Supplementary Material (ESI) for Chemical Communications
Electronic Supporting Information for the article:

Anomalous thermal transition and crystallization of ionic liquids confined in graphene multilayers**

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Confinement of ionic liquids in the graphene multilayers

Graphene oxides (GOs) were synthesized through the acidification, oxidation, and exfoliation of natural graphite through modified Hummers method.[1] The resultant GOs (5mg) were fully exfoliated and dissolved in deionized (DI) water (10 mL). The GOs were reduced into reduced graphene oxide (RGO) by 10 μL of hydraize solution at 95 ^{o}C for 12 hours. The quality of RGO was confirmed in our previous reports.[2] The graphene multilayers (GMLs) were obtained from the filtering of homogeneous RGO solution in N,N-dimethylformamide (DMF) through anodic alumina oxide (AAO) membrane filter (47 mm in diameter, 0.2 μm pore size, Whatman). The GML powders were dried in air and isolated from the filter membrane.

The GMLs (2 mg) were mixed with 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4], 0.4 mL), and the mixture was ground with an agate mortar for 20 min. [bmim][BF_4] was confined in the GMLs and crystallized through π-π stacking and hydrogen bonding interactions in the course of grinding. The resultant suspension gradually turned into a black paste. [bmim][BF_4]@GML was isolated from the bulk [bmim][BF_4], not confined in GMLs, through the centrifugation (18,000 rpm, 60 min). [bmim][BF_4]@GML was finally collected by removing the supernatant with a pipet. [bmim][PF_6]@GML and [bmim][Tf_2N]@GML were synthesized, following the same procedure of [bmim][BF_4]@GML.

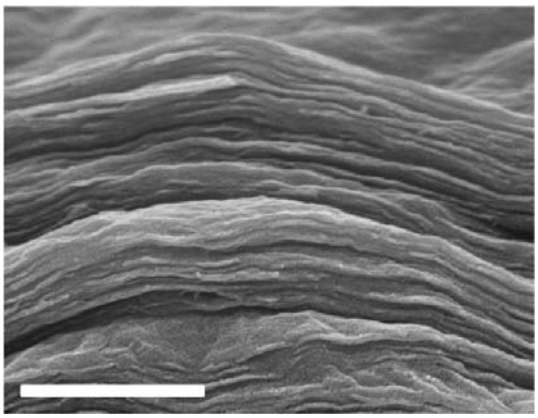

Fig. S1. Cross-sectional SEM image of GML (500 nm bar).

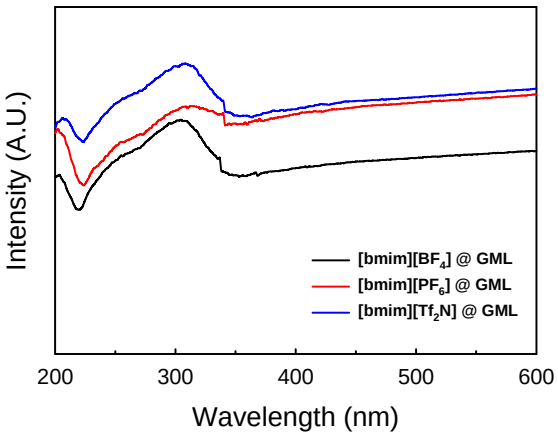

Fig. S2. UV-vis spectra of [bmim][BF_4]@GML, [bmim][PF_6]@GML, and [bmim][Tf_2N]@GML.

UV spectra of the three RTILs@GMLs showed different locations of a characteristic band of GML at around 230 nm, which is ascribed to the π-π* transition.[3]

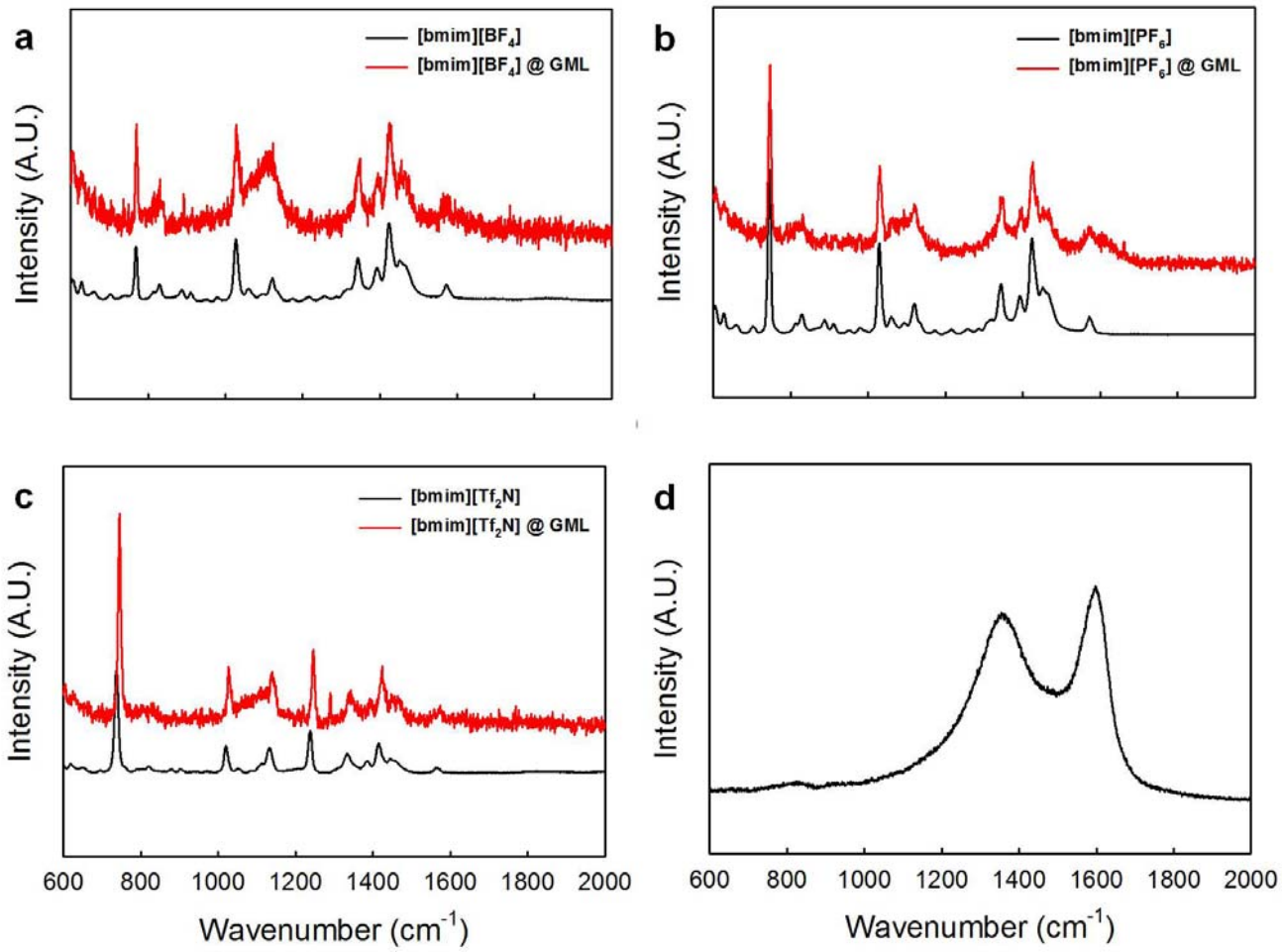

Fig. S3. Raman spectra of (a) [bmim][BF_4] and [bmim][BF_4]@GML, (b) [bmim][PF_6] and [bmim][PF_6]@GML, (c) [bmim][Tf_2N] and [bmim][Tf_2N]@GML, and (d) GML.

As shown in the Raman spectra of GML, three RTILs, and three RTILs @ GMLs, the characteristic bands of pristine GML and RTILs well matched with previous literature.[4] In a similar manner to FT-IR and XRD spectra of the three RTILs@GML, however, the characteristic bands of GMLs in the RTILs@GMLs were not observed due to small volume fraction relative to RTILs.[4] The bulk RTILs revealed C−C and C−N stretching vibrations of the imidazolium ring at around 1570 cm^{-1}, out-plane vibration of imidazolium ring at around 1460 cm^{-1}, symmetrical deformation vibrations of alkyl chain at around 1420 cm^{-1}, and in-plane wagging vibrations of alkyl chain at around 1020 cm^{-1}.[4] In contrast,

the vibrational bands of anions are assigned in the 770 − 740 cm^{-1} region due to the expansion and contraction of the respective anions.[5] The characteristic bands of imidazolium rings and anions at around 1570 cm^{-1}, 1460 cm^{-1}, and 770 − 740 cm^{-1} were shifted to higher wavenumbers after the confinement in the layers of GMLs through π-π stacking interactions with the conjugated structures of GMLs and different hydrogen bonding interactions of respective anions.

Ref.

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

2. B. G. Choi, W. H. Hong, Y. M. Jung and H. S. Park, *Chem. Commun.*, 2011, **47**, 10293; B. G. Choi, J. Hong, W. H. Hong, P. T. Hammond and H. S. Park, *ACS Nano*, 2011, **5**, 7205; B. G. Choi, H. S. Park, T. J. Park, M. H. Yang, J. S. Kim, S. Y. Jang, N. S. Heo, S. Y. Lee, K. Kong and W. H. Hong, *ACS Nano*, 2010, **4**, 2910.

3. B. G. Choi, W. H. Hong, Y. M. Jung and H. S. Park, *Chem. Commun.*, 2011, **47**, 10293.

4. F. Shi and Y. Deng, *Spectrochim. Acta Part A*, 2005, **62**, 239.

5. M. Herstedt, M. Smirnov, P. Johansson, M. Chami, J. Grondin, L. Servant and J. C. Lassègues, *J. Raman Spectrosc.*, 2005, **36**, 762.