Supporting Information

Hydrogen/deuterium isotope effect of the host material on the lifetime of organic light-emitting diodes

by

Hayato Tsuji,^{*a,b,**} Chikahiko Mitsui^{*a*} and Eiichi Nakamura^{*a,**}

 ^a Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: tsuji@chem.s.u-tokyo.ac.jp, nakamura@chem.s.u-tokyo.ac.jp
^b JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

Experimental section

Instrumentation. Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on a JEOL ECA-500 (500 MHz) NMR spectrometer. Chemical shift data for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent (CDCl₃: δ 7.26, CDCl₂CDCl₂: δ 6.00). Carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 125 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent (CDCl₃: δ 77.0, CDCl₂CDCl₂: δ 74.0, acetone- d_6 : δ 29.8, 206.5). The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiplet resonances, br = broad, brs = broad singlet), coupling constant in Hertz (Hz), and integration. Train sublimation was performed on an ALS Technology P-HT100 instrument. Pressure was maintained below 20 mTorr by rotary pump. Melting points of solid materials were determined on a Mel-Temp II capillary melting-point apparatus and uncorrected. IR spectra recorded on a React IR 1000 Reaction Analysis System equipped with DuraSample IR (ASI Applied System) are reported in cm⁻¹. Routine mass spectra were acquired by atmospheric pressure ionization (APCI) using a time-of-flight mass analyzer on a JEOL JMS-T100LC (AccuTOF) spectrometer.

Materials. Unless otherwise noted, commercial reagents were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and used as purchased. Butyllithium was purchased from Kanto, passed over a pad of Celite under nitrogen and the concentration was determined by titration with menthol in the presence of 2,2'-bipyridyl. CD₃I was purchased from Isotec (minimum 99.5 atom%D). Anhydrous tetrahydrofuran (THF) was purchased from Wako Ltd., and purified by successively passing it over a molecular sieves column, then an alumina column. Lithium (dispersion) was purchased from Wako Co., and was washed with distilled hexane and dried over before use. The water content of the solvent was confirmed with a Karl-Fischer moisture titrator to be less than 20 ppm. Synthesis of

2,5-Bis(1-propynyl)-1,4-benzenediol has been already reported.¹

1. Synthesis

3,7-Bis[4-(N-carbazolyl)phenyl]-2,6-dimethylbenzo[1,2-b:4,5-b']difuran



A solution of *n*-butyllithium in hexane (0.38 mL, 1.56 mol/L, 0.60 mmol) was added to a solution of 2,5-di(1-propynyl)-1,4-benzenediol (55.9 mg, 0.300 mmol) in THF (0.3 mL) at 0 °C. The resulting yellow suspension was allowed to warm to ambient temperature and stirred for 30 min. After a solution of zinc chloride in THF (0.6 mL, 1.0 mol/L, 0.6 mmol) was added, the volatiles were removed in *vacuo*, and then toluene (0.6 mL) was added. The resulting yellow solution was heated to 120 °C and stirred for 3 h at this temperature. After cooling to ambient temperature, Pd₂(dba)₃·CHCl₃ (31.0 mg, 0.03 mmol), P(t-Bu)₃ in toluene (120 µL, 1.0 mol/L, 0.12 mmol), NMP (0.15 mL), and 4-bromophenylcarbazole (232 mg, 0.72 mmol) were successively added. The resulting mixture was stirred at 60 °C for 10 h. After cooling to ambient temperature, the reaction mixture was filtrated and washed several times with ethyl acetate. The resulting crude solid product was purified by gradient vacuum sublimation (pressure < 20 mTorr) at 320-330 °C to obtain the title compound (112 mg, 0.167 mmol, 56%) as a white powder. After extraction of the organic layer in the resulting mother liquor with CH₂Cl₂, solvent was removed in vacuo. The crude material was subjected to flash column chromatography on silica gel employing hexane:toluene (90:10-70:30) to afford the title compound (33 mg, 0.049 mmol, 16%). Total yield was 72%. Mp: 389 °C (TG-DTA). ¹H NMR (500 MHz, CDCl₂CDCl₂): δ 2.63 (s, 6H, CH₃), 7.29 (dd, J

¹ Mitsui, C.; Tanaka, H.; Tsuji, H.; Nakamura, E. Chem. Asian J. **2011**, *6*, 2296–2300.

= 7.5 Hz, 7.5 Hz, 4H, carbazole), 7.43 (dd, J = 8.1 Hz, 8.1 Hz, 4H), 7.52 (d, J = 8.1 Hz, 4H), 7.67 (d, J = 8.1 Hz, 4H, phenylene), 7.72 (s, 2H, benzodifuran), 7.75 (d, J = 8.5 Hz, 4H, phenylene), 8.13 (d, J = 7.5 Hz, 4H, carbazole). ¹³C NMR (125 MHz, CDCl₂CDCl₂): δ 13.2, 100.3, 110.0, 116.6, 120.2, 120.3, 123.7, 126.1, 126.5, 127.5, 130.3, 132.4, 136.8, 141.2, 151.5, 152.5. Anal. Calcd for C₄₈H₃₂N₂O₂: C, 86.20; H, 4.82; N, 4.19. Found: C, 86.32; H, 4.67; N, 4.06. MS (APCI+): 669 (M+1).

2-{2,5,-Bis[1-(3,3,3-²H₃)propynyl]-4-(tetrahydro-2*H*-2-pyranyloxy)phenoxy}tetrahydro-2*H*-pyran



A solution of *n*-butyllithium in hexane (6.66 mL, 1.56 mol/L, 10.4 mmol) was added to a suspension of 2-[2,5-diethynyl-4-(tetrahydro-2*H*-2-pyranyloxy)phenoxy]tetrahydro-2*H*-pyran (1.31 g, 4.00 mmol) in 15 mL THF at 0 °C. The resulting dark blue suspension was allowed to warm to ambient temperature and stirred for 30 min. After iodomethane- d_3 (996 µL, 16.0 mmol) was added, the resulting pale yellow suspension was stirred at ambient temperature for 22 h. After addition of water, organic layer was extracted with CH₂Cl₂. After removing the solvent *in vacuo*, the crude material was subjected to flash silica gel column chromatography employing hexane:ethyl acetate (97:3–90:10) to afford the titled compound (1.35 g, 94%) as white solid. Total yield was 94%. Mp: 178–179 °C (decomp); ¹H NMR (500 MHz, CDCl₃): δ 1.58–1.72 (m, 6H, *CH*₂), 1.80–1.87 (m, 2H, *CH*₂), 1.92–1.94 (m, 2H, *CH*₂), 2.00–2.08 (m, 2H, *CH*₂), 3.57–3.61 (m, 2H, OCH₂CH₂), 3.95–4.00 (m, 2H, OCH₂CH₂), 5.37 (s, 2H, OCHO), 7.08 (s, 2H, aromatic proton). ²D NMR (75 MHz, CDCl₃): δ 2.04 (s, 6D, CD₃). ¹³C NMR (125 MHz, CDCl₃): δ 18.5, 25.3, 30.3, 61.8, 75.9, 90.7, 97.5, 115.3, 121.1, 152.1. HRMS (APCI+) calcd for C₂₂H₂₁D₆O₄⁺ ([M + H]⁺) 361.2286, found: 361.2284.

2,5-Bis[1-(3,3,3-²H₃)propynyl]-1,4-benzenediol



p-Toluenesulfonic acid (28.5 mg, 0.150 mmol) was added to a suspension of 2-{2,5,-bis[1-(3,3,3- $^{2}H_{3})$ propynyl]-4-(tetrahydro-2*H*-2-pyranoyloxy) phenoxy}tetrahydro-2*H*-pyran (1.08 g, 3.00 mmol) in dichloromethane (30 mL) and methanol (15 mL). After stirring at ambient temperature for 30 min, solvent was removed *in vacuo* to 5 mL. The resulting white precipitate was collected by filtration and washed with Et₂O to afford the title compound (490 mg, 85%) as white solid. To the resulting mother liquor, sat. NaHCO₃ aqueous solution was added to quench the reaction. Organic layer was extracted twice with CH₂Cl₂, washed with brine, and then dried over MgSO₄. After removal of the solvent *in vacuo*, the crude material was subjected to flash silica gel column chromatography employing hexane:ethyl acetate (90:10–70:30) as an eluent to afford the titled compound (63 mg, 10%) as white solid. Total yield was 95%. Mp: 220–221°C (decomp); ¹H NMR (500 MHz, CDCl₃): δ 5.39 (s, 2H, OH), 6.83 (s, 2H, aromatic proton). ²D NMR (75 MHz, CDCl₂DCl₂): δ 2.04 (s, 6D, CD₃). ¹³C NMR (125 MHz, acetone-*d*₆): δ 3.7 (m), 75.9, 92.5, 112.7, 118.8, 151.7. HRMS (APCI+) calcd for C₁₂H₄D₆O₂ (M⁺) 192.1057, found: 192.1062.

3,7-Bis[4-(N-carbazolyl)phenyl]-2,6-di(²H₃)methylbenzo[1,2-b:4,5-b']difuran



A solution of *n*-butyllithium in hexane (3.85 mL, 1.56 mol/L, 6.00 mmol) was added to a solution of 2,5-bis[1-(3,3,3-²H₃)propynyl]-1,4-benzenediol (577 mg, 3.00 mmol) in

THF (3.0 mL) at 0 °C. The resulting yellow suspension was allowed to warm to ambient temperature and stirred for 30 min. After a solution of zinc chloride in THF (6.0 mL, 1.0 mol/L, 6.0 mmol) was added, the volatiles were removed in vacuo, and then toluene (6.0 mL) was added. The resulting yellow solution was heated to 120 °C and stirred for 3 h at this temperature. After cooling to ambient temperature, NMP (1.5 mL), Pd₂(dba)₃·CHCl₃ (311 mg, 0.30 mmol), P(t-Bu)₃ in toluene (1.2 mL, 1.0 mol/L, 1.2 mmol), and 4-bromophenylcarbazole (2.32 g, 7.20 mmol) were successively added. The resulting mixture was stirred at 60 °C for 22 h. After cooling to ambient temperature, the reaction mixture was filtrated and washed several times with ethyl The resulting crude solid was purified by gradient vacuum sublimation acetate. (pressure < 20 mTorr) at 350–360 °C to afford the title compound (2.07 mg, 69%) as a white powder. Mp: 384 °C (TG-DTA). ¹H NMR (500 MHz, CDCl₂CDCl₂) δ 7.29 (dd, J = 7.5 Hz, 7.5 Hz, 4H, carbazole), 7.43 (dd, J = 7.5 Hz, 7.5 Hz, 4H, carbazole), 7.52 (d, J = 7.5 Hz, 4H, carbazole), 7.67 (d, J = 8.0 Hz, 4H, phenylene), 7.72 (s, 2H, benzodifuran), 7.75 (d, J = 8.0 Hz, 4H, phenylene), 8.13 (d, J = 7.5 Hz, 4H). ²D NMR (75 MHz, CDCl₂CDCl₂, 100 °C): δ 2.64 (s, 6H, CD₃). ¹³C NMR (100 MHz, CDCl₂CDCl₂, 130 °C): δ 100.3, 110.0, 116.7, 120.2, 120.3, 123.8, 126.1, 126.6, 127.5, 130.3, 132.5, 137.0, 141.4, 151.6, 152.4, (CD₃ carbons were not observed due to the poor solubility and multiplicity). HRMS (APCI+) calcd for C₄₈H₂₇D₆N₂O₂ (M+H): 675.2919, found: 675.2905.

2-[2,5,-Bis(3,3-dimethylbut-1-ynyl)-4-(tetrahydro-2*H*-2-pyranoyloxy)phenoxy]tetra hydro-2*H*-pyran



Nitrogen was bubbled through a solution of piperidine (200 mL) for 30 min. 2-[2,5-Dibromo-4-(tetrahydro-2*H*-2-pyranyloxy)phenoxy]tetrahydro-2*H*-pyran (17.4 g, 40.0 mmol) followed by CuI (610 mg, 3.20 mmol), PPh₃ (841 mg, 3.20 mmol), and Pd(PPh₃)₄ (1.85 mg, 1.60 mmol) were added. The mixture was stirred at 65 °C for 15 h. After cooling to ambient temperature, solvent was removed *in vacuo* and the organic

layer was extracted three times with CHCl₃. After removing the solvent *in vacuo*, recrystallization from CHCl₃ gave the title compound (12.9 g, 74%) as a white powder. The second crop was obtained from the mother liquor. After removal of the solvent *in vacuo*, the crude material was purified by flash column chromatography on silica gel employing hexane:ethyl acetate = 95:5 to afford the title compound (3.2 g, 19%). Total yield was 93%. Mp: 202–203 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.31 (s, 18H, CH₃), 1.58–1.71 (m, 6H, *CH*₂), 1.83–1.87 (m, 2H, *CH*₂), 1.92–1.95 (m, 2H, *CH*₂), 2.01–2.09 (m, 2H, *CH*₂), 3.58–3.62 (m, 2H, OCH₂CH₂), 3.99–4.01 (m, 2H, OCH₂CH₂), 5.43 (brs, 2H, OCHO), 7.06 (s, 2H, aromatic proton). ¹³C NMR (125 MHz, CDCl₃): δ 18.2, 25.4, 28.2, 30.3, 31.0, 61.5, 75.3, 97.2, 103.4, 115.4, 120.9, 152. MS (APCI+): 439 (M+1). Anal. Calcd. For C₂₈H₃₈O₄: C, 76.68; H, 8.73. Found: C, 76.40; H, 8.70.

2,5-Bis(3,3-dimethylbut-1-ynyl)-benzene-1,4-diol



p-Toluenesulfonic acid (47.6 mg, 0.250 mmol) was added to a suspension of 2-[2,5-bis(3,3-dimethylbut-1-ynyl)-4-(tetrahydro-2*H*-2-pyranoyloxy)phenoxy]tetrahydro-2*H*-pyran (2.19 g, 5.00 mmol) in dichloromethane (50 mL) and methanol (25 mL). After stirring at ambient temperature for 3 hour, solvent was removed *in vacuo* to 5 mL. The resulting white precipitate was collected by filtration and washed with Et₂O to afford the title compound (1.05 g, 78%) as white solid. To the resulting mother liquor, NaHCO₃ aqueous solution was added to quench the reaction. Organic layer was extracted twice with CH₂Cl₂, washed with brine, and then dried over MgSO₄. After removal of the solvent *in vacuo*, the crude material was subjected to flash silica gel column chromatography employing hexane:ethyl acetate (95:5–90:10) as an eluent to afford the titled compound (0.23 g, 17%) as white solid. Total yield was 95%. Mp: 80 °C (decomp). ¹H NMR (500 MHz, CDCl₃): δ 1.34 (s, 18H, Me), 5.36 (brs, 2H, OH), 6.84 (s, 2H, aromatic proton). ¹³C NMR (125 MHz, acetone-*d*₆): δ 28.8, 31.2, 75.5, 104.4, 112.7, 119.2, 151.2. MS (APCI+): 271 (M+1). Anal. Calcd. For C₁₈H₂₂O₂: C, 79.96; H, 8.02. Found: C, 79.68; H, 8.28.

3,7-Bis[4-(*N*-carbazolyl)phenyl]-2,6-bis(3,3-dimethylbut-1-ynyl)-benzo[1,2-*b*:4,5-*b*'] difuran



A solution of n-butyllithium in hexane (2.01 mL, 1.49 mol/L, 3.00 mmol) was added to a suspension of 2,5-bis(3,3-dimethylbut-1-ynyl)-benzene-1,4-diol (406 mg, 1.50 mmol) in THF (3.0 mL) at 0 °C. The resulting yellow suspension was allowed to warm to ambient temperature and stirred for 30 min. After a solution of zinc chloride in THF (3.0 mL, 1.0 mol/L, 3.0 mmol) was added, the volatiles were removed in vacuo, and then toluene (6.0 mL) was added. The resulting yellow solution was heated to 120 °C and stirred for 38 h at this temperature. After cooling to ambient temperature, NMP (0.8 mL), Pd₂(dba)₃·CHCl₃ (155 mg, 0.15 mmol), P(t-Bu)₃ in toluene (0.6 mL, 1.0 mol/L, 0.6 mmol), and 4-bromophenylcarbazole (1.16 g, 3.6 mmol) were successively added. The resulting mixture was stirred at 60 °C for 22 h. After cooling to ambient temperature, the reaction mixture was filtrated and washed several times with methanol and ethyl acetate. The resulting crude solid was purified by gradient vacuum sublimation (pressure < 20 mTorr) at 350–360 °C to afford the title compound (529 mg, 0.703 mmol, 47%) as a white powder. Mp: 434 °C (TG-DTA). ¹H NMR (500 MHz, $CDCl_2CDCl_2$) δ 1.31 (s, 18H, CH₃), 7.29 (t, J = 7.5 Hz, 4H, carbazole), 7.31 (s, 2H, benzodifuran), 7.44 (t, J = 7.5 Hz, 4H, carbazole), 7.52 (d, J = 8.0 Hz, 4H, carbazole), 7.58–7.63 (m, 8H, phenylene), 8.13 (d, J = 8.0 Hz, 4H, carbazole). ¹³C NMR (125 MHz, CDCl₂CDCl₂, 130 °C) & 100.4, 110.1, 116.4, 120.3, 120.5, 123.3, 126.1, 126.3, 127.3, 130.3, 136.3, 140.8, 151.3, 152.6. MS (APCI+): 753 (M+1). Anal. Calcd. For C₅₄H₄₄ N₂O₂: C, 86.14; H, 5.89; N, 3.72. Found: C, 86.21; H, 5.99; N, 3.51.

2. Spectral measurements and basic properties



Figure S1 UV-vis absorption spectra of alkyl-CZBDFs measured in 1,2-dichloroethane solution at room temperature.



Phosphorescence spectra

UV-vis absorption spectra

Figure S2 Phosphorescence spectra of alkyl-CZBDFs measured in 2-Me-THF glass matrix at 77 K. (a) CH₃CZBDF, (b) CD₃CZBDF, and (c) *t*-BuCZBDF.

	$IP(eV)^{a}$	$\Delta Eg~(eV)^{b}$	EA (eV) ^c	$T_1 (eV)$
CH ₃ CZBDF	6.04	3.49	2.55	2.64
CD ₃ CZBDF	6.03	3.49	2.54	2.65
t-BuCZBDF	6.00	3.49	2.51	2.67

Table S1 Summary of properties of alkyl-CZBDFs

^a Ionization potentials determined using photoemission yield spectroscopy (PYS). ^b Optical gap obtained from absorption spectra at room temperature (Figure S1). ^c Electron affinities obtained from the following equation: $EA = IP - \Delta Eg$. ^d Triplet energy levels determined by phosphorescent measurements at 77 K (Figure S2).

3. Device fabrication and evaluation

Fabrication of OLED devices

To fabricate the OLED devices, a clean glass substrate pre-coated with 165-nm-thick indium-tin-oxide (ITO) layer with a sheet resistance of 8.4 Ω /sq was used as anode electrode. Prior to device fabrication, ITO substrates were treated with UV ozone for 3 min. On the ITO coated substrate, 70 nm thickness of PEDOT:PSS (AI4083) with a sheet resistance of 100,000 Ω /sq was spin coated as hole-injection layer at a rate of 3000 rpm for 30 sec.

Then, organic layers were deposited sequentially by thermal evaporation from resistively heated tantalum boats onto the substrates at a rate of 1-5 Å. The base pressure at room temperature was $2-3 \times 10^{-5}$ Torr. The rate for single component layers was controlled using one crystal monitor that was located near the substrate. A second crystal monitor located near the evaporation source of the dopant was used to control the rate of dopant molecule incorporation into the host matrix. The additional monitor was screened from the host evaporation, allowing for increased precision of the dopant concentration.

After organic film deposition, a cathode consisting of 800–1000 Å thickness of aluminum was deposited at a rate of 3–10 Å. OLEDs were formed at the 2×2 mm squares where the ITO (anode) and Al (cathode) stripes intersected. The fabricated devices were encapsulated and evaluated within 2 h of fabrication.

Evaluation of *L***-***V* **and** *J***-***V* **characteristic of OLED devices**

The luminance-voltage (L-V) and current-voltage (J-V) characteristics of OLED devices were measured by PRECISE GAUGES, EL 1003. All the measurements were carried out under an ambient atmosphere using the encapsulated devices.