Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Bridge-tuned through-space charge transfer for TADF and HLCT emissions

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Table S1. Calculated HOMO levels (eV) of molecule **Cz-XAN-TRZ** (XCT) with different DFT functionals with a fixed percentage of nonlocal Hartree-Fock exchange (HF_{exc}).

	B3LYP 20%	PBE0 25%	PBE0-1/3 33.33%	PBE38 37.5%	Exp[a]
HOMO	**-5.45**	**-5.73**	**-6.14**	**-6.21**	**-5.58**

[a] Experimental values obtained from ref. 45.

Table S2. Calculated absorption wavelength (λ_{abs}: nm) and emission wavelength (λ_{em}: nm) of molecule **Cz-XAN-TRZ** (XCT) with different DFT functionals with a fixed percentage of nonlocal Hartree-Fock exchange (HF_{exc}).

	B3LYP 20%	PBE0 25%	PBE0-1/3 33.33%	PBE38 37.5%	Exp[a]
λ_{abs}	**408**	**382**	**344**	**328**	**341**
λ_{em}	**484**	**452**	**407**	**392**	**419**

[a] Experimental values obtained from ref. 45.

Table S3. HOMO and LUMO levels, HOMO-LUMO energy gaps (eV) of commonly used acceptors and donors in their ground states.

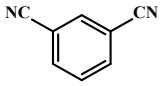
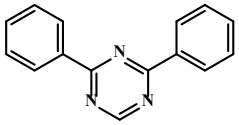
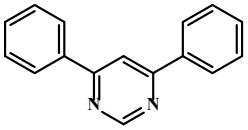
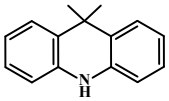
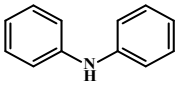
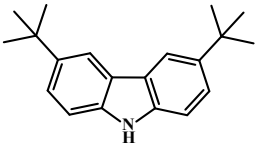
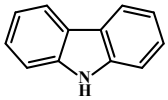
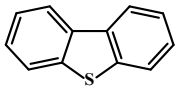
Mol.	HOMO	LUMO	gap
 **isophthalonitrile (IPN)**	**-7.84**	**-2.25**	**5.59**
 **2,4-diphenyl-1,3,5-triazine (TRZ)**	**-6.73**	**-1.91**	**4.82**
 **4,6-diphenylpyrimidine (PM)**	**-6.52**	**-1.72**	**4.80**
 **9,9-dimethyl-9,10-dihydroacridine (DMAC)**	**-4.89**	**-0.08**	**4.81**
 **diphenylamine (DPA)**	**-5.10**	**-0.14**	**4.96**
 **3,6-di-tert-butyl-9H-carbazole (tBuCz)**	**-5.23**	**-0.61**	**4.62**
 **9H-carbazole (Cz)**	**-5.46**	**-0.66**	**4.80**
 **dibenzo[b,d]thiophene (DBT)**	**-5.83**	**-0.96**	**4.86**

Table S4. Calculated vertical ΔE_{ST} (eV) for the investigated molecules in this work.

Mol.	ISC	ΔE_{ST}
DPA-XAN-TRZ	T_1-S_1	0.02
	T_2-S_1	-0.04
	T_3-S_1	-0.08
DPA-AN-TRZ	T_1-S_1	0.96
	T_2-S_1	0.11
	T_3-S_1	-0.23
Cz-XAN-TRZ	T_1-S_1	0.31
	T_2-S_1	0.22
	T_3-S_1	0.12
Cz-AN-TRZ	T_1-S_1	1.18
	T_2-S_1	0.16
	T_3-S_1	-0.09
tBuCz-XAN-TRZ	T_1-S_1	0.12
	T_2-S_1	0.08
	T_3-S_1	0.02
tBuCz-AN-TRZ	T_1-S_1	1.06
	T_2-S_1	0.10
	T_3-S_1	-0.14

Table S5. Geometrical parameters (in Å or degree) for **tBuCz-XAN-TRZ** and **tBuCz-AN-TRZ** in their ground and excited states.

Mol.	S_0			S_1			T_1		
	d	α_1	α_2	*d*	α_1	α_2	*d*	α_1	α_2
tBuCz-XAN-TRZ	4.70	51.40	44.61	4.65	56.17	43.37	4.65	53.00	40.65
tBuCz-AN-TRZ	5.02	55.14	33.34	4.99	57.87	22.65	4.98	49.86	25.68

Figure S1. Optimized ground-state structures and dihedral angles of the investigated molecules and molecules with only the donor or acceptor connected with the bridge.

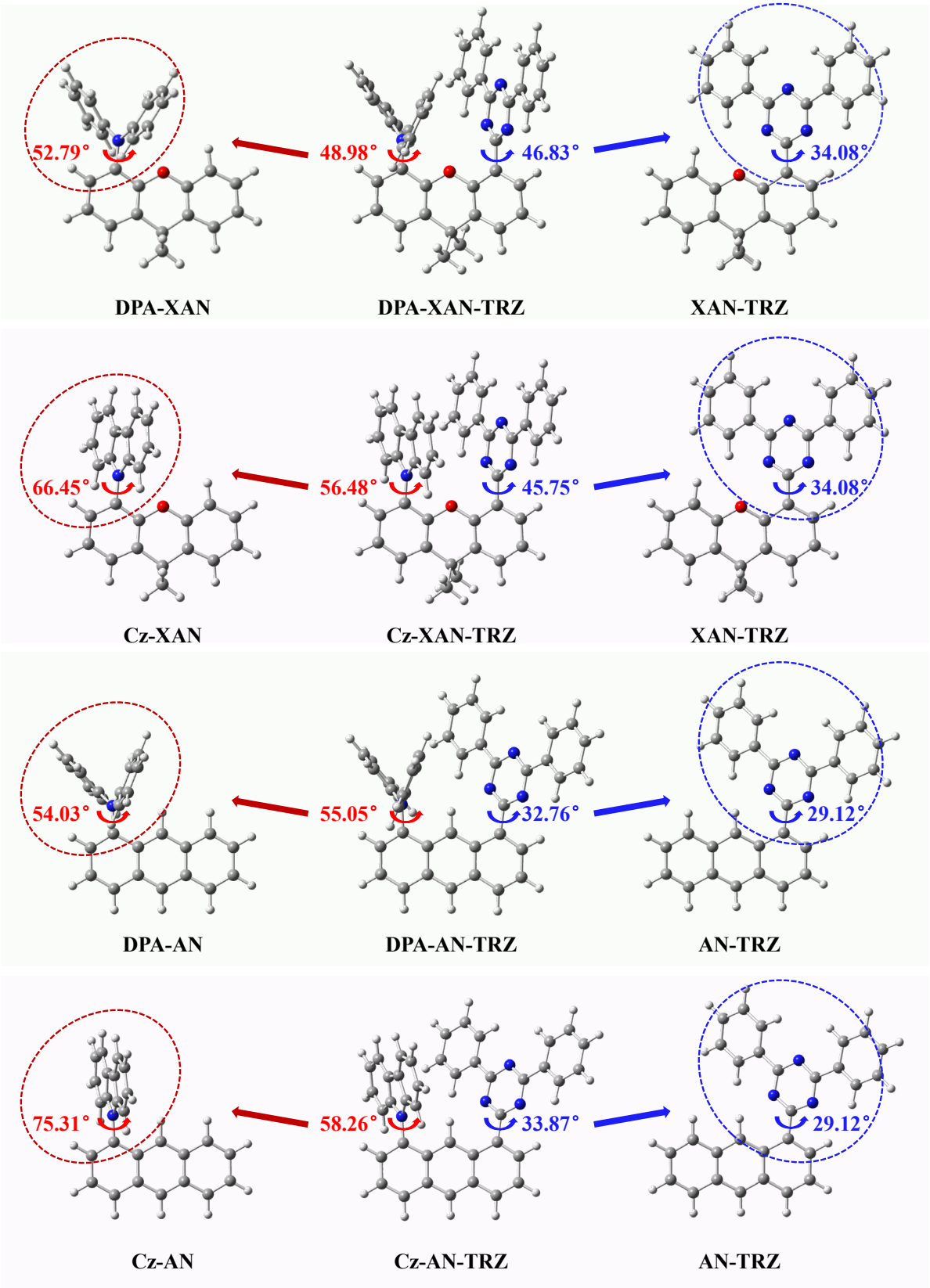
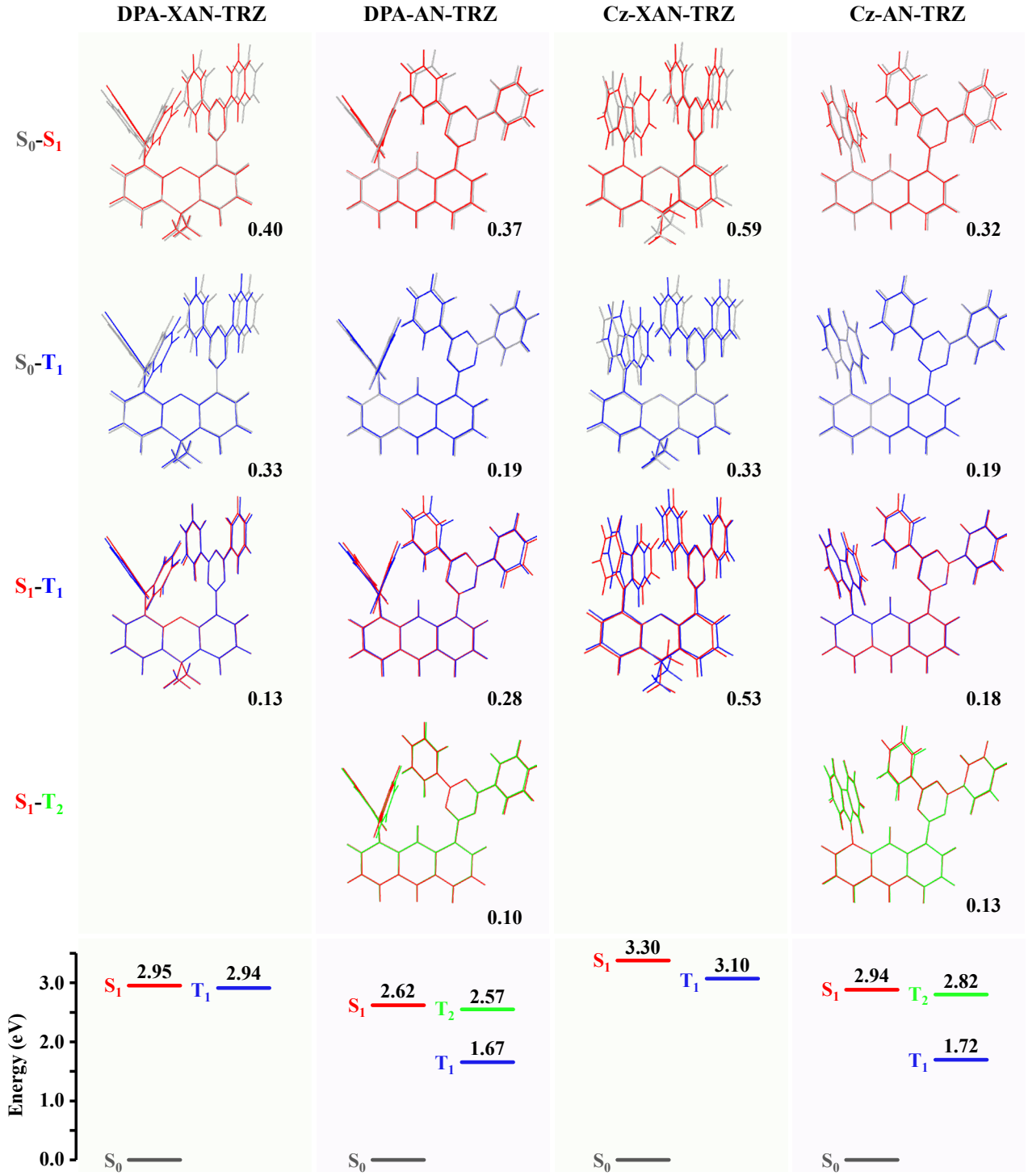


Figure S2. Structural changes between two states with their RMSDs and the corresponding relative energy levels (S_0, S_1, T_1, and T_2 are shown in gray, red, blue, and green, respectively).



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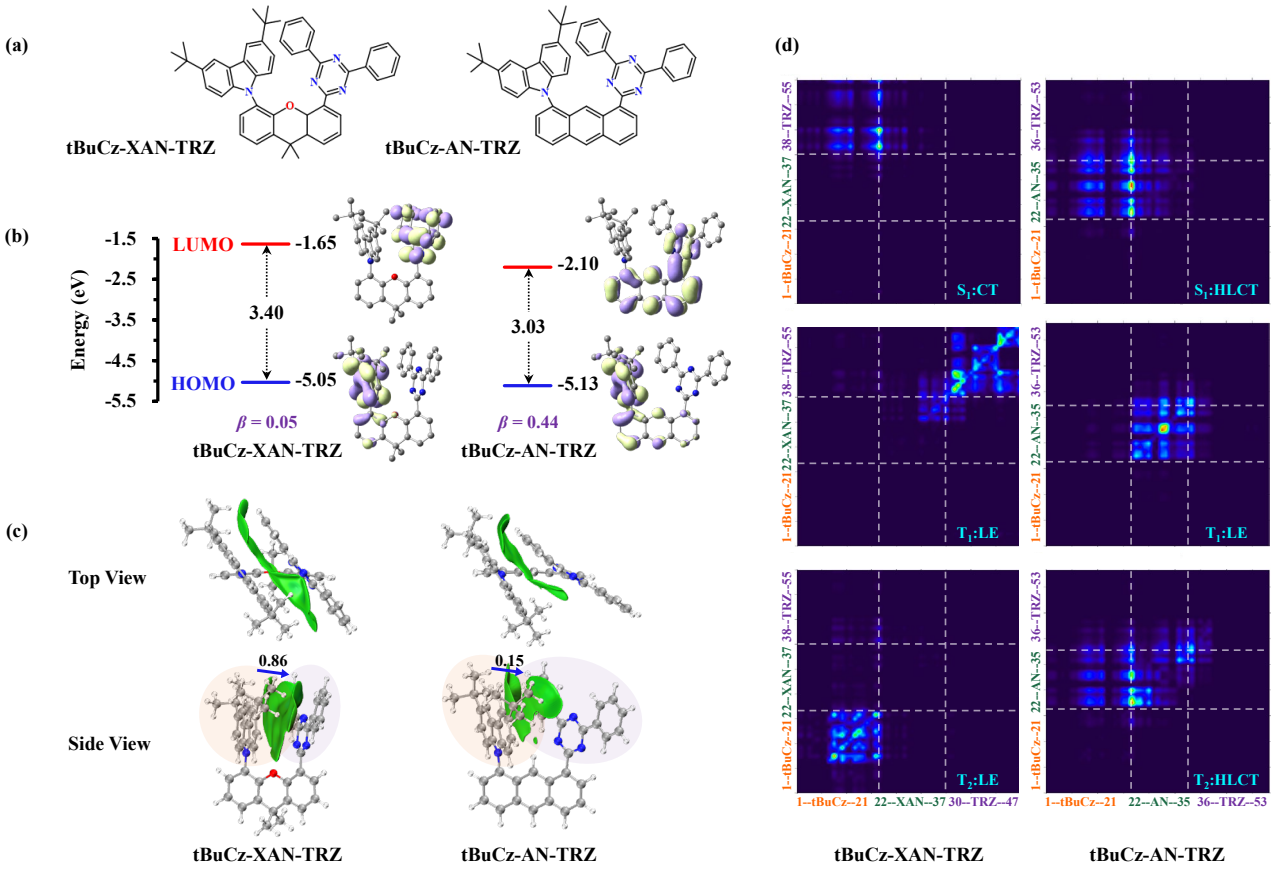

(e)

	S1 Hole	S1 Electron	LE	E (eV)	T1 Hole	T1 Electron	LE	E (eV)	T2 Hole	T2 Electron	LE	E (eV)
tBuCz-XAN-TRZ		v = 1.00 CT	1%	3.45		v = 0.55 LE	77%	3.33		v = 0.80 LE	86%	3.37
tBuCz-AN-TRZ		v = 0.99 CT+LE	18%	3.01		v = 0.93 LE	83%	1.95		v = 0.77 CT+LE	38%	2.91