Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information for

Aggregation induced blue-shifted emission – molecular picture from QM/MM study

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Contents:

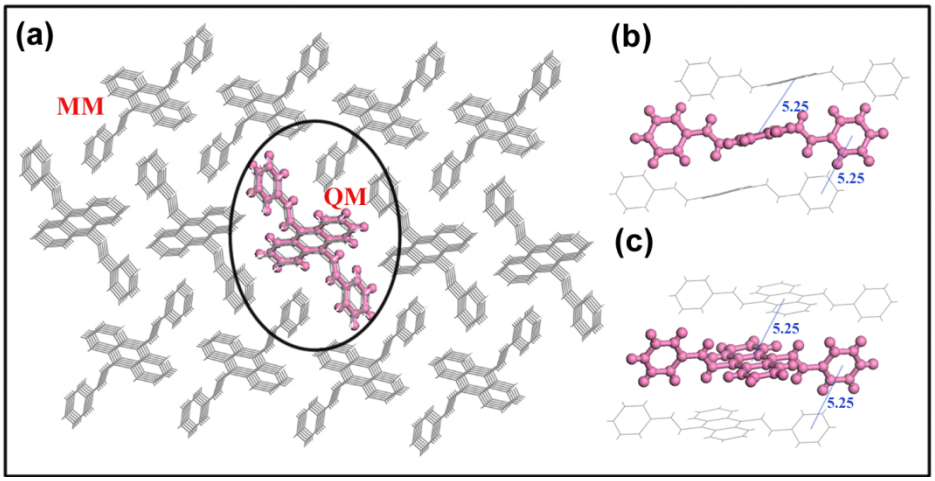


Fig. S1 (a) Setup of the QM/MM model for **DSA** (a cluster of 65 molecules consisting of 52 QM atoms and 3328 MM atoms). (b) and (c) Side views of the residues within 7.50 Å of QM centroid. The nearest intermolecular π-π interaction distance is 5.25 Å.

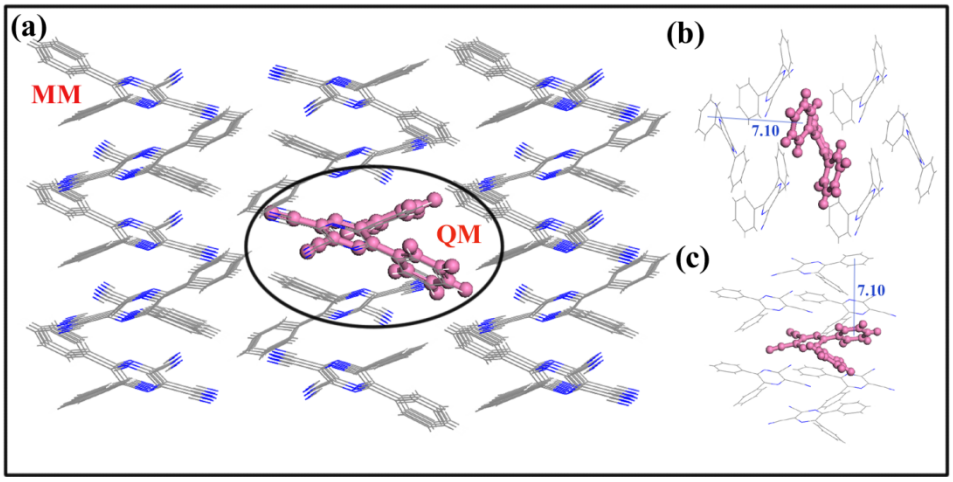


Fig. S2 (a) Setup of the QM/MM model for **DCDPP** (a cluster of 50 molecules consisting of 32 QM atoms and 1568 MM atoms). (b) and (c) Side views of the residues within 7.50 Å of QM centroid. The nearest intermolecular π-π interaction distance is 7.10 Å.

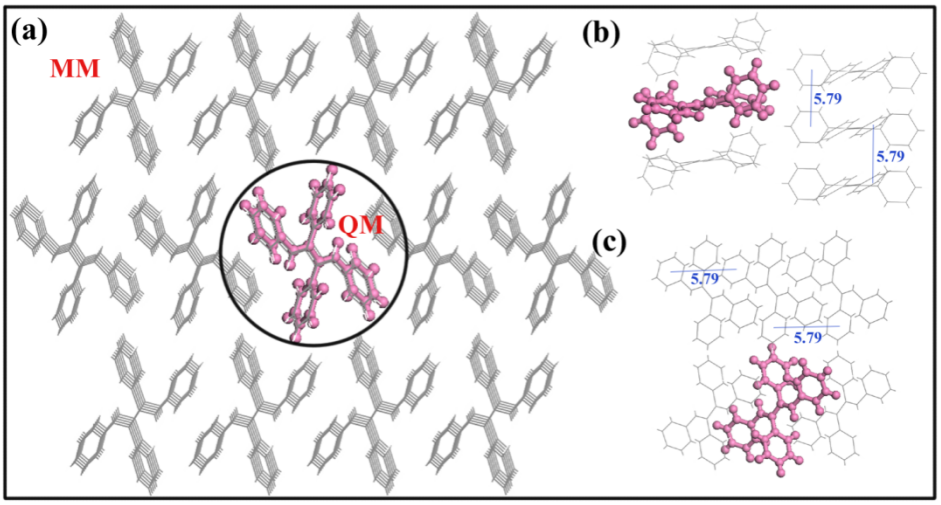


Fig. S3 (a) Setup of the QM/MM model for **TPBD** (a cluster of 65 molecules consisting of 50 QM atoms and 3200 MM atoms). (b) and (c) Side views of the residues within 7.50 Å of QM centroid. The nearest intermolecular π-π interaction distance is 5.79 Å.

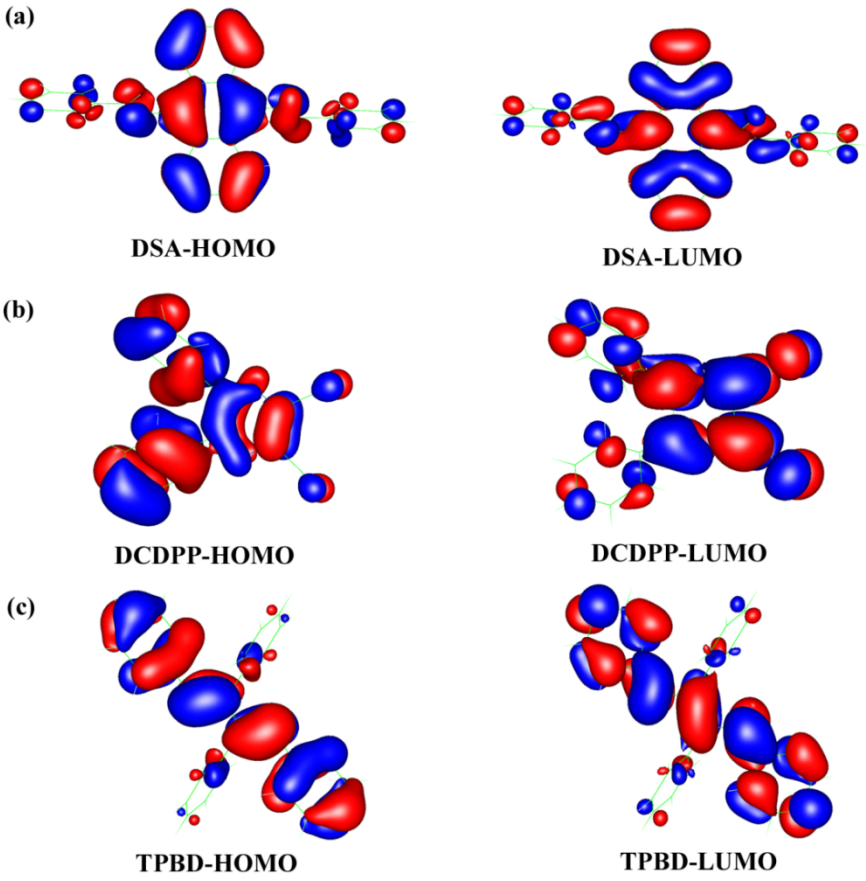
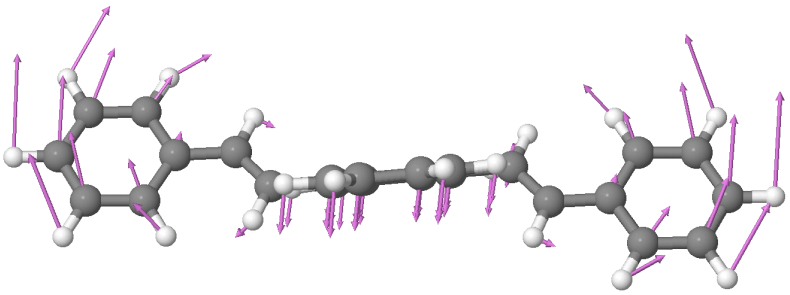
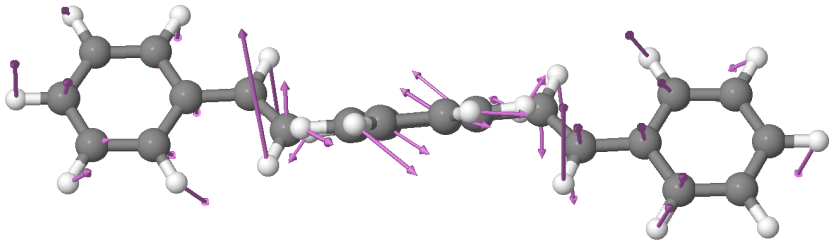


Fig. S4 Electron density contours of HOMOs and LUMOs for **DSA**, **DCDPP** and **TPBD** in aggregate (isovalue = 0.02 a.u.) at the PBE0-D3(bj)/6-31G* level. The shapes of the frontier orbitals in aggregate are almost the same as those in solution.

(a)



14 cm^{-1} mode 3



105 cm^{-1} mode 9

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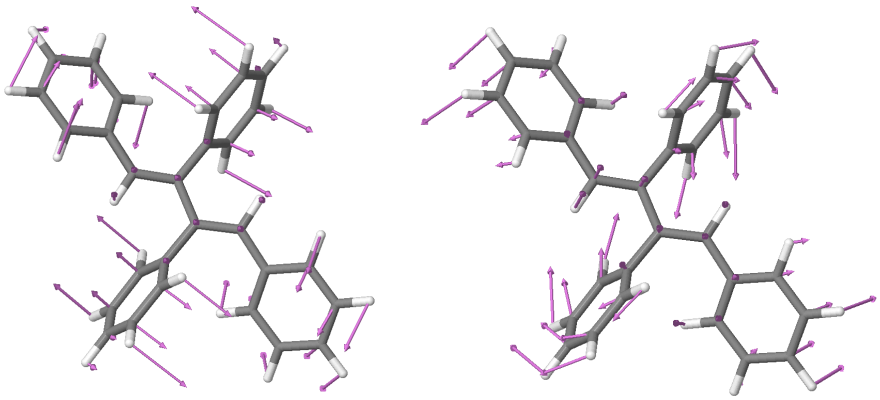

22 cm^{-1} mode 2 39 cm^{-1} mode 4

Fig. S5 Diagrammatic illustrations of the selected normal modes in solution with evidently decreased HR factor from solution to aggregate for **DSA** (a) and **TPBD** (b).

Table S1 Selected bond lengths (in Å), bond angles (in deg) and torsion angles (in deg) for **DSA** in aggregate and in THF solution. The minimum of the $\mathbf{S_0}$ ($\mathbf{S_1}$) was optimized at the (TD)-PBE0-D3(bj)/6-31G* level.

	DSA in aggregate			**DSA** in solution			Crystal[a]
	S_0	S_1	$\|\Delta(S_0\text{-}S_1)\|$	S_0	S_1	$\|\Delta(S_0\text{-}S_1)\|$	
C31-C32	1.4744	1.4387	0.0357	1.4694	1.4147	0.0547	1.49
C5-C6	1.4744	1.4386	0.0358	1.4694	1.4302	0.0392	1.49
C28-C32	1.3425	1.3626	0.0201	1.3444	1.3796	0.0352	1.30
C6-C2	1.3425	1.3626	0.0201	1.3444	1.3692	0.0248	1.30
C28-C38	1.4630	1.4458	0.0172	1.4627	1.4354	0.0273	1.47
C2-C12	1.4629	1.4458	0.0171	1.4627	1.4438	0.0189	1.47
C31-C32-C28	123.16	124.80	1.64	125.02	128.12	3.10	124.36
C5-C6-C2	123.15	124.82	1.67	125.02	129.02	4.00	124.35
C32-C28-C38	127.51	127.31	0.20	126.68	125.66	1.02	128.86
C6-C2-C12	127.50	127.28	0.22	126.68	125.59	1.09	128.86
C8-C4-C1-C10	-2.59	-4.51	1.92	-1.64	-10.17	8.53	-3.13
C36-C27-C30-C34	2.61	4.54	1.93	1.64	3.42	1.78	3.13
C31-C4-C1-C5	-1.65	-4.91	3.26	-1.01	-10.90	9.89	-1.69
C31-C27-C30-C5	1.67	4.94	3.27	1.01	4.64	3.63	1.68
C27-C31-C32-C28	-63.14	-41.96	21.18	-53.00	-15.65	37.35	-74.95
C1-C5-C6-C2	63.24	41.93	21.31	53.00	33.75	19.25	74.93
C32-C28-C38-C45	-6.54	-20.04	13.50	-9.69	-9.95	0.26	4.64
C6-C2-C12-C19	6.45	20.10	13.65	9.68	13.36	3.68	-4.68
C31-C32-C28-C38	177.49	178.36	0.87	-179.26	-179.29	0.03	177.28
C5-C6-C2-C12	-177.58	-178.51	0.93	179.26	-178.51	2.23	-177.21

[a]Ref. 14

Table S2 Selected bond lengths (in Å), bond angles (in deg) and torsion angles (in deg) for **DSA** in aggregate and in THF solution. The minimum of the $\mathbf{S_0}$ ($\mathbf{S_1}$) was optimized at the (TD)-B3LYP-D3(bj)/6-31G* level.

	DSA in aggregate			**DSA** in solution			Crystal[a]
	S_0	S_1	$\lvert\Delta(S_0\text{-}S_1)\rvert$	S_0	S_1	$\lvert\Delta(S_0\text{-}S_1)\rvert$	
C31-C32	1.4792	1.4437	0.0355	1.4735	1.4189	0.0546	1.49
C5-C6	1.4792	1.4437	0.0355	1.4735	1.4340	0.0395	1.49
C28-C32	1.3447	1.3650	0.0203	1.3466	1.3820	0.0354	1.30
C6-C2	1.3446	1.3650	0.0204	1.3466	1.3720	0.0254	1.30
C28-C38	1.4666	1.4491	0.0175	1.4658	1.4384	0.0274	1.47
C2-C12	1.4665	1.4491	0.0174	1.4658	1.4463	0.0195	1.47
C31-C32-C28	123.28	124.91	1.63	125.27	128.35	3.08	124.36
C5-C6-C2	123.27	124.93	1.66	125.27	129.18	3.91	124.35
C32-C28-C38	127.56	127.42	0.14	126.84	125.73	1.11	128.86
C6-C2-C12	127.56	127.40	0.16	126.84	125.76	1.08	128.86
C8-C4-C1-C10	-2.55	-4.38	1.83	-1.69	-9.96	8.27	-3.13
C36-C27-C30-C34	2.57	4.41	1.84	1.69	3.34	1.65	3.13
C31-C4-C1-C5	-1.64	-4.73	3.09	-1.04	-10.78	9.74	-1.69
C31-C27-C30-C5	1.67	4.76	3.09	1.04	4.40	3.36	1.68
C27-C31-C32-C28	-62.89	-42.46	20.43	-52.51	-15.99	36.52	-74.95
C1-C5-C6-C2	62.98	42.42	20.56	52.52	33.62	18.90	74.93
C32-C28-C38-C45	-6.23	-19.23	13.00	-7.43	-9.77	2.34	4.64
C6-C2-C12-C19	6.13	19.28	13.15	7.43	12.26	4.83	-4.68
C31-C32-C28-C38	177.42	178.14	0.72	-179.25	-179.32	0.07	177.28
C5-C6-C2-C12	-177.51	-178.29	0.78	179.25	-178.48	2.27	-177.21

[a]Ref. 14

Table S3 Selected bond lengths (in Å), bond angles (in deg) and torsion angles (in deg) for **DCDPP** in aggregate and in THF solution. The minimum of the $\mathbf{S_0}$ ($\mathbf{S_1}$) was optimized at the (TD)-PBE0-D3(bj)/6-31G* level.

	DCDPP in aggregate			**DCDPP** in solution			Crystal[a]
	S_0	S_1	$\lvert\Delta(S_0\text{-}S_1)\rvert$	S_0	S_1	$\lvert\Delta(S_0\text{-}S_1)\rvert$	
C1-C2	1.4289	1.4402	0.0113	1.4303	1.4633	0.0330	1.43
C2-C3	1.4738	1.4505	0.0233	1.4743	1.4424	0.0319	1.48
C2-N9	1.3283	1.3426	0.0143	1.3317	1.3317	0.0000	1.33
N9-C11	1.3331	1.3144	0.0187	1.3307	1.3251	0.0056	1.33
C11-C13	1.4331	1.4256	0.0075	1.4344	1.4197	0.0147	1.45
C1-C2-C3	122.50	121.39	1.11	124.32	121.66	2.66	122.11
C1-C2-C3-C4	-45.20	-31.20	14.00	38.26	22.21	16.05	-46.55
C2-C1-C5-C6	-42.73	-33.53	9.20	38.26	22.21	16.05	-43.80
N10-C1-C2-C3	175.02	174.58	0.44	-166.84	-161.15	5.69	174.01
N9-C2-C1-C5	171.12	168.54	2.58	-166.84	-161.15	5.69	170.60
C11-N9-C2-C3	-177.85	-175.41	2.44	172.24	168.84	3.40	-177.30
C12-N10-C1-C5	-174.03	-172.58	1.45	172.25	168.84	3.41	-173.74
C3-C2-C1-C5	-7.23	-10.65	3.42	14.63	20.74	6.11	-8.12

[a]Ref. 16

Table S4 Selected bond lengths (in Å), bond angles (in deg) and torsion angles (in deg) for **DSA** in aggregate and in THF solution. The minimum of the $\mathbf{S_0}$ ($\mathbf{S_1}$) was optimized at the (TD)-B3LYP-D3(bj)/6-31G* level.

	DCDPP in aggregate			**DCDPP** in solution			Crystal[a]
	S_0	S_1	$\lvert\Delta(S_0\text{-}S_1)\rvert$	S_0	S_1	$\lvert\Delta(S_0\text{-}S_1)\rvert$	
C1-C2	1.4333	1.4314	0.0019	1.4346	1.4663	0.0317	1.43
C2-C3	1.4780	1.4606	0.0174	1.4780	1.4520	0.0260	1.48
C2-N9	1.3337	1.3570	0.0233	1.3370	1.3335	0.0035	1.33
N9-C11	1.3388	1.3154	0.0234	1.3361	1.3332	0.0029	1.33
C11-C13	1.4356	1.4322	0.0034	1.4365	1.4188	0.0177	1.45
C1-C2-C3	122.53	122.00	0.53	124.22	121.88	2.34	122.11
C1-C2-C3-C4	-45.19	-34.83	10.36	38.30	24.92	13.38	-46.55
C2-C1-C5-C6	-42.81	-37.59	5.22	38.30	24.91	13.39	-43.80
N10-C1-C2-C3	175.10	175.83	0.73	-166.71	-161.85	4.86	174.01
N9-C2-C1-C5	171.12	168.96	2.16	-166.72	-161.85	4.87	170.60
C11-N9-C2-C3	-177.91	-176.48	1.43	172.12	169.26	2.86	-177.30
C12-N10-C1-C5	-173.98	-173.16	0.82	172.13	169.26	2.87	-173.74
C3-C2-C1-C5	-7.22	-9.25	2.03	14.88	20.51	5.63	-8.12

[a]Ref. 16

Table S5 Selected bond lengths (in Å) and torsion angles (in deg) for **TPBD** in aggregate and in acetone solution. The minimum of the $\mathbf{S_0}$ ($\mathbf{S_1}$) was optimized at the (TD)-PBE0-D3(bj)/6-31G* level.

	TPBD in aggregate			**TPBD** in solution			Crystal[a]
	S_0	S_1	$\lvert\Delta(S_0\text{-}S_1)\rvert$	S_0	S_1	$\lvert\Delta(S_0\text{-}S_1)\rvert$	
C1-C2	1.3564	1.4117	0.0553	1.3570	1.4195	0.0625	1.36
C4-C5	1.3564	1.4117	0.0553	1.3570	1.4195	0.0625	1.36
C4-C2	1.4761	1.4327	0.0434	1.4739	1.4177	0.0562	1.48
C1-C29	1.4664	1.4235	0.0429	1.4625	1.4163	0.0462	1.47
C5-C40	1.4664	1.4235	0.0429	1.4625	1.4163	0.0462	1.47
C2-C7	1.4922	1.4851	0.0071	1.4862	1.4743	0.0119	1.50
C4-C18	1.4922	1.4851	0.0071	1.4862	1.4743	0.0119	1.50
C1-C2-C4-C5	180.00	180.00	0.00	-164.81	-153.78	11.03	180.00
C1-C2-C7-C9	-69.07	-61.11	7.96	64.35	41.27	23.08	-70.02
C5-C4-C18-C20	69.08	61.13	7.95	64.33	41.24	23.09	69.95
C4-C5-C40-C42	33.47	17.89	15.58	25.71	13.96	11.75	32.10
C2-C1-C29-C31	-33.46	-17.88	15.58	25.69	13.97	11.72	-31.96

[a]Ref. 30

Table S6 Selected bond lengths (in Å) and torsion angles (in deg) for **TPBD** in aggregate and in acetone solution. The minimum of the $\mathbf{S_0}$ ($\mathbf{S_1}$) was optimized at the (TD)-B3LYP-D3(bj)/6-31G* level.

	TPBD in aggregate			**TPBD** in solution			Crystal[a]
	S_0	S_1	$\lvert\Delta(S_0\text{-}S_1)\rvert$	S_0	S_1	$\lvert\Delta(S_0\text{-}S_1)\rvert$	
C1-C2	1.3589	1.4140	0.0551	1.3596	1.4219	0.0623	1.36
C4-C5	1.3590	1.4140	0.0550	1.3596	1.4219	0.0623	1.36
C4-C2	1.4804	1.4385	0.0419	1.4777	1.4223	0.0554	1.48
C1-C29	1.4701	1.4274	0.0427	1.4657	1.4193	0.0464	1.47
C5-C40	1.4701	1.4274	0.0427	1.4657	1.4193	0.0464	1.47
C2-C7	1.4972	1.4900	0.0072	1.4907	1.4783	0.0124	1.50
C4-C18	1.4972	1.4900	0.0072	1.4907	1.4783	0.0124	1.50
C1-C2-C4-C5	180	180	0.00	-165.15	-153.26	11.89	180.00
C1-C2-C7-C9	-69.08	-61.02	8.06	64.88	41.52	23.36	-70.02
C5-C4-C18-C20	69.09	61.04	8.05	64.84	41.52	23.32	69.95
C4-C5-C40-C42	33.16	18.14	15.02	24.85	13.96	10.89	32.10
C2-C1-C29-C31	-33.15	-18.14	15.01	24.74	13.97	10.77	-31.96

[a]Ref. 30

Table S7 Electronic energies (E) and ZPE (V) at crucial points (*a*, *b*, *c* and *d*) of the adiabatic potential energy surfaces (PES) for **DSA**, **DCDPP** and **TPBD** in aggregate (E^{aggr}, V^{aggr}) and in solution (E^{solu}, V^{solu}) at the (TD)-PBE0-D3(bj)/6-31G* level.

molecule		E^{aggr} /a.u.	E^{solu} /a.u.	V^{aggr} /a.u.	V^{solu} /a.u.
DSA	*a*	-1155.129022	-1155.139345	0.435144	0.427125
	b	-1155.020265	-1155.036915	0.430202	0.425820
	c	-1155.034540	-1155.048160	0.430202	0.425820
	d	-1155.119710	-1155.123381	0.435144	0.427125
DCDPP	*a*	-909.893883	-909.899216	0.242449	0.237389
	b	-909.765718	-909.776488	0.237845	0.233793
	c	-909.778311	-909.793601	0.237845	0.233793
	d	-909.876043	-909.877830	0.242449	0.237389
TPBD	*a*	-1078.987343	-1079.000461	0.420520	0.414462
	b	-1078.846687	-1078.867469	0.416482	0.411865
	c	-1078.860329	-1078.886379	0.416482	0.411865
	d	-1078.973956	-1078.981213	0.420520	0.414462

Table S8 Electronic energies (E) and ZPE (V) at crucial points (*a*, *b*, *c* and *d*) of the adiabatic PES for **DSA**, **DCDPP** and **TPBD** in aggregate (E^{aggr}, V^{aggr}) and in solution (E^{solu}, V^{solu}) at the (TD)-B3LYP-D3(bj)/6-31G* level.

molecule		E^{aggr} /a.u.	E^{solu} /a.u.	V^{aggr} /a.u.	V^{solu} /a.u.
DSA	*a*	-1155.805302	-1156.568656	0.431971	0.424414
	b	-1155.700131	-1156.469721	0.427019	0.423137
	c	-1155.713719	-1156.480146	0.427019	0.423137
	d	-1155.796769	-1156.553813	0.431971	0.424414
DCDPP	*a*	-910.440695	-910.993866	0.240044	0.235431
	b	-910.318894	-910.877540	0.235564	0.231502
	c	-910.330364	-910.894225	0.235564	0.231502
	d	-910.427048	-910.978986	0.240044	0.235431
TPBD	*a*	-1079.621850	-1080.342287	0.417761	0.411746
	b	-1079.485246	-1080.213025	0.413946	0.409263
	c	-1079.498015	-1080.231138	0.413946	0.409263
	d	-1079.609346	-1080.324070	0.417761	0.411746

Table S9 Oscillator strengths and dominant assignments for S_1 of **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the TD-PBE0-D3(bj)/6-31G* level. $f_{ab}^{aggr(solu)}$ denotes the absorption oscillator strength, and $f_{em}^{aggr(solu)}$ is the emission oscillator strength. H (L) denotes HOMO (LUMO), the contributions respect to aggregate and solution are in the parentheses, respectively.

	Absorption			Emission		
S_1 state	f_{ab}^{aggr}	f_{ab}^{solu}	Assignment	f_{em}^{aggr}	f_{em}^{solu}	Assignment
DSA	0.44	0.59	H→L(98.1%, 99.3%)	0.67	0.79	H→L(98.7%, 98.4%)
DCDPP	0.11	0.15	H→L(92.2%, 97.5%)	0.05	0.04	H→L(98.0%, 98.2%)
TPBD	1.12	1.06	H→L(98.0%, 99.1%)	1.19	0.76	H→L(98.3%, 98.0%)

Table S10 Oscillator strengths and dominant assignments for S_1 of **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the TD-B3LYP-D3(bj)/6-31G* level. $f_{ab}^{aggr(solu)}$ denotes to the absorption oscillator strength, and $f_{em}^{aggr(solu)}$ is the emission oscillator strength. H (L) denotes HOMO (LUMO).

	Absorption			Emission		
S_1 state	f_{ab}^{aggr}	f_{ab}^{solu}	Assignment	f_{em}^{aggr}	f_{em}^{solu}	Assignment
DSA	0.42	0.58	H→L(97.7%, 99.3%)	0.64	0.78	H→L(98.7%, 98.3%)
DCDPP	0.09	0.13	H→L(91.3%, 96.5%)	0.05	0.04	H→L(97.4%, 97.7%)
TPBD	1.08	1.03	H→L(97.6%, 98.9%)	1.16	0.74	H→L(98.0%, 97.8%)

Table S11 Calculated electronic vertical transition energies considering ZPE correction for **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the TD-PBE0-D3(bj)/6-31G* level. The available experimental values are presented in the parentheses.

	Absorption			Emission		
	E_{ab}^{aggr} /eV	E_{ab}^{solu} /eV	$\Delta E_{ab}^{aggr-solu}$ /eV	E_{em}^{aggr} /eV	E_{em}^{solu} /eV	$\Delta E_{em}^{aggr-solu}$ /eV
DSA	2.82 (2.99)	2.75 (3.05)	0.07 (-0.06)	2.18 (2.39)	2.01 (2.03)	0.17 (0.36)
DCDPP	3.36 (3.65)	3.24 (3.65)	0.12 (0.00)	2.53 (3.00)	2.19 (2.93)	0.34 (0.07)
TPBD	3.72 (3.60)	3.55 (3.71)	0.17 (-0.11)	2.98 (3.18)	2.51 (3.04)	0.47 (0.14)

Table S12 Reorganization energies for **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the (TD)-PBE0-D3(bj)/6-31G* level.

	Aggregate			Solution			Difference
	λ_{gs} /eV	λ_{es} /eV	λ^{aggr} /eV	λ_{gs} /eV	λ_{es} /eV	λ^{solu} /eV	$\lambda^{solu\text{-}aggr}$ /eV
DSA	0.25	0.39	0.64	0.43	0.31	0.74	0.10
DCDPP	0.49	0.34	0.83	0.58	0.47	1.05	0.22
TPBD	0.36	0.37	0.73	0.52	0.51	1.03	0.30

Table S13 The electronic vertical transition energies corresponding to absorption and emission peaks for **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the level of TD-B3LYP-D3(bj)/6-31G*. The available experimental values are presented in the parentheses.

	Absorption			Emission		
	E_{ab}^{aggr} /eV	E_{ab}^{solu} /eV	$\Delta E_{ab}^{aggr-solu}$ /eV	E_{em}^{aggr} /eV	E_{em}^{solu} /eV	$\Delta E_{em}^{aggr-solu}$ /eV
DSA	2.86 (2.99)	2.69 (3.05)	0.17 (-0.06)	2.26 (2.39)	2.00 (2.03)	0.26 (0.36)
DCDPP	3.31 (3.65)	3.17 (3.65)	0.14 (0.00)	2.63 (3.00)	2.31 (2.93)	0.32 (0.07)
TPBD	3.72(3.60)	3.52 (3.71)	0.20 (-0.11)	3.03 (3.18)	2.53 (3.04)	0.50 (0.14)

Table S14 Calculated electronic vertical transition energies considering ZPE correction for **DSA**, **DCDPP** and **TPBD** in aggregate and in solution, respectively at the level of TD-B3LYP-D3(bj)/6-31G*. The available experimental values are presented in the parentheses.

	Absorption			**Emission**		
	E_{ab}^{aggr} /eV	E_{ab}^{solu} /eV	$\Delta E_{ab}^{aggr-solu}$ /eV	E_{em}^{aggr} /eV	E_{em}^{solu} /eV	$\Delta E_{em}^{aggr-solu}$ /eV
DSA	2.73 (2.99)	2.66 (3.05)	0.07 (-0.06)	2.13 (2.39)	1.97 (2.03)	0.16 (0.36)
DCDPP	3.19 (3.65)	3.06 (3.65)	0.13 (0.00)	2.51 (3.00)	2.20 (2.93)	0.31 (0.07)
TPBD	3.61 (3.60)	3.45 (3.71)	0.16 (-0.11)	2.92 (3.18)	2.46 (3.04)	0.46 (0.14)

Table S15 Reorganization energies for **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the (TD)-B3LYP-D3(bj)/6-31G* level.

	Aggregate			**Solution**			**Difference**
	λ_{gs} /eV	λ_{es} /eV	λ^{aggr} /eV	λ_{gs} /eV	λ_{es} /eV	λ^{solu} /eV	$\lambda^{solu\text{-}aggr}$ /eV
DSA	0.23	0.37	0.60	0.40	0.28	0.68	0.08
DCDPP	0.37	0.31	0.68	0.40	0.45	0.85	0.17
TPBD	0.34	0.35	0.69	0.50	0.49	0.99	0.30

Table S16 Adiabatic excitation energies for **DSA**, **DCDPP** and **TPBD** at the (TD)-PBE0-D3(bj)/6-31G* and (TD)-B3LYP-D3(bj)/6-31G* level. $\Delta E_{ad}^{aggr(solu)}$ corresponds to the electronic energy in aggregate and solution, and $\Delta E_{adZPE}^{aggr(solu)}$ is related to the values taking ZPE into account.

		Aggregate		**Solution**	
	Functional	ΔE_{ad}^{aggr} /eV	ΔE_{adZPE}^{aggr} /eV	ΔE_{ad}^{solu} /eV	ΔE_{adZPE}^{solu} /eV
	PBE0-D3(bj)	2.57	2.44	2.48	2.46
DSA	B3LYP-D3(bj)	2.49	2.35	2.41	2.37
	PBE0-D3(bj)	3.14	3.02	2.87	2.78
DCDPP	B3LYP-D3(bj)	3.00	2.88	2.71	2.60
	PBE0-D3(bj)	3.46	3.35	3.10	3.03
TPBD	B3LYP-D3(bj)	3.37	3.27	3.02	2.96

Table S17 The electronic vertical transition energies corresponding to absorption and emission peaks for **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the level of TD-CAM-B3lYP-D3(bj)/6-31G*//(TD)-PBE0-D3(bj)/6-31G*. The available experimental values are presented in the parentheses.

	Absorption			**Emission**		
	E_{ab}^{aggr} /eV	E_{ab}^{solu} /eV	$\Delta E_{ab}^{aggr-solu}$ /eV	E_{em}^{aggr} /eV	E_{em}^{solu} /eV	$\Delta E_{em}^{aggr-solu}$ /eV
DSA	3.25 (2.99)	3.07 (3.05)	0.18 (-0.06)	2.52 (2.39)	2.18 (2.03)	0.34 (0.36)
DCDPP	4.03 (3.65)	3.88 (3.65)	0.15 (0.00)	3.14 (3.00)	2.71 (2.93)	0.43 (0.07)
TPBD	4.12 (3.60)	3.90 (3.71)	0.22 (-0.11)	3.25 (3.18)	2.74 (3.04)	0.51 (0.14)

Table S18 Reorganization energies for **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the (TD)-CAM-B3lYP-D3(bj)/6-31G*//(TD)-PBE0-D3(bj)/6-31G* level.

	Aggregate			**Solution**			**Difference**
	λ_{gs} /eV	λ_{es} /eV	λ^{aggr} /eV	λ_{gs} /eV	λ_{es} /eV	λ^{solu} /eV	$\lambda^{solu\text{-}aggr}$ /eV
DSA	0.37	0.36	0.73	0.60	0.29	0.89	0.16
DCDPP	0.58	0.31	0.89	0.71	0.45	1.16	0.27
TPBD	0.48	0.39	0.87	0.68	0.49	1.17	0.30

Table S19 The electronic vertical transition energies corresponding to absorption and emission peaks for **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the level of TD-PBE0-D3(bj)/TZVP//(TD)-PBE0-D3(bj)/6-31G*. The available experimental values are presented in the parentheses.

	Absorption			**Emission**		
	E_{ab}^{aggr} /eV	E_{ab}^{solu} /eV	$\Delta E_{ab}^{aggr-solu}$ /eV	E_{em}^{aggr} /eV	E_{em}^{solu} /eV	$\Delta E_{em}^{aggr-solu}$ /eV
DSA	2.90 (2.99)	2.74 (3.05)	0.16 (-0.06)	2.27 (2.39)	2.00 (2.03)	0.27 (0.36)
DCDPP	3.46 (3.65)	3.31 (3.65)	0.15 (0.00)	2.64 (3.00)	2.27 (2.93)	0.37 (0.07)
TPBD	3.75 (3.60)	3.54 (3.71)	0.21 (-0.11)	3.02 (3.18)	2.49 (3.04)	0.53 (0.14)

Table S20 The electronic vertical transition energies corresponding to absorption and emission peaks for **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the level of TD-PBE0-D3(bj)/6-31+G*//(TD)-PBE0-D3(bj)/6-31G*. The available experimental values are presented in the parentheses.

	Absorption			Emission		
	E_{ab}^{aggr} /eV	E_{ab}^{solu} /eV	$\Delta E_{ab}^{aggr-solu}$ /eV	E_{em}^{aggr} /eV	E_{em}^{solu} /eV	$\Delta E_{em}^{aggr-solu}$ /eV
DSA	2.91 (2.99)	2.74 (3.05)	0.17 (-0.06)	2.28 (2.39)	2.00 (2.03)	0.28 (0.36)
DCDPP	3.45 (3.65)	3.29 (3.65)	0.16 (0.00)	2.63 (3.00)	2.26 (2.93)	0.37 (0.07)
TPBD	3.75 (3.60)	3.54 (3.71)	0.21 (-0.11)	3.02 (3.18)	2.49 (3.04)	0.53 (0.14)

Table S21. Reorganization energies for **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the (TD)-PBE0-D3(bj)/TZVP//(TD)-PBE0-D3(bj)/6-31G* level.

	Aggregate			Solution			Difference
	λ_{gs} /eV	λ_{es} /eV	λ^{aggr} /eV	λ_{gs} /eV	λ_{es} /eV	λ^{solu} /eV	$\lambda^{solu\text{-}aggr}$ /eV
DSA	0.28	0.35	0.63	0.45	0.29	0.74	0.11
DCDPP	0.53	0.29	0.82	0.62	0.43	1.05	0.23
TPBD	0.40	0.33	0.73	0.58	0.47	1.05	0.32

Table S22. Reorganization energies for **DSA**, **DCDPP** and **TPBD** in aggregate and in solution at the (TD)-PBE0-D3(bj)/6-31+G*//(TD)-PBE0-D3(bj)/6-31G* level.

	Aggregate			Solution			Difference
	λ_{gs} /eV	λ_{es} /eV	λ^{aggr} /eV	λ_{gs} /eV	λ_{es} /eV	λ^{solu} /eV	$\lambda^{solu\text{-}aggr}$ /eV
DSA	0.26	0.37	0.63	0.44	0.30	0.74	0.11
DCDPP	0.50	0.32	0.82	0.59	0.45	1.04	0.22
TPBD	0.37	0.36	0.73	0.53	0.51	1.04	0.31

Table S23. The predicted harmonic vibrational frequencies at the minimum of $\mathbf{S_0}$ for **DSA** in THF solution at the PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
11	12	14	25	46	55	74	83	105	125
131	150	159	189	237	255	264	305	309	349
366	403	407	412	413	433	447	460	488	505
511	513	537	571	607	621	622	628	632	633
666	680	707	707	724	754	765	769	778	782
803	817	851	857	859	870	876	877	894	896
930	934	943	957	978	980	981	981	1003	1005
1008	1008	1018	1019	1024	1025	1067	1068	1073	1075
1081	1119	1121	1134	1149	1189	1189	1189	1203	1211

1214	1215	1252	1252	1259	1284	1311	1314	1338	1343
1350	1354	1372	1375	1393	1394	1423	1431	1439	1484
1498	1500	1504	1505	1548	1553	1555	1600	1601	1635
1657	1657	1684	1684	1693	1706	1723	1725	3179	3179
3187	3187	3208	3208	3215	3215	3218	3218	3224	3224
3231	3231	3232	3232	3241	3242	3246	3246	3259	3260

Table S24. The predicted harmonic vibrational frequencies at the minimum of $\mathbf{S_1}$ for **DSA** in THF solution at the TD-PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
11	28	36	40	48	51	74	99	119	138
146	158	173	213	229	246	292	309	316	322
380	388	413	414	420	433	440	462	486	500
507	522	542	576	606	613	625	626	629	630
661	672	696	700	722	737	759	764	768	773
785	814	843	848	854	866	872	883	889	899
921	925	945	947	955	957	973	975	979	980
994	999	1003	1005	1010	1014	1062	1064	1092	1096
1106	1121	1124	1135	1165	1188	1188	1192	1194	1199
1211	1212	1257	1263	1265	1292	1306	1312	1333	1348
1356	1361	1377	1383	1394	1400	1404	1409	1421	1447
1490	1493	1500	1506	1517	1544	1548	1558	1588	1611
1621	1632	1633	1636	1644	1670	1676	1680	3179	3203
3205	3208	3208	3214	3215	3219	3222	3223	3224	3225
3232	3233	3235	3236	3241	3242	3246	3248	3252	3261

Table S25. The predicted harmonic vibrational frequencies at the minimum of $\mathbf{S_0}$ for **DCDPP** in THF solution at the PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
27	47	49	62	79	90	110	151	162	192
236	259	277	325	332	405	412	418	444	459
490	510	545	558	596	605	628	630	686	700
707	713	715	728	768	790	792	842	866	867
952	953	965	990	992	1018	1018	1021	1023	1062
1069	1112	1123	1127	1173	1192	1193	1215	1216	1284
1306	1350	1354	1366	1386	1391	1439	1460	1499	1504
1551	1554	1577	1604	1660	1660	1682	1685	2388	2391
3223	3223	3232	3232	3239	3239	3246	3246	3251	3251

Table S26. The predicted harmonic vibrational frequencies at the minimum of S_1 for **DCDPP** in THF solution at the TD-PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
31	58	59	77	77	99	111	153	160	203
226	252	283	290	330	385	406	410	423	427
484	498	501	536	549	598	611	615	650	664
690	695	702	708	741	773	775	794	842	864
907	937	948	985	992	1003	1004	1013	1014	1043
1048	1082	1108	1120	1141	1191	1193	1196	1198	1214
1286	1290	1330	1349	1385	1404	1411	1416	1470	1484
1497	1499	1531	1546	1595	1609	1626	1647	2319	2325
3233	3234	3239	3240	3247	3247	3255	3256	3260	3261

Table S27. The predicted harmonic vibrational frequencies at the minimum of S_0 for **TPBD** in acetone solution at the PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
13	22	27	39	40	53	57	66	67	115
132	178	192	196	201	241	266	267	318	338
412	412	416	417	452	486	494	517	527	560
584	612	623	627	631	634	641	689	710	710
711	716	720	741	773	776	786	807	808	863
863	867	867	888	905	905	926	940	945	945
956	983	983	985	985	1009	1009	1010	1011	1018
1018	1022	1022	1062	1066	1069	1069	1109	1114	1115
1123	1137	1187	1187	1187	1187	1207	1207	1214	1215
1217	1260	1261	1298	1342	1345	1352	1364	1378	1379
1384	1388	1413	1449	1494	1494	1499	1500	1546	1548
1552	1553	1646	1650	1656	1657	1669	1680	1682	1684
1691	1692	3196	3196	3207	3207	3213	3213	3216	3216
3218	3218	3226	3226	3226	3226	3233	3233	3239	3239
3242	3242	3253	3253						

Table S28. The predicted harmonic vibrational frequencies at the minimum of S_1 for **TPBD** in acetone solution at the TD-PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
15	21	37	47	47	60	61	71	85	129
130	172	185	207	209	256	274	278	310	322
413	414	418	421	454	462	481	507	524	543
545	604	616	622	624	629	643	661	685	686
699	713	716	743	745	764	782	798	801	826
830	848	852	863	864	885	895	910	912	941
942	977	978	983	984	997	997	998	1004	1007
1007	1017	1018	1055	1055	1060	1064	1111	1114	1115
1124	1139	1183	1184	1186	1186	1188	1203	1207	1209
1212	1266	1270	1325	1338	1342	1358	1363	1383	1384
1389	1408	1409	1443	1463	1487	1493	1501	1518	1523
1530	1543	1549	1579	1604	1604	1639	1640	1653	1666
1669	1674	3188	3188	3206	3206	3214	3214	3214	3215
3221	3221	3224	3224	3230	3230	3236	3236	3239	3239
3242	3243	3256	3256						

Table S29. The predicted harmonic vibrational frequencies at the minimum of $\mathbf{S_0}$ for **DSA** in aggregate at the PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
67	77	91	106	109	143	156	158	160	168
173	183	195	212	264	314	320	323	330	379
383	407	429	446	464	465	466	476	522	522
536	547	552	578	618	628	636	637	639	639
672	702	729	744	747	772	805	808	821	822
825	825	872	882	902	903	907	910	912	918
953	966	974	975	1000	1001	1014	1015	1022	1023
1023	1024	1037	1039	1050	1051	1073	1074	1080	1081
1081	1129	1132	1140	1149	1204	1209	1210	1215	1219
1230	1231	1261	1261	1275	1301	1317	1327	1347	1349
1351	1365	1383	1386	1416	1418	1421	1447	1448	1499
1500	1504	1510	1510	1550	1560	1561	1604	1615	1647
1667	1667	1693	1694	1702	1713	1736	1737	3200	3200
3206	3206	3223	3223	3229	3229	3229	3230	3244	3245
3245	3245	3249	3253	3254	3255	3271	3271	3278	3282

Table S30. The predicted harmonic vibrational frequencies at the minimum of $\mathbf{S_1}$ for

DSA in aggregate at the TD-PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
71	74	80	91	102	121	122	134	137	153
161	170	170	212	259	297	299	303	323	357
390	402	417	433	439	439	459	468	485	524
526	531	536	578	605	618	620	626	634	635
663	675	721	722	722	728	764	776	784	790
795	816	863	872	877	878	879	884	895	898
938	939	949	950	958	964	972	979	992	996
1000	1000	1019	1019	1023	1023	1073	1074	1091	1098
1109	1127	1129	1138	1158	1199	1206	1211	1211	1211
1221	1222	1260	1261	1278	1294	1309	1316	1334	1340
1361	1368	1383	1385	1408	1411	1414	1416	1423	1438
1492	1495	1506	1509	1518	1549	1552	1563	1604	1618
1620	1626	1647	1651	1665	1670	1686	1686	3182	3183
3213	3214	3217	3218	3225	3226	3230	3230	3240	3241
3247	3247	3248	3249	3251	3256	3262	3264	3273	3274

Table S31. The predicted harmonic vibrational frequencies at the minimum of $\mathbf{S_0}$ for **DCDPP** in aggregate at the PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
94	111	114	127	142	147	149	189	200	213
263	274	289	333	358	420	440	446	468	481
498	530	562	582	611	616	636	639	693	703
719	727	745	755	782	802	814	862	894	907
973	976	978	1011	1017	1026	1029	1037	1045	1072
1082	1121	1132	1134	1185	1209	1210	1232	1234	1293
1319	1355	1361	1374	1405	1413	1448	1469	1511	1513
1557	1561	1592	1614	1668	1668	1694	1696	2388	2398
3239	3244	3247	3250	3252	3266	3274	3281	3283	3294

Table S32. The predicted harmonic vibrational frequencies at the minimum of $\mathbf{S_1}$ for **DCDPP** in aggregate at the TD-PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
92	101	109	123	130	145	147	167	195	214

255	263	291	324	331	413	417	429	438	475
498	508	526	547	561	607	611	624	661	671
693	696	714	733	766	779	791	809	874	893
925	944	961	997	1008	1009	1017	1025	1031	1052
1060	1084	1100	1124	1128	1180	1196	1205	1209	1213
1281	1309	1342	1349	1382	1398	1413	1425	1486	1491
1508	1530	1553	1589	1612	1627	1637	1645	2305	2349
3235	3241	3248	3254	3262	3262	3273	3276	3289	3294

Table S33. The predicted harmonic vibrational frequencies at the minimum of $\mathbf{S_0}$ for **TPBD** in aggregate at the PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
73	82	93	97	101	128	129	134	140	140
163	186	204	209	221	247	281	286	334	365
437	438	442	444	462	492	503	535	547	571
599	619	627	633	637	643	643	702	704	726
727	735	749	760	788	798	798	818	823	882
883	892	894	896	907	927	940	961	963	965
971	996	997	1002	1002	1020	1020	1023	1024	1026
1026	1027	1027	1065	1070	1080	1081	1116	1124	1125
1136	1145	1197	1197	1207	1207	1216	1219	1220	1234
1236	1262	1265	1301	1349	1350	1357	1372	1392	1392
1396	1407	1413	1446	1497	1497	1507	1507	1552	1553
1557	1558	1654	1657	1662	1663	1677	1685	1690	1690
1695	1695	3210	3210	3216	3216	3217	3217	3231	3231
3232	3232	3244	3244	3248	3248	3253	3253	3259	3259
3263	3263	3284	3284						

Table S34. The predicted harmonic vibrational frequencies at the minimum of $\mathbf{S_1}$ for **TPBD** in aggregate at the TD-PBE0-D3(bj)/6-31G* level.

Harmonic vibrational frequencies / cm^{-1}									
70	72	93	97	101	110	113	123	128	136
165	183	204	210	216	246	280	283	288	300
425	428	430	435	450	483	495	511	515	537
563	606	615	625	628	637	639	665	685	692
698	730	744	755	760	775	792	811	815	832
834	858	868	890	893	895	898	916	920	961

964	979	980	998	999	999	1000	1004	1009	1020
1020	1024	1025	1064	1065	1067	1070	1117	1122	1122
1134	1146	1191	1197	1197	1200	1200	1216	1217	1226
1232	1269	1275	1322	1337	1346	1364	1367	1375	1392
1392	1417	1418	1443	1475	1491	1498	1502	1525	1528
1533	1550	1552	1580	1601	1601	1652	1652	1662	1677
1678	1690	3214	3215	3216	3216	3217	3218	3228	3228
3231	3231	3243	3243	3247	3248	3248	3248	3263	3264
3267	3268	3279	3280						