## Supporting Information Submission

## Experimental Section

Chemicals were used directly as received. Solvents were distilled, dried and degassed prior to use. NMR spectra were recorded on DPX 400 spectrometer operating at 400.13 MHz for <sup>1</sup>H, and 100.61 MHz for <sup>13</sup>C, and were standardised with respect to TMS. UV/vis spectra were obtained using a Shimadzu UV-2401PC, spectrophotometer. Fluorescence spectra were recorded using a Perkin Elmer LS50B luminescence spectrometer. Electrospray ionization mass spectra were recorded on a micromass LCT electrospray mass spectrometer using nitrogen as drying and nebulizing gas.

**di-(pyrimdin-3,5-yl)ethyne 5**. Modification of the procedure reported for dipyridylacetylenes<sup>1</sup> so as to couple 5-ethynylpyrimidine and 5-bromopyrimidine gave **5** (0.388g, 74% yield): mp 172-174°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C, TMS)  $\delta$  9.19 (s, 2H), 8.89 (s, 4H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, 25°C, TMS)  $\delta$  158.3, 157.1, 118.3, 88.6; ESI-MS (CH<sub>3</sub>CN) *m/z*(%) (MH)<sup>+</sup> 183.5 (100); (calcd 182.2). Anal. Calcd for C<sub>10</sub>H<sub>6</sub>N<sub>4</sub>: C, 65.92; H, 3.32; N, 30.76. Found: C, 65.39; H, 3.42; N, 30.64.

## 1,2-dipyrimidyl-3,4,5,6-tetra-(4-tert-

**butylphenyl)benzene 6**. Benzophenone (4.5 g), di-(pyrimidin-3,5-yl)ethyne **5** (120 mg, 0.657 mmol), and 2,3,4,5-tetra-(4tert-butylphenyl)cyclopentadien-1-one **4** (400 mg, 0.657 mmol) were heated to reflux for 1 h. Chromatography (SiO<sub>2</sub>, Et<sub>2</sub>O) and crystallisation from ethylacetate/petroleum ether gave colourless crystals (0.406 g, 81% yield): mp >300°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C, TMS) δ 8.77 (s 2H), 8.26 (s, 4H), 6.93 (d, 4H, *J*(H,H)=9 Hz), 6.85 (d, 4H, *J*(H,H)=9 Hz), 6.71 (d, 4H, *J*(H,H)=9 Hz), 6.68 (d, 4H, *J*(H,H)=9 Hz), 1.13 (s, 18H), 1.11 (s, 18H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, 25°C, TMS) δ 157.6, 155.4, 148.6, 147.9, 142.6, 141.2, 136.0, 135.2, 133.7, 132.2, 130.4, 130.1, 123.7, 122.9, 33.7, 33.6, 30.70, 30.68; ESI-MS (CH<sub>3</sub>CN) *m/z*(%)(MH)<sup>+</sup> 763.6(100); (calcd 763.0). Anal. Calcd for C<sub>54</sub>H<sub>58</sub>N<sub>4</sub>: C, 84.99; H, 7.66; N, 7.34. Found C, 84.84; H, 8.01; N, 6.92.

## Tetra-peri-(tert-butyl-benzo)-di-peri-(pyrimidino)-

coronene (Heterosuperbenzene) 1. 6 (200 mg, 0.262 mmol), AlCl<sub>2</sub> (555 mg, 4.16 mmol), and CuCl<sub>2</sub> (564 mg, 4.19 mmol) were stirred in CS<sub>2</sub> (60 mL) at 295 K for 72 h. The black solid was stirred in dilute ammonia solution, extracted into chloroform and dried. Chromatography (SiO<sub>2</sub>, 1:9methanol:toluene), and crystallisation from toluene/petroleum ether gave red/orange crystals (0.096 g, 49% yield): mp > 300°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C, TMS) δ 9.79 (s, 2H), 9.42 (s, 2H), 9.07 (s, 2H), 9.01 (s, 2H), 8.94 (s, 2H), 1.95 (s, 18H), 1.87 (s, 18H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, 25°C, TMS) δ 155.5, 153.1, 149.5, 149.3, 149.1, 129.5, 128.9, 128.8, 127.4, 124.0, 122.3, 121.6, 121.4, 119.8, 118.7, 118.4, 117.6, 117.3, 114.1, 35.42, 35.40, 31.7, 31.6; Elemental analysis could not be obtained for **1**. Non-invasive methods are usually employed for thermally stable graphene systems similar to these.<sup>6</sup> ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>); m/z(%): (MH)<sup>+</sup> 751.3382(100); ES-MS (toluene); calculated for  $C_{54}H_{47}N_4$ : (MH)<sup>+</sup> m/z 751.3840, found: 751.3801.



Figure 3. Thermogravimetric analysis of heterosuperbenzene 1 showing 5-10% solvent loss and *tert*-butyl decomposition.



Scheme 2. The atom labeling scheme showing the 23 chemically distinct carbon atoms of heterosuperbenzene 1.

Carbon atom label	<sup>1</sup> H NMR assignment (ppm)	<sup>13</sup> C NMR assignment (ppm)
22 or 23, CH <sub>3</sub>	1.87	31.58
22 or 23, CH <sub>3</sub>	1.95	31.67
13 or 14, CH	8.94	118.36
13 or 14, CH	9.01	118.70
15	9.07	122.28
16	9.42	121.55
19	9.79	155.46

Table 1. Assignment of  ${}^{13}C$  and  ${}^{1}H$  NMR signals from HMQC experiments on 1.

<sup>&</sup>lt;sup>1</sup> Ames D. E.; Bull D.; Takundwa C. Synthesis 1981, 364



Figure 4. <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub> of heterosuperbenzene 1 showing the assigned 23 signals.



Figure 5. HMQC CH-COSY spectrum in  $*CDCl_3$  of heterosuperbenzene 1 showing the coupling of the aromatic CH signals and the absence of any additional signals other than those assigned to 1.



Figure 6. The ESI-mass spectrum of heterosuperbenzene 1 in toluene showing the isotopic distribution pattern for  $(MH)^{+}$  in the presence of Na ions (from glass).