Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Exciton Transfer Free Energy from Car-Parrinello Molecular Dynamics

Supplementary Information

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Theory

Implementation

The implemented restraining potentials that act on Wannier centres can be invoked in our modified CPMD code by using the following keywords:

```
WAN POT {EXCI}, {LINE, REL}
 Activates restraining potentials acting on Wannier centres.
 The following lines contain the number of restrained centres N.
 This is followed by one line per centre containing the index of
 the centre I_i, the force constant K_i and the equilibrium
 position X_i, Y_i and Z_i.
 N
   I_1, K_1, X_1, Y_1, Z_1
   I_2, K_2, X_2, Y_2, Z_2
   ...
   I_N, K_N, X_N, Y_N, Z_N

 The keyword EXCI is used to restrain the c.o.m. of the specified
 orbitals instead of the individual orbitals.

 The keyword LINE defines a reaction coordinate as the lien connecting
 the c.o.m.s of two groups of atoms, read from the next lines. The line
 containing the number of atoms M is followed by two lines, each containing
 M indices of the atoms AT_i comprising the respective group. The number of
 atoms in each group has to be the same.
 M
  AT_1, AT_2, ..., AT_M
  AT_M, AT_M+1, ..., AT_2M

 note: if LINE is specified, only the X coordinate of the orbital
 restraining input is used and corresponds to the 1D reaction coordinate.
 The lines specifying the groups of atoms have to appear before the lines
 specifying the orbitals.

 The keyword REL indicates that the specified X, Y and Z coordinates are
 to be taken relative to the c.o.m. of the molecule.
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Example input for a simulation of Di-P3MT with an intermolecular distance of $d = 4.0\,\text{Å}$ and an exciton restraint at $\xi_{\text{ref}} = 0.5$ with force constant $K_{\xi} = 0.2\,\text{a.u.}$:

```
&CPMD
  RESTART COORDINATES WAVEFUNCTION VELOCITIES NOSEP LATEST
  QUENCH BO
  MOLECULAR DYNAMICS CP
  ROKS
  SUBTRACT COMVEL ROTVEL
   100
  NOSE IONS
    300 2500
  CONVERGENCE ORBITALS
   1.0D-7
  MAXSTEP
   10000
  VDW CORRECTION ON
  TRAJECTORY XYZ
  TIMESTEP
   4.0
  EMASS
   400
  PCG MINIMIZE
  ANDERSON MIXING
   0.4
  BROYDEN MIXING
   0.5 350 0.01 5 5 0
  REAL SPACE WFN KEEP
  DIPOLE DYNAMICS WANNIER
  WANNIER REFERENCE
   -1.09389937       1.63228834      -1.33474410
  WAN POT LINE EXCI
   5
    2 16 17 18 19
    7 47 50 52 54
   2
    152 0.2 0.5 0 0
    153 0.2 0.5 0 0
  NOSE ELECTRONS
   0.07266 30835
  NOSE PARAMETERS
   4 12 4 9 9 1
&END

&VDW
  VDW PARAMETERS
   ALL GRIMME
   S6GRIM
    PBE
```

```
&END

&DFT
  FUNCTIONAL PBE
  GC-CUTOFF
   1.0d-06
&END

&SYSTEM
  ANGSTROM
  SYMMETRY
   8
  CELL ABSOLUTE
   28.0 19.0 16.0 0.0 0.0 0.0
  CUTOFF
   70
&END
&ATOMS

CONSTRAINTS
  RESTRAINTS
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  DIST  1 38 4.24 0.1
  DIST  2 52 4.24 0.1
  DIST  2 54 4.24 0.1
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  DIST  3 48 4.24 0.1
  DIST  4 58 4.24 0.1
  DIST  4 59 4.24 0.1
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  DIST  5 46 4.24 0.1
  DIST  6 32 4.24 0.1
  DIST  6 33 4.24 0.1
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  DIST  7 18 4.24 0.1
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  DIST  8 13 4.24 0.1
  DIST  9 26 4.24 0.1
  DIST  9 27 4.24 0.1
  DIST 10 21 4.24 0.1
  DIST 10 22 4.24 0.1
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```

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    -8.767149930    -0.075252000     0.298076000
    -8.899220470     0.617493990    -3.419254060
    -1.114495990     2.084117890    -3.438569070
    -4.521377090    -0.790813030    -3.656286950
     6.570835110     3.667284010    -3.238698960
     3.155884980     1.074179050    -2.682812930

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    -6.375994210     1.261808990     0.239333000
    -3.286045070    -0.792075990    -0.005262000
    -2.577074050     2.369817970     0.209962990
    -2.171637060     3.664936070    -0.012140000
    -0.746613980     3.964303020     0.110022000
    -0.028003000     2.793148040     0.430754010
     1.379547000     2.574078080     0.804162980
     1.898998020     1.300623060     1.095988040
     3.359126090     1.222293020     1.303204060
     3.920820000     2.515064950     1.107223030
     4.138638020    -0.049197000     1.567415000
     5.236975190     2.988991020     1.053235050
     5.613279820     4.209552760     0.539502980
     6.941484930     4.586558820     0.590417980
     7.722219940     3.520988940     0.997673990
     7.575149060     5.880370140     0.189546000
    -0.127130000     5.326170920     0.101273000
    -7.793631080     1.387627960     0.187169000
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    -9.979931830     2.207859990     0.120676000
   -10.287369730     0.847692010     0.224316000
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    -5.632522110     1.525336030    -3.511876110
    -4.285267830     1.764431000    -3.406761880
    -9.840561870    -0.803650020    -3.349548100
     0.974861030     4.336192130    -3.476720090
    -5.993988040     0.204517010    -3.610390900
    -7.372260090    -0.406823990    -3.507960080
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    -9.159602170    -1.986698990    -3.238550900
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```

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*H_MT_PBE.psp  KLEINMAN-BYLANDER
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```

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&END
```

Exact Exchange in ROKS

The exchange-correlation energy within ROKS is defined as[1–3]

$$E_{\mathrm{xc}}^{\mathrm{ROKS}} = 2E_{\mathrm{xc}}[\rho_m^\alpha, \rho_m^\beta] - E_{\mathrm{xc}}[\rho_t^\alpha, \rho_t^\beta]$$

for the mixed-state Slater-determinant m and the triplet determinant t; the spin-densities for α– and β–spin are defined as:

$$\rho_m^\alpha = \sum_{i=1}^{n} |\phi_i^\alpha(\boldsymbol{r})|^2, \;\; \rho_m^\beta = \sum_{i=1}^{n-1} \left|\phi_i^\beta(\boldsymbol{r})\right|^2 + \left|\phi_{n+1}^\beta(\boldsymbol{r})\right|^2,$$

$$\rho_t^\alpha = \sum_{i=1}^{n+1} |\phi_i^\alpha(\boldsymbol{r})|^2, \;\; \rho_t^\beta = \sum_{i=1}^{n-1} \left|\phi_i^\beta(\boldsymbol{r})\right|^2.$$

Within unrestricted Kohn-Sham (UKS) theory, the Hartree-Fock exchange (HFX) contribution of hybrid density functionals has the form

$$E^{\mathrm{HFX}} = -\frac{1}{2} \sum_{i,j,\sigma} f_i^\sigma f_j^\sigma \, (i^\sigma j^\sigma | j^\sigma i^\sigma)$$

with occupation numbers f_i^σ for spin $\sigma\%in\{\alpha,\beta\}$ and the shorthand notation

$$(ij|kl) = \iint \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\, \phi_i^*(\boldsymbol{r})\phi_j(\boldsymbol{r}) \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \phi_k^*(\boldsymbol{r}')\phi_l(\boldsymbol{r}').$$

for two–electron integrals. The HFX energy expression for the mixed and triplet densities is then

$$\begin{aligned} E^{\mathrm{HFX}}[\rho_m^\alpha, \rho_m^\beta] = &-\frac{1}{2} \sum_{i,j=1}^{n} (i^\alpha j^\alpha | j^\alpha i^\alpha) - \frac{1}{2} \sum_{i,j=1}^{n-1} (i^\beta j^\beta | j^\beta i^\beta) \\ &- \frac{1}{2} \sum_{i=1}^{n-1} (i^\beta (n+1)^\beta | (n+1)^\beta i^\beta) - \frac{1}{2} \sum_{j=1}^{n} ((n+1)^\beta j^\beta | j^\beta (n+1)^\beta) \\ &- \frac{1}{2} ((n+1)^\beta (n+1)^\beta | (n+1)^\beta (n+1)^\beta), \end{aligned}$$

$$E^{\mathrm{HFX}}[\rho_t^{\alpha},\rho_t^{\beta}] = -\frac{1}{2}\sum_{i,j=1}^{n+1}(i^{\alpha}j^{\alpha}|j^{\alpha}i^{\alpha}) - \frac{1}{2}\sum_{i,j=1}^{n-1}(i^{\beta}j^{\beta}|j^{\beta}i^{\beta}),$$

where all occupation numbers were set to $f_i = 1$, as each orbital contains exactly one electron within UKS. In the ROKS formulation all orbitals except the two SOMOs are doubly occupied and have the same spatial wavefunction for both spins. Therefore, the expressions containing the doubly occupied orbitals can be reduced to the restricted Kohn-Sham (RKS) formulation:

$$\begin{aligned}
&\phi_i^{\alpha}(\boldsymbol{r}) = \phi_i^{\beta}(\boldsymbol{r}) \equiv \phi_i(\boldsymbol{r}) \ \forall i \in \{1,\ldots,n+1\} \\
\Rightarrow E_{\mathrm{ROKS}}^{\mathrm{HFX}} = &-\frac{1}{2}\sum_{i,j=1}^{n-1}(ij|ji) - \frac{1}{2}\sum_{i=1}^{n-1}(in|ni) - \frac{1}{2}\sum_{j=1}^{n-1}(nj|jn) - \frac{1}{2}(nn|nn) \\
&-\frac{1}{2}\sum_{i=1}^{n-1}(i(n+1)|(n+1)i) + \frac{1}{2}(n(n+1)|(n+1)n) \\
&-\frac{1}{2}\sum_{j=1}^{n-1}((n+1)j|j(n+1)) + \frac{1}{2}((n+1)n|n(n+1)) \\
&-\frac{1}{2}((n+1)(n+1)|(n+1)(n+1)).
\end{aligned}$$

Using the symmetry of the two–electron orbitals[4]

$$(ij|ji) = (ji|ij)$$

the terms can be further simplified:

$$\begin{aligned}
E_{\mathrm{ROKS}}^{\mathrm{HFX}} = &-\sum_{i,j=1}^{n-1}(ij|ji) - \frac{1}{2}\sum_{i=1}^{n+1}\sum_{j=n}^{n+1}(ij|ji) - \frac{1}{2}\sum_{j=1}^{n+1}\sum_{i=n}^{n+1}(ij|ji) \\
&-\frac{1}{2}\sum_{i=n}^{n+1}(ii|ii) + \frac{1}{2}\sum_{\substack{i=n,\\ j=n,\\ i\neq j}}^{n+1}(ij|ji)
\end{aligned}$$

or using the shorthand notation $a,b \in \{1,\ldots,n-1\}$:

$$\begin{aligned}
E_{\mathrm{ROKS}}^{\mathrm{HFX}} = &-\sum_{a,b}(ab|ba) - \frac{1}{2}\sum_{a,k}(ak|ka) - \frac{1}{2}\sum_{a,k}(ka|ak) \\
&-\frac{1}{2}\sum_{k}(kk|kk) + \frac{1}{2}\sum_{k\neq l}(kl|lk).
\end{aligned}$$

Here, the terms containing doubly occupied orbitals (a and b) have been separated from the SOMO terms (k and l) for clarity. Now the occupation numbers

$$f_a = f_b = 2$$

$$f_k = f_l = 1$$

are explicitly substituted:

$$
\begin{aligned}
E_{\text{ROKS}}^{\text{HFX}} = & -\frac{1}{4}\sum_{a,b} f_a f_b\,(ab|ba) - \frac{1}{4}\sum_{a,k} f_a f_k\,(ak|ka) - \frac{1}{4}\sum_{a,k} f_k f_a\,(ka|ak) \\
& -\frac{1}{2}\sum_{k} f_k f_k\,(kk|kk) + \frac{1}{2}\sum_{k\neq l} f_k f_l\,(kl|lk) \\
= & -\frac{1}{4}\Bigg[\sum_{a,b} f_a f_b\,(ab|ba) + \sum_{a,k} f_a f_k\,(ak|ka) + \sum_{a,k} f_k f_a\,(ka|ak) \\
& +2\sum_{k} f_k f_k\,(kk|kk) - 2\sum_{k\neq l} f_k f_l\,(kl|lk)\Bigg].
\end{aligned}
$$

The differences between doubly and singly occupied orbitals can be summarized in the prefactor matrix $\boldsymbol{P}$:

$$
E_{\text{ROKS}}^{\text{HFX}} = -\frac{1}{4}\sum_{i,j=1}^{n+1} P_{i,j}\, f_i f_j\,(ij|ji)
$$

with

$$
\begin{aligned}
P_{n,n} &= P_{n+1,n+1} = 2, \\
P_{n,n+1} &= P_{n+1,n} = -2, \\
P_{i,j} &= 1, \text{ else.}
\end{aligned}
$$

These prefactors correspond to the Roothaan parameters for excitations without specified symmetry within the restricted open-shell Hartree-Fock method[5].

The implementation and performance of ROKS with hybrid functionals is verified by calculating vertical excitation energies for various organic molecules. For all molecules structures were relaxed in the ground state before single point calculations with ROKS were performed. The vertical excitation energies are then the difference between S_1 and S_0 energies (see Tab. S1). The excitation character is determined from the shape of the SOMOs.

Table S1 ROKS vertical excitation energies for various organic molecules compared with literature results from ROKS calculations(RO-PBE0/6-31G*[6]), as well as benchmark *ab initio* results ((d) CASPT2, CC2, CCSD und CC3 best estimates[6,7]) and experimentally determined energies ((b) experiment, in solution[8,9] and (f) experiment[10,11]).

		Excitation energy ΔE / eV					
Molecule	Type	BLYP	PBE	B3LYP	PBE0	Reference	Estimate
Diazene	$n \rightarrow \pi^*$	2.68	2.68	2.87	2.88	3.54^a	3.50^b
Azobenzene	$n \rightarrow \pi^*$	2.21	2.18	2.34	2.43	2.61^a	2.79^b
Formaldehyde	$n \rightarrow \pi^*$	3.57	3.54	3.65	3.62	3.67^c	3.88^d
Acetone	$n \rightarrow \pi^*$	3.94	3.96	4.08	4.09	4.10^c	4.40^d
Guanine	$n \rightarrow \pi^*$	4.02	3.96	4.30	4.42	4.87^e	4.55^f
Thymine	$\pi \rightarrow \pi^*$	4.10	4.12	4.67	4.82	4.96^c	4.82^d
Cytosine	$\pi \rightarrow \pi^*$	4.13	4.18	4.58	4.71	4.63^c	4.66^d
Uracil	$\pi \rightarrow \pi^*$	4.25	4.27	4.84	4.99	5.06^c	4.80^d
Adenine	$\pi \rightarrow \pi^*$	4.11	4.15	4.69	4.93	4.94^c	5.25^d

The results are consistent with previous implementations and deviations can be attributed to basis set differences[6]. Hybrid functionals alleviate the usual shortcomings of ROKS especially in the case of $\pi \rightarrow \pi^*$ excitations.

Results and Discussion

Investigated Molecules

In the Di-P3MT system intermolecular distances are restrained by fixing the bonds between sulfur and carbon atoms of thiophene rings which lie on top of each other. The interatomic distances d' which lead to the specified intermolecular distances d are shown in Tab. S2.

Table S 2 Restrained S–C bond distances d' resulting from the defined intermolecular distances d between P3MT monomers in the Di-P3MT system.

d / Å	d' / Å
3.0	3.31
3.5	3.76
4.0	4.24
4.5	4.71
5.0	5.19

Without restraining the intermolecular distance, the monomers drift apart in longer simulations. Fig. S1 shows the intermolecular distance measured during a 2.9 ps simulation of Di-P3MT without restrained bonds, but with the exciton coordinate restrained to $\xi_{\text{ref}} = 0.5$. The resulting structure is shown in Fig. S2

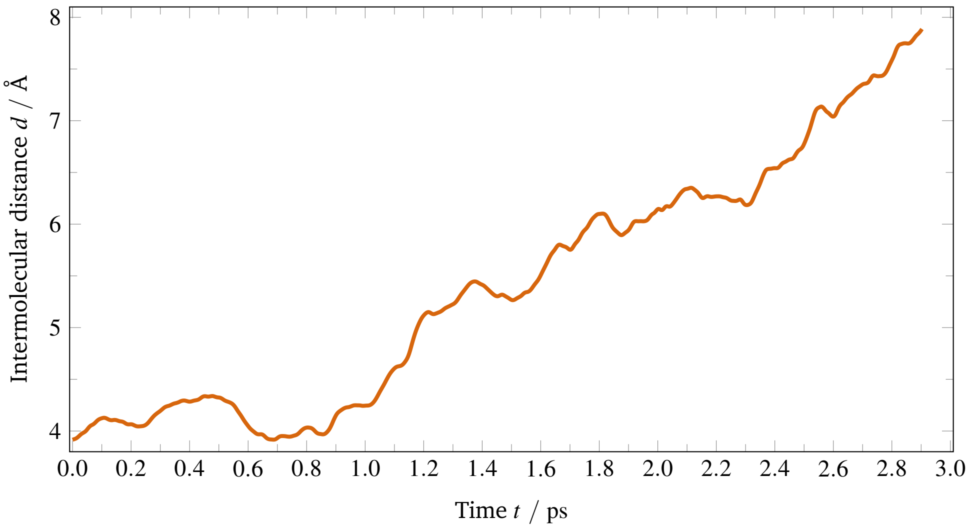

Fig. S 1 Time evolution of the intermolecular distance from a simulation of Di-P3MT over 2.9 ps. The exciton coordinate is kept at $\xi_{\text{ref}} = 0.5$ with a harmonic potential with force constant $K_{\xi} = 0.2\,\text{a.u.}$ and no bonds between P3MT monomers are restrained.

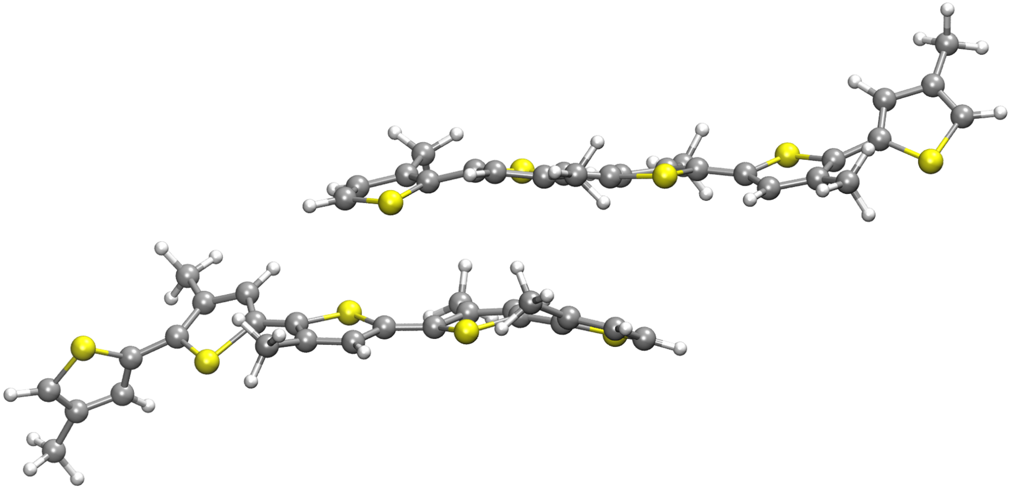

Fig. S2 Structure of Di-P3MT after a $2.9\,\mathrm{ps}$ simulation without restrained bonds, but with the exciton coordinate restrained to $\xi_{\text{ref}} = 0.5$.

Restraining Potentials

The effect of the restraining potentials depends on the force constant K_ξ, as larger force constants restrict deviations of the exciton coordinate from the reference coordinate. Fig. S3 shows the average deviations for different force constants.

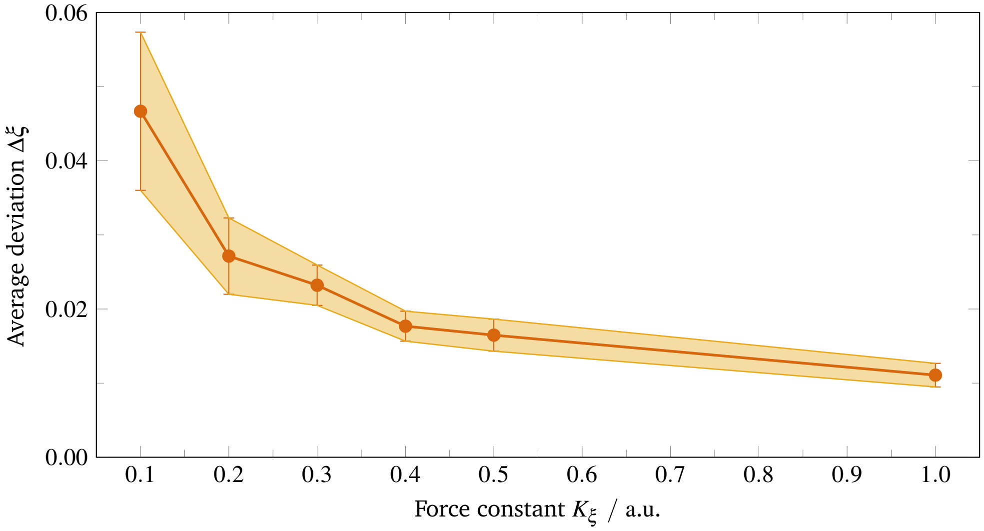

Fig. S3 Average deviation of the exciton coordinate averaged over time and windows, i.e. $\Delta\xi = \frac{1}{N}\sum_{i=0}^{N} \left|\langle\xi_i\rangle - \xi_{\text{ref},i}\right|$ for different force constants K_ξ. The error bars indicate the average standard deviation $\sigma = \frac{1}{N}\sum_{i=0}^{N}\sigma_i$.

As restraining potentials acting on Wannier centres induce low frequency oscillations in the orbital system, energy can be transferred from the ions, increasing the orbital temperature. An exemplary temperature profile from a $1\,\mathrm{ps}$ simulation of Di–P3MT with an intermolecular distance $d = 4.0\,\text{Å}$ and with $K_\xi = 0.2\,\mathrm{a.u.}$ and $\xi_{\text{ref}} = 0.0$ is shown in Fig. S4.

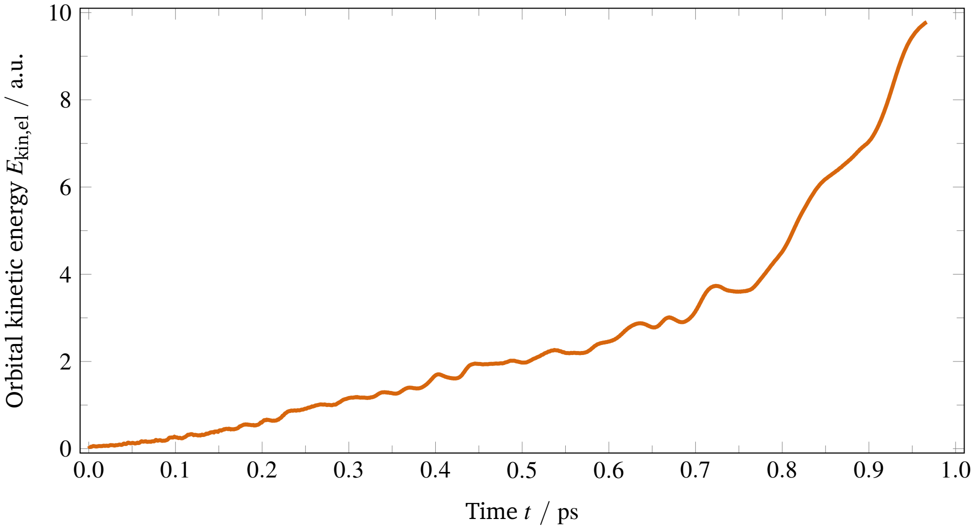

Fig. S4 Time evolution of the total orbital kinetic energy of the from a simulation of Di-P3MT over $1\,\text{ps}$. The exciton coordinate is kept at $\xi_{\text{ref}} = 0.0$ with a harmonic potential with force constant $K_\xi = 0.2\,\text{a.u.}$ and the P3MT monomers are kept at an intermolecular distance of $d = 4.0\,\text{Å}$.

The vibrational spectrum of Di-P3MT was calculated for the un–restrained, optimized structure in the harmonic approximation. As intensities are not calculated by default in the CPMD code, the intensities for each mode are normalised to 1. Lorentzian broadening with a width of $\Delta\omega = 20\,\text{cm}^{-1}$ is applied to the line spectrum for visualisation (see Fig. S5).

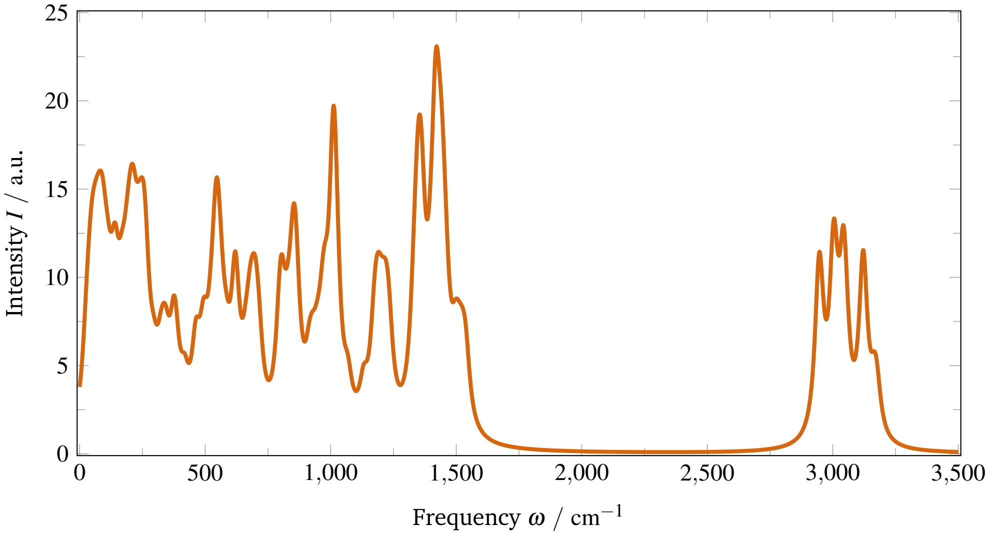

Fig. S5 Harmonic vibrational spectrum of optimized Di–P3MT. The intensities for each mode are normalised to 1. Lorentzian broadening with a width of $\Delta\omega = 20\,\text{cm}^{-1}$ is applied to the line spectrum.

References

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