

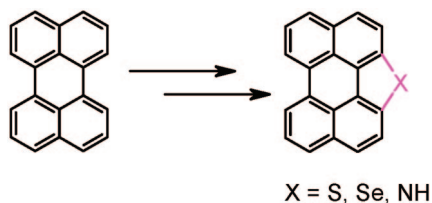
Heteroatom-Annulated Perylenes: Practical Synthesis, Photophysical Properties, and Solid-State Packing Arrangement

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A practical strategy for the preparation of a series of heterocyclic annulated perylenes in good yields is presented. UV-vis absorption spectra indicate hypsochromic shift of the absorption maxima relative to the corresponding parent perylene. Single-crystal X-ray diffraction analysis reveals that they all adopt planar conformation, but the solid-state packing arrangements are significantly altered by annulation of various heterocycles.

Highly π -extended heteroarenes, which contain chalcogen, nitrogen, etc. in fused aromatic rings, are the subjects of considerable current research interest due to their fundamental optoelectronic properties and their potential applications such as organic field-effect transistors (OFETs), light emitting diodes (LEDs), photovoltaic devices, and other organic optoelectronic devices.¹ Attempts to construct bay-region heterocyclic annulated polycyclic aromatic hydrocarbons (PAHs) such as triphenylene, pyrene, perylene, and perylene bisimides have been performed during the past decades.² However, due to the difficulty in the establishment of efficient and practical synthetic protocols, further investigation of structure/properties relationship of the heterocyclic annulated PAHs is rather limited.

Perylene is unique in the family of PAHs and has been extensively studied due to its excellent optical and electronic

properties.³ Incorporating heteroatoms into its skeleton is an intriguing target because the introduction of heteroatoms would induce a variety of intermolecular interactions, such as van der Waals interactions and heteroatom-heteroatom interactions (S...S or Se...Se interactions), which is essential to achieve highly ordered supramolecular self-assembled structure,⁴ and eventually excellent device performance.⁵

S-heterocyclic annulated perylene, namely perylo[1,12-*b,c,d*]thiophene (PET, **3**), which has first prepared from 3,4:9,10-perylenetetracarboxylic dianhydride by Rogovik,⁶ has been synthesized by several groups in harsh conditions such as flash vacuum pyrolysis (FVP).⁷ However, its electrical property is rarely studied, probably due to the difficulties in scale-up, long reaction sequences, and poor yields. Recently, we reported its extraordinary solid-state packing arrangement with marked S...S short contacts of 3.51 Å between the neighboring columns and the likelihood of double-channel superstructure, which is responsible for effective intermolecular carrier transport.^{5c} Herein, we describe our endeavors to develop a new and practical synthetic route toward PET up to gram-scale successfully. Furthermore, Se-heterocyclic annulated perylene is synthesized by incorporating selenium into the perylene skeleton. Accordingly, detailed investigation of photophysical properties and single-crystal analysis of heterocyclic annulated perylenes is presented to fully explore the influence of different heteroatoms on the inherent electronic properties and solid-state packing arrangement.

The key starting material is 1-nitroperylene **2**. Previous synthetic reports⁸ of **2** were unsatisfactory in that the yield of the regioselective mononitration of perylene at position 1 was rather low or the reaction was irreproducible.⁹ Successful preparation of **2** from perylene is achieved in a modified mononitration of the perylene process, by which the temperature is reduced and the reaction time is shortened to 25–30 min. There are three main fractions in the crude products. The first

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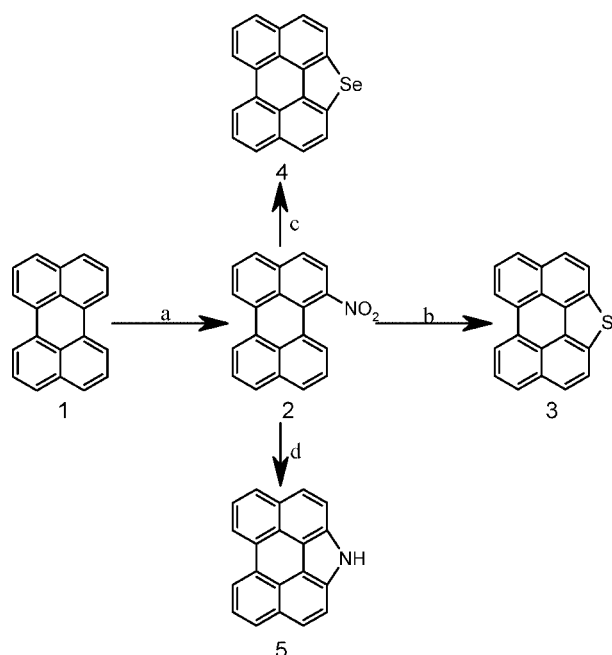
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SCHEME 1. Preparation of Heterocyclic Annulated Perylenes^a

^a Reagents and conditions: (a) fuming $\text{HNO}_3/\text{H}_2\text{O} = 1/1.6$ (v/v), 1,4-dioxane, 60 °C, 25–30 min; (b) sulfur powder, NMP, 180 °C, 5 h; (c) selenium powder, 180 °C, 5 h; (d) triethyl phosphite, reflux, 2 h.

fraction is perylene, while the second and the third fractions are determined to be 1-nitroperylene and 3-nitroperylene, respectively. Notably, the yield of the desired product **2** is improved up to 30% and can be obtained in 10-g scale, which is a prerequisite for the synthesis of a series of heterocyclic annulated perylenes and investigation of their material properties.

Chalcogen-annulated perylenes are prepared in high yield by a surprisingly simple one-pot procedure from the readily available precursor **2**. The key step is carried out in *N*-methylpyrrolidone (NMP) with sulfur or selenium powder at 180 °C in 5 h, following purification by column chromatography to give the desired heteroatom-annulated products in 70% and 65% yield for **3** and **4**, respectively (Scheme 1). Treatment of 1-nitroperylene with triethyl phosphite in reflux temperature in 2 h directly afforded the yellow-brown product **5** in high yield.⁸ The compounds **3–5** exhibit moderate solubility in common solvents, such as dichloromethane and tetrahydrofuran. Their structures are unambiguously characterized by mass spectrometry, NMR spectroscopy, elemental analyses, and X-ray single-crystal analysis.

As an extension of this synthetic methodology, heterocyclic annulated benzoperylene bearing two carboxylate substituents has been synthesized. The introduction of two carboxylate substituents is expected to not only increase the solubility, but also have a further influence on its solid-state packing mode.¹⁰

S-heterocyclic annulated benzoperylene **7** has been prepared following the synthetic route shown in Scheme 2. Diels–Alder reaction of 1-nitroperylene with diethyl maleate, following dehydrogenation by chloranil affords **6** as bright yellow solids (51%). The crucial final step with sulfur powder in NMP is the same as the above-described, and **7** is obtained as light yellow solids in a yield of 52%.

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Crystals of **4**, **5**, and **7** suitable for single-crystal X-ray analysis are obtained by slow evaporation of their dilute solution. The crystal structure of perylo[1,12-*b,c,d*]selenophene **4** shows almost planar molecular conformations, which are regularly stacked along the *b* axis, with similar interplanar distances as PET (3.47 Å).¹¹ In addition, marked $\text{Se}\cdots\text{Se}$ short contacts (3.49 Å) shorter than $\text{S}\cdots\text{S}$ short contacts (3.51 Å) in PET molecules are observed between molecules of neighboring stacks, indicating that **4** has a more compressed packing structure (Figure 1a). This extraordinary double-channel superstructure makes **4** an attractive candidate for device applications.

The introduction of nitrogen into the perylene backbone does not induce a significant change in packing motif. The crystal structure of **5** exhibits a nearly planar molecular conformation with a packing arrangement consisting of edge-to-face dimers (sandwich-herringbone packing, Figure 1b). The dimers adopt an antiparallel manner, with an interplanar distance of 3.48 Å, while the perylene molecules have interplanar distances of 3.47 Å.¹²

Differing from the packing motif of **4** and **5**, the crystal structure of **7** reveals a marked difference in solid-state packing in which the dipole–dipole interaction is dominant over chalcogen–chalcogen interactions and other factors. Recently, a weak dipole–dipole interaction has been utilized for inducing a columnar phase.¹³ In molecules of **7**, the carboxylate–carboxylate moiety would generate a dipole that would be expected to organize the molecules in an antiparallel manner to produce a columnar structure. The perpendicular separation between the discs is 3.34 Å (Figure 1c). This π -stacked columnar structure represents a promising packing motif to explore its charge transfer properties.¹⁴

The photophysical properties of heterocyclic annulated perylenes **3–5** are summarized in Table 1, together with the data of perylene **1** for comparison. The UV–vis absorption spectra showed that they all exhibit well-defined vibronic π – π^* transition bands with the longest maximum at 412.0, 416.5, and 425.0 nm for **3**, **4**, and **5**, respectively. They are all slightly blue-shifted relative to the corresponding parent compound perylene ($\lambda_{\text{max}} = 438.5$ nm) as a reflection of the extended aromatic core along the short molecular axis.¹⁵ Perylene bisimides have proven to have a similar effect in which the enlargement of the π system along the short molecular axis always causes a hypsochromic shift.⁴ In comparison with **3**, the maximum absorption of **4** is bathochromically shifted about 4.5 nm. The heteroatom annulated perylenes presented here possess small Stokes shifts of about 6, 7.5, and 11 nm for **3**, **4**, and **5**, respectively.

Cyclic voltammetry of **3–5** in acetonitrile shows a reversible oxidation wave (for charts, see the Supporting Information). The oxidation peaks ($E^{1/2}$ values) of **3**, **4**, and **5** are found at 1.12, 1.08, and 0.89 V vs Ag/AgCl, respectively. Given the silver

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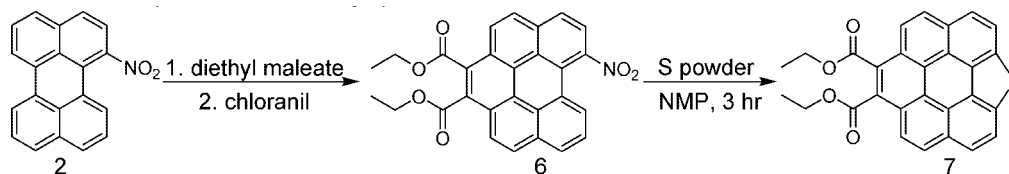
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SCHEME 2. Synthesis of S-Heterocyclic Annulated Benzoperylene 7



wire as a quasireference electrode and the ferrocene/ferrocenium (Fc/Fc⁺) couple as the internal potential standard,¹⁶ HOMO levels estimated by oxidation onsets are -5.42 , -5.39 , and -5.18 eV, respectively.¹⁷

In conclusion, we have developed a practical synthetic procedure for the synthesis of heterocyclic annulated perylenes and benzoperylene from the readily available 1-nitroperylene. Single-crystal X-ray diffraction analysis demonstrates that chalcogen-annulated perylenes have a similar slipped π -stacked packing motif with marked chalcogen–chalcogen interactions

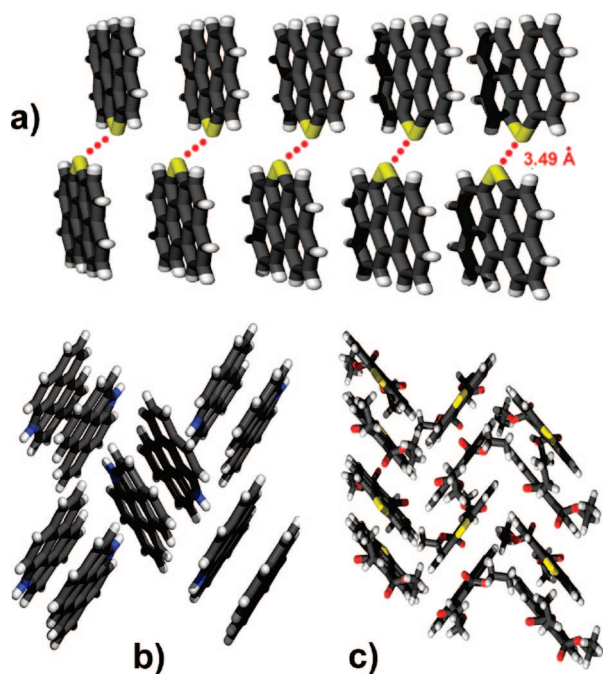


FIGURE 1. Crystal packing view of (a) the double-channel packing mode of **4**, (b) the sandwich-herringbone arrangement of **5**, and (c) the π -stacked columnar structure of **7**.

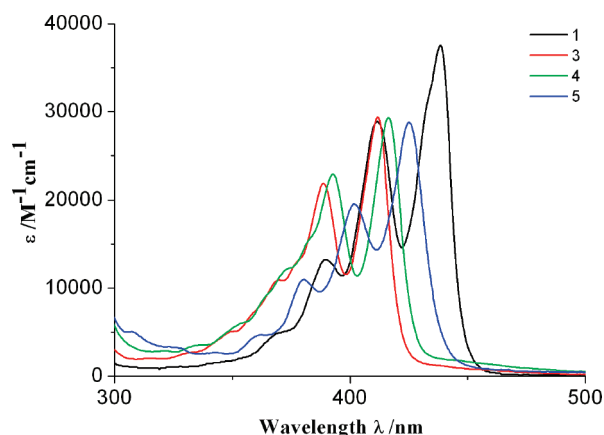


FIGURE 2. UV–vis absorption spectra of **1** (black line), **3** (red line), **4** (green line), and **5** (blue line) in CHCl_3 at room temperature (1.0×10^{-5} M).

TABLE 1. UV–vis and Electrochemical Data of **1** and **3–5** Together with Estimated HOMO Levels

comps	abs _{max} ^a /nm	fluo _{max} ^b /nm	$E^{1/2}_{\text{ox}}$ ^c /V	E_{HOMO} ^d /eV
1	438.5	443	1.05	-5.38
3	412.0	418	1.12	-5.42
4	416.5	424	1.08	-5.39
5	425.0	436	0.89	-5.18

^a Measured in dilute CHCl_3 solution (1.0×10^{-5} M). ^b Excited at the absorption maxima, and measured in dilute CHCl_3 solution (1.0×10^{-6} M). ^c Versus Fc/Fc⁺, performed in $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ (0.1 M), scan rate = 100 mV/s. ^d Estimated from the onset of the oxidation peak, ref 17.

between neighboring columns, which is expected to facilitate effective charge transport. Further studies on the application of these molecules to electronic devices such as OFETs are currently underway.

Experimental Section

1-Nitroperylene (2). To a hot solution of perylene (30.0 g, 118.8 mmol) in 1,4-dioxane (1.2 L) was added a mixture of 24.0 mL of water and 15.0 mL of nitric acid ($d = 1.5$) dropwise. The resulting solution was heated to 60°C with vigorous stirring for 25–30 min, and then cooled and poured into 5 L of water. The solid was collected, washed, dried, and purified by column chromatography on silica gel with petroleum ether as eluent to afford **2** (10.56 g, 30%) as a brick-red crystal. ¹H NMR (DMSO, 400 MHz, ppm) δ 8.52 (dd, 2H), 8.01–7.93 (m, 4H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.76 (dd, 2H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 8.0$ Hz, 1H). ¹³C NMR (DMSO, 100 MHz, ppm) δ 146.0, 134.3, 133.8, 131.3, 130.2, 129.0, 128.9, 128.8, 128.0, 127.8, 127.6, 127.2, 126.8, 125.6, 124.8, 122.8, 122.7, 122.2. EI-MS m/z (%) 297 (M^+ , 100%). Elemental analysis calcd for $\text{C}_{20}\text{H}_{11}\text{NO}_2$: C, 80.80; H, 3.73; N, 4.71. Found: C, 80.55; H, 3.66; N, 4.74. Mp 170 – 171°C .

Perylo[1,12-*b,c,d*]thiophene (3). Sulfur (1.72 g, 53.84 mmol) was dissolved in *N*-methylpyrrolidone (NMP, 80 mL, 70°C), then 1-nitroperylene **2** (1.6 g, 5.36 mmol) was added under argon. The mixture was heated to 180°C with vigorous stirring for 5 h until the starting material could not be detected by TLC. Upon cooling to room temperature, the reaction mixture was poured into 1 L of 2 M HCl, then the precipitate was collected by vacuum filtration, washed with water, dried, and purified by column chromatography on silica gel (petroleum ether/dichloromethane = 5/1) to give **3** (1.06 g, 70%) as a bright yellow needle. ¹H NMR (DMSO, 400 MHz, ppm) δ 8.82 (d, $J = 7.6$ Hz, 2H), 8.35 (d, $J = 8.8$ Hz, 2H), 8.23 (d, $J = 8.0$ Hz, 2H), 8.11 (d, $J = 9.2$ Hz, 2H), 7.92 (t, $J = 7.6$ Hz, 2H). EI-MS m/z (%) 282 (M^+ , 100%). Elemental analysis calcd for $\text{C}_{20}\text{H}_{10}\text{S}$: C, 85.07; H, 3.57. Found: C, 85.02; H, 3.70. Mp $<280^\circ\text{C}$.

Perylo[1,12-*b,c,d*]selenophene (4). This compound was synthesized by a similar procedure as for the synthesis of **3**. Selenium (4.2 g, 53.84 mmol) was allowed to react with **2** (1.6 g, 5.36 mmol) in NMP under argon for 5 h analogously to yield **4** as a yellow-brown needle (1.15 g, 65%). ¹H NMR (DMSO, 400 MHz, ppm) δ 8.76 (d, $J = 7.6$ Hz, 2H), 8.38 (d, $J = 8.4$ Hz, 2H), 8.16 (d, $J = 8.0$ Hz, 2H), 8.02 (d, $J = 8.8$ Hz, 2H), 7.86 (t, $J = 7.6$ Hz, 2H). ¹³C NMR (DMSO, 100 MHz, ppm) δ 136.5, 131.9, 131.0, 130.1, 126.7, 126.5, 125.7, 125.3, 121.1. EI-MS m/z (%) 330 (M^+ , 100%). Elemental analysis calcd for $\text{C}_{20}\text{H}_{10}\text{Se}$: C, 72.96; H, 3.06. Found: C, 72.85; H, 3.02. Mp 270 – 271.5°C .

6H-Phenanthro[1,10,9,8-c,d,e,f,g]carbazole (5). Compound **5** was synthesized according to the literature by J. J. Looker. ¹H NMR (DMSO, 400 MHz, ppm) δ 12.19 (s, NH, 1H), 8.76 (d, *J* = 7.2 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 2H), 7.98 (dd, 4H), 7.82 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (DMSO, 100 MHz, ppm) δ 130.6, 129.7, 128.3, 125.0, 124.5, 124.2, 123.5, 120.8, 116.9, 115.5. EI-MS *m/z* (%) 265 (M⁺, 100%). Elemental analysis calcd for C₂₀H₁₁N: C, 90.54; H, 4.18; N, 5.28. Found: C, 90.23; H, 4.15; N, 5.21. Mp >280 °C.

Diethyl 7-Nitrobenzo[*g,h,i*]perylene-1,2-dicarboxylate (6). 1-Nitroperylene **2** (0.5 g, 1.68 mmol) was added to diethyl maleate (20 mL), the mixture was heated to 180 °C with vigorous stirring for 5 h and cooled to room temperature, then chloranil (1.0 g) was added. The resulting mixture was stirred for another 24 h at 180 °C. Upon cooling to room temperature, the reaction mixture was poured into 150 mL of hexane, and the precipitate was collected by vacuum filtration, washed with hexane, dried, and purified by column chromatography on silica gel (petroleum ether/dichloromethane = 1/1) to give **6** (400 mg, 51%) as bright yellow solids. ¹H NMR (DMSO, 400 MHz, ppm) δ 8.61 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 8.8 Hz, 2H), 8.51–8.46 (m, 4H), 8.43 (d, *J* = 9.2 Hz, 1H), 8.17 (t, *J* = 7.6 Hz, 1H), 4.63 (q, *J* = 7.2 Hz, 4H), 1.46 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (CDCl₃, 150 MHz, ppm) δ 168.1, 168.0, 146.0, 133.0, 131.2, 129.4, 129.2, 128.8, 128.7, 127.9, 127.0, 126.7, 126.5, 125.7, 125.4, 125.3, 125.0, 124.4, 124.3, 124.1, 123.8, 123.7, 122.4, 121.7, 62.49, 62.45, 14.44, 14.40. EI-MS *m/z* (%) 465 (M⁺, 100%). Elemental analysis calcd for C₂₈H₁₉NO₆: C, 72.25; H, 4.11; N, 3.01. Found: C, 72.15; H, 4.16; N, 3.13. Mp 210–211 °C.

Diethyl Benzoperylo[7,8-*b,c,d*]thiophene-1,2-dicarboxylate (7). Sulfur (138 mg, 4.3 mmol) was dissolved in *N*-methylpyrrolidone (NMP, 10 mL, 70 °C), then benzoperylene **6** (200 mg, 0.43 mmol) was added under argon. The mixture was heated to 180 °C with

vigorous stirring for 3 h until the starting material could not be detected by TLC. Upon cooling to room temperature, the reaction mixture was poured into 200 mL of 2 M HCl, then the precipitate was collected by vacuum filtration, washed with water, dried, and purified by column chromatography on silica gel (petroleum ether/dichloromethane = 1/1) to give **7** (100 mg, 52%) as light yellow solids. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 8.61 (d, *J* = 9.2 Hz, 2H), 8.34 (t, *J* = 8.8 Hz, 4H), 8.22 (d, *J* = 8.4 Hz, 2H), 4.78 (q, *J* = 7.2 Hz, 4H), 1.66 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 168.4, 135.5, 128.3, 127.7, 126.7, 126.5, 124.5, 124.2, 123.2, 122.9, 121.2, 120.2, 62.1, 14.4. EI-MS *m/z* (%) 450 (M⁺, 100%). Elemental analysis calcd for C₂₈H₁₈O₄S: C, 74.65; H, 4.03. Found: C, 74.56; H, 4.05. Mp 225–226 °C.

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Supporting Information Available: Further experimental details, NMR spectra for all new compounds, as well as crystallographic data for **4**, **5**, and **7** presented in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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