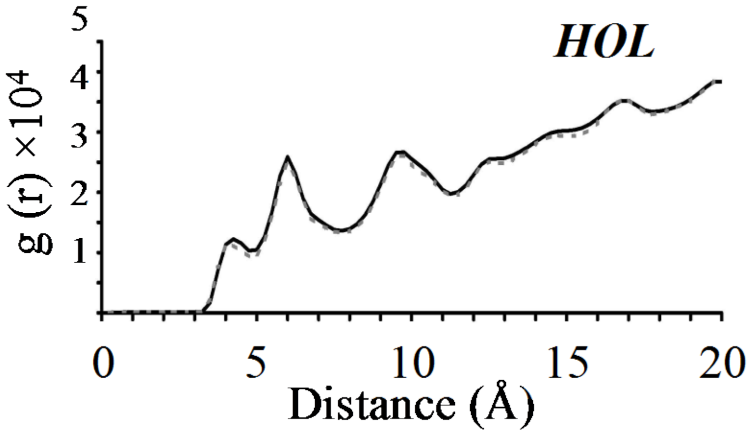


Figure S5.- Accumulated radial distribution of EDOT-ClO_4^- mass centers distances for the last ns. Solid lines depict the computed results for all polymer chains and dashed grey line for the central residues of each PEDOT oligomer. From to top to bottom: *ORD*, *DOR* and *HOL* models.