Supporting information

Control on the Arrangement of Dipolar Orientation of Pyrimidine inside the Conjugated Backbone

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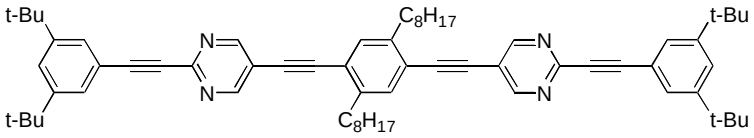
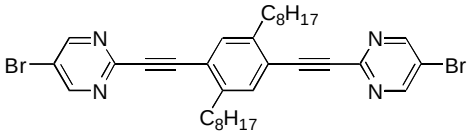
General.

All reactions were performed under argon and were magnetically stirred. Solvents were distilled from appropriate dying agent prior to use: THF from sodiumand benzophenone, iPr_2NH from calcium hydride. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Macherey-Nagel pre-coated aluminum foil sheets (0.20 mm with fluorescent indicator UV_{254}). Compounds were visualized with UV light at 254 nm and 365nm. Column Chromatography was carried out using flash silica gel from Macherey-Nagel (230~400 mesh). Melting points were measured on a Fargo MP-1D and are uncorrected. Infra-red (IR) spectra were recorded within KBr on a Nicolet FT-IR spectrometer. ^{1}H-NMR and ^{13}C-NMR were recorded using a Bruker or Varian spectrometer at 400 MHz and 100 MHz respectively. Low and high resolution mass spectra were recorded using a Jeol SX-102A spectrometer in FAB mode.



3

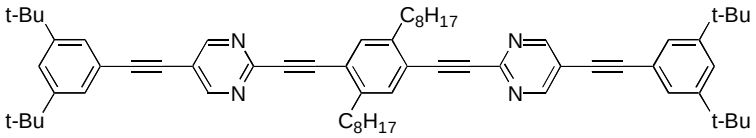
To a solution of compound **2** (158 mg, 0.5 mmol) and 1,4-diiodo3,5-dioctylbenzene (139 mg, 0.25 mmol), $Pd(PPh_3)_4$ (100 mg, 0.09 mmol), CuI (10 mg, 0.05 mmol) in THF (25 mL) was stirred for 10 min, iPr_2NH (0.14 mL, 0.95 mmol) was introduced, the mixture was refluxed for 1 hour. After cooled to room temperature, MeOH (30 mL) was added to precipitate the product, the resulting suspension was filtered to afford crude product which can be reprecipitated from MeOH/$CHCl_3$ and further washed with hot hexane to afford **3** as a pale yellow solid (126 mg, 54%). mp 249~251 ^oC; IR (KBr) υ2961 (w), 2928 (w), 2861 (w), 2218 (w), 1591 (w), 1492 (s), 1184 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.86~0.89 (m, 6H), 1.27~1.39 (m, 56H), 1.67~1.74 (m, 4H), 2.80~2.84 (t, *J* = 7.8 Hz, 4H), 7.42 (s, 2H), 7.50 (t, *J* = 1.8 Hz, 4H), 7.57 (d, *J* = 1.8 Hz, 4H), 8.84 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.7, 29.3, 29.5, 30.7, 31.3, 31.9, 34.1, 34.9, 87.1, 87.6, 92.0, 96.5, 117.7, 120.1, 122.3, 124.6, 127.2, 132.7, 142.8, 151.0, 158.7; MS (m/z, FAB^+) 931 (30), 784 (2), 743 (3), 631 (50), 575 (2), 460 (6), 307 (100), 289 (65), 242 (8); HRMS cacld for $C_{66}H_{82}N_4$: 930.6539; found 930.6578.



4

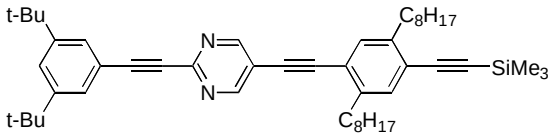
To a solution of 1,4-diethynyl-2,5-dioctylbenzene (868 mg, 2.34 mmol), 5-bromo-2-iodopyrimidine (1.35 g, 4.74 mmol), $Pd(PPh_3)_4$ (100 mg, 0.09 mmol) and CuI (10 mg, 0.05 mmol) in THF (60 mL) was stirred for 10 min., iPr_2NH (1.27 mL, 9 mmol) was introduced. The mixture was stirred for another 2.5 hours at 30 ^oC. The ammonium salt formed was removed by filtered through a short Al_2O_3 column and washed with Et_2O (2 x 20 mL). The combined filtrate was concentrated in vacuo and further purified by column chromatography on silica gel and eluted with EtOAc/hexanes (1/12). Recrystallized from hexane and EtOH afforded yellow solid (2.01 g, 82%). mp 140~142 ^oC; IR (KBr) υ 2926 (m), 2856 (m), 2212 (m), 1529 (m), 1392 (m), 1238 (w), 1175 (w), 1109 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.84~0.90 (m, 6H), 1.24~1.36 (m, 20H), 1.64~1.72 (m, 4H), 2.83~2.87 (t, *J* = 7.8 Hz, 4H), 7.52 (s, 2H), 8.800 (s, 4H); ^{13}C NMR ($CDCl_3$,100 MHz) δ 14.1, 22.6, 29.2, 29.4, 30.5, 31.9, 33.8, 63.8, 87.9, 92.1, 119.1, 122.1, 133.5, 143.6, 151.1, 158.1; MS (m/z, FAB^+) 664 (42), 553 (3), 460 (7), 304 (100), 289 (50),

242 (4); HRMS cacld for $C_{34}H_{41}{}^{79}Br_2N_4$: 663.1698; found 663.1680, cacld for $C_{34}H_{41}{}^{79}Br^{81}BrN_4$: 665.1677; found 665.1680, cacld for $C_{34}H_{41}{}^{81}Br_2N_4$: 663.1657; found 667.1688.



5

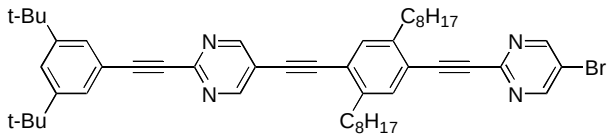
To a mixture of compound **4** (665 mg, 1 mmol), 1,3,-di-*t*-butyl-5-ethynylbenzene (429 mg, 2 mmol), $Pd(PPh_3)_4$ (57 mg, 0.05 mmol) and CuI (10 mg, 0.05 mmol) in THF (25 mL) was stirred for 10 min. iPr_2NH (0.54 mL, 3.8 mmol) was introduced, the resulting solution was stirred for another 1 hour under reflux. MeOH (30 mL) was added to precipitate the product. The resulting crude solid after filtered was reprecipitated from MeOH/$CHCl_3$ and further washed with hot hexane to afford **5** as a pale yellow solid (677 mg, 71%). mp 239~242 ^oC; IR (KBr) υ2959 (w), 2861 (w), 2212 (w), 1568 (w), 1498 (s), 1400 (w), 1180 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.85~0.89 (m, 6H), 1.26~1.38 (m, 20H), 1.66~1.74 (m, 4H), 2.85~2.89 (t, J = 7.6 Hz, 4H), 7.42 (d, J = 1.8 Hz, 4H), 7.48 (t, J = 1.8 Hz, 2H), 7.55 (s, 2H), 8.85 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.7, 29.2, 29.5, 30.5, 31.3, 31.9, 33.8, 34.9, 81.6, 88.5, 93.0, 99.2, 118.2, 120.8, 122.2, 124.0, 126.1, 133.5, 143.6, 150.5, 151.2; MS (m/z, FAB^+) 931 (50), 876 (5), 820 (4), 613 (3), 460 (8), 307 (65), 289 (43), 202 (3); HRMS cacld for $C_{66}H_{82}N_4$: 930.6539; found 930.6517.



6

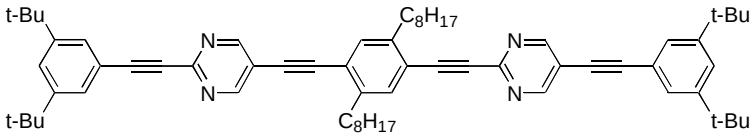
To a mixture of **2** (1.25 g, 2.34 mmol) and 1-ethynyl-4-iodo-2,5-dioctylbenzene (904 mg, 2.86 mmol), $Pd(PPh_3)_4$ (100 mg, 0.09 mmol) and CuI (10 mg, 0.05 mmol) in THF (60 mL) was stirred for 10 mins at room temperature. iPr_2NH (0.64 mL, 4.52 mmol) was introduced, the resulting mixture was refluxed for another 6 hours. The cold mixture was filtered through a short Al_2O_3 column and washed with Et_2O (2 x 25 mL). The combined filtrate was concentrated in vacuo to afford crude product which can be purified by column chromatography on silica gel and eluted with Hexane/EtOAc (9/1) to afford a pale yellow solid (1.59 g, 94%). mp 68~70 ^oC; IR (KBr)υ2927 (m), 2857 (w), 2220 (m), 2150 (w), 1444 (m), 843 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.27 (s, 9H), 0.85~0.89 (m, 6H), 1.26~1.33 (m, 38H), 1.62~1.67 (m, 4H), 2.74 (m, J = 6.0 Hz, 4H), 7.32 (s, 1H), 7.34 (s, 1H), 7.49 (t, J = 2.0 HZ, 1H), 7.56 (d, J = 2.0 Hz, 2H), 8.82 (s,

1H), 8.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ –0.1, 14.0, 29.2, 29.3, 29.4, 29.6, 30.4, 31.2, 31.8, 33.8, 34.0, 34.8, 87.0, 91.8, 96.8, 99.8, 103.5, 117.8, 120.1, 123.7, 124.4, 127.1, 132.6, 133.1, 142.9, 150.7, 151.0, 158.6; MS (m/z, FAB$^+$) 713(100), 698 (20), 658 (14), 642 (35), 628 (10), 586 (8), 555 (4); HRMS cacld for $C_{49}H_{69}N_2Si$: 713.5230; found 713.5221.



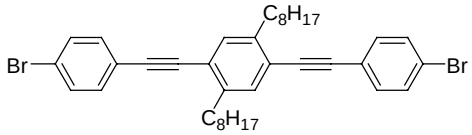
7

Compound **6** (1.59 g, 2.23 mmol) was dissolved in THF (25 mL) and MeOH (10 mL), 2N NaOH (1.5 mL, 1.5 mmol) was added, the resulting mixture was stirred at room temperature for 24 hours. Removed the solvents in vacuum vacuo, the residue was added H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 20 mL), the combined organic solution was dried over $MgSO_4$ and concentrated in vacuo to afford brownish solid (1.34g, 94%) which was used for the next coupling reaction without further purification. Further coupling reaction was carried out by mixing **1** (544 mg, 1.9 mmol) with $Pd(PPh_3)_4$ (100 mg, 0.09 mmol) and CuI (10 mg, 0.05 mmol) in THF (60 mL). To this solution was stirred for 10 min. at room temperature. iPr_2NH (1.27 mL, 9 mmol) was added, the mixture was refluxed for another 8 hours and filtered through a short Al_2O_3 column. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel and eluted with hexane/EtOAc (3/1) to afford **7** as a pale yellow solid (1.46 g, 96%). mp 166~168 ^{o}C; IR (KBr) υ2958 (m), 2858 (m), 2218 (m), 1442 (m), 1397 (m), 1184 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84~0.87 (m, 6H), 1.18~1.38 (m, 38H), 1.62~1.72 (m, 4H), 2.78~2.82 (t, *J* = 7.8 Hz, 2H), 2.85~2.89 (t, *J* = 7.8 Hz, 2H), 7.41 (s, 1H), 7.49 (t, *J* = 1.6 Hz, 1H), 7.53 (s, 1H), 7.57 (d, *J* = 1.6 Hz, 2H), 8.81 (s, 2H), 8.84 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.6, 29.2, 29.4, 29.5, 30.5, 30.6, 31.3, 31.8, 33.9, 34.0, 34.9, 87.0, 87.6, 92.0, 96.5, 117.7, 119.1, 120.1, 121.7, 122.7, 124.5, 127.2, 132.6, 133.6, 142.6, 146.8, 151.1, 158.1, 158.8; MS (m/z, FAB$^+$) 797 (90), 741 (8), 641 (40), 587 (10), 307 (100), 289 (14), 202 (10); HRMS cacld for $C_{50}H_{62}{}^{79}BrN_4$: 797.4158; found 797.4129, cacld for $C_{50}H_{62}{}^{81}BrN_4$: 799.4137; found 799.4149.



8

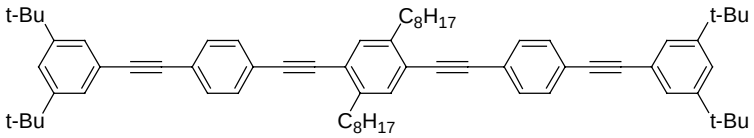
To a solution of **7** (753 mg, 1 mmol), 1,3-di-t-butyl-5-ethynylbenzene (220 mg, 1.1 mmol), $Pd(PPh_3)_4$ (57 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol) in THF (25 mL) was stirred at room temperature for 10 min. iPr_2NH (0.25 mL, 1.9 mmol) was introduced, the resulting mixture was refluxed for 1 hour. After cooled to room temperature, MeOH (30 mL) was added to precipitate the crude product, pure product as a pale yellow solid (684 mg, 79%) was isolated by reprecipitation from MeOH/$CHCl_3$ and further washed with hot hexane. mp 236~238 ^oC; IR (KBr) υ2960 (m), 2929 (m), 2219 (w), 1495 (w), 1366 (w), 1247 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.86~0.87 (m, 6H), 1.26~1.35 (m, 56H), 1.71 (m, 4H), 2.78~2.82 (t, *J* = 7.5 Hz, 2H), 2.88~2.91 (t, *J* = 7.5 Hz, 2H), 7.41~7.42 (m, 3H), 7.48 (t, *J* = 1.8 Hz, 1H), 7.49 (t, *J* = 1.8 Hz, 1H), 7.55 (s, 1H), 7.57 (d, *J* = 1.8 Hz, 2H), 8.84 (s, 2H), 8.87(s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.6, 29.2, 29.3, 30.5, 31.3, 31.9, 33.9, 34.5, 81.5, 87.1, 93.0, 96.6, 117.7, 118.3, 120.1, 121.9, 122.6, 124.1, 126.1, 132.6, 133.7, 142.6, 143.8, 150.5, 151.2, 158.8; MS (m/z, FAB^+) 931 (50), 876 (2), 613 (3), 460 (7), 307 (100), 289 (50), 242 (3); HRMS cacld for $C_{66}H_{82}N_4$: 930.6539; found 930.6542.



9

To a mixture of 1,4-diethynyl-2,5-dioctylbenzene (1.69 g, 4.8 mmol), 2-bromo-4-iodobenzene (2.72 g, 9.62 mmol), $Pd(PPh_3)_4$ (100 mg, 0.09 mmol), CuI (40 mg, 0.21 mmol) in THF (60 mL) was stirred for 10 min. iPr_2NH (2.68 mL, 19 mmol) was introduced, the resulting solution was stirred at room temperature for 10 hrs. The ammonium salt was removed by filtration through a short Al_2O_3 column and washed with Et_2O (2 x 20 ml). The combined filtrate was concentrated in vacuo. Pure **9** (2.89 g) as a pale yellow solid was isolated in 91% yield by column chromatography on silica gel and eluted with EtOAc/hexane (9/1). mp 59~61^oC; IR (KBr)υ2923 (m), 2359 (w), 1501 (w), 1461 (m), 1071 (w), 824 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.85~0.89 (m, 6H), 1.26~1.39 (m, 20H), 1.65~1.72 (m, 4H), 2.76~2.80 (t, *J* = 7.8 Hz, 4H), 7.34 (s, 2H), 7.39 (d, *J* = 4 Hz, 4H), 7.48 (t, *J* = 4 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.6,

29.3, 29.4, 29.5, 30.6, 31.8, 34.1, 89.5, 92.9, 122.4, 122.5, 131.7, 132.3, 132.8, 142.3; MS (m/z, FAB^+) 660 (88), 580 (10), 482 (12), 307 (16), 289 (20), 215 (20); HRMS cacld for $C_{38}H_{44}{}^{79}Br_2$: 658.1810; found 658.1769, cacld for $C_{38}H_{44}{}^{79}Br^{81}Br$: 660.1789; found 660.1780, cacld for $C_{38}H_{44}{}^{81}Br_2$: 662.1769; found 662.1749.



10

To a solution of **9** (504 mg, 0.76 mmol), 1,3-di-t-butyl-5-ethynylbenzene (343 mg, 1.6 mmol), $Pd(PPh_3)_4$ (46 mg, 0.04 mmol), CuI (10 mg, 0.05 mmol) in THF (25 mL) was stirred for 10 min. at room temperature. iPr_2NH (0.41 mL, 2.9 mmol) was introduced. The resulting mixture was refluxed for 3 hours. After cooled to room temperature, MeOH (30 mL) was added to precipitate the crude product. Pure **10** (651 mg) was isolated in 92% yield as a yellow solid from recrystallization with MeOH/$CHCl_3$. mp 99~101 ^oC; IR (KBr) υ2963 (m), 2925 (m), 2861 (w), 2363 (w), 2341 (w), 1588 (w), 1470 (w), 1363 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.85~0.88 (m, 6H), 1.25~1.39 (m, 56H), 1.66~1.70 (m, 4H), 2.76~2.80 (t, J = 7.6 Hz, 4H), 7.35~7.50 (m, 16H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.7, 29.3, 29.5, 30.6, 31.3, 31.9, 34.1, 34.8, 72.9, 82.5, 87.0, 89.5, 91.7, 92.9, 120.9, 121.8, 122.2, 122.4, 123.0, 125.8, 125.9,126.7, 131.6, 132.3, 150.9; MS (m/z, FAB^+) 931 (3), 797 (4), 660 (7), 460 (15), 307 (100), 289 (50), 242 (4); HRMS cacld for $C_{70}H_{86}$: 926.6730; found 926.6738.