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A Bifunctional Approach to the Preparation of Graphene and Ionic Liquid-Based Hybrid Gels

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Electronic Supplementary Information

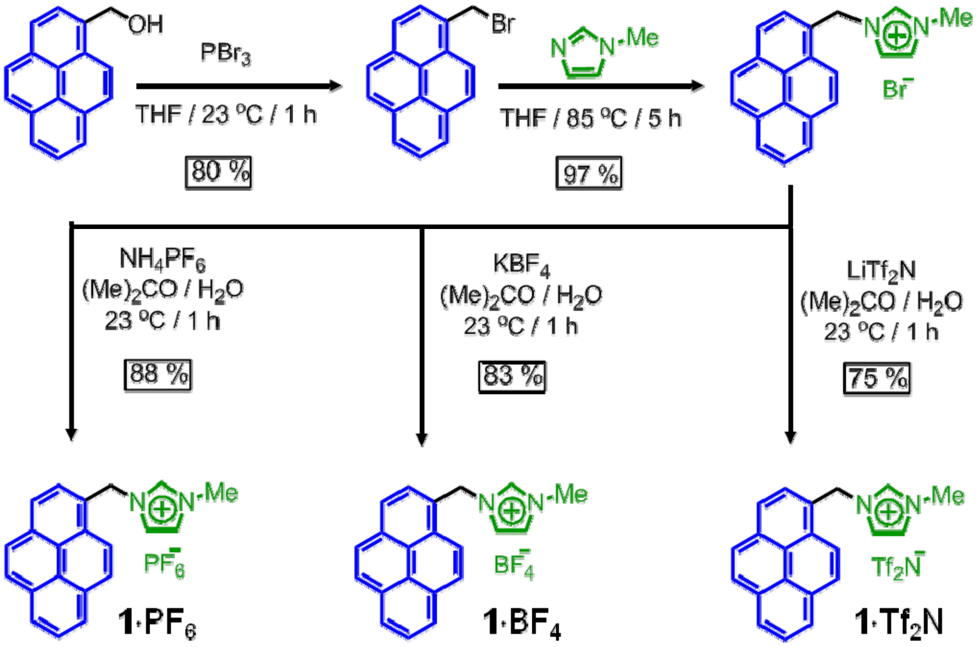
Table of Contents

Section A. Materials / General Methods / Instrumentation

Anhydrous tetrahydrofuran (THF), was obtained from an EMD Chemicals DrySolv® system, while $CDCl_3$, CD_2Cl_2, $(CD_3)_2NCDO$ and $(CD_3)_2SO$ were purchased from Aldrich and used without further purification. Graphite powder (synthetic, conducting grade, 325 mess, 99.9995, metals basis) was obtained from Alfa Aesar. All other reagents and solvents were purchased from commercial sources and were used without further purification, unless indicated otherwise. All reactions were carried out under N_2 atmosphere in flame-dried flasks using anhydrous solvents. Thin-layer chromatography (TLC) was performed using glass or aluminum plates, precoated with silica-gel 60 containing a fluorescent indicator (Whatman LK6F). The plates were inspected by UV light. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX500 (500 MHz) spectrometer. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents. Mass spectra (MS) were recorded on a Finnigan LCQ iontrap mass spectrometer (MS-ESI). High resolution mass spectra (HRMS) were measured on a MICROTOF-Q II high resolution hybrid tandem LC-MS/MS. Raman spectra were obtained using a Nanophoton Raman-11 microscope with a Laser power of 0.3 mW and an exitation Laser source of 532 nm. X-Ray photoelectron spectroscopy (XPS) measurments were conducted on a XPS (Omicron ESCA probe) instrument with an emission current of 2 μA and a beam energy of 10 eV. High resolution XPS spectra were collected on an Omicron ESCALAB (Omicron, Taunusstein, Germany), configured with a monochromated Al Kα (1486.8 eV) 300-W X-ray source with a 1.5 mm circular spot size under an ultrahigh vacuum ($<10^{-8}$). All binding energies were calibrated using the C(1s) carbon peak (284.6 eV). FT-IR studies were conducted using a Perkin Elmer precisely spectrum spotlight 300 FT-IR-microscope instrument. Transmission electron microscopy (TEM) studies were conducted using TEM-JEOL-2100F and TEM-HD-2300 instrument at a 200 kV accelerating electron voltage. SEM imaging was performed on a FEI Quanta 600F sFEG ESEM scanning electron microscope (SEM) at an accelerating electron voltage of 30 kV. Atomic force microscopy (AFM) studies were conducted using Veeco ICON PT system under tapping mode. Rheology studies were performed using a modular compact rheometer Anton Paar MCR150 Physica instrument with 25 mm diameter parallel plate geometry.

Section B. Synthetic Protocols

*1) Syntheses of **1**·PF_6, **1**·BF_4, and **1**·Tf_2N (Scheme S1)*



Scheme S1. The preparation of **1**·PF_6, **1**·BF_4 and **1**·Tf_2N.

1-Bromomethylpyrene: Phosphorus tribromide (875 mg, 3.2 mmol) was added to a solution of 1-pyrenemethanol (500 mg, 2.1 mmol) in dry THF (2 mL) and the mixture was stirred for 1 h at room temperature. It was filtered and the residue was washed with Et_2O to yield the desired product (510 mg, 80 %) as a light yellow solid.[1] ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) δ = 5.26 (2H, s), 8.03 (3H, m), 8.12 (2H, m), 8.24 (3H, m), 8.39 (1H, d, *J* = 9.0 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) δ = 32.2, 122.9, 124.7, 124.9, 125.2, 125.6, 125.7, 126.3, 127.4, 127.8, 128.1, 128.3, 129.1, 130.6, 130.8, 131.2, 132.0 ppm. ESI-MS $[M]^+$ Mass calculated : 294.00, Mass found : 293.92.

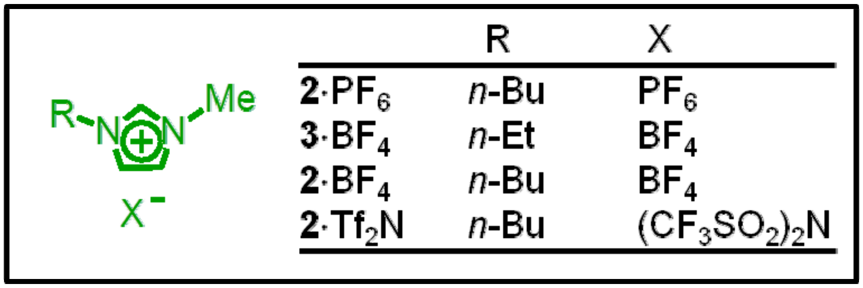
1-Methyl-3-(pyren-1-ylmethyl)-1H-imidazol-3-ium Bromide: *N*-Methylimidazole (205 mg, 2.5 mmol) was added at room temperature under an argon atmosphere to the solution of 1-bromomethylpyrene (250 mg, 0.85 mmol) in dry THF (30 mL). The reaction mixture was heated under reflux for 5 h. It was filtered and the residue was washed with Et_2O to yield the desired product (310 mg, 97%) as a pale yellow solid. ^{1}H NMR (500 MHz, CD_3SOCD_3, 25 ºC) δ = 3.86 (3H, s), 6.27 (2H, s), 7.78 (1H, b), 7.92 (1H, b), 8.19 (2H, m), 8.3 (2H, m), 8.42 (4H, m), 8.52 (1H, d, *J* = 9.5 Hz), 9.21 (1H, s) ppm. ^{13}C NMR (125 MHz, CD_3SOCD_3, 25 ºC) δ = 36.8, 50.9, 123.3, 123.6, 124.6, 124.9, 125.1, 126.2, 126.8, 127.0, 127.7, 128.3, 128.4, 128.9, 129.2, 129.6, 129.8, 131.1, 131.7, 132.5, 137.7 ppm. HRMS (ESI) $[M - Br]^+$ Mass calculated : 297.1386, Mass found : 297.1381.

1·PF$_6$: 1-Methyl-3-(pyren-1-ylmethyl)-1H-imidazol-3-ium bromide (240 mg, 0.64 mmol) was dissolved in Me_2CO/H_2O (20 mL/4 mL) at room temperature. NH_4PF_6 (1 g, 6.1 mmol) was added to the reaction mixture which was stirred for 1 h. It was then filtered and the remaining solid was washed with H_2O to yield **1**·PF$_6$ (250 mg, 88%) as a solid. ^{1}H NMR (500 MHz, CD_3SOCD_3, 25 ºC) δ = 3.82 (3H, s), 6.22 (2H, s), 7.71 (1H, b), 7.91 (1H, b), 8.18 (2H, m), 8.30 (2H, m), 8.42 (4H, m), 8.42 (1H, d, *J* = 9.0 Hz), 9.19 (1H, s) ppm. ^{13}C NMR (125 MHz, CD_3SOCD_3, 25 ºC) δ = 36.8, 50.9, 123.4, 123.7, 124.6, 124.9, 125.1, 126.2, 126.8, 127.0, 127.7, 128.3, 128.4, 128.9, 129.2, 129.6, 129.8, 131.1, 131.7, 132.5, 137.7 ppm. HRMS (ESI) $[M - \mathrm{PF_6}]^+$ Mass calculated : 297.1386, Mass found : 297.1383.

1·$\mathbf{BF_4}$: 1-Methyl-3-(pyren-1-ylmethyl)-1H-imidazol-3-ium bromide (240 mg, 0.64 mmol) was dissolved in Me_2CO/H_2O (20 mL/4 mL) at room temperature. KBF_4 (235 mg, 1.89 mmol) was added and the reaction mixture was stirred for 1 h. It was then filtered and the remaining solid was washed with H_2O to yield **1**·BF_4 (215 mg, 83%) as a solid. ^{1}H NMR (500 MHz, $(CD_3)_2NCDO$, 25 ºC) δ = 4.21 (3H, s), 6.59 (2H, s), 8.09 (1H, b), 8.26 (1H, b), 8.37 (1H, m), 8.45-8.57 (4H, m), 8.62 (3H, m), 8.76 (1H, d, *J* = 9.0 Hz), 9.51 (1H, s) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2NCDO$, 25 ºC) δ = 36.0, 50.7, 122.6, 123.2, 124.4, 124.4, 124.9, 125.6, 126.2, 126.4, 127.0, 127.5, 127.7, 128.6, 128.61, 129.2, 129.4, 130.9, 131.5, 132.4, 137.7 ppm. HRMS (ESI) $[M - \mathrm{BF_4}]^+$ Mass calculated : 297.1386, Mass found : 297.1378.

1·$\mathbf{Tf_2N}$: 1-Methyl-3-(pyren-1-ylmethyl)-1H-imidazol-3-ium bromide (320 mg, 0.84 mmol) was dissolved in Me_2CO/H_2O (20 mL/4 mL) at room temperature. $LiN(CF_3SO_2)_2$ (800 mg, 2.8 mmol) was added and the reaction mixture was stirred for 1 h. The solvents were removed under vacuum and the residue was extracted with CH_2Cl_2 and washed with H_2O. The product **1**·Tf_2N (380 mg, 75%) was obtained as a solid after removing the solvent under reduced pressure. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 ºC) δ = 3.92 (3H, s), 6.1 (2H, s), 7.22 (2H, b), 8.09-8.17 (4H, m), 8.23 (1H, d, *J* = 9.0 Hz), 8.27-8.35 (4H, m), 8.73 (1H, s) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, 25 ºC) δ = 37.0, 52.2, 121.5, 122.6, 124.0, 124.3, 124.7, 125.4, 125.7, 126.6, 126.9, 127.1, 127.6, 129.0, 129.3, 129.8, 130.3, 130.8, 131.5, 133.3, 136.3 ppm. HRMS (ESI) $[M - \mathrm{Tf_2N}]^+$ Mass calculated : 297.1386, Mass found : 297.1386.

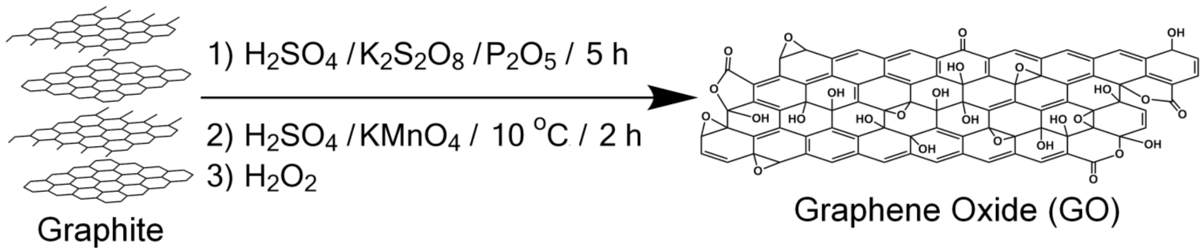
2) Structural formulas of ionic liquids (ILs) (Scheme S2)



	R	X
2·PF_6	*n*-Bu	PF_6
3·BF_4	*n*-Et	BF_4
2·BF_4	*n*-Bu	BF_4
2·Tf_2N	*n*-Bu	$(CF_3SO_2)_2N$

Scheme S2. Structural formulas of ionic liquids (ILs)

3) Synthesis of GO from graphite (Scheme S3)



Scheme S3. The preparation of GO from graphite

Synthesis of Graphene Oxide (GO): GO was synthesized from graphite powder by using a modification of Hummer's method.[2-4] Briefly, graphite powder (0.3 g) (Alfa Aesar, 325 mesh) was added into a mixed solution of concentrated H_2SO_4 (98 %) (2.4 mL), $K_2S_2O_8$ (0.5 g) and P_2O_5 (0.5 g), and the solution was kept at 80°C for 5 h. The mixture was slowly diluted with deionized (DI) H_2O (100 mL) and left to stand overnight. The resulting preoxidized product was filtered and washed with large amount of DI H_2O to get rid of acid residue and then dried. The preoxidized graphite was then added to concentrated H_2SO_4 (98 %) (12 mL). $KMnO_4$ (1.5 g) was added slowly to the mixture under stirring and ice-cooling. The mixture was stirred at 35°C for 2 h, followed by the addition of DI H_2O (70 mL). The reaction mixture was injected with 30%

H_2O_2 (2 mL), a bright yellow solution was obtained. The mixture was filtered and washed with 3.5 M HCl solution (125 mL) and the GO was filtered and dried. Exfoliation of GO was achieved by ultrasonication of GO dispersion in H_2O (60 mg in 3 mL) using a ultrasonic bath sonicator resulting in the formation of a brown dispersion, which was subjected to dialysis for 2 weeks.

General Procedure for the Preparation of Hybrid Gels: GO and **1**·**X** (X = PF_6, BF_4, TF_2N) was added to ILs and sonicated for 30 min in a ultrasound sonic bath sonicator. The dispersed GO in the solution of **1**·X/ILs was heated at 150°C for 1 h. The reduction process can be visualised by observing the color change in the solution from brown to black and the gelation. The critical gelation concentration of $\mathbf{1}^+$ was determined by varying the concentration of $\mathbf{1}^+$ in the initial soultion in ILs. Above the critical gel concentraion, the thermal process results in the formation of stable hybrid gel material. The nanocomposite materials were obtained by dispersing the hybrid gel in DMF and then removing the solvent under vacuum by filtration.

Sample Prepartion for Experiments**:** Samples for XPS experiments were prepared by placing the hybrid gel material over a silicon wafer. The TEM samples were prepared by drop-casting the dispersed nanocomposite solution on a carbon-coated Cu grid before being dried under vacumm at room temperature for 3 d. The Raman and SEM samples were prepared by dropping the nanocompoiste materials onto a silicon wafer.

Section C. Rheology and FT-IR

1) *Rheology studies of* RGO/**1**.PF_6/**2**.PF_6, b) RGO/**1**.BF_4/**2**.BF_4 and c) RGO/**1**.Tf_2N/**2**.Tf_2N *(Fig. S1)*

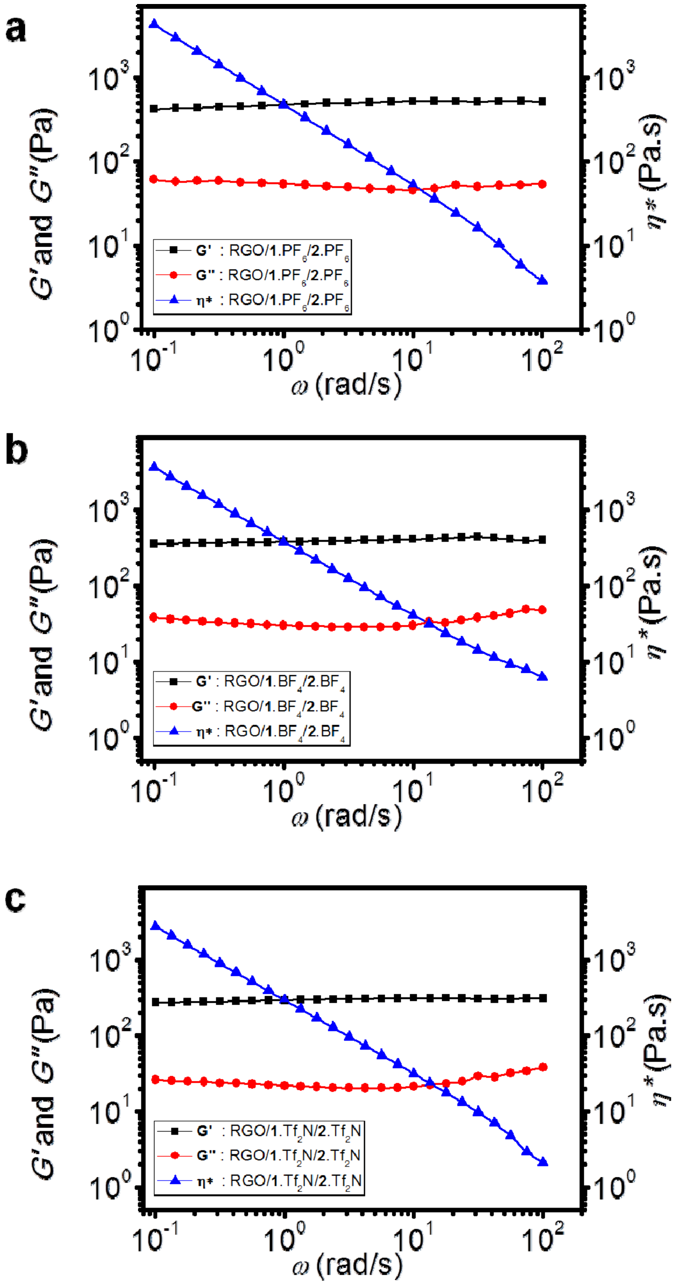


Fig. S1. Angular frequency dependencies of dynamic storage (*G'*) loss modules (*G''*) and complex viscosity (η*) of hybrid gels a) RGO/**1**.PF_6/**2**.PF_6, b) RGO/**1**.BF_4/**2**.BF_4 and c) RGO/**1**.Tf_2N/**2**.Tf_2N at a strain amplitude (γ) of 0.1.

1) *Microscope FT-IR of* GO, **1**.PF_6, and RGO/**1**.PF_6/**2**.PF_6 *(Fig. S2)*

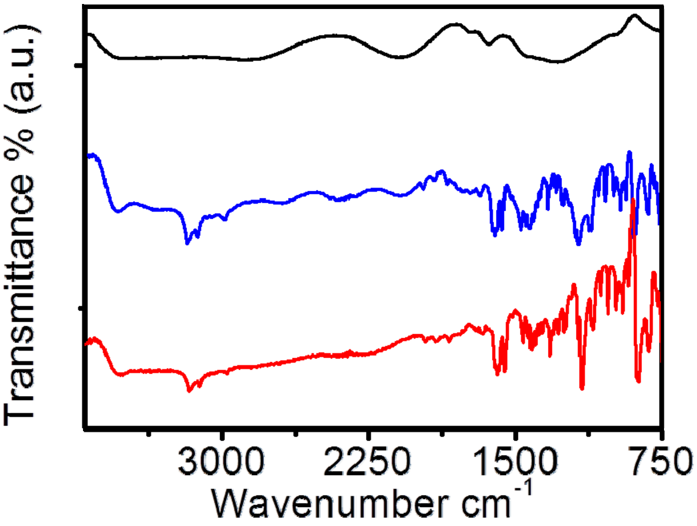


Fig. S2. FT-IR spectra of GO (black), **1**.PF_6 (blue) and RGO/**1**.PF_6/**2**.PF_6 (red). FT-IR analysis was performed using a Perkin Elmer precisely spectrum spotlight 300 FT-IR-microscope instrument under ambient conditions. Samples were prepared by drop-casting the GO dispersion in H_2O, **1**.PF_6 solution in DMF and a diluted solution of RGO/**1**.PF_6/**2**.PF_6 in DMF onto a silicon wafer.

Section C. Microscopic Images

1) *TEM images of GO (Fig. S3)*

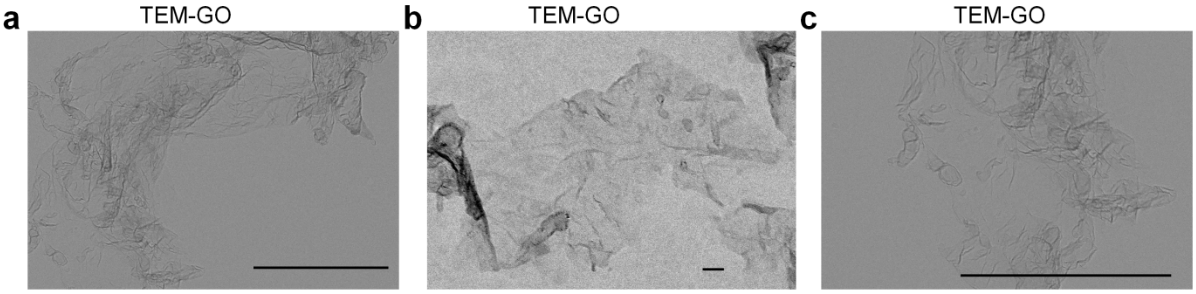


Fig. S3. TEM images (**a-c**) of different sections of GO reveal the presence of GO sheets with folds and wrinkles. Imaging was performed using a TEM instrument at 200 kV accelerating electron voltage. Samples were prepared by drop-casting the GO dispersion in H_2O onto a carbon-coated Cu grid after which the solvent was evaporated under vacuum at room temperature. Scale bars are 1 µm.

2) *TEM images of RGO/**1**·PF_6/**2**·PF_6 (Fig. S4)*

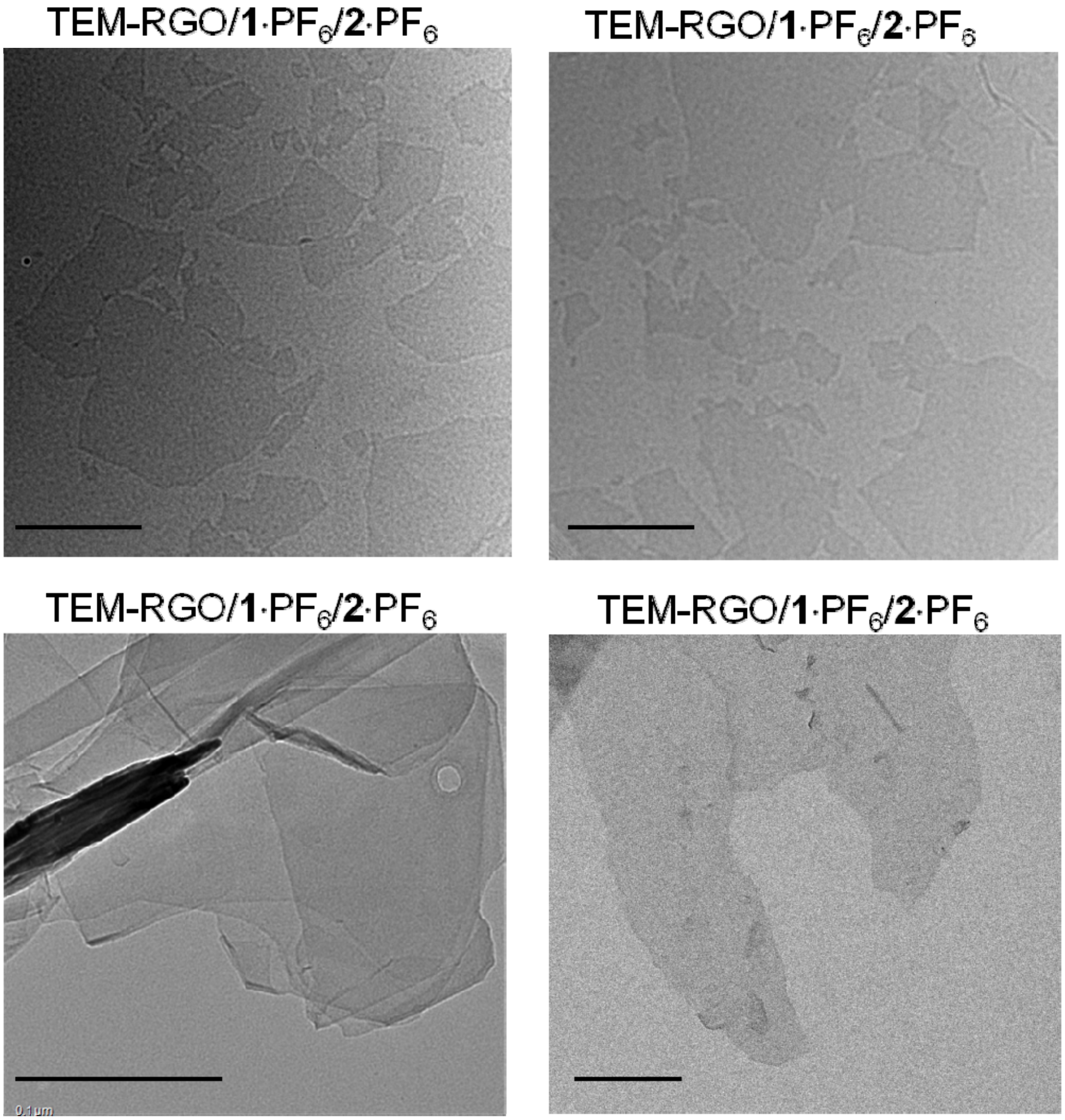


Fig. S4. TEM images of reduced graphene sheets (**a-d**) obtained from **1**·PF_6/**2**·PF_6, reveal graphene sheets with occasional folds. Imaging was performed using a TEM instrument at 200 kV accelerating electron voltage. Samples were prepared by drop-casting the nanocomposite dispersion in DMF onto the carbon-coated Cu grid after which the solvent was evaporated under vacuum at room temperature. All scale bars are 300 nm.

3) *TEM, Z-Contrast and SEM images of GO and RGO/**1**·PF$_6$/**2**·PF$_6$ (Fig. S5)*

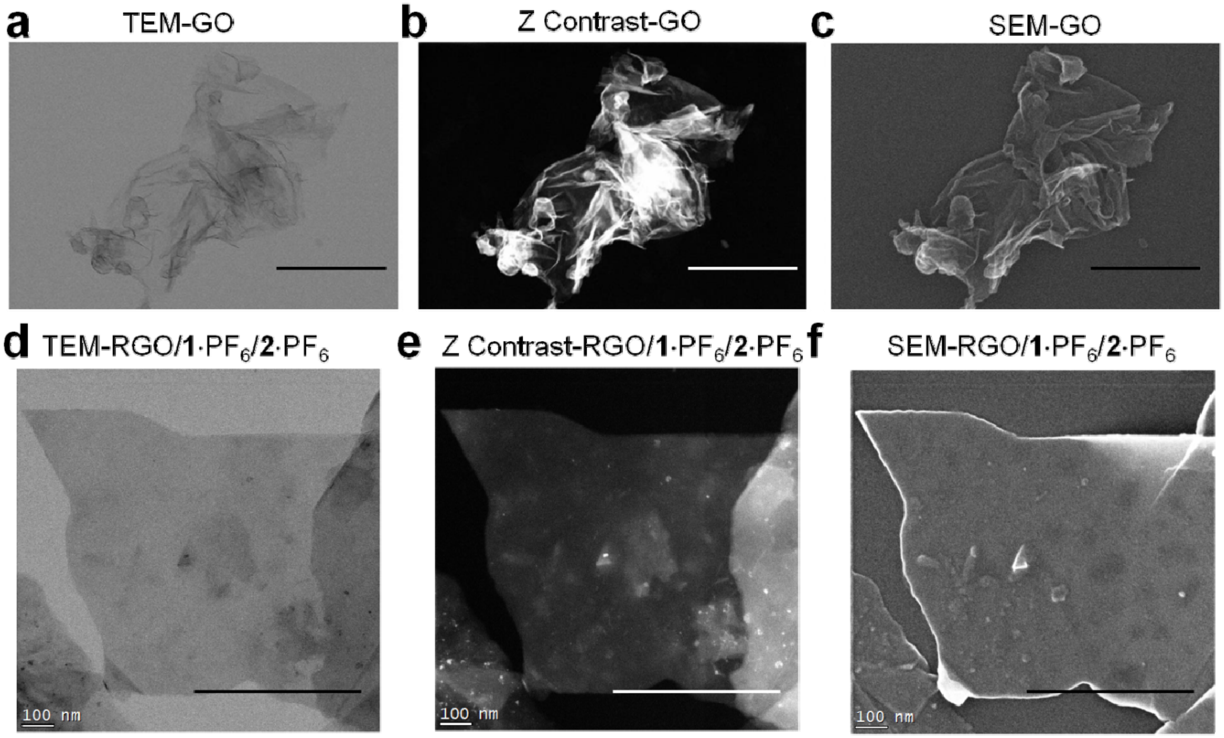


Fig. S5. Microscopic images of GO (**a-c**) and RGO/**1**·PF$_6$/**2**·PF$_6$ (**d-f**) under different viewing modes in the same screening area. Samples were prepared by drop-casting the nanocomposite dispersion in DMF onto the carbon-coated Cu grid after which the solvent was evaporated under vacuum at room temperature. All scale bars are 500 nm.

4) *SEM images of RGO/**1**·BF$_4$/**2**·BF$_4$, RGO/**1**·BF$_4$/**3**·BF$_4$ and RGO/**1**·TF$_2$N/**2**·TF$_2$N (Fig. S6)*

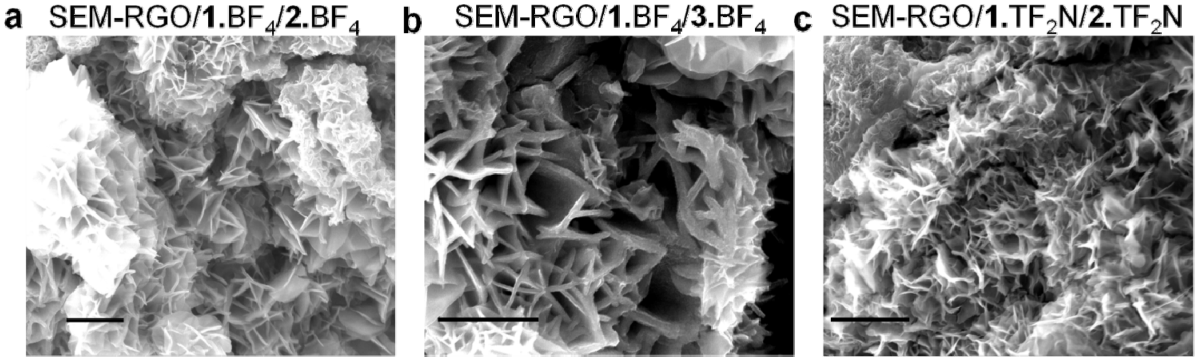


Fig. S6. SEM images of a) RGO/**1**·BF$_4$/**2**·BF$_4$, b) RGO/**1**·BF$_4$/**3**·BF$_4$ and c) RGO/**1**·TF$_2$N/**2**·TF$_2$N. The SEM images illustrate the highly porous networks of the hybrid gels. All scale bars are 5 µm.

Section D. References

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