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Synthesis of a Pentalene Centered Polycyclic Fused System

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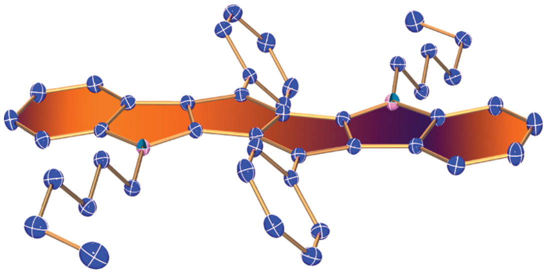
ABSTRACT



A novel pentalene-centered polycyclic 24π-electron system, IB1, was synthesized via a Pd-catalyzed homocoupling reaction. The geometry structure was studied by X-ray diffraction and theoretical method. The HOMO level of IB1 was studied by electrochemical experiment and DFT methods. The IB1 molecule shows a strong electro-donating property and can form a charge transfer complex with electro-acceptor TCNQ, indicating fascinating potential in the field of organic electronics.

Linear polyacenes with extended π-conjugation, such as pentacene and rubrene, have become a primary focus in the field of organic electronics. This species has been widely used in the construction of organic electronic devices (e.g., OFET, OLED)[1] and is considered to be among the most promising organic semiconductors with incredible carrier mobility. However, the poor solubility and oxidative degradation restrict the further application of these materials. Pentalene (as shown in Figure 1), as a 4nπ-electron system, provides corresponding stable dianion and dication species leading to highly amphoteric redox properties.[2] In particular, the more stable extended pentalene derivatives,[3] and related polyindenoindenes,[4] though scarcely studied, represent an interesting alternative to classic polyacenes in several fields. Among them, the dichalcogenophene derivatives of pentalene have demonstrated extraordinary potential as high-performance semiconductors.[5] Recently,

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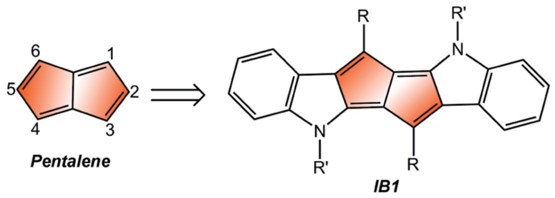
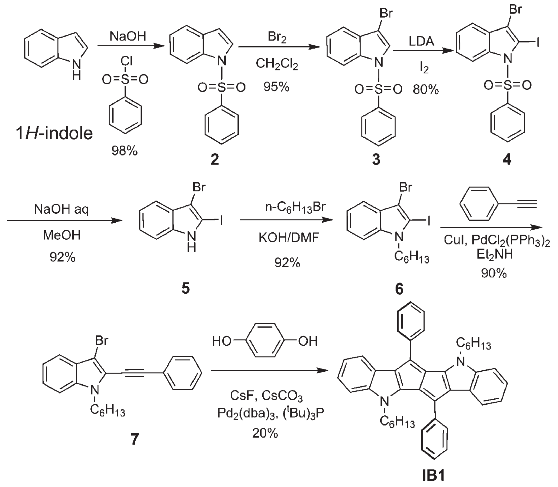


Figure 1. Structure of pentalene and **IB1**.

Scheme 1. Synthesis Route of **IB1**



tremendous progress has been made on synthetic methodologies for accessing indenoindenes and dibenzopentalenes,[6,7] thus promoting research on their application for organic electronics.[6b]

In this work, we synthesized a pentalene-centered, six-ring fused system with two outstretched units of indole, named **IB1** (Figure 1). This molecule shows a strong electro-donating property with a high HOMO level. Interestingly, **IB1** can be oxidized to a radical cation by oxidative reagents and form a charge transfer complex with TCNQ, which renders enormous potential as an organic semiconductor/conductor.

IB1 was synthesized via the Pd-catalyzed homocoupling of 3-bromo-1-hexyl-2-(phenylethynyl)-1*H*-indole (**7**) which was obtained from bare indole in six steps (Scheme 1). First, phenylsulfyl-protected indole was brominated and iodinated successively to obtain **4**. Then deprotection occurred in methanol with aqueous sodium hydroxide, which was followed by condensation with 1-bromohexane to obtain **6**. **6** was coupled with phenylacetylene via a Sonagashira cross coupling reaction to afford **7**. **IB1** was obtained in a similar method as reported by Tilley's group.[7b] In the presence of hydroquinone, Cs_2CO_3, and CsF, a coupling reaction with 2 equiv of **7** occurred utilizing a Pd(0) catalyst in an inert atmosphere to afford **IB1** as purple needle crystals in 20% yield. Different from traditional polyacenes, **IB1** showed incredible solubility and thermostability. A TGA experiment reveals that the decomposition temperature is ca. 350 °C (Figure S1).

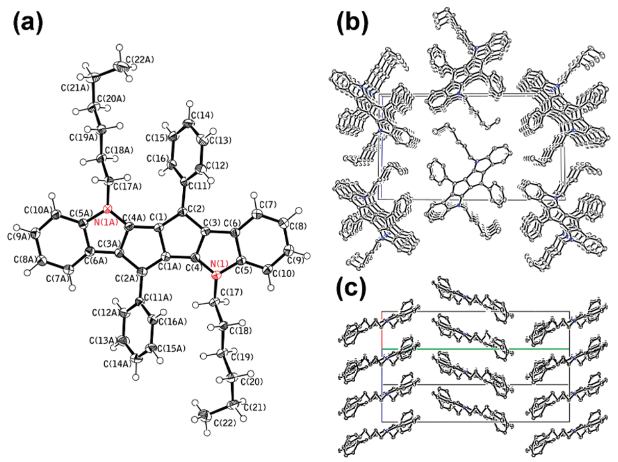


Figure 2. (a) Molecular structure of **IB1**, ellipsoids drawn at 50% probability level; (b) **IB1** packing along the *a*-axis; (c) **IB1** packing from side view.

After careful purification by alumina column, **IB1** was recrystallized by slow evaporation of a solution in acetone to afford a small amount of crystalloids suitable for X-ray diffraction. Consistent with the reported molecular structure of dibenzopentalenes,[8] the molecular structure (Figure 2) reveals that the fused ring system is essentially planar with a slight dihedral angle of ca. 10° between the planes of indole and pentalene. The two benzene rings substituted on the pentalene have a torsion angle of ca. 51° to the plane of pentalene, and they experience steric hindrance due to the neighboring alkyl chains, of which the nearest distance is ca. 3 Å (Figure S2). Due to the shielding effect of the phenyl ring, chemical shifts of hydrogen on the alkyl chain were split from each other and display a high-field shift in varying degrees (Figure S2). Especially, the hydrogen on the carbon connected with the nitrogen atom has a marked high-field shift of about 1 ppm. The slightly high-field shift of the hydrogen on the benzene of indole might be due to the paratropicity of pentalene.

In accordance with the reported structures of pentalene derivatives, the alternating long (1.442(3) and 1.443(3)Å for C(2)−C(3) and C4−C(1A), respectively) and short (1.398(3) and 1.405(3) Å for C(1)−C(2) and C(3)−C(4), respectively) bonds in the central pentalene core were seen, whereas the peripheral benzene bonds are relatively homogeneous (1.382−1.399 Å). At the same time, the fully structural optimization of **IB1** was carried out by Gaussian 03 at the RB3LYP/6-31+G* level. The calculated result

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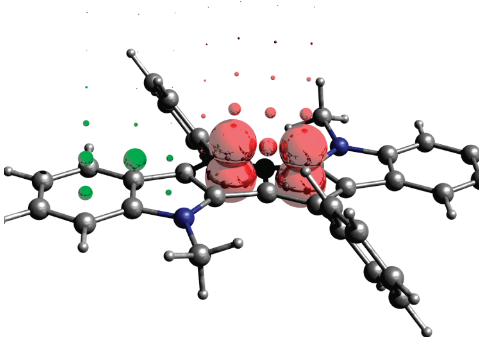

Figure 3. NICS grid plot of **IB1** (GIAO-RB3LYP/6-31+G*) (red, positive value; green, negative value); the size of the sphere relates to its absolute value.

matches well with the crystallographic data with the exception of some small deviations (less than 0.01 Å) on C(3)−C(4) and C(5)−C(6) (Figure S3, Table S1). Such good agreement suggests the good feasibility of the molecular model we optimized for further study.

IB1 exhibited a column packing mode along the *a*-axis (Figure 2), and the major contacts in the unit cell are C−H...π between hydrogens on the phenyl ring, alkyl chains, and the central pentalene ring. The average distance between two neighboring molecules is 3.83 Å.

Nucleus-independent chemical shift (NICS) calculation was used to investigate the antiaromatic character of **IB1**. NICS was introduced by Schleyer and co-workers as a measure of electron delocalization and induced ring current.[9] A negative NICS value is indicative of the presence of diatropic ring current, while a positive value is related to paratropic ring current. A series of NICS values with different positions relative to **IB1** were calculated at the GIAO-RB3LYP/6-31+G* level (Figure 3, Table S2). The results showed that the NICS values of pentalene ring and benzene of indole were +28 and −7.8, respectively. The highly positive value of pentalene ring, which is even higher than pentalene itself (+18.42), indicated a high antiaromaticity, whereas the benzene ring showed slightly less aromaticity than that of benzene itself (−11.31).

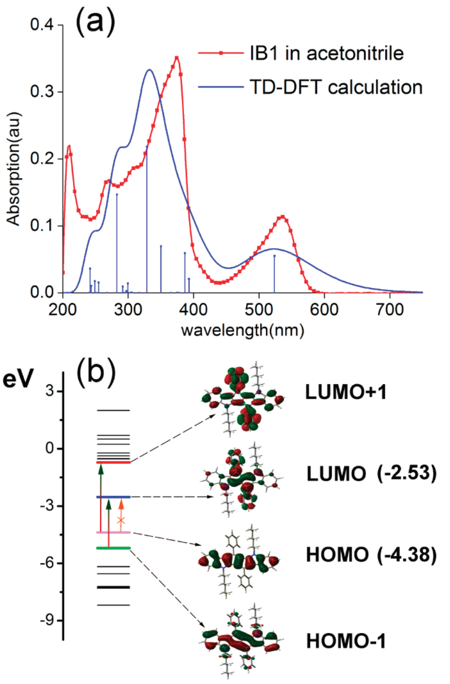

Figure 4. (a) TD-DFT calculated electro spectra of IB1 compared with experimental electronic spectra (in acetonitrile, 1 × 10^{-5} M). (b) The molecular orbitals and energy diagrams (eV) of IB1 calculated with the B3LYP/6-31+G* method.

The photophysical property of **IB1** was studied by both experimental and theoretical methods. The electronic spectra of **IB1** were measured in different solvents (Figure S4). The results show that **IB1** has two main absorption bands at 380 and 540 nm without a solventchromic effect. The absorptions at 280 and 530 nm in hexane are due to the bad solubility of **IB1** which leads to formation of aggregation. Theoretical calculation of the excited state was carried out by the TD-DFT method at the B3LYP/6-31+G* level (Figure 4). The result indicated that the absorption band located at about 530 nm is attributable to HOMO−1→LUMO transition, while the transition of HOMO→LUMO is symmetry forbidden which is typical for 4nπ-electron systems (Table S2). We also investigated the molecular orbitals of **IB1** at B3LYP/6-31+G* (Figure 4), which indicated that **IB1** has an unusually high HOMO of about −4.4 eV, and the gap between HOMO and LUMO is 1.85 eV. The distribution of the HOMO reveals the delocalization of electrons on the main part of **IB1**, which might be due to its good planarity. Upon comparison with the reported HOMO of acenes like rubrene and tetracene,[10] the unusually high HOMO of **IB1** should be due to the higher composition of the antibonding orbital in the HOMO of **IB1.**

Subsequently, electrochemical experiments were carried out to study the redox property of **IB1** (Figure S5, Table S4). Oxidative (two) and reductive (one) processes were observed with good reversibility. Interestingly, the first oxidation revealed an extremely low oxidative potential which is −270 mV versus that of ferrocene, indicating a strong electro-donating property of **IB1** with a HOMO level of ca. −4.5 eV. The formation of **IB1**$^{2+}$ occurs at a potential ca. 340 mV more positive than that for **IB1**$^{+}$, and the formation of **IB1**$^{-}$ occurs at the potential of −1.76 V versus Fc^{+}/Fc. The DPV result shows that all of these redox processes are equally one-electron processes.

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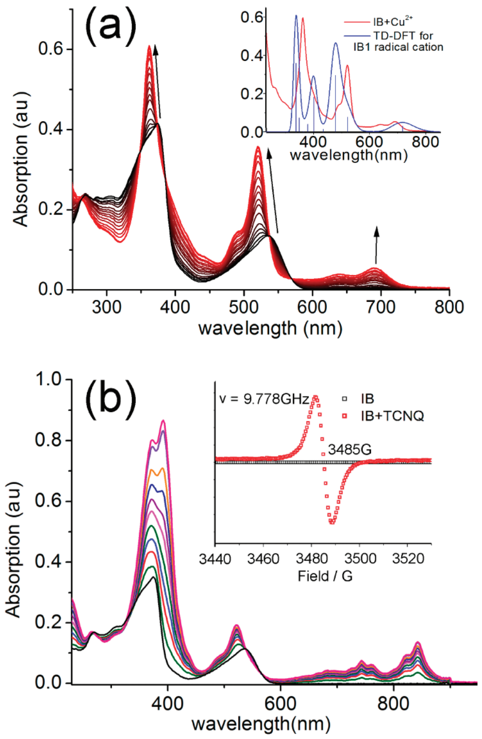

Figure 5. (a) UV−vis titration of **IB1** (1×10^{-5} M) with Cu^{2+}. Inset: TD-DFT calculation for the **IB1** radical cation at the UB3LYP/6-31+G* level. (b) Titration of **IB1** in acetonitrile (1×10^{-5} M) with TCNQ; ESP spectra of [**IB1**][TCNQ].

As a strong electro-donor, **IB1** can be oxidized easily by oxidative chemicals and form a radical cation. Titration of **IB1** with Cu^{2+} was carried out in a solution of **IB1** in acetonitrile (1×10^{-5} M, Figure 5). As the amount of Cu^{2+} increased, the absorption at 380 and 540 nm blue-shifted for ca. 20 nm, and the intensity increased by about 50% and 100% respectively. Another relatively weak absorption peak appears at 690 nm. TD-DFT calculation (UB3LYP/6-31+G* level) result (Table S6) for the **IB1** radical cation supported the blue shift mentioned above, as well as the new absorption at 690 nm which could be assigned to the transition from 159β to 161β (SOMO). The clear isosbestic points also support a clean conversion to the radical cation.

Furthermore, **IB1** can form a charge transfer complex with TCNQ in polar solvents. The titration of **IB1** with TCNQ was carried out in acetonitrile (1×10^{-5} M, Figure 5b). As the amount of TCNQ increased, absorption of the **IB1** radical cation at 370, 530, and 690 nm appeared as well as the typical absorption of the TCNQ radical anion at 700−800 nm and 800−900 nm.[11] The solution, which was light-purple initially, turned to dark brown. ESR spectroscopy was carried out to confirm the formation of a radical complex in acetonitrile (Figure 5b). The result showed that the resonance occurred at 3485 G under a frequency of ca. 9.8 GHz, indicating the *g* factor is 2.0049. Theoretical calculation was carried out at the B3LYP/6-31+G* level with the BSSE method to study the interaction between the neutral molecule of TCNQ and **IB1** (Figure S6). The result revealed a strong interaction between **IB1** and TCNQ with a dipole−dipole binding energy of about 54 kJ/mol, which is much stronger than that of a typical hydrogen bond. Such a strong interaction is the driving power of the intermolecular electron transfer.

In conclusion, a six-ring fused system including pentalene, **IB1**, was synthesized and the structure was confirmed by X-ray diffraction. Theoretical calculation was used to study the geometric structure and MO energy level of **IB1** which showed good agreement with the experimental results. The alternating bond lengths and positive NICS value support the strong antiaromaticity of **IB1**. Electrochemical experiments and theoretical calculations showed that **IB1** has an extremely high HOMO level indicating a strong electro-donating property. As a consequence, a charge-transfer complex can be formed with the TCNQ molecule as an electron acceptor. Further research on the application of **IB1** for organic electronics is still in progress.

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Supporting Information Available. Detailed experimental procedures, characterization data, crystal structure tabulated data, UV−vis absorption spectra, electrochemistry data, and results of theoretical calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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