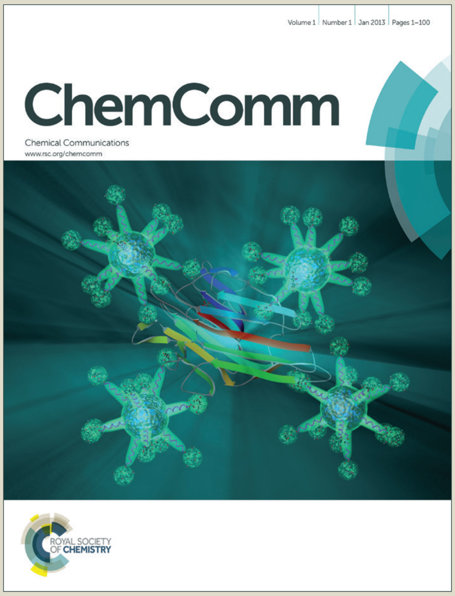

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Facile synthesis of pyrrole-fused dibenzo[*a*,*e*]pentalene and application as a new extended, ladder-type fused aromatic system

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A novel ladder-type pyrrole-fused dibenzo[*a*,*e*]pentalene, in which two benzo[*a*,*e*]pentalene units are held coplanar by a nitrogen bridge, is synthesized via double intermolecular Pd-catalyzed cascade crossover annulations. The introduction of nitrogen bridge not only has a substantial influence on the optoelectronic properties but also improves the processability and stability.

In recent years, dibenzo[*a*,*e*]pentalenes (DBPs, **1**, Fig. 1) have attracted considerable interest due to their distinct physical and chemical properties,[1] and utility in organic electronic devices.[2] Since the first synthesis in 1912, DBPs have had a long history of studies on their synthesis, structures, electronic properties, and their convenient synthetic method has been developed only recently.[3] For example, Jin reported the effective synthesis of multisubstituted DBPs through a Pd-catalyzed cascade carbopalladation and C-H activation.[4] Kawase and co-workers reported a new π-extended pentalene derivatives, 6,13-diphenyldinaphtho[*a*,*e*]pentalenes (DNPs, **2**, n = 1, Fig. 1), via a nickel-mediated reaction.[5] Xi disclosed the facile synthesis of perfluoronated DBPs and DNPs via intramolecular C-F and C-H bond cleavage promoted by butadienyl heavy Grignard reagents.[6] Quite recently, dianthraceno[*a*,*e*]pentalene (DAP, **2**, n = 2, Fig. 1) was also obtained by some of us under the $Pd(OAc)_2/n\text{-}Bu_4NOAc$ system.[7]

Ladder-type heteroatom-fused polycyclic aromatic hydrocarbons (PAHs) with extended π-conjugation are of great interest because of their potential applications in organic field-effect transistors (OFETs), light-emitting diodes (LEDs), and organic photovoltaics (OPVs).[8] DBPs, which possess a 4*n*π-electron periphery and fairly stable with a planar structure, are considered as one of the most promising building blocks for π-extended ladder-type polycyclic hydrocarbons. However, despite the great progress in the synthesis of DBPs, extended DBP derivatives are scarcely studied due to the limited synthetic methodologies. Meanwhile, the application of DBPs to organic semiconductor devices is still underdeveloped because they are commonly susceptible to oxidative degradation and often suffer from poor solubility.[9] Thus, appropriate modification such as the introduction of heteroatom-bridge may be one of the most effective way.

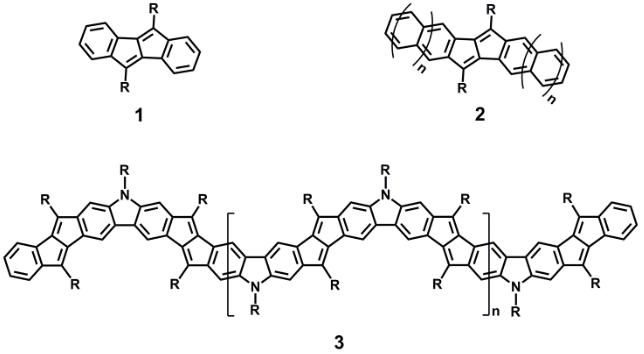
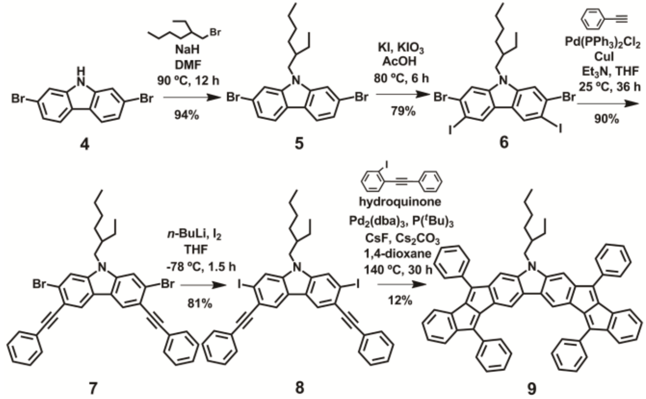


Fig. 1 Chemical structures of DBPs (**1**), DNPs (**2**, n = 1), DAPs (**2**, n = 2), and ladder-type pyrrole-fused dibenzo[*a*,*e*]pentalene-based derivatives (**3**).

We are particularly interested in the design and synthesis of ladder-type heteroatom-fused PAHs. In previous work, we reported the facile synthesis of S-, Se-, and N-annulated perylenes which have unique optoelectronic properties and supramolecular self-assembly behavior.[10] Furthermore, π-extended ladder-type N-annulated perylene derivatives, bis-N-annulated quaterrylene and tri-N-annulated hexarylene, were also synthesized efficiently, both of which exhibit good solubility owing to the introduction of alkyl nitrogen-atoms.[11] Quite recently, we reported the effective synthesis of a series of heterocyclic acene diimides and their potential application in OFETs.[12]

Inspired by previous work, herein, we designed and synthesized a novel extended ladder-type fused aromatic system, pyrrole-fused dibenzo[*a*,*e*]pentalene (**9**, Scheme 1), via double intermolecular Pd-catalyzed cascade crossover annulations, which could be considered as the model compound for pyrrole-fused dibenzo[*a*,*e*]pentalene-based derivatives (**3**, Fig. 1). The introduction of nitrogen bridge in the pyrrole-fused dibenzo[*a*,*e*]pentalene not only improves the processability and stability, but also holds two benzo[*a*,*e*]pentalene units coplanar which will definitely has a substantial influence on the optical and electronic properties. Moreover, OFETs based on the assembled microribbons of pyrrole-fused dibenzo[*a*,*e*]pentalene are also investigated which make it particularly attractive for electronic applications.



Scheme 1 Synthesis of pyrrole-fused dibenzo[*a*,*e*]pentalene.

The synthesis of pyrrole-fused dibenzo[*a*,*e*]pentalene is shown in Scheme 1. The starting material 2,7-dibromocarbazole **4** and 1-iodo-2-(phenylethynyl)benzene were prepared according to known procedures.[13] Compound **5** was achieved by deprotonation of **4** with NaH and subsequent alkylation with branched 2-ethylhexyl bromide in 94% yield. Compound **6** was synthesized by iodization of **5** using potassium iodide and potassium iodate in acetic acid at 80 ℃ in 79% yield, which was then subjected to Sonogashira Coupling with phenylacetylene to furnish compound **7** in 90% yield. It should be noted that the reaction temperature is very important in the synthesis of **7**. The Sonogashira reaction usually takes place just in the iodine-substituted (3,6-) position of **6** at room temperature whereas it contains the bromine-substituted (2,7-) position at high temperature because of different reactivity. In order to deliver an even more reactive building block, the bromine atoms of **7** were substituted by iodines by lithium-bromine exchange and subsequent quenching with iodine to yield **8** in 81% yield.

Pd-catalyzed coupling reactions are considered as one of the most effective methods for the synthesis of DBPs. However, the synthetic methodologies for extended ladder-type pentalene derivatives are scarcely studied. After screening of various reaction conditions, pyrrole-fused dibenzo[*a*,*e*]pentalene was synthesized via double intermolecular Pd-catalyzed cascade crossover annulations. When using Pd$_2$(dba)$_3$ as the catalyst, P(^{t}Bu)$_3$ as the ligand, hydroquinone as the reductant, CsF and Cs$_2$CO$_3$ as the base, the crossover annulations of **8** and 1-iodo-2-(phenylethynyl)benzene proceed successfully in 1,4-dioxane at 140 ℃ for 30 h, and the final product **9** was separated after column chromatography in 12% yield. It should be noted that although the yield is moderate, considering the more complicated structure of **8** than that of diphenylacetylene, and the double intermolecular cascade crosssover annulations between **8** and 1-iodo-2-(phenylethynyl)benzene, the Pd$_2$(dba)$_3$/ P(^{t}Bu)$_3$/ hydroquinone/ CsF/ Cs$_2$CO$_3$ system is effective for the crossover annulation via C-I/C-I cascade.

For comparison, 5,10-diphenyldibenzopentalene (**1**, R = phenyl), which was synthesized via homoannulation of 1-iodo-2-(phenylethynyl)benzene, was also gained as a byproduct. It is worth mentioning that except of **9**, pyrrole-fused dibenzo[*a*,*e*]pentalene-based *o*-alkynylaryliodide **10** (Fig. S1, ESI†) is also observed, which has a good solubility and provides a very important precursor for the synthesis of larger ladder-type pyrrole-fused dibenzo[*a*,*e*]pentalene-based derivatives (**3**, n = 1) via homoannulation.

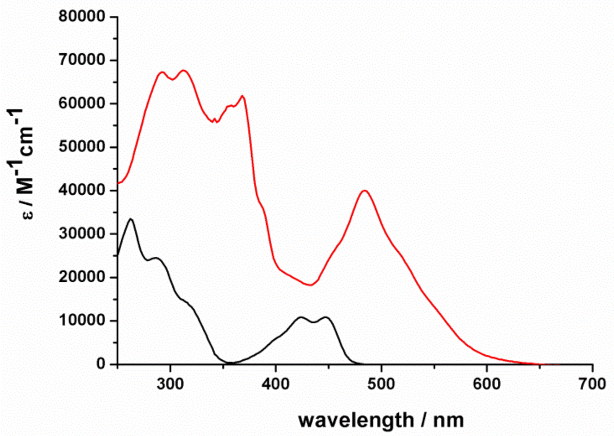


Fig. 2 UV/vis absorption spectra of 5,10-diphenyldibenzopentalene **1** (black) and pyrrole-fused dibenzo[*a*,*e*]pentalene **9** (red) in CHCl$_3$ (1×10^{-5} M) at room temperature.

Pyrrole-fused dibenzo[*a*,*e*]pentalene **9** has a good solubility in common organic solvents such as CH$_2$Cl$_2$, CHCl$_3$ and toluene. The thermal properties of pyrrole-fused dibenzo[*a*,*e*]pentalene **9** is investigated by thermogravimetric analysis (TGA), which reveals that the dibenzopentalene having a pyrrole moiety significantly improved its thermal stability might due to the π-extension of the conjugation. (430 ℃ corresponding to 5% weight loss under nitrogen flow) (Fig. S3, ESI†). Room temperature absorption spectra of 5,10-diphenyldibenzopentalene **1** and pyrrole-fused dibenzo[*a*,*e*]pentalene **9** in CHCl$_3$ are shown in Fig. 2, whereas the fluorescence of both compounds are not detected. 5,10-diphenyldibenzopentalene **1** has two major absorption bands in the 250-500 nm range with low-energy maxima at 448 nm (ε_{max} = 10861 M^{-1} cm^{-1}). Pyrrole-fused dibenzo[*a*,*e*]pentalene **9** displays broad absorption over much of the visible region, suggesting the possible application as active layers in organic photovoltaic cells.[14] Pyrrole-fused dibenzo[*a*,*e*]pentalene **9** exhibits two major absorption bands in the 250-650 nm range with low-energy maxima at 484 nm, bathochromically shifted by 36 nm in comparison with 5,10-diphenyldibenzopentalene **1**, as a reflection of a larger π-extended ladder-type fused aromatic system. It should be noted that instead of a simple superposition of the absorption of two DBP units, pyrrole-fused dibenzo[*a*,*e*]pentalene **9** shows a higher molar extinction coefficient (ε_{max} = 40018 M^{-1} cm^{-1}).

Table 1 Electronic properties and energy levels of 5,10-diphenyldibenzopentalene **1** and pyrrole-fused dibenzo[*a*,*e*]pentalene **9**

	E_{1r} [a]	E_{1o} [b]	LUMO [c]	HOMO [d]	E_g [e]
1	-1.71	—	-3.32	-5.95	2.63
9	-1.75	0.46	-3.22	-5.31	2.09

[a] Half-wave reductive potentials (in V vs Fc/Fc$^+$) measured in CH$_2$Cl$_2$ at a scan rate of 0.1 V/s with ferrocene as an internal potential marker. [b] Half-wave oxidative potentials (in V vs Fc/Fc$^+$) measured in CH$_2$Cl$_2$ at a scan rate of 0.1 V/s with ferrocene as an internal potential marker. [c] Estimated from the onset potential of the first reduction wave (in eV). [d] Estimated from LUMO levels and E$_g$ (in eV). [e] Obtained from the edge of the absorption spectra (in eV).

The electrochemical properties of 5,10-diphenyldibenzopentalene **1** and pyrrole-fused dibenzo[*a*,*e*]pentalene **9** are also investigated by cyclovoltammetry in dichloromethane (vs Fc/Fc^+), and their reductive potentials, oxidative potentials, and the energy levels are shown in Table 1. 5,10-diphenyldibenzopentalene **1** exhibits one reversible reduction waves (-1.71 V vs Fc/Fc^+). On the contrary, pyrrole-fused dibenzo[*a*,*e*]pentalene **9** shows not only two reversible reduction waves (-1.75 V and -1.86 V) but also two reversible oxidation waves (0.46 V and 0.92 V), indicating that the introduction of nitrogen bridge into two DBP units makes pyrrole-fused dibenzo[*a*,*e*]pentalene **9** potential electron-donor material. From the energy levels we can also see that pyrrole-fused dibenzo[*a*,*e*]pentalene **9** has a much smaller band gap (E_g) than that of 5,10-diphenyldibenzopentalene **1**, and the HOMO levels go up to -5.31 eV implying that the hole is more easily to be injected.

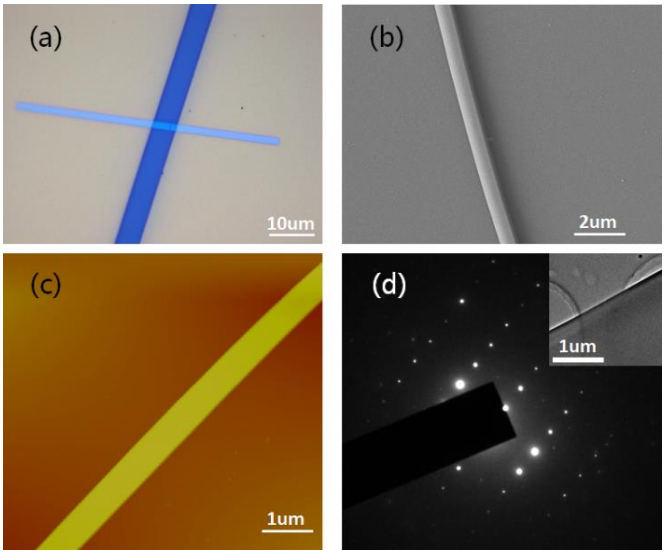


Fig. 3 (a) OM image of the single-crystal transistor based on **9**. (b) SEM image of the microribbon. (c) AFM image of the microribbon. (d) TEM image of the microribbon and its corresponding SAED pattern.

In order to demonstrate the viability of our concept, transistors based on single-crystal microribbons of pyrrole-fused dibenzo[*a*,*e*]pentalene **9** were fabricated using a doped n-type silicon wafer as the gate electrode, octadecyltrichlorosilane (OTS)-modified SiO_2 as the dielectric layer, and Au as the source and drain electrodes based on the fact that the HOMO level of compound **9** (5.3 eV) was very close to the work function of gold (5.1 eV). Single-crystal microribbons of pyrrole-fused dibenzo[*a*,*e*]pentalene **9** were grown by a simple slowly solvent evaporation process. A saturated solution of **9** in toluene was prepared and poured over the OTS-treated SiO_2/Si substrates directly.[15] After the solvent evaporation, long, thin microribbons of **9** were obtained on substrates as shown in Fig. S4 (ESI†). The low-magnification optical microscopy (OM) image of the microribbon in the device configuration is shown in Fig. 3a. From the scanning electron microscopy (SEM) image (Fig. 3b), it can be seen that the surface of the single-crystal microribbons was very smooth. The atomic force microscopy (AFM) image (Fig. 3c) further confirmed that the crystals were well-defined and the thickness of the crystals was about dozens of nanometers. The transmission electron microscopy (TEM) image (Fig. 3d) of the microribbons revealed that the single-crystal microribbons exhibited very neat morphology and the corresponding electron diffraction patterns showed sharp and well-defined diffraction spots. Field-effect transistors based on individual micro- or nanoribbons of compound **9** were fabricated by using "organic nanowires mask" technique. All characterizations of the organic single crystal transistors were performed under ambient conditions. The representative output and transfer characteristics of the transistors are presented in Fig. 4. The devices exhibited excellent p-type transistor behaviors as we expected with the highest mobility of 0.57 $cm^2\ V^{-1}\ s^{-1}$ and an on/off ratio of 10^4 along the growth direction. The average mobility of 20 devices was 0.18 $cm^2\ V^{-1}\ s^{-1}$, and the average threshold voltage was -24.1 V.

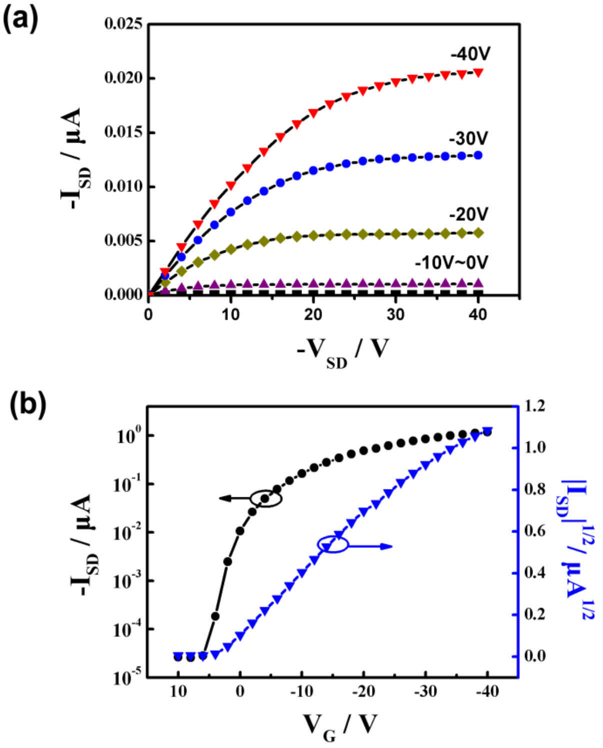


Fig. 4 Output (a) and transfer (b) characteristics of representative single crystal device based on pyrrole-fused dibenzo[*a*,*e*]pentalene **9**.

In conclusion, a novel π-extended, ladder-type fused aromatic system, pyrrole-fused dibenzo[*a*,*e*]pentalene, was successfully synthesized via double intermolecular Pd-catalyzed cascade crossover annulations. The introduction of nitrogen bridge in the pyrrole-fused dibenzo[*a*,*e*]pentalene not only improves the processability and stability but also holds two benzo[*a*,*e*]pentalene units coplanar, which has a substantial influence on the optical and electronic properties such as drastic bathochromic-shifted absorption and remarkable energy increase of the HOMO level. Moreover, the single-crystal transistors based on microribbons of pyrrole-fused dibenzo[*a*,*e*]pentalene display excellent p-type behavior with the highest mobility of up to 0.57 $cm^2\ V^{-1}\ s^{-1}$. Extension of this synthetic strategy to higher ladder-type pyrrole-fused dibenzo[*a*,*e*]pentalene-based derivatives and applications in electronic devices are currently underway.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization, MS spectra, and copies of ^{1}H and ^{13}C NMR spectra for all new compounds. See DOI: 10.1039/c000000x/

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