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Highly Efficient Deep-Blue Electrophosphorescence Enabled by Solution-Processed Bipolar Tetraarylsilane Host with Both a High Triplet Energy and a High-Lying HOMO Level

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Phosphorescent organic light-emitting diodes (PhOLEDs) offer a bright future for the next generation flat-panel displays and lighting sources due to their high quantum efficiency compared with fluorescent OLEDs.^[1,2] To date, green and red PhOLEDs with 100% internal quantum efficiency have been achieved,^[3,4] but highly efficient and stable blue PhOLEDs, especially deepblue PhOLEDs, remain to be further developed. Many works on blue PhOLEDs have focused on the blue phosphor of iridium(III) bis(4,6-(difluorophenyl)pyridine- $N, C^{2'}$) picolinate (FIrpic).^[5-8] Among these, Kido et al.^[8] reported the highest external quantum efficiencies (EQE) of 26% and 25% at a practical luminance of 100 and 1000 cd m⁻², respectively. Despite the efficiency improvement for the FIrpic-based blue PhOLEDs, their color purity with Commission International de l'Eclairage (CIE) coordinates of (0.17, 0.34)^[5b] is not ideal for the practical applicability of blue PhOLEDs in full-color displays and solid lighting. To improve the color quality of blue PhOLEDs, Thompson and co-workers reported a phosphor of iridium(III) bis(4',6'-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate (FIr6), and the corresponding devices show deep-blue emission with CIE coordinates of (0.16, 0.26).^[9] Since then, elegant materials and elaborate device structures have been developed to improve the performance of FIr6-based devices.^[10-12] For example, Fukagawa et al. reported a highly efficient, low-voltage deep-blue PhOLED with a maximum EQE of 19% (33 lm W⁻¹) by adopting both hole- and electron-transporting hosts in a double-emission-layer structured device;^[11] Xue et al. demonstrated a maximum EQE of 20% (36 lm W⁻¹) by incorporating a double emissive layer into a p-i-n type cell architecture.^[12] It is noticed that the highly efficient FIr6-based devices have

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been achieved by complicated device configurations. One of the reasons is the lack of adequate host materials for deep-blue phosphor. As an effective host for deep-blue phosphor, its triplet energy ($E_{\rm T}$) has to be larger than that of FIr6 (2.72 eV)^[13] to maintain effective energy transfer from host to guest, whereas a high triplet energy generally associates with a low-lying highest occupied molecular orbital (HOMO) level, which may cause inefficient hole injection from the indium tin oxide (ITO) anode. To compensate the scarcity, multiple hole-transporting-layers (HTLs) with gradient energy pathway for the injection of holes into the emissive layer have to be adopted.^[11,12] This inevitably increases the complexity of the devices.

Solution-processable OLEDs are considered critical to the realization of low-cost and large-area displays.^[14] Obvious progress for red, green, and sky-blue PhOLEDs by solution processes has been made.^[15–17] However, several challenges make it difficult to generate a high efficiency, deep-blue phosphorescent OLED using a solution process. Primary among these is the design of a host material that should combine a high triplet energy (>2.72 eV) and a high-lying HOMO level to match the Fermi level of poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS, 5.1 eV),^[18] which is commonly used as hole-injection material in solution-processed devices. In this case, the emissive layer, consisting of host and triplet guest, is usually coated on the PEDOT:PSS layer directly, and thus one cannot insert several stepped HTLs as in the vacuumdeposition devices, except for using thermally cross-linkable hole-transporting materials.^[19] Providing that one also expects the host to possess good film-forming ability and bipolar transporting characteristics, in addition to high $E_{\rm T}$ and a high-lying HOMO level, it becomes a very big challenge for the search of the host material for solution-processable deep-blue PhOLEDs.

In our recent work, we demonstrated a bipolar siliconbridged host material that has a triplet energy of 2.69 eV and a HOMO level of 5.27 eV.^[20] The HOMO value is close to that of PEDOT:PSS, but the triplet energy is not high enough to host deep-blue phosphor FIr6. Here, we successfully design a new bipolar tetraarylsilane derivative with both a sufficiently high triplet energy (2.93 eV) and a high-lying HOMO level (5.28 eV) by incorporating diphenylamine and 1,2,4-triazole units into a silicon-bridged framework. Additionally, the Si compounds with multiple arylsilane groups as well as the rigid 1,2,4-triazole unit would enhance the likelihood that the material forms morphologically stable amorphous films. As a



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result, an efficient deep-blue phosphorescent device employing the new host material via a solution process has been realized with the maximum current efficiency of 12.5 cd A^{-1} (6.2 lm W^{-1} , 6.3%). Remarkably, the current efficiency still remains as high as 11.4 cd A^{-1} with a low roll-off value of 8.8% at the practical brightness of 1000 cd m⁻². To the best of our knowledge, this is the first report of a small-molecule-based, solutionprocessed, FIr6-based PhOLED. Additionally, the performance is the highest ever reported for solution-processed FIr6-based devices. Furthermore, the new host material is also applicable for the widely used sky-blue emitter-FIrpic, and the solutionprocessed device has achieved a maximum current efficiency of 23.7 cd A^{-1} (11.8 lm W^{-1} , 11.2%), which is among the highest for FIrpic-based PhOLEDs by solution processes ever reported.

The new tetraarylsilane derivative, namely {4-[{4-[5-(4-*tert*butylphenyl)-4-phenyl-4*H*-1,2,4-triazol-3-yl]phenyl}(diphenyl)silyl]phenyl}diphenylamine (*p*-TAZSiTPA, the inset of **Figure 1**), was synthesized in two steps. The electron-withdrawing 1,2,4triazole moiety and the electron-donating diphenylamine segment were sequentially introduced to the tetraphenylsilane skeleton (Scheme S1, Supporting Information). The chemical structure was fully characterized by ¹H NMR and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis. The absorption and fluorescence spectra of *p*-TAZSiTPA are shown in Figure 1. The triplet energy of the compound was determined to be 2.93 eV by the highest-energy vibronic sub-band of the phosphorescence spectrum in 2-methyltetrahydrofuran at 77 K, which is substantially higher than that of deep-blue phosphor FIr6 (2.72 eV).

The good thermal stability of *p*-TAZSiTPA is indicated by the high decomposition temperatures (T_d , corresponding to 5% weight loss) of 421 °C in the thermogravimetric analysis (TGA), and the glass transition temperature (T_g) of 119 °C through differential scanning calorimetry (DSC) (Figure S1, Supporting Information), which is much higher than those of previously reported tetraarylsilane compounds, such as the UGH (ultrahigh energy gap hosts) series (26–53 °C).^[13] The high T_g value of *p*-TAZSiTPA should benefit the stability of film morphology. As



Figure 1. The absorption and emission spectra of *p*-TAZSiTPA in hexane at 5×10^{-6} M at room temperature, and phosphorescence spectrum of *p*-TAZSiTPA in 2-methyltetrahydrofuran at 77 K. Inset: the molecular structure of *p*-TAZSiTPA.

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Figure 2. AFM topographic images (angled and top views) of the solutionprocessed *p*-TAZSiTPA films doped with a) 10 wt% FIr6 and b) 15 wt% FIrpic after drying at 80 °C under nitrogen atmosphere.

shown in **Figure 2**, the atomic force microscopy (AFM) images of solution-processed *p*-TAZSiTPA films doped with FIr6 or FIrpic display the smooth and homogeneous film morphologies, with small values of root-mean-square (RMS) roughness of 0.36 and 0.42 nm, respectively. We believe that the silicon tetrahedral configuration^[21] and the rigid 1,2,4-triazole unit could provide a stabilizing environment for dopants and keep films integrity throughout the entire fabrication process.

The electrochemical properties of *p*-TAZSiTPA were probed using cyclic voltammetry (CV). The compound exhibits one quasi-reversible, one-electron oxidation process (Figure S2, Supporting Information). The HOMO energy level evaluated from the onset of the oxidation potential is 5.28 eV with regard to the energy level of ferrocene (4.8 eV below vacuum). This HOMO level is consistent with the calculated HOMO value (5.31 eV) from density functional theory (DFT) calculations (Figure S3, Supporting Information). The matched HOMO level with PEDOT:PSS (5.1 eV) should result in a low hole-injection barrier from PEDOT:PSS to the host.

To evaluate the bipolar character of *p*-TAZSiTPA, a holeonly device with the structure of Al/MoO₃ (5 nm)/*p*-TAZSiTPA (200 nm)/MoO₃ (5 nm)/Al and an electron-only device with the configuration of Al/LiF (1 nm)/*p*-TAZSiTPA (200 nm)/LiF (1 nm)/ Al were fabricated. The current density versus voltage curves show that the electron current density is comparable to the hole current density in *p*-TAZSiTPA (Figure S4, Supporting Information), indicating the bipolar transporting property of *p*-TAZSiTPA.

The high triplet energy, the high-lying HOMO level, the bipolar transporting character, and the good film-forming ability for the new compound make it a good candidate as a solution-processed host for deep-blue PhOLEDs. We initially fabricated the FIr6-based blue phosphorescent device (device A) with the device architecture of ITO/PEDOT:PSS (40 nm)/*p*-TAZSiTPA:FIr6





Figure 3. a) Current density and luminance versus driving voltage characteristics for devices A (FIr6-based device, circles) and B (FIrpic-based device, triangles). Inset: device structure for devices A and B. b) Current efficiency and power efficiency versus luminance curves for device A. Inset: the normalized electroluminescence (EL) spectra of device A at a driving voltage of 7 V. c) Current efficiency and power efficiency versus luminance curves for device B. Inset: the normalized EL spectra of device B at a driving voltage of 7 V.

(10 wt%, 40 nm)/1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (Tm3PyPB, 5 nm)/1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI, 30 nm)/LiF (1 nm)/Al (100 nm). Tm3PyPB^[7b] and TPBI were used as the hole/exciton-blocking and electron-transporting layers, respectively; PEDOT:PSS and LiF served as hole- and electron-injecting layers, respectively; and FIr6 doped in *p*-TAZSiTPA was used as the emitting layer. As depicted in the inset of **Figure 3**b,



the electroluminescence (EL) spectrum originated from the triplet emission of FIr6 with CIE coordinates of (0.16, 0.27), indicative of efficient energy transfer from the host *p*-TAZSiTPA to FIr6. The deep-blue phosphorescent device achieved a maximum current efficiency ($\eta_{c,max}$) of 12.5 cd A⁻¹, a maximum power efficiency ($\eta_{p,max}$) of 6.2 lm W⁻¹, and a maximum external quantum efficiency ($\eta_{ext,max}$) of 6.3% (Figure 3). These values are over two times higher than those of the solution-processed polymer device using poly(9-vinylcarbazole) (PVK) as host ($\eta_{c,max}$ of 3.66 cd A⁻¹ and $\eta_{ext,max}$ of 1.48%).^[22] It is worth noting that the current efficiency still remains as high as 11.4 cd A⁻¹ with a low roll-off value of 8.8% at the brightness of 1000 cd m⁻². To the best of our knowledge, this is the first report of small-molecule-based deepblue PhOLED by solution-processed emissive layer and the device performance is the highest ever reported for solution-processed FIr6-based devices.

To evaluate the utility of the compound as host material for other blue phosphorescent emitters, we then fabricated the device B with the same configuration as device A, with the exception of using 15 wt% FIrpic as the dopant. The FIrpic-based device achieved $\eta_{c,max}$ of 23.7 cd A⁻¹, $\eta_{p,max}$ of 11.8 lm W⁻¹ and $\eta_{ext,max}$ of 11.2% (Figure 3), respectively, with CIE coordinates of (0.15, 0.32) at 7 V. Moreover, the device showed rather low efficiency roll-off; at the luminance of 1000 cd m⁻², η_c was still as high as 23.1 cd A⁻¹ with a very low roll-off value of 2.5%. The performance of the device B is among the highest for solution-processed FIrpic-based PhOLEDs ever reported.^[17,23]

The high efficiencies and low efficiency roll-off at high luminance for blue and deep-blue PhOLEDs can be attributed to the superiority of the host *p*-TAZSiTPA: the high triplet energy ensures efficient energy transfer from the host to the phosphor and triplet exciton confinement on the phosphor; the high-lying HOMO level facilitates efficient hole injection to the emitting layer; and bipolar feature renders balanced charge fluxes and a broad distribution of recombination region within the emitting layer.

In summary, we have developed a new tetraarylsilane derivative by incorporating an electron-donor diphenylamine group and an electron-acceptor 1,2,4-triazole unit into the siliconbridged structure. Such molecular design endows the material with a high triplet energy and a high-lying HOMO level simultaneously. Along with the good film-forming ability and bipolar property, the new compound enables a solution-processed deepblue PhOLED with high efficiency and low efficiency roll-off. Further application of the new compound as a host material in solution-processable white PhOLEDs is in progress.

Experimental Section

Device Fabrication and Measurement: The hole-injection material, PEDOT:PSS, and electron-transporting material, TPBI, were commercially available. Commercial ITO-coated glass with a sheet resistance of 10 Ω square⁻¹ was used as the starting substrates. Before device fabrication, the ITO glass substrates were precleaned carefully and treated by oxygen plasma for 2 min. PEDOT:PSS was spin-coated to smooth the ITO surface and promote hole injection, and then the emissive layer (EML) was spincoated from chlorobenzene solution. The samples were annealed at 80 °C for 30 min to remove residual solvent. The thickness of the EML was about 40 nm. Finally, a hole/exciton-blocking layer of Tm3PyPB (5 nm),



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an electron-transporting layer of TPBI (30 nm), and a cathode composed of lithium fluoride (1 nm) and aluminum (100 nm) were sequentially deposited onto the substrate by vacuum deposition in a vacuum with a pressure of 10^{-6} Torr. The current density–voltage–luminance (*J*–*V*–*L*) measurements of the devices were recorded with a Keithley 2400 Source meter and a Keithley 2000 Source multimeter equipped with a calibrated silicon photodiode. The EL spectra were measured using a JY SPEX CCD3000 spectrometer. The EQE values were calculated according to previously reported methods.^[24] All measurements were carried out at room temperature under ambient conditions.

Synthesis of {4-[{4-[5-(4-tert-butylphenyl)-4-phenyl-4H-1,2,4-triazol-3-yl]phenyl}(diphenyl)silyl]phenyl}diphenylamine (p-TAZSiTPA): A mixture of p-TAZSi-Br (2.07 g, 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), and (tBu)₃PHBF₄ (52 mg, 0.18 mmol) in 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/CH2Cl2 (1:15 by vol) as the eluent to give a white powder. Yield: 45%. ¹H NMR (300 MHz, CDCl₃) δ [ppm]: 7.53-7.48 (m, 6H), 7.46-7.40 (m, 6H), 7.38-7.29 (m, 11H), 7.24-7.19 (m, 6H), 7.13 (d, J = 7.2 Hz, 4H), 7.07-7.00 (m, 4H), 1.28 (s, 9H). ^{13}C NMR (75 MHz, CDCl₃) δ [ppm]: 154.82, 154.46, 152.70, 149.07, 147.11, 137.12, 136.61, 136.23, 135.27, 133.93, 129.93, 129.58, 129.25, 128.21, 127.81, 127.65, 125.30, 125.08, 123.83, 123.42, 121.33, 34.64, 31.06. MS (EI): m/z 778.3 [M⁺]. Anal. calcd for C₅₄H₄₆N₄Si (%): C 83.25, H 5.95, N 7.19; found: C 83.21, H 6.15, N 6.94.

Supporting Information

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

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