# **Supporting Information**

# Efficient Light-Harvesters Based on Modified Bi-fluorenylidenes.

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# 1. General

NMR spectra (<sup>1</sup>H, <sup>13</sup>C) were recorded at room temperature on Bruker DPX 300 MHz and Bruker AVIII. 500 MHz data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C). Mass spectrometry was carried out by the services at the Universidad Complutense de Madrid. UV-vis spectra were recorded in a Varian Cary 50 spectrometer at a constant temperature of 25 °C in diluted dimethylsulfoxide solution (ca.  $10^{-5}$  mol L<sup>-1</sup>). Compounds F1,<sup>1</sup> 1,<sup>2</sup> 2,<sup>3</sup> 3,<sup>4</sup> 10,<sup>5</sup> and 13<sup>6</sup> were synthesized according to already described procedures.

## 2-Synthesis of fluorene derivatives (F series)



Scheme S1. Synthesis of F2a, F3a, and F3b.

#### 2.1 Synthesis of fluorenone derivatives

**4**: **2** (60 mg, 0.17 mmol), *n*-Bu<sub>4</sub>NBr (112 g, 0.35 mmol),  $K_2CO_3$  (100 g, 0.71 mmol) and diphenyl-(4-vinyl-phenyl)-amine (54 g, 0.2 mmol) were dissolved in 25 mL of dry DMF under argon atmosphere. Pd(OAc)<sub>2</sub> (catalytic amount, 2–3 % mmol) was then added under an argon flow. The mixture was heated at 80–90 °C overnight. The crude was poured in water to precipitate **4** that was then filtered. Purification by column chromatography over silica gel afford **4** as a red solid (53 % yield).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): *δ* ppm 7.63 (s, 2H), 7.55 (d, 2H, *J* = 7.7 Hz), 7.35 (d, 4H, *J* = 8.5 Hz), 7.29 (s, 1H), 7.23-7.18 (m, 10H), 7.13 (s, 1H), 7.07-6.92 (s, 18H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): *δ* ppm 148.3, 147.5, 144.7, 144.2, 133.9, 131.3, 130.6, 129.5, 127.9, 127.5, 126.1, 125.0, 124.8, 123.6, 123.1, 117.5. MS: (ESI<sup>+</sup>); calculated: *m/z* 718.30; found *m/z*: 741.3 [M+Na]<sup>+</sup>, 742.3 [M+H+Na]<sup>+</sup>. IR: 1736, 1700, 1587, 1496, 1324, 1281, 754, 668.

#### 2.2 General procedure for Knoevenagel condensation:

Compounds 5, 6, and 7 were successfully obtained only in neat conditions. The use of solvents, such as DCM or chloroform yielded only traces of the titled compounds. The corresponding ketones were dissolved in 10 eq of cyano-acetic acid methyl ester, 4-methyl-morpholine (10 eq). Then TiCl<sub>4</sub> (10 eq) was carefully added dropwise, *via* a syringe. The reaction was performed in vial or in a 10mL schlenk flask. After the addition of TiCl<sub>4</sub>, the reaction was gently heated at 60 °C until no more starting materials was observed by TLC. The crude was poured in water (100 mL) and extracted with DCM (2 × 25 mL). In case of emulsion, the solution was filter over celite and ammonium chloride was added to the water phase. The organic layers were collected, dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure. The crude solid was purified by chromatography column (hexanes / DCM; 3 : 7 in all cases). The target compound, which contained a large excess of cyano-acetic acid methyl ester, was further purified by washing with MeOH, giving pure derivatives 5, 6, and 7. Relative low yields are reported as follows due to the additional purification process.

### **5:** a bluish green solid was obtained (47 % yield)

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ ppm 8.19 (bs, 2H), 7.4–7.1 (m, 24H), (3.5, s, 3H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ ppm 152.9, 147.45, 136.5, 135.6, 129.5, 127.3, 124.5, 122.1, 121.6, 123.4, 120.0, 115.4, 53.2MS: (ESI<sup>-</sup>); calculated: *m/z* 595.23; found: *m/z*: 537.0 [M-COOCH<sub>3</sub>], 568.1 [M-CN]. IR: 3031, 2925, 2856, 2205, 1588, 1489, 1462, 1322, 1274, 754, 696.



Figure S2. <sup>13</sup>C-NMR of compound 5.



Figure S3. MS of compound 5.

**6:** a dark solid was obtained (43 % yield).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.40 (d, 1H,  $J_3$  = 8.5 Hz), 8.14 (d, 1H,  $J_3$  = 8.7 Hz), 7.30–7.27 (m, 8H), 7.12–7.09 (m, 12H), 6.98 (dd, 2H,  $J_3$  = 10.8 Hz,  $J_4$  = 2.0 Hz), 6.77 (dd, 1H,  $J_3$  = 8.8 Hz,  $J_4$  = 2.2 Hz), 6.69 (dd, 1H,  $J_3$  = 8.7 Hz,  $J_4$  = 2.2 Hz), 3.91 (s, 3H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 164.2, 156.4, 152.2, 152.1, 146.6, 146.5, 143.9, 143.6, 130.7, 129.7, 128.5, 128.1, 125.9, 125.8, 125.7, 124.7, 120.9, 120.5, 118.5, 112.7, 112.4, 92.8, 53.1; MS: (ESI<sup>+</sup>); calculated: *m/z* 595.23; found: *m/z*: 618.3 [M+Na]<sup>+</sup>, 634.3 [M+K]<sup>+</sup>. IR: 3062, 2924, 2855, 2204, 1726, 1586, 1489, 1276, 1238, 1099, 760, 698.



Figure S4. <sup>1</sup>H-NMR of compound 6.



Figure S5. <sup>13</sup>C-NMR of compound 6.



Figure S6. MS of compound 6.

7: a dark solid was obtained (37 % yield).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.54 (d, 1H,  $J_3 = 13$  Hz), 8.16 (d, 1H,  $J_3 = 13$  Hz), 7.73 (d, 2H,  $J_3 = 8$  Hz), 7.45–7.41 (m, 4H), 7.38–7.35 (m, 2H), 7.31–7.28 (m, 7H), 7.22 (d, 1H,  $J_3 = 5.6$  Hz), 7.14–7.05 (m, 18H), 6.99 (d, 2H,  $J_3 = 10.5$  Hz), 4.00 (s, 3H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 163.8, 156.2, 148.6, 147.7, 143.2, 142.9, 135.4, 134.3, 131.5, 131.4, 130.8, 130.9, 129.8, 128.3, 127.5, 127.3, 127.0, 126.2, 125.3, 123.9, 123.8, 123.4, 123.3, 117.7, 117.4, 117.3, 97.3; MS: (ESI<sup>+</sup>); calculated: *m/z* 799.32; found: *m/z*: 822.3[M+Na]<sup>+</sup>; 823.4 [M+H+Na]<sup>+</sup>, IR: 3030, 1730, 1541, 1497, 1280, 1236, 1180, 1100, 959, 831, 754, 665.



Figure S7. <sup>1</sup>H-NMR of compound 7.



Figure S8. <sup>13</sup>C-NMR of compound 7.



Figure S9. MS of compound 7.

#### 2.3 Hydrolysis of esters

Due to intrinsic solubility issues of some of the described final materials (F2a, F3a and F3b), its complete characterization by NMR techniques was difficult to perform. However in all these materials, it is possible to appreciate the disappearance of the methoxy group, therefore confirming the hydrolysis of the esters. Additionally, it is important to remark here, that those materials difficult to study by NMR were correctly characterized by MS, HR-MS and FT-IR techniques.

**F2a**: ester derivative **5** (0.18 mmol) was dissolved in CH<sub>3</sub>CN (30 mL) and treated with LiOH (excess, 86.4 mg, 3.6 mmol) dissolved in water (10 mL). The reaction was stirred at RT for 5–6 hrs and monitored by TLC (eluent mixture: DCM : hexanes; 1 : 1). Acetonitrile was removed under reduced pressure and the crude was extracted with AcOEt ( $3 \times 25$  mL) and a 10 % HCl water solution. The combined organic layers were dried over MgSO<sub>4</sub> and concentrated affording bluish green solid **F2a** (% yield).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ ppm 8.2 (bs, 2H), 7.7 (bs, 2H), 7.4–6.9 (m, 22H); MS: (ESI-); calculated: *m/z* 581.21; found: *m/z*: 604.2 [M+Na]<sup>-</sup>, 620.1 m/z: [M +K]<sup>-</sup>; HR MS: (ESI<sup>-</sup>); calculated: *m/z* 581.2103; found: *m/z*: 581.2079 [M]<sup>+</sup>; IR: 3031, 2925, 2856, 2205, 1588, 1489, 1462, 1322, 1274, 754, 696.



Figure S10. <sup>1</sup>H-NMR of compound F2a.



Figure S11. MS of compound F2a.



Figure S12. HR MS of compound F2a.

**F3a:** ester derivative **6** (0.20 mmol) was dissolved in 40 mL of a CH<sub>3</sub>CN / methanol (1:1 v/v) solvent mixture and treated with an excess of NaOH (20–25 mL of a 3M water solution). The reaction was gently heated at 40–50 °C until no more ester was observed by TLC. Acetonitrile and methanol were removed under reduced pressure and the crude was extracted with DCM ( $3 \times 30$  ml) and a 10 % HCl solution. The organic layers were gathered, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The solid was washed with cyclohexane affording dark solid **F3a** (yield 42 %).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.40 (d, 1H,  $J_3$  = 8.5 Hz), 8.20 (d, 1H,  $J_3$  = 8.7 Hz), 7.30–7.27 (m, 8H), 7.12–7.09 (m, 12H), 6.98 (m, 2H), 6.77 (dd, 1H,  $J_3$  = 8.8 Hz,  $J_4$  = 2.2 Hz), 6.69 (dd, 1H,  $J_3$  = 8.7 Hz,  $J_4$  = 2.2 Hz); MS: (ESF); calculated: *m/z* 581.66; found: *m/z*:535.9 [M-COOH]<sup>+</sup>; IR: broad 3367, 3051, 2923, 2855, 2198, 1692, 1587, 1489, 1276, 754, 696.



Figure S14. MS of compound F3a.

**F3b:** ester derivative 7 (0.20 mmol) was dissolved in 40 mL of a CH<sub>3</sub>CN / methanol (1:1 v/v) solvent mixture and treated with an excess of NaOH (20–25 mL of a 3M water solution). The reaction was gently heated at 40–50 °C until no more ester was observed by TLC. Acetonitrile and methanol were removed under reduced pressure and the crude was extracted with DCM ( $3 \times 30$  ml) and a 10 % HCl solution. The organic layers were gathered, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The solid was washed with cyclohexane and pentane, **F3b** (yield 8 8%).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ ppm 8.05 (bs, 2H), 7.73 (bs, 2H), 7.5-6.9 (m, 34H); MS: (ESI<sup>-</sup>); calculated: *m/z* 785.93; found: *m/z*: 740.1 [M-COOH]<sup>+</sup>; IR: broad 3359, 3199, 2201, 1663, 1619, 1394, 753, 696.



Figure S15. <sup>1</sup>H-NMR of compound F3b.



Figure S16. MS of compound F3b.

## 3 Synthesis of 9'9-fluorenylidene derivatives (BF series)



Scheme S2. Synthesis of BF1, BF3a, BF3b, and BF3c.

#### 3.1 Synthesis of tosylhydrazone

**8:** 4-carboxymethyl fluoren-9-one (1.0 g, 4.2 mmol), was refluxed in methanol in the presence of tosylhydrazine (1.2 g; 6.3 mmol) and a catalytic amount of HCl (36%). After heating for a few hours the suspension turned pale yellow. TLC (eluent : DCM) was used to monitor the reaction. The cooled solution gave a pale yellow precipitate of **8** that was filtered on Buchner. (1.4 g, yield 82%).

<sup>1</sup>H-NMR (500 MHz, [D<sub>6</sub>]DMSO):  $\delta$  ppm mixture of isomers: 8,33 (dd,  $J_3 = 8$  Hz,  $J_4 = 1$  Hz), 8,18 (dd,  $J_3 = 7$  Hz,  $J_4 = 1.0$  Hz), 8.15 (dd,  $J_3 = 9$  Hz,  $J_4 = 1.0$  Hz), 7,95–7.93 (m), 7,82 (dd,  $J_3 = 7$  Hz,  $J_4 = 1.0$  Hz), 7.77 (dd,  $J_3 = 8$  Hz,  $J_4 = 1$  Hz), 7.64 (dd,  $J_3 = 7$  Hz,  $J_4 = 0.4$  Hz), 7.58–7.50 (m), 7.47–7.42 (m), 7.38 (td,  $J_3 = 7$  Hz,  $J_4 = 1$  Hz), 3.96 (s), 3.94 (s), 2.39 (s). <sup>13</sup>C-NMR (125 MHz, [D<sub>6</sub>]DMSO):  $\delta$  ppm mixture of isomers: 167.5, 167.4, 150.0, 150.0, 143.9, 143.9, 139.6, 139.4, 137.5, 137.5, 137.4, 136.6, 135.0, 135.0, 132.2, 131.8, 131.7, 130.8, 130.5, 130.2, 129.5, 129.4, 129.1, 128.9, 128.3, 128.1, 128.0, 128.0, 127.6, 126.7, 126.4, 124.6, 124.5, 124.2, 121.2, 52.6, 20.99. MS: (ESI-); calculated: *m/z* 406.10; found: *m/z*: 404.8 [M-H]<sup>-</sup>. IR: 2923, 2855, 1708, 1596, 1439, 1343, 1276, 1168, 957, 879, 816, 772, 735, 682.

#### 3.2 Synthesis of fluroene-thione derivatives

11: the corresponding fluorenone derivative 3 (103 mg, 0.2 mmol) and Lawesson's reagent (80 mg, 0.2 mmol) were heated in toluene (100 mL) at 90–100 °C for 5–6 hrs. The reaction was protected from the light with aluminum foil and monitored by TLC (hexanes/DCM 1:1). The solvent was removed under reduced pressure and the residue purified by chromatography column over silica gel (eluent: hexanes/DCM 1:1) to afford brown solid **11** (67% yield).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 7.63 (d, 2H,  $J_3 = 8.3$  Hz), (s, 2H), 7.32–7.29 (m, 8H), 7.15–7.11 (m, 12H), 6.94 (d, 2H,  $J_1 = 1.9$  Hz), 6.73 (d, 2H,  $J_3 = 8.3$  Hz,  $J_4 = 1.9$  Hz). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 219.68, 153.3, 146.7, 144.7, 136.6, 129.7, 125.8, 125.6, 124.7, 121.2, 112.4. MS: (ESI<sup>+</sup>); calculated: *m/z* 530.68; found: *m/z*: 529.2 [M-H]<sup>-</sup>, 530.2 [M]<sup>+</sup>, 531.2 [M+H]<sup>+</sup>. IR: 1585, 1484, 1327, 1274, 1105, 754, 697, 654.

**12: 4** (143 mg, 0.2 mmol) and Lawesson's reagent (80 mg, 0.2 mmol) were heated in toluene (120 mL) at 90–100 °C for 5–6 hrs. The reaction was protected from the light with aluminum foil and monitored by TLC (hexanes/DCM 1:1). The solvent was removed under reduced pressure and the residue purified by chromatography column over silica gel (eluent: hexanes/DCM 1 : 1) to afford brown solid **12** (83% yield).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ ppm 7.74 (d, 2H, *J*<sub>3</sub> = 7.7 Hz), 7.76 (s, 2H), 7.43 (d, 5H, *J*<sub>3</sub> = 8.2 Hz), 7.30–7.27 (m, 7H), 7.14–7.13 (m, 10H), 7.08–7.05 (m, 12H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ ppm 223.8, 148.3, 147.5, 144.1, 143.7, 141.1, 131.2, 130.7, 129.5, 129.5, 128.0, 127.4, 126.4, 125.0, 124.8, 124.7, 124.6, 123.6, 123.1, 116.9. MS: (ESI<sup>-</sup>); calculated: *m/z* 734.28; found: *m/z*: 734.2 [M]<sup>-</sup>, 735.1 [M+H]<sup>-</sup>. IR: 2923, 2854, 1588, 1496, 1323, 1269, 1216, 1097, 1028, 804, 757, 697, 669.

#### 3.3 Barton's two fold coupling: general procedure for the synthesis of esters (13, 14, 15).

A solution of hydrazone **8** (295 mg, 3 eq, 1.2 mmol ) was dissolved in 100 mL of anhydrous THF. Activated manganese oxide (100 mg, 10 eq, 12 mmol) was added to the solution and stirred at RT under  $N_2$ . The reaction was monitored by TLC using DCM as the eluent. The solution was filtered on celite and washing with dry THF to collect all the diaza-intermediate. The filtrate, without any further purification, was quickly added to 0.40 mmol (1 eq) of the corresponding thione **10, 11, 12**, and **13**. The reaction was stirred overnight at room temperature and covered with aluminum foil. The solvent was removed under reduced pressure, and the residue was purified by column chromatography.

**14:** the crude was purified by chromatography column over silica gel (eluent: hexanes/DCM 4 : 6), affording orange solid **14** (75% yield).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.55 (d, 1H,  $J_3 = 8.1$  Hz), 8.43, (d, 1H,  $J_3 = 8.1$  Hz), 8.37 (d, 1H,  $J_3 = 7.7$  Hz), 8.23 (d, 1H,  $J_3 = 7.9$  Hz), 8.19 (d, 1H,  $J_3 = 7.9$  Hz), 7.60 (d, 3H,  $J_3 = 7.3$  Hz), 7.35–7.31 (m, 3H), 7.25–7.18 (m, 4H), 4.05 (s, 3H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 168.9, 141.7, 141.7, 141.6, 140.3, 140.1, 139.6, 139.1, 138.4, 138.3, 130.6, 129.7, 129.6, 129.5, 129.4, 127.6, 127.2, 127.2, 127.1, 127.0, 126.8, 126.5, 126.0, 124.8, 120.2, 120.1, 52.6. MS: (ESI<sup>+</sup>); calculated: *m/z* 381.1; found: *m/z*: 409.1 [M+Na]<sup>+</sup>; IR: 3059, 2924, 2856, 1718, 1604, 1445, 1262, 1190, 1137, 1088, 736.



Figure S17. <sup>1</sup>H-NMR of compound 14.



Figure S18. <sup>13</sup>C-NMR of compound 14.



Figure S19. MS of compound 14.

**15:** the crude was purified by chromatography column over silica gel (eluent: hexanes/DCM 6:4), affording red solid **15** (67% yield).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.52 (d, 1H,  $J_3 = 8.2$  Hz), 8.39 (d, 1H,  $J_3 = 7.9$  Hz), 8.22–8.20 (m, 2H), 8.06 (d, 1H,  $J_3 = 8.8$  Hz), 7.66 (d, 1H,  $J_3 = 7.5$  Hz), 7.31–7.27 (m, 11H including CDCl<sub>3</sub>), 7.23 (q, 2H,  $J_3 = 7.7$  Hz), 7.17–7.15 (m, 8H), 7.07 (t, 4H,  $J_3 = 7.7$  Hz), 6.85–6.81 (m, 2H), 4.06 (s, 3H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 169.1, 149.3, 149.2,147.4, 147.4, 142.7, 142.5, 141.1, 140.2, 139.3, 138.7, 138.6, 135.7, 133.1, 133.0, 129.5, 129.4, 129.2, 128.2, 128.2, 127.9, 127.2, 126.6, 126.0, 125.6, 125.0, 124.5, 123.7, 123.6, 122.1, 122.0, 114.6, 114.6, 52.48. MS: (ESI<sup>-</sup>); calculated: *m/z* 720.28; found: *m/z*: 743.3 [M+Na]<sup>+</sup>,744.3 [M+H+Na]<sup>+</sup>; IR: 3062, 2923, 2855, 2258, 1726, 1589, 1488, 1447, 1329, 1271, 1129, 761, 695.



Figure S20. <sup>1</sup>H-NMR of compound 15.



Figure S21. <sup>13</sup>C-NMR of compound 15.



Figure S22. MS of compound 15.

**16:** the crude was purified by chromatography column over silica gel (eluent: hexanes/DCM 1:1), affording dark solid **16** (50% yield).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.52 (d, 1H,  $J_3 = 7.5$  Hz), 8.40 (d, 1H,  $J_3 = 7.8$  Hz), 8.30 (d, 1H,  $J_3 = 8.3$  Hz), 8.20 (d, 1H,  $J_3 = 8.0$  Hz), 8.16 (d, 1H,  $J_3 = 8.3$  Hz), 7.87 (s, 2H), 7.68 (d, 1H,  $J_3 = 7.5$  Hz), 7.44 (d, 4H,  $J_1 = 8.4$  Hz), 7.35-7.21 (m, 13H including CDCl<sub>3</sub>), 7.14–7.04 (m, 20H), 4.05 (s, 3H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 168.9, 147.9, 147.9, 147.6, 142.0, 141.8, 141.2, 140.2, 139.4, 139.3, 139.2, 139.1, 139.0, 138.0, 137.9, 131.3, 131.3, 130.3, 129.6, 129.5, 129.4, 129.4, 129.1, 127.7, 127.5, 127.4, 127.2, 126.9, 126.9, 126.7, 126.4, 125.9, 125.5, 125.5, 124.8, 123.5, 123.4, 117.6, 117.6, 52.55. MS (Maldi-TOF); DCM/Ditranol; calculated: *m/z* 924.37; found *m/z*: 924.4 [M]<sup>+</sup>, 925.4 [M+H]<sup>+</sup>, 926.4 [M+2H]<sup>+</sup>; IR: 3013, 2948, 2061, 1722, 1592, 1428, 1265, 1190, 1138, 1087, 751.



Figure S23. <sup>1</sup>H-NMR of compound 16.



Figure S24. <sup>13</sup>C-NMR of compound 16.

**17:** the crude was purified by chromatography column over silica gel (eluent: hexanes/DCM 1:1) affording red solid (54% yield).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 8.47 (dd, 1H,  $J_1 = 7.8$  Hz,  $J_2 = 0.9$ Hz), 8.36 (dd, 1H,  $J_1 = 7.8$  Hz,  $J_2 = 0.9$ Hz), 8.22 (t, 2H,  $J_1 = 8.7$  Hz), 8.08 (d, 1H,  $J_1 = 8.7$  Hz), 7.65 (dd, 1H,  $J_1 = 7.7$  Hz,  $J_2 = 1.0$  Hz), 7.30 (td, 1H,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz), 7.26-7.13 (m, 4H), 6.75–6.70 (m, 2H), 4.05 (s, 3H), 3.92 (s, 3H), 3.91(s, 3H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 169.0, 161.3, 161.3, 143.3, 143.2, 141.3, 140.2, 139.2, 138.8, 138.7, 135.6, 132.2, 132.1, 129.5, 129.2, 128.5, 128.3, 128.3, 127.2, 126.6, 125.9, 125.6, 124.6, 113.1, 105.3, 55.7, 52.5. MS: (ESI<sup>+</sup>); calculated: *m/z* 446.15; found: *m/z*: 469.1[M+Na]<sup>+</sup>; IR: 2927, 2844, 1722, 1607, 1489, 1461, 1433, 1295, 1239, 1202, 1167, 1131, 1031, 953, 765.



Figure S25. <sup>1</sup>H-NMR of compound 17.



Figure S26. MS of compound 17.

### 3.4 Hydrolysis of 9'9-fluorenylidene ester derivatives

**BF1**: **14** (0.18 mmol) was dissolved in CH<sub>3</sub>CN (30 mL) and treated with LiOH (excess, 86.4 mg, 3.6 mmol) dissolved in water (10 mL). The reaction was stirred at RT for 5–6 hrs and monitored by TLC (eluent mixture: DCM : hexanes; 1 : 1). Acetonitrile was removed under reduced pressure and the crude was extracted with AcOEt ( $3 \times 25$  mL) and a 10% HCl water solution. The combined organic layers were dried over MgSO<sub>4</sub> and concentrated to dryness under reduced pressure affording orange solid **BF1** which was recrystallized from hot cyclohexane (75% yield).

<sup>1</sup>H-NMR (500 MHz, *d6*-Acetone):  $\delta$  ppm 8.60 (dd, 1H,  $J_1 = 7.9$  Hz,  $J_2 = 0.9$  Hz), 8.46 (d, 1H,  $J_1 = 7.5$  Hz), 8.42 (d, 1H,  $J_1 = 7.7$  Hz), 8.40 (d, 1H,  $J_1 = 8.1$  Hz), 8.29 (d, 1H,  $J_1 = 7.9$  Hz), 7.86 (d, 2H,  $J_1 = 7.5$  Hz), 7.82 (d, 2H,  $J_1 = 7.6$  Hz,  $J_2 = 0.9$  Hz), 7.42–7.36 (m, 3H), 7.34–7.26 (m, 3H). <sup>13</sup>C-NMR (125 MHz, *d6*-Acetone):  $\delta$  ppm 141.98, 139.9, 139.03, 131.10, 129.73, 127.94, 127.58, 127.36, 125.43, 120.61. MS: (ESF); calculated: *m/z* 372.12; found: *m/z*: 370.9 [M-H]<sup>-</sup>; IR: 3067, 2924, 2857, 1697, 1438, 1342, 1279, 1151, 934, 764, 726.





Figure S28. <sup>13</sup>C-NMR of compound BF1.



Figure S29. MS of compound BF1.

### General procedure for BF3a, BF3b, and BF3d

The corresponding ester derivatives **15**, **16**, and **17** (0.20 mmol) were dissolved in 40 mL of a CH<sub>3</sub>CN / methanol (1:1 v/v) solvent mixture and treated with an excess of NaOH (20–25 mL of a 3M water solution). The reaction was gently heated at 40–50 °C until no more ester was observed by TLC. Reaction time varies from 5 hrs to 12 hrs. Work up: acetonitrile and methanol were removed under reduced pressure and the crude was extracted with DCM ( $3 \times 30$  ml) and a 10% HCl solution. The organic layers were gathered, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The solid was washed with cyclohexane or pentane, yielding corresponding acids BF3a, BF3b, and BF3d.

BF3a: A dark violet solid was obtained by washing with hot pentane (yield 90%).

<sup>1</sup>H-NMR (500 MHz, [D<sub>6</sub>]DMSO): δ ppm 8.33 (d, 1H, *J* = 8.0 Hz), 8.25 (m, 2H), 8.12 (d, 1H, *J* = 8 Hz), 8.06 (d, 1H, *J* = 8 Hz), 7.55 (d, 1H, *J* = 8 Hz), 7.40–6.90 (m, 25H), 6.75 (m, 2H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ ppm 170.1, 149.5, 146.9,146.4, 142.2, 140.05, 139.2, 138.7, 138.4, 136.9, 135.07, 132.3, 130.01, 129.22, 128.78, 128.42, 128.19, 127.6, 126.6, 126.16, 125.76, 125.25, 124.42, 121.60, 113.7.MS: (ESI<sup>-</sup>); calculated: *m*/*z* 706.26; found: *m*/*z*: 705.3 [M-H]<sup>+</sup>, 706.0 [M]<sup>+</sup>; HR MS: (ESI<sup>+</sup>); calculated: *m*/*z* 706.2620; found: *m*/*z*: 706.2648; IR: broad 3600-3400, 3030, 2924, 2857, 1694, 1589, 1487, 1320, 1272, 754, 695.



Figure S30. <sup>1</sup>H-NMR of compound BF3a.



Figure S31. <sup>13</sup>C-NMR of compound BF3a.



Figure S32. MS of compound BF3a.



Figure S33. HR MS of compound BF3a.

BF3b: A dark solid was obtained by washing with hot pentane (yield 42%).

<sup>1</sup>H-NMR (500 MHz, [D<sub>6</sub>]DMSO): δ ppm 8.40–8.10 (m, 5H), 7.6–6.9 (m, 32 H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ ppm 147.6, 147.3, 131.4, 130.1, 128.3, 124.85, 123.9, 123.26. MS: (ESI<sup>-</sup>); calculated: *m/z* 909.08; found: *m/z*: 909.1 [M]<sup>+</sup>; HR MS: (ESI<sup>+</sup>); calculated: *m/z* 908.3403; found: *m/z*: 908.3403 [M+H]<sup>+</sup>; IR: broad 3400, 2924, 2856, 1714, 1650, 1497, 1280, 752, 696.



Figure S34. <sup>1</sup>H-NMR of compound BF3b.



Figure S35. <sup>13</sup>C-NMR of compound BF3b.



Figure S36. MS of compound BF3b.



Figure S37. HR MS of compound BF3b.

BF3c: A red solid was obtained by washing with hot cyclohexane (yield 95%).

<sup>1</sup>H-NMR (500 MHz,  $d_6$ -Acetone):  $\delta$  ppm 8.53 (d, 1H,  $J_I = 7.7$  Hz), 8.39 (d, 1H,  $J_I = 7.7$  Hz), 8.25 (d, 1H,  $J_I = 8.8$  Hz), 8.15 (d, 1H,  $J_I = 8.8$  Hz), 7.78. (d, 1H,  $J_I = 7.7$  Hz), 7.46 (d, 2H,  $J_I = 2.7$  Hz), 7.39–7.28 (m, 4H), 6.86–6.83 (m, 2H), 3.95 (s, 6H); <sup>13</sup>C-NMR (125 MHz,  $d_6$ -Acetone):  $\delta$  ppm 169.6, 162.7, 162.6, 144.4, 144.3, 142.2, 140.7, 139.8, 139.7, 139.2, 135.8, 132.4, 132.3, 130.5, 129.7, 129.2, 129.0, 128.9, 128.2, 128.1, 126.7, 126.5, 125.8, 114.3, 106.4, 106.4, 56.1. MS: (ESI<sup>-</sup>); calculated: *m/z* 432.14; found: *m/z*: 430.9 [M-H]<sup>+</sup>, 431.9 [M]<sup>+</sup>; HR MS: (ESI<sup>-</sup>); calculated: *m/z* 432.1362; found: *m/z*: 433.1417 [M+H]<sup>+</sup>; IR: 3416, 2925, 2854, 1604, 1461, 1401, 1300, 1236, 1030, 765.



Figure S38. <sup>1</sup>H-NMR of compound BF3c.



Figure S39. <sup>13</sup>C-NMR of compound BF3c.



Figure S40. MS of compound BF3c.



Figure S41. HR MS of compound BF3c.

# **Theoretical calculations**



**Figure S42.** B3LYP/cc-pVDZ-optimized geometries calculated for **F1**, **F2a**, **F3b**, **BF1** and **BF3c** in dichloromethane. The rotational angle between the fluorene unit and the acceptor cyanoacrylic acid group in **F1**, **F2a** and **F3b** and between the two fluorene units in **BF1** and **BF3c** are indicated.



**Figure S43.** Energy diagram showing the isovalue contours (±0.03 a.u.) computed for the HOMOs and LUMOs of the representative dyes **F3a** and **BF3a** at the B3LYP/cc-pVDZ level.



**Figure S44.** Representation of the electron spin densities calculated for the optimized cationic species at the B3LYP/cc-pVDZ level in dichloromethane.

**Table S1.** Lowest-energy singlet excited states calculated for all the investigated dyes using the TD-DFT approach and dimethylformamide as solvent. Vertical excitation energies (E), oscillator strengths (f), dominant monoexcitations with contributions (within parentheses) greater than 40%, and description of the excited state are summarized. H and L denote HOMO and LUMO, respectively.

Dye	State	E(eV)	E (nm)	f	Monoexcitations	%	Description
F1	$\mathbf{S}_1$	2.4298	510	0.0011	H→L	99	СТ
	$S_2$	3.4695	357	0.2864	H-1→L	56	Core+Acceptor
					H-2→L	40	СТ
	$S_3$	3.4942	355	0.2460	H-2→L	54	СТ
					H-1→L	41	Core+Acceptor
	$S_6$	4.7593	261	0.7128	$H \rightarrow L+1$	88	Core
F2a	$\mathbf{S}_1$	1.3353	929	0.0358	H→L	99	СТ
	$S_2$	1.9617	632	0.0010	H-1→L	100	СТ
	$S_4$	3.1407	395	0.6063	$H \rightarrow L+1$	86	Donor
	$S_6$	3.3876	366	0.3764	H-5→L	71	СТ
F3a	$\mathbf{S}_1$	1.9131	648	0.2640	H→L	97	СТ
	$S_2$	2.3720	523	0.5242	H-1→L	99	СТ
	$S_3$	2.8377	437	0.1263	H-2→L	95	СТ
	$S_4$	3.4358	361	0.1901	$H \rightarrow L+1$	87	Core+Donor
	$S_5$	3.5959	345	0.1260	H-3→L	82	Core+Acceptor
F3b	$\mathbf{S}_1$	1.6024	774	0.6920	H→L	97	СТ
	$\mathbf{S}_2$	1.8065	686	0.4811	H-1→L	100	СТ
	$\mathbf{S}_3$	2.3299	532	0.0019	H-2→L	88	CT
	$\mathbf{S}_4$	2.8114	441	0.4643	H-3→L	98	Core+Acceptor
	$S_5$	2.8788	431	0.5799	H-4→L	80	СТ
	$\mathbf{S}_6$	3.0389	408	0.6747	$H \rightarrow L+1$	95	Donor
	$S_7$	3.0859	402	0.4811	H-1→L+1	83	Donor
BF1	$\mathbf{S}_1$	2.4411	508	0.5841	H→L	100	Core
	$S_4$	3.2820	378	0.0342	$H \rightarrow L+1$	98	CT
	$S_5$	3.4961	355	0.0301	H-3→L	89	Core
	$S_6$	3.5928	345	0.0322	H-4→L	76	Core
BF3a	$\mathbf{S}_1$	1.9397	639	0.1989	H-1→L	98	СТ
	$S_2$	1.9915	623	0.8444	H→L	100	Core
	$S_5$	2.8564	434	0.0715	H-4→L	89	СТ
	$S_6$	2.8929	429	0.0789	H-2→L	85	Core
	<b>S</b> <sub>9</sub>	3.4297	362	0.1644	H-1→L+2	90	Donor
BF3b	$\mathbf{S}_1$	1.7215	720	0.5113	H-1→L	97	СТ
	$S_2$	1.7784	697	0.8792	H→L	100	СТ
	$S_3$	2.3332	531	0.3243	H-2→L	99	Core
	$S_7$	2.9242	424	1.2990	$H\rightarrow L+2$	77	Donor
	$\mathbf{S}_{10}$	3.0581	405	0.5816	H-1→L+2	88	Donor
BF3c	$\mathbf{S}_1$	2.3526	527	0.7128	H→L	100	Core
	$S_4$	3.0643	405	0.0342	$H \rightarrow L+1$	98	СТ
	$S_5$	3.3389	371	0.0733	H-3→L	92	Core

**Table S2.** Lowest-energy doublet excited states calculated for the cationic species of representative dyes using the TD-DFT approach. Vertical excitation energies (E), oscillator strengths (f), dominant monoexcitations with contributions (within parentheses) greater than 40%, and description of the excited state are summarized. H and L denote HOMO and LUMO, respectively.

Cation	State	E(eV)	E (nm)	f	Monoexcitations	%	Description
F2a	$\mathbf{D}_1$	0.9877	1255	0.487	H-1→SOMO	94	Donor
	$D_2$	1.4480	856	0.1327	SOMO→L	92	СТ
	$D_9$	2.2179	559	0.0116	H-6→SOMO	50	Donor
F3a	$\mathbf{D}_1$	0.3793	3269	0.0835	H-1→SOMO	98*	Donor
	$D_2$	1.2310	1007	0.0234	H-2→SOMO	94	Donor
	$D_3$	1.5924	779	0.1314	H-3→SOMO	91	Donor
	$D_4$	1.6050	773	0.015	H-1→L	59	СТ
	$D_5$	1.8024	688	0.0042	H-4→SOMO	97	Donor
	$D_6$	1.8328	676	0.014	H-5→SOMO	98	Donor
	$D_7$	1.9492	636	0.0099	H-6→SOMO	93	Donor
	D <sub>13</sub>	2.2058	562	0.1298	SOMO→L	85	Donor
F3b	$\mathbf{D}_1$	0.3112	3984	0.2207	H-1→SOMO	99*	Donor
	$D_2$	1.0220	1213	0.1204	H-2→SOMO	94	Donor
	$D_3$	1.1725	1057	0.2727	H-3→SOMO	98	Donor
	$D_4$	1.4159	876	0.0098	H-1→L	61	СТ
	$D_5$	1.4996	827	0.0557	H-4→SOMO	88	Donor
	$D_6$	1.7759	698	0.2864	SOMO→L	65	СТ
	D <sub>11</sub>	2.0456	606	0.2581	H-7→SOMO	40	Donor
BF3a	$\mathbf{D}_1$	0.5362	2312	0.0639	H-1→SOMO	94	СТ
	$D_4$	1.4711	843	0.0234	H-1→L	64	СТ
	$D_5$	1.6480	752	0.0998	H-4→SOMO	61	СТ
	$D_6$	1.6530	750	0.4312	SOMO→L	40	Core
	$\mathbf{D}_7$	1.8555	668	0.2588	H-1→L	55	СТ
	$D_8$	2.0833	595	0.0224	H-7→SOMO	47	Donor
BF3b	$D_1$	0.3218	3853	0.2014	H-1→SOMO	98*	Donor
	$D_2$	0.7906	1568	0.1911	H-2→SOMO	87	Donor
	$D_3$	1.1308	1096	0.1569	H-3→SOMO	94	Donor
	$D_6$	1.3178	941	0.4011	SOMO→L	42	СТ
	$D_7$	1.5648	792	0.6233	H-1→L	57	СТ
	$D_{10}$	1.8069	686	0.1614	H-5→SOMO	45	Donor
	$D_{19}$	2.2500	551	0.1745	H-2→L	44	Core

## **Photophysical measurements**



**Figure S45.** Differential absorption spectra obtained upon femtosecond flash photolysis ( $\lambda_{exc} = 480$  nm) of 3 µm-thick TiO<sub>2</sub> films sensitized with **BF3a** (top) and **BF3b** (bottom) with several time delays at room temperature showing the spectral characteristics of the oxidized states generated after charge injection into TiO<sub>2</sub>.



**Figure S46.** Differential absorption spectra obtained upon femtosecond flash photolysis ( $\lambda_{exc} = 480$  nm) of 3 µm-thick TiO<sub>2</sub> films sensitized with **F2a** (top), **F3b** (middle) and **F3a** (bottom) with several time delays at room temperature showing the spectral characteristics of the oxidized states generated after charge injection into TiO<sub>2</sub>.

#### **Photovoltaic measurements**



**Figure S47.** Photocurrent density-voltage characteristic curves of devices sensitized with **F3a**, **F3b**, **BF3a**, **BF3b** and **BF3c** measured under AM 1.5G simulated sunlight illumination (100 mW cm<sup>-2</sup>) and in dark with different dyes.

**Table S3**. Detailed photovoltaic parameters of devices measured under AM 1.5G simulated sunlight illumination (100 mW cm<sup>-2</sup>).

Dye	J <sub>sc</sub> / mA cm <sup>-2</sup>	V <sub>oc</sub> / mV	FF	PCE / %
F3a	4.802	577	0.767	2.11
F3b	4.777	540	0.758	1.94
BF3a	1.702	530	0.738	0.66
BF3b	6.840	629	0.772	3.29
BF3c	1.514	584	0.766	0.67

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