Electronic Supplementary Material (ESI) for Soft Matter.

Elucidating Structure of Donor-acceptor Conjugated Polymer Aggregates in the Liquid Solution

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Supplementary Information

Table S1 Partial charge calculations for CPDT-BBT (Dimer) using various implicit solvents (octanol, chloroform, and chlorobenzene) and comparison of charges with octanol and other solvents.

Atom No.	Octanol	Chloro-benzene	Difference (Oct/ChlB)	Chloroform	Difference (Oct/ChlF)
1	0.118914	0.117890	0.001024	0.117426	0.001488
2	-0.107884	-0.108105	0.000221	-0.108200	0.000316
3	0.049029	0.049024	0.000005	0.049056	-0.000027
4	-0.033547	-0.032735	-0.000812	-0.032372	-0.001175
5	-0.037594	-0.036861	-0.000733	-0.036538	-0.001056
6	-0.112223	-0.112033	-0.000190	-0.111947	-0.000276
7	0.116046	0.115055	0.000991	0.114622	0.001424
8	-0.022803	-0.022178	-0.000625	-0.021899	-0.000904
9	-0.041149	-0.040343	-0.000806	-0.040002	-0.001147
10	-0.015091	-0.014153	-0.000938	-0.013749	-0.001342
11	0.048140	0.046640	0.001500	0.045999	0.002141
12	-0.018553	-0.017786	-0.000767	-0.017453	-0.001100
13	-0.099375	-0.098642	-0.000733	-0.098325	-0.001050
14	-0.013731	-0.013397	-0.000334	-0.013260	-0.000471
15	-0.106060	-0.105950	-0.000110	-0.105897	-0.000163
16	-0.015137	-0.014770	-0.000367	-0.014611	-0.000526
17	-0.106395	-0.105893	-0.000502	-0.105674	-0.000721
18	0.101579	0.101634	-0.000055	0.101652	-0.000073
19	0.038098	0.036991	0.001107	0.036508	0.001590
20	0.100839	0.099968	0.000871	0.099591	0.001248
21	0.050601	0.049567	0.001034	0.049107	0.001494
22	0.101815	0.101133	0.000682	0.100832	0.000983
23	0.100740	0.101108	-0.000368	0.101246	-0.000506
24	-0.104520	-0.103535	-0.000985	-0.103127	-0.001393
25	-0.028304	-0.027714	-0.000590	-0.027455	-0.000849
26	0.048514	0.049649	-0.001135	0.050195	-0.001681
27	-0.003610	-0.003270	-0.000340	-0.003134	-0.000476
28	0.103570	0.103520	0.000050	0.103500	0.000070
29	-0.337185	-0.336398	-0.000787	-0.336051	-0.001134
30	0.461909	0.458364	0.003545	0.456757	0.005152
31	-0.333331	-0.333286	-0.000045	-0.333247	-0.000084
32	0.108876	0.108838	0.000038	0.108820	0.000056
33	-0.011266	-0.011001	-0.000265	-0.010872	-0.000394
34	0.104210	0.104165	0.000045	0.104145	0.000065
35	-0.338877	-0.338167	-0.000710	-0.337834	-0.001043
36	0.465399	0.461970	0.003429	0.460428	0.004971
37	-0.323297	-0.322972	-0.000325	-0.322861	-0.000436
38	0.108702	0.108633	0.000069	0.108599	0.000103
39	-0.022043	-0.021408	-0.000635	-0.021133	-0.000910
40	0.048939	0.050210	-0.001271	0.050812	-0.001873
41	-0.028970	-0.028363	-0.000607	-0.028084	-0.000886
42	-0.037243	-0.036544	-0.000699	-0.036237	-0.001006
43	-0.107830	-0.107248	-0.000582	-0.106979	-0.000851
44	0.105249	0.104966	0.000283	0.104849	0.000400
45	-0.021370	-0.020604	-0.000766	-0.020265	-0.001105
46	-0.037230	-0.036521	-0.000709	-0.036218	-0.001012

Table S1 Partial charge calculations for CPDT-BBT (Dimer) using various implicit solvents (octanol, chloroform, and chlorobenzene) and comparison of charges with octanol and other solvents.

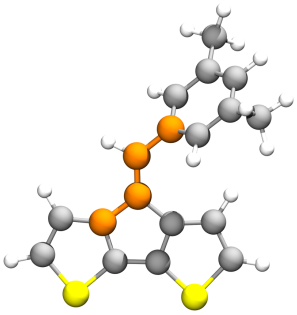
Atom No.	Octanol	Chloro-benzene	Difference (Oct/ChlB)	Chloroform	Difference (Oct/ChlF)
47	-0.014654	-0.013760	-0.000894	-0.013367	-0.001287
48	0.050572	0.049148	0.001424	0.048514	0.002058
49	-0.018660	-0.017871	-0.000789	-0.017528	-0.001132
50	-0.106033	-0.105553	-0.000480	-0.105345	-0.000688
51	-0.014980	-0.014644	-0.000336	-0.014501	-0.000479
52	-0.105755	-0.105698	-0.000057	-0.105668	-0.000087
53	-0.013750	-0.013431	-0.000319	-0.013293	-0.000457
54	-0.099364	-0.098658	-0.000706	-0.098353	-0.001011
55	0.102086	0.101407	0.000679	0.101104	0.000982
56	0.050916	0.049829	0.001087	0.049338	0.001578
57	0.100997	0.100089	0.000908	0.099693	0.001304
58	0.037764	0.036564	0.001200	0.036035	0.001729
59	0.101681	0.101699	-0.000018	0.101702	-0.000021
60	0.101393	0.101764	-0.000371	0.101908	-0.000515
61	-0.102840	-0.101817	-0.001023	-0.101389	-0.001451
62	-0.026500	-0.026101	-0.000399	-0.025921	-0.000579
63	0.052918	0.054083	-0.001165	0.054641	-0.001723
64	0.002954	0.003622	-0.000668	0.003908	-0.000954
65	0.107297	0.107164	0.000133	0.107107	0.000190
66	-0.325906	-0.325528	-0.000378	-0.325390	-0.000516
67	0.460965	0.457336	0.003629	0.455719	0.005246
68	-0.357426	-0.356534	-0.000892	-0.356091	-0.001335
69	0.101293	0.101244	0.000049	0.101231	0.000062
70	-0.092910	-0.093272	0.000362	-0.093408	0.000498
71	0.101009	0.100963	0.000046	0.100953	0.000056
72	-0.357633	-0.356776	-0.000857	-0.356352	-0.001281
73	0.460307	0.457203	0.003104	0.455789	0.004518
74	-0.340094	-0.339314	-0.000780	-0.338972	-0.001122
75	0.101494	0.101362	0.000132	0.101308	0.000186
76	0.126308	0.126032	0.000276	0.125908	0.000400

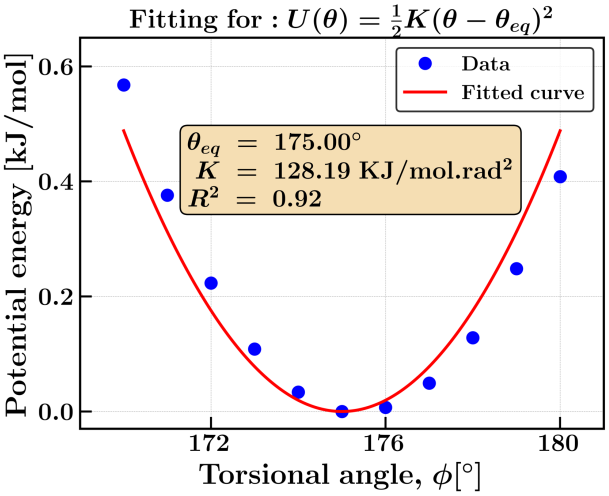
Table S2 Radius of gyration (R_g) of oligomers and their correlation length (ξ) compared to the corresponding (cubic) simulation box length. Here, the largest R_g value of the oligomers is reported for each system.

T = 298 K			
Chain length, n	**R_g (nm)**	**Correlation length, ξ (nm)** when $R_g = \sqrt{3}\xi$	**Simulation box length (nm)**
Dimer (n = 2)	6.66	3.84	10.99
Tetramer (n = 4)	8.35	4.82	13.80
Octamer (n = 8)	10.16	5.87	17.38
Hexadecamer (n = 16)	13.57	7.84	21.89

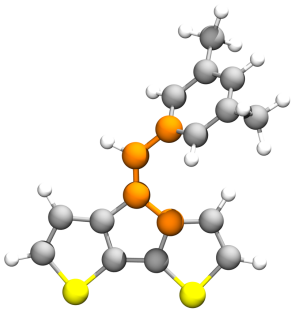
T = 323 K			
Chain length, n	**R_g (nm)**	**Correlation length, ξ (nm)** if $R_g = \sqrt{3}\xi$	**Simulation box length (nm)**
Dimer (n = 2)	7.82	4.53	11.10
Tetramer (n = 4)	7.08	4.09	13.92
Octamer (n = 8)	8.40	4.85	17.54
Hexadecamer (n = 16)	12.50	7.22	22.08

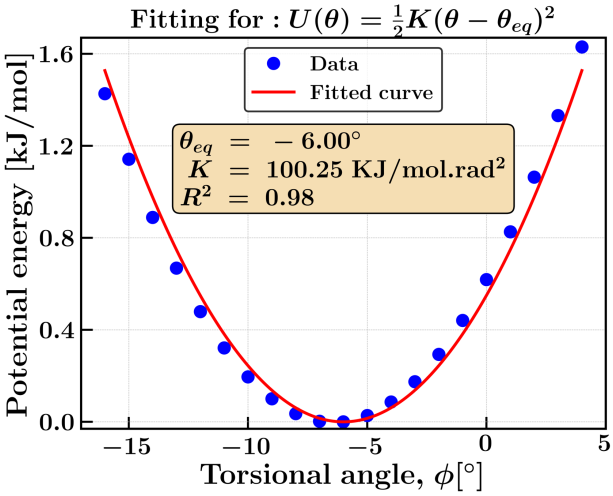
(A)




Fitting for : $U(\theta) = \frac{1}{2}K(\theta - \theta_{eq})^2$
Data
Fitted curve
θ_{eq} = 175.00°
K = 128.19 KJ/mol.rad^2
R^2 = 0.92
Potential energy [kJ/mol]
Torsional angle, ϕ[°]

(B)

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Data
Fitted curve
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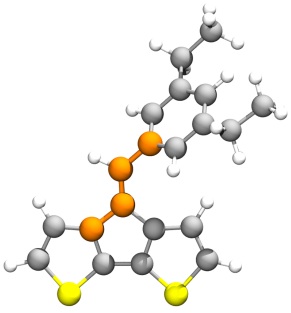
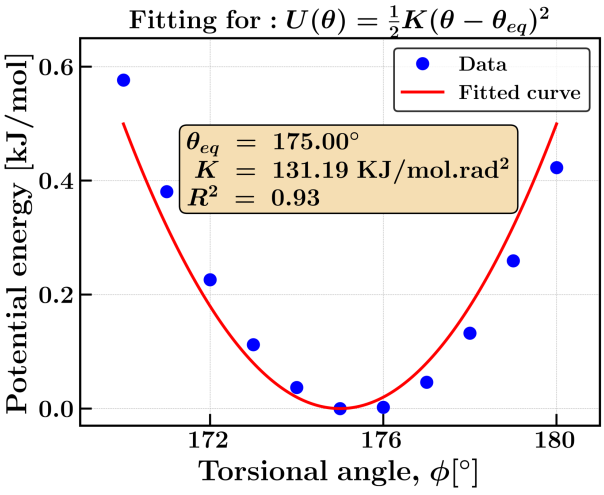
Torsional angle, ϕ[°]

(C)




Fitting for : $U(\theta) = \frac{1}{2}K(\theta - \theta_{eq})^2$
Data
Fitted curve
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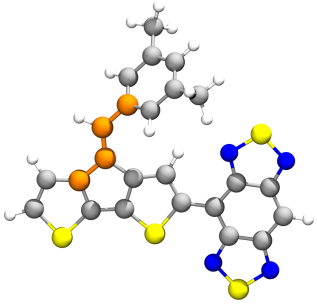
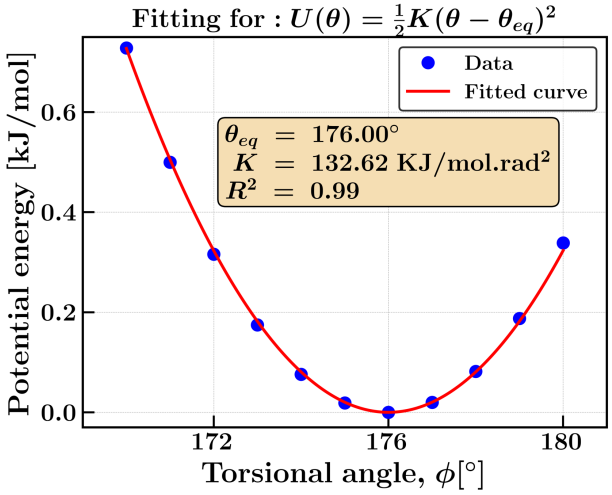
K = 131.19 KJ/mol.rad^2
R^2 = 0.93
Potential energy [kJ/mol]
Torsional angle, ϕ[°]

(D)




Fitting for : $U(\theta) = \frac{1}{2}K(\theta - \theta_{eq})^2$
Data
Fitted curve
θ_{eq} = 176.00°
K = 132.62 KJ/mol.rad^2
R^2 = 0.99
Potential energy [kJ/mol]
Torsional angle, ϕ[°]

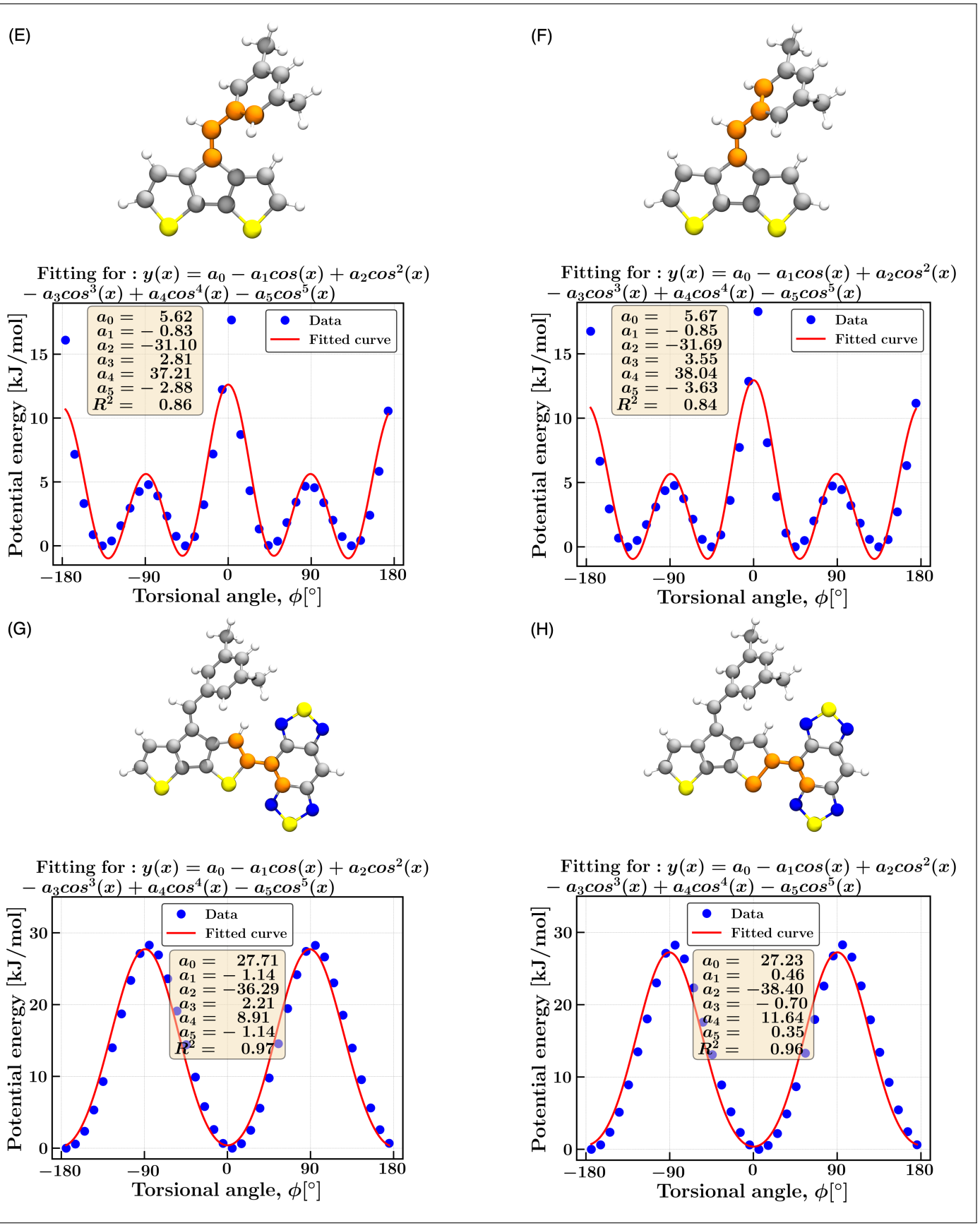


Fig. S1 Potential energy surface scanning was performed for the dihedral angle indicated by the orange colored atoms. The scanning was conducted in two different ways: rigid scanning (A-D) and regular scanning (E-H). The obtained data from the scanning was fitted using two different equations: the Improper potential equation for the rigid scanning (A-D) and the Ryckaert-Bellemans potential equation for the regular scanning (E-H).

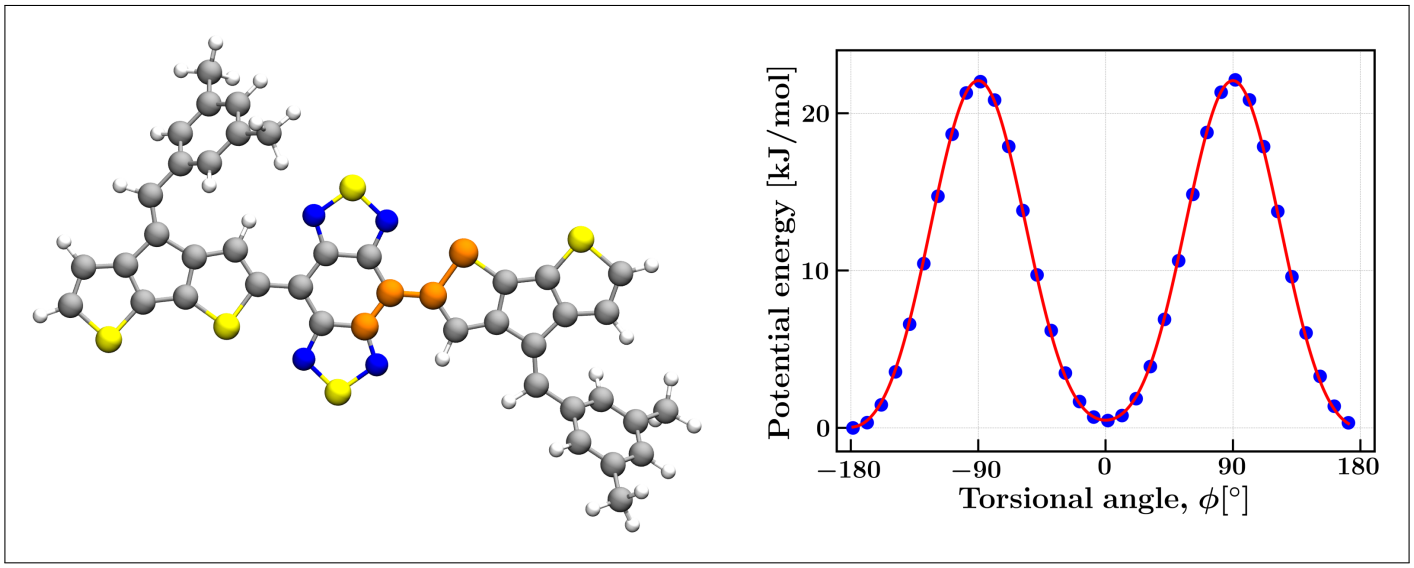


Fig. S2 Energy plot in the figure depicts the energy variation of the cis and trans configurations of the CPDT-BBT repeating unit in the oligomers, with the dihedral angle represented by the orange colored atoms.

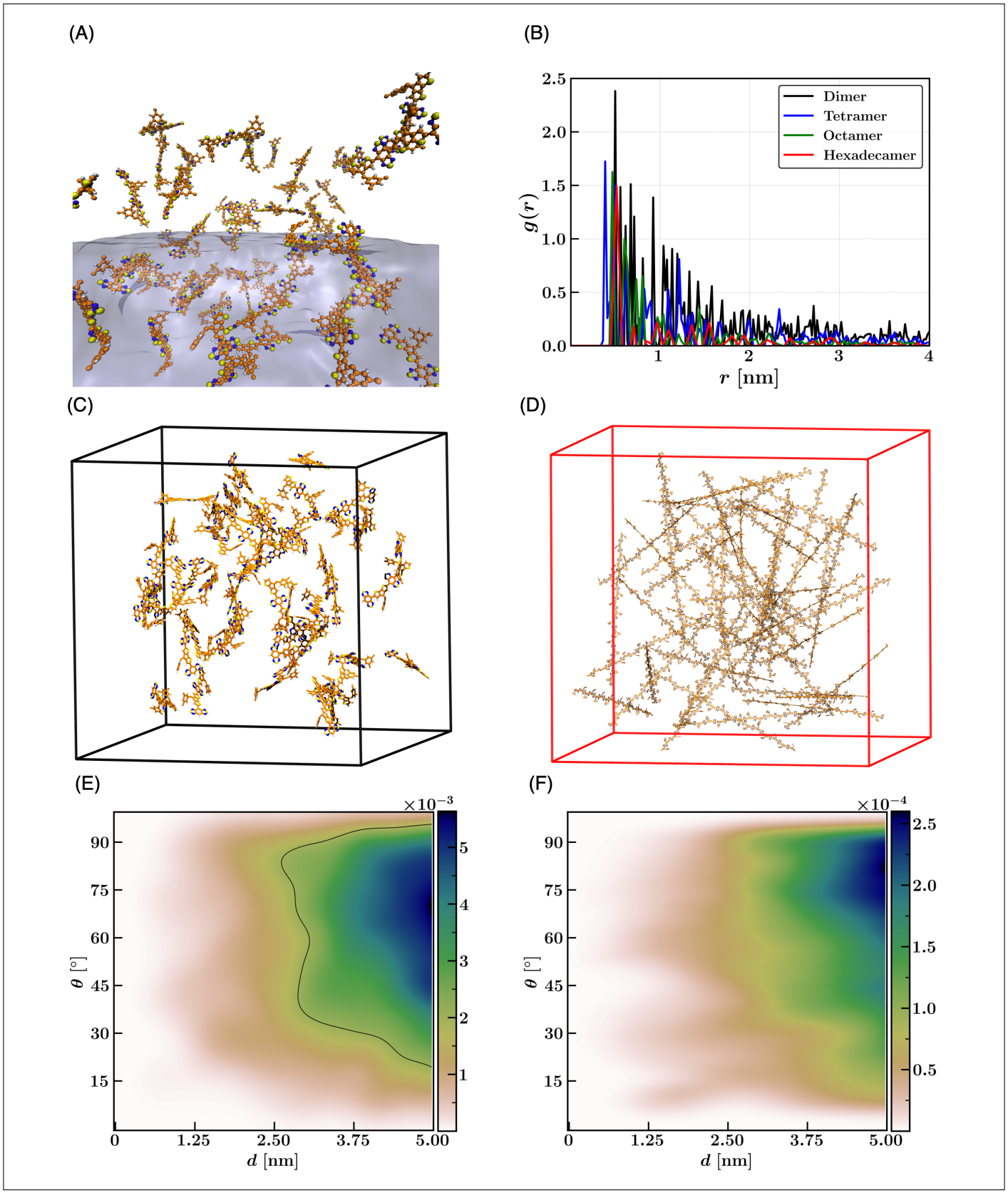


Fig. S3 (A) Snapshot of molecular dynamics simulation (initial) system of CPDT-BBT ($n = 2$) and the box is shown shown half-filled for better visualization. (B) Inter-chain RDFs ($g(r)$) of the aromatic ring-center along the CPDT-BBT backbone. Initial packing of CPDT-BBT for $n = 2$ and $n = 16$ are shown in (C) and (D), respectively, without chloroform solvent. The probability (density) map of angle (θ) between stacked aromatic ring (plane) with respect to the distance (d) between these rings for $n = 2$ (E) and $n = 16$ (F).

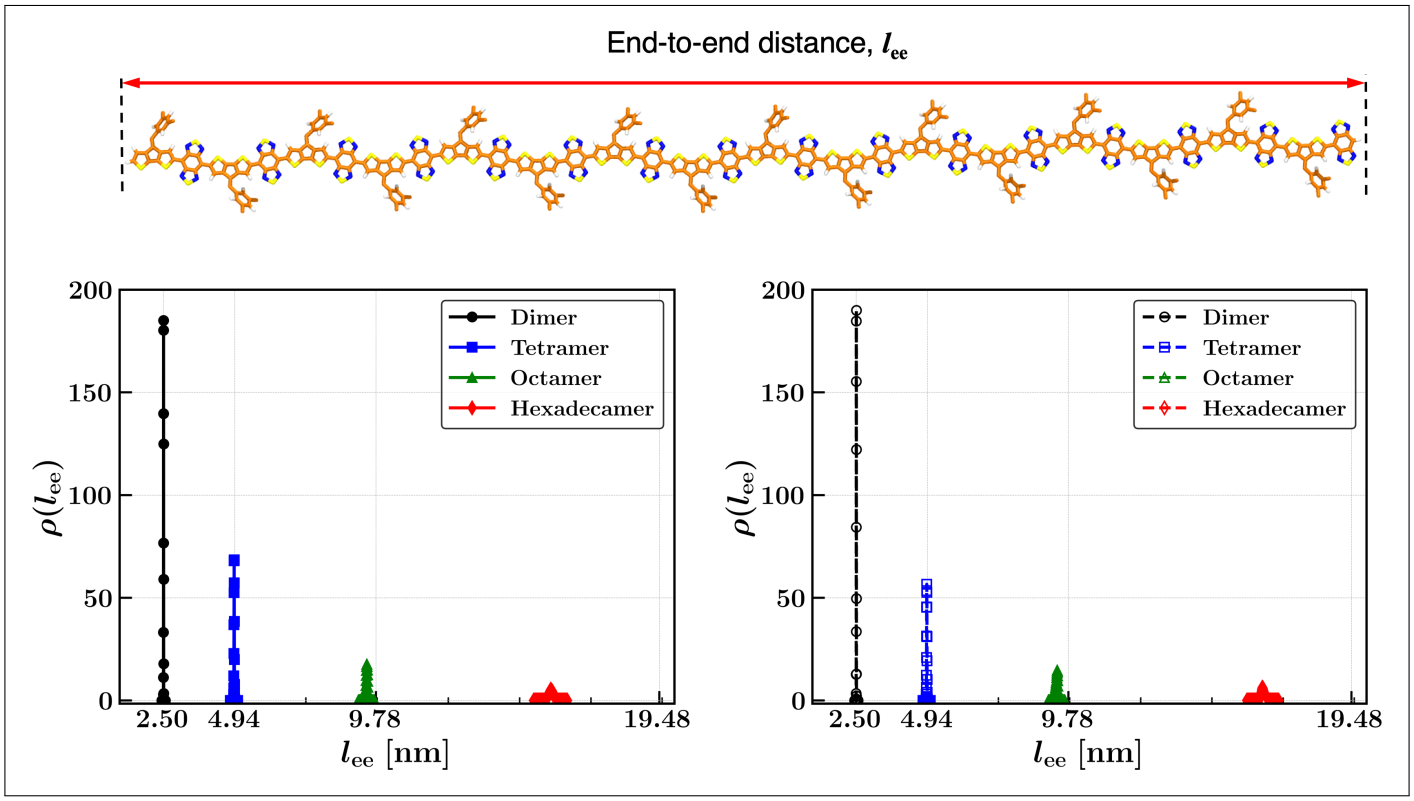


Fig. S4 End-to-end (E2E) distance distribution ($\rho(l_{ee})$) of CPDT-BBT oligomers as a function of E2E distance, l_{ee}. Isolated single chain extended length is shown as x-axis scale points in the figure. Filled (left) and unfilled (right) markers are for T = 298 and 323 K, respectively.

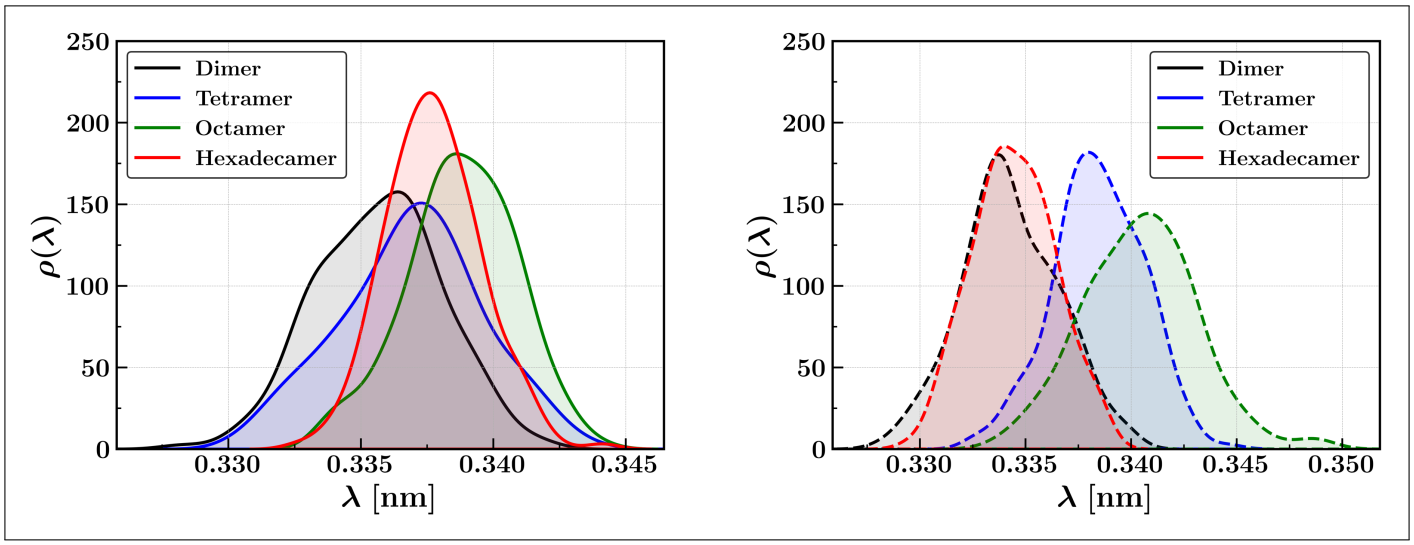


Fig. S5 π-π stacking distribution of CPDT-BBT oligomers in chloroform solvent at temperature T = 298 K (left) and T = 323 K (right).

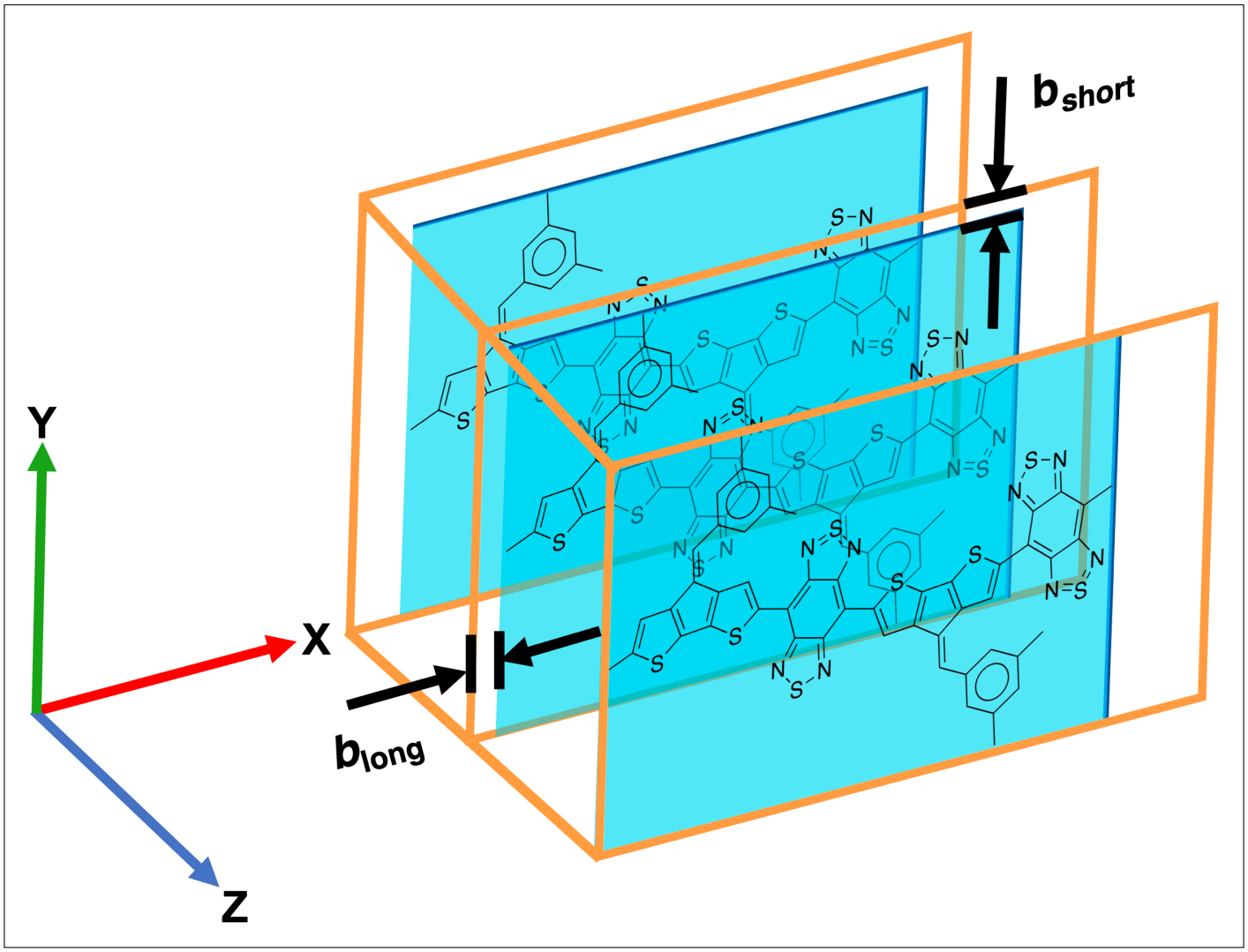
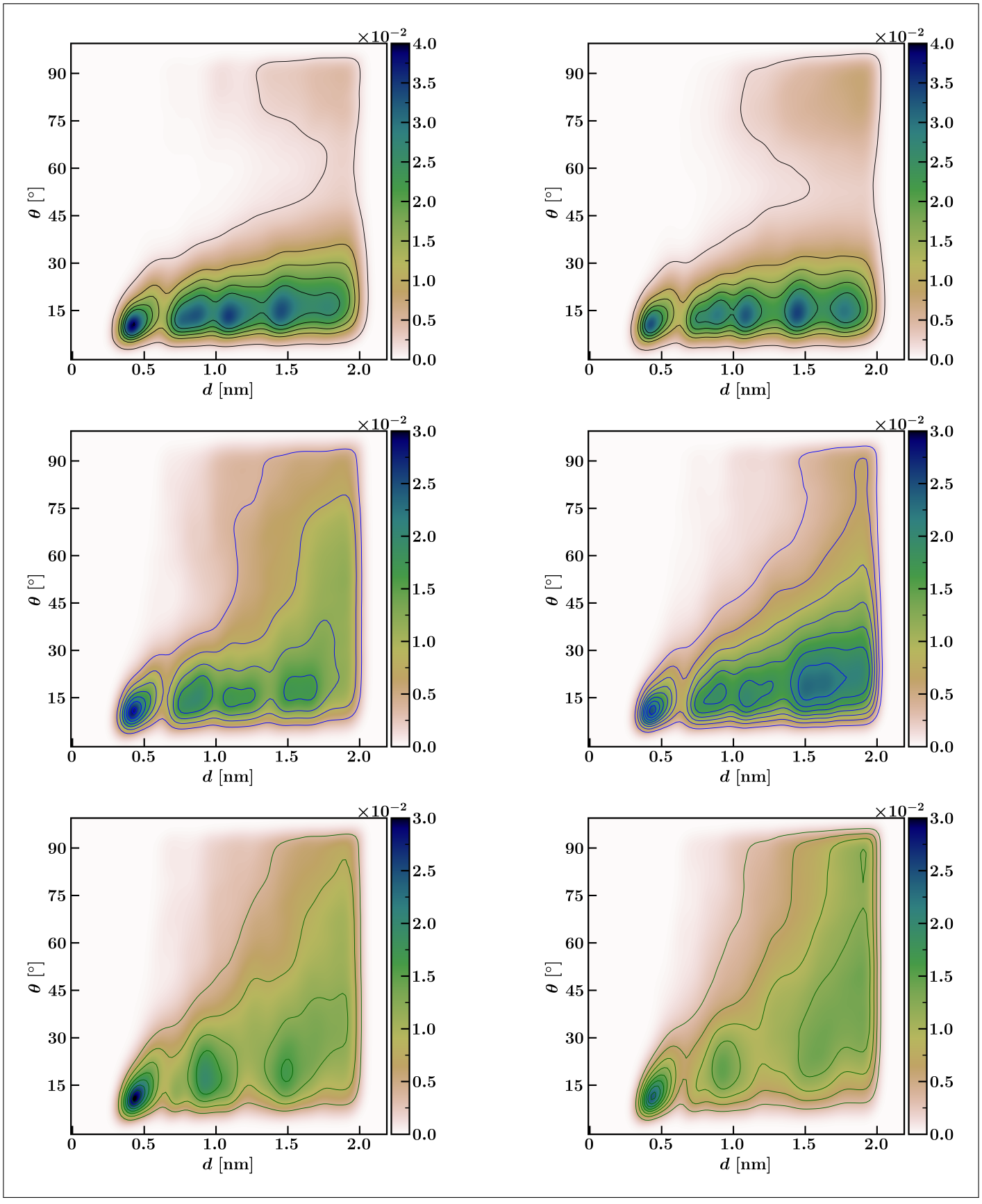


Fig. S6 Schematic of displacement between two neighboring π-stacked CPDT-BBT oligomers in chloroform.

Table S3 Displacement distances of different oligomers at two different temperatures, where b_{long} and b_{short} represent long and short displacements, respectively.

Chain length, n	$T = 298$ **K**		$T = 323$ **K**	
	b_{long} [Å]	b_{short} [Å]	b_{long} [Å]	b_{short} [Å]
Dimer ($n = 2$)	1.793 ± 0.010	1.010 ± 0.008	1.812 ± 0.010	0.981 ± 0.008
Tetramer ($n = 4$)	1.917 ± 0.024	1.155 ± 0.017	1.802 ± 0.021	0.963 ± 0.015
Octamer ($n = 8$)	2.122 ± 0.020	0.702 ± 0.021	1.819 ± 0.157	1.192 ± 0.077
Hexadecamer ($n = 16$)	2.038 ± 0.026	1.228 ± 0.029	1.768 ± 0.042	1.060 ± 0.027


×10−2
θ [°]
d [nm]
0
0.5
1.0
1.5
2.0
15
30
45
60
75
90
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

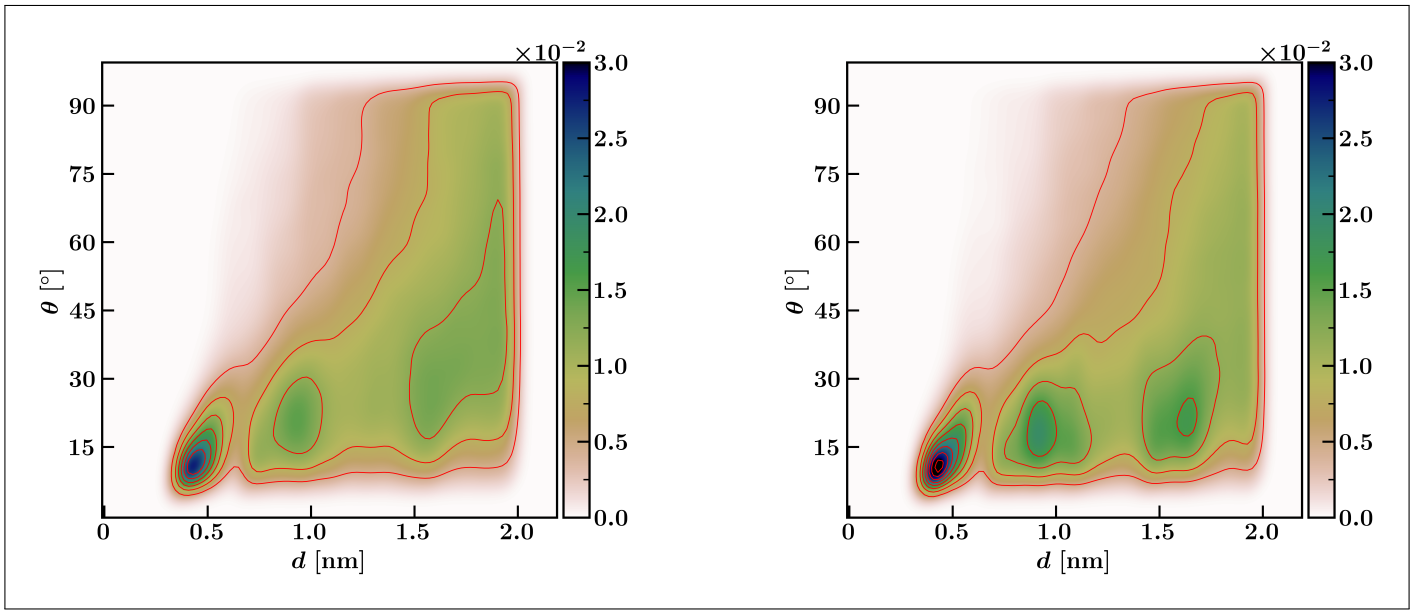


Fig. S7 The probability (density) map of angle (θ) between stacked aromatic ring (plane) with respect to the distance (d) between these rings. First, second, third and fourth rows are representing the results for dimer, tetramer, octamer and hexadecamer, respectively at $T = 298$ K (left column) and $T = 323$ K (right column).

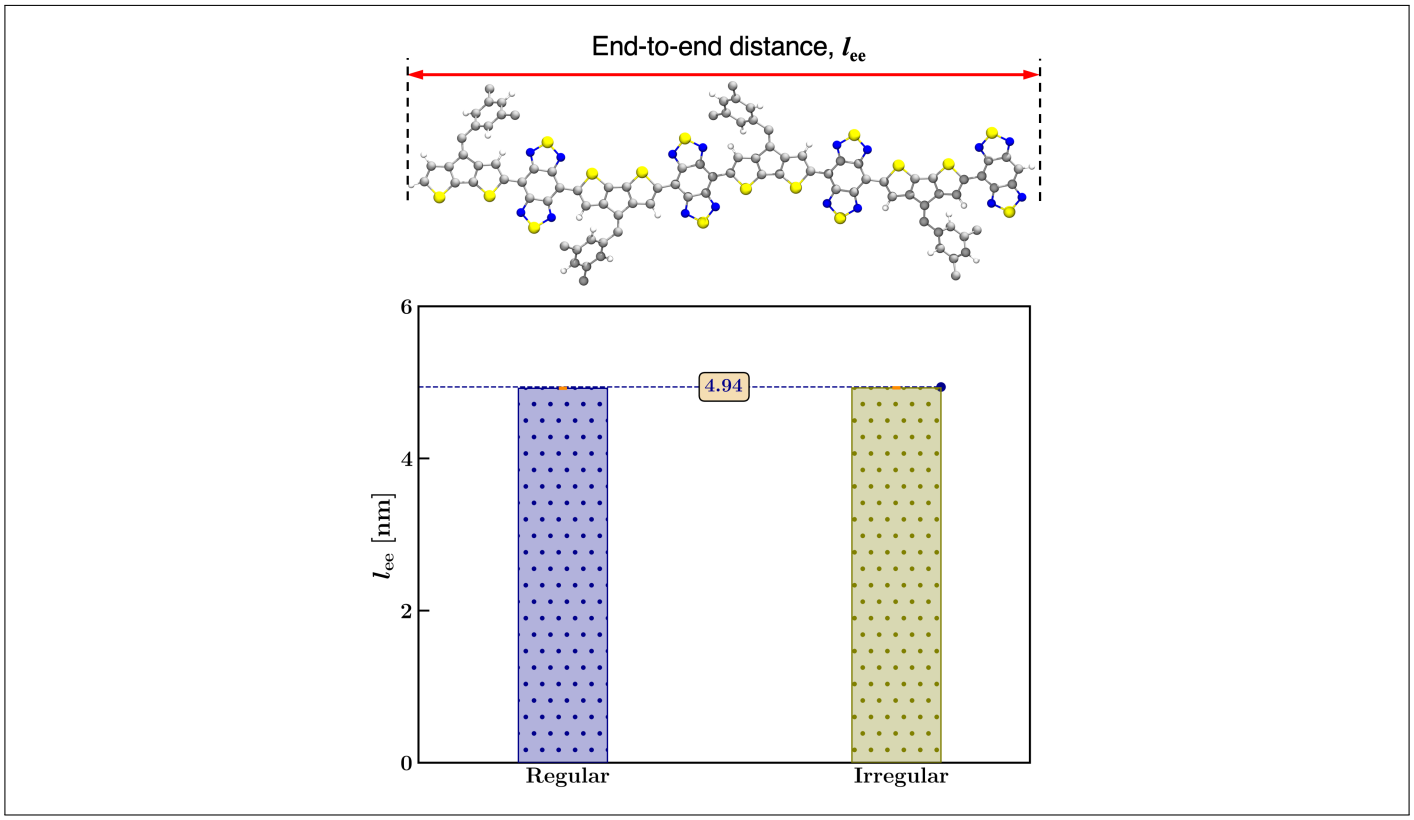


Fig. S8 End-to-end distance of CPDT-BBT tetramer with regio-regular and regio-irregular lateral groups in chloroform solvent. Isolated single chain elongated length is shown as the horizontal dashed line with the associated value. The tetramer with regio-irregular conformation is shown here.

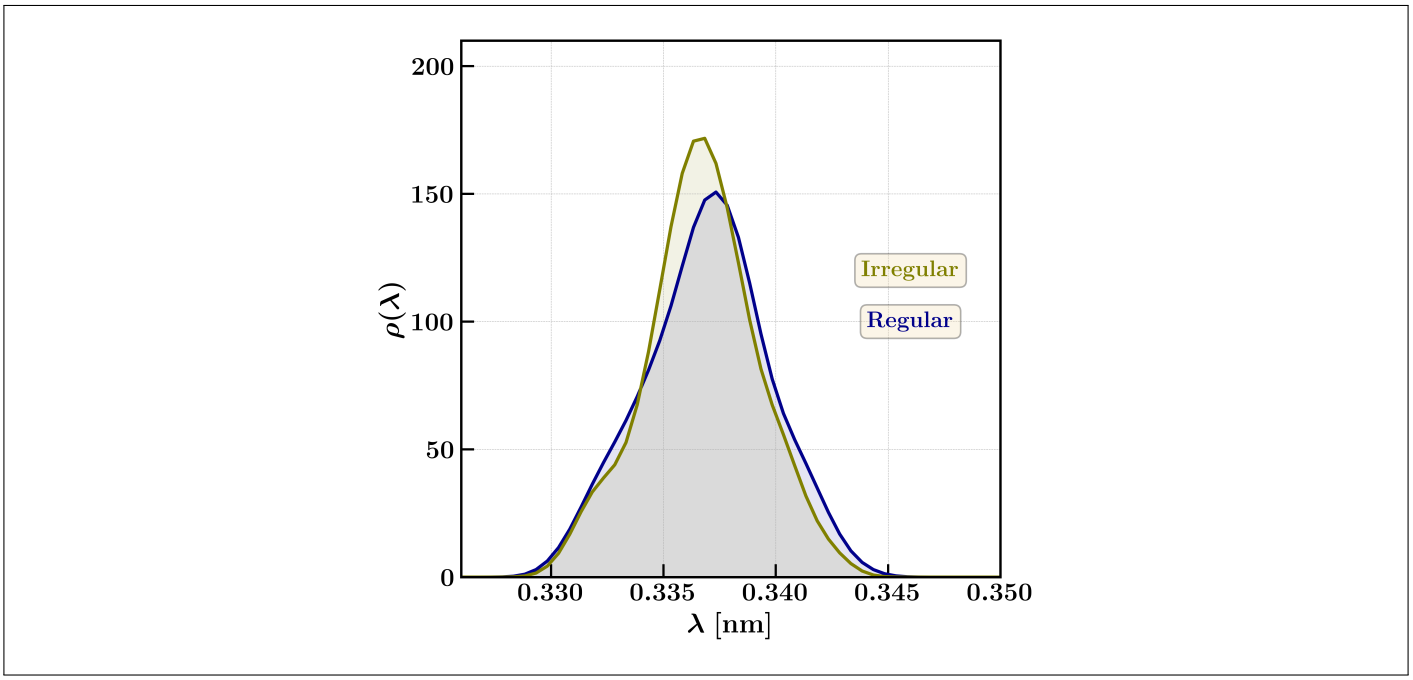


Fig. S9 π-π Stacking distribution of CPDT-BBT tetramer with regio-regular and regio-irregular lateral groups in chloroform solvent.

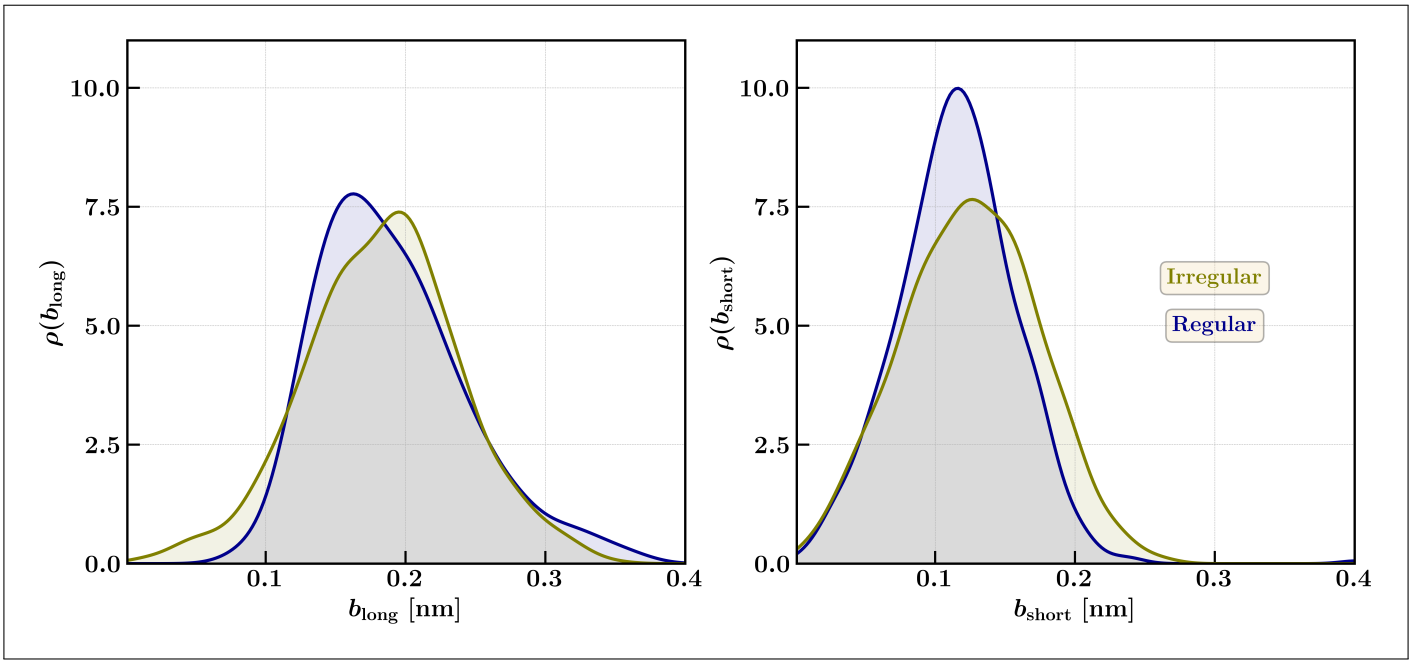


Fig. S10 The distribution of parallel displacement along the long-axis (left) and the short-axis (right) of CPDT-BBT with regio-regular and regio-irregular lateral groups in chloroform solvent.

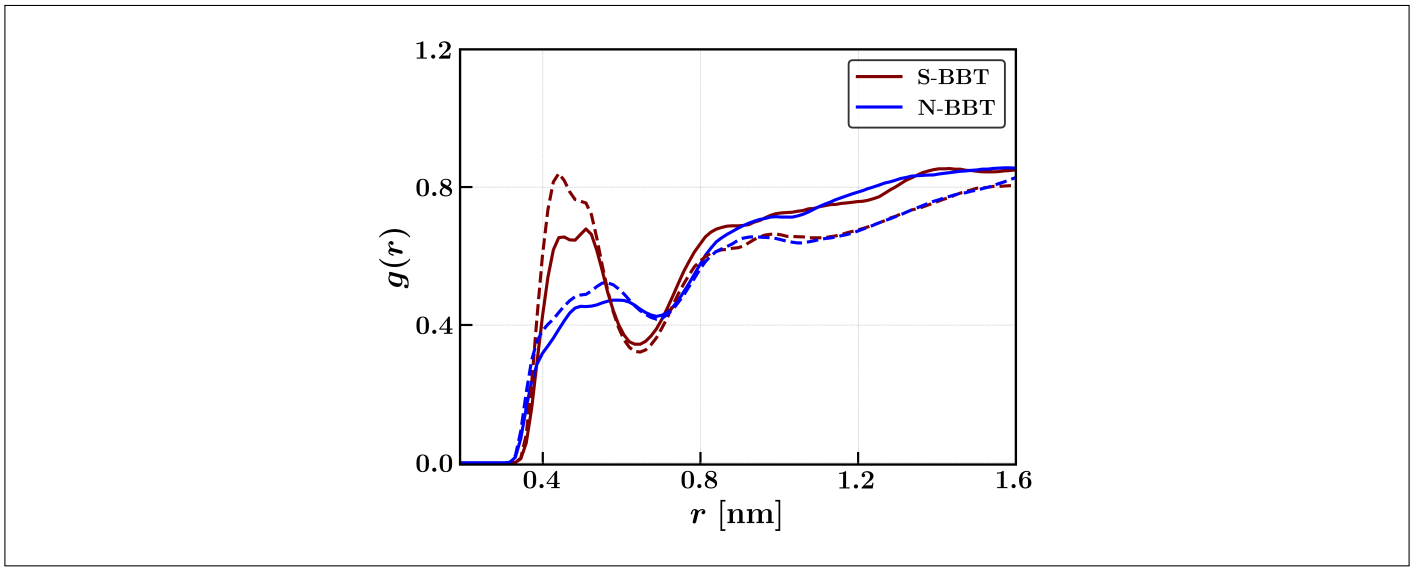


Fig. S11 Radial distribution function (RDF), $g(r)$, of solvent (chloroform) molecules around the regio-irregular CPDT-BBT tetramer. The RDF is plotted as a function of distance (r) between C-atoms of chloroform and S-atoms in BBT moieties (maroon), and C-atoms of chloroform and N-atoms in BBT moieties (blue). The solid and dashed lines represent the distribution for lateral groups pointed toward and opposite to the BBT (acceptor) moities, respectively.

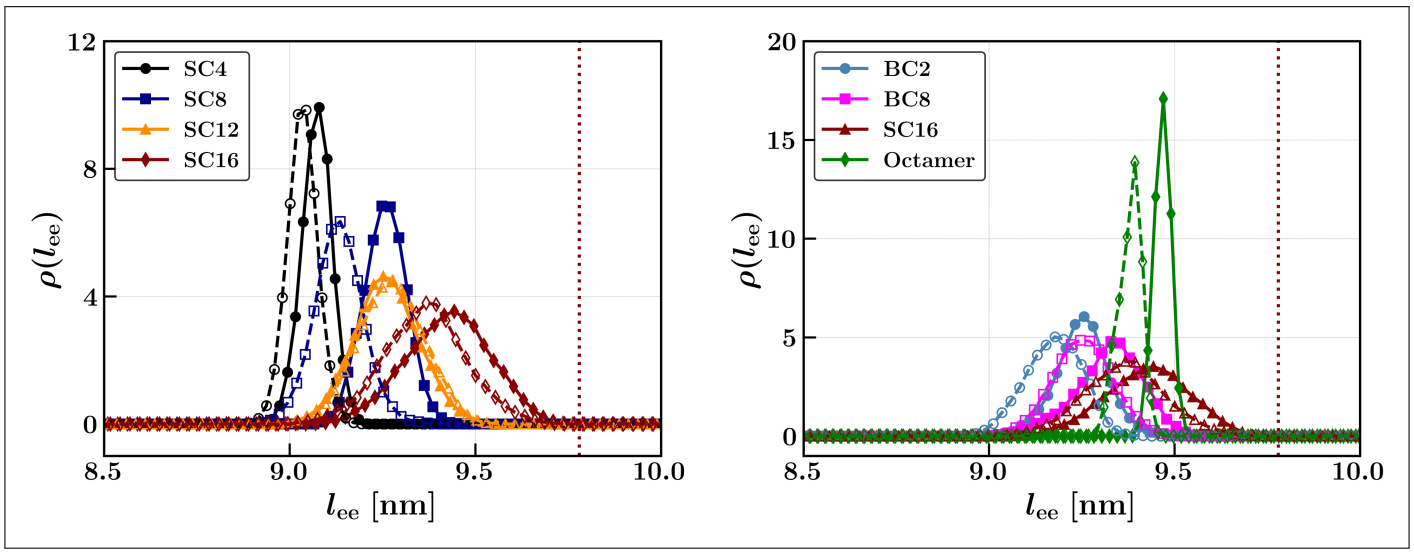


Fig. S12 End-to-end distance distribution ($\rho(l_{ee})$) of octamer with alkyl side chains of different length (C_4, C_8, C_{12} and C_{16} respectively denoted as SC4, SC8, SC12 and SC16.) (left) and of octamer with C_{16} side chains branched at different positions (C_2 and C_8 respectively denoted as BC2 and BC8) (right). The isolated single chain extended length of the octamer is indicated by the dotted vertical lines. Filled and unfilled markers are for $T = 298$ and 323 K, respectively.

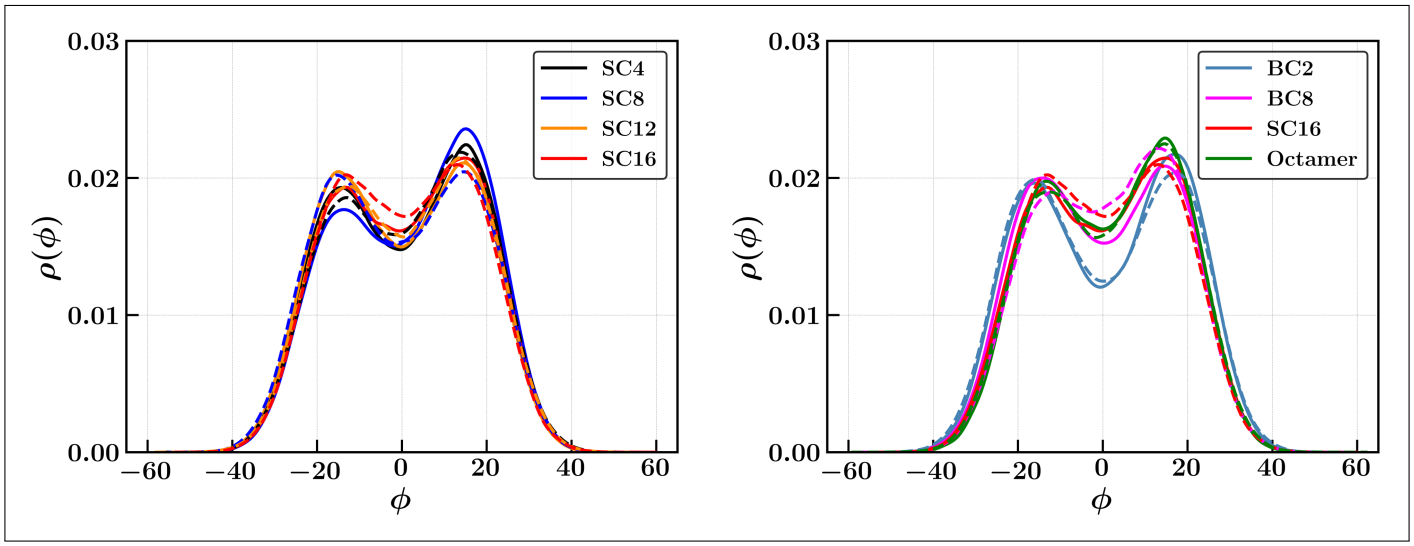


Fig. S13 Dihedral distribution ($\rho(\phi)$) of donor-acceptor adjoin angle (ϕ). Effect of linear alkyl side chain on $\rho(\phi)$ is shown left where side chain length varies from SC4 (C_4) to SC16 (C_{16}). The effect of branching position (at C_2 (BC2) and C_8 (BC8)) is compared with octamer of CPDT-BBT and CPDT-BBT with linear side chain of equal length C_{16} (SC16) is shown right. The solid and dashed lines represent the distribution at $T = 298$ and 323 K, respectively.

Table S4 Displacement distances of octamer with different side chains at two different temperatures, where b_{long} and b_{short} represent long and short displacements, respectively.

Chain length, n	$T = 298$ **K**		$T = 323$ **K**	
	b_{long} [Å]	b_{short} [Å]	b_{long} [Å]	b_{short} [Å]
Octamer ($n = 8$)	2.122 ± 0.020	0.702 ± 0.021	1.819 ± 0.157	1.192 ± 0.077
SC4	2.674 ± 0.354	1.413 ± 0.279	1.754 ± 0.034	1.396 ± 0.033
SC8	2.310 ± 0.032	1.079 ± 0.028	2.288 ± 0.067	1.539 ± 0.063
SC12	2.276 ± 0.051	1.348 ± 0.060	2.344 ± 0.059	1.504 ± 0.054
SC16	2.407 ± 0.045	1.138 ± 0.030	2.444 ± 0.031	1.152 ± 0.027
BC8	2.340 ± 0.055	1.359 ± 0.044	2.305 ± 0.032	1.173 ± 0.034

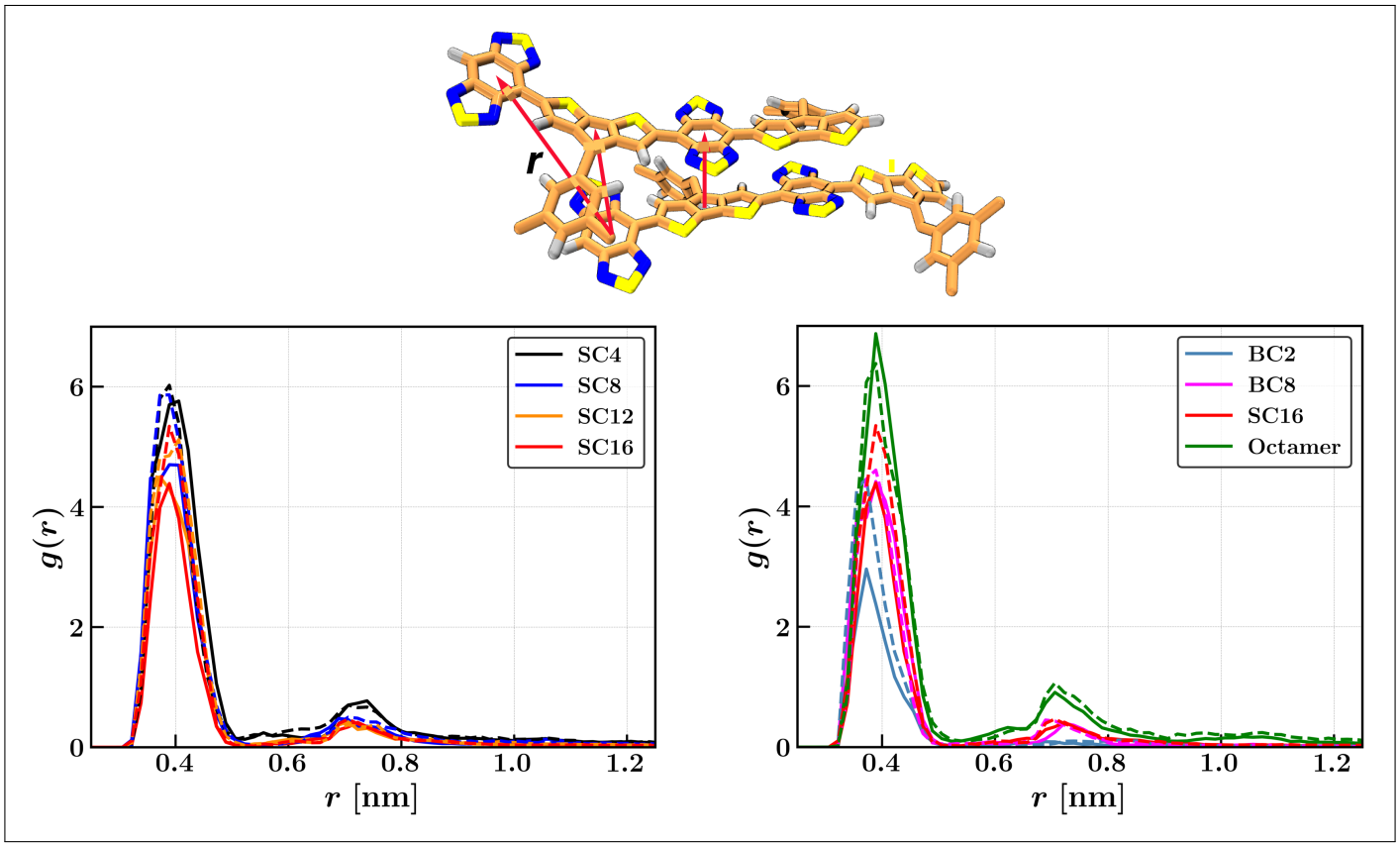


Fig. S14 Inter-chain RDFs ($g(r)$) for the aromatic ring-center belonging to the CPDT-BBT backbone with different side chains. SC represents the linear alkyl side chain and associated number is for the number of carbon in the chain. BC represents the branched alkyl side chain and associated number indicates the branching position. The solid and dashed lines represent the distribution at T = 298 and 323 K, respectively.

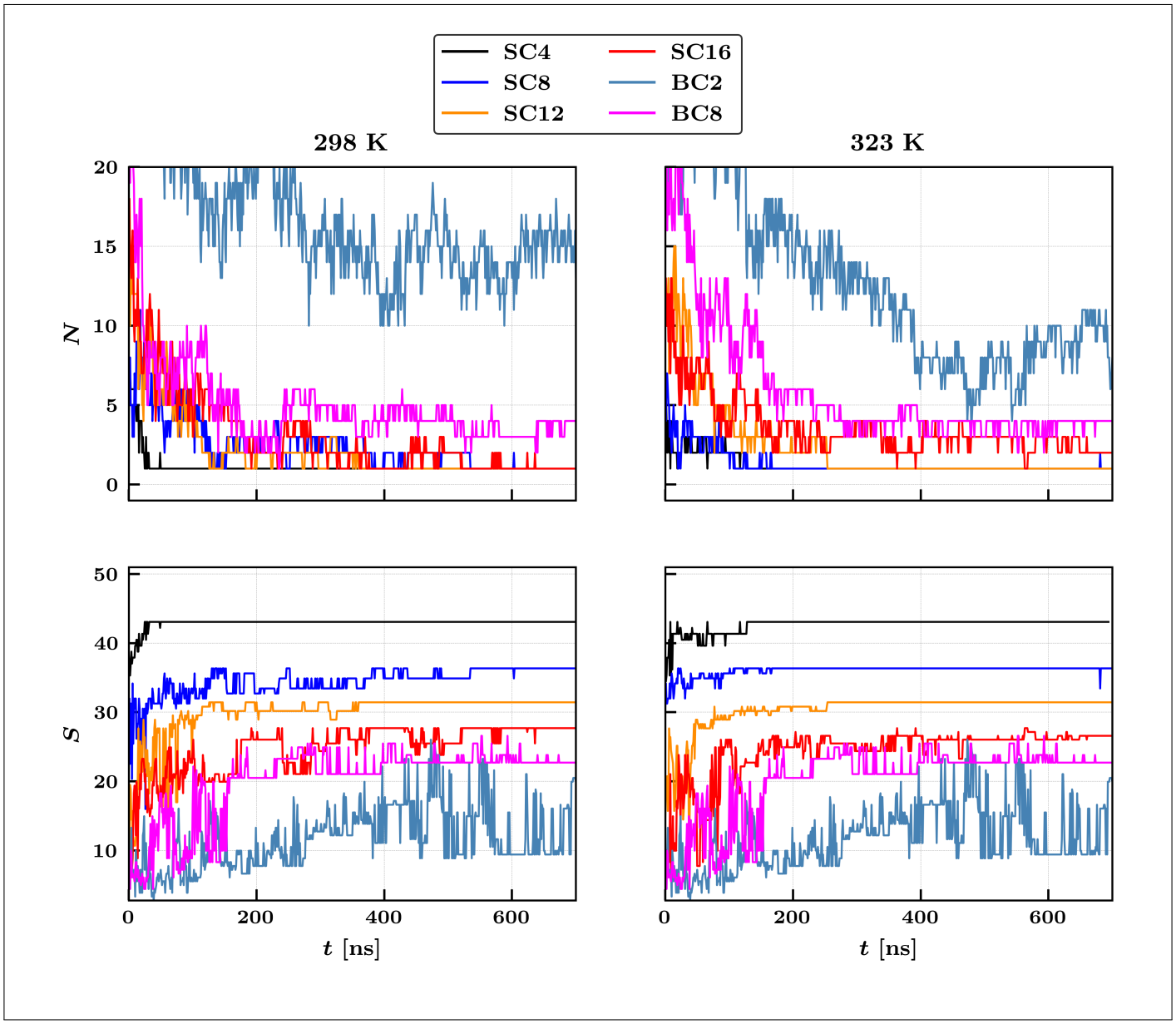


Fig. S15 The growth of cluster in terms of number of clusters (N) and size of the largest cluster (S), as the number of oligomers in the cluster, are plotted as the simulation time (t) progress. Left column for $T = 298$ K and right column for $T = 323$ K. Linear alkyl side chains designated as SC and size is represented as the number of carbons (i.e. C_4 as SC4). Branched alkyl side chain designated as BC and the number represents the branching position (i.e. branching at position 2 of alkyl chain as BC2).