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Scalable, Chromatography-Free Synthesis of Alkyl-Tethered Pyrene-Based Materials. Application to First-Generation "Archipelago Model" Asphaltene Compounds

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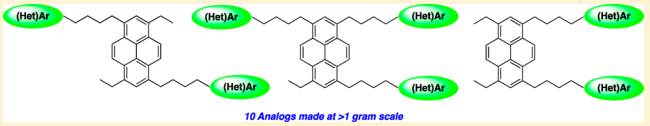
Supporting Information

ABSTRACT: In this paper, we report a highly efficient, scalable approach to the total synthesis of conformationally unrestricted, electronically isolated arrays of alkyl-tethered polycyclic aromatic chromophores. This new class of modular molecules consists of polycyclic aromatic "islands" comprising significant structural fragments present in unrefined heavy petroleum, tethered together by short saturated alkyl chains, as represented in the "archipelago model" of asphaltene structure. The most highly branched archipelago compounds reported here share an architecture with first-generation dendrimeric constructs, making the convergent, chromatography-free synthesis described herein particularly attractive for further extensions in scope and applications to materials chemistry. The syntheses are efficient, selective, and readily adaptable to a multigram scale, requiring only inexpensive, "earth-abundant" transition-metal catalysts for cross-coupling reactions and extraction and fractional crystallization for purification. This approach avoids typical limitations in cost, scale, and operational practicality. All of the archipelago compounds and synthetic intermediates have been fully characterized spectroscopically and analytically. The solid-state structure of one archipelago model compound has been determined by X-ray crystallography.



INTRODUCTION

The archipelago model for asphaltene structure is characterized by polycyclic aromatic, partially aromatic, and heteroaromatic "islands" linked together by short, saturated alkyl tethers and further decorated with short alkyl side chains.[1] Mixtures of asphaltene molecules irreversibly associate into poorly characterized supramolecular aggregates,[2] compromising the efficiency of conventional upgrading technologies.[3] "Hyperbranched" members of the asphaltene class are well described as first-generation dendrimers of random but oligomeric composition.

The synthesis of dendrimeric and semidendrimeric molecules containing electronically active residues, such as aromatic chromophores, is an active area of research.[4] This has provided a broad class of hyperbranched compounds varying in size, shape, rigidity, and electronic properties.[5] There remains, however, much room for the development of efficient, practical regiocontrolled methodology for large-scale synthesis of such materials, delivering gram quantities of pure materials without resorting to chromatographic purifications. Specifically in the area of carbon−carbon coupling reactions, precious metal catalysts and specialized ligands continue to dominate a landscape populated largely by alkynyl- and vinylarylation procedures.[6] Access to electronically isolated, saturated-alkyl-tethered archipelago-like structures is currently limited to isolated examples containing only two or three polycyclic aromatic residues.[7]

Our interest in synthesizing "authentic" asphaltene structural mimics[8] prompted us to develop operationally robust strategies for the preparation of pyrene-based archipelago compounds tethered to other polycyclic chromophores by saturated hydrocarbon linkages. For proof of principle and optimization studies, we targeted both carbocyclic and heterocyclic appendages, here represented by phenanthrene and *N*-alkylcarbazole, respectively (Figure 1). In all cases, the pyrene core is 1,3,6,8-tetrasubstituted, with nontethering positions capped by ethyl groups, consistent with the "short-chain" terminal alkyl groups ubiquitous in natural asphaltenes.[9] The use of different length terminal substituents and tethering

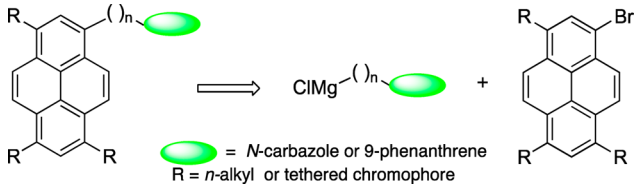


Figure 1. Retrosynthesis of pyrene-anchored archipelago.

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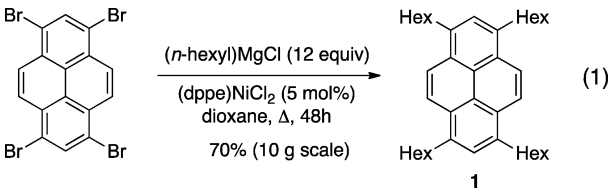
chains in this demonstration was guided by the more or less random distribution of short alkyl substituents/chains identified in natural asphaltenes,[3b] the lengths of which may prove important in driving aggregation. Although fortuitous, the installation of ethyl substituents provided the key to avoiding chromatography for the separation of 1,6- and 1,8-difunctionalized intermediates, a significant bottleneck in previously reported pyrene syntheses.[10]

RESULTS AND DISCUSSION

Alkylation and polyalkylation of pyrenes have been demonstrated via various metal-catalyzed cross-coupling methods, but even the most recent report fails to offer a preparatively practical, scalable solution to the problem, relying extensively on chromatographic separations.[11] The use of HPLC in particular limits scalability and scope, in turn inhibiting investigations of physical properties and structure/activity relationships, all required for the development of real-world applications. Here, we report robust, *chromatography-free* procedures for the synthesis of alkylated pyrene derivatives on a multigram scale, providing organic-soluble pyrene-based building blocks for further manipulation.

As proof of concept, the 4-fold alkylation of 1,3,6,8-tetrabromopyrene (TBP) with excess commercial *n*-hexylmagnesium chloride was conducted under standard reaction conditions (eq 1).[12] Despite the poor solubility of tetrabromopyrene, the selectivity is nearly perfect, providing tetra-*n*-hexylpyrene (**1**) cleanly and in high yield after crystallization on a decagram scale. Previous approaches to the convergent poly-*n*-alkylation of polycyclic aromatic compounds require more than one step[7b,c] or proved to be unselective.[13] In comparison, the classic metal-catalyzed alkynylation/hydrogenation sequence returns lower yields and requires chromatography to obtain the products in reasonably pure form.[14]



To demonstrate that this protocol is adaptable to polycyclic "island-terminated" haloalkyl segments, *N*-(4-chlorobutyl)-carbazole[15] (**2**) was prepared, converted to the magnesium salt **3**, and subjected to TBP under standard Kumada conditions (Scheme 1). As a concession to the greater value of the nucleophile, the excess of Grignard was reduced to 1.5 equiv per coupling site without compromising selectivity or yield. Further reduction in relative stoichiometry was counterproductive. Upon quenching, the crude archipelago compound was obtained as a solid by suction filtration. After being rinsed with ether and water to remove both organic impurities and magnesium salts, the nearly colorless material was recrystallized from chloroform. Final drying to constant weight required prolonged treatment under high vacuum to remove persistent residual solvent(s). The five-island, symmetrical first-generation dendrimer **4** was nonetheless obtained analytically pure in 74% yield on a one-gram scale.

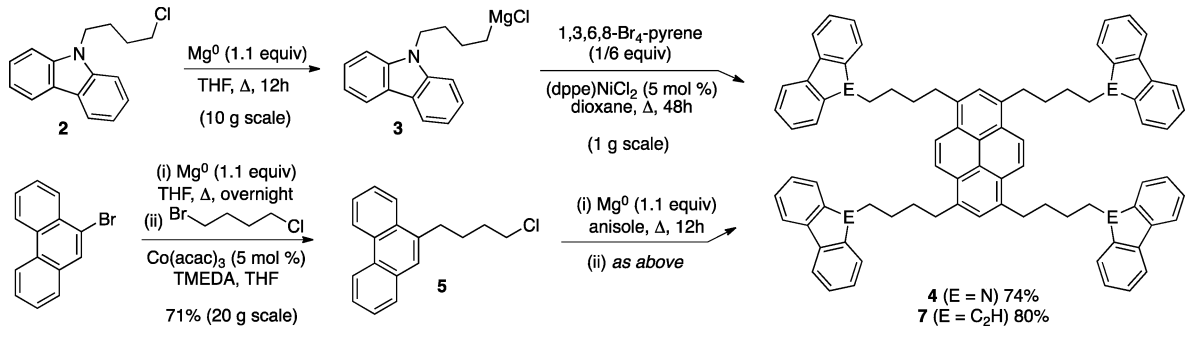
Extension of this protocol to the analogous phenanthrene derivative required the synthesis of chloroalkylated phenanthrene **5**. In general, chloroalkylated polycycles must be synthesized from the aromatic core using a difunctional electrophile. Here, we adopt known methodology, the cobalt-catalyzed arylation of α,ω-bromochloroalkanes,[16] which proceeds by highly selective displacement of the bromide. In this way, 9-(4-chlorobutyl)phenanthrene **5** was prepared cleanly from 9-bromophenanthrene and 1-bromo-4-chlorobutane (Scheme 1). The cross-coupling to produce **5** proved quite efficient and was conveniently run on a 20 g scale.

9-(Chlorobutyl)phenanthrene **5** is only sparingly soluble in conventional ethereal solvents but dissolves readily in hot anisole, which became the solvent of choice for preparation of the corresponding Grignard reagent.[17] In the event, the 4-fold Kumada cross-coupling with TBP proceeds without issue, yielding the hydrocarbon archipelago **7** after a similar workup and crystallization. Solutions of the Grignard reagents derived from **2** and **5**, in THF and anisole solutions, respectively, can be prepared on a decagram scale and stored for months under inert atmosphere without appreciable loss of activity.

The efficiency of this procedure encouraged us to target the complete series of pyrene/carbazole and pyrene/phenanthrene pseudoasphaltenes to make possible a systematic study of intra- and intermolecular aggregation as a function of the complexity, symmetry, and polarization of the component residues. Thus, all possible two-, three-, and four-island structures in each series have been prepared from the corresponding bromopyrenes, substituting one, two, or three terminal ethyl substituents in place of tethered islands.

Regioselective synthesis of dibrominated pyrene derivatives such as **8** and **9** is not a simple problem, particularly on a multigram scale, where chromatography becomes increasingly costly and tedious. Procedures for the preparation of 1-bromopyrene, 1,6- and 1,8-dibromopyrenes, and 1,3,6-tribromopyrene are found in the literature,[18] not all of which reliably provide pure materials even after chromatography. The

Scheme 1. Synthesis of Tetrasubstituted Pyrene Archipelago Compounds



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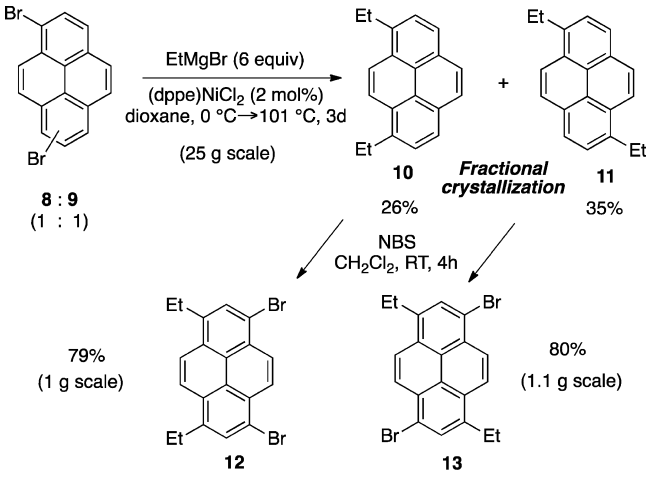
J. Org. Chem. 2015, 80, 1719−1726

Iwasa group, however, recently reported the preparation of 1,6-dibromo-3,8-di-*n*-butylpyrene,[19] closely analogous to the diethyl derivatives targeted for archipelago construction. Unfortunately, the reported approach requires multiple steps and chromatographic purifications and gives only one of the two dibrominated isomers in purified form.

In order to circumvent the issues described above, we have developed an efficient, chromatography-free synthesis of isomerically pure C_2- and C_s-symmetric dibromodialkylpyrenes on a substantial scale. Rather than engage the poorly soluble dibromides **8** and **9**,[20] the 1:1 mixture was converted without separation to the more lipophilic diethyl isomers (Scheme 2).

Scheme 2. Synthesis of Dibromopyrenes 12 and 13

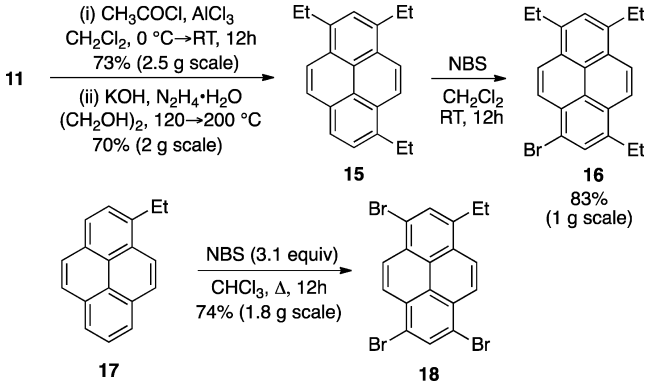


Despite the greater solubility of the ethylated derivatives, the polarity difference between the isomers remains substantial, leading to a dramatic improvement in the efficiency of fractional crystallization. In this way, both 1,8- and 1,6-diethylpyrenes **10** and **11** were obtained as pure compounds after a single crystallization. The material balance is reasonable and can be improved by further manipulation of the mother liquor, if desired. At this stage, double bromination of each isomer afforded central island templates **12** and **13**, respectively, cleanly and in high yield.

The remaining central island templates were prepared by bromination of 1,3,6-triethylpyrene **15**, generating bromopyrene **16**, and tribromination of 1-ethylpyrene[21] **17**, giving tribromopyrene **18** (Scheme 3). 1,3,6-Triethylpyrene **15** was obtained by standard acylation/reduction of diethylpyrene **11**.

Using the halogenated mono-, di-, and triethylated pyrenes, two-, three-, and four-island archipelago compounds **19**–**26** were synthesized by Kumada coupling, completing the series of four-carbon-tethered carbazole- and phenanthrene-decorated pyrene derivatives (Scheme 4). All of the cross-coupling reactions were conducted conveniently in THF, except for the four-island archipelago compounds derived from **18**, which required the use of dioxane. Lower symmetry archipelago compounds generally show greater solubility; as a consequence, two- and four-island systems were isolated by conventional workups and purified by subsequent crystallizations. The less-soluble three- and five-island systems precipitated directly from solution and were isolated by simple filtrations. Subsequent recrystallizations from a halogenated solvent and drying under high vacuum provided pure products.

Scheme 3. Synthesis of Bromopyrene 16 and Tribromopyrene 18



All reported compounds have been fully characterized spectroscopically and analytically. Despite spectroscopic purity and consistent HRMS analysis, combustion analysis often returned measurements low in carbon, even upon addition of standard combustion aids. Incomplete combustion is endemic to compounds incorporating extensively cumulated quaternary carbon centers.[22] Single crystals of the C_2-symmetric three-island carbazole **21** were grown from saturated dimethylacetamide, and the solid-state structure was determined by X-ray crystallography.[23] ORTEP diagrams of the compound and the extended lattice unit are shown in Figure 2. The carbazole units of neighboring molecules show face-to-face π-stacking along the long-molecular axis. The remainder of the close contacts, on the other hand, reveals the dominant role of both intermolecular dispersion interactions and edge-to-face stacking in the crystal packing of the molecule.

CONCLUSION

In summary, efficient, robust, gram-scale syntheses of alkyl-bridged first-generation dendrimeric and semidendrimeric compounds have been developed to provide model compounds for investigation of archipelago model asphaltene structures. Strategically convergent, scalable, and adaptable to a broad range of polycyclic aromatic and partially aromatic systems, this methodology is expected to assist developments in a range of chemistries based on arrays of chromophores embedded within a single molecular matrix. Applications of such compounds to the characterization of solution aggregation in natural asphaltenes will be reported in due course.

EXPERIMENTAL SECTION

1,3,6,8-Tetrahexylpyrene (1). To a stirred suspension of 1,3,6,8-tetrabromopyrene (10.000 g, 19.311 mmol) and $NiCl_2$(dppe) (0.510 g, 0.966 mmol) in dioxane (600 mL) at 0 °C under nitrogen was added 154 mL of 1.5 M HexMgCl in THF slowly via cannula. The reaction mixture was warmed to reflux and maintained there for 48 h, after which the resulting solution was cooled to 0 °C and quenched by slow addition of 1 M HCl (150 mL). The reaction mixture was taken up in 400 mL of ether and washed with 400 mL of brine. The organic layer was separated, dried over magnesium sulfate, and filtered. The solvent was removed under vacuum, and the crude product taken up in a minimal amount of hot chloroform. This solution was layered with an equal volume of methanol and allowed to diffuse slowly at rt overnight. The product, lightly colored (lime green), was collected by suction filtration to yield 7.320 g (70%) of spectroscopically and analytically pure compound. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 4H), δ 7.71 (s, 2H), 3.32 (t, J = 8 Hz, 8H), 1.87 (m, 8H), 1.52 (m, 8H), 1.435–1.33 (m, 16H), 0.94 (t, J = 7 Hz, 12H). ^{13}C{^{1}H} NMR

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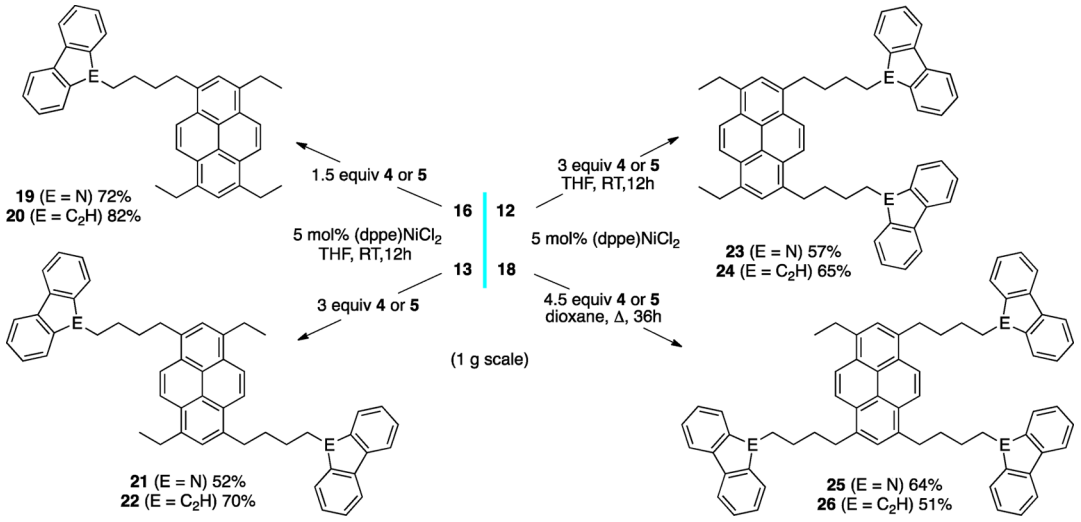
J. Org. Chem. 2015, 80, 1719–1726

Scheme 4. Synthesis of Two-, Three-, and Four-Island Compounds 19−26



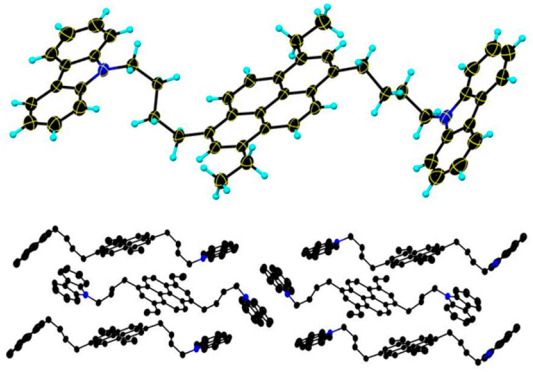


Figure 2. (Top) ORTEP diagram of the solid-state structure of compound **21**, shown with 50% thermal ellipsoids. Hydrogen atoms are shown in aqua, nitrogen in blue. (Bottom) Extended unit cell with hydrogen atoms omitted for clarity.

(125 MHz, $CDCl_3$): δ 136.2, 128.7, 127.2, 126.4, 122.3, 33.8, 31.9, 31.9, 29.6, 22.7, 14.1. EI HRMS: exact mass calcd for $C_{40}H_{58}$ (M^+) 538.45386, found 538.45457. Anal. Calcd for $C_{40}H_{58}$: C, 89.15; H, 10.85. Found: C, 89.36; H, 10.68. Repeat Found: C, 89.35; H, 10.72.

(4-(9*H*-Carbazol-9-yl)butyl)magnesium Chloride (3) [~0.5 M in THF]. In a glass reactor sealed with a high vacuum Teflon stopcock, magnesium turnings (1.040 g, 42.80 mmol) in THF (3 mL) were activated by addition of ethylene bromide (0.17 mL, 1.948 mmol) via syringe under a stream of nitrogen, followed by heating the suspension at reflux for 1 h. To the resulting solution/suspension was added 9-(4-chlorobutyl)-9*H*-carbazole (10.000 g, 38.895 mmol) in THF (75 mL), and the reactor was resealed and heated to 70 °C overnight. At this time, only a small amount of magnesium remained visible, and the brown solution was used without further purification.

A small amount of this Grignard reagent was quenched with 1 M HCl at 0 °C and subjected to standard workup. Analysis of the crude product by ^{1}H NMR spectroscopy revealed the presence of only N-butylcarbazole, with no evidence for olefinic or dimeric material. Thus, we assumed the magnesiation proceeded to completion and the molarity of the resulting solution was estimated based on quantitative conversion. The Grignard solution was stored in the drybox, remaining stable over months when kept at rt sealed with an unpunctured septum.

1,3,6,8-Tetrakis(4-(9*H*-carbazol-9-yl)butyl)pyrene (4). In a glass reactor topped by a Teflon high-vacuum stopcock was added a suspension of 1,3,6,8-tetrabromopyrene (1.000 g, 1.931 mmol) and $NiCl_2$(dppe) (0.051 g, 0.097 mmol) in dioxane (60 mL) at rt. To the stirred solution was added (4-(9*H*-carbazol-9-yl)butyl)magnesium chloride (23 mL of a 0.5 M solution in THF) under a nitrogen atmosphere. The reaction mixture was heated to 100 °C for 48 h, cooled to 0 °C, and quenched with 1 M HCl (5 mL). The product was collected by suction filtration and washed multiple times with hot water, ether, and hexanes, in that order. The remaining material was dissolved in a minimal amount of hot chloroform and placed in the freezer overnight. The product was collected by suction filtration and rinsed with cold dichloromethane. The light yellow, spectroscopically pure powder was dried under high vacuum to yield 1.548 g (74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (ddd, J = 8, 1, 1 Hz, 8H), 8.06 (s, 4H), 7.44 (s, 2H), 7.41 (ddd, J = 8, 7, 2 Hz, 8H), 7.34 (ddd, J = 8, 1, 1 Hz, 8H), 7.20 (ddd, J = 7, 7, 1 Hz, 8H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.4, 135.5, 128.9, 127.3, 126.4, 125.7, 122.9, 122.4, 120.4, 118.8, 108.7, 43.0, 33.3, 29.2, 28.9. MALDI-FT-ICR HRMS: exact mass calcd for (M^+) $C_{80}H_{70}N_4$ 1086.55950, found 1086.55821. Anal. Calcd for $C_{80}H_{70}N_4$: C, 88.36; H, 6.49; N, 5.15. Found: C, 88.24; H, 6.62; N 5.10. Repeat Found: C, 88.24; H, 6.62; N, 5.10.

9-(4-Chlorobutyl)phenanthrene (5). In a dry 250 mL RBF fitted with a stir bar and condenser attached to a nitrogen pressure inlet were added magnesium turnings (2.080 g, 85.56 mmol) and 80 mL of THF. Ethylene bromide (0.337 mL, 3.89 mmol) was added via syringe and the mixture heated to reflux for 1 h. The reaction mixture was cooled to rt, and 9-bromophenanthrene (20.000 g, 77.782 mmol) in THF (80 mL) was added by cannula transfer. The resulting reaction mixture was heated to reflux overnight and then cooled to rt. In a separate 500 mL RBF fitted with a stir bar and condenser and placed under nitrogen was added $Co(acac)_3$ (1.392 g, 3.907 mmol) in THF (40 mL), followed by TMEDA (0.583 mL, 3.89 mmol) and 4-chlorobromobutane (9.9 mL, 86 mmol). The resulting solution was cooled to 0 °C, and the solution of 9-phenanthrylmagnesium bromide was transferred into the reaction flask via cannula. After 4 h at 0 °C, the reaction mixture was heated to reflux overnight and then cooled to rt and quenched with 1 M HCl (100 mL). To this was added 100 mL of ether in a separatory funnel. After separation of the layers, the organic phase was washed with brine (100 mL) and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under vacuum and the crude product dissolved in a minimal amount of hot 2-propanol. After slow cooling, 14.823 g (71%) of an off-white product was collected by suction filtration after rinsing with cold 2-propanol and drying under high vacuum. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.76 (dd, J = 10, 2 Hz, 1H), 8.67 (d, J = 9 Hz, 1H), 8.11 (dd, J = 7, 3 Hz, 1H), 7.85 (dd, J = 7, 2 Hz, 1H), 7.57−7.70 (m, 5H), 3.63 (t, J = 6 Hz, 2H), 3.18 (t, J = 7 Hz, 2H), 1.98 (m, 4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.0, 131.9, 131.2, 130.8, 129.8, 128.1, 126.7, 126.6, 126.3, 126.3, 126.1, 124.3, 123.3, 122.5, 44.9, 32.7, 32.6, 27.4. EI HRMS: exact mass calcd for $C_{18}H_{17}{}^{35}Cl$ (M^+) 268.10187, found 268.10155.

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Anal. Calcd for $C_{18}H_{17}Cl$: C, 80.43; H, 6.38. Found: C, 80.71; H, 6.33. Repeat Found: C, 80.47; H, 6.35.

(4-(Phenanthren-9-yl)butyl)magnesium Chloride (6) [~0.3 M in 4.66:1 Anisole/THF]. In a glass reactor equipped with a Teflon high vacuum stopcock were placed magnesium turnings (1.193 g, 49.09 mmol), and the vessel was placed under nitrogen. The Mg was suspended in THF (26 mL) and activated by the addition of ethylene bromide (0.193 mL, 2.24 mmol) via syringe under a stream of N_2, followed by heating to reflux for 1 h. In a separate glass reactor, 9-(4-chlorobutyl)phenanthrene (12.000 g, 44.646 mmol) under nitrogen was dissolved in dry, deoxygenated anisole (121 mL). To the activated magnesium suspension was added the solution of 9-(4-chlorobutyl)-phenanthrene in anisole. The reactor was sealed and heated to 70 °C overnight. At this time, only a small amount of magnesium remained visible in the brown solution.

A small amount of this Grignard reagent was quenched with 1 M HCl at 0 °C and subjected to standard workup. Analysis of the crude product by ^{1}H NMR spectroscopy revealed the presence of only 9-butylphenanthrene, with no evidence for olefinic or dimeric material. Thus, we assumed the magnesiation proceeded to completion and the molarity of the resulting solution was estimated on the basis of quantitative conversion. The Grignard solution was stored in the drybox, remaining stable over months when kept at rt under an unpunctured septum.

1,3,6,8-Tetrakis(4-(phenanthren-9-yl)butyl)pyrene (7). To a stirred suspension of 1,3,6,8-tetrabromopyrene (1.000 g, 1.931 mmol, 1 equiv) and $NiCl_2$(dppe) (0.051 g, 0.097 mmol) in dioxane (40 mL) under nitrogen at rt was added (4-(phenanthren-9-yl)butyl)-magnesium chloride (39 mL, 0.3 M in anisole/THF (4.7:1 v/v)). The reactor was sealed and heated to 100 °C for 48 h. The reaction mixture was cooled to 0 °C and quenched by dropwise addition of aq 1 M HCl (5 mL). The crude product was collected by suction filtration, washed multiple times with hot water, and then washed successively with water, ether, and hexanes. The remaining material was dissolved in a minimal amount of hot chloroform and placed in the freezer overnight. The product, a spectroscopically homogeneous white powder, was collected by suction filtration, rinsed with cold dichloromethane, and dried under vacuum to yield 1.753 g (80%) of compound 7. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.71 (dd, J = 8, 2 Hz, 4H), 8.63 (d, J = 8 Hz, 4H), 8.08 (dd, J = 8, 1 Hz, 4H), 7.74 (dd, J = 8, 2 Hz, 4H), 7.68 (s, 2H), 7.65−7.5 (m, 20H), 3.36 (t, J = 6 Hz, 8H), 3.16 (t, J = 6 Hz, 8H), 2.01 (app t, J = 4 Hz, 16H), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.6, 135.9, 132.0, 131.3, 130.8, 129.7, 128.9, 128.1, 127.3, 126.6, 126.5, 126.5, 126.2, 126.1, 125.9, 124.5, 123.3, 122.6, 122.5, 33.6, 33.4, 31.9, 30.2. MALDI-FT-ICR HRMS: exact mass calcd for (M^+) $C_{88}H_{74}$ 1130.57850, found 1130.57702. Anal. Calcd for $C_{88}H_{74}$: C, 93.41; H, 6.59. Found: C, 92.89; H, 6.61. Repeat Found: C, 92.87; H, 6.63.

1,6-Diethylpyrene (11). In a dry, three-neck RBF fitted with a condenser and under a nitrogen atmosphere was placed a 1:1 mixture of 1,6- and 1,8-dibromopyrene (25.000 g, 69.852 mmol) and $NiCl_2$(dppe) (0.729 g, 1.38 mmol) in dioxane (500 mL). The solution was cooled to 0 °C, and EtMgBr (138 mL, 3 M in Et_2O) was added slowly. The resultant reaction mixture was heated to 100 °C for 36 h, cooled to 0 °C, and quenched by dropwise addition of saturated NH_4Cl (300 mL) followed by the addition of ether (500 mL) and water (200 mL). This mixture was partitioned in a separatory funnel and the organic layer washed with brine (500 mL), dried over magnesium sulfate, and filtered. After removal of the solvent under reduced pressure, the crude solid was dissolved in minimum of dichloromethane, and an equal amount of methanol was layered on top. The biphasic mixture was allowed to diffuse overnight in the freezer. 1,8-Diethylpyrene deposited first and was collected by suction filtration. Rinsing with methanol and drying under high vacuum gave a bright yellow solid, 6.167 g (35%), pure by spectroscopic analysis. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, J = 9 Hz, 2H), 8.14 (d, J = 8 Hz, 2H), 8.10 (d, J = 10 Hz, 2H), 7.91 (d, J = 8 Hz, 2H), 3.41 (q, J = 8 Hz, 4H), 1.52 (t, J = 8 Hz, 6H), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.4, 129.6, 128.7, 127.4, 126.4, 125.5, 124.7, 122.5, 26.7, 16.1. EI HRMS: exact mass calcd for $C_{20}H_{18}$ (M^+) 258.14084, found 258.14067. Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.61; H, 6.95.

1,6-Diethylpyrene (10). The filtrate remaining after isolation of 1,8-diethylpyrene was concentrated under reduced pressure. The resulting sludge was dissolved in a minimal amount of hot THF and filtered through a short pad of Fluorisil. The solvent was removed under vacuum, providing a yellow oil which solidified upon standing overnight at room temperature. The crude solid was dissolved in a minimal amount of hot hexanes and allowed to crystallize in the refrigerator overnight. The 1,6-diethylpyrene was collected by suction filtration, rinsed with cold hexanes, and dried under high vacuum, giving a spectroscopically pure dark yellow solid, 5.224 g (26%). Mp = 77 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (s, 2H), 8.09 (d, J = 8 Hz, 2H), 7.96 (s, 2H), 7.87 (d, J = 8 Hz, 2H), 3.39 (q, J = 7 Hz, 4H), 1.50 (t, J = 7 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 138.2, 130.1, 128.2, 126.7, 126.3, 125.5, 124.8, 123.1, 26.6, 16.1. EI HRMS: exact mass calcd for $C_{20}H_{18}$ (M^+) 258.14084, found 258.14088. Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.11; H, 7.20. Repeat Found: C, 92.81; H, 7.03.

1,8-Dibromo-3,6-diethylpyrene (12). A 100 mL RBF open to the atmosphere was charged with a solution of 1,8-diethylpyrene (1.000 g, 3.874 mmol) in dichloromethane (35 mL) at room temperature. To this solution was added NBS (1.447 g, 8.130 mmol) and the reaction mixture stirred magnetically for 4 h. The solvent was removed under vacuum and the crude product mixture dissolved in a minimal amount of hot chloroform, which was layered with an equal volume of ethanol and allowed diffuse at rt overnight. The product was collected by suction filtration, rinsed with ethanol, and dried under high vacuum providing a spectroscopically pure, off-white powder (1.271 g, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (s, 2H), 8.29 (s, 2H), 8.17 (s, 2H), 3.35 (q, J = 7 Hz, 4H), 1.49 (t, J = 7 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 139.8, 131.0, 128.4, 128.1, 126.8, 126.3, 123.2, 120.5, 26.4, 15.8. EI HRMS: exact mass calcd for $C_{20}H_{16}{}^{81}Br_2$ (M^+) 417.95779, found 417.95826. Anal. Calcd for $C_{20}H_{16}Br_2$: C, 57.72; H, 3.88. Found: C, 57.50; H, 3.77. Repeat Found: C, 57.56; H, 3.89.

1,6-Dibromo-3,8-diethylpyrene (13). A 100 mL RBF open to the atmosphere was charged with a solution of 1,6-diethylpyrene (1.107 g, 4.288 mmol) in DCM (40 mL) at room temperature. To this solution was added NBS (1.601 g, 8.995 mmol) and the reaction mixture stirred magnetically for 4 h. The solvent was removed under vacuum, and the crude product mixture was dissolved in a minimal amount of hot chloroform, layered with an equal volume of ethanol, and allowed to diffuse at rt overnight. The product was collected by suction filtration as a spectroscopically pure, off-white powder (1.432 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, J = 10 Hz, 2H), 8.26 (d, J = 10 Hz, 2H), 8.15 (s, 2H), 3.34 (q, J = 8 Hz, 4H), 1.48 (t, J = 8 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 139.8, 131.0, 128.2, 128.1, 126.2, 126.2, 123.8, 120.6, 26.5, 15.8. EI HRMS: exact mass calcd for $C_{20}H_{16}{}^{79}Br_2$ (M^+) 413.96188, found 413.96283. Anal. Calcd for $C_{20}H_{16}Br_2$: C, 57.72; H, 3.88. Found: C, 57.41; H, 3.91.

1-(3,8-Diethylpyren-1-yl)ethanone (14). A three-necked 250 mL RBF under nitrogen was charged with 1,6-diethylpyrene (3.000 g, 11.61 mmol), dissolved in dichloromethane (60 mL), and cooled to 0 °C. To this stirred solution was added a solution of acetyl chloride (0.83 mL, 12 mmol) and aluminum trichloride (1.548 g, 11.61 mmol) in dichloromethane (30 mL). The reaction mixture was allowed to warm to rt and stirred overnight. The reaction mixture was cooled to 0 °C and quenched by slow addition of 1 M HCl (30 mL). The reaction mixture was allowed to warm to rt over 30 min, at which point 50 mL of water was added, and the resulting two-phase mixture was separated in a separatory funnel. The organic layer was washed with 100 mL of brine and dried over magnesium sulfate. The mixture was filtered, and the solvent was removed under vacuum. The crude product was dissolved in a minimal amount of hot hexanes and placed in the refrigerator overnight. The product, a spectroscopically pure yellow powder, was collected by suction filtration, rinsed with cold hexanes, and dried under high vacuum. Yield = 2.532 g (73%). IR (DCM cast, cm^{-1}): 3039 (w), 2990 (s), 2964 (s), 2930 (m), 2878 (m), 1660 (s, C═O). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.00 (d, J = 10 Hz, 1H), 8.39

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J. Org. Chem. 2015, 80, 1719−1726

(d, J = 10 Hz, 1H), 8.24 (d, J = 8 Hz, 1H), 8.23 (s, 1H), 8.17 (d, J = 8 Hz, 1H), 8.16 (d, J = 9 Hz, 1H), 7.92 (d, J = 8 Hz, 1H), 3.41 (q, J = 7 Hz, 2H), 3.40 (q, J = 8 Hz, 2H), 2.91 (s, 3H), 1.51 (t, J = 7 Hz, 3H), 1.50 (t, J = 8 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 202.5, 139.9, 137.1, 131.8, 131.8, 129.7, 129.4, 128.2, 127.8, 127.5, 126.9, 126.1, 126.0, 125.2, 124.8, 124.7, 122.1, 30.6, 26.9, 26.8, 16.3, 16.0. EI HRMS: exact mass calcd for $C_{22}H_{20}O$ (M^+) 300.15143, found 300.15131. Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.91; H, 6.76. Repeat Found: C, 87.80; H, 6.76.

1,3,6-Triethylpyrene (15). To a suspension of 1-(3,8-diethylpyren-1-yl)ethanone **14** (2.000 g, 6.658 mmol) and potassium hydroxide (3.883 g, 69.21 mmol) in ethylene glycol (36 mL) in a 100 mL RBF fitted with a reflux condenser and open to the air was added hydrazine hydrate (5.50 mL, 0.113 mol) via syringe. The mixture was heated to 120 °C for 2 h, after which time the condenser was removed and the reaction mixture heated to 200 °C for 1 h to drive off water. At this point, the reaction mixture was cooled to rt and taken up in dichloromethane and water. The organic layer was separated, washed with brine, dried with magnesium sulfate, and filtered, and the solvent was removed under vacuum. The resulting orange sludge was filtered through a short silica pad using hexanes. Removal of the solvent provided a white solid that was dissolved in a minimal amount of hot toluene, diluted with an equal volume 2-propanol, and placed in the freezer overnight. The product, a spectroscopically pure white solid was collected by suction filtration, rinsed with cold 2-propanol, and dried under high vacuum. Yield = 1.13g (70%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, J = 9 Hz, 1H), 8.25 (d, J = 9 Hz, 1H), 8.19 (d, J = 9 Hz, 1H), 8.06 (d, J = 8 Hz, 1H), 7.99 (d, J = 9 Hz, 1H), 7.85 (d, J = 8 Hz, 1H), 7.75 (s, 1H), 3.40−3.33 (m, 6H, 3 overlapping quartets w/J = 8 Hz each), 1.51−1.46 (m, 9H, 3 overlapping triplets w/J = 8 Hz each). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 138.2, 138.0, 138.0, 129.9, 128.5, 127.3, 127.2, 126.8, 126.5, 126.2, 126.0, 125.9, 124.5, 123.2, 122.5, 122.2, 26.8, 26.7, 26.7, 16.2, 16.2, 16.1. EI HRMS: exact mass calcd for $C_{22}H_{22}$ (M^+) 286.17215, found 286.17244. Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.91; N, 0.35.

1-Bromo-3,6,8-triethylpyrene (16). A 50 mL RBF open to the air was charged with 1,3,6-triethylpyrene (1.000 g, 3.494 mmol) dissolved in dichloromethane (30 mL). To this solution was added NBS (0.653 g, 3.67 mmol). The reaction mixture was allowed to stir at rt overnight. The solvent was removed under vacuum, and the crude product, a brown sludge, was dissolved in a minimal amount of warm dichloromethane, combined with an equal volume of methanol, and placed in a freezer overnight. The product, a light brown, spectroscopically pure powder, was collected by suction filtration, rinsed with methanol, and dried under high vacuum. Yield = 1.054 g (83%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, J = 9 Hz, 1H), 8.31 (d, J = 8 Hz, 1H), 8.29 (d, J = 8 Hz, 1H), 8.20 (d, J = 9 Hz, 1H), 8.11 (s, 1H), 7.79 (s, 1H), 3.39−3.31 (6 line m, 6H, 3 overlapping quartets w/J = 8 Hz each), 1.51−1.47 (m, 9H, 3 overlapping triplets w/J = 8 Hz each). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 138.9, 138.9, 138.7, 130.2, 128.2, 128.1, 127.8, 127.2, 127.1, 126.9, 125.4, 124.9, 124.1, 123.5, 121.9, 119.4, 26.8, 26.7, 26.4, 16.2, 16.2, 15.8. EI HRMS: exact mass calcd for $C_{22}H_{21}{}^{81}Br$ (M^+) 366.08063, found 366.08224. Anal. Calcd for $C_{22}H_{21}Br$: C, 72.33; H, 5.79. Found: C, 72.47; H, 5.82.

1,3,6-Tribromo-8-ethylpyrene (18). A 100 mL RBF fitted with a condenser and open to the air was charged with a solution of 1-ethylpyrene (1.840 g, 7.990 mmol) in chloroform (60 mL) at rt. To this solution was added NBS (4.408 g, 24.78 mmol), and the reaction mixture was heated overnight at reflux. The reaction mixture was cooled to rt, and the crude product collected by suction filtration, rinsed with cold chloroform and methanol, and then dried under vacuum to provide 2.758 g (74%) of a spectroscopically pure beige powder. ^1H NMR (500 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.52 (d, J = 9 Hz, 1H), 8.44 (d, J = 9 Hz, 1H), 8.42 (d, J = 10 Hz, 1H), 8.35 (d, J = 8 Hz, 1H), 8.21 (s, 1H), 3.36 (q, J = 8 Hz, 2H), 1.50 (t, J = 8 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 140.8, 134.0, 131.8, 129.4, 129.1, 128.2, 128.1, 128.0, 128.0, 126.5, 125.9, 125.3, 124.9, 121.5, 119.9, 119.8, 26.5, 15.9. EI HRMS: exact mass calcd for $C_{18}H_{11}{}^{81}Br_3$ (M^+) 469.83493, found 469.83462. Anal. Calcd for $C_{18}H_{11}Br_3$: C, 46.29; H, 2.37. Found: C, 46.49; H, 2.42. Repeat Found: C, 46.66; H, 2.43; N, 0.15.

9-(4-(3,6,8-Triethylpyren-1-yl)butyl)-9*H*-carbazole (19). A 50 mL RBF under nitrogen was charged with 1-bromo-3,6,8-triethylpyrene (1.000 g, 2.737 mmol) and $NiCl_2$(dppe) (0.043 g, 0.082 mmol) in THF (20 mL). To the resulting suspension was added (4-(9*H*-carbazol-9-yl)butyl)magnesium chloride (8 mL of a 0.5 M solution in THF) at room temperature. The reaction mixture was allowed to stir overnight, cooled to 0 °C, and quenched slowly with 1 M HCl (5 mL). The crude reaction mixture was taken up in ether and washed with water and brine. The organic layer was dried over magnesium sulfate and filtered, and the solvent was removed under vacuum. The crude solid was dissolved in a minimal amount of hot *sec*-butanol and allowed to precipitate from solution overnight at room temperature, providing a yellow, spectroscopically pure powder that was collected by suction filtration, rinsed with *sec*-butanol, and dried under high vacuum. Yield = 0.995 g (72%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 10 Hz, 1H), 8.20 (d, J = 10 Hz, 1H), 8.19 (d, J = 9 Hz, 1H), 8.12 (d, J = 10 Hz, 1H), 8.10 (d, J = 8 Hz, 2H), 7.74 (s, 1H), 7.61 (s, 1H), 7.44 (dd, J = 6, 1 Hz, 2H), 7.40 (ddd, J = 8, 8, 1 Hz, 2H), 7.22 (ddd, J = 8, 7, 1 Hz, 2H), 4.35 (t, J = 7 Hz, 2H), 3.37−3.28 (m, 8H), 2.07 (m, 2H), 1.98 (m, 2H), 1.49 (t, J = 8 Hz, 3H), 1.48 (t, J = 8 Hz, 3H), 1.44 (t, J = 8 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 140.5, 137.9, 137.9, 137.6, 135.2, 127.9, 127.2, 127.2, 127.1, 127.0, 127.0, 126.5, 126.4, 125.7, 122.9, 122.4, 122.2, 122.1, 120.4, 118.8, 108.7, 43.1, 33.4, 29.3, 29.0, 26.8, 26.8, 26.7, 16.2, 16.2, 16.1. APPI-TOF HRMS: exact mass calcd for ($[M + H]^+$) $C_{38}H_{38}N$ 508.2999, found 508.3003. Anal. Calcd for $C_{38}H_{37}N$: C, 89.90; H, 7.35; N, 2.76. Found: C, 89.63; H, 7.35; N, 2.85. Repeat Found: C, 89.71; H, 7.37; N, 2.83.

1,3,6-Triethyl-8-(4-(phenanthren-9-yl)butyl)pyrene (20). A 50 mL RBF was charged with 1-bromo-3,6,8-triethylpyrene (1.000 g, 2.737 mmol) and $NiCl_2$(dppe) (0.043 g, 0.082 mmol) and dissolved in THF (15 mL). To this suspension was added (4-(phenanthren-9-yl)butyl)magnesium chloride (14 mL of a 0.3 M in anisole/THF (4.7:1 v/v)). The resulting reaction mixture was allowed to stir at overnight at room temperature. The reaction mixture was then cooled to 0 °C and quenched carefully with 1 M HCl (5 mL). The reaction mixture was taken up in chloroform and washed with water, followed by brine. The organic layer was dried over magnesium sulfate and filtered and the solvent removed under vacuum. The crude solid was dissolved in a minimal amount hot *sec*-butanol, and the product, a spectroscopically pure white powder, precipitated out of solution at overnight. The product was collected by suction filtration, rinsed with *sec*-butanol, and dried under high vacuum. Yield = 1.158 g (82%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.74 (dd, J = 10, 2 Hz, 1H), 8.65 (d, J = 8 Hz, 1H), 8.23 (d, J = 10 Hz, 1H), 8.20 (d, J = 10 Hz, 1H), 8.20 (d, J = 10 Hz, 1H), 8.18 (d, J = 10 Hz, 1H), 8.12 (dd, J = 8, 1 Hz, 1H), 7.77 (dd, J = 7, 1 Hz, 1H), 7.73 (s, 1H) δ 7.71 (s, 1H), 7.67−7.53 (m, 5H), 3.41−3.30 (m, 8H), 3.21 (t, J = 7 Hz, 2H), 2.06−2.03 (m, 4H), 1.53−1.44 (m, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 137.8, 137.8, 137.6, 136.7, 136.0, 132.0, 131.4, 130.8, 129.7, 128.1, 127.9, 127.3, 127.1, 127.1, 127.0, 127.0, 126.6, 126.5, 126.5, 126.4, 126.2, 126.1, 125.9, 124.5, 123.3, 122.5, 122.3, 122.3, 122.2. APPI-TOF HRMS: exact mass calcd for ($[M + H]^+$) $C_{40}H_{39}$ 519.3046, found 519.3045. Anal. Calcd for $C_{40}H_{38}$: C, 92.62; H, 7.38. Found: C, 91.79; H, 7.38. Repeat Found: C, 91.89; H, 7.41.

9,9′-((3,8-Diethylpyrene-1,6-diyl)bis(butane-4,1-diyl))bis-(9*H*-carbazole) (21). A 100 mL RBF was charged with 1,6-dibromo-3,8-diethylpyrene (1.000 g, 2.403 mmol) and $NiCl_2$(dppe) (0.063 g, 0.12 mmol) in THF (50 mL). To this suspension was added (4-(9*H*-carbazol-9-yl)butyl)magnesium chloride (14 mL of a 0.5 M solution in THF) at room temperature and the reaction mixture allowed to stir overnight. After being cooled to 0 °C, the reaction was quenched with 1 M HCl (5 mL). The crude product was collected by suction filtration and washed multiple times with hot water, followed by ether, followed by hexanes. This washed product was then dissolved in a minimal amount of hot chloroform and placed in the freezer overnight. The product was collected by suction filtration and rinsed with cold dichloromethane. The resulting white powder was then dried under

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J. Org. Chem. 2015, 80, 1719−1726

high vacuum to yield spectroscopically pure **21**. Yield = 0.883 g (52%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, J = 11 Hz, 2H), 8.12 (d, J = 11 Hz, 2H), 8.10 (dd, J = 8, 1 Hz, 4H), 7.61 (s, 2H), 7.43 (ddd, J = 8, 7, 1 Hz, 4H), 7.39 (d, J = 8 Hz, 4H), 7.22 (ddd, J = 8, 7, 1 Hz, 4H), 4.34 (t, J = 7 Hz, 4H), 3.33−3.29 (m, 8H), 2.07 (tt, J = 8, 8 Hz, 4H), 1.97 (tt, J = 8, 7 Hz, 4H), 1.44 (t, J = 8 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.4, 137.7, 135.4, 127.9, 127.2, 127.1, 126.4, 125.6 122.9, 122.4, 122.2, 120.4, 118.8, 108.7, 43.1, 33.4, 29.3, 28.9, 26.7, 16.1. MALDI-FT-ICR HRMS: exact mass calcd for (M^+) $C_{52}H_{48}N_2$ 700.38120, found 700.38105. Anal. Calcd for $C_{52}H_{48}N_2$: C, 89.10; H, 6.90; N, 4.00. Found: C, 88.72; H, 6.87; N, 4.02. Repeat Found: C, 88.79; H, 6.80; N, 4.04.

1,6-Diethyl-3,8-bis(4-(phenanthren-9-yl)butyl)pyrene (22). A 100 mL RBF under nitrogen was charged with 1,8-dibromo-3,6-diethylpyrene (1.000 g, 2.403 mmol) and $NiCl_2$(dppe) (0.063 g, 0.12 mmol) in THF (40 mL) and stirred at room temperature. To this suspension was added (4-(phenanthren-9-yl)butyl)magnesium chloride (24 mL of a 0.3 M in anisole/THF (4.7:1 v/v)). The reaction mixture was allowed to stir overnight at rt, after which time it was cooled to 0 °C and quenched with 1 M HCl (5 mL). The precipitated product was collected by suction filtration and washed multiple times with hot water, then ether, then hexanes. The crude product was dissolved in a minimal amount of hot chloroform and allowed to precipitate from solution overnight. The product, a spectroscopically pure white powder, was collected by suction filtration, washed with cold dichloromethane, and dried under high vacuum. Yield = 1.214 g (70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74 (dd, J = 8, 1 Hz, 2H), 8.65 (d, J = 8 Hz, 2H), 8.21 (d, J = 10 Hz, 2H), 8.17 (d, J = 10 Hz, 2H), 8.12 (d, J = 8 Hz, 2H), 7.77 (d, J = 8 Hz, 2H), 7.71 (s, 2H), δ 7.68−7.50 (m, 10H), 3.40 (t, J = 7 Hz, 4H), 3.32 (q, J = 8 Hz, 4H), 3.20 (t, J = 8 Hz, 4H), 2.07−2.03 (m, 8H), 1.45 (t, J = 5 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.6, 136.7, 136.1, 132.0, 131.4, 130.8, 129.7, 128.1, 128.0, 127.3, 127.1, 126.6, 126.5, 126.5, 126.2, 126.1, 125.9, 124.5, 123.3, 122.5, 122.4, 122.3, 33.7, 33.4, 31.9, 30.3, 26.7, 16.2. APPI-TOF HRMS: exact mass calcd for ([M + H]$^+$) $C_{56}H_{51}$ 723.3985, found 723.3971. Anal. Calcd for $C_{56}H_{50}$: C, 93.03; H, 6.97. Found: C, 91.38; H, 6.96. Repeat Found: C, 91.39; H, 6.94.

9,9′-((3,6-Diethylpyrene-1,8-diyl)bis(butane-4,1-diyl))bis(9*H*-carbazole) (23). A 100 mL RBF under nitrogen atmosphere was charged with 1,8-dibromo-3,6-diethylpyrene (1.000 g, 2.403 mmol) and $NiCl_2$(dppe) (0.063 g, 0.12 mmol) in THF (50 mL). To this suspension was added (4-(9*H*-carbazol-9-yl)butyl)magnesium chloride (14 mL of a 0.5 M solution in THF) at room temperature, and the reaction mixture was allowed to stir at rt overnight. The reaction mixture was then cooled to 0 °C and quenched with 1 M HCl (5 mL). The crude product was collected by suction filtration and washed multiple times with hot water, then ether, then hexanes. The crude product was then dissolved in a minimal amount of warm dichloromethane and allowed to precipitate out of solution overnight. The product, a spectroscopically pure light yellow powder, was collected by suction filtration, washed with cold dichloromethane, and dried under high vacuum. Yield = 0.954 g (57%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 2H), 8.10 (ddd, J = 8, 1, 1 Hz, 4H), 8.08 (s, 2H), 7.62 (s, 2H), 7.43 (ddd, J = 8, 7, 2 Hz, 4H), 7.39 (dd, J = 7, 1 Hz, 4H), 7.22 (ddd, J = 8, 7, 1 Hz, 4H), 4.35 (t, J = 7 Hz, 4H), 3.33−3.28 (m, 8H), 2.11−2.05 (m, 4H), 2.01−1.95 (4, 4H), 1.44 (6, J = 7 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.5, 137.8, 135.4, 127.9, 127.2, 127.2, 126.4, 125.7, 122.9, 122.4, 122.3, 120.4, 118.8, 108.7, 43.1, 33.4, 29.4, 29.0, 26.7, 16.2. APPI-TOF HRMS: exact mass calcd for ([M + H]$^+$) $C_{52}H_{49}N_2$ 701.3890, found 701.3879. Anal. Calcd for $C_{52}H_{48}N_2$: C, 89.10; H, 6.90; N, 4.00. Found: C, 88.24; H, 6.96; N, 4.07. Repeat Found: C, 88.35; H, 6.88; N, 4.05.

1,8-Diethyl-3,6-bis(4-(phenanthren-9-yl)butyl)pyrene (24). A 100 mL RBF under nitrogen was charged with 1,6-dibromo-3,8-diethylpyrene (1.000 g, 2.403 mmol) and $NiCl_2$(dppe) (0.063 g, 0.12 mmol) in THF (40 mL). To this suspension was added (4-(phenanthren-9-yl)butyl)magnesium chloride (24 mL of a 0.3 M solution in anisole/THF (4.7:1 v/v)) at room temperature. The reaction mixture was allowed to stir at rt overnight. The reaction mixture was cooled to 0 °C and quenched with 1 M HCl (5 mL). The precipitated product was collected by suction filtration and washed multiple times with hot water, then ether, then hexanes. This material was then dissolved in a minimal amount of warm dichloromethane and allowed to precipitate from solution overnight in a freezer. The product, a spectroscopically pure white powder, was collected by suction filtration, rinsed with cold dichloromethane, and dried under high vacuum. Yield = 1.136 g (65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (dd, J = 8, 1 Hz, 2H), 8.68 (d, J = 8 Hz, 2H), 8.25 (s, 2H), 8.20 (s, 2H), 8.15 (dd, J = 8, 1 Hz, 2H), 7.80 (dd, J = 7, 1 Hz, 2H), 7.75 (s, 2H), 7.70−7.56 (m, 10H), 3.42 (t, J = 7 Hz, 4H), 3.38 (q, J = 7 Hz, 4H), 3.24 (t, J = 7 Hz, 4H), 2.08 (m, 8H), 1.49 (t, J = 8 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.6, 136.7, 136.0, 132.0, 131.4, 130.8, 129.7, 128.1, 128.0, 127.2, 127.1, 126.6, 126.5, 126.5, 126.2, 126.1, 125.9, 124.5, 123.3, 122.5, 122.4, 122.3, 33.7, 33.4, 31.9, 30.3, 26.7, 16.2. APPI-TOF HRMS: exact mass calcd for ([M + H]$^+$) $C_{56}H_{51}$ 723.3985, found 723.3977. Anal. Calcd for $C_{56}H_{50}$: C, 93.03; H, 6.97. Found: C, 91.27; H, 7.28. Repeat Found: C, 91.49; H, 6.95.

9,9′,9″-((8-Ethylpyrene-1,3,6-triyl)tris(butane-4,1-diyl))tris(9*H*-carbazole) (25). To a glass reactor topped by a Teflon high vacuum stopcock under nitrogen were added 1,3,6-tribromo-8-ethylpyrene (1.000 g, 2.141 mmol) and $NiCl_2$(dppe) (0.057 g, 0.11 mmol) in dioxane (60 mL). To this suspension was added (4-(9*H*-carbazol-9-yl)butyl)magnesium chloride (19 mL of a 0.5 M solution in THF) at room temperature. The reactor was sealed and heated to 100 °C for 36 h. The resulting reaction mixture was cooled to 0 °C and quenched with 1 M HCl (5 mL). The mixture was taken up in ether and washed with water, followed by brine. The organic layer was dried over magnesium sulfate and filtered, and the solvents were removed under vacuum. The crude product was taken up in a minimal amount of hot chloroform and placed in the freezer overnight, at which point the product, a spectroscopically pure yellow powder, was collected by suction filtration and washed with cold dichloromethane. Yield = 1.224 g (64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, J = 10 Hz, 1H), 8.12−8.10 (m, 8H), 8.06 (d, J = 9 Hz, 1H), 7.62 (s, 1H), 7.45−7.33 (m, 13H), 7.24−7.19 (m, 6H), 4.36 (t, J = 7 Hz, 2H), 4.30−4.26 (m, 4H), 3.33−3.22 (m, 8H), δ 2.11−1.87 (m, 12H), 1.45 (t, J = 7 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.4, 140.4, 140.4, 137.9, 135.5, 135.2, 135.1, 128.8, 128.0, 127.4, 127.3, 127.1, 127.1, 126.4, 126.3, 125.6, 125.6, 125.6, 125.6, 125.6, 122.9, 122.9, 122.9, 122.9, 122.5, 122.4, 122.2, 122.2, 120.4, 120.4, 118.8, 118.8, 108.7, 108.7, 43.1, 43.0, 33.4, 33.2, 29.3, 29.2, 29.0, 28.9, 28.9, 26.7, 16.2. APPI-TOF HRMS: exact mass calcd for ([M + H]$^+$) $C_{66}H_{60}N_3$ 894.4782, found 894.4774. Anal. Calcd for $C_{66}H_{59}N_3$: C, 88.65; H, 6.65; N, 4.70. Found: C, 86.04; H, 6.96; N, 4.57. Repeat Found: C, 86.51; H, 6.87; N, 4.62.

1-Ethyl-3,6,8-tris(4-(phenanthren-9-yl)butyl)pyrene (26). To a suspension of 1,3,6-tribromo-8-ethylpyrene (1.000 g, 2.141 mmol) and $NiCl_2$(dppe) (0.057 g, 0.11 mmol) in dioxane (50 mL) in a glass reactor topped by a Teflon vacuum stopcock was added (4-(phenanthren-9-yl)butyl)magnesium chloride (32 mL of a 0.3 M solution in anisole/THF (4.7:1 v/v)) at room temperature. The reactor was sealed and heated to 100 °C for 36 h. The reaction mixture was cooled to 0 °C and quenched carefully with 1 M HCl (5 mL). The resulting mixture was taken up in chloroform and washed with water, followed by brine. The organic layer was dried over magnesium sulfate, filtered, and evaporated to dryness. The crude product was dissolved in a minimal amount of hot chloroform and placed in the freezer overnight. The precipitated product, a light yellow spectroscopically pure powder, was collected by suction filtration, washed with cold dichloromethane, and dried under high vacuum. Yield = 1.022 g (51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74−8.70 (m, 3H), 8.66−8.62 (m, 3H), 8.20 (d, J = 9 Hz, 1H), 8.18 (d, J = 9 Hz, 1H), 8.16 (s, 1H), 8.16 (s, 1H), δ 8.12 (dd, J = 8, 2 Hz, 1H), δ 8.08−8.06 (m, 2H), 7.77 (dd, J = 8, 2 Hz, 1H), 7.75−7.73 (m, 2H), 7.72 (s, 1H), 7.68 (s, 1H), 7.66−7.50 (m, 15H), 3.40−3.30 (m, 8H), 3.22−3.14 (m, 6H), 2.07−2.00 (m, 12H), 1.46 (t, J = 8 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.7, 136.6, 136.6, 136.1, 135.9, 135.9, 132.0, 131.4, 131.3, 130.8, 130.8, 129.7, 129.7, 128.9, 128.1, 128.1, 128.0, 127.4, 127.3, 127.2, 127.1, 126.6, 126.6, 126.5, 126.5, 126.5, 126.2, 126.2, 126.1, 126.1, 125.9, 125.9, 124.5, 124.5, 123.3, 123.3, 122.5, 122.5,

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J. Org. Chem. 2015, 80, 1719−1726

122.4, 122.4, 122.3, 33.7, 33.6, 33.4, 33.4, 33.4, 31.9, 31.9, 31.8, 30.3, 30.2, 30.2, 26.7, 16.2. APPI-TOF HRMS: exact mass calcd for ([M + H]$^+$) $C_{72}H_{63}$ 927.4924, found 927.4927. Anal. Calcd for $C_{72}H_{62}$: C, 93.26; H, 6.74. Found: C, 91.05; H, 6.62. Repeat Found: C, 90.96; H, 6.62.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra and crystallographic details (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(23) Details of the X-ray structure solution for compound **21** are provided as Supporting Information.

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J. Org. Chem. 2015, 80, 1719−1726