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

Supporting information

Theoretical Design and Performance Prediction of Deep-red/Near-infrared Thermally Activated Delayed Fluorescent Molecules with Through Space Charge Transfer

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In order to analyze TSCT ratio quantitatively, the non-relaxation part of charge transfer should be determined by analyzing the hole-electron distribution for excited molecule. This CT ratio is analyzed by inter-fragment charge transfer (IFCT) method, achieved by following function:

$$Q_{R,S} = \Theta_{R,hole}\Theta_{S,ele}$$

Here $Q_{R,S}$ means the charge transfer quantity, $\Theta_{R,hole}$ is the excited electron occupied by part R, $\Theta_{S,ele}$ represents the arrived electron occupied by part S, then pure amount of electron transfer can be calculated by following formula:

$$p_{S\to R} = Q_{S,R} - Q_{R,S}$$

$$\Delta p_R = \sum_{s \neq R} Q_{S,R} - Q_{R,S}$$

Where, $p_{S\to R}$ represents the pure amount of electron transfer of two parts, Δp_R is the charge variation of one part. Based on these functions, the charge transfer ratio can be calculated quantitatively. Among these, the direct CT ratio between D-A can be regarded as through-space CT, the CT ratios of D-π and π-A are regard as through-bond CT.

However, if there is no spatial overlap between holes and electrons in one molecule, the transition is forbidden although with large charge transfer. In other words, this part of charge transfer does not contribute to the absorption or emission. So, what we concerned about is that the CT transition which can contribute to emission and absorption. To solve this issue, we analyze the transition density by the following function:

$$\rho_{TB} = \rho_{tot} - \rho_{TS}$$

Here, ρ_{tot} means the transition density integral of the whole molecule, and ρ_{TS} represents the transition density integral of the molecule with deleted π bridge, ρ_{TB} is then obtained. Following the abovementioned method, we should define the donor part, acceptor part and bridge part.

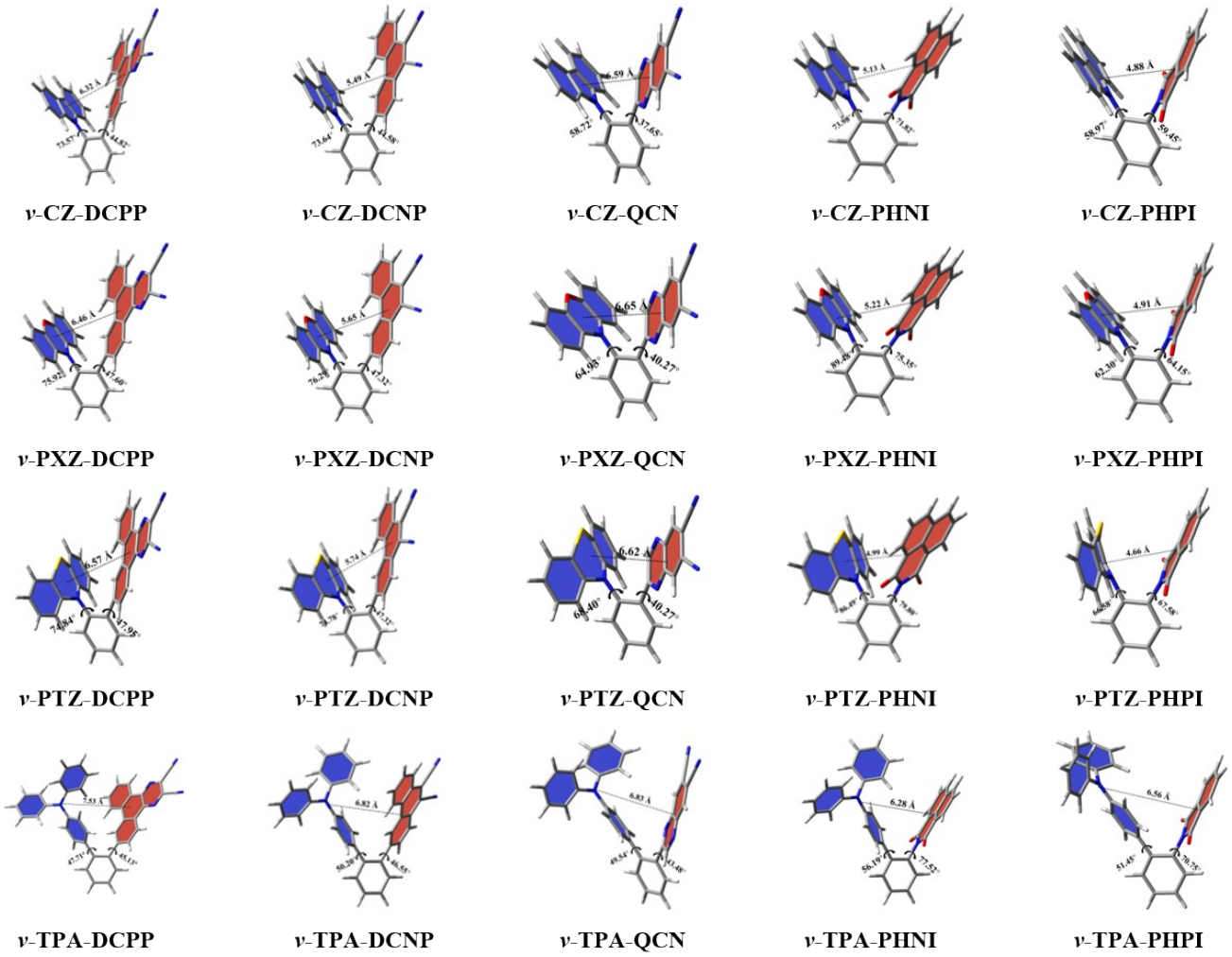

Figure S1. The geometric parameters of all *v*-shaped molecules in Toluene.

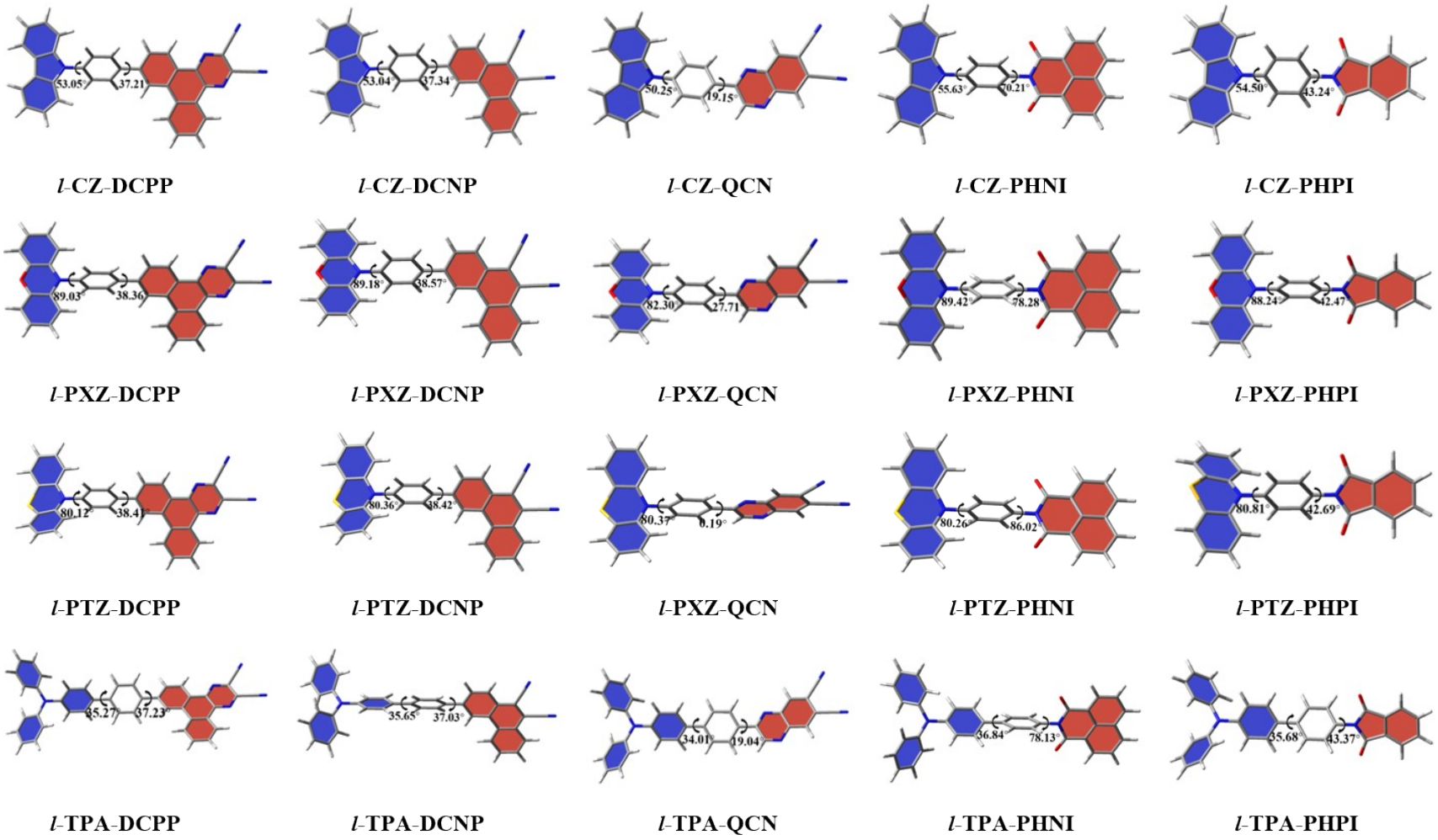

Figure S2. The geometric parameters of all *l*-shaped molecules in Toluene.

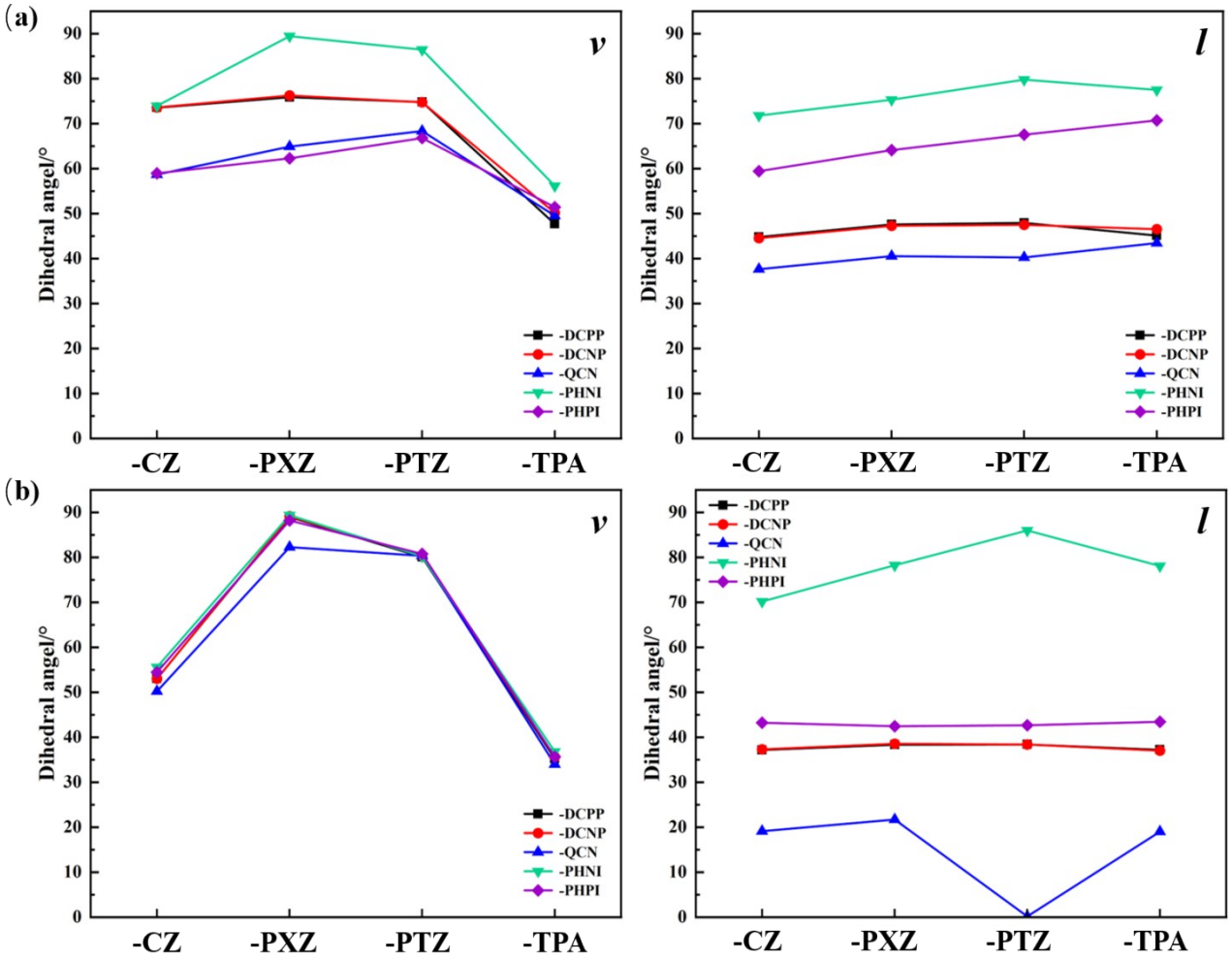

Figure S3. The dihedral angles of B and D (a), B and A (b) for all molecules in Toluene.

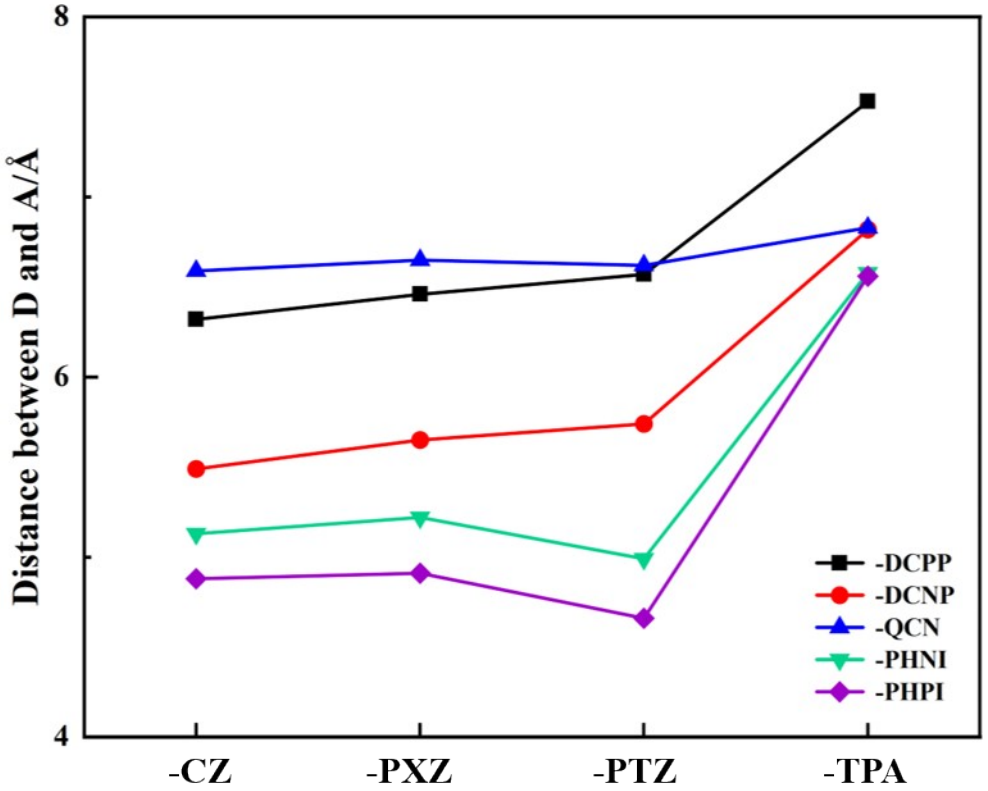

Figure S4. The Distance between D and A for all *v*-shaped molecules in Toluene.

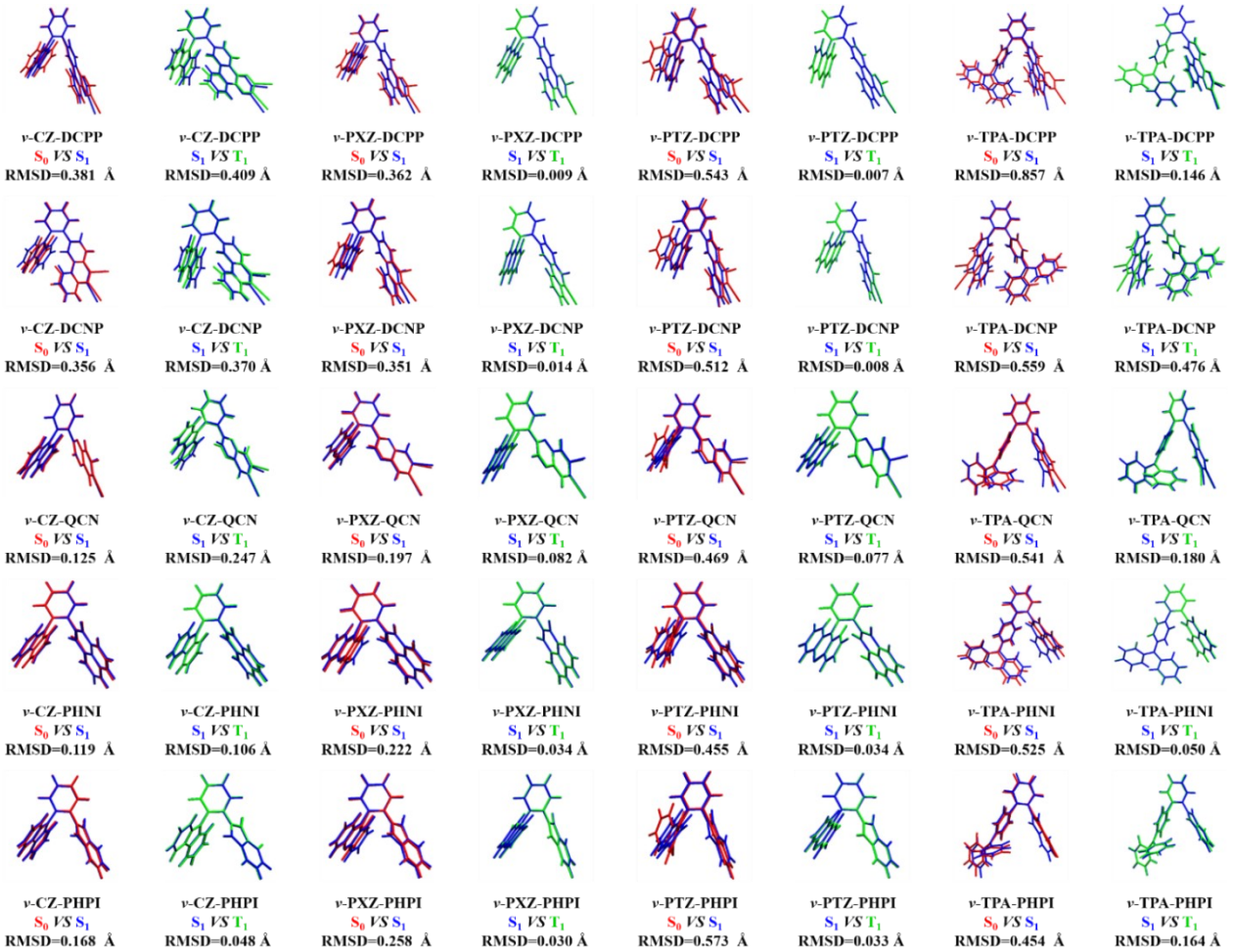

Figure S5. Geometry comparisons and RMSD values of all *v*-shaped molecules between S_0 (red), S_1 (blue), and T_1 (green) in Toluene, respectively.

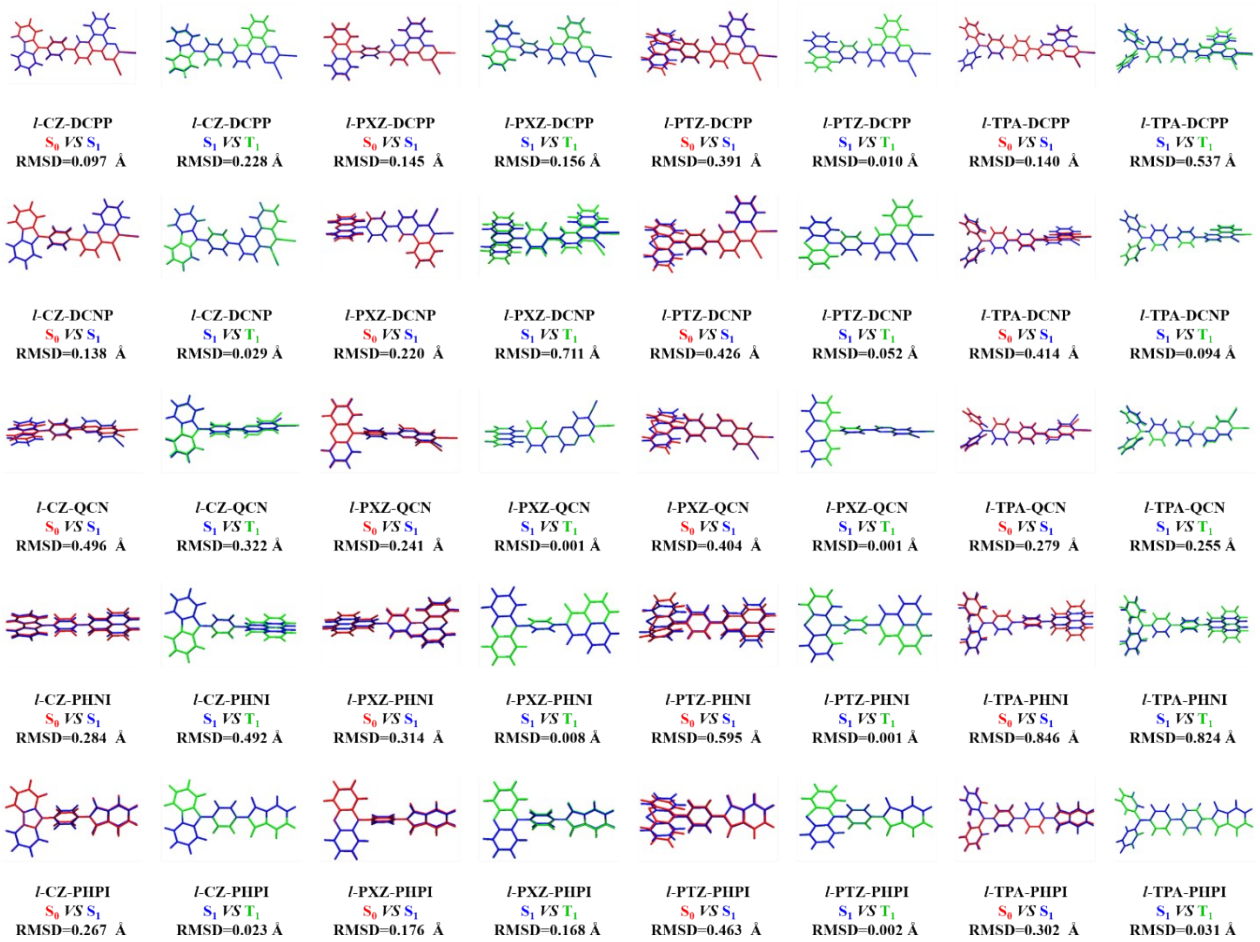

Figure S6. Geometry comparisons and RMSD values of all *l*-shaped molecules between S_0 (red), S_1 (blue), and T_1 (green) in Toluene, respectively.

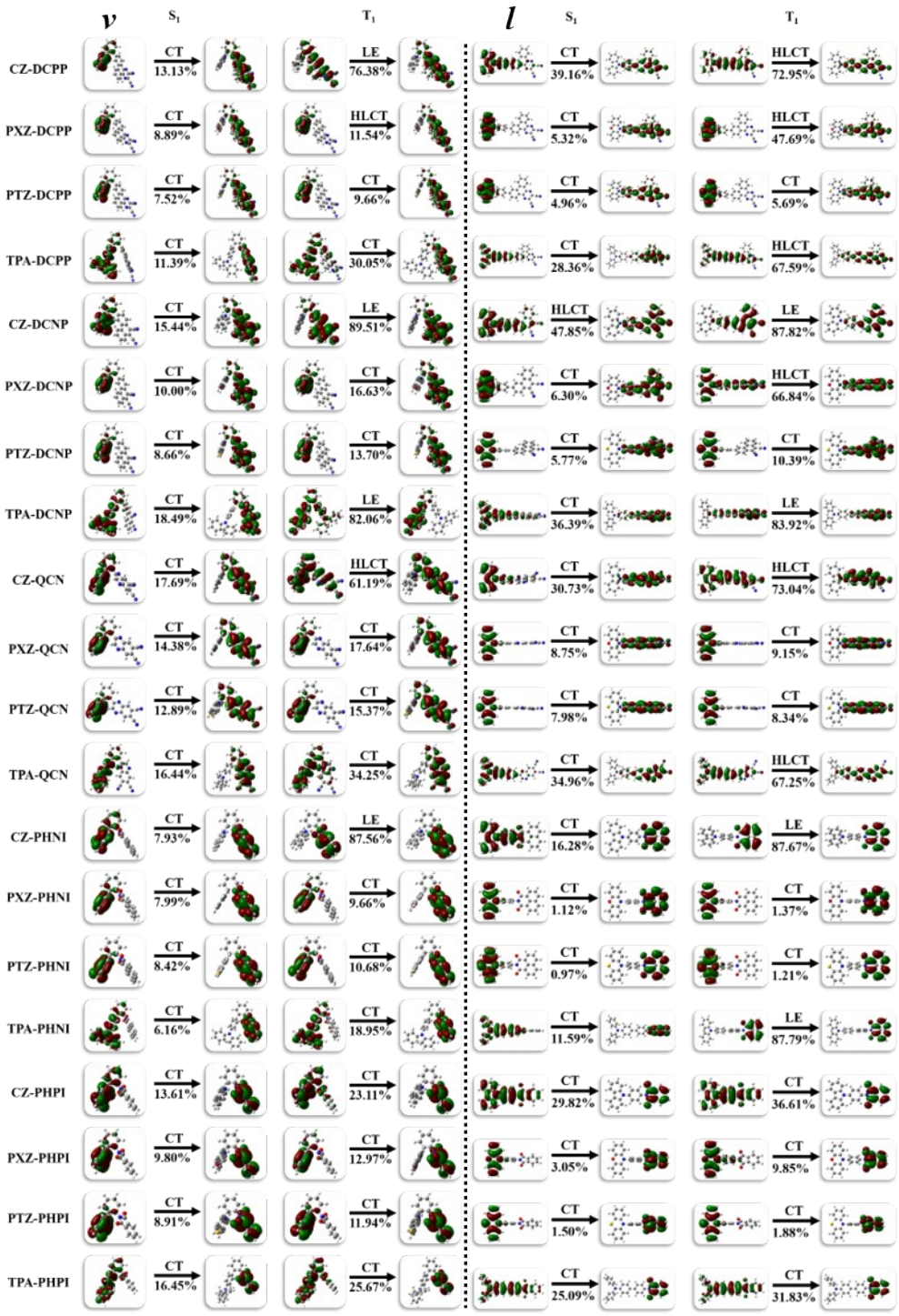

Figure S7. Natural transition orbitals (NTOs) of the S_1 and T_1 states for all *v*-shaped molecules and *l*-shaped molecules in Toluene, respectively.

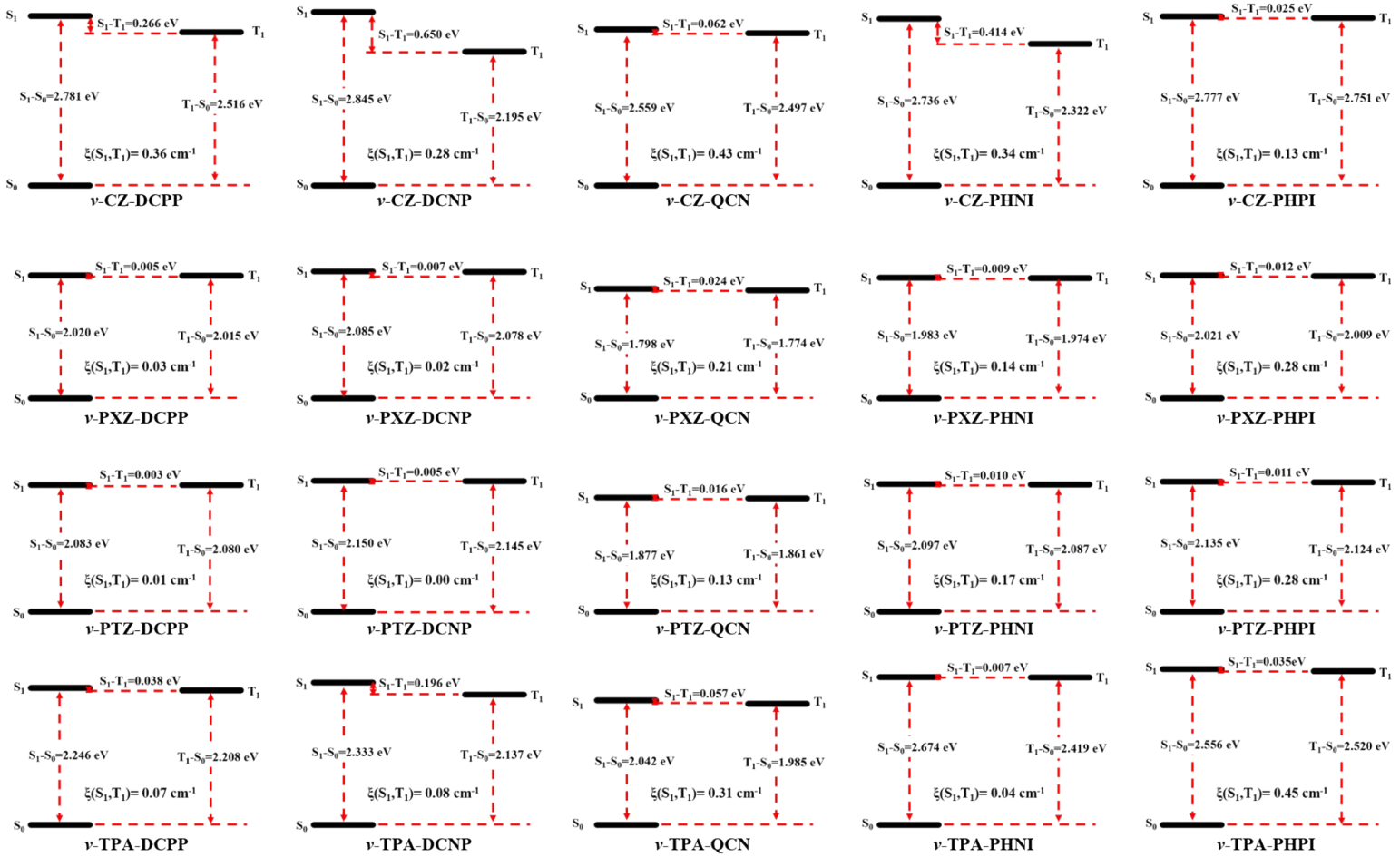

Figure S8. The energy levels of molecules of all *ν*-shaped molecules in Toluene.

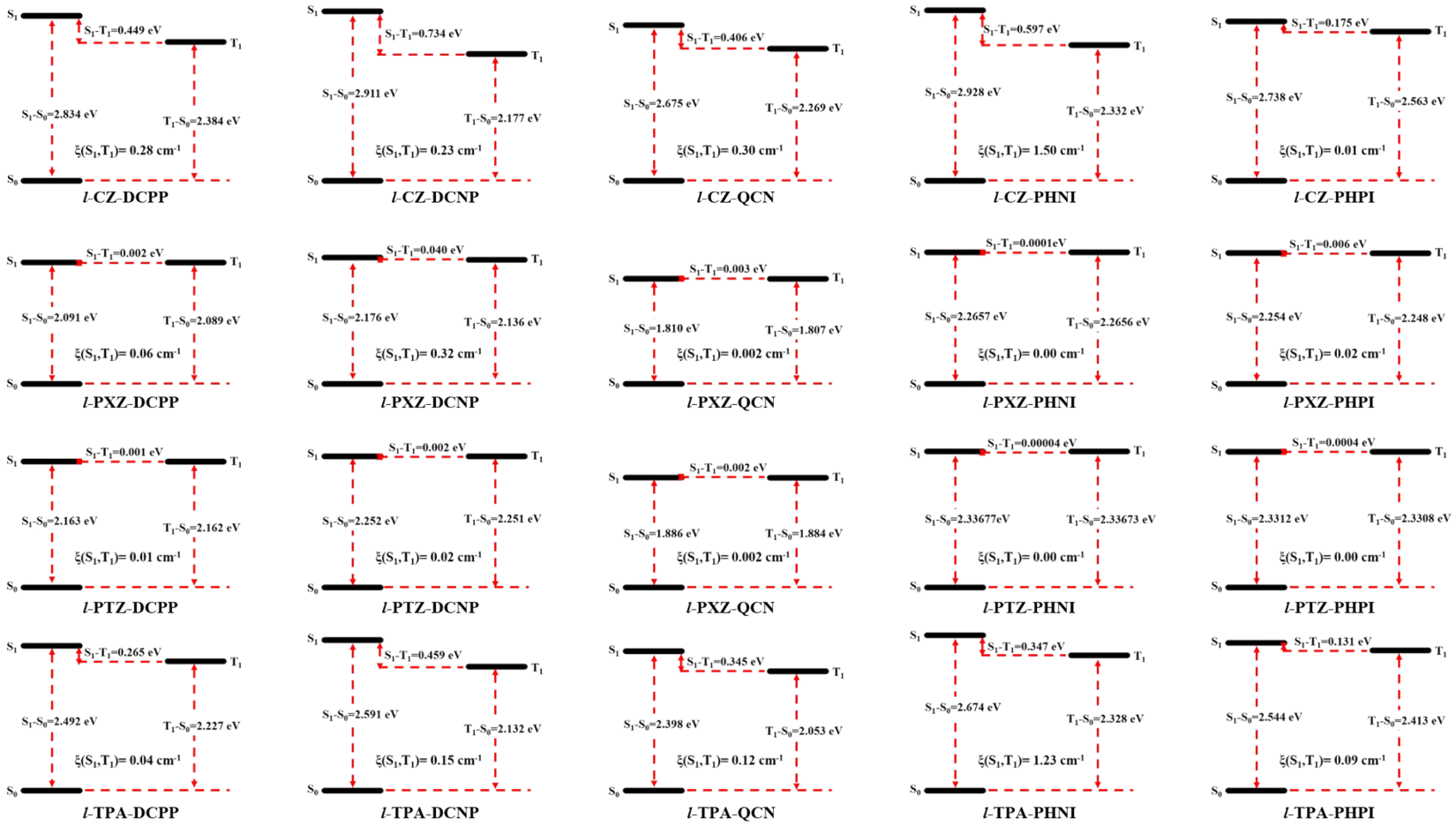

Figure S9. The energy levels of molecules of all *l*-shaped molecules in Toluene.

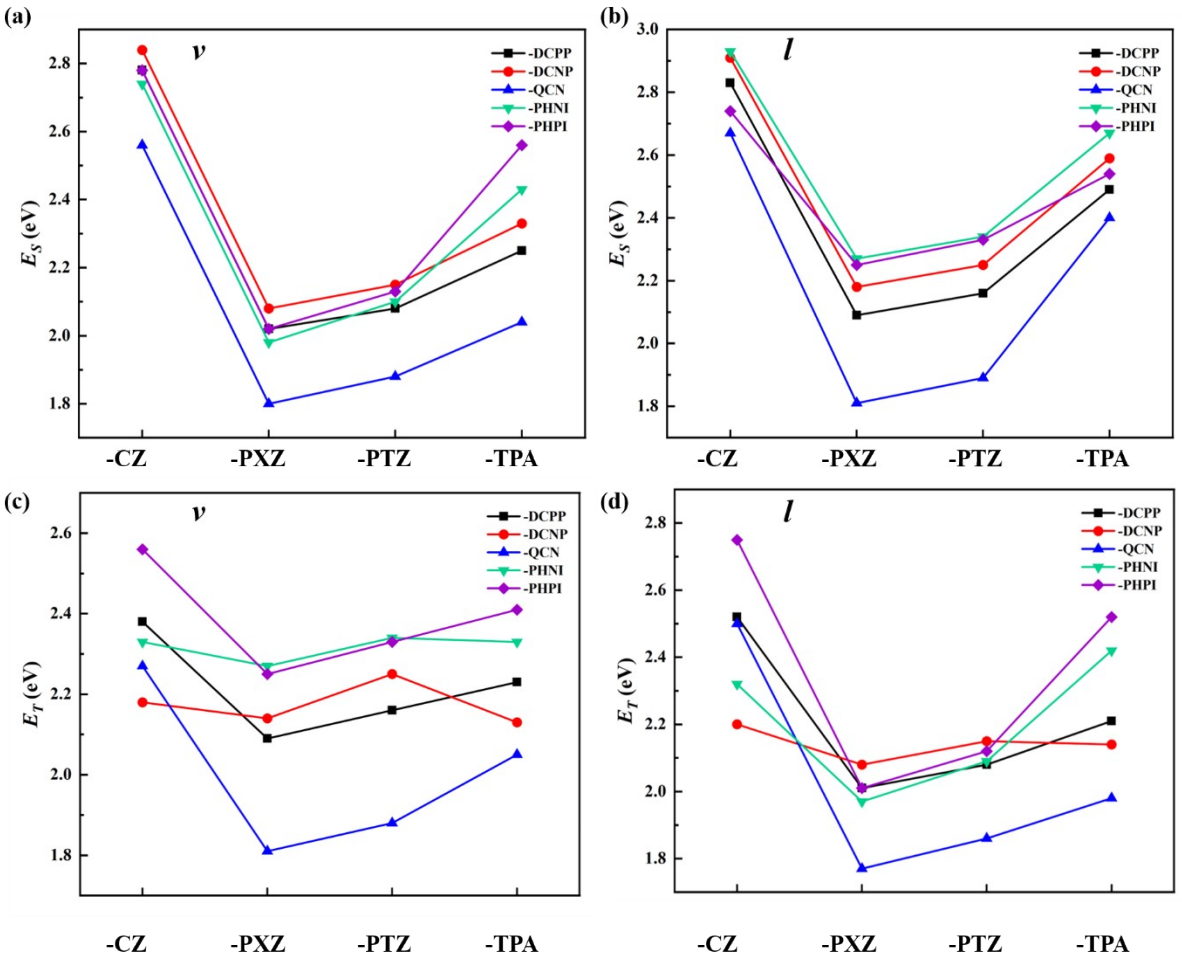

Figure S10. The S_1(a,b) and T_1(c,d) energies of all *v*-shaped molecules and *l*-shaped molecules in Toluene.

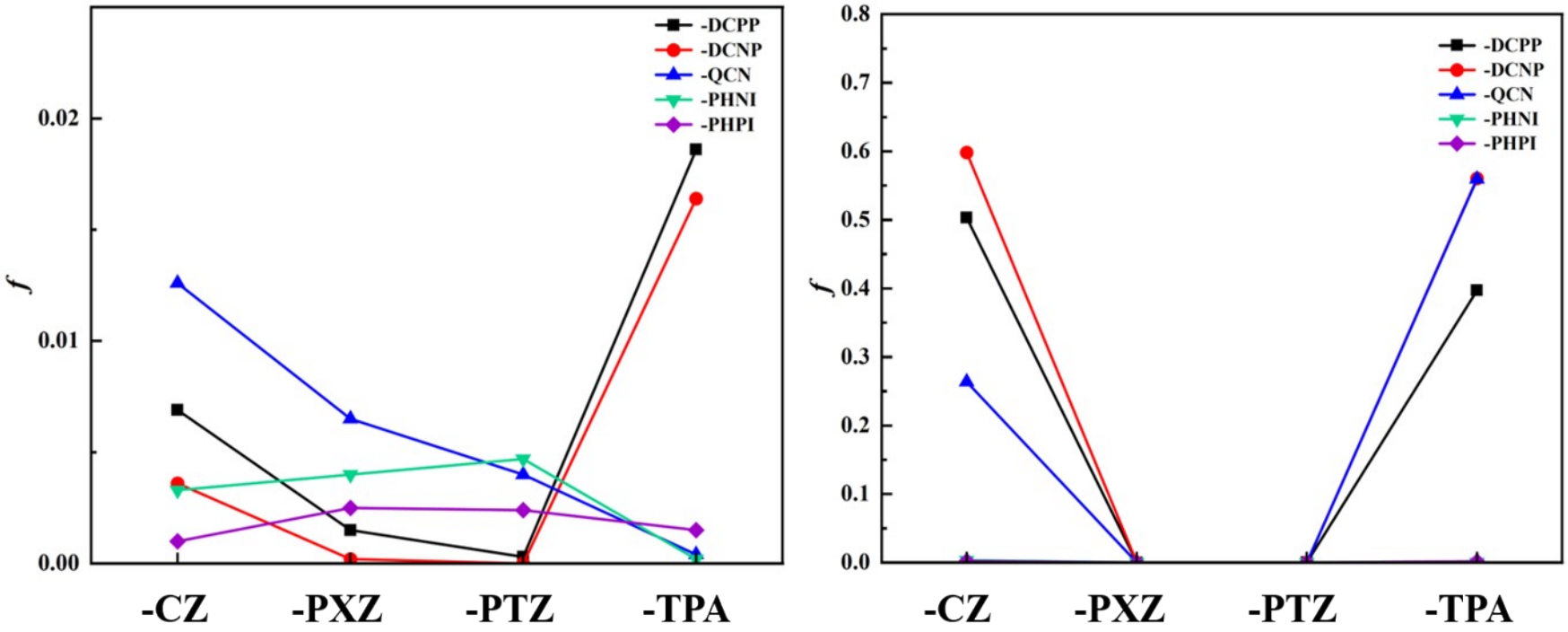

Figure S11. Oscillator strength (*f*) from S_1 to S_0 for all *v*-shaped molecules and *l*-shaped molecules in Toluene, respectively.

Table S1. The emission wavelengths (nm) of *v*-CZ-PHNI and *v*-CZ-PHPI calculated by different functionals and experimentally measured emission wavelengths in toluene.

	b3lyp	bmk	m062x	wb97xd	pbe0	pbe33	exp.
CZPHNI	646.04	471.69	427.72	414.55	581.05	503.56	517
CZPHPI	682.56	487.49	436.36	427.5	607.78	525.33	520

Table S2 Energy gap between S_1 and T_1 calculated with LC-WPBE with optimized w and PBE33.

	w	LC-WPBE (ΔE_{ST})	Pbe33 (ΔE_{ST})
v-CZ-DCPP	0.1801	0.623	0.266
v-PXZ-DCPP	0.1797	0.016	0.005
v-PTZ-DCPP	0.1774	0.011	0.003
v-TPA-DCPP	0.1726	0.094	0.038
v-CZ-DCNP	0.1841	0.965	0.650
v-PXZ-DCNP	0.1830	0.025	0.007
v-PTZ-DCNP	0.1807	0.018	0.005
v-TPA-DCNP	0.1751	0.544	0.196
v-CZ-QCN	0.1843	0.154	0.062
v-PXZ- QCN	0.1843	0.033	0.024
v-PTZ- QCN	0.1828	0.025	0.016
v-TPA- QCN	0.1843	0.193	0.057
v-CZ-PHNI	0.1945	0.789	0.414
v-PXZ- PHNI	0.1931	0.016	0.009
v-PTZ- PHNI	0.1913	0.019	0.010
v-TPA- PHNI	0.1848	0.253	0.007
v-CZ- PHPI	0.2024	0.084	0.025
v-PXZ- PHPI	0.2014	0.02	0.012
v-PTZ- PHPI	0.1994	0.019	0.011
v-TPA- PHPI	0.1957	0.117	0.035

Table S3. Geometric parameters of all *v*-shaped molecules in toluene.

	Dihedral angel/°		Distance between D and A/Å
	D-B	**A-B**	
v-CZ-DCPP	73.57	44.82	6.32
v-PXZ-DCPP	75.92	47.60	6.46
v-PTZ-DCPP	74.84	47.95	6.57
v-TPA-DCPP	47.71	45.13	7.53
v-CZ-DCNP	73.64	44.58	5.49
v-PXZ-DCNP	76.29	47.32	5.65
v-PTZ-DCNP	74.78	47.54	5.74
v-TPA-DCNP	50.20	46.55	6.82
v-CZ-QCN	58.72	37.65	6.59
v-PXZ-QCN	64.93	40.56	6.65
v-PTZ-QCN	68.40	40.27	6.62
v-TPA-QCN	49.54	43.48	6.83
v-CZ-PHNI	73.98	71.82	5.13
v-PXZ-PHNI	89.48	75.35	5.22
v-PTZ-PHNI	86.49	79.80	4.99
v-TPA-PHNI	56.19	77.52	6.58
v-CZ-PHPI	58.97	59.45	4.88
v-PXZ-PHPI	62.30	64.15	4.91
v-PTZ-PHPI	66.84	67.58	4.66
v-TPA-PHPI	51.45	70.75	6.56

Table S4. Geometric parameters of all *l*-shaped molecules in toluene.

	Dihedral angel/°	
	D-B	**A-B**
l-CZ-DCPP	53.05	37.21
l-PXZ-DCPP	89.03	38.36
l-PTZ-DCPP	80.12	38.41
l-TPA-DCPP	35.27	37.23
l-CZ-DCNP	53.04	37.34
l-PXZ-DCNP	89.18	38.57
l-PTZ-DCNP	80.36	38.42
l-TPA-DCNP	35.65	37.03
l-CZ-QCN	50.25	19.15
l-PXZ- QCN	82.30	21.71
l-PTZ- QCN	80.37	0.19
l-TPA- QCN	34.01	19.04
l-CZ-PHNI	55.63	70.21
l-PXZ- PHNI	89.42	78.28
l-PTZ- PHNI	80.26	86.02
l-TPA- PHNI	36.84	78.13
l-CZ- PHPI	54.50	43.24
l-PXZ- PHPI	88.24	42.47
l-PTZ- PHPI	80.81	42.69
l-TPA- PHPI	35.68	43.47

Table S5. Through space/bond CT transition densities between the donor and acceptor of all molecules based on optimized S_1 structures.

Molecule	Through space CT		Through bond CT		Total Density
	Density	Ratio	Density	Ratio	
v-CZ-DCPP	0.109	78.55%	0.030	21.44%	0.138
v-PXZ-DCPP	0.082	84.66%	0.015	15.33%	0.097
v-PTZ-DCPP	0.071	85.67%	0.012	14.32%	0.083
v-TPA-DCPP	0.155	93.42%	0.011	6.57%	0.166
v-CZ-DCNP	0.130	76.95%	0.039	23.04%	0.169
v-PXZ-DCNP	0.090	81.20%	0.021	18.79%	0.111
v-PTZ-DCNP	0.081	83.33%	0.016	16.66%	0.097
v-TPA-DCNP	0.188	88.07%	0.025	11.92%	0.213
v-CZ-QCN	0.173	78.79%	0.047	21.20%	0.220
v-PXZ- QCN	0.154	84.83%	0.028	15.16%	0.182
v-PTZ- QCN	0.138	85.91%	0.023	14.08%	0.161
v-TPA- QCN	0.149	84.67%	0.027	15.32%	0.176

Table S6. λ_{em} (nm) is the emission wavelength of all *l*-shaped molecules, E_S is the adiabatic energy of S_1 state, E_T is the adiabatic energy of T_1 state, and ΔE_{ST} is the adiabatic energy difference between S_1 state and T_1 state of the molecules, f is the vibration strength of the molecule in Toluene.

	λ (nm)	**E_S (eV)**	**E_T (eV)**	**ΔE_{ST} (eV)**	**f**
l-CZ-DCPP	463.78	2.83	2.38	0.499	0.5032
l-PXZ-DCPP	670.15	2.09	2.09	0.002	0
l-PTZ-DCPP	679.22	2.16	2.16	0.001	0.0002
l-TPA-DCPP	536.09	2.49	2.23	0.265	0.397
l-CZ-DCNP	451.73	2.91	2.18	0.734	0.5984
l-PXZ-DCNP	635.35	2.18	2.14	0.040	0
l-PTZ-DCNP	642.17	2.25	2.25	0.002	0.0001
l-TPA-DCNP	511.40	2.59	2.13	0.459	0.5606
l-CZ-QCN	469.52	2.67	2.27	0.406	0.2637
l-PXZ-QCN	785.47	1.81	1.81	0.003	0
l-PTZ-QCN	793.84	1.89	1.88	0.002	0
l-TPA-QCN	551.50	2.40	2.05	0.345	0.5597
l-CZ-PHNI	481.83	2.93	2.33	0.597	0.0033
l-PXZ-PHNI	628.68	2.27	2.27	0.0001	0
l-PTZ-PHNI	633.35	2.34	2.34	0.00004	0
l-TPA-PHNI	531.13	2.67	2.33	0.347	0.0018
l-CZ-PHPI	590.62	2.74	2.56	0.175	0.0022
l-PXZ-PHPI	688.96	2.25	2.25	0.006	0
l-PTZ-	694.87	2.33	2.33	0.0003	0

PHPI *l*-TPA-PHPI	639.02	2.54	2.41	0.131	0.0018

Table S7. Radiative and internal conversion rates from S_1 to S_0 as well as the ISC and RISC rates between S_1 and T_1 for all *l*-shaped molecules in Toluene.

	SOC_{T_1}(cm^{-1})	k_{ISC} (s^{-1})	k_{RISC} (s^{-1})	k_r (s^{-1})	k_{nr} (s^{-1})
l-CZ-DCPP	0.277	1.06×10^{7}	0	1.56×10^{8}	1.35×10^{7}
l-PXZ-DCPP	0.064	5.16×10^{6}	6.49×10^{6}	0	3.09×10^{5}
l-PTZ-DCPP	0.009	5.40×10^{5}	6.34×10^{5}	2.89×10^{4}	3.39×10^{5}
l-TPA-DCPP	0.038	4.23×10^{3}	0	9.21×10^{7}	9.19×10^{6}
l-CZ-DCNP	0.235	3.04×10^{5}	0	1.96×10^{8}	1.22×10^{7}
l-PXZ-DCNP	0.321	3.44×10^{3}	2.83×10^{3}	0	3.84×10^{5}
l-PTZ-DCNP	0.018	1.33×10^{6}	1.12×10^{6}	1.62×10^{4}	4.71×10^{5}
l-TPA-DCNP	0.149	3.17×10^{6}	1.34×10^{0}	1.43×10^{8}	9.59×10^{6}
l-CZ-QCN	0.299	1.02×10^{7}	0	7.14×10^{7}	2.50×10^{7}
l-PXZ-QCN	0.002	6.20×10^{3}	2.05×10^{4}	0	3.33×10^{6}
l-PTZ-	0.002	9.67×10^{3}	1.51×10^{4}	0	1.19×10^{6}

QCN					
l-TPA-QCN	0.115	6.18×10^{5}	1.42×10^{0}	1.23×10^{8}	2.08×10^{7}
l-CZ-PHNI	1.499	7.39×10^{7}	0	9.48×10^{5}	1.21×10^{6}
l-PXZ-PHNI	0	0	0	0	1.17×10^{4}
l-PTZ-PHNI	0	0	0	0	9.59×10^{3}
l-TPA-PHNI	1.232	5.31×10^{4}	0	4.26×10^{5}	4.21×10^{5}
l-CZ-PHPI	0.009	2.05×10^{3}	1.68×10^{1}	4.21×10^{5}	6.50×10^{6}
l-PXZ-PHPI	0.020	3.10×10^{5}	1.84×10^{5}	0	4.29×10^{4}
l-PTZ-PHPI	0	0	0	0	3.67×10^{4}
l-TPA-PHPI	0.092	1.61×10^{6}	2.30×10^{4}	2.94×10^{5}	4.14×10^{6}