Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Proposal of fluorescence lifetime in chloroform as a convenient parameter for electron injection of efficient indoline dyes in dye-sensitized solar cell

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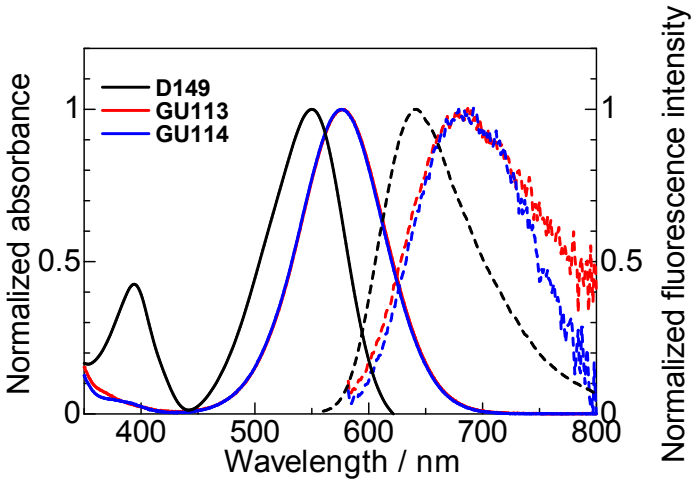

Figure S1. Normalized UV-vis absorption and fluorescence spectra of **GU113**, **GU114**, and **D149** measured on 1.0 x 10^{-5} mol dm^{-3} at 25°C. Solid and dotted lines represent UV-vis absorption and fluorescence spectra,

respectively.

*Synthesis of pyridone ethyl acetates **4***

To ethanol (2 mL) were added glycine hydrochloric acid ethyl ester **3** (2.80 g, 20.0 mmol) and triethylamine (3.00 g, 29.7 mmol) and stirred for 5 min at room temperature, Then, to the mixture were added ethyl alkanoylacetate **1** (20.0 mmol), ethyl cyanoacetate **2** (2.22 g, 20.0 mmol), and piperidine (0.522 g, 6.13 mmol) and refluxed for 9 h. After the reaction was completed, the mixture was concentrated and water (4 mL) was added. This mixture was added to 10% aqueous hydrochloric acid (30 mL) at 0°C. In the case of **4a**, the resulting viscous compound was recrystallized from ethyl acetate. In the case of **4b**, the resulting viscous compound, obtained in a 10% yield, was used to next step without further purification.

4a: Yield 8.5%; mp 178-180°C; IR (KBr) ν = 1223, 1497, 1616, 1740, 2218; ^{1}H NMR (DMSO-d_6) δ = 1.20 (t, J = 7.1 Hz, 3H), 2.23 (s, 3H), 4.13 (q, J = 7.1 Hz, 2H), 4.66 (s, 3H), 5.59 (s, 1H); ^{13}C NMR (DMSO-d_6) δ = 14.0, 20.7, 39.9, 61.1, 86.6, 92.9, 117.7, 158.4, 160.6, 160.7, 167.8; FABMS (NBA) *m/z* 237 (MH^+); Anal. Found: 55.90; H, 5.15; N, 11.94%. Calcd for $C_{11}H_{12}N_2O_4$: C, 55.93, H, 5.12; N, 11.86%.

*Synthesis of pyridine acetic acids **5***

Compound **4** (400 mg, 1.69 mmol) was refluxed in acetic acid-conc. hydrochloric acid mixed solvent (2:1, 3 mL) for 3 h. After the reaction was completed, the resulting powder was washed with cold water and dried.

5a: Yield 44%; mp 195-197°C; IR (KBr) ν = 1535, 1670, 2222, 2970; ^{1}H NMR ($CDCl_3$) δ = 2.23 (s, 3H), 4.58 (s, 2H), 6.00 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 20.6, 41.6, 86.9, 92.5, 117.6, 158.3, 160.4, 160.5, 169.0; FABMS (NBA) *m/z* 209 (MH^+); Anal. Found: 52.05; H, 4.03; N, 13.24%. Calcd for $C_9H_8N_2O_4$: C, 51.93, H, 3.87; N, 13.46%.

5b: Yield 50.9%; mp 203-205°C; IR (KBr) ν = 1539, 1754, 2222, 2936; ^{1}H NMR (DMSO-d_6) δ = 0.91 (t, J = 7.2 Hz, 3H), 1.34 (quint, J = 7.2 Hz, 2H), 1.54 (q, J = 7.2 Hz, 2H), 2.51 (t, J = 7.2 Hz, 2H), 4.58 (s, 2H), 5.58 (s, 1H); ^{13}C NMR ((DMSO-d_6) δ = 11.4, 19.6, 28.7, 31.7, 39.5, 84.2, 89.5, 115.4, 158.5, 158.6, 160.1, 166.9; FABMS (NBA) *m/z* 251 (MH^+); Anal. Found: C, 57.84; H, 5.69; N, 11.33%. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.59, H, 5.64; N, 11.19%.

*Synthesis of **GU113** and **GU114***

To absolute ethanol (10 mL) were added **5** (0.70 mmol) and **6** (400 mg, 0.86 mmol) and stirred at room temperature for 1 day. After the reaction was completed, the solvent was removed *in vacuo*. The product was dissolved in dichloromethane (6 mL) and poured into hexane (100 mL). The resulting precipitate was collected by centrifugal separation and dried *in vacuo*.

GU113: Yield 82.2%; mp 206-208°C; IR (KBr) ν = 1454, 1651, 2222; ^{1}H NMR (DMSO-d_6) δ = 0.48-0.57 (m, 4H), 0.62 (t, J = 7.2 Hz, 3H), 0.67 (t, J = 7.2 Hz, 3H), 0.99-1.08 (m, 4H), 1.39-1.43 (m, 1H), 1.66-1.80 (m, 4H), 1.97-2.12 (m, 5H), 2.61 (s, 3H), 3.88 (t, J = 8.6 Hz, 1H), 4.54 (s, 2H), 5.32 (t, J = 8.6 Hz, 1H), 6.80 (d, J = 8.6 Hz, 1H), 7.31-7.36 (m, 2H), 7.43-7.46 (m, 2H), 7.55 (s, 1H), 7.82 (d, J = 6.9 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.93 (s, 1H), 8.11 (d, J = 8.6 Hz, 1H), 8.37 (s, 1H); Exact FABMS (NBA) *m/z* (MH^+): 654.3342. Calcd for $C_{42}H_{45}N_3O_4$: 654.3332.

GU114: Yield 88.1%; mp 206-208°C; IR (KBr) ν = 1442, 1651, 2218; ^{1}H NMR (DMSO-d_6) δ = 0.48-0.58 (m, 4H), 0.62 (t, J = 7.2 Hz, 3H), 0.67 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H), 0.98-1.08 (m, 4H), 1.38-1.48 (m, 3H), 1.57 (quint, J = 7.3 Hz, 2H), 1.65-1.80 (m, 4H), 1.97-2.12 (m, 5H), 2.66-3.08 (m, 2H), 3.89 (t, J = 8.9 Hz, 1H), 4.53 (s, 2H), 5.32 (t, J = 8.9 Hz, 1H), 6.80 (d, J = 8.6 Hz, 1H), 7.31-7.36 (m, 2H), 7.43-7.46 (m, 2H), 7.56 (s, 1H), 7.82 (d, J = 6.8 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.91 (s, 1H), 8.11 (d, J = 8.6 Hz, 1H), 8.40 (s, 1H); Exact FABMS (NBA) *m/z* (MH^+): 696.3831.

Calcd for $C_{45}H_{51}N_3O_4$: 696.3801.