A new class of non-conjugated bipolar hybrid hosts for phosphorescent organic light-emitting diodes†

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Comprising hole- and electron-transporting moieties with flexible linkages, representative non-conjugated bipolar hybrids have been synthesized and characterized for a demonstration of their potential use as host materials for the fabrication of phosphorescent organic light-emitting diodes. The advantages of this material class include solution processing into amorphous films with elevated glass transition temperatures, stability against phase separation and crystallization, and provision of LUMO/HOMO levels and triplet energies contributed by the two independent moieties without constraint by the electrochemical energy gap. While exciplex formation between the hole- and electron-transporting moieties is inevitable, its adverse effects on spectral purity and device efficiency can be avoided by trapping charges on triplet emitters, as demonstrated for Ir(mppy)3 in TRZ-3Cz(MP)2 and TRZ-1Cz(MP)2. With these two bipolar hybrids and hole-transporting Cz(MP)2 as the host, the maximum current efficiency of the bilayer PhOLED is achieved with TRZ-3Cz(MP)2, but the driving voltage decreases monotonically with an increasing TRZ content.

Introduction

Since the invention of relatively efficient fluorescent organic light-emitting diodes (OLEDs) in 1987, a new generation of flat-panel displays has emerged with a potential for capturing a substantial market share of consumable electronics, such as television sets and computer monitors. While full-color OLED displays require the emission of blue, green and red light, white OLEDs are potentially useful for efficient and inexpensive solid-state lighting and as backlights for liquid crystal displays.2–4 Compared to molecular materials that can be vacuum-deposited into thin films, solution-processable materials, such as π-conjugated polymers and monodisperse oligomers, offer cost advantage and ease of scale-up to large-area thin films. Fluorescence or phosphorescence is responsible for light emission from organic luminophores. Electrophosphorescence is superior to electroluminescence in terms of readily accessible internal quantum yield, 100 versus 25%. Despite the intensive efforts worldwide over the past decade, device efficiency and lifetime have remained critical issues. For the fabrication of an efficient phosphorescent OLED, a triplet emitter is typically doped in a host material with sufficiently high triplet energy, $E_T$, to realize blue, green or red emission.5–8 A higher $E_T$ of the host than the guest ensures exciton transfer from the former to the latter where light emission occurs. In cases where the triplet emitters serve as charge traps, exciton formation is expected at the emitter without back-transfer to the host because of the higher $E_T$ of the latter. Compared to exciton transfer from the host, charge trapping on the emitter as the source of phosphorescence is advantageous in terms of the higher internal quantum yield, $\eta$, less concentration quenching because of the lower doping level,9–11 and the emission spectrum solely from the emitter,11,12 albeit at the higher driving voltage.13

Most of the existing triplet host materials are capable of preferentially transporting holes or electrons.7,13,14 Charge injection and transport layers are added between electrodes and the emitting layer as needed to improve efficiency.5–8,13,15 Nevertheless, charge recombination tends to occur close to the interface with the charge-transport layer for lack of bipolar transport capability in general of the emitting layer.16,17 Under a high current density pertaining to practical application, confinement of excitons to the interfacial region could expedite triplet-triplet annihilation, resulting in efficiency roll-off.16–21 Furthermore, a narrow recombination zone is detrimental to operational stability because only a fraction of molecules contribute to charge transport, exciton formation, and light emission.22–24 To substantially improve device efficiency and lifetime, it is imperative that excitons be evenly distributed through the emitting layer and that the accumulation of charges and excitons at interfaces be prevented. To this effect, it has been demonstrated that mixed hosts can effectively decrease driving voltage while improving device efficiency sustainable at high current densities.11,12,25–30 A typical phosphorescent layer is comprised of a host mixed with a charge-transport component at 25 to 50 wt%, to which 1 to 10 wt% of a triplet emitter is doped. The desired bipolar transport capability entails a high concentration of the charge-transport additive, at which doping level phase separation is destined to take place over time unless miscibility has been taken into account in the design of both components, thus adversely affecting long-term operational stability of OLEDs. Bipolar charge-transport host materials via...
chemical modification represent a viable approach to circumventing the potential phase-separation problem. A bipolar compound can be constructed by chemically bonding an electron- and a hole-transport moiety with and without a finite extent of π-conjugation between the two moieties, resulting in conjugated and non-conjugated bipolar compounds, respectively. For all the conjugated bipolar host materials that have been developed for full-color emission,31–40 few non-conjugated bipolar compounds have been reported,41,42 of which none carry a flexible linkage consisting of σ-bonds between the two moieties. Conjugated and non-conjugated bipolar hybrid molecules without a flexible linkage tend to be rigid and bulky, thus limiting solubility and the ability to form morphologically stable glassy films. This study aims at a new class of non-conjugated bipolar hybrids comprising aliphatic linkages between the two charge-transport moieties. Representative compounds have been synthesized and characterized to assess their potential for use as hosts for triplet emitters. Furthermore, the ability of bipolar hybrid hosts to modulate charge injection into and transport through the emitting layer has been unraveled through the fabrication and characterization of PhOLEDs.

Results and discussion

In addition to precluding phase separation, the flexible linkages connecting the two charge-transport moieties in the non-conjugated bipolar hybrid molecules serve to increase entropy because of the more abundant conformations, which is conducive to solubility in benign solvents to facilitate materials purification and solution processing. Furthermore, the increased entropy with flexible linkages presents a higher free energy barrier to crystallization from a glassy state, thereby improving morphological stability against crystallization over relatively rigid conjugated and non-conjugated bipolar hybrid molecules without flexible linkages. Depicted in Chart 1 are three representative non-conjugated bipolar hybrid compounds with propylene linkages, TRZ-1Cz(MP)2, TRZ-3Cz(MP)2, and OXD-2Cz(MP)2 that were synthesized for an investigation of their thermal, morphological, electrochemical, fluorescence, and phosphorescence properties. These hybrid compounds consist of a hole-transport Cz(MP)243–45 and an electron-transport TRZ46–49 or OXD.27,30,49,50

The results from thermogravimetric analysis compiled in Fig. 1 reveal their thermal stability to 400 °C at about 5 wt% weight loss. Solid morphologies of the three independent building blocks, three bipolar compounds, and their corresponding mixtures, TRZ:1Cz(MP)2, TRZ:3Cz(MP)2, and OXD:2Cz(MP)2, were characterized by differential scanning calorimetry and hot-stage polarizing optical microscopy. The DSC thermograms compiled in Fig. 2 indicate that the building blocks and their mixtures are crystalline, semicrystalline or amorphous with a glass transition temperature, \( T_g \), below 65 °C, while all the hybrid compounds are amorphous with a \( T_g \) near or above 100 °C.

![Fig. 1](image)

**Fig. 1** TGA thermograms of hybrid compounds recorded at a heating rate of 10 °C/min under nitrogen atmosphere. The decomposition temperatures at a weight loss of 5% are 399, 403 and 407 °C for TRZ-1Cz(MP)2, TRZ-3Cz(MP)2 and OXD-2Cz(MP)2, respectively.

**Chart 1** Representative non-conjugated bipolar compounds as well as independent electron- and hole-transport moieties with their thermal transition temperatures determined by DSC heating scans shown in Fig. 2 below. Symbols: G, glassy; K, crystalline; I, isotropic.
The amorphous OXD:2Cz(MP)₂ mixture observed under differential scanning calorimetry and polarizing optical microscopy was further evaluated for phase separation via thermal annealing at 32 °C for 3 days. While the pristine, spin-cast film of OXD:2Cz(MP)₂ was amorphous under polarizing optical microscopy (Fig. 3a), phase separation and/or crystallization occurred upon thermal annealing at 32 °C for 3 days (Fig. 3b). The thermally annealed film was further characterized by polarizing optical microscopy to yield melting points at 150 and 185 °C, which fall between the melting points of Cz(MP)₂ (144 °C) and OXD (240 °C) also determined by polarizing optical microscopy for spin-cast films left at room temperature for 2 to 3 days. These results suggest a complex phase behavior of the OXD:2Cz(MP)₂ mixture. As shown in Fig. 3c, the amorphous character persisted in the OXD-2Cz(MP)₂ film upon thermal annealing at 100 °C, i.e. the same reduced temperature and annealing time as for OXD:2Cz(MP)₂, indicating that the hybrid compound is not vulnerable to phase separation and that it is resistant to thermally activated crystallization. Poly(N-vinylcarbazole), PVK, mixed with OXD at a 70:30 mass ratio was employed as the host for iridium(III) bis[2-(4,6-difluorophenyl)-pyridinato-N,C₂]0 picolinate (FIrpic). The pristine, spin-cast film of this bipolar host material was found to be amorphous with the same optical micrograph as shown in Fig. 3a or c, but phase separation and/or crystallization emerged in Fig. 3d upon thermal annealing at 100 °C for 3 days. Moreover, the crystallites observed under polarizing optical microscopy were found to melt at 230 °C, close to the melting point of OXD.

The electrochemical properties of the non-conjugated bipolar compounds and their building blocks are characterized by cyclic voltammetry. The oxidation and reduction scans are shown in Fig. 4, illustrating that the oxidation and reduction scans of the hybrids are represented by the composites of those of their constituent hole- and electron-transport moieties. The key data summarized in Table 1 indicates that the HOMO levels of TRZ-1Cz(MP)₂, TRZ-3Cz(MP)₂ and OXD-2Cz(MP)₂ are placed at −5.2 eV, a value identical to that of the hole-transporting Cz(MP)₂. The LUMO levels of −2.6 eV for TRZ-1Cz(MP)₂ and TRZ-3Cz(MP)₂, and −2.5 eV for OXD-2Cz(MP)₂, are also equal within error to those of the electron-transporting TRZ and OXD, respectively. With a HOMO level at −5.2 eV, which is close to the work function of PEDOT:PSS at 5.1 eV, and a LUMO level at −2.5 to −2.6 eV, which is relatively close to the work function of LiF/Al at 2.9 eV, these non-conjugated bipolar compounds are expected to facilitate hole and electron injection in phosphorescent OLED devices. With an interruption of π-conjugation between the two moieties by a propylene linkage, the HOMO and LUMO levels of non-conjugated bipolar hybrid compounds are essentially imported from those of the hole- and electron-transport moieties as independent chemical entities. The
Table 1  Electrochemical properties of compounds determined by the oxidation and reduction scans presented in Fig. 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}^{\text{red}}$ (V)</th>
<th>$E_{1/2}^{\text{oxd}}$ (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRZ</td>
<td>-1.67</td>
<td>-1.86</td>
<td>-4.86</td>
<td>-1.97</td>
</tr>
<tr>
<td>OXD</td>
<td>-0.92</td>
<td>-0.89</td>
<td>-4.85</td>
<td>-1.80</td>
</tr>
<tr>
<td>TRZ:1Cz(MP)2</td>
<td>-1.86</td>
<td>-1.72</td>
<td>-4.44</td>
<td>-1.92</td>
</tr>
<tr>
<td>Cz(MP)2</td>
<td>-1.83</td>
<td>-1.83</td>
<td>-4.44</td>
<td>-1.83</td>
</tr>
</tbody>
</table>

$E_{1/2}$ and $E_{1/2}^{\text{oxd}}$ were determined as the average of forward and reverse reduction or oxidation peaks. Calculated with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte.

Half-wave potentials, $E_{1/2}^{\text{red}}$ determined as the average of forward and reverse reduction or oxidation peaks. Calculated with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte.

HOMO and LUMO levels in conjugated bipolar hybrid compounds, however, are generally affected by the finite extent of σ-conjugation between the two moieties.

In addition to phase separation detected by microscopy (see Fig. 3), fluorescence spectroscopy was employed to uncover molecular aggregation in non-conjugated bipolar compounds and their equivalent mixtures. To facilitate data interpretation, TRZ:1Cz(MP)2 was used along with TRZ:1Cz(MP)2 based on the facts that TRZ was found to be essentially nonemissive and that OXD showed fluorescence in the 400 to 450 nm region largely overlapping with that of Cz(MP)2. Approximately 45 nm-thick amorphous films of TRZ:1Cz(MP)2, TRZ:1Cz(MP)2, and Cz(MP)2 prepared by spin-coating from chlorobenzene were photoexcited at 360 nm, and their fluorescence spectra normalized with film thickness are presented in Fig. 5. The pristine TRZ:1Cz(MP)2 and TRZ:1Cz(MP)2 films exhibited similar fluorescence in the same spectral range from 450 to 600 nm, representing a red-shift from that of Cz(MP)2 by about 90 nm. These broad and red-shifted fluorescence peaks at 2.4 eV originated from exciplex formation between TRZ and Cz(MP)2 moieties in the hybrid compound and their equimolar mixture, as expected of the offset between the HOMO level of Cz(MP)2 and the LUMO level of TRZ in addition to the Coulomb attraction energy. The lower fluorescence intensity from the pristine film of TRZ:1Cz(MP)2 than that of TRZ:1Cz(MP)2 could have arisen from the less extent of inter- and/or intra-molecular exciplex formation in the former caused by steric hindrance in the presence of a propylene spacer. Thermal annealing of the TRZ:1Cz(MP)2 film at 20 °C above its $T_g$ for ½ h did not result in any change in the amorphous character and the fluorescence spectrum. Upon thermal annealing under the same condition, poly-crystalline domains emerged from the pristine TRZ:1Cz(MP)2 film with a melting point at 178 °C, which is distinct from those of TRZ and Cz(MP)2 at 242 and 144 °C, respectively as noted above. The polarizing optical micrographs of thermally annealed TRZ:1Cz(MP)2 and TRZ:1Cz(MP)2 films are displayed in Fig. S1 (ESI†). As shown in Fig. 5, phase separation accompanied by crystallization led to much reduced, blue-shifted exciplex emission as well as weak emission between 400 and 450 nm attributable to Cz(MP)2. Thus, the hybrid compound is preferable over its equivalent mixture from the standpoint of morphological stability, but the issue of exciplex formation in both material systems must be addressed. Whereas exciplex emission involving bipolar mixed hosts is frequently observed in phospholuminescence where triplet emitters serve as charge traps with improved device efficiencies at lower driving voltages compared to the constituent unipolar hosts. To ensure effective charge trapping on the emitter, its LUMO level must be lower than that of the electron-transport component, while its HOMO level must be higher than that of the hole-transport component, an idea to be incorporated in the design of non-conjugated bipolar hybrid compounds.

The absorption spectra of Cz(MP)2, OXD, and OXD-2Cz(MP)2 at 10⁻⁷ to 10⁻⁶ M in chloroform are presented in Fig. 6a, serving to identify selective photoexcitation wavelengths for the determination of their lowest triplet energies, $E_T$, to within ±0.02 eV through phosphorescence measurements. Phosphorescence spectra were obtained for Cz(MP)2, OXD, and OXD-2Cz(MP)2 at 10⁻⁴ M in ethyl acetate at −196 °C (or 77 K).
As illustrated in Fig. 6b, Cz(MP)2 shows a 0,0-phosphorescence band corresponding to an $E_T$ at 2.77 eV upon excitation at 360 nm. The OXD moiety shows only very weak phosphorescence due largely to inefficient intersystem crossing. Thus, butyl iodide was added at 10 wt% to the OXD and OXD-2Cz(MP)2 solutions to enhance phosphorescence, particularly the 0,0-vibronic transition, and to help confirm the identity of the emitting state. With photoexcitation at 332 nm, the relatively sharp highest-energy 0,0-vibronic band shown in Fig. 6c establishes an $E_T$ of 2.71 eV for OXD. When the hybrid compound OXD-2Cz(MP)2 is excited at 360 nm (Fig. 6d), its phosphorescence spectrum is identical to that of OXD (Fig. 6c) even though OXD is not excited at 360 nm. These results indicate highly efficient triplet energy transfer from Cz(MP)2 ($E_T = 2.77$ eV) to OXD ($E_T = 2.71$ eV) in OXD-2Cz(MP)2 and further suggest that the two moieties retain their energy levels as independent entities and that the effective $E_T$ of the hybrid equals that of the lower-$E_T$ moiety due to efficient intramolecular triplet energy transfer. Phosphorescence spectra were also collected for TRZ and TRZ-3Cz(MP)2 to arrive at $E_T = 3.03$ and 2.75 eV, respectively, an observation also consistent with highly efficient triplet energy transfer from TRZ to the lower energy Cz(MP)2 moiety. Furthermore, the $E_T$ value of a non-conjugated bipolar hybrid compound is determined by the lower value of the two independent moieties. The $E_T$ value of a conjugated bipolar compound, however, is consistently less than those of the two independent moieties because of the finite $\pi$-conjugation between them. 29,31,54

Let us proceed to assess yet another merit of non-conjugated bipolar compounds compared to their conjugated counterparts. In a conjugated bipolar compound, the $E_T$ value is consistently less than $E_G$, the LUMO–HOMO energy gap, 31–40 by the sum of singlet–triplet splitting, $\Delta_{ST}$, 55 and exciton binding energy, $E_B$. 56

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**Fig. 4** Cyclic voltammetric scans of compounds in acetonitrile/toluene (1:1 by volume) at $10^{-3}$ M with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte.

**Fig. 5** Fluorescence spectra with excitation at 360 nm of approximately 45 nm-thick, spin-cast films of Cz(MP)2, TRZ-1Cz(MP)2, and TRZ-1Cz(MP)2; thermal annealing was performed at 20°C above $T_g$ under argon for ½ h.

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**Fig. 6** (a) UV-vis absorption spectra in molecular extinction coefficients, $\varepsilon$, of OXD-2Cz(MP)2, Cz(MP)2 and OXD. Phosphorescence spectra of (b) Cz(MP)2, (c) OXD, and (d) OXD-2Cz(MP)2 at 77 K in ethyl acetate at $10^{-4}$ M, for which the $E_T$ values were determined by the 0–0 transitions as indicated by arrows.
For example, CzOXD has its HOMO/LUMO levels at −5.6/−2.4 eV based on the reported half-wave potentials with an $E_T$ at 2.5 eV, which is 0.7 eV less than $E_G$ (see Fig. 7a).

On the other hand, the $E_T$ value of a non-conjugated bipolar compound, such as TRZ-1Cz(MP)2, is not limited by its $E_G$. The oxidation potentials of TRZ and OXD and the reduction potential of Cz(MP)2 are beyond our CV measurement range. Their optical bandgaps were estimated at the onset of their absorption spectra in dilute solutions to yield HOMO levels at −6.7 and −6.2 eV for TRZ and OXD, respectively, and LUMO level at −1.8 eV for Cz(MP)2. As shown in Fig. 7b, the $E_T$s of independent electron- and hole-transport moieties are less than their respective $E_G$s as in a typical conjugated system. The Cz(MP)2 moiety is characterized by an $E_T$ and HOMO/LUMO levels at 2.8 eV, and −5.2/−1.8 eV, respectively, while the TRZ moiety carries an $E_T$ and HOMO/LUMO levels at 3.0 eV, and −6.7/−2.6 eV, respectively (see Fig. 7b). The hybrid TRZ-1Cz(MP)2 has an $E_T$ at 2.8 eV, as verified by low temperature phosphorescence spectroscopy, and HOMO/LUMO levels at −5.2/−2.6 eV by cyclic voltammetry. In contrast to CzOXD, TRZ-1Cz(MP)2 has an $E_T$ greater than its $E_G$ and its HOMO/ LUMO levels corresponding to the hole- and electron-transport moieties without modification in the absence of inter-moiety conjugation. The caveat here is that the $E_T$s of both the electron- and hole-transport moieties must be greater than the hybrid’s $E_G$ to arrive at a non-conjugated bipolar compound with an $E_T$ greater than its $E_G$, as is also applicable to TRZ-3Cz(MP)2 and OXD-2Cz(MP)2.

Bipolar hybrid TRZ-3Cz(MP)2 and TRZ-1Cz(MP)2 and hole-transporting Cz(MP)2 were employed as hosts for the fabrication of bilayer phosphorescent OLEDs in the device architecture, ITO/ MoO$_3$(10 nm)/emitting layer(40–50 nm)/1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI)(30 nm)/CsF(1 nm)/Al(100 nm).

Prepared by spin casting, the emitting layer consisted of a host doped with green-emitting tris(2-(p-methylphenyl)pyridine)iridium, Ir(mppy)$_3$ at a 10:1 mass ratio. While MoO$_3$ and CsF were applied as the hole- and electron-injection layers, respectively, TPBI was applied as the electron-transporting and hole-blocking layer. A typical electroluminescence spectrum is shown as the inset in Fig. 8a, consistent with the triplet emission of Ir(mppy)$_3$, suggesting effective confinement of triplet excitons on the emitter. This is expected of the higher $E_T$s of all three hosts than that of Ir(mppy)$_3$, 2.8 eV for Cz(MP)2 over 2.4 eV for Ir(mppy)$_3$. Furthermore, Ir(mppy)$_3$ has a HOMO level at −5.0 eV, 0.2 eV higher than those of the hosts, thus serving as a hole trap to preclude exciplex formation between the TRZ and Cz(MP)2 moieties.

It is also shown in Fig. 8a that driving voltage decreases with an increasing TRZ content in the hybrid hosts, suggesting improved electron injection from the adjacent TPBI into the emitting layer. Current efficiency and luminance as functions of driving voltage for phosphorescent OLEDs with emitting layers comprising Cz(MP)2, TRZ-3Cz(MP)2, and TRZ-1Cz(MP)2 doped with Ir(mppy)$_3$ at a 10:1 mass ratio. Inset: electroluminescence (EL) spectrum with TRZ-3Cz(MP)2 as the host. (b) Luminance and current efficiency as functions of current density for the same phosphorescent OLEDs as described in (a).
current density are shown in Fig. 8b. Compared to Cz(MP)2, the higher efficiency with TRZ-3Cz(MP)2 as the host is attributable to the more balanced electron and hole fluxes through the emitting layer, which leads to the more efficient electron-hole recombination. Furthermore, the presence of electron-transporting TRZ in TRZ-3Cz(MP)2 generates a broader charge recombination zone to alleviate efficiency roll-off at high current densities. As shown in Fig. 8b, at the current density of 0.5 mA/cm², the device with Cz(MP)2 as the host has a luminance of 105 cd/m², corresponding to current efficiency of 21 cd/A and external quantum efficiency of 5.9%, which diminish to 5.4 cd/A and 1.5% at 100 mA/cm², respectively, representing a 74% loss in efficiency. In contrast, at the current density of 0.5 mA/cm², the device with TRZ-3Cz(MP)2 as the host has a luminance of 160 cd/m², corresponding to current efficiency of 32 cd/A and external quantum efficiency of 9.2%, which roll off to 16.8 cd/A and 4.9% at 100 mA/cm², respectively, representing a 47% loss in efficiency. The efficiencies achieved with TRZ-3Cz(MP)2 as the host are among the best of solution-processed phosphorescent OLEDs using bipolar hosts.\textsuperscript{12,13,34,61} Implemented in more sophisticated device architectures, optimum non-conjugated bipolar hybrids can be expected to yield much higher efficiencies than the bilayer device architecture as presently reported. With a further increase in the TRZ content, however, TRZ-1Cz(MP)2 resulted in current efficiencies comparable to those with Cz(MP)2 as the host, presumably because of exciton quenching by MoO₃ as the recombination zone is shifted toward the anode at an increased electron transport.\textsuperscript{58} The results obtained to date have demonstrated the potential of non-conjugated bipolar hybrid hosts with flexible linkages for substantially improving PhOLED device performance through optimization of change injection into and transport through the emitting layer.

Experimental section

Material synthesis and characterization

\textsuperscript{1}H NMR spectra were acquired in CDCl₃ with an Avance-400 spectrometer (400 MHz) at 298 K using trimethylsilane (TMS) as an internal standard. Elemental analysis was carried out by Quantitative Technologies, Inc. Molecular weights were measured with a ToFSpec2E MALDI/TOF mass spectrometer (Micromass, Inc., Manchester, U.K.) with 2-[2(E)-3-(4-tert-butylphenyl)-2-methylpropenylidene]malononitrile (DCTB) as the matrix. The target compounds were synthesized and purified according to Scheme 1 following the procedures described in the ESI.\textsuperscript{†}

Morphology, thermal stability, and phase transition temperatures

Thermogravimetric analysis was performed in a TGA/DSC system (SDT Q600, TA Instruments) at a ramping rate of 10 °C/min under a nitrogen flow of 50 ml/min. Thermal transition temperatures were determined by differential scanning calorimetry (Perkin-Elmer DSC-7) with a continuous N₂ purge at 20 ml/min. Samples were preheated to above Tₘ and then cooled down to −30 °C at −100 °C/min before the reported second heating and cooling scans were recorded at 20 °C/min. The nature of phase transition was characterized by hot-stage polarizing optical microscopy (DMLM, Leica, FP90 central processor and F882 hotstage, Mettler Toledo). Absorption spectra of dilute solutions in chloroform at a concentration of 10⁻⁷ to 10⁻⁶ M were acquired on a UV-vis-NIR spectrophotometer (Lambda–900, Perkin-Elmer).

Electrochemical characterization

Cyclic voltammetry was conducted on an EC-Epsilon potentiostat (Bioanalytical Systems Inc.) at a concentration of 10⁻³ M in acetonitrile/toluene (1:1 by volume) containing 0.1 M tetraethylammonium tetrafluoroborate as the supporting electrolyte. A silver/silver chloride (Ag/AgCl) wire, a platinum wire, and a glassy carbon disk (3 mm diameter) were used as the reference, counter, and working electrodes, respectively, to complete a standard 3-electrode cell. The supporting electrolyte was purified as described previously,\textsuperscript{59} and the solvents acetonitrile and toluene were distilled over calcium hydride and sodium/benzophenone, respectively. The dilute sample solutions in acetonitrile/toluene (1:1 by volume) exhibit reversible reduction and oxidation waves against the Ag/AgCl reference electrode. The reduction and oxidation potentials were adjusted to ferrocene serving as an internal standard with an oxidation potential of 0.51 ± 0.02 V over Ag/AgCl. The resultant reduction and oxidation potentials, E₁/₂(red) and E₁/₂(oxd), relative to (Fc/Fc⁺) were used to calculate the LUMO and HOMO levels as −4.8eV − qE₁/₂(red) and −4.8eV − qE₁/₂(oxd), respectively, where q is the electron charge.\textsuperscript{60,61}

Triplet energy measurement

Phosphorescence spectra were gathered using a Fluorolog-3 spectrofluorimeter (Jobin Yvon, Horiba) and were corrected for the efficiency of the monochromator and the spectral response of the photomultiplier tube. Samples (10⁻⁴ M) were dissolved in ethyl acetate in NMR tubes and inserted into a small liquid nitrogen Dewar to measure the phosphorescence spectra at 77 K. As has been customary,\textsuperscript{54,62} the maximum of highest-energy 0–0 vibronic band in the phosphorescence spectrum was assigned as the energy of the lowest triplet state. Phosphorescence measurements were also carried out with 10% butyl iodide added to the ethyl acetate to enhance the 0–0 vibronic transition\textsuperscript{63} and to help differentiate between phosphorescence and fluorescence.

Thin film preparation and characterization

Films of hybrid compounds and mixtures were prepared by spin coating from 2 wt% chlorobenzene solutions at 2500 rpm on microscope glass slides followed by drying under vacuum overnight. The thicknesses of the resultant films were determined by optical interferometry ( Zygo New Views 5000). Thermal annealing was performed under argon at elevated temperatures. The film morphology, including melting points where applicable, was characterized by hot-stage polarizing optical microscopy. Photoluminescence was characterized using a spectrofluorimeter (Quanta Master C-60SE, Photon Technology International) with a liquid light guide directing excitation at 360 nm onto the sample film at normal incidence.
Phosphorescent OLED device fabrication and characterization

Glass substrates coated with patterned ITO were thoroughly cleaned and treated with oxygen plasma prior to deposition of a 10 nm thick MoO₃ layer by thermal evaporation at 0.1 nm/s. The emitting layers comprising host:Ir(mppy)₃ at a mass ratio of 10:1 were then prepared by spin-coating from 2.0 wt% toluene solutions at 4000 rpm for 2 min in a nitrogen-filled glove box with oxygen level less than 1 ppm. The resultant film thickness was 40–50 nm determined by optical interferometry (Zygo NewView 5000). Layers of TPBI (30 nm) and CsF (1 nm) were then consecutively deposited at rates of 0.1 nm/s and 0.02 nm/s, respectively. The devices were completed by thermal evaporation of Al (100 nm) at 1 nm/s through a shadow mask to define an active area of 0.1 cm². All evaporation processes were carried out at a base pressure less than 4 × 10⁻⁶ Torr. All devices were encapsulated with cover glass and glue for characterization with a source-measure unit (Keithley 2400) and a spectroradiometer (PhotoResearch PR650). Only the front-view performance data were collected.

Summary

Potentially useful as the host materials for the fabrication of efficient and stable, single-layer phosphorescent OLEDs for information display and solid-state lighting, a new class of non-conjugated bipolar compounds have been synthesized and characterized for their thermal, morphological, electrochemical, fluorescence, and phosphorescence properties. Comprising hole- and electron-transport moieties chemically bonded by an aliphatic spacer, the potential of these materials has been demonstrated for solution processing and for the formation of thin films with elevated glass transition temperatures with superior stability against phase separation and thermally
activated crystallization. Because of the absence of π-conjugation between the two charge-carrier moieties, the LUMO/HOMO levels and the triplet energies of the two moieties as independent entities are retained in the resultant non-conjugated bipolar compounds. Furthermore, the flexibility in molecular design is enhanced by the fact that the triplet energy of a non-conjugated bipolar compound is not constrained by its electrochemical energy gap. Exciplex formation is inevitable in neat films between the hole- and electron-transport moieties, but its adverse effects on spectral purity and device efficiency can be prevented by having triplet emitters serve as charge traps. All these material traits are conducive to the optimization of properties for intended device applications. The current efficiencies of PhOLEDs consisting of Ir(mppy)3 doped in Cz(MP)2, TRZ-3Cz(MP)2, and TRZ-1Cz(MP)2 at an increasing TRZ content reach the maximum at 32 cd/A with TRZ-3Cz(MP)2, which is among the best of solution processed devices using bipolar hosts. The driving voltage, however, decreases monotonically with an increasing TRZ content, suggesting improved electron injection from the adjacent TPBI layer into the emitting layer.

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