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Solvent Effects on Electronic Structures and Chain Conformations of α-Oligothiophenes

in Polar and Apolar Solutions

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3T; and (c) the central ($g_{mid}(r)$) and terminal ($g_{end}(r)$) ring of **9T,** respectively. The statistical error is ±0.05 Å.

Figure S8. Radial distribution functions: $g_{H...O}(r)$ for hydrogen (H in thiophene) to oxygen (O in water). The statistical error is ±0.05 Å.

Table S1. Various Charges near the Equilibrium Structures of Thiophene-water and Thiophene-carbon Tetrachloride Dimers
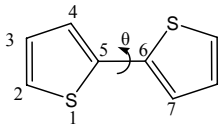
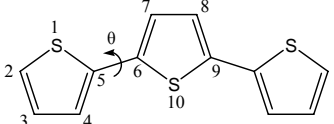|	PCFF	Mulliken	ESP
S…H-O interaction ($r_{S…H}$=2.4 Å)			
S1	0.0240	0.046088	0.085736
C2	-0.1388	-0.267338	-0.262202
C3	-0.1388	-0.267338	-0.262202
C4	-0.1268	-0.151514	-0.056418
C5	-0.1268	-0.151514	-0.056418
H6	0.1268	0.204741	0.198037
H7	0.1268	0.204741	0.198037
H8	0.1268	0.181764	0.107059
H9	0.1268	0.181764	0.107059
H10	0.3991	0.390378	0.386466
O11	-0.7982	-0.731877	-0.838754
H12	0.3991	0.360106	0.393600
π...H-O interaction (r_{CEN}=2.4 Å)			
S1	0.0240	0.038044	0.048691
C2	-0.1388	-0.306073	-0.256728
C3	-0.1388	-0.307277	-0.262372
C4	-0.1268	-0.105456	-0.051646
C5	-0.1268	-0.104457	-0.048959
H6	0.1268	0.203040	0.199384
H7	0.1268	0.203040	0.201590
H8	0.1268	0.182678	0.114512
H9	0.1268	0.182683	0.114340
H10	0.3991	0.381398	0.359602
O11	-0.7982	-0.727886	-0.816188
H12	0.3991	0.360267	0.397774
C-H…Cl interaction ($r_{H…Cl}$=2.6 Å)			
S1	0.024	-0.092887	0.020483
C2	-0.139	-0.154089	-0.191063
C3	-0.139	-0.486272	-0.234763
C4	-0.127	-0.199385	-0.126336
C5	-0.127	0.194130	-0.046229
H6	0.127	0.182119	0.172709
H7	0.127	0.190204	0.178175
H8	0.127	0.170808	0.107451
H9	0.127	0.174045	0.114562
Cl10	-0.184	-0.037102	0.029281
C11	0.736	-0.125658	-0.123638
Cl12	-0.184	0.193314	0.030064
Cl13	-0.184	-0.004614	0.034652
Cl14	-0.184	-0.004614	0.034652

Table S2. The Number of Solvents Corresponding to a Solute Molecule. The Concentration of Solution is Assumed to be 0.1 M, and the Density of Solution is Replaced by that of Pure Solvents

	n-hexane	1,4-dioxane	carbon tetrachloride	chloroform	water
T		117			551
2T	75	116	102	123	546
3T	74	115	102	123	542
4T	73	114	101	122	537
5T	72	113	101	121	533
6T	71	112	100	120	528
7T	70	111	100	120	524
8T	69	110	99	119	519
9T	68	109	99	118	514
10T	67	108	98	118	510

Table S3. Geometrical Parameters of **2T** and **3T** (Bond Length in Å, Dihedral Angel in Degree) Optimized in Gas Phase, *n*-Hexane, 1,4-Dioxane, Chloroform, and Water, Respectively, at the B3LYP/6-31G (d) Level

	gas (expt.[a])	*n*-hexane	1,4-dioxane	chloroform	water
S1-C2	1.736 (1.719)	1.736	1.736	1.737	1.738
C2-C3	1.368 (1.363)	1.368	1.368	1.368	1.368
C3-C4	1.424 (1.452)	1.425	1.425	1.425	1.426
C4-C5	1.378 (1.370)	1.378	1.378	1.378	1.378
C5-S1	1.756 (1.733)	1.757	1.757	1.758	1.759
C5-C6	1.451 (1.456)	1.451	1.451	1.452	1.452
C2-S1-C5	91.8 (91.7)	91.8	91.8	91.8	91.8
S1-C2-C3	111.6 (112.3)	111.6	111.6	111.5	111.5
C2-C3-C4	112.9 (112.3)	112.9	112.9	113.0	113.0
C3-C4-C5	113.6 (111.9)	113.6	113.6	113.6	113.6
C4-C5-S1	110.1 (111.8)	110.1	110.1	110.0	110.0
C4-C5-C6	129.1 (126.3)	129.1	129.2	129.2	129.2
θ	157.6 (148.4)	157.9	158.4	159.0	160.7

|	gas	*n*-hexane	1,4-dioxane	chloroform	water
S1-C2	1.735	1.736	1.736	1.737	1.737
C2-C3	1.368	1.368	1.368	1.368	1.369
C3-C4	1.424	1.424	1.424	1.425	1.425
C4-C5	1.379	1.379	1.379	1.380	1.380
C5-S1	1.757	1.758	1.758	1.759	1.759
C5-C6	1.448	1.448	1.448	1.448	1.449
C6-C7	1.379	1.379	1.379	1.379	1.380
C7-C8	1.417	1.417	1.417	1.418	1.418
C6-S10	1.756	1.757	1.757	1.758	1.758
C5-S1-C2	91.8	91.8	91.8	91.8	91.8
S1-C2-C3	111.6	111.6	111.6	111.6	111.6
C2-C3-C4	112.9	112.9	112.9	113.0	113.0
C3-C4-C5	113.6	113.6	113.6	113.6	113.6
C4-C5-S1	110.1	110.1	110.1	110.0	110.0
C9-S10-C6	92.1	92.1	92.1	92.1	92.1
S10-C6-C7	110.1	110.1	110.1	110.1	110.1
C4-C5-C6	129.1	129.1	129.1	129.1	129.1
θ	161.4	161.4	161.5	161.7	161.9

[a] Reference 83.
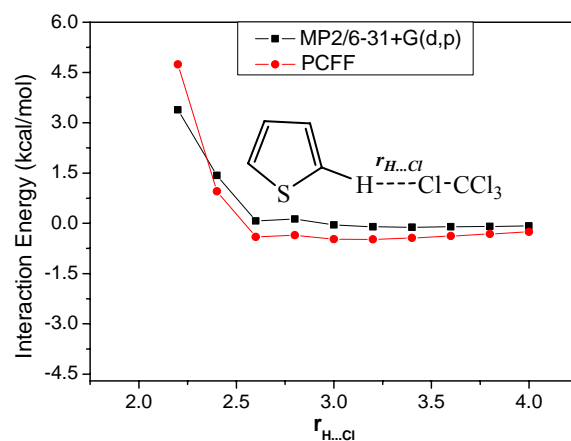
Figure S1. Evolution of the interaction potentials of C-H…Cl interactions as a function of the intermolecular distance, $r_{H…Cl}$. The interaction energy corresponds to the energy difference between the isolated molecules. The structures of dimers were obtained by fixing H…Cl distances at $r_{H…Cl}$, and minimizing other variables at MP2/6-31+G(d, p) level.
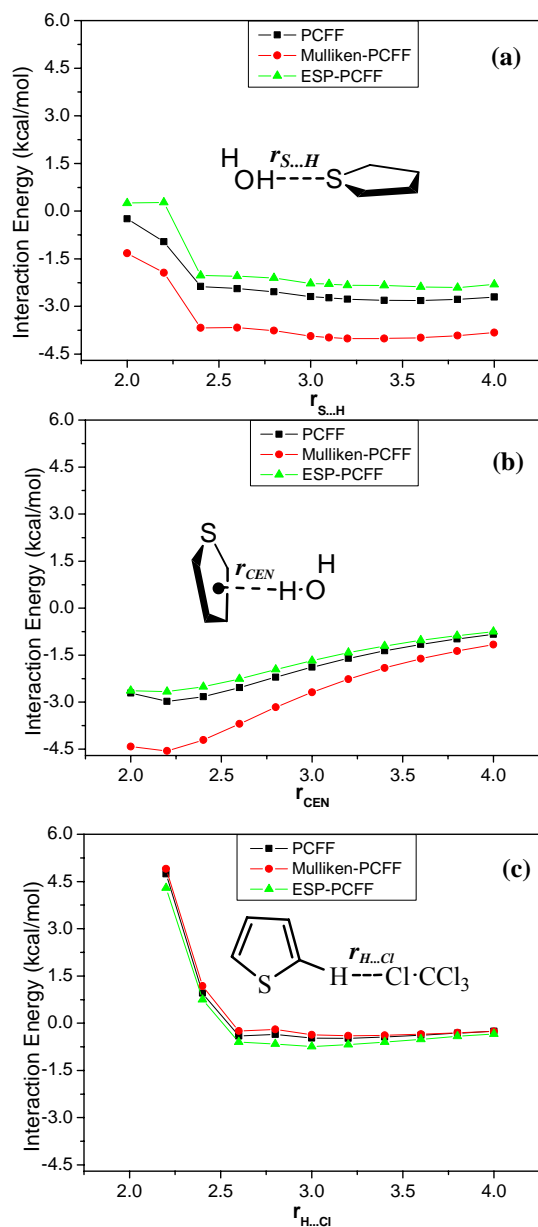
Figure S2. Evolution of the relative energy of (a) S…H-O; (b) π…H-O; and (c) C-H…Cl interactions with partial charges taken from PCFF, Mulliken, ESP as a function of the intermolecular distance, $r_{S…H}$, r_{CEN}, and $r_{H…Cl}$, respectively. The interaction energy corresponds to the energy difference between the isolated molecules.
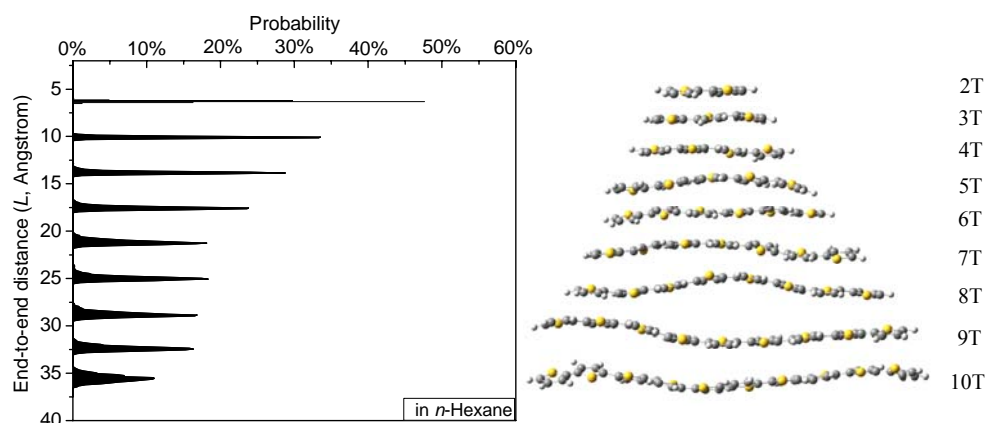
Figure S3. Probability of end-to-end distance, *L,* (in units of Å) of *n***T**s and the representative conformations in *n*-hexane. The data come from the statistical analysis of MD simulations.
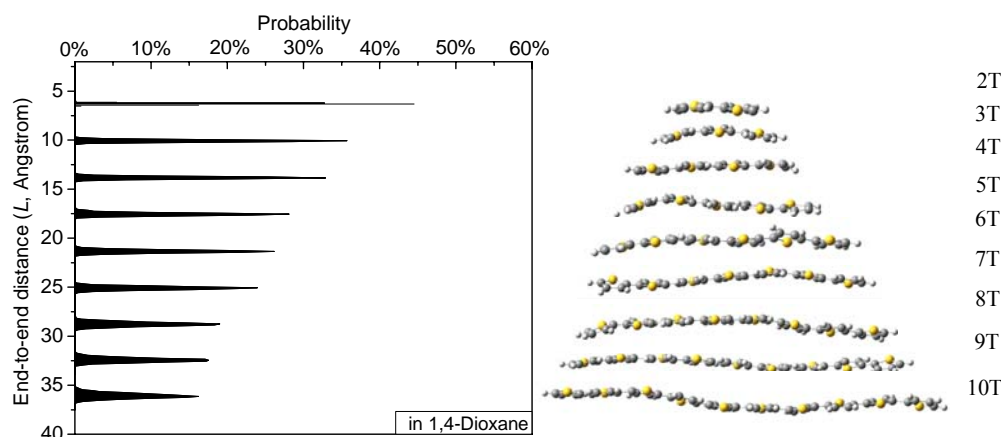

Figure S4. Probability of end-to-end distance, *L,* (in units of Å) of *n***T**s and the representative conformations in 1,4-dioxane. The data come from the statistical analysis of MD simulations.
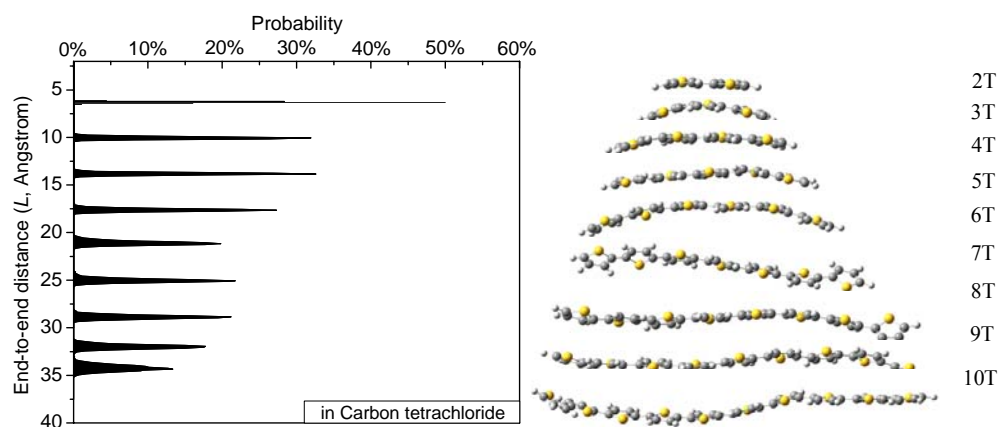
Figure S5. Probability of end-to-end distance, *L,* (in units of Å) of *n***T**s and the representative conformations in carbon tetrachloride. The data come from the statistical analysis of MD simulations.
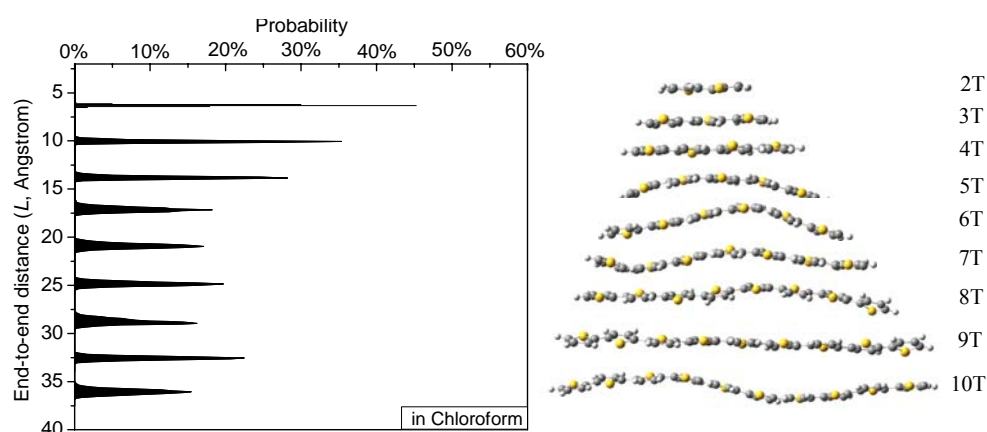

Figure S6. Probability of end-to-end distance, *L,* (in units of Å) of *n***T**s and the representative conformations in chloroform. The data come from the statistical analysis of MD simulations.

(a) **T** in water

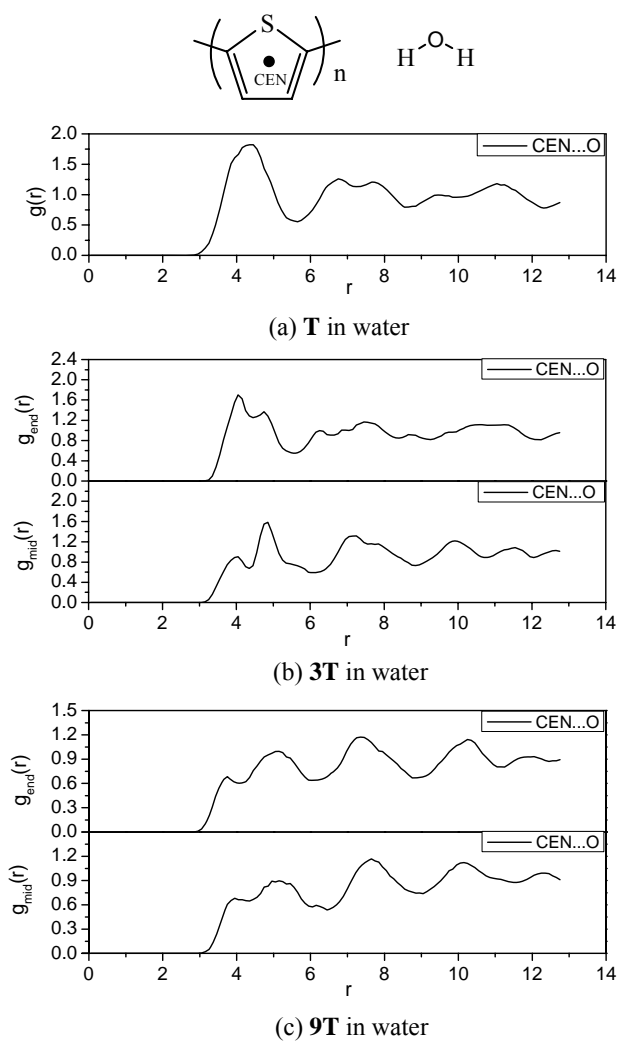(b) **3T** in water

(c) **9T** in water

Figure S7. Radial distribution functions between the geometric center (CEN) of oligothiophene ring and oxygen (O) in water for: (a) **T** (thiophene); (b) the central ($g_{mid}(r)$) and terminal ($g_{end}(r)$) ring of **3T**; and (c) the central ($g_{mid}(r)$) and terminal ($g_{end}(r)$) ring of **9T**, respectively. The statistical error is ±0.05 Å.
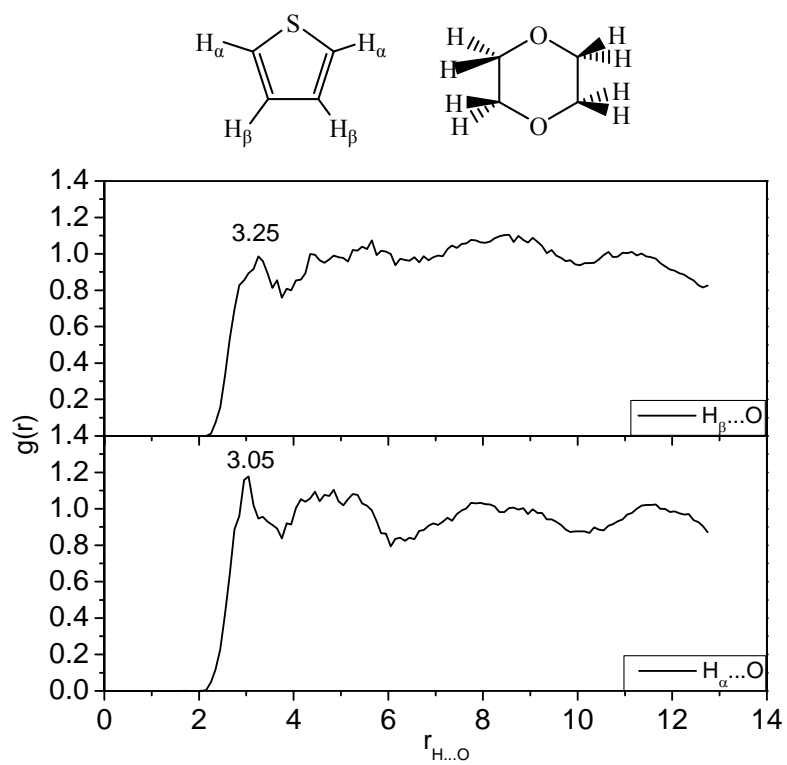
Figure S8. Radial distribution functions: $g_{H \cdots O}(r)$ for hydrogen (H in thiophene) to oxygen (O in water).

The statistical error is ±0.05 Å.