

# Room-temperature chemical synthesis of C<sub>2</sub>

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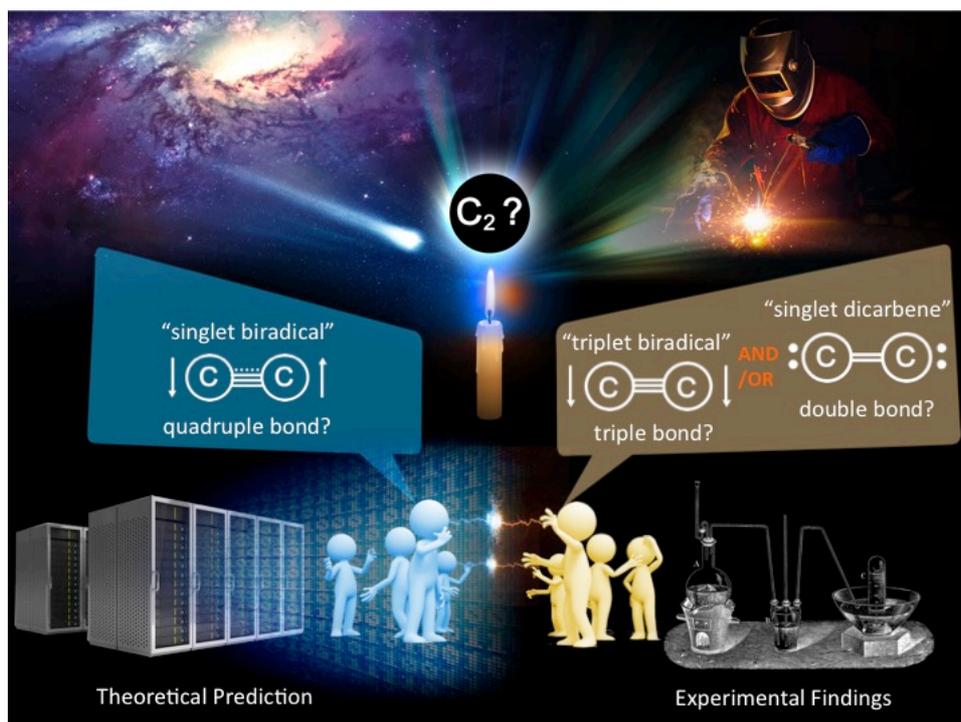
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**Diatomic carbon (C<sub>2</sub>) exists in carbon vapour, comets, the stellar atmosphere, and interstellar matter, but although it was discovered in 1857,<sup>1</sup> it has proved frustratingly difficult to characterize (Figure 1), since C<sub>2</sub> gas occurs/exists only at extremely high temperatures (above 3500°C).<sup>2</sup> Since 1930, several experimental methods to generate C<sub>2</sub> have been developed by using extremely high energy processes, such as electric carbon arc and multiple photon excitation,<sup>3,4</sup> and the C<sub>2</sub> species obtained were reported to exhibit singlet dicarbene (double bond) and/or triplet biradical (triple bond) behavior.<sup>5-7</sup> In contrast, recent theoretical simulations suggest that C<sub>2</sub> in the ground state should have a singlet biradical (quadruple bond) character.<sup>8,9</sup> Here, we present a straightforward room-temperature/pressure synthesis of C<sub>2</sub> in a flask. We show that C<sub>2</sub> generated under these conditions behaves exclusively as a singlet biradical, as predicted by theory. We also show that spontaneous, solvent-free reaction of *in situ*-generated C<sub>2</sub> under an argon atmosphere results in the formation of graphene, carbon nanotubes (CNTs) and fullerene (C<sub>60</sub>) at room temperature. This is not only the first *chemical* synthesis of nanocarbons at *ordinary temperature and pressure*, but also provides experimental evidence that C<sub>2</sub> may serve as a key intermediate of various sp<sup>2</sup>-carbon allotropes.**



34

35 **Figure 1 | Long-standing dispute between experimental and theoretical chemists**  
 36 **concerning the nature of diatomic carbon ( $C_2$ ).**

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38 Diatomic carbon ( $C_2$ ) is historically an elusive chemical species. Considerable efforts  
 39 have been made to generate/capture  $C_2$  experimentally and to measure its  
 40 physicochemical properties. The first successful example of artificial generation of  $C_2$ ,  
 41 which was confirmed spectroscopically, involved the use of an electric carbon arc under  
 42 high vacuum conditions.<sup>10</sup> Subsequent chemical trapping studies pioneered by Skell  
 43 indicated that  $C_2$  behaves as a mixture of singlet dicarbene (double bond) and triplet  
 44 biradical (triple bond) states in a ratio of 7:3 to 8:2 (Supplementary Fig. S1A).<sup>3,6</sup>  
 45 Multiple photon dissociation of two-carbon small molecules (acetylene, ethylene,  
 46 tetrabromoethylene, *etc.*) by infrared or UV irradiation in the gas phase was also  
 47 developed to generate  $C_2$ , but this photo-generated  $C_2$  also exhibited several electronic  
 48 states.<sup>4</sup> Recently, other approaches for the isolation of  $C_2$  have been reported, using  
 49 potent electron-donating ligands to stabilize  $C_2$  by means of dative interactions  
 50 ( $L:\rightarrow C_2\leftarrow:L$ ), but such stabilized complexes no longer retain the original character of  
 51  $C_2$  (Supplementary Fig. S1B).<sup>11-14</sup> Instead, theoretical/computational simulation has  
 52 been applied recently, and the results indicated that  $C_2$  has a *quadruple bond* with a  
 53 singlet biradical character in the ground state (Fig. 1). These various theoretical and

54 experimental findings have sparked extensive debate on the molecular bond order and  
55 electronic state of C<sub>2</sub> in the scientific literature, probably because of the lack of a  
56 method for the synthesis of ground-state C<sub>2</sub>.

57 For the present work, we focused on hypervalent iodane chemistry, aiming to utilize  
58 the phenyl-λ<sup>3</sup>-iodanyl moiety as a hyper-leaving group (*ca.* 10<sup>6</sup> times greater leaving  
59 ability than triflate (–OSO<sub>2</sub>CF<sub>3</sub>), a so-called super-leaving group).<sup>15</sup> We designed  
60 [β-(trimethylsilyl)ethynyl](phenyl)-λ<sup>3</sup>-iodane **1a**,<sup>16</sup> in the expectation that it would  
61 generate C<sub>2</sub> upon desilylation of **1a** with fluoride ion to form anionic ethynyl-λ<sup>3</sup>-iodane  
62 **11**, followed by facile reductive elimination of iodobenzene (Fig. 2A). Gratifyingly,  
63 exposure of **1a** to 1.2 equivalents of *tetra*-*n*-butylammonium fluoride (Bu<sub>4</sub>NF) in  
64 dichloromethane resulted in smooth decomposition at –30 °C with the formation of  
65 acetylene and iodobenzene, indicating the generation of C<sub>2</sub>! However, all attempts to  
66 capture C<sub>2</sub> with a range of ketones and olefins, such as acetone (**3**),  
67 1,3,5,7-cyclooctatetraene (**4**), styrene (**7**), and 1,3,5-cycloheptatriene, failed, though  
68 they smoothly reacted with arc-generated C<sub>2</sub> on an argon matrix at –196 °C  
69 (Supplementary Fig. S1).<sup>7,17</sup> These findings immediately suggested that the putative C<sub>2</sub>  
70 synthesized here at –30 °C has a significantly different character from C<sub>2</sub> generated  
71 under high-energy conditions (Supplementary Fig. S2). Taking account of the fact that  
72 quantum-chemical calculations suggest a relatively stable singlet biradical C<sub>2</sub> with  
73 quadruple bonding in the ground state, we next examined an excellent hydrogen donor.  
74 9,10-Dihydroanthracene (**12**) has very weak C–H bonds (bond dissociation energy of  
75 **12**: 76.3 kcal mol<sup>–1</sup> vs CH<sub>2</sub>Cl<sub>2</sub>: 97.3 kcal mol<sup>–1</sup>)<sup>18,19</sup> that might effectively trap the  
76 putative singlet biradical C<sub>2</sub>. When **12** was added to the reaction mixture, anthracene  
77 (**13**) was obtained accompanied with the quantitative formation of acetylene (Fig. 2A),  
78 which clearly suggests that the generation of C<sub>2</sub> and subsequent hydrogen abstraction  
79 from **12** gave acetylene. The formation of acetylene was confirmed by Raman  
80 spectroscopy after AgNO<sub>3</sub> trapping, and the amount of acetylene was estimated by the  
81 quantitative analysis of Ag<sub>2</sub>C<sub>2</sub> thus generated. These results strongly support the  
82 relatively stable (singlet) biradical nature of our C<sub>2</sub>, in accordance with the theoretical  
83 calculations. Thus, we turned our attention to the galvinoxyl free (stable) radical **14** in  
84 order to trap C<sub>2</sub> directly. To our delight, *O*-ethynyl ether **15** was obtained in 14% yield,  
85 accompanied with the formation of acetylene (84%) (Fig. 2B). The structure of **15** was  
86 fully characterized by <sup>1</sup>H/<sup>13</sup>C NMR spectra: an upfield-shifted acetylenic proton was

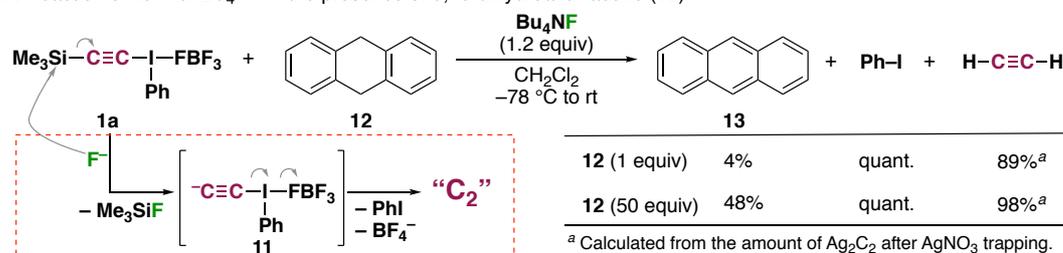
87 seen at 1.78 ppm in the  $^1\text{H}$  NMR, as well as considerably separated  $^{13}\text{C}$  NMR chemical  
88 shifts of two acetylenic carbons ( $\text{C}_\alpha$ : 90.4 ppm,  $\text{C}_\beta$ : 30.0 ppm), clearly indicating the  
89 presence of an ethynyl ether unit.<sup>20</sup> In solution, di-galvinoxyl alkyne **16** was  
90 undetectable or barely detectable even when excess amounts of **14** were used, though **15**  
91 was obtained as almost the sole product in all cases. On the other hand, when we  
92 performed the trapping reaction in the presence of 2 equivalents of **14** under  
93 solvent-free conditions, **16** was clearly observed by atmospheric pressure chemical  
94 ionization (APCI) mass (MS) spectrometry, although in very small quantity  
95 (Supplementary Fig. S3).<sup>21</sup> These findings are consistent with the valence bond model  
96 of a singlet biradical species, according to which the energy barrier of the second  
97 hydrogen abstraction is lower by approximately 10 kcal/mol compared with the first  
98 hydrogen abstraction, which has to overcome the bonding energy of the singlet  
99 biradical.<sup>22</sup> It should be noted that the *O*-phenylated product was not formed at all,  
100 excluding alternative single electron transfer (SET) pathways, such as those *via*  
101 ethynyl(phenyl)- $\lambda^2$ -iodanyl radical (Supplementary Fig. S4).<sup>23</sup>

102 In order to obtain more direct information about the generation of  $\text{C}_2$  “gas”, we  
103 designed a connected-flask, solvent-free experiment (Fig. 2C): a solvent-free chemical  
104 synthesis of  $\text{C}_2$  using **1a** with 3 equivalents of CsF was carried out in one of a pair of  
105 connected flasks (Flask A), and 3 equivalents of **14** was placed in the other flask (Flask  
106 B). The reaction mixture in Flask A was vigorously stirred at room temperature for 72  
107 hours under argon. As the reaction proceeds in Flask A, generated  $\text{C}_2$  gas should pass  
108 from Flask A to Flask B. Indeed, the color of **14** in Flask B gradually changed from  
109 deep purple to deep brown as the reaction progressed. After 72 hours, the formation of  
110 **15** and **16** was confirmed by APCI–MS analysis of the residue in Flask B.

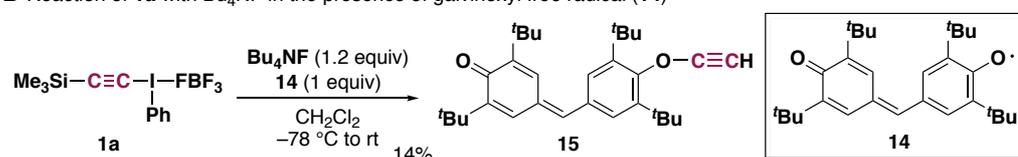
111 We then performed a  $^{13}\text{C}$ -labeling experiment using **1b**- $^{13}\text{C}_\beta$ , which was synthesized  
112 from  $\text{H}_3^{13}\text{C}$ -I in 8 steps.<sup>24</sup> Treatment of **1b**- $^{13}\text{C}_\beta$  (99%  $^{13}\text{C}$ ) with  $\text{Bu}_4\text{NF}$  in the presence  
113 of **14** in  $\text{CH}_2\text{Cl}_2$  gave a mixture of **15**- $^{13}\text{C}_\alpha$  and **15**- $^{13}\text{C}_\beta$ , suggesting that  $\text{C}_2$  is generated  
114 before the *O*-ethynyl bond-forming reaction with **14** (Fig. 2D). The observed  $O$ - $^{13}\text{C}/^{12}\text{C}$   
115 selectivity (71:29) may be related to very fast radical pairing between  $\text{C}_2$  and **14** prior to  
116 ejection of iodobenzene from the solvent cage.<sup>25</sup> We also carried out  $^{13}\text{C}$ -labeling  
117 experiments using **1b**- $^{13}\text{C}_\beta$  in *solvents of different viscosities*. The observed  $O$ - $^{13}\text{C}/^{12}\text{C}$   
118 selectivity decreased as the viscosity decreased, and the regioselectivity was almost lost  
119 (52:48) under solvent-free conditions. Similarly, the  $O$ - $^{13}\text{C}/^{12}\text{C}$  selectivity was 51:49 in

120 the connected-flask experiment. All these findings rule out stepwise  
 121 addition/elimination mechanisms (Supplementary Fig. S5).  
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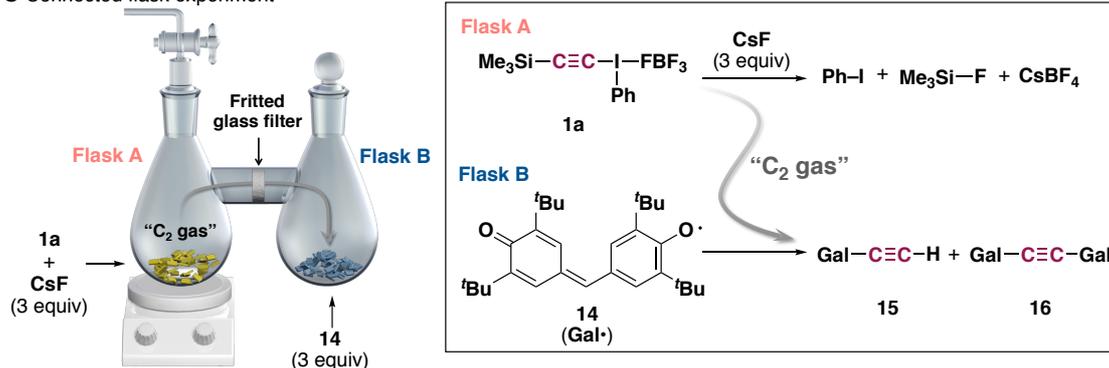
**A** Reaction of **1a** with Bu<sub>4</sub>NF in the presence of 9,10-dihydroanthracene (**12**)



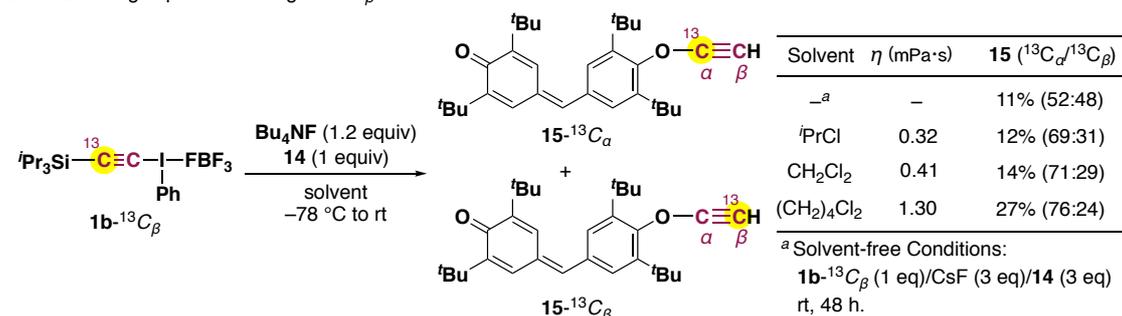
**B** Reaction of **1a** with Bu<sub>4</sub>NF in the presence of galvinoxyl free radical (**14**)



**C** Connected flask experiment



**D** <sup>13</sup>C-Labeling experiment using **1b**-<sup>13</sup>C<sub>β</sub> with/without solvent



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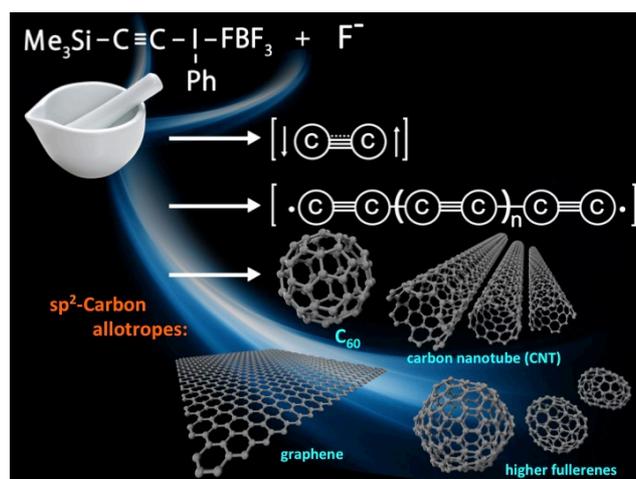
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**Figure 2 | Chemical trapping of C<sub>2</sub> synthesized at low temperature. A,** Reaction of **1a** with Bu<sub>4</sub>NF in the presence of 9,10-dihydroanthracene (**12**). **B,** Reaction of **1a** with Bu<sub>4</sub>NF in the presence of galvinoxyl free radical **14**. **C,** Connected-flask experiment. **D,** <sup>13</sup>C-Labeling experiments using **1b**-<sup>13</sup>C<sub>β</sub>.

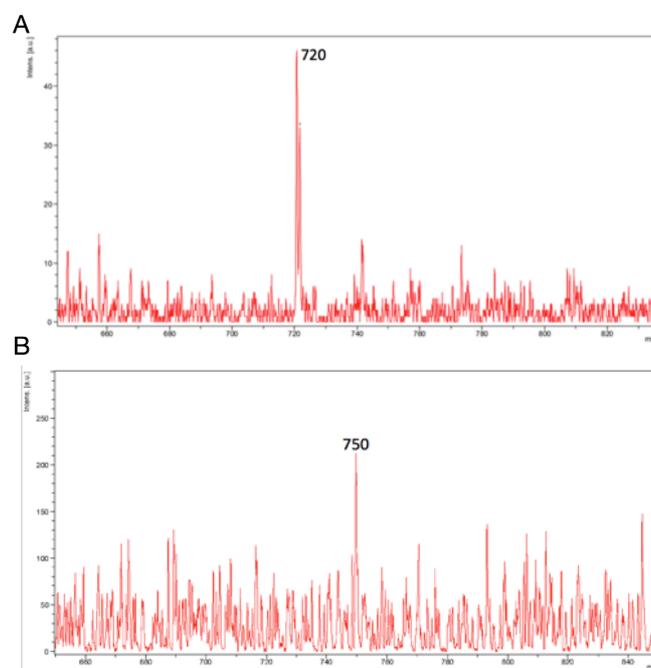
Given that C<sub>2</sub> generated at room temperature or below behaves exclusively as a

130 singlet biradical, as theoretically predicted for the ground state, we examined whether  
131 this ground-state C<sub>2</sub> would serve as a molecular element for the formation of various  
132 carbon allotropes. Today, sp<sup>2</sup>-carbon allotropes such as graphene, carbon nanotubes  
133 (CNT) and fullerenes, in which sp<sup>2</sup>-carbon takes the form of a planar sheet, tube,  
134 ellipsoid, or hollow sphere, are at the heart of nanotechnology.<sup>26</sup> But, in contrast with  
135 the rapid growth of their practical applications, the mechanisms of their formation  
136 remain unclear. Various models and theories for the growth of sp<sup>2</sup>-carbon allotropes  
137 have been proposed, most of which include the addition/insertion of C<sub>2</sub> into a growing  
138 carbon cluster as a key step.<sup>27,28</sup> However, this idea lacks experimental verification. To  
139 investigate this issue, we examined the solvent-free reaction of the present singlet  
140 biradical C<sub>2</sub> in order to avoid hydrogen quenching. Notably, simple grinding of CsF and  
141 1.5 equivalents of **1a** in a mortar & pestle at ambient temperature for 10 min under an  
142 argon atmosphere resulted in the formation of a dark-brown solid containing various  
143 sp<sup>2</sup>-carbon allotropes, as determined by resonance Raman spectroscopy (Supplementary  
144 Fig. S6), matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass  
145 spectrometry (MS) (Fig. 3A) and electrospray ionization (ESI) MS (Supplementary Fig.  
146 S7). Careful examination of the Raman spectra and high-resolution transmission  
147 electron micrograph (HRTEM) images indicated that high-quality graphite with few  
148 defects and an interlayer distance of 0.33 nm (Fig. 4A–C) and amorphous carbon had  
149 been mostly synthesized (Supplementary Fig S6A), together with very small amounts  
150 (<0.0001%) of C<sub>60</sub> and CNTs (*ca.* 0.5–7 nm in diameter, Fig. 4D and Supplementary  
151 Fig. S6B, S7, S8, and S9A), and we did not detect larger fullerenes, such as C<sub>70</sub>, C<sub>76</sub>,  
152 C<sub>78</sub>, and C<sub>84</sub>. This specificity may reflect the ambient temperature/pressure condition, as  
153 the electric carbon arc method generally affords a fearsome mixture of sp<sup>2</sup>-carbon  
154 allotropes. By using **1b**-<sup>13</sup>C<sub>β</sub>, we further confirmed that C<sub>60</sub> is synthesized from C<sub>2</sub>.  
155 Grinding of **1b**-<sup>13</sup>C<sub>β</sub> with CsF under the same reaction conditions as above afforded  
156 C<sub>60</sub>-<sup>13</sup>C<sub>30</sub>, which was detected by means of MALDI-TOF and ESI MS, while  
157 non-labeled C<sub>60</sub> was not detected at all (Fig. 3B, Fig. S9B). The formation of this unique  
158 fullerene is solid evidence for the role of C<sub>2</sub>, as its occurrence probability in nature is  
159 extremely small (0.01)<sup>30</sup>.



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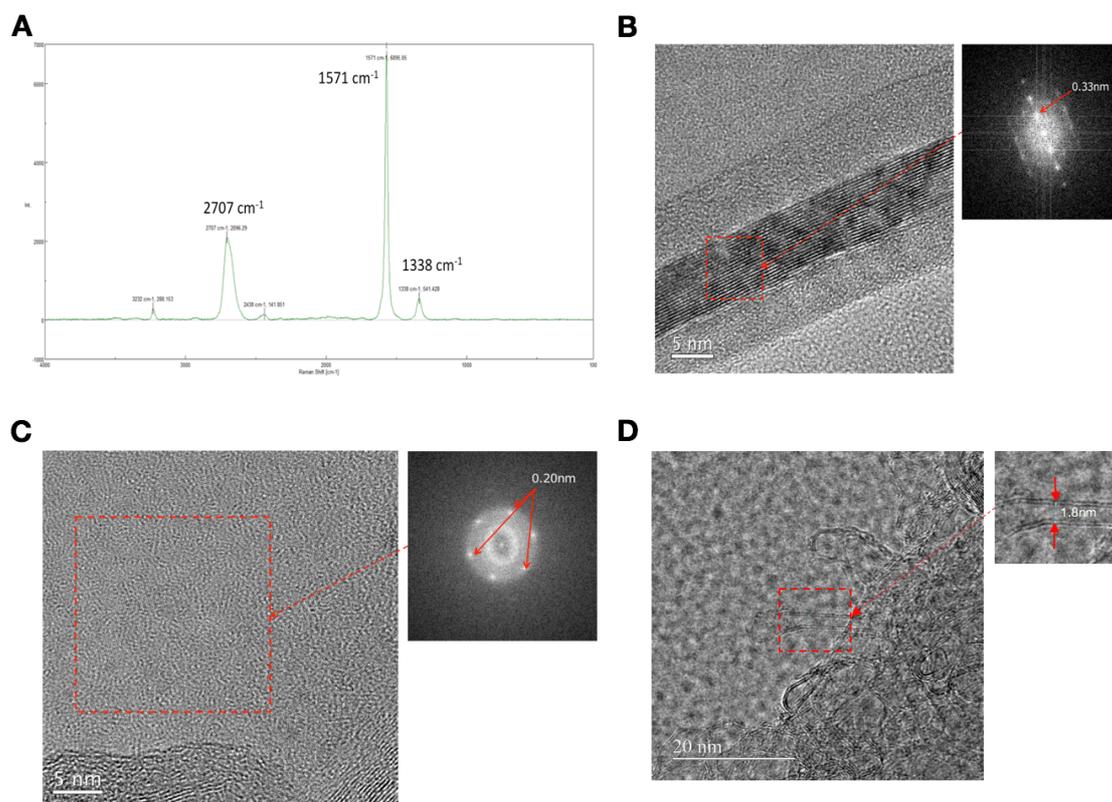
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**Figure 3 | Solvent-free reaction of *in-situ*-generated  $\text{C}_2$  in a mortar at room temperature leads to spontaneous formation of  $\text{sp}^2$ -carbon allotropes. MALDI-TOF mass spectra of **A**, Ground **1a** and CsF. **B**, Ground **1b**- $^{13}\text{C}_\beta$  and CsF.**



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168 **Figure 4 | Raman spectra and HRTEM images (and their power spectra) of carbon**  
 169 **allotropes.** **A**, Raman spectrum of graphite-containing sample. **B**, HRTEM image and  
 170 power spectrum of graphite-containing sample corresponding to the (002) lattice plane.  
 171 **C**, HRTEM image and power spectrum of graphite-containing sample corresponding to  
 172 the (100) lattice plane. **D**, HRTEM image of carbon nanotube-containing sample.

173

174 In conclusion, we have generated  $C_2$  at *ordinary temperature and pressure* for the  
 175 first time. Further, we have established that it has a singlet biradical character at low  
 176 temperature, settling a long-standing difference of opinion between experimental and  
 177 theoretical chemists. We also observed spontaneous formation of  $sp^2$ -carbon allotropes  
 178 such as graphite, carbon nanotube (CNT) and  $C_{60}$  from  $C_2$  at ambient temperature,  
 179 providing the first experimental support for the generally held belief that the formation  
 180 mechanism of  $sp^2$ -carbon allotropes involves the addition/insertion of  $C_2$  into a growing  
 181 carbon cluster as a key step. This is also represents the first *chemical* synthesis of  
 182 nanocarbons at *ordinary temperature and pressure* from  $C_2$  in the ground state. Easy  
 183 synthetic access to *in-situ*-generated  $C_2$  should be helpful in opening up new areas of  
 184 chemistry and materials science, including further studies on the hot topic of the growth

185 mechanisms of  $sp^2$ -carbon allotropes from  $C_2$ .

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271 **Supplementary Information** is available in the online version of the paper.

272 **Acknowledgements** This paper is dedicated to the memory of Professor Keiji  
273 Morokuma, an inspirational leader to all of us who have pondered the mysteries of the  
274 generation/formation of  $\text{C}_{60}$  and other carbon allotropes with the aid of computational  
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