

## Supporting Information

### An Organic D- $\pi$ -A Dye for Record Efficiency Solid-State Sensitized Heterojunction Solar Cells

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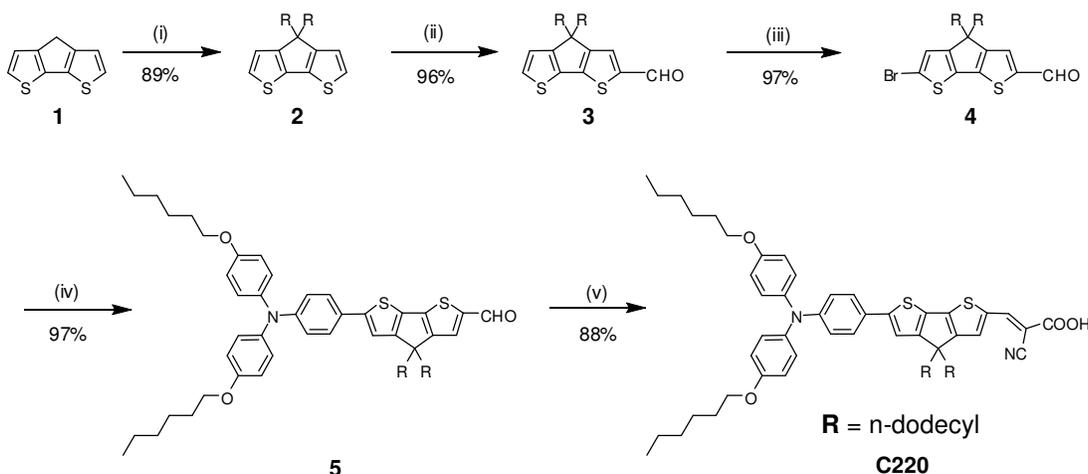
#### I) Synthesis of C220

#### II) Emission measurements

## I) Synthesis of C220

All solvents and reagents, unless otherwise stated, were of puriss quality and used as received. Phosphoryl trichloride, *N*-bromosuccinimide, Pd(OAc)<sub>2</sub>, 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos), 2-cyanoacetic acid, and piperidine was purchased from Aldrich, The synthesis of 4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**1**) and 4,4,5,5-tetramethyl-2-{4-[*N,N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolanewere described in our previous paper.<sup>17</sup>

### Synthetic Route of the C220 Dye



Reaction conditions: (i) 2.0 eq. 1-bromododecane, 3.0 eq. *t*-BuOK, THF, RT, overnight; (ii) 1.2 eq. POCl<sub>3</sub>, 2.8 eq. DMF, 1,2-dichloroethane, 0°C, 4 h; (iii) 1.1 eq. NBS, THF, 0 °C , RT, 5 h; (iv) 1.2 eq. 4,4,5,5-tetramethyl-2-{4-[*N,N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane, 2% Pd(OAc)<sub>2</sub>, 2% SPhos, 5.0 eq. K<sub>3</sub>PO<sub>4</sub>, dioxane/H<sub>2</sub>O (5/1, *v/v*), 40°C, 2h; (v) 3.0 eq. cyanoacetic acid, 7.0 eq. piperidine, CHCl<sub>3</sub>, reflux, 18 h.

### Preparation of 4,4-didodecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**2**)

To a solution of **1** (0.400 g, 2.24 mmol) and 1-bromododecane (1.118 g, 4.49 mmol) in dry tetrahydrofuran (20 mL) was added potassium *tert*-butoxide (0.755 g, 6.73 mmol) under argon. The

reaction mixture was stirred overnight at room temperature and then water (100 mL) added. The crude product was extracted into diethyl ether, and the organic layer was washed with saturated sodium chloride aqueous solution and water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether 60–90 °C) on silica gel to yield a yellowish oil (1.020 g, 89% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.14 (d, *J*=4.8 Hz, 2H), 6.92 (d, *J*=4.8 Hz, 2H), 1.81 (m, 4H), 1.25 (m, 24H), 1.12 (m, 12H), 0.93 (m, 4H), 0.87 (t, *J*=6.9 Hz, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 158.15, 136.44, 124.39, 121.65, 53.26, 37.73, 31.92, 30.03, 29.62, 29.59, 29.39, 29.34, 24.53, 22.68, 14.11. MS (ESI) *m/z* calcd. for (C<sub>33</sub>H<sub>54</sub>S<sub>2</sub>): 514.37. Found: 515.66 ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>33</sub>H<sub>54</sub>S<sub>2</sub>: C, 76.97; H, 10.57%. Found: C, 77.01; H, 10.52%.

### **Preparation of 4,4-didodecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (3)**

To a cold solution of **2** (0.500 g, 0.97 mmol) and *N,N*-dimethylformide (0.199 g, 2.72 mmol) in 1,2-dichloroethane (10 mL) at 0 °C was added phosphoryl trichloride (0.176 g, 1.15 mmol). The reaction solution was stirred at the same temperature for 4 h and then saturated sodium acetate aqueous solution (20 mL) added. The mixture was further stirred at room temperature for 2 h. The crude product was extracted into dichloromethane, and the organic layer was washed with brine and water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/30, *v/v*) on silica gel to yield a yellowish oil (0.509 g, 96% yield). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 9.83 (s, 1H), 7.99 (s, 1H), 7.70 (d, *J*=4.8 Hz, 1H), 7.19 (d, *J*=4.8 Hz, 1H), 1.88 (m, 4H), 1.22 (m, 24H), 1.09 (m, 12H), 0.86 (m, 4H), 0.85 (t, *J*=6.9 Hz, 6H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ: 182.94, 162.15, 157.81, 145.95, 142.63, 134.48, 131.22, 130.41, 121.92, 53.06, 36.34, 30.86, 28.76, 28.54, 28.53, 28.43, 28.36, 28.22, 28.18, 23.63, 21.63, 13.44. MS (ESI) *m/z* calcd. for (C<sub>34</sub>H<sub>54</sub>OS<sub>2</sub>): 542.36. Found: 543.72 ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>34</sub>H<sub>54</sub>OS<sub>2</sub>: C, 75.22; H, 10.03%. Found: C, 75.18; H, 10.08%.

### **Preparation of 6-bromo-4,4-didodecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (4)**

To a cold solution of **3** (0.450 g, 0.83 mmol) in tetrahydrofuran (25 mL) was added *N*-bromosuccinimide (0.162 g, 0.91 mmol) at 0 °C under argon. The reaction mixture was warmed to room temperature and stirred for 5 h and then water (25 mL) added. The crude product was extracted into dichloromethane, and the organic layer was dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography(ethyl acetate/petroleum ether 60–90 °C, 1/30, *v/v*) on silica gel to yield a yellowish solid (0.500 g, 97% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 9.83 (s, 1H), 7.55 (s, 1H), 7.01 (s, 1H), 1.84 (m, 4H), 1.23 (m, 24H), 1.14 (m, 12H), 0.93 (m, 4H), 0.87 (t, *J*=6.9 Hz, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 182.53, 161.07, 157.16, 146.74, 143.53, 135.94, 129.82, 124.92, 116.18, 54.60, 37.50, 31.89, 29.87, 29.60, 29.54, 29.31, 24.53, 22.66, 14.09. MS (ESI)*m/z* calcd. for(C<sub>34</sub>H<sub>53</sub>BrOS<sub>2</sub>): 620.27. Found: 621.53 ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>34</sub>H<sub>53</sub>BrOS<sub>2</sub>: C, 65.67; H, 8.59%. Found: C, 65.75; H, 8.50%.

**Preparation of 6-{4-[*N,N*-bis(4-hexyloxyphenyl)amino]phenyl}-4,4-didodecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (**5**)**

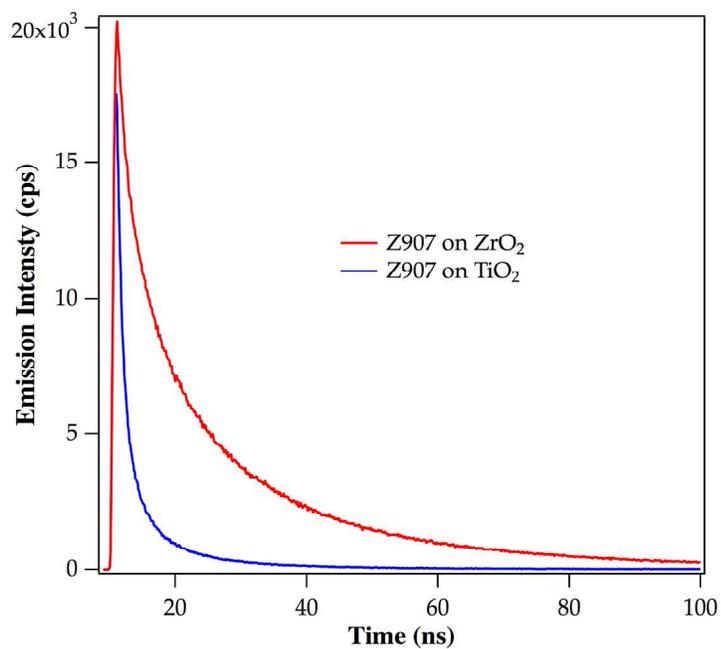
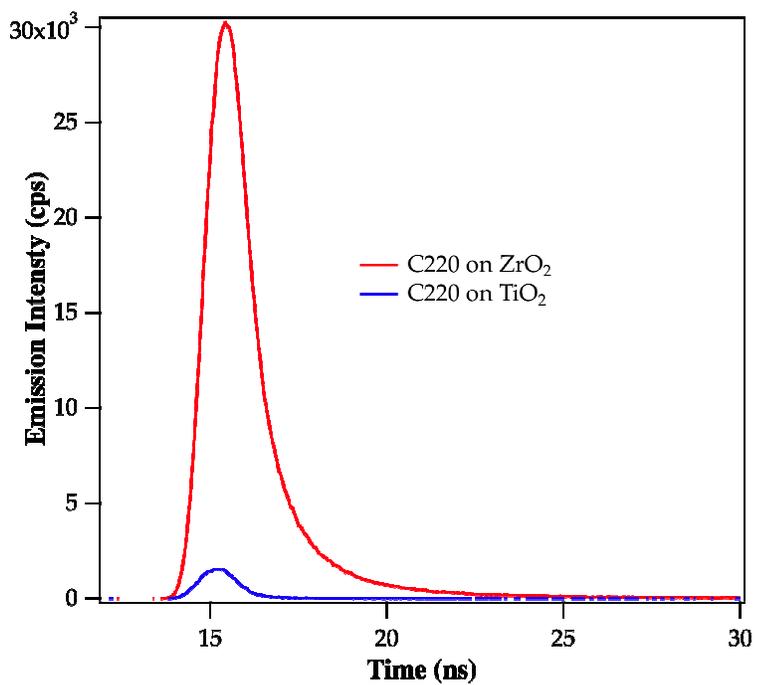
To a suspended solution of **4** (0.870 g, 1.40 mmol), Pd(OAc)<sub>2</sub> (0.006 g, 0.03 mmol), SPhos (0.011 g, 0.03 mmol) and K<sub>3</sub>PO<sub>4</sub> (1.480 g, 7.00 mmol) in dioxane/H<sub>2</sub>O (5/1, *v/v*)(24 mL) was added 4,4,5,5-tetramethyl-2-{4-[*N,N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane (0.960 g, 1.68 mmol). The reaction mixture was reacted at 40 °C for 2 h under argon and then water (50 mL) added. The crude compound was extracted into ethyl acetate, washed with brine and water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography(ethyl acetate/petroleum ether 60–90 °C, 1/50, *v/v*) on silica gel to yield a viscous orange oil (1.340 g, 97% yield). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>)δ: 9.80 (s, 1H), 7.96 (s, 1H), 7.51 (d, *J*=8.8 Hz, 2H), 7.46 (s, 1H), 7.03 (d, *J*=8.8 Hz, 4H), 6.92 (d, *J*=8.8 Hz, 4H), 6.77 (d, *J*=8.8 Hz, 2H), 3.94 (t, *J*=6.4 Hz, 4H), 1.84 (m, 4H), 1.70 (m, 4H), 1.42 (m, 4H), 1.31 (m, 8H), 1.14 (m, 36H), 0.88 (m, 10H), 0.83 (t, *J*=7.2 Hz, 6H). <sup>13</sup>C NMR(150 MHz, CDCl<sub>3</sub>) δ: 182.28, 163.65, 157.16, 155.80, 150.06, 148.86, 148.44, 142.58, 140.16, 133.25, 129.88, 126.80, 126.22, 126.14, 120.16, 116.10, 115.34, 68.28, 54.03, 37.74,

31.89, 31.59, 29.95, 29.60, 29.57, 29.35, 29.31, 25.75, 24.57, 22.66, 22.60, 14.09, 14.02. MS (ESI) $m/z$  calcd. for (C<sub>64</sub>H<sub>91</sub>NO<sub>3</sub>S<sub>2</sub>): 985.64. Found: 987.02 ([M+H]<sup>+</sup>). Anal. Calcd. for C<sub>64</sub>H<sub>91</sub>NO<sub>3</sub>S<sub>2</sub>: C, 77.92; H, 9.30; N, 1.42%. Found: C, 77.85; H, 9.40; N, 1.39%.

**Preparation of 2-cyano-3-{6-[4-[N,N-bis(4-hexyloxyphenyl)amino]phenyl]-4,4-didodecyl-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-yl}acrylic acid (C220)**

To a stirred solution of **5** (0.650 g, 0.66 mmol) and cyanoacetic acid (0.168 g, 1.98 mmol) in chloroform (35 mL) was added piperidine (0.392 g, 4.61 mmol). The reaction mixture was refluxed under argon for 18 h and then acidified with hydrochloric acid aqueous solution (2 M, 35 mL). The crude product was extracted into chloroform, washed with water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by flash chromatography with chloroform and methanol/chloroform (1/50, *v/v*) in turn as the eluent to yield a purple powder (0.610 g, 88%). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 13.34 (s, 1H), 8.40 (s, 1H), 7.92 (s, 1H), 7.51 (d, *J*=9.0 Hz, 2H), 7.47 (s, 1H), 7.03 (d, *J*=8.8 Hz, 4H), 6.91 (d, *J*=8.8 Hz, 4H), 6.77 (d, *J*=9.0 Hz, 2H), 3.94 (t, *J*=6.6 Hz, 4H), 1.88 (m, 4H), 1.70 (m, 4H), 1.41 (m, 4H), 1.31 (m, 8H), 1.14 (m, 36H), 0.88 (m, 10H), 0.83 (t, *J*=7.2 Hz, 6H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 168.82, 165.25, 158.23, 155.94, 152.35, 152.12, 149.23, 148.02, 140.00, 135.52, 133.28, 131.48, 126.93, 126.41, 125.73, 119.91, 117.02, 116.10, 115.38, 91.26, 68.30, 54.16, 37.80, 31.90, 31.60, 29.90, 29.62, 29.57, 29.35, 29.32, 25.76, 24.57, 22.67, 22.61, 14.10, 14.03. HR-MS (ESI)  $m/z$  calcd. for (C<sub>67</sub>H<sub>92</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>): 1052.64985. Found: 1051.64205 ([M-H]<sup>-</sup>). Anal. Calcd. for C<sub>67</sub>H<sub>92</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C, 76.38; H, 8.80; N, 2.66%. Found: C, 76.30; H, 8.90; N, 2.55%.

## II) Emission measurements



**Figure S1.** Emission decay traces of **C220** and **Z907** adsorbed on ZrO<sub>2</sub> or TiO<sub>2</sub> in presence of spiro-OMeTAD. Excitation wavelength: 460 nm. Photoluminescence was measured under ambient conditions

at 740 nm for **Z907** and at 670 nm for **C220**.

**Table S1.** Electron injection efficiency  $\eta_{inj}$  of **C220** and **Z907** determined by emission measurements, involving the determination of a) the halftime (after excitation with a 460 nm laser diode), b) the area under the emission decay curves (after excitation with a 460 nm laser diode) and c) the area under the emission profiles.

<b>Sensitizer</b>	in presence of Spiro-MeOTAD		$\eta_{inj}/\%$ (lower limit)
	on ZrO <sub>2</sub>	on TiO <sub>2</sub>	
<b>a) Halftime [ns]</b>			
<b>C220</b>	1.30	$\leq 0.11$	<b>92</b>
<b>Z907</b>	4.26	$\leq 0.67$	<b>85</b>
<b>b) Intensity decay</b>			
<b>C220</b>	1	0.03	<b>97</b>
<b>Z907</b>	1	0.12	<b>88</b>
<b>c) Intensity Steady State</b>			
<b>C220</b>	$5.10 \times 10^7$	$1.62 \times 10^6$	<b>97</b>

