

## Supporting information

# **High-Performance Organic Solar Cells Featuring Double Bulk Heterojunction Structures with Vertical-Gradient Selenium Heterocyclic Nonfullerene Acceptor Concentrations**

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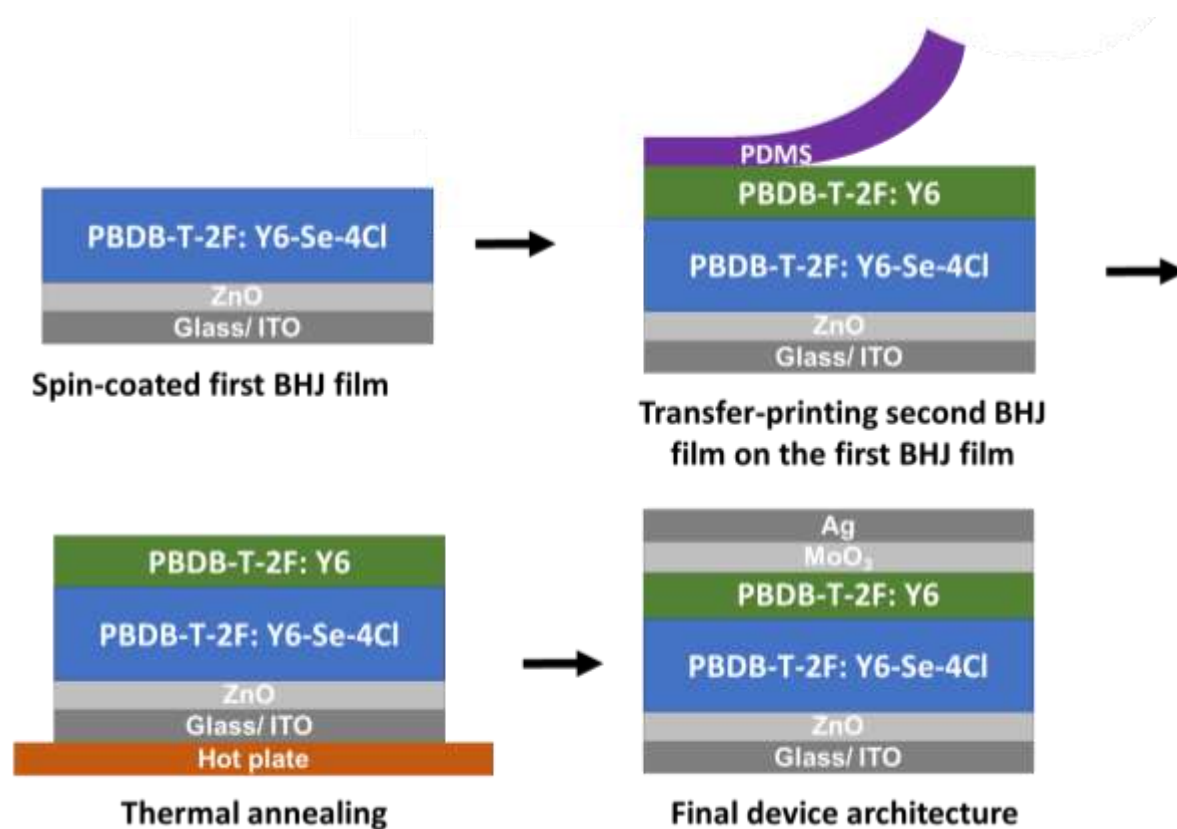
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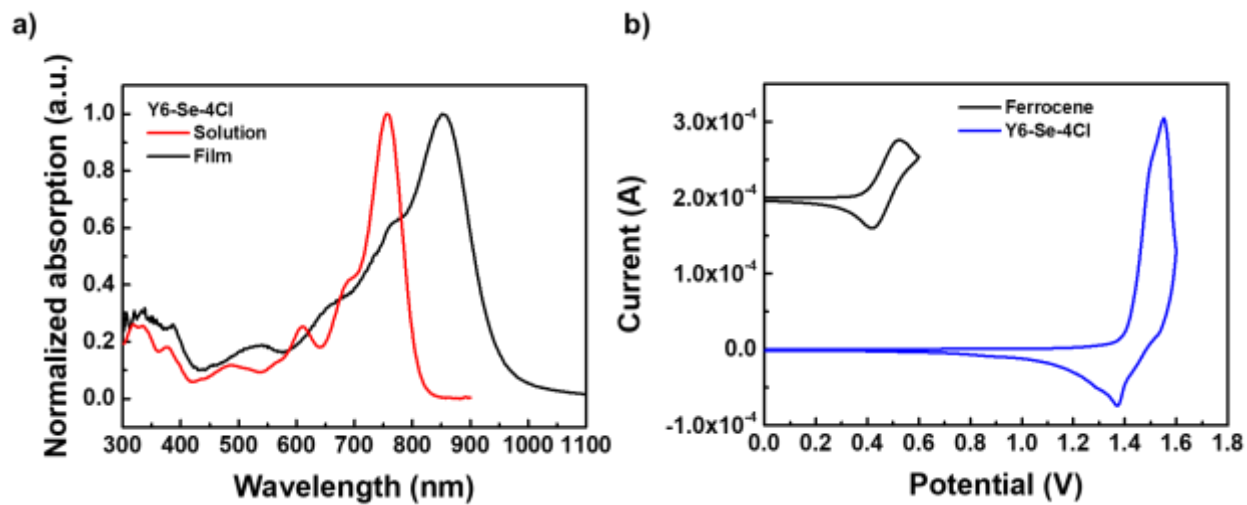
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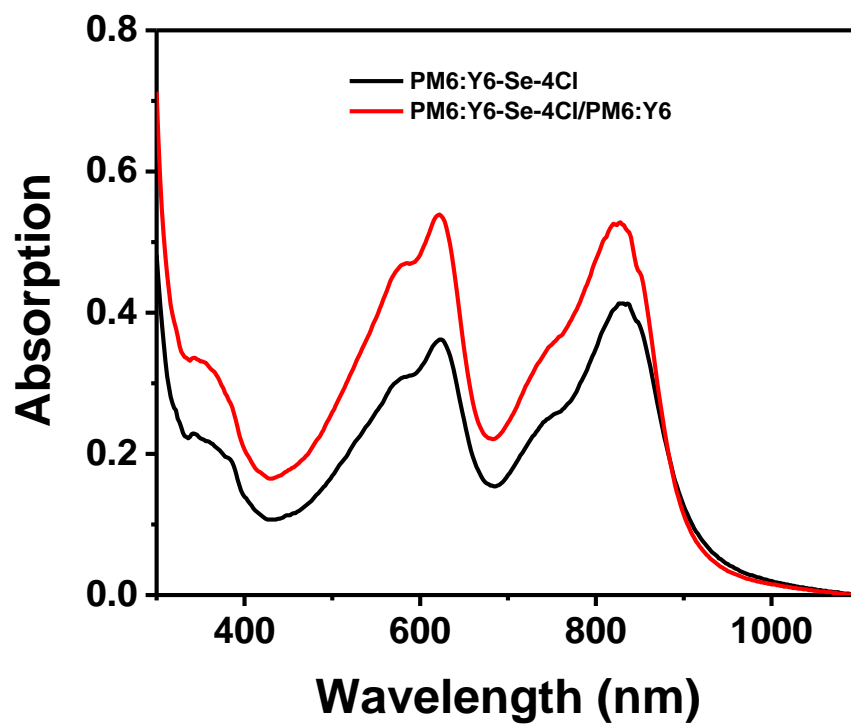
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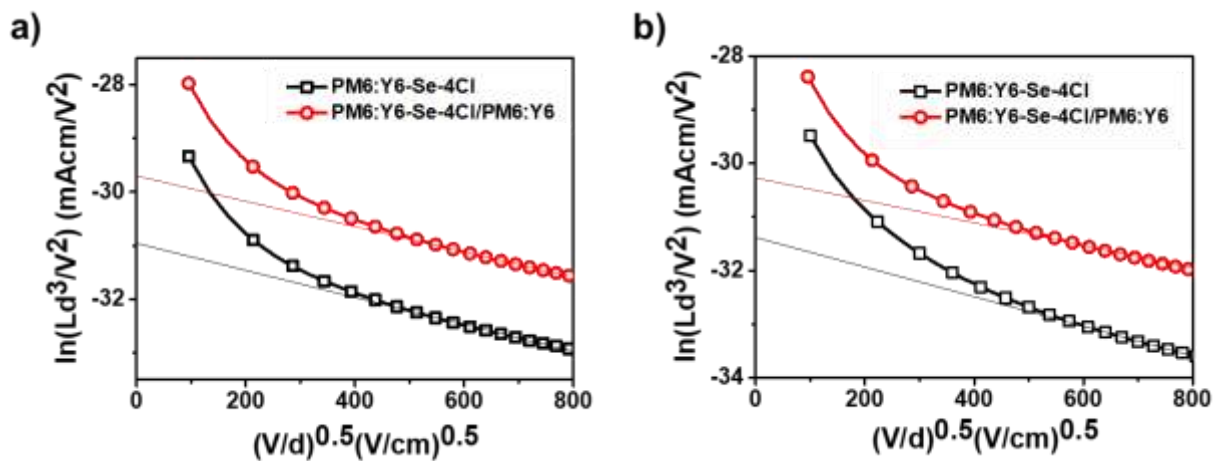
**Figure S1.** The scheme of the process of preparing the double-BHJ structure devices via transfer-printing process.



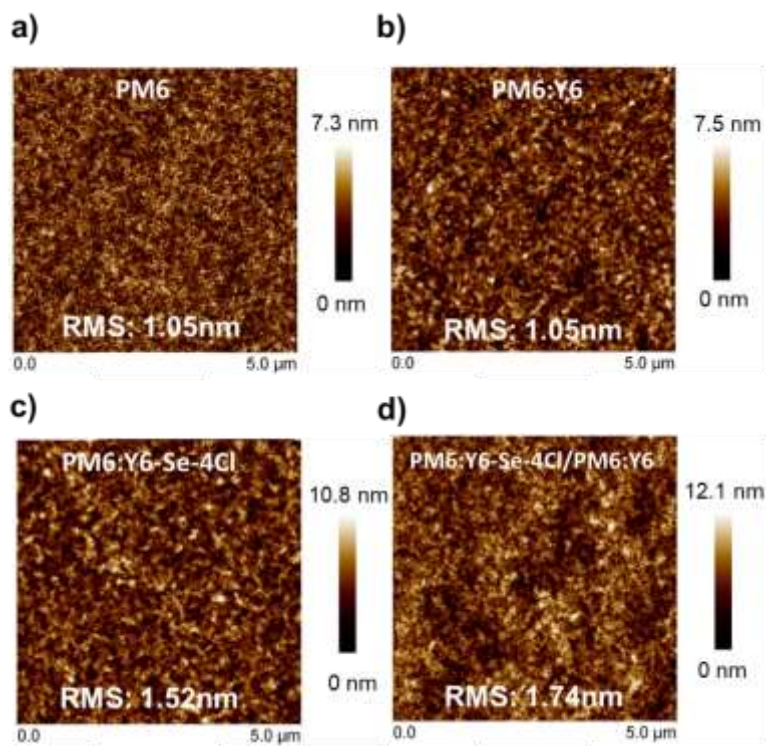
**Figure S2.** a) The normalized absorption of Y6-Se-4Cl in film and solution. b) The cyclic voltammetry curve of Y6-Se-4Cl.



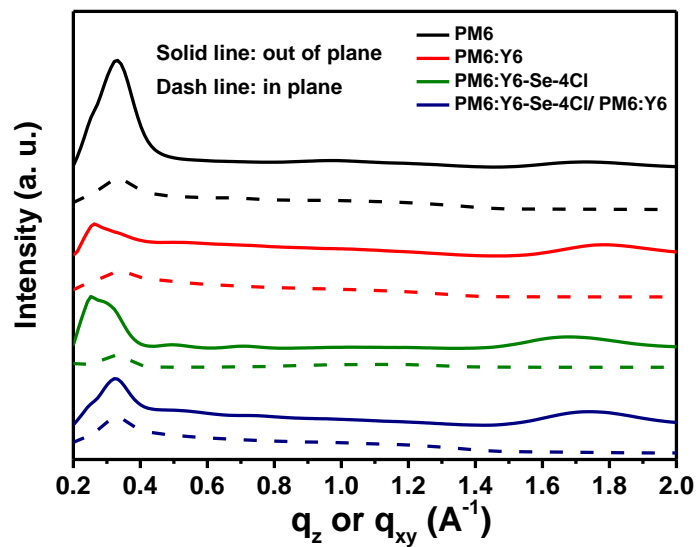
**Figure S3.** The absorption spectrum of PM6:Y6-Se-4Cl (one-BHJ structure) and PM6:Y6-Se-4Cl/PM6:Y6 (double-BHJ structure) films.



**Figure S4** a) and b) Hole-only and electron-only based on the PM6:Y6-Se-4Cl (one-BHJ structure) and PM6:Y6-Se-4Cl/ PM6:Y6 (double-BHJ structure) devices.

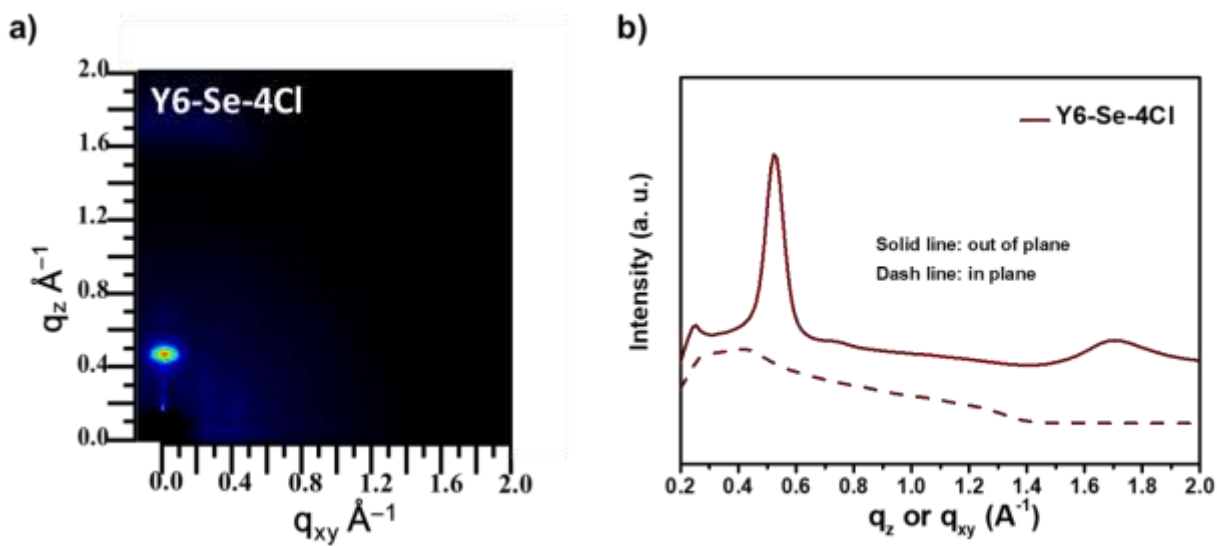


**Figure S5.** a-d) AFM height images (5 x 5 μm) of films of pure PM6, PM6:Y6, PM6:Y6-Se-4Cl and PM6:Y6-Se-4Cl/ PM6:Y6 films.



**Figure S6.** The one-dimensional GIWAX patterns of pure PM6, PM6:Y6, PM6:Y6-Se-4Cl and PM6:Y6-Se-4Cl/ PM6:Y6 films.





**Figure S7.** a) 2D and b) 1D GIWAX patterns of pure Y6-Se-4Cl film.

**Table S1.** Photovoltaic performance of the champion devices based on PM6:Y6-Se-4Cl, PM6:Y6, PM6:IT-4Cl, PM6:Y6-Se-4Cl/PM6:Y6, and PM6:Y6-Se-4Cl/PM6:IT-4Cl.

	Active layer structure	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	Champion PCE (%)
<b>PM6:Y6-Se-4Cl (120 nm)</b>	Traditional	0.84	26.4	67.7	15.0
<b>PM6:Y6 (100 nm)</b>	Traditional	0.84	25.9	70.6	15.4
<b>PM6:IT-4Cl (100 nm)</b>	Traditional	0.80	21.4	67.6	11.6
<b>PM6:Y6-Se-4Cl (100 nm) /PM6:Y6 (20 nm)</b>	Double-BHJ	0.84	26.6	73.3	16.4
<b>PM6:Y6-Se-4Cl (100 nm) /PM6:IT-4Cl (20 nm)</b>	Double-BHJ	0.83	27.6	68.8	15.8

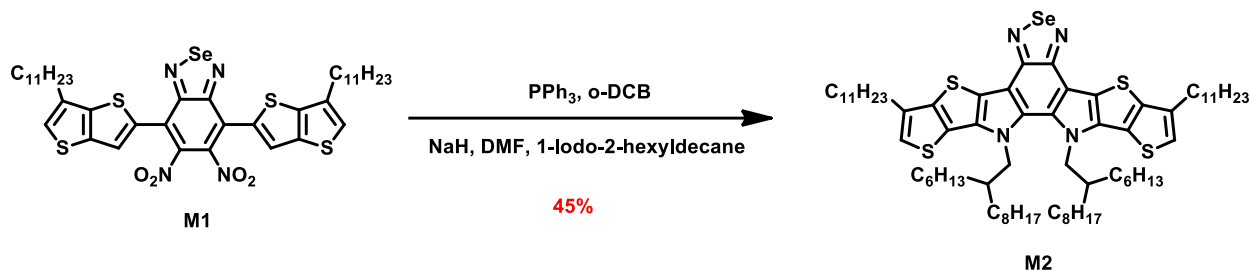
**Table S2.** The optimization of the photovoltaic performance for the devices based on double-BHJ devices (PM6:Y6-Se-4Cl/PM6:Y6, and PM6:Y6-Se-4Cl/PM6:IT-4Cl) with different thickness of the second BHJ layer.

First BHJ	Second BHJ	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
PM6:Y6-Se-4Cl (100nm)	None	0.84±0.01	25.1±0.2	66.4±0.2	14.0±0.3
PM6:Y6-Se-4Cl (100nm)	PM6:Y6 (10 nm)	0.84±0.01	26.3±0.4	70.4±0.2	15.6±0.3
PM6:Y6-Se-4Cl (100nm)	PM6:Y6 (20 nm)	0.84±0.01	26.3±0.2	73.0±0.2	16.1±0.2
PM6:Y6-Se-4Cl (100nm)	PM6:Y6 (30 nm)	0.84±0.01	27.3±0.4	68.0±0.3	15.6±0.1
PM6:Y6-Se-4Cl (100nm)	PM6:IT-4Cl (10 nm)	0.83±0.01	26.4±0.2	67.9±0.3	14.9±0.3
PM6:Y6-Se-4Cl (100nm)	PM6:IT-4Cl (20 nm)	0.83±0.01	27.4±0.3	68.5±0.1	15.5±0.2
PM6:Y6-Se-4Cl (100nm)	PM6:IT-4Cl (30 nm)	0.83±0.01	27.6±0.3	63.8±0.1	14.6±0.2

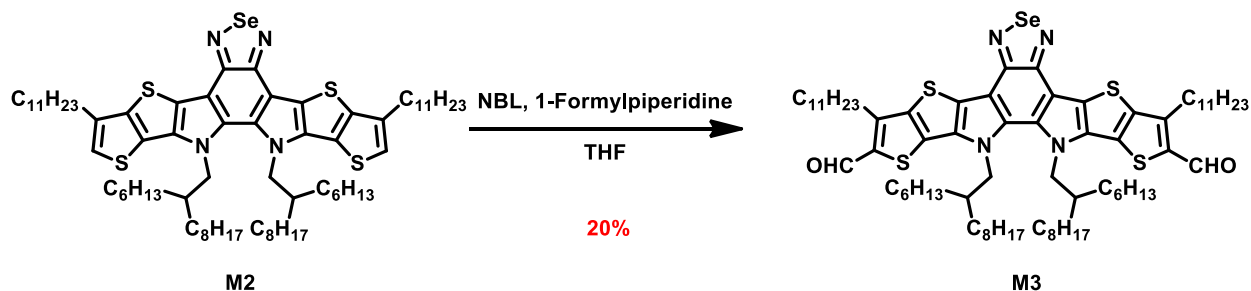
**Table S3.** Photovoltaic performance of the PM6:Y6-Se-4Cl:Y6 based ternary-blend devices.

Active layer (ratio, wt%)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
PM6:Y6-Se-4Cl (1:1.2, 20 mg mL <sup>-1</sup> )	0.84±0.01	25.9±0.3	67.2±0.3	14.6±0.2
PM6:Y6-Se-4Cl:Y6 (1:1.2:0.1, 20 mg mL <sup>-1</sup> )	0.83±0.01	26.3±0.3	69.6±0.2	15.2±0.3
PM6:Y6-Se-4Cl:Y6 (1:1.2:0.2, 20 mg mL <sup>-1</sup> )	0.82±0.01	27.1±0.3	63.8±0.3	14.2±0.3
PM6:Y6-Se-4Cl:Y6 (1:1.2:0.3, 20 mg mL <sup>-1</sup> )	0.82±0.01	26.8±0.2	61.8±0.3	13.6±0.1
PM6:Y6-Se-4Cl:Y6 (1:1.2:0.4, 20 mg mL <sup>-1</sup> )	0.82±0.01	26.2±0.2	59.7±0.2	12.8±0.2

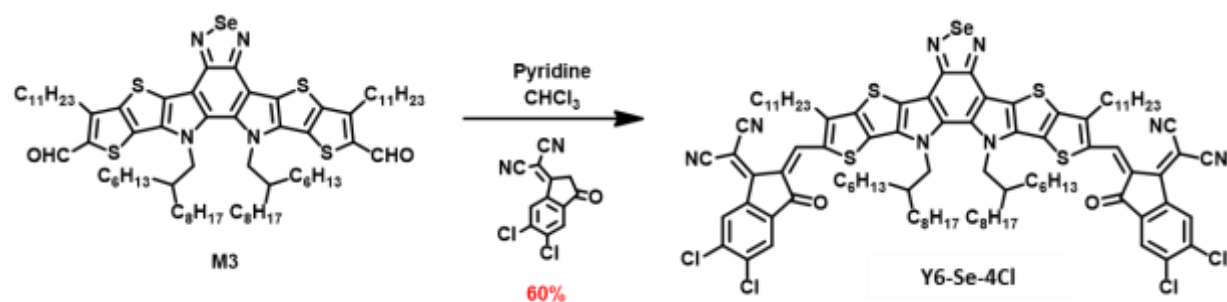
## Synthesis route of Y6-Se-4Cl



A mixture of M1 (6 g, 8.0 mmol), triphenylphosphine (21 g, 80.4 mmol) and 1,2-dichlorobenzene (173 mL) was degassed for 30 minutes and refluxed for 22 hours. After cooling to room temperature, methanol was added and the mixture was filtered under reduced pressure. The residue was purified by column chromatography (heptane/dichloromethane, v/v, 1/1) to give an orange solid. Subsequently, the orange intermediate was then mixed with NaH (60% in oil, 2.1 g, 51.7 mmol), 1-iodo-2-hexyldecane (20.5 g, 58.2 mmol) and anhydrous DMF (100 mL) were mixed under argon and stirred at 80 °C overnight. The mixture was extracted with ethyl acetate for three times. The combined organic phase was washed with water followed by brine. Then, the solution was dried over  $\text{Mg}_2\text{SO}_4$  and concentrated under reduced pressure. The residue was purified by column chromatography (heptane/dichloromethane, v/v, 1/1), to give an orange solid 3.6 g, 45% yield, two steps).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.97 (s, 2H), 4.52 (d,  $J=8.0$  Hz, 4H), 2.79 (t,  $J=7.8$  Hz, 4H), 2.09-2.04 (m, 2H), 1.83 (p,  $J=7.6$  Hz, 4H), 1.45-0.79 (m, 92H), 0.66 (d,  $J=7.0$  Hz, 6H) °.



A mixture of compound M2 (800 mg, 0.64 mmol) and anhydrous THF (32 mL), 2.5 M n-butyl lithium (0.6 mL, 1.4 mmol) was added dropwise slowly at -78 °C under argon. The mixture was stirred at -78 °C for 30 minutes, and then anhydrous 1-formylpiperidine (0.71 mL, 6.4 mmol) was added. The mixture was stirred 30 minutes at room temperature. Brine was added and the mixture was extracted with ethyl acetate for three times. The combined organic phase was washed with water followed by brine. Then the solution was dried over  $\text{Mg}_2\text{SO}_4$  and concentrated under reduced pressure. The residue was purified by column chromatography (heptane/dichloromethane, 1/1, v/v) to get the product as orange solid (157 mg, 20%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.11 (s, 2H), 4.55 (d,  $J=8.0$  Hz, 4H), 3.17 (t,  $J=7.8$  Hz, 4H), 2.04-2.01 (m, 2H), 1.90 (p,  $J=7.6$  Hz, 4H), 1.48-0.78 (m, 92H), 0.66 (d,  $J=7.0$  Hz, 6H) .



A mixture of compound M3 (510 mg, 0.39 mmol) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (515 mg, 1.96 mmol) in chloroform (15 mL) was degassed before pyridine (0.5 mL) was added. The reaction was kept at 65 °C under argon for 30 minutes. The solvent was removed under reduced pressure and the residue was washed by methanol and acetone to get the product as dark blue solid (421 mg, 60%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.15 (s, 2H), 8.77 (s, 4H), 7.93 (s, 2H), 4.70 (d,  $J=7.5$  Hz, 4H), 3.20 (t,  $J=8$  Hz, 4H), 2.14-2.09 (m, 2H), 1.85 (p,  $J=7.8$  Hz, 4H), 1.51-0.75 (m, 92H), 0.67 (d,  $J=6.8$  Hz, 6H) .

## NMR

