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De Novo Design of Silicon-Bridged Molecule Towards a Bipolar Host: All-Phosphor White Organic Light-Emitting Devices Exhibiting High Efficiency and Low Efficiency Roll-Off

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White organic light-emitting diodes (WOLEDs) continue to attract intensive interest due to their applications in full color flat-panel displays and lighting sources.^[1,2] Among various approaches to realize WOLEDs, adopting all phosphorescent emitters has great potential because electrophosphorescence can, in theory, achieve unity internal quantum efficiency through harvesting both singlet and triplet excitons.^[3] Allphosphor WOLEDs have made considerable progress in recent years;^[4–6] however, they are still a long way from commercialization. Firstly, a major bottleneck is the lack of highly efficient and stable blue-emitting electrophosphorescence, which is indispensable to WOLEDs. Secondly, all-phosphor WOLEDs usually exhibit significant efficiency roll-off at the luminance required for practical light sources. Thirdly, the two or multiple emitting layer (EML) structures widely adopted in WOLEDs inevitably result in higher complexity, control difficulties and higher operational voltages during fabrication.^[5,7] To address these issues, elegant materials and elaborate device structures have to be developed. In terms of material, a bipolar host capable of hosting blue phosphor can play a vital role in solving the above-mentioned problems because a bipolar host can not only broaden the exciton-formation zone - consequently reducing the efficiency roll-off - but also simplify the device structure by employing a single emitting layer comprised of a bipolar host and two or more phosphors. However, the design of such a host is a significant challenge because three tradeoffs have to be managed: i) the high enough triplet energy required to host blue phosphor and bipolar transporting characteristics, since the p- and n-type segments integrated into the molecule structure unavoidably lower the band gap of the material due to intramolecular charge-transfer;^[8] ii) the high triplet energy and minimum energy barrier between the host material and

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adjacent charge-transporting layer – a high triplet energy generally signifies a large electrical band gap, i.e., a low-lying highest occupied molecular orbital (HOMO) and/or high-lying lowest occupied molecular orbital (LUMO) level, which are not easily matched in the energy levels of adjacent layers; and, iii) the high triplet energy and good morphologically stability needed – a high triplet energy usually requires limited conjugation length and molecular size, which makes it difficult for the materials to acquire morphological stability.^[9]

To date, the host materials for blue phosphorescent OLEDs (PhOLEDs) have mainly been based on carbazole-based compounds.^[10] Most recently, diphenylphosphine oxide derivatives of aromatic molecules have emerged as a new class of bipolar host materials for blue PhOLEDS.[11] In addition, a series of tetraarylsilicon compounds with ultrahigh singlet (around 4.5 eV) and triplet (around 3.5 eV) energies as host materials for deep blue electrophosphorescence have also been reported.^[12] Although the tetraarylsilicon host materials have high triplet energy levels, they show a poor charge-transporting ability and a very high hole-injection barrier. The synthetic versatility of organic materials allows the optimization of their physical properties, including energy level, charge transport and morphological stability. In this communication, we report the de novo design of a silicon-bridged molecule by integrating electrondonating and -accepting moieties into the tetraarylsilicon skeleton. We anticipated that the electron-donating and -accepting groups would impart the material with bipolar transporting nature; meanwhile, the whole molecule would maintain relative high triplet energy owing to silicon-interrupted conjugation of two segments. The new silicon-bridged compound, combining p-type triphenylamine and n-type benzimidazole groups, namely *p*-BISiTPA, shows a high triplet energy level of 2.69 eV. Hole- and electron-only devices indicate its bipolar transporting feature. Devices with p-BISiTPA as host show excellent performance, with external quantum efficiencies as high as 16.1% for blue, 20.4% for orange and 19.1% for white electrophosphorescence at a practical brightness of 100 cd m⁻². Even at a brighter emission of 1000 cd m⁻², the efficiencies were still 14.2%, 18.9% and 17.4%, respectively.

The bipolar molecule *p*-BISiTPA was synthesized in two steps (**Scheme 1**). The electron-withdrawing benzimidazole moiety was first introduced into the silicon-containing skeleton by a cyclization of *N*-phenyl-*o*-phenylenediamine and 4-[(4-bromophenyl)(diphenyl)silyl]benzoyl chloride. Then, the electron-donating diphenylamine segment was connected to the skeleton through the palladium-catalyzed C–N coupling

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Scheme 1. Synthesis of *p*-BISiTPA.

reaction of the intermediate *p*-BISi–Br with diphenylamine.^[13] The chemical structure of *p*-BISiTPA was fully characterized by ¹H NMR and ¹³C NMR spectroscopies, mass spectrometry and elemental analysis.

The good thermal stability of *p*-BISiTPA is indicated by the high decomposition temperatures (T_d , corresponding to 5% weight loss) of 405 °C in the thermogravimetric analysis, and the glass transition temperature (T_g) of 102 °C through differential scanning calorimetry (DSC), which is substantially higher than those of carbazole-based 1,3-bis(9-carbazolyl)benzene (*m*CP, 60 °C)^[10a] and tetraarylsilicon compounds (26–53 °C).^[12] The high T_g and T_d values of *p*-BISiTPA can improve the film morphology and reduce the possibility of phase separation upon heating.

The absorption and fluorescence spectra of *p*-BISiTPA are shown in **Figure 1**. The absorption peak at 308 nm (log ε = 4.9) can be attributed to the π - π * transition. It is noteworthy that charge transfer absorption from the electron-donating triphenylamine to the electron-withdrawing benzimidazole



Figure 1. The absorption and emission spectra of *p*-BISITPA in toluene at 5×10^{-6} M at room temperature, and phosphorescence spectrum of *p*-BISITPA in 2-methyltetrahydrofuran at 77 K.

group cannot be observed,^[14] indicating the disruption of the π -conjugation between the two parts owing to the silicon-bridged linkage mode. The triplet energy of the compound was determined to be 2.69 eV by the highest energy vibronic sub-band of the phosphorescence spectrum in 2-methyltetrahydrofuran at 77 K, which is higher than that of blue phosphor iridium(III) bis(4,6-(difluorophenyl)pyridine- $N, C^{2'}$) picolinate (FIrpic, 2.65 eV).^[15]

The electrochemical properties of *p*-BISiTPA were investigated by cyclic voltammetry (CV). The compound exhibits one quasi-reversible, one-electron oxidation process (see Figure S1 in the Supporting Information), which can be assigned to the oxidation of arylamine moiety. The HOMO energy level determined from the onset of the oxidation potential is 5.27 eV with regard to the energy level of ferrocene (4.8 eV below vacuum), which is much higher than the approximately 7.0 eV of tetraarylsilicon compounds. The HOMO level of the compound is even higher than that of most widely used hole transporting material 1,4-bis[(1-naphthylphenyl)amino]biphenyl (NPB, 5.4 eV),^[16] suggesting no hole–injection barriers from NPB to the compound.

To gain insight into the electronic state of the new compound, DFT calculations were performed. The calculated HOMO and LUMO values are 5.22 and 1.78 eV, respectively. Moreover, HOMO and LUMO levels distribute over aryamine and benzimidazole segments, respectively (See Figure S2 in the Supporting Information). Complete separation is preferable for efficient hole- and electron-transporting properties, and the prevention of reverse energy transfer.^[17]

To evaluate the bipolar character of *p*-BISiTPA, we fabricated a hole-only device having the structure ITO/MoO₃ (10 nm)/ NPB (80 nm)/4,4',4"-tri(*N*-carbazolyl)triphenylamine (TCTA, 5 nm)/*p*-BISiTPA (20 nm)/1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI, 40 nm)/MoO₃ (40 nm)/Al (100 nm) and an electron-only device having the configuration ITO/TPBI (40 nm)/NPB (80 nm)/TCTA (5 nm)/*p*-BISiTPA (20 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm). MoO₃ and TPBI layers were used to prevent electron- and hole-injection from the cathode and anode, respectively. The current density versus voltage

Table 1. Electroluminescence Characteristics of the Devices.[a]

| Device | V _{on} [V] | $L_{\rm max}$ [cd m ⁻²] (V at $L_{\rm max}$ [V]) | $\eta_{ m c}$ [b] [cd A ⁻¹] | $\eta_{ m p}$ [b] [lm W ⁻¹] | η_{ext} [b] [%] | CIE [c] [x, y] |
|--------|---------------------|--|---|---|-------------------------------|----------------|
| В | 3.5 | 17 798 (14.1) | 35.1, 35.1, 31.1 | 26.1, 24.5, 15.5 | 16.1, 16.1, 14.2 | 0.18, 0.32 |
| 0 | 3.1 | 47 756 (13.1) | 57.8, 57.3, 53.2 | 51.9, 43.9, 29.3 | 20.5, 20.4, 18.9 | 0.52, 0.48 |
| W | 3.1 | 45 398 (14.5) | 51.8, 51.7, 47.3 | 42.7, 37.8, 25.2 | 19.1, 19.1, 17.4 | 0.38, 0.44 |

[a] Abbreviations: V_{on} : turn-on voltage; L_{max} : maximum luminance; V: voltage; η_{ext} : external quantum efficiency; η_c : current efficiency; η_c : power efficiency; CIE [x, γ]: Commission International de l'Eclairage coordinates; [b] Order of measured value: maximum, then values at 100 and 1000 cd m⁻²; [c] Measured at 7 V.

curves show that the electron-current density is slightly higher than the hole-current density in *p*-BISiTPA (see Figure S3 in the Supporting Information), which indicates the bipolar charge-transport nature of *p*-BISiTPA.

We initially examined the performance of FIrpic-based blue phosphorescent device (device B) with the structure ITO/MoO₂ (10 nm)/NPB (80 nm)/TCTA (5 nm)/p-BISiTPA: FIrpic (8 wt.-%, 20 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm). NPB and TPBI were used as the hole- and electron-transporting layers, respectively. TCTA was used as the electron/exciton-blocking layer. MoO3 and LiF served as the hole- and electron-injecting layers, respectively; FIrpic doped in p-BISiTPA was used as the emitting layer. The blue phosphorescent device achieved a maximum current efficiency ($\eta_{c, max}$) of 35.1 cd A⁻¹, a maximum power efficiency ($\eta_{p, max}$) of 26.1 lm W⁻¹ and a maximum external quantum efficiency ($\eta_{\text{ext. max}}$) of 16.1% (see Figure S4 in the Supporting Information and Table 1). It is worth noting that the external quantum efficiencies still remain as high as 14.2% at a brightness of 1000 cd m⁻². These values are inferior to the best performance reported for FIrpic-based devices^[11,18] presumably because the triplet energy of *p*-BISiTPA is not high enough relative to FIrpic. However, this is a worthy sacrifice to acquire a compromise among the triplet energy, bipolar transporting nature and carrier-injection barrier.

Next we fabricated an orange phosphorescent device (device O) with the same configuration as device B except for using bis[2-(9,9-diethyl-9*H*-fluoren-2-yl)-1-phenyl-1*H*-benzoimidazol-N,C³]-iridium(acetylacetonate) [(fbi)₂Ir(acac)] as the dopant. The device achieved $\eta_{c, max}$ of 57.8 cd A⁻¹, $\eta_{p, max}$ of 51.9 lm W⁻¹ and $\eta_{ext, max}$ of 20.5%, respectively. Moreover, the device displays low external quantum efficiency roll-off, with a roll-off value of 7.8% at a luminance of 1000 cd m⁻². The performance of the device O is among the highest for orange PhOLEDs ever reported.^[19]

Finally, we demonstrated a two-color based phosphorescent WOLED (device W) with the configuration ITO/MoO₃ (10 nm)/NPB (80 nm)/TCTA (5 nm)/*p*-BISiTPA: 8 wt.-% FIrpic: 0.67 wt.-% (fbi)₂Ir(acac) (20 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm). FIrpic and (fbi)₂Ir(acac) were co-doped into the bipolar host *p*-BISiTPA as the single emitting layer. The device had $\eta_{c, max}$ of 51.8 cd A⁻¹, $\eta_{p, max}$ of 42.7 lm W⁻¹ and $\eta_{ext, max}$ of 19.1% (Figure 2 and Figure S4 in the Supporting Information). To the best of our knowledge, the device efficiencies are among the highest reported for single emitting layer WOLEDs.^[20] Remarkably, the device shows rather low efficiency roll-off: at a luminance of 1000 cd m⁻², η_{ext} is still as high as 17.4% with a roll-off value of 8.9%, and at the extremely high luminance of 10 000 cd m⁻², η_{ext} is still 12.2%. The roll-off values

are significantly reduced compared to our previously reported results using similar device structures having the conventional host material mCP, in which the external quantum efficiency reached a maximum value of 19.3% at a very low luminance of 7 cd m⁻²;^[20b] at a luminance of 1000 cd m⁻², η_{ext} dropped to 12.3% with a roll-off value of 36.3%, and at a luminance of 10 000 cd m⁻², η_{ext} declined to only 6.3%. The high efficiencies and low efficiency roll-off at high luminance for device W can be attributed to the use of the bipolar host *p*-BISiTPA, which may have resulted in balanced charge fluxes and a broad distribution of recombination region within the emitting layer. Additionally, the white light are quite stable, and the Commission International de l'Eclairage (CIE) coordinates of the device remain almost invariable when the luminance going from 4 774 cd m⁻² (0.37, 0.43) to 24 295 cd m⁻² (0.36, 0.43) (inset of Figure 2). The color-rendering index (CRI) of 67 for the current WOLED is not high due to the two-color system.

In summary, we have developed a new molecular design strategy for bipolar host material by incorporating both electron donor and electron acceptor into the silicon-bridged structure. The new silicon-bridged compound *p*-BISiTPA finds a balance between the high triplet energy and bipolar transporting nature, carrier-injection barrier, plus morphological stability. The new compound was demonstrated to be an efficient host for blue and orange phosphors. A two-color, all-phosphor and single-emitting-layer WOLED hosted by *p*-BISiTPA was fabricated



Figure 2. Current efficiency and power efficiency versus luminance for device W. Inset: the normalized EL spectra of device W at various voltages.



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and displayed very high efficiency and low roll-off. We note the device performance is achieved without fine optimization for device structures. We believe that the efficiency, color purity and CRI of this white light device can be further improved by optimizing device configurations, and this work is in progress.

Experimental Section

Synthesis of (4-{Diphenyl[4-(1-phenyl-1H-benzimidazol-2-vl)phenyl]silvl} phenyl)diphenylamine (p-BISiTPA): Amixture of p-BISi-Br (1.82g, 3.00 mmol), diphenylamine (0.54 g, 3.20 mmol), Pd(OAc)₂ (13 mg, 0,06 mmol), tBuONa (0.35 g, 3.60 mmol), (tBu)₃PHBF₄ (52 mg, 0.18 mmol) and toluene (20 mL) was refluxed under argon for 18 h. After cooling, the reaction mixture was extracted with brine and CH₂Cl₂, and dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum (1:5 v/v) as the eluent to give a white powder. Yield: 72%. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3) \delta$ [ppm]: 8.35 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.67-7.57 (m, 6H), 7.52-7.34 (m, 12H), 7.32-7.27 (m, 8H), 7.14 (d, J = 7.8 Hz, 4H), 7.07–7.00 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ [ppm]: 152.28, 149.45, 147.52, 142.69, 137.52, 137.42, 137.16, 137.02, 136.63, 134.35, 130.74, 130.25, 129.93, 129.62, 129.06, 128.82, 128.17, 127.67, 125.44, 123.90, 123.77, 123.54, 121.75, 119.99, 110.84. MS (ESI): m/z 696 $[M + H]^+$. Anal. calcd for C₄₉H₃₇N₃Si (%): C 84.57, H 5.36, N 6.04; found: C 84.72, H 5.12, N 5.95.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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