PCDTBT: Accurate Force Field Derivation and Molecular Dynamics Simulation

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π-Conjugated polymers are essential building blocks in a bulk heterojunction architecture for organic solar cells. Polymer poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] known as PCDTBT (Fig. 1a) is a carbazole based co-polymer, with a donor-acceptor structure. It consists of electron-donating and electron-withdrawing subunits and features a low band gap. In this work we apply ab-initio computations to construct an accurate force field for modelling PCDTBT at the fully atomistic level. More specifically, the LC-ωPBE long range corrected functional along with the 6-31G(d,p) basis set were employed to extract torsional profiles around the PCDTBT backbone. These were subsequently used to reparametrize the General Amber Force Field [1]. In order to validate the new parameterization a series of large-scale Molecular Dynamics simulations were performed at different chain lengths and different initial conditions. The calculated mass density at 300K is close to experimental measurements [2] and in addition, predictions on conformational properties namely persistence length (Fig. 1b), Kuhn length and conjugation length are compatible with existing experimental literature [3]. The outcome from Molecular Dynamics simulations suggests that the improved force field can reproduce successfully essential properties of PCDTBT which are relevant in further modelling of this polymer as a donor material in an organic photovoltaic device.

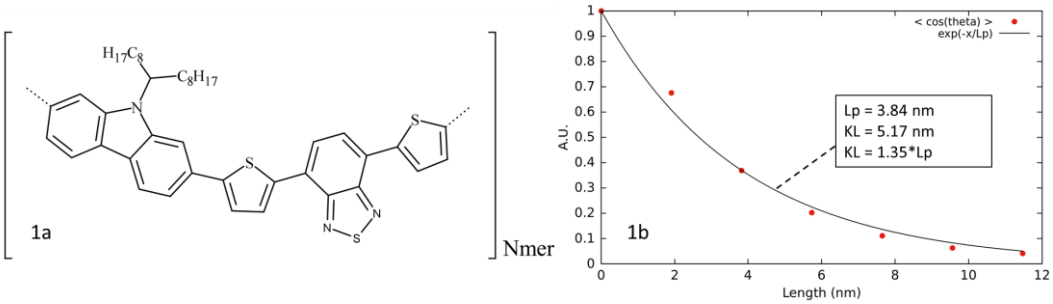

Figure 1: PCDTBT polymer (Fig. 1a) and PCDTBT persistence length (Lp) and Kuhn length (KL) (Fig. 1b).

References

[1] Wang, J., Wolf, R. M.; Caldwell, et al. “Development and testing of a general AMBER force field”. *J. Comput. Chem.*, **2004**, 25, 1157-1174.
[2] Martin Streiter, Daniel Beer, Fabian Meier et al. “Homocoupling Defects in a Conjugated Polymer Limit Exciton Diffusion”. *Adv. Func. Mater.*, **2019**, 29, 46.
[3] Pieter van der Scheer, Ties van de Laar & Joris Sprakel. “Chain length-dependent luminescence in acceptor-doped conjugated polymers”. *Sci. Rep.*, **2019**, 9, 11217.