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Sonogashira reactions for the synthesis of polarized pentacene derivatives

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Abstract: Five dissymmetrically functionalized anthracene analogues (**3a**–**e**) were synthesized from commercially available 9,10-dibromoanthracene through an efficient bromine–iodine exchange followed by two successive Sonogashira coupling reactions. The resulting TMS-anthracene analogues are interesting building blocks for the preparation of highly π-conjugated dissymmetric pentacene-based dyads, which could be used as active semiconducting layers for organic field-effect transistors (OFETs).

Key words: Sonogashira reaction, anthracene, pentacene, organic field-effect transistors

1. Introduction

During the past few years, organic field-effect transistors (OFETs) have attracted a great deal of interest due to the possibility to design flexible, large-area, low-cost, and lightweight devices.[1−7] Among all organic molecules investigated, a lot of studies have been devoted to pentacene derivatives, which combine high reproducibility of thin films and good electronic performance.[8,9] Dissymmetric pentacenes-based dyads have particularly been widely examined as promising candidates for OFETs.[10−15] Indeed, such compounds may be composed of both a triisopropylsilylethynyl part, providing sufficient solubility of the pentacene core, and an extended π-conjugated system, increasing the charge mobility and the degree of crystal formation in the film.[16] Dissymmetric TIPS-pentacenes were reported in a series of inspiring and insightful publications by Tykwinski,[10−15] the aromatic end-part being then composed of diverse acenes including phenyl, naphthyl, or anthracenyl groups. These polycyclic aromatic hydrocarbons were attached to the pentacene through an ethynyl linker to provide extended conjugation.[11] Pentacene derivatives have also found potential applications in photoredox catalysis as pure organic photocatalysts that can be an alternative to expensive iridium complexes.[17]

In this work, we report on the practical synthesis of dissymmetric TMS-anthracene building blocks **3** for the preparation of new polarized pentacene derivatives **5** (Scheme 1). As indicated in the synthetic blueprint, the first logical building block is commercially available 9,10-dibromoanthracene that needs to be first and selectively alkynylated using a metal-catalyzed cross-coupling reaction with different phenylacetylenes substituted with electron-withdrawing or electron-donating substituent in the para position. To achieve this selectivity, it was

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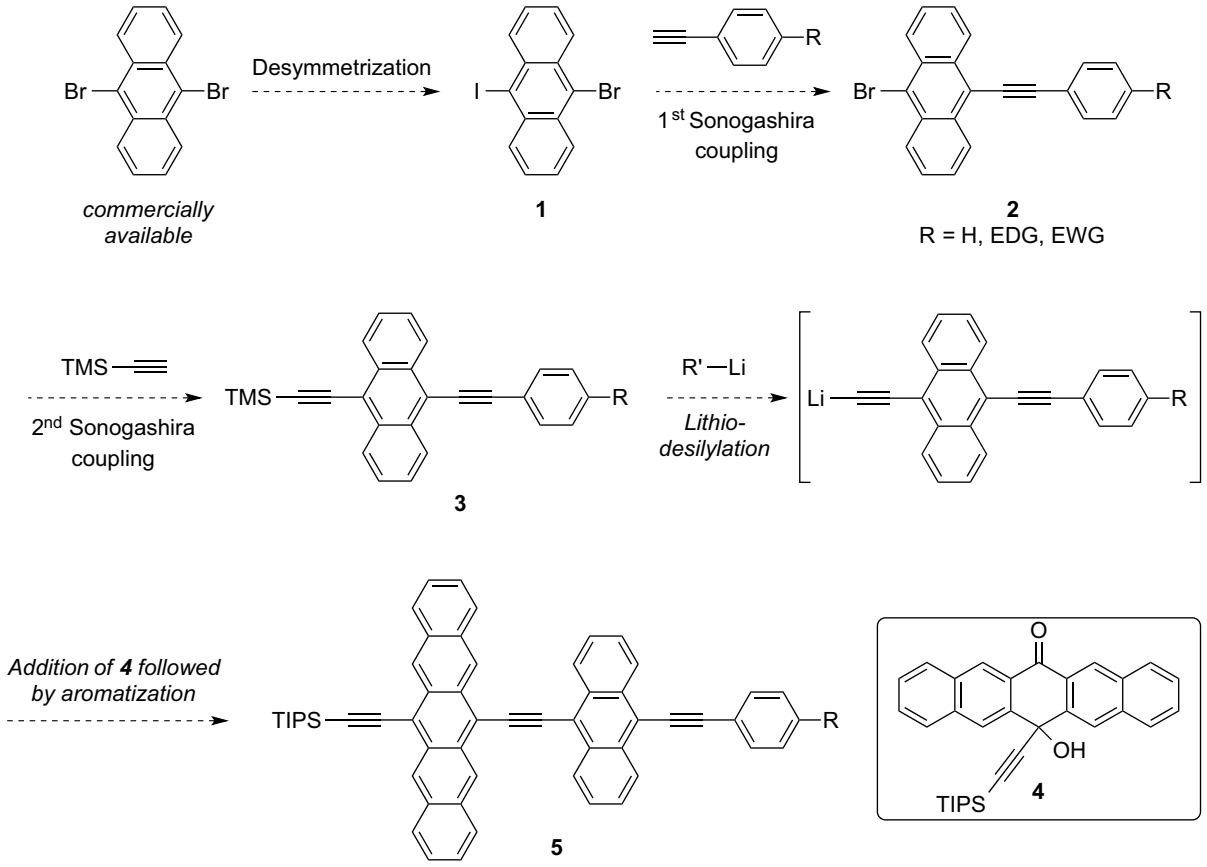
envisioned to transform 9,10-dibromoanthracene into the corresponding mono-iodinated derivative **1**. Then a second metal-catalyzed cross-coupling reaction could be applied, leading to a series of anthracenes **3**. The latter could then undergo an in situ lithio-desilylation reaction, offering a transient lithium acetylide that could add onto the known aromatic ketone **4**.[10–15] Completion of the synthesis of the pentacene dyads **5** finally calls for a classical aromatization reaction.[10–15]



Scheme 1. Synthetic blueprint for the preparation of the pentacene dyads **5**.

2. Results and discussion

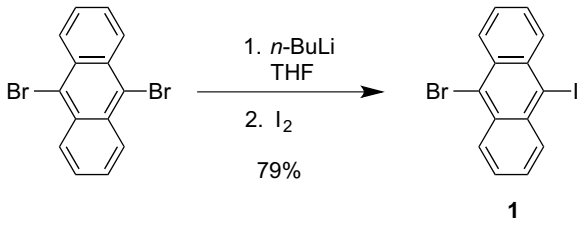
2.1. Desymmetrization of 9,10-dibromoanthracene

As shown in Scheme 2, commercially available 9,10-dibromoanthracene can be converted into 9-bromo-10-iodo-anthracene **1** through a monoiodination reaction.[18] Indeed, upon addition of 1 equivalent of n-butyllithium to a THF solution of 9,10-dibromoanthracene, a very clean mono bromine-lithium exchange occurred. Addition of iodine then led to the formation of the expected compound **1** in 79% isolated yield. This key transformation is scalable and was routinely done on a decagram scale, allowing us to easily and selectively functionalize the anthracenyl motif through two successive Sonogashira coupling reactions.

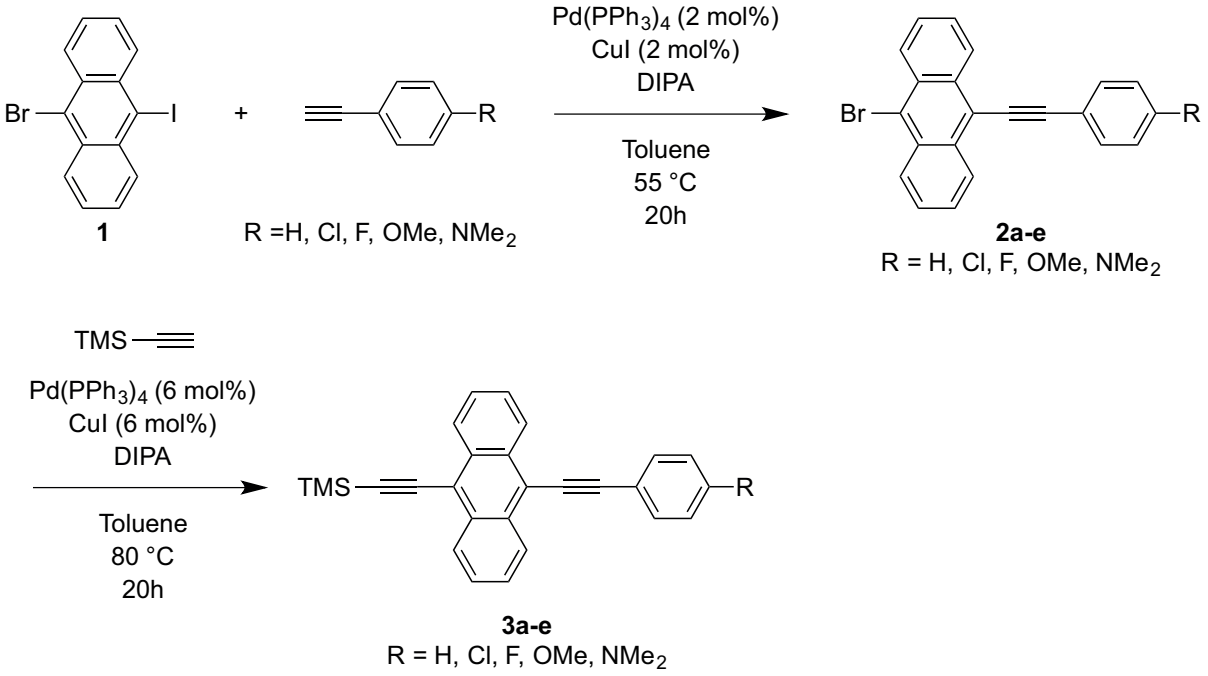
2.2. Selective Sonogashira coupling reactions

A first Sonogashira coupling reaction was carried out between 9-bromo-10-iodo-anthracene **1** and a series of 5 para-substituted phenylacetylenes using 2 mol% of $Pd(PPh_3)_4$ and a copper(I) co-catalyst (2 mol%) in toluene

at 55 °C (Scheme 3).[18] The chemoselectivity of the cross-coupling was excellent as none of the 9,10-dialkynylated anthracene was observed by ^{1}H NMR analysis of the crude material. As shown in the Table, this first coupling reaction was very efficient and provided the 5 expected para-substituted bromoanthracenes **2** with excellent yields either from phenylacetylene itself (**2a**, 74%, entry 1), or electron-deficient (**2b**, **2c**, 67%–94%, entries 2 and 3) or electron-rich (**2d**, **2e**, 72%–75%, entries 4 and 5) phenylacetylene derivatives.



Scheme 2. Halogen swap of 9,10-dibromoanthracene according to Swager et al.



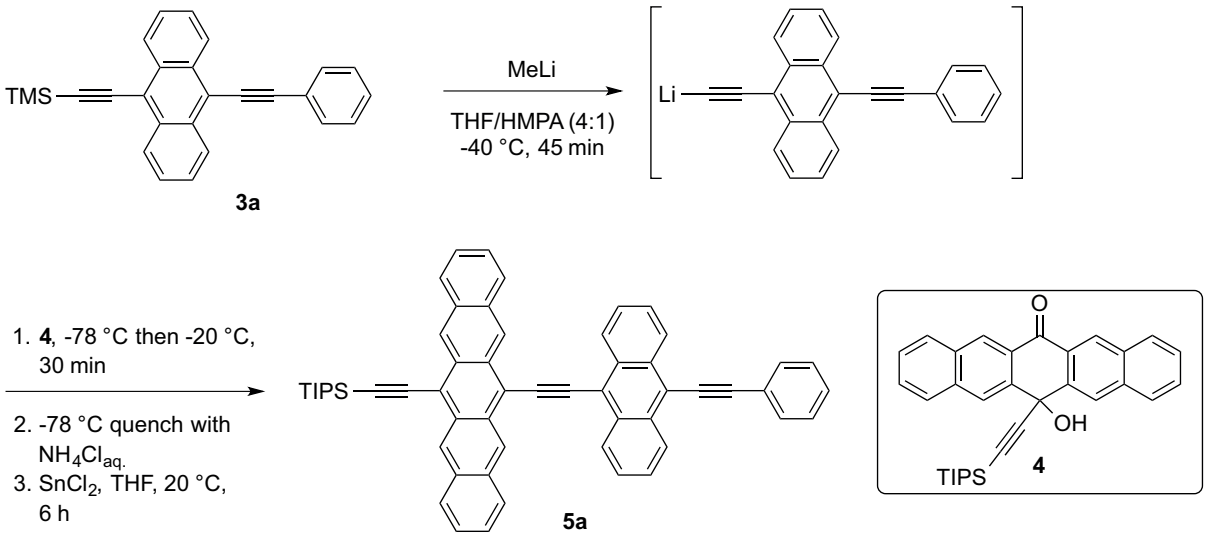
Scheme 3. Successive Sonogashira coupling reactions.

Table. Two successive Sonogashira couplings on 9-bromo-10-iodo-anthracene **1**.

Entry	R	1st coupling (Yield)[a]	2nd coupling (Yield)[b]
1	H	**2a** (74%)	**3a** (66%)
2	4-Cl	**2b** (94%)	**3b** (65%)
3	4-F	**2c** (67%)	**3c** (90%)
4	4-OMe	**2d** (75%)	**3d** (98%)
5	4-NMe_2	**2e** (72%)	**3e** (93%)

Reaction conditions: [a] **1** (1 equiv.), alkyne (1 equiv.), $Pd(PPh_3)_4$ (2%), CuI (2%) in toluene/diisopropylamine, 55 °C, 20 h. Isolated yields. [b] **2** (1 equiv.), TMS-acetylene (1 equiv.), $Pd(PPh_3)_4$ (6%), CuI (6%) in toluene/diisopropylamine, 80 °C, 20 h. Isolated yields.

The next step of the synthesis of the 5 building blocks **3** involved a second Sonogashira reaction between the bromo-anthracene derivatives **2a**–**e** and TMS-acetylene (Scheme 3).[18] For this coupling, an excess of TMS-acetylene (3 equivalents) was employed and the reaction was carried out at 80 °C in toluene using a threefold amount of catalyst (6 mol%) and co-catalyst (6 mol%) compared to the first Sonogashira cross-coupling. As shown in the Table, this second coupling reaction led to the formation of the 5 expected asymmetric anthracenes **3a**–**e** with good to excellent yields (65%–98%).



Scheme 4. Preliminary results for the synthesis of **5a** from **3a**.

3. Application to the synthesis of polarized pentacene derivatives

Having in hand these stable 9,10-dialkynylated anthracenes **3a**–**e**, we briefly explored the reactivity of **3a** as a representative compound in the synthesis of extended π-conjugated pentacene-based dyads **5**. It was quickly discovered that the lithio-desilylation of **3a** using methyllithium was not a trivial task, leading either to the unchanged starting material or to complete degradation. After extensive experimentation, it was found that the optimal conditions for this lithio-desilylation required running the reaction at –40 °C for 45 min, in a mixture of THF and HMPA (4:1). Addition of this lithium acetylide to the known ketone **4**[10–15] at –78 °C followed by warming the reaction mixture at –20 °C for 20 min led to the desired product alongside numerous unidentified side products, even after a –78 °C quench with aqueous ammonium chloride. Immediate aromatization of the crude mixture using tin(II) chloride in degassed THF led to an intricate mixture from which several very apolar and UV active products could be isolated as minor components ($<$10%) by flash chromatography. Although the targeted pentacene derivative **5a** was present in this green powder (as demonstrated by extensive 2D NMR experiments), it was contaminated by inseparable isomers that seem to be partially reduced forms of one of the alkynes embedded in **5a**.

Further optimization of these last two steps is obviously required in order to provide a more general synthetic access to this class of electronically diverse trialkynyl-pentacenes **5**.

3.1. Conclusions

We have reported an efficient synthesis of electronically diverse 9,10-dialkynylated anthracenes **3a**–**e** thanks to 2 successive Sonogashira cross-coupling reactions. This sequence is practical and can be performed routinely on

decagrams. The reactivity of these building blocks as competent partners for the synthesis of pentacene-based dyads has been briefly explored and demonstrated that access to pentacenes such as **5** is not a trivial task. Optimization of the last 2 steps of the sequence is currently under study and will be communicated in due course.

4. Experimental

4.1. General remarks

NMR spectra were recorded on Bruker AV 300 or AV 400 spectrometer at 300 MHz or 400 MHz for ^{1}H NMR, at 75 or 100 MHz for ^{13}C NMR, and at 376 MHz for ^{19}F NMR. The spectra were calibrated using undeuterated solvent as internal reference, unless otherwise indicated. Coupling constants (J) were reported in Hertz. Melting points were recorded on a Büchi 510 melting point apparatus. All reactions were carried out in oven-dried glassware under a nitrogen atmosphere using dry solvents, unless otherwise noted. Tetrahydrofuran (THF) was distilled under nitrogen from sodium-benzophenone, and toluene and dichloromethane were distilled over CaH_2. Reagents were purchased from Aldrich, Acros, or Alfa Aesar. Yields refer to chromatographically homogeneous materials, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on Merck TLC silica gel 60 F254 glass-coated plates, using UV light or potassium permanganate as visualizing agents. All separations were performed by flash chromatography on Merck silica gel 60 (40-63 μm), on a Combiflash Companion from Teledyne Isco.

4.2. Synthesis of 9-bromo-10-iodo-anthracene (1)[18]

A round-bottom flask, equipped with a magnetic stirring bar and dry nitrogen inlet, was successively charged with 9,10-dibromoanthracene (10.0 g, 29.9 mmol) and THF (200 mL). n-BuLi (2 M in hexane, 16 mL, 32.3 mmol) was then added at –78 °C to the solution and the mixture was stirred at –78 °C for 3 h. At –78 °C, a solution of iodine (9.9 g, 38.9 mmol) in THF (50 mL) was then slowly added on the anion and the mixture was stirred at room temperature for 16 h. The solvent was evaporated under reduced pressure (to 10% of the initial volume) and a saturated aqueous $Na_2S_2O_3$ solution was added thus triggering the formation of a yellow precipitate. The solid was recovered by filtration and washed with a saturated aqueous solution of $Na_2S_2O_3$, water, and cold ethanol. Compound **1** was obtained as a yellow powder (9.0 g, 79% yield).

Mp: 221 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.58–8.55 (m, 4H), 7.60–7.63 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 134.6, 134.4, 134.2, 128.7, 128.1, 127.6, 125.7, 106.6.

This product has been previously described and spectral data are in agreement with those reported in the literature.[18]

4.3. General procedure for the first Sonogashira coupling

A round-bottom flask, equipped with a magnetic stirring bar and a dry nitrogen inlet, was successively charged with **1** (500 mg, 1.31 mmol), toluene (5.6 mL), diisopropylamine (2.4 ml), and the corresponding alkyne (1 equiv.). Copper(I) iodide (5 mg, 0.026 mmol) and palladium(0)tetrakis(triphenylphosphine) (30 mg, 0.026 mmol) were added to the solution and the mixture was stirred at 55 °C for 20 h. Dichloromethane was added at room temperature to dissolve the precipitate and the resulting clear solution was successively washed with water and brine. The organic layer was dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. The crude material was purified by column chromatography on silica gel to provide the desired product **2**.

4.3.1. 9-Bromo-10-(2-phenylethynyl)anthracene (2a)

Compound **2a** was obtained following the general procedure from phenylacetylene (143 μL, 1.31 mmol). The crude material was purified by chromatography on silica gel (cyclohexane) to afford **2a** as a yellow powder (345 mg, 74%).

Mp: 171 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.68–8.73 (m, 2H), 8.56–8.61 (m, 2H), 7.76–7.80 (m, 2H), 7.60–7.69 (m, 4H), 7.42–7.50 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 133.1, 131.8, 130.4, 128.9, 127.7, 128.4, 127.6, 127.4, 126.9, 124.3, 123.5, 118.4, 101.9, 86.1.

This product has been previously described and spectral data are in agreement with those reported in the literature.[18]

4.3.2. 9-Bromo-10-[2-(4-chlorophenyl)ethynyl]anthracene (2b)

Compound **2b** was obtained following the general procedure from 4-chlorophenylacetylene (178 mg, 1.31 mmol). The crude material was purified by chromatography on silica gel (cyclohexane) to afford **2b** as a yellow powder (485 mg, 94%).

Mp: 187 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.65–8.69 (m, 2H), 8.56–8.60 (m, 2H), 7.73–7.78 (m, 2H), 7.61–7.68 (m, 4H), 7.13–7.19 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 134.9, 133.1, 132.9, 130.4, 129.1, 128.4, 127.6, 127.2, 127.1, 124.7, 122.0, 117.9, 100.7, 87.1.

4.3.3. 9-Bromo-10-[2-(4-fluorophenyl)ethynyl]anthracene (2c)

Compound **2c** was obtained following the general procedure from 1-ethynyl-4-fluorobenzene (150 μL, 1.31 mmol). The crude material was purified by chromatography on silica gel (cyclohexane) to afford **2c** as a yellow powder (326 mg, 67%).

Mp: 204 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.65–8.69 (m, 2H), 8.56–8.60 (m, 2H), 7.76 (dd, J_{H-H} = 8.6 Hz, J_{H-F} = 3.5 Hz, 2H), 7.61–7.68 (m, 4H), 7.16 (t, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 163.0 (d, J_{C-F} = 249 Hz), 133.7 (d, J_{C-F} = 8 Hz), 133.1, 130.4, 128.4, 127.6, 127.3, 127.0, 124.4, 119.6, 116.1 (d, J_{C-F} = 21 Hz), 105.8, 100.8, 85.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ (ppm) –109.2 (tt, J= 8.6 Hz, J= 5.7 Hz). HRMS-ESI m/z calcd for $C_{22}H_{12}BrF$ $[M+H]^+$ 375.0179, found 375.0178).

4.3.4. 9-Bromo-10-[2-(4-methoxyphenyl)ethynyl]anthracene (2d)

Compound **2d** was obtained following the general procedure from 4-(methoxyphenyl)acetylene (169 μL, 1.31 mmol). The crude material was purified by chromatography on silica gel (cyclohexane) to afford **2d** as a yellow powder (378 mg, 75%).

Mp: 132 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.65–8.71 (m, 2H), 8.53–8.58 (m, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.57–7.66 (m, 4H), 6.97 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 160.2, 133.3, 133.0, 130.4, 128.3, 127.5, 127.5, 126.8, 123.8, 118.8, 115.6, 114.4, 102.2, 84.9, 55.5.

This product has been previously described and spectral data are in agreement with those reported in the literature.[19]

4.3.5. 4-[2-(10-Bromoanthracen-9-yl)ethynyl]-*N,N*-dimethylaniline (2e)

Compound **2e** was obtained following the general procedure from 4-ethynyl-*N*,*N*-dimethylaniline (190 mg, 1.31 mmol). The crude material was purified by chromatography on silica gel (cyclohexane) to afford **2e** as an orange powder (374 mg, 72%).

Mp: 233 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.70–8.75 (m, 2H), 8.53–8.58 (m, 2H), 7.65 (d, J = 9 Hz, 2H) 7.60–7.64 (m, 4H), 6.75 (d, J = 9 Hz, 2H), 3.05 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 150.9, 133.3, 133.1, 130.8, 128.5, 128.0, 127.8, 126.8, 123.2, 120.0, 112.4 (2C), 104.1, 84.6, 40.7.

This product has been previously described and spectral data are in agreement with those reported in the literature.[20]

4.4. Procedures for the second Sonogashira coupling

4.4.1. Trimethyl({2-[10-(2-phenylethynyl)anthracen-9-yl]ethynyl})silane (3a)

A sealed tube, equipped with a magnetic stirring bar, was successively charged with **2a** (270 mg, 0.76 mmol), toluene (3.5 mL), diisopropylamine (1.6 mL), and trimethylsilylacetylene (325 μL, 2.27 mmol). Copper(I) iodide (9 mg, 0.045 mmol) and palladium(0)tetrakis(triphenylphosphine) (52 mg, 0.045 mmol) were added to the solution and the mixture was stirred at 80 °C for 20 h. Dichloromethane was added at room temperature to dissolve the precipitate and the resulting clear solution was filtered through a pad of silica gel. The solvent was evaporated under reduced pressure and the crude material was purified by column chromatography on silica gel (cyclohexane) to afford **3a** as a yellow powder (186 mg, 66% yield).

Mp: 129 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.65–8.70 (m, 2H), 8.58–8.63 (m, 2H), 7.76–7.79 (m, 2H), 7.60–7.66 (m, 4H), 7.42–7.50 (m, 3H), 0.44 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 132.5, 132.1, 131.8, 128.8, 128.7, 127.4, 127.3, 127.0, 126.9, 123.5, 118.8, 118.4, 108.2, 102.6, 101.8, 86.6, 0.4.

This product has been previously described and spectral data are in agreement with those reported in the literature.[18]

4.4.2. (2-{10-[2-(4-Chlorophenyl)ethynyl]anthracen-9-yl} ethynyl)trimethylsilane (3b)

A sealed tube, equipped with a magnetic stirring bar, was successively charged with **2b** (420 mg, 1.07 mmol), toluene (5.3 mL), diisopropylamine (2.3 mL), and trimethylsilylacetylene (458 μL, 3.22 mmol). Copper(I) iodide (12 mg, 0.064 mmol) and palladium(0)tetrakis(triphenylphosphine) (74 mg, 0.064 mmol) were added to the solution and the mixture was stirred at 80 °C for 20 h. Dichloromethane was added at room temperature to dissolve the precipitate and the resulting clear solution was passed through a pad of silica gel. The solvent was evaporated under reduced pressure and the crude material was purified by column chromatography on silica gel (cyclohexane) to afford **3b** as a yellow powder (283 mg, 65% yield).

Mp: 173 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.57–8.66 (m, 4H), 7.69 (d, J = 8.6 Hz, 2H), 7.60–7.66 (m, 4H), 7.43 (d, J = 8.6 Hz, 2H), 0.44 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 134.9, 133.0, 132.5, 132.1, 129.1, 127.5, 127.2, 127.1, 127.0, 122.0, 118.7, 118.3, 108.5, 101.6, 101.3, 87.5, 0.3. HRMS-ESI m/z calcd for $C_{27}H_{21}ClSi$ $[M+H]^+$ 409.1174, found 409.1175).

4.4.3. (2-{10-[2-(4-Fluorophenyl)ethynyl]anthracen-9-yl} ethynyl)trimethylsilane (3c)

A sealed tube, equipped with a magnetic stirring bar, was successively charged with **2c** (291 mg, 0.78 mmol), toluene (3.9 mL), diisopropylamine (1.7 mL), and trimethylsilylacetylene (331 μL, 2.33 mmol). Copper(I) iodide (9 mg, 0.046 mmol) and palladium(0)tetrakis(triphenylphosphine) (54 mg, 0.046 mmol) were added to the solution and the mixture was stirred at 80 °C for 20 h. Dichloromethane was added at room temperature to dissolve the precipitate and the resulting clear solution was passed through a pad of silica gel. The solvent was evaporated under reduced pressure and the crude material was purified by column chromatography on silica gel (cyclohexane) to afford **3c** as a yellow powder (275 mg, 90% yield).

Mp: 154 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.54–8.59 (m, 4H), 7.69 (dd, J_{H-H} = 8.8 Hz, J_{H-F} = 3.3 Hz, 2H), 7.55–7.59 (m, 4H), 7.10 (t, J = 8.8 Hz, 2H), 0.42 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 163.0 (d, J_{C-F} = 250 Hz), 133.7 (d, J_{C-F} = 8 Hz), 132.5, 132.1, 127.5, 127.2, 127.1, 127.0, 119.6 (d, J_{C-F} = 4 Hz), 118.6, 118.5, 116.1 (d, J_{C-F} = 22 Hz), 108.4, 101.7, 101.4, 86.3, 0.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ (ppm) –105.6 (tt, J = 8.6 Hz, J = 5.7 Hz). HRMS-ESI m/z calcd for $C_{27}H_{21}FSi$ $[2M+H]^+$ 785.2866, found 785.2865).

4.4.4. (2-{10-[2-(4-Methoxyphenyl)ethynyl]anthracen-9-yl} ethynyl)trimethylsilane (3d)

A sealed tube, equipped with a magnetic stirring bar, was successively charged with **2d** (354 mg, 0.91 mmol), toluene (4.6 mL), diisopropylamine (2 mL), and trimethylsilylacetylene (390 μL, 2.74 mmol). Copper(I) iodide (11 mg, 0.055 mmol) and palladium(0)tetrakis(triphenylphosphine) (63 mg, 0.055 mmol) were added to the solution and the mixture was stirred at 80 °C for 20 h. Dichloromethane was added at room temperature to dissolve the precipitate and the resulting clear solution was passed through a pad of silica gel. The solvent was evaporated under reduced pressure and the crude material was purified by column chromatography on silica gel (cyclohexane/dichloromethane 9:1) to afford **3d** as an orange powder (361 mg, 98% yield).

Mp: 150 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.64–8.70 (m, 2H), 8.56–8.62 (m, 2H), 7.71 (d, J = 8.8 Hz, 2H), 7.59–7.65 (m, 4H), 6.98 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 0.43 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 160.2, 133.3, 132.6, 132.0, 127.4, 127.4, 127.0, 126.8, 119.3, 117.9, 115.7, 114.4, 108.0, 102.8, 101.8, 85.4, 55.3, 0.4. HRMS-ESI m/z calcd for $C_{28}H_{24}OSi$ $[M+H]^+$ 405.1669, found 405.1671).

4.4.5. *N,N*-Dimethyl-4-(2-{10-[2-(trimethylsilyl)ethynyl]anthracen-9-yl} ethynyl)aniline (3e)

A sealed tube, equipped with a magnetic stirring bar, was successively charged with **2e** (328 mg, 0.82 mmol), toluene (2.1 mL), diisopropylamine (1.8 mL), and trimethylsilylacetylene (350 μL, 2.46 mmol). Copper(I) iodide (9 mg, 0.049 mmol) and palladium(0)tetrakis(triphenylphosphine) (57 mg, 0.049 mmol) were added to the solution and the mixture was stirred at 80 °C for 20 h. Dichloromethane was added at room temperature to dissolve the precipitate and the resulting clear solution was passed through a pad of silica gel. The solvent was evaporated under reduced pressure and the crude material was purified by column chromatography on silica gel (cyclohexane/dichloromethane: 9/1) to afford **3e** as a red powder (317 mg, 93% yield).

Mp: 208 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.65–8.70 (m, 2H), 8.53–8.59 (m, 2H), 7.62 (d, J = 8.9 Hz, 2H), 7.55–7.62 (m, 4H), 6.73 (d, J = 8.9 Hz, 2H), 3.03 (s, 6H), 0.41 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 150.6, 133.0, 132.6, 131.7, 127.6, 127.3, 127.0, 126.5, 120.2, 117.0, 112.0, 110.2, 107.6, 104.6, 102.0, 84.9, 40.4, 0.4. HRMS-ESI m/z calcd for $C_{29}H_{27}NSi$ $[M+H]^+$ 418.1986, found 418.1987).

4.5. Synthesis of a pentacene derivative [2-(13-{2-[10-(2-Phenylethynyl)anthracen-9-yl]ethynyl} pentacen-6-yl)ethynyl]-tris(propan-2-yl)silane (5)

In a round-bottom flask equipped with a magnetic stirring bar, a dry nitrogen inlet, and a septum, MeLi (1.28 M) (1.41 mL, 1.8 mmol) was added at –40 °C to a solution of **3a** (704 mg, 1.88 mmol) in THF (6 mL) and HMPA (1.5 mL). The reaction mixture was stirred at –40 °C for 45 min and the resulting anion solution was added at –78 °C to a solution of **4** (184 mg, 0.38 mmol) in THF (2 mL). The mixture was then stirred for 30 min at –20 °C and quenched with NH_4Cl sat. at –78 °C. After extraction with dichloromethane, the organic phase was dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure. The crude material was then dissolved in degassed THF (4 mL) and a solution of tin(II) chloride dihydrate (270 mg, 1.2 mmol) in degassed THF (4 mL) was added. The reaction mixture was stirred at room temperature for 6 h. After addition of water, the green/blue mixture was extracted with dichloromethane and the organic layer was dried over $MgSO_4$. After filtration, the solvents were evaporated under reduced pressure. From an intricate crude material, several very apolar and UV active products could be isolated as minor components (22 mg, $<10\%$) by flash chromatography (cyclohexane/dichloromethane: 8/2). Although the targeted pentacene derivative **5a** was present in this green powder, it was contaminated by inseparable isomers that seem to be partially reduced forms of one of the alkynes embedded in **5a** as demonstrated by HRMS (HRMS-APCI m/z calcd for $C_{57}H_{48}Si$ $[M+H]^+$ 761.3604, found 761.3579). Extensive 2D NMR experiments demonstrated that **5a** was present as a mixture with (at least) three other compounds. Data for **5a**: ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 9.41 (s, 2H), 9.28 (s, 2H), 8.85 (d, $J = 8.0$ Hz, 2H), 8.80 (d, $J = 8.8$ Hz, 2H), 8.00 (d, $J = 8.8$ Hz, 2H), 7.93 (d, $J = 8.4$ Hz, 2H), 7.73–7.22 (13H), 1.43 (s, 3H), 1.41 (s, 18H).

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