Supplementary Information

Structure-Property Relationship Study of Blue Thermally Activated Delayed Fluorescence Molecules with Different donor and position substitutions: Theoretical Perspective and Molecular Design

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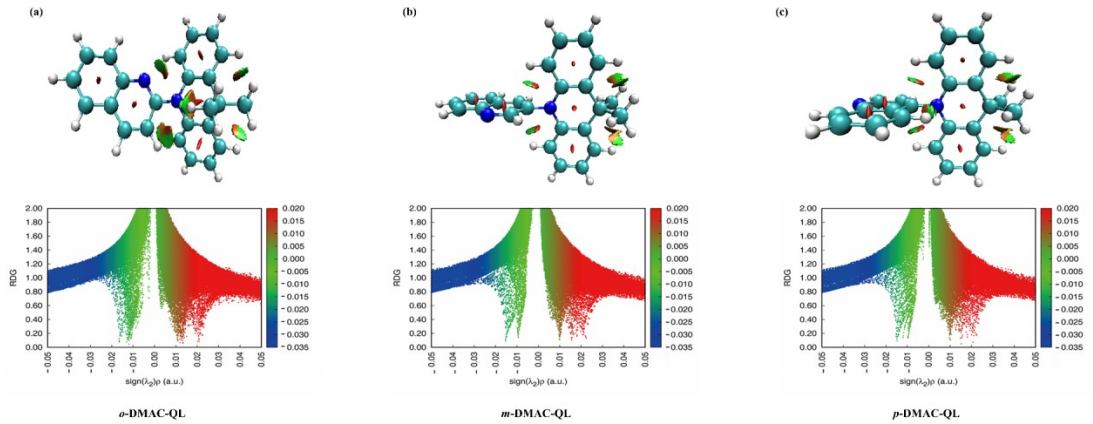

Figure S1. Reduced density gradient (RDG) isosurface maps (upper) and scatter graphs (lower) of RDG versus sign(λ_2) ρ(a.u.) of *o*-DMAC-QL, *m*-DMAC-QL and *p*-DMAC-QL.

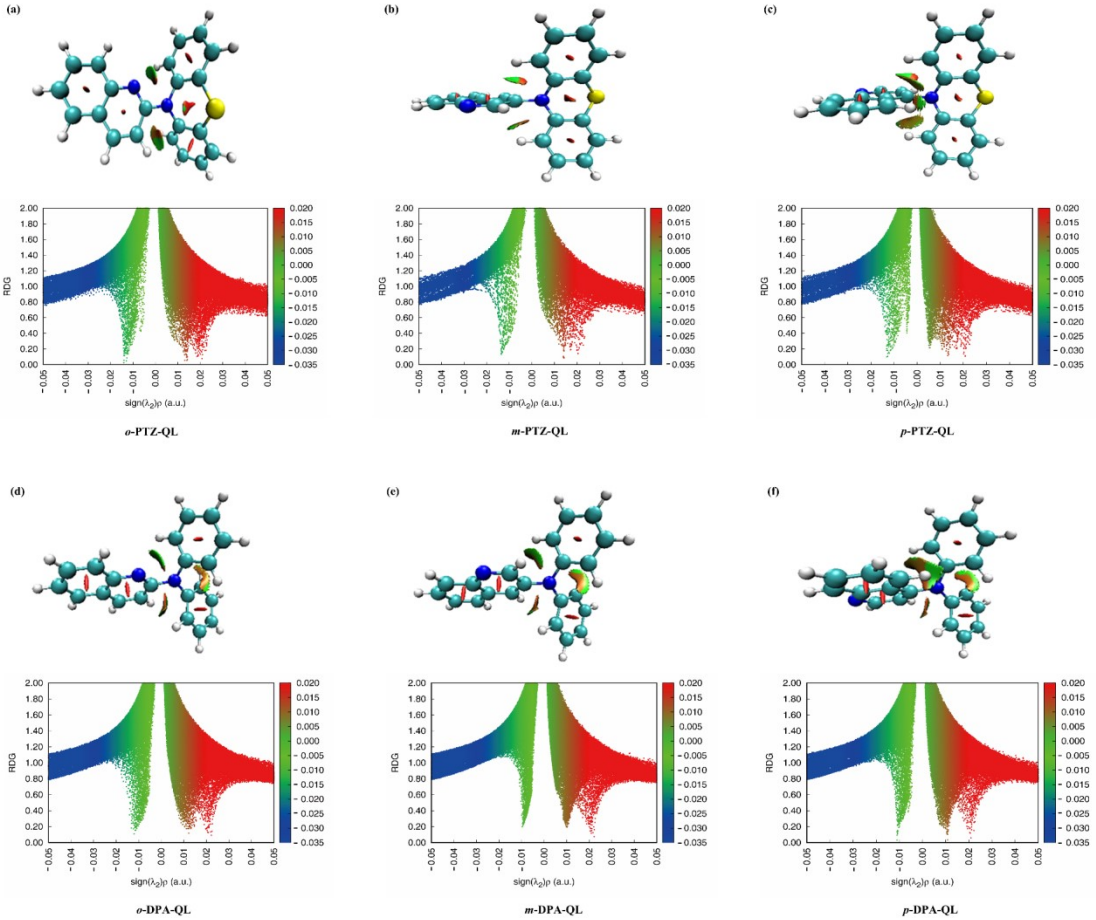

Figure S2. Reduced density gradient (RDG) isosurface maps (upper) and scatter graphs (lower) of RDG versus sign(λ_2) ρ(a.u.) of *o*-PTZ-QL, *m*-PTZ-QL, *p*-PTZ-QL, *o*-DPA-QL, *m*-DPA-QL and *p*-DPA-QL.

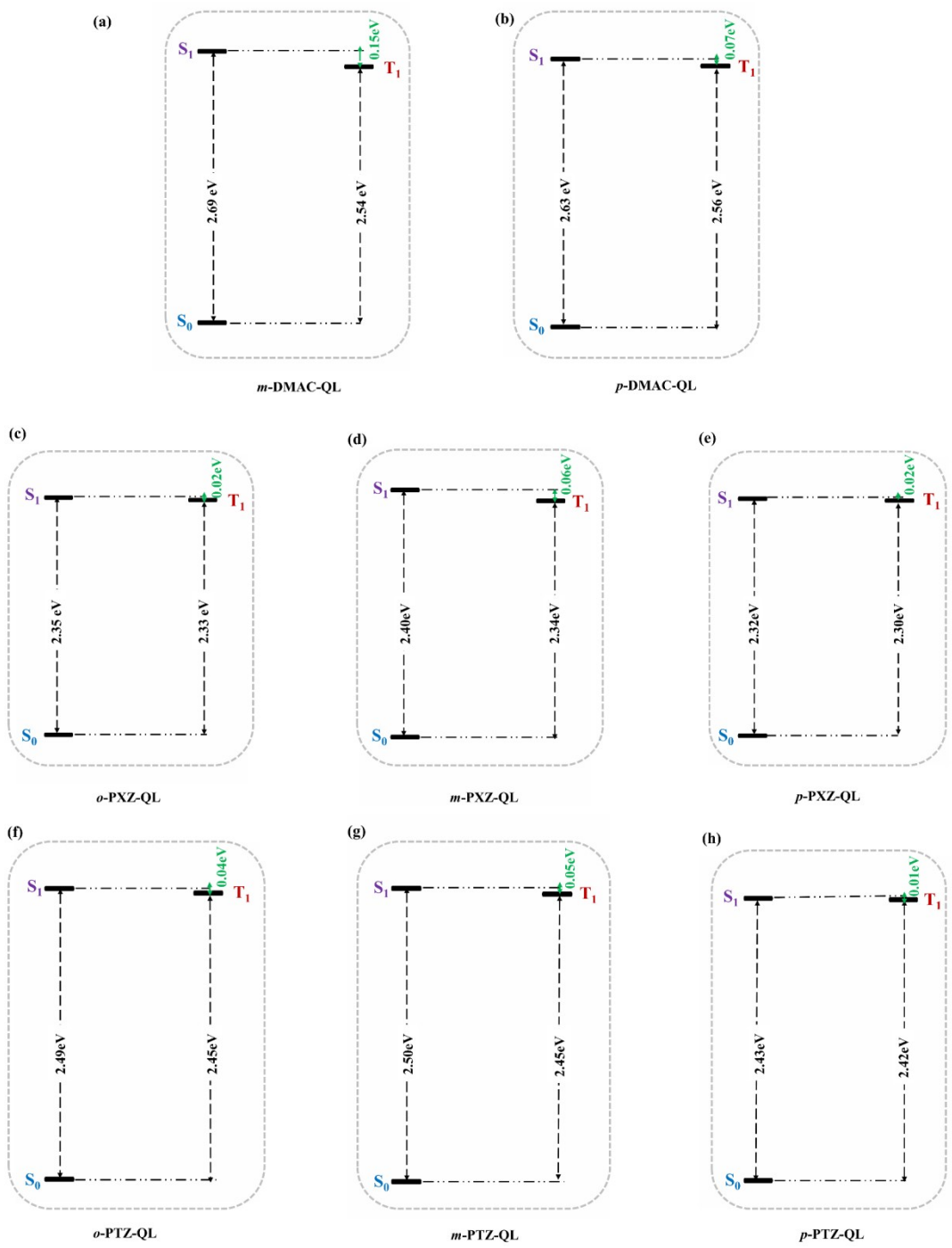

Figure S3. Adiabatic excitation energies for *m*-DMAC-QL, *p*-DMAC-QL, *o*-PXZ-QL, *m*-PXZ-QL, *p*-PXZ-QL, *o*-PTZ-QL, *m*-PTZ-QL and *p*-PTZ-QL in tetrahydrofuran, respectively.

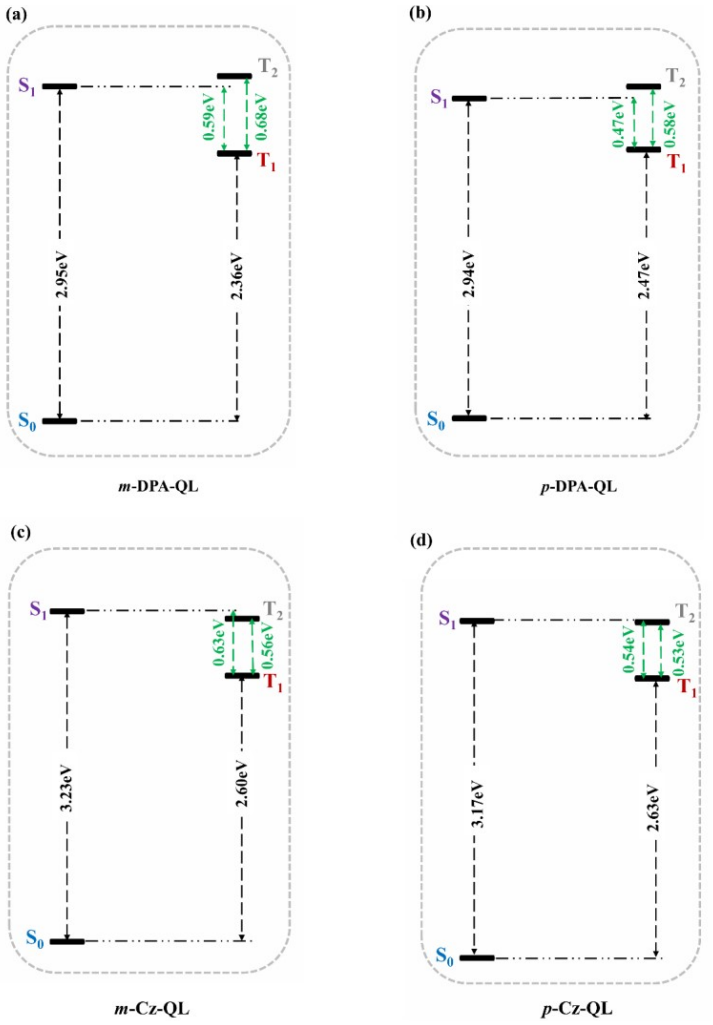

Figure S4. Adiabatic excitation energies for *m*-DPA-QL, *p*-DPA-QL, *m*-Cz-QL and *p*-Cz-QL, respectively.

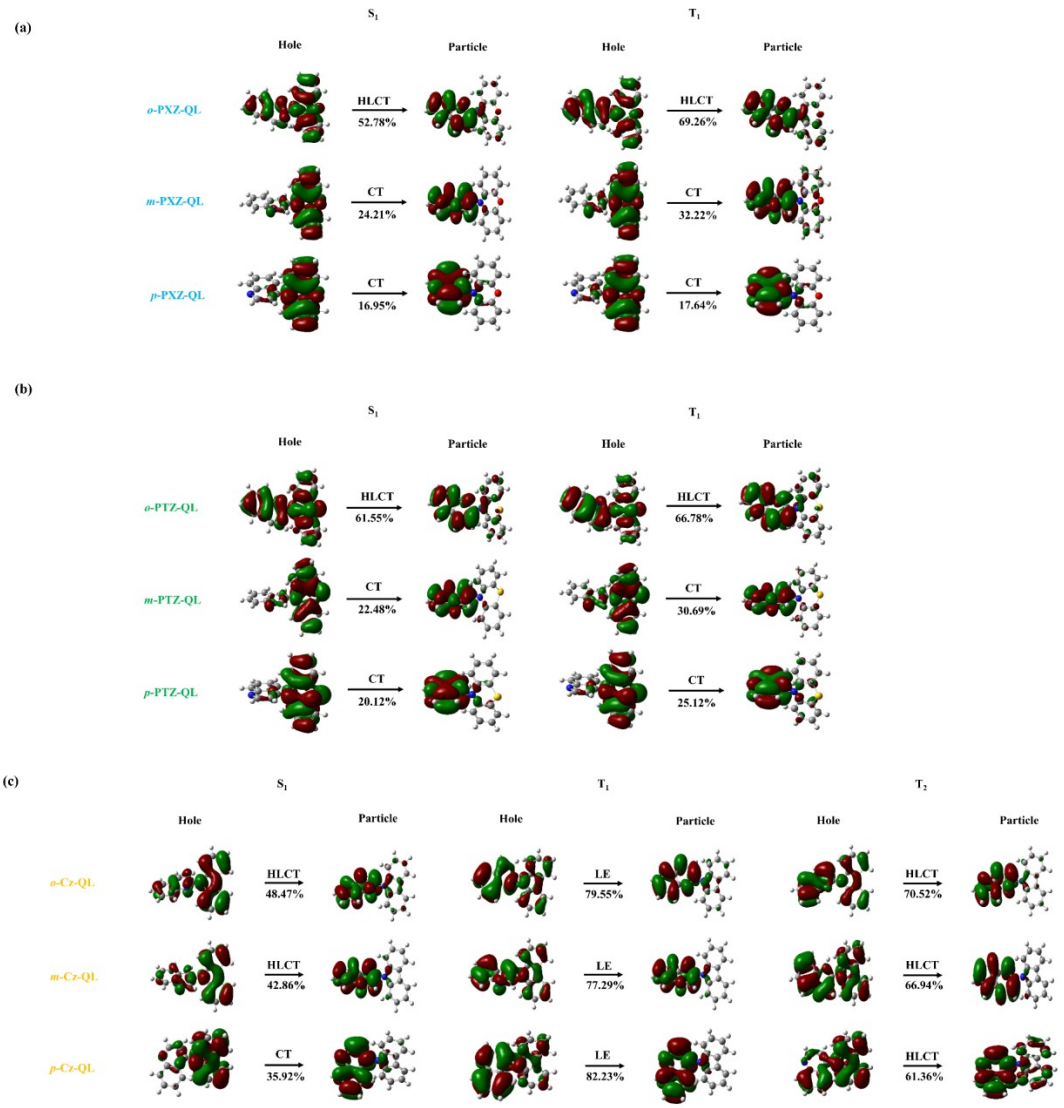

Figure S5. Natural transition orbitals (NTOs) of the S_1 and T_n states for *o*-PXZ-QL, *m*-PXZ-QL, *p*-PXZ-QL, *o*-PTZ-QL, *m*-PTZ-QL, *p*-PTZ-QL, *o*-Cz-QL, *m*-Cz-QL and *p*-Cz-QL in tetrahydrofuran. The values below the arrows are the LE proportion in excitation.

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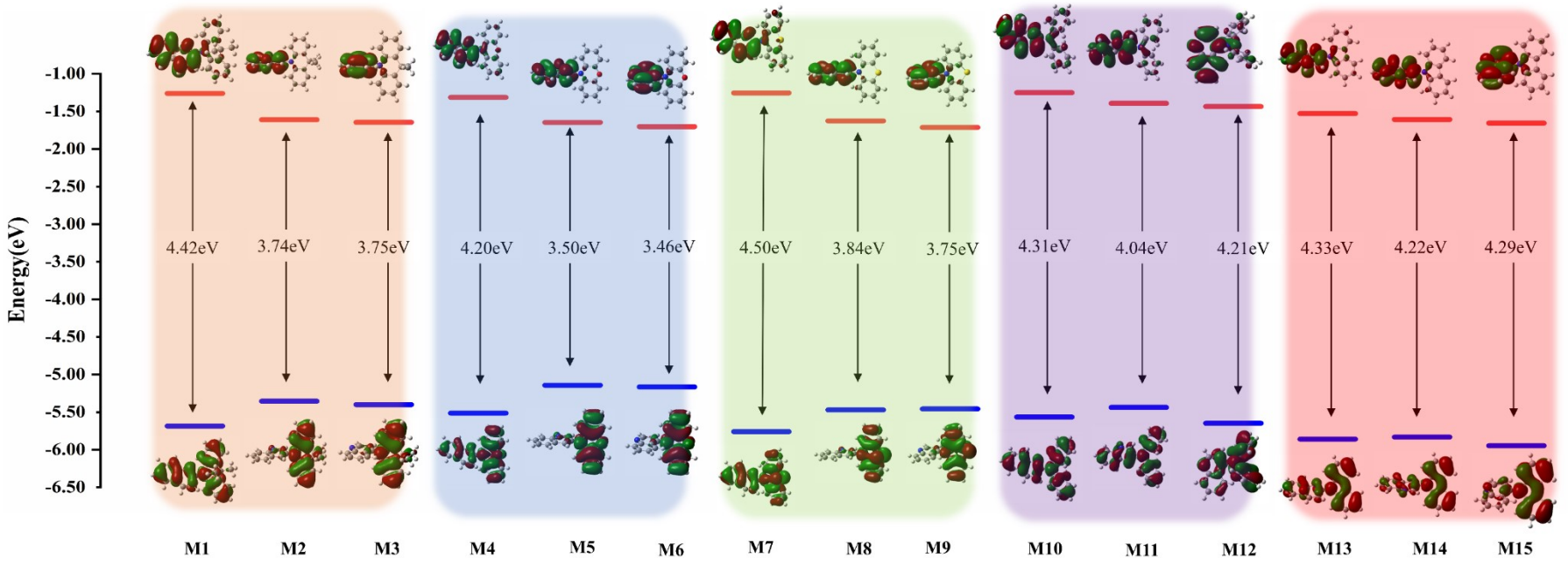

Figure S6. Energies and distributions of HOMO (blue lines) and LUMO (red lines) for all molecules in tetrahydrofuran.

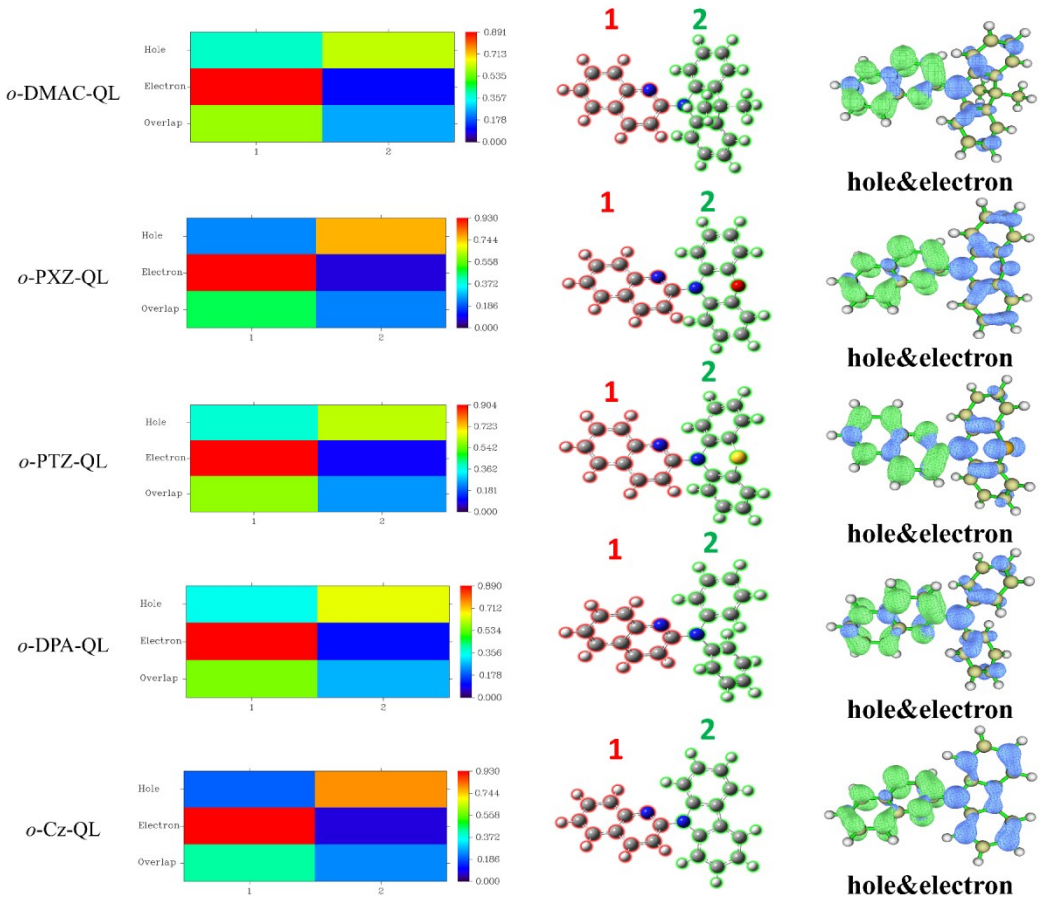

Figure S7. Isosurface distributions of holes and electrons and heat map of the S_1 state for *o*-DMAC-QL, *o*-PXZ-QL, *o*-PTZ-QL, *o*-DPA-QL and *o*-Cz-QL in tetrahydrofuran.

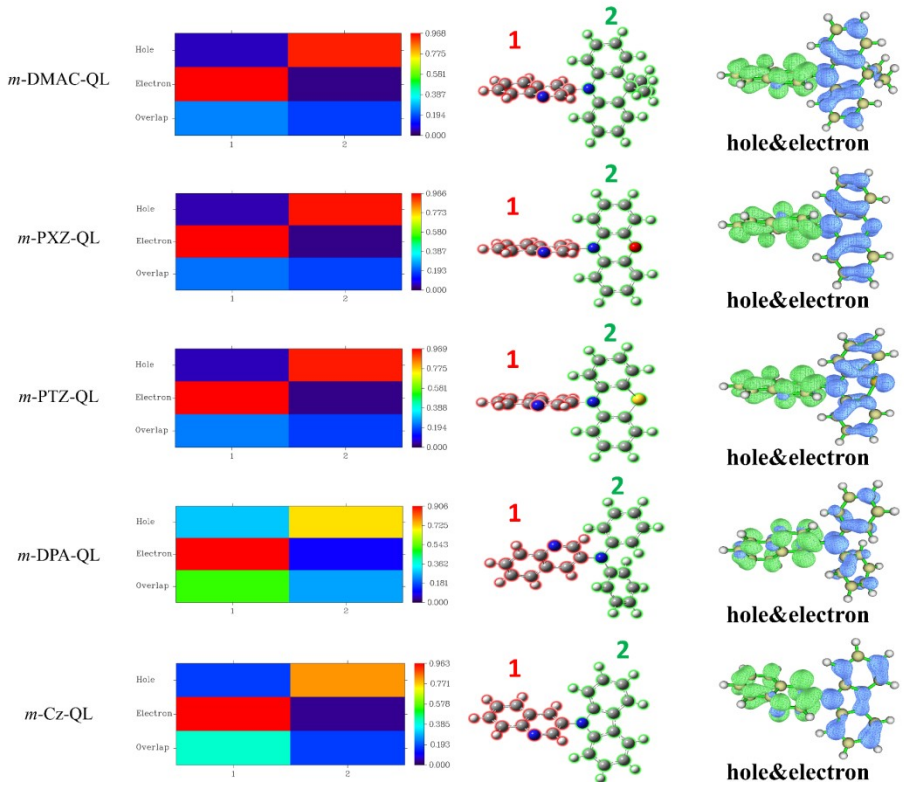

Figure S8. Isosurface distributions of holes and electrons and heat map of the S_1 state for *m*-DMAC-QL, *m*-PXZ-QL, *m*-PTZ-QL, *m*-DPA-QL and *m*-Cz-QL in tetrahydrofuran.

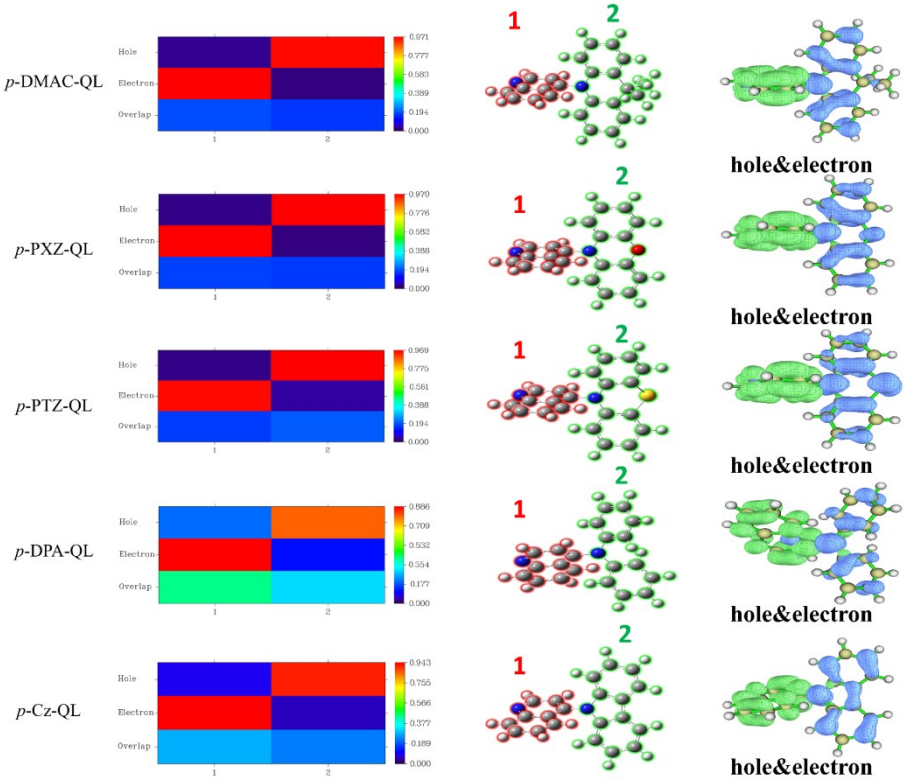

Figure S9. Isosurface distributions of holes and electrons and heat map of the S_1 state for *p*-DMAC-QL, *p*-PXZ-QL, *p*-PTZ-QL, *p*-DPA-QL and *p*-Cz-QL in tetrahydrofuran.

Table S1. Orbital energies of HOMO and LUMO, energy gaps (ε_{gap}) and overlaps (S).

	HOMO (eV)	LUMO (eV)	ε_{gap} (eV)	S
***o*-DMAC-QL**	-5.68	-1.26	4.42	0.61
***m*-DMAC-QL**	-5.35	-1.61	3.74	0.21
***p*-DMAC-QL**	-5.40	-1.64	3.75	0.15
***o*-PXZ-QL**	-5.51	-1.31	4.20	0.52
***m*-PXZ-QL**	-5.14	-1.65	3.50	0.21
***p*-PXZ-QL**	-5.16	-1.70	3.46	0.15
***o*-PTZ-QL**	-5.76	-1.25	4.50	0.60
***m*-PTZ-QL**	-5.47	-1.63	3.84	0.20
***p*-PTZ-QL**	-5.46	-1.71	3.75	0.17
***o*-DPA-QL**	-5.56	-1.25	4.31	0.60
***m*-DPA-QL**	-5.44	-1.39	4.04	0.61
***p*-DPA-QL**	-5.65	-1.43	4.21	0.58
***o*-Cz-QL**	-5.86	-1.53	4.33	0.47
***m*-Cz-QL**	-5.83	-1.61	4.22	0.42
***p*-Cz-QL**	-5.95	-1.66	4.29	0.37

The ε_{gap} and S are the energy gap and the orbital overlap integral between the HOMO and LUMO, respectively.

Table S2. The LE proportion in excitation and the difference of LE components between S_1 and T_n states for total 15 molecules.

	S_1	T_1	T_2	Difference between T_1-S_1	Difference between T_2-S_1
***o*-DMAC-QL**	60.71%	75.47%	\	14.75%	\
***m*-DMAC-QL**	24.22%	29.97%	\	5.74%	\
***p*-DMAC-QL**	17.54%	19.02%	\	1.48%	\
***o*-PXZ-QL**	52.78%	69.26%	\	16.48%	\
***m*-PXZ-QL**	24.21%	32.22%	\	8.01%	\
***p*-PXZ-QL**	16.95%	17.64%	\	0.69%	\
***o*-PTZ-QL**	61.55%	66.78%	\	5.23%	\
***m*-PTZ-QL**	22.48%	30.69%	\	8.21%	\
***p*-PTZ-QL**	20.12%	25.12%	\	4.99%	\
***o*-DPA-QL**	60.47%	74.26%	82.99%	13.79%	22.52%
***m*-DPA-QL**	59.28%	76.07%	77.28%	16.79%	18.00%
***p*-DPA-QL**	55.41%	77.62%	75.51%	22.21%	20.09%
***o*-Cz-QL**	48.47%	79.55%	70.52%	31.08%	22.05%
***m*-Cz-QL**	42.86%	77.29%	66.94%	34.43%	24.08%
***p*-Cz-QL**	35.92%	82.23%	61.36%	46.31%	25.44%

Table S3. Calculated intersystem crossing rates (K_{ISC}) and reverse intersystem crossing rates (K_{RISC}) between the singlet and triplet excited states of all molecules.

	K_{ISC} ($S_1 \rightarrow T_1$) (s^{-1})	K_{ISC} ($S_1 \rightarrow T_2$) (s^{-1})	K_{RISC} ($T_1 \rightarrow S_1$) (s^{-1})	K_{RISC} ($T_2 \rightarrow S_1$) (s^{-1})
***o*-DMAC-QL**	1.75×10^4		8.84×10^6	
***m*-DMAC-QL**	3.34×10^6		6.09×10^5	
***p*-DMAC-QL**	2.88×10^5		2.18×10^7	
***o*-PXZ-QL**	6.08×10^4		3.30×10^8	
***m*-PXZ-QL**	2.44×10^6		2.47×10^7	
***p*-PXZ-QL**	5.38×10^5		1.23×10^8	
***o*-PTZ-QL**	8.52×10^4		1.04×10^5	
***m*-PTZ-QL**	5.45×10^6		2.54×10^6	
***p*-PTZ-QL**	7.85×10^5		4.48×10^6	
***o*-DPA-QL**	3.13×10^7	1.04×10^7	1.41×10^1	1.07×10^7
***m*-DPA-QL**	1.72×10^7	7.07×10^5	2.16×10^{-2}	3.18×10^8
***p*-DPA-QL**	1.52×10^8	6.85×10^4	2.41×10^0	1.64×10^7
***o*-Cz-QL**	3.77×10^6	2.85×10^8	2.04×10^0	8.14×10^5
***m*-Cz-QL**	9.83×10^6	2.59×10^8	7.84×10^{-4}	1.89×10^7
***p*-Cz-QL**	3.69×10^7	4.33×10^5	7.27×10^{-3}	2.11×10^5

Table S4. Total reorganization energies between S_1 and S_0 of 15 molecules in tetrahydrofuran.

	Reorganization energy (cm^{-1})
***o*-DMAC-QL**	16093.94

***m*-DMAC-QL**	1492.42
***p*-DMAC-QL**	1490.64
***o*-PXZ-QL**	10171.06
***m*-PXZ-QL**	2071.93
***p*-PXZ-QL**	1827.46
***o*-PTZ-QL**	17080.32
***m*-PTZ-QL**	4407.28
***p*-PTZ-QL**	3019.29
***o*-DPA-QL**	5838.92
***m*-DPA-QL**	2818.24
***p*-DPA-QL**	4660.44
***o*-Cz-QL**	1994.44
***m*-Cz-QL**	1457.75
***p*-Cz-QL**	1978.16

Table S5. Calculated spin–orbit coupling constants (in cm $^{-1}$) between the S_0 and T_1 for all molecules in tetrahydrofuran (THF).

	$\langle S_0 \vert \hat{H}_{so} \vert T_1 \rangle$			
	X-component (cm $^{-1}$)	**Y-component (cm $^{-1}$)**	**Z-component (cm $^{-1}$)**	**Total (cm $^{-1}$)**
***o*-DMAC-QL**	2.78	-1.36	1.79	3.57
***m*-DMAC-QL**	1.54	-1.36	-2.27	3.06
***p*-DMAC-QL**	1.46	-1.03	-1.14	1.92
***o*-PXZ-QL**	1.87	1.06	-2.48	3.28
***m*-PXZ-QL**	-1.61	1.59	-2.43	3.32
***p*-PXZ-QL**	-1.93	-3.00	0.48	2.02
***o*-PTZ-QL**	-2.27	-9.62×10^{-4}	2.28	3.21
***m*-PTZ-QL**	1.19	5.61×10^{-4}	-2.85	3.09
***p*-PTZ-QL**	-1.03	-1.98×10^{-4}	5.99	1.12
***o*-DPA-QL**	2.31	0.84	0.80	2.59
***m*-DPA-QL**	-1.14	-1.03	-1.14	1.92
***p*-DPA-QL**	-1.15	0.26	0.16	1.19
***o*-Cz-QL**	-0.67	-0.92	0.86	1.43
***m*-Cz-QL**	-1.23	1.05	1.19	2.00
***p*-Cz-QL**	-0.53	0.33	-0.17	0.65

Table S6. Electric emission transition dipole moments of total 15 molecules.

	μ（Debye）
***o*-DMAC-QL**	0.28

***m*-DMAC-QL**	0.29
***p*-DMAC-QL**	0.07
***o*-PXZ-QL**	0.04
***m*-PXZ-QL**	0.06
***p*-PXZ-QL**	0.05
***o*-PTZ-QL**	0.13
***m*-PTZ-QL**	0.20
***p*-PTZ-QL**	0.05
***o*-DPA-QL**	2.45
***m*-DPA-QL**	2.99
***p*-DPA-QL**	2.20
***o*-Cz-QL**	2.77
***m*-Cz-QL**	2.37
***p*-Cz-QL**	0.04