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ARTICLE

Oxidative Cyclodehydrogenation of a Perylene Derivative: Different Reagents Give Different Products

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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An efficient synthesis of 3-fluoroterrylene, a promising molecular nanoprobe for single electron optical sensing, is described. The key synthetic steps comprised the palladium-catalysed cross-coupling reaction of 3-bromoperylene and 4-fluoronaphthalene-1-boronic acid pinacol ester to give 3-(4-fluoronaphthalen-1-yl)perylene, followed by oxidative cyclodehydrogenation to give selectively either 3-fluoroterrylene or its isomer 10-fluorobenzo[4,5]indeno[1,2,3-*cd*]perylene. The selectivity of the Scholl oxidation under $AlCl_3$/chlorobenzene or DDQ/TfOH conditions was confirmed by ^{19}F NMR.

Introduction

Oligo(*peri*-naphthylene)s, known as rylenes,[1a] with the general structure **1** (Fig. 1) are a class of *peri*-condensed nanosized graphenes nano-ribbons with armchair edges.[1b] Due to the outstanding chemical, thermal and photochemical inertness, and low cost, in connection with the ease of accessibility,[1b] perylene **1a** (n = 0) and its derivatives have been intensively studied and found applications ranging from laser dyes,[2a,b] photochemical sensitizers,[2c-e] absorbers for sunlight collectors[2f-m] to applications in liquid-crystalline phases[3] and organic semiconductors.[4] Incorporation of additional naphthalene units along the molecular axis of perylene **1a**, to form its higher rylenes (*e.g.* terrylene **1b** and quaterrylene **1c**), extends the conjugation length and has been proven to be an effective method to obtain long wavelength rylenes (560 nm for **1b**, and 662 nm for **1c**).[1b]

Terrylene **1b** has several important properties, including photostability,[5a] semiconductivity,[5b] and a high fluorescence quantum yield.[5c] In the field of single-molecule spectroscopy terrylene **1b** is the most studied compound due to its extremely high-photostability[6a] under continuous high intensity irradiation and because its UV-vis. absorption maximum (around 570 nm) fits well with standard laser emission wavelengths.[6b] However the study of terrylene **1b** and its derivatives remains challenging, due to difficult syntheses as well as their limited processability caused by their low solubilities.[1a,7]

In connection with our previous work on single molecule optics,[8a] we wish to report in this paper a facile access to 3-fluoroterrylene **2**, a potential nanoprobe for optical single electron sensing.[8b] Furthermore we herein describe selectivity of the Scholl oxidation to obtain either **2** or **3**, under $AlCl_3$/chlorobenzene or DDQ/TfOH conditions, respectively, as confirmed by ^{19}F NMR.

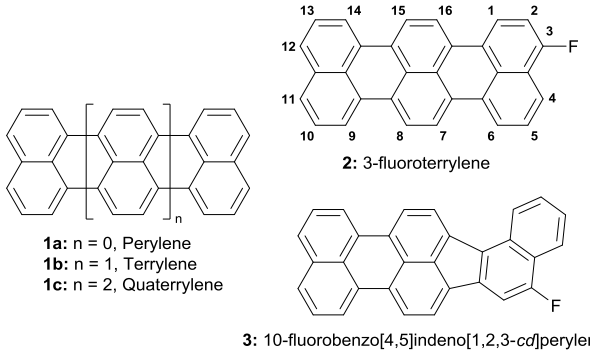

Fig. 1 General structure of rylenes **1**, 3-fluoroterrylene **2** and 10-fluorobenzo[4,5]indeno[1,2,3-*cd*]perylene **3**.

The retrosynthetic analysis of **2** and **3** is shown in Scheme 1. Disconnection of the C6-C7 bond suggested that **2** or **3** might be formed by cyclodehydrogenation of 3-(4-fluoronaphthalen-1-yl)perylene **4**. Several inter- and intramolecular oxidative cyclodehydrogenation reactions have been reported,[9] however the outcome (the new C-C bond between two unfunctionalized aryl vertices) might sometimes be unpredictable, and depends on the conditions used and the topology and nature of the substituents.[9p,q] Moreover, the cyclodehydrogenation reaction can also be effected by electrochemical oxidation.[9s-u] Further disconnection on 3-(4-fluoronaphthalen-1-yl)perylene **4** suggested that it could be accessed by employing our previously reported optimised palladium-catalysed cross-coupling reaction conditions[10] between 3-bromoperylene **5** and 4-fluoronaphthalene-1-boronic acid pinacol ester **6** (Scheme 1).

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† Electronic Supplementary Information (ESI) available: Copies of ^{1}H, ^{13}C, and ^{19}F NMR, HRMS, UV/Vis and fluorescence spectra. See DOI: 10.1039/x0xx00000x

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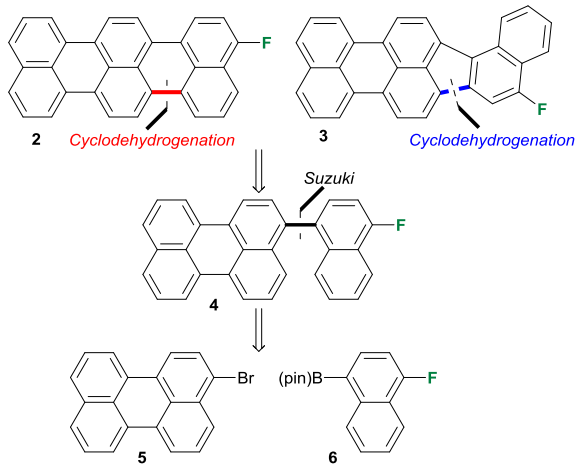
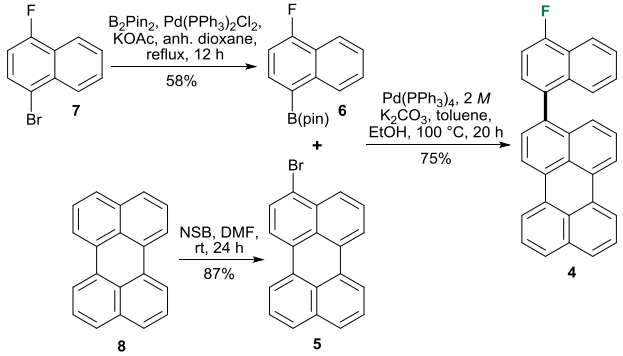


Scheme 1 Retrosynthesis of **2** and **3**.

Results and discussion

The synthetic route started with the preparation of 2-(4-fluoronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **6**, which was obtained in 58 % yield by Miyaura borylation of 1-bromo-4-fluoronaphthalene **7**, using a modified procedure to that reported by Miyaura *et al.*[11] 3-Bromoperylene **5** was obtained in 87 % yield by NBS bromination of perylene **8**, following the procedure reported by Mitchell *et al.*[12] in combination with our previously reported improved purification method.[10] The ^{1}H-NMR data of **5** was in a good agreement with our previous report.[10]

Subjecting 2-(4-fluoronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **6** with 3-bromoperylene **5** under modified Suzuki cross-coupling conditions[10,13] afforded the key intermediate 3-(4-fluoronaphthalen-1-yl)perylene **4** in 75% yield. Despite the low solubility of **4**, purification by column chromatography on silica gel was successfully performed using a mixture of hexane-toluene-DCM (10 : 0.5 : 0.5) as eluent.



Scheme 2 Preparation of 3-(4-fluoronaphthalen-1-yl)perylene **4**.

The structure of **4** was confirmed by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy, and by UV and mass spectrometry. Characteristically the absorption spectrum of **4** (λmax 445 nm) is shifted bathochromically by 6 nm compared to perylene **8**[14] due to conjugation with the naphthalene moiety (Fig. 2). In addition compound **4** possesses an intense green fluorescence with larger Stokes shift (14 nm) than perylene (7 nm),[14] which is in good agreement with the reported values by Müllen *et al.* for 3-(1-naphthyl)perylene.[9r]

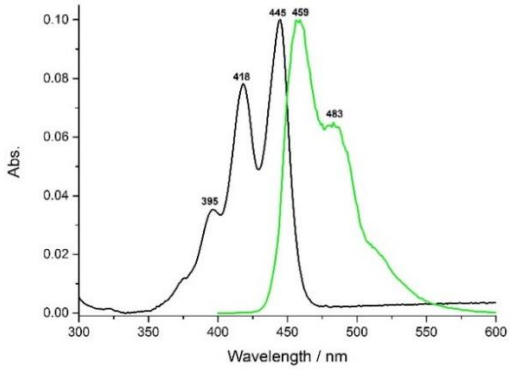
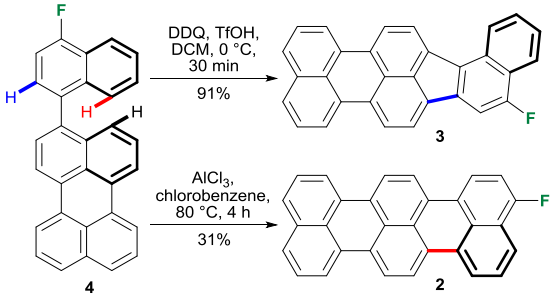


Fig. 2 Absorption and emission spectra of **4** in dichloromethane.

Having obtained the key intermediate 3-(4-fluoronaphthalen-1-yl)perylene **4**, attention was then turned to cyclodehydrogenation reactions. Recently Rathore *et al.*[15] demonstrated that the DDQ/H$^+$ oxidation system (which is known to oxidize a variety of electron donors with oxidation potential as high as ~1.7 V to the corresponding cation radicals) can be effectively employed for a variety of oxidative cyclodehydrogenation reactions. The procedure described therein with DDQ/H$^+$ rather than most commonly utilised oxidants (*e.g.* $FeCl_3$,[9f,g,r,10,16a,b] $CuCl_2$ or $Cu(OTf)_2$ and $AlCl_3$,[9a,c,r,10,] $Tl(O_2CCF_3)_3$ in CF_3CO_2H or BF_3•OEt_2,[9o] $Pb(OAc)_4/BF_3$• Et_2O in MeCN,[9n] triethyloxonium hexachloroantimonate ($Et_3O^+SbCl_6^-$),[16c,d] $SbCl_5$,[16e-g] $MoCl_5$,[9h-j,16h] *etc.*) for the Scholl reaction eliminates problems such as chlorination of the polyaromatic products and the use of large excess of oxidants.

A typical DDQ/H$^+$ cationic cyclodehydrogenation procedure, involved the treatment of 3-(4-fluoronaphthalen-1-yl)perylene **4**, in dry DCM, with one equivalent of DDQ at 0 °C followed by the addition of ten equivalents of trifluoromethanesulfonic acid at 0 °C (Scheme 3). Following a standard workup an orange-red residue was obtained which was washed with hexane and purified by column chromatography on silica gel (hexane : toluene : DCM = 10 : 2 : 2) to give **3** as a red solid in 91%. The MALDI micro TOF LD$^+$ mass spectrum, using DCTB as the matrix, of the purified product showed the [M]$^+$ (100%) molecular ion at 394.1 *m/z* confirming the successful cyclodehydrogenation reaction (-2H$^+$).



Scheme 3 Cyclodehydrogenation of 3-(4-fluoronaphthalen-1-yl)perylene **4**.

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Furthermore, the low solubility of **3** in $C_2D_2Cl_4$ at 100 °C allowed the structure confirmation by ^1H and ^{19}F NMR spectroscopy (Table 1). However the ^{13}C NMR could not be measured. The $^1H\{^{19}F\text{-coupled}\}$ spectrum of **3** displayed a doublet at δ_H 7.86 ($^3J_{HF\text{-}o}$ = 10.5 Hz) which upon ^{19}F-decoupling the signal collapses to give a singlet. In contrast the $^1H\{^{19}F\text{-coupled}\}$ spectrum of **6** displayed doublet of doublets at δ_H 7.15 ($^3J_{HF\text{-}o}$ = 10.5 Hz, $^3J_{HH\text{-}o}$ = 7.8 Hz) which upon ^{19}F-decoupling the signal collapses to give a doublet ($^3J_{HH\text{-}o}$ = 7.8 Hz) due to the *meta*-hydrogen. In addition, the $^{19}F\{^1H\text{-coupled}\}$ spectrum of **3** displayed a doublet of multiplets at δ_F -122.05 ($^3J_{FH\text{-}o}$ = 10.9 Hz), whereas the $^{19}F\{^1H\text{-coupled}\}$ spectrum of **6** displayed a ddd pattern at δ_F -117.5 ($^3J_{FH\text{-}o}$ = 10.4 Hz, $^4J_{FH\text{-}m}$ = 6.2 Hz, ^5J = 2.0 Hz), a splitting similar to the one observed in the spectrum of **4** (Table 1).

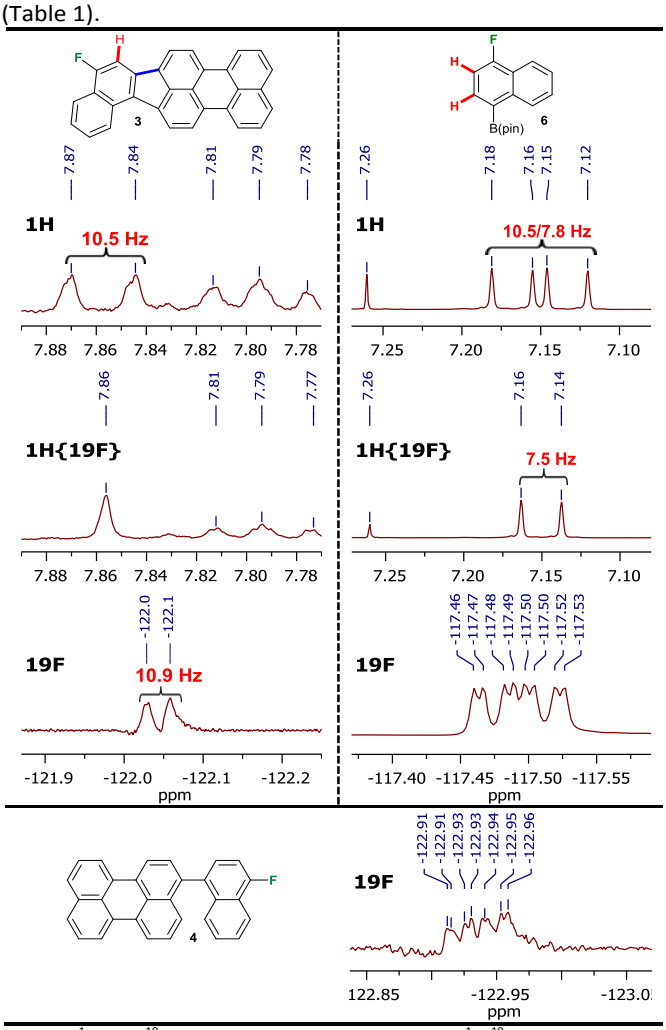

Table 1 ^1H and ^{19}F NMR of **6** (300 MHz, $CDCl_3$, top: $^1H\{^{19}F\text{-coupled}\}$, middle: $^1H\{^{19}F\text{-decoupled}\}$, bottom (282 MHz, $C_2D_2Cl_4$): $^{19}F\{^1H\text{-coupled}\}$), **3** (400 MHz, $C_2D_2Cl_4$, 100 °C, top: $^1H\{^{19}F\text{-coupled}\}$, middle: $^1H\{^{19}F\text{-decoupled}\}$, bottom (376 MHz, $CDCl_3$): $^{19}F\{^1H\text{-coupled}\}$), and **4** (282 MHz, $C_2D_2Cl_4$, 45 °C: $^{19}F\{^1H\text{-coupled}\}$).

As expected the absorption spectrum of **3** (λmax 503 nm) is shifted hypsochromically by 57 nm, compared to 3-methylterrylene,[10] due to a smaller extension of conjugation (Fig. 3). Compound **3** showed no fluorescence upon excitation at 300–600 nm.

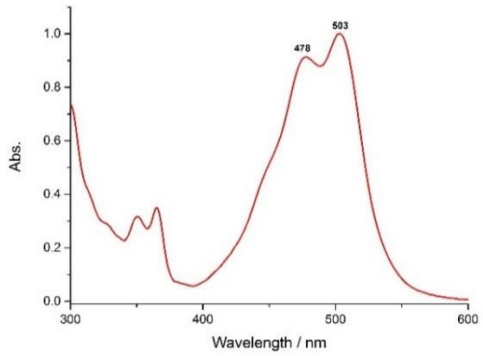

Fig. 3 Absorption spectra of **3** in dichloromethane.

In spite of numerous attempts using the DDQ/TfOH cyclodehydrogenation procedure, such as different reagents addition orders, or slight increase in the reaction temperature, from 0 °C to room temperature, the conditions proved to selectively give the isomer 10-fluorobenzo[4,5]indeno[1,2,3-*cd*]perylene **3**. An alternative cyclodehydrogenation procedure of **4** involved the use of eight equivalents of aluminium chloride in chlorobenzene and the mixture was stirred at 80 °C for 4 h (Scheme 3). Following a standard workup the precipitate was then washed thoroughly with dichloromethane and extracted in a Soxhlet apparatus with toluene. The orange solution was decanted and the solid product was collected from the flask walls, rinsed with petroleum ether and dried in vacuum to give the targeted product 3-fluoroterrylene **2** as a purple solid in 31% yield. As observed by ^{19}F NMR and UV-vis spectra, the product **2** did not contain terrylene isomer **3**. However the ^1H NMR and ^{13}C NMR spectra of **2** could not be measured due to the very poor solubility in all solvents.

As expected the signal in the $^{19}F\{^1H\text{-decoupled}\}$ NMR spectrum of **2** moved downfield from δ_F -122.94 (for **4**) to δ_F -120.96, whereas the signal for the isomer **3** was observed at δ_F -122.05 (all obtained in $C_2D_2Cl_4$), see supplementary information. Furthermore, the DCI-CH_4 TOF MS CI^+ spectrum showed a peak at 394.1167 for $C_{30}H_{15}F$ $[M]^+$, confirming the cyclodehydrogenation reaction. Finally, the UV-vis spectrum of **2** (λmax 557 nm) is in good agreement with the literature values for terrylene (λmax = 560 nm),[9r] and for 3-methylterrylene (λmax = 560 nm).[10] Compound **2** possesses an intense fluorescence with a small Stoke shift (10 nm) as expected for a rigid molecule (Fig. 4).

Such selectivity in cyclodehydrogenation (Fig. 3) is puzzling and may imply that two different mechanisms are involved depending on the reaction conditions. Similar, but less selective, sensitivity has already been observed for the preparation of terrylene[9b] and 3-methylterrylene[10] with $AlCl_3$ favouring the formation of terrylene and $FeCl_3$ yielding preferentially the benzoindenoperylene isomers.

Considering the growing importance of these reactions for the preparation of PAHs and graphene nanoribbons, further theoretical[18] and experimental explorations seem highly important.

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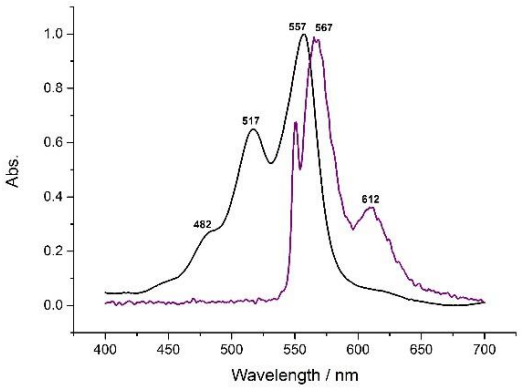

Fig. 4 Absorption and emission spectra of **2** in dichloromethane.

Conclusions

To develop investigations on halogenated nanoprobes for electron sensing by single molecule optics, an efficient synthetic strategy has been developed for the preparation of 3-fluoroterrylene and its isomer 10-fluorobenzo[4,5]indeno[1,2,3-*cd*]perylene. The target compounds were obtained by palladium-catalysed cross-coupling reaction between 3-bromoperylene and 4-fluoronaphthalene-1-boronic acid pinacol ester, followed by selective oxidative cyclodehydrogenation under $AlCl_3$/chlorobenzene or DDQ/TfOH conditions, respectively. Despite the limited processability of these type of compounds, caused by their low solubility, 10-fluorobenzo[4,5]indeno[1,2,3-*cd*]perylene was successfully purified by column chromatography and the structure was confirmed by ^{1}H and ^{19}F NMR, UV-vis and mass spectroscopy, in comparison with the spectra data of 2-(4-fluoronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 3-(4-fluoronaphthalen-1-yl)perylene. The preparation of 3-fluoroterrylene was confirmed by ^{19}F NMR and UV-vis spectra, from which it was also confirmed the absence of its isomer. The reported synthesis could also serve as the starting point for the preparation of new derivatives by suitable editing of the fluoro-position, and/or introduction of new functionalities on the naphthalene core.

Experimental

General

All reagents and solvents were purchased from commercial sources and either used as supplied or purified using the appropriate standard procedures.[17] Column chromatography was carried out using Merck silica gel 60H (40-60 nm, 230-300 mesh). Thin-layer chromatography (TLC) was carried out using aluminum plates coated with Merck HF254/366 silica gel. Visualisation was performed under a 254 nm ultraviolet (UV) light source and/or by immersion in potassium permanganate ($KMnO_4$) or phosphomolybdic acid (PMA) solutions, followed by heating. EI and DCI-CH_4 mass spectra were recorded on a GCT 1er Waters spectrometer. DCI-NH_3 mass spectra were recorded on a DSQ Thermo Fisher Scientific spectrometer. Electrospray (ES±) mass spectra were recorded on a UPLC Xevo G2 Q TOF Waters spectrometer. MALDI mass spectra were recorded on a MALDI Micro MX Waters spectrometer. High resolution mass spectra (HRMS) were recorded on a GCT 1er Waters spectrometer. UV-vis spectra were recorded on a Varian 5000 UV-VIS-NIR and luminescence spectra were recorded in dichloromethane on a Hitachi F-4500 spectrometer, at excitation wavelengths of λ = 275 nm for **2** and λ = 257 nm for **4**. NMR spectra were recorded using deuterated chloroform ($CDCl_3$) as solvent unless otherwise stated. ^{1}H NMR spectra were recorded either on a Bruker Avance III 500 Ultrashield Plus (500 MHz), Bruker Avance III 400 (400 MHz), or on a Bruker Avance 300 (300 MHz) spectrometer. Residual non-deuterated solvent was used as the internal standard. Chemical shifts (δH) are quoted in parts per million (ppm) downfield from tetramethylsilane (TMS). ^{13}C NMR spectra were recorded either on a Bruker Avance III 500 Ultrashield Plus (125 MHz), Bruker Avance III 400 (100 MHz), or on a Bruker Avance 300 (75 MHz) spectrometer, using a carbon signal of the solvent as the internal standard. Chemical shifts (δC) are quoted in parts per million (ppm) downfield from tetramethylsilane (TMS). ^{19}F NMR spectra were recorded either on Bruker Avance 300 (282 MHz), or on a Bruker Avance III 400 (376 MHz). Chemical shifts for fluorine (δF) are reported in parts per million (ppm) on the δ scale relative to trichloro-fluoro-methane (CCl_3F) as the external standard. Peak assignments were aided by ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC and/or ^{1}H{^{19}F-decoupling}, whenever necessary. The resonance multiplicity patterns are described as singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), quintet (quin.), multiplet (m), or combinations of these. Coupling constants (J) are quoted in hertz (Hz).

2-(4-Fluoronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6): 1-Bromo-4-fluoronaphthalene **7** (495 mg, 2.2 mmol), bis(pinacolato)diboron (614 mg, 2.4 mmol), potassium acetate (648 mg, 6.6 mmol) and bis(triphenylphosphine)palladium(II) dichloride (92.6 mg, 0.13 mmol) were suspended in 20 mL anhydrous dioxane in a dry 50 mL single-necked round-bottomed flask fitted with a condenser and a magnetic stirrer. The yellow suspension was flushed with argon for 30 minutes and then refluxed for twelve hours. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave an oil which was purified by column chromatography on silica gel (hexane : EtOAc = 9.5 : 0.5) to afford product **6** as a colourless oil (347 mg, 58%). Rf (SiO_2, hexane : EtOAc = 9.5 : 0.5) = 0.62. **^{1}H NMR** (300 MHz, $CDCl_3$, ^{19}F-coupled): δH 8.82 (^{1}H, dm, J = 8.4 Hz, C(5)H), 8.14 (1H, dm, J = 8.4 Hz, C(8)H), 8.06 (1H, dd, ^{3}JHH-o = 7.8 Hz, ^{4}JHF-m = 6.0 Hz, C(2)H), 7.63-7.52 (2H, m, C(6)H & C(7)H), 7.15 (1H, dd, ^{3}JHF-o = 10.5 Hz, ^{3}JHH-o = 7.8 Hz, C(3)H). **^{13}C NMR** (75 MHz, $CDCl_3$, ^{19}F-coupled): δC 161.21 (d, ^{1}JCF = 254.8 Hz, C-4), 138.77 (d, ^{4}JCF = 4.8 Hz, C-1), 136.18 (d, ^{3}JCF = 8.9 Hz, C-2), 128.31 (d, ^{4}JCF = 2.9 Hz, C-5 (or) C-8), 127.31 (C-6 and C-7), 125.82 (d, ^{4}JCF = 1.9 Hz, C-5 (or) C-8), 123.53 (d, ^{2}JCF = 14.9 Hz, C-5a), 120.57 (d, ^{3}JCF = 6.2 Hz, C-8a), 108.80 (d, ^{2}JCF = 18.8 Hz, C-3), 83.57 (BOC), 24.96 (CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$, 1H-coupled): δF -118.12 (ddd, ^{3}JFH-o = 10.4 Hz, ^{4}JFH-m = 6.2 Hz, ^{5}J = 2.0 Hz). ^{19}F NMR (282 MHz, $C_2D_2Cl_4$, ^{1}H-decoupled): δF -117.5. **HRMS** (DCI-CH_4, TOF MS CI$^+$): calculated for $C_{16}H_{18}BO_2F$ $[M]^+$ requires 272.1384; found: 272.1380.

3-(4-Fluoronaphthalen-1-yl)perylene (4): 3-Bromoperylene **5** (100 mg, 0.3 mmol) and 2-(4-fluoronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **6** (110 mg, 0.4 mmol) were dissolved in a mixture of toluene (40 mL) and ethanol (2 mL) in a 100 mL Schlenk flask and flushed with argon. After stirring at 95 °C for 20 minutes, 2 M aqueous K_2CO_3 (0.5 mL) and $Pd(PPh_3)_4$ (105 mg, 0.09 mmol) were added to the solution. The reaction mixture was stirred at 100 °C for 20 hours under argon. The reaction mixture was then cooled to room temperature, washed with water and extracted with toluene. The combined organic extracts were evaporated in vacuo and 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. Finally the yellow solid was purified by column chromatography on silica gel (hexane : toluene : DCM = 10 : 0.5 : 0.5) to afford product **4** as a yellow solid (89 mg, 75%). Rf (SiO_2, hexane : toluene : DCM = 10 : 0.5 : 0.5) = 0.57. **^{1}H NMR** (400 MHz, $C_2D_2Cl_4$, 45 °C): δH 8.37 (1H, d, J = 7.6 Hz), 8.34 (1H, d, J = 8.4 Hz), 8.30-8.25 (3H, m), 7.80 (2H, d, J = 7.6 Hz), 7.65-7.52 (6H, m), 7.46 (1H, ddd, J = 8.4, 6.8, 1.2 Hz), 7.40-7.34 (2H, m), 7.30 (1H,

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dd, J = 9.2, 1.2 Hz). **^{13}C NMR** (100 MHz, $C_2D_2Cl_4$, 50 °C ^{19}F-^{1}J & ^{2}J-decoupled): δC 159.50, 138.46, 135.73, 135.38, 135.25, 135.00, 132.30 (d, ^{3}JCF = 7.9 Hz), 132.11 (d, ^{4}JCF = 1.8 Hz), 130.01, 129.84, 129.63, 129.04 (d, ^{4}JCF = 3.5 Hz), 128.54, 128.10, 127.78, 127.71, 127.50 (d, ^{3}JCF = 6.2 Hz), 127.27, 124.76, 121.72, 121.57, 121.44 (d, ^{4}JCF = 3.0 Hz), 120.93, 110.17. **^{19}F NMR** (282 MHz, $C_2D_2Cl_4$, 45 °C, ^{1}H-decoupled): δF -122.94. **HRMS** (DCI-CH_4, TOF MS CI^+): calculated for $C_{30}H_{17}F$ $[M]^+$ requires 396.1314; found: 396.1297. **UV-vis** (CH_2Cl_2) λmax/nm (ε/dm^{3}mol^{-1}cm^{-1}): 445 (8520), 418 (6640), 395 (2745).

10-Fluorobenzo[4,5]indeno[1,2,3-cd]perylene (3): To a solution of 3-(4-fluoronaphthalen-1-yl)perylene **4** (11 mg, 0.028 mmol) in dry CH_2Cl_2 (10 mL) was added 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (6.3 mg, 0.028 mmol) at 0 °C. After stirring for 5 min, trifluoromethanesulfonic acid (0.025 mL, 0.28 mmol) was added to the mixture which was further stirred for 30 minutes at 0 °C. The reaction mixture was neutralized with sat. $NaHCO_3$ aq., and then extracted with CH_2Cl_2. The combined organic phase was dried over anh. $MgSO_4$ and the solvent was removed under reduced pressure. The orange-red residue was washed with hexane and further purified by column chromatography on silica gel (hexane : toluene : DCM = 10 : 2 : 2) to afford product **3** as red solid (10 mg, 91%). **^{1}H NMR** (400 MHz, $C_2D_2Cl_4$, 100 °C, ^{19}F-coupled): δH 8.81 (1H, dm, J = 8.4 Hz), 8.57-8.45 (5H, m), 8.30 (1H, dm, J = 8.8 Hz), 8.16 (1H, dm, J = 7.6 Hz), 7.96 (2H, d, J = 8.0 Hz), 7.86 (1H, d, ^{3}JHF-o = 10.4 Hz), 7.80 (1H, t, J = 7.2 Hz), 7.72 (2H, td, J = 7.6, 2.4 Hz), 7.65 (1H, t, J = 7.6 Hz). The ^{13}C NMR could not be measured due to the poor solubility. **^{19}F NMR** (376 MHz, $C_2D_2Cl_4$, 100 °C, ^{1}H-coupled): δF -122.05 (dm, ^{3}JFH-o = 10.9 Hz). **MS** (MALDI micro, TOF LD$^+$, DCTB), m/z (rel. intensity %): 394.1 (M^+, 100%). UV-vis (CH_2Cl_2) λmax/nm (ε/dm^{3}mol^{-1}cm^{-1}): 503 (16365), 478 (14955), 447 (7870).

3-Fluoroterrylene (2): A mixture of 3-(4-fluoronaphthalen-1-yl)perylene **4** (4 mg, 0.01 mmol), anhydrous aluminium chloride (10.7 mg, 0.08 mmol) and chlorobenzene (2 mL) were placed in a dry 5 mL single-necked round-bottomed flask fitted with a condenser and a magnetic stirrer. The reaction mixture was flushed with argon and stirred at 80 °C for 4 h. The mixture was cooled to room temperature and quenched with diluted (10%) HCl (1 mL). The resulting two-phase system was filtered under suction and the precipitate from the filter and the reaction flask were rinsed thoroughly with dichloromethane and extracted in a Soxhlet apparatus with toluene (2-3 days). The extract was cooled to room temperature and the orange solution was decanted. The solid product was collected from the flask walls, rinsed with petroleum ether and dried in vacuum to afford product **2** as a purple solid (1.2 mg, 31%). The product did not contain terrylene isomer **3** according to the ^{19}F NMR and UV-vis spectra. The ^{1}H NMR and ^{13}C NMR spectra of **2** could not be measured due to the poor solubility. **^{19}F NMR** (376 MHz, $C_2D_2Cl_4$, ^{1}H-decoupled): δF -120.96. **HRMS** (DCI-CH_4, TOF MS CI^+): calculated for $C_{30}H_{15}F$ $[M]^+$ requires 394.1158; found: 394.1167. UV-vis (CH_2Cl_2) λmax/nm (ε/dm^{3}mol^{-1}cm^{-1}): 557 (28200), 517 (19920), 482 (11130).

Acknowledgements

We gratefully acknowledge the European Commission for financial support within the project PAMS "Planar Atomic and Molecular Scale devices" (contract number: 610446) and the Nanosciences group at CEMES-CNRS for valuable assistance.

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