

# Impact of Fluorine-Induced Effects on Co-Sensitization Systems in Dye-Sensitized Solar Cells

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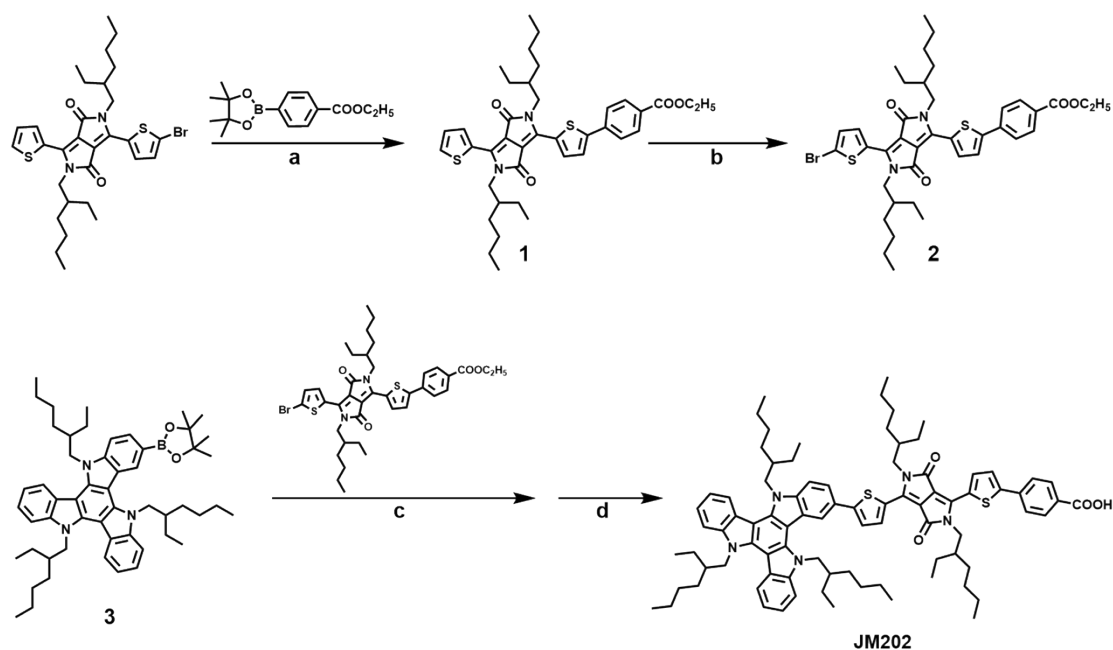
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## 1. General methods for synthesis

All the reactions were performed under an argon atmosphere unless mentioned. THF, DMF, and toluene were dried using solvent purification columns (Glass contour) under an argon atmosphere.  $^1\text{H}$  NMR spectroscopy measurements were recorded on a Varian INOVA 400NMR or 500NMR apparatus. Chemical shifts were calibrated against TMS as an internal standard. Mass spectra (MALDI-TOF MS) were measured on a Micromass GCT-MS spectrometer. The UV-vis data were recorded by Agilent 8453 spectrophotometer, the path length through the sample is 1 cm.

### Synthetic route to JM102

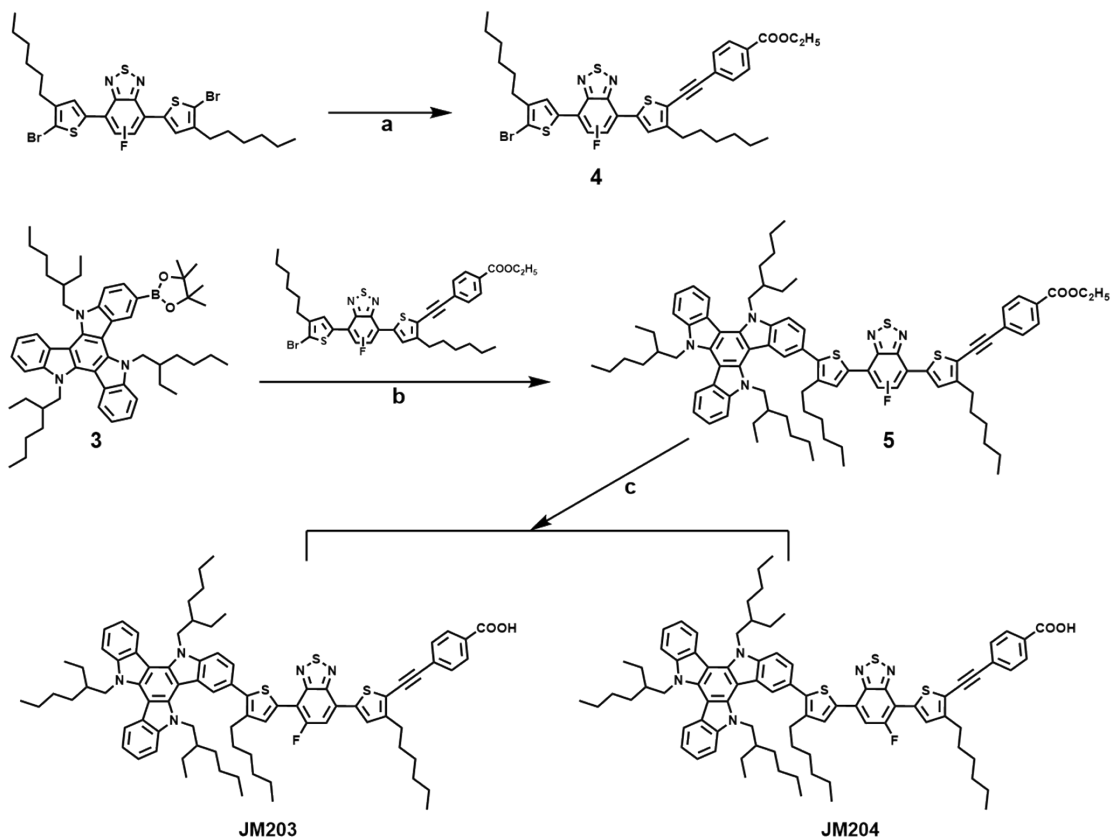


(a) (c)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{K}_2\text{CO}_3$ , 1,4-dioxane,  $\text{H}_2\text{O}$ , reflux; (b) NBS, THF,  $0^\circ\text{C}$ ; (d) KOH, THF,  $\text{H}_2\text{O}$ , reflux.

Compounds 1, 2, and 3 are synthesized by following the cited literature procedures.<sup>1, 2</sup>

**JM202 (4-(5-(2,5-bis(2-ethylhexyl)-3,6-dioxo-4-(5-(5,10,15-tris(2-ethylhexyl)-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazol-3-yl)thiophen-2-yl)-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)thiophen-2-yl)benzoic acid):** Compound 3 (200 mg, 0.25 mmol) and compound 2 (175 mg, 0.25 mmol) were sequentially added to a 100 mL two-neck flask, followed by the addition of  $\text{K}_2\text{CO}_3$  (138 mg, 1 mmol),  $\text{H}_2\text{O}$

(5 mL), and 1,4-dioxane (35 mL). The mixture was bubbled with nitrogen for 15 min. After Pd(PPh<sub>3</sub>)<sub>4</sub> (28 mg, 0.025 mmol) was added under nitrogen protection, the reaction mixture was stirred and heated to 80 °C for 12 h. When the reaction was cooled to room temperature, water was added and the mixture was extracted by CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was concentrated and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered to remove impurities, and the filtrate was obtained as a crude product. The crude product was further purified by silica gel column chromatography using petroleum ether and dichloromethane eluent (V<sub>CH<sub>2</sub>Cl<sub>2</sub></sub>/V<sub>PE</sub>=1:5), yielding 0.27 g of orange powder (78% yield). Then, a mixture of the compounds obtained (673 mg, 0.5 mmol), KOH (380 mg, 7 mmol) dissolved in water (5 mL), and THF (15.0 mL) in a round bottom flask is heated refluxing for 36 h. After cooling to room temperature, the reaction is quenched with water, to which is then added 2 M HCl for neutralizing to pH = 1-3, and the organic layer is extracted with CH<sub>2</sub>Cl<sub>2</sub>, then to recrystallize with methanol to accept orange-yellow solid (91%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.30 (s, 2H), 8.13 (s, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.65 (s, 3H), 7.44 (d, *J* = 6.5 Hz, 2H), 7.36 (s, 2H), 4.96 (m, 9H), 2.06 (m, 4H), 1.81-1.50 (m, 22H), 1.37- 1.21 (m, 11H), 1.14- 0.72 (m, 31H), 0.71- 0.61 (m, 7H), 0.60- 0.38 (m, 8H). MS (MALDI-TOF) Calcd for C<sub>77</sub>H<sub>93</sub>F<sub>2</sub>N<sub>5</sub>O<sub>2</sub>S<sub>2</sub> (M<sup>+</sup>): 1323.7608; Found: 1323.7589.



(a) CuI, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, THF, Et<sub>3</sub>N, reflux; (b) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, 1,4-dioxane, H<sub>2</sub>O, reflux; (c) KOH, THF, H<sub>2</sub>O, reflux.

Compound 3 is synthesized by following the cited literature procedures.

**Compounds 4 ethyl 4-((5-(7-(5-bromo-4-hexylthiophen-2-yl)-6-fluorobenzo[c][1,2,5]thiadiazol-4-yl)-3-hexylthiophen-2-yl)ethynyl)benzoate and ethyl 4-((5-(7-(5-bromo-4-hexylthiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazol-4-yl)-3-hexylthiophen-2-yl)ethynyl)benzoate :** To a 25 mL two of the flask equipped with a magnetic stirring bar are added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (14.5 mg, 0.015 mmol), CuI (1.9 mg, 7 0.01 mmol), ethyl 4-ethynylbenzoate (175 mg, 1 mmol), 4,7-bis(5-bromo-4-hexylthiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (650 mg, 1 mmol), and 50 mL of toluene under an nitrogen atmosphere. Then, 2 mL of trimethylamine solution (0.5 M, 1.0 mmol) is added to the mixture and the flask was heated at 80°C for 12 h. After cooling to room temperature, the solution is washed with water and the aqueous layer is extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers are dried over anhydrous magnesium sulfate and concentrated under reduced pressure to leave a crude oil, which is purified by chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>: petroleum ether

(1:2, v/v) to afford 550 mg red solid (75%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): 8.05 (d, J = 6 Hz, 2H), 7.77-7.70 (m, 1H), 7.58 (d, J = 6 Hz, 2H), 7.17 (s, 1H), 7.11 (s, 1H), 4.42-4.37 (m, 2H), 2.87-2.68 (m, 4H), 1.81-1.67 (m, 4H), 1.44-1.28 (m, 15H), 0.90 (t, 6H). MS (MALDI-TOF) m/z calculated for C<sub>37</sub>H<sub>38</sub>BrFN<sub>2</sub>O<sub>2</sub>S<sub>3</sub>: 737.80; found, 737.8.

**JM203**            **4-((5-(6-fluoro-7-(4-hexyl-5-(5,10,15-tris(2-ethylhexyl)-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazol-3-yl)thiophen-2-**

**yl)benzo[c][1,2,5]thiadiazol-4-yl)-3-hexylthiophen-2-yl)ethynyl)benzoic acid:**

Compound 3 (100 mg, 0.125 mmol), compound 4 (95 mg, 0.125 mmol), K<sub>2</sub>CO<sub>3</sub> (13.8 mg, 1 mmol) in 35 mL 1,4-dioxane, 10 mL H<sub>2</sub>O was added under N<sub>2</sub>. After that, the Pd (PPh<sub>3</sub>)<sub>4</sub> (28 mg, 0.025 mmol) were added into the flask. The mixture was allowed to heat at 85 °C for 12 h and then extracted with CH<sub>2</sub>Cl<sub>2</sub> and water. The combined organic layers are dried over anhydrous magnesium sulfate and concentrated under reduced pressure to leave a yellow solid, which is purified by chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>: CH<sub>3</sub>OH (20:1, v/v) to afford 273 mg orange solid (78%). After then, the product was dissolved in H<sub>2</sub>O (10 mL), and THF (30 mL) · KOH (0.38 g, 0.07 mmol) dissolved in water was added and refluxed 20 h. After cooling to room temperature, 2 M HCl was added slowly in 2 h for neutralizing to pH=1-3, the organic was collected and evaporated to obtain an orange solid. The residue was purified by chromatography using CH<sub>2</sub>Cl<sub>2</sub> to provide JM203 as an orange solid (260 mg). a 100 mL two of the flask equipped with a magnetic stirring bar are added 4,7-bis(5-bromo-4-hexylthiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (650 mg, 1 mmol), ethyl 4-ethynylbenzoate (261 mg, 1.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (14.5 mg, 0.015 mmol), CuI (1.9 mg, 0.01 mmol) and 15 mL of toluene under a nitrogen atmosphere. Then, 2 mL of trimethylamine solution (0.5 M, 1.0 mmol) is added to the mixture and the flask was heated at 80 °C for 12 h. After cooling to room temperature, the solution is washed with water and the aqueous layer is extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers are dried over anhydrous magnesium sulfate and concentrated under reduced pressure to leave a crude oil, which is purified by chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>: CH<sub>3</sub>OH (20:1, v/v) to afford 550 mg red solid (75%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm) 8.42 (s, 1H), 8.28 (s, 2H), 8.10 (d, J = 10 Hz, 2H), 7.93 (s, 1H), 7.79 (d, J = 9 Hz, 1H), 7.62 (s, 4H), 7.53 (s, 1H),

7.44 (s, 2H), 7.34 (s, 2H), 4.95 (m, 6H), 3.38 (t, J = 6 HZ, 1H), 2.85 (m, 4H), 2.39 (d, J = 6 HZ, 1H), 2.39 (t, J = 6 HZ, 1H), 2.16–1.94 (m, 4H), 1.86–1.70 (m, 4H), 1.52–1.15 (m, 19H), 1.14–0.73 (m, 23H), 0.72–0.59 (m, 8H), 0.58–0.36 (m, 7H), 0.07 (s, 1H). MS (MALDI-TOF) m/z calculated for C<sub>83</sub>H<sub>96</sub>FN<sub>5</sub>O<sub>2</sub>S<sub>3</sub>: 1309.6710; found, 1309.6668

**JM204**            **4-((5-(5-fluoro-7-(4-hexyl-5-(5,10,15-tris(2-ethylhexyl)-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazol-3-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3-hexylthiophen-2-yl)ethynyl)benzoic acid:**

Synthetic steps is following the **JM203** synthesis method to accept purple blue solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, ppm): 8.42 (s, 1H), 8.28 (s, 2H), 8.10 (d, J = 10 HZ, 2H), 7.93 (s, 1H), 7.79 (d, J = 9 HZ, 1H), 7.62 (s, 4H), 7.53 (s, 1H), 7.44 (s, 2H), 7.34 (s, 2H), 4.95 (m, 6H), 3.38 (t, J = 6 HZ, 1H), 2.85 (m, 4H), 2.39 (d, J = 6 HZ, 1H), 2.39 (t, J = 6 HZ, 1H), 2.16–1.94 (m, 4H), 1.86–1.70 (m, 4H), 1.52–1.15 (m, 19H), 1.14–0.73 (m, 23H), 0.72–0.59 (m, 8H), 0.58–0.36 (m, 7H), 0.07 (s, 1H). MS (MALDI-TOF) m/z calculated for C<sub>83</sub>H<sub>96</sub>FN<sub>5</sub>O<sub>2</sub>S<sub>3</sub>: 1309.6710; found, 1309.6648

## 2. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS). The electrochemical impedance spectroscopy (EIS) measurements are carried out at an impedance/gain-phase analyzer (Zahner Zennium, Serial No. 40037) electrochemical work station with frequency range from 1 MHz to 0.1 Hz and the applied amplitude bias is 10 mV, and the data is fitted with the Zahner Analysis.

## 3. Cyclic voltammetry

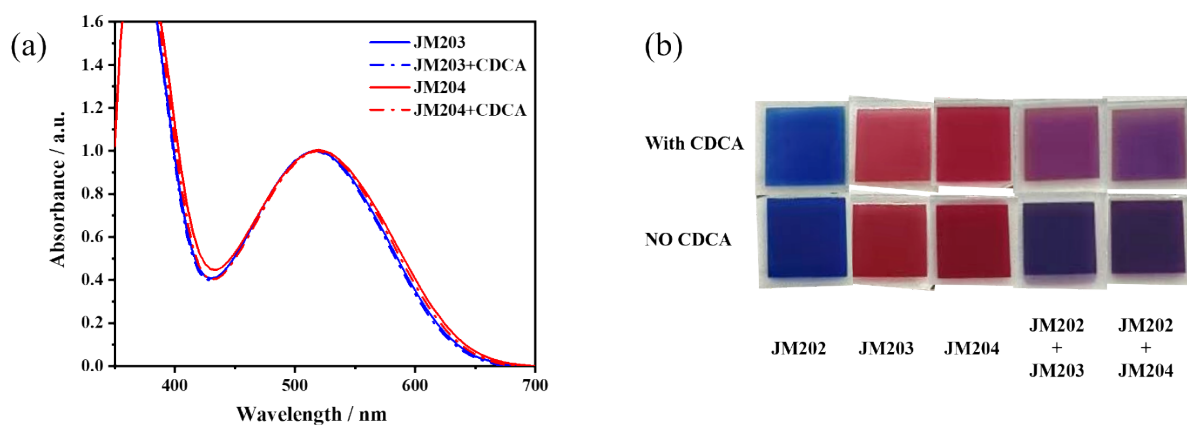
Cyclic voltammograms are recorded with a CHI660E (CH Instruments, Inc.) Electrochemical workstation. Ag/AgCl and platinum wire are treated as reference electrode, and counter electrode, respectively, 0.1 M 10 tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) solution as supporting electrolyte and the scan rate is 50 mV/s. For the energy level testing of a single dye, a glassy carbon electrode was used as the working electrode. For the testing of TiO<sub>2</sub> film with co-adsorbed dyes of different proportions, the TiO<sub>2</sub> film itself served as the working electrode.

#### 4. Dye loading amount measurements

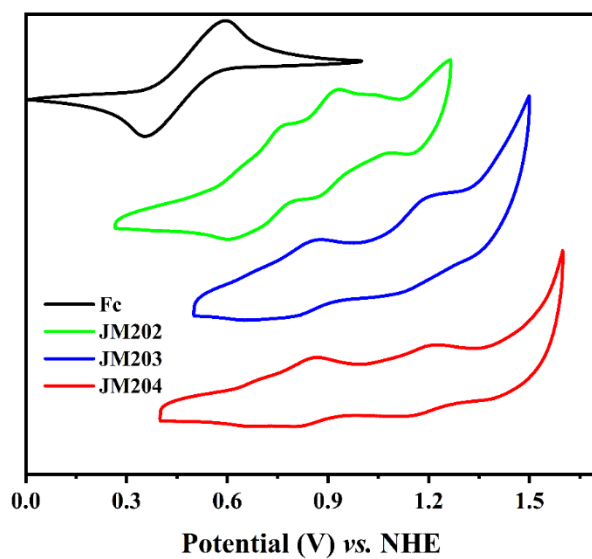
The dye loading was measured by the method described in the literature.<sup>3</sup> In brief, a dye stock solution (12 ml) was prepared by dissolving 50  $\mu\text{M}$  **JM202** and 50  $\mu\text{M}$  **JM203/JM204** in  $\text{CH}_2\text{Cl}_2$  and divided into three equal parts (solutions 1, 2 and 3) followed by immersing an FTO glass covered with 6- $\mu\text{m}$ -thick transparent  $\text{TiO}_2$  film and a blank sheet of FTO glass of the same size into solutions 1 and 2, respectively. Then, the  $\text{TiO}_2$  film was taken out of solution 1 and carefully washed with acetonitrile to remove the weakly adsorbed dyes. The dye stock solution was combined with  $\text{CH}_2\text{Cl}_2$  to have a total weight of 5 g. The bare FTO glass in solution 2 was treated by the same procedure as the  $\text{TiO}_2$  film in solution 1.  $\text{CH}_2\text{Cl}_2$  (1 g) was also added into solution 3. Furthermore,  $\text{CH}_2\text{Cl}_2$  solvent (3 g) was added into each bottle of solutions 1, 2, and 3 to ensure that the dyes were completely dissolved. Finally, the UV-vis spectra of these three solutions were measured. The amount of dye loading expressed by the number of adsorbed moles of dye per unit film area and unit film thickness (cm) was calculated from the equation:

$$C_m = \frac{(Abs_2 - Abs_1) \times c \times V}{Abs_3 \times A \times d}$$

where  $Abs_1$ ,  $Abs_2$  and  $Abs_3$  are the absorbance values of final solutions 1, 2 and 3 at the same wavelength, respectively;  $c$  and  $V$  are the concentration and volume of fresh solutions 1, 2, and 3, respectively;  $A$  and  $d$  are the area and thickness of the  $\text{TiO}_2$  film, respectively. In this study, for the **JM202+JM203**, **JM202+JM204**  $\text{TiO}_2$  film, the dye loading amount of **JM202** can be easily derived by the absorbance at a long wavelength where **JM203** and **JM204** do not absorb. Assuming that the absorption spectrum of a binary dye solution of **JM202** and **JM203/JM204** is the simple physical overlap of an individual solution, we could further estimate the amount of dye loading of **JM203/JM204** via spectral decomposition.

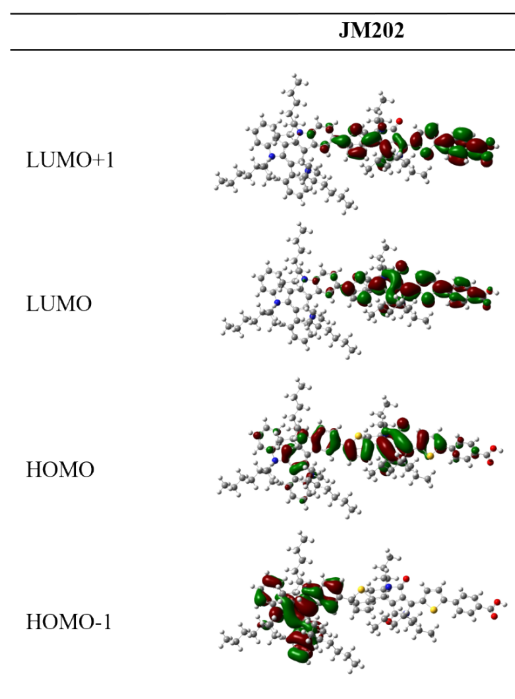


**Figure S1.** (a) UV-vis absorption spectra of sensitizers JM203/JM203+CDCA and JM204/JM204+CDCA attached on 4µm TiO<sub>2</sub> film immersed in CH<sub>3</sub>CN solutions with 0.1 M LiClO<sub>4</sub>. (b) Photograph of dye adsorption on 6µm TiO<sub>2</sub>.

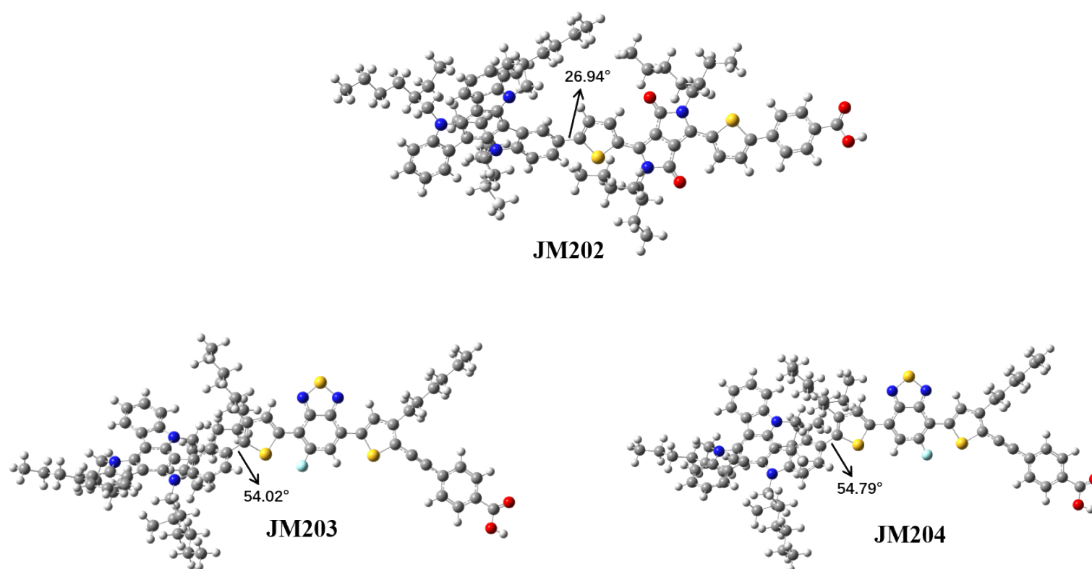


**Figure S2.** Cyclic voltammograms of JM202, JM203 and JM204 sensitizers

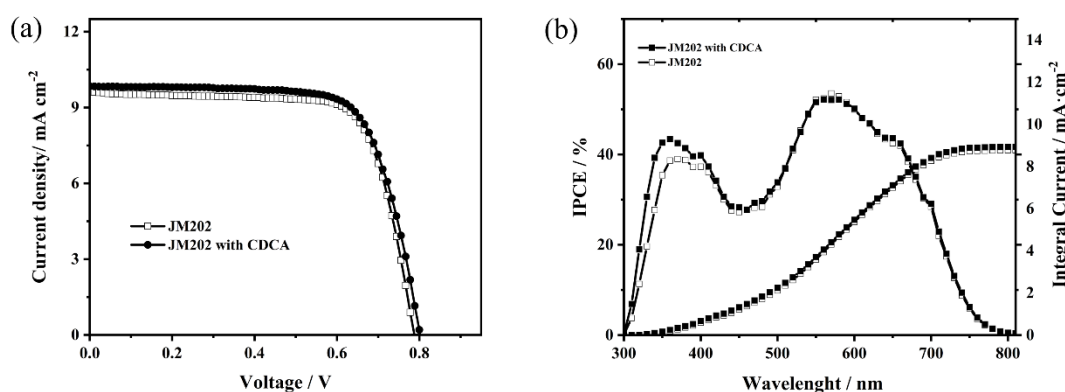




**Figure S3.** The electron distribution in HOMO, HOMO-1 and LUMO, LUMO+1 levels of JM202 by DFT calculations..



**Figure S4.** Dihedral angles between the neighboring units calculated from optimized structures.

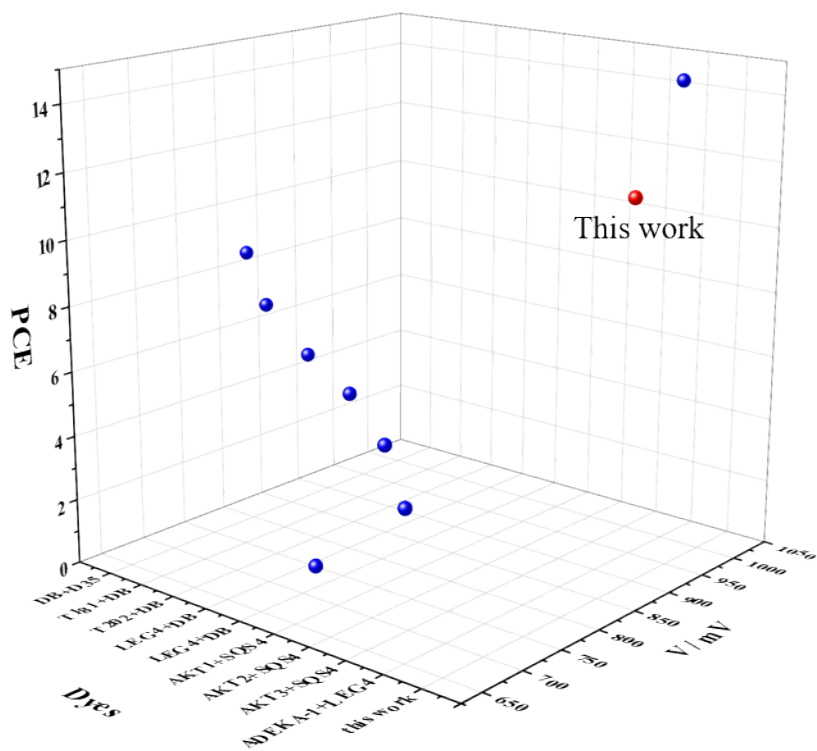


**Figure S5.** (a) Current–voltage (J–V) characteristics of the DSSCs measured under simulated AM1.5G. (b) IPCE spectra and integrated photocurrents of the DSSCs based on JM202.

**Table S1.** Photophysical and electrochemical properties of sensitizers on DFT calculations

Dye	$E_{0-0}^{\text{DFT[a]}}$ (eV)	$E_{\text{H-1}}^{\text{DFT[b]}}$ (eV)	$E_{\text{H}}^{\text{DFT[b]}}$ (eV)	$E_{\text{L}}^{\text{DFT[b]}}$ (eV)	$E_{\text{L+1}}^{\text{DFT[b]}}$ (eV)
<b>JM202</b>	2.14	-5.24	-4.98	-2.84	-1.90
<b>JM203</b>	2.07	-5.14	-5.07	-3.00	-2.16
<b>JM204</b>	2.18	-5.21	-5.14	-2.96	-2.08

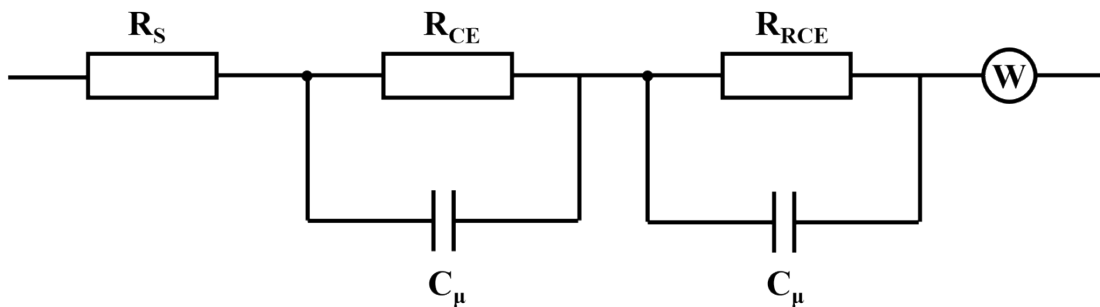
[a] Energy gaps ( $E_{0-0}^{\text{DFT}}$ ), [b]H, H-1 and L, L+1 represent HOMO, HOMO-1 and LUMO, LUMO+1 respectively. The frontier orbital energy levels ( $E_{\text{H}}^{\text{DFT}}$  and  $E_{\text{L}}^{\text{DFT}}$ ) with respect to vacuum are calculated at the B3LYP/6-311G(d,p) level of theory for dye in vacuum,  $\lambda_{\text{abs max}}^{\text{DFT}}$  is derived from DFT calculation at the B3LYP/6-311G(d,p) level of theory for dye in vacuum, Energy gaps (DFT) are calculated via  $E_{0-0}^{\text{DFT}} = E_{\text{L}}^{\text{DFT}} - E_{\text{H}}^{\text{DFT}}$ .



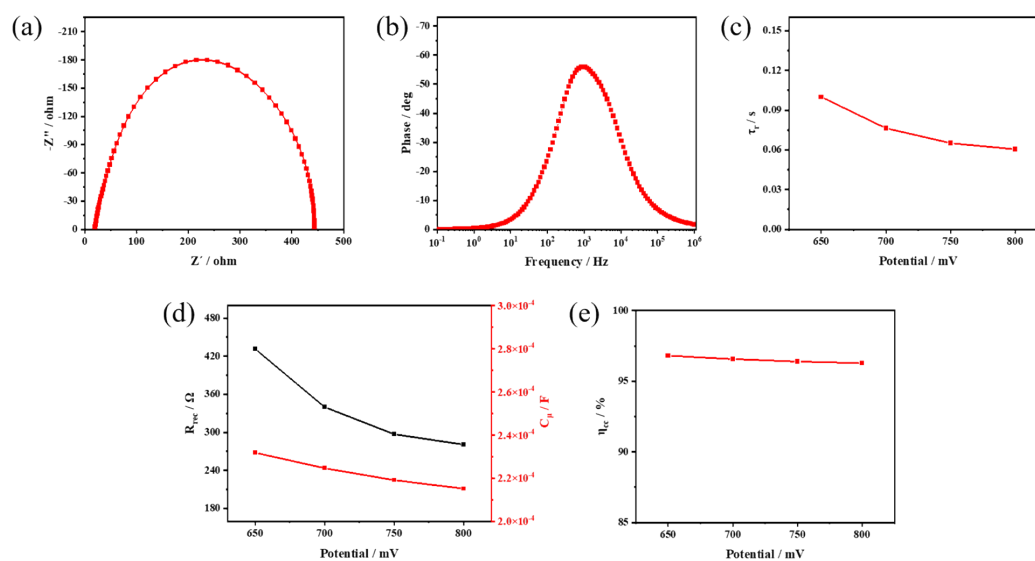
**Figure S6.** Comparison of reported and current work on cobalt electrolyte-based pure organic photosensitizers for co-sensitization.

**Table S2.** Optimization data of DSSCs devices based on JM202-JM204 and co-sensitization under different conditions.

Dye	Electrolyte	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$ (%)	$PCE$ (%)
<b>JM202</b>	[Cu(tmby) <sub>2</sub> ] <sup>2+/+</sup>	0.82	8.61	70.76	5.0
<b>JM203</b>	[Cu(tmby) <sub>2</sub> ] <sup>2+/+</sup>	0.96	5.19	75.91	3.8
<b>JM204</b>	[Cu(tmby) <sub>2</sub> ] <sup>2+/+</sup>	0.99	8.57	75.00	6.3
<b>JM202:JM203</b> (60 μM:40μM)	[Co(bpy) <sub>3</sub> ] <sup>3+/2+</sup>	0.82	13.04	68.81	7.4
<b>JM202:JM203</b> (50 μM:50μM)	[Co(bpy) <sub>3</sub> ] <sup>3+/2+</sup>	0.83	14.93	67.63	8.5
<b>JM202:JM203</b> (40 μM:60μM)	[Co(bpy) <sub>3</sub> ] <sup>3+/2+</sup>	0.84	13.95	66.58	7.8
<b>JM202:JM204</b> (60 μM:40μM)	[Co(bpy) <sub>3</sub> ] <sup>3+/2+</sup>	0.86	17.88	69.15	10.7
<b>JM202:JM204</b> (50 μM:50μM)	[Co(bpy) <sub>3</sub> ] <sup>3+/2+</sup>	0.89	20.38	64.24	11.7
<b>JM202:JM204</b> (40 μM:60μM)	[Co(bpy) <sub>3</sub> ] <sup>3+/2+</sup>	0.89	18.39	66.08	10.8



**Figure S7.** Equivalent circuit for EIS data fitting.



**Figure S8.** Nyquist plots (a) and bode plots (b) of DSSCs based on JM202. (d) interfacial charge-recombination resistance ( $R_{rec}$ ), and chemical capacitance ( $C_{\mu}$ ), (e) electron lifetime ( $\tau_r$ ), (f) Charge-collection efficiency ( $\eta_{cc}$ ) fitted from impedance analysis under a series applied bias for DSSCs based on dye JM202.

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