# Supporting Information for Accurate and scalable electronic structure calculation of crystalline conjugated polymers

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## S1 Abbreviations

| | | | |
|---|---|---|---|
| a3p | Ahlrichs triple-ζ basis Def2-TZVP | MD | Molecular Dynamics |
| AO | Atomic Orbital | MO | Molecular Orbital |
| BLA | Bond Length Alternation | NN | Nearest Neighbors |
| BMCOS | Benchmark Dataset of Crystalline Organic Semiconductors | PAW | Projector Augmented Wave |
| | | PES | Potential Energy Surface |
| CIF | Crystallographic Information File | p2p | Pople double-ζ polarized basis 6-31G* |
| DFT | Density Functional Theory | RMS | Root-Mean Square |
| DFT-D | Dispersion-corrected DFT | SCF | Self-Consistent Field |
| ECG | Electronic Coarse-Graining | TB | Tight Binding |
| HOMO | Highest Occupied Molecular Orbital | TBH | Tight Binding Hamiltonian |
| LMO | Localized Molecular Orbital | VB | Valence Band |
| LUMO | Lowest Unoccupied Molecular Orbital | ZPE | Zero-Point Energy |

## S2 Notations for TBH elements

In the present work we use the TBH notations described at `https://cmsos.github.io/cmsos/TBH`. In these notations the TBH elements are labeled as $t^{XY}_{anbmcl}$, where indices $X, Y$ enumerate different LMOs (TBH sites) within the unit cell and indices $n, m, l$ enumerate cells along a,b,c-translation vectors. The following shortcuts are used: a2b0c1=aac, a(-1)b(-2)c(-3)=ijjk3 and so on. See illustrations in Fig. S1 and Table S1.

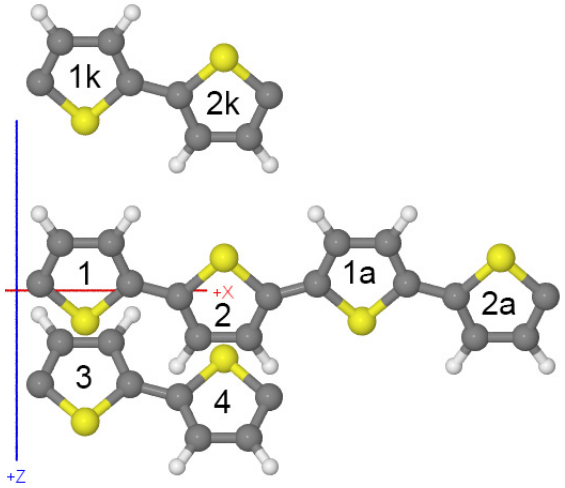



Figure S1: Illustration of monomer notations for aH-PT.

Table S1: Nonzero TBH elements of the high-symmetry $\pi$-stack of PPP. Each 3×3 block corresponds to TBH elements between the symmetry unique monomer (1,1) (asymmetric unit) and its symmetry-generated replica.

| | 1i | 1 | 1a | 1aa |
|---|---|---|---|---|
| 1 | $t_{\mathrm{a}}^{\mathrm{AA}}$ $-t_{\mathrm{a}}^{\mathrm{AC}}$<br>$t_{\mathrm{a}}^{\mathrm{BB}}$<br>$t_{\mathrm{a}}^{\mathrm{AC}}$ $t_{\mathrm{a}}^{\mathrm{CC}}$ | $\epsilon^{\mathrm{A}}$<br>$\epsilon^{\mathrm{B}}$<br>$\epsilon^{\mathrm{C}}$ | $t_{\mathrm{a}}^{\mathrm{AA}}$ $t_{\mathrm{a}}^{\mathrm{AC}}$<br>$t_{\mathrm{a}}^{\mathrm{BB}}$<br>$-t_{\mathrm{a}}^{\mathrm{AC}}$ $t_{\mathrm{a}}^{\mathrm{CC}}$ | $t_{\mathrm{aa}}^{\mathrm{AA}}$ $t_{\mathrm{aa}}^{\mathrm{AC}}$<br>$t_{\mathrm{aa}}^{\mathrm{BB}}$<br>$-t_{\mathrm{aa}}^{\mathrm{AC}}$ $t_{\mathrm{aa}}^{\mathrm{CC}}$ |
| 1c | $t_{\mathrm{ac}}^{\mathrm{AA}}$ $-t_{\mathrm{ac}}^{\mathrm{AC}}$<br>$t_{\mathrm{ac}}^{\mathrm{BB}}$<br>$t_{\mathrm{ac}}^{\mathrm{AC}}$ $t_{\mathrm{ac}}^{\mathrm{CC}}$ | $t_{\mathrm{c}}^{\mathrm{AA}}$<br>$t_{\mathrm{c}}^{\mathrm{BB}}$<br>$t_{\mathrm{c}}^{\mathrm{CC}}$ | $t_{\mathrm{ac}}^{\mathrm{AA}}$ $t_{\mathrm{ac}}^{\mathrm{AC}}$<br>$t_{\mathrm{ac}}^{\mathrm{BB}}$<br>$-t_{\mathrm{ac}}^{\mathrm{AC}}$ $t_{\mathrm{ac}}^{\mathrm{CC}}$ | $t_{\mathrm{aac}}^{\mathrm{AA}}$ $t_{\mathrm{aac}}^{\mathrm{AC}}$<br>$t_{\mathrm{aac}}^{\mathrm{BB}}$<br>$-t_{\mathrm{aac}}^{\mathrm{AC}}$ $t_{\mathrm{aac}}^{\mathrm{CC}}$ |

## S3 Analytic solutions for PPP and aH-PT

High-symmetry crystals allow for analytic solutions of a TBH at least at some k-points, simplifying analysis of the dependence of the electronic structure on TBH elements. Molecular crystals rarely have higher symmetry than monoclinic. Here we consider the perfectly aligned $\pi$-stack of PPP as a model structure. The Hamiltonian of the occupied $\pi$-system is

$$\begin{pmatrix} \varepsilon^{\mathrm{A}} & 0 & \mathrm{i}\tau^{\mathrm{AC}} \\ 0 & \varepsilon^{\mathrm{B}} & 0 \\ -\mathrm{i}\tau^{\mathrm{AC}} & 0 & \varepsilon^{\mathrm{C}} \end{pmatrix}, \tag{S1}$$

where

$$\varepsilon^{\mathrm{X}} = \sum_{n,m\in\mathbb{Z}} t^{\mathrm{XX}}_{ancm} \mathrm{e}^{\mathrm{i}nk_x+\mathrm{i}mk_z}, \quad t^{\mathrm{XX}}_{\mathrm{a0c0}} \equiv \epsilon^{\mathrm{X}}, \tag{S2}$$

$$\tau^{\mathrm{AC}} = -\mathrm{i} \sum_{n,m\in\mathbb{Z}} \mathrm{sgn}(n)\, t^{\mathrm{AC}}_{ancm} \mathrm{e}^{\mathrm{i}nk_x+\mathrm{i}mk_z}, \quad t^{\mathrm{AC}}_{\mathrm{a0c0}} \equiv 0, \tag{S3}$$

and the k-vector is given in the coordinate system with $x$-axis directed along the polymer chain and $z$-axis directed along the $\pi$-stack. The high symmetry of the Hamiltonian (S1) allows to write its eigenvalues explicitly:

$$E_{1,3} = \frac{\varepsilon^{\mathrm{A}} + \varepsilon^{\mathrm{C}}}{2} \pm \sqrt{\left(\frac{\varepsilon^{\mathrm{A}} - \varepsilon^{\mathrm{C}}}{2}\right)^2 + (\tau^{\mathrm{AC}})^2}, \quad E_2 = \varepsilon^{\mathrm{B}}. \tag{S4}$$

The valence band edge is at $\Gamma$-point. The width of the frontier band along the $\pi$-stacking direction is

$$\varepsilon^{\mathrm{A}}\big|_{k=\Gamma} - \varepsilon^{\mathrm{A}}\big|_{k=\mathrm{Z}} = \sum_{n,m\in\mathbb{Z}} t^{\mathrm{AA}}_{ancm} \left(1 - (-1)^m\right) = 2t^{\mathrm{AA}}_{\mathrm{c}} + 4t^{\mathrm{AA}}_{\mathrm{ac}} + \ldots \tag{S5}$$

For aH-PT crystal, the two upper valence $\pi$-bands are not hybridized at $\Gamma$-point yielding

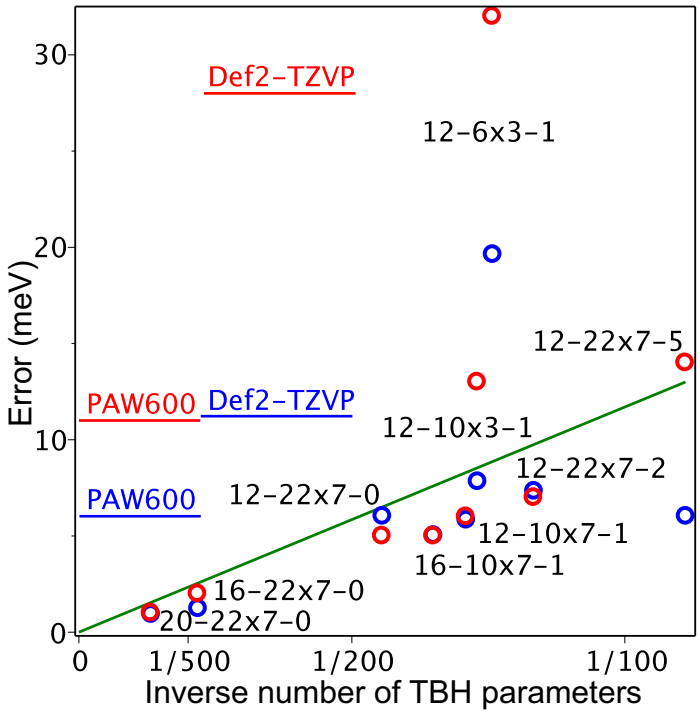
$$t^{\Gamma}_{12} = \frac{t_{13} + t_{24}}{2} - (t_{14} + t_{23}) + (t_{13\mathrm{a}} + t_{24\mathrm{i}}) - (t_{14\mathrm{a}} + t_{23\mathrm{i}}) + \ldots \tag{S6}$$

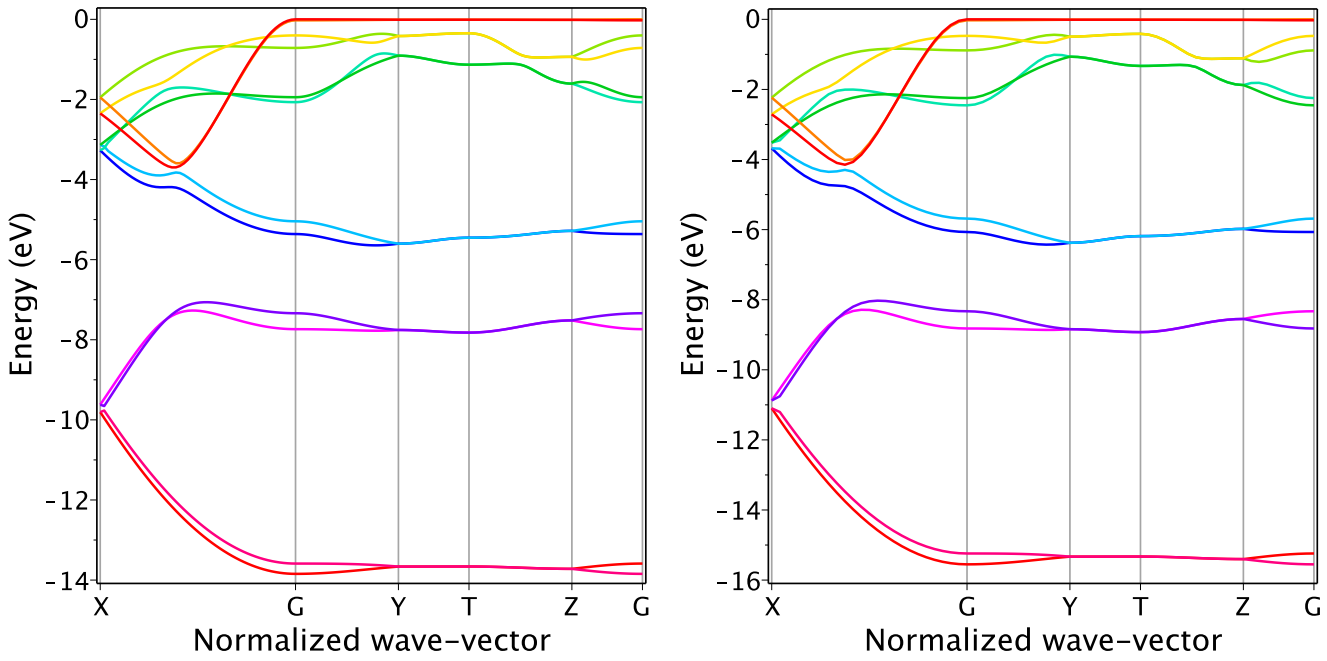
where all the couplings are between the frontier monomer orbitals.

## S4 Additional figures and tables

Table S2: Benchmarking the used in this work ECG approach for the energy of valence bands of PET. The reference band structure is calculated by PBE/6-31G* on the geometry optimized by PBE-D3/PAW900. The model specification is given by the size of the symbolic TB Hamiltonian $R$ (maximum separation between sites in a digitized geometrical model), the size of the cluster used for it parametrization including number of monomers per oligomer $N_{\mathrm{mon}}$ and number of oligomers (molecules) in the cluster $N_{\mathrm{mol}}$, cutoff for electronic couplings "cut" in meV, and number of independent parameters in the resulting numerical TB Hamiltonian, $N_{\mathrm{par}}$. Rows are ordered by the complexity of models, namely, by $R$, $N_{\mathrm{mon}}$, $N_{\mathrm{mol}}$, and $N_{\mathrm{par}}$, sequentially. The last two rows show how the band structure changes upon basis set change for geometry or single point calculations relative to the reference method. When calculating errors, the energy of the top of the valence band is set to zero. Then "RMS" is the root mean square error, "min/mean/max" are the minimum, mean, and maximum deviation over the uniform Γ-centered k-grid of size $18 \times 10 \times 6$. The last column shows the label of this model in the main text. The table is visualized below with labels abbreviated as "$R$-$N_{\mathrm{mon}}$x$N_{\mathrm{mol}}$-cut"; red-colored are RMS errors, blue-colored are maximum absolute errors divided by 10.

| Model | | | | | Errors | | | | Label |
|---|---|---|---|---|---|---|---|---|---|
| $R$ | $N_{\mathrm{mon}}$ | $N_{\mathrm{mol}}$ | cut | $N_{\mathrm{par}}$ | RMS | min | mean | max | |
| 12 | 6 | 3 | 1 | 132 | 32 | -2 | 137 | 196 | 6 monomers |
| 12 | 10 | 3 | 1 | 137 | 13 | -78 | 16 | 69 | dimers only |
| 12 | 10 | 7 | 1 | 141 | 6 | -58 | 10 | 40 | optimal model |
| 12 | 22 | 7 | 5 | 90 | 14 | -60 | 0 | 59 | 5 meV cutoff |
| 12 | 22 | 7 | 2 | 120 | 7 | -73 | 3 | 37 | 2 meV cutoff |
| 12 | 22 | 7 | 1 | 142 | 6 | -66 | 4 | 32 | |
| 12 | 22 | 7 | 0 | 180 | 5 | -60 | 3 | 32 | cutoff by distance |
| 16 | 10 | 7 | 1 | 154 | 5 | -50 | 8 | 35 | |
| 16 | 22 | 7 | 1 | 154 | 5 | -56 | 2 | 28 | |
| 16 | 22 | 7 | 0 | 459 | 2 | -11 | 3 | 12 | cutoff by distance |
| 20 | 22 | 7 | 0 | 758 | 1 | -4 | 1 | 9 | cutoff by distance |
| geometry by PAW600 | | | | | 11 | -60 | 3 | 47 | geometry error |
| single point by Def2-TZVP | | | | | 28 | -2 | 72 | 112 | basis set error |

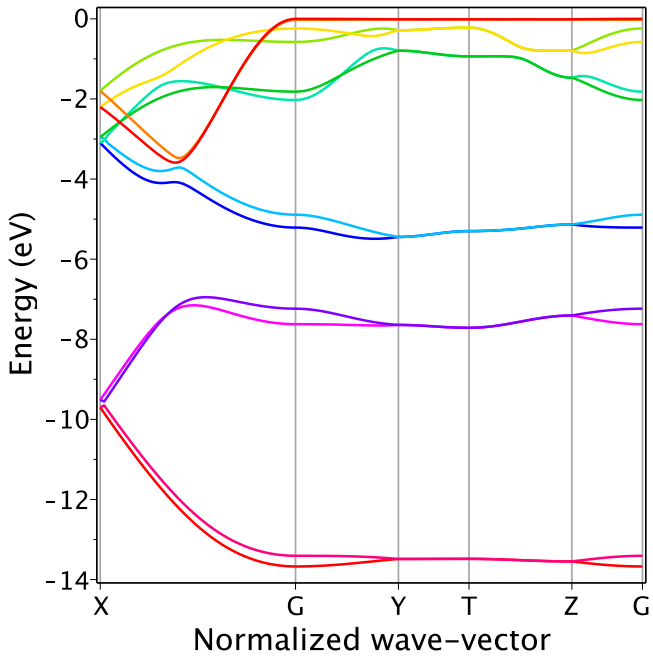




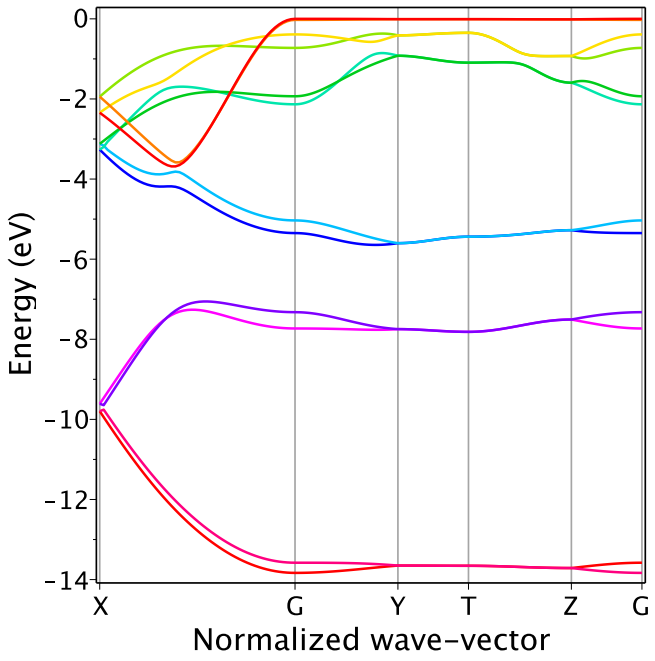

(a) PBE




(b) CAM-B3LYP

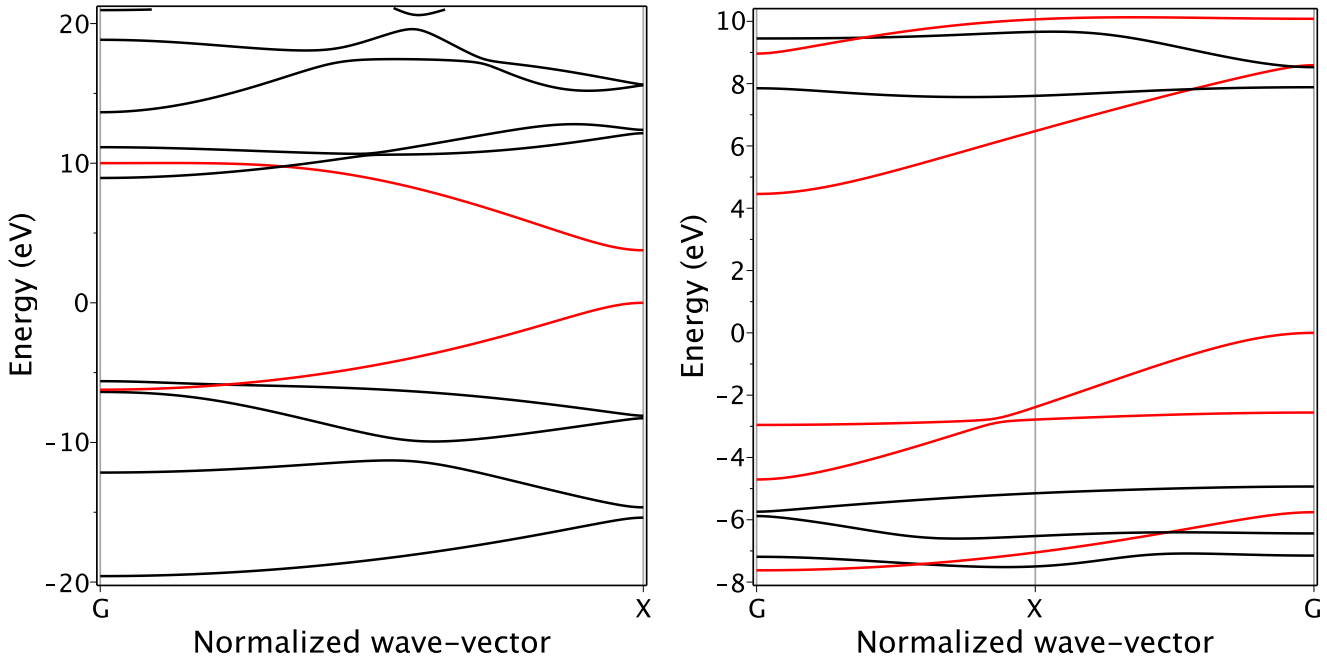



(c) x6m3




(d) x10m7

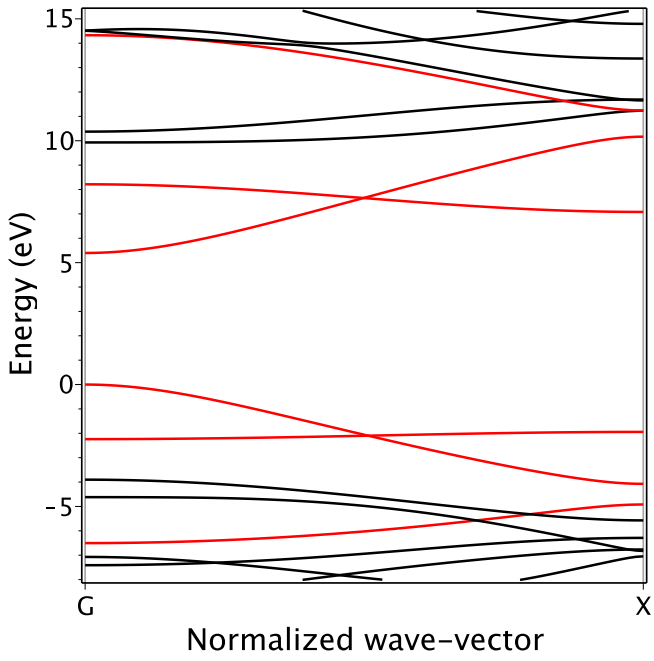
Figure S2: Valence band structure of crystalline PET.



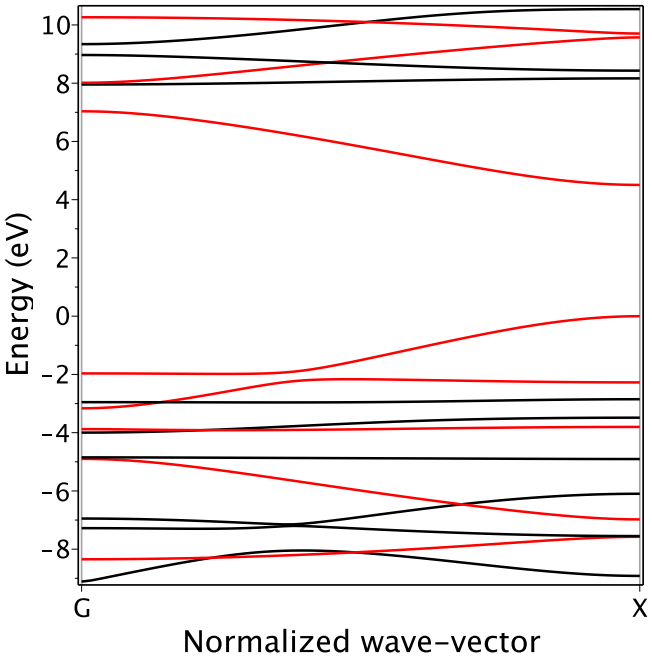

(a) tPA




(b) PT

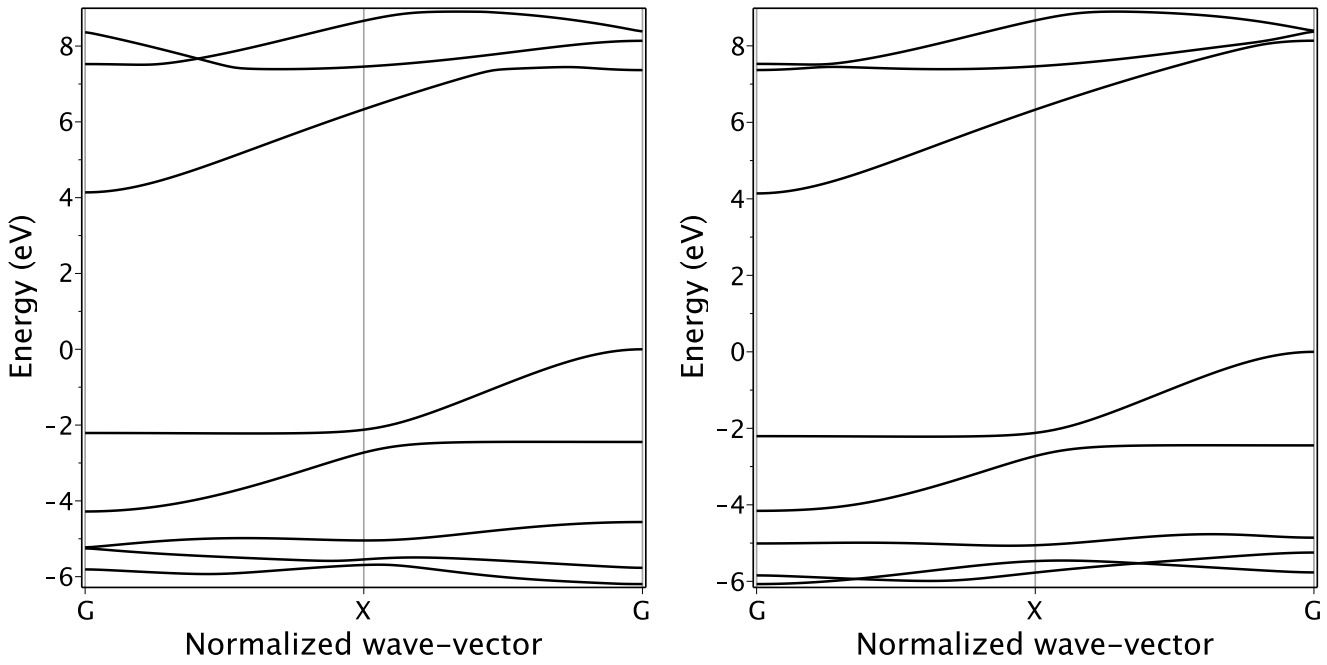



(c) PPP




(d) polyTzTz

Figure S3: Band structure of a single polymer chain calculated in all-electron basis in periodic boundary conditions. The energy window is chosen to include all valence $\pi$-bands which are highlighted by red color. For PT the band structure is unfolded because its chemical period is half the translation period.




(a) $\alpha$-PEDOT (b) $\beta$-PEDOT

Figure S4: Band structure of PEDOT single polymer chain in $\alpha$ and $\beta$ conformations, calculated in all-electron basis in periodic boundary conditions. Since the polymer is nonplanar, $\pi$-bands cannot be rigorously separated.

Table S3: PT polymorphs including oligomers (o2,o4,o6) and arbitrarily shifted structures (ax,ay) [URL].

Herringbone polymorphs by PBE-D3paw900 (total energies in meV/mol, mol=7 atoms, P212121*=P212121:084yx):

| | SG | V1 Ao^3 | 23s4 | RMSD Ao | phi deg | xi2 | y2 Ao | z3 Ao | d Ao | xi | Eacc meV | E meV | ZPE meV | E(T) meV | F(T) meV | frequenc meV | meV | elastic eigenval GPa | GPa | GPa |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| a | P21/nxz | 11.60 | 00+0 | .014 | 62.02 | 0.301 | 7.527 | 5.544 | 4.674 | 0.150 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3.74 | 7.42 | 1.89 | 2.41 | 5.73 |
| c | P212121* | 11.58 | 00-+ | .039 | 66.03 | 0 | 7.238 | 5.752 | 4.623 | 1/4 | 2.5 | 2.9 | 1.7 | 2.6 | 2.3 | 1.90 | 6.52 | -16.74 | 0.30 | 0.46 |
| b | P21/cxz | 11.58 | 00-0 | .009 | -69.40 | -0.378 | 7.065 | 5.891 | 4.599 | -0.189 | 6.1 | 6.4 | 4.7 | 6.2 | 5.3 | -1.71 | 6.00 | 0.83 | 0.88 | 3.25 |
| aH | Pmcn | 11.65 | 00+0 | .030 | 64.39 | 0 | 7.428 | 5.641 | 4.663 | 0 | 11.2 | 11.2 | 9.4 | 4.0 | 9.2 | -2.90 | 6.67 | -0.86 | 0.55 | 4.76 |
| bH | Pmnb | 11.86 | 00-0 | .012 | -63.12 | 0 | 7.559 | 5.642 | 4.716 | 0 | 24.3 | 24.7 | 21.9 | 23.5 | 22.0 | 1.59 | 4.20 | -0.35 | 0.57 | 3.22 |
| -----Shifted---------- | | | | | | | | | | | | | | | | | | | | |
| ax | P21/nxz | 11.61 | 00+0 | .015 | 62.30 | 0.285 | 7.517 | 5.553 | 4.673 | 0.143 | 0.1 | 0.1 | -0.3 | 0.0 | -0.6 | 3.44 | 7.15 | 0.53 | 1.12 | 2.87 |
| ay | P21/nxz | 11.65 | 00+0 | .012 | 62.26 | 1/3 | 7.527 | 5.564 | 4.680 | 1/6 | 0.5 | | | | | | | | | |

-----Oligomers----------

| | SG | V1 | 23s4 | RMSD | phi | xi2 | y2 | z3 | d | xi | z2 | xi3 | file |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| o2 | P21/c | 11.72 | +0-+ | .230 | 59.77 | 0.370 | 7.583 | 5.652 | 4.599 | 0.152 | -0.447 | -0.066 | bithiophene/cryst_PBE-D3paw900 |
| o4 | P21/cxz | 11.73 | +0-+ | .086 | 62.59 | 0.371 | 7.486 | 5.647 | 4.667 | 0.180 | -0.072 | -0.011 | oligothiophene4/cryst_PBE-D3paw900 |
| o6 | P21/cxz | 11.70 | +0-+ | .075 | 62.19 | 0.343 | 7.498 | 5.605 | 4.672 | 0.169 | -0.031 | -0.004 | oligothiophene6/cryst_PBE-D3paw900 |

Polymorph notations:
a - in-phase
b - anti-phase
c - in-phase zigzag
H - high-symmetry

Table S4: PEDOT polymorphs [URL].

Polymorphs by PBE-D3paw900 (total energies in meV/mol, mol=13 atoms):

| | code | * | SG | E | * | SG | E | comment |
|---|---|---|---|---|---|---|---|---|
| polym-a | ++ | | q2/c11x | 0 | | | | |
| polym-b | +- | | q2221zy | 0.8 | | | | |
| pistack-aa | ++++ | H | a2/b11x | 5.6 | | | | |
| pistack-ab | ++-- | H | pbaaxz | 0 | L | pb21a:400xz | -21.7 | shifted |
| | | | | | T | p2/b11xz | -13.8 | tilted, unstable |
| pistack-ba | +-+- | H | pbaa:440y | 0.8 | L | p21/b11:440xz | -27.6 | shifted and tilted |
| pistack-bb | +--+ | H | c222:400y | 7.0 | L | c2111xz | -9.5 | tilted |
| cryst-ab | ++-- | | | | Tx | P2/c11 | 23.0 | tilted, Kim08, Shi15 |
| | | | | | T | | -11.8 | large tilt |
| | | | | | Lx | Pc11 | 30.7 | shifted and tilted |
| | | | | | L | | -29.5 | large tilt and shift |
| cryst-ba | +-+- | | | | L | P21/c:044yx | 0 | shifted and tilted |
| cryst-bb | +--+ | | | | T | P2111 | -34.9 | large tilt |

Notations:
Code is the list of signs encoding orientation of C2H4 group in XZ-plane for each monomer in unit cell
There are only four combinations of signs encoded as 'aa','ab','ba','bb'
High-symmetry polymorphs are labeled with 'H'
Low-symmetry polymorphs are labeled with 'T' if only tilt is present and 'L' otherwise
Incompletely relaxed structures are additionally labeled with 'x'

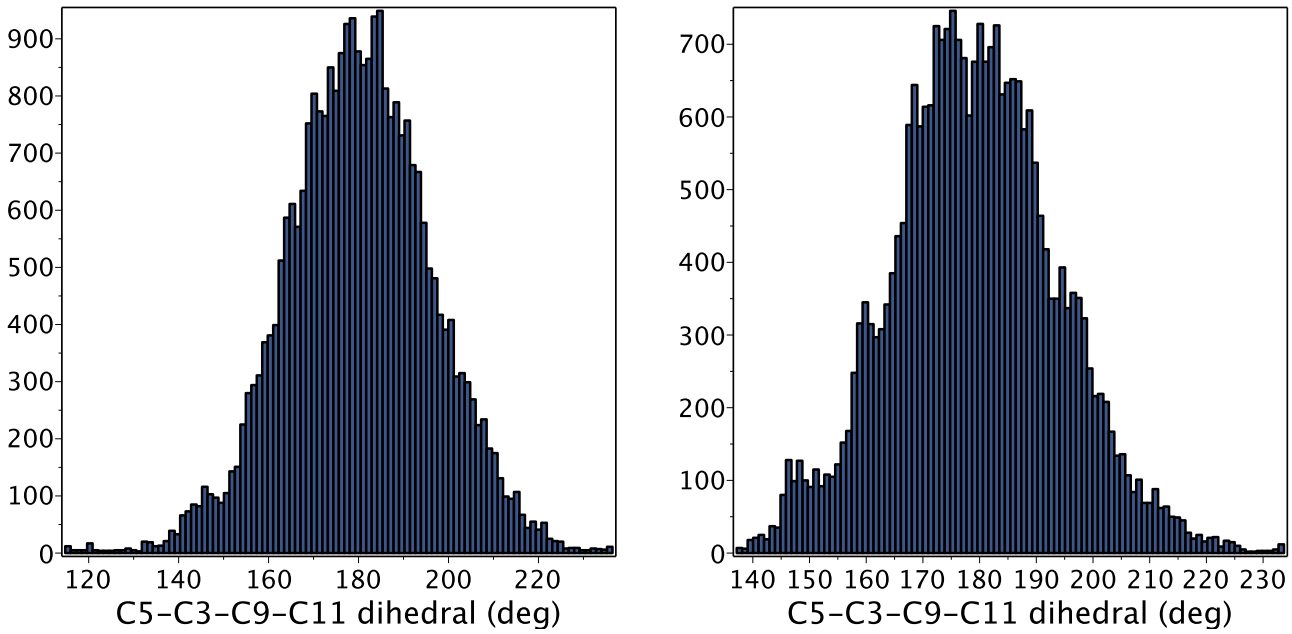
Symmetry:
Monomer symmetry is 1/2-x,+y,-z (rotation around Y-axis)
NN-monomers are generated by one of 4 point-symmetry operations {x or 1/2-x},-y,±z combined with X- or Z-translations

Table S5: P3HT polymorphs [URL].

Pistack polymorphs (mol=25 atoms,
total energies by PBE-D3paw900,
band structure parameters* by CAM-B3LYPp2p):

| | dE meV/mol | EGX eV | dEG eV | |
|---|---|---|---|---|
| CAaac | 0 | 2.23 | 0.50 | |
| AAaac | 7 | 2.35 | 0.13 | |
| BAab | 12 | 2.31 | 0.76 | |
| CAab | 12 | 2.01 | 0.05 | |
| CBaac | 15 | 2.11 | 0.38 | |
| CAaac+aac | 25 | | | |
| BDa | 28 | 2.29 | 0.13 | also amorphous** |
| DAaac | 31 | 2.53 | 0.54 | |
| BAaac | 36 | 2.49 | 0.74 | |
| CAabab | 43 | 1.94 | 0.32 | |
| BBaac | 44 | 2.19 | 0.29 | |
| BAacc | 46 | | | |
| CBab | 55 | | | |
| BAa | 56 | | | |
| BAa-min2 | 59 | | | |
| BDab | 60 | | | |
| BBa | 64 | | | |
| CBabab | 70 | | | |
| BCa | 78 | | | |
| ABaac | 105 | 1.94 | 0.31 | |
| CA | 105 | 2.07 | 0.48 | |
| C | 113 | 2.46 | 0.49 | also amorphous |
| CBb | 116 | | | |
| CAb | 118 | | | |
| CAa | 127 | | | |
| CCa | 137 | | | |
| B | 150 | | | also amorphous |
| CDa | 153 | | | |
| CBa | 169 | | | also amorphous |
| AAa | 181 | | | |
| ---crystals--- | | | | |
| iL | -1.4 | | | fully relaxed interdigitated |
| i | 0 | 2.29 | 0.13 | monoclinic interdigitated |
| CA | 86 | 2.19 | 0.40 | Dudenko's structure relaxes to CA |
| C | 127 | 2.46 | 0.52 | |

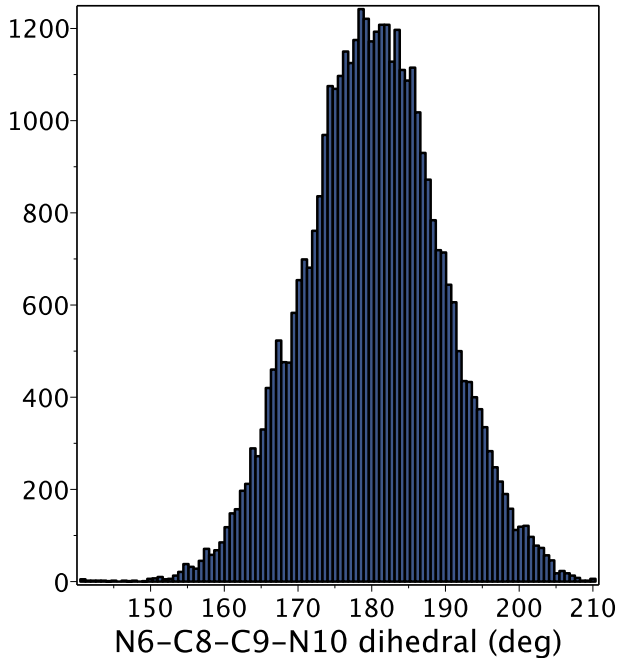
* EGX=E1(X)-E1(Gamma), dEG=E1(Gamma)-E2(Gamma),
where numbers enumerate eigenergies from top of VB
**Only 4 polymorphs with ordered backbone and disordered side chains
can be obtained by melt-quench above 300K with force field [Moreno10]



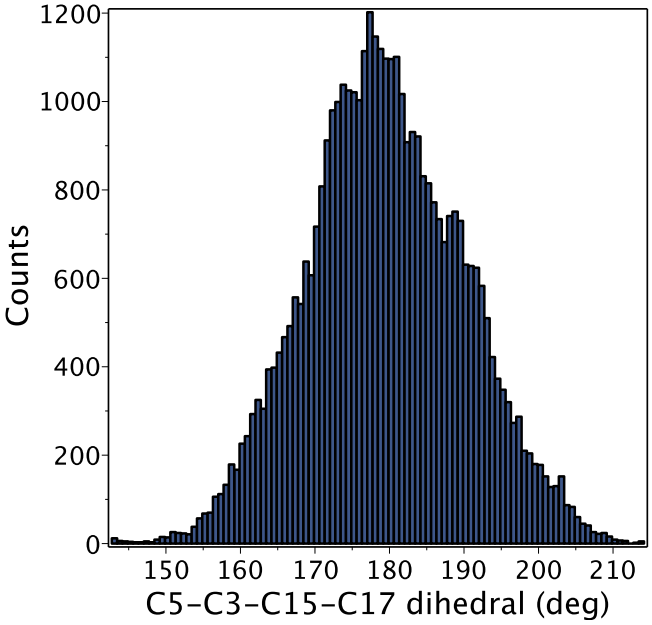

(a) aH-PT($2 \times 2 \times 3$)




(b) ay-PT($2 \times 2 \times 3$)

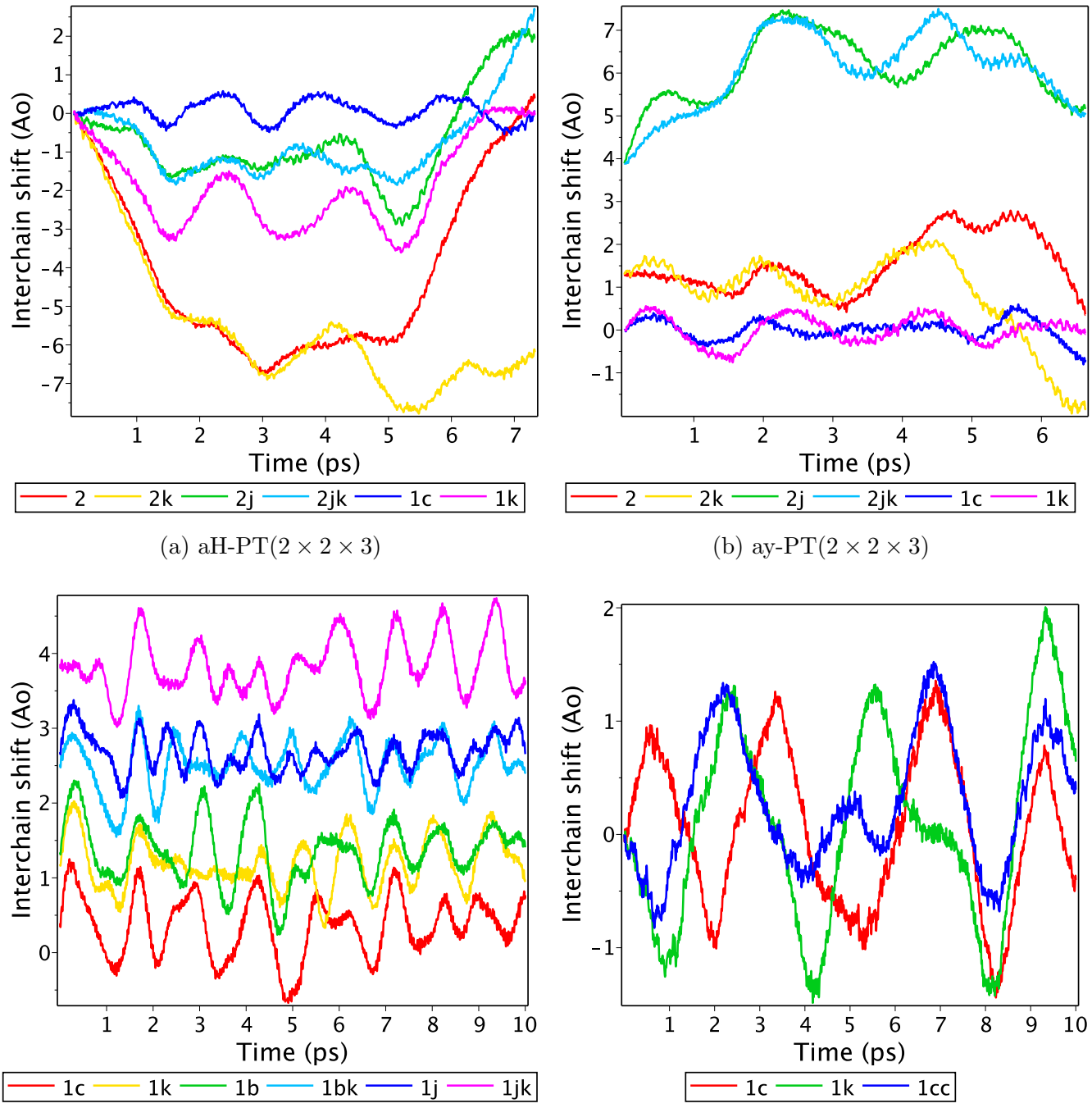



(c) a-PTzTz($2 \times 3 \times 4$)




(d) abH-PEDOT($2 \times 2$)

Figure S5: Distribution of flexible intrachain dihedrals in crystalline polymers at 400 K starting from the optimized geometry. The supercell is indicated in parentheses.



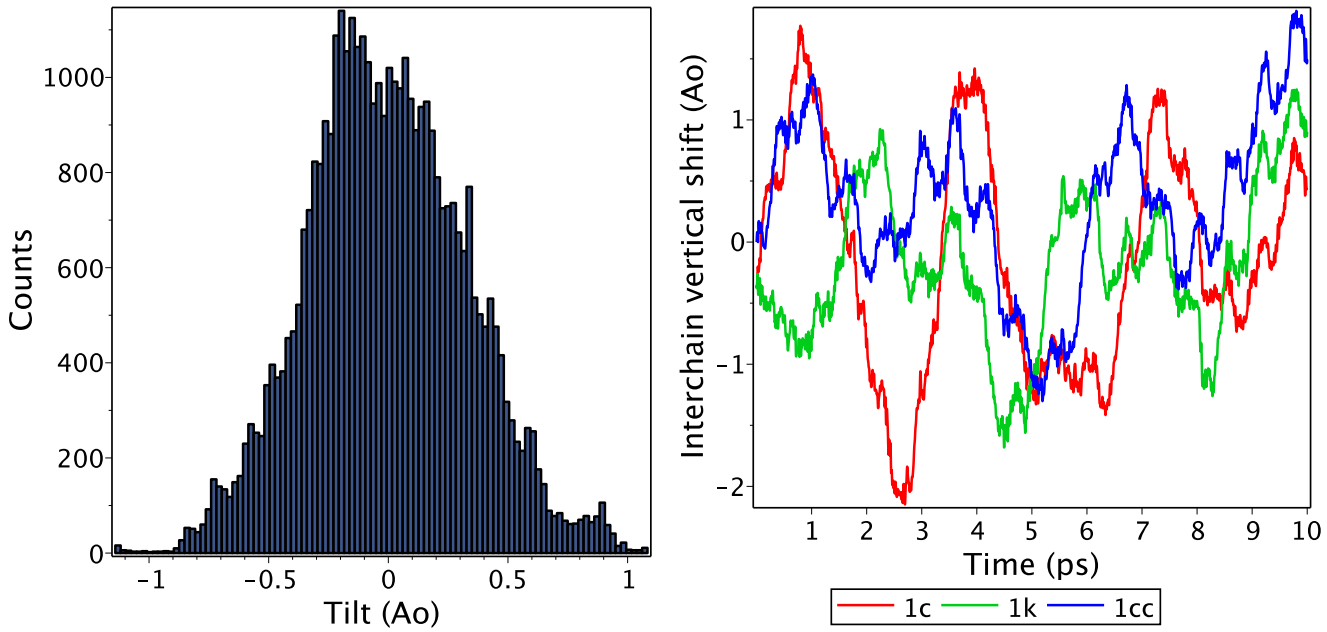

(a) aH-PT($2 \times 2 \times 3$)

(b) ay-PT($2 \times 2 \times 3$)

(c) a-PTzTz($2 \times 3 \times 4$)

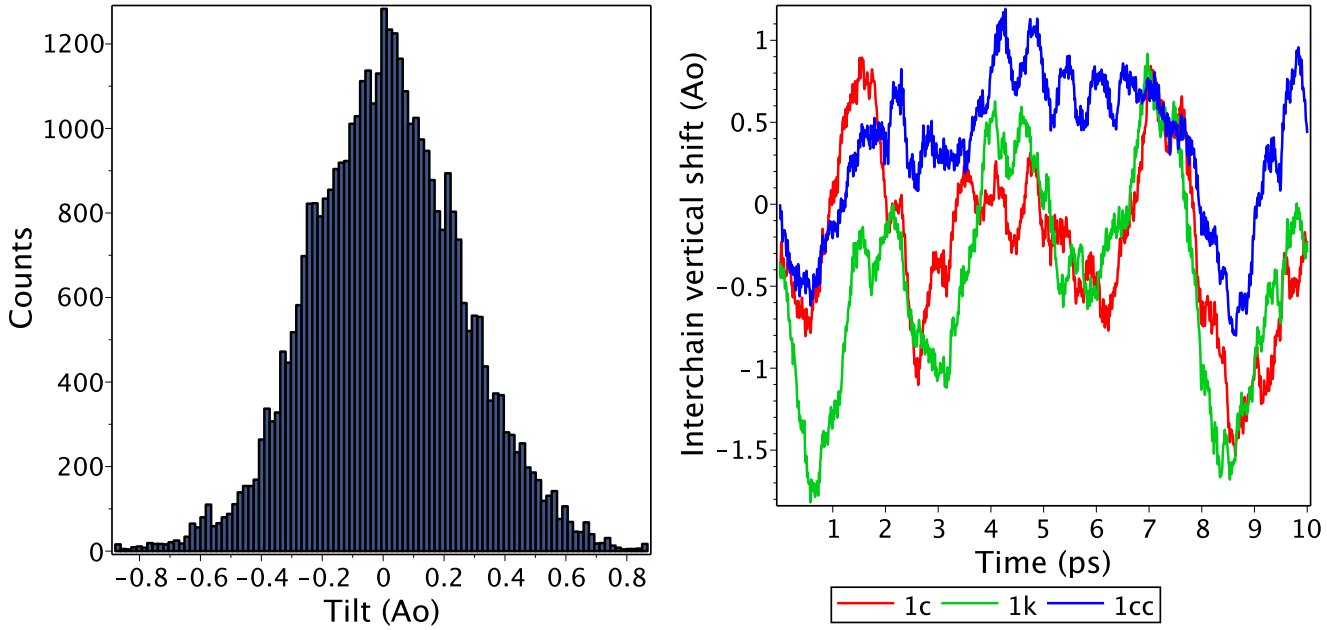
(d) abH-PEDOT($2 \times 2$)

Figure S6: Dynamics of the interchain shift for the nearest neighbors in crystalline polymers at 400 K starting from the optimized geometry. The supercell is indicated in parentheses.



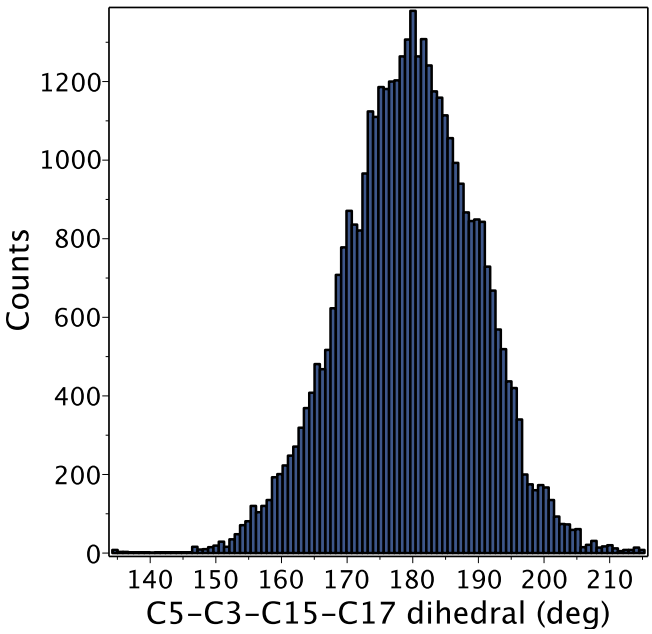

(a) tilt (b) vertical shift

Figure S7: Dynamics of the tilt and relative vertical shift in abH-PEDOT $\pi$-stack at 400 K starting from the optimized geometry. The tilt is calculated as z-coordinate difference between atoms S1 and C4 which is 0.02 Å for 'abL' and 0.6 Å for 'abT'.

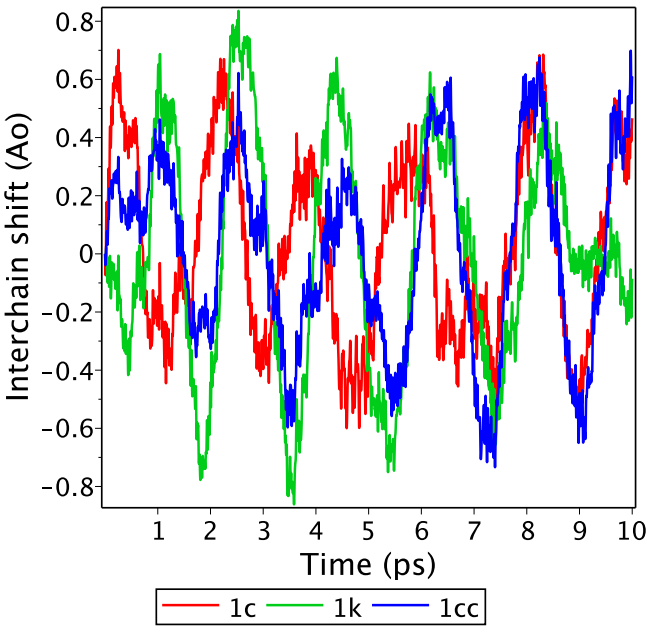



(a) tilt (b) vertical shift

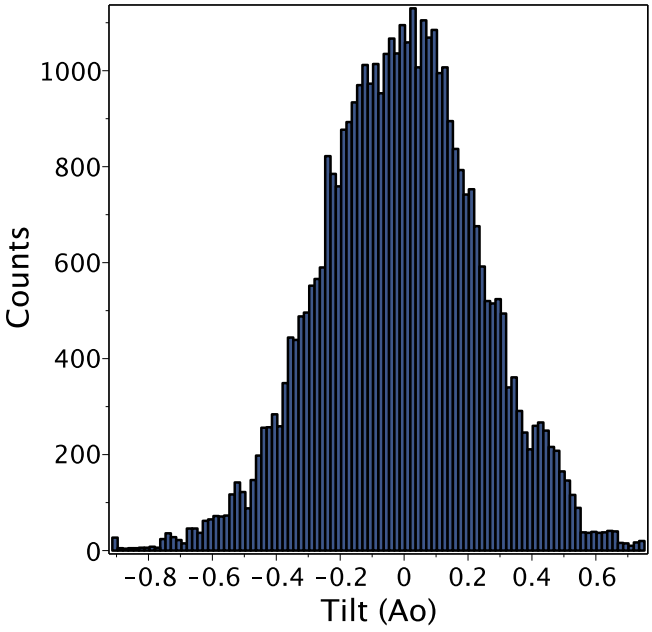
Figure S8: The same as in Fig. S7 but at 300 K.



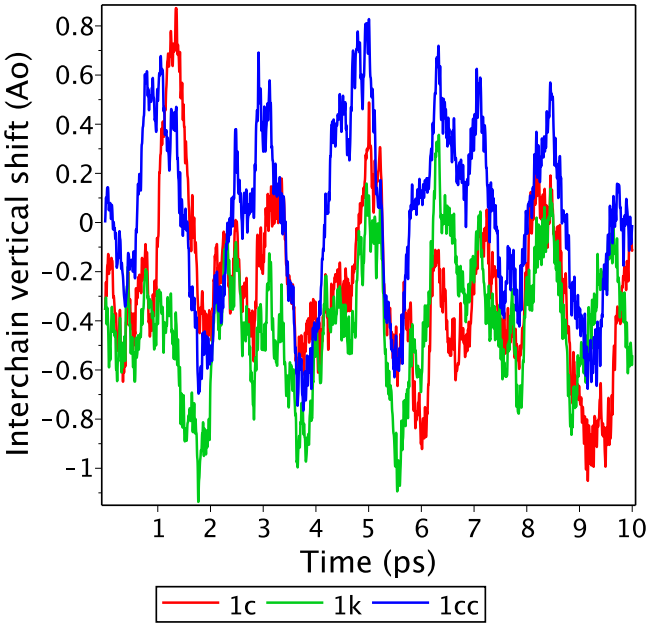

(a) dihedral




(b) shift

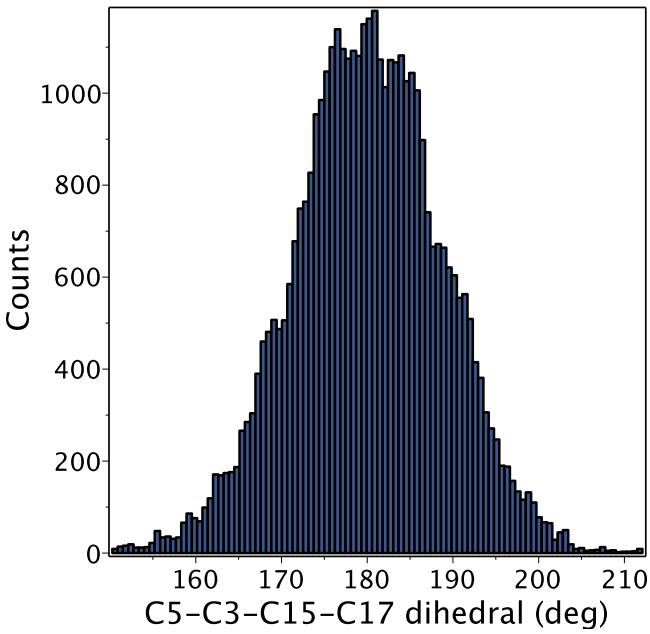



(c) tilt

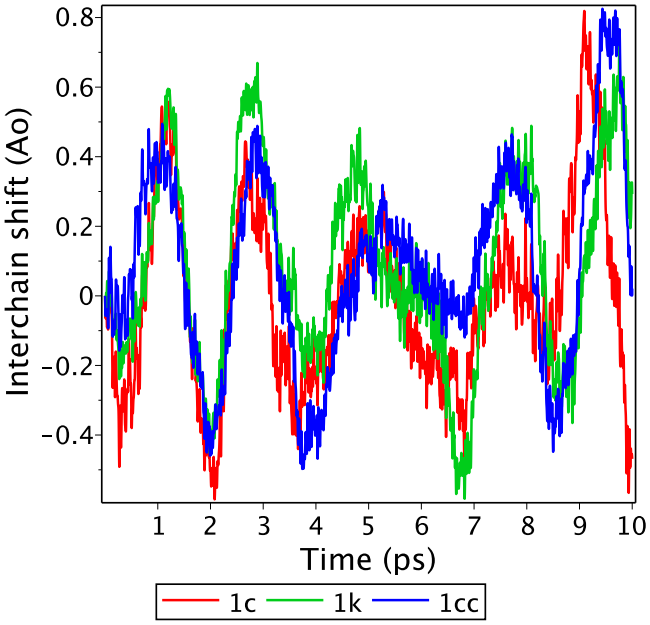



(d) vertical shift

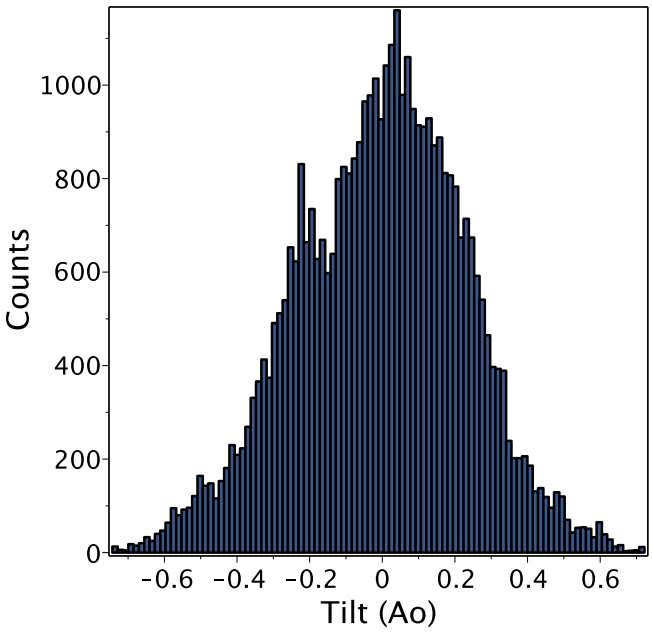
Figure S9: Dynamics of the fluorinated abH-PEDOT at 400 K.



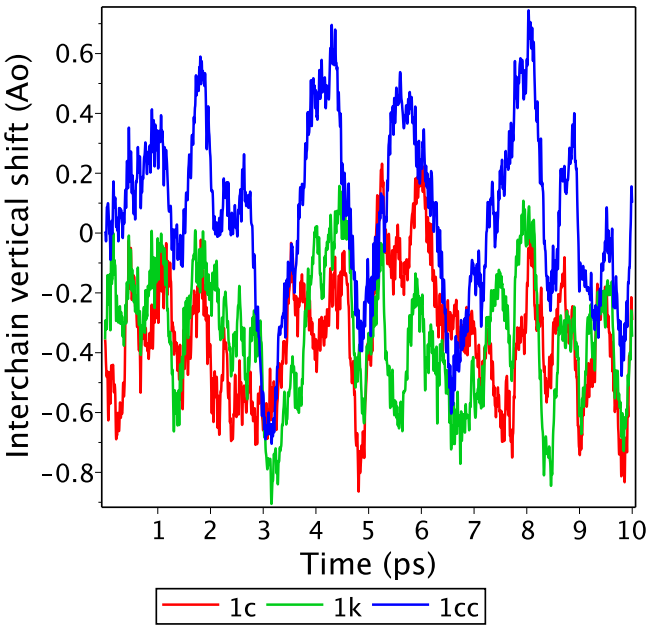

(a) dihedral




(b) shift




(c) tilt




(d) vertical shift

Figure S10: Dynamics of the fluorinated abH-PEDOT at 300 K.

Table S6: Tight-binding Hamiltonian for high-symmetry $\pi$-stack of PPP [URL].

| | 1i4 | | | 1i3 | | | 1ii | | | 1i | | | 1 | | | 1a | | | 1aa | | | 1a3 | | | 1a4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 6 | . | -3 | 24 | . | -12 | 118 | . | -66 | 992 | . | -641 | 0 | . | . | 992 | . | 641 | 118 | . | 66 | 24 | . | 12 | 6 | . | 3 |
| . | . | . | . | . | . | . | . | 2 | . | . | -74 | . | . | 191 | . | . | -74 | . | . | 2 | . | . | . | . | . | . | . |
| . | 3 | . | . | 12 | . | -6 | 66 | . | -35 | 641 | . | -390 | . | . | -3352 | -641 | . | -390 | -66 | . | -35 | -12 | . | -6 | -3 | . | . |
| 1c | . | . | . | -1 | . | . | -3 | . | 2 | -16 | . | 9 | 248 | . | . | -16 | . | -9 | -3 | . | -2 | -1 | . | . | . | . | . |
| . | . | . | . | . | . | . | . | . | . | . | 7 | . | . | 267 | . | . | 7 | . | . | . | . | . | . | . | . | . | . |
| . | . | . | . | . | . | . | -2 | . | . | -9 | . | 5 | . | . | 290 | 9 | . | 5 | 2 | . | . | . | . | . | . | . | . |

In polymer basis:

| | |
|---|---|
| 1 | 2282 |
| 1k | 206 |

| | 1i4 | | | 1i3 | | | 1ii | | | 1i | | | 1 | | | 1a | | | 1aa | | | 1a3 | | | 1a4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | tAAa4 | . | -tACa4 | tAAa3 | . | -tACa3 | tAAaa | . | -tACaa | tAAa | . | -tACa | eA | . | . | tAAa | . | tACa | tAAaa | . | tACaa | t | | | | | | |
| . | . | . | . | . | . | . | . | . | tBBaa | . | . | tBBa | . | . | eB | . | . | tBBa | . | . | tBBaa | . | | | | | | |
| . | tACa4 | . | . | tACa3 | . | tCCa3 | tACaa | . | tCCaa | tACa | . | tCCa | . | . | eC | -tACa | . | tCCa | -tACaa | . | tCCaa | -t | | | | | | |
| 1c | . | . | . | tAAa3c | . | . | tAAaac | . | -tACaac | tAAac | . | -tACac | tAAc | . | . | tAAac | . | tACac | tAAaac | . | tACaac | tA | | | | | | |
| . | . | . | . | . | . | . | . | . | . | . | . | tBBac | . | . | tBBc | . | . | tBBac | . | . | . | . | | | | | | |
| . | . | . | . | . | . | . | tACaac | . | . | tACac | . | tCCac | . | . | tCCc | -tACac | . | tCCac | -tACaac | . | . | . | | | | | | |

Table S7: Tight-binding Hamiltonian for a-PTzTz [URL].

| | 1i4 | | | 1i3 | | | 1ii | | | 1i | | | 1 | | | 1a | | | 1aa | | | 1a3 | | | 1a4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | . | . | . | -27 | -5 | -2 | 12 | -3 | -5 | -773 | -139 | -8 | 0 | -30 | . | -773 | -139 | 8 | 12 | -3 | 5 | -27 | -5 | 2 | . | . | . |
| . | . | . | . | -5 | . | . | -3 | . | . | -139 | 30 | 10 | -30 | -674 | . | -139 | 30 | -10 | -3 | . | . | -5 | . | . | . | . | . |
| . | . | . | . | 2 | . | . | 5 | . | 11 | 8 | -10 | -41 | . | . | -1519 | -8 | 10 | -41 | -5 | . | 11 | -2 | . | . | . | . | . |
| 1c | . | . | . | 7 | . | . | . | -3 | -6 | 71 | 13 | -5 | 176 | 68 | 56 | -53 | 19 | 7 | -7 | 4 | 6 | -10 | . | 2 | -4 | . | . |
| . | . | . | . | . | . | -1 | -3 | . | -3 | 13 | -1 | 13 | 68 | 116 | 16 | 19 | 14 | 6 | 4 | 2 | . | . | 1 | . | . | . | . |
| . | . | . | . | . | 1 | . | 6 | 3 | . | 5 | -13 | 4 | -56 | -16 | 5 | -7 | -6 | 2 | -6 | . | . | -2 | . | 4 | . | . | . |
| 1k | -4 | . | . | -10 | . | -2 | -7 | 4 | -6 | -53 | 19 | -7 | 176 | 68 | -56 | 71 | 13 | 5 | . | -3 | 6 | 7 | . | . | . | . | . |
| . | . | . | . | . | 1 | . | 4 | 2 | . | 19 | 14 | -6 | 68 | 116 | -16 | 13 | -1 | -13 | -3 | . | 3 | . | . | 1 | . | . | . |
| . | . | . | . | 2 | . | 4 | 6 | . | . | 7 | 6 | 2 | 56 | 16 | 5 | -5 | 13 | 4 | -6 | -3 | . | . | -1 | . | . | . | . |
| 1b | . | . | . | 3 | . | 3 | 8 | -14 | . | 26 | -38 | 18 | -8 | 3 | -16 | -7 | -19 | -29 | -2 | . | -4 | -3 | . | -3 | . | . | . |
| . | . | . | . | . | . | . | -14 | -9 | 6 | -38 | 130 | -8 | 3 | -93 | -88 | -19 | -8 | -16 | . | . | . | . | . | . | . | . | . |
| . | . | . | . | -3 | . | -2 | . | -6 | . | -18 | 8 | -2 | 16 | 88 | 35 | 29 | 16 | 10 | 4 | . | . | 3 | . | . | . | . | . |
| 1j | . | . | . | -3 | . | 3 | -2 | . | 4 | -7 | -19 | 29 | -8 | 3 | 16 | 26 | -38 | -18 | 8 | -14 | . | 3 | . | -3 | . | . | . |
| . | . | . | . | . | . | . | . | . | . | -19 | -8 | 16 | 3 | -93 | 88 | -38 | 130 | 8 | -14 | -9 | -6 | . | . | . | . | . | . |
| . | . | . | . | -3 | . | . | -4 | . | . | -29 | -16 | 10 | -16 | -88 | 35 | 18 | -8 | -2 | . | 6 | . | 3 | . | -2 | . | . | . |
| 1bk | . | . | . | 2 | . | . | 2 | . | 4 | 3 | -3 | 1 | . | -4 | -2 | 1 | 3 | 10 | . | . | . | . | . | . | . | . | . |
| . | . | . | . | . | . | . | . | . | -2 | -3 | -9 | -6 | -4 | 14 | 32 | 3 | . | 3 | . | . | . | . | . | . | . | . | . |
| . | . | . | . | . | . | -2 | -4 | 2 | -4 | -1 | 6 | 10 | 2 | -32 | 111 | -10 | -3 | 57 | . | . | -5 | . | . | -3 | . | . | . |
| 1jc | . | . | . | . | . | . | . | . | . | 1 | 3 | -10 | . | -4 | 2 | 3 | -3 | -1 | 2 | . | -4 | 2 | . | . | . | . | . |
| . | . | . | . | . | . | . | . | . | . | 3 | . | -3 | -4 | 14 | -32 | -3 | -9 | 6 | . | . | 2 | . | . | . | . | . | . |
| . | . | . | . | . | . | -3 | . | . | -5 | 10 | 3 | 57 | -2 | 32 | 111 | 1 | -6 | 10 | 4 | -2 | -4 | . | . | -2 | . | . | . |

In polymer basis:

| | |
|---|---|
| 1 | 1649 |
| 1c | 156 |
| 1b | -13 |
| 1bk | -4 |

Table S8: Interchain couplings for herringbone PT in dimer approximation [URL].

```
Interchain couplings in dimer approximation
from oligomer HOMO by PBE-D3paw900/CAM-B3LYPp2p
----------------------------
    shift 1+2  1+1c  dE
          meV  meV  meV/mol
----------------------------
aH  .000   26  -12   11
ax  .143  -29  -13    0.1
a   .150  -32  -13    0
o2  .152  -45  +13
ay  .167  -40  -13    0.5
o6  .169  -48   -8
o4  .180  -55   -2
c   .250  -61  -10    2.5
b   .311  -33   -7    6
bH  .500   79  -12   24
-----Oligomer polymorphs-----
o4aL    -19/27 -26
```

Table S9: Tight-binding Hamiltonian for herringbone polymorphs of PT.

(a) aH [URL]

```
    2ii  .  1i  .    2i    .  1    .     2    .  1a   .  2a  .
1   -58  .  37 10 -1124  -42  0    . -1124   42  37 -10 -58  .
.     .  . -10  3    42 -100  . -465   -42 -100  10   3   .  .
2    -2 -3  -4  6   -17  -34 77    .   -17   34  -4  -6  -2  3
.     3  .   .  .    41   -3  . -160   -41   -3   .   .  -3  .
2j   -2 -3 -10  .   -17  -41 24    .   -17   41 -10   .  -2  3
.     3  .   3  .    34   -3  .  -83   -34   -3  -3   .  -3  .
2k    .  .  -4  .    27    6 77    .    27   -6  -4   .   .  .
.    -3  .  -6  .   -18   -8  . -160    18   -8   6   .   3  .
2jk   .  3 -10 -3    27   18 24    .    27  -18 -10   3   . -3
.     .  .   .  .    -6   -8  .  -83     6   -8   .   .   .  .
1c    . -3  -4  .     .  -32 11    .     .   32  -4   .   .  3
.     3  .   .  .    32    2  . -121   -32    2   .   .  -3  .
1k    2  2  -4  .    13   13 11    .    13  -13  -4   .   2 -2
.    -2  .   .  .   -13  -11  . -121    13  -11   .   .   2  .

In polymer basis:
1   2438
2     29
1c   -13
```

(b) a [URL]

```
    2ii  .  1i  .    2i    .   1    .     2   . 1a   .  2a  .
1   -55  .  46  9 -1121 -36   .    . -1111  22 46 -12 -53  .
.     .  . -12  3    36 -96   . -501   -22 -96  9   3   .  .
2     .  .   3  .    19   .  13  -64   -21  18 -2  -4  -3  2
.     4  .  -3  .    39 -18 -54 -119   -14   .  .   .   .  .
2j   -3  .  -2 -3   -21 -14 -14  -12    19  39 -7   .   .  4
.     2  .   5  .    18   .  82  -50     . -18  3   .   .  .
2k    8  .   3  3    92  -5  13   54   -31  -6 -2   .  -6  .
.     2  .   .  .    54 -23  64 -119    31   .  4   .   3  .
2jk  -6  3  -2 -5   -31  31 -14  -82    92  54 -7  -3   8  2
.     .  .   3  .    -6   .  12  -50    -5 -23  .   .   .  .
1c    2 -3  -5  .     . -36  13    .     .  37 -5   .   2  3
.     3  .   .  .    36   .  -2 -141   -37   .  .   .  -3  .
1k    3  2  -5  .    17  16  13   -2    16 -15 -5   .   3 -2
.    -2  .   .  .   -16 -13   . -141    15 -13  .   .   2  .

In polymer basis:
1   2431
2    -33
1c   -18
```

Table S10: Tight-binding Hamiltonian for $\pi$-stack polymorphs of PEDOT.

(a) abH [URL]

| | 2ii | . | 1i | . | 2i | . | 1 | . | 2 | . | 1a | . | 2a | . |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -46 | 10 | 101 | . | -1077 | 126 | . | . | -1077 | -126 | 101 | . | -46 | -10 |
| . | -10 | 2 | . | 2 | -126 | 51 | . | -52 | 126 | 51 | . | 2 | 10 | 2 |
| 2 | 2 | . | 31 | -6 | -11 | 15 | -243 | -15 | -11 | -10 | 31 | 7 | 2 | . |
| . | . | . | 7 | . | -10 | . | -15 | 302 | 15 | . | -6 | . | . | . |
| 2k | 2 | . | 31 | -7 | -11 | 10 | -243 | 15 | -11 | -15 | 31 | 6 | 2 | . |
| . | . | . | 6 | . | -15 | . | 15 | 302 | 10 | . | -7 | . | . | . |

In polymer basis:

| | |
|---|---|
| 1 | 2448 |
| 2 | -161 |

(b) abL [URL]

| | 2ii | . | 1i | . | 2i | . | 1 | . | 2 | . | 1a | . | 2a | . |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -41 | 7 | 106 | 14 | -1070 | 67 | . | 42 | -1070 | -153 | 106 | 7 | -41 | -7 |
| . | -7 | 1 | 7 | 3 | -153 | 49 | 42 | -67 | 67 | 49 | 14 | 3 | 7 | 1 |
| 2 | 19 | -5 | 10 | . | 133 | -35 | -75 | 59 | -211 | -15 | 36 | 14 | -20 | -4 |
| . | 6 | -1 | . | . | 32 | -5 | -78 | 253 | 31 | 9 | -10 | -2 | 6 | . |
| 2k | 19 | -6 | 10 | . | 133 | -32 | -75 | 78 | -211 | -31 | 36 | 10 | -20 | -6 |
| . | 5 | -1 | . | . | 35 | -5 | -59 | 253 | 15 | 9 | -14 | -2 | 4 | . |

In polymer basis:

| | |
|---|---|
| 1 | 2443 |
| 2 | 34 |

(c) abT [URL]

| | 2ii | . | 1i | . | 2i | . | 1 | . | 2 | . | 1a | . | 2a | . |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -46 | 8 | 103 | -1 | -1071 | 126 | . | 10 | -1067 | -164 | 103 | 2 | . | . |
| . | -8 | 1 | 2 | 1 | -126 | 47 | 10 | -51 | 164 | 63 | -1 | 1 | . | . |
| 2 | 5 | -1 | 40 | . | 13 | -10 | -156 | 3 | -6 | -3 | 40 | 5 | . | . |
| . | . | . | 5 | . | -20 | -3 | 3 | 143 | 35 | -4 | . | . | . | . |
| 2k | 5 | . | 21 | -7 | 13 | 20 | -290 | 38 | -6 | -35 | 21 | 12 | . | . |
| . | 1 | . | 12 | -2 | 10 | -3 | 38 | 234 | 3 | -4 | -7 | -2 | . | . |

In polymer basis:

| | |
|---|---|
| 1 | 2391 |
| 2 | -174 |

(d) baL [URL]

| | 2ii | . | 1i | . | 2i | . | 1 | . | 2 | . | 1a | . | 2a | . |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -34 | 7 | 115 | 8 | -1054 | 123 | . | 36 | -1054 | -129 | 115 | 3 | -34 | -6 |
| . | -6 | 1 | 3 | 3 | -129 | 54 | 36 | -84 | 123 | 54 | 8 | 3 | 7 | 1 |
| 2 | 19 | -5 | 10 | 4 | 138 | -29 | -76 | 122 | -190 | -39 | 53 | 8 | -15 | -5 |
| . | 4 | . | -4 | 2 | 14 | -3 | -122 | 204 | 19 | 3 | -8 | -4 | 4 | . |
| 2k | 19 | -4 | 16 | -5 | 138 | -14 | -120 | 15 | -190 | -19 | 26 | 15 | -15 | -4 |
| . | 5 | . | 5 | -1 | 29 | -3 | -15 | 231 | 39 | 3 | -15 | -2 | 5 | . |

In polymer basis:

| | |
|---|---|
| 1 | 2409 |
| 2 | -4 |

Table S11: Tight-binding Hamiltonian for P3HT.

(a) cryst-i [URL]

| | 2ii | . | 1i | . | 2i | . | 1 | . | 2 | . | 1a | . | 2a | . |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -41 | 17 | 58 | 10 | -1009 | 314 | 0 | -1 | -1009 | 263 | 58 | -13 | -41 | 12 |
| . | 12 | -6 | -13 | . | 263 | -163 | -1 | -420 | 314 | -163 | 10 | . | 17 | -6 |
| 2 | 18 | -6 | 11 | 3 | 50 | -22 | 4 | 85 | 9 | 82 | 37 | -49 | -3 | . |
| . | -6 | 2 | -3 | . | -22 | 6 | 61 | 14 | 82 | 127 | 19 | . | . | -2 |
| 2k | . | . | 11 | -3 | -19 | 6 | 4 | 61 | -58 | 19 | 37 | 19 | 2 | -5 |
| . | . | -1 | 3 | . | 6 | -3 | 85 | 14 | 19 | 168 | -49 | . | -5 | 5 |

In polymer basis:

| | |
|---|---|
| 1 | 2369 |
| 2 | 31 |

(b) pistack-C [URL]

| | 2ii | . | 1i | . | 2i | . | 1 | . | 2 | . | 1a | . | 2a | . |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -51 | 13 | 72 | 22 | -1076 | 263 | 0 | -14 | -1076 | 240 | 72 | -7 | -51 | 7 |
| . | 7 | -3 | -7 | -6 | 240 | -66 | -14 | -516 | 263 | -66 | 22 | -6 | 13 | -3 |
| 2 | -12 | 7 | -16 | 5 | -60 | 62 | -56 | . | 159 | -3 | 23 | -18 | 17 | -3 |
| . | 7 | -2 | 5 | -3 | 62 | -19 | . | -145 | -3 | -93 | -18 | 6 | -3 | . |
| 2k | -12 | 7 | -16 | 5 | -60 | 62 | -56 | . | 159 | -3 | 23 | -18 | 17 | -3 |
| . | 7 | -2 | 5 | -3 | 62 | -19 | . | -145 | -3 | -93 | -18 | 6 | -3 | . |

In polymer basis:

| | |
|---|---|
| 1 | 2494 |
| 2 | -122 |

(c) pistack-CA [URL]

| | 2ii | . | 1i | . | 2i | . | 1 | . | 2 | . | 1a | . | 2a | . |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -50 | 15 | 63 | 14 | -1052 | 285 | 0 | -22 | -1052 | 257 | 63 | -3 | -50 | 8 |
| . | 8 | . | -3 | -6 | 257 | -76 | -22 | -516 | 285 | -76 | 14 | -6 | 15 | . |
| 2 | 10 | -10 | 19 | 2 | 154 | -184 | 5 | 39 | -110 | 19 | -17 | 15 | -24 | 8 |
| . | -10 | 3 | 2 | -7 | -184 | 12 | -170 | -216 | 19 | 9 | . | -4 | 8 | -2 |
| 2k | 36 | -9 | 19 | 2 | 288 | -60 | 5 | -170 | -110 | 38 | -17 | . | -25 | 9 |
| . | -9 | 2 | 2 | -7 | -60 | 49 | 39 | -216 | 38 | -13 | 15 | -4 | 9 | -4 |

In polymer basis:

| | |
|---|---|
| 1 | 2447 |
| 2 | -124 |

(d) cryst-CA [URL]

| | 2ii | . | 1i | . | 2i | . | 1 | . | 2 | . | 1a | . | 2a | . |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -52 | 13 | 74 | 17 | -1066 | 274 | 0 | -6 | -1066 | 249 | 74 | -3 | -52 | 12 |
| . | 12 | -4 | -3 | -6 | 249 | -67 | -6 | -482 | 274 | -67 | 17 | -6 | 13 | -4 |
| 2 | -20 | 4 | -42 | 3 | 52 | -29 | 149 | -11 | -107 | -25 | . | 8 | -11 | . |
| . | 4 | . | 12 | -4 | -29 | -6 | -192 | -41 | -25 | 35 | -11 | . | . | 3 |
| 2k | 15 | . | -42 | 12 | 210 | 22 | 149 | -192 | -56 | 31 | . | -11 | -6 | 3 |
| . | . | . | 3 | -4 | 22 | 156 | -11 | -41 | 31 | -23 | 8 | . | 3 | -2 |

In polymer basis:

| | |
|---|---|
| 1 | 2484 |
| 2 | 99 |

(e) pistack-CAaac [URL]

| | 2ii | . | 1i | . | 2i | . | 1 | . | 2 | . | 1a | . | 2a | . |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -34 | 17 | 71 | 13 | -1011 | 297 | 0 | -23 | -1011 | 280 | 71 | -9 | -34 | 14 |
| . | 14 | -7 | -9 | -5 | 280 | -145 | -23 | -453 | 297 | -145 | 13 | -5 | 17 | -7 |
| 2 | -27 | 7 | -39 | 6 | -9 | 12 | 132 | -35 | -106 | -13 | -15 | 10 | -26 | . |
| . | 7 | . | 12 | -3 | 12 | -20 | -144 | -46 | -13 | 30 | -9 | 3 | . | 5 |
| 2k | 13 | -7 | -39 | 12 | 175 | -25 | 132 | -144 | -42 | 13 | -15 | -9 | -22 | 5 |
| . | -7 | 4 | 6 | -3 | -25 | 47 | -35 | -46 | 13 | -7 | 10 | 3 | 5 | . |

In polymer basis:

| | |
|---|---|
| 1 | 2385 |
| 2 | 125 |

(f) pistack-BAab [URL]

| | 2ii | . | 1i | . | 2i | . | 1 | . | 2 | . | 1a | . | 2a | . |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -42 | 15 | 60 | . | -998 | 269 | 0 | -34 | -998 | 260 | 60 | -16 | -42 | 19 |
| . | 19 | . | -16 | 3 | 260 | -139 | -34 | -382 | 269 | -139 | . | 3 | 15 | . |
| 2 | . | . | 50 | . | 17 | -2 | -58 | 29 | 13 | -8 | 50 | -17 | 13 | . |
| . | . | . | -17 | . | -42 | 24 | 29 | -102 | 60 | -56 | . | . | . | . |
| 2k | 13 | . | . | . | 13 | 60 | -311 | 99 | 17 | -42 | . | . | . | . |
| . | . | . | . | . | -8 | -56 | 99 | 112 | -2 | 24 | . | . | . | . |

In polymer basis:

| | |
|---|---|
| 1 | 2353 |
| 2 | -189 |

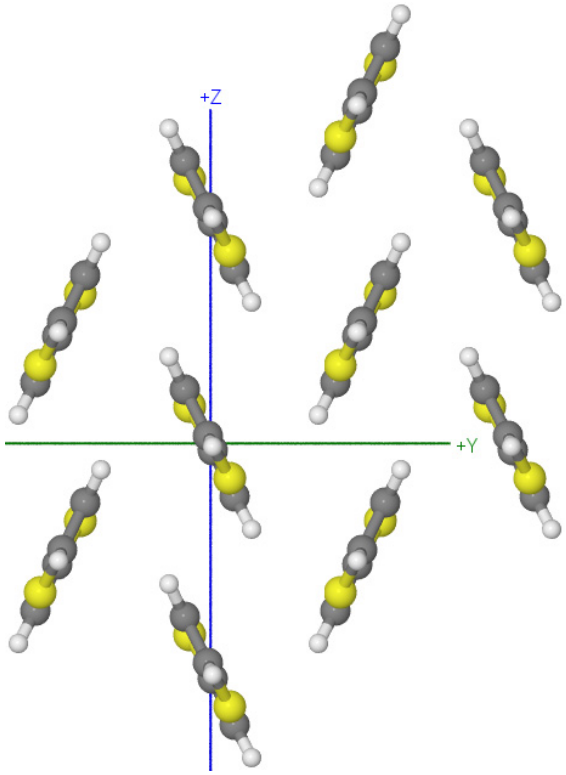



Figure S11: Example of a PT cluster used for the determination of interchain couplings.

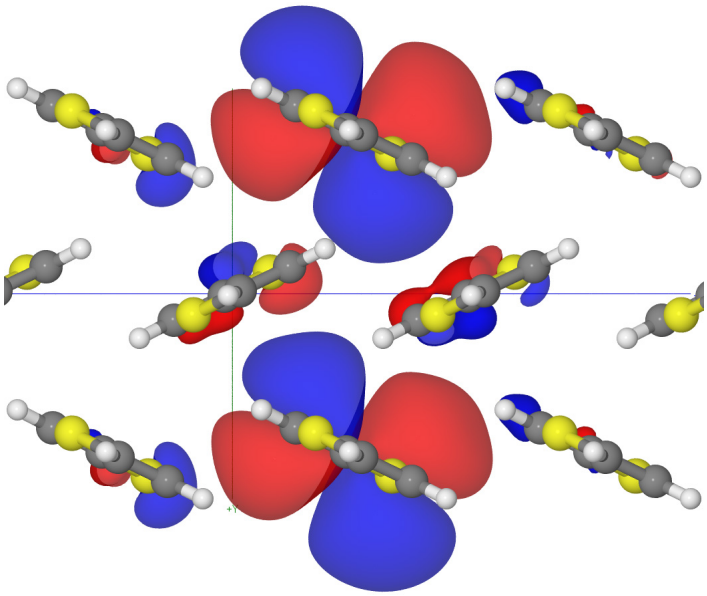


Figure S12: Illustration of a next-nearest-neighbor coupling in PT exceeding 10 meV due to through-neighbor tunneling. Shown here is a linear combination of two coupled LMOs. The Jmol isosurface value is reduced to 0.005 to visualize the spread of these orthogonalized LMOs on neighbor chains.

Table S12: Dependence of onsite energies on cluster size and shape. Here 'e1' and 'e2' are onsite energies (in eV) for the highest and the next-highest LMOs, 'e12' is their difference, 'psi^2' is the weight of the HOMO of the cluster on the monomer at which the onsite energies are taken, that monomer number is denoted by 'm', 'r' is the distance from the center of that monomer to the center of the cluster in lattice coordinates.

| e1 | e2 | e12 | psi^2 | r | m | cluster |
|---|---|---|---|---|---|---|
| polyT/cryst-a | | | | | | |
| -7.939 | -8.440 | -0.501 | 0.042 | 0.29 | 4 | 1+2+2j+2k+2jk+1c+1k |
| -7.899 | -8.399 | -0.500 | 0.000 | 0.34 | 13 | 1+2+1b+2j+1c+2k+1bc+2jk+1k+2c |
| -7.894 | -8.394 | -0.500 | 0.002 | 0.40 | 4 | 1+2+1b+2j+1c+2k+1bc+2jk+1k+2c |
| -7.932 | -8.433 | -0.501 | 0.012 | 0.41 | 4 | 1+1c+2+2j+2k+2jc+2jk+2c+1k+1cc |
| -7.884 | -8.388 | -0.504 | 0.003 | 0.51 | 5 | 1+2+1b+2j+1c+2k+1bc+2jk+1k+2c |
| -7.969 | -8.444 | -0.475 | 0.001 | 0.54 | 21 | 1+1c+2+2j+2k+2jc+2jk+2c+1k+1cc |
| -8.071 | -8.604 | -0.533 | 0.200 | 0.29 | 4 | 1 |
| -7.823 | -8.346 | -0.523 | 0.199 | 0.34 | 13 | 1+2 |
| -8.139 | -8.724 | -0.585 | 0.001 | 0.40 | 4 | 1+2 |
| -8.091 | -8.590 | -0.499 | 0.100 | 0.41 | 4 | 1+1c |
| -8.215 | -8.747 | -0.532 | 0.001 | 0.51 | 5 | 1+2 |
| PEDOT/pistack-abH | | | | | | |
| -6.658 | -6.709 | -0.051 | 0.129 | 0.28 | 4 | 1+2+2k |
| -6.657 | -6.709 | -0.052 | 0.130 | 0.28 | 5 | 1+2+2k |
| -6.575 | -6.629 | -0.054 | 0.088 | 0.37 | 4 | 1+2+2k+1c |
| -6.574 | -6.628 | -0.054 | 0.089 | 0.37 | 5 | 1+2+2k+1c |
| -7.122 | -7.152 | -0.030 | 0.208 | 0.28 | 4 | 1 |
| -7.121 | -7.152 | -0.031 | 0.209 | 0.28 | 5 | 1 |
| -6.870 | -6.914 | -0.044 | 0.105 | 0.37 | 4 | 1+2 |
| -6.871 | -6.914 | -0.043 | 0.104 | 0.37 | 5 | 1+2 |
| P3HT/cryst-CA | | | | | | |
| -7.420 | -7.902 | -0.482 | 0.071 | 0.27 | 5 | 1+2+2k+1c |
| -7.498 | -8.007 | -0.509 | 0.038 | 0.37 | 12 | 1+2+2k |
| -7.451 | -7.932 | -0.481 | 0.104 | 0.38 | 5 | 1+2+2k |
| -7.484 | -7.994 | -0.510 | 0.045 | 0.50 | 21 | 1+2+2k |
| -7.539 | -8.044 | -0.505 | 0.088 | 0.27 | 5 | 1+2 |
| -7.647 | -8.160 | -0.513 | 0.210 | 0.45 | 4 | 1 |
| -7.663 | -8.183 | -0.520 | 0.187 | 0.45 | 5 | 1 |
| polTzTz/cryst-a | | | | | | |
| -8.269 | -8.925 | -0.656 | 0.075 | 0.00 | 5 | 1+1c+1k+1b+1j+1bk+1jc |
| -8.226 | -8.887 | -0.661 | 0.041 | 0.50 | 5 | 1+1b+1c+1bk+1k+1bc+1jc+1bbk+1j+1bb |
| -8.240 | -8.893 | -0.653 | 0.040 | 0.50 | 5 | 1+1c+1b+1jc+1bk+1jcc+1j+1bc+1k+1cc |
| -8.380 | -9.126 | -0.746 | 0.177 | 0.00 | 5 | 1 |
| -8.338 | -9.056 | -0.718 | 0.088 | 0.50 | 5 | 1+1b |
| -8.387 | -9.122 | -0.735 | 0.088 | 0.50 | 5 | 1+1c |

Table S13: Difference between solid-state and cluster TBH diagonal elements (onsite energies) for the monomer next to the one used for the parametrization. Here $\varepsilon_1$ is the energy of the top valence orbital in meV and $\varepsilon_{12} = \varepsilon_1 - \varepsilon_2$ is the difference between energies of the two upper valence orbitals on the same site.

| system | polymorph | $\Delta\varepsilon_1$ | $\Delta\varepsilon_{12}$ |
|---|---|---|---|
| polyT | cryst-aH | 10 | 1 |
| polyT | cryst-a | 8 | 0 |
| PEDOT | pistack-abH | 12 | 4 |
| P3HT | pistack-C | 7 | 4 |
| P3HT | pistack-Caac | 8 | 6 |
| polyTzTz | cryst-a | 6 | 1 |