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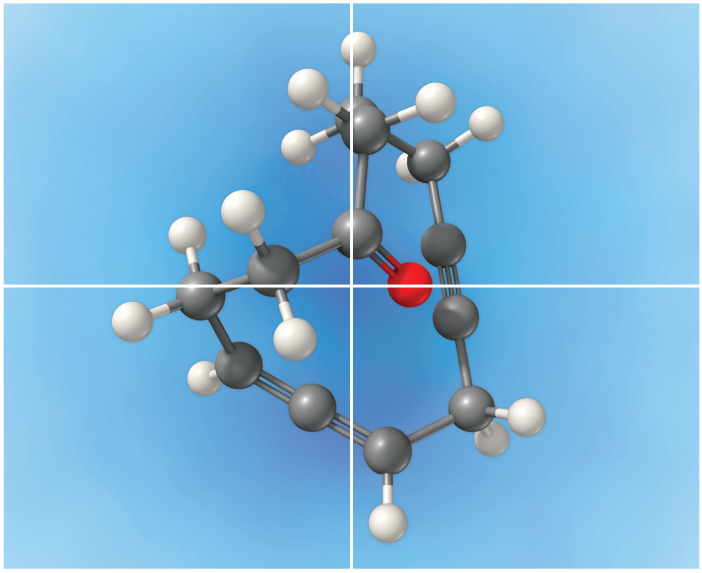

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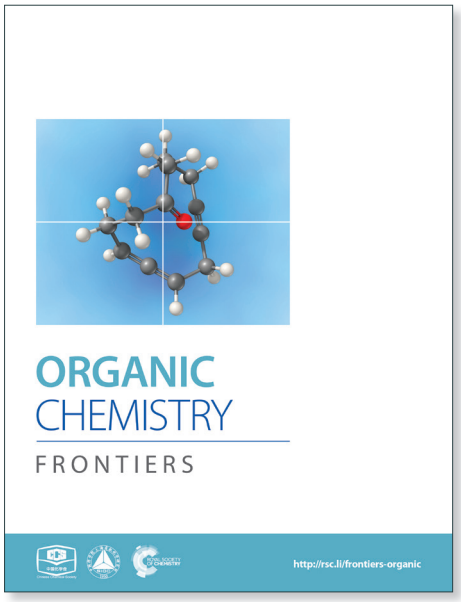

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ARTICLE TYPE

A divergent synthesis of 3,10-dialkylpicenes

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The abstract should be a single paragraph which summarises the content of the article.

A series of 3,10-dialkylated picenes has been synthesized from 3,10-dimethoxypicene through a divergent approach involving Ni-catalyzed alkynylation of a C–O bond, alkylation, and hydrogenation.

Introduction

Fused aromatic compounds containing π-conjugated systems are notable for their utility in organic semiconductors and organic field-effect transistors (OFETs).[1-8] Research in these field emerged following pioneering discoveries of organic conductors in 1954[9] and OFETs in 1986.[10] Advantageous features of fused aromatic compounds for OFET devices include their mechanical flexibility, light weight, and low costs, relative to inorganic-based FET devices. As a result a number of synthetic approaches to these molecules have been developed.

The most frequently studied class of organic semiconductors contain [*n*]acenes, in particular pentacene derivatives, due to their excellent transistor characteristics.[11] Nevertheless, the poor solubility of pentacene and higher acenes in common organic solvents hinders their processability. In addition, because of their narrow energy gaps and high HOMO energy levels, [*n*]acenes are sensitive to light and oxidants, especially in the internal rings.[12,13] Due to this reason, recently [*n*]phenacenes, armchair-structure molecules have received much attention because of high stability even in the presence of O_2 and H_2O.[14]

Picene ([5]phenacene) is an isomer of pentacene with notably high stability resulting from its large band gap (E_g = 3.3 eV) and higher ionization potential (IP = 5.5 eV).[15] An OFET device with a picene thin film displayed a high μ value, more than 1.1 $cm^2\ V^{-1}\ s^{-1}$, and, significantly, the μ value as well as the on-off ratio were dramatically improved under air/O_2 conditions.[16] Very recently, we reported an efficient synthetic route to picene by Suzuki-Miyaura coupling or Wittig reaction and sequential intramolecular cyclization via C–H bond activation.[17] With this methodology in hand, various methoxy-substituted picene derivatives were elaborated.[18] Results of theoretical calculations of HOMO and LUMO levels in methoxypicenes indicated that methoxy groups in the 3,10-positions can stabilize the HOMO energy level, the crystal structure of 3,10-dimethoxypicene revealed a 3D-herringbone structure, leading to a higher charge mobility ($1.4 \times 10^{-2}\ cm^2\ V^{-1}\ s^{-1}$) than other methoxy-substituted picenes. Despite the promising properties of 3,10-dimethoxypicene toward OFETs, its poor solubility in organic solvents limited its utilization for device fabrication by a solution process, which is desired for application in organic electronic devices. A general strategy to improve the solubility and, as a result, processability is to install long alkyl substituents onto the parent core.[19,20]

In recent years, various synthetic methods for substituted picenes have been reported. In 2010, Nakano *et al.* reported the synthesis of 3,10-dialkylpicenes through the Pt-catalyzed cycloaromatization reaction of terminal alkynes (Scheme 1A).[21] However, a drawback of this protocol is the need of an initial stage for the introduction of alkyl groups: Suzuki-Miyaura coupling of alkyl-substituted arylboronic acids with halobenzene, which limits the diversity derivatization of alkylated picenes that can be obtained. In general, although a divergent synthesis might allow for a more benign and straightforward route for the preparation of alkylated picenes, to the best of our knowledge, there is only one known example on the installation of alkyl groups onto a picene core at later stage.[22] We herein report the first general and straightforward synthesis of various 3,10-alkylated picenes from 3,10-dimethoxypicene as the common staring material. This involves introduction of alkyl groups through the Ni-catalyzed alkynylation of a C–O bond as the key step. (Scheme 1B).

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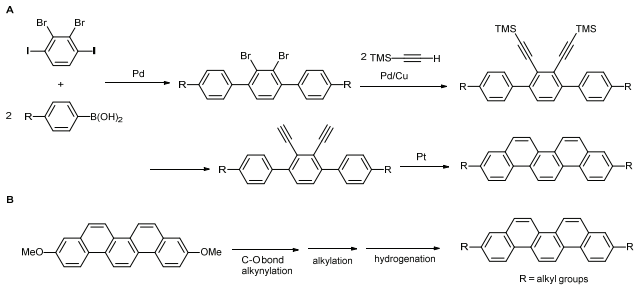
† This paper is dedicated to Professor Ei-ichi Negishi on the occasion of his 80th birthday.

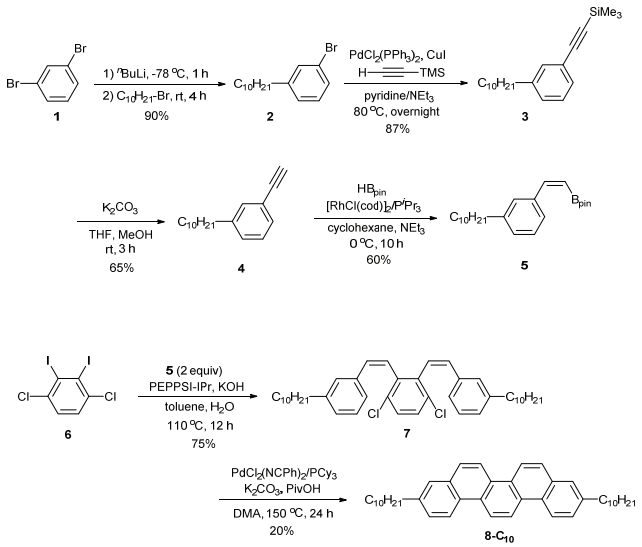
‡ Electronic Supplementary Information (ESI) available: Experimental procedures and the characterization data of the new compounds. See DOI: 10.1039/c000000x/



Scheme 1 A synthetic strategy for 3,10-alkylated picenes.

Results and discussion

To synthesize 3,10-didecylpicene (**8-C_{10}**) as a benchmark compound, we started to apply our previously reported procedure.[17] A synthetic scheme is shown in Scheme 2. A decyl group was incorporated by the reaction of 1,3-dibromobenzene (**1**) with an equimolar amount of ^{n}BuLi, followed by 1-bromodecane to afford **2** in 90% yield. Preparation of **3** was accomplished by Sonogashira-Hagihara coupling of **2** with trimethylsilylethyne. After desilylation of **3**, Rh-catalyzed hydroboration of the obtained terminal alkyne **4** with HB_{pin} gave a stereodefined (*Z*)-alkenylboronate **5** in 60% yield. Precursor **7** was prepared by Pd-catalyzed Suzuki-Miyaura coupling of **5** with 1,4-dichloro-2,3-diiodobenzene (**6**). Finally, an intramolecular double cyclization of **7** via C–H bond activation furnished the target product **8-C_{10}**, albeit in 20% yield.

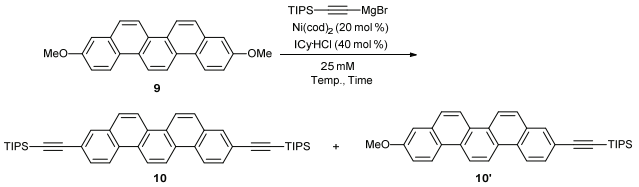


Scheme 2 Synthesis of 3,10-didecylpicene (**8-C_{10}**).

Although alkylated picene **8-C_{10}** could be obtained, the synthetic route shown in Scheme 2 is not ideal for the synthesis of a serious of alkylated picenes because the alkyl group has to be introduced at an initial stage. Therefore, we started to investigate more efficient syntheses of 3,10-dialkylpicenes through C–O bond functionalization of 3,10-dimethoxypicene (**9**)[18] as the common starting material. Because of the high stability of the C–O bond, the direct transformations of the C–O bond is a challenging objective.[23-36]

Very recently, Tobisu and Chatani have reported the direct C–O bond alkynylation reaction of anisole derivatives.[37] Inspired by this straightforward transformation of the C–O bond, we optimized the conditions for the double alkynylation of **9** and the results are summarized in Table 1.

Table 1 Alkynylation of 3,10-dimethoxypicene (**9**) via C–O bond activation[a]



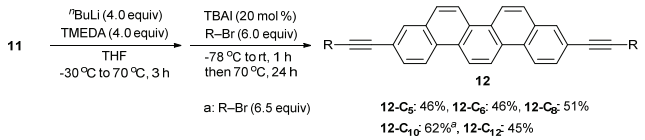
Entry	Solvent	Temp. (ºC)	Time (h)	Yield[b] (%)	
				10	**10'**
1	1,4-dioxane	120	18	0	0
2	triglyme	160	18	0	0
3	NMP	160	18	0	0
4	diphenyl ether	160	18	0	0
5	mesitylene	160	18	47	25
6	mesitylene	150	18	70	0
7	mesitylene	140	18	33	17
8	mesitylene	130	72	22	20
9	mesitylene	140	72	76[c]	9[c]

[a] 3,10-Dimethoxypicene (**9**) (0.05 mmol), the in situ prepared triisopropylsilylethynylmagnesium bromide (0.2 mmol), $Ni(cod)_2$ (0.01 mmol), ICy•HCl (0.02 mmol) in the solvent. [b] NMR yields based on 1,4-dioxane as an internal standard. [c] Isolated yields (0.59 mmol for **9**).

According to the original reaction conditions,[37] a mixture of **9** (1.0 equiv) and triisopropylsilylethynylmagnesium bromide (4.0 equiv) was heated in 1,4-dioxane (500 mM) at 120 °C for 18 h in the presence of $Ni(cod)_2$ (20 mol %) and ICy•HCl (40 mol %) as the catalyst system (ICy = 1,3-dicyclohexylimidazol-2-ylidene). Unfortunately, however, no desired product **10** was detected and all the substrates were recovered. At a lower concentration (25 mM), the reaction proved similarly unsuccessful (entry 1). In an attempt to identify effective solvents, triglyme, NMP, diphenyl ether, and mesitylene were also evaluated (entries 2-4). To our delight, when mesitylene was used as the solvent, the desired doubly alkynylated product **10** was formed in 47% NMR yield (entry 5). Further optimization of the reaction conditions revealed that reaction at 150 °C gave **10** up to 70% yield (entries 6-8). Consequently, the best result was obtained by the reaction at 140 °C for 72 h; the desired product was obtained in 76% isolated yield (entry 9).

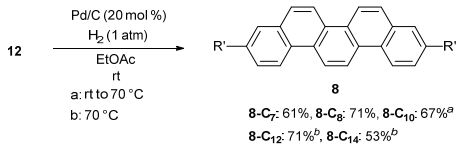
When compound **10** was treated with ^{n}Bu$_4$NF, desilylated diethynylpicene (**11**) was generated in 91% yield.[38]

We next screened the reaction conditions for alkyne alkylation by using ^{n}BuLi followed by the addition of alkyl bromides in THF.[39] When the reaction temperature was increased and 20 mol % of TBAI was added, a wide range of alkylated products **12** were obtained in 46-62% yields (Scheme 3).



Scheme 3. Alkylation of **11**.

After obtaining successful alkylation of **11** with different types of alkylating agents, we proceeded to hydrogenate the products to complete the synthesis of alkylpicenes (Scheme 4).[40] Interestingly, when using atmospheric pressures of hydrogen gas for hydrogenation we observed low reactivity for substrates bearing longer alkyl chains, and found that a higher reaction temperature (70 ºC) was necessary. Gratifyingly, a slight alteration of the reaction conditions (e.g., reaction temperatures and times) afforded full conversion of **12** and reasonable yields of the desired products **8**.



Scheme 4. Synthesis of alkylpicenes **8** via hydrogenation of **12**.

The solubility of a series of alkylpicenes **8** was determined to confirm the solubilizing effect of alkyl substituents. Although the parent picene was almost insoluble in chloroform at room temperature, introduction of the alkyl groups did enhance the solubility (2.9 g/L for **8-C$_7$**, 3.1 g/L for **8-C$_8$**, 4.0 g/L for **8-C$_{10}$**, 1.1 g/L for **8-C$_{12}$**, and 0.4 g/L for **8-C$_{14}$**). We observed that the solubility of picenes with longer alkyl chains (C_{12} and C_{14}) decreased once the number of carbon atoms in the chain exceeds ten. We believe this is due to the hydrophobic interaction between the alkyl chains, which typically enhance an intermolecular interaction, leading to the lower solubility. This is the so-called "fastener effect".[41-43]

Conclusions

In summary, we have developed a new synthetic route to an array of alkyl-substituted picenes via C–O bond activation/alkynylation sequences. This sequence successfully delivered five dialkylated picenes in yields up to 71%. A further elucidation of the physical properties of these compounds, in particular their FET characteristics, is presently underway in our laboratory.

Experimental section

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 GF_{254}, 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 ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Mercury-300 (300 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.[18]

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 ^{n}BuLi (12.3 mL, 20 mmol, 1.63 M in hexane) at –78 ºC over 10 min. After the reaction 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 $MgSO_4$. 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). ^{1}H NMR ($CDCl_3$, 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); ^{13}C{^{1}H} NMR ($CDCl_3$, 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. MS (EI, m/z (relative intensity)): 296 (M^+, 14), 172 (44), 171 (22), 170 (48), 169 (20), 105 (6), 104 (11), 91 (100), 90 (19), 89 (12), 71 (6). HRMS (EI) Calcd for $C_{16}H_{25}Br$: 296.1140. Found: 296.1162.

Preparation of ((3-Decylphenyl)ethynyl)trimethylsilane (3). To a two-necked round bottom flask, were added compound **2** (5.0 g, 17 mmol), $PdCl_2(PPh_3)_2$ (119 mg, 0.17 mmol, 1 mol %), CuI (162 mg, 0.85 mmol, 5 mol %), trimethylamine (40 mL), pyridine (40 mL), and trimethylsilylethyne (3.88 mL, 20.4 mmol) under an argon atmosphere. The reaction mixture was heated up to 80 ºC 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 ($CDCl_3$, 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); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 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. Calcd for $C_{21}H_{34}Si$: C, 80.18; H, 10.89%. Found: C, 80.43; H, 11.07%.

Preparation of Ethynyl-3-decylbenzene (4). To a solution of **3** (4.4 g, 14 mmol) in THF (50 mL) and MeOH (30 mL), was added K_2CO_3 (2.89 g, 21 mmol) and H_2O (1.2 mL). The solution was stirred at room temperature for 3 h prior to quenching with saturated aqueous NH_4Cl. The reaction mixture was extracted with diethyl ether, washed with brine, and dried over $MgSO_4$. 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), 2855 (s), 1600 (w), 1481 (w), 1466 (m), 793 (m), 694 (m), 606 (m). ^1H NMR ($CDCl_3$, 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); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 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, 129.6, 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) Calcd for $C_{18}H_{26}$: 242.2035. Found: 242.2055.

Preparation of 4,4,5,5-tetramethyl-2-[(1*Z*)-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), $^iPr_3P$ (0.057 mL, 0.3 mmol, 6 mol %), NEt_3 (5 mL), and HB_{pin} (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 (m), 808 (m), 698 (m). ^1H NMR ($CDCl_3$, 400 MHz, rt): δ 0.88 (t, J = 7.2 Hz, 3H), 1.22-1.34 (m, 26H), 1.61 (q, J = 7.7 H, 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); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.1 MHz, rt) δ 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 $C_{24}H_{39}BO_2$: C, 77.83; H, 10.61%. Found: C, 77.51; H, 10.41%.

Preparation of 1,4-dichloro-2,3-bis[(1*Z*)-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_2O (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), 1600 (w), 1456 (m), 1435 (m), 1128 (m), 903 (w), 804 (s), 696 (s). ^1H NMR ($CDCl_3$, 300 MHz, rt): δ 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); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, rt) δ 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 $C_{42}H_{56}Cl_2$: C, 79.84; H, 8.93%. Found: C, 79.52; H, 8.71%.

Preparation of 3,10-didecylpicene (8-C_{10}). To a 50 mL Schlenk tube charged with a magnetic stirrer bar, were added PCy_3 (11.5 mg, 0.04 mmol, 20 mol %), $PdCl_2(NCPh)_2$ (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_2CO_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 $CHCl_3$. The crude product was purified by column chromatography to yield **8-C_{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 ($CDCl_3$, 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); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 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 $C_{42}H_{54}$: 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 prepared [(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 CH_2Cl_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 °C. The crude product was purified by column chromatography (hexane:$CHCl_3$ = 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 ($CDCl_3$, 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); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 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; $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 119 MHz, rt) δ –1.63. Anal. Calcd for $C_{44}H_{54}Si_2$: C, 82.69; H, 8.52%. Found: C, 82.47; H, 8.28%.

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 $^nBu_4NF$ (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). ^1H NMR ($CDCl_3$, 600 MHz, rt): δ 3.23 (s, 2H), 7.81 (d, J = 8 Hz, 2H), 7.99 (d, J = 9 Hz, 2H), 8.18 (s, 2H), 8.79 (bd, J = 4 Hz, 4H), 8.91 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 78.3, 83.9, 119.4, 120.5, 122.2, 122.5, 123.5, 127.4, 129.9, 131.7, 132.8, 138.4, 159.2. HRMS (EI) Calcd for $C_{26}H_{14}$: 326.1096. Found: 326.1078.

General 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 °C. 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 1M HCl. The crude mixture was extracted with CH_2Cl_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), 1467 (m), 1445 (w), 1274 (m), 887 (m), 810 (s), 750 (m). ^1H NMR ($CDCl_3$, 600 MHz, rt): δ 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); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt) δ 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.

General 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 ($CDCl_3$, 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 = 8.6 Hz, 2H), 8.90 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 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.

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