Supporting Information

Electronic Processes in Conjugated Diblock Oligomers Mimicking Low Band-gap Polymers: Experimental and Theoretical Spectral Analysis

Jodi M. Szarko^{§, $\Delta \Box$}, Brian S. Rolczynski^{§, $\Delta \Box$}, Jianchang Guo^{$\Delta^{\circ,\Box}$}, Yongye Liang^{\circ}, Feng He^{\circ}, Michael W. Mara^{§, $\Delta \Box$}, Luping Yu^{\circ^*} and Lin X. Chen^{§, $\Delta \Box^*$}

§Department of Chemistry, Northwestern University, Evanston, Illinois 60208

^A Chemical Sciences and Engineering Division, Argonne National Laboratory,

Argonne, Illinois 60439

Argonne-Northwestern Solar Energy Research (ANSER) Center, Northwestern

University, 2145 Sheridan Road, Evanston, IL 60208, USA

ODepartment of Chemistry and The James Franck Institute, The University of Chicago,

929 E 57th. Street, Chicago, Illinois, 60637

Synthesis and molecular characterizations

Scheme 1. Synthesis of the oligomers.

^{*} email:lchen@anl.gov, lupingyu@uchicago.edu



The oligomers are synthesized by a similar method reported in literature.¹ A general approach is to incorporate regioregular oligothiophene on both sides of thieno [3,4-b]thiophene through Stille coupling reaction and regioregular oligomers can be obtained. (Scheme 1)





Figure S1: ¹HNMR (CDCl₃) of M3: δ 0.90-1.00 (12H, m), 1.33-1.39 (18H, m),

1.54-1.74 (7H, m), 2.60-2.65 (4H, m), 4.26-4.28 (2H), 6.91 (1H, s), 6.94 (1H, s), 7.09 (1H, s), 7.13 (1H, s), 7.95 (1H,s). The * indicates trace amounts of methylene chloride.



Figure S2: ¹HNMR (CDCl₃) of M5: δ 0.90-1.0 (18H, m), 1.33-1.67 (41H, m), 2.61-2.64 (4H, m), 2.76-2.79 (4H, m), 4.27-4.29 (2H), 6.92 (1H, s), 6.94 (1H, s), 7.01 (1H, s), 7.03 (1H, s) 7.06 (1H, s), 7.11 (1H, s), 7.98 (1H, s)

M9 characterization



Figure S3: ¹HNMR (CDCl₃) of M9: δ 0.88-1.00 (30H, m), 1.31-1.70 (73H, m), 2.60-2.62 (4H, t, J = 8 Hz), 2.76-2.84 (12H, m), 4.28-4.31 (2H, d, J = 6 Hz), 6.91 (2H, s), 6.96-7.00 (4H, m), 7.02 (1H, s) 7.03 (1H, s), 7.08 (1H, s), 7.12 (1H, s), 8.01 (1H,s). The * indicates trace amounts of methylene chloride.

M17 characterization



Figure S4: ¹HNMR (CDCl₃) of M17: δ 0.89-0.93 (54H, m), 1.25-1.70 (137H, m), 2.60-2.63 (4H, t, J = 8 Hz), 2.74-2.82 (28H, m), 4.38-4.39 (2H, d, J = 7 Hz), 6.90 (2H, s), 6.90-7.01 (12H, m), 7.03 (1H, s) 7.04 (1H, s), 7.09 (1H, s), 7.13 (1H, s), 8.01 (1H,s).

Calculations

Supplemental Table 1: Bond lengths of the M5 oligomer. T5 and TT5 oligomers are also shown for comparison. The geometry was optimized using the AM1 method.

bond nun	T5		TT5		M5	
	ground	excited	ground	excited (Å)	ground	excited (Å)
	(Å)	(Å)	(Å)		(Å)	
1	1.3833	1.3869	1.3794	1.3817	1.3835	1.3849
2	1.4294	1.4229	1.4578	1.4554	1.4294	1.4265
3	1.3878	1.3973	1.3936	1.4054	1.388	1.3924
4	1.423	1.4056	1.4168	1.394	1.4228	1.4144

5	1.3951	1.4212	1.392	1.4096	1.3957	1.4091
6	1.4239	1.3906	1.4516	1.4389	1.4233	1.4049
7	1.389	1.4295	1.3959	1.4264	1.3898	1.4121
8	1.4236	1.37	1.4157	1.365	1.4206	1.3873
9	1.3946	1.4491	1.3933	1.4285	1.3893	1.4139
10	1.4325	1.3782	1.4516	1.4314	1.4538	1.439
11	1.3936	1.4488	1.3962	1.4278	1.3924	1.4316
12	1.4246	1.3706	1.4155	1.3663	1.4219	1.3638
13	1.3902	1.4288	1.3938	1.4229	1.3886	1.4422
14	1.4236	1.3912	1.4512	1.4377	1.427	1.3875
15	1.3949	1.4206	1.3967	1.4109	1.3921	1.4162
16	1.423	1.4062	1.4164	1.3953	1.4257	1.402
17	1.3872	1.3963	1.3931	1.4018	1.3902	1.4049
18	1.4303	1.424	1.4568	1.4542	1.4291	1.424
19	1.3823	1.3857	1.3839	1.3846	1.3825	1.3803

Frontier molecular orbital levels of M series and related compounds

The frontier molecular orbitals of the thiophene and thienothiophene oligomers are shown for comparison. These orbitals were investigated mainly 1) to compare the localization of the LUMO level in the M series to its homocyclic counterparts, namely thiophene oligomers and thienothiophene oligomers and 2) to compare the LUMO+1 levels of the M series molecules. The ZINDO/S calculations show the $S_0 \rightarrow S_1$ transition has nearly 100% HOMO \rightarrow LUMO character while the $S_0 \rightarrow S_2$ transition has nearly 100% HOMO \rightarrow LUMO+1 character. For the homo 17-mers of thiophene or thienothiophene, the molecular orbitals have electron density extend over the entire backbone of the fragment. It is interesting to note that the thienothiophene oligomer shows an asymmetry in the HOMO and LUMO orbitals, which is typically attributed to a charge transfer process in a donor-acceptor pair. It has been shown previously that similar homocyclic compounds can have donor-acceptor character.² For the M series molecules, the smaller oligomers show a very asymmetric LUMO+1 orbital state. For longer oligomers, the LUMO+1 more closely resemble that of corresponding thiophene oligomers. This could be due to the fact that the LUMO and LUMO+1 levels of the longer thiophene oligomer chains are lower in energy. If the longer thiophene chain becomes similar in energy with the thienothiophene ring unit, then there can be a competing process for the electron distribution in this molecular orbital. More work will be done to verify this claim.



Figure S5: Molecular structure, HOMO (green and blue), LUMO (red and yellow), and LUMO+1 (violet and black) orbitals of M series oligomers



Figure S6: Molecular structure, HOMO (green and blue), LUMO (red and yellow),

and LUMO+1 (violet and balck) orbitals of the thiophene pentamer



Figure S6: Molecular structure, HOMO (green and blue), LUMO (red and yellow), and LUMO+1 (violet and black) orbitals of the 17 unit thiophene oligomer (left) and thienothiophene oligomer (right). The orbitals extend through the entire backbone chain of these molecules.

AM1 geometric analysis of the ground and excited states

The geometries of the ground and excited states were also investigated. The electronic and structural natures of the oligomers are closely related. The nature of the excited state, particularly the relaxation of the excited state, typically has a significant effect on the molecular excitonic coupling.³ It has been reported previously that the lower energy gap oligomers are typically more rigid and planar due to the more quinoidal character of the ground state.⁴ Since the quinoidal contribution to the ground state is relatively small for these molecules, it would be interesting to investigate the structural characteristics of this molecule and how they compare to their oligothiophene counterparts. For this analysis, only the bond lengths are discussed as a means to

measure the degree of bond alternation change due to the TT moiety. The bond alternation has been used previously in many reports as a means to determine the character of the quinoidal and aromatic character of the conjugated systems.^{5,6} The bond lengths along the oligomer backbone in the ground and the excited states were calculated. These calculations are based on the assumption that the oligomers are more aromatic in the ground state. This assumption is supported by both previous reported theoretical calculation results on the TT oligomers and polymers⁷ and our experimental results. The thiophene rings further stabilize the aromatic structure of the material compared to the TT oligomers.

The geometry of the M5 molecule with labeled bond positions is shown in Figure S7a. The long alkyl chains were left off for simplicity in this figure. The molecule was also calculated with the hexane and ester side groups, and no significant change in the bond length was observed. The conjugated bond lengths are shown in Table S1. The bond length shows a bond alternation pattern typical of heterocyclic conjugated molecules. This molecule was compared to the thiophene (T) and thienothiophene (TT) pentamers. The change in the conjugated bond lengths between the thiophene and thienothiophene rings varies by less than 0.01 Å, which is not significant. The aromaticity is related to the bond alternation in the oligomer and was found by using the relationship⁶

$$\delta \mathbf{r}_{i} = 0.5(\mathbf{C}_{2i+1} + \mathbf{C}_{2i-1} - 2^{*}(\mathbf{C}_{2i})) \tag{1}$$

where δr_i is the aromaticity, C is the bond length and i is the bond number. For aromatic compounds, this number is negative while δr_i is positive for quinoidal structures. This

relation finds the bond differences for every other bond. An aromatic or quinoidal molecule will have an alternating bond sequence along the backbone chain, but this number should remain relatively constant for a uniform backbone chain. For the odd values of i, the bond alternation measures the bond change within the ring while the even values of i measure the bond alternation between the rings. As the aromatic nature of the molecules increases, this number becomes more negative. The relationship of δr_i versus bond site is shown in Figure S7b for M5, the thiophene pentamer (T5), and the thienothiophene pentamer (TT5). In comparing the T5 and TT5 molecules, it is observed that the aromaticity varies much more in the TT5 molecule, but the average aromaticity does not decrease. The bond lengths between the rings are shorter for the TT5 molecule, but the bond alternation is increased within the thiophene rings. This behavior is more indicative of a donor-acceptor material. It should be noted that donor-acceptor materials also show an increased electron density between the rings, which increases the rigidity of the molecule and creates a more quinoidal state. However, inside the thiophene rings, the TT5 molecule has a less quinoidal character. The M5 molecule shows a slight difference around the center of the ring, but the bond length differences are not observed for the entire molecule.



Figure S7. a) The structure of the M5 oligomer with labeled bond numbers used for bond alternation determinations. b) Aromaticity of the M5 oligomer as a function of bond length. The homocyclic analogs, T5 and TT5, are also shown for comparison purposes.

The structural differences between M5 are more noticeable in the excited state compared to the ground state. The bond distances for the excited state for the M5 molecule labeled in Figure S7a are also shown in Table S1. The "bond perturbation," or the difference in the bond length between the excited and ground states, for M5, T5, and TT5 are shown in Figure S8a. Although the TT5 molecule does show a smaller bond difference between the ground and excited states, it appears as though the M5 molecule shows the smallest bond changes on one side of the molecule while the other side has

remarkably similar bond changes compared to T5. This asymmetry is not fully understood, but it most likely comes from the asymmetry of the fused thiophene ring. The geometry dependencies indicate the effect of the lower bandgap is due mainly to the structural and electronic changes in the excited state. As a consequence, the quinoidal character for the M5 molecule is decreased in the excited state compared to the T5 molecule, which means the excited states structural differences for M5 are smaller compared to T5. This relationship is shown in Figure S8b.



Figure S8. Change in bond length in the excited state of M5, T5, and TT5 b) Aromaticity of M5, T5, and TT5 in the excited state.

TT substituent groups

The effect of the substituent group on the TT ring was also investigated. The unsubstituted TT ring was not studied in these experiments. It has been reported previously that the unsubstituted TT polymer is not ideal for solar cell applications because the HOMO level is too high compared to the PCBM acceptor levels for efficient charge separation.⁸ By adding the COOR group, the HOMO level is sufficiently lowered to effectively promote charge separation.⁹ It has also been discovered that adding a fluorinated group further facilitates the synthesis of well-characterized polymer species by lowering reactivity of the protons in the thiophene rings neighboring the thienothiophene unit.¹ These additional side groups also affect the donor character, electron spacing levels, and structure. For instance, the absorption and fluorescence spectra of PF and MF, which are the fluorinated form of M17 and its polymer, have been reported previously. The S1 peak maximum for PF and MF is 2.37 eV (523 nm) while the S1 peak maximum for M17 is 2.32 eV (535 nm). It is assumed that the fluorinated side group slightly lowers the electron withdrawing character of the fused ring, which facilitates regioregular polymerization of this oligomer species.¹ Although the ester and the fluorinated alkane groups both withdraw electron density from the fused ring, the COOR group could enhance the conjugated character of the unit, which will increase the acceptor nature of the TT unit. The calculated optical bandgap, HOMO and LUMO energy levels of M3 with different substitute groups, -COOR, -CF₃, -CH₃ and -H are shown in Table 2. The experimental

results are mimicked in these calculations. The COOR group shows the smallest optical bandgap.

Supplemaental Table 2. Substituent dependence of the HOMO and LUMO energetic

levels.

group	E _{opt} (eV)	HOMO (eV)	LUMO (eV)
-COOR	2.70	-6.658	-1.254
-CF3	2.82	-6.677	-1.054
-CH3	2.86	-6.386	-0.701
-H	2.86	-6.453	-0.765

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