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Three-Step Synthesis of End-Substituted Pentacenes

Matthew T. Stone* and Harry L. Anderson

Department of Chemistry, Chemistry Research Laboratory, University of Oxford, 12 Mansfield Road, Oxford OX1 3TA, U.K.

matthew.stone@chem.ox.ac.uk

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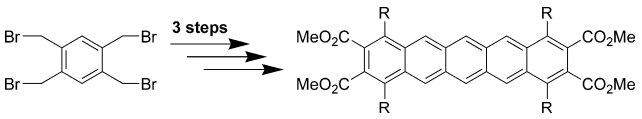
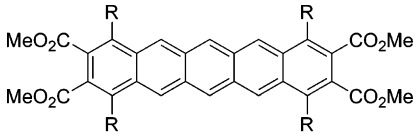


A concise, three-step synthesis of 1,4,8,11-substituted 2,3,9,-10-tetrakis(methoxycarbonyl)pentacenes from commercially available 1,2,4,5-tetrakis(bromomethyl)benzene was established. Efficient alkynylation, followed by formation of four fused rings via a zirconacyclopentadiene intermediate, and then oxidation with DDQ gave pentacenes **1a**−**c**. The process was compatible with methyl, phenyl, and trimethylsilyl substituents, which have good solubility in various organic solvents.

Pentacenes represent a promising class of molecules for application as organic semiconductors and have been shown to have excellent mobilities in thin film transistors.[1−5] However, unsubstituted pentacene is difficult to work with due to its lack of stability and solubility. To address these problems and control organization in the solid state, a number of pentacene derivatives have been synthesized and characterized.[6−9] Toward the same end, we have begun to explore a supramolecular strategy to control the properties of acenes by threading them inside macrocycles to form rotaxanes.[10] The advantage of this approach is that it should permit the isolation of longer and less stable acene systems that have potential applications in organic electronics and would allow the evaluation of theoretical studies of their properties.[11−14] Our previous investigation of a β-cyclodextrin anthracene rotaxane supported this concept as the insulated acene moiety was significantly more resistant to fluorescence quenching and photobleaching than the uninsulated analog.[10] However, to extend this approach to longer acenes, we were presented with the challenge of synthesizing a pentacene with sterically bulky end groups.

While a number of pentacene derivatives have been isolated, relatively few synthetic approaches have been established to access such molecules. The most commonly employed strategies proceed via the reduction of a pentacenequinone precursor which can be used to synthesize a variety of 6,13-substituted pentacenes.[15,16] However, using this methodology to install substituents at other positions can require a number of additional steps in order to access the substituted pentacenequinone precursor.[8,17,18] An alternative homologation approach was reported by Takahashi and co-workers that allowed the synthesis of highly substituted acenes; however, this methodology required eight steps to synthesize pentacenes.[19,20] Building on Takahashi's homologation approach, here we report a symmetric route to synthesize end-substituted pentacenes in only three steps. We demonstrated its application to the synthesis of end-functionalized pentacenes **1a**−**c**.



1a R = Me
1b R = Ph
1c R = TMS

Synthesis of end-substituted pentacenes **1a**−**c** proceeded from commercially available 1,2,4,5-tetrakis(bromomethyl)benzene **2** by reaction with various alkynes to give tetraalkynes **3a**−**c** (Scheme 1). All attempts at reacting **2** with alkynyllithium compounds gave an unidentified mixture of products, which might be attributed to the lithiation of the relatively acidic benzylic hydrogens generated after displacement of the bromide. Successful synthesis of tetraalkynes **3a**−**c** was achieved by reaction with the appropriate alkynylmagnesium bromides in the presence of copper(I) bromide as described by Gopalsamuthiram and Wulff for coupling of trimethylsilylacetylene.[21]

* To whom correspondence should be addressed. Tel: +44 01865 275983. Fax: +44 01865 285002.

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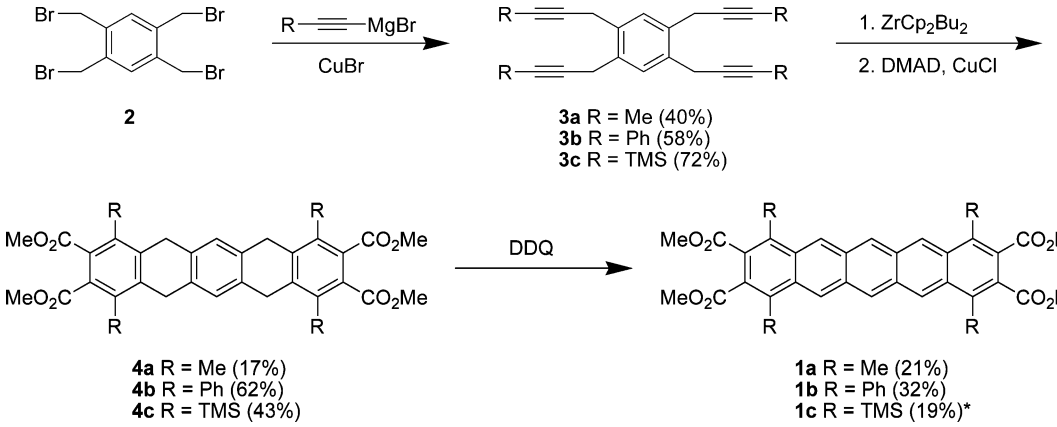
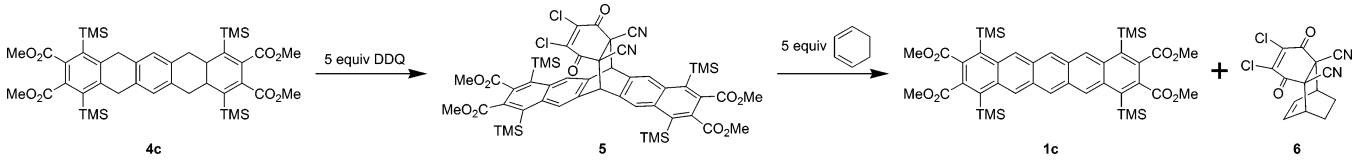
SCHEME 1. Synthesis of Pentacenes 1a−c[a]



[a] Modified conditions were used for oxidation to give **1c**.

SCHEME 2. Modified Conditions for Oxidation To Give 1c[23]



These conditions were also found to be compatible with methyl- and phenyl-substituted acetylenes. Full conversion was crucial to isolation of the pure compounds since incompletely coupled byproducts were impractical to separate.

Tetraalkynes **3a−c** were then converted to 5,7,12,14-tetrahydropentacenes **4a−c** providing four of the fused rings of the pentacene skeleton. First, tetraalkynes **3a−c** were treated with dibutylzirconocene (Negishi's reagent), generated from zirconocene dichloride and *n*-butyllithium, to afford two zirconacyclopentadienes that formed the second and fourth ring of the pentacene skeleton. The first and fifth rings of the pentacene skeleton were formed by reacting the zirconacyclopentadiene compound in situ with copper(I) chloride and dimethylacetylenedicarboxylate acid (DMAD).[19,20] The yield of the reaction was highly dependent on the quality of zirconocene dichloride; exposure to moisture in the air was found to deactivate the reagent.

Tetrahydropentacenes **4a−c** were then transformed into pentacenes **1a−c** by reacting with 2,3-dicyano-5,6-dichloroparabenzoquinone (DDQ) at 100 °C in toluene. DDQ (2 equiv) was used for tetramethyl-substituted pentacene **1a** and tetraphenyl-substituted pentacene **1b**, and any incompletely oxidized byproducts were separated by precipitation with methanol. However, trimethylsilyl-substituted pentacene **1c** was relatively soluble even in methanol and was difficult to separate from incompletely oxidized byproducts by chromatography. This problem was addressed by reacting **4c** with an excess of DDQ (5 equiv) to eliminate incompletely oxidized byproducts. However, under these conditions, pentacene **1c** then underwent cycloaddition with the excess DDQ to give Diels−Alder adduct **5** (Scheme 2). To recover the pentacene, Diels−Alder adduct **5** was treated with 5 equiv of 1,3-cyclohexadiene at 100 °C in toluene to drive the retro-Diels−Alder reaction.[22] The evolution of pentacene **1c** after addition of the 1,3-cyclohexadiene was apparent as the solution developed a deep indigo color.

Pentacenes **1a−c** are deep blue powders when precipitated from solution and have good solubility in a variety of organic solvents. Consistent with previously reported pentacene derivatives, **1a−c** were photosensitive, and thus, reactions were performed under nitrogen and shielded from light.[4,24−26] The compounds were purified and characterized open to the air in the dark and showed no evidence of degradation under these conditions.

The photophysical properties of compounds **1a−c** are consistent with pentacene and it derivatives.[4,6,9,27,28] However, the substituents cause some differences between the colors of the three pentacene derivatives. This was noticeable to the eye, as in solution pentacenes **1b** and **1c** were both indigo whereas tetramethyl derivative **1a** was red-violet. The absorbance spectra are consistent with these observations, as pentacenes **1b** and **1c** have nearly identical absorbance maxima at 600 and 602 nm, respectively, while the absorbance maximum of **1a** is hypsochromically shifted 20 nm to 580 nm (Figure 1, Table 1). The same hypsochromic shift was observed in the fluorescence spectra where methyl-substituted pentacene **1a** was also about 20 nm less than **1b** and 30 nm less than **1c**. Since all three substituents are only weakly electron-donating/withdrawing groups, the shift in the spectra might be attributed to their steric influence on the carboxylate groups. The larger phenyl and trimethylsilyl substituents act to force the carboxylates further out of conjugation than the smaller methyl groups.

(22) A thermally driven retro-Diels−Alder reaction to produce substituted pentacenes from thin films of the corresponding *p*-chloranil pentacence adduct is reported in the patent: Yoshitoku, N.; Kazuto, O. (Asahi Kasei Co.). *Jpn. Kokai Tokkyo Koho* 2005232136, 2005.

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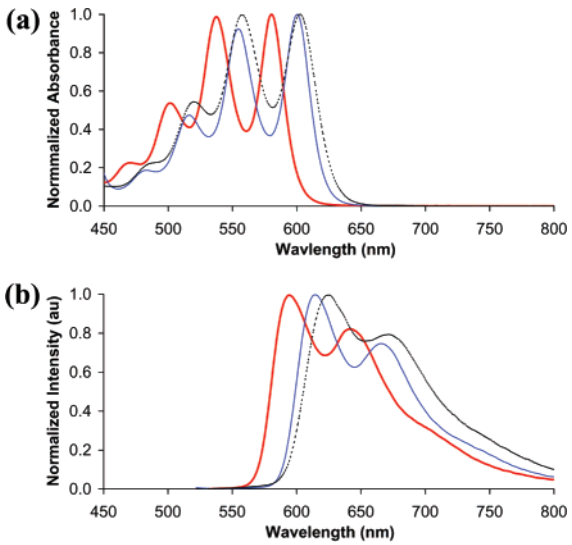

FIGURE 1. UV (a) and fluorescence emission (b) spectra of pentacenes **1a** (bold red), **1b** (blue), and **1c** (dotted black) in dichloromethane at 120 μM and 6 μM, respectively. Fluorescence spectra were excited at 500 nm.

TABLE 1. Spectroscopic Data for Compounds 1a−c

compd	R	π_{max}abs (nm)	π_{max}em (nm)
1a	Me	580	594
1b	Ph	600	615
1c	TMS	602	625

In conclusion, a concise three-step synthesis of end-substituted pentacenes has been established. Efficient conditions were determined to give complete alkynylation of 1,2,4,5-tetrakis(bromomethyl)benzene. Subsequently, a powerfully simplifying transform utilizing Negishi's reagent was used to form the four remaining fused rings of the pentacene skeleton. Oxidation afforded pentacenes with good solubility in various organic solvents. The scheme is compatible with methyl, phenyl, and trimethsilyl groups, although further optimization is necessary to obtain the larger quantities required for rotaxane synthesis. Our next goal will be to identify clipping reactions that will allow the synthesis of rotaxanes from these end-substituted pentacenes. We are particularly interested in aromatic macrocycles that would facilitate charge transfer in the solid state.

Experimental Section

Preparation of 1,2,4,5-Tetrakis(3-phenyl-2-propynyl)benzene (3b). To a 100 mL two-neck round-bottom flask outfitted with a reflux condenser were added tetrahydrofuran (5 mL) and phenylacetylene (2.0 mL, 1.86 g, 18 mmol) under nitrogen. The flask was subsequently cooled to 0 °C, and a solution of ethylmagnesium bromide (17 mL, 1.0 M) in tetrahydrofuran was added via syringe. The solution was allowed to react for 30 min and then allowed to warm to room temperature for 30 min. Copper(I) bromide (65 mg, 0.45 mmol) was then added to the resulting slurry and allowed to react for 30 min. Then 1,2,4,5-tetrakis(bromomethyl)benzene **2** (0.64 g, 1.4 mmol) was added, and the reaction mixture was refluxed for 72 h. After the mixture was cooled to room temperature, the reaction was quenched with saturated aqueous ammonium chloride (100 mL) and then extracted with ether (3 × 75 mL). The combined organic layers were washed with brine (100 mL), dried with sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (ethyl acetate/dichloromethane, 3/7) to give 433 mg (0.833 mmol, 58%) of pure **3b** as a white solid: mp 162−163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.40 (dd, J = 8.0, 1.5, 8H), 7.24 (s, 12H), 3.92 (s, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.5, 131.7, 129.5, 128.2, 127.8, 123.5, 86.7, 83.2, 23.3; HRMS (EI) m/z $[M]^+$ calcd for $C_{42}H_{30}$ 534.2347, found 534.2327. Anal. Calcd for $C_{42}H_{30}$: C, 94.34; H, 5.66. Found: C, 94.33; H, 5.68.

Preparation of 1,4,8,11-Tetraphenyl-2,3,9,10-tetrakis(methoxycarbonyl)-5,7,12,14-tetrahydropentacene (4b). To a 25 mL round-bottom flask outfitted with a side arm adapter was added zirconocene dichloride (377 mg, 0.44 mmol) and then tetrahydrofuran (9 mL). The flask was evacuated and filled with nitrogen (3×) and then cooled to −76 °C (dry ice/2-propanol). Then a solution of *n*-butyllithium (1.7 mL, 1.6 M) in hexane was added, and the reaction mixture was allowed to stir for 1 h. A solution of **3b** (292 mg, 0.55 mmol) in tetrahydrofuran (12 mL) was added via cannula, and the solution was allowed to warm to room temperature and react for 3 h. Then dimethyl acetylenedicarboxylate (0.55 mL, 4.4 mmol) was added followed quickly by copper(I) chloride (340 mg, 3.4 mmol). The reaction mixture was then heated to 40 °C for 18 h and then quenched with acetic acid (1.5 mL). The precipitated product was collected by centrifugation and washed with ether (3×) to remove the more soluble byproduct formed by trimerization of dimethyl acetylenedicarboxylate. The solid was dissolved in chloroform and passed through a plug of silica gel eluting with ethyl acetate/chloroform (2/3) to give 279 mg (0.341 mmol, 62%) of pure **4b** as a white solid: mp 309 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (m, 12H), 7.23 (d, J = 7.9, 8H), 6.84 (s, 2H), 3.63 (s, 8H), 3.43 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 138.3, 138.2, 138.1, 134.1, 130.4, 129.2, 128.2, 127.6, 125.8, 52.0, 34.0; MS (ESI) m/z $[M + Na]^+$ calcd for $C_{54}H_{42}NaO_8$ 841.2772, found 841.2776. Anal. Calcd $C_{54}H_{42}O_8$: C, 79.20; H, 5.17. Found: C, 79.14; H, 5.19.

Preparation of 1,4,8,11-Tetraphenyl-2,3,9,10-tetrakis(methoxycarbonyl)pentacene (1b). To a 50 mL round-bottom flask outfitted with a sidearm adapter were added **4b** (100 mg, 0.12 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (55 mg, 0.24 mmol). The flask was evacuated and backfilled with nitrogen (3×), and then toluene (25 mL) was added. The solution was then degassed (3×), and the flask was heated to 100 °C for 18 h. After the solution was cooled to room temperature, the solvent was removed in vacuo. The residue was dissolved in a minimum amount of dichloromethane and then precipitated with methanol. The product was recovered by centrifugation and washed with methanol (3×). The crude product was purified by silica gel column chromatography (dichloromethane) to give 32 mg (0.039 mmol, 32%) of pure **1b** as a dark blue solid: mp 330 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 2H), 8.34 (s, 4H), 7.55−7.50 (m, 12H), 7.45−7.43 (m, 8H), 3.52 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.6, 140.0, 137.5, 130.7, 130.3, 129.9, 128.5, 128.2, 128.14, 128.08, 127.6, 52.1; MS (ESI) m/z $[M + Na]^+$ calcd for $C_{54}H_{38}NaO_8$ 837.2464, found 837.2459.

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Supporting Information Available: Experimental procedures for **1a**,**c**, **3a**,**c**, and **4a**,**c** and spectroscopic data (^{1}H NMR and ^{13}C NMR) for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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