Synthesis and Application of Pyridine-Based Ambipolar Hosts: Control of Charge Balance in Organic Light-Emitting Devices by Chemical Structure Modification
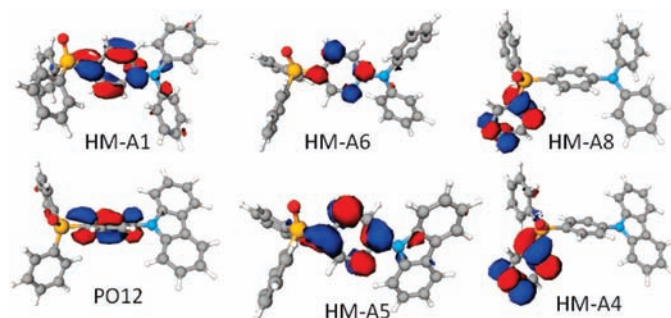
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ABSTRACT

We studied the influence of a pyridine moiety versus a phenyl moiety when introduced in the molecular design of an ambipolar host. These pyridine-based host materials for organic light-emitting diodes (OLEDs) were synthesized in three to five steps from commercially available starting materials. The isomeric hosts have similar HOMO/LUMO energies; however, data from OLEDs fabricated using the above host materials demonstrate that small structural modification of the host results in significant changes in its carrier-transporting characteristics.

The continued development of materials for efficient and stable blue devices is of interest for both displays[1] and energy-saving solid-state lighting[2] based on organic light-emitting device (OLED) technology. In blue phosphorescent OLEDs, energy is transferred from both singlet and triplet states of the host to the triplet states of the phosphorescent emitter/dopant[3] which results in nearly 100% internal quantum efficiency (IQE).[4] This process mandates that the triplet excited state of the host and the exciton-confining properties of the surrounding transport materials be higher than that of the phosphorescent emitter to prevent quenching

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of the dopant emission.[5] Previously, we reported phosphorescent blue OLEDs with low drive voltages using phosphine oxide (PO)-based wide bandgap host/charge transporting materials and the sky blue emitter iridium(III)bis(4,6-(difluorophenyl)pyridinato-N,C2)picolinate (FIrpic).[6,7] For these materials, the P=O moiety acts to break the conjugation between adjacent aryl groups resulting in a triplet energy greater than 2.7 eV. Here, we report the design, synthesis, electrochemical characterization, and OLED properties of four new ambipolar phosphine oxide based hosts (4-(9H-carbazol-9-yl)phenyl)(phenyl)(pyridin-3-yl)phosphine oxide (**HM-A4**), (5-(9H-carbazol-9-yl)pyridin-2-yl)diphenylphosphine oxide (**HM-A5**), and (5-(diphenylamino)pyridin-2-yl)diphenylphosphine oxide (**HM-A6**), (4-(diphenylamino)phenyl)(phenyl)(pyridin-3-yl)phosphine oxide (**HM-A8**) (Schemes 1 and 2). The device properties of these hosts were compared to those of two previously reported hosts (4-(diphenylamino)phenyl)diphenylphosphine oxide (**HM-A1**)[8] and (4-(9H-carbazol-9-yl)phenyl)diphenylphosphine oxide (**PO12**) (Figure 1).[8b,9]
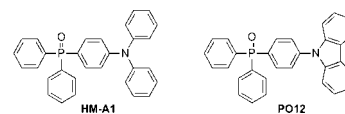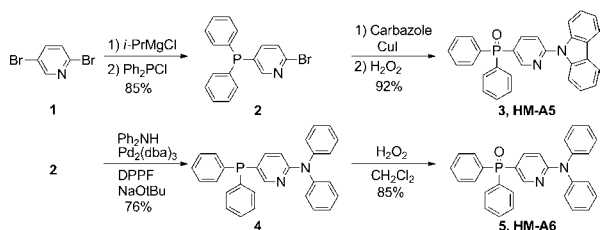

Figure 1. Chemical structures for hosts HM-A1 and PO12.

Scheme 1. Syntheses of HM-A5 and HM-A6

Scheme 2. Syntheses of HM-A4 and HM-A8

Our design strategy takes advantage of the pyridine moiety which has been shown to enhance electron transport because

most host materials preferentially transport holes rather than electrons.[10] Pyridine rings have low-lying lowest unoccupied molecular orbital (LUMO) energies. This, coupled with the E_{LUMO} lowering properties of the appendant diphenylphosphine oxide group, results in enhanced electron injection and transport. Hole transport and injection are accomplished by using either of the well-known and commonly used hole transport moieties carbazole or triphenylamine. Compounds **HM-A4**, **HM-A5**, **HM-A6**, and **HM-A8** are combinations of the functional groups above and are designed to produce ambipolar host materials for blue phosphorescent OLEDs.
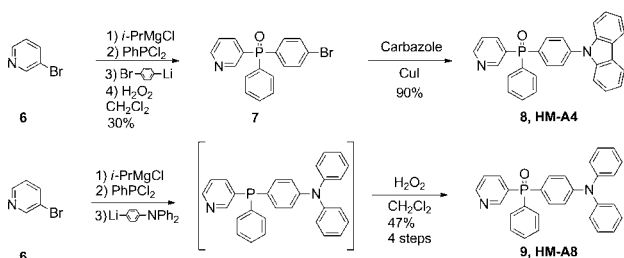
The synthesis of the pyridine bridge hosts **HM-A5** and **HM-A6** starts with Grignard metathesis of the commercially available 2,5-dibromopyridine **1** using i-PrMgCl followed by treatment with chlorodiphenylphosphine to afford the common intermediate 2-bromo-5-diphenylphosphanylpyridine **2** (Scheme 1). Copper-catalyzed N-amination of this intermediate **2** in the presence of carbazole followed by H_2O_2 oxidation of the resulting product furnishes **HM-A5** in excellent yields. This product was characterized by ^{1}H, ^{13}C, ^{31}P, FTIR, and HRMS. The regiochemistry of the nitrogen of the central pyridyl ring was assigned on the basis of ^{13}C NMR analysis. The ^{13}C NMR spectrum of **HM-A5** contains two diagnostic doublets at 153.0 and 142.3 ppm, a product of ^3J [13]C$-$[31]P coupling, corresponding to two of the three pyridyl protons. Only the **HM-A5** regioisomer shown in Scheme 1 is consistent with this pattern. This observation is consistent with the literature report indicating that the Grignard methathesis takes place preferentially at the 5-position of the 2,5-dibromopyridine.[11] **HM-A6**, a derivative of **HM-A5** containing a diphenylamine group in place of the carbazole moiety, was synthesized via a copper-catalyzed N-amination of compound **2** in the presence of diphenylamine to afford the intermediate **4** in good yield. Subsequent oxidation using H_2O_2 affords **HM-A6** in excellent yield. Both **HM-A5** and **HM-A6** were purified by column chromatography, followed by multiple gradient sublimations to obtain high purity materials.

Synthesis of the more challenging p-chiral phosphine oxide based hosts **HM-A4** and **HM-A8** was achieved via Grignard metathesis of 3-bromopyridine **6** using i-PrMgCl followed by reaction with an excess (2 equiv) of dichlorophenylphosphine (Scheme 2). This was performed so as to obtain 1 equiv of the monosubstituted chlorophenyl(3-pyridyl)phosphine. Subsequent reaction of this product with 4-bromophenyllithium affords the

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desired chiral phosphine and 2 equiv of bis(4-bromophenyl)phenylphosphine as a byproduct. The chiral phosphine was oxidized using H_2O_2 to afford compound **7**. **HM-A4** was obtained from compound **7** via copper-catalyzed *N*-arylation using conditions similar to those for **HM-A5**. Synthesis of **HM-A8** is analogous to that of **HM-A4**, starting with Grignard metathesis followed by reaction with chlorodiphenylphosphine to provide an intermediate which is then reacted with 2 equiv of (4-(diphenylamino)phenyl)lithium to give the intermediate *N,N*-diphenyl-4-(phenyl(pyridin-3-yl)phosphino)aniline. This intermediate was partially purified by column chromatography to remove the byproduct 4,4′-(phenylphosphinediyl)bis(*N,N*-diphenylaniline). Oxidation of this crude intermediate using hydrogen peroxide followed by chromatographic purification affords **HM-A8** in modest yields.

Having successfully synthesized the host materials, electrochemical characterization was performed in order to estimate the energies of highest occupied molecular orbital (HOMO) and LUMO levels. Knowledge of HOMO/LUMO energy levels of OLED materials is important as they may affect the charge injection from adjacent layers. It is established that there exists a correlation between the HOMO/LUMO energy levels derived from direct methods such as ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) and much simpler solution-based electrochemical methods.[12] In this work, we measured the oxidation and reduction potentials of all of the materials in solution and used these electrochemical values to estimate the orbital energies based on the published protocols.[12a,13] The oxidation and reduction potentials, E_{HOMO} and E_{LUMO} values derived from cyclic voltammetry, and the experimentally obtained triplet energy (E_T) values for the hosts are shown in Table 1.

Table 1. Solution Oxidation and Reduction Potentials, Electrochemistry-Based Frontier Orbital Energies, and Triplet Energies Obtained from Low Temperature Delayed Luminescence Spectra

	E_{ox}, V	E_{red}, V	E_{HOMO},[a] eV	E_{LUMO},[b] eV	E_T,[c] eV
HM-A1	0.71	−2.91	−5.59	−2.56	2.80
PO12	0.96	−2.85	−5.94	−2.52	2.84
HM-A4	0.89	−2.69	−5.85	−2.78	2.99
HM-A5	0.96	−2.56	−5.94	−2.91	2.99
HM-A6	0.80	−2.80	−5.72	−2.68	2.80
HM-A8	0.65	−2.78	−5.51	−2.69	2.82
PO15	n/a[d]	−2.61	−6.55[e]	−2.86	3.10

[a] Calculated from the oxidation potential using the equation $E_{HOMO} = -1.4E_{ox} - 4.6$ eV according to ref 12a unless stated otherwise. [b] Calculated from reduction potentials using a bicarbazole biphenyl (CBP) LUMO as a reference, as described in ref 13. [c] Estimated from the photoluminescence of frozen dichloromethane solutions at 77 K. [d] Outside the solvent window. [e] Estimated from the optical gap using the onset of the absorption spectrum.

Geometry optimization was carried out using PNNL's *NWChem* package at the B3LYP/6-31G* level to extract theoretical electronic properties and correlate with experimental trends. The HOMO of the host molecules are predominantly localized on the TPA or carbazole fragments which are responsible for the hole transport. The LUMO is localized on the lowest energy aryl group around the P=O moiety (see the Supporting Information). For nonpyridine-containing hosts **PO12** and **HM-A1**, the LUMO state is localized on the bridging phenyl group, whereas for pyridine-containing hosts the LUMO is localized on the pyridine. The E_{LUMO}'s of the pyridine-containing hosts are deeper than those of the aryl-bridged hosts as a consequence of the electronegative nature of the pyridine moiety (Table 1). The HOMO levels of the hosts are determined by the hole transport moiety (HTm). As a result, changes in the electron-transporting moiety have a minor effect on the HOMO levels of the molecules.

Charge balance in an OLED, particularly in the light-emitting region of the organic stack, strongly influences the quantum efficiency of the emitting device.[14] Our chemistry approach based on functionalization of host materials with charge-transporting groups allows for the control of charge transport and charge balance in the emissive zone of an OLED. A method to determine whether the host material provides ambipolar charge transport or is predominantly hole- or electron-conductive is to monitor the emission zone in an operating device. The location of the emission zone during device operation correlates with the charge-transport character of the host materials.[15] For a host with ambipolar character, the emission zone is expected to be broad with the maximum emission coming from the bulk of the emissive layer (EML). On the other hand, if a given host preferentially transports one sign of carriers, then the emission zone is narrowed and moved to the interface of the EML with the opposite sign charge transporting layer, as depicted in Figure 2. On the basis of the location of the
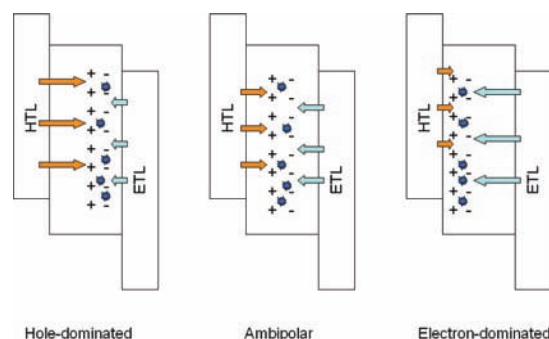

Figure 2. Schematic representation of the organic layers of OLEDs in which a host material possesses different degrees of charge balance.

maximum emission region, conclusions can be drawn regarding the charge transport in a given host material. We examined the

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shifts in the OLED emission region as a function of the host material chemical structure and categorized the hosts on the basis of their charge-transport type. The results are summarized in Table 2.

Table 2. Charge-Transport Character of the Emissive Layer of Blue OLEDs Based on Phosphine Oxide Host Materials Augmented by Different Functional Groups[a]

	functionality	charge transport character
HM-A1	TPA, no py	hole-dominant
HM-A6	TPA + py bridge	electron-dominant
HM-A8	TPA + py in outer position	ambipolar
PO12	CBz, no py	ambipolar to electron-dominant
HM-A5	CBz + py bridge	electron-dominant
HM-A4	CBz + py in outer position	electron-dominant

[a] "py" is pyridine, "TPA" is triphenylamine, and "CBz" is carbazole.

It can be seen from Table 2 how a minor chemical modification in the host determines the preference for hole or electron transport in the emissive layer of an operating OLED. Replacement of a phenyl linkage with a pyridine in both **PO12** and **HM-A1** results in an increase in electron transport, which induces a shift of the emission zone toward the HTL interface (compare **HM-A5** with **PO12**). When the charge transport in **HM-A1** and **PO12**-based devices is compared, it can be seen that **HM-A1** is hole-dominant, and **PO12** is mostly ambipolar with a slight preference for electron transport. When a pyridine bridge is placed between the phosphine oxide and TPA/CBz moieties instead of a simple phenyl bridge (compounds **HM-A6** and **HM-A5**), we see that the pyridine moiety overwhelms hole transport for either a TPA or CBz group, resulting in materials that, overall, are electron-transporting. When the pyridine ring is moved from between the phosphine oxide and TPA/CBz group and affixed to the phosphine oxide at an outer position (compounds **HM-A8** and **HM-A4**), the result depends on the HTm in the host molecule. For the TPA-containing **HM-A8**, the charge-transport character shifts from electron-

dominated to balanced ambipolar compared to the electron-dominant **HM-A6**. However, **HM-A4** and **HM-A5** both exhibit electron-dominated transport characteristics. This observation demonstrates that the location of the pyridine ring in an HM-Ax structure has a greater influence on charge transport when a TPA moiety is present than when a CBz moiety is present.

In summary, slight but distinct structural changes were incorporated into host design to study the impact of structural modification on carrier-transport properties. We have reported the synthesis of host materials (**HM-A4**, **HM-A5**, **HM-A6**, and **HM-A8**) as well as their corresponding electrochemical properties. The syntheses utilize known, well established methods. More importantly, from emission zone location data we identified differences in transport properties of host materials described herein. Compounds **HM-A4**, **HM-A5**, and **HM-A6** show preference for electron transport, while **HM-A8** shows ambipolar characteristics. The electronic changes associated with structural modification of the host materials have a significant effect on the charge transport properties of the hosts in an OLED and allow for the control of the charge balance.

Supporting Information Available: ^{1}H, ^{13}C, and ^{31}P NMR spectra for all novel compounds, orbital density maps, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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