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

Design of BPEA-based Derivatives with High Singlet Fission Performance: A theoretical Perspective

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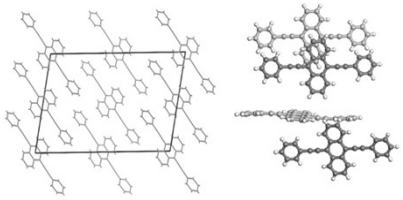
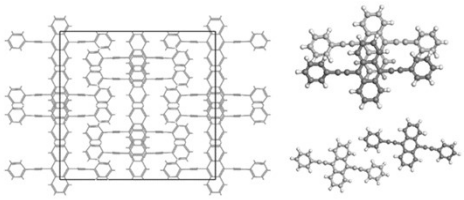
Further calculations are detailed in the Supplementary information. The crystal structure information of BPEA and its derivatives is given in Section A. Section B is about the selection of functionals and basis sets, and gives the detailed calculation data. Section C deals with further analysis of electronic states.

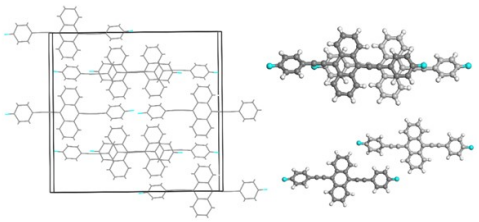
A. Crystal structure information



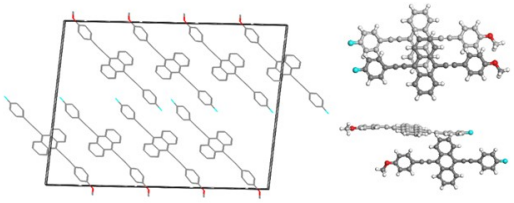
BPEA (C2/c)



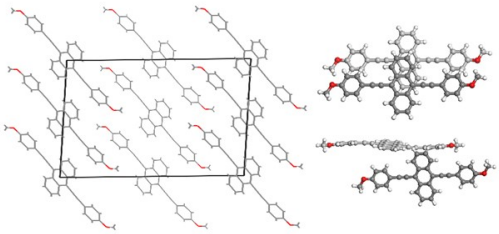
BPEA (Pbcn)



1 (P21/C)



2 (P21/C)



3 (C2/C)

Figure S1. Crystal packing structures and selected dimers of **BPEA**, derivative **1, 2,** and **3.** Data come from ref[1,2 3]

Table S1. Summary of crystal parameters for **BPEA** and its derivatives, ref[1-3].

	BPEA(C2/c)	**BPEA**(Pbcn)	**1** (P21/C)	**2** (P21/C)	**3** (C2/C)
a	22.866(5) Å	24.305(4) Å	6.8920 (9) Å	24.7160 (10) Å	26.095(5) Å
b	5.3567(11) Å	11.512(1) Å	11.8321 (16) Å	5.2272 (2) Å	5.1784(11) Å
c	16.930(3) Å	7.099(1) Å	25.181 (4) Å	16.6641 (8) Å	16.585(3) Å
α	90 °	90 °	90 °	90 °	90 °
β	99.72(3) °	90 °	92.247 (6) °	95.493 (2) °	93.988(5)
γ	90 °	90 °	90 °	90 °	90 °
CCDC	715257	1205622	1909837	1907242	234275

B. Selection of functional and basis group

Basis sets test

Table S2. Comparing the theoretical E(S_1) and E(T_1) of monomers calculated by different basis sets with experiments. The functional is ωB97X-D and the experimental data come from ref[1-3]. (unit: eV).

		6-31g**	6-31+g**	6-311g**	6-311+g**	6-311++g**	Exp
BPEA	S_1	2.918	2.885	2.888	2.873	2.873	2.64
	T_1	1.339	1.349	1.348	1.351	1.351	--
1	S_1	2.764	2.736	2.736	2.723	2.723	2.65
	T_1	1.138	1.153	1.149	1.154	1.154	1.12-1.3
2	S_1	2.793	2.763	2.763	2.751	2.751	2.59
	T_1	1.215	1.227	1.225	1.229	1.229	1.12-1.3
3	S_1	2.832	2.799	2.801	2.788	2.788	2.59
	T_1	1.265	1.275	1.273	1.276	1.276	1.12-1.3

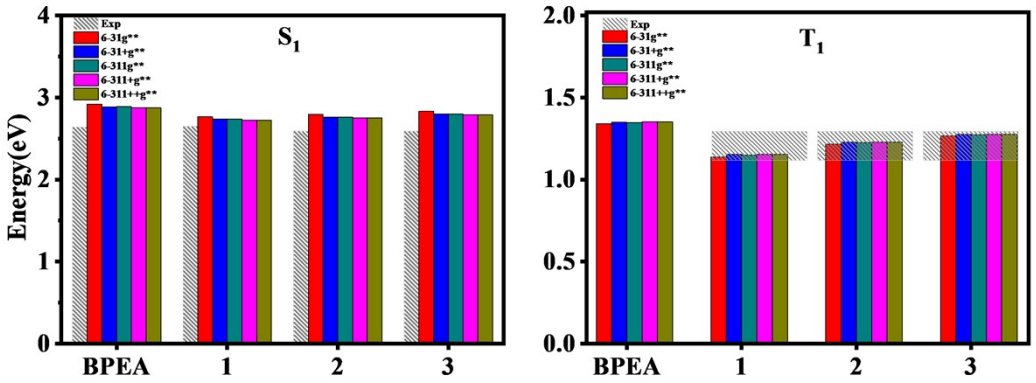


Figure S2. Comparing the theoretical E(S_1) and E(T_1) of monomers calculated by different basis sets with experiments. The experimental data come from ref[1-3].

Selection of functional

Table S3. Comparing the theoretical E(S_1) and E(T_1) of monomers calculated by different functionals with experiments. The basis set is 6-311+g**. The experimental data come from ref[1-3]. (unit: eV).

		PBE0	M06-2X	M06-HF	CAM-B3LYP	ωB97X-D	Exp
BPEA	S_1	2.608	2.865	2.559	2.843	2.873	2.64
	T_1	1.358	1.741	1.376	1.257	1.351	--
1	S_1	2.471	2.714	2.424	2.694	2.723	2.65
	T_1	1.203	1.577	1.219	1.052	1.154	1.12-1.3
2	S_1	2.473	2.737	2.432	2.718	2.751	2.59
	T_1	1.258	1.639	1.266	1.131	1.229	1.12-1.3
3	S_1	2.49	2.769	2.453	2.752	2.788	2.59
	T_1	1.293	1.672	1.309	1.179	1.276	1.12-1.3

Table S4. Comparing the theoretical E(S_1) and E(T_1) of dimers calculated by different functionals with experiments. The basis set is 6-311+g**. The experimental data come from ref[1-3]. (unit: eV).

		PBE0	M06-2X	M06-HF	CAM-B3LYP	ωB97X-D	Exp
BPEA	S_1	2.411	2.793	2.406	2.779	2.814	2.43
	T_1	1.329	1.694	1.315	1.236	1.325	1.24
1	S_1	2.306	2.667	2.306	2.652	2.682	2.48
	T_1	1.186	1.549	1.165	1.040	1.142	1.12-1.3
2	S_1	2.277	2.666	2.273	2.658	2.691	2.34
	T_1	1.226	1.589	1.194	1.101	1.200	1.12-1.3
3	S_1	2.301	2.704	2.297	2.701	2.735	2.34
	T_1	1.258	1.619	1.235	1.147	1.244	1.12-1.3

Table S5. Comparing the theoretical E(S_1-$2T_1$) of monomers and dimers calculated by different functionals with experiments. The basis set is 6-311+g**. The experimental data come from ref[1-3]. (unit: eV).

		PBE0	M06-2X	M06-HF	CAM-B3LYP	ωB97X-D	Exp
BPEA	monomer	-0.109	-0.616	-0.193	0.329	0.171	-
	dimer	-0.247	-0.595	-0.224	0.307	0.164	0-0.19
1	monomer	0.066	-0.439	-0.014	0.591	0.416	0.35-0.69
	dimer	-0.065	-0.433	-0.025	0.571	0.398	0.1-0.42
2	monomer	-0.044	-0.540	-0.100	0.455	0.292	0.35-0.69
	dimer	-0.174	-0.511	-0.115	0.456	0.292	0.1-0.42
3	monomer	-0.096	-0.575	-0.164	0.394	0.237	0.35-0.69
	dimer	-0.216	-0.534	-0.173	0.407	0.248	0.1-0.42

Table S6. The calculated lowest three singlet excited state of the monomers of **BPEA** and its derivatives. The basis set is 6-311+g**. (unit: eV).

		PBE0	M06-2X	M06-HF	CAM-B3LYP	ωB97X-D
BPEA	S_1	2.608	2.865	2.559	2.843	2.873
	S_2	3.740	3.930	3.644	3.895	3.913
	S_3	3.867	4.400	3.855	4.400	4.480
1	S_1	2.471	2.714	2.424	2.694	2.723
	S_2	3.624	3.832	3.553	3.799	3.817
	S_3	3.648	4.172	3.625	4.205	4.290
2	S_1	2.473	2.737	2.432	2.718	2.751
	S_2	3.477	3.898	3.476	3.867	3.886
	S_3	3.704	4.085	3.612	4.116	4.227
3	S_1	2.490	2.769	2.453	2.752	2.788
	S_2	3.471	3.885	3.485	3.853	3.872
	S_3	3.607	4.135	3.590	4.176	4.313

Table S7. The calculated lowest three triplet excited state of the monomers of **BPEA** and its derivatives. The basis set is 6-311+g**. (unit: eV).

		PBE0	M06-2X	M06-HF	CAM-B3LYP	ωB97X-D
BPEA	T_1	1.358	1.741	1.376	1.257	1.351
	T_2	2.983	3.468	3.022	3.116	3.236
	T_3	3.132	3.569	3.171	3.246	3.370
1	T_1	1.203	1.577	1.219	1.052	1.154
	T_2	2.785	3.260	2.816	2.883	3.009
	T_3	2.886	3.367	2.915	2.959	3.089
2	T_1	1.258	1.639	1.266	1.131	1.230
	T_2	2.788	3.262	2.810	2.920	3.042
	T_3	2.927	3.407	2.949	3.023	3.150
3	T_1	1.293	1.672	1.309	1.179	1.276
	T_2	2.841	3.318	2.875	2.978	3.101
	T_3	2.902	3.381	2.938	3.043	3.166

Table S8. The calculated lowest three singlet excited state of the dimers of **BPEA** and its derivatives. The basis set is 6-311+g**. (unit: eV).

		PBE0	M06-2X	M06-HF	CAM-B3LYP	ωB97X-D
BPEA	S_1	2.411	2.793	2.406	2.779	2.814
	S_2	2.463	2.804	2.457	2.868	2.851
	S_3	2.614	3.266	2.608	3.317	3.596
1	S_1	2.306	2.666	2.306	2.652	2.682
	S_2	2.376	2.671	2.368	2.666	2.702
	S_3	2.430	3.120	2.439	3.228	3.456
2	S_1	2.277	2.666	2.273	2.658	2.691
	S_2	2.336	2.673	2.332	2.684	2.729
	S_3	2.471	3.113	2.468	3.221	3.447
3	S_1	2.301	2.704	2.297	2.701	2.735
	S_2	2.374	2.708	2.372	2.716	2.765
	S_3	2.487	3.144	2.485	3.251	3.478

Table S9. The calculated lowest three triplet excited state of the dimers of **BPEA** and its derivatives. The basis set is 6-311+g**. (unit: eV).

		PBE0	M06-2X	M06-HF	CAM-B3LYP	ωB97X-D
BPEA	T_1	1.329	1.694	1.315	1.236	1.325
	T_2	1.362	1.737	1.364	1.248	1.358
	T_3	2.517	3.220	2.547	3.047	3.215
1	T_1	1.186	1.549	1.165	1.040	1.142
	T_2	1.209	1.577	1.198	1.063	1.164
	T_3	2.379	3.079	2.419	2.857	2.982
2	T_1	1.226	1.589	1.194	1.101	1.199
	T_2	1.265	1.638	1.251	1.143	1.239
	T_3	2.382	3.083	2.415	2.908	3.030
3	T_1	1.258	1.619	1.235	1.147	1.244
	T_2	1.301	1.672	1.295	1.191	1.287
	T_3	2.411	3.121	2.445	2.969	3.092

C Analysis of the Electronic States

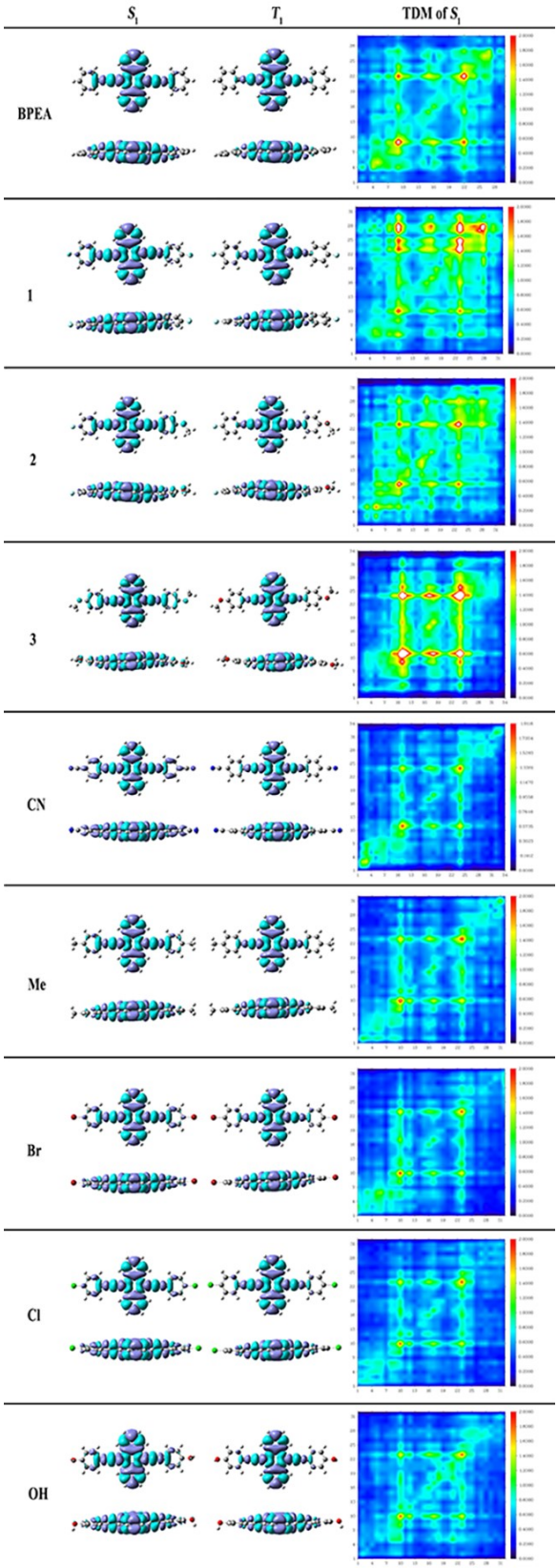


Figure S3. The CDDs of S_1 and T_1 and the heat map of $S_0 \rightarrow S_1$ transition density matrix (TDM) for all **BPEA** derivatives.

Table S10 The calculated transition electric dipole moments of the monomers of BPEA and its derivatives. The methods is ωB97X-D with 6-311+G**. (unit: Au).

	X	Y	Z	Dip
CN	4.3665	-0.0003	0.0056	19.0667
Cl	4.2134	-0.0001	0.0063	17.7528
Br	4.3028	0.0001	0.0077	18.5139
1	3.7261	0.1563	0.0178	13.9088
BPEA	-3.6421	0.0544	0.0609	13.2714
Me	4.1181	-0.0003	-0.0052	16.9591
3	-2.7349	-0.3573	-2.7922	15.4032
OH	-4.0493	-0.0001	-0.0055	16.3966

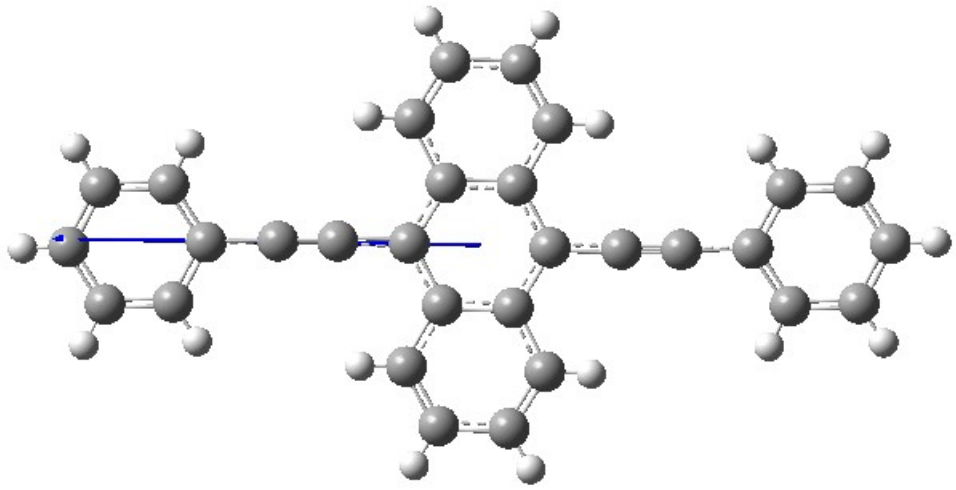


Figure S4. The Transition dipole moment direction of **BPEA** monomer.

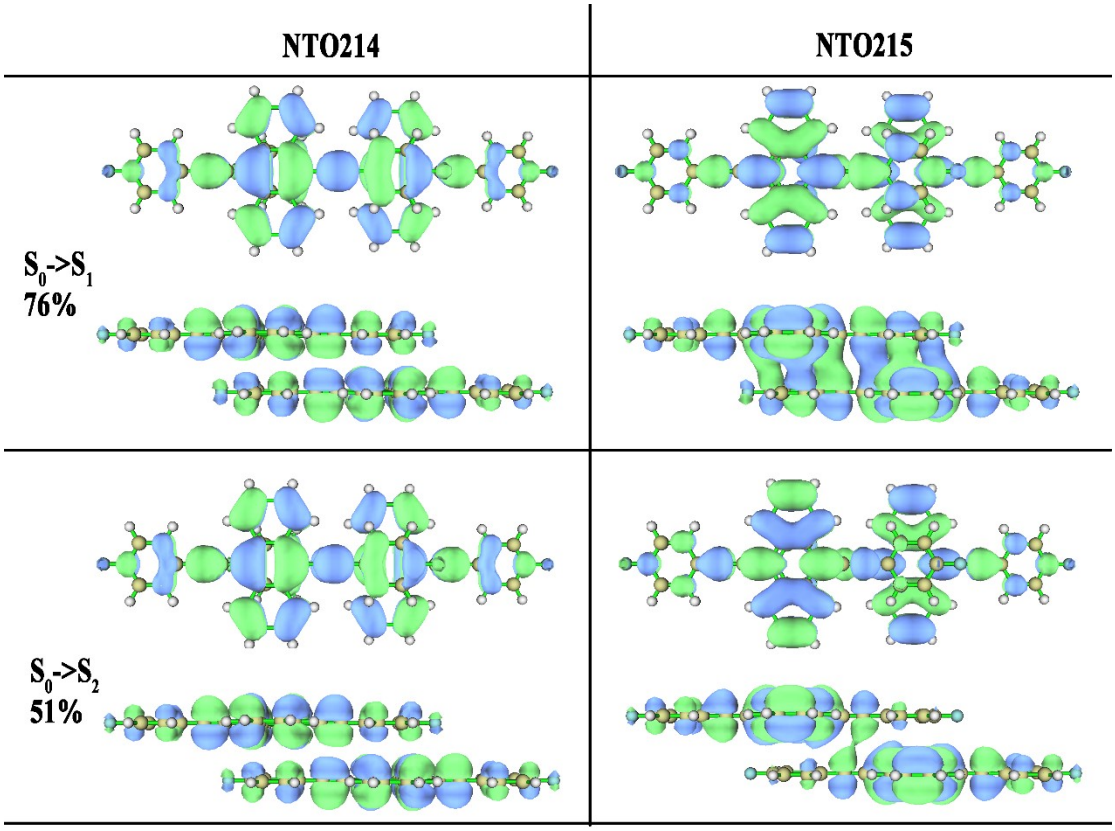


Figure S5.The natural orbital(orbit214->orbit215) diagram of the transition of derivative 1 from the ground state to the first two singlet excited states at the minima point in the X direction.(x=6.7Å)

Table S11 The first five excitation energies of the singlet and triplet states of BPEA and its derivatives at the minima point in the X direction. (unit: eV)

	BPEA (6.9Å)	1 (6.7Å)	2 (6.9Å)	3 (6.7Å)	Br (6.7Å)	Cl (6.7Å)	CN (6.9Å)	Me (6.7Å)	OH (6.7Å)
S_1	2.4896	2.4828	2.4596	2.4314	2.3830	2.4136	2.3786	2.4351	2.4577
S_2	2.6147	2.6134	2.5853	2.5725	2.5733	2.5854	2.5552	2.5940	2.6065
S_3	3.4673	3.4431	3.3364	3.2905	3.4005	3.4155	3.3971	3.4023	3.3910
S_4	3.5029	3.4806	3.4734	3.3516	3.4599	3.4664	3.4506	3.4511	3.5128
S_5	3.6767	3.6878	3.7248	3.7189	3.6648	3.6712	3.6464	3.6709	3.6829
T_1	1.0386	1.0372	1.0359	1.0325	1.0001	1.0118	1.0020	1.0199	1.0281
T_2	1.0934	1.0926	1.0821	1.0789	1.0761	1.0807	1.0749	1.0851	1.0940
T_3	2.7784	2.7627	2.7295	2.7016	2.6873	2.7026	2.6613	2.7400	2.7462
T_4	2.9641	2.9511	2.9212	2.8929	2.8730	2.8940	2.8441	2.9466	2.9440
T_5	3.0260	2.9983	2.9448	2.9426	2.8875	2.9035	2.8695	2.9899	2.9813

Reference

[1] Y. J. Bae, J. A. Christensen, G. Kang, J. Zhou, R. M. Young, Y. L. Wu, R. P. Van Duyne, G. C. Schatz, and M. R. Wasielewski, J Chem Phys **151** (4), 044501 (2019).

[2] Y. J. Bae, G. Kang, C. D. Malliakas, J. N. Nelson, J. Zhou, R. M. Young, Y. L. Wu, R. P. Van Duyne, G. C. Schatz, and M. R. Wasielewski, J Am Chem Soc **140** (45), 15140 (2018).

[3] Biswajit Manna, Amitabha Nandi, and Rajib Ghosh, The Journal of Physical Chemistry C **122** (36), 21047 (2018).