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Letter

Benzo- and Thieno-Annulated Tetracenes: A One-Pot Synthesis via Cross-Dehydrogenative Annulation

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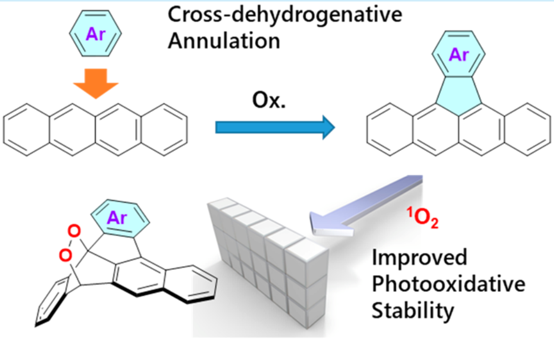
ABSTRACT: A facile method for the direct cross-annulation of unfunctionalized tetracene is reported. The one-pot oxidative cross-dehydrogenative coupling (CDC) between tetracene and aromatic compounds, such as benzene or 2-methylthiophene, furnished annulated products with an extended π-network. Moreover, relative to the benzo-annulated tetracenes, thieno-annulated tetracenes exhibited notably improved photooxidative stability. This behavior stands in sharp contrast with that of tetracene and its derivatives, such as rubrene, which readily engage in photoinduced oxidation reactions.



Oligoacenes that consist of linearly fused benzene rings have attracted substantial interest due to their unusual optoelectronic properties. For example, oligoacenes possess a singlet biradical ground state, a small HOMO−LUMO gap, and a high charge-carrier mobility, and can undergo singlet exciton fission.[1] However, larger oligoacenes, such as tetracene and pentacene, suffer from significant practical drawbacks associated with, for example, a high susceptibility to engage in photochemical oxidation and dimerization reactions as well as limited solubility.[2] For example, the representative tetracene derivative rubrene shows an exceptionally high charge-carrier mobility but simultaneously shows a high propensity to engage in rapid photooxidative degradation.[3] Whereas a number of oligoacene derivatives have been intensively studied,[4] the development of novel synthetic strategies for the versatile functionalization of acene derivatives and the improvement of their photooxidative stability remain of paramount importance for the continued progress of acene-based materials chemistry.

Recently, efficient methods to extend the π-network of oligoacenes using intramolecular Scholl cyclizations have been reported.[5] The Scholl cyclization is one of the most effective and versatile C−C bond-forming reactions for the generation of polycyclic aromatic hydrocarbons.[6] For example, the two-fold intramolecular Scholl cyclization of 5,11-diaryltetracenes furnishes dibenzo- or dithieno-annulated structures. These electron-deficient polyaromatic compounds, such as **1**, exhibit a narrow HOMO−LUMO gap (Figure 1).[5a,d] Chi and coworkers reported that bisindeno-annulated pentacene derivatives,[5b] obtained via the two-fold Scholl cyclization of 6,13-diarylpentacenes, exhibit an enhanced stability toward photooxidation, which is even higher than that of 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene).[1a]

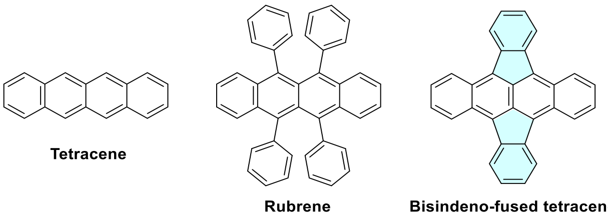


Figure 1. Structures of tetracene, rubrene, and bisindeno-fused tetracene **1**.

Although the annulation of indeno-type structures is effective for the generation of semiconductor materials with enhanced photooxidative stability, most synthetic pathways used for the π-extension of acenes require a transition-metal-catalyzed cross-coupling or a multistep process.[6,7] Herein we report a simple and powerful route to an indeno-annulated structure from tetracene. The use of a one-pot cross-dehydrogenative annulation (CDA) enables the synthesis of a series of π-extended tetracenes. Moreover, systematic studies clarified that the introduction of a thieno-annulated structure significantly enhances the photooxidative stability of the tetracene core.

The first route that we examined for the synthesis of indeno-annulated tetracene was the oxidative cross-dehydrogenative

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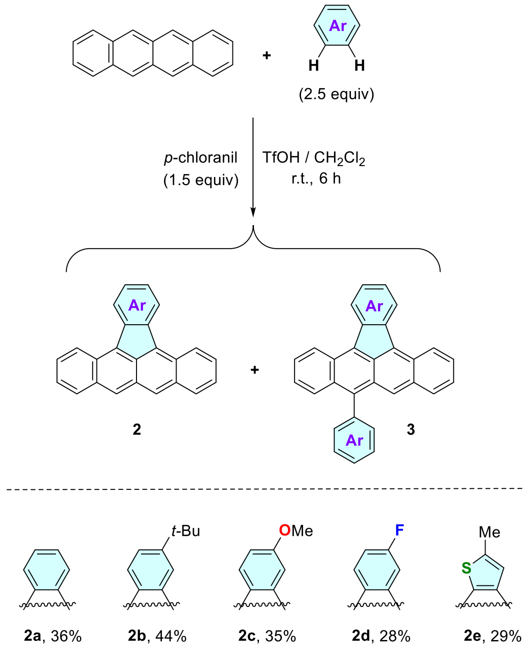
coupling (CDC) between unfunctionalized tetracene and benzene. Even though the formation of C−C bonds in CDC reactions tends to suffer from low selectivity, this issue can partly be addressed by the judicious choice of oxidants or techniques, for example, hypervalent iodine reagents[8] or "radical cation pools".[9] It should also be noted here that single-step cross-annulation reactions have been developed and extensively studied by Itami and coworkers.[10] On the contrary, tetracene, which is an electron-rich relative of simple arenes or heteroarenes, is a suitable substrate for direct CDA reactions. When tetracene was subjected to a one-pot treatment at room temperature with unfunctionalized benzene using a *p*-chloranil/TfOH system (typical conditions for the Scholl reaction), indenotetracene **2a** (36%) was obtained together with **3a** (19%), which contains an additional phenyl group (Scheme 1). The yield of **3a** improved to 49% upon increasing the amount of benzene (5 equiv) and *p*-chloranil (2 equiv), whereas **1** was not generated. *t*-Butylbenzene, anisole, fluorobenzene, and 2-methylthiophene could also be used instead of benzene to give **2b**−**e**. Uncyclized products, that is, 5-aryltetracenes, were not observed in these reactions, which is indicative of facile intramolecular cyclizations. The rapid cyclization relative to the initial C−C bond formation was, assuming a dicationic mechanism[5f] for the Scholl cyclization (for details, see the Supporting Information), supported by density functional theory (DFT) calculations.[11] We did not observe the formation of an indeno-annulated product when anthracene was used instead of tetracene.

Scheme 1. One-Pot Oxidative Cross-Dehydrogenative Annulation (CDA) between Unfunctionalized π-Systems



The structure of **2a** was unambiguously determined by single-crystal X-ray diffraction analysis (Figure 2). Within the crystals, molecules of **2a** adopt a herringbone packing motif, similar to that of the parent tetracene[12] with predominant edge-to-face interactions between the C−H bonds and the π-surface of adjacent molecules. Moreover, because of this extended π-network, **2a** forms π-stacked columns with intermolecular distances of 3.29 to 3.39 Å, which are within the range of typical π-stacked structures (3.4 to 3.7 Å).[13] This result stands in sharp contrast with tetracene, which arranges in a significantly slipped fashion.[1c] In the crystalline states, **2a** and disordered **2d** form a packing structure through two effective interactions, that is, π−π and C−H/π interactions (for details, see the Supporting Information), insight that will be useful for the design of molecular arrangements in the solid state.

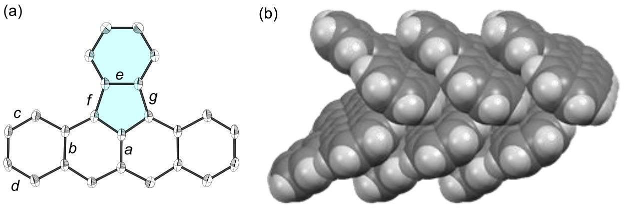


Figure 2. Single-crystal X-ray diffraction structure of **2a**. (a) Molecular structure with thermal ellipsoids at 50% probability. Only one of the two crystallographically independent molecules is shown, and hydrogen atoms are omitted for clarity. (b) Herringbone structure of **2a** with the van der Waals surface. Selected bond lengths (Å) for **2a**: *a*, 1.410(2); *b*, 1.451(2); *c*, 1.362(2); *d*, 1.358(2); *e*, 1.4326(18); *f*, 1.472(2); *g*, 1.470(2).

The absorption spectra of **2a** and **2e** were recorded (Figure 3), and the electronic properties were examined. The absorption spectrum of **2a** showed its longest-wavelength absorption at λ_{max} = 566 nm (log ε = 3.76). Whereas **2e** showed an absorption band in a region similar to that of **2a**, the absorption band of **2e** also had a tail that extended to 720 nm. Time-dependent (TD) DFT calculations at the CAM-B3LYP/6-31G*//B3LYP/6-31G* level of theory suggested that the longest wavelength absorption band of **2a** has an oscillator strength of *f* = 0.17 and arises from a π−π* transition with a major contribution from the HOMO → LUMO transition. In contrast, the longest-wavelength absorption of **2e** has a much smaller oscillator strength (*f* = 0.029) and likely stems from a π−π* transition with a major contribution from the HOMO−1 → LUMO transition.

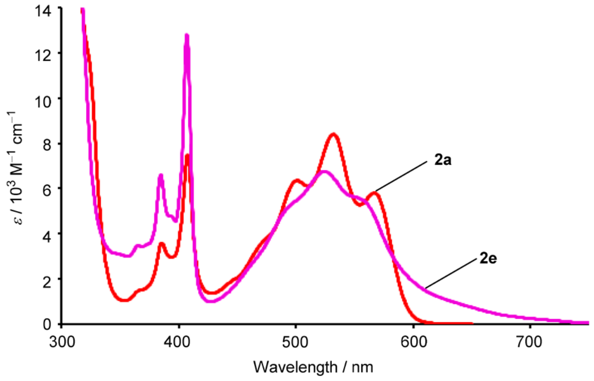


Figure 3. UV−vis absorption spectra of benzo- and thieno-annulated tetracenes **2a** and **2e** in toluene.

During our study, we noticed that the addition of an indeno-annulated moiety to tetracene induces markedly improved stability toward photooxidation (Figure 4). Thus the photo-oxidation behavior of **2a** and **2e** under ambient conditions was studied by monitoring the decay of each absorption band compared with the behavior of tetracene and rubrene. The results indicate that indeno-annulation has a notable effect on the stability toward photooxidation. In contrast, rubrene,

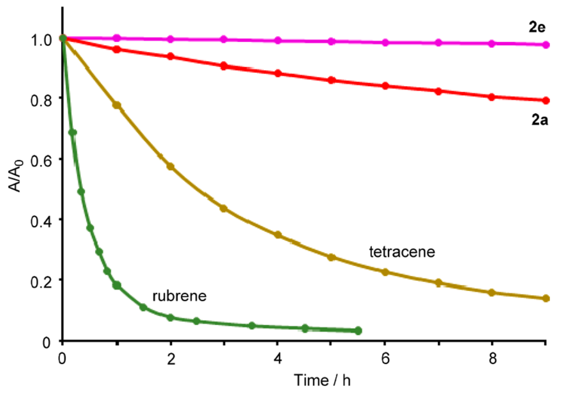
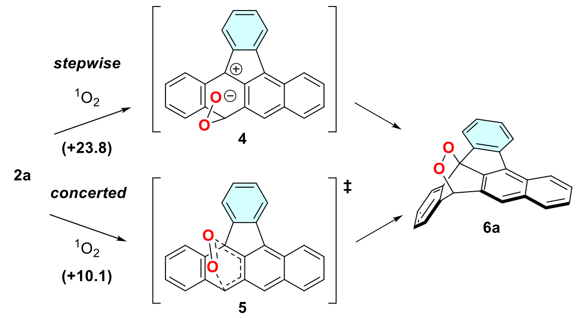


Figure 4. Decay profiles of the absorption maximum of **2a**, **2e**, tetracene, and rubrene upon photoirradiation with artificial light (32 W fluorescent lightning strips) in a toluene solution (1.0×10^{-4} M) under atmospheric conditions.

which contains four additional phenyl groups relative to tetracene, undergoes very rapid degradation in comparison with tetracene. Regardless of whether the derivative contains an electron-donating or -withdrawing group, slightly improved photooxidative stability was observed for **2b**−**d**. (For details, see the Supporting Information.) Moreover, we found that the stability is further enhanced by the addition of a thiophene ring to the structure. The degradation of **2e** in a dilute toluene solution was negligible under atmospheric conditions in the presence of the artificial light (32 W fluorescent lighting strips).

Even though the photooxidation of acenes and their substituted derivatives has been extensively studied, the underlying mechanism remains a matter of debate.[4,14] A lowered LUMO level plays an important role for the stabilization of TIPS-pentacene by suppressing the generation of the radical anion $O_2^{\bullet-}$ via an electron transfer.[14a] Cyclic voltammograms of **2a** and **2e** in CH_2Cl_2 each show one reversible reduction wave ($E_{1/2} = -1.58$ V and -1.59 V vs Fc/Fc$^+$, respectively), indicating that the LUMO levels of **2a** and **2e** are comparable. (For details, see the Supporting Information.) On the contrary, 9,10-diarylanthracenes are thought to react with singlet oxygen ($^1O_2$) via a stepwise pathway that involves a zwitterionic intermediate.[4c,14] This stepwise pathway proceeds faster than the concerted [4 + 2] cycloaddition with $^1O_2$.[4c] Rubrene is considered to be oxidized rapidly, which is, at least in part, due to the stabilization of its polar intermediate by its phenyl groups. However, on the basis of our DFT calculations at the M06-2X/6-31G* level of theory, the barrier for the generation of the polar intermediate **4** ($\Delta G^\ddagger = 23.8$ kcal/mol) is likely to be significantly higher than the barrier for the concerted pathway to give **6a** via transition state **5** ($\Delta G^\ddagger = 10.1$ kcal/mol) (Scheme 2). Reflecting its rigid annulated skeleton, the barrier for the concerted pathway of **2a** is higher than that of tetracene and rubrene ($\Delta G^\ddagger = 8.9$ and 6.1 kcal/mol, respectively) and therefore corroborates the experimental data. The high photooxidative stability imparted by the thieno-annulated framework of **2e** is not completely explained by the concerted mechanism, that is, $\Delta G^\ddagger = 10.0$ kcal/mol for the photooxidation of **2e**. This suggests that the thieno-annulated framework might additionally induce a rapid nonradiative decay[3c] that suppresses the photochemical generation of the reactive species $^1O_2$ and $O_2^{\bullet-}$.

Scheme 2. Proposed Pathways for the Photooxygenation of Indeno-Annulated Tetracene 2a with Calculated Barriers ($\Delta G^\ddagger$ in kcal/mol)



In summary, we have demonstrated a one-pot direct annulation based on an oxidative CDA between unfunctionalized tetracene and simple aromatic compounds such as benzene and 2-methylthiophene. A single-crystal X-ray diffraction analysis of indeno-annulated tetracene (**2a**) revealed that the crystal packing involves effective π−π and C−H/π interactions. Moreover, this synthetic strategy allowed us to carry out systematic studies on the photooxidative stability of the extended π-network of tetracenes. We discovered that the introduction of a thieno-annulated structure significantly suppresses the photochemical degradation relative to indeno-annulated structures. Further studies on (hetero)arene-annulated acenes synthesized via CDAs for applications in semiconducting materials are currently in progress in our laboratory, and the results will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01244.

> Experimental details, characterization data for all new compounds, crystallographic data for **2a** and **2d**, and the details of the computational studies (PDF)

Accession Codes

CCDC 1995329−1995330 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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