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Letter

Planar versus Twist: Two Conformers of a 5,7,12,14-Tetrakis(triisopropylsilylethynyl)pentacene in the Solid State

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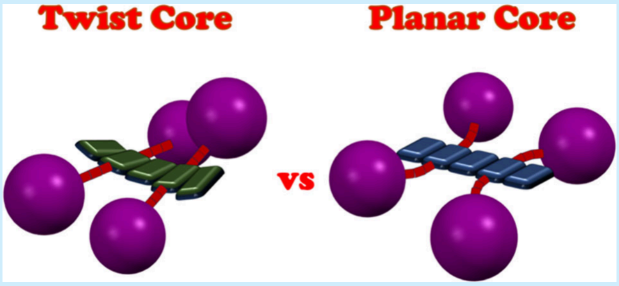
ABSTRACT: We synthesized **4TIPS-pen**, a pentacene derivative bearing TIPS-ethynyl groups at the 5,7,12,14-positions via a modified route. The compound showed polymorphism, forming green crystals with a twisted backbone and blue crystals with a planar backbone. UV−vis spectra and theoretical calculations revealed distinct optical behaviors linked to structural differences. **4TIPS-pen** is photo-unstable, and we confirmed the product structure using X-ray analysis. These results highlight structure−property relationships and offer design guidelines for extended π-conjugated pentacenes.



Acenes are renowned for their exceptional optical properties, which result from effective conjugation, and are utilized in electronic materials such as organic transistors.[1] As the conjugated system expands, the carrier mobility and other functions of acenes improve. At the same time, higher acenes beyond pentacene show significantly reduced stability and solubility in organic solvents, making pentacene the most studied compound both practically and in fundamental research.[2] One of the most direct strategies to address these issues is the introduction of suitable substituents. The formation of parent pentacene and higher acenes without substituents is currently limited to experimental techniques such as on-surface synthesis under inert conditions.[3]

The triisopropylsilyl (TIPS)-ethynyl-substituted pentacene at the 6,13-positions (**TIPS-pen**) is frequently examined as a benchmark for pentacene derivatives (Figure 1).[4] **TIPS-pen** was first reported by Anthony in 2001, and various analogues have been designed since then.[4,5] The advantages of the TIPS-ethynyl groups include 1) improved molecular solubility due to the bulky and stable TIPS groups, 2) expanded conjugation while maintaining planarity due to the acetylene triple bond, 3) control of packing in crystals, and 4) reversible detachment of the oxygen molecule at the 6,13-positions, resulting in stabilization against oxygenation.[6]

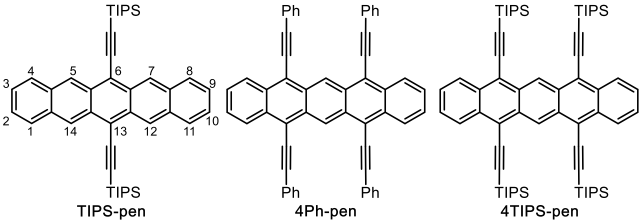


Figure 1. Pentacene derivatives bearing multiple π-conjugated substituents.

Most pentacene derivatives, including **TIPS-pen**, are disubstituted compounds introduced at the 6,13-positions. Compounds with substituents introduced at the other positions or with more than two substituents are rare.[7] **4Ph-pen** has phenyl-ethynyl groups introduced at 5,7,12,14-positions, exhibiting a long-wavelength shift in the maximum absorption wavelength to 705 nm in *o*-dichlorobenzene.[7] But it has the disadvantage of being insoluble in most organic solvents. No examples have been reported for nearly half a century, since the introduction of the same substituent that directly extends π-conjugation at the 5,7,12,14-positions.[8] Recently, Bunz reported the synthesis of 4-fold TIPS-ethynyl pentacene **4TIPS-pen** (Figure 1) to octacene and their physical properties as well as their stability in solution.[9] Meanwhile, in our independent efforts to create pentacene derivatives that exhibit absorption in the long-wavelength region by introducing four TIPS-ethynyl groups, we gained interesting insights into the crystal polymorphism of **4TIPS-pen**.

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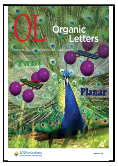

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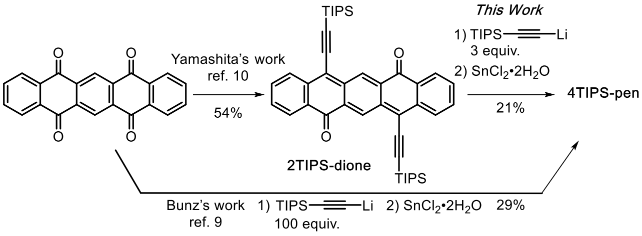
Here, we synthesized **4TIPS-pen** using a modified route that was not previously reported. **4TIPS-pen** exhibited crystalline polymorphism, yielding green and blue single crystals from the same solvent system. Single-crystal X-ray analysis revealed that the blue crystal has a structure where the pentacene skeleton is planar, while the green crystal has a twisted pentacene skeleton structure. The color difference was also examined by comparing the UV−visible absorption spectra of each single crystal.

In synthesizing **4TIPS-pen**, we referred to the report by Yamashita et al. in 2009.[10] They used commercially available 5,7,12,14-pentacene-tetraone as the starting material and synthesized the compound with TIPS-ethynyl groups introduced at the diagonal 5,12-positions (**2TIPS-dione**) (Scheme 1). They reported that only two positions reacted even when an excess amount of TIPS-acetylene was added; thus, we considered that by isolating this **2TIPS-dione** and performing the same reaction once again, it would be possible to introduce TIPS-ethynyl groups into the two remaining ketone positions.

Scheme 1. Synthesis of 4TIPS-pen



The synthesis of **4TIPS-pen** was performed according to Scheme 1. Although Bunz's group directly obtained **4TIPS-pen** from pentacene-tetraone in 29% yield, they need a large excess amount of lithiated TIPS-acetylene (100 equiv) in hexane.[9] In our synthetic route, 3 equiv of TIPS-ethynyl lithium were reacted with **2TIPS-dione** at room temperature for 24 h and the corresponding diol was reduced with $SnCl_2$ under hydrochloric acid conditions at 60 °C in an oil bath to obtain **4TIPS-pen** as a dark-green solid with a yield of 21%. When the reduction was carried out at room temperature, the yield was reduced to 10%.

The UV−vis absorption spectrum of **4TIPS-pen** showed a long-wavelength shift relative to those of pristine pentacene and **TIPS-pen** due to the introduction of the ethynyl groups. The maximum absorption wavelength in the absorption spectrum was observed to be slightly affected by the polarity of the solvents: in hexane (675 nm), dichloromethane (684 nm), chloroform (684 nm), chlorobenzene (687 nm), and tetrahydrofuran (690 nm) (Figure S7). No fluorescent emission was observed, probably because the thermal rotation of the bulky TIPS groups accelerated the nonradiative decay.

When the single crystals of **4TIPS-pen** were prepared using dichloromethane as the good solvent and methanol as the poor solvent at room temperature, green and blue crystals were obtained (Figure 2).[11] Under optical microscope observation, the number of blue crystals was less than that of green crystals (Figure S8). Analysis by single-crystal X-ray diffraction was successful for both.[12] It was found that the molecular structure in the green crystal (**4TIPS-pen(G)**) has a twisted pentacene skeleton (20.0°) while that in the blue crystal (**4TIPS-pen(B)**) has a flat pentacene skeleton with TIPS-ethynyl groups bent outward. The blue and green crystals had similar molecular packings within the crystals (Figure S9).

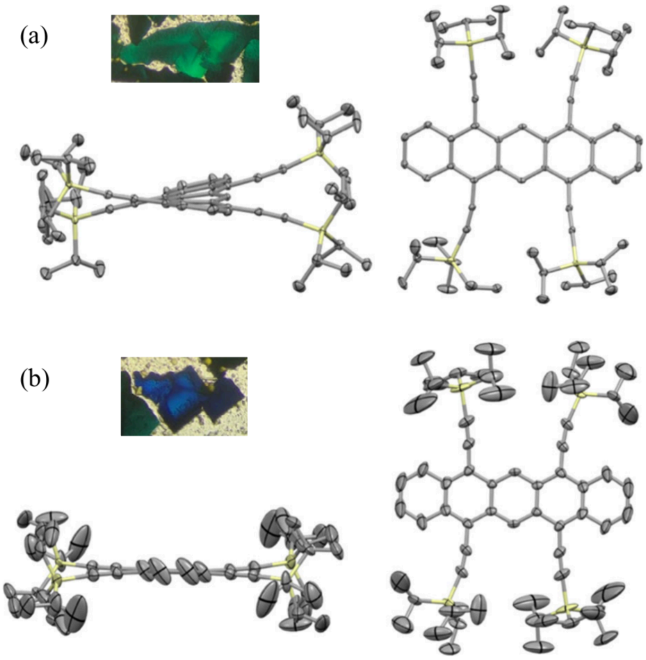


Figure 2. Single-crystal X-ray structures of (a) **4TIPS-pen(G)** and (b) **4TIPS-pen(B)** (top and side views) and photographs of crystals observed under an optical microscope. The ellipsoids are scaled at 50% probability. Hydrogen atoms and disordered parts were omitted for clarity.

The Δ*G* of each molecule in the crystal was calculated using density functional theory (DFT) methods (B3LYP/3-21G* level), and it was found that the structure in the blue crystal had a higher energy (ΔΔ*G* = 1.48 kcal/mol) than that in the green crystal. This result indicates that to mitigate the repulsion of bulky TIPS groups, twisting the pentacene plane can be achieved at a lower energy than distorting the four TIPS-ethinyl groups, which possess higher flexibility. That is, the blue crystals represent a kinetic product that precipitates at a relatively fast rate while the structure in the green crystals is a thermally stable one. According to these energy calculations, the phase-transition behavior between crystal polymorphs was investigated by heating the blue crystal by using a melting-point apparatus. As shown in Figure S10, the color of a crystal was observed to change from blue to green at 270−280 °C. Once the crystal color changed to green upon heating, the crystals did not regain their blue color even after cooling.

The UV−vis absorption spectra of these single crystals were recorded (Figure 3). That of **4TIPS-pen(G)** exhibits relatively large absorption at 400−440 nm for the $S_0 \rightarrow S_2$ transition compared to the 550−700 nm range for the $S_0 \rightarrow S_1$ transition. On the other hand, that of **4TIPS-pen(B)** exhibits comparatively small absorption at 400−440 nm. The fact that the oscillator strengths at 536 and 467 nm are zero for **4TIPS-pen(B)**, based on the time-dependent (TD)-DFT calculations, suggests that the $S_0 \rightarrow S_2$ absorption is symmetry-forbidden. In contrast, the oscillator strength at the same wavelengths is nonzero for **4TIPS-pen(G)**, indicating that $S_0 \rightarrow S_2$ absorption becomes partially allowed due to the twisting of the backbone. The absorption on the blue side (400−440 nm) could result in the green color of the crystal, which agrees with the experimental absorption spectrum.

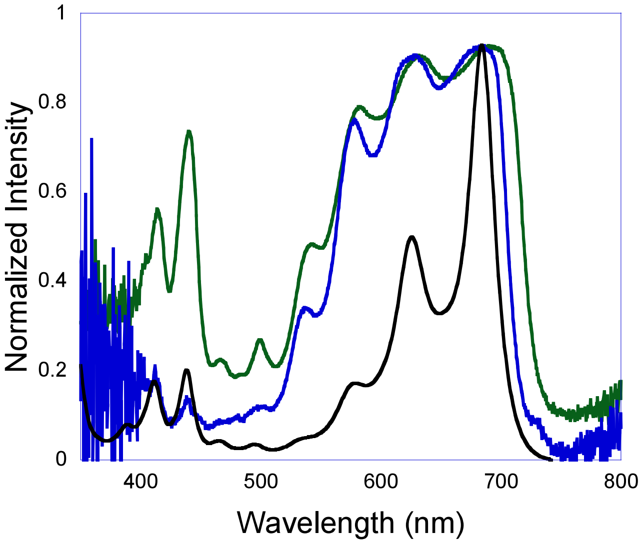


Figure 3. UV−vis absorption spectra of single crystals of **4TIPS-pen(G)** (green) and **4TIPS-pen(B)** (blue) along with that in $CHCl_3$ solution (black).

Higher acenes form endoperoxides by adding an oxygen molecule to the central benzene ring of the parent skeleton when exposed to light in the presence of oxygen.[6,13] We evaluated the photostability of **4TIPS-pen** by leaving it in a chloroform solution under ambient conditions. **4TIPS-pen** peaks in the ^{1}H NMR spectra completely disappeared after 2 weeks (Figure S11).[9] When a chloroform solution of **4TIPS-pen** was left in the dark, no significant changes were observed on the same time scale. This confirmed that **4TIPS-pen** is stable in solution under atmospheric conditions as long as it is protected from light.

The structure of the **4TIPS-pen(O_2)** photodegradation product was identified by ^{1}H NMR spectroscopy and single-crystal X-ray structural analysis (Figure 4).[12] The crystal structure confirms that the addition of an oxygen molecule causes the pentacene skeleton to bend at the central benzene ring and break the conjugation. The literature claims that anthracene endoperoxide readily converts to the corresponding quinone,[14] yet there are also reports indicating that the anthracene skeleton can be restored by heating.[15] We confirmed that heating **4TIPS-pen(O_2)** in degassed tetrachloroethane-d_2 at 120 °C in an oil bath resulted in its complete decomposition within 1 h.

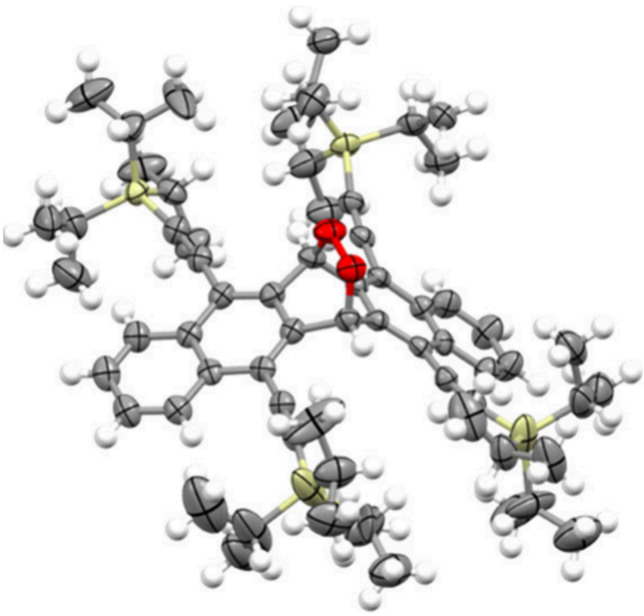


Figure 4. Single-crystal X-ray structure of the photodegradation product of **4TIPS-pen**. The ellipsoids are scaled at 50% probability. The disordered parts were omitted for clarity.

In summary, we synthesized pentacene derivative **4TIPS-pen** with TIPS-ethynyl groups introduced at the 5,7,12,14-positions via the modified synthetic route and evaluated its physical properties. **4TIPS-pen** exhibited polymorphic behavior, yielding green and blue single crystals from the same solvent system. Single-crystal X-ray analysis revealed that the blue crystal had a planar pentacene skeleton with TIPS-ethynyl groups bent outward while the green crystal had a twisted pentacene skeleton. It was found that the structure in the blue crystal had a higher energy than that in the green crystal. This indicates that the blue crystals represent a kinetic product while the structure in the green crystals is a thermally stable one. The color differences were also examined by comparing the UV−visible absorption spectra of each single crystal and TD-DFT calculations. The instability of **4TIPS-pen** was monitored by ^{1}H NMR, and we confirmed the structure of the endoperoxide product. These characteristics are unique to **4TIPS-pen**, which lacks substituents at positions 6 and 13. This study experimentally demonstrates insights into the physical properties and reactivity of the 5,7,12,14-tetrasubstituted pentacene derivative and provides useful guidelines for the molecular design of novel pentacene derivatives with extended π-conjugation.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.5c03674.

> Experimental procedures, compound characterization data, spectral data, X-ray structural data, and computational details (PDF)

Accession Codes

Deposition Numbers 2483982−2483984 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Author Contributions

The manuscript was written through the contributions of all authors.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Kitamura, M.; Arakawa, Y. Pentacene-based organic field-effect transistors. *J. Phys.: Condens. Matter* **2008**, *20*, 184011.

(2) Dimitrakopoulos, C. D.; Mascaro, D. J. Organic thin-film transistors: A review of recent advances. *IBM J. Res. Dev.* **2001**, *45*, 11–27.

(3) (a) Tönshoff, C.; Bettinger, H. F. Pushing the Limits of Acene Chemistry: The Recent Surge of Large Acenes. *Chem.—Eur. J.* **2021**, *27*, 3193–3212. (b) Lerena, L.; Zuzak, R.; Godlewski, S.; Echavarren, A. M. The Journey for the Synthesis of Large Acenes. *Chem.—Eur. J.* **2024**, *30*, No. e202402122. (c) Hayashi, H.; Yamada, H. Exploring the Chemistry of Higher Acenes: From Synthesis to Applications. *Chem. Sci.* **2025**, *16*, 11204–11231.

(4) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. Functionalized Pentacene: Improved Electronic Properties from Control of Solid-State Order. *J. Am. Chem. Soc.* **2001**, *123*, 9482.

(5) Sheraw, C. D.; Jackson, T. N.; Eaton, D. L.; Anthony, J. E. Functionalized Pentacene Active Layer Organic Thin-Film Transistors. *Adv. Mater.* **2003**, *15*, 2009.

(6) Fudickar, W.; Linker, T. Why Triple Bonds Protect Acenes from Oxidation and Decomposition. *J. Am. Chem. Soc.* **2012**, *134*, 15071–15082.

(7) (a) Maulding, D. R.; Roberts, B. G. Infrared Liquid-Phase Chemiluminescence from Reactions of Bis(2,4,6-trichlorophenyl) Oxalate, Hydrogen Peroxide, and Infrared Fluorescent Compounds. *J. Org. Chem.* **1969**, *34*, 1734–1735. (b) Rauhut, M. M.; Roberts, B. G.; Maulding, D. R.; Bergmark, W.; Coleman, R. Infrared liquid-phase chemiluminescence from reactions of bis(2,4,6-trichlorophenyl) oxalate, hydrogen peroxide, and infrared fluorescent compounds. *J. Org. Chem.* **1975**, *40*, 330–335.

(8) Glocklhofer, F.; Petritz, A.; Karner, E.; Bojdys, M. J.; Stadlober, B.; Frohlicha, J.; Unterlass, M. M. Dicyano- and tetracyanopentacene: foundation of an intriguing new class of easy-to-synthesize organic semiconductors. *J. Mater. Chem. C* **2017**, *5*, 2603–2610.

(9) Zeitter, N.; Hippchen, N.; Baur, P.; Unterreiner, T. V.; Rominger, F.; Freudenberg, J.; Bunz, U. H. F. Pentacene to Octacene: The Limit of Fourfold TIPS-Ethynylation. *Organic Materials* **2024**, *6*, 12–17.

(10) Nishida, J.-i.; Fujiwara, Y.; Yamashita, Y. Synthesis Crystal Structure, and Physical Properties of 7,14-Disubstituted Pentacene-5,12-diones Containing a Methylenequinoid Structure. *Org. Lett.* **2009**, *11*, 1813–1816.

(11) Previous research has also analyzed the same green single crystal (ref 9), but since it was measured at 200 K, we aligned the measurement conditions at 90 K this time for both.

(12) **4TIPS-pen(G)**: $C_{66}H_{94}Si_4$, Mw = 999.77, monoclinic, space group $C2/c$ (no. 15), a = 54.876(7), b = 14.8416(19), c = 15.1296(18) Å, β = 94.474(2)°, V = 12285(3) Å^3, Z = 8, T = 90(2) K, D_{calcd} = 1.081 g cm^{-3}, R_1 = 0.0619 ($I > 2\sigma(I)$), R_w = 0.1228 (all data), GOF = 1.090. **4TIPS-pen(B)**: $C_{66}H_{94}Si_4$, Mw = 999.77, monoclinic, space group $P2_1/c$ (no. 14), a = 15.538(2), b = 15.2022(19), c = 15.0461(19) Å, β = 118.252(2)°, V = 3130.7(7) Å^3, Z = 2, T = 90(2) K, D_{calcd} = 1.061 g cm^{-3}, R_1 = 0.1133 ($I > 2\sigma(I)$), R_w = 0.2776 (all data), GOF = 1.040. **4TIPS-pen(O_2)**: $C_{66}H_{94}O_2Si_4$, Mw = 1031.77, orthorhombic, space group $Pbca$ (no. 61), a = 15.986(2), b = 24.614(3), c = 32.352(4) Å, V = 12730(3) Å^3, Z = 8, T = 90(2) K, D_{calcd} = 1.077 g cm^{-3}, R_1 = 0.0781 ($I > 2\sigma(I)$), R_w = 0.2326 (all data), GOF = 1.172.

(13) Purushothaman, B.; Bruzek, M.; Parkin, S. R.; Miller, A.-F.; Anthony, J. E. Synthesis and Structural Characterization of Crystalline Nonacenes. *Angew. Chem., Int. Ed.* **2011**, *50*, 7013–7017.

(14) (a) Yamashita, K.-i.; Sugiura, K.-i. Photochemical reaction of anthracene with dioxygen catalyzed by platinum(II) porphyrin. *Tetrahedron Lett.* **2019**, *60*, 151081. (b) Do, T. A. T.; Imae, T. Photodynamic and Photothermal Effects of Carbon Dot-Coated Magnetite- and Porphyrin-Conjugated Confeito-Like Gold Nanoparticles. *Bull. Chem. Soc. Jpn.* **2021**, *94*, 2079–2088.

(15) (a) De Bonfils, P.; Nun, P.; Coeffard, V. Unsymmetrical Anthracene Platforms as Singlet Oxygen Batteries: Effects of Substituents on Photooxygenation and Endoperoxide Thermolysis. *Eur. J. Org. Chem.* **2024**, *27*, No. e202400099. (b) Klaper, M.; Wessig, P.; Linker, T. Base catalysed decomposition of anthracene endoperoxide. *Chem. Commun.* **2016**, *52*, 1210–1213.