Supporting Information

Multiscale computational analysis of molecular stacking and charge transfer mechanisms on the performance of PM6: BTP-x OSCs

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Computational methods and Marcus theory

The charge transfer process of D-A molecules can be approximated as the following two processes, the donor molecules change from neutral to cationic by electron transfer after excitation; The acceptor molecule changes from neutral to anion through hole transfer after excitation. The charge transfer rates constant k_{CT} for the CT states can be estimated according to the semiclassical Marcus theory as follows.

$$k_{CT} = \frac{2\pi}{\hbar}|V_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda T k_B}} \exp\left[-\frac{(\Delta G + \lambda)^2}{4T\lambda k_B}\right] \quad (1)$$

In Eq. 1, $\hbar$ is the approximate Planck constant; k_B is the Boltzmann constant; T is the temperature, set to 298.15 K; V_{DA} denotes the generalized Mulliken-Hush (GMH)[1] method to calculate the electronic coupling; λ is the reorganization energy (including the internal recombination λ_i energy and the external reorganization energy λ_s). For the D/A dimer, internal reorganization energy can be calculated using Eq. 2.[2]

$$\lambda_i = \frac{\lambda_{i1} + \lambda_{i2}}{2} \quad (2)$$

For hole transfer:

$$\lambda_{i1} = [E^0 D^+ + E^* A^-] - [E^0 D^0 + E^* A^-] \quad (3)$$

$$\lambda_{i2} = [E^+ D^0 + E^- A^*] - [E^+ D^+ + E^- A^-] \quad (4)$$

For electron transfer:

$$\lambda_{i1} = [E^* D^+ + E^* A^-] - [E^0 D^0 + E^* A^*] \quad (5)$$

$$\lambda_{i2} = \left[E^+ D^* + E^- A^0\right] - \left[E^+ D^+ + E^- A^-\right] \quad (6)$$

where $E^*/E^0/E^+/E^-$ refer to the energy of excited/basic/cationic/anionic states, respectively; $D^*/D^0/D^+$ denotes the equilibrium geometry of the donor molecule in excited/basic/cationic states; $A^*/A^0/A^-$ denotes the equilibrium geometry of the acceptor molecule in excited/basic/anionic states.

In Eq. 1, ΔG is the difference of the Gibbs free energy during the exciton separation process. The ΔG can be calculated using the Rehm-Weller equation[3,4] as follows.

$$\Delta G_{CS} = -\Delta G_{CR} - \Delta E_{S_1} - \Delta E_b \quad (7)$$

In Eq. 7, ΔE_{S1} is the first excitation energy of the donor and ΔE_b is the exciton binding energy.

In Eq. 1 V_{DA} is the electron coupling integral, which can be calculated by the Generalized Mulliken–Hush (GMH)[5] method as follows.

$$V_{DA} = \frac{\Delta E \mu_{ij}}{\sqrt{\Delta \mu_{ij}^{\ 2} + 4\mu_{ij}^{\ 2}}} \quad (8)$$

In Eq.8, ΔE is the excitation energy difference between the initial and final states; μ is the leap dipole moment between the initial and final states; $\Delta \mu_{ij}$ is the dipole moment difference between the initial and final states.

$$E_b = E_g^{fund} - E_g^{opt} \quad (9)$$

$$E_g^{fund} = IP - EA \quad (10)$$

In Eq.9, ΔE_b is defined as the energy difference between the fundamental band gap and the optical band gap, and E_{opt} refers to the energy level difference from S_0 to S_1. E_{fund} in Eq.10 refers to the difference between ionization energy and affinity energy, the units of both E_{fund} and E_{opt} are chosen as eV.

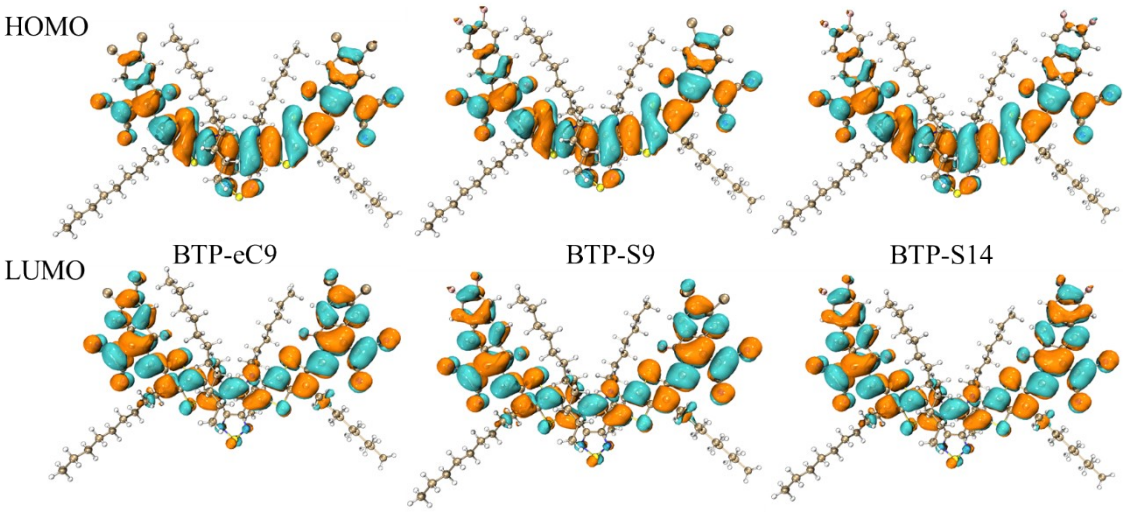

Figure S1 The electron density distribution of HOMO and LUMO orbitals of BTP-eC9 , BTP-S9 and BTP-S14 molecules (iso-value=0.005 a.u.)

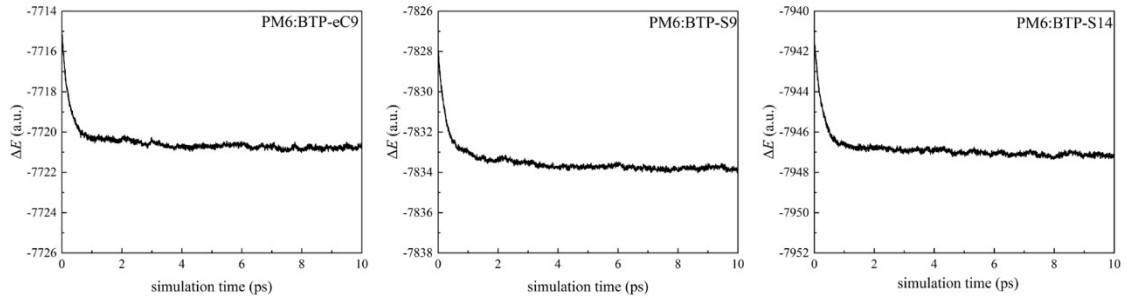

Figure S2 The plots between the potential energy and simulation time in PM6: BTP-x systems during annealing process

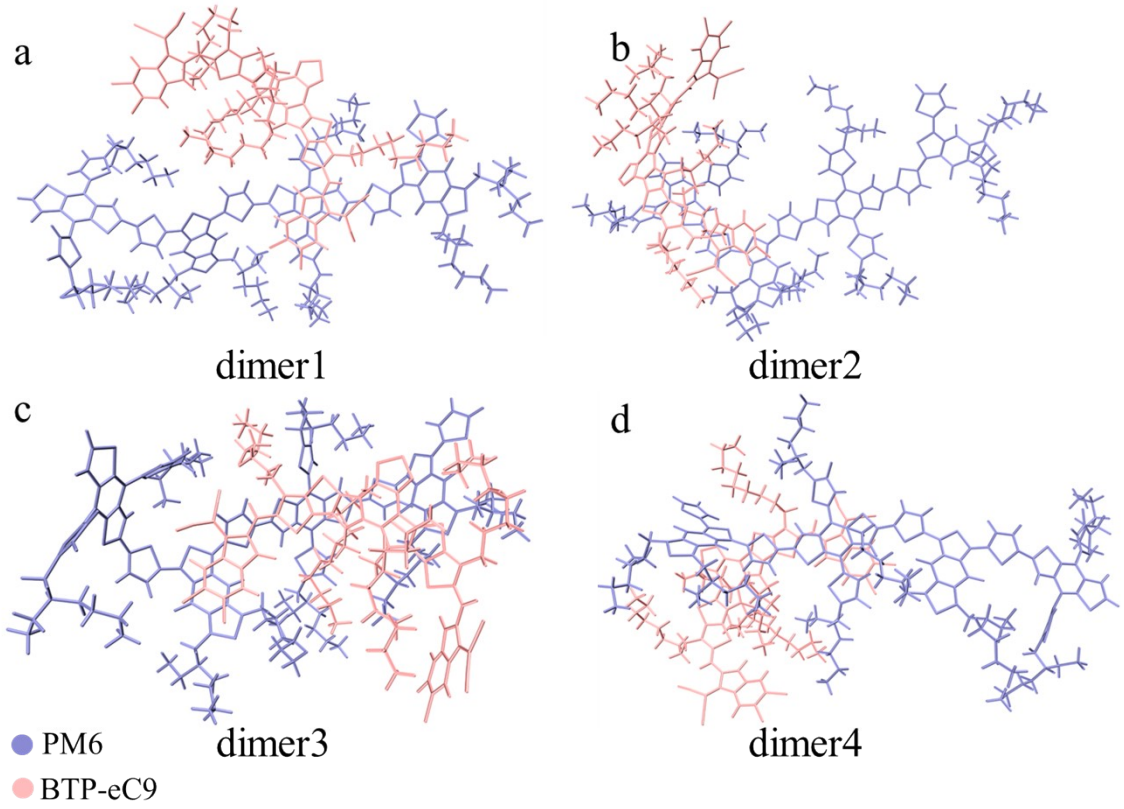

Figure S3 Top view of PM6: BTP-eC9 dimers

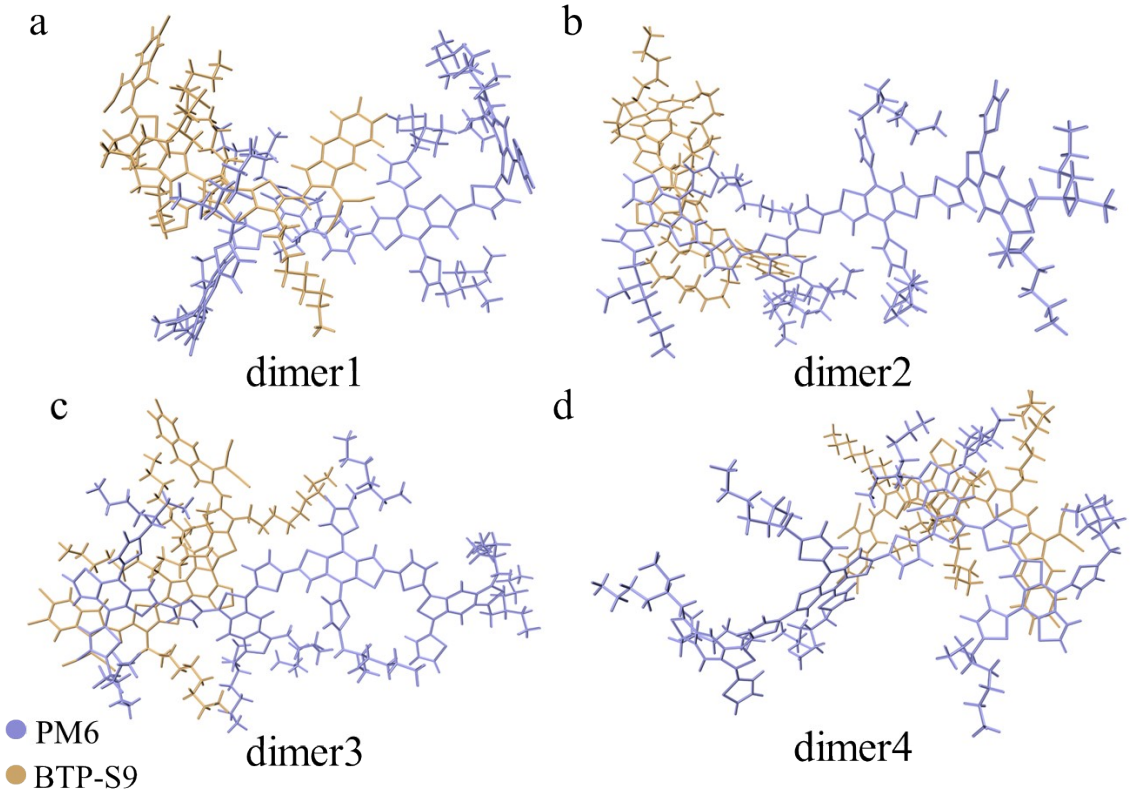

Figure S4 Top view of PM6: BTP-S9 dimers

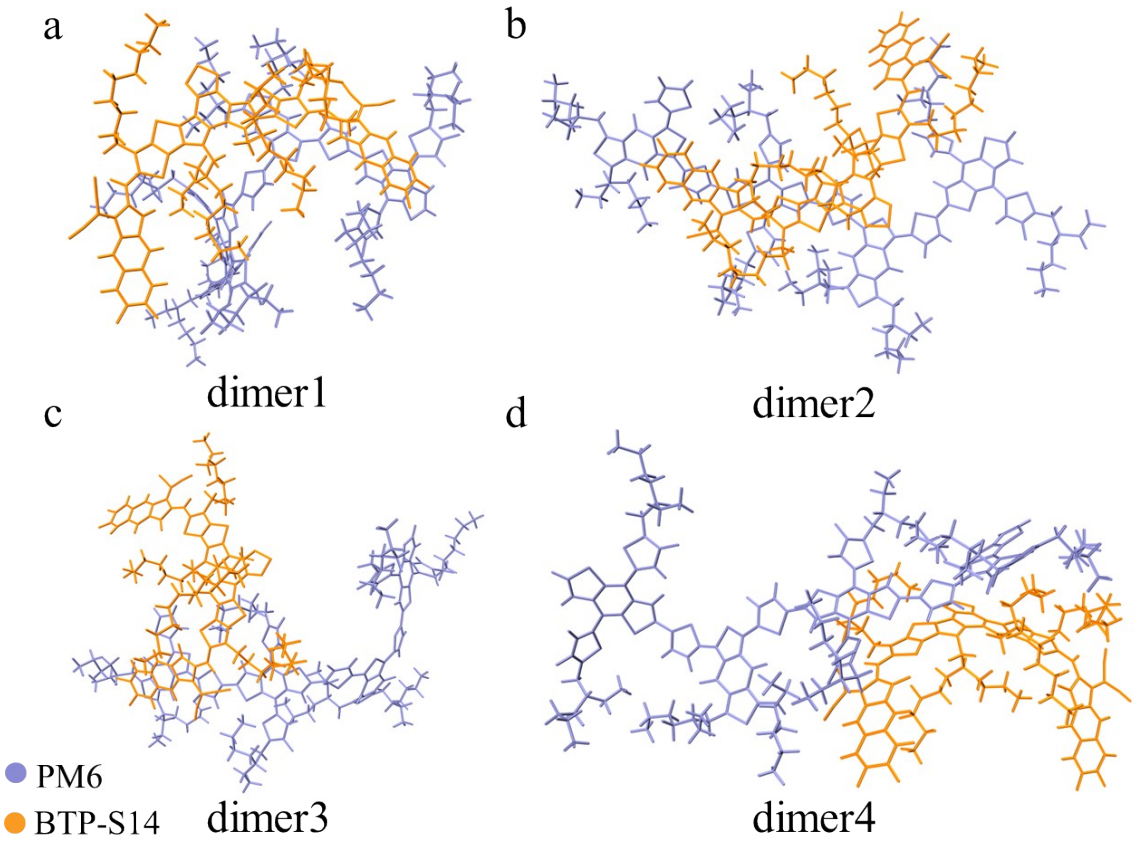

Figure S5 Top view of PM6: BTP-S14 dimers

Table S1 The open circuit voltage (V_{OC}), short circuit (J_{SC}) and fill factor (FF) of PM6: BTP-x OSCs

Blend films	V_{OC}[V]	J_{SC}[Ma cm^{-2}]	FF[%]	PCE[%]
PM6: BTP-eC9	0.845	27.57	77.95	18.0
PM6: BTP-S9	0.853	26.72	77.05	17.5
PM6: BTP-S14	0.855	25.07	76.69	16.4

Table S2 The excited states information of BTP-eC9 molecule in chloroform solvent calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.6763	739.62	2.2207	S_{16}	3.1090	398.79	0.0000
S_2	2.0005	619.78	0.1572	S_{17}	3.1679	391.38	0.0018
S_3	2.2600	548.60	0.1108	S_{18}	3.2281	384.08	0.0002
S_4	2.3468	528.31	0.0130	S_{19}	3.2327	383.53	0.0842
S_5	2.3540	526.71	0.0005	S_{20}	3.2384	382.85	0.2221
S_6	2.4735	501.25	0.6651	S_{21}	3.2666	379.55	0.0062
S_7	2.5265	490.73	0.0956	S_{22}	3.3048	375.16	0.0028
S_8	2.6338	470.74	0.0767	S_{23}	3.3128	374.26	0.0102
S_9	2.6834	462.04	0.0027	S_{24}	3.3223	373.19	0.0008
S_{10}	2.7260	454.82	0.0353	S_{25}	3.3417	371.02	0.0009
S_{11}	2.8570	433.96	0.0042	S_{26}	3.3604	368.96	0.0753
S_{12}	2.9565	419.36	0.0467	S_{27}	3.4003	364.63	0.0275
S_{13}	3.0342	408.62	0.0505	S_{28}	3.4723	357.06	0.0960
S_{14}	3.0388	408.00	0.0122	S_{29}	3.4883	355.43	0.0708
S_{15}	3.0760	403.07	0.0378	S_{30}	3.5368	350.55	0.0249

Table S3 The excited states information of BTP-S9 molecule in chloroform solvent calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.6663	744.08	2.2445	S_{16}	3.0699	403.87	0.0012
S_2	2.0076	617.59	0.2176	S_{17}	3.0738	403.35	0.0414
S_3	2.2857	542.44	0.0705	S_{18}	3.1052	399.29	0.0256
S_4	2.3560	526.25	0.0011	S_{19}	3.1764	390.33	0.0111
S_5	2.4310	510.01	0.4746	S_{20}	3.2375	382.97	0.0156
S_6	2.5227	491.48	0.1453	S_{21}	3.2460	381.96	0.1781
S_7	2.5369	488.73	0.0863	S_{22}	3.2663	379.58	0.0200
S_8	2.6292	471.56	0.0924	S_{23}	3.2842	377.52	0.0708
S_9	2.6768	463.19	0.0023	S_{24}	3.3160	373.90	0.1077
S_{10}	2.7142	456.80	0.0933	S_{25}	3.3179	373.68	0.0275
S_{11}	2.7230	455.33	0.0668	S_{26}	3.3354	371.73	0.0127
S_{12}	2.8642	432.87	0.0088	S_{27}	3.3789	366.94	0.0329
S_{13}	2.9659	418.03	0.0578	S_{28}	3.4049	364.13	0.0221

S_{14}	3.0120	411.64	0.0393	S_{29}	3.4254	361.96	0.0145
S_{15}	3.0575	405.51	0.0060	S_{30}	3.4444	359.96	0.0668

Table S4 The excited states information of BTP-S14 molecule in chloroform solvent calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.6580	747.79	2.2752	S_{16}	3.0707	403.77	0.0237
S_2	2.0211	613.45	0.2641	S_{17}	3.0738	403.36	0.0001
S_3	2.3615	525.03	0.0036	S_{18}	3.0748	403.23	0.0000
S_4	2.4109	514.27	0.4434	S_{19}	3.0917	401.03	0.0026
S_5	2.4684	502.29	0.0538	S_{20}	3.1417	394.65	0.0112
S_6	2.5335	489.37	0.1256	S_{21}	3.1784	390.08	0.1139
S_7	2.5355	488.99	0.0857	S_{22}	3.2169	385.41	0.1534
S_8	2.6214	472.97	0.1008	S_{23}	3.2418	382.46	0.0605
S_9	2.6696	464.43	0.0083	S_{24}	3.2758	378.48	0.0273
S_{10}	2.7127	457.05	0.0018	S_{25}	3.2791	378.11	0.0289
S_{11}	2.7250	455.00	0.0281	S_{26}	3.3254	372.84	0.0090
S_{12}	2.7365	453.07	0.2366	S_{27}	3.3471	370.42	0.2280
S_{13}	2.8693	432.11	0.0222	S_{28}	3.3979	364.88	0.0473
S_{14}	3.0286	409.38	0.0441	S_{29}	3.4038	364.25	0.0347
S_{15}	3.0372	408.21	0.0012	S_{30}	3.4270	361.79	0.0928

Table S5 The excited states information of BTP-eC9-dimer1 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.1150	1111.98	0.0027	S_{16}	2.0198	613.83	0.0409
S_2	1.3211	938.48	0.0040	S_{17}	2.0420	607.16	0.0993
S_3	1.4082	880.44	0.0003	S_{18}	2.0653	600.32	0.0422
S_4	1.4797	837.92	0.6332	S_{19}	2.0974	591.14	0.1554
S_5	1.5650	792.24	0.3037	S_{20}	2.1188	585.16	0.2189
S_6	1.6243	763.32	0.5202	S_{21}	2.1339	581.01	0.0070
S_7	1.6333	759.12	0.4633	S_{22}	2.1552	575.28	0.1530
S_8	1.6917	732.89	0.0084	S_{23}	2.1906	565.99	0.0862
S_9	1.7133	723.66	0.0190	S_{24}	2.2066	561.88	0.0279
S_{10}	1.7463	709.96	1.0785	S_{25}	2.2268	556.78	0.1200
S_{11}	1.7820	695.74	0.3570	S_{26}	2.2404	553.40	0.0213
S_{12}	1.8570	667.67	0.0032	S_{27}	2.2673	546.83	0.0161
S_{13}	1.9400	639.10	0.1996	S_{28}	2.2690	546.42	0.0509
S_{14}	1.9460	637.12	0.0018	S_{29}	2.2717	545.78	0.2631
S_{15}	2.0006	619.73	0.0026	S_{30}	2.2933	540.63	0.2878

Table S6 The excited states information of BTP-eC9-dimer2 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.1881	1043.52	0.0008	S_{16}	2.0065	617.91	0.0121
S_2	1.4183	874.18	0.0003	S_{17}	2.0279	611.41	0.0040
S_3	1.4296	867.24	0.0007	S_{18}	2.0407	607.56	0.3067
S_4	1.6176	766.47	1.0025	S_{19}	2.0947	591.90	0.5103
S_5	1.6254	762.79	0.0120	S_{20}	2.1405	579.24	0.0003
S_6	1.6600	746.90	1.0677	S_{21}	2.1551	575.32	0.0009
S_7	1.6683	743.18	0.5966	S_{22}	2.1671	572.12	0.0389
S_8	1.6792	738.34	0.2434	S_{23}	2.1751	570.02	0.1422
S_9	1.7081	725.86	0.0015	S_{24}	2.1825	568.08	0.1264
S_{10}	1.8133	683.76	0.2378	S_{25}	2.1864	567.06	0.0020
S_{11}	1.8192	681.53	0.0043	S_{26}	2.2450	552.26	0.1220
S_{12}	1.8796	659.63	0.0001	S_{27}	2.2651	547.36	0.0247
S_{13}	1.8999	652.59	0.0008	S_{28}	2.2828	543.12	0.0002
S_{14}	1.9082	649.74	0.0310	S_{29}	2.2922	540.90	0.1271
S_{15}	1.9141	647.74	0.2931	S_{30}	2.3012	538.77	0.0001

Table S7 The excited states information of BTP-eC9-dimer3 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.2280	1009.65	0.0093	S_{16}	2.0979	590.99	0.1546
S_2	1.4129	877.49	0.0136	S_{17}	2.1051	588.98	0.0272
S_3	1.4730	841.69	0.0016	S_{18}	2.1473	577.39	0.0061
S_4	1.5886	780.48	0.7937	S_{19}	2.1623	573.39	0.0386
S_5	1.6682	743.23	0.0045	S_{20}	2.1741	570.28	0.0148
S_6	1.6836	736.43	0.1377	S_{21}	2.1931	565.34	0.1055
S_7	1.7273	717.78	0.0023	S_{22}	2.2291	556.21	0.1208
S_8	1.7655	702.25	0.0420	S_{23}	2.2426	552.87	0.0047
S_9	1.8080	685.74	0.2255	S_{24}	2.2517	550.63	0.0245
S_{10}	1.8752	661.19	1.1119	S_{25}	2.2641	547.60	0.0132
S_{11}	1.8991	652.84	0.0010	S_{26}	2.2668	546.96	0.0468
S_{12}	1.9351	640.71	0.0115	S_{27}	2.2743	545.16	0.0570
S_{13}	1.9533	634.74	0.0327	S_{28}	2.3143	535.74	0.0524
S_{14}	1.9929	622.14	0.0082	S_{29}	2.3265	532.92	0.0432
S_{15}	2.0809	595.83	0.1353	S_{30}	2.3418	529.45	0.0955

Table S8 The excited states information of BTP-eC9-dimer4 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.1310	1096.22	0.0213	S_{16}	2.0695	599.11	0.0715
S_2	1.3385	926.32	0.0045	S_{17}	2.0915	592.79	0.0057
S_3	1.4754	840.34	0.0163	S_{18}	2.1051	588.97	0.0017
S_4	1.5156	818.04	0.1148	S_{19}	2.1409	579.11	0.0823
S_5	1.6091	770.52	1.1212	S_{20}	2.1540	575.61	0.1117
S_6	1.6540	749.61	0.0116	S_{21}	2.1803	568.65	0.0786

S_7	1.7023	728.34	1.4841	S_{22}	2.2045	562.42	0.1477
S_8	1.7194	721.10	0.0060	S_{23}	2.2161	559.47	0.0185
S_9	1.8025	687.85	0.0112	S_{24}	2.2258	557.03	0.0251
S_{10}	1.8660	664.45	0.0286	S_{25}	2.2362	554.44	0.0150
S_{11}	1.8780	660.19	0.2050	S_{26}	2.2691	546.40	0.0229
S_{12}	1.9020	651.85	0.0919	S_{27}	2.2921	540.92	0.1189
S_{13}	1.9154	647.29	0.0059	S_{28}	2.3101	536.71	0.0090
S_{14}	2.0247	612.36	0.1719	S_{29}	2.3262	532.98	0.2045
S_{15}	2.0324	610.05	0.0358	S_{30}	2.3736	522.35	0.0959

Table S9 The excited states information of BTP-S9-dimer1 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
	1.3439	922.54	0.0151	S_{16}	2.2663	547.07	0.0072
S_2	1.5806	784.39	0.1343	S_{17}	2.2677	546.74	0.0253
S_3	1.6007	774.58	0.0435	S_{18}	2.2747	545.06	0.0319
S_4	1.6882	734.43	1.3559	S_{19}	2.3146	535.67	0.0189
S_5	1.8056	686.65	0.1024	S_{20}	2.3235	533.60	0.0060
S_6	1.8864	657.24	0.0011	S_{21}	2.3286	532.44	0.0273
S_7	1.9145	647.60	0.0148	S_{22}	2.3476	528.13	0.0983
S_8	1.9293	642.64	0.3910	S_{23}	2.3863	519.57	0.0071
S_9	2.0338	609.63	0.1069	S_{24}	2.3942	517.85	0.0551
S_{10}	2.0606	601.70	0.0028	S_{25}	2.4165	513.07	0.1571
S_{11}	2.0758	597.29	0.0308	S_{26}	2.4354	509.09	0.2233
S_{12}	2.0885	593.66	0.2207	S_{27}	2.4565	504.72	0.1470
S_{13}	2.1689	571.66	0.1770	S_{28}	2.4731	501.33	0.0269
S_{14}	2.2074	561.66	0.0731	S_{29}	2.5030	495.34	0.0026
S_{15}	2.2196	558.59	0.6415	S_{30}	2.5155	492.88	0.0117

Table S10 The excited states information of BTP-S9-dimer2 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.3298	932.33	0.0333	S_{16}	2.1355	580.58	0.0307
S_2	1.4523	853.70	0.0231	S_{17}	2.1551	575.30	0.1446
S_3	1.5031	824.87	0.0105	S_{18}	2.1759	569.80	0.0003
S_4	1.6199	765.36	0.0043	S_{19}	2.1854	567.33	0.0002
S_5	1.6729	741.15	1.3021	S_{20}	2.1985	563.94	0.0020
S_6	1.7952	690.65	0.3439	S_{21}	2.2746	545.08	0.6376
S_7	1.8002	688.73	1.1010	S_{22}	2.2924	540.84	0.0395
S_8	1.8792	659.76	0.1557	S_{23}	2.3007	538.91	0.0797
S_9	1.9114	648.64	0.0009	S_{24}	2.3285	532.46	0.0210
S_{10}	1.9221	645.04	0.0217	S_{25}	2.3300	532.13	0.0181
S_{11}	1.9524	635.02	0.0900	S_{26}	2.3798	520.99	0.0056
S_{12}	2.0260	611.98	0.0013	S_{27}	2.3954	517.59	0.0067
S_{13}	2.0314	610.33	0.2560	S_{28}	2.3965	517.35	0.0021
S_{14}	2.0776	596.75	0.2366	S_{29}	2.3999	516.61	0.0159

S_{15}	2.0827	595.29	0.0153	S_{30}	2.4191	512.53	0.0559

Table S11 The excited states information of BTP-S9-dimer3 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.1957	1036.88	0.0855	S_{16}	2.0963	591.43	0.0187
S_2	1.2995	954.12	0.0095	S_{17}	2.1151	586.19	0.0024
S_3	1.4716	842.53	0.0785	S_{18}	2.1399	579.39	0.0033
S_4	1.4963	828.63	1.1946	S_{19}	2.1508	576.46	0.0933
S_5	1.5989	775.45	0.0169	S_{20}	2.1780	569.27	0.1454
S_6	1.6821	737.07	0.0403	S_{21}	2.1839	567.73	0.1448
S_7	1.7611	704.00	0.0063	S_{22}	2.2488	551.33	0.0017
S_8	1.7888	693.12	0.1944	S_{23}	2.2759	544.78	0.0576
S_9	1.8175	682.17	0.0004	S_{24}	2.2768	544.56	0.0113
S_{10}	1.8935	654.78	1.2944	S_{25}	2.2972	539.72	0.0191
S_{11}	1.9447	637.54	0.0034	S_{26}	2.3292	532.31	0.0267
S_{12}	1.9750	627.78	0.3374	S_{27}	2.3319	531.70	0.0340
S_{13}	1.9949	621.51	0.0511	S_{28}	2.3485	527.92	0.0770
S_{14}	2.0153	615.21	0.0740	S_{29}	2.3572	525.99	0.2456
S_{15}	2.0875	593.93	0.1109	S_{30}	2.3632	524.64	0.4102

Table S12 The excited states information of BTP-S9-dimer4 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.3282	933.51	0.0534	S_{16}	2.2135	560.14	0.0236
S_2	1.4732	841.62	0.0028	S_{17}	2.2363	554.42	0.5713
S_3	1.5844	782.55	1.7675	S_{18}	2.2634	547.77	0.0001
S_4	1.7016	728.65	0.0367	S_{19}	2.2799	543.82	0.1076
S_5	1.7191	721.23	0.0396	S_{20}	2.2846	542.69	0.0176
S_6	1.7935	691.31	0.0002	S_{21}	2.3158	535.39	0.2749
S_7	1.9438	637.83	0.0972	S_{22}	2.3432	529.13	0.1126
S_8	1.9476	636.60	0.0010	S_{23}	2.3638	524.51	0.0090
S_9	2.0217	613.26	0.2116	S_{24}	2.3868	519.46	0.6562
S_{10}	2.0429	606.91	0.0139	S_{25}	2.4197	512.38	0.0022
S_{11}	2.0602	601.81	0.0076	S_{26}	2.4258	511.12	0.0415
S_{12}	2.0864	594.24	0.0023	S_{27}	2.4360	508.97	0.0005
S_{13}	2.1458	577.81	0.0635	S_{28}	2.4760	500.74	0.0329
S_{14}	2.1611	573.70	0.0330	S_{29}	2.4765	500.64	0.0123
S_{15}	2.1755	569.92	0.1480	S_{30}	2.4854	498.86	0.0119

Table S13 The excited states information of BTP-S14-dimer1 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.1818	1049.08	0.0240	S_{16}	2.1600	573.99	0.0298
S_2	1.4055	882.12	0.0095	S_{17}	2.1717	570.92	0.2226
S_3	1.5470	801.47	1.0409	S_{18}	2.1889	566.43	0.0137

S_4	1.5742	787.62	0.4823	S_{19}	2.2541	550.04	0.2233
S_5	1.6102	770.01	0.4067	S_{20}	2.2720	545.72	0.1132
S_6	1.7622	703.59	0.9346	S_{21}	2.2777	544.33	0.1178
S_7	1.7935	691.28	0.0070	S_{22}	2.2994	539.19	0.1172
S_8	1.8158	682.80	0.0065	S_{23}	2.3156	535.43	0.0144
S_9	1.9494	636.01	0.0225	S_{24}	2.3544	526.61	0.1252
S_{10}	1.9685	629.84	0.1123	S_{25}	2.3662	523.97	0.0252
S_{11}	1.9993	620.13	0.0434	S_{26}	2.3668	523.85	0.2761
S_{12}	2.0011	619.57	0.1406	S_{27}	2.3785	521.26	0.0269
S_{13}	2.0696	599.08	0.1280	S_{28}	2.3924	518.24	0.1916
S_{14}	2.1136	586.61	0.0409	S_{29}	2.4026	516.05	0.0623
S_{15}	2.1546	575.43	0.1772	S_{30}	2.4171	512.95	0.0364

Table S14 The excited states information of BTP-S14-dimer2 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.2575	985.94	0.0143	S_{16}	2.1529	575.91	0.0231
S_2	1.4716	842.53	0.0816	S_{17}	2.1629	573.24	0.0077
S_3	1.5857	781.90	0.7776	S_{18}	2.2015	563.19	0.2577
S_4	1.6049	772.51	0.0537	S_{19}	2.2241	557.47	0.1250
S_5	1.6579	747.82	0.3419	S_{20}	2.2380	554.00	0.0263
S_6	1.7314	716.08	0.2474	S_{21}	2.2460	552.02	0.0400
S_7	1.7985	689.38	0.0455	S_{22}	2.2801	543.076	0.2272
S_8	1.8152	683.04	1.4442	S_{23}	2.2914	541.08	0.0292
S_9	1.9130	648.11	0.2267	S_{24}	2.3080	537.20	0.0252
S_{10}	1.9777	626.92	0.0058	S_{25}	2.3186	534.74	0.2216
S_{11}	2.0123	616.13	0.1186	S_{26}	2.3349	531.00	0.1114
S_{12}	2.0315	610.30	0.0837	S_{27}	2.3718	522.74	0.0208
S_{13}	2.0707	598.77	0.0338	S_{28}	2.3874	519.32	0.1218
S_{14}	2.0907	593.03	0.0025	S_{29}	2.3934	518.03	0.0088
S_{15}	2.1188	585.15	0.0780	S_{30}	2.4175	512.85	0.0441

Table S15 The excited states information of BTP-S14-dimer3 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.2773	970.70	0.0026	S_{16}	2.1115	587.18	0.1715
S_2	1.5070	822.71	0.0042	S_{17}	2.1292	582.32	0.1075
S_3	1.6031	773.41	1.6142	S_{18}	2.1605	573.88	0.0001
S_4	1.6296	760.83	0.0032	S_{19}	2.1923	565.54	0.1326
S_5	1.6631	745.50	1.5350	S_{20}	2.2597	548.67	0.1340
S_6	1.7650	702.46	0.0412	S_{21}	2.2862	542.32	0.0050
S_7	1.8010	688.44	0.0022	S_{22}	2.3207	534.24	0.0029
S_8	1.8707	662.76	0.0010	S_{23}	2.3337	531.27	0.0446
S_9	1.9407	638.87	0.2256	S_{24}	2.3449	528.75	0.0013
S_{10}	1.9596	632.69	0.0416	S_{25}	2.3508	527.41	0.1089
S_{11}	1.9711	628.99	0.0397	S_{26}	2.3739	522.29	0.0917

S_{12}	1.9932	622.03	0.2911	S_{27}	2.3947	517.74	0.0631
S_{13}	2.0213	613.38	0.0344	S_{28}	2.4149	513.41	0.0290
S_{14}	2.0559	603.05	0.0007	S_{29}	2.4334	509.50	0.0050
S_{15}	2.1024	589.74	0.1726	S_{30}	2.4499	506.08	0.0755

Table S16 The excited states information of BTP-S14-dimer4 calculated by DFT calculation

Excited states	*E*/eV	*λ*/nm	f	Excited states	*E*/eV	λ/nm	f
S_1	1.3120	944.97	0.0154	S_{16}	2.2930	540.71	0.0594
S_2	1.5681	790.66	0.0219	S_{17}	2.2968	539.81	0.1284
S_3	1.6471	752.75	0.0034	S_{18}	2.3051	537.87	0.0597
S_4	1.6971	730.56	1.5658	S_{19}	2.3120	536.26	0.0010
S_5	1.7953	690.61	0.1247	S_{20}	2.3510	527.37	0.0526
S_6	1.8504	1.8504	0.0032	S_{21}	2.3620	524.90	0.0014
S_7	1.8661	664.42	0.0010	S_{22}	2.3664	523.94	0.1525
S_8	1.9003	652.45	1.8219	S_{23}	2.3723	522.64	0.3174
S_9	2.0442	607.12	0.0911	S_{24}	2.4086	514.76	0.1536
S_{10}	2.0520	604.23	0.0929	S_{25}	2.4298	510.26	0.0383
S_{11}	2.1169	585.70	0.0070	S_{26}	2.4550	505.03	0.0464
S_{12}	2.1250	583.45	0.2535	S_{27}	2.4771	500.52	0.0558
S_{13}	2.1590	574.25	0.0312	S_{28}	2.4850	498.93	0.0090
S_{14}	2.1876	566.76	0.0676	S_{29}	2.4920	497.53	0.1832
S_{15}	2.2926	540.81	0.0049	S_{30}	2.5059	494.77	0.0634

Table S17 The PM6: BTP-x dimers with singlet charge transfer state (CT_1), triplet charge transfer state ($^3CT_1$), triplet local excited state (T_1) energy levels

	E_{CT_1}	$E_{^3CT_1}$	E_{T_1}	$\Delta E_{^3CT_1\text{-}CT_1}$	$\Delta E_{^3CT_1\text{-}T_1}$
BTP-eC9-dimer1	1.1150	1.1142	1.0990	-0.0008	0.0152
BTP-eC9-dimer2	1.1881	1.1872	1.0847	-0.0009	0.1025
BTP-eC9-dimer3	1.2280	1.1770	1.2402	-0.0510	-0.0632
BTP-eC9-dimer4	1.1310	1.0832	1.1330	-0.0478	-0.0498
BTP-S9-dimer1	1.3439	1.3016	1.2317	-0.0423	0.0699
BTP-S9-dimer2	1.3298	1.3546	1.2246	0.0248	0.1300
BTP-S9-dimer3	1.1957	1.1919	1.0107	-0.0038	0.1812
BTP-S9-dimer4	1.3282	1.3158	1.1073	-0.0124	0.2085
BTP-S14-dimer1	1.1818	1.3956	1.0960	0.2138	0.2996
BTP-S14-dimer2	1.2575	1.4799	1.1889	0.2224	0.2910
BTP-S14-dimer3	1.2773	1.2885	1.0221	0.0112	0.2664
BTP-S14-dimer4	1.3120	1.3188	1.2402	0.0068	0.0786

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