

## Electronic Supplementary Information (ESI)

### **A Non-Volatile Memory Device Consisting of Graphene Oxide Covalently Functionalized with Ionic Liquid**

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- **Synthetic experimental procedure**
- **Characterization by IR, Raman and TGA**
- **Full scale XPS spectra of GO and PrGO-IL (Figure S1)**
- **High-resolution C1s, N1s and Br3d XPS spectra (Figure S2)**
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- **AFM image of exfoliated GO (Figure S5)**

## 1. Experimental section

### 1.1 Chemicals.

Natural graphite (Bay Carbon, SP-1 graphite), sulphuric acid (95-97%), hydrogen peroxide (30 wt.%), potassium permanganate, sodium nitrate, were obtained from commercial sources. 3-Bromopropylamine hydrobromide ( $\geq 98\%$ ), 1-Methylimidazole, Sodium methoxide, *N,N'*-Dicyclohexylcarbodiimide (DCC), *N,N'*-Dimethylformamide (reagent grade), Ethanol (reagent grade), Methanol (reagent grade) were obtained from Aldrich and used as received. Unless otherwise stated, other reagents were of analytical grade and were used as received.

### 1.2 Instruments.

All X-ray photoelectron spectroscopy (XPS) measurements were made by a SIGMA PROBE (ThermoVG, U.K.) with a monochromatic Al-K $\alpha$  X-ray source at 100. W Raman spectroscopy measurements were taken using a micro-Raman system (Renishaw, RM1000-In Via) with an excitation energy of 2.41 eV (514 nm). FT-IR spectra was collected using a Thermo Nicolet AVATAR 320 instrument. NMR spectroscopy was performed on a Virian 200 MHz. Thermal properties were characterized by TGA (Polymer Laboratories, TGA 1000 plus). I-V data were collected from Keithley 4200 semiconductor characterization system unit. GO layers was characterized by AFM (Agilent Technologies 5500 AFM/SPM System).

### 1.3 Preparation of Graphene oxide (GO)

GO was prepared from natural graphite powder by the modified Hummers and Offenman's method using sulphuric acid, potassium permanganate, and sodium nitrate.<sup>1</sup>

### 1.4 Preparation of IL-NH<sub>2</sub> (Br<sup>-</sup>).

1-(3-aminopropyl)-3-methylimidazolium bromide (IL-NH<sub>2</sub> (Br<sup>-</sup>)) was prepared according to the literature,<sup>2</sup> 3-bromopropylamine hydrobromide (12 g, 0.05 mol) and 1-methylimidazole (4.35 mL, 0.05 mol) were added to 125 mL ethanol, forming a colorless solution, which was refluxed under nitrogen for 24 h. The resulting turbid mixture was purified by re-crystallization from ethanol, with ethyl acetate as anti-solvent. Finally, the resulting white powder was dried under vacuum at 60°C for overnight to afford the product. Yield 12.5g (75%) of the product.

To afford the free amine from the corresponding hydrobromide salt, it (10g, 0.033 mol) was dissolved in dry methanol (50 mL) followed by addition of sodium methoxide (4g, 0.037 mol). The reaction mixture was stirred for 30 min under N<sub>2</sub> atmosphere. Then the methanol was evaporated to get a white solid, into which immediately 50 mL dichloromethane was added and stirred for 1h under N<sub>2</sub> in room temperature. Then it was filtered and to afford the desired free amine the filtrate was evaporated under vacuum. Yield 7g (95%). IL-NH<sub>2</sub> (Br<sup>-</sup>) is soluble in DMF and DMSO, and well soluble in water. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 10.5 ppm (s, 1H), 7.4 ppm (s, 1H), 7.3 ppm (s, 1H), 4.5 ppm (t, 2H), 4.1 ppm (s, 3H), 2.8 ppm (t, 2H), 2.0 ppm (m, 2H).

### 1.5 Preparation of chemically converted graphene oxide (PrGO-IL).

PrGO-IL was synthesised following the literature,<sup>3</sup> by addition of IL-NH<sub>2</sub> (Br<sup>-</sup>) (40 mg), *N,N'*-Dicyclohexylcarbodiimide (DCC, 40 mg) to a GO (20 mg) solution in DMF (40 mL) under stirring under N<sub>2</sub> atmosphere. The reaction mixture was heated at 50°C for 24h. The it was filtered through membrane filter paper (0.2 μm) and washed with DMF twice, Water twice and Ethenol twice to remove the excess reagents. Then it was dried in vacuum oven for 12h to afford product.

### 1.6 Characterization of PrGO-IL.

The Raman spectrum of the as-made GO (Figure S3(i)) using a laser excitation wavelength of 514 nm displayed the well known broad G peak at  $1607\text{ cm}^{-1}$  corresponding to first-order scattering of the  $E_{2g}$  mode, a prominent D peak at  $1351\text{ cm}^{-1}$  associated with structural defects, amorphous carbon, or edges that can break the symmetry and selection rule, and a 2D peak at  $2690\text{ cm}^{-1}$  originating from a two phonon double resonance Raman process (not shown in the spectra).<sup>4</sup> The Raman spectrum of the PrGO-IL was also characterized by a D peak at  $1353\text{ cm}^{-1}$  and a G peak at  $1594\text{ cm}^{-1}$ . There was a slight shift of the G peak down ( $13\text{ cm}^{-1}$ ) with almost the same intensity ratio ( $r=I_D/I_G$ , 0.91 to 0.92) as observed for as-made GO, indicating little reduction compared to the as-made GO.

The successful functionalization of GO nanosheets with IL-NH<sub>2</sub>(Br<sup>-</sup>) was also reflected by the thermogravimetric analysis (TGA) curves (Figure S3(ii)). TGA was performed on as-made GO and PrGO-IL up to 900°C at a heating rate of  $1^\circ\text{C min}^{-1}$  under N<sub>2</sub>. GO was thermally unstable and started to lose mass upon heating below 100°C due to evaporation of intercalated water. At around 200°C and 580°C, there were two significant mass losses. The former was because of labile functional groups, yielding CO, CO<sub>2</sub>, and steam, while the latter was due to pyrolysis of the carbon skeleton of GO.<sup>5</sup> In contrast, in the case of PrGO-IL with fewer thermally labile oxygen functional groups, the slow mass loss in the range of 170-350°C was attributed to the decomposition of surface-attached IL-NH<sub>2</sub>(Br<sup>-</sup>) molecules.<sup>6</sup> The mass loss at around 600°C was due to pyrolysis of the carbon skeleton of GO. Therefore, the TGA curves confirmed the attachment of IL-NH<sub>2</sub>(Br<sup>-</sup>) to GO.

We used Fourier transform infrared (FT-IR) spectroscopy (Figure. S3(iii)) to determine the characteristic absorption of the functional groups on GO sheets as well as on PrGO-IL. The FT-IR spectra of the as-made GO sheets were characterized by a strong band at  $1726\text{ cm}^{-1}$

corresponding to C=O and a band at  $1624\text{ cm}^{-1}$  for the aromatic C=C stretching frequency. In the FT-IR spectra of PrGO-IL, a characteristic new band appeared at  $1639\text{ cm}^{-1}$  due to amide bonds<sup>7</sup> and ring in-plane asymmetric stretching arising from the imidazolium ring was observed at  $1168\text{ cm}^{-1}$ ,<sup>8</sup> indicating the successful attachment of IL-NH<sub>2</sub>(Br<sup>-</sup>) to the GO nanosheets.

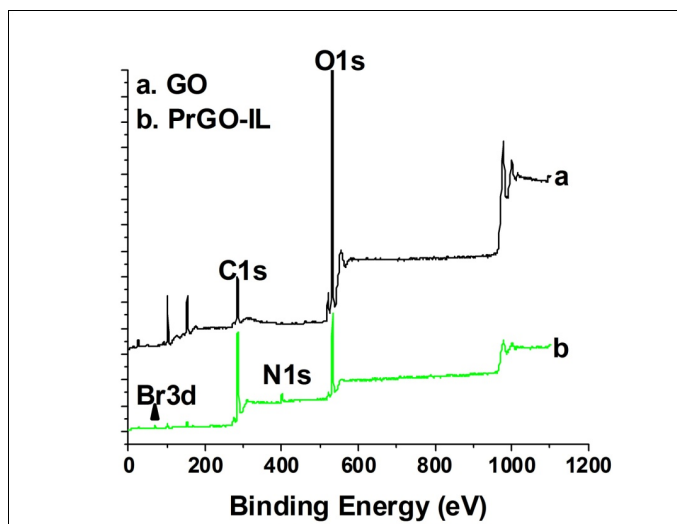


Fig. S1. Full scale XPS spectra of GO and PrGO-IL.

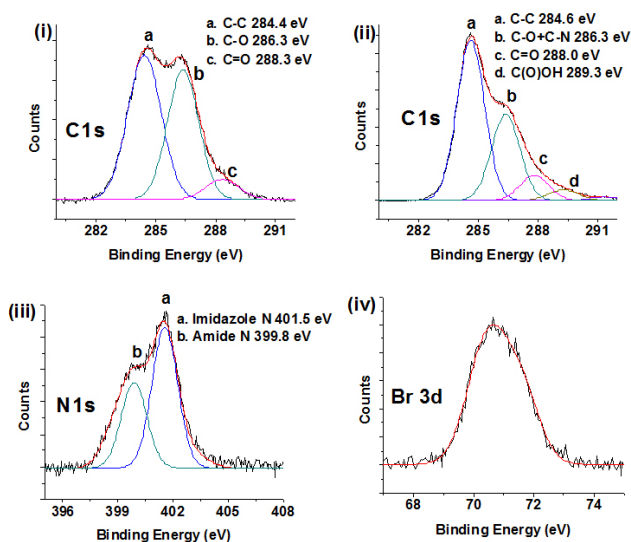


Figure S2. (i) C1s XPS spectra of GO (ii) C1s (iii) N1s and (iv) Br3d XPS spectra of PrGO-IL.

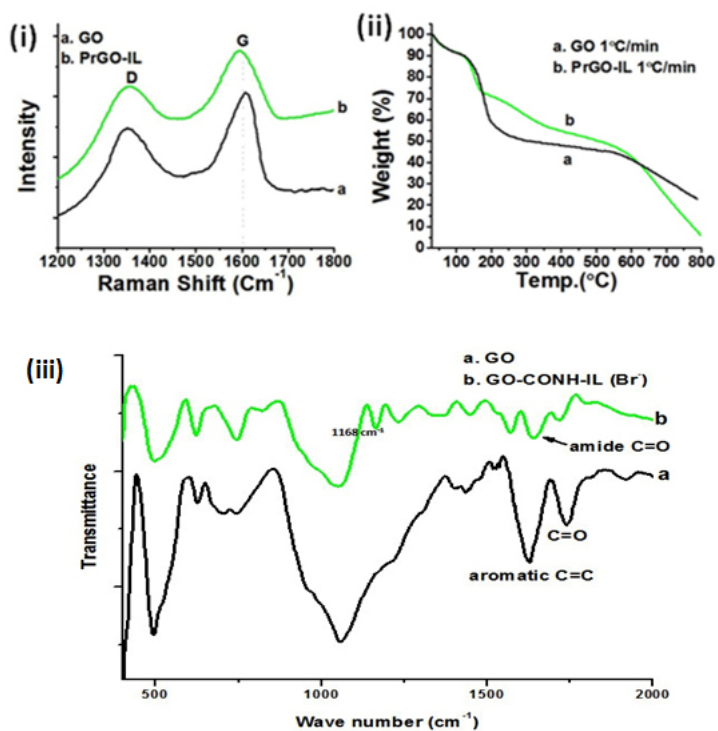


Fig. S3. (i) Raman spectra and (ii) TGA curve (iii) FT-IR spectra of GO and PrGO-IL.

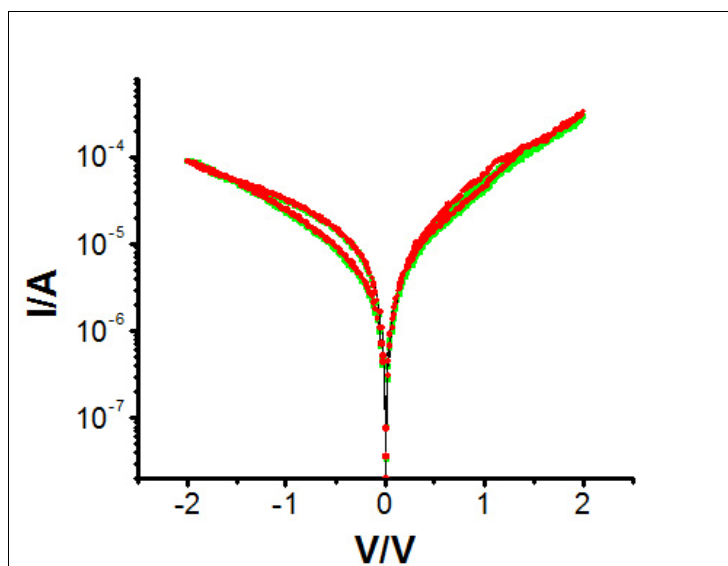
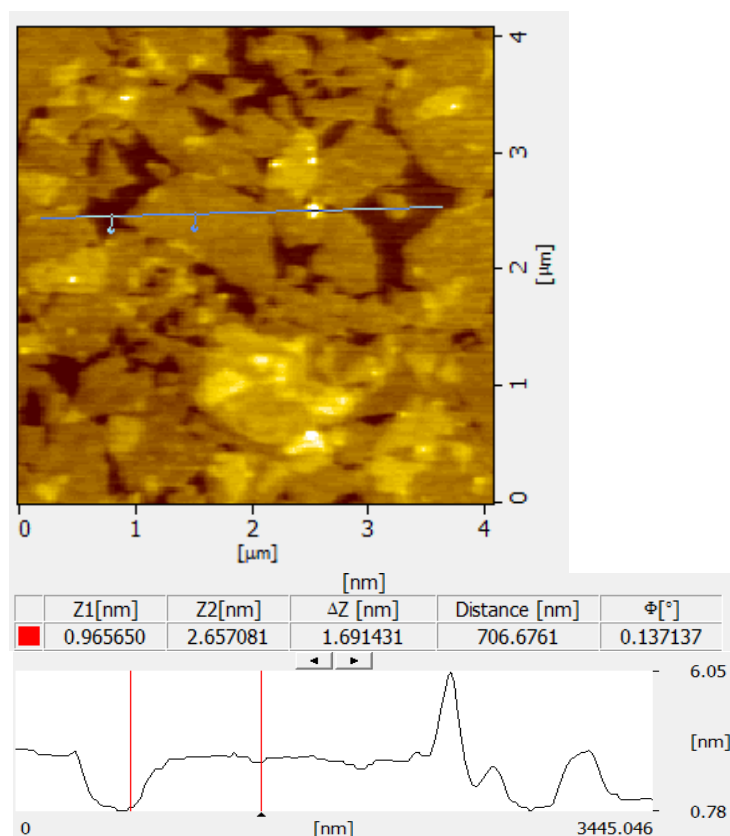


Fig. S4. Control experiment: Hysteretic I-V characteristics of the molecular device (ITO/ GO (heated at 50°C)/Au). The I-V characteristics of the devices were recorded by scanning the applied voltage from 0 to +2 V and then to -2 V, followed by reverse scan from -2 to 0 V.



**Fig. S5.** AFM image of GO solution in water (0.5mg/mL) 50 μL on SiO<sub>2</sub> substrate through spin-coating and high profile along the lines shown in AFM image.

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