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

Supporting Information

Boosting Electron Mobilities of Dimeric Perylenediimides by Simultaneously Enhancing Intermolecular and Intramolecular Interactions

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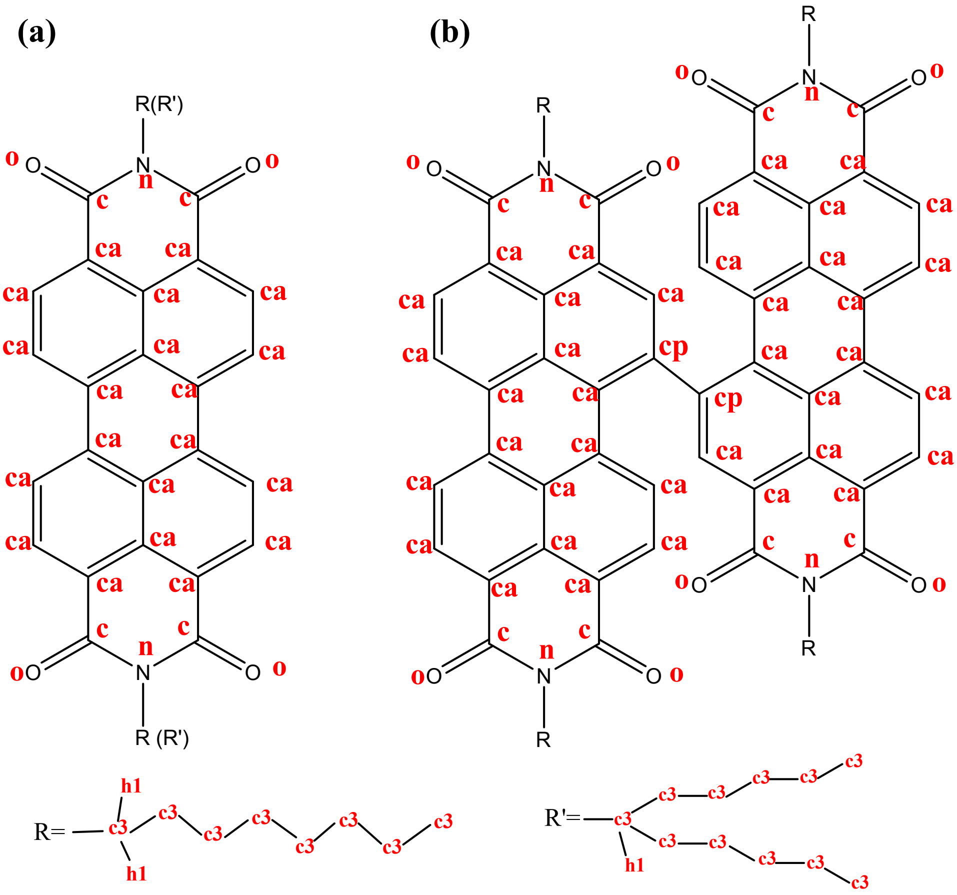
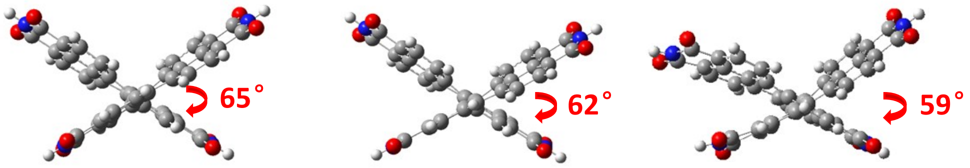


Figure S1. Atomic type definition for M1, M2, DN1/DN2 (a) and DC1/DC2 (b) from the general AMBER force field. The hidden hydrogen atoms on the c3 and ca atoms are defined as hc and ha, respectively.

(a) minimum 1



(b) minimum 2

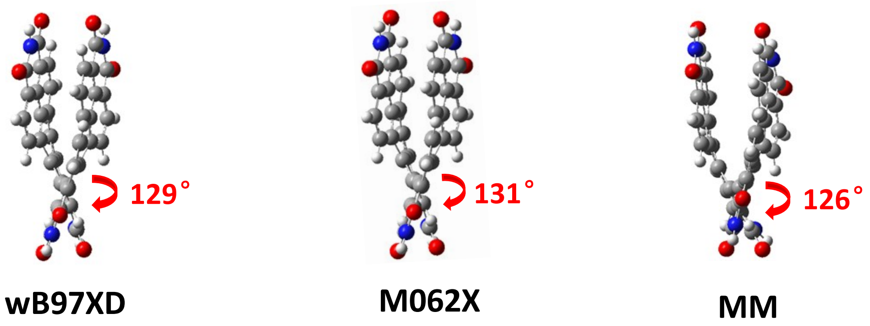


Figure S2. Two local minimum geometries of the π-conjugated backbone of DC1/DC2 optimized by different levels of methods (wB97XD, M062X, and MM), which are similar to those obtained by B3LYP-D3 provided in Figure 2a of the main manuscript.

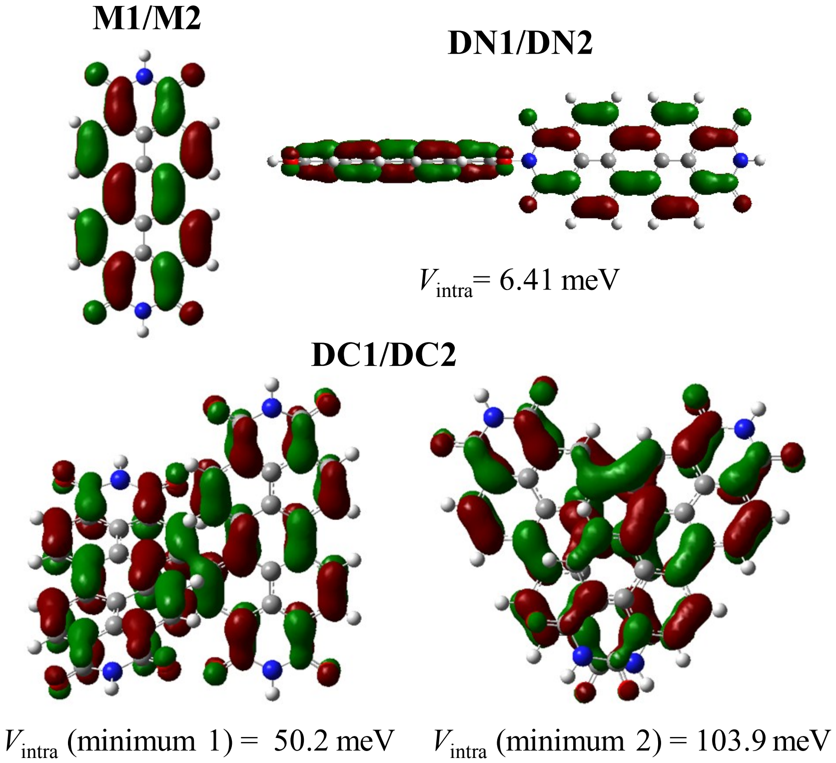


Figure S3. Pictorial representation of the LUMO of the π-conjugated backbones of the monomeric and dimeric PDIs and the intramolecular electronic couplings for the N-N and C-C bonding dimeric PDIs calculated by the ZINDO method.

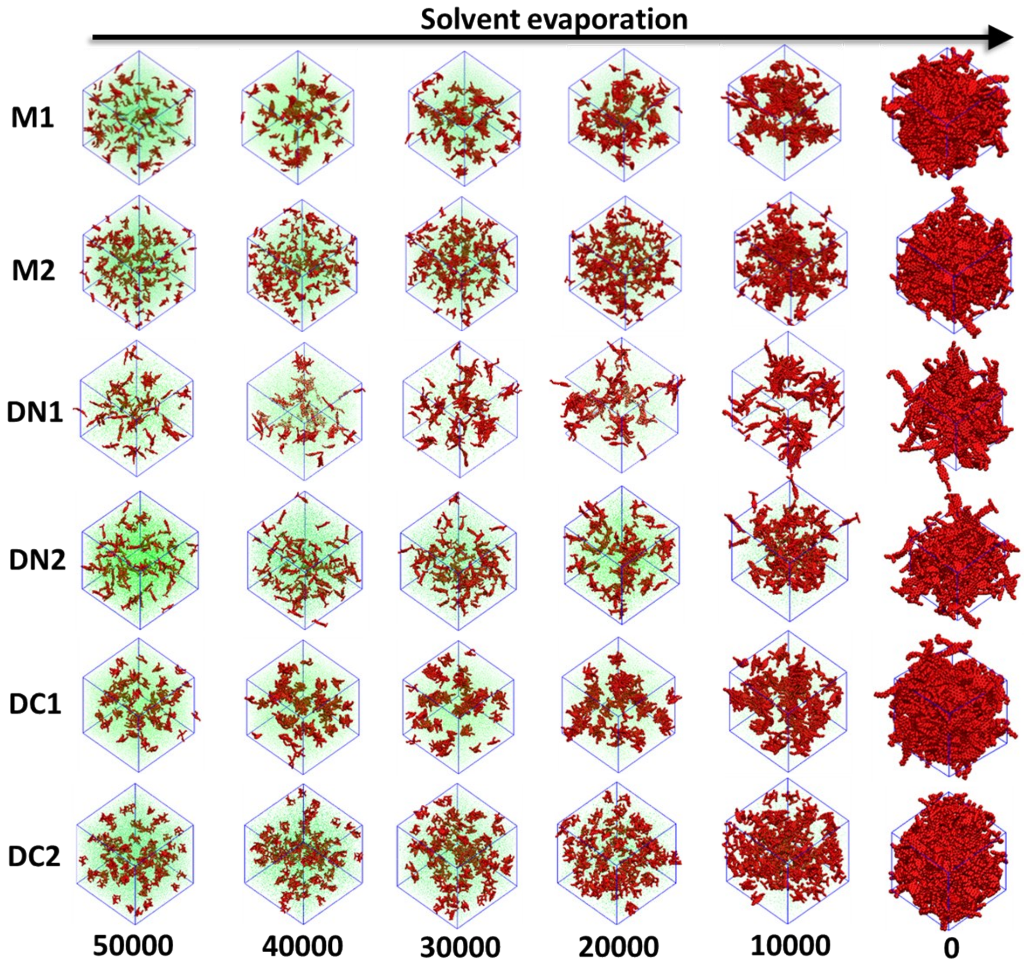


Figure S4. Representative snapshots with decreasing number of chloroform molecules during solvent evaporation of the PDI derivatives. For clarity, alkyl chains and hydrogen atoms are omitted here.

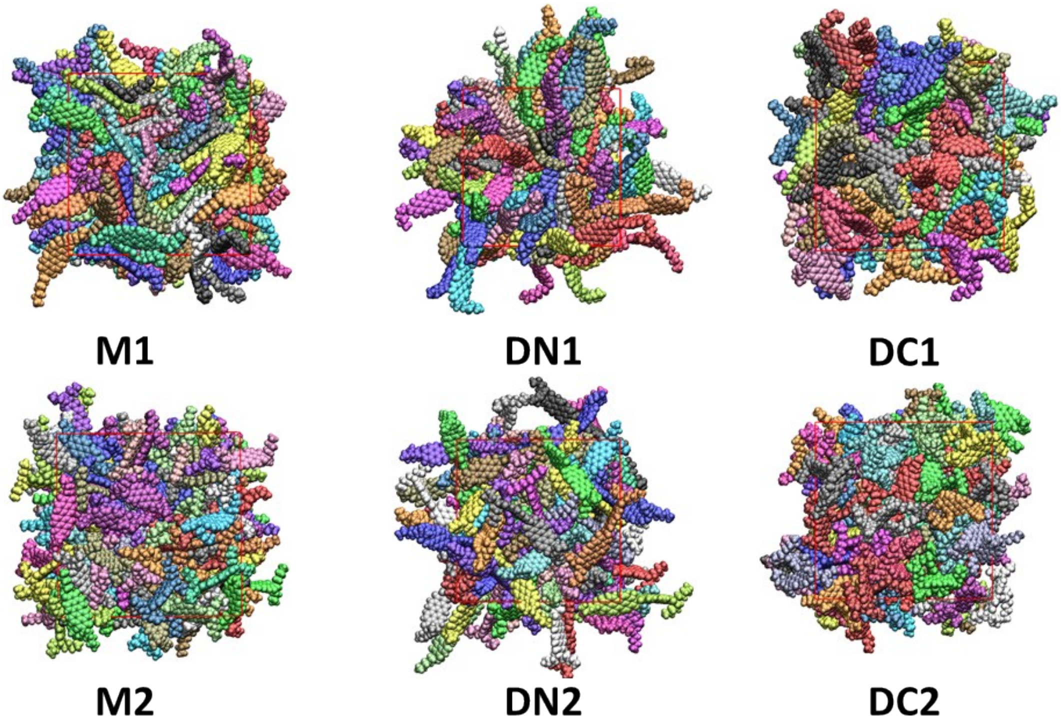


Figure S5. Representation of molecular packing morphologies for the annealed films of the PDI derivatives.

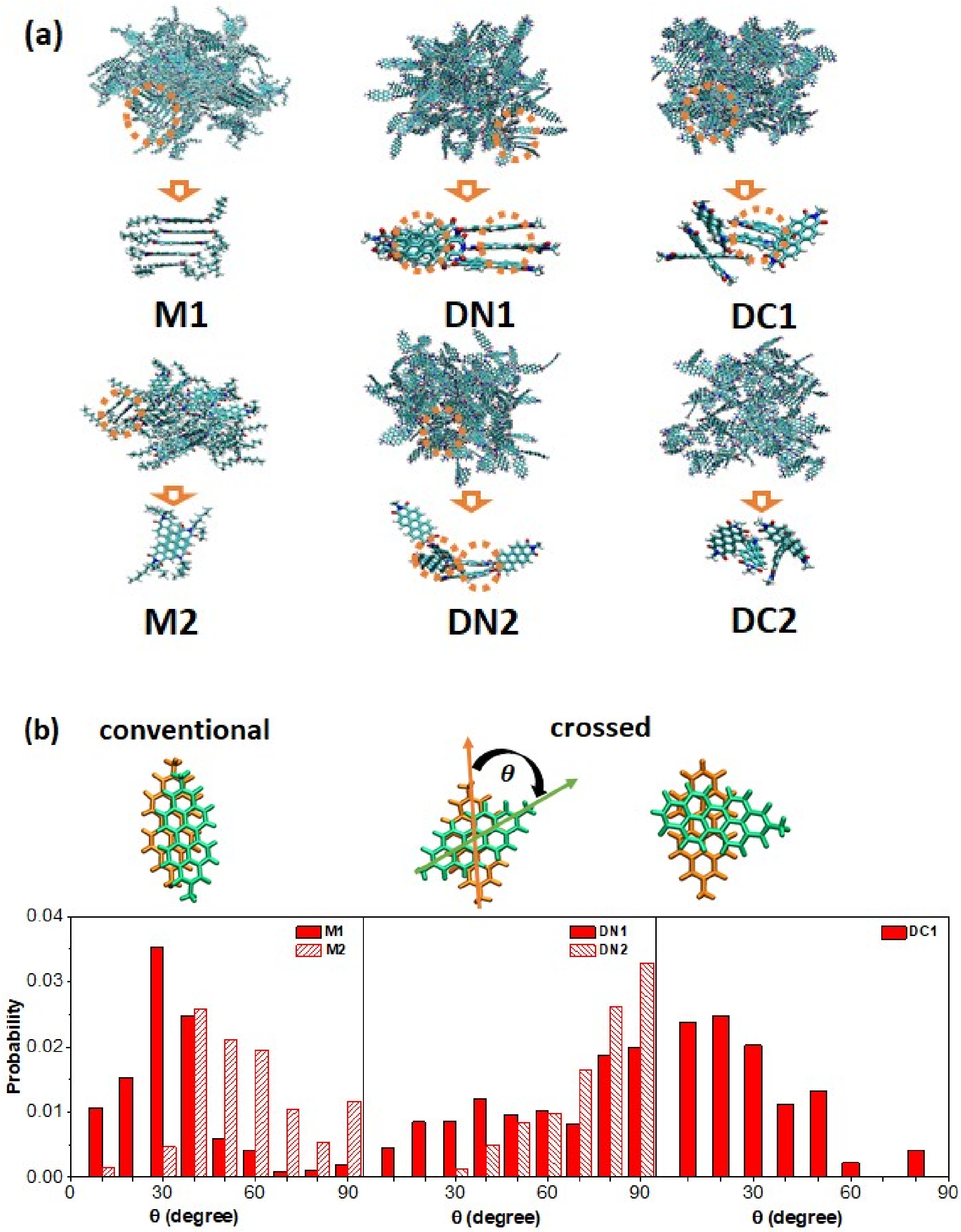


Figure S6. (a) Representative molecular stacking structures in the films of the PDI derivatives. For clarity, alkyl chains are omitted for DN1/DN2 and DC1/DC2 here. (b) Representative conventional and crossed π-π stacking structures (top) and distributions of the angles between the long-axes of two π-π stacking PDI units (below).

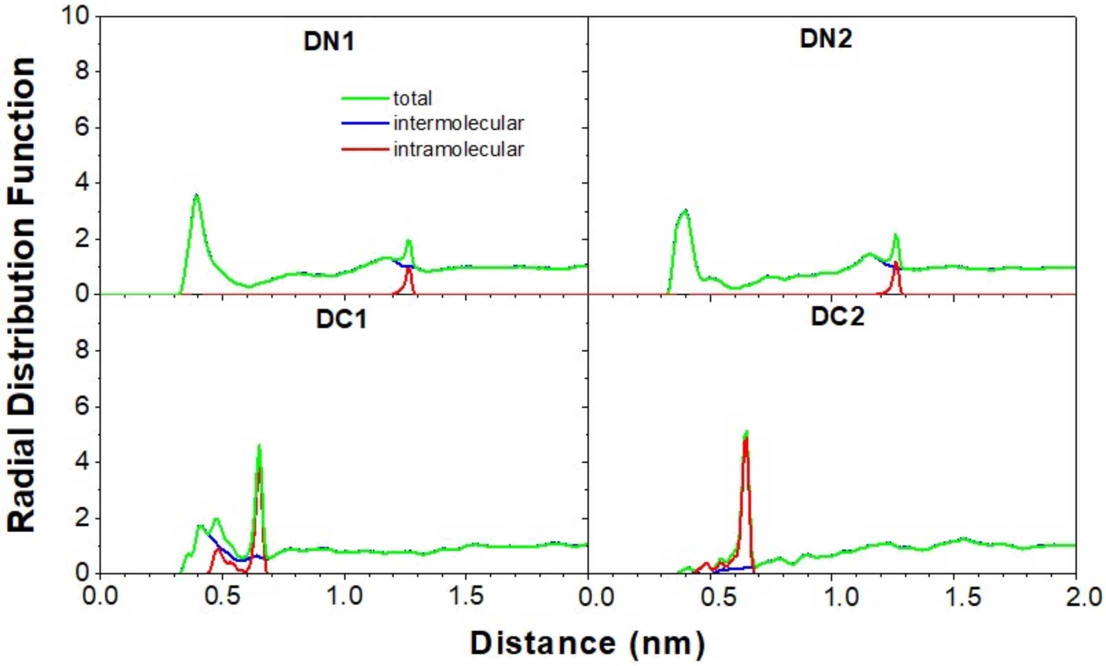
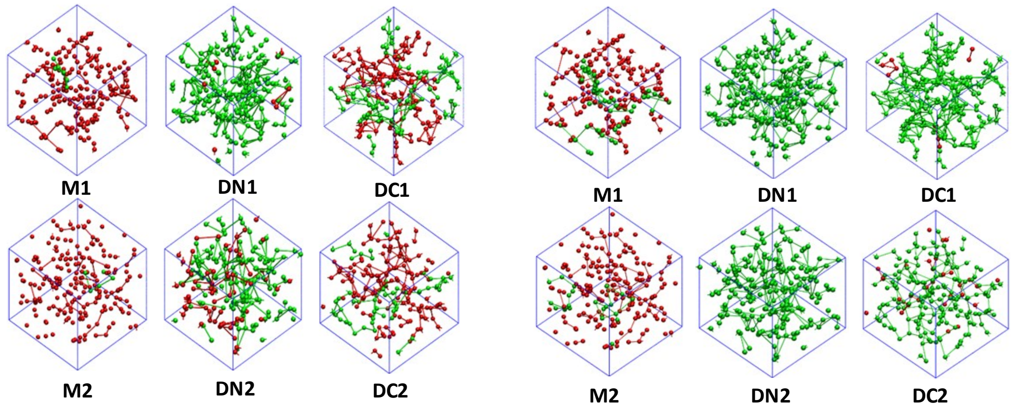


Figure S7. Center-of-mass radial distribution functions of intermolecular and intramolecular PDI units for the films of DN1/DN2 and DC1/DC2.

(a) distance=3.1 Å **(b) distance=3.2 Å**



(c) distance=3.3 Å **(d) distance=3.4 Å**

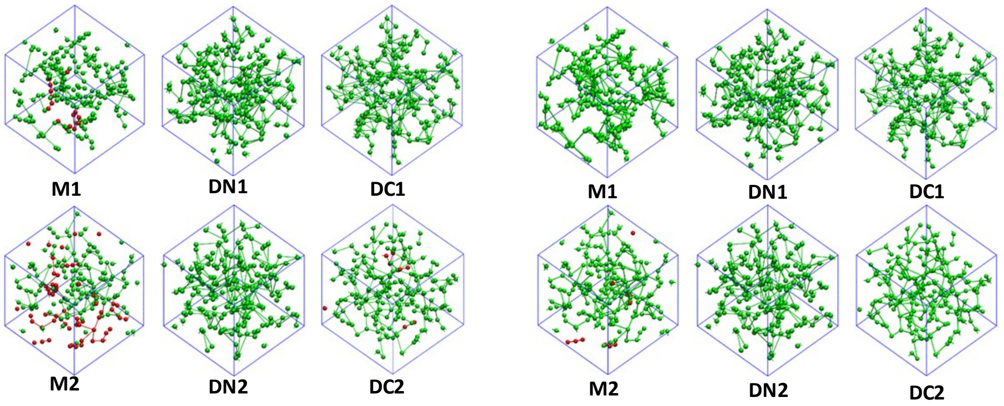


Figure S8. Illustration of connection network of PDI units in the films of the PDI derivatives within a cut-off distance from 3.1 to 3.4 Å between closest heavy atoms. The balls denote the center of mass of the PDI backbones. The green balls and lines belong to the maximum connection network; the red balls and lines belong to the rest of isolated networks.

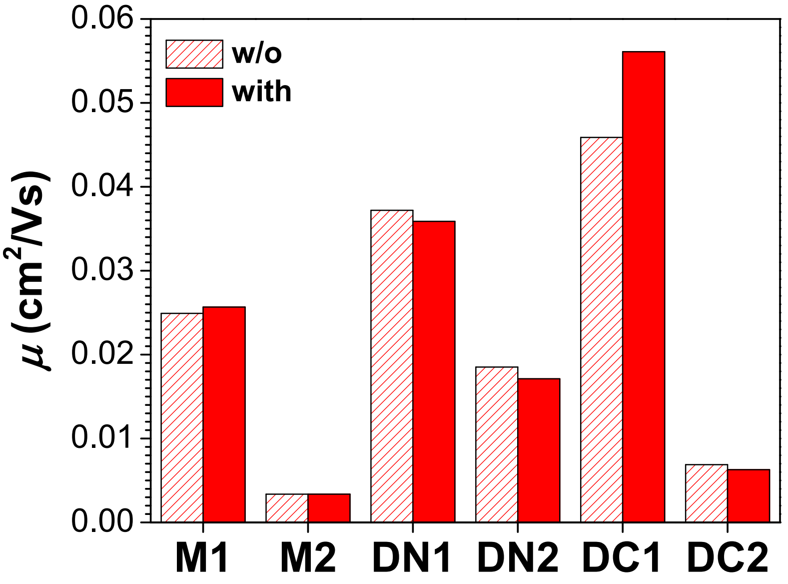


Figure S9. Electron mobilities estimated without/with consideration of static disorder of site energies for the thin films of the PDI derivatives.

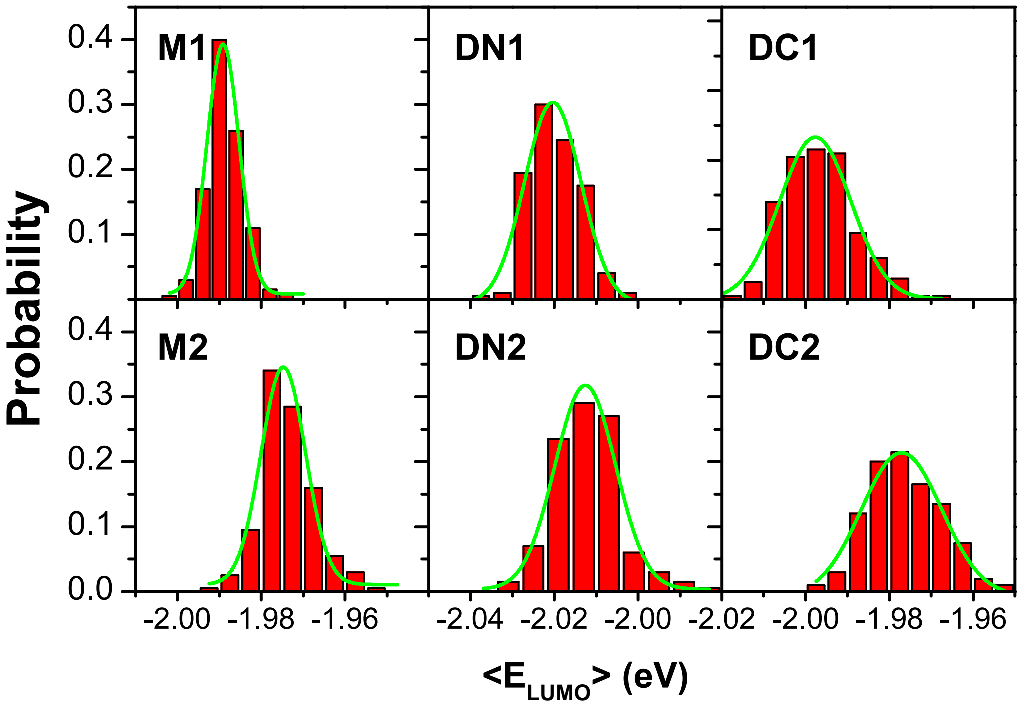


Figure S10. Distribution of the average LUMO energies over 1000 snapshots for the 200 PDI units in the films of the PDI derivatives.

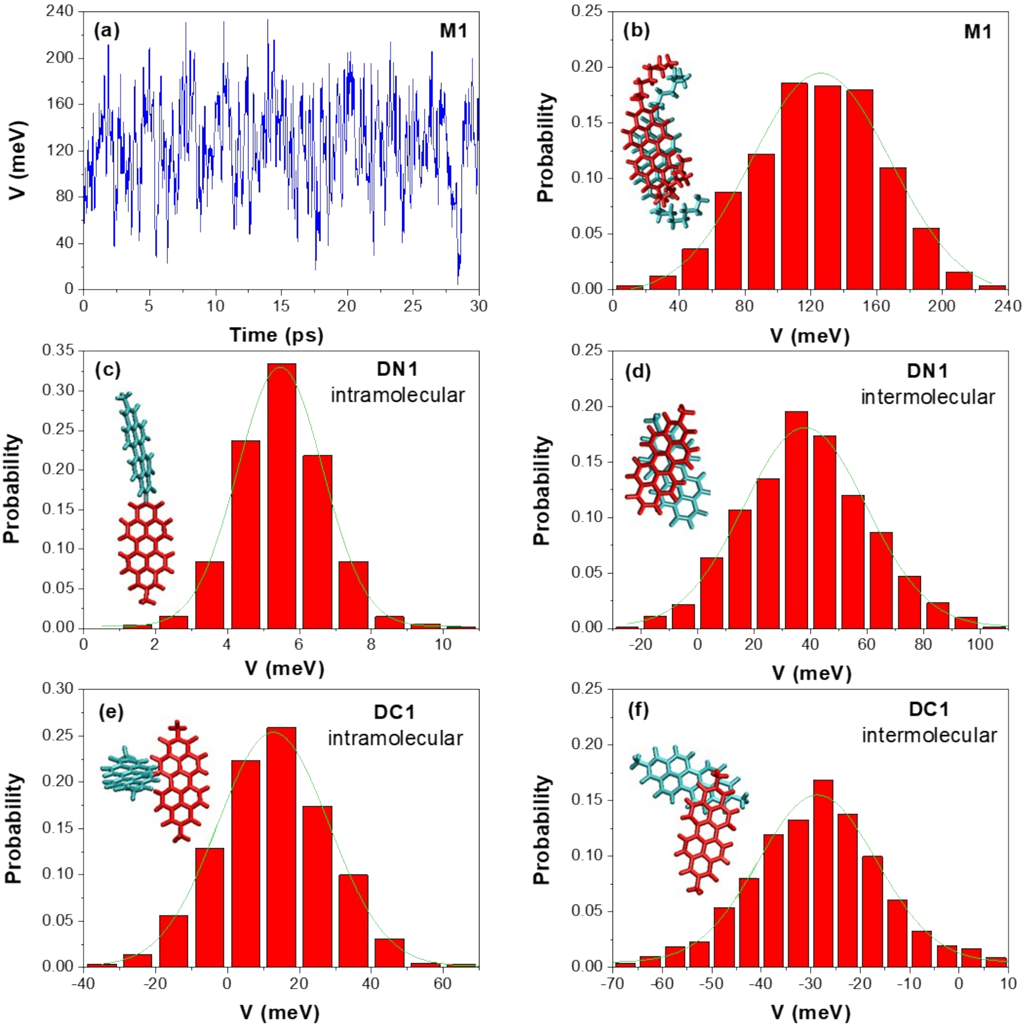


Figure S11. a, b) Evolution of the transfer integral as a function of MD simulation time (a) and Gaussian fitting of the distribution of transfer integrals (b) for a selected PDI pair in the M1 film; c-f) Gaussian fitting of the distribution of transfer integrals for a selected intramolecular PDI pair (c, e) and a selected intermolecular PDI pair (d, f) in the films of DN1 (c, d) and DC1 (e, f).

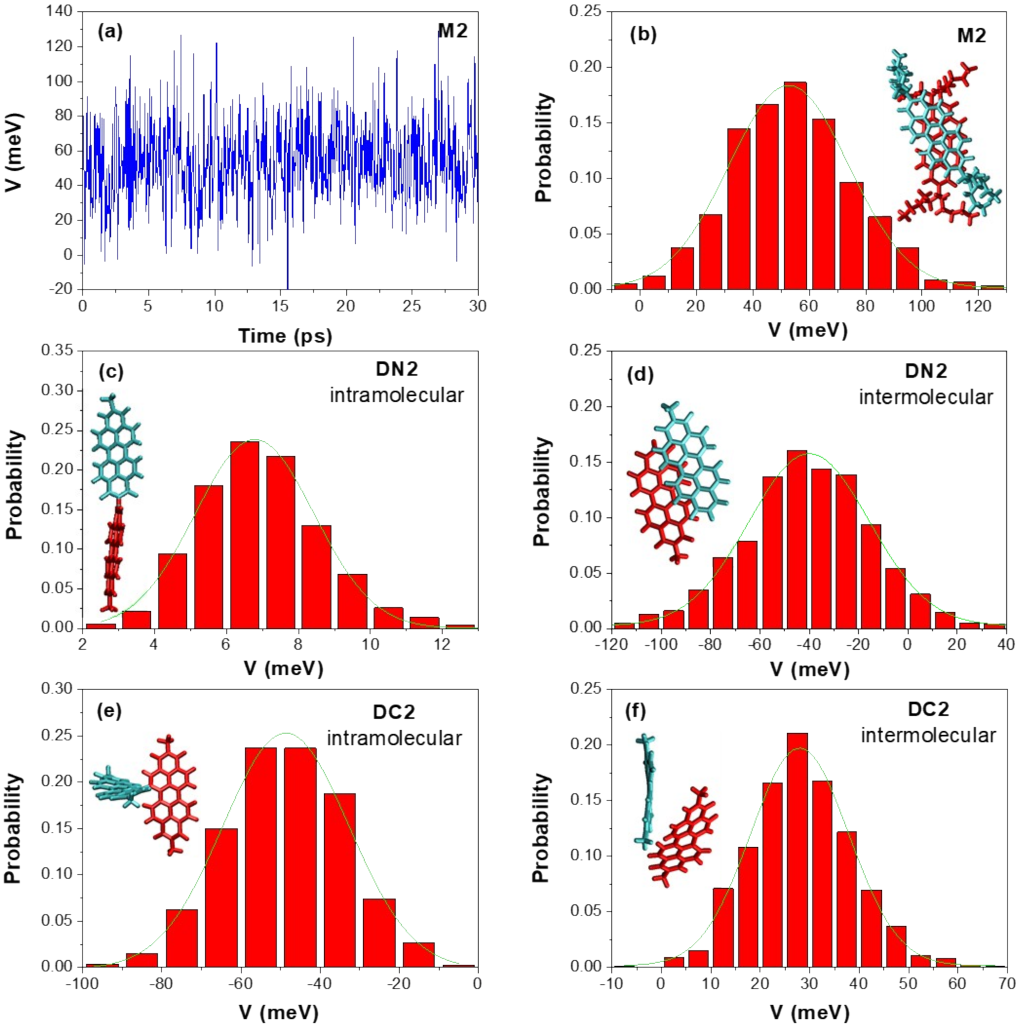


Figure S12. a, b) Evolution of the transfer integral as a function of MD simulation time (a) and Gaussian fitting of the distribution of transfer integrals (b) for a selected PDI pair in the M2 film; c-f) Gaussian fitting of the distribution of transfer integrals for a selected intramolecular PDI pair (c, e) and a selected intermolecular PDI pair (d, f) in the films of DN2 (c, d) and DC2 (e, f).

Details for simulating charge carrier mobilities in the PDI films

In disordered organic systems, charge transport is controlled by the thermally activated hopping mechanism, which can be characterized by a Brownian particle's random diffusion process. Charge carriers hop between adjacent molecules according to the charge transfer rates. In the high-temperature limit, electron transfer rates can be estimated by the semi-classical Marcus theory:[1]

$$k_{ij} = \frac{{V_{ij}}^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_B T}}\,exp[-\frac{(\Delta G_{ij}+\lambda)^2}{4\lambda k_B T}] \tag{1}$$

where $\hbar$ and k_B denote the reduced Planck's constant and the Boltzmann constant, respectively. T is the temperature (300 K). ΔG_{ij}, the Gibbs free energy, is estimated as the difference between the average LUMO energies of involved PDI units i and j over 1000 snapshots. λ, the reorganization energy, consists of external (intermolecular) and internal (intramolecular) contributions. The external λ, a challenging quantity to be calculated exactly, is negligible for nonpolar systems, as considered here. The intramolecular λ can be estimated by the four-point potential energy surface approach; the associated optimal geometries and single-point energies of the neutral and anionic states were obtained by density functional theory at the B3LYP/6-31G** level. Since λ is hardly influenced by alkyl substitutions,[2] it is estimated to be ca. 0.28 eV for electron transfer based on the PDI moiety. V_{ij} is the transfer integral between the LUMOs of two involved PDI units i and j. To assess the thermal fluctuation of V_{ij}, i.e., the magnitude of nonlocal electron-phonon coupling, V_{ij} for each PDI pair was computed for 1000 sampled snapshots; the average $<V_{ij}>$ and variance σ_{ij} were then obtained by the

Gaussian fitting (**Figures S11** and **S12**). Accordingly, the charge-transfer rates and mobilities were estimated without and with considering thermal disorder effect when the square of transfer integral corresponds to $<V_{ij}>^2$ and $<V_{ij}^2> = <V_{ij}>^2 + \sigma_{ij}^2$, respectively. It is noted that most of V_{ij} values are much smaller than λ, confirming the feasibility of the non-adiabatic hopping model.

In the low field limit, the carrier mobility can be expressed by the Einstein relation:

$$\mu = \frac{eD}{k_B T} \tag{2}$$

Therefore, the calculation of the Brownian mobility can be performed by evaluating the diffusion coefficient D with a set of kinetic Monte Carlo (KMC) simulations.[3-5] For an n-dimensional system, D is defined as the ratio between the mean-square displacement and the diffusion time t:

$$D = \frac{1}{2n} \lim_{t \to \propto} \frac{< r^2 >}{t} \tag{3}$$

For a three-dimensional system, D can be obtained with n=3. In each KMC simulation, the charge carrier is randomly situated on one PDI unit in the sample as the starting point. Then the charge hops to the neighboring molecules with a probability of $P_{ij} = k_{ij} / \sum_{j'} k_{ij'}$. At each step, a uniform random number x ranging from 0 to 1 is introduced to determine the next site of the charge. If $\sum_{j'=1}^{j-1} P_{ij'} < x \le \sum_{j'=1}^{j} P_{ij'}$ the charge carrier is assumed to hop to the jth PDI unit, and the simulation time t is incremented by $-\ln(y) / \sum_{j'} k_{ij'}$, where y is a uniform random number between 0 and

1. The hopping distance corresponds to the center-of-mass distance of PDI moieties involved in the electron transfer process. In this work, the KMC simulations will be terminated until the diffusion time reaches 100 ns and 2000 independent KMC simulations have been performed to calculate the diffusion coefficients.

References:

[1] R. A. Marcus, *Rev. Mod. Phys.* **1993**, *65*, 599.

[2] Z. Ma, H. Geng, D. Wang, Z. Shuai, *J. Mater. Chem. C* **2016**, *4*, 4546.

[3] L. Wang, G. Nan, X. Yang, Q. Peng, Q. Li, Z. Shuai, *Chem. Soc. Rev.* **2010**, *39*, 423.

[4] L. Wang, Q. Li, Z. Shuai, L. Chen, Q. Shi, *Phys. Chem. Chem. Phys.* **2010**, *12*, 3309.

[5] Z. Shuai, L. Wang, Q. Li, *Adv. Mater.* **2011**, *23*, 1145.