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Methylterrylene isomers

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ABSTRACT

2-Methyl and 3-methylterrylenes have been obtained by Suzuki coupling of 3-bromoperylene and corresponding methylnaphthylboronic acids or esters, giving methylnaphthylperylene isomers, followed by Scholl cyclodehydrogenation; the latter reaction gave also the other cyclodehydrogenation isomers 10- (respectively, 9-) methylbenzo[4,5]indeno[1,2,3-*cd*]perylene.

1. Introduction

Terrylene is a much studied compound for single-molecule spectroscopy because, in contrast with almost all other single-molecule systems, it shows extremely high-photostability[1] under continuous, high intensity irradiation and because its UV–visible absorption maximum (around 570 nm) fits well with standard laser emission wavelengths. Terrylene is the main workhorse in the rapidly developing field of single-photon source.[2] However, its main drawbacks were, until recently, a laborious synthesis, a difficult purification, a lack of solubility, and the absence of anchoring groups for functionalization of biomolecules for instance. Along these lines we wished to open new routes to substituted terrylene in particular isomers of methylterrylene **1** and **2** shown in Fig. 1.

In particular, our initial objective with these two compounds was:

(1) to investigate the low-temperature tunnel rotation of a single methyl group linked to a fluorophore,[3]
(2) to explore the limits of imaging of frontier orbitals of a single molecule by low-temperature STM as recently described.[4] We have shown in this latter article that it was possible to detect the contribution of the benzyl hydrogen orbital to the HOMO and the LUMO contours and this electronic signature of benzylic hyperconjugation has been clearly demonstrated.

2. Results and discussion

Both isomers were prepared by cyclodehydrogenation of the corresponding methyl derivative of naphthylperylene in the Scholl conditions. These latter compounds were obtained by Suzuki coupling of 3-bromoperylene and methylnaphthalene boronic acids or esters. This route has also been recently used by Müllen et al.,[5] for the synthesis of terrylene from naphthylperylene for which we present improved Suzuki coupling conditions. Due to the relatively low solubilities of the naphthylperylene compounds in non-polar eluents, which leads to laborious chromatography, we have optimized the coupling conditions so that purification steps are limited

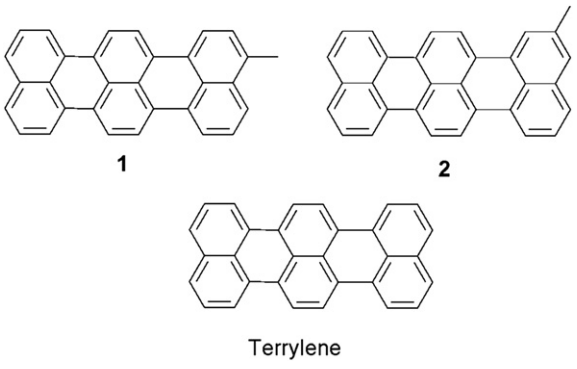

Fig. 1. 3-Methylterrylene **1** and 2-methylterrylene **2**, and terrylene.

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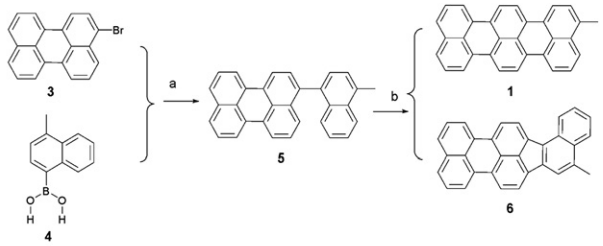
to washings and recrystallizations. The 3-bromoperylene was obtained by NBS bromination of perylene in dry DMF as suggested by Mitchell et al.[6,7] and recrystallized from toluene.

2.1. Terrylene

3-(1-Naphthyl)perylene was obtained by Suzuki coupling of 3-bromoperylene **3** in toluene, and 2-fold excess of commercial naphthalene boronic acid with air stable $PdCl_2(PPh_3)_2/PPh_3$ as a catalyst and potassium carbonate/water as a base. The reaction sequence is analogous to that given in Scheme 1 for the methyl derivative **1**. The purification steps involved first a washing by boiling ethanol, then filtration of the suspension in boiling toluene through a plug of silica gel, and recrystallization from toluene (yield 88%). The cyclodehydrogenation step by aluminum chloride in chlorobenzene was done as in Ref. 5, but, for an unknown reason and despite numerous attempts in various conditions, we have never been able to obtain the published yields of pure terrylene (40%). In our case the typical yield was limited to 15%.



Scheme 1. Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, PPh_3, 2 M K_2CO_3, toluene; (b) $AlCl_3$, chlorobenzene (or $FeCl_3$/DCM, CH_3NO_2 for **6**).

2.2. Isomer (1): 3-methylterrylene

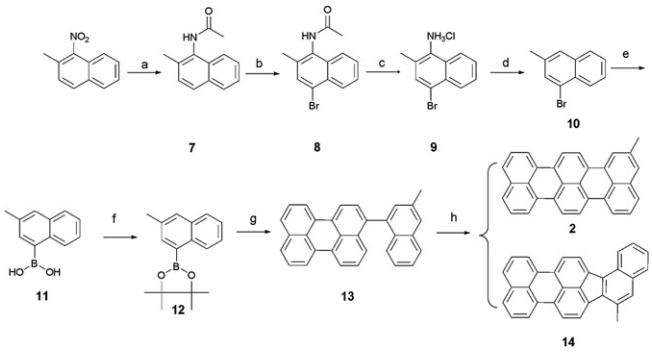
Similarly, the 3-methylterrylene **1** was obtained by cyclodehydrogenation of 3-(4-methylnaphthalen-1-yl)perylene **5**.

This latter compound **5** was prepared by Suzuki coupling of (4-methylnaphthyl-1)boronic acid **4**,[8] synthesized from commercial 1-bromo-4-methyl naphthalene (90% yield) and 3-bromoperylene **3** in 72% yield. The higher solubility of the methyl derivative **4** in boiling ethanol during the washing procedure reduces the yield but at the benefit of simple and efficient purification steps. Furthermore this coupling can be easily scaled up to the gram scale without trouble. The cyclodehydration step was carried out with aluminum chloride in chlorobenzene to provide **1** in 24% yield. The main by-products of this reaction are chlorinated 3-methylterrylenes and a benzoindenoperylene **6** analogous to the one described in Ref. 5. Similarly, **6** can be prepared in 26% yield by cyclodehydrogenation of **5** using anhydrous iron chloride in dichloromethane/nitromethane solution. Compound **6** is a red product soluble enough in $C_2D_2Cl_4$ at 100 °C for proton NMR spectroscopy. However the NMR spectra show broad and poorly resolved peaks indicating aggregation even at this temperature.

2.3. Isomer (2): 2-methylterrylene

2-Methylterrylene **2** was obtained from the corresponding methylnaphthylperylene isomer **13** as shown in Scheme 2.

1-Bromo-3-methylnaphthalene **10** was prepared from commercial 2-methyl-1-nitronaphthalene by an improved procedure.[9] First, reduction of the nitro group and acetylation gave **7** in 91%



Scheme 2. Reagents and conditions: (a) NH_2NH_2/Pd/C or ferrihydrite; Ac_2O; (b) Br_2, AcOH; (c) HCl; (d) $NaNO_2$, AcOH, HCl, H_3PO_2; (e) *n*-BuLi; $B(O\text{-}i\text{-}Pr)_3$, HCl; (f) pinacol, molecular sieves; (g) $Pd(PPh_3)_2Cl_2$, PPh_3, 2 M K_2CO_3, toluene; (h) $AlCl_3$, chlorobenzene (or $FeCl_3$/DCM, CH_3NO_2 for **14**).

yield. The reduction step by hydrazine hydrate in the presence of ferrihydrite[10] or palladium on charcoal revealed as much more convenient in terms of yield and workup than the published procedure by Raney nickel under hydrogen pressure[11] or Fe/HCl.[12] *N*-(2-Methyl-1-naphthyl)acetamide **7** was brominated in *para* position and deacetylated by hydrochloric acid according to Ref. 8 to yield the hydrochlorhydrate **9**, which was used in the dediazoniation step to provide 1-bromo-3-methylnaphthalene **10** in 49% yield. Borylation of **10** by lithiation, then reaction with tri(*iso*-propyl)borate and hydrolysis gave the crude boronic acid **11**. Unfortunately, this compound is not pure enough for the next step and attempts to purify it by recrystallization or chromatography have been unsuccessful. In consequence, the Suzuki coupling with bromoperylene was carried out with the boronic ester **12**, obtained from the acid and purified by chromatography. It gave **13** (in 72% yield), which was cyclodehydrogenated by $AlCl_3$ in chlorobenzene to give **2** in 12% yield. As for the isomer **1**, the main by-products of this reaction are chlorinated 2-methylterrylenes and a benzoindenoperylene **14** analogous to **6**. Similarly, **14** can be also be synthesized in 15% yield by cyclodehydrogenation of **13** by anhydrous iron(III) chloride in dichloromethane/nitromethane solution. The ^1H NMR of **14** in $C_2D_4Cl_2$ at 100 °C shows two broad close peaks at 3.01 and 3.15 ppm (integrating in a ratio ca. 2:1) that can be attributed to the sterically hindered methyl protons. In contrast, the NMR spectrum of **6** in the same conditions shows a single peak at 2.90 ppm, indicating a freely rotating methyl group.

2.4. Absorption and emission

The absorption and emission properties of isomers **1** and **2** are, as expected, very similar to the one of terrylene. Fig. 2 shows the well-structured absorption spectrum of **1** in dichloromethane with absorption peaks at 560, 520, and 483, 440 (sh) nm. Fig. 2 also shows the absorption spectra of the indenobenzoperylene **6** with peaks at 504, 478, and a weak shoulder at 440 nm. The emission spectrum of **1** in dichloromethane (λ_{exc}: 560 nm) displays two maxima at 578 and 620 nm mirroring (in energy) the absorption peaks with a small Stoke shift (18 nm) as expected for this rigid molecule.

Absorption spectra for the isomer **2**, with peaks at 558, 514, 482, and 440 (sh) nm and for **14**, with peaks at 482 and 511 nm, and emission spectra for **2**, with peaks at 576 and 618 nm, are very similar to those for the couple **1**/**6**.

In contrast, the indenoperylenes **6** and **14** were found only marginally luminescent.

Similarly the peaks in the visible part are at 511, 482, and 440 nm for **14**. Hypsochromic shift of 57 nm of the absorption maximum of **6** compared to the methylterrylene **1** (respectively,

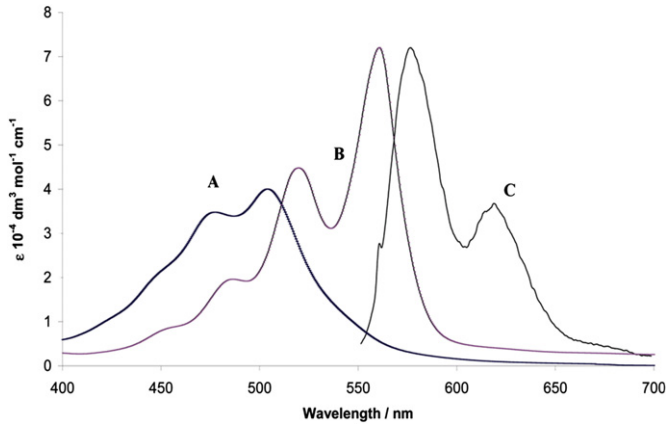


Fig. 2. Absorption spectra of **6** (A) and **1** (B) and emission spectrum of **1** (C, arbitrary units) in toluene.

47 nm for the couple **14**/**2**) can be easily explained by the extension of the conjugation length in the oligorylenes **1** and **2**, in comparison with the corresponding indenoperylenes **6** and **14**. These values are close to those of the terrylene and benzo[4,5]indeno[1,2,3-*cd*]perylene (respectively, 560 and 508 nm in toluene)[5] so that the presence and the position of the methyl group on the polyaromatic cores has little influence on the absorption spectra in the visible range.

3. Experimental section

3.1. General

All chemicals and reagents were purchased from Aldrich or Acros Company and were used without further purification. The solvents were purified using standard protocols. ^{1}H and ^{13}C (300 MHz at room temperature or 500 MHz, at 100 °C) NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, or $C_2D_4Cl_2$ solutions using solvent residue as internal standard ($CDCl_3$ δ_H: 7.25 ppm, δ_C: 77.0 ppm; CD_2Cl_2 δ_H: 5.30 ppm, δ_C: 53.8 ppm; $C_2D_4Cl_2$ δ_H: 6.00 ppm; DMSO-d_6: δ_H: 2.50 ppm). Chemical shifts are reported in parts per million on the δ scale and coupling constants, *J*, are in hertz. Elemental analyses were done by the Service d'Analyse de l'ICSN (Paris).[13] Mass spectra were obtained in the CI mode with Nermag R10-R10. High Resolution Mass Spectra (HRMS) were obtained with GCT 1er Waters. UV and fluorescence spectra were recorded in Varian 5000 UV–vis–NIR and Hitachi F-4500 spectrometers, respectively, using dichloromethane as solvent.[14] Chromatographic separations were effected over Merck 60 silica gel. The ferrihydrite catalyst was prepared according to Ref. 10 and ground with one drop of water half an hour before use.

3.2. 3-Bromoperylene 3

A solution of *N*-bromosuccinimide (706 mg, 3.97 mmol) in dry DMF (20 mL) was added to a solution of perylene (1 g, 3.96 mmol) in dry DMF (250 mL) and stirred at room temperature under nitrogen for 24 h. Addition of water (750 mL) to the mixture gave a suspension which was extracted with dichloromethane (3×200 mL). The grouped organic phases were then washed with water (5×100 mL) and dried ($MgSO_4$). Rotoevaporation of the solvent gave crude 3-bromoperylene, which was recrystallized from toluene. Yield: 90%; ^{1}H (300 MHz, CD_2Cl_2): δ 8.16–8.27 (m, 3H), 7.93–8.15 (m, 2H), 7.68–7.79 (m, 3H), 7.46–7.62 (m, 3H);[13] ^{13}C (75 MHz, CD_2Cl_2): δ 150.0, 134.6, 133.1, 131.6, 131.2, 130.7, 130.6, 130.4, 129.8, 128.4, 128.3, 127.9, 127.8, 122.3, 121.1, 120.9, 120.6, 120.5 ppm; MS (CI, CH_4): *m*/*z* calcd for $C_{20}H_{11}Br$: 331.1; found 331.1 [M^+]. Anal. Calcd for $C_{20}H_{11}Br$: C, 72.53; H, 3.35. Found : C, 73.12; H, 3.36.

3.3. Synthesis of 3-(1-naphthyl)perylene

In a Schlenk tube, a solution of 3-bromoperylene (200 mg, 0.60 mmol), 1-naphthalene boronic acid (172 mg, 1 mmol) in toluene was purged with argon and stirred 15 min at 80 °C with argon bubbling. After addition of degassed aqueous potassium carbonate 2 M solution (0.5 mL, 1 mmol), of $Pd(PPh_3)_2Cl_2$ (12 mL, 0.18 mmol), PPh_3 (38 mg, 0.036 mmol), the mixture was stirred 15 h at 110 °C under argon. The suspension was then evaporated and the residue was stirred in 50 mL of boiling ethanol and filtered. The precipitate was dissolved in 100 mL of boiling toluene, then the hot solution was filtered on a 2 cm plug of silica gel and the plug was washed with 100 mL of boiling toluene. Evaporation of the solvent gave pure 3-(1-naphthyl)perylene **5** as a yellow powder. Yield: 201 mg (88%).

3.4. 4-Methyl-1-naphthylboronic acid 4

A solution of *n*-BuLi (1.7 M in hexane, 10 mL) was slowly added to a cooled (−78 °C) solution of 1-bromo-4-methyl naphthalene (1.5 g, 6.78 mmol) in dry ether (200 mL). The mixture was then allowed to warm up and stirred at room temperature for 2 h. It was then cooled back (−78 °C) and a solution of tri-*iso*-propyl borate (4 g, 4.91 mL, 21.27 mmol) in ether (20 mL) was rapidly added. The mixture was stirred at −78 °C for 30 min and then at room temperature for 15 h. Then, 100 mL of HCl (2 M) was added and milky white emulsion gradually became clear. The ethereal layer was then separated and the aqueous layer was extracted with ether (3×100 mL). The combined ether solutions were dried ($MgSO_4$) and the solvent was rotoevaporated. The residual solid was recrystallized from hot CH_2Cl_2 to give white solid. Yield: 95%; ^{1}H (300 MHz, CD_2Cl_2): δ 9.33 (d, *J*=9.3 Hz, 1H), 8.59 (d, *J*=7.0 Hz 1H), 8.16 (d, *J*=9.5 Hz, 1H), 7.65 (dd, 2H), 7.54 (d, *J*=7.6 Hz, 1H), 2.82 (s, 3H); ^{13}C (75 MHz, CD_2Cl_2): δ 140.3, 137.5, 132.8, 132.3, 128.6, 126.5, 126.3, 125.9, 125.7, 124.6, 19.5; MS (CI, CH_4): *m*/*z* calcd for $C_{11}H_{11}BO_2$: 186.1; found 186.1 [M^+]. Anal. Calcd for $C_{11}H_{11}BO_2 \cdot H_2O$: C, 64.75; H, 6.42. Found: C, 62.91; H, 5.64.[13]

3.5. *N*-(2-Methylnaphthalen-1-yl)acetamide 7

2-Methyl-1-nitronaphthalene (15.53 g, 82.96 mmol) in ethanol (100 mL) was heated to 65 °C under argon, ferrihydrite catalyst (2.5 g) (or 10% Pd/C, 2 g), hydrazine hydrate (10 mL, 10.32 g, 205.6 mmol) were added and this mixture was stirred for 3 h at 65 °C. Filtration over Celite, rotoevaporation, and vacuum drying gave the raw amine as brown oil, which was then dissolved in dichloromethane (20 mL). After dropwise addition of acetic anhydride (10 mL, 10.8 g, 105.8 mmol) in dichloromethane (15 mL), the mixture was stirred 1 h at room temperature and rotoevaporated. Recrystallization of the residue in ethanol gave the acetamide in 91% yield (86% when catalyzed by Pd/C) as white crystals. ^{1}H (300 MHz, DMSO-d_6): 9.70 (s, 1H), 7.89 (d, *J*=6.6 Hz, 1H), 7.86 (d, *J*=7.8 Hz, 1H), 7.77 (d, *J*=8.5 Hz, 1H), 7.53–7.45 (m, 2H), 7.41 (d, *J*=8.5 Hz, 1H), 2.30 (s, 3H), 2.17 (s, 3H); ^{13}C (75 MHz, $CDCl_3$): δ 164.6, 149.9, 128.7, 128.1, 127.6, 126.6, 125.2, 122.2, 23.2, 18.6; MS (CI, CH_4): *m*/*z* calcd for $C_{13}H_{13}NO$: 199.2; found 200.1 [MH^+]. Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.34; H, 6.62; N, 7.01.

3.6. *N*-(4-Bromo-2-methylnaphthalen-1-yl)acetamide 8

To a solution of **7** (15 g, 75.28 mmol) in acetic acid (200 mL), a solution of bromine (3.9 mL, 12.17 g, 76.3 mmol) in acetic acid

(50 mL) was added dropwise over 4 h and stirred overnight at 55 °C. The suspension was filtered and 500 mL of water was added to the filtrate, which provided the product. The filtration/dilution operation was repeated for three more times and the precipitates were regrouped, dried under vacuum, and recrystallized in ethanol. Yield: 17.8 g (85%); ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.79 (br s, 1H, NH), 8.11–8.08 (m, 1H), 7.97–7.93 (m, 1H), 7.85 (s, 1H), 7.64–7.61 (m, 2H); ^{13}C NMR (300 MHz, DMSO-d_6): 168.5, 133.8, 132.2, 131.8, 131.6, 130.0, 127.0, 126.8, 126.3, 123.8, 119.6, 22.6, 17.8; MS (CI, CH_4): m/z calcd for $C_{13}H_{12}BrNO$: 278.1; found: 278.0 [M^+]. Anal. Calcd for $C_{13}H_{12}BrNO$: C, 56.14; H, 4.35; N, 5.04. Found: C, 56.15; H, 4.15; N, 5.06.

3.7. 4-Bromo-2-methylnaphthalen-1-amine hydrochloride 9

About 15 g (53.93 mmol) of **8** was dissolved in boiling ethanol (300 mL). After addition of concentrated HCl (80 mL), the mixture was refluxed for 24 h, cooled to room temperature, and filtered giving 9 g of white needles. To the filtrate was added again 80 mL of concentrated HCl; after 24 h reflux, cooling, and filtration gave a new crop of 5.1 g of product. The acidification sequence was repeated and furnished 0.2 g of product. Total yield of 4-bromo-2-methylnaphthalen-1-amine hydrochloride **9**: 14 g (95%). ^{1}H (300 MHz, DMSO-d_6): δ 8.24 (d, J=9.0 Hz, 1H), 8.0 (d, J=9.3 Hz, 1H), 7.62–7.54 (m, 3H), 4.07 (br s, 2H), 2.52 (s, 3H).

3.8. 1-Bromo-3-methylnaphthalene 10

9 was suspended in a mixture of acetic acid (100 mL), water (50 mL), concentrated HCl (10 mL), and the suspension was cooled to 2–5 °C by an external ice. Then a cold solution of sodium nitrite (4.2 g, 60.87 mmol) in water (15 mL) was added dropwise, stirred for 30 min at 2–5 °C. This cold solution was then poured in cold 50% aqueous solution of hypophosphorous acid (120 mL) and stirred overnight at room temperature, and then 1 h at 100 °C. The suspension was then extracted with ether (3×250 mL); washing of the organic phase with water (3×250 mL), drying ($MgSO_4$), and evaporation of the solvent left crude brown oil that was purified by chromatography on silica (eluent: petroleum ether). Yield: 7.50 g, 66%; ^{1}H (300 MHz, CD_2Cl_2): δ 8.24 (d, J=7.8 Hz, 1H), 7.78 (d, J=8.4 Hz, 1H), 7.69 (s, 1H, b), 7.59–7.52 (m, 3H); ^{13}C (75 MHz, CD_2Cl_2): δ 137.1, 135.4, 132.7, 130.9, 128.4, 127.7, 127.4, 127.3, 127.1, 122.9, 21.8; MS (CI, CH_4): m/z calcd for $C_{11}H_9Br$: 221; found 221 [M^+]. Anal. Calcd for $C_{11}H_9Br$: C, 59.76; H, 4.10. Found: C, 60.31; H, 4.24.

3.9. 4,4,5,5-Tetramethyl-2-(3-methylnaphthalen-1-yl)-1,3,2-dioxaborolane 12

A solution of **10** (880 mg, 3.98 mmol) in dry ether (20 mL) was cooled to −78 °C and then *n*-BuLi (1.6 M in hexane, 3 mL, 4.8 mmol) was added dropwise. The bath was removed and the mixture was stirred at room temperature for 2 h. The reaction mixture was then cooled to −78 °C and a solution of tri-*iso*-propyl borate (1.3 mL, 1.059 g, 5.76 mmol) in dry ether (10 mL) was added rapidly. The mixture was stirred at −78 °C for half an hour and then at room temperature overnight. Then, aqueous HCl (2 M, 50 mL) was added and milky white emulsion gradually became clear. The ethereal layer was separated and the aqueous layer was extracted with ether (3×100 mL). The combined ether solution was dried ($MgSO_4$). After filtration, the solution of **11** was rotoevaporated and the white residue was dissolved in DCM (50 mL). Pinacol (4.5 mmol, 531 mg) and molecular sieves were added and the mixture was stirred for 2 days at room temperature. After filtration and evaporation, the residue was chromatographed using silica gel with cyclohexane/dichloromethane (4:1) as eluent. Yield: 85%; ^{1}H (300 MHz, DMSO): 9.79 (br s, 1H), 8.10 (m, 1H), 7.95 (m, 1H), 7.85 (s, 1H), 7.63 (m, 2H), 2.31 (s, 3H), 2.19 (s, 3H); ^{13}C (75 MHz, CD_2Cl_2): δ 137.0, 135.4, 132.7, 130.9, 128.4, 127.7, 127.4, 127.4, 127.1, 123.0, 21.8; MS (CI, CH_4): m/z calcd for $C_{17}H_{21}BO_2$: 268.2; found 269.2 [MH^+]. Anal. Calcd for $C_{17}H_{21}BO_2$: C, 76.14; H, 7.89. Found: C, 75.89; H, 7.82.

3.10. 3-(4-Methylnaphthalen-1-yl)perylene 5 and 3-(3-methylnaphthalen-1-yl)perylene 13

A solution of **3** (200 mg, 0.6 mol) and **4** (186 mg, 1 mmol)/**12** (215 mg, 0.8 mmol) in toluene (25 mL) was stirred at 80 °C for 20 min with argon bubbling. To this solution, $Pd(PPh_3)_2Cl_2$ (12 mg, 0.18 mmol), triphenylphosphine (38 mg, 0.36 mmol), and 0.5 mL of a 2 M aqueous potassium carbonate solution (1 mmol) were added . The mixture was then stirred overnight at 110 °C under argon and the solvent was evaporated. The residue was stirred in 50 mL of boiling ethanol and filtered. The precipitate was then dissolved in 100 mL of boiling toluene and the hot solution was filtered on a small plug of silica gel. The solution was then concentrated and cooled to −20 °C to give a yellow solid.

*3.10.1. 3-(4-Methylnaphthalen-1-yl)perylene **5**.* Yield: 81%; ^{1}H (300 MHz, CD_2Cl_2): δ 8.34 (d, J=7.8 Hz, 1H), 8.26–8.31 (m, 2H), 8.22 (d, J=8.9 Hz, 1H), 8.13 (d, J=8.4 Hz, 1H), 7.75 (d, J=8.3 Hz, 2H), 7.40–7.57 (m, 6H), 7.22–7.37 (m, 4H), 2.81 (s, 3H); ^{13}C (75 MHz, CD_2Cl_2): δ 136.5, 136.3, 135.6, 135.2, 134.4, 133.6, 129.4, 126.7, 126.6, 125.5, 125.0, 124.8, 124.7, 121.9, 120.9, 120.8, 120.5, 120.0, 20.4; MS (CI, NH_3): m/z calcd for $C_{31}H_{20}$: 392.1; found 392 [M^+]. Anal. Calcd for $C_{31}H_{20}$: C, 94.86; H, 5.14. Found: C, 94.41; H, 5.45.

*3.10.2. 3-(3-Methylnaphthalen-1-yl)perylene **13**.* Yield: 72%; ^{1}H (300 MHz, CD_2Cl_2): δ 8.17–8.27 (m, 5H), 7.96–8.12 (m, 3H), 7.68–7.79 (m, 5H), 7.60 (dd, J=7.6 Hz, J=8.4 Hz, 1H), 7.46 7.53 (m, 3H), 2.12 (s, 3H); ^{13}C (75 MHz, CD_2Cl_2): δ 138.3, 138.1, 135.3, 134.8, 134.1, 133.9, 131.2, 131.1, 130.0, 128.7, 128.6, 127.8, 127.5, 126.8, 126.7, 126.5, 126.1, 25.9, 125.1, 120.4, 120.3, 119.9, 21.4; MS (CI, NH_3): m/z calcd for $C_{31}H_{20}$: 392.1; found 392 [M^+]. Anal. Calcd for $C_{31}H_{20}$: C, 94.86; H, 5.14. Found: C, 94.61; H, 5.58.

3.11. Methylterrylenes 1 and 2

To a solution of **5** (respectively, **13**) (200 mg, 0.509 mmol) in dry chlorobenzene (25 mL) was added anhydrous aluminum chloride (600 mg, 4.5 mmol) and the mixture was stirred at 80 °C under argon for 4 h. After cooling to room temperature, 10% HCl (50 mL) was added; after 1 h stirring, the mixture was filtered over paper. The filter paper and the precipitate were then extracted in a Soxhlet apparatus with toluene for 48 h. The toluene solution was then cooled to room temperature and centrifuged giving a dark black colored powder. ^{1}H NMR and ^{13}C NMR could not be measured due to the poor solubility of the methylterrylene.

*3.11.1. Isomer (**1**).* Yield: 24%; MS (CI, NH_3): m/z calcd for $C_{31}H_{18}$: 390.5; found 391.5 [MH^+]; HRMS (DCI, CH_4): m/z calcd for $C_{31}H_{19}$ [MH^+]: 391.1487; found: 391.1481; UV–vis: λ_{max} (CH_2Cl_2)/nm 560 (ε/dm^3 mol^{-1} cm^{-1} 72,000), 520 (44,800), 483 (19,400), 440 sh;[14] emission λ_{max} (toluene)/nm (λ_{exc}: 560 nm): 578, 620. Anal. Calcd for $C_{31}H_{18}$: C, 95.35; H, 4.65. Found: C, 94.9; H, 4.8.[13]

*3.11.2. Isomer (**2**).* Yield: 12%; MS (CI, NH_3): m/z calcd for $C_{31}H_{18}$: 390.5; found 391.2 [MH^+]; HRMS (DCI, CH_4): m/z calcd for $C_{31}H_{19}$ [MH^+]: 391.1487; found: 391.1489; UV–vis: λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 482 (59,035); 514 (87,510); 558 (88,150).[14] Anal. Calcd for $C_{31}H_{18}$: C, 95.35; H, 4.65. Found: C, 94.8; H, 4.95.[13]

3.12. 10-Methylbenzo[4,5]indeno[1,2,3-*cd*]perylene 6 and 14

Methylnaphthylperylene **5** (respectively, **13**) (39 mg, 0.1 mmol) was dissolved in dry dichloromethane (20 mL) and stirred in argon at room temperature. After 30 min, a solution of anhydrous iron(III) chloride (130 mg, 0.80 mmol) in dry nitromethane (1 mL) was injected and the mixture was stirred for 48 h under argon. Dry methanol (15 mL) was added to the solution and allowed to stand for 2 h. The resulting dark brown precipitate was filtered, washed with methanol, and dried. The product was then crystallized from chloroform/methanol (1:1) and dried under vacuum three times. ^{13}C NMR could not be measured due to the poor solubility of the indenoperylenes.

3.12.1. Compound ***6***. Yield: 26%. ^{1}H (500 MHz, $C_2D_2Cl_4$, 100 °C):[15] δ 8.79 (d, J=8.4 Hz, 1H), 8.39–8.53 (m, 5H), 8.14 (br t, 2H), 8.00 (s, 1H), 7.89 (d, J=8.5 Hz, 2H), 7.57–7.70 (m, 4H), 2.9 (s, 3H); ^{13}C NMR could not be measured due poor solubility; HRMS (DCI, CH_4): m/z calcd for $C_{31}H_{19}$ [MH^+]: 391.1487; found 391.1472; UV–vis: λ_{max} (CH_2Cl_2)/nm 504 (ε/dm^3 mol^{-1} cm^{-1} 40,000), 477 (34,500), 445 sh.[14]

3.12.2. Compound ***14***. Yield: 15%. ^{1}H (500 MHz, $C_2D_2Cl_4$, 100 °C):[15] δ 8.76 (d, J=9.9 Hz, 1H), 8.23–8.59 (br m, 6H), 7.89 (br s, 3H), 7.51–7.67 (m, 5H), 3.15 (br s, 1H, CH_3), 3.01 (br s, 2H, CH_3); ^{13}C NMR could not be measured due to poor solubility; HRMS (DCI, CH_4): m/z calcd for $C_{31}H_{19}$ [MH^+]: 391.1487; found 391.1494 [MH^+]; UV–vis: λ_{max} (CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}): 482 (83,840); 511 (95,540).[14]

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.09.033. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. Moerner, W. E. *New J. Phys.* **2004**, *6*, 88.
2. Grangier, P.; Sanders, B.; Vuchovic, J. *New J. Phys.* **2004**, *6* (Issue 1). Focus issue: Single Photons on Demand and references therein.
3. Sigl, A.; Scharmagl, C.; Friedrich, J.; Gourdon, A.; Orrit, M. *J. Chem. Phys.* **2008**, *128*, 044508-1–044508-9.
4. Javier Villagomez Ojeda, C.; Zambelli, T.; Gauthier, S.; Gourdon, A.; Barthes, C.; Stojkovic, S.; Joachim, C. *Chem. Phys. Lett.* **2007**, *450*, 107–111.
5. Avlasevich, Y.; Kohl, C.; Müllen, K. *J. Mater. Chem.* **2006**, *16*, 1053–1057.
6. Mitchell, R. H.; Lai, Y.-H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733–4735.
7. Maeda, H.; Nanai, Y.; Mizuno, K.; Chiba, J.; Takeshima, S.; Inouye, M. *J. Org. Chem.* **2007**, *72*, 8990–8993.
8. Cammidge, A. N.; Gopee, H. *Chem.—Eur. J.* **2006**, *12*, 8609–8613.
9. Bongue-Boma, R.; Rinaudo, J.; Bonnier, J.-M. *Bull. Soc. Chim. Fr.* **1982**, *2*, 52–58.
10. Lauwiner, M.; Rys, P.; Wissmann, J. *Appl. Catal., A* **1998**, *172*, 141–148.
11. Baker, B. R.; Carlson, G. H. *J. Am. Chem. Soc.* **1942**, *64*, 2657–2664.
12. Marion, L.; McRae, J. A. *Can. J. Res.* **1940**, *18*, 265–271.
13. As commonly observed, the chemical analyses of large PAH and aromatic boronic acids are very often imprecise due to incomplete combustion or/and the presence of solvates.
14. The absorption coefficients of the poorly soluble compounds **1**, **6**, **2**, **14** could not be determined with high accuracy due to partial aggregation in even dilute solutions.
15. In contrast with non-methylated analogues (Ref. 5), the NMR peaks of compounds **6** and **14** are very broad, even at 100 °C, confirming partial aggregation.