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A *m*-Terphenyl-Modifed Sulfone Derivative as a Host Material for High-Efficiency Blue and Green Phosphorescent OLEDs

Hisahiro Sasabe,*[†,‡] Yuki Seino,[†] Masato Kimura,[†] and Junji Kido*[†,‡]

[†]Department of Organic Device Engineering and [‡]Research Center for Organic Electronics (ROEL), Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

Supporting Information

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High-efficiency organic light-emitting devices (OLEDs) have received considerable attention for energy-saving solid-state lighting and eco-friendly flat panel display applications.[1] For an energy-saving illumination light source beyond the fluorescent tube, the use of phosphorescent OLED technology is imperative because a phosphorescent emitter can yield an internal quantum efficiency as high as 100%.[2] In phosphorescent OLEDs, a host material plays a key role in determining OLED performances.[3] Among the known host materials, a host material with an electron-accepting moiety, such as pyridine, pyrimidine, and phosphine-oxide, can realize high performances in blue and green OLEDs.[4] This type of host can promote electron injection as well as electron transport, creating an improved carrier balance of holes and electrons in an emissive layer (EML).[5]

In this regard, a sulfone-containing material is an attractive candidate to present a great opportunity for a phosphorescent host material, because a sulfone moiety possesses a strong electron-accepting nature. Some sulfone-containing materials have been used as an emitter[6] and an electron transporter[7] to realize high-performance fluorescent OLEDs so far. On the other hand, Hsu and co-workers have reported triphenylamine/bisphenylsulfonyl-substituted fluorene material for red phosphorescent OLEDs.[8] Most recently, Kim and co-workers have developed a solution-processed blue phosphorescent OLED with an external quantum efficiency (η_{ext}) of 6.9% and a current efficiency (η_{c}) of 12.9 cd A^{-1} at 100 cd m^{-2} using 4,4′-bis(phenylsulfonyl)biphenyl (SO1) and a common blue phosphorescent emitter iridium(III) bis[(4,6-difluorophenyl)-pyridinate-$N,C^{2'}$]picolinate (FIrpic).[9] Even though sulfone-containing derivatives can hold tremendous promises as a host material in phosphorescent OLEDs, their performances are limited and the full potential is yet to be explored. We have already reported that *m*-terphenyl-modified carbazole derivative (CzTP) has a high thermal stability and a triplet energy (E_{T}) of 2.70 eV to realize high-performance blue and green OLEDs.[10] In this communication, we introduce a *m*-terphenyl-modified sulfone derivative, 5′,5″″-sulfonyl-di-1,1′:3′,1″-terphenyl (BTPS, Figure 1) as a host material for phosphorescent blue and green OLEDs.

Prior to material preparation, we conducted the density functional theory (DFT) calculations.[4g,5] An optimized structure was calculated at the RB3LYP 6-31G(d) level for the ground state. The single-point energy was calculated at the corresponding RB3LYP 6-311+G(d,p) level. The calculated highest occupied molecular orbital (HOMO) energy of BTPS was estimated to be 6.58 eV, and the lowest unoccupied molecular orbital (LUMO) energy was 1.88 eV. On the other hand, as we reported previously, the corresponding HOMO/LUMO energies of a common host material, *N,N′*-dicarbazolyl-3,5-benzene (mCP), were estimated to be 5.80 and 1.26 eV, respectively.[4e] The LUMO energy of BTPS was evaluated to be 0.62 eV deeper than that of mCP, probably because of the strong electron-accepting nature of a sulfone moiety. This result suggests that BTPS can promote electron injection, creating superior carrier balance of holes and electrons in an EML. We also calculated an E_{T} from TD-DFT calculation at the RB3LYP 6-31G(d) level using an optimized structure mentioned above. An E_{T} was evaluated to be 3.11 eV, which is slightly lower than that of mCP (3.18 eV). These results suggest an effective confinement of phosphorescent blue emitter in BTPS.

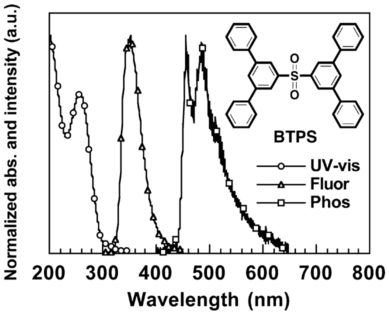

Figure 1. Absorption and photoluminescence (PL) spectra of BTPS film.

BTPS was prepared via a Suzuki coupling reaction of bis(3,5-dichlorophenyl)sulfone[11] with phenylboronic acid using Pd$_2$(dba)$_3$/PCy$_3$/K$_3$PO$_4$ catalyst system in 71% yield. The characterization was established on the basis of ^{1}H NMR, mass spectrometry, and elemental analysis. The product was purified by the train sublimation method before device fabrication. The

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purity of BTPS thus obtained was confirmed to be >99.0% by HPLC analysis.

The thermal properties were measured by differential scanning calorimetry (DSC). The melting point (T_m) was observed at 282 °C, and the glass transition temperature (T_g) was not observed. The decomposition temperature with 5% loss (T_{d5}) was estimated at 385 °C by using a thermogravimetric analysis (TGA). The ionization potential (I_p) was observed at 6.7 eV by a photoelectron yield spectroscopy (PYS)[12] under the vacuum (~10^{-3} Pa). The electron affinity (E_a) was estimated to be 2.9 eV by subtraction of the optical energy gap (E_g) from the I_p. The phosphorescent spectrum was measured by a streak camera at 5 K. The onset phosphorescence was observed at 2.79 eV for BTPS (Figure 1). Therefore, BTPS is considered to be applicable for blue and green phosphorescent OLEDs.

Prior to the device fabrication, photophysical properties of 5−15 wt % iridium(III) bis[(4,6-difluorophenyl)-pyridinate-*N*,$C^{2'}$]picolinate (FIrpic)-doped host films (30 nm) were evaluated. The photoluminescent quantum yield (η_{PL}) was measured under N_2 flow using an integrating sphere, using an excitation wavelength of 331 nm, and with a multichannel spectrometer as the optical detector. η_{PL}s of BTPS/FIrpic films were estimated to be 81 ± 1% for 5 wt %-doped film, 71 ± 1% for 10 wt %-doped film, and 50 ± 1% for 15 wt %-doped film, respectively. The transient PL decay curve of 5 wt % FIrpic-doped film exhibited almost single-exponential decay with a τ_p of 1.4 μs at room temperature (see Supporting Information in detail). These values are almost similar to that of the mCP/FIrpic film,[14] indicating effective suppression of the triplet extion of FIrpic.

First, to investigate the function of BTPS as a host material, several blue phosphorescent OLEDs using FIrpic as an emitter were fabricated. We used 1,1-bis[4-[*N*,*N*-di(*p*-tolyl)amino]-phenyl]cyclohexane (TAPC) as a hole-transporting layer (HTL) and 3,3″,5,5″-tetra(3-pyridyl)-1,1′;3′,1″-terphenyl (B3PyPB)[13] as an electron-transporting layer (ETL); these materials have higher E_T than that of FIrpic. Therefore, the triplet exciton quenching of FIrpic at the HTL/EML and/or EML/ETL interface(s) can be minimized. On the other hand, due to the deep I_p of BTPS (6.7 eV), there can be a large hole-injection barrier between HTL/EML. For effective hole-injection from TAPC (5.6 eV) to EML (BTPS and/or FIrpic, 6.2 eV), we used 4,4′,4″-tris(*N*-carbazolyl)triphenylamine (TCTA, 5.8 eV), which has higher triplet energy than FIrpic, between TAPC and EML.[15] Then, we fabricated a blue phosphorescent OLED with a structure of [ITO (130 nm)/TAPC (15 nm)/TCTA (5 nm)/FIrpic 5−15 wt % doped BTPS (10 nm)/B3PyPB (50 nm)/Liq (1 nm)/Al (100 nm)]. EL spectra showed an emission only from FIrpic with no emission from neighboring materials (inset in Figure 2b). The current density−voltage−luminance (*J*−*V*−*L*) and the power efficiency−luminance (*PE*−*L*) characteristics are shown in Figure 2a,b, respectively. An OLED with BTPS/15 wt %-FIrpic showed a much reduced operating voltage of 3.33 V at 100 cd m^{-2} and gave an $\eta_{p,100}$ of 46.0 lm W^{-1} (48.6 cd A^{-1}, η_{ext} 21.8%) at 100 cd m^{-2} and 31.4 lm W^{-1} (39.4 cd A^{-1}, η_{ext} 17.7%) at 1000 cd m^{-2}, respectively. The average performance was 43.7 lm W^{-1} at 100 cd m^{-2}, which was derived from four devices. These are among the best performances in FIrpic-based OLEDs.[13,16] In these series of OLEDs, higher doped OLEDs showed reduced operating voltages. Therefore, electron injection from B3PyPB to EML is greatly enhanced by doping of FIrpic.

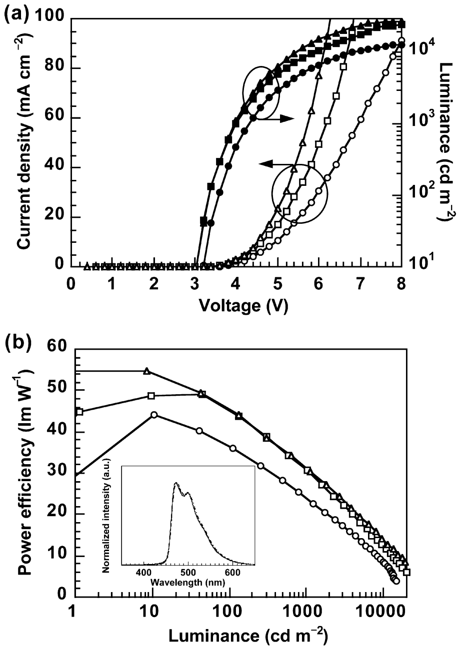

Figure 2. (a) *J*−*V*−*L* characteristics and (b) PE−*L* characteristics of blue OLEDs using BTPS. 5 wt % (circle), 10 wt % (square), and 15 wt % (triangle) FIrpic-doped device, respectively. Inset: EL spectra of the devices.

We also tried to estimate green OLED performances using a common green phosphohrescent emitter *fac*-tris(2-phenylpyridyl)iridium(III) [$Ir(ppy)_3$]. Prior to the device fabrication, photophysical properties of 5−15 wt % $Ir(ppy)_3$-doped host films (30 nm) were evaluated. η_{PL}s of BTPS/$Ir(ppy)_3$ films were estimated to be 72 ± 1% for 5 wt %-doped film, 70 ± 1% for 10 wt %-doped film, and 56 ± 1% for 15 wt %-doped film, respectively. The transient PL decay curve of the 5% $Ir(ppy)_3$-doped film exhibited almost single-exponential decay with a τ_p of 1.4 μs at room temperature.

A green phosphorescent OLED with a structure of [ITO (130 nm)/TAPC (30 nm)/5−15 wt % $Ir(ppy)_3$-doped BTPS (10 nm)/B3PyPB (50 nm)/Liq (1 nm)/Al (100 nm)] was fabricated. The *PE*−*L* characteristics are shown in Figure 3. Compared with 5 wt %-doped OLED, higher doped OLEDs showed a much reduced operating voltage of 3.0 V at 100 cd m^{-2}. Thus, carrier injection to EML is greatly enhanced by doping of $Ir(ppy)_3$. This result clearly shows that electro-

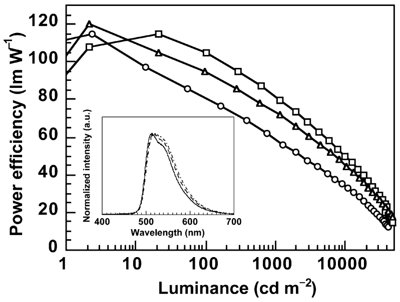

Figure 3. PE−*L* characteristics of green OLEDs using BTPS. 5 wt % (circle), 10 wt % (square), and 15 wt % (triangle) $Ir(ppy)_3$-doped device, respectively. Inset: EL spectra of the devices.

phosphorescence is generated by the guest carrier trapping process in 10−15 wt % Ir(ppy)$_3$-doped green OLEDs. Further, these operating voltages are much lower than that with mCP (3.2 V)[10] and CzTP (3.6 V)[10] and comparable that with mCaP (2.9 V),[4e] probably because the electron-accepting nature of BTPS can promote electron-injection in EML. The 10 wt %-doped device showed a very high $\eta_{p,100}$ of 105 lm W^{-1} ($\eta_{c,100}$: 100 cd A^{-1}, $\eta_{ext,100}$: 28%) at 100 cd m^{-2} and an $\eta_{p,1000}$ of 82 lm W^{-1} ($\eta_{c,1000}$: 75 cd A^{-1}, $\eta_{ext,1000}$: 26%) at 1000 cd m^{-2}, respectively. The average performance was 100 lm W^{-1} at 100 cd m^{-2}, which was derived from five devices. The angular dependence of luminous intensity is well-fitted by a Lambertian distribution (Lambertian factor: 0.968; see Supporting Information). Associated relative expanded uncertainty with the luminous flux measurement is lower than a few percent. In 10−15 wt %-doped devices, reduced efficiency roll-off was also observed at high luminance. To estimate the efficiency roll-off, we calculated a current density ($J_{1/2}$) at half the maximum η_{ext}, and the $J_{1/2}$ value is evaluated to be 71−91 mA cm^{-2}. Compared with previously reported phosphorescent OLEDs, the $J_{1/2}$ value is quite large despite the high-doping concentration of Ir(ppy)$_3$.[1g] Although a 15 wt %-doped film showed relatively low η_{PL} of 56%, a green OLED with this film gave extremely high $\eta_{ext,100}$ of 25%. The angular dependence of luminous intensity is almost fitted by a Lambertian distribution (Lambertian factor: 0956; see Supporting Information). These results suggest that an η_{ext} estimated from an η_{PL}[17] might be underestimated because an imperfect energy transfer process from host to guest can be included in an η_{PL} evaluation.

In summary, we developed a novel high E_T host material BTPS with sulfone and *m*-terphenyl moieties for phosphorescent OLED. By using BTPS as a host material, we successfully developed high-performance blue and green OLEDs. These performances are the highest levels in the scientific literature. Investigation of the device performances with different dopant concentrations shows that the electrophosphorescence is generated by the carrier trapping process. Our results promise that a high-efficiency phosphorescent OLED can be realized by using guest charge trapping even though an EML exhibits a low η_{PL} in an exciton-confining high E_T host material.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedure and characterization, transient phosphorescence decay curves, angular dependence of luminous intensity in OLEDs, and summary of OLED performances (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: h-sasabe@yz.yamagata-u.ac.jp, kid@yz.yamagata-u.ac.jp.

Notes

The authors declare no competing financial interest.

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