How does PEDOT combine with PSS ? Insights from experiment and theory

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Supporting Information :

<u>SEM</u>



Fig. S-1 : SEM image of PEDOT-PSS solution after sonication

Theoretical modeling

Studies of oligomeric 3,4-ethylenedioxythiophene (EDOT), Styrene sulphonic acid

(SS) and EDOT-SS complex were performed using density functional theory (DFT) as implemented in the Gaussian 03[1] suite of programs. The structures of all isolated molecules and complexes were determined by full geometry optimization in the gas-phase using B3LYP [2,3] functional with the 6-31G** basis set, frequency calculations were performed to ascertain the stationary points. The Mulliken charges [4] are obtained from Mulliken population analysis and provide the partial atomic charges on the individual atoms of a molecule using linear combination of atomic orbitals molecular orbitals (LCAO-MO) method as implemented in G03 software. For each system studied we have provided the nature of the HOMO and LUMO molecular orbitals along with the respective energies in eV. The energy gap between HOMO and LUMO orbital is an important factor controlling the current through the molecule and comparison of the values for different complexes give an idea about the ease with which their electron densities can be modified. HOMO-LUMO gaps calculated using B3LYP method are reported here as they are more reliable [5] than non-DFT based methods. However it is known that the energies of HOMO, LUMO and the gaps are predicted with varying accuracies for different theoretical methods. [6] The binding energies for PEDOT-PSS complex formation of are calculated using following expression:

$E_{binding} = [E_{EDOT} + E_{SS}] - E_{EDOT-SS}$

We have first considered a small oligomeric unit, trimer of EDOT. In neutral and singlet form, this is a completely planer molecule (see Figure S-5 for structure). The HOMO-LUMO gap is 3.30 eV and the HOMO and LUMO is extended over the thiophene backbone of the planer molecule. The Mulliken atomic charges(averaged over one EDOT unit) is shown in Figure S-5 and it is found that small (-) ve charges are present in the edge units with small (+) ve charge on the central unit. The monocation of the trimer EDOT is in doublet state and the atomic charges on all the units are (+) ve and nearly same (0.33, 0.34, 0.33) Figure S-6a. The HOMO-LUMO gap is 2.19 eV with extended HOMO and LUMO. The dication of the trimer EDOT is in singlet state and the atomic charges on all the units are (+) ve and are 0.60, 0.69, 0.60 (Figure S-6b). The HOMO-LUMO gap is 1.97 eV with extended LUMO and LUMO+1.



Figure S-2: Structure and Mulliken atomic charges for neutral, singlet EDOT trimer.





Figure S-3: (a) Structure and Mulliken atomic charges for EDOT⁺ (doublet) trimer and (b) EDOT²⁺ (singlet) trimer.

When the trimer of EDOT and the monomer of SS interact, the monocation & monoanion interaction gives rise to a stable complex which is neutral as a whole and in doublet state with negligible spin contamination. The optimized structure of the EDOT (trimer)-SS (monomer) is shown in Figure S-7 (a), which shows that EDOT remains planer and the styrene sulphonate unit approximately points to the central portion of EDOT, trimer. The atomic charges calculated on the rings after complexation with monomeric SS⁻ are (+) ve and are 0.26, 0.30, 0.29 on three units respectively (Figure S-7b). The optimized structure of the EDOT²⁺(trimer)-SS²⁻(dimer) is shown in the Figure S-7 c and d, which shows that EDOT²⁺ is bent and the dimeric styrene sulphonate approximately points to the central portion of EDOT²⁺, trimer. The atomic charges calculated on all the units after complexation with SS²⁻ are (+) ve and are 0.49, 0.54, 0.48 on the three units respectively (Figure S-7e).



Figure S-4: (a) Optimized structure for EDOT⁺-SS⁻ (monocation- monoanion) neutral as a whole, (b) Mulliken atomic charges for EDOT⁺-SS⁻ (c) &(d) Optimized structure for EDOT²⁺-SS²⁻ (dication- dianion) neutral as a whole but doublet state, top view and side views are shown (d) Mulliken atomic charges for EDOT²⁺-SS²⁻.

When studying the eight unit oligomer of EDOT, we have chosen to reduce the size of PEDOT 8-mer by removing the ethylene oxide rings connected to the two edge thiophene rings. This slight modification

of structure, does not affect the molecular orbitals, and Mulliken charge distribution of the EDOT unit as we have shown in Figures S-8 and S-9. This study justifies the use of modified EDOT 8 mer (Figure S-8.c) for all the detailed studies instead of EDOT 8-mer shown in Figure S-8d.



Figure S-5. a) HOMO and LUMO for EDOT⁴⁺(singlet) 8-mer (b) HOMO and LUMO for EDOT2+(singlet) 8-mer (c) HOMO and LUMO for EDOT 8-mer with modified end rings marked by blue square (singlet). (d) HOMO and LUMO for EDOT 8-mer without modified end rings (singlet). The energies are given in eV.



Figure S-6. a) Mulliken atomic charges for EDOT with modified end rings marked by blue square (singlet). (b) Mulliken atomic charges for EDOT without modified end rings (singlet). It is seen that in spite of the modified end rings the charges on the S atoms of the thiophene backbone remains nearly unaffected.



Figure S7. a) The UV-Vis spectrum for PEDOT²⁺ (without any counter ion thus straight). (b) 200-600 nm is expanded for better viewing (c) PEDOT²⁺, slightly bent to inteact with dianion (d) 200-600 nm is expanded for better viewing (e) PEDOT⁴⁺ bending is more when interacts with tetracation (f) 200-600 nm is expanded for better viewing.

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