Acenes Generated from Precursors and Their Semiconducting Properties

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CONSPECTUS

Acenes are a class of aromatic hydrocarbons composed of linearly fused benzene rings. Noteworthy features of these molecules include their extended flat structure and the narrow gap between the HOMO and LUMO energy levels. However, the preparation of larger acenes, those that are larger than pentacene, has been challenging. These molecules are relatively unstable and have low solubility in typical solvents. Recently researchers have developed a new synthesis route for higher acenes using stable and soluble "precursors," which generate these structures on demand by either heating or irradiation of light. Using this method, nonsubstituted hexacene, heptacene, octacene, and nonacene were successfully prepared.

In this Account, we summarize the preparation of nonsubstituted acenes from corresponding precursors, describe their physical properties, and discuss potential applications including potential usage in organic semiconductor devices. We first introduced the concept of using a precursor in the work with pentacene. Overall, we divide this methodology into two categories: masking pentacene itself with a dienophile to form a cycloadduct and the construction of higher acenes through conventional synthetic procedures. For the first category, a diverse array of dienophiles could be chosen, depending on the processing needs, especially for use in field-effect transistors (FETs). For the second category, researchers synthesized the pentacene precursor molecules using a multistep procedure. Upon proper activation, these molecules expel small fragments to generate pentacene readily. This strategy enabled the production of pentacene andunprepared higher acenes ranging from hexacene to nonacene. This new method provides a way to unravel the fascinating chemistry of higher acenes.
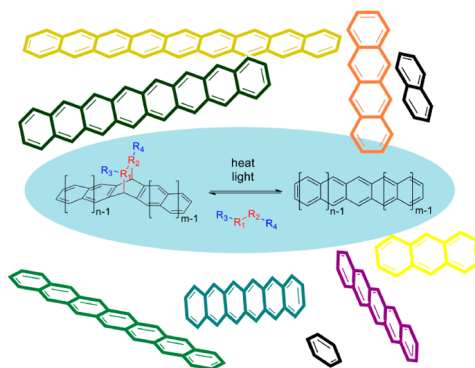
1. Introduction

Acenes are a class of aromatic hydrocarbons composed of linearly fused benzene rings. The structure of acenes is considered as linearly extended one-dimensional graphene, while their chemistry attracts wide interest in both materials[1] and theoretical science.[2] One of the most noteworthy features of their electronic structures is the narrow gap between HOMO−LUMO energy levels. This energy gap is reduced dramatically while the molecular length is increased.[2,3] Acenes have already been effectively used in a number of opto-electronic devices, such as organic field effect transistors (OFETs),[1,4] organic photovoltaic cells (OPVs),[5] organic light-emitting diodes (OLEDs),[6] and organic chemosensors,[7] among others. A wide variety of derivatives has been designed and synthesized in order to adjust the properties of acenes and to improve device performance. As reported in literature, many kinds of bulky groups[1b] and electron withdrawing/releasing groups have been added onto the structure of acenes, such as phenyl,[8] arylthio,[8,9] alkylsilylethynyl,[10] halo, cyano, and many

others.[11] The structural modifications enhance the stability of acenes and the efficiency of the devices. For example, the OFET devices made with alkylsilylethynyl-substituted acenes[10,12] and thiophene-fused heteroacenes[13,14] have displayed remarkably high charge carrier mobility. Nonsubstituted acenes with molecular sizes larger than pentacene, on the contrary, are difficult to obtain due to their low stability under ambient environments.[15−21] It was generally accepted that nonsubstituted acenes higher than pentacene are not accessible under normal conditions. Recently the synthesis of several higher acenes has been reported, yet they can only be isolated in inert matrixes.[3] They were easily oxidized by oxygen in air, or underwent self-dimerization readily. In this Account, we highlight the synthesis of nonsubstituted acenes through various types of precursors, that are stable in common environments and can be converted to acenes readily on demand. The transformation was believed to proceed through a unimolecular process, initiated either by heating or by light. The reaction type generally involves retro-cyclization or cheletropic expulsion reaction as depicted in Figure 1. The acenes generated from the precursors were pure enough to be used directly on device fabrication. Moreover, a recent work on the synthesis of hexacene indicated that, by using a proper precursor, it may become possible to obtain higher acenes under ordinary conditions and use them to manufacture semiconducting devices.
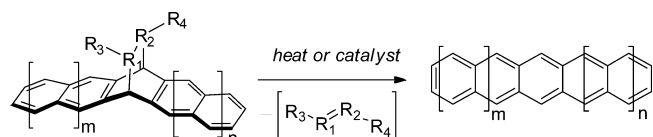
2. Pentacene Precursors for Improving the Solubility

It is generally recognized that, for practical usage on OFETs, the charge carrier mobility must be higher than $0.1-1.0$ cm^2 V^{-1} s^{-1}.[22] Pentacene has been shown to display a mobility higher than 5 cm^2 V^{-1} s^{-1}.[23] However, the practical value of pentacene is severely limited by its low stability and low solubility in usual solutions. A way to overcome the solubility problem is to prepare its soluble precursors, then transform them into pentacene at the proper stage during processing. The first example of soluble pentacene precursor was reported by Müllen et al. in 1996.[24a] These materials were prepared either from low molecular weight starting materials (conventional synthesis, type 2), or by masking the existing acenes with a protecting group (mask method, type 1).

2.1. Soluble Pentacene Precursors via Conventional Synthesis. A typical example for the synthesis of pentacene precursors of type 2 is shown in Figure 2.[24] 5,6,7,8-Tetramethylenebicyclo[2.2.2]oct-2-ene (**1**) was used as the starting material, which underwent a double ring annulation with benzyne, followed by oxidative aromatization to give 6,13-dihydro-6,13-ethenopentacene (**3**) in two steps. Reaction of **3** with tetrahalo-substituted thiophenedioxide yielded the triaryl-fused bicyclo[2.2.2] precursor **4** in 70−75% yield. The reaction was conducted under a high pressure (6 kbar) in order to speed up the cyclization reaction. Compound **4** was found to be quite soluble in CH$_2$Cl$_2$ and in toluene (∼1.5 wt %), from which thin films can be prepared by spin-coating. The films of **4** were converted to pentacene (**5**) quantitatively through a retro Diels−Alder

FIGURE 1. Strategy of acenes generation from precursors, where *m* and *n* are integers, R$_1$ and R$_2$ denote the dienophile leaving group, and R$_3$ and R$_4$ denote functional substituents.
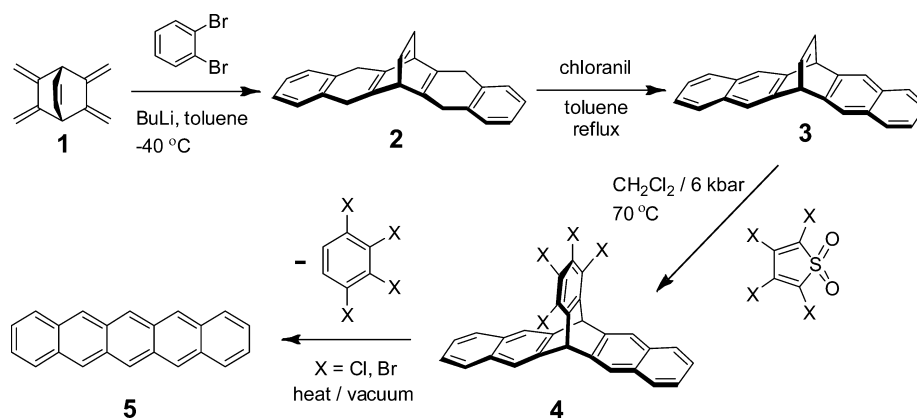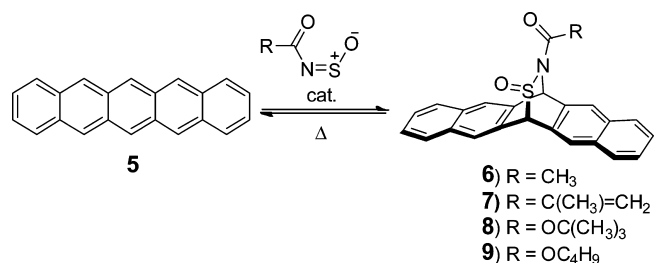
FIGURE 2. Synthesis and the thermal reaction of pentacene precursor **4**.

FIGURE 3. Synthesis of pentacene precursor **6**−**9**.

FIGURE 4. Photo patterning process using pentacene precursor **7**. The steps are (a) spin-coated thin film of compound **7**; (b) selective polymerization by UV irradiation through a patterned mask, followed by post exposure bake and washing with methanol; and (c) thermal generation of pentacene at 150−200 °C under N_2.

type reaction by heating at 200 °C for 5 min. The microcrystalline pentacene obtained in these films was similar to those prepared by vapor deposition method. The highest mobility found in these devices was 0.2 cm^2 V^{-1} s^{-1}.

2.2. Soluble Pentacene Precursors Made by Masking the Benzene Rings. In a different approach (type 1), Afzali et al. developed a one-step method to mask pentacene in the form of a bicyclic adduct.[25] Through this method as shown in Figure 3, soluble precursors can be obtained avoiding tedious synthetic operations (Figure 3). Pentacene (**5**) was heated with an excess amount of *N*-sulfinylacetamide in CHCl$_3$ with a catalytic amount of methyltrioxorhenium to yield the adduct **6** in 90% yield.[26a] The solubility of **6** is high in most organic solvents, such as THF, dioxane, and chlorinated hydrocarbons (∼50 g/L). Thin films of **6** were prepared from solutions by spin-coating method, and then were transformed back to pentacene by heating at 120−200 °C. The OFET devices made with **6** displayed the highest hole mobility of 0.89 cm^2 V^{-1} s^{-1} with an on/off ratio >10^6. This compound was also processed using an inkjet printing technique. Volkman et al. prepared a bottom-contact OFET device by inkjet method using an anisole solution of precursor **6** (1 wt %). The film was heated at 160 °C for several min to regenerate pentacene. The device showed a charge carrier mobility 0.02 cm^2 V^{-1} s^{-1} with an on/off ratio 10^5.[26b]

Pentacene films prepared from the precursors were also prepatterned using a photochemical process from a shadow mask. An *N*-sulfinylmethacrylamide type precursor **7** was prepared by the cycloaddition with pentacene upon acid catalysis, and then used as a photosensitive pentacene precursor. Compound **7** can be converted back to pentacene by heating at 120−200 °C. The photopatterning process is shown in Figure 4. A solution of **7** was spin-coated to produce a thin film, then the film was irradiated with light through a patterning mask, while the methacrylate moiety was polymerized. The polymerized film was baked briefly at 120 °C, and then washed with methanol to remove the 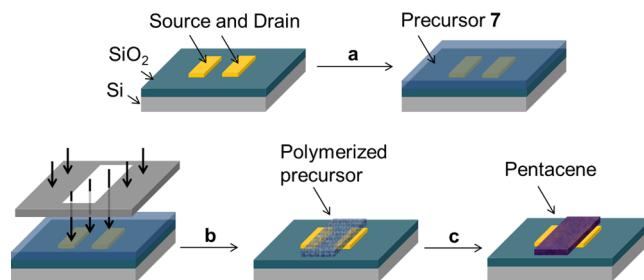nonpolymerized precursor. It was then heated at 200 °C to release pentacene, after then a bottom contact OFET device was fabricated. It showed a charge mobility of 2.1 × 10^{-2} cm^2 V^{-1} s^{-1} with on/off ratio 2 × 10^5.[27a] The mobility value was further improved by a similar "*t*-BOC resist" functionality, whereas a labile *tert*-butoxycarbonyl group can be cleaved by heating in the presence of a photogenerated acid.[28] In this case, a spin-coated thin-film of **8** was exposed under UV light through a photo patterning mask in an acidic medium, and was then annealed at 130 °C to convert the photopatterned film to pentacene. The OFET device fabricated by using **8** in a bottom-contact configuration showed a high charge mobility of 0.25 cm^2 V^{-1} s^{-1} with on/off ratio 8 × 10^4.[27b]

An inkjet printing process was developed by Afzali et al. by using an alcohol soluble pentacene precursor. The pentacene adduct of *N*-sulfinylbutyl carbamate **9** was soluble in ethanol (>15 g/L), isopropanol, and butanol. A solution of **9** (20 g/L) in isopropanol was spin-coated into a film, and transformed into pentacene by heating at 120 °C for 20 h. The charge mobility was found to be 6.8 × 10^{-2} cm^2 V^{-1} s^{-1} with an on/off ratio 2 × 10^5.[29a] Compound **9** was also blended into poly(9-vinylcarbazole) (PVC) (4:1) to form films.[29b] The charge mobility was found to be 2.2 × 10^{-2} cm^2 cm^2 V^{-1} s^{-1} with a 2 × 10^6 on/off ratio.

The grain size and crystalinity of thin films depend significantly on the processing conditions, such as solvent, annealing time, and temperature.[30] Recently, we developed a new processing methodology, that substantially improved the morphology of pentacene films. This process was successfully demonstrated with compound **10**. It was prepared readily via a cycloaddition with diethyl ketomalonate (Figure 5a),[31] and is soluble in most organic solvents (ca. 50 g/L). By using a multiple "spin-heat" procedure, films of relatively smooth surface was achieved, for example, with a root-mean-square roughness of ∼70 nm. In a typical
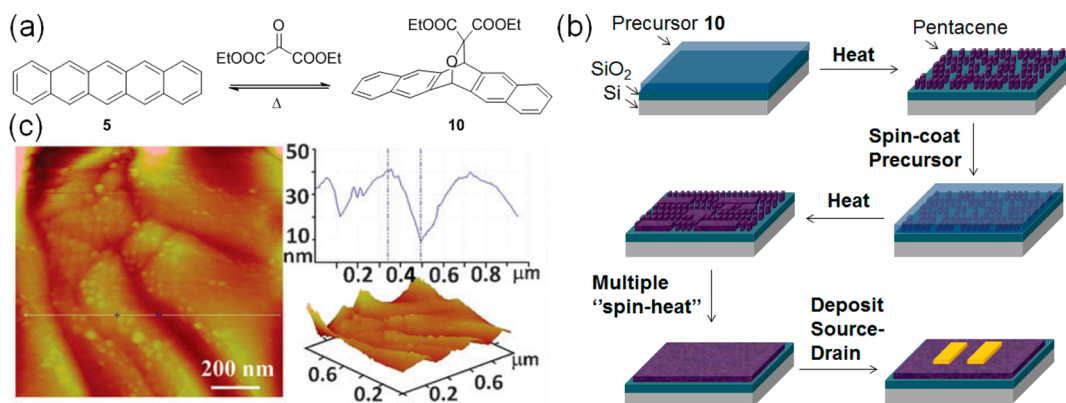
FIGURE 5. (a) Cycloaddition reaction of pentacene with diethyl ketomalonate to yield an adduct **10**. (b) Multiple spin-heat process. (c) AFM image of pentacene thin-film after multiple spin-heat process.

process, a solution of **10** in CHCl$_3$ (50 g/L) was spin-coated on top of the substrate, then was heated at 210 °C for 7 min to converted it back to pentacene. A second layer of precursor **10** was then spin-coated on top of the first pentacene layer. The combined film was heated again at 210 °C for 7 min. The spin-heat sequence was repeated six times to complete the whole process (Figure 5b). During each sequence, the microcrystals of **10** tended to fill gaps of pentacene colonies that were formed in the previous step. Thus, the film obtained a smooth surface suitable for fabrication of a top contact FET device (Figure 5c). The device displayed the highest charge mobility of 0.38 cm^2 V^{-1} s^{-1} with a 10^6 on/off ratio. The relatively high temperature required in these processes, however, may become a drawback in practical applications.[32]

3. Photogeneration of Acenes via Diketone-Type Precursors

Acene precursors composed of a bicyclo[2.2.2]octa-2,3-dione framework (abbreviated as diketone precursor) showed a high thermal stability under an ambient condition. Many of them were synthesized through conventional multistep procedures (type 2). These compounds are thermally stable, yet undergo a double CO expulsion reaction when irradiated with light to generate corresponding acenes. This method has been successfully used for the synthesis of higher acenes, i.e., hexacene, heptacene, octacene, and nonacene.

The photoexpulsion of α-diketone was found by Starting et al. in 1969.[33] They examined the thermal and photochemical properties of bicycle[2.2.2]octa-2,3-dione derivatives **11**−**15** (Table 1). When these compounds were heated, double C=O expulsion occurred in low efficiency. For example, compound **11** melted at 200 °C and remained unchanged until 350 °C was reached, while the C=O

TABLE 1. Pyrolytic and Photolysis Reactions of Diketone Precursors

Reactant	Product	Pyrolytic conditions		Photolysis yield[a]
11	**16**	350 °C	<20%[b]	100%
12	**17**	180 °C	32%	97%
13	**18**	220 °C	N.D.	95%[c], (53%)[d]
14	**19**	230 °C	Black tar.	43%[e]
15	**20**	N.D.	N.D.	60%

[a]Benzene solution, UV with Pyrex filter. [b]80% recovered of **11**. [c]Crude yield. [d]Isolated yield. [e]Isolated yield as benzo[α]phenazine.

expulsion happened in <20% yield. In comparison, the photoinduced C=O expulsion proceeded in benzene, while the yields of **16**−**20** were promoted to 43−100%.

3.1. Pentacene Generated from Diketone Precursors via Photodissociation Reactions. Two kinds of pentacene diketone precursors **21** and **22** were prepared by the Yamada and Uno groups (Figure 6).[34,35] Compounds **21** and **22** showed a high thermal stability in an ambient environment and were slightly soluble in toluene (2.3 g/L for **21** and 0.44 for **22**). When **21** was irradiated with UV/vis light in a toluene solution for 15 min, the expulsion of C=O occurred, leading to the formation of pentacene in 74% yield (Table 2). The conversion rate could determine by fluorescence
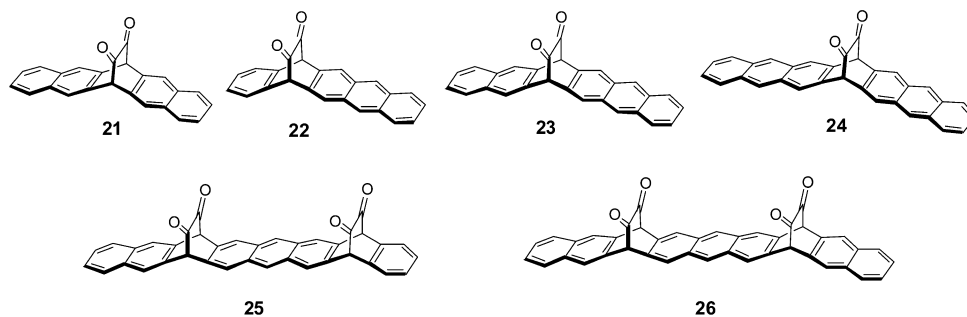
FIGURE 6. Diketone precursors of acenes.

quantum efficiency, which showed 2.3% for **21** and 2.4% for **22**. However, the photoconversion reactions were sensitive to oxygen. When the solution or thin-film was irradiated in air, the color of pentacene faded rapidly to indicate that air oxidation had occurred. Effective OFET devices can be fabricated from the use of these solutions with charge carrier mobility 0.34 cm^2 V^{-1} s^{-1} were achieved.[36]

3.2. Higher Acenes Generated from the Diketone Precursors. Although acenes higher than pentacene have drawn considerable attention for more than 70 years, their properties have not yet been unambiguously described due to their unstable nature. The first synthesis of hexacene was achieved by Clar and Marschalk in 1939[16] and heptacene in 1942 and 1943.[17] An improved synthesis of **30** and **31** was reported in 1955,[18] yet the yields were severely limited by the instability of the products.[19−21] The first reproducible syntheses of the two compounds were completed by Neckers and co-workers in 2006 and 2007 from the use of diketone precursors **23** and **24**.[37,38] Pure hexacene and heptacene were isolated by matrix isolation in poly(methyl methacrylate) (PMMA). When the PMMA matrix of **23** was irradiated with 395 nm UV light, the characteristic *para*-bands of hexacene at 550−700 nm (λ_{max} = 672 nm) appeared, along with the diminishing of the absorption band of the precursor (**23**) at 465 nm. A similar transformation for heptacene took place, while the corresponding *para*-bands appeared at 600−825 nm (λ_{max} = 760 nm). Hexacene was stable in the PMMA matrix for more than 12 h in air, but heptacene persisted only for 4 h in the same conditions. In addition to the matrix of PMMA, a cryogenic matrix isolation was performed by vaporizing compounds **21**, **23**, and **24** with low pressure, and doped into an argon or xenon matrix.[39] The photoexpulsion reactions were conducted by irradiating the matrixes with UV light (high-pressure mercury lump) at 30 K. The CO molecule that was expelled from the precursors displayed distinctive absorption peaks at 2133−2188 cm^{-1}. The photoionization property of the

acenes in the argon matrix was examined by shining on them at 185 nm. The formation of radical ions was evidenced by the absorption bands at 800−1250 nm in near IR region, while the wavelengths shifted with the number of benzene rings in a manner predicted by the theoretical model. In an argon matrix, pentacene and hexacene remained stable in the range of 10−294 K, while heptacene started to decompose at 39 K.
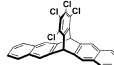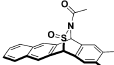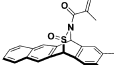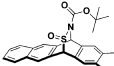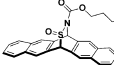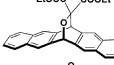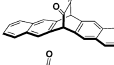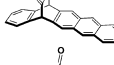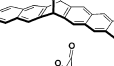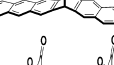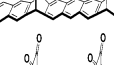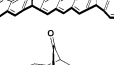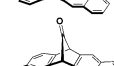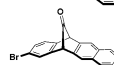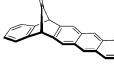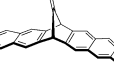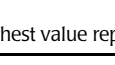
Octacene and nonacene were obtained from the diketone precursors **25** and **26**, respectively, by vaporization at a low pressure into an argon matrix.[3] The photolysis was taken by a sequential irradiation, first in the visible range (>360 nm), followed by UV (305−320 nm) light. New bands were generated at 806 nm for octacene, and at 865 nm for nonacene. When octacene and nonacene were irradiated at 185 nm, the corresponding radical ion species were detected in NIR region, that is, at 1476 nm for octacene and 1772 nm for nonacene.

The mechanism of photodecarbonylation was analyzed at room temperature by time-resolved spectra. It was clear that the CO expulsion process was initiated within several hundred picoseconds, and completed in the range of nanoseconds (∼7 ns) at room temperature.[40] A computational analysis based on B3LYP/6-311+G** suggested that an initial cleavage of the C−C bond happened between the bridgehead and one carbonyl atom to form a biradical intermediate. The subsequent loss of two CO molecules led to the production of a triplet acene.[41] The computational results complied well with the experimental.

4. Generation of Acene by Monoketone-Type Precursors

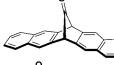Acene precursors consist of one or more carbonyl bridges across the benzene rings, i.e., with a norbornadiene-7-one moiety, are abbreviated as monoketone precursors in this report (Figure 7).[42] This series of compounds showed nearly

TABLE 2. Conversion Conditions of the Acene Precursors and Physical Parameters of the Products

| Precursor	Conversion Condition	Yield (%)	Stability of the product	Mobility[a] ($cm^2V^{-1}s^{-1}$)	Ref.
4	180 °C	>99	stable for OFET	0.2	24
6	130-200 °C	>99	stable for OFET	0.02 – 0.89	26a,b
7	hν (UV), then 120-200 °C	-	stable for OFET	0.021	27a
8	hν (UV), then 130 °C	-	stable for OFET	0.25	27b
9	120 °C, or 160 °C with PVK	>99	stable for OFET	0.022-0.054	29a,b
10	210 °C	>99	stable for OFET	0.38	31a
21	>300 nm w/o 120 °C	74	air oxidation	0.34	34a,36
22	405 nm or 468 nm	-	air oxidation	-	35
23	395nm or 385-450 nm	-	more than 12 h in matrix	-	37, 39
24	395nm or 385-450 nm	-	4 h in matrix	-	38, 39
25	>360 nm, then 305-320 nm	-	matrix isolated	-	3
26	>360 nm, then 305-320 nm	-	matrix isolated	-	3
30	106 °C	>99	stable in dark	0.064-0.56	49
30b	91 °C	>99	stable in dark	0.0022	50
30c	98 °C	>99	stable in dark	0.0046	50
31	150 °C, or 385 nm	>99	stable in solid state	0.0013	47, 48
35	128 °C, or 385 nm	>99	stable in solid state	0.0088	48
37	180 °C	>99	stable in solid state	4.3	51

[a]The highest value reported in literature, of either single crystal or thin film.

quantitative yields on either a thermal or a photochemical conversion to the corresponding acenes through a cheletropic decarbonylation. This method provides an alternative yet more effective way to access higher acenes of high purity.

The cheletropic thermal decarbonylation of norbornadiene-7-one (**27**) derivatives have been well documented.[43–46] The thermal stability was enhanced when the number of
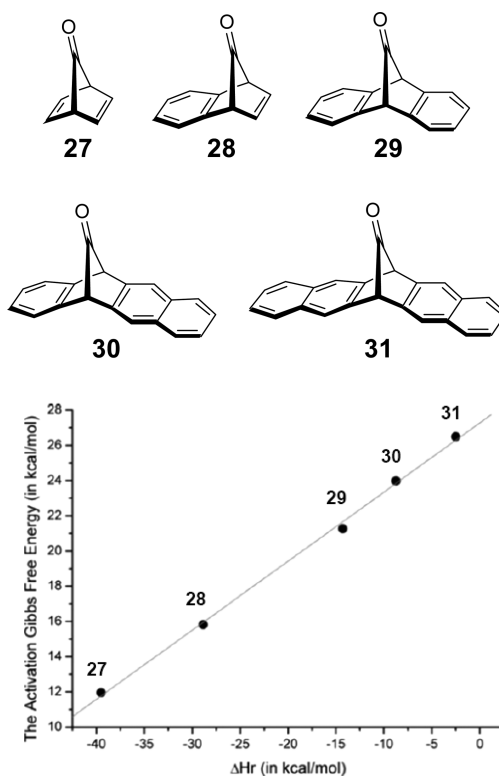
FIGURE 7. Linear fitting of **27**–**31** for the activation Gibbs free energy ($\Delta G^{\ddagger}$) and the reaction heat (ΔH_r).

benzene rings on either side of the norbordiene-7-one was extended (Figure 7). The gradual increase of the decomposition temperature with the number of rings was further supported by an ab initio modeling, and indicated that the activation energy ($\Delta G^{\ddagger}$) of C=O expulsion is proportional to the number of benzene rings.[42] The calculation indicated that for compound **31**, the decomposition temperature for the production of pentacene was in the proximity of 400 K. These results encouraged us to synthesize the tetracene and pentacene analogues **30** and **31**, which were predicted to be stable under ambient conditions.

4.1. Pentacene Monoketone Precursors. The synthesis of pentacene monoketone precursors can be approached through several pathways (Figure 8). Compound **31** was obtained from **32**, that was prepared from 7-*tert*-butoxynorbornadiene in one step via a double annulation of two naphthalene rings.[47] The net yield of **31** from 7-*tert*-butoxynorbornadiene was 27%. The CO bridge is shifted away from the center of **31** to an unsymmetrical structure of **35**, for the purpose of promoting higher solubility. Compound **35** was synthesized through a multistep sequence starting from a benzonorbornadiene derivative **33a** in a total yield of 40%.[48] Both **31** and **35** are stable in air and can be stored for a long period of time under an ambient temperature
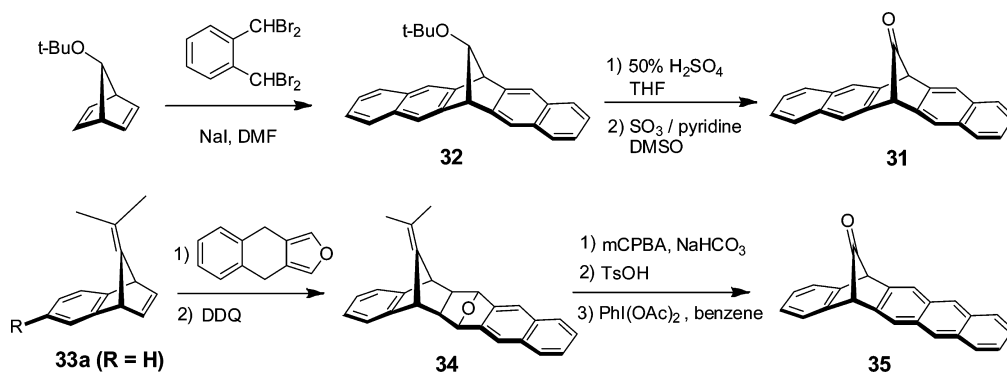
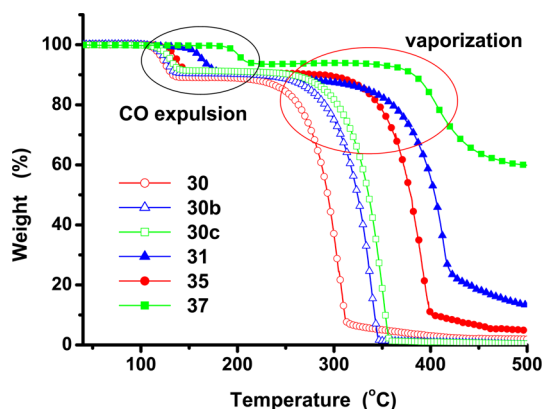**FIGURE 8.** Synthesis of monoketone precursors of pentacene **31** and **35**.

FIGURE 9. TGA profiles of acene precursors.

FIGURE 10. Absorption spectra of **31** in a degassed THF, excited at 310 nm, as a function of exposure times 0–40 s with each increment of 5 s.

($\leq$25 °C). They exhibit limited solubility in organic solvents, such as CHCl$_3$, CH$_2$Cl$_2$, benzene, toluene, acetone, and THF ($\sim$0.7 g/L). Both compounds **31** and **35** can produce pentacene through a cheletropic C=O expulsion reaction in high yields. Upon heating at ca. 150 °C, the C=O absorption band at around 1780 cm^{-1} in IR spectra diminished rapidly. The thermal conversion profile is clearly depicted in a thermal gravimetric analysis (TGA) (Figure 9). The conversion reaction was also achieved via photochemical reactions. When a degassed solution of **31** was irradiated with UV light, the characteristic absorption bands of pentacene at 400–600 nm arose (Figure 10). The yield of photochemical conversions was also high, yet it seemed inevitable to observe the formation of dimers in the process. The dimerization of pentacene is a photochemically labile reaction, and proceeds very fast in solutions.

The thin films prepared from the precursors by spin-coating usually displayed a polycrystalline morphology. The highest charge carrier mobility of the devices made with **31** through heating was 8.8 $\times$ 10^{-3} cm^2 V^{-1} s^{-1}, and that of **35** was 1.3 $\times$ 10^{-3} cm^2 V^{-1} s^{-1}.[47,48] The devices made with an equal molar mixture of **31** and **35** through UV

irradiation showed the highest charge mobility of 2.4 $\times$ 10^{-3} cm^2 V^{-1} s^{-1}.

4.2. Tetracene Derivatives and Their Monoketone Precursors. The monoketone precursors of tetracene derivatives have also been studied. The 2-halogen substituted tetracene was obtained from the corresponding precursor compounds **30b,c** in high yields.[49,50] These compounds were synthesized from the cycloaddition reactions of **33a–c** with naphthaquinone, followed by aromatization of the ring and the ozonolysis of C=C bond (Figure 11). The overall yield of **30** through five steps was ca. 30%. All three derivatives showed a good thermal stability under ambient conditions, and underwent CO expulsion while heated above 106 °C (Figure 9). They are highly soluble in most organic solvents, for example, CH$_2$Cl$_2$ and CHCl$_3$ (ca. 15 g/L). When a toluene solution of **30** (0.6 wt %) was heated at 110 °C, the color turned to yellow-orange readily. Orange plate shape crystals of tetracene 150–600 μm in diameter precipitated out of the solution, and used directly for the fabrication of OFET devices (Figure 12). The charge mobility found was quite high, that is, 0.56 cm^2 V^{-1} s^{-1}, with an

FIGURE 11. Synthesis of monoketone precursors of tetracene **30** and **30b**,**c**.

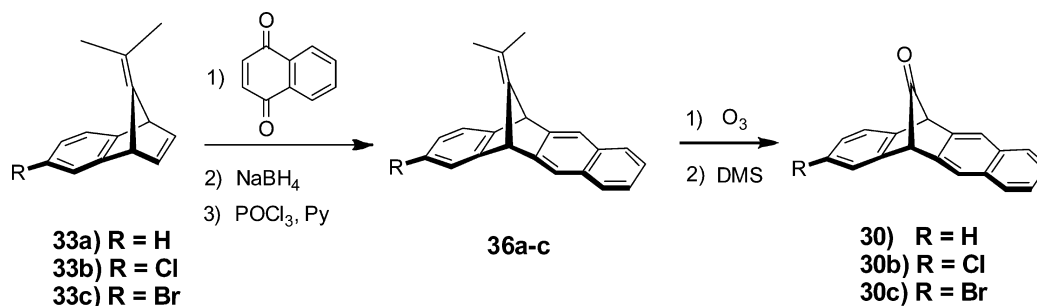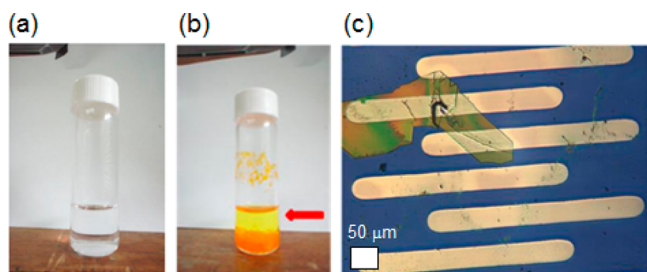**FIGURE 12.** (a) Solutions of **30** in toluene. (b) Orange precipitates of tetracene formed after heating. (c) Crystal of tetracene on top of a SiO$_2$/Si substrate across gold source and drain electrodes.
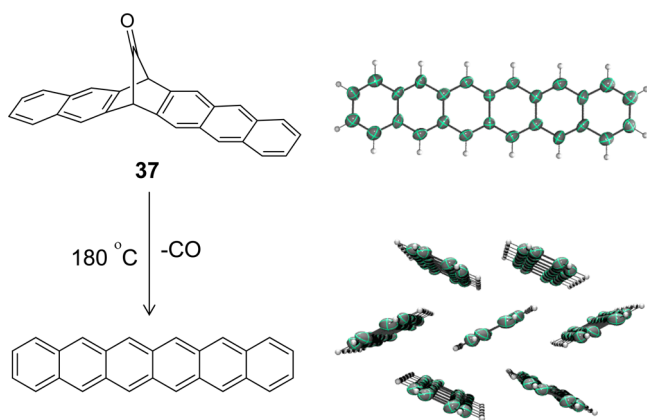

FIGURE 13. Synthesis of hexacene from its precursor (left); ORTEP drawing of hexacene in crystal and its herringbone packing motif (right).

on/off ratio of 1.0×10^5. In a different design, thin film devices were also made from saturated solutions of **30** through spin-coating. Such devices showed the highest charge mobility of 6.4×10^{-2} cm^{2}V^{-1}s^{-1}, substantially lower than those made with single crystals.

4.3. Hexacene Generated from the Monoketone Precursor. The synthesis of hexacene was also achieved from the use of corresponding monoketone precursor **37** (Figure 13).[51] The conversion was best performed by heating a solid sample of **37** to 180 °C in a nitrogen atmosphere. During heating, the color changed rapidly from white to

blue-green. In the IR spectrum, the characteristic carbonyl peak of **37** at 1784 cm^{-1} diminished. The thermal stability of crystalline hexacene was found to be remarkably high. It can be stored at room temperature for more than 30 days without apparent decomposition. Hexacene in solution is much more sensitive to light, which initiated the process of dimerization. When a solution of **37** in THF was irradiated with a UV light (365 nm) under an oxygen-free condition, new absorption bands at 557, 611, and 667 nm appeared, to indicate the formation of hexacene. However, these bands persisted briefly then disappeared. Single crystals of hexacene of good quality can be obtained from the use of physical vapor transport method. The structure of hexacene was successfully resolved with X-ray diffraction analysis. The packing pattern of hexacene was similar to that of pentacene, while both were arranged in a herringbone motif (Figure 13). Theoretical calculations based on X-ray crystal data of hexacene revealed smaller reorganization energy (λ^+) as well as a higher electronic coupling (τ^+) than pentacene. These results implied high charge mobility. The OFET devices made with a single crystal of hexacene were successfully fabricated. The results showed a charge carrier mobility of 4.3 cm^2 V^{-1} s^{-1}. Such a performance is among the best for all known organic semiconductors to date.

5. Summaries and Outlook

Utilizing suitable precursors for the production of acenes has proven to be an effective method to obtain these sensitive high quality materials. There are many advantages from the use of these precursors; for instance, they are stable in ambient environments and soluble enough for spin-coating processes. These precursors are composed of an acene and a smaller fragment, namely, a dienophile, to form a cyclic adduct. Each type of dienophile possesses its unique advantages; therefore, they may be selected according to the needs of a particular experiment. For example, the bulky *N*-sulfinylamide groups can enhance the solubility of the

materials and are, therefore, suitable for solution processing in general. The diketone precursors are photolabile, so that the acenes can be produced by photolysis at low temperatures in frozen glasses. This type of precursor has been used in the preparation of nonacene, which is the longest acene known to date. The monoketone precursors showed lower activation energy; that is, they are workable either by heating or by irradiation. An OFET device made with a single crystal of hexacene has been achieved recently in our laboratory from the use of monoketone precursor.

The method of using precursors for the production of acenes has opened new routes toward the preparation of higher acenes that were not previously accessible. There are many attractive properties of higher acenes that are awaiting to be explored. Examples of these attractive properties are higher conductivity and antiferrimagnetic properties, among others. With these new methods, we expect major advancements in the fascinating chemistry of these materials.

BIOGRAPHICAL INFORMATION

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Tahsin J. Chow completed his BS degree in National Taiwan University (1972), then a Ph.D. degree in the University of Cincinnati (1980). He spent two years in the University of Utah as a postdoctoral fellow. Form 1982, he was appointed to the position of an Associate Research Fellow in Academia Sinica, and was promoted in 1986 to a Research Fellow. In the meantime, he was also appointed as an Adjunct Associate Professor and Professor in National Taiwan University. His research interests are in the fields of organic and physical organic chemistry, and in recent years with a particular focus on organic materials.

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