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Optimised exfoliation conditions enhance isolation and solubility of grafted graphenes from graphite intercalation compounds

Takuya Morishita,[†] [‡] Adam J. Clancy,[†] and Milo S. P. Shaffer*,[†]

[†] Department of Chemistry, Imperial College London, London, SW7 2AZ, UK

[‡] Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan

*Corresponding author. E-mail: m.shaffer@imperial.ac.uk

Supplementary figures

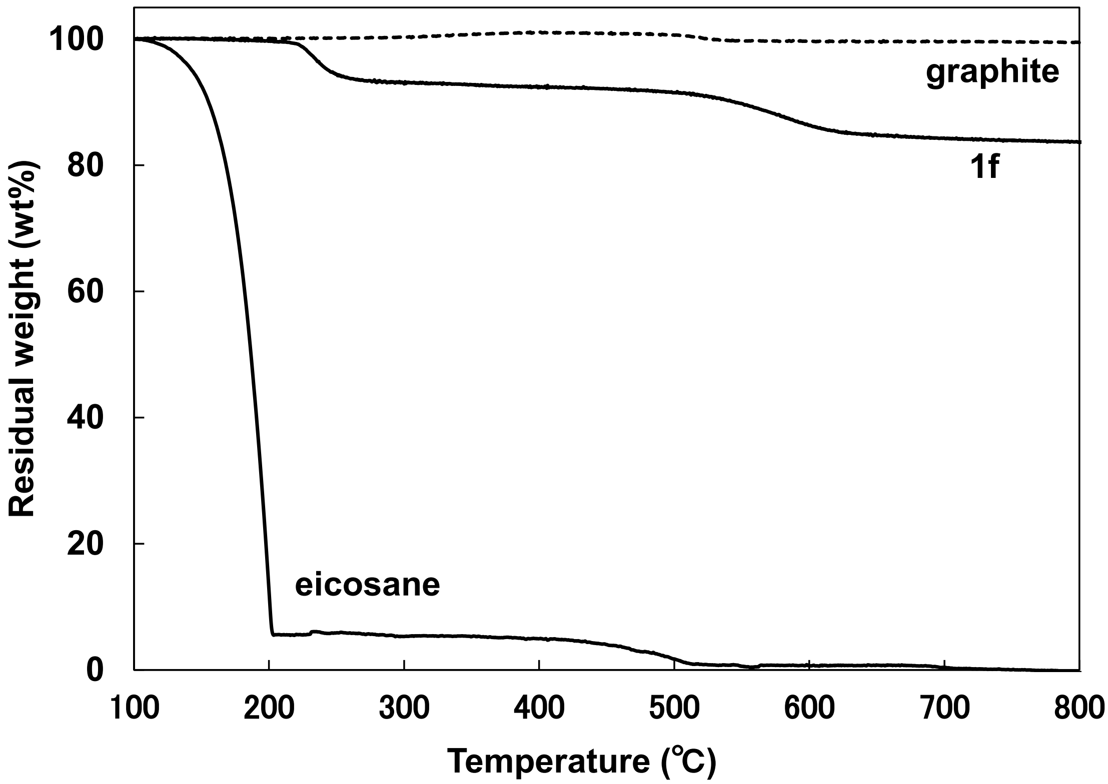

Fig. S1. TGA data (heating rate = 10°C min^{-1}, under N_2) for eicosylated graphene **1f**, pristine graphite, and eicosane. A pure eicosane control decomposed predominantly below 200°C with a small amount of char disappearing about ~550°C. A very small weight loss of **1f** below 210°C can be ascribed to decomposition of remaining physical adsorbed alkane. The two step weight loss of **1f** observed from

210°C to 800°C is ascribed predominantly to decomposition of eicosyl chains to graphenes, although some THF may also be present (see Fig. S2). Alkyl chains grafted to graphene,[1a] and SWNTs[1b] synthesised by reacting with alkyl iodide, are also known to show two step weight losses from ~200°C to ~700°C, as confirmed by TGA-MS observations.[1a]

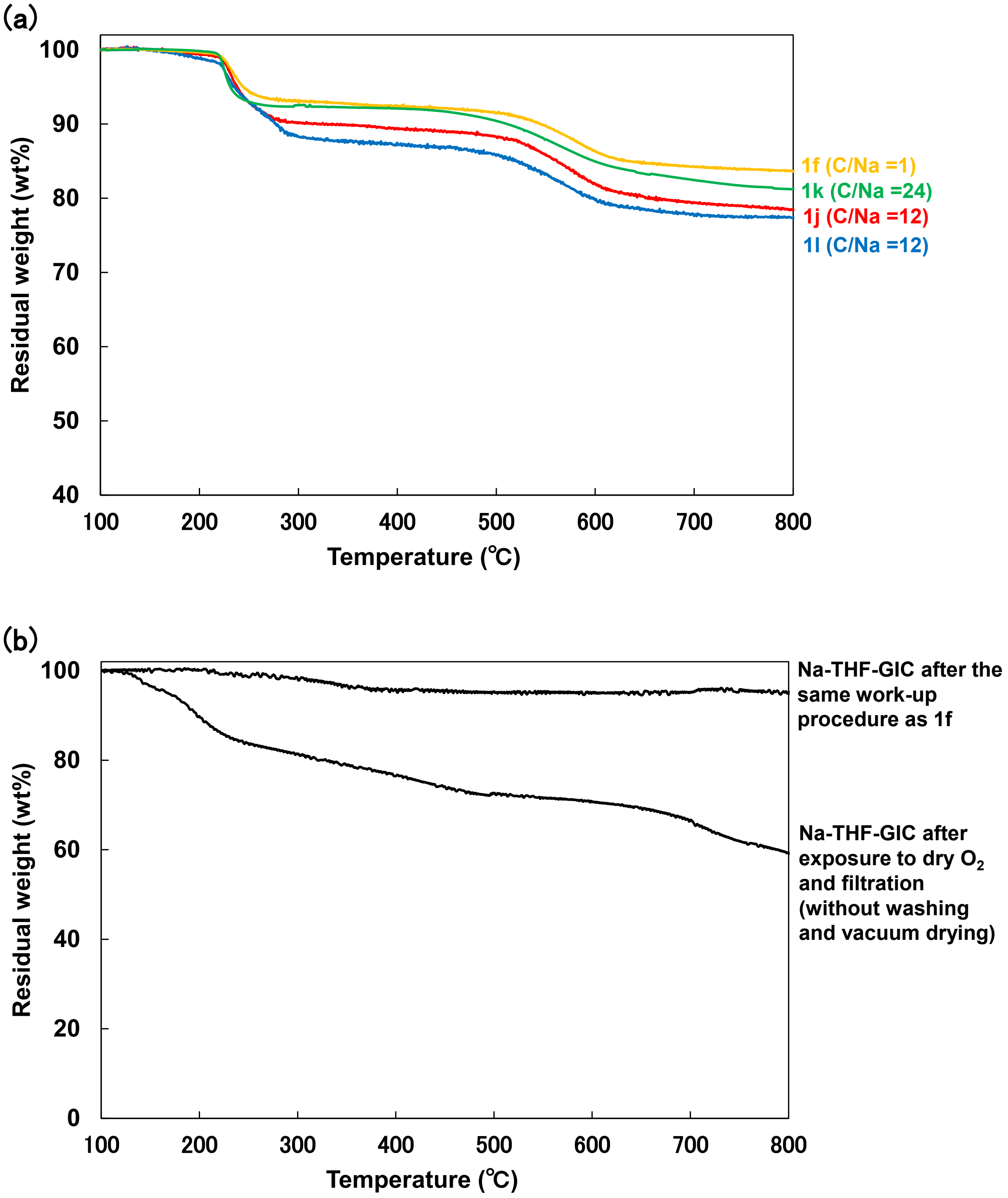

Fig. S2. (a) TGA data (heating rate = 10°C min^{-1}, under N_2) for eicosylated graphene **1f**, **1j**, **1k**, and **1l**. Eicosyl chains grafted to graphene showed two step weight losses from ~210°C to ~700°C, which are the similar type of weight losses as shown in alkylated graphenes.[1a] (b) TGA data (heating rate = 10°C min^{-1}, under N_2) for Na-THF-GIC (synthesised with C/Na ratio = 12) after the same work-up procedure as **1f**, and Na-THF-GIC after exposure to dry O_2 and filtration (without washing and vacuum drying). Na-THF-GIC after exposure to dry O_2 and filtration (but without washing and vacuum drying) showed weight losses which are likely due to volatilisation of remaining THF and naphthalene. The weight loss from ~200°C to ~500°C is ascribed to intercalated THF volatilisation. For comparison, a weight loss due to intercalated alkylamine volatilisation of stage-1 Na-alkylamine-GICs is known[2a] to be observed from 50°C to 500°C. After reaching ~650°C, the trace oxygen present presumably led to some decomposition of graphene itself [2a]. Na-tetrabutylammonium (TBA)-GIC showed weight losses due to intercalated TBA volatilisation at 150°C to 500°C.[2b] Na-THF-GIC prepared by the same work-up procedure as **1f** showed a very small weight loss at ~200°C to ~500°C, which is ascribed to volatilisation of remaining intercalated THF, since this sample did not show any characteristic naphthalene peaks in the Raman and IR spectra. During the work-up procedure using dry O_2, most of the Na cations reacted with dry O_2 producing Na_2O during charge quenching (Na-THF-GICs can be converted into the pristine graphite), and the resulting Na_2O was removed by washing with water several times. Most of the remaining THF between layers can be removed by drying at 80 °C under vacuum overnight. Note that the amount of Na-THF-GIC remaining unreacted in the alkyl reacted samples is very small (3% for **1f** and 0% for **1l**, see caption S3 below) and the Na-THF-GIC itself shows a very small weight loss after appropriate washing and drying (see above). Therefore, the possible contribution of remaining THF or other Na-THF-GIC species to the TGA weight loss of the alkylated graphenes should be small in the current case, and in any case does not affect the clear trends observed.

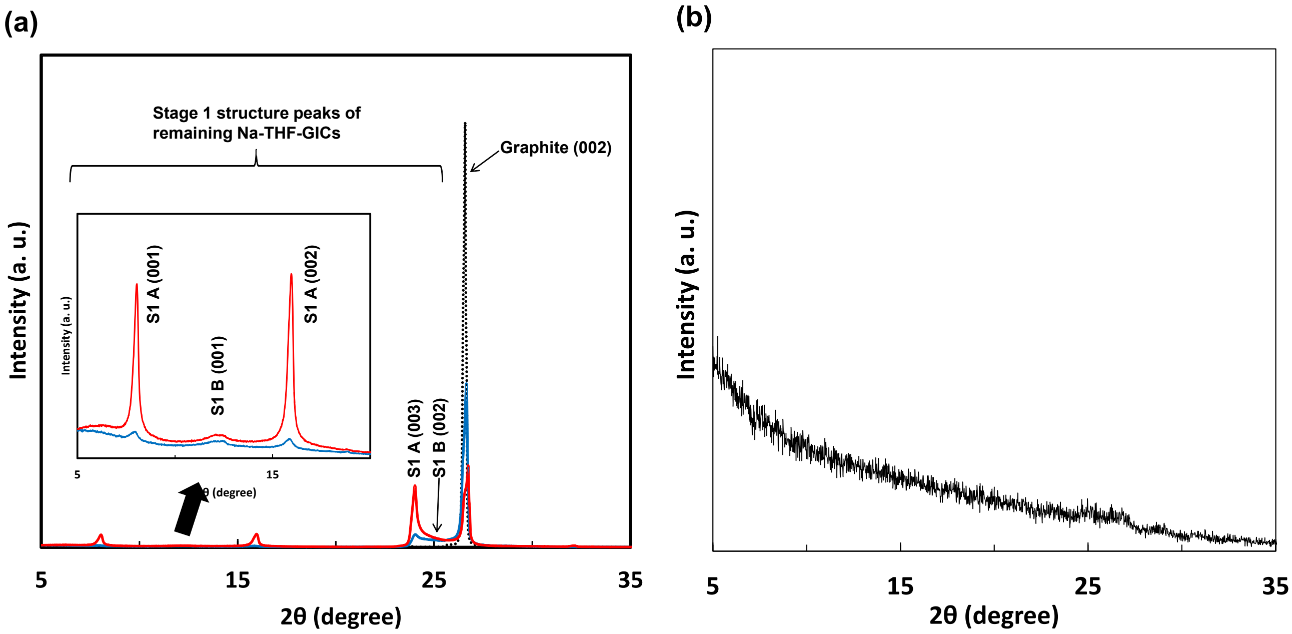

Fig. S3. (a) Enlarged XRD diffractogram of eicosylated graphene **1f** (blue), Na-THF-GIC obtained after filtration under air (without washing and drying) (red), and pristine graphite (dotted line). Remaining stage-1 Na-THF-GIC structure peaks are indexed as (001) lines by using two values of the characteristic period I_c, 1.12 and 0.72 nm, indicated as stage-1 phases A (S1 A) and B (S1 B),[3] respectively, in the figure. The thickness of intercalate layer is calculated as 0.79 nm for phase A, and 0.39 nm for phase B, by a subtraction of the thickness of carbon layers (0.335 nm). Phase B is formed by exposing phase A to air. From these values of I_c, both phases are reasonably supposed to have the stage-1 structure.[3] The content of remaining Na-THF-GIC in **1f** is very small (estimated as ~3% based on the XRD peak intensity ratio of S1 A (001) in **1f** (blue) to that of Na-THF-GIC (red))). (b) Enlarged XRD diffractogram of eicosylated graphene **1l** (C/Na = 12), under optimum conditions. The enlarged diffractogram does not show any S1 A peaks, and shows only a very small trace at ~25.5 degrees**.**

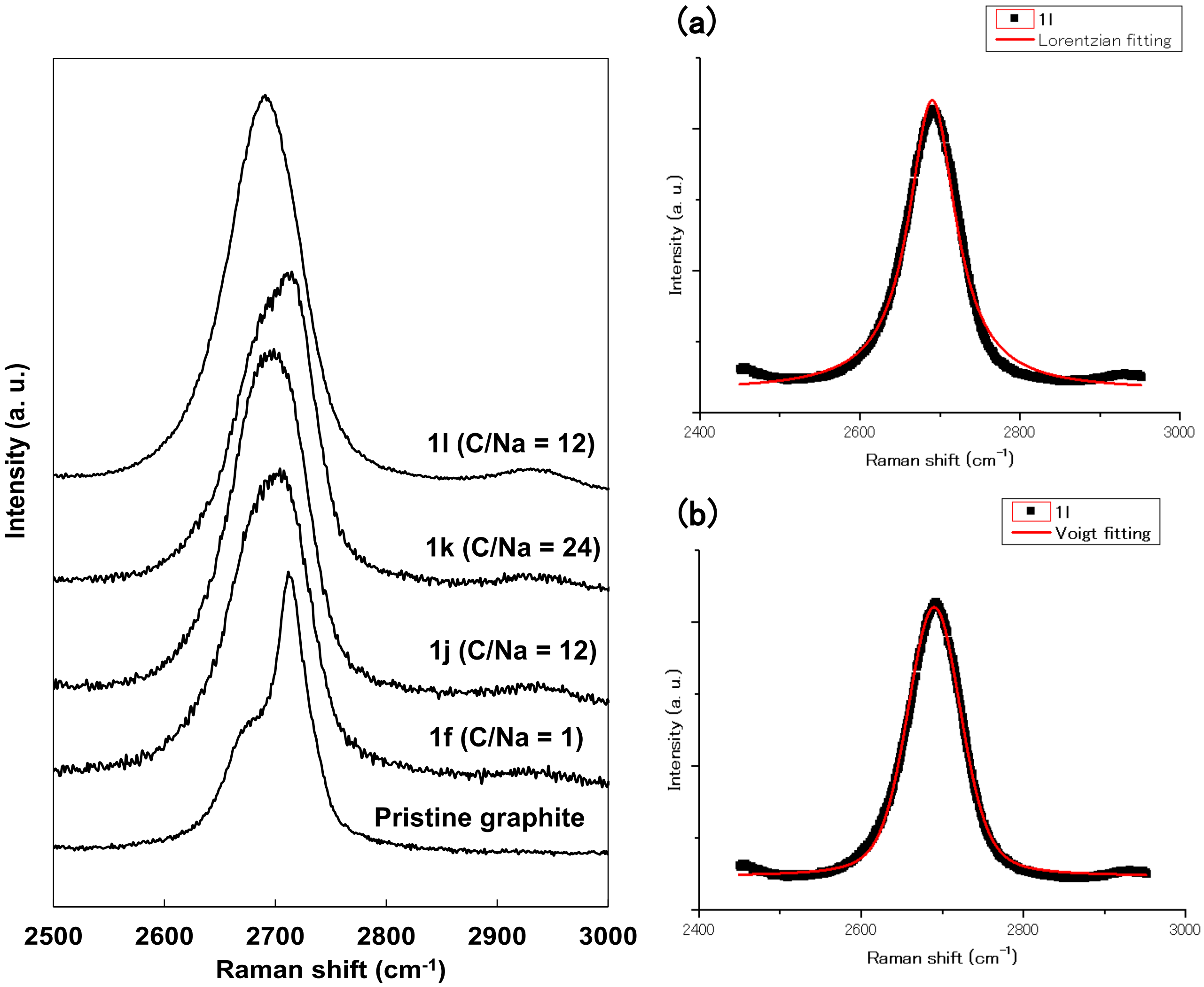

Fig. S4. (left) Raman 2D bands (normalised by the intensity of the G peak) of pristine graphite and eicosylated graphenes **1f**, **1j**, **1k**, and **1l**. (right) (a) Lorentzian peak fitting of the 2D peak of eicosylated graphene **1l**. The 2D peak of **1l** have a single symmetric line profile ($R^2 = 0.989$) with a full width at half magnitude (FWHM) value of 71.9 cm^{-1}: this characteristic 2D peak indicates the existence of a single layer graphene sheet.[4–6] In the case of a single-layer graphene, the 2D peak is generally higher than the intensity of G peak. However, it is known that a single-layer graphene after chemical reaction shows significantly reduced and broadened 2D peak compared with non-functionalised single-layer graphene.[5] (b) Voigt peak fitting of the 2D peak of eicosylated graphene **1l**. Voigt functions have been proposed for graphenes incorporating different environments[7] and here provide an even better fit ($R^2 = 0.997$), indicating possibly a combination of Lorentzian line shape with a Gaussian variation of functionalisation/defect density.

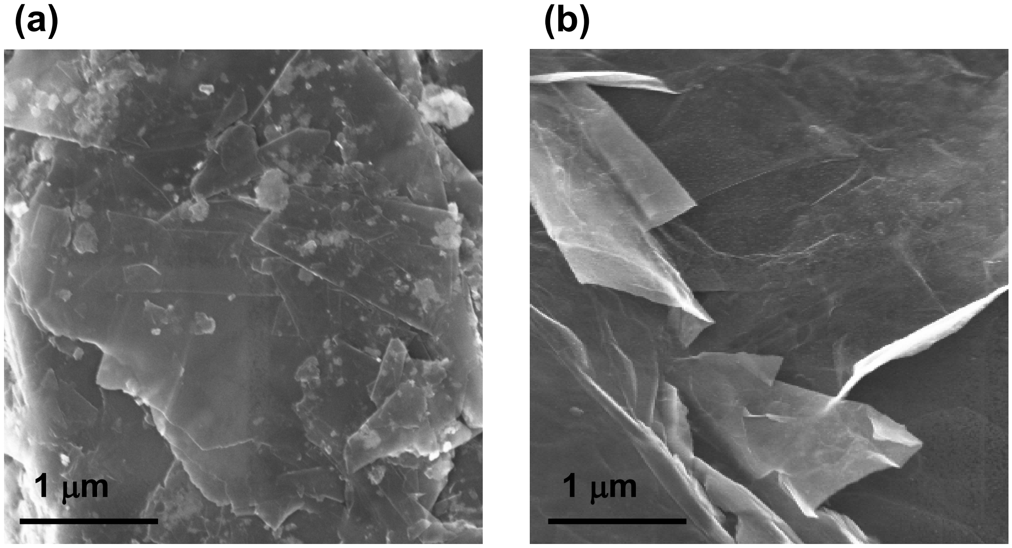

Fig. S5. SEM images of (a) pristine graphite (flake graphite G2369) and (b) eicosylated graphene **1j** (C/Na = 12). The SEM image of **1j** shows crumpled sheets with blunter edges, due to the exfoliation reaction and functionalisation.

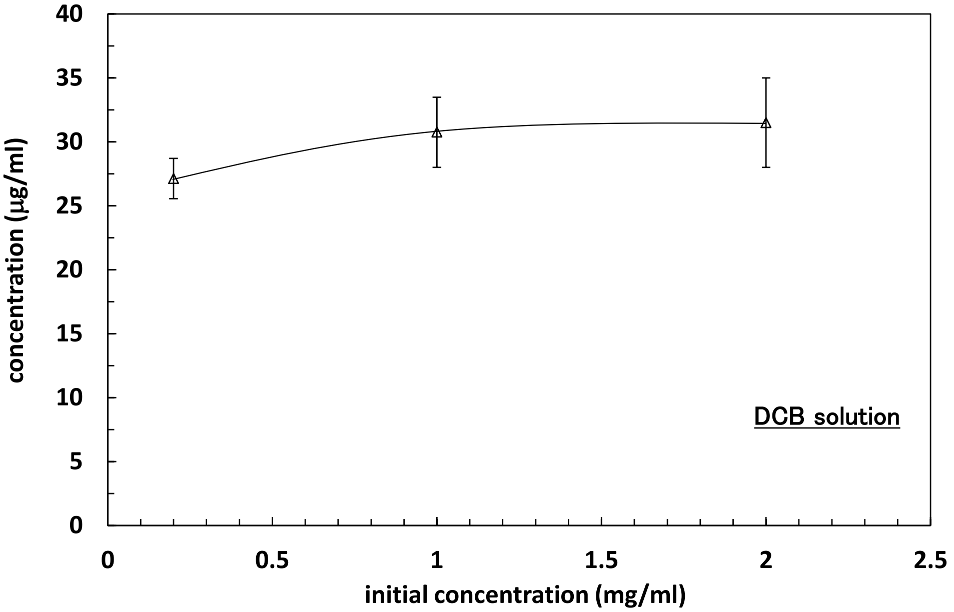

Fig. S6. Concentrations of supernatant after mild centrifugation (1,000 rpm (87 g), 5 min) of eicosylated graphene **1j**-dispersed DCB solution (initial concentration: 0.2, 1, and 2 mg/ml).

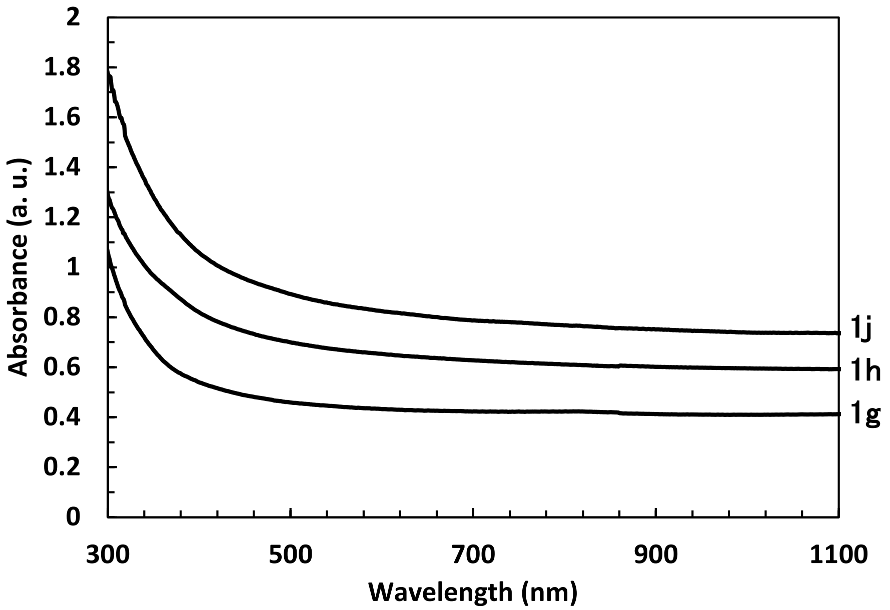

Fig. S7. UV-vis spectra of supernatant solutions after mild centrifugation of butylated graphene (**1g**) in DCB, dodecylated graphene (**1h**) in DCB, and eicosylated graphene (**1j**) in DCB.

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