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Exploiting the versatility of organometallic cross-coupling reactions for entry into extended aromatic systems

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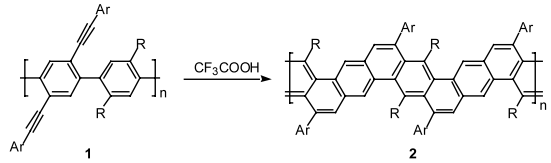
Abstract

Using a variety of Pd-catalyzed cross-coupling techniques, we have prepared several pendant arene derivatives (**5**, **6**, **12**, **15**). From these materials, we have expanded upon earlier work and developed new electrophilic cyclization strategies. By employing sufficiently strong electrophile sources, we may efficiently effect double annulations to afford polycyclic aromatics **10**, **11**, **13** and **16**. This chemistry allows for the participation of both heteroaromatic and heteroatomic moieties thus providing an electronically diverse array of extended aromatic systems. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polycyclic aromatics; Electrophilic; Dehydrogenation; Cyclization; Pyrylium

1. Introduction

Fully aromatic ladder polymers represent extended electronic structures of high stability for potential utilization in a variety of electronic applications. Schlüter first elaborated the synthesis of such fully aromatized ribbons by dehydrogenation of a polymeric Diels–Alder adduct [1]. In 1993, Chmil and Scherf disclosed a ketone condensation route to phenacene-type graphite ribbons; [2] shortly thereafter, our group reported a structurally similar polymer by way of an acid-induced electrophilic cyclization of the alkyne appended polyphenylene **1** to provide the aromatized ribbon **2** [3]. Very recently, Bard utilized the inherent stability of such fused ladder polymers in the design of robust electrochromic materials [4]. Common to all these approaches, the verification of the 'polymer-analogous' chemistry requires study of appropriate molecular models that allow for more rigorous structural characterization. With respect to **1** and **2**, our group studied smaller terphenyl and quinquephenyl systems with appropriately substituted alkoxy donors as models for **1**. We found conditions to effect high yielding, often quantitative, cyclization to the corresponding benzo- and phenanthro-fused anthracenes [5]. The potential for utilizing such discrete polycyclic aromatics as higher mobility FET materials has spurned the development of synthetic methods for new and otherwise challenging polycyclic scaffolds. Notably, Müllen has elegantly applied a cyclodehydrogenation scheme to the synthesis of 'superacene' graphite sheets, [6] while Anthony has recently developed a strategy to access higher acenes and rylenes through sequential Bergman cyclizations [7]. In this study, we report an extension of our methodology [5] where we now utilize stronger amine donors as cyclization directing groups. Key to the study of this cyclization chemistry, the model compounds presented herein shall attest to the power and specificity of organometallic cross-coupling methodologies towards constructing extended, differentially functionalized polyaromatic systems.



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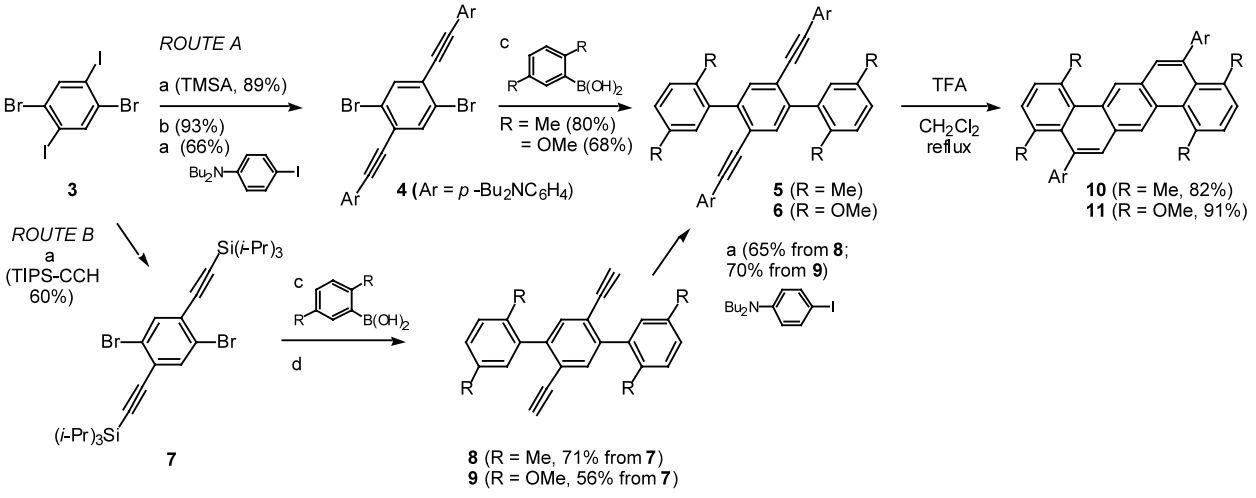
2. Results and discussion

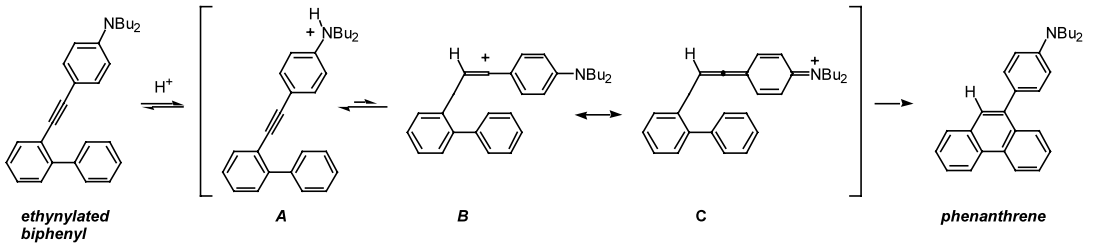
We developed two different synthetic routes to obtain the desired amine-donor terphenyl models **5** and **6**, both of which rely on Sonogashira and Suzuki protocols [8,9]. Scheme 1 depicts both of these synthetic routes, as well as the final cyclization step. The first route (Route A) installs the dibutylamine donor early and allows entry to polymerizable substrates, in analogy with our previous studies [5a]. Starting from the halide **3**, [10] Sonogashira cross-coupling of TMS acetylene installed two alkynes chemoselectively at the iodo positions. Subsequent protiodesilylation and Sonogashira cross coupling of *N*,*N*-dibutyliodoaniline [11] provided the dibromide **4**, again taking advantage of the differential reactivity between bromo- and iodo-substituted arenes. From **4**, Suzuki cross-coupling of dimethyl- or dimethoxy phenylboronic acid provided the terphenyls **5** and **6**, respectively, in high yields. The second route (Route B) initially constructs a desired terphenyl, allowing for the addition of a donor directing functionality at a later stage. Analogous to the preparation of **4**, chemoselective Sonogashira cross-coupling of TIPS acetylene provided the dibromide **7**. The robustness of the TIPS protecting groups allowed for clean Suzuki cross-coupling with dimethyl- or dimethoxy phenylboronic acid without apparent desilylation. Fluoride-promoted deprotection of the TIPS moieties then provided **8**–**9** in modest overall yields from **7**. From these terminal alkynes, Sonogashira cross-coupling with *N*,*N*-dibutyliodoaniline again provided **5**–**6** in high yield. Over both four-step procedures, Route A provided higher overall yields from the halide parent **3**:**5** (Route A, 44%; Route B, 30%), **6** (Route A, 37%; Route B, 25%).

With these precursor models readily available, we could assess the competency of the stronger amine donors in the electrophilic cyclization. In line with our previous results, the starting terphenyls reacted immediately upon addition of trifluoroacetic acid; however, a basic work-up only regenerated the starting materials. We postulated that the enhanced basicity of the amine-substituted terphenyls allowed for mere protonation of the amino moiety rather than an electrophilic attack and cyclization on the acetylene. To support this claim, we performed NMR experiments with **5** at room temperature that indicated no new aryl or olefinic protons upon TFA addition. These measurements revealed that the alkynes persisted under such acidic conditions (^{13}C resonances at 92.1 and 91.6 ppm) while the *N*-butyl amine chains exhibited an α-methylene resonance at 59.9 ppm, significantly downfield from the value of 50.9 ppm exhibited by **5**. The absence of any new products resulting from rehybridization of the alkynes of **5** confirms that the protonated donor ***A*** was the most favorable species under the cyclization conditions at room temperature (depicted in Scheme 2). Subsequently, we found that the cyclization proceeded smoothly under refluxing conditions to provide the cyclized dibenz[*a*,*h*]-anthracene systems **10**–**11** in excellent yields. Consistent with earlier findings, the enhanced degree of aromaticity in the cyclized materials provided downfield shifts in the proton NMR for the dibenzanthracene ring protons. Furthermore, the extension of the π-conjugated pathway via rigidification provided red-shifted (ca. 28 nm between **6** and **11**), weakly-allowed transitions often observed in similar polycyclic aromatic systems.

One of the limitations of our earlier methodology arose from the fact that ethynyl cyclization onto a thienyl moiety (as opposed to an arene) often provided



Scheme 1. Reagents and conditions: (a) Sonogashira: $(Ph_3P)_2PdCl_2$, CuI, PhMe, DIPA; (b) deprotection: K_2CO_3, THF, MeOH, rt; (c) Suzuki: $Pd(PPh_3)_4$, Na_2CO_3, PhMe, EtOH, H_2O, reflux; (d) deprotection: TBA, THF, H_2O, rt.



Scheme 2.

rearrangement products, and unsubstituted thienyls did not undergo cyclization at all [5a]. To test if the amine donor would allow for more efficient entry into thiophene-fused anthracenes, we prepared bisthienyl derivative **12** through Stille cross coupling between **4** and tributyltin thiophene (Scheme 3) [12]. Initial cyclization attempts with TFA provided no reaction, even under refluxing conditions. Fortunately, when we employed the much stronger triflic acid as the electrophilic proton source, we obtained the cyclized anthracene **13** in moderate yield. We envisioned that an unsubstituted thiophene-based monomer such as **13** would allow for electrodeposition of highly stable, electroactive polymer films; however, the readily oxidized aryl amines pendant to the aromatic scaffold complicated efforts to characterize the electrochemical behavior of **13**. As a result, anodic oxidation led to completely irreversible activity but no apparent polymer film deposition. We have observed that other thiophene-based polycyclic aromatics of comparable size to **13** afford highly stable, multiply charged species upon electrochemical oxidation and that polymers incorporating such units exhibit electrochromicity and robust environmental stability [13].

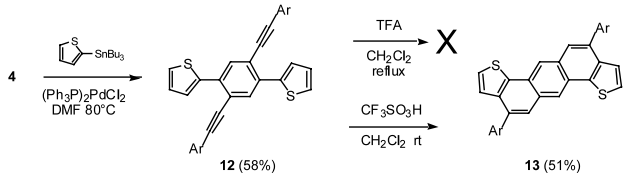
We found that a similar methodology applied to hetero*atoms* in addition to arenes and heterocycles, where we could employ a carbonyl oxygen in place of an arene to trap the electrophilic site of intermediate *B* (Scheme 2) [14]. Our group has studied a number of amide-containing poly(*p*-phenyleneethynylene)s (PPEs), [15] and we saw them as attractive candidates for post-polymerization modification involving a pyrylium intermediate. From the halide **14**, [15a] Sonogashira cross-coupling afforded **15**, a model for the amide PPE system (Scheme 4). Much like the situation for **12**, subjection of **15** to the TFA cyclization conditions failed to provide any isolable, cyclized materials. The use of a stronger acid (HBF_4) allowed the deep burgundy-colored cyclized salt **16** to precipitate upon addition of ethyl ether to the reaction solution. Our studies on smaller isobenzopyrylium compounds demonstrated that this cyclization reaction could couple with additional chemical ring transformations in one synthetic step, thus providing isoquinoline ring systems from readily available aryl alkynes [14,16]. In line with our findings for dibenz[*a*,*h*]anthracenes (vide supra), these salts exhibit lower energy charge-transfer optical transitions upon cyclization ($\lambda_{max} = 539$ nm in $CHCl_3$ for **16**). Our current investigations seek to utilize this chemistry towards the construction of larger electron deficient aromatics.

3. Concluding remarks

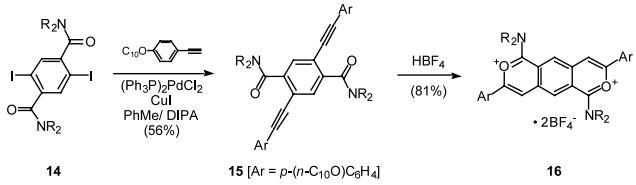
In closing, we have described extensions to an acid-induced electrophilic cyclization of pendant alkynes to provide electronically diverse families of polycyclic aromatics. By harnessing the versatility of the organometallic cross-coupling reaction, we may readily construct a variety of substrates through which we may design and examine new reaction manifolds. The array of polyaromatics available on behalf of this generality stands to provide exciting new materials for current electronics and photonics applications.

4. Experimental

General: all air and water sensitive synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques. All chemicals were of reagent grade and used as received: anhydrous diiso-



Scheme 3.



Scheme 4.

propylamine (DIPA), methylene chloride and tetrahydrofuran (THF) were purchased from Aldrich and used without further purification. The following abbreviations have been used: *N*,*N*-dibutyl-4-iodoaniline (BuNI); 2,5-dimethylphenyl boronic acid ($Me_2B(OH)_2$); 2,5-dimethoxyphenyl boronic acid ($(MeO)_2B(OH)_2$). Column chromatography was performed using Baker 40 μm silica gel. All organic extracts were dried over $MgSO_4$ and filtered prior to removal. NMR spectra were obtained on a Bruker AC-250, Varian Mercury-300 or Varian Inova-500 spectrometers, and all chemical shifts are referenced to $CHCl_3$ (7.26 ppm for ^1H, 77.23 ppm for ^{13}C) and TMS or $CHDCl_2$ (5.32 ppm). High resolution mass spectra were obtained at the MIT Department of Chemistry Instrumentation Facility (DCIF) on a Finnigan MAT 8200 using a peak matching protocol to determine the mass and error range of the molecular ion; FAB spectra were obtained using a 3-nitrobenzyl alcohol matrix. UV–vis measurements were obtained on a Hewlett–Packard 8452A diode array spectrophotometer. Fluorescence measurements were recorded on a SPEX Fluorolog-τ2 fluorimeter (model FL112, 450 W Xe lamp). Elemental analyses were obtained at Desert Analytics (Tucson, AZ). Melting points are uncorrected.

4.1. 2,5-Bis(trimethylsilylethynyl)-1,4-dibromobenzene (en route to **4**)

Under an argon atmosphere, 125 ml THF was added to **3** (6.00 g, 12.3 mmol), $(Ph_3P)_2PdCl_2$ (860.3 mg, 1.266 mmol) and CuI (745.4 mg, 3.91 mmol). After the addition of 15 ml DIPA, the solution was stirred at room temperature (r.t.) for 15 min followed by the dropwise addition of TMS acetylene (3.65 ml, 25.8 mmol). After stirring for 17 h at r.t., an ethereal solution of the reaction mixture was washed with NH_4Cl ($\times 2$) and brine. The organic phase was dried and removed in vacuo to provide crude material that was chromatographed on silica gel (hexane) to yield the desired product (4.67 g, 10.90 mmol, 89%) as a pale yellow solid which was used without further purification. ^1H-NMR (250 MHz, $CDCl_3$): 7.67 (s, 2H), 0.27 (s, 18H). ^{13}C-NMR (125 MHz, $CDCl_3$): 136.62, 126.63, 123.91, 103.27, 101.56, −0.10.

4.2. 2,5-Bisethynyl-1,4-dibromobenzene (en route to **4**)

A solution of 2,5-bis(trimethylsilylethynyl)-1,4-dibromobenzene (4.439 g, 10.36 mmol) and K_2CO_3 (5.73 g, 41.5 mmol) in 65 ml THF and 65 ml MeOH was stirred at r.t. for 7 h. The reaction was diluted with ether and washed with brine and NH_4Cl ($\times 2$), and the organic layer was dried and removed in vacuo to yield a light brown solid (2.734 g, 9.63 mmol, 93%) which was of limited stability and was, therefore, used without further purification. ^1H-NMR (250 MHz, $CDCl_3$): 7.72 (s, 2H), 3.50 (s, 2H). HR–MS (EI): found $m/z = 281.8680 \pm 0.00056$ (M^+); calc. for $C_{10}H_4Br_2$: 281.8680%.

4.3. 2,5-Bis(4-(*N*,*N*-dibutylamino)phenylethynyl)-1,4-dibromobenzene (**4**)

A solution of BuNI (7.14 g, 21.56 mmol), $(Ph_3P)_2PdCl_2$ (519 mg, 0.739 mmol) and CuI (541 mg, 2.84 mmol) in THF (75 ml) and DIPA (10 ml) was stirred under argon for 20 min. To this, a solution of 2,5-bisethynyl-1,4-dibromobenzene (2.77 g, 9.76 mmol) in THF (25 ml) was transferred dropwise under argon, followed by a THF rinse (25 ml). The reaction was stirred at r.t. for 17 h at which point it was diluted with ether and NH_4Cl (aq.). The organic layer was washed with NH_4Cl and NaCl, dried and removed in vacuo to provide a crude material that was chromatographed on silica gel (4:1 hexane/CH_2Cl_2). Recrystallization from CH_2Cl_2/MeOH yielded the product as an orange powder (4.47 g, 6.47 mmol, 66%). Melting point (m.p.) 143–144.5 °C. ^1H-NMR (250 MHz, $CDCl_3$): 7.69 (s, hH), 7.39 (d, 4H, $J = 8.56$ Hz), 6.58 (d, 4H, $J = 8.65$ Hz), 3.29 (t, 8H, $J = 7.22$ Hz), 1.57 (quin, 8H, $J = 6.30$ Hz), 1.35 (sex, 8H, $J = 7.43$ Hz), 0.96 (t, 12H, $J =$ 7.20Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): 148.62, 135.43, 133.36, 126.43, 123.30, 111.35, 107.88, 98.66, 85.65, 50.90, 29.55, 20.52, 14.22. FTIR (KBr): ν (cm^{-1}): 2955, 2929, 2870, 2208, 1604, 1520, 1373, 1287, 1191, 1144, 1055, 811, 423. HR–MS (EI): found $m/z = 688.2028 \pm 0.0014$ (M^+); calc. for $C_{38}H_{46}Br_2N_2$: 688.2028%.

4.4. 2′,5′-Bis(4-(*N*,*N*-dibutylamino)phenyl)ethynyl-2,2″,5,5″-tetramethyl[1,1′:4′,1″]terphenyl (**5**)

A mixture of **4** (100 mg, 0.144 mmol), $Me_2B(OH)_2$ (108 mg, 0.721 mmol), KOH (113 mg, 2.01 mmol) and $Pd(PPh_3)_4$ (18 mg, 0.016 mmol) were placed under argon followed by the addition of 1.5 ml toluene, 0.5 ml ethanol and 1.0 ml water. A reflux condenser was attached under a purge of argon, and the reaction was stirred at reflux for 20 h at which point the solution was cooled to r.t. and diluted with toluene, ether and 2 M KOH (aq.). The organic layer was washed with 2 M KOH, 1 M HCl and brine, dried and removed in vacuo to provide a reddish oil. Chromatography on silica (3.5:1 hexane/CH_2Cl_2) yielded the desired product as a yellow solid (86 mg, 0.116 mmol, 80%). M.p. 123–124.5 °C. ^1H-NMR (250 MHz, $CDCl_3$): 7.44 (s, 2H), 7.19 (d, 2H, $J = 7.6$ Hz), 7.15 (s, 2H), 7.11 (d, 2H, $J = 7.60$ Hz), 6.98 (d, 4H, $J = 8.70$ Hz), 6.46 (d, 4H, $J = 8.82$ Hz), 3.22 (t, 8H, $J = 7.30$ Hz), 2.37 (s, 6H), 2.27 (s, 6H), 1.50 (quin, 8H, $J = 6.18$ Hz), 1.32 (sex, 8H, $J = 7.57$ Hz), 0.93 (t, 12H, $J = 7.19$ Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): 147.97, 142.80, 140.41, 134.64,

133.69, 132.89. 132.16, 130.85, 129.68, 128.29, 122.77, 111.25, 109.14, 95.23, 87.27, 50.87, 29.56, 21.22, 20.51, 19.82, 14.19. FTIR (KBr): ν (cm^{-1}): 2955, 2928, 2870, 2202, 1605, 1521, 1367, 1193, 1136, 811. HR–MS (EI): found $m/z = 740.5070 \pm 0.0015$ (M^+); calc. for $C_{54}H_{64}N_2$: 740.5070%.

4.5. 2′,5′-Bis(4-(N,N-dibutylamino)phenyl)ethynyl-2,2″,5,5″-tetramethoxy[1,1′:4′,1″]terphenyl (6)

A mixture of **4** (340 mg, 0.492 mmol), $(MeO)_2B(OH)_2$ (534 mg, 2.93 mmol), Na_2CO_3 (858 mg, 8.09 mmol) and $Pd(PPh_3)_4$ (80 mg, 0.069 mmol) was placed under argon followed by the addition of toluene (19 ml), ethanol (4 ml) and water (4 ml). The system was opened and purged for 10 min to allow for attachment of a reflux condenser, and the reaction was stirred at reflux for 19 h. The reaction was worked up as for compound **5** and subsequent chromatography on silica (1:1 hexane/CH_2Cl_2) yielded 306 mg of the desired product as a reddish white solid. Recrystallization from CH_2Cl_2/MeOH yielded a pure product as a fluffy pale yellow solid (269 mg, 0.334 mmol, 68%). M.p. 168–169 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.57 (s, 2H), 7.05 (d, 4H, $J = 8.7$ Hz), 7.02 (d, 2H, $J = 2.4$ Hz), 6.93 (m, 4H), 6.47 (d, 4H, $J = 9.0$ Hz), 3.81 (s, 6H), 3.78 (s, 6H), 3.23 (t, 8H, $J = 7.8$ Hz), 1.53 (quin, 8H, $J = 8.1$ Hz), 1.33 (sex, 8H, $J = 7.5$ Hz), 0.94 (t, 12H, $J = 7.2$ Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): 153.33, 151.65, 147.88, 139.30, 133.15, 132.90, 130.55, 122.98, 116.76, 114.63, 112.52, 111.25, 109.40, 94.71, 87.58, 56.69, 56.05, 50.88, 29.56, 20.52, 14.20. FTIR (KBr): ν (cm^{-1}): 2951, 2921, 2863, 2013, 1604, 1520, 1473, 1366, 1225, 1194, 1054, 812. UV–vis ($CHCl_3$) λ (nm) ($\log \varepsilon$): 314 (4.46), 387 (4.74), 402 (4.73). Emission ($CHCl_3$) λ_{max} (nm): 437. HR–MS (EI): found $m/z = 804.4866 \pm 0.0016$ (M^+); calc. for $C_{54}H_{64}N_2O_4$: 804.4866%.

4.6. 5,12-Bis(4-(N,N-dibutylamino)phenyl)ethynyl-1,4,8,11-tetramethyldibenz[a,h]anthracene (10)

To a solution of **5** (20 mg, 0.027 mmol) in CH_2Cl_2 (3 ml) under argon was added trifluoroacetic acid (TFA, 80 μl), and the reaction was refluxed for 2 days, cooled and quenched with $NaHCO_3$ (aq.). After dilution with CH_2Cl_2, the organic layer was washed with $NaHCO_3$ and brine, dried and removed in vacuo. The crude solid was chromatographed on silica (1:1 hexane/CH_2Cl_2) to yield the desired product as a yellow solid (16 mg, 0.022 mmol, 82%). M.p. 211–213 °C. ^{1}H-NMR (300 MHz, CD_2Cl_2): 9.09 (s, 2H), 7.72 (s, 2H), 7.44 (d, 2H, $J = 7.5$ Hz), 7.26 (d, 2H, $J = 7.5$ Hz), 7.21 (d, 4H, $J = 8.4$ Hz), 6.72 (d, 4H, $J = 8.7$ Hz), 3.34 (t, 8H, $J = 7.5$ Hz), 3.20 (s, 6H), 2.11 (s, 6H), 1.64 (quin, 8H, $J = 7.8$ Hz), 1.40 (sex, 8H, $J = 8.1$ Hz), 0.99 (t, 12H, $J = 7.2$ Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): 147.35, 139.10, 134.37, 133.28, 132.79, 132.57, 132.25, 130.86, 130.28, 130.06, 129.98, 129.88, 129.47, 127.07, 111.48, 51.13, 29.70, 26.93, 25.38, 20.66, 14.30. FTIR (KBr): ν (cm^{-1}): 2954, 2930, 2868, 1609, 1517, 1457, 1365, 1180, 1105, 915, 817, 784. HR–MS (EI): found $m/z = 740.5070 \pm 0.0015$ (M^+); calc. for $C_{54}H_{64}N_2$: 740.5070%.

4.7. 5,12-Bis(4-(N,N-dibutylamino)phenyl)ethynyl-1,4,8,11-tetramethoxydibenz[a,h]anthracene (11)

To a solution of **6** (49 mg, 0.061 mmol) in CH_2Cl_2 (6 ml) under argon was added 60 μl TFA, and the reaction was refluxed for 20 h. After working up as for compound **10**, the residual crude solid was chromatographed on silica (3:2 CH_2Cl_2/hexane) to yield the desired product as a yellow solid (44 mg, 0.055 mmol, 91%). ^{1}H-NMR (250 MHz, $CDCl_3$): 10.10 (s, 2H), 7.84 (s, 2H), 7.30 (d, 4H, $J = 8.45$ Hz), 7.19 (d, 2H, $J = 8.62$ Hz), 7.07 (d, 2H, $J = 8.75$ Hz), 6.73 (d, 4H, $J = 8.38$ Hz), 4.14 (s, 6H), 3.47 (s, 6H), 3.34 (t, 8H, $J = 7.15$ Hz), 1.62 (quin, 8H, $J = 6.28$ Hz), 1.40 (sex, 8H, $J = 7.53$ Hz), 0.99 (t, 12H, $J = 7.18$ Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): 154.26, 151.96, 146.72, 136.05, 133.69, 132.87, 131.29, 129.12, 128.12, 127.94, 125.12, 122.88, 111.67, 111.10, 109.66, 57.62, 56.51, 51.26, 29.80, 20.67, 14.31. FTIR (KBr): ν (cm^{-1}): 2928, 2868, 1612, 1518, 1428, 1371, 1254, 1186, 1115, 1068, 1033, 922, 796, 731, 415. UV–vis ($CHCl_3$) λ (nm) ($\log \varepsilon$): 251 (4.60), 281 (4.76), 319 (4.71), 405 (4.22), 431 (4.15). Emission ($CHCl_3$) λ_{max} (nm): 437, 468. HR–MS (EI): found $m/z = 804.4866 \pm 0.0016$ (M^+); calc. for $C_{54}H_{64}N_2O_4$: 804.4866%.

4.8. 2,5-Bis(triisopropylsilylethynyl)-1,4-dibromobenzene (7)

Under an argon atmosphere, 200 ml THF was added to **3** (9.88 g, 20.26 mmol), $(Ph_3P)_2PdCl_2$ (1.01 g, 1.43 mmol) and CuI (0.596 g, 3.13 mmol). After the addition of 25 ml DIPA, the solution was stirred at r.t. for 15 min followed by the dropwise addition of triisopropylsilylacetylene (10 ml, 44.58 mmol). After stirring for 40 h at r.t., the reaction was worked up as described for **4**. The crude material was pushed through a silica gel plug to provide 11 g of a white solid contaminated with the starting diiodide. Recrystallization from CH_2Cl_2/hexane provided a total of 4.75 g of a purer product, and further recrystallization from isopropanol provided an additional 3.77 g. All collected solids were further chromatographed on silica (hexanes) to yield 6.62 g of the desired product as a white solid in pure form next to 0.95 g of a mixture containing an additional 0.686 g of the desired product as determined by ^{1}H-NMR integration against an internal standard. In addition, 534 mg of the starting material was recovered (1.09

mmol, 5.4%). Total desired product: 7.31 g (12.25 mmol, 64% based on recovered starting material). ^{1}H-NMR (250 MHz, $CDCl_3$): 7.67 (s, 2H), 1.14 (s, 42H). ^{13}C-NMR (125 MHz, $CDCl_3$): 136.74, 126.81, 123.95, 103.41, 100.00, 18.87, 11.46. FTIR (KBr): ν (cm^{-1}): 2924, 2864, 2164, 1460, 1342, 1064, 883, 811, 674, 585.

4.9. 2′,5′-Bis(triisopropylsilylethynyl)-2,2″,5,5″-tetramethyl[1,1′:4′,1″]terphenyl (en route to **8**)

A 100 Schlenk flask was charged with **7** (1.004 g, 1.683 mmol), $Me_2B(OH)_2$ (1.111 g, 7.41 mmol), KOH (1.5 g, 26.7 mmol) and $Pd(PPh_3)_4$ (278 mg, 0.241 mmol) and placed under argon. Toluene (19 ml), ethanol (10 ml) and water (15 ml) were added, and the system was purged for 15 min to allow for the installation of a reflux condenser. The reaction was heated at reflux for 14 h and worked up similar to **5**. The crude material was chromatographed on silica gel (hexanes) to yield the desired product as a white solid (820 mg, 1.267 mmol, 75%). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.39 (s, 2H), 7.10 (d, 2H, $J = 8.0$ Hz), 7.04 (m, 4h), 2,32 (s, 3H), 2.17 (s, 3H), 0.90 (s, 42H). ^{13}C-NMR (125 MHz, $CDCl_3$): 143.86, 140.00, 134.88, 133.27, 130.27, 129.89, 128.49, 123.05, 105.72, 95.35, 21.07, 19.80, 18.64, 11.36. FTIR (KBr): ν (cm^{-1}): 2941, 2863, 2157, 1482, 1460, 1188, 995, 882, 808, 677, 594, 422. HR–MS (EI): found $m/z = 646.4390 \pm 0.0013$ (M^+); calc. for $C_{44}H_{62}Si_2$: 646.4390%.

4.10. 2′,5′-Bis(triisopropylsilylethynyl)-2,2″,5,5″-tetramethoxy[1,1′:4′,1″]terphenyl (en route to **9**)

A 100 Schlenk flask was charged with **7** (1.005 g, 1.684 mmol), $(MeO)_2B(OH)_2$ (1.347 g, 7.40 mmol), KOH (1.4 g, 26.7 mmol) and 278 mg $Pd(PPh_3)_4$ (278 mg, 0.241 mmol) and placed under argon. Toluene (19 ml), ethanol (10 ml) and water (15 ml) were added, and the system was purged for 15 min to allow for the installation of a reflux condenser. The reaction was heated at reflux for 14 h and worked up similar to **5**. The crude material was chromatographed on silica gel (2:1 hexanes/CH_2Cl_2) to yield the desired product as a white solid (750 mg, 1.055 mmol, 63%). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.48 (s, 2H), 8.86 (m, 6H), 3.77 (s, 6H), 3.74 (s, 6H), 0.93 (s, 42H). ^{13}C-NMR (125 MHz, $CDCl_3$): 153.46, 151.31, 140.46, 134.06, 130.26, 123.40, 116.92, 114.21, 112.27, 106.11, 94.78, 56.48, 55.97, 18.70, 11.38. HR–MS (EI): found $m/z = 710.4187 \pm 0.0014$ (M^+); calc. for $C_{44}H_{62}O_4Si_2$: 710.4187%.

4.11. 2′,5′-Diethynyl-2,2″,5,5″-tetramethyl-[1,1′:4′,1″]terphenyl (**8**)

The TIPS tetramethyl terphenyl (listed at 4.8, 301 mg, 0.465 mmol) was placed in a 50 ml round bottom flask followed by THF (25 ml) and water (2 ml). The system was briefly purged with a stream of argon at which point a 1 M solution of TBAF in THF (5 ml, 5 mmol) was added dropwise. The reaction was stirred at r.t. for 45 h and the reaction was diluted with ether and washed with NaCl ($\times$ 3). The organic layer was dried and removed in vacuo to yield a white solid (148 mg, 0.442 mmol, 95%) which was used without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.44 (s, 2H), 7.17 (d, 2H, $J = 8$ Hz), 7.12 (d, 2H, $J = 7.5$ Hz), 7.07 (s, 2H), 3.01 (s, 2H), 2.36 (s, 6H), 2.20 (s, 6H).

4.12. 2′,5′-Diethynyl-2,2″,5,5″-tetramethoxy-[1,1′:4′,1″]terphenyl (**9**)

The TIPS tetramethoxy terphenyl (listed at 4.9, 300 mg, 0.421 mmol) was placed in a 100 ml round bottom flask followed by THF (35 ml) and water (2 ml). The system was briefly purged with a stream of argon at which point a 1 M solution of TBAF in THF (5 ml, 5 mmol) was added dropwise. The reaction was stirred at r.t. for 5 days, and an additional 5 ml of TBAF solution (5 mmol) was added. After a total of 6 days, workup as described for **8** provided a white solid (149 mg, 0.375 mmol, 89%) that was used without further purification. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.57 (s, 2H), 6.92 (bm, 6H), 3.80 (s, 6H), 3.78 (s, 6H), 3.03 (s, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): 153.41, 151.25, 140.27, 134.99, 129.36, 122.46, 116.97, 114.58, 112.50, 82.88, 80.83, 56.45, 56.01.

4.13. **5** (Route B)

BuNI (336 mg, 1.01 mmol) was placed in a 10 ml Schlenk flask under argon and diluted with toluene (3 ml). To another 10 ml Schlenk flask was added **8** (148 mg, 0.4419 mmol) and toluene (3 ml). A 25 ml Schlenk flask was charged with $(Ph_3P)_2PdCl_2$ (31 mg, 0.044 mmol) and CuI (28 mg, 0.145 mmol) and was placed under argon. The BuNI solution was then transferred into the catalyst mixture followed by a toluene rinse (1 ml) and the dropwise addition of DIPA (0.6 ml). This solution was stirred for 10 min at which point the solution of **8** was cannulated in dropwise followed by a toluene rinse (1 ml) and a THF rinse (1 ml). The reaction was stirred at r.t. for 20 h and worked up similar to **4**. Silica gel chromatography (4:1 hexanes/CH_2Cl_2) yielded 212 mg of clean product as a oily yellow solid (0.286 mmol, 70%). Recrystallization from CH_2Cl_2/EtOH again yielded the desired product as a yellow solid (151 mg, 71% recovery). Characterization data described above.

4.14. **6** (Route B)

BuNI (290.6 mg, 0.877 mmol) was placed in a 10 ml Schlenk flask under argon and diluted with THF (3 ml). To another 10 ml Schlenk flask was added **9** (149 mg, 0.375 mmol) and THF (3 ml). A 25 ml Schlenk flask was charged with $(Ph_3P)_2PdCl_2$ (26 mg, 0.038 mmol) and CuI (22 mg, 0.116 mmol) and was placed under argon. Following the procedure for **5** (Route B), the reaction was stirred at r.t. for 2 days and worked up similar to **4**. Silica gel chromatography (1:1 hexanes/CH_2Cl_2) yielded 211 mg of product as a pale yellow solid (0.262 mmol, 70%). Recrystallization from CH_2Cl_2/MeOH provided the desired compound as a off-white-beige needles (141 mg, 67% recovery). Characterization data described above.

4.15. 2,5-Bis(4-(N,N-dibutylamino)phenylethynyl)-1,4-bis(thiophen-2-yl)benzene (**12**)

A 50 ml Schlenk flask was charged with **4** (1.000 g, 1.448 mmol) and $(Ph_3P)_2PdCl_2$ (50 mg, 0.071 mmol) and placed under argon. DMF was added (15 ml) and heated to 80 °C. Upon complete dissolution of the solids, 2-(tributylstannyl)thiophene was added dropwise (1.13 ml, 3.56 mmol), and the reaction stirred at 80 °C for 68 h. Upon cooling, the mixture was pushed through a pad of celite, and the organic eluent was diluted with ether, washed with brine (× 3), dried and removed in vacuo. The crude material was pushed through a silica plug (hexane to 1:1 hexane/CH_2Cl_2) to provide a brown material, which was subjected to further column chromatography (hexane to 2:1 hexane/CH_2Cl_2). Removal of the solvents provided the desired product as a bright yellow solid (753 mg, 1.080 mmol, 75%). M.p. 157.5–158.5 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.82 (s, 2H), 7.74 (d, 2H, $J = 2.5$ Hz), 7.37 (d, 4H, $J = 8.5$ Hz), 7.14 (dd, 2H, $J = 4.5$, 4.5 Hz), 6.59 (d, 4H, $J = 8.5$ Hz), 3.29 (t, 8H, $J = 7.0$ Hz), 1.58 (m, 8H), 1.36 (sex, 8H, $J = 8.0$ Hz), 0.97 (t, 12H, $J = 7.5$ Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): 148.30, 141.68, 133.80, 133.29, 133.00, 127.30, 126.96, 126.00, 120.78, 111.38, 108.80, 97.26, 87.52, 50.91, 29.56, 20.53, 14.23. FTIR (KBr): ν (cm^{-1}): 2953, 2927, 2868, 2198, 1604, 1520, 1367, 1192, 1135, 810. UV–vis ($CHCl_3$) λ (nm) (log ε): 289 (4.54), 334 (4.68), 417 (4.73). HR–MS (EI): found $m/z = 696.3572 \pm 0.0014$ (M^+); calc. for $C_{46}H_{52}N_2S_2$: 696.3572%.

4.16. 4,10-Bis(4-(N,N-Dibutyl)phenyl)-bisthien[2,3-a,h]-anthracene (**13**)

A 200 ml Schlenk flask was charged with **12** (205 mg, 0.294 mmol) and placed under argon. CH_2Cl_2 (100 ml) was added and stirred vigorously as TfOH was added dropwise (0.52 ml, 5.88 mmol). After 2 h, the reaction was quenched with $NaHCO_3$ and the organic phase was washed with $NaHCO_3$ (× 2) and brine, dried and removed. The crude material was purified on silica gel (3:1 hexane/CH_2Cl_2) to provide the desired product as a deep burgundy–red solid (105 mg, 0.151 mmol, 51%). M.p. 208–209 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.76 (s, 2H), 7.59 (d, 4H, $J = 8$,5 Hz), 7.48 (s, 2H), 7.46 (d, 2H, $J = 5.0$ Hz), 7.14 (d, 2H, $J = 5.0$ Hz), 6.70 (d, 4H, $J = 9.0$ Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): 148.45, 145.57, 142.05, 141.88, 132.72, 131.79, 129.34, 126.99, 125.14, 123.54, 123.25, 111.21, 110.58, 50.98, 29.68, 20.58, 14.26. FTIR (KBr): ν (cm^{-1}): 2954, 2858, 1594, 1520, 1367, 1186, 1140. UV–vis ($CHCl_3$) λ (nm) (log ε): 287 (4.46), 314 (4.53), 361 (4.55), 470 (4.74). HR–MS (EI): found $m/z = 696.3561 \pm 0.0020$ (M^+); calc. for $C_{46}H_{52}N_2S_2$: 696.3572%. Anal: calc. for $C_{46}H_{52}N_2S_2$: C, 79.26; H, 7.52; N, 4.02. Found: C, 78.98; H, 7.74; N, 3.89%.

4.17. 2,5-Bis(4-decyloxyphenylethynyl)-1,4-di(N,N-dioctylcarbamoyl)benzene (**15**)

A 10 ml Schlenk flask was charged with **14** (400 mg, 0.463 mmol), $(Ph_3P)_2PdCl_2$ (18 mg, 0.026 mmol) and CuI (11 mg, 0.056 mmol) and placed under argon. THF (2 ml) and DIPA (1 ml) were added and the solution was stirred at r.t. during the addition of a solution of (*p*-decyloxy)phenylacetylene (254 mg. 0.983 mmol) in THF (0.5 ml). After addition, very thick precipitates formed, and toluene was added to facilitate stirring (1 ml). After 3 h at r.t., the reaction was worked up similar to **4** while subsequent purification on silica gel (9:1 hexane/EtOAc) yielded a yellowish solid (310 mg, 0.275 mmol, 60%). ^{1}H-NMR (250 MHz, $CDCl_3$): 7.42 (s, 2H), 7.38 (d, 4H, $J = 8.7$ Hz), 6.83 (d, 4H, $J = 8.81$ Hz), 3.95 (t, 4H, $J = 6.5$ Hz), 3.75 (bm, 2H), 3.16 (bm, 6H), 1.0–1.9 (bm, 80H), 0.85 (m, 18H). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.9, 159.8, 139.8, 133.4, 130.2, 120.5, 114.67, 114.63, 95.2, 85.2, 68.3, 48.8, 44.9, 32.1, 31.9, 29.77, 29.71, 29.60, 29.53, 29.44, 29.39, 29.32, 28.8, 27.9, 27.4, 26.9, 26.2, 22.88, 22.83, 14.34, 14.28. FTIR (KBr): ν (cm^{-1}): 2923, 2853, 2212, 1636, 1603, 1512, 1249, 1173, 837. HR–MS (FAB): found $m/z =$ 1125.9304 $(M + H)^+$; calc. for $C_{76}H_{120}N_2O_4 + H$: 1125.9326%.

4.18. 3,7-Bis(4-decyloxyphenylethynyl)-1,5-di(N,N-dioctylcarbamoyl)-2,6-dioxanthracene (**16**)

A 100 ml Schlenk flask was charged with **15** (80 mg, 0.071 mmol) and placed under argon. After the addition of CH_2Cl_2 (15 ml), the solution was stirred vigorously as HBF_4 (0.5 ml of a 40% solution in diethyl ether, 3.63 mmol) was added dropwise. The reaction stirred for 1 h at which point diethyl ether was added. The intensely colored material that precipitated was

collected by filtration and washed with ether to provide a fluffy burgundy solid product (75 mg, 0.57 mmol, 81%). ^{1}H-NMR (300 MHz, CD_3CN): 8.32 (s, 2H), 7.84 (d, 4H, $J = 8.7$ Hz), 7.51 (s, 2H), 7.13 (d, 4H, $J = 9.0$ Hz), 4.10 (m, 12H), 1.80 (m, 4H), 1.7–1.2 (bm, 76H), 0.89 (m, 18H). UV–vis ($CHCl_3$) λ (nm) ($\log \varepsilon$): 302 (4.40), 389 (4.74), 539 (3.79).

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