Supporting Information For: Multi-state emission properties and the inherent mechanism of D-A-D type asymmetric organic boron complexes

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Experimental

Measurement and characterization

$^1$H NMR spectra were obtained with a Varian inova-400-MHz instrument using tetramethylsilane (TMS) as the internal standard. $^{13}$C NMR spectra were recorded on a Varian inova-100-MHz spectrometer by using CDCl$_3$ as the solvent in all cases. The UV-vis absorption spectra were obtained on a MaPada UV-3200PCS spectrophotometer. Fluorescent emission spectra were obtained on a Hitachi F-2500 fluorescence spectrophotometer. Fluorescent quantum yields of solids were obtained by Fsl980 full-featured Steady/Transient Fluorescence Spectrometer (Edinburgh). Glass transition temperature and melting point was determined by DSC measurements carried out using DSC Q2000 (TA, America). ESI/MS spectra were obtained on a Waters GCT Premier. MALDI/HRMS were record on an UltrafleXtreme MALDI-TOF/TOF mass spectrometer (Bruker, Germany). Powder XRD measurements were conducted on D8 Advance (Bruker) with Cu Kα radiation in the range 10° < 2θ < 90°. Digital photographs were taken by Canon 550D (Canon, Japan) digital cameras. Fluorescence lifetimes were obtained on an Edinburgh Instrument FLSP920 fluorescence spectrophotometer. Fluorescence microscopy photos were obtained on OLYMPUS BX53. The theoretical calculation were calculated by density functional theory (DFT) in Gaussian 09 at the B3LYP/6-31G (d,p) level. Fluorescence quantum yields in solution, for TPEDKBF$_2$-derivatives in various solvent were calculated versus quinine sulphate in 0.1 M sulfuric acid solution (Φ$_r$= 0.55) as the standard using the following values: Φ(Hexane) = 1.375, Φ(Toluene) = 1.496, Φ(CH$_2$Cl$_2$)= 1.424, Φ(THF) =1.405 Φ(DMSO) = 1.478, and Φ(H$_2$O) = 1.333. Optically dilute solutions of TPEDKBF$_2$-derivatives and quinine sulphate standard were prepared in 10 mL volumetric flasks with absorbances < 0.05. Quantum yield measurements were performed with excitation at λ$_{ex}$ = 350 nm.

Materials and Synthesis.

THF, DMF and CH$_2$Cl$_2$ were dried according to standardized procedures previously described. All the other chemicals and reagents used in this study were of analytical grade without further purification. In general, all the intermediates and final compounds were purified by column chromatography on silica gel (200-300 mesh), and crystallization from analytical grade solvents. Reactions were monitored by using thin layer chromatography (TLC). The synthetic routes for TPEDKBF$_2$Ca, TPEDKBF$_2$DBeA, and TPEDKBF$_2$DMeA are shown in Scheme 1. Firstly, TPE was synthesized by using benzophenone as the reagent according to the reported procedures; then Friedel-Crafts acylation reaction occurred between TPE and acetyl chloride, to thus give compound Ac-TPE; The boron complexes were synthesized by Claisen condensation with methyl benzoate derivatives and NaH (60%) to generate the β-diketones intermediates, followed by boronation with
BF₃·OEt₂ in CH₂Cl₂. The target molecules were characterized by ¹H NMR, ¹³C NMR, and MALDI-TOF mass spectrometry.

4-(4-(dibenzylamino)phenyl)-2,2-difluoro-6-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide (TPEDKBF₂,DBeA)

methyl 4-(dibenzylamino)benzoate (500 mg, 1.5 mmol), acetyl-TPE (520 mg, 1.40 mmol) and NaH (60%, 120 mg, 3.0 mmol) were added sequentially to a 100 mL round-bottom flask containing THF (30 mL). The mixture was refluxed under 90 °C for 24 h in argon atmosphere, it was cooled to room temperature. After that, the mixture was acidified with dilute HCl. The mixture was poured into water and extracted with dichloromethane three times. Then the organic phase was combined and dried over anhydrous Na₂SO₄. Removing the solvent under reduced pressure and an orange residue solid was collected. The residue was purified by column chromatography on silica gel eluting with petroleum ether/CH₂Cl₂, v/v = 3/1 to give the diketone precursor, 1-(4-(dibenzylamino)phenyl)-3-(4-(1,2,2-triphenylvinyl)phenyl)propane-1,3-dione as a yellow solid (500 mg, 53%) Then, the pure diketone precursor was dried under vacuum followed by dissolving in CH₂Cl₂ (50 mL). The boron trifluoride diethyl ether complex (0.3 mL, 2.4 mmol) was added to the above solution, which was stirred under an atmosphere of argon at room temperature for 24 h. Water was added in order to quench the reaction. The organic layer was separated and dried over Na₂SO₄. After removal of the solvent, the crude product was purified by column chromatography (silica gel, petroleum ether/CH₂Cl₂, v/v = 2/1) to afford TPEDKBF₂,DBeA (428.5 mg) as a red solid, yield 80%, m.p. 190.0–192.0 °C. ¹H NMR (400 MHz, CDCl₃) δ/ppm = 7.98 (d, J = 8.0, 2H), 7.80 (d, J = 8.0, 2H), 7.39-7.29 (m, 6H). 7.21 (d, J = 8.0, 4H), 7.16-7.12 (m, 11H). 7.04-7.00 (m, 6H). 6.88 (s, 1H). 6.81 (d, J = 9.2, 2H), 4.78 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ/ppm = 180.63, 178.10, 154.84, 150.18, 143.18, 143.11, 143.02, 142.89, 139.73, 136.26, 131.99, 131.35, 131.32, 131.28, 130.57, 129.06, 127.75, 127.68, 127.16, 126.90, 126.39, 119.44, 112.14, 91.61, 54.19. HRMS (MALDI-TOF): m/z 721.2951, calculated 721.2964.

4-(4-(dimethylamino)phenyl)-2,2-difluoro-6-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide (TPEDKBF₂,DMeA)

Compound TPEDKBF₂,DMeA was prepared by following the synthetic procedure for compound TPEDKBF₂,DBeA. The crude diketone precursor, 1-(4-(dimethylamino)phenyl)-3-(4-(1,2,2-triphenylvinyl)phenyl)propane-1,3-dione, was purified by column chromatography (silica gel, petroleum ether/CH₂Cl₂, v/v = 3/1), to afford pure diketone precursor (401 mg, 55%) as a yellow solid. Then, boronation with BF₃·OEt₂ in CH₂Cl₂, the crude product was purified by column chromatography (silica gel, petroleum ether/CH₂Cl₂, v/v = 2/1) to obtain TPEDKBF₂,DMeA (385 mg) as a red solid, yield 88%, m.p. 350.0–353.0 °C. ¹H NMR (400 MHz, CDCl₃) δ/ppm = 8.05 (d, J = 8.0, 2H), 7.85 (d, J = 8.4, 2H), 7.19-7.13 (m, 11H), 7.07-7.04 (m, 6H), 6.93 (s, 1H), 3.17 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ/ppm = 155.09, 149.97, 143.12, 143.08, 143.04, 142.90, 139.75, 131.84, 131.82, 131.34, 131.31, 131.27, 127.98, 127.92, 127.77, 127.72, 127.59, 126.87, 111.39, 99.98, 40.18. HRMS (MALDI-TOF): m/z 569.2334, calculated 569.2338.

4-(4-(9H-carbazol-9-yl)phenyl)-2,2-difluoro-6-(4-(1,2,2-triphenylvinyl)phenyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide (TPEDKBF₂,Ca)

Compound TPEDKBF₂, Ca was prepared by following the synthetic procedure for compound TPEDKBF₂,DBeA. The crude diketone precursor, 1-(4-(9H-carbazol-9-yl)phenyl)-3-(4-(1,2,2-triphenylvinyl)phenyl)propane-1,3-dione, was purified by column chromatography (silica gel, petroleum ether/CH₂Cl₂, v/v = 3/1), to afford pure diketone precursor (459 mg, 51%) as a yellow solid. Then, boronation with BF₃·OEt₂ in CH₂Cl₂, the crude product was purified by column chromatography (silica gel, petroleum ether/CH₂Cl₂, v/v = 2/1) to obtain TPEDKBF₂, Dca (420 mg) as a red solid, yield 85%, m.p. 268.0–270.0 °C. ¹H NMR (400 MHz, CDCl₃) δ/ppm = 8.39 (d, J = 8.8, 2H), 8.17 (d, J = 8.0, 2H), 7.96 (d, J = 8.0, 2H), 7.85 (d, J = 8.8, 2H), 7.56 (d, J = 8.0, 2H), 7.48
(td, J=8.0, 2H), 7.37 (td, J=8.0), 7.26 (d, J=8.8, 2H), 7.20-7.15 (m, 10H), 7.09-7.04 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm = 182.62, 180.99, 152.08, 144.11, 143.95, 142.87, 142.66, 139.83, 139.46, 132.21, 131.35, 131.26, 130.62, 130.00, 129.57, 128.56, 128.11, 128.06, 127.79, 127.38, 127.07, 126.51, 126.42, 124.19, 121.15, 120.59, 109.84, 99.98, 93.33. HRMS (MALDI-TOF): m/z 672.2518, [[M-F]$^+$, calculated 672.2510].

**Figure S1.** Lippert–Mataga plot of TPEDKBF$_2$Ca, TPEDKBF$_2$DBeA and TPEDKBF$_2$DMeA vs the solvent polarity.

**Figure S2.** Optimized structures for the $S_0$ ($S_0$) and $S_1$ ($S'_1$) electronic states and an energy diagram for TPEDKBF$_2$Ca, calculated at the B3LYP/SV(P) level of theory.
**Figure S3.** The UV-Vis absorption spectrum of TPEDKBF$_2$DBeA from 20 to 50% water content (4nm red-shift)

**Figure S4.** The frontier orbital plots of the HOMO and LUMO of molecular TPEDKBF$_2$Ca, TPEDKBF$_2$DBeA, TPEDKBF$_2$DMeA in single crystal.
Figure S5. Emission maxima of TPEDKBF$_2$Ca(Oc) during the grinding-annealing cycles. As = the prepared crystals of TPEDKBF$_2$Ca (Oc), G = ground sample; Fn = Fuming sample (fuming with DCM for 2h). The numbers after G or Fn represent cycle numbers.

Figure S6. Fluorescent spectra of TPEDKBF$_2$DBeA ($\Phi_F$ = 0.538) and TPEDKBF$_2$Ca ($\Phi_F$ = 0.570) at the melt-cooled amorphous states.

Table S1. Peak absorption/emission wavelengths ($\lambda$, in nm) and quantum yields ($\Phi_F$) of three compounds in different solvents.

<table>
<thead>
<tr>
<th></th>
<th>$\Phi_F$/%</th>
<th>$\lambda_{\text{abs}}$/nm</th>
<th>$\lambda_{\text{em}}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPEDKBF$_2$Ca</td>
<td>1.3</td>
<td>448/500</td>
<td>453/497</td>
</tr>
<tr>
<td>TPEDKBF$_2$DBeA</td>
<td>13.9</td>
<td>457/544</td>
<td>465/522</td>
</tr>
<tr>
<td>TPEDKBF$_2$DMeA</td>
<td>11.4</td>
<td>459/590</td>
<td>474/556</td>
</tr>
<tr>
<td>Hexane</td>
<td>469/531</td>
<td>479/565</td>
<td>472/563</td>
</tr>
<tr>
<td>Toluene</td>
<td>488/577</td>
<td>492/585</td>
<td></td>
</tr>
<tr>
<td>DCM</td>
<td>462/606</td>
<td></td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>488/585</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>462/606</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table S2. HOMO/LUMO energy levels of TPEDKBF$_2$Ca, TPEDKBF$_2$DBeA, TPEDKBF$_2$DMeA.

<table>
<thead>
<tr>
<th></th>
<th>single molecular state/single crystal</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gap (eV)</td>
<td>LUMO (eV)</td>
<td>HOMO (eV)</td>
</tr>
<tr>
<td>TPEDKBF$_2$Ca(Oc)</td>
<td>2.908/2.915</td>
<td>-2.689/-2.691</td>
<td>-5.597/-5.606</td>
</tr>
<tr>
<td>TPEDKBF$_2$Ca(Rc)</td>
<td>2.908/2.694</td>
<td>-2.689/-2.792</td>
<td>-5.597/-5.486</td>
</tr>
<tr>
<td>TPEDKBF$_2$DBeA</td>
<td>3.181/3.182</td>
<td>-2.282/-2.294</td>
<td>-5.463/-5.476</td>
</tr>
<tr>
<td>TPEDKBF$_2$DMeA</td>
<td>3.189/ --</td>
<td>-2.255/ --</td>
<td>-5.445/ --</td>
</tr>
</tbody>
</table>

Table S3. Peak emission wavelengths (λ, in nm), fluorescent lifetime (τ, in μs) and quantum yields of five compounds in different states.

<table>
<thead>
<tr>
<th>Entry</th>
<th>λ$_{ultrasonic}$</th>
<th>λ$_{crystal}$</th>
<th>λ$_{ground}$</th>
<th>λ$_{annealed}$</th>
<th>Δλ$_{max}$</th>
<th>Φ$_{crystal}$</th>
<th>Φ$_{ground}$</th>
<th>τ$_{crystal}$</th>
<th>τ$_{ground}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPEDKBF$_2$DBeA</td>
<td>617</td>
<td>642</td>
<td>597</td>
<td>603</td>
<td>600</td>
<td>45</td>
<td>0.188</td>
<td>0.545</td>
<td>8.503</td>
</tr>
<tr>
<td>TPEDKBF$_2$DMeA</td>
<td>624</td>
<td>628</td>
<td>636</td>
<td>630</td>
<td>628</td>
<td>12</td>
<td>0.157</td>
<td>0.211</td>
<td>0.268</td>
</tr>
<tr>
<td>TPEDKBF$_2$Ca(Oc)</td>
<td>581</td>
<td>586</td>
<td>616</td>
<td>582</td>
<td>583</td>
<td>35</td>
<td>0.550</td>
<td>0.566</td>
<td>3.839</td>
</tr>
<tr>
<td>TPEDKBF$_2$Ca(Rc)</td>
<td>582</td>
<td>624</td>
<td>615</td>
<td>583</td>
<td>583</td>
<td>9</td>
<td>0.485</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure S7 $^1$H NMR (400 MHz) spectrum of compound TPEDKBF$_2$Ca in CDCl$_3$.

Figure S8 $^{13}$C NMR (100 MHz) spectrum of compound TPEDKBF$_2$Ca in CDCl$_3$. 
Figure S9 ¹H NMR (400 MHz) spectrum of compound TPEDKBF₂DBeA in CDCl₃.

Figure S10 ¹³C NMR (100 MHz) spectrum of compound TPEDKBF₂DBeA in CDCl₃.
Figure S11 $^1$H NMR (400 MHz) spectrum of compound TPEDKBF$_2$DMeA in CDCl$_3$.

Figure S12 $^{13}$C NMR (100 MHz) spectrum of compound TPEDKBF$_2$DMeA in CDCl$_3$. 
**Figure S13** MALDI/TOF MS spectrum of compound TPEDKF$_2$Ca.

**Figure S14** MALDI/TOF MS spectrum of compound TPEDKF$_2$DBeA.
Figure S15: MALDI/TOF MS spectrum of compound TPEDKBF$_2$DMeA.

Table S4: Crystal data and structure refinement for the single crystals

<table>
<thead>
<tr>
<th></th>
<th>TPEDKBF$_2$Ca (Oc)</th>
<th>TPEDKBF$_2$DBeA</th>
<th>TPEDKBF$_2$Ca (Rc)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C47 H32 B F2 N O2</td>
<td>C49 H38 B F2 N O2</td>
<td>C47 H32 B F2 N O2</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>691.55</td>
<td>721.61</td>
<td>691.55</td>
</tr>
<tr>
<td><strong>Temperature, K</strong></td>
<td>296(2)</td>
<td>296(2)</td>
<td>296(2)</td>
</tr>
<tr>
<td><strong>Wavelength, Å</strong></td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>space group</strong></td>
<td>P-1</td>
<td>P-1</td>
<td>P2(1)/n</td>
</tr>
<tr>
<td><strong>a, Å</strong></td>
<td>8.3426(9)</td>
<td>8.393(5)</td>
<td>14.917(2)</td>
</tr>
<tr>
<td><strong>b, Å</strong></td>
<td>11.4056(11)</td>
<td>11.122(7)</td>
<td>24.663(3)</td>
</tr>
<tr>
<td><strong>c, Å</strong></td>
<td>19.6777(18)</td>
<td>21.214(13)</td>
<td>20.762(3)</td>
</tr>
<tr>
<td><strong>α, deg.</strong></td>
<td>81.770(3)</td>
<td>97.698(17)</td>
<td>90.00</td>
</tr>
<tr>
<td><strong>β, deg.</strong></td>
<td>84.375(3)</td>
<td>96.901(15)</td>
<td>93.468(5)</td>
</tr>
<tr>
<td><strong>γ, deg.</strong></td>
<td>87.955(4)</td>
<td>91.598(18)</td>
<td>90.00</td>
</tr>
<tr>
<td><strong>Volume, Å$^3$</strong></td>
<td>1843.7(4)</td>
<td>1946(2)</td>
<td>7624.1(19)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td><strong>Calculated density</strong></td>
<td>1.246 Mg/m$^3$</td>
<td>1.231 Mg/m$^3$</td>
<td>1.205 Mg/m$^3$</td>
</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
<td>0.082 mm$^{-1}$</td>
<td>0.080 mm$^{-1}$</td>
<td>0.079 mm$^{-1}$</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>720</td>
<td>756</td>
<td>2880</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
<td>0.21 x 0.17 x 0.19 mm</td>
<td>0.20 x 0.19 x 0.18 mm</td>
<td>0.22 x 0.20 x 0.18 mm</td>
</tr>
<tr>
<td><strong>Theta range for data</strong></td>
<td>1.05 to 24.96 deg.</td>
<td>0.98 to 25.11 deg.</td>
<td>1.28 to 25.00 deg.</td>
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<tr>
<td></td>
<td>-9 &lt;= h &lt;= 8, -13 &lt;= k &lt;= 13, -23 &lt;= l &lt;= 23</td>
<td>-9 &lt;= h &lt;= 9, -9 &lt;= k &lt;= 13, -25 &lt;= l &lt;= 23</td>
<td>-15 &lt;= h &lt;= 17, -29 &lt;= k &lt;= 28, -24 &lt;= l &lt;= 24</td>
</tr>
<tr>
<td>-------------------------</td>
<td>---------------------------------------------</td>
<td>---------------------------------------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td><strong>Limiting indices</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reflections collected / unique</strong></td>
<td>11808/6382 [R(int)=0.0381]</td>
<td>12304/6820 [R(int)=0.0941]</td>
<td>14145/7034 [R(int)=0.0293]</td>
</tr>
<tr>
<td><strong>Completeness to theta</strong></td>
<td>24.96°, 98.6%</td>
<td>25.11°, 98.4%</td>
<td>25.00°, 99.9%</td>
</tr>
<tr>
<td><strong>Absorption correction</strong></td>
<td>Semi-empirical from equivalents</td>
<td>Semi-empirical from equivalents</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td><strong>Max. and min. transmission</strong></td>
<td>0.9847 and 0.9816</td>
<td>0.9857 and 0.9841</td>
<td>0.9859 and 0.9828</td>
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<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on F^2</td>
<td>Full-matrix least-squares on F^2</td>
<td>Full-matrix least-squares on F^2</td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>6382 / 0 / 479</td>
<td>6820 / 0 / 496</td>
<td>13413 / 48 / 956</td>
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<tr>
<td><strong>Goodness-of-fit on F^2</strong></td>
<td>0.967</td>
<td>0.937</td>
<td>1.479</td>
</tr>
<tr>
<td><strong>Final R indices [I &gt; 2sigma(I)]</strong></td>
<td>R_1 = 0.0558, wR_2 = 0.1287</td>
<td>R_1 = 0.1140, wR_2 = 0.3079</td>
<td>R_1 = 0.1564, wR_2 = 0.4437</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R_1 = 0.1148, wR_2 = 0.1613</td>
<td>R_1 = 0.2587, wR_2 = 0.3985</td>
<td>R_1 = 0.2517, wR_2 = 0.4936</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
<td>0.238 and -0.262 e. Å^3</td>
<td>0.283 and -0.338 e. Å^3</td>
<td>2.797 and -0.460 e. Å^3</td>
</tr>
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