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Preparation of a Homologous Series of Graphite Alkylamine Intercalation Compounds Including an Unusual Parallel Bilayer Intercalate Arrangement

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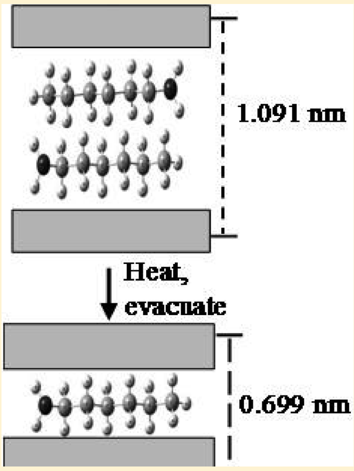
Supporting Information

ABSTRACT: New ternary graphite intercalation compounds (GICs) containing Na^+ and linear alkylamines (Na-Cx-GIC) are reported. The following new GICs with indicated stages and intercalate arrangements are obtained: stage 1, monolayer (C3, C4); stage 1, bilayer (C6, C8); and stage 2 bilayer (C12, C14). Two features new to donor-type GICs found are (i) an intercalate bilayer arrangement with guest alkyl chains parallel to encasing graphene layers, and (ii) the transition from an intercalate bilayer to monolayer arrangement upon evacuation for C6. Although there are many reports on the intercalation of short, medium, and long-chain alkylamines in layered hosts, this is the first example of a homologous compound series for GICs. The products obtained are characterized using powder X-ray diffraction, thermogravimetric analysis, and differential scanning calorimetry.



KEYWORDS: graphite intercalation compounds, GIC, alkylamine, X-ray diffraction

INTRODUCTION

Intercalation chemistry results in changes in both layered host and guest and allows the study of molecular confinement in two dimensions.[1] The properties and subsequent chemistry of intercalation compounds can be more clearly developed and controlled by understanding the intercalate composition and arrangement within the expanded galleries. Alkylamines and alkylammonium ions are among the most commonly employed intercalate guests. Details of complex transitions in intercalate arrangements have been obtained for some layered hosts. For example, the evolution of a hexadecylamine ($C_{16}H_{33}NH_2$) intercalate arrangement from parallel monolayer, to parallel bilayer, to perpendicular (or tilted) monolayer, to perpendicular (or tilted) bilayer, was observed with increasing intercalate content in bentonite.[2,3] Similar structural changes, with an added bilayer-to-trilayer transition, were reported for a R_4N^+-exchanged smectite clay.[4] These organoclays have several potential applications, including the adsorption of toxins, use as photo and electro-functional materials, and as precursors in the formation of clay—polymer nanocomposites with enhanced mechanical properties.[5]

Although the intercalation and exfoliation of layered materials using alkylamine intercalates (or the associated ammonium cations) is well-known in the literature,[1,6] similar behavior has never been reported for graphite. In the donor-type graphite intercalation compounds (GICs), graphene sheets are reduced and cations intercalate between the carbon layers. Ternary GICs, in which the solvent molecules coordinate to the M cations and are cointercalates, can be synthesized using either direct or indirect methods. In the direct method, an alkali metal is dissolved in a polar, highly ionizing liquid such as liquid ammonia,[7−9] methylamine,[7] or ethylenediamine.[7] The electrons/radicals/anions thus generated reduce the graphene sheets, and the solvated cations intercalate to satisfy the charge neutralization. In the indirect method, a preformed binary GIC, e.g., KC_{24} or KC_{36}, is further reacted with a cointercalate in the liquid or gas phase, examples include the cointercalation of N,N,N',N'-tetramethylethylenediamine (TMEDA),[10] triethylamine,[10] and the cryptand "K222".[11] In some cases, such as with methylamine, GIC's have been synthesized by both direct and indirect methods.[7,12] We recently reported the synthesis of the ternary GICs containing the alkali metal M (M = Li, Na, K) and 1,2-diaminopropane,[13] which provides an unusual example of cation-directed orientation of organic cointercalates. However, no extended homologous series for alkylamines has been reported to date. This contrasts the extensive literature on amine intercalation for other layered hosts such as transition metal dichalcogenides and clays where homologous series of amines have been prepared and their structure—property relations evaluated.[1]

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We report herein the synthesis of several new GICs containing Na$^+$ cations and a series of linear alkylamines with 3, 4, 6, 8, 12, 14 carbon atoms. These compounds exhibit two features new to donor-type GICs, an intercalate bilayer arrangement with guest alkyl chains parallel to encasing graphene layers, and a transition from an intercalate bilayer to monolayer arrangement. Both as prepared ("wet") and dried products were studied, as the intercalate arrangement can depend strongly on drying conditions. The GIC products are characterized using powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

■ EXPERIMENTAL SECTION

All synthesis and handling of the air-sensitive reagents and the resulting GICs were done under an inert atmosphere using a drybox or septum-syringe techniques. In a typical synthesis, 0.25 g of graphite powder (SP-1, Union Carbide, average particle diameter 100 μm) was mixed with 0.06 g of Na metal (99.95%, Alfa Aesar) (mol C/mol Na = 8) and the amine (4 mL for *n*-propyl to *n*-octylamine, 0.75 g for *n*-dodecylamine and *n*-tetradecylamine). Anthracene (0.05 g) was added as an electron transfer catalyst for the C12 and C14 amines. The reaction mixtures were continuously stirred for 1−7 days at the following temperatures: *n*-propylamine (C3) and *n*-butylamine (C4) 20 °C; *n*-hexylamine (C6) 90 °C; *n*-octylamine (C8) 140 °C, and *n*-dodecylamine (C12) and *n*-tetradecylamine (C14) 90 °C. For the C12 synthesis, an additional experiment was performed using only 0.25 g of the amine. For some reactions, Li metal was used to prepare Li-C*x*-GICs by the same methods. The liquid amines were removed by centrifugation immediately (C3−C8), or by washing with dry toluene followed by centrifugation (C12, C14). GIC products denoted "wet" were characterized after centrifugation without further processing, those denoted "dried" were placed under vacuum (<100 μm) at 20 °C (C3−C4) or 50 °C (C6−C14) for 6 h.

PXRD data were collected on a Rigaku MiniFlex II, using Ni-filtered Cu Kα radiation, with 0.02° 2θ steps from 3° to 60°. Sample holders were sealed with a plastic tape window to prevent decomposition in air during the PXRD measurement. The (00*l*) reflections were indexed according to the relation $I_c = d_i + (n - 1)(0.335 \text{ nm})$, where I_c is the identity period obtained directly by diffraction data, d_i is the gallery height, n is the GIC stage number, and 0.335 nm is the distance between two adjacent graphene sheets. Peak positions (00*l*) of all GIC phases reported in this work can be found in Table S1 in the Supporting Information. The samples were digested in conc. HCl and the sodium content in the liquid was analyzed with ICP-AES using the Jobin Yvon Emission JY2000. TGA was performed using a Shimadzu TGA-50 under flowing Ar gas (20 mL/min) from RT to 800 at 5 °C/min. DSC measurements were performed on a Shimadzu DSC-50, with samples (~5 mg) hermetically sealed in aluminum pans. The DSC samples were heated from ambient to 150 at 5 °C/min. Only the heating curves were recorded.

■ RESULTS AND DISCUSSION

Short- to Medium-Chain Amines. Figure 1a shows the PXRD pattern of the blue stage 1 GIC product, Na-C3-GIC (d_i = 0.701 nm), obtained with *n*-propylamine after RT drying under vacuum. The wet product shows the same PXRD pattern. This product has well-ordered galleries as evidenced by the presence of up higher order reflections. Neglecting the contribution of Na$^+$, which has a smaller diameter (≈ 0.2 nm) than the minimum amine dimension along any axis, the intercalate monolayer height within the graphene gallery is therefore 0.701 − 0.335 = 0.366 nm. The relationship between the orientation of alkyl chains and interactions with the Na$^+$ cation will be discussed later. This monolayer height is similar to that reported previously for Li-methylamine-GIC (0.36 nm),[7] but smaller than those reported for Li-ethylenediamine-GIC (0.51 nm)[7] and K-TMEDA-GIC (0.56 nm).[10] The larger dimension for the TMEDA gallery is readily understood due to the increased steric requirement for the methyl group substituents on the amine.

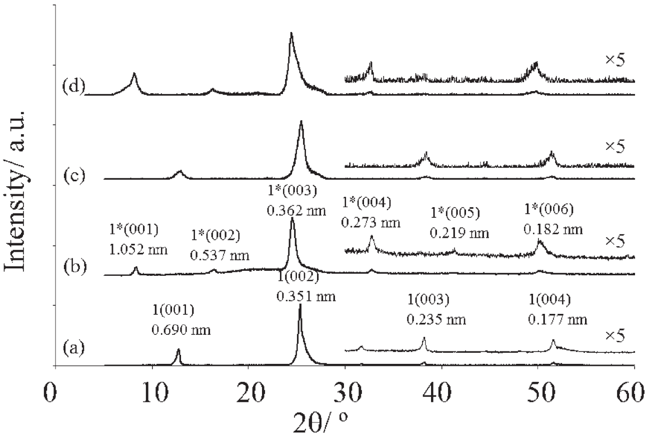

Figure 1. PXRD pattern of (a) Na-C3-GIC, (b) Na-C6-GIC (wet), (c) Na-C6-GIC (dried), and (d) Na-C8-GIC. The numbers 1 and 1* indicate the stage 1 monolayer and bilayer, respectively, with the assigned (00*l*) indices and the observed d values indicated. The PXRD patterns of Na-C3-GIC and Na-C8-GIC are the same for the wet and dry samples.

Na-C4-GIC (d_i = 0.704 nm), Li-C3-GIC (d_i = 0.700 nm), and Li-C4-GIC (d_i = 0.697 nm) can all be prepared similarly, and the products have monolayer heights comparable to Na-C3-GIC. From steric considerations, and the equivalent gallery heights for M-C3-GIC and M-C4-GICs (M = Li, Na), it is clear that these short-chain alkylamine intercalates must form monolayers with long molecular axes lying parallel to the graphene sheets, as shown in Figure 2a. The synthesis of Cs-C*x*-GIC (for C4, C5, and C6 alkane) have also been previously reported through the reaction of CsC_{24} and the alkane vapor.[14] Although the d_i values of those GICs were not directly stated by the authors, the data included in the publication indicates that these GICs contained parallel alkane monolayers.

The wet Na-C6-GIC product is a blue stage 1 GIC with d_i = 1.091 nm, corresponding to an intercalate dimension of 0.756 nm. As shown in Figure 1b, the presence of reflections up to (006) indicates well-ordered domains along the stacking direction. These galleries are assigned a bilayer arrangement, since the intercalate dimension is nearly twice that of the monolayer arrangement described above for M-C3-GIC and M-C4-GIC (M = Li, Na). After drying, a new C6 monolayer GIC structure appears with d_i = 0.699 nm (Figure 1c), indicating a transition to the monolayer arrangement described above. This transition of bilayer-to-monolayer arrangement for alkyl-chain intercalates, indicated in the scheme in Figure 2b, is new for GICs. A bilayer structure is also observed in the wet product obtained with *n*-octylamine − the blue stage 1 Na-C8-GIC (d_i = 1.093 nm). However, Na-C8-GIC does not change structure after drying. The bilayer to monolayer transition was also not observed for the alkane-containing Cs-C5-GIC or Cs-C6-GIC.[14] The number of steps in the TGA mass loss curves further supports the monolayer and bilayer assignments (see below).

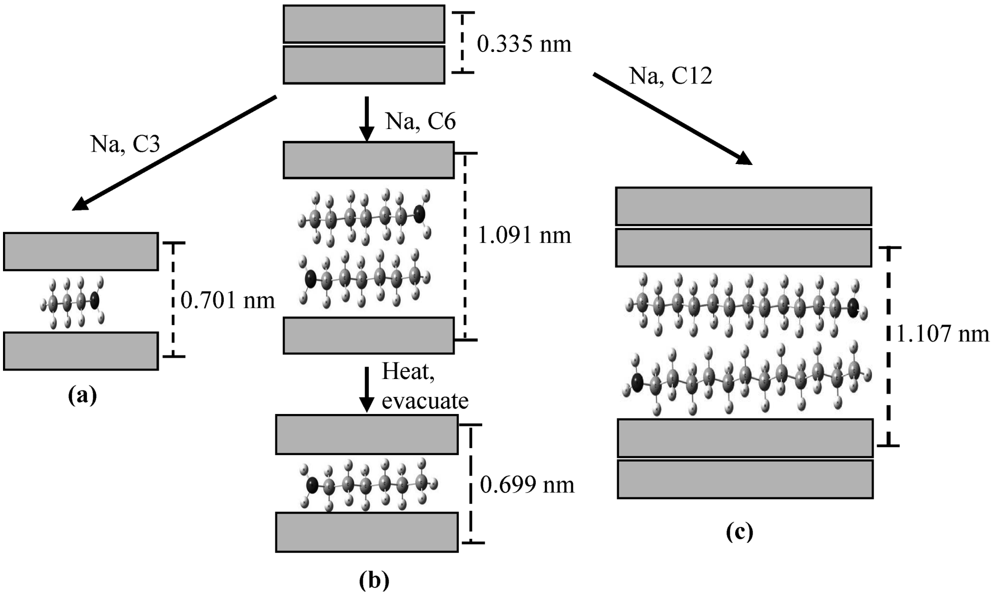

Figure 2. (a) Monolayer structure in Na−C3-GIC, (b) the bilayer structure in wet Na−C6-GIC and its transformation to the monolayer structure by drying, and (c) the bilayer structure in stage 2 Na-C12-GIC. The gallery dimensions, d_i, are shown in each case. The locations of the Na^+ intercalates are not shown.

The formation of radicals/anions/solvated electrons through the reaction of alkali metal with liquid ammonia, ethylenediamine, and small chain amines is well-established in the literature.[15] The analogous reactions with longer-chain amines have received less attention. However, the successful formation of Na-C6-GIC and Na-C8-GIC suggests that such reactive intermediates exist and can provide the strong reducing conditions necessary to form donor-type GICs. Because the highest Na content in a well-characterized binary Na-graphite is the stage 6 NaC_{48} (synthesized from the reaction of graphite and a molten Na−Ca alloy at 250−300 °C),[16] it is unlikely that the indirect method is operative in these reactions. Much more likely, these GICs are formed by a direct method—coinsertion of cation and solvent. The intermediate formation of a binary alkali metal GIC has not been proposed in other reports of GICs containing amines.[7−9,12]

Long-Chain Amines. Preparation of the black Na-C12-GIC product requires the addition of anthracene, likely due to the low reaction rate of sodium metal with the larger amines. Although the reaction details of alkali metals in liquid ammonia,[17] or small amines like ethylamine[18] or ethylenediamine,[19] are reported, we are not aware of similar reports for long-chain amines. Control experiments, where either anthracene or the amines were omitted, yielded only graphite, as evidenced by a strong and sharp (002) graphite reflection in the resulting PXRD (not shown). The use of electron transfer agents, including naphthalene and phenanthrene, has been reported previously in the synthesis of GICs containing alkali metals and ethers.[20,21] Figure 3a shows the PXRD obtained for Na-C12-GIC, with reflections observed up to index (008). Na-C14-GIC is prepared under the same synthetic conditions, the product PXRD is shown in Figure 3c.

Na-C12-GIC (d_i = 1.107 nm) and Na-C14-GIC (d_i = 1.095 nm) are stage 2 compounds. These assignments give layer heights of 0.386 and 0.380 nm, respectively, consistent with a parallel oriented bilayer structure as described above. An alternate structure model, a stage 1 trilayer, would give intercalate layer heights around 0.37 nm, but was discarded because of the product's black colors and TGA mass losses indicating organic content comparable to a bilayer arrangement (see thermal analysis discussion below). Interestingly, the same stage 2 Na-C12-GIC and unreacted graphite are obtained when the amount of C12 reagent is reduced by 2/3, Figure 3b. These conditions favor the formation of mixed phases rather than higher-stage GIC products. The PXRD patterns of Na-C12-GIC and Na-C14-GIC do not change after drying.

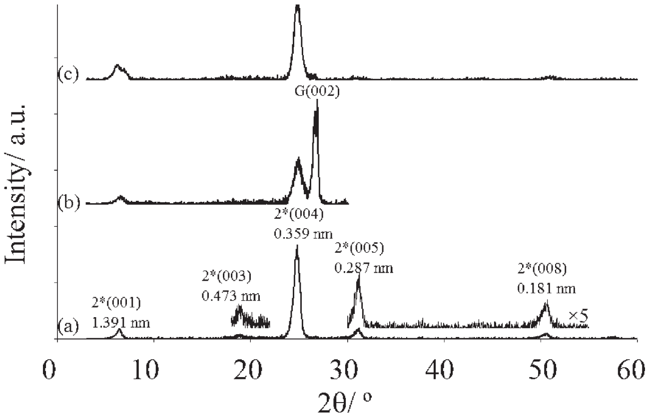

Figure 3. PXRD patterns of: (a) Na-C12-GIC, (b) the mixture of Na-C12-GIC and graphite obtained by decreasing the amine reactant (see text), and (c) Na-C14-GIC. The 2*(00*l*) labels indicate reflections for the stage 2 parallel bilayer structure. The reflection from graphite is labeled G(002).

Although the synthesis of intercalation compounds containing short-, medium-, and long-chain alkylamine for other layered hosts is common in the literature,[1] we believe that this is the first report of such a series for GICs. A summary of the prepared GICs and structure assignments is provided in Table 1.

A simple model for understanding the number of layers formed by the alkylamine intercalates can focus on the relative strength of alkyl

Table 1. Structural and Compositional Data of the Prepared M-alkylamine-GICs

amine	stage no. n	d_i (nm)	intercalate arrangement	wt % amine	wt % Na	experimental composition
C3	1	0.701 (0.700)[a]	monolayer	15.4	9.3	$Na(C3)_{0.7}C_{16}$
C4	1	0.704 (0.697)[a]	monolayer	(14.8)[a]		
C6 wet	1	1.091	bilayer			
C6 dried	1	0.699	monolayer			
C8	1	1.093	bilayer	29.3	3.3	$Na(C8)_{1.6}C_{40}$
C12	2	1.107	bilayer	18.0		
C14	2	1.095	bilayer	14.5		

[a] Values in parentheses indicate M = Li, all others are for M = Na.

chain hydrophobic interactions. The attractive forces between Na^+ cation intercalates and negatively charged graphene sheets strongly favors the formation of GICs with a minimum gallery height, in this case the parallel monolayer arrangement. However, interchain interactions grow in relative strength as the alkyl chain lengths increase. Thus, for Na-C3-GIC and Na-C4-GIC, only parallel monolayers are observed, whereas for Na-C8-GIC, which has more significant interchain interactions, a bilayer arrangement is produced and is preserved even after the GIC is dried. An intermediate behavior is observed in Na-C6-GIC, which undergoes the bilayer to monolayer transition upon drying. Unlike clay hosts where a trilayer structure has been reported for longer chain amines,[4] the bilayer structure persists for Na-C12-GIC and Na-C14-GIC. The change to stage 2 products rather than stage 1 for these GICs may also be associated with the retention of the bilayer arrangement.

Thermal and Elemental Analysis. Representative mass loss curves for the GIC products obtained are depicted in Figure 4a. All show mass losses from ~50−300 °C that are absent in the graphite starting reagent. These losses are followed by a higher temperature mass loss with onset around 600−650 °C, also seen in graphite, which is ascribed to the decomposition of the graphitic host lattice. A single mass loss region is observed for Na-C3-GIC. Together with analysis of the sodium content, we can obtain a GIC composition of $Na(C3)_{0.7}C_{16}$. The Na to amine ratio (1/0.7) and the ~15% amine content of this phase are similar to previous reports for comparable GICs, namely K(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)$_{0.7}$C$_{37}$ (14.4% mass loss),[10] Cs(*n*-pentane)$_{1.0}$C$_{24}$ (14.6%),[14] Li(ethylenediamine)$_{1.0}$C$_{28}$ (14.9%),[7] Cs(*n*-hexane)$_{0.9}$C$_{24}$ (15.6%),[14] and Li(methylamine)$_2$C$_{12}$ (17.4%).[7]

For Na-C8-GIC, the presence of two, rather than one, mass-loss steps agrees with the assignment as a bilayer intercalate. The greater mass loss for the stage 1 bilayer Na-C8-GIC (approximately 29%) also supports this assignment. However, we did not attempt to separate the intermediate phase monolayer Na-C8-GIC by thermal decomposition of the bilayer Na-C8-GIC. The obtained composition of $Na(C8)_{1.6}C_{40}$ shows a significantly decreased Na/amine mole ratio as compared to the propylamine GIC (1/1.6 as compared to 1/0.7), but the amine/graphite ratio is similar in each case. The mass losses of the stage 2 bilayer Na−C12-GIC and stage 1 monolayer Na-C3-GIC are similar (Table 1). This appears reasonable considering the equivalent ratio of intercalate and graphene layers in the two structures. The determination of the amine content in the stage 2 bilayer structure may appear less reliable because of the overlap of the mass loss events (Figure 4a). However, the same GICs prepared in separate experiments showed organic contents that agreed within 2%, and the Na contents in these cases agreed to within 0.6% for Na-C3-GIC and 0.2% for Na-C8-GIC.

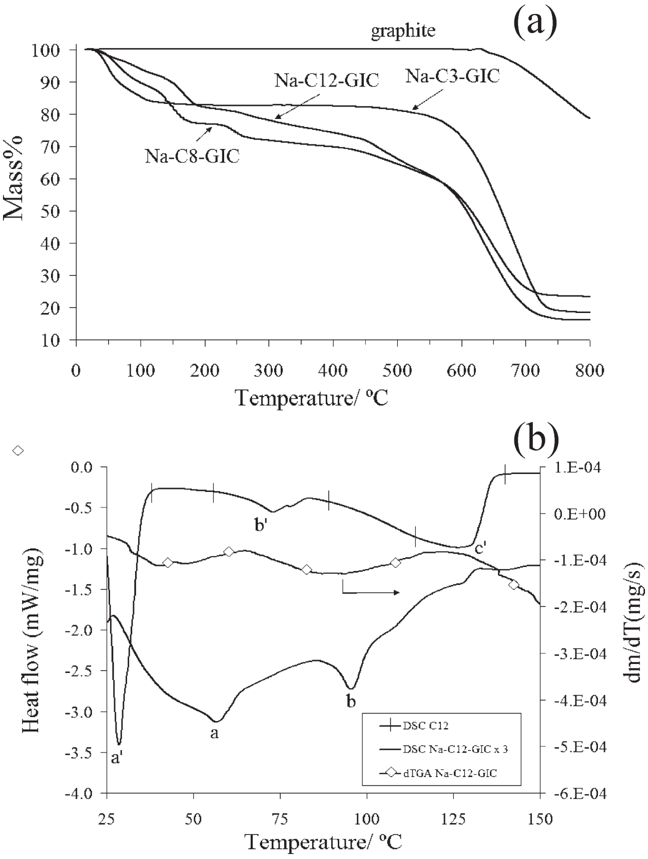

Figure 4. (a) Selected TGA mass loss data for GIC products, and (b) DSC curve for Na-C12-GIC, C12 amine, and the respective dTGA curve for Na-C12-GIC.

We can determine the packing densities of the intercalate galleries by comparing the experimentally obtained compositions and structural data of these Na-C*x*-GICs with the known dimensions of the intercalates. For Na-C3-GIC, the values required are the ionic volume of Na^+ (0.0060 nm^3), the van der Waals molecular volume of *n*-propylamine (0.0714 nm^3),[22] the surface area per carbon atom in a graphene layer (0.0261 nm^2), and the experimentally determined composition and intercalate gallery expansion, $Na(C3)_{0.7}C_{16}$ and 0.366 nm. The packing density, or fraction of volume in the opened galleries occupied by intercalate, can be determined by the following calculation

$$[(0.0060\ \text{nm}^3 + (0.7)(0.0714\ \text{nm}^3)] / (16)(0.0261\ \text{nm}^2)(0.366\ \text{nm}) = 0.37$$

A similar calculation for the bilayer stage 1 GIC $Na(C8)_{1.6}C_{40}$ using the molecular volume for *n*-octylamine (0.158 nm^3)[22] and the gallery expansion (0.758 nm) yields a similar packing density of 0.33. Mono- and bilayer arrangements of short- and long-chain amines appear to produce similar packing efficiencies within the GIC galleries.

The DSC heating curve for Na-C12-GIC and the amine reagent are shown in Figure 4b. The amine reagent shows a strong, sharp melting endotherm at 29 °C, and two additional endotherms at 74 and 130 °C (labeled *a*′−*c*′ respectively). The *n*-dodecylamine boiling point occurs at ∼250 °C and is beyond the temperature range studied. Endotherms for Na−C12-GIC are observed at 58 and 96 °C (labeled as *a* and *b*, respectively). These coincide with peaks in the dTGA curve also shown in Figure 4b. The disappearance of the free amine melting endotherm, and appearance of two new endothermic transitions between 50 and 100 °C for amines intercalates confined in galleries are all consistent with previous observations on amine-intercalated montmorillonite.[2]

Surface studies of *n*-alkylamine (e.g., C8) on graphite show a parallel orientation of the amine long axis to the graphite basal plane,[23] similar to that described above for the GIC galleries. The adsorption of C6−C16 monolayers on graphite has also been reported.[24] In those cases, as in this study, the other orientation details, such as whether the H−C−H or H−N−H face orients toward the graphene layer, remain an unanswered and interesting question.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Tables of PXRD (00*l*) reflections for the reported GICs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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