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Highly efficient, deep-red organic light-emitting devices using energy transfer from exciplexes;

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We developed a highly efficient, deep-red organic light-emitting device (OLED) with an external quantum efficiency of nearly 18% with a very low turn-on voltage of 2.41 V and an electrolumines-cence emission wavelength (λ_{EL}) of 670 nm using energy transfer from an exciplex host to a deep-red phosphorescent emitter, bis(2,3-diphenylquinoxaline)iridium(dipivaloylmethane)[(DPQ)₂Ir(dpm)].

Organic light-emitting devices (OLEDs) have several outstanding characteristics compared to other light sources; for example, OLEDs are thin, light-weight, flexible, and low-power-consuming.^{1,2} Among the emitters for highly efficient OLEDs, phosphorescent and/or thermally activated delayed fluorescent (TADF) emitters have received considerable attention because these emitters can realize 100% conversion from electrons to photons by harvesting all the electrically generated molecular excitons.^{1,2}

Although orange, green, and sky-blue OLEDs have already achieved an external quantum efficiency (η_{ext}) of over 30% by using phosphorescent³ and/or TADF emitters,⁴ the η_{ext} values of deep-red OLEDs with an electroluminescence (EL) emission wavelength (λ_{EL}) of approximately 680 nm have been reported to be significantly low, around 10% (Table S1, ESI†).⁵

For example, Fujii and co-workers synthesized a deep-red phosphorescent emitter, bis(2,3-diphenylquinoxaline)iridium-(acetylacetone) [(QH)₂Ir(acac)], with a photoluminescence quantum efficiency (η_{PL}) of 79% in dichloromethane solution. A deep-red OLED based on (QH)₂Ir(acac) showed an η_{ext} of 10.2%, a λ_{EL} of 675 nm, and Commission Internationale de l'Eclairage (CIE) coordinates of (0.70, 0.27) using 3-(4-biphenylyl)-4-phenyl-5-(4-*tert*-buthylphenyl)-1,2,4-triazole as an electron-transporting host material.^{5a} Jou and co-workers synthesized

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Mascaren Center for Organic Electronics (NOLE), Fronter Center for Organic Materials (FROM) Yamagata University, Yonezawa, Yamagata, 992-8510, Japan † Electronic supplementary information (ESI) available: Synthetic route, results [bis(spirofluorenedibenzosuberene[*d*]quinoxaline-C²,*N*)-monoacetylacetone]iridium(m) with an $\eta_{\rm PL}$ of 51% in dichloromethane solution. The corresponding deep-red OLED employing a co-host system of *N*,*N*'-di(naphthalene-1-yl)-*N*,*N*'-diphenylbenzidine (NPD) and bis(10hydroxybenzo[h]quinolinato)beryllium (BeBq₂) showed a maximum $\eta_{\rm ext}$ of 11.2%, a $\lambda_{\rm EL}$ of 688 nm, and CIE coordinates of (0.70, 0.27).^{5b} Recently, Wang and co-workers synthesized the TADF emitter, 7,10bis(4-(diphenylamino)phenyl)dibenzo[*f*,*h*]quinoxaline-2,3-dicarbonitrile (TPA-DCPP), which exhibited a $\eta_{\rm PL}$ of 50% in a co-doped film. An OLED based on TPA-DCPP showed an $\eta_{\rm ext}$ of 9.8%, a $\lambda_{\rm EL}$ of 668 nm, and CIE coordinates of (0.70, 0.29).^{5c} As can be seen from these examples, in order to improve the $\eta_{\rm ext}$ values of deepred OLEDs, sophisticated device engineering along with the development of a deep-red emitter with a high $\eta_{\rm PL}$ is necessary.

In this context, we developed deep-red OLEDs based on the iridium complex, bis(2,3-diphenylquinoxaline)iridium(dipivaloylmethane) [(DPQ)₂Ir(dpm)]. By using energy transfer from exciplexes, these OLEDs exhibit a record-breaking η_{ext} of nearly 18% with a $\lambda_{\rm EL}$ of 670 nm. We designed and synthesized three new types of electron-transporting host materials composed of dibenzothiophene (DBT) and azine units: 2-(3'-(dibenzo[b,d]thiophen-4yl)-[1,1'-biphenyl]-3-yl)-4,6-diphenylpyrimidine (4DBT46PM), 4-(3'-(dibenzo[b,d]thiophen-4-yl)-[1,1'-biphenyl]-3-yl)-2,6-diphenylpyrimidine (4DBT26PM), and 2-(3'-(dibenzo[b,d]thiophen-4-yl)-[1,1'biphenyl]-3-yl)-4,6-diphenyl-1,3,5-triazine (4DBT46TRZ). These host materials formed exciplexes in co-deposited films with di(naphthalene-1-yl)-N,N'-diphenylbenzidine (NPD). Combining (DPQ)₂Ir(dpm) with these exciplex hosts, the co-deposited films showed reasonably high $\eta_{\rm PL}$ values of over 50%. Finally, we fabricated OLEDs using the exciplex host systems, and the optimized OLED showed an η_{ext} of 17.9% with a very low turn-on voltage of 2.41 V, and CIE coordinates of (0.70, 0.29). This value of η_{ext} is 1.6 times higher than that of the current state-of-the-art deep-red OLED.5

First, we designed three types of electron-transporting host materials: **4DBT46PM**, **4DBT26PM**, and **4DBT46TRZ**. Azine units, such as pyrimidine and triazine, were introduced into these host materials to improve their electron-transporting properties.

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of DFT calculation, UV-vis absorption spectra, phosphorescence lifetime of codeposited films, and energy diagrams of OLEDs. See DOI: 10.1039/c6tc04979f



The azine units are expected to interact with electron-donating moieties such as arylamines and carbazoles to form exciplexes.^{6,7} Furthermore, the azine units are connected via meta-conjugation to enhance the solubility in organic solvents and film uniformity to prevent crystallization of solid films. Prior to preparing the materials, we conducted a density functional theory (DFT) calculation using the Gaussian 09 program package. The molecular structures of the employed materials are shown in Fig. 1, and all the calculated data are summarized in Table 1. The DFT calculation indicated that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are completely separated; the HOMO is located on the DBT unit, whereas the LUMO is located on the azine unit (Fig. S1, ESI[†]). The HOMO energy levels were calculated to be approximately 6.00 eV, and the LUMO energy levels were approximately 2.10 eV. We also calculated the triplet energy (E_T) by TD-DFT calculations. The studied derivatives had high $E_{\rm T}$ values of over 2.90 eV, which are sufficiently high to confine the triplet excitons on the phosphorescent emitter (DPQ)₂Ir (dpm) ($E_{\rm T}$ = 1.95 eV).

The synthetic route to the DBT-azine derivatives is shown in Schemes S1–S5 (ESI†). Three derivatives were easily synthesized on a multigram scale *via* Suzuki–Miyaura cross-coupling reactions with dibenzothiophene-containing boron derivatives and azine-containing bromides in 62–81% yields. The products were purified by column chromatography and train sublimation, and confirmed using ¹H and ¹³C NMR and mass spectrometry. The purities were confirmed by high-performance liquid chromatography to be over 99.0%.

We investigated the thermal properties, including the glass transition temperature (T_g), melting point (T_m), and decomposition temperature (T_{d5}), using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen flow. The thermal properties are listed in Table 1. Among these materials, **4DBT46TRZ** showed a high T_g of over 100 °C, which

led to the ability of **4DBT46TRZ** to form an amorphous film with good thermal stability. Actually, DBT-azine derivatives gave smooth films with a small roughness of approximately 0.2 nm (Fig. S2, ESI†). The ionization potential (I_p) was obtained by photoelectron yield spectroscopy (PYS) in a vacuum of 10^{-3} Pa. The DBT-azine derivatives showed I_p values of approximately 6.2 eV. The UV-vis absorption edges of the DBT-azine derivatives were located at nearly the same wavelength of 350 nm, which is equivalent to an energy gap (E_g) of approximately 3.54 eV. The electron affinities (E_a) were estimated from the I_p and E_g values at 2.71 eV for **4DBT46PM**, 2.71 eV for **4DBT26PM**, and 2.79 eV for **4DBT46TRZ**. The electron affinity (E_a) values were all estimated to be approximately 2.7 eV by subtracting E_g from I_p .

In the photoluminescence (PL) spectra (Fig. 2), the emission peaks (λ_{em}) were located at 405 nm for 4DBT46TRZ, 397 nm for 4DBT46PM, and 392 nm for 4DBT26PM. We then investigated exciplex formation between the DBT-azine derivatives and NPD. An exciplex is an excited complex formed between a donor material and an acceptor material. The donor material contains electrondonating groups such as triphenylamine and carbazole derivatives, while the acceptor material contains electron-withdrawing groups such as pyrimidine and triazine. Therefore, the DBT-azine derivatives can be expected to form exciplexes with NPD. To confirm exciplex formation, we recorded the UV-vis absorption and PL spectra of co-deposited films of DBT-azine derivatives and NPD (1:1 weight ratio). The additional absorption peak derived from the chargetransfer (CT) complex was not observed in the UV-vis absorption spectra (Fig. S3, ESI⁺). The DBT-azine derivatives showed strong absorption derived from π - π * transition around 260 nm and broad absorption derived from $n-\pi^*$ transition around 330 nm. In contrast, in the PL spectra of the co-deposited films, a novel emission, completely different from those of the DBT-azine derivatives and NPD, was observed at 522 nm for 4DBT46TRZ, 495 nm for 4DBT46PM, and 500 nm for 4DBT26PM. These novel emissions can be attributed to the exciplexes.

We then evaluated the $\eta_{\rm PL}$ values of exciplex host films doped with 1 wt% (DPQ)₂Ir(dpm). The $\eta_{\rm PL}$ value was measured under N₂ flow using an integrating sphere excited at 330 nm using a multichannel spectrometer as the optical detector. The $\eta_{\rm PL}$ values were measured to be 52% to 54%. The transient phosphorescence spectra of the (DPQ)₂Ir(dpm)-doped exciplex host films were recorded at room temperature. The phosphorescence decay curves showed a single exponential decay curve with a phosphorescence lifetime ($\tau_{\rm p}$) of approximately 1.0 µs (Fig. S4, ESI†). Thus, these exciplex hosts can confine the triplet excitons of (DPQ)₂Ir(dpm).

Table 1 Physical properties of DBT-azine derivatives						
	$T_{\rm g}{}^a/T_{\rm m}{}^a/T_{\rm d5}{}^b \left[^{\circ}{ m C}\right]$	HOMO/LUMO/ $\Delta E_{\mathrm{H-L}}^{c}$ [eV]	$E_{\rm S}/E_{\rm T}/\Delta E_{\rm ST}^d$ [eV]	$I_{\rm p}^{\ e}/E_{\rm g}^{\ f}/E_{\rm a}^{\ g}$ [eV]	${\Phi_{ ext{PL}}}^h$ [%]	
4DBT46PM 4DBT26PM 4DBT46TRZ	92/n.d./445 88/261/444 104/248/438	5.96/2.10/3.86 5.97/2.09/3.88 6.04/2.22/3.82	3.59/2.90/0.69 3.63/2.93/0.70 3.55/2.94/0.61	6.25/3.54/2.71 6.25/3.54/2.71 6.23/3.44/2.79	$53 \pm 1 \\ 52 \pm 1 \\ 54 \pm 1$	

^{*a*} Determined by DSC measurements. ^{*b*} Obtained from TGA. ^{*c*} Calculated at the RB3LYP 6-311(d,p)//RB3LYP 6-31G(d) level; $\Delta E_{H-L} =$ HOMO-LUMO. ^{*d*} E_S and E_T are energies from TD-DFT at the RB3LYP 6-31G(d)//RB3LYP 6-31G(d) level; calculated using E_S and E_T . ^{*e*} Obtained from PYS. ^{*f*} Taken as the point of intersection of the normalized absorption spectra. ^{*g*} Calculated using I_p and E_g . ^{*h*} Φ_{PL} of the DBT-host:NPD film doped with 1 wt% Ir(DPQ)₂(dpm).



To investigate the functionality of the exciplex hosts, we fabricated OLEDs using the $(DPQ)_2Ir(dpm)$ -doped exciplex hosts as emission layers. We used 1,4-di(1,10-phenanthrolin-2-yl)benzene $(DPB)^8$ as an electron transporter, and 8-quino-linolatolithium (Liq) as an electron-injection layer. The structures of the resultant devices were [ITO (130 nm)/triphenylamine-containing polymer: 4-isopropyl-4-methyldiphenyl-iodonium

tetrakis(pentafluorophenyl)borate (PPBI)9 (20 nm)/NPD (20 nm)/ NPD:DBT-azine derivatives: (DPQ)₂Ir (dpm) (50:50:1) (wt/ratio) (40 nm)/DBT-azine derivatives (20 nm)/DPB (30 nm)/20 wt% Liq doped DPB (20 nm)/Liq (1 nm)/Al (80 nm)]. The energy diagram of this device is shown in Fig. S5 (ESI[†]). The EL spectra showed deep-red emission with an EL emission peak at 670 nm and CIE coordinates of (0.63, 0.30) for 4DBT46PM, (0.68, 0.29) for 4DBT26PM, and (0.70, 0.29) for 4DBT46TRZ (Fig. S6, ESI⁺). When 4DBT46PM or 4DBT26PM was used as the host, weak exciplex emission was observed, likely because of the inefficient energy transfer from the exciplex host to the emitter. The **4DBT46TRZ**-based device showed the highest η_{ext} of 17.9% at 100 cd m^{-2} ; this record-breaking efficiency is approximately 1.6 times higher than the η_{ext} of the current state-of-the-art deep-red OLED.⁵ It can be considered that an EQE of nearly 18% is realized by a contribution of horizontal molecular orientation because Ir(DPQ)₂(dpm) is a heteroleptic complex.¹⁰ The current density-voltage-luminance (I-V-L)characteristics are shown in Fig. 3(a). The 4DBT46TRZ-based device showed a very low turn-on voltage (Von) of 2.41 V at 1 cd m^{-2} , while the **4DBT26PM**-based device showed a higher $V_{\rm on}$ of 3.66 V. To investigate the differences in the device performances, we fabricated and evaluated electron only devices with a structure of [ITO (130 nm)/DPB (40 nm)/DBTazine derivatives (40 nm)/DPB (30 nm)/20 wt% Liq doped DPB (20 nm)/Liq (1 nm)/Al (80 nm)]. The energy diagram of the electron only device is shown in Fig. S7 (ESI†). As a result, 4DBT46PM showed superior electron transporting ability than 4DBT26PM (Fig. S8, ESI[†]). At this stage, it can be deduced that 4DBT46PM has less steric bulkiness around the electron cloud of LUMO compared to 4DBT26PM leading to better overlapping of LUMOs for higher electron mobility. The η_{ext} -luminance characteristics are shown in Fig. 3(b). Compared with the 4DBT26PM-based device, the 4DBT46TRZbased device showed a much higher current density due to the deeper $E_{\rm a}$, which is attributed to the superior electron injection from DPB. Moreover, the 4DBT46TRZ-based device showed a long device lifetime (LT₇₀) of approximately 890 h at 7.75 mA cm⁻² (Fig. 3(c)), which is equivalent to approximately 5,000 cd m⁻² for a yellow OLED ($\lambda_{\rm EL}$ = 585 nm).⁷ Assuming that the acceleration factor is 1.5, the device lifetime is equivalent to an LT_{70} of approximately 1970 h at 100 cd m⁻² $(4.04 \text{ mA cm}^{-2})$. All the device performances are summarized in Table 2.

In conclusion, we designed and synthesized a series of DBT-azine host materials. By combining DBT-azine and NPD as an exciplex-forming host system, we developed highly efficient and long-lifetime deep-red OLEDs with an η_{ext} of nearly 18% and an LT₇₀ of 890 h at 7.75 mA cm⁻² (1970 h at 4.04 mA cm⁻²). These results clearly show the strong advantages of an exciplex host system that can create superior carrier balance by changing the ratio of hole-transporting and electron-transporting hosts without preparing the materials for realizing high η_{ext} , low-driving voltage, and long-lifetime deep-red OLEDs. Finally, the achieved η_{ext} is 1.6 times higher than that of the current state-of-the-art deep-red OLED.⁵



Fig. 3 Device performances: (a) J-V-L characteristics, (b) $\eta_{ext}-L$ characteristics (inset: EL spectra), and (c) normalized luminance of a (DPQ)₂Ir(dpm) emitterbased OLED as a function of operating time at an initial luminance of approximately 170 cd m⁻².

Table 2	Summary	of OLED	performances
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	V_{on}^{a} [V]	$\frac{V_{100}/\eta_{\rm p,100}/\eta_{\rm c,100}/\eta_{\rm ext,100}}{[\rm V/lm~W^{-1}/cd~A^{-1}/\%]}$	$\frac{V_{1000}/\eta_{\rm p,1000}/\eta_{\rm c,1000}/\eta_{\rm ext,1000}}{[\rm V/lm~W^{-1}/cd~A^{-1}/\%]}$
4DBT46PM	2.61	3.65/2.03/2.36/15.0	5.89/0.99/1.87/11.6
4DBT26PM	3.66	4.93/1.49/2.34/16.6	7.00/0.86/1.93/12.7
4DBT46TRZ	2.41	3.50/2.21/2.47/17.9	5.80/1.06/1.96/13.5

^{*a*} Turn-on voltage (V_{on}) at 1 cd m⁻². ^{*b*} Driving voltage (V), power efficiency (η_p), current efficiency (η_c), and external quantum efficiency (η_{ext}) at 100 cd m⁻². ^{*c*} V, η_p , η_c , and η_{ext} at 1000 cd m⁻².

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Notes and references

- (a) J. Kido, M. Kimura and K. Nagai, *Science*, 1995, 267, 1332;
 (b) Y. Sun, N. C. Giebink, H. Kannno, B. Ma, M. E. Thompson and S. R. Forrest, *Nature*, 2006, 440, 998; (c) S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lüssem and K. Leo, *Nature*, 2009, 459, 234; (d) M. G. Helander, Z. B. Wang, J. Qiu, M. T. Greiner, D. P. Puzzo, Z. W. Liu and Z. H. Lu, *Science*, 2011, 332, 944; (e) T.-H. Han, Y. Lee, M.-R. Choi, S.-H. Woo, S.-H. Bae, B. H. Hong, J.-H. Ahn and T.-W. Lee, *Nat. Photonics*, 2012, 6, 105.
- 2 (a) H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, *Nature*, 2012, 492, 234; (b) H. Sasabe and J. Kido, *J. Mater. Chem. C*, 2013, 1, 1699; (c) H. Sasabe and J. Kido, *Eur. J. Org. Chem.*, 2013, 7653.
- 3 (a) D. Tanaka, H. Sasabe, Y.-J. Li, S.-J. Su, T. Takeda and J. Kido, Jpn. J. Appl. Phys., 2007, 46, L10; (b) C. W. Lee and J. Y. Lee, Adv. Mater., 2013, 25, 5450; (c) K.-H. Kim, S. Lee, C.-K. Moon, S.-Y. Kim, Y.-S. Park, J.-H. Lee, J. W. Lee, J. Huh, Y. You and J.-J. Kim, Nat. Commun., 2014, 5, 4769; (d) Y. Seino, H. Sasabe, Y.-J. Pu and J. Kido, Adv. Mater., 2014, 26, 1612; (e) K.-H. Kim, J.-L. Liao, S. W. Lee, B. Sim, C.-K. Moon, G.-H. Lee, H. J. Kim, Y. Chi and J.-J. Kim, Adv. Mater., 2016, 28, 2526.
- 4 (a) J. W. Sun, J.-H. Lee, C.-K. Moon, K.-H. Kim, H. Shin and J.-J. Kim, *Adv. Mater.*, 2014, 26, 5684; (b) H. Kaji, H. Suzuki, T. Fukushima, K. Shizu, K. Suzuki, S. Kubo, T. Komino, H. Oiwa, F. Suzuki, A. Wakamiya, Y. Murata and C. Adachi, *Nat. Commun.*, 2014, 6, 8476; (c) T.-A. Lin, T. Chatterjee, W.-L. Tsai, W.-K. Lee, M.-J. Wu, M. Jiao, K.-C. Pan, C.-L. Yi, C.-L. Chung, K.-T. Wong and C.-C. Wu, *Adv. Mater.*, 2016, 28, 6976; (d) Y. Seino, S. Inomata, H. Sasabe, Y.-J. Pu and J. Kido, *Adv. Mater.*, 2016, 28, 2638.
- 5 (a) H. Fujii, H. Sakurai, K. Tani, K. Wakisaka and T. Hirao, *IEICE Electron. Express*, 2005, 2, 260; (b) J.-H. Jou, Y.-T. Su, M.-T. Hsiao, H.-H. Yu, Z.-K. He, S.-C. Fu, C.-H. Chiang, C.-T. Chen, C.-H. Chou and J.-J. Shyue, *J. Phys. Chem. C*, 2016, 120, 18794; (c) S. Wang, X. Yan, Z. Cheng, H. Zhang, Y. Liu and Y. Wang, *Angew. Chem., Int. Ed.*, 2015, 54, 13068; (d) M. Ikai, F. Ishikawa, N. Aratani, A. Osuka, S. Kawabata, T. Kajioka, H. Takeuchi, H. Fujikawa and Y. Taga, *Adv. Funct. Mater.*, 2006, 1, 515; (e) M. Shimizu, R. Kaki, Y. Takeda, T. Hiyama, N. Nagai, H. Yamagishi and H. Furutani, *Angew. Chem., Int. Ed.*, 2012, 51, 4095.
- 6 K. Goushi, K. Yoshida, K. Sato and C. Adachi, *Nat. Photonics*, 2012, **6**, 253.
- 7 S. Seo, S. Shitagaki, N. Ohsawa, H. Inoue, K. Suzuki, H. Nowatari and S. Yamazaki, *Jpn. J. Appl. Phys.*, 2014, 53, 042102.
- 8 Y.-J. Pu, G. Nakata, H. Satoh, H. Sasabe, D. Yokoyama and J. Kido, *Adv. Mater.*, 2012, **24**, 1765.
- 9 J. Kido, G. Harada, M. Komoda, H. Shinomiya and K. Nagai, ACS Symp. Ser., 1997, 672, 381.
- 10 (a) D. Yokoyama, *J. Mater. Chem.*, 2011, 21, 19187;
 (b) M. Flämmich, J. Frischeisen, D. S. Setz, D. Michaelis,
 B. C. Krummacher, T. D. Schmidt, W. Brütting and N. Danz, *Org. Electron.*, 2011, 12, 1663.