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Supporting Information

Unraveling the unusual effect of fluorination on crystal packing in organic semiconductor

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1. Synthetic details

Synthesis of *N*, *N*'-diphenyl-NDI (Ph-NDI)^{S1}: A mixture of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (0.30 g, 1 mmol), aniline (0.21 g, 0.20 ml, 2 mmol) in dry DMF (20 ml) was heated at 80 °C for 2 h. When the reaction mixture reached the room temperature, a crystalline solid precipitated out, which was collected by filtration.

Synthesis of *N*, *N*'-bis(4-fluorophenyl)-NDI (p-FPh-NDI)^{S2}: A mixture of 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.53 g, 2 mmol), 4-fluoroaniline (0.44 g, 0.38 ml, 4 mmol) in dry DMF (25 ml) was heated under reflux for 24 h. When the reaction mixture reached room temperature, a crystalline solid precipitated out, which was collected by filtration.

The molecular structures were characterized by ¹H, ¹³C NMR spectroscopy (Figure S2-S5) and elemental analysis.



Figure S1. Synthetic route to Ph-NDI and p-FPh-NDI.

N, *N*'-Diphenyl-NDI (2,7-diphenylbenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone): The crude product was purified by recrystallization from DMF, the target compound was off-white crystalline solid in 82% yield (0.41 g, 0.9 mmol). ¹H (DMSO d₆, 400 MHz) δ /ppm: 8.74 (4H, *s*, Naph), 7.46-7.60 (10H, *m*, Ph). ¹³C NMR (100 MHz, CDCl₃) δ /ppm: 162.83, 135.52, 130.36, 128.93, 128.85, 128.37, 126.94, 126.65. Found, %: C 74.37; H 3.42; N 6.81. C₂₆H₁₄N₂O₄. Calculated, %: C 74.64; H 3.37; N 6.70.

N, *N*'-Bis(4-fluorophenyl)-NDI (2,7-bis(4-fluorophenyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone): The crude product was purified by two-staged gradient high-vacuum sublimation to obtain target compound as an yellow crystalline solid in 80% yield (0.73 g, 1.6 mmol). The spatial separation of the crude material into fractions during gradient vacuum sublimation occurred at a pressure of ~1×10⁻⁶ mbar in a smooth temperature gradient of 0.6 K cm⁻¹. The sublimation temperature was about 250°C, and the precipitation temperature was 230– 190°C. Each purification stage lasted about 24 hours. ¹H (DMSO d₆, 400 MHz) δ /ppm: 8.76 (4H, *s*, Naph), 7.56 (4H, *dd*, *J* = 9.01 Hz, Ph), 7.41 (4H, *t*, *J*₁ = 8.75 Hz, *J*₂ = 8.88 Hz, Ph). ¹³C NMR (100 MHz, CDCl₃) δ /ppm: 162.89, 162.74, 160.46, 131.53, 131.50, 131.01, 130.93, 130.29, 126.85, 126.57, 115.73, 115.49. Found, %: C 68.58; H 2.68; N 6.30. C₂₆H₁₂F₂N₂O₄. Calculated, %: C 68.73; H 2.66; N 6.17.



Figure S2. ¹H NMR spectrum of Ph-NDI.



Figure S3. ¹³C NMR spectrum of Ph-NDI.



Figure S4. ¹H NMR spectrum of **p-FPh-NDI**.



Figure S5. ¹³C NMR spectrum of p-FPh-NDI.

2. CV measurements and optical properties

The cyclic voltammetry method (CV) was used to study the electrochemical behavior and to estimate the value of LUMO energy level of the **Ph-NDI** and **p-FPh-NDI**. E_{LUMO} (eV) = $[-e(E^{red}_{onsetvsAg/AgCI} - E_{FcvsAg/AgCI} + 4.80)]$, where 4.8 eV is the energy level of ferrocene below the vacuum level.^{S3} The oxidation potential of Fc⁺/Fc against Ag/AgCl was recorded in DMF-Et₄N⁺ClO⁻₄ (0.1 M) solution to be 0.50 V, therefore the herein half-wave potentials are converted to Fc/Fc⁺ by subtracting 0.50 V from Ag/AgCl values. CV data are shown in Figure S6.



Figure S6. CV curves of Ph-NDI (blue line) and p-FPh-NDI (red line).

To address the impact of fluorination on the optical characteristics of **Ph-NDI**, absorption and photoluminescence spectra of **Ph-NDI** and **p-FPh-NDI** (Table S1) were recorded. UV-Vis absorption spectra were recorded in standard $10 \times 10 \times 45$ mm quartz cuvettes using a Shimadzu UV-2600 spectrophotometer for **Ph-NDI** and **p-FPh-NDI** solutions in DMSO at a concentration of 1 x 10⁻⁵ mol L⁻¹. Photoluminescence spectra of these solutions were recorded with a Shimadzu RF-5301 PC spectrofluorophotometer. The solvent was dried and distilled before using as described in Ref. ^{S4}

The introduction of fluorine atoms does not significantly change the optical characteristics of **Ph-NDI**. The absorption maxima of both **Ph-NDI** and **p-FPh-NDI** in solution are located in UV region, which are usually ascribed to the $\pi - \pi^*$ transition of the conjugated backbone.

| Comp | E _{HOMO} , eV ^a | E_{LUMO}, eV^{b} | λ^{abs}_{max} , nm ^c | λ^{emi}_{max} , nm ^c | E_g^{opt} , eV^d |
|-----------|-------------------------------------|--------------------|---|---|----------------------|
| Ph-NDI | -7.03 | -3.96 | 360, 380 | 407, 436 | 3.07 |
| p-FPh-NDI | -7.12 | - 4.02 | 360, 380 | 414, 436 | 3.10 |
| | nt E hE | | | 1 4 0 0 1 | 1 40 17 |

 ${}^{a}E_{HOMO} = E_{g}{}^{opt} - E_{LUMO}$; ${}^{b}E_{LUMO}$ (eV) = [-e($E^{red}_{onsetvsAg/AgCl} - E_{FcvsAg/AgCl} + 4.80$)], where 4.8 eV is the energy level of ferrocene below the vacuum level.^{S3} cAbsorption and emission maxima in DMSO solutions; ${}^{d}E_{g}{}^{opt} = 1240/\lambda_{onset}$, λ_{onset} is the long-wavelength absorption edge.



Figure S7. Absorption (a) and emission (b) spectra of **Ph-NDI** (blue line) and **p-FPh-NDI** (red line) in DMSO solution ($C = 1*10^{-5}$ M).

3. Calculated molecular properties: orbitals, Mulliken charges and optical transitions

The calculated patterns of highest occupied molecular orbitals – HOMO, HOMO-1 and HOMO-2 – for **Ph-NDI** and **p-FPh-NDI** are shown in Figure S8. The HOMO-1 and HOMO-2 are very close in energy to the HOMO in both compounds, and each of these three orbitals of **Ph-NDI** has a similar counterpart in **p-FPh-NDI**. The HOMO is localized mainly at the NDI core, whereas, in HOMO-1 and HOMO-2 are localized at the phenyl rings.



Figure S8. Calculated HOMO, HOMO-1 and HOMO-2 patterns for **Ph-NDI** (left) and **p-FPh-NDI** (right) in DMSO. Energies of the orbitals are labeled.



Figure S9. Representation of Mulliken charges for **Ph-NDI** (a) and **p-FPh-NDI** (b). The red and blue colors designate large positive and negative Mulliken charges, respectively; orange and light-blue show small positive and negative Mulliken charges, correspondingly.

TDDFT calculations yielded that lowest-energy transitions from the ground state to singlet excited state peak at 3.247 eV (382 nm) and 3.276 eV (379 nm) in **Ph-NDI** and **p-FPh-NDI**, respectively, in perfect correspondence with the experimental data (Section 2). These transitions correspond mostly to HOMO–LUMO transitions. Their oscillator strengths are rather low — 0.33 and 0.48 for **Ph-NDI** and **p-FPh-NDI**, correspondingly, — and are in line with weak luminescence of both compounds.

4. Thermal analysis

Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) was performed by using Netzsch DSC 214 Polyma: the scan rate was 10°C/min under nitrogen atmosphere. **p-FPh-NDI** was studied by simultaneous thermal analysis and differential scanning calorimetry (Figure S10).

High thermal stability is important for OFETs since it is directly related to the device longevity. The introduction of fluorine atoms into the phenyl substituents of **Ph-NDI** increases its decomposition temperature. For **Ph-NDI**, decomposition to a 10% loss of weight occurs at 390°C.^{S5} According to our TG data (Figure S10), **p-FPh-NDI** underwent thermal decomposition with a mass loss accompanied by an endothermic effect starting at 407–408°C so that the temperature of 430 °C corresponds to a 10% loss of weight. Therefore, the fluorination results in the higher thermal stability of **p-FPh-NDI**, which is beneficial for applications in electronic devices.



Figure S10. Thermal analysis of **p-FPh-NDI**. Blue solid curve: DSC; green solid curve: TG; green dashed curve: TG derivative.

5. XRD analysis

Crystal Data of **p-FPh-NDI**. C₂₆H₁₂F₂N₂O₄, M = 454.38, monoclinic, a = 16.538(5) Å, b = 8.3933(15) Å, c = 7.2050(18) Å, $\beta = 101.82(3)^{\circ}$, V = 978.9(4) Å³, T = 295(2), space group $P2_1/c$, Z = 2, μ (Mo K α) = 0.118 mm⁻¹. The final refinement parameters: $R_1 = 0.0606$, $wR_2 = 0.1658$ [for observed 1539 reflections with $I > 2\sigma(I)$]; $R_1 = 0.0897$, $wR_2 = 0.1963$ (for all independent 2368 reflections, $R_{int} = 0.0333$), S = 1.098. Largest diff. peak and hole 0.238 and $- 0.241 \text{ e}\text{Å}^{-3}$.

CCDC 1956469 (for **p-FPh-NDI**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

For crystal directions with slipped face-to-face arrangement of the NDI cores (a_1 , a_3 for **Ph-NDI** and a_1 for **p-FPh-NDI**, see Figure 8), the slip distances along the long (D_x) and short (D_y) axes of the NDI core were calculated as described in Ref. S8. For **Ph-NDI** in direction a_1 : $D_x = 0$ Å, $D_y = 4.341$ Å; in direction a_3 , $D_x = 5.662$ Å, $D_y = 3.367$ Å; for **p-FPh-NDI** in direction a_1 : $D_x = 3.097$ Å, $D_y = 5.821$ Å. The interplanar distances for these directions are 3.463 Å for **Ph-NDI** and 2.903 Å for **p-FPh-NDI**.



Figure S11. Molecular structure of **Ph-NDI** (a) and **p-FPh-NDI** (c) with labeled atoms and torsion angles; side view on the stacks with the dihedral angle and inter-centroid distances for **Ph-NDI** (b) and **p-FPh-NDI** (d).

6. Hirshfeld surface analysis

Curvedness is a function which is the root-mean-square curvature of the surface (Figure S12b). Flat areas of the surface, indicated in green, have a low curvedness and areas of sharp curvature, indicated in blue, have a high curvedness. The comparison of curvedness mapping for **Ph-NDI** and **p-FPh-NDI** shows significant differences: the surface for **Ph-NDI** has a flat region (large green spot) over the NDI core, indicating planar stacking between the molecules, whereas the curvedness plot for **p-FPh-NDI** shows no flat surface patches, which corresponds to the absence of any signs of planar stacking.

Shape index mapping (Figure S12c) represents the fine changes in the surface shape, especially in the regions with low curvature and highlights the regions where the two molecular Hirshfeld surfaces touch one another. This mapping uses red and blue color schemes for complementary pairs of hollows and bumps. This is very useful feature suitable for identifying interface regions where surfaces of adjacent molecules touch one another. The front and back

view of the Hirshfeld surfaces for both **Ph-NDI** and **p-FPh-NDI** are quite similar indicating that the two sides of the molecules are involved in a quite similar crystal packing.



Figure S12. Molecular diagrams of **Ph-NDI** and **p-FPh-NDI** (a), curvedness (b), shape-index (c) and 2D fingerprint plots with d_i and d_e ranging from 0.5 to 2.9 Å (d).

Figure S12d shows the associated fingerprint plots of the two compounds. For any given d_i and d_e pairs, the change in color shows the raise in occurrence: the white color for no occurrence, the blue green, and red ones for most frequent occurrence. These plots give the percentage contribution of each contacts to the total Hirshfeld surface area (Table S2). The major contribution to the total Hirshfeld area for **Ph-NDI** is from H···H contacts, which is about 34.0%, whereas it is only 16% for **p-FPh-NDI**. This is explained by the planar stack packing of **Ph-NDI**, which promotes H···H contacts from the core hydrogens of adjacent molecules. On the other hand, herringbone packing of **p-FPh-NDI** prohibits such contacts, modifying them into C-

H… π contacts. The remaining significant contributions are from C…H, O…H and F…all (for **p**-**FPh-NDI**). The extended symmetrical 'spikes' in Figure S12d are the characteristics of O…H intermolecular hydrogen bond interactions, which appear for both compounds. But for **p**-**FPh-NDI** double symmetrical 'spikes' are observed, since the second pair of spikes correspond to F…H intermolecular hydrogen bond interactions. The relative contributions of the various intermolecular interactions to the Hirshfeld surfaces are illustrated in Figure S13, which shows that the whole amount of H…H contacts for **Ph-NDI** has split into H…H and F…H contacts for **p**-**FPh-NDI**. Also, the change in packing motif from π -stacking to herringbone one naturally resulted in the decrease in number of C…C contacts.



Figure S13. Distribution of reciprocal intermolecular contacts in Ph-NDI and p-FPh-NDI.

 Table S2. Percentage of individual intermolecular interactions (reciprocal) in Ph-NDI and p

 FPh-NDI.

| Molecule | Н…Н | С…Н | C…C | О…Н | O…C | 00 | O…N | C…N | ···N | N···H | F…H | F…other |
|----------|------|------|-----|------|-----|-----|-----|-----|------|-------|------|---------|
| Ph-NDI | 34.1 | 26.7 | 6.6 | 25.3 | 6.5 | 0.2 | 0.2 | 0 | 0 | 0.3 | 0 | 0 |
| p-FPh- | | | | | | | | | | | | 4.5 |
| NDI | 15.9 | 28.2 | 2.6 | 21.1 | 9.7 | 0 | 0.8 | 0 | 0 | 0.6 | 16.6 | |

Figure S14 and Figure S15 show how the breakdown of the fingerprint plot can be used to identify the patterns associated with specific interactions (C···C, C···O and F···all). Moreover, a deeper insight can be obtained by mapping just those surface areas that contribute to particular interactions, and in Figure S14 and Figure S15 the shape index mapping is used to illustrate this. As shown in the left column of Figure S14, C···C contacts for **Ph-NDI** cover significant area above the NDI core. Furthermore, there is a complementary stamp of red and blue triangles on the surface of **Ph-NDI** — a 'bow tie' pattern. Such a pattern on the shape index mapping alongside with the flat region on curvedness mapping strongly indicate π ... π stacking between adjacent molecules through this area. But for **p-FPh-NDI** with herringbone packing of molecules neither large regions with low curvature nor complementary red and blue triangles are observed. On the contrary, C···O contacts cover a large area of the Hirshfeld surface for both molecules, and for each molecule two red depressions over the core ring can be readily matched to the corresponding blue buldges over the oxygen, illustrating how these C···O contacts occur.

Among the fluorine contacts (21%) in **p-FPh-NDI**, the most part of them are with hydrogen (16.6%) and carbon (3.5%).



Figure S14. Fingerprint plots for **Ph-NDI** and **p-FPh-NDI** molecules broken down into contributions from specific pairs of atom types. For each plot, the grey shadow is an outline of the complete fingerprint plot (see Figure S12d). Surfaces above highlight the relevant surface patches associated with the specific contacts, with the shape index is mapped in the same manner as in Figure S12c.



Figure S15. Fingerprint plot for **p-FPh-NDI** molecule, only F...all (reciprocal) contributions are shown. See Figure S12 for details.

6.1. Electrostatic interaction energies contribution into packing

Here we elaborate further on the concept of "electrostatic complementarity" between touching surface patches in adjacent molecules^{S7}, with Figure S16 and S17 showing small clusters of molecules extracted from the crystal structures, with the molecular ESP mapped on the Hirshfeld surfaces, along with values of the electrostatic interaction energy computed directly from the two molecular charge (electron + nuclear) distributions.

Ph-NDI

A number of clusters of several **Ph-NDI** dimers (Figure S16) with ESPs onto the Hirshfeld surfaces was generated to illustrate an electrostatic contribution to molecular packing. The clusters for intralayer and interlayer packing are presented in Figure S16a-b and Figure S16c-d, respectively. Figure S16a shows an obvious complementarity between ESP maps for the molecules involved in the edge-to-edge pairs (Figure S16a), with a good matching of zero potential (the white lines), and electronegative (red) patches paired with electropositive (blue) patches in adjacent molecules. The computed electrostatic energy for these pairs, -23 kJ mol⁻¹, reflects rather strong complementarity. The face-to-face pairs (Figure S16b) exhibit less ESP complementarity, mostly due to the electropositive hydrogen on the phenyl rings and electronegative oxygen in the carboxylic group (-33 kJ mol⁻¹ and -9 kJ mol⁻¹). The ESP complementarity for the interlayer clusters is much weaker, very close to zero for half of the dimers (Figure S16c-d). The other half of the dimers have red-blue complementarity over a small phenyl area where the electropositive para-hydrogen is adjacent to the electronegative phenyl core (-5.5 kJ mol⁻¹).

p-FPh-NDI

Similar to Ph-NDI several clusters of p-FPh-NDI dimers (Figure S17) with ESPs onto the Hirshfeld surfaces were generated. Because of herringbone packing, the most intralayer interactions are between the edge-to-face dimers (Figure S17a-b). The ESP complementarity is observed in the following areas: between the carboxylic oxygen (red) and the NDI core (blue), between the carboxylic oxygen (red) and phenyl hydrogen (blue), between the phenyl ring (red) and phenyl hydrogen (blue). The total electrostatic energy for this pair is -26 kJ mol⁻¹ (for comparison the ESP complementarity for face-to-face dimers is minimal and the electrostatic energy is around -1 kJ mol⁻¹). As for the interlayer dimers, the ESP complementarity occurs as often as the uncomplimentarity (Figure S17c-d). The ESP complementarity is observed for two dimers (-x, y+1/2, -z+1/2), where the blue surface region of the phenyl hydrogen is adjacent to the red surface region of the fluorine (the electrostatic energy is around -4 kJ mol⁻¹). Meanwhile, one of the two remaining dimers contributes only -4 kJ mol⁻¹ because of weak interaction. The last one dimer shows an ESP uncomplimentarity as the electronegative oxygen in the carboxylic group is adjacent to the electronegative fluorine region with the electrostatic energy as high as +4 kJ mol⁻¹. Such destabilization is of the order of magnitude to the stabilizing electrostatic energy from other two dimers.



Figure S16. Ph-NDI: ESP mapped on the Hirshfeld surfaces for a small molecular cluster in the crystal. Color mapping and range for ESP as for Figure 4a in the main text, and the electrostatic

interaction energies (kJ mol⁻¹) for the nearest neighbor pairs of molecules are indicated in orange.



Figure S17. P-FPh-NDI: ESP mapped on the Hirshfeld surfaces for a small molecular cluster in the crystal. Color mapping and range for ESP as for Figure 4a in the main text, and the electrostatic interaction energies (kJ mol⁻¹) for the nearest neighbor pairs of molecules are indicated in orange.

6.2. Close contacts for other fluorinated NDIs

a)



Figure S18. Close contacts for *N*, *N'*-bis(2,2,3,3,4,4,4-heptafluorobutyl)-NDI (a) and *N*, *N'*-bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-NDI (b) as obtained from Hirshfeld analysis.

7. Energy frameworks and lattice energies



Figure S19. The graphical representation of total energy (blue) for the **Ph-NDI** (a) and **p-FPh-NDI** (b) crystals (for details see Figure 7 in the main text).

Table S3. Different interaction energies of the molecular pairs for **Ph-NDI** in kJ mol⁻¹: N is the number of pairs, R is the distance between the molecule centroids, E_ele is the classical electrostatic energy of interaction between monomer charge distributions, E_pol is the polarization energy estimated as a sum over atoms with terms of the kind $-\frac{1}{2}\alpha|F|^2$, where the electric field *F* is computed at each atomic nucleus from the charge distribution of the other monomer and α are isotropic atomic polarizabilities, E_dis is Grimme's D2 dispersion correction summed over all intermolecular atom pairs, E_rep is the exchange–repulsion energy, obtained from the antisymmetric product of the monomer spin orbitals,^{S8} and E_tot is the total energy.

| N | R (A) | E_ele | E_pol | E_dis | E_rep | E_tot |
|---|-------|-------|-------|-------|-------|-------|
| 2 | 9.11 | -22.7 | -5.1 | -16.5 | 21.8 | -28.6 |
| 2 | 5.14 | -32.8 | -8.0 | -87.1 | 62.1 | -78.2 |
| 4 | 13.64 | -0.3 | -0.4 | -8.9 | 3.6 | -6.2 |
| 4 | 13.55 | -5.5 | -1.6 | -16.3 | 9.2 | -15.6 |
| 2 | 7.52 | -8.7 | -2.8 | -43.3 | 20.6 | -36.2 |

Table S4. Different interaction energies of the molecular pairs for p-FPh-NDI in kJ mol⁻¹.

| N | R (A) | E_ele | E_pol | E_dis | E_rep | E_tot |
|---|-------|-------|-------|-------|-------|-------|
| 4 | 18.29 | -4.2 | -0.5 | -8.2 | 6.2 | -8.1 |
| 2 | 19.58 | -0.1 | -0.1 | -2.5 | 0.0 | -2.3 |
| 4 | 5.53 | -26.1 | -7.2 | -75.3 | 51.3 | -66.7 |
| 2 | 16.63 | 4.0 | -0.3 | -12.3 | 2.0 | -5.5 |
| 2 | 7.20 | -1.4 | -3.0 | -35.4 | 17.3 | -23.9 |

In **Ph-NDI**, the intralayer interactions consist mostly of energies between the face-to-face dimers (Figure S19a, black-yellow and black-violet pairs) and the edge-to-edge dimers (black-red pairs). The interactions between the face-to-face dimers are the most important: the dispersion energy is the largest (-87 kJ mol^{-1} and $-43.3 \text{ kJ mol}^{-1}$), and it is much less for the edge-to-edge neighbors (-16 kJ mol^{-1}), while the electrostatic energy for the face-to-face ($-32.8 \text{ kJ mol}^{-1}$) and edge-to-edge dimers ($-22.7 \text{ kJ mol}^{-1}$) is quite close. For **p-FPh-NDI**, the edge-to-face pairs (Figure S19b, black-green pairs) have the most important interactions ($-75.3 \text{ kJ mol}^{-1}$ dispersion term and $-26.1 \text{ kJ mol}^{-1}$ electrostatic term), while the interaction between face-to-face dimers (black-violet pairs) is two times weaker ($-35.4 \text{ kJ mol}^{-1}$ dispersion term and -1.4 kJ mol^{-1} electrostatic term).

The lattice energy, E_{latt} , was calculated for a 25Å-cluster for both **Ph-NDI** and **p-FPh-NDI** according to the technique described in the methods section. As the **Ph-NDI** and **p-FPh-NDI** molecules are centrosymmetric, their molecular dipole moments are equal to zero, and the lattice energy was estimated as the halved sum of all dimer's of interaction energies. The resulting distribution of partial sums to E_{latt} is presented in Figure S20: the partial energy contributions as well as the E_{latt} values are close to each other for both compounds. Remarkably, the dispersion contribution in E_{latt} is a little higher for **p-FPh-NDI**, while the electrostatic contribution is slightly lower. This fact is fully consistent with the ESP complementarity and energy framework diagrams discussed above.



Figure S20. Distribution of halved sum of the interaction energies (absolute values) for 25Åcluster of Ph-NDI and p-FPh-NDI. E_tot*N is the total lattice energy $E_{\text{latt.}}$

8. Charge mobility calculation details

8.1. Transfer integrals

Table S5. Center-to-center distances r, electron transfer integrals J, and electron transfer rates k for charge transport directions in the studied crystals.

| direction | <i>r</i> , A | J, meV | <i>k</i> , 10 ¹¹ s ⁻¹ | | | | | |
|-----------------------|--------------|--------|---|--|--|--|--|--|
| Ph-NDI | | | | | | | | |
| a ₁ | 5.16 | 68 | 27 | | | | | |
| a ₂ | 9.16 | 19 | 2.0 | | | | | |
| a ₃ | 7.56 | 16 | 1.5 | | | | | |
| p-FPh-NDI | | | | | | | | |
| a ₁ | 7.24 | 61 | 19 | | | | | |
| a ₂ | 5.56 | 28 | 4.1 | | | | | |

| a ₃ | 5.56 | 24 | 3.0 |
|----------------|------|----|-----|
| | | | |

8.2. LUMO overlap

a) a_1 (face-to-face 1)



b) a_2 (edge-to-edge)



c) a_3 (face-to-face 2)



d) a_1 (face-to-face 1)



Figure S21. LUMO overlap for molecular pairs along the main charge transport directions in **Ph-NDI**: $a_1(a)$, $a_2(b)$ and $a_3(c)$ and in **p-FPh-NDI**: $a_1(d)$.

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