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Design of Efficient Ambipolar Host Materials for Organic Blue Electrophosphorescence: Theoretical Characterization of Hosts Based on Carbazole Derivatives

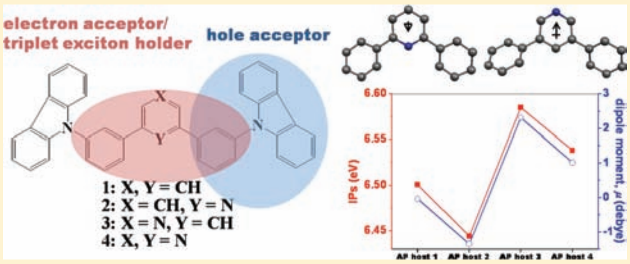
Dongwook Kim,*[,†,‡] Veaceslav Coropceanu,[†] and Jean-Luc Brédas*[,†,#]

[†]School of Chemistry and Biochemistry, and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, United States

[‡]Department of Chemistry, Kyonggi University, San 94-6 Iui-Dong, Yeongtong-Gu, Suwon 443-760, Korea

Supporting Information

ABSTRACT: Density functional theory calculations were carried out to investigate the electronic structures of representative ambipolar hosts for blue electroluminescence, based on two carbazole end groups and *meta*-terphenyl (*m*TP)-like bridges. The bridge molecular segments include *m*TP, 2,6-bisphenylpyridine, 3,5-bisphenylpyridine, and 2,6-bisphenylpyrimidine. While the ionization potentials and electron affinities of these molecules are mainly determined by their hole- and electron-transport subunits, respectively, each subunit impacts the electronic properties of the other upon their binding, mainly in an inductive way. Importantly, the lowest triplet state of the hosts is determined to be confined into the *m*TP-like bridges since these are the subunits with lowest individual triplet energy. Extension of the phenyl-based π-conjugated system via *meta* linkages is found to be effective in modulating the electron affinity value while maintaining a high triplet energy.



1. INTRODUCTION

Since the discovery of electroluminescence in organic small molecules[1] and polymers,[2] organic light-emitting diodes (OLEDs) have attracted major interest due to their potential for lighting and display applications.[3] They pave the way toward more energy-efficient, low-cost, and flexible and/or transparent devices. While blue-light emission represents an essential ingredient for both solid-state lighting and full-color displays, advances in (deep) blue OLEDs have not paralleled those for red or green OLEDs. One of the major hurdles in developing blue OLEDs is the obvious need for compounds with large optical gaps, which translates into relatively high ionization potentials (IPs) and low electron affinities (EAs); as a result, high operating voltages are required to inject charges efficiently from both the cathode and anode sides, and the injection process leads to the formation of highly energetic species that are prone to side reactions detrimental to device lifetime.

In electrophosphorescent OLEDs, the emissive layer (EML) is composed of a phosphorescent emitter dispersed within a host material in order to prevent concentration quenching of the phosphorescence. The host molecules must fulfill a number of requirements, including (i) high rates for charge and energy (exciton) transfers; (ii) triplet excited-state energies higher than those of the emitter molecules, in order to avoid guest-to-host back energy transfer (since the hosts are usually pure organic molecules, their triplet states correspond to dark states); and (iii) facile and balanced charge injection from the neighboring hole-transport layer (HTL) and electron-transport layer (ETL).

A large number of host materials have been developed, many of which present essentially a so-called unipolar character; this means that these materials favor injection/diffusion of one type of charge carrier over the other, which can result in unbalanced charge injection into the EML.[4−16] To circumvent this issue, considerable efforts have been placed into the development of ambipolar (AP) host materials.[16−23]

Efficient AP hosts have been recently reported. Of note are the synthesis and exploitation by Kido and co-workers of AP host molecules based on *meta*-terphenyl (*m*TP)-like derivatives of carbazole: pyridine-based 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine and 3,5-bis(3-(carbazol-9-yl)phenyl)pyridine,[19] and pyrimidine-based 2,6-bis(3-(carbazol-9-yl)phenyl)pyrimidine[24] (see compounds **2**−**4** in Figure 1a). These authors fabricated blue OLEDs with an EML composed of one of these hosts and iridium(III) bis((4,6-difluorophenyl)pyridinato-*N*,$C^{2'}$) picolinate (FIrpic) as the guest phosphor.[19,24] The devices operate with high efficiency and reduced roll-off at high current density and luminescence; external quantum efficiencies (EQEs) as high as 24% at 100 cd/m^2 and 22% at 1000 cd/m^2 were obtained with AP host **2**. Using phosphine-oxide-based AP hosts, Hsu et al. fabricated devices with ~20% EQE at 100 cd/m^2 and a turn-on voltage as low as 2.6 V.[20,21] Cho and Cheng also reported "universal" AP host molecules for red, green, and blue OLEDs;[22] their blue

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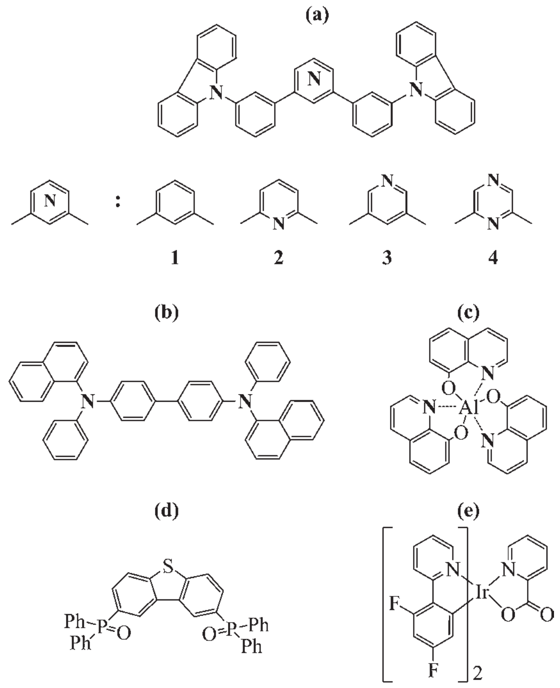

Figure 1. Chemical structures of molecules studied in this work: (a) ambipolar (AP) host molecules with bridges including *m*TP (AP host **1**), 2,6-bisphenylpyridine (AP host **2**), 3,5-bisphenylpyridine (AP host **3**), and 2,6-bisphenylpyrimidine (AP host **4**); (b) *N,N*′-bis-(1-naphthyl)-*N,N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPD) as a hole-transport molecule; (c) tris(8-hydroquinolinato)aluminum (Alq3) as an electron-transport molecule; (d) 2,8-bis(diphenylphosphoryl)dibenzothiophene (*m*BTPO) as a host molecule with good electron-injection properties; (e) iridium(III) bis((4,6-difluorophenyl)pyridinato-$N,C^{2'}$) picolinate (FIrpic) as blue phosphor.

devices exhibited EQEs similar to those reported by the Kido group.

Here, our goal is to develop a better understanding of the structure−property relationships for AP hosts. We chose as representative molecules those reported in refs 19 and 24. We thus describe the results of density functional theory (DFT) calculations on compound **1** and its pyridine/pyrimidine analogues (see Figure 1a) and discuss how the molecular subunits affect the system energetics as well as the charge-injection properties. Our results allow us to draw a number of conclusions, of help in the design of efficient AP host materials.

2. COMPUTATIONAL DETAILS

The chemical structures of the AP molecular hosts considered here are shown in Figure 1a. The hosts are based on carbazole units on both ends and *m*TP-like bridges in the center; the bridges include *m*TP, 2,6-bisphenylpyridine, 3,6-bisphenylpyridine, and 2,6-bisphenylpyrimidine. These AP hosts are referred to as compounds **1**−**4** hereafter. The geometric and electronic structures and energetics of the molecular hosts and their building blocks were calculated at the DFT level using the B3LYP functional and a split-valence SV(P) basis set as implemented in the TURBOMOLE program (version 5.9).[25−27] The geometries in the ground state (S_0) were optimized via spin-restricted DFT calculations, while those in the lowest triplet state (T_1) and in the positively or negatively charged (ionic) states were conducted at the spin-unrestricted DFT level. Vibrational frequency calculations were also carried out to confirm that all the optimized structures correspond to minima on the potential energy surfaces.

Table 1. Frontier Molecular Orbital Energies and Ionization Potentials (IPs)/Electron Affinities (EAs) of Ambipolar (AP) Host Molecules, Hole- and Electron-Transport Molecules, and the Blue Phosphor, FIrpic[a]

AP host	HOMO-1	HOMO	LUMO	IP	EA
1	−5.50	−5.50	−1.37	6.50	−0.34
2	−5.41	−5.41	−1.63	6.44	−0.51
3	−5.58	−5.58	−1.56	6.59	−0.51
4	−5.51	−5.51	−1.96	6.54	−0.76
NPD		−4.88	−1.36	5.74	−0.46
Alq3		−5.33	−1.85	6.48	−0.72
*m*BTPO		−6.27[b]	−1.52[b]	7.37[b]	−0.43[b]
FIrpic		−5.61[b]	−1.87[b]	6.68[b]	−0.68[b]

[a] All energies are in eV. [b] Data from ref 31.

Our previous work on mixed-valence systems suggests that the radical-cations of **1**−**4** should undergo broken-symmetry effects, with localization of the positive charge on one of the carbazole units.[28] Since current DFT methods usually fail to account for such localization effects, the geometries of $\mathbf{1}^+-\mathbf{4}^+$ were derived at the unrestricted Hartree−Fock level of theory, followed by final reoptimization at the DFT level. The lowest triplet energies as well as the adiabatic IPs/EAs were assessed by means of the ΔSCF method on the basis of the optimized structures for the respective electronic states; in the case of the triplet energies, zero-point vibrational energy (ZPVE) corrections were considered. To get a better insight into the nature of the T_1 state, we performed natural transition orbital (NTO) analyses[29,30] based on time-dependent DFT (TD-DFT) calculations carried out at the optimized T_1-state geometries.

To complement our investigations, we also conducted similar theoretical studies of the geometric and electronic structures of representative molecules used for the following purposes: molecular material for HTL, *N,N*′-bis-(1-naphthyl)-*N,N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPD, Figure 1b); molecular material for ETL, tris(8-hydroquinolinato)aluminum (Alq3, Figure 1c); and blue phosphorescent emitter (FIrpic, Figure 1e). (Note that it was reported that direct hole injection from the HTL into FIrpic is also possible.[16,17]) In addition, we reproduce here the results we obtained earlier[24] for another host molecule for blue electroluminescence with a low barrier for electron injection,[16,17,31] 2,8-bis(diphenylphosphoryl)dibenzothiophene (*m*BTPO, Figure 1d).

3. RESULTS AND DISCUSSION

3.1. HOMO/LUMO Energies and IP/EA Values. A major drive to develop new AP hosts is to lower and balance the charge-injection barriers from the neighboring HTL/ETL layers into the EML. In this context, we first computed the IP and EA values of the AP hosts and the other molecules in Figure 1 at both Koopmans's theorem (HOMO/LUMO energies) and ΔSCF levels of theory. The results are given in Table 1.

Since the IPs and EAs computed at the Koopmans's theorem and ΔSCF levels show exactly the same trends, we focus here on the latter. Our calculations indicate that the IPs of the AP hosts **1**−**4** (∼6.44−6.59 eV) are smaller by ∼0.1−0.2 eV than that of FIrpic but significantly larger (by ∼0.7−0.85 eV) than that of NPD. Among the AP hosts in this study, **2** has the smallest IP; this means that the smallest barrier for hole injection could be obtained with **2**, which is qualitatively consistent with the experimental data that provide a higher EQE for the devices based on **2** than those based on **3**.[19,24] Table 1 also shows that the EAs of the

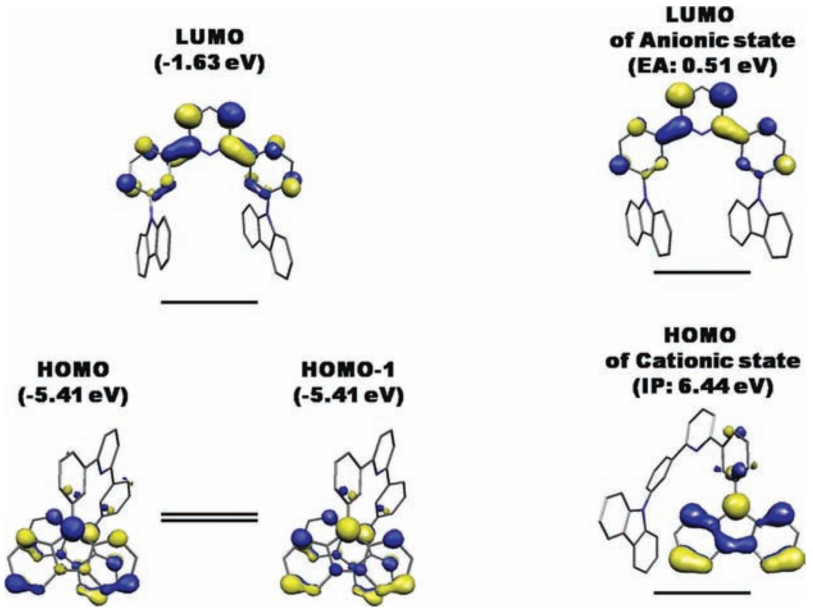

Figure 2. Frontier molecular orbitals of AP host **2** in the neutral (left) and ionic states (right).

AP hosts **1**−**3** are smaller in magnitude than those of both Alq3 and FIrpic. However, they are larger than that of *m*BTPO (−0.43 eV), except for host **1** (−0.34 eV); the latter result is due to the lack of any electron-withdrawing character within the *m*TP bridge. Thus, AP hosts **2** and **3** can be expected to present reduced energy barriers for electron injection compared to *m*BTPO and potentially help in lowering the device turn-on voltage. On the other hand, in the case of host **4**, its slightly larger EA (−0.76 eV) than that of Alq3 (0.72 eV), which is due to the strong electron-pulling nature of pyrimidine, points to facile electron injection; however, electron transfer from **4** to the guest phosphor, FIrpic (EA = −0.68 eV), might become more difficult and reduce device performance, which is consistent with recent experimental observations.[24]

Clearly, there is still room for further improvement of device performance by reducing the energy barriers for charge injection, which can be achieved by having a somewhat more destabilized cationic state and more stabilized anionic state of the host compared to **1**−**3**. In this context, it is important not only to identify the hole- and electron-transport subunits of the host molecules but also to gain a detailed understanding of how each subunit affects the properties of the other and of the whole molecule. We now turn to such a discussion.

The HOMO/HOMO-1 and LUMO wave functions of AP host **2** are depicted in Figure 2. As expected,[19] the HOMO and HOMO-1 wave functions are delocalized mainly on the carbazole subunits, with small contributions from the phenyl substituents on the carbazole N atoms. In contrast, the LUMO wave function resides on the *m*TP-like bridge. The HOMO and HOMO-1 orbitals are energetically nearly degenerate and represent linear combinations of HOMOs of the two carbazole subunits. The near degeneracy between HOMO and HOMO-1 implies that the electronic interactions between the two carbazoles are negligible, which is precisely the reason why the cationic species $\mathbf{1}^{+}$−$\mathbf{4}^{+}$ exhibit symmetry-broken geometries.[28] In order to explore the impact of the binding of the subunits, we compare in Figure 3 the EAs and IPs of the whole AP hosts to those of their individual electron- and hole-transport moieties.

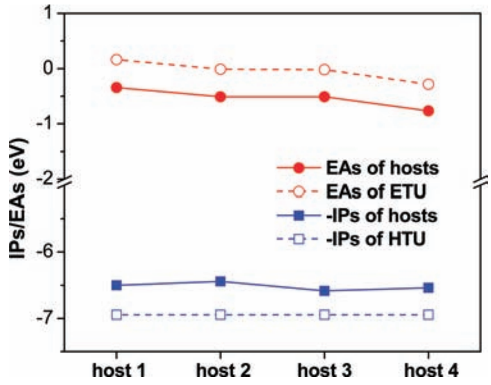

Figure 3. Plots of ionization potentials (IPs) and electron affinities (EAs) of AP hosts (full symbols), and their hole- and electron-transport units (HTU/ETU) (open symbols).

With regard to EAs, the AP hosts **1**−**4** and their electron-transport segments follow the exact same trends. It is useful to note that the carbazole units linked to the bridge via their N atoms exert an inductive electron-withdrawing effect; natural bond orbital analyses show that the terphenyl-like bridge carries a total net charge of ∼+0.4 |e| in **1**−**4**. The interesting consequence is that the anionic state gets stabilized (higher, more exothermic EA) by about 0.5 eV. We also note that the EAs of AP hosts **2** and **3** are nearly the same, which indicates a negligible impact of the exact position of the N atom in the central pyridine ring with respect to the positions of the phenyl substituents in these compounds.

In contrast, although the cationic states of all AP hosts in this study are dominated by the same *N*-phenylcarbazole subunits, their IPs appears to depend to some extent on the detailed chemical structure of the bridge; in particular, the position of the pyridine N atom impacts the IPs of the host molecules. The fact that the IP of AP host **1** lies in between those of hosts **2** and **3** suggests that the bridge might exert an electrostatic effect. To verify this point,

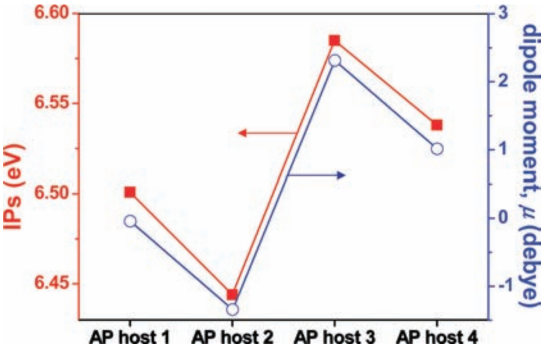

Figure 4. Plots of IPs of AP hosts (full squares) and of the dipole moment, μ, of their electron-transport *m*TP-like bridge (open circles).

Table 2. Adiabatic Lowest Triplet Energies of the Ambipolar Host Molecules and the Blue Phosphor, FIrpic[a]

AP host	$\Delta E_{\text{trip.}}$[b]	$\Delta E^0_{\text{trip.}}$[b]	expt	ref
1	2.94	2.81	2.72	24
2	2.85	2.71	2.71	19, 24
3	2.93	2.78	2.71	19, 24
4	2.78	2.63		
FIrpic	2.67	2.56	2.65/2.66	5/33

[a] All energies are in eV. [b] $\Delta E_{\text{trip.}}$ and $\Delta E^0_{\text{trip.}}$ denote the lowest triplet energy without and with ZPVE correction.

a comparison between the IPs of the hosts and the dipole moments, μ, of their terphenyl-like bridges is illustrated in Figure 4 (since μ is a vector quantity, its direction is also taken into account). The correlation shown in Figure 4 indeed suggests that the IPs of the hosts are affected mainly in an electrostatic way by the charge distribution in the bridge. The potential impact of such an effect needs to be borne in mind in the design of new AP host materials, since modulations of IP and/or EA values by just a few tenths of an electronvolt can lead to marked variations in charge-injection rates.

3.2. Triplet Energy. As already pointed out above, to suppress the back energy transfer from guest to host, the lowest triplet energy of the host must be higher than that of the guest. The computed adiabatic triplet energies of the AP hosts are collected in Table 2, along with that of FIrpic. The theoretical results are in good agreement with experiment and confirm that all the AP hosts considered here exhibit a higher T_1 energy than FIrpic, by over 0.07 eV based on ZPVE-corrected values at the DFT-B3LYP level. In the case of blue electrophosphorescence, the design of efficient AP hosts thus requires that we maintain a sufficiently high triplet energy while reducing the energy gap (transport gap) between the cationic and anionic states. A detailed understanding of the factors impacting the nature of the triplet state is therefore critical.

In the cases of AP hosts **2** and **3**, the calculated triplet energies of 2.71 and 2.78 eV compare very well with the experimental values of 2.71 eV measured in the solid state for both compounds (it must be borne in mind, however, that intermolecular interactions occurring in the condensed phase are not taken into account in the calculations). Interestingly, we note that, in ref 19, these high triplet energies were assumed to arise from the carbazole subunits.[19] However, the calculated triplet energies are actually significantly smaller than that of the carbazole molecule, ~3.05 eV both from theory[31] and experiment.[32] This large (3.05 − 2.71 = 0.34 eV) difference in triplet energy can hardly be attributed to any substituent effect. Hence, our results imply that other subunits might be related to the triplet state of host molecules **2** and **3**. Therefore, the triplet energies of the *m*TP-like bridges have also been calculated; the results are presented in Figure 5.

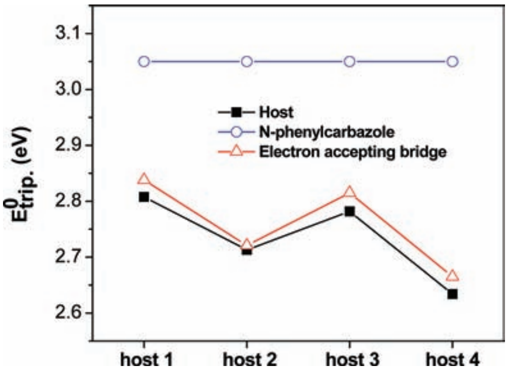

Figure 5. Triplet energies of the AP host molecules (full squares), *N*-phenylcarbazole subunits (open circles), and *m*TP-like subunits (open triangles). All values include ZPVE corrections.

Figure 5 demonstrates that there is a close one-to-one correspondence between the triplet energies of compounds **1**−**4** and their respective bridges. Thus, these results strongly suggest that it is the *m*TP-like bridge rather than the carbazole subunit that is responsible for the triplet state of the AP hosts. A further confirmation comes from the NTO analyses, carried out on the basis of the optimized T_1-state geometries of the AP hosts and illustrated in Figure 6. The NTO hole−particle wave functions are observed to be centered indeed on a biphenyl-like moiety of the bridge. We note that these results are in fact not surprising when one takes into account that the triplet energy of the electron-transport bridge is lower than that of a carbazole molecule, and that the triplet energy of an AP host molecule can be expected to be determined by the subunit with lowest triplet energy.[15]

4.3. Fine Modulation of the EA Value without Modification of the Triplet Energy. Carbazole is widely used as a host molecule because of its very good hole-transport properties, appropriate IP for facile hole injection, and high triplet energy.[9] New AP hosts for blue electroluminescence have thus often been developed by considering a suitable electron-transport unit and combining it with carbazole subunit(s).[16−23] Importantly, the electron-transport nature of π-conjugated molecules can be modulated not only by introducing electron-withdrawing substituents, as we have discussed so far in this work, but also by tuning the length of the π-conjugated pathway. In this context, we now discuss how the EA and triplet energy values of phenyl-based π-conjugated systems can be modulated via their connectivity and size.

We first address the difference between the *m*TP-like compounds and their *para*-terphenyl (*p*TP) counterparts. We have evaluated and compared the triplet energies of *p*TP and *m*TP (details are provided in the Supporting Information, see Table S1). The triplet energy of *p*TP (2.55 eV) is found to be significantly lower than that of *m*TP (2.84 eV) and comparable to that of FIrpic (2.56 eV). The triplet energy difference between *m*TP and *p*TP can be explained from an NTO analysis (see Figure S1 for details); while the hole−particle NTOs for *p*TP expand across the whole molecule, for *m*TP they become localized on a biphenyl segment. We note that, as expected, the EA of *p*TP is

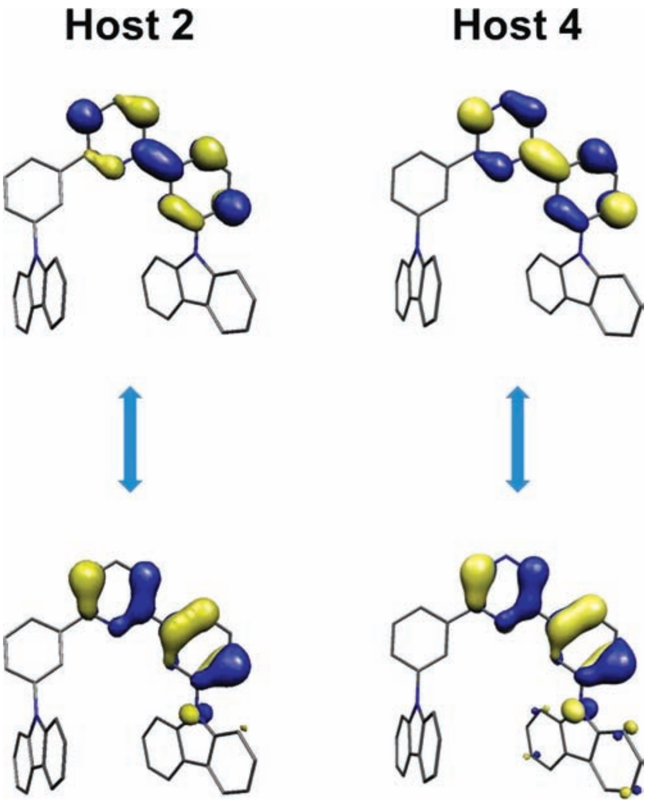

Figure 6. Natural transition orbitals describing the T_1 state of AP hosts **2** and **4**. The orbitals on the top correspond to the particle (electron) wave functions, and those at the bottom to the hole wave functions.

more exothermic than that of *m*TP by some 0.2−0.3 eV, which suggests that electron injection might possibly be more efficient when a *p*TP rather than *m*TP subunit is considered (see Table S1). Thus, when the *m*TP bridge is replaced with *p*TP, the host is expected to display a more facile electron injection but becomes less promising with regard to blue electroluminescence; however, the *p*TP triplet energy is sufficiently high to be useful for red and/or green OLEDs.

The fact that the T_1 state of *m*TP is nearly identical to that of biphenyl points to the fact that longer phenyl-based π-conjugated molecules can be expected to retain high enough a triplet energy to be incorporated in an AP host for blue OLEDs as long as all the phenyl rings are linked in *meta* positions. At the same time, their anionic states might be expected to become more stable as more phenyl rings are added.

To verify this hypothesis, we calculated the evolutions of the EA values and triplet energies upon going from benzene to *meta*-quaterphenyl (*m*QP) (details can be found in the SI, see Figure S2). The elongation of the π-conjugated pathway indeed leads to more stable anionic states (by ~0.31 eV from biphenyl to *m*TP and by ~0.15 eV from *m*TP to *m*QP). At the same time, the change in triplet energy when going from biphenyl to *m*QP is minimal (2.86 vs 2.84 eV). Since AP host **1** shows a less interesting EA value with respect to **2** and **3**, arising from the less stable anionic state of the *m*TP bridge, device performance with **1** could possibly be improved by integrating one more phenyl substituent in the *meta* position into the bridge. Furthermore, since the triplet energy of *m*QP is higher than those of the bisphenylpyridines of AP hosts **2** and **3**, it might be exploitable with deeper blue electrophosphorescent guests than FIrpic.

4. SYNOPSIS

We have evaluated the geometric and electronic structures of conjugated molecules based on carbazole hole-transport subunits and *meta*-terphenyl-like bridges, taken as representative for ambipolar hosts in organic electrophosphorescent devices. The results of DFT calculations confirm that the carbazole subunits and the *m*TP-like bridge are mainly responsible for the cationic states (IP values) and anionic states (EA values) of the hosts, respectively. Importantly, however, the IP and EA values of the host molecules are seen to be modulated by electrostatic/inductive effects coming from the electron-transport and hole-transport parts of the molecule, respectively; these factors must be taken into account when tuning the energy levels of the host molecules to those of the HTL and ETL materials for facile and balanced charge injections.

In contrast to the original expectation,[19] the T_1 states of the AP host molecules **1**−**4** are dominated by the *m*TP-like bridges, and not the carbazole subunits, due to the intrinsic lower triplet energy of the former segments. Therefore, when designing AP host materials for blue electroluminescence, care has to be exercised to examine the electronic structure of every molecular segment in order to assess the lowest triplet energy.

Since carbazole is a widely used hole-transport molecule, potentially useful AP hosts for blue OLEDs can be designed by associating carbazole to appropriate electron-accepting/transporting units. An investigation of phenyl-based π-conjugated molecules highlights that, as long as the phenyl rings are connected via *meta* linkages, the EA values of the AP hosts can be finely tuned by varying the size of the phenyl-based bridges, while the triplet energy can be kept very close to the high value observed for biphenyl.

Although this work was restricted to host molecules that combine carbazole and phenyl/pyridine-type molecules, webelieve that the findings of this study will prove very informative in the design and development of new AP hosts for blue electroluminescence.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Illustrations of EAs and lowest T_1 energies for *p*- and *m*TP; LUMO wave functions of anionic state and hole−particle NTOs in the T_1 state of *p*- and *m*TP evolution of EAs and T_1 energies of *m*-oligophenyls as a function of the number of phenyl rings; and all the calculated geometries in xyz-coordinate file format and their absolute energies. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

dongwook-kim@kgu.ac.kr; jean-luc.bredas@chemistry.gatech.edu

Notes

[#] Also affiliated with Department of Chemistry, King Abdulaziz University, Jeddah 21589, Saudi Arabia

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