Supporting Information
for

A divergent synthesis of 3,10-dialkylpicenes

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1. Experimental Details

General

All reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (150 ºC) and heated under reduced pressure prior to use. Solvents employed as eluents and other routine operations, as well as anhydrous solvents were purchased from commercial suppliers and employed without any further purification. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. Silica gel column chromatography was carried out using Silica gel 60 N (spherical, neutral, 40-100 μm) from Kanto Chemicals Co., Ltd. The 1H and 13C{1H} NMR spectra were recorded on Mercury-300 (300 MHz), 400-NMR ASW (400 MHz), and Varian INOVA-600 (600 MHz) spectrometers. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu Capillary Column (CBP1-M25-025) and Shimadzu C-R6A-Chromatopac integrator. GC/MS analyses were carried out on a SHIMADZU GC-17A equipped with a SHIMADZU QP-5050 GC-MS system. High-resolution mass spectra (HRMS) analyses were carried out on a JEOL JMS-700 MStation. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyser at Okayama University.

1,4-Dichloro-2,3-diiodobenzene (6) and 3,10-dimethoxypicene (9) were synthesized according to the literature.1

Preparation of 1-Bromo-3-decylbenzene (2). To a solution of 1,3-dibromobenzene (4.7 g, 20 mmol) in diethyl ether, was added dropwise a solution of nBuLi (12.3 mL, 20 mmol, 1.63 M in hexane) at –78 ºC over 10 min. After the reaction mixture was stirred at –78 ºC for 1 h, 1-bromodecane (4.8 g, 22 mmol) was added and the solution was allowed to warm to room temperature. After 4 h, the reaction was quenched with water, extracted with diethyl ether, washed by brine, and dried over MgSO4. After the volatiles were removed under vacuum, the crude product was subjected to column chromatography (hexane as eluent) to afford the desired product 2 (5.34 g, 18 mmol) in 90% yield as colorless liquid. FT-IR (neat, cm\(^{-1}\)): 2955 (m), 2924 (s), 2853 (s), 1595 (w), 1568 (w), 1468 (w), 1070 (w), 777 (w), 692 (w). 1H NMR (CDCl3, 600 MHz, rt): δ 0.90 (t, \(J = 7.2\) Hz, 3H), 1.28-1.35 (m, 14H), 1.60 (quin, \(J = 7.2\) Hz, 2H), 2.58 (t, \(J = 7.8\) Hz, 2H), 7.10 (d, \(J = 7.8\) Hz, 1H), 7.14 (t, \(J = 7.8\) Hz, 1H), 7.31 (dt, \(J = 7.8\) and 1.2 Hz, 1H), 7.34 (t, \(J = 1.2\) Hz, 1H); 13C{1H} NMR (CDCl3, 151 MHz, rt) δ 14.3, 22.8, 29.4, 29.5, 29.6, 29.7, 29.8, 31.4, 32.1, 35.8, 122.5, 127.2, 128.8, 129.9, 131.6, 145.4.
Preparation of ((3-Decylphenyl)ethynyl)trimethylsilane (3). To a two-necked round bottom flask, were added compound 2 (5.0 g, 17 mmol), PdCl2(PPh3)2 (119 mg, 0.17 mmol, 1 mol %), CuI (162 mg, 0.85 mmol, 5 mol %), trimethylamine (40 mL), pyridine (40 mL), and trimethylsilylethylene (3.88 mL, 20.4 mmol) under an argon atmosphere. The reaction mixture was heated up to 80 °C and stirred overnight. After being cooled to room temperature, the mixture was filtered through Celite. Removal of the solvents by evaporation afforded the crude product, which was purified by column chromatography on silica gel (hexane as eluent) to afforded 3 (4.65 g, 14.8 mmol) as colorless liquid in 87% yield. FT-IR (neat, cm⁻¹): 2957 (s), 2926 (s), 2855 (s), 2153 (m), 1600 (w), 1481 (m), 1466 (m), 1250 (s), 854 (s), 843 (s), 793 (w), 760 (m), 694 (m), 648 (w). 1H NMR (CDCl3, 400 MHz, rt): δ 0.25 (s, 9H), 0.89 (t, \( J = 6.8 \) Hz, 3H), 1.26-1.30 (m, 16H), 2.56 (t, \( J = 7.8 \) Hz, 2H), 7.12 (d, \( J = 7.6 \) Hz, 1H), 7.20 (t, \( J = 7.5 \) Hz, 1H), 7.27 (d, \( J = 6 \) Hz, 1H), 7.30 (s, 1H); 13C{1H} NMR (CDCl3, 101 MHz, rt) δ 0.0, 14.1, 22.7, 29.2, 29.3, 29.5, 29.56, 29.60, 31.3, 31.9, 35.7, 93.5, 105.5, 122.8, 128.1, 128.8, 129.2, 131.9, 142.9. MS (EI, m/z (relative intensity)): 314 (M⁺, 26), 300 (29), 299 (100), 173 (56), 172 (23), 73 (80). Anal. Caled for C21H34Si: C, 80.18; H, 10.89%. Found: C, 80.43; H, 11.07%.

Preparation of 1-Decyl-3-ethynylbenzene (4). To a solution of 3 (4.4 g, 14 mmol) in THF (50 mL) and MeOH (30 mL), was added K2CO3 (2.89 g, 21 mmol) and H2O (1.2 mL). The solution was stirred at room temperature for 3 h prior to quenching with saturated aqueous NH4Cl. The reaction mixture was extracted with diethyl ether, washed with brine, and dried over MgSO4. The target product 4 (2.2 g, 9.08 mmol, 65% yield) was isolated by silica gel column chromatography using hexane as eluent. FT-IR (neat, cm⁻¹): 3312 (m), 2955 (s), 1481 (w), 1466 (m), 793 (m), 694 (m), 648 (w). 1H NMR (CDCl3, 400 MHz, rt): δ 0.89 (t, \( J = 7.2 \) Hz, 3H), 1.27-1.31 (m, 16H), 2.58 (t, \( J = 7.8 \) Hz, 2H), 3.05 (s, 1H), 7.17 (d, \( J = 7.5 \) Hz, 1H), 7.23 (t, \( J = 7.3 \) Hz, 1H), 7.32 (d, \( J = 7.2 \) Hz, 1H), 7.33 (s, 1H); 13C{1H} NMR (CDCl3, 101 MHz, rt) δ 14.3, 22.8, 29.4, 29.5, 29.6, 29.7, 29.8, 31.4, 32.1, 35.8, 76.8, 84.1, 122.0, 128.3, 129.2, 132.2, 143.2. MS (EI, m/z (relative intensity)): 242 (M⁺, 4), 157 (17), 131 (19), 130 (21), 129 (27), 128 (25), 118 (21), 117 (30), 116 (67), 115 (100). HRMS (EI) Caled for C18H26: 242.2035. Found: 242.2055.

Preparation of 4,4,5,5-Tetramethyl-2-[(1Z)-2-(3-decylphenylethenyl)]-1,3,2-dioxaborolane (5). To a two-necked round bottom flask equipped with a magnetic stirrer bar, were added [RhCl(cod)]2 (37 mg, 0.075 mmol, 1.5 mol %), cyclohexane (15 mL), \( ^{3} \text{Pr}_3 \text{P} \) (0.057 mL, 0.3 mmol, 6 mol %), NEt3 (5 mL), and HBpin (0.725 mL, 5 mmol) under argon. After the mixture was stirred at 0 °C for 30 min, 4 (2.4 g, 10 mmol) was added. The reaction mixture was then stirred at 0 °C for an additional 10 h prior to quenching with MeOH. The
reaction mixture was filtrated through Celite and the volatiles were evaporated under vacuum to afford brown oil, which was purified by bulb to bulb distillation to give compound 5 (2.23 g, 6.0 mmol) in 60% yield as colourless liquid. FT-IR (neat, cm⁻¹): 2955 (s), 2926 (s), 2855 (s), 1620 (s), 1427 (m), 1371 (m), 1258 (s), 1144 (s), 968 (s), 808 (m), 698 (m). 

\[^{1}\text{H NMR (CDCl}_3, 400 MHz, rt): \delta \] 0.88 (t, J = 7.2 Hz, 3H), 1.22-1.34 (m, 26H), 1.61 (q, J = 7.7 Hz, 2H), 2.58 (t, J = 7.6 Hz, 2H), 5.56 (d, J = 15.2 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.17-7.21 (m, 1H), 7.21 (d, J = 15.2 Hz, 1H), 7.32 (d, J = 7.7 Hz, 1H), 7.45 (bs, 1H); 

\[^{13}\text{C}\{^{1}\text{H}\} \text{NMR (CDCl}_3, 101 MHz, rt) \delta \] 14.3, 22.8, 25.0 (x 2), 29.5, 29.6, 29.69, 29.76, 29.78, 31.6, 32.1, 36.2, 83.6, 126.4, 128.0, 128.3, 128.7, 138.4, 142.7, 148.6. The carbon signal adjacent to B was not observed due to low intensity. MS (EI, m/z (relative intensity)): 370 (M⁺, 28), 313 (28), 285 (28), 284 (12), 242 (22), 157 (25), 144 (39), 143 (100), 129 (26), 117 (23), 85 (42), 84 (93). 

Anal. Calcd for C\textsubscript{24}H\textsubscript{39}BO\textsubscript{2}: C, 77.83; H, 10.61%. Found: C, 77.51; H, 10.41%.

**Preparation of 1,4-Dichloro-2,3-bis[(1Z)-2-(3-decylphenyl)ethenyl]benzene (7).** To a 50 mL Schlenk tube charged with a magnetic stirrer bar, were successively added 1,4-dichloro-2,3-diiodobenzene (6) (199 mg, 0.5 mmol), 5 (407 mg, 1.1 mmol), PEPPSI-IPr (34 mg, 0.05 mmol, 10 mol %), KOH (168 mg, 3 mmol), H\textsubscript{2}O (0.2 mL) and toluene (1 mL). The reaction mixture was stirred at 110 °C for 12 h. After being cooled to room temperature, the reaction mixture was quenched with 1 M HCl and extracted by diethyl ether. The volatiles were removed under vacuum to give the crude product, which was purified by column chromatography to afford 7 (236 mg, 0.374 mmol) in 75% yield as yellow oil. FT-IR (neat, cm⁻¹): 2954 (s), 2924 (s), 2853 (s), 2357 (w), 1601 (w), 1456 (m), 1435 (m), 1128 (m), 903 (w), 804 (s), 696 (s). 

\[^{1}\text{H NMR (CDCl}_3, 300 MHz, rt): \delta \] 0.89 (t, J = 7.2 Hz, 6H), 1.26-1.43 (m, 32H), 2.43 (t, J = 7.5 Hz, 4H), 6.00 (d, J = 12.1 Hz, 2H), 6.49 (d, J = 12.1 Hz, 2H), 6.74 (s, 2H), 6.77 (d, J = 7.5 Hz, 2H), 6.96 (d, J = 7.5 Hz, 2H), 7.07 (t, J = 7.5 Hz, 2H), 7.29 (s, 2H); 

\[^{13}\text{C}\{^{1}\text{H}\} \text{NMR (CDCl}_3, 101 MHz, rt) \delta \] 14.3, 22.9, 29.3, 29.5, 29.66, 29.74, 29.8, 31.3, 32.1, 35.9, 125.5, 125.6, 127.9, 128.2, 128.3, 129.2, 132.2, 133.6, 136.9, 137.7, 142.8. 

Anal. Calcd for C\textsubscript{42}H\textsubscript{56}Cl\textsubscript{2}: C, 79.84; H, 8.93%. Found: C, 79.52; H, 8.71%.

**Preparation of 3,10-Didecylpicene (8-C\textsubscript{10}).** To a 50 mL Schlenk tube charged with a magnetic stirrer bar, were added PCy\textsubscript{3} (11.5 mg, 0.04 mmol, 20 mol %), PdCl\textsubscript{2}(NCPh)\textsubscript{2} (7.6 mg, 0.02 mmol, 10 mol %), and DMA (1 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 10 min, Cs\textsubscript{2}CO\textsubscript{3} (130 mg, 0.4 mmol), PivOH (8.3 mg, 0.08 mmol, 40 mol %), and 7 (126 mg, 0.2 mmol) were successively added to the reaction mixture. The reaction mixture was heated up to 150 °C and stirred for 24 h prior to quenching with 1 M HCl, and filtered through Celite, and extracted with CHCl\textsubscript{3}. The crude product was purified by column chromatography to yield 8-C\textsubscript{10} (22.3 mg, 0.04 mmol) in 20% yield as a white solid. 

MP:
>300 °C. FT-IR (neat, cm⁻¹): 2955 (s), 2922 (s), 2897 (s), 2872 (s), 2855 (s), 2826 (s), 1713 (m), 1466 (m), 1263 (m), 1096 (m), 1076 (m), 785 (m), 507 (m). ¹H NMR (CDCl₃, 600 MHz, rt): δ 0.88 (t, J = 7.2 Hz, 6H), 1.28-1.41 (m, 28H), 1.77 (quin, J = 7.5 Hz, 4H), 2.86 (t, J = 7.8 Hz, 4H), 7.58 (dd, J = 8.5 and 1.2 Hz, 2H), 7.78 (s, 2H), 7.97 (d, J = 9.1 Hz, 2H), 8.74 (d, J = 9.2 Hz, 2H), 8.75 (d, J = 8.5 Hz, 2H), 8.90 (s, 2H); ¹³C{¹H} NMR (CDCl₃, 151 MHz, rt) δ 14.3, 22.8, 29.5, 29.6, 29.72, 29.77, 29.79, 31.7, 32.1, 36.1, 121.66, 121.73, 123.1, 127.4, 127.5, 128.2, 128.4, 128.6, 128.8, 132.2, 141.5. HRMS (EI) Calcd for C₄₂H₅₄: 558.4226. Found: 558.4240.

Preparation of 3,10-Bis[(triisopropylsilyl)ethynyl]picene (10). To a 50 mL Schlenk tube containing ethynyltriisopropylsilane (525 μL, 2.36 mmol) under an argon atmosphere, was added dropwise ethylmagnesium bromide (THF solution, 2.6 mmol) at 0 °C and the reaction mixture was stirred at 50 °C for 1 h to prepare [(triisopropylsilyl)ethynyl]magnesium bromide. After the mixture was cooled to room temperature, Ni(cod)₂ (32.5 mg, 0.12 mmol, 20 mol %), ICy•HCl (63.4 mg, 0.24 mmol, 40 mol %), and 3,10-dimethoxypicene (9) (200 mg, 0.59 mmol) were added. After 3 min, the volatiles were removed under vacuum. To the resulting mixture, 23.6 mL of mesitylene was added and the reaction mixture was stirred at 140 °C for 72 h. After the reaction mixture was extracted with CH₂Cl₂ and washed with water, the volatiles were removed by a rotary evaporator, and high-boiling mesitylene was removed under reduced pressure (1 mmHg) at 150 °C. The crude product was purified by column chromatography (hexane:CHCl₃ = 1:1), followed by washing with hexane to afford the desired product 10 (287 mg, 0.45 mmol) in 76% yield as a white solid. Mp: 242-243 °C. FT-IR (neat, cm⁻¹): 2943 (s), 2889 (s), 2864 (s), 1593 (w), 1462 (s), 1382 (w), 1244 (m), 997 (m), 951 (s), 883 (s), 804 (s), 748 (s), 685 (s). ¹H NMR (CDCl₃, 600 MHz, rt): δ 1.20 (s, 42H), 7.78 (dd, J = 8.6 and 1.7 Hz, 2H), 7.95 (d, J = 9.1 Hz, 2H), 8.14 (d, J(long-range) = 1.6 Hz, 2H), 8.73 (d, J = 8.2 Hz, 4H), 8.85 (s, 2H); ¹³C{¹H} NMR (CDCl₃, 151 MHZ, rt) δ 11.6, 18.9, 91.9, 107.3, 121.9, 122.0, 122.4, 123.3, 127.3, 128.7, 129.1, 130.08, 130.12, 131.7, 132.4; ²⁹Si{¹H} NMR (CDCl₃, 119 MHZ, rt) δ −1.63. Anal. Calcd for C₄₄H₄₂Si₂: C, 82.69; H, 8.52%. Found: C, 82.47; H, 8.28%.

Preparation of 10 using a Microwave Reactor. To a 20 mL Schlenk tube containing ethynyltriisopropylsilane (79 μL, 0.35 mmol) under an argon atmosphere, was added dropwise ethylmagnesium bromide (THF solution, 0.39 mmol) at 0 °C and the reaction mixture was stirred at 50 °C for 1 h to prepare [(triisopropylsilyl)ethynyl]magnesium bromide. After the mixture was cooled to room temperature, Ni(cod)₂ (4.88 mg, 0.036 mmol, 20 mol %), ICy•HCl (9.51 mg, 0.036 mmol, 40 mol %), and 3,10-dimethoxypicene (9) (30 mg, 0.088 mmol) were added. After 3 min, the volatiles were removed under vacuum. To the resulting mixture, 3.5 mL of mesitylene was added and the reaction mixture was stirred at 140 °C for 10 min. Then, the
mixture was transferred to a 5 mL vial via syringe and heated at 140 °C for 12 h in a microwave reactor. After being cooled to room temperature, the reaction mixture was extracted with CH$_2$Cl$_2$ and washed with water, the volatiles were removed by a rotary evaporator, and high-boiling mesitylene was removed under reduced pressure (1 mmHg) at 150 ºC. The mixture was containing the desired product 10 in 75% NMR yield.

**3-Methoxy-10-[2-[tris(1-methylethyl)silyl]ethynyl]picene (10’).** White solid. Yield was 9% (27 mg, 0.05 mmol). Mp: >300 °C. FT-IR (neat, cm$^{-1}$): 2943 (s), 2891 (m), 2864 (s), 2151 (s), 1624 (m), 1464 (s), 1254 (s), 1173 (m), 883 (s), 806 (s), 745 (s), 683 (s). $^1$H NMR (CDCl$_3$, 600 MHz, rt): $\delta$ 1.20 (s, 21H), 4.01 (s, 3H), 7.35-7.39 (m, 2H), 7.77 (dd, $J = 9.0$ and 1.8 Hz, 1H), 7.95 (dd, $J = 9.1$ and 1.9 Hz, 2H), 8.13 (d, $J = 2$ Hz, 1H). 8.72-8.76 (m, 4H), 8.85 (bs, 2H); $^{13}$C$\{^1$H$\}$ NMR (CDCl$_3$, 151 MHz, 40 ºC) $\delta$ 11.7, 18.9, 55.6, 91.8, 107.5, 108.3, 118.1, 121.6, 121.86, 121.93, 122.3, 122.4, 123.2, 125.0, 125.3, 127.2, 127.3, 127.5, 128.0, 129.32, 129.33, 130.0, 130.4, 131.2, 132.4, 133.7, 158.7. HRMS (EI) Calcd for C$_{34}$H$_{36}$OSi: 488.2535. Found: 488.2529.

**Preparation of 3,10-Diethynylpicene (11).** To a 50 mL Schlenk tube equipped with a magnetic stirrer bar, were added 10 (204 mg, 0.319 mmol) dissolved in THF (25 mL) and a solution of $^n$Bu$_4$NF (0.96 mL, 0.96 mmol, 1 M in THF). After being stirred at room temperature for 1 h, the reaction was quenched with 1 M HCl. The product was extracted with dichloromethane and water, and the volatiles were removed by rotary evaporation. The crude material was purified by washing with hexane, a small portion of acetone, and methanol to afford the title product 11 (95 mg, 0.291 mmol) in 91% yield as a white solid. Mp: 170 °C (dec). FT-IR (neat, cm$^{-1}$): 3304 (s), 1593 (m), 1468 (m), 1267 (s), 897 (s), 810 (s), 754 (s), 650 (s), 621 (s). $^1$H NMR (CDCl$_3$, 600 MHz, rt): $\delta$ 3.23 (s, 2H), 7.81 (d, $J = 7.9$ Hz, 2H), 7.99 (d, $J = 8.6$ Hz, 2H), 8.18 (s, 2H), 8.79 (bd, $J = 4.0$ Hz, 4H), 8.91 (s, 2H); $^{13}$C$\{^1$H$\}$ NMR (CDCl$_3$, 151 MHz, 40 ºC) $\delta$ 78.3, 83.9, 120.5, 122.2, 122.5, 123.5, 127.4, 128.8, 129.2, 130.0, 130.5, 131.7, 132.8. HRMS (EI) Calcd for C$_{26}$H$_{14}$: 326.1096. Found: 326.1078.

**Representative Procedure for the Alkylation of 11.** **Preparation of 3,10-Di(1-heptynyl)picene (12-C$_5$).** To a solution of 11 (32 mg, 0.1 mmol) in THF (10 mL) in a 50 mL Schlenk tube, was added dropwise TMEDA (60 μL, 0.4 mmol) and $^n$BuLi (250 μL, 0.4 mmol) at −30 ºC. After the solution mixture was stirred at 70 °C for 3 h, the mixture was cooled to −78 °C, then TBAI (7.4 mg, 0.02 mmol, 20 mol %) and 1-bromopentane (74 μL, 0.6 mmol, 6.0 equiv) were added. The reaction mixture was stirred at −78 °C for 1 h, and heated to a gentle reflux (70 °C) for 24 h. The mixture was cooled to room temperature and quenched with 1 M HCl. The crude mixture was extracted with CH$_2$Cl$_2$, washed with brine, and dried over MgSO$_4$. After the volatiles were evaporated, the crude product was purified by column chromatography (hexane:CHCl$_3$ = 1:1) to afford 12-C$_5$ (21.5 mg, 0.046 mmol) in 46% yield as a white solid. Mp: 243-244 °C. FT-IR (neat, cm$^{-1}$): 2953 (m),
2930 (s), 2860 (m), 1445 (w), 1274 (m), 887 (m), 810 (s), 750 (m). $^1$H NMR (CDCl$_3$, 600 MHz, rt): $\delta$ 0.97 (t, $J = 7.5$ Hz, 6H), 1.39-1.45 (m, 4H), 1.49-1.54 (m, 4H), 1.70 (quin, $J = 7.2$ Hz, 4H), 2.50 (t, $J = 6.9$ Hz, 4H), 7.70 (dd, $J = 8.4$ and 1.8 Hz, 2H), 7.91 (d, $J = 9.0$ Hz, 2H), 8.03 (d, $J$(long-range) = 1.2 Hz, 2H), 8.69 (d, $J = 9.0$ Hz, 4H), 8.80 (s, 2H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 151 MHz, rt) $\delta$ 14.2, 19.7, 22.4, 28.7, 31.4, 80.8, 91.8, 121.9, 122.2, 122.4, 123.2, 127.2, 128.6, 128.8, 129.6, 129.9, 131.6, 131.8. HRMS (EI) Calcd for C$_{36}$H$_{34}$: 466.2661. Found: 466.2651.

3,10-Di(1-octynyl)picene (12-C$_6$). White solid. Yield was 46% (17 mg, 0.035 mmol). Mp: 241-242 °C. FT-IR (neat, cm$^{-1}$): 2961 (s), 2930 (s), 2857 (m), 1466 (m), 1445 (w), 1261 (s), 1090 (s), 1028 (s), 893 (m), 810 (s). $^1$H NMR (CDCl$_3$, 600 MHz, rt): $\delta$ 0.94 (t, $J = 7.2$ Hz, 6H), 1.36-1.39 (m, 8H), 1.50-1.55 (m, 4H), 1.69 (quin, $J = 7.2$ Hz, 4H), 2.50 (t, $J = 7.2$ Hz, 4H), 7.70 (dd, $J = 8.4$ and 1.8 Hz, 2H), 7.91 (d, $J = 9.0$ Hz, 2H), 8.03 (d, $J$(long-range) = 1.2 Hz, 2H), 8.69 (d, $J = 9.0$ Hz, 4H), 8.81 (s, 2H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 151 MHz, rt) $\delta$ 14.3, 19.8, 22.8, 28.86, 28.94, 31.6, 80.8, 91.8, 121.9, 122.2, 122.4, 123.2, 127.2, 128.6, 128.8, 129.6, 129.9, 131.6, 131.8. HRMS (EI) Calcd for C$_{38}$H$_{38}$: 494.2974. Found: 494.2961.

3,10-Di(1-decynyl)picene (12-C$_8$). White solid. Yield was 51% (15 mg, 0.027 mmol). Mp: 235-236 °C. FT-IR (neat, cm$^{-1}$): 2957 (s), 2926 (s), 2855 (s), 1593 (w), 1466 (s), 1261 (s), 1090 (s), 1022 (s), 893 (s), 810 (s). $^1$H NMR (CDCl$_3$, 600 MHz, rt): $\delta$ 0.92 (t, $J = 6.9$ Hz, 6H), 1.32-1.39 (m, 16H), 1.51-1.54 (m, 4H), 1.69 (quin, $J = 7.8$ Hz, 4H), 2.50 (t, $J = 7.2$ Hz, 4H), 7.70 (dd, $J = 8.4$ and 1.8 Hz, 2H), 7.91 (d, $J = 9.6$ Hz, 2H), 8.03 (d, $J$(long-range) = 1.2 Hz, 2H), 8.69 (d, $J = 9.0$ Hz, 4H), 8.81 (s, 2H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 151 MHz, rt) $\delta$ 14.1, 19.6, 22.7, 28.8, 29.0, 29.18, 31.9, 80.7, 91.6, 121.8, 122.0, 122.3, 123.1, 127.1, 128.4, 128.7, 129.5, 129.7, 131.4, 131.6. HRMS (EI) Calcd for C$_{42}$H$_{46}$: 550.3600. Found: 550.3578.

3,10-Di(1-dodecynyl)picene (12-C$_{10}$). White solid. Yield was 62% (37 mg, 0.060 mmol). Mp: 215-216 °C. FT-IR (neat, cm$^{-1}$): 2957 (m), 2920 (s), 2851 (m), 1470 (s), 1261 (s), 1096 (m), 1020 (m), 893(m), 810 (s), 752 (m). $^1$H NMR (CDCl$_3$, 600 MHz, rt): $\delta$ 0.90 (t, $J = 7.2$ Hz, 6H), 1.31-1.39 (m, 16H), 1.51-1.54 (m, 4H), 1.69 (quin, $J = 7.8$ Hz, 4H), 2.50 (t, $J = 7.2$ Hz, 4H), 7.69 (dd, $J = 8.4$ and 1.2 Hz, 2H), 7.91 (d, $J = 9.6$ Hz, 2H), 8.03 (d, $J$(long-range) = 1.2 Hz, 2H), 8.68 (d, $J = 9.0$ Hz, 4H), 8.80 (s, 2H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 151 MHz, rt) $\delta$ 14.3, 19.8, 22.9, 29.0, 29.2, 29.4, 29.5, 29.7, 29.8, 32.1, 80.8, 91.8, 121.9, 122.2, 122.4, 123.2, 127.2, 128.6, 128.8, 129.6, 129.9, 131.6, 131.8. HRMS (EI) Calcd for C$_{46}$H$_{54}$: 606.4226. Found: 606.4213.

3,10-Di(1-tetradecynyl)picene (12-C$_{12}$). White solid. Yield was 45% (18 mg, 0.027 mmol). Mp: 209-210 °C. FT-IR (neat, cm$^{-1}$): 2959 (m), 2918 (s), 2849 (m), 1470 (m), 1261 (s), 1098 (s), 1020 (s), 893(m), 806 (s), 752 (w). $^1$H NMR (CDCl$_3$, 600 MHz, rt): $\delta$ 0.89 (t, $J = 7.2$ Hz, 6H), 1.28-1.38 (m, 32H), 1.49-1.55 (m, 4H), 1.68 (quin, $J = 7.2$ Hz, 4H), 2.50 (t, $J = 7.2$ Hz, 4H), 7.70 (dd, $J = 8.4$ and 1.2 Hz, 2H), 7.92 (d, $J = 9.0$ Hz, 4H).
Representative Procedure for Hydrogenation of 8. Preparation of 3,10-Diheptylpicene (8-C_7). To a 20 mL Schlenk tube, were added Pd/C (5 wt %, 10 mg, 0.005 mmol of Pd, 20 mol %), 12-C_5 (11.2 mg, 0.024 mmol) and ethyl acetate (2.4 mL) were added, the hydrogen gas (1 atm) was introduced to the reaction vessel. After being stirred for 18 h, the reaction mixture was filtered through Celite. The volatiles were removed under reduced pressure to afford the crude product, which was washed with hexane to give the desired product 8-C_7 (7 mg, 0.0147 mmol) in 61% yield as a white solid. Mp: >300 °C. FT-IR (neat, cm⁻¹): 2955 (s), 2922 (s), 2872 (m), 2853 (s), 1625 (w), 1466 (m), 1271 (m), 1098 (w), 1022 (w), 880 (m), 808 (s), 752 (m). ¹H NMR (CDCl₃, 600 MHz, rt): δ 0.90 (t, J = 7.2 Hz, 6H), 1.28-1.43 (m, 16H), 1.78 (quin, J = 7.8 Hz, 4H), 2.86 (t, J = 7.8 Hz, 4H), 7.57 (dd, J = 8.5 and 1.8 Hz, 2H), 7.78 (d, J (long-range) = 1.2 Hz, 2H), 7.96 (d, J = 9.0 Hz, 2H), 8.74 (d, J = 9.2 Hz, 2H), 8.75 (d, J = 8.5 Hz, 2H), 8.90 (s, 2H); ¹³C⁰¹H NMR (CDCl₃, 151 MHz, rt) δ 14.3, 22.8, 29.4, 29.5, 31.7, 32.0, 36.1, 121.66, 121.73, 123.1, 127.4, 127.5, 128.2, 128.4, 128.6, 128.8, 132.2, 141.4. HRMS (EI) Calcd for C_{36}H_{42}: 474.3287. Found: 474.3304.

3,10-Dioctylpicene (8-C_8). At room temperature for 18 h. White solid. Yield was 71% (13 mg, 0.025 mmol). Mp: >300 °C. FT-IR (neat, cm⁻¹): 2957 (s), 2920 (s), 2872 (s), 2851 (s), 1626 (w), 1601 (w), 1466 (s), 1261 (s), 1097 (m), 1020 (m), 881 (m), 808 (s), 754 (m). ¹H NMR (CDCl₃, 600 MHz, rt): δ 0.89 (t, J = 7.2 Hz, 6H), 1.25-1.43 (m, 20H), 1.77 (quin, J = 7.2 Hz, 4H), 2.86 (t, J = 7.2 Hz, 4H), 7.57 (dd, J = 8.4 and 1.8 Hz, 2H), 7.78 (s, 2H), 7.97 (d, J = 9.0 Hz, 2H), 8.74 (d, J = 9.2 Hz, 2H), 8.75 (d, J = 8.5 Hz, 2H), 8.90 (s, 2H); ¹³C⁰¹H NMR (CDCl₃, 151 MHz, rt) δ 14.3, 22.8, 29.4, 29.5, 31.7, 32.0, 36.1, 121.66, 121.73, 123.1, 127.4, 127.5, 128.2, 128.4, 128.6, 128.8, 132.2, 141.4. HRMS (EI) Calcd for C_{38}H_{46}: 502.3600. Found: 502.3582.

3,10-Didecylpicene (8-C_10). At room temperature for 18 h, then 70 °C for 3 h. White solid. Yield was 67% (15 mg, 0.027 mmol). Mp: >300 °C. FT-IR (neat, cm⁻¹): 2955 (s), 2922 (s), 2872 (s), 2855 (s), 2826 (s), 1713 (m), 1466 (m), 1263 (m), 1096 (m), 1076 (m), 785 (m), 507 (m). ¹H NMR (CDCl₃, 600 MHz, rt): δ 0.88 (t, J = 7.2 Hz, 6H), 1.28-1.41 (m, 28H), 1.77 (quin, J = 7.5 Hz, 4H), 2.86 (t, J = 7.8 Hz, 4H), 7.58 (dd, J = 8.5 and 1.2 Hz, 2H), 7.78 (s, 2H), 7.97 (d, J = 9.1 Hz, 2H), 8.74 (d, J = 9.2 Hz, 2H), 8.75 (d, J = 8.5 Hz, 2H), 8.90 (s, 2H); ¹³C⁰¹H NMR (CDCl₃, 151 MHz, rt) δ 14.3, 22.8, 29.4, 29.5, 29.7, 29.9, 31.7, 32.1, 36.1, 121.66, 121.73, 123.1, 127.4, 127.5, 128.2, 128.4, 128.6, 128.8, 132.2, 141.4. HRMS (EI) Calcd for C_{42}H_{54}: 558.4226. Found: 558.4240.
3,10-Didodecylpicene (8-C12). At 70 °C for 24 h. White solid. Yield was 71% (21.8 mg, 0.036 mmol). Mp: 245-246 °C. FT-IR (neat, cm⁻¹): 2965 (s), 2922 (m), 2851 (w), 1721 (m), 1465 (w), 1414 (s), 1261 (m), 1013 (s), 866 (s), 789 (s), 700 (m), 662 (m). ¹H NMR (CDCl₃, 600 MHz, rt): δ 0.87 (t, J = 7.2 Hz, 6H), 1.28-1.43 (m, 36H), 1.77 (quin, J = 7.2 Hz, 4H), 2.86 (t, J = 7.8 Hz, 4H), 7.57 (dd, J = 8.5 and 1.8 Hz, 2H), 7.78 (s, 2H), 7.97 (d, J = 9.0 Hz, 2H), 8.74 (d, J = 9.2 Hz, 2H), 8.75 (d, J = 8.4 Hz, 2H), 8.90 (s, 2H); ¹³C {¹H} NMR (CDCl₃, 151 MHz, rt) δ 14.3, 22.8, 29.5, 29.6, 29.7, 29.77, 29.79, 29.80, 29.83, 29.85, 31.6, 32.1, 36.1, 121.66, 121.73, 123.1, 127.4, 127.5, 128.2, 128.4, 128.6, 128.8, 132.2, 141.5. HRMS (EI) Calcd for C₄₆H₆₂: 614.4852. Found: 614.4826.

3,10-Ditetradecylpicene (8-C14).² At 70 °C for 72 h. White solid. Yield was 53% (10 mg, 0.015 mmol). Mp: 209-210 °C. FT-IR (neat, cm⁻¹): 2957 (m), 2918 (s), 2851 (s), 1464 (m), 1271 (s), 806 (s), 721 (s). ¹H NMR (CDCl₃, 600 MHz, 40 °C): δ 0.88 (t, J = 7.2 Hz, 6H), 1.27-1.44 (m, 44H), 1.77 (quin, J = 7.8 Hz, 4H), 2.87 (t, J = 7.8 Hz, 4H), 7.57 (dd, J = 8.4 and 1.2 Hz, 2H), 7.78 (s, 2H), 7.96 (d, J = 9.0 Hz, 2H), 8.74 (d, J = 8.9 Hz, 2H), 8.75 (d, J = 8.3 Hz, 2H), 8.90 (s, 2H); ¹³C {¹H} NMR (CDCl₃, 151 MHz, 40 °C) δ 14.2, 22.8, 29.5, 29.6, 29.7, 29.77, 29.82, 29.83, 29.84 (∗ 2), 29.9, 31.6, 32.1, 36.1, 121.7, 121.8, 123.2, 127.4, 127.5, 128.2, 128.5, 128.7, 129.0, 132.3, 141.5.
2. Copies of $^1$H and $^{13}$C$^1$H} NMR Charts for the New Compounds

The $^1$H and $^{13}$C$^1$H} NMR spectra of 2 (in CDCl$_3$).
The $^1$H and $^{13}$C$^{(1)}$H NMR spectra of 3 (in CDCl$_3$).
The $^1$H and $^{13}$C($^1$H) NMR spectra of 4 (in CDCl$_3$).
The $^1$H and $^{13}$C($^1$H) NMR spectra of 5 (in CDCl$_3$).
The $^1$H and $^{13}$C $^1$H NMR spectra of 7 (in CDCl$_3$).
The $^1$H and $^{13}$C($^1$H) NMR spectra of 8-C$_{10}$ (in CDCl$_3$).
The $^1$H and $^{13}$C-$^1$H NMR spectra of 10 (in CDCl$_3$).
The $^1$H and $^{13}$C,$^1$H NMR spectra of 10' (in CDCl$_3$).
The $^1$H and $^{13}$C$_{^1}$H NMR spectra of 11 (in CDCl$_3$).
The $^1$H and $^{13}$C-$^1$H NMR spectra of 12-C$_5$ (in CDCl$_3$).
The $^1$H and $^{13}$C{$^1$H} NMR spectra of 12-C$_6$ (in CDCl$_3$).
The $^1$H and $^{13}$C{$^1$H} NMR spectra of 12-C$_8$ (in CDCl$_3$).
The $^1\text{H}$ and $^{13}\text{C}[^1\text{H}]$ NMR spectra of 12-C$_{10}$ (in CDCl$_3$).
The $^1$H and $^{13}$C($^1$H) NMR spectra of 12-C$_{12}$ (in CDCl$_3$).
The $^1$H and $^{13}$C $^{[1]}$H NMR spectra of 8-C$_7$ (in CDCl$_3$).
The $^1$H and $^{13}$C ($^1$H) NMR spectra of 8-C$_8$ (in CDCl$_3$).
The $^1\text{H}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 8-C$_{12}$ (in CDCl$_3$).
The $^1$H and $^{13}$C-$^1$H NMR spectra of 8-C$_{14}$ (in CDCl$_3$).
3. **Reference**
