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A Road Map to Stable, Soluble, Easily Crystallized Pentacene Derivatives

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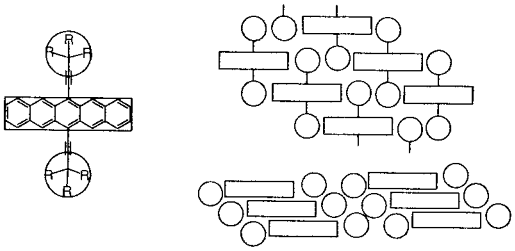
ABSTRACT



A series of 6,13-disubstituted pentacenes, in which the substituents are functionalized ethyne units, were synthesized and analyzed by X-ray crystallography. The resulting pentacene derivatives were highly soluble and oxidatively stable and exhibited a significant amount of π-stacking in the crystal.

Organic semiconductors based on extended aromatic systems are growing in importance as components for electronic devices.[1] Recent studies on the solid state order of these materials in relation to device performance, particularly in the area of thin-film transistors (TFTs), have served to underscore the importance of molecular close contacts and π-stacking to the fabrication of efficient devices: materials that yield ordered, π-stacked arrays in the solid state lead to devices with significantly higher charge mobilities.[2] Pentacene, one of the most promising organic compounds for device applications,[3] has a crystalline order (often referred to as "herringbone" packing) with only minimal π-stacking (Figure 1).[4]

This solid-state order results in a poor dispersion of the electronic bands in the solid, implying that pentacene's transport properties may be limited by its crystal packing.[5] Recent studies on a new crystalline polymorph of pentacene have shown that even slight increases in carbon−carbon close contacts lead to dramatically improved device function.[6] Numerous attempts have been made to increase close contacts and π-stacking in pentacene by variations in deposition methods or by substrate modification.[7] We report here our approach to increasing pentacene π-stacking by directed functionalization.

Approach. Apart from the potential for improved electronic properties, acenes are an attractive target for an exercise in noncovalent self-assembly because they are rigid, elongated plate-shaped molecules with no hydrogen bonding groups to consider.[8] Thus, the crystalline state can be controlled by consideration of size, shape, and aromatic interactions (both edge-to-face and face-to-face). The her-

Figure 1. Solid-state order of unsubstituted pentacene.

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[1] For a recent review, see: Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359.

[2] (a) Li, X.-C.; Sirringhaus, H.; Garnier, F.; Holmes, A. B.; Moratti, S. C.; Feeder, N.; Clegg, W.; Teat, S. J.; Friend, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 2206. (b) Garnier, F.; Horowitz, G.; Fichou, D.; Yassar, D. *Synth. Met.* **1996**, *81*, 163. (c) Dimitrakopoulos, C. D.; Furman, B. K.; Graham, T.; Hegde, S.; Purushothaman, S. *Synth. Met.* **1998**, *92*, 47. (d) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. *Adv. Mater.* **1997**, *9*, 36.

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ringbone packing motif of unsubstituted pentacene represents a simple combination of edge-to-face and face-to-face interactions.

Our goal is to disrupt edge-to-face interactions by substitution at one or more of the *peri* positions of the acene with a relatively bulky group. This substituent must be chosen with care: if this group were attached directly to the acene, π-stacking interactions would also be disrupted. We therefore separate the substituent from the acene by a rigid alkyne spacer (Figure 2, left). The only strong interaction left to influence solid-state order is thus aromatic face-to-face interactions, which we assume will lead to a separation between acene planes of 3.4 Å. For derivatives with approximately spherical alkyne substituents, the most efficient two-dimensional packing is shown in Figure 2 (right). This arrangement requires a ~7 Å diameter for the substituent, since *two* of these units must occupy the same in-plane area as *one* pentacene unit (length ~ 14 Å).[9] The third dimension of the crystal (the π-stacking axis) will be comprised of slip-stacked pentacene units, with the spacing between the stacks related to the size of the substituent. The size of the substituent will also influence the amount of π-overlap along the pentacene long axis between any two adjacent acenes.

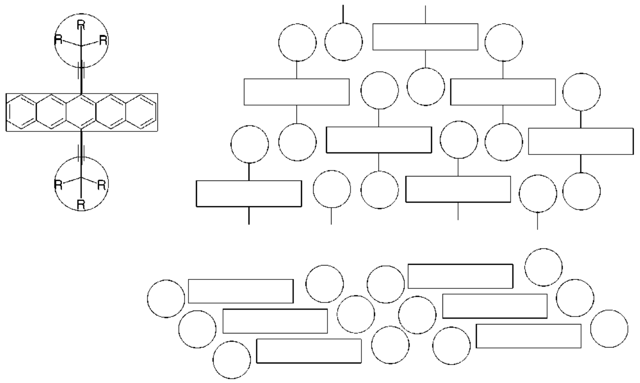
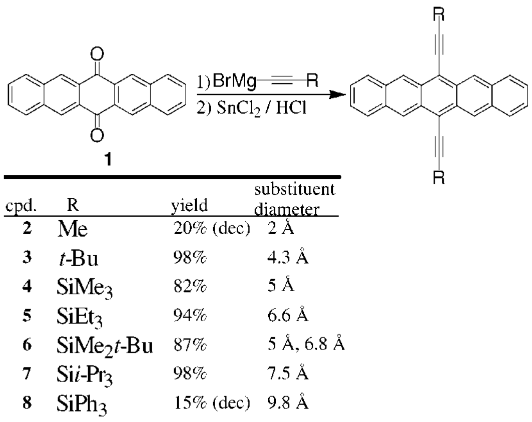


Figure 2. Strategy to enhance π-stacking in substituted pentacene. Left: Representation of substituted pentacene. Right, top: Expected order, view normal to plane of aromatic rings. Right, bottom: Expected order, view normal to short axis of aromatic rings, showing slip-stacking of the acenes.

Synthesis. Pentacenes substituted at the 6,13-positions are easily prepared from pentacenequinone by methods that have been known since the 1940s (Scheme 1).[10] Pentacenequinone is added to a solution of the alkynyl Grignard reagent in THF and stirred at 60 °C until it dissolves. To this solution is then carefully added a solution of 10% HCl that has been saturated with stannous chloride; the deep blue pentacene is formed immediately. Workup involves flushing this solution through a pad of silica gel with methylene chloride, evaporation, and recrystallization. Noteworthy is the excellent yield of this reaction: the formation of aryl or alkyl pentacenes by this method typically gives yields less than 40%.[11] Derivatives **2**−**8** are easily prepared on a multigram scale from relatively inexpensive starting materials; all are soluble in common organic solvents, and most of these derivatives crystallize readily from organic solvents.

Scheme 1. Functionalized Pentacene Synthesis



cpd.	R	yield	substituent diameter
2	Me	20% (dec)	2 Å
3	*t*-Bu	98%	4.3 Å
4	$SiMe_3$	82%	5 Å
5	$SiEt_3$	94%	6.6 Å
6	$SiMe_2$*t*-Bu	87%	5 Å, 6.8 Å
7	Si*i*-Pr_3	98%	7.5 Å
8	$SiPh_3$	15% (dec)	9.8 Å

Solid-State Analysis. Single crystals of derivatives **3**−**7** were analyzed by X-ray crystallography. The solid-state arrangement we envisioned (Figure 2) does indeed describe the general crystalline order for compounds **3**−**5** and for one of the polymorphs of **6** (the *tert*-butyldimethylsilyl (TBDMS) group is elliptical rather than spherical; thus, derivative **6** crystallized in two different polymorphs, **6** and **6′**). Interplane distance for all of these pentacene derivatives is 3.41 ± 0.03 Å (essentially at a van der Waals radius). This arrangement of acenes leads to an excellent overlap of the acene π-surfaces between adjacent molecules in the stack. A typical example (the trimethylsilyl derivative **4**) is shown in Figure 3. While the size of the alkyne substituent does indeed influence the amount of $\pi-\pi$ overlap along the pentacene long axis, unpredictable slipping along the pentacene *short*

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(3) (a) Schön, J. H.; Kloc, Ch.; Batlogg, B. *Science* **2000**, *288*, 2338. (b) Schön, J. H.; Berg, S.; Kloc, Ch.; Batlogg, B. *Science* **2000**, *287*, 1022. (c) Schön, J. H.; Kloc, Ch.; Batlogg, B. *Science* **2000**, *406*, 702. (d) Schön, J. H.; Kloc, Ch.; Bucher, E.; Batlogg, B. *Synth. Met.* **2000**, *115*, 177. (e) Dimitrakopoulos, C. D.; Purushothaman, S.; Kymissis, J.; Callegari, A.; Shaw, J. M. *Science* **1999**, *283*, 822. (f) Dimitrakopoulos, C. D.; Kymissis, J.; Purushothaman, S.; Neumayer, D. A.; Duncombe, P. R.; Laibowitz, R. B. *Adv. Mater.* **1999**, *11*, 1372.

(4) Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem. Eur. J.* **1999**, *5*, 3399.

(5) Cornil, J.; Calbert, J. Ph.; Brédas, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 1250.

(6) Siegrist, T.; Kloc, C.; Schön, J. H.; Batlogg, B.; Haddon, R. C.; Berg, S.; Thomas, G. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1732.

(7) Gundlach, D. J.; Lin, Y. Y.; Jackson, T. N.; Nelson, S. F.; Schlom, D. G. *IEEE Electron Device Lett.* **1997**, *18*, 87.

(8) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: New York, 1989.

(9) Substituted pentacenes were constructed in the MacSpartan program (version 1.1.7, Wavefunction, Inc.). All distances reported are internuclear distances.

(10) (a) Allen, C. F. H.; Bell, A. *J. Am. Chem. Soc.* **1942**, *64*, 1253. (b) Funk, R. L.; Young, E. R. R.; Williams, R. M.; Flanagan, M. F.; Cecil, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 3291. (c) Miller, G. P.; Mack, J.; Briggs, J. *Org. Lett.* **2000**, *2*, 3983.

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

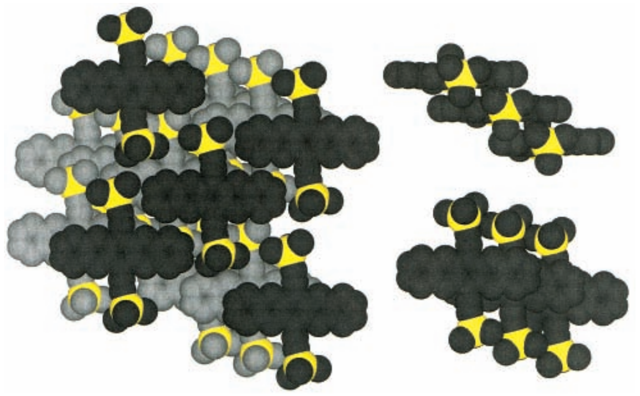

Figure 3. Crystallographic order of compound **4**. Left: View normal to the plane of the pentacenes (cf. Figure 2). Top right: View down the short axis of the pentacene showing slip-stacking. Bottom right: Top−down view of slip-stack.

axis (Figure 3, lower right) precludes the development of a general formula relating substituent size to total π-overlap. Among these derivatives, projected π-overlap varies from 20% π-surface overlap for **6** to nearly 40% π-surface overlap for **5**.[12]

Among the derivatives **3**−**6**, the only significant deviation from the pattern described in Figure 2 occurs when the diameter of the substituent is *significantly* smaller than 7 Å (e.g., the *tert*-butyl group). While the view down the crystallographic *b*-axis (Figure 4, left) closely resembles the expected view described in Figure 2, an examination of the view at 90° to that axis reveals that the pentacene ring systems of adjacent stacks are not parallel. To accommodate the small substituent, the pentacene units of this derivative must move closer together, which requires the pentacenes in adjacent stacks to tilt in opposite directions (Figure 4, center). Although adjacent stacks are significantly tilted with respect to each other, the molecules within each stack are still slip-stacked (Figure 4, right), with good π-overlap within each stack.

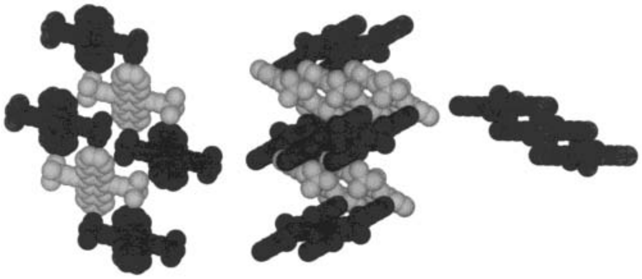

Figure 4. Crystallographic order of compound **3**. Left: View down crystallographic *b*-axis. Middle: View 90° to crystallographic *b*-axis showing “tilted” pentacene stacks. Right: Within each slip-stacked column, the pentacene units maintain significant π-overlap.

Groups smaller than *tert*-butyl do not occupy enough volume to fulfill the requirements for packing as described in Figure 2, explaining why methyl derivative **2** formed amorphous powders rather than crystals. As has been reported for other pentacene derivatives, stability in these systems is highly dependent on substitution.[13] Here, pentacene derivatives with substituents that did not enhance crystallinity were not stable in the solid state. Thus, powders of compound **2** begin to show a color change signifying decomposition within hours after isolation.

If the diameter of the alkyne substituent is significantly *larger* than 7 Å (i.e., roughly twice the pentacene stack spacing), the solid-state ordering described in Figure 2 can no longer hold, and the arrangement of molecules in the solid-state becomes more difficult to predict. For the triphenylsilyl derivative **8**, we were only able to isolate powders that decomposed rapidly, implying (by analogy with the methyl derivative **2**) that there is no efficient solid-state arrangement for pentacenes with such large substituents. As we have reported previously, the triisopropylsilyl derivative **7** packs with the silyl groups segregated from the pentacene units, leading to a two-dimensional “running bond” packing of the acenes.[14]

In the second polymorph of the TBDMS derivative (**6′**), both of the bulky *tert*-butyl groups point toward the same end of the molecule, making the packing described in Figure 2 impossible. This polymorph crystallizes as columnar stacks of pentacenes, with the *tert*-butyl groups alternating to avoid interaction down the stack (Figure 5).

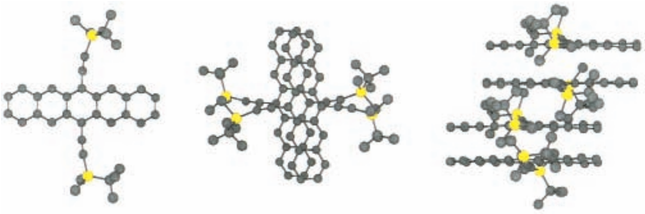

Figure 5. Crystallographic order of compound **6′** (second polymorph of **6**). Left: Single molecule showing distorted alkynes. Middle: View down a column of pentacene units. Right: Columnar order, view down the pentacene short axis.

The severe distortion of the alkynes caused by crystallization in the polymorph depicted in Figure 5 ($C_{Ar}-C_{sp}-C_{sp} = 173°$ and $C_{sp}-C_{sp}-Si = 168°$), as well as the excellent π-overlap present in the columnar arrangement of the acenes, led us to consider whether we could induce a similar columnar motif without alkyne distortion by preparing an

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[12] Overlap refers to the projected area shared between two stacked pentacene units.

(13) Miller, G. P.; Mack, J. *Org. Lett.* **2000**, *2*, 3979.

(14) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482.

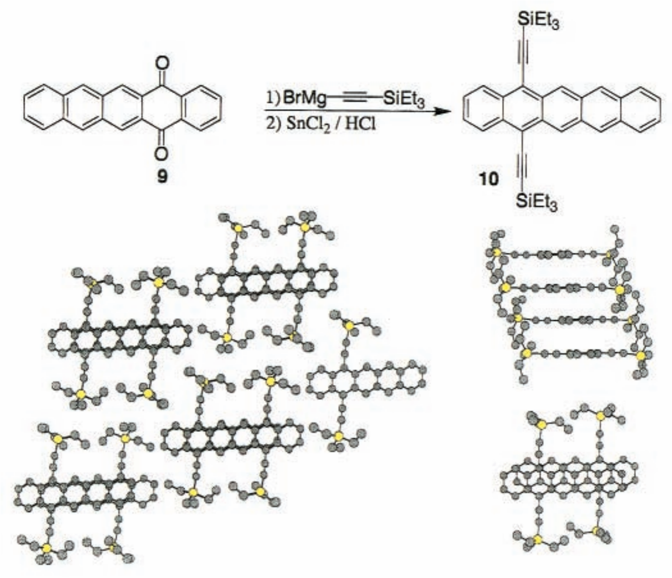

Figure 6. Synthesis and crystallographic order of **10**. Left: View down crystallographic *b*-axis. Top right: Single column, view down pentacene long axis. Bottom right: View normal to the plane of the pentacenes showing significant π-overlap.

unsymmetrical (offset) pentacene derivative. We reasoned that an alkyne substituent on the offset pentacene with a diameter slightly smaller than the *long* axis of the TBDMS group (6.8 Å) should allow columnar packing without distortion. Thus, triethylsilyl derivative **10** was prepared, which did indeed crystallize in nearly columnar stacks, with no distortion of the alkyne and with excellent overlap (~55% projected area overlap) between adjacent molecules in the stack.

Although the amount of π-overlap varies significantly between these derivatives, particularly when comparing slip-stacked **3**−**6** with columnar-stacked **10**, this difference has little bearing on the resistivity of the crystals. Along the π-stacking axis, resistivities were relatively consistent from derivative to derivative, with an average of ~10^8 ohm cm.[15] Any slight variation in measured resistivity across this series of derivatives appears to arise more from changes in orientation of the pentacene units in the stack than from the absolute amount of π-overlap.[16]

With several stable, crystalline pentacene derivatives in hand, we were anxious to determine whether any of these derivatives possessed crystalline order when prepared as thin films. Due to their remarkably high solubility, acceptable thin films of the invariably nonviscous solutions of these pentacene derivatives could not be formed by spin-casting techniques. We thus turned to thin film deposition by evaporation, which provided uniform thin films (~1000 Å) of **3**−**6** and **10**. The stability of the various pentacene derivatives in thin films was revealed almost immediately: while all of these pentacene derivatives were stable as crystals, films of the offset compound **10** decomposed within a few hours, turning from the deep blue color of pentacene to pale yellow. Stable films of **3**−**6** were analyzed by powder X-ray diffraction analysis showing that, for the most part, these materials possessed little crystalline order. Only the TMS derivative **4** showed weak absorptions distinguishable above baseline noise, giving a *d*-value of ~4.4 Å. This spacing would correspond to the pentacene π-face stacking on the glass substrate, leading to slip-stacked columns growing perpendicular to the glass.

In conclusion, we have developed a functionalization model for pentacene that yields materials that crystallize with a predominant π-stacked order. We have demonstrated a simple method for the preparation of these stable, soluble pentacene derivatives, leading to materials that are easily crystallized from organic solvents. All of these compounds possessed resistivities several orders of magnitude lower than that measured in crystals of unsubstituted pentacene. Although evaporated thin films of these materials did not show a high degree of crystalline order, we are still investigating their applicability to electronic device fabrication.

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Supporting Information Available: Spectroscopic data for compounds **3**−**6** and **10** and crystallographic data for compounds **3**, **4**, **6′**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] This value is still several orders of magnitude lower than that reported for unsubstituted pentacene (10^{14} ohm cm: Schön, J. H.; Kloc, Ch.; Batlogg, B. *Appl. Phys. Lett.* **2000**, *77*, 2473).

[16] A more detailed study of the electronic and photophysical properties of these crystals is currently underway: Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Matson, J. R. Manuscript in preparation.