Supporting Information

Rational designs of structurally similar TADF and HLCT emitters with benzo- or naphtho-carbazole units as electron donors

Jiaqi Li, Tingyu Li, Mingfan Zhang, Dongxue Guo, and Houyu Zhang*

State Key Laboratory of Supramolecular Structure and Materials,

Institute of Theoretical Chemistry, College of Chemistry, Jilin University,

Changchun 130012, P.R. China

*Email: houyuzhang@jlu.edu.cn

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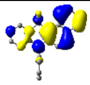
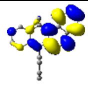
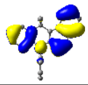
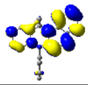
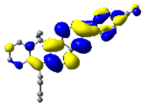
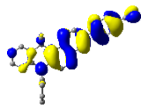
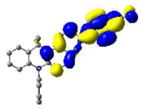
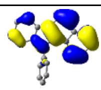
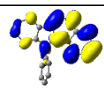
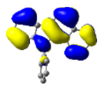
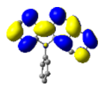
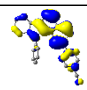
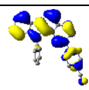
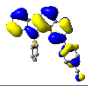
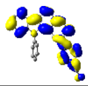
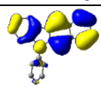
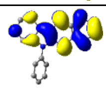
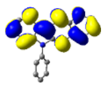
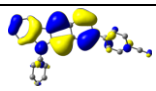
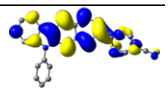
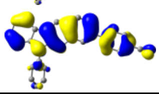
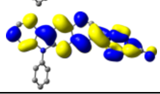
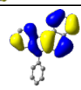
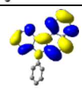
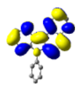
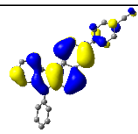
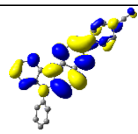
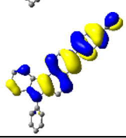
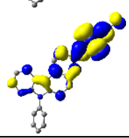
Table S1. NTO distributions and main transition excitations of T_1 and T_2 states for the donor fragments and **BN**-based D–A type molecules, estimated by TD-DFT at the BMK/6-31G(d, p) level.

	State	Excitation	*E* (eV)	Eigenvalues	NTOs Hole	NTOs Electron
DMBA	T_1	H → L (68.9%)	2.72	0.93		
		H-2 → L (17.4%)				
	T_2	H-2 → L (54.5%)	3.56	0.75		
		H → L (13.8%)				
DMBA-BN	T_1	H → L (54.5%)	2.57	0.91		
		H → L+1 (16.7%)				
	T_2	H → L+1 (24.0%)	3.28	0.76		
		H-2 → L (15.6%)				
		H → L (5.6%)				
PB[*a*]CZ	T_1	H → L (66.0%)	2.93	0.85		
		H → L+1 (4.3%)				
	T_2	H → L+1 (66.1%)	3.52	0.83		
		H → L (9.7%)				
PB[*a*]CZ-BN	T_1	H → L (43.7%)	2.75	0.84		
		H → L+1 (21.0%)				
	T_2	H → L+1 (52.2%)	3.29	0.73		
		H → L (12.5%)				
PB[*b*]CZ	T_1	H → L (80.9%)	2.55	0.94		
	T_2	H-1 → L (72.9%)	3.44	0.89		
		H → L (10.1%)				
PB[*b*]CZ-BN	T_1	H → L (63%)	2.44	0.93		
		H → L+1 (15%)				
	T_2	H-1 → L (65%)	3.24	0.80		
		H → L (6%)				
PB[*c*]CZ	T_1	H → L (68.7%)	2.87	0.89		
		H-1 → L (16.7%)				
	T_2	H-1 → L (59.8%)	3.55	0.89		
		H → L (20.1%)				
PB[*c*]CZ-BN	T_1	H → L (44.2%)	2.77	0.84		
		H → L+1 (19.9%)				
	T_2	H → L+1 (39.1%)	3.31	0.72		
		H → L (24.8%)				

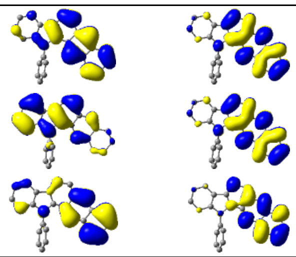
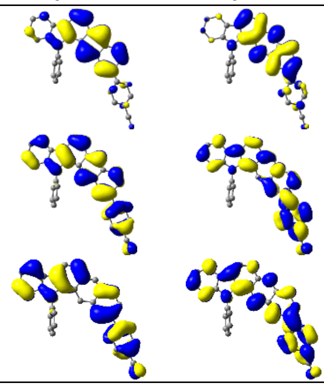
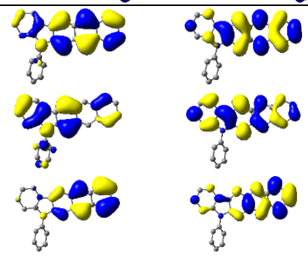
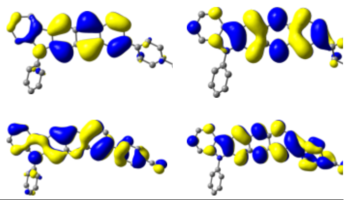
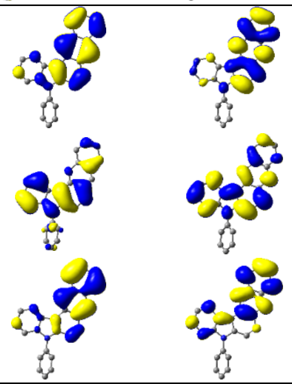
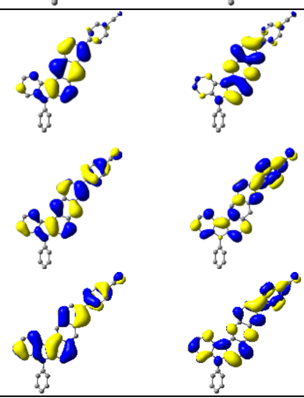
PN[*a*]CZ	T_1	H → L (87.1%)	2.05	0.95	
	T_2	H → L+1 (48.1%)	3.29	0.70	
		H-2 → L (23.2%)		0.25	
		H → L+4 (5.6%)			
PN[*a*]CZ-BN	T_1	H → L (73%)	1.98	0.95	
		H → L+1 (12%)			
	T_2	H → L+1 (44%)	3.09	0.61	
		H-2 → L (25%)		0.32	
PN[*b*]CZ	T_1	H → L (89.4%)	1.73	0.98	
	T_2	H-2 → L (24.8%)	3.10	0.54	
		H → L+1 (21.4%)		0.43	
		H-1 → L (12.8%)			
		H → L+4 (11.7%)			
PN[*b*]CZ-BN	T_1	H-2 → L+1 (83%)	1.68	0.97	
	T_2	H-1 → L (36%)	2.96	0.94	
		H → L+1 (14%)			
PN[*c*]CZ	T_1	H → L (87.2%)	2.06	0.95	
	T_2	H-2 → L (27.1%)	3.19	0.66	
		H-1 → L (22.6%)		0.28	
		H → L+2 (18.5%)			
PN[*c*]CZ-BN	T_1	H → L (79%)	2.01	0.94	
	T_2	H → L+1 (42%)	3.05	0.62	
		H-2 → L (26%)		0.31	

Table S2. Calculated HOMO-LUMO overlap integral (β) of the investigated molecules in S_0 state.

Mol.	$\boldsymbol{\beta}$
PB[*b*]CZ-BN	0.6236
PB[*b*]CZ-BPN	0.0856
PN[*b*]CZ-BN	0.7550
PN[*b*]CZ-BPN	0.0979
PN[*a*]CZ-BN	0.7240
PN[*a*]CZ-BPN	0.1019
PN[*c*]CZ-BN	0.7923
PN[*c*]CZ-BPN	0.1194

Table S3. Calculated absorption wavelengths (**λ**) and energies (ΔE), oscillator strengths (f), and dominant orbital excitations from TD-DFT calculation for the investigated molecules.

Mol.	**State**	**λ (nm)**	**ΔE (eV)**	f	**Excitation**
PB[*b*]CZ-BN	S_1	357	3.47	0.0813	H → L (90%)
	S_2	308	4.03	0.4632	H-1 → L (71%); H → L+1 (8%)
	T_1	508	2.44	0	H → L (63%); H → L+1 (15%)
	T_2	382	3.24	0	H-1 → L (65%); H → L (6%)
	T_3	358	3.46	0	H-3 → L (25%); H-1 → L+1 (21%)
	T_4	334	3.71	0	H → L+2 (32%); H → L+5 (13%)
PB[*b*]CZ-BPN	S_1	560	2.21	0.0013	H → L (96%)
	S_2	497	2.49	0.0733	H → L+1 (95%)
	S_3	420	2.95	0.0081	H-1 → L (94%)
	S_4	381	3.25	0.3983	H-1 → L+1 (92%)
	S_5	342	3.62	0.0436	H → L+2 (87%)
	S_6	337	3.68	0.0014	H-2 → L (93%)
	S_7	314	3.95	0.0077	H-2 → L+1 (83%); H → L+2 (5%)
	T_1	577	2.15	0	H → L+1 (57%); H → L+2 (20%); H → L (8%)
	T_2	566	2.19	0	H → L (86%)
	T_3	454	2.73	0	H-1 → L+1 (33%); H → L+1 (16%)
PN[*b*]CZ-BN	S_1	430	2.88	0.0599	H → L (97%)
	S_2	340	3.64	0.1085	H-1 → L (53%); H → L+2 (16%)
	T_1	736	1.68	0	H → L (83%)
	T_2	419	2.96	0	H-1 → L (36%); H → L+1 (14%)
	T_3	392	3.16	0	H-1 → L (39%); H-2 → L (30%)

PN[*b*]CZ-BPN	S_1	656	1.89	0.0011	H → L (96%)
	S_2	575	2.16	0.1161	H → L+1 (94%)
	S_3	417	2.98	0.0137	H-1 → L (78%); H → L+1 (13%)
	S_4	415	2.99	0.0477	H → L+2 (80%); H-1 → L (13%)
	S_5	386	3.22	0.4255	H-1 → L+1 (87%)
	T_1	794	1.56	0	H → L+2 (48%); H → L+1 (39%)
	T_2	665	1.86	0	H → L (93%)
	T_3	549	2.25	0	H → L+1 (48%); H → L+2 (36%)
PN[*a*]CZ-BN	S_1	390	3.18	0.0881	H → L (95%)
	S_2	340	3.65	0.0407	H → L+1 (49%); H-1 → L (28%)
	T_1	626	1.98	0	H → L (73%); H → L+1 (12%)
	T_2	402	3.09	0	H → L+1 (44%); H-2 → L (25%)
	T_3	366	3.38	0	H-1 → L (35%); H → L+6 (10%)
PN[*a*]CZ-BPN	S_1	630	1.97	0.0011	H → L (96%)
	S_2	552	2.24	0.1422	H → L+1 (95%)
	S_3	435	2.85	0.0016	H-1 → L (97%)
	S_4	405	3.07	0.0484	H-1 → L+1 (82%)
	S_5	388	3.20	0.0072	H-2 → L (89%)
	S_6	377	3.29	0.1484	H → L+2 (83%)
	S_7	357	3.48	0.1893	H-2 → L+1 (88%)
	S_8	325	3.81	0.0144	H-1 → L+2 (39%); H → L+3 (38%)
	T_1	695	1.79	0	H → L+1 (49%); H → L+2 (35%)
	T_2	640	1.94	0	H → L (93%)
	T_3	521	2.38	0	H → L+2 (45%); H → L+1 (36%)
PN[*c*]CZ-BN	S_1	382	3.24	0.0956	H → L (94%)
	S_2	339	3.65	0.0017	H → L+1 (40%); H-1 → L (40%)
	T_1	617	2.01	0	H → L (79%)
	T_2	406	3.05	0	H → L+1 (42%); H-2 → L (26%)
	T_3	388	3.20	0	H-1 → L (61%); H-1 → L+1 (11%)
	T_4	355	3.50	0	H-2 → L+1 (20%); H → L+5 (11%)
PN[*c*]CZ-BPN	S_1	593	2.09	0.0018	H → L (96%)
	S_2	517	2.40	0.2311	H → L+1 (94%)
	S_3	436	2.85	0.0028	H-1 → L (95%)
	S_4	403	3.08	0.1244	H-1 → L+1 (83%)
	S_5	372	3.33	0.1747	H → L+2 (85%)
	S_6	367	3.47	0.0062	H-2 → L (89%)
	S_7	332	3.74	0.1171	H-2 → L+1 (70%); H-1 → L+2 (15%)
	S_8	327	3.79	0.0361	H-3 → L (73%); H-1 → L+2 (6%)
	S_9	325	3.81	0.0791	H-1 → L+2 (46%); H-2 → L+1 (17%)
	T_1	657	1.89	0	H → L+1 (43%); H → L+2 (40%)
	T_2	606	2.05	0	H → L (92%)
	T_3	514	2.41	0	H → L+2 (42%); H → L+1 (39%)

Table S4. Calculated the related orbital distributions and vertical excitation energies of LE states.

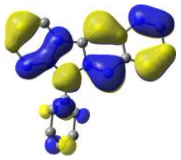
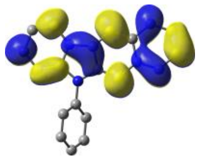
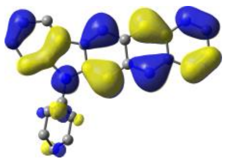
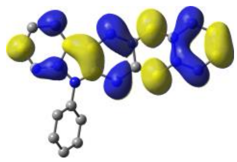
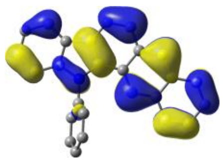
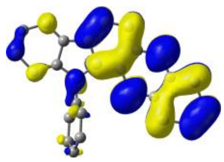
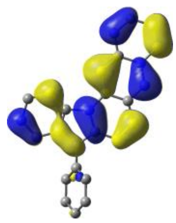
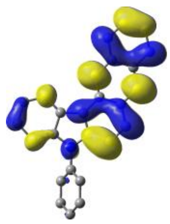
	Hole	Particle	$E_{1_{\mathrm{LE}}}$	$E_{3_{\mathrm{LE}}}$
PB[*b*]CZ			3.71 eV	2.55 eV
PN[*b*]CZ			3.03 eV	1.76 eV
PN[*a*]CZ			3.38 eV	2.04 eV
PN[*c*]CZ			3.37 eV	2.06 eV

Table S5. Calculated vertical excitation energies of singlet and triplet states, energy gaps between S_1 and related T_n states of the investigated molecules by BMK/6-31G(d, p) level (energy unit in eV).

Mol.	E_{T_1}	E_{T_2}	E_{T_3}	E_{S_1}	E_{S_2}	$\Delta E_{T_2-T_1}$	$\Delta E_{S_1-T_1}$	$\Delta E_{S_1-T_2}$	$\Delta E_{S_1-T_3}$
PB[*b*]CZ-BN	2.44	3.24	3.46	3.47	4.03	0.80	1.03	0.23	0.01
PB[*b*]CZ-BPN	2.15	2.19	2.73	2.21	2.49	0.04	0.06	0.02	--
PN[*b*]CZ-BN	1.68	2.96	3.16	2.88	3.64	1.28	1.20	-0.08	--
PN[*b*]CZ-BPN	1.56	1.86	2.26	1.89	2.16	0.30	0.33	0.03	--
PN[*a*]CZ-BN	1.98	3.09	3.38	3.18	3.65	1.11	1.20	0.09	--
PN[*a*]CZ-BPN	1.79	1.94	2.38	1.97	2.24	0.15	0.18	0.03	--
PN[*c*]CZ-BN	2.01	3.05	3.20	3.24	3.65	1.04	1.23	0.19	0.04
PN[*c*]CZ-BPN	1.89	2.05	2.41	2.09	2.40	0.16	0.20	0.04	--

Table S6. Calculated adiabatic excitation energies of S_1 and T_1 states and their energy gaps at BMK/6-31G (d, p) level (energy unit in eV).

Mol.	$E_{T_1-S_0}$	$E_{S_1-S_0}$	ΔE_{ST}
PB[*b*]CZ-BN	2.41	3.30	0.89
PB[*b*]CZ-BPN	1.96	1.97	0.02
PN[*b*]CZ-BN	1.71	2.74	1.03
PN[*b*]CZ-BPN	1.58	1.66	0.08
PN[*a*]CZ-BN	1.97	2.96	0.99
PN[*a*]CZ-BPN	1.53	1.70	0.17
PN[*c*]CZ-BN	2.01	3.05	1.04
PN[*c*]CZ-BPN	1.62	1.85	0.23

Table S7. Calculated $\Delta E_{T_2-T_1}$ and NAC constants between T_2 and T_1 states for the investigated molecules.

Mol.	**PB[*b*]CZ-BN**	**PN[*b*]CZ-BN**	**PN[*a*]CZ-BN**	**PN[*c*]CZ-BN**
$\Delta E_{T_2-T_1}$ **(eV)**	0.80	1.28	1.11	1.04
NAC (bohr^{-1})	2.86	2.12	2.30	2.47
Mol.	**PB[*b*]CZ-BPN**	**PN[*b*]CZ-BPN**	**PN[*a*]CZ-BPN**	**PN[*c*]CZ-BPN**
$\Delta E_{T_2-T_1}$ **(eV)**	0.04	0.30	0.15	0.16
NAC (bohr^{-1})	4.15	3.53	4.18	4.13

Figure S1. HOMO and LUMO spatial distributions, energy levels, and their energy gaps of the investigated molecules in their ground states.

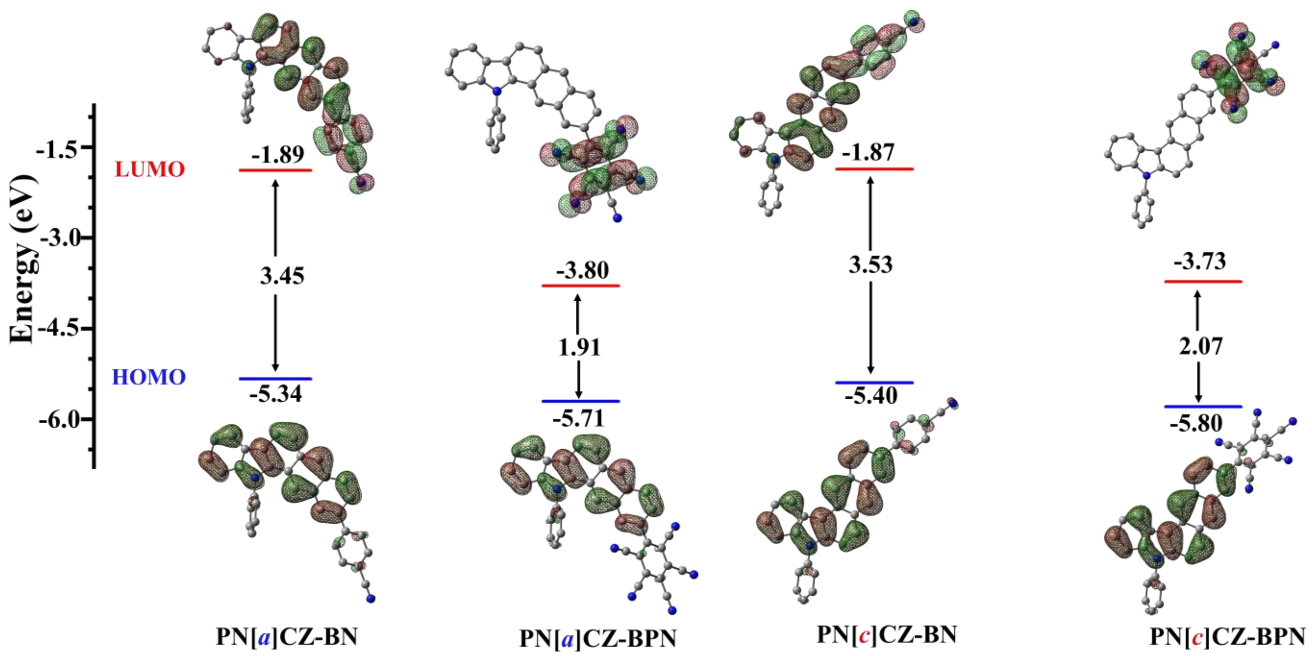


Figure S2. NTO plots for the selected singlet and triplet excited states of the investigated molecules.

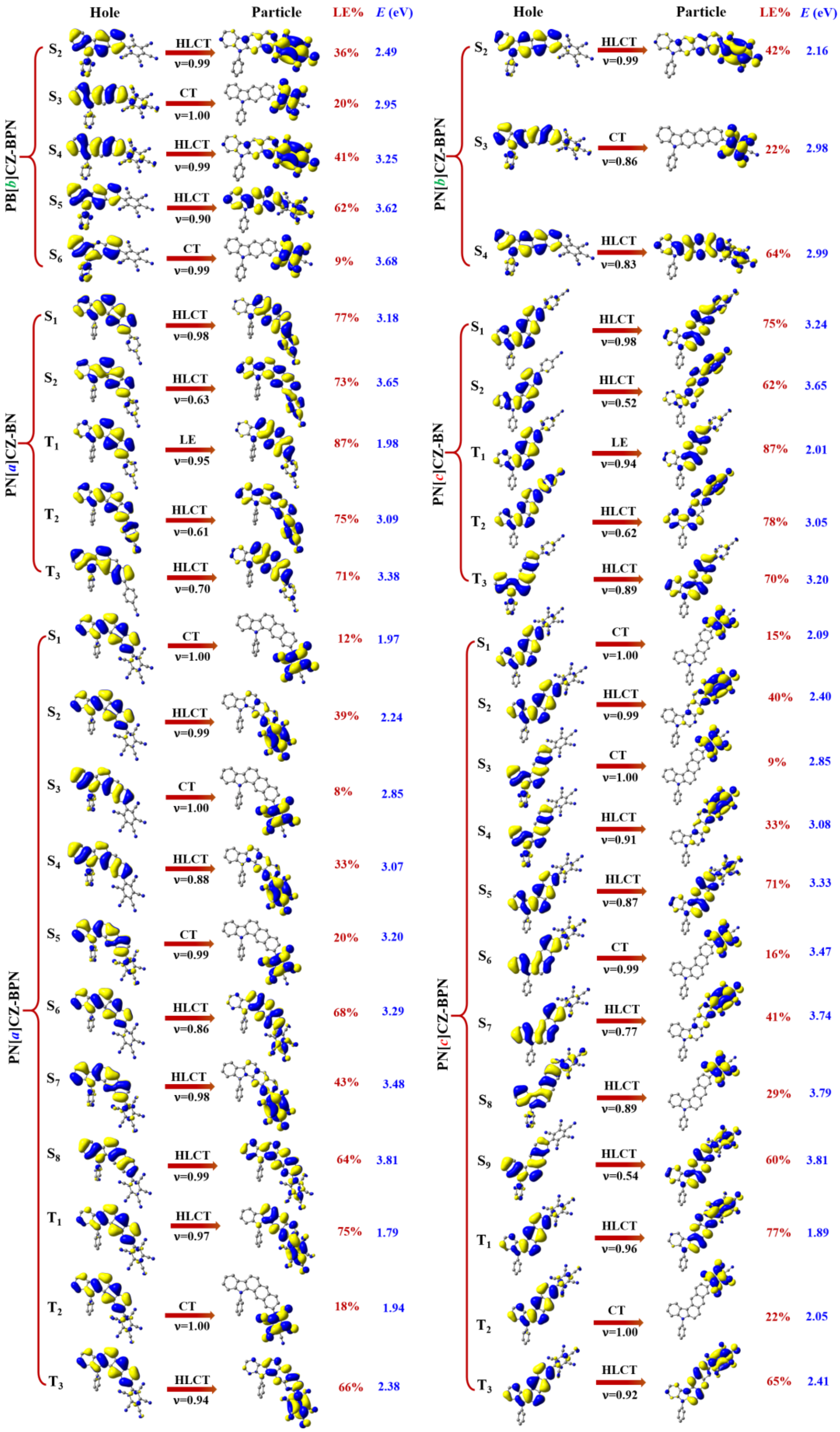
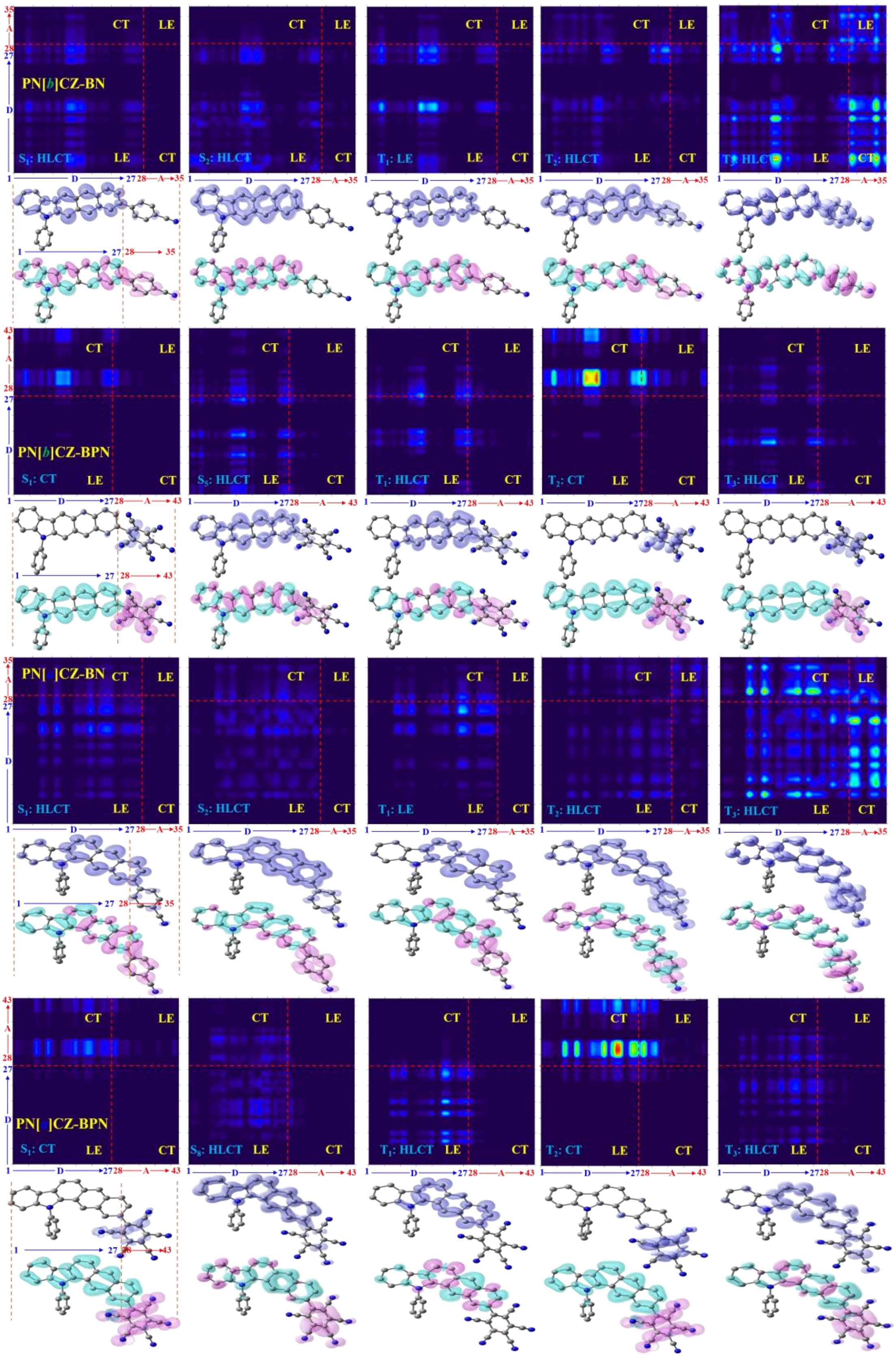


Figure S3. The TDM maps, the overlaps and distributions of electron-hole wavefunctions for the investigated molecules.



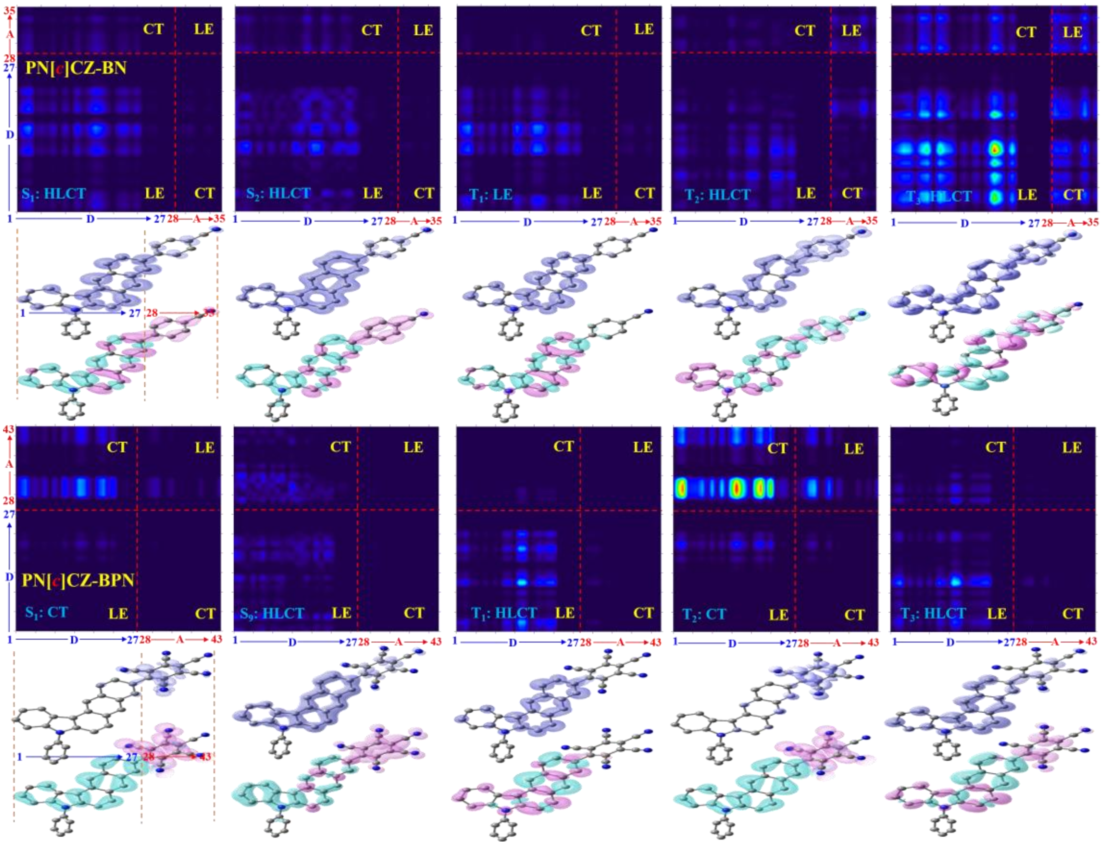


Figure S4. Energy diagram for the state hybridization of LE and CT state for both singlet and triplet subspaces.