Charge-Transfer Diamondoid Lattices: An Unprecedentedly Huge and Highly Catenating Diamondoid Network Arising from a Tetraphenol as a Tetrahedral Node and Benzoquinone as a Linear Spacer**

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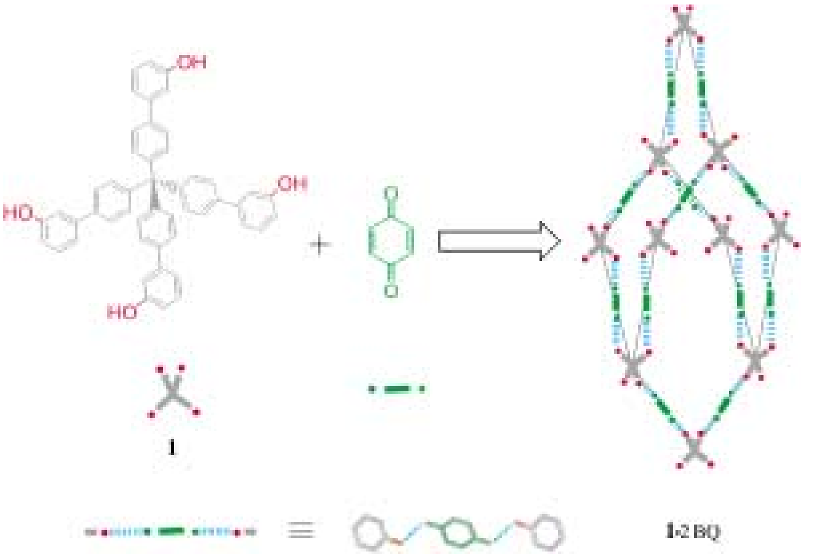
Diamondoid lattices have been a subject of intense recent attention in the area of crystal engineering.[1] Organic,[2–4] organometallic,[5] and inorganic[6] diamondoid materials can be obtained by connecting tetrahedral centers. Metallic or organic components of T_d symmetry as tetrahedral nodes may be assembled by covalent linkage, metal coordination, hydrogen bonding, or donor–acceptor interaction as a node connector. In particular, self-complementary multiple hydrogen bonding has been used to link tetrahedral carboxylic acid,[2] amide (pyridone),[3] and diaminotriazine[7] derivatives. To the best of our knowledge, all known hydrogen-bonded organic diamondoid materials obtained so far are unimolecular species.[2, 3] An interesting extension would be to develop multicomponent organic diamondoid networks, especially from the viewpoint of functional materials design, whereas the use of linear spacers as hydrogen-bonded node connectors remains a challenge.[8] Another point of fundamental importance is how large the superadamantane framework could be and, if the huge cavity left is to be filled by self-clathration, how high the extent of interpenetration or polycatenation would be. Here we report the crystal structure of the hydrogen-bonded 1:2 complex of tetrakis[4-(3-hydroxyphenyl)phenyl]methane (**1**) and benzoquinone (BQ). We notice the largest known (76 Å) superadamantane framework that undergoes the highest recorded (11-fold) catenation, which results in alternate donor–acceptor (phenol–quinone) charge-transfer stacking.



Scheme 1. Formation of a hydrogen-bonded superadamantane framework from **1** and benzoquinone. The benzene rings, quinone guests, and OH groups are in gray, green, and red, respectively, and hydrogen bonds are shown in blue.

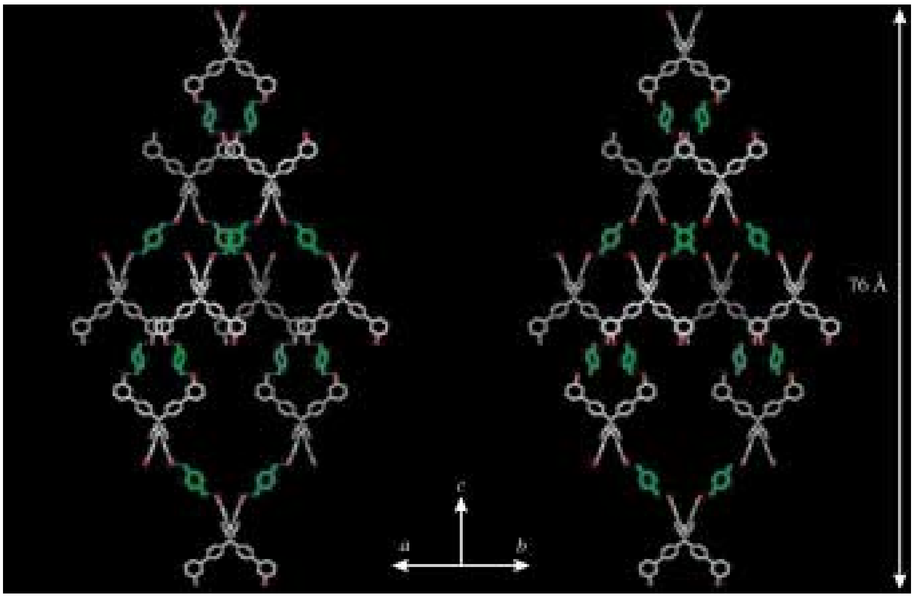


Figure 1. Stereoview of the hydrogen-bonded superadamantane framework in the crystal structure of the adduct **1**·2BQ. The colors have the same meanings as in Scheme 1.

Slow evaporation of an ethanol solution of **1** and benzoquinone afforded brilliantly red crystals of a 1:2 adduct **1**·2BQ (Scheme 1).[9] The crystal packing of this adduct reveals a hydrogen-bonded (O⋯O bond length 2.84 Å) phenol–quinone–phenol triad with a phenol–quinone interplanar angle of 55.6° (Scheme 1). Compound **1** is linked with four quinone molecules in this way. This arrangement leads to an infinite hydrogen-bonded diamondoid network with the tetraphenol **1** as a tetrahedral node and the quinone as a spacer. The resultant superadamantane framework with a tetragonal elongation, as in the case of methanetetraacetic acid,[2b] is illustrated schematically in Scheme 1 and its actual crystal structure is shown in Figure 1. It is composed of 22 organic molecules (10 of **1** and 12 of quinone) linked together

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by 24 single O–H$\cdots$O hydrogen bonds and represents the largest superadamantane lattice known with a top-to-bottom length of 76 Å; the adjoining tetrahedral nodes are separated by 23 Å. The cavity is filled by self-clathration along the tetragonal *c* axis to give an 11-fold nonconnected interpenetration (catenation) of the networks separated from each other by 6.9 Å, as illustrated in Figure 2, where only one quinone column is shown for clarity. The observed 11-fold catenation is the highest degree of interpenetration known. The 9-fold catenation of $[Ag(4,4'\text{-biphenyldicarbonitrile})_2]^+PF_6^-$ was the highest previously recorded.[10]

A set of polycatenated **1**–quinone–**1** arrays is shown in Figure 3, together with its plan view. Thus, the acceptor (quinone) column is surrounded by the framework of four donor (phenol) columns along its *c* axis (Figure 3b). In the direction perpendicular to this axis, there is alternate donor–acceptor stacking (Figure 3a) roughly of the face-to-face type (the shortest interatomic distance between the phenol and quinone units is ca. 3.3 Å, the interplanar distance is ca. 4.5 Å, and the interplanar angle 30°), which might be the origin of charge-transfer coloration.

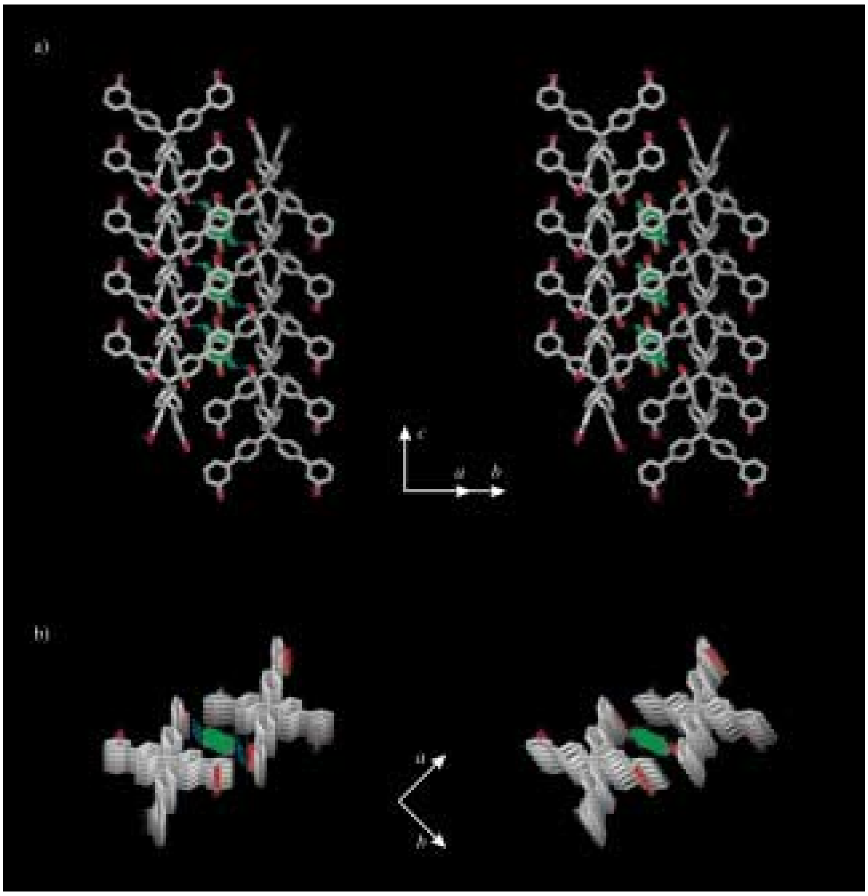

Figure 3. a) Stereoview of a set of polycatenated **1**–quinone–**1** arrays, showing alternate phenol–quinone stacking; b) plan view of (a). The colors have the same meanings as in Scheme 1.

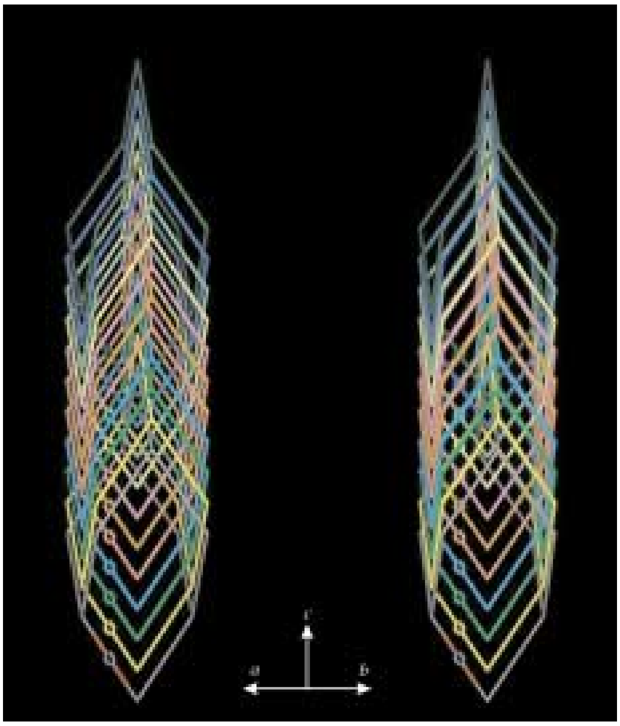

Figure 2. Schematic stereoview of the 11-fold catenation of the hydrogen-bonded superadamantane frameworks, shown in different colors, in the crystal structure of adduct **1**$\cdot$2BQ, in which only one quinone column is shown for clarity.

The quinone-mediated dimerization of phenols may be compared to the dimerization of carboxylic acids. As the zero-, one-, and two-dimensional hydrogen-bonded nets found in 2:1 hydroquinone:benzoquinone,[11a] 1:1 hydroquinone:benzoquinone,[11b] and 1:2 anthracenebisresorcinol:benzoquinone[12] complexes correspond to those of benzoic, terephthalic,[13] and trimesic[14] acids, so does the present three-dimensional net compare to that of adamantane-1,3,5,7-tetracarboxylic acid[2a] or methanetetraacetic acid.[2b]

Experimental Section

1: A mixture of tetrakis(4-bromophenyl)methane (3.3 g, 5.18 mmol), 3-methoxyphenylboronic acid (5.0 g, 33.3 mmol), and $[Pd(PPh_3)_4]$ (300 mg, 0.25 mmol) in a 1/1 mixture (20 mL) of THF and 1N aqueous Na_2CO_3 was heated at 80°C for 48 h. The usual workup procedure gave 3.29 g (84%) of tetrakis[4-(3-methoxyphenyl)phenyl]methane, which was demethylated with a stoichiometric amount of BBr_3 in dry CH_2Cl_2 at room temperature for 12 h to give **1**: ^1H NMR (400 MHz, $[D_6]$DMSO, 25°C, TMS): $\delta = 6.75$ (m, 4H), 7.09 (m, 8H), 7.38 (m, 11H), 7.61 (m, 8H), 9.51 (s, 4H; OH). Adduct **1**$\cdot$2BQ was obtained by slow evaporation of an ethanol solution of a 1:2 mixture of compound **1** and benzoquinone; elemental analysis for $C_{61}H_{44}O_8$ (904.97): calcd: C 80.96, H 4.89; found: C 80.63, H 4.97.

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[9] Crystal data for $\mathbf{1}\cdot 2\,BQ$: $[C_{61}H_{44}O_8]$, $M = 905.01\ \mathrm{g\,mol^{-1}}$, crystal dimensions $0.05 \times 0.05 \times 0.05$ mm, tetragonal, space group $I4_1/a$ (No. 88), $a = 25.753(3)$, $b = 6.909(3)$ Å, $V = 4582(1)$ Å^3, $Z = 4$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.86\ \mathrm{cm^{-1}}$, $2\theta_{max} = 54.9°$, $T = 273$ K, $\rho_{calc} = 1.312\ \mathrm{g\,cm^{-3}}$, $F(000) = 1896$; 2836 unique reflections, 710 observed reflections with $I > 2\sigma(I)$, 157 parameters, $R = 0.071$, $Rw = 0.10$, GOF = 1.64, shift/esd$_{max} = 0.01$, residual electron density $= -0.21\ \mathrm{e\,Å^{-3}}$. The poor quality of the reflection data is at least partly due to the small size of the crystals obtained. Data collection on a Rigaku AFC7R diffractometer by using a ω-2θ scan. The structure was solved by direct methods (SHELXS 86) and refined using the full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were fixed at calculated positions. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143768. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Catalyst Screening Using an Array of Thermistors[**]

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The use of combinatorial techniques to discover and optimize chemical and biological catalysts is becoming increasingly widespread.[1] Methodology for the production of catalyst libraries is now advanced, particularly in the case of biological catalysts with the advent of DNA shuffling and error-prone PCR.[2] Efficient screening methodology is less advanced; although the literature abounds with ingenious screens contrived to suit a particular reaction there are few general screens. Recently IR thermography has emerged as a potentially general technique to monitor reactions associated with a temperature change.[3] Several groups, notably those of Reetz[3a, 3b] and Morken,[3c] have demonstrated the power of IR thermography in catalyst screening, but the method suffers from a number of problems including relatively low resolution of temperature change (±10 mK), the requirement for visualization to be effected through IR-transparent materials, and inconvenient data analysis techniques. In pioneering work Danielsson and co-workers have demonstrated the use of thermistors to monitor temperature changes downstream of an immobilized enzyme in a continuous flow of substrate.[4] We now report that a multiplexed array of thermistors can be used as an alternative to IR thermography for chemical and biochemical catalyst screening.

The apparatus we constructed is shown in Figure 1. A commercially available 96-well plate dispenser (Multi-

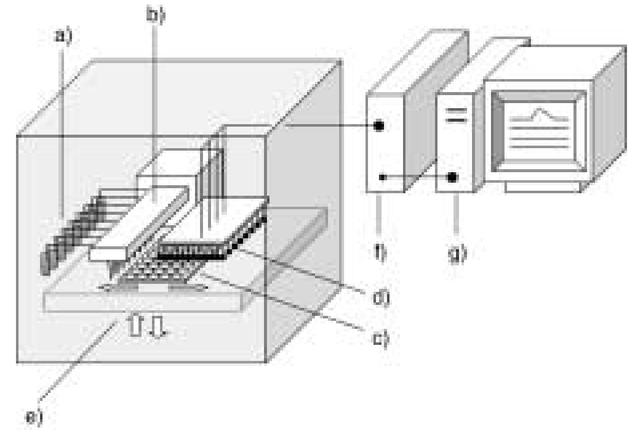

Figure 1. Thermistor array apparatus comprising: a) 8 reagent/substrate reservoirs, b) an 8-channel dispensing head, c) a 96 well plate and holder (movable in x-dimension), d) an 8×12 thermistor array, e) a base plate (movable in z-dimension), f) a multiplexing apparatus, g) a microcomputer.

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