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Photochemical Synthesis of 2,6-Linked Anthracene Oligomers without Introducing Extra Substituents

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Photoconvertible precursors of 2,6-linked anthracene oligomers (trimer, tetramer, and pentamer) are synthesized through repeated Suzuki–Miyaura cross-coupling reactions. Upon exposure of these precursors to light at 450 nm, which corresponds to the *n*–π* transition of diketone moieties, yellow precipitates are formed, suggesting the conversion to the corresponding anthracene oligomers from the precursors. The disappearance of ^{1}H nuclear magnetic resonance peaks after photoirradiation indicates the formation of anthracene oligomers with less solubility. High-resolution (HR) mass spectrometry evidently indicates the oligomer formations, and infrared (IR) spectral analysis for thin films show the disappearance of peaks originating from the carbonyl groups, also supporting the conversion. The absorption spectra after photoirradiation indicate a red shift in the absorption peaks accompanying oligomer formations, suggesting an extension of the π-conjugated system. The low solubility of the resulting anthracene oligomers in organic solvents highlights the effectiveness of this synthetic strategy using the photoconvertible precursor. This study provides a practical method to synthesize acene oligomers without the introduction of extra substituents.

1. Introduction

Anthracene has been widely used as an organic semiconductor,[1–5] fluorescence material,[6] and molecular building block[7–13] due to its rigid and planar structure with high air stability. Compared to linear [*n*]acenes,[14–18] anthracene and its derivatives possess an appropriate highest occupied molecular orbital level and better solubility. More importantly, the ease of chemical modification to tune the packing structure has facilitated the derivatizations and functionalizations of anthracene, resulting in several efficient *p*-type semiconductors.[1,4,5] Pristine anthracene single crystal exhibits hole mobilities of 0.02 cm^2 V^{-1} s^{-1}.[19] Specifically, π-elongation at 2,6-positions of anthracene, achieved through oligomerization or functionalization, presents a promising strategy for preparing *p*-type organic field-effect transistor (OFET) materials due to the most extended π-conjugation and highest planarity. For instance, 2,6-diphenylanthracene exhibited an excellent hole mobility of 34 cm^2 V^{-1} s^{-1}.[4,5] Its simple molecular structure with no additional solubilizing groups facilitates effective molecular packing leading to high hole mobility. Therefore, utilizing anthracene oligomers as a planar backbone could potentially improve π–π interactions in the packing, resulting in superior OFET properties. However, π-extension of anthracene at the 2,6-positions without introducing extra solubilizing groups poses a challenge. Indeed, 2,6-dianthracenylanthracene (**3mer**) and even those with hexyl groups at the edges of anthracene exhibited extremely low solubility in organic media, although they demonstrated comparable hole mobility (0.3 cm^2 V^{-1} s^{-1}) to amorphous silicon.[20]

In this study, we employed the photochemical precursor method to synthesize 2,6-linked anthracene oligomers, including trimer (**3mer**), tetramer (**4mer**), and pentamer (**5mer**), without any functional groups (**Figure 1**). In particular, **4mer** and **5mer** are among the longest 2,6-linked anthracene oligomers without solubilizing groups. Due to their low solubility, conventional synthesis methods are not applicable, and if the synthesis was possible, the purification would remain challenging.

Photochemical precursor method utilizes the Strating–Zwanenburg reaction,[21] whereby α-diketone groups undergo visible-light-induced photodecarbonylation at the final stage to generate anthracenes (**Figure 2**). The irradiation of α-diketone-type precursors at the n–π* absorption (≈450–500 nm) leads to the release of two molecules of CO, enabling the quantitative preparation of the corresponding acenes in solutions or films.[14,22–25] Therefore, purification of the resulting products is unnecessary if the purity of the precursor is sufficient, as the reaction produces only gaseous byproducts. In addition, photochemical precursor molecules are often more soluble and stable than their resultant products.

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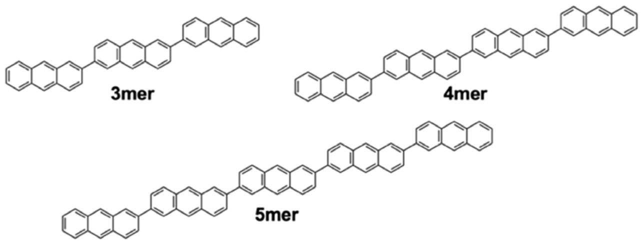


Figure 1. Anthracene oligomers were synthesized in this study.

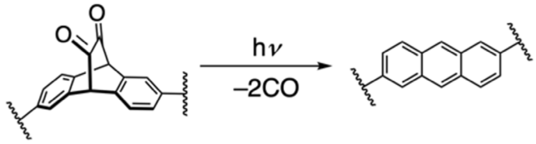
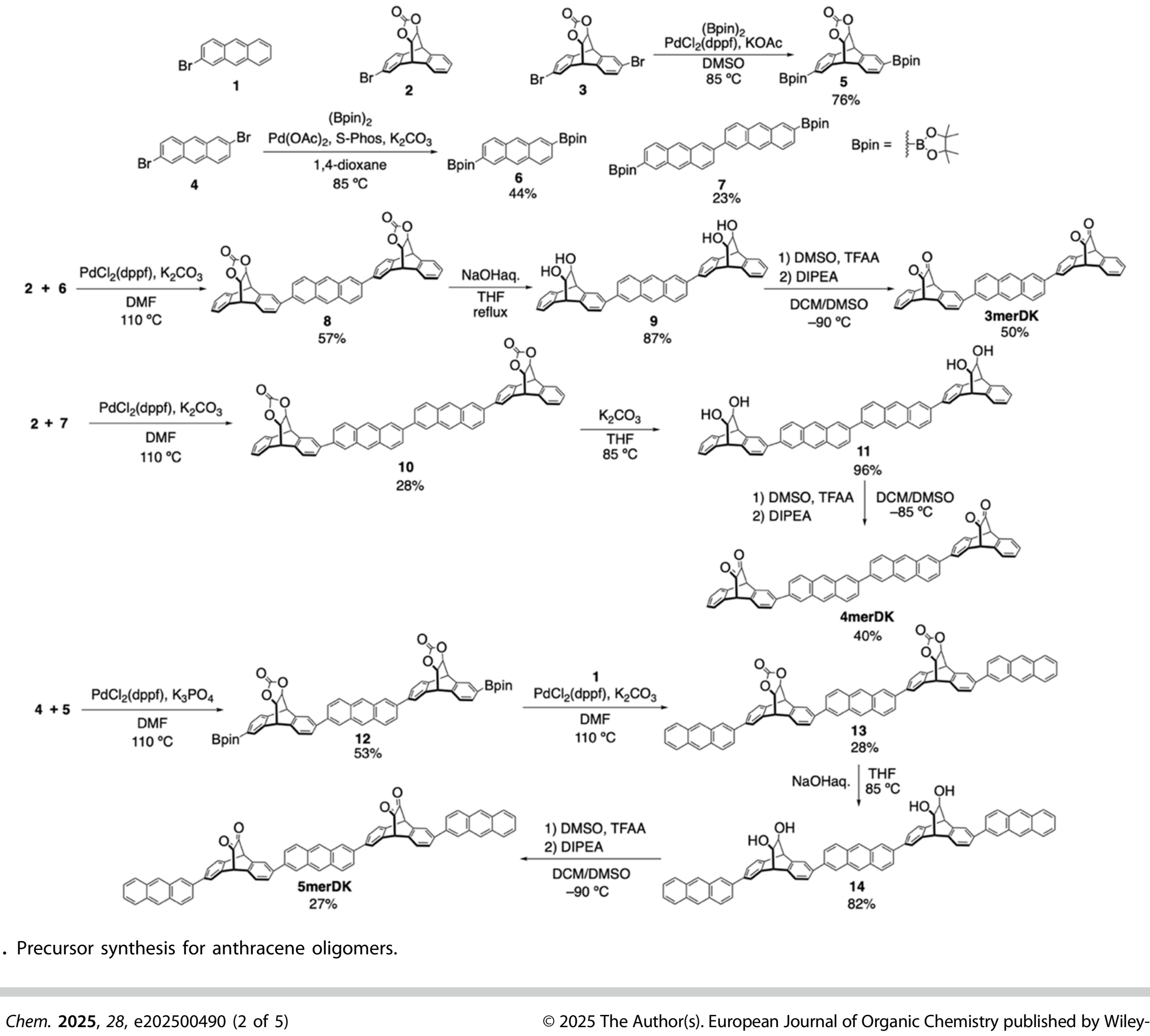


Figure 2. Anthracene formation *via* visible-light-induced photodecarbonylation.

Here, precursors of anthracene oligomers with α-diketone groups were synthesized through multiple Suzuki–Miyaura cross-coupling reactions, and these precursors were then converted to the corresponding anthracene oligomers by simple photoirradiation. The optical properties of these anthracene oligomers were investigated. Through this study, we demonstrated a practical method to synthesize acene oligomers without the introduction of extra substituents.

2. Results and Discussion

Molecular structures of the photochemical precursors (**3merDK**, **4merDK**, and **5merDK**) are depicted in **Scheme 1**. To ensure sufficient solubility, each precursor was designed to incorporate two anthracenes bearing α-diketone group.[22] Initially, essential building blocks for synthesizing these photochemical precursors were prepared. Vinylene carbonate (VC) groups were introduced to brominated anthracenes (2-bromoanthracene and 2,6-dibromoanthracene) through Diels–Alder reactions, yielding compounds **2** and **3**, in alignment with previous reports.[23,26] Subsequently, pinacoloronic esters were introduced to compound **3** via palladium-catalyzed reactions to form compound **5**. Similarly, a coupling reaction between compound **4** and bis(pinacol)diboronic acid with palladium catalysis produced compound **6** and its byproduct of anthracene dimer with bis(pinacol)boronic esters (compound **7**).[27–30] Synthesis of **3merDK** was initiated using the Suzuki–Miyaura cross-coupling reaction between compound **2** and compound **6**, resulting in an anthracene trimer bearing VC-introduced anthracenes at 2,6-positions



Scheme 1. Precursor synthesis for anthracene oligomers.

(compound **8**) with 57% yield. VC groups were deprotected using NaOH aqueous solution to yield compound **9** with 87% yield. Finally, Swern oxidation of compound **9** afforded **3merDK** with 50% yield. Similarly, **4merDK** was synthesized through a coupling reaction with building blocks (compound **2** and compound **7**), yielding a key intermediate for anthracene tetramer (compound **10**) with 28% yield. Deprotection of the VC groups led to bis-diol compound **11**, and Swern oxidation yielded **4merDK**. For synthesizing **5merDK**, a key intermediate (compound **12**) was prepared *via* a Suzuki–Miyaura cross-coupling reaction. Subsequent reactions mirrored those used for **3merDK** and **4merDK**, with the Swern oxidation of bis-diol compound **14** yielding **5merDK**. Notably, **3merDK**, **4merDK**, and **5merDK** all exhibited reasonable solubility in organic solvents such as dichloromethane (DCM), chloroform, tetrahydrofuran, *N*,*N*-dimethylformamide, and dimethyl sulfoxide, which is in contrast to **3mer** shows minimal solubility in organic media.

The UV–vis absorption spectra of **3merDK**, **4merDK**, and **5merDK** in DCM are shown in **Figure 3**. These precursors displayed vibrational peaks characteristic of anthracene, along with broad peaks at ≈450–500 nm, attributed to the *n*–*π** transition of the α-diketone moiety.[22,23] Given that the anthracene moiety does not absorb light beyond 400 nm, photoirradiation at 450–500 nm can selectively excite the *n*–*π** transition in the precursors, thereby converting them to the corresponding anthracene oligomers. Note that **4merDK** shows a red shift in absorption maxima of longer wavelengths, which corresponds to the presence of directly linked anthracene dimer in the system.

The photoconversion of these precursors in $CDCl_3$ was examined in nuclear magnetic resonance (NMR) tubes. Prior to photoirradiation, the solution was bubbled with Ar gas for 30 min. A blue LED (470 ± 10 nm, 200 mW cm^{-2}) or a metal halide lamp (>390 nm) served as the light source for photoconversion. In the case of **5merDK**, the ^1H NMR spectrum before photoirradiation showed several peaks in the aromatic region, indicating reasonable solubility (**Figure 4**). A notable peak at 5.2 ppm, corresponding to bridgehead protons of the α-diketone group, confirmed the presence of precursors. Upon photoirradiation, the ^1H NMR signals of **5merDK** completely vanished after 10 min, with no signals from the product detected after photoconversion, indicating the low solubility of the resultant products in $CDCl_3$. Yellow precipitates formed in the NMR tube are most likely insoluble compounds like **5mer**, generated during photoirradiation. HR matrix-assisted-laser-desorption/ionization time-of-flight mass spectrometry detected parent ion peaks at $m/z = 882.3287$ (calcd. for $C_{70}H_{42} = 882.3281$ $[M]^+$) for **5mer** (see Supporting Information). Similarly, **3merDK** and **4merDK** were also photoconverted in NMR tubes to the corresponding oligomers, **3mer** and **4mer**, respectively (Figure S1, Supporting Information), with clear parent ion peaks observed, confirming successful photoconversion from precursors to anthracene oligomers (see Supporting Information).

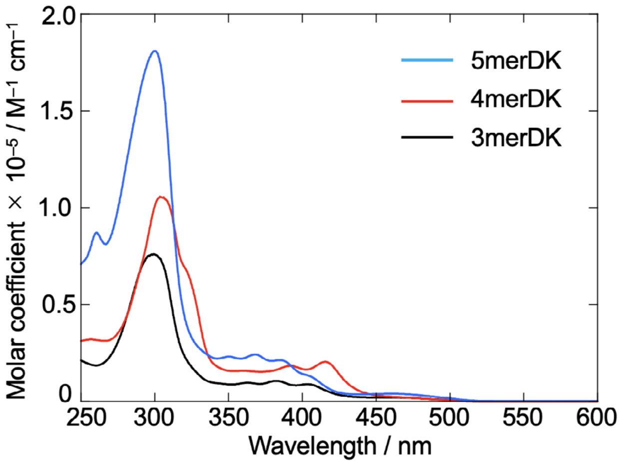


Figure 3. Absorption spectra of photochemical precursors in DCM.

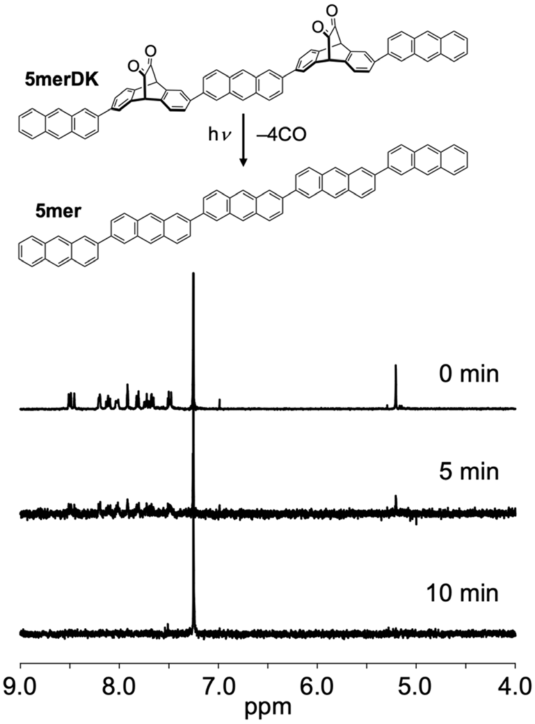


Figure 4. ^1H NMR spectra changing upon photoirradiation to **5merDK** in $CDCl_3$. The corresponding photochemical reaction is also shown.

The conversion of these materials during photoirradiation was further investigated in DCM, judging from changes in absorption spectra (**Figure 5**). Upon photoirradiation of **5merDK**, new peaks at 447 and 484 nm emerged, with the broad peak corresponding to the *n*–*π** transition of the α-diketone moiety disappearing (Figure 5b). Photoirradiation afforded precipitates of **5mer**, affecting the baseline of the absorption spectra. Prior reports showed oligo(2,6-anthrylene)s with solubilizing groups at the 9,10-positions of anthracene, where pentamer absorption bands at the long wavelength were well-resolved and observed at 425, 448, and 483 nm.[31] These findings further support the successful photoconversion in this study. Similar photoconversions were performed for **3merDK** and **4merDK**, resulting in long-wavelength absorption maxima at 460 nm for **3mer** and 478 nm for **4mer** (Figure S2, Supporting Information). The degree of red shift in absorption maxima upon oligomerization agrees well with anthracene oligo(2,6-anthrylene)s with solubilizing

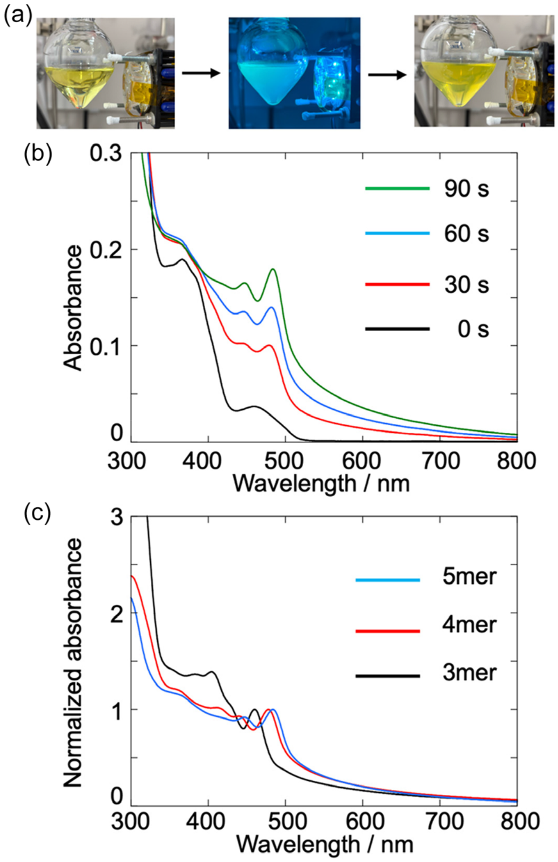


Figure 5. a) Images of color change before (left), during (middle), and after (right) photoirradiation with a blue LED lamp. b) Absorption spectra of **5merDK** during photoirradiation. c) Normalized absorption spectra of **5mer**, **4mer**, and **3mer** obtained by photoirradiation for 90 s (**5mer** and **4mer**) and 120 s (**3mer**).

groups,[31] indicating small but effective π-conjugation between repeated anthracene units (Figure 5c). The obtained anthracene oligomers exhibited no significant degradation over time, indicating those stabilities under ambient conditions.

Solubility of these oligomers in organic solvents promoted us to perform the solution-processable film fabrication of anthracene oligomers, specifically targeting **5mer** film preparation. **3mer** was previously deposited on substrates by sublimation;[20] however, oligomers such as **5mer** faced challenges in sublimation due to there large molecular weight. In this study, a solution of **5merDK** in DCM was firstly drop-casted on a glass substrate. Photoirradiation of the drop-cast films was then performed using a blue LED (470 ± 10 nm, 200 mW cm^{-2}). Upon photoirradiation, the film exhibited an absorption peak at ≈480 nm (**Figure 6**a), consistent with photoconversion from a DCM solution (Figure 5b). IR spectroscopy directly verified photoconversion; the IR spectra of thin films showed the disappearance of the characteristic C=O stretching band at 1786 cm^{-1} corresponding to α-diketone groups upon photoirradiation (Figure 6b), indicating efficient photoreaction even in thin-film states. This photochemical approach demonstrates the capability to prepare organic thin films previously limited by solution processing due to poor solubility or by vacuum deposition due to the large molecular weight. These results significantly contribute to developing methods for preparing various types of organic thin films, paving the way for applications in organic devices such as OFETs and organic photovoltaics (OPVs).[14,25]

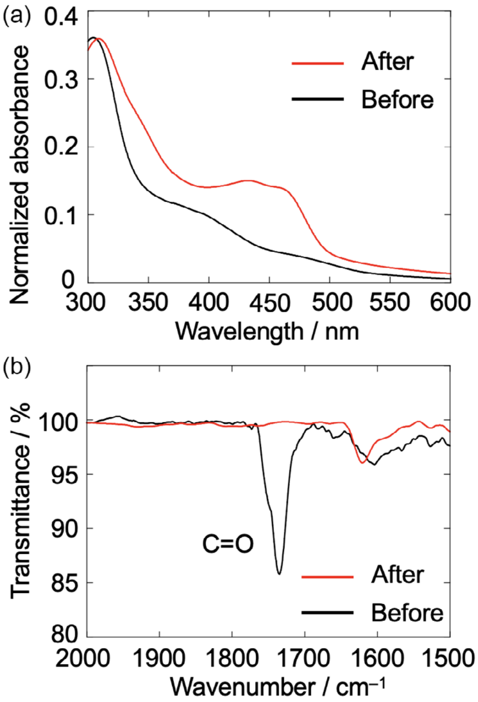


Figure 6. a) Normalized absorption and b) IR spectra of **5merDK** film on a glass substrate. Red line: after photoirradiation. Black line: before photoirradiation.

3. Conclusion

In summary, this study has successfully demonstrated a photochemical approach to synthesize 2,6-linked anthracene oligomers without introducing solubilizing groups, achieving notable advancements in both synthesis methodology and material application. Through the strategic design of photochemical precursors (**3merDK**, **4merDK**, and **5merDK**), we addressed solubility challenges and facilitated effective π-conjugation between anthracene units. In contrast to the utilization of the thermal conversion method,[8,14,32–34] the ability to convert these precursors into anthracene oligomers through selective photoirradiation highlights the versatility of the Strating–Zwanenburg reaction for creating advanced organic materials. The observed solubility of precursors in various organic solvents emphasizes the significance of α-diketone moiety incorporation in enhancing solubility and facilitating solution-processable film fabrication. Furthermore, the successful photoconversion to the corresponding anthracene oligomers, **3mer**, **4mer**, and **5mer** in both solution and thin-film states, confirmed by UV–vis and IR spectroscopy as well as NMR analysis, provides compelling evidence for the method's efficacy. Thus, this photochemical approach not only opens new avenues for the synthesis of π-conjugated systems but also contributes significantly to the material science field by enabling the fabrication of organic thin films that are challenging to produce through conventional methods. This advancement has potential applications in organic electronics, including OFETs and OPVs, where such films can greatly enhance device performance and broaden the scope of organic materials utilized in technological innovations.[35,36]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: anthracenes · multi-step synthesis · oligomers · photoconversions · precursor approaches

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