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# The hydrogen/deuterium isotope effect of the host material on the lifetime of organic light-emitting diodes†

Hayato Tsujii,\*<sup>ab</sup> Chikahiko Mitsui<sup>a</sup> and Eiichi Nakamura\*<sup>a</sup>

**The hydrogen/deuterium primary kinetic isotope effect provides useful information about the degradation mechanism of OLED host materials. Thus, replacement of labile C–H bonds in the host with C–D bonds increases the device lifetime by a factor of five without loss of efficiency, and replacement with C–C bonds by a factor of 22.5.**

Organic light-emitting diodes (OLEDs) being innovative devices for display and illumination,<sup>1,2</sup> their device lifetime and hence the mechanism of device degradation remain the most pressing subjects of research.<sup>3–5</sup> Many of the studies reported thus far have focused on the analysis of the degradation products,<sup>6</sup> while a few have reported on the kinetics of the molecular processes of the degradation.<sup>7</sup> We focused on the hydrogen/deuterium (H/D) primary kinetic isotope effect (KIE) as a mechanistic probe, where the rate of a chemical reaction slows down by a factor of 6.5 (a theoretical value at 298 K)<sup>8</sup> when the cleavage of the C–H(D) bond in question is the rate determining step in the overall reaction sequence.<sup>9–14</sup> We report here a finding that deuteration of the benzylic methyl groups in a green phosphorescent host material (*i.e.*, CH<sub>3</sub>CZBDF *vs.* CD<sub>3</sub>CZBDF in Fig. 1a) increases the device lifetime by a factor of five (from 0.2 h to 1.0 h) without affecting the other properties of the device much. This rate retardation factor of five is consistent with the KIE value reported for the heterolysis of a benzylic C–H bond.<sup>15</sup> Taking together the isotope effect and the resonance-stabilizing effect of a furan ring (Fig. 1b), we consider the degradation of the methyl group in CH<sub>3</sub>CZBDF to be involved as a critical step of the degradation process; that is, the molecule is oxidized to a radical cation (*i.e.*, hole formation) during operation of the OLED device and suffers from the loss of either a proton or a hydrogen radical. Guided by this analysis,

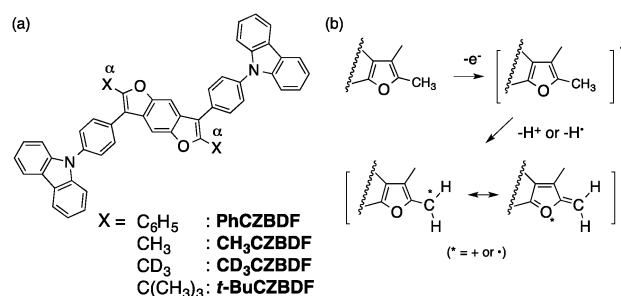


Fig. 1 Host materials discussed in this study. (a) Chemical structures of CZBDF derivatives and (b) a plausible degradation path of CH<sub>3</sub>CZBDF.

we replaced the heterolytically labile C–H bonds in CH<sub>3</sub>CZBDF with more stable C–CH<sub>3</sub> bonds (*t*-BuCZBDF) and found the lifetime to increase by a factor of 22.5 under the same device configuration. The lifetime enhancement by a factor of five through H to D change in the OLED performance makes an interesting contrast to a reported decrease of solar cell performance by 50% where no C–H(D) cleavage is involved.<sup>16</sup> These data indicate that isotope effects are of considerable practical and mechanistic values in organic electronic research.<sup>17,18</sup>

The host material CH<sub>3</sub>CZBDF, which we focus on in this work, was designed on the basis of our previous host material PhCZBDF (Fig. 1a),<sup>19–21</sup> whose triplet energy (T<sub>1</sub>) level of PhCZBDF, *ca.* 2.0 eV, was too low to be suitable as a host for green and blue phosphorescent OLEDs (PHOLEDs). We thus designed a less conjugated host CH<sub>3</sub>CZBDF in order to raise the T<sub>1</sub> level (Fig. 1a; synthesis in ESI†), having a concern about the device durability due to the intrinsically labile benzylic methyl groups (*cf.* Fig. 1b). Thus, we also synthesized the deuterated (CD<sub>3</sub>CZBDF) and the *tert*-butyl analogues (*t*-BuCZBDF) for comparison.

We first found that CH<sub>3</sub>CZBDF and CD<sub>3</sub>CZBDF have essentially the same photophysical properties. This is reasonable because the C–H(D) bonds are not directly involved in the photoexcitation processes (see ESI†, Table S1). The ionization potentials (IPs) of CH<sub>3</sub>CZBDF and CD<sub>3</sub>CZBDF were the same (6.04 and 6.03 eV, respectively), as determined using photoemission yield spectroscopy

<sup>a</sup> Department of Chemistry, School of Science, The University of Tokyo, Hongo,

Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: tsujii@chem.s.u-tokyo.ac.jp, nakamura@chem.s.u-tokyo.ac.jp

<sup>b</sup> JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

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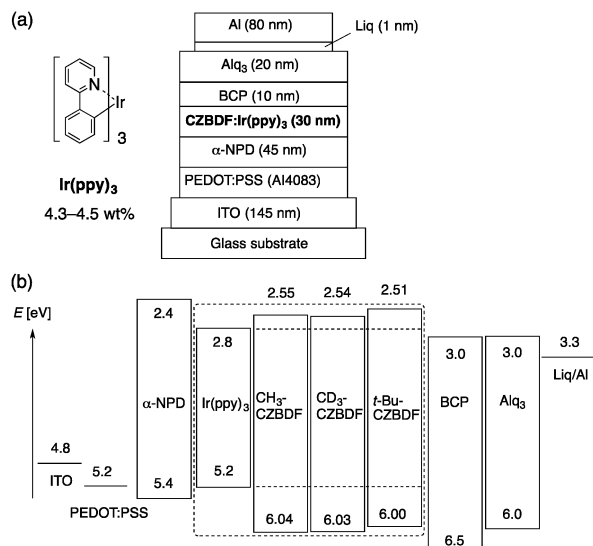


Fig. 2 Materials and device structure of the CZBDF-based PHOLEDs. (a) Chemical structure of Ir(ppy)<sub>3</sub> and device structure. (b) Energy diagram of the materials.

(PYS).<sup>22</sup> The IP of *t*-BuCZBDF was slightly lower (6.00 eV). The optical band gap ( $\Delta E_g$ ) was the same for all compounds (3.49 eV). Using the IP and the  $\Delta E_g$  values, the electron affinities (EAs) were calculated to be 2.55, 2.54 and 2.51 eV for CH<sub>3</sub>CZBDF, CD<sub>3</sub>CZBDF and *t*-BuCZBDF, respectively, which are large enough to confine carriers within green phosphorescent Ir(ppy)<sub>3</sub><sup>23</sup> (Fig. 2b). As determined by phosphorescence measurements at 77 K, the triplet energy levels ( $E_T$ ) are also high enough to suppress energy transfer from Ir(ppy)<sub>3</sub> ( $E_T = 2.4$  eV) to the host materials: 2.64, 2.65 and 2.67 eV for CH<sub>3</sub>CZBDF, CD<sub>3</sub>CZBDF and *t*-BuCZBDF, respectively.

PHOLED devices were fabricated using alkyl-CZBDF as a host material in the emission layer doped with green phosphorescent Ir(ppy)<sub>3</sub> with a standard heterojunction configuration as follows: ITO/PEDOT:PSS/ $\alpha$ -NPD/alkyl-CZBDF:Ir(ppy)<sub>3</sub>/BCP/Alq<sub>3</sub>/Liq/Al, where PEDOT:PSS and  $\alpha$ -NPD serve as hole injection and transport layers, BCP as a hole-blocking layer, and Alq<sub>3</sub> and Liq as electron transport and injection layers, respectively (Fig. 2a). The PEDOT:PSS layer was spin-coated, and the other layers were deposited under vacuum. Electroluminescence from Ir(ppy)<sub>3</sub> was observed from all devices (Fig. 3a), indicating that the carriers are appropriately confined within Ir(ppy)<sub>3</sub>.

A comparison of the performances of the CH<sub>3</sub>CZBDF- and CD<sub>3</sub>CZBDF-based devices indicates that deuteration of the host material significantly enhanced the device stability without affecting the electroluminescence spectra (Fig. 3a) and the device efficiency (Fig. 3b and c). Thus, the driving voltage and luminance efficiency at 1000 cd m<sup>-2</sup> ( $V_{1000}$  and  $\eta_{1000}$ , respectively) and external quantum efficiency (EQE) barely changed ( $V_{1000} = 7.0$  and 6.9 V;  $\eta_{1000} = 8.9$  and 8.4 lm W<sup>-1</sup>; EQE = 5.5 and 5.5% for devices A and B, respectively; Table 1). The maximum luminance of the CD<sub>3</sub>CZBDF device was higher than that of the CH<sub>3</sub>CZBDF device, 22 270 and 13 800 cd m<sup>-2</sup>, respectively, because the former device degraded much less during the measurement. In consonance

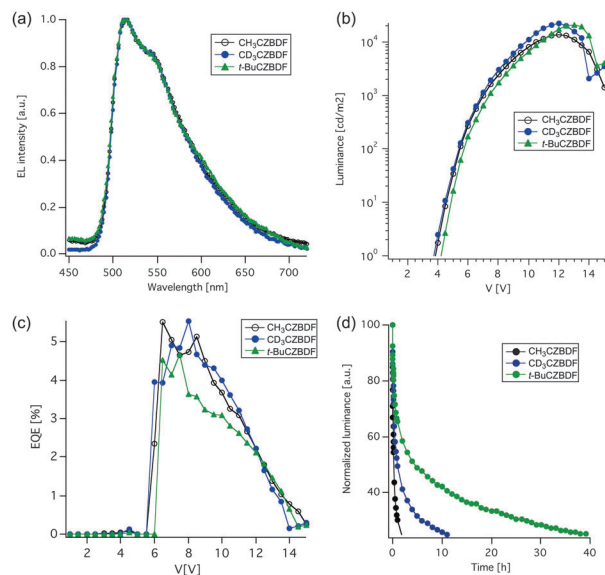


Fig. 3 Device performance of the CZBDF-based PHOLEDs. (a) EL spectra. (b)  $L$ - $V$  characteristics. (c) EQE- $V$  characteristics. (d) Normalized  $L$ - $t$  characteristics.

Table 1 Summary of the OLED performance data<sup>a</sup>

Host	$V_{1000}$ <sup>b</sup> [V]	$\eta_{1000}$ <sup>c</sup> [lm W <sup>-1</sup> ]	EQE <sub>max</sub> <sup>d</sup> [%]	$L_{max}$ <sup>e</sup> [cd A <sup>-1</sup> ]	$\tau_{1/2}$ <sup>f</sup> [h]
CH <sub>3</sub> CZBDF	7.0	8.9	5.5	13 800	0.2
CD <sub>3</sub> CZBDF	6.9	8.4	5.5	22 270	1.0
<i>t</i> -BuCZBDF	7.4	6.1	4.5	20 770	4.5

<sup>a</sup> These data were collected at a luminance of 1000 cd m<sup>-2</sup>. <sup>b</sup> Driving voltage. <sup>c</sup> Luminance efficiency. <sup>d</sup> Maximum external quantum efficiency. <sup>e</sup> Maximum luminance. <sup>f</sup> Device half-lifetime measured at a constant current density of 12.5 mA cm<sup>-2</sup>.

with this data, the half-life of the former was five times longer than the latter (1.0 h and 0.2 h, respectively, Fig. 3d and Table 1). This difference of stability is consistent with the reported KIE values for the heterolysis of a benzylic C-H bond,<sup>11,15</sup> and hence suggests that the degradation of the  $\alpha$ -methyl groups in CH<sub>3</sub>CZBDF (Fig. 1b) is a rate-determining step in this rapidly degrading device.

We next considered the possibility that the conversion of the  $\alpha$ -C-H bonds into heterolytically more stable C-C bonds will further elongate the device lifetime (Fig. 1a). Consistent with this expectation, the *t*-BuCZBDF device achieved a 22.5 times longer lifetime (Fig. 3d, Table 1) and higher maximum luminance (20 770 cd m<sup>-2</sup>) than the CH<sub>3</sub>CZBDF-based device. There were slight increases in the driving voltage (7.4 V) and lower efficiencies ( $\eta_{1000} = 6.1$  lm W<sup>-1</sup>, EQE = 4.5%), which was possibly caused by the difference of molecular packing.<sup>24</sup> In a similar vein, a similar device using PhCZBDF (having a heterolytically stable phenyl-furyl bond) has a very long lifetime of > 4000 h.<sup>19</sup>

In conclusion, we have shown that the hydrogen/deuterium exchange of a heterolytically labile C-H bond in an OLED host material increases the lifetime of the device. The deuterium atoms in CD<sub>3</sub>CZBDF did not change the device performance much except for the lifetime (and the maximum luminance which is related to the lifetime), because the photophysical and



electrical processes as well as morphological changes do not include C–H(D) bond cleavage (*cf.* secondary kinetic isotope effects). Identification of the heterolytically labile C–H bonds in CH<sub>3</sub>CZBDF then led us to replace these bonds with C–C bonds to achieve a further increase in the lifetime. We expect that some of the data reported in the literature and patents on the favourable effects of deuterated materials may be rationalized in terms of the kinetic and equilibrium isotope effects.

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