Electronic Supplementary Information

## Electronic and optical properties of $\pi$ -bridged

## perylenediimide derivatives: the role of $\pi$ -bridges

Yuan Guo,<sup>ab</sup> Guangchao Han,<sup>a</sup> Zeyi Tu,<sup>ab</sup> and Yuanping Yi\*<sup>ab</sup>

<sup>a</sup>Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China;

<sup>b</sup>University of Chinese Academy Sciences, Beijing 100049, China.

	geom-1	geom-2
bb'-(p-Ph)PDI		
bo'-(p-Ph)PDI		
oo'-(p-Ph)PDI		na a na a
bb'-(m-Ph)PDI		ູ້ມີ ຈູ້ຍັງຍີ່ ເບັນ ເວັນອີດ ເວັນອີ ເວັນອີດ ເວັນອີດ ເວັນອີດ ເວັນອີ ເວັ ເວັນອີ ເວັ ເວັນອີ ເວັ ເວັ ເວັ ເວັ ເວີ ເວັ ເວີ ເວັ ເວີ ເວັ ເວີ ເວັ ເວີ ເວີ ເວີ ເວັ ເວີ ເວັ ເວີ ເວັ ເວີ ເວັ ເວີ ເວັ ເວີ ເວັ ເວີ ເວີ ເວີ ເວັ ເວີ ເວັ ເວີ ເວັ ເວີ ເວັ ເວີ ເວີ ເວີ ເວີ ເວີ ເວັ ເວີ ເວີ ເວີ ເວີ ເວີ ເວີ ເວີ ເວີ ເວີ ເວີ
<i>bo'-(m-</i> Ph)PDI		• 5 • 5 • 5 • 5 • 5 • 5 • 5 • 5 • 5 • 5 • 5 • 5
<i>oo'-(m-</i> Ph)PDI		
bb'-(m-Ta)PDI		
bo'-( <i>m</i> -Ta)PDI		
oo'-(m-Ta)PDI		

**Figure S1**. Molecular geometries (left: top view; right: side view) optimized by DFT-B3LYP/6-31G (d,p) for all the investigated PDI derivatives.



**Figure S2**. Top view and side view of the optimized geometries of *bb*'-(*p*-Ph)PDI at the B3LYP/6-31G (d,p) level.



**Figure S3**. Evolution of super-exchange coupling as a function of the number of  $\pi$ -bridge levels of geom-1 for *bb*'-(*p*-Ph)PDI, *bb*'-(*m*-Ph)PDI and *bb*'-(*m*-Ta)PDI.



**Figure S4**. Torsion potential calculations under fixed dihedral angle ( $\theta_2$ ) and the corresponding super-exchange coupling of *bb*'-(*p*-Ph)PDI, *bo*'-(*p*-Ph)PDI and *oo*'-(*p*-Ph)PDI for geom-1.



**Figure S5**. Representative snapshots with decreasing number of chloroform molecules (purple color) during solvent evaporation and the as-cast film of *bb*'-(*p*-Ph)PDI (green color). The inherent hydrogen atoms are omitted here for clarity.



**Figure S6.** Frontier molecular orbital energy levels of geom-1 for  $bb'-(p-Ph)PDI\sim oo'-(m-Ta)PDI$  at the  $\omega$ B97XD/6-31G (d,p) level.



**Figure S7.** Frontier orbital energies and pictorial representation of geom-1 for bb'-(*p*-Ph)PDI~oo'-(*m*-Ta)PDI at the  $\omega$ B97XD/6-31G (d,p) level.

	geom-1			geom-2			
	$ heta_l$	$\theta_2$	Ψ	$ heta_l$	$ heta_2$	Ψ	$\Delta E_{12}$
<i>bb'-(p-</i> Ph)PDI	55	56	67	55	57	3.5	1.76
<i>bo'-(p-</i> Ph)PDI	60	57	59	60	57	5.2	0.07
<i>oo</i> '-( <i>p</i> -Ph)PDI	65	63	54	62	63	1.0	1.48
bb'-(m-Ph)PDI	55	53	55	55	57	2.4	4.47
<i>bo</i> '-( <i>m</i> -Ph)PDI	55	55	21	58	73	6.2	8.46
<i>oo</i> '-( <i>m</i> -Ph)PDI	65	62	46	63	67	7.4	3.16
bb'-(m-Ta)PDI	42	42	75	45	38	6.6	4.44
bo'-(m-Ta)PDI	49	73	24	45	52	4.8	3.92
oo'-(m-Ta)PDI	58	56	54	50	66	46	0.20

**Table S1.** Dihedral angles ( $\theta_1$  and  $\theta_2$ , °) between  $\pi$ -bridge (*p*-Ph, *m*-Ph and *m*-Ta) and each PDI units and twist angles ( $\psi$ , °) between two PDI units, and relative energies ( $\Delta E_{12}=E^{\text{geom-2}}-E^{\text{geom-1}}$ , kJ·mol<sup>-1</sup>) between the two energy minima for all the investigated dimeric PDI derivatives.

**Table S2**. Calculated LUMO charge density of PDI ( ${\rho}_{L}^{PDI}$ ) and HOMO, LUMO and LUMO+1 charge density ( ${\rho}_{H}^{\pi}$ ,  ${\rho}_{L}^{\pi}$ , and  ${\rho}_{L}^{\pi}$ +1) of *p*-Ph, *m*-Ph and *m*-Ta at linkage atom at the B3LYP/6-31G (d,p) level.

		geom-1				geom-2			
	PDI	$o^{\pi}$	$o^{\pi}$	$^{\pi}$		$o^{\pi}$	$o^{\pi}$	$a^{\pi}$	
<i>bb'-(p</i> -Ph)PDI	0.057	0.332	0.329	_		0.323	0.329	_	
<i>bo'-(p</i> -Ph)PDI	0.044	0.328	0.328	_		0.308	0.328	_	
<i>oo'-(p</i> -Ph)PDI	0.034	0.267	0.328	_		0.332	0.328	_	
<i>bb'-(m</i> -Ph)PDI	0.057	0.231	0.245	_		0.085	0.245	_	
<i>bo'-(m-</i> Ph)PDI	0.044	0.218	0.244	_		0.240	0.243	_	
<i>oo'-(m-</i> Ph)PDI	0.034	0.133	0.245	_		0.078	0.244	_	
<i>bb'-(m</i> -Ta)PDI	0.057	_	0 299	0 108		_	0 298	0 107	
<i>bo'-(m-</i> Ta)PDI	0.044	_	0.297	0.105		_	0.293	0.101	
<i>oo'-(m-</i> Ta)PDI	0.034	_	0.298	0.105		_	0.286	0.095	

sample1 sample2 sam	sample3		
$\mu^{\rm SE}$ $\mu^{ m direct}$ $\mu^{ m SE}$ $\mu^{ m direct}$ $\mu^{ m SE}$	$\mu^{ ext{direct}}$		
<b>snapshot-1</b> 2.897 0.410 2.847 0.456 2.526	0.402		
<b>snapshot-2</b> 2.847 0.458 2.978 0.484 2.655	0.487		
<b>snapshot-3</b> 2.687 0.425 2.626 0.390 2.504	0.447		
<b>snapshot-4</b> 2.748 0.395 2.621 0.416 2.497	0.409		
<b>snapshot-5</b> 2.807 0.386 2.822 0.428 2.479	0.413		
Average2.7970.4152.7780.4352.532±deviation+0.082+0.028+0.153+0.036+0.070	0.432 +0.035		

**Table S3** Electron mobilities  $(10^{-2} \text{ cm}^{-2} \cdot \text{V}^{-1} \cdot \text{s}^{-1})$  estimated with intramolecular transport considered as the super-exchange  $(\mu^{\text{SE}})$  or direct  $(\mu^{\text{direct}})$  coupling mechanism of five snapshots extracted from MD simulations for three independent *bb*'-(*p*-Ph)PDI thin-film samples.

**Table S4** Excitation wavelengths ( $\lambda$ , nm), oscillator strengths (f), and main electronic transitions and corresponding weights for the excited states of all PDI derivatives in chloroform solutions.

bb'-(p-Ph)PDI       S1       513       1         S2       509       0         S3       378       0         bo'-(p-Ph)PDI       S1       513       0         S2       494       1       53       390       0         oo'-(p-Ph)PDI       S1       491       0       0         s2       485       1       53       388       0         bb'-(m-Ph)PDI       S1       515       0       0         bb'-(m-Ph)PDI       S1       515       0       0         bb'-(m-Ph)PDI       S1       515       0       0         bb'-(m-Ph)PDI       S1       514       0       0         s3       385       0       0       0       0         bo'-(m-Ph)PDI       S1       514       0       0         s3       385       0       0       0       0         bo'-(m-Ph)PDI       S1       494       0       0         s2       486       1       0       0       0         s2       486       1       0       0       0         s2       486       1       0       0	.084	HæL( $61\%$ ) H-1æL+1( $34\%$ )
bo'-(p-Ph)PDI       S1       513       0         S2       494       1         S3       390       0         oo'-(p-Ph)PDI       S1       491       0         S2       485       1         S3       388       0         bb'-(m-Ph)PDI       S1       515       0         bb'-(m-Ph)PDI       S1       515       0         S2       505       1       55       359       0         bo'-(m-Ph)PDI       S1       514       0       0         S2       495       1       53       385       0         bo'-(m-Ph)PDI       S1       494       0       0         S2       486       1       0       0       0         s2       486       1       0       0       0	).345 ).425	H $\sim$ L+1(52%),H-1 $\sim$ L(42%) H-2 $\sim$ L(41%), H-1 $\sim$ L+1(33%)
oo'-(p-Ph)PDI       S1       491       0         S2       485       1         S3       388       0         bb'-(m-Ph)PDI       S1       515       0         S2       505       1         S5       359       0         bo'-(m-Ph)PDI       S1       514       0         S2       495       1         S3       385       0         bo'-(m-Ph)PDI       S1       494       0         S2       486       1	).534 .128 ).172	H&L+1(71%),H&L(21%) H-1&L(71%),H-1&L+1(21%) H-2&L(44%),H&L(26%)
bb'-(m-Ph)PDI       S1       515       0         S2       505       1         S5       359       0         bo'-(m-Ph)PDI       S1       514       0         S2       495       1         S3       385       0         oo'-(m-Ph)PDI       S1       494       0         S2       486       1	).637 262 ).263	H&L(49%),H-1&L+1(47%) H-1&L(50%),H&L+1(47%) H-2&L(74%)
bo'-(m-Ph)PDI       S1       514       0         S2       495       1         S3       385       0         oo'-(m-Ph)PDI       S1       494       0         S2       486       1	0.305 160 0.156	H&L+1(51%),H-1&L(47%) H&L(47%),H-1&L+1(38%) H-2&L+1(42%),H-3&L(28%)
<i>oo</i> '-( <i>m</i> -Ph)PDI S1 494 0 S2 486 1	).526 .179 ).126	H&L+1(89%),H-1&L(8%) H-1&L(88%),H&L+1(7%) H-2&L(58%),H&L(25%)
<b>S3</b> 377 0	).427 415 ).151	H&L+1(36%),H- 1&L(35%),H&L(14%) H-1&L(32%),H&L+1(30%), H&L(18%) H-2&L+1(57%),H-3&L(17%)
<i>bb</i> '-( <i>m</i> -Ta)PDI S1 516 0 S2 507 0 S15 318 0	).461 ).994 ).415	H&L+1(42%),H-1&L(49%), H&L(52%),H-1&L+1(40%) H&L+2(42%)
bo'-(m-Ta)PDI         S1         510         0           S2         491         1           S10         327         0	).124 487 ).116	H&L+1(23%),H-1&L(75%) H&L+1(75%),H-1&L(22%) H-4&L+1(51%)
<i>oo</i> '-( <i>m</i> -Ta)PDI S1 496 0 S2 489 1 S11 324 0	).527 .292 ).092	H $\approx$ L+1(26%),H- 1 $\approx$ L(26%),H $\approx$ L(24%) H- 1 $\approx$ L(36%),H $\approx$ L+1(33%),H $\approx$ L(14%) H 5 5 L+1(20%)

## **Computational Details**

**Excited state properties.** In the TDDFT calculations of the excited states and optical properties with the long-range corrected functional ( $\omega$ B97XD), the range-separation parameter ( $\omega$ ) was tuned by minimizing the following expression in gas phase:<sup>1, 2</sup>

$$J_{gap}^{2}(\omega) = |E_{HOMO} + IP|^{2} + |E_{LUMO} + EA|^{2}$$
(1)

where IP is ionization potential, the energy difference between the cationic and neutral states ( $IP = E^+ - E^0$ ); EA is electron affinity, the energy difference between the neutral and anionic states ( $EA = E^0 - E^-$ );  $E_{HOMO}$ , the energy of the highest occupied molecular orbital (HOMO);  $E_{LUMO}$ , the LUMO energy.

**Super-exchange electronic couplings.** The electronic properties of the PDI- $\pi$ -PDI molecules can be described by the following secular equation:

$$HC = ESC \tag{2}$$

The Hamiltonian (*H*) and the overlap matrix (*S*) of the PDI- $\pi$ -PDI system can be projected to the PDI and  $\pi$ -bridge fragment orbitals as follows:

$$H = \begin{pmatrix} \varepsilon_{1} & V_{12} & V_{1B} \\ V_{21} & \varepsilon_{2} & V_{2B} \\ V_{B1} & V_{B2} & \varepsilon_{B} \end{pmatrix}$$
(3)

$$S = \begin{pmatrix} 1 & S_{12} & S_{1B} \\ S_{21} & 1 & S_{2B} \\ S_{B1} & S_{B2} & 1 \end{pmatrix}$$
(4)

Here, the matrix element  $\varepsilon_i = \langle \psi_i | H | \psi_i \rangle$ ,  $V_{ij} = V_{ji} = \langle \psi_i | H | \psi_j \rangle$  and  $S_{ij} = S_{ji} = \langle \psi_i | \psi_j \rangle$ .  $\psi_{i/j}$  denotes the localized orbitals of the isolated PDI or  $\pi$ -bridge moieties saturated by hydrogen atoms. For electron transport,  $\psi_{1/2}$  is the LUMO of each PDI unit and  $\psi_B$  represents the molecular orbitals of the  $\pi$ -bridge. After Löwdin's symmetric transformation,<sup>3</sup> the Hamiltonian based on an orthogonalized basis can be obtained:

$$\tilde{H} = S^{-1/2} H S^{-1/2} = \begin{pmatrix} \tilde{\varepsilon}_1 & \tilde{V}_{12} & \tilde{V}_{1B} \\ \tilde{V}_{21} & \tilde{\varepsilon}_2 & \tilde{V}_{2B} \\ \tilde{V}_{B1} & \tilde{V}_{B2} & \tilde{\varepsilon}_B \end{pmatrix}$$
(5)

Then in the framework of perturbation scheme, the effective electronic coupling can be obtained by means of Larsson partition:<sup>4, 5</sup>

$$V_{12}^{eff} = \tilde{V}_{12} + \sum_{b \in B} \frac{\tilde{V}_{1B} \tilde{V}_{B2}}{E - \tilde{\varepsilon}_B}$$
(6)

Here, the first and second terms denote the implicit and explicit contributions to the super-exchange coupling, respectively.

**Molecular dynamic simulations.** The atomistic MD simulations for *bb*'-(*p*-Ph)PDI compound were performed with the Gromacs-4.6.7 software package based on the general AMBER force field with the RESP charges.<sup>6-8</sup> A spherical cutoff of 1.4 nm was set for the summation of van der Waals (VDW) interactions. The particle-mesh Ewald (PME) solver was used to compute the long-range Coulomb interaction with a cutoff of 1.0 nm and a tolerance of  $1.0 \times 10^{-5}$ . The MD simulations were carried out with three-dimensional periodic boundary conditions using the leap-frog integrator with a time step of 1.0 fs.

The bb'-(p-Ph)PDI thin-film molecular packing structure was obtained according to the following procedure: (i) constructing a  $20 \times 20 \times 20$  nm<sup>3</sup> box containing 100 molecules with various conformations and 50000 chloroform solvent molecules by randomly placing PDI molecules into the solvent; (ii) 1 ns simulation under high pressure (100 bar) and then 20 ns simulation under normal pressure (1 bar) at room temperature (300 K) to make the bb'-(p-Ph)PDI molecules and solvent molecules disperse homogeneously; (iii) randomly removing 100 solvent molecules from the solution every 200 ps to simulate solvent evaporation processes at the room temperature and normal pressure; (iv) after removing all solvent molecule, 70 ns equilibration was carried out at 300 K and 1 bar. The Berendsen barostat9 and velocity rescaling thermostat<sup>10</sup> under the NPT ensemble were applied to control the pressure and temperature, respectively. For the final 10 ns of equilibration, the Parrinello-Rahman barostat<sup>11</sup> and Nosé-Hoover thermostat<sup>12, 13</sup> were used to obtain better equilibrium conformations. The procedure was repeated three times with different initial models to obtain three different samples. The final box size for bb'-(p-Ph)PDI is ca. 6.20 nm in three dimensions. Representative molecular packing morphology for the as-cast film of the bb'-(p-Ph)PDI is shown in **Figure S5.** For each sample, the last 50 ps of equilibration was sampled every 10 ps to generate 5 snapshots to consider the thermal fluctuation effect. Total 15 snapshots were used to calculate the average carrier mobility for the bulk system.

**Electron mobility calculations.** The electronic couplings for the intermolecular PDI pairs (the shortest inter-atomic distance between the PDI units is less than 0.6 nm) were computed at the DFT-B3LYP/6-31G (d,p) level. In each snapshot extracted from the MD simulated *bb*'-(*p*-Ph)PDI thin films, there are about 620 neighboring intermolecular PDI pairs.

Since the electronic couplings are relatively weak, we employ the hopping model to calculate the electron mobilities for the simulated amorphous films. The electron transfer rate between neighboring PDI units can be evaluated by the semi-classical Marcus theory:<sup>14</sup>

$$k_{ij} = \frac{V_{ij}^{2}}{\hbar} \sqrt{\frac{\pi}{\lambda k_{B}T}} exp\left[-\frac{\left(\Delta G_{ij} + \lambda\right)^{2}}{4\lambda k_{B}T}\right]$$
(7)

here,  $\hbar$  denotes the reduced Planck's constant;  $V_{ij}$ , the electronic couplings, including the intermolecular couplings and intramolecular couplings between PDI units;  $k_B$ , the Boltzmann constant; T, the temperature (300 K);  $\lambda$ , the reorganization energy that includes internal and external contributions. The external  $\lambda$ , a challenging quantity to be calculated exactly, is negligible for nonpolar systems, as considered here. The internal  $\lambda$  for electron transfer was estimated to be about 0.26 eV at the DFT-B3LYP/6-31G(d,p) level based on the PDI moiety since it is hardly influenced by the alkyl substitutions.<sup>15</sup>  $\Delta G_{ij}$  is the Gibbs free energy and set to be zero, associated with the selfexchange process and the limit of zero filed considered here.

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

$$\mu = \frac{eD}{k_B T} \tag{8}$$

$$D = \frac{1}{2n_{t \to \infty}} \frac{\langle r^2 \rangle}{t}$$
<sup>(9)</sup>

where e is the elementary charge of an electron and D is the charge diffusion coefficient. The evolution of charge carrier position r as a function of diffusion time t was obtained by kinetic Monte Carlo (KMC) simulations according to the computed charge-transfer rates.<sup>16, 17</sup> In this work, 2000 independent diffusion trajectories were simulated to calculate the diffusion coefficient for each snapshot.

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