JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

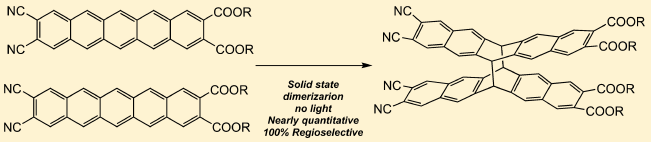
Face-to-Face Packing of 2,3,9,10-Tetrasubstituted Pentacene Derivatives Revealed through a Solid State [4 + 4] Thermal Cycloaddition and Molecular Dynamic Simulation

Bikash Pal, Bo-Chao Lin, Mark Vincent Carreon dela Cerna, Chao-Ping Hsu,* and Chih-Hsiu Lin*

Institute of Chemistry, Academia Sinica, Academia Road, Section 2, No. 128, Taipei, Taiwan, Republic of China

Supporting Information

ABSTRACT: 2,3,9,10-Substituted pentacene tetraesters and pentacene diester-dinitriles were synthesized. These pentacene derivatives underwent an unusual solid state [4 + 4] thermal dimerization with good efficiency and complete stereoselectivity. This observation indicates this series of pentacene derivatives adopt $\pi-\pi$ stacking geometry with large mutual overlap in solid state. This notion was confirmed by molecualr dynamic simulation.

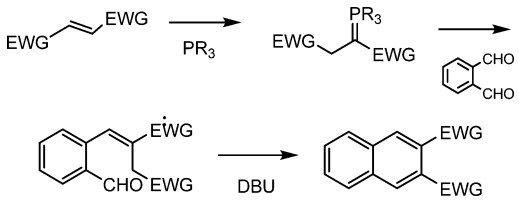


INTRODUCTION

The pursuit of organic electronic material has matured into an interdisciplinary research endeavor which unites synthetic chemistry, physical chemistry, and engineering.[1] In designing charge transporting materials, it is recognized that both the structures of the constitutive molecules and their solid state arrangement must be optimized to achieve high mobility.[2] As synthetic chemistry furnishes control over the molecular architecture, crystal engineering attempts to rationally design intermolecular packing pattern in searching for good organic charge transporters. By studying the crystal structures of a series of synthetic compounds, intermolecular forces governing solid state packing can be gradually tuned to achieve the optimal structure. However, two major obstacles must be overcome when applying this concept to pentacene derivatives, the archetype of organic charge transporters.[3] First, selective synthesis of multisubstituted pentacene is challenging. Second, studying single crystals of pentacene derivatives is difficult due to low stability. This article describes the attempt to solve both problems through innovative synthetic strategy, investigation of unique solid state reactivity, and computational simulation.

The synthesis of pentacene derivatives from soluble thermal or photoprecursors is well documented.[4] This approach is frequently employed to overcome the solubility problem encountered during the fabrication of acene based devices. Among these protocols, Yamada-Ono's photochemical precursor route seems particularly amenable to generate 2,3,9,10-tetrasubstituted pentacene derivatives. We perceived that the Wittig–Knoevenagel benzannulation methodology[5] (Scheme 1) can provide an efficient entry into appropriate photoprecursors to pentacene derivatives with terminal ring substitutions. Therefore, a series of pentacene derivatives become accessible by combining these two protocols.

Scheme 1. Wittig–Knoevenagel Benzannulation



RESULT AND DISCUSSION

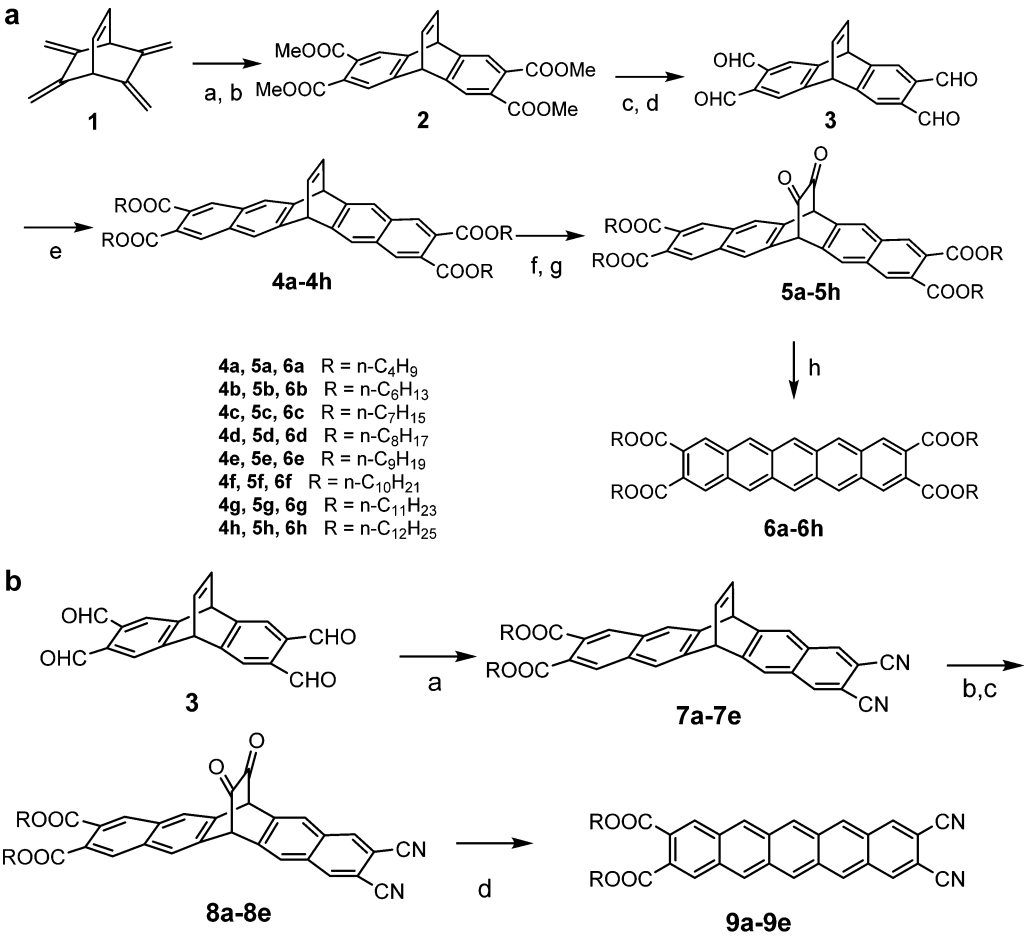
The synthesis starts with the known bicyclic penta-ene 2,3,5,6-tetramethylenebicyclo[2.2.2]oct-7-ene[6] (**1** in Scheme 2a). The exocyclic diene units first undergo Diels–Alder reaction with dimethyl dicarboxylate acetylene. The bisadduct was then dehydrogenated to establish the etheno-anthracene **2**. The *ortho*-diester units were converted to *ortho*-aldehyde in a two-step redox sequence (Dibal-H then Swern oxidation). Tetra-aldehyde **3** is the diverging intermediate in the preparation of a series of pentacene derivatives hence forward. The *ortho*-dialdehyde was elongated with Wittig–Knoevenagel benzannulation (dialkyl maleate, PEt_3, then DBU) to give etheno-pentacene **4a–4h**. According to Yamada-Ono's work, the etheno-bridge was first converted to 1,2-diketone **5a–5h** (OsO_4, NMO, then Swern oxidation) and then removed photochemically to give the target pentacene tetraester **6a–6h**. It should be noted that this series of pentacene tetraesters cannot be prepared by simple trans-esterification due to the inherent instability of the pentacene chromophore.

We then venture to employ a similar strategy to construct pentacene derivatives with unsymmetric substituents at terminal rings, namely, pentacene diester dinitrile (Scheme 2b). A two-stage Wittig–Knoevenagel annulation was utilized

Received: March 28, 2016
Published: June 30, 2016

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223–6234

Scheme 2. (a) Synthesis of 2,3,9,10-Pentacene Tetraester via Wittig–Knoevenagel Condensation and Photolysis and (b) Synthesis of 2,3,9,10-Pentacene Diester Dinitrile via Wittig–Knoevenagel Condensation and Photolysis[a]



[a](a) Reagents and conditions: (a) DMAD, toluene, (b) chloranil, toluene, reflux, over two steps 91%, (c) DibalH, toluene, (d) $(COCl)_2$, DMSO, Et_3N, over two steps 79%, (e) diethyl maleate, PEt_3, then DUB, 49–51%, (f) OsO_4, NMO, acetone, 73–76%, (g) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, 76–81%, (h) photolysis, $h\nu$ = 365 nm, 49–56%. (b) Reagents and conditions: (a) diethyl maleate, PEt_3, DUB, then fumaronitrile, PEt_3, DBU, 19–22%, (b) OsO_4, NMO, acetone, 74–78%, (c) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, 73–76%, (d) photolysis, $h\nu$ = 365 nm, 56–60%.

(first fumaronitrile/PEt_3, then dialkyl maleate/PEt_3) to fulfill this purpose. The diester–dinitrile etheno-pentacene precursors **7a–7e** were easily separated from the symmetric side products. The subsequent oxidation and photolysis were carried out accordingly to furnish the target pentacene diester dinitrile **9a–9e**. It should be noted that such unsymmetrical pentacene derivatives are quite rare in the literature.[7] This strategy affords a new entry to this class of pentacene that are hitherto hard to access.

The photophysical and electrochemical properties of these pentacene derivatives are probed with UV–vis spectra and cyclic voltammetry (CV), respectively. The λ_{max} values of tetraester derivatives **6a–6h** in CH_2Cl_2 are near 590 nm, while those of diester dinitirle **9a–9e** are red-shifted to near 605 nm. These numbers are quite consistent with other terminal ring substituted pentacene derivatives reported.[8] The CV measurements revealed the LUMO of **6a** at −3.3 eV (quasi-reversible wave), while that of **9a** is 0.2 eV more positive at −3.5 eV (reversible reduction), attributable to the stronger electron withdrawing power of the nitrile group. More noteworthy photophysical results were obtained for films of **6a–6h**. While absorptions near 590 nm are still visible in film state, a new broad peak near 670 nm now emerges (Figure 1). Since the wavelength of this new peak is comparable to the pentacene derivatives shifts with face-to-face packing patterns in solid state,[9] the absorption is reasonably attributed to excimer-like stacking in the condensed phase. The most remarkable feature of this series of film spectra is that the intensity of this excimer-like absorption increase as the alkyl chain length increases (the monomeric absorption near 590 nm is normalized). This observation strongly suggests that the interactions between the neighboring pentacene chromophores are enhanced by the alkyl–alkyl interactions in the side chains.

The unsubstituted acene compounds adopt herringbone arrangement in solid states due to the C–H-π interaction.[10] However, the π–π stacking mode can become the preferred

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223–6234

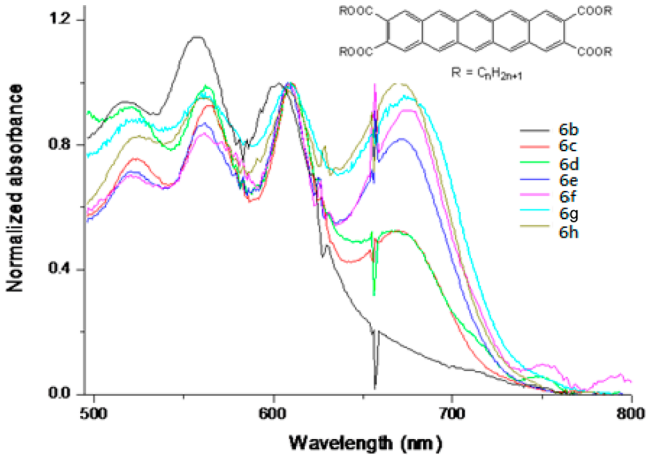


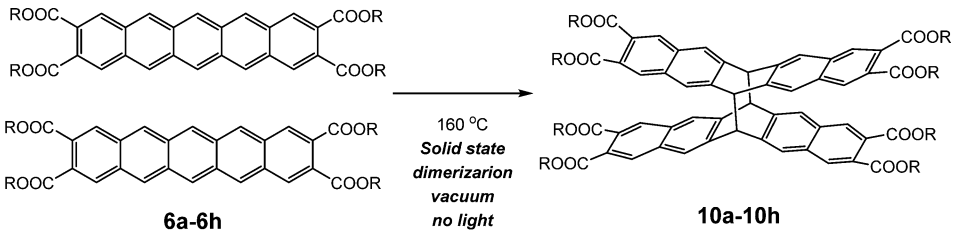
Figure 1. UV−vis absorption spectra of solution cast film of **6b**−**6h**.

packing mode when such C−H-π interaction is disrupted by substitutions at central rings like 6,13 positions in pentacene..[11] Our results hint at a new approach to induce π−π stacking in acene solids by installing alkyl ester substitutions at terminal rings. Since the π−π stacking geometry is often cited to facilitate the charge mobility, we next attempt to employ the tetraester pentacene derivative **6h** in a field effect transistor.

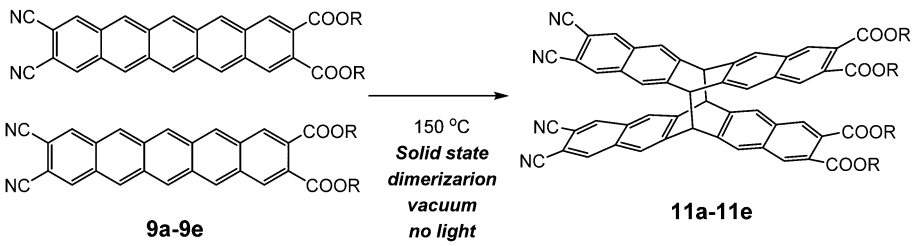
To our disappointment, the devices fabricated from **6h** did not exhibit any measurable charge mobility ($\mu < 10^{-5}$). This is quite puzzling since the system is composed of an optimal charge transporter-pentacene, in its optimal packing mode, π−π-stacking.[12] However, it was soon discovered that the pentacene tetraester films lose their distinct blue-purple color within a few hours upon mild heating (150 °C), indicating complete degradation. The only identifiable component (according to ^{1}H NMR and later X-ray crystallography of the octamethylester derivative, **12**) in this decomposed mixture is the pentacene dimer **10h**, which is produced in over 70% yield.

Although dimerization is a well-known decay pathway for pentacene derivatives in solution,[13] it should be emphasized that the solid state thermal dimerization with such efficiency is quite unusual. (One notable example of the solid state reaction of pentacene is the [4 + 2] polymerization of 2,3,9,10-tetachloropentacene at 400 °C reported by Wudl's group.[13d]) Furthermore, when other pentacene tetraesters **6a**−**6g** were subjected to the same condition, corresponding pentacene dimers **10a**−**10g** were isolated in similar yields in each case (Scheme 3). The generality of this dimerization reaction not only explains the vanishing of charge mobility in the device fabricated from **6h** but also implies π−π stacking solid state structure that the film UV spectrum result suggested. In order to understand the nature of this unusual reaction, several control experiments were carried out. The solution phase reaction ($CDCl_3$ under ambient temperature and light) produces a complex mixture where the yield of the dimer is lower than 10%. Clearly, the solid state structure not only holds the reaction partners in proximity to facilitate the reaction but also prevents other decomposition pathways from taking place. When a thin film composed of **6h** was heated under vacuum in the absence of light, yields similar to those obtained from previous runs without such precautions were observed. However, no dimerization was observed when the film was irradiated for 12 hours at ambient temperature. These results confirm this dimerization reaction is a purely thermal [4 + 4] cycloaddition. Since such a reaction is "forbidden" according to Woodward−Hoffmann's rule, the facile dimerization is likely the result of π−π alignment of pentacene skeletons directed by the intermolecular alkyl−alkyl interactions. Incidentally, Takahashi reported that the thermal dimerization of teramethyl 2,3,9,10-pentacene tetraester in dodecane solution proceeded in good yield.[8] The efficiency of that reaction could also be due to the face-to-face alignment of the pentacene skeleton induced by the dodecane solution matrix.

Scheme 3. Solid State Dimerization of Pentacene Derivatives



6a, 10a R = n-C_4H_9 Yield = 72% **6b, 10b** R = n-C_6H_{13} Yield = 72%
6c, 10c R = n-C_7H_{15} = 74% **6d, 10d** R = n-C_8H_{17} =73%
6e, 10e R = n-C_9H_{19} = 73% **6f, 10f** R = n-$C_{10}H_{21}$ =73%
6g, 10g R = n-$C_{11}H_{23}$ = 74% **6h, 10h** R = n-$C_{12}H_{25}$ = 75%



9a, 11a R = n-C_4H_9 Yield = 90% **9d, 11d** R = n-$C_{10}H_{21}$ Yield = 95%
9b, 11b R = n-C_6H_{13} = 89% **9e, 11e** R = n-$C_{12}H_{25}$ = 94%
9c, 11c R = n-C_8H_{17} =92%

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223−6234

The solid state dimerization of diester dinitrile pentacene derivatives **9a**–**9e** is accomplished at the same reaction temperature, albeit requiring longer reaction time (5 h). The yields for dimerization approach quantitative levels in all five cases. The stereoselectivity of the dimerization is more curious. Because of the unsymmetric substitution pattern, there are two possible dimer products, head-to-head and head-to-tail. However, after carefully inspecting the spectral data, it is concluded the reaction proceeds with 100% stereoselectivity with only one of the two isomers formed. If the intermolecular arrangement in diester dinitrile pentacene derivatives resembles that found in the tetraester derivatives, the dimers thus formed are most likely the head-to-head isomer since the ester terminal of each pentacene monomer must align with that of its neighboring molecule to ensure the alkyl–alkyl packing. Although there are a plethora of solid state organic reactions reported in the literature, the hitherto examples are dominated by photoinduced reactions in crystals.[14,15] The present results therefore constitute a rare example of thermal cycloaddition in condensed phase.

In principle, the proposed π–π stacking structure can be verified by X-ray crystallography. Unfortunately, single crystal of pentacene derivatives are unobtainable due to their poor stability (solution half-life <12 h in the dark under nitrogen). Theoretical simulations were therefore carried out to provide more support to the hypothesis. Previous computational work on such forbidden pentacene dimerization indicates a two-stage mechanism. With two pentacene moieties in face-to-face arrangement, the first bond is formed between the C_6 of the two molecules. To furnish the dimer, one of the pentacene fragments in the diradical intermediate must then rotate 180° to form of the second bond between C13.[16] Such a drastic conformational switch in solid phase, however, is very unlikely due to the van der Waals interactions imposed by neighboring molecules. In the following section, we employ molecular dynamics (MD) simulation to study whether the alkyl directed intermolecular packing can make the [4 + 4] cyclization feasible. Pentacene tetraester **6f** was chosen as an example.

The first key question in the subsequent computational study is whether the dispersive interactions of the alkyl chains are strong enough to hold a cluster of molecules of **6a**–**h** together. We further verify whether the pentacene skeletons are aligned in a face-to-face configuration that allows a fast dimerization reaction in such clusters. To answer these questions, closely packed clusters of **6f** were built by keeping the packing among decyl chains similar to that found in a decane crystal structure.[17] In the decane structure, the regular arrangement of terminal C atoms are shown as an array of dots in Figure 2a, and two possible pairs of neighboring decanes were picked, indicated as solid (**I**) and dashed (**II**) ellipses, with each pair connected to one pentacene with an ester linkage, as shown in Figure 2b. In this way, two different close-packed clusters composed of 32 molecules, arranged in an 8 × 4 array, were created for further tests (left panels of Figure 3).

In order to test how molecule **6f** may stack, MD simulation was performed with further details included in the Supporting Information. The equilibrated snapshots (right panels of Figure 3) demonstrate that the both clusters maintain their parallel stacking configurations. Structure **I** becomes denser after equilibrium, and it is more stable than the equilibrated structure **II** (by 3.5 kcal/mol).

In order to see the π–π stacking conformation in the equilibrated structure, we collected the π–π stacking

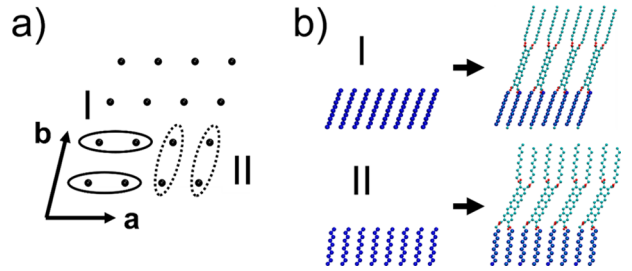


Figure 2. (a) [001] lattice plane of the decane crystal, with each dot represent one terminal C in decane. In forming **6f**, two decane fragments were attached to one side of the tetraester pentacene core. The solid and dashed ellipses mark the two different ways of assigning two decane fragments to one **6f** molecule, forming two different cluster structures, **I** and **II**. The two lattice axes, **a** and **b**, are indicated with arrows. (b) Formation of the two closed-packed structures of **6f** following the decane crystal structure.

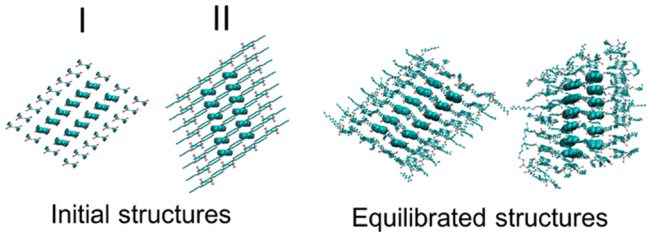


Figure 3. Two different clusters **I** and **II** in their initial construct and those equilibrated from MD simulations.

configurations from the middle 6 × 2 molecules, and the pentacene π–π stacking is depicted in Figure 4. For each pair of parallel **6f** molecules, we placed one of the pentacene cores fixed in a reference position (shown in black), while the position of another pentacene moiety is shown in yellow (starting structure) or as thin green rods (equilibrated structure). Initially, the pentacene cores are displaced along the short axes of pentacene in structure **I**, and that displacement was much reduced after equilibrium. For structure **II**, the initial displacement is in both short and long axes. The displacement in the short-axis is also reduced after equilibrium. With the alkyl side chains, the π–π stacking is enhanced in a cluster. Such arrangement is indeed promising starting structures for dimerization. Therefore, the MD simulation results are very consistent with the experimental observation. The alkyl groups in molecules **6a**–**6h** are competent to bring the pentacene core structures together in face-to-face π–π stacking configurations with small displacement, allowing for a dimerization reaction without cumbersome structural changes.

■ CONCLUSIONS

In summary, by combining photochemical precursor pathway and the Wittig–Knoevenagel benzannulation protocols, we have successfully synthesized a series of pentacene tetraester and pentacene diester–dinitrile derivatives. The UV spectra of the tetraester pentacene films clearly reveal intermolecular π–π packing structure directed by alkyl–alkyl interaction. Furthermore, pentacene tetraesters **6a**–**6h** and pentacene diester–dinitrile **9a**–**9e** readily dimerize in solid state under thermal conditions with very high yields and complete stereoselectivity. The efficiency of these forbidden thermal [4 + 4] strongly suggests that the pentacene derivatives adopt face-to face stacking structure in solid state with substantial overlap of the

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223–6234

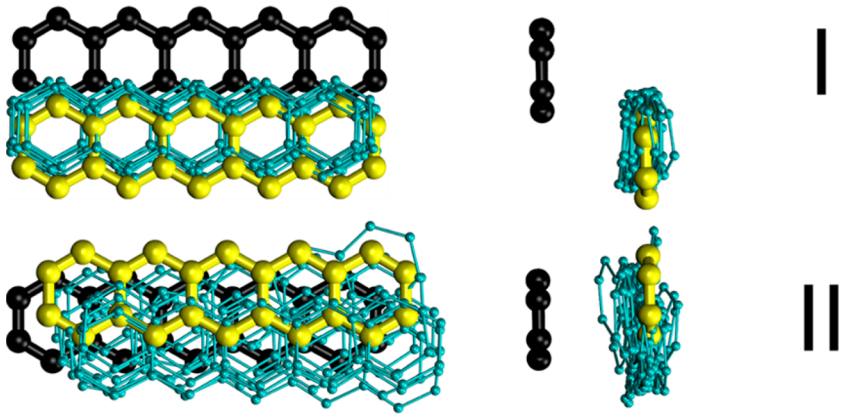


Figure 4. $\pi-\pi$ stacking configurations of the pentacene cores of **6f** from two viewing angles. Shown are pairs of $\pi-\pi$ stacked pentacene cores derived from the initial and the equilibrated clusters. In each pair, one reference pentacene moiety is overlapped to the model in black, while the other pentacene is shown in yellow (initial) or thin green rod (equilibrated) structures.

pentacene π systems. Molecular dynamics simulation confirmed that the alkyl side chains are sufficient to induce stacking with large face-to-face overlaps. In the constructed cluster of **6f**, the pentacene moieties are well aligned for the [4 + 4] cycloaddition to occur. We believe the current study demonstrates a reliable platform to maximize face-to-face π overlap, which is crucial in designing charge transporting materials. The challenge to prevent pentacene dimerization in such π stacking assemblies should be the emphasis of future studies.

EXPERIMENTAL SECTION

General Procedure. All reactions were performed under 1 atm of dried nitrogen and well mixed with magnetic stirring devices. Reagent grade chemicals and solvents were used in all reactions. Diethyl ether and tetrahydrofuran for reactions were distilled over metallic sodium with benzophenone radical anion as the indicator. Dichloromethane was distilled from CaH_2. Reaction vessels were dried in an oven before use. Flash column chromatography was performed with silica gel 60 (1.11567.9025, 0.040−0.063 mm) as the stationary phase. All reported ratios of mixed eluents were based on volume. ^1H and ^{13}C NMR spectra were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C; 400 MHz for ^1H and 100 MHz for ^{13}C spectrometers. Chemical shifts are reported in parts per million (ppm, δ) referenced to the residual $CHCl_3$ in deuterated solvents. Splitting patterns are designated as follows: s, singlet; br, broad; d, doublet; t, triplet; q, quartet; and m, multiplet. Mass spectra were recorded with a direct inlet on a double-focusing high-resolution magnetic-sector mass analyzer operating in fast atom bombardment (FAB) mode, electrospray ionization (ESI) mode, matrix-assisted laser desorption/ionization (MALDI) mode, or electron impact (EI) mode.

The films for absorption spectra were prepared by dissolving the sample (ca. 1 mg) in 1 mL of dichloromethane. A few drops of the solution were placed on a glass slide, and the solvent was slowly evaporated under inert atmosphere to form a thin film. The absorptions were monitored between 300 and 700 nm. Cyclic voltammetry samples were prepared in dichloromethane solution with $TBAPF_6$ as the supporting electrolyte. The measurements were carried with a scan-rate of 100−150 mV/s.

The dialkyl fumarates used in the Wittig−Knoevenagel annulation were synthesized from maleic anhydride in two steps. Their synthetic procedure and spectroscopic characterization are given in this section.

General Procedure for the (3-Alkyloxy Carbonyl) Acrylic Acid.[17] To a solution of alcohol (10 mmol) in CH_2Cl_2 (10 mL), triethylamine (1.7 mL, 12.2 mmol) was added, and the mixture was stirred at room temperature. Maleic anhydride (1.0 g, 10.2 mmol) was added to the solution, and the mixture was refluxed at 55 °C for 1 h under nitrogen atmosphere. After the reaction was cooled to room temperature, 1.5 M aq. HCl solution (20 mL) was added to the solution, and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was then removed under reduced pressure to yield the product as a light tan oil.

(3-Butyloxy Carbonyl) Acrylic Acid. Light tan oil (1.7 g, 99%). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 6.40 (d, J = 12.0 Hz, 1H), 5.86 (d, J = 12.0 Hz, 1H), 4.28 (t, J = 6.7 Hz, 2H), 1.63−1.52 (m, 2H), 1.37−1.28 (m, 2H), 0.87 (t, J = 6.6 Hz, 3H).

(3-Hexyloxy Carbonyl) Acrylic Acid. Light tan oil (2.0 g, 99%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.40 (d, J = 12.8 Hz, 1H), 5.86 (d, 12.8 Hz, 1H), 4.26 (t, J = 6.7 Hz, 2H), 1.75−1.63 (m, 2H), 1.41−1.25 (m, 6H), 0.87 (t, J = 6.6 Hz, 3H).

(3-Heptyloxy Carbonyl) Acrylic Acid. Light tan oil (2.1 g, 99%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ6.40 (d, J = 12.8 Hz, 1H), 5.86 (d, 12.8 Hz, 1H), 4.26 (t, J = 6.7 Hz, 2H), 1.76−1.64 (m, 2H), 1.34−1.24 (m, 9H), 0.87 (t, J = 6.9 Hz, 3H).

(3-Octyloxy Carbonyl) Acrylic Acid. Light tan oil (2.3 g, 99%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ6.40 (d, J = 12.8 Hz, 1H), 5.86 (d, 12.8 Hz, 1H), 4.25 (t, J = 6.7 Hz, 2H), 1.75−1.63 (m, 2H), 1.36−1.23 (m, 10H), 0.86 (t, J = 6.8 Hz, 3H).

(3-Nonanyloxy Carbonyl) Acrylic Acid. Light tan oil (2.4 g, 99%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ6.40 (d, J = 12.8 Hz, 1H), 5.86 (d, 12.8 Hz, 1H), 4.27 (t, J = 6.7 Hz, 2H), 1.76−1.64 (m, 2H), 1.38−1.23 (m, 12H), 0.86 (t, J = 6.8 Hz, 3H).

(3-Decyloxy Carbonyl) Acrylic Acid. Light tan oil (2.57 g, 99%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ6.40 (d, J = 12.8 Hz, 1H), 5.86 (d, 12.8 Hz, 1H), 4.26 (t, J = 6.7 Hz, 2H), 1.75−1.64 (m, 2H), 1.40−1.22 (m, 14H), 0.86 (t, J = 6.7 Hz, 3H).

(3-Undecyloxy Carbonyl) Acrylic Acid. Light tan oil (2.7 g, 99%). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ6.40 (d, J = 12.8 Hz, 1H), 5.86 (d, 12.8 Hz, 1H), 4.26 (t, J = 6.7 Hz, 2H), 1.75−1.64 (m, 2H), 1.39−1.22 (m, 16H), 0.85 (t, J = 6.8 Hz, 3H).

(3-Dodecyloxy Carbonyl) Acrylic Acid. Light tan oil (2.8 g, 99%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ6.40 (d, J = 12.8 Hz, 1H), 5.86 (d, 12.8 Hz, 1H), 4.26 (t, J = 6.7 Hz, 2H), 1.75−1.63 (m, 2H), 1.40−1.22 (m, 18H), 0.85 (t, J = 6.8 Hz, 3H).

General Procedure for the Synthesis of Dialkyl Fumerate.[18] A solution of EDCI (2.5 g, 13.0 mmol) and DMAP (145 mg, 1.19 mmol) in CH_2Cl_2 (100 mL) was added to a stirred solution of (3-alkyloxy carbonyl) acrylic acid (10 mmol) and the corresponding alcohol (10 mmol) in CH_2Cl_2 (100 mL) at room temperature under nitrogen atmosphere. After 24 h, the solvent was washed with dilute hydrochloric acid (100 mL), and the aqueous layer was further extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude oil was purified by column chromatography on silica gel (hexane−CH_2Cl_2, 1:1 to 100% CH_2Cl_2).

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223−6234

Dibutyl Fumerate. White solid (1.16 g, 51%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.82 (s, 2H), 4.18 (t, J = 6.6 Hz, 4H), 1.70−1.59 (m, 4H), 1.46−1.32 (m, 4H), 0.93 (t, J = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.1, 133.6, 65.2, 30.5, 19.08, 13.6.

Dihexyl Fumerate. White solid (1.48 g, 52%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.81 (s, 2H), 4.16 (t, J = 6.7 Hz, 4H), 1.70−1.59 (m, 4H), 1.40−1.24 (m, 12H), 0.86 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 164.8, 133.4, 65.3, 31.2, 28.31, 25.4, 22.4, 13.8.

Diheptyl Fumerate. White solid (1.72 g, 55%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.82 (s, 2H), 4.17 (t, J = 6.8 Hz, 4H), 1.70−1.60 (m, 4H), 1.36−1.24 (m, 16H), 0.86 (t, J = 5.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.1, 133.6, 65.5, 31.7, 28.9, 28.5, 25.8, 22.6, 14.0.

Dioctyl Fumerate. White solid (1.8 g, 53%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.82 (s, 2H), 4.16 (t, J = 6.7 Hz, 4H), 1.71−1.59 (m, 4H), 1.38−1.23 (m, 20H), 0.86 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.1, 133.6, 65.5, 31.8, 29.2, 29.1, 28.5, 25.9, 22.6, 14.1.

Dinonyl Fumerate. White solid (2.03 g, 55%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.82 (s, 2H), 4.17 (t, J = 6.7 Hz, 4H), 1.70−1.59 (m, 4H), 1.39−1.23 (m, 24H), 0.86 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.1, 133.6, 65.5, 31.8, 29.4, 29.2, 28.5, 25.9, 22.6, 14.1.

Didecyl Fumerate. White solid (2.14 g, 54%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.82 (s, 2H), 4.16 (t, J = 6.8 Hz, 4H), 1.71−1.58 (m, 4H), 1.40−1.22 (m, 28H), 0.85 (t, J = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.1, 133.6, 65.5, 31.9, 29.5, 29.3, 29.2, 28.5, 28.4, 25.9, 22.7, 14.1.

Diundecyl Fumerate. White solid (2.42 g, 57%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.82 (s, 2H), 4.17 (t, J = 6.7 Hz, 4H), 1.71−1.59 (m, 4H), 1.39−1.22 (m, 32H), 0.85 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.1, 133.6, 65.5, 31.9, 29.6, 29.6, 29.5, 29.3, 29.2, 28.5, 25.9, 22.7, 14.1.

Didodecyl Fumerate. White solid (2.44 g, 54%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.82 (s, 2H), 4.16 (t, J = 6.8 Hz, 4H), 1.71−1.59 (m, 4H), 1.40−1.21 (m, 36H), 0.85 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.1, 133.6, 65.5, 31.9, 29.62, 29.6, 29.5, 29.3, 29.2, 29.2, 28.5, 25.9, 22.7, 14.1.

9,10-Dihydro-9,10-ethenoanthracene-2,3,6,7-tetracarboxylic Acid Tetramethyl Ester[5] ***(2).*** Colorless solid (5.3 g, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.60 (s, 4H), 6.97 (t, J = 3.6 Hz, 2H), 5.27 (t, J = 3.6 Hz, 2H), 3.84 (s, 12H).

9,10-Dihydro-2,3,6,7-tetrakis(hydroxymethyl)-9,10-ethenoanthracene[5] ***(2′).*** Colorless solid (3.62 g, 92%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 7.29 (s, 4H), 6.98 (t, J = 3.6 Hz, 2H), 5.20 (t, J = 3.6 Hz, 2H), 4.90 (t, J = 5.4 Hz, 4H)), 4.41 (d, J = 5.4 Hz, 8H).

9,10-Dihydro-2,3,6,7-tetrakis(carbaldehyde)-9,10-ethenoanthracene[5] ***(3).*** Brown-yellow solid (2.68 g, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 10.46 (s, 4H), 7.90 (s, 4H), 7.07 (t, J = 3.6 Hz, 2H), 5.54 (brt, 2H).

General Procedure for the Synthesis of Etheno-pentacene Tetraester 4a−4h from Tetraldehyde 3. The triethylphosphine solution (2.5 mmol in THF) was added dropwise via syringe to a stirred CH_2Cl_2 solution of dialkyl fumerate (2.5 mmol, 2 mmol/mL) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 30 min. The Wittig reagent thus generated was transferred dropwise via syringe to a stirred CH_2Cl_2 solution of tetraaldehyde **3** (0.5 mmol, 5 mmol/mL) at room temperature. After the completion of the addition, a CH_2Cl_2 solution of DBU (0.2 mmol, 5 mmol/mL) was added dropwise via syringe to the reaction mixture. The reaction mixture was stirred at room temperature for another 3 h. Water was added, and the mixture was extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous $MgSO_4$, and the volatiles were removed under reduced pressure. The resulting slurry was purified by column chromatography on silica gel (hexane−CH_2Cl_2, 1:1 and 1:3 to pure CH_2Cl_2).

6,13-Dihydro-6,13-etheno-2,3,9,10-tetracarboxylic Acid Tetrabutyl Ester Pentacene ***(4a).*** Colorless solid (172 mg, 49%). IR (Neat, ν) 2959, 2873, 1722, 1441, 1280, 1206, 1123, 1045, 788 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.08 (s, 4H), 7.77 (s, 4H), 7.04 (t, J = 3.7 Hz, 2H), 5.37 (t, J = 3.7 Hz, 2H), 4.29 (t, J = 6.8 Hz, 8H), 1.78−1.62 (m, 8H), 1.49−1.35 (m, 8H), 0.93 (t, J = 7.4 Hz, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.8, 144.2, 137.9, 131.9, 129.3, 128.8, 122.0, 65.4, 50.1, 30.5, 19.1, 13.6; EIMS m/z (%) 704 (M^+, 100), 680 (8), 666 (13), 654 (18); HREIMS m/z 704.3354 (M^+, calcd for $C_{44}H_{48}O_8$ 704.3349).

6,13-Dihydro-6,13-etheno-2,3,9,10-tetracarboxylic Acid Tetrahexyl Ester Pentacene ***(4b).*** Colorless solid (204 mg, 50%). IR (Neat, ν) 2955, 2930, 2858, 1723, 1441, 1278, 1204, 1123, 1051, 788 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.08 (s, 4H), 7.77 (s, 4H), 7.03 (t, J = 3.5 Hz, 2H), 5.37 (t, J = 3.5 Hz, 2H), 4.28 (t, J = 6.8 Hz, 8H), 1.76−1.65 (m, 8H), 1.42−1.34 (m, 8H), 1.33−1.25 (m, 16H), 0.87 (t, J = 7.0 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.9, 144.3, 137.9, 131.9, 129.4, 128.9, 122.1, 65.8, 50.1, 31.5, 28.5, 25.6, 22.5, 13.9; EIMS m/z (%) 816 (100), 804 (32), 792 (30), 766 (35), 754 (25), 742 (32); HREIMS m/z 816.4614 (M^+, calcd for $C_{52}H_{64}O_8$ 816.4601).

6,13-Dihydro-6,13-etheno-2,3,9,10-tetracarboxylic Acid Tetraheptyl Ester Pentacene ***(4c).*** Colorless solid (231 mg, 51%). IR (Neat, ν) 2927, 2857, 1723, 1446, 1275, 1206, 1125, 1044, 925 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.07 (s, 4H), 7.76 (s, 4H), 7.03 (t, J = 3.7 Hz, 2H), 5.36 (t, J = 3.7 Hz, 2H), 4.28 (t, J = 6.8 Hz, 8H), 1.77−1.66 (m, 8H), 1.44−1.23 (m, 32H), 0.86 (t, J = 6.7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.9, 144.3, 137.9, 131.9, 129.4, 128.9, 122.1, 65.8, 50.1, 31.7, 28.9, 28.6, 25.9, 22.6, 14.0; EIMS m/z (%) 872 (100), 854 (10), 842 (9), 828 (8), 816 (10), 804 (12); HREIMS m/z 872.5226 (M^+, calcd for $C_{56}H_{72}O_8$ 872.5227).

6,13-Dihydro-6,13-etheno-2,3,9,10-tetracarboxylic Acid Tetraoctyl Ester Pentacene ***(4d).*** Colorless solid (236 mg, 51%). IR (Neat, ν) 2941, 2926, 2855, 1725, 1441, 1277, 1205, 1124, 1044, 788 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.08 (s, 4H), 7.77 (s, 4H), 7.03 (t, J = 3.7 Hz, 2H), 5.36 (t, J = 3.7 Hz, 2H), 4.28 (t, J = 6.8 Hz, 8H), 1.77−1.65 (m, 8H), 1.42−1.23 (m, 40H), 0.85 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.9, 144.3, 137.9, 131.9, 129.4, 128.9, 122.1, 65.8, 50.1, 31.8, 29.3, 29.2, 28.6, 25.9, 22.6, 14.1; EIMS m/z (%) 928 (100), 927 (3), 903 (5), 902 (5), 892 (2); HREIMS m/z 928.5847 (M^+, calcd for $C_{60}H_{80}O_8$ 928.5853).

6,13-Dihydro-6,13-etheno-2,3,9,10-tetracarboxylic Acid Tetrananonyl Ester Pentacene ***(4e).*** Colorless solid (246 mg, 50%). IR (Neat, ν) 2926, 2851, 1724, 1446, 1380, 1274, 1206, 1125, 1045, 921, 787 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.08 (s, 4H), 7.76 (s, 4H), 7.03 (t, J = 3.7 Hz, 2H), 5.36 (t, J = 3.7 Hz, 2H), 4.28 (t, J = 6.8 Hz, 8H), 1.77−1.66 (m, 8H), 1.44−1.22 (m, 48H), 0.85 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.9, 144.3, 137.9, 131.9, 129.4, 128.9, 122.1, 65.8, 50.1, 31.9, 29.5, 29.3, 29.2, 28.6, 25.9, 22.7, 14.1; EIMS m/z (%) 984 (100), 966 (3), 954 (3), 942 (3), 928 (4), 904 (5); HREIMS m/z 984.6470 (M^+, calcd for $C_{64}H_{88}O_8$ 984.6479).

6,13-Dihydro-6,13-etheno-2,3,9,10-tetracarboxylic Acid Tetradecyl Ester Pentacene ***(4f).*** Colorless solid (265 mg, 51%). IR (Neat, ν) 2925, 2854, 1723, 1443, 1380, 1276, 1206, 1125, 1047, 920, 788 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.08 (s, 4H), 7.77 (s, 4H), 7.03 (t, J = 3.4 Hz, 2H), 5.36 (t, J = 3.4 Hz, 2H), 4.28 (t, J = 6.6 Hz, 8H), 1.76−1.65 (m, 8H), 1.42−1.22 (m, 56H), 0.85 (t, J = 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.9, 144.3, 137.9, 131.9, 129.4, 128.9, 122.1, 65.8, 50.1, 31.9, 29.5, 29.3, 28.6, 25.9, 22.7, 14.1; FABMS m/z 1041 ([M + H]$^+$; HRFABMS m/z 1041.7164 ([M + H]$^+$, calcd for $C_{68}H_{97}O_8$ 1041.7183).

6,13-Dihydro-6,13-etheno-2,3,9,10-tetracarboxylic Acid Tetraundecyl Ester Pentacene ***(4g).*** Colorless solid (279 mg, 51%). IR (Neat, ν) 2925, 2854, 1724, 1447, 1380, 1275, 1206, 1126, 1047, 924, 786 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.08 (s, 4H), 7.77 (s, 4H), 7.03 (t, J = 3.6 Hz, 2H), 5.36 (t, J = 3.6 Hz, 2H), 4.28 (t, J = 6.7 Hz, 8H), 1.77−1.66 (m, 8H), 1.41−1.21 (m, 64H), 0.85 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.9, 144.3, 137.9, 131.9, 129.4, 128.9, 122.1, 65.8, 50.1, 31.89, 29.6, 29.5, 29.3, 29.3, 28.6, 25.9, 22.7, 14.1; EIMS m/z (%) 1096 (100), 942 (15); HREIMS m/z 1096.7708 (M^+, calcd for $C_{72}H_{104}O_8$ 1096.7731).

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223−6234

*6,13-Dihydro-6,13-etheno-2,3,9,10-tetracarboxylic Acid Tetradodecyl Ester Pentacene (**4h**).* Colorless solid (288 mg, 50%). IR (Neat, ν) 2924, 2854, 1726, 1462, 1380, 1276, 1206, 1126, 1048, 920, 788 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.08 (s, 4H), 7.77 (s, 4H), 7.03 (q, J = 3.6 Hz, 2H), 5.36 (t, J = 3.6 Hz, 2H), 4.28 (t, J = 6.8 Hz, 8H), 1.77−1.65 (m, 8H), 1.41−1.21 (m, 72H), 0.85 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.8, 144.3, 137.9, 131.9, 129.4, 128.9, 122.1, 65.8, 50.1, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 28.6, 25.9, 22.7, 14.1; FABMS m/z 1152 (M^+); HRFABMS m/z 1152.8331 (M^+, calcd for $C_{76}H_{112}O_8$ 1152.8357).

General Method for the Dihydroxylation of 4a−4h to 4a′−4h′. To a stirred acetone solution of 4-methylmorpholine-*N*-oxide (110 mg, 0.94 mmol/20 mL), a 2.5% (w) solution of osmium tetroxide in *t*-butanol (0.16 mL, diluted with 2 mL of acetone) was slowly added under a nitrogen atmosphere at 0 °C. The mixture was stirred for 20 min at 0 °C. An acetone solution of 6,13-dihydro-6,13-etheno-2,3, 9,10-tetracarboxylic acid tetraalkyl ester pentacene (0.25 mmol/20 mL) was then added slowly. The mixture was stirred at room temperature for an additional 5 h. Sodium dithionite (150 mg) was added to the reaction mixture, and the slurry was stirred for another 20 min. The solvent was removed under reduced pressure at 40 °C, and the residue was purified by column chromatography on silica gel (passed dichloromethane to remove impurity) using ethyl acetate as eluent. The desired product was obtained as a colorless solid.

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetrabutyl Ester-cis-23,24-diol (**4a′**).* Colorless solid (136 mg, 74%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.18 (s, 2H), 8.15 (s, 2H), 7.91 (s, 2H), 7.86 (s, 2H), 4.70 (brs, 2H), 4.31 (t, J = 6.6 Hz, 8H), 4.22 (brs, 2H), 1.77−1.64 (m, 8H), 1.50−1.36 (m, 8H), 0.94 (t, J = 7.4 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.7, 167.6, 139.6, 138.4, 132.8, 129.6, 129.1, 129.0, 125.9, 124.3, 67.9, 65.64, 65.59, 51.3, 30.6, 19.2, 13.7; FABMS m/z 739 $[M + H]^+$; HRFABMS m/z 739.3486 ($[M + H]^+$, calcd for $C_{44}H_{51}O_{10}$ 739.3482).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetrahexyl Ester-cis-23,24-diol (**4b′**).* Colorless solid (157 mg, 74%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.16 (s, 2H), 8.14 (s, 2H), 7.88 (s, 2H), 7.83 (s, 2H), 4.68 (brs, 2H), 4.30 (t, J = 6.8 Hz, 8H), 4.19 (brs, 2H), 1.78−1.66 (m, 8H), 1.45−1.34 (m, 8H), 1.33−1.26 (m, 16H), 0.87 (t, J = 6.9 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.8, 167.7, 139.7, 138.5, 132.8, 129.6, 129.1, 128.9, 125.9, 124.2, 67.9, 66.0, 65.9, 51.4, 31.5, 28.5, 25.6, 22.5, 13.9; FABMS m/z 851 $[M + H]^+$; HRFABMS m/z 851.4714 ($[M + H]^+$, calcd for $C_{52}H_{67}O_{10}$ 851.4734).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetraheptyl Ester-cis-23,24-diol (**4c′**).* Colorless solid (165 mg, 73%). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.16 (s, 2H), 8.14 (s, 2H), 7.88 (s, 2H), 7.83 (s, 2H), 4.68 (brs, 2H), 4.30 (t, J = 6.8 Hz, 8H), 4.19 (brs, 2H), 1.77−1.67 (m, 8H), 1.44−1.21 (m, 32H), 0.86 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.8, 167.7, 139.7, 138.6, 132.8, 129.6, 129.1, 128.9, 125.9, 124.2, 67.9, 66.0, 65.9, 51.4, 31.7, 28.9, 28.6, 25.9, 22.6, 14.0; FABMS m/z 907 $[M + H]^+$; HRFABMS m/z 907.5347 ($[M + H]^+$, calcd for $C_{56}H_{75}O_{10}$ 907.5360).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetraoctyl Ester-cis-23,24-diol (**4d′**).* Colorless solid (180 mg, 75%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.16 (s, 2H), 8.14 (s, 2H), 7.88 (s, 2H), 7.83 (s, 2H), 4.67 (brs, 2H), 4.29 (t, J = 6.8 Hz, 8H), 4.18 (brs, 2H), 1.78−1.66 (m, 8H), 1.42−1.23 (m, 40H), 0.85 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.8, 167.7, 139.7, 138.5, 132.8, 129.6, 129.1, 128.9, 125.9, 124.2, 67.9, 66.0, 65.9, 51.4, 31.8, 29.2, 29.2, 28.6, 25.9, 22.6, 14.1; FABMS m/z 963 $[M + H]^+$; HRFABMS m/z 963.5988 ($[M + H]^+$, calcd for $C_{60}H_{83}O_{10}$ 963.5986).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetranonyl Ester-cis-23,24-diol (**4e′**).* Colorless solid (191 mg, 75%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17 (s, 2H), 8.15 (s, 2H), 7.90 (s, 2H), 7.85 (s, 2H), 4.69 (brs, 2H), 4.29 (t, J = 6.8 Hz, 8H), 4.21 (brs, 2H), 1.77−1.66 (m, 8H), 1.42−1.22 (m, 48H), 0.85 (t, J = 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.8, 167.7, 139.6, 138.4, 132.8, 129.6, 129.2, 129.0, 125.9, 124.2, 67.9, 66.0, 65.9, 51.4, 31.8, 29.5, 29.3, 29.2, 28.6, 25.9, 22.6, 14.1; FABMS m/z 1019 $[M + H]^+$; HRFABMS m/z 1019.6613 ($[M + H]^+$, calcd for $C_{64}H_{91}O_{10}$ 1019.6612).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetradecyl Ester-cis-23,24 diol (**4f′**).* Colorless solid (204 mg, 76%). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.16 (s, 2H), 8.14 (s, 2H), 7.88 (s, 2H), 7.82 (s, 2H), 4.67 (brs, 2H), 4.29 (t, J = 6.7 Hz, 8H), 4.18 (brs, 2H), 1.77−1.65 (m, 8H), 1.42−1.21 (m, 56H), 0.84 (t, J = 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.8, 167.7, 139.7, 138.5, 132.7, 129.6, 129.1, 128.9, 125.9, 124.2, 67.9, 66.0, 65.9, 51.3, 31.9, 29.5, 29.3, 28.6, 25.9, 22.6, 14.1; FABMS m/z 1075 $[M + H]^+$; HRFABMS m/z 1075.7267 ($[M + H]^+$, calcd for $C_{68}H_{99}O_{10}$ 1075.7238).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetraundecyl Ester-cis-23,24-diol (**4g′**).* Colorless solid (209 mg, 74%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17 (s, 2H), 8.15 (s, 2H), 7.90 (s, 2H), 7.85 (s, 2H), 4.69 (brs, 2H), 4.29 (t, J = 6.8 Hz, 8H), 4.21 (brs, 2H), 1.78−1.66 (m, 8H), 1.42−1.21 (m, 64H), 0.84 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.8, 167.7, 139.6, 138.4, 132.8, 129.6, 129.1, 128.9, 125.9, 124.2, 67.9, 66.0, 65.9, 51.4, 31.9, 29.6, 29.5, 29.3, 28.6, 25.9, 22.7, 14.1; FABMS m/z 1131 $[M + H]^+$; HRFABMS m/z 1131.7888 ($[M + H]^+$, calcd for $C_{72}H_{107}O_{10}$ 1131.7864).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetradodecyl Ester-cis-23,24-diol (**4h′**).* Colorless solid (225 mg, 76%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17 (s, 2H), 8.15 (s, 2H), 7.90 (s, 2H), 7.84 (s, 2H), 4.69 (brs, 2H), 4.29 (t, J = 6.7 Hz, 8H), 4.21 (brs, 2H), 1.78−1.66 (m, 8H), 1.42−1.21 (m, 72H), 0.85 (t, J = 6.7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.8, 167.7, 139.6, 138.4, 132.8, 129.6, 129.2, 129.0, 125.9, 124.2, 67.9, 66.0, 65.9, 51.4, 31.9, 29.7, 29.63, 29.61, 29.6, 29.3, 28.6, 25.9, 22.7, 14.1; FABMS m/z 1187 $[M + H]^+$; HRFABMS m/z 1187.8479 ($[M + H]^+$, calcd for $C_{76}H_{115}O_{10}$ 1187.8490).

General Method for the Oxidation of 4a′−4h′ to 5a−5h (Swern Oxidation). A mixture of DMSO and CH_2Cl_2 (1:2, 6 mL) was added dropwise via syringe to a stirred solution of oxalyl chloride (0.2 mL, 2.4 mmol) in CH_2Cl_2 (4 mL) at −80 °C under nitrogen atmosphere. The mixture was stirred for 30 min. A solution of 6,13-dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic acid tetrabutyl ester-*cis*-23,24-diol (0.22 mmol) in DMSO and CH_2Cl_2 (1:2, 9 mL) was added slowly via syringe at the same temperature, and the reaction mixture was stirred for another 3 h before triethylamine (0.75 mL, distilled) was slowly added. The reaction mixture was stirred at the low temperature for another 1 h before being warmed back to room temperature. Water (50 mL) was added at this point, and the reaction mixture was extracted three times with CH_2Cl_2. The combined organic layer was washed with water three times and dried over anhydrous $MgSO_4$. The solution was concentrated in vacuo, and the remaining solid was purified by column chromatography on silica gel (passed through hexane/dichloromethane = 1:1 and then dichloromethane to remove impurities) using a mixture of dichloromethane and ethyl acetate (3:1 to 7:1) as eluent. The desired product was obtained as a brownish-yellow solid.

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetrabutyl Ester-23,24-dione (**5a**).* Brownish-yellow solid (123 mg, 76%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.19 (s, 4H), 7.98 (s, 4H), 5.34 (s, 2H), 4.33 (t, J = 6.6 Hz, 8H), 1.78−1.67 (m, 8H), 1.50−1.37 (m, 8H), 0.95 (t, J = 7.4 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.8, 167.3, 134.1, 133.6, 130.3, 129.7, 126.2, 65.8, 60.7, 30.6, 19.2, 13.7; FABMS m/z 735 $[M + H]^+$; HRFABMS m/z 735.3164 ($[M + H]^+$, calcd for $C_{44}H_{47}O_{10}$ 735.3169).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetrahexyl Ester-23,24-dione (**5b**).* Brownish-yellow solid (147 mg, 79%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.18 (s, 4H), 7.97 (s, 4H), 5.34 (s, 2H), 4.32 (t, J = 6.8 Hz, 8H), 1.79−1.68 (m, 8H), 1.45−1.28 (m, 24H), 0.87 (t, J = 7.0 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.8, 167.3, 134.0, 133.5, 130.2, 129.7, 126.2, 66.2, 60.6, 31.4, 28.5, 25.6, 22.5, 13.9; FABMS m/z 847 $[M + H]^+$; HRFABMS m/z 847.4438 ($[M + H]^+$, calcd for C_{52} $H_{63}O_{10}$ 847.4421).

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223−6234

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetraheptyl Ester-23,24-dione (**5c**).* Brownish-yellow solid (153 mg, 77%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.21 (s, 4H), 8.02 (s, 4H), 5.36 (s, 2H), 4.31 (t, J = 6.8 Hz, 8H), 1.79−1.68 (m, 8H), 1.43−1.24 (m, 32H), 0.86 (t, J = 6.7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 183.8, 167.2, 134.1, 133.6, 130.4, 129.8, 126.2, 66.2, 60.8, 31.7, 28.9, 28.6, 25.9, 22.6, 14.0; FABMS m/z 903 $[M + H]^+$; HRFABMS m/z 903.5052 ($[M + H]^+$, calcd for C_{56} $H_{71}O_{10}$ 903.5047).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetraoctyl Ester-23,24-dione (**5d**).* Brownish-yellow solid (164 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.21 (s, 4H), 8.01 (s, 4H), 5.36 (s, 2H), 4.31 (t, J = 6.6 Hz, 8H), 1.79−1.67 (m, 8H), 1.45−1.23 (m, 40H), 0.85 (t, J = 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.8, 167.2, 134.1, 133.6, 130.3, 129.7, 126.2, 66.2, 60.7, 31.8, 29.2, 29.1, 28.5, 25.9, 22.6, 14.1; FABMS m/z 959 $[M + H]^+$; HRFABMS m/z 959.5667 ($[M + H]^+$, calcd for C_{60} $H_{79}O_{10}$ 959.5673).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetranonyl Ester-23,24-dione (**5e**).* Brownish-yellow solid (181 mg, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.20 (s, 4H), 8.01 (s, 4H), 5.35 (s, 2H), 4.31 (t, J = 6.7 Hz, 8H), 1.77−1.68 (m, 8H), 1.44−1.22 (m, 48H), 0.85 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.8, 167.3, 134.1, 133.6, 130.3, 129.8, 126.2, 66.2, 60.7, 31.8, 29.5, 29.3, 29.2, 28.6, 25.9, 22.6, 14.1; FABMS m/z 1015 $[M + H]^+$; HRFABMS m/z 1015.6310 ($[M + H]^+$; calcd for C_{64} $H_{87}O_{10}$ 1015.6299).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetradecyl Ester-23,24-dione (**5f**).* Brownish-yellow solid (186 mg, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.20 (s, 4H), 7.99 (s, 4H), 5.35 (s, 2H), 4.31 (t, J = 6.7 Hz, 8H), 1.79−1.67 (m, 8H), 1.43−1.21 (m, 56H), 0.84 (t, J = 6.7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.8, 167.3, 134.1, 133.6, 130.3, 129.7, 126.2, 66.2, 60.7, 31.9, 29.5, 29.3, 28.6, 25.9, 22.6, 14.1; FABMS m/z 1071 $[M + H]^+$; HRFABMS m/z 1071.6925 ($[M + H]^+$; calcd for $C_{68}H_{95}O_{10}$ 1071.6923).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetraundecyl Ester-23,24-dione (**5g**).* Brownish-yellow solid (193 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.21 (s, 4H), 8.02 (s, 4H), 5.36 (s, 2H), 4.31 (t, J = 6.7 Hz, 8H), 1.79−1.67 (m, 8H), 1.43−1.21 (m, 64H), 0.84 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.8, 167.3, 134.1, 133.6, 130.3, 129.8, 126.2, 66.2, 60.7, 31.9, 29.6, 29.5, 29.32, 29.3, 28.6, 25.9, 22.7, 14.1; FABMS m/z 1127 $[M + H]^+$; HRFABMS m/z 1127.7552 ($[M + H]^+$, calcd for $C_{72}H_{103}O_{10}$ 1127.7551).

*6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic Acid Tetradodecyl Ester-23,24-dione (**5h**).* Brownish-yellow solid (205 mg, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.21 (s, 4H), 8.01 (s, 4H), 5.36 (s, 2H), 4.31 (t, J = 6.7 Hz, 8H), 1.79−1.67 (m, 8H), 1.42−1.21 (m, 72H), 0.85 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 183.8, 167.3, 134.1, 133.6, 130.3, 129.8, 126.2, 66.2, 60.7, 31.9, 29.64, 29.62, 29.6, 29.5, 29.33, 29.3, 28.6, 25.9, 22.7, 14.1′; FABMS m/z 1183 $[M + H]^+$; HRFABMS m/z 1183.8170 ($[M + H]^+$, calcd for $C_{76}H_{111}O_{10}$ 1183.8177).

General Method for the Photolysis of Precursor 5a−5h to Pentacene-2,3,9,10-tetraester 6a−6h. A $CDCl_3$ solution of 6,13-dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic acid tetra alkyl ester-23,24-dione (0.03 mmol in 2 mL) was taken in an NMR tube under nitrogen atmosphere. The NMR tube was sealed by septum and parafilm. While the solution was irradiated under a 365 nm UV lamp, the photochemical conversion was monitored by NMR spectrum until completion (2−4 h). Flash chromatography (under nitrogen atmosphere, pure CH_2Cl_2 and CH_2Cl_2: E.A. 50:1 to 20:1) provided a pure sample of pentacene.

*Pentacene-2,3,9,10-tetracarboxylic Acid Tetrabutyl Ester (**6a**).* Deep purple solid (10 mg, 49%). IR (Neat, ν) 2960, 2928, 2868, 1722, 1454, 1382, 1276, 1218, 1118, 1045, 919, 779 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.99 (s, 2H), 8.73 (s, 4H), 8.33 (s, 4H), 4.35 (t, J = 6.2 Hz, 8H), 1.81−1.68 (m, 8H), 1.54−1.40 (m, 8H), 0.98 (t, J = 7.4 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.6, 131.7, 131.1, 130.3, 128.9, 128.2, 128.1, 65.6, 30.7, 19.3, 13.8; FABMS m/z 678 (M^+); HRFABMS m/z 678.3188 (M^+, calcd for $C_{42}H_{46}O_8$ 678.3193).

*Pentacene-2,3,9,10-tetracarboxylic Acid Tetrahexyl Ester (**6b**).* Deep purple solid (13.3 mg, 56%). IR (Neat, ν) 2956, 2930, 2858, 1723, 1455, 1380, 1276, 1220, 1122, 1055, 925, 788 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.04 (s, 2H), 8.78 (s, 4H), 8.37 (s, 4H), 4.35 (t, J = 6.8 Hz, 8H), 1.83−1.72 (m, 8H), 1.48−1.31 (m, 24H), 0.90 (t, J = 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.6, 131.8, 131.1, 130.3, 128.9, 128.2, 128.1, 65.9, 31.5, 28.6, 25.7, 22.6, 14.0; EIMS m/z (%) 790 (100); HREIMS m/z 790.4459 (M^+, calcd for C_{50} $H_{62}O_8$ 790.4445).

*Pentacene-2,3,9,10-tetracarboxylic Acid Tetraheptyl Ester (**6c**).* Deep purple solid (14.2 mg, 56%). IR (Neat, ν) 2929, 2860, 1720, 1457, 1382, 1276, 1123, 1054, 931, 777 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.02 (s, 2H), 8.76 (s, 4H), 8.36 (s, 4H), 4.35 (t, J = 6.8 Hz, 8H), 1.83−1.72 (m, 8H), 1.48−1.26 (m, 32H), 0.88 (t, J = 6.9 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.6, 131.8, 131.1, 130.3, 128.9, 128.3, 128.2, 65.9, 31.8, 29.0, 28.7, 26.0, 22.6, 14.1; FABMS m/z 846 (M^+); HRFABMS m/z 846.5082 (M^+, calcd for C_{54} $H_{70}O_8$ 846.5071).

*Pentacene-2,3,9,10-tetracarboxylic Acid Tetraoctyl Ester (**6d**).* Deep purple solid (14.9 mg, 55%). IR (Neat, ν) 2941, 2925, 2855, 1722, 1455, 1381, 1269, 1221, 1123, 1048, 933, 787 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 9.04 (s, 2H), 8.78 (s, 4H), 8.37 (s, 4H), 4.35 (t, J = 6.8 Hz, 8H), 1.83−1.72 (m, 8H), 1.46−1.21 (m, 40H), 0.87 (t, J = 6.7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.6, 131.9, 131.1, 130.3, 128.9, 128.3, 128.2, 65.9, 31.8, 29.3, 29.2, 28.7, 26.1, 22.7, 14.1; EIMS m/z (%) 902 (100); HREIMS m/z 902.5681 (M^+, calcd for $C_{58}H_{78}O_8$ 902.5697).

*Pentacene-2,3,9,10-tetracarboxylic Acid Tetranonyl Ester (**6e**).* Deep purple solid (15.5 mg, 54%). IR (Neat, ν) 2925, 2857, 1719, 1460, 1384, 1278, 1223, 1124, 1052, 930, 773 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.03 (s, 2H), 8.77 (s, 4H), 8.36 (s, 4H), 4.35 (t, J = 6.8 Hz, 8H), 1.83−1.72 (m, 8H), 1.48−1.21 (m, 48H), 0.86 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.6, 131.8, 131.1, 130.3, 128.9, 128.3, 128.2, 65.9, 31.9, 29.5, 29.4, 29.3, 28.7, 26.1, 22.7, 14.1; FABMS m/z 958 (M^+); HRFABMS m/z 958.6336 (M^+, calcd for $C_{62}H_{86}O_8$ 958.6323).

*Pentacene-2,3,9,10-tetracarboxylic Acid Tetradecyl Ester (**6f**).* Deep purple solid (16.4 mg, 54%). IR (Neat, ν) 2923, 2854, 1718, 1458, 1382, 1284, 1221, 1125, 1052, 933, 725 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.03 (s, 2H), 8.77 (s, 4H), 8.36 (s, 4H), 4.34 (t, J = 6.7 Hz, 8H), 1.83−1.72 (m, 8H), 1.47−1.23 (m, 56H), 0.86 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.6, 131.8, 131.1, 130.3, 128.9, 128.3, 128.2, 65.9, 31.9, 29.6, 29.4, 29.3, 28.7, 26.1, 22.7, 14.1; FABMS m/z 1014 (M^+); HRFABMS m/z 1014.6937 (M^+, calcd for $C_{66}H_{94}O_8$ 1014.6949).

*Pentacene-2,3,9,10-tetracarboxylic Acid Tetraundecyl Ester (**6g**).* Deep purple solid (17 mg, 53%). IR (Neat, ν) 2923, 2854, 1719, 1461, 1382, 1281, 1223, 1126, 1051, 931, 771 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 9.04 (s, 2H), 8.78 (s, 4H), 8.37 (s, 4H), 4.35 (t, J = 6.7 Hz, 8H), 1.82−1.72 (m, 8H), 1.47−1.23 (m, 64H), 0.85 (t, J = 7.0 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.6, 131.8, 131.1, 130.3, 128.9, 128.3, 128.2, 65.9, 31.9, 29.7, 29.6, 29.4, 28.7, 26.1, 22.7, 14.1; FABMS m/z 1070 (M^+); HRFABMS m/z 1070.7583 (M^+, calcd for $C_{70}H_{102}O_8$ 1070.7575).

*Pentacene-2,3,9,10-tetracarboxylic Acid Tetradodecyl Ester (**6h**).* Deep purple solid (18.6 mg, 55%). IR (Neat, ν) 2923, 2853, 1722, 1461, 1382, 1281, 1218, 1126, 1051, 932, 785 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.99 (s, 2H), 8.74 (s, 4H), 8.34 (s, 4H), 4.34 (t, J = 6.8 Hz, 8H), 1.83−1.72 (m, 8H), 1.46−1.22 (m, 72H), 0.85 (t, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.6, 131.8, 131.1, 130.3, 128.9, 128.3, 128.2, 65.9, 31.9, 29.7, 29.6, 29.4, 28.7, 26.1, 22.7, 14.1; FABMS m/z 1126 (M^+); HRFABMS m/z 1126.8206 (M^+, calcd for $C_{74}H_{110}O_8$ 1126.8201).

General Procedure for the Synthesis of Dicyano Diester Etheno-pentacene 7a−7e from Tetraldeyde 3. A solution of triethylphosphine (1.0 M in THF, 1.2 equiv) was diluted with CH_2Cl_2 (equal volume to THF solution). This phosphine solution was added dropwise via syringe to a stirred CH_2Cl_2 solution of fumaronitrile (1.1

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223−6234

mmol, 1.5 mmol/mL) at 0 °C under nitrogen atmosphere. The reaction mixture was then stirred at the same temperature for 30 min. In another flask, triethylphosphine (1.3−1.4 mmol) was added dropwise via syringe to a stirred CH_2Cl_2 solution of dialkyl fumerate (1.2−1.3 mmol, 2 mmol/mL) at room temperature under nitrogen atmosphere. The reaction mixture was also stirred at room temperature for 30 min. Then, the Wittig reagent generated from fumaronitrile was added dropwise via syringe to a stirred CH_2Cl_2 solution of tetraaldehyde **3** (1 mmol, 5 mmol/mL) at 0 °C. The reaction mixture was stirred at the same temperature for 10 min. Then, the other Wittig reagent was added dropwise via syringe to a stirred reaction mixture at 0 °C. After the completion of the addition, a CH_2Cl_2 solution of DBU (0.1 mmol, 5 mmol/mL) was added dropwise via syringe to the reaction mixture. The reaction mixture was stirred at room temperature for another 3 h. Water was added, and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was dried over anhydrous $MgSO_4$, and the volatiles were removed under reduced pressure. The resulting slurry was purified by column chromatography on silica gel (hexane−E.A., 5:1 to 1:1 and hexane−CH_2Cl_2, 1:1 to 1:3).

*6,13-Dihydro-6,13-etheno-9,10-dicyano-2,3-dicarboxylic Acid Dibutyl Ester Pentacene (**7a**).* Colorless solid (105 mg, 19%). IR (Neat, ν) 2960, 2932, 2873, 2233, 1721, 1609, 1441, 1281, 1207, 1124, 1046, 918, 789 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.18 (s, 2H), 8.08 (s, 2H), 7.81 (s, 2H), 7.80 (s, 2H), 7.06 (t, J = 3.8 Hz, 2H), 5.43 (t, J = 3.6 Hz, 2H), 4.30 (t, J = 6.8 Hz, 4H), 1.76−1.65 (m, 4H), 1.47−1.37 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.7, 147.1, 143.2, 137.8, 135.0, 132.1, 131.9, 129.4, 129.2, 122.6, 121.9, 115.9, 109.9, 65.6, 50.1, 30.6, 19.2, 13.7; FABMS m/z 555 $[M + H]^+$; HRFABMS m/z 555.2277 ($[M + H]^+$, calcd for $C_{36}H_{31}O_4N_2$ 555.2284).

*6,13-Dihydro-6,13-etheno-9,10-dicyano-2,3-dicarboxylic Acid Dihexyl Ester Pentacene (**7b**).* Colorless solid (122 mg, 20%). IR (Neat, ν) 2927, 2861, 2232, 1721, 1603, 1449, 1273, 1206, 1125, 1047, 925, 799 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.18 (s, 2H), 8.08 (s, 2H), 7.81 (s, 2H), 7.80 (s, 2H), 7.06 (t, J = 3.6 Hz, 2H), 5.43 (t, J = 3.6 Hz, 2H), 4.28 (t, J = 6.8 Hz, 4H), 1.77−1.65 (m, 4H), 1.42−1.26 (m, 12H), 0.87 (t, J = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.8, 147.1, 143.3, 137.8, 135.1, 132.1, 132.0, 129.4, 129.2, 122.6, 122.0, 115.9, 110.0, 65.9, 50.1, 31.5, 28.6, 25.6, 22.5, 14.0; EIMS m/z (%) 610 (100), 604 (7), 592 (6), 580 (5); HREIMS m/z 610.2817 ($[M^+]$, calcd for $C_{40}H_{38}O_4N_2$ 610.2832).

*6,13-Dihydro-6,13-etheno-9,10-dicyano-2,3-dicarboxylic Acid Dioctyl Ester Pentacene (**7c**).* Colorless solid (140 mg, 21%). IR (Neat, ν) 2954, 2926, 2855, 2232, 1721, 1610, 1442, 1280, 1206, 1125, 1046, 915, 789 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17 (s, 2H), 8.08 (s, 2H), 7.80 (s, 2H), 7.79 (s, 2H), 7.06 (t, J = 3.8 Hz, 2H), 5.43 (t, J = 3.6 Hz, 2H), 4.28 (t, J = 6.8 Hz, 4H), 1.77−1.66 (m, 4H), 1.40−1.22 (m, 20H), 0.85 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.7, 147.1, 143.2, 137.8, 135.0, 132.0, 131.9, 129.4, 129.2, 122.5, 121.9, 115.9, 109.9, 65.9, 50.1, 31.8, 29.2, 29.1, 28.6, 25.9, 22.6, 14.1; EIMS m/z (%) 666 (100), 665 (10), 654 (7), 616 (6); HREIMS m/z 666.3458 ($[M^+]$, calcd for $C_{44}H_{46}O_4N_2$ 666.3453).

*6,13-Dihydro-6,13-etheno-9,10-dicyano-2,3-dicarboxylic Acid Didecyl Ester Pentacene (**7d**).* Colorless solid (152 mg, 21%). IR (Neat, ν) 2925, 2854, 2233, 1722, 1441, 1280, 1206, 1126, 1047, 918, 778 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.17 (s, 2H), 8.08 (s, 2H), 7.81 (s, 2H), 7.79 (s, 2H), 7.06 (q, J = 3.6 Hz, 2H), 5.43 (t, J = 3.6 Hz, 2H), 4.28 (t, J = 6.8 Hz, 4H), 1.76−1.66 (m, 4H), 1.41−1.22 (m, 28H), 0.84 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.7, 147.1, 143.2, 137.8, 135.0, 132.1, 131.9, 129.4, 129.2, 122.5, 121.9, 115.9, 109.9, 65.9, 50.1, 31.9, 29.5, 29.3, 28.6, 25.9, 22.6, 14.1; EIMS m/z (%) 722 (100), 721 (6), 704 (7); HREIMS m/z 722.4079 ($[M^+]$, calcd for $C_{48}H_{54}O_4N_2$ 722.4084).

*6,13-Dihydro-6,13-etheno-9,10-dicyano-2,3-dicarboxylic Acid Didodecyl Ester Pentacene (**7e**).* Colorless solid (171 mg, 22%). IR (Neat, ν) 2925, 2856, 2232, 1722, 1450, 1279, 1206, 1128, 1048, 924, 787 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.17 (s, 2H), 8.08 (s, 2H), 7.81 (s, 2H), 7.79 (s, 2H), 7.06 (t, J = 3.6 Hz, 2H), 5.43 (t, J = 3.6 Hz, 2H), 4.28 (t, J = 6.8 Hz, 4H), 1.77−1.65 (m, 4H), 1.42−1.21 (m, 36H), 0.85 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.7, 147.1, 143.2, 137.8, 135.0, 132.1, 131.9, 129.4, 129.2, 122.5, 121.9, 115.9, 109.9, 65.9, 50.1, 31.9, 29.63, 29.6, 29.57, 29.5, 29.3, 29.28, 28.6, 25.9, 22.7, 14.1; EIMS m/z (%) 778 (100), 766 (33), 754 (28), 740 (22), 716 (38), 704 (35); HREIMS m/z 778.4724 ($[M^+]$, calcd for $C_{52}H_{62}O_4N_2$ 778.4710).

*General Method for the Dihydroxylation of **7a**−**7e** to **7a′**−**7e′**.* To a stirred acetone solution of 4-methylmorpholine-*N*-oxide (110 mg, 0.94 mmol/20 mL), a 2.5% (w) solution of osmium tetroxide in *t*-butanol (0.16 mL, diluted with 2 mL acetone) was slowly added under a nitrogen atmosphere at 0 °C. The mixture was stirred for 20 min at 0 °C. An acetone solution of 6,13-dihydro-6,13-etheno-9,10-dicyano-2,3-dicarboxylic acid dialkyl ester pentacene (0.25 mmol/20 mL) was then added slowly. The mixture was stirred at room temperature for an additional 16 h. Sodium dithionite (150 mg) was added to the reaction mixture, and the slurry was stirred for another 1 h. The solvent was removed under reduced pressure at 40 °C, and the residue was purified by column chromatography with silica gel (dichloromethane was first passed through to remove some impurities) using ethyl acetate as the eluent. The desired product was obtained as a colorless solid.

*6,13-Dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarboxylic Acid Dibutyl Ester-cis-23,24-diol (**7a′** Mixture of Diastereomers).* Colorless solid (109 mg, 74%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.27 (s, 2H), 8.18 (s, 1H), 8.15 (s, 1H), 7.95 (s, 1H), 7.92 (s, 1H), 7.87 (s, 2H), 4.76 (brs, 2H), 4.31 (t, J = 6.6 Hz, 4H), 4.27 (s, 1H), 4.23 (s, 1H), 1.77−1.67 (m, 4H), 1.47−1.38 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.8, 167.7, 142.6, 141.9, 138.8, 137.7, 135.4, 132.8, 132.5, 129.6, 129.3, 129.1, 126.2, 125.8, 124.5, 124.3, 115.9, 115.8, 110.1, 109.6, 67.7, 67.5, 65.8, 51.4, 30.6, 19.2, 13.7; FABMS m/z 589 $[M + H]^+$; HRFABMS m/z 589.2331 ($[M + H]^+$, calcd for $C_{36}H_{33}O_6N_2$ 589.2339).

*6,13-Dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarboxylic Acid Dihexyl Ester-cis-23,24-diol (**7b′** Mixture of Diastereomers).* Colorless solid (121 mg, 75%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.26 (brs, 2H), 8.17 (s, 1H), 8.15 (s, 1H), 7.94 (s, 1H), 7.92 (s, 1H), 7.90 (s, 1H), 7.86 (s, 1H), 4.76 (s, 1H), 4.70 (s, 1H), 4.30 (t, J = 6.8 Hz, 4H), 4.27 (s, 1H), 4.23 (s, 1H), 1.78−1.67 (m, 4H), 1.42−1.26 (m, 12H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.6, 142.6, 141.8, 138.7, 137.5, 135.4, 132.8, 132.6, 129.6, 129.4, 126.3, 125.8, 124.5, 124.3, 115.9, 115.8, 109.9, 67.8, 67.6, 66.1, 51.5, 51.4, 31.4, 28.5, 25.6, 22.5, 13.9; FABMS m/z 645 $[M + H]^+$; HRFABMS m/z 645.2957 ($[M + H]^+$, calcd for $C_{40}H_{41}O_6N_2$ 645.2965).

*6,13-Dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarboxylic Acid Dioctyl Ester-cis-23,24-diol (**7c′** Mixture of Diastereomers).* Colorless solid (135 mg, 77%). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.26 (s, 1H), 8.22 (s, 1H), 8.15 (s, 1H), 8.14 (s, 1H), 7.93 (s, 1H), 7.91 (s, 1H), 7.90 (s, 1H), 7.85 (s, 1H), 4.75 (brs, 2H), 4.29 (t, J = 6.8 Hz, 4H), 4.24 (s, 1H), 4.22 (s, 1H), 1.77−1.67 (m, 4H), 1.40−1.22 (m, 20H), 0.85 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.7, 142.7, 141.8, 138.8, 137.6, 135.4, 132.8, 132.6, 129.6, 129.4, 126.2, 125.8, 124.5, 124.3, 115.9, 115.8, 110.2, 109.8, 67.7, 67.5, 66.1, 51.5, 51.4, 31.8, 29.23, 29.16, 28.6, 25.9, 22.6, 14.0; FABMS m/z 701 $[M + H]^+$; HRFABMS m/z 701.3589 ($[M + H]^+$, calcd for $C_{44}H_{49}O_6N_2$ 701.3591).

*6,13-Dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarboxylic Acid Didecyl Ester-cis-23,24-diol (**7d′** Mixture of Diastereomers).* Colorless solid (148 mg, 78%). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.27 (s, 2H), 8.18 (s, 1H), 8.15 (s, 1H), 7.95 (s, 1H), 7.92 (s, 2H), 7.87 (s, 1H), 4.77 (brs, 2H), 4.30 (t, J = 6.8 Hz, 4H), 4.28 (s, 1H), 4.24 (s, 1H),1.78−1.66 (m, 4H), 1.42−1.22 (m, 28H), 0.85 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.6, 142.6, 141.8, 138.8, 137.5, 135.4, 132.8, 132.6, 129.6, 129.4, 126.2, 125.8, 124.5, 124.3, 115.9, 115.8, 110.2, 109.9, 67.8, 67.6, 66.1, 51.5, 51.4, 31.9, 29.5, 29.3, 28.6, 25.9, 22.6, 14.1; FABMS m/z 757 $[M + H]^+$; HRFABMS m/z 757.4222 ($[M + H]^+$, calcd for $C_{48}H_{57}O_6N_2$ 757.4217).

*6,13-Dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarboxylic Acid Didodecyl Ester-cis-23,24-diol (**7e′** Mixture of Diastereomers).* Colorless solid (158 mg, 78%). ^1H NMR ($CDCl_3$, 400 MHz,

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223−6234

ppm): δ 8.26 (s, 2H), 8.18 (s, 1H), 8.15 (s, 1H), 7.95 (s, 1H), 7.92 (s, 2H), 7.87 (s, 1H), 4.77 (brs, 2H), 4.30 (t, J = 6.6 Hz, 4H), 4.28 (s, 1H), 4.24 (s, 1H), 1.78−1.66 (m, 4H), 1.42−1.21 (m, 36H), 0.85 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.6, 142.6, 141.7, 138.7, 137.4, 135.4, 132.8, 132.6, 129.6, 129.4, 126.3, 125.8, 124.5, 124.3, 115.9, 115.8, 110.3, 109.9, 67.8, 67.6, 66.1, 51.5, 51.4, 31.9, 29.63, 29.61, 29.58, 29.53, 29.31, 29.29, 28.6, 25.9, 22.7, 14.1; FABMS *m/z* 813 $[M + H]^+$; HRFABMS *m/z* 813.4856 ($[M + H]^+$, calcd for $C_{52}H_{65}O_6N_2$ 813.4843).

General Method for the Oxidation to 7a′−7e′ to 8a′−8e′ 6,13-Dihydro-6,13- ethenopentacene-9,10-dicyano-2,3-dicarboxylic Acid Dialkyl Ester-23,24-dione. A mixture of DMSO and CH_2Cl_2 (1:2, 10 mL) was added dropwise via syringe to a stirred CH_2Cl_2 solution of oxalyl chloride (0.2 mL, 2.4 mmol in 4 mL) at −80 °C under nitrogen atmosphere. The mixture was stirred for 30 min. A solution of 6,13- dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarboxylic acid dialkyl ester-*cis*-23,24-diol (0.22 mmol) in DMSO and CH_2Cl_2 (1:2, 18 mL) was added slowly via syringe at the same temperature, and the reaction mixture was further stirred for 3 h before triethylamine (0.75 mL, distilled) was slowly added. The reaction mixture was stirred at the low temperature for another 1 h before being warmed back to room temperature. Water (50 mL) was added at this point, and the reaction mixture was extracted three times with CH_2Cl_2. The combined organic layer was washed with water three times and dried over anhydrous $MgSO_4$. The solution was concentrated in vacuo, and the remaining solid was purified by column chromatography on silica gel (passed hexane/dichloromethane = 1:1 and then dichloromethane to remove impurities) using a mixture of dichloromethane and ethyl acetate (3:1 to 5:1) as eluent. The desired product was obtained as a tan-yellow solid.

*6,13-Dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarboxylic Acid Dibutyl Ester-23,24-dione (**8a**).* Tan-yellow solid (94 mg, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.35 (s, 2H), 8.22 (s, 2H), 8.10 (s, 2H), 8.05 (s, 2H), 5.43 (s, 2H), 4.33 (t, J = 6.8 Hz, 4H), 1.78−1.67 (m, 4H), 1.50−1.36 (m, 4H), 0.95 (t, J = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 182.8, 167.1, 137.2, 135.6, 133.7, 133.4, 133.2, 130.7, 129.8, 126.6, 126.2, 115.3, 111.6, 65.9, 60.8, 30.6, 19.2, 13.7; FABMS *m/z* 585 $[M + H]^+$; HRFABMS *m/z* 585.2023 ($[M + H]^+$, calcd for $C_{36}H_{29}O_6N_2$ 585.2026).

*6,13-Dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarboxylic Acid Dihexyl Ester-23,24-dione (**8b**).* Tan-yellow solid (104 mg, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.35 (s, 2H), 8.22 (s, 2H), 8.10 (s, 2H), 8.04 (s, 2H), 5.43 (s, 2H), 4.32 (t, J = 6.7 Hz, 4H), 1.79−1.67 (m, 4H), 1.43−1.27 (m, 12H), 0.87 (t, J = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 182.8, 167.2, 137.1, 135.5, 133.7, 133.4, 133.2, 130.6, 129.7, 126.5, 126.2, 115.3, 111.6, 66.3, 60.7, 31.4, 28.5, 25.6, 22.5, 13.9; FABMS *m/z* 641 $[M + H]^+$; HRFABMS *m/z* 641.2644 ($[M + H]^+$, calcd for $C_{40}H_{37}O_6N_2$ 641.2652).

*6,13-Dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarboxylic Acid Dioctyl Ester-23,24-dione (**8c**).* Tan-yellow solid (116 mg, 76%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.35 (s, 2H), 8.22 (s, 2H), 8.10 (s, 2H), 8.04 (s, 2H), 5.44 (s, 2H), 4.31 (t, J = 6.8 Hz, 4H), 1.79−1.67 (m, 4H), 1.43−1.21 (m, 20H), 0.85 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 182.9, 167.1, 137.1, 135.5, 133.7, 133.4, 133.2, 130.6, 129.7, 126.5, 126.2, 115.3, 111.6, 66.3, 60.7, 31.8, 29.24, 29.18, 28.6, 25.9, 22.6, 14.1; FABMS *m/z* 697 $[M + H]^+$; HRFABMS *m/z* 697.3288 ($[M + H]^+$, calcd for $C_{44}H_{45}O_6N_2$ 697.3278).

*6,13-Dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarboxylic Acid Didecyl Ester-23,24-dione (**8d**).* Tan-yellow solid (126 mg, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.35 (s, 2H), 8.22 (s, 2H), 8.10 (s, 2H), 8.04 (s, 2H), 5.43 (s, 2H), 4.31 (t, J = 6.8 Hz, 4H), 1.79−1.68 (m, 4H), 1.41−1.21 (m, 28H), 0.84 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 182.9, 167.2, 137.1, 135.6, 133.6, 133.4, 133.2, 130.6, 129.7, 126.5, 126.2, 115.3, 111.5, 66.3, 60.7, 31.9, 29.5, 29.3, 28.5, 25.9, 22.6, 14.1; FABMS *m/z* 753 $[M + H]^+$; HRFABMS *m/z* 753.3911 ($[M + H]^+$, calcd for $C_{48}H_{53}O_6N_2$ 753.3904).

*6,13-Dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarboxylic Acid Didodecyl Ester-23,24-dione (**8e**).* Tan-yellow solid (133 mg, 75%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.35 (s, 2H), 8.22 (s, 2H), 8.10 (s, 2H), 8.05 (s, 2H), 5.43 (s, 2H), 4.31 (t, J = 7.0 Hz, 4H), 1.76−1.66 (m, 4H), 1.43−1.21 (m, 36H), 0.85 (t, J = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 182.8, 167.1, 137.1, 135.5, 133.7, 133.4, 133.2, 130.6, 129.7, 126.5, 126.2, 115.3, 111.6, 66.3, 60.7, 31.9, 29.64, 29.61, 29.6, 29.5, 29.32, 29.29, 28.6, 25.9, 22.7, 14.1; FABMS *m/z* 809 $[M + H]^+$; HRFABMS *m/z* 809.4532 ($[M + H]^+$, calcd for $C_{52}H_{61}O_6N_2$ 809.4530).

General Method for the Photolysis of Precursor 8a−8e to 9a−9e Pentacene-9,10-dicyano-2,3-diester. A $CDCl_3$ solution of 6,13-dihydro-6,13-ethenopentacene-9,10-dicyano-2,3-dicarb- oxylic acid dialkyl ester-23,24-dione (0.032 mmol in 2 mL) was taken in an NMR tube under nitrogen atmosphere. The NMR tube was sealed by septum with parafilm. While the solution was irradiated under a 365 nm UV lamp, the photochemical conversion was monitored by NMR spectrum until completion (2−4 h). Flash chromatography (under nitrogen atmosphere, pure CH_2Cl_2 and CH_2Cl_2/E.A. 20:1 to 50:1) provided a pure sample of pentacene.

*Pentacene-9,10-dicyano-2,3-dicarboxylic Acid Dibutyl Ester (**9a**).* Deep purple solid (9.5 mg, 56%). IR (Neat, ν) 2959, 2922, 2851, 2227, 1706, 1620, 1451, 1384, 1304, 1261, 1118, 1048, 931, 799 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.09 (s, 2H), 8.81 (s, 4H), 8.46 (s, 2H), 8.37 (s, 2H), 4.36 (t, J = 6.8 Hz, 4H), 1.82−1.71 (m, 4H), 1.54−1.41 (m, 4H), 0.98 (t, J = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.4, 138.7, 131.6, 131.1, 130.9, 130.3, 129.14, 129.09, 128.9, 128.6, 116.1, 107.9, 65.8, 30.7, 19.3, 13.8; FABMS *m/z* 528 $[M^+]$; HRFABMS *m/z* 528.2045 ($[M^+]$, calcd for $C_{34}H_{28}O_4N_2$ 528.2049).

*Pentacene-9,10-dicyano-2,3-dicarboxylic Acid Dihexyl Ester (**9b**).* Deep purple solid (10.8 mg, 58%). IR (Neat, ν) 2928, 2851, 2225, 1715, 1632, 1456, 1380, 1272, 1220, 1122, 1056, 925, 798 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 9.11 (s, 2H), 8.83 (s, 4H), 8.48 (s, 2H), 8.40 (s, 2H), 4.36 (t, J = 6.8 Hz, 4H), 1.84−1.73 (m, 4H), 1.49−1.29 (m, 12H), 0.91 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.4, 138.7, 131.6, 131.1, 130.9, 130.3, 129.2, 129.1, 128.9, 128.6, 116.1, 107.9, 66.1, 31.5, 28.6, 25.7, 22.6, 14.0; FABMS *m/z* 584 $[M^+]$; HRFABMS *m/z* 584.2676 ($[M^+]$, calcd for $C_{38}H_{36}O_4N_2$ 584.2675).

*Pentacene-9,10-dicyano-2,3-dicarboxylic Acid Dioctyl Ester (**9c**).* Deep purple solid (12 mg, 59%). IR (Neat, ν) 2950, 2923, 2846, 2225, 1720, 1454, 1377, 1267, 1119, 1042, 924, 798 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.10 (s, 2H), 8.83 (s, 4H), 8.48 (s, 2H), 8.39 (s, 2H), 4.35 (t, J = 6.8 Hz, 4H), 1.84−1.72 (m, 4H), 1.48−1.26 (m, 20H), 0.87 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.4, 138.7, 131.6, 131.1, 130.9, 130.3, 129.2, 129.1, 128.9, 128.6, 116.1, 107.9, 66.1, 31.8, 29.3, 29.2, 28.7, 26.0, 22.7, 14.1; FABMS *m/z* 640 $[M^+]$; HRFABMS *m/z* 640.3297 ($[M^+]$, calcd for $C_{42}H_{44}O_4N_2$ 640.3301).

*Pentacene-9,10-dicyano-2,3-dicarboxylic Acid Didecyl Ester (**9d**).* Deep purple solid (13.4 mg, 60%). IR (Neat, ν) 2917, 2851, 2225, 1722, 1706, 1451, 1259, 1122, 1089, 1015, 927, 798 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.09 (s, 2H), 8.82 (s, 4H), 8.47 (s, 2H), 8.38 (s, 2H), 4.35 (t, J = 6.8 Hz, 4H), 1.83−1.72 (m, 4H), 1.48−1.25 (m, 28H), 0.86 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.4, 138.7, 131.6, 131.1, 130.9, 130.3, 129.13, 129.08, 128.9, 128.6, 116.1, 107.9, 66.1, 31.9, 29.6, 29.3, 28.7, 26.0, 22.7, 14.1; FABMS *m/z* 697 $[M + H]^+$; HRFABMS *m/z* 697.4001 ($[M + H]^+$, calcd for $C_{46}H_{53}O_4N_2$ 697.4005).

*Pentacene-9,10-dicyano-2,3-dicarboxylic Acid Didodecyl Ester (**9e**).* Deep purple solid (14.4 mg, 60%). IR (Neat, ν) 2956, 2912, 2846, 2225, 1712, 1465, 1300, 1259, 1124, 1094, 1015, 930, 801 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 9.11 (s, 2H), 8.84 (s, 4H), 8.48 (s, 2H), 8.40 (s, 2H), 4.35 (t, J = 6.8 Hz, 4H), 1.83−1.73 (m, 4H), 1.47−1.21 (m, 36H), 0.85 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.4, 138.7, 131.6, 131.1, 130.9, 130.3, 129.2, 129.1, 128.9, 128.6, 116.1, 107.9, 66.1, 31.9, 29.69, 29.66, 29.64, 29.58, 29.4, 28.7, 26.1, 22.7, 14.1; FABMS *m/z* 752 $[M^+]$; HRFABMS *m/z* 752.4545 ($[M^+]$, calcd for $C_{50}H_{60}O_4N_2$ 52.4553).

General Procedure for the Solid State Dimerization of Pentacene Tetraester 6a−6h to 10a−10h. A CH_2Cl_2 solution of

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223−6234

pentacene-2,3,9,10-tetracarboxylic acid tetra alkyl ester (0.008 mmol) was taken in a 10 mL round-bottomed flask. The solvent was slowly evaporated under reduced pressure to form a film at the bottom. The flask was then heated at 160 °C under high vacuum for 30−75 min. The crude product of compounds **10c** and **10h** were purified by column chromatography on silica gel (CH_2Cl_2−E.A, 100:1 to 50:1) as eluent, but yields of the other products are calculated by calibration with 1,4-dimethoxybenzene as an internal standard.

*Octabutyl-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphthaleno)cycloocta[1,2-b:5,6-b′]dinaphthalen-2,3,10,11,21,22,29,30-octacarboxylate (**10a**).* Yield 72%. IR (Neat, ν) 2960, 2928, 2868, 1723, 1679, 1455, 1382, 1262, 1215, 1122, 1015, 941, 801 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.91 (s, 8H), 7.54 (s, 8H), 5.20 (s, 4H), 4.27−4.19 (m, 16H), 1.73−1.62 (m, 16H), 1.43−1.36 (m, 16H), 0.91 (t, J = 7.2 Hz, 24H); HRMALDIMS m/z 1379.6284 ($[M + Na]^+$, calcd for $C_{84}H_{92}O_{16}Na$ 1379.6283).

*Octahexyl-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphthaleno)cycloocta[1,2-b:5,6-b′]dinaphthalen-2,3,10,11,21,22,29,30-octacarboxylate (**10b**).* Yield 72%. IR (Neat, ν) 2956, 2925, 2851, 1727, 1679, 1454, 1380, 1262, 1119, 1096, 1017, 924, 799 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.91 (s, 8H), 7.53 (s, 8H), 5.20 (s, 4H), 4.25−4.19 (m, 16H), 1.73−1.61 (m, 16H), 1.33−1.19 (m, 48H), 0.86 (t, J = 6.6 Hz, 24H); HRMALDIMS m/z 1603.8790 ($[M + Na]^+$, calcd for $C_{100}H_{124}O_{16}Na$ 1603.8787).

*Octaheptyl-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphthaleno)cycloocta[1,2-b:5,6-b′]dinaphthalen-2,3,10,11,21,22,29,30-octacarboxylate (**10c**).* White solid (10 mg, 74%). IR (Neat, ν) 2956, 2925, 2851, 1723, 1679, 1455, 1380, 1263, 1215, 1122, 1017, 924, 801 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.91 (s, 8H), 7.53 (s, 8H), 5.20 (s, 4H), 4.27−4.17 (m, 16H), 1.71−1.61 (m, 16H), 1.35−1.19 (m, 64H), 0.85 (t, J = 6.6 Hz, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.7, 142.1, 132.1, 129.4, 128.9, 126.6, 65.9, 53.6, 31.7, 28.9, 28.5, 25.9, 22.6, 14.0; HRMALDIMS m/z 1716.0042 ($[M + Na]^+$, calcd for $C_{108}H_{140}O_{16}Na$ 1716.0039).

*Octaoctyl-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphthaleno)cycloocta[1,2-b:5,6-b′]dinaphthalen-2,3,10,11,21,22,29,30-octacarboxylate (**10d**).* Yield 73%. IR (Neat, ν) 2956, 2925, 2855, 1728, 1679, 1456, 1377, 1271, 1215, 1124, 1047, 954, 802 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.91 (s, 8H), 7.53 (s, 8H), 5.19 (s, 4H), 4.26−4.18 (m, 16H), 1.71−1.61 (m, 16H), 1.35−1.21 (m, 80H), 0.85 (t, J = 6.6 Hz, 24H); HRESIMS m/z 1806.1466 ($[M + H]^+$, calcd for $C_{116}H_{157}O_{16}$ 1806.1461).

*Octanonyl-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphthaleno)cycloocta[1,2-b:5,6-b′]dinaphthalen-2,3,10,11,21,22,29,30-octacarboxylate (**10e**).* Yield 73%. IR (Neat, ν) 2956, 2924, 2854, 1727, 1679, 1456, 1380, 1271, 1124, 1091, 1017, 924, 801 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.91 (s, 8H), 7.53 (s, 8H), 5.19 (s, 4H), 4.24−4.19 (m, 16H), 1.72−1.61 (m, 16H), 1.38−1.21 (m, 96H), 0.85 (t, J = 6.3 Hz, 24H); HRMALDIMS m/z 1940.2548 ($[M + Na]^+$, calcd for $C_{124}H_{172}O_{16}Na$ 1940.2543).

*Octadecyl-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphthaleno)cycloocta[1,2-b:5,6-b′]dinaphthalen-2,3,10,11,21,22,29,30-octacarboxylate (**10f**).* Yield 73%. IR (Neat, ν) 2956, 2922, 2851, 1728, 1679, 1454, 1377, 1267, 1122, 1094, 1017, 798 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.91 (s, 8H), 7.53 (s, 8H), 5.19 (s, 4H), 4.25−4.18 (m, 16H), 1.72−1.63 (m, 16H), 1.44−1.21 (m, 112H), 0.85 (t, J = 6.7 Hz, 24H); HRMALDIMS m/z 2052.3796 ($[M + Na]^+$, calcd for $C_{132}H_{188}O_{16}Na$ 2052.3795).

*Octaundecyl-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphthaleno)cycloocta[1,2-b:5,6-b′]dinaphthalen-2,3,10,11,21,22,29,30-octacarboxylate (**10g**).* Yield 74%. IR (Neat, ν) 2956, 2922, 2846, 1725, 1679, 1454, 1380, 1263, 1122, 1094, 1015, 798 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.91 (s, 8H), 7.53 (s, 8H), 5.19 (s, 4H), 4.25−4.18 (m, 16H), 1.72−1.61 (m, 16H), 1.44−1.21 (m, 128H), 0.86 (t, J = 6.2 Hz, 24H); HRMALDIMS m/z 2164.5049 ($[M + Na]^+$, calcd for $C_{140}H_{204}O_{16}Na$ 2164.5047).

*Octadodecyl-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphthaleno)cycloocta[1,2-b:5,6-b′]dinaphthalen-2,3,10,11,21,22,29,30-octacarboxylate (**10h**).* White solid (13.7 mg, 76%). IR (Neat, ν) 2954, 2923, 2853, 1727, 1674, 1455, 1378, 1274, 1213, 1124, 1049, 925, 802 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.91 (s, 8H), 7.53 (s, 8H), 5.19 (s, 4H), 4.26−4.17 (m, 16H), 1.73−1.63 (m, 16H), 1.37−1.21 (m, 144H), 0.86 (t, J = 6.7 Hz, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.7, 142.1, 132.1, 129.4, 128.9, 126.6, 65.9, 53.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 28.5, 25.9, 22.7, 14.1; HRFABMS m/z 2251.6196 ($[M − 2H]^+$, calcd for $C_{148}H_{218}O_{16}$ 2251.6225).

General Procedure for the Solid State Reaction of Pentacene-9,10-dicyano-2,3-dicarboxylic Acid Dialkyl Ester. A CH_2Cl_2 solution of pentacene-9,10-dicyano-2,3-dicarboxylic acid dialkyl ester (0.008 mmol) was taken in a 10 mL round-bottom flask. The solvent was slowly evaporated under reduced pressure to make a film of unified thickness. After that, the flask was heated at 160 °C under high vacuum for 4−6 h to afford the title compound as a white solid. The crude product of compounds **11a**, **11d**, and **11e** were purified by column chromatography on silica gel (hexane−E.A., 1:1 to 1:3). However, yields of the other products are calculated by calibration with 1,4-dimethoxybenzene as an internal standard.

*Tetrabutyl-21,22,29,30-tetracyano-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphtha-aleno)cycloocta[1,2-b:5,6-b′]-dinaphthalene-2,3,10,11-tetracarboxylate (**11a**).* White solid (7.5 mg, 90%). IR (Neat, ν) 2958, 2928, 2868, 2234, 1724, 1632, 1453, 1377, 1282, 1212, 1123, 1059, 927, 750 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.03 (s, 4H), 7.91 (s, 4H), 7.60 (s, 4H), 7.57 (s, 4H), 5.27 (s, 4H), 4.25 (t, J = 6.6 Hz, 8H), 1.73−1.61 (m, 8H), 1.46−1.32 (m, 8H), 0.93 (t, J = 7.4 Hz, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.4, 144.4, 140.8, 135.1, 132.2, 132.0, 129.5, 129.3, 126.9, 126.6, 115.6, 110.6, 65.8, 53.5, 30.6, 19.2, 13.7; FABMS m/z 1057 [M^+]; HRFABMS m/z 1057.4175 ([M^+], calcd for $C_{68}H_{57}O_8N_4$ 1057.4176).

*Tetrahexyl-21,22,29,30-tetracyano-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphtha-aleno)cycloocta[1,2-b:5,6-b′]-dinaphthalene-2,3,10,11-tetracarboxylate (**11b**).* Yield 89%. IR (Neat, ν) 2956, 2926, 2855, 2233, 1724, 1673, 1453, 1374, 1261, 1122, 1089, 1018, 800 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.03 (s, 4H), 7.91 (s, 4H), 7.60 (s, 4H), 7.57 (s, 4H), 5.27 (s, 4H), 4.24 (t, J = 6.8 Hz, 8H), 1.77−1.64 (m, 8H), 1.44−1.21 (m, 24H), 0.87 (t, J = 6.6 Hz, 12H); FABMS m/z 1169 [$M + H]^+$; HRFABMS m/z 1169.5428 ($[M + H]^+$, calcd for $C_{76}H_{73}O_8N_4$ 1169.5408).

*Tetraoctyl-21,22,29,30-tetracyano-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphtha-aleno)cycloocta[1,2-b:5,6-b′]-dinaphthalene-2,3,10,11-tetracarboxylate (**11c**).* Yield 92%. IR (Neat, ν) 2956, 2924, 2854, 2234, 1725, 1679, 1453, 1377, 1262, 1122, 1089, 1018, 800 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.03 (s, 4H), 7.91 (s, 4H), 7.60 (s, 4H), 7.57 (s, 4H), 5.26 (s, 4H), 4.24 (t, J = 6.8 Hz, 8H), 1.74−1.62 (m, 8H), 1.41−1.21 (m, 40H), 0.86 (t, J = 6.8 Hz, 12H); FABMS m/z 1281 [$M + H]^+$; HRFABMS m/z 1281.6698 ($[M + H]^+$, calcd for $C_{84}H_{89}O_8N_4$ 1281.6680).

*Tetradecyl-21,22,29,30-tetracyano-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naph-thaleno)cycloocta[1,2-b:5,6-b′]-dinaphthalene-2,3,10,11-tetracarboxylate (**11d**).* White solid (10.5 mg, 95%). IR (Neat, ν) 2961, 2922, 2853, 2233, 1723, 1678, 1454, 1399, 1261, 1212, 1091, 1019, 800 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.03 (s, 4H), 7.91 (s, 4H), 7.60 (s, 4H), 7.57 (s, 4H), 5.26 (s, 4H), 4.24 (t, J = 6.8 Hz, 8H), 1.73−1.62 (m, 8H), 1.40−1.22 (m, 56H), 0.86 (t, J = 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.5, 144.4, 140.7, 135.1, 132.2, 132.0, 129.4, 129.3, 126.9, 126.6, 115.4, 111.0, 66.1, 53.4, 31.9, 29.7, 29.5, 29.3, 28.5, 25.9, 22.7, 14.1; FABMS m/z 1393 [$M + H]^+$; HRFABMS m/z 1393.7913 ([$M + H]^+$, calcd for $C_{92}H_{105}O_8N_4$ 1393.7932).

*Tetradodecyl-21,22,29,30-tetracyano-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]napht-haleno)cycloocta[1,2-b:5,6-b′]-dinaphthalene-2,3,10,11-tetracarboxylate (**11e**).* White solid (11.3 mg, 94%). IR (Neat, ν) 2959, 2923, 2853, 2234, 1725, 1633, 1453, 1402, 1261, 1211, 1092, 1015, 799 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.03 (s, 4H), 7.91 (s, 4H), 7.60 (s, 4H), 7.57 (s, 4H), 5.26 (s, 4H), 4.24 (t, J = 6.6 Hz, 8H), 1.74−1.62 (m, 8H), 1.42−1.22 (m, 72H), 0.85 (t, J = 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.4, 144.4, 140.7, 135.1, 132.2, 132.0, 129.4, 129.3, 126.9, 126.6, 115.6, 110.6, 66.1, 53.5, 31.9, 29.6, 29.5, 29.33, 29.29, 28.6, 25.9, 22.7, 14.1; FABMS m/z 1504 [M^+]; HRFABMS m/z 1504.9111 ([M^+], calcd for $C_{100}H_{120}O_8N_4$ 1504.9106).

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223−6234

*Octamethyl-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]-naphthaleno)cycloocta [1,2-b:5,6-b′]dinaphthalen-2,3,10,11,21,22,29,30-octacarboxylate (**12**).* A solution of octadodecyl-6,7,14,15-tetrahydro-6,15:7,14-bis([2,3]naphthaleno) cycloocta-[1,2-b:5,6-*b*′]dinaphthalen-2,3,10,11,21,22,29,30-octacarboxylate (**10h**) (23 mg, 0.01 mmol), iodotrimethylsilane (0.22 mL, 1.6 mmol), and iodine (15 mg, 0.06 mmol) in 1,2-dichloroethane (10 mL) was heated under reflux at about 120 °C for 4 h. The mixture was allowed to cool at room temperature and stirred. After that, dry methanol (0.5 mL, 12 mmol) was added, and the mixture was again heated under reflux at the same temperature for 16 h. The mixture was then allowed to cool at room temperature, quenched by 5% sodium hydrogen carbonate solution (10 mL), and extracted with dichloromethane (3 × 50 mL). The organic layer was washed with brine solution and dried over anhydrous $MgSO_4$. The organic layer was removed under reduced pressure, and the resulting slurry was purified by column chromatography on silica gel (hexane−E.A., 1:1 to 1:3 and finally 100% E.A.).

White solid (8 mg, 76%). IR (Neat, ν) 2958, 2923, 2852, 1717, 1454, 1280, 1210, 1122, 1050, 939, 803, 734 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.92 (s, 8H), 7.52 (s, 8H), 5.21 (s, 4H), 3.84 (s, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 168.0, 142.1, 132.1, 129.5, 128.5, 126.6, 53.6, 52.6; HRMALDIMS *m*/*z* 1043.2535 ([M + Na]$^+$, calcd for $C_{60}H_{44}O_{16}Na$ 1043.2527).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00526.

Details of MD simulation protocols and results (PDF)

Initial and final structures (ZIP)

Crystallography data for the characterization of dimer **10h** (CIF)

^1H and ^{13}C NMR spectra for most new compounds reported (PDF)

Crystallographic characterization of pentacene tetraester dimer **10h** (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*(C.-P.H.) E-mail: chemopera@gate.sinica.edu.tw.

*(C.-H.L.) E-mail: cherri@chem.sinica.edu.tw.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are thankful to Academia Sinica, Taiwan for financial support.

■ REFERENCES

(1) (a) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (b) Sasabe, H.; Kido, J. *J. Mater. Chem. C* **2013**, *1*, 1699. (c) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2474.

(2) (a) Lin, B.-C.; Cheng; You, Z.-Q.; Hsu, C.-P. *J. Am. Chem. Soc.* **2005**, *127*, 66. (b) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J. L. *Chem. Rev.* **2007**, *107*, 926.

(3) (a) Nelson, S. F.; Lin, Y.-Y.; Gundlach, D. J.; Jackson, T. N. *Appl. Phys. Lett.* **1998**, *72*, 1854. (b) Jurchescu, O. D.; Baas, J.; Palstra, T. T. M. *Appl. Phys. Lett.* **2004**, *84*, 3061.

(4) (a) Afzali, A.; Dimitrakopoulos, C.; Breen, T. *J. Am. Chem. Soc.* **2002**, *124*, 8812. (b) Chen, K.-Y.; Hsieh, H.-H.; Wu, C.-C.; Hwang, J.−J.; Chow, T.-J. *Chem. Commun.* **2007**, 1065. (c) Yamada, H.; Yamashita, Y.; Kikuchi, M.; Watanabe, H.; Okujima, T.; Uno, H.; Ogawa, T.; Ohara, K.; Ono, N. *Chem. - Eur. J.* **2005**, *11*, 6212.

(5) (a) Lin, K.-L.; Pal, B.; Tsou, L.-D.; Lin, C.-H. *Chem. Commun.* **2009**, 803. (b) Hsu, D.-T.; Lin, C.-H. *J. Org. Chem.* **2009**, *74*, 9180. (c) Lin, Y.-C.; Lin, C.-H.; Chen, C.-Y.; Sun, S.-S.; Pal, B. *Org. Biomol. Chem.* **2011**, *9*, 4507.

(6) Gabioud, R.; Vogel, P. *Tetrahedron* **1980**, *36*, 149.

(7) Tönshoff, C.; Bettinger, H. F. *Chem. - Eur. J.* **2012**, *18*, 1789.

(8) Li, S.; Li, Z.; Nakajima, K.; Kanno, K.-I.; Takahashi, T. *Chem. - Asian J.* **2009**, *4*, 294.

(9) (a) Li, J.; Wang, M.; Ren, R.; Gao, X.; Li, W. H.; Zhu, D. *J. Mater. Chem.* **2012**, *22*, 10496. (b) Schwaben, J.; Klues, M.; Hofmann, B. P.; Harms, K.; Witte, G.; Koert, U. *Chem. - Eur. J.* **2015**, *21*, 13758.

(10) (a) Campbell, R. B.; Robertson, J. M.; Trotter, J. *Acta Crystallogr.* **1961**, *14*, 705. (b) Watanabe, M.; Chang, Y. J.; Liu, S. W.; Chao, T. H.; Goto, K.; Islam, M. M.; Yuan, C. H.; Tao, Y. T.; Shinmyozu, T.; Chow, T. J. *Nat. Chem.* **2012**, *4*, 574.

(11) (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482. (b) Moon, H.; Zeis, R.; Borkent, E. J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, C.; Bao, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15322.

(12) Very low mobility was recently observed in 2,3,9,10-tetraalkylpentacene based devices. Katsuta, S.; Saeki, H.; Tanaka, K.; Murali, Y.; Kuzuhara, D.; Misaki, M.; Aratani, N.; Masuo, S.; Ueda, Y.; Yamada, H. *J. Mater. Chem. C* **2014**, *2*, 986.

(13) (a) Chien, C.-T.; Chiang, T.-C.; Watanabe, M.; Chao, T.-H.; Chang, Y. J.; Lin, Y.-D.; Lee, H.-K.; Liu, C.-Y.; Tu, C.-H.; Sun, C.-H.; Chow, T. J. *Tetrahedron Lett.* **2013**, *54*, 903. (b) 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**, 66. (c) Ref 8. (d) Perepichka, D. F.; Bendikov, M.; Meng, H.; Wudl, F. *J. Am. Chem. Soc.* **2003**, *125*, 10190.

(14) Toda, F. *Organic Solid State Reactions*; Springer, The Netherlands, 2005.

(15) Zade, S. S.; Zamoshchik, N.; Reddy, A. R.; Fridman-Marueli, G.; Sheberla, D.; Bendikov, M. *J. Am. Chem. Soc.* **2011**, *133*, 10803.

(16) Bond, A. D.; Davies, J. E. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2002**, *58*, 1690.

(17) Watts, P.; Wiles, C.; Haswell, S. J.; Pombo-Villa, E. *Tetrahedron* **2002**, *58*, 5427−5439.

(18) Kiss, V.; Egri, G.; Balint, J.; Ling, I.; Barkoczi, J.; Forgassy, E. *Tetrahedron: Asymmetry* **2006**, *17*, 2220−2234.

DOI: 10.1021/acs.joc.6b00526
J. Org. Chem. 2016, 81, 6223−6234