Pyrene-fused pyrazaacenes with eight rectilinearly arranged aromatic rings

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Abstract: A series of pyrene-fused azaacene-type conjugated molecules containing two pyrazine units and up to eight rectilinearly arranged aromatic rings were prepared by condensation coupling reactions in moderate yields. The geometries and electronic structures associated with **2** and **5** were evaluated by density functional theory calculations. Photophysical properties indicated that these systems possess delocalized structures, and their optoelectronic properties can be tuned by extending the π-conjugated length and introducing electronic-withdrawing groups. The compounds were thoroughly investigated by X-ray diffraction studies, electrochemistry and DFT calculations. High thermal stability and tunable energy levels make them excellent candidates as a new class of organic molecular materials.

Introduction

Heterocyclic organic conjugated compounds with multiple fused aromatic rings are of great importance and interest as molecular materials for use in organic light emitting diodes (OLEDs),[1] organic field-effect transistors (OFET),[2] and organic photovoltaic cells (OPVs).[3] The introduction of heteroatoms among these molecules can dramatically tune their properties, such as the nature of charge transport, the band gap, solubility, stability, and supramolecular

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organization.[4] In particular, azaacenes having undergone "doping" of the imine nitrogen atoms have been demonstrated to be vital elements in organic photoelectronics.[5]

Pyrene-fused pyrazaacenes (PPAs),[4a] possess cross conjugation with a nitrogenated ribbon-like structure, and provide a substantial increase in the azaacene-based materials. Such molecules are attractive for studying optoelectronic properties due to the extended sp²-hybridized scaffolds both at transverse and longitudinal positions. PPAs are generally prepared using pyrene-4,5-diketone and pyrene-4,5,9,10-tetraketone as the key starting materials. A number of new synthetic approaches to reactive intermediates have been developed. The first examples of the synthesis of the pyrene-4,5-diketone and the pyrene-4,5,9,10-tetraketone were reported in 1937, and involved multistep synthetic routes.[6] With a slow and sustained improvement of synthetic methodology, more economic and efficient synthetic routes were developed. Direct synthesis using OsO_4 and RuO_2 catalyzed oxidation replaced the multi-step routes,[7] and more environment-friendly "green chemical reagents" phased out the toxic catalyst.[8] Significant progress has been made, especially in recent decades, in the development of facile and efficient methodology for the oxidation of pyrene.[9] Even a scalable method, on a 15g scale, was performed comfortably using standard laboratory equipment.[10] Based on these two types of reactive intermediates, a straightforward strategy was developed to prepare pyrene-fused pyrazazcences.[9a] As a prelude to the discussion and investigation of the synthesis of PPAs, it is appropriate that some of the physical and chemical properties be first presented. For instance, following the characterization of the structure of the simplest diazatetracene (pyrene-4',5',2,3-quinoxaline),[7a] the low solubility of this compound motivated researchers to enhance the low overall solubility. Near-infrared (NIR) absorption attracted great interest because of its wide application in optical and electronic areas.[11] Thus, a large number of short pyrene-fused [n]acenes (4 ≤ n ≤ 6) were designed and synthesized. To enhance the solubility, several attempts were performed by introducing different substituent groups at the pyrene core or the longitude peripheral ends of the [n]acene.[4a] On the other hand, high pyrene-fused [n]acenes (n > 6) remain rare, such as heptacene,[9a,12] octacene,[13] nonacene,[14] or those possessing even more than ten rectilinearly arranged aromatic rings.[15] PPAs with low LUMO levels exhibit a wide range of applications, such as field-effect transistors,[15c,16] solar cells[17] etc.

Previous research[6,9a,18] has been revealed that insoluble PPA molecules hindered the development of materials in the absence of solubilizing groups. Thus, much work was carried out to enhance the solubility of PPAs. In our group, a series of pyrene-fused hexaacenes were designed and synthesized using an efficient synthetic approach, and they exhibited good solubility and high stabilities by functionalization of both the

active sites (1,3-) and the K-region (4,5,9,10-) of pyrene.[9e] Herein, we report the synthesis and physicochemical properties of a series of new derivatives. The aim of this study is to investigate the effect of the properties of the higher pyrene-fused [8]acene. We attempt to demonstrate another approach to lowering the bandgap of the PPAs with low LUMO levels by attaching multiple electron-withdrawing groups at the appropriate positions of the pyrene-fused pyrazaacenes moiety.

Results and Discussion

Taking all these aspects into consideration, firstly, a pyrene-fused [6]acene **2** was prepared by a Knoevenagel condensation reaction based on our previous work.[9e] The synthesis is outlined in Scheme 1. In comparison, the dicyanoethenyl groups (–CH=C(CN)$_2$) were chosen as strong electron-withdrawing groups to replace the –CHO groups, which we expected to result in an intramolecular charge transfer (ICT) compared with the precursor. Accordingly, a combined strategy (enhanced the intramolecular charge transfer and extended lateral π-conjugation) has been employed to synthesize a series of stable and soluble pyrene-fused [8]acenes **5** by two crucial steps using compound **3** as an intermediate. Donor/Acceptor groups were introduced by a Suzuki cross-coupling reaction, and introducing *o*-naphthylenediamine groups by a cyclocondensation reaction in moderate yields; the synthetic procedures for the three compounds are depicted in Scheme 2, which could dramatically tune the HOMO and LUMO levels as a result of intramolecular charge transfer.[19] Finally, the desired dicyanoethenyl pyrene-fused [8]acene **5d** was prepared by using Knoevenagel condensation reaction (Scheme 3), which could exhibit a lower LUMO level than the aforementioned compounds because of the stronger acceptor moieties present. The more extended pyrene-fused pyrazaacenes **2**, **5**, with high stability and solubility, are promising candidates as useful organic materials, such as electron acceptors in solar cells and electron-transport materials in field-effect transistors.[20] The as-prepared compounds were confirmed by ^{1}H NMR, ^{13}C NMR spectroscopy, and High Mass spectrometry (Figures S1-9).
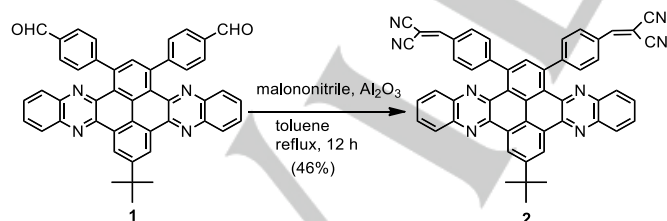
Scheme 1. The synthetic route for the preparation of **2**.
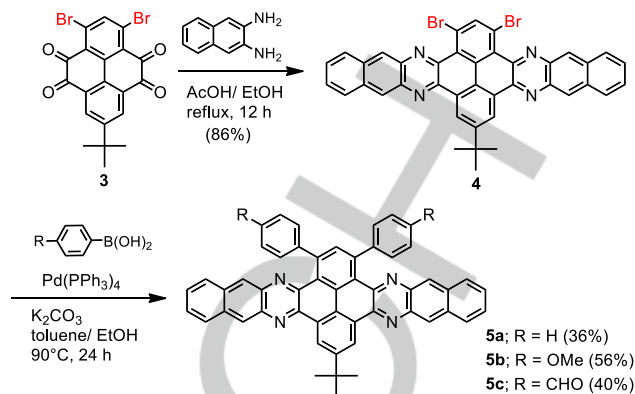
Scheme 2. Synthesis of pyrene-fused pyrazaacenes **5a**–**c**.
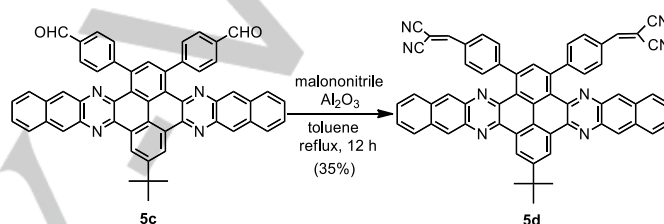
Scheme 3. Synthesis of pyrene-fused pyrazaacenes **5d**.

Single-crystals of **5a**, suitable for analysis by X-ray diffraction, have been prepared from a solution of dichloromethane/hexane. The asymmetric unit contains a single pyrene-fused azaacene molecule (Figure 1 and Table S1). The length measured between the two terminal H atoms of the naphthalene is 20.9 Å. The two phenyl groups are twisted by 80.92(13)° (C41 > C46) and 75.77(11)° (C47 > C52) relative to the plane of the central pyrene ring (C23 > C36). The two imine-bridged naphthalene substituents fused to the K-region of the pyrene, are slightly twisted away from both the plane of the pyrene ring and each other. The torsion angles of the fused azaacene, relative to the central pyrene ring (C23 > C36), are: 15.36(19)° (C1 > C6) and 11.4(2)° (C11 > C16).

The molecules pack with their pyrene cores co-aligned in parallel planes by a slightly offset aggregation where the two *tert*-butyl and four phenyl groups of two adjacent molecules are placed in the "bays" between the pyrene units. The pyrene core of each molecule is approached from above, by the ring C1 > C6 on one immediately adjacent molecule, and from below, by the ring C11 > C16 on a second, immediately adjacent molecule. The centroid-centroid distances of these two π···π interactions are 3.82 Å and 3.75 Å respectively. This π···π bonding array is observed at each molecule, running continuously through each plane. Molecules in adjacent planes pack with their *tert*-butyl groups approaching one another and their two phenyl substituents approaching one another. Where the phenyl groups approach one another, a single very weak intermolecular π···π interaction of distance 4.52 Å is observed between the symmetry-related C41 > C46 rings on neighbouring molecules.

Additionally, the arrangement of planarity is further stabilized by additional CH···π interactions of the phenyl moieties with the π–plane of the octacene core unit of an adjacent molecule.
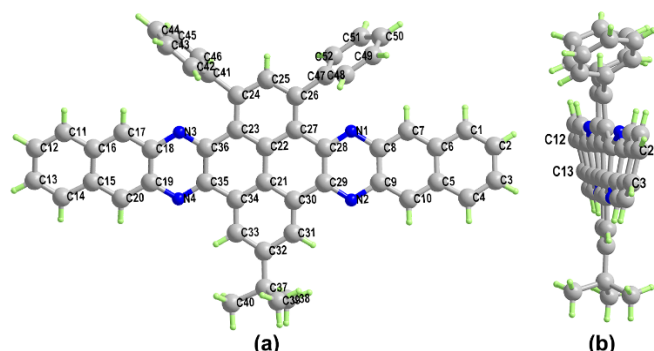

Figure 1. Single-crystal X-ray structure of **5a**: a) top view and b) side view showing Ph rings almost perpendicular to the pyrene core, and the slight twist along the [8]acene spine.
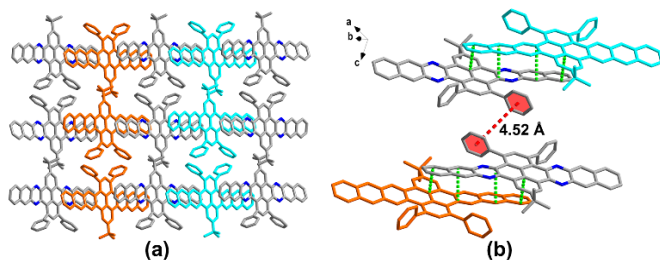

Figure 2. a) Packing viewed parallel to the crystallographic *a*-axis. To highlight the packing motif, every second molecule is depicted in a different colour; b) details of the intermolecular π···π interactions; green dashes are π···π separations of ca. 3.8 Å. The hydrogen atoms are omitted for clarity.

The UV–vis absorption spectra of **2** and **5** were measured in CH₂Cl₂ solution (Figure 3). These spectra present well-resolved absorption bands with legible vibronic features consistent with the structure and the electronic nature of the substituents.[9e,21] Specifically, significant spectral differences were observed, attributable to the differences between the substituents at the para position on the phenyl groups at the 1, 3-positions, especially for compounds **2** and **5d** compared with **5a**–**c**. Two sets of short wavelengths at 250–290 nm and 320–370 nm were attributed to the π–π* and n–π* transitions of the phenyl group and pyrene core, respectively. Furthermore, the different lengths of lateral π-conjugated aromatic rings result in slight shifts to short wavelengths (λ_{abs} < 370 nm). On the other hand, in comparison to **5a**–**c**, **2** and **5d** showed distinctive absorption bands at longer wavelengths, which might be the result of charge transfer between the 1, 3-moieties and the pyrene core, associated with the ability of the electron-withdrawing substituents at the *para*-positions of the phenyl group.[22] Such results indicate the potential tunability of the electronic properties of pyrene-fused azaacenes.
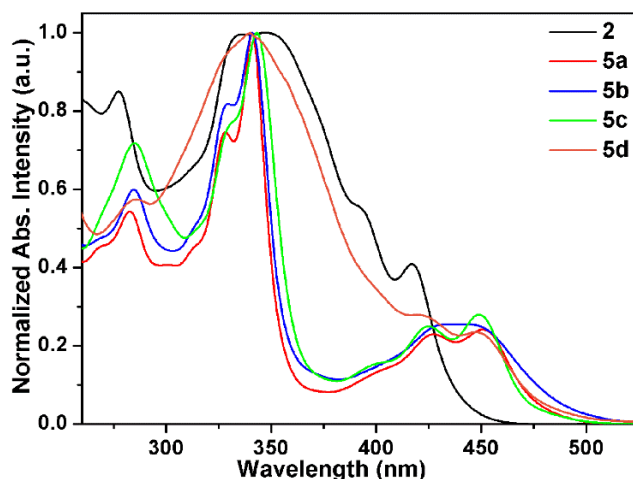

Figure 3. UV-vis absorption spectra of **2**, and **5** in CH₂Cl₂ solution.

To elucidate the effects of the substituents on the electronic structures of the compounds mentioned above, density functional theory (DFT) calculations were performed at the B3LYP/6-31G* level. As depicted in Figure 4, the LUMO levels of compounds **5** were evaluated at the B3LYP/6-31G* level, and the values show a significant downwards trend on increasing the electronegativity or electron-withdrawing ability following the order **5b** > **5a** > **5c** > **5d**. Furthermore, compound **2** also exhibited a lower LUMO level compared with the other pyrene-fused [6]acenes with different *para*-substituents (such as H, OMe, CHO),[9e] even **5a**−**c**. This indicated that intramolecular charge transfer plays a crucial role when designing and synthesizing this type of compound with lower LUMO levels. In addition, cyclic voltammetry was performed in 0.1 M CH₂Cl₂ with a scan rate of 100 mV s⁻¹ (Figure S11), all of the compounds displayed irreversible oxidation processes with distinct positive potentials. The HOMOs of compounds **2** and **5** were estimated to be −6.12 eV (**2**), −5.96 eV (**5a**), −5.92 eV (**5b**), and −5.99 eV (**5c**), respectively. Although the data for **5d** is deficient because of the limited sample, the consistent trend of the other four compounds (**2** and **5a**−**c**) in the DFT and voltammetry work indicates that an efficient strategy was established by tuning the *para*-substituents of the phenyl groups.
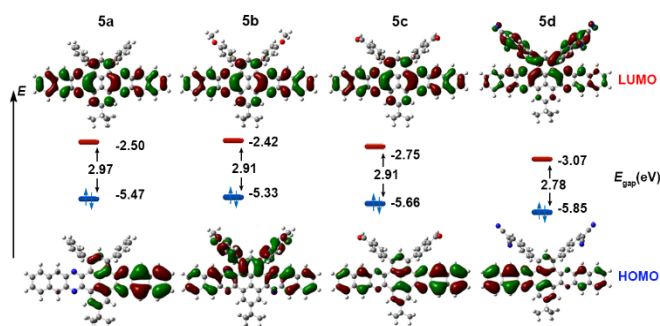

Figure 4. Frontier-molecular-orbital distributions and energy level diagrams of **5a**−**d** by DFT calculations.

Table 1. Linear and nonlinear optical properties of compounds **2** and **5**.

Compds	λ_{abs},[a] nm	$E_{HOMO (CV)}$,[b] eV	$E_{HOMO (calcd)}$,[c] eV	$E_{LUMO (calcd)}$,[c] eV	$E_{gap (calcd)}$,[c] eV	$E_{gap (optical)}$,[d] eV	T_d,[e] °C
2	278, 348, 417	–6.12	–6.26	–2.99	3.27	2.72	410
5a	283, 341, 427, 451	–5.96	–5.47	–2.50	2.97	2.65	460
5b	285, 341, 435	–5.92	–5.33	–2.42	2.91	2.45	436
5c	285, 343, 425, 449	–5.99	–5.66	–2.75	2.91	2.49	434
5d	286, 340, 420, 447	nd[f]	–5.85	–3.07	2.78	2.43	nd

[a] Measured in CH_2Cl_2. [b] Measured from the oxidation potential in 0.1 M CH_2Cl_2 with a scan rate of 100 mV s^{-1} by cyclic voltammetry. [c] DFT/B3LYP/6-31G* using Gaussian. [d] Estimated from the absorption edge of UV-Vis data. [e] Obtained from TGA analysis. [f] nd: not detected.

Conclusions

In summary, a set of new pyrene-fused azaacenes **2** and **5** were designed and synthesized with rectilinearly arranged aromatic rings. Based on intramolecular charge transfer, they all show low LUMO levels by introducing different donor or acceptor moieties at the *para* position of the phenyl groups. Their photophysical properties, including thermostability, absorption properties, electrochemical properties and DFT calculation results, indicated that this work provides an efficient and widely tunable strategy to reduce the LUMO levels of pyrene-fused [*n*]acenes. This preliminary study has demonstrated the efficiency of tuning LUMO levels using this strategy, and further detailed investigations aimed at developing electronic devices are ongoing in our group.

Experimental Section

Materials: Unless otherwise stated, all reagents used were purchased from commercial sources and used without further purification. The preparations of compounds **1** and **3** were described previously.[9e]

All melting points (Yanagimoto MP-S₁) are uncorrected. ¹H/¹³C NMR spectra (400 MHz) were recorded on a Varian-400MR-vnmrs 400 with SiMe₄ as an internal reference. Mass spectra were obtained with a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. UV/ Vis spectra were obtained with a Perkin–Elmer Lambda 19 UV/Vis/NIR spectrometer in various organic solvents. Thermogravimetric analysis (TGA) was undertaken using a SEIKO EXSTAR 6000 TG/ DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The quantum chemistry calculation was performed on the Gaussian 03W (B3LYP/6–31G* basis set) software package.

Synthesis of 2-*tert*-butyl-10,12-bis(4-dicyanoethenylphenyl)tetraazahexacene (2)
2-*tert*-Butyl-10,12-bis(4-formylphenyl)tetraazahexacene (**1**) (300 mg, 0.447 mmol), basic aluminum oxide (228 mg, 2.24 mmol), malononitrile (295 mg, 4.47 mmol), and toluene (20 mL) was added to a round-bottomed flask. The mixture was refluxed for 12 h, cooled to room temperature, and filtered, and the residue was washed with chloroform. The filtrate was evaporated, and the solid obtained was purified by chromatography (SiO₂, chloroform). The procedure afforded pure 2-*tert*-butyl-10,12-bis(4-dicyanoethenylphenyl)tetraazahexacene (**2**) as a yellow powder (156 mg, 46 %). M.p. > 400 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.77 (9H, s, *t*Bu), 7.17 (2H, d, *J* = 8.0 Hz, –CH=C(CN)₂), 7.61 (4H, d, *J* = 8.0 Hz, Ar–*H*), 7.68–7.70. (4H, m, Ar–*H*), 7.83 (2H, t, *J* = 8.4 Hz, Ar–*H*), 7.95 (1H, s, pyrene–*H*), 8.04 (4H, d, *J* = 8.0 Hz, Ar–*H*), 8.33 (2H, d, *J* = 8.4 Hz, Ar–*H*) and 9.86 (2H, s, pyrene–*H*) ppm. ¹³C NMR (100 MHz, CDCl₃): δ= 30.7, 34.9, 80.8, 111.9, 113.1, 124.1, 124.4, 126.0, 127.9, 128.1, 128.3, 128.6, 128.9, 129.0, 129.1, 129.5, 129.5, 129.7, 132.6, 139.3, 140.4, 140.7, 141.6, 151.1, 151.9 and 158.7 ppm. FAB-HRMS: *m*/z calcd. for $C_{52}H_{30}N_8$ 766.2593 [M⁺]; found 766.2590 [M⁺].

Synthesis of 2-*tert*-butyl-12,14-dibromotetraazaoctacene (4)
A mixture of 1,3-dibromo-7-*tert*-butylpyrene-4,5,9,10-tetraone (**3**) (400 mg, 0.85 mmol) and 2,3-diaminonaphtalene (185 mg, 1.70 mmol) were placed in a reaction flask containing AcOH (50 mL) under an argon atmosphere. The solution was then refluxed for 4 h. The reaction mixture was poured into a large excess of water and extracted with dichloromethane (50 mL × 2). The combined organic extracts were washed with water and brine, then dried with anhydrous MgSO₄ and evaporated. The residue was purified by column chromatography using dichloromethane/hexane, 2:1 as eluent to provide a yellow solid (435 mg, 83%), which was used in the next reaction without further purification.[23]

Synthesis of 2-*tert*-butyl-12,14-diphenyltetraazaoctacene (5a)
A mixture of compound **4** (250 mg, 0.347 mmol), phenyl boronic acid (846 mg, 6.94 mmol) in toluene (50 mL) and ethanol (20 mL) at room temperature was stirred under argon, and a 2M aqueous solution of K₂CO₃ (5 mL) and Pd(PPh₃)₄ (80mg, 0.07 mmol) was added. After the mixture was stirred for 30 min. at room temperature under argon, the mixture was heated to 90 °C for 48 h with stirring. After cooling to room temperature, the mixture was quenched with water, extracted with CH₂Cl₂ (2 × 30 mL), washed with water and brine. The organic extracts were dried with MgSO₄ and evaporated. The residue was purified by column chromatography eluting with CHCl₃/hexane (3:1) to give **5a** as a brown solid (95 mg, 36%). M.p. 337–338 °C. ¹H NMR (400 MHz, CDCl₃): *δ* = 1.79 (9H, s, *t*Bu), 7.43–7.50. (14H, m, Ar–*H*), 7.83 (2H, s, Ar–*H*), 7.88 (1H, s, pyrene–*H*), 7.96 (2H, d, *J* = 8.0 Hz, Ar–*H*), 8.09 (2H, d, *J* = 8.0 Hz, Ar–*H*), 8.84 (2H, s, Ar–*H*) and 9.83 (2H, s, pyrene–*H*) ppm. ¹³C NMR (100 MHz, CDCl₃): δ= 31.8, 35.8, 125.7, 126.2, 126.5, 126.6, 126.7, 126.9, 127.6, 128.0, 128.4, 128.6, 130.4, 131.1, 133.8, 134.3, 136.2, 137.4, 138.1, 143.5, 143.7, 144.6, 145.9 and 151.5 ppm. FAB-HRMS: *m*/z calcd. for $C_{52}H_{34}N_4$ 714.2783 [M⁺]; found 714.2778 [M⁺].

Synthesis of 2-*tert*-butyl-12,14-bis(4-methoxylphenyl)tetraaza-octacene (5b)
A mixture of compound **4** (300 mg, 0.416 mmol), 4-methoxyphenyl boronic acid (1.26 g, 8.32 mmol) in toluene (50 mL) and ethanol (20 mL) at room temperature was stirred under argon, and a 2M aqueous solution of K₂CO₃ (5 mL) and Pd(PPh₃)₄ (96 mg, 0.08 mmol) was added. After the mixture was stirred for 30 min. at room temperature under argon, the

mixture was heated to 90 °C for 48 h with stirring. After cooling to room temperature, the mixture was quenched with water, extracted with CH_2Cl_2 (2 × 30 mL), washed with water and brine. The organic extracts were dried with $MgSO_4$ and evaporated. The residue was purified by column chromatography eluting with $CHCl_3$/hexane (3:1) to give **5b** as an orange solid. Recrystallization from CH_2Cl_2/hexane (3:1) gave **5b** (176 mg, 56%) as orange prisms. M.p. 326–327 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (s, 9H, *t*Bu), 3.99 (s, 6H, OMe–*H*), 7.06 (d, *J* = 8.4 Hz, 4H, Ar–*H*), 7.43 (d, *J* = 8.4 Hz, 4H, Ar–*H*), 7.46–7.52. (m, 4H, Ar–*H*), 7.86 (s, 1H, pyrene–*H*), 7.95 (s, 2H, Ar–*H*), 7.99 (d, *J* = 8.0 Hz, 2H, Ar–*H*), 8.11 (d, *J* = 7.8 Hz, 2H, Ar–*H*), 8.86 (s, 2H, Ar–*H*) and 9.82 (s, 2H, pyrene–*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.7, 35.8, 55.6, 113.5, 125.6, 126.2, 126.4, 126.5, 126.8, 126.9, 127.5, 128.4, 128.6, 129.8, 130.3, 131.3, 133.8, 134.2, 136.8, 137.5, 138.0, 138.8, 143.5, 144.0, 144.3, 151.4 and 158.5 ppm. FAB-HRMS: *m/z* calcd. for $C_{54}H_{38}O_2N_4$ 775.3028 [M$^+$]; found 775.3046 [M$^+$].

Synthesis of 2-*tert*-butyl-12,14-bis(4-formylphenyl)tetraazaoctacene (5c)

A mixture of compound **4** (300 mg, 0.416 mmol), 4-formylphenyl boronic acid (1.03 g, 8.32 mmol) in toluene (50 mL) and ethanol (20 mL) at room temperature was stirred under argon, and a 2M aqueous solution of K_2CO_3 (5 mL) and Pd(PPh$_3$)$_4$ (96 mg, 0.08 mmol) was added. After the mixture was stirred for 30 min. at room temperature under argon, the mixture was heated to 90 °C for 48 h with stirring. After cooling to room temperature, the mixture was quenched with water, extracted with CH_2Cl_2 (2 × 30 mL), washed with water and brine. The organic extracts were dried with $MgSO_4$ and evaporated. The residue was purified by column chromatography eluting with $CHCl_3$/hexane (3:1) to give **5c** as an orange solid. Recrystallization from CH_2Cl_2–hexane (3:1) gave **5c** (125 mg, 40%) as orange prisms. M.p. 332–333 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.81 (s, 9H, *t*Bu), 7.40–7.47 (m, 4H, Ar–*H*), 7.60–7.62. (m, 6H, Ar–*H*), 7.67 (s, 1H, pyrene–*H*), 7.85 (d, *J* = 8.0 Hz, 2H, Ar–*H*), 8.03–8.05. (m, 4H, Ar–*H*), 8.80 (s, 2H, Ar–*H*), 9.80 (s, 2H, pyrene–*H*) and 10.23 (s, 2H, C*H*O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.7, 35.9, 125.7, 126.0, 126.4, 126.7, 126.9, 127.0, 127.1, 128.3, 128.5, 129.2, 129.6, 130.2, 130.9, 133.8, 134.3, 134.4, 134.5, 136.9, 137.9, 142.7, 142.8, 143.3, 151.9, 152.5 and 192.2 ppm. FAB-HRMS: *m/z* calcd. for $C_{54}H_{38}O_2N_4$ 771.2760 [M$^+$]; found 771.2746 [M$^+$].

Synthesis of 2-*tert*-butyl-12,14-bis(4-dicyanoethenylphenyl)tetraazaoctacene (5d)

2-*tert*-Butyl-12,14-bis(4-formylphenyl)tetraazaoctacene (**5c**) (60 mg, 0.08 mmol), basic aluminum oxide (66 mg, 0.65 mmol), malononitrile (52 mg, 0.78 mmol), and toluene (12 mL) was added to a round-bottom flask. The mixture was refluxed for 12 h, cooled to room temperature, and filtered, and the residue was washed with chloroform. The filtrate was evaporated, and the solid obtained was purified by chromatography (SiO$_2$, chloroform). The procedure afforded pure 2-*tert*-butyl-12,14-bis(4-dicyanoethenylphenyl)tetraazaoctacene (**5d**) as a yellow powder (23 mg, 35%). M.p. > 400 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (s, 9H, *t*Bu), 7.52–7.57 (m, 4H, Ar–*H*), 7.66 (d, *J* = 9.5 Hz, 4H, Ar–*H*), 7.71 (s, 1H, pyrene–*H$_2$*), 7.74 (s, 2H, C*H*=C(CN)$_2$), 7.97 (d, *J* = 8.3 Hz, 4H, Ar–*H*), 8.07 (d, *J* = 8.1 Hz, 4H, Ar–*H*), 8.13 (d, *J* = 7.6 Hz, 2H, Ar–*H*), 8.92 (s, 2H, Ar–*H*) and 9.86 (s, 2H, pyrene–*H$_{6,8}$*) ppm. As very little sample was obtained, it was not further characterized by ^{13}C NMR. FAB-HRMS: *m/z* calcd. for $C_{60}H_{34}N_8$ 866.2906 [M$^+$]; found 866.2901 [M$^+$].

Crystallography for 5a

A suitable single crystal of **5a** was obtained from solution of dichloromethane/hexane. Diffraction data was collected at the ALS, beam line 11.3.1, using silicon 111-monochromated synchrotron radiation (λ = 0.7749 Å). Data was corrected for Lorentz and polarisation effects and for absorption from multiple and symmetry equivalent measurements.[24] The structure was solved by a charge-flipping dual space algorithm and refined by full-matrix least-squares methods on F^2.[25] The diffraction data were non-merohedrally twinned via a 180° rotation about reciprocal axis (0 1 −1) and the structure was refined as a two-component twin with a major:minor component ratio of 53.5:46.5(2)%. The refinement was otherwise routine and the details are supplied the supplementary information. CCDC-1853980 contains the supplementary crystallographic data for this paper. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 144-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

A series of pyrene-fused azaacene-type conjugated molecules containing two pyrazine units and up to eight rectilinearly arranged aromatic rings were prepared and possess significant delocalization and tunable optoelectronic properties.
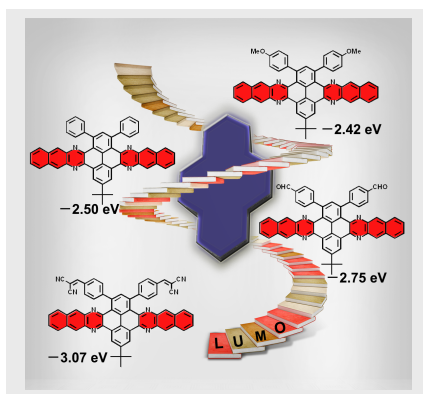
Chuan-Zeng Wang,[*a,b] *Xing Feng,*[c] *Mark R.J. Elsegood,*[d] *Thomas G. Warwick,*[d] *Simon J. Teat,*[e] *Carl Redshaw,*[f] *Yu-Sui Bi,*[a] *and Takehiko Yamato*[*b]

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Pyrene-fused pyrazaacenes with eight rectilinearly arranged aromatic rings