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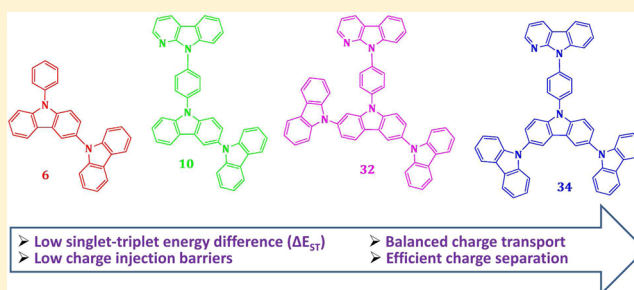
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Rational Design of Carbazole- and Carboline-Based Ambipolar Host Materials for Blue Electrophosphorescence: A Density Functional Theory Study

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S Supporting Information

ABSTRACT: Density functional theory has been employed to design 41 host molecules for blue electrophosphorescence by incorporating electron donor (carbazole (cbz)) and electron acceptor (α -carboline (Cb1)) units into *N*-phenyl-carbazole (PhCbz). We have systematically investigated the influence of the number (mono-, di-, and trisubstituted) and positions of Cb1 and Cbz substitution on an array of electronic properties of the designed hosts. The results underline that the substitution of the *N*-phenyl ring with a carboline unit yields host molecules with low charge injection barriers, balanced charge transport, efficient charge separation, high triplet energy (E_T), and low singlet–triplet energy difference (ΔE_{ST}). For disubstituted hosts, the second subunit can either be Cb1 or Cbz substituted at the 2/7 position of PhCbz, while substituting the 2 and 3 positions of PhCbz with Cbz subunits generates trisubstituted hosts with efficient electronic properties. Thus, our results indicate that both number and position of subunit substitution in PhCbz play a decisive role in designing hosts with appropriate electronic properties. Among the 41 systems considered in the study, we have identified the two most efficient hosts, and their electronic properties are found to be very promising compared to some of the experimentally reported analogous hosts.



1. INTRODUCTION

Phosphorescent organic light-emitting diodes (PhOLEDs) based on heavy-metal complexes have recently attracted a great deal of attention because these materials can efficiently harvest both singlet and triplet excitons and hence can achieve high internal quantum efficiency.^{1–3} In typical PhOLED devices, to prevent concentration quenching of the phosphorescence and triplet–triplet annihilation, the emitters are usually doped into a suitable host.⁴ Hence, development of host materials for an efficient PhOLED device is as critical as that of the emitter. For blue PhOLED, the host materials are required to have higher triplet energy ($E_T > 2.9$ eV) than the guest (emitter) to prevent the back energy transfer from the guest to the host and to facilitate the exothermic energy transfer from host to guest.^{5,6} In addition to that, to achieve low operating voltage, the HOMO and LUMO levels of the host molecule should be appropriately aligned with respect to the neighboring hole transport layer (HTL) and electron transport layer (ETL). In other words, the host molecule should have high HOMO (IP) and low LUMO (EA) with respect to HTL and ETL. Besides, the host materials should have good charge-carrier transport properties. These constraints make the design of efficient host materials for blue PhOLEDs particularly challenging compared to red and green. A number of experimental and theoretical studies have been reported in designing ideal host materials with high triplet energy for blue

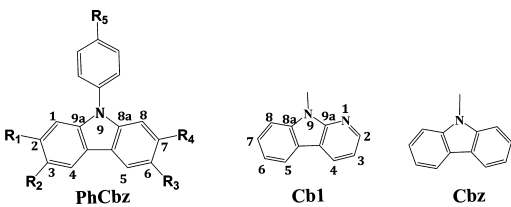
PhOLEDs.^{7–18} Carbazole-based derivatives are among the most successful host molecules for blue PhOLED due to their efficient hole-transport properties, well-positioned IP, low exchange energy between singlet and triplet states, and high triplet energy.^{6,12,14,15,19–24} An example of a carbazole-based host molecule for blue emitter iridium(III) bis[[4,6-difluorophenyl] pyridinato- $N,C^{2'}$]picolate (FIrpic) is *N,N'*-dicarbazolyl-3,5-benzene (mCP), which has an E_T of 2.90 eV.⁵ However, this host has poor electron injection due to the shallow LUMO levels with respect to ETL and unipolar character. These drawbacks have been rectified by substituting various electron transport units such as diphenylphosphine oxide, oxadiazole, 1,3,5-triazines, and triazole with a carbazole core to yield efficient bipolar host materials.^{11,12,17,25,26} Forrest, Thompson, and co-workers have reported ultrahigh energy gap host materials based on *p*-bis(triphenylsilyl)benzene (UGH2) for deep blue emitting PhOLEDs.²⁷ The exciton formation in these kinds of hosts is by charge trapping mechanism which reduces the emitter concentration in the emissive layer, and the resultant exciton formation leads to high driving voltage. Theoretical calculations have confirmed that asymmetric substitution of the hole and electron transport materials into

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Scheme 1. Chemical Structure of Core and Subunits Used to Design New Host Molecules



Hosts	R ₁	R ₂	R ₃	R ₄	R ₅	Hosts	R ₁	R ₂	R ₃	R ₄	R ₅
1	H	H	H	H	Cb1	22	Cbz	H	Cbz	H	H
2	Cb1	H	H	H	H	23	Cbz	H	H	Cbz	H
3	H	Cb1	H	H	H	24	H	Cbz	Cbz	H	H
4	H	H	H	H	Cbz	25	Cb1	H	Cb1	H	Cb1
5	Cbz	H	H	H	H	26	Cb1	H	H	Cb1	Cb1
6	H	Cbz	H	H	H	27	H	Cb1	Cb1	H	Cb1
7	Cb1	H	H	H	Cb1	28	Cb1	H	Cbz	H	Cb1
8	H	Cb1	H	H	Cb1	29	Cb1	H	H	Cbz	Cb1
9	Cbz	H	H	H	Cb1	30	H	Cb1	Cbz	H	Cb1
10	H	Cbz	H	H	Cb1	31	H	Cb1	H	Cbz	Cb1
11	Cb1	H	H	H	Cbz	32	Cbz	H	Cbz	H	Cb1
12	H	Cb1	H	H	Cbz	33	Cbz	H	H	Cbz	Cb1
13	Cbz	H	H	H	Cbz	34	H	Cbz	Cbz	H	Cb1
14	H	Cbz	H	H	Cbz	35	Cbz	H	Cbz	H	Cbz
15	Cb1	H	Cb1	H	H	36	Cbz	H	H	Cbz	Cbz
16	Cb1	H	H	Cb1	H	37	H	Cbz	Cbz	H	Cbz
17	H	Cb1	Cb1	H	H	38	Cbz	Cb1	Cbz	H	H
18	H	Cb1	H	Cbz	H	39	Cbz	H	Cbz	Cb1	H
19	Cb1	H	H	Cbz	H	40	Cbz	Cb1	H	Cbz	H
20	H	Cb1	Cbz	H	H	41	Cb1	Cbz	Cbz	H	H
21	Cb1	H	Cbz	H	H						

such a UGH2 moiety improves the charge transport and charge injection barrier of UGH2.¹⁰ Recently, great efforts have been made to develop ideal host molecules with ambipolar character which can transport both hole and electron. Efficient ambipolar host materials for blue emitters have been developed by Kido and co-workers using carbazole and pyridine-based terphenyl-like subunits, with external quantum efficiency (EQE) of 24%.¹⁶ In addition to that, many ambipolar host molecules for the blue PhOLED have been reported experimentally using hole transporting carbazole and different electron transporting units.^{12,17,18,25,26} A large number of host molecules have also been designed using quantum chemical methods.^{7–13} Pyridine-modified heteroring-based compounds have also been recently used as electron transport materials to develop bipolar host materials.^{27–30} One of the best known pyridine-modified heteroring derivatives is pyridoindole (carboline), based on which a few host materials have been reported.^{28–33} In a recent communication, Kim et al. proposed an efficient host molecule (9-(4-(9H-pyrido[2,3-b]indol-9-yl)phenyl)-9H-3,9-bicarbazole (pBCb2Cz)) for blue phosphorescence based on carbazole and the α -carboline unit.³⁴ The authors could demonstrate that the device has a considerably high quantum efficiency of 23% in which pBCb2Cz is used as the host along with Flrpic as the blue emitter.

To the best of our knowledge, a systematic study of ambipolar host molecules based on phenylcarbazole (PhCbz) and α -carboline (Cb1) moieties has not been reported. In this study our aim is to develop efficient ambipolar host molecules using carbazole (Cbz) and α -carboline (Cb1) moieties by taking Flrpic as the reference blue emitters and di[4-(*N,N*-ditolyl-amino)-phenyl]cyclohexane (TAPC) and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) as reference hole and electron transport materials, respectively. Since, the host pBCb2Cz (host 10 in Scheme 1) has been synthesized, the same has been chosen as a reference for screening the other

host molecules designed in this study.³⁴ This host has a carboline unit attached at the R₅ position and Cbz at R₂ of the parent PhCbz core. On the other hand, host 6 (Scheme 1) also has been synthesized and differs from 10 by the absence of the Cb1 unit at the R₅ position; however, the device performance is rather poor (~13% EQE with Flrpic). This observation highlights that a small variation in the structure of the host can drastically change the quantum efficiency of the device. This prompted us to undertake the present study to obtain a deeper understanding of these carbazole-/carboline-based materials which will help in the rational design of new host molecules for blue PhOLEDs. One of the main objectives of this study is to analyze the variation in the electronic properties of the complementary carbazole and carboline systems. We would like to investigate if there is any particular site in the PhCbz unit (R₁, R₂, R₃, R₄, and R₅) which when substituted by Cb1 or Cbz would yield an ambipolar host with improved electronic properties compared to those already reported (10 and 6). We would also like to investigate how the number (mono-, di-, and tri-substituted) and position (R₁, R₂, R₃, R₄, and R₅) of Cb1 and Cbz units at the PhCbz unit would influence the electronic properties such as E_T , HOMO and LUMO, ΔE_{ST} , charge injection, and charge transport properties.

2. COMPUTATIONAL DETAILS

All the structures in their ground state were optimized at the B3LYP/6-31G* level of theory.^{35,36} The structures were characterized as minima by frequency analysis which yielded all positive frequencies. The vertical singlet (E_{S1}) and triplet (E_{T1}) excitation energies were evaluated at B3LYP/6-31G* by TD-DFT formalism on optimized ground-state geometry (S_0). It is evident from the previous reports that the TD-DFT energies of the excited states depend on the choice of the DFT functional. In order to analyze how the variation in the choice

of functional can alter the vertical E_{S1}/E_{T1} excitation energies, we carried out excited state calculations with functionals like B3LYP, TPSSh, CAM-B3LYP, M06, M06-2X, PBE0, and ω B97X in conjunction with the 6-31G* basis set. The B3LYP/6-31G* optimized geometries were used for benchmarking various functionals. Among the various functionals considered in this study, B3LYP and TPSSh exhibit good correlation with experimental data (Figure S1, Supporting Information). Thus, we have restricted all the analysis to the B3LYP functional with 6-31G* basis set. The adiabatic triplet energy (E_T) was calculated by using the Δ SCF method employing the optimized geometries of the triplet excited (T_1) and ground (S_0) states. The adiabatic IP and EA were determined for the selected systems via the Δ SCF method based on the optimized geometries of the respective electronic states. To get more insights into the nature of the triplet state, natural transition orbital analysis (NTO)³⁷ was performed based on the TD-DFT approach, using the optimized geometries of the excited triplet state. All calculations were carried out with the Gaussian 09 package.³⁸

We choose *N,N'*-dicarbazolyl-3,5-benzene (mCP) as a reference host molecule for blue electrophosphorescence and di[4-(*N,N*-ditolyl-amino)-phenyl]cyclohexane (TAPC) and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) as reference hole and electron transport materials, respectively. Iridium(III) bis((4,6-difluorophenyl) pyridinato-*N,C*^{2'}) picolate (FIrpic) was taken as the reference blue emitting material. The geometry optimization of the reference emitter was carried out at the B3LYP level with LANL2DZ basis set for the iridium atom and 6-31G* for the rest of the atoms.

2.1. Internal Reorganization Energy. It is evident from the previous studies that the charge mobility of organic molecules can be well described by the incoherent hopping model^{39–42} where charge transport is viewed as a charge exchange reaction



where M^n represents the neutral state of the system and M^i represents the ionic state of the system. The hole/electron transfer rate can be expressed by the standard Marcus–Hush eq 2.^{43–45}

$$K_{\text{hole/electron}} = \left(\frac{4\pi^2}{h} \right) \frac{1}{\sqrt{4\pi k_B T \lambda_{\text{hole/electron}}}} \exp \left(-\frac{\lambda_{\text{hole/electron}}}{4k_B T} \right) \quad (2)$$

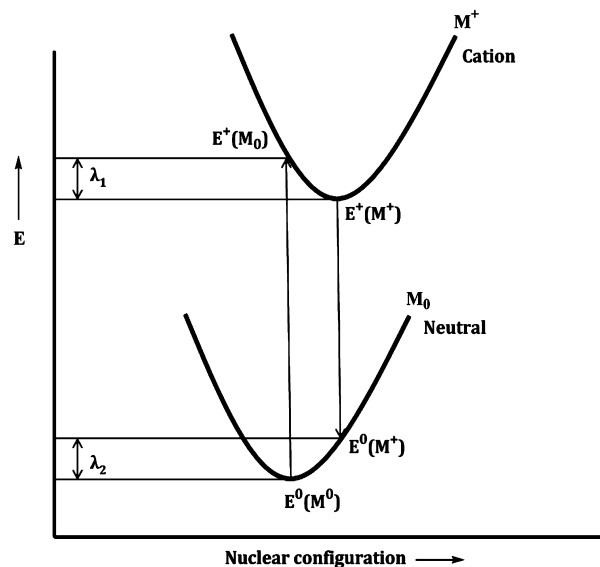
where T is the temperature; λ is the reorganization energy; V is the electronic coupling matrix element (transfer integral) between neighboring molecules in the organic single crystal; h is the Planck constant; and k_B is the Boltzmann constant. It is evident from the above relation (eq 2) that there are two key parameters which determine the charge transfer rate, the λ and V . The experimentally determined coupling matrix, V , for organic molecules is however reported to be rather narrow due to the direct contact in the amorphous solid films.^{46,47} Thus, one can assume that the charge (hole and electron) mobility of the designed hosts will be dominated by the respective reorganization energies, although such an assumption would be too simplistic. However, such an assumption is widely used to calculate the charge mobility of organic molecules.^{9,10,13,47–51} We have additionally calculated the charge

transfer integrals within Koopman's approximation by taking into consideration the neutral stacked dimer conformation of some selected hosts. Since it is difficult to predict the most stable dimer structure, five different dimer conformations have been considered as shown in Figure S8 (Supporting Information) for which the transfer integrals for hole and electron were evaluated (Table S4, Supporting Information). These small charge transfer integral values indicate a weak electron coupling between the dimer complexes considered, and hence the mobility of the designed hosts will largely be governed by the respective reorganization energies. According to the Marcus–Hush theory, lower λ means higher charge mobility. In this study the internal reorganization energy (for hole and electron) is calculated by using the following eqs 3 and 4 and is schematically presented in Scheme 2.

$$\begin{aligned} \lambda_+ &= \lambda_1 + \lambda_2 \\ \lambda_1 &= E^+(M_0) - E^+(M^+) \\ \lambda_2 &= E^0(M^+) - E^0(M_0) \end{aligned} \quad (3)$$

$$\begin{aligned} \lambda_- &= \lambda_3 + \lambda_4 \\ \lambda_3 &= E^-(M_0) - E^-(M^-) \\ \lambda_4 &= E^0(M^-) - E^0(M_0) \end{aligned} \quad (4)$$

Scheme 2. Internal Reorganization Energy for Hole (λ_h) in Arbitrary Units



where $E^0(M_0)$, $E^+(M^+)$, and $E^-(M^-)$ denote the total energy of the neutral, cation, and anion species at their respective optimized geometries. $E^+(M_0)$ and $E^0(M^+)$ denote the total energy of the cation and neutral species at the optimized geometry of M_0 and M^+ , respectively. Similarly, $E^-(M_0)$ and $E^0(M^-)$ represent the total energy of the anion and neutral species at the optimized geometry of M_0 and M^- , respectively. The reorganization energies for electrons (λ_-) and holes (λ_+) were calculated at the B3LYP/6-31G* level.

2.2. Triplet Exciton Generation Fraction. It is evident from the previous observations that the formation of a triplet exciton in the host matrix can be qualitatively calculated from the triplet exciton generation fraction (χ_T).^{9,13} It is another

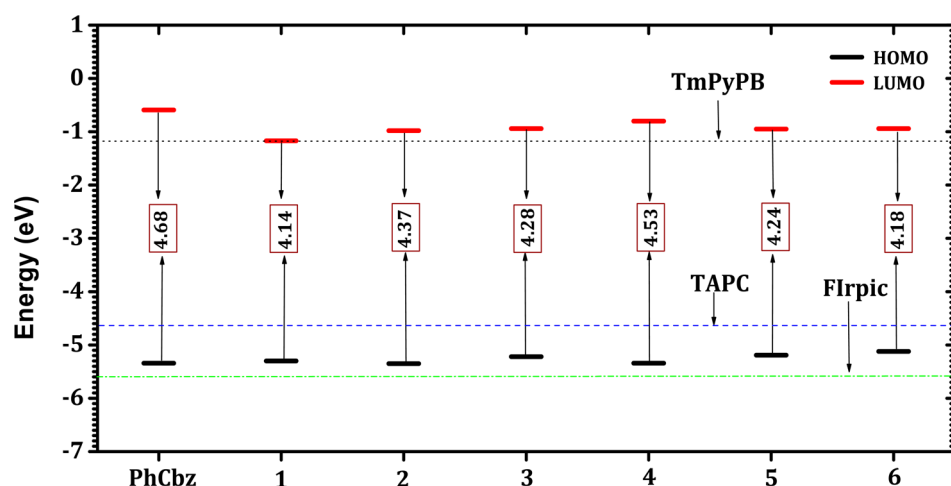


Figure 1. HOMO and LUMO energy levels (in eV) and HOMO/LUMO energy gap (E_g) of monosubstituted hosts and reference HTL (TAPC), ETL (TmPyPB), and emitter (Flrpic) as obtained at the B3LYP/6-31G* level.

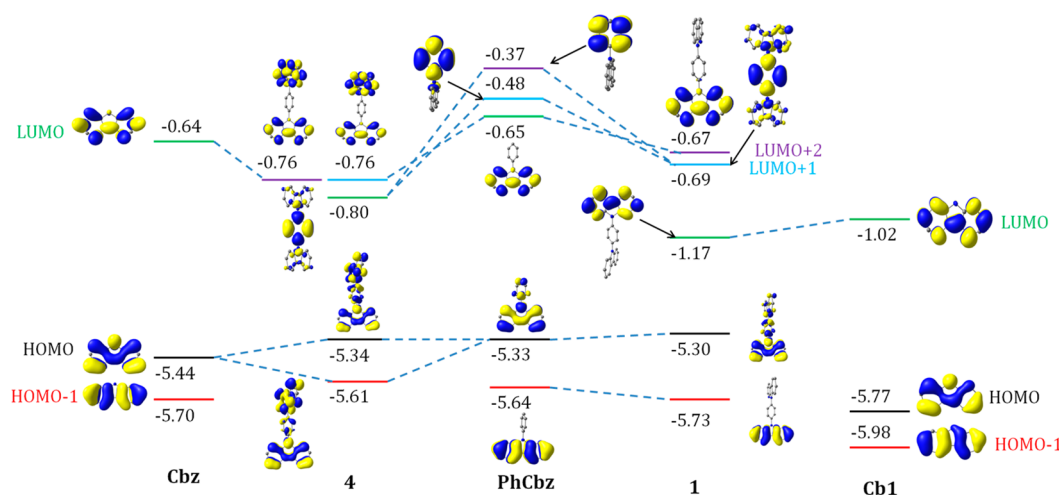


Figure 2. Correlation diagram for the frontier orbitals (FMOs in eV) of PhCbz, Cbz, and Cb1 and hosts 1 and 4 (isosurface value = 0.025 au). The hydrogen atoms are omitted here for clarity.

parameter to identify the potential host molecules, which is related to the formation of a triplet exciton in the host matrix. In the case of the host–guest system, the triplet exciton generation fraction (χ_T) value is a tool to characterize the intersystem crossing (ISC) process.⁵² In addition to that, a higher χ_T in host molecule is a direct indication of more triplet states being formed in the host molecules. Furthermore, the energy/electron transfer between the host and guest depends upon the exciton (singlet/triplet) formation in the host matrix. The energy transfer (Förster) between triplet states of the donor to singlet state of the acceptor might be very efficient if the donor is phosphorescent. In this study the χ_T of carbazole and α -carboline based ambipolar host was calculated from the following eq 5.⁵³

$$\chi_T = \frac{3\sigma_T}{\sigma_S + 3\sigma_T} \quad (5)$$

where σ_S and σ_T are the formation cross-section of the singlet and triplet excitons, respectively.

$$\frac{\sigma_S}{\sigma_T} = \frac{E_{bT}}{E_{bS}} = \frac{E_g - E_{T1}}{E_g - E_{S1}} \quad (6)$$

where E_{bS} and E_{bT} are the binding energies of the singlet and triplet exciton, respectively. E_g is the band gap calculated by the energy difference between HOMO and LUMO, and E_{T1} and E_{S1} denote excitation energies of the triplet and singlet, respectively.

3. RESULTS AND DISCUSSION

3.1. Monosubstituted Hosts. In the present study, PhCbz is considered as the core unit. New host molecules are designed by introducing the hole-transporting (Cbz) and electron-transporting (Cb1) subunits to the core. We adopted a step by step approach to introduce subunits in the PhCbz unit to analyze how the electronic properties are altered in the presence of the substituents. The subunits Cb1 and Cbz can be substituted at the R_S , R_1 , and R_2 positions of PhCbz (Scheme 1), and if monosubstitution is considered, it results in the hosts 1, 2, 3 and 4, 5, 6, respectively. A comparison of the HOMO–LUMO (H–L) gap of PhCbz and the designed hosts (Figure 1) indicates a more profound variation in the LUMO energies of the hosts which are significantly stabilized by 0.15–0.52 eV. The HOMO levels are less sensitive to the subunits introduced. The maximum variation of 0.21 eV is seen in the HOMO of 6. Such an effect has already been reported for hosts based on

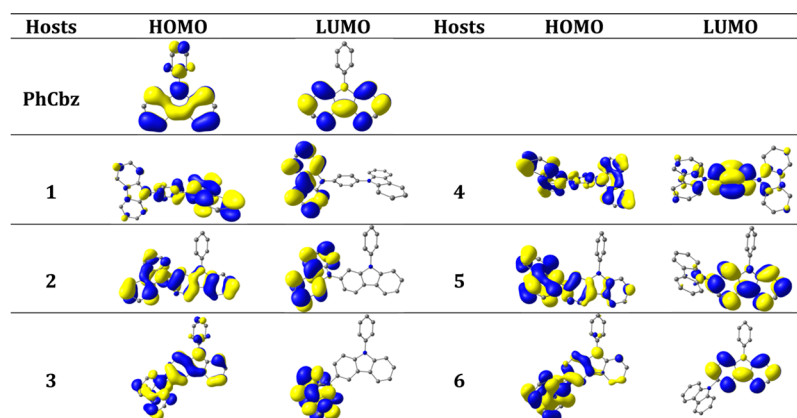


Figure 3. Contour plots (isosurface value = 0.025 au) of the HOMO and LUMO levels of the core and designed monosubstituted host molecules. The hydrogen atoms are omitted here for clarity.

carbazole.^{11,14} The figure also presents the HOMO, LUMO of the HTL, ETL and emissive layer. The HOMO and LUMO energies are important parameters in designing host materials for OLED applications. A potential host molecule should have high HOMO and low LUMO energy levels to reduce the charge injection barrier. It is well-known that for an efficient hole transport the HOMO of the host molecules should be close to that of the HTL and also in between that of the HTL and emissive layers. Similarly, if the LUMO of the host molecules is close to that of the ETL, a facile electron transport will be mediated between the two layers. For exciton blocking, the HOMO of the host should be greater than that of the HTL, and its LUMO needs to be greater than that of the ETL. A close analysis of the HOMO (Figure 1 and Table S1, Supporting Information) of the monosubstituted hosts elicits that they can efficiently mediate hole transport between the HTL and the emissive layer as their HOMO values (−5.12 to −5.35 eV) lie in between that of the HTL (−4.66 eV) and emissive layer (−5.54 eV). Interestingly, the HOMO of the designed systems is higher in energy than that of the reference host mCP (−5.41 eV). For a facile electron injection, the LUMO of the hosts should lie close to that of the ETL, and this criterion is well satisfied by the designed hosts. The H–L gap also plays an important role in the design of ambipolar host molecules as a reduced H–L gap is a prerequisite for balanced and facile charge transfer. Figure 1 indicates that substituting the R_5 position by a Cb1 unit yields a host (1) with low H–L gap (4.14 eV). Equally noteworthy is that the LUMO of 1 is lower than mCP (reference host) and its HOMO higher in energy than mCP. This may reflect the fact that 1 may mediate both hole and electron more efficiently than mCP. The figure also shows that among the six monosubstituted hosts 1 will be most efficient to transport both hole and electron with low barriers. Though the other hosts may also transport electrons, it will be at the expense of a higher turn-on voltage compared to 1.

In order to analyze why host 1 has a stabilized LUMO, molecular orbital analysis of *N*-phenylcarbazole (PhCbz), carbazole (Cbz), carboline (Cb1), and hosts 1 and 4 (Figure 2) were carried out. We start by comparing the MOs of unsubstituted carbazole and carboline wherein the presence of a pyridine ring of the pyridoindole moiety significantly stabilizes the LUMO of carboline (−1.02 eV) over carbazole (−0.65 eV). The high stability of LUMO of 1 can be traced to the localization of its LUMO on the carboline subunit, which

can be clearly seen from the figure. Similarly, LUMO and LUMO+1, LUMO+2 of *N*-phenylcarbazole give rise to the LUMO+2 and LUMO+1 of host 1, respectively. In the case of host 4, the LUMO orbital which is localized on the phenyl ring arises from the LUMO+1, LUMO+2 of the *N*-phenylcarbazole which lies higher in energy than the MO of the carboline unit. Hence, the substitution of the Cb1 unit stabilizes the LUMO of host 1.

The frontier molecular orbital distribution and composition of the monosubstituted hosts are presented in Figure 3 and Table S2 (Supporting Information), respectively. Both the figure and table clearly reveal that a clear charge separation is obtained only for host 1 with HOMO localized on Cbz (89.1%) and LUMO (97.9%) on the Cb1 unit. In the case of 2 and 3, even though the LUMO is solely concentrated on the Cb1 unit (ca. 97%), the HOMO is delocalized on both Cb1 and Cbz units. This charge separation reflects that 1 may function as an ambipolar host.^{7,14,54} Thus, one can say that substitution of Cb1 at R_5 over R_1 and R_2 positions induces a clear charge separation. For the monosubstituted Cbz hosts, irrespective of whether the Cbz subunit is introduced at the R_5 , R_1 , or R_2 positions of PhCbz, a clear charge separation is not seen as the HOMO is delocalized over the Cbz skeleton of the core (20–30%) and the Cbz subunit (70–80%) introduced.

In order to get a rational explanation as to why a clear charge-separated state is obtained only for 1 and not for other hosts, we looked at the MO distribution of the individual subunits and of these hosts. In the core PhCbz, the phe and Cbz units are linked via the C–N linkage due to which the −I inductive effect predominates and the carbazole ring carries a high negative charge (−0.203 lel (NPA charges), −0.276 lel (Mulliken charges)) compared to the benzene ring.^{7,11} The HOMO of PhCbz is localized on the Cbz unit with a node present on the C2 and C7 carbon atoms (Figure 2 and Scheme 1).⁵⁴ Also, the HOMO is characterized by high electron density on the amine nitrogen (N9) which suggests its electron-donating nature. The HOMO−1, on the other hand, has electron density delocalized on all carbon atoms and a node on the N9 nitrogen atom. As mentioned before, host 1 is derived by substituting Cb1 at the R_5 position of the phenyl ring. This substitution does not stabilize the HOMO of the PhCbz significantly to interact with the highly stabilized HOMO of the Cb1 subunit (see Figure 2). Therefore, in the case of host 1 the HOMO gets localized on the electron-rich PhCbz and LUMO on the electron-deficient Cb1 subunit.

Table 1. Calculated Reorganization Energies for Hole (λ_+) and Electron (λ_-), Adiabatic Triplet Energies (E_T), and Singlet/Triplet Vertical Excitation Energies $E(S_0 \rightarrow S_1)/E(S_0 \rightarrow T_1)$ at the B3LYP/6-31G* Method (All Values are in eV)

hosts	λ_+	λ_-	E_T	$E(S_0 \rightarrow S_1)$	$E(S_0 \rightarrow T_1)$	ΔE_{ST}
1	0.21	0.19	3.06	3.71	3.12	0.59
2	0.31	0.16	3.05	3.76	3.06	0.70
3	0.30	0.16	3.05	3.70	3.12	0.58
4	0.16	0.14	3.19	3.89	3.18	0.71
5	0.21	0.26	2.95	3.71	3.03	0.68
6	0.24	0.26	3.07(3.00 ^a)	3.62(3.32 ^a)	3.15	0.46(0.32 ^a)
mCP	-	-	3.16(2.90 ^a)	4.01(3.56 ^a)	3.18	0.83(0.66 ^a)
Flrpic	-	-	2.73(2.65 ^b)	-	-	-

^aData from ref 15. ^bData from ref 5.

The HOMO of the PhCbz is characterized by the presence of a node at the C2 carbon atom. Hence, the HOMO of **2** arises from the HOMO–1 of the PhCbz core which lies energetically closer to the HOMO of the Cb1 unit. This leads to an effective conjugation between the two subunits due to which the HOMO of **2** is delocalized on both Cb1 and Cbz units. Further, the presence of a node on the N9 atom of Cbz prevents the delocalization of the HOMO on the phenyl unit.

The HOMO of host **3** also arises from the HOMO of PhCbz. However, unlike host **1**, the electron-deficient Cb1 is now substituted on the electron-rich biphenyl unit of PhCbz. This substitution (C–N linkage with strong $-I$ inductive effect⁷) stabilizes the HOMO of the PhCbz due to which its coupling with the HOMO of Cb1 strengthens. Additionally the absence of any node on the N9 atom in the HOMO of Cbz further extends the conjugation to the phenyl ring. Therefore, the HOMO is delocalized on the three units (phenyl, Cbz, and Cb1), while the LUMO is localized on the electron-deficient Cb1 unit.

In the case of host **4**, the $-I$ inductive effect of the carbazole predominates as both the Cbz units are attached via C–N linkage to the phenyl ring. The HOMO hence is delocalized on the electron-rich Cbz unit and the LUMO on the electron-deficient phenyl ring. The MO distribution of hosts **5** and **6** is very similar to that of hosts **2** and **3** where the effective conjugation between the subunit at the R₁ or R₂ position and the Cbz core delocalizes the HOMO on the two subunits. The LUMO of both Cbz and PhCbz is nearly degenerate. However, upon the addition of the subunit, the central carbazole attains a positive charge due to which its LUMO gets stabilized compared to the LUMO of the carbazole present at the R₁ or R₂ position (Table S5, Supporting Information). This explains the localization of the LUMO on the central carbazole core. This discussion thus highlights the importance of the phenyl ring (R₅ position) which separates the electron-rich Cbz and electron-deficient Cb1, thereby localizing the HOMO on the Cbz unit and LUMO on the Cb1 unit as seen in host **1**.

In order to evaluate the charge mobility, the reorganization energies (Table 1) of the hosts were evaluated from the hole and electron relaxation energies (Table S1, Supporting Information). The reorganization energy can in principle give a qualitative indication of the charge carrier mobility with low reorganization energies being associated with higher transport rate of the carriers. It is interesting to note that the formation of a charge-separated state can be related to the reorganization energies. A closer look at the HOMO of **1** reveals the presence of a node at the C8a and C9a atoms of the Cb1 unit which localizes the electron density on the PhCbz unit and pyrrole nitrogen of Cb1. The presence of these nodes leads to

nonbonding interactions between the two subunits. In the case of hosts **2** and **3**, the MO picture elicits antibonding interactions between the Cbz and Cb1 units due to which the electron density in both hosts is delocalized over the two subunits. This delocalization of the HOMO on the electron transport Cb1 unit increases the hole (λ_+) reorganization energy of **2** and **3**, while **1**, where the HOMO is localized on the hole transport unit (Cbz), exhibits lower λ_+ . The LUMO of all three hosts is also characterized by the presence of a node at the N9 atom of the Cb1 unit which localizes the electron density on the Cb1 unit which may be the reason why the electron (λ_-) reorganization energies of **1**, **2**, and **3** are quite comparable. A similar argument can be extended to hosts **4**, **5**, and **6**. In **4**, the concentration of the HOMO (on Cbz) and LUMO (phenyl) on different subunits can be traced to its low λ_+ and λ_- energies, while the delocalization in the HOMO leads to higher λ_+ values in **5** and **6**. The high λ_- values of **5** and **6** are because the LUMO is localized on the core Cbz unit which acts as the electron transport unit. The hole (λ_+) and electron (λ_-) reorganization energies of **1**, **2**, **3**, **4**, **5**, and **6** (Table 1) elicit that a balanced charge transport is exhibited by **1**, **4**, and **6** as the reorganization energies for their hole and electron are comparable ($\Delta\lambda = 0.02$ eV). The hosts **2** and **3** with low λ_- (0.16 eV as LUMO is localized on Cb1) and high λ_+ (0.30–0.31 eV as HOMO is delocalized) will have a higher affinity to transport electrons, while the hosts **5** and **6** with low λ_+ (0.21–0.24 eV) are more appropriate for hole transport. It is worthy to note that, compared to **1** and **4**, the charge mobility of **6** is low which can be traced to its higher relaxation energies for both hole and electron. This observation further affirms that R₅ substitution which can induce charge separation by localizing the electron density on different subunits (HOMO on the electron-donating group and LUMO on the electron-accepting group) leads to a balanced charge transport with low barriers compared to R₁ and R₂ substitutions.

Triplet energy is a key parameter which determines the potential performance of host molecules as phosphorescent blue emitters. It is evident from the previous studies that in order to prohibit the back energy transfer from the guest to host and to enhance the tendency of confinement of all excitons in the emitter the lowest E_T of the host molecule should be higher than that of the guest. As mentioned previously, for a blue emitter, the E_T of the host should be higher than ~ 3 eV. The computed adiabatic triplet energies (E_T) of the studied systems are collected in Table 1, along with the experimentally reported value of **6**, reference blue emitters (Flrpic), and popular host molecule (mCP). It can be seen from the table that the calculated E_T value of **6** (3.07 eV) is in good agreement with the experimental reports (3.00 eV) which

may reflect the suitability of the method employed. The triplet energy of hosts **1**, **2**, and **3** (3.05–3.06 eV) is rather insensitive to the position of the substitution. This can be traced to the triplet spin density distribution (Figure 4) which shows that in

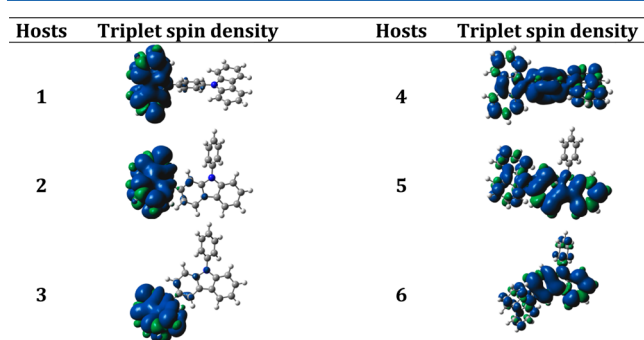


Figure 4. Triplet spin density (isosurface value = 0.0004 au) of the monosubstituted designed host molecules.

the case of **1**, **2**, and **3** the triplet electron density is distributed solely on the Cb1 unit. Therefore, the E_T value is close to that of the lone Cb1 ($E_T = 3.01$ eV) unit. However, depending on the position of Cbz substitution in **4**, **5**, and **6**, the triplet spin density is delocalized over the phenyl ring, central Cbz unit, and on the Cbz substituent at the R_1 or R_2 positions, and the E_T can vary from 2.95 to 3.19 eV. Furthermore, irrespective of whether the triplet spin density is localized or delocalized on subunits, all the host molecules studied here exhibit higher E_T energy (2.95–3.19 eV) than the reference emitter Flrpic (2.73 eV).

We further carried out NTO analyses (Figure 5) to shed light on the nature of the lowest triplet state. It is evident from the previous studies that the difference in the E_T energy values of the host molecules can be clearly understood by inspecting the NTOs.^{7,8,11,55,56} From Figure 5, we can see that for the hosts **1**, **2**, and **3** the hole–electron pair of the NTOs corresponds to a localized transition within the Cb1 unit. Hence, the E_T value is close to that of Cb1. A similar observation was also obtained from the triplet spin density distribution. In the case of hosts **4**, **5**, and **6**, hole and electron wave functions vary depending upon the position of the Cbz substitution. In host **4**, the T_1 state is characterized by transition confined to the phenyl unit. In the case of **5** and **6**, the T_1 state corresponds to transition

predominantly in the core carbazole unit. Hence, the E_T value is close to that of the Cbz core as seen in the case of triplet spin density distribution.

The ΔE_{ST} values (0.46–0.71 eV) of the designed hosts (Table 1) are lower than the reference host mCP (0.83 eV). When compared to the ΔE_{ST} of PhCbz (0.89 eV), the same is found to decrease for the mono Cbz and Cb1 substituted hosts (details are provided in the Supporting Information, see Table S3 and discussion). It is evident from the previous studies that the triplet exciton generation fraction (χ_T) can be used as an indicator to identify potential host molecules. The calculated χ_T values of monosubstituted hosts are shown in Table S6 (Supporting Information). The χ_T values (56.95–62.25) of Cbz-substituted hosts (**4**, **5**, and **6**) are slightly higher than the Cb1-substituted hosts (**1**, **2**, and **3**), and the position of substitution (R_1 , R_2 , and R_3) hardly influences the triplet exciton generation fractions.

The preceding discussion gives a clear indication as to where and what type of subunits need to be introduced in the PhCbz core to design efficient host molecules. First, an electron-withdrawing Cb1 unit should be present at the R_3 position of PhCbz to obtain a clear charge separation due to MO localization and not at the R_1 and R_2 positions as they tend to increase the λ_+ by delocalizing the HOMO. Thus, among the six monosubstituted hosts considered in the study, **1** may outperform the other hosts based on its lower charge injection barrier, balanced charge transport, clear charge-separated state, and lower ΔE_{ST} value.

3.2. Disubstituted Hosts. We now consider the hosts where two subunits are introduced in the PhCbz core at the R_1 , R_2 , R_3 , R_4 , and R_5 positions. They can further be subclassified into homo- and hetero-disubstituted systems, and we have considered a total of 18 such possible hosts in the current study. We start the discussion with the hosts **7**, **8**, **9**, and **10** wherein the R_3 position is substituted by the Cb1 unit and R_1 / R_2 position by Cb1/Cbz. Figure 6 depicts the HOMO and LUMO energy levels of the disubstituted systems along with those of the HTL, ETL, and emissive layer which clearly indicates that these systems are marked by low injection barrier for both hole and electron. The localization of the HOMO and LUMO (Figure 7 and Table S2, Supporting Information) of all the considered hosts on different subunits ensures charge separation and indicates a possible ambipolar character.⁵⁴ The E_T (2.95–3.06 eV) of the hosts is also high when compared to

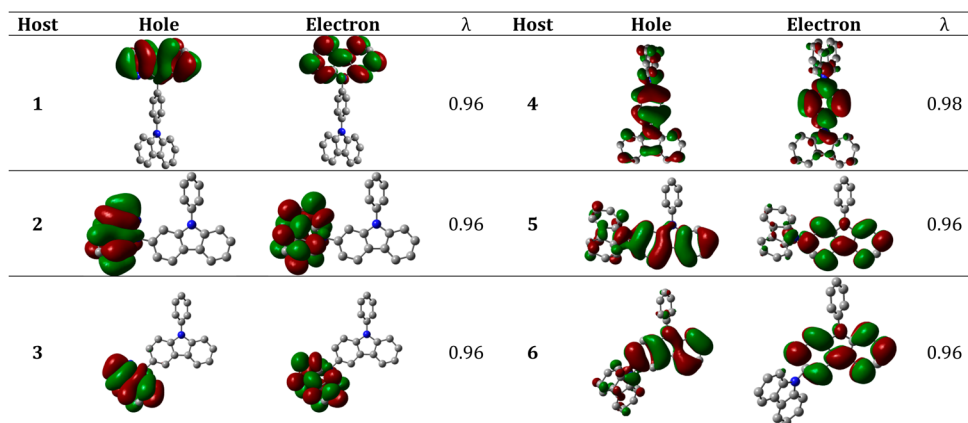


Figure 5. Hole–particle pairs of natural transition orbitals (NTOs) of the monosubstituted host molecules for the T_1 state (isosurface value = 0.020 au). The hydrogen atoms are omitted here for clarity.

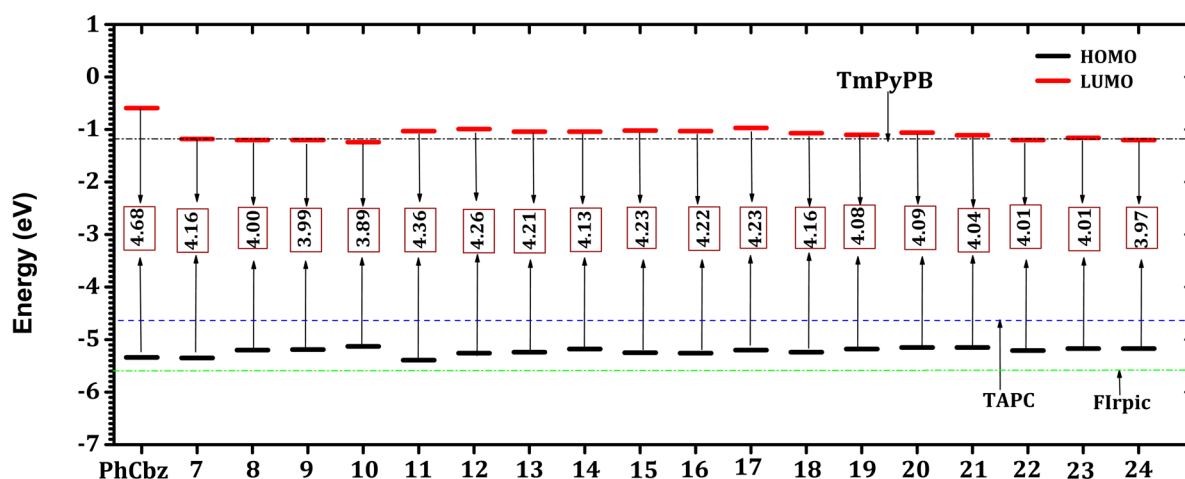


Figure 6. HOMO and LUMO energy levels and HOMO/LUMO energy gap (E_g) of disubstituted hosts with reference HTL (TAPC), ETL (TmpyPB), and emitter (FIrpic) in the ground state.

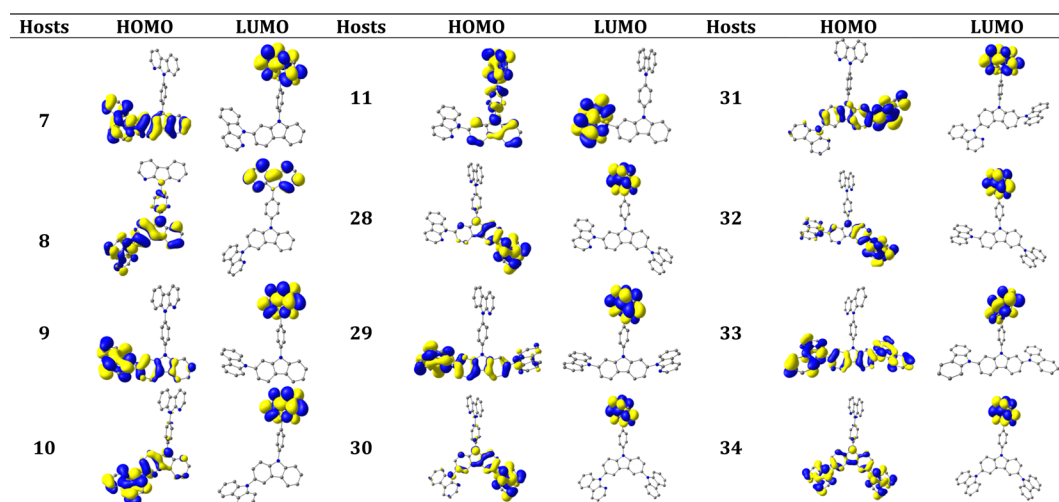


Figure 7. HOMO and LUMO contour plots (isosurface value = 0.025 au) of selected di- and trisubstituted host molecules. The hydrogen atoms are omitted here for clarity.

the emitter (Table 2), and the distribution of the triplet spin density indicates localization on the Cb1 subunit (Figure S3, Supporting Information). A similar trend is seen from the NTOs analysis (Figure S4, Supporting Information). Thus, the four hosts behave similarly in terms of their injection barrier, charge separation, and adiabatic triplet energies, and the difference arises only in their charge mobility and ΔE_{ST} . The reorganization energies of the hosts indicate a balanced charge transport only for 7 (λ_+ (0.17 eV), λ_- (0.14 eV)) and 9 (λ_+ (0.13 eV), λ_- (0.14 eV)) and a higher electron mobility for 8 (λ_+ (0.27 eV), λ_- (0.15 eV)) and 10 (λ_+ (0.21 eV), λ_- (0.14 eV)). This can be explained by analyzing the MO's of the respective hosts. In the case of hosts 7 and 9 the HOMO comes from the HOMO-1 of core carbazole. Therefore, the delocalization is limited to the R_1 substituent and the core Cbz unit. The HOMO of 8 and 10 arises from the HOMO of the PhCbz unit wherein a significant electron density is present on the N9 atom due to which the HOMO of these complexes is delocalized over the phenyl ring and pyrrole nitrogen of Cb1 also. This extended delocalization on different subunits increases the λ_+ in the hosts with R_2 substitution. The vertical ΔE_{ST} is generally low when the subunits are introduced at the R_2 position (8 and 10) in addition to the R_5 position. Even

though the ΔE_{ST} of the hosts is slightly high, it is still lower than that of the reference host mCP. It is also interesting at this point to compare the reorganization energies of hosts 7, 8, 9, and 10 (with Cb1 at R_5) with those of hosts 2, 3, 5, and 6 (no Cb1 unit at the R_5 position). The presence of the Cb1 unit at the R_5 position leads to the localization of the HOMO and LUMO on spatially separated subunits and hence a decrease in the reorganization energy.

In the next set of hosts 11, 12, 13, and 14, the Cb1 unit at the R_5 position of the hosts 7, 8, 9, and 10 is replaced by the Cbz unit. Such a substitution will highlight the influence of the nature of the substituent present at the R_5 position in determining the electronic properties of the hosts. A close analysis of the HOMO and LUMO levels reveals that replacing the R_5 position by a Cbz unit destabilizes the LUMO thereby by increasing the electron injection barrier of the new hosts (Figure 6) which can be attributed to the inductive effect of the Cbz unit and the Cb1 unit. It is seen that the hosts with Cbz at the R_5 position have lower λ_+ values compared to similar hosts with Cb1 at the R_5 position as the HOMO is delocalized on both Cbz units (core and R_5 substituent). Hence, most of the hosts (except 14) have an unbalanced charge transport and in general have a higher mobility for hole (Table 2). Even though

Table 2. Calculated Singlet/Triplet Vertical Excitation Energies $E(S_0 \rightarrow S_1)/E(S_0 \rightarrow T_1)$, Adiabatic Triplet Energies (E_T), and Reorganization Energies for Hole (λ_+) and Electron (λ_-) at the B3LYP/6-31G* Method (All Values Are in eV)

hosts	λ_+	λ_-	E_T	$E(S_0 \rightarrow S_1)$	$E(S_0 \rightarrow T_1)$	ΔE_{ST}
7	0.17	0.14	3.05	3.76	3.04	0.72
8	0.27	0.15	3.05	3.65	3.12	0.53
9	0.13	0.14	2.95	3.70	3.03	0.68
10	0.21	0.14	3.06	3.61	3.13	0.48
10	-	-	(2.93 ^a)	(3.43 ^a)	-	(0.50 ^a)
11	0.12	0.17	3.06	3.78	3.04	0.74
12	0.21	0.10	3.05	3.71	3.12	0.59
13	0.08	0.18	2.94	3.67	3.02	0.65
14	0.17	0.14	3.07	3.58	3.15	0.43
15	0.32	0.12	3.05	3.72	3.03	0.68
16	0.34	0.17	2.89	3.70	2.95	0.76
17	0.28	0.12	3.08	3.69	3.12	0.57
18	0.22	0.21	3.05	3.63	3.00	0.63
19	0.25	0.19	2.85	3.58	2.92	0.66
20	0.22	0.20	3.03	3.53	3.11	0.42
21	0.26	0.18	2.94	3.53	3.02	0.50
22	0.16	0.33	2.90	3.47	2.98	0.50
23	0.18	0.38	2.82	3.50	2.89	0.60
24	0.17	0.34	2.98	3.42	3.06	0.36

^aData from ref 34.

these hosts have comparable E_T and ΔE_{ST} values with their Cb1 analogues, **11** alone displays a clear charge separation (Figure 7, Table S2, Supporting Information) and hence an ambipolar characteristic compared to the other three hosts.

The noteworthy points that emerge from the preceding discussion are as follows: first, the presence of a Cb1 unit at the R_5 position is necessary to design hosts with low electron injection barrier and a clear charge-separated state as it ensures that HOMO and LUMO are localized on units which are spatially separated. Second, the other subunit which can either be Cb1 or Cbz must be present at the R_1 position (to limit the delocalization of HOMO) to ensure that the hosts possess a balanced charge transport character.

In order to verify the generality of the above statement, we have substituted the Cb1 unit present in the R_5 position of **7** and **8** at the R_3 and R_4 positions which results in the hosts **15**, **16**, and **17**. The findings clearly point out that such a structural modification leads to an apparent increase in the electron injection barrier as the LUMO of the designed hosts is more destabilized and lies higher in energy than that of the ETL. The destabilization of LUMO leads to higher H–L gap (4.22–4.23 eV) in these new hosts. Compared to host **7** with a balanced charge transport, hosts **15** and **16** possess higher transport rate for electron, as reflected from their lower electron reorganization energies, making them more suitable building blocks for electron transport. The increase in the λ_+ values is due to the delocalization of the HOMO on the electron-deficient Cb1 units. Also, the E_T values of these hosts are comparable with **7** and **8** (except **16**). The low E_T value of the **16** might be due to the effective and extended conjugation between the subunits at the R_1 and R_4 positions and the central carbazole unit (Figure S3, Supporting Information). The NTO analysis also supports the high triplet energy of **15** due to its localized transitions within the Cb1 unit. The comparatively low E_T of **16** can be mapped to the delocalization of the hole-particle wave

functions over the central Cbz and the substituted Cb1 units (Figure S4, Supporting Information).

Similarly, we can generate the hosts **18**, **19**, **20**, and **21** by substituting the Cb1 present at the R_5 position of **9** and **10** at the R_3 and R_4 positions. The results clearly indicate that the absence of the Cb1 unit at the R_5 position results in hosts which in general have higher barrier for electron injection due to destabilized LUMO. Also, such hosts lack either a clear charge separation (Figure S2, Supporting Information) or balanced charge mobility (Table 2). We did not observe any appreciable change in both the E_T and ΔE_{ST} values of these hosts. It is interesting to note that even though **18** and **20** exhibit balanced charge transport they exhibit higher reorganization energies for both hole (HOMO delocalization extends slightly to Cb1 also) and electron (LUMO is localized on the central carbazole core) than **9** and **10**. The presence of a node at the C3 atom in the LUMO of carbazole is responsible for the localization of the LUMO to the carbazole unit rather than Cb1 present at the R_2 position. The hosts **19** and **21** with lower λ_- (0.18–0.19 eV), due to the concentration of the LUMO on the Cb1 unit, are more suitable for electron transport. Hence, this discussion reaffirms the importance of the substitution of a Cb1 unit at the R_5 position in controlling the electronic properties of the disubstituted hosts.

We have also considered hosts where both the subunits are Cbz (**22**, **23**, and **24**) for comparison, and such hosts have been reported earlier.^{7,15,19–21} As expected, these systems have a higher mobility for hole as indicated by their low λ_+ (0.16–0.18 eV) due to the delocalization of the HOMO on the Cbz units and low mobility for electron due to the localization of the LUMO on the central Cbz unit. Apart from their higher hole mobility, these systems exhibit low barrier for both hole and electron injection, low ΔE_{ST} values, and small band gap. Also the E_T values of these hosts are slightly lower than the Cb1-substituted hosts (**15**, **16**, and **17**). The variation in the E_T is due to the delocalized triplet spin density on the PhCbz and subunits (Figure S3, Supporting Information). The NTO analysis also indicates that the electron wave function is localized on the central carbazole, while that of the hole is delocalized on both the central and side-substituted Cbz units. This delocalization of the hole–electron wave functions may result in the lowering of the E_T in **22**, **23**, and **24** (Figure S4, Supporting Information). The calculated χ_T values of disubstituted hosts are shown in Table S6 (Supporting Information). The χ_T values of hosts **11**, **12**, **13**, and **14** (Cbz at R_5 position) are higher than **7**, **8**, **9**, and **10** (Cb1 at R_5 position), indicating that triplet exciton formation values increase with the increase in the number of Cbz substitutions in PhCbz. Hence, the χ_T values of hosts **14** and **24** (62.91–64.34) are higher than **7** and **8**. It is also interesting to note that χ_T values increase when the R_5 position is substituted by a Cbz unit rather than Cb1. Hence, the χ_T value of hosts **11**, **12**, **13**, and **14** (56.75–62.91) is higher than **7**, **8**, **9**, and **10** (47.39–54.04). It is also found that substitutions at the R_2 and R_3 or R_1 and R_3 positions are more effective than the R_1 and R_4 . Thus, the χ_T values of hosts **15**, **17**, **18**, **20**, **21**, **22**, and **24** (56.16–64.34) are higher than **16**, **19**, and **23** (54.98–58.01). The above discussion implies that both position and nature of the substituents may influence the triplet exciton generation formation.

From the preceding discussion, we can conclude that the presence of a Cb1 unit at the R_5 position is quite essential to design hosts with low injection barrier for electrons specifically.

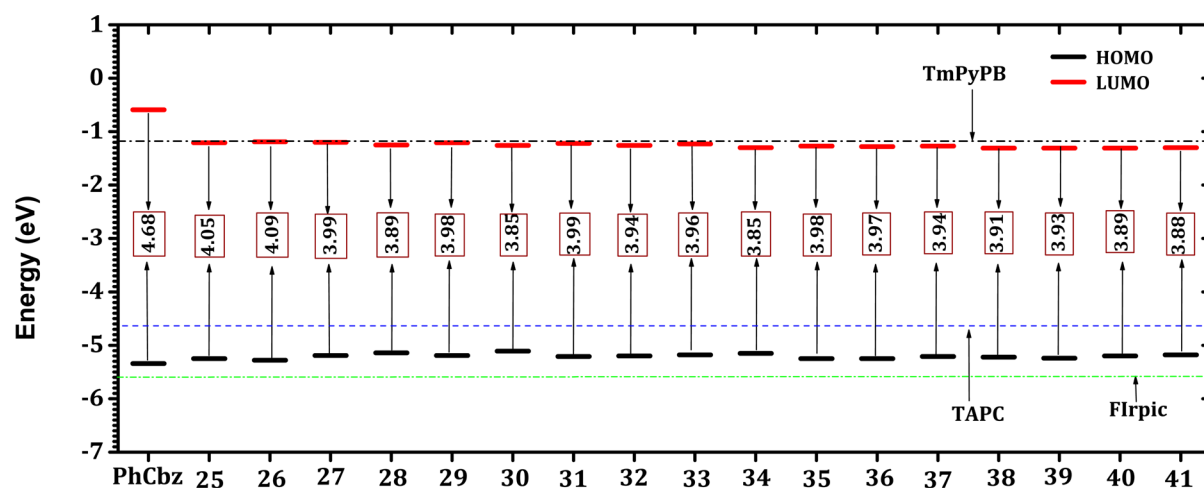


Figure 8. HOMO and LUMO energy levels and HOMO/LUMO energy gap (E_g) of the trisubstituted hosts with reference HTL (TAPC), ETL (TmPyPB), and emitter (Flrpic) in the ground state.

In order to have a well-balanced charge transport, with low reorganization energy for both hole and electron, the second subunit should be present at the R_1 position.

3.3. Trisubstituted Hosts. On the basis of the results obtained from the disubstituted systems, we designed trisubstituted hosts wherein the Cb1 unit at the R_5 position was fixed. We have considered ten host molecules in this series. The hosts **25**, **26**, and **27** are generated from **7** or **8** by introducing the Cb1 unit at the appropriate positions. The array of electronic properties evaluated clearly reveals that the addition of the third Cb1 unit does not yield hosts with improved features. The third Cb1 unit appreciably improves neither the electron or hole injection barriers nor the ΔE_{ST} or the band gap (Figure 8, Table 3). This can clearly be understood if we analyze the MOs (Figure S7, Supporting Information). The electron density distribution of the central Cbz unit in **25** and **27** resembles the HOMO of the PhCbz

Table 3. Calculated Singlet/Triplet Vertical Excitation Energies $E(S_0 \rightarrow S_1)/E(S_0 \rightarrow T_1)$, Adiabatic Triplet Energies (E_T), and Reorganization Energies for Hole (λ_+) and Electron (λ_-) at the B3LYP/6-31G* Method (All Values Are in eV)

hosts	λ_+	λ_-	E_T	$E(S_0 \rightarrow S_1)$	$E(S_0 \rightarrow T_1)$	ΔE_{ST}
25	0.28	0.10	3.05	3.71	3.03	0.68
26	0.37	0.08	2.86	3.75	2.94	0.81
27	0.32	0.09	3.06	3.67	3.12	0.55
28	0.22	0.11	3.07	3.51	3.01	0.50
29	0.29	0.11	2.84	3.57	2.91	0.66
30	0.23	0.12	3.03	3.51	3.10	0.41
31	0.20	0.11	3.05	3.62	3.00	0.62
32	0.16	0.16	2.90	3.47	2.98	0.48
33	0.21	0.17	2.81	3.47	2.88	0.59
34	0.18	0.16	2.98	3.41	3.05	0.37
35	0.12	0.27	2.90	3.44	2.97	0.47
36	0.15	0.32	2.81	3.46	2.87	0.58
37	0.14	0.25	2.98	3.39	3.04	0.35
38	0.17	0.30	3.06	3.36	2.97	0.39
39	0.15	0.28	2.86	3.39	2.92	0.47
40	0.17	0.30	3.06	3.35	2.88	0.47
41	0.16	0.27	3.16	3.34	2.99	0.35

unit. The presence of a node at the C2 atom in the HOMO of PhCbz prevents any delocalization of electron density between the core and the R_1 substituent as seen in the case of **25**. This may be why the HOMO and LUMO of **25** are similar in energy to the disubstituted host **8**. Unlike **25**, there can be an effective coupling between the core and substituent subunits in the case of **26** and **27**. However, the antibonding interaction between the two subunits destabilizes the HOMO of these trisubstituted hosts which appear closer in energy to that of the corresponding disubstituted hosts **7** and **8**, respectively. The triplet energies (3.05 eV) of the above-mentioned trisubstituted hosts are almost the same as that of their disubstituted counterparts. The only exception is seen in the case of **26** with E_T of 2.86 eV. Such a decrease in the triplet energies for hosts with R_1 and R_4 substitutions has previously been reported and has been attributed to more effective and extended conjugation (Figure S5, Supporting Information). The NTO analysis also clearly elicits that localization of the hole and particle wave functions on the Cb1 subunit in **25** and **27** leads to high E_T in these hosts. The relatively low triplet energy of **26** may be due to the delocalization of hole wave function on the central Cbz and side Cb1 subunits, thereby reducing its triplet energy (Figure S6, Supporting Information). Also, as expected, these hosts with only a Cb1 unit will have higher mobility for electron transport (as LUMO is localized on the Cb1 unit present at the R_5 position) as exemplified by their lower reorganization energies for electron over hole ($\lambda_- = 0.08$ – 0.10 eV).

The next class of hosts, **28**, **29**, **30**, and **31**, was designed by introducing Cbz as the third subunit at the R_3 and R_4 position of **7** and **8**, respectively. The HOMO and LUMO of these hosts (Figure 8) indicate improved barriers for both hole and electron compared to **7** and **8** as the addition of the Cbz unit destabilizes the HOMO and stabilizes the LUMO of the designed hosts. The same can be attributed to the small variation in the HOMO–LUMO gap observed in this class. Formation of a clear charge-separated state is seen with HOMO localized on the central Cbz and the subunits present on the same and the LUMO localized solely on the Cb1 present at the R_5 position (Figure 7 and Table S2, Supporting Information). However, the E_T of these hosts is almost identical (except **29**) to disubstituted hosts (**7** and **8**). The lower triplet energy of the host **29** is due to the effective conjugation of the

R_1 - and R_4 -substituted system. Such a decrease in the triplet energy for host **29** is very clear from the NTO analysis, wherein hole–electron wave functions are slightly delocalized over the two carbazole units (Figure S6, Supporting Information). In the case of **28** and **31** the T_1 state corresponds to a localized transition only on the Cb1 unit. The reorganization energies of these systems reveal a small change in the case of the electron for all the four hosts considered here, and these hosts are more suitable for electron transport (Table 3). This discussion points to the fact that the addition of either Cb1 or Cbz subunit in a homo (Cb1) disubstituted system does not improve the electronic properties of the hosts, and such hosts tend to exhibit higher mobility for electron (as LUMO is localized on the Cb1 unit present at the R_5 position) over hole (as HOMO is delocalized over core Cbz and Cb1/Cbz units present at the R_3 and R_4 positions). Thus, none of the seven trisubstituted hosts considered so far exhibited a balanced charge transport.

Apart from **7**, the disubstituted host **9** ($R_1 = \text{Cbz}$ and $R_5 = \text{Cb1}$) had also exhibited electronic properties desirable for an efficient host. Hence, we modified the structure of **9** and **10** by introducing an additional Cbz unit at the R_3 and R_4 positions resulting in hosts **32**, **33**, and **34**. The most striking result here is that all the designed hosts have a balanced charge transport (Table 3) and a very good charge-separated state (Figure 7). The difference in the reorganization energies of the hole and electron is as low as 0.02–0.04 eV. It is interesting to note that in the case of **32** the reorganization energy for both hole and electron is identical (0.16 eV). The electronic distribution shows the localization of the electron density over the core carbazole and the subunits (ca. 80%) in the case of the HOMO and over the Cb1 unit at the R_5 position in the case of the LUMO (ca. 97%) and thus the formation of a clear charge-separated state. From Figure 8, we can observe that such structural modification however does not appreciably improve the charge injection properties. The HOMO and LUMO of these three trisubstituted hosts are similar to that of their disubstituted counterparts. This can be traced to the presence of a node at the C2 position in **32** and the antibonding interactions between the two subunits as explained in the previous case of hosts **25**, **26**, and **27**. However, it is to be emphasized that these trisubstituted systems have low barrier for the injection of electron and hole. The variation in the E_T of the trisubstituted hosts **32** (2.90 eV), **33** (2.81 eV), and **34** (2.81 eV) can be explained on the basis of their triplet spin density distribution and NTO analysis (Figures S5 and S6, Supporting Information). The triplet spin density distribution and hole–electron wave function distribution of **32** are similar to **9** (2.95 eV) and so is its E_T . In the case of **33**, the E_T value being lower than **9** can be ascribed to the effective conjugation of the R_1 and R_4 substituents as seen in the case of **29** also. The host **34** exhibits much lower E_T than **10** because of the delocalization of the triplet spin density and hole–electron wave functions over the Cbz units against **10** wherein the electron density and NTO are located on the Cb1 unit. We have also looked at the vertical ΔE_{ST} (0.37–0.59 eV) of the three trisubstituted hosts under consideration which is found to be much lower than their disubstituted hosts. This variation is due to a more profound change in the singlet energy. The addition of a Cbz unit is found to stabilize the singlet excited state selectively, and hence a reduction in the ΔE_{ST} value is seen. Such a decrease in the S_1 is already discussed in the monosubstituted host (Table S3, Supporting Information). It is worth noting that the hosts **32** and **34** exhibit ΔE_{ST} as low as

0.48 and 0.37 eV, respectively. Also, introducing a Cbz unit converts the host **10** with a higher mobility for electron to a host (**34**) with balanced charge transport character. This discussion highlights that an efficient trisubstituted host requires substitution of one carboline subunit at the R_5 position and two Cbz units which are substituted at the R_3 and R_1/R_2 positions.

One can say that our results may be biased in terms of the preference of the Cb1 unit at the R_5 position as we had fixed this substitution in all the trisubstituted systems considered so far. Hence, in order to test whether the presence of a Cb1 at the R_5 position is mandatory for the better performance of the hosts, we took into consideration seven more hosts. Three of the hosts, **35**, **36**, and **37**, are obtained by replacing the Cb1 unit in **32**, **33**, and **34** with Cbz. These systems, with the Cbz unit alone in their skeleton, will be more efficient as hole transporting hosts as reflected by their lower reorganization energies for hole even though they fair very well in terms of other electronic properties. The other four hosts (**38**, **39**, **40**, and **41**) have the Cb1 unit substituted in the central carbazole core. Such a change in the structure helps to improve the triplet energy and the ΔE_{ST} when compared to the host systems (**32**, **33**, and **34**) where the Cb1 unit is present in the R_5 position. However, these hosts exhibit higher charge mobility for hole and also do not have a very clear charge separation (Figure S7 and Table S2, Supporting Information). Hence, one can state that presence of a Cb1 unit at the R_5 position will decide balanced mobility of the charge carriers and a clear charge separation.

This preceding discussion clearly highlights the importance of the number and position of substitution of Cb1 and Cbz units to design efficient hosts. An efficient trisubstituted host requires at the R_5 position one carboline subunit and at the R_3 position and R_1/R_2 position two Cbz units. Thus, the hosts **32** and **34** stand out as the most efficient hosts based on the electronic properties considered.

4. HOSTS SCREENED FOR THEIR BETTER ELECTRONIC PROPERTIES

On the basis of the electronic properties considered in the study, we screened nine hosts (**6**, **7**, **8**, **9**, **10**, **30**, **32**, **33**, and **34**) from the 41 which were initially considered. The charge injection barriers for the hosts were addressed by taking into consideration the HOMO and LUMO values as they qualitatively reflect the IP and EA if the Koopmans' theorem is invoked. However, the poor performance of the Koopmans' theorem has been shown previously when it is combined with DFT.⁵⁷ Hence, we have calculated the IPs and EAs of selected hosts (Table 4) using both the Koopmans' theorem and ΔSCF method. From Table 4, the adiabatic IP values of the host molecules are in between those of TAPC and FIrpic, which indicates the potential to mediate the hole from TAPC to FIrpic. A similar conclusion was drawn from the Koopman's theorem. Similarly, the computed adiabatic EA values also follow the same trend as the LUMO values. It is evident from the previous studies that the triplet exciton generation fraction (χ_T) is an indicator to identify the potential host molecules. Higher χ_T values are associated with better performance. The calculated χ_T values are given in Table 4 which indicates that hosts with higher content of Cbz in their structure (**6**) have higher χ_T values than the others. Very interestingly, both hosts **32** and **34** have higher χ_T values than the experimentally reported carbazole- and carboline-based host **10**. In addition,

Table 4. Calculated Adiabatic Ionization Potential (IP in eV), Electron Affinity (EA in eV) and Triplet Exciton Generation Fraction (χ_T) for the Selected Designed Hosts and Reference Systems at the B3LYP/6-31G* Level

hosts	HOMO	LUMO	IP	EA	χ_T
6	−5.12	−0.94	6.24	0.28	59.72
7	−5.35	−1.18	6.34	−0.09	45.19
8	−5.20	−1.20	6.14	−0.14	45.62
9	−5.19	−1.20	6.30	−0.09	37.75
10	−5.13	−1.24	6.14	−0.10	42.55
30	−5.11	−1.26	6.01	−0.26	50.98
32	−5.20	−1.26	6.11	−0.30	55.83
33	−5.18	−1.23	6.07	−0.29	53.28
34	−5.15	−1.30	6.03	−0.30	58.14
mcp	−5.41	−0.77	6.55	0.31	–
TAPC	−4.66	−0.28	5.58	0.59	–
TmPyPB	−6.15	−1.18	7.16	−0.28	–
FIrpic	−5.54	−1.74	6.62	−0.59	–

the χ_T value of the host **34** is very close to that of the carbazole-based host **6**.

5. CONCLUSION

We have carried out a systematic search to propose efficient hosts based on carbazole (C**bz**) which is primarily a hole-transporting subunit and carboline (C**bl**) which is an electron-transporting subunit. By taking phenyl carbazole as the central core unit, we have designed 41 hosts for blue electrophosphorescence by introducing one, two, or a maximum of three carbazole or carboline subunits into the phenyl carbazole core. Theoretical calculations at the density functional theory level, B3LYP/6-31G*, were employed to screen the designed hosts based on an array of electronic properties, viz., E_T , HOMO and LUMO, ΔE_{ST} , charge injection barriers, and charge mobilities from the reorganization energies. Overall our results highlight that substituting the phenyl carbazole core with a C**bl** subunit at the R_5 position ensures that HOMO and LUMO are localized on units which are spatially separated, and a further substitution of C**bl** or C**bz** subunit at the R_1 position limits the delocalization of HOMO. The resultant disubstituted hosts have low barriers for both hole and electron transport and well charge separated states. However, the main drawback here will be the high ΔE_{ST} values of these hosts. This drawback can however be overcome by adding another carbazole unit. In the trisubstituted case, the most desirable electronic properties will be obtained only when the R_5 position is substituted by the C**bl** unit and C**bz** unit substituted at the R_1/R_2 and R_3 positions. Thus, the hosts **32** and **34** stand out as the most efficient hosts based on the electronic properties considered, and their computed electronic properties are better than some of the already reported hosts. These two hosts exhibit low barrier for hole and electron injection, clear charge-separated state, balanced charge transport for both hole and electron, and low ΔE_{ST} .

■ ASSOCIATED CONTENT

■ Supporting Information

The HOMO and LUMO energies, HOMO/LUMO energy gaps, and relaxation energy (λ_1 , λ_2 , λ_3 , and λ_4) for the designed host molecules; percentage contributions of molecular orbital contribution of the HOMO and LUMO of the PhC**bz** and the subunits; dominant transitions corresponding to the lowest

singlet (S_1) and triplet (T_1) states; the charge transfer integrals and the average intermolecular distance for the hosts **32** and **34**; NPA and Mulliken charges for the monosubstituted host molecules; triplet exciton generation fraction for the host molecules; ΔE_{ST} values for the hosts **6**, **10**, and mCP in different functionals; HOMO and LUMO contour plots of di- and trisubstituted hosts; triplet spin density of di- and trisubstituted hosts; NTOs of di- and trisubstituted hosts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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