Electronic Supplementary Material (ESI) for RSC Advances.

Unrevealing the interaction between O_2 molecules and Poly(3-hexylthiophene-2,5-diyl) (P3HT)

Marcelo Fernandes[1†], Ernesto Osvaldo Wrasse[1], Caio Junji Kawata Koyama[1], Florian Steffen Günther[2], Douglas José Coutinho[1*]

[1]Federal University of Technology – Paraná (UTFPR), 85902-490 Toledo-PR, Brazil.
[2]São Carlos Institute of Physics, University of São Paulo, P.O.Box 369, 13560-970 São Carlos-SP, Brazil.
**Corresponding author: douglascoutinho@utfpr.edu.br*

Keywords: poly(3-hexyl)thiophene (P3HT), DFT, polymer oxidation and degradation, doping, singlet/triplet oxygen.

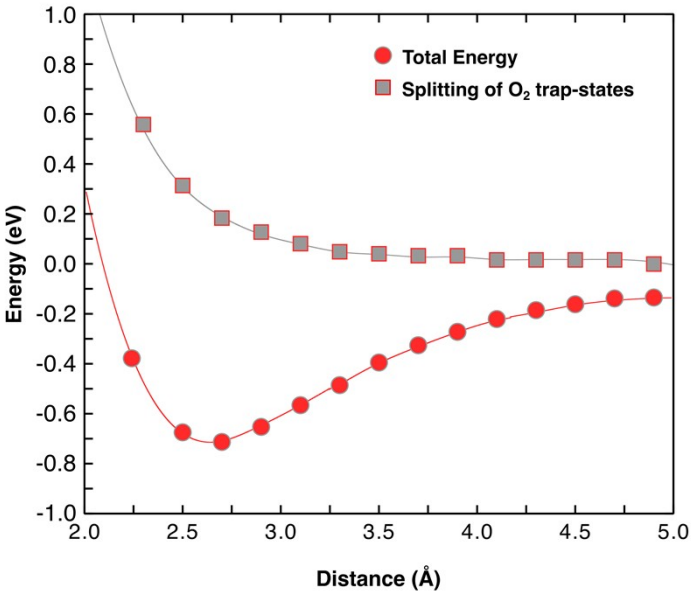

Fig. SM1 - Calculated energy as a function of the distance between a O_2 molecule and the thiophene ring. The red circles show the total energy, and the grey squares the split for the trap-state levels.

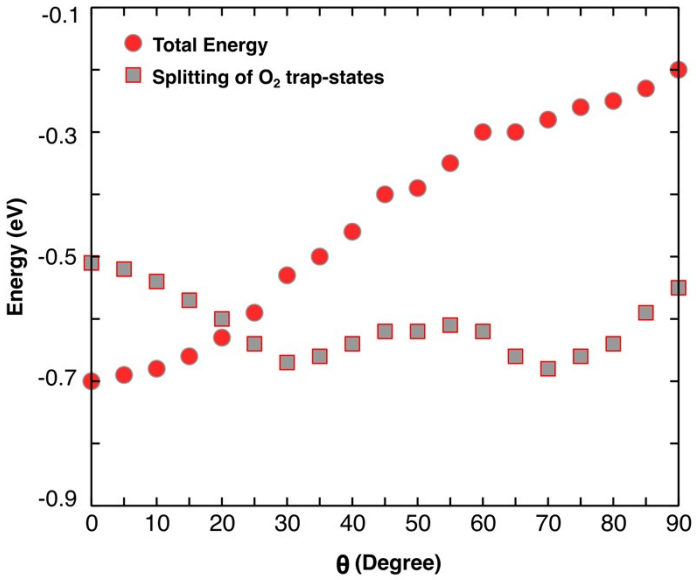

Fig. SM2 - Calculated energy for in-plane rotations of the O_2 molecule. The red circles show the total energy, and the grey squares the energy split for the O_2 trap-states.

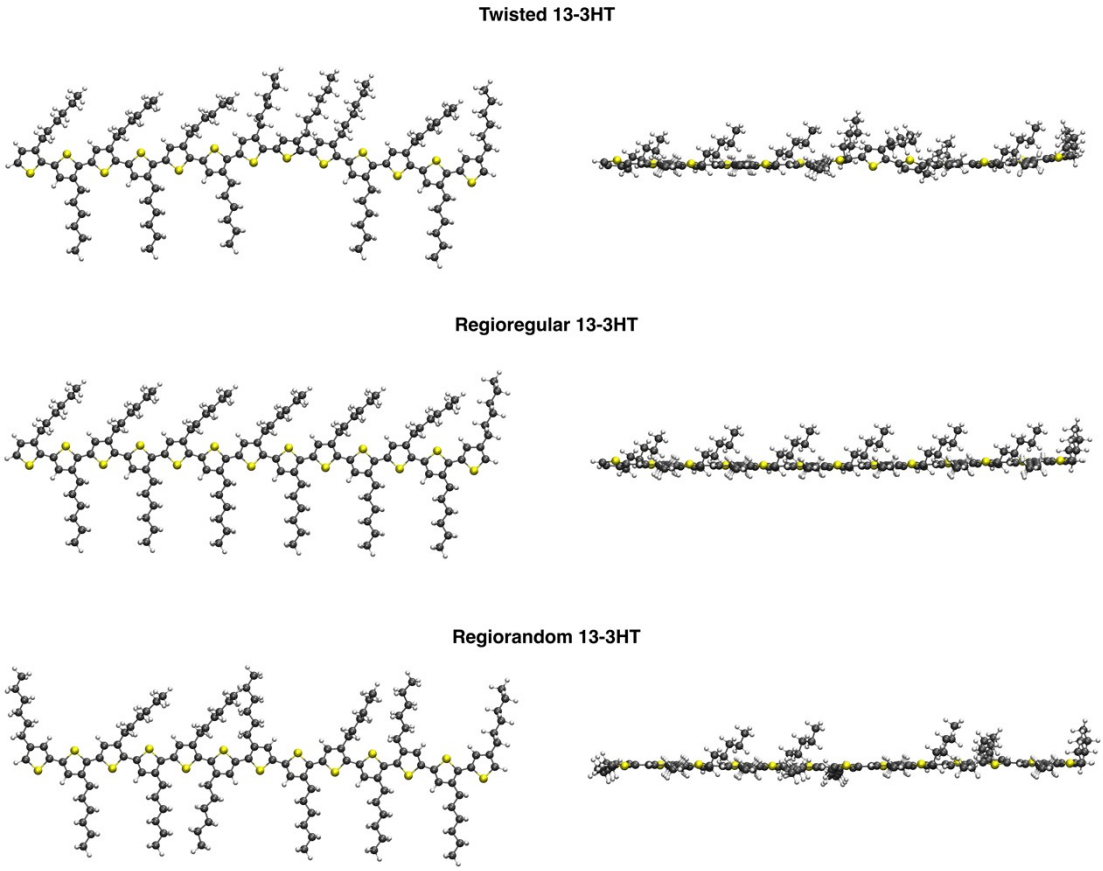

Fig. SM3 - Top and side view of the relaxed geometries of a twisted, regioregular (Rr) and regiorandom (Ra) 13-3HT oligomers.

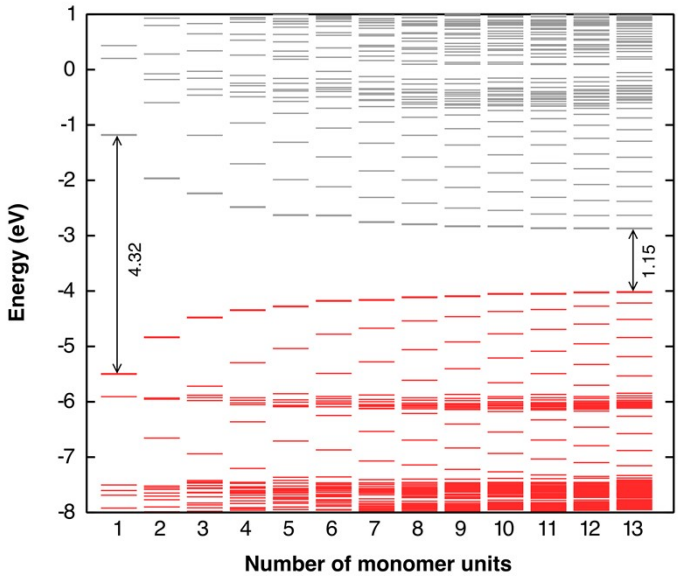

Fig. SM4 - Orbital energies as a function of the oligomer length N. Occupied levels are given in red and unoccupied levels in grey. The energy gaps for N = 1 and N = 13 are indicated.

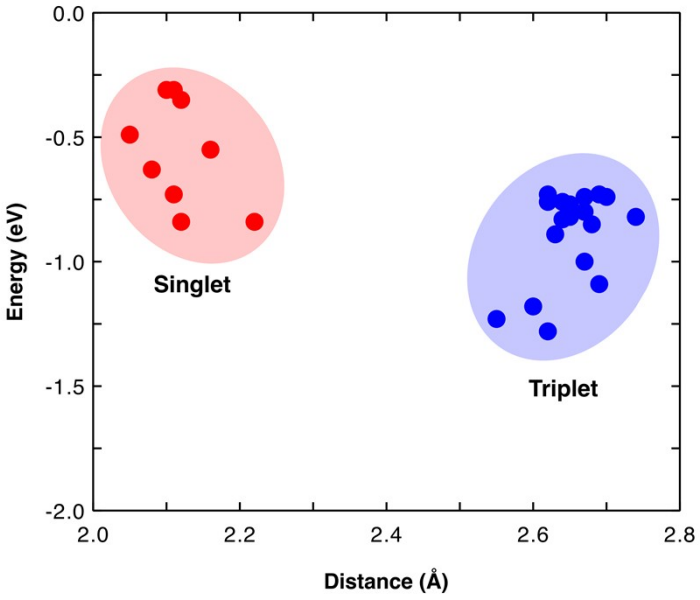

Fig. SM5 – Calculated interaction energy of P3HT:O_2 as a function of the distance *d* between the oxygen molecule and the thiophene ring for the models represented in Fig. SM3.

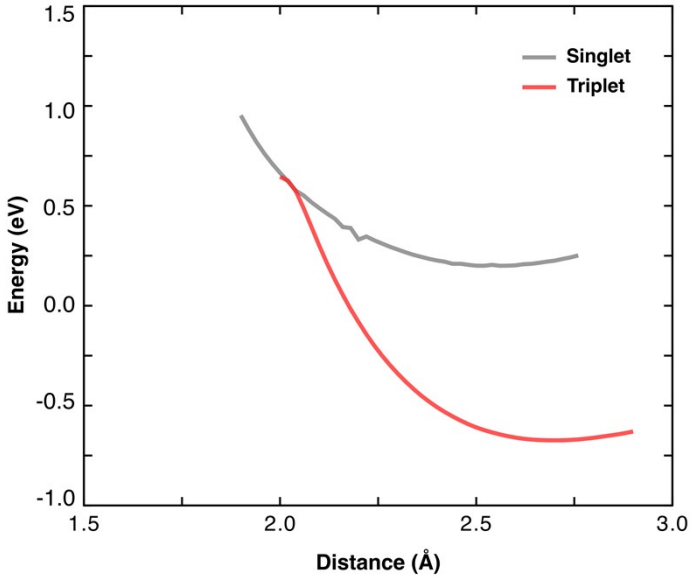

Fig. SM6 - Calculated energy for the O_2 molecule interacting with the P3HT monomer as a function of the distance d for the singlet (grey line) and triplet (red line) multiplicities.

Atomic position of 3HT:O_2 model in Angstroms

Atom	X	Y	Z
S	8.425196	7.021245	6.87264
C	9.791333	9.078836	6.116628
C	8.425672	9.348841	5.800664
C	9.932485	7.839634	6.703298
C	7.575829	8.322051	6.148169
C	10.904524	10.058884	5.936687
C	10.662383	11.350343	6.700593
C	11.820002	12.320348	6.618687
C	11.556975	13.6278	7.334615
C	12.726302	14.589815	7.292128
C	12.441503	15.898031	7.996521
H	6.482498	8.265043	6.018051
H	10.860485	7.371896	7.073661
H	8.075223	10.288051	5.331095
H	11.044487	10.292601	4.850111
H	11.862594	9.594287	6.276658
H	10.433307	11.110101	7.769831
H	9.732082	11.839553	6.314089
H	12.066165	12.525607	5.544616
H	12.738324	11.840334	7.045111
H	11.283453	13.420529	8.401452
H	10.653829	14.120802	6.890377
H	13.002904	14.78168	6.224565
H	13.622012	14.096572	7.747385

H	13.310695	16.593445	7.958918
H	12.190966	15.730499	9.070894
H	11.570593	16.421457	7.535393
O	8.433582	10.119957	8.486365
O	8.74854	9.045371	8.999731