

Influence of material impurities in the hole-blocking layer on the lifetime of organic light-emitting diodes

Hiroshi Fujimoto,^{1,2,a)} Masayuki Yahiro,^{1,2,3} Satoshi Yukiwaki,¹ Keiko Kusuhara,² Nozomi Nakamura,^{2,4} Takashi Suekane,⁵ Hong Wei,⁶ Katsuya Imanishi,⁷ Ko Inada,² and Chihaya Adachi^{1,2,3,4,8,b)}

¹Fukuoka i³-Center for Organic Photonics and Electronics Research (i³-OPERA), 5-14 Kyudai-shinmachi, Nishi, Fukuoka 819-0388, Japan

²Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan

³Institute of System, Information Technology and Nanotechnology (ISIT), 2-1-22 Momochihama, Sawara, Fukuoka 819-0395, Japan

⁴International Institute for Carbon Neutral Energy Research (WPI-I²CNER), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan

⁵Technology Innovation Center, Sumika Chemical Analysis Service, Ltd. (SCAS), 7-5, Kikumoto-cho 1-chome, Niihama, Ehime 792-0801, Japan

⁶Osaka Laboratory, Sumika Chemical Analysis Service, Ltd. (SCAS), 1-135, Kasugade-Naka 3-chome, Konohana-ku, Osaka 554-0022, Japan

⁷Technology Innovation Center, Sumika Chemical Analysis Service, Ltd. (SCAS), 1-135, Kasugade-Naka 3-chome, Konohana-ku, Osaka 554-0022, Japan

⁸Japan Science and Technology Agency (JST), ERATO, Adachi Molecular Exciton Engineering Project, Fukuoka 819-0395, Japan

(Received 23 August 2016; accepted 29 November 2016; published online 16 December 2016)

We evaluated the influence of impurities in an organic material used for the fabrication of organic light-emitting diodes (OLEDs) on the lifetime of the fabricated devices. Despite no differences in the current-density–voltage characteristics and external quantum efficiencies of the devices, the lifetime was approximately nine times longer for devices with high-purity 2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine (T2T), which was used as a hole-block layer. Chlorine-containing impurities derived from T2T had the greatest influence on the lifetime of the OLEDs even though the amount of halogen in the source material was at most 0.9 ppm. On the other hand, the lifetime was not greatly influenced by other impurities even with concentrations up to 0.2%. Therefore, the purities of materials other than the emitter must also be closely controlled. *Published by AIP Publishing.*

[<http://dx.doi.org/10.1063/1.4972055>]

Organic light-emitting diodes (OLEDs) offer greater artificial contrast ratios and wider viewing angles than the liquid crystal displays because of their self-luminescence. Therefore, the development of a next generation of commercially viable smart phone displays, large-screen television, and flexible displays based on OLEDs has intensified around the world in recent years.^{1–3} Such devices require organic materials with high efficiencies and long lifetimes under electrical operation. For achieving a high efficiency, emitter materials based on phosphorescence and thermally activated delayed fluorescence (TADF) were developed and can reach the internal quantum efficiencies (η_{int}) of 100%.^{4–6} However, since the light extraction efficiency is often limited to around 20%, efforts have been growing to improve the light outcoupling efficiency.^{7–12} While reasonably long lifetimes have been achieved in these high-efficiency devices, further improvements through the development of highly durable device structures and organic materials based on the concurrently evolving understanding of degradation mechanisms are underway.^{13–26}

The degradation mechanisms affecting the lifetime of OLEDs can be either intrinsic or extrinsic. Degradation

mechanisms intrinsic to the organic materials or device structure include interfacial degradation such as at the organic/cathode or organic/anode interface,^{13,14} trap formation,¹⁵ and quencher formation.^{16–18} Reported sources of extrinsic degradation include residual water in the vacuum chamber during fabrication,^{19,20} impurities on the indium tin oxide (ITO) substrate surface,^{21–23} halogen impurities in the organic material,^{24,25} and impurities floating in the vacuum chamber.²⁶ Such impurities can have a significant effect on the lifetime of devices.

In this study, we investigate the impurities in an OLED material used as a hole-blocking layer (HBL) and their impact on the lifetime of highly efficient TADF-based OLEDs. We find that the lifetime is significantly different even though similar initial characteristics are obtained for the devices. We show that the lifetime dependence in this case was related to the synthesis lot of the HBL material 2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine (T2T) in our device and report the origin of this dependence.

Devices were fabricated by thermal evaporation on ITO-coated glass substrates (Atsugi Micro Co., Ltd.), which were pre-patterned with polyimide bank structures to define an active device area of 0.04 cm². The materials used in this experiment include 1,4,5,8,9,11-hexaazatriphenylenehexa-carbonitrile (HAT-CN) as the hole-injection layer (HIL),

^{a)}fujimoto@opera.kyushu-u.ac.jp

^{b)}adachi@cstf.kyushu-u.ac.jp

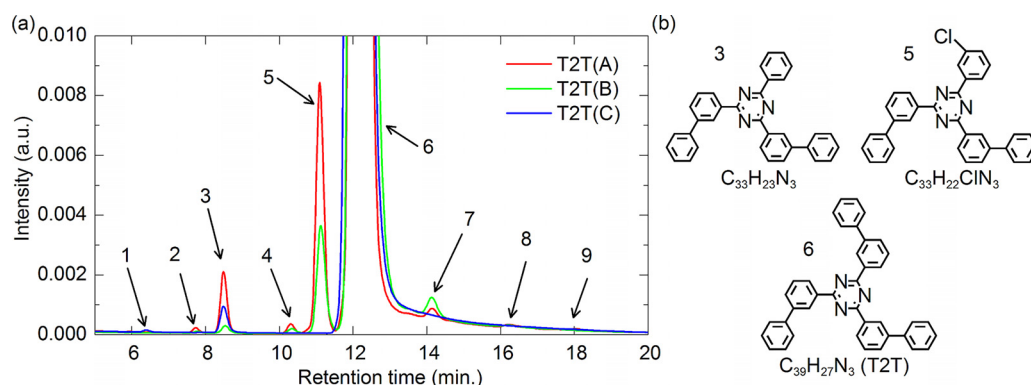


FIG. 1. (a) Chromatograms of three synthesis lots of T2T. (b) Structures of some of the materials that could be tentatively assigned peaks 3 and 5 in the LC-MS signals along with the structure of T2T (peak 6).

9,9',9''-triphenyl-9H,9'H,9''H-3,3':6',3''-tercarbazole (Tris-PCz) as hole-transport layer, 3,3-di(9H-carbazol-9-yl)biphenyl (mCBP) doped with (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl) isophthalonitrile (4CzIPN) as emitter layer, T2T as HBL, 2,7-bis(2,2'-bipyridine-5-yl)triphenylene (Bpy-TP2) as electron-transport layer, and LiF as electron-injection layer. Cathodes were deposited by the evaporation of Al. The device structure was ITO/HAT-CN (10 nm)/Tris-PCz (30 nm)/15% 4CzIPN:mCBP (30 nm)/T2T (10 nm)/Bpy-TP2 (40 nm)/LiF (0.8 nm)/Al (100 nm). Three synthesis lots (A, B, and C) of the material T2T were prepared, with lots A and B being synthesized in-house via the same route and lot C being synthesized by an outside source via an undisclosed route. All lots of T2T were purified in-house by sublimation before use.

An external quantum efficiency measurement system (C9920-12, Hamamatsu Photonics K. K.) was used to measure the current-density (J)-voltage (V) characteristics and external quantum efficiencies (η_{ext}) of the OLEDs. Device lifetimes were measured with a lifetime measurement system (System Giken Co., Ltd.) at a constant temperature of 30 °C and a constant current for an initial luminance of 1000 cd/m². High-performance liquid chromatography coupled to UV detection and mass spectrometry (LC-UV/MS) analyses were performed to measure the material purity using a Waters e2695 liquid chromatography system equipped with a Waters 2489 UV/Visible detector and a Waters 3100 mass detector. The amount of halogen in the material was measured using a Dionex DX-600 ion chromatography system and conductivity detector (Thermo Fisher Scientific Inc.). Thermally-stimulated current (TSC) has been widely used to analyze and evaluate the carrier traps in organic materials and to investigate the degradation in OLEDs.²⁷ TSC characteristics were measured to analyze the carrier traps in the devices using a TSC-FETT EL2000 (Rigaku Co.). The device being measured was cooled to 90 K using liquid nitrogen and then biased with a constant current flow of 1 mA/cm² for 2 min to fill the traps with charge carriers. The TSC current generated by the charge carriers being thermally activated from traps was measured using a collection bias of 0.01 V while increasing the temperature by 5 K/min until 340 K.

Figure 1(a) shows chromatograms for three synthesis lots (A, B, and C) of the material T2T, and Fig. 1(b) shows estimated structures of three of the detected materials, with **Peak**

6 corresponding to the principal body of T2T. The material purities of T2T (A), T2T (B), and T2T (C) measured by LC-UV were 99.0%, 99.6%, and 99.9%, respectively. Although we measured LC-UV for up to 30 min, no additional peaks or impurities were observed after 20 min. **Peak 5** corresponds to an impurity containing a halogen (Cl). The amount of halogen in T2T (A) was 0.9 ppm as determined by ion chromatography. The initial characteristics (J - V - η_{ext} characteristics) of the devices using these different lots of T2T were all very similar (Figs. 2(a) and 2(b)). However, the lifetimes until a 10% drop in luminance (LT90) were 30 h, 59 h, and 516 h in the order of increasing material purity, with corresponding increases in driving voltage of 0.26 V, 0.20 V, and 0.11 V, respectively (Fig. 2(c)). The increase in lifetime by approximately nine times with a small increase of material purity from 99.6% for T2T (B) to 99.9% for T2T (C) indicates the strong influence of purity on lifetime.

To more closely evaluate the influence of impurities on the device lifetime, the amounts of impurities 3 and 5 were plotted along with the lifetimes as shown in Fig. 3(b). Similar plots for the other peaks, which were found in significantly lower amounts compared to 3 and 5, are provided in Fig. 3(c). While a correlation between the lifetime and the amount of impurity 3 was not observed, the lifetime clearly improved as the amount of impurity 5 reduced. These results suggest that impurity 5, which is a Cl-containing compound, influences the lifetime. Similar correlations for impurities 2, 4, 8, and 9, the structures of which are unknown, were also observed (Fig. 3(c)). Although these impurities may also influence the lifetime, the amount of these impurities is much smaller since the LC-UV area ratio of these impurities were smaller than those of **Peaks 5** and **3** by 1 and 2 orders of magnitude (see [supplementary material](#) Note 1 for details). Therefore, the influence on the lifetime of impurities 2, 4, 8, and 9 is likely much smaller than that of the halogen-containing compound corresponding to **Peak 5**. On the other hand, impurities 1, 3, and 7 increased in T2T (B) or T2T (C) even though these devices had longer lifetimes, suggesting that these impurities have a much smaller impact on the lifetime. Thus, the strength of the influence on lifetime varies from impurity to impurity.

Generally, halogens have a great influence on the lifetime of OLEDs.^{24,25} Halogens from such compounds can be released due to the electrochemical degradation when current

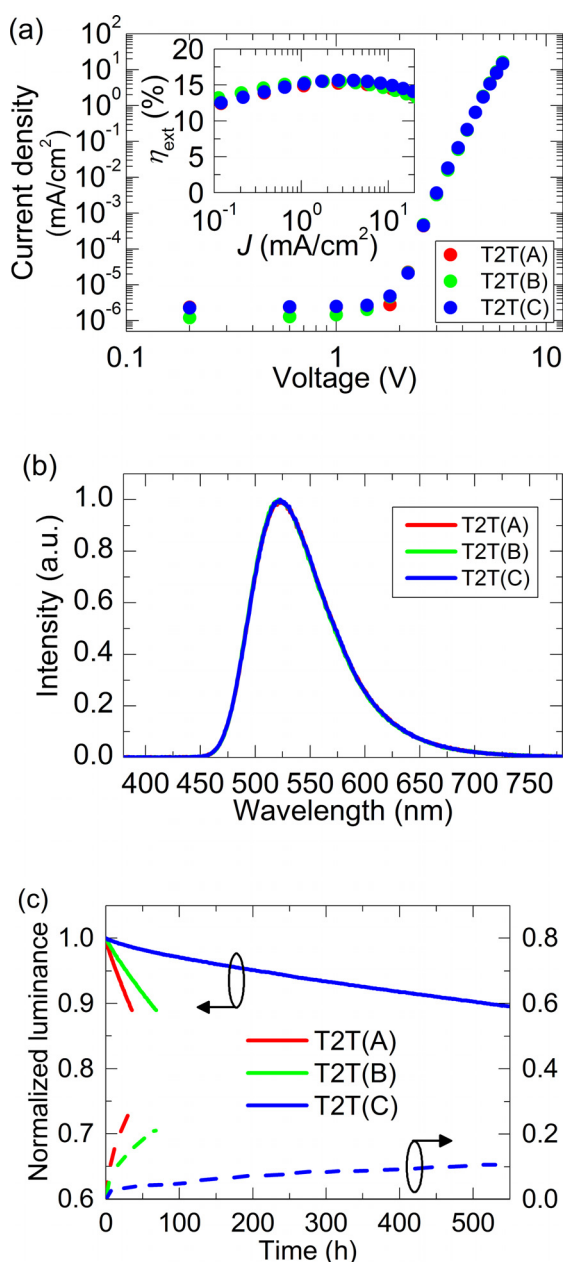


FIG. 2. (a) Representative J - V and (inset) η_{ext} - J characteristics, and (b) emission spectra at $J = 1 \text{ mA}/\text{cm}^2$ of devices fabricated with different lots of T2T and the structure ITO (100 nm)/HAT-CN (10 nm)/Tris-PCz (30 nm)/15% 4CzIPN:mCBP (30 nm)/T2T (10 nm)/Bpy-TP2 (40 nm)/LiF (0.8 nm)/Al (100 nm). (c) Luminance and change in the driving voltage as a function of time for OLEDs fabricated with lots of T2T and driven at a constant current for an initial illumination of $1000 \text{ cd}/\text{m}^2$.

flows through the device and move to the anode side as free halogen anions. In TADF-based OLEDs, the light-emitting site is mainly located in the vicinity of the 4CzIPN-doped mCBP/T2T interface since the hole-transporting mCBP is more abundant than the electron-transporting 4CzIPN.²⁸ Therefore, free halogen anions from T2T may diffuse toward the light-emitting site and act as quenchers, considerably decreasing the lifetime.²⁴ Through such a mechanism, the lifetime may be significantly decreased by the halogen-containing impurities in concentration of only 0.3%, even with source materials that have high purities such as 99.6%. In the most impure lot, the amount of Cl measured by ion chromatography was only 0.9 ppm, a figure which includes

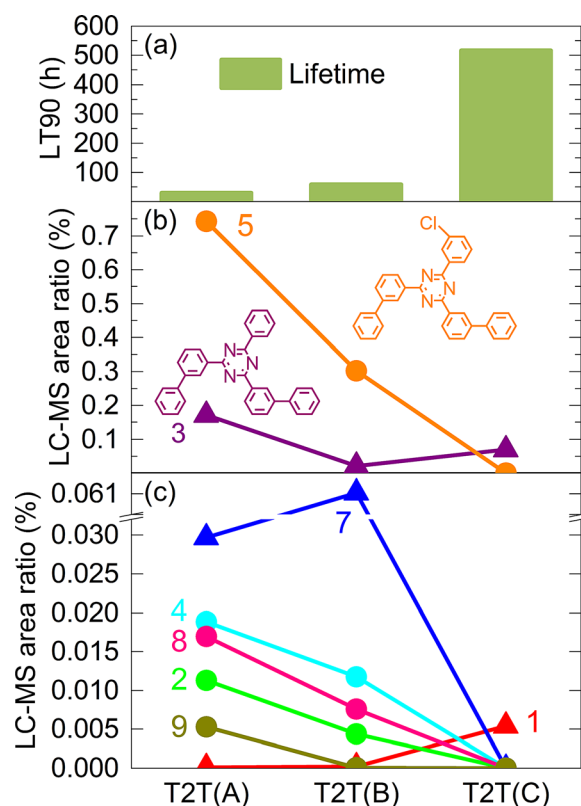


FIG. 3. (a) Device lifetime for OLEDs fabricated with the lots of T2T. (b) Relationship between lifetime and amounts of impurities 3 and 5, and (c) impurities 1, 2, 4, 7, 8, and 9 corresponding to the peaks in Fig. 1(a).

both free Cl and Cl incorporated into molecules. This highlights how large of an impact such extremely small amounts of halogen can have on the lifetime of OLEDs. On the other hand, the lifetime was not influenced by impurities such as 3 even in a concentration of approximately 0.1%–0.2%. Thus,

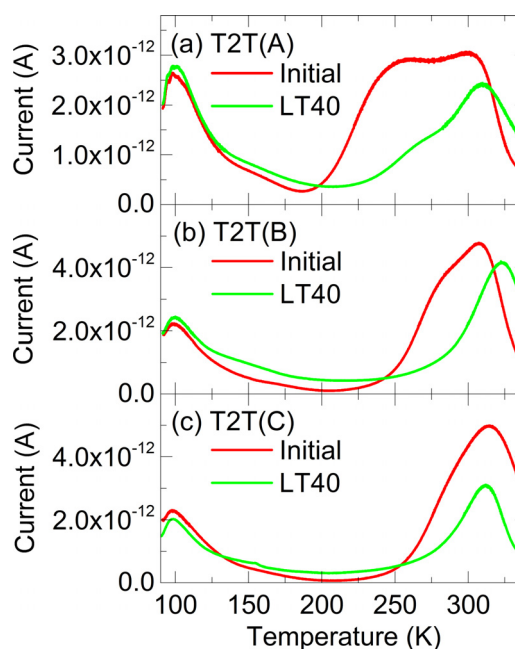


FIG. 4. The TSC spectra of OLEDs with (a) T2T(A), (b) T2T(B), and (c) T2T(C) before lifetime testing (initial) and LT40 at a constant current density of $10 \text{ mA}/\text{cm}^2$.

the removal of impurities should target those that actually affect the lifetime.

To investigate the cause of the increasing driving voltage, traps in the devices before and after driving at a constant current of 10 mA/cm² until LT40 using T2T(A), T2T(B), and T2T(C) were measured by TSC (Fig. 4). The total number of traps and the number of energies at which traps are found in the range of 250–300 K increased with the amount of impurities. In this range, many of the shallower traps disappeared after degradation for devices with T2T(A) and T2T(B) (Figs. 4(a) and 4(b)). On the other hand, the trap spectral shape of the device with the highest purity T2T barely changed after degradation (Fig. 4(c)). Based on these results, the increase of driving voltage is attributed to an increased injection barrier at the interface and/or decreased carrier mobility in the organic layers.²⁹

In a previous report, the accumulation of extra carriers in deep traps formed near the hole-transport layer (HTL)/emission layer (EML) interface caused dissociative reactions of arylamines of the HTL materials, leading to a significant increase of driving voltage.^{29,30} Such degradation has been ascribed to the breaking of molecular bonds when a high energy polaron is formed by exciton-polaron annihilation between excitons and accumulated carriers in the traps,^{31,32} and Tsang *et al.* have demonstrated a reduction in traps and increase in lifetime by introducing ultrathin interlayers of 8-hydroxyquinolino lithium on both sides of the T2T layer in a device with the same structure as ours.³² Thus, the additional traps formed for impure T2T may increase the exciton-polaron annihilation, leading to the degradation of organic materials and thereby increasing the driving voltage and reducing the lifetime. Since the amount of impurities in our experiments is very small, the traps might disappear after device degradation. Furthermore, the high polarity of Cl-containing compounds (supplementary material, Table S1) originating from the high electronegativity of the halogen makes such impurities especially likely to form traps.³³

In this device, we found that removing halogen-containing impurities in T2T greatly improved the lifetime. This is despite the impurities being contained in a material that does not contribute to emission. Therefore, the purity of materials other than the emitters must be carefully considered. Furthermore, in this paper, these impurities were still present in the materials even though they had been purified by sublimation. These results highlight the importance of using materials with a sufficiently high purity when evaluating the intrinsic properties of newly synthesized organic materials.

See supplementary material for discussion of the relative amounts of the impurities and the polarity of the impurities.

This work was supported in part by the International Institute for Carbon Neutral Energy Research (WPI-I²CNER) sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT). The help of Dr. William J. Potscavage, Jr., of Kyushu University in the

preparation of this manuscript is gratefully acknowledged. We also acknowledge Mr. Yasuhiro Hatae (i³-OPERA) for support with the density functional theory (DFT) calculations for T2T and impurities.

- ¹Y. H. Tak, C. W. Han, H. S. Kim, B. C. Kim, J. W. Kim, T. S. Kim, B. S. Kim, C. H. Oh, S. Y. Cha, and B. C. Ahn, *Proc. SPIE* **8829**, 88290R (2013).
- ²N. Ohsawa, S. Idojiri, K. Kumakura, S. Obana, Y. Kobayashi, M. Kataniwa, T. Ohide, M. Ohno, H. Adachi, N. Sakamoto, S. Yatsuzuka, T. Aoyama, and S. Yamazaki, *SID Symp. Dig. Tech. Pap.* **44**, 923 (2013).
- ³T. Tsujimura, J. Fukawa, K. Endoh, Y. Suzuki, K. Hirabayashi, and T. Mori, *J. Soc. Inf. Disp.* **22**, 412 (2014).
- ⁴C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *J. Appl. Phys.* **90**, 5048 (2001).
- ⁵A. Endo, M. Ogasawara, A. Takahashi, D. Yokoyama, Y. Kato, and C. Adachi, *Adv. Mater.* **21**, 4802 (2009).
- ⁶H. Uoyama, K. Goushi, K. Shizu, H. Nomura, and C. Adachi, *Nature* **492**, 234 (2012).
- ⁷T. Yamasaki, K. Sumioka, and T. Tsutsui, *Appl. Phys. Lett.* **76**, 1243 (2000).
- ⁸C. F. Madigan, M. H. Lu, and J. C. Sturm, *Appl. Phys. Lett.* **76**, 1650 (2000).
- ⁹S. Möller and S. R. Forrest, *J. Appl. Phys.* **91**, 3324 (2002).
- ¹⁰M. Fujita, T. Ueno, K. Ishihara, T. Asano, S. Noda, H. Ohata, T. Tsuji, H. Nakada, and N. Shimoji, *Appl. Phys. Lett.* **85**, 5769 (2004).
- ¹¹W. H. Koo, S. M. Jeong, F. Araoka, K. Ishikawa, S. Nishimura, T. Toyooka, and H. Takezoe, *Nat. Photonics* **4**, 222 (2010).
- ¹²H. Fujimoto, M. Yahiro, T. Kawashima, K. Konno, Q. Chen, K. Sawaya, S. Kawakami, and C. Adachi, *Appl. Phys. Express* **8**, 082102 (2015).
- ¹³T. Y. Chu, Y. H. Lee, and O. K. Song, *Appl. Phys. Lett.* **91**, 223509 (2007).
- ¹⁴R. Phatak, T. Y. Tsui, and H. Aziz, *J. Appl. Phys.* **111**, 054512 (2012).
- ¹⁵D. Y. Kondakov, J. R. Sandifer, C. W. Tang, and R. H. Young, *J. Appl. Phys.* **93**, 1108 (2003).
- ¹⁶F. So and D. Kondakov, *Adv. Mater.* **22**, 3762 (2010).
- ¹⁷D. Y. Kondakov, W. C. Lenhart, and W. F. Nichols, *J. Appl. Phys.* **101**, 024512 (2007).
- ¹⁸J. R. Gong, L. J. Wan, S. B. Lei, C. L. Bai, X. H. Zhang, and S. T. Lee, *J. Phys. Chem. B* **109**, 1675 (2005).
- ¹⁹H. Yamamoto, J. Brooks, M. S. Weaver, J. J. Brown, T. Murakami, and H. Murata, *Appl. Phys. Lett.* **99**, 033301 (2011).
- ²⁰H. Yamamoto, C. Adachi, M. S. Weaver, and J. J. Brown, *Appl. Phys. Lett.* **100**, 183306 (2012).
- ²¹Y. Fukushi, H. Kominami, Y. Nakanishi, and Y. Hatanaka, *Appl. Surf. Sci.* **244**, 537 (2005).
- ²²H. T. Lu and M. Yokoyama, *J. Cryst. Growth* **260**, 186 (2004).
- ²³D. Lu, Y. Wu, J. Guo, G. Lu, Y. Wang, and J. Shen, *Mater. Sci. Eng. B* **97**, 141 (2003).
- ²⁴A. Fleissner, K. Stegmaier, C. Melzer, H. von Seggern, T. Schwalm, and M. Rehahn, *Chem. Mater.* **21**, 4288 (2009).
- ²⁵H. Becker, I. Bach, M. Holbach, J. Schwaiger, and H. Spreitzer, *SID Symp. Dig. Tech. Pap.* **41**, 39 (2010).
- ²⁶H. Fujimoto, T. Suekane, K. Imanishi, S. Yukiwaki, H. Wei, K. Nagayoshi, M. Yahiro, and C. Adachi, *Sci. Rep.* **6**, 38482 (2016).
- ²⁷H. Fujimoto, W. J. Potscavage, Jr., T. Edura, and C. Adachi, *Org. Electron.* **15**, 2783 (2014).
- ²⁸H. Nakanotani, K. Masui, J. Nishide, T. Shibata, and C. Adachi, *Sci. Rep.* **3**, 2127 (2013).
- ²⁹S. Scholz, D. Kondakov, B. Lüssem, and K. Leo, *Chem. Rev.* **115**, 8449 (2015).
- ³⁰D. Y. Kondakov, *J. Appl. Phys.* **104**, 084520 (2008).
- ³¹N. C. Giebink, B. W. D'Andrade, M. S. Weaver, J. J. Brown, and S. R. Forrest, *J. Appl. Phys.* **105**, 124514 (2009).
- ³²D. P. K. Tsang, T. Matsushima, and C. Adachi, *Sci. Rep.* **6**, 22463 (2016).
- ³³Y. Noguchi, Y. Miyazaki, Y. Tanaka, N. Sato, Y. Nakayama, T. D. Schmidt, W. Brütting, and H. Ishii, *J. Appl. Phys.* **111**, 114508 (2012).