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Heterosuperbenzenes: A New Family of Nitrogen-Functionalized, Graphitic Molecules

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There has been a strategic shift in research and development toward so-called “soft”’ materials (e.g., polymer LED) as part of an ongoing development of molecular materials within the electronics industry. The electrical and optoelectronic properties of such molecules rely heavily on extended π-conjugation. Müllen et al. have developed a route to a series of predefined all-carbon superbenzenes via the cyclodehydrogenation of polyphenylene precursors.[1]

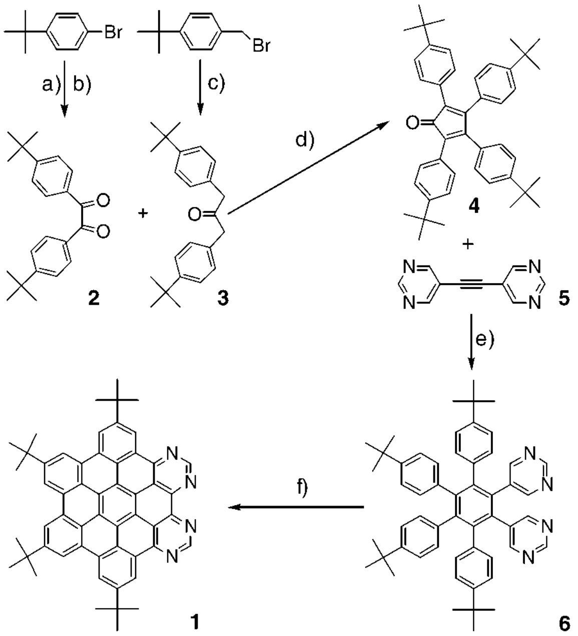
Herein we present our initial result, which promises the establishment of a host of heterosuperbenzenes with intrinsic carbon−nitrogen frameworks. The members of this new heterosuperbenzene family are molecular models of active graphitic nanostructures with electroactive imines on the periphery. The integration of molecular functions within the C framework renders these materials sensitive toward external triggers and highly processible. In the context of LED applications, the systematic replacement of carbon atoms with electronegative nitrogen atoms enhances the carrier transport of the system. There is a paucity of processable forms of electron-acceptor materials with desired thermal stability. Our *N*-heterosuperbenzenes offer a significant advance in this regard. Compound **1** was prepared as the first member of this new heterosuperbenzene family.

Central to the work is the introduction of heteroatoms into a polyphenylene precursor. Carbon polyphenylene precursors are usually generated by the cyclotrimerization[2] of phenyl-substituted ethynes, or the Diels−Alder [2+4] cycloaddition of the same with tetraphenylcyclopentadienone.[3] We chose to modify the established synthetic protocol of the latter by incorporating pyrimidine substituents into the alkyne.

We achieved **6**, the precursor of compound **1**, synthetically in a stepwise manner by the Diels−Alder [2+4] cycloaddition of di(pyrimdin-3,5-yl)ethyne (**5**) to 2,3,4,5-tetra(4-*tert*-butylphenyl)cyclopentadien-1-one (**4**), (Scheme 1). The careful choice of starting materials and the established stereochemistry of [2+4] cycloaddition reactions meant that the system was chemioselective ensuring the ortho arrangement of the pyrimidine subunits on the generated benzene core of **6**. Subsequent oxidative cyclodehydrogenation of **6** generated the *N*-functionalized heterosuperbenzene **1**.

An alternative synthetic method is to incorporate pyrimidine substituents into the cyclopentadienone. This increases the number of options available for the positioning and number of pyrimidine subunits and opens up the possibility of first, generating structural isomers of **1** and second, systematically increasing the degree of *N*-doping in the resultant heterosuperbenzene.

Scheme 1. The Systematic Synthesis of **1**[a]



[a] Conditions: (a) BuLi, THF, −78 °C; (b) DMPD, THF, −78 °C, 70%;[4] (c) $Ca(OH)_2$, $Bu_4N^+HSO_4^-$, $Fe(CO)_5$, 1:1 CH_2Cl_2/H_2O, room temperature, 5 h; 65%;[5] (d) KOH, EtOH, 3 h, 65%;[6] (e) Ph_2O, melt, 1 h, 81%; (f) $AlCl_3$, $CuCl_2$, CS_2, 72 h, room temperature, 49%.

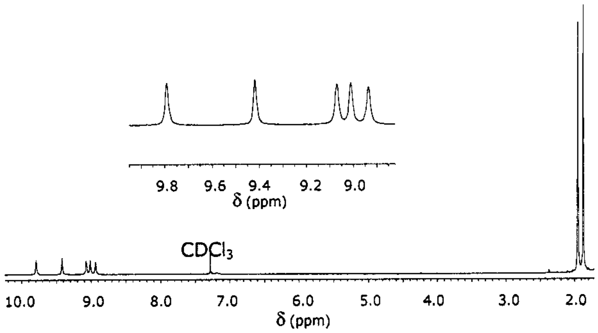


Figure 1. The ^1H NMR spectrum of **1** (400 MHz, $CDCl_3$, 25 °C, TMS).

1 was purified by chromatography and extracted in $CHCl_3$. Coronene and its derivatives are insoluble in this solvent, ensuring that such graphene materials were not present in the sample. Accurate mass spectral data, ^{13}C and ^1H NMR spectra, heteronuclear CH COSY (HMQC, HMBC), and 135° DEPT NMR spectra in $CDCl_3$ were obtained of **1**. All data were cooperative and no signals other than those assigned to **1** were observed. The proposed structure of **1** is simplified by the presence of a C_2 plane of symmetry running through the molecule. The methyl groups of each *tert*-butyl group rotate, rendering them equivalent on the NMR timescale. ^1H NMR spectra of **1** show two sets of aliphatic signals integrating for 18 hydrogen atoms each, corresponding to the two pairs of equivalent *tert*-butyl protons, and five aromatic signals, each integrating for two hydrogen atoms (Figure 1). The aromatic

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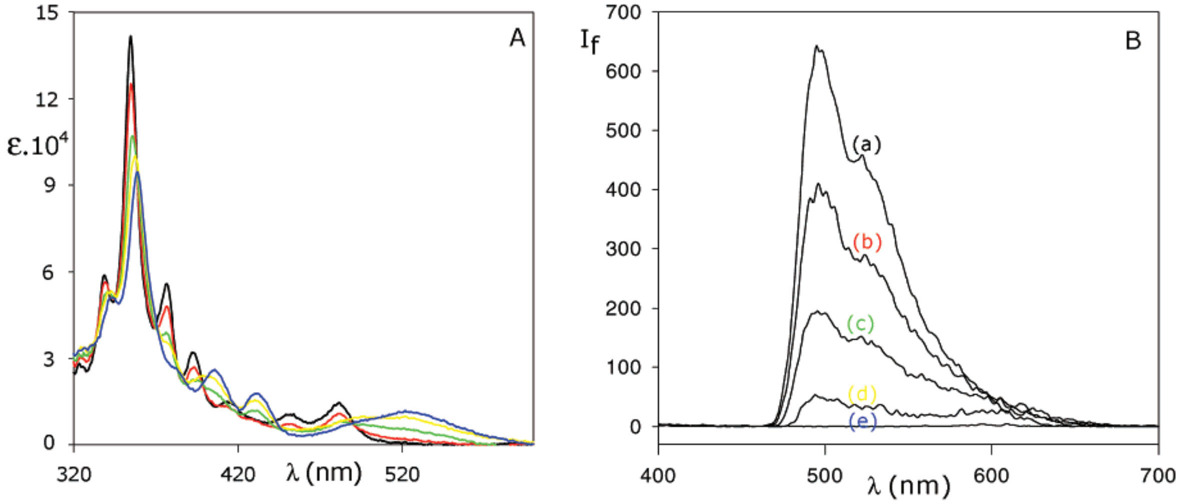

Figure 2. The UV/vis spectrum (A) and fluorescence spectrum (B) of **1** (toluene, 0.67 μM, 20 °C) on addition of trifluoroacetic acid (0.1 M): (a) black line, 0 mol, (b) red line, 0.5 μmol, (c) green line, 1.0 μmol, (d) yellow line, 3.0 μmol, and (e) blue line, 10.0 μmol.

signal at highest field is assigned to the two hydrogen atoms located between the imine nitrogen atoms.

1 formally combines superbenzene and bipyrimidine and experimentally exhibits desirable properties of both. The enhanced π-electron mobility of **1** is evident from the polar nature of the molecule ,which is supporting structurally opposing electronegative nitrogen atoms and weakly donating *tert*-butyl groups. **1** is soluble in a variety of organic solvents (polar and nonpolar). A UV−visible spectrum recorded in toluene (unsubstituted graphenes are insoluble in this solvent) shows the characteristic bands of hexa-*peri*-benzocoronene (in dichlorobenzene) together with two weak bands at 450 and 490 nm (Figure 2A(a)). There is also a characteristic band at 372 nm that is not found in the all-benzene analogue.[7] A reduction in ϵ_{max} (355 nm, ϵ_{max} 140 000) compared to the hexa-*peri*-benzocoronene (ϵ_{max} 177 000) is observed in agreement with the depletion of π-electron density as a result of the imine nitrogen atoms, thus rendering the molecule overall electron-acceptor characteristics.

It has been reported that the linear extension of π-conjugation on phenanthroline gives a vast increase in the fluorescence of the resulting material.[8] We observe a similar dramatic effect but the extension to our π-system is supramolecular rather than linear. **1** exhibits strong green emission under both visible and UV light. A very strong fluorescent band (quantum yield 4.00 ± 0.01) was observed in toluene at 545 nm by exciting at 355 nm. The unstructured nature of the band suggests strong interaction between the solvent and the polarized compound in the excited state. Protonation of the peripheral nitrogen atoms by the gradual addition of acid quenches the fluorescence (Figure 2B) and changes the UV/vis spectrum (Figure 2A). The decrease in intensity of the 355 nm absorption band along with the disappearance of the 375 nm band in the UV/vis spectrum indicates that nitrogen protonation has a profound electronic effect on the π-electron density throughout the system. The UV/vis spectrum is independent of concentration in the region studied (10^{-1} to 10^{-7} M).

Thermogravimetric analysis of **1** indicates compound stability to around 450 °C. Decomposition at this temperature agrees with mass loss of the flexible *tert*-butyl groups. Examination of the residue remaining at 800 °C confirms the retention of N. This suggests that pristine heterosuperbenzenes without substituents are likely to be highly thermally stable and particularly suitable for many LED applications where thermally sensitive polymer materials fail.

In conclusion the essential steps in the formation of intrinsically nitrogen-doped graphite nanostructures in a controlled and systematic manner have been proven. The presence of imine N atoms has rendered overall electron-accepting properties to **1** compared to its all-C analogue. The preliminary emission studies undertaken on **1** suggest that the optoelectronic properties of this emerging heterosuperbenzene family will be promising. Synthetic control of the extent and position of N doping such as demonstrated here allows molecular tuning of the optoelectronic properties of the resultant material and provides the potential for ligand-based functionality.

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Supporting Information Available: Full experimental and spectroscopic details for all the compounds reported and HMQC, ^{13}C NMR data, ESI-mass spectrum, and thermogravimetric analysis of **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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