Supporting Information

Improving the Robustness of Organic Semiconductors through Hydrogen-Bonding

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Figure S1. $^1$H-NMR (400 MHz) and $^{13}$C-NMR (50 MHz) spectra of compound 1 in CDCl$_3$. 
Figure S2. $^1$H-NMR (300 MHz) and $^{13}$C-NMR (100 MHz) spectra of ADI in DMSO-$d_6$. 
**Thermal properties**

![Thermogravimetric analysis](image)

**Figure S3.** Thermogravimetric analysis.

**Theory and computational results**

Marcus–Levitch–Jortner (MLJ) Rate Constant and its Parameters. Within a hopping mechanism, a MLJ rate constant has been selected since the MLJ rate incorporates quantum tunneling effects through an effective vibrational normal mode coordinate. The non-adiabatic electron-transfer MLJ rate is expressed as follows:

\[
K_{ij} = \frac{2\pi}{\hbar} \left\langle t_{ij}^2 \right\rangle \frac{1}{4\pi\sigma^2_{ij}} e^{-\frac{1}{2} \sum_{n} FCI_{n'} S_{n'}} \frac{1}{\sum_{n} \exp \left[ \frac{-\left( \Delta E_{ij} + \lambda_{ij} + (n' - n)b \omega_{ij} \right)^2}{4\lambda_{ij}k_B T} \right]} \text{ (S1)}
\]

where \( t_{ij} \) is the transfer integral between the hopping sites \( i \) and \( j \). \( \left\langle t_{ij}^2 \right\rangle \) incorporates the effect of the thermal fluctuation since \( \left\langle t_{ij}^2 \right\rangle = \left\langle t_{ij} \right\rangle^2 + \sigma_{ij}^2 \), where \( \sigma_{ij}^2 \) denotes the variance of \( t_{ij} \). \( \lambda_{ij} \) is the external reorganization energy, \( k_B \) is the Boltzmann constant, \( T \) is the temperature (298 K) and \( \hbar \) is the reduced Planck constant. \( \Delta E_{ij} \) is the site energy difference, which in an ideal crystal structure is zero. Here, the energy difference (\( \Delta E_{ij} = -q\vec{F}_{ij} \)) is caused by an external electric field \( \vec{F} \), where \( q \) is the charge (positive unit charge) and \( \vec{F}_{ij} \) is the distance vector between sites \( i \) and \( j \). \( FCI_{n'} S_{n'} \) denotes the Franck–Condon integrals between the initial \( (n) \) and final \( (n') \) vibrational levels between the initial \( i \) and final \( j \) molecular sites which have been calculated using an analytic expression under the harmonic approximation.\(^1\) \( S_{\text{eff}} \) corresponds to the Huang–Rhys (HR) factor for an effective normal mode with frequency \( \omega_{\text{eff}} \). Finally, \( P_f(n) \) represents the Boltzmann probability that a vibrational state \( n \) on an initial site \( i \) is occupied at a certain temperature.
The transfer integral $t_{ij}$ (also known as electronic coupling) have been calculated according to the approach developed by Baumeier et al.,\textsuperscript{2} in which the molecular orbitals of a dimer are projected on the basis of the molecular orbitals of the individual molecules.

To take into account the impact of the thermal motions on $t_{ij}$, molecular dynamics (MD) simulations (10 ps of equilibration and 100 ps of production) of cubic cells of 91 molecules for ADI and 125 molecules for ADAI were carried out at the GFN-FF level,\textsuperscript{3} where the molecules in the edge of the crystal were kept frozen since periodic boundary conditions are not implemented in the xTB code. From the production simulation, 1000 snapshots with timesteps of 0.1 ps were extracted. For each snapshot, the transfer integrals $t_{ij}$ for the most relevant dimers were calculated at the B3LYP/6-31G** level using a homemade program. Relevant dimers were considered to be those that displayed significant couplings ($t_{ij} > 1$ meV) at the experimental crystal structure (Table S1). Average transfer integral values ($\langle t_{ij} \rangle$) and their corresponding standard deviations ($\sigma_{t_{ij}}$) have been collected in Table S1.

The reorganization energy ($\lambda$) is a key parameter for the evaluation of electron transfer rates and is associated with the energy change owing to electronic redistribution and nuclear rearrangement in electron-transfer events.\textsuperscript{4} Generally, $\lambda$ is split into the internal and external reorganization components ($\lambda = \lambda_{\text{int}} + \lambda_{\text{ext}}$). The former is related to the energy cost due to the intramolecular nuclear relaxation of the molecular systems during the electron-transfer reaction whereas the latter comes from the environmental effects; i.e., polarization and reorientation of neighboring molecules as a response of the charge (electron or hole) injection in a molecular system.

The internal reorganization energy $\lambda_{\text{int}}$ has been estimated by using the four-point approach.\textsuperscript{4} $\lambda_{\text{int}}$ values of 159 and 183 meV have been calculated at the DFT level (B3LYP/6-31G**) for ADI and ADAI, respectively. $\lambda_{\text{int}}$ has been also decomposed into contributions for each normal mode according to $\lambda_{\text{int}} = \sum_k \hbar \omega_k S_k$, where $\omega_k$ is the vibrational frequency of the normal mode $k$ and $S_k$ corresponds to the Huang–Rhys (HR) factor. The HR factors have been estimated according to Ref. 5. In the MLJ expression (Eq. S1), the rate constant is simplified because it makes use of only a single effective normal mode coordinate with frequency $\omega_{\text{eff}} = \sum_k \omega_k S_k / \sum_k S_k$ and an effective HR factor $S_{\text{eff}} = \lambda_{\text{int}} / \hbar \omega_{\text{eff}}$.\textsuperscript{6} For ADI (ADAI), $S_{\text{eff}}$ and $\omega_{\text{eff}}$ values of 1.235 (1.415) and 1036 cm$^{-1}$ (1046 cm$^{-1}$) were obtained.

The external reorganization energy $\lambda_{\text{ext}}$ for electron-transfer processes in molecular crystals is generally small\textsuperscript{7} and is commonly neglected. Here, a common value of $\lambda_{\text{ext}} = 50$ meV has been set for both ADI and ADAI compounds in line with values reported for other similar systems.\textsuperscript{8}
Master Equation and Mobilities. The charge transport can be described by solving a kinetic master equation. In the case of low charge-carrier densities, the master equation acquires the simple linear expression:

$$\frac{d\rho_i}{dt} = \sum_j (k_j \rho_j - k_{ji} \rho_i),$$

where $\rho_i$ corresponds to the probability that the site $i$ is occupied by a charge (hole/electron) carrier. When the dynamic balance is reached (steady state), the occupation probabilities for the sites do not change anymore ($d\rho_i/dt = 0$). Eq. S2 can be rewritten in a matrix form as

$$\hat{0} = \hat{\rho} \mathbf{N},$$

where $\hat{\rho}$ contains the unknown $\rho_i$ and $\mathbf{N}$ is a negative semidefinite sparse matrix that collects all electron-transfer rates $k_{ji}$. $\mathbf{N}$ is approximated by a finite matrix by applying cyclic boundary conditions. In this work, a crystal super-cell model ($4 \times 4 \times 4$) of grid points corresponding to the molecular centroids of the ADI (128 sites) and a $5 \times 5 \times 5$ super-cell (125 sites) for ADAI molecules were used to solve Eq. S3. Once all the $\rho_i$ probabilities are obtained and the normalization condition ($\sum_i \rho_i = 1$) has taken into account, the hole mobility in the external electric field direction is calculated according to:

$$\mu = \frac{1}{F} \sum_j \rho_j \bar{r}_{ji} \bar{F}_j$$

**Figure S4.** Crystal structure views of the ab (a), ac (b), and bc (c) crystallographic planes of ADI. d) Grid representation of the crystal unit cell of ADI, where all different and non-negligible $t_{ji}$ values starting from the central molecule are shown (see Table S1). H atoms have been omitted for simplicity.
Figure S5. a) Crystal structure of ADAI. b) Grid representation of the crystal structure shown in (a) where all different and non-negligible $t_{ij}$ values involving the central molecule are shown (see Table S1). H atoms have been omitted for simplicity. Dotted blue lines indicates the molecules that form H-bonds.
Figure S6. a) 2D map of $t_{ij}$ (in meV) for a face-to-face π-stacked dimer of ADAI calculated by moving one of the molecules along the $x$ and $z$ directions starting from the crystal structure ($x = 0$ Å and $z = 0$ Å). b) Topologies of the HOMOs for a face-to-face π-stacked dimer of ADAI at the crystal structure (top and bottom molecules are represented with bright and faded colors, respectively).
Table S1. Average transfer integrals ($\langle t_{ij} \rangle$) and standard deviations ($\sigma_{t_{ij}}$) in meV calculated for the different molecular pairs of ADI and ADAI crystals from MD simulations (300K) (Figure S4 and S5). $t_{ij}$ corresponds to transfer integrals computed at the experimental crystal structure. Transfer integrals were computed at the B3LYP/6-31G** level. The $t_{ij}$ values for the face-to-face π-stacked dimers in both ADI and ADAI are highlighted in blue.

|       | ADI               |        | ADAI               |        |
|-------|-------------------|--------|--------------------|--------|
| $t_{ij}$ | $t_{ij}$ | $\langle t_{ij} \rangle$ | $\sigma_{t_{ij}}$ | $t_{ij}$ | $t_{ij}$ | $\langle t_{ij} \rangle$ | $\sigma_{t_{ij}}$ |
| $t_{1,2} = t_{1,3} = t_{1,4} = t_{1,5}$ | 14.4   | -6.8   | 16.9               | 11.1   | 0.0    | 57.8               |
| $t_{1,6} = t_{1,7} = t_{1,8} = t_{1,9}$ | 6.7    | -8.1   | 10.6               | 0.7    | -      | -                  |
| $t_{1,10} = t_{1,11}$ | 40.0   | 37.7   | 14.5               | 0.4    | -      | -                  |
| $t_{1,12} = t_{1,13}$ | 0.3    | -      | -                  | 0.0    | -      | -                  |

OFETs parameters at different temperatures

Table S2. OFETs parameters.

|       | ADI               |        | ADAI               |        |
|-------|-------------------|--------|--------------------|--------|
| T (°C) | $\mu$ [cm$^2$ V$^{-1}$ s$^{-1}$] | $V_{on}$ [V] | $I_{on}/I_{off}$ | $\mu$ [cm$^2$ V$^{-1}$ s$^{-1}$] | $V_{on}$ [V] | $I_{on}/I_{off}$ |
| 25    | 4.0×10$^{-4}$ ± 1×10$^{-4}$ | -48 ± 1 | 5×10$^4$ | 7.9×10$^{-3}$ ± 4×10$^{-4}$ | -16 ± 3 | 2×10$^4$ |
| 60    | 1.0×10$^{-3}$ ± 2×10$^{-4}$ | -35 ± 4 | 3×10$^4$ | 9.0×10$^{-3}$ ± 3×10$^{-4}$ | -5 ± 1 | 2×10$^6$ |
| 80    | 1.3×10$^{-3}$ ± 1×10$^{-4}$ | -33 ± 4 | 4×10$^4$ | 1.0×10$^{-3}$ ± 2×10$^{-3}$ | -9 ± 3 | 6×10$^4$ |
| 100   | 1.9×10$^{-3}$ ± 5×10$^{-4}$ | -29 ± 3 | 3×10$^5$ | 1.2×10$^{-2}$ ± 2×10$^{-3}$ | -8 ± 2 | 4×10$^4$ |
| 120   | 3.1×10$^{-3}$ ± 3×10$^{-4}$ | -26 ± 3 | 6×10$^3$ | 1.3×10$^{-2}$ ± 2×10$^{-3}$ | -7 ± 2 | 6×10$^4$ |
| 145   | 1.0×10$^{-3}$ ± 2×10$^{-3}$ | -25 ± 3 | 2×10$^5$ | 1.5×10$^{-2}$ ± 1×10$^{-3}$ | -8 ± 2 | 5×10$^4$ |
| 180   | 2.0×10$^{-3}$ ± 3×10$^{-3}$ | -29 ± 3 | 5×10$^6$ | 1.6×10$^{-3}$ ± 1×10$^{-3}$ | -10 ± 2 | 7×10$^4$ |
| 220   | 9.0×10$^{-3}$ ± 1×10$^{-3}$ | -22 ± 2 | 4×10$^5$ | 1.1×10$^{-2}$ ± 2×10$^{-3}$ | -9 ± 2 | 3×10$^4$ |

Average values and standard deviations obtained from six devices.
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