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Revisiting zethrene: synthesis, reactivity and semiconductor properties†

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Zethrene, a unique polycyclic aromatic hydrocarbon with formally fixed C–C double bonds, is predicted to have interesting properties and potential applications as an optical and electronic material. Here we report a novel synthesis of zethrene with improved yield, which presumably involves dinaphtho[10]-annulene as an unstable intermediate. With this convenient access to zethrene, we used zethrene as a p-type semiconductor in thin film transistors for the first time. It is found that Diels–Alder addition to the bay region of zethrene leads to new derivatives of benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene, which behave as n-type organic semiconductors.

Introduction

Zethrene is a polycyclic aromatic hydrocarbon (PAH) that is characterized by its formally fixed C–C double bonds as shown in Fig. 1a. Early interest in zethrene was mainly associated with its unique structure in terms of aromaticity, while the recently revived interest in zethrene and its derivatives has arisen due to their potential applications as functional materials.[1,2] As suggested by their theoretically predicted second-order hyperpolarizability[3] and singlet diradical character,[4] zethrene and its derivatives may function as nonlinear optical materials and near-infrared dyes.[1,2] In view of the structural similarity of zethrene to tetracene and pentacene, two well-known organic semiconductors, zethrene and its derivatives are also expected to function as organic semiconductors.[5] These interesting applications were proposed mainly on the basis of computational or theoretical studies,[6] but have remained experimentally unexplored, mainly because of the difficulty involved in the synthesis of zethrene. Here we report a novel synthesis of zethrene, which led to new findings regarding the reactivity of zethrene and fabrication of thin film transistors of zethrene for the first time. It was found that zethrene functions as a p-type semiconductor in organic thin film transistors (OTFTs) with a field effect mobility of up to 0.05 $cm^2 V^{-1} s^{-1}$.

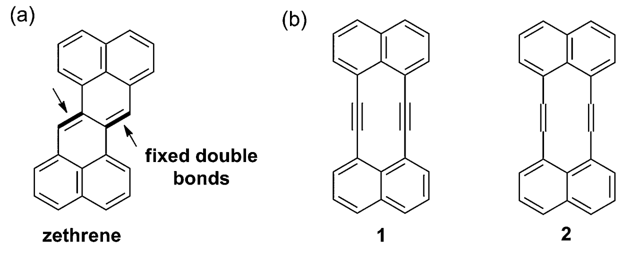

Fig. 1 Molecular structures of (a) zethrene with the fixed double bonds highlighted and (b) two reported synthetic precursors of zethrene.

The first synthesis of zethrene was reported by Clar and co-workers from chrysene through an inefficient route in 1955.[7] A more convenient route to zethrene *via* cross-coupling of Cu(I) acetylides and iodoarenes was later reported by Staab[8] and Sondheimer[9] during their attempted syntheses of tetradehydrodinaphtho[10]annulene (**1** as shown in Fig. 1b), which was suggested to form zethrene through spontaneous trans-annular cyclization. However, this mechanism remains unproven,[1,10] and the overall yields of zethrene in these syntheses were relatively low.[11] In close relation to the transformation of **1** to zethrene, a series of zethrene derivatives were recently synthesized *via* Pd-catalyzed coupling reactions of alkynes,[5,12,13] which nevertheless did not improve the yield of zethrene itself. Another documented synthetic precursor of zethrene is dinaphtho[10]annulene (**2** as shown in Fig. 1b), which was reported to result in zethrene through 7,14-dihydrozethrene when oxidized in air.[14] However, **2** was prepared *via* a Wittig reaction in very low yield (2%),[14] and the identity of **2** appears controversial since a compound with the same spectroscopic properties was later assigned a structure of 7,7*a*-dihydrozethrene.[15]

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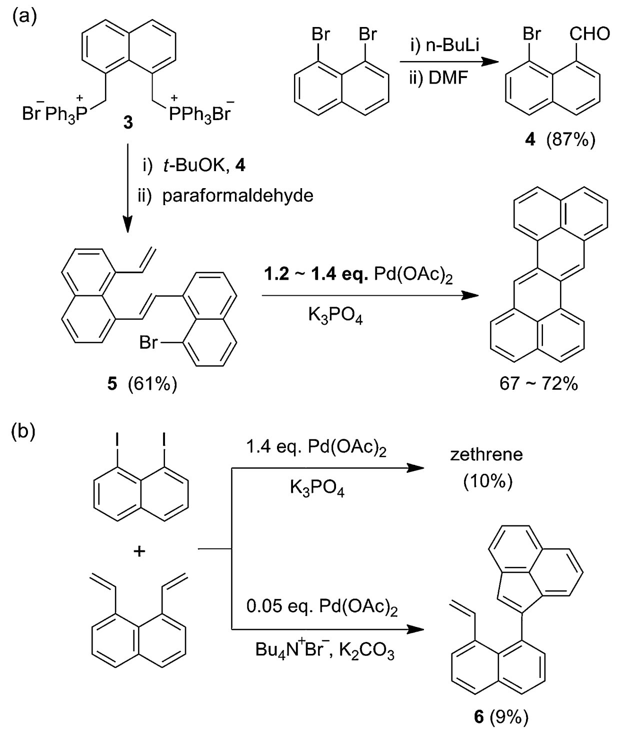
Results and discussion

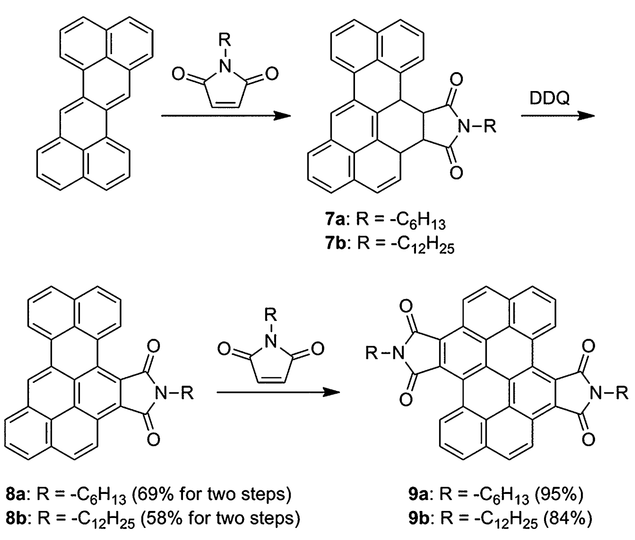
Inspired by the reported conversion of **2** to zethrene,[14] we designed a new synthesis of zethrene, which presumably involves **2** as an unstable intermediate. As shown in Scheme 1a, this synthesis involves a Wittig reaction followed by a Heck reaction to link two naphthalene moieties together. The Wittig reaction has bis(triphenylphosphonium) **3**[16] reacting with two aldehydes, subsequently leading to diene **5**. It is particularly worth noting that more than one equivalent of palladium acetate is necessary in the reaction of **5** to achieve a good yield of zethrene. When a catalytic amount (10%) of palladium acetate was applied in this reaction, zethrene was isolated in a low yield of 7%, possibly because annulene **2** either deactivated Pd(0) by strong coordination or consumed Pd(II) during its conversion to zethrene. In comparison, an alternative approach to zethrene from 1,8-divinylnaphthalene[17] and 1,8-diiodonaphthalene[18] led to zethrene in a much lower yield (10%) under the same conditions as shown in Scheme 1b. When reacting under typical Heck reaction conditions with a catalytic amount of palladium acetate, the two starting materials yielded compound **6** instead of zethrene.

The reactivity of zethrene was studied in terms of bromination and Diels–Alder reactions. Bromination of zethrene under different conditions, such as Br_2, H_2O_2/HBr and NBS, was found to result in formation of a complex mixture of products, while brominated products due to simple addition on the central double bonds were not isolated. This indicates that the reactivity of zethrene is not only governed by the formally fixed double bonds, in agreement with the recent finding that catalytic hydrogenation of zethrene occurs not on the fixed double bonds but on the naphthalene rings.[13] As shown in Scheme 2, heating zethrene with *N*-alkyl maleimide at reflux in toluene led to an adduct (**7a** or **7b**), which was obtained as a mixture with the corresponding oxidized product (**8a** or **8b**, respectively). This Diels–Alder reaction employs zethrene as the diene with one of its fixed double bonds and one of its naphthalene ring involved. Oxidation of **7a**/**b** with DDQ yielded **8a**/**b** leading to π-expansion of zethrene. Further reaction of **8a**/**b** with an excess of the corresponding *N*-alkyl maleimide in refluxing diphenyl ether directly led to diimide **9a**/**b**, possibly because the Diels–Alder adduct was oxidized by air. With two electron-withdrawing imide moieties attached to the large π-face of benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene, **9a** and **9b** can be considered as potential n-type organic semiconductors.

Single crystals of zethrene suitable for X-ray crystallography were grown from solutions in chloroform. The crystal structure of zethrene is shown in Fig. 2, and it confirms the formally fixed C–C double bonds and reveals π-stacking. As shown in red in Fig. 2a, the C7–C7a and C14–C14a bonds have a bond length of 1.35 Å, which is very close to the typical length (1.31–1.34 Å) for a C(sp^2)–C(sp^2) double bond in alkenes, but shorter than the typical length (1.38–1.40 Å) for a C(sp^2)–C(sp^2) aromatic bond in arenes.[19] The C7a–C14a bond shown in green has a bond length of 1.46 Å, which is typical for a single bond between two sp^2 carbon atoms (1.45–1.46 Å).[20] These bond lengths are in agreement with the fixed C–C double bonds in zethrene. Unlike pentacene and tetracene, which exhibit well-known herringbone packing, zethrene forms offset π-stacks in two directions as illustrated in Fig. 2b. The π-to-π distance between two parallel neighbours within a stack is 3.45 Å, and the angle between π-planes in neighboring stacks is 78.6°. Such molecular packing of zethrene is also known as the γ-type packing of PAHs, which arises from the increased relative importance of C⋯C interactions over C⋯H interactions according to Desiraju and Gavezzotti's predictive model.[20] Unlike the γ-type packing,



Scheme 1 (a) Synthesis of zethrene; (b) attempted synthesis of zethrene from 1,8-divinylnaphthalene.



Scheme 2 Diels–Alder reactions of zethrene and π-expansion.

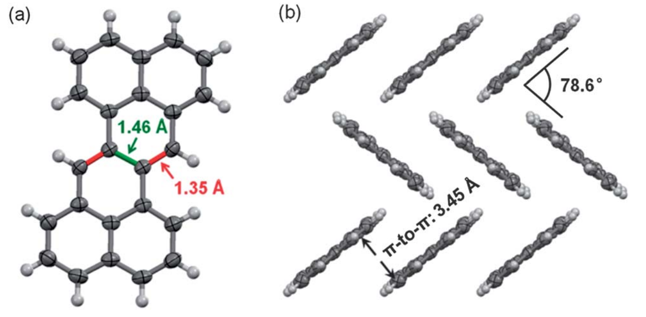


Fig. 2 (a) Structure of zethrene in the single crystal with carbon atom positions shown as 50% probability ellipsoids; (b) π-stacking of zethrene in the single crystal.

simple herringbone packing has nearest neighbouring PAH molecules nonparallel to each other leading to more C⋯H interactions throughout the crystal lattice. Zethrene ($C_{24}H_{14}$) adopts γ-type packing rather than herringbone packing because it, in comparison to pentacene ($C_{22}H_{14}$), has an increased number of carbon atoms relative to hydrogen atoms and furthermore, the additional carbon atoms are core atoms that promote face-to-face π-stacking.

Besides molecular packing in the solid state, the energy level of frontier molecular orbital is another key factor governing semiconductor properties of conjugated molecules. Therefore zethrene and diimide **9a** were investigated using cyclic voltammetry and UV-vis absorption spectroscopy to determine the energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The cyclic voltammogram of zethrene as measured from a solution in dichloromethane exhibited a reversible reduction peak at −1.79 V and a quasi-reversible oxidation peak at 0.27 V *versus* ferrocenium/ferrocene as shown in ESI.† From these potentials, the energy levels of HOMO and LUMO for zethrene are estimated as −5.07 eV and −3.01 eV, respectively.[21] The UV-vis absorption spectrum of zethrene (shown in ESI†) was recorded using a solution in chloroform and revealed a HOMO–LUMO energy gap of 2.16 eV based on the absorption edge at 575 nm. This gap is in agreement with the HOMO and LUMO energy levels estimated from the electrochemical potentials. The cyclic voltammogram of **9a** from a solution in dichloromethane (shown in ESI†) exhibited two reversible reduction waves with half-wave reduction potentials at −1.52 V and −1.73 V *versus* ferrocenium/ferrocene. From the first reduction wave, the LUMO energy level of **9a** is estimated as −3.28 eV. This value, to our surprise, is much higher than the reported LUMO energy levels of zethrene diimide (−3.96 eV),[12] naphthalene diimides (about −3.8 eV) and perylene diimides (about −3.8 eV).[22] A solution of **9a** in dichloromethane exhibited an absorption edge at 561 nm corresponding to a HOMO–LUMO energy gap of 2.21 eV (shown in ESI†). The relatively high HOMO energy level along with the γ-type π-packing suggests that zethrene is a promising candidate as a p-type semiconductor for OTFTs.[23] In contrast, the LUMO of **9a** is not sufficiently low to promise a high performance in n-channel OTFTs.

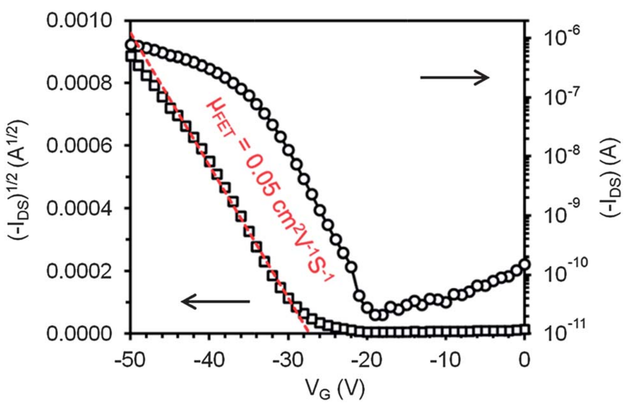


Fig. 3 Drain current (I_{DS}) *versus* gate voltage (V_G) with drain voltage (V_{DS}) at −50 V for the best-performing OTFT of zethrene with an active channel of W = 1 mm and L = 150 μm as measured in air.

To test the semiconductor properties of zethrene and diimide **9a** in OTFTs, thin films were deposited by thermal evaporation under high vacuum onto silicon wafers, whose SiO_2 dielectric surface was pre-treated with a self-assembled monolayer of octadecyltrimethoxysilane.[24] When the substrate temperature was kept at 60 °C during deposition, the resulting films of zethrene were polycrystalline, exhibiting a polymorph different from the bulk crystals as found from X-ray diffraction (XRD).[25] Atomic force microscopy (AFM) images of the films of zethrene exhibited a terraced morphology that is typical for vacuum-deposited films of organic semiconductors. The device fabrication was completed by depositing a layer of gold onto the zethrene films through a shadow mask to form top-contact source and drain electrodes. The resulting devices had highly doped silicon as the gate electrode and a 300 nm-thick layer of SiO_2 as dielectrics. As measured from these devices, zethrene functioned as a p-type organic semiconductor with field effect mobility in the range of 0.01 to 0.05 $cm^2\ V^{-1}\ s^{-1}$. Fig. 3 shows typical transfer *I*–*V* curves for the best-performing OTFT of zethrene as tested in air. When measured under vacuum, the OTFTs of **9a** exhibited an n-channel field effect with electron mobility of up to $2 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$ and a threshold voltage larger than 40 V. In contrast, the films of **9a** appeared insulating when measured in ambient air because of electron trapping by oxygen and water. The low air stability and large threshold voltage of **9a** can be attributed to its high-lying LUMO. Moreover, the high-lying LUMO leads to high-energy mobile electrons in the film of **9a**, which are easily trapped by defects. Such electron trapping can in principle make the measured electron mobility much lower than the intrinsic value.

Conclusions

In summary, the above studies demonstrate not only a new synthesis of zethrene with improved yield, but also for the first time that zethrene functions as a p-type semiconductor in thin film transistors. Moreover, Diels–Alder addition to the bay region of zethrene is found to allow π-expansion leading to new derivatives of benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene, which behave as n-type organic semiconductors in thin film transistors.

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