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Oligoindenopyrenes: A New Class of Polycyclic Aromatics

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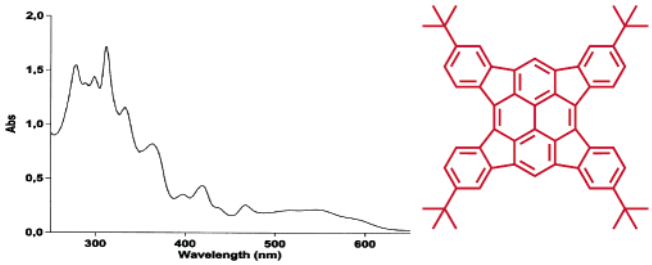
Received July 5, 2006



A new class of polycyclic aromatic hydrocarbons—oligoindenopyrenes—has been synthesized featuring a Pd-catalyzed Suzuki−Heck coupling cascade. The oligoindenopyrenes are robust, highly colored substructures of C_{70} and have properties that might prove useful in new organic materials or devices. After excitation, the tetraindenopyrene derivative **3d** undergoes efficient deactivation (99%) by internal conversion to the ground state. The small fluorescence quantum yield (0.004) is in accordance with the short (0.6 ns) fluorescence decay time.

Introduction

Information on the class of indenopyrenes is scarce. To date, only indeno[1,2,3-*cd*]pyrene (**1**) has been reported.[1−3] Structurally similar compounds, such as benzo[*b*]fluoranthene, show strong carcinogenic effects in animals and are suspected to act similarly in humans. We have begun exploring synthetic routes to the other members of this interesting family of aromatics, the di-, tri-, and tetraindenopyrenes, to learn what unusual properties they might have. Special interest in these nonalternant polycyclic aromatic hydrocarbons (PAHs) stems from their identity as partial structures of C_{70}-fullerene (**2**) and its higher homologues, their potential to show unusual physical and photophysical properties, e.g., high electron affinities and anomalous fluorescence,[4,5] and the carcinogenicity exhibited by other nonalternant PAHs.[6,7] Herein we report the previously unknown diindenopyrenes **3a** and **3b**, triindenopyrene **3c**, and tetraindenopyrene **3d**. The *tert*-butyl groups on **3c** and **3d** were incorporated to enhance the solubility of these large PAHs. An overview of the properties of these new hydrocarbons, including their absorption and fluorescence spectra, fluorescence quantum yields, and decay times, is presented first, and a summary of the synthetic procedures used then follows.

Results and Discussion

Properties of the Indenopyrenes. In 2002, Havenith and co-workers reported extensive calculations on all the cyclopenta-

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10.1021/jo0613939 CCC: $33.50
Published on Web 10/21/2006

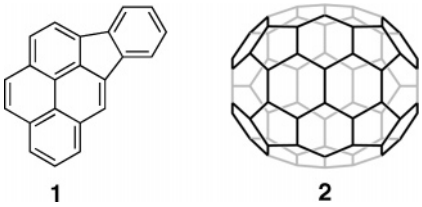

FIGURE 1. Monoindenopyrene (**1**) and tetraindenopyrene mapped onto C_{70} (**2**).

fused pyrenes, which represent truncated substructures of the indenopyrenes considered here.[8] Besides interesting magnetic and electronic properties, all of the structural parameters were also predicted. Interestingly, tetracyclopenta[*cd*,*fg*,*jk*,*mn*]pyrene was computed to be bowl shaped. To date, however, no synthesis of this compound has been published. Our own calculations (B3LYP/6-31G*)[9] predict a curved structure as well for tetraindeno[1,2,3-*cd*:1′,2′,3′-*fg*:1″,2″,3″-*jk*:1‴,2‴,3‴-*mn*]-pyrene **3d**. The slightly longer *o*-phenylene bridges, however, relax the pinching effect of the five-membered rings and lower the calculated inversion barrier to just 0.33 kcal/mol. With derivative **3d** now in hand, it should be possible to test these calculations. Unfortunately, we have so far been unable to obtain a single-crystal suitable for X-ray analysis.

The NMR spectra of the indenopyrenes are unexceptional. Incorporation of successive indeno groups causes only minor changes in the chemical shifts of the remaining hydrogens attached to the pyrene core. The only apparent exception to this behavior is seen with the tetraindenopyrene **3d**; in this case, the signal for the remaining two equivalent hydrogens on the pyrene core shifts upfield by ca. 0.8 ppm. Eventually, however, we learned that the unusual shift is a consequence of aggregation of **3d** in solution; the signal returns to the expected region when the spectrum is recorded on very dilute solutions. A more thorough discussion of the NMR spectra of the neutral oligoindenopyrenes and of their dianions and other charged states is reported in a separate publication.[10]

One property of these new compounds that adds to their attractiveness for possible uses in material science is their extreme stability. Diindenopyrene **3a** remains solid up to 250 °C, and decomposition of **3b** begins only at 240 °C. The melting points for **3c** and **3d** are both over 325 °C.

Absorption Spectra of the Indenopyrenes. In their absorption spectra, the diindenopyrenes **3a** and **3b** exhibit two main absorption maxima (Figure 2), appearing at 267 (log ϵ = 1.94) and 307 nm (log ϵ = 2.44) for **3a** and at 264 (log ϵ = 3.01) and 316 nm (log ϵ = 2.56) for **3b**. These correlate with the absorption maxima for pyrene itself at 242 (log ϵ = 8.84) and 273 nm (log ϵ = 5.36), but are shifted to longer wavelengths.[11] The red colors of the diindenopyrenes result from their extended π-systems, which give rise to additional lower intensity maxima at 388 (log ϵ = 1.08) and 411 nm (log ϵ = 1.24) for **3b** and at even longer wavelength for **3a** at 410 (log ϵ = 0.77), 429 (log ϵ = 0.77), and 455 nm (log ϵ = 0.97). Monoindenopyrene **1** shows long wavelength absorptions also in this region at 376 (log ϵ = 1.40) and 386 nm (log ϵ = 1.16), which emphasizes the trend: the more indeno groups attached, the further the maxima shift to longer wavelength. This trend continues with the higher homologues of the indenopyrenes. The triindenopyrene **3c** exhibits strong maxima in its UV−vis spectrum at 276 nm (log ϵ = 1.43), 312 nm (log ϵ = 1.92), and up to 325 nm (log ϵ = 1.00) and also in the region from 400 nm to beyond 500 nm. The tetraindenopyrene **3d** shows distinct absorption maxima well beyond 500 nm (545 nm (log ϵ = 0.21)) and an

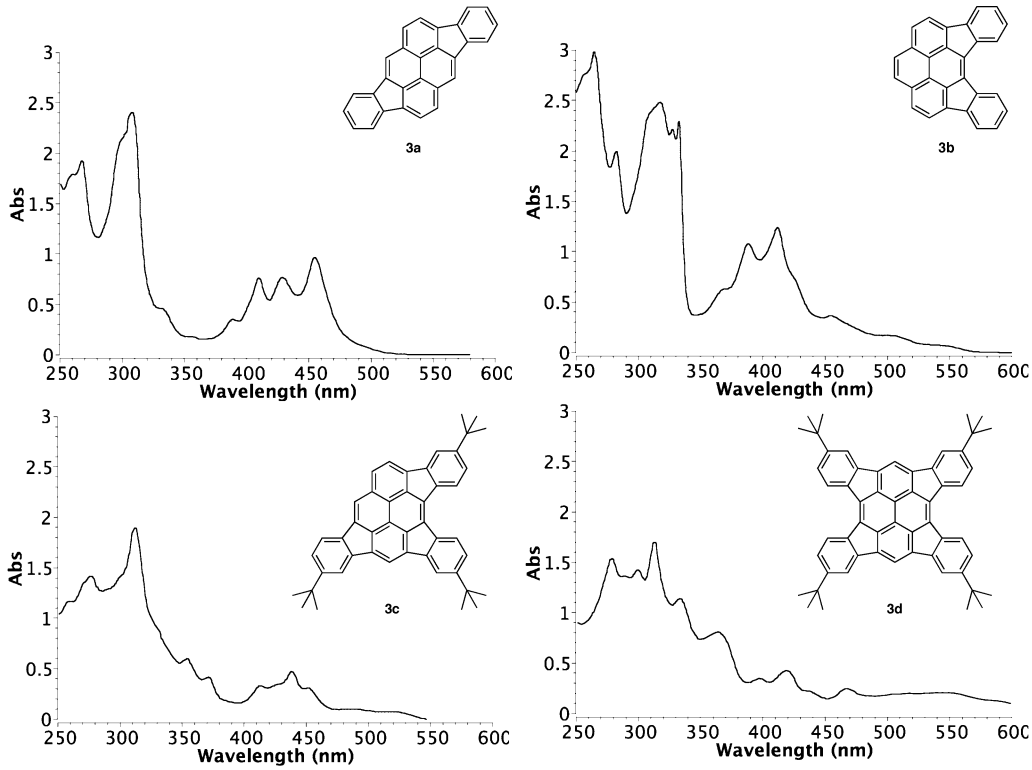

FIGURE 2. Absorption spectra in $CHCl_3$ at room temperature of diindeno[1,2,3-*cd*:1′,2′,3′-*jk*]pyrene (**3a**) (top left), diindeno[1,2,3-*cd*:1′,2′,3′-*fg*]-pyrene (**3b**) (top right), 2,7,11-tri-*tert*-butyltriindeno[1,2,3-*cd*:1′,2′,3′-*fg*:1″,2″,3″-*jk*]pyrene (**3c**) (bottom left), and 2,7,11,16-tetra-*tert*-butyltetraindeno-[1,2,3-*cd*:1′,2′,3′-*fg*:1″,2″,3″-*jk*:1‴,2‴,3‴-*mn*]pyrene (**3d**) (bottom right).

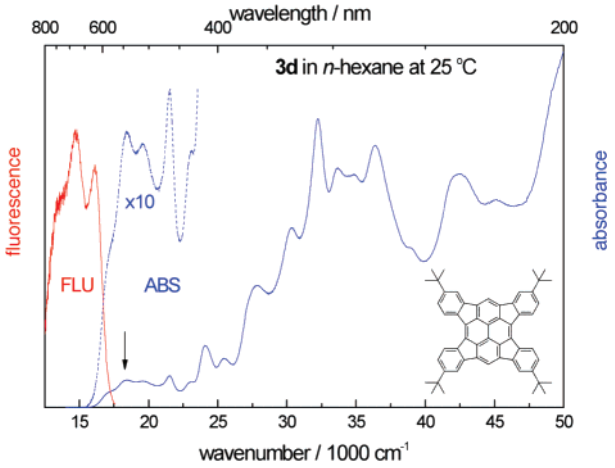

FIGURE 3. Absorption (ABS) and fluorescence (FLU) spectra of 2,7,-11,16-tetra-*tert*-butyltetraindeno[1,2,3-*cd*:1′,2′,3′-*fg*:1″,2″,3″-*jk*:1‴,2‴,3‴-*mn*]pyrene (**3d**) in *n*-hexane at 25 °C. The excitation wavelength for the fluorescence spectrum (550 nm) is indicated by an arrow.

TABLE 1. Fluorescence Quantum Yields Φ_f, Lifetimes τ, and Energies $E(S_1)$ of the First Excited Singlet State S_1 of 3d in Three Solvents at 25 °C[a]

solvent	*n*-hexane	toluene	diethyl ether
Φ_f	0.0037	0.0043	0.0043
τ/ns	0.610	0.606	0.618
$E(S_1)$[b]/cm^{-1}	16590	16500	16600
flu max/cm^{-1}	14720	14590	14708
first abs max/cm^{-1}	18445	18320	18465
τ_f/ns	165	141	144

[a] The fluorescence (flu) and absorption (abs) maxima are also listed. The radiative lifetime τ_f is equal to the reciprocal of the radiative rate constant $k_f = \Phi_f/\tau$. [b] Determined from the crossing point of the normalized absorption and fluorescence spectra of **3d** in Figure 3.

absorption tail that extends beyond 600 nm. These long wavelength absorption bands make the indenopyrenes appealing as candidates for new dyes and photoelectronic materials.[12]

Absorption and Fluorescence Spectra of the Tetraindenopyrene 3d. The absorption spectrum of **3d** in *n*-hexane at 25 °C (Figure 3) is similar to that of the other indenopyrenes **3a**−**c** in Figure 2, with the predominant pyrene features around 32 000 cm^{-1} (313 nm) and a considerably weaker low-energy maximum at 18 445 cm^{-1} (542 nm). The fluorescence spectrum of **3d**, with a maximum at 14 720 cm^{-1} (679 nm) and vibrational structure (progression of approximately 1350 cm^{-1}), shows a mirror-image with respect to the lowest energy absorption band in *n*-hexane and also in the two other solvents (toluene and diethyl ether) investigated (Table 1). This is an indication that the molecular structure of **3d** does not undergo a substantial change upon excitation to the equilibrated lowest excited singlet state S_1, similar to what is observed for alternant aromatic hydrocarbons such as pyrene as well as for the nonalternant hydrocarbon fluoranthene. Practically no change occurs in the fluorescence spectra of **3d** in toluene and diethyl ether upon cooling (Figure 4). In *n*-hexane, only a room temperature spectrum is available because of solubility problems at lower temperatures.[13]

Internal Conversion of the Tetraindenopyrene 3d. The fluorescence quantum yield Φ_f of **3d** is very small: 0.0037 in *n*-hexane at 25 °C, and 0.0043 in toluene and diethyl ether at this temperature (Table 1). Upon cooling, a small increase of Φ_f occurs, for example, to 0.005 for **3d** in toluene at −91 °C.

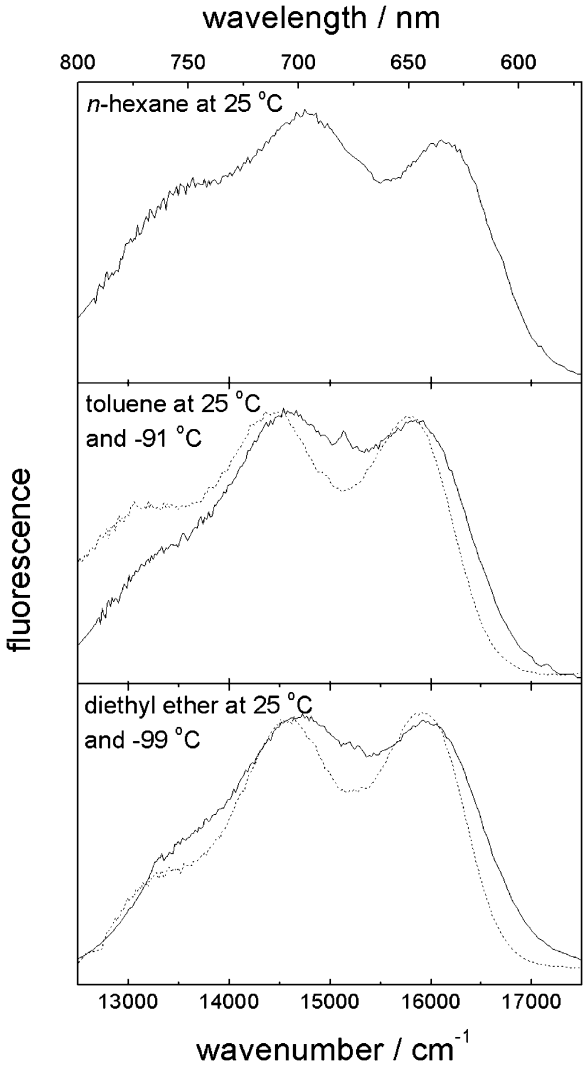

FIGURE 4. Fluorescence spectra of **3d** in *n*-hexane, toluene, and diethyl ether at 25 °C. For toluene and diethyl ether, fluorescence spectra are also presented for lower temperatures (dashed curves). Such a low-temperature spectrum is absent for *n*-hexane, because of solubility problems with **3d** in this solvent upon cooling.

Triplet−triplet transient absorption laser measurements with **3d** in *n*-hexane (XeCl, 308 nm) over a detection range covering the entire spectrum (350−750 nm) did not reveal the presence of a triplet state, indicating that the quantum yield of intersystem crossing Φ_{ISC} is effectively zero. This shows that the S_1 state of **3d** is mainly (more than 99%) deactivated by internal conversion (IC), as $\Phi_{IC} = 1 - \Phi_f - \Phi_{ISC}$. The efficiency of the IC deactivation channel is due to the relatively small S_1-S_0 energy gap (16 590 cm^{-1} in *n*-hexane, Table 1) of **3d,** which leads via $k_{IC} = \Phi_{IC}/\tau$ to an IC rate constant of 1.6×10^9 s^{-1}.

Deactivation by IC in the series of aromatic hydrocarbons from benzene to hexacene is likewise governed by the energy gap law.[14] In cyclohexane at 25 °C, the IC rate constant k_{IC} increases from 8×10^2 (benzene) to 6.3×10^8 s^{-1} (hexacene), with a decrease of the energy $E(S_1)$ of the first excited singlet state from 37 080 to 14 500 cm^{-1}.[14c] For anthracene, with $E(S_1) = 26\,580$ cm^{-1}, the IC yield Φ_{IC} under these conditions is still practically zero ($\Phi_{IC} = 1.6 \times 10^{-3}$), as calculated from k_{IC} (3.5×10^5 s^{-1}) and the fluorescence lifetime τ (4.7 ns) by using the expression $\Phi_{IC} = k_{IC}\tau$.[14c] Not before an energy gap between S_1 and S_0 of 20 950 cm^{-1} (tetracene) is reached is an appreciable

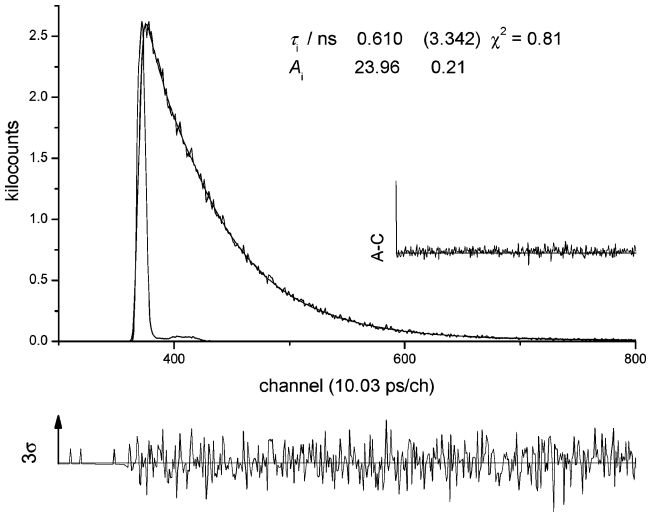

FIGURE 5. Fluorescence decay of **3d** in *n*-hexane at 25 °C. The decays τ_i were obtained by using picosecond laser excitation at 298 nm, with 10.03 ps/channel. The decay times and their preexponential factors A_i are given. The decay time in parentheses (3.342 ns) is considered to be an impurity. The weighted deviations, expressed as 3σ (expected deviations), the autocorrelation function A−C, and the value for χ^2 are also indicated.

yield Φ_{IC} observed, rapidly increasing as $E(S_1)$ becomes smaller: 0.083 (tetracene, 20 950 cm^{-1}), 0.75 (pentacene, 17 000 cm^{-1}), and 0.95 (hexacene, 14 500 cm^{-1}).[14c]

Fluorescence Decays of the Tetraindenopyrene 3d. The fluorescence decay of **3d** in *n*-hexane is single exponential, with a decay time τ of 610 ps at 25 °C (Figure 5). Similar decay times are observed in toluene (606 ps) and diethyl ether (618 ps) (Table 1). The fluorescence decay times become somewhat longer upon cooling, 705 ps in toluene at −91 °C, for example, corresponding with the minor increase in the corresponding fluorescence quantum yields mentioned above.

The observation of these relatively short decay times (similar values around 600 ps in toluene and diethyl ether at 25 °C, Table 1) is in line with the absence of ISC, as the forbidden character of the singlet to triplet ISC generally leads to ISC rates of the order of 10 ns or slower.[15] The forbidden character of the fluorescence of **3d** can be seen from the values for the radiative lifetime τ_f of around 150 ns (Table 1). With pyrene in cyclohexane τ_f = 690 ns, due to its symmetry-forbidden S_1 state (L_b), whereas for fluoranthene τ_f = 210 ns has been found.[15] These data show that the bowl shaped form of **3d** (see Introduction) has only a small impact on internal conversion.

Syntheses of the Indenopyrenes. Our first synthesis of indenopyrenes begins with a Suzuki coupling of a brominated pyrene **4** with *o*-methoxybenzeneboronic acid (**5a**) (Scheme 1). To enhance the solubility of the final products, 5-*tert*-butyl-2-methoxybenzeneboronic acid (**5b**) was used for the synthesis of tri- and tetraindenopyrenes. After the coupling, the ether **6** was demethylated with BBr_3, and the resulting phenol **7** was converted to the corresponding triflate **8** with triflic anhydride. Palladium-catalyzed cyclization gave the desired oligoindenopyrene **3**. A similar four-step sequence has recently been used by Echavarren for the synthesis of other polycyclic aromatic hydrocarbons.[16]

For the synthesis of diindeno[1,2,3-*cd*:1′,2′,3′-*jk*]pyrene (**3a**) and diindeno[1,2,3-*cd*:1′,2′,3′-*fg*]pyrene (**3b**), a mixture of 1,6- and 1,8-dibromopyrene (**4a** and **4b**) was subjected to the Suzuki coupling, and the isomeric coupling products **6a** and **6b** were subsequently separated by a simple treatment with acetone.

The 2,7,11-tri-*tert*-butyltriindeno[1,2,3-*cd*:1′,2′,3′-*fg*:1″,2″,3″-*jk*]pyrene (**3c**) and 2,7,11,16-tetra-*tert*-butyltetraindeno[1,2,3-*cd*:1′,2′,3′-*fg*:1″,2″,3″-*jk*:1‴,2‴,3‴-*mn*]pyrene (**3d**) were synthesized by the same procedure. The starting materials, tribromopyrene (**4c**) and tetrabromopyrene (**4d**), were prepared by selective bromination of pyrene.[17]

Unfortunately, the final cyclization reactions give low yields, especially for the tri- and tetraindenopyrenes. Therefore, efforts were undertaken to improve the synthesis by replacing the triflate with a bromine atom and then making use of the one-step methodology developed in our labs, which had been successfully applied to the synthesis of the monoindenopyrene (**1**) (Scheme 2).[18]

When applied to a mixture of the two dibromopyrenes **4a** and **4a**, however, this reaction furnished a mixture of diindenopyrenes (**3a** and **3b**) that could not be separated. To obtain **3a** and **3b** separately, therefore, a two-step variant was pursued. After the first Suzuki coupling, the isomeric bis(2-bromophenyl)pyrenes **11a** and **11b** could be separated by fractional crystallization (Scheme 3). Subsequent optimization of the cyclization conditions revealed that $Pd(PPh_3)_2Cl_2$ (10 mol %/cyclization) and DBU in DMF at 155 °C gave the best results and boosted the yield to 44% for the diindeno[1,2,3-*cd*:1′,2′,3′-*fg*]pyrene (**3a**).

With these improved conditions, the synthesis of tetraindenopyrene **3d** was reexamined. Different substituents on the phenyl groups were assayed (H, OMe, OEt), but only the *tert*-butyl groups enhanced the solubility enough to allow purification of the cyclized product by column chromatography. The *tert*-butyl-substituted 2-bromobenzeneboronic acid **10b** required for this synthesis was prepared in four steps starting from 4-*tert*-butylbromobenzene (**12**) (Scheme 4).

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(9) Calculations on tetraindenopyrene were performed at the B3LYP/6-31G* level of theory, using Spartan 02 (Linux version) from Wavefunction, Inc., Irvine, CA 92612. The C_{2v} structure was found to be an energy minimum (zero imaginary frequencies), whereas the D_{2h} structure was found to be the transition state for bowl-to-bowl inversion (one imaginary frequency).

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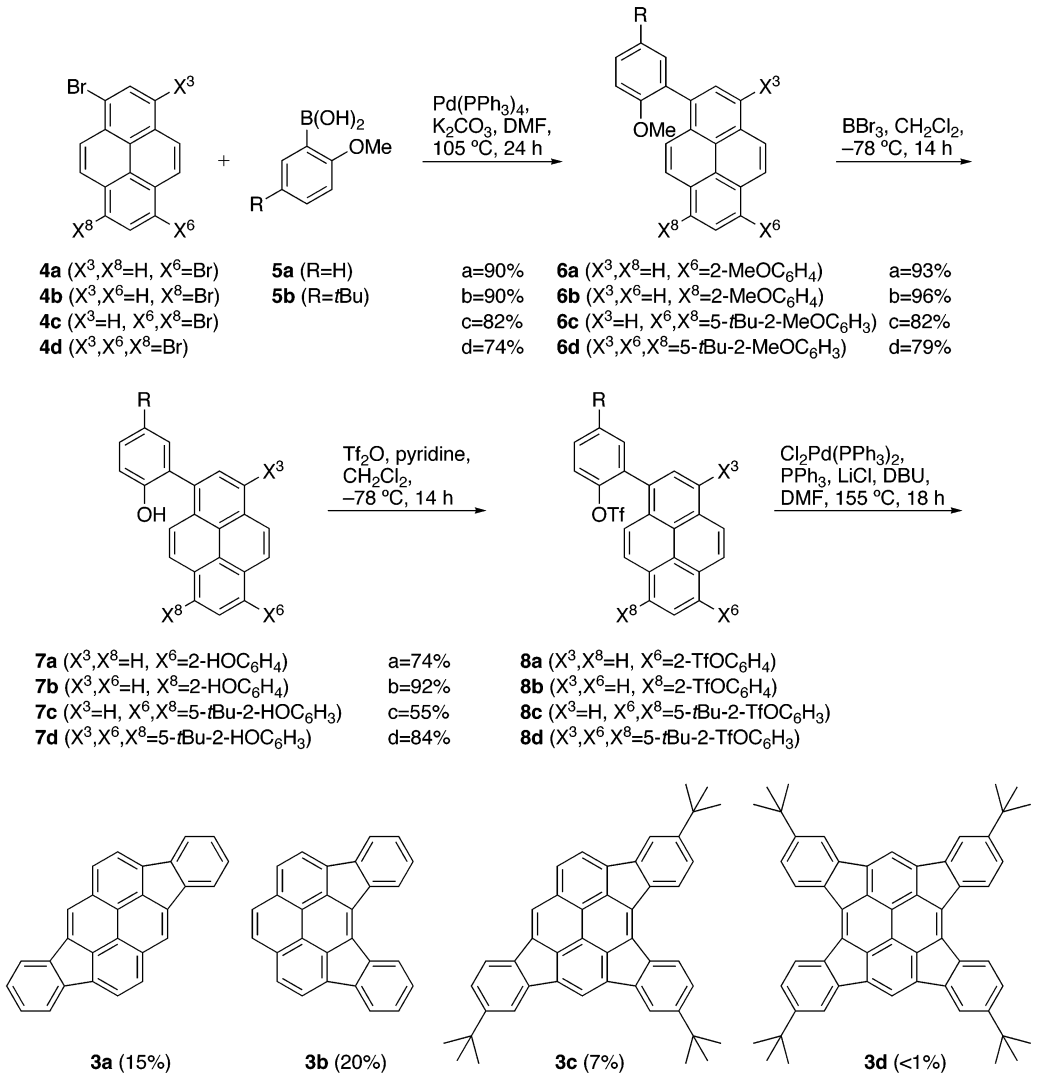
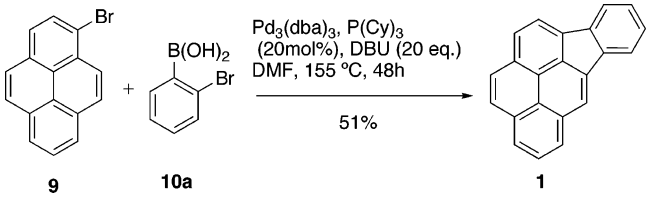
SCHEME 1. General Synthetic Route for the Preparation of Indenopyrenes 3



SCHEME 2. Synthesis of Monoindenopyrene (1) in a One-Pot Reaction



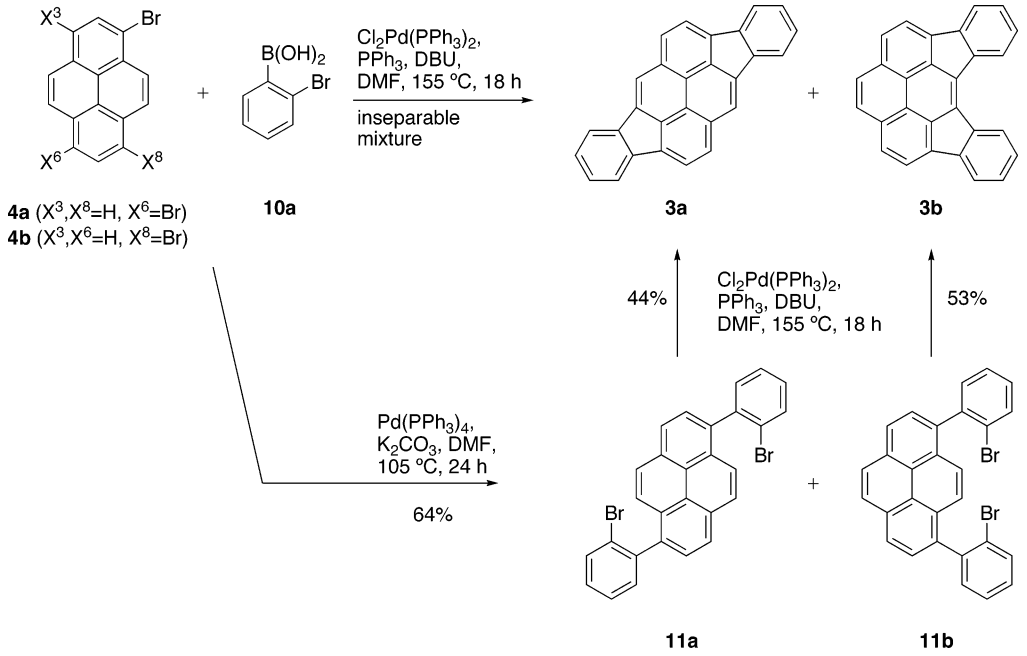
The one-pot preparation of the tetraindenopyrene **3d** was ultimately achieved reproducibly in 1% yield. Using the pinacolboronic ester of **10b** did not further improve the yield. Likewise, increasing the equivalents of boronic acid from 1.2 to 5.0 had no effect. Application of this methodology to the synthesis of the triindenopyrene **3c** gave the desired product in 4% yield.

One side product of the one-pot indenoannelation process is the replacement of Br with H. Interestingly the use of *o*-chlorobenzeneboronic acid (**17**) in the model system 1,4-dibromonaphthalene (**16**) gave nearly quantitatively the desired product **18**, compared to 51% with *o*-bromobenzeneboronic acid (**10a**) (Scheme 5).[18] Unfortunately, this modification did not improve the result with 1,3,6,8-tetrabromopyrene (**4d**); the reaction had a similar outcome as with 2-bromobenzeneboronic acid (**10a**).

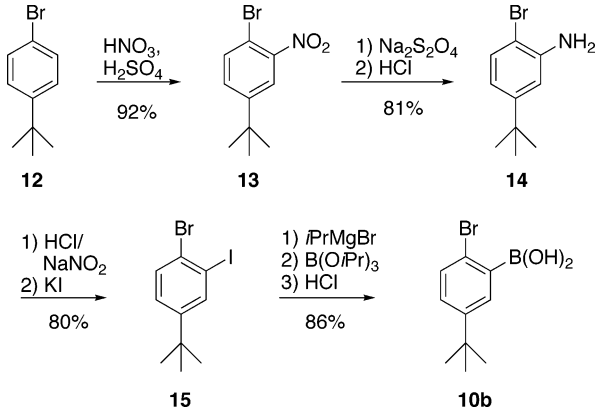
Conclusions

The syntheses reported here for oligoindenopyrenes, a new class of polycyclic aromatics, demonstrate the utility of palladium-catalyzed cross-coupling reactions, especially the Suzuki coupling. The tetraindenopyrene derivative **3d** in its first excited singlet state undergoes efficient deactivation (99%) by internal conversion to the ground state. The short (0.6 ns) fluorescence decay time is in line with the small fluorescence quantum yield (0.004). The intense red colors of the oligoindenopyrenes along

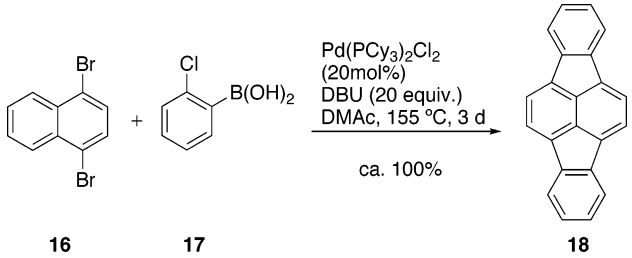
SCHEME 3. Synthesis of Diindenopyrenes 3a and 3b from 1,6- and 1,8-Dibromopyrene 4a and 4b



SCHEME 4. Synthesis of 2-Bromo-5-*tert*-butylbenzeneboronic Acid (10b)



SCHEME 5. Improved Yield of the Pd-Catalyzed Indenoannelation Reaction with *o*-Chlorobenzeneboronic Acid (17)



with their thermal stabilities make them potentially useful as long wavelength dyes for special high-temperature applications.

Experimental Section

Spectroscopic Studies on the Oligoindenopyrenes. The tetraindenopyrene derivative **3d** was purified by HPLC. The solvent *n*-hexane was used as received. Diethyl ether was chromatographed over alumina, and toluene was refluxed from potassium in a nitrogen atmosphere. The solutions, with an optical density between 0.02 and 0.10 at the maximum of the first band in the absorption spectrum, were deaerated by bubbling with nitrogen for 15 min. The fluorescence spectra were measured with a quantum-corrected (modified)[19] spectrofluorometer. The fluorescence quantum yields Φ_f, with an estimated reproducibility of 5%, were determined with quinine sulfate in 1.0 N H_2SO_4 as a standard ($\Phi_f = 0.546$ at 25 °C),[20] with equal optical density at the excitation wavelength. The difference in refractive index between the standard solution and the alkanes was not taken into account. The fluorescence decay times were obtained with a picosecond laser (λ_{exc}: 296 nm) single-photon counting (SPC) setup described elsewhere.[21]

1,6-Bis(2-methoxyphenyl)pyrene (6a) and 1,8-Bis(2-methoxyphenyl)pyrene (6b). A mixture of 1,6-dibromopyrene and 1,8-dibromopyrene[17] (0.600 g, 1.66 mmol, isomer ratio ~1:2), 2-methoxybenzeneboronic acid (0.607 g, 4.01 mmol), K_2CO_3 (2.30 g, 16.7 mmol), and $Pd(PPh_3)_4$ (0.385 g, 0.333 mmol) in 10 mL of anhydrous and oxygen-free DMF was stirred at 155 °C for 24 h. After cooling to ambient temperature the mixture was diluted with CH_2Cl_2, washed with HCl (10%), $NaHCO_3$, and water, and dried over $MgSO_4$. After evaporation under reduced pressure the crude product was treated with acetone (15 mL). The precipitate was filtered and yielded 0.399 g (0.963 mmol) of 1,6-bis(2-methoxyphenyl)pyrene. The residue was purified by column chromatography (silica gel, CH_2Cl_2/*n*-pentane 1:2) to give 0.220 g (0.531 mmol) of 1,8-bis(2-methoxyphenyl)pyrene as a pale yellow solid (90% total yield).

1,6-Bis(2-methoxyphenyl)pyrene (6a): mp 242 °C; IR (KBr) ν 3041, 3002, 2956, 2930, 2829, 1596, 1582, 1504, 1484, 1459, 1430, 1298, 1272, 1234, 1177, 1111, 1052, 1026, 1006, 845, 822, 795, 765, 707 cm^{-1}; ^1H NMR (300 MHz, $C_2D_2Cl_4$, 125 °C) δ 3.78 (s, 6H), 7.10−7.18 (m, 4H), 7.40−7.52 (m, 4H), 7.84 (d, $^3J = 9.2$ Hz, 2H), 7.93 (d, $^3J = 8.0$ Hz, 2H), 7.99 (d, $^3J = 9.2$ Hz, 2H), 8.18 (d, $^3J = 8.0$ Hz, 2H); ^{13}C NMR (75.5 MHz, $C_2D_2Cl_4$, 125 °C, additional APT) δ 55.8 (+), 112.2 (+), 120.6 (+), 123.9 (+), 124.8 (−), 125.5 (+), 126.7 (+), 128.0 (+), 128.7 (+), 129.4 (−), 130.2 (−), 130.5 (−), 132.2 (+), 134.4 (−), 157.6 (−); MS (70 eV, EI),

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m/z (%) 414 (100) [M$^+$], 384 (16) [M − OMe], 353 (7) [M − 2 OMe]; $C_{30}H_{22}O_2$ calcd 414.1620 (correct HRMS).

1,8-Bis(2-methoxyphenyl)pyrene (6b): mp 98−103 °C; IR (KBr) ν 3026, 2937, 2831, 1596, 1575, 1486, 1461, 1434, 1263, 1236, 1180, 1121, 1048, 1027, 853, 827, 754 cm^{-1}; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 125 °C) δ 3.72 (s, 6H), 7.10−7.20 (m, 4H), 7.40−7.55 (m, 4H), 7.81 (s, 2H), 8.00 (d, ^3J = 8.0 Hz, 2H), 8.17 (s, 2H), 8.25 (d, ^3J = 8.0 Hz, 2H); ^{13}C NMR (75.5 MHz, $C_2D_2Cl_4$, 125 °C, additional APT) δ 55.8 (+), 112.2 (+), 120.6 (+), 124.0 (+), 124.8 (−), 125.2 (+), 127.0 (+), 127.9 (+), 128.7 (+), 129.0 (−), 130.3 (−), 130.6 (−), 132.2 (+), 134.3 (−), 157.5 (−); MS (70 eV, EI), *m/z* (%) 415 (32) [M$^+$], 414 (100) [M], 384 (16) [M − OMe], 353 (5) [M − 2 × OMe]; $C_{30}H_{22}O_2$ calcd 414.1620 (correct HRMS).

1,6-Bis(2-hydroxyphenyl)pyrene (7a). A mixture of 1,6-bis(2-methoxyphenyl)pyrene (**6a**) (402 mg, 0.97 mmol) in 20 mL of anhydrous CH_2Cl_2 and 10 mL of a 1 M solution of BBr_3 (10.0 mmol) in CH_2Cl_2 was stirred at −78 °C for 14 h. The reaction mixture was quenched with water, and the organic phase was dried over $MgSO_4$. Evaporation of the solvent gave 347 mg (0.898 mmol, 93%) of the product as a yellow solid: mp 233 °C dec; IR (KBr) ν 3538, 3038, 1576, 1482, 1456, 1330, 1280, 1227, 1195, 1096, 1007, 850, 754 cm^{-1}; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 125 °C) δ 7.08−7.12 (m, 4H), 7.34−7.43 (m, 4H), 7.93 (d, ^3J = 9.3 Hz, 2H), 8.00 (d, ^3J = 7.8 Hz, 2H), 8.07 (d, ^3J = 9.3 Hz, 2H), 8.25 (d, ^3J = 7.8 Hz, 2H); ^{13}C NMR (75.5 MHz, $C_2D_2Cl_4$, 125 °C, additional APT) δ 115.8 (+), 120.6 (+), 125.0 (−), 125.1 (+), 126.9 (−), 127.8 (+), 128.4 (+), 129.4 (+), 129.6 (−), 131.0 (−), 131.4 (+), 131.9 (−), 153.2 (−); MS (70 eV, EI), *m/z* (%) 386 (100) [M$^+$], 368 (10) [M − H_2O], 292 (17) [M − phenyl − OH]; $C_{28}H_{18}O_2$ (386.5).

1,6-Bis(2-trifluoromethylsulfonylphenyl)pyrene (8a). A mixture of 1,6-bis(2-hydroxyphenyl)pyrene (**7a**) (301 g, 0.780 mmol) in 50 mL of anhydrous CH_2Cl_2, pyridine (5 mL, 62.1 mmol), and Tf_2O (3 mL, 18.3 mmol) was stirred at −78 °C for 14 h. The reaction was quenched with water, and the mixture was diluted with CH_2Cl_2. The organic phase was washed with HCl (10%), $NaHCO_3$, and water and dried ($MgSO_4$). After evaporation of the solvents the crude product was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane 1:4*)* to yield 374 mg (0.575 mmol, 74%) of the product as a pale yellow solid: mp 198 °C; IR (KBr) ν 3045, 2965, 1610, 1580, 1481, 1414, 1400, 1248, 1211, 1149, 1093, 1042, 889, 846, 818, 783, 772 cm^{-1}; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 125 °C) δ 7.66−7.48 (m, 8H), 7.81 (d, ^3J = 9.3 Hz, 2H), 7.95 (d, ^3J = 7.8 Hz, 2H), 8.04 (d, ^3J = 9.3 Hz, 2H), 8.21 (d, ^3J = 7.8 Hz, 2H); ^{13}C NMR (75.5 MHz, $C_2D_2Cl_4$, 125 °C, additional APT) δ 121.5 (+), 124.4 (+), 124.6 (−), 124.9 (+), 127.7 (+), 127.8 (+), 128.0 (+), 129.3 (+), 129.4 (−), 130.7 (−), 131.0 (−), 133.5 (+), 134.4 (−), 147.5 (−) (O_3SCF_3 is missing because of coupling with F); MS (70 eV, EI), *m/z* (%) 650 (100) [M − H], 517 (16) [M − SO_2CF_3], 383 (80) [M$^+$ − 2SO_2CF_3], 355 (17), 292 (8); $C_{30}H_{16}F_6O_6S_2$ (650.6).

Diindeno[1,2,3-*cd*:1′,2′,3′-*jk*]pyrene (3a). An oxygen free solution of dry LiCl (150 mg, 3.54 mmol), 1,6-bis(2-trifluoromethylsulfonylphenyl)pyrene (**8a**) (75.0 mg, 0.115 mmol), $Pd(PPh_3)_2Cl_2$ (16.2 mg, 23.1 μmol), PPh_3 (24.2 mg, 92.2 μmol), and 0.75 mL of DBU in 5 mL of anhydrous DMF was stirred in a sealed thick-walled Pyrex flask at 170 °C for 24 h. After cooling to ambient temperature the reaction mixture was diluted with 50 mL of CH_2Cl_2 and stirred with 30 mL of H_2O_2 (15%) for 3 h. Then the mixture was washed with 50 mL of HCl (10%), 50 mL of $NaHCO_3$, and 50 mL of H_2O. After drying over $MgSO_4$ the solvent was removed under reduced pressure. The crude product was treated with 5 mL of $CHCl_3$, and the resulting precipitate was filtered off to yield 6 mg (17.3 μmol, 15%) of the product as a red solid: mp >250 °C; IR (KBr) ν 3033, 2960, 1652, 1437, 1258, 1077, 826, 740 cm^{-1}; UV λ_{max} ($CHCl_3$) nm (log ϵ) 455 (0.97), 429 (0.77), 410 (0.77), 389 (0.35), 334 (0.45), 307 (2.44), 298 (2.14), 267 (1.94), 260 (1.81), 248 (1.76); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 125 °C) δ 7.29 (m, 4H), 7.79 (m, 2H), 7.88 (m, 2H), 8.01 (d, ^3J = 8.0 Hz, 2H), 8.18 (d, ^3J = 8.0 Hz, 2H), 8.21 (s, 2H); ^{13}C NMR (75.5 MHz, $C_2D_2Cl_4$, 125 °C) δ 120.1, 120.4, 121.1, 122.2, 122.6, 127.7, 128.5, 128.6, 131.48, 131.54, 135.4, 136.6, 140.4, 141.8; MS (70 eV, EI), *m/z* (%) 351 (28) [M$^+$], 350 (100) [M], 277 (6), 200 (18) [M + 2H − 2 × C_6H_4]; $C_{28}H_{14}$ calcd 350.1096 (correct HRMS).

1-Bromo-4-*tert*-butyl-2-nitrobenzene (13). Concentrated sulfuric acid (31.6 mL, 594 mmol) was added slowly to nitric acid (27.4 mL, 396 mmol) at 0 °C. This cold mixture was added carefully to 4-bromo-*tert*-butylbenzene (56.2 g, 264 mmol). The temperature was kept below 10 °C, and the mixture was stirred for an additional 20 h at ambient temperature, then poured into water (750 mL). The organic layer was separated, and the water layer was washed with Et_2O (200 mL). The combined organic phases were dried over $MgSO_4$. Removal of the solvents under reduced pressure and distillation (bp 190 °C, at 40 mbar) gave 62.7 g of the title compound (243 mmol, 92%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.33 (s, 9H), 7.44 (dd, ^3J = 7.4 Hz, ^4J = 1.9 Hz, 1H), 7.63 (d, ^3J = 7.4, 1H), 7.83 (d, ^4J = 1.9 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 30.9, 34.9, 111.1, 122.7, 130.6, 134.5, 152.5, 157.2; $C_{10}H_{12}BrNO_2$ (258.1). The analytical data agreed with those reported in the literature.[22]

2-Bromo-5-*tert*-butylaniline (14). A mixture of 1-bromo-4-*tert*-butyl-2-nitrobenzene (**13**) (59.1 g, 229 mmol) and $Na_2S_2O_4$ (146.4 g, 841 mmol) in glycol monomethyl ether (350 mL) and water (350 mL) was heated under reflux for 6 h. Water (300 mL) and concentrated hydrochloric acid (300 mL) were added to the warm solution; then the mixture was heated under reflux for 15 min and poured into ice water (500 mL). Solid Na_2CO_3 was added until the mixture was basic. The organic layer was separated and the water layer extracted with Et_2O (200 mL). The combined organic phases were dried over $MgSO_4$. Removal of the solvents under reduced pressure and distillation of the residue (bp 153 °C, at 35 mbar) gave 42.3 g (185 mmol, 81%) of the title compound: IR (KBr) ν 3473, 3382, 2963, 2905, 2869, 1616, 1487, 1416, 1394, 1363, 1312, 1241, 1203, 1159, 1114, 1090, 1017, 935, 861, 801, 701, 667, 641 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.29 (s, 9H), 3.96 (br s, 2H), 6.48 (dd, ^3J = 7.4 Hz, ^4J = 1.9 Hz, 1H), 6.80 (d, ^4J = 1.9 Hz, 1H), 7.33 (d, ^3J = 7.4 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 31.2, 34.4, 106.3, 113.1, 117.0, 132.0, 143.5, 151.8; $C_{10}H_{14}BrN$ (228.1). The analytical data agreed with those reported in the literature.[23]

1-Bromo-2-iodo-4-*tert*-butylbenzene (15). A solution of $NaNO_2$ (13.3 g, 193 mmol) in water (40 mL) was added dropwise to a mixture of 2-bromo-5-*tert*-butylaniline (**14**) (40.0 g, 175 mmol) in water (275 mL) and concentrated hydrochloric acid (66.2 mL) below 5 °C, and the mixture was stirred for 10 min. Then a solution of potassium iodide (43.7 g, 263 mmol) in water (67 mL) was added. The mixture was stirred for 15 min without cooling, then at 50 °C for 15 min and at 80 °C for 15 min. After that the mixture was cooled to 0 °C, and a solution of 5% aqueous sodium sulfite (50 mL) was added. The organic layer was separated, and the water layer extracted with Et_2O (200 mL, 3 times). The combined organic phases were dried over $MgSO_4$. After removal of the solvents under reduced pressure the crude product was purified by column chromatography (silica gel, *n*-pentane) to yield 47.6 g of the title compound (141 mmol, 80%): IR (KBr) ν 2963, 2905, 2868, 1576, 1547, 1475, 1452, 1375, 1272, 1257, 1203, 1118, 1006, 881, 848, 819, 753, 704, 657, 583 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.28 (s, 9H), 7.22 (dd, ^3J = 7.4 Hz, ^4J = 1.9 Hz, 1H), 7.50 (d, ^3J = 7.4 Hz, 1H), 7.83 (d, ^4J = 1.9 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 31.0, 34.4, 101.1, 126.3, 126.9, 132.1, 137.4, 152.0; MS (70 eV, EI), *m/z* (%) 341 (5), 340 (55), 339 (4), 338 (53) [M$^+$], 326 (8), 325 (98), 324 (6), 323 (100) [M$^+$ − CH_3], 297 (16), 295 (15), 277 (12), 198 (16), 196 (14), 127 (12), 117 (28) [M$^+$ − CH_3 − Br − I], 115 (31); $C_{10}H_{12}BrI$ (339.0).

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2-Bromo-5-*tert*-butylbenzeneboronic Acid (10b). To a solution of 1-bromo-2-iodo-4-*tert*-butylbenzene (**15**) (0.460 g, 1.36 mmol) in 40 mL of a mixture of THF and Et_2O (1:1) was added dropwise at −78 °C isopropylmagnesium bromide (2.3 m in Et_2O, 0.59 mL, 1.36 mmol). After the mixture was stirred for 2 h at that temperature $B(OiPr)_3$ (588 mg mL, 3.13 mmol) was added. The solution was warmed to room temperature overnight; then 40 mL of HCl (10%) was added, and the resulting mixture was stirred for 30 min at room temperature. The aqueous layer was extracted with Et_2O (50 mL, 3 times). Drying over Na_2SO_4 and evaporation of the solvent gave 300 mg of the crude product (86%).

For spectroscopic characterization the crude product was treated with pinacol (355 mg, 3.00 mmol) in dioxane (50 mL) to give a quantitative yield of 2-(2-bromo-5-*tert*-butylphenyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane: mp 71 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.30 (s, 9H), 1.39 (s, 12H), 7.26 (dd, ^3J = 8.5 Hz, ^3J = 2.6 Hz, 1H), 7.49 (d, ^3J = 8.5 Hz, 1H), 7.57 (d, ^4J = 2.6 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 24.8, 31.2, 34.2, 84.2, 124.8, 129.2, 132.2, 133.0, 149.1 (C-1, is missing because of coupling with B); MS (70 eV, EI), *m*/*z* (%) 341 (5), 340 (36), 339 (14), 338 (34), 337 (6) [M^+], 326 (15), 325 (100), 324 (40), 323 (98), 322 (23) [$M^+ - CH_3$], 259 (33), 239 (11), 225 (19), 223 (18), 197 (8), 161 (12); $C_{16}H_{24}BBrO_2$ (339.08).

2,7,11-Tri-*tert*-butyltriindeno[1,2,3-*cd*:1′,2′,3′-*fg*:1″,2″,3″-*jk*]-pyrene (3c) (one-pot procedure). A 50 mL Schlenk flask was equipped with a magnetic stirring bar, $Pd_2(dba)_3$ (894 mg, 0.976 mmol), $P(Cy)_3$ (1.09 g, 3.90 mmol), 1,3,6-tribromopyrene[17] (**4c**) (1.07 g, 2.44 mmol), and 2-bromo-5-*tert*-butylbenzeneboronic acid (3.76 g, 14.6 mmol) in DMF (30 mL). After degassing the mixture, DBU (9.1 mL) was added. The resulting mixture was stirred at 155 °C for 36 h. After dilution with 300 mL of CH_2Cl_2, the mixture was washed three times with 50 mL each of HCl (10%) and once each with 50 mL of $NaHCO_3$ and twice 50 mL of H_2O. Drying of the organic phase over $MgSO_4$ and evaporation of the solvent gave the crude product, which was subjected to chromatography on flash silica gel, eluting with pentane/CH_2Cl_2 (10:1) and then (6:1). The isolated red product (R_f 0.28) was then further purified by column chromatography on flash silica gel, eluting with pentane/CH_2Cl_2 (6:1) and then suspended in pentane (10 mL) in the sonicator followed by separation in a centrifuge. This procedure was repeated until the pentane fraction was colorless (five times) to yield 60 mg of **3c** (4%): mp >325 °C; UV λ_{max} ($CHCl_3$) nm (log ϵ) 259 (1.18), 276 (1.43), 298 (1.41), 312 (1.92), 325 (1.00), 354 (0.60), 371 (0.42), 413 (0.34), 438 (0.48), 451 (0.32), 487 (0.11); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 125 °C) δ 1.52 (s, 9H), 1.54 (s, 9H), 1.58 (s, 9H), 7.22−7.41 (m, 3H), 7.43−7.58 (m, 1H), 7.68−7.85 (m, 2H), 7.88−7.95 (m, 2H), 7.96−8.05 (m, 2H), 8.07−8.22 (m, 3H); ^{13}C NMR (75.5 MHz, $C_2D_2Cl_4$, 125 °C, additional APT) δ 31.0 (+), 31.16 (+), 31.21 (+), 34.7 (−), 34.75 (−), 34.82 (−), 112.4 (+), 118.9 (+), 119.05 (+), 119.13 (+), 119.3 (+), 119.9 (+), 122.3 (+), 123.9 (+), 124.9 (+), 125.8 (+), 125.9 (+), 128.0 (+), 129.0 (+), 131.28 (−), 131.32 (−), 131.68 (−), 131.73 (−), 131.8 (−), 131.9 (−), 135.5 (−), 136.6 (−), 136.7 (−), 136.8 (−), 137.8 (−), 138.1 (−), 138.3 (−), 143.1 (−), 143.3 (−), 144.1 (−), 152.0 (−), 152.49 (−), 152.54 (−); MS (70 eV, EI), *m*/*z* (%) 595 (7), 594 (20), 593 (46), 592 (100) [M^+], 579 (3), 578 (13), 577 (25) [$M^+ - CH_3$], 465 (4), 464 (13), 563 (40), 462 (90) [$M^+ - 2 \times t$Bu − CH_3 − H], 449 (3), 448 (11), 447 (32) [$M^+ - 2 \times t$Bu − 2 CH_3 − H]; $C_{46}H_{40}$ calcd 592.3130 (correct HRMS).

2,7,11,16-Tetra-*tert*-butyltetraindeno[1,2,3-*cd*:1′,2′,3′-*fg*:1″,2″,3″-*jk*:1‴,2‴,3‴-*mn*]pyrene (3d) (one-pot procedure). A 50 mL Schlenk flask was equipped with a magnetic stirring bar, $Pd_2(dba)_3$ (1.88 g, 1.82 mmol), $P(Cy)_3$ (2.11 g, 7.53 mmol), 1,3,6,8-tetrabromopyrene[17] (**4d**) (2.44 g, 4.71 mmol), and 2-bromo-5-*tert*-butylbenzeneboronic acid (7.26 g, 28.3 mmol) in DMF (60 mL). After degassing the mixture, DBU (18 mL) was added. The resulting mixture was stirred at 155 °C for 36 h. After dilution with 300 mL of CH_2Cl_2, the mixture was washed twice with 150 mL of HCl (10%) and once each with 150 mL of $NaHCO_3$ and 50 mL of H_2O. Drying of the organic phase over $MgSO_4$ and evaporation of the solvent gave the crude product, which was subjected to chromatography on flash silica gel, eluting with pentane/CH_2Cl_2 (3:1). The isolated red product (R_f 0.28) was then further purified by column chromatography on flash silica gel, eluting with pentane/CH_2Cl_2 (3:1) and then suspended in pentane (5 mL) in the sonicator followed by separation in a centrifuge. This procedure was repeated three times. The resulting solid was dissolved in CH_2Cl_2 (10 mL) and then precipitated by adding pentane (30 mL). The product was then again suspended in pentane (5 mL) in the sonicator followed by separation in a centrifuge. This procedure was repeated until the pentane fraction was colorless (six times) to yield 18 mg of **3d** (1%): mp >325 °C; UV λ_{max} ($CHCl_3$) nm (log ϵ) 278 (1.55), 288 (1.38), 298 (1.44), 312 (1.72), 333 (1.16), 363 (0.82), 397 (0.35), 419 (0.43), 437 (0.24), 467 (0.25), 545 (0.21); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 125 °C) δ 1.57 (s, 36H), 7.27 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 4H), 7.39 (s, 2H), 7.58 (d, ^3J = 8.0 Hz, 4H), 7.62 (d, ^4J = 1.5 Hz, 4H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 125 °C) δ 31.1, 34.7, 118.9, 119.0, 124.2, 125.65, 125.72, 133.1, 137.6, 139.4, 143.6, 152.1, 153.8; MS (70 eV, EI), *m*/*z* (%) 723 (3) [M^+], 708 (3) [$M^+ - CH_3$], 481 (10), 421 (22), 393 (15), 309 (28), 268 (14), 222 (16), 167 (18), 153 (19), 139 (26), 125 (37), 111 (55), 97 (98), 57 (100); $C_{56}H_{50}$ calcd 722.39125 (correct HRMS).

Acknowledgment. This work was supported by the State of Niedersachsen (Germany) and the U.S. National Science Foundation. H.A.W. is indebted to the German National Merit Foundation (Studienstiftung des Deutschen Volkes) as well as the Fonds der Chemischen Industrie for a graduate fellowship. Generous gifts of chemicals by BASF, Bayer, Degussa-Hüls AG, and Chemetall GmbH have been provided. We thank Mr. J. Bienert (MPIfbC, Göttingen) for HPLC purification of the 2,7,11,16-tetra-*tert*-butyltetraindenopyrene (**3d**) used for the fluorescence and absorption measurements.

Supporting Information Available: Experimental procedures for **3b**−**d**, **6b**−**d**, **7b**−**d**, and **8b**−**d** and ^{1}H and ^{13}C NMR spectra for **3a**−**d**, **6a**−**d**, **7a**−**d**, **8a**−**d**, and the pinacol ester of **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0613939