Supplementary Information for

Theoretical insights into the central "acceptor" bridge function on whole visible light and near-infrared emission in tetraphenylpyrazine-based luminogens

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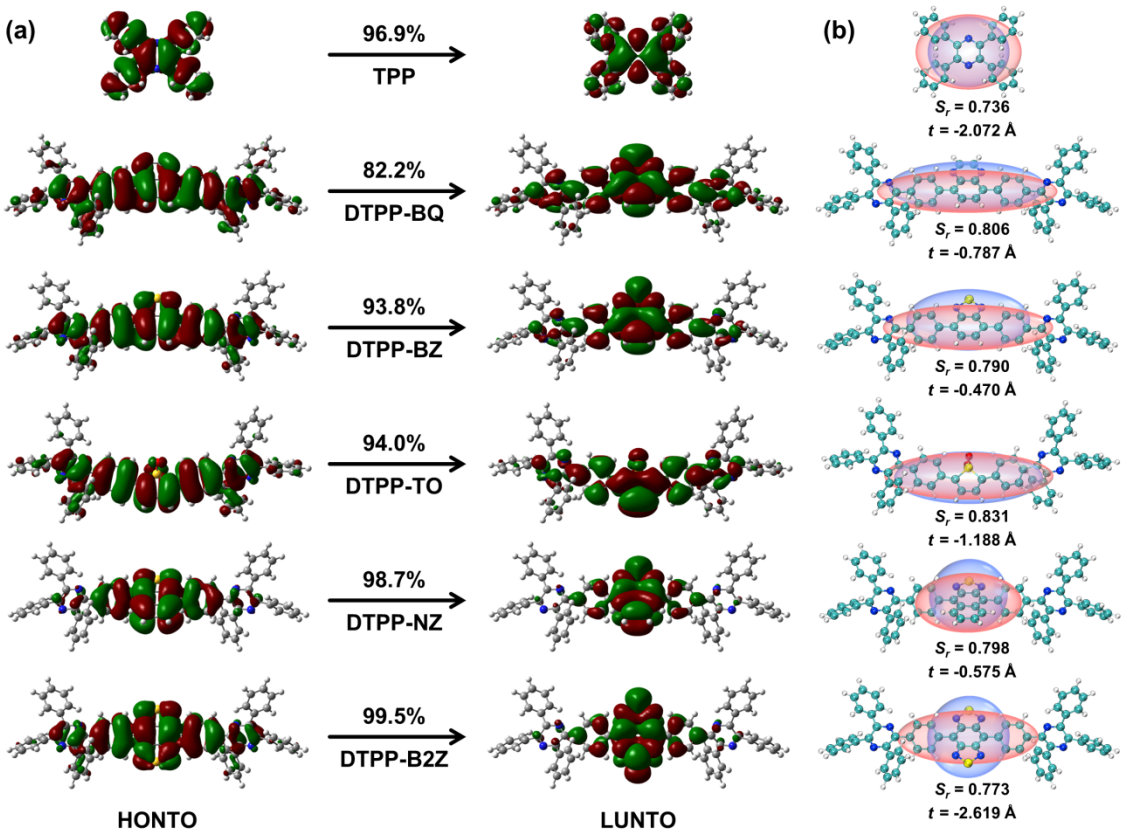

Fig. S1 NTO characters and transition proportions for TPP and its derivatives at the S_0-optimized geometries in solution (a). Centroids of holes (red region) and electrons (blue region) for the corresponding transition (b).

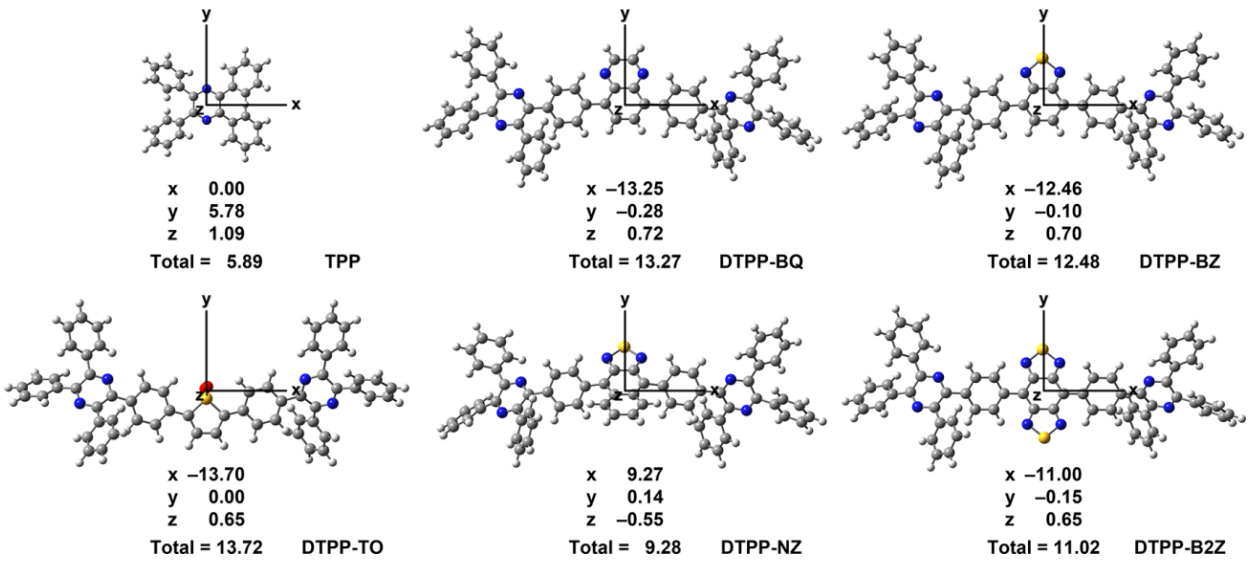

Fig. S2 Electric transition dipole moment values (in Debye) for TPP and its derivatives at their S_1-optimized geometries in solution.

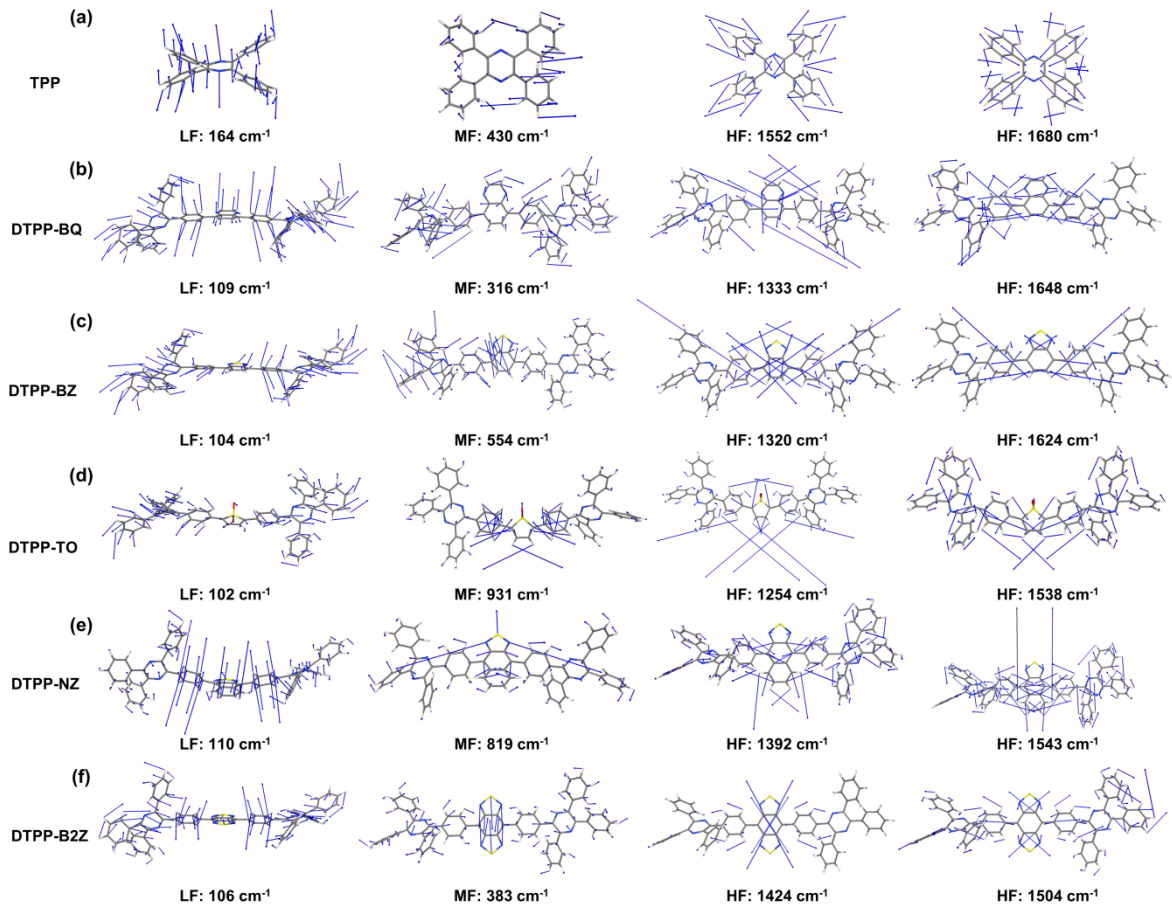

Fig. S3 Diagrammatic illustration of selected normal modes with major λ_j in LF, MF and HF regions for TPP and its derivatives in solution.

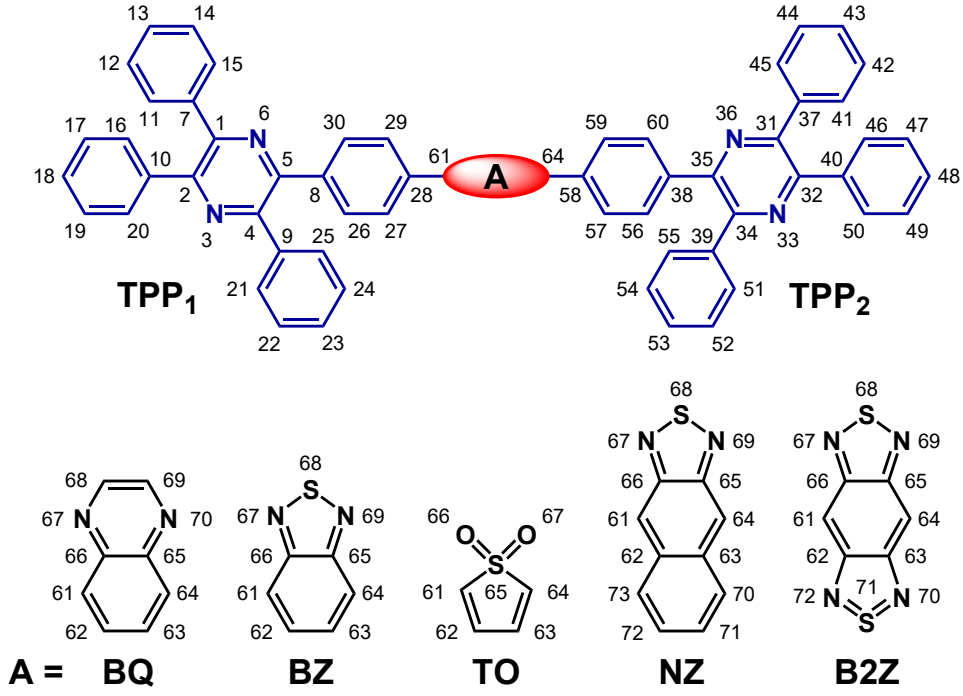

Fig. S4 Molecular structures of TPP derivatives with the labeled atom index.

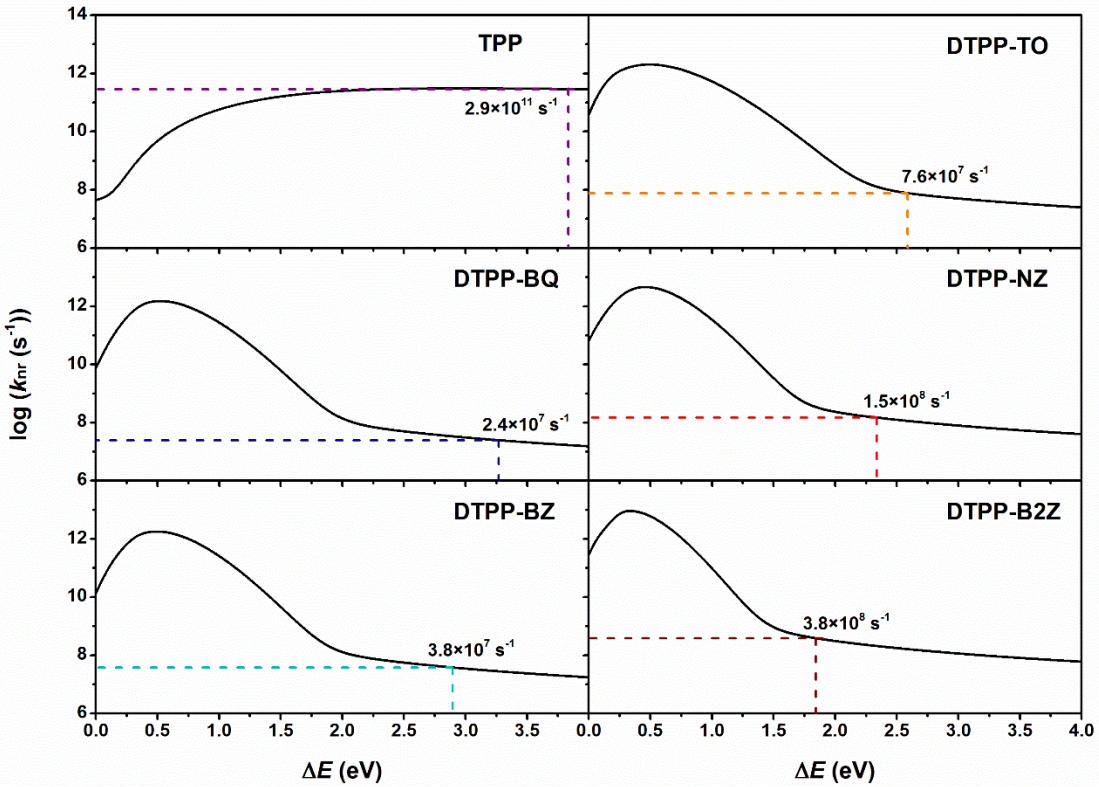

Fig. S5 Calculated logarithm of the non-radiative decay rate log (k_{nr}) *versus* the energy gap ΔE for TPP and its derivatives in solution. The vertical dash line indicates the position of the adiabatic energy gap ΔE_{ad}.

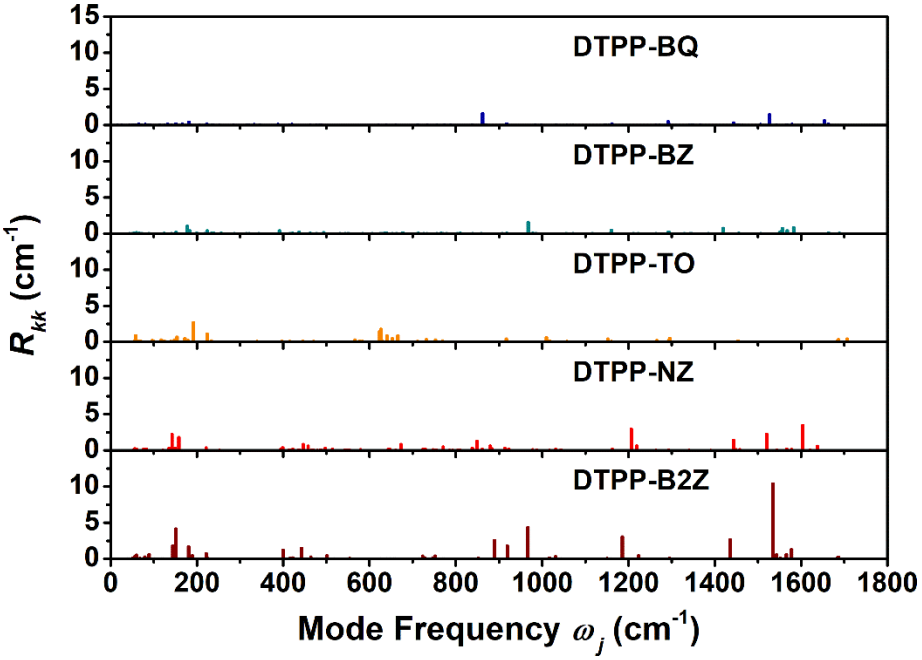

Fig. S6 Diagonal elements R_{kk} of the electronic coupling matrix R_{kl} *versus* mode frequency ω_j for TPP derivatives in solution.

Table S1 Calculated SOC constants between S_1 and low triplet excited states (T_1, T_2, T_3) for TPP derivatives (all at S_1-optimized geometries) at the CAM-B3LYP/6-31G(d) level.

$\langle S_1 \quad \lvert\hat{H}_{SOC}\rvert \quad T_n\rangle$	T_1	T_2	T_3
DTPP-BQ	0.04	0.13	0.16
DTPP-BZ	0.07	0.12	0.09
DTPP-TO	0.00	0.06	0.07
DTPP-NZ	0.00	0.07	0.19
DTPP-B2Z	0.00	0.16	0.15

Table S2 Selected dihedral angles (in deg.) for TPP and its derivatives in solution. S_0/S_1 and Δ represent the geometric parameters extracted from the optimized S_0/S_1 states and the modifications between the two states, respectively.

	S_0	S_1	Δ	S_0	S_1	Δ	S_0	S_1	Δ
	TPP			DTPP-BQ			DTPP-BZ		
1 -	44.05	36.26	7.79	37.42	36.02	1.40	37.18	35.98	1.20
2 -	44.06	36.26	7.80	37.25	32.85	4.40	36.80	34.01	2.79
3 -	–44.04	–15.29	28.75	37.95	34.46	3.49	37.59	35.15	2.43
4 -	–44.06	–15.29	28.77	36.03	25.51	10.52	35.73	27.36	8.37
1′-	—	—	—	37.01	36.49	0.52	37.12	36.44	0.69
2′-	—	—	—	37.28	33.55	3.73	37.15	33.83	3.32
3′-	—	—	—	36.91	34.52	2.38	37.41	34.97	2.44
4′-	—	—	—	36.53	27.56	8.97	36.44	28.00	8.43
5 -	—	—	—	–42.56	–24.78	17.78	–35.34	–17.47	17.87
5′-	—	—	—	42.95	25.79	17.16	36.07	17.12	18.95
	DTPP-TO			DTPP-NZ			DTPP-B2Z		
1 -	37.15	35.97	1.18	37.54	36.74	0.80	37.02	36.21	0.81
2 -	36.88	32.98	3.90	37.03	35.50	1.53	36.71	34.20	2.51
3 -	37.64	34.91	2.73	37.78	36.97	0.81	37.16	35.47	1.69
4 -	35.02	26.35	8.67	36.59	31.32	5.27	34.97	29.12	5.85
1′-	37.18	35.92	1.26	37.25	36.83	0.42	37.33	36.55	0.78
2′-	36.79	33.01	3.78	37.03	35.84	1.19	36.94	34.90	2.04
3′-	37.39	34.86	2.53	36.99	36.53	0.46	37.12	35.70	1.42
4′-	35.13	26.52	8.61	36.90	32.22	4.68	36.19	30.81	5.38
5 -	–20.26	–2.60	17.66	–56.64	–38.99	17.65	–39.16	–28.68	10.48
5′-	18.65	2.02	16.63	57.48	39.93	17.55	39.39	28.95	10.44

Table S3 Calculated vertical transition energies ΔE_{vert} related to absorption (Abs.) and emission (Emi.) peaks as well as available experimental (Exp.) values (in eV and nm), oscillator strengths f and HONTO→LUNTO (H→L) components for TPP and its derivatives in solution.

		ΔE_{vert}	Exp.	f	H→L
TPP	Abs.	4.22 (294)	3.67 (338)	0.62	96.9%
	Emi.	3.17 (391)	3.18 (390)	0.42	97.8%
DTPP-BQ	Abs.	3.61 (343)	N. A.	1.80	82.2%
	Emi.	2.79 (444)	N. A.	1.87	92.4%
DTPP-BZ	Abs.	3.22 (385)	3.08 (403)	1.31	93.8%
	Emi.	2.45 (506)	2.44 (509)	1.45	96.3%
DTPP-TO	Abs.	2.94 (422)	2.91 (426)	1.56	94.0%
	Emi.	2.08 (596)	2.34 (529)	1.49	97.0%
DTPP-NZ	Abs.	2.61 (475)	N. A.	0.53	98.7%
	Emi.	1.91 (649)	N. A.	0.62	99.5%
DTPP-B2Z	Abs.	2.04 (608)	N. A.	0.68	99.5%
	Emi.	1.56 (795)	N. A.	0.72	99.9%

Table S4 Bond lengths with large relaxation energies (>1 meV) for TPP and its derivatives in solution.

TPP	meV	DTPP-BQ	meV	DTPP-BZ	meV
PRZ		**BQ**		**BZ**	
C4-C5	46.21	C61-C62	23.13	C62-C63	35.43
C1-C2	44.64	C63-C64	22.82	C63-C64	30.68
C2-N3	1.11	C62-C63	22.07	C61-C62	30.42
C1-N6	1.10	N67-C68	12.83	N67-S68	12.30
Junction		C68-C69	12.65	S68-N69	12.06
C4-C9	30.59	C69-N70	12.38	**Junction**	
C5-C8	30.53	C61-C66	1.64	C28-C61	16.40
C1-C7	7.40	C64-C65	1.56	C58-C64	15.52
C2-C10	7.38	**Junction**		**TPP**	
Phenyl		C28-C61	19.92	C28-C29	4.49
C9-C25	8.99	C58-C64	16.96	C5-C8	4.42
C8-C26	8.97	**TPP**		C27-C28	4.19
C9-C21	5.97	C5-C8	7.21	C58-C59	4.04
C8-C30	5.97	C28-C29	5.42	C57-C58	4.02
C28-C29	3.98	C35-C38	5.11	C35-C38	3.88
C22-C23	3.98	C27-C28	4.79	C8-C26	2.24
C29-C30	2.44	C58-C59	4.54	C38-C56	2.06
C21-C22	2.44	C57-C58	3.89	C26-C27	2.06
C7-C11	2.14	C8-C26	3.42	C56-C57	1.89
C10-C16	2.13	C26-C27	2.65	C8-C30	1.78
C7-C15	1.69	C38-C56	2.59	C29-C30	1.76
C10-C20	1.68	C8-C30	2.51	C38-C60	1.57
		C29-C30	2.36	C59-C60	1.57
		C56-C57	2.08	C1-C2	1.04
		C38-C60	1.93		
		C59-C60	1.75		
		C1-C2	1.61		
		C4-C5	1.23		
		C31-C32	1.22		
DTPP-TO		DTPP-NZ		DTPP-B2Z	
TO		**NZ**		**B2Z**	
C62-C63	73.42	N67-S68	18.89	N67-S68	11.50
C61-C62	53.77	S68-N69	18.63	S71-N72	11.47
C63-C64	53.43	C71-C72	16.92	S68-N69	11.33
C64-S65	4.10	C61-C62	13.31	N70-S71	11.32
C61-S65	3.96	C63-C64	13.09	C64-C65	4.58
S65-O66	1.51	C72-C73	12.08	C61-C62	4.53
S65-O67	1.24	C70-C71	11.94	C63-C64	4.50
Junction		C62-C73	6.28	C61-C66	4.39

C58-C64	19.07	C63-C70	6.18	C62-N72	3.30
C28-C61	19.01	C62-C63	5.45	C66-N67	3.28
TPP		C61-C66	1.91	C63-N70	3.28
C5-C8	5.76	C64-C65	1.74	C65-N69	3.26
C35-C38	5.64	**Junction**		**Junction**	
C28-C29	5.14	C28-C61	8.84	C28-C61	7.95
C58-C59	5.03	C58-C64	8.21	C58-C64	7.45
C27-C28	4.71	**TPP**		**TPP**	
C57-C58	4.56	C27-C28	1.32	C28-C29	1.97
C38-C60	2.98	C28-C29	1.26	C58-C59	1.83
C8-C30	2.93	C57-C58	1.08	C27-C28	1.77
C29-C30	2.49	C58-C59	1.06	C5-C8	1.70
C59-C60	2.48			C57-C58	1.63
C8-C26	1.74			C35-C38	1.36
C38-C56	1.71				
C26-C27	1.52				
C56-C57	1.46				
C34-C35	1.14				
C4-C5	1.11				
C1-C2	1.10				
C31-C32	1.07				

Table S5 Bond angles with large relaxation energies (>1 meV) for TPP and its derivatives in solution.

TPP	meV	DTPP-BQ	meV	DTPP-BZ	meV
Junction		**Junction**		**BZ**	
N3-C4-C9	2.46	C58-C64-C63	1.01	N67-S68-N69	4.85
N6-C5-C8	2.46			**Junction**	
C4-C5-C8	1.26			C28-C61-C62	2.17
C5-C4-C9	1.26			C58-C64-C63	2.09
C4-C9-C21	1.19				
C5-C8-C30	1.19				
Phenyl					
C21-C9-C25	1.07				
C26-C8-C30	1.07				
DTPP-TO		DTPP-NZ		DTPP-B2Z	
TO		**NZ**		**B2Z**	
O66-S65-O67	5.35	N67-S68-N69	11.60	N67-S68-N69	12.93
C61-S65-O66	1.05	C66-C65-N69	1.99	N70-S71-N72	12.88
C64-S65-O67	1.02	C65-C66-N67	1.95	C62-C61-C66	2.57
C63-C64-S65	1.00	C71-C72-C73	1.16	C63-C64-C65	2.50
Junction		C70-C71-C72	1.15	C65-C66-N67	1.32
C58-C64-C63	1.57			C63-C62-N72	1.30
C28-C61-C62	1.45			C62-C63-N70	1.27
TPP				C66-C65-N69	1.26
C27-C28-C29	1.01				

Table S6 Dihedral angles with large relaxation energies (>1 meV) for TPP and its derivatives in solution.

TPP	meV	DTPP-BQ	meV	DTPP-BZ	meV
PRZ		**Junction**		**Junction**	
N3-C4-C5-N6	3.67	C57-C58-C64-C63	19.06	C27-C28-C61-C66	14.40
C4-N3-C2-C10	2.04	C29-C28-C61-C62	18.99	C29-C28-C61-C66	14.05
C5-N6-C1-C7	2.04	C27-C28-C61-C62	18.85	C27-C28-C61-C62	13.81
N3-C2-C1-N6	1.37	C59-C58-C64-C63	18.66	C29-C28-C61-C62	13.52
Phenyl		C29-C28-C61-C66	17.98	C57-C58-C64-C65	12.29
C4-C5-C8-C26	54.14	C27-C28-C61-C66	17.91	C59-C58-C64-C65	11.98
C5-C4-C9-C25	54.11	C57-C58-C64-C65	17.70	C57-C58-C64-C63	11.63
C6-C5-C8-C26	50.99	C59-C58-C64-C65	17.26	C59-C58-C64-C63	11.33
C3-C4-C9-C25	50.96	**TPP**		**TPP**	
C4-C5-C8-C30	38.65	C6-C5-C8-C26	6.78	C6-C5-C8-C26	3.72
C5-C4-C9-C21	38.60	C6-C5-C8-C30	6.52	C36-C35-C38-C60	3.51
C6-C5-C8-C30	37.37	C4-C5-C8-C26	4.58	C36-C35-C38-C56	3.19
C3-C4-C9-C21	37.33	C36-C35-C38-C60	4.48	C6-C5-C8-C30	3.08
C1-C2-C10-C16	9.80	C4-C5-C8-C30	4.23	C34-C35-C38-C60	2.39
C2-C1-C7-C11	9.79	C36-C35-C38-C56	4.18	C4-C5-C8-C26	2.19
C1-C2-C10-C20	8.57	C34-C35-C38-C60	3.04	C34-C35-C38-C56	2.14
C2-C1-C7-C15	8.56	C34-C35-C38-C56	2.83	C4-C5-C8-C30	1.50
C3-C2-C10-C20	4.61				
C6-C1-C7-C15	4.60				
C3-C2-C10-C16	4.57				
C6-C1-C7-C11	4.55				
DTPP-TO		DTPP-NZ		DTPP-B2Z	
TO		**NZ**		**Junction**	
C28-C61-S65-O67	1.56	C28-C61-C62-C63	2.88	C57-C58-C64-C65	7.45
C31-C64-S65-O67	1.30	C62-C63-C64-C31	2.87	C57-C58-C64-C63	7.13
Junction		C28-C61-C66-C65	2.68	C59-C58-C64-C65	7.04
C27-C28-C61-C65	7.24	C28-C61-C62-C73	2.55	C59-C58-C64-C63	6.72
C27-C28-C61-C62	6.87	C70-C63-C64-C31	2.55	C27-C28-C61-C66	6.70
C29-C28-C61-C65	5.78	C31-C64-C65-C66	2.43	C29-C28-C61-C66	6.67
C57-C58-C64-C65	5.55	C69-C65-C66-C61	1.20	C27-C28-C61-C62	6.45
C29-C28-C61-C62	5.53	C28-C61-C66-C67	1.12	C29-C28-C61-C62	6.42
C57-C58-C64-C63	5.20	C66-C61-C62-C63	1.09	**TPP**	
C59-C58-C64-C65	4.25	C62-C61-C66-C65	1.09	C6-C5-C8-C26	1.98
C59-C58-C64-C63	4.00	C62-C63-C64-C65	1.06	C6-C5-C8-C30	1.92
TPP		**Junction**		C36-C35-C38-C60	1.51
C36-C35-C38-C60	4.63	C29-C28-C61-C62	22.81	C36-C35-C38-C56	1.40
C36-C35-C38-C56	3.87	C59-C58-C64-C63	21.99	C4-C5-C8-C26	1.36
C34-C35-C38-C60	3.38	C27-C28-C61-C62	20.42	C4-C5-C8-C30	1.28
C6-C5-C8-C26	3.32	C29-C28-C61-C66	19.84	C34-C35-C38-C60	1.08

C6-C5-C8-C30	2.96	C57-C58-C64-C63	19.44
C34-C35-C38-C56	2.73	C59-C58-C64-C65	19.13
C4-C5-C8-C26	2.18	C27-C28-C61-C66	17.62
C4-C5-C8-C30	1.79	C57-C58-C64-C65	16.74
		TPP	
		C36-C35-C38-C56	1.46
		C34-C35-C38-C56	1.03
		C36-C35-C38-C60	1.02