Supporting Information

Cyclic Oligothiophenes: Novel Organic Materials and Models for Polythiophene. A Theoretical Study

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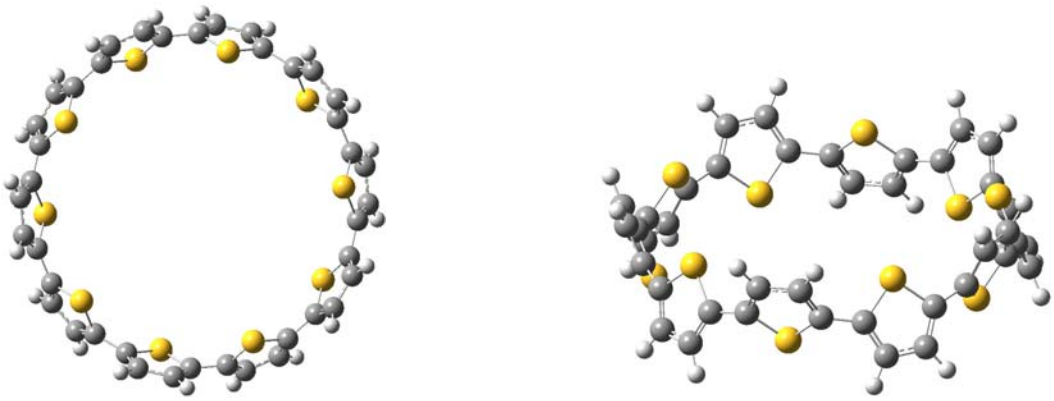
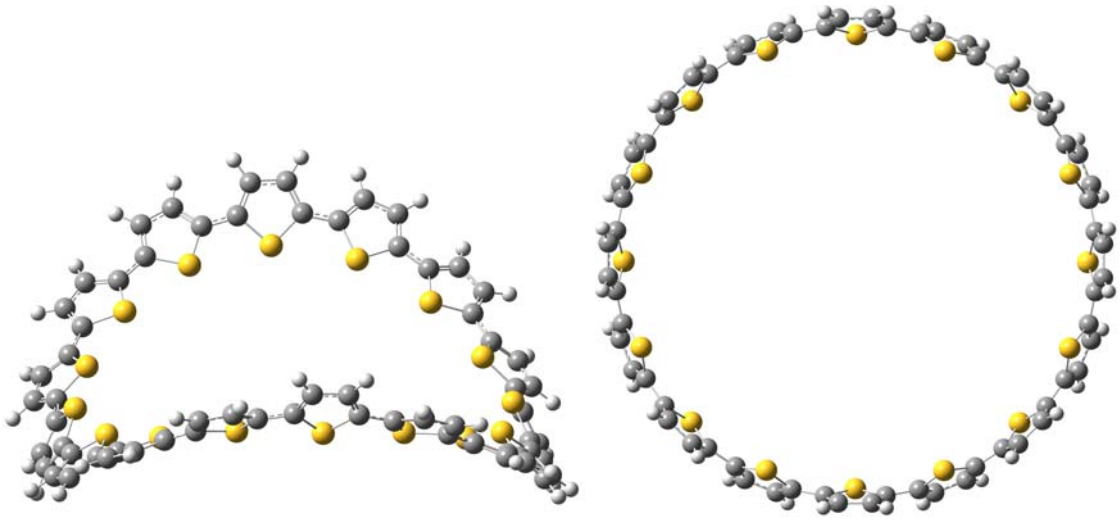


(a) (b)

Figure S1: Two views of optimized structure of C10T-anti.



(a) (b)

Figure S2. Views of optimized (a) C16T-syn and (b) C16T-anti

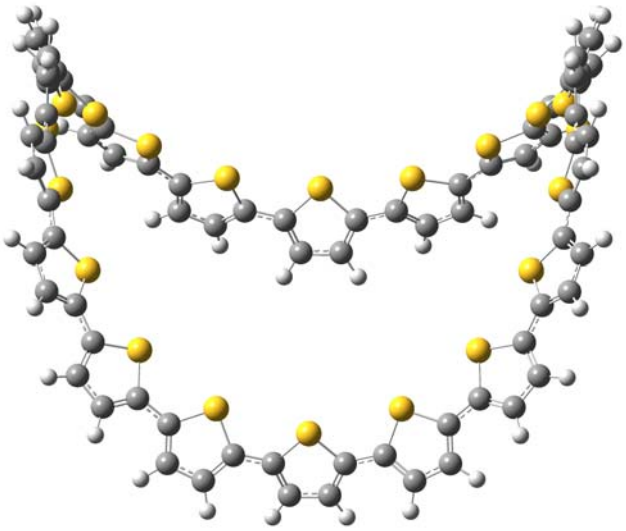
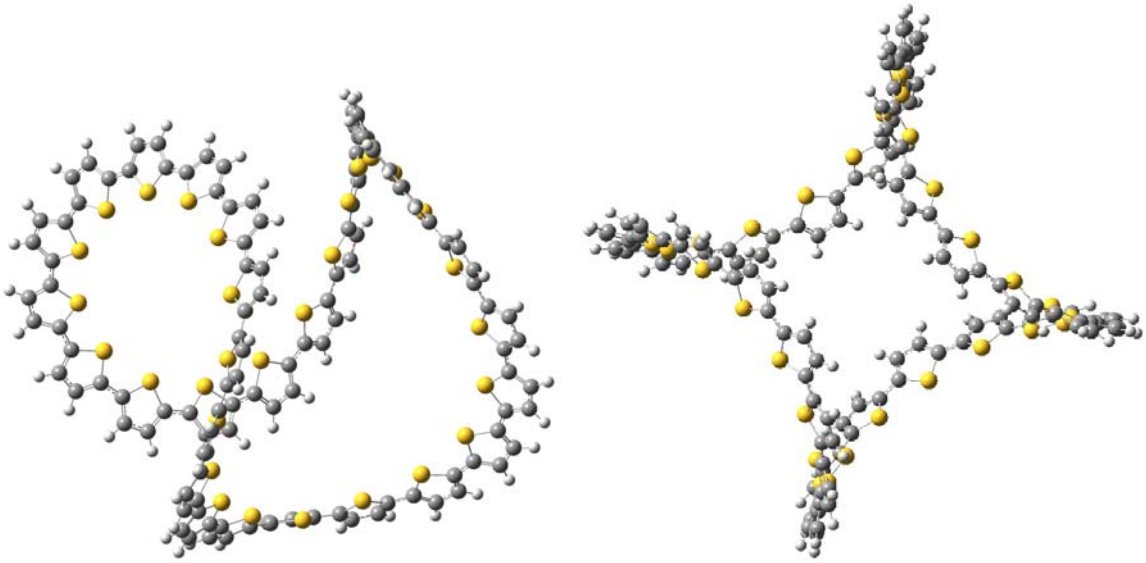


Figure S3. A view of optimized C20T-syn



(a) (b)

Figure S4. Two views of optimized C30T-syn

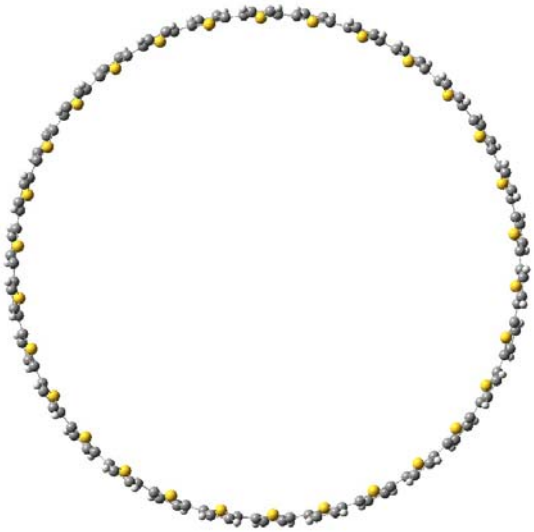
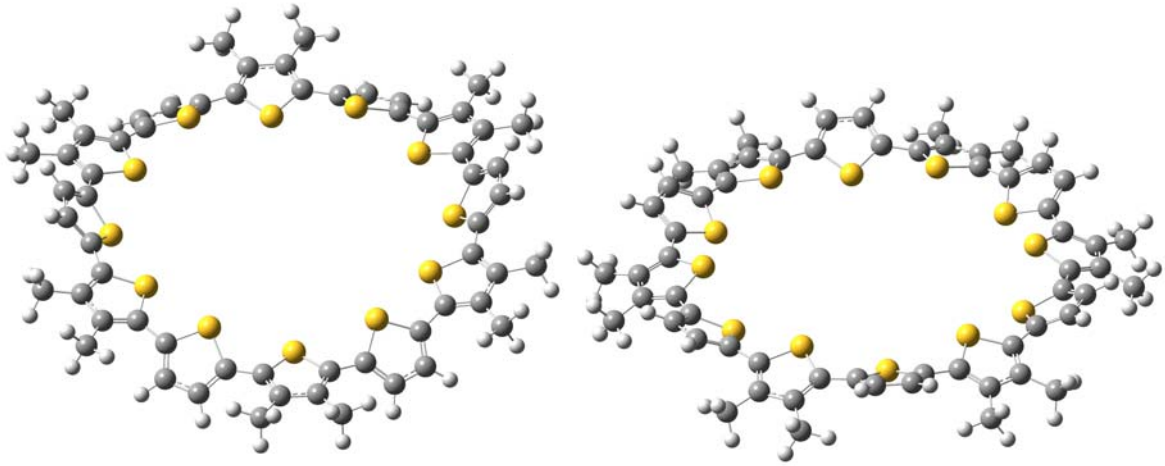
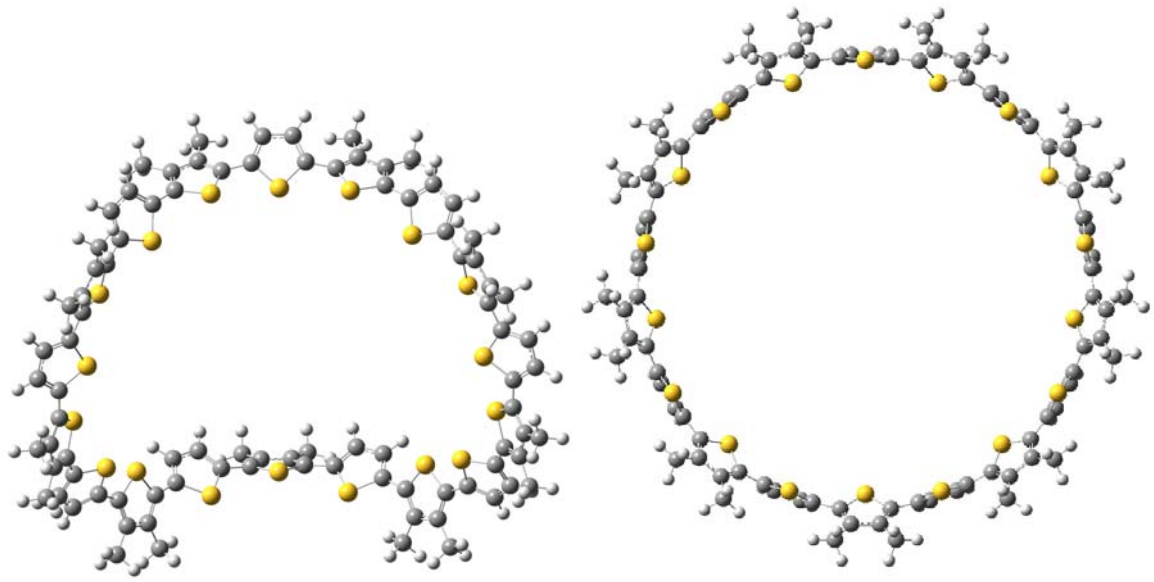


Figure S5: A view of optimized structure of C30T-anti.



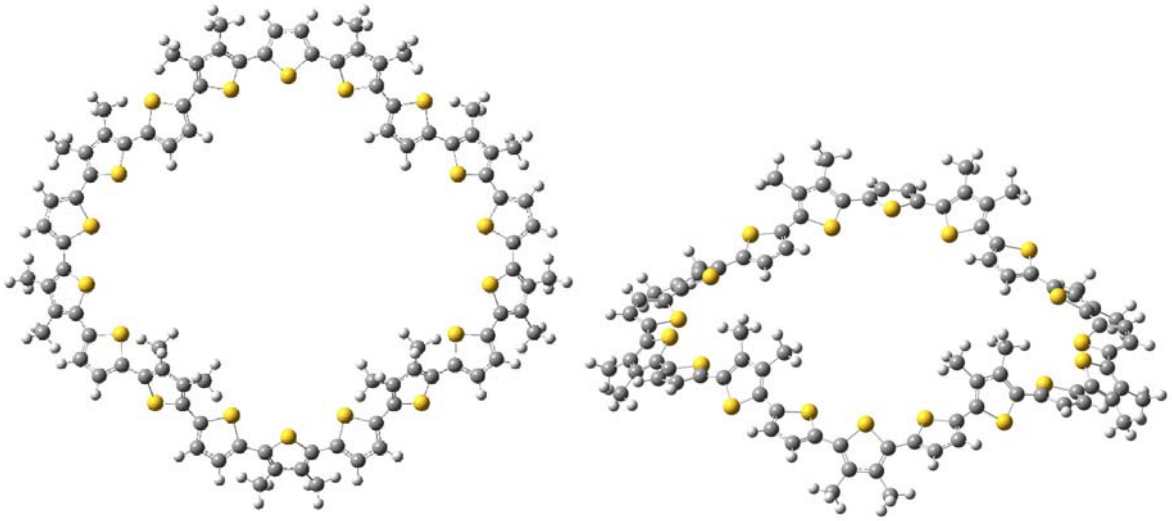
(a) (b)

Figure S6. The optimized structures of C12T having two dimethyl substituents on alternate rings (a) C12T-Me-a; (b) C12T-Me-b (spider-like).



(a) (b)

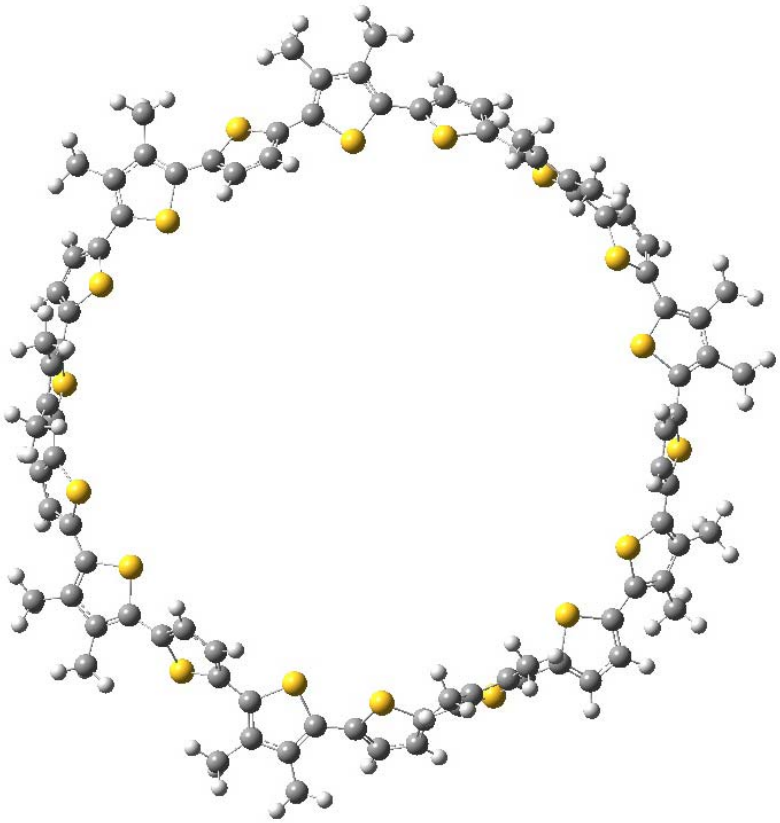
Figure S7. Views of optimized (a) C18T-Me-syn and (b) C18T-Me-anti



(a) (b)

Figure S8. Two views of optimized C18T-Me-a

(a)



(b)

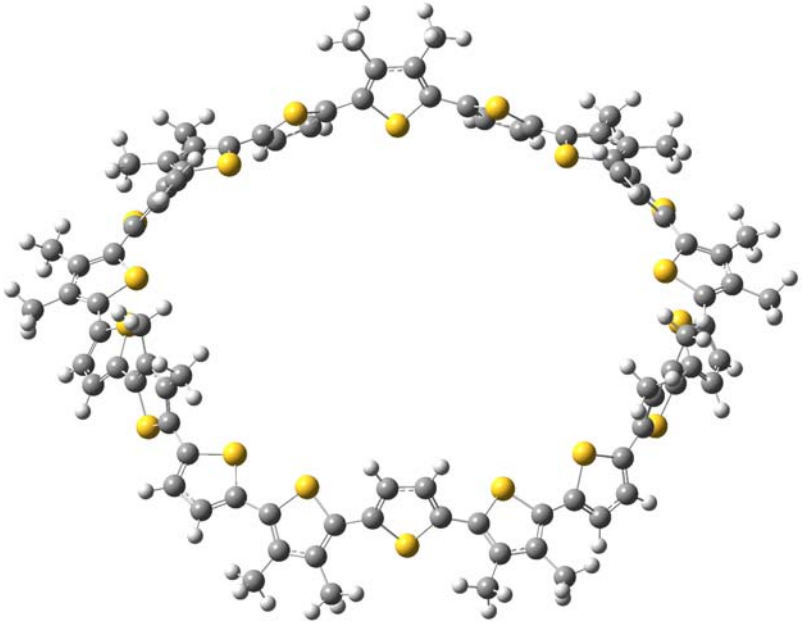


Figure S9. Two views of optimized C18T-Me-b

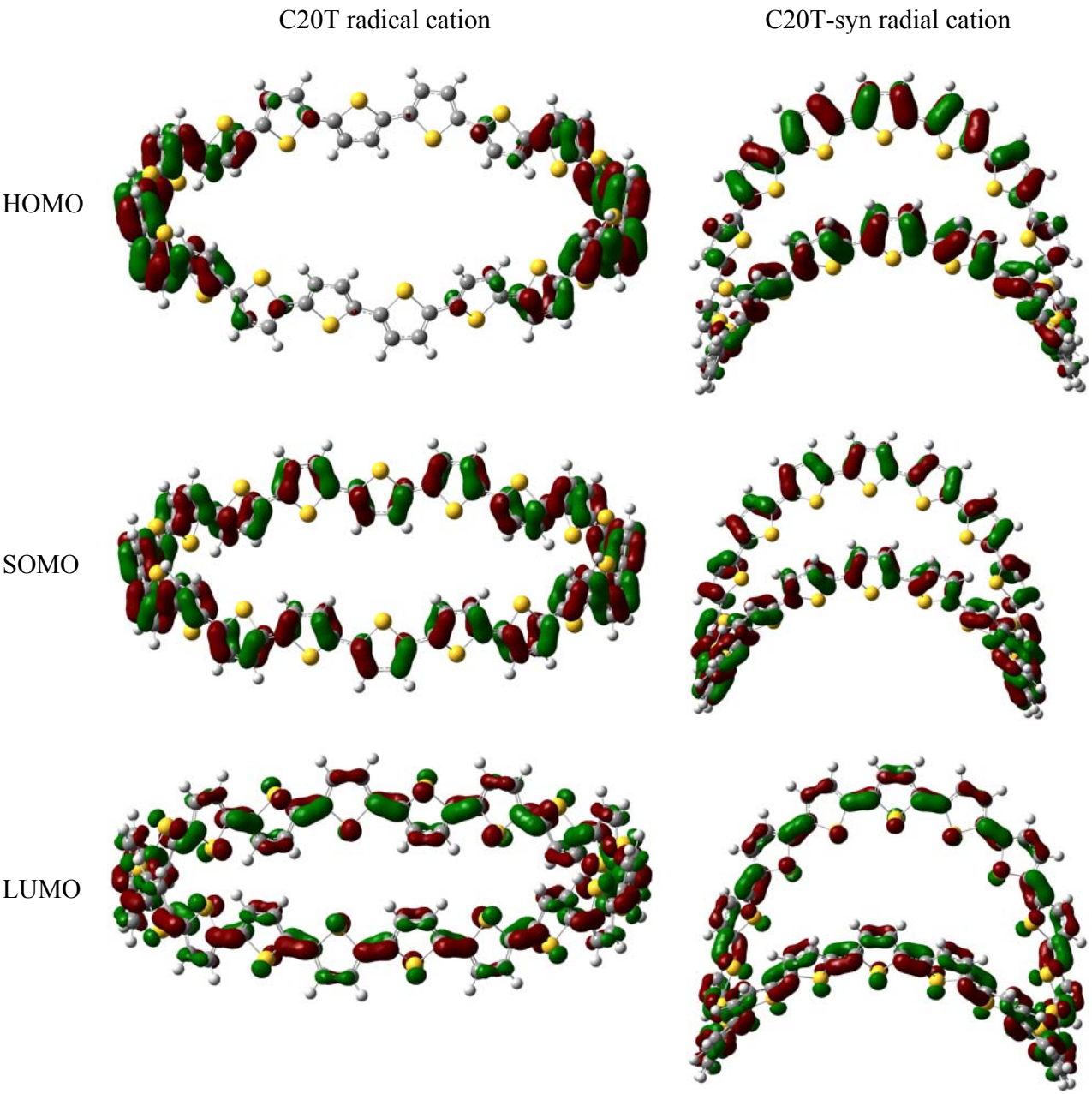


Figure S10. Frontier molecular orbital for C20T radical cation in syn and anti conformation

The plot of the dihedral angles relates linearly with the inverse of chain length for s-transoid cyclic oligomer (Figure S5).

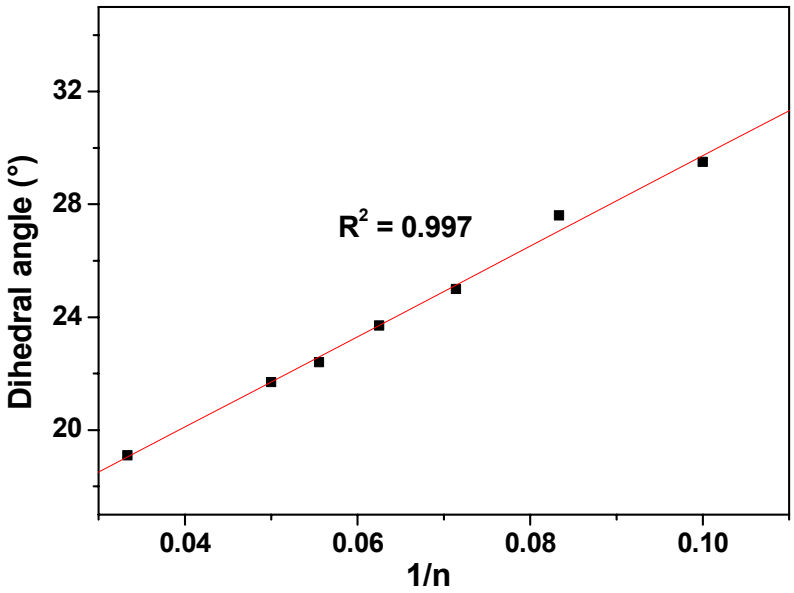


Figure S11. Dihedral angle vs. reciprocal of chain length for s-transoid cyclic oligomers

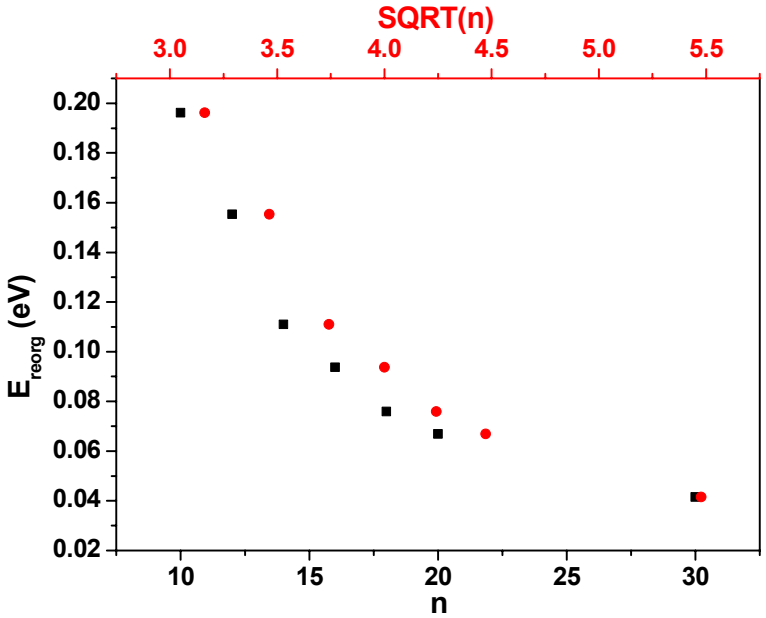


Figure S12. Reorganization energy for anti cyclic oligomers vs. n (squares) and vs. square root of n (circles).

Table S1: The average interring dihedral angle in s-cisoid (syn-) and s-transoid (anti-conformer) cyclic oligothiophenes.

Cyclic Oligomer	Interring dihedral angle	
	s-transoid	s-cisoid
C8T	33.7	36.9
C10T	29.5	24.1
C12T	27.6	13.6
C14T	25.0	0
C16T	23.7	22.0
C18T	22.4	23.4
C20T	21.7	23.7
C30T	19.1	17.1

Table S2: Absolute energies of the optimized structures.

Compound	Energy at B3LYP/6-31G*
C6T-anti	-3310.7582588
C6T-syn	-3310.7446069
C8T-anti	-4414.4274279
C8T-syn	-4414.4490769
C10T-anti	-5518.0790619
C10T-syn	-5518.1190967
C12T-anti	-6621.7234710
C12T-syn	-6621.7631029
C14T-anti	-7725.3639499
C14T-syn	-7725.3893595
C16T-anti	-8829.0019335
C16T-syn	-8829.0198690
C18T-anti	-9932.6382336
C18T-syn	-9932.6466503
C20T-anti	-11036.2734508
C20T-syn	-11036.2741549
C30T-anti	-16554.4396804
C30T-syn	-16554.4108598
C12T-Me-a	-7093.5696762
C12T-Me-b	-7093.5701254
C18T-Me-anti	-10640.3422556
C18T-Me-syn	-10640.3505912
C18T-Me-a	-10640.3500688
C18T-Me-b	-10640.3454566
$[C10T\text{-}anti]^{+}$	-5517.8683406
$[C12T\text{-}anti]^{+}$	-6621.5181928
$[C14T\text{-}anti]^{+}$	-7725.1626816
$[C14T\text{-}syn]^{+}$	-7725.2048602
$[C16T\text{-}anti]^{+}$	-8828.8038724
$[C18T\text{-}anti]^{+}$	-9932.4426076
$[C20T\text{-}anti]^{+}$	-11036.0798886
$[C20T\text{-}syn]^{+}$	-11036.0849741
$[C30T\text{-}anti]^{+}$	-16554.2525150
$[C30T\text{-}syn]^{+}$	-16554.2284175
$[C10T\text{-}anti]^{++}$	-5517.5796869
$[C12T\text{-}anti]^{++}$	-6621.2428153
$[C14T\text{-}anti]^{++}$	-7724.8976065
$[C16T\text{-}anti]^{++}$	-8828.5472263
$[C18T\text{-}anti]^{++}$	-9932.1927722
$[C20T\text{-}anti]^{++}$	-11035.8359153
$[C30T\text{-}anti]^{++}$	-16554.0276983

Table S3. NICS (0.5-5) values for C6T-C12T (syn and anti, even only) at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d).

	0[a]	**0.5**[a]	**1**[a]	**2**[a]	**3**[a]	**4**[a]	**5**[a]	**-0.5**[a]	**-1**[a]	**-2**[a]	**-3**[a]	**-4**[a]	**-5**[a]
Thiophene	-18.6	-15.9	-11.1	-4.3	-1.7	-0.8	-0.4	-15.9	-11.1	-4.3	-1.7	-0.8	-0.4
Benzene	-8.1	-9.9	-10.2	-4.8	-1.9	-0.9	-0.5	-9.9	-10.2	-4.8	-1.9	-0.9	-0.5
C6T-anti	-1.3	-1.3	-1.1	-0.7	-0.4	-0.1	0.0	-1.3	-1.1	-0.8	-0.4	-0.2	-0.1
C6T-syn	3.0	2.6	2.1	1.3	0.7	0.5	0.3	3.2	3.2	2.9	2.2	1.5	1.0
C8T-anti	-1.1	-1.1	-1.1	-0.8[b]	-0.6	-0.4	-0.2	-1.1	-1.1	-0.9[b]	-0.6	-0.4	-0.2
C8T-syn	1.3	1.3	1.2	0.8	0.5	0.2	0.1	1.3	1.2	0.9	0.5	0.3	0.1
C10-anti	-0.8	-0.8	-0.8	-0.7	-0.5	-0.4	-0.2	-0.8	-0.8	-0.7	-0.5	-0.3	-0.2
C10T-syn	1.2	1.2	1.1	0.9	0.6	0.4	0.2	1.2	1.1	0.9	0.6	0.4	0.2
C12T-anti[c]	-0.7	-0.7	-0.7	-0.6	-0.7	-0.7	-0.6	-0.5	-0.4	-0.3	-0.5	-0.4	-0.3
C12T-syn	0.8	0.8	0.7	0.6	0.5	0.3	0.2	0.8	0.7	0.6	0.5	0.3	0.2

[a] The perpendicular distance of the ghost-atom from the centre of the molecular plane.

[b] The inclusion of more decimal points results in values of -0.849 and -0.861 ppm which are practically same.

[c] Calculated with Gaussian 98, since we did not succeed to achieve convergence with Gaussian 03.