Synthesis and physical properties of brominated hexacene and hole-transfer properties of thin-film transistors†

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A halide-substituted higher acene, 2-bromohexacene, and its precursor with a carbonyl bridge moiety were synthesized. The precursor was synthesized through 7 steps in a total yield of 2.5%. The structure of precursor and thermally converted 2-bromohexacene were characterized by solid state NMR, IR, and absorption spectra, as well as by DFT computation analysis. It exhibited high stability in the solid state over 3 months, therefore can be utilized in the fabrication of opto-electronic devices. The organic thin-film transistors (OFETs) were fabricated by using 2-bromohexacene and parent hexacene through vacuum deposition method. The best film mobility of 2-bromohexacene was observed at 0.83 cm² V⁻¹ s⁻¹ with an on/off ratio of 5.0 × 10⁴ and a threshold of −52 V, while the best film mobility of hexacene was observed at 0.076 cm² V⁻¹ s⁻¹ with an on/off ratio of 2.4 × 10² and a threshold of −21 V. AFM measurement of 2-bromohexacene showed smooth film formation. The averaged mobility of 2-bromohexacene is 8 fold higher than the non-substituted hexacene.

1. Introduction

Acenes are amongst the most representative hydrocarbons for analysing the physical properties of polycyclic hydrocarbon materials. Along with the increase in the number of aromatic benzene rings, acenes exhibit a reduction of both the HOMO-LUMO gap and the reorganisation energy. The chemistry of acenes higher than pentacene, particularly their open-shell characteristics and high charge transport properties, has attracted considerable attention. Hence, these compounds and their analogs such thieonoacene based semiconductor are suitable for use in organic electronic devices such as organic field-effect transistors. The extended π-conjugation of higher acenes also induce an interesting phenomenon of singlet fission that can be used on light harvesting. Bulky substituents can enhance the thermal and photo-stability of acenes by lowering the radical characteristic in the ground state. The isolation of higher acenes, from hexacene to nonacene and derivatives, has been achieved by applying this strategy. The modification of physical properties of acenes in the solid state requires a crystal engineering approach; however, their isolation steps are either difficult or tedious in order to obtain qualified structures due to their high thermal and light sensitivity in solutions. To overcome the difficulty, stable precursors of acenes are prepared first, which can then be converted to the corresponding acenes quantitatively in demand through either a thermal or a photo-driven process. The synthesis of nonacene derivatives has been achieved by this approach utilising a diketone precursor through photo-induced transformation. Recently, the dimer structure of heptacene was converted to heptacene via a thermal retro-cyclization reaction, therefore showing its feasibility for further processes. The precursor method can be used to produce higher acenes in large quantity that is required to become usable materials. Acenes have certain valuable potential applications, such as organic semi-conductors, singlet fission materials, and organic biradical sources. Our group has developed the method of producing higher acene molecules from either monoketone...
precursors or from diethylketomalonate precursors. Both types of precursor can be cleanly converted to hexacene either thermally or photo-chemically. In addition, our group has generated halide-substituted tetracene and pentacene from their corresponding monoketone precursors. They were used successfully as the semiconductors in electronic devices. In these devices, single crystal bromopentacene device exhibits a significant superior hole mobility (>5 cm² V⁻¹ s⁻¹) to the parent pentacene (1.4 cm² V⁻¹ s⁻¹). Such a high performance is comparable with other related materials, such as trisopropylysilylethynylpentacene (>1 cm² V⁻¹ s⁻¹).22-26 alkylated dinaphtho[2,3-b:2’,3’-f]thieno[3,2-b]thiophenes (>10 cm² V⁻¹ s⁻¹).27,28 and the crystal of tetracene analogous of rubrene (>18 cm² V⁻¹ s⁻¹).29,30 In previous reports, the charge mobility of hexacene and derivatives were measured in the devices either made with single crystals,31 or with crystalline thin films prepared through solution method.32,33 However, the physical properties and transistor characteristics of hexacene thin film that is prepared by vacuum deposition method have not yet been reported.

It is believed that the bromine substituent can provide a suitable size to improve crystal packing. Judged by the past high-performance of brominated tetracene and pentacene, it is therefore in demand to explore the possibility of brominated analogue of hexacene. In this regard, the brominated analogue of hexacene, i.e., 2-bromohexacene (1a), is synthesized and its charge-transport property is examined. Precursor 2a is cleanly converted to 1a by thermal decomposition, and 1a exhibits high thermal stability in the dark over 90 days (Fig. 1). This is the first example of the charge-transport property of a stable vacuum-deposited thin-film of hexacene and halogenated hexacene for electronic devices.

2. Results and discussion

2.1. Synthesis

The synthesis of 2a is shown in Scheme 1. Dimethylfulvene derivative 3 and benzoquinone 4 were treated with s-tetrazine, affording diketone 5 as an endo-exo mixture, then the double bond of 5 was reduced using zinc in acetic acid, affording adduct 6. The aldol reaction of 6 with dialdehyde 7 afforded diketone 8 as an endo compound in 17% yield (from 3, three steps). Pure endo-8 was crystallized probably due to steric influence by the bromo-substituent. It was reduced by NaBH₄, and further treatment with POCl₃/pyridine afforded aromatic compound 9 in 48% yield (from 8, two steps). The exo-double bond was treated with OsO₄ to give a diol, followed by treatment with Ph(OAc)₂ to give desired 2a in 31% yield. The total yield was 2.5% in 7 steps.

The absorption spectrum of 2a in 1,2,4-trichlorobenzene exhibited characteristic 1A→1L₅ transitions of the anthracene chromophore at 353, 371, 391 and 408 nm, with vibronic progressions, which were red-shifted from the peaks of parent 2b at 350, 368 and 391 nm in the 1,2,4-trichlorobenzene solution (Fig. S1†). When the solution of 2a was heated at 230 °C, the solution changed from colorless to pale-green, which exhibited characteristic acene vibration absorption bands at 573, 623 and 679 nm. However, this colour changed to yellow within a few minutes owing to the dimerization or oxidation of 1a.

2.2. Physical properties

The absorption maximum in the visible range was observed at 679 nm, whereas parent hexacene 1b exhibited the peak maximum at 675 nm in 1,2,4-trichlorobenzene (Fig. S1†). The peaks were red-shifted from those of parent hexacene 1b by 4 nm, indicating the reduction of HOMO–LUMO gap of 1a by the bromo substituent. This phenomenon has similarly been observed in the pairs of tetracene (473 nm in THF) and 2-bromotetracene (477 nm in THF),23 as well as pentacene (575 nm in THF) and 2-bromopentacene (578 nm in THF).22 To compare with the reported hexacene analogues, the peak maximum was shown to be red-shifted from that of pentacene[2,3-b]thiophene (640 nm in o-DCB)20 due to the increase of aromaticity. In comparison with other substituent group effect, however, it showed a blue shift from those of tricyclohexylsilylthethyl-6,11,12-tri-tert-butylsilylhexacyclopentacene (725 nm),21 tri-tetrahexylsilylhexacyclopentacene (738 nm),21,24 and trialkylsilylthethyl-azahexacene (823–842 nm in hexane)24 due to the electron-donating effect of the trialkylsilylthethyl acetylene units.

In the thermal gravimetric analysis (TGA) profile of 2a, the first weight loss (8.5%, calcd 6.5%) was observed at approximately 200 °C to generate 1a. The thermal weight loss profile did not change up to 360 °C. Then it was followed by the second weight loss caused by the vaporisation as well as the decomposition of 1a at temperatures greater than 400 °C (Fig. 2a). Decarbonylation at 200 °C was confirmed by infrared (IR) spectroscopy, which revealed the disappearance of the characteristic C=O stretching band at 1786 cm⁻¹ after heating at 230 °C (Fig. 2b). The high-resolution FAB-MS spectrum revealed
a molecular ion signal at $m/z$ 406.0387 [M+, calc 406.03571, error = +7.4 ppm], which corresponded to 1a. The purity was also confirmed by correct elemental analysis. The absorption spectra of 2a, fabricated by drop-casting a saturated chloro-benzene solution on a quartz substrate, exhibited a similar vibration structure to that of 2a in solution, with characteristic peaks at 403, 380 and 364 nm, indicative of the fabrication of film of 2a. In contrast, after heating at 230 °C under nitrogen, a broad band was observed at 500–900 nm, and the peaks at 360–400 nm, which are characteristic of the anthracene moiety, disappeared.

These structures were different from that of 1a in solution. Film 1a exhibited characteristic peaks at 833 and 776 and at 708 and 661 nm. These peaks exhibited the appearance of Davydov splitting effect. The same pattern appeared in other related acene structures in the solid state, including parent 1b, at 840 nm, 765 nm, 708 nm and 654 nm. The first bands at 833 and 775 nm corresponded to the 0–0 band, and those at 708 and 654 nm corresponded to the 0–1 band (Fig. 2c). The high thermal stability of 1b in the solid state was confirmed by solid-state NMR that maintained invariant over 1 month. Comparing it with heptacene under a similar situation, the latter dimerised slightly after 1 month. To verify the thermal stability of 1a, $^{13}$C CP-MAS NMR spectra were recorded for monitoring the variation of the carbon skeleton. Compound 2a exhibited three main peaks at 193.2 (bridge position of C=C=O), 137–114 (aromatic carbon atoms) and 54.4 ppm (bridgehead tertiary carbon atom).

After the conversion to 1a, the spectrum exhibited aromatic carbon peaks at 125.7 and 122.9 ppm only, indicating a quantitative transformation. After maintaining 1a for 90 days in the dark under air atmosphere, no changes were observed in the CP-MAS spectrum, indicative of the high thermal stability of 1a (Fig. 2d). This high thermal stability can be compared with the reported property of hexacene (>1 month in dark) and tricyclohexylsilyl ethynyl hexacene (several month). The film of 1a was grown by vacuum sublimation and exhibited a structure similar to the film in Fig. 2c (Fig. S3†). The ionisation potential ($E_{ip}$) and electron affinity ($E_{ea}$) of the film 1a were $–5.24$ and $–3.30$ eV, respectively, while those of 1b were $–4.81$ and $–2.70$ eV, respectively (Fig. S4†). The $E_{ip}$ of thin film 1b ($–4.81$ eV) was consistent with that of the crystalline powder reported previously ($–4.96$ eV). The energy gap of 1a (1.94 eV) was less than that of 1b (2.11 eV). Theoretical computation results (DFT, B3LYP/6-31G(d) level) revealed the HOMO and LUMO of 1b to be $–4.68$ and $–2.90$ eV, respectively, while the corresponding values for 1a were $–4.81$ eV and $–3.04$ eV, respectively. The HOMO and LUMO were lowered by bromination compared with those of 1a, indicative of the electron-withdrawing effect by the bromo substituent. The HOMO-LUMO gap of 1a was 1.77 eV, whereas that of 1b was 1.78 eV, supporting the experimental results (Table 1).

### 2.3. Charge transport properties

The properties of organic field-effect transistors (OFETs) made with the films of 1a–b were examined. The OFET devices were fabricated by vacuum sublimation of 1a–b under a pressure of 8 $\times$ 10$^{-6}$ torr to deposit the thin films on an HMDS/SiO$_2$/Si substrate, followed by the deposition of gold electrodes on top of the films. The film thickness of 1a–b was 60 nm. The channel dimension of the source/drain electrodes was 45 $\times$ 2000 μm. The output parameters were measured on a selected film across a source–drain channel, followed by the plot of drain current ($I_D$) vs drain source voltage ($V_{DS}$) at various gate voltages ($V_G$). The corresponding transfer characteristics were plotted for $\log(I_D)$ vs $V_G$ at a $V_{DS}$ of $–100$ V and $I_D$ vs $V_{DS}$

| Sample | Ionization potential ($E_{ip}$, eV)$^a$ | Electron affinity ($E_{ea}$, eV)$^b$ | Energy gap (eV)$^c$ | Optical gap (eV)$^d$ | HOMO ($E_{H}$, eV)$^e$ | LUMO ($E_{L}$, eV)$^f$ | Energy gap (eV)$^g$ | Reorganization energy ($\chi^*,$ meV)$^h$ |
|--------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 1a     | $–5.24$                 | $–3.30$                 | 1.94                    | 1.47                    | $–4.81$                 | $–3.04$                 | 1.77                    | 85                     |
| 1b     | $–4.81$                 | $–2.70$                 | 2.11                    | 1.41                    | $–4.68$                 | $–2.90$                 | 1.78                    | 79                     |

$^a$ Estimated by photoelectron yield spectroscopy. $^b$ Estimated by low-energy inverse photoemission spectroscopy. $^c$ $E_{ip} – E_{ea}$. $^d$ Estimated by the edge of absorption spectra of thin-film. $^e$ B3LYP/6-31G(d). $^f$ $E_H – E_L$. $^g$ $E_{ip} – E_{ea}$. $^h$ $E_H – E_L$.
in the saturation mode. The field-effect hole mobility of 1a was measured, and the mobility values ranged from 0.21 to 0.83 cm² V⁻¹ s⁻¹ with threshold voltages of −50 to −69.3 V. The averaged performance of six independent devices was 0.52 cm² V⁻¹ s⁻¹ and a threshold of −56.3 V. The best mobility of bromohexacene 1a was observed at 0.83 cm² V⁻¹ s⁻¹ with an on/off ratio of 5.0 × 10⁴ and a threshold of −52 V (Fig. 3a–b). To compare the hole mobility, parent 1b was also tested. The mobility of 1b in the saturation mode ranged from 0.072 to 0.076 cm² V⁻¹ s⁻¹ with a threshold voltage ranging from −19 to −22 V. The averaged performance of six independent devices was 0.074 cm² V⁻¹ s⁻¹ and a threshold of −20.7 V. The best film mobility of 1b was observed at 0.076 cm² V⁻¹ s⁻¹ with an on/off ratio of 2.4 × 10² and a threshold of −21 V (Fig. 3c–d). Previously, the hole mobility of hexacene 1b has been reported in the single-crystal phase and in the spin-coated thin-film phase by the precursor method. The best hole-transfer mobility by spin-coated 1b was 0.035 cm² V⁻¹ s⁻¹, with a similar surface treatment on SiO₂/Si substrate. Although our fabrication conditions were not fully optimised, the mobility of the vacuum-deposited film was greater than that of the spin-coated one. It indicates that better crystalline films of 1b were formed by thermal deposition. The mobility of film 1a exhibited a larger range of randomness compared to 1b. However, a higher hole-transfer efficiency of 1a ranging 7- to 10-folds compared with that of 1b was observed in all tested devices. This result indicated that the packing moiety and/or film morphology possessing a better charge-transfer pathway may account for the mobility. Previously, a single-crystal bromopentacene was found to exhibit a 4-fold faster hole-transfer speed than that of non-substituted pentacene, while their reorganization energies were estimated to be 102 meV and 95 meV (B3LYP/6-31Gd level), respectively. DFT computations revealed that the reorganisation energy between the radical cation and ground state of 1a was 85 meV (B3LYP/6-31Gd level). This value was quite close to that of 1b (79 meV), suggesting a similar energy loss during structure reorganization in the hexacenes 1a and 1b.

2.4. TEM, XRD, and AFM measurements of hexacene films

To investigate the morphology of thin-film, we performed a surface analysis on the films 1a and 1b. Fig. 4 showed cross-section of transmission electron microscope (TEM) image of ca. 60 nm deposited films 1a and 1b on HMDS/SiO₂/Si surface. The ion milling method allows us to examine a cross-section of substrate at the interface of 1a–b and HMDS/SiO₂/Si. The TEM image show a good continuous growth of 1a and 1b films on HMDS/SiO₂/Si surface, suggesting both films were deposited uniformly on the substrate.

The parent structure of hexacene 1b exhibited a herringbone arrangement, where the face-to-edge stacking arrangement between adjacent molecules avoided the progress of dimerization and led to a high thermal stability in the solid state. The vacuum-deposited film of 1b exhibited out-of-plane X-ray diffraction (XRD) peaks along (00l) direction and in-plane XRD along (hk0) direction (Fig. S4†).

These patterns indicated that the molecules in the deposited film are oriented vertical to the surface along their long axis. In addition, this film orientation was consistent with the reported out-of-plane pattern of heat-converted film 1b from corresponding precursor compound. The (001) peak was observed at 4.84° corresponding to an interplanar distance of 18.3 Å. This value can be compared with the d-spacing in the single crystal of 1b, which has been estimated to be 16.4 Å. It indicates that the molecules in the crystalline film 1b are tilted on the surface of HMDS/SiO₂/Si substrate. The out-of-plane and in-plane XRD peaks of vacuum-deposited film 1a exhibited (00l) and (hk0) patterns, indicating that molecules in film 1a is oriented along the long axis normal to the surface (Fig. S4†). Although film 1a exhibited weaker XRD diffraction peaks compared with that of 1b, the 2θ angle of 1a observed at a smaller angle of 4.43° on the HMDS/SiO₂/Si substrate. The d-spacing of bromohexacene molecules is estimated to be 20.0 Å. The larger d-spacing revealed that the molecules interact through the a–b axis.

To further study of finding the difference of mobility between 1a and 1b, the atomic force microscope (AFM) analysis was investigated. The films 1b revealed a high surface roughness of 12.01 nm (Fig. 5). In contrast, film 1a revealed a lower roughness of 6.48 nm. This smoother
During data acquisition, $^1$H decoupling by spinal-$^6$4 was polarization transfer, the contact-time was set to $1.75$ ms.

### 3. Materials and methods

#### 3.1. General information

The $^1$H and $^{13}$C NMR spectra were recorded in solutions on a BrukerAV600 (600 MHz) spectrometer. The $^1$H and the $^{13}$C NMR chemical shifts were reported as $\delta$ values (ppm) relative to external Me$_3$Si. The coupling constants (J) were given in hertz. High resolution FAB mass spectra were recorded on a JMS-700 MStation spectrometer. FAB MS spectra were measured with 3-nitrobenzyl alcohol (NBA) as the matrix. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F$_{254}$ Merck. Column chromatography was performed on KANTOSil60N (neutral). Absorption and reflectance spectra were recorded on a SHIMADZU UV-3600. IR spectra were performed by SHIMADZU IRPrestige-21 spectrophotometer. AFM measurements were tested by SHIMADZU SPM-9700. The elemental analyses were recorded on a Yanaco CHN recorder MT-6. THF was distilled from sodium benzophenone ketyl. Toluene was distilled from CaH$_2$. Other solvents and reagents were of reagent quality, purchased commercially, and used without further purification.

#### 3.2. $^{13}$C CP/MAS NMR

The $^{13}$C CP/MAS NMR spectra were acquired with a Bruker Avance 400 MHz NMR spectrometer, equipped with a 4 mm double resonance probe operating at the $^1$H and the $^{13}$C Larmor frequencies of $400.13$ and $100.63$ MHz, respectively. For the polarization transfer, the contact-time was set to $1.75$ ms. During data acquisition, $^1$H decoupling by spinal-64 was applied. Powdered samples were packed in 4 mm zirconium oxide MAS rotors with Kel-F cap. A sample spinning frequency of $12$ kHz was used and regulated by a spinning controller within $\pm 1$ Hz. All CP-MAS experiments were carried out at ambient temperature. The $^{13}$C NMR chemical shifts are referenced to the methyl signal ($=17.36$ ppm) of hexamethylbenzene, which was used as an external standard. All measurements were performed in air, and the sample tube was kept in the dark between measurements.

#### 3.3. FET measurement

The electrical measurements were carried out in vacuum using a semiconductor parameter analyzer (B1500A, Keysight). The saturation mobility ($\mu_{sat}$) was extracted from the slope of the square root of the drain current plot vs. $V_G$ from eqn (1).

$$I_{D, sat} = \frac{W}{2L}C_i\mu_{sat}(V_G - V_T)^2$$

where $I_{D, sat}$ is the drain-to-source saturated current; $W/L$ is the channel width to length ratio; $C_i$ is the capacitance of the insulator per unit area, and the $V_G$ and $V_T$ are gate voltage and threshold voltage, respectively. A heavily doped silicon (Si) wafer was used for a back gate electrode, which was covered with a $300$ nm-thick thermally grown SiO$_2$ ($G = 10.2$ nF cm$^{-2}$) as the gate insulator. Channel length ($L$) and width ($W$) were $2000$ $\mu$m and $45$ $\mu$m.

#### 3.4. TEM measurement

The organic films were vacuum sublimation of 1a-b under a pressure of $8 \times 10^{-6}$ torr to deposit the thin films for 350 nm on a HMDS/SiO$_2$/Si substrate. Cross-sectional TEM samples for all of the films were prepared by mechanical thinning and ion milling. The transmission electron microscope used in this study was a JEOL JEM-2100F, which was operated at an accelerating voltage of $200$ kV.

#### 3.5. Synthesis of materials

##### 3.5.1. Synthesis of (6 aS,14aR,15S)-10-bromo-17-(propan-2-ylidene)-6,6a,14a,15-tetrahydro-6,15-methanohexacene-7,14-dione 8

A solution of 1R,4S-11(propan-2-ylidene)-1,4-dihydro-1,4-methanoanthracene 3 (232 mg, 1.00 mmol), benzoquinone 4 (108 mg, 1.00 mmol), and 3,6-bis(2-pyridyl)tetrazine (248 mg, 1.05 mmol) in toluene (50 mL) was heated at $95^\circ$C for $24$ h under a nitrogen atmosphere. After the reaction, the mixture was quenched with $30\%$ H$_2$SO$_4$, extracted with CH$_2$Cl$_2$, and the organic solution was dried over MgSO$_4$ and concentrated in vacuo. The crude product was purified by a silica gel chromatography eluted with CH$_2$Cl$_2$ to afford a mixture of endo and exo geometrical isomers of 5 (163 mg) as yellow solids. The mixture was used for next step without further purification.

The mixture of 5 (163 mg, 0.519 mmol) and zinc (600 mg) and glacial acetic acid (50 mL) was sonicated for $30$ min at room temperature. After reaction, the suspension was filtered and the solution was evaporated to give the crude product. Silica gel chromatography of the crude product with CH$_2$Cl$_2$ and treatment with iced MeOH afforded dione 6 (114 mg). The mixture was used for next step without further purification.

A mixture of diketone 6 (114 mg, 0.361 mmol) and 4-bromomethylaldehyde 7 (76.1 mg, 0.361 mmol) was dissolved in EtOH (50 mL). The EtOH solution was bubbled by nitrogen gas for $20$ min to remove oxygen. To the mixture was added $10\%$ KOH/EtOH solution (2–3 drops) in the nitrogen atmosphere and stirred $72$ h at room temperature under nitrogen gas. The mixture gradually became dark, and pale-yellow powder precipitated. After reaction, the precipitate was filtered and washed with EtOH and hexane to afford endo-8 (86.2 mg, 17% in three steps). Pale yellow powder (EtOH). $\delta_{1H}$ (CDCl$_3$, 600 MHz) 1.23 (d, $J = 4.8$, 6H), 3.17 (s, 2H), 4.47 (s, 2H), 7.45 (dd, $J = 6.0, 3.0$ Hz, 2H), 7.76 ($J = 9.0, 7.7$ Hz, 1H), 7.78 (s, 2H), 7.82 (dd, $J = 4.8, 6H$).
6.0, 2.4 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 8.24 (s, 1H), 8.53 (s, 1H), 8.61 (s, 1H). δC (CDCl3, 125 MHz) 19.7, 51.3, 52.9, 117.9, 119.0, 124.1, 125.6, 127.5, 127.9, 128.6, 131.4, 131.9, 132.2, 132.8, 132.9, 133.5, 136.0, 142.3, 143.7, 197.0, 197.8.

3.5.2. Synthesis of (6S,15R)-10-bromo-17-(propan-2-ylidene)-6,15-dihydro-6,15-methanohexacene 9. To a solution of dione 8 (220 mg, 0.446 mmol) in MeOH (50 mL) and THF (50 mL) in an ice bath was added NaBH4 (74 mg, 1.65 mmol). A mixture of olefinylidene)-6,15-dihydro-6,15-methanohexacene 9. To a solution containing precipitates was extracted with CH2Cl2. The organic layer was washed with water, and was extracted with CH2Cl2. The crude product was purified by silica gel chromatography eluted with hexane/CH2Cl2 (1:4) to give the aromatized compound 9 (98.8 mg, 48%) as pale yellow powder. Physical data of 9: pale yellow powder (EtOH). δH (CDCl3, 600 MHz) 1.72 (s, 6H), 5.06 (s, 2H), 7.35 (dd, J = 6.0, 3.0, 2H), 7.43 (dd, J = 9.0, 7.2 Hz, 1H), 7.70 (d, J = 6.0, 3.0 Hz, 2H), 7.72 (d, J = 2H, 1H), 7.77–7.79 (m, 3H), 8.08 (s, 1H), 8.12 (s, 1H), 8.19 (s, 1H). δC (CDCl3, 125 MHz) 19.8, 51.4, 113.2, 118.3, 118.4, 118.9, 119.0, 119.02, 124.9, 125.5, 126.1, 127.7, 128.3, 129.6, 131.3, 131.3, 132.2, 132.4, 145.2, 145.3, 145.6, 153.8.

3.5.3. Synthesis of (6S,15R)-10-bromo-6,15-dihydro-6,15-methanohexacene-17-one 2a. A mixture of olefin 9 (200 mg, 0.433 mmol) and N-methylmorpholine N-oxide (NMO) (50% in H2O, 1.5 mL) in a mixed solvent of acetone (50 mL) and H2O (1.5 mL) was stirred at room temperature until 9 was dissolved completely. Then the solution was added a few drops of OsO4 (4% H2O soln). The reaction was monitored by TLC until completion, and the mixture was quenched with 15% aqueous Na2S2O5. The aqueous solution was washed with diethylether, dried over Na2SO4, and evaporated. The product was purified by a silica gel chromatograph eluted with CH2Cl2 to give diol 10 (79 mg), which was directly used in the next step. The diol 10 (79 mg) and Phl(OAc)2 (120 mg) in benzene (100 mL) was stirred at 60 °C for 12 h. After reaction, the mixture was cooled in an ice bath, while white precipitates formed. The solids were collected by suction filtration to give compound 2a (59 mg, 31% in two steps) as a white powder. Physical data of 2a: m.p. 181 °C. (TGA, decomp.); IR (KBr): v = 1786 cm⁻¹ (s, C=O); 13C CP/MAS NMR (12 000 rpm, 100 MHz): 54.0, 118.5, 120.6, 122.5, 123.9, 126.1, 130.5, 133.2, 135.2, 197.2.

3.5.4. Synthesis of 2-bromohexacene 1a. Proper amount of precursor 2a was loaded in a glass container, and the powder was sealed. The mixture was heated at 210 °C for 5 min under a nitrogen atmosphere. The color of 2a changed from white to green to give 2-bromohexacene 1a in a quantitative yield. M.p. 340 °C. (TGA, sublimes); 13C CP/MAS NMR (12 000 rpm, 100 MHz): 123.1, 126.0; HRMS: m/z 406.0387 [M+, calcld 406.0357]; EA: found, %: C, 76.2; H, 3.7. For C24H13Br. Calculated, %: C, 76.1; H, 3.7.

4. Conclusions

A novel hexacene precursor was successfully synthesised, which can be quantitatively converted at around 200 °C to the corresponding 2-bromohexacene. It exhibited high thermal stability over 3 months in the dark. The bromine atom affected the hexacene crystal packing and decreased the HOMO–LUMO energy gap. The thin-film of 1a was fabricated by using both spin-coating and vacuum sublimation methods, and both films exhibited exciton coupling, indicative the presence of herringbone arrangement in the polycrystalline film. The film of 1a exhibited a more efficient hole-transport property compared with that of parent 1b. Hence, film 1a exhibits a higher hole mobility of 0.83 cm² V⁻¹ s⁻¹ than that of 1b (0.074 cm² V⁻¹ s⁻¹).

Although these hole mobility were lower than that of single crystal hexacene (4.28 cm² V⁻¹ s⁻¹), it was comparable with the reported value of solution-processed single crystal tricyclohexylsilylethynyloctafluorohexacene (0.1 cm² V⁻¹ s⁻¹). To the best of our knowledge, this is the first study on the charge-transport property of a stable vacuum-deposited thin-film of hexacene for electronic devices. Currently, other derivatives of halogenated hexacene are prepared, and their properties related to optoelectronic devices are being examined. The results will be reported in due course.

Author’s contributions

MW designed and performed the experiments and theoretical calculations; TM, CTC, MS and SSS were synthesized, measured and analysed the materials and physical properties; TM and CA designed the devices and analysed the data; JM measured and analysed the TEM; MW and TI were measured and analysed the NMR data; MW, TM and TJC co-wrote the manuscript; all authors gave final approval for publication.

Conflicts of interest

There are no conflicts to declare.

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