Supporting Information for PCCP

Ultrafast Internal Conversion in a Low Band Gap Polymer for Photovoltaics: Experimental and Theoretical Study

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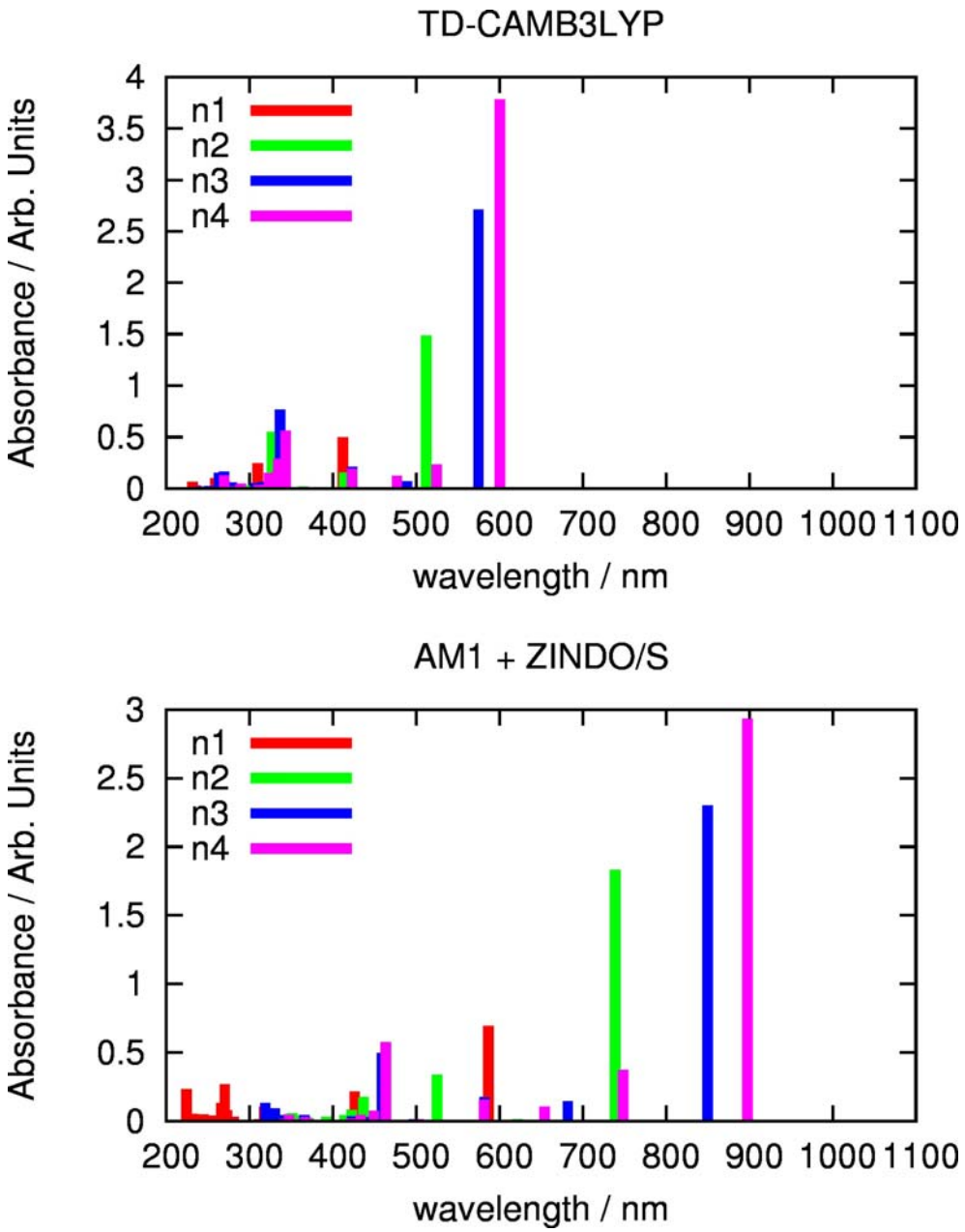
S1) DFT (CAM-B3LYP, B3LYP and wB97XD/6-31G**) total energy for $CPDTBT_4$ in its ground state singlet (S0) and triplet (T1) state:

S_0: $CPDTBT_4$ flat geometry (CAM-B3LYP/6-31G**) = -7830.95572666 Ha
S_0: $CPDTBT_4$ distorted geometry (CAM-B3LYP/6-31G**) = -7830.95622708 Ha
S_0: $CPDTBT_4$ distorted geometry (wB97XD/6-31G**) = -7831.51193128 Ha
S_0: $CPDTBT_4$ distorted geometry (B3LYP/6-31G**) = -7832.72377798 Ha

T_1: $CPDTBT_4$ (UCAM-B3LYP/6-31G**) = -7830.91916325 Ha

S2) Evaluation of the vertical excited state energies for $CPDTBT_{1\text{-}4}$ with: ZINDO/S calculations on AM1 optimized geometries and TD-CAMB3LYP calculations on CAM-B3LYP optimized geometries.



S3) Calculated TD-CAM-B3LYP/6-31G** Franck-Condon (FC) factors for S0→S1 transition for $CPDTBT_1$.

Freq (cm-1)	FC
26.6	0.0000
41.1	0.0000
74.8	0.0965
85.0	0.0000
105.3	0.0000
127.8	0.0000
158.3	0.4548
160.2	0.0000
198.4	0.0000
207.2	0.2858
224.6	0.0000
246.8	0.0000
257.4	0.2959
260.6	0.0000
284.0	0.0410
305.2	0.2729
319.5	0.0963
389.3	0.0000
396.7	0.0000
419.4	0.0000
443.4	0.0059
450.8	0.0235
481.6	0.1905
492.6	0.0000
501.6	0.0000
530.3	0.0013
548.2	0.0000
578.9	0.1096
607.0	0.0149
624.7	0.0000
638.5	0.0407
678.6	0.0333
694.1	0.0305
696.1	0.0000
702.5	0.1282
711.3	0.0000
724.6	0.0000
765.0	0.0000
770.8	0.0000
796.2	0.1414
808.2	0.0208
818.7	0.0001
840.4	0.0304
882.3	0.0000
883.3	0.0008
909.6	0.0000
912.3	0.0017
922.7	0.0000
954.6	0.0015
965.5	0.0000

970.8	0.0000
1007.0	0.0001
1011.9	0.0022
1045.8	0.0000
1106.6	0.0024
1122.6	0.0004
1134.5	0.0004
1168.3	0.0000
1194.8	0.0000
1201.8	0.0187
1209.6	0.0128
1226.5	0.0001
1275.3	0.0092
1296.6	0.0008
1354.4	0.0620
1384.8	0.0504
1396.3	0.0280
1410.5	0.0489
1423.3	0.0000
1430.2	0.0136
1443.4	0.0001
1450.4	0.0140
1472.2	0.0733
1487.2	0.0302
1503.0	0.0299
1503.1	0.0002
1506.3	0.0000
1521.9	0.0002
1524.6	0.0019
1536.5	0.1015
1551.6	0.0126
1567.0	0.0577
1592.1	0.2575
1626.1	0.0467
3072.5	0.0000
3075.4	0.0000
3149.4	0.0000
3153.4	0.0000
3162.9	0.0000
3164.1	0.0000
3210.4	0.0000
3227.1	0.0000
3243.3	0.0000
3251.0	0.0000
3272.2	0.0000
3287.8	0.0000

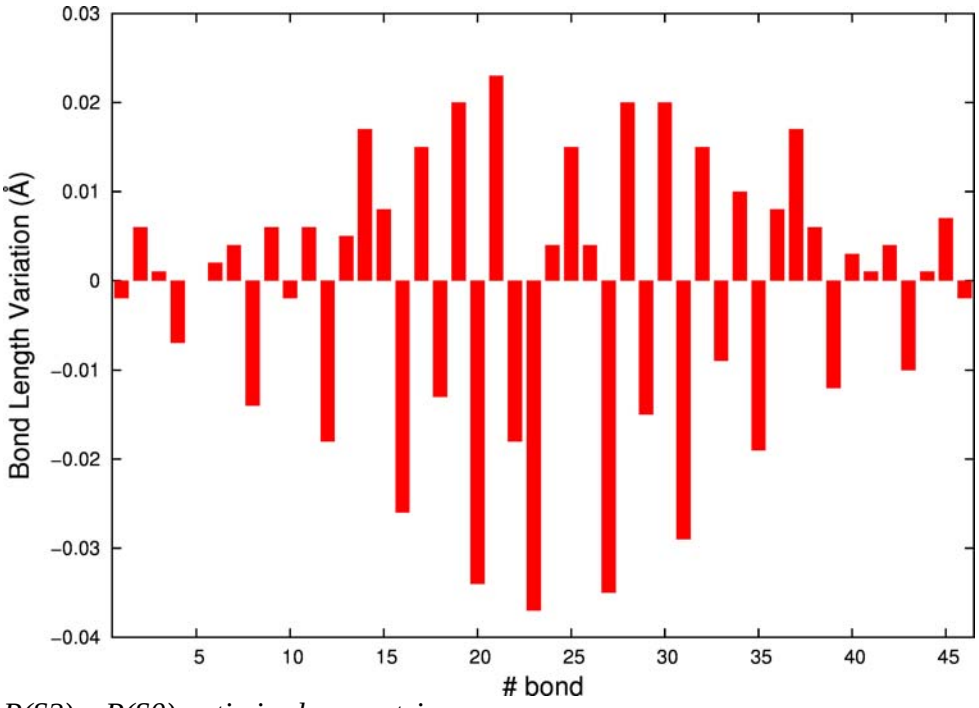
S4) Calculated TD-CAM-B3LYP/6-31G** Franck-Condon (FC) factors for S0→S2 transition for $CPDTBT_1$.

Freq (cm-1)	FC
17.2	0.0000
34.2	0.0000
73.2	0.0000
75.5	0.0335
108.1	0.0000
124.5	0.0000
143.6	0.0000
157.3	0.2922
183.2	0.0000
205.8	0.1181
216.5	0.0000
234.3	0.0000
256.9	0.0687
271.0	0.0000
276.8	0.1701
299.2	0.2493
317.5	0.3180
365.8	0.0000
379.2	0.0000
438.0	0.0510
438.1	0.0000
448.7	0.0171
471.8	0.0000
490.7	0.0000
497.2	0.0092
531.8	0.2130
539.9	0.0000
570.7	0.1016
608.2	0.0125
620.1	0.0495
624.4	0.0000
661.7	0.0000
676.6	0.0786
683.7	0.0000
690.9	0.1016
700.2	0.0275
724.2	0.0000
727.5	0.0000
785.2	0.0059
806.7	0.0000
823.8	0.0192
842.8	0.0005
867.4	0.0217
895.7	0.0543
911.6	0.0000
917.6	0.0168
932.2	0.0000
945.1	0.0016
946.7	0.0000
957.8	0.0000

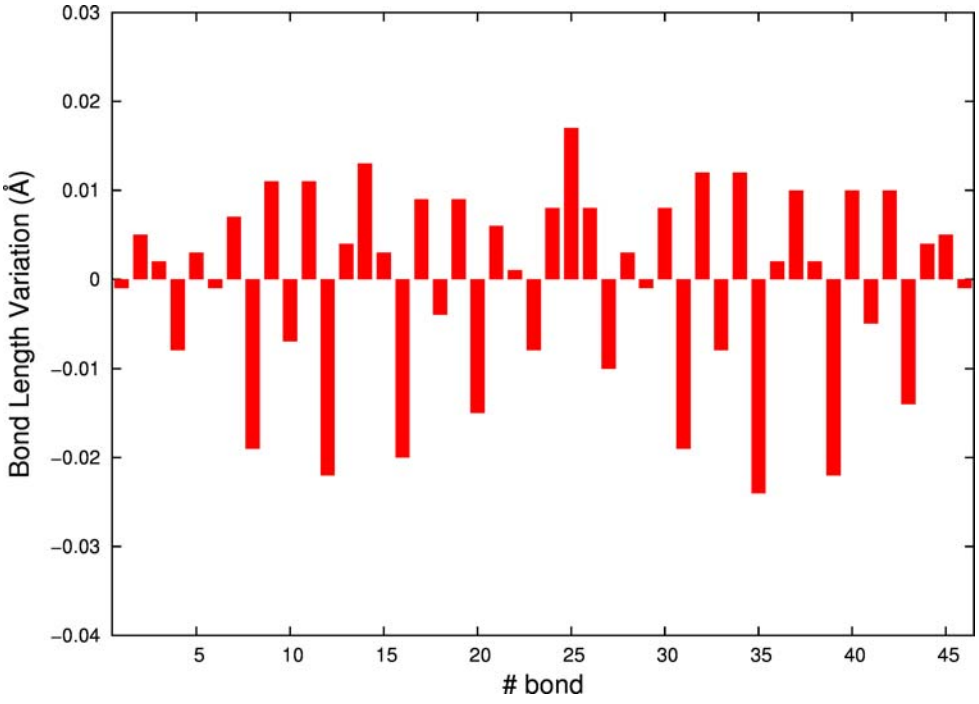
988.5	0.0083
991.8	0.0000
1001.8	0.0175
1034.9	0.0000
1097.7	0.0001
1112.8	0.0000
1134.6	0.0090
1167.4	0.0001
1185.0	0.0800
1185.1	0.0005
1207.0	0.0315
1239.5	0.0064
1273.3	0.0001
1284.5	0.0124
1326.4	0.0098
1341.2	0.0026
1369.2	0.1315
1390.0	0.0000
1407.9	0.0688
1417.5	0.0000
1438.0	0.0065
1442.9	0.0079
1465.5	0.1037
1481.8	0.0105
1501.6	0.0000
1502.9	0.0000
1509.7	0.0041
1516.0	0.0200
1517.7	0.0064
1530.3	0.0094
1553.4	0.0001
1581.8	0.0389
1608.3	0.3855
1659.4	0.0059
3064.2	0.0000
3068.1	0.0000
3139.1	0.0000
3143.8	0.0000
3160.7	0.0000
3162.3	0.0000
3215.1	0.0000
3231.9	0.0000
3245.1	0.0000
3250.3	0.0000
3271.1	0.0000
3286.0	0.0000

S5) Bond length differences as evaluated at the (TD)-CAMB3LYP/6-31G** level for optimized structures in S0, S1 and S2 states. Oligomer $CPDTBT_4$.

R(S1) – R(S0) optimized geometries



R(S2) – R(S0) optimized geometries



S6) Evaluation of the non radiative adiabatic S2→S1 excited state transition rate, following the energy gap-law equation.

Non radiative decay rate [G. Lanzani, et. al., *Phys. Rev. Lett.*, *2001*, **87**, 187402]:

$k_{nr} = A^{ij} \exp(-\Delta E^{ij}/B^{ij})$

where:
A is the pre-exponential factor related to the electronic coupling between states *i* and *j*;
ΔE^{ij} is the adiabatic energy (zero point energy) difference between states *i* and *j*;
B^{ij} is related to the relaxation energy for the *i*→*j* transition.

For $CPDTBT_4$ we have:

$\Delta E\ (S_1\text{-}S_0) = 1.67$ eV
$\Delta E\ (S_2\text{-}S_1) = 0.35$ eV
B, expressed in terms of effective frequency:
$\omega_M\ (S_1\text{-}S_0)$ as evaluated by FC factors calculated for $S_1 \rightarrow S_0$ transition (see **S3**) = $1618 cm^{-1}$
$\omega_M\ (S_2\text{-}S_1)$ as evaluated by FC factors calculated for $S_2 \rightarrow S_1$ transition (see list below reported) = $1410 cm^{-1}$

The ratio between $S_1 \rightarrow S_0$ and $S_2 \rightarrow S_1$ for non radiative rate transitions is expressed as:

$k_{nr}\ (S_1 \rightarrow S_0) / k_{nr}\ (S_2 \rightarrow S_1) = A^{1\text{-}0} \exp(-\Delta E^{1\text{-}0}/B^{1\text{-}0}) / A^{2\text{-}1} \exp(\Delta E^{2\text{-}1}/B^{2\text{-}1})$

by considering, in a first approximation, $A^{1\text{-}0} = A^{2\text{-}1}$, we have:

$k_{nr}\ (S_1 \rightarrow S_0) / k_{nr}\ (S_2 \rightarrow S_1) = 0.00179$

By knowing (see manuscript): $k_{nr}(S_1 \rightarrow S_0) = 5.95 \times 10^9\ s^{-1}$
(determined by knowing the quantum yield and the radiative decay rate $k_{nr}(S_1 \rightarrow S_0)$)

we have:

$k_{nr}\ (S_2 \rightarrow S_1) = 3.36 \times 10^{12}\ s^{-1}$

hence

$\tau_{nr}(S_2 \rightarrow S_1) = 300$fs

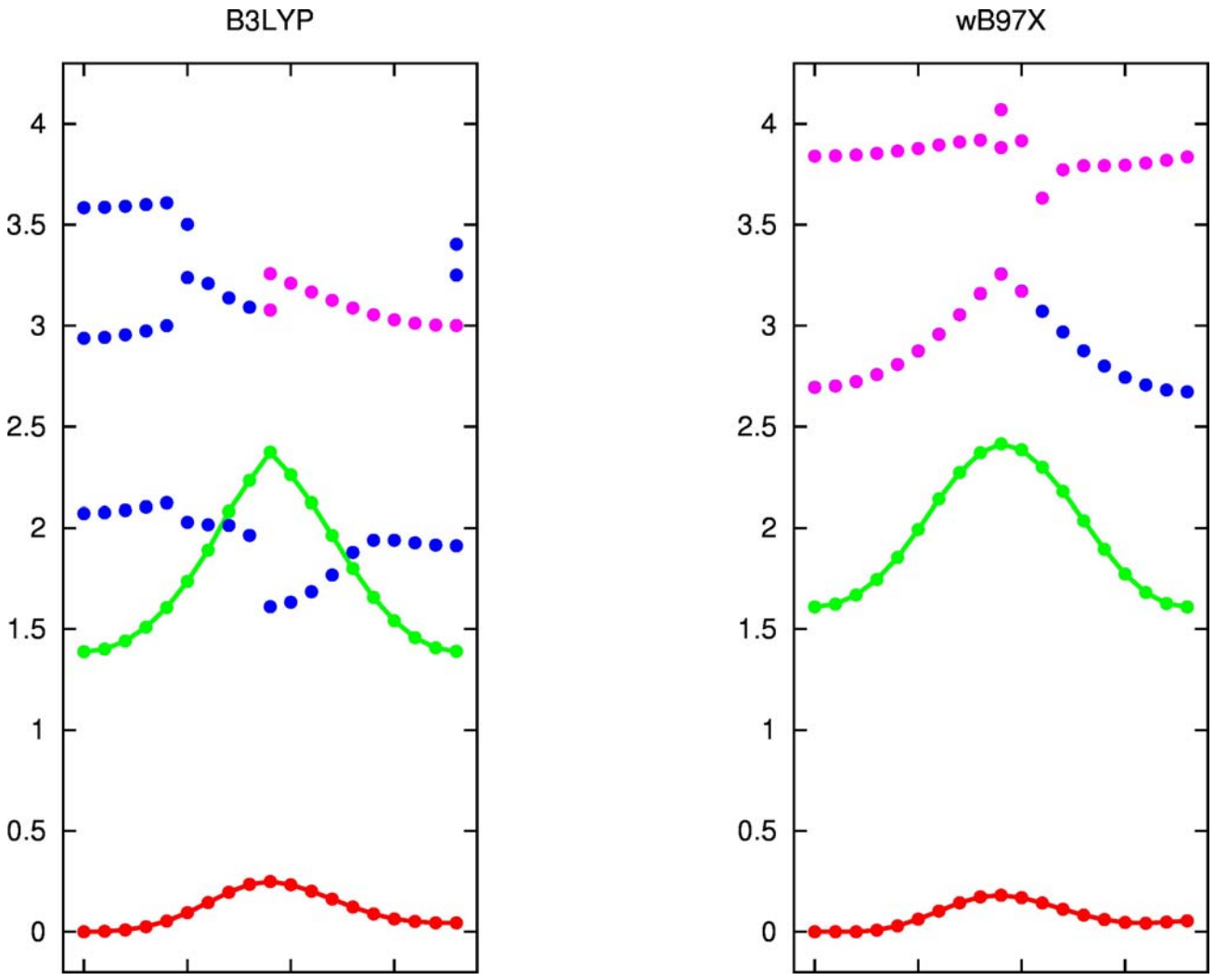
FC factors evaluated for the $S_2 \rightarrow S_1$ transition ($CPDTBT_1$)

Freq (cm^{-1})	FC
-2.8	0.0000
-1.8	0.0000
0.6	0.0000
1.2	0.0000
3.8	0.0000

5.3	0.0000
26.6	0.0000
41.1	0.0000
74.8	0.0168
85.0	0.0000
105.3	0.0000
127.8	0.0000
158.3	0.0173
160.2	0.0000
198.4	0.0000
207.2	0.0314
224.6	0.0000
246.8	0.0000
257.4	0.1048
260.6	0.0000
284.0	0.0312
305.2	0.0012
319.5	0.0499
389.3	0.0000
396.7	0.0000
419.4	0.0000
443.4	0.0037
450.8	0.0010
481.6	0.2498
492.6	0.0000
501.6	0.0000
530.3	0.1824
548.2	0.0000
578.9	0.0143
607.0	0.0222
624.7	0.0000
638.5	0.0025
678.6	0.0016
694.1	0.0026
696.1	0.0000
702.5	0.0020
711.3	0.0000
724.6	0.0000
765.0	0.0000
770.8	0.0000
796.2	0.0104
808.2	0.0137
818.7	0.0019
840.4	0.0065
882.3	0.0000
883.3	0.0051
909.6	0.0000
912.3	0.0003
922.7	0.0000
954.6	0.0002
965.5	0.0000
970.8	0.0000
1007.0	0.0007
1011.9	0.0093
1045.8	0.0000
1106.6	0.0033
1122.6	0.0000
1134.5	0.0026
1168.3	0.0002
1194.8	0.0000
1201.8	0.0078
1209.6	0.0002
1226.5	0.0436
1275.3	0.0017
1296.6	0.0027
1354.4	0.0665
1384.8	0.0086
1396.3	0.0094
1410.5	0.1633

1423.3	0.0000
1430.2	0.0466
1443.4	0.0029
1450.4	0.0117
1472.2	0.0073
1487.2	0.0136
1503.0	0.0051
1503.1	0.0000
1506.3	0.0000
1521.9	0.0050
1524.6	0.0037
1536.5	0.0009
1551.6	0.0039
1567.0	0.0030
1592.1	0.0085
1626.1	0.0000
3072.5	0.0000
3075.4	0.0001
3149.4	0.0000
3153.4	0.0000
3162.9	0.0000
3164.1	0.0000
3210.4	0.0000
3227.1	0.0000
3243.3	0.0000
3251.0	0.0000
3272.2	0.0000
3287.8	0.0000

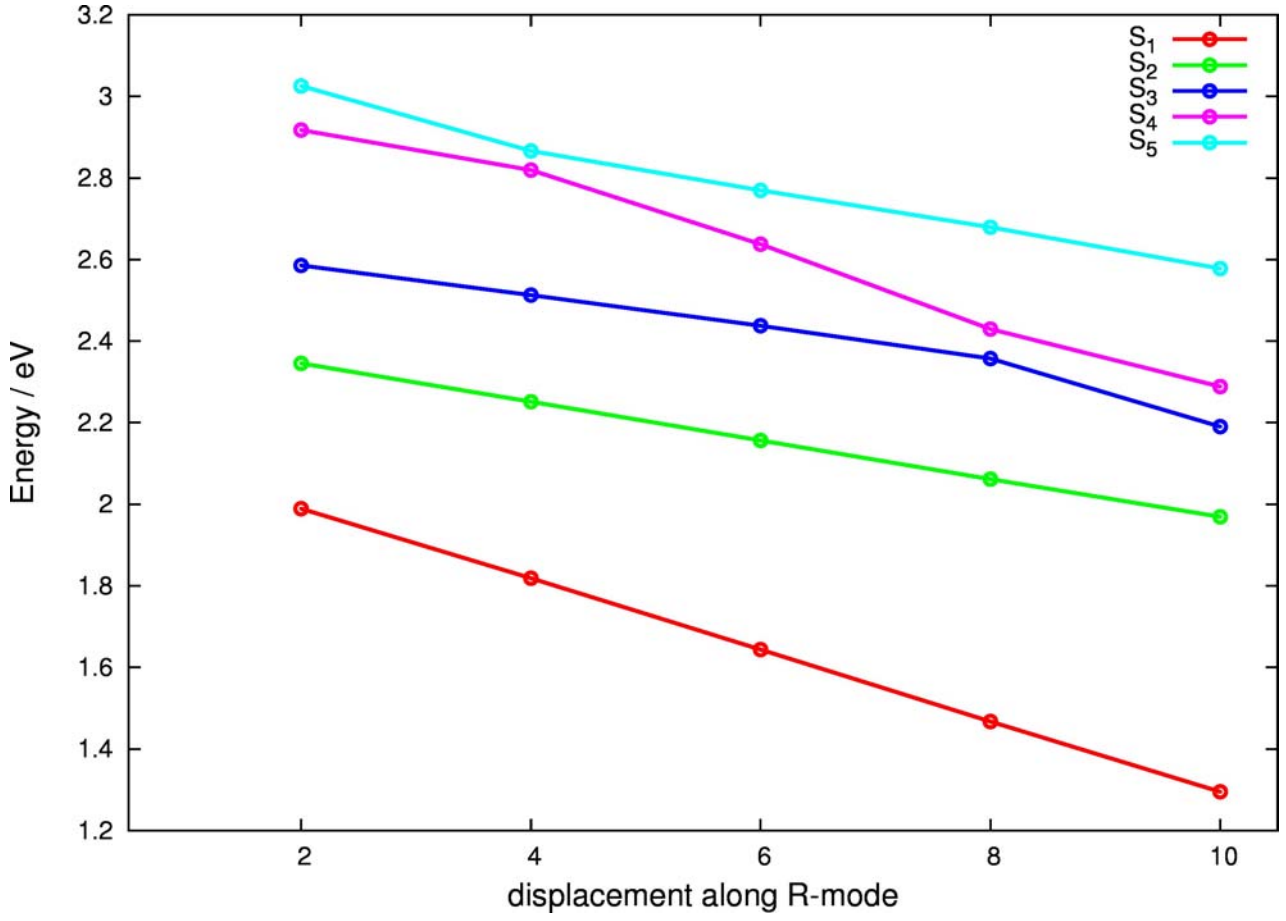
S7) TDDFT relaxed potential energy profiles as evaluated at the TDB3LYP and TDwB97X/6-31G** level for S0 (red circles), S1 (blue), S2 (purple) and T1 (green).



S8) Excited state energies for $CPDTBT_4$ as evaluated with TDCAM-B3LYP, TDwB97XD, TDB3LYP/6-31G**

	TDCAMB3LYP	TDwB97XD	TDB3LYP
S0→S1	2.06 (f = 3.78)	2.36 (f = 3.70)	1.31 (f = 3.31)
S0→S2	2.36 (f = 0.23)	2.62 (f = 0.21)	1.57 (f = 0.05)
S0→S3	2.60 (f = 0.12)	2.83 (f = 0.13)	1.71 (f = 0.14)
S0→S4	2.93 (f = 0.19)	3.17 (f = 0.20)	1.73 (f = 0.004)
S0→S8	3.61 (f = 0.56)	3.82 (f = 0.92)	

S9) TDDFT (CAM-B3LYP/6-31G**)excited state energy variations as evaluated by displacing the nuclear geometry of $CPDTB_4$ along the most Raman active mode (ECC-mode)



S10) PCM (SCRF) TDDFT (CAM-B3LYP/6-31G) excited state energies for PCPDTBT$_{1,4}$ oligomers (optimized geometries PCM-CAM-B3LYP/6-31G**, cholorobenzene as solvent).**

n	S0-S1 (*vacuum*)	S0-S1 (*chlorobenzene*)
1	3.01 (f=0.49)	2.93 (f=0.62)
4	2.15 (f=3.70)	2.01 (f=3.93)