

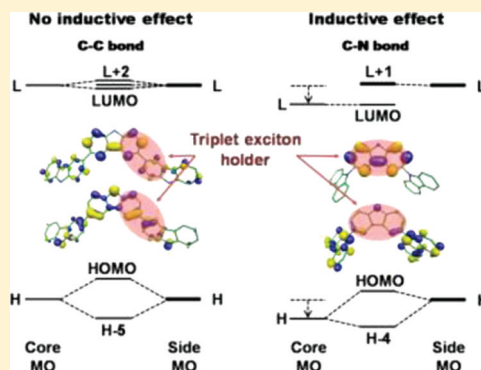
Theoretical Investigation of Triscarbazole Derivatives As Host Materials for Blue Electrophosphorescence: Effects of Topology

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S Supporting Information

ABSTRACT: We have investigated the electronic structure of triscarbazole derivatives used as host materials in blue phosphorescent organic light-emitting diodes. The results of density functional theory calculations show that, in the case of triscarbazole derivatives where the carbazole units are linked via C–C bonds, the frontier molecular orbital energies are modulated by strong molecular orbital interactions between the central and side carbazole units. On the other hand, in the case of triscarbazoles linked via C–N bonds, the combination of inductive effects and molecular orbital interactions tunes the frontier level energies and, interestingly, gives rise to an ambipolar character. In the C–N linked systems, the lowest triplet states are characterized mainly by an electronic transition localized within the central carbazole, while in the C–C linked compounds it is the longest oligo-*para*-phenyl segment to be found in the chemical structure that defines the lowest triplet transition. When the N–H group of the central carbazole unit is replaced by other groups [O, S, CH₂, C(CH₃)₂, C(CH₃)(CF₃), and C(CF₃)₂], the HOMO/LUMO energies fluctuate substantially in the absence of the side carbazoles, but these variations are significantly reduced in their presence; also, the singlet–triplet energy differences decrease substantially when going from the isolated central unit to the triscarbazole-like derivatives.

KEYWORDS: blue OLEDs, ambipolar hosts, triscarbazoles, singlet–triplet energy differences, density functional theory (DFT) calculations



I. INTRODUCTION

Phosphorescent organic light-emitting diodes (PhOLEDs) based on heavy-metal complexes have recently attracted considerable attention because of the high quantum efficiency they achieve by harvesting both singlet and triplet excitons, as a result of efficient intersystem crossing.^{1–3} In PhOLED devices, to prevent concentration quenching of the phosphorescence, the emitters are usually doped into a suitable host organic material. Thus, the development of host materials is as critical as that of emitters for the fabrication of efficient devices. Important criteria that the host needs to fulfill include (i) a triplet energy larger than that of the phosphorescent guest,^{4,5} which facilitates an exothermic energy transfer from the host to the guest and prevents back energy transfer (that could lead to luminescence quenching); and (ii) appropriate values of ionization potential (IP, that can be approximated by the energy of the HOMO level) and electron affinity (EA, energy of the LUMO level) to facilitate charge injection from adjacent hole-transport and electron-transport layers.

Although efficient and stable red- and green-emitting PhOLEDs have been demonstrated,^{2,6} the realization of high-performance, deep blue PhOLEDs remains a challenge. Part of the issue is related to the fact that the host material is then required to display a high triplet energy (~3.0 eV), which

normally means a large HOMO–LUMO gap (high IP and low EA). In molecules with high triplet energy, the extent of π -conjugation usually needs to remain small and the resulting large band gap leads to appreciable charge-injection barriers and high device turn-on voltage. This explains that the number of efficient host materials for blue electrophosphorescent devices is still limited.

Carbazole-based materials have received special attention for their excellent hole-transport properties, well-positioned IP, and high triplet energy.^{4,7–19} For instance, N,N'-dicarbazolyl-3,5-benzene (mCP) is commonly used along with the phosphorescent iridium complex iridium(III)bis[[4,6-difluorophenyl]pyridinato-*N*,*C*^{2'}]picolate (FIrpic) to fabricate blue phosphorescent devices with high quantum efficiency.⁴ The high triplet energy of carbazole is maintained when the molecule is functionalized with phenylsilane¹¹ or biphenylphosphoryl moieties^{13–16} where silicon and phosphine oxide act as breaking points of π -conjugation. However, there is still room for improvement, as these host materials still present

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issues related to large band gaps, unbalanced charge transport, and low device power efficiency.¹⁴

Lately, it has been shown that linking monomer moieties with a large energy gap to form oligomers can produce host materials with large triplet energies suitable for blue electrophosphorescence. With regard to carbazole-based oligomers, although polycarbazoles linked via C–C bonds have been suggested as host materials for OLED applications,^{7–9} little attention had been paid to oligo-carbazoles linked via C–N bonds, until a study on triscarbazoles (TCzs) with a 3(6),9'-linked topology (see Figure 1);¹² blue devices based on this

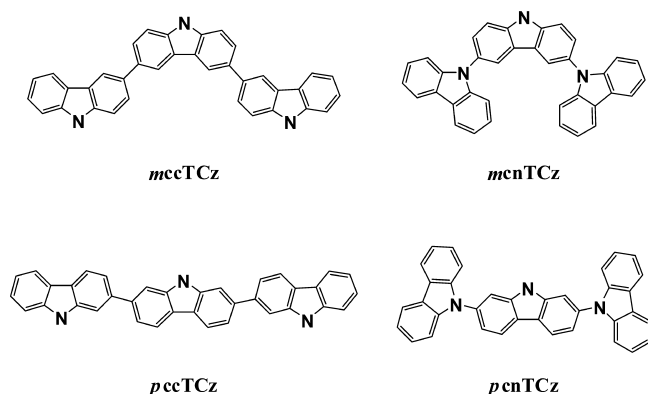


Figure 1. Chemical structures of the triscarbazoles (TCzs) examined in this study.

type of molecular architecture turn on at approximately 3 V and yield maximum external quantum efficiencies (EQE) as high as 15% (31 cd/A) and maximum power efficiencies of 28 lm/W.¹² The performance of these devices indicates that such TCz molecules possess not only high triplet energies but also relatively low energy barriers for charge injection from adjacent layers. However, a detailed understanding of how this type of molecules can achieve good device performance is still missing.

Here, we report on quantum-mechanical investigations of the electronic structure of the series of TCz derivatives shown in Figure 1. In addition, to gain better insight into the charge transport levels and triplet exciton confinement, we performed electronic-structure calculations on *N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPD), tris(8-hydroquinolino)aluminum (Alq3), and FIrpic, chosen as representative systems for hole-transport, electron-transport, and blue light-emitting materials, respectively. On the basis of our results, we discuss how molecular topology affects the photophysical and charge-injection properties of TCz molecules. We also address the effect of substitution of the N–H group of the central carbazole (referred to below as the “core” unit while the terminal carbazoles are referred to as the “side” units) with X = O, S, CH₂, C(CH₃)₂, C(CH₃)(CF₃), and C(CF₃)₂ on the energies of the frontier molecular orbitals (FMOs) as well as on

the lowest-lying excited singlet (*S*₁) and triplet states (*T*₁) of these molecules.

II. COMPUTATIONAL DETAILS

The optimized geometries and relevant energies of the TCz derivatives were obtained by means of density functional theory (DFT) calculations using the hybrid B3LYP functional and 6-31G* basis set. Spin-restricted DFT calculations were carried out for ground-state (*S*₀) geometries, and spin-unrestricted calculations for the lowest triplet states (*T*₁) and ionic states. All geometries were confirmed to be minima by additional vibrational frequency calculations. The lowest triplet energies and IPs/EAs were evaluated via the Δ SCF method based on optimized geometries. To get a better insight into the nature of the triplet state, natural transition orbital (NTO) analyses^{20,21} were performed following time-dependent (TD) DFT calculations,²² using the *T*₁-optimized geometries. To confirm the reliability of the B3LYP functional to assess the charge-transfer states in the molecules under study, the ω B97X functional²³ was also employed; the singlet (*S*₁) and triplet (*T*₁) vertical excitation energies of the core molecules and their TCz derivatives were compared. All the calculations were carried out with the Gaussian-03 package,²⁴ except for the NTO analyses performed with the TurboMole package.^{25–27}

III. RESULTS AND DISCUSSION

1. Effect of Topology: C–C Linkage versus C–N Linkage. To assess energy barriers for charge injection from adjacent layers, the FMO energies and IP/EA values of the TCz derivatives are collected in Table 1 and compared with those of NPD, Alq3, and FIrpic. All four TCzs have their HOMO energies (ranging from –4.92 to –5.23 eV) in between those of NPD (–4.74 eV) and FIrpic (–5.47 eV), which indicates the potential for the TCz molecules to mediate hole transport from NPD to FIrpic. The comparison of the IP values draws the same picture: The IPs of TCzs fall in between those of NPD and FIrpic. However, a closer examination distinguishes *mccTCz* from the other molecules in that its HOMO (and IP) is more energetically distant from that of FIrpic, while those of the other TCzs are located in a more balanced way between NPD and FIrpic. Hence, hole transfer from NPD to FIrpic would be expected to be least facile when *mccTCz* is used as the host material. Regarding electron injection, the LUMOs of Alq3 and FIrpic are comparable (–1.68 eV vs –1.72 eV) while those of the TCzs are positioned at higher energies with the *mccTCz* LUMO very high (–0.67 eV), and the *pccTCz*, *mcnTCz*, and *pcnTCz* LUMOs at similar energies (–1.23 eV). This points to *mccTCz* having the largest electron-injection barrier. The comparison of the EAs is consistent with this observation. Thus, from the perspective of charge injection, *mccTCz* appears to be the least promising molecule among the TCz derivatives investigated in our study.

To better understand the impact of the topologies of the TCz molecules on their FMO energy levels, natural population analyses (NPA) were carried out. The C–C linkages do not alter the overall electron density of each carbazole moiety in TCz, as the NPA results confirm the neutrality of the core

Table 1. DFT/B3LYP Calculated FMO Energy Levels and Adiabatic IPs/EAs of TCz Derivatives NPD, Alq3, and FIrpic.^a

	Cz	<i>mccTCz</i>	<i>pccTCz</i>	<i>mcnTCz</i>	<i>pcnTCz</i>	NPD	Alq3	FIrpic
LUMO	–0.65	–0.67	–1.23	–1.23	–1.23	–1.15	–1.68	–1.72
EA ^b	0.91	0.25	–0.35	0.00	–0.07	–0.24	–0.54	–0.59
HOMO	–5.44	–4.92	–5.14	–5.20	–5.23	–4.74	–5.20	–5.47
IP	7.11	5.89	6.06	6.18	6.18	5.60	6.36	6.56

^aAll values are in eV. ^bEA is defined as E(anionic state) – E(neutral state).

carbazole (zero net charge for both ccTCzs). On the other hand, there occurs a net charge transfer from the core carbazole to the side carbazoles in the case of C–N linkages; the total net charge of the core carbazole is +0.43 lel and +0.40 lel for *mcnTCz* and *pcnTCz*, respectively. Thus, the variations in linking patterns in the chemical structures of the carbazole moieties lead to markedly different inductive effects; these are negligible for the ccTCz molecules and substantial for the cnTCz molecules. As a result, in the ccTCz molecules, the MO energies of the core and side carbazoles remain nearly in resonance (that is, at the same energy); hence, as long as the linking atoms contribute substantially to an MO, the interactions between the subunits for that MO will be significant. As seen from Figure 2, the HOMO wave functions

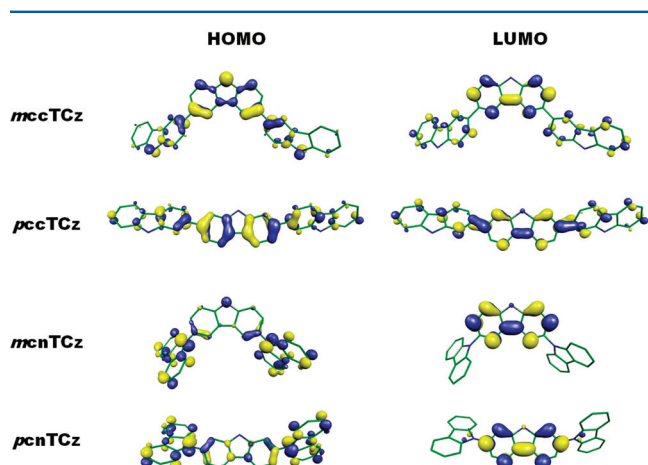


Figure 2. Sketch of the HOMO and LUMO wave functions of the triscarbazole derivatives.

of the ccTCz molecules are delocalized over the whole system. Consequently, antibonding combinations between the HOMOs of each carbazole moiety give rise to the destabilization of the TCz HOMO with respect to an isolated unit. The LUMO of *pccTCz* shows a similar picture; there, bonding-type interactions result in a stabilized TCz LUMO. However, in *mccTCz*, orbital mixing and energy-level splitting are expected to be modest because the LUMO wave functions of the subunits present nodes at the linking carbon atoms; indeed, the LUMO energy of *mccTCz* is very close to that of the carbazole molecule itself.

In the cnTCz molecules where substantial inductive effects are present, there occur energy-level offsets between the subunits and, as a result, the MO interactions between subunits weaken. The net positive charge of the core unit pushes its frontier orbitals down in energy, resulting in the localization of the cnTCz LUMOs on the core units (see Figure 2) and in a more stable LUMO energy (and EA) than for the carbazole molecule itself (Table 1). On the other hand, the side carbazoles contribute predominantly to the HOMO; some additional antibonding MO interactions between the core and side carbazoles lead to a destabilization of the HOMO in the cnTCzs derivatives.

Interestingly, the fact that the HOMO and LUMO of the cnTCz molecules are localized on different subunits and present higher and lower energy, respectively, than in carbazole itself, suggests that molecules of this type might possess an ambipolar charge-transport character. This is an intriguing proposition because it points to the possibility that ambipolar host molecules for blue OLED applications can be synthesized from a single building block.²⁸ This feature arises in the cnTCz molecules from the interplay between the inductive stabilization of the core MOs and the less effective MO interactions between subunits. The weaker MO interactions in cnTCzs are also consistent with the fact that their HOMO energy levels

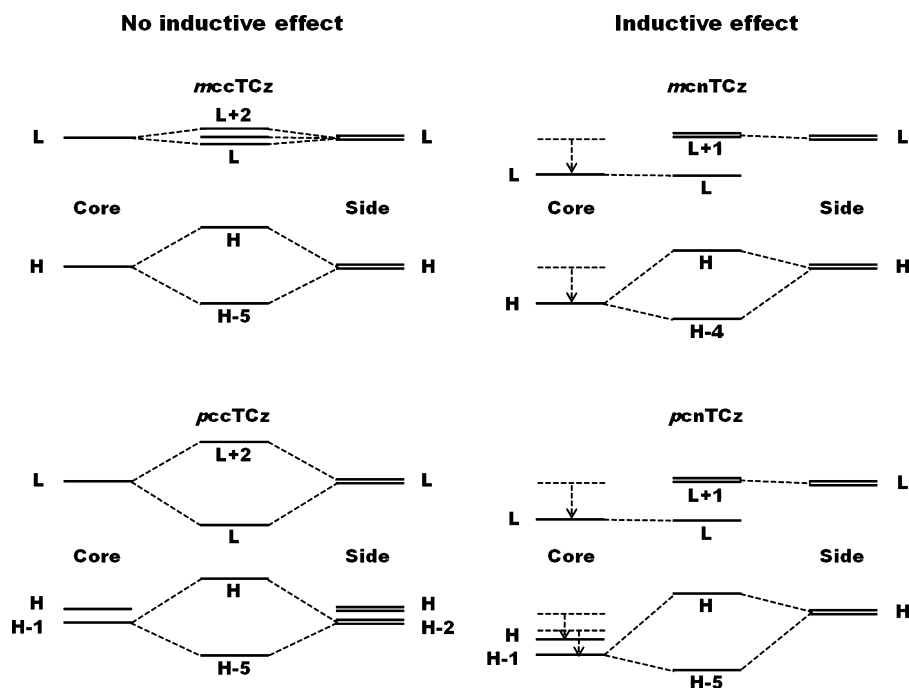


Figure 3. Correlation diagram for the frontier molecular orbitals of the triscarbazole derivatives: C–C linked TCzs are displayed on the left and C–N linked TCzs on the right. For the sake of simplicity, only the HOMO/LUMO (H/L) levels are depicted.

tend to be lower than those of ccTCzs (Table 1). The evolution of the FMO energies in going from carbazole to the TCz derivatives is illustrated in the form of a correlation diagram in Figure 3.

The host molecules in the emissive layer are also required to have high triplet energies to eventually confine all of the excitons on the guest emitters. The calculated lowest triplet energies of the TCzs are listed in Table 2. While *mccTCz*,

Table 2. Calculated and Experimental Triplet Energies of the Triscarbazole Derivatives and FIrpic.^a

	<i>mccTCz</i>	<i>pccTCz</i>	<i>mcnTCz</i>	<i>pcnTCz</i>	FIrpic
E_T^b	2.98	2.59	3.01	2.83	2.69
$E_T^0^b$	2.82	2.46	2.87	2.71	2.58
expt.	2.73 ^c	2.37 ^c	2.92 ^c		2.65/2.66
ref	7	7	12		4/39

^aAll values are in eV. ^b E_T and E_T^0 denote adiabatic triplet energy without and with zero-point vibrational energy correction, respectively.

^cThe actual compounds to which *mccTCz*, *pccTCz*, and *mcnTCz* are compared are [3,3':6'3"]-ter(9-octylcarbazole), 2,7-bis(9,9-[3,7-dimethyloctyl]fluorene-2-yl)-9-octylcarbazole, and 3,6-bis(carbazole-9-yl)-9-2-ethylhexyl-carbazole, respectively. See refs 7 and 12.

mcnTCz, and *pcnTCz* show higher triplet energies (>2.71 eV) than that of FIrpic (2.58 eV), *pccTCz* exhibits a significantly lower triplet energy (2.46 eV). This difference can be understood by inspecting the natural transition orbitals (NTOs) defining the T_1 state that are depicted in Figure 4.

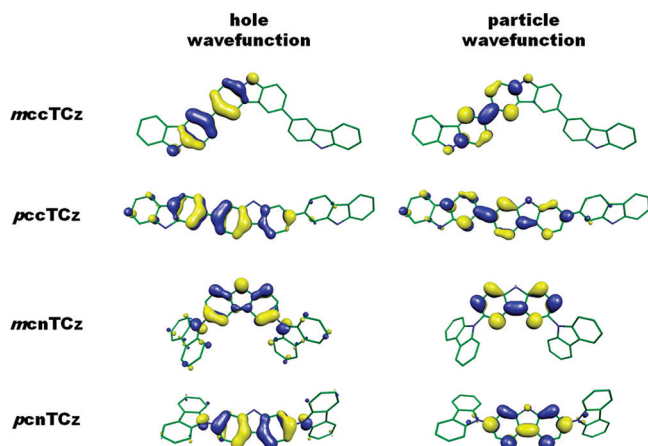


Figure 4. Hole-particle pairs of natural transition orbitals (NTO) of the triscarbazole derivatives for the T_1 state. The NTO eigenvalues, λ , are very close to 1 (0.9365, 0.9407, 0.9724, and 0.9623 for *mccTCz*, *pccTCz*, *mcnTCz*, and *pcnTCz*, respectively), which indicates that the hole-particle pairs illustrated here dominate the description of the S_0 – T_1 transition.

Clearly, high triplet energies are explained by localized transitions within subunits with high triplet energy. The T_1 states of the cnTCz molecules are characterized predominantly by a transition localized in the core carbazole; in *mccTCz*, the biphenyl segment between adjacent carbazole units defines where the triplet transition occurs.⁷ In the case of *pccTCz*, however, the T_1 state corresponds to a transition between hole-particle wave functions delocalized over three to four *para*-phenyl subunits;⁷ this is due to the strong MO interactions across the subunits in the FMO levels of *pccTCz*. Since the energy gap between these delocalized hole-particle wave

functions is expected to be small, *pccTCz* has a relatively lower triplet energy, which makes *pccTCz* inappropriate as host material in blue PhOLEDs.

It is also of interest to consider the dihedral angles between the core and side carbazole units in the various electronic states considered in this study, see Table 3. By and large, the more

Table 3. Dihedral Angles in the Tris-Carbazole Molecules between the Core and Side Carbazole Units for the Electronic States Explored in This Study.^a

	<i>mccTCz</i>	<i>pccTCz</i>	<i>mcnTCz</i>	<i>pcnTCz</i>
ground (S_0) state	33.4°, 33.4°	38.1°, 38.1°	61.3°, 61.3°	56.1°, 56.1°
T_1 state	2.2°, 38.2°	13.8°, 25.7°	46.0°, 45.3°	48.7°, 48.7°
cationic state	29.4°, 29.4°	28.0°, 28.0°	48.4°, 48.4°	45.5°, 45.5°
anionic state	28.3°, 28.3°	24.5°, 24.5°	64.2°, 64.2°	68.3°, 68.3°

^aDihedral angles are taken by considering the linkage atoms and adjacent C atoms.

localized character of the electronic states in the cnTCz molecules is reflected in much larger dihedral angles. For instance, in the T_1 state, the cnTCz dihedral angles reach values on the order of 45–50°, while those in the ccTCz molecules can be as small as 2–14°.

We also note that concerns have been recently raised regarding the possibility of triplet excimer formation in carbazole derivatives,^{29–31} which would lead to a decrease in triplet-state energy and thus degrade the performance of blue-emitting devices based on such host molecules. However, the triplet-state wave functions of cnTCz molecules reside on the central carbazole unit. Because rather bulky, significantly twisted substituents are present, intermolecular interactions between the central carbazole moieties of adjacent molecules should be very limited,³⁰ which is consistent with the good performance of *mcnTCz* derivatives as host materials for blue devices.¹²

To summarize, the ccTCz molecules suffer either from unbalanced energy barriers for charge injection (*mccTCz*) or from low triplet energy (*pcnTCz*). On the other hand, the cnTCz molecules display ambipolar transport characteristics and high triplet energy, which make them promising host molecules for blue electrophosphorescence; this conclusion is consistent with the high EQE of devices based on *mcnTCz* analogs.¹² Because *mcnTCz* presents a higher T_1 state energy and more appropriate IP and EA values (i.e., a stronger ambipolar character due to a smaller HOMO–LUMO energy gap) than its *para* counterpart, we have chosen to discuss in more detail the electronic structures of *mcnTCz* and its analogs formed by replacing the N–H group of the core unit; the corresponding molecules are shown in Figure 5.

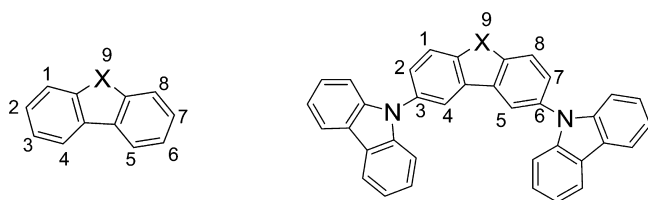


Figure 5. Chemical structure of the core compounds (left) and their triscarbazole-like derivatives (right) where X = NH, O, S, CH₂, C(CH₃)₂, C(CH₃)(CF₃), or C(CF₃)₂.

2. *mcnTCz* and Its Analogs. (i). *Electronic Structure*.

To eventually gain a good insight into the electronic structures of *mcnTCz* and its derivatives, especially regarding the role of the side carbazole units, it is useful first to investigate the core molecules themselves. The FMO energies of carbazole and its analogs are collected in Table 4. Carbazole ($X = \text{NH}$) exhibits

Table 4. FMO Energies of the Core Molecules and Their 3(6),9'-Triscarbazole Derivatives (*mcnTCzs*).^a

X	core			TCz		
	HOMO	LUMO	$\Delta E_{\text{H-L}}$ ^b	HOMO	LUMO	$\Delta E_{\text{H-L}}$ ^b
NH	−5.44	−0.64	4.80	−5.20	−1.23	3.97
O	−6.01	−0.92	5.09	−5.38	−1.44	3.94
S	−5.82	−0.95	4.87	−5.36	−1.43	3.93
CH ₂	−5.75	−0.71	5.04	−5.33	−1.23	4.10
C(CH ₃) ₂	−5.73	−0.74	4.99	−5.32	−1.25	4.07
C(CH ₃)(CF ₃)	−6.00	−0.99	5.01	−5.43	−1.45	3.98
C(CF ₃) ₂	−6.25	−1.25	5.00	−5.52	−1.64	3.88

^aAll values are in eV. ^b $\Delta E_{\text{H-L}}$ denotes the energy gap between the HOMO and LUMO levels.

the highest HOMO and LUMO energies in the series; the substitution of $X = \text{NH}$ with O, S, CH₂, C(CH₃)₂, C(CH₃)(CF₃), and C(CF₃)₂ stabilizes the HOMO level by 0.3 to 0.8 eV and the LUMO level by 0.1 to 0.6 eV. However, the HOMO–LUMO energy gap is hardly affected by these substitutions and remains in the range of 4.9 ± 0.1 eV within the series. This is related to the fact that the X groups actually contribute only moderately to the HOMO and LUMO wave functions, see Figure 6 (note that in the cases of carbazole and

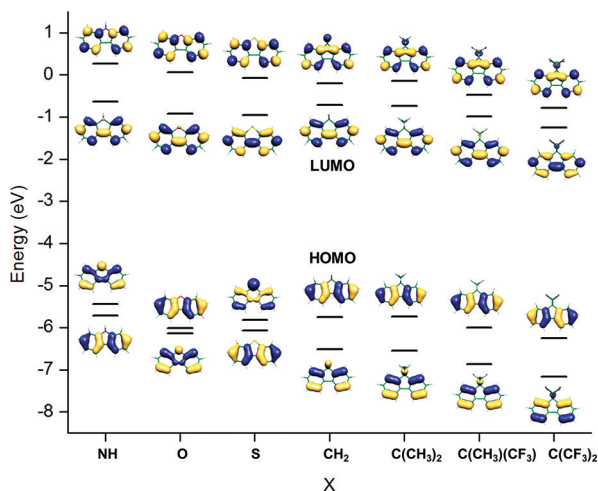


Figure 6. Frontier molecular orbitals of the core molecules associated with the lowest singlet (S_1) and triplet (T_1) excited states as a function of the nature of the X group. Note the interchange in the electronic description of HOMO and HOMO-1 in the cases of $X = \text{NH}$ and S with respect to the other compounds.

dibenzothiophene ($X = \text{S}$), the HOMO and HOMO-1 characteristics are interchanged with respect to the other molecules and the X groups contribute to the HOMO wave functions; however, the magnitude of the shift of the HOMO level itself remains marginal).

On the other hand, with two additional carbazoles linked via *meta* positions (3,6 positions in Figure 4), the HOMO–LUMO energy gaps of the molecules in the series are significantly

reduced by ca. 1 eV (Table 3); as discussed, this effect arises from the interplay between inductive effects and MO interactions among the core and side carbazoles. In addition, the variations in the HOMO or LUMO energies are much smaller in the TCz-like derivatives; while changes of 0.8 and 0.6 eV are observed in the HOMOs and LUMOs of the core molecules, respectively, the HOMOs in the TCz-like molecules vary only by 0.32 eV and the LUMOs by 0.41 eV. This is at least partly due to the fact that the X groups of the core molecules contribute even less to the HOMO/LUMO wave functions in the presence of the side carbazoles.

(ii). *Singlet versus Triplet Energy*. The energy difference between the singlet (S_1) and triplet (T_1) excited states, ΔE_{ST} ,^{32,33} has often been used as an indicator of the potential performance of host molecules, since a smaller ΔE_{ST} energy gap has been observed to correlate to a better performance.^{7,34} In this context, the lowest singlet and triplet energies evaluated at the optimized ground-state geometries are given in Table 4.

When considering the core molecules, moving away from carbazole leads to an increase in the singlet energy. For instance, substitution of the N atom with O or CH₂ increases the singlet energy by 0.38 and 0.25 eV, respectively. On the other hand, the triplet energy depends less on the choice of the X group; for example, the triplet energy decreases by 0.1 eV upon replacing the NH group with the CH₂ group. Substitution of CH₂ with C(CH₃)₂, C(CH₃)(CF₃), and C(CF₃)₂, however, hardly influences either the singlet or the triplet energy. The ΔE_{ST} singlet–triplet energy difference (Table 5) is found to be

Table 5. TD-DFT/B3LYP Calculated Energies E of the Singlet (S_1) and Triplet (T_1) Excited States along with the Singlet–Triplet Energy Difference (ΔE_{ST}) for the Core Molecules and Their 3(6),9'-Triscarbazole-Like Derivatives (*mcnTCzs*).^a

X	core			TCz		
	$E(S_1)$	$E(T_1)$	ΔE_{ST}	$E(S_1)$	$E(T_1)$	ΔE_{ST}
NH	4.15	3.19	0.96	3.34	3.08	0.26
O	4.53	3.21	1.32	3.34	3.13	0.21
S	4.20	3.16	1.04	3.35	3.08	0.27
CH ₂	4.40	3.09	1.31	3.56	3.00	0.56
C(CH ₃) ₂	4.39	3.06	1.33	3.41	2.97	0.44
C(CH ₃)(CF ₃)	4.39	3.05	1.34	3.41	2.94	0.47
C(CF ₃) ₂	4.41	3.03	1.38	3.35	2.89	0.46

^aAll values are in eV.

in the range 1.0–1.4 eV and slightly larger than those of many small molecules (0.7–1 eV).^{35,36} The introduction of the side carbazole units, however, substantially diminishes the singlet–triplet energy difference; ΔE_{ST} ranges from 0.21 to 0.56 eV and is smaller by ca. 0.7–1.1 eV than in the core molecules.

To shed light on the nature of the excited states, the MO transitions that present the largest contributions to the excited states have been investigated and are listed in Table 6. The triplet states of the TCz-like derivatives remain localized on the core units, giving rise to triplet energies similar to those of the core molecules. However, the singlet excited states are calculated to be dominated by a HOMO-to-LUMO transition with strong intramolecular charge transfer (ICT) character, that is, from a HOMO localized on the side carbazoles to a LUMO localized on the core units (see Figures 2 and 7). Therefore, the lowering of the singlet transition energy and hence the reduced singlet–triplet energy difference when going from the core

Table 6. Dominant Transitions Corresponding to the Lowest Singlet (S_1) and Triplet (T_1) States of the Core Molecules and Their 3(6),9'-Triscarbazole-Like Derivatives (*mcnTCzs*).^a

X	core		TCz	
	S_1	T_1	S_1	T_1
NH	H→L	H-1→L	H→L	H→L, H-4→L
O	H-1→L	H→L	H→L	H-4→L
S	H→L	H-1→L	H→L	H-5→L
CH ₂	H→L, H→L+1	H→L	H→L	H-4→L
C(CH ₃) ₂	H→L	H→L	H→L	H-4→L
C(CH ₃)(CF ₃)	H→L+1, H→L	H→L	H→L	H-4→L
C(CF ₃) ₂	H→L+1, H→L	H→L	H→L	H-4→L

^aH and L denote HOMO and LUMO, respectively.

molecules to their TCz-like derivatives appears related to this shift from a localized transition to an ICT transition. At this stage, it is useful to note that conventional DFT methodologies are susceptible to evaluating incorrectly ICT transition energies, as a result of the self-interaction error present in traditional (local) exchange-correlation functionals.^{37,38} Hence, we checked the reliability of the B3LYP ICT energies by conducting calculations using the long-ranged corrected ω B97X functional,²³ which is expected to handle ICT transition energies appropriately; the results are given in Tables S3 and S4 in the Supporting Information. When X = NH and S, the ω B97X functional also describes the S_1 state of the TCz derivatives as an ICT state. For the other TCz derivatives, however, the S_1 states have a localized character on one of the side carbazole units. Importantly, however, the B3LYP and ω B97X results are in mutual agreement in that the singlet–triplet energy differences are significantly diminished with the addition of the side carbazoles; as mentioned, this reduced ΔE_{ST} points to the better potential of the TCz-like derivatives.^{7,34}

3. Charge Injection Efficiency into the Hosts. All the *mcnTCz* analogs studied here display higher triplet energies than FIrpic (Table S5 in the Supporting Information); therefore, the eventual performance of these molecules as hosts for blue OLEDs can depend upon the charge-injection barriers they present with respect to the adjacent layers. The IPs and EAs of the TCz derivatives are listed in Table 7. To a

Table 7. Ionization Potentials (IPs) and Electron Affinities (EAs) of 3(6),9'-Triscarbazole Derivatives Evaluated at the B3LYP/6-31G* Level^a

	NH	O	S	CH ₂	C(CH ₃) ₂	C(CH ₃)(CF ₃)	C(CF ₃) ₂
IP	6.18	6.40	6.46	6.36	6.34	6.45	6.54
EA	0.00	−0.21	−0.24	−0.05	−0.10	−0.31	−0.52

^aAll values are in eV.

first approximation, that is, when basing the discussion only on these energies, it appears that *mcnTCz* might most efficiently transfer holes from NPD to FIrpic because of a lower injection barrier (0.58 eV for *mcnTCz* vs 0.74 eV or higher for the analogs). On the other hand, with respect to electron injection, *mcnTCz* has the largest barrier (0.54 eV) and would be the least efficient when Alq3 is employed as an electron-transport layer. However, the charge-injection barriers for this molecule (0.58 eV for hole injection vs 0.54 eV for electron injection) are well balanced and the singlet–triplet energy difference (0.26 eV) is one of the smallest. Therefore, *mcnTCz* appears to be a most promising host among the molecules investigated in this study.

IV. SUMMARY

By conducting quantum–mechanical calculations on the electronic structures of triscarbazole derivatives, we find that the coupling of the carbazole subunits via C–N bonds allows the fine turning of the HOMO and LUMO energies via a combination of inductive effects and MO interactions between

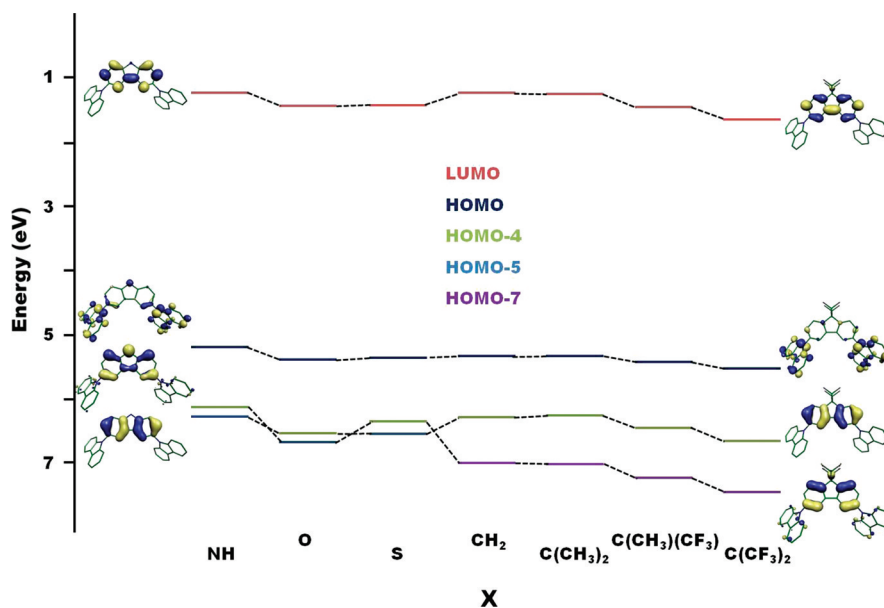


Figure 7. Frontier molecular orbitals of the triscarbazole derivatives involved in their lowest singlet (S_1) and triplet (T_1) excited states. Orbitals of a similar nature are connected by dotted lines. The HOMO-5s, when X = NH, O, and S, or HOMO-7s, when X = CH₂, C(CH₃)₂, C(CH₃)(CF₃), and C(CF₃)₂, are depicted for the sake of completeness.

the subunits. Interestingly, an ambipolar character is obtained in terms of hole and electron injections, which is an intriguing finding, since it represents the uncommon example of an ambipolar host molecule made from a single building block. Variations of the X group in the core units do affect the HOMO and LUMO energy levels for the isolated molecules; however, the variations significantly decrease when side carbazole units are present. While the introduction of side carbazoles hardly influences the triplet energy, it reduces significantly the singlet energy and thus the singlet–triplet energy difference.

In summary, the coupling of three carbazoles via C–N linkages imparts the molecules with an ambipolar character with regard to charge injection while keeping the triplet energy as high as that of the carbazole monomer. This qualifies the *meta* C–N linked TCz molecules as good host materials for blue PhOLEDs. We think that the findings described in this theoretical work are useful for the design and development of new efficient host materials.

■ ASSOCIATED CONTENT

● Supporting Information

Results obtained with different computational methodologies; results on the core and TCz derivatives at the DFT wB97X/6-31G* level of theory; comparison of adiabatic triplet energies of the TCz derivatives and FLrpic; the frontier molecular orbitals of the TCz derivatives, including the ones related to the lowest triplet state. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ REFERENCES

- (1) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, 395, 151.
- (2) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Appl. Phys. Lett.* **2000**, 77, 904.
- (3) Kawamura, Y.; Goushi, K.; Brooks, J.; Brown, J. J.; Sasabe, H.; Adachi, C. *Appl. Phys. Lett.* **2005**, 86, 071104.
- (4) Holmes, R. J.; Forrest, S. R.; Tung, Y. J.; Kwong, R. C.; Brown, J. J.; Garon, S.; Thompson, M. E. *Appl. Phys. Lett.* **2003**, 82, 2422.
- (5) Tokito, S.; Iijima, T.; Suzuri, Y.; Kita, H.; Tsuzuki, T.; Sato, F. *Appl. Phys. Lett.* **2003**, 83, 569.
- (6) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Lamansky, S.; Thompson, M. E.; Kwong, R. C. *Appl. Phys. Lett.* **2001**, 78, 1622.
- (7) Brunner, K.; van Dijken, A.; Börner, H.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W. *J. Am. Chem. Soc.* **2004**, 126, 6035.
- (8) van Dijken, A.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W.; Rothe, C.; Monkman, A.; Bach, I.; Stössel, P.; Brunner, K. *J. Am. Chem. Soc.* **2004**, 126, 7718.
- (9) Avilov, I.; Marsal, P.; Bredas, J. L.; Beljonne, D. *Adv. Mater.* **2004**, 16, 1624.
- (10) Shih, P. I.; Chiang, C. L.; Dixit, A. K.; Chen, C. K.; Yuan, M. C.; Lee, R. Y.; Chen, C. T.; Diau, E. W. G.; Shu, C. F. *Org. Lett.* **2006**, 8, 2799.
- (11) Tsai, M. H.; Lin, H. W.; Su, H. C.; Ke, T. H.; Wu, C. C.; Fang, F. C.; Liao, Y. L.; Wong, K. T.; Wu, C. I. *Adv. Mater.* **2006**, 18, 1216.
- (12) Tsai, M. H.; Hong, Y. H.; Chang, C. H.; Su, H. C.; Wu, C. C.; Matoliukstyte, A.; Simokaitiene, J.; Grigalevicius, S.; Grazulevicius, J. V.; Hsu, C. P. *Adv. Mater.* **2007**, 19, 862.
- (13) Sapochak, L. S.; Padmaperuma, A. B.; Vecchi, P. A.; Qiao, H.; Burrows, P. E. *Proc. SPIE* **2006**, 6333, 57.
- (14) Sapochak, L. S.; Padmaperuma, A. B.; Vecchi, P. A.; Cai, X.; Burrows, P. E. *Proc. SPIE* **2007**, 6655, 65506.
- (15) Cai, X.; Padmaperuma, A. B.; Sapochak, L. S.; Vecchi, P. A.; Burrows, P. E. *Appl. Phys. Lett.* **2008**, 92, 083308.
- (16) Sapochak, L. S.; Padmaperuma, A. B.; Cai, X. Y.; Male, J. L.; Burrows, P. E. *J. Phys. Chem. C* **2008**, 112, 7989.
- (17) Kim, D.; Salman, S.; Coropceanu, V.; Salomon, E.; Padmaperuma, A. B.; Sapochak, L. S.; Kahn, A.; Brédas, J.-L. *Chem. Mater.* **2010**, 22, 247.
- (18) Su, S.-J.; Sasabe, H.; Takeda, T.; Kido, J. *Chem. Mater.* **2008**, 20, 1691.
- (19) Chou, H.-H.; Cheng, C.-H. *Adv. Mater.* **2010**, 22, 2468.
- (20) Martin, R. L. *J. Chem. Phys.* **2003**, 118, 4775.
- (21) Batista, E. R.; Martin, R. L. Natural transition orbitals. In *Encyclopedia of Computational Chemistry*, Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F. I., Schreiner, P. R., Eds.; John Wiley & Sons: Chichester, UK, 2004.
- (22) Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, 52, 997.
- (23) Chai, J.-D.; Head-Gordon, M. *J. Chem. Phys.* **2008**, 128, 084106.
- (24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, J. T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; M. A. Al-Laham; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian-03*; Gaussian, Inc.: Wallingford, CT, 2004.
- (25) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, 256, 454.
- (26) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1997**, 264, 573.
- (27) Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2002**, 117, 7433.
- (28) Usually, ambipolar host molecules for blue OLEDs are synthesized by combining hole-accepting (higher HOMO) and electron-accepting (lower LUMO) units; thus, their HOMO and LUMO are localized on the respective subunits. As a result, hole and electron injections can be more facile and more balanced compared to either single subunit.
- (29) Tani, K.; Tohda, Y.; Takemura, H.; Ohkita, H.; Ito, S.; Yamamoto, M. *Chem. Commun.* **2001**, 1914.
- (30) Hoffmann, S. T.; Schrögel, P.; Rothmann, M.; Albuquerque, R. Q.; Strohhriegel, P.; Köhler, A. *J. Phys. Chem. B* **2011**, 115, 414.
- (31) Jankus, V.; Monkman, A. P. *Adv. Funct. Mater.* **2011**, 21, 3350.
- (32) Strictly speaking, the energy difference between singlet and triplet states can be considered as exchange energy only if both states are of the same nature and there's no geometry relaxation. Upon relaxation, triplet state wave function tends to shrink more than that of singlet state and hence the electrostatic attraction between nucleus and electron becomes more important (see ref 33). Because singlet and

triplet states are different in nature, in particular for TCz derivatives, we would not take here the singlet–triplet energy difference as exchange energy.

- (33) Rioux, F. *J. Chem. Educ.* **2007**, *84*, 358.
- (34) Su, S.-J.; Cai, C.; Kido, J. *Chem. Mater.* **2011**, *23*, 274.
- (35) Bässler, H.; Arkhipov, V. I.; Emelianova, E. V.; Gerhard, A.; Hayer, A.; Im, C.; Rissler, J. *Synth. Met.* **2003**, *135*, 377.
- (36) TD-DFT/B3LYP/6-31G* calculations of the vertical excitation energies tend to give T_1 energies comparable to the experimental values but underestimate S_1 energies. Therefore, the singlet–triplet energy differences calculated here are expected to be somewhat underestimated. However, one should note that geometry relaxation effects are not taken into account in the assessment of excited-state energy. For comparison of various computational results with the experimental values, see Tables S1 and S2 in Supporting Information.
- (37) Dreuw, A.; Weisman, J. L.; Head-Gordon, M. *J. Chem. Phys.* **2003**, *119*, 2943.
- (38) Dreuw, A.; Head-Gordon, M. *J. Am. Chem. Soc.* **2004**, *126*, 4007.
- (39) American Dye Source, Inc., Quebec, Canada.