Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Electronic and Structural Properties of Fluorene-Thiophene Copolymers as Function of the Composition Ratio Between the Moieties: A Theoretical Study.

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1. Model Structures and Computational Methods

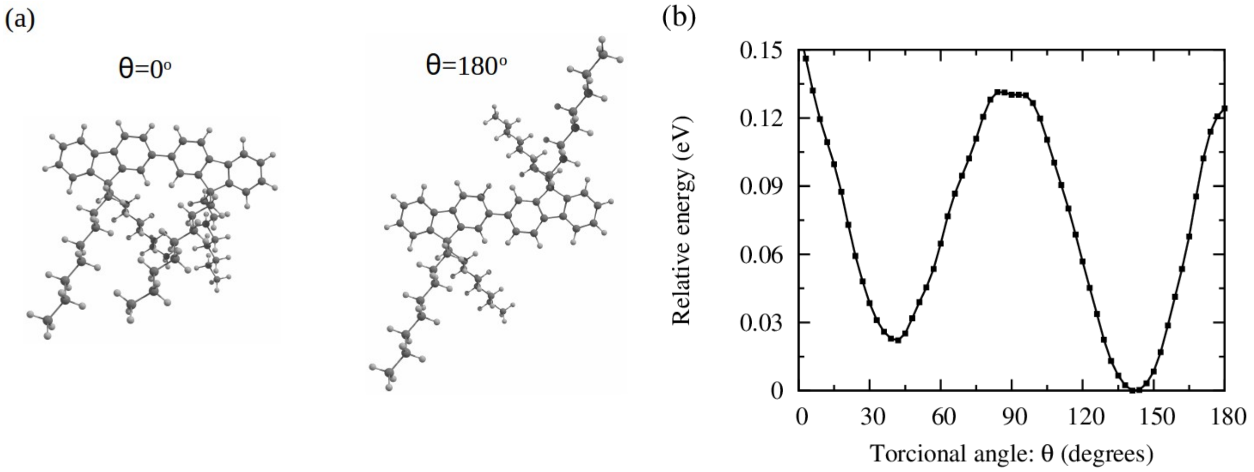

Figure S1 - (a) Structure of the two dioctilfluorenes used to calculate the torsional potential curve in $\theta=0^o$ and $\theta=180^o$. (b) Rigid torsional potential energy profiles (B3LYP/6-31G**).

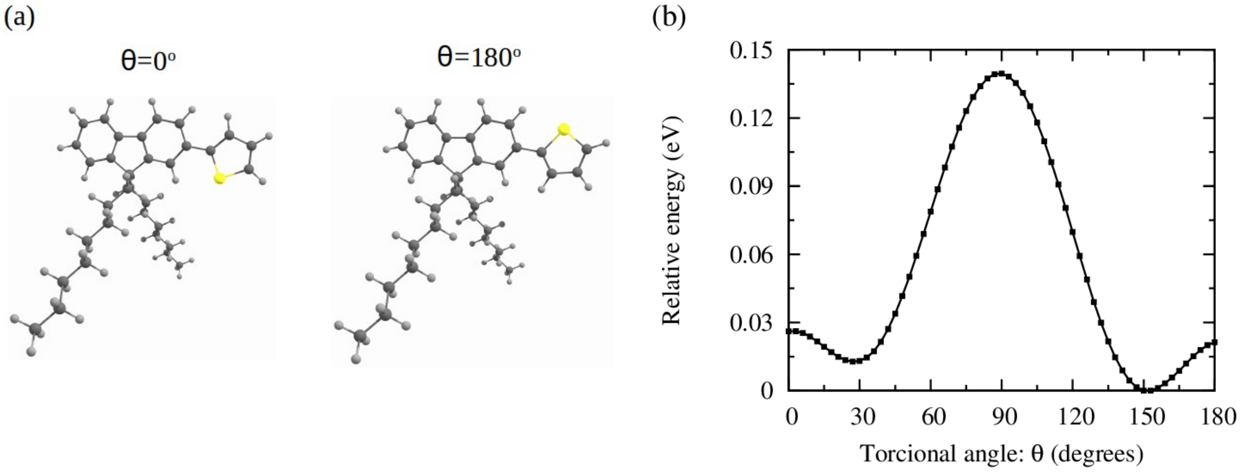

Figure S2 - (a) Structure of the dioctilfluorene and thiophene used to calculate the torsional potential curve in $\theta=0^o$ and $\theta=180^o$. (b) Rigid torsional potential energy profiles (B3LYP/6-31G**).

Table S1 – Maximum absorption wavelength (λ_{max}) for different functionals (B3LYP[1], M06[2], PBE1PBE[3], CAM-B3LYP[4] and LC-wPBE[5]) and basis sets and experimental data extracted of Saeki et al.[6] for (1,2)-*anti* copolymer in chloroform. Theoretical values of λ_{max} are the main electronic transition of TD-DFT calculation for a two mer copolymer. λ_d is the wavelength difference between the simulated and the experimental result.

Copolymer	Method	λ_{max} (nm)	λ_d (nm)
(1,2)-*anti*	UV-vis absorption	460	
	B3LYP/cc-pVDZ	472	12
	B3LYP/6-31+G**	479	19
	B3LYP/6-311G**	476	16
	B3LYP/6-31G**	470	10
	B3LYP/6-31G*	469	9
	B3LYP/3-21G*	452	-8
	M06/6-31G**	453	-7
	PBE1PBE/6-31G**	449	-11
	CAM-B3LYP/6-31G**	391	-69
	LC-wPBE/6-31G**	350	-110

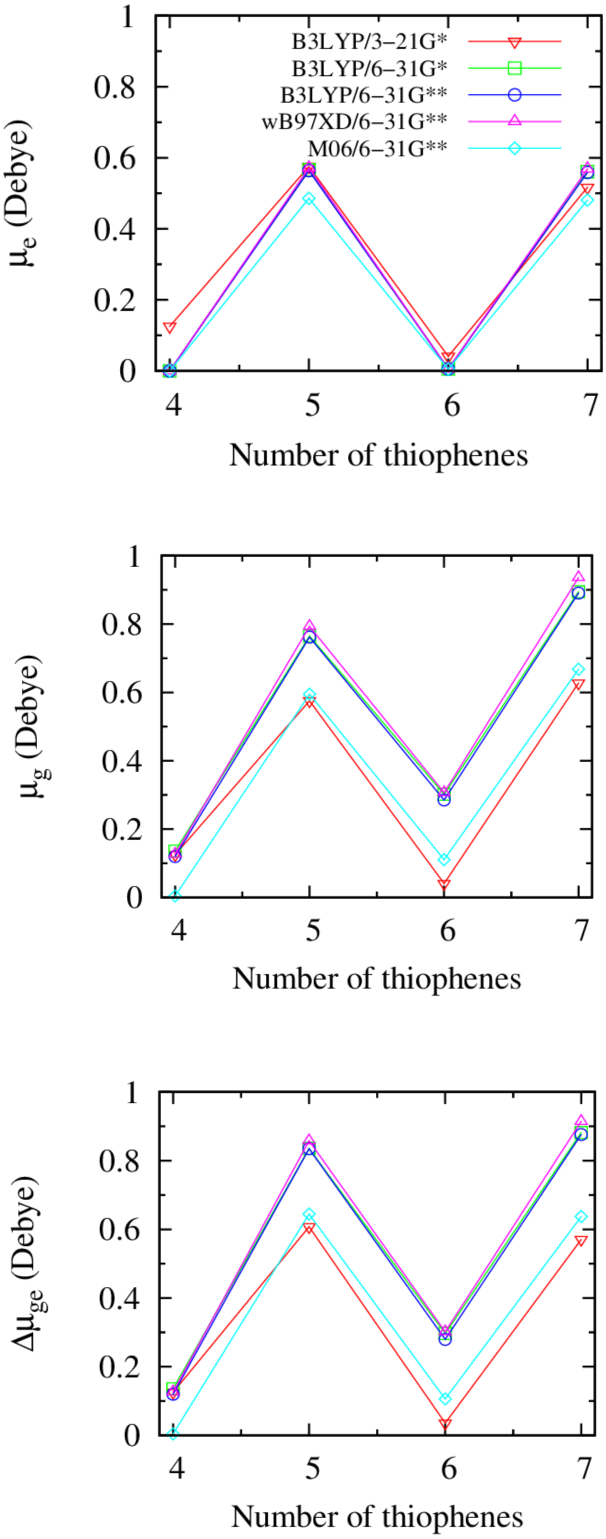

Figure S3 – The magnitude of (a) μ_e, (b) μ_g and (c) $\Delta\mu_{ge}$ with increasing number of thiophene in the dimetylfluorene-(4-7)thiophene-dimetylfluorene molecule for different functionals (B3LYP[1], wB97XD[7] and M06[2]) and basis sets.

2. F-(T)$_n$-F Molecules

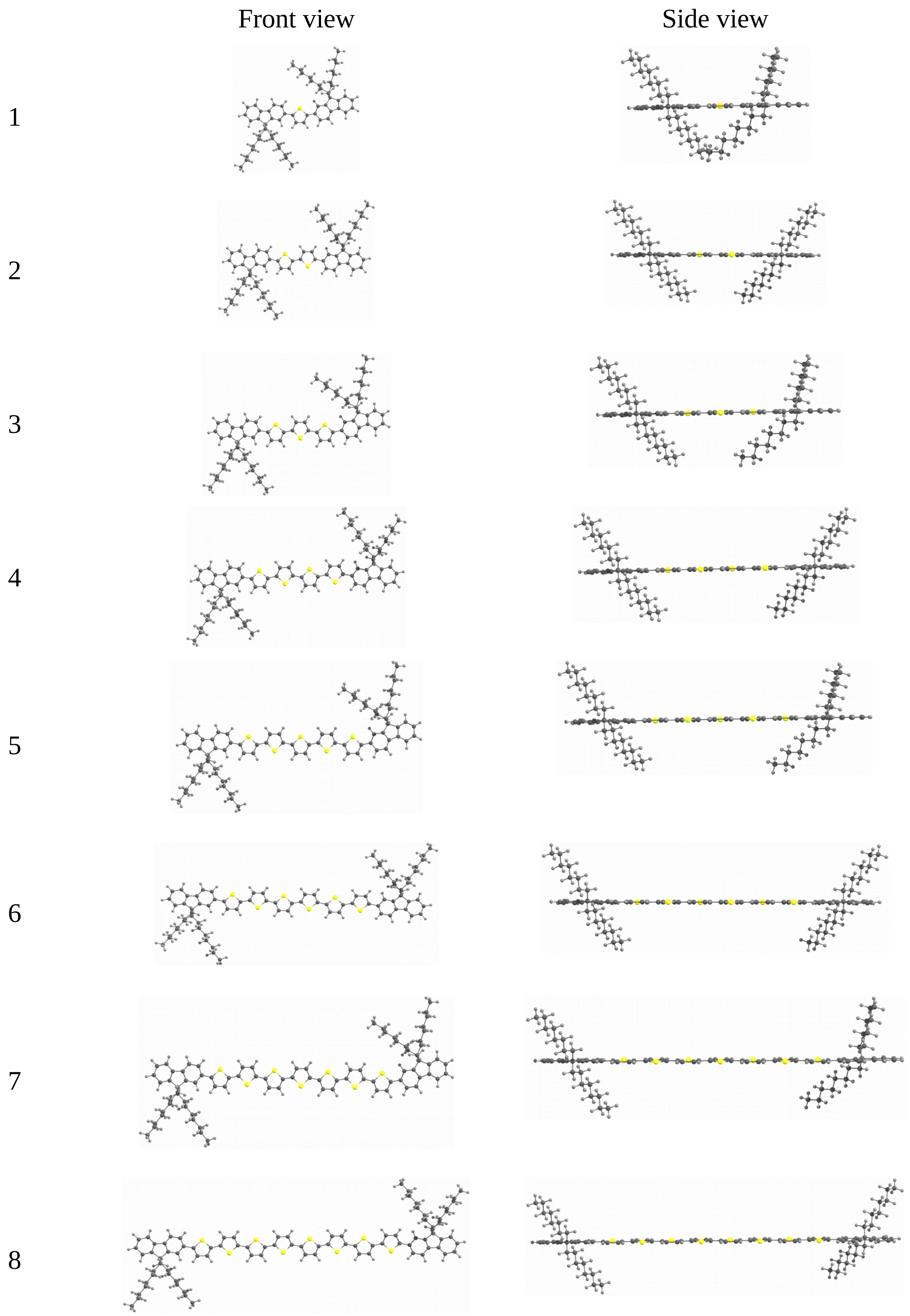

Figure S4 - Excited state optimized geometry of F-(T)$_n$-F molecules (TD-PM3 optimization).

Table S2 - The calculation results of dipole moment of F-(T)$_n$-F molecules. B3LYP/6-31G* calculation.

Number of thiophenes	$\boldsymbol{\mu}_g$ (xyz)	μ_g	$\boldsymbol{\mu}_e$ (xyz)	μ_e	$\Delta\mu_{ge}$	Angle
1	0.4771 0.3513 0.1911	0.6226	0.6094 0.0269 0.2881	0.6746	0.3635	32.2318
2	-0.0574 0.1823 -0.0468	0.1967	0.0004 0.0228 -0.0004	0.0228	0.1758	22.2963
3	0.2979 0.4788 -0.3675	0.6731	0.5253 0.0067 -0.3694	0.6422	0.5240	46.8835
4	-0.0137 0.0440 -0.0173	0.0492	-0.0001 0.0070 -0.0002	0.0070	0.0429	24.8472
5	0.1401 0.7310 0.2130	0.7742	0.5999 0.0343 0.2185	0.6393	0.8347	71.6712
6	-0.0485 0.0828 -0.0003	0.0959	-0.0001 0.0023 -0.0002	0.0024	0.0939	28.2417
7	-0.2502 -0.8260 0.1747	0.8806	-0.2979 -0.0012 0.5646	0.6384	0.9135	71.9514
8	0.0284 -0.1966 -0.0756	0.2126	0.0004 -0.0057 -0.0004	0.0057	0.2070	17.3216

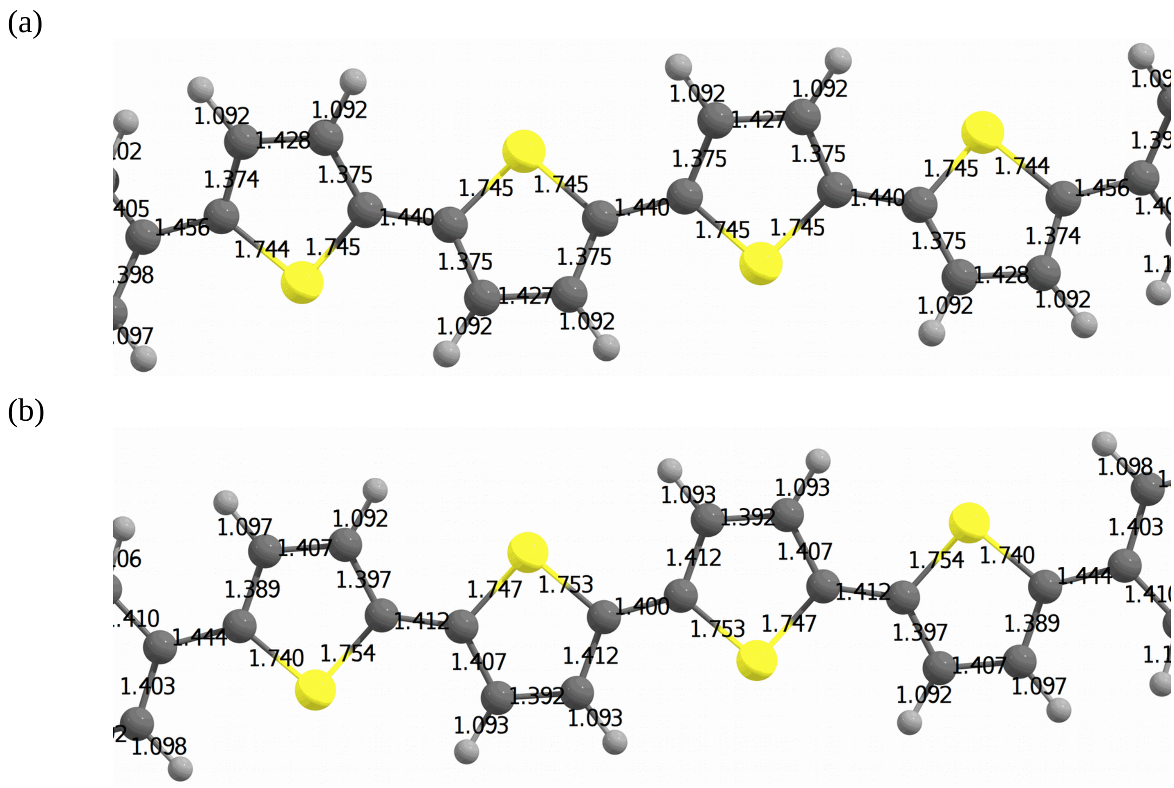

Figure S5 - Bond lengths of thiophenes for dioctylfluorene-(4)thiophene-dioctylfluorene molecule in (a) ground state and (b) excited state.

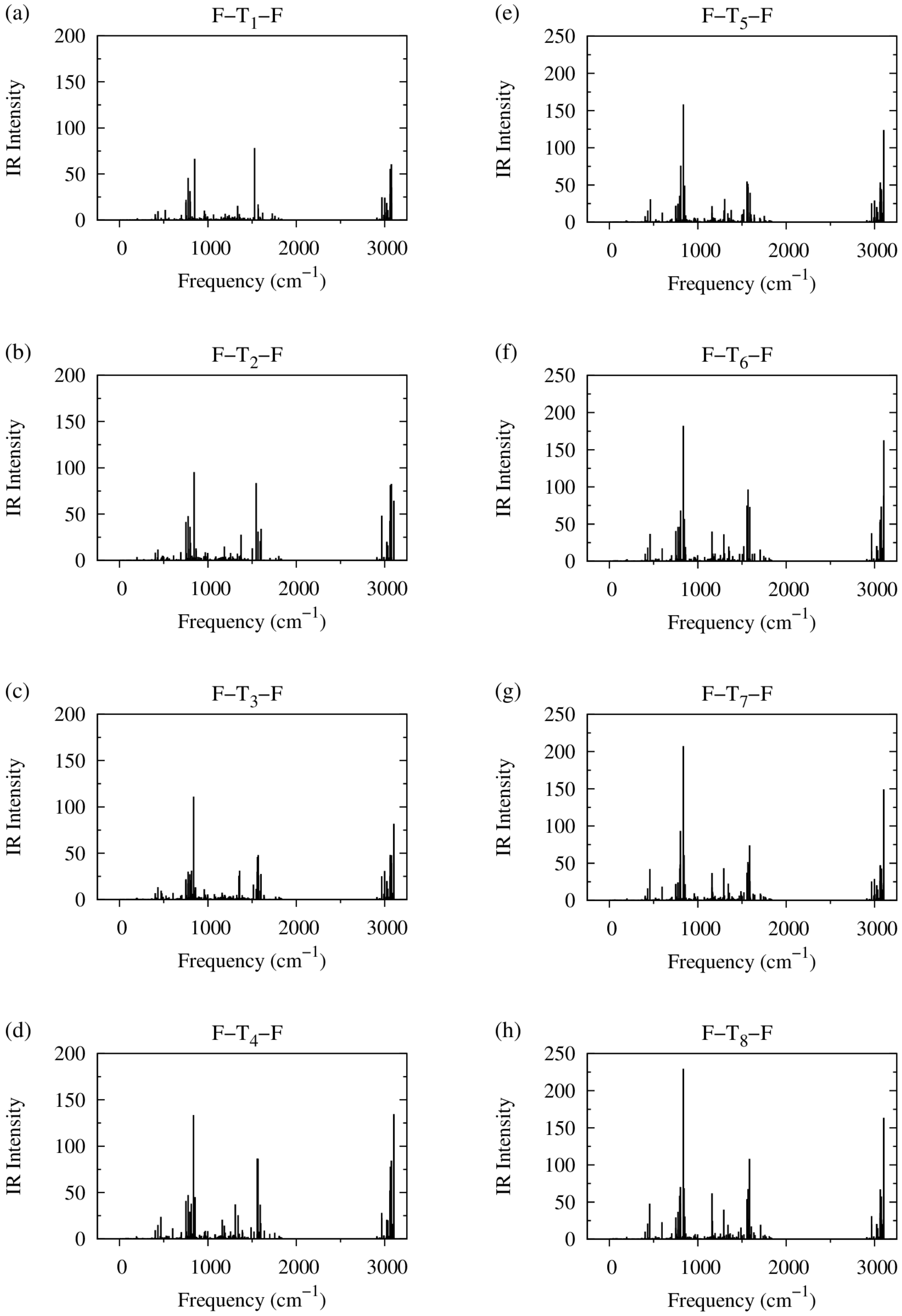

Figure S6 - Frequency analysis for F-T$_n$-F molecules in geometry of first excited state (a) F-T$_1$-F, (b) F-T$_2$-F, (c) F-T$_3$-F, (d) F-T$_4$-F, (e) F-T$_5$-F, (f) F-T$_6$-F, (g) F-T$_7$-F and (h) F-T$_8$-F. PM3 calculation.

3. F-(T2)$_n$-F Molecules

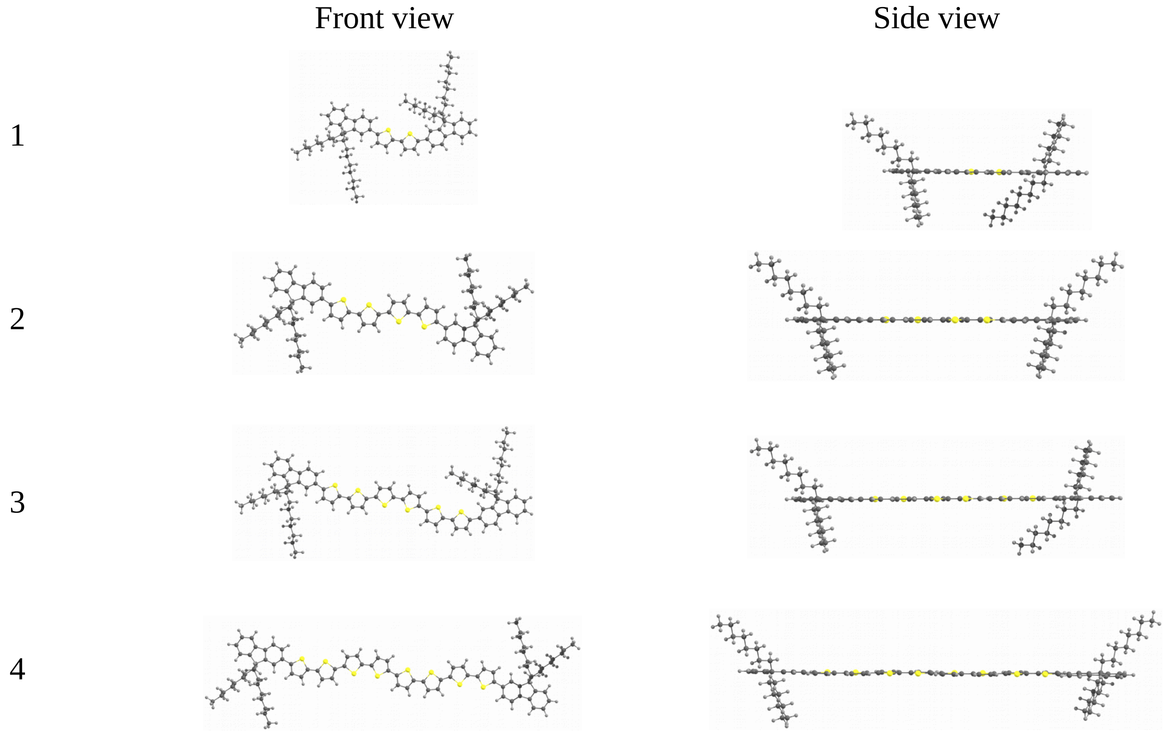

Figure S7 - Excited state optimized geometry of F-(T2)$_n$-F molecules (TD-PM3 optimization).

Table S3 - The calculation results of dipole moment of F-(T2)$_n$-F molecules. B3LYP/6-31G* calculation.

Number of bithiophenes	$\boldsymbol{\mu}_g$ (xyz)	μ_g	$\boldsymbol{\mu}_e$ (xyz)	μ_e	$\Delta\mu_{ge}$	Angle
1	-0.8470 -0.7355 0.3961	1.1896	-1.2205 0.0067 0.1360	1.2281	0.8706	42.1762
2	0.1324 -0.4422 0.1173	0.4763	0.0005 -0.0114 0.0000	0.0114	0.4655	19.9886
3	-0.0206 0.7921 0.8825	1.1860	0.5943 -0.0623 1.0038	1.1682	1.0596	53.4934
4	0.1593 -0.5028 0.1509	0.5486	0.0002 -0.0049 0.0003	0.0049	0.5439	19.4952

4. F-(T)$_n$-F Molecules changing octyl to metyl

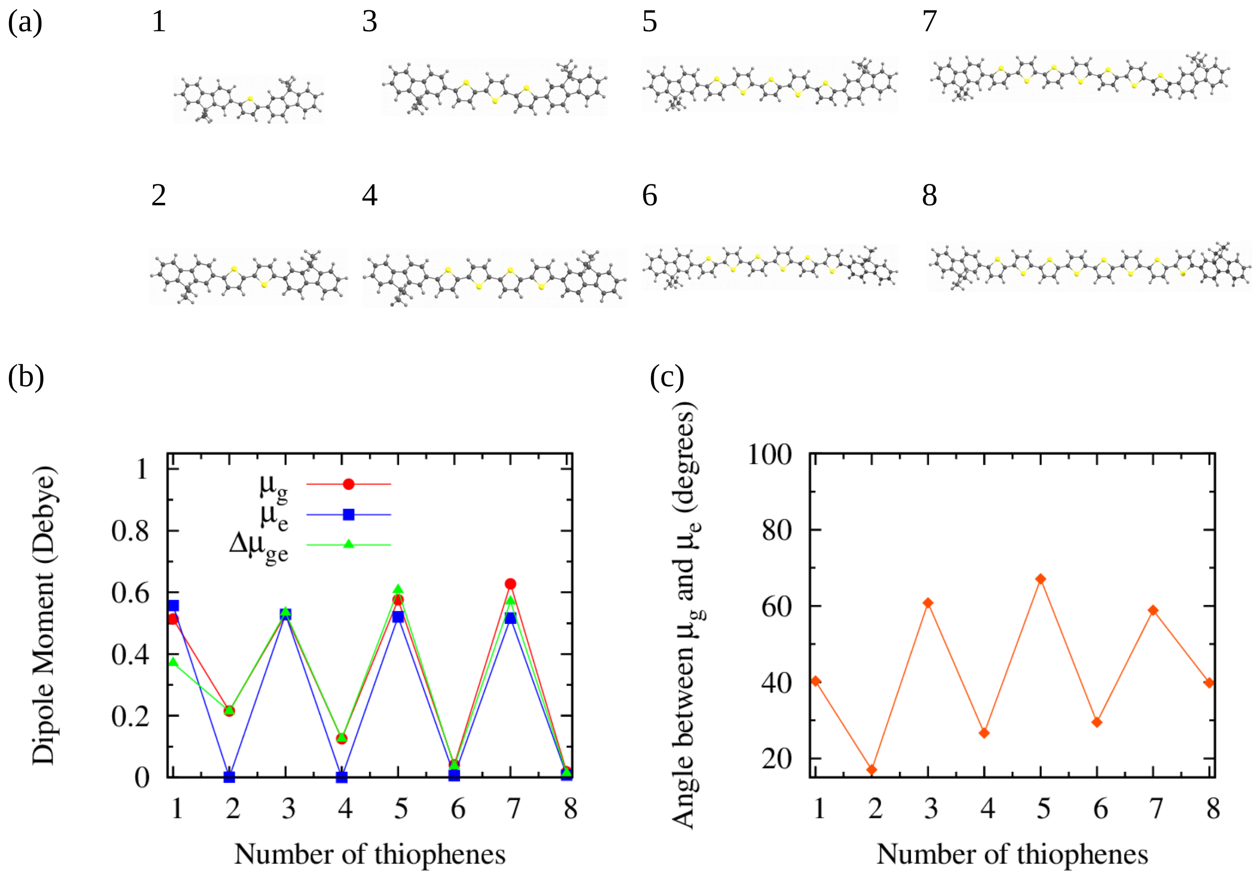

Figure S8 – (a) Ground state geometry of molecules containing dimetylfluorene-(1-8)thiophene-dimetylfluorene. (b) The magnitude of μ_g, μ_e, $\Delta\mu_{ge}$ with increasing number of bithiophene groups in the molecule, and (c) the angular change between the vectors μ_e and μ_g with the number of thiophene groups in the molecule. B3LYP/3-21G* calculation.

Table S4 - The calculation results of dipole moment of dimetylfluorene-(1-8)thiophene(anti)-dimetylfluorene molecules.

Trimers	$\boldsymbol{\mu}_g$ (xyz)	μ_g	$\boldsymbol{\mu}_e$ (xyz)	μ_e	$\Delta\mu_{ge}$	Angle
1	-0.4459 0.2545 0.0022	0.5134	-0.4909 0.0003 -0.2640	0.5574	0.3708	40.2591
2	-0.0645 0.1985 -0.0519	0.2151	-0.0001 0.0007 0.0000	0.0007	0.2143	17.0437
3	0.2415 0.4343 0.1769	0.5274	0.5260 -0.0004 0.0512	0.5285	0.5345	60.8201
4	0.0554 -0.1122 0.0101	0.1255	0.0000 -0.0001 0.0000	0.0001	0.1255	26.6521
5	0.1252 0.5182 0.2168	0.5756	0.4381 0.0012 0.2811	0.5206	0.6077	67.1321
6	-0.0105 0.0348 -0.0183	0.0407	0.0000 -0.0056 -0.0002	0.0056	0.0359	29.4691
7	0.0587 -0.5222 0.3423	0.6272	0.2726 -0.0021 0.4388	0.5166	0.5705	58.909
8	0.0036 -0.0132 0.0107	0.0174	0.0000 -0.0075 0.0001	0.0075	0.0127	39.8155

Table S5 – Gas phase calculations for dimetylfluorene-(4-8)thiophene(anti)-dimetylfluorene molecules of vertical ionization potential (IP), vertical electron affinity (EA), optical gap (E_{opt}) and biding energy (E_b) with wB97XD/6-31+G** for geometry optimization of the ground state and single point calculations of cation and anion.

F-(T)$_n$-F	IP	EA	E_{opt}	E_b
n=4	6.6706	0.7245	3.2583	2.6879
n=5	6.6451	0.8100	3.1701	2.6650
n=6	6.6634	0.8267	3.1571	2.6796
n=7	6.6416	0.8900	3.0842	2.6674
n=8	6.6478	0.8989	3.0713	2.6776

Table S6 – The average of the dihedral angles between the chemical groups of dimetylfluorene-(4-8)thiophene(anti)-dimetylfluorene molecules in ground state geometry (wB97XD/6-31+G** calculation).

Pair of chemical moiety	Dihedral angle				
	n=4	n=5	n=6	n=7	n=8
1-2	35.026	33.603	35.551	34.873	34.118
2-3	26.784	25.405	28.672	29.183	29.146
3-4	28.838	28.834	28.485	26.977	28.719
4-5	25.272	25.223	29.310	28.626	28.867
5-6	35.571	28.811	29.148	26.484	28.683
6-7		35.824	31.819	28.845	28.879
7-8			32.250	27.035	28.769
8-9				34.239	29.052
9-10					34.474
Mean	30.298	29.617	30.695	29.521	30.130

Table S7 - The calculation results of the angle (θ) between the ground state dipole moment (**μ_g**) and transition dipole moment (**μ_{ex}** between HOMO → LUMO states) of dimetylfluorene-(4-8)thiophene(anti)-dimetylfluorene molecules (wB97XD/6-31+G** calculation). Also the result of cos(180^o - θ^o).

F-(T)$_n$-F	θ^o	cos(180^o - θ^o)
n=4	93.56	0.062
n=5	77.01	-0.225
n=6	91.17	0.020
n=7	82.90	-0.124
n=8	90.07	0.001

Table S8 – Gas phase calculations for dimetylfluorene-(4-8)thiophene(anti)-dimetylfluorene molecules of vertical ionization potential (IP), vertical electron affinity (EA), optical gap (E_{opt}) and biding energy (E_b) with wB97XD/6-31G** for geometry optimization of the ground state and single point calculations of cation and anion.

$F\text{-}(T)_n\text{-}F$	IP	EA	E_{opt}	E_b
n=4	6.4944	0.4720	3.2931	2.7293
n=5	6.4723	0.5612	3.2043	2.7068
n=6	6.4869	0.5897	3.1714	2.7258
n=7	6.4565	0.6702	3.0923	2.6940
n=8	6.4710	0.6812	3.0749	2.7149

Table S9 – The average of the dihedral angles between the chemical groups of dimetylfluorene-(4-8)thiophene(anti)-dimetylfluorene molecules in ground state geometry (wB97XD/6-31G** calculation).

Pair of chemical moiety	Dihedral angle				
	n=4	n=5	n=6	n=7	n=8
1-2	30.362	33.361	32.239	32.785	32.181
2-3	28.081	21.463	28.466	29.782	27.938
3-4	26.480	30.825	24.067	22.542	25.929
4-5	26.182	20.830	29.585	28.123	28.464
5-6	33.406	28.594	25.927	21.480	25.897
6-7		31.318	29.423	29.235	27.832
7-8			33.114	22.029	22.887
8-9				34.717	28.614
9-10					32.204
Mean	28.902	27.732	28.974	27.587	27.994

5. F-(T2)$_n$-F Molecules changing octyl to metyl

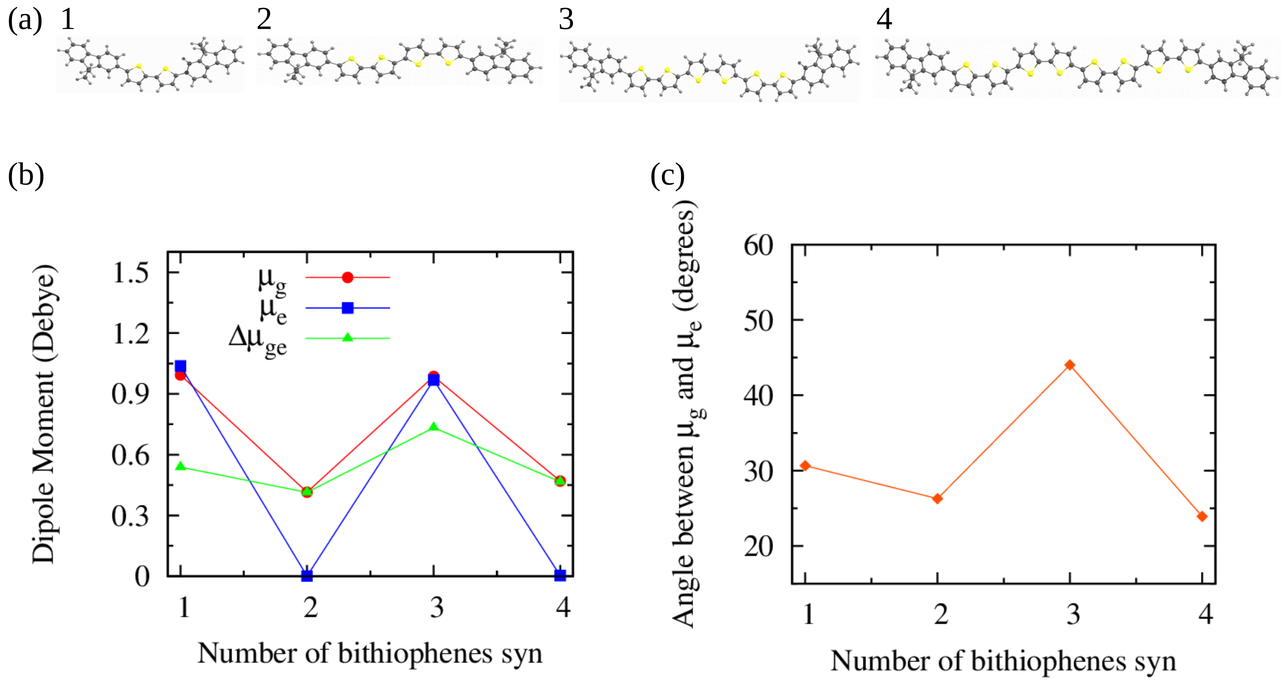

Figure S9 – (a) Ground state geometry of molecules containing dimetylfluorene-(1-4)bithiophene (syn)-dimetylfluorene. (b) The magnitude of μ_g, μ_e, $\Delta\mu_{ge}$ with increasing number of thiophene rings in the molecule, and (c) the angular change between the vectors μ_e and μ_g with the number of thiophene in the molecule. B3LYP/3-21G* calculation.

Table S10 - The calculation results of dipole moment of dimetylfluorene-(1-3)bithiophene (syn)-dimetylfluorene molecules.

Trimers	$\boldsymbol{\mu}_g$ (xyz)	μ_g	$\boldsymbol{\mu}_e$ (xyz)	μ_e	$\Delta\mu_{ge}$	Angle
F-2T-F	-0.8869 0.0683 -0.4425	0.9935	-1.0353 0.0003 0.0710	1.0377	0.5388	30.6668
F-4T-F	-0.1459 0.3840 -0.0578	0.4149	0.0000 0.0007 0.0001	0.0007	0.4141	26.2759
F-6T-F	0.0247 0.6544 0.7373	0.9861	0.2995 0.0002 0.9212	0.9687	0.7330	44.0352
F-8T-F	-0.1791 0.4294 -0.0649	0.4698	0.0000 -0.0037 0.0000	0.0037	0.4663	23.9237

6. Results for α4T and α5T

Table S11 - Theoretical values – TDDFT calculations with B3LYP/6-31G* – of the HOMO energy and λ_{max} for α4T and α5T molecules compared to experimental data[8].

Molecules	HOMO (eV)		λ_{max} (nm)	
	Calculated	Observed	Calculated	Observed
α4T	-5.15	-5.79[a]	383	391[c]
α5T	-5.05	-5.85[b]	415	418[c]

[a] Estimated using the optical gap. [b] From electrochemical data: $E_g^{CV} = E_1^{1/2}$ (Ox) – $E_1^{1/2}$ (Red). [c] In THF solution.

Table S12 - The calculation results of $\Delta\mu_{ge}$ and E_b for α4T and α5T with the same procedure performed for F-(T)$_n$-F molecules.

Molecules	$\Delta\mu_{ge}$	E_b
α4T	0.2098	2.9863
α5T	0.6863	2.8449

Table S13 – Computed geometric parameters of α4T and α5T molecules.

Molecules	Length (Å)[a,b,c]	
	Core	Maximum
α4T	17.51 (17.48, 17.55)	18.62 (18.17)
α5T	21.28	22.30

[a] Core length refers to the maximum distance from ring carbon to ring carbon atom along the thiophene core, while the maximum length is the greatest extent of the molecule, including hydrogens. Both lengths include standard van der Waals radii for carbon (1.70Å) and hydrogen atoms (1.20Å). [b] Theoretical results with PM3 optimization. [c] Numbers in parentheses indicate experimental values from X-ray crystal structures[8].

7. Copolymers

Table S14 - The average of the dihedral angles between the chemical groups of F8T2 (1,2), (1,3), (2,2), (2,3), (3,2) and (3,3) for the *anti* and *syn* conformation. The pair of chemical moiety follows the sequence from left to right for the copolymers of Figure 6.

Pair of chemical moiety	Dihedral angle											
	(1,2)		(1,3)		(2,2)		(2,3)		(3,2)		(3,3)	
	syn	*anti*	*syn*	*anti*	*syn*	*anti*	*syn*	*anti*	*syn*	*anti*	*syn*	*anti*
1-2	36.80	37.06	36.55	37.07	46.82	47.41	46.77	47.35	46.82	46.78	46.77	47.38
2-3	29.61	32.93	29.67	32.89	36.53	37.01	36.49	36.95	47.40	47.35	47.36	46.79
3-4	32.65	33.50	32.81	33.01	29.71	33.17	29.67	32.78	36.76	36.96	36.51	37.09
4-5	29.66	33.00	29.71	32.11	32.77	33.41	32.57	32.67	29.66	32.88	29.66	32.52
5-6	36.75	37.08	33.27	33.07	29.71	33.26	29.68	31.97	32.48	33.21	32.73	32.91
6-7	36.50	36.85	29.61	32.94	36.54	37.01	33.04	32.68	29.68	32.93	29.72	31.77
7-8	29.80	32.96	38.15	37.03	46.84	47.44	29.61	32.89	36.76	36.95	31.01	32.90
8-9	32.56	33.38	36.69	36.83	36.52	36.98	38.07	36.95	47.41	47.36	29.82	32.58
9-10	30.07	35.44	29.67	32.79	29.73	33.30	46.77	47.39	46.84	46.80	38.22	36.40
10-11			32.89	32.98	32.55	33.37	36.48	36.94	36.05	36.79	47.34	46.90
11-12			29.73	32.24	30.05	35.53	29.66	32.85	29.79	32.81	46.79	47.38
12-13			32.71	32.24			32.64	32.60	32.69	33.09	36.48	36.98
13-14			30.02	35.45			29.70	32.05	30.09	35.23	29.68	32.87
14-15							32.44	32.70			32.62	32.66
15-16							30.01	35.19			29.70	32.07
16-17											32.45	32.73
17-18											30.02	35.23
Mean	32.71	34.69	32.42	33.90	35.25	37.08	34.24	35.60	37.11	38.40	35.70	36.90

Table S15 - The calculation results of dipole moment of (1,2), (1,3), (2,2), (2,3), (3,2) and (3,3) copolymers for the *anti* and *syn* conformation. B3LYP/6-31G* calculation.

Structures		$\boldsymbol{\mu}_g$ (xyz)	μ_g	$\boldsymbol{\mu}_e$ (xyz)	μ_e	$\Delta\mu_{ge}$
$(1,2)_2$	*syn*	-0.4932	0.8187	-0.1106	0.8370	0.7874
		0.5315		0.0102		
		0.3803		0.8296		
	anti	-0.3482	0.6866	-0.2940	0.8806	0.2971
		-0.2948		-0.5738		
		0.5131		0.5998		
$(1,3)_2$	*syn*	-1.5338	1.7033	-1.7428	1.8614	0.9242
		-0.7107		0.0742		
		0.2085		0.6496		
	anti	-0.5243	0.9599	-0.3698	0.9857	0.3007
		0.8040		0.8835		
		0.0123		-0.2332		
$(2,2)_2$	*syn*	-0.6547	1.2948	-0.9816	1.2426	0.4853
		1.1128		0.7616		
		0.0972		0.0238		
	anti	-0.3159	0.3751	-0.6110	0.6491	0.3571
		-0.0570		-0.2098		
		0.1941		0.0633		
$(2,3)_2$	*syn*	0.2230	2.2870	-0.2489	2.5634	0.7601
		-1.0424		-0.6459		
		2.0234		2.4682		
	anti	-0.4483	0.5228	-0.5398	0.5628	0.3206
		-0.2042		0.0990		
		0.1750		0.1248		
$(3,2)_2$	*syn*	-0.4755	1.5181	-0.1674	1.1443	0.6534
		1.4369		1.0124		
		0.1169		0.5066		
	anti	0.1840	0.3032	-0.1917	0.5178	0.4570
		-0.2373		-0.4774		
		0.0422		-0.0582		
$(3,3)_2$	*syn*	-0.2053	2.4285	-0.2185	1.9830	1.4454
		1.5434		0.1018		
		-1.8637		-1.9683		
	anti	0.1549	0.8351	0.0286	0.4824	0.9862
		-0.6651		-0.2559		
		-0.4806		0.4078		

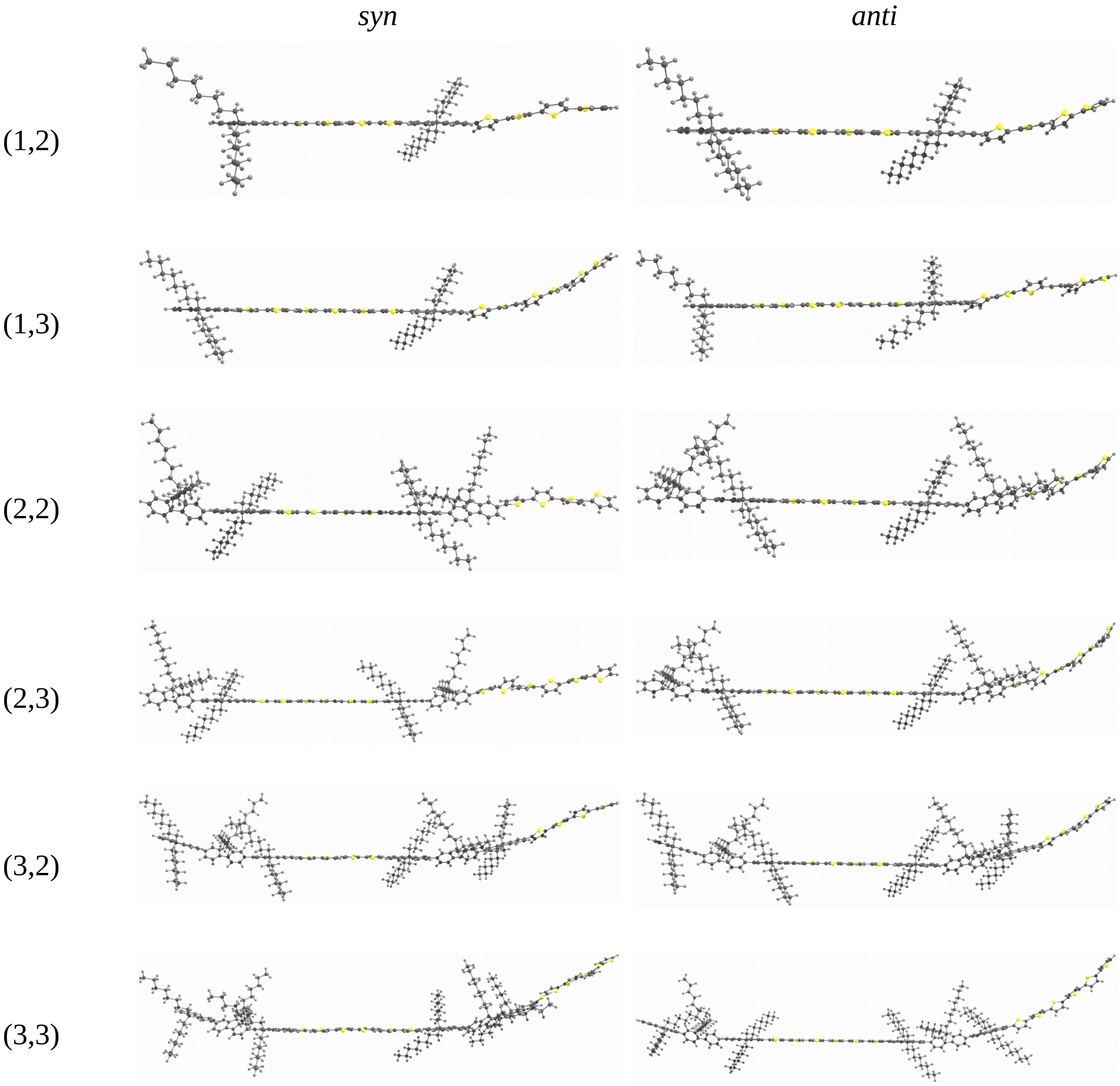

Figure S10 - Side view of excited state optimized geometry for the (1,2), (1,3), (2,2), (2,3), (3,2) and (3,3) copolymers for the *anti* and *syn* conformation (TD-PM3 optimization).

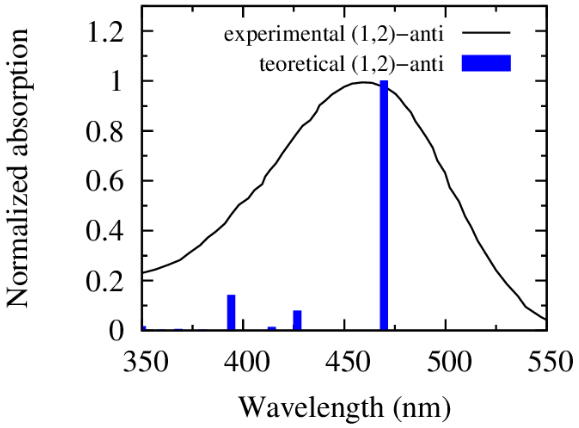

Figure S11 - Vertical electronic transitions of (1,2)-anti structure (solid blue bars) and experimental result (line) of light absorption obtained from Ref.[6] for (1,2)-anti structure in chloroform. The experimental data are for a 50% composition ratio of T units. B3LYP/6-31G* calculation.

Table S16 – Gas phase calculations for (1,2)-*syn* and (1,3)-*syn* with one mer of vertical ionization potential (IP), vertical electron affinity (EA), optical gap (E_{opt}) and biding energy (E_B) with wB97XD/6-31+G** for geometry optimization of the ground state and single point calculations of cation and anion.

Copolymer	IP	EA	E_{opt}	E_b
(1,2)-*syn*	6.855	0.544	3.496	2.815
(1,3)-*syn*	6.770	0.716	3.309	2.744

8. References

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