Supporting Information

Oligomeric Interface Modifiers in Hybrid Polymer Solar Cell Prototypes Investigated by Fluorescence Voltage Spectroscopy

B. Reeja-Jayan[†], *Katherine A. Koen*[§], *Robert J. Ono*[§], *David A. Vanden Bout*[§],
Christopher W. Bielawski[§], *and Arumugam Manthiram*[†,*]

[†]*Materials Science and Engineering Program*
[§] *Center for Nano and Molecular Science and Technology and the Department of Chemistry*
The University of Texas at Austin
Austin, Texas 78712, USA

Table S1. Summary of photovoltaic parameters

Polymer sample	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	Efficiency (%)
P3HT	0.12	0.26	27	0.01
P3HT- oligothiophene	0.29	0.37	39	0.04
P3HT- carboxylated oligothiophene	0.51	0.34	61	0.11
10:1 blend of P3HT and carboxylated oligothiophene	0.32	0.18	38	0.02

Figure S1. Fluorescence intensity (FL) as a function of (a) time and (b) bias for devices incorporating premixed blends of P3HT and carboxylated oligothiophene. No hysteresis was seen in blend devices, unlike in the case of pure P3HT devices.

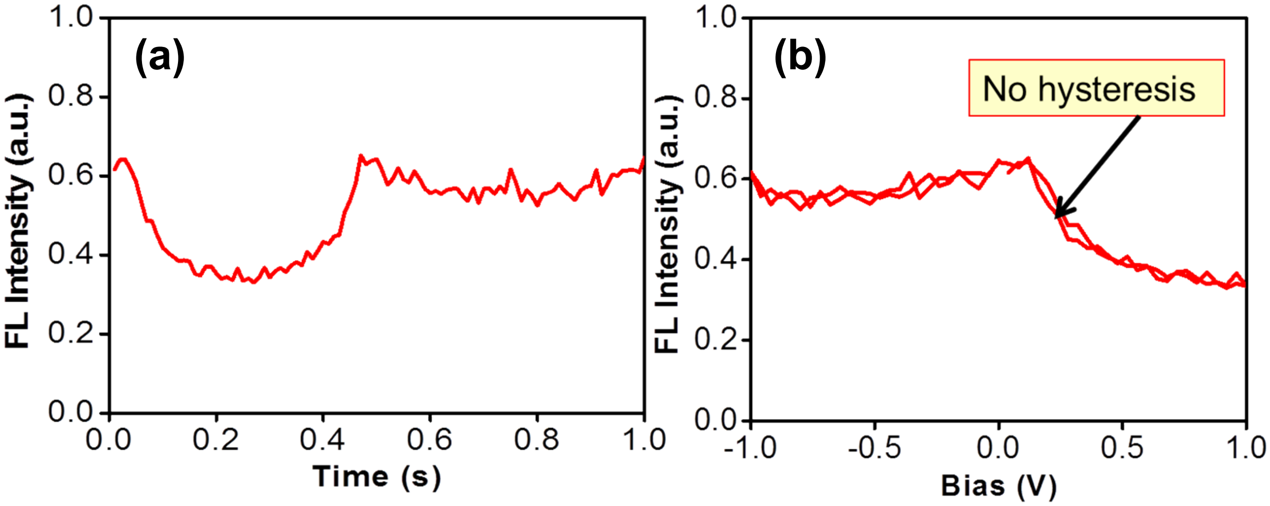

Figure S2. Enclosed absolute area between the forward and reverse curves of the fluorescence intensity versus bias plot against the photovoltaic parameters (a) V_{oc} and (b) fill factor

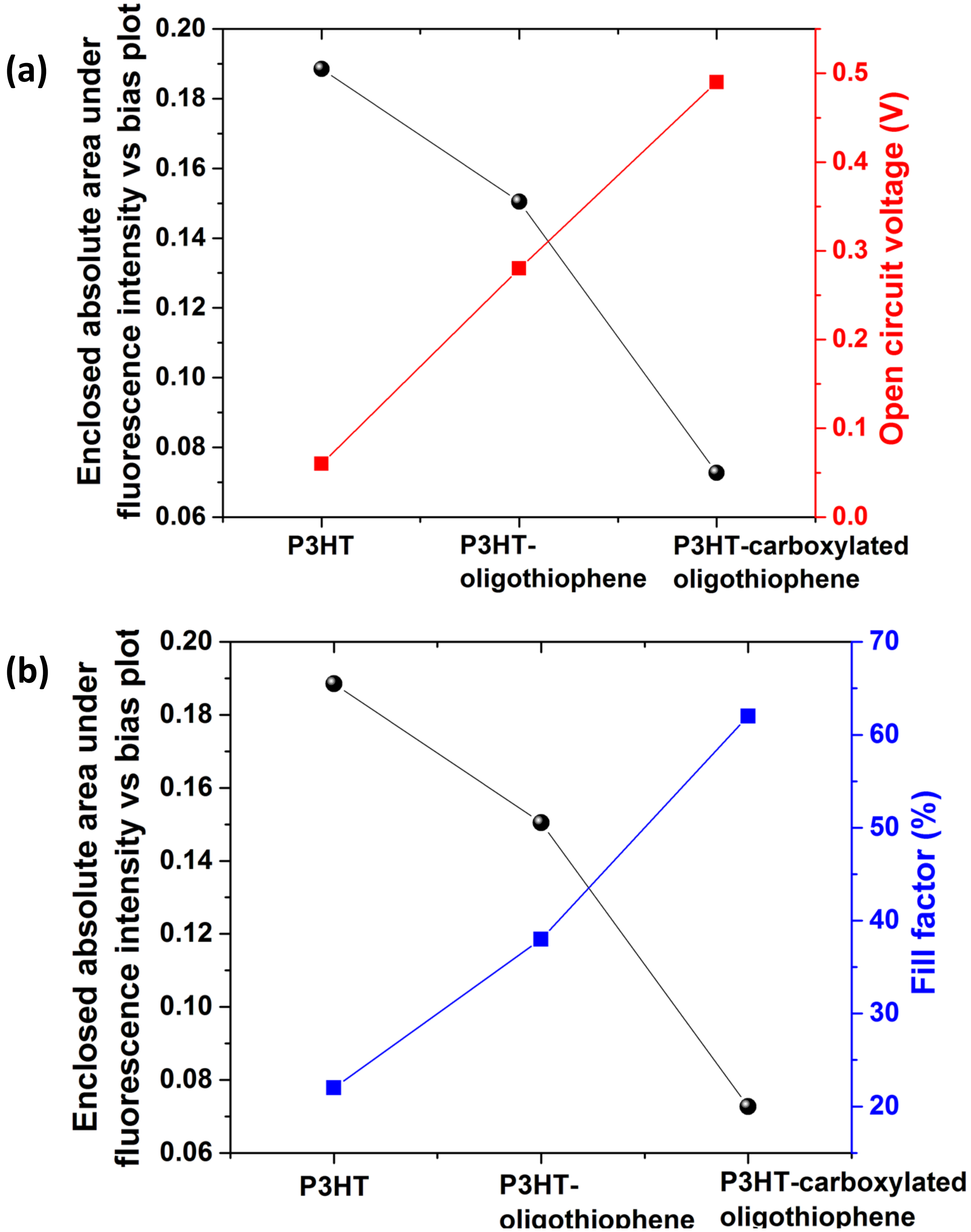

Figure S3. Emission spectra of polymer P3HT with and without bias show no change

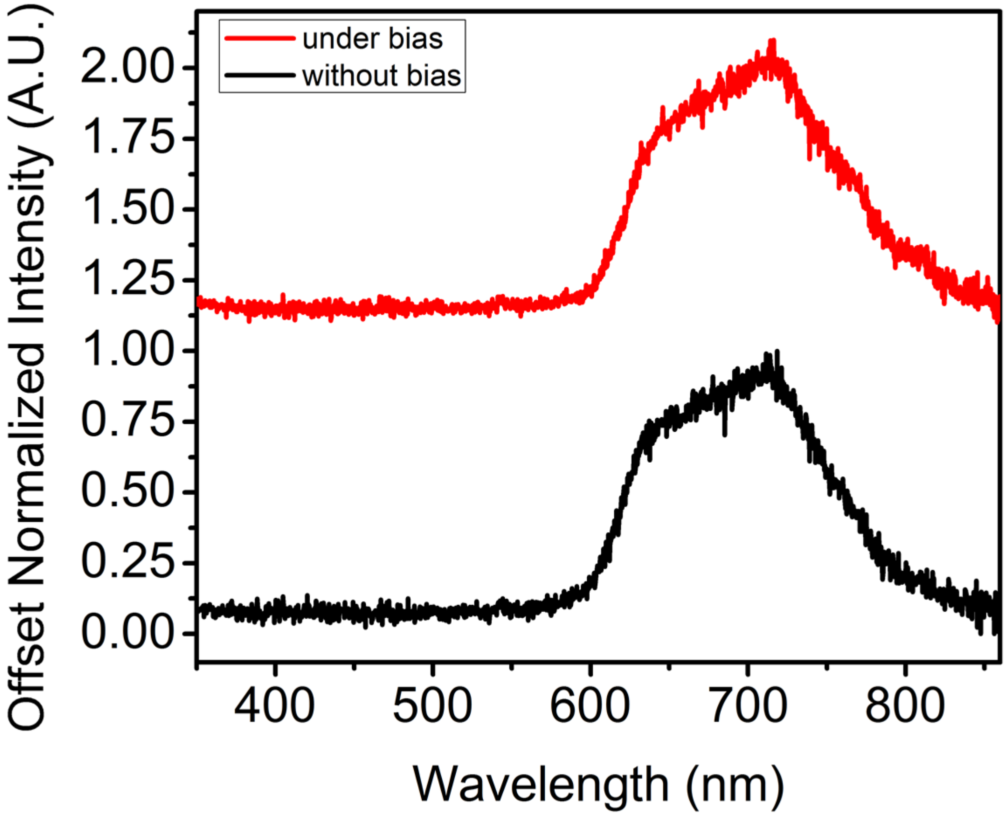

Figure S4. XPS Ti2p and O1s spectra

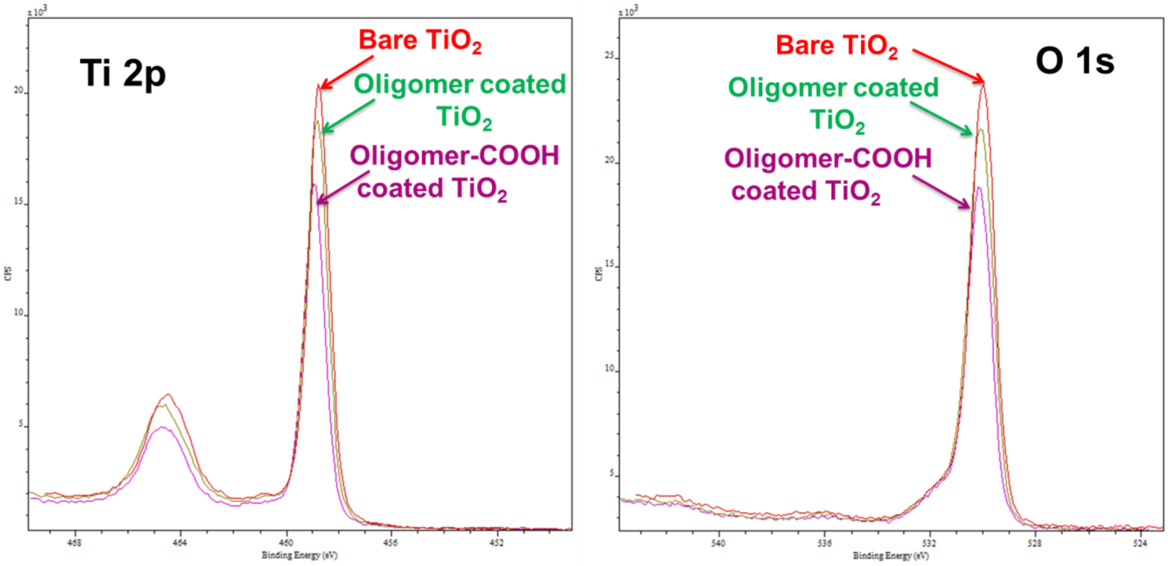

Figure S5. (a) Ball and stick Spartan model of carboxylated oligothiophene. This model was generated by building the molecule in Spartan molecular modeling package and finding the lowest energy configuration. This is a Hartree-Fock calculation and does not account for solvent. Red balls – oxygen, gray balls – carbon, white balls – hydrogen, space filling model for (b) horizontally and (c) vertically oriented chain configuration.

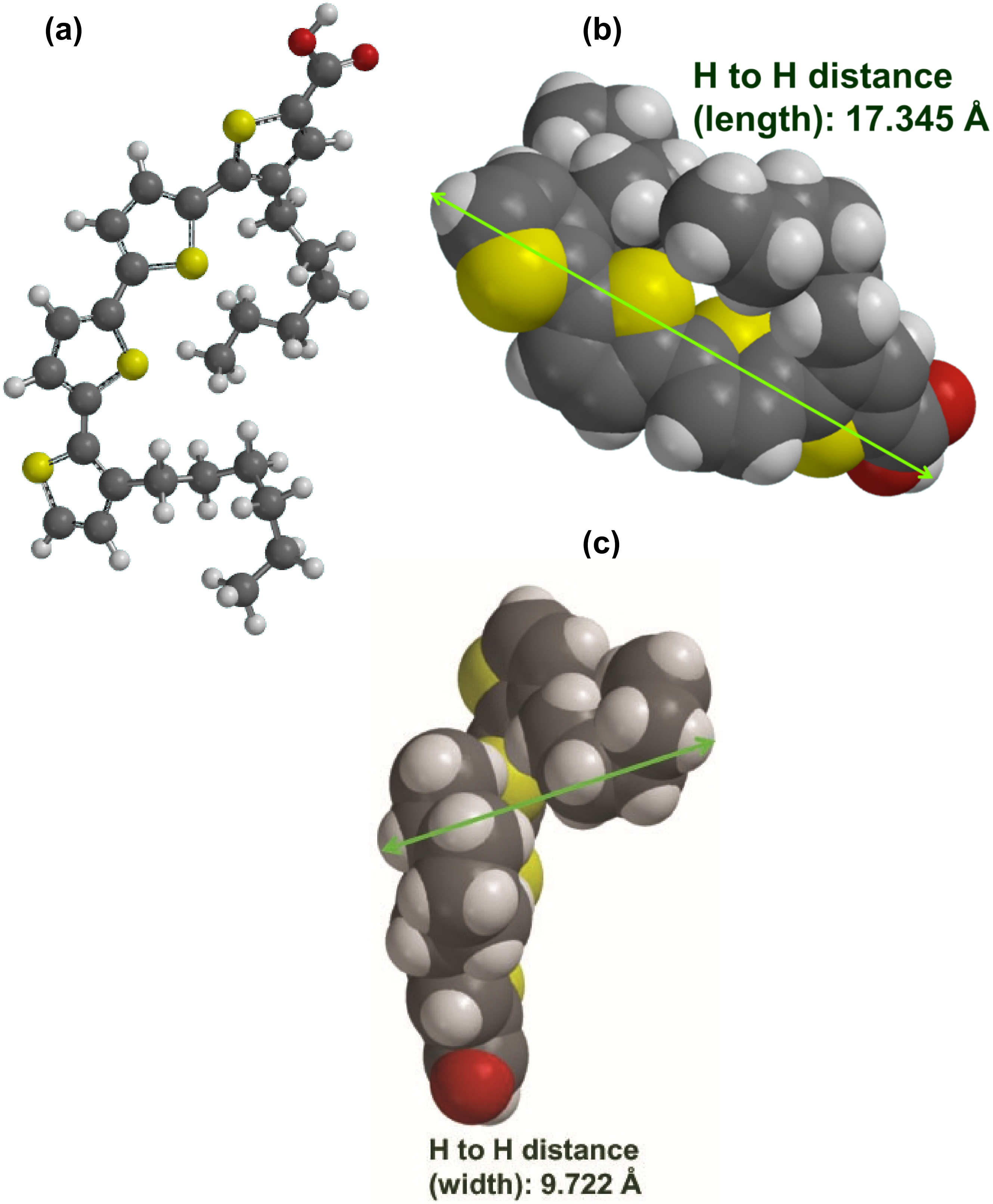

Figure S6. If the carboxylated oligothiophene orients so that its length lies in contact with the TiO_2 surface, then it can potentially explore a circle of surface area whose radius is defined by the length of the molecule. This is the greatest possible surface area one carboxylated oligothiophene molecule could occupy. If the carboxylated oligothiophene does not rotate, but its length is still in contact with the surface, then the surface area it covers is a rectangle whose length and width are those of the molecule.

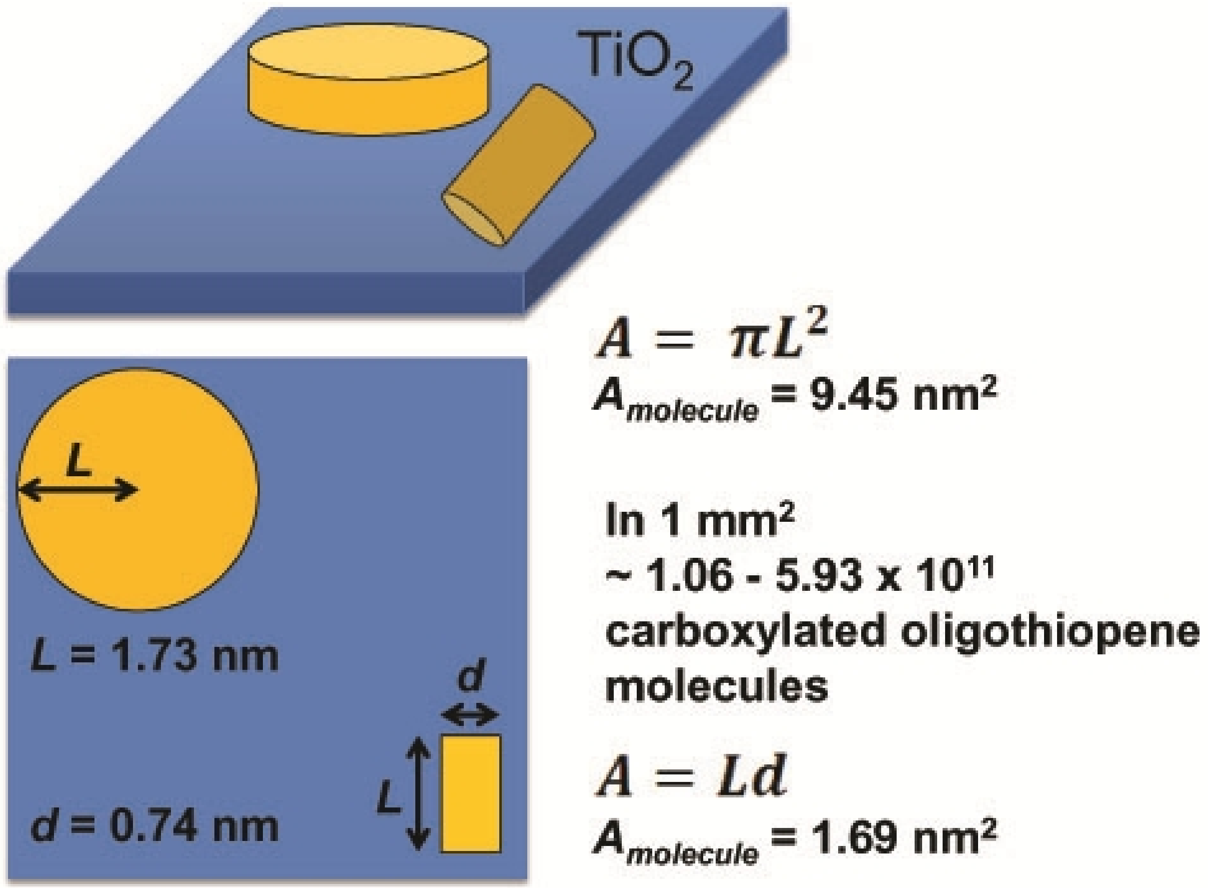

Figure S7. If the carboxylated oligothiophene orients such that its contact with the TiO_2 is limited to its carboxyl moiety and the oligothiophene tail is normal to the surface, the surface area each molecule occupies is a circle whose diameter is equal to the width of the molecule. This is the smallest possible surface area each carboxylated oligothiophene molecule could occupy.

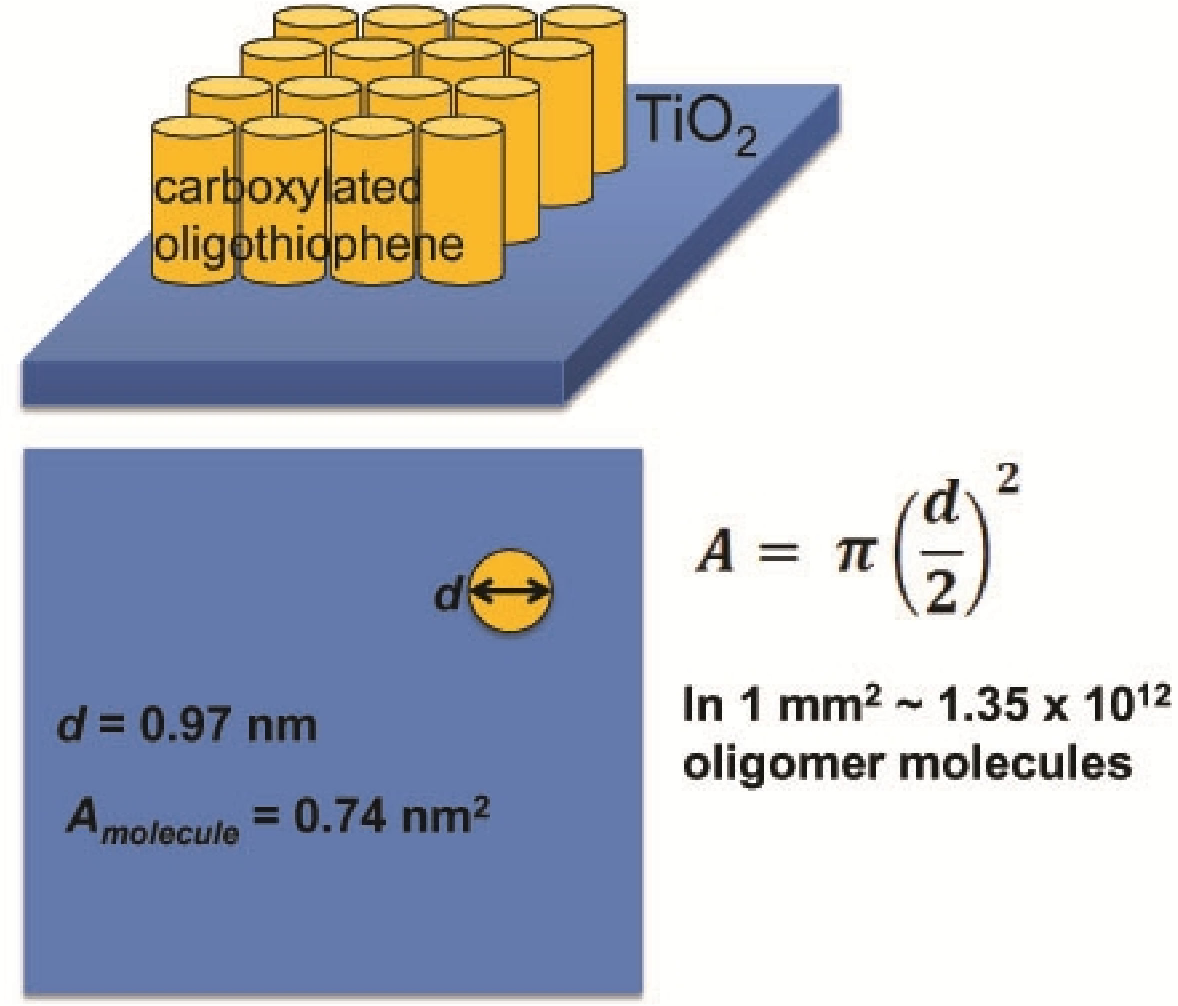

Figure S8. Photographs comparing oligothiophene coated TiO_2 (top) and bare TiO_2 (bottom) samples show no difference in appearance between the samples. Absorption spectra of the TiO_2 layer on the right also remains unchanged.