

Cite this: *Chem. Commun.*, 2011, **47**, 3616–3618

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COMMUNICATION

Thienyl directed polyaromatic C–C bond fusions: S-doped hexabenzocoronenes†

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Received 28th November 2010, Accepted 20th January 2011

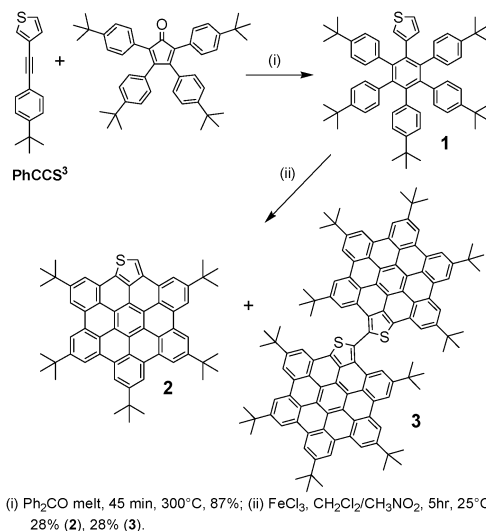
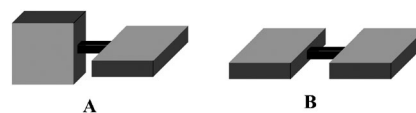
DOI: 10.1039/c0cc05231k

With a view to combining the desirable electronic and photochemical properties of hexabenzocoronene (HBC) and the C–C bond forming capabilities of thiophenes, 1-(3-thienyl)-2,3,4,5,6-penta(4-*tert*-butyl-phenyl)benzene (**1**) was oxidised using FeCl₃. The resulting products, superaromatic thiophene (**2**) and its 5,5'-dimer (**3**), are S-HBC systems and provide a new pair of spectral comparators.

The enhanced reactivity of thiophenes and their polymer forming capabilities mean that there are distinct and expanded potential applications that arise upon the incorporation of thiophene subunits into carbon frameworks.¹ Herein is described the careful design of a polyphenylene precursor with a strategically positioned 3-thienyl moiety and the formation of a fully cyclised thienyl-hexabenzocoronene along with its 5,5' dimer. Although some sulfur containing polycyclic aromatic hydrocarbons have been previously reported,² these systems are the first sulfur containing hexabenzocoronenes. The full photochemical and electrochemical characterisation of these new molecules is discussed.

Polyphenylenes are readily formed from the [2 + 4] Diels–Alder reactions of appropriately substituted alkynes and cyclopentadienones.³ Monosubstitution on the polyphenylene requires the use of an asymmetric alkyne such as (4-*tert*-butyl-phenyl)(3-thienyl)acetylene (PhCCS).⁴ The reaction of this with *tert*-butyl substituted tetraphenyl cyclopentadienone results in the formation of monothiophene **1** which undergoes oxidative cyclodehydrogenation in the presence of FeCl₃ (Scheme 1).

Looking at the products formed, the rationale behind the choice of a 3-thiophene becomes self-evident; **1** provides two carbon sites (2- and 4-) for subsequent C–C bond formation. On complete cyclisation only one isomer of the product can be formed, irrespective of the twist of the thiophene about its point of attachment to the polyphenylene fragment (Scheme 2A). Cyclodehydrogenation produces both thienyl-hexabenzocoronene **2** and its dimer **3** (each in 28% yield). The reactivity of the 2-position in thiophenes is well-established, however the

Scheme 1 The synthetic route *via* **1** of fully cyclised S-HBCs **2** and **3**.Scheme 2 Twisted (A) and coplanar (B) conformations proposed for the dimeric system **3**.

formation of the 5,5' dimer **3** appears to be possible only after the precursor polyphenylene has been oxidised and aromatised. This implies that in **1** the intramolecular cyclodehydrogenations between both the 2- and 4-positions of the thiophene and the polyphenylene core are more facile than the intermolecular dimerisation at the 5-position.

The ¹H NMR spectrum of **2** shows five aliphatic signals for the five sets of *tert*-butyl groups between δ 1.89 and 1.72 ppm. These integrate for nine protons each leaving eleven aromatic methine signals for the hydrogens on the periphery of the compound (Fig. 1). Ten of these (2–11, Fig. 1) resonate between δ 9.31 and 8.94 ppm but one appears more upfield at δ 8.22 ppm (1, Fig. 1). Through correlation spectroscopy this has been assigned as the phenyl proton closest to the sulfur atom. The rest were fully assigned using 2D correlation and nOe experiments.

For **3**, aliphatic singlets for the *tert*-butyl groups are observed between δ 1.90 and 1.79 ppm, each integrating for

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† Electronic supplementary information (ESI) available: Experimental data along with tables of photochemical data are available. See DOI: 10.1039/c0cc05231k

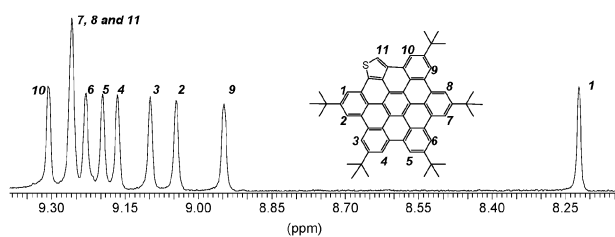


Fig. 1 The ^1H NMR spectrum of **2** (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$).

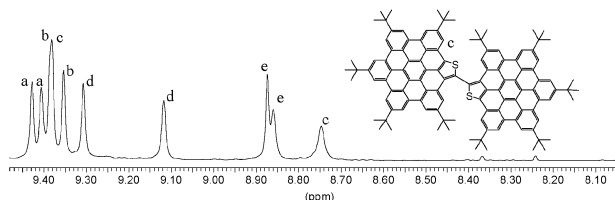


Fig. 2 The ^1H NMR spectrum of **3** (CDCl_3 , 600 MHz, 25 $^\circ\text{C}$).

eighteen protons. A total of ten aromatic signals, each integrating for two protons, are observed between δ 9.46 and 8.70 ppm (Fig. 2). These signals appear broader than those of **2**, due to increased aggregation effects in this larger graphene. Although the ^1H NMR spectrum of **3** could not be assigned fully, five pairs of aromatic signals (a–e) for the two protons on each aromatic ring have been identified using TOCSY spectroscopy. The signal at δ 8.75 ppm has been assigned to position c due to its proximity to the sulfur (Fig. 2).

In solution cyclic voltammetry experiments monothiophene hexabenzocoronene **2** (Fig. 3, solid line) reveals three fully reversible oxidations leading to cation formation with $E_{1/2} = +0.38$, $+0.56$ and $+1.01$ V vs. Fc/Fc^+ which closely match those observed in its dimeric twin **3** (Fig. 3, dashed line) ($E_{1/2} = +0.38$, $+0.59$ and $+1.04$ V).

These compare to just two oxidations at $E_{1/2} = +0.45$ and $+0.88$ V in all-carbon hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene, reported vs. SCE and converted to Fc/Fc^+ (conversion SCE to Fc/Fc^+ is -0.54 V in chloroform).⁴ The first oxidation on both **2** and **3** occurs at the same potential ($+0.38$ V) indicating that this is positioned on the aromatic phenyl-based platforms and as such is unaffected upon dimerisation. This first oxidation is at a slightly lower potential than that seen for the all carbon analogue ($+0.45$ V) as a result of the increased electron density due to the presence of sulfur in the thiophene graphenes. The second and third, fully reversible oxidation processes (one of which is missing from the all-carbon hexabenzocoronene) are more influenced by the

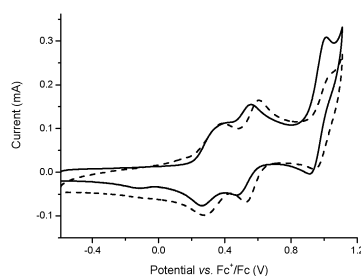


Fig. 3 Cyclic voltammograms of **2** (solid line) and its dimer **3** (dashed line) vs. Fc/Fc^+ (chloroform, 10^{-2} M).

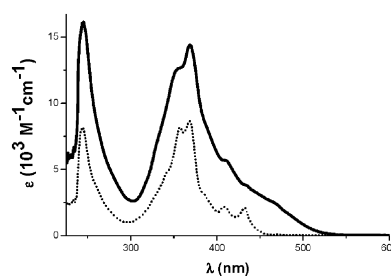


Fig. 4 UV/Vis absorption spectra (chloroform, 10^{-5} M) of **2** (dotted line) and **3** (solid line).

fused thiophene unit. These peaks are affected upon dimerisation—indicative of the additional intermolecular 5,5'/C–C bond fusion between the two thiophene units in **3**, shifting the oxidation peaks to higher potential in comparison with **2**.

To further elucidate the electronic character of the compounds photophysical investigations were carried out (Tables S1–S3, ESI †). S-containing graphene monomer **2** exhibits two intense structured absorptions (λ_{max} 358 and 369 nm) (Fig. 4, dotted line) similar to those of symmetric, alkyl substituted hexabenzocoronene (HBC).⁵ These correspond to the β and p absorption bands generally observed for HBCs.⁶ In addition longer wavelength absorptions with λ_{max} 408 and 432 nm are seen; these $\pi \rightarrow \pi^*$ transitions are usually symmetry forbidden in all carbon HBC but appear in **2** due to its lower symmetry.

For the dimeric compound **3**, the absorption (Fig. 4, solid line) is slightly more intense than **2** but the spectrum exhibits a similar profile, with the addition of a new absorption shoulder that tails out to 550 nm. The appearance of this tail is independent of concentration, precluding the formation of any aggregated ground state species (concentration range 10^{-3} – 10^{-5} M). The new low-energy absorption could be due to the increased conjugation that would arise if the two graphene subunits in **3** become coplanar. If this is the case, then it would reflect the proportion of coplanar molecules in solution (Scheme 2B).⁷

Despite the presence of sulfur heteroatoms, the emission spectrum of **2** closely matches that of alkyl substituted HBCs.⁷ It is very structured (λ_{max} 475 and 505 nm are the most intense peaks, chloroform, 10^{-3} M) and remains unchanged in shape and position when different excitation wavelengths and concentrations (range 10^{-3} – 10^{-5} M) are employed (Fig. 5).⁸ This is similar to other HBC systems in which the overall complexity of the fluorescence spectrum suggests that there are several singlet excited states that are close in energetic proximity, each having its own vibronic progression and contributing to the fluorescence.

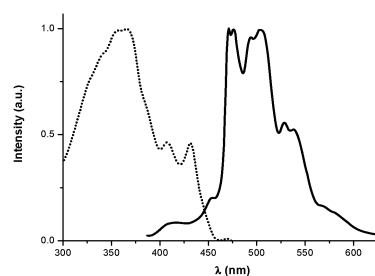


Fig. 5 Normalised excitation (λ_{exc} 540 nm) and emission (λ_{em} 367 nm) spectra of **2** (chloroform, 10^{-3} M) at 298 K.

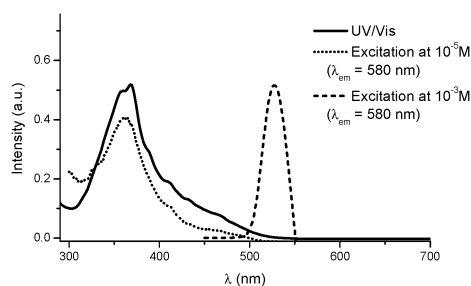


Fig. 6 UV/Vis absorption (10^{-3} M) and excitation spectra of **3** at high (10^{-3} M) and low (10^{-5} M) concentrations (chloroform 298 K).

The emission is biexponential. This is unusual but has been observed for HBC derived fluorescence in a family of platinum–HBC acetylides.⁹ The lifetimes vary depending on the excitation and emission wavelength (Table S3, ESI[†]). The excited state lifetime for the emission at 476 and 504 nm is short lived (both components in the ns range); while at 580 nm, the emission is composed of both a short fluorescence-derived (12 ns (32%)) and a significantly longer-lived (374 ns (68%)) component. This suggests the onset of a longer lived emissive excited state at longer wavelengths which we tentatively assign as a weak triplet emission, an assignment corroborated by the appearance of a new broad emission band at 77 K between 610 and 700 nm (λ_{max} 634 nm) (Fig. S1, ESI[†]).

The dimeric system **3** exhibits dual luminescence that varies with concentration. In dilute solution (chloroform, 10^{-5} M) (Fig. 6), the excitation spectra correspond to the absorption spectra but with the absence of the low-energy absorption shoulder for which a planar conformation was responsible (Scheme 2B).¹⁰ At higher concentration (chloroform, 10^{-3} M) the excitation spectra exhibit a new low-energy band between λ 500 and 550 nm (λ_{max} 527 nm) at similar λ to the tail of the lowest energy absorption band in the UV/Vis spectrum. This suggests that a planar conformation (Scheme 2B) is observed in concentrated solution.

At low concentration the emission of **3** (Fig. 7) shows structured high-energy bands similar in position to the emission observed for the monomer **2** between λ 450 and 550 nm (λ_{max} 494 nm) and a second broader lower-energy emission between λ 550 and 675 nm (λ_{max} 565 nm). In more concentrated solutions (chloroform, 10^{-3} M) this broad low-energy emission (Fig. 7) dominates (λ_{max} 580 nm), suggesting that a planar conformation is observed in concentrated solutions that gives rise to excited state aggregates and the formation of excimeric species.¹¹

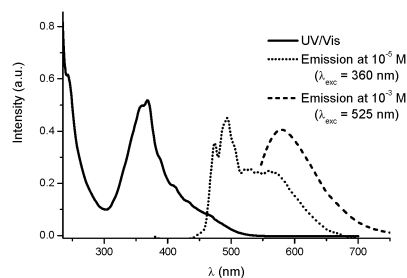


Fig. 7 UV/Vis absorption (10^{-3} M) and emission spectra of **3** at high (10^{-3} M) and low (10^{-5} M) concentrations (chloroform) at 298 K.

Dual luminescence can be dependent on the polarity of the solvent or related to temperature dependent excimeric processes.¹² In our case, an excimeric species forms only for the dimeric system **3** and is not observed for the monomeric compound **2**. Although dual luminescence related to the twisting of monomeric aromatic subunits has been described previously in the literature,^{11,12} this is the first time in which the solubility allows exploration of the conformational consequences of attaching two HBC platforms *via* a single carbon–carbon bond. The low luminescence quantum yields of **2** and **3** (0.024 and 0.011, respectively, in oxygen) are consistent with other fused polyaromatic systems.¹³ The quantum yields increase in an argon atmosphere, as oxygen quenching of triplet excited states is prevented (Table S2, ESI[†]).

The reactivity of the thienyl-polyphenylene precursor **1** has led to the preparation of two sulfur-containing hexabenzocoronene derivatives. The new thienyl-hexabenzocoronene **2** and its dimer **3** resemble all-carbon analogues with photochemical and electrochemical properties similar to those reported in the literature for hexa alkyl-substituted coronenes. However dimeric species **3** also has optical properties which vary with concentration as a result of the orientation of the two HBC platforms about the newly formed dimer bond. This luminescence variation is new to HBC-based systems.

Notes and references

- L. N. Lucas, J. J. D de Jong, J. H. van Esch, R. M. Kellogg and B. L. Feringa, *Eur. J. Org. Chem.*, 2003, 155–166; J. H. Hou, Z. Tan, Y. J. He, C. H. Yang and Y. F. Li, *Macromolecules*, 2006, **39**, 4657–4662; R. D. McCullough, *Adv. Mater.*, 1998, **10**, 93–116; J. Roncali, *Chem. Rev.*, 1997, **97**, 173–205.
- X. L. Feng, J. S. Wu, M. Ai, W. Pisula, L. J. Zhi, J. P. Rabe and K. Mullen, *Angew. Chem., Int. Ed.*, 2007, **46**, 3033–3036.
- D. J. Gregg, E. Bothe, P. Höfer, P. Passaniti and S. M. Draper, *Inorg. Chem.*, 2005, **44**, 5654–5660; D. J. Gregg, C. M. A. Ollagnier, C. M. Fitchett and S. M. Draper, *Chem.–Eur. J.*, 2006, **12**, 3043–3052; R. D. J. Roberts, D. J. Gregg, C. M. Fitchett and S. M. Draper, *Organometallics*, 2010, **29**, 6541–6547.
- P. T. Herwig, V. Enkelmann, O. Schmelz and K. Mullen, *Chem.–Eur. J.*, 2000, **6**, 1834–1839.
- W. Hendel, Z. H. Khan and W. Schmidt, *Tetrahedron*, 1986, **42**, 1127–1134.
- E. Clar, *The Aromatic Sextet*, John Wiley and Sons, 1972.
- J. S. Wu, M. D. Watson, L. Zhang, Z. H. Wang and K. Mullen, *J. Am. Chem. Soc.*, 2004, **126**, 177–186.
- S. Ito, P. T. Herwig, T. Bohme, J. P. Rabe, W. Rettig and K. Mullen, *J. Am. Chem. Soc.*, 2000, **122**, 7698–7706; J. S. Wu, A. Fechtenkotter, J. Gauss, M. D. Watson, M. Kastler, C. Fechtenkotter, M. Wagner and K. Mullen, *J. Am. Chem. Soc.*, 2004, **126**, 11311–11321; M. Biasutti, J. Rommens, A. Vaes, S. DeFeyer, F. de Schryver, P. Herwig and K. Mullen, *Bull. Soc. Chim. Belg.*, 1997, **106**, 659–664.
- K. Y. Kim, S. Liu, M. E. Köse and K. S. Schanze, *Inorg. Chem.*, 2006, **45**, 2509–2519.
- X. N. Zhang, M. Kohler and A. J. Matzger, *Macromolecules*, 2004, **37**, 6306–6315; N. DiCesare, M. Belletete, A. Donat-Bouillud, M. Leclerc and G. Durocher, *Macromolecules*, 1998, **31**, 6289–6296; N. DiCesare, M. Belletete, F. Raymond, M. Leclerc and G. Durocher, *J. Phys. Chem. A*, 1997, **101**, 776–782; S. A. Lee, S. Hotta and F. Nakanishi, *J. Phys. Chem. A*, 2000, **104**, 1827–1833.
- Q. Yan, Y. Zhou, B. B. Ni, Y. G. Ma, J. Wang, J. Pei and Y. Cao, *J. Org. Chem.*, 2008, **73**, 5328–5339; N. DiCesare, M. Belletete, E. R. Garcia, M. Leclerc and G. Durocher, *J. Phys. Chem. A*, 1999, **103**, 3864–3875.
- Z. R. Grabowski, K. Rotkiewicz and W. Rettig, *Chem. Rev.*, 2003, **103**, 3899–4032.
- Y. S. Liu, P. Mayo and W. R. Ware, *J. Phys. Chem.*, 1993, **97**, 5595–6001.