

Supporting Information

The intercalation of *N,N,N',N'*-tetramethyl-ethane-1,2-diamine (tmeda) into C₆Li and C₁₂Li

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EXPERIMENTAL DETAILS

Graphite powder (Aldrich, synthetic; particle size 1-2 μm ; or naturally occurring Ceylon graphite, sieved and soxhlet extracted with toluene, particle size 53 μm -90 μm) was evacuated at a vacuum line for several hours and then transferred to the glove box (VAC DRI-LAB) containing an argon atmosphere of less than 10 ppm oxygen. Lithium (Analytical reagent, BDH) was rinsed in HPLC-grade hexane to remove the protective liquid paraffin, dried and then stored in a glove box. Surface oxides were removed from the lithium with a scalpel. Prior to use tmeda was stored over 3 Å molecular sieves.

Li intercalation A solvent-less route was used to prepare C₆Li and C₁₂Li.¹ At the glove box, a stainless steel Parr reactor equipped with a stainless steel propeller was charged with a small excess of lithium (0.2g, 29 mmol) and graphite (2.0g, 166.5 mmol) and the reactor sealed. At the bench the mixture was heated to 200 °C on a hotplate and stirred at 450-600 rpm for 30 minutes, allowed to cool to room temperature and then returned to the glove box. Where C₁₂Li was required the procedure was similar to the preparation of C₆Li but with the following modifications: lithium (0.1g, 14.4 mmol) and graphite (2.04g, 170 mmol) were heated between 230-250 °C with stirring at 450-600 rpm for two hours. For X-ray diffraction analysis, an aliquot of the gold C₆Li or purple C₁₂Li was loaded into a glass capillary (2 mm diameter, 80 mm long, wall thickness 1/100th mm) and the capillary closed with a screw rotaflow stopcock. The characterisation of C₆Li and C₁₂Li prepared by this method has been described elsewhere.²

Tmeda intercalation All manipulations were conducted under argon using Schlenk manifold techniques. The ternaries were prepared by adding the liquid amine onto solid C₆Li or C₁₂Li. A typical preparation is as follows. An excess of tmeda (2.3 g, 20 mmol) was added to C₆Li

(0.82 g, 10 mmol) and the mixture stirred in an argon atmosphere for 4 days. The flask was then equipped with a condenser that had been heated, evacuated and backfilled with argon, and the mixture refluxed for five hours under argon. Excess tmeda was removed by filter cannula followed by primary pumping for 10 minutes to yield a free-flowing black powder. Found: **C**, 72.95 %; **H**, 3.55%; **N**, 4.77%; **Li**, 5.06%.

X-ray diffraction (XRD): Measurements were recorded on a diffractometer based on a Huber 422 2-circle horizontal turntable goniometer, requiring the sample to be vertical. The diffractometer was equipped with a Philips generator operating at 40 kV and 20 mA and using a wavelength (λ) of 1.54 Å. The capillaries were mounted vertically into the diffractometer in transmission geometry. The data were recorded as intensity (I) as a function of angle (2θ). Identity periods (I_c) were obtained from $I_c = \frac{2\pi}{Q}$ where Q the scattering vector, is $\frac{4\pi \sin \theta}{\lambda}$.

Small angle X-ray scattering (SAXS): Measurements were recorded using a 1.638m Huxley-Holmes camera with an Elliott type GX-13 rotating anode X-ray generator operating at 34kV and 36 mA, of 1.54 Å.

¹³C NMR spectroscopy: Spectra were obtained with a Varian Zeeman-Inova500 spectrometer, with samples in an 11.78 T magnetic field.

Microanalyses: Lithium content was obtained by inductively couple plasma-optical emission spectroscopy (ICP-OES) using an argon plasma. Carbon, hydrogen and nitrogen contents, as obtained by combustion using the Carlo Erba method, are averages from three preparations.

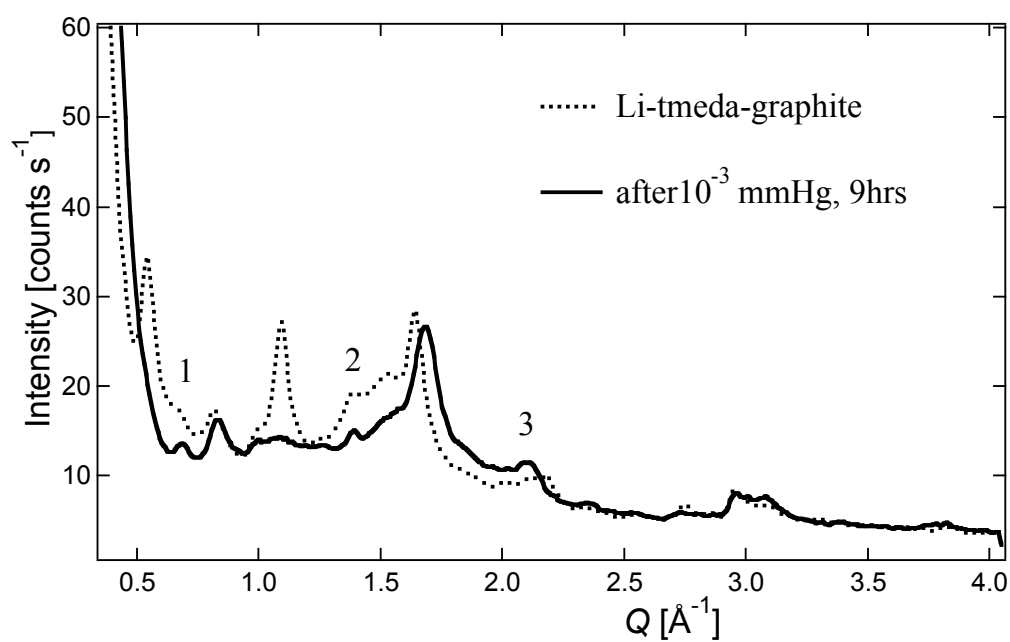


Figure S1. X-ray diffraction patterns displayed as I vs Q of Li-tmeda-graphite (dotted line) and after vacuum treatment at 10^{-3} mmHg for 9 hrs showing the first three (00ℓ) reflections for the 9 Å identity period (full line). $\lambda = 1.54$ Å.

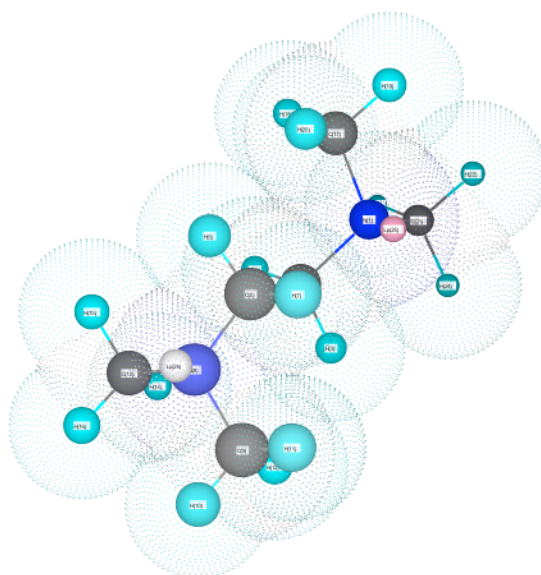


Figure S2. Tmeda molecule considered as a short cylinder of length 7.4 Å and 4.8 Å width.

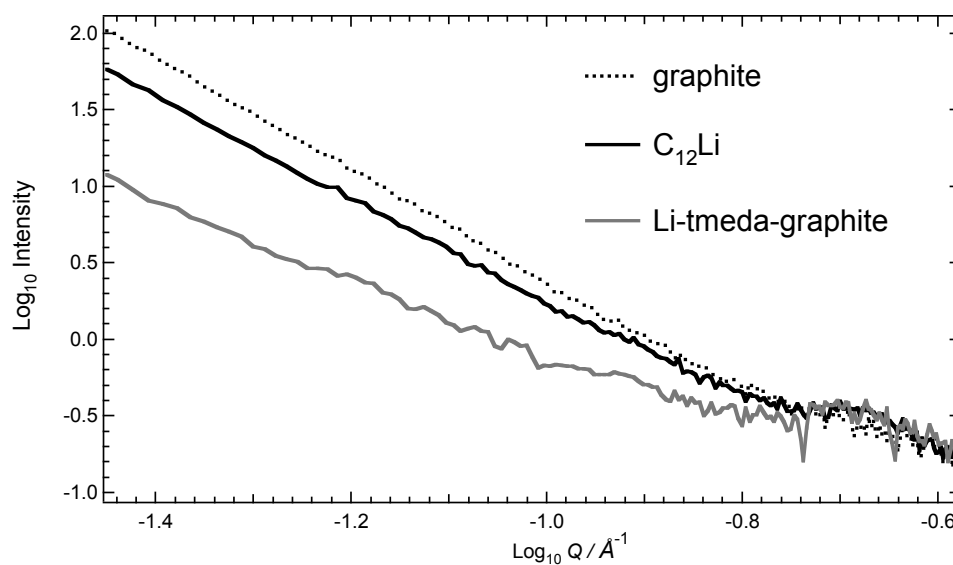


Figure S3. Small angle X-ray scattering measurements displayed as $\log_{10} I$ vs $\log_{10} Q$ of Ceylon graphite (dotted line), C₁₂Li (black line) and C₁₂Li after refluxing with tmeda (grey line). $\lambda = 1.54 \text{ \AA}$. Data from Figure 2.

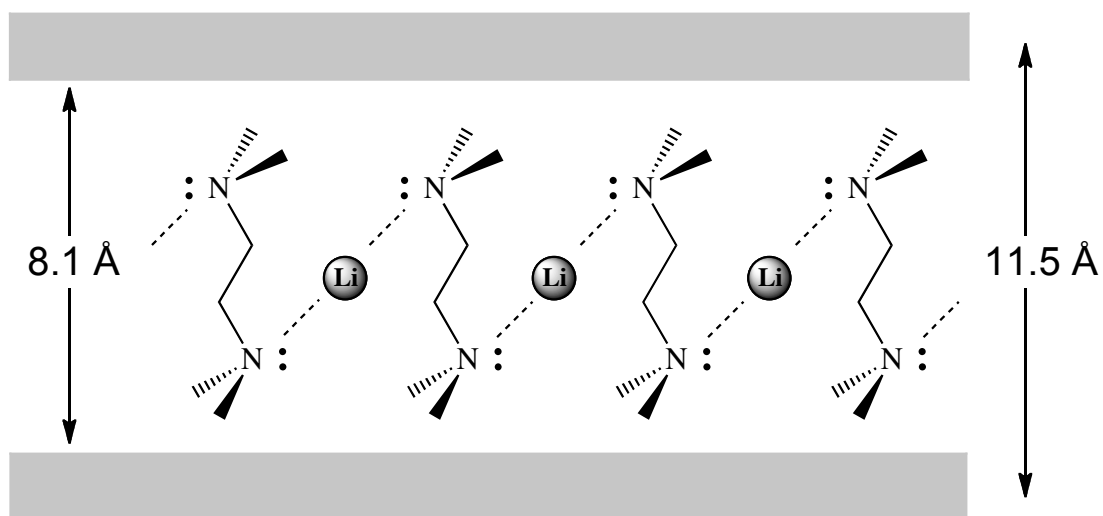


Figure S4. Stylized image of the Li-tmeda-graphite ternary compound showing tmeda molecules normal to the graphene planes.

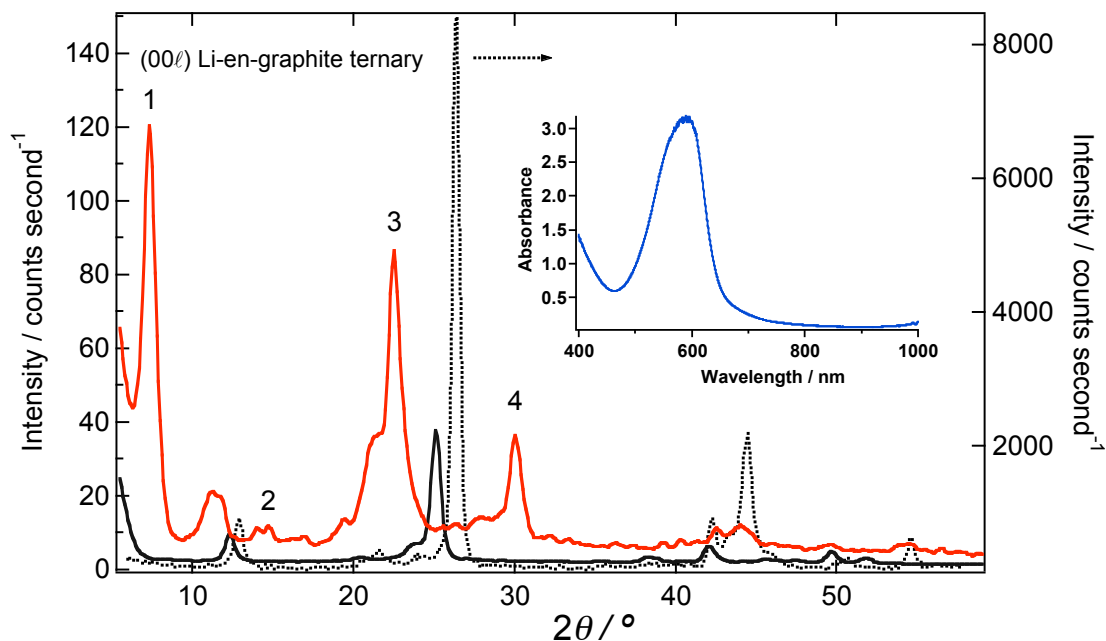


Figure S5. X-ray diffraction patterns displayed as I vs 2θ of (i) graphite (dotted line) (ii) C₁₂Li (black line) and (iii) C₁₂Li exposed to liquid ethylenediamine (en) (red line) at room temperature 15 days after the reaction was commenced in a sealed capillary. $\lambda = 1.54$ Å. Inset shows the UV-Vis absorption spectrum obtained from the filtrate after an attempted scale-up of the reaction.

1. Postnikov, V. A.; Kakuliya, T. V.; Khananashvili, L. M.; Isaev, Y. V.; Novikov, Y. N.; Volpin, M. E., *Russ. Chem. Bull.* **1979**, 28, 626-627.
2. Henderson, M. J.; White, J. W., *Int. J. Energy Engineering* **2011**, 1, 19-26.