Two-Dimensional Carbon Compounds Derived from Graphyne with Chemical Properties Superior to Those of Graphene

Jia-Jia Zheng1,2, Xiang Zhao1, Yuliang Zhao2 & Xingfa Gao2,3

1Institute for Chemical Physics & Department of Chemistry, State Key Laboratory of Electrical Insulation and Power Equipment, Xi’an Jiaotong University, Xi’an 710049, China, 2CAS Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China, 3College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China.

Computational studies considering both thermodynamic and kinetic aspects revealed that graphyne, a carbon material that has recently been of increasing interest, favours unprecedented homogeneous “in-plane” addition reactions. The addition of dichlorocarbene to the C(sp)-C(sp) bond, a site with outstanding regioselectivity in graphyne, proceeds via a stepwise mechanism. Due to their homogeneous nature, additions occurring at C(sp)-C(sp) bonds yield structurally ordered two-dimensional carbon compounds (2DCCs). 2DCCs have electronic band structures near the Fermi level that are similar to those of graphene and are either electrically semi-conductive or metallic depending on whether the reactions break the hexagonal symmetry. Notably, 2DCCs can be further functionalised through substitution reactions with little damage to the extended π-electron conjugation system. These results suggest that 2DCCs derived from graphyne have physical properties comparable to those of graphene and chemical properties superior to those of graphene. Therefore, 2DCCs are expected to be better suited to practical applications.

Carbon is able to make chemical bonds with nearly all elements in the periodic table, including itself. It can adopt three types of hybridisation, sp, sp2 and sp3. These types of hybridisation result in the formation of carbon geometries with linear, trigonal planar and tetrahedral shapes, respectively. Among hybridised carbons, sp3 carbons form σ bonds with electrons that are primarily confined to the vicinity of the carbons, whereas sp and sp2 carbons form conjugated π bonds with delocalised electrons. This versatile bonding ability makes carbon the key building atom for organic compounds, which are the basis of not only life but also modern organic electronics.

The first characterised carbon allotrope consisting of sp2 carbon is graphite. Graphite has a planar, multi-layered structure, with each layer consisting of sp2 carbons arranged in a hexagonal lattice. It exists abundantly in nature and has a variety of uses, e.g., as pencil lead, lubricants and anodes in battery technologies. Polyacetylene is a stable organic polymer with repeating sp2 carbon dimers (HC=CH) along the polymer chain that is electrically semi-conductive. After functional doping, the conductivity of polyacetylene can be strikingly increased1, and therefore this polymer is well known as an “electrically conductive plastic”. In addition to graphite and polyacetylene, sp2 carbon atoms are found in polycyclic aromatic hydrocarbons (PAHs)3, which are two-dimensional organic π-systems with sizes ranging from several to several tens of nanometers. PAHs have served as important models for molecular orbital theory and spectroscopy and also have potential applications in organic electronics. Experimental observations of fullerenes in 19854, carbon nanotubes (CNTs) in 19915 and graphene in 20046 spurred renewed interest in sp2 carbon materials. Because of their unprecedented structures, electronic properties and versatility in applications, fullerenes, CNTs and graphene have attracted intense and sustained interest in multidisciplinary fields in recent decades.

These sp2 carbon materials have a common feature: with the exception of polyacetylene, these materials have molecular surfaces that consist almost entirely of sp2 carbon atoms forming extended π-electron conjugation systems, which provide the foundation for their intriguing electronic properties. Chemical functionalisation of these materials is usually necessary prior to practical use. For example, the solubility of sp2 carbon materials must be increased to permit their use in biological systems. Depending on their structural composition, sp2 carbon materials can be functionalised via chemical addition reactions in which the carbon atoms are converted from sp2 to sp3 hybrids to bond with the chemical groups being added. Such addition reactions unavoidably disrupt the
extended π-conjugation system (Figure 1a). The deterioration of π-conjugation can severely damage the electronic performance, which is based on the conjugated system. For example, after solubilisation via oxidation reactions, the electrical conductivity of CNTs and graphene may be reduced by more than a thousandfold. Furthermore, addition reactions on sp² materials such as graphene usually proceed in an aggregate manner, making the functionalisation process difficult to control.

In this work, we propose a new type of two-dimensional carbon compound (2DCC, Figure 1b). 2DCCs have large extended π-conjugation systems and electronic properties similar to those of graphene. Unlike graphene, they may have intrinsic components suitable for chemical substitution reactions (e.g., the H and OH groups in III and IV are substitutable, Figure 1b). Consequently, 2DCCs can be functionalised through chemical substitution rather than addition, therefore eliminating the loss of π-conjugation. Structurally, these 2DCCs can be viewed as derivatives of graphyne, a 2D carbon sheet consisting of sp and sp² carbon atoms. By considering both thermodynamic and kinetic aspects, we computationally studied addition and multiple addition reactions of graphyne. For the first time, we found that graphyne favours homogeneous “in-plane” addition reactions, which can lead to the formation of 2DCCs. The resulting 2DCCs can be semi-conductive or metallic depending on whether the additions break the hexagonal symmetry. After functionalisation via chemical substitution reactions, these 2DCCs retain electronic band structures near the Fermi level. For example, 2DCC IV (Figure 1b) is expected to exhibit considerable electric conductivity and aqueous solubility simultaneously, making it suitable for use in biological systems and under other aqueous conditions. This simultaneous electric conductivity and aqueous solubility is a unique feature not shared by conventional sp² carbon materials. The results suggest that 2DCCs are a conceptually new family of carbon materials that have physical properties comparable to those of graphene and chemical properties superior to those of graphene. Therefore, 2DCCs are expected to be better suited to chemical tailoring and applications.

**Results**

Homogeneous “in-plane” reactivity. 2DCCs can be regarded as derivatives of graphyne, a 2D material consisting of sp and sp² carbon atoms. Although the structural and electronic properties of graphyne have been extensively studied experimentally and theoretically, only a few studies have been devoted to its chemical properties. Therefore, we first studied the reactivity of graphyne to explore the feasibility of deriving 2DCCs from this material. The sp and sp² carbons of graphyne can form three types of carbon-carbon bonds: sp-sp, sp-sp² and sp²-sp². All of these bond types can be found in β-graphyne (Figure 2a). Therefore, we first focused on β-graphyne in the reactivity study. For simplicity and without loss of generality, the epoxidation reaction of β-graphyne was considered first.

The addition of one oxygen atom into a unit cell of β-graphyne may yield four possible atomic arrangements. Figures 2b and 2c show configurations with oxygen added to the carbon triple bond (sp-sp), while Figures 2d and 2e show those with oxygen added to the sp-sp² and sp²-sp² bonds, respectively. The epoxidation of the sp-sp² and sp²-sp² bonds gives “on-top” products, with oxygen protruding upwards from the basal plane of graphyne (Figures 2d and 2e). This “on-top” configuration is characteristic of addition products of sp² carbon materials and has previously been reported for fullerenes, carbon nanotubes and graphene. In sharp contrast, the epoxidation of sp-sp bonds yields amazing “in-plane” products in which the oxygen lies within the basal plane of graphyne (Figures 2b and 2c). This “in-plane” configuration perfectly maintains the planarity of pristine graphyne. Interestingly, the “in-plane” configuration shown in Figure 2b is thermodynamically more stable than the “on-top” configurations: (b) is lower in energy than (d) and (e) by 15.4 and 21.2 kcal mol⁻¹ per unit cell, respectively. The “in-plane” structure of (c) is thermodynamically less stable than that of (b) by
15.7 kcal mol$^{-1}$. Obviously, the lower stability of (c) relative to (b) can be ascribed to that the additional oxygen in (c) is located in a 12-membered ring (12-MR), whereas the oxygen in (b) is in an 18-membered ring (18-MR). Therefore, (c) is more sterically hindered than (b). The “on-top” configuration (e) is less stable than the “on-top” configuration (d) by 5.8 kcal mol$^{-1}$. This result is in agreement with the fact that (d) is produced by addition to the sp$^2$-sp$^2$ carbon bond of graphyne, which is more chemically “unsaturated” than the sp$^2$-sp$^2$ bond, the addition site for (e).

The thermodynamic selectivity for addition to various bonds is in accordance with the bond lengths. The lengths of the sp-sp, sp-sp$^*$ and sp$^*$-sp$^*$ bonds in β-graphyne are calculated to be 1.23, 1.39 and 1.46 Å, respectively (Figure 2a). For these bonds, a shorter bond length indicates a greater degree of chemical unsaturation, and consequently, greater reactivity. Reactions occurring at the shortest sp-sp bonds thus release the most energy and result in the most thermodynamically stable adducts. The right panel of Figure 2a shows the unhybridised $p_x$ and $p_y$ orbitals for representative carbons of β-graphyne. All $p_y$ orbitals are orthogonal to $p_x$ orbitals. The $p_x$ orbitals are perpendicular to the basal plane of graphyne, are distributed on all carbons and contribute to the extended π-electron conjugation system; the $p_y$ orbitals lie in the basal plane of graphyne and are distributed only on sp carbons. During the “in-plane” additions, the adatoms react only with the $p_y$ orbitals of sp carbons, resulting in little change to the orthogonal $p_x$ orbitals and the extended π-electron conjugation. Therefore, “in-plane” reactions provide a unique approach to the covalent functionalisation of graphyne while simultaneously maintaining electronic properties near the Fermi level. This behaviour is in sharp contrast to that of conventional sp$^2$ carbon materials such as fullerenes, carbon nanotubes and graphene, for which any covalent functionalisation severely changes their electronic properties.

We further studied the kinetic selectivity of the three different carbon-carbon bonds of graphyne by investigating their reactions with dichlorocarbene (CCl$_2$), a reactive species that has been previously used for the functionalisation of fullerenes and carbon nanotubes$^{21,22}$. Similar to oxygenation (Figures 2b–2d), four sites in β-graphyne are able to form unique products with CCl$_2$. These sites are labelled 1 through 4 in the cluster model of graphyne (insert of Figure 3). The corresponding products are denoted as p1 through p4. Since the solvent effect and biradical character were found to have slight influences on the reaction barriers and thermodynamics for dichlorocarbene additions (Fig. S1 and Table S1 of Supplementary Information), we will focus on the reaction pathways in the gas phase in the following discussion. As shown in Figure 3, p1, in which the CCl$_2$ group is added to site 1 (i.e., the sp-sp bond) and located in the 18-MR side, has the greatest exothermicity, with a reaction energy ($E_r$) of $-56.2$ kcal·mol$^{-1}$. The $E_r$ values of p2, p3 and p4
are approximately 18.0, −35.8 and −39.8 kJ mol⁻¹, respectively. The thermodynamic preference of CCl₂ for reacting with the sp-sp bond from the 18-MR side was confirmed by extended-model calculations with periodic boundary conditions (Supplementary Fig. S3), in good agreement with the above results for graphyne oxygenation. The Eₘ of 18.0 kJ mol⁻¹ for p₂ suggests that the formation of p₂ is not thermodynamically favoured. This thermodynamic unavailability can be ascribed to the high steric repulsion encountered when inserting a CCl₂ group into a small 12-MR.

According to Figure 3, the most convenient pathway to p₁ corresponds to a stepwise mechanism. In the first step, CCl₂ approaches the sp-sp bond to form intermediate int₁ via transition state ts₁. The activation energy (Eᵃ) of this step is 6.5 kJ mol⁻¹. In int₁, the CCl₂ moiety is nearly perpendicular to the graphyne plane. In the second step, the CCl₂ of int₁ rotates to lie in the 18-MR to form p₁ with an activation energy of 3.2 kJ mol⁻¹. The small Eᵃ of both steps suggests that the formation of p₁ via the reaction of CCl₂ and graphyne is very facile. Figure 3 also shows the reaction paths for p₃ and p₄: p₄ is linked to p₃ via ts₃, with Eᵃ = 26.8 kJ mol⁻¹; p₃ is linked to int₁ via ts₄, with Eᵃ = 11.2 kJ mol⁻¹. Thus, p₃ and p₄, if formed, will readily transform into p₁ upon thermal annealing. Hence, the formation of p₁ is uniquely favoured with respect to both thermodynamic and kinetic aspects, suggesting that the sp-sp bond of β-graphyne is highly regioselective in chemical reactions. A similarly high regioselectivity is also observed for the sp-sp bond of α-graphyne (Supplementary Fig. S4).

Another important issue regarding graphyne reactivity is its regioselectivity in multiple addition reactions. Reportedly, sp² carbon materials (fullerenes, carbon nanotubes and graphene) thermodynamically favour an inhomogeneous mode of multiple additions in which chemical groups tend to be added aggregately so as to destroy fewer π-bonds and maintain a larger π-conjugated area. Such inhomogeneous additions yield products consisting of separated areas of sp² and sp carbon. Because the “in-plane” addition reactions of graphyne cause no damage to the π-electron conjugation system, the inhomogeneous mode should not predominate for graphyne.

Indeed, we observed that graphyne tends to undergo multiple addition reactions homogeneously. Depending on their orientations, the sp-sp bonds of α-graphyne can be classified into three groups: sites I, II and III, which are perpendicular to the three arrows in Figure 4a. To study multiple additions, we added four H₂ molecules to four sp-sp bonds of a 2 × 2 supercell of α-graphyne using different combinations of the three types of sp-sp bonds. The addition of H₂ to two adjacent sp-sp bonds of α-graphyne can occur in two different ways, yielding the armchair (Figure 4b) and zigzag (Figure 4c) configurations for the hydrogenated carbon chains. The armchair configuration (Figure 4b) was found to be lower in energy than the zigzag one (Figure 4c) by 0.9 kJ mol⁻¹. Consequently, we focused on the armchair configurations when adding four H₂. We exhausted the armchair products and then calculated their energies after full geometry optimisations (Supplementary Fig. S5). Figure 4d presents the results. Along the absissa app: addword: abscissa of Figure 4d, 4S₁

**Figure 3 | Energy profiles for CCl₂ additions to α-graphyne calculated with the B3LYP/6-31G(d) method.** The insert panel shows the cluster model of graphyne used in the calculations. Numbers 1 through 4 denote the addition sites; p₁ through p₄ represent the products in which CCl₂ was added to sites 1 through 4, respectively. The unit of energy is kJ mol⁻¹. C, green; Cl, brown; H, light blue.

**Figure 4 | Thermodynamic selectivity of multiple hydrogenations of α-graphyne.** (a) Sites I, II and III represent three groups of sp-sp bonds perpendicular to the dashed arrow lines. (b) and (c) are two different atomic arrangements for H₂ additions occurring at neighbouring sp-sp bonds. (d) Relative energies of the products with four H₂ molecules added to the different positions of a 2 × 2 supercell of α-graphyne. C, green; H, light blue.
corresponds to the products in which the four H2 were all added to site I sp-sp bonds; 3SII–1SIII represents the products with three and one H2 added to site I and site II; 2SII–2SIII denotes the products with the four H2 added equally to site II and site III; and 2SII–1SII–1SIII are the products with two H2 added to site I and one each added to site II and site III, respectively. The numbers of symmetrically unique products belonging to the series of 4SII, 3SII–1SIII, 2SII–2SIII and 2SII–1SII–1SIII were found to be 1, 3, 7 and 8. This increase in the number of products is consistent with the fact that more types of sp-sp bonds are reacted in the products along the series. Figure 4d shows that the energy barrier for the addition of H2 to the sp-sp bond of graphyne has been estimated to be 48.4 kcal mol\(^{-1}\). Therefore, it is predicted that the hydrogenation of graphdiyne by H2 requires a catalytic pathway\(^2\)\(^5\). As shown in Figure 4, H-2DCC, F-2DCC and O-2DCC have electronic band structures calculated by DFT methods, the middle panel shows the 2 \times 2 supercell of the structure, and the bottom panel shows the symmetry of the hexagonal lattice. C, green; H, light blue; F, magenta; O, red.

**Electronic band gap tuning.** Owing to the zero band gap of graphene, graphene transistors have small on/off ratios, typically less than 10\(^{-2}\). As a result, graphene transistors are hard to turn off, preventing their application in electronic devices. Chemical addition reactions such as hydrogenation\(^2\)\(^9\) and oxidation\(^2\)\(^9\) have been proposed to open the band gap of graphene. To open large band gaps by these reactions, dispersive additions following certain patterns are required\(^2\)\(^9\)\(^-\)\(^3\)\(^1\). However, because graphene thermodynamically prefers aggregate additions\(^3\)\(^2\)\(^3\)\(^2\), the gap-opening process is difficult to control. Moreover, since this gap opening occurs at the expense of the conversion of the carbons of graphene from sp\(^2\) to sp\(^3\) hybrids, the electron mobility of graphene deteriorates severely after gap opening.

Graphyne also has the gapless problem\(^1\)\(^0\)\(^-\)\(^1\). Here, we predicted that the band gap opening of graphyne can be achieved via hexagonally asymmetric addition reactions. Due to the homogeneous “in-plane” reactivity of graphyne, such gap opening should be easy to control and free from substantial electron-mobility reduction. Figures 5a–5e show the 2 \times 2 hexagonal supercells and electronic band structures of graphyne, H-2DCC, F-2DCC, HF-2DCC and O-2DCC (see, respectively, the middle and top panels for each species). The latter four species are derivatives of graphyne while maintaining its main electronic properties. This ability is in agreement with the above fascinating characteristics of “in-plane” addition reactions, which tune the band gaps of graphene while maintaining its main electronic properties. This ability is in agreement with the above
finding that “in-plane” addition reactions have little effect on the \( p_z \) orbitals and the extended \( \pi \)-electron conjugation system of graphyne.

The band gap openings of HF-2DCC, O\(_{2/3}\)-2DCC and O\(_{1/3}\)-2DCC can be understood based on their non-hexagonally symmetric addition patterns. For HF-2DCC, the additions of H and F divide the six corner carbons of \( \alpha \)-graphyne’s 18-MR into two types with different chemical environments: one is C(CH)\(_3\), i.e., an \( sp^3 \) carbon bonded to three CH units, and the other is C(CF)\(_3\), i.e., an \( sp^3 \) carbon bonded to three CF units. By contrast, the chemical environments of the six edges of the 18-MR are identical, with each edge consisting of a C-C-(H)-(C)-(F)-C unit linked to two other such units through a shared carbon. Therefore, the symmetry-breaking pattern of HF-2DCC can be represented by the bottom panel of Figure 5d, in which the corners belong to two different types while the six edges are identical. In terms of O\(_{2/3}\)-2DCC, the six corner carbons of the 18-MR are symmetrically identical, whereas the edges can be classified into two types, with and without oxygen. Therefore, O\(_{2/3}\)-2DCC has a different symmetry-breaking pattern, as shown in the bottom of Figure 5f. Similarly, one can understand the symmetry-breaking pattern for O\(_{1/3}\)-2DCC and that the additions in H-2DCC, F-2DCC and O-2DCC do not break the hexagonal symmetry. Therefore, according to Figure 5, the band gap openings of HF-2DCC, O\(_{2/3}\)-2DCC and O\(_{1/3}\)-2DCC can be ascribed to their hexagonally asymmetric addition patterns, whereas the band gap closings of H-2DCC, F-2DCC and O-2DCC can be ascribed to the hexagonal symmetry of their addition patterns. A similar symmetry-breaking mechanism for band gap opening also holds for graphane\(^{16,39}\) and has been previously used to open graphene’s band gap.

The band gap evolution of graphyne with respect to the extent of addition reactions is strikingly different from that of graphene. When graphene is fully reacted with chemical addition groups, the resulting products have a wide band gap. For example, the band gap of fully hydrogenated graphyne (i.e., graphene) is over 4.0 eV, being electrically insulating\(^{2,21,22}\). By contrast, a metallic to semiconductive transition occurs in solvents such as dichlorobenzene and toluene, the respective solvent structures in the reaction paths, which confirmed the structures to be minimal or transition states. Because dichloroacarbene addition and O-2DCC isomerisation usually occur in solvents such as dichlorobenzene and toluene, the respective solvent effects were further evaluated via single-point (SP) energy calculations with the polarisable continuum model (PCM)\(^{23}\) using B3LYP/6-31G(d)-optimised geometries. For dichloroacarbene additions, energy profiles considering a biradical character and the effect of a larger basis set were also computed via SP calculations. The results of these SP calculations are presented in Fig. S1, Table S1 and Table S2 of the Supplementary Information.

**Discussion**

The above thermodynamic and kinetic data consistently suggest the high regioselectivity of the \( sp-sp \) bonds in graphyne. These bonds undergo homogeneously “in-plane” addition reactions, perfectly maintaining the planarity of graphyne without damaging the extended \( \pi \)-electron conjugation system. Therefore, graphyne can serve as an ideal precursor to produce structurally ordered 2DCCs, whose electronic structures are predicted to be semi-conductive or metallic depending on whether the additions break the hexagonal symmetry. Interestingly, the “in-plane” addition of chemical species with substitutable groups to graphyne, such as Cl\(_2\), Cl\(_2\)H, yields 2DCCs capable of undergoing substitution reactions. Substitution reactions can also be used to adjust the band gap of graphyne according to the same hexagonal-symmetry breaking mechanism while causing little deterioration to the extended \( \pi \)-electron conjugation system. These chemical properties are not shared by conventional \( sp^2 \) carbon materials such as graphene. The results suggest that 2DCCs are a conceptually new family of carbon materials with physical properties comparable to those of graphene and chemical properties superior to those of graphene. Therefore, 2DCCs are expected to be better suited for chemical tailoring and practical applications.

**Methods**

Geometry optimisation and electronic structure calculations were performed with the Vienna Ab-initio Simulation Package (VASP)\(^{24}\). The generalized gradient approximation (GGA) with the exchange-correlation functional of the Perdew-Burke-Ernzerhof functional (PBE)\(^{25}\) was employed. The ion-electron interaction was described using the projector-augmented wave method\(^{26}\) with a kinetic energy cut-off of 500 eV, and the convergence criterion in the self-consistency process was set to 10\(^{-5}\) eV. The vacuum space along the Z direction was 15 Å, which is sufficiently large to prevent interaction between the nearest images. For the geometry optimisations of a unit cell and a 2 \( \times \) 2 supercell, \( 7 \times 7 \times 1 \) and \( 3 \times 3 \times 1 \) Monkhorst-Pack meshes\(^{30}\) of \( k \) points were used, respectively, to sample the first Brillouin zone.

**Table 1 | Calculated Fermi velocities \( v_F \) and effective masses of holes and electrons \( m_{h/e} \)** near the Dirac points along the K\( \Gamma \) direction for \( \alpha \)-graphyne, H-2DCC, F-2DCC and O-2DCC. The Fermi velocity and effective masses of carriers for graphene are taken from ref. 33 and 5.

|  | **graphene** | **\( \alpha \)-graphyne** | **H-2DCC** | **F-2DCC** | **O-2DCC** |
|---|---|---|---|---|---|
| \( v_F \) [m/s] | \( -1 \times 10^8 \) | \( 6.34 \times 10^3 \) | \( 5.67 \times 10^3 \) | \( 4.72 \times 10^3 \) | \( 3.27 \times 10^3 \) |
| \( m_{h} \) [m\(_h\)] | \( -0.06 \) | \( 0.34 \) | \( 0.77 \) | \( 0.93 \) | \( 1.74 \) |
| \( m_{e} \) [m\(_e\)] | \( -0.03/-0.1 \) | \( 0.32 \) | \( 0.77 \) | \( 0.69 \) | \( 1.04 \) |

1. Chiang, C. K. et al. Electrical conductivity in doped polyacetylene. *Phys. Rev. Lett.* **39**, 1098–1101 (1977).
2. Randić, M. Aromaticity of polycyclic conjugated hydrocarbons. *Chem. Rev.* **103**, 3449–3605 (2003).
3. Kroto, H. W., Heath, J. R., O’Brien, S. C., Curl, R. F. & Smalley, R. E. C. 60: Buckminsterfullerene. *Nature* **318**, 162–163 (1985).
4. Iijima, S. Helical microtubules of graphitic carbon. *Nature* **354**, 56–58 (1991).
5. Novoselov, K. S. et al. Electric field effect in atomically thin carbon films. *Science* **306**, 666–669 (2004).
6. Baughman, R. H., Eckhardt, H. & Kertesz, M. Structure property predictions for novel planar forms of carbon: Layered phases containing sp2 and sp atoms. *J. Chem. Phys.* **87**, 6687–6699 (1987).
7. Bunz, U. H. F., Rubin, Y. & Tohe, T. Polyethylene and cationic \( \pi \)-systems: scaffolds for novel two- and three-dimensional carbon networks. *Chem. Soc. Rev.* **28**, 107–119 (1999).
8. Diederich, F. Carbon scaffolding: building acetylenic all-carbon and carbon-rich compounds. *Nature* **369**, 199–207 (1994).
9. Narita, N., Nagai, S., Suzuki, S. & Nakao, K. Optimized geometries and electronic structures of graphyne and its family. *Phys. Rev. B* **58**, 11009–11014 (1998).
10. Malko, D., Neiss, C., Vines, F. & Gorling, A. Competition for graphene: Graphynes with direction-dependent Dirac cones. *Phys. Rev. Lett.* **108**, 086804 (2012).
11. Kim, B. G. & Choi, H. J. Graphyne: Hexagonal network of carbon with versatile Dirac cones. *Phys. Rev. B* **86**, 115435 (2012).
12. Kehoe, J. M. et al. Carbon networks based on dehydrobenzoannulenes. *Synthesis of graphene substructures*. *Org. Lett.*, 2, 969–972 (2000).
13. Haley, M. M. Synthesis and properties of annulenic subunits of graphyne and graphdiyne nanoarchitectures. *Pure Appl. Chem.* **80**, 519–532 (2008).
14. Li, G. et al. Architecture of graphdiyne nanoscale films. *Chem. Commun.* **46**, 3256–3258 (2010).
15. Diederich, F. & Kivala, M. All-carbon scaffolds by rational design. *Adv. Mater.* **22**, 803–812 (2010).
16. Kang, J., Li, J., Wu, F., Li, S.-S. & Xia, J.-B. Elastic, electronic, and optical properties of two-dimensional graphyne sheet. *J. Phys. Chem. C* **115**, 20466–20470 (2011).
17. Wu, P., Du, P., Zhang, H. & Cai, C. Graphyne as a promising metal-free electrocatalyst for oxygen reduction reactions in acidic fuel cells: A DFT Study. *J. Phys. Chem. C* **116**, 20472–20479 (2012).
18. Heymann, D. et al. C$_2$O$_2$, a fullerene ozonide: Synthesis and dissociation to C$_2$O and O$_2$. *J. Am. Chem. Soc.* **122**, 11473–11479 (2000).
19. Lu, X., Yuan, Q. & Zhang, Q. Sidewall epoxidation of single-walled carbon nanotubes: A theoretical prediction. *Org. Lett.* **5**, 3527–3530 (2003).
20. Kim, S. et al. Room-temperature metastability of multilayer graphene oxide films. *Nat. Mater.* **11**, 544–549 (2012).
21. Liu, C. et al. Carbene-functionalized single-walled carbon nanotubes and their electrical properties. *Small* **7**, 1257–1263 (2011).
22. Hu, H. et al. Sidewall functionalization of single-walled carbon nanotubes by addition of dichlorocarbene. *J. Am. Chem. Soc.* **125**, 14893–14900 (2003).
23. Wang, L. et al. Stability of graphene oxide phases from first-principles calculations. *Phys. Rev. B* **82**, 161406 (2010).
24. Gao, X., Zhao, Y., Liu, B., Xiang, H. & Zhang, S. B. P-$\pi$-Bond maximization of graphene in hydrogen addition reactions. *Nanoscale* **4**, 1171–1176 (2012).
25. Psaltiannis, G. M. & Proudakis, G. E. Computational prediction of new hydrocarbon materials: The hydrogenated forms of graphdiyne. *J. Phys. Chem. C* **116**, 19211–19214 (2012).
26. Reid, T. Graphene: Switch if off. *Nat. Nanotechnol.* (2008).
27. Balog, R. et al. Bandgap opening in graphene induced by patterned hydrogen adsorption. *Nat. Mater.* **9**, 315–319 (2010).
28. Nourbakhsh, A. et al. Bandgap opening in oxygen plasma-treated graphene. *Nanoletters* **21**, 435203 (2010).
29. Pedersen, T. G. et al. Graphene antidot lattices: Designed defects and spin qubits. *Phys. Rev. Lett.* **100**, 136804 (2008).
30. Martinazzo, R., Casolo, S. & Tantardini, G. F. Symmetry-induced band-gap opening in graphene superlattices. *Phys. Rev. B* **81**, 245420 (2010).
31. Gao, X., Wei, Z., Meunier, V., Sun, Y. & Zhang, S. B. Opening a large band gap for graphene by covalent addition. *Chem. Phys. Lett.* **555**, 1–6 (2013).
32. Sun, T. & Fabris, S. Mechanisms for oxidative unzipping and cutting of graphene. *Nano. Lett.* **12**, 17–21 (2012).
33. Avouris, P., Chen, Z. & Perebeinos, V. Carbon-based electronics. *Nat. Nanotechnol.* **2**, 605–615 (2007).
34. Peng, X. & Ahuja, R. Symmetry breaking induced bandgap in epitaxial graphene layers on SiC. *Nano. Lett.* **8**, 4464–4468 (2008).
35. Dong, X. et al. Symmetry breaking of graphene monolayers by molecular decoration. *Phys. Rev. Lett.* **102**, 135501 (2009).
36. Sofo, J. O., Chaudhari, A. S. & Barber, G. D. Graphane: A two-dimensional hydrocarbon. *Phys. Rev. B* **75**, 153401 (2007).
37. Lébée, S., Klintenberg, M., Eriksson, O. & Kataenelson, M. I. Accurate electronic band gap of pure and functionalized graphane from GW calculations. *Phys. Rev. B* **79**, 245117 (2009).
38. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
39. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
40. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).
41. Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **13**, 5188–5192 (1976).
42. Frisch, M. J. et al. Gaussian 09, Revision C.01, Gaussian, Inc.: Wallingford CT, 2010 (see Supplementary Information for full citation).
43. Miertusiński, S., Scrocco, E. & Tomasi, J. Electrostatic interaction of a solute with a continuum. A direct utilization of ab initio molecular potentials for the prediction of solvent effects. *Chem. Phys.* **55**, 117–129 (1981).

**Acknowledgments**

This work was supported by the National Key Basic Research Project of China (973 programs: 2012CB934001, 2011CB933043, 2012CB932504, 2012CB720904), the National Natural Science Foundation of China (21171138, 21274164, 21144001), and CAS Hundreds Elite Program (Y229182053).

**Author contributions**

X.G. conceived the initial idea of this research. J.Z. demonstrated the initial idea and collected all data. X.Z. and Y.Z. participated in the discussions. J.Z. and X.G. wrote the paper. X.G. and X.Z. guided the work.

**Additional information**

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

**Competing financial interests:** The authors declare no competing financial interests.

License: This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported License. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-nd/3.0/

How to cite this article: Zheng, J., Zhao, X., Zhao, Y. & Gao, X. Two-Dimensional Carbon Compounds Derived from Graphyne with Chemical Properties Superior to Those of Graphene. *Sci. Rep.* **3**, 1271; DOI:10.1038/srep01271 (2013).