SUPPLEMENTARY INFORMATION

Self-assembly of donar-accepter semiconductor polymers in thin solution films: molecular dynamics simulation study

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S.1 GROMACS molecular topology file

The GROMACS molecular topology file with parameters of the GAFF force field [1] in the following form [2],

$$\begin{aligned} V_{total} &= \sum_{bonds} \frac{k_r}{2}(r - r_{eq})^2 \\ &+ \sum_{angles} \frac{k_\theta}{2}(\theta - \theta_{eq})^2 \\ &+ \sum_{dihedrals} k_\phi\{1 + \cos(n\phi - \phi_0)\} \\ &+ \sum_{atomic\ pairs} \left[4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right\} + \frac{q_i q_j}{4\pi\varepsilon r_{ij}} \right], \end{aligned}$$

can be found in the separate supplementary information file.

S.2 Comparison of simulated crystal cell parameters of NTz2T-Me with XRD study values

Comparison of simulated crystal cell parameters of NTz2T-Me with XRD study values [3] is shown in Table S1.

Table S1: Comparison of simulated crystal cell parameters with XRD study values.

-	a(nm)	b(nm)	c(nm)	α(degree)	β(degree)	γ(degree)
XRD (293 K)	1.17957	0.85620	1.88140	90.000	106.720	90.000
MD* (293 K)	1.32117	0.80617	1.93033	90.745	107.860	90.020
MD (293 K)	1.16526	0.83516	1.91063	88.997	106.995	90.023

In this table, the line with MD* corresponds to the results with original general AMBER (GAFF) parameters. In this case, simulated cell parameters were obtained with a maximum deviation of 12% (in a-axis) from the values reported in the XRD study. Whereas, the line with MD corresponds to the results with replacing the sulfur Lennard-Jones parameters to those of the GROMOS force field [4] with following our previous study [5]. Simulated cell parameters were obtained with a maximum deviation of 2.5% (in b-axis) from the XRD values and it is acceptable for the current purpose. We thus utilized the GROMOS sulfur parameters for the rest of the studies.

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S.3 PNTz4T packing views without chains

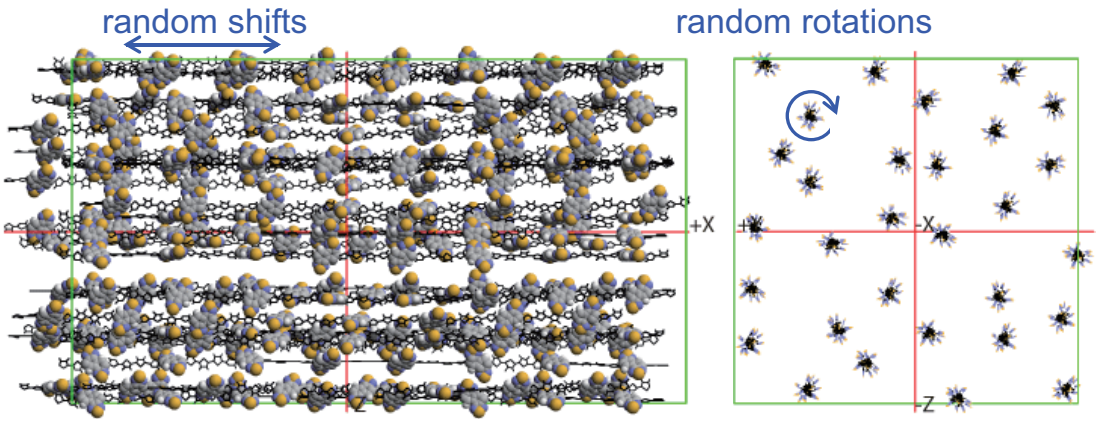

Figure S1: PNTz4T packing views without chains for clarity. Left): View along z axis. Right): View along x axis.

S.4 Validation of the DCB solvent model used in this study.

We tested our DCB solvent model with simulation at the room temperature under normal pressure. Our DCB model is similar to the one in the literature [6] which also modeled with the general AMBER force field. The initial structure was firstly made by random placements of 512 DCB molecules within a cubic box by using GROMACS utility program genbox, and then stacking it twice in the three coordinate directions to make the system with 4096 molecules. Time evolution of the density is shown in the following.

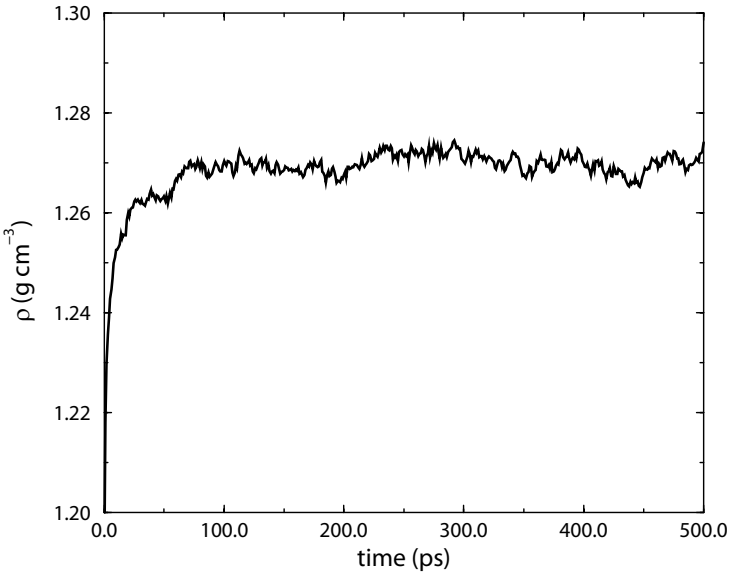

Figure S2: Time evolution of the density of the pure DCB solvent simulation.

Averaged density over the last 100 ps was 1.27 g cm^{-3} which is slightly (2.3 %) lower than the experimental value 1.3 g cm^{-3} [6] and it is acceptable for the current purpose.

S.5 Time evolution of the order parameter in four times smaller PNTz4T concentration than the simulation shown in Figure 7.

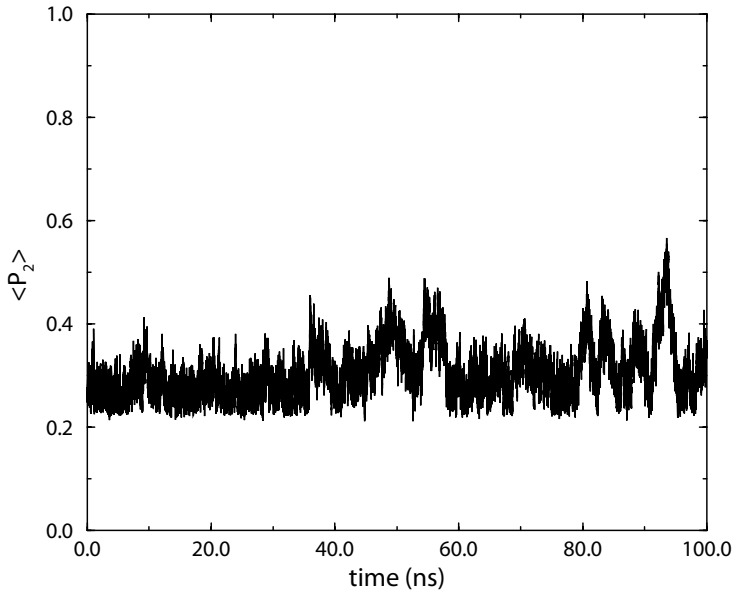

Figure S3: Time evolution of the orientational order parameter $< P_2 >$ of the PNTz4T accepter part core vectors.

S.6 Comparison of simulated crystal cell parameters of $PC_{61}BM$ with XRD study values

Comparison of simulated crystal cell parameters of $PC_{61}BM$ with XRD study values [7, 8] is shown in Table S2.

Table S2: Comparison of simulated crystal cell parameters with XRD study values.

-	a(nm)	b(nm)	c(nm)	α(degree)	β(degree)	γ(degree)
XRD (100 K)	13.47	15.10	19.01	90.00	106.9	90.00
MD (100 K)	13.60	16.44	18.71	90.00	105.5	90.01

Simulated cell parameters were obtained with a maximum deviation of 8.9% (in b-axis) from the XRD values and it is acceptable for the current purpose.

S.7 Time evolution of the order parameter during the simulation shown in Figure 13.

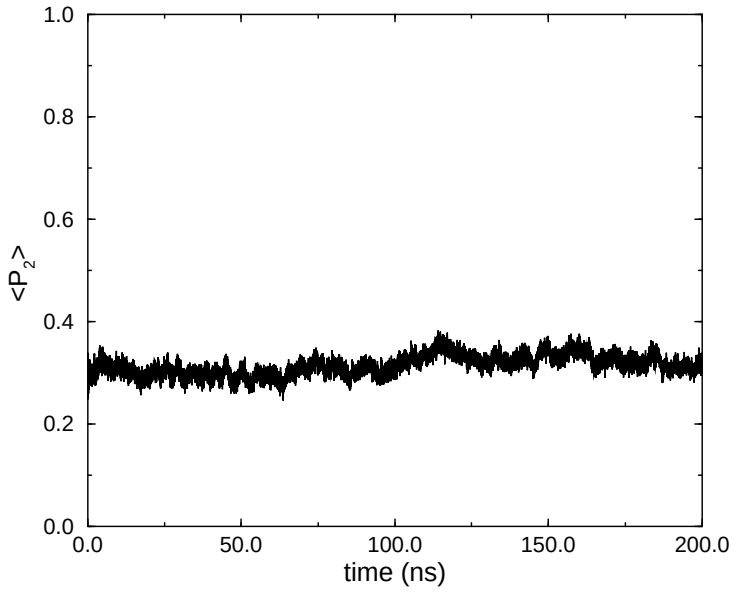

Figure S4: Time evolution of the orientational order parameter $< P_2 >$ of the PNTz4T accepter part core vectors.

References

[1] Junmei Wang, Romain M. Wolf, James W. Caldwell, Peter A. Kollman, and David A. Case. Development and testing of a general Amber force field. *J. Comput. Chem.*, 25:1157, 2004.

[2] B. Hess, C. Kutzner, D. Van Der Spoel, and E. Lindahl. GROMACS 4: Algorithms for highly efficient, load-balanced, and scalable molecular simulation. *J. Chem. Theory Comput.*, 4(3):435–447, 2008.

[3] Itaru Osaka, Masafumi Shimawaki, Hiroki Mori, Iori Doi, Eigo Miyazaki, Tomoyuki Koganezawa, and Kazuo Takimiya. Synthesis, characterization, and transistor and solar cell applications of a naphthobisthiadiazole-based semiconducting polymer. *Journal of the American Chemical Society*, 134(7):3498–3507, 2012.

[4] Lukas D Schuler, Xavier Daura, and Wilfred F Van Gunsteren. An improved gromos96 force field for aliphatic hydrocarbons in the condensed phase. *Journal of Computational Chemistry*, 22(11):1205–1218, 2001.

[5] Satoru Inoue, Hiromi Minemawari, Jun'ya Tsutsumi, Masayuki Chikamatsu, Toshikazu Yamada, Sachio Horiuchi, Mutsuo Tanaka, Reiji Kumai, Makoto Yoneya, and Tatsuo Hasegawa. Effects of substituted alkyl chain length on solution-processable layered organic semiconductor crystals. *Chemistry of Materials*, 27(11):3809–3812, 2015.

[6] James S Peerless, G Hunter Bowers, Albert L Kwansa, and Yaroslava G Yingling. Fullerenes in aromatic solvents: Correlation between solvation-shell structure, solvate

formation, and solubility. *The Journal of Physical Chemistry B*, 119(49):15344–15352, 2015.

[7] Giuseppe Paternò, Anna J Warren, Jacob Spencer, Gwyndaf Evans, Victoria García Sakai, Jochen Blumberger, and Franco Cacialli. Micro-focused x-ray diffraction characterization of high-quality [6, 6]-phenyl-c 61-butyric acid methyl ester single crystals without solvent impurities. *Journal of Materials Chemistry C*, 1(36):5619–5623, 2013.

[8] Mosè Casalegno, Stefano Zanardi, Francesco Frigerio, Riccardo Po, Chiara Carbonera, Gianluigi Marra, Tommaso Nicolini, Guido Raos, and Stefano Valdo Meille. Solvent-free phenyl-c61-butyric acid methyl ester (pcbm) from clathrates: insights for organic photovoltaics from crystal structures and molecular dynamics. *Chemical Communications*, 49(40):4525–4527, 2013.