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Improving lifetime of phosphorescent organic light-emitting diodes by using a non-conjugated hybrid host

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ABSTRACT

Three hybrid host materials, mCP-PhSiPh3, mCP-L-PhSiPh3, and *t*Bu-mCP-L-PhSiPh3, have been synthesized and characterized for their thermal, morphological, electrochemical, fluorescence, phosphorescence, and electroluminescence properties. The flexible spacer in mCP-L-PhSiPh3 and *t*Bu-mCP-L-PhSiPh3 makes them maintain high triplet energies at about 3.00 eV due to the interruption of π-conjugation. The introduction of the *tert*-butyl group at the electrochemically active C3 and C6 sites of the carbazole moiety greatly improves thermal and electrochemical stability of the host *t*Bu-mCP-L-PhSiPh3. Blue and green phosphorescent organic light-emitting diodes (PhOLEDs) based on the non-conjugated hosts exhibit external quantum efficiencies at around 15 and 21%, respectively. Higher current densities in PhOLEDs hosted by mCP-PhSiPh3 produce current leakage, resulting in lower efficiencies, especially in green PhOLEDs. The green PhOLEDs using non-conjugated hosts show improved device lifetime in comparison with the mCP-PhSiPh3 based PhOLED because of enhanced morphological stability. The operational stability of the *t*Bu-mCP-L-PhSiPh3 based device is further raised because of improved electrochemical stability by employing the *tert*-butyl group. Our results demonstrate that both the flexible linkage and the blocking of the electrochemically active sites are crucial measures to realize long-lived PhOLED devices.

1. Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) offer a bright future for the next generation flat-panel displays and solid-state lighting sources due to their high quantum efficiency compared with fluorescent OLEDs. The triplet emitter is preferably dispersed into a host at the molecular level to prevent concentration quenching. Host materials with sufficiently high triplet energies (E_Ts) used to prepare the emitting layer (EML), are crucial to triplet emitters for excitons to remain on dopant molecules, especially in blue PhOLEDs with adequate longevity, which have remained the main barrier to practical applications. To substantially improve device efficiency and lifetime simultaneously, it is imperative that excitons be evenly distributed through EML, and that the accumulation of charges and excitons at interfaces be prevented. The effective design strategy of host materials to achieve high and balanced electric flux is to bond electron-donating and electron-accepting moieties chemically into a single bipolar molecule. The capability of the bipolar hybrid hosts has been demonstrated for facilitating injection and transport of holes and electrons, broadening the recombination zone, and consequentially alleviating efficiency roll-off [1–4]. To attain sufficiently high E_T, so that the hosts are amenable to blue phosphors, π-conjugation between the electron- and hole-transport moieties should be minimized or prevented altogether through a large torsion angle [5], *meta*-or *ortho*-substitution [6], or insertion of an sp^3-hybridized C or Si atoms [7–10]. The host material comprising hole- and electron-transport moieties chemically bonded by an aliphatic spacer has been demonstrated to be the least susceptible to charge transfer complex formation compared to the hosts using the same transport moieties but with *para*- and *meta*-linkages, allowing accommodation of the most singlets and triplets following charge recombination [11]. More important, bipolar hybrid compounds with flexible linkages have been demonstrated for superior morphological stability against crystallization [7]. In our recent report, a mixed host, mCP:SiPh4 at a 1:1 M ratio, and its hybrid counterpart, mCP-L-PhSiPh3, are used to elucidate how thermally activated morphological changes in the EML may affect PhOLED performance [12].

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Compared to physical mixing, the concept of chemical hybrids with a flexible linkage holds promise for long-lived PhOLED devices by elevating glass transition temperatures while preventing crystallization of an amorphous EML. However, the unblocked active sites of C3 and C6 of carbazoles in mCP-L-PhSiPh3 could lead to problems with electrochemical stability [13,14], which may hurt the device lifetime since charge transport by organic semiconductors is intrinsically a repeated oxidation/reduction process.

In the present study, by substituting C3 and C6 positions of carbazoles with *tert*-butyl groups, a new mCP/SiPh4 hybrid host, namely *t*Bu-mCP-L-PhSiPh3, was designed and synthesized. Due to the introduction of the bulky *tert*-butyl group and the blocking of the electrochemically active sites, the new host is expected to have enhanced morphological stability and significantly improved electrochemical stability while retaining a large E_T value because of the non-conjugated spacer. Another new host material without the substituent group and the flexible spacer, mCP-PhSiPh3, was also prepared for comparison. In addition to the material property characterizations of the new hosts, the PhOLED device performance, especially the device lifetime, has been systematically investigated to illustrate our idea.

2. Experimental section

2.1. General information

All chemicals, reagents, and solvents were used as received from commercial sources without further purification. All reactions were carried out under nitrogen and anhydrous conditions unless noted otherwise. ^{1}H NMR (400 MHz) spectra were measured on a Bruker Avance spectrometer using $CDCl_3$ as a solvent and the spectral data were reported in ppm relative to tetramethylsilane (TMS) as an internal standard. Molecular weights were measured with a Brüker Autoflex III MALDI-TOF mass spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. UV–Vis absorption spectra were recorded on a Perkin-Elmer Lambda-900 spectrophotometer. PL spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer and phosphorescence spectra at 77 K were recorded on a Perkin-Elmer LS 50B spectrofluorometer. DSC was performed on a Perkin-Elmer DSC-7 differential scanning calorimetry with nitrogen flow at 20 mL/min. Samples were preheated to above their melting points, and then cooled down to −30 °C at −100 °C/min before the second heating and cooling scans were recorded at 20 °C/min. The T_g was determined from the second heating scan. TGA was undertaken with a TA instrument Q600 at a scanning rate of 10 °C/min under nitrogen. CV was conducted on an EC-Epsilon potentiostat (Bioanalytical Systems Inc.). A silver/silver chloride (Ag/AgCl) wire, a platinum wire, and a glassy carbon disk with a 3-mm diameter were used as the reference, counter, and working electrodes, respectively. Tetraethylammonium tetrafluoroborate was used as the supporting electrolyte. Samples were dissolved at a concentration of 10^{-3} M in acetonitrile/toluene (1:1 by volume) containing 0.1 M supporting electrolyte. CV was carried out at a scan rate of 100 mV/s.

2.2. Synthesis

2.2.1. Triphenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)silane (**2**)

n-BuLi (2.5 M in hexane, 1.27 mL, 3.2 mmol) was added dropwise into a solution of **1** (1.01 g, 2.4 mmol) in THF (30 mL) at −78 °C, where the mixture was stirred for 3 h before adding 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (0.91 g, 4.9 mmol) in one portion. The reaction mixture was allowed to warm up to room temperature over a period of 12 h, quenched with water, and then extracted with ether. The organic extracts were combined, washed with brine and water, and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate 19:1 (v/v) as the eluent to yield **2** (0.66 g, 58%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.81 (d, J = 7.5 Hz 2H), 7.59 (d, J = 7.5 Hz 2H), 7.57–7.54 (m, 6H), 7.46–7.41 (m, 3H), 7.39–7.35 (m, 6H), 1.35 (m, 12H).

2.2.2. 9,9′-(4′-(Triphenylsilyl)-[1,1′-biphenyl]-3,5-diyl)bis(9H-carbazole) (mCP-PhSiPh3)

Toluene (10 mL) and H_2O (6 mL) were added into a mixture of **2** (0.60 g, 1.30 mmol), **3** (0.69 g, 1.42 mmol), $Pd(PPh_3)_4$ (0.030 g, 0.026 mmol), and Na_2CO_3 (1.27 g, 12.00 mmol). The reaction mixture was stirred at 90 °C for 12 h, cooled to room temperature, and extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product was purified by gradient column chromatography on silica gel with hexane/chloroform 3:1 (v/v) to yield mCP-PhSiPh3 (0.50 g, 52%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.17–8.15 (d, J = 7.6 Hz 4H), 7.94 (s, 2H), 7.81–7.80 (d, J = 1.6 Hz 1H), 7.73–7.71 (m, 4H), 7.61–7.58 (m, 10H), 7.46–7.29 (m, 17H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.53, 140.65, 140.28, 139.92, 137.31, 136.46, 134.92, 133.96, 129.82, 128.05, 126.65, 126.30, 124.37, 123.99, 123.75, 120.57, 120.49, 109.82. LDI TOF MS m/z ([M]$^+$): 742.2. Anal. calcd for $C_{54}H_{38}N_2Si$ (%): C 87.29, H 5.16, N 3.77; found: C 87.20, H 5.02, N 3.64.

2.2.3. 9,9′-(5-(3-(4-(Triphenylsilyl)phenyl)propyl)-1,3-phenylene) bis(3,6-di-tert-butyl-9H-carbazole) (tBu-mCP-L-PhSiPh3)

9-BBN (0.5 M in THF, 10.0 mL, 5.0 mmol) was added dropwise into a solution of **4** (0.63 g, 1.67 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at room temperature for 15 min and then at 35 °C for 3 h before transferring into a mixture of **5** (0.95 g, 1.34 mmol), $Pd(PPh_3)_4$ (0.039 g, 0.033 mmol), Na_2CO_3 (4.45 g, 42.0 mmol), H_2O (21 mL) and toluene (35 mL). The reaction mixture was stirred at 90 °C for 24 h, cooled down to room temperature, and extracted with chloroform. The organic extracts were combined, washed with water, and dried over $MgSO_4$. Upon evaporating off the solvent, the crude product was purified by column chromatography on silica gel with hexane/chloroform 4:1 (v/v) as the eluent to yield *t*Bu-mCP-L-PhSiPh3 (1.05 g, 78%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.13 (s, 4H), 7.62 (s, 1H), 7.56–7.54 (m, 6H), 7.50–7.46 (m, 11H), 7.43–7.35 (m, 10H), 7.25–7.22 (m, 2H), 2.89–2.85 (m, 2H), 2.81–2.77 (m, 2H), 2.18–2.09 (m, 2H), 1.46 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 145.80, 143.44, 143.19, 139.63, 139.07, 136.68, 136.46, 134.47, 131.38, 129.61, 128.19, 127.92, 124.98, 123.83, 123.63, 121.92, 116.41, 109.32, 35.68, 35.62, 34.83, 32.79, 32.10. LDI TOF MS m/z ([M]$^+$): 1008.4. Anal. calcd for $C_{73}H_{76}N_2Si$ (%): C 86.85, H 7.59, N 2.78; found: C 86.59, H 7.53, N 2.68.

2.3. PhOLED device fabrication and characterization

The hole-injection material MoO_3 (Acros), hole-transporting materials TAPC (Nichem) and NPB (Nichem), blue emitter FIrpic (Nichem), green emitter $Ir(ppy)_2(acac)$ (Nichem), hole/exciton-blocking material TmPyPB (Nichem) and BCP (Sigma-Aldrich), electron-transporting material Alq_3 (Nichem), and electron-injection material LiF (Alfa) were commercially available. Devices were grown on ITO-coated glass substrates by thermal evaporation of the materials without breaking vacuum. Current–-brightness–voltage characteristics were measured using Keithley source measurement units (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The electroluminescence spectra were measured using a SpectraScan PR650 spectrophotometer. All the measurements except the lifetime testing were carried out in