# **Supporting Information**

# Phosphorescence within Benzotellurophenes and Color Tunable Tellurophenes under Ambient Conditions

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## **Experimental Section**

### 1. Materials and instrumentation

General. All reactions were performed using standard Schlenk and glovebox (MBraun) techniques under a nitrogen atmosphere. All solvents were dried and degassed using a Grubbs-type solvent purification system manufactured by Innovative Technology, Inc., and stored under an atmosphere of nitrogen prior to use. 3,3"'-Dihexyl-2,2':5',2":5",2"'-quaterthiophene (DH4T) was purchased from Sigma-Aldrich. Diphenyl zirconocene (Cp<sub>2</sub>ZrPh<sub>2</sub>),<sup>1</sup> bipy•TeCl<sub>2</sub>,<sup>2</sup> 1,2-bis(4,4,5,5-tetramethyl[1,3,2] dioxaborolan-2-yl)ethyne (PinBC=CBPin),<sup>3</sup> 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaboro lane (PhC=CBPin)<sup>4</sup> were prepared according to literature procedures. All other chemicals were obtained from Aldrich and used without further purification.  ${}^{1}H$ ,  ${}^{13}C{}^{1}H$  and  ${}^{11}B{}^{1}H$  NMR spectra were recorded on Varian Inova-400 or Varian Inova-500 spectrometers and referenced externally to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}) and F<sub>3</sub>B•OEt<sub>2</sub> (<sup>11</sup>B{<sup>1</sup>H}). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. High resolution mass spectra were obtained on an Agilent 6220 spectrometer. Melting points were obtained in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected. UV/vis measurements were performed using a Varian Cary 300 Scan spectrophotometer. The luminescence measurements were conducted on a Photon Technology International (PTI) MP1 fluorescence system. The aggregates in THF-water mixture were prepared using a typical method: a tellurophene or benzotellurophene was dissolved into THF, and then water was added rapidly with stirring. To accelerate the aggregation, each suspension was sonicated for 10 min (FS60 sonicator, Fisher Scientific). Thermogravimetric analyses (TGA) were conducted on a Metter Toledo TGA/DSC Star System under a heating rate of 10 °C/min under N<sub>2</sub>. X-ray diffraction (XRD) on the tellurophene films were acquired using a Bruker D8 Discover instrument with a sealed Cu tube X-ray source. Solid state samples for photo-luminescence measurements were made into thin films on quartz. The data were collected using an integrating sphere and the quantum yields were determined according to know method from the literature.<sup>5</sup> Further quantum yield corrections to account for waveguiding were applied.<sup>6</sup> Lifetime measurements were taken using a 337 nm pulsed nitrogen laser; pulses were 4 ns in duration at 30 Hz. Photoluminescence from the sample entered a monochromator, then a photomultiplier tube and the signal was recorded with an oscilloscope. The decay of the signal was fit to an exponential and the time constant was taken to be the lifetime. Lifetime data for all samples was greater than 1 microsecond, indicating phosphorescence. Lifetimes for all the compounds were verified at higher excitation intensities using a fast response (20 ns rise-time) photodiode.

### 2. Computational methods

The ground state equilibrium structures of **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** and **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** were determined at the B3LYP/cc-pVTZ (cc-pVTZ-pp for Te) level of theory<sup>7</sup> in the gas-phase; for convenience, these computations will simply be referred to as B3LYP/cc-pVTZ. The convergence criteria for the maximum of force and displacement are 0.000015 and 0.000060, respectively, and the convergence criteria for the RMS of force and displacement are 0.000010 and 0.000040. The vertical excitation energies of these two compounds were determined via time-dependent density functional theory (TD-DFT) at the B3LYP/aug-cc-pVDZ (aug-cc-pVDZ-pp for Te) level of theory.<sup>7c,8</sup> The UV/Vis absorption spectrum was also determined from the results of the TD-DFT computations.

The structures of **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** and **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** in the T<sub>1</sub> state were optimized using UHF- and ROHF-B3LYP/cc-pVTZ (cc-pVTZ-pp for Te).<sup>7b,c,9</sup> The energy gap between T<sub>1</sub> and S<sub>0</sub> at the T<sub>1</sub> equilibrium geometry was determined at the same level of theory. The molecular orbitals (MO) and the geometrical parameters of the two compounds were analyzed based on the S<sub>0</sub> and T<sub>1</sub> equilibrium structures. All the computations above were carried out using the Gaussian (G09) software package.<sup>10</sup> All computations are for the structures with the -CH<sub>3</sub> groups on BPin replaced by hydrogen atoms.

### 3. Synthetic procedures

Synthesis of 2,3-diphenyl-benzo[*b*]zirconocene, Benzo-ZrCp<sub>2</sub>-Ph<sub>2</sub>. This compound was synthesized according to a modification of a literature procedure.<sup>11</sup> Cp<sub>2</sub>ZrPh<sub>2</sub> (1.350 g, 3.59 mmol) and diphenylacetylene (0.625 g, 3.52 mmol) were dissolved in toluene (30 mL) and the mixture heated to 110 °C stirring for 48 h. The mixture was allowed to cool to room temperature and the volatiles were removed under reduced pressure. The product was extracted with 20 mL of THF and the mixture was filtered through Celite. The solvent was removed from the filtrate to afford 2,3-diphenyl-benzo[*b*]zirconocene as an analytically pure red solid (1.66 g, 97 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.12–6.38 (m, 14 H, Ar-*H*), 6.38 (s, 10 H, Cp-*H*). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  194.5, 184.9, 147.1, 146.7, 146.0, 141.2, 136.3, 130.3, 127.7, 127.3, 126.4, 125.4, 125.1, 125.0, 123.5, 122.7 (Ar-*C*), 112.8 (Cp-*C*). Anal. Calcd. for C<sub>20</sub>H<sub>14</sub>Zr: C, 62.90; H, 3.69. Found: C, 63.17; H, 3.81. Mp (°C): 138–141 (dec, color changed to dark). UV/vis (in THF):  $\lambda_{max} = 254$  nm,  $\varepsilon = 4.26 \times 10^4$  L/(mol•cm).



Synthesis of 2,3-diphenyl-benzo[b]tellurophene, Benzo-Te-Ph<sub>2</sub>. 2,3-Diphenylbenzo[b]zirconocene (0.44 g, 0.92 mmol) and bipy•TeCl<sub>2</sub> (0.33 g, 1.02 mmol) were dissolved in 10 mL of THF. The resulting mixture was allowed to stir at room temperature for 48 h and filtered. The solvent was then removed from the filtrate, and the crude yellow product was purified by column chromatography (silica gel with hexanes:THF (10:1) as the eluent,  $R_f = 0.35$ ) and the product fraction was evaporated to dryness to give **Benzo-Te-Ph<sub>2</sub>** as a crystalline yellow powder (0.21 g, 59

%). Yellow crystals of suitable quality for X-ray crystallography were grown form a hexanes solution at -30 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.95 (d, 1 H, <sup>3</sup>*J*<sub>HH</sub>= 7.6 Hz, Ar-*H*), 7.40–7.13 (m, 13 H, Ar-*H*). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  149.3, 144.4, 139.8, 138.8, 138.6, 132.2, 131.8, 130.8, 130.0, 128.9, 128.5, 128.2, 127.2, 127.0, 125.3, 124.9 (Ar-*C*). HR-MS (EI) (C<sub>20</sub>H<sub>14</sub>Te): m/z; Calcd. 384.0158. Found: 384.0176 ( $\Delta$  ppm = 4.6). Anal. Calcd. for C<sub>20</sub>H<sub>14</sub>Te: C, 62.90; H, 3.69. Found: C, 63.17; H, 3.81. Mp (°C): 117–118. UV/vis (in THF):  $\lambda_{max} = 261$  nm,  $\varepsilon = 3.05 \times 10^4$  L/(mol·cm);  $\lambda_{max} = 320$  nm,  $\varepsilon = 1.19 \times 10^4$  L/(mol·cm),  $\lambda_{max} = 361$  nm,  $\varepsilon = 2.73 \times 10^3$  L/(mol·cm).



Synthesis of 3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-benzo[*b*]zirconocene, Benzo-ZrCp<sub>2</sub>-BPin-Ph. Cp<sub>2</sub>ZrPh<sub>2</sub> (1.76 g, 4.68 mmol) and PhC=CBPin (1.05 g, 4.60 mmol) were combined in 60 mL of THF and the mixture was heated 110 °C for 24 h. The mixture was then cooled down to room temperature, and the solvent was removed under reduced pressure. The product was extracted with 60 mL of toluene, and the mixture was filtered through Celite. Removal of the solvent from the filtrate gave **Benzo-ZrCp<sub>2</sub>-BPin-Ph** as an orange solid (1.72 g, 70 %). Orangeyellow crystals were obtained by cooling a saturated hexanes solution to -30 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.26–6.66 (m, 9 H, Ar-*H*), 6.43 (s, 10 H, Cp-*H*), 0.97 (s, 12 H, C*H*<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  185.8, 150.3, 146.4, 144.9, 135.9, 128.6, 127.5, 125.5, 125.10, 125.08, 123.8 (Ar-C), 112.8 (Cp-C), 82.0 (C-O), 24.6 (CH<sub>3</sub>). <sup>11</sup>B {<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>):  $\delta$  30.5 (br). Anal. Calcd. for C<sub>30</sub>H<sub>31</sub>BO<sub>2</sub>Zr: C, 68.55; H, 6.94. Found: C, 68.27; H, 6.82. Mp (°C): 101–103. UV/vis (in THF):  $\lambda_{max} = 255$  nm,  $\varepsilon = 2.39 \times 10^4$  L/(mol•cm).



Synthesis of 3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-benzo[b]tellurophene, Benzo-Te-BPin-Ph. Benzo-ZrCp<sub>2</sub>-BPin-Ph (0.30 g, 0.57 mmol) and bipy•TeCl<sub>2</sub> (0.22 g, 0.62 mmol) were dissolved in 10 mL of THF and the resulting mixture was allowed to stir at room temperature for 24 h. The solution was filtered and the volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (silica gel with hexanes:THF (10:1) as the eluent,  $R_f = 0.39$ ) to give Benzo-Te-BPin-Ph as a yellow solid. This product was recrystallized from hexanes at -30 °C to give Benzo-Te-BPin-Ph as yellow crystals (0.15 g, 61 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.03 (d, 1 H, <sup>3</sup>*J*<sub>HH</sub> = 8.5 Hz, Ar-*H*), 7.51–7.22 (m, 8 H, Ar-*H*), 1.17 (s, 12 H, *CH*<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  154.4, 149.5, 140.9, 135.1, 132.2, 130.1, 129.6, 127.7, 127.3, 125.3, 124.8 (Ar-*C*), 84.0 (*C*-O), 24.6 (*C*H<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>):  $\delta$  31.2 (br). HR-MS (EI) (C<sub>19</sub>H<sub>30</sub>B<sub>2</sub>O<sub>4</sub>Te): m/z; Calcd. 434.0697. Found: 434.0696 ( $\Delta$  ppm = 0.3). Anal. Calcd. for C<sub>20</sub>H<sub>21</sub>BO<sub>2</sub>Te: C, 55.63; H, 4.90. Found: C, 55.69; H, 5.06. Mp (°C): 143–144. UV/vis (in THF):  $\lambda_{max} = 262$  nm,  $\varepsilon = 1.96 \times 10^4$  L/(mol·cm);  $\lambda_{max} = 357$  nm,  $\varepsilon = 4.90 \times 10^3$  L/(mol·cm).



Synthesis of 2,3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-benzo[*b*]zirconocene, Benzo-ZrCp<sub>2</sub>-BPin<sub>2</sub>. Cp<sub>2</sub>ZrPh<sub>2</sub> (1.53 g, 4.08 mmol) and 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)ethyne, PinBC=CBPin (1.11 g, 4.00 mmol) were dissolved in toluene (30 mL) and the mixture was stirred at 110 °C for 48 h and then allowed to cool to room temperature. The solvent was removed under reduced pressure and the product was extracted with hexanes (100 mL) and the mixture was filtered through Celite. The solvent was removed from the filtrate to afford **Benzo-**ZrCp<sub>2</sub>-BPin<sub>2</sub> as a yellow-orange powder (2.01 g, 87 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.48 (d, 1 H, <sup>3</sup>*J*<sub>HH</sub> = 8.0 Hz, Ar-*H*), 6.96–6.92 (m, 1 H, Ar-*H*), 6.78–6.74 (m, 1 H, Ar-*H*), 6.53 (d, 1 H, <sup>3</sup>*J*<sub>HH</sub> = 8.4 Hz, Ar-*H*), 6.36 (s, 10 H, Cp-*H*), 1.30 (s, 12 H, CH<sub>3</sub>), 1.28 (s, 12 H, CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  185.0 (Zr-C=*C*),  $\delta$  144.8 (Zr-*C*=*C*), 135.9, 127.1, 125.5, 123.4 (Ar-*C*), 112.6 (Cp-*C*), 83.1, 82.2 (*C*-O), 25.3, 24.9 (CH<sub>3</sub>). <sup>11</sup>B {<sup>1</sup>H} NMR (128.3 MHz, CDCl<sub>3</sub>):  $\delta$  26.6 (br). Anal. Calcd. for C<sub>38</sub>H<sub>44</sub>B<sub>2</sub>O<sub>4</sub>Zr: C, 62.61; H, 6.66. Found: C, 62.56; H, 6.94. Mp (°C): 80–82. UV/vis (in THF):  $\lambda_{max}$ = 256 nm,  $\epsilon$  = 1.69 × 10<sup>4</sup> L/(mol•cm).



Synthesis of 2,3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-benzo[*b*]tellurophene, Benzo-Te-BPin<sub>2</sub>. Benzo-Zr-BPin<sub>2</sub> (0.42 g, 0.73 mmol) and bipy•TeCl<sub>2</sub> (0.28 g, 0.79 mmol) were dissolved in 10 mL of THF. The resulting mixture was allowed to stir at room temperature for 48 h. The solution was filtered and the solvent was removed from the filtrate. The crude product was purified by column chromatography (silica gel with hexanes:ethyl acetate (10:1) as the eluent,  $R_f = 0.45$ ) and dried under dynamic vacuum for 24 h to give a yellow powder (0.14 g, 46 %). <sup>1</sup>H NMR (500 MHz,

CDCl<sub>3</sub>):  $\delta$  8.17 (d, 1 H,  ${}^{3}J_{\text{HH}} = 8.0$  Hz, Ar-*H*), 7.98 (d, 1 H,  ${}^{3}J_{\text{HH}} = 8.0$  Hz, Ar-*H*), 7.36 (t, 1 H,  ${}^{3}J_{\text{HH}} = 8.0$  Hz, Ar-*H*), 7.16 (d, 1 H,  ${}^{3}J_{\text{HH}} = 8.4$  Hz, Ar-*H*), 1.44 (s, 12 H, CH<sub>3</sub>), 1.36 (s, 12 H, CH<sub>3</sub>).  ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  154.3, 138.2, 131.9, 129.5, 124.8, 124.5 (Ar-C), 84.5 (C-O), 84.1 (C-O), 25.1 (CH<sub>3</sub>), 24.9 (CH<sub>3</sub>).  ${}^{11}\text{B}\{{}^{1}\text{H}\}$  NMR (128 MHz, CDCl<sub>3</sub>):  $\delta$  31.4 (br). HR-MS (EI) (C<sub>20</sub>H<sub>28</sub>B<sub>2</sub>O<sub>4</sub>Te): m/z; Calcd. 484.1236. Found: 484.1237 ( $\Delta$  ppm = 0.2). Anal. Calcd. for C<sub>20</sub>H<sub>28</sub>B<sub>2</sub>O<sub>4</sub>Te: C, 49.87; H, 5.86. Found: C, 49.88; H, 5.90. Mp (°C): 114–115. UV/vis (in THF):  $\lambda_{\text{max}} = 262$  nm,  $\varepsilon = 1.20 \times 10^{4}$  L/(mol·cm),  $\lambda_{\text{max}} = 288$  nm,  $\varepsilon = 5.42 \times 10^{3}$  L/(mol·cm);  $\lambda_{\text{max}} = 359$  nm,  $\varepsilon = 2.15 \times 10^{3}$  L/(mol·cm).



Synthesis of 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-diphenylzirconocene (2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-ZrCp<sub>2</sub>) and 2,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,5-diphenylzirconocene (2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-ZrCp<sub>2</sub>). To a solution of Cp<sub>2</sub>ZrCl<sub>2</sub> (2.655 g, 9.08 mmol) in THF (60 mL) at -78 °C was added dropwise a solution of <sup>n</sup>BuLi (7.3 mL, 2.5 M in hexanes, 18 mmol). After the mixture was stirred at -78 °C for 1 h, a solution of 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (4.1 g, 18 mmol), PhC=CBPin in 20 mL of THF was added at -78 °C. The temperature was allowed to rise to room temperature, and the mixture was stirred for another 5 h. The volatiles were removed under reduced pressure and the product was extracted with 60 mL toluene, and the mixture was filtered through Celite. The solvent was removed from the filtrate under vacuum to give a mixture of two zirconocene regioisomers as a red solid (4.3 g, 70 %). In one recrystallization attempt from toluene (-30 °C) crystals of 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-ZrCp<sub>2</sub> were

isolated and characterized by single-crystal X-ray crystallography. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.28–6.78 (m, Ar-*H*), 6.47 (s, Cp-*H*), 6.32 (s, Cp-*H*), 1.05 (s, C*H*<sub>3</sub>), 0.64 (s, C*H*<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, CDCl<sub>3</sub>):  $\delta$  28.7 (br). Anal. Calcd. for C<sub>38</sub>H<sub>44</sub>B<sub>2</sub>O<sub>4</sub>Zr: C, 67.36; H, 6.55. Found: C, 66.35; H, 6.75.



2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-ZrCp<sub>2</sub> 2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-ZrCp<sub>2</sub>

Synthesis of 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-diphenyltellurophene (2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te) 2,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,5and diphenyltellurophene (2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te). The above mentioned mixture of 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-**ZrCp**<sub>2</sub> and **2,4-BPin**<sub>2</sub>**-3,5-Ph**<sub>2</sub>**-ZrCp**<sub>2</sub> (0.74 g, 1.1 mmol) was combined with bipy•TeCl<sub>2</sub> (0.43 g, 1.2 mmol) in 20 mL of THF. The resulting mixture was allowed to stir at room temperature for 24 h. The solution was then filtered and the volatiles were removed from the filtrate. The crude product was then extracted with 10 mL of hexanes and filtered through a 4 cm plug of silica gel. The solvent was removed from the filtrate under vacuum to give a crude product that was recrystallized from hexanes at -30 °C to give a mixture of 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te and 2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te as pale yellow crystals. The two isomers showed different emission color under UV light ( $\lambda = 365$  nm), which enabled us to manually separate the crystals of each isomer. For 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te (isolated yield, 0.15 g, 24 %): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.11–6.97 (m, 10 H, Ar-*H*), 1.12 (s, 24 H, C*H*<sub>3</sub>).  $^{13}C{^{1}H}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  161.5 (TeC=C), 142.7, 130.3, 126.9, 126.2 (Ar-C), 83.8 (C-O), 24.5 (CH<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>):  $\delta$  31.4 (br). HR-MS (EI) (C<sub>19</sub>H<sub>30</sub>B<sub>2</sub>O<sub>4</sub>Te): m/z; Calcd. 586.1705. Found: 586.1705 ( $\Delta$  ppm = 0.0). Anal. Calcd. for C<sub>28</sub>H<sub>34</sub>B<sub>2</sub>O<sub>4</sub>Te: C, 57.61; H, 5.87. Found: C, 57.69; H, 5.95. Mp (°C): 204–205. UV/vis (in THF):  $\lambda_{max} = 284$  nm,  $\varepsilon = 1.73 \times 10^4$ 

L/(mol·cm);  $\lambda_{max} = 348 \text{ nm}$ ,  $\varepsilon = 8.32 \times 10^3 \text{ L/(mol·cm)}$ . For **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** (isolated yield, 0.26 g, 41 %): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.56–7.27 (m, 10H, Ar-*H*), 1.43 (s, 12H, CH<sub>3</sub>), 0.90 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  164.9 (TeC=*C*), 159.6 (Te*C*=*C*), 142.8, 142.1, 129.7, 128.7, 128.2, 127.5, 127.1, 126.8 (Ar-*C*), 83.7 (*C*-O), 83.6 (*C*-O), 24.6 (CH<sub>3</sub>), 24.5 (CH<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>):  $\delta$  31.6 (br). HR-MS (EI) (C<sub>19</sub>H<sub>30</sub>B<sub>2</sub>O<sub>4</sub>Te): m/z; Calcd. 586.1705. Found: 586.1704 ( $\Delta$  ppm = 0.2). Anal. Calcd. for C<sub>28</sub>H<sub>34</sub>B<sub>2</sub>O<sub>4</sub>Te: C, 57.61; H, 5.87. Found: C, 57.83; H, 5.96. Mp (°C): 151–152. UV/vis (in THF):  $\lambda_{max} = 287 \text{ nm}$ ,  $\varepsilon = 1.36 \times 10^4 \text{ L/(mol·cm)}$ ;  $\lambda_{max} = 310 \text{ nm}$ ,  $\varepsilon = 1.17 \times 10^3 \text{ L/(mol·cm)}$ .



2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-ZrCp<sub>2</sub>

2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-ZrCp<sub>2</sub>





2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te

2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te

### 4. Single-crystal X-ray structure determinations

**X-ray Crystallography**. Crystals of appropriate quality for X-ray diffraction studies were removed from a vial (in a glove box) and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then selected, attached to a glass fiber, and quickly placed in a glass vial. All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo K $\alpha$  or Cu K $\alpha$  radiation. The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using the direct methods programs SHELXS-97,<sup>12</sup> and refinements were completed using the program SHELXL-97.<sup>12</sup>



**Figure S1.** Molecular structure of **Benzo-ZrCp<sub>2</sub>-BPin-Ph** with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)—Zr 2.263(4), C(12)—Zr 2.277(5), C(1)—B 1.539(7), C(2)—C(21) 1.510(6); C(1)—Zr—C(12) 79.18(16), Zr—C(1)—B 127.7(3), C(1)—C(2)—C(21) 123.3(4), Zr—C(12)—C(13) 133.8(4).

## Table S1. Crystallographic experimental details for Benzo-ZrCp<sub>2</sub>-BPin-Ph

A. Crystal Data	
formula	C30H31BO2Zr
formula weight	525.58
crystal dimensions (mm)	$0.11 \times 0.09 \times 0.07$
crystal system	orthorhombic
space group	<i>Pbca</i> (No. 61)
unit cell parameters <sup>a</sup>	
<i>a</i> (Å)	10.3097 (2)
<i>b</i> (Å)	15.5055 (3)
<i>c</i> (Å)	32.3133 (7)
$V(Å^3)$	5165.51 (18)
Ζ	8
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.352
$\mu (\mathrm{mm}^{-1})$	3.665
B. Data Collection and Refinement Condi	tions
diffractometer	Bruker D8/APEX II CCD <sup>b</sup>
radiation ( $\lambda$ [Å])	Cu K $\alpha$ (1.54178) (microfocus source)
temperature (°C)	-100
scan type	$\omega$ and $\phi$ scans (1°) (5 s exposures)
data collection $2\theta$ limit (deg)	145.43
total data collected	$33381 \ (-12 \le h \le 12,  -19 \le k \le 19,  -39 \le l \le 39)$
independent reflections	$5118 (R_{int} = 0.0726)$
number of observed reflections (NO)	$4323 \ [F_0^2 \ge 2\sigma(F_0^2)]$
structure solution method	intrinsic phasing (SHELXT <sup>c</sup> )
refinement method	full-matrix least-squares on $F^2$ (SHELXL-2013 <sup>C</sup> )
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.8230-0.6910
data/restraints/parameters	5118 / 0 / 307
goodness-of-fit (S) <sup>d</sup> [all data]	1.131
final R indices <sup>e</sup>	
$R_1 [F_0^2 \ge 2\sigma(F_0^2)]$	0.0611
$wR_2$ [all data]	0.1531
largest difference peak and hole	1.618 and $-1.165$ e Å <sup>-3</sup>

*a*Obtained from least-squares refinement of 9951 reflections with  $5.46^{\circ} < 2\theta < 144.56^{\circ}$ .

<sup>b</sup>Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

<sup>c</sup>Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112–122.

 $dS = [\Sigma w (F_0^2 - F_c^2)^2 / (n - p)]^{1/2} (n = \text{number of data; } p = \text{number of parameters varied; } w = [\sigma^2 (F_0^2) + (0.0606P)^2 + 15.2414P]^{-1} \text{ where } P = [Max(F_0^2, 0) + 2F_c^2]/3).$ 

$$e_{R_1} = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|; \ w_{R_2} = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^4)]^{1/2}.$$



**Figure S2.** Molecular Structure of **Benzo-Te-Ph**<sub>2</sub> with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)—Te 2.0985(14), C(4)—Te 2.0789(14), C(1)—C(11) 1.4765(18), C(2)—C(21) 1.4928(19); C(1)—Te—C(4) 82.27(5), Te—C(1)—C(11) 118.65(10), C(1)—C(2)—C(21) 123.45(12), Te—C(4)—C(5) 128.15(11).

# Table S2. Crystallographic Experimental Details for Benzo-Te-Ph<sub>2</sub>

A. Crystal Data	
formula	C20H14Te
formula weight	381.91
crystal dimensions (mm)	$0.82 \times 0.18 \times 0.17$
crystal system	triclinic
space group	<i>P</i> <b>1</b> (No. 2)
unit cell parameters <sup>a</sup>	
<i>a</i> (Å)	5.7439 (4)
<i>b</i> (Å)	11.1587 (7)
<i>c</i> (Å)	12.0325 (8)
$\alpha$ (deg)	80.1921 (7)
$\beta$ (deg)	87.5978 (7)
$\gamma$ (deg)	79.9810 (6)
$V(Å^3)$	748.30 (9)
Ζ	2
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.695
$\mu (\mathrm{mm}^{-1})$	1.977
<i>B</i> Data Collection and Refinement Cond	itions
diffractometer	Bruker D8/APEX II CCD <sup>b</sup>
radiation $(\lambda [Å])$	graphite-monochromated Mo K $\alpha$ (0.71073)
temperature (°C)	-100
scan type	$\omega$ scans (0.3°) (15 s exposures)
data collection $2\theta$ limit (deg)	56.58
total data collected	$6591 (-7 \le h \le 7, -14 \le k \le 14, -16 \le l \le 15)$
independent reflections	$3553 (R_{int} = 0.0076)$
number of observed reflections (NO)	$3513 [F_0^2 \ge 2\sigma(F_0^2)]$
structure solution method	Patterson/structure expansion (DIRDIF-2008 <sup>C</sup> )
refinement method	full-matrix least-squares on $F^2$ (SHELXL–2013d)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.7917-0.2814
data/restraints/parameters	3553 / 0 / 190
goodness-of-fit (S) <sup>e</sup> [all data]	1.127
final R indices <sup>f</sup>	
$R_1 [F_0^2 \ge 2\sigma(F_0^2)]$	0.0146
wR <sub>2</sub> [all data]	0.0396
largest difference peak and hole	0.328 and –0.576 e Å <sup>-3</sup>

*a*Obtained from least-squares refinement of 9533 reflections with  $4.66^{\circ} < 2\theta < 56.58^{\circ}$ .

- <sup>b</sup>Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.
- <sup>c</sup>Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M.; Garcia-Granda, S.; Gould, R. O. (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen, The Netherlands.

dSheldrick, G. M. Acta Crystallogr. 2008, A64, 112-122.

- ${}^{e}S = [\Sigma w(F_0{}^2 F_c{}^2)^2 / (n p)]^{1/2} (n = \text{number of data; } p = \text{number of parameters varied; } w = [\sigma^2(F_0{}^2) + (0.0194P)^2 + 0.3735P]^{-1} \text{ where } P = [Max(F_0{}^2, 0) + 2F_c{}^2]/3).$
- $f_{R_1} = \Sigma ||F_0| |F_c|| / \Sigma |F_0|; \ w_{R_2} = [\Sigma w (F_0^2 F_c^2)^2 / \Sigma w (F_0^4)]^{1/2}.$



**Figure S3.** Molecular structure of **Benzo-Te-BPin-Ph** with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)—Te 2.090(3), C(4)—Te 2.071(3), C(1)—B 1.548(4), C(2)—C(21) 1.488(3); C(1)—Te—C(4) 82.01(10), Te—C(1)—B 116.02(18), C(1)—C(2)—C(21) 121.8(2), Te—C(4)—C(5) 126.9(2).

Table S3. Crystallographic experimental details for Benzo-Te-BPin-Ph

A. Crystal Data	
formula	C <sub>20</sub> H <sub>21</sub> BO <sub>2</sub> Te
formula weight	431.78
crystal dimensions (mm)	$0.39 \times 0.37 \times 0.08$
crystal system	orthorhombic
space group	<i>Pbca</i> (No. 61)
unit cell parameters <sup>a</sup>	
a (Å)	8.2167 (8)
$b(\mathbf{A})$	20.788 (2)
c (A)	22.069 (2)
$V(Å^3)$	3769.4 (6)
Ζ	8
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.522
$\mu (\mathrm{mm}^{-1})$	1.586
B. Data Collection and Refinement Condition	ons
diffractometer	Bruker D8/APEX II CCD <sup>b</sup>
radiation ( $\lambda$ [Å])	graphite-monochromated Mo K $\alpha$ (0.71073)
temperature (°C)	-100
scan type	$\omega$ scans (0.3°) (15 s exposures)
data collection $2\theta$ limit (deg)	56.61
total data collected	$33186 (-10 \le h \le 10, -27 \le k \le 27, -29 \le l \le 29)$
independent reflections	$4681 \ (R_{\text{int}} = 0.0189)$
number of observed reflections (NO)	$4321 \ [F_0^2 \ge 2\sigma(F_0^2)]$
structure solution method	Patterson/structure expansion (DIRDIF-2008 <sup>C</sup> )
refinement method	full-matrix least-squares on $F^2$ (SHELXL-2013d)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9390-0.6463
data/restraints/parameters	4681 / 0 / 219
goodness-of-fit (S) <sup>e</sup> [all data]	1.037
final $R$ indices $f$	
$R_1 [F_0^2 \ge 2\sigma(F_0^2)]$	0.0341
$wR_2$ [all data]	0.0966
largest difference peak and hole	1.738 and -1.181 e Å <sup>-3</sup>

*a*Obtained from least-squares refinement of 9972 reflections with  $4.34^{\circ} < 2\theta < 45.62^{\circ}$ .

<sup>b</sup>Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

<sup>c</sup>Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M.; Garcia-Granda, S.; Gould, R. O. (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen, The Netherlands.

dSheldrick, G. M. Acta Crystallogr. 2008, A64, 112-122.

 $eS = [\Sigma w(F_0^2 - F_c^2)^2/(n-p)]^{1/2}$  (n = number of data; p = number of parameters varied;  $w = [\sigma^2(F_0^2) + \sigma^2(F_0^2)^2/(n-p)]^{1/2}$ 

$$(0.0456P)^{2} + 7.9485P]^{-1} \text{ where } P = [\text{Max}(F_{0}^{2}, 0) + 2F_{c}^{2}]/3).$$
  
$$f_{R_{1}} = \Sigma ||F_{0}| - |F_{c}||/\Sigma |F_{0}|; w_{R_{2}} = [\Sigma w(F_{0}^{2} - F_{c}^{2})^{2}/\Sigma w(F_{0}^{4})]^{1/2}.$$



**Figure S4.** Molecular structure of **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** with thermal ellipsoids presented at a 30% probability. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)—Te 2.068(3), C(4)—Te 2.060(3), C(1)—B(1) 1.553(4), C(2)—C(31) 1.479(4), C(4)—B(2) 1.555(4), C(3)—C(41) 1.493(4); C(1)—Te—C(4) 82.79(11), Te—C(1)—B(1) 116.5(2), C(1)—C(2)—C(31) 121.8(2), C(2)—C(31)—C(41) 121.4(3), Te—C(4)—B(2) 117.8(2).

A. Crystal Data	
formula	C28H36B2O4Te
formula weight	583.77
crystal dimensions (mm)	$0.20 \times 0.13 \times 0.11$
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters <sup>a</sup>	
<i>a</i> (Å)	10.6313 (6)
b (Å)	21.4729 (12)
<i>c</i> (Å)	13.1595 (7)
$\beta$ (deg)	113.0417 (6)
$V(Å^3)$	2764.4 (3)
Ζ	4
$\rho$ calcd (g cm <sup>-3</sup> )	1.403
$\mu (\text{mm}^{-1})$	1.106
B. Data Collection and Refinement Cond	litions
diffractometer	Bruker PLATFORM/APEX II CCD <sup>b</sup>
radiation $(\lambda [Å])$	graphite-monochromated Mo K $\alpha$ (0.71073)
temperature (°C)	-100
scan type	$\omega$ scans (0.3°) (20 s exposures)
data collection $2\theta$ limit (deg)	55.04
total data collected	$24418 \ (-13 \le h \le 13,  -27 \le k \le 27,  -17 \le l \le 17)$
independent reflections	$6356 (R_{int} = 0.0428)$
number of observed reflections (NO)	$5130 \ [F_0^2 \ge 2\sigma(F_0^2)]$
structure solution method	intrinsic phasing (SHELXT <sup>c</sup> )
refinement method	full-matrix least-squares on $F^2$ (SHELXL–2013 <sup>c</sup> )
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9280-0.8565
data/restraints/parameters	6356 / 0 / 333
goodness-of-fit $(S)^d$ [all data]	1.039
final <i>R</i> indices <sup><i>e</i></sup>	
$R_1 \left[ F_0^2 \ge 2\sigma(F_0^2) \right]$	0.0371
wR <sub>2</sub> [all data]	0.0896
largest difference peak and hole	1.358 and -1.134 e Å- <sup>3</sup>

Table S4. Crystallographic experimental details for for 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te

<sup>*a*</sup>Obtained from least-squares refinement of 9459 reflections with  $4.58^{\circ} < 2\theta < 51.42^{\circ}$ .

<sup>b</sup>Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

<sup>c</sup>Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112–122.

$$dS = [\Sigma w (F_0^2 - F_c^2)^2 / (n-p)]^{1/2} (n = \text{number of data; } p = \text{number of parameters varied; } w = [\sigma^2 (F_0^2) + (0.0383P)^2 + 2.8177P]^{-1} \text{ where } P = [Max(F_0^2, 0) + 2F_c^2]/3).$$

$$e_{R_1} = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|; w_{R_2} = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^4)]^{1/2}.$$



**Figure S5.** Molecular structure of **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** with thermal ellipsoids presented at a 30% probability. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)—Te 2.062(2), C(4)—Te 2.069(2), C(1)—B(1) 1.551(3), C(2)—C(31) 1.492(3), C(3)—B(2) 1.576(3), C(4)—C(41) 1.482(3); C(1)—Te—C(4) 82.65(9), Te—C(1)—B(1) 115.73(17), C(1)—C(2)—C(31) 122.6(2), C(2)—C(3)—B(2) 120.0(2), C(3)—C(4)—C(41) 127.3(2).

## Table S5. Crystallographic Experimental Details for 2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te

A. Crystal Data	
formula	C28H34B2O4Te
formula weight	583.77
crystal dimensions (mm)	$0.38 \times 0.17 \times 0.06$
crystal system	triclinic
space group	<i>P??1??</i> (No. 2)
unit cell parameters <sup>a</sup>	
a (Å)	7.0792 (11)
<i>b</i> (Å)	12.1454 (19)
<i>c</i> (Å)	16.953 (3)
$\alpha$ (deg)	75.2698 (17)
$\beta$ (deg)	82.0304 (19)
$\gamma$ (deg)	80.2126 (19)
$V(Å^3)$	1382.2 (4)
Z	2
$\rho_{\text{calcd}}(\text{g cm}^{-3})$	1.403
$\mu (\text{mm}^{-1})$	1.106
B. Data Collection and Refinement Cond	litions
diffractometer	Bruker D8/APEX II CCD <sup>b</sup>
radiation ( $\lambda$ [Å])	graphite-monochromated Mo K $\alpha$ (0.71073)
temperature (°C)	-100
scan type	$\omega$ scans (0.3°) (16 s exposures)
data collection $2\theta$ limit (deg)	55.21
total data collected	$47499 \ (-9 \le h \le 9,  -15 \le k \le 15,  -22 \le l \le 22)$
independent reflections	$6307 (R_{int} = 0.0926)$
number of observed reflections (NO)	$5781 \ [F_0^2 \ge 2\sigma(F_0^2)]$
structure solution method	intrinsic phasing (SHELXT-2013 <sup>C</sup> )
refinement method	full-matrix least-squares on $F^2$ (SHELXL-2013 <sup>c</sup> )
absorption correction method	multi-scan (TWINABS)
range of transmission factors	0.9517-0.4698
data/restraints/parameters	6307 / 0 / 317
goodness-of-fit (S) <sup>d</sup> [all data]	1.056
final R indices <sup>e</sup>	
$R_1 [F_0^2 \ge 2\sigma(F_0^2)]$	0.0313

*a*Obtained from least-squares refinement of 9888 reflections with  $4.76^{\circ} < 2\theta < 54.86^{\circ}$ .

0.0796

wR<sub>2</sub> [all data]

largest difference peak and hole

<sup>b</sup>Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. The crystal used for data collection was found to display non-merohedral twinning. Both components of the twin were indexed with the program *CELL\_NOW* (Bruker AXS Inc., Madison, WI, 2004). The second twin component can be related to the first component by a 4.6° rotation about the  $[^{-1}/_{4} 1 0]$  axis in real space and about the  $[0 1 \frac{1}{3}]$  axis in reciprocal space. Integrated intensities for the reflections from the two components were written into a *SHELXL-2013* HKLF 5

1.094 and -0.572 e Å<sup>-3</sup>

reflection file with the data integration program *SAINT* (version 7.68A), using all reflection data (exactly overlapped, partially overlapped and non-overlapped). The refined value of the twin fraction (*SHELXL-2013* BASF parameter) was 0.1399(11).

<sup>c</sup>Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112–122.

 $dS = [\Sigma w(F_0^2 - F_c^2)^2 / (n - p)]^{1/2} (n = \text{number of data; } p = \text{number of parameters varied; } w = [\sigma^2(F_0^2) + (0.0446P)^2 + 0.3629P]^{-1} \text{ where } P = [Max(F_0^2, 0) + 2F_c^2]/3).$ 

 $e_{R_1} = \sum ||F_0| - |F_c|| / \sum |F_0|; \ w_{R_2} = \left[\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^4)\right]^{1/2}.$ 

5. Molecular packing of Benzo-Te-Bpin-Ph in the solid state



Figure S6. Packing diagram for Benzo-Te-Bpin-Ph. The shortest Te-Te distance is ca. 4.55 Å.



Figure S7. UV/vis spectra of Benzo-Te-Ph<sub>2</sub>, Benzo-Te-BPin-Ph and Benzo-Te-BPin<sub>2</sub> in THF.



Figure S8. UV/vis spectra of 2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te and 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te in THF.

### 7. Thermogravimetric analysis (TGA) measurements



**Figure S9.** TGA thermograms of **Benzo-Te-Ph<sub>2</sub>**, **Benzo-Te-BPin-Ph** and **Benzo-Te-BPin<sub>2</sub>** measured under N<sub>2</sub> (10 °C/min).



**Figure S10.** TGA thermograms of **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** and **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** measured under N<sub>2</sub> (10 °C/min).

# 8. NMR measurements



Figure S11. <sup>1</sup>H NMR spectra of Benzo-Te-Ph<sub>2</sub>, Benzo-Te-BPin-Ph, Benzo-Te-BPin<sub>2</sub>, 2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te and 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te in CDCl<sub>3</sub>.

9. Photoluminescence spectra of Benzo-Bin-Ph-Te, 2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te and 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te in THF/water (5:95) mixtures

![](_page_28_Figure_1.jpeg)

Figure S12. PL excitation and emission spectra of Benzo-Te-Bin-Ph in THF/water (5:95). [Benzo-Te-BPin-Ph] =  $600 \mu$ M.

![](_page_28_Figure_3.jpeg)

Figure S13. PL excitation and emission spectra of 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te in THF/water (5:95). [2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te] =  $600 \mu$ M.

![](_page_29_Figure_0.jpeg)

**Figure S14.** PL excitation and emission spectra of **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** in THF/water (5:95). [**2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te**] = 600  $\mu$ M. The maxima of scattering peaks are dependent on the excitation wavelength.

![](_page_30_Picture_0.jpeg)

**Figure S15.** Photo of aggregates of **Benzo-Te-Ph**<sub>2</sub>, **Benzo-Te-BPin-Ph**, **Benzo-Te-BPin**<sub>2</sub>, **2,4-BPin**<sub>2</sub>-**3,5-Ph**<sub>2</sub>-**Te** and **2,5-BPin**<sub>2</sub>-**3,4-Ph**<sub>2</sub>-**Te** in THF/water (5:95) under UV light ( $\lambda_{\text{excit.}} = 365 \text{ nm}$ ).

10. Photoluminescence spectra of Benzo-Te-Ph<sub>2</sub>, Benzo-Te-BPin-Ph and Benzo-Te-BPin<sub>2</sub> in the film state

![](_page_31_Figure_1.jpeg)

**Figure S16.** PL of **Benzo-Te-Ph<sub>2</sub>**, **Benzo-Te-BPin-Ph**, **Benzo-Te-BPin<sub>2</sub>** in the film state. ( $\lambda_{\text{excit.}} = 337$  nm). The maxima of the scattering peaks are dependent on the excitation wavelength.

![](_page_31_Figure_3.jpeg)

**Figure S17.** PL of 10 wt % of **Benzo-Te-BPin-Ph** in the PMMA drop-coated film. ( $\lambda_{\text{excit.}} = 337 \text{ nm}$ ).

### **11.** Computational results

![](_page_32_Figure_1.jpeg)

**Figure S18.** HOMO (left) and LUMO (right) of **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** at the S<sub>0</sub> equilibrium geometry as determined at the B3LYP/cc-pVTZ level of theory in the gas-phase.

![](_page_32_Figure_3.jpeg)

**Figure S19.** HOMO (left) and LUMO (right) of **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** for the S<sub>0</sub> state at the (ROB3LYP/cc-pVTZ) T<sub>1</sub> equilibrium geometry as determined at the B3LYP/cc-pVTZ level of theory in the gas-phase.

![](_page_33_Figure_0.jpeg)

**Figure S20.** Lower energy SOMO (left) and higher energy SOMO (right) of **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** for the  $T_1$  state at the  $T_1$  equilibrium geometry as determined at the ROB3LYP/cc-pVTZ level of theory in the gas-phase.

![](_page_33_Figure_2.jpeg)

**Figure S21.** Lower energy SOMO (left) and higher energy SOMO (right) of **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** for the  $T_1$  state at the  $T_1$  equilibrium geometry as determined at the UB3LYP/cc-pVTZ level of theory in the gas-phase.

![](_page_34_Picture_0.jpeg)

**Figure S22.** HOMO (left) and LUMO (right) of **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** at the S<sub>0</sub> equilibrium geometry as determined at the B3LYP/cc-pVTZ level of theory in the gas-phase.

![](_page_34_Figure_2.jpeg)

**Figure S23.** HOMO (left) and LUMO (right) of **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** for the S<sub>0</sub> state at the (ROB3LYP/cc-pVTZ) T<sub>1</sub> equilibrium geometry as determined at the B3LYP/cc-pVTZ level of theory in the gas-phase.

![](_page_35_Figure_0.jpeg)

**Figure S24.** Lower energy SOMO (left) and higher energy SOMO (right) of **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** for the  $T_1$  state at the  $T_1$  equilibrium geometry as determined at the ROB3LYP/cc-pVTZ level of theory in the gas-phase.

![](_page_35_Figure_2.jpeg)

**Figure S25.** Lower energy SOMO (left) and higher energy SOMO (right) of **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** for the  $T_1$  state at the  $T_1$  equilibrium as determined at the UB3LYP/cc-pVTZ level of theory in the gas-phase.

**Table S6.** The specific bond length and specific dihedral angles in **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** at S<sub>0</sub> and T<sub>1</sub> geometries (optimized via both ROB3LYP and UB3LYP). Optimizations were done using the cc-pVTZ basis set cc-pvTZ-PP + ECP for Te). **Figure S5** was used in designation of the atoms in the molecular structure.

Bond	Bond length [Å] (S <sub>0</sub> geometry)	Bond Length [Å] (T <sub>1</sub> geometry, ROB3LYP optimized)	Bond Length [Å] (T <sub>1</sub> geometry, UB3LYP optimized)	Experimental
Te-C(1)	2.08401	2.07422	2.07722	2.062(2)
Te-C(4)	2.08585	2.15905	2.15799	2.069(2)
C(1)-C(2)	1.37429	1.45586	1.45495	1.373(3)
C(2)-C(3)	1.44696	1.37497	1.37305	1.459(3)
C(3)-C(4)	1.37157	1.45216	1.45751	1.372(3)
C(1)-B(1)	1.53703	1.52679	1.52791	1.551(3)
C(2)-C(31)	1.49182	1.48863	1.48984	1.492(3)
C(3)-B(2)	1.56836	1.56495	1.56453	1.576(3)
C(4)-C(41)	1.46960	1.40332	1.40140	1.482(3)
Dihedral	Angle [°]	Angle [°]	Angle [°]	Angle [°]
Te-C(1)-B(1)-O(2)	-175.42941	-175.53845	-175.83475	-163.3(2)
C(1)-C(2)-C(31)-C(32)	-116.50389	-112.89968	-111.13304	-124.6(3)
C(4)-C(3)-B(2)-O(3)	-110.60203	-116.31378	-117.24387	-86.6(3)
C(3)-C(4)-C(41)-C(42)	-135.06786	-171.71968	-172.29676	137.3(3)

**Table S7.** The specific bond length and specific dihedral angles in **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** at  $S_0$  and  $T_1$  geometries (optimized via both ROB3LYP and UB3LYP). Optimizations were done using cc-pVTZ basis set (cc-pVTZ-PP + ECP for Te). **Figure S4** was used in designation of the atoms in the molecular structure.

Bond	Bond length [Å] (S <sub>0</sub> geometry)	Bond Length [Å] (T <sub>1</sub> geometry; ROB3LYP optimized)	Bond Length [Å] (T <sub>1</sub> geometry; UB3LYP optimized)	Experimental
Te-C(4)	2.07703	2.05466	2.05778	2.060(3)
Te-C(1)	2.07703	2.17084	2.16864	2.068(3)
C(4)-C(3)	1.37615	1.48551	1.49469	1.365(4)
C(3)-C(2)	1.44939	1.41696	1.41118	1.461(4)
C(2)-C(1)	1.37615	1.38981	1.39511	1.368(4)
C(4)-B(2)	1.54116	1.51526	1.51695	1.555(4)
C(1)-B(1)	1.54116	1.52302	1.52664	1.553(4)
C(3)-C(41)	1.49232	1.46135	1.46211	1.493(4)
C(2)-C(31)	1.49232	1.49538	1.49575	1.479(4)
Dihedral	Angle [°]	Angle [°]	Angle [°]	Angle [°]
Te-C(4)-B(2)-O(4A)	170.09295	169.78131	168.63686	-126.3(3)
C(4)-C(3)-C(41)-C(46)	113.11589	136.45157	137.28154	-125.1(3)
C(1)-C(2)-C(31)-C(32)	113.11553	106.64526	104.96882	-120.8(3)
C(2)-C(1)-B(1)-O(1)	176.53660	-177.18840	-177.71585	-178.3(3)

**Table S8.** The excitation energies at the TD-B3LYP/ aug-cc-pVTZ level of theory for **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** and **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** at their S<sub>0</sub> geometries. The states highlighted in red are the states that are suspected to be involved in the intersystem crossing responsible for phosphorescence.

2,5-BPin <sub>2</sub> -3,4-Ph <sub>2</sub> -Te			2,4-BPin <sub>2</sub> -3,5-Ph <sub>2</sub> -Te			
Excited State	Energy (eV)	Oscillator Strength	Excited State	Energy (eV)	Oscillator Strength	
T <sub>1</sub>	2.6659	0.000	T <sub>1</sub>	2.5995	0.000	
$T_2$	2.7313	0.000	$T_2$	2.9932	0.000	
$\mathbf{S}_1$	3.5590	0.134	T <sub>3</sub>	3.4918	0.000	
$T_3$	3.6149	0.000	$T_4$	3.6115	0.000	
$T_4$	3.7101	0.000	$\mathbf{S}_1$	3.6435	0.084	
T <sub>5</sub>	3.7992	0.000	$T_5$	3.7478	0.000	
$S_2$	4.0860	0.061	$S_2$	3.9231	0.231	
$S_3$	4.1164	0.000	$S_3$	3.9707	0.028	
$S_4$	4.1903	0.002	$S_4$	4.3102	0.068	
$S_5$	4.3283	0.044	$S_5$	4.3246	0.047	

![](_page_39_Figure_0.jpeg)

**Figure S26.** UV/Vis Absorption Spectra of **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** and **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** at the TD-B3LYP/ aug-cc-pVTZ level of theory. The Oscillator Strength of **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** at 295.88 nm is multiplied by 10 for clarity. The FWHM of the peaks is set at 0.66 eV, which is then converted to wavelength.

Table S9. Computational and experimental phosphorescence emission wavelengths of 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te and 2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te. The wavelengths are computed at the UB3LYP/cc-pVTZ and ROB3LYP/cc-pVTZ levels of theory.

	UB3LYP		ROB3LYP		experiment	
2,5-BPin <sub>2</sub> -3,4-Ph <sub>2</sub> -Te	2.02 eV	614 nm	2.16 eV	575 nm	2.40 eV	517 nm
2,4-BPin <sub>2</sub> -3,5-Ph <sub>2</sub> -Te	1.62 eV	764 nm	1.74 eV	711 nm	2.15 eV	577 nm

Table S10. Gas phase DFT/cc-pVTZ determined xyz coordinates (in Å) for all studied species.

A. 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te at S<sub>0</sub> equilibrium geometry using B3LYP/cc-pVTZ level of theory

Te 0.000005 2.365942 -0.000002 O -3.282919 2.470702 0.046489 O -3.910225 0.287105 -0.234526 O 3.282928 2.470692 -0.046496 O 3.910230 0.287096 0.234536 C -1.368082 0.803289 0.022656 C -0.724513 -0.413083 0.016194 C 0.724514 -0.413086 -0.016181 C 1.368087 0.803284 -0.022649 C -4.716558 2.495442 0.000021 C -5.119037 1.050402 -0.365232 C 4.716567 2.495431 -0.000028 C 5.119043 1.050393 0.365236 B -2.866236 1.157885 -0.047750 B 2.866242 1.157877 0.047752 Н 5.094615 2.798774 -0.977824 Н 5.039666 3.225653 0.741109 H 5.476809 0.965106 1.392553 H 5.875138 0.639162 -0.302608 H -5.875132 0.639177 0.302615 H -5.476803 0.965108 -1.392548 Н -5.039657 3.225659 -0.741121 H -5.094606 2.798793 0.977815 C -2.216101 -3.738959 -1.028588 C -2.955670 -4.081537 0.097678 C -2.966433 -3.229708 1.195339 C -2.244723 -2.043405 1.164619 C -1.495491 -1.690578 0.041145 C -1.489151 -2.556244 -1.054569 Н -2.203211 -4.394743 -1.889237 Н -3.518054 -5.005617 0.119336 Н -3.538077 -3.487658 2.077278 Н -2.257707 -1.381760 2.020536 Н -0.914660 -2.298595 -1.933777 C 2.955651 -4.081552 -0.097685 C 2.216099 -3.738967 1.028590 C 1.489156 -2.556248 1.054578 C 1.495485 -1.690586 -0.041139 C 2.244699 -2.043420 -1.164623 C 2.966402 -3.229727 -1.195349 Н 3.518030 -5.005636 -0.119348 H 2.203218 -4.394748 1.889241 H 0.914678 -2.298594 1.933794 Н 2.257673 -1.381779 -2.020542 Н 3.538032 -3.487683 -2.077296

**B.** 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te at T<sub>1</sub> equilibrium geometry using ROB3LYP/cc-pVTZ level of theory Te 0.222903 2.347228 -0.104259 O 3.436807 2.277271 0.118622 O 3.939068 0.055173 0.416740 O -3.035027 2.674213 -0.136815 O -3.918954 0.556835 -0.054988 C 1.463817 0.710317 -0.056461 C 0.663957 -0.540589 -0.009713 C -0.744830 -0.427213 0.091539 C -1.326699 0.833927 0.041304 C 4.860765 2.217199 0.245720 C 5.146261 0.773200 0.700800 C -4.457302 2.853998 -0.114090 C -5.029912 1.432799 -0.290252 B 2.940443 0.976924 0.154515 B -2.768986 1.315944 -0.042644 H -4.740547 3.299917 0.841625 H -4.748991 3.532027 -0.915456 H -5.404978 1.261228 -1.301319 H -5.824623 1.204691 0.419335 Н 5.975658 0.314054 0.163232 Н 5.348931 0.711793 1.772507 H 5.194401 2.962989 0.966932 Н 5.314604 2.440893 -0.722880 C 1.712333 -4.124954 0.574696 C 2.692399 -4.282119 -0.400962 C 3.015685 -3.209483 -1.227514 C 2.377076 -1.992336 -1.072321 C 1.356673 -1.822858 -0.116887 C 1.043732 -2.920101 0.708239 H 1.467331 -4.946546 1.234470 Н 3.206251 -5.227926 -0.509552 Н 3.777943 -3.320753 -1.987122 H 2.645162 -1.162012 -1.708189 Н 0.290119 -2.813023 1.472454 C -3.383810 -3.813926 0.241803 C -2.675471 -3.532221 -0.920645 C -1.816179 -2.442084 -0.968941 C -1.650233 -1.616175 0.144121 C -2.376430 -1.900135 1.301642 C -3.232350 -2.992634 1.353000 Н -4.051556 -4.664383 0.279943 Н -2.792429 -4.161465 -1.793214 Н -1.267782 -2.227994 -1.876381 Н -2.266015 -1.259014 2.166146 Н -3.783748 -3.200292 2.260669

C. 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te at T<sub>1</sub> equilibrium geometry using UB3LYP/c-pVTZ level of theory Te 0.214736 2.354099 -0.155798 O 3.444021 2.277088 0.139398 O 3.911921 0.058703 0.509734 O -3.049828 2.659610 -0.132861

O -3.913456 0.536512 -0.020352 C 1.462049 0.720266 -0.059562 C 0.664414 -0.543066 -0.016182 C -0.738067 -0.430877 0.092820 C -1.321438 0.834974 0.032470 C 4.862284 2.207764 0.319294 C 5.119795 0.769551 0.809909 C -4.473497 2.829013 -0.092763 C -5.037899 1.400646 -0.238179 B 2.934476 0.984106 0.192382 B -2.772138 1.306076 -0.032124 H -4.746095 3.288577 0.859340 Н -4.780917 3.491728 -0.900924 Н -5.436251 1.212923 -1.237175 H -5.812176 1.173884 0.493950 Н 5.956755 0.290686 0.302167 Н 5.295024 0.726596 1.887193 Н 5.175379 2.963755 1.039057 Н 5.352184 2.411334 -0.635908 C 1.740402 -4.130990 0.505249 C 2.723162 -4.262729 -0.471300 C 3.038983 -3.171873 -1.276608 C 2.389727 -1.963117 -1.099669 C 1.366817 -1.819118 -0.143031 C 1.062335 -2.933688 0.660940 H 1.500558 -4.966573 1.149239 Н 3.244768 -5.202194 -0.596622 Н 3.803635 -3.262210 -2.036662 H 2.653074 -1.118913 -1.719561 H 0.306963 -2.847847 1.426053 C -3.380221 -3.813200 0.283996 C -2.702091 -3.522748 -0.894159 C -1.842309 -2.433559 -0.955691 C -1.645253 -1.618224 0.159773 C -2.340484 -1.911172 1.333774 C -3.197591 -3.002146 1.398022 H -4.048553 -4.662673 0.332341 Н -2.842865 -4.144463 -1.768604 Н -1.316930 -2.212681 -1.875075 Н -2.205289 -1.278710 2.201250 H -3.725171 -3.216859 2.318128

**D.** 2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te at S<sub>0</sub> equilibrium geometry using B3LYP/cc-pVTZ level of theory Te -0.052293 -2.334529 -0.061635 O 3.211454 -2.612249 -0.011872 O 3.970734 -0.455360 0.112681 C -1.339783 -0.694506 -0.002907 C -0.639009 0.484522 -0.002672 C 0.805238 0.400729 -0.031480 C 1.398670 -0.838607 -0.055336 C 4.642098 -2.715481 -0.014443 C 5.134296 -1.281194 0.270682

B 2.871568 -1.272966 0.010739 Н 4.953225 -3.429903 0.746871 Н 4.966877 -3.080431 -0.990586 Н 5.904948 -0.950910 -0.424857 Н 5.509654 -1.165729 1.288947 O -2.050190 2.328895 1.146485 O -1.402705 2.750533 -1.007742 C -2.673768 3.576414 0.796659 C -2.045441 3.956201 -0.558727 B -1.370675 1.870909 0.045847 Н -2.782198 4.266466 -1.298290 Н -1.289745 4.737171 -0.462974Н -2.474351 4.307995 1.578228 Н -3.751363 3.418472 0.727481 C 3.074305 4.045776 0.038218 C 3.151555 3.195744 -1.059182 C 2.426819 2.011916 -1.079733 C 1.607724 1.658083 -0.006643C 1.533006 2.521518 1.090076 C 2.263789 3.703655 1.114104 Н 3.641793 4.966866 0.054902 Н 3.777437 3.455633 -1.902834H 2.487280 1.355912 -1.936989 H 0.909818 2.257501 1.934409 H 2.203182 4.354005 1.977070 C -2.799465 -0.861818 -0.035661 C -3.584842 -0.121405 -0.930221 C -4.964066 -0.278742 -0.965357 C -5.590190 -1.181898 -0.114462 C -4.822986 -1.930513 0.771414 C -3.444727 -1.775180 0.808240 Н -3.104302 0.559983 -1.619043 Н -5.549434 0.297446 -1.669967 Н -6.664304 -1.305989 -0.145020 Н -5.299654 -2.635487 1.439618 Н -2.857745 -2.349063 1.513299

**E. 2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** at T<sub>1</sub> equilibrium geometry using ROB3LYP/cc-pVTZ level of theory Te -0.181251 -2.341625 0.210951

O 3.029412 -2.755578 0.039543 O 3.891549 -0.634412 -0.110179 C -1.450165 -0.601492 0.058294 C -0.629019 0.595489 0.016844 C 0.732972 0.427121 -0.067840 C 1.301498 -0.912833 -0.038860 C 4.447529 -2.927332 -0.076922 C 5.021436 -1.502473 0.057834 B 2.748184 -1.400817 -0.045594H 4.796148 -3.600958 0.705175 Н 4.670545 -3.373656 -1.048325Н 5.768050 -1.271504 -0.701233 Н 5.457519 -1.323619 1.042706

O -1.865875 2.449035 1.321656 O -1.212214 2.993947 -0.802953 C -2.379589 3.771375 1.088751 C -1.722988 4.211769 -0.233800 B -1.237972 2.028554 0.173582 Н -2.425961 4.666240 -0.930358 H -0.888526 4.896628 -0.075451 H -2.116513 4.411622 1.929304 Н -3.467414 3.715077 1.016775 C 3.334522 3.833702 -0.230477 C 3.255553 2.960257 -1.310910 C 2.429267 1.848166 -1.252599 C 1.651284 1.597595 -0.119967 C 1.740903 2.477091 0.962278 C 2.578121 3.586350 0.907617 Н 3.984898 4.697210 -0.275444 H 3.840922 3.146641 -2.201645 H 2.374095 1.172454 -2.094879 H 1.162486 2.280816 1.855350 H 2.642253 4.252120 1.758452 C -2.832757 -0.740788 -0.137487 C -3.657192 0.321123 -0.627573 C -5.007926 0.149282 -0.822948 C -5.625930 -1.074948 -0.543884 C -4.849787 -2.136461 -0.077324 C -3.494328 -1.982383 0.115146 H -3.208007 1.263614 -0.900879 Н -5.596422 0.970600 -1.210826 Н -6.689008 -1.198532 -0.695963 H -5.313277 -3.090164 0.138067 H -2.921202 -2.816368 0.498197

**F. 2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** at T<sub>1</sub> equilibrium geometry using UB3LYP/cc-pVTZ level of theory Te -0.191762 -2.342198 0.231409

O 3.022726 -2.761540 0.040966 O 3.884744 -0.642821 -0.136143 C -1.455219 -0.601036 0.061267 C -0.627373 0.597697 0.016015 C 0.731822 0.423789 -0.071168 C 1.295483 -0.917100 -0.036993 C 4.439766 -2.936030 -0.086530 C 5.016361 -1.510102 0.025550 B 2.742329 -1.407909 -0.053225 Н 4.794779 -3.600384 0.700578 H 4.653140 -3.394584 -1.054313 Н 5.752508 -1.287564 -0.746120 Н 5.465943 -1.321029 1.002338 O -1.861203 2.443461 1.332681 O -1.194802 3.007034 -0.783153 C -2.367047 3.770790 1.111150 C -1.701907 4.221509 -0.203627 B -1.230165 2.031737 0.183167

Н -2.399216 4.686912 -0.898656 Н -0.864665 4.900305 -0.034227 H -2.104705 4.400874 1.959569 H -3.454791 3.720861 1.033422 C 3.351351 3.817213 -0.238897 C 3.242778 2.961630 -1.330884 C 2.409593 1.854515 -1.272091 C 1.655859 1.591145 -0.126515 C 1.774723 2.452398 0.967003 C 2.617965 3.557162 0.911350 H 4.006432 4.677125 -0.284617 Н 3.809924 3.158206 -2.231177 H 2.330701 1.192779 -2.123634 H 1.213268 2.246395 1.868725 H 2.704342 4.209638 1.770478 C -2.834838 -0.732938 -0.146490 C -3.650308 0.335183 -0.641798 C -5.000147 0.170924 -0.849332 C -5.627460 -1.050930 -0.577755 C -4.860429 -2.118336 -0.105789 C -3.506331 -1.972064 0.098779 H -3.193826 1.276112 -0.908422 H -5.580933 0.996163 -1.240492 H -6.689913 -1.168488 -0.738902 Н -5.331197 -3.069730 0.103955 H -2.940548 -2.809992 0.484248

# 12. Photostability study

![](_page_46_Figure_1.jpeg)

**Figure S27.** Time dependence of the emission intensity of **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** drop-cast thin films and DH4T film under sodium lamp<sup>13</sup> (the distance of the lamp from the film was 8 cm). The structure of DH4T is shown in Figure S28.

![](_page_46_Figure_3.jpeg)

Figure S28. Structure of DH4T.

![](_page_47_Figure_0.jpeg)

**Figure S29.** UV/vis spectra of drop-cast thin film **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** before and after exploring a 360 W mercury lamp.

![](_page_48_Figure_0.jpeg)

13. Photoluminescence spectra of 2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te film under N<sub>2</sub>, air and O<sub>2</sub>

**Wavelength (nm) Figure S30.** Photoluminescence spectra of **2,5-BPin2-3,4-Ph2-Te** film under N<sub>2</sub>, air and O<sub>2</sub>. The pressure of O<sub>2</sub> was *ca.* 4 atm.

![](_page_48_Picture_3.jpeg)

![](_page_48_Figure_4.jpeg)

### 14. X-ray diffraction (XRD) study of film crystallization

![](_page_49_Figure_1.jpeg)

**Figure S32.** X-ray diffraction (XRD) patterns for **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** drop-coated film in different states: Fresh prepared film (less than 30 min) (Blue), same Film left for 7 days at ambient condition (Red) and simulated XRD pattern from single-crystal structure (Black).

![](_page_49_Figure_3.jpeg)

**Figure S33.** X-ray diffraction (XRD) patterns for **2,4-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** drop-coated film in different states: Fresh prepared film (less than 30 min) (Blue), same Film left for 7 days at ambient condition (Red) and simulated XRD pattern from single-crystal structure (Black).

![](_page_50_Figure_0.jpeg)

### 15. Study of the effect of film crystallization on emission lifetimes

**Figure S34.** Time-resolved photoluminescence of **2,5-BPin<sub>2</sub>-3,4-Ph<sub>2</sub>-Te** (A) Freshly prepared dropcoated film (less than 30 min) and (B) Same film left for 7 days in ambient conditions.

![](_page_50_Figure_3.jpeg)

**Figure S35.** Time-resolved photoluminescence of **2,3-BPin<sub>2</sub>-3,5-Ph<sub>2</sub>-Te** (A) Freshly prepared dropcoated film (less than 30 min) and (B) Same film left for 7 days in ambient conditions.

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