Atomistic Simulations of P(NDI2OD-T2) Morphologies: from Single Chain to Condensed Phases

Supporting Information

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1 Force Field

In the Amber force field, the torsionals are expressed as a sum of harmonic terms such as:

$$U(\phi) = \sum_{i=1}^{n} A_i [1 + cos(m_i \phi - \delta_i)] \tag{1}$$

Keeping the functional form unaltered, we have modified this force field by substituting the potential parameters for some dihedrals with:

$$U(\phi_{ss-cc-cc-ss}) = 0.19[1 + cos(\phi - 14)] + 1.80[1 + cos(2\phi - 190)]$$
$$+0.04[1 + cos(3\phi - 18)] + 0.33[1 + cos(4\phi - 361)] \tag{2}$$

$$U(\phi_{ss-cc-ca-ca}) = 1.47[1 + cos(2\phi - 150)] \tag{3}$$

$$U(\phi_{cd-cc-cc-ss}) = 0 \tag{4}$$
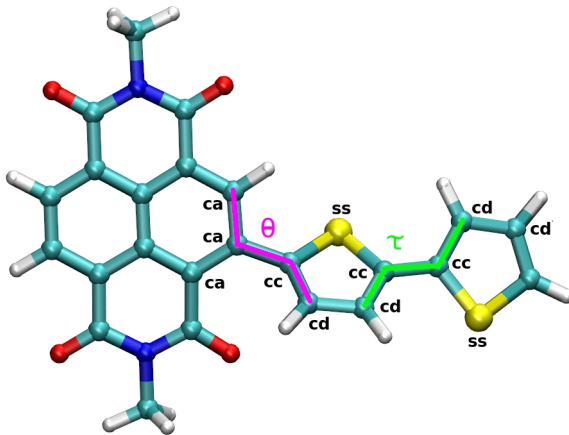
$$U(\phi_{cd-cc-cc-cd}) = 0 \tag{5}$$

Figure 1: Atom labeling for the definition of the potential parameters.

In Fig.2,3 we report the comparison between the PEP obtained *ab initio* and with the two force fields. In particular, Fig.2 shows the *unrelaxed* PEP, while Fig.3 shows the *relaxed* PEP. The *unrelaxed* PEP is obtained *ab initio* by rigidly rotating the two planes defining either
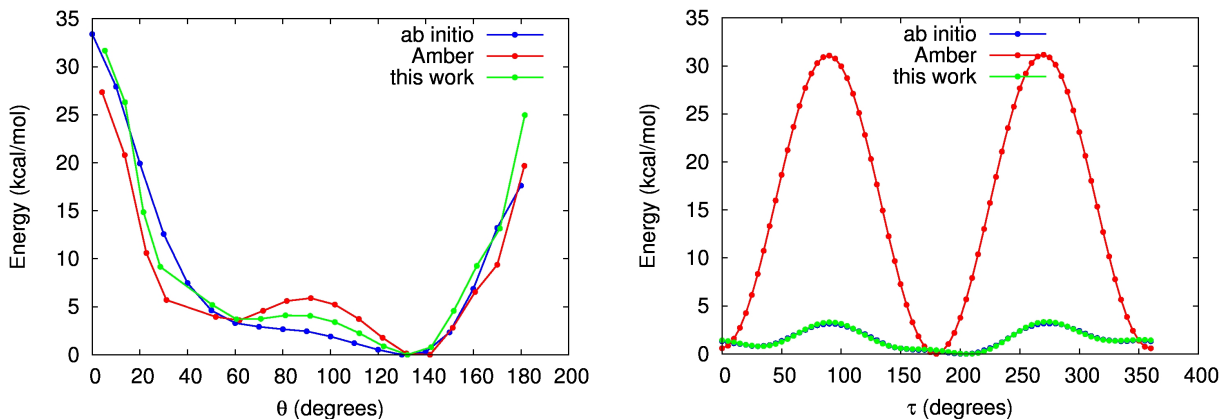
Figure 2: Comparison between the unrelaxed PEP obtained *ab initio*, with the Amber force field and with our new force field for the two dihedral angles θ (left) and τ (right)
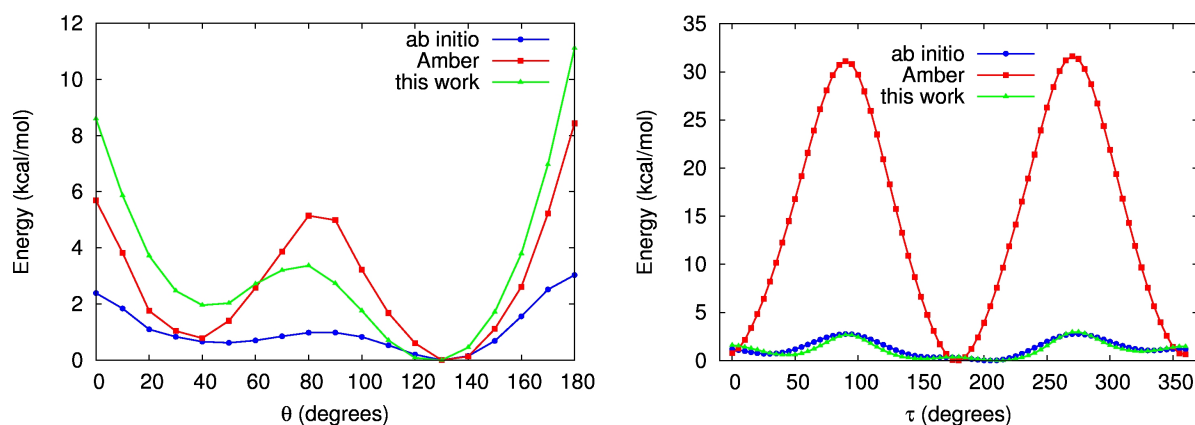

Figure 3: Comparison between the relaxed PEP obtained *ab initio*, with the Amber force field and with our new force field for the two dihedral angles θ (left) and τ (right)

the NDI2OD and T2 units (for angle θ) or the two thiophenes (for angle τ) and calculating the potential energy for each conformation without any geometry minimization (only the wavefunction is relaxed): this procedure gives high energy barriers since all the atoms of the molecules are constrained and high repulsions are possible in some configuration. The classical *unrelaxed* PEP is obtained starting from the DFT *unrelaxed* configurations for all angles, keeping the atoms which are involved in the dihedral fixed at the *ab initio* positions and performing a conjugate gradient minimization.

Conversely, the *relaxed* PEP (Fig.3) has been obtained *ab initio* by performing a geometry minimization while constraining only the dihedral of interest. In this way, the atoms which

are not involved in the dihedral can rearrange in order to lower the energy. The classical PEP for angle τ has been obtained starting from the DFT *relaxed* configurations, by (i) constraining the dihedral (and not the atoms as in the unrelaxed case) and performing a conjugate-gradient minimization (ii) releasing the constraint and calculating the energy for that configuration. For angle θ, during phase (i) we have also performed a low-temperature dynamics until the energy had reached an equilibrium value (10 ps), in order to achieve a better relaxed configuration.

For the relaxed curves, however, absolute energy barriers obtained with a classical, fixed-charges potential are expected to be higher than their *ab initio* counterparts. Here, this phenomenon is particularly evident for dihedral angle θ. The reason of these differences can be explained by considering that for some configurations a charge displacement would be required in order to keep the energy low. This is not possible in a fixed-charges potential, and a complete reparametrization of the force field (which includes charges, van der Waals parameters etc.) would be needed to reproduce the absolute barriers. Here we have chosen to modify only the dihedrals part of the potential, focusing on keeping the shape of the PEP and the ratio between the barriers heights as similar as possible to the *ab initio* curve. In particular, it is important to have a small barrier for $\theta = 90°$, since a high barrier would hinder the monomer torsions which are responsible for the self-aggregation of long chains.

2   Diffusion coefficients

The values of D have been calculated in two ways: (i) by simple fitting of $MSD(t)$ along a 10 ns trajectory with the function $f(t) = 6Dt$; (ii) by fitting all the possible sub-trajectories of $MSD(t)$ and averaging the resulting values of D. An example of $MSD(t)$ plots for 12 sub-trajectories is shown in Figure 4. Table 1 reports the values calculated with the two methods.
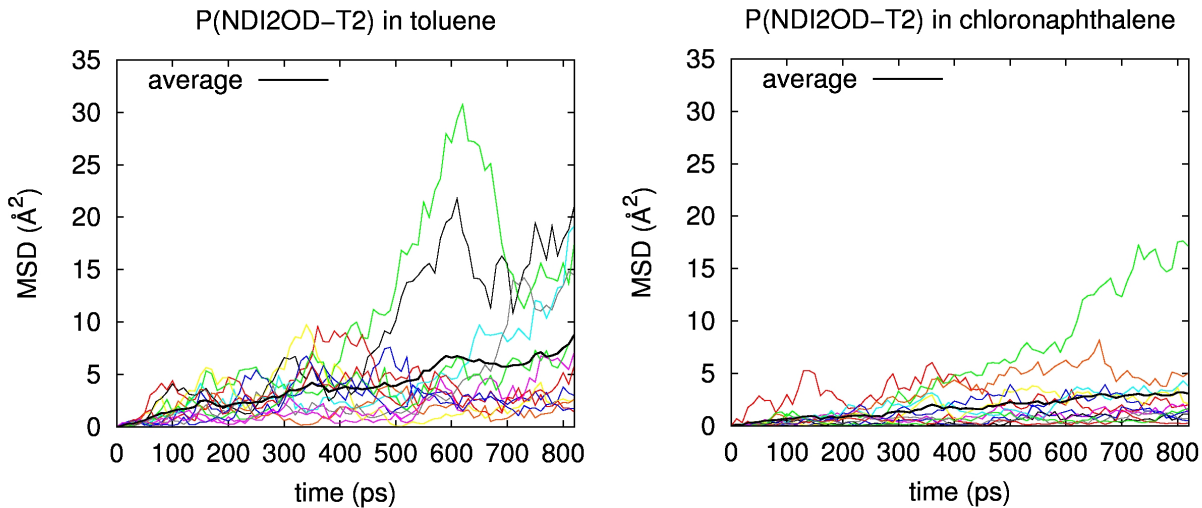
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Figure 4: Mean squared displacement curves as obtained from averaging 12 sub-trajectories of P(NDI2OD-T2) in toluene (left) and chloronaphthalene (right). Black thick lines represent the average MSD.

Table 1: **P(NDI2OD-T2) diffusion coefficients as calculated with the two methods explained above.**

	D (10^{-7}cm^2/s)	
solvent	10 ns trajectory	all sub-trajectories
toluene	1.31	1.36
chloronaphtalene	0.93	1.04

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3 References

Full citation for Gaussian 09:

Gaussian 09, Revision D.01; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox. Gaussian, Inc., Wallingford, CT, 2009.