

Supporting Information for

**Geometry and Electronic Coupling in Perylenediimide Stacks: Mapping Structure - Charge Transport Relationships.**

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**1. Computational details and discussion**

The geometry of the PDI-H monomer used in the dimer calculation was optimized using B3LYP/6-31G\*. Values reported in Figure 2 were calculated by stacking two PDI-H monomers with short axis (x) shifts from 0 to 3.5 Å in intervals of 0.5 Å, and long axis (y) shifts from 0 to 6 Å in intervals of 0.5 Å. The plane-to-plane distance was fixed at 3.5 Å. Binding energies (Figure 2a) were calculated as:

$$\text{Binding Energy} = E_{\text{dimer}} - 2E_{\text{monomer+ghost}}$$

Where *monomer+ghost* includes the atoms of one PDI-H and additional basis functions placed at the locations of the other PDI-H atoms in the dimer to correct for basis set superposition error.

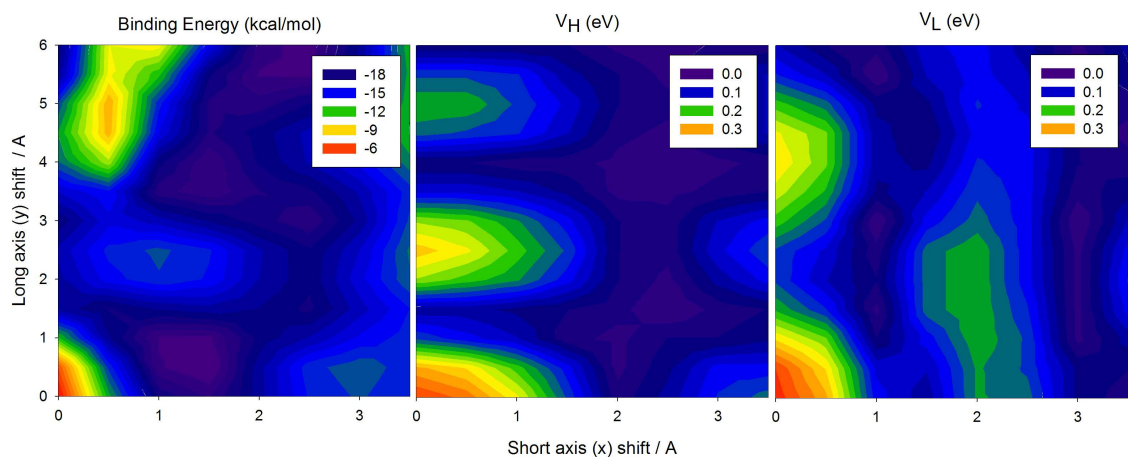
We note that in the case of the  $\pi$ -stacked benzene dimer, two-body effects dominate the binding energy, with the addition of a third and fourth benzene to the stack contributing only 10% to the total binding energy (normalized for the number of benzenes)<sup>1</sup>

Electronic coupling matrix element  $V_H$  ( $V_L$ ) reported in Figures 2b (2c) was calculated as half the energy difference between the HOMO and HOMO-1 (LUMO and LUMO+1) dimer

orbitals (see Figure 1c). This method is well suited for symmetric dimers where the HOMO and HOMO-1 of the dimer are linear combinations of the HOMOs of each monomer, with little contribution from lower-lying monomer orbitals (with corresponding requirements for LUMO orbitals). In this case, the HOMO-1 and LUMO+1 of the PDI-H monomer are at least 1.3 eV separated from the HOMO and LUMO, so have little effect on the dimer orbitals. This model also requires the dimer to be symmetric, and would be inappropriate for herringbone crystals such as that of pentacene (see ref 17 in the main text and refs 2 and 3 below). However, several functionalized tetracenes and pentacenes form planar  $\pi$ -stacks<sup>4</sup> and could be studied using this method. We also note that to avoid confusion we have reported the absolute value of  $V_H$  and  $V_L$ , since the sign of the coupling is not relevant to the charge transport properties in the hopping regime.

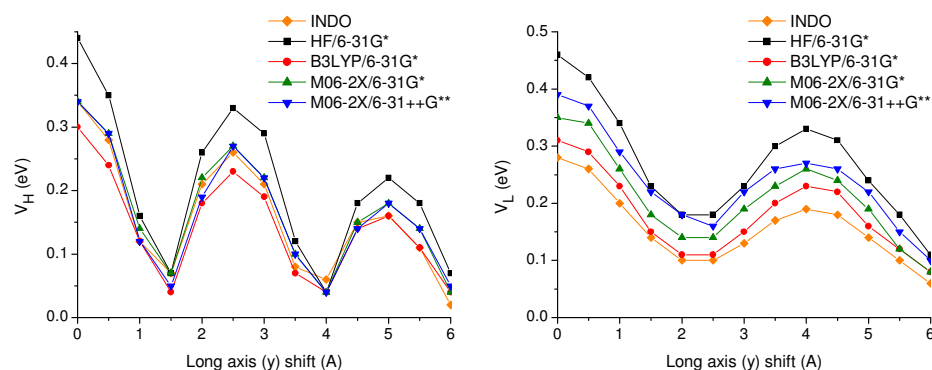
The coupling values reported in Table 1 were obtained by extracting the relative (x,y,z) shifts or rotation angles from the crystal structure of each molecule, then constructing a PDI-H dimer with those coordinates, followed by the calculation described above. Test calculations using full dimers extracted from the crystal structure (including the R groups) gave answers within 0.02 eV of the simple model calculations.

All values reported were calculated using the M06-2X functional with the 6-31++G\*\* basis set. Use of the smaller 6-31G\* basis set gave qualitatively similar results, as shown in Figure S1. The SG1 grid was used, with energy tolerances of 1E-8. During the preparation of this manuscript, Johnson et al.<sup>5</sup> reported oscillations in meta-GGA potential energy surfaces with certain grids. The SG1 grid appeared to be sufficient to avoid this problem for our system, and we did not observe such oscillations when scanning the binding energy vs plane-to-plane distance.



**Figure S1:** Binding energy and electronic coupling for hole and electron transfer of PDI dimers vs stacking geometry ( $z=3.5\text{\AA}$ ), computed using the smaller 6-31G\* basis set. The z axis (binding energy or electronic coupling) scale is identical to that of Figure 2 in the main text. The strong similarity of this figure with Figure 2 indicates that we have reached convergence of these properties with respect to basis set size.

Earlier papers in the literature have used less computationally intensive methods such as INDO to calculate electronic coupling matrix elements. Figure S2 shows  $V_H$  and  $V_L$  as a function of y axis shift ( $x$  shift =  $0\text{\AA}$ ,  $z$  shift =  $3.5\text{\AA}$ ) using five different methods: INDO, HF/6-31G\*, B3LYP/6-31G\*, M06-2X/6-31G\*, and M06-2X/6-31++G\*\*. While the results are nearly quantitative for  $V_H$ , it should be noted that the  $V_L$  values calculated using M06-2X/6-31++G\*\* are on average ~30% higher than those calculated using INDO, so caution should be taken when comparing these predictions with earlier results. The INDO calculations were performed in Gaussian98<sup>6</sup>.



**Figure S2:**  $V_H$  and  $V_L$  as a function of long axis shift calculated using several different methods/basis sets

## 2. Dimer geometries for Table 1

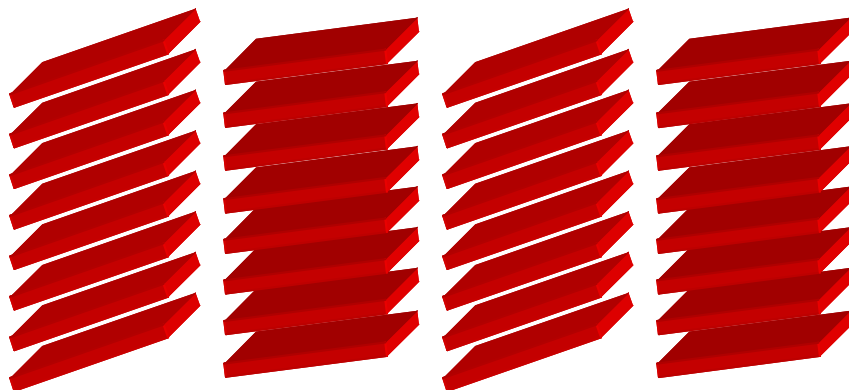
The x,y,z shifts for the molecules discussed in the main text and listed in Table 1 are given in Table S1, with the monomer geometry optimized with B3LYP/6-31G\* given in Table S2. Several form crystals with two inequivalent stacks (Figure S3). In these cases the values for dimers from each stack are listed on separate rows (e.g. **2a** and **2b**). In Table 1 in the main text, these values were combined into one row (e.g.  $V_L = 0.01, 0.03$  for **2**). Molecules **1-4**, **6-17** were taken from ref. 14a in the main text, molecule **5** was taken from ref. 5c, and molecules **18-20** were taken from refs 14b-d, respectively. Stacks in **2**, **18**, and **20** feature rotation as well as translation, so only the z shift is given in the table.

**Table S1:** Electronic couplings matrix elements and dimer (x,y,z) shifts for PDI derivatives

| #   | R                                                                                                                                                                             | V <sub>H</sub> (eV) | V <sub>L</sub> (eV) | x shift (Å) | y shift (Å) | z shift (Å) |
|-----|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|---------------------|-------------|-------------|-------------|
| 1   | —CH <sub>3</sub>                                                                                                                                                              | 0.04                | 0.14                | 1.60        | 0.94        | 3.40        |
| 2a  | —CH <sub>2</sub> CH <sub>3</sub>                                                                                                                                              | 0.09                | 0.01                | n/a         | n/a         | 3.41        |
| 2b  |                                                                                                                                                                               | 0.09                | 0.03                | n/a         | n/a         | 3.44        |
| 3a  | —(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>                                                                                                                              | 0.04,               | 0.20                | 2.48        | 2.05        | 3.41        |
| 3b  |                                                                                                                                                                               | 0.20                | 0.10                | 0.79        | 3.11        | 3.40        |
| 4   | —(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>                                                                                                                              | 0.15                | 0.07                | 1.31        | 3.10        | 3.34        |
| 5   | —(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>                                                                                                                              | 0.17                | 0.07                | 1.12        | 3.05        | 3.28        |
| 6   | —CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>                                                                                                          | 0.14                | 0.03                | 0.98        | 5.45        | 3.42        |
| 7   | —CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>                                                                                                             | 0.13                | 0.05                | 1.28        | 3.23        | 3.35        |
| 8   | —(CH <sub>2</sub> ) <sub>3</sub> OCH <sub>3</sub>                                                                                                                             | 0.19                | 0.13                | 0.68        | 3.15        | 3.44        |
| 9   | —(CH <sub>2</sub> ) <sub>3</sub> OCH <sub>2</sub> CH <sub>3</sub>                                                                                                             | 0.15                | 0.05                | 1.26        | 3.06        | 3.40        |
| 10a | —(CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> OH                                                                                                                           | 0.19                | 0.13                | 0.76        | 3.22        | 3.36        |
| 10b |                                                                                                                                                                               | 0.19                | 0.11                | 0.70        | 3.06        | 3.51        |
| 11a | —(CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> OH                                                                                                                           | 0.15                | 0.01                | 1.10        | 3.19        | 3.40        |
| 11b |                                                                                                                                                                               | 0.19                | 0.08                | 0.85        | 3.13        | 3.42        |
| 12  | —CH <sub>2</sub> —                                                                           | 0.16                | 0.00                | 1.10        | 3.08        | 3.42        |
| 13  | —CH <sub>2</sub> —  —OCH <sub>3</sub>                                                        | n/a                 | 0.16                | 0.36        | 2.67        | 3.46        |
| 14  | —CH <sub>2</sub> CH <sub>2</sub> —                                                           | 0.12                | 0.14                | 0.39        | 3.20        | 3.48        |
| 15  | —CH <sub>2</sub> CH(CH <sub>3</sub> )—                                                     | 0.01                | 0.07                | 3.40        | 1.23        | 3.43        |
| 16a |  —OCH <sub>2</sub> CH <sub>3</sub>                                                         | 0.03                | 0.01                | 3.09        | 1.56        | 3.55        |
| 16b |                                                                                                                                                                               | 0.12                | 0.04                | 3.50        | 0.55        | 3.47        |
| 17  |  —N=N—  | 0.08                | 0.10                | 3.96        | 0.81        | 3.48        |
| 18  |  —      | 0.03                | 0.09                | n/a         | n/a         | 3.33        |
| 19  |  —      | 0.04                | 0.16                | 1.69        | 0.91        | 3.31        |
| 20  |  —      | 0.08                | 0.04                | n/a         | n/a         | 3.46        |

**Table S2:** Geometry of PDI-H monomer optimized with B3LYP/6-31G\*, with absolute energy = -1331.121232 Hartree

|   |          |          |   |
|---|----------|----------|---|
| C | 2.425929 | 2.877042 | 0 |
| C | 2.431692 | 1.478377 | 0 |
| C | 1.249698 | 0.735668 | 0 |
| C | 0        | 1.434695 | 0 |
| C | 0        | 2.865043 | 0 |
| C | 1.230871 | 3.573191 | 0 |
| C | -1.2497  | 0.735668 | 0 |
| C | -2.43169 | 1.478377 | 0 |
| C | -2.42593 | 2.877042 | 0 |
| C | -1.23087 | 3.573191 | 0 |
| C | 1.249698 | -0.73567 | 0 |
| C | 0        | -1.4347  | 0 |
| C | -1.2497  | -0.73567 | 0 |
| C | 2.431692 | -1.47838 | 0 |
| C | 2.425929 | -2.87704 | 0 |
| C | 1.230871 | -3.57319 | 0 |
| C | 0        | -2.86504 | 0 |
| C | -1.23087 | -3.57319 | 0 |
| C | -2.42593 | -2.87704 | 0 |
| C | -2.43169 | -1.47838 | 0 |
| C | 1.253155 | -5.05612 | 0 |
| N | 0        | -5.66637 | 0 |
| C | -1.25316 | -5.05612 | 0 |
| C | -1.25316 | 5.056118 | 0 |
| N | 0        | 5.66637  | 0 |
| C | 1.253155 | 5.056118 | 0 |
| O | -2.27551 | 5.724343 | 0 |
| O | 2.275511 | 5.724343 | 0 |
| O | -2.27551 | -5.72434 | 0 |
| O | 2.275511 | -5.72434 | 0 |
| H | 3.355369 | 3.436985 | 0 |
| H | 3.392235 | 0.977632 | 0 |
| H | -3.39224 | 0.977632 | 0 |
| H | -3.35537 | 3.436985 | 0 |
| H | 3.392235 | -0.97763 | 0 |
| H | 3.355369 | -3.43699 | 0 |
| H | -3.35537 | -3.43699 | 0 |
| H | -3.39224 | -0.97763 | 0 |
| H | 0        | -6.68172 | 0 |
| H | 0        | 6.68172  | 0 |



**Figure S3:** Schematic representation of a crystal with two inequivalent stacks

### 3. Full citation for ref. 10:

Shao, Y.; Molnar, L. F.; Jung, Y.; Kussmann, J.; Ochsenfeld, C.; Brown, S. T.; Gilbert, A. T. B.; Slipchenko, L. V.; Levchenko, S. V.; O'Neill, D. P.; DiStasio, R. A.; Lochan, R. C.; Wang, T.; Beran, G. J. O.; Besley, N. A.; Herbert, J. M.; Lin, C. Y.; Van Voorhis, T.; Chien, S. H.; Sodt, A.; Steele, R. P.; Rassolov, V. A.; Maslen, P. E.; Korambath, P. P.; Adamson, R. D.; Austin, B.; Baker, J.; Byrd, E. F. C.; Dachsel, H.; Doerksen, R. J.; Dreuw, A.; Dunietz, B. D.; Dutoi, A. D.; Furlani, T. R.; Gwaltney, S. R.; Heyden, A.; Hirata, S.; Hsu, C.-P.; Kedziora, G.; Khalliulin, R. Z.; Klunzinger, P.; Lee, A. M.; Lee, M. S.; Liang, W.; Lotan, I.; Nair, N.; Peters, B.; Proynov, E. I.; Pieniazek, P. A.; Rhee, Y. M.; Ritchie, J.; Rosta, E.; Sherrill, C. D.; Simmonett, A. C.; Subotnik, J. E.; Woodcock, H. L.; Zhang, W.; Bell, A. T.; Chakraborty, A. K.; Chipman, D. M.; Keil, F. J.; Warshel, A.; Hehre, W. J.; Schaefer, H. F.; Kong, J.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2006**, 8, 3172-3191.

### 4. References for Supporting Information:

- (1) Tauer, T. P.; Sherrill, C. D. *J. Phys. Chem. A* **2005**, 109, 10475-10478.
- (2) Valeev, E. F.; Coropceanu, V.; da Silva, D. A.; Salman, S.; Bredas, J. L. *J. Am. Chem. Soc.* **2006**, 128, 9882-9886.
- (3) Yang, X. D.; Li, Q. K.; Shuai, Z. G. *Nanotechnology* **2007**, 18, 424029
- (4) Anthony, J. E. *Chem. Rev.* **2006**, 106, 5028-5048.
- (5) Johnson, E. R.; Becke, A. D.; Sherrill, C. D.; DiLabio, G. A. *J. Chem. Phys.* **2009**, 131, 034111.
- (6) Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998