Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Supplementary Information

## Conformational and Aggregation Properties of PffBT4T Polymers: Atomistic Insight into the Impact of Alkyl-Chain Branching Positions

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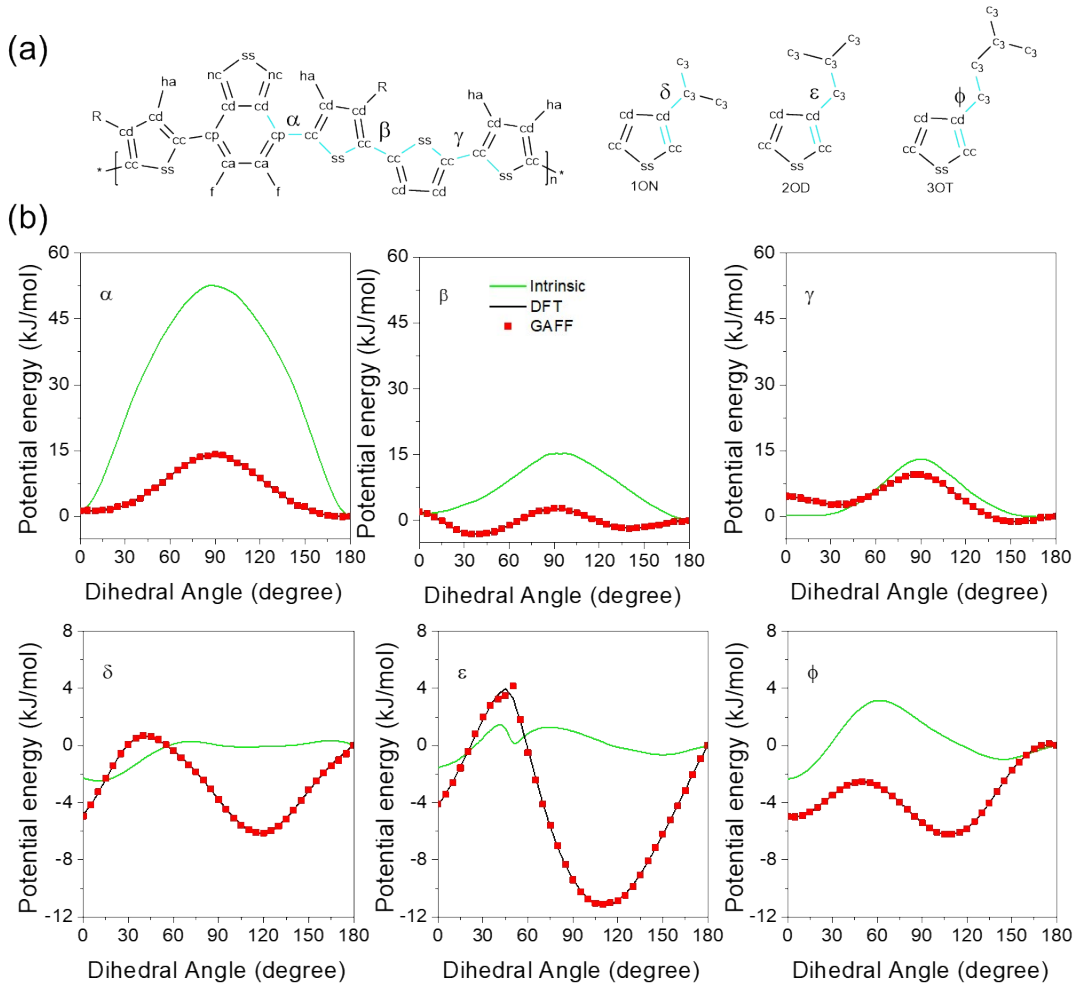


**Fig. S1** (a) Definition of atomic types for PffBT4T-based polymers using the general AMBER force field (GAFF). The hidden hydrogen and carbon atoms on alkyl chains are defined as hc and c3, respectively. (b) Potential energies for dihedrals highlighted in (a) calculated by DFT at the ωB97XD/6-31G(d,p) level and GAFF along with the fitted intrinsic torsion potential.

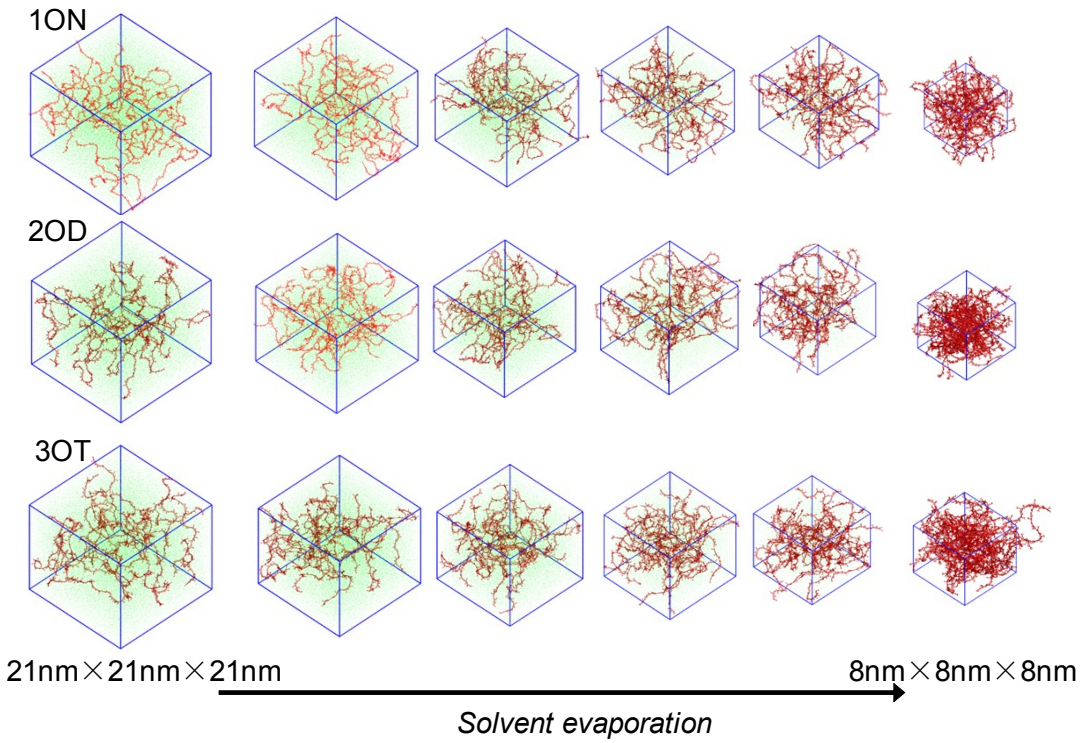


**Fig. S2** Construction of a polymer solution and simulations of the supramolecular self-assemblies of polymer chains during solvent evaporation (CB: chlorobenzene). The initial box sizes are all set to be about 23nm×23nm×23nm, after equilibrium, the boxes size of the three systems in solvent and thin film are all about 21nm×21nm×21nm and 8nm×8nm×8nm, respectively, they are all larger than the equilibrium length of the polymers. For clarity, the alkyl chains after the branched positions are shortened to methyl groups, and all hydrogen atoms are omitted.

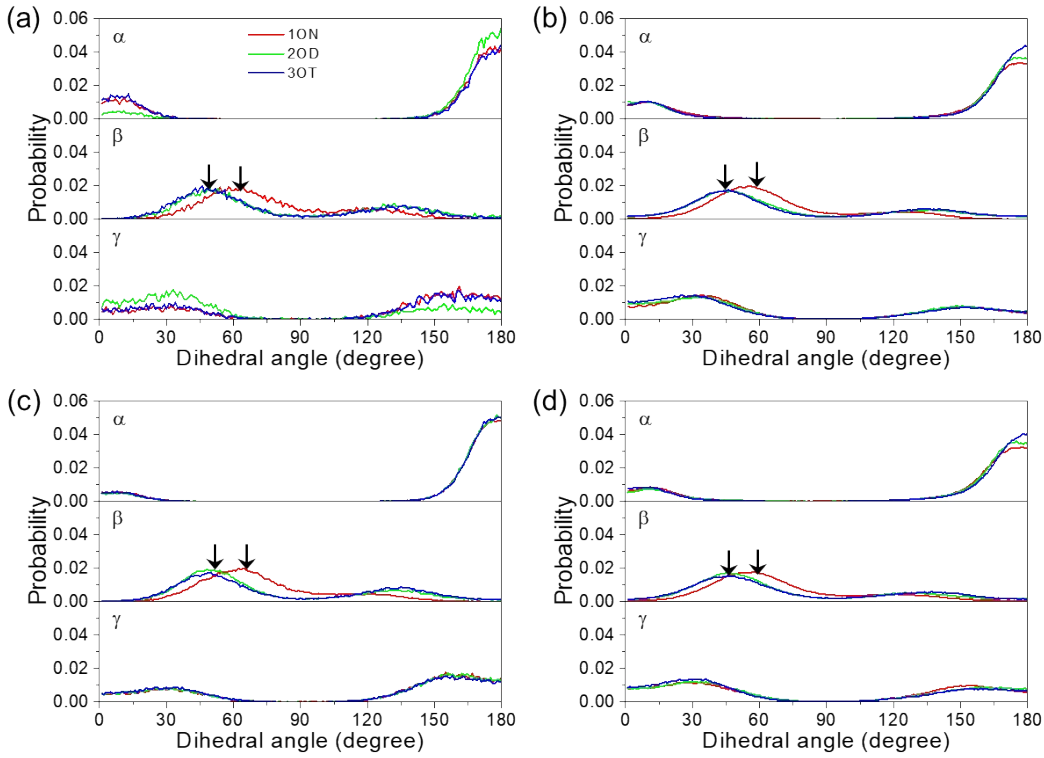


**Fig. S3** Distribution of the dihedral angles α, β, and γ along the π-conjugated backbone extracted from (a) single polymer chain in solution, (b) 30 polymer chains in neat film, (c) 30 polymer chains in solution with $PC_{71}BM$ molecules, and (d) 30 polymer chains in blending film at room temperature (300 K).

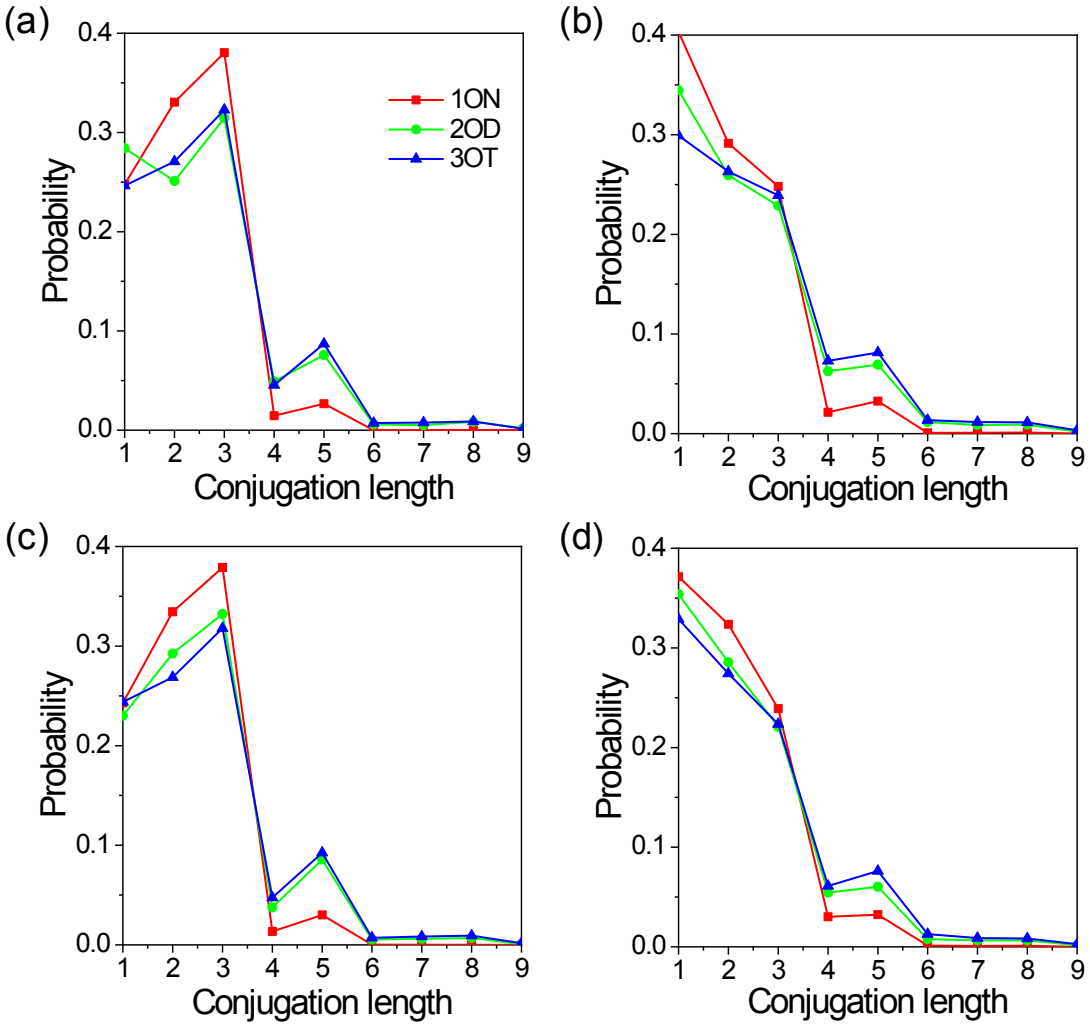


**Fig. S4** Probability of conjugation length for (a) single polymer chain in solution, (b) 30 polymer chains in neat film, (c) 30 polymer chains in solution with $PC_{71}BM$ molecules, (d) 30 polymer chains in blending film.

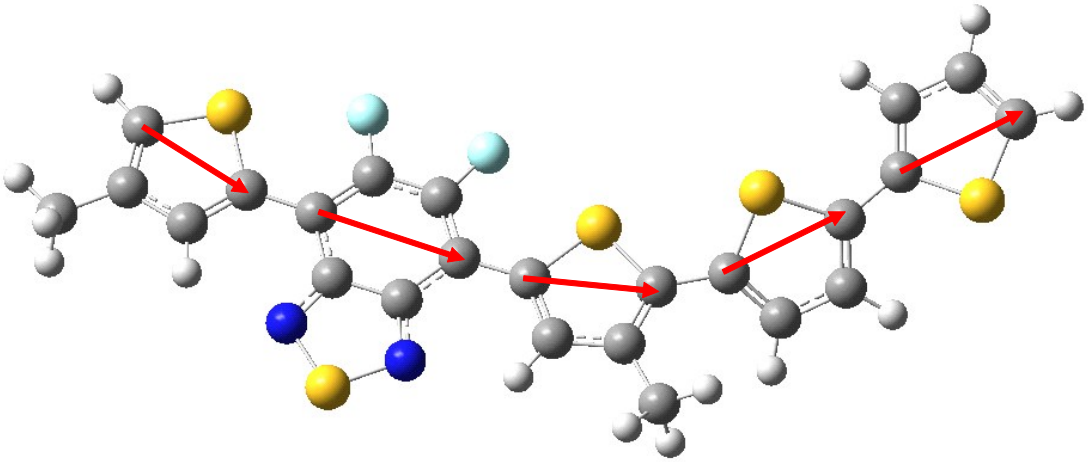

**Fig. S5** Schematic representation of a PffBT4T segment and the definition of persistence length vector used in persistence length calculations.

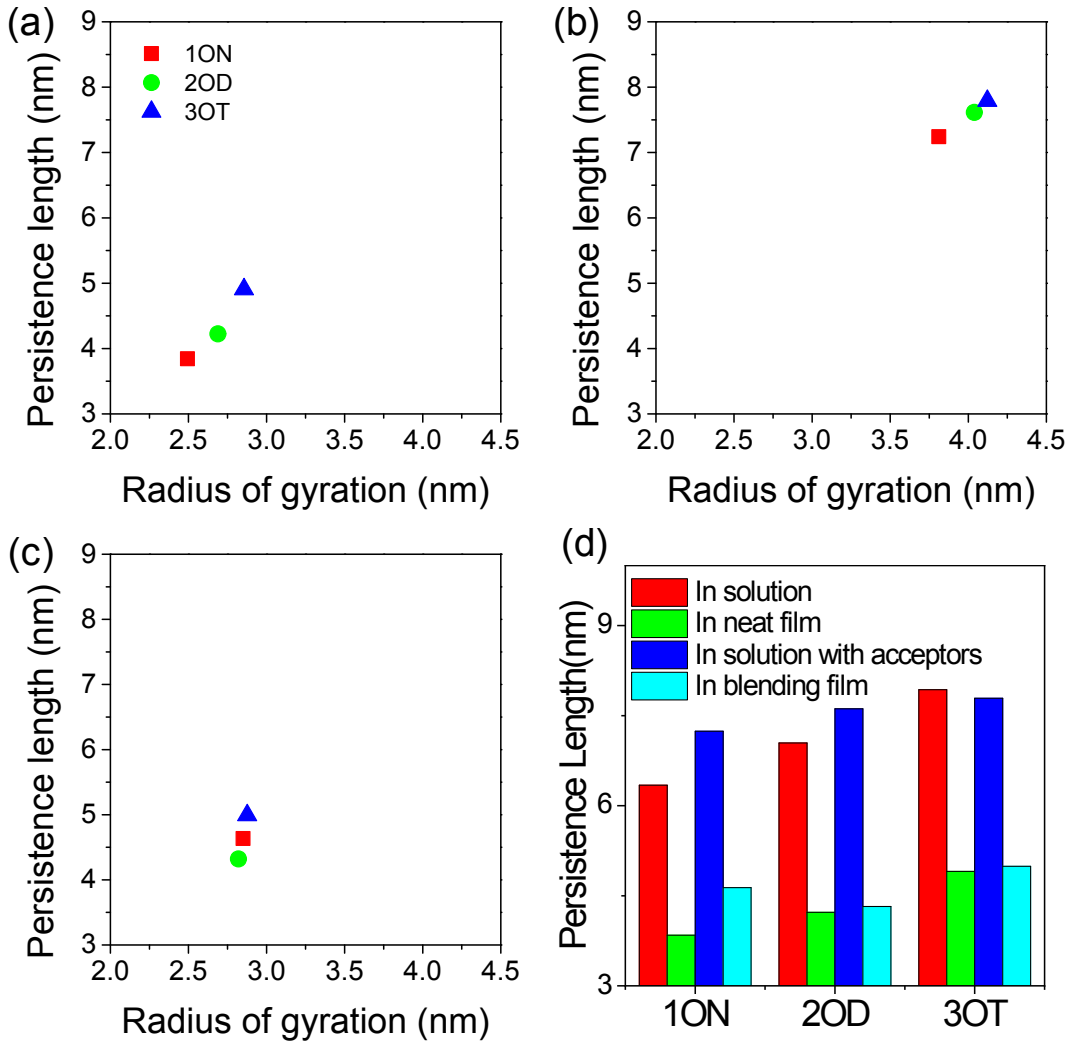


**Fig. S6** Average persistence length versus average radius of gyration for (a) 30 polymer chains in neat film, (b) 30 polymer chains in solution with $PC_{71}BM$ molecules, and (c) 30 polymer chains in blending film. (d) Average persistence length for 30 polymer chains in different cases.

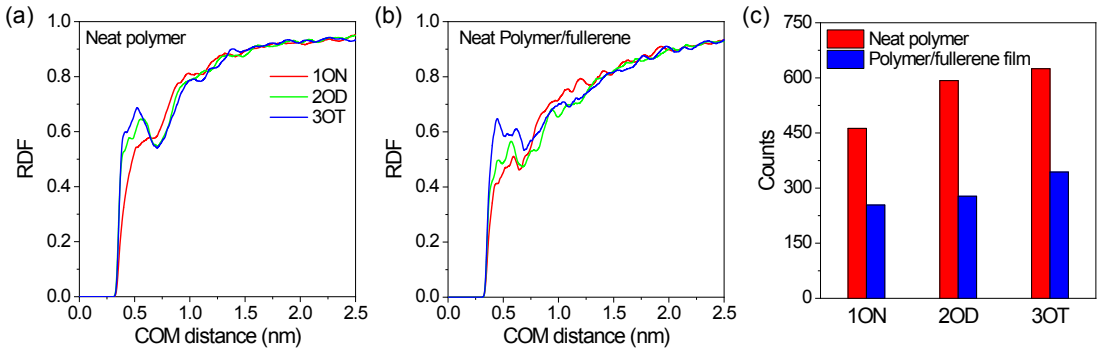


**Fig. S7** Inter-chain radial distribution functions (RDFs) of conjugated rings in the polymer backbones in (a) neat polymer film and (b) polymer/$PC_{71}BM$ film. (c) The number of local π-π stacks in neat polymer film and polymer/$PC_{71}BM$ film (the pair of inter-chain rings is treated as a local π-π stack if the center-of-mass distance is < 0.5 nm).