Double Diels−Alder Strategies to Soluble 2,9- and 2,9,6,13-Tetraethynylpentacenes, Photolytic [4 + 4] Cycloadditions, and Pentacene Crystal Packing

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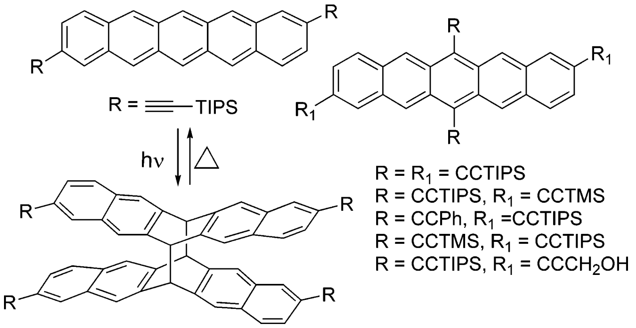

Four new classes of organic solvent soluble ethynylpentacene derivatives (2,9-, 2,10-, 2,6,9,13-, 2,6,-10,13-) have been prepared by complementary, versatile, double Diels−Alder strategies. Functional groups on the A, C, and E rings can be manipulated to increase the solubility, modulate the electronics, and alter the solid-state packing. Cycloaddition reactions with diene **2** and 1,4,5,8-anthradiquinone (**3**) or *ortho*-quinodimethane **19** with 1-butyl-3-methylimidazolim iodide (**18**) as the iodide source (a significant improvement over NaI) and benzoquinone (**20**) followed by in situ aromatization afforded the quinones **4**, **5**, **21**, and **22**, respectively. For the 2,9- and 2,10- families, a one-pot desilylation/triflation was developed. Palladium(0) coupling and reductive aromatization afforded 2,9-di(triisopropylsilylethynyl)pentacene (**10**) and 2,10-di(triisopropylsilylethynyl)pentacene (**11**), respectively. Photodimerization of these pentacenes afforded the air-stable [4 + 4] cycloaddition pentacene precursors (tetrakisnaphthotricyclo[4.2.2.2^{2,5}]-dodecanes, **12**−**15**). Thermal cycloreversion of the dimers (∼13 J/g, ∼4 kcal/mol) produces the parent pentacenes (**10** or **11**). The tetrasubstituted family utilized a parallel route with extra versatility as the timing of the Grignard and palladium(0) coupling step may be varied depending upon the functional group combinations desired. The subsequent reactions provided the tetraethynylpentacenes **28**−**30**, **33**−**35** (para-isomers), and **38** (meta-isomer). X-ray crystallography analysis of **28**, **29**, and **33** revealed various π−π stacked packing motifs that differ from the unfavorable herringbone pattern of pentacene.

Introduction

Pentacene (**1**) is among the most widely employed small molecule p-type organic semiconductor for organic thin film transistors[1] because of high hole mobilities in excess of 1 cm^2/V per s compared to that of other organic compounds.[2] Pentacene is insoluble in common organic solvents and sensitive to light and atmospheric oxygen. Consequently, the development of solution-based processing of pentacene for organic electronic

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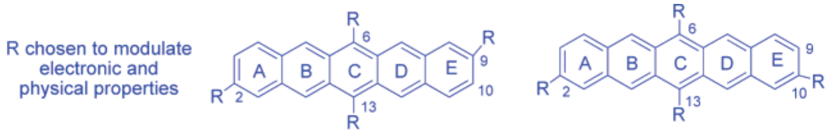

1 (*para*-, 2,9-) **1**(*meta*-, 2,10-)

FIGURE 1. Pentacene framework for diverse derivatives.

devices is hindered by these properties,[3] although Gelinck et al. constructed a single sheet transistor display from 1888 pentacene transistors.[4] Two strategies have emerged to overcome these difficulties. The first approach utilizes soluble pentacene precursors equipped for thermal retro-Diels−Alder reactions to generate pentacene.[5] The second approach involves pentacene derivatives with solubilizing groups.[6] In general, these syntheses were not designed for further functionalization. We wish to describe four new classes of pentacene derivatives (Figure 1) with functional groups on the terminal A and E or A, C, and E rings designed to increase the solubility, modulate the electronics, and alter the solid-state packing.[7]

Results and Discussion

Synthesis and Photochemical Dimerization of Pentacenes 10 and 11. Pentacene reacts preferentially at the electron-rich C ring; thus, direct reactions at the terminal rings are challenging.[8] Therefore, a new double Diels−Alder strategy for pentacenes was designed to facilitate early introduction of a substituent onto the terminal A and E rings (Scheme 1). Reaction of Danishefsky's diene **2**[9] and anthradiquinone **3**[10] followed by air oxidation over silica gel afforded diquinones **4** and **5** (1:1, 60%). The isomers were separated by fractional crystallization from $CHCl_3$. Ditriflate **6** was prepared in a one-pot desilylation/triflation sequence from the corresponding diquinone to avoid precipitation of the initial diol. Silyl ether **4** was disilylated (TBAF/THF) and treated directly with $PhNTf_2$ to afford **6** in 98% yield.[11] Sonogashira coupling of ditriflate **6** and TIPS−acetylene gave diquinone **8**. Ditriflate **6** was sparingly soluble (THF, 1 mg/5 mL) and required complete dissolution before reagent addition. The most reliable reductive deoxygenation/aromatization procedure employed a Meerwein−Ponndorf−Verley reduction (Al, $HgCl_2$, CBr_4, cyclohexanol, reflux).[12] Reductive/aromatization of **8** afforded the 2,9-disubstituted pentacene **10**. The identical reaction sequence transformed **5** into the 2,10-disubstituted pentacene **11**. Pentacenes **10** and **11** were deep purple and soluble in common organic solvents (CH_2Cl_2, THF, Et_2O, hexane). This solubility rendered them particularly sensitive to atmospheric oxygen.[13] The initial peroxide product is unstable and is rapidly oxidized to the C ring quinone. This could provide an alternative, inefficient route to **24** for tetrafunctionalized 2,6,9,13-pentacenes! Fritzsche observed 140 years ago that anthracene underwent a photochemically induced [4 + 4] cycloaddition to generate tetrakisbenzotricyclo[4.2.2.2^{2,5}]dodecane,[14] and subsequent research revealed the dimer afforded anthracene upon thermolysis.[15] In the interim, the photochemistry of anthracene has been thoroughly investigated.[16] Its photolytic cycloaddition reactivity is due to high singlet energy, excitation to an encounter exciplex in equilibrium with a more stable exciplex complex that combines to generate the dimer.[17,18] We anticipated that the solubility and enhanced diene character of pentacenes **10** and **11** would facilitate a photodimerization capable of thermal reversion. This was the case as independent photolysis of **10** and **11** afforded a regiochemical mixture (1:1) composed of the individual isomers (**12**, **13**, and **14**, **15**), which were separated by flash chromatography (Scheme 2).[19,20] The pentacene cycloaddition photochemistry likely parallels anthracene, in which these pentacenes act as their own singlet

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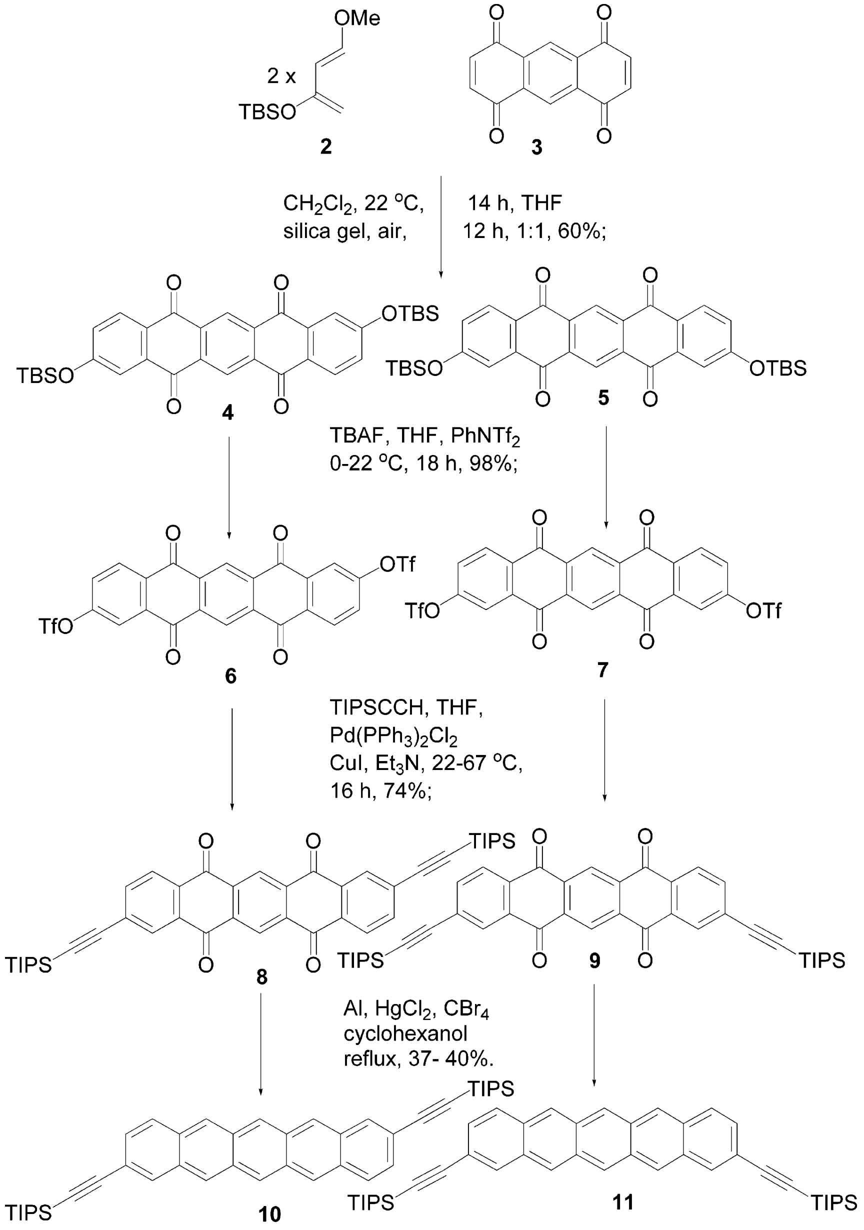
SCHEME 1. Double Cycloaddition Route to Pentacenes 10 and 11



sensitizer to form an exciplex complex that collapses to the [4 + 4] cycloaddition products.

Differential scanning calorimetry (DSC) measurements established that the thermal reversion onset temperature was 167 °C with a low value of the enthalpy of dissociation (∼13 J/g, ∼4 kcal/mol), a consequence of the elongated C1−C23 bond (1.60 Å) and the stabilized bisbenzylic radical intermediates from bond cleavage. The tilted nature of the naphthalene rings is reflected in the 2.81 Å distance between C2 and C24, compared to the increased distance of 7.33 Å between C6 and C28. The X-ray crystal structure of **14** (from acetone) confirmed the structural assignment and its interesting "biplanar" motif (Figure A in the Supporting Information).[21,22]

These photochemical adducts may have other attributes by analogy with tetrahydroanthracene if they can be converted to tetrahydropentacenes. Tetrahydroanthracene is a precursor for the synthesis of both tubelike structures[23] and a Möbius aromatic hydrocarbon.[24] This implies that tetrahydropentacenes have the

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(19) A SciFinder structure search for tetrakisnaphthotricyclo$[4.2.2.2^{2,5}]$-dodecane failed. It is in the literature named *s*-dipentacene. Photolysis of pentacene (**1**) in 1-chloronaphthalene afforded *s*-dipentacene, although the thermal retro-reaction was not investigated. Berg, O.; Chronister, E. L.; Yamashita, T.; Scott, G. W.; Sweet, R. M.; Calabrese, J. *J. Phys. Chem. A* **1999**, *103*, 2451.

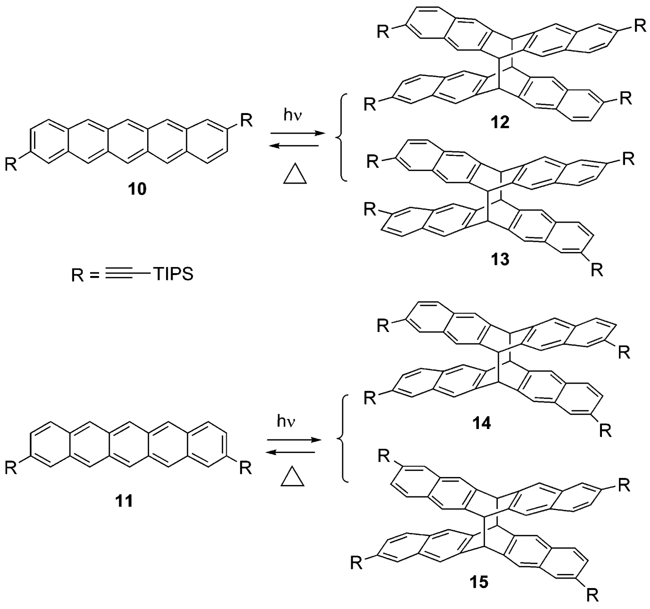
(20) In parallel with our atmospheric oxygen experiments and photochemical studies, Wong and co-workers[12c] reported the rapid reaction with oxygen to form a peroxide of their soluble 2,3,9,10-tetrakis(trimethylsilyl)pentacene. In the absence of air, it was stable for 7 days in chloroform. They also observed the dimerization of their pentacene in sunlight in concentrated hexane solution during crystallization.

(21) X-ray data for compounds **14**, **28**, **29**, and **33** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 297309, 652161, 652162, and 652163, respectively. Copies of the data may be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. Fax: (+44) 1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.

(22) See ref. 19.

(23) Kammermier, S.; Jones, P. G.; Herges, R. *Angew. Chem., Int. Ed.* **1996**, *35*, 2669.

SCHEME 2. Photochemical [4 + 4] Dimerization of Pentacenes 10 and 11 and Their Thermal Reversion

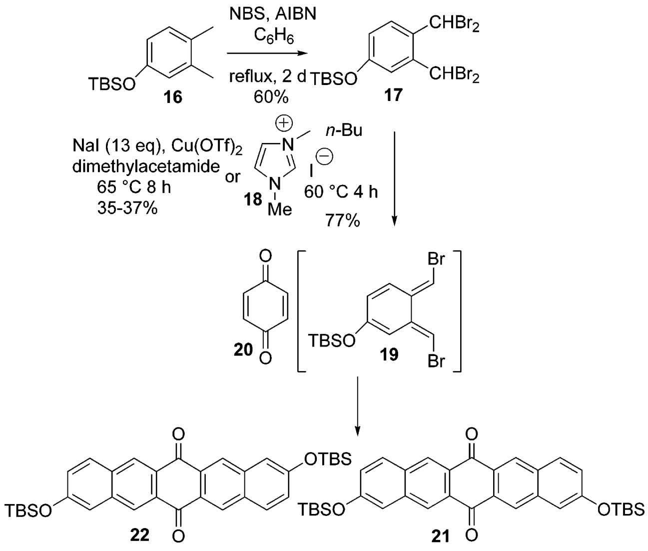


potential to provide access to new members of both these homologous structural types.

Unfortunately, despite the interesting chemistry above, nature presented us with several insurmountable complications. Pentacene **10** dimerizes immediately when exposed to ambient laboratory light (3−5 min). The thermal reversion may be followed visually because of the appearance of the purple pentacene, but this method did not afford pentacene **10** with the purity required for thin film electronics. In addition, the ^{13}C NMR spectra could not be recorded nor could the mobility be measured. Consequently, these results were not publishable in an independent article.[25]

Synthesis of Tetrasubstituted Ethynylpentacenes 28−30, 33−35 (*para*-, 2,9-), and 38 (*meta*-, 2,10-). To solve the problems presented by the reactivity of pentacenes **10** and **11**, we embarked on the synthesis of more highly substituted pentacenes with 6,13-alkylsilylethynyl functionality to moderate the reactivity of the central ring and improve crystal packing. The desirable 2,9-substituents were retained to aid the solubility, mix and match the silyl groups, explore their effect on the crystal packing and the potential to extend the chromophore, and attach heterocyclic groups. This new class of tetrasubstituted pentacene derivatives possesses functionalized ethynyl groups on the terminal A, C, and E rings that may be varied as desired. On the basis of Scheme 1, a related double Diels−Alder tandem elimination strategy for these new pentacenes was designed to facilitate introduction of the substituents onto the terminal A and E rings and allow ring C functionalization (Scheme 3). The most reliable route to the requisite *ortho*-quinodimethane, despite the investigation of alternative synthetic methods,[26] was the Cava procedure in which a tetrabromo-*ortho*-xylene is treated with an iodide source.[27] This appears to be the first example of an ionic halide source for this transformation. The *ortho*-xylene TBS ether **17** was prepared from the xylene **16** by free radical bromination. The initial conditions to generate the desired diene intermediate **19** involved the exposure of **17** to sodium iodide and copper triflate in DMF for 8 h (65 °C) in the presence of benzoquinone (**20**). These conditions resulted in disappointing 35−37% yields of the Diels−Alder adducts **21** and **22** (1:1). A significant improvement of this literature method involved the replacement of sodium iodide with the iodo-ionic liquid **18** (1-butyl-3-methylimidazolim iodide) as the halogen source. The yield of the Diels−Alder adducts **21** and **22** (1:1) was doubled (77%), the reaction time was halved, and the workup was facilitated. The two quinones were separated by fractional crystallization from CH_2Cl_2.

SCHEME 3. Preparation of *ortho*-Quinodimethane 19: Improved Cycloadditions with an Ionic Liquid Iodide Source



The requisite transformations to the new pentacenes followed a sequence similar to those established above, as summarized in Scheme 4. The desired 2,9-regioisomer **22** was treated with fluoride, and the diol product reacted with *N*-phenyltrifluoromethanesulfonimide to afford the ditriflate **23** in 90% overall yield. Sonogashira coupling with TIPS−acetylene gave silylacetylene **24** in excellent yield (90−93%).

This was followed by double addition of the appropriate lithium acetylides (TIPS−C≡CLi or TMS−C≡CLi or Ph−C≡CLi) to provide the diols **25**−**27**, respectively. Aromatization was accomplished using tin(II) chloride under acidic conditions to afford the 2,6,9,13-tetrasubstituted pentacenes **28**−**30** in 78−93% yield.

Reordering the experimental steps from the 2,9-disilylquinone **22** afforded a versatile alternate route to the pentacene family in Scheme 4. This is preferred because of the concomitant silyl ether deprotection/aromatization step and potential for the addition of diverse functionality at the 2,9-positions. Double addition of the appropriate Grignard reagent was conducted initially with quinone **22** to add the C6 and C13 substituents and generate the tertiary diol **31** (Scheme 5). Subsequent exposure to tin chloride generated the 2,9-diols (not illustrated). Triflation provided the ditriflate compound **32**, which was converted to the pentacenes **28** and **33**−**35** by palladium(0)-

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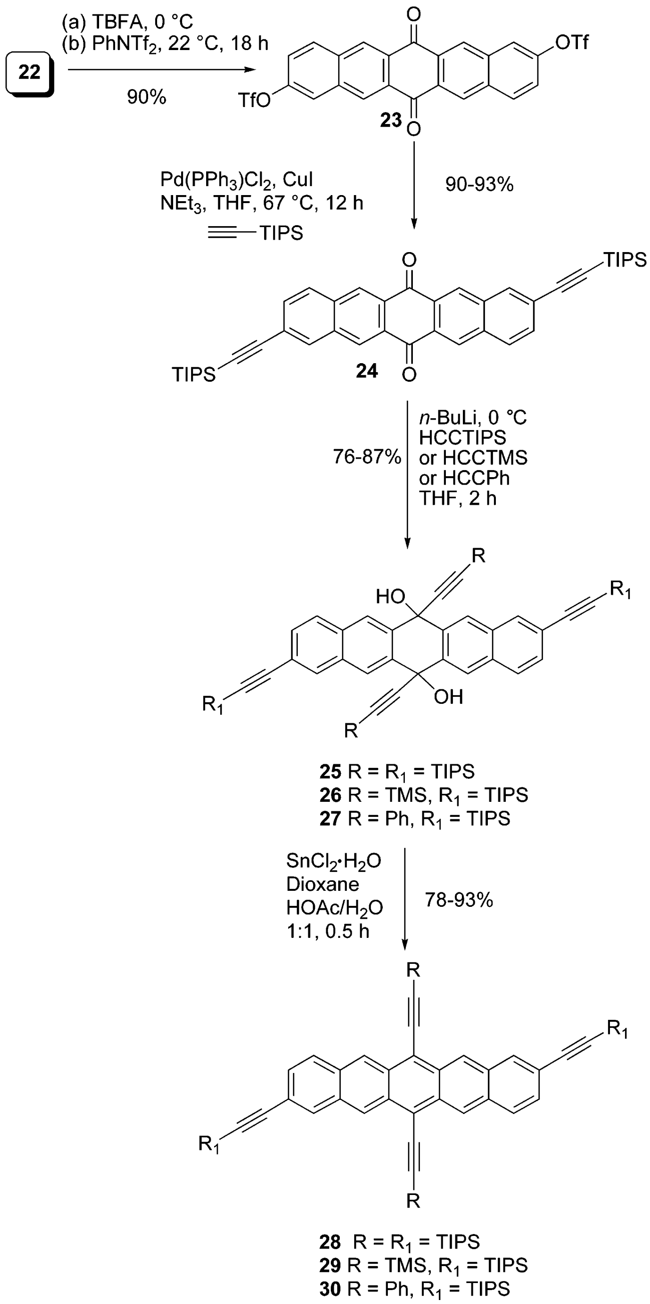
SCHEME 4. Synthesis of Tetraethynylpentacenes 28−30 from Quinone 22

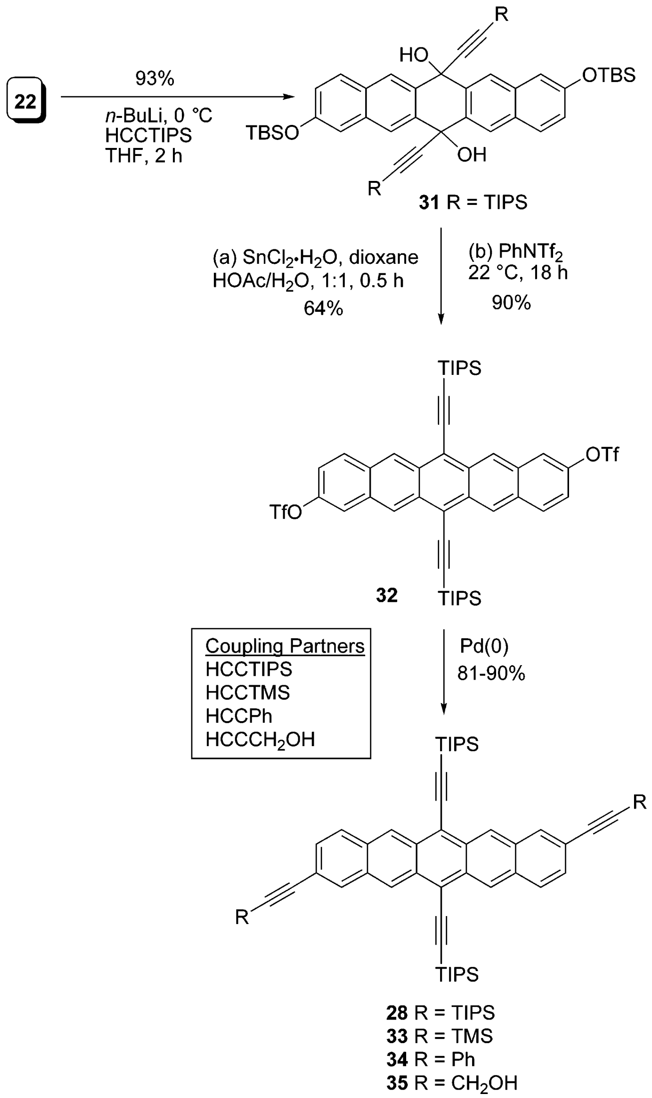


mediated coupling with the appropriate acetylenic component. The triflates **23** and **32** are versatile intermediates for the preparation of various A and E ring 2,9-pentacene derivatives for the attachment of heterocyclic and electronically useful groups that have not been available previously.

The 2,10-pentacene isomer **21** was converted in a parallel manner following the reaction sequence in Scheme 6 to afford the 2,6,10,13-tetrasilylethynylpentacene **38** in the meta-series.

Crystal Packing Studies: X-ray Analyses of Pentacenes 28, 29, and 33. The excellent recent review by Anthony[28] contains a detailed analysis of pentacene packing motifs. Pentacene itself prefers to pack in a herringbone pattern, and the same pattern is adopted by 6,13-TMS−ethynyl substitution

SCHEME 5. Alternate Synthesis of Tetrasubstituted Pentacenes 28 and 33−35 from Quinone 22



because of increased edge-to-face interactions that are present. In contrast, replacement of TMS groups with TIPS groups, which are essentially spherical and have an approximate diameter equal to or less than one-half the pentacene length, induces a change in the packing arrangement. Consequently, 6,13-TIPS−ethynyl groups prefer a 2-D parallel geometry, sometimes referred to as a “bricklayer” arrangement, whereas *n*-propyl substitution results in a “slipped-stack” parallel geometry.

The tetra-TIPS pentacene **28** forms stacked parallel sheets in which the pentacenes are superimposed (Figure 2). The individual molecules are separated by 10.5 Å. This large separation is caused by the steric repulsion between the C6 and C13 TIPS groups, which extend into the edge of the π-system in rings B and D and cause a ring shift in the overlapping pair. This feature prevents the close π-stacking of the aromatic rings. This arrangement can be identified more easily in the ORTEP diagram in which the packing arrangement is viewed perpendicular to the pentacene plane (Figure B in the Supporting Information). In principle, the most facile way to remove this interaction is to replace the silyl group with hydrogen and compare the X-ray data. Unfortunately, the resulting 6,13-diethynylpentacene could not be properly characterized because

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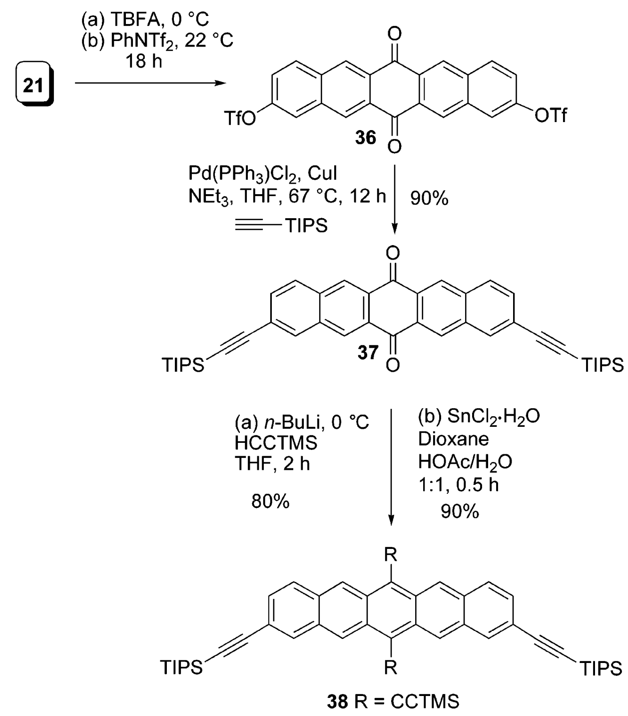
[28] Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028.

SCHEME 6. Synthesis of Tetrasubstituted Pentacene 38 from Quinone 21



of its instability, and the corresponding bromoacetylene behaved similarly. Additional nonbonded interactions between the C9 TIPS group of the top ring and the C2 TIPS substituent of the lower ring are also restrictive. Despite the magnitude of the separation of the overlapping pentacenes, the presence of the TIPS groups has lived up to their reputation of creating a very ordered mode of crystal packing. Figure 3 shows the crystal packing of **29**.

This beneficial feature is apparent in the X-ray of the 6,13-TMS compound **33** (Figure 4). The C rings in two pentacenes are nearly superimposed but are splayed into an X-like orientation because of rotation about the C ring by the steric interference between the C13-TMS on the top ring group with the C9-TIPS group of the nearest neighbor. This inhibits the alignment for full overlap that might otherwise occur. In addition, the TIPS groups at the C2 and C9 positions disrupt rather than aid the alignment. If **33** were a tetra-TMS compound instead of mixed it is possible the overlap might be improved. The final crystal structure is for compound **33**. The 6,13-TIPS groups face each other in an interlocking manner like "anthers about to clash" and dictate the orientation of the other functionality. Consequently, there is no close π-overlap between the aromatic rings of the acenes. Instead, they are oriented as a parallel series of steps along the long axis of the pentacenes. The 2,9-phenylenynylpentacene samples continually cocrystallized with the solvent, and thus the X-rays were disordered and further analysis was not informative.

On the basis of the simplistic possibility that 2,9-proparyl alcohol groups might facilitate hydrogen bonding in the crystal, while retaining the benefit of the 6,13-TIPS substituents, the compound **35** was prepared, but unfortunately, its crystal packing could not be determined because of its very poor crystal quality.

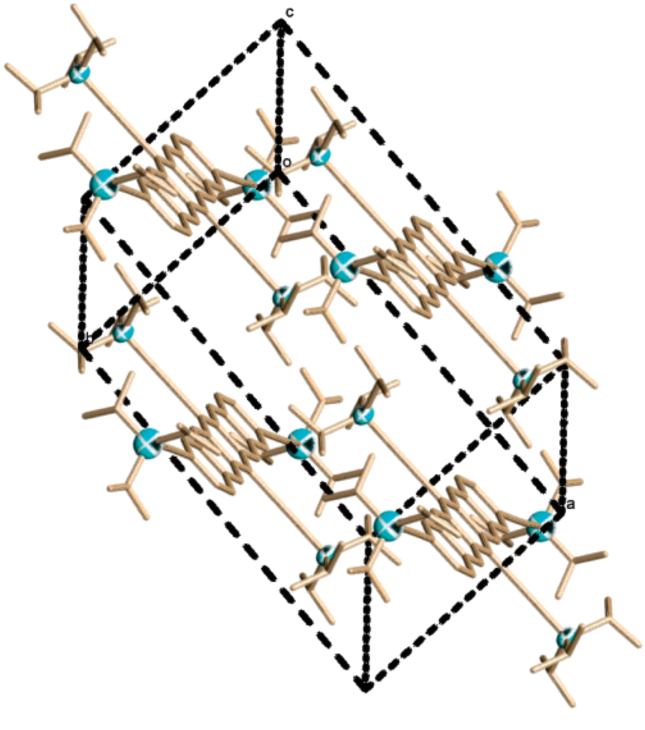


FIGURE 2. Crystal packing: 2,6,9,13-tetrakis(triisopropylsilylethynyl)-6,13-pentacene (**28**).

Device Characteristics. The mobility characteristics were determined for the tetra-TIPS molecule **28**. Thin semiconductor films were then deposited by either spin coating or drop casting from chlorobenzene or 1,2-dichlorobenzene. The films were measured before and after annealing at 100 °C.[29] The best results were obtained for films that were drop cast from 1,2-dichlorobenzene onto substrates heated at 90 °C. The saturated mobility was 3×10^{-4} cm^2/V per s, whereas the linear mobility was an order of magnitude lower at 10^{-5} cm^2/V per s for a 10-μm device. The devices were turned on near 0 V and showed a reasonable ON/OFF ratio of 10^3 in saturation mode. A comparison of pentacene and 6,13-TIPS pentacene films recorded values of 0.02−0.04 and 0.01−0.06 cm^2/V per s, respectively.[30] These values are considerably better than those for **28**.

Spectral Data. Electronic absorption and fluorescence spectra of phenylethynyl-substituted acenes including pentacenes were reported several years ago.[31] More recently, Kafafi and coworkers[32] have examined the photophysical properties of dioxolane-substituted pentacene derivatives with 6,13-triisopropylsilylethynyl groups dispersed in tris(quinolin-8-olato)aluminum(III). Our spectra for **29**, **30**, and **32** are illustrated in Figures 5 and 6, but the variation in the substitution patterns between TMS and TIPS had little effect on the absorbance spectra. It is also interesting that the spectral characters for the ditriflate **32** were very similar to that of the silyl ethynyl compounds. The normalized fluorescence spectra of these pentacenes in n-hexane displayed the near absence of Stokes' shift in the fluorescence spectra consistent with the rigidity of these molecules. For

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(29) Unfortunately for our collaborators and us, vapor disposition methods were not available.

(30) Ostroverkhova, O.; Shcherbyna, S.; Cooke, D. G.; Egerton, R. F.; Hegmann, F. A.; Tykwinski, R. R.; Parkin, S. R.; Anthony, J. E. *J. Appl. Phys.* **2005**, *98*, 33701.

(31) Maulding, D. R.; Roberts, B. G. *J. Org. Chem.* **1969**, *34*, 1734.

(32) Wolak, M. A.; Melinger, J. S.; Lane, P. A.; Palilis, L. C.; Landis, C. A.; Delcamp, J.; Anthony, J. E.; Kafafi, Z. H. *J. Phys. Chem. B* **2006**, *110*, 7928.

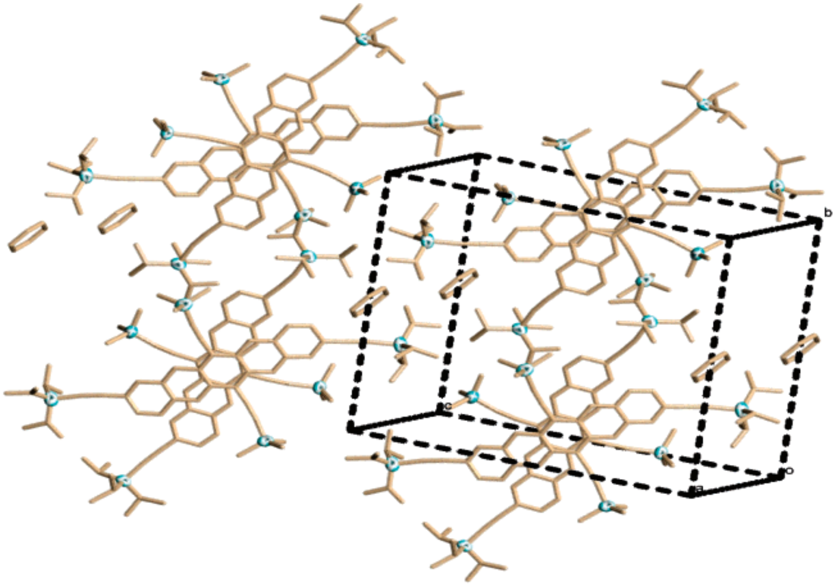

FIGURE 3. Crystal packing: 2,9-bis(triisopropylsilylethynyl)-6,13-bis(trimethylsilylethynyl)pentacene (**29**).

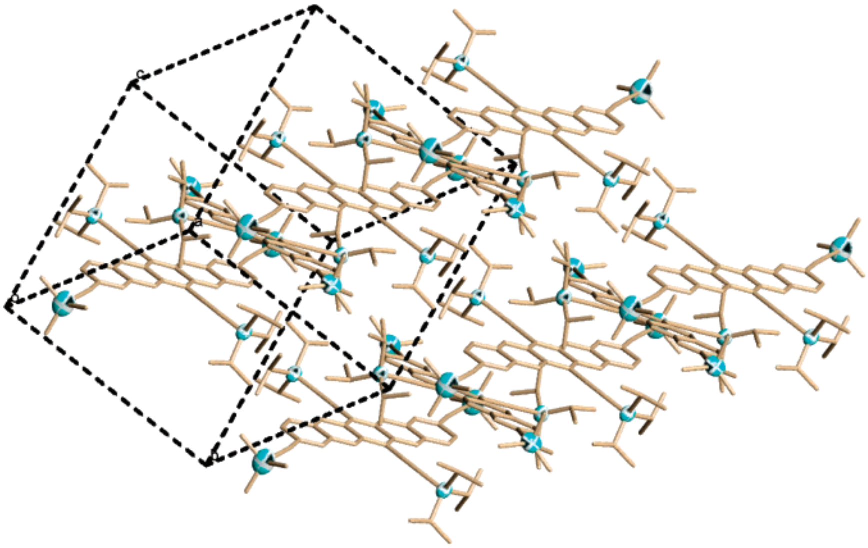

FIGURE 4. Crystal packing: 2,9-bis(2-(trimethylsilyl)ethynyl)-6,13-bis(2-(triisopropylsilyl)ethynyl)pentacene (**33**).

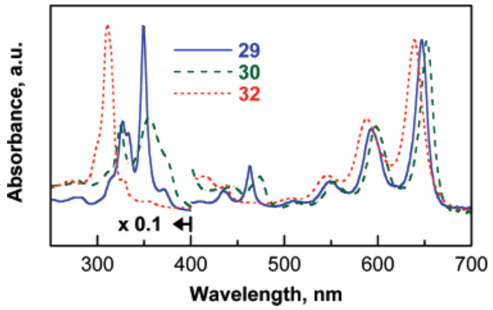

FIGURE 5. UV–vis absorption spectra of pentacenes **29**, **30**, and **32** in *n*-hexane (normalized at $\lambda_{max} \approx$ 650 nm).

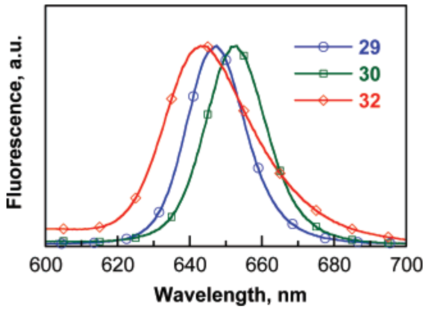

FIGURE 6. Normalized fluorescence spectra of pentacenes **29**, **30**, and **32** in *n*-hexane (open to air).

example, the absorption maximum for **29** is centered at 647 nm and the emission maximum shifts by less than 1 nm. This observation indicates that little conformational change occurs between the ground state and the first singlet excited state. The fluorescence quantum yield (Φ_f) was found to be ~0.1 for **28**, **29**, **30**, and **32** in *n*-hexane under air when compared to Nile Red in dioxane ($\Phi_f = 0.7$).[33] The absorbance and fluorescence peaks near 650 nm were also very narrow. The full width at

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[33] Sackett, D. L.; Wolff, J. *Anal. Biochem*. **1987**, *167*, 228.

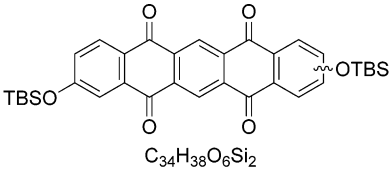
half-maximum (fwhm) for compound **29** is 16.5 and 20 nm for absorption and fluorescence, respectively. This compares favorably with that of CdSe nanoparticles, noted for their narrow emission spectra that afford fwhm of ∼30 nm.[34]

Conclusions

In summary, we have developed versatile four-step syntheses of soluble silyl-protected 2,9-, 2,10-, 2,6,9,13-, and 2,6,10,13-ethynylpentacenes by a double Diels−Alder strategy that may be extended to other molecules. The knowledge gained from this study should lead to new pentacenes with potential as organic thin film semiconductors. Pentacene without C ring substituents underwent light inducted dimerization to tetrakisnaphthotricyclo[4.2.2.2^{2,5}]dodecanes cycloaddition adducts. An ionic liquid is the preferred halide source for the generation of *ortho*-quinodimetanes from bromoxylenes. In addition, the appropriate members of these families are useful building blocks for both *para*-pentacenes **23** and **29**−**33** and *meta*-pentacenes **36** and **38** helical cyclophanes with pentacene caps. In particular, the meta-compounds are key intermediates for shape-persistent, π-stacked, helical pentacene cyclophanes that parallel our previous research with benzene in which the superimposed aromatic rings are separated by ∼3.5 Å, a consequence of the restricted geometry imposed by the bridges.[35]

Experimental Section

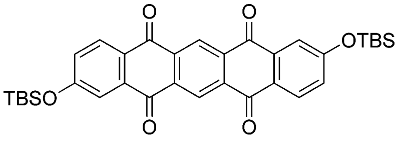
2,9/2,10-Bis(*t*-butyldimethylsiloxy)-5,7,12,14-pentacenediquinone (4, 5).



$C_{34}H_{38}O_6Si_2$
Mol. Wt.: 598.83

1,4,5,8-Anthradiquinone (**3**) (2.45 g, 10.3 mmol, 1 equiv) and *trans*-3-(*t*-butyldimethylsiloxy)-1-methoxy-1,3-butadiene (**2**) (5.14 mL, 21.6 mmol, 2.1 equiv) were combined in CH_2Cl_2 and stirred at room temperature (22 °C) for 20 h. The reaction was concentrated and taken up in THF, silica gel was added, and the suspension was stirred open to air for 24 h. The reaction was filtered through a silica gel plug with CH_2Cl_2 to afford **4** and **5**. The plug was flushed with THF to recover unaromatized material. Silica gel was added to the THF fraction, and this slurry was stirred open to air for 24 h. Filtration through a silica gel plug with CH_2Cl_2 afforded additional **4** and **5**. The silica gel oxidation/filtration was repeated until all of the unaromatized material was converted to **4** and **5**. The diquinones were isolated as a yellow solid (3.72 g, 60%) as mixture of **4** and **5** (1:1). Isomers **4** and **5** could be separated by preparative HPLC (CH_2CL_2/hexane, 70:30) or preferably by fractional crystallization from chloroform.

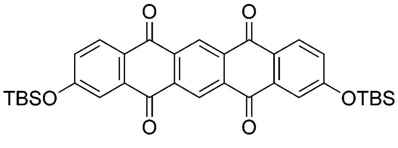
2,9-Bis(*t*-butyldimethylsiloxy)-5,7,12,14-pentacenediquinone (4).



$C_{34}H_{38}O_6Si_2$
Mol. Wt.: 598.83

Mp: >270 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 2H), 8.28 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 2.5 Hz, 2H), 7.24 (dd, J = 8.5, 2.6 Hz, 2H), 1.01 (s, 18 H), 0.30 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.8 (s), 180.7 (s), 161.9 (s), 136.9 (s), 136.7 (s), 135.6 (s), 130.4 (d), 127.5 (s), 127.0 (d), 126.5 (d), 117.7 (d), 25.5 (q), 18.3 (s), −4.3 (q); MS (EI) m/z 541.2 ($M^+ - t$-Bu, 100), 485.1 (8), 242.0 (19), 162.0 (34); IR ($CDCl_3$) ν 2957.6, 2930.7, 1677.7, 1591.9 cm^{-1}; HRMS calcd for $C_{30}H_{29}O_6Si_2$ 541.1502 ($M^+ - t$-Bu), found 541.1510.

2,10-Bis(*t*-butyldimethylsiloxy)-5,7,12,14-pentacenediquinone (5).



$C_{34}H_{38}O_6Si_2$
Mol. Wt.: 598.83

Mp: >270 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (s, 1H), 9.14 (s, 1H), 8.28 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 2.4 Hz, 2H), 7.24 (dd, J = 8.2, 2.6 Hz, 2H), 1.01 (s, 18 H), 0.30 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.8 (s), 180.7 (s), 161.9 (s), 137.0 (s), 136.6 (s), 135.6 (s), 130.4 (d), 127.5 (s), 127.1 (d), 127.0 (d), 126.5 (d), 117.7 (d), 25.5 (q), 18.3 (s), −4.3 (q); IR ($CDCl_3$) ν 2955.8, 2927.2, 1675.0, 1590.9 cm^{-1}; MS (EI) m/z 541.2 ($M^+ - t$-Bu, 15), 504.9 (3), 162.0 (18), 57.1 (100); HRMS calcd for $C_{30}H_{29}O_6Si_2$ 541.1502 ($M^+ - t$-Bu), found 541.1516.

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Supporting Information Available: Experimental methods and characterization data for new compounds and complete ref 4 and CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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