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The CA.M lattice revisited. Gel formation from a linear bis-isocyanuric acid and 2-amino-4,6-bis-(4-*tert*-butylphenylamino)-1,3,5-triazine

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Abstract—Five bis(isocyanuric) acid dimers have been prepared and characterised. The introduction of flexible alkyl chains was necessary to aid solubility. On mixing with *N*,*N*-bis(4-*tert*-butyphenyl)melamine in THF followed by slow evaporation, a viscous gel can form which is interpreted as evidence for the assembly of an infinite 2-D hydrogen bonded network.

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1. Introduction

The cyanuric acid–melamine lattice (CA.M)[1,2] has been a source of inspiration[3,4] for the study of hydrogen bonded aggregates. By mixing melamine derivatives and isocyanuric acid or dialkylbarbituric acid derivatives, hydrogen bonding is restricted to give discrete aggregates which can be studied in solution and in some cases crystallised.[4,5] The crystallisation of diethylbarbituric acid with *N*,*N*-bis(4-substituted phenyl)melamines gives either linear tape, crinkled tape or a rosette motif depending upon the substituents on the aryl rings.[5] If 4-*tert*-butyl substituted aryl rings are used as substituents then the rosette motif (Fig. 1) crystallises. The steric bulk of the *tert*-butyl groups disfavours linear or crinkled tapes. This structure prepared by us is very similar to the original rosette crystallised by the group of Whitesides.[5] The motif is not quite planar in contrast to the cyclic motif observed in the crystal structure of the CA.M lattice[2] suggesting that the deviation from planarity is a consequence of crystal packing forces since there are no steric interactions between the substituents.

In the structure of components **1** and **2**, rosette motifs form sheets that extend in $\{1\bar{1}\bar{1}\}$ planes. These sheets are packed in parallel fashion. Adjacent sheets within the stack are related by inversion symmetry. In two of the three independent molecules of **1**, the alkyl chains adopt an all-*trans* conformation resulting in an essentially planar $H_3C(CH_2)_3C(CH_2)_3CH_3$ unit. The mean plane of this unit is approximately perpendicular to that of the ring. In the third independent molecule of **1**, both alkyl chains are in end-*gauche* conformation

Our approach to preparing new networked materials was to attempt to ‘expand’ the CA.M lattice by introducing a linear spacer between pairs of cyanuric acids. The anticipated 2-D hydrogen bonded network is shown in Figure 2. It would consist of sheets with hexagonal cavities which are lined by six *N*,*N*-bis(4-*tert*-butyphenyl) groups of the melamines. This example would represent a macrocyclic architecture formed by supramolecular chemistry that can bind to a multiple number of six exchangeable melamine derivatives with convergent functionality that forms a cavity.

2. Results and discussion

Initially we prepared the linear bis-isocyanuric acids **11** and **15** (Schemes 1 and 2). Biuret **3** was nitrated to give nitrobiuret **4**[5] then reacted with 4-iodoaniline or 2-chloro-4-iodoaniline to give compounds **5** and **6**, respectively. Cyclisation was achieved by heating with NaOEt in EtOH with $(EtO)_2C{=}O$.[3] To our surprise, compound **7** underwent Sonogashira coupling with trimethylsilylacetylene despite possessing the acidic functionality of the isocyanuric acid group. Building block **10** was formed by removing the trimethylsilyl group with KOH/MeOH. Coupling of compound **7** with **10** gave the first isocyanuric acid dimer **11**.

Keywords: 2-Amino-4,6-bis-(4-*tert*-butylphenylamino)-1,3,5-triazine; Cyanuric acid; Hydrogen bonding; Rosette motif.

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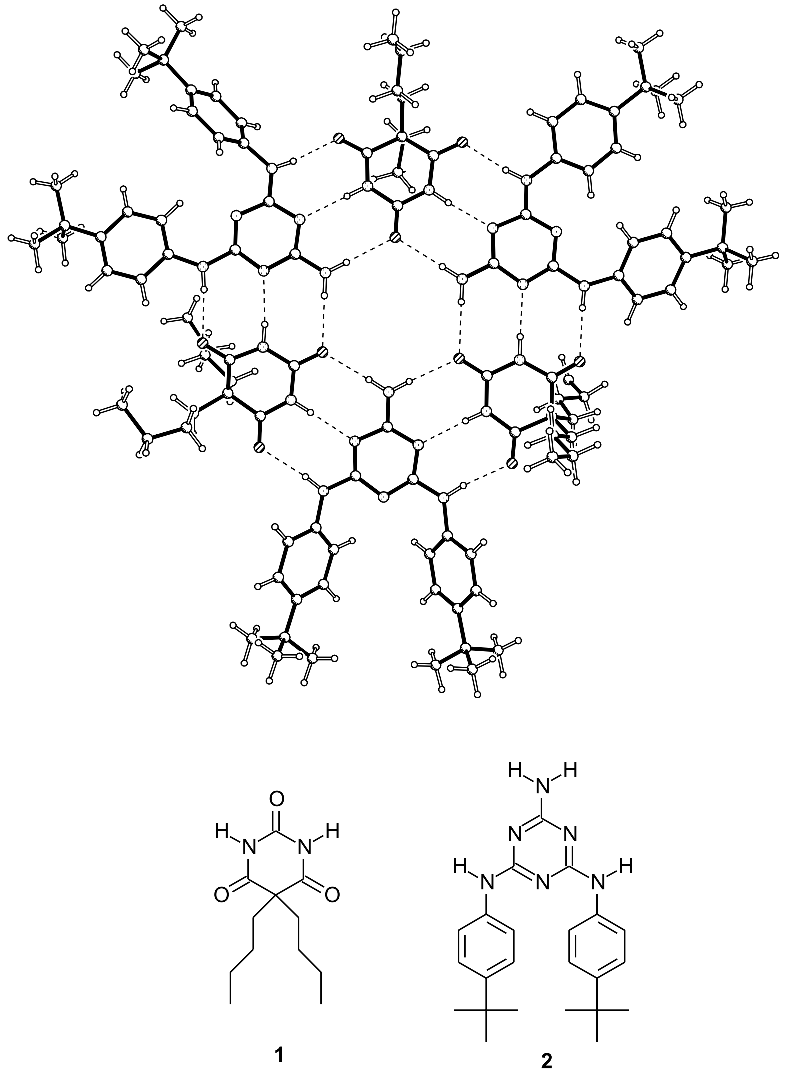


Figure 1. Crystal structure of a rosette formed from components **1** and **2**.

Dimer **15** was prepared by palladium catalysed coupling of diethnylbenzene **14**[6] with 4-iodophenylisocyanuric acid **7**.

Both dimers **11** and **15** are poorly soluble but were of interest because they might have packed well in a crystal lattice. They dissolved in DMSO allowing good proton and carbon spectra to be obtained but were too involatile to provide mass spectral molecular ions. Ideally for rosette formation, solubility in $CHCl_3$ is desired because in this relatively non-polar solvent strong hydrogen bonding between components can occur. In contrast, in polar solvents such as DMSO and THF, hydrogen bonding between components is much weaker and rosette aggregates break up. However, we anticipated that for a concentrated solution in a polar solvent, 2-D network formation may still occur because of cooperative stabilisation owing to the infinite network. A 2-D network should be more stable than 1-D chains which should be more stable than discrete aggregates. However, all attempts made to form a network from dimers **11** and **15** with *N*,*N*-bis(4-*tert*-butylphenyl)-melamine in THF and DMSO were unsuccessful. In all cases, slow evaporation of solvent gave a powder which could not be characterised.

Given that $CHCl_3$ is a more desirable solvent for these studies a further series of dimers **29**–**31** were prepared which contained solubilising alkyl chains in the centre (Scheme 3). The synthesis of diethnyl precursors **26**–**28**[7,8] follows standard methods and indeed all of the intermediates have been previously reported.[7–11] Palladium coupling of compounds **27**–**28** with 4-iodophenylisocyanuric acid **7** gave the extended dimers **29** and **31**, respectively. Palladium coupling of precursor **26** was less successful. The purification was aided by the flexible alkyl chains, which enhance solubility and give the compounds surfactant-like properties. Excess iodophenylisocyanuric acid is easily removed by extraction of the crude solid with aqeous NaOH. The sodium salt of this is water soluble while the sodium salt, mono or bis, of the dimer is still insoluble in acid or base. The dimer is then treated with acid to ensure reprotonation. The dimers are much more soluble than the unsubstituted dimers **11** and **15** and can be dissolved in THF. The molecular ion in the MALDI mass spectrum showed the same peak intensity pattern as that calculated theoretically which aided characterisation. However, although good proton and carbon spectra were obtained, the MALDI spectra showed evidence of oligomers of compounds **26**–**28** coupled terminally with isocyanuric

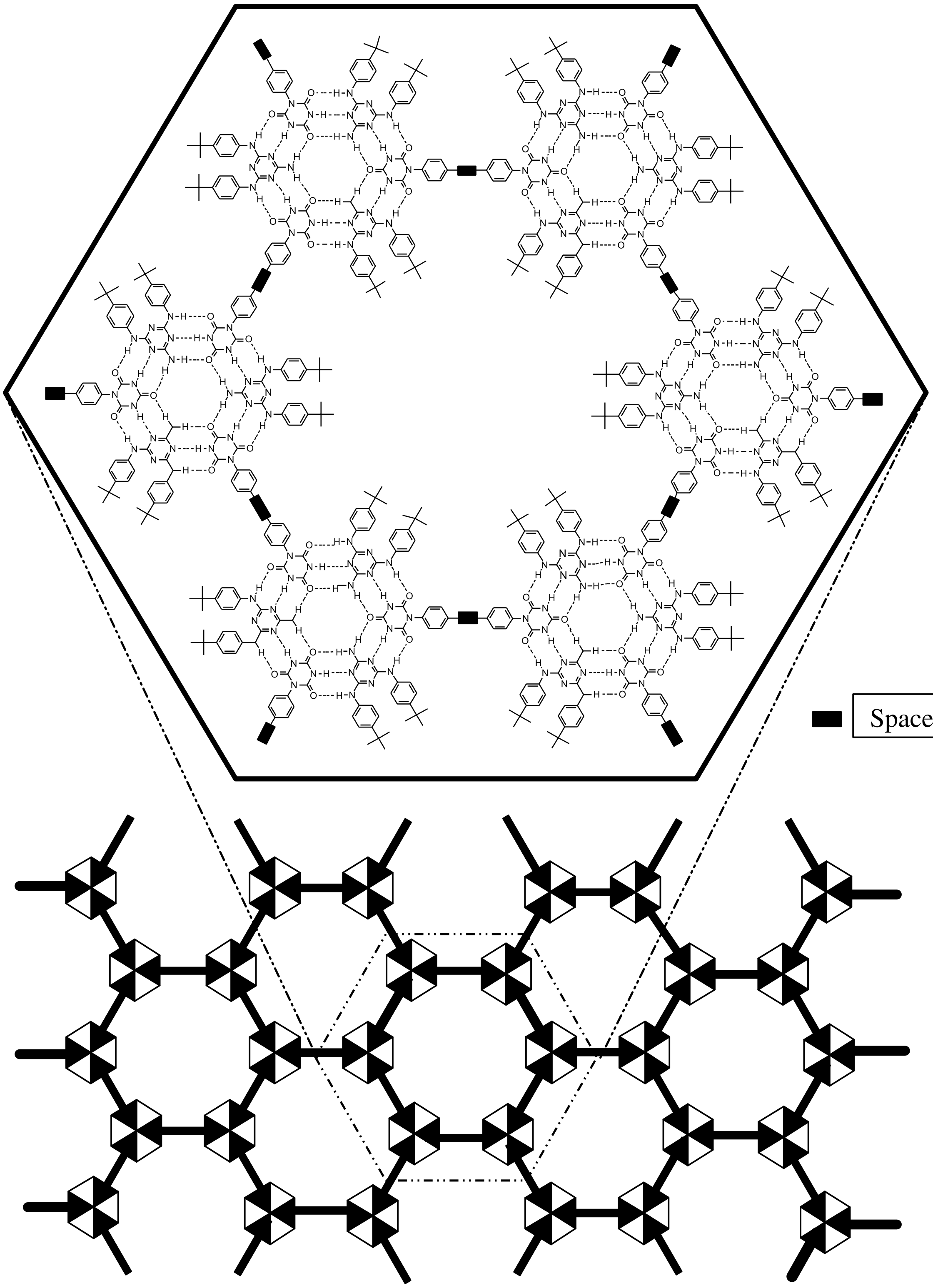
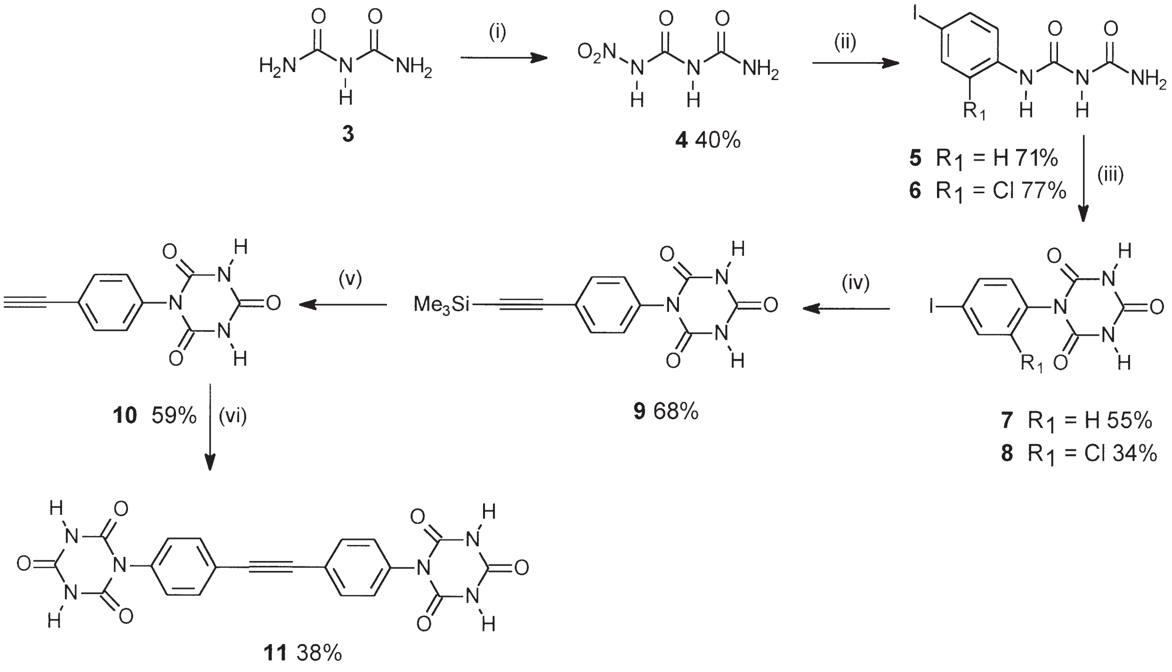


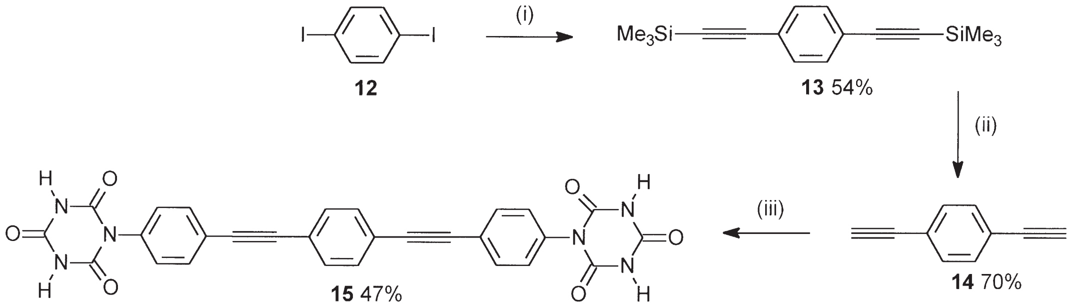
Figure 2. Drawing of the proposed 2-D structural motif formed between compounds **29** and **2**.

acids. For this reason an alternative route to prepare **29** was used which involved coupling *N*-(4-ethynylphenyl)isocyanuric acid **10** with 1,4-didecyloxy-2,5-diiodobenzene **21**. This route avoids the formation of similar polymeric oligomers and gives a product of greater purity (Scheme 4). Unfortunately dimers **29** and **31**, which possesses a longer side chain, are not soluble in $CHCl_3$. To enhance solubility in $CHCl_3$, dimer **30** was prepared which has a chlorine substituent adjacent to each isocyanuric acid. This should cause some molecular twisting and reduce the symmetry and so enhance solubility. Compound **30** has a slight solubility in $CHCl_3$ because a suspension of **30** in $CHCl_3$ turns yellow in colour although the solubility is not enough to obtain NMR data in $CHCl_3$.

2-D network formation was studied in concentrated THF



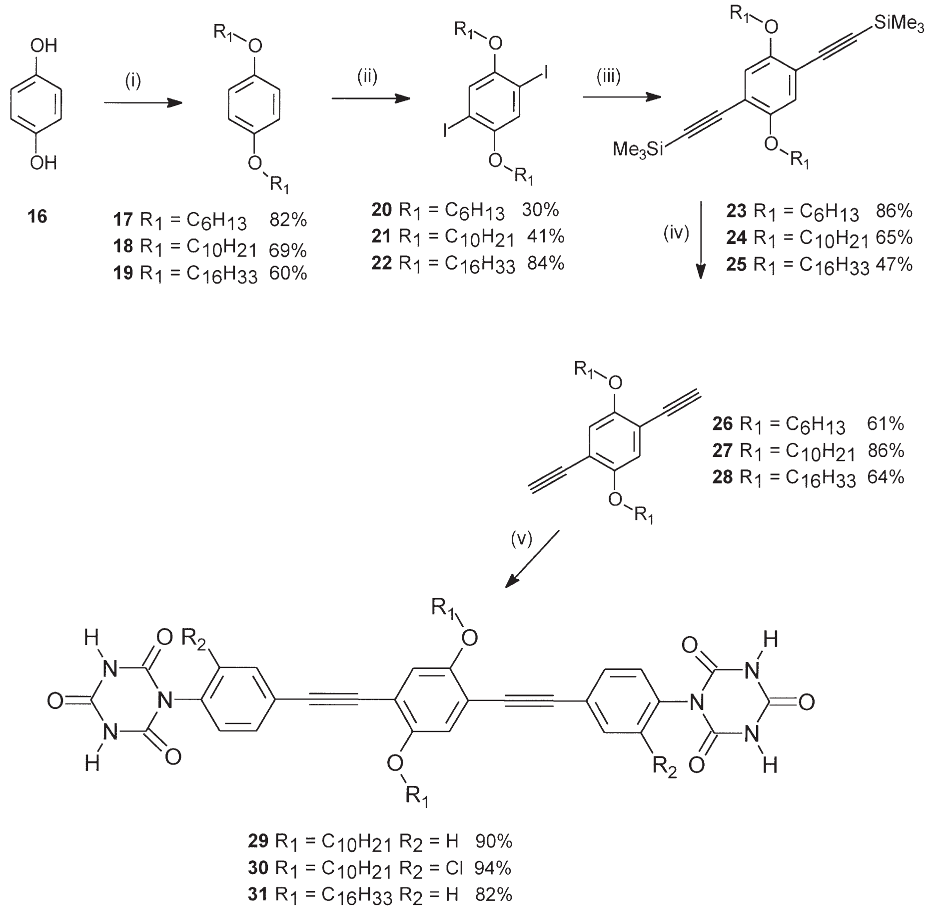
Scheme 1. Reagents and conditions: (i) HNO_3/H_2SO_4 (40%); (ii) 4-iodoaniline or 2-chloro-4-iodoaniline/H_2O/Δ; (iii) diethyl carbonate/Na/EtOH/Δ; (iv) **7**/TMS–$C_2H/(PPh_3)_2PdCl_2/CuI/Et_3N$/RT/THF/1–3 days; (v) KOH/MeOH/rt/15; (vi) **7**/$(PPh_3)_2PdCl_2/CuI/Et_3N$.



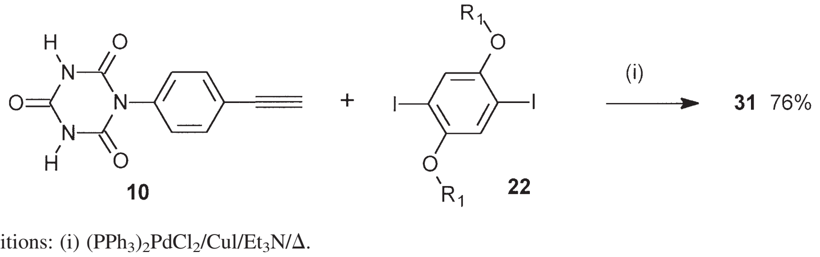
Scheme 2. Reagents and conditions: (i) TMS–$C_2H/(PPh_3)_2PPCl_2/CuI/Et_3N$/rt/THF; (ii) KOH/MeOH/rt/15 min; (iii) **7**/$(PPh_3)_2PdCl_2/CuI/Et_3N$/rt.

solution. An interesting result was obtained from mixing THF solutions of dimer **29** with *N*,*N*-bis(4-*tert*-butyphenyl)-melamine **1**. A solution of the dimer in THF was mixed with a solution of compound **1** and allowed to slowly evaporate in a sample vial. In one case this was done over a few months in an NMR tube. As the solvent slowly evaporates the solutions become thick and viscous with gel like properties. A skin could form on the surface which redissolved on mixing and heating. The gel would not pour from the vessel. If desolvation was continued the sample eventually reverted to a dry flaky powder. In contrast if the dimer **29** alone or the melamine **1** alone is slowly concentrated in THF no gel like phase is observed but a powder eventually forms. Also concentration of a solution of the dimer with *N*,*N*-bis(phenyl)melamine does not give a viscous gel like phase but forms a powder as the components precipitate from solution. The viscous gel phase is interesting evidence for the formation of extended 2-D sheets depicted in diagram 2 which are still in solution. On slow solvent evaporation an extended network of hydrogen bonds could form, stabilised by the infinite network. A concentrated solution is necessary because of the polar solvent THF which would normally break up rosettes. *N*,*N*-bis(4-*tert*-butyphenyl)melamine **1** favours rosette formation over other structural motifs, so the motif depicted in Figure 2 is our proposal. Dimers **30** and **31** did not form gels with melamine **1** from THF showing that the gel formation is sensitive to the dimer structure. The precipitated material may still consist of extended networks but it is difficult to characterise. Evidently a dimer soluble in $CHCl_3$ is desired because the network formation could be studied in a less concentrated solution and may be easier to crystallise. Furthermore the methodology to produce compounds with this type of spacer structure that are soluble in water is known[12] so isocyanuric acid dimers with these spacers might allow assembly in water to be studied.

In conclusion, linear bis(isocyanuric) acid dimers have been prepared and characterised. On mixing one with *N*,*N*-bis(4-*tert*-butyphenyl)melamine in THF followed by slow evaporation, a gel forms which is interpreted as evidence for the assembly of an infinite and soluble 2-D hydrogen bonded network The network is predicted to have hexagonal like cavities each of which binds six exchangeable melamines on the inside with the *tert*-butylphenyl groups pointing inwards forming a cavity.[13]



Scheme 3. Reagents and conditions: (i) hexylbromide, decylbromide or hexadecylbromide/K_2CO_3/acetone/Δ; (ii) I_2/KIO_3/H_2SO_4/HOAc/H_2O; (iii) TMS–C_2H/$(PPh_3)_2PdCl_2$/CuI/Et_3N/rt/THF; (iv) KOH/MeOH/THF/2 h; (v) **7** or **8**/$(PPh_3)_2PdCl_2$/CuI/Et_3N/Δ.



Scheme 4. Reagents and conditions: (i) $(PPh_3)_2PdCl_2$/CuI/Et_3N/Δ.

3. Experimental

3.1. General

Melting points were carried out using a Kofler hot-stage microscope and are uncorrected. Butterworth Laboratories, using a PE.2400 CHN analyser, conducted elemental analysis. Ultraviolet spectra were recorded on a Perkin–Elmer Lambda 15 UV–VIS spectrometer using DCM, THF and DMSO as the solvents. Infrared spectra were recorded on an ATI Mattson FTIR spectrometer. ^1H and ^{13}C NMR spectra were obtained at 250 and 62.9 MHz, respectively, on a Brucker AC 250 spectrometer and at 400 and 100.5 MHz, respectively on a Varian 400 spectrometer. Chemical shifts (δ) are given in ppm relative to the residual solvent. Coupling constants, (J) are given in Hz. All compounds were prepared to a high standard of purity, greater than 95% as determined by ^1H NMR spectra. Low-resolution mass spectra were obtained using electrospray ionization on a Finnigan Navigator Mass Spectrometer and accurate mass at the University of Wales. Swansea using fast atom bombardment methods and MALDI. For dimers **29**, **30** and **31** the theoretical peak pattern for the MALDI spectrum is listed. Aldrich, Lancaster Synthesis, Avocado and BDH supplied starting materials. Et_3N was dried by distillation from CaH_2, EtOH was dried by distillation from magnesium, toluene from sodium, and THF from potassium using benzophenone as the indicator. All dried solvents were transferred from the stills to the reaction vessels using oven dried glass syringes under nitrogen. Reactions requiring anhydrous conditions were carried out in three-necked r.b. flasks, which were flame dried while under vacuum and then purged three times with either argon or nitrogen.

3.1.1. 1-Nitrobiuret 4.[3] Biuret **3** (51.5 g, 0.5 mol) was added in 1 g portions to a mixture of sulphuric acid (125 mL, ~97%) and nitric acid (30 mL, ~69%), chilled in an ice bath, over 30 min. After the mixture had been stirred for 2 h, all the solid had dissolved, and the solution was poured onto ice (1 kg). The ice was allowed to melt and the precipitate was filtered. The precipitate was suspended in water (1 L), chilled in an ice bath, and sodium hydroxide (400 mL, 1 M) was added to bring the pH to ~8.5. The solution was filtered cold and the product precipitated with concentrated HCl to pH~2, filtered, washed with water and dried under vacuum to give the title compound (30 g, 40%) as a white powder; δ_H (250 MHz; DMSO-d_6) 4.95 (2H, s, br, NH_2), 7.07–7.39 (1H, d, NH) and 9.42 (1H, s); δ_C (62.9 MHz; DMSO-d_6)148.8 and 153.2; *m*/*z* (ES) 147.0 (M^++Na, 100%).

3.1.2. 1-(4-Iodophenyl)biuret 5. *General procedure*. A mixture of 1-nitrobiuret **4** (4.78 g, 32 mmol) and 4-iodoaniline (5.14 g, 25 mmol) in water (50 mL) was heated at reflux for 2 h. The precipitated product was filtered hot, washed with water and MeOH to give the title compound (5.4 g, 71%) as a grey powder, mp >230 °C. (Found: C, 31.7; H, 2.6; N, 13.8. $C_8H_8IN_3O_2$ requires C, 31.5; H, 2.6; N, 13.8%); ν_{max} (KBr)/cm^{-1} 3386vs, 3311m, 3241m, 3207m, 3151m, 3050m, 2979m, 2923m, 1729vs, 1689vs, 1581vs, 1533vs, 1508vs, 1481s, 1429vs, 1384vs, 1299vs, 1213vs, 1118s, 1078m, 991w, 879w, 815s, 732m, 682w and 651; δ_H (250 MHz; DMSO-d_6) 6.90 (2H, vbs, NH_2), 7.29 (2H, d, *J*=8.6 Hz), 7.61 (2H, d, *J*=8.6 Hz), 8.93 (1H, s) and 10.05 (1H, s); δ_C (62.9 MHz; DMSO-d_6) 86.3, 121.3, 137.5, 138.1, 151.9 and 155.5; *m*/*z* 305.9741 (M^++H. $C_8H_9IN_3O_2$ requires 305.9739).

3.1.3. 1-(2-Chloro-4-iodophenyl)biuret 6. 3.1 g, 77%. Grey powder, mp >230 °C (decomp. from water) ν_{max}(KBr)/cm^{-1} 3441m, 3256m, 3194m, 1704s, 1621m, 1590s, 1578s, 1505s, 1370m, 1351m, 1297m, 1272m, 1257s, 1232s and 818m; δ_H (250 MHz; [$^2H_6$]DMSO) 6.9 (2H, br s, NH_2), 7.64 (1H, d, *J*=8.9 Hz, Ar), 7.83 (1H, s, Ar), 8.03 (1H, d, *J*=8.6 Hz, Ar), 9.34 (1H, s, NH) and 10.9 (1H, s, NH); δ_C(62.9 MHz; DMSO-d_6) 61.2, 86.3, 122.6, 123.1 135.2, 136.5, 151.6 and 155.8; *m*/*z* (EI) 357.0 (M^++NH_4, 100%) and 340.0 (M^++H, 31), *m*/*z* (EI) 339.9351 (M^++H, 100. $C_8H_7ClIN_3O_2$ requires 339.9344).

3.1.4. *N*-(4-Iodophenyl)isocyanuric acid 7. *General procedure*. Sodium ethoxide was prepared by dissolving sodium (0.49 g, 21 mmol) in dry ethanol (60 mL) under an argon atmosphere. Biuret **5** (1.83 g, 6 mmol) and diethyl carbonate (1.42 g, 12 mmol) were added to this solution. The mixture was heated at reflux for 24 h, allowed to cool and toluene was added. The sodium salt was filtered, washed with toluene and dried. The solid was dissolved in water, filtered and dilute HCl was added and the precipitate was filtered, washed with water and dried under vacuum to give the title compound (1.1 g, 55%) as a white powder, mp >200 °C. (Found: C, 32.1; H, 1.8; N, 12.3. $C_9H_6IN_3O_3$ requires C, 32.6; H, 1.8; N, 12.7%); ν_{max} (KBr)/cm^{-1} 3212s, 3064s, 2831m, 1799vs, 1762vs, 1693vs, 1479vs, 1402vs, 1211m, 1114w, 1068w, 1010w, 881w, 823m and 744vs; δ_H (250 MHz; DMSO-d_6) 7.16 (2H, d, *J*=8.5 Hz), 7.82 (2H, d, *J*=8.5 Hz), and 11.58 (2H, bs); δ_C (62.9 MHz; DMSO-d_6) 94.9, 131.6, 134.2, 137.7, 148.9 and 149.6; *m*/*z* 331.1 (M^+, 100%).

3.1.5. *N*-(2-Chloro-4-iodophenyl)isocyanuric acid 8. 0.54 g, 34%. White powder, mp >260 °C (from water). ν_{max}(KBr)/cm^{-1} 3420br, 3208br, 3082br, 2847w, 1751s, 1704s, 1574m, 1476s, 1419s, 1408s, 1375m, 830m, 789m, 761m, 603m, 555m and 533m; δ_H (250 MHz; DMSO-d_6) 7.33 (1H, d, *J*=8.2 Hz, Ar), 7.81 (1H, d, *J*=7.9 Hz, Ar), 8.05 (1H, s, Ar) and 11.9 (2H, br s, NH); δ_C (62.9 MHz; DMSO-d_6) 96.3, 131.6, 133.1, 133.6, 137.1, 137.2, 148.7 and 148.8; *m*/*z* (ES$^-$) 364.3 (M−H, 100%); *m*/*z* (ES$^-$) 363.8987 (M−H, 100% $C_9H_5ClIN_3O_3$ requires 363.8991).

3.1.6. *N*-(4-Trimethylsilylethynylphenyl)isocyanuric acid 9. A mixture of isocyanuric acid **7** (0.4 g, 1 mmol), trimethylsilylacetylene (0.23 g, 2 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg, 28 μmol), CuI (4 mg, 21 μmol) in THF (25 mL) and Et_3N (4 mL) under an argon atmosphere was stirred, at rt, for 8 h. The solvent was removed under reduced pressure and the residue, dissolved in DCM, filtered through silica to elute impurities followed by elution with ethyl acetate. The solvent was removed under reduced pressure and the residue washed with light petroleum to give the title compound (0.25 g, 68%) as an off white solid, mp >250 °C. (Found: C, 55.0; H, 5.0; N, 12.9. $C_{11}H_{10}N_3O_3$ requires C, 55.8; H, 5.0; N, 13.9%); ν_{max} (KBr)/cm^{-1} 2969vs, 2939vs 2759vs, 2678vs, 2474m, 1463vs, 1413s, 1359m, 1162s, 1064w, 1029vs, 842w and 798m; δ_H (250 MHz; DMSO-d_6) 0.24 (9H, s, Si–Me), 7.34 (2H, d, *J*=8.2 Hz), 7.53 (2H, d, *J*=8.2 Hz) and 11.58 (2H, bs); δ_C (62.9 MHz; DMSO-d_6) −0.1, 95.1, 104.5, 122.3, 129.7, 132.0, 134.7, 148.9 and 149.6; *m*/*z* (ES) 301 (M^++Na, 100%); *m*/*z* (ES) 319.1224 (M+NH_4, 100% $C_{14}H_{15}N_3SiO_3$ requires 319.1221).

3.1.7. *N*-(4-Ethynylphenyl)isocyanuric acid 10. Isocyanuric acid **9** (0.71 g, 2.3 mmol) was suspended in ethanol (40 mL). Aqueous sodium hydroxide (40 mL, 1 M) was added and the solution stirred. After 1 h the solvent was reduced to 50 mL and concentrated HCl was added to adjust the pH to 7. The precipitate was filtered and the residue was washed with water to give the title compound (0.32 g, 59%) as off white solid, mp >200 °C (from water). (Found: C, 57.1; H, 3.2; N, 17.3. $C_{11}H_{10}N_3O_3$ requires C, 57.6; H, 3.1; N, 18.3%); ν_{max} (KBr)/cm^{-1} 3484w, 3413m, 3303m, 3226vs, 3201vs, 3097vs, 3054vs, 2875s, 2420m, 2358vs, 2329vs, 1984m, 1810vs, 1675vs, 1612m, 1502vs, 1380vs, 1267w, 1211m, 1095m, 908w, 840m, 809w, 754vs, 725vs, 632vs, 547s, 474w and 428s; δ_H (250 MHz; DMSO-d_6) 4.27 (1H, s, CCH), 7.36 (2H, d, *J*=8.3 Hz), 7.56 (2H, d, *J*=8.3 Hz), and 11.59 (2H, s); δ_C (62.9 MHz; DMSO-d_6) 81.6, 82.9, 122.0, 129.7, 132.2, 134.7, 148.9 and 149.6; *m*/*z* 228.1 (M^+−H, 100%) *m*/*z* 247.0827 (M^++NH_4, 100% $C_{11}H_7N_3O_3$ requires 247.0827).

3.1.8. Bis-1,2-ethynyl-(4-phenylisocyanuric acid) 11. A stirred solution of 1-(4-ethynylphenyl)isocyanuric acid **10** (250 mg, 1.09 mmol),1-(4-iodophenyl)isocyanuric acid **7** (360 g, 1.09 mmol) and CuI and $(PPh_3)_2PdCl_2$ in catalytic amounts dissolved in degassed anhydrous THF (40 mL) was treated with Et_3N (3 mL). The mixture was refluxed for 24 h, then another aliquot of 1-(*p*-iodophenyl)isocyanuric acid (200 g) was added. The organic solvent was removed under reduced pressure before the remaining solid was partially dissolved up in 10% sodium hydroxide (40 mL). The insoluble material was collected by filtration then stirred as a suspension in THF (60 mL) and water (60 mL) whilst conc. hydrochloric acid (15 mL) was added dropwise. The acidic mixture was allowed to stir for 2 h, followed by removal of the organic solvent under reduced pressure, addition of water (30 mL), filtration and a final wash with fresh water (20 mL) to give the title compound (180 mg, 38%) as a brown powder, mp >250 °C (from tetrahydrofuran) ν_{max}(KBr)/cm^{-1} 3454br, 3216m, 3070m, 2833m, 1791s, 1762s, 1522s, 1444s, 1408s, 1214w, 840m, 756m, 744m, 734m, 721m, and 549m; δ_H(250 MHz; DMSO-d_6) 7.41 (4H, d, J=7.6 Hz, Ar), 7.65 (4H, d, J=7.3 Hz, Ar) and 11.64 (4H, s, NH); δ_C(250 MHz; DMSO-d_6) 89.4, 122.3, 129.8, 131.9, 134.6, 148.9 and 149.8.

3.1.9. 1,4-Bis(trimethylsilylethynyl)benzene 13.[6] Trimethylsilylacetylene (3.57 g, 0.036 mol) was added to a stirred solution of 1,4-diiodobenzene (4.0 g, 0.012 mol), CuI and $(PPh_3)_2PdCl_2$ in catalytic amounts dissolved in degassed anhydrous Et_3N (60 mL). The reaction mixture was refluxed for 8 h under a nitrogen atmosphere then the solvent was removed under reduced pressure. The residue was taken up in DCM and filtered through a silica plug. Afterwards the solvent was removed under reduced pressure. The residue was dissolved in (1:1) methanol/ethylacetate (40 mL) and cooled in an ice water bath for 3 h. The product readily crystallised and was collected by filtration to yield the title compound (1.75 g, 54%) as clear crystalline material, mp 121–123 °C (from methanol/ethylacetate 1:1) (lit. 122 °C) δ_H(250 MHz; $CDCl_3$) 0.24 (18H, s, Si(CH_3)$_3$) and 7.38 (4H, s, Ar); δ_C(62.9 MHz; $CDCl_3$) −0.06, 96.3, 104.6, 123.2 and 131.8.

3.1.10. 1,4-Diethynylbenzene 14.[6] To a stirred solution of 1,4-bis(trimethylsilylethynyl)benzene **13** (1.5 g, 5.55 mmol) in DCM (25 mL) and methanol (25 mL), was added dropwise potassium hydroxide (1 M, 10 mL). The mixture was left to stir for 3 h, then the organic solvent was removed under reduced pressure. Water (30 mL) was added and the mixture was extracted with ether (3×30 mL), dried with $MgSO_4$ and treated with decolourising charcoal. The solvent was removed under reduced pressure to yield the title compound (0.48 g, 70%) as a white solid, mp 94–95 °C (from diethyl ether) (lit 95–96 °C) δ_H(250 MHz; $CDCl_3$) 3.2 (2H, s, acetylenic H) and 7.45 (4H, s, Ar); δ_C(62.9 MHz; $CDCl_3$) 79.1, 83.1, 122.6 and 132.0.

3.1.11. 1,4-Phenylethynyl-(4-phenylisocyanuric acid) 15. A stirred solution of 1,4-diethynylbenzene 14 (200 mg, 3.17 mmol), 1-(4-iodophenyl)isocyanuric acid 7 (2.1 g, 12.7 mmol) and CuI and $(PPh_3)_2PdCl_2$ in catalytic amounts dissolved in degassed anhydrous THF (60 mL) was treated with Et_3N (5 mL). The mixture was refluxed for 12 h, then the organic solvent was removed under reduced pressure, redissolved in a large volume of THF and filtred through a silica plug. After concentration, the remaining solid was partially dissolved up in 10% sodium hydroxide (40 mL). The insoluble material was collected by vacuum filtration then stirred as a suspension in THF (60 mL) and water (60 mL) whilst conc. hydrochloric acid (15 mL) was added dropwise. The acidic mixture was allowed to stir for 2 h, followed by removal of the organic solvent under reduced pressure, addition of water (30 mL), filtration and a final wash with fresh water (20 mL) to give the title compound (393 mg, 47%) as a pale yellow powder, mp >250 °C (from water). (Found C: 62.6, H, 3.6. $C_{28}H_{16}N_6O_6$ requires C, 63.2; H, 3.0%); λ_{max}(DMSO)/nm 325 (log ε 4.6); ν_{max}(KBr)/cm^{-1} 3783w, 3258s, 3098s, 3063s, 1796s, 1754vs, 1692vs, 1488vs, 1460s, 1418s, 1390m, 838w and 787vs; δ_H(250 MHz; DMSO-d_6) 7.41 (4H, d, J=8.2 Hz, Ar), 7.63 (4H, s, Ar), 7.66 (4H, d, J=8.6 Hz, Ar) and 11.64 (4H, s, NH); δ_C(62.9 MHz; DMSO-d_6) 89.6, 90.8, 122.2, 122.4, 129.7, 131.8, 132.0, 134.7, 148.9 and 149.7.

3.1.12. 1,4-Dihexyloxybenzene 17.[9] *General procedure*. A solution of hydroquinone (18.2 g, 0.110 mol), bromohexane (40.4 g, 0.242 mol) and K_2CO_3 (15.2 g) in acetone (400 mL), was refluxed under a nitrogen atmosphere for 3 days. Toluene (300 mL) was added, then the solution was filtered hot, and the filtrate was concentrated to a brown solid which was redissolved in DCM. Washed twice with dilute sodium dithionate and dilute sodium hydroxide, dried over $MgSO_4$, and reduced to 10 mL appearing as an orange solution. This was then passed through a silca plug and concentrated to give the title compound (25.1 g, 82%), as a crystalline solid, mp 44–45 °C (from acetone). ν_{max}(KBr)/cm^{-1} 2924vs, 2871vs, 1509s, 1476m, 1396m, 1286m, 1237vs, 1115m, 1033s, 996m, 828s, 773m and 730w; δ_H(250 MHz; $CDCl_3$) 0.90 (6H, t, J=6.5 Hz, Me), 1.34 (12H, m, CH_2), 1.75 (4H, m, CH_2), 3.89 (4H, t, J=6.6 Hz, OCH_2) and 6.81 (4H, s, Ph); δ_C(62.9 MHz; $CDCl_3$) 14.1, 22.7, 25.8, 29.4, 31.7, 68.7, 115.4 and 153.2; *m/z* (EI) 278.2245 (M$^+$, $C_{18}H_{30}O_2$ requires 278.2240), *m/z* (ES) 279.1 (M$^+$+Na, 100%).

3.1.13. 1,4-Didecyloxybenzene 18.[10] 18.3 g, 69%. White powder, mp 67–68 °C (from ethanol/dichloromethane 1:1); ν_{max}(KBr)/cm^{-1} 2961s, 2936s, 2857s, 1509s, 1476m, 1396m, 1380w, 1287m, 1244vs, 1115m, 1032s, 828s, 772m and 659m; δ_H(250 MHz; $CDCl_3$) 0.88 (6H, t, J=6.6 Hz, Me), 1.26 (28H, m, CH_2), 1.77 (4H, m, O$CH_2$$CH_2$), 3.89 (4H, t, J=6.5 Hz, OCH_2) and 6.81 (4H, s, Ph); δ_C(62.9 MHz; $CDCl_3$)14.2, 22.7, 22.9, 29.2, 29.3, 29.4, 29.6, 31.9, 68.7, 115.4 and 153.2 (one resonance is missing); *m/z* (EI) 290.4 (M$^+$, 100%).

3.1.14. 1,4-Dihexadecyloxybenzene 19.[7] 15.2 g, 60%. White solid, mp 82–84 °C (from ethanol); ν_{max}(KBr)/cm^{-1}; δ_H(250 MHz; $CDCl_3$) 0.84 (6H, br t, Me), 1.25 (52H, m, $C_{13}H_{23}$), 1.73 (4H, m, O$CH_2$$CH_2$), 3.88 (4H, t, J=6.7 Hz, OCH_2) and 6.8 (4H, s, Ph); δ_C(62.9 MHz; $CDCl_3$) 14.2, 22.7, 26.1, 29.4, 29.6, 29.7, 32.0, 69.7, 115.4 and 153.2 (8 missing resonances).

3.1.15. 1,4-Dihexyloxy-2,5-diiodobenzene 20.[11] *General procedure*. A solution of 1,4-dihexyloxy **17** benzene (1.0 g, 3.6 mmol), KIO_3 (0.92 g, 1.8 mmol) and iodine (0.23 g, 4.3 mmol) in acetic acid (50 mL), sulphuric acid (1 mL) and water (5 mL), was refluxed for 4 h. To the reaction was added iodine (0.2 g, 1.58 mmol) and KIO_3 (0.5 g, 2.34 mmol), and reflux continued for another 7 h. A solution of sodium thionite (2.0 g in water 20 mL) was added and a colour change from orange to yellow was observed. The precipate was filtered to give the title compound (0.58 g, 30%) as yellow/white crystalline blocks mp 58–59 °C (from ethanol) ν_{max}(KBr)/cm^{-1} 3493m, 3424m, 2943s, 2851m, 1451s, 1347m, 1209vs, 1061m, 993m and 937m; δ_H(250 MHz; $CDCl_3$) 0.90 (6H, t, *J*=6.9 Hz, Me), 1.33 (12H, m, CH_2), 1.79 (4H, m, CH_2), 3.92 (4H, t, *J*=6.4 Hz, CH_2) and 7.16 (2H, s, Ph); δ_C(62.9 MHz; $CDCl_3$) 14.1, 22.6, 25.8, 29.2, 31.5, 70.4, 86.3, 122.8 and 152.9; *m/z* (ES) 530.1 (M^+, 100%).

3.1.16. 1,4-Didecyloxy-2,5-diiodobenzene 21.[8] 2.7 g, 41%. White powder, mp 62–63 °C (from ethanol). (Found: C, 48.2; H, 6.7. $C_{26}H_{44}I_2O_2$ requires C, 48.6; H, 6.9%); ν_{max}(KBr)/cm^{-1} 2940s, 2925vs, 2846s, 1487m, 1447m, 1388m, 1354m, 1264w, 1216s, 1071m, 1053m and 847m; δ_H(250 MHz; $CDCl_3$) 0.87 (6H, t, *J*=6.6 Hz, Me), 1.27 (28H, m, CH_2)1.8 (4H, m, OCH_2CH_2), 3.9 (4H, t, *J*=6.4 Hz, OCH_2) and 7.2 (2H, s, Ph); δ_C(62.9 MHz; $CDCl_3$) 14.2, 22.7, 26.1, 29.2, 29.3, 29.4, 29.6, 32.0, 70.4, 86.4, 122.8 and 152.9 (one missing resonance); *m/z* (EI) 660 (M^++NH_4, 100%) and 642.3 (M^+, 75).

3.1.17. 1,4-Dihexadecyloxy-2,5-diiodobenzene 22.[7] 6.07 g, 84%. White powder, mp 77–79 °C (from ethanol/dichloromethane 1:1) δ_H(250 MHz; $CDCl_3$) 0.87 (6H, br t, CH_3), 1.25 (52H, m, CH_2), 1.78 (4H, br t, OCH_2CH_2), 3.91 (4H, br t, OCH_2) and 7.16 (2H, s, Ar); δ_C(62.9 MHz; $CDCl_3$) 14.2, 22.7, 26.1, 29.2, 29.3, 29.4, 29.6, 29.7, 29.9, 32.0, 70.4, 86.3, 122.8 and 152.9 (6 resonances are overlapping).

3.1.18. 1,4-Bis(trimethylsilylethynyl)-2,5-dihexyloxybenzene 23.[7] *General procedure*. A stirred solution of 1,4-dihexyloxy-2,5-diiodobenzene **20** (1.24 g, 0.92 mmol) trimethylsilylacetylene (0.92 g, 9.35 mmol), $(PPh_3)_2PdCl_2$ (60 mg, 0.086 mmol) and of CuI (40 mg, 0.21 mmol) in anhydrous THF (20 mL) was treated with Et_3N (2 mL, 0.014 mol) under nitrogen at room temperature. The reaction was stirred for 24 h after which the solvent was removed in vacuo. The solid was dissolved in CH_2Cl_2 (10 mL), filtered through a 4 cm silica plug and eluted with dichloromethane to give the title compound (0.48 g, 86%) as a grey crystalline solid, mp 91–92 °C (from methanol) λ_{max}(CH_2Cl_2)/nm 237 (log ε 5.2), 270 (5.3), 285 (5.7) and 344 (5.0); ν_{max}(KBr)/cm^{-1} 2960s, 2939s, 2868m, 2156m, 1500m, 1469m, 1408m, 1386s, 1249s, 1225s, 1203s, 1032s, 894s, 867vs, 758m, 730m, 693m, 664m and 625m; δ_H(250 MHz; $CDCl_3$) 0.24 (18H, s, $SiMe_3$), 0.89 (6H, br t, Me), 1.3 (8H, m, C_2H_4), 1.55 (4H, m, CH_2), 1.75 (4H, m, CH_2), 3.93 (4H, t, *J*=6.3 Hz, OCH_2) and 6.88 (2H, s, Ph); δ_C(62.9 MHz; $CDCl_3$) −0.03, 14.0, 22.7, 25.7, 29.3, 31.6, 69.4, 100.1, 101.1, 113.9, 117.2 and 154.0; *m/z* (ES) 471.3104 (M^++H, 100%) $C_{28}H_{47}Si_2O_2$ requires 471.3109), *m/z* (ES) 470.2 (M, 87%), 431.3 (35), 359.2 (53), 293.1 (40) and 279.1 (100).

3.1.19. 1,4-Bis(trimethylsilylethynyl)-2,5-didecyloxybenzene 24.[8] 2.17 g, 65%. Grey crystalline solid, mp 72–73 °C (from methanol) λ_{max}(CH_2Cl_2)/nm 237 (log ε 4.2), 270 (4.2), 285 (4.5) and 345 (3.9); ν_{max}(KBr)/cm^{-1} 2943s, 2851m, 2157m, 1500m, 1471m, 1388m, 1225s, 1204m, 1032m, 893s, 855s and 759m; δ_H(250 MHz; $CDCl_3$) 0.24 (18H, s, $SiMe_3$), 0.89 (6H, m, Me), 1.23 (24H, m, C_6H_{12}), 1.45 (4H, m, CH_2), 1.75 (4H, m, CH_2), 3.93 (4H, t, *J*=6.3 Hz, OCH_2) and 6.85 (2H, s, Ph); δ_C(62.9 MHz; $CDCl_3$) −0.04, 8.8, 14.1, 22.7, 26.0, 29.3, 29.4, 29.6, 29.65, 31.9, 46.5, 69.4, 100.1, 101.0, 113.9, 117.1 and 154.0; *m/z* (EI) 583.5 (M^++H, 100%).

3.1.20. 1,4-Bis(trimethylsilylethynyl)-2,5-dihexadecyloxybenzene 25.[7] 0.87 g, 47%. Off-white solid, mp 65–66 °C (from dichloromethane) δ_H(250 MHz; $CDCl_3$) 0.24 (18H, s, $Si(CH_3)_3$), 0.87 (6H, br t, CH_3), 1.25 (52H, m, $C_{14}H_{28}$), 3.93 (4H, t, *J*=6.3 Hz, OCH_2) and 6.88 (2H, s, Ar); δ_C(62.9 MHz; $CDCl_3$) 0.0, 14.2, 22.7, 26.1, 29.4, 29.5, 29.7, 32.0, 69.5, 100.1, 101.1, 113.9, 117.2 and 154.0 (8 resonances are overlapping).

3.1.21. 1,4-Diethynyl-2,5-dihexyloxybenzene 26.[7] *General procedure*. A stirred solution of 1,4-bis-trimethylsilylethynyl-2,5-dihexyloxybenzene **23** (250 mg, 0.53 mmol) in anhydrous THF (20 mL) and methanol (20 mL) was treated with (4 mL) 20% KOH, and continued to stir for another 3 h. The reaction mixture was reduced to the aqueous slurry, where more water (30 mL) was added and extracted with dichloromethane (3×50 mL). The combined extracts were dried and evaporated under reduced pressure to give the title compound (100 mg, 61%) as a yellow crystalline solid, mp 69–71 °C (from methanol) λ_{max}(CH_2Cl_2)/nm 233 (log ε 4.0) and 271 (4.3); ν_{max}(KBr)/cm^{-1} 3266s, 2959s, 2939s, 2917s, 2852s, 1499s, 1468s, 1385s, 1218vs, 1197s, 1029s, 997m, 862m and 652m; δ_H(250 MHz; $CDCl_3$) 0.89 (6H, m, 2×CH_3), 1.33 (12H, m, 2×C_3H_6), 1.76 (4H, m, 2×OCH_2CH_2), 3.35 (2H, s, 2×C_2H), 3.96 (4H, t, *J*=6.4 Hz, 2×OCH_2) and 6.94 (2H, s, Ph); δ_C(62.9 MHz; $CDCl_3$) 14.1, 22.6, 25.6, 28.1, 31.5, 69.6, 79.2, 83.0, 113.3, 117.7 and 154.8; *m/z* (ES) 470.2 (M^+, 87%), 431.3 (35), 359.2 (53), 293.1 (40) and 279.1 (100).

3.1.22. 1,4-Diethynyl-2,5-didecyloxybenzene 27.[8] 1.06 g, 86%. Yellow powder, mp 70–72 °C (from methanol) λ_{max}(CH_2Cl_2)/nm 232 (log ε 4.0), 262 (4.3), 271 (4.5), 337 (3.9); ν_{max}(KBr)/cm^{-1} 3285s, 2927vs, 2850s, 1502m, 1471m, 1384s, 1270m, 1215s, 1048m, 1028m, 992m, 867m, 667m and 646m; δ_H(250 MHz; $CDCl_3$) 0.86 (6H, m, Me), 1.25 (28H, m, C_7H_{14}), 1.77 (4H, m, OCH_2CH_2), 3.3 (2H, s, CH), 3.95 (4H, t, *J*=6.6 Hz, OCH_2) and 6.93 (2H, s, Ph); δ_C(62.9 MHz; $CDCl_3$) 14.2, 22.7, 25.9, 29.1, 29.4, 29.6, 31.9, 69.6, 79.8, 82.4, 113.2, 117.7 and 154.0 (2 missing resonances); *m/z* (ES) 456.3836 (M^++NH_4) $C_{30}H_{46}O_2$ requires 456.3836); *m/z* (EI) 456.6 (M^++NH_4, 83%) and 439.5 (M^++H, 100).

3.1.23. 1,4-Diethynyl-2,5-dihexadecyloxybenzene 28.[7] 0.51 g, 64%. Yellow solid, mp 87–88 °C (lit. 89–90 °C) (from methanol) δ_H(250 MHz; $CDCl_3$) 0.87 (6H, br t, CH_3), 1.25 (52H, m, $C_{13}H_{26}$), 1.75 (4H, br t, OCH_2CH_2), 3.32 (2H, s, CCH), 3.95 (4H, t, *J*=6.3 Hz, OCH_2) and 6.94 (2H, s, Ar); δ_C(62.9 MHz; $CDCl_3$) 14.1, 22.7, 25.9, 29.2, 29.4, 29.6, 29.7, 32.0, 69.7, 79.8, 82.4, 113.3, 117.7 and 154.0 (7 resonances are missing).

3.1.24. 1,4-Bis[4-(isocyanuric acid)phenylethynyl)-2,5-didecyloxybenzene 29. *General procedure Method 1*. To a stirred solution of *N*-(4-iodophenyl)isocyanuric acid **7**

(0.5 g, 1.14 mmol), 1,4-diethynyl-2,5-dihexyloxybenzene **26** (1.13 g, 3.42 mmol), copper(I) iodide (40 mg, 0.21 mmol), bis(triphenylphosphine)palladium(II) chloride (40 mg, 0.0567 mmol) in anhydrous THF (30 mL) degassed for 20 min, was added freshly distilled anhydrous triethylamine (5 mL). This was left to stir for 24 h, then concentrated and redissolved in fresh tetrahydrofuran and purified by flash column chromatography on silica using initally dichloromethane to elute an orange impurity, followed by tetrahydrofuran. Concentration gave a brown solid which was sonicated first with 10% sodium hydroxide and filtered, then sonicated with 10% hydrochloric acid and filtered to give the title compound (0.87 g, 90%) as a yellow powder, mp >280 °C (from tetrahydrofuran) λ_{max}(THF)/nm 270 (log ε 5.0) and 396 (4.3); ν_{max}(KBr)/cm^{-1} 2952m, 2924m, 2851m, 1754s, 1719vs, 1513w, 1493w, 1441m, 1408w, 1275w, 1217m, 1025w, 870w and 660w; δ_H(400 MHz; THF-d$_8$) 0.56 (6H, br t, CH_3), 0.98 (24H, m, CH_2), 1.27 (4H, m, $CH_2CH_2CH_2O$), 1.53 (4H, m, CH_2CH_2O), 3.74 (4H, t, J=6.1 Hz, OCH_2), 6.78 (2H, s, Ar), 6.97 (4H, d, J=8.6 Hz, Ar), 7.23 (4H, d, J=8.6 Hz, Ar) and 10.34 (4H, br s, NH); δ_C(100.5 MHz; THF-d$_8$) 15.5, 24.6, 28.1, 31.2, 31.3, 31.4, 31.6, 31.7, 33.9, 71.2, 88.8, 95.7, 116.0, 118.6, 125.7, 131.1, 133.4, 150.2, 151.1 and 155.9; m/z (MALDI) 2154.2 (8%), 1717.9 (27) and 1280.6 (94), 847.4 (4), 846.3 (18), 845.3 (56), 844.3 (100) $C_{48}H_{56}N_6Cl_2O_8$ requires 847.4 (3%), 846.4 (17), 845.4 (57), 844.4 (100).

3.1.25. 1,4-Bis[4-(isocyanuric acid)-3-chlorophenylethynyl)-2,5-didecyloxybenzene 30. 0.50 g, 94%. Yellow powder, mp 265 and 289 °C by DSC (from tetrahydrofuran) λ_{max}(THF)/nm 243 (log ε 4.7), 309 (4.7) and 376 (4.6); ν_{max}(KBr)/cm^{-1} 3221w, 3087m, 2923s, 2852m, 2213w, 1792m, 1725vs, 1594m, 1506m, 1490m, 1421s, 1277w, 1216m, 1079m, 759m, 595m and 531m; δ_H(400 MHz; THF-d_8) 0.77 (6H, br t, CH_3), 1.29 (28H, m, C_7H_{14}), 1.75 (4H, m, OCH_2CH_2), 3.95 (4H, br t, OCH_2), 7.05 (2H, s, Ar), 7.30 (2H, br d, Ar), 7.40 (2H, br d, Ar), 7.55 (2H, s, Ar) and 11.75 (4H, s, NH); δ_C(100.5 MHz; THF-d$_8$)14.0, 23.1, 26.6, 29.8, 29.9, 30.1, 30.2, 32.4, 69.7, 88.7, 92.9, 114.2, 117.0, 126.4, 130.7, 131.8, 132.5, 132.6, 134.0, 148.6, 148.8 and 154.5 (1 resonance is missing); m/z (MALDI) 1348.9 (16%) 918.5 (3), 917.5 (8), 916.5 (15), 915.5 (40), 914.5 (78), 913.5 (58) and 912.5 (100) $C_{48}H_{54}N_6Cl_2O_8$ requires 918.3 (2%), 917.3 (8), 916.3 (15), 915.3 (40), 914.3 (80), 913.3 (57) and 912.3 (100).

3.1.26. 1,4-Bis[4-(isocyanuric acid)phenylethynyl)-2,5-dihexadecyloxybenzene 31. 0.44 g, 82%. Pale yellow powder, mp 142–175 °C (from tetrahydrofuran) λ_{max}(THF)/nm 229 (log ε 4.7), 279 (4.8) and 357 (4.5); ν_{max}(KBr)/cm^{-1} 3221br, 3087br, 2921s, 2852m, 1752m, 1716s, 1515m, 1496m, 1442m, 1220m, 760 and 550; δ_H(250 MHz; THF-d$_8$) 0.90 (6H, br d, CH_3), 1.25 (48H, m, $C_{12}H_{24}$), 1.50 (4H, m, CH_2), 1.75 (4H, m, OCH_2CH_2), 3.95 (4H, br t, OCH_2), 7.00 (2H, s, Ar), 7.20 (4H, br d, Ar), 7.45 (4H, br d, Ar) and 10.70 (4H, s, NH); δ_C(62.9 MHz; THF-d$_8$) 14.0, 23.1, 29.4, 29.5, 29.6, 29.7, 29.9, 30.2, 32.4, 69.7, 87.3, 94.2, 114.4, 117.2, 124.2, 129.6, 131.8, 134.7, 148.7, 149.6 and 154.4; m/z (MALDI) 1012.5 (53%), 819.6 (100) 1016.6 (2), 1015.7 (6), 1014.5 (20), 1013.5 (55) and 1012.5 (100) $C_{60}H_{80}N_6O_8$ requires 1016.6 (2%), 1015.6 (7), 1014.6 (25), 1013.6 (70) and 1012.6 (100).

Method 2. To a stirred solution of N-(4-ethynylphenyl)isocyanuric acid **10** (250 mg, 1.09 mmol), 1,4-dihexadecyloxy-2,5-diiodobenzene **21** (0.49 g, 0.606 mmol), copper(I) iodide (15 mg, 0.79 mmol), bis(triphenylphosphine)-palladium(II) chloride (20 mg, 0.029 mmol) in anhydrous THF (40 mL) degassed for 20 min, was added freshly distilled anhydrous Et_3N (2 mL). This was left to reflux for 48 h then concentrated and redissolved in fresh THF to dry load onto a column, and purified by flash column chromatography on silica initially using dichloromethane to elute an orange impurity, followed by tetrahydrofuran. Concentration gave a brown solid which was sonicated first with 10% sodium hydroxide and filtered, then sonicated with 10% hydrochloric acid and filtered to give the title compound (0.44 g, 82%) identical to that reported previously.

3.2. Crystal structure determination[14]

Intensity data were recorded at 150 K, using a Nonius Kappa CCD area-detector diffractometer mounted at the window of a rotating anode FR591 generator with a molybdenum anode (λ=0.71073 Å). ϕ and ω scans were carried out to fill the Ewald sphere. An empirical absorption correction was applied using SORTAV. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares refinements. Crystallographic data: Formula $C_{105}H_{150}N_{24}O_9$; M=1892.49, triclinic space group $P\bar{1}$, unit cell dimensions a=14.0756(11) Å, b=18.494(2) Å, c=22.732(3) Å, α=84.478(8)° β=86.697(9)° γ=69.622(4)°, U=5519.6(10) Å^3, Z=2, D_c=1.139 Mg/m^3, μ(Mo Kα)=0.075 mm^{-1}. Colourless plate, crystal size 0.10×0.02×0.02 mm^3. θ range for data collection 2.3–25.1°; 27,949 collected reflections of which 17,899 are independent [R_{int}=0.142]. Structure refinement with 17,899 data for 1253 parameters, GOF=1.13, final R indices for data with [$F2>2\sigma(F2)$] $R1$=0.1331, $wR2$=0.1690; R indices for all data $R1$=0.2819, $wR2$=0.2008. CCDC 225189.

References and notes

1. Wang, Y.; Wei, B.; Wang, Q. *J. Crystallogr. Spectrosc. Res.* **1990**, *20*, 79–84.
2. Ranganathan, A.; Pedireddi, V. R.; Rao, C. N. R. *J. Am. Chem. Soc.* **1999**, *121*, 1752–1753.
3. Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 905–916.
4. (i) Timmerman, P.; Vreekamp, R. H.; Hulst, R.; Verboom, W.; Reinhoudt, D. N.; Rissanen, K.; Udachin, K. A.; Ripmeester, J. *Chem. Eur. J.* **1997**, *3*, 1823–1832. (ii) Arduini, M.; Crego-Calama, M.; Timmermann, P.; Reinhoudt, D. N. *J. Org. Chem.* **2003**, *68*, 1097–1106. (iii) Bielejewska, A. G.; Marjo, C. E.; Prins, L. J.; Timmerman, P.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2001**, *123*, 7518–7533.
5. (i) Zerkowski, J. A.; Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 5473–5475. (ii) Zerowski, J. A.; Seto, C. T.; Wierda, D. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 9025–9026.
6. (i) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C.-W.; Chen, J.; Wang, W.; Campbell, I. *Chem. Eur. J.* **2001**, *23*,

5118–5134. (ii) Kang, S. K.; Ryu, H. C.; Hong, Y. T. *J. Chem. Soc., Perkin Trans. 1* **2001**, *7*, 736–739.

7. (i) Pelter, A.; Jones, D. E. *J. Chem. Soc., Perkin Trans. 1* **2000**, *14*, 2289–2294. (ii) Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886–4893.
8. Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593–12602.
9. Maruyama, S.; Kawanishi, Y. *J. Mater. Chem.* **2002**, *12*, 2245–2249.
10. Mohr, B.; Enkelmann, V.; Wegner, G. *J. Org. Chem.* **1994**, *59*, 635–638.
11. Peng, Z.; Gharavi, A. R.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 4622–4632.
12. Kuroda, K.; Swager, T. M. *J. Chem. Soc., Chem. Commun.* **2003**, 26–27.
13. We have named this proposed network 'The Garden of Eden' owing to its aesthetic symmetry and its anticipated potential, with mixtures of modified melamines, to mimic a process by which life might have originated on earth. The Garden of Eden described in the Bible is not ascribed hexagonal symmetry though. The painting by Masaccio 'Adam and Eve Banished from Paradise' (1424–1428), Brancacci Chapel, Florence, Italy, depicts the descent of Adam and Eve, hence 'life' from The Garden of Eden.
14. Data collection and cell refinement: Otwinowski, D. Z.; Minor, W. *Methods Enzymol.* **1997**, 276–307. Carter, C. W., Jr., Sweet, R. M., Eds. Macromolecular crystallography, part A; Academic, pp 307–326. Blessing, R. H. Absorption correction. *SORTAV Acta Crystallogr.* **1995**, *A51*, 33–38. Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421–426. Sheldrick, G. M. Structure solution and refinement: SHELXS97. *Acta Crystallogr.* **1990**, *A46*, 467–473. Sheldrick, G. M. *SHELXL97*; University of Göttingen: Germany, 1997. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 225189 **1**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).