

S-heterocyclic annelated perylene bisimide: synthesis and co-crystal with pyrene†‡

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An S-heterocyclic annelated perylene bisimide (PBI) has been prepared from readily available tetrachloro-PBI by a one-step palladium-catalyzed reaction; when co-crystallized with pyrene it gives a unique columnar arrangement of 1 : 2 complexes.

Due to exceptional chemical, thermal and photochemical stabilities and high fluorescence quantum yields,¹ perylene-3,4:9,10-tetracarboxylbisimides (PBIs) **1** (Fig. 1) are among the most intensively investigated chromophores in dye chemistry. They also serve as important functional units in a wide range of applications including electron-transfer systems, energy transfer cascades,² liquid crystals,³ photovoltaic devices,⁴ organic field effect transistors,⁵ light emitting diodes⁶ and other organic electronic devices.

Recently, there has been increasing interest in the extension of the aromatic core of PBIs to modulate their structure and properties. Extension along the long molecular axis from PBI **1** to terrylene and quaterrylene bisimides **2**⁷ induces a large bathochromic shift with an absorbance maximum at 780 nm for $n = 3$. However, enlargement of the π system along the short molecular axis as dibenzocoronene diimides **3**⁸ and coronene derivatives³ always causes a hypsochromic shift. Annelation of PBIs with heterocycles in one bay region has also been investigated.⁹

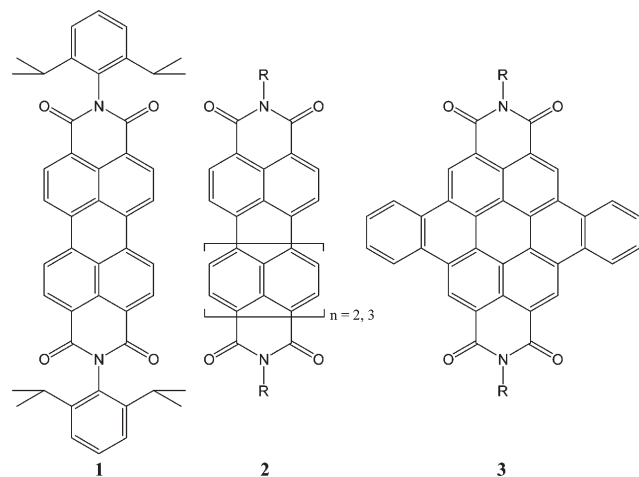


Fig. 1 PBIs and core-extended PBIs.

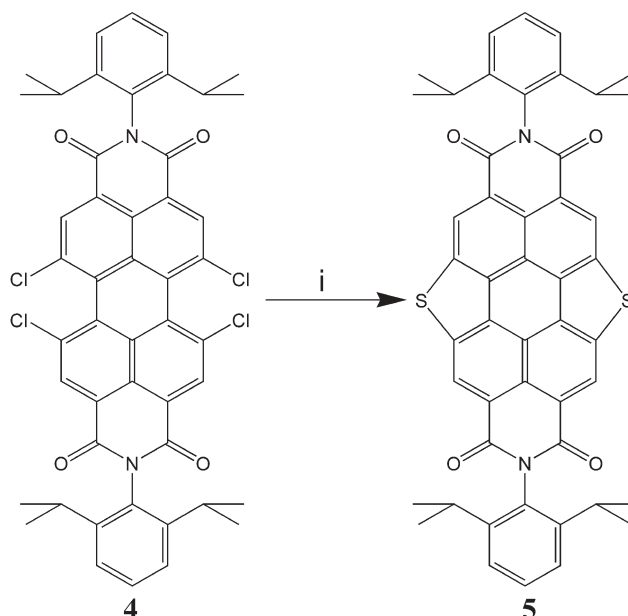
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† Electronic supplementary information (ESI) available: Experimental details and characterization of compounds **4** and **5**; X-ray crystallography. See DOI: 10.1039/b610765f

‡ Dedicated to Professor Dr Klaus Müllen on the occasion of his 60th birthday.

In search of high performance organic semiconductors for molecular devices, fused and extended heteroarenes are recognized as one of the most promising molecular scaffolds.¹⁰ Herein we present our initial studies which promise the establishment of a new synthetic protocol to novel S-heterocyclic annelated perylene bisimides, a new PBI family that is expected to display extraordinary supramolecular self-assembly behaviour. Accordingly, we elucidate the structures of crystalline inclusion complexes of a new S-heterocyclic PBI with benzene, toluene and pyrene, the self-assembly of which is controlled mainly by hydrogen-bonding (for benzene and toluene) and electrostatic interactions (for pyrene).

Central to this work is a double S-heterocyclic annelation of PBI in the two bay regions. PBI **5** is obtained in high yield by a surprisingly simple procedure from the readily available precursor. *N,N'*-diisopropylphenyl-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxyl bisimide **4**¹¹ is synthesized by heating 2,6-diisopropylaniline and 1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisanhydride in propionic acid. The subsequent key step, a palladium-catalyzed reaction of **4** with $\text{Bu}_3\text{SnSSnBu}_3$ in toluene under N_2 , affords **5** in 72% yield (Scheme 1). The aromatic core of tetrachloro PBIs is highly twisted because of the electrostatic repulsion and steric encumbrance of the chlorine substituents in the bay regions.¹² Surprisingly, the



Scheme 1 Reagents, conditions and yield: (i) $\text{Pd}(\text{PPh}_3)_4$, $\text{Bu}_3\text{SnSSnBu}_3$, toluene, reflux, 10 h, 72%.

extremely twisted molecule **4** is easily converted to the planar molecule **5** by the one-step Stille type reaction which reduces the strain of the tetrachloro precursor.

The conventional methodology to prepare S-heterocyclic PBIs⁹ relies on 1-nitroperylenebisimide precursors which are prepared by the regioselective mononitration of **1** utilizing N_2O_4 in CH_2Cl_2 . This method suffers from the harsh conditions needed for nitration, difficulty in separation, and low yield of both the nitration intermediate and subsequent sulfur annelated product (the latter step is carried out in DMF or NMP). 1,7-Dinitroperylenebisimides are obtained in poor yield by nitration of perylene tetracarboxylic acid bisanhydride using HNO_3 ,¹³ and cyclization of the 1,7-dinitroperylenebisimides at high temperatures affords mixtures without the desired product. The new palladium-catalyzed double S-heterocyclic annelation of PBI reported here is facile and highly efficient. Kosugi¹⁴ reported this Stille type coupling of bis(tributylstannyl) sulfide with aryl bromide and we have now extended this chemistry to integrate intramolecular sulfur bridges into the two bay regions of PBIs.

Aided by the presence of solubilizing 2,6-diisopropylphenyl groups, PBI **5** is soluble in common organic solvents such as dichloromethane and toluene. Room-temperature UV/Vis absorption and fluorescence spectra of **5** in CHCl_3 are shown in Fig. 2. In comparison with **1**, the UV/Vis spectrum of compound **5** is hypsochromically shifted by 47 nm with a maximum at 480 nm, reflecting the larger π - π^* transition band gap which accompanies the enlargement of the aromatic system along the short molecular axis. The extinction coefficient of **5** at its maximum absorption (480 nm, $\epsilon = 82,000 \text{ M}^{-1} \text{ cm}^{-1}$) is lower than that of **1**.¹⁵ The emission spectrum of **5** in CHCl_3 exhibits a Stokes shift of 8.2 nm ($\lambda_{\text{max}} = 488.2 \text{ nm}$, $\Phi_{\text{f}} = 0.15$, see supporting information).

To determine the structure of **5**, crystals suitable for a single-crystal X-ray structure analysis are obtained by slow evaporation of a solution of **5** in benzene at room temperature. The crystal structure reveals that **5** has crystallographically imposed inversion symmetry, and the perylene core is almost planar; the carbon and sulfur atoms are coplanar to within 0.092 Å (Fig. 3). Owing to the steric bulk of the isopropyl groups which inhibit rotation about the C13–N1 bond, a dihedral angle of 94.7° between the perylene plane and the diisopropylphenyl plane is observed. The perylene forms a columnar structure with benzene molecules filling the

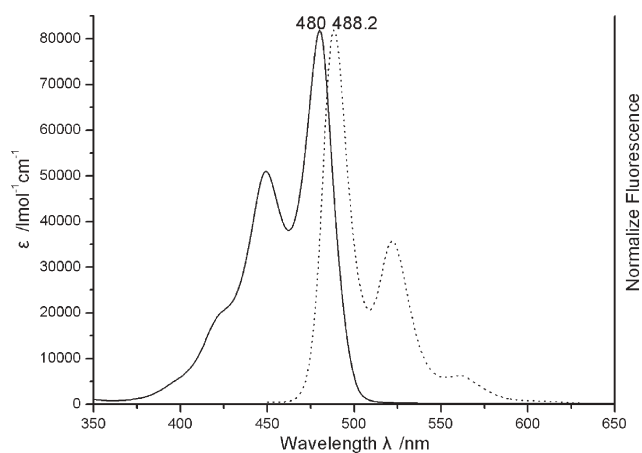


Fig. 2 UV/Vis absorption (10^{-5} M , solid line) and normalized fluorescence spectra (440 nm excit., dotted line) of **5** in CHCl_3 .

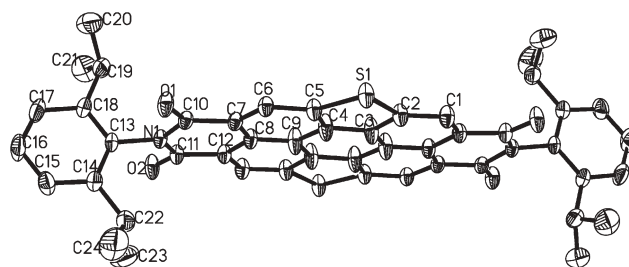


Fig. 3 ORTEP drawing of the structure of **5** with 30% probability ellipsoids.

voids without strong π - π interactions (perylene–benzene interplanar distance 3.75 Å). Interestingly, the crystal structure contains unique ribbons of **5**. The inversion-related pairs of bisimide **5** molecules in the crystal of **5**·Ph are linked by weak C6–H6···O1 [at $(1 - x, 1 - y, z)$] hydrogen bonds with $\text{H} \cdots \text{O}$ 2.34 Å and $\text{C} - \text{H} \cdots \text{O}$ 140° (Fig. 4). To the best of our knowledge, such hydrogen bonding ribbons have not been reported for normal PBIs.¹⁶ Their presence in this case is possibly due to the subtle influence of hetero atoms on the molecular electronic structure.

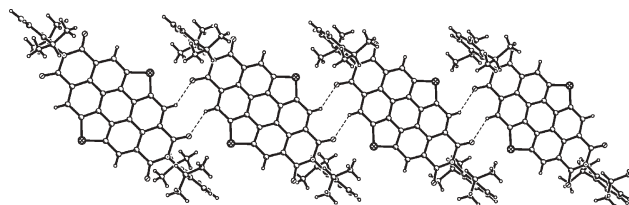


Fig. 4 Weak hydrogen bonding interactions in the crystal structure of **5**·Ph.

It should be noted that the tendency of **5** to build up hydrogen bonding ribbons is independent of the solvent used in the crystallization. **5**·PhMe is obtained when toluene instead of benzene is utilized as the solvent; it possesses the same stoichiometry (1 : 1) as **5**·Ph, and shows identical lattice parameters. The observation that similar structures are formed from different solvents suggests that hydrogen bonding ribbons are probably an intrinsic property of **5**.

A further step towards the control of supramolecular arrangements of **5** in single crystals concerns the introduction of larger size guest molecules. Pyrene was chosen as an inclusion guest as favourable face-to-face stacking between electron-rich guest and electron-poor host molecules of almost similar shape and size was anticipated.

Red crystals were obtained by slow evaporation of a solution of **5** and pyrene (1 : 1) in CH_2Cl_2 . Within the crystals of **5**·(pyrene)₂·(CH₂Cl₂)₃, one molecule **5** is sandwiched by two pyrene molecules (interplanar distance 3.55 Å), and the adjacent sandwiches are offset slightly to form unique columnar structures through weak π - π interactions of the pyrenes (interplanar distance 3.67 Å, close to the distance between dimers found in the crystal structure of pyrene) (Fig. 5). Similarly to **5**·Ph and **5**·PhMe, hydrogen bonding ribbons are also generated in **5**·(pyrene)₂·(CH₂Cl₂)₃. The bisimide **5** molecules in this structure are linked by weak C1–H1A···O4 [at $(1 - x, 1 - y, z)$] hydrogen bonds with $\text{H} \cdots \text{O}$ 2.45 Å and $\text{C} - \text{H} \cdots \text{O}$ 124°. In addition, a well-defined C83–H83B···O1 [at $(1 - x, 1 - y, z)$] hydrogen bond with

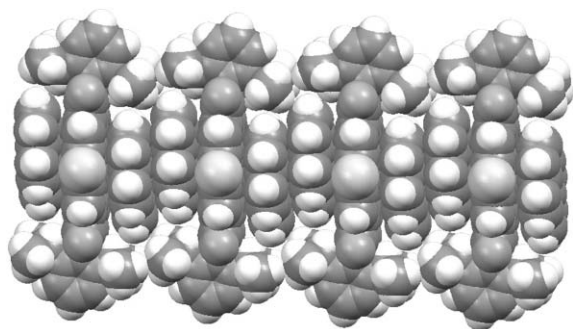


Fig. 5 Space-filling diagram of **5**·(pyrene)₂·(CH₂Cl)₃.

H···O 2.36 Å and C–H···O 164° is formed between one of the dichloromethane molecules and the bisimide **5** molecule. §

In summary, we report the facile synthesis of a novel PBI that is S-heterocyclic annelated in two bay regions. The palladium-catalyzed reaction of bis(tributylstannyl) sulfide with aryl chloride easily converts an extremely twisted precursor molecule to a planar product. This powerful synthetic methodology is expected to offer a versatile, high-yielding route to a variety of S-heterocyclic annelated polycyclic aromatic hydrocarbons. The supramolecular arrangement in the single crystals is tunable by the inclusion of different guest molecules. The S-heterocyclic annelated PBI **5** is expected to serve as a new building block in a wide range of applications such as electron transfer systems, molecular sensors and liquid crystalline materials.

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Notes and references

§ Crystal data of **5-Ph**. The measurements were made on a Bruker SMART CCD area detector with graphite monochromated Mo-K α radiation (λ 0.71073 Å) at 294 K. All calculations were performed using SHELXL-97. C₆₆H₅₆N₂O₄S₂, $M = 1005.25$, orange-red, crystal dimensions 0.22 × 0.14 × 0.12 mm, triclinic, space group $P\bar{1}$, $a = 8.317(3)$, $b = 11.425(4)$, $c = 15.518(5)$ Å, $\alpha = 106.441(5)$, $\beta = 104.475(6)$, $\gamma = 94.316(6)^\circ$, $V = 1352.3(8)$ Å³, $Z = 1$, $D_c = 1.234$ g cm⁻³, $\mu = 0.150$ mm⁻¹, θ range 1.43–25.00°. Of the 6745 reflections that were collected, 4727 were unique ($R_{\text{int}} = 0.0378$), GOF = 1.007, 363 parameters, $R_1 = 0.0557$, $wR_2 = 0.1229$ for reflections with $I > 2\sigma(I)$. Largest diff. peak and hole, 0.232 and -0.226 e/Å³.

Crystal data of **5-PhMe**. The measurements were made on a Bruker SMART CCD area detector with graphite monochromated Mo-K α radiation (λ 0.71073 Å) at 294 K. All calculations were performed using SHELXL-97. C_{34.5}H₃₁NO₂S, $M = 523.66$, orange-red, crystal dimensions 0.40 × 0.34 × 0.30 mm, triclinic, space group $P\bar{1}$, $a = 8.264(2)$, $b = 11.438(3)$, $c = 15.204(4)$ Å, $\alpha = 101.119(4)$, $\beta = 100.521(4)$, $\gamma = 91.278(4)^\circ$, $V = 1383.9(7)$ Å³, $Z = 2$, $D_c = 1.257$ g cm⁻³, $\mu = 0.149$ mm⁻¹, θ range 1.39–26.39°. Of the 7866 reflections that were collected, 5578 were unique

($R_{\text{int}} = 0.0135$), GOF = 1.030, 352 parameters, $R_1 = 0.0499$, $wR_2 = 0.1396$ for reflections with $I > 2\sigma(I)$. Largest diff. peak and hole, 0.500 and -0.371 e/Å³.

Crystal data of **5**·(pyrene)₂·(CH₂Cl)₃. The measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-K α radiation (λ 0.71070 Å) at 113 K. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97. C₈₃H₆₄N₂O₄S₂Cl₆, $M = 1430.27$, red-black, crystal dimensions 0.34 × 0.32 × 0.22 mm, triclinic, space group $P\bar{1}$, $a = 10.435(2)$, $b = 17.055(3)$, $c = 20.962(4)$ Å, $\alpha = 108.740(3)$, $\beta = 101.183(3)$, $\gamma = 94.073(2)^\circ$, $V = 3430.1(12)$ Å³, $Z = 2$, $D_c = 1.385$ g cm⁻³, $\mu = 0.367$ mm⁻¹, θ range 1.27–27.86°. Of the 30321 reflections that were collected, 16044 were unique ($R_{\text{int}} = 0.0266$), GOF = 1.065, 902 parameters, $R_1 = 0.0552$, $wR_2 = 0.1351$ for reflections with $I > 2\sigma(I)$. Largest diff. peak and hole, 0.449 and -0.418 e/Å³.

CCDC 612066–612068. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610765f

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