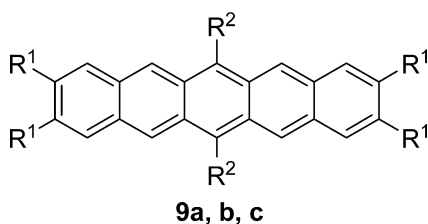## Design, Synthesis, and Properties of New Derivatives of Pentacene

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9a, b, c

Stable, soluble ethynylated derivatives of pentacene (**9a**−**c**) were synthesized, and the ethynyl moieties on the terminal rings were used to tune the electronic properties of these compounds. Their oxidation potentials are higher and their reduction potentials are lower than those of pentacene. The HOMO−LUMO gaps are among the lowest reported for pentacene derivatives.

Pentacene has been extensively studied as an active material in organic field effect transistors (OFET) because of its high hole transport mobility (p-type semiconductor).[1−5] Its practical uses are limited by its sensitivity to air (O_2), poor solubility in common organic solvents, and herringbone packing in the solid state.[6−8] It is well-known that the performance of electronic devices is related not only to the properties of individual molecules but also to their spatial arrangements in the solid state. Many research groups are currently working on the design and synthesis of novel substituted pentacenes seeking improved performance in OFETs. Anthony et al. reported that attaching trialkylsilylethynyl moieties in the center ring not only imparted solubility to the pentacene derivatives but also enhanced

π-stacking in the solid state.[9−11] Introducing substituents on the 2, 3, 9, and 10 positions of the terminal rings variously affects the electronic properties due to the different electronic properties of the substituents.[12−15] In this Note, in an attempt to produce stable, soluble derivatives of pentacene that might evidence modified π-stacking and rationally modifiable electronic properties, we report the successful synthesis and the electronic properties of three novel derivatives of pentacene. Furthermore, we report the successful introduction of ethynyl moieties on both the central ring and the terminal rings.

We designed an eight-step synthetic scheme (Scheme 1). By starting with commercially available phthalimide **1**, iodization[16] and subsequent hydrolysis yielded the desired 4,5-diiodobenzene-1,2-dicarboxylic acid **3** in moderate yield (65%) on a scale of tens of grams. Via BH_3 reduction, **3** was converted to dimethanol **4**, which was then oxidized to the corresponding 4,5-diiodobenzene-1,2-dicarbaldehyde in good yield with a modification of a literature procedure.[17] Sonogashira coupling[18] between **5** and four different terminal alkynes led to **6a**−**d**. A subsequent 4-fold aldol condensation between ethynylated phthalaldehydes and 1,4-cyclohexanedione[19] was efficient in yielding pentacenequinones (100%−60%). Pentacenequinones were converted to the corresponding pentacenediols using a standard ethynylation approach.[9,20,21] To avoid purifying final products at the last step, the pentacenediols were separated and purified to the extent that they passed elemental analysis prior to their subsequent use. This strategy turned out to be practical and produced pentacenes **9a**−**c** of good quality (Table 1). Up to now, we have failed to separate **9d**, in that it was unstable and decomposed during workup. A similar report was documented by Anthony et al. in attempts to prepare acyclic ethers of pentacene derivatives.[11] We are currently working on modifying the synthetic procedure to isolate **9d**. In general, the scheme proved viable in synthesizing new ethynyl derivatives of pentacene with acceptable yields; for example, the overall yield of **9a** is around 15%.

Compounds **9a** and **9b** are blue solids and are soluble in common organic solvents, whereas **9c** is a green-blue solid and is less soluble than the others. These compounds are stable when exposed to air under laboratory conditions in the solid state for months. If sealed free from air (O_2), solutions can be kept for

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(1) Würthner, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1037.
(2) Klauk, H.; Gundlach, J.; Nichols, J. A.; Sheraw, C. D.; Bonse, M.; Jackson, T. N. *Solid State Technol.* **2000**, *43*, 63.
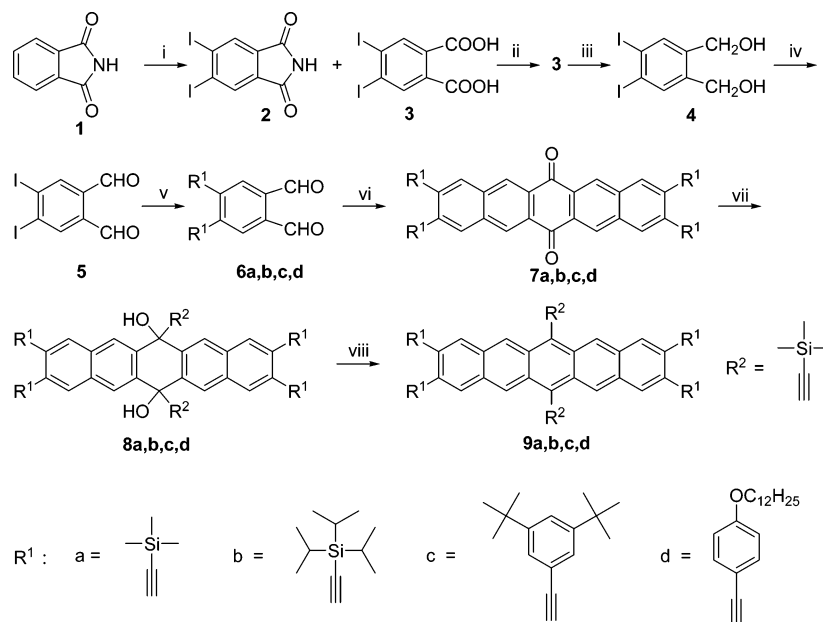(3) Nelson, S. F.; Lin, Y.-Y.; Gundlach, D. J.; Jackson, T. N. *Appl. Phys. Lett.* **1998**, *72*, 1854.
(4) Dimitrakopoulos, C. D.; Furman, B. K.; Graham, T.; Hedge, S.; Purushothaman, S. *Synth. Met.* **1998**, *92*, 47.
(5) Gundlach, D. J.; Lin, Y. Y.; Jackson, T. N.; Nelson, S. F.; Schlom, D. G. *IEEE Electron Device Lett.* **1997**, *18*, 87.
(6) Ponomarev, V. I.; Filipenko, O. S.; Atovmyan, L. O. *Kristallografiya* **1976**, *21*, 392.
(7) Brock, C. P.; Dunitz, J. D. *Acta Crystallogr., B* **1990**, *46*, 795.
(8) Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem.−Eur. J.* **1999**, *5*, 3399.
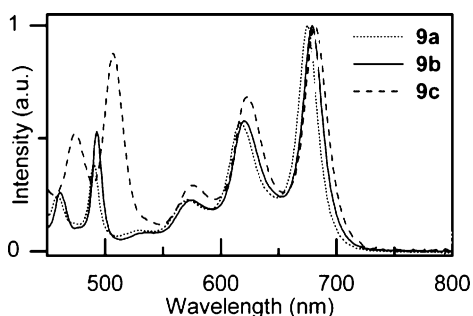
(9) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482.
(10) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15.
(11) Payne, M. M.; Delcamp, J. H.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 1609.
(12) Meng, H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegrist, T.; Kloc, C.; Chen, C.-H. *Adv. Mater.* **2003**, *15*, 1090.
(13) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138.
(14) Chan, S. H.; Lee, H. K.; Wang, Y. M.; Fu, N. Y.; Chen, X. M.; Cai, Z. W.; Wong, H. N. C. *Chem. Commun.* **2005**, *2005*, 66.
(15) Swartz, C. R.; Parkin, S. R.; Bullock, J. E.; Anthony, J. E.; Mayer, A. C.; Malliaras, G. G. *Org. Lett.* **2005**, *7*, 3163.
(16) Terekhov, D. S.; Nolan, K. J. M.; McArthur, C. R.; Leznoff, C. C. *J. Org. Chem.* **1996**, *61*, 3034.
(17) Perepichka, D. F.; Bendikov, M.; Meng, H.; Wudl, F. *J. Am. Chem. Soc.* **2003**, *125*, 10190.
(18) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.
(19) Ried, W.; Anthöfer, F. *Angew. Chem.* **1953**, *65*, 601.
(20) Funk, R. L.; Young, E. R. R.; Williams, R. M.; Flanagan, M. F.; Cecil, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 3291.
(21) Miller, G. P.; Mack, J.; Briggs, J. *Org. Lett.* **2000**, *2*, 3983.

SCHEME 1[a]

TABLE 1. Photophysical Properties of **9a−c**

entry	ϵ/M⁻¹ cm⁻¹ [a] (λmax/nm)	ϕ_{fl} benzene	ϕ_{fl} CH₂Cl₂	ϕ_{fl} THF	τ_{fl}/ns[b]
9a	105000 (676)	0.18	0.16	0.18	9.29
9b	22400 (679)	0.19	0.10	0.12	8.06
9c	12100 (681)	0.15	0.08	0.13	8.58

[a] Absorption in CH₂Cl₂. [b] Recorded in CH₂Cl₂ at room temperature.

TABLE 2. Electrochemical Properties[a]

entry	**9a**	**9b**	**9c**
E_{ox}/V	0.455	0.460	0.393
E_{red1}/V	−1.28	−1.30	−1.30
E_{red2}/V	−1.69	−1.69	−1.70
HOMO/LUMO gap/eV	1.735	1.760	1.693

[a] Performed in a 0.1 M solution of Bu₄NPF₆ in CH₂Cl₂ using a Pt electrode, a Ag/AgCl reference electrode, a scan rate of 150 mV/s, and Ferrocene as an internal reference.
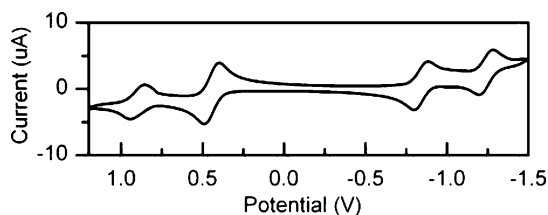

FIGURE 1. Absorption spectra of **9a−c** in CH₂Cl₂.

FIGURE 2. Cyclic voltammogram of **9a**. Recorded at the same conditions as those in Table 2.

weeks without change. When saturated with O₂, the solutions are also quite stable, an increased stability that can be partly explained by their low LUMO orbital energy compared to that of pentacene.[22] We recorded absorption (Figure 1) and emission spectra, as well as cyclic voltammograms (Table 2 and Figure 2), for each. In solution, these compounds were strongly absorbing evidencing large molar extinction coefficients (Table 1) and fluoresced in the deep red region, though the Stokes shift was small. Compared to 6,13-bis(triisopropylsilylethynyl)-pentacene,[9] **9a−c** each evidenced a relative red shift of at least 30 nm in their absorptions, indicating extended π-conjugation

along the long axis of the molecules. Fluorescence was most efficient in benzene, and fluorescence quantum yields, which were less than 20%, were measured in benzene, CH₂Cl₂, and THF. The fluorescence bands were narrow ($h_{1/2}$ of **9a−c** is 32, 38, and 39 nm, respectively). A lifetime of ca. 10 ns was observed for each in CH₂Cl₂ at room temperature (Table 1). No phosphorescence was observed at room temperature.

Compounds **9a−c** show one reversible oxidation and two reversible reductions (Table 2). Their oxidation and reduction potentials are quite comparable to those of 2,3,9,10-tetrabromo-6,13-bis(triisopropylsilylethynyl)pentacene but significantly different from those of 6,13-bis(triisopropylsilylethynyl)pentacene.[15] The compounds demonstrate almost the same reduction potentials, but **9c** differs in oxidation potential from **9a** and **9b**. Correspondingly, the LUMO energy level was essentially

(22) Maliakal, A.; Raghavachari, K.; Katz, H.; Chandross, E.; Siegrist, T. *Chem. Mater.* **2004**, *16*, 4980.
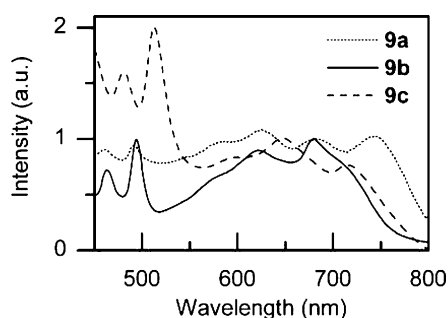
FIGURE 3. Thin-film absorption spectra of **9a**−**c**.

unchanged from each at −1.30 eV (vs ferrocene), whereas **9c** differs in the HOMO energy level from **9a** and **9b**. The difference in the HOMO energy level may be attributed to the weakly π-donating property of 3,5-di-*tert*-butylphenyl moieties and the weakly π-accepting property of the silyl groups. We anticipate that attaching different electron-donating or -accepting moieties to the terminal rings of pentacene may tune or even alter the electronic properties of pentacene derivatives. The attachment of substituents on the terminal ring can be realized by the reliable palladium-based coupling reaction with 4,5-diiodobenzene-1,2-dicarbaldehyde. The HOMO−LUMO gaps estimated from the oxidation and reduction potentials are 1.735, 1.760, and 1.693 eV for **9a**, **9b**, and **9c**, respectively. Those values are among the lowest HOMO−LUMO gaps reported in the literature for pentacene derivatives.[12−15]

Compared with their absorptions in solution, compounds **9a**−**c** all demonstrated a significant red shift (or displacement) of the absorption spectrum in thin films grown from their CHCl₃ solutions (Figure 3). The red shifts, characteristic for conjugated organic compounds, indicate strong electronic interaction between molecules in the films.[23,24] A displacement of 68, 37, and 35 nm with respect to the absorptions in CH₂Cl₂ solutions was obtained in films for compounds **9a**, **9b**, and **9c**, respectively. In addition, peak broadening was also observed in their thin-film absorptions, indicating strong intermolecular interaction. These thin films were quite stable. When exposed to the light and air in the lab, no significant change was observed in their absorptions for two weeks.

We have shown that the synthetic scheme designed is viable for the preparation of symmetrical silylethynylated pentacenes. The attachment of ethynyl moieties on terminal rings offers more opportunities to tune the electronic properties of the molecules. Prompted by the results that they are soluble and stable and by their strong aggregation in thin films, investigation of their potential charge-carrier mobility is currently underway.

Experimental Section

4,5-Diiodobenzene-1,2-dicarbaldehyde (5). Oxalyl chloride (10 mL, 0.116 mol) was dissolved in CH₂Cl₂ (187 mL) at −78 °C. A solution of DMSO (18.75 mL, 0.264 mol) in CH₂Cl₂ (37.5 mL) was added in 2.5 h. The solution was stirred at −78 °C for another 10 min. A solution of **4** (14.6 g, 0.037 mol) in DMSO (7.5 mL) and THF (75 mL) was added slowly in 1.5 h at −78 °C. After the reaction mixture was stirred at −78 °C for 5 h, NEt₃ (53 mL) was slowly added. The temperature was raised slowly to room temper-

ature, and the reaction mixture was stirred overnight. Water and CH₂Cl₂ were added to the reaction mixture in sequence. The CH₂-Cl₂ extract was dried over anhydrous Na₂SO₄ and concentrated to dryness. Chromatography of the residue with CH₂Cl₂ afforded **5** (13.73 g, 95%). Mp: 185 °C (dec.). ¹H NMR (300 MHz, CDCl₃): δ 10.414 (2H, s), 8.373 (2H, s). ¹³C NMR (75 MHz, THF-d_8): δ 191.1, 141.9, 137.2, 116.2. IR (neat): 1692. HREI: calcd for (C₈H₄O₂I₂) 385.830 083, found 385.829 281.

4,5-Bis(trimethylsilylethynyl)benzene-1,2-dicarbaldehyde (6a). **5** (0.772 g, 2 mmol), trimethylsilylacetylene (0.45 mL, 3.2 mmol), CuI (0.03 g, 0.16 mmol), and Pd(PPh₃)₂Cl₂ (0.056 g, 0.08 mmol) were put together and purged with argon for 10 min. THF (20 mL) and NEt₃ (8 mL) were added in sequence. The reaction mixture was stirred at room temperature under argon overnight. After all solvents were removed, CH₂Cl₂ and water were added to the residue. The CH₂Cl₂ layer was separated and dried with anhydrous Na₂SO₄. Removal of CH₂Cl₂ resulted in a solid residue. Chromatography of the residue with CH₂Cl₂ gave a yellow solid (**6a**, 0.52 g, 79%). Mp: 135−137 °C. ¹H NMR (300 MHz, CDCl₃): δ 10.457 (2H, s), 8.025 (2H, s), 0.299 (18H, s). ¹³C NMR (75 MHz, CDCl₃): 190.9, 134.9, 134.7, 130.9, 104.88, 101.3, −0.25. IR (neat): 1694. HREI: calcd for (C₁₈H₂₂O₂Si₂) 326.115 837, found 326.115 193.

2,3,9,10-Tetrakis(trimethylsilylethynyl)-6,13-pentacenequinone (7a). **6a** (0.163 g, 0.5 mmol) and 1,4-cyclohexanedione (0.031 g, 0.276 mmol) were dissolved in C₂H₅OH (9 mL) at room temperature. KOH (1 M aqueous, 0.1 mL) was added to it. The reaction mixture was stirred at 55 °C for 5 min. The red-brown precipitate was collected with vacuum filtration, washed with water, and then dried at 60 °C in a vacuum oven overnight to give a yellow solid **6a** (0.102 g, 60%). Mp: >320 °C. ¹H NMR (300 MHz, THF-d_8): δ 8.833 (4H, s), 8.369 (4H, s), 0.329 (4H, s). ¹³C NMR (75 MHz, THF-d_8): δ 182.0, 135.1, 135.0, 132.8, 129.5, 126.38, 103.6, 101.0, 0.1. IR (neat): 1675. HREI: calcd for (C₄₂H₄₄O₂Si₄) 692.241 845, found 692.242 263.

2,3,6,9,10,13-Hexa(trimethylsilylethylnyl)-6,13-dihydropentacene-6,13-diol (8a). Isopropylmagnesium chloride (2 M in THF, 2.2 mL, 4.4 mmol) and trimethylsilylacetylene (0.62 mL, 4.35 mmol) were dissolved in THF (5 mL) and heated for 2 h at 60 °C. **7a** (0.22 g, 0.32 mmol) was added. The reaction mixture was stirred at 60 °C overnight and quenched by adding 6% aqueous NH₄Cl. CH₂Cl₂ was added. The CH₂Cl₂ extract was washed with saline twice and then with water and dried with anhydrous Na₂SO₄. Removal of CH₂Cl₂ resulted in a solid residue, chromatography of which with CH₂Cl₂/hexane (2:1) produced a yellow solid **8a** (0.192 g, 67%). Mp: 250 °C (dec.). ¹H NMR (300 MHz, THF-d_8): δ 8.505 (4H, s), 8.110 (4H, s), 5.960 (2H, s), 0.307 (36H, s), 0.210 (18H, s). ¹³C NMR (75 MHz, THF-d_8): δ 140.3, 133.3, 132.8, 126.1, 123.5, 109.1, 104.4, 98.3, 91.2, 69.4, 0.4, 0.2. IR(neat): 2143, 839. Anal. Calcd: C, 70.21; H, 7.25. Found: C, 70.16; H, 7.31.

2,3,6,9,10,13-Hexa(trimethylsilylethynyl)pentacene (9a). **8a** (0.136 g, 0.15 mmol) was dissolved in THF (5 mL). A solution of SnCl₂ (0.172 g) in 3 M HCl (0.86 mL) was added with a syringe under argon. The reaction mixture was sonicated for 2.5 h. Filtration under argon gave a deep blue solid **9a** (0.124 g, 95%). Mp: 285 °C (dec.). ¹H NMR (300 MHz, CDCl₃): δ 9.047 (4H, s), 8.198 (4H, s), 0.557 (18H, s), 0.361 (36H, s). ¹³C NMR (75 MHz, CDCl₃): δ 133.7, 131.0, 130.6, 126.4, 121.7, 118.9, 111.3, 103.5, 102.0, 99.2, 0.3, 0.1. IR(neat): 2144, 837. HRFAB: calcd for (C₅₂H₆₂Si₆ + H) 855.354 548, found 855.355 000.

(23) Ostroverkhova, O.; Shcherbyna, S.; Cooke, D. G.; Egerton, R. F.; Hegmann, F. A.; Parkin, S. R.; Anthony, J. E. *J. Appl. Phys.* **2005**, *98*, 033701.

(24) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic crystals and Polymers*, 2nd ed.; Oxford University Press: New York, 1999.

Supporting Information Available: Synthetic procedures and characterization of **3** and **4**. Characterization of **6b−d**, **7b−d**, **8b−d**, and **9b,c**. Spectral data of compounds in Scheme 1. Fluorescence spectra of **9a−c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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