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Benzo[4,5]cyclohepta[1,2-*b*]fluorene: an isomeric motif for pentacene containing linearly fused five-, six- and seven-membered rings†

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Benzo[4,5]cyclohepta[1,2-*b*]fluorene (**5a**), a new π -conjugated polycyclic hydrocarbon containing linearly fused six-, five-, six-, seven- and six-membered rings (C₆-C₅-C₆-C₇-C₆), was designed and its stable derivatives **5b** and **5c** were synthesized. With 22 π electrons, **5a** is an isomer of pentacene with quinoidal, dipolar ionic and diradical resonance forms. Molecules **5b** and **5c** were experimentally investigated with cyclic voltammetry, electronic absorption spectroscopy and X-ray crystallographic analysis, and theoretically studied by calculating the NICS value, diradical character and dipole moment. A comparison of **5a-c** with pentacene and other pentacene analogues containing linearly fused five- or seven-membered rings was also conducted and discussed. It was found that **5b** behaved as a p-type organic semiconductor in solution-processed thin film transistors with a field effect mobility of up to 0.025 cm² V⁻¹ s⁻¹.

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Introduction

Pentacene (**1a** in Fig. 1a) is a leading p-type organic semiconductor for applications in light-weight, flexible and low-cost organic electronic devices,¹ and has been used as a benchmark in comparison with new materials for applications in organic thin film transistors (OTFTs).² Pentacene has been molecularly engineered with three strategies in order to modify electronic structure, tune molecular packing in the solid state, improve solubility and stability, and better understand its structure-property relationship. As extensively studied, the first strategy is to substitute H atoms in pentacene with a variety of functional groups.³ The most successful example of this strategy is 6,13-bis((triisopropylsilyl)ethynyl)-pentacene (**1b** in Fig. 1a),⁴ which is a solution-processed high-mobility p-type semiconductor^{5,6}

with brickwork arrangement of π -planes. The second strategy is to replace C atoms in pentacene with hetero atoms, such as B,⁷ N,⁸ and S.^{9,10} Among the resultant heteropentacenes, *N*-heteropentacenes were most extensively studied, and have recently arisen as a class of organic semiconductors with high performance in OTFTs.¹¹ The third strategy is to replace six-membered rings in pentacene with five- or seven-membered rings, leading to recently reported pentacene analogues containing C₆-C₅-C₆-C₅-C₆¹²⁻¹⁴ and C₆-C₇-C₆-C₇-C₆¹⁵ polycyclic frameworks, such as **2-4** in Fig. 1a. With 20 π electrons, **2a** and **3a** both have two π electrons less than pentacene, while **4a** has two more π electrons. Therefore, their electronic structure and physical properties are distinctively different from those of pentacene. In this study, we explore a novel linearly fused pentacene analogue, benzo[4,5]cyclohepta[1,2-*b*]fluorene (**5a** in Fig. 1a), which contains an unprecedented C₆-C₅-C₆-C₇-C₆ polycyclic framework. Unlike other pentacene analogues, **5a** is a constitutional isomer of pentacene having both five- and seven-membered rings in the linear π -backbone with 22 π electrons. Besides the quinoidal resonance structure, one dipolar ionic resonance form (**5a'**) and one open-shell diradical form (**5a''**) can be also drawn for **5a** (Fig. 1b). The existence of one more aromatic sextet ring (shaded in blue) in **5a'** and **5a''** suggests that these two resonance forms might make a significant contribution to the ground state structure. Like all other pentacene analogues, bulky triisopropylsilylethynyl (in **5b**) or mesityl (in **5c**) groups are introduced to the reactive sites so that soluble and stable materials can be obtained. Detailed below are their synthesis, ground-state structures, physical properties and their applications for OTFTs. A comparison with pentacene and other

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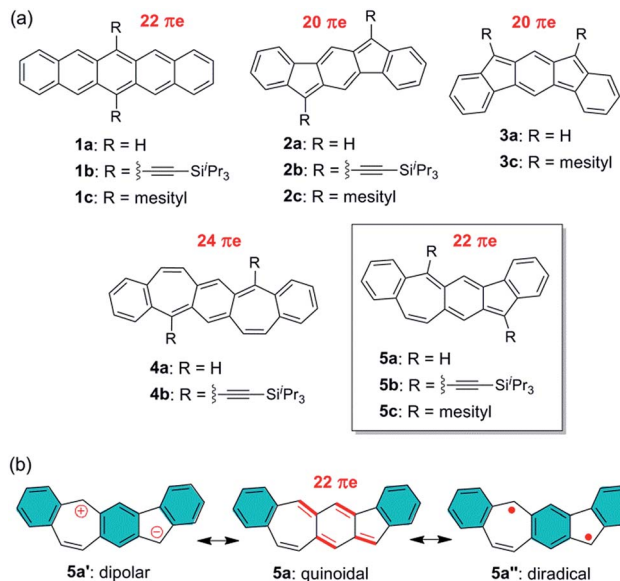


Fig. 1 (a) Chemical structures of pentacene and its analogues; (b) three typical resonance forms of 5a.

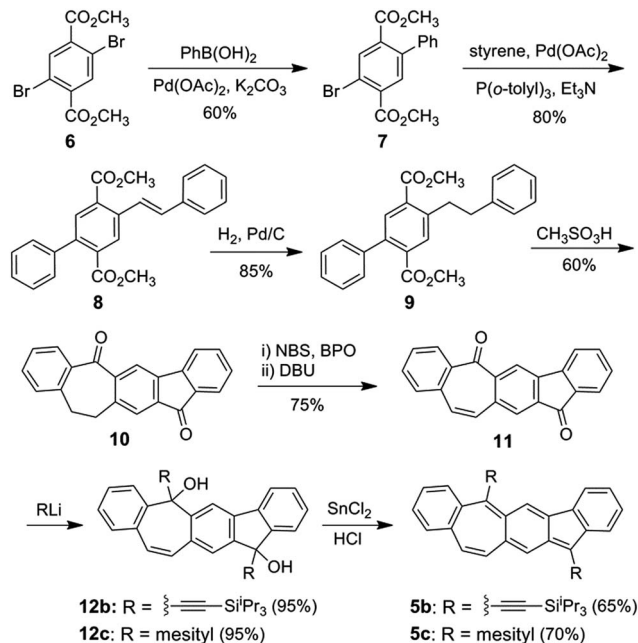
pentacene analogues is also made to better understand the structure–property relationship.

Results and discussion

Synthesis and characterization

Scheme 1 shows the synthesis of **5b** and **5c** starting from commercially available dimethyl 2,5-dibromoterephthalate **6**, which was coupled with phenyl boronic acid and styrene subsequently in the Suzuki reaction and Heck reaction, respectively, resulting in the diester **8**. Pd/C-catalyzed hydrogenation of **8** followed by treatment with methanesulfonic acid at 100 °C led to cyclized product **10**. Bromination of **10** and subsequent elimination of HBr yielded the dehydrogenated dione **11**. X-Ray crystallographic analysis of the single crystals of **11** revealed a non-planar geometry (Fig. S6 in ESI[†]), which can explain its moderate solubility in common organic solvents. Nucleophilic addition of (triisopropylsilyl)ethynyl and mesityl lithium to **11** resulted in the diols **12b** and **12c**, respectively, which both were obtained as a mixture of *cis* and *trans*-isomers. Reduction of intermediate diols **12b** and **12c** in THF with a solution of concentrated HCl that was saturated with SnCl₂ led to **5b** and **5c**, respectively, both as deep green solids in moderate yield. Dione **10** was also synthesized from 2,5-dibromo-*p*-xylene in a similar approach in higher overall yield but more steps (Scheme S1 in ESI[†]). The ¹H NMR spectra of **5b** and **5c** (ESI[†]) both show sharp splitting and narrow line widths indicating that they behave more like closed-shell compounds in the ground state.¹⁶

The redox behaviors of **5b/5c** in solution were investigated with cyclic voltammetry. In the test window of cyclic voltammetry, **5b** exhibits a reversible reduction (**5b/5b⁻**) wave and an irreversible oxidation (**5b/5b⁺**) wave, while **5c** exhibits a reversible reduction (**5c/5c⁻**) wave and a reversible oxidation (**5c/5c⁺**)



Scheme 1 Synthesis of **5b/5c**.

wave as shown in Fig. 2a. The half-wave reduction potentials ($E_{1/2}^{\text{red}}$) of **5b** and **5c** are -1.30 V and -1.77 V versus the ferrocenium/ferrocene (Fc^+/Fc) redox couple, respectively, from which the lowest unoccupied molecular orbital (LUMO) energy levels of **5b** and **5c** are estimated as -3.80 eV and -3.33 eV, respectively.¹⁷ Similarly, the highest occupied molecular orbital (HOMO) energy levels of **5b** and **5c** are estimated as -5.36 eV and -5.27 eV from the half-wave oxidation potential ($E_{1/2}^{\text{ox}} = 0.26$ V and 0.17 V vs. Fc^+/Fc , respectively).¹⁷ The lower LUMO and HOMO energy levels of **5b** in comparison with **5c** can be attributed to the facts that the ethynyl substituents with sp hybridized carbons in **5b** are electron withdrawing and the substituting phenyl groups in **5c** are almost orthogonal to the polycyclic backbone with poor conjugation. Table 1 compares **5b/5c** with those of the related molecules **1–4** in terms of electrochemical potentials and frontier molecular orbital energy levels. It is found that **5b** and **5c** have a higher HOMO energy level and a lower LUMO energy level than the corresponding pentacene derivatives **1b** and **1c**, respectively. Furthermore, the oxidation potential of **5b** is almost the same as that of **4b**, and the reduction potential of **5b** is close to that of **2b**. Molecule **5c** has a reduction potential close to that of **3c**, which has the same mesityl substituents. These findings are in agreement with the assumption that the first reduction of **5b/5c** occurs on the five-membered ring leading to an aromatic cyclopentadienide anion and the first oxidation of **5b/5c** occurs on the seven-membered ring leading to an aromatic cycloheptatrienium cation.

As shown in Fig. 2b, **5b** and **5c** in CH₂Cl₂ exhibit electronic absorption spectra very different from those of pentacene and other analogues. The broad absorption band in the visible-near infrared (vis-NIR) region could be attributed to the HOMO → LUMO transition based on time-dependent density functional theory (TDDFT) calculations (ESI[†]). The intense absorption



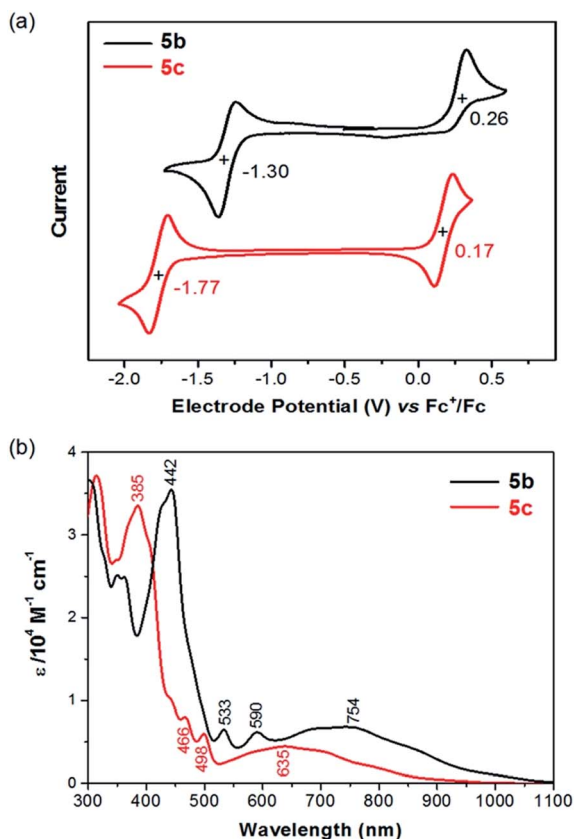


Fig. 2 (a) Cyclic voltammograms of **5b** and **5c** recorded in CH_2Cl_2 with Fc^+/Fc as the external standard at a scan rate of 50 mV s^{-1} ; (b) UV-vis-NIR absorption of **5b** and **5c** in CH_2Cl_2 .

Table 1 Electrochemical potentials and frontier molecular orbital energy levels of **1–5**

| | $E_{1/2}^{\text{red}}/V$ | $E_{1/2}^{\text{ox}}/V$ | LUMO ^b /eV | HOMO ^c /eV | E_g^{ECd}/eV |
|-------------------------|--------------------------|-------------------------|-----------------------|-----------------------|-----------------------|
| 1b ¹⁸ | -1.50 | 0.37 | -3.60 | -5.47 | 1.87 |
| 1c ¹⁰ | -1.92 | 0.22 | -3.18 | -5.32 | 2.14 |
| 2b ¹² | -1.15 | 0.74 | -3.95 | -5.84 | 1.89 |
| 2c ¹³ | -1.58 | 0.64 | -3.52 | -5.74 | 2.22 |
| 3c ¹⁴ | -1.13 | 0.13 | -3.97 | -5.23 | 1.26 |
| 4b ¹⁵ | -1.66 | 0.12 | -3.44 | -5.32 | 1.78 |
| 5b | -1.30 | 0.26 | -3.80 | -5.36 | 1.56 |
| 5c | -1.77 | 0.17 | -3.33 | -5.27 | 1.94 |

^a $E_{1/2}^{\text{red}}$ and $E_{1/2}^{\text{ox}}$ are the half-wave potential (vs. Fc^+/Fc) of the first oxidation and reduction wave, respectively. ^b Estimated from $\text{LUMO} = -5.10 - E_{\text{red}}$ (eV). ^c Estimated from $\text{HOMO} = -5.10 - E_{\text{ox}}$ (eV). ^d $E_g^{\text{EC}} = \text{LUMO} - \text{HOMO}$.

band at the UV-vis region can be mainly attributed to the $\text{HOMO}-1 \rightarrow \text{LUMO}$ and $\text{HOMO} \rightarrow \text{LUMO}+1$ transitions. The optical energy gaps (E_g^{opt}) of **5b** and **5c** were estimated to be 1.13 eV and 1.25 eV, respectively, from the lowest energy absorption onset. The optical energy gap of **5b/5c** is significantly smaller than the $\text{HOMO}-\text{LUMO}$ gap (E_g^{EC}) as estimated from electrochemical potentials. A similar phenomenon was also observed from azulene, which has an optical energy gap of 1.75 eV (about 710 nm)¹⁹ and an electrochemical energy gap of

2.35 eV.²⁰ Azulene has a lower transition energy than anticipated from the $\text{HOMO}-\text{LUMO}$ gap because the excited state of azulene has a smaller repulsive energy between the two electrons occupying HOMO and LUMO due to the nonalternant nature of azulene.^{21–23} This explanation may also account for the smaller optical energy gap of **5b/5c**, whose pentacyclic backbone is also nonalternant.

Single crystals of **5c** selected for X-ray crystallographic analysis were grown by slow diffusion of acetonitrile into a solution in CH_2Cl_2 .²⁴ It is found that the unit cell of this crystal contains crystallized solvent (CH_3CN) molecules with disorder as shown in Fig. 3a. In the crystal structure of **5c**· CH_3CN , the pentacyclic backbone of **5c** (Fig. 3b) is essentially flat and is almost perpendicular to the substituting mesityl groups with dihedral angles of 80.2° and 87.9° . Examination of the bond lengths in the central six-membered ring reveals four C–C single bonds (C5a–C12a, C5a–C6, C6a–C11a, C11a–C12) with bond lengths of 1.42–1.48 Å and two C–C double bonds (C6–C6a, C12–C12a) with bond lengths of 1.35–1.37 Å.²⁵ Moreover, the central six-membered ring is bonded to C5 and C11 with relatively short bond lengths (C5–C5a: 1.39 Å; C11–C11a: 1.37 Å). The above bond lengths are similar to the corresponding bond lengths in

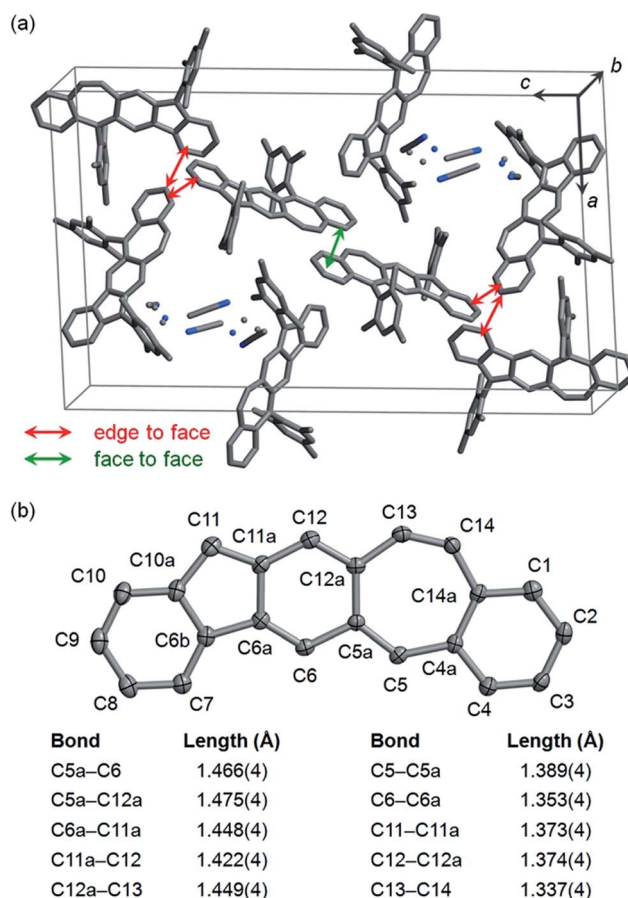


Fig. 3 Crystallographic structure of **5c**· CH_3CN with hydrogen atoms removed for clarification: (a) a unit cell with disordered atoms of CH_3CN shown as dots; (b) the pentacyclic backbone of **5c** with carbon atoms labeled and some bond lengths highlighted (carbon atoms are shown as ellipsoids at the 50% probability level).



the crystallographic structures of **2b**,¹² **2c**,¹³ and **4b**,¹⁵ indicating a *p*-quinodimethane structure with large bond length alternation. In addition to the C5–C5a bond, the seven-membered ring contains another C–C double bond (C13–C14) with a bond length (1.34 Å) typical for alkenes. Neighboring molecules of **5c** exhibit poor π – π interactions between the pentacyclic backbones presumably because the bulky mesityl substituting groups block π – π interactions. Only a small face-to-face overlap with a π -to- π distance of 3.40 Å and a small number of edge-to-face contacts are observed as shown in Fig. 3a.

Computational studies

Density functional theory (DFT) calculations at the (U)CAM-B3LYP/6-31G* level of theory were conducted to better understand the ground state structures of **5a–c**. It is found that the solution of the open-shell singlet (OS) state has a lower energy than the closed-shell (CS) state for **5b**, thus defining an open-shell singlet ground state. The singly occupied molecular orbitals (SOMO) of the α and β spins are partially disjointed (Fig. 4a), in accordance with a calculated small diradical character ($\nu_0 = 4.7\%$). The spins are delocalized throughout the whole π -conjugated framework, including the C–C triple bonds (Fig. 4a). This result indicates that the diradical resonance form **5a'** indeed contributes to the ground state of **5b** to a certain extent. On the other hand, **5a** and **5c** are calculated to have a closed-shell ground state with zero diradical character. The HOMO and LUMO of **5a** and **5c** are delocalized through the whole backbone with slight segregation as shown in Fig. S1 (ESI)[†] and **4a**, respectively. The above results suggest that the

ethynyl substituents can help to stabilize the diradical resonance form. The dipole moments of **5b** and **5c** were calculated to be 3.179 and 2.647 debye, respectively, at the CAM-B3LYP/6-31G* level of DFT, which are larger than that of azulene (1.268 debye) as calculated with the same method. This reflects the contribution of the dipolar ionic form **5a'** to the ground state of both **5b** and **5c**.

To provide further insight into the aromaticity of each individual ring of these π -conjugated polycyclic hydrocarbons, nucleus independent chemical shift (NICS) of **1a**, **2a**, **4a** and **5a** were also calculated. Fig. 4b compares the calculated NICS(1)zz values of these molecules. Large negative values are found for all rings in **1a**, in agreement with its known aromatic character. In **2a**, a large negative value is calculated for ring A while both ring B and ring C show positive values, indicating that it can be regarded as a dibenzo-fused anti-aromatic *s*-indacene structure. In **4a**, the central ring C is less positive compared with that in **2a**, indicating its less anti-aromatic character. The seven-membered ring B however has a large positive value. In **5a**, the central ring C and the five-membered ring B both become negative, and the seven-membered ring D is much less positive than that in **4a**, indicating that a balance of three resonance forms leads to a weak aromatic character of the central C₅–C₆–C₇ framework. The outmost benzenoid rings (A and E) are aromatic with large negative values. In agreement with the negative NICS value for the central ring C in **5a**, the protons on the same ring in **5b** exhibit a downfield singlet peak at 8.95 ppm as well as a singlet peak 7.10 ppm in the ¹H NMR spectrum. In comparison to this, the corresponding protons on the central ring C in **2b**¹² and **4b**¹⁵ exhibit singlet peaks at 7.26 and 7.16 ppm, respectively, in the ¹H NMR spectra taken from the same solution (CDCl₃).

Semiconductor properties

One interesting aspect of **5b** is its semiconducting properties since it is a constitutional isomer of pentacene **1b**, a well-known solution-processed p-type organic semiconductor. To test the semiconducting properties of **5b**, top-contact transistors were fabricated on dip-coated films of **5b**, which were formed by immersing a SiO₂/Si substrate in a solution of **5b** (2.5 mg mL⁻¹) in *n*-hexane and then pulling it up with a constant speed of 5.3 $\mu\text{m s}^{-1}$. As shown in the polarized-light micrograph in Fig. 5a, the dip-coated films of **5b** on SiO₂ are composed of crystalline fibers roughly aligned in the pulling direction; X-ray diffraction patterns from the films of **5b** (Fig. S4 in ESI[†]) exhibit an intense peak at *d*-spacing of 18.88 Å ($2\theta = 4.68^\circ$) accompanied with three higher-order peaks at 9.44 Å ($2\theta = 9.37^\circ$), 6.29 Å ($2\theta = 14.07^\circ$), and 4.72 Å ($2\theta = 18.80^\circ$), indicating a crystalline film with a layered structure. As measured in air from these devices, **5b** functions as a p-type semiconductor with a field-effect mobility of up to 0.025 cm² V⁻¹ s⁻¹ (average 0.018 ± 0.003 cm² V⁻¹ s⁻¹). Fig. 5b shows the transfer *I*–*V* curve in the saturation region for one of the best-performing OTFTs of **5b** measured in air. From this transfer *I*–*V* curve, the field mobility is extracted using the equation: $I_{\text{DS}} = (\mu WC_i/2L)(V_G - V_T)^2$, where I_{DS} is the drain current, μ is field-effect mobility, C_i is the

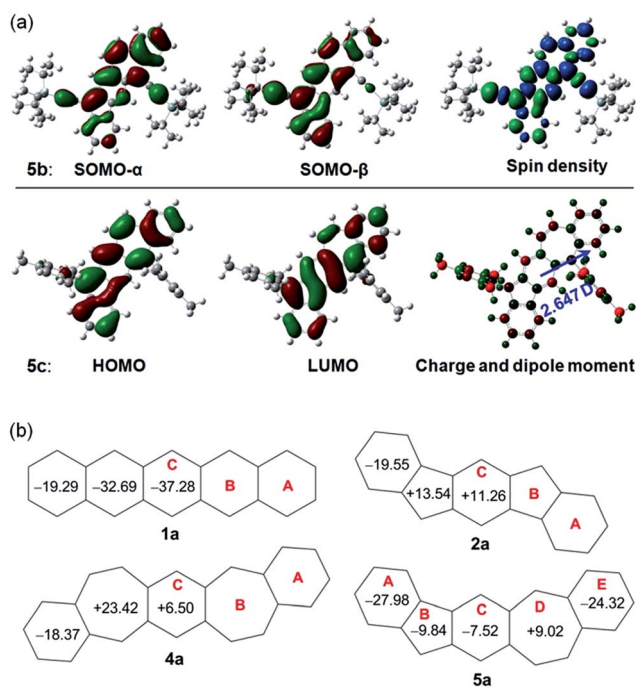


Fig. 4 (a) Calculated frontier MO profiles of **5b** and **5c**, spin density map of singlet diradical of **5b**, and Mulliken charge distribution (–0.528 (red) to 0.528 (green)) and dipole moment of **5c**; (b) calculated NICS(1)zz values for pentacene and its analogues.



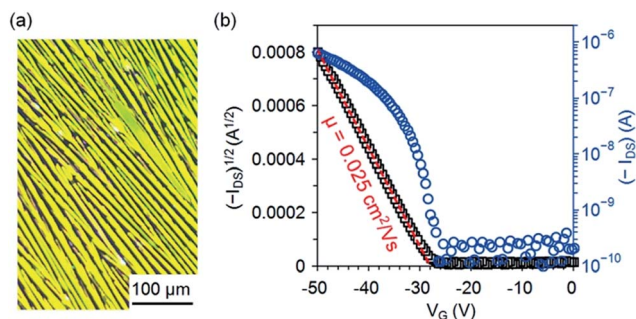


Fig. 5 (a) Reflection polarized-light micrograph for a dip-coated film of **5b** on SiO₂; (b) drain current (I_{DS}) versus gate voltage (V_G) with drain voltage (V_{DS}) at -50 V for an OTFT of **5b** with an active channel of $W = 1$ mm and $L = 100$ μm as measured in air.

capacitance per unit area (11 nF cm^{-2}) for the 300 nm-thick dielectric layer of SiO₂, W is the channel width, L is the channel length, and V_G and V_T are the gate and threshold voltage, respectively. The mobility of **5b** is lower than those of **1b**²⁶ and **4b**¹⁵ in solution-processed OTFTs on bare SiO₂ by one order of magnitude likely because of the unsymmetrical arrangement of silylethynyl substituting groups, which presumably leads to unfavorable molecular packing with poor π - π interactions.

Conclusions

In summary, the above study puts forth a new class of conjugated polycyclic molecules that contain a C₆-C₅-C₆-C₇-C₆ framework isomeric to pentacene. The benzo[4,5]cyclohepta[1,2-*b*]fluorene derivatives **5b/5c** display different optical and electrochemical properties in comparison with pentacene and its analogues **2-4**. As found from the crystal structure, **5b** has a nearly flat pentacyclic π -backbone with a quinoidal core. The computational studies indicate that the dipolar ionic resonance form contributes to the ground states of both **5b** and **5c**, while the diradical characters in the ground state depends on the substituting groups. **5b** has a calculated diradical character (γ_0) in the ground state as small as 4.7%, which is not spectroscopically detectable, while **5c** has a closed-shell ground state with zero diradical character. As a constitutional isomer of pentacene **1b**, **5b** functions as a p-type organic semiconductor in solution-processed OTFTs with field effect mobility of up to $0.025 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. As an extension from this study, synthesis of novel polycyclic arenes containing both five- and seven membered rings is in progress in our laboratories. These molecules may exhibit interesting physical properties that are not available for their benzenoid analogues as suggested by a recent theoretical study.²⁷

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- 25 The bond length is 1.45–1.46 Å for a typical single bond between two sp² carbon atoms, 1.38–1.40 Å for a typical C–C 1.5 bond in arenes, and 1.31–1.34 Å for a typical C–C double bond in alkenes. See: E. V. Anslyn and D. A. Dougherty, *Modern Physical Organic Chemistry*, University Science Books, Sausalito, 2004, ch. 1, p. 22.
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