

### Supporting information

Pyridomethene-BF<sub>2</sub> complex/phenothiazine-hybrid sensitizer with high molar extinction coefficient for efficient sensitized solar cells

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#### Table of contents:

Page	Contents
S3	Synthesis of dyes <b>K</b> , <b>R1</b> and <b>P3</b>
S4	Computation method
S6	<b>Scheme S1</b> Synthetic scheme for the dyes <b>K1</b> and <b>K2</b> .
S7	<b>Scheme S2</b> Synthetic Scheme for the dyes <b>K3-K5</b> .
S8	<b>Scheme S3</b> Synthetic Scheme for the dyes <b>K6 – K8</b> .
S9	<b>Scheme S4</b> Synthetic Scheme for the compounds <b>R1</b> and <b>P3</b> .
S10	Characterization data of <b>2</b> , <b>5</b> and <b>6</b>
S11	Characterization data of <b>8</b>
S12	Characterization data of <b>11</b> , <b>12</b> and <b>14</b>
S13	Characterization data of <b>15</b> and <b>16</b>
S14	Characterization data of <b>17</b> and <b>19</b>
S15	Characterization data of <b>20</b> , <b>21</b> and <b>22</b>
S16	Characterization data of <b>23</b> and <b>24</b>
S17	Characterization data of <b>25</b>
S18	Characterization data of <b>26</b> , <b>K1</b> and <b>K2</b>
S19	Characterization data of <b>K3</b> and <b>K4</b>
S20	Characterization data of <b>K5</b> and <b>K6</b>
S21	Characterization data of <b>K7</b> and <b>K8</b>
S22	Characterization data of <b>P3</b> and <b>R1</b>

S23-24	<b>Figure S1.</b> Absorption spectra of (a) <b>K1</b> , (b) <b>K2</b> , (c) <b>K3</b> , (d) <b>K4</b> , (e) <b>K5</b> , (f) <b>K6</b> , (g) <b>K7</b> , (h) <b>K8</b> , (i) <b>R1</b> , and (j) <b>R2</b> in different solvents.
S25	<b>Figure S2.</b> Absorption spectra of (a) <b>K2</b> , (b) <b>K4</b> , (c) <b>K5</b> , (d) <b>K6</b> , (e) <b>K7</b> , (f) <b>K8</b> , and (g) <b>R1</b> in THF solutions before and after the addition of TEA.
S26	<b>Figure S3.</b> Cyclic voltammograms of the <b>K</b> and <b>R</b> dyes recorded in THF solutions.
S27	<b>Figure S4.</b> Frontier orbitals of the <b>K</b> and <b>R</b> dyes optimized with DFT at the B3LYP/6-31G(d,p) level.
S28	<b>Figure S5.</b> Frontier orbitals of the <b>K</b> and <b>R</b> dyes optimized with DFT at the B3PW91/6-31G (d,p) level.
S29	<b>Figure S6.</b> Frontier orbitals of the <b>K</b> and <b>R</b> dyes optimized with Hartree-Fock 6-31G (d,p) basis set.
S30	<b>Figure S7.</b> Calculated gas-phase absorption spectra of (a) dyes <b>K1– K5</b> and (b) dyes <b>K6– K8, R1</b> and <b>R2</b> by using DFT at the B3LYP/6-31G (d,p) level.
S31	<b>Figure S8.</b> Calculated gas-phase absorption spectra of (a) dyes <b>K1– K5</b> and (b) dyes <b>K6– K8, R1</b> and <b>R2</b> by using DFT at the B3PW91/6-31G(d,p) level.
S32	<b>Figure S9.</b> Calculated gas-phase absorption spectra of (a) dyes <b>K1– K5</b> and (b) dyes <b>K6– K8, R1</b> and <b>R2</b> by using Hartree-Fock 6-31G (d,p) basis set.
S33	<b>Figure S10.</b> (a) The IPCE and (b) current-voltage plots for the DSSC made with dye <b>K1</b> with or without DCA.
S34	<b>Figure S11.</b> The electrochemical impedance spectra of (a) Nyquist plots, and (b) Bode phase plots for the DSSC based on <b>K</b> and <b>R</b> with DCA.
S35	<b>Figure S12.</b> Absorption spectra of (a) <b>K2</b> , (b) <b>K3</b> , (c) <b>K5</b> , (d) <b>K6</b> , (e) <b>K7</b> , and (f) <b>K8</b> absorbed on nanocrystalline TiO <sub>2</sub> films before and after light irradiation (30 min).
S36-37	<b>Table S1</b> Calculated TDDFT excitation energies ( <i>E</i> ), oscillator strengths ( <i>f</i> ), MO compositions and characters, are compared with experimental absorptions based on DFT at the B3LYP/6-31G (d,p) level.
S38-39	<b>Table S2</b> Calculated TDDFT excitation energies ( <i>E</i> ), oscillator strengths ( <i>f</i> ), MO compositions and characters, are compared with experimental absorptions based on DFT at the B3PW91/6-31G (d,p) level.
S40-41	<b>Table S3</b> Calculated TDDFT excitation energies ( <i>E</i> ), oscillator strengths ( <i>f</i> ), MO compositions and characters, are compared with experimental absorptions based on Hartree-Fock 6-31G (d,p) basis set.
S42	<b>Table S4</b> DSSC performance parameters of dye <b>K1</b> with or without DCA as co-adsorbent.

*Synthesis of dyes K, R1 and P3*

The synthetic route of organic dyes **K**, **R1** and **P3** are depicted in Scheme S1–S4. Reaction of the pyridomethene-BF<sub>2</sub> complex **1**<sup>S1</sup> with the commercially available bis(pinacol)borane in the presence of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and KOAc in refluxing toluene affords the desired pyridomethene-BF<sub>2</sub> complex pinacolboronates **2** in good yields. Suzuki coupling reaction on **2** with compound **3**<sup>S2</sup> or **4**<sup>S2</sup> result in the corresponding aldehyde or bromo derivatives. Bromo derivative **6** was coupled with **7**<sup>S3</sup> by a Stille coupling reaction, by following acidic hydrolysis to afford **8**. A Knoevenagel reaction was then used to condense compound **5** or **8** with 2-cyanoacrylic acid to obtain the target dyes **K1** and **K2**. Compound **11** and **12** were synthesized through a Suzuki coupling reaction of thiophene derivatives **9** and **10**, respectively. Compound **14**, **15** and **17** were synthesized through Suzuki coupling reaction to afforded corresponding aldehyde precursors, followed by treatment with 2-cyanoacrylic acid in the presence of ammonium acetate afforded the dyes **K3**, **K4**, and **K5**, respectively. The synthesis of dye **K6–K8** started from phenothiazine, which was coupled with 1,4-dibromobenzene through a palladium-catalyzed aromatic C-N bond formation. A Vilsmeier reaction of **18** with a mixture of DMF and POCl<sub>3</sub> produced compound **19**. Bromination of **19** with NBS, followed by a Suzuki coupling reaction of the obtained intermediate **20** with compound **2**, gave compound **21**. Further treatment of this intermediate with bis(pinacol)borane affords the desired **22** that was coupling with compound **10** and **12**, respectively yielding the corresponding aldehyde derivatives **23** and **24**, respectively. A Suzuki coupling reaction between intermediate **23** and pinacol ester of pyridomethene-BF<sub>2</sub> complex **2** afforded compound **25**. Subsequent Knoevenagel condensation of **25** and **24** with 2-cyanoacrylic acid in the presence of ammonium acetate afforded the dyes **K6** and **K7**. In addition, compound **19** is react with **2** under Suzuki coupling condition to give compound **26**. Finally, Knoevenagel condensation of aldehyde **26** and cyanoacetic acid give the dye **K8**.

Compound **28** was made from **13**<sup>S4</sup> with **27** by a Suzuki coupling reaction, followed by Knoevenagel condensation to construct the reference **R1**. In addition, the parent compound **P3** was synthesized via Suzuki coupling reaction of **1** with phenylboronic acid.

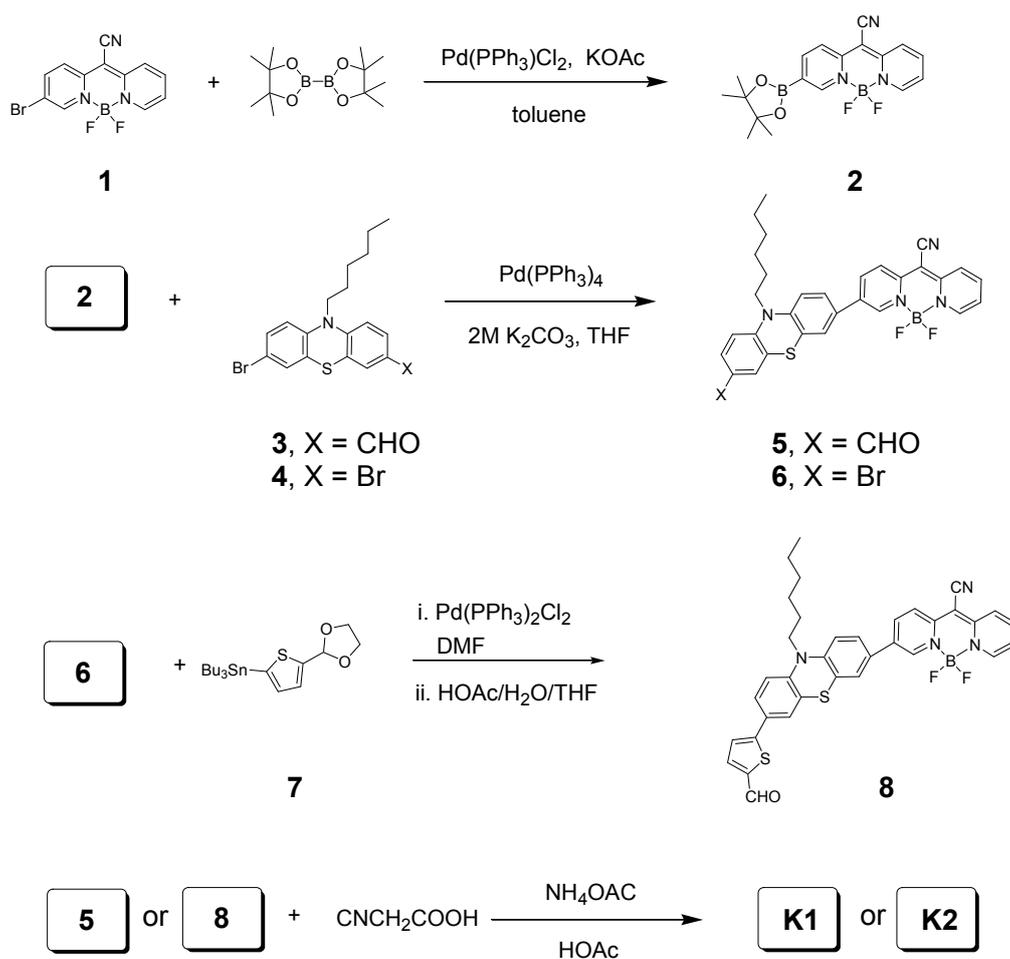
#### *Computation method*

The entire quantum chemical calculations have been performed at DFT (B3LYP and B3PW91) and Hartree-Fock with 6-31G (d,p) basis sets using the Gaussian 03W program.<sup>S5</sup>

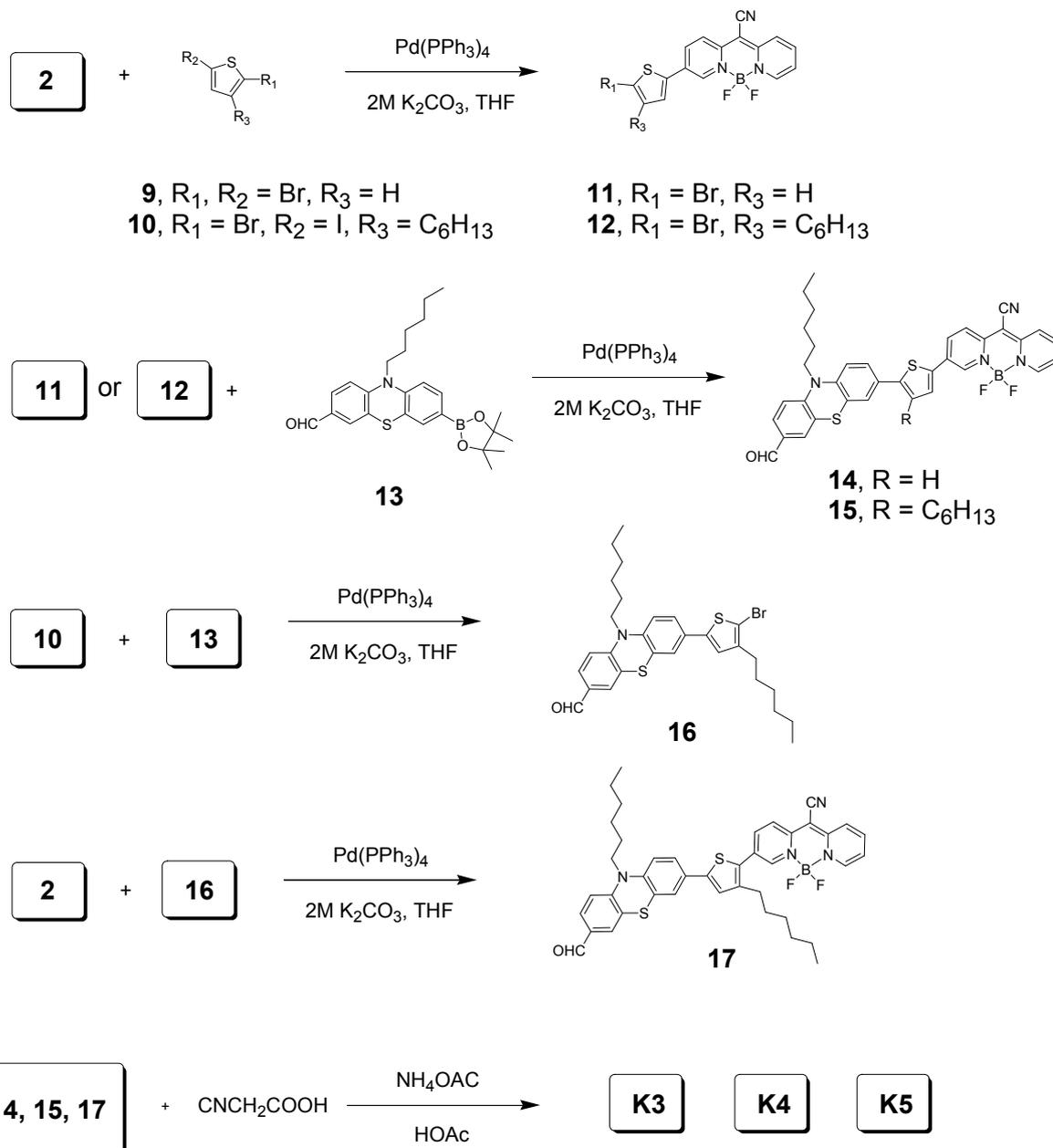
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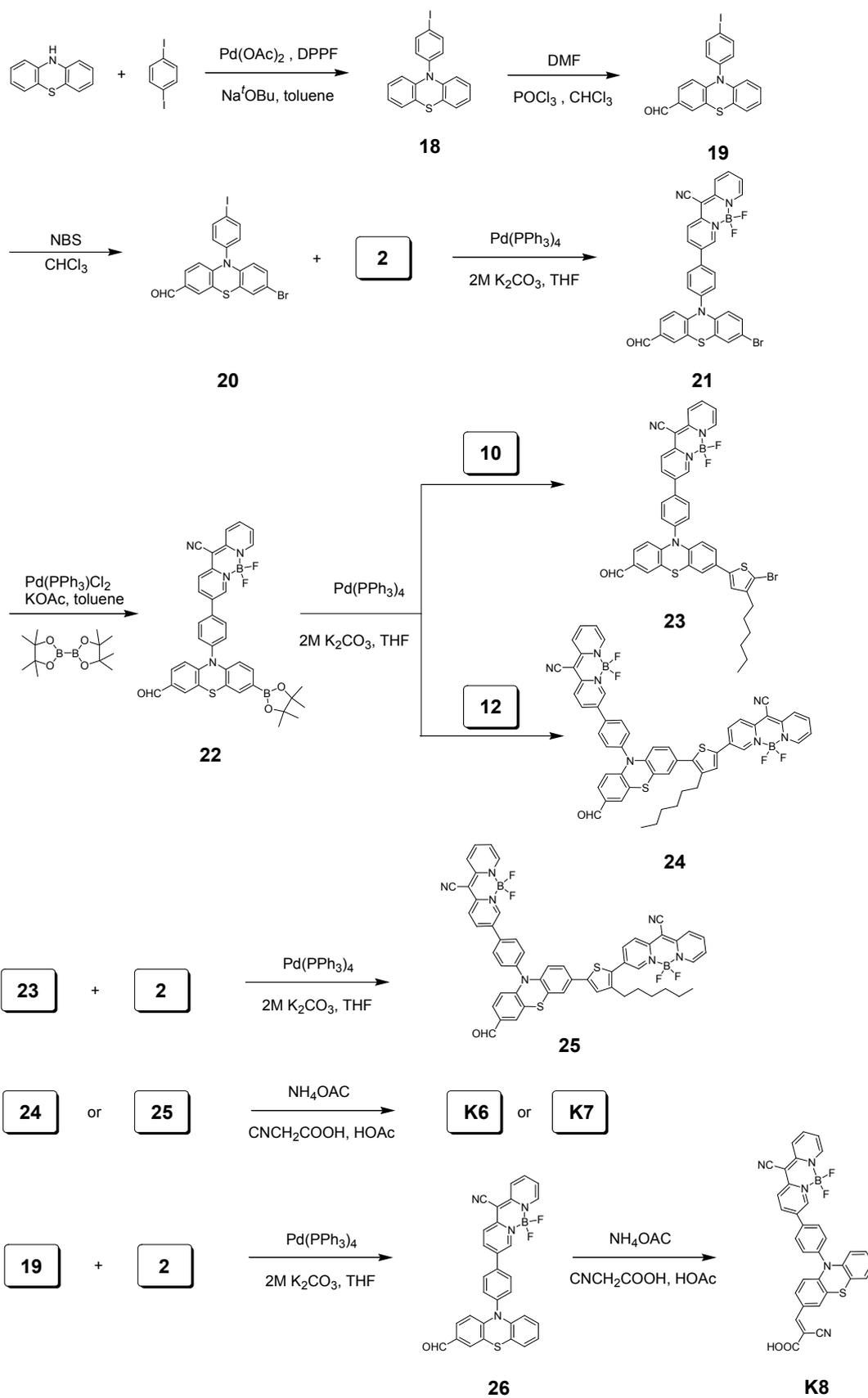
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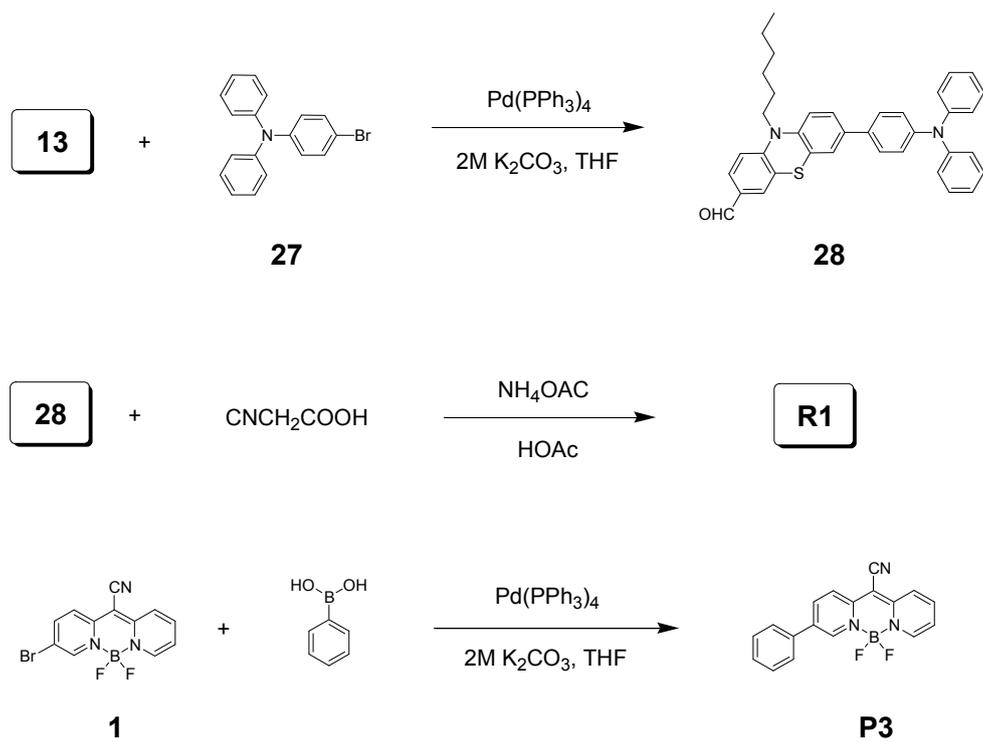
**Scheme S1** Synthetic Scheme for the dyes **K1** and **K2**.



**Scheme S2** Synthetic Scheme for the dyes **K3-K5**.



**Scheme S3** Synthetic Scheme for the dyes **K6–K8**.



**Scheme S4** Synthetic Scheme for the compounds **R1** and **P3**.

**Synthesis of compound 2.** Compound **1** (2.1 g, 6.52 mmol), bis(pinacolato)diboron (1.99 g, 7.83 mmol), KOAc (1.91 g, 19.56 mmol), and Pd(PPh<sub>3</sub>)Cl<sub>2</sub> (0.234 g, 0.326 mmol) in 65 mL of anhydrous toluene under nitrogen was heated at 120 °C for 18 h. The solution was cooled and then 30 mL of CH<sub>2</sub>Cl<sub>2</sub> was added. The insoluble residue was filtered off and the filtrate was concentrated *in vacuo* to afford the crude product. Further purification was performed by column chromatography, using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and n-hexane (2:1) as the elution to provide white solids in 94% yield. Mp 185—186 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.55 (s, 1H), 8.23 (s, 1H), 7.76—7.73 (m, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 6.97 (s, 1H), 1.35 (s, 12H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 151.34, 150.68, 145.32, 143.76, 139.75, 138.46, 120.43, 119.11, 118.95, 115.66, 84.80, 70.89, 25.05 ppm; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ -138.21 (q, *J* = 30.1 Hz, 2F); FAB-HRMS calcd for C<sub>18</sub>H<sub>19</sub>B<sub>2</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub> (M<sup>+</sup>) 369.1631, found 369.1629.

**Synthesis of compound 5.** Compound **5** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and n-hexane (2:1) as the elution to provide yellow solids in 82 % yield. Mp 236—237 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.78 (s, 1H), 8.41 (s, 1H), 8.34 (s, 1H), 8.33 (s, 1H), 8.00 (t, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.63—7.60 (m, 3H), 7.55—7.51 (m, 2H), 7.22—7.18 (m, 3H), 4.00 (t, *J* = 7.0 Hz, 2H), 1.72 (t, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 2H), 1.28—1.26 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 191.08, 149.96, 149.71, 148.38, 143.52, 141.47, 139.15, 138.75, 134.73, 131.50, 130.71, 130.32, 128.34, 127.40, 126.16, 125.20, 124.07, 123.56, 120.14, 119.82, 118.89, 117.43, 116.87, 116.20, 68.85, 47.53, 31.23, 26.50, 26.13, 22.51, 14.29 ppm; <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>): δ -138.60 (q, *J* = 30.1 Hz, 2F); FAB-HRMS calcd for C<sub>31</sub>H<sub>27</sub>BF<sub>2</sub>N<sub>4</sub>OS (M<sup>+</sup>) 552.1967, found 552.1974.

**Synthesis of compound 6.** Compound **6** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and n-

hexane (1:1) as the elution to provide yellow solids in 58 % yield. Mp 235—236 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 8.44 (s, 1H), 8.33 (s, 1H), 8.32 (s, 1H), 8.00 (t, *J* = 8.0 Hz, 1H), 7.99—7.51 (m, 4H), 7.37 (s, 1H), 7.36 (s, 1H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.12 (d, *J* = 9.0 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 1H), 3.89 (t, *J* = 7.0 Hz, 2H), 1.68 (t, *J* = 7.0 Hz, 2H), 1.39 (t, *J* = 7.0 Hz, 2H), 1.26—1.24 (m, 4H), 0.83 (t, *J* = 7.0 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 149.72, 148.29, 144.91, 144.14, 141.42, 139.18, 138.74, 134.60, 130.72, 129.50, 129.48, 127.62, 126.12, 125.17, 124.29, 120.14, 119.81, 118.91, 118.05, 116.89, 116.83, 114.39, 68.84, 47.12, 31.25, 26.47, 26.20, 22.52, 14.29 ppm; <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>): δ -138.52 (q, *J* = 30.1 Hz, 2F); FAB-HRMS calcd for C<sub>30</sub>H<sub>26</sub>BBrF<sub>2</sub>N<sub>4</sub>S (M<sup>+</sup>) 604.1123, found 604.1119.

**Synthesis of compound 8.** Compound **6** (0.4 g, 0.66 mmol), compound **7** (0.29 g, 0.66 mmol), and Pd(PPh<sub>3</sub>)Cl<sub>2</sub> (0.014 g, 0.02 mmol) in 3 mL of anhydrous DMF under nitrogen was heated at 90 °C for 18 h. The solution was cooled and then 30 mL of CH<sub>2</sub>Cl<sub>2</sub> was added. The insoluble residue was filtered off and the filtrate was concentrated *in vacuo* to afford the crude product. A mixture of this compound (0.38 g, 0.56 mmol), acetic acid (3 mL), THF (1.5 mL), and water (0.6 mL) was heated at 60 °C for 4 h. The reaction mixture was diluted with ethyl acetate, washed with water and saturated NaHCO<sub>3</sub>. The organic layer was dried over anhydrous MgSO<sub>4</sub>. The filtrate was concentrated under reduced pressure. Column chromatograph with a mixture of CH<sub>2</sub>Cl<sub>2</sub> and n-hexane (1:1) as the elution afforded the desired product as yellow solid (0.33 g, 92 % yield). Mp 260—261 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.88 (s, 1H), 8.46 (s, 1H), 8.34—8.33 (m, 2H), 8.02—7.99 (m, 2H), 7.68—7.51 (m, 7H), 7.20—7.10 (m, 3H), 3.96 (t, *J* = 7 Hz, 2H), 1.71 (t, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 2H), 1.29—1.26 (m, 4H), 0.84 (t, *J* = 7.0 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 151.80, 149.27, 147.80, 145.17, 143.90, 141.17, 140.98, 139.42, 138.74, 138.25, 134.15, 129.18, 127.13, 126.94, 126.71, 125.96, 125.67, 124.70, 124.47, 124.02, 123.82, 123.58, 119.63, 119.34, 118.46, 116.45, 116.25, 46.74, 30.79, 26.06, 25.73, 22.06, 13.83 ppm; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ -138.52 (q, *J* =

30.1 Hz, 2F); FAB-HRMS calcd for  $C_{35}H_{29}BF_2N_4OS_2$  ( $M^+$ ) 634.1844, found 634.1838.

**Synthesis of compound 11.** Compound **11** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of  $CH_2Cl_2$  and n-hexane (1:1) as the elution to provide yellow solid in 58 % yield. Mp 236—237 °C;  $^1H$  NMR (500 MHz,  $DMSO-d_6$ ):  $\delta$  8.23 (s, 1H), 8.19 (s, 1H), 8.16 (s, 1H), 7.79—7.61 (m, 1H), 7.59—7.54 (m, 2H), 7.05 (d,  $J = 11.5$  Hz, 2H), 6.97 (t,  $J = 7.0$  Hz, 1H) ppm;  $^{13}C$  NMR (125 MHz,  $DMSO-d_6$ ):  $\delta$  150.19, 148.92, 139.66, 139.24, 138.08, 137.89, 136.61, 134.03, 131.23, 124.33, 120.58, 120.33, 118.56, 115.63, 112.71 ppm;  $^{19}F$  NMR (470 MHz,  $DMSO-d_6$ ):  $\delta$  -138.53 (q,  $J = 30.1$  Hz, 2F); FAB-HRMS calcd for  $C_{16}H_9BBrF_2N_3S$  ( $M^+$ ) 404.9762, found 404.9758.

**Synthesis of compound 12.** Compound **12** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of  $CH_2Cl_2$  and n-hexane (1:1) as the elution to provide yellow solid in 77 % yield. Mp 239—240 °C;  $^1H$  NMR (500 MHz,  $DMSO-d_6$ ):  $\delta$  8.28 (s, 1H), 8.21 (s, 1H), 8.27 (d,  $J = 9.0$  Hz, 1H), 7.80—7.72 (m, 2H), 7.58 (t,  $J = 8.2$  Hz, 2H), 7.01 (s, 1H), 6.98 (t,  $J = 6.8$  Hz, 1H), 2.58 (t,  $J = 7.5$  Hz, 2H), 1.66—1.58 (m, 2H), 1.40—1.31 (m, 6H), 0.90 (t,  $J = 6.7$  Hz, 3H) ppm;  $^{13}C$  NMR (125 MHz,  $DMSO-d_6$ ):  $\delta$  149.69, 148.58, 144.01, 142.22, 141.29, 138.63, 137.67, 137.45, 133.32, 126.49, 122.34, 120.37, 119.81, 118.10, 116.91, 108.45, 31.53, 29.47, 29.42, 28.76, 22.49, 13.91 ppm;  $^{19}F$  NMR (470 MHz,  $CDCl_3$ ):  $\delta$  -138.51 (q,  $J = 30.1$  Hz, 2F); FAB-HRMS calcd for  $C_{23}H_{23}BBrF_2N_3S$  ( $M^+$ ) 501.0857, found 501.0850.

**Synthesis of compound 14.** Compound **14** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using  $CH_2Cl_2$  as the elution to provide orange solid in 60 % yield. Mp 275—276 °C;  $^1H$  NMR (500 MHz,  $DMSO-d_6$ ):  $\delta$  9.80 (s, 1H), 8.41 (s, 1H), 8.37 (s, 1H), 8.28 (d,  $J = 9.5$  Hz, 1H), 8.03 (t,  $J = 7$  Hz, 1H), 7.72 (t,  $J = 11.5$  Hz, 1H), 7.70 (s, 1H), 7.63 (s, 1H), 7.57—7.54 (m, 5H), 7.23—7.19 (m, 2H), 7.29 (t,  $J = 8$  Hz, 1H) ppm;  $^{13}C$  NMR (125 MHz,  $DMSO-d_6$ ):  $\delta$  191.05, 149.89, 149.56, 148.25, 143.04, 142.62, 141.65, 138.84, 137.88,

136.52, 133.17, 131.47, 130.71, 129.11, 128.36, 126.93, 125.49, 125.30, 124.15, 123.92, 123.34, 122.99, 120.52, 119.96, 119.71, 117.40, 117.21, 116.17, 69.60, 47.56, 31.23, 26.50, 26.12, 22.51, 14.29 ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  -138.61 (q,  $J$  = 30.1 Hz, 2F); FAB-HRMS calcd for  $\text{C}_{35}\text{H}_{29}\text{BF}_2\text{N}_4\text{OS}_2$  ( $\text{M}^+$ ) 634.1844, found 634.1834.

**Synthesis of compound 15.** Compound **15** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using  $\text{CH}_2\text{Cl}_2$  as the elution to provide orange solid in 68 % yield. Mp 202—203 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  9.78 (s, 1H), 8.36 (s, 2H), 8.24 (d,  $J$  = 9.0 Hz, 1H), 8.02 (t,  $J$  = 80 Hz, 1H), 7.74 (d,  $J$  = 9 Hz, 1H), 7.66 (s, 1H), 7.62 (s, 1H), 7.53 (d,  $J$  = 9.0 Hz, 2H), 7.32 (d,  $J$  = 8.5 Hz, 1H), 7.23-7.16 (m, 4H) 3.99 (t,  $J$  = 7.0 Hz, 2H), 2.62 (t,  $J$  = 7.0 Hz, 2H), 1.72 (t,  $J$  = 7.0 Hz, 2H), 1.62 (t,  $J$  = 7.0 Hz, 2H), 1.42 (t,  $J$  = 7.0 Hz, 2H), 1.27—1.23 (m, 10H), 0.83 (t,  $J$  = 7.0 Hz, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  191.09, 150.00, 149.61, 148.25, 143.10, 141.64, 140.59, 138.85, 137.91, 136.48, 135.47, 133.16, 131.53, 130.76, 129.18, 128.83, 128.40, 128.35, 127.42, 123.59, 123.49, 123.04, 123.02, 120.52, 119.98, 118.77, 117.21, 116.23, 69.50, 47.58, 31.42, 31.27, 30.40, 28.96, 28.71, 26.52, 26.16, 22.53, 22.49, 14.43, 14.31 ppm;  $^{19}\text{F}$  NMR (470 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  -138.58 (q,  $J$  = 30.1 Hz, 2F); FAB-HRMS calcd for  $\text{C}_{41}\text{H}_{42}\text{BF}_2\text{N}_4\text{OS}_2$  ( $\text{M}+\text{H}^+$ ) 719.2861, found 719.2853.

**Synthesis of compound 16.** Compound **16** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of  $\text{CH}_2\text{Cl}_2$  and n-hexane (1:2) as the elution to provide yellow solid in 35 % yield. Mp 270—271 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  9.79 (s, 1H), 8.73 (d,  $J$  = 2.0 Hz, 1H), 7.61 (s, 1H), 7.42—7.40 (m, 2H), 7.33 (s, 1H), 7.17 (d,  $J$  = 8.5 Hz, 1H), 7.08 (d,  $J$  = 8.5 Hz, 1H), 3.95 (t,  $J$  = 7.0 Hz, 2H), 3.95 (t,  $J$  = 7.0 Hz, 2H), 1.73—1.65 (m, 2H), 1.59—1.56 (m, 2H), 1.42—1.37 (m, 2 H), 1.29—1.24 (m, 12 H), 0.89—0.79 (m, 6 H), ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  190.96, 149.89, 143.64, 142.91, 141.97, 131.43, 130.65, 128.97, 128.26, 125.12, 124.93, 123.93, 123.80, 123.35, 117.31, 116.09, 107.18, 47.51,

31.38, 31.16, 29.39, 28.93, 28.64, 26.45, 26.05, 22.50, 22.41, 14.33, 14.21 ppm; FAB-HRMS calcd for  $C_{29}H_{34}BrNOS_2$  ( $M^+$ ) 555.1265, found 555.1263.

**Synthesis of compound 17.** Compound **17** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of  $CH_2Cl_2$  and n-hexane (2:1) as the elution to provide orange solid in 80 % yield. Mp 271—272 °C;  $^1H$  NMR (500 MHz,  $DMSO-d_6$ ):  $\delta$  9.80 (s, 1H), 8.56 (s, 1H), 8.16 (s, 1H), 8.06—8.02 (m, 2H), 7.75—7.73 (m, 1H), 7.63—7.50 (m, 6H), 7.24—7.19 (m, 2H), 7.12 (d,  $J = 8.5$  Hz, 1H), 3.98 (t,  $J = 7.0$  Hz, 2H), 2.63 (t,  $J = 7.0$  Hz, 2H), 1.71 (t,  $J = 7.0$  Hz, 2H), 1.64 (t,  $J = 7.0$  Hz, 2H), 1.43 (t,  $J = 7.0$  Hz, 2H), 1.27—1.24 (m, 10H), 0.83 (t,  $J = 7.0$  Hz, 6H) ppm;  $^{13}C$  NMR (125 MHz,  $DMSO-d_6$ ):  $\delta$  191.07, 150.09, 149.69, 148.49, 143.03, 142.23, 141.73, 141.53, 141.14, 138.86, 136.28, 131.49, 130.77, 129.20, 128.71, 128.37, 126.81, 125.35, 124.02, 123.90, 123.36, 122.54, 120.39, 119.97, 118.71, 117.39, 117.27, 116.17, 47.54, 31.40, 31.22, 30.44, 28.94, 28.81, 26.50, 26.11, 22.48, 22.47, 14.29, 14.28 ppm;  $^{19}F$  NMR (470 MHz,  $DMSO-d_6$ ):  $\delta$  -138.74 (q,  $J = 30.1$  Hz, 2F); FAB-HRMS calcd for  $C_{41}H_{41}BF_2N_4OS_2$  ( $M^+$ ) 718.2783, found 718.2787.

**Synthesis of compound 19.** To a solution compound **18** (3.0 g, 7.48 mmol) in 50 mL of  $CHCl_3$  was cooled at 0 °C under  $N_2$  atmosphere.  $POCl_3$  (0.84 mL, 8.98 mmol) was added slowly. The reaction mixture was heated at 90 °C for 18 h. After cooling, the reaction solution was extracted with  $CH_2Cl_2$ . The combined organic layer dried over  $MgSO_4$  and evaporated under reduced pressure. Further purification was performed by column chromatography, using a mixture of  $CH_2Cl_2$  and n-hexane (1:3) as the elution to provide white solid in 52% yield. Mp 198—199 °C;  $^1H$  NMR (500 MHz,  $DMSO-d_6$ ):  $\delta$  9.71 (s, 1H), 8.06 (d,  $J = 9.0$  Hz, 2H), 7.53 (d,  $J = 2.5$  Hz, 1H), 7.43 (d,  $J = 10$  Hz, 1H), 7.30 (d,  $J = 7.5$  Hz, 2H), 7.08 (t,  $J = 5.0$  Hz, 1H), 6.95—6.90 (m, 2H), 6.20 (d,  $J = 9.0$  Hz, 1H), 6.10 (d,  $J = 8.0$  Hz, 1H) ppm;  $^{13}C$  NMR (125 MHz,  $DMSO-d_6$ ):  $\delta$  190.37, 148.02, 141.78, 140.37, 139.18, 132.91, 131.06, 129.89, 127.71, 127.42, 126.75, 123.95, 119.28, 118.30, 116.49, 115.38, 95.73, 54.94 ppm;  $^{19}F$  NMR

(470 MHz, DMSO- $d_6$ ); FAB-HRMS calcd for  $C_{19}H_{12}INOS$  ( $M^+$ ) 428.9684, found 428.9679.

**Synthesis of compound 20.** Under  $N_2$  atmosphere, to a solution compound **19** (2.0 g, 4.66 mmol) in 30 mL of  $CHCl_3$ , was added *N*-bromosuccinimide (1.0 g, 5.59 mmol). The reaction mixture was heated at 60 °C for 4 h. The reaction solution was extracted with  $CH_2Cl_2$ . The combined organic layer dried over  $MgSO_4$  and evaporated under reduced pressure. Further purification was performed by column chromatography, using a mixture of  $CH_2Cl_2$  and *n*-hexane (1:5) as the elution to provide white solid in 64% yield. Mp 230—231 °C;  $^1H$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  9.72 (s, 1H), 8.06 (d,  $J = 8.0$  Hz, 2H), 7.53 (s, 1H), 7.44 (d,  $J = 8.5$  Hz, 1H), 7.29 (d,  $J = 8.0$  Hz, 3H), 7.10 (d,  $J = 8.5$  Hz, 1H), 6.20 (d,  $J = 9.0$  Hz, 1H), 6.00 (d,  $J = 9.0$  Hz, 1H) ppm;  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  190.80, 147.98, 141.72, 140.95, 139.31, 133.23, 131.68, 130.64, 130.47, 128.94, 127.95, 121.33, 119.01, 118.42, 115.98, 115.67, 96.48 ppm; FAB-HRMS calcd for  $C_{19}H_{11}BrINOS$  ( $M^+$ ) 508.8789, found 508.8781.

**Synthesis of compound 21.** Compound **21** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of  $CH_2Cl_2$  and *n*-hexane (3:1) as the elution to provide yellow solid in 80% yield. Mp 263—264 °C;  $^1H$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  9.72 (s, 1H), 8.58 (s, 1H), 8.46 (d,  $J = 2.0$  Hz, 1H), 8.40 (s, 1H), 8.10 (d,  $J = 8.5$  Hz, 2H), 8.05 (t,  $J = 8.0$  Hz, 1H), 7.62 (d,  $J = 8.0$  Hz, 3H), 7.56 (t,  $J = 2.0$  Hz, 2H), 7.46 (d,  $J = 8.5$  Hz, 1H), 7.34 (s, 1H), 7.23 (t,  $J = 7.0$  Hz, 1H), 7.11 (d,  $J = 7.0$  Hz, 1H), 6.26 (d,  $J = 8.5$  Hz, 1H), 6.07 (d,  $J = 8.5$  Hz, 1H) ppm;  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  190.80, 149.73, 148.93, 148.20, 141.92, 141.73, 139.61, 138.88, 136.12, 135.87, 131.71, 130.89, 130.61, 130.45, 130.21, 129.80, 128.96, 127.99, 121.33, 120.37, 119.93, 119.31, 118.99, 118.80, 118.24, 117.20, 116.00, 115.65 ppm;  $^{19}F$  NMR (470 MHz, DMSO- $d_6$ ):  $\delta$  -138.54 (q,  $J = 30.1$  Hz, 2F); FAB-HRMS calcd for  $C_{31}H_{18}BBrF_2N_4OS$  ( $M^+$ ) 624.0446, found 624.0440.

**Synthesis of compound 22.** Compound **21** (0.7 g, 1.12 mmol), bis(pinacolato)diboron (0.34 g, 1.3

mmol), KOAc (0.33 g, 3.36 mmol), and Pd(PPh<sub>3</sub>)Cl<sub>2</sub> (0.039 g, 0.056 mmol) in 11 mL of anhydrous toluene under nitrogen was heated at 120 °C for 18 h. The solution was cooled and then 20 mL of dry toluene was added. The insoluble residue was filtered off and the filtrate was concentrated *in vacuo* to afford the crude product. Further purification was performed by column chromatography, using CH<sub>2</sub>Cl<sub>2</sub> as the elution to provide yellow solid in 49% yield. Mp 266—267 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.72 (s, 1H), 8.61 (s, 1H), 8.47 (d, *J* = 2.0 Hz, 1H), 8.41 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 8.05 (t, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 2.0 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.39 (s, 1H), 7.29 (s, 1H), 7.24 (t, *J* = 7.0 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 6.26 (d, *J* = 8.5 Hz, 1H), 6.14 (d, *J* = 8.5 Hz, 1H), 1.29 (s, 12H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 190.19, 149.43, 148.60, 147.67, 144.49, 141.12, 139.40, 139.05, 138.31, 135.62, 135.35, 134.05, 132.44, 131.48, 131.24, 129.61, 129.20, 127.33, 127.06, 119.92, 119.55, 119.48, 118.19, 117.78, 116.63, 115.94, 115.73, 83.74, 68.87, 24.62 ppm; <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>): δ -137.59 (q, *J* = 30.1 Hz, 2F); FAB-HRMS calcd for C<sub>37</sub>H<sub>30</sub>B<sub>2</sub>F<sub>2</sub>N<sub>4</sub>O<sub>3</sub>S(M<sup>+</sup>) 670.2193, found 670.2201.

**Synthesis of compound 23.** Compound **23** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane (2:1) as the elution to provide yellow solid in 71% yield. Mp 267—268 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.74 (s, 1H), 8.58 (s, 1H), 8.45—8.43 (m, 1H), 8.38 (s, 1H), 8.10—8.03 (m, 3H), 7.65—7.62 (m, 3H), 7.58—7.56 (m, 2H), 7.46—7.44 (m, 1H), 7.36 (s, 1H), 7.25—7.22 (m, 2H), 7.13—7.11 (m, 1H), 6.29 (d, *J* = 8.5 Hz, 1H), 6.19 (d, *J* = 8.5 Hz, 1H), 2.57 (t, *J* = 8.5 Hz, 2H), 1.59 (t, *J* = 8.5 Hz, 2H), 1.33—1.25 (m, 6H), 0.87 (t, *J* = 8.5 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 190.13, 147.62, 141.45, 141.13, 139.44, 139.07, 138.32, 135.34, 131.31, 131.22, 129.82, 129.23, 127.36, 124.55, 124.39, 122.92, 119.50, 118.94, 116.91, 116.63, 115.56, 106.84, 68.87, 30.92, 29.05, 28.93, 28.19, 21.92, 13.81 ppm; <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>): δ -137.59 (q, *J* = 30.1 Hz, 2F); FAB-HRMS calcd for C<sub>41</sub>H<sub>32</sub>BBrF<sub>2</sub>N<sub>4</sub>OS<sub>2</sub> (M<sup>+</sup>) 788.1262, found 788.1254.

**Synthesis of compound 24.** Compound **24** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and n-hexane (3:1) as the elution to provide orange solid in 72% yield. Mp 267–268 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.74 (s, 1H), 8.57 (s, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 8.42–8.35 (m, 3H), 8.20 (d, *J* = 2.0 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 2H), 8.04–8.00 (m, 2H), 7.65–7.62 (m, 3H), 7.57–7.44 (m, 6H), 7.22–7.15 (m, 2H), 7.15 (s, 1H), 7.06–7.04 (m, 1H), 6.31–6.26 (m, 2H), 2.60 (t, *J* = 8.5 Hz, 2H), 1.61 (t, *J* = 8.5 Hz, 2H), 1.29–1.26 (m, 6H), 0.84 (t, *J* = 8.5 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 190.09, 149.41, 149.24, 148.59, 147.89, 147.74, 141.52, 141.10, 140.99, 140.24, 139.39, 139.01, 138.30, 138.28, 137.39, 135.82, 135.67, 135.33, 135.05, 132.71, 131.35, 131.27, 129.82, 129.23, 129.07, 127.94, 127.78, 127.36, 127.09, 125.35, 122.55, 119.93, 119.47, 119.13, 119.06, 118.16, 118.08, 116.67, 116.60, 115.57, 69.16, 68.85, 30.94, 29.90, 28.46, 28.31, 21.96, 13.83 ppm; <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>): δ -137.51 (q, *J* = 30.1 Hz, 4F); FAB-HRMS calcd for C<sub>53</sub>H<sub>39</sub>B<sub>2</sub>F<sub>4</sub>N<sub>7</sub>OS<sub>2</sub> (M<sup>+</sup>) 951.2780, found 951.2768.

**Synthesis of compound 25.** Compound **25** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and n-hexane (3:1) as the elution to provide orange solid in 92% yield. Mp 262–263 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.74 (s, 1H), 8.57 (s, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 8.37–8.33 (m, 2H), 8.15 (s, 1H), 8.11–8.01 (m, 5H), 7.63 (d, *J* = 8.5 Hz, 3H), 7.57–7.53 (m, 4H), 7.46–7.42 (m, 3H), 7.24–7.20 (m, 3H), 6.29 (d, *J* = 8.5 Hz, 1H), 6.21 (d, *J* = 8.5 Hz, 1H), 2.61 (t, *J* = 8.5 Hz, 2H), 1.63 (t, *J* = 8.5 Hz, 2H), 1.32–1.25 (m, 6H), 0.83 (t, *J* = 8.5 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 190.10, 149.42, 149.33, 148.60, 148.10, 147.62, 141.70, 141.42, 140.85, 140.56, 139.45, 139.04, 138.29, 135.84, 135.64, 135.34, 131.29, 131.24, 129.99, 129.79, 129.22, 129.11, 127.36, 124.53, 123.08, 122.06, 119.93, 119.86, 119.47, 118.97, 118.05, 116.90, 116.67, 115.55, 69.06, 68.86, 30.89, 29.96, 28.41, 28.26, 21.92, 13.75 ppm; <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>): δ -137.66 (q, *J* = 30.1 Hz, 4F);

FAB-HRMS calcd for  $C_{53}H_{39}B_2F_4N_7OS_2$  ( $M^+$ ) 951.2780, found 951.2780.

**Synthesis of compound 26.** Compound **26** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of  $CH_2Cl_2$  and n-hexane (2:1) as the elution to provide yellow solid in 84% yield. Mp 258—259 °C;  $^1H$  NMR (500 MHz,  $DMSO-d_6$ ):  $\delta$  9.72 (s, 1H), 8.59 (s, 1H), 8.45 (d,  $J = 9.0$  Hz, 1H), 8.40 (s, 1H), 8.10 (d,  $J = 8.5$  Hz, 2H), 8.05 (t,  $J = 8.5$  Hz, 1H), 7.64—7.55 (m, 5H), 7.45 (d,  $J = 8.5$  Hz, 1H), 7.23 (t,  $J = 7.0$  Hz, 1H), 7.11 (d,  $J = 7.5$  Hz, 1H), 6.98—6.91 (m, 2H), 6.28 (d,  $J = 8.5$  Hz, 1H), 6.18 (d,  $J = 8.5$  Hz, 1H) ppm;  $^{13}C$  NMR (125 MHz,  $DMSO-d_6$ ):  $\delta$  190.80, 158.84, 149.73, 148.91, 148.68, 142.41, 141.71, 139.90, 139.64, 138.87, 135.92, 135.83, 131.81, 130.32, 129.68, 128.13, 127.55, 127.22, 124.38, 123.15, 121.84, 120.36, 119.92, 119.69, 118.82, 118.74, 117.00, 115.84 ppm;  $^{19}F$  NMR (470 MHz,  $DMSO-d_6$ ):  $\delta$  -137.26 (q,  $J = 30.1$  Hz, 2F); FAB-HRMS calcd for  $C_{31}H_{19}BF_2N_4OS$  ( $M^+$ ) 544.1341, found 544.1337.

**Synthesis of compound K1.** Compound **K1** was obtained according to the standard Knoevenagel condensation reaction. Further purification was performed by column chromatography, using a mixture of  $CH_2Cl_2$  and acetic acid (19/1) as the elution to provide black solid in 72 % yield. Mp 238—239 °C;  $^1H$  NMR (500 MHz,  $DMSO-d_6$ ):  $\delta$  8.42 (s, 1H), 8.32—8.26 (2H), 8.14 (s, 1H), 7.98 (t,  $J = 8$  Hz, 1H), 7.90 (d,  $J = 7$  Hz, 1H), 7.29 (t,  $J = 8.7$  Hz, 1H), 7.80 (s, 1H), 7.55 (s, 2H), 7.48 (d,  $J = 8.7$  Hz, 2H), 7.18—7.10 (m, 3H) ppm;  $^{13}C$  NMR (125 MHz,  $DMSO-d_6$ ):  $\delta$  164.16, 152.69, 149.70, 148.65, 148.36, 143.17, 141.45, 139.07, 138.74, 134.70, 132.04, 130.31, 129.56, 127.33, 126.32, 125.16, 123.58, 123.17, 120.14, 119.81, 118.88, 117.34, 117.30, 116.87, 116.24, 68.90, 47.47, 31.24, 26.47, 22.53, 14.30 ppm;  $^{19}F$  NMR (470 MHz,  $DMSO-d_6$ ):  $\delta$  -137.06 (q,  $J = 30.1$  Hz, 2F); FAB-HRMS calcd for  $C_{34}H_{28}BF_2N_5O_2S$  ( $M^+$ ) 619.2025, found 619.2041.

**Synthesis of compound K2.** Compound **K2** was obtained according to the standard Knoevenagel condensation reaction. Further purification was performed by column chromatography, using a mixture of  $CH_2Cl_2$  and acetic acid (19/1) as the elution to provide black solid in 64 % yield. Mp

280–281 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 8.45 (d, *J* = 14.0 Hz, 2H), 8.34–8.32 (m, 2H), 8.02–7.96 (m, 2H), 7.71 (s, 1H), 7.70–7.60 (m, 4H), 7.59–7.51 (m, 2H), 7.20–7.11 (m, 3H), 3.95 (t, *J* = 7.0 Hz, 2H), 1.72 (t, *J* = 7 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 2H), 1.29–1.25 (m, 4H), 0.83 (t, *J* = 7 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 164.03, 149.72, 148.57, 148.31, 145.66, 144.27, 144.09, 141.70, 141.43, 139.18, 138.73, 134.62, 134.49, 129.97, 129.69, 127.62, 127.35, 126.47, 126.11, 125.15, 124.84, 124.32, 124.28, 120.15, 119.82, 118.91, 117.33, 117.14, 116.94, 116.83, 68.85, 47.26, 31.27, 26.54, 26.22, 22.54, 14.31 ppm; <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>): δ -137.13 (q, *J* = 30.1 Hz, 2F); FAB-HRMS calcd for C<sub>38</sub>H<sub>30</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>2</sub>S<sub>2</sub>(M<sup>+</sup>) 701.1902, found 701.1917.

**Synthesis of compound K3.** Compound **K3** was obtained according to the standard Knoevenagel condensation reaction. Further purification was performed by column chromatography, using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and acetic acid (19/1) as the elution to provide black solid in 78 % yield. Mp 278–279 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 8.40 (s 1H), 8.37 (s, 1H), 8.29 (q, *J* = 2 Hz, 1H), 8.03 (t, *J* = 7.5 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.79 (s, 1H), 7.70 (s, 1H), 7.56–7.53 (m, 5H), 7.21 (t, *J* = 6.5 Hz, 1H), 7.16 (t, *J* = 8.5 Hz, 1H), 7.11 (t, *J* = 9.5 Hz, 1H) 3.96 (t, *J* = 7 Hz, 2H), 1.72 (t, *J* = 7 Hz, 2H), 1.42 (t, *J* = 7 Hz, 2H), 1.29–1.23 (m, 4H), 0.85 (t, *J* = 7 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 163.80, 149.56, 148.23, 147.86, 143.00, 142.66, 142.28, 141.63, 138.84, 137.86, 136.47, 136.05, 134.52, 133.15, 131.42, 129.09, 128.95, 126.92, 125.47, 125.24, 124.15, 123.59, 123.00, 122.93, 120.52, 119.95, 118.95, 118.71, 118.34, 117.17, 116.24, 69.57, 47.42, 31.25, 26.50, 26.15, 22.54, 14.31 ppm; <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>): δ -137.17(q, *J* = 30.1 Hz, 2F); TOF-HRMS calcd for C<sub>38</sub>H<sub>29</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>2</sub>S<sub>2</sub> (M-H<sup>+</sup>) 700.1824, found 700.1829.

**Synthesis of compound K4.** Compound **K4** was obtained according to the standard Knoevenagel condensation reaction. Further purification was performed by column chromatography, using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and acetic acid (19/1) as the elution to provide black solid in 81 % yield. Mp 275–276 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 8.37 (s, 1H), 8.17 (s, 1H), 8.14 (s, 1H), 8.06–8.04 (m,

2H), 7.92 (d,  $J = 1.1$  Hz, 1H), 7.83 (s, 1H), 7.58—7.49 (m, 5H), 7.23—7.18 (m, 2H), 7.11 (d,  $J = 7.2$  Hz, 1H), 3.97 (t,  $J = 7$  Hz, 2H), 2.61 (t,  $J = 7$  Hz, 2H), 1.70 (t,  $J = 7$  Hz, 2H), 1.62 (t,  $J = 7$  Hz, 2H), 1.42 (t,  $J = 7$  Hz, 2H), 1.30—1.24 (m, 10H), 0.85—0.80 (t,  $J = 7$  Hz, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  164.10, 149.66, 148.56, 148.43, 142.66, 142.12, 141.71, 141.45, 141.11, 138.85, 136.27, 131.94, 130.27, 129.57, 129.21, 126.79, 126.34, 125.35, 124.03, 123.44, 122.95, 122.53, 120.38, 119.96, 118.68, 117.45, 117.25, 116.23, 47.47, 31.40, 31.24, 30.45, 28.94, 28.82, 26.49, 26.12, 22.53, 22.50, 14.35, 14.30 ppm;  $^{19}\text{F}$  NMR (470 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  -137.39 (q,  $J = 30.1$  Hz, 2F); TOF-HRMS calcd for  $\text{C}_{44}\text{H}_{41}\text{BF}_2\text{N}_5\text{O}_2\text{S}_2$  ( $\text{M-H}^+$ ) 784.2763, found 784.2755.

**Synthesis of compound K5.** Compound **K5** was obtained according to the standard Knoevenagel condensation reaction. Further purification was performed by column chromatography, using a mixture of  $\text{CH}_2\text{Cl}_2$  and acetic acid (19/1) as the elution to provide black solid in 79 % yield. Mp 258–259 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  8.47 (s, 1H), 8.36 (t,  $J = 8.5$  Hz, 1H), 8.24 (t,  $J = 8.5$  Hz, 1H), 8.10—8.02 (m, 2H), 7.90 (s, 1H), 7.81 (s, 1H), 7.66 (s, 1H), 7.54 (d,  $J = 10.5$  Hz, 2H), 7.31 (t,  $J = 8.5$  Hz, 1H), 7.24—7.16 (m, 4H), 3.98 (t,  $J = 8.5$  Hz, 2H), 2.63 (t,  $J = 8.5$  Hz, 2H), 1.72 (t,  $J = 8.5$  Hz, 2H), 1.62 (t,  $J = 8.5$  Hz, 2H), 1.42 (t,  $J = 8.5$  Hz, 2H), 1.28—1.24 (m, 10H), 0.86—0.81 (m, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  162.52, 159.34, 157.76, 151.12, 148.82, 148.25, 147.83, 147.37, 146.51, 144.63, 142.77, 142.17, 141.56, 140.59, 138.81, 137.89, 136.45, 135.46, 133.27, 133.12, 131.98, 129.59, 129.50, 128.79, 128.29, 127.39, 126.41, 123.15, 120.48, 118.09, 52.88, 47.52, 31.37, 31.23, 30.35, 29.91, 28.72, 26.51, 26.13, 22.47, 14.35, 14.24;  $^{19}\text{F}$  NMR (470 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  -137.13 (q,  $J = 30.1$  Hz, 2F); TOF-HRMS calcd for  $\text{C}_{44}\text{H}_{41}\text{BF}_2\text{N}_5\text{O}_2\text{S}_2$  ( $\text{M-H}^+$ ) 784.2763, found 784.2765.

**Synthesis of compound K6.** Compound **K6** was obtained according to the standard Knoevenagel condensation reaction. Further purification was performed by column chromatography, using a mixture of  $\text{CH}_2\text{Cl}_2$  and acetic acid (19/1) as the elution to provide black solid in 62 % yield. Mp 256–257 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  8.58 (s, 1H), 8.44 (d,  $J = 10.5$  Hz, 1H), 8.39—8.36 (m,

3H), 8.20 (d,  $J = 12.0$  Hz, 1H), 8.12–7.99 (m, 5H), 7.23 (s, 1H), 7.65–7.44 (m, 8H), 7.24–7.17 (m, 3H), 7.04 (d,  $J = 10.5$  Hz, 1H), 6.24–6.21 (m, 2H), 2.58 (t,  $J = 8.5$  Hz, 2H), 1.60 (t,  $J = 8.5$  Hz, 2H), 1.27–1.24 (m, 6H), 0.84 (t,  $J = 8.5$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  162.63, 149.66, 149.48, 148.84, 148.10, 146.33, 141.80, 141.62, 141.52, 140.64, 140.55, 139.50, 139.46, 138.81, 138.76, 137.68, 136.08, 136.05, 135.79, 135.34, 133.01, 131.74, 131.64, 131.57, 129.70, 129.35, 129.21, 128.29, 128.20, 127.85, 127.49, 127.42, 126.72, 122.86, 120.37, 120.29, 119.87, 119.37, 119.27, 119.18, 119.15, 118.72, 118.64, 117.09, 116.90, 115.98, 69.44, 69.14, 31.42, 30.37, 29.09, 28.74, 22.49, 14.39;  $^{19}\text{F}$  NMR (470 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  -137.07 (q,  $J = 30.1$  Hz, 2F); TOF-HRMS calcd for  $\text{C}_{56}\text{H}_{39}\text{B}_2\text{F}_4\text{N}_8\text{O}_2\text{S}_2$  (M-H<sup>+</sup>) 1017.2760, found 1017.2761.

**Synthesis of compound K7.** Compound **K7** was obtained according to the standard Knoevenagel condensation reaction. Further purification was performed by column chromatography, using a mixture of  $\text{CH}_2\text{Cl}_2$  and acetic acid (19/1) as the elution to provide black solid in 65 % yield. Mp 250–251 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  8.60 (s, 1H), 8.46 (d,  $J = 10.5$  Hz, 1H), 8.40–8.36 (m, 3H), 8.16–7.98 (m, 7H), 7.75 (s, 1H), 7.66–7.62 (m, 3H), 7.58–7.53 (m, 4H), 7.48–7.46 (m, 2H), 7.25–7.20 (m, 3H), 6.23–6.17 (m, 2H), 2.60 (t,  $J = 8.5$  Hz, 2H), 1.62 (t,  $J = 8.5$  Hz, 2H), 1.31–1.24 (m, 6H), 0.83 (t,  $J = 8.5$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  163.59, 151.03, 149.74, 149.65, 148.92, 148.43, 148.36, 148.30, 142.17, 142.11, 141.82, 141.71, 141.25, 141.12, 139.67, 139.57, 139.42, 138.86, 136.27, 136.07, 136.03, 135.88, 131.76, 131.67, 130.46, 130.33, 129.93, 129.77, 129.57, 129.45, 129.33, 127.60, 126.79, 124.94, 123.53, 122.48, 122.45, 120.36, 119.93, 119.61, 119.32, 119.12, 118.82, 118.68, 117.24, 117.18, 116.05, 115.97, 31.39, 30.47, 29.94, 28.80, 22.47, 14.35;  $^{19}\text{F}$  NMR (470 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  -137.24 (q,  $J = 30.1$  Hz, 4F); TOF-HRMS calcd for  $\text{C}_{56}\text{H}_{39}\text{B}_2\text{F}_4\text{N}_8\text{O}_2\text{S}_2$  (M-H<sup>+</sup>) 1017.2760, found 1017.2766.

**Synthesis of compound K8.** Compound **K8** was obtained according to the standard Knoevenagel condensation reaction. Further purification was performed by column chromatography, using a

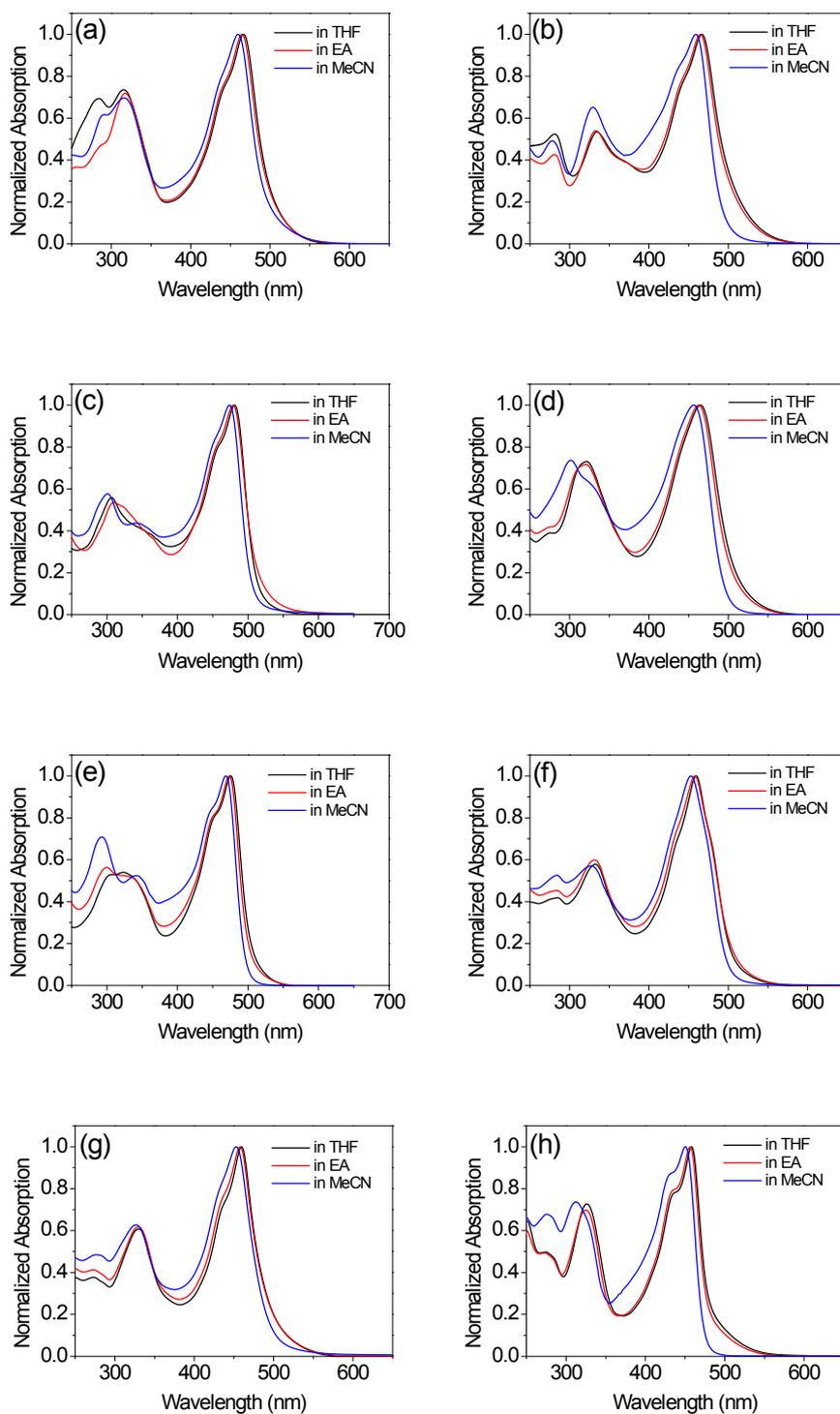
mixture of CH<sub>2</sub>Cl<sub>2</sub> and acetic acid (19/1) as the elution to provide black solid in 75 % yield. Mp 256–257 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 8.58 (s, 1H), 8.46–8.43 (m, 2H), 8.40–8.02 (m, 4H), 7.75 (s, 1H), 7.66–7.35 (m, 6H), 7.25 (s, 1H), 7.21 (t, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.22 (d, *J* = 11.0 Hz, 1H), 6.07 (d, *J* = 2.5 Hz, 1H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 164.14, 152.36, 149.68, 148.86, 147.47, 142.21, 141.72, 141.31, 139.66, 138.89, 135.98, 135.86, 131.90, 131.71, 129.72, 129.35, 128.69, 128.17, 127.59, 127.25, 126.37, 124.41, 120.33, 119.92, 119.59, 118.85, 118.51, 117.18, 116.96, 115.87, 108.57, 100.72, 79.65, 69.67 ppm; <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>): δ -137.07 (q, *J* = 30.1 Hz, 2F); TOF-HRMS calcd for C<sub>34</sub>H<sub>19</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>2</sub>S (M-H<sup>+</sup>) 610.1321, found 610.1326.

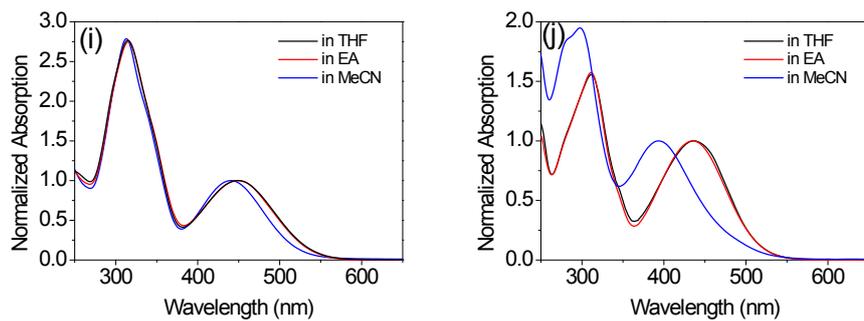
**Synthesis of compound P3.** Compound **P3** was synthesized via the typical Suzuki reaction procedure. Further purification was performed by column chromatography, using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and n-hexane (2:1) as the elution to provide yellow solid in 72 % yield. Mp 197–198 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 8.36 (s, 1H), 8.17 (s, 1H), 7.94 (dd, *J* = 6.4, 9.2 Hz, 1H), 7.71–7.67 (m, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.56–7.52 (m, 3H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.40–7.37 (m, 1H), 6.91 (t, *J* = 7.5 Hz, 1H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 150.54, 149.14, 139.39, 138.48, 138.11, 135.61, 129.51, 129.18, 128.67, 126.41, 120.51, 120.33, 119.06, 115.29, 69.89 ppm; <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>): δ -137.59 (q, *J* = 30.1 Hz, 2F); FAB-HRMS calcd for C<sub>18</sub>H<sub>12</sub>BF<sub>2</sub>N<sub>3</sub> (M<sup>+</sup>) 319.1092, found 319.1087.

**Synthesis of compound R1.** Compound **R1** was obtained according to the standard Knoevenagel condensation reaction. Further purification was performed by column chromatography, using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and acetic acid (19/1) as the elution to provide black solid in 59% yield. Mp 145–147 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.10 (s, 1H), 7.92 (dd, 1H, *J* = 2.0, 8.8 Hz), 7.69 (d, 1H, *J* = 2.0 Hz), 7.33-7.40 (m, 3H), 7.25-7.29 (m, 5H), 7.10-7.13 (m, 6H), 7.03 (t, 2H, *J* = 7.2 Hz), 6.86-6.91 (m, 2H), 3.90 (t, 2H, *J* = 7.2 Hz), 1.80-1.86 (m, 2H), 1.45-1.47 (m, 2H), 1.33-1.34 (m, 4H), 0.89 (t, 3H, *J* = 2.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) : δ 168.7, 154.5, 149.9, 147.6, 147.2, 141.3, 136.5, 133.2, 131.9,

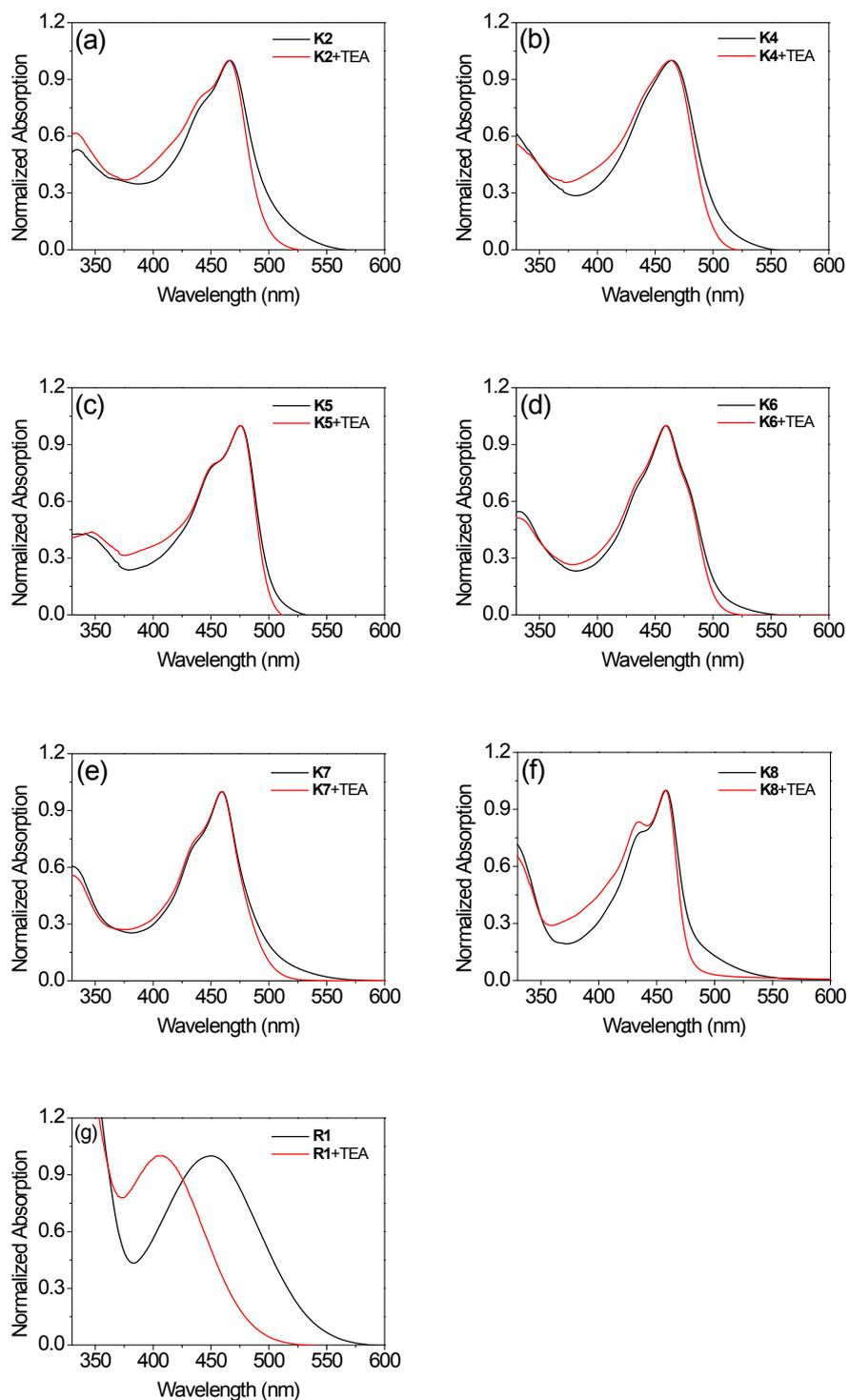
130.4, 129.3, 127.1, 125.7, 125.3, 125.3, 124.5, 124.2, 123.8, 123.5, 123.0, 116.0, 114.8, 97.5, 48.2,

31.4, 26.6, 26.5, 22.6, 14.0; FAB-HRMS calcd for  $C_{40}H_{36}O_2N_3S$  ( $M+H^+$ ) 622.2528, found 622.2527.

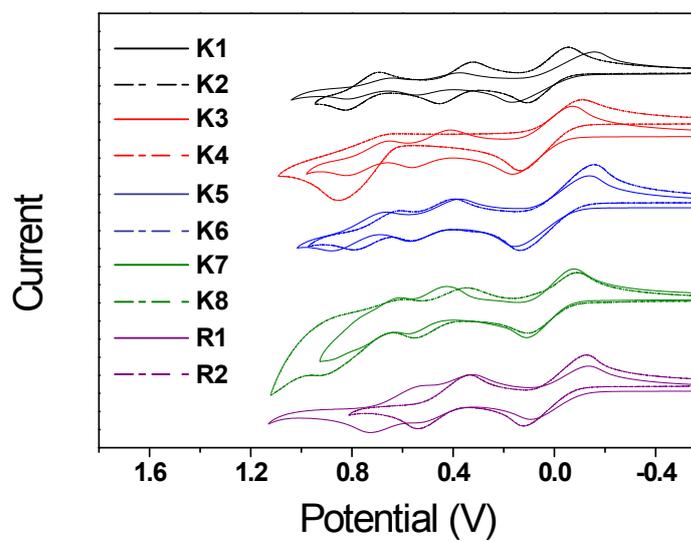




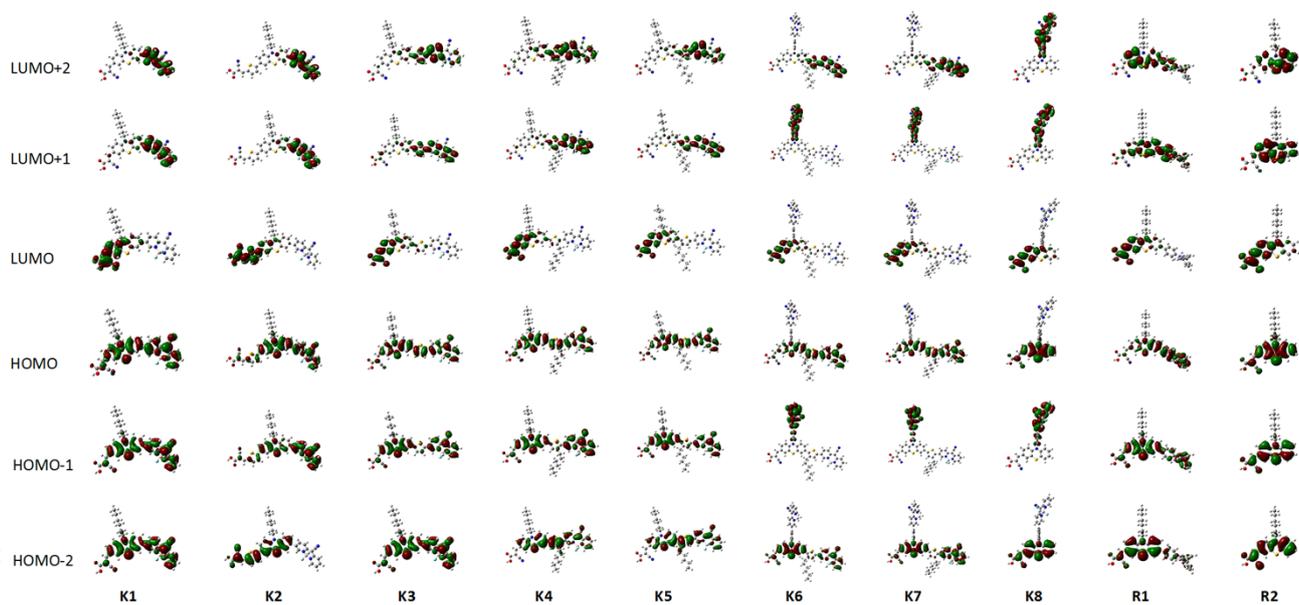
**Figure S1.** Absorption spectra of (a) **K1**, (b) **K2**, (c) **K3**, (d) **K4**, (e) **K5**, (f) **K6**, (g) **K7**, (h) **K8**, (i) **R1**, and (j) **R2** in different solvents.



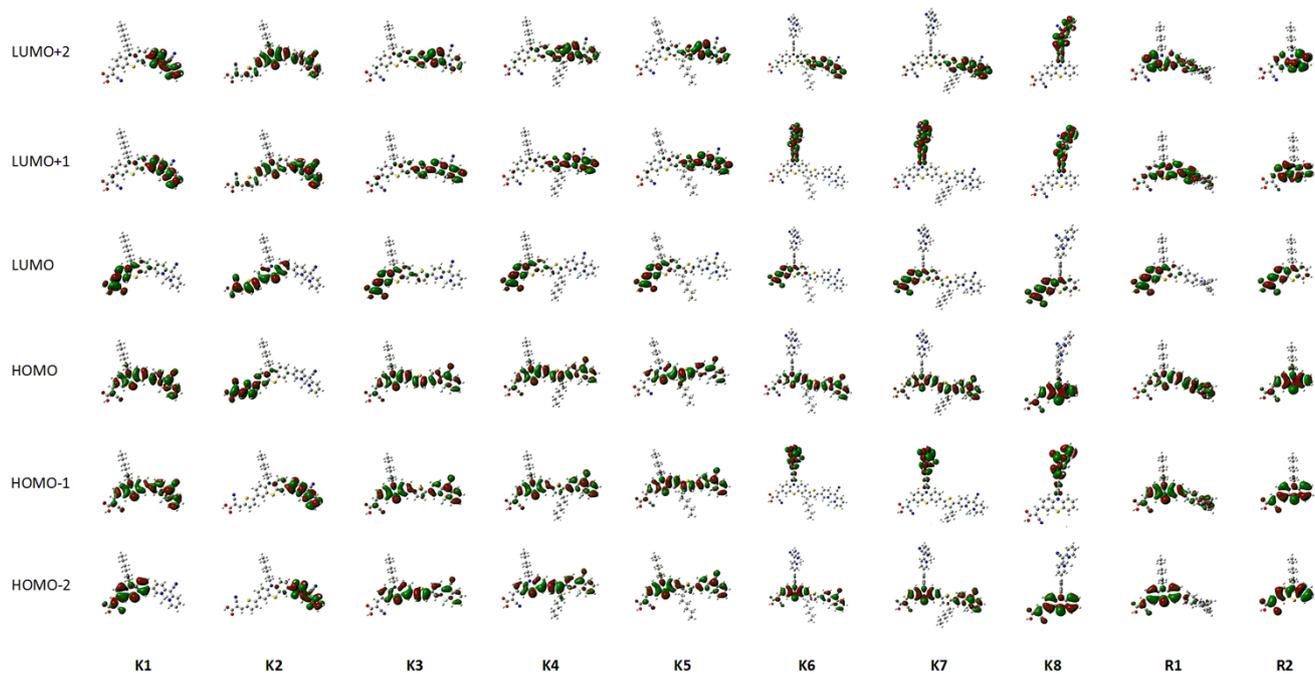
**Figure S2.** Absorption spectra of (a) **K2**, (b) **K4**, (c) **K5**, (d) **K6**, (e) **K7**, (f) **K8**, and (g) **R1** in THF solutions before and after the addition of TEA.



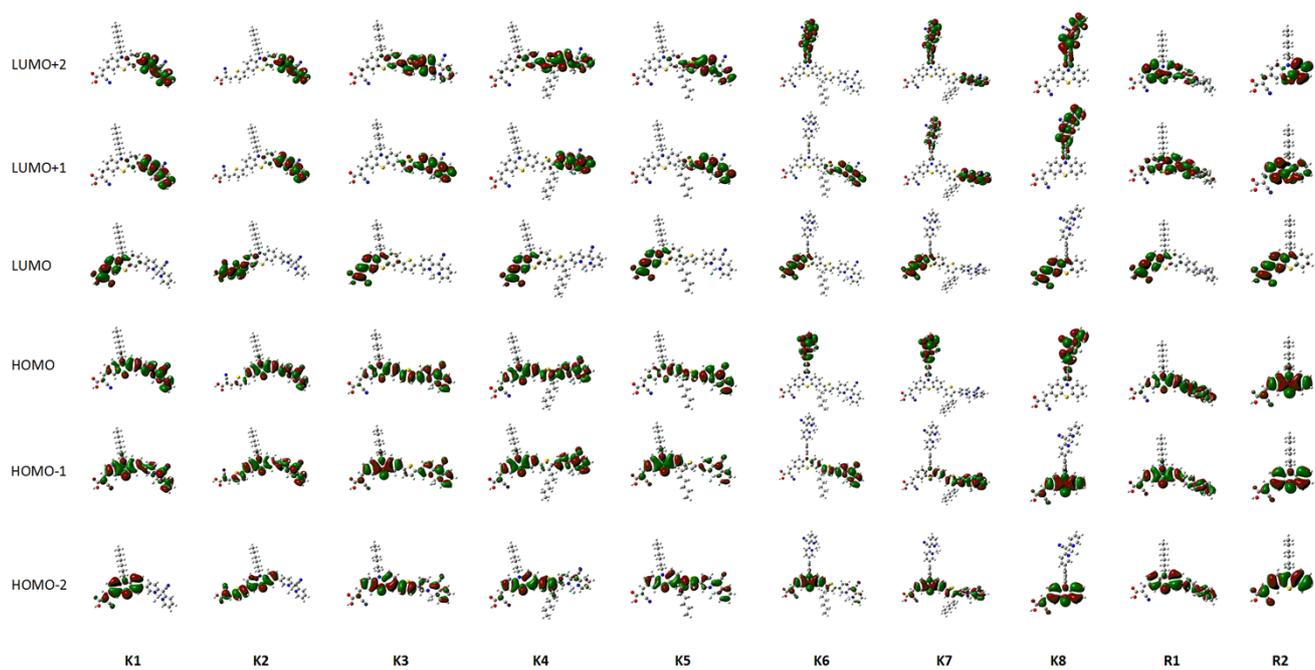
**Figure S3.** Cyclic voltammograms of the K and R dyes recorded in THF solutions.



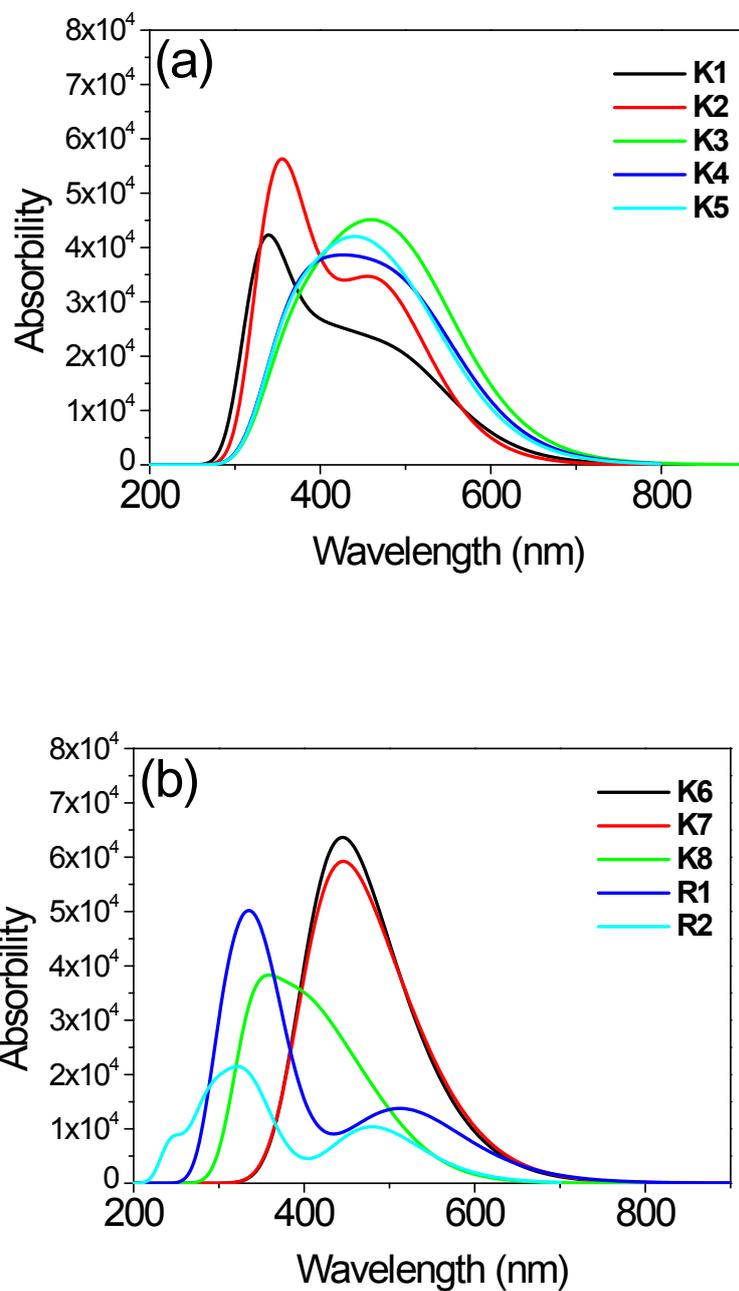
**Figure S4.** Frontier orbitals of the **K** and **R** dyes optimized with DFT at the B3LYP/6-31G (d,p) level.



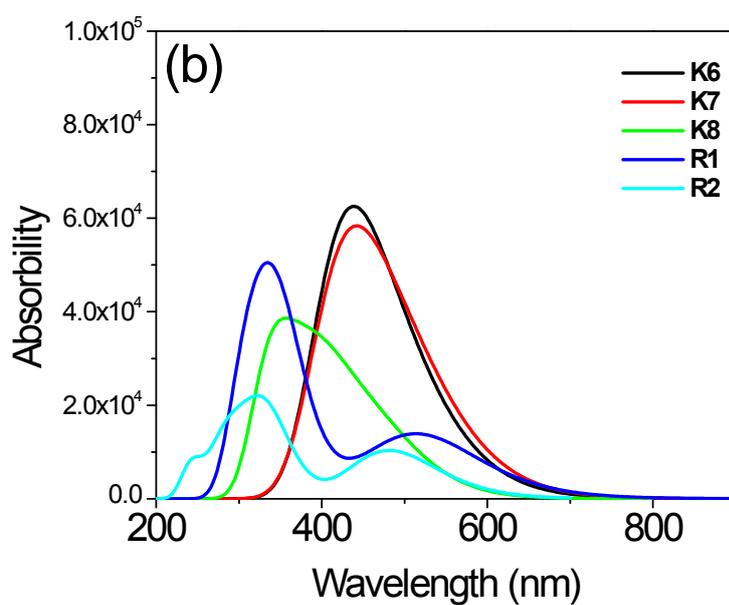
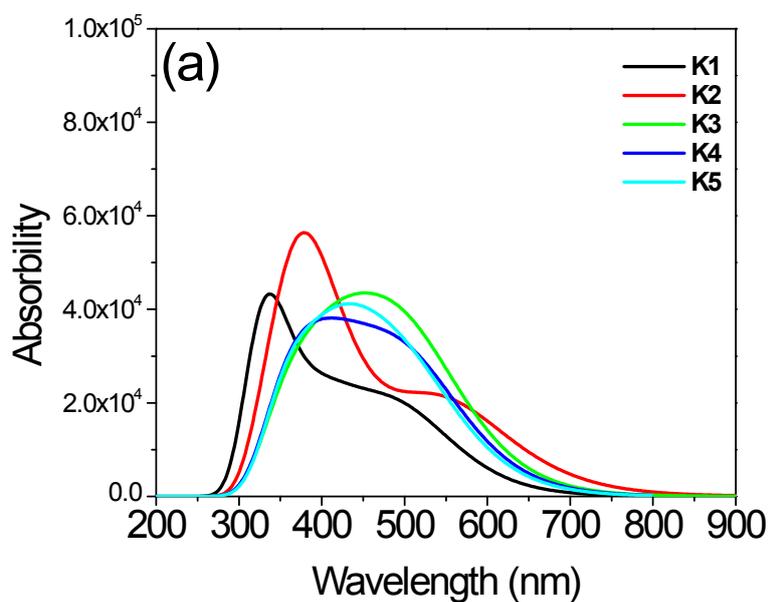
**Figure S5.** Frontier orbitals of the d **K** and **R** yes optimized with DFT at the B3PW91/6-31G (d,p) level.



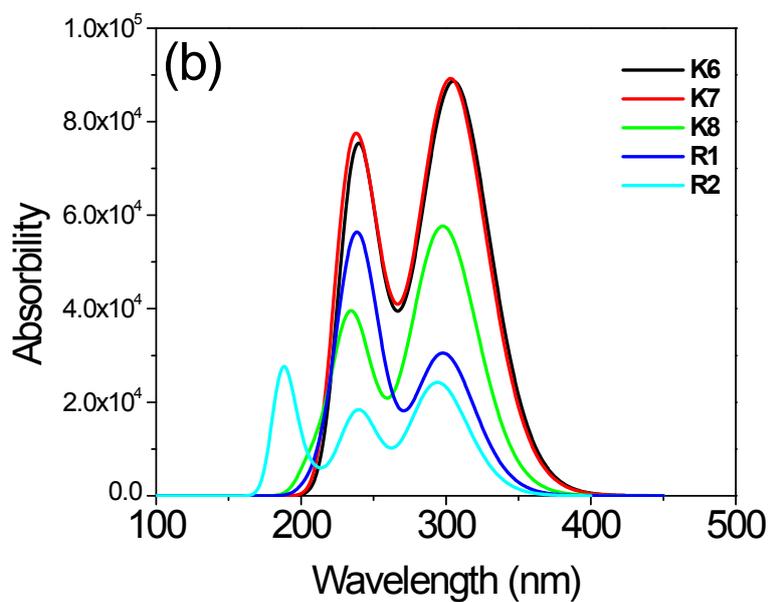
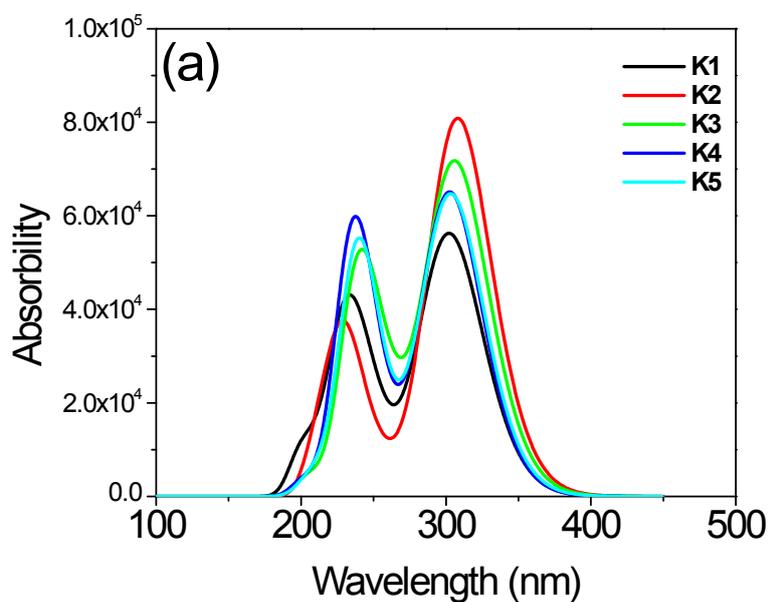
**Figure S6.** Frontier orbitals of the **K** and **R** dyes optimized with Hartree-Fock 6-31G (d,p) basis set.



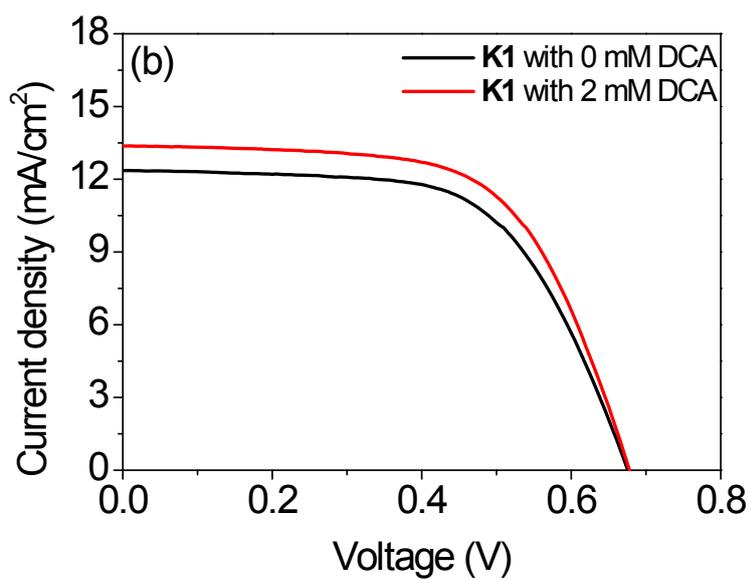
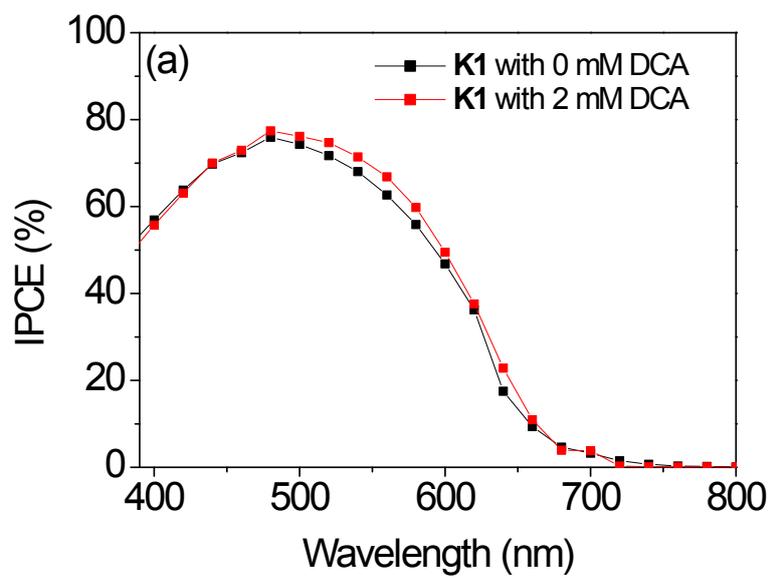
**Figure S7.** Calculated gas-phase absorption spectra of (a) dyes **K1– K5** and (b) dyes **K6– K8, R1** and **R2** by using DFT at the B3LYP/6-31G (d,p) level.



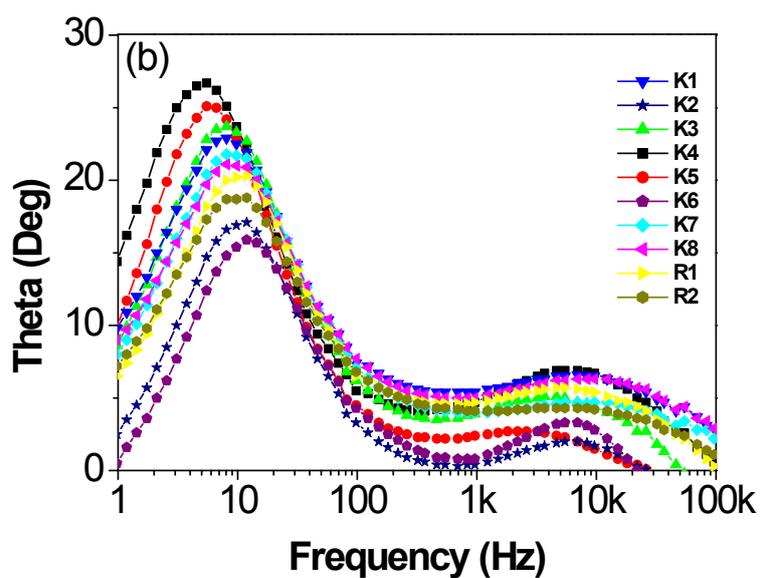
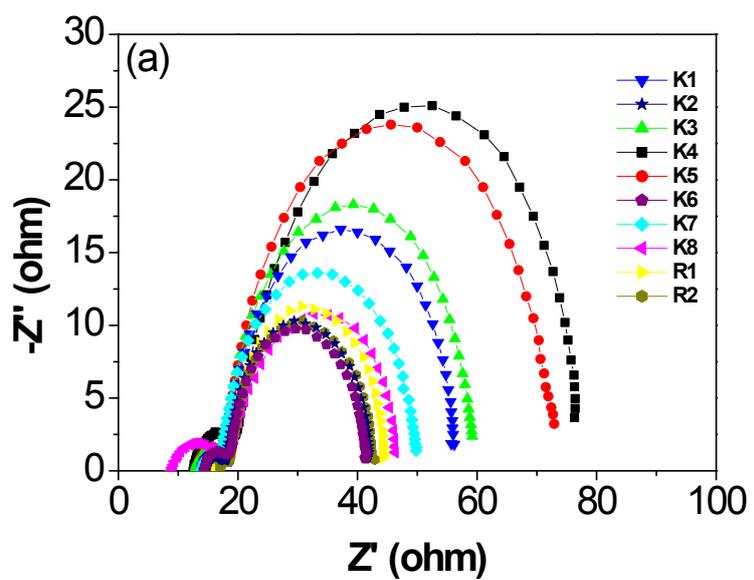
**Figure S8.** Calculated gas-phase absorption spectra of (a) dyes **K1– K5** and (b) dyes **K6– K8, R1** and **R2** by using DFT at the B3PW91/6-31G(d,p) level.



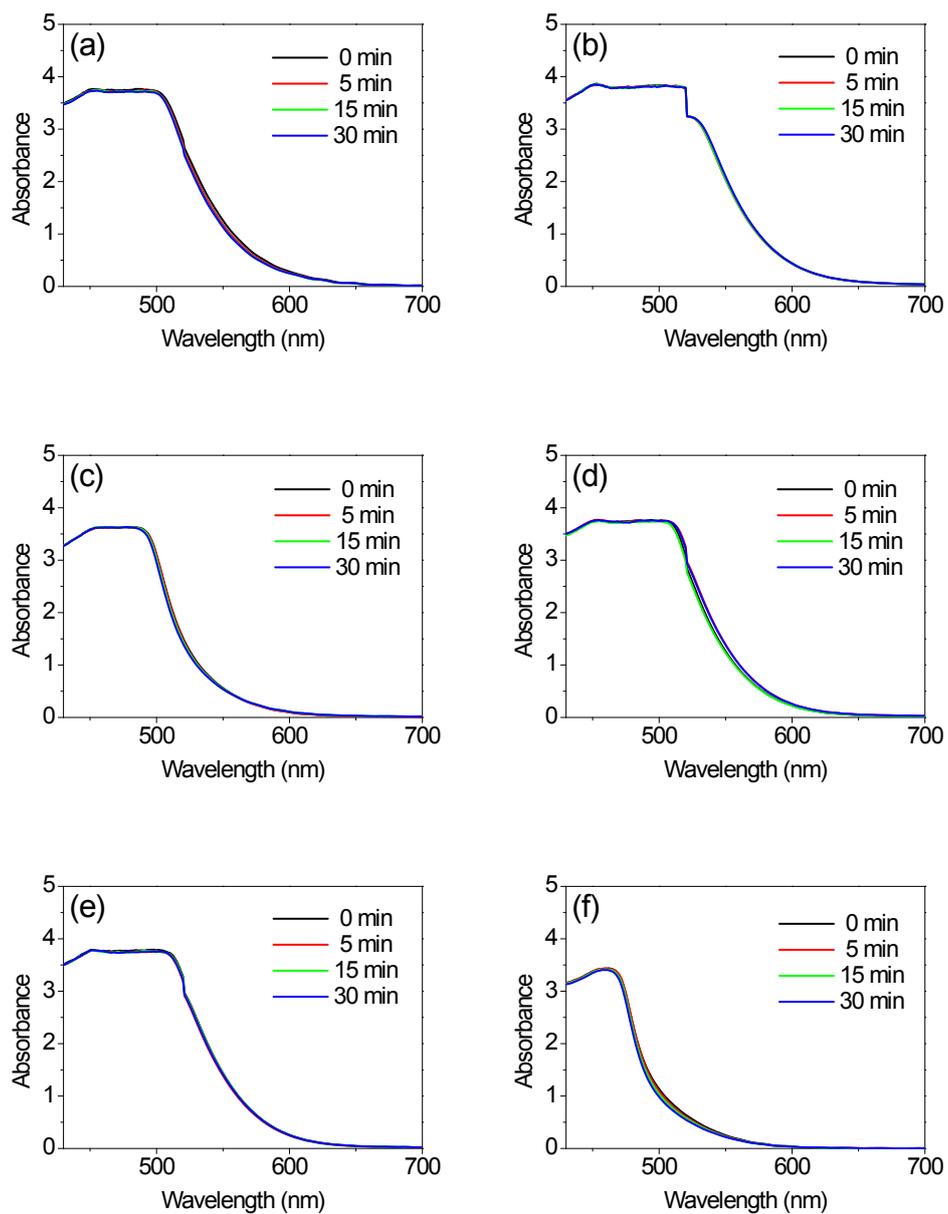
**Figure S9.** Calculated gas-phase absorption spectra of (a) dyes **K1– K5** and (b) dyes **K6– K8, R1** and **R2** by using 6-31G (d,p) basis set at Hartree-Fock level.



**Figure S10.** (a) The IPCE and (b) current-voltage plots for the DSSC made with dye **K1** with or without DCA.



**Figure S11.** The electrochemical impedance spectra of (a) Nyquist plots, and (b) Bode phase plots for the DSSC based on **K** and **R** with DCA.



**Figure S12.** Absorption spectra of (a) K2, (b) K3, (c) K5, (d) K6, (e) K7, and (f) K8 absorbed on nanocrystalline TiO<sub>2</sub> films before and after light irradiation (30 min).

**Table S1** Calculated TDDFT excitation energies ( $E$ ), oscillator strengths ( $f$ ), MO compositions and characters, are compared with experimental absorptions based on DFT at the B3LYP/6-31G (d,p) level.

Dye	$n^a$	$E$ (ev, nm)	$f$	Composition	Character	exptl (ev, nm)
<b>K1</b>	1	2.47 (503)	0.39	93% HOMO→LUMO	CT	2.66 (467)
	3	2.97 (418)	0.37	89% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	3.78 (328)
	5	3.28 (378)	0.10	92% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	4.41 (281)
	6	3.49 (355)	0.20	43% HOMO→LUMO+3	$\pi$ - $\pi^*$ (3)	
	8	3.67 (338)	0.22	36% HOMO-1→LUMO+3	$\pi$ - $\pi^*$ (4)	
<b>K2</b>	9	3.77 (329)	0.50	46% HOMO-1→LUMO+4	$\pi$ - $\pi^*$ (5)	
	1	2.24 (554)	0.47	96% HOMO→LUMO	CT	2.66 (467)
	3	2.86 (433)	0.37	93% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	3.70 (335)
	5	3.22 (386)	0.32	86% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	4.41 (281)
	6	3.26 (380)	0.64	73% HOMO-2→LUMO	$\pi$ - $\pi^*$ (3)	
<b>K3</b>	9	3.65 (340)	0.39	29% HOMO→LUMO+4	$\pi$ - $\pi^*$ (4)	
	1	2.40 (516)	0.70	90% HOMO→LUMO	CT	2.58 (481)
	3	2.82 (439)	0.60	83% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	4.05 (306)
	5	3.14 (395)	0.13	92% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	
	6	3.28 (377)	0.31	73% HOMO→LUMO+3	$\pi$ - $\pi^*$ (3)	
<b>K4</b>	9	3.61 (343)	0.12	57% HOMO-1→LUMO+3	$\pi$ - $\pi^*$ (4)	
	1	2.42 (513)	0.60	91% HOMO→LUMO	CT	2.67 (465)
	3	2.85 (434)	0.51	91% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	3.88 (320)
	5	3.18 (390)	0.13	91% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	
	6	3.31 (375)	0.31	59% HOMO→LUMO+3	$\pi$ - $\pi^*$ (3)	
<b>K5</b>	9	3.61 (344)	0.13	57% HOMO-1→LUMO+3	$\pi$ - $\pi^*$ (4)	
	1	2.43 (510)	0.56	89% HOMO→LUMO	CT	2.61 (475)
	3	2.85 (434)	0.63	92% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	3.82 (325)
	6	3.34 (371)	0.41	68% HOMO→LUMO+3	$\pi$ - $\pi^*$ (2)	
<b>K6</b>	9	3.62 (343)	0.11	37% HOMO-1→LUMO+3	$\pi$ - $\pi^*$ (3)	
	1	2.45 (507)	0.49	90% HOMO→LUMO	CT	2.70 (460)
	3	2.74 (453)	0.13	80% HOMO-2→LUMO	$\pi$ - $\pi^*$ (1)	3.76 (330)
	4	2.83 (439)	0.72	56% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	
<b>K7</b>	6	2.89 (429)	0.43	61% HOMO→LUMO+2	$\pi$ - $\pi^*$ (3)	
	1	2.44 (508)	0.55	90% HOMO→LUMO	CT	2.70 (459)
	3	2.76 (449)	0.11	82% HOMO-2→LUMO	$\pi$ - $\pi^*$ (1)	3.73 (332)
	4	2.83 (439)	0.56	52% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	
<b>K8</b>	6	2.89 (429)	0.43	67% HOMO→LUMO+2	$\pi$ - $\pi^*$ (3)	
	1	2.64 (469)	0.31	92% HOMO→LUMO	CT	2.71(458)

	4	3.08 (402)	0.56	90% HOMO-1→LUMO+1	π-π* (1)	3.82(325)
	8	3.56 (348)	0.34	42% HOMO-2→LUMO	π-π* (2)	
	9	3.62 (342)	0.27	70% HOMO-1→LUMO+3	π-π* (3)	
	10	3.70 (335)	0.17	64% HOMO→LUMO+4	π-π* (4)	
<b>R1</b>	1	2.34 (530)	0.27	97% HOMO→LUMO	CT	2.76 (450)
	2	2.68 (462)	0.12	91% HOMO-1→LUMO	π-π* (1)	3.94 (315)
	3	3.43 (361)	0.50	57% HOMO→LUMO+1	π-π* (2)	
	4	3.59 (345)	0.15	54% HOMO-2→LUMO	π-π* (3)	
	5	3.71 (334)	0.47	50% HOMO-1→LUMO+1	π-π* (4)	
	7	3.88 (320)	0.10	22% HOMO→LUMO+2	π-π* (5)	
	9	4.04 (307)	0.19	91% HOMO→LUMO+5	π-π* (6)	
<b>R2</b>	1	2.58 (480)	0.26	93% HOMO→LUMO	CT	2.84 (437)
	2	3.56 (348)	0.19	73% HOMO-1→LUMO	π-π* (1)	3.99 (311)
	3	3.79 (327)	0.29	75% HOMO→LUMO+1	π-π* (2)	
	5	4.22 (294)	0.18	49% HOMO-2→LUMO	π-π* (3)	
	10	5.08 (244)	0.13	47% HOMO-1→LUMO+1	π-π* (4)	

<sup>a</sup> Order of calculated transitions according to energy.

**Table S2** Calculated TDDFT excitation energies ( $E$ ), oscillator strengths ( $f$ ), MO compositions and characters, are compared with experimental absorptions based on DFT at the B3PW91/6-31G (d,p) level.

Dye	$n^a$	$E$ (ev, nm)	$f$	Composition	Character	exptl (ev, nm)
<b>K1</b>	1	2.46	0.40	93% HOMO→LUMO	CT	2.66 (467)
	3	2.99	0.37	89% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	3.78 (328)
	5	3.30	0.11	91% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	4.41 (281)
	6	3.50	0.17	45% HOMO-1→LUMO+2	$\pi$ - $\pi^*$ (3)	
	8	3.68	0.22	36% HOMO→LUMO+3	$\pi$ - $\pi^*$ (4)	
	9	3.78	0.55	43% HOMO→LUMO+4	$\pi$ - $\pi^*$ (5)	
<b>K2</b>	1	2.24	0.46	96% HOMO→LUMO	CT	2.66 (467)
	3	2.88	0.37	93% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	3.70 (335)
	5	3.23	0.31	87% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	4.41 (281)
	6	3.28	0.67	71% HOMO-2→LUMO	$\pi$ - $\pi^*$ (3)	
	9	3.66	0.42	37% HOMO→LUMO+4	$\pi$ - $\pi^*$ (4)	
<b>K3</b>	1	2.41	0.69	90% HOMO→LUMO	CT	2.58 (481)
	3	2.84	0.62	87% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	4.05 (306)
	5	3.15	0.15	92% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	
	6	3.31	0.30	69% HOMO→LUMO+3	$\pi$ - $\pi^*$ (3)	
	9	3.62	0.14	56% HOMO-1→LUMO+3	$\pi$ - $\pi^*$ (4)	
<b>K4</b>	1	2.42	0.60	91% HOMO→LUMO	CT	2.67 (465)
	3	2.87	0.51	92% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	3.88 (320)
	5	3.19	0.14	90% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	
	6	3.32	0.29	56% HOMO→LUMO+3	$\pi$ - $\pi^*$ (3)	
	9	3.62	0.16	57% HOMO-1→LUMO+3	$\pi$ - $\pi^*$ (4)	
<b>K5</b>	1	2.43	0.56	89% HOMO→LUMO	CT	2.61 (475)
	3	2.87	0.63	93% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	3.82 (325)
	5	3.17	0.10	92% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	
	6	3.36	0.39	64% HOMO→LUMO+3	$\pi$ - $\pi^*$ (3)	
	9	3.63	0.13	37% HOMO-1→LUMO+3	$\pi$ - $\pi^*$ (4)	
<b>K6</b>	1	2.46	0.48	89% HOMO→LUMO	CT	2.70 (460)
	3	2.76	0.11	81% HOMO-2→LUMO	$\pi$ - $\pi^*$ (1)	3.76 (330)
	4	2.86	0.67	60% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (2)	
	6	2.92	0.47	69% HOMO→LUMO+2	$\pi$ - $\pi^*$ (3)	
<b>K7</b>	1	2.44	0.56	90% HOMO→LUMO	CT	2.70 (459)
	4	2.83	0.34	52% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	3.73 (332)
	5	2.86	0.27	43% HOMO→LUMO+1	$\pi$ - $\pi^*$ (2)	
	6	2.91	0.45	70% HOMO→LUMO+2	$\pi$ - $\pi^*$ (3)	

<b>K8</b>	1	2.63	0.31	92% HOMO→LUMO	CT	2.71(458)
	4	3.11	0.57	91% HOMO-1→LUMO+1	π-π* (1)	3.82(325)
	8	3.57	0.23	41% HOMO-2→LUMO	π-π* (2)	
	9	3.63	0.37	74% HOMO-1→LUMO+3	π-π* (3)	
	10	3.70	0.18	49% HOMO→LUMO+4	π-π* (4)	
<b>R1</b>	1	2.34	0.28	96% HOMO→LUMO	CT	2.76 (450)
	2	2.67	0.11	91% HOMO-1→LUMO	π-π* (1)	3.94 (315)
	3	3.44	0.48	61% HOMO→LUMO+1	π-π* (2)	
	4	3.61	0.15	54% HOMO-2→LUMO	π-π* (3)	
	5	3.71	0.49	50% HOMO-1→LUMO+1	π-π* (4)	
	9	4.05	0.19	91% HOMO→LUMO+5	π-π* (5)	
<b>R2</b>	10	4.09	0.29	79% HOMO-3→LUMO	π-π* (6)	
	1	2.57	0.25	93% HOMO→LUMO	CT	2.84 (437)
	2	3.57	0.17	69% HOMO-1→LUMO	π-π* (1)	3.99 (311)
	3	3.79	0.33	71% HOMO→LUMO+1	π-π* (2)	
	5	4.24	0.16	46% HOMO-1→LUMO+3	π-π* (3)	
	7	4.44	0.10	39% HOMO-2→LUMO	π-π* (4)	
	9	5.07	0.11	50% HOMO-1→LUMO+1	π-π* (5)	

<sup>a</sup> Order of calculated transitions according to energy.

**Table S3** Calculated TDDFT excitation energies ( $E$ ), oscillator strengths ( $f$ ), MO compositions and characters, are compared with experimental absorptions based on 6-31G (d,p) basis set at Hartree-Fock level.

Dye	$n^a$	$E$ (ev, nm)	$f$	Composition	Character	exptl (ev, nm)
<b>K1</b>	1	4.04	0.98	87% HOMO→LUMO+1	CT	2.66 (467)
	2	4.24	0.48	37% HOMO-1→LUMO	$\pi$ - $\pi^*$ (1)	3.78 (328)
	3	4.92	0.20	63% HOMO→LUMO+2	$\pi$ - $\pi^*$ (2)	4.41 (281)
	4	5.09	0.24	17% HOMO-1→LUMO+5	$\pi$ - $\pi^*$ (3)	
	6	5.37	0.49	22% HOMO→LUMO+5	$\pi$ - $\pi^*$ (4)	
	7	5.46	0.26	22% HOMO→LUMO+5	$\pi$ - $\pi^*$ (5)	
	8	5.85	0.12	22% HOMO→LUMO+6	$\pi$ - $\pi^*$ (6)	
	10	6.22	0.13	15% HOMO→LUMO+7	$\pi$ - $\pi^*$ (7)	
<b>K2</b>	1	4.00	1.69	25% HOMO→LUMO+1	CT	2.66 (467)
	2	4.13	0.33	31% HOMO→LUMO+1	$\pi$ - $\pi^*$ (1)	3.70 (335)
	4	4.94	0.12	44% HOMO→LUMO+2	$\pi$ - $\pi^*$ (2)	4.41 (281)
	6	5.35	0.51	14% HOMO→LUMO+4	$\pi$ - $\pi^*$ (3)	
	7	5.44	0.26	17% HOMO→LUMO+6	$\pi$ - $\pi^*$ (4)	
	9	5.83	0.13	70% HOMO-6→LUMO	$\pi$ - $\pi^*$ (5)	
	10	5.84	0.14	7% HOMO-3→LUMO+3	$\pi$ - $\pi^*$ (6)	
<b>K3</b>	1	4.02	1.46	48% HOMO→LUMO+1	CT	2.58 (481)
	2	4.18	0.35	35% HOMO-1→LUMO	$\pi$ - $\pi^*$ (1)	4.05 (306)
	3	4.80	0.37	50% HOMO→LUMO+2	$\pi$ - $\pi^*$ (2)	
	5	5.17	0.77	11% HOMO-1→LUMO+3	$\pi$ - $\pi^*$ (3)	
	6	5.22	0.30	35% HOMO-3→LUMO	$\pi$ - $\pi^*$ (4)	
	<b>K4</b>	1	4.08	1.40	32% HOMO→LUMO+1	CT
2		4.18	0.21	23% HOMO-1→LUMO	$\pi$ - $\pi^*$ (1)	3.88 (320)
3		4.94	0.34	33% HOMO→LUMO+2	$\pi$ - $\pi^*$ (2)	
6		5.27	1.14	10% HOMO→LUMO+5	$\pi$ - $\pi^*$ (3)	
<b>K5</b>	1	4.05	1.18	66% HOMO→LUMO+1	CT	2.61 (475)
	2	4.20	0.46	49% HOMO-1→LUMO	$\pi$ - $\pi^*$ (1)	3.82 (325)
	3	4.88	0.22	65% HOMO→LUMO+2	$\pi$ - $\pi^*$ (2)	
	4	5.07	0.12	24% HOMO-1→LUMO+4	$\pi$ - $\pi^*$ (3)	
	5	5.19	0.94	30% HOMO→LUMO+3	$\pi$ - $\pi^*$ (4)	
	6	5.22	0.17	33% HOMO-3→LUMO	$\pi$ - $\pi^*$ (5)	
<b>K6</b>	1	3.94	0.82	85% HOMO→LUMO+2	CT	2.70 (460)
	2	4.05	1.06	79% HOMO-1→LUMO+1	$\pi$ - $\pi^*$ (1)	3.76 (330)
	3	4.33	0.59	54% HOMO-2→LUMO	$\pi$ - $\pi^*$ (2)	
	5	4.88	0.26	61% HOMO-1→LUMO+3	$\pi$ - $\pi^*$ (3)	

	6	5.11	0.36	13% HOMO-1→LUMO+5	π-π* (4)	
	7	5.22	0.83	10% HOMO-1→LUMO+5	π-π* (5)	
	8	5.25	0.34	11% HOMO→LUMO+6	π-π* (6)	
	9	5.29	0.16	18% HOMO→LUMO+6	π-π* (7)	
<b>K7</b>	1	3.94	0.78	65% HOMO→LUMO+2	CT	2.70 (459)
	2	4.10	1.14	54% HOMO-1→LUMO+1	π-π* (1)	3.73 (332)
	3	4.30	0.50	42% HOMO-2→LUMO	π-π* (2)	
	4	4.81	0.11	62% HOMO→LUMO+4	π-π* (3)	
	5	4.95	0.53	32% HOMO-1→LUMO+3	π-π* (4)	
	6	5.01	0.18	32% HOMO-1→LUMO+5	π-π* (5)	
	7	5.25	0.19	11% HOMO→LUMO+6	π-π* (6)	
	8	5.28	0.19	31% HOMO→LUMO+6	π-π* (7)	
	9	5.32	1.07	9% HOMO-2→LUMO+10	π-π* (8)	
<b>K8</b>	1	4.08	1.05	85% HOMO→LUMO+1	CT	2.71(458)
	2	4.36	0.53	60% HOMO-1→LUMO	π-π* (1)	3.82(325)
	3	4.93	0.12	76% HOMO→LUMO+2	π-π* (2)	
	4	5.20	0.24	21% HOMO-1→LUMO+4	π-π* (3)	
	5	5.26	0.29	32% HOMO-2→LUMO	π-π* (4)	
	6	5.38	0.40	47% HOMO→LUMO+3	π-π* (5)	
<b>R1</b>	1	4.15	0.75	39% HOMO-1→LUMO	CT	2.76 (450)
	2	5.00	0.39	45% HOMO→LUMO+1	π-π* (1)	3.94 (315)
	3	5.18	0.28	12% HOMO-1→LUMO+1	π-π* (2)	
	4	5.23	0.65	6% HOMO→LUMO+4	π-π* (3)	
	7	5.49	0.19	45% HOMO→LUMO+5	π-π* (4)	
<b>R2</b>	1	4.21	0.20	65% HOMO→LUMO	CT	2.84 (437)
	2	5.12	0.25	50% HOMO→LUMO+1	π-π* (1)	3.99 (311)
	3	5.21	0.20	36% HOMO-1→LUMO	π-π* (2)	
	7	6.58	0.35	11% HOMO-3→LUMO	π-π* (3)	
	9	6.63	0.29	17% HOMO-1→LUMO+1	π-π* (4)	

<sup>a</sup> Order of calculated transitions according to energy.

**Table S4** DSSC performance parameters of dye **K1** with or without DCA as co-adsorbent.

dye	DCA	Amount <sup>a</sup> / mol cm <sup>-2</sup>	V <sub>oc</sub> /V	J <sub>sc</sub> /mA cm <sup>-2</sup>	ff	η (%)
<b>K1</b>	0 mM	4.08×10 <sup>-7</sup>	0.65	11.31	0.58	4.25 <sup>b</sup>
	0 mM	2.28×10 <sup>-7</sup>	0.68	12.36	0.61	5.15 <sup>c</sup>
	2 mM	1.97×10 <sup>-7</sup>	0.68	13.37	0.62	5.66 <sup>c</sup>
	10 mM	1.66×10 <sup>-7</sup>	0.69	14.05	0.63	6.02 <sup>b</sup>

<sup>a</sup> Amount of dye adsorbed on TiO<sub>2</sub> film. <sup>b</sup> Experiments were conducted with TiO<sub>2</sub> photoelectrodes with 10 μm transparent and 5 μm scattering thickness and 0.25 cm<sup>2</sup> working area on the FTO (8 Ω/sq.) substrates. <sup>c</sup> Experiments were conducted with TiO<sub>2</sub> photoelectrodes with 5 μm transparent and 5 μm scattering thickness and 0.25 cm<sup>2</sup> working area on the FTO (8 Ω/sq.) substrates.