

Supporting Information for
Effects of *ortho*-Linkages on the Molecular Stability of Organic Light-Emitting Diode Materials

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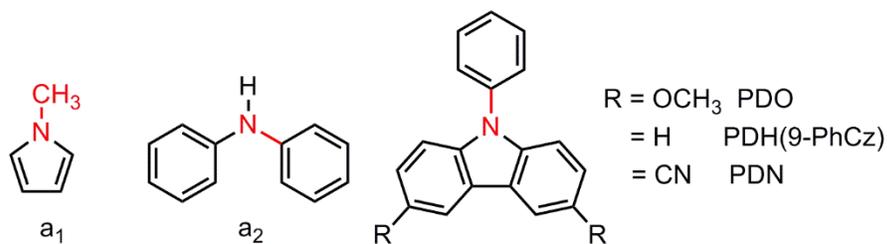


Figure S1. Chemical structures of the compounds selected for the comparative calculation. BDE_f values of the fragile D- π bonds (those labeled in red) were calculated.

Table S1. Experimental Values and Calculated Values at Different Levels of the Selected Compounds in Figure S1

method	experimental	B3LYP	B3LYP	M06-2X	M06-2X
BDE (eV)	value ^a	6-31G(d)	6-311+G(d,p)	6-31G(d)	6-311+G(d,p)
a ₁	3.53	3.23	3.14	3.63	3.52
a ₂	3.79	3.54	3.58	4.05	3.94
PDO		3.26	3.12	3.80	3.74
PDH		3.54	3.41	4.15	4.03
PDN		3.68	3.56	4.29	4.18

^a Ref 1.

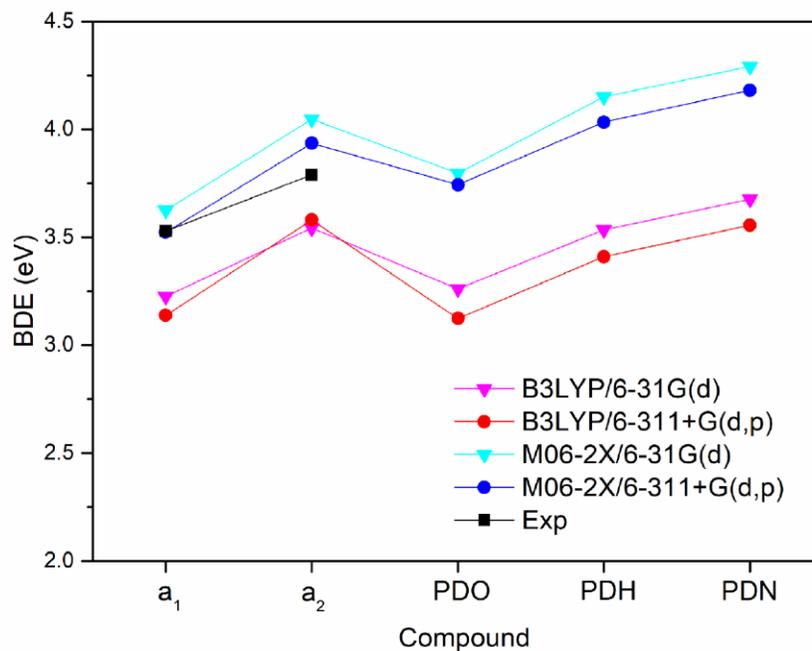


Figure S2. The variation tendency of the experimental BDEs and calculated BDEs at different levels.

Table S2. Calculated and Experimental Values of Vertical Absorption Energies of S₁ States [$E_{VA}(S_1)$] of Molecules in Figure 1, Group A, B, and F

compound	OHF /%	$E_{VA}(S_1)^a$ /eV				ref
		q -OHF ^a	ω B97XD	LC- ω PBE	exptl ^b	
9-PhCz	3.9	3.68	4.43	4.62	3.66	2
CBP	28.7	3.84	4.38	4.60	3.80	2
mCP	1.1	3.50	4.45	4.63	3.66	Figure S3
DCzTrz	34.1	3.41	4.04	4.50	3.69	3
Cz2BP	33.4	3.54	3.78	3.86	3.52	4
<i>p</i> -CzTrz	34.1	3.55	4.13	4.48		
DMCzTrz	37.1	3.68	4.37	4.62		
BPCzTrz	36.0	3.50	4.12	4.57		
TCzTrz	34.5	3.31	3.94	4.37	3.42	5
4CzIPN	31.4	2.85	3.39	3.89	2.85	2
5CzBN	30.4	3.07	3.68	4.18	3.11	6
2CzPN	31.8	3.20	3.79	4.23	3.19	2
PDOTrz	35.5	3.24	3.83	4.16		
PDMTrz	34.4	3.45	4.04	4.38	3.29	7
PDFTrz	33.4	3.88	4.38	4.63		
PDNTrz	33.9	3.95	4.36	4.56		

^aThe excitation energies were calculated based on B3LYP/6-31G(d) optimized geometries. In the q -OHF method developed by Adachi et al., $E_{0-0}(S_1) = E_{VA}(S_1, \text{OHF}) - \Delta E_V - \Delta E_{\text{Stokes}}$, ΔE_V is vibrational energy loss, 0 for 9-PhCz and 0.15 eV others. ΔE_{Stokes} is the Stokes-shift energy loss, 0.09 eV. ^bThe experimental $E_{VA}(S_1)$ values are determined from the absorption peaks in the toluene solution of the corresponding materials (for 9-PhCz, mCP, CBP, Cz2BP, 2CzPN, 4CzIPN, and PDMTrz) or polystyrene films (for DCzTrz, TCzTrz, and 5CzBN).

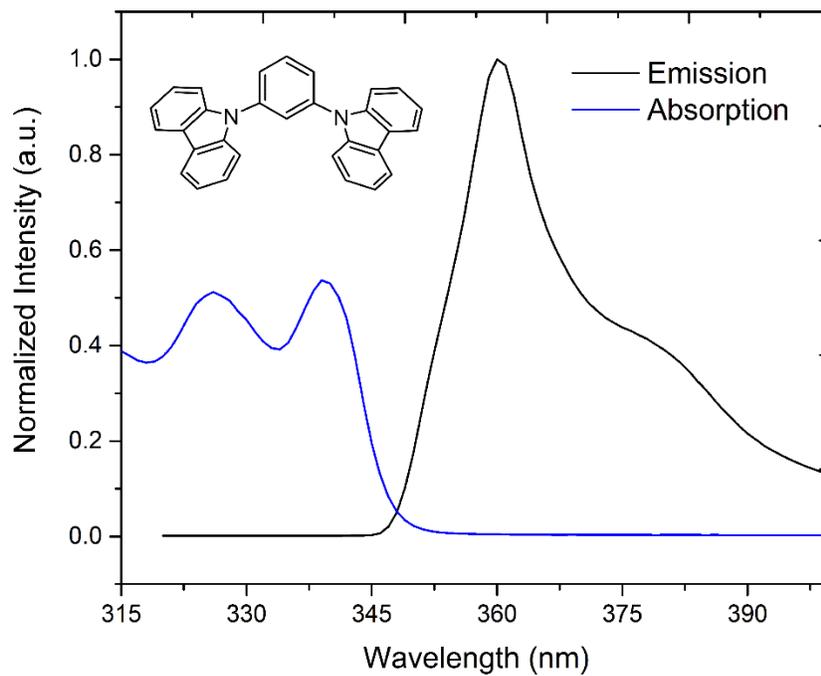


Figure S3. The chemical structure (inset), absorption and emission spectra of mCP in toluene solution ($\sim 10^{-5}$ M) under room temperature. The absorption spectra were recorded using an UV–visible spectrophotometer (Agilent 8453). The emission spectra were recorded using a fluorospectrophotometer (JobinYvon, FluoroMax-3).

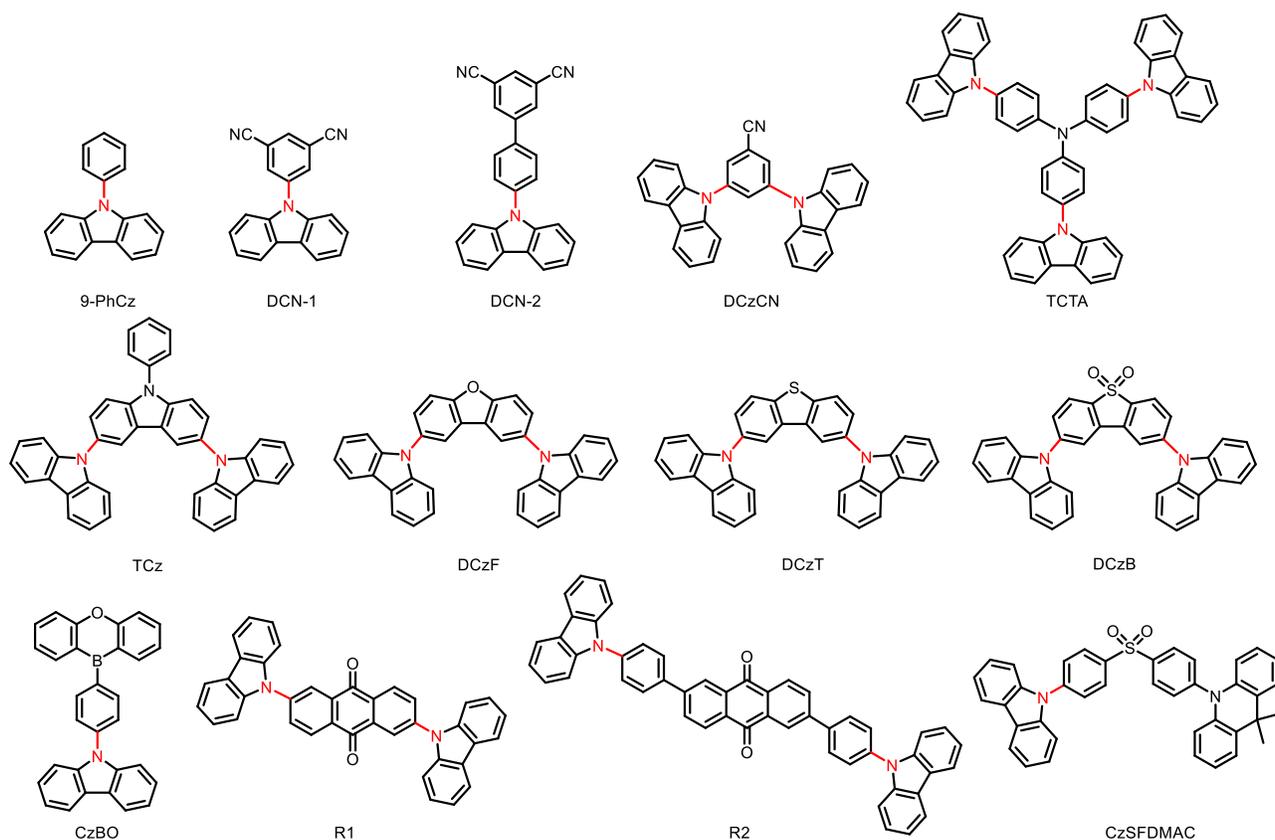


Figure S4. Chemical structures of the additional Cz-based molecules with non-*ortho*-substituents on the π -side. BDE_f values of the fragile D- π bonds (those labeled in red) were calculated.

Table S3. B3LYP/6-31G(d) Absolute (BDE_f) and Relative (ΔBDE_f) Bond Dissociation Energies of the Fragile D- π Bonds, Dihedral Angles between Carbazoles and the Phenyl Groups ($\angle D-\pi$) of Molecules in Figure S4

molecule	BDE_f (eV)	ΔBDE_f (eV) ^a	$\angle D-\pi$ (deg)
9-PhCz	3.54	0	56
DCN-1	3.50	-0.04	51
DCN-2	3.53	-0.01	53
DCzCN	3.49	-0.05	53
TCTA	3.56	0.02	56
TCz	3.55	0.01	61
DCzF	3.54	0	59
DCzT	3.53	-0.01	57
DCzB	3.52	-0.02	52
CzBO	3.54	0	55
R1	3.52	-0.02	50
R2	3.55	0.01	53
CzSFDMAC ^b	3.53	-0.01	50

^aFor one molecule, $\Delta BDE_f = BDE_f - BDE_f(9\text{-PhCz})$. ^bFor CzSFDMAC, Cz-phenyl bond is not the weakest bond in this molecule, here its BDE is listed only for comparison.

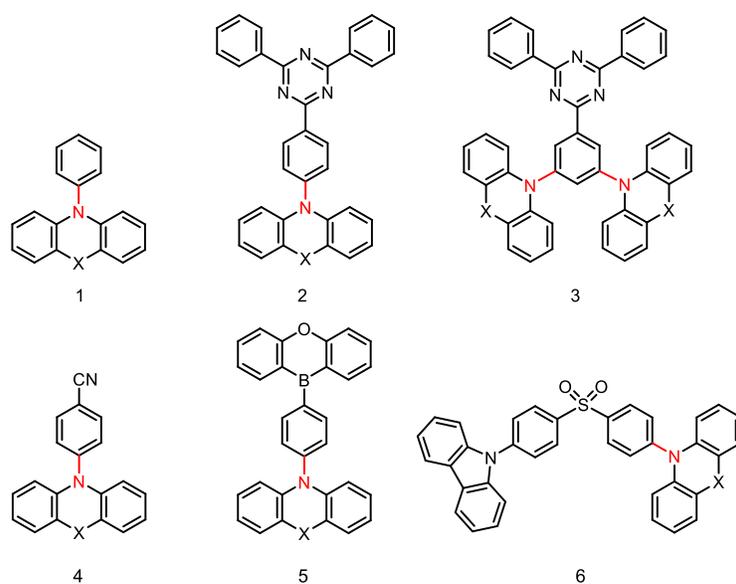


Figure S5. 9,9-dimethyl-9,10-dihydroacridine (DMAC, X = CMe₂) and phenoxazine (Px, X = O) based molecules with non-*ortho*-substituents on the π -side. BDE_f values of the fragile D- π bonds (those labeled in red) were calculated.

Table S4. B3LYP/6-31G(d) Bond Dissociation Energies of the Fragile D- π Bonds (BDE_f), Dihedral Angles between Donors and the Phenyl Groups ($\angle D-\pi$) of Molecules in Figure S5

structure	X = CMe ₂ (DMAC as donor)		X = O (Px as donor)	
	BDE_f /eV	$\angle D-\pi$ (deg)	BDE_f /eV	$\angle D-\pi$ (deg)
1	2.89	90	2.64	90
2	2.88	88	2.63	90
3	2.83	90	2.57	84
4	2.87	90	2.61	90
5	2.89	90	2.64	87
6	2.87	90	2.61	87

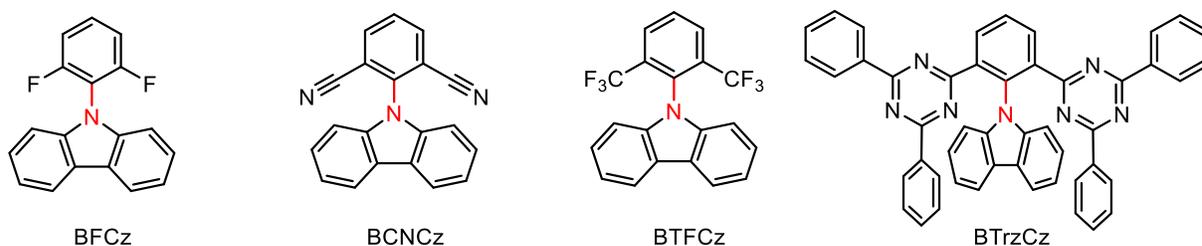


Figure S6. Chemical structures of the Cz-based molecules with *ortho*-electron-withdrawing substituents on the π -side. BDE_f values of the fragile D- π bonds (those labeled in red) were calculated.

Table S5. B3LYP/6-31G(d) Absolute (BDE_f) and Relative (ΔBDE_f) Bond Dissociation Energies of the Fragile D- π Bonds, Dihedral Angles between Carbazoles and the Phenyl Groups ($\angle D-\pi$) of 9-PhCz and Molecules in Figure S6

molecule	BDE_f (eV)	ΔBDE_f (eV) ^a	$\angle D-\pi$ (deg)
9-PhCz	3.54	0	56
BFCz	3.60	0.06	60
BCNCz	3.45	-0.09	90
BTFCz	3.28	-0.26	90
BTrzCz	3.10	-0.44	70

^aFor one molecule, $\Delta BDE_f = BDE_f - BDE_f(9\text{-PhCz})$.

Discussion of the results in Table S5:

The BDE_f values of BFCz, BCNCz, BTFCz, and BTrzCz are 3.60 eV, 3.45 eV, 3.28 eV, and 3.10 eV, respectively. It can be found that the BDE_f and the volume of the substituent have a negative correlation. The fluorine atoms have the smallest volume (slightly larger than the hydrogen atom) within these substituents, and the BDE_f of BFCz is not even decreased (compared with that of 9-PhCz); the increase of the dihedral angle between Cz and the phenyl group is only 4°. Cyano groups have a small volume, and the effect on the BDE_f is also relatively small (~0.1 eV). Trifluoromethyl groups (CF₃) have a large volume, and they decrease the BDE_f of BTFCz by over 0.2 eV. Such influence is similar to the situation in ODF [9-phenyl-1,8-bis(trifluoromethyl)-9H-carbazole], where two *ortho*-CF₃ on D-side have decreased the BDE_f of ODF to 3.35 eV. 4,6-Diphenyl-1,3,5-triazin-2-yl (Trz) groups have the largest volume, and they can conjugate with the phenyl group; thus, they tend to drive away the donor. As a result, the BDE_f of BTrzCz is largely decreased by over 0.4 eV. Despite the large volume of Trz, the dihedral angle between Cz and the central Ph does not increase much, because Trz and Cz both tend to conjugate with the central Ph and they would arrange in a propeller shape. Of note, the electronic characters of CN and CH₃ groups are quite different. However, their effects on BDE_f values are similar due to the similar volumes. Thus, on the π -side, the effect of a substituent on BDE_f mainly depends on the steric hindrance that it brings to the D- π bond, rather than its electronic character.

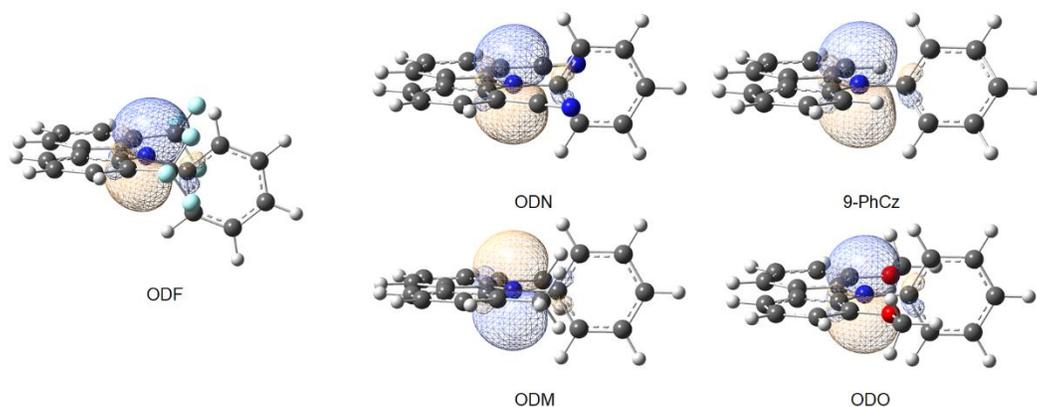


Figure S7. Profiles of lone-pairs of the N atoms in 9-PhCz and its 1,8-substituted derivatives, obtained by the natural bond orbital (NBO) method.

Table S6. Compositions of Lone-Pairs of the N Atoms in 9-PhCz and Its 1,8-Substituted Derivatives in Figure S7, Analyzed by NBO Method at B3LYP/6-31G(d) Level

molecule	composition of the lone-pair /%	
	<i>s</i> component of the N atom	<i>p</i> component of the N atom
ODF	1.8	98.2
ODN	0	100
9-PhCz	0	100
ODM	0	100
ODO	0	100

Discussion of the results in Table S6:

The NBO results show that except ODF who has 1.8% *s* component in the lone-pair of the N atom, those of the other molecules are purely contributed by *p* component of the N atom (which is a typical sp^2 character). Thus, compared with other molecules, N atom in ODF has some sp^3 character.

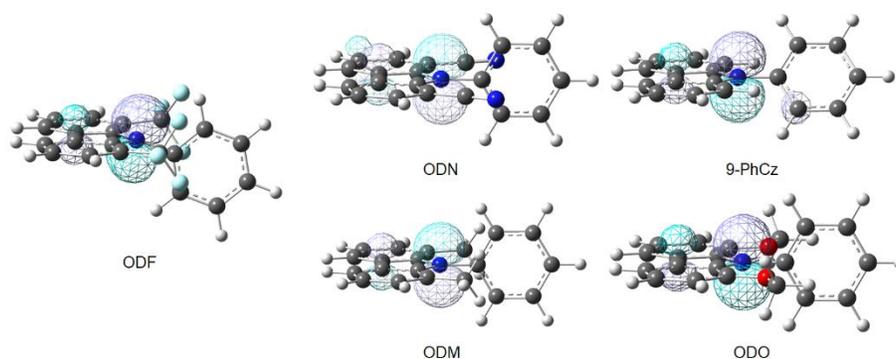


Figure S8. Profiles of “lone-pair orbitals” (i.e., orbitals that are mainly contributed by the lone-pairs of the N atoms) of 9-PhCz and its 1,8-substituted derivatives, obtained by the adaptive natural density partitioning (AdNDP) method.

Table S7. Compositions of Lone-Pair Orbitals of 9-PhCz and Its 1,8-Substituted Derivatives in Figure S8, Analyzed by AdNDP Method at B3LYP/6-31G(d) Level

molecule	composition of the lone-pair orbital/%		
	total contribution of the N atom	<i>s</i> component of the N atom	<i>p</i> component of the N atom
ODF	82.0	2.3	79.7
ODN	81.5	0	82.3
9-PhCz	82.3	0	82.3
ODM	85.8	0	85.8
ODO	84.4	0	84.4

Details and Discussions of the results in Table S7:

To further confirm the hybridization character of ODF, AdNDP analysis is further performed by Multiwfn^{8,9}. Orbitals that are dominated by the N atoms (called “lone-pair orbitals” for discussion) are picked and their components are analyzed. From Table S7, it can be clearly observed that only the lone-pair orbital of ODF has a fraction of *s* component of the N atom. Thus, it can be concluded that only N atom in ODF has some sp^3 hybridization character.

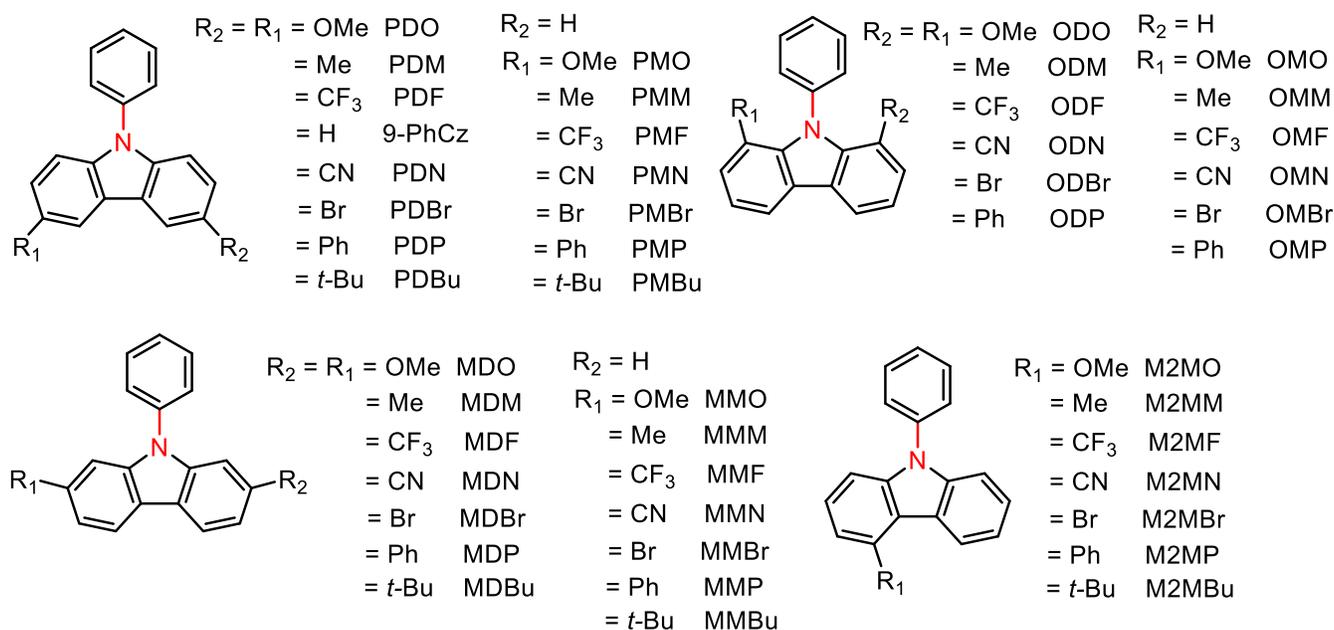


Figure S9. Derivatives of 9-PhCz investigated in Figure 5. BDE_f values of the fragile D- π bonds (those labeled in red) were calculated.

Table S8. B3LYP/6-31G(d) Hirshfeld Charges of the N Atoms (q_N), Bond Dissociation Energies of Fragile Bonds (BDE_f) of the Derivatives of 9-PhCz and Real OLED Molecules

molecule	substituent ^a	substituted sites ^a	q_N	BDE_f /eV
PDO	Methoxyl	3,6	-0.02568	3.26
PDM	Methyl	3,6	-0.02171	3.46
9-PhCz	H	3,6	-0.02133	3.54
PDF	Trifluoromethyl	3,6	-0.01536	3.65
PDN	Cyano	3,6	-0.01198	3.68
PDBr	Bromine	3,6	-0.01839	3.53
PDP	Phenyl	3,6	-0.01926	3.46
PDBu	<i>tert</i> -Butyl	3,6	-0.02220	3.46
PMO	Methoxyl	3	-0.02358	3.38
PMM	Methyl	3	-0.02148	3.50
PMF	Trifluoromethyl	3	-0.01817	3.60
PMN	Cyano	3	-0.01614	3.61
PMBr	Bromine	3	-0.01987	3.53
PMP	Phenyl	3	-0.02039	3.50
PMBu	<i>tert</i> -Butyl	3	-0.02191	3.50

ODO	Methoxyl	1,8	-0.01998	3.24
ODM	Methyl	1,8	-0.02761	3.15
ODF	Trifluoromethyl	1,8	-0.02332	3.33
ODN	Cyano	1,8	-0.01176	3.56
ODBr	Bromine	1,8	-0.01879	3.31
ODP	Phenyl	1,8	-0.02308	2.98
OMO	Methoxyl	1	-0.02052	3.38
OMM	Methyl	1	-0.02612	3.35
OMF	Trifluoromethyl	1	-0.02118	3.46
OMN	Cyano	1	-0.01791	3.54
OMBr	Bromine	1	-0.02194	3.43
OMP	Phenyl	1	-0.02408	3.30
MDO	Methoxyl	2,7	-0.02173	3.55
MDM	Methyl	2,7	-0.02123	3.53
MDF	Trifluoromethyl	2,7	-0.01654	3.64
MDN	Cyano	2,7	-0.01516	3.68
MDP	Phenyl	2,7	-0.02092	3.55
MDBr	Bromine	2,7	-0.01742	3.62
MDBu	<i>tert</i> -Butyl	2,7	-0.02321	3.50
MMO	Methoxyl	2	-0.02167	3.53
MMM	Methyl	2	-0.02128	3.53
MMF	Trifluoromethyl	2	-0.01891	3.59
MMN	Cyano	2	-0.01818	3.61
MMBr	Bromine	2	-0.01930	3.57
MMP	Phenyl	2	-0.02116	3.54
MMBu	<i>tert</i> -Butyl	2	-0.02233	3.52
M2MO	Methoxyl	4	-0.02054	3.53
M2MM	Methyl	4	-0.02138	3.52
M2MF	Trifluoromethyl	4	-0.01992	3.56
M2MN	Cyano	4	-0.01908	3.58
M2MBr	Bromine	4	-0.01974	3.53

M2MP	Phenyl	4	-0.02172	3.50
M2MBu	<i>tert</i> -Butyl	4	-0.02229	3.47
PDOTrz	-	-	-0.02239	3.29
PDMTrz	-	-	-0.01905	3.48
<i>p</i> -CzTrz	-	-	-0.01903	3.55
PDFTrz	-	-	-0.01374	3.62
PDNTrz	-	-	-0.01061	3.67
DCzTrz	-	-	-0.02142	3.50
mCP	-	-	-0.02166	3.50
Cz2BP	-	-	-0.01917	3.54
CBP	-	-	-0.02124	3.55

^aCompounds are mainly derivatives of 9-PhCz; some real OLED materials with complete D- π -A structures are also investigated; *substituted sites* refers to introduced positions of the carbazole of 9-PhCz.

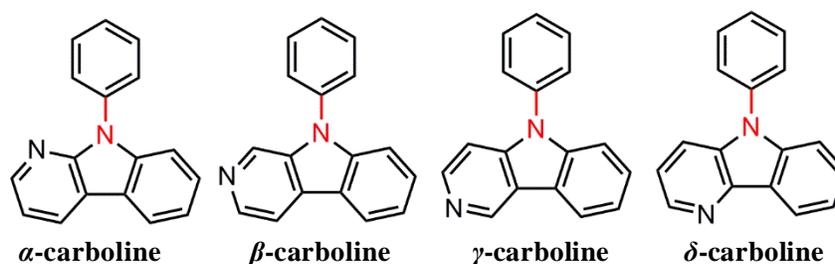


Figure S10. Chemical structures of the molecules with carboline subunits. BDE_f values of the fragile D- π bonds (those labeled in red) were calculated.

Table S9. B3LYP/6-31G(d) Bond Dissociation Energies of Fragile Bonds (BDE_f), Dihedral Angles ($\angle D-\pi$) between Carboline and the Phenyl Group ($\angle D-\pi$) and Hirshfeld Charges (q_N) of Molecules with Carboline Subunits

molecule	BDE_f (eV)	$\angle D-\pi$ (deg)	$10^2 \times q_N$
α -carboline	3.78	51	-1.9
β -carboline	3.56	56	-1.9
γ -carboline	3.66	57	-1.7
δ -carboline	3.58	55	-2.1

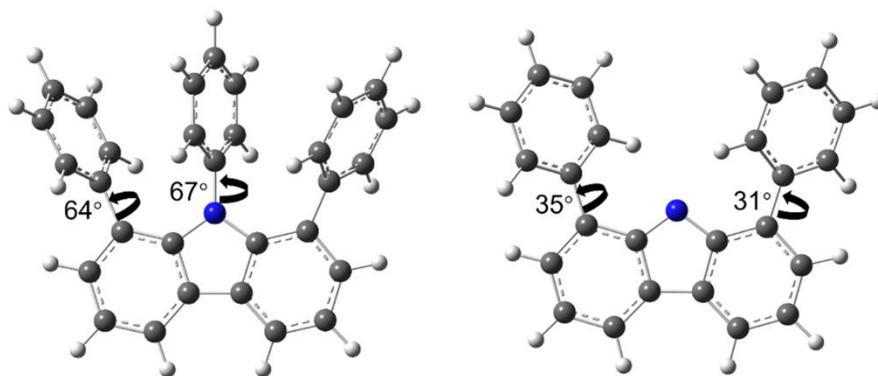


Figure S11. Geometries of ODP before and after the phenyl group on 9-position of Cz is taken off.

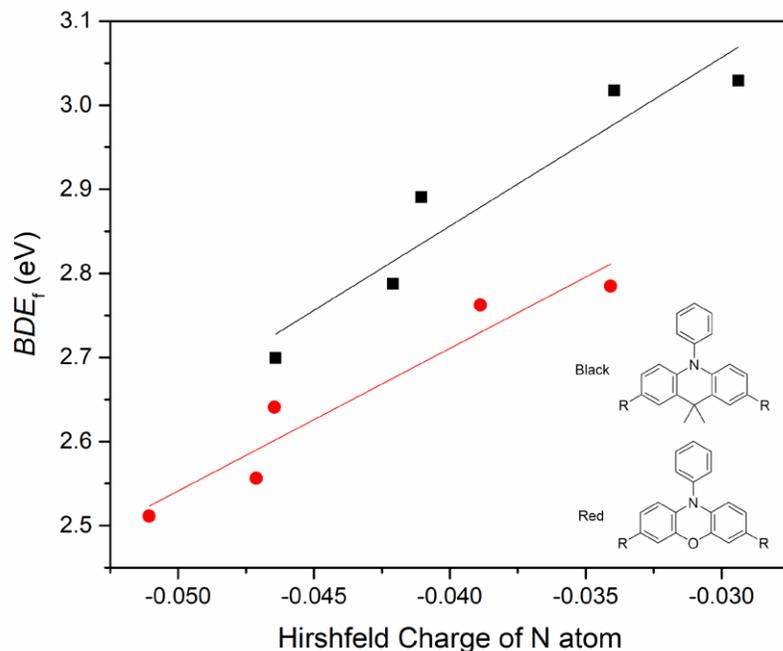


Figure S12. The correlation between the B3LYP/6-31G(d) Hirshfeld charge of N atom (q_N) and BDE_f in derivatives of 9,9-dimethyl-10-phenyl-9,10-dihydroacridine (PhDMAC, black dots) and 10-phenyl-10*H*-phenoxazine (PhPx, red dots). Group R is selected from methoxyl group, methyl group, H atom, trifluoromethyl group, or cyano group.

Table S10. B3LYP/6-31G(d) Bond Dissociation Energies of Fragile Bonds (BDE_f) and Hirshfeld Charges of the N Atoms (q_N) of Derivatives of PhDMAC and PhPx

substituents on 3,6-positions	derivatives of PhDMAC		derivatives of PhPx	
	BDE_f (eV)	q_N	BDE_f (eV)	q_N
Methoxyl group	2.70	-0.0464	2.51	-0.0519
Methyl group	2.78	-0.0421	2.57	-0.0471
H atom	2.89	-0.0410	2.64	-0.0465
Trifluoromethyl	3.02	-0.0339	2.76	-0.0389
Cyano group	3.03	-0.0294	2.78	-0.0341

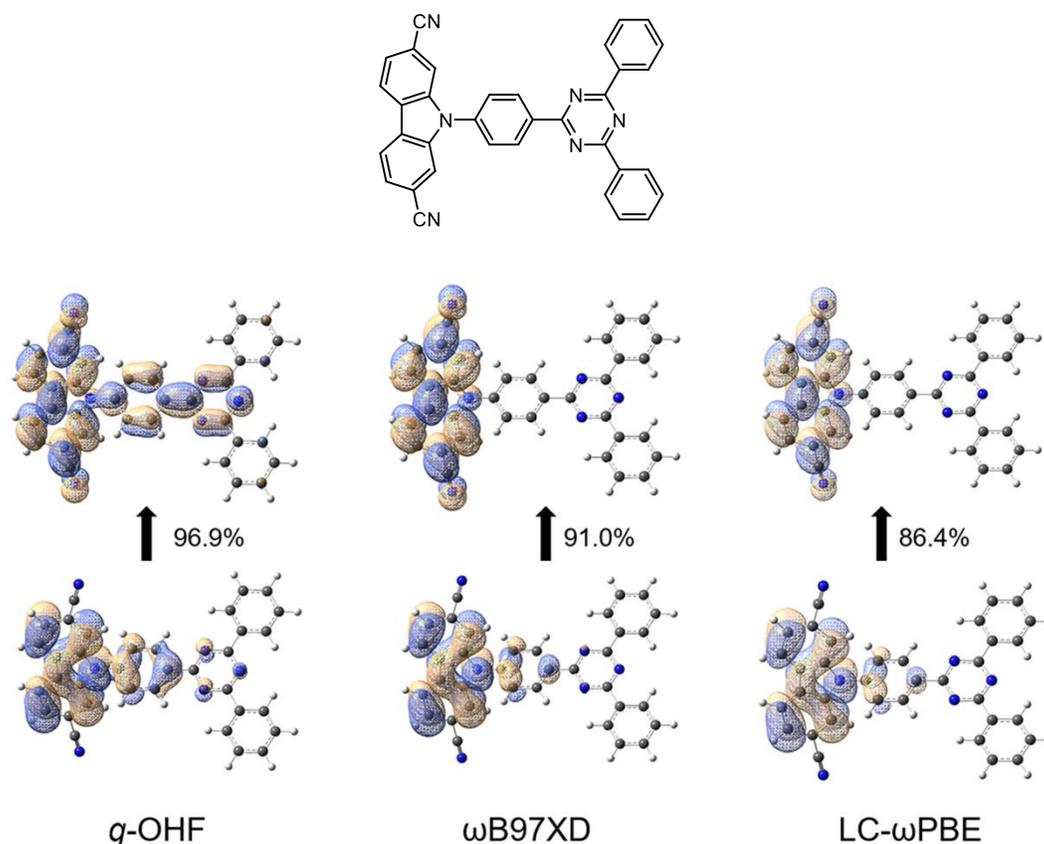


Figure S13. Chemical structure of MDNTrz; natural transition orbitals (NTOs) of its S_1 state and the weights; calculated by the *q*-OHF (OHF% = 18.2%) method, ω B97XD and LC- ω PBE functionals.

Reference

- Internet Bond-energy Databank (pK_a and BDE)-iBonD Home Page. <http://ibond.chem.tsinghua.edu.cn> (accessed April 2018).
- Huang, S.; Zhang, Q.; Shiota, Y.; Nakagawa, T.; Kuwabara, K.; Yoshizawa, K.; Adachi, C. Computational Prediction for Singlet- and Triplet-Transition Energies of Charge-Transfer Compounds. *J. Chem. Theory Comput.* **2013**, *9*, 3872–3877.
- Kim, M.; Jeon, S. K.; Hwang, S.-H.; Lee, J. Y. Stable Blue Thermally Activated Delayed Fluorescent Organic Light-Emitting Diodes with Three Times Longer Lifetime than Phosphorescent Organic Light-Emitting. *Adv. Mater.* **2015**, *27*, 2515–2520.
- Lee, S. Y.; Yasuda, T.; Yang, Y. S.; Zhang, Q.; Adachi, C. Luminous Butterflies: Efficient Exciton Harvesting by Benzophenone Derivatives for Full-Color Delayed Fluorescence OLEDs. *Angew. Chem. Int. Ed.* **2014**, *53*, 6402–6406.
- Lee, D. R.; Kim, M.; Jeon, S. K.; Hwang, S.-H.; Lee, C. W.; Lee, J. Y. Design Strategy for 25% External Quantum Efficiency in Green and Blue Thermally Activated Delayed Fluorescent Devices. *Adv. Mater.* **2015**, *27*, 5861–5867.
- Cho, Y. J.; Jeon, S. K.; Lee, J. Y. Molecular Engineering of High Efficiency and Long Lifetime Blue Thermally Activated Delayed Fluorescent Emitters for Vacuum and Solution Processed Organic Light-Emitting Diodes. *Adv. Opt. Mater.* **2016**, *4*, 688–693.
- Cui, L.-S.; Nomura, H.; Geng, Y.; Kim, J. U.; Nakanotani, H.; Adachi, C. Controlling Singlet-Triplet Energy Splitting for Deep-Blue Thermally Activated Delayed Fluorescence Emitters. *Angew. Chem. Int. Ed.* **2016**, *55*, 1–6.
- Zubarev, D. Y.; I. Boldyrev, A. I. Developing paradigms of chemical bonding: adaptive natural density partitioning. *Phys. Chem. Chem. Phys.*, **2008**, *10*, 5207–5217.
- Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580–592.