# **Electronic Supplementary Information**

### A theoretical discussion on the relationships among molecular

## packings, intermolecular interactions, and electron transport

## properties for naphthalene tetracarboxylic diimides derivatives

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#### The site energy corrected method

The site energy corrected method is used to calculate the effective electronic coupling and effective site energies from the spatial overlap integral  $S_{ij}$ , electronic coupling  $V_{ij}$  and site energies  $\mathcal{E}_{i(j)}$ ,

$$V_{12}^{eff} = \frac{V_{12} - \frac{1}{2} (\varepsilon_1 + \varepsilon_2) S_{12}}{1 - S_{12}^2}$$
(S1)

$$\varepsilon_{1(2)}^{eff} = \frac{1}{2} \frac{(\varepsilon_1 + \varepsilon_2) - 2V_{12}S_{12} \pm (\varepsilon_1 - \varepsilon_2)\sqrt{1 - S_{12}^2}}{1 - S_{12}^2}$$
(S2)

Assuming that H is the Hamiltonian of the dimer system and  $\psi_i$  and  $\psi_j$  are the highest occupied molecular orbitals (HOMO) of two monomers,  $S_{ij}$ ,  $V_{ij}$ , and  $\varepsilon_{i(j)}$  needed for the calculation of electronic coupling for p-type organic materials can be obtained from

$$S_{ij} = \left\langle \psi_i \middle| \psi_j \right\rangle \tag{S3}$$

$$\varepsilon_{i} = \left\langle \psi_{i} \left| \hat{H} \right| \psi_{i} \right\rangle \tag{S4}$$

$$V_{ij} = \left\langle \psi_i \left| \hat{H} \right| \psi_j \right\rangle \tag{S5}$$

#### The electrostatic potential (ESP)

The electrostatic potential can be defined in the gas-phase by the following expression:

$$V\left(\vec{r}\right) = \sum_{A} \frac{Z_{A}}{\left|\vec{r} - \vec{R}_{A}\right|} - \int \frac{\rho\left(\vec{r}'\right)}{\left|\vec{r} - \vec{r}'\right|} d\vec{r}'$$
(S6)

Where  $Z_A$  and  $\overline{R}_A$  are the charge and position of nucleus A, respectively, and  $\rho(\overline{r}')$  is the electron density at position  $\overline{r}'$ . The first term corresponds to the classical electrostatic potential of the nuclei and the second term corresponds to the quantum-mechanical electrostatic potential of the electrons. The ESP at a given point near a molecule is a measure of the electrostatic energy. A positive unit test charge would experience at that point. For instance, in Fig. 7 of manuscript, negative ESPs in blue correspond to an attractive interaction with this test charge, while positive ESPs in red indicate repulsion.

**Table S1** Bond lengths (Å), dihedral angles (°), the lowest unoccupied molecular orbital (LUMO) energy levels (eV), and adiabatic electron affinities (AEA eV) in full optimized geometries based on B3LYP/6-31G(d,p), compared with experimental values <sup>a</sup>.

	1		2	2		3	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	
N1-C2	1.411	1.398	1.399	1.398	1.404	1.394	
C2-O3	1.219	1.213	1.219	1.219	1.215	1.174	
C2-C4	1.486	1.477	1.484	1.469	1.495	1.533	
C4-C5	1.416	1.390	1.417	1.422	1.427	1.451	
C4-C6	1.386	1.380	1.378	1.361	1.393	1.370	
C6-C7	1.407	1.402	1.409	1.399	1.429	1.421	
C7-C8	1.386	1.360	1.397	1.395	1.395	1.387	
C8-C9	1.416	1.425	1.428	1.436	1.429	1.444	
C5-C9	1.421	1.434	1.425	1.406	1.425	1.350	
C8-C10	1.486	1.490	1.494	1.493	1.498	1.509	
N1-C2-C4-C6	-177.5	-176.1	-178.1	-178.9	-162.4	-170.5	
LUMO	-3.74	-3.72	-3.94	-4.01	-4.06	-4.13	
AEA	2.44		2.71	—	2.90	—	

<sup>a</sup> Data from ref [22].



Fig. S1 The definition of the perpendicular distance P (a) and the evolution of the electron transfer integrals as functions of P for the three simplified models cofacial dimers. There is no displacement both along the long axis and short axis.



**Fig. S2** The geometries of dimers *A* of **1-3** before and after optimization and the corresponding bond labels.

1		2	2	3		
	Bond length <sup>a</sup>	Bond length <sup>b</sup>	Bond length <sup>a</sup>	Bond length <sup>b</sup>	Bond length <sup>a</sup>	Bond length <sup>b</sup>
1	1.338	1.313	1.341	1.348	1.341	1.338
2	1.552	1.539	1.551	1.518	1.552	1.465
3	1.357	1.325	1.357	1.356	1.360	1.356
4	1.546	1.513	1.549	1.537	1.550	1.574
5	1.365	1.357	1.364	1.361	1.363	1.328
6	1.527	1.521	1.526	1.519	1.524	1.500
7	1.461	1.468	1.462	1.467	1.465	1.503
8	1.415	1.387	1.403	1.398	1.405	1.397
9	1.217	1.224	1.217	1.219	1.213	1.181
10	1.485	1.490	1.486	1.470	1.495	1.509
11	1.418	1.425	1.419	1.422	1.428	1.444
12	1.387	1.360	1.379	1.361	1.397	1.387
13	1.408	1.402	1.413	1.399	1.733	1.706
14	1.387	1.380	1.739	1.721	1.430	1.421
15	1.422	1.434	1.398	1.395	1.734	1.746
16	1.417	1.390	1.428	1.436	1.394	1.370
17	1.485	1.477	1.426	1.406	1.426	1.451
18	1.218	1.213	1.494	1.493	1.426	1.350
19	1.412	1.398	1.213	1.207	1.493	1.533
20			1.421	1.419	1.212	1.174
21					1.406	1.394

 Table S2
 The monomer bond lengths (Å) in dimers before and after optimization.

<sup>a</sup> The bond lengths before optimization;

<sup>b</sup> The bond lengths after optimization.



**Fig. S3** The convergences of total dimer energies during geometrical optimization process for all dimers *A*. The total dimer energies before optimization are set to 0 eV.

	L (Å)		X(A	$X(\text{\AA})$		$P(\text{\AA})$		C-C (Å)	
	Before	After	Before	After		Before	After	Before	After
1	3.082	2.864	2.316	1.076		3.476	3.396	5.191	4.571
2	3.662	1.825	3.286	2.246		3.318	3.473	5.935	4.521
3	1.511	1.263	3.648	2.998		3.233	3.402	5.104	4.707

**Table S3** The relative orientations before and after optimizations for  $1-3^a$ .

<sup>a</sup> The C-C values refer to centroid to centroid distances, P is the perpendicular distance between the two NDI core planes, L refers to the displacement along the molecular long axis, and X is the displacement along the short axis.



**Fig. S4** Schematic description of the intramolecular reorganization energy of compound **1** calculated using different functionals, BLYP, B3LYP, B $\lambda$ LYP, and BH&HLYP with the same basis set 6-31G(d,p).



Fig S5 The contributions of vibrations to the geometry relaxation for 1-3.



**Fig S6** Band structures of three crystals: (a) **1** (Triclinic space group  $P\overline{I}$ , a = 5.191 Å, b = 10.146 Å, c = 11.599 Å, and  $\alpha = 66.69^{\circ}$ ,  $\beta = 79.06^{\circ}$ ,  $\gamma = 89.12^{\circ}$ ), (b) **2** (Monoclinic space group  $P2_1/c$ , a = 11.870 Å, b = 16.633 Å, c = 5.935 Å, and  $\alpha = \gamma = 90^{\circ}$ ,  $\beta = 110.90^{\circ}$ ), and (c) **3** (Triclinic space group  $P\overline{I}$ , a = 5.104 Å, b = 10.358 Å, c = 12.395 Å,  $\alpha = 111.08^{\circ}$ ,  $\beta = 90.07^{\circ}$ ,  $\gamma = 96.67^{\circ}$ ,). The energies are plotted along directions in the first Brillouin zone connecting the point:  $\Gamma = (0, 0, 0)$ ,

X = (0.5, 0, 0), Y = (0, 0.5, 0), Z = (0, 0, 0.5), T = (0, 0.5, 0.5), V = (0.5, 0.5, 0), U = (0.5, 0, 0.5)and R = (0.5, 0.5, 0.5) for the band structure of **1**;  $\Gamma = (0, 0, 0), B = (0.5, 0, 0), Y = (0, 0.5, 0), Z = (0, 0, 0.5), A = (0.5, 0.5, 0), C = (0, 0.5, 0.5), D = (0.5, 0, 0.5)$  and E = (0.5, 0.5, 0.5, 0.5) for the band structure of **2**;  $\Gamma = (0, 0, 0), X = (0.5, 0, 0), Y = (0, 0.5, 0), Z = (0, 0, 0.5), T = (0, 0.5, 0.5), V = (0.5, 0.5), O = (0.5, 0.5), O = (0.5, 0.5), C = (0, 0.5, 0.5), C = (0, 0.5, 0.5), D = (0.5, 0.5), C = (0, 0.5, 0.5), D = (0.5, 0.5), C = (0, 0.5, 0.5), C = (0, 0.5, 0.5), D = (0.5, 0.5), C = (0, 0.5, 0.5), D = (0.5, 0.5), C = (0, 0.5, 0.5), C = (0, 0.5,$ 



**Fig. S7** Illustration of projecting different hopping pathways to a transistor channel in the *a-b* plane of **1** crystal;  $\theta_P$ ,  $\theta_{T1}$ ,  $\theta_{T2}$  and  $\theta_{T3}$  are the angles of *P*,  $T_1$ ,  $T_2$ , and  $T_3$  dimers relative to the reference crystallographic axis *a* (*L* dimer is also shown);  $\Phi$  is the angle of a transistor channel relative to the reference crystallographic axis *a*.



**Fig. S8** Illustration of projecting different hopping pathways to a transistor channel in the *b-c* plane of **2** crystal;  $\theta_P$ ,  $\theta_{T1}$ , and  $\theta_{T2}$  are the angles of *P*,  $T_1$ , and  $T_2$  dimers relative to the reference crystallographic axis *c* (*L* dimer is also shown);  $\Phi$  is the angle of a transistor channel relative to the reference crystallographic axis *c*.



**Fig. S9** Illustration of projecting different hopping pathways to a transistor channel in the *a-b* plane of a **3** crystal;  $\theta_P$ ,  $\theta_{T1}$ ,  $\theta_{T2}$  and  $\theta_{T3}$  are the angles of *P*,  $T_1$ ,  $T_2$ , and  $T_3$  dimers relative to the reference crystallographic axis *a* (*L* dimer is also shown);  $\Phi$  is the angle of a transistor channel relative to the reference crystallographic axis *a*.



Fig. S10 The electron mobility as a function of temperature for 1-3.