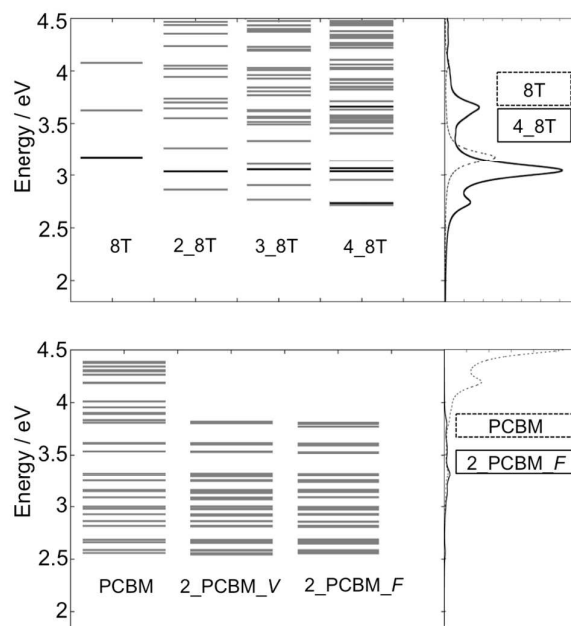


SUPPORTING INFORMATION

Vertical excitation energies computed at the TD-ωB97X-D/6-31G* level for homogeneous clusters.	P2
Excited-state classification for each cluster investigated in the manuscript.	P3
Excited-state classification for <i>large</i> clusters containing two PCBM molecules.	P9
S₁ optimized structure and state characterization for 1 8T/1 PCBM:<i>t</i>.	P15
Comparison between vertical excitations of 4 8T/1 PCBM clusters computed with different approaches (gas-phase, C PCM, and tuned ω value).	P16

Figure SI1

Vertical excitation energies computed at the TD- ω B97X-D/6-31G* level for different homogeneous clusters. Donors: 8T (oligothiophene octamer chain), 2_8T, 3_8T and 4_8T, featuring 2, 3 and 4 π - π stacked oligothiophenes. Acceptors: PCBM (single molecule) and two PCBM in face-to-face (2_PCBM:f) or vertical (2_PCBM:v) configuration. Absorption spectra were calculated as a convolution of Lorentzian functions of the computed TD-DFT vertical energies and oscillator strengths. Marked in black are the strongest dipole allowed singlet excited states.



Excited-state classification for each cluster investigated and reported in Figure 1, 2 and 3 of the manuscript.

TD- ω B97X-D/6-31G* results obtained at optimized ground-state structures. *D* stands for *Donor* (i.e. oligothiophene domain), *A* for *Acceptor* (i.e. PCBM), *CT* for *Charge Transfer* and *deloc* for *delocalized*.

The thresholds necessary to classify the excited states as Rydberg, CT, localized or diffused (details regarding the state-classification can be found in Theor. Chem. Acc. (2012) 131:1237) are set to 1.0 for the Rydberg state and 0.6 for the CT.

1_8T/1_PCBM_t

State	E (eV)	Osc - <i>f</i>	Classification
1	2.5611	0.0017	loc (A)
2	2.5890	0.0001	loc (A)
3	2.6642	0.0000	loc (A)
4	2.6835	0.0000	loc (A)
5	2.8218	0.0002	loc (A)
6	2.8594	0.0005	loc (A)
7	2.9284	0.0000	loc (A)
8	2.9632	0.0004	loc (A)
9	2.9795	0.0022	loc (A)
10	3.0692	0.0035	loc (A)
11	3.1317	1.0570	loc (D)
12	3.1526	0.2394	loc (A)
13	3.1634	0.0769	loc (A)
14	3.2126	0.2722	loc (A)
15	3.2547	0.0269	CTD->A
16	3.2862	0.1149	loc (A)
17	3.3122	0.0110	loc (A)
18	3.3580	0.2753	CTD->A
19	3.4646	0.0839	CTD->A
20	3.5291	0.0012	loc (A)
21	3.6041	0.0008	loc (A)
22	3.6134	0.0014	loc (A)
23	3.6256	0.0771	loc (D)
24	3.8038	0.0091	loc (A)
25	3.8209	0.0107	loc (A)
26	3.8337	0.0002	loc (A)
27	3.8774	0.0030	loc (A)
28	3.8997	0.0000	loc (A)
29	3.9475	0.0486	loc (A)
30	3.9815	0.0201	CTD->A
31	4.0107	0.0372	loc (A)
32	4.0335	0.2648	loc (D)
33	4.0732	0.0124	CTD->A
34	4.1634	0.0278	loc (A)
35	4.1801	0.0676	loc (A)
36	4.1912	0.0487	CTD->A

37	4.2531	0.0011	loc (A)
38	4.2875	0.0094	loc (A)
39	4.2962	0.0102	loc (A)
40	4.3313	0.0007	loc (A)

1_8T/1_PCBM_e

State	E (eV)	Osc - f	Classification
1	2.5678	0.0018	loc (A)
2	2.5901	0.0002	loc (A)
3	2.6498	0.0000	loc (A)
4	2.6750	0.0000	loc (A)
5	2.8041	0.0002	loc (A)
6	2.8515	0.0002	loc (A)
7	2.9244	0.0000	loc (A)
8	2.9695	0.0011	loc (A)
9	3.0000	0.0007	loc (A)
10	3.0844	0.0011	loc (A)
11	3.1393	0.0047	loc (A)
12	3.1495	0.0010	loc (A)
13	3.1856	0.0079	CTD->A
14	3.2497	0.9210	loc (D)
15	3.2691	0.9679	deloc
16	3.2793	0.0866	loc (A)
17	3.3163	0.0094	loc (A)
18	3.3739	0.2492	CTD->A
19	3.4707	0.0807	CTD->A
20	3.5340	0.0005	loc (A)
21	3.5931	0.1239	loc (D)
22	3.6076	0.0177	loc (A)
23	3.6246	0.0007	loc (A)
24	3.7946	0.0018	loc (A)
25	3.8187	0.0001	loc (A)
26	3.8265	0.0065	loc (A)
27	3.8826	0.0031	loc (A)
28	3.8842	0.0002	loc (A)
29	3.9310	0.0116	CTD->A
30	3.9481	0.0146	loc (A)
31	3.9767	0.0006	CTD->A
32	3.9925	0.0001	loc (A)
33	4.0600	0.0573	loc (D)
34	4.0871	0.0007	CTD->A
35	4.1782	0.0286	loc (A)
36	4.1845	0.1126	loc (A)
37	4.2638	0.0025	loc (A)
38	4.2798	0.0035	loc (A)
39	4.3086	0.0114	loc (A)
40	4.3429	0.0022	loc (A)

2_8T/1_PCBM_t

State	E(eV)	Osc - f	Classification
1	2.5592	0.0015	loc (A)
2	2.5857	0.0001	loc (A)
3	2.6640	0.0000	loc (A)
4	2.6800	0.0000	loc (A)
5	2.8173	0.0001	loc (A)
6	2.8264	0.0164	loc (D)
7	2.8544	0.0004	loc (A)
8	2.9334	0.0009	loc (A)
9	2.9410	0.0001	loc (A)
10	2.9646	0.0572	loc (A)
11	3.0064	4.6722	loc (D)
12	3.0736	0.0636	CTD->A
13	3.0893	0.0005	loc (A)
14	3.1398	0.0206	loc (A)
15	3.1662	0.0010	loc (A)
16	3.1857	0.0144	loc (A)
17	3.2053	0.0515	CTD->A
18	3.2112	0.0347	loc (A)
19	3.2596	0.0353	deloc
20	3.2787	0.0413	loc (A)
21	3.3218	0.0153	loc (A)
22	3.5125	0.0133	loc (D)
23	3.5289	0.0034	loc (A)
24	3.5797	0.0058	loc (D)
25	3.6009	0.0003	loc (A)
26	3.6140	0.0022	loc (A)
27	3.6251	0.0282	loc (D)
28	3.7003	0.0159	loc (D)
29	3.7443	0.0001	CTD->A
30	3.7594	0.0007	CTD->A
31	3.8045	0.0050	loc (A)
32	3.8207	0.0108	loc (A)
33	3.8318	0.0006	loc (A)
34	3.8788	0.0024	loc (A)
35	3.8923	0.0003	loc (A)
36	3.9030	0.0731	loc (D)
37	3.9332	0.0930	CTD->A
38	3.9418	0.0080	loc (A)
39	3.9658	0.0023	CTD->A
40	3.9714	0.0092	CTD->A

2_8T/1_PCBM_e

State	E(eV)	Osc - f	Classification
1	2.5533	0.0023	loc(A)
2	2.5770	0.0001	loc(A)
3	2.6527	0.0001	loc(A)
4	2.6818	0.0000	loc(A)
5	2.8019	0.0004	loc(A)
6	2.8486	0.0019	loc(A)
7	2.8835	0.0436	loc(D)
8	2.9062	0.2199	loc(D)
9	2.9180	0.0021	loc(A)
10	2.9476	0.0020	CTD->A
11	2.9782	0.0010	loc(A)
12	2.9979	0.0115	loc(A)
13	3.0474	3.9094	loc(D)
14	3.0820	0.0130	loc(A)
15	3.1057	0.1932	CTD->A
16	3.1247	0.0882	loc(A)
17	3.1473	0.0000	loc(A)
18	3.1754	0.0145	CTD->A
19	3.1914	0.2405	CTD->A
20	3.2591	0.0137	loc(A)
21	3.2824	0.0032	loc(A)
22	3.2964	0.1079	loc(D)
23	3.3250	0.0375	loc(A)
24	3.4284	0.0001	CTD->A
25	3.5247	0.0069	loc(A)
26	3.5370	0.0308	loc(D)
27	3.5957	0.0006	loc(A)
28	3.6036	0.0021	loc(A)
29	3.6841	0.0004	CTD->A
30	3.7185	0.0298	loc(D)
31	3.7427	0.0002	CTD->A
32	3.7636	0.0740	loc(D)
33	3.7848	0.1403	loc(D)
34	3.7999	0.0021	loc(A)
35	3.8263	0.0139	loc(A)
36	3.8300	0.0009	loc(A)
37	3.8727	0.0002	CTD->A
38	3.8814	0.0035	loc(A)
39	3.9032	0.0003	loc(A)
40	3.9401	0.0471	CTD->A

4_8T/1_PCBM_t

State	E(eV)	Osc - f	Classification
1	2.5627	0.0017	loc(A)
2	2.5947	0.0000	loc(A)
3	2.6548	0.0002	loc(A)
4	2.6798	0.0000	loc(A)
5	2.7091	0.1508	loc(D)
6	2.7388	0.5093	loc(D)
7	2.8254	0.0006	loc(A)
8	2.8576	0.0032	loc(A)
9	2.8869	1.3805	loc(D)
10	2.9233	0.0226	loc(A)
11	2.9435	0.0110	loc(A)
12	2.9748	0.0003	loc(A)
13	3.0254	4.2581	loc(D)
14	3.0397	0.1327	loc(A)
15	3.0586	0.6701	loc(D)
16	3.0694	0.3433	CTD->A
17	3.1134	0.0403	loc(A)
18	3.1442	0.0201	loc(D)
19	3.1562	0.0009	loc(A)
20	3.1666	0.0095	loc(A)
21	3.2006	0.0325	loc(A)
22	3.2543	0.0053	loc(A)
23	3.3055	0.0059	loc(A)
24	3.3378	0.0140	loc(A)
25	3.3785	0.1467	loc(D)
26	3.4092	0.0109	loc(D)
27	3.4565	0.0131	loc(D)
28	3.4607	0.0065	loc(D)
29	3.5033	0.0607	loc(D)
30	3.5054	0.0016	CTD->A
31	3.5302	0.0015	loc(A)
32	3.5424	0.0176	CTD->A
33	3.5529	0.0750	CTD->A
34	3.5679	0.0197	loc(D)
35	3.5774	0.4160	loc(D)
36	3.5965	0.5218	loc(D)
37	3.6081	0.0116	loc(A)
38	3.6176	0.0040	loc(A)
39	3.6681	0.9418	loc(D)
40	3.7150	0.0066	loc(D)

4_8T/1_PCBM_e

State	E(eV)	Osc - f	Classification
1	2.5106	0.0103	CTD->A
2	2.5460	0.0032	loc(A)
3	2.5727	0.0006	loc(A)
4	2.5806	0.0068	CTD->A
5	2.6567	0.0004	loc(A)
6	2.6788	0.0048	loc(A)
7	2.6932	0.0086	CTD->A
8	2.7018	0.0696	CTD->A
9	2.7317	0.0029	CTD->A
10	2.7443	0.0408	loc(D)
11	2.7659	0.2845	loc(D)
12	2.7914	0.3110	CTD->A
13	2.8101	0.0117	loc(A)
14	2.8224	0.0706	CTD->A
15	2.8544	0.0096	loc(A)
16	2.9122	0.0002	loc(A)
17	2.9291	0.0247	CTD->A
18	2.9544	0.0304	loc(A)
19	2.9659	0.1571	loc(D)
20	2.9826	0.0011	loc(A)
21	3.0366	0.1833	CTD->A
22	3.0549	0.2110	loc(A)
23	3.0612	5.7212	loc(D)
24	3.0806	0.3646	loc(D)
25	3.0987	0.0490	CTD->A
26	3.1049	0.0446	loc(A)
27	3.1311	0.0032	loc(A)
28	3.1473	0.0132	loc(A)
29	3.1531	0.2350	loc(D)
30	3.2330	0.0149	loc(A)
31	3.2357	0.0140	CTD->A
32	3.2820	0.0249	loc(A)
33	3.2926	0.0180	loc(A)
34	3.3010	0.0017	CTD->A
35	3.3538	0.0032	CTD->A
36	3.4137	0.0828	loc(D)
37	3.4528	0.0125	CTD->A
38	3.4582	0.0359	CTD->A
39	3.4727	0.0126	loc(D)
40	3.4978	0.0029	CTD->A

Excited-state classification for *large* clusters containing 2 PCBM molecules, as reported in [Figure 1](#) of the manuscript.

1_8T/2_PCBM:tf

State	E(eV)	Osc - f	Classification
1	2.5406	0.0019	loc (A)
2	2.5519	0.0020	loc (A)
3	2.5619	0.0000	loc (A)
4	2.5895	0.0001	loc (A)
5	2.6401	0.0003	loc (A)
6	2.6704	0.0000	loc (A)
7	2.6757	0.0001	loc (A)
8	2.6842	0.0001	loc (A)
9	2.8044	0.0021	loc (A)
10	2.8266	0.0002	loc (A)
11	2.8516	0.0007	loc (A)
12	2.8566	0.0005	loc (A)
13	2.9173	0.0012	loc (A)
14	2.9212	0.0001	loc (A)
15	2.9490	0.0150	loc (A)
16	2.9562	0.0108	loc (A)
17	2.9849	0.0014	loc (A)
18	2.9896	0.0038	loc (A)
19	3.0512	0.7193	deloc
20	3.0630	0.0332	loc (A)
21	3.0691	0.5524	loc (A)
22	3.1252	0.0364	loc (A)
23	3.1288	0.0020	loc (A)
24	3.1456	0.1245	loc (A)
25	3.1504	0.0096	loc (A)
26	3.1646	0.0043	loc (A)
27	3.2021	0.1980	CTD->A
28	3.2214	0.0478	CTD->A
29	3.2339	0.0124	loc (A)
30	3.2487	0.0098	loc (A)
31	3.2679	0.0228	loc (A)
32	3.3053	0.0075	loc (A)
33	3.3078	0.0051	loc (A)
34	3.3155	0.0070	loc (A)
35	3.3371	0.0027	loc (A)
36	3.4710	0.0252	CTD->A
37	3.5070	0.0148	CTD->A
38	3.5133	0.0097	loc (A)
39	3.5195	0.0042	CTD->A
40	3.5400	0.0401	loc (D)

1_8T/2_PCBM:tv

State	E(eV)	Osc - f	Classification
1	2.5532	0.0019	loc (A)
2	2.5559	0.0016	loc (A)
3	2.5798	0.0000	loc (A)
4	2.5865	0.0000	loc (A)
5	2.6537	0.0000	loc (A)
6	2.6608	0.0000	loc (A)
7	2.6623	0.0000	loc (A)
8	2.6802	0.0000	loc (A)
9	2.8136	0.0002	loc (A)
10	2.8160	0.0001	loc (A)
11	2.8556	0.0003	loc (A)
12	2.8577	0.0004	loc (A)
13	2.9156	0.0001	loc (A)
14	2.9300	0.0000	loc (A)
15	2.9376	0.0002	loc (A)
16	2.9646	0.0007	loc (A)
17	2.9787	0.0005	loc (A)
18	2.9867	0.0003	loc (A)
19	3.0578	0.0001	loc (A)
20	3.0903	0.0021	loc (A)
21	3.1377	0.0576	loc (A)
22	3.1444	0.0066	loc (A)
23	3.1482	0.0022	loc (A)
24	3.1649	0.0001	loc (A)
25	3.1669	0.1615	deloc
26	3.1769	0.0083	CTD->A
27	3.2118	0.1560	loc (A)
28	3.2256	0.0001	loc (A)
29	3.2416	0.3406	loc (D)
30	3.2661	0.0061	loc (A)
31	3.3010	0.0049	loc (A)
32	3.3035	0.0059	loc (A)
33	3.3149	0.0048	loc (A)
34	3.3183	0.0196	loc (A)
35	3.5096	0.0013	loc (A)
36	3.5212	0.0021	loc (A)
37	3.5832	0.0002	loc (A)
38	3.5873	0.0005	loc (A)
39	3.5970	0.0389	loc (A)
40	3.6040	0.0007	loc (A)

2_8T/2_PCBM:tf

State	E(eV)	Osc - f	Classification
1	2.5407	0.0024	loc (A)
2	2.5473	0.0007	loc (A)
3	2.5769	0.0000	loc (A)
4	2.5822	0.0001	loc (A)
5	2.6406	0.0002	loc (A)
6	2.6513	0.0002	loc (A)
7	2.6580	0.0001	loc (A)
8	2.6723	0.0001	loc (A)
9	2.8079	0.0031	loc (A)
10	2.8136	0.0003	loc (A)
11	2.8512	0.3016	loc (D)
12	2.8519	0.0032	loc (A)
13	2.8583	0.0350	loc (A)
14	2.9062	0.0016	loc (A)
15	2.9185	0.0000	loc (A)
16	2.9223	0.0002	loc (A)
17	2.9532	0.0277	loc (A)
18	2.9581	0.0033	loc (A)
19	2.9743	0.0018	loc (A)
20	3.0189	1.2638	loc (D)
21	3.0442	1.2142	deloc
22	3.0545	0.3621	loc (A)
23	3.0703	0.5837	deloc
24	3.0807	0.1115	loc (A)
25	3.1383	0.0253	loc (A)
26	3.1424	0.0032	loc (A)
27	3.1518	0.0034	loc (A)
28	3.1566	0.0023	loc (A)
29	3.1849	0.0814	loc (A)
30	3.1914	0.0094	loc (A)
31	3.2078	0.0012	loc (A)
32	3.2358	0.0226	loc (A)
33	3.2540	0.0002	CTD->A
34	3.2598	0.1422	loc (D)
35	3.2851	0.0054	loc (A)
36	3.2885	0.0455	loc (A)
37	3.3239	0.0006	loc (A)
38	3.3286	0.0018	loc (A)
39	3.4078	0.0540	loc (A)
40	3.5011	0.0459	loc (D)

2_8T/2_PCBM:tv

State	E(eV)	Osc - f	Classification
1	2.5484	0.0017	loc (A)
2	2.5537	0.0016	loc (A)
3	2.5794	0.0000	loc (A)
4	2.5830	0.0001	loc (A)
5	2.6574	0.0000	loc (A)
6	2.6632	0.0000	loc (A)
7	2.6761	0.0000	loc (A)
8	2.6795	0.0000	loc (A)
9	2.8142	0.0002	loc (A)
10	2.8157	0.0097	loc (D)
11	2.8173	0.0002	loc (A)
12	2.8561	0.0002	loc (A)
13	2.8611	0.0004	loc (A)
14	2.9277	0.0000	loc (A)
15	2.9290	0.0007	loc (A)
16	2.9518	0.0411	loc (A)
17	2.9587	0.0036	loc (A)
18	2.9723	0.0002	loc (A)
19	2.9922	0.0352	loc (A)
20	2.9941	4.6982	loc (D)
21	3.0751	0.0049	loc (A)
22	3.0835	0.0033	CTD->A
23	3.0934	0.0023	loc (A)
24	3.1455	0.0008	loc (A)
25	3.1475	0.0039	loc (A)
26	3.1628	0.0000	loc (A)
27	3.1669	0.0029	loc (A)
28	3.1823	0.0389	deloc
29	3.1987	0.0019	loc (A)
30	3.2074	0.0355	CTD->A
31	3.2357	0.0003	loc (A)
32	3.2407	0.0345	loc (D)
33	3.2764	0.0088	loc (A)
34	3.3055	0.0029	loc (A)
35	3.3166	0.0190	loc (A)
36	3.3200	0.0081	loc (A)
37	3.4780	0.0378	loc (D)
38	3.5187	0.0018	loc (A)
39	3.5274	0.0014	loc (A)
40	3.5566	0.0054	loc (D)

4_8T/2_PCBM_tf

State	E(eV)	Osc - f	Classification
1	2.5514	0.0019	loc (A)
2	2.5581	0.0012	loc (A)
3	2.5893	0.0001	loc (A)
4	2.5917	0.0001	loc (A)
5	2.6463	0.0001	loc (A)
6	2.6495	0.0001	loc (A)
7	2.6642	0.0001	loc (A)
8	2.6768	0.0000	loc (A)
9	2.6964	0.1298	loc (D)
10	2.7284	0.0552	loc (D)
11	2.8166	0.9218	loc (A)
12	2.8189	0.3671	loc (A)
13	2.8238	0.7753	loc (A)
14	2.8490	0.0762	loc (A)
15	2.8543	0.0029	loc (A)
16	2.9135	0.0074	loc (A)
17	2.9193	0.0048	loc (A)
18	2.9211	0.0025	loc (A)
19	2.9522	0.0029	loc (A)
20	2.9556	0.0021	loc (A)
21	2.9592	0.0015	loc (A)
22	2.9737	0.0007	CTD->A
23	2.9839	0.0174	CTD->A
24	3.0226	3.9408	loc (D)
25	3.0474	0.0050	loc (A)
26	3.0576	0.4740	loc (D)
27	3.0657	0.0032	loc (A)
28	3.0863	0.1701	CTD->A
29	3.1155	0.0954	CTD->A
30	3.1357	0.0035	loc (A)
31	3.1465	0.0072	loc (A)

4_8T/2_PCBM_tv

State	E(eV)	Osc - f	Classification
1	2.5487	0.0017	loc (A)
2	2.5544	0.0015	loc (A)
3	2.5792	0.0000	loc (A)
4	2.5845	0.0000	loc (A)
5	2.6563	0.0000	loc (A)
6	2.6621	0.0000	loc (A)
7	2.6758	0.0000	loc (A)
8	2.6788	0.0000	loc (A)
9	2.7222	0.1028	loc (D)
10	2.7478	0.5777	loc (D)
11	2.8135	0.0002	loc (A)
12	2.8197	0.0002	loc (A)
13	2.8557	0.0026	loc (A)
14	2.8611	0.0004	loc (A)
15	2.9138	0.8958	loc (D)
16	2.9293	0.0002	loc (A)
17	2.9294	0.0014	loc (A)
18	2.9422	0.0146	loc (A)
19	2.9554	0.0009	loc (A)
20	2.9718	0.0002	loc (A)
21	2.9920	0.0006	loc (A)
22	3.0357	5.1918	loc (D)
23	3.0511	0.2400	CTD->A
24	3.0642	0.6392	loc (D)
25	3.0801	0.0019	loc (A)
26	3.0963	0.0023	loc (A)
27	3.1337	0.0161	loc (D)
28	3.1400	0.0439	CTD->A
29	3.1475	0.0004	loc (A)
30	3.1561	0.0072	loc (A)

S₁ OPTIMIZED STRUCTURE AND STATE CHARACTERIZATION FOR 1_8T/1_PCBM:t.

TD- ω B97XD/6-31G* optimized molecular structure of the first excited state (S₁) for the 1_8T/1_PCBM:t dimer case.

The computed relaxation energy (E_{rel}), from the FC region (vertical excitation) to the S₁ minimum, is E_{rel} = 0.27 eV.

The S₁ state is localized on the acceptor (PCBM) both in the FC region and in the relaxed S₁ minimum.

In **Figure SI2** we report the electron-hole density map in the relaxed S₁ state.

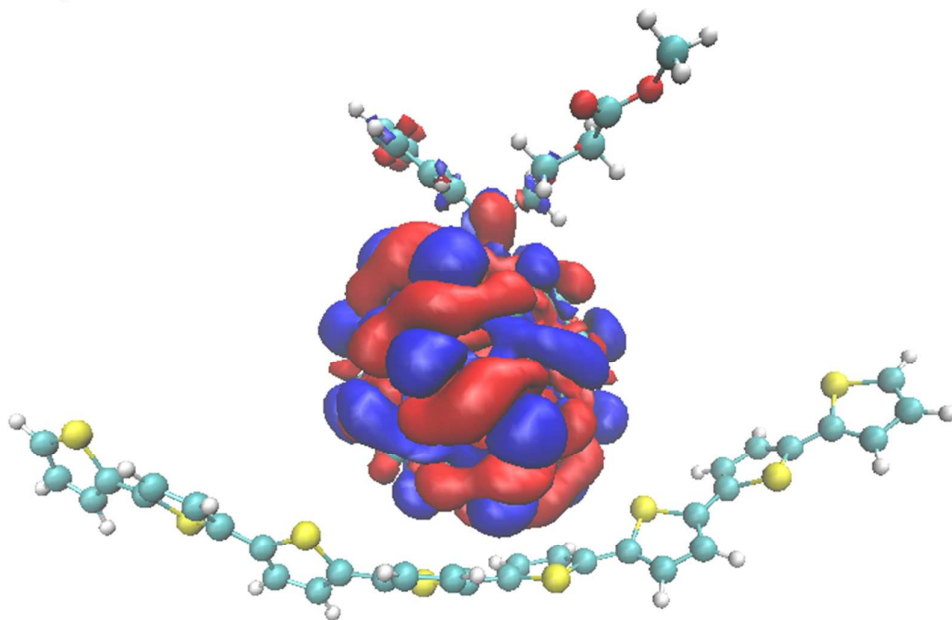


Figure SI2: Electron-hole density map computed at the TD- ω B97XD/6-31G* level for the relaxed S₁ state of 1_8T/1_PCBM:t (in the equilibrium geometry).

Comparison between the vertical excitations of 4_8T/1_PCBM clusters computed with different approaches (gas-phase, C-PCM and tuned ω value).

Vertical excitations were computed at the TD- ω B97X-D/6-31G* level on the optimized ground state (gas-phase) geometries of 4_8T/1_PCBM:t and 4_8T/1_PCBM:e.

Three cases were considered for each cluster:

- 1) gas phase (as all the results reported in the main text);
- 2) conductor polarizable continuum model CPCM, dielectric constant $\epsilon = 3.0$;
- 3) tuned range-separated parameter ω : the default value as implemented in Gaussian09 is $\omega = 0.20 \text{ bohr}^{-1}$, while our tuned optimized ω value is 0.17 bohr^{-1} , in agreement with Ref. 18.

In the following we report the results for the computed vertical excitations for each case. Highlighted are the relevant low-lying active excited states localized on the donor cluster (called *loc(D)*, here the 4_P3HT cluster) and the first charge-transfer states (*CT*).

As mentioned in the main text, we find energy shifts between the different sets of results, and hence also changes in the energy differences $\Delta E = E(CT) - E(\text{active})$. However, these changes do not alter the proposed photovoltaic mechanisms and our qualitative interpretations and conclusions.

Case 1): gas phase (already reported above)

$$\Delta E = E(CT) - E(\text{active}) = 3.07 \text{ eV} - 3.02 \text{ eV} = +0.05 \text{ eV}$$

4_8T/1_PCBM_t

State	E (eV)	Osc - f	Classification
1	2.5627	0.0017	loc (A)
2	2.5947	0.0000	loc (A)
3	2.6548	0.0002	loc (A)
4	2.6798	0.0000	loc (A)
5	2.7091	0.1508	loc (D)
6	2.7388	0.5093	loc (D)
7	2.8254	0.0006	loc (A)
8	2.8576	0.0032	loc (A)
9	2.8869	1.3805	loc (D)
10	2.9233	0.0226	loc (A)
11	2.9435	0.0110	loc (A)
12	2.9748	0.0003	loc (A)
13	3.0254	4.2581	loc (D)
14	3.0397	0.1327	loc (A)
15	3.0586	0.6701	loc (D)
16	3.0694	0.3433	CTD->A
17	3.1134	0.0403	loc (A)
18	3.1442	0.0201	loc (D)

19	3.1562	0.0009	loc (A)
20	3.1666	0.0095	loc (A)
21	3.2006	0.0325	loc (A)
22	3.2543	0.0053	loc (A)
23	3.3055	0.0059	loc (A)
24	3.3378	0.0140	loc (A)
25	3.3785	0.1467	loc (D)
26	3.4092	0.0109	loc (D)
27	3.4565	0.0131	loc (D)
28	3.4607	0.0065	loc (D)
29	3.5033	0.0607	loc (D)
30	3.5054	0.0016	CTD->A
31	3.5302	0.0015	loc (A)
32	3.5424	0.0176	CTD->A
33	3.5529	0.0750	CTD->A
34	3.5679	0.0197	loc (D)
35	3.5774	0.4160	loc (D)
36	3.5965	0.5218	loc (D)
37	3.6081	0.0116	loc (A)
38	3.6176	0.0040	loc (A)
39	3.6681	0.9418	loc (D)
40	3.7150	0.0066	loc (D)

Case 2): CPCM, $\epsilon = 3.0$

$$\Delta E = E(CT) - E(\text{active}) = 3.03 \text{ eV} - 2.94 \text{ eV} = +0.09 \text{ eV}$$

4_8T/1_PCBM_t

State	E (eV)	Osc - f	Classification
1	2.5535	0.0035	loc (A)
2	2.5917	0.0001	loc (A)
3	2.6536	0.0003	loc (A)
4	2.6760	0.0000	loc (A)
5	2.6811	1.5816	loc (D)
6	2.7044	0.5749	loc (D)
7	2.8195	2.7505	loc (D)
8	2.8277	0.0110	loc (A)
9	2.8560	0.0048	loc (A)
10	2.9142	0.0084	loc (A)
11	2.9301	0.0127	loc (A)
12	2.9440	4.1682	loc (D)
13	2.9707	0.0015	loc (A)
14	3.0199	0.0312	loc (D)
15	3.0317	0.1081	CTD->A
16	3.0402	0.0713	loc (A)
17	3.0904	0.0061	loc (A)
18	3.0982	0.0221	loc (D)
19	3.1391	0.0072	loc (A)
20	3.1516	0.0071	CTD->A
21	3.1780	0.0232	loc (D)

22	3.2327	0.0043	loc (A)
23	3.2871	0.0760	loc (A)
24	3.2966	0.0174	loc (A)
25	3.3230	0.0487	loc (A)
26	3.3671	0.0028	loc (A)
27	3.3823	0.1634	loc (D)
28	3.4042	0.0001	loc (A)
29	3.4205	0.0317	loc (A)
30	3.4343	0.0021	loc (A)

Case 3): $\omega = 0.17 \text{ bohr}^{-1}$

$$\Delta E = E(CT) - E(\text{active}) = 2.98 \text{ eV} - 2.93 \text{ eV} = +0.05 \text{ eV}$$

4_8T/1_PCBM_t

State	E (eV)	Osc - f	Classification
1	2.4630	0.0015	loc (A)
2	2.5083	0.0000	loc (A)
3	2.5609	0.0002	loc (A)
4	2.5843	0.0000	loc (A)
5	2.6271	0.2137	loc (D)
6	2.6516	0.4358	loc (D)
7	2.7147	0.0054	loc (A)
8	2.7394	0.0094	loc (A)
9	2.7701	0.0661	loc (A)
10	2.7923	1.0223	loc (D)
11	2.8149	0.1579	loc (A)
12	2.8583	0.0428	loc (A)
13	2.8631	0.0006	loc (A)
14	2.8990	0.0112	loc (A)
15	2.9356	3.7701	loc (D)
16	2.9664	0.0074	loc (A)
17	2.9755	0.6231	loc (D)
18	2.9855	0.3785	CTD->A
19	3.0251	0.0084	loc (A)
20	3.0414	0.0108	loc (D)
21	3.0500	0.0067	loc (A)
22	3.0987	0.0031	loc (A)
23	3.1745	0.0088	loc (A)
24	3.1926	0.0830	CTD->A
25	3.1982	0.0091	CTD->A
26	3.2307	0.1201	loc (D)
27	3.2435	0.0066	loc (A)
28	3.2830	0.0001	loc (A)
29	3.2889	0.2289	loc (A)
30	3.3420	0.0070	loc (A)

Case 1): gas phase (already reported above)

$$\Delta E = E(CT) - E(\text{active}) = 2.51 \text{ eV} - 3.06 \text{ eV} = -0.55 \text{ eV}$$

4_8T/1_PCBM_e

State	E (eV)	Osc - f	Classification
1	2.5106	0.0103	CTD->A
2	2.5460	0.0032	loc (A)
3	2.5727	0.0006	loc (A)
4	2.5806	0.0068	CTD->A
5	2.6567	0.0004	loc (A)
6	2.6788	0.0048	loc (A)
7	2.6932	0.0086	CTD->A
8	2.7018	0.0696	CTD->A
9	2.7317	0.0029	CTD->A
10	2.7443	0.0408	loc (D)
11	2.7659	0.2845	loc (D)
12	2.7914	0.3110	CTD->A
13	2.8101	0.0117	loc (A)
14	2.8224	0.0706	CTD->A
15	2.8544	0.0096	loc (A)
16	2.9122	0.0002	loc (A)
17	2.9291	0.0247	CTD->A
18	2.9544	0.0304	loc (A)
19	2.9659	0.1571	loc (D)
20	2.9826	0.0011	loc (A)
21	3.0366	0.1833	CTD->A
22	3.0549	0.2110	loc (A)
23	3.0612	5.7212	loc (D)
24	3.0806	0.3646	loc (D)
25	3.0987	0.0490	CTD->A
26	3.1049	0.0446	loc (A)
27	3.1311	0.0032	loc (A)
28	3.1473	0.0132	loc (A)
29	3.1531	0.2350	loc (D)
30	3.2330	0.0149	loc (A)
31	3.2357	0.0140	CTD->A
32	3.2820	0.0249	loc (A)
33	3.2926	0.0180	loc (A)
34	3.3010	0.0017	CTD->A
35	3.3538	0.0032	CTD->A
36	3.4137	0.0828	loc (D)
37	3.4528	0.0125	CTD->A
38	3.4582	0.0359	CTD->A
39	3.4727	0.0126	loc (D)
40	3.4978	0.0029	CTD->A

Case 2): CPCM, $\epsilon = 3.0$

4_8T/1_PCBM_e

State	E (eV)	Osc -f	Classification
1	2.5445	0.0051	CTD->A
2	2.5720	0.0003	loc(B)
3	2.6564	0.1424	loc(B)
4	2.6600	0.1119	CTD->A
5	2.6782	0.0553	loc(B)
6	2.7187	0.2651	loc(A)
7	2.7238	1.1652	loc(A)
8	2.7511	0.3320	CTD->A
9	2.8030	0.0046	loc(B)
10	2.8458	0.0187	loc(B)

Case 3): $\omega = 0.17$ bohr⁻¹

$$\Delta E = E(CT) - E(\text{active}) = 2.26 \text{ eV} - 2.97 \text{ eV} = -0.71 \text{ eV}$$

4_8T/1_PCBM_e

State	E (eV)	Osc -f	Classification
1	2.2603	0.0041	CTD->A
2	2.3272	0.0039	loc(A)
3	2.4217	0.0030	CTD->A
4	2.4454	0.0099	CTD->A
5	2.4556	0.0058	CTD->A
6	2.4777	0.0000	CTD->A
7	2.4901	0.0004	CTD->A
8	2.5316	0.0012	loc(A)
9	2.5617	0.0030	loc(A)
10	2.5781	0.0001	loc(D)
11	2.5856	0.0000	loc(D)
12	2.6443	0.0066	loc(A)
13	2.6785	0.5251	loc(D)
14	2.6938	0.1832	CTD->A
15	2.7008	0.0131	loc(A)
16	2.7429	0.0008	loc(A)
17	2.7688	0.0011	CTD->A
18	2.7983	0.0006	loc(A)
19	2.8292	0.0014	loc(A)
20	2.8426	0.0006	loc(A)
21	2.8518	0.0435	loc(A)
22	2.8821	0.1059	loc(D)
23	2.8872	0.0036	CTD->A
24	2.9465	0.0237	CTD->A
25	2.9583	1.4807	loc(D)
26	2.9792	4.1596	loc(D)
27	2.9877	0.2248	loc(D)

28	2.9962	0.0560	CTD->A
29	3.0076	0.0245	CTD->A
30	3.0341	0.0360	loc(A)