Phenacenes: A Family of Graphite Ribbons. 2. Syntheses of Some [7]Phenacenes and an [11]Phenacene by Stilbene-like Photocyclizations

Frank B. Mallory,*,† Kelly E. Butler,† Amanda C. Evans,† Emilie J. Brondyke,† Clelia W. Mallory,‡ Changqing Yang,† and Aviva Ellenstein†

Contribution from the Departments of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010, and University of Pennsylvania, Philadelphia, Pennsylvania 19104

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Abstract: It is proposed that members of the family of polycyclic aromatic compounds with an extended phenanthrene-like structural motif be designated as [*n*]phenacenes, where *n* is the number of fused benzene rings. [*n*]Phenacene molecules are related to layers of graphite in the way that ribbons are related to sheets. In order to investigate the properties of [*n*]phenacenes as materials, methods for the syntheses of these molecules have been developed that involve Wittig reactions and stilbene-like photocyclizations for the construction of carbon−carbon bonds. The solubilities of the unsubstituted [*n*]phenacene molecules decrease dramatically with increasing *n*; [7]phenacene, the largest known example, melts with decomposition at 565 °C and is essentially intractable for chemical investigation owing to its extreme insolubility. This solubility problem was solved by incorporating alkyl substituents. 2,13-Di-*n*-pentyl[7]phenacene, 2,13-di-*tert*-butyl[7]phenacene, and 15,18-di-*n*-pentyl[7]phenacene (mp 325, 290, and 235 °C, respectively) were synthesized and found to be moderately soluble compounds. As a first step in the exploration of the chemistry of larger phenacenes, 2,17,21,24-tetra-*n*-pentyl[11]phenacene was synthesized.

Using Wittig reactions followed by stilbene-like photocyclizations[1] as the key steps for the construction of carbon−carbon bonds, we have developed methods for the synthesis of various members of the family of polycyclic aromatic compounds having fused benzene rings in an extended phenanthrene-like structural motif. We propose to designate these compounds as [*n*]phenacenes, where *n* is an integer that indicates the number of fused benzene rings. As illustrated by the bold outlines in the schematic representation of a layer of graphite shown in Figure 1, these phenacene molecules are related to layers of graphite as ribbons are to sheets. In view of this structural analogy, and in view of the practical importance of graphite as a material, it is our hope that [*n*]phenacenes with large values of *n* might show interesting and potentially useful properties (*e.g.*, as electrical conductors or as nonlinear optical materials).

Prior to our recent work,[2] there appear to have been no reports in the literature of any simple unsubstituted phenacenes with more than six rings. This limitation can be attributed to solubility problems, which increase dramatically with increasing values of *n* as a consequence of the very favorable crystal packing interactions for molecules of this shape. This is illustrated by the trend in the melting points of the four previously known unsubstituted phenacenes: phenanthrene ([3]-phenacene), 101 °C; chrysene ([4]phenacene), 256 °C; picene ([5]phenacene), 364 °C; and fulminene ([6]phenacene), 467 °C. In line with this trend, [7]phenacene (**1**), a compound whose synthesis we reported recently[2] (Scheme 1), melts with decomposition at 565 °C.[3]

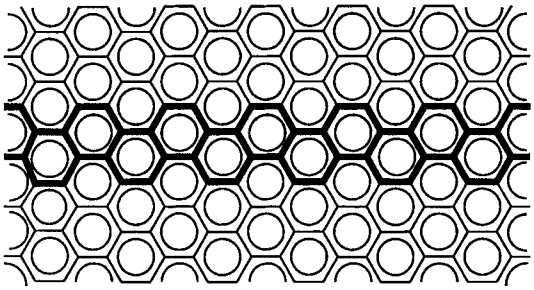
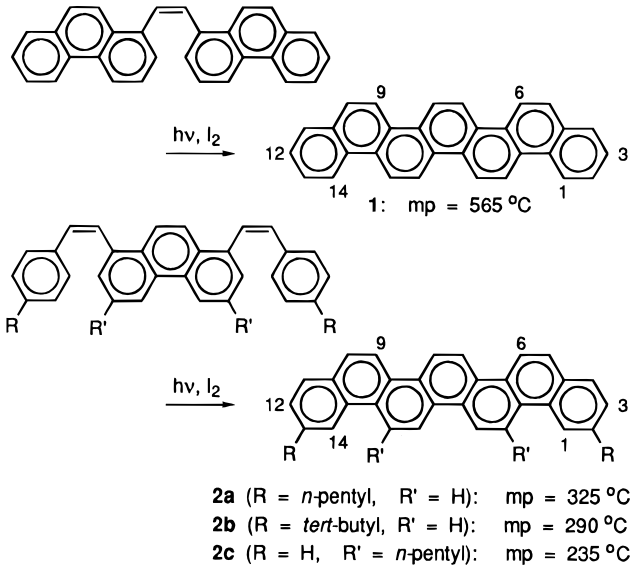


Figure 1. Representation of a layer of graphite illustrating that [*n*]-phenacene molecules can be regarded as graphite ribbons.

Scheme 1



[7]Phenacene (**1**) is very insoluble. To obtain its ^{1}H NMR spectrum (see the Experimental Section), we had to resort to

† Bryn Mawr College.
‡ University of Pennsylvania.
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(1) Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1−456.
(2) (a) For Part 1 in this series, see: Mallory, F. B.; Butler, K. E.; Evans, A. C.; Mallory, C. W. *Tetrahedron Lett.* **1996**, *40*, 7173−7176. (b) Mallory, F. B.; Butler, K. E.; Evans, A. C.; Mallory, C. W. 1995 International Chemical Congress of Pacific Basin Societies, Abstract #3294. (c) Butler, K. E. M.A. Thesis, Bryn Mawr College, 1996.

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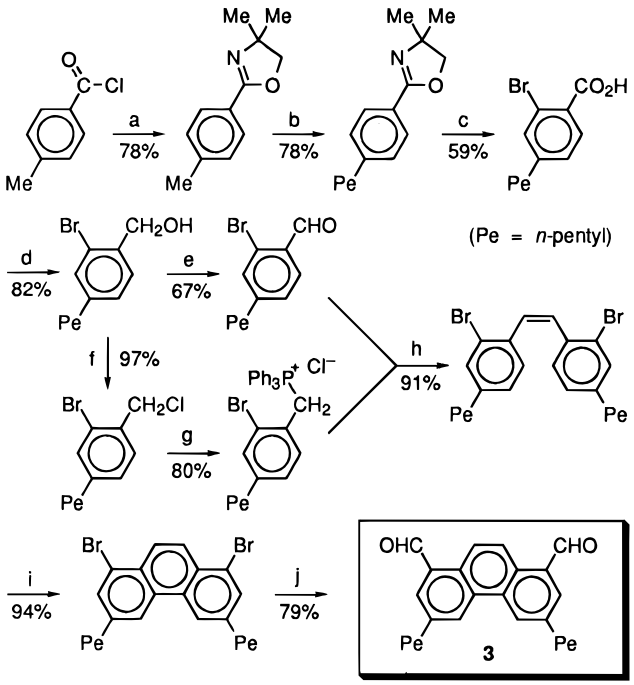
carrying out the measurement at 150 °C in 1,2,4,5-tetrachloro-3,6-dideuteriobenzene[4] as the solvent. This spectrum is fully consistent with the proposed structure of **1**. In the region characteristic of aromatic bay hydrogens (δ 8.9−9.4) there are the expected five signals: one singlet (H-7,8), one doublet with coupling constant of about 8.5 Hz (H-1,14), and three doublets with coupling constants of about 9.1 Hz (H-6,9; H-15,18; and H-16,17). In the region characteristic of aromatic α hydrogens (δ 8.0−8.2) there is the expected doublet with a coupling constant of about 8.5 Hz (H-4,11) and the expected doublet with a coupling constant of about 9.1 Hz (H-5,10). In the region characteristic of aromatic β hydrogens (δ 7.6−8.0) there are the expected two broad triplets with coupling constants of about 8 Hz (H-2,13 and H-3,12).

[7]Phenacene (**1**) is so insoluble that we had to employ an experimental trick even to measure its ultraviolet absorption spectrum. We placed an appropriately dilute solution of 1,2-di-1-phenanthrylethylene in air-saturated benzene in a 1-cm spectrometer cuvette, irradiated this cuvette briefly with ultraviolet light from a mercury lamp to produce **1** by oxidative photocyclization (Scheme 1),[5] and then quickly placed the cuvette in a spectrometer and recorded a spectrum (see the Experimental Section). At this stage the concentration of dissolved **1** temporarily exceeded its thermodynamic solubility in benzene; over a period of minutes, the spectrum gradually disappeared as the solution came to equilibrium by precipitating **1** onto the walls of the cuvette.

To meet our ultimate goal of synthesizing and characterizing [*n*]phenacenes with large values of *n*, it is obvious that we must find ways to solubilize these otherwise intractable compounds. The strategy we have adopted for this purpose involves incorporating alkyl groups as substituents in order to disrupt the close-packing intermolecular associations found in the crystals of the parent systems. Specifically, we have synthesized 2,13-di-*n*-pentyl[7]phenacene (**2a**),[2] 2,13-di-*tert*-butyl[7]phenacene (**2b**),[2] and 15,18-di-*n*-pentyl[7]phenacene (**2c**) (see Scheme 1) and have found that these are moderately soluble compounds with melting points of 325, 290, and 235 °C, respectively. These results suggest that alkyl groups are more effective as solubilizing substituents when they are located at bay positions such as 15 and 18 rather than at uncrowded positions such as 2 and 13, an effect we attribute to the twisting of the polycyclic framework that bay substituents are expected to cause.

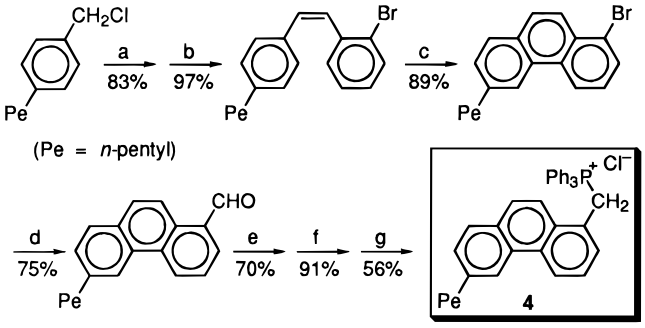
With these preliminary results in hand, we turned our attention to the synthesis of a significantly larger solubilized phenacene. As illustrated[6] in Schemes 2 and 3, we first prepared two key intermediates: 3,6-di-*n*-pentylphenanthrene-1,8-dicarboxaldehyde (**3**) and the phosphonium salt **4** obtained from the reaction of 1-(chloromethyl)-6-*n*-pentylphenanthrene with triphenylphosphine. As illustrated[6] in Scheme 4, these two intermediates were assembled by a Wittig reaction to give the bis(arylvinyl)-phenanthrene **5**, which was then photocyclized to give 2,17,21,24-tetra-*n*-pentyl[11]phenacene (**6**).

Scheme 2[a]



[a] (a) $H_2NCMe_2CH_2OH$; (b) $LiN(i\text{-}Pr)_2$, *n*-BuBr; (c) *n*-BuLi, THF, Br_2, hydrolysis; (d) BH_3, THF; (e) PCC; (f) $SOCl_2$; (g) Ph_3P; (h) aqueous NaOH, CH_2Cl_2; (i) $h\nu$, I_2; (j) *n*-BuLi, DMF, hydrolysis.

Scheme 3[a]



[a] (a) Ph_3P; (b) aqueous NaOH, CH_2Cl_2, *o*-bromobenzaldehyde; (c) $h\nu$, I_2; (d) *n*-BuLi, DMF, hydrolysis; (e) $NaBH_4$; (f) $SOCl_2$; (g) Ph_3P.

The ^{1}H NMR spectrum of **6**, measured in 1,2,4,5-tetrachloro-3,6-dideuteriobenzene[4] solution at 147 °C, is fully in accord with the proposed structure (see the Experimental Section). There are the expected eight signals for aromatic bay hydrogens (δ 8.9−9.4): one broad singlet (H-1,18), two sharp singlets (H-9,10 and H-22,23), and five doublets with coupling constants of about 9.1 Hz (H-6,13; H-7,12; H-8,11; H-19,26; and H-20,25). Also there are the expected two signals for aromatic α hydrogens (δ 8.0−8.2): a doublet with a coupling constant of about 8.5 Hz (H-4,15) and a doublet with a coupling constant of about 9.1 Hz (H-5,14). In the region characteristic of aromatic β hydrogens (δ 7.6−8.0), the expected broad doublet with a coupling constant of about 8.5 Hz (H-3,16) is obscured by the signal from incompletely deuterated molecules of the solvent. Finally, the region characteristic of aliphatic hydrogens (δ 0.9−4.2) contains the five signals expected for the pentyl groups at positions 2 and 17 and also the five signals expected for the somewhat more deshielded pentyl groups at positions 21 and 24.

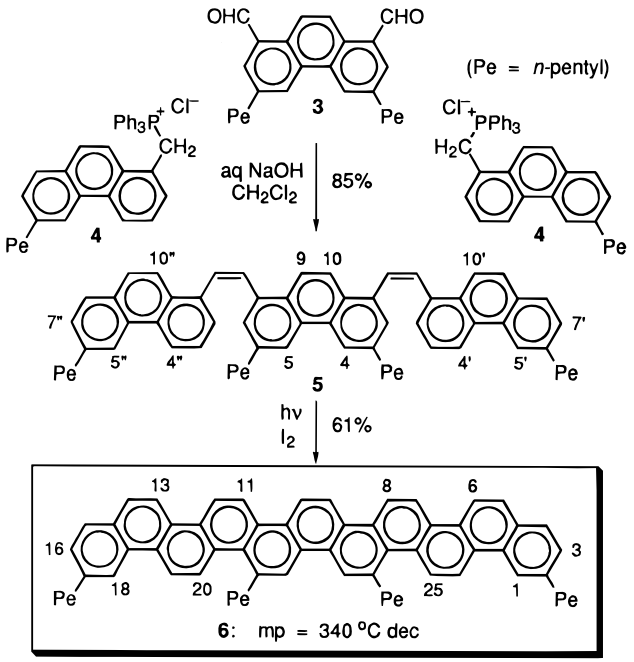
(3) We are grateful to Dr. Andrew R. McGhie of the University of Pennsylvania for determining the melting behavior of [7]phenacene (**1**) by differential scanning calorimetry.

(4) 1,2,4,5-Tetrachloro-3,6-dideuteriobenzene was prepared for use as a high-temperature NMR solvent as described in the following: Zimmerman, H. *Mol. Cryst. Liq. Cryst.* **1978**, *49*, 1−5.

(5) Under these conditions, the dihydrophenanthrene type of intermediate generated in this photocyclization reaction is trapped oxidatively to give **1** by reaction with dissolved O_2.

(6) For convenience the stilbene analogues in Schemes 2−4 are depicted as *Z* isomers, although the Wittig reactions shown in these schemes actually produce mixtures of *E* and *Z* isomers. For purposes of purification and characterization, we routinely use catalysis by atomic iodine (produced from I_2 by irradiation with visible light) to isomerize these product mixtures in cyclohexane solution to the thermodynamically favored *E* isomer, which is then recrystallized to high purity. Although stilbene-like photocyclization ultimately requires absorption of an ultraviolet photon by the *Z* isomer, either the *E* or the *Z* isomer can be used as the starting material because they are interconverted by ultraviolet irradiation. It is sometimes convenient to carry out photocyclizations starting with the *E*,*Z* mixture that is obtained from a Wittig reaction.

Scheme 4



The ultraviolet absorption spectrum of the [11]phenacene derivative **6** shows the typical pattern of peaks characteristic of the previously known smaller phenacenes but with the expected shift of the pattern to longer wavelengths. The magnitudes of the red shifts in phenacenes as a function of the number of rings *n* can be gauged by using as an index for each particular phenacene the wavelength of its so-called para band,[7] which is the longest-wavelength peak in the set of intense peaks in its electronic absorption spectrum. The wavelength of this peak depends not only on the value of *n* but also on the nature of the substituents. For example, the peak for the unsubstituted [7]-phenacene (**1**) is at 344 nm, but for each of the 2,13-dialkyl derivatives **2a**,**b**, the peak is red-shifted by 4 nm, and for the 15,18-dialkyl derivative **2c**, the peak is red-shifted by 14 nm. Perhaps steric effects account for our observation that the two intramolecularly crowded bay-region alkyl groups in **2c** cause a larger red shift (14 nm) than the two uncrowded alkyl groups in **2a**,**b** (4 nm). The tetraalkyl[11]phenacene derivative **6** has its para band at 400 nm. This compound has two bay-region alkyl groups and two uncrowded alkyl groups. If the red shifts arising from these two types of alkyl substitution are assumed for simplicity to be approximately additive, one might expect that they would amount to a total of 18 nm for compound **6**. On this basis one might predict roughly that the *unsubstituted* [11]phenacene would have its para band at about 382 nm. The measured values of the para bands for the unsubstituted [*n*]-phenacenes with *n* ranging from 4 through 7, along with the value of 382 nm estimated here for the unsubstituted [11]-phenacene, are plotted against *n* in Figure 2. The slope of this plot is only about 9 nm/ring, which suggests that we may be required to go to quite large values of *n* to obtain highly colored phenacenes with small band gaps. For our long-term objectives it is promising that at least up to $n = 11$ there is no indication that this 9 nm/ring slope has begun to decrease with increasing *n*.

The tetra-*n*-pentyl[11]phenacene **6**, with its rather high mp of 340 °C, is not as soluble as we had hoped it would be. Accordingly, in the ongoing work in progress in our laboratory on the synthesis of alkyl-substituted [*n*]phenacenes with large values of *n*, we have adjusted our approach in two ways. First, we have decided to employ *tert*-butyl groups as the alkyl substituents because they appear to be somewhat more effective than *n*-pentyl groups as solubilizing substituents, as judged by our observation that the melting point of the di-*tert*-butyl compound **2b** is lower than that of its di-*n*-pentyl analogue **2a**. Second, we have adopted a modified method of synthesis that is designed to produce phenacenes with a higher ratio of the number of solubilizing substituents to the number of rings. We hope to report soon on the implementation of this revised strategy for the synthesis of solubilized phenacenes.

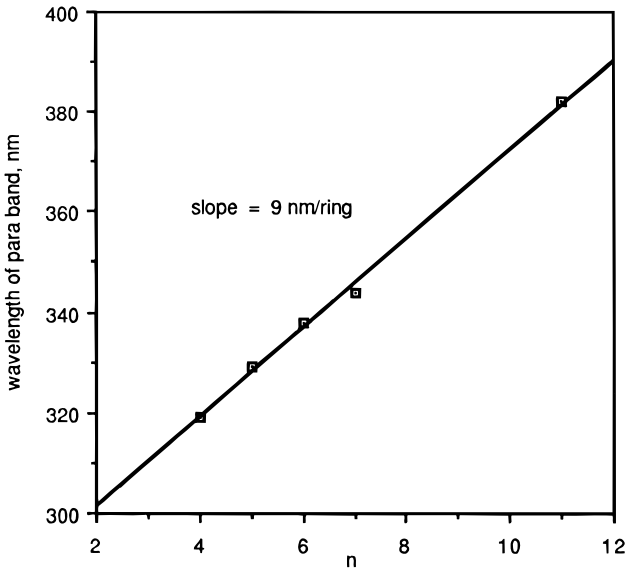


Figure 2. Wavelength of the para band (the longest-wavelength peak among the set of intense peaks in the electronic absorption spectrum) for each of a series of five different [*n*]phenacenes in benzene solution plotted as a function of *n*: [4]phenacene (chrysene), 319 nm;[8] [5]phenacene (picene), 329 nm;[8] [6]phenacene (fulminene), 338 nm;[8] [7]phenacene (**1**), 344 nm; and [11]phenacene, 382 nm (estimated as described in the text).

Experimental Section

General Procedure. Melting points were determined with an oil-bath apparatus and are uncorrected. Unless specified otherwise, ^{1}H NMR spectra were measured at 300 MHz in $CDCl_3$ solution at ambient temperature. A sample of 1,2,4,5-tetrachloro-3,6-dideuteriobenzene was prepared as previously reported;[4] the ^{1}H NMR signal at δ 7.67 arising from incompletely deuterated material in this sample was used as the reference for ^{1}H NMR spectra measured in this solvent. Mass spectra were obtained using GC/MS instrumentation. Photocyclizations were carried out using ultraviolet irradiation either from a Hanovia 450-W mercury lamp or from a set of 16 Rayonet 300-nm lamps. Elemental analyses were performed by M-H-W Laboratories, P.O. Box 15149, Phoenix, AZ 85018.

Wittig Reactions. Stilbene analogues were synthesized by Wittig reactions using the following general procedure. The appropriate (arylmethyl)phosphonium salt was prepared by treating the corresponding arylmethyl bromide or arylmethyl chloride with triphenylphosphine in refluxing xylenes, after which the reaction mixture was cooled and the phosphonium salt was collected by filtration, washed with cold xylenes, and allowed to dry. A solution of the phosphonium salt and an aromatic aldehyde in CH_2Cl_2 was stirred vigorously at room temperature while a solution of 50% aqueous NaOH was added dropwise. Subsequently the reaction mixture was heated at 50 °C for about 1 h and then was allowed to cool and poured into water. The layers were separated, and the aqueous layer was extracted with diethyl ether. This ether extract was combined with the original organic layer, which was then washed with H_2O, dried over Na_2SO_4, filtered, and evaporated. Cyclohexane was added to the residue, and the insoluble

(7) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964.
(8) Lang, K. F.; Buffleb, H.; Kalowy, J. *Chem. Ber.* **1964**, *97*, 494−497.

triphenylphosphine oxide was removed by filtration. A small crystal of I_2 was added to the filtrate, and the solution was irradiated for about 18 h with visible light to effect *Z*-to-*E* isomerization. Evaporation of the solvents followed by chromatography of the residue on silica gel with hexanes as eluent yielded the *E* isomer of the stilbene analogue.

(*E*)-1,2-Di-1-phenanthrylethylene. *o*-Methylstilbene, produced by a Wittig reaction of *o*-tolualdehyde with benzyltriphenylphosphonium bromide, was photocyclized to give 1-methylphenanthrene.[9] The reaction of 1-methylphenanthrene with 1 equiv of NBS gave 1-(bromomethyl)phenanthrene,[10] and the reaction of 1-methylphenanthrene with 2 equiv of NBS followed by hydrolysis gave phenanthrene-1-carboxaldehyde.[11]

Treatment of 1.90 g (7.0 mmol) of 1-(bromomethyl)phenanthrene with 1.83 g (7.0 mmol) of triphenylphosphine gave 3.38 g (91%) of the phosphonium salt. The Wittig reaction of 3.20 g (6.0 mmol) of this phosphonium salt with 1.24 g (6.0 mmol) of phenanthrene-1-carboxaldehyde gave, after recrystallization of the crude product from toluene, 1.70 g (74%) of (*E*)-1,2-di-1-phenanthrylethylene as a yellow solid. The characterization of this hydrocarbon was reported earlier.[2a]

[7]Phenacene (1). The photocyclization of (*E*)-1,2-di-1-phenanthrylethylene to give [7]phenacene (**1**) and some aspects of the characterization of **1** were reported earlier.[2a] Additional characterization of **1** is provided here: ^{1}H NMR (1,2,4,5-tetrachloro-3,6-dideuteriobenzene,[4] 150 °C) δ 9.23 and 9.12 (ABq, J = 9 Hz, 4 H; H-15,16,17,18), 9.16 (s, 2 H; H-7,8), 9.01 (d, J = 8 Hz, 2 H; H-1,14), 9.00 (d, J = 9 Hz, 2 H; H-6,9), 8.20 (d, J = 9 Hz, 2 H; H-4,11 or H-5,10), 8.17 (d, J = 9 Hz, 2 H; H-5,10 or H-4,11), 7.92 (br t, J = 8 Hz, 2 H; H-2,13 or H-3,12), 7.83 (br t, J = 8 Hz, 2 H; H-3,12 or H-2,13); UV (benzene, nm [relative intensity]) 344 [1.0], 320 [2.0], 304 [2.9] (see text for details).

(*E*)-2,2′-Dibromostilbene. Treatment of 3.0 g (12 mmol) of 2-bromobenzyl bromide with 3.14 g (12 mmol) of triphenylphosphine gave 5.8 g (94%) of the phosphonium salt. The Wittig reaction of this phosphonium salt with 2.09 g (11.3 mmol) of 2-bromobenzaldehyde gave 3.74 g (98%) of (*E*)-2,2′-dibromostilbene as a white solid that was recrystallized from 95% ethanol to give white needles: mp 110−111 °C (lit.[12] mp 108.0−108.5 °C); ^{1}H NMR δ 7.73 (dd, J = 7.8 Hz, 1.5 Hz, 2 H; H-6,6′), 7.60 (dd, J = 8.0 Hz, 1.1 Hz, 2 H; H-3,3′), 7.40 (s, 2 H; H-α,α′), 7.35 (td, J = 7.6 Hz, 1.1 Hz, 2 H; H-5,5′), 7.15 (td, J = 7.5 Hz, 1.5 Hz, 2 H; H-4,4′); MS *m/z* (relative intensity) 340 (M^+, 6), 338 (M^+, 13), 336 (M^+, 6), 178 (100). Anal. Calcd for $C_{14}H_{10}Br_2$: C, 49.74; H, 2.98. Found: C, 49.63; H, 2.89.

1,8-Dibromophenanthrene. A solution of 5.0 g (14.8 mmol) of (*E*)-2,2′-dibromostilbene, 3.81 g (15.0 mmol) of I_2, and 174.2 g (3.0 mol) of propylene oxide[13] in 560 mL of cyclohexane was irradiated (Rayonet) for 7 d. Evaporation of the solvent gave 4.93 g (98%) of 1,8-dibromophenanthrene as a yellow solid. Recrystallization from 95% ethanol/toluene gave white needles: mp 223−225 °C (lit.[14] mp 225 °C); ^{1}H NMR δ 8.66 (br d, J = 8.3 Hz, 2 H; H-4,5), 8.31 (s, 2 H; H-9,10), 7.93 (dd, J = 7.6 Hz, 0.8 Hz, 2 H; H-2,7), 7.53 (dd, J = 8.3 Hz, 7.8 Hz, 2 H; H-3,6); MS *m/z* (relative intensity) 338 (M^+, 45), 336 (M^+, 90), 334 (M^+, 45), 176 (100). Anal. Calcd for $C_{14}H_8Br_2$: C, 50.04; H, 2.40. Found: C, 49.83; H, 2.29.

Phenanthrene-1,8-dicarboxaldehyde (6). A stirred mixture of 3.0 g (8.9 mmol) of the partly soluble 1,8-dibromophenanthrene and 90 mL of anhydrous diethyl ether was cooled in an ice bath. A solution consisting of 14.2 mL (35.5 mmol) of 2.5 M *n*-BuLi in hexanes and 10 mL of anhydrous diethyl ether was added dropwise under N_2. Stirring was continued for an additional 30 min, after which 4.39 g (60 mmol) of anhydrous DMF was added dropwise. The reaction mixture was allowed to warm to room temperature and then poured onto 1 M H_3PO_4. The resulting precipitate was collected by filtration, washed with water and diethyl ether, and dried to give 1.91 g (92%) of **6** as a yellow solid. Recrystallization from 95% ethanol/toluene gave pale yellow crystals: mp 207−208 °C; ^{1}H NMR δ 10.57 (s, 2 H; CHO), 9.36 (s, 2 H; H-9,10), 9.03 (d, J = 8.4 Hz, 2 H; H-4,5), 8.18 (d, J = 7.2 Hz, 2 H; H-2,7), 7.89 (dd, J = 8.0 Hz, 7.7 Hz, 2 H; H-3,6). Anal. Calcd for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 81.96; H, 4.41.

2-(4-*n*-Pentylphenyl)-4,4-dimethyl-2-oxazoline. Treatment of 75 g (0.48 mol) of *p*-toluoyl chloride with 91 g (1.02 mol) of 2-amino-2-methylpropanol followed by 172 g (1.45 mol) of thionyl chloride as described previously[15] gave 71.1 g (78%) of 2-(4-methylphenyl)-4,4-dimethyl-2-oxazoline as a clear, colorless liquid: ^{1}H NMR δ 7.82 (d, J = 8.2 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 4.09 (s, 2 H), 2.38 (s, 3 H), 1.37 (s, 6 H); MS *m/z* (relative intensity) 189 (M^+, 8), 174 (100).

A solution of 11.1 g (110 mmol) of diisopropylamine in 250 mL of anhydrous THF was cooled in an ice bath and treated under N_2 with 43.2 mL (108 mmol) of a 2.5 M solution of *n*-BuLi in hexanes followed by 13.7 g (72 mmol) of 2-(4-methylphenyl)-4,4-dimethyl-2-oxazoline. After 30 min, 20.5 g (150 mmol) of 1-bromobutane was added and the reaction mixture was allowed to warm to room temperature. Aqueous workup followed by distillation (95−120 °C, 0.002 mm) gave 14.4 g (82%) of 2-(4-*n*-pentylphenyl)-4,4-dimethyl-2-oxazoline as a clear, colorless liquid: ^{1}H NMR δ 7.84 (d, J = 8.2 Hz, 2 H; H-2′,6′), 7.21 (d, J = 8.2 Hz, 2 H; H-3′,5′), 4.09 (s, 2 H; H-5), 2.63 (t, J = 7.7 Hz, 2 H), 1.61 (quintet, J = 7.2 Hz, 2 H), 1.37 (s, 6 H), 1.32−1.27 (m, 4 H), 0.88 (t, J = 6.9 Hz, 3 H); MS *m/z* (relative intensity) 245 (M^+, 6), 230 (100). Anal. Calcd for $C_{16}H_{23}NO$: C, 78.32; H, 9.45. Found: C, 78.40; H, 9.29.

2-Bromo-4-*n*-pentylbenzoic Acid. A stirred solution of 10.0 g (40.8 mmol) of 2-(4-*n*-pentylphenyl)-4,4-dimethyl-2-oxazoline in 100 mL of anhydrous THF was maintained at -45 °C (cyclohexanone−dry ice) under N_2 while 25 mL (62.5 mmol) of a 2.5 M solution of *n*-BuLi in hexanes was added dropwise. After an additional 2 h, 3.2 mL (62.5 mmol) of Br_2 was added dropwise and then the reaction mixture was allowed to stir at room temperature overnight. Aqueous workup gave 13 g (99%) of 2-(2-bromo-4-*n*-pentylphenyl)-4,4-dimethyl-2-oxazoline as an orange liquid: ^{1}H NMR δ 7.57 (d, J = 7.9 Hz, 1 H; H-6), 7.44 (d, J = 1.5 Hz, 1 H), 7.13 (dd, J = 7.9 Hz, 1.5 Hz, 1 H), 4.14 (s, 2 H), 2.58 (t, J = 7.7 Hz, 2 H), 1.59 (quintet, J = 7.2 Hz, 2 H), 1.42 (s, 6 H), 1.31−1.27 (m, 4 H), 0.88 (t, J = 6.7 Hz, 3 H).

A suspension of 10.0 g (30.8 mmol) of this oxazoline in 100 mL of 3 M HCl was heated under reflux for 1 h. The cooled reaction mixture was neutralized with Na_2CO_3 and extracted with ethyl acetate. This extract was evaporated, and the residue was heated under reflux for 1 h with a mixture of 50 mL of methanol and a solution of 30 g of NaOH in 100 mL of H_2O. Extraction with diethyl ether followed by aqueous workup and recrystallization from hexanes gave 4.98 g (60%) of 2-bromo-4-*n*-pentylbenzoic acid as a white solid, mp 52−54 °C. Further recrystallization from hexanes gave white crystals: mp 59−60 °C; ^{1}H NMR δ 7.95 (d, J = 8.0 Hz, 1 H; H-6), 7.54 (d, J = 1.6 Hz, 1 H; H-3), 7.21 (dd, J = 8.0 Hz, 1.6 Hz, 1 H; H-5), 2.63 (t, J = 7.7 Hz, 2 H), 1.63 (quintet, J = 7.5 Hz, 2 H), 1.36−1.28 (m, 4 H), 0.90 (t, J = 6.9 Hz, 3 H). Anal. Calcd for $C_{12}H_{15}BrO_2$: C, 53.16; H, 5.58. Found: C, 53.26; H, 5.67.

2-Bromo-4-*n*-pentylbenzyl Alcohol. A solution of 1.64 g (6.1 mmol) of 2-bromo-4-*n*-pentylbenzoic acid, 5 mL of THF, and 12.2 mL (12.2 mmol) of a 1.0 M solution of borane in THF was heated under reflux for 4 h. Aqueous workup followed by distillation (96−112 °C, 0.01 mm) gave 1.28 g (82%) of 2-bromo-4-*n*-pentylbenzyl alcohol as a clear, colorless liquid: ^{1}H NMR δ 7.37 (d, J = 1.6 Hz, 1 H; H-3), 7.35 (d, J = 7.8 Hz, 1 H; H-6), 7.13 (dd, J = 7.7 Hz, 1.5 Hz, 1 H; H-5), 4.71 (d, J = 5.8 Hz, 2 H), 2.57 (t, J = 7.7 Hz, 2 H), 2.05 (br s, 1 H; OH), 1.59 (quintet, J = 7.5 Hz, 2 H), 1.36−1.26 (m, 4 H), 0.89 (t, J = 6.8 Hz, 3 H). Anal. Calcd for $C_{12}H_{17}BrO$: C, 56.05; H, 6.63. Found: C, 56.26; H, 6.64.

2-Bromo-4-*n*-pentylbenzaldehyde. A solution of 2.90 g (11.3 mmol) of 2-bromo-4-*n*-pentylbenzyl alcohol in 10 mL of CH_2Cl_2 was added to a suspension of 3.65 g (16.9 mmol) of pyridinium chlorochromate in 10 mL of CH_2Cl_2, and the black mixture was stirred at room temperature under N_2 for 1.5 h. Anhydrous diethyl ether (20 mL) was added, and the supernatant liquid was decanted. The insoluble

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residue was washed with diethyl ether, and the combined organic solution was filtered through Celite and evaporated to give 1.93 g (67%) of 2-bromo-4-*n*-pentylbenzaldehyde as a pale green liquid that was chromatographed on silica gel with 5% ethyl acetate in hexanes as eluent to give a pale yellow liquid: ^{1}H NMR δ 10.31 (s, 1 H; CHO), 7.83 (d, J = 7.9 Hz, 1 H; H-6), 7.47 (d, J = 1.1 Hz, 1 H; H-3), 7.24 (br d, J = 7.9 Hz, 1 H; H-5), 2.64 (t, J = 8.1 Hz, 2 H), 1.63 (quintet, J = 7.5 Hz, 2 H), 1.35−1.31 (m, 4 H), 0.90 (t, J = 6.8 Hz, 3 H); MS *m/z* (relative intensity) 256 (M^+, 37), 254 (M^+, 37), 91 (100). Anal. Calcd for $C_{12}H_{15}BrO$: C, 56.49; H, 5.93. Found: C, 56.69; H, 5.81.

2-Bromo-4-*n*-pentylbenzyl Chloride. A solution of 4.0 g (15.6 mmol) of 2-bromo-4-*n*-pentylbenzyl alcohol in 13 mL of benzene was cooled in an ice bath, and 3.71 g (31.2 mmol) of thionyl chloride was added dropwise. A drop of pyridine was added, and the reaction mixture was maintained in the ice bath for 1 h and then heated under reflux for 2 h before being poured onto water and extracted with diethyl ether. Aqueous workup followed by chromatography on silica gel with hexanes as eluent gave 4.15 g (97%) of 2-bromo-4-*n*-pentylbenzyl chloride as a pale yellow liquid: ^{1}H NMR δ 7.41 (d, J = 1.5 Hz, 1 H; H-3), 7.36 (d, J = 7.8 Hz, 1 H; H-6), 7.12 (dd, J = 7.8 Hz, 1.6 Hz, 1 H; H-5), 4.68 (s, 2 H), 2.57 (t, J = 7.8 Hz, 2 H), 1.59 (quintet, J = 7.5 Hz, 2 H), 1.35−1.29 (m, 4 H), 0.89 (t, J = 6.8 Hz, 3 H); MS *m/z* (relative intensity) 278 (M^+, 5), 276 (M^+, 25), 274 (M^+, 15), 103 (100). Anal. Calcd for $C_{12}H_{16}BrCl$: C, 52.29; H, 5.85. Found: C, 52.09; H, 5.87.

***(Z)*-2,2′-Dibromo-4,4′-di-*n*-pentylstilbene.** Treatment of 4.15 g (15 mmol) of 2-bromo-4-*n*-pentylbenzyl chloride with 5.24 g (20 mmol) of triphenylphosphine gave 6.48 g (80%) of the phosphonium salt. The Wittig reaction of 4.03 g (7.5 mmol) of this phosphonium salt with 1.9 g (7.5 mmol) of 2-bromo-4-*n*-pentylbenzaldehyde gave, after purification by molecular distillation at reduced pressure, 3.26 g (91%) of a pale yellow liquid consisting predominantly of *(Z)*-2,2′-dibromo-4,4′-di-*n*-pentylstilbene: ^{1}H NMR δ 7.39 (d, J = 1.1 Hz, 2 H; H-3,3′), 6.91 (d, J = 7.9 Hz, 2 H; H-6,6′); 6.81 (dd, J = 7.9 Hz, 1.4 Hz, 2 H; H-5,5′), 6.70 (s, 2 H; H-α,α′), 2.51 (t, J = 7.7 Hz, 4 H), 1.63−1.51 (m, 4 H), 1.37−1.22 (m, 8 H), 0.88 (t, J = 6.7 Hz, 6 H); MS *m/z* (relative intensity) 480 (M^+, 50), 478 (M^+, 100), 476 (M^+, 50). Anal. Calcd for $C_{24}H_{30}Br_2$: C, 60.27; H, 6.32. Found: C, 60.15; H, 6.38.

The ^{1}H NMR spectrum of the Wittig product also exhibited peaks consistent with the presence of a small amount of (*E*)-2,2′-dibromo-4,4′-di-*n*-pentylstilbene: ^{1}H NMR δ 7.62 (d, J = 8 Hz), 7.41 (d, J = 1.5 Hz), 7.35 (s), 7.19 (br d, J = 8 Hz), 2.56 (t, J = 7 Hz), 1.63−1.51 (m), 1.37−1.22 (m), 0.89 (t, J = 7 Hz).

1,8-Dibromo-3,6-di-*n*-pentylphenanthrene. A solution of 3.26 g (6.8 mmol) of predominantly *(Z)*-2,2′-dibromo-4,4′-di-*n*-pentylstilbene, 1.73 g (6.8 mmol) of I_2, and 79.0 g (1.36 mol) of propylene oxide[13] in 500 mL of cyclohexane was irradiated (Rayonet) for 68 h. Evaporation of the solvent followed by chromatography on silica gel with hexanes as eluent gave 3.03 g (94%) of 1,8-dibromo-3,6-di-*n*-pentylphenanthrene as a white solid. Recrystallization from 95% ethanol/toluene gave white crystals: mp 86.5−88.5 °C; ^{1}H NMR δ 8.41 (br s, 2 H; H-4,5), 8.18 (s, 2 H; H-9,10), 7.77 (d, J = 1.2 Hz, 2 H; H-2,7), 2.84 (t, J = 7.8 Hz, 4 H), 1.76 (quintet, J = 7.5 Hz, 4 H), 1.42−1.36 (m, 8 H), 0.92 (t, J = 7.0 Hz, 6 H); MS *m/z* (relative intensity) 478 (M^+, 50), 476 (M^+, 100), 474 (M^+, 50). Anal. Calcd for $C_{24}H_{28}Br_2$: C, 60.52; H, 5.93. Found: C, 60.39; H, 5.86.

3,6-Di-*n*-pentylphenanthrene-1,8-dicarboxaldehyde (3). A stirred solution of 0.79 g (1.66 mmol) of 1,8-dibromo-3,6-di-*n*-pentylphenanthrene in 25 mL of anhydrous diethyl ether was cooled in an ice bath. A solution consisting of 2.7 mL (6.64 mmol) of 2.5 M *n*-BuLi in hexanes and 5 mL of anhydrous diethyl ether was added dropwise under N_2. Stirring was continued for an additional 1 h, after which 1.0 mL (13 mmol) of anhydrous DMF was added dropwise. The reaction mixture was allowed to warm to room temperature and then was poured onto 1 M H_3PO_4. Extraction with diethyl ether followed by aqueous workup and chromatography on silica gel with 5% ethyl acetate in hexanes as eluent gave 0.49 g (79%) of **3** as a yellow solid. Recrystallization from 95% ethanol gave pale yellow crystals: mp 87.0−87.5 °C; ^{1}H NMR δ 10.56 (s, 2 H; CHO), 9.21 (s, 2 H; H-9,10), 8.78 (br s, 2 H; H-4,5), 8.00 (d, J = 1.4 Hz, 2 H; H-2,7), 2.98 (t, J = 7.8 Hz, 4 H), 1.83 (quintet, J = 7.6 Hz, 4 H), 1.45−1.41 (m, 8 H), 0.93 (t, J = 6.9 Hz, 6 H); MS *m/z* (relative intensity) 374 (M^+, 100). Anal. Calcd for $C_{26}H_{30}O_2$: C, 83.38; H, 8.07. Found: C, 83.46; H, 7.86.

2,13-Di-*n*-pentyl[7]phenacene (2a). The reaction of 10.0 g (52 mmol) of 4-*n*-pentylbenzoic acid with 2.0 g (53 mmol) of $LiAlH_4$ in 100 mL of anhydrous THF gave 5.4 g (60%) of 4-*n*-pentylbenzyl alcohol[16] as a pale yellow liquid: ^{1}H NMR δ 7.27 (d, J = 7.9 Hz, 2 H; H-2,6), 7.17 (d, J = 7.7 Hz, 2 H; H-3,5), 4.64 (s, 2 H), 2.59 (t, J = 7.7 Hz, 2 H), 1.84 (br s, 1 H; OH), 1.60 (quintet, J = 7.1 Hz, 2 H), 1.34−1.30 (m, 4 H), 0.88 (t, J = 6.5 Hz, 3 H).

Treatment of 5.4 g (31 mmol) of 4-*n*-pentylbenzyl alcohol with 26.2 g (62 mmol) of triphenylphosphine dibromide in 60 mL of anhydrous DMF gave 6.2 g (83%) of 4-*n*-pentylbenzyl bromide[17] as a pale yellow liquid: ^{1}H NMR δ 7.30 (d, J = 8.1 Hz, 2 H; H-2,6), 7.15 (d, J = 8.0 Hz, 2 H; H-3,5), 4.49 (s, 2 H), 2.59 (t, J = 7.7 Hz, 2 H), 1.60 (quintet, J = 7.5 Hz, 2 H), 1.37−1.29 (m, 4 H), 0.89 (t, J = 6.9 Hz, 3 H); MS *m/z* (relative intensity) 242 (M^+, 2), 240 (M^+, 2), 161 (100).

Treatment of 1.0 g (4.1 mmol) of 4-*n*-pentylbenzyl bromide with 1.1 g (4.2 mmol) of triphenylphosphine gave 1.5 g (73%) of the phosphonium salt. The Wittig reaction of 1.0 g (2.0 mmol) of this salt with 0.21 g (0.9 mmol) of phenanthrene-1,8-dicarboxaldehyde (**6**) gave 0.29 g (62%) of *(E,E)*-1,8-bis(4-*n*-pentylstyryl)phenanthrene. The characterization of this stilbene analogue and a description of its photocyclization to give 2,13-di-*n*-pentyl[7]phenacene (**2a**) were reported earlier.[2a]

2,13-Di-*tert*-butyl[7]phenacene (2b). Treatment of 2.12 g (9.3 mmol) of 4-*tert*-butylbenzyl bromide with 3.7 g (14 mmol) of triphenylphosphine gave 3.77 g (83%) of the phosphonium salt. The Wittig reaction of 2.03 g (4.15 mmol) of this salt with 0.47 g (2.0 mmol) of phenanthrene-1,8-dicarboxaldehyde (**6**) gave 0.45 g (45%) of *(E,E)*-1,8-bis(4-*tert*-butylstyryl)phenanthrene. The characterization of this stilbene analogue and a description of its photocyclization to give 2,13-di-*tert*-butyl[7]phenacene (**2b**) were reported earlier.[2a]

3,6-Di-*n*-pentyl-1,8-distyrylphenanthrene. The Wittig reaction of 0.78 g (2.0 mmol) of benzyltriphenylphosphonium chloride with 0.25 g (0.67 mmol) of 3,6-di-*n*-pentylphenanthrene-1,8-dicarboxaldehyde (**3**) gave 0.24 g (69%) of *(E,E)*-3,6-di-*n*-pentyl-1,8-distyrylphenanthrene as a white solid that was recrystallized from 95% ethanol/toluene: mp 132−133 °C; ^{1}H NMR δ 8.48 (br s, 2 H; H-4,5), 8.10 (s, 2 H; H-9,10), 7.94 (d, J = 16.0 Hz, 2 H; H-α,α′), 7.70 (br s, 2 H; H-2,7), 7.64 (d, J = 7.3 Hz, 4 H; H-2′,6′,2″,6″), 7.42 (t, J = 7.5 Hz, 4 H; H-3′,5′,3″,5″), 7.31 (t, J = 7.3 Hz, 2 H; H-4′,4″), 7.17 (d, J = 16.0 Hz, 2 H; H-β,β′), 2.91 (t, J = 7.8 Hz, 4 H), 1.83 (quintet, J = 7.5 Hz, 4 H), 1.47−1.41 (m, 8 H), 0.94 (t, J = 7.0 Hz, 6 H). Anal. Calcd for $C_{40}H_{42}$: C, 91.90; H, 8.10. Found: C, 91.76; H, 7.80.

15,18-Di-*n*-pentyl[7]phenacene (2c). A solution of 160 mg (0.31 mmol) of 3,6-di-*n*-pentyl-1,8-distyrylphenanthrene, 160 mg (0.62 mmol) of I_2, and 8.7 mL (124 mmol) of propylene oxide[13] in 300 mL of cyclohexane was irradiated (Rayonet) for 5 d. The solvents were evaporated, and the orange residue was dissolved in a small amount of toluene. Chromatography on silica gel with hexanes as eluent gave 60 mg (52%) of 15,18-di-*n*-pentyl[7]phenacene (**2c**) as a yellow solid that was recrystallized from 95% ethanol/toluene: mp 234.5−235 °C; ^{1}H NMR δ 8.89 (br s, 4 H; H-7,8,16,17), 8.88 (d, J = ∼9 Hz, 4 H; H-1,6,9,14), 8.04 (dd, J = 7.7 Hz, 1.5 Hz, 2 H; H-4,11), 8.02 (d, J = 8.8 Hz, 2 H; H-5,10), 8.18−7.63 (m, 4 H; H-2,3,12,13), 3.73 (t, J = 7.9 Hz, 4 H), 2.10 (quintet, J = 7.7 Hz, 4 H), 1.67−1.44 (m, 8 H), 0.99 (t, J = 7.2 Hz, 6 H); UV (benzene, nm [relative intensity]) 358 [1.0], 342 [1.1], 324 (shoulder) [2.4], 309 [4.3]. Anal. Calcd for $C_{40}H_{38}$: C, 92.62; H, 7.38. Found: C, 92.73; H, 7.45.

(*E*)-2-Bromo-4′-*n*-pentylstilbene. The reaction of 4-*n*-pentylbenzyl alcohol[16] with thionyl chloride in benzene gave 4-*n*-pentylbenzyl chloride[18] as a pale yellow liquid: ^{1}H NMR δ 7.30 (d, J = 8.1 Hz, 2 H; H-2,6), 7.17 (d, J = 8.1 Hz, 2 H; H-3,5), 4.57 (s, 2 H), 2.60 (t, J = 7.8 Hz, 2 H), 1.58 (quintet, J = 7.5 Hz, 2 H), 1.36−1.27 (m, 4 H), 0.89 (t, J = 6.9 Hz, 3 H). Treatment of 8.8 g (45 mmol) of 4-*n*-pentylbenzyl

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chloride with 15.9 g (61 mmol) of triphenylphosphine gave 17.1 g (83%) of the phosphonium salt. The Wittig reaction of 1.0 g (2.2 mmol) of this phosphonium salt with 0.4 g (2.2 mmol) of 2-bromobenzaldehyde gave 0.7 g (97%) of (*E*)-2-bromo-4′-*n*-pentylstilbene as a pale yellow liquid that was further purified by molecular distillation under reduced pressure: ^{1}H NMR δ 7.66 (dd, J = 7.8 Hz, 1.5 Hz, 1 H; H-6), 7.57 (dd, J = 8.0 Hz, 1.1 Hz, 1 H; H-3), 7.47 (d, J = 8.2 Hz, 2 H; H-2′,6′), 7.42 (d, J = 16.2 Hz, 1 H; H-α), 7.30 (td, J = 7.6 Hz, 1.1 Hz, 1 H; H-5), 7.19 (d, J = 8.1 Hz, 2 H; H-3′,5′), 7.10 (td, J = 7.6 Hz, 1.6 Hz, 1 H; H-4), 7.02 (d, J = 16.2 Hz, 1 H; H-α′), 2.61 (t, J = 7.7 Hz, 2 H), 1.63 (quintet, J = 7.5 Hz, 2 H), 1.35−1.30 (m, 4 H), 0.90 (t, J = 6.9 Hz, 3 H); MS *m/z* (relative intensity) 330 (M^+, 80), 328 (M^+, 76), 271 (100). Anal. Calcd for $C_{19}H_{21}Br$: C, 69.31; H, 6.41. Found: C, 69.06; H, 6.10.

1-Bromo-6-*n*-pentylphenanthrene. A solution of 3.7 g (11 mmol) of a mixture of the *E* and *Z* isomers of 2-bromo-4′-*n*-pentylstilbene, 2.87 g (11 mmol) of I_2, and 131 mL (1.9 mol) of propylene oxide[13] in 1.06 L of cyclohexane was irradiated (Hanovia) for 40 h. Evaporation of the solvent followed by chromatography on silica gel with hexanes as eluent gave 3.3 g (89%) of 1-bromo-6-*n*-pentylphenanthrene as a yellow liquid: ^{1}H NMR δ 8.19 (d, J = 8.4 Hz, 1 H; H-4), 8.45 (br s, 1 H; H-5), 8.14 (d, J = 9.2 Hz, 1 H; H-10), 7.87 (dd, J = 7.7 Hz, 0.9 Hz, 1 H; H-2), 7.84 (d, J = 7.8 Hz, 1 H; H-8), 7.81 (d, J = 8.5 Hz, 1 H; H-9), 7.49 (d, J = 8.2 Hz, 1 H; H-7), 7.47 (t, J = 7.9 Hz, 1 H; H-3), 2.87 (t, J = 7.7 Hz, 2 H), 1.76 (quintet, J = 7.6 Hz, 2 H), 1.40−1.36 (m, 4 H), 0.91 (t, J = 7.0 Hz, 3 H); MS *m/z* (relative intensity) 328 (M^+, 60), 326 (M^+, 60), 271 (100). Anal. Calcd for $C_{19}H_{19}Br$: C, 69.73; H, 5.85. Found: C, 69.54; H, 5.75.

6-*n*-Pentylphenanthrene-1-carboxaldehyde. A stirred solution of 4.6 g (14 mmol) of 1-bromo-6-*n*-pentylphenanthrene in 135 mL of anhydrous diethyl ether was cooled in an ice bath. A solution of 14 mL (35 mmol) of 2.5 M *n*-BuLi in hexanes was added dropwise under N_2, followed by the addition of 65 mL of anhydrous diethyl ether. Stirring was continued for an additional 20 min, after which 4.34 mL (56 mmol) of anhydrous DMF in 70 mL of anhydrous diethyl ether was added dropwise. The reaction mixture was allowed to warm to room temperature and then was poured onto 1 M H_3PO_4. Extraction with diethyl ether and aqueous workup followed by chromatography on silica gel, first with hexanes and then 10% ethyl acetate in hexanes as eluents, gave 2.9 g (75%) of 6-*n*-pentylphenanthrene-1-carboxaldehyde as an off-white solid: mp 49−50 °C; ^{1}H NMR δ 10.54 (s, 1H; CHO), 9.09 (d, J = 9.3 Hz, 1 H; H-10), 9.02 (br d, J = 8.4 Hz, 1 H; H-4), 8.50 (br s, 1 H; H-5), 8.10 (dd, J = 7.2 Hz, 0.9 Hz, 1 H; H-2), 7.94 (d, J = 9.3 Hz, 1 H; H-9), 7.88 (d, J = 8.1 Hz, 1 H; H-8), 7.82 (dd, J = 8.2 Hz, 7.4 Hz, 1 H; H-3), 7.52 (dd, J = 8.2 Hz, 1.4 Hz, 1 H; H-7), 2.90 (t, J = 7.7 Hz, 2 H), 1.78 (quintet, J = 7.5 Hz, 2 H), 1.45−1.38 (m, 4 H), 0.92 (t, J = 7.0 Hz, 3 H); MS *m/z* (relative intensity) 276 (M^+, 50), 219 (100). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.78; H, 7.25.

1-(Hydroxymethyl)-6-*n*-pentylphenanthrene. A stirred solution of 330 mg (1.2 mmol) of 6-*n*-pentylphenanthrene-1-carboxaldehyde in 1 mL of methanol was cooled in an ice bath. The ice bath was removed, and a solution of 23 mg (0.6 mmol) of $NaBH_4$ in 0.5 mL of aqueous 2 M NaOH was added dropwise. After 1 h the reaction mixture was subjected to aqueous workup to give, after recrystallization from hexanes, 232 mg (70%) of 1-(hydroxymethyl)-6-*n*-pentylphenanthrene as an off-white solid: mp 99−100 °C; ^{1}H NMR δ 8.72 (dd, $\sum J$ = 6.2 Hz + 3.3 Hz = 9.5 Hz, 1 H; H-4), 8.49 (br s, 1 H; H-5), 8.02 (d, J = 9.1 Hz, 1 H; H-10 or H-9), 7.83 (d, J = 8.4 Hz, 1 H; H-8), 7.80 (d, J = 9.7 Hz, 1 H; H-9 or H-10), 7.65−7.59 (m, 2 H; H-2,3), 7.47 (dd, J = 8.1 Hz, 1.5 Hz, 1 H; H-7), 5.21 (s, 2 H; CH_2OH), 2.88 (t, J = 7.7 Hz, 2 H), 1.77 (quintet, J = 7.5 Hz, 2 H), 1.44−1.35 (m, 4 H), 0.91 (t, J = 7.0 Hz, 3 H). Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.12; H, 8.06.

1-(Chloromethyl)-6-*n*-pentylphenanthrene. A solution of 232 mg (0.83 mmol) of 1-(hydroxymethyl)-6-*n*-pentylphenanthrene, 198 mg (1.66 mmol) of $SOCl_2$, and a drop of pyridine in 2 mL of benzene was stirred in an ice bath for 1 h and then was heated under reflux for 2 h. Aqueous workup gave 225 mg (91%) of 1-(chloromethyl)-6-*n*-pentylphenanthrene as a beige solid that was recrystallized twice from hexanes to give beige crystals: mp 67.0−67.5 °C; ^{1}H NMR δ 8.74 (dd, J = 7.1 Hz, 2.3 Hz, 1 H; H-4), 8.47 (s, 1 H; H-5), 8.01 (d, J = 9.2 Hz, 1 H; H-10), 7.84 (d, J = 8.9 Hz, 2 H; H-8 and H-9), 7.62−7.56 (m, 2 H; H-2 and H-3), 7.47 (dd, J = 8.1 Hz, 1.4 Hz, 1 H; H-7), 5.09 (s, 2 H; CH_2Cl), 2.87 (t, J = 7.7 Hz, 2 H), 1.76 (quintet, J = 7.5 Hz, 2 H), 1.41−1.35 (m, 4 H), 0.91 (t, J = 7.0 Hz, 3 H); MS *m/z* (relative intensity) 298 (M^+, 35), 296 (M^+, 100). Anal. Calcd for $C_{20}H_{21}Cl$: C, 80.93; H, 7.13. Found: C, 80.76; H, 7.22.

Bis(arylvinyl)phenanthrene 5. Treatment of 86 mg (0.29 mmol) of 1-(chloromethyl)-6-*n*-pentylphenanthrene with 76 mg (0.29 mmol) of triphenylphosphine gave 91 mg (56%) of phosphonium salt **4**. The Wittig reaction of 300 mg (0.54 mmol) of **4** with 100 mg (0.27 mmol) of 3,6-di-*n*-pentylphenanthrene-1,8-dicarboxaldehyde (**3**) gave, after chromatography of the crude product on silica gel with 5% ethyl acetate in hexanes as eluent, 200 mg (85%) of *(E,E)*-3,6-di-*n*-pentyl-1,8-bis-[2-(6-*n*-pentyl-1-phenanthryl)ethenyl]phenanthrene (**5**) as a yellow solid. Recrystallization from 95% ethanol/toluene gave yellow crystals: mp 139.5−141 °C; ^{1}H NMR δ 8.74 (br d, J = 8.1 Hz, 2 H; H-4′,4″), 8.57 (br s, 2 H; H-4,5 or H-5′,5″), 8.52 (br s, 2 H; H-5′,5″ or H-4,5), 8.17 (d, J = ∼8 Hz, 2 H; H-10′,10″), 7.98 (s, 4 H; alkene hydrogens), 7.85 (s, 2 H; H-9,10), 7.83 (d, J = ∼8 Hz, 2 H; H-8′,8″), 7.79 (d, J = 9.2 Hz, 2 H; H-9′,9″), 7.71 (t, J = 7.8 Hz, 2 H; H-3′,3″), 7.49 (br s, 2 H; H-2,7), 7.47 (d, J = ∼8 Hz, 2 H; H-2′,2″), 7.18 (d, J = ∼8 Hz; 2 H; H-7′,7″), 2.98 (t, J = 7.5 Hz, 4 H), 2.89 (t, J = 7.7 Hz, 4 H), 1.89 (m, 4 H), 1.79 (m, 4 H), 1.47 (m, 8 H), 1.41 (m, 8 H), 0.97 (t, J = 7.1 Hz, 6 H), 0.95 (t, J = 7.3 Hz, 6 H). Anal. Calcd for $C_{66}H_{70}$: C, 91.83; H, 8.17. Found: C, 92.00; H, 8.04.

2,17,21,24-Tetra-*n*-pentyl[11]phenacene (6). A solution of 190 mg (0.22 mmol) of bis(arylvinyl)phenanthrene **5**, 64 mg (0.25 mmol) of I_2, and 2.56 g (44 mmol) of propylene oxide[13] in 400 mL of benzene was irradiated (Rayonet) for 18 h. Filtration of the reaction mixture gave 100 mg (61%) of 2,17,21,24-tetra-*n*-pentyl[11]phenacene (**6**) as a yellow solid: mp 340 °C (dec); ^{1}H NMR (1,2,4,5-tetrachloro-3,6-dideuteriobenzene, 147 °C) δ 9.37, 9.30, 9.21, 9.13 (each of these four signals is a 2 H doublet with J = ∼9 Hz; H-7,12, H-8,11, H-19,26, H-20,25), 9.29 (s, 2 H; H-9,10), 9.19 (s, 2 H; H-22,23), 8.99 (d, J = 9.5 Hz, 2 H; H-6,13), 8.90 (br s, 2 H; H-1,18), 8.19 (d, J = 9.1 Hz, 2 H; H-5,14), 8.12 (d, J = 8.8 Hz, 2 H; H-4,15), ∼7.67 (expected 2 H br d signal for H-3,16 obscured by solvent peak), 4.21 (t, J = 7.3 Hz, 4 H), 3.27 (t, J = 6.8 Hz, 4 H), 2.54 (quintet, J = 7.4 Hz, 4 H), 2.21 (quintet, J = 7.0 Hz, 4 H), 2.00 (quintet, J = 6.8 Hz, 4 H), 1.93−1.75 (m, 12 H), 1.33−1.27 (m, 12 H); UV (benzene, nm [relative intensity]) 400 [1.0], 374 [1.5], 344 [2.5], 328 [2.8], 312 [3.0] Anal. Calcd for $C_{66}H_{66}$: C, 92.26; H, 7.74. Found: C, 92.41; H, 7.58.

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