Supporting Information

Facile approach to synthesize oxo-functionalized graphene/polymer composite for low-voltage operating memory devices

Zhenxing Wang,[a,†,‡] Siegfried Eigler,[b,†,*], Yoshitaka Ishii,[c,*] Yichen Hu,[c] Christian Papp,[d] Ole Lytken,[d] Hans-Peter Steinrück,[d] Marcus Halik[a,*]

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[a] *Organic Materials & Devices (OMD), Institute of Polymer Materials, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Martensstraße 7, 91058 Erlangen, Germany. E-mail: Marcus.Halik@fau.de*

[b] *Department of Chemistry and Pharmacy and Institute of Advanced Materials and Processes (ZMP), Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Dr.-Mack-Straße 81, 90762 Fürth, Germany. E-mail: Siegfried.Eigler@fau.de*

[c] *Department of Chemistry, University of Illinois at Chicago, 845 W Taylor St, Chicago IL 60607, USA. E-mail: YIshii@uic.edu*

[d] *Institute of Physical Chemistry II and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Egerlandstraße 3, 91058 Erlangen, Germany.*

† Both authors contributed equally to this work.

‡ Current address: Advanced Microelectronic Center Aachen (AMICA), AMO GmbH, Otto-Blumenthal-Straße 25, 52074 Aachen, Germany.

Experimental Section:

Natural flake graphite was obtained from Asbury Carbon. Grade 3061 was used. Potassium permanganate, sodium nitrate, sulfuric acid, dodecylamine (DA), sodium hydroxide, hydriodic acid 57% in water and trifluoroacetic acid were obtained from Sigma-Aldrich® and used as received. 2-Propanol and tetrahydrofuran were obtained from VWR and used after distillation. ^{15}N-Dodecylamine (^{15}N-DA) was purchased from Cambridge Isotope Laboratories and used as received. Poly(styrene-*b*-ethylene oxide), (abbreviation used: PSEO) was purchased from Biopolymer source. The semiconductor material α,α´-didecylsexithiophene (Dec-6T-Dec) was obtained from H. C. Starck and the SAM molecule 3-methyl-1-(12-phosphonododecyl)imidazolium bromide (IMI-PA) was purchased from Sikemia. Centrifugation was accomplished by a Sigma 4K15 centrifuge, Sigma Laborzentrifugen GmbH, Germany. Elemental analysis was performed by combustion and gas chromatographic analysis with a VarioMicro CHNS analyzer from Elementar Analysensysteme GmbH, Hanau, Germany. Thermogravimetric analysis (TGA) equipped with a mass spectrometer (MS) was accomplished on a Netzsch STA 409 CD instrument equipped with a Skimmer QMS 422 mass spectrometer (MS/EI) with the following programmed time dependent temperature profile: RT-700 °C (TGA-MS) with 10 K/min gradient, and cooling to RT. The initial sample weights were about 6 to 7 mg and the whole experiment was accomplished under inert gas atmosphere with a He gas flow of 80 ml/min. This TGA-MS was used for the characterization of oxo-G_1, def-GO and def-GO/DA. Thermogravimetric analysis (TGA) equipped with a mass spectrometer (MS) was accomplished on a Pyris1 TGA equipped with a Clarus SQ 8 C mass spectrometer with the following programmed time dependent temperature profile: RT–700 °C (TGA-MS) with 20 $Kmin^{-1}$ gradient and cooling to RT. TGA was coupled with a gas chromatograph from Perkin Elmer, Clarus 680, operated under He (10 ml /min) and the temperature ramp used was 40-80 °C (20 min), 80-280 °C (10 min) and 280-700 °C (21 min). TGA was also coupled with FTIR spectrometer Frontier from Perkin Elmer for recording FTIR spectra. The initial sample weights were about 1 to 3 mg and the whole experiment was accomplished under inert gas atmosphere with a N_2 gas flow of 70 ml/min. The whole coupling was TGA-FTIR-GC-MS. Langmuir-Blodgett films were prepared using Langmuir-Blodgett Minitrough from KSV NIMA and films are prepared from MeOH/water mixtures on water as subphase if not otherwise stated at a pressure of 1.5 mN/m to yield slightly over packed films. These films were used for AFM imaging and scanning Raman spectroscopy. Films of dodecylamine functionalized GO were prepared by drop casting, from a solution with a concentration of 0.001 mg/ml. The pH was measured using a pH100 from VWR. Optical microscope images are made with Axio M1m Imager, Carl Zeiss, Germany. Scanning Raman spectroscopy was accomplished on a Horiba Jobin Yvon LabRAM Aramis confocal Raman microscope with an excitation wavelength of 532 nm. The spot size was about 1 µm using an Olympus LMPlanFl 100, NA 0.80 objective in back-scattering geometry. A silicon detector array charge coupled device (CCD) was used at -70 °C for gathering Raman spectra. The spectrometer was calibrated in frequency using crystalline graphite. A motorized x,y table was used to scan the sample area using swift-mode. The sample was mounted on the x,y table and it was ensured that the focus of the laser is constant within the scanned area. The increment of scanning for an area of 150 x 150 μm^2 was 4 µm, 0.25 s exposure time with a laser intensity of about 1 mW, grating 600, laser excitation 532 nm. For the analysis of Raman spectra, gathering and evaluation of statistical information, the preparation of histograms and creating SRM images a combination of software was used, Labspec 5, python modules from SciPy.org and OriginPro 9. The 2D peak was fitted by one Lorentz function.[1]

ssNMR experiments:

The ssNMR experiments were performed at static magnetic fields of 9.4 or 11.7 T. The freeze-dried oxo-G_1/DA sample of 16.1-18.3 mg was packed in a MAS rotor for solid state NMR. The ^{13}C chemical shifts were referenced to neat TMS using the secondary reference of adamantane CH_2 peak at 38.48 ppm [2, 3] and the ^{15}N chemical shifts were referenced to liquid $^{15}NH_3$ at 0 ppm using the indirect referencing of a ^{13}C signal. Basic 1D ssNMR experiments were conducted using a Bruker Avance III NMR spectrometer and a home-built 2.5mm MAS probe at a ^{1}H NMR frequency of 400.21 MHz with a Varian Inifinity-plus MAS controller and a variable temperature (VT) system. The temperature of VT cooling air was set at -10 °C with a flow rate of 360 L/h so that the sample temperature was maintained at ~14 °C. The MAS spinning speed was set to 20,000 ± 10 Hz. The 1D ^{13}C and ^{15}N MAS spectra in Figure 3A, B were collected with excitation by a $\pi/2$-pulse of 4.5 μs and 6.5 μs widths, respectively. For the 1D ^{13}C or ^{15}N MAS spectrum, a rotor-synchronized echo scheme was used with an interval of two rotation periods (100 μs) before the signal acquisition after the excitation $\pi/2$-pulse and a π-pulse was applied in the middle of the interval. A total of 4096 scans were accumulated without any ^{1}H RF decoupling. The spectra were apodized with Lorentzian line broadenings of 200 Hz and 100 Hz for ^{13}C and ^{15}N, respectively. The ^{15}N cross polarization experiment was acquired with 4096 scans using ^{1}H-^{15}N contact time of 0.4 ms and 150 Hz Lorentzian line broadening was used for the spectrum.

2D $^{1}H/^{15}N$ and $^{1}H/^{13}C$ correlation ssNMR experiments and ^{13}C-{^{15}N} REDOR experiments in Figure 3C-E were conducted at a static magnetic field of 11.7 T using a Bruker Avance III wide-bore NMR spectrometer with a Bruker 3.2-mm triple-resonance E-free MAS probe at a ^{1}H NMR frequency of 500.2 MHz. The temperature of VT cooling air was set to 275K at a flow rate of 1070 L/h. The MAS spinning speed was set to 22,000 ± 5 Hz. For the 2D ^{15}N-^{1}H-correlation experiment in Figure 3C, 64 t_1 points were acquired using a CP mixing time of 0.4 ms with 2048 scans for each real or imaginary t_1 data point with a t_1 increment of 45.45 μs. The total experimental time was 4.3 h. The carrier frequencies for ^{15}N and ^{1}H were set at 50 and 3.5 ppm, respectively. The spectra were processed with Lorentzian broadening of 300 and 200 Hz in the ^{15}N and ^{1}H dimensions, respectively. For the 2D ^{13}C-^{1}H-correlation experiment in Figure 3D, 48 t_1 points were collected using a mixing time of 0.7 ms with 10,240 scans for each real or imaginary t_1 data point with a t_1 increment of 45.45 μs. The carrier frequencies for ^{13}C and ^{1}H were set at 100 ppm and 3.5 ppm, respectively. The total experimental time was 15 h. The spectra were processed with 300 and 200 Hz Lorentzian line-broadening for the ^{13}C and ^{1}H dimensions. For the ^{13}C-{^{15}N} REDOR experiments in Figure 3E, prior to ^{15}N dipolar dephasing, CP from ^{1}H

spins was used with a contact time of 0.7 ms to enhance ^{13}C signals. A ^{13}C-^{15}N dipolar dephasing period of 8.7 ms or 11.6 ms was used by changing the repetition number of ^{15}N dephasing π-pulses in the REDOR sequence. A π-pulse width of 11 μs was used for ^{15}N, while a π-pulse width of 10 μs was used for ^{13}C. Due to fast relaxation of ^{1}H and use of CP from ^{1}H, these experiments with a mixing time of 8.7 ms and 11.6 ms were conducted with short recycle delay of 0.5 s and 0.64 s, respectively. A total of 73,728 scans (~10.7 h) and 32,768 scans (~6 h) were respectively accumulated for each experiment with or without ^{15}N dephasing π-pulses. The carrier frequencies for the ^{13}C, ^{15}N and ^{1}H channels were set at 100, 50 and 3.5 ppm respectively. The spectra were processed with 800 Hz Lorentzian line-broadening.

Ab-initio calculations:

Structural optimizations and ^{15}N chemical-shift calculations were performed using Gaussian 03 (Revision E.01)[4] on a UNIX workstation with two quad-core CPUs (ASA Computers Inc., Mountain View, CA, USA). Dodecylamine, dodycylammonium and the simplified oxo-G_1/DA structural models were geometry optimized at the B3LYP/6-31G* level of theory.[5-8] Chemical shielding tensors for ^{15}N of dodecylamine and dodecylammonium were calculated using GIAO[9] with BPW91 and a 6-311+G* basis set, which was optimized from a previous study on aminopyrimidines and aminobenzenes.[10] The chemical shielding tensors for ^{15}N were converted to the chemical shift tensor as follows. Ammonia ($^{15}NH_3$) was used as the theoretical reference compound. The isotropic chemical shielding of ^{15}N in an isolated ammonia molecule was calculated at the BPW91/6-311+G* level of theory, after geometry optimization at the same level of theory. The calculated shielding for ammonia gas was converted to the shielding of liquid ammonia by adding the experimentally confirmed difference (−20.7 ppm) between the chemical shift of gas-phase ammonia and that of liquid-phase neat ammonia.[11, 12] This gave the calculated shielding of neat liquid ammonia, which was 236.6 ppm. The calculated shielding tensor values of each nitrogen species of our interest were then subtracted from the calculated isotropic shielding of liquid ammonia at the same level of theory in order to calculate the ^{15}N chemical-shift tensor values. The average of the principal values of the chemical shift tensor yielded the isotropic ^{15}N chemical-shift value.

Preparation of oxo-G_1:

The method for preparation is adopted from an earlier publication.[13]

No pre-treatment of graphite was applied. Graphite (1 g, 83 mmol grade 3061, Asbury Carbon) and sodium nitrate (0.5 g, 5.9 mmol) were dispersed in concentrated sulphuric acid

(24 mL). The dispersion was cooled to about 0 °C. After that, over a period of three hours potassium permanganate (3.0 g, 19 mmol) was added. The temperature of the reaction mixture was kept below 10 °C and stirred for an additional 16 h. The reaction mixture was still cooled and during cooling the reaction mixture was continuously diluted with water (80 mL, 12 h). The temperature of the reaction mixture remained below 10 °C. The reaction mixture was then poured on ice (500 mL) and hydrogen peroxide (20 mL, 3%) was added drop wise until gas evolution was completed. The temperature of the mixture remained below 10 °C. The obtained graphite oxide was purified by repeated centrifugation and dispersion in cooled water (below 10 °C) until the pH of the supernatant was neutral. Graphite oxide already delaminates to single layers. However, GO was yielded by mild sonication using a bath sonicator. The suspension was finally centrifuged three times at 5,000 g to remove remaining graphite oxide. Finally the oxo-G_1 was dispersed in water and a part of that stock solution was freeze dried for analysis and to determine the concentration of the stock solution, which was 0.5 mg/ml. For further experiments the stock solution was used.

Elemental Analysis: C 46.33, H 2.36, N 0.02, S 6.47. Total weight loss according to thermogravimetric analysis (N_2, 25-800 °C): 51.8 %; yield: 650 mg freeze dried.

Considerations about the terminology oxo-G_1:

There is a lack in terminology on graphene derivatives, as well as types of graphene oxide. Therefore, systematics are proposed to make it easier for the reader to understand what type of material authors referring.[14, 15]

$$S/{}^{s,d}G_n-(R)_f/A$$

S: substrate, s: size of graphene, d: structural defect density of graphene within the carbon framework, in % G: graphene; n: number of layers of graphene R: addend; f: degree of functionalization given in %, based on C-atoms; A: non-covalently bound molecules; no S: reactions applied in dispersion.

Here, we use a simplified terminology that does not cover all possible details. We use G_1 to indicate that single layers of a material are prepared that is based on the honeycomb lattice. The density of defects can be estimated by Raman to about 0.3% (Figure S1). However, densities of defects in oxo-G_1 are constant and thus, the density of defects is not throughout the manuscript. Typical flake size is roughly 2-10 µm as depicted in AFM images (Figure S6-S8). Moreover, about 5% of C atoms are functionalized with organosulfate groups, in addition to other sp^3-hybridized carbon due to epoxy groups and hydroxyl groups. In addition we determined by ssNMR a ratio of sp^2 and sp^3 hybridized carbon of about 1:1.

Titration of oxo-G_1 with sodium hydroxide:

A dispersion of oxo-G_1 in a 1/1 mixture of 2-propanol and water was prepared by dispersion of 7 mg GO from an aqueous stock solution of oxo-G_1. The final concentration of oxo-G_1 was 35 µg/ml and the volume was 200 ml. A stock solution of sodium hydroxide at a concentration of 0.54 mmol/ml (21.6 mg/L) was used for the titration experiment. The titration was continued until a pH of about 8 was reached. Within 1 h the pH increased to about 7.5 as a consequence of the buffer effect of oxo-G_1.

Titration of oxo-G_1 with dodecylamine:

A dispersion of oxo-G_1 in a 1/1 mixture of 2-propanol and water was prepared by dispersion of 7 mg GO from an aqueous stock solution of oxo-G_1. The final concentration of oxo-G_1 was 35 µg/ml and the volume was 200 ml. A stock solution of dodecylamine at a concentration of 0.54 mmol/ml (100 mg/L) was used for the titration experiment. The titration was continued until a pH of about 8.5 was reached. Within 1 h the pH increased to about 7.4 as a consequence of the buffer effect of oxo-G_1.

Preparation of oxo-G_1/DA and oxo-G_1/^{15}N-DA:

A dispersion of oxo-G_1 (15 mg, 30 ml of stock solution, 0.5 mg/ml) was used to prepare a dispersion of oxo-G_1 in a 1/1 mixture of 2-propanol and water at a concentration of 100 µg/ml. The dispersion was stirred at room temperature (rt) and DA or ^{15}N-DA (6 mg in 50 ml of 2-propanol) was added dropwise. A precipitate was formed within 10 min and the dispersion was stirred for an additional 30 min. The mixture was centrifuged (5000 g, 15 min 10 °C) and dispersed in a 1/1 mixture of 2-propanol and water (200 ml), two times. Finally, the centrifuged product was soaked in pure water for freeze drying to yield 20 mg of freeze dried product.

Elemental Analysis: C 57.47, H 4.88, N 1.94, S 2.40. Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 56 %.

Preparation of def-GO:

GO with introduced defects (def-GO) was prepared from oxo-G_1 dispersion. To an aqueous dispersion of oxo-G_1 (100 mg, 200 ml, 0.5 mg/ml) was added sodium hydroxide (16 mg, 0.4 mmol) and the dispersion was heated to reflux for one hour. The mixture was centrifuged (20.000 g, 30 min) and dispersed in water (200 ml) for three times. The final product was freeze dried for analysis.

Elemental Analysis: C 48.20, H 2.84, N 0.04, S 0.59. Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 43 %; rt-95 °C: 6.8%; 95 °C-210 °C: 21.0%; 210-700 °C: 15.0%.

Preparation of def-GO/DA:

The preparation was done according to the procedure of oxo-G_1/DA preparation, using the same amount of material and reagents.

Elemental Analysis: C 58.10, H 4.09, N 1.19, S 0.53. Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 39.9 %; rt-120 °C: 2.9%; 120 °C-200 °C: 17.1%; 200-490 °C: 17.4%.

Preparation of oxo-G_1/DA/PSEO:

The polymer-composite oxo-G_1/DA/PSEO was prepared by dispersing oxo-G_1/DA (10 mg) in tetrahydrofuran (100 ml) and the dropwise addition of the polymer dispersion (40 mg polymer in 100 ml THF). As polymer, a block-co-polymer Poly(styrene-*b*-ethylene oxide), of styrene and ethylene oxide was used, with molecular mass contributions of about 105.000 and 3.000. The mixture was stirred for 30 min and the mixture was centrifuged and dispersed in THF (80 ml) to remove excess of polymer (three times).

Elemental Analysis: C 65.20, H 6.78, N 0.21, S 0.58. Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 79 %; rt-240 °C: 23%; 240-400 °C: 12%; 400-700 °C.: 43%.

Preparation of def-GO/DA/PSEO:

The preparation was accomplished using the same procedure as for the preparation of oxo-G_1/DA/PSEO.

Elemental Analysis: C 73.58, H 6.44, N 0.27, S 0.16. Total weight loss according to thermogravimetric analysis (N_2, 25-700 °C): 73 %; rt-200 °C: 14%; 200-350 °C: 8%; 350-700 °C.: 51%.

Solvent exchange: From oxo-G_1 in water to oxo-G_1 in THF (and preparation of films on wafer):

A dispersion of oxo-G_1 in water (150 ml, 0.1 mg/ml) was centrifuged (20.000 g, 45 min) and dispersed in 150 ml THF, followed by another centrifugation and dispersion step. A part of the dispersion of oxo-G_1 in THF was further diluted to a concentration of 0.001 mg/ml and a drop was deposited on a 300 nm SiO_2 / Si wafer for AFM analysis.

Reference experiment using oxo-G_1 in THF and PSEO:

A dispersion of oxo-G_1 in THF (0.1 mg/ml, 20 ml) was mixed with PSEO in THF (1 mg/ml, 8 ml). The dispersion was sonicated with a bath sonicator for about 5 min. However, the dispersion was not stable and a precipitate was formed within minutes.

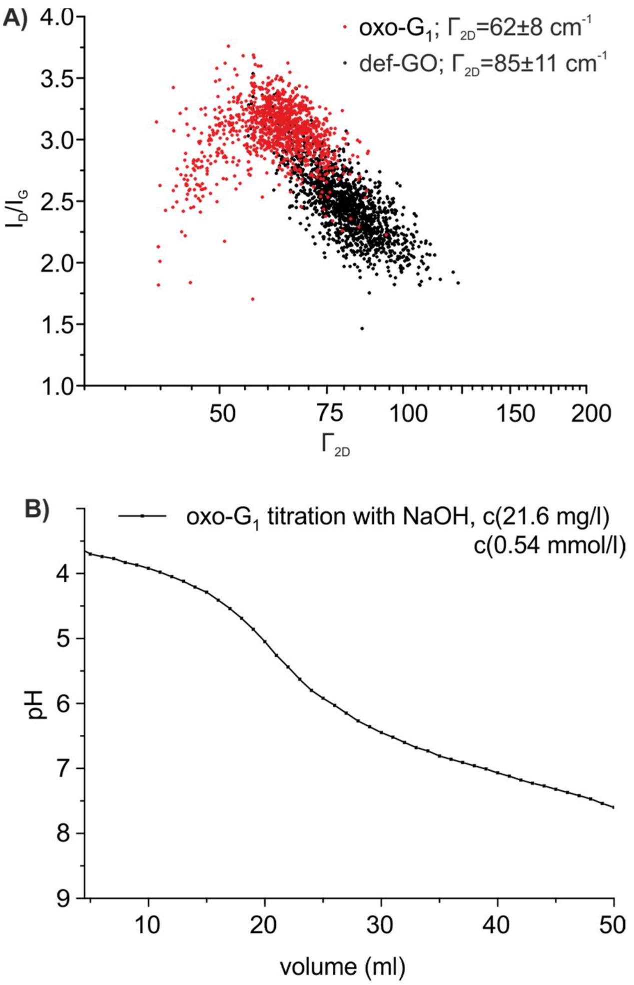

Figure S1. A) Statistical Raman analysis of a film of flakes of oxo-G_1 and def-GO by plotting I_D/I_G against full-width at half-maximum (Γ) of the 2D band of Raman spectra. B) pH titration of oxo-G_1 with sodium hydroxide in *i*-propanol/water (1/1).

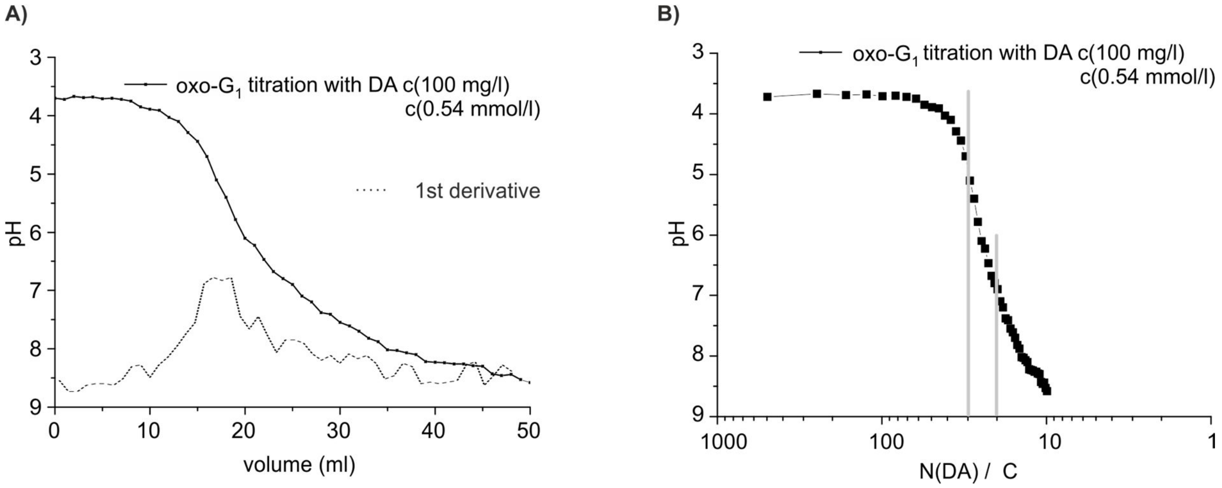

Figure S2. A) pH titration of oxo-G_1 with dodecylamine in *i*-propanol/water (1/1). B) recalculated curve of A) correlating the volume of added dodecylamine to the number of titrated dodecylamine molecules per amount of carbon atoms.

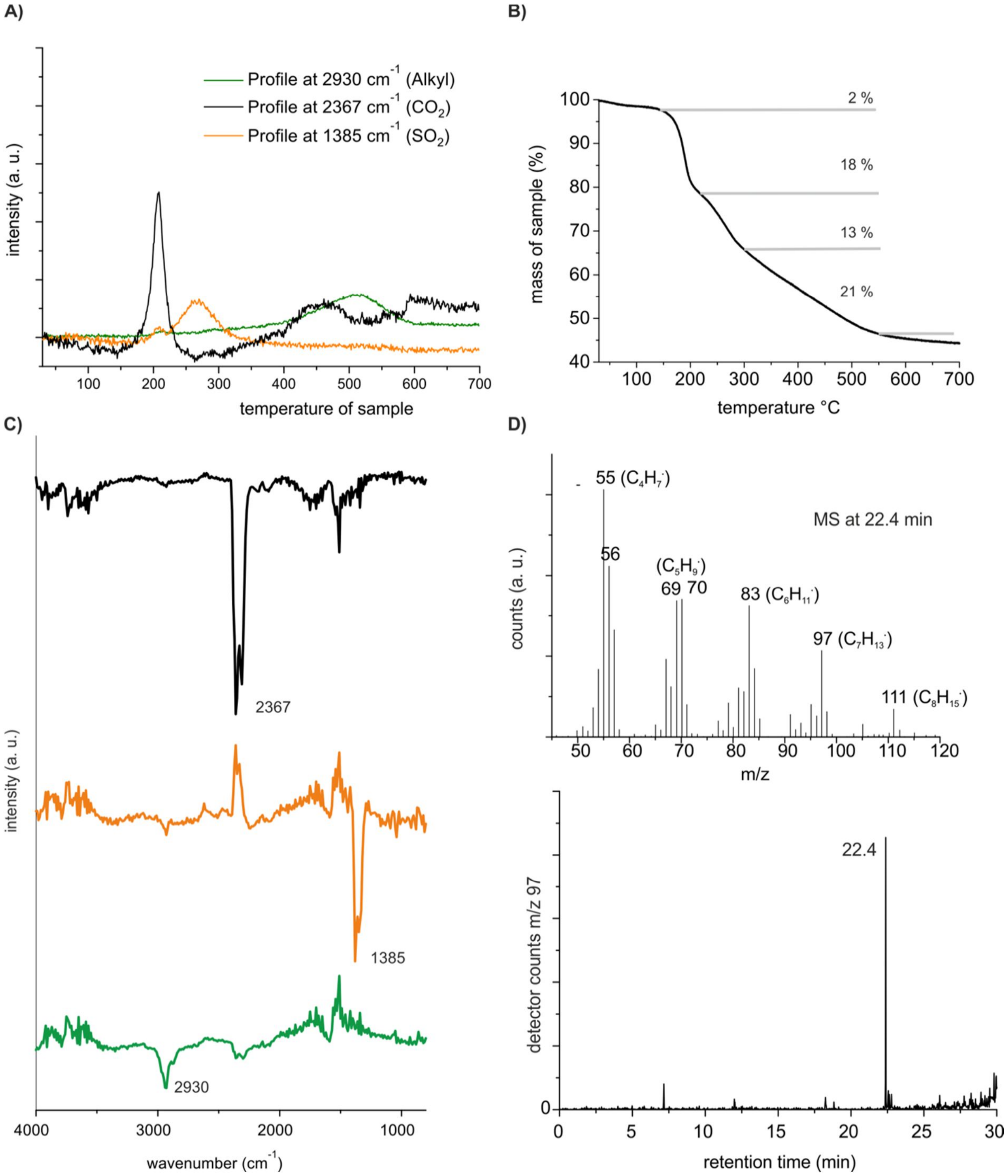

Figure S3. A) TGA of oxo-G_1/DA between 30 °C and 700 °C and the temperature-profiles of cleaved alky, CO_2 and SO_2 formation, identified by FTIR. B) TGA profile of oxo-G_1. C) FTIR spectra of gases formed at 200 °C (black), 280 °C (orange) and 470 °C (green). D) MS of gas produced at 470 °C and separated by gas chromatography at an elution time of 22.4 min.

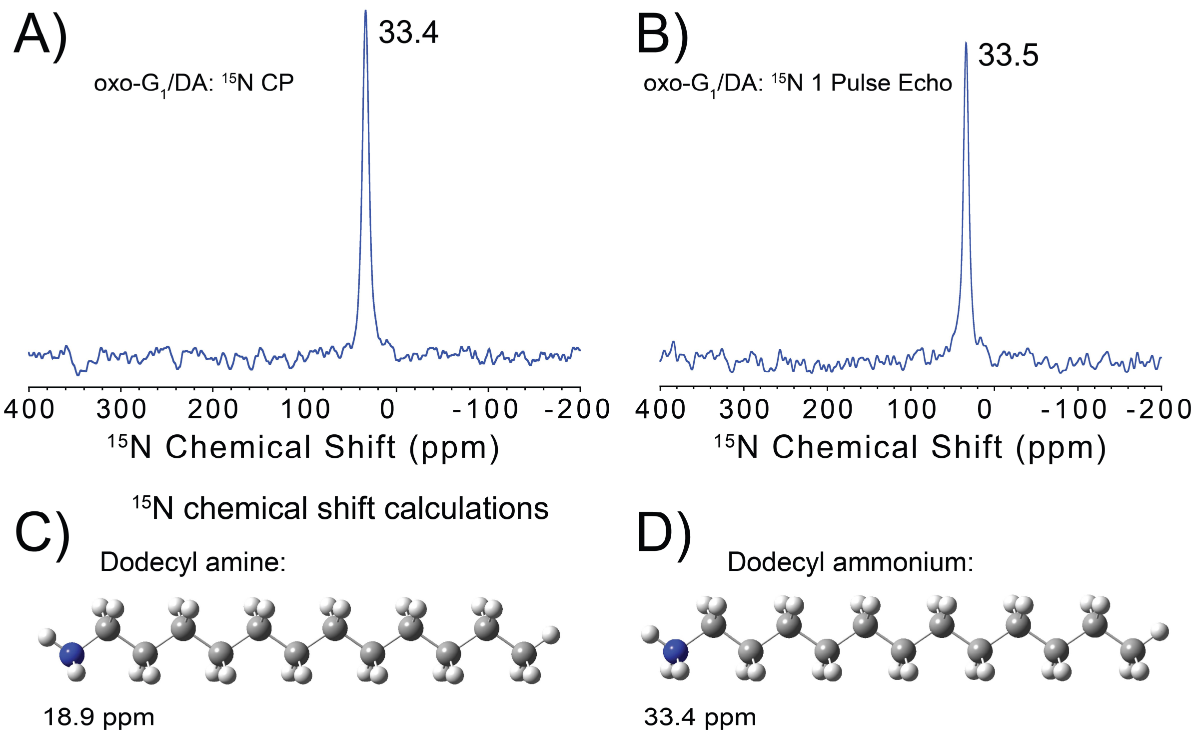

Figure S4. A, B) ^{15}N MAS ssNMR spectra of oxo-G$_1$/DA by A) CP and B) a π/2-pulse excitation. C, D) Molecular models with calculated ^{15}N NMR shifts for C) dodecyl amine and D) dodecyl ammonium, respectively.

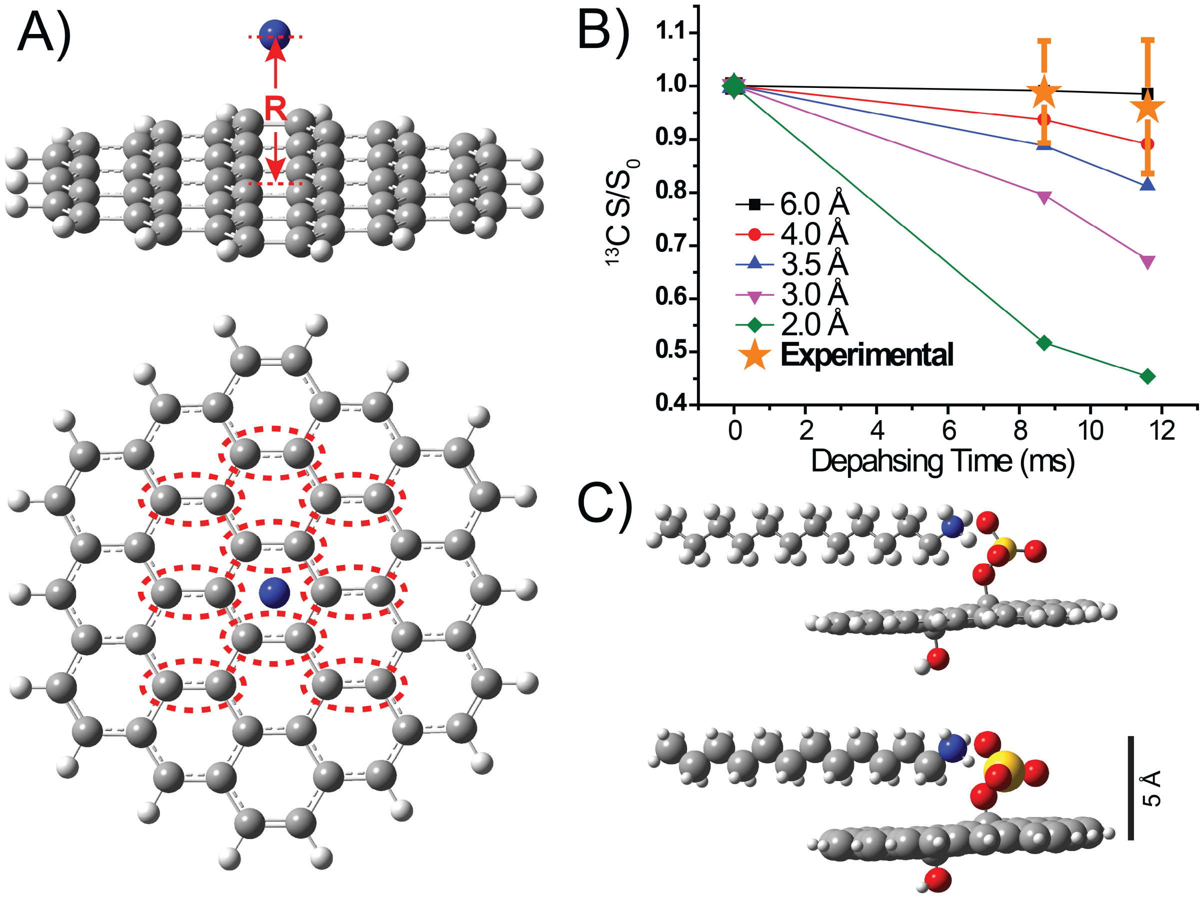

Figure S5. A) A model of nitrogen atom (^{15}N) and graphene to simulate the REDOR dephasing effect for the oxo-G$_1$/DA system. (top) The distance *R* denotes the distance between ^{15}N and the carbon plane. (bottom) 18 circled carbons (this number corresponds to synthetic condition) from graphene plane consist of a unit which is closest to the ^{15}N atom in the center. We consider one ^{15}N for every 18 carbons in oxo-G$_1$. Only the dipolar interactions between ^{15}N and the neighboring 18 carbons were considered to simulate the dephasing. B) A ^{13}C-{^{15}N} REDOR dephasing curve for oxo-G$_1$/^{15}N-DA with simulation curves for varied distance *R*. C) A structural model of oxo-G$_1$/DA obtained by *ab-initio* geometry optimization. (top) a ball and stick model and (bottom) a space filling model with a scale bar. The distance between ^{15}N and the sp^2 carbon surface is around 4 Å.

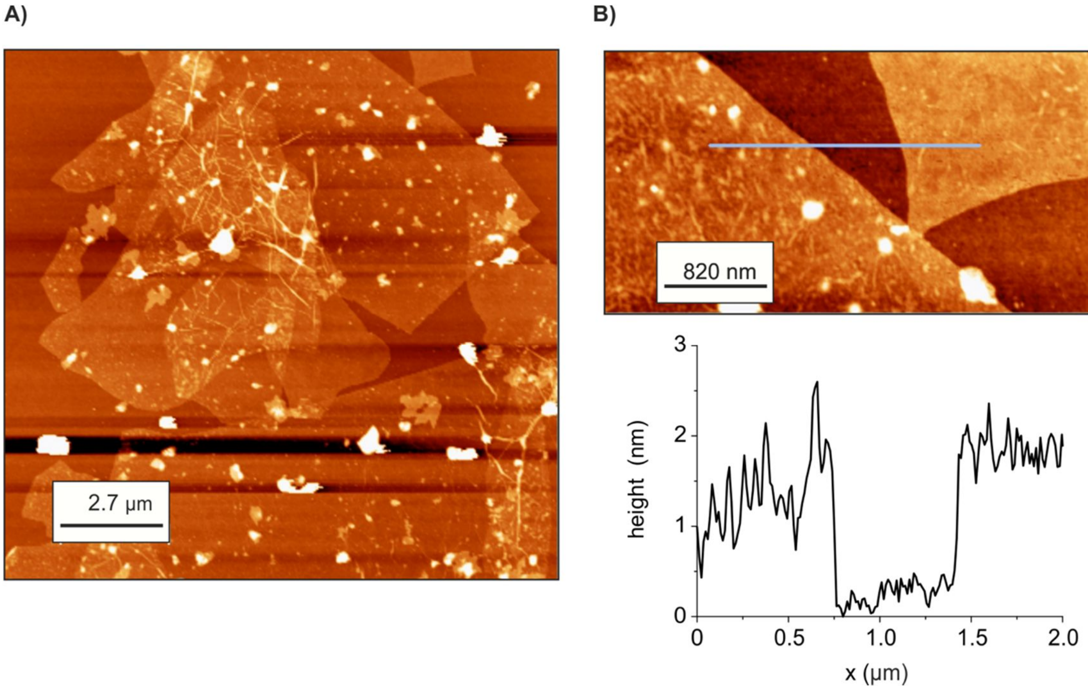

Figure S6. A) and B) AFM images of oxo-G_1/DA on SiO_2/Si substrate processed from THF by drop-casting and height-profile.

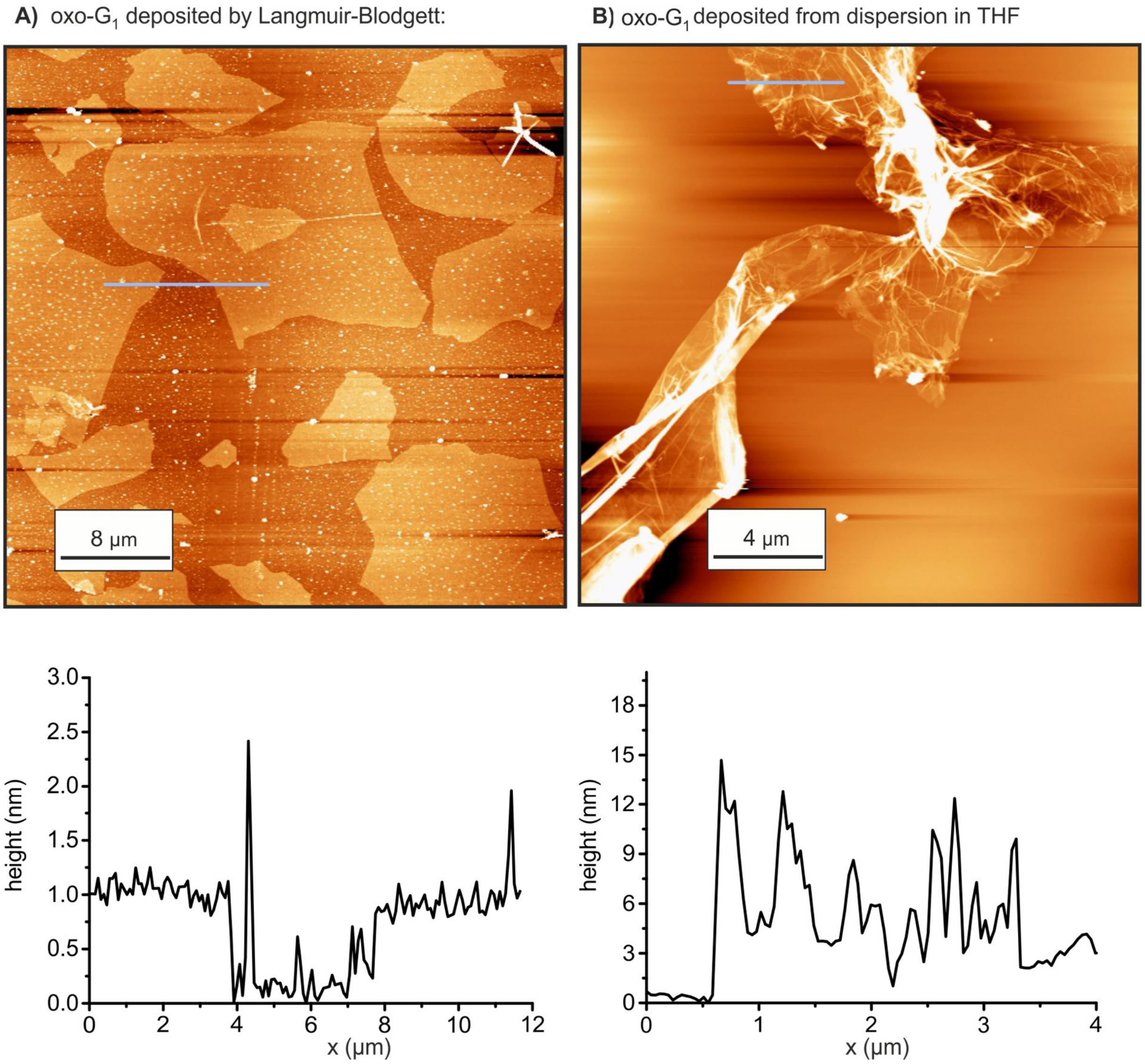

Figure S7. A) AFM image of oxo-G_1 on SiO_2/Si substrate processed by Langmuir-Blodgett technique from a dispersion of oxo-G_1 in MeOH/water (1/1) on a water subphase, processed at a pressure of 0.6 mN/m. B) AFM image of oxo-G_1 on SiO_2/Si substrate processed by drop-casting from THF after solvent exchange.

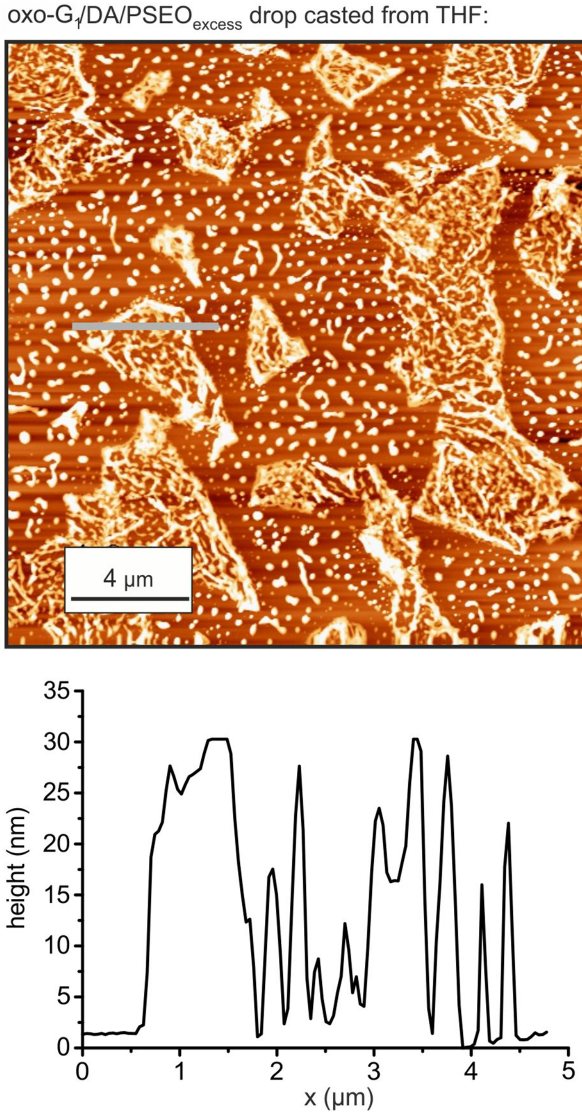

Figure S8. AFM image of oxo-G$_1$/DA/PSEO$_{excess}$ on SiO_2/Si substrate processed by drop-casting from THF. Excess of PSEO is visible as dots between flakes.

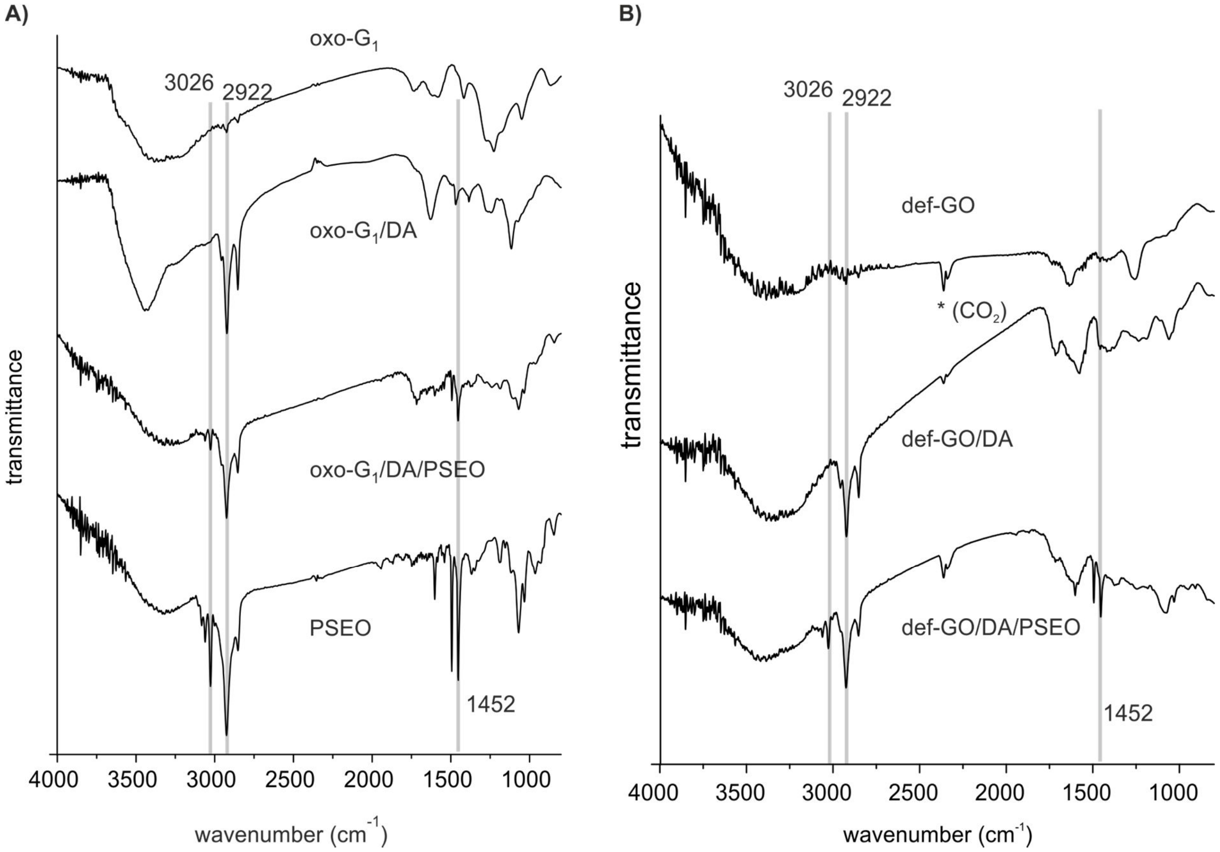

Figure S9. FTIR spectra of A) oxo-G$_1$, oxo-G$_1$/DA, oxo-G$_1$/DA/PSEO and PSEO and B) def-GO, def-GO/DA and def-GO/DA/PSEO.

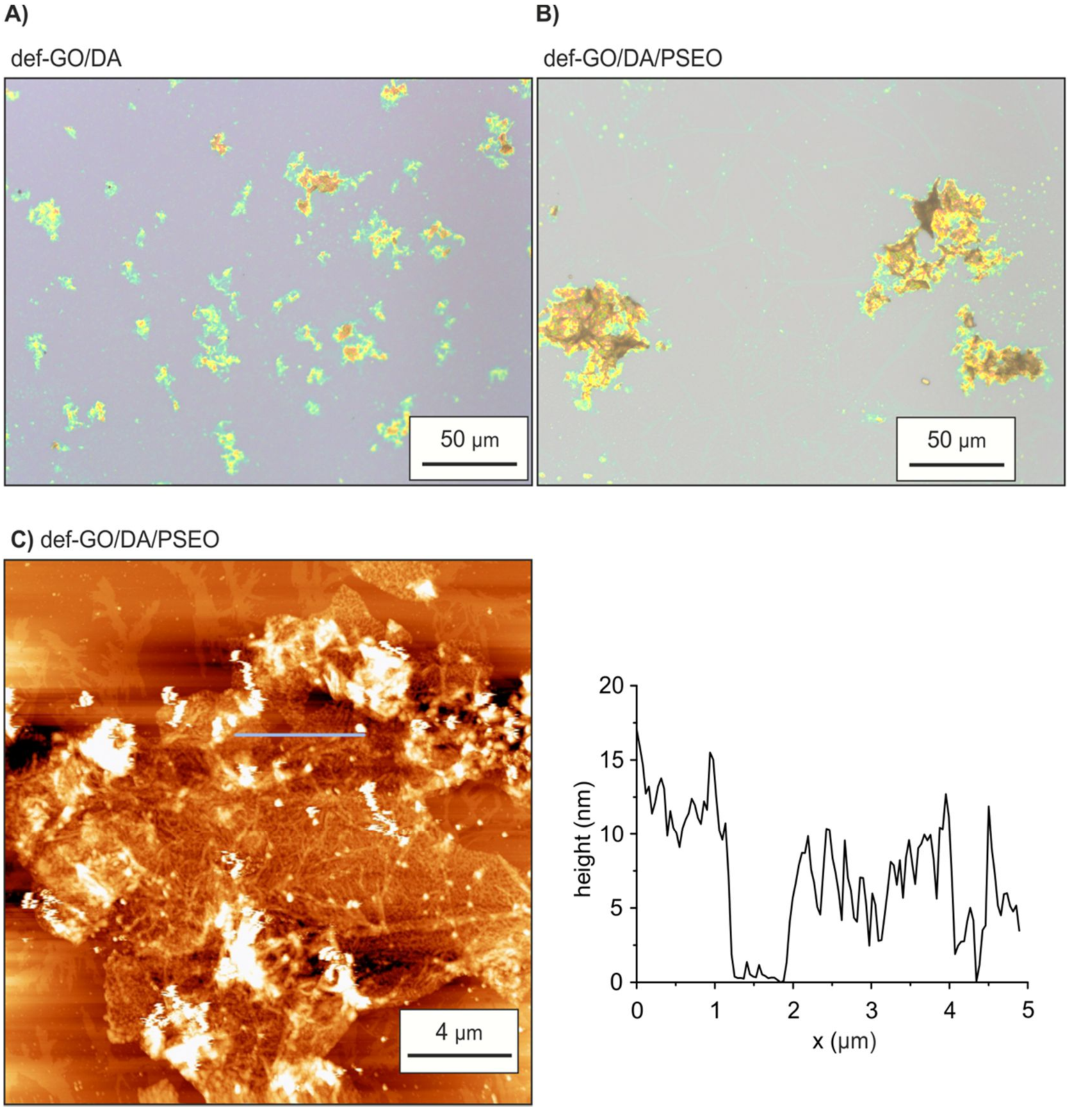

Figure S10. A) and B) Optical microscope images of def-GO/DA and def-GO/DA/PSEO processed by drop-casting from THF on 300 nm SiO_2/Si substrate. C) AFM image of def-GO/DA/PSEO flake on SiO_2/Si substrate with height profile.

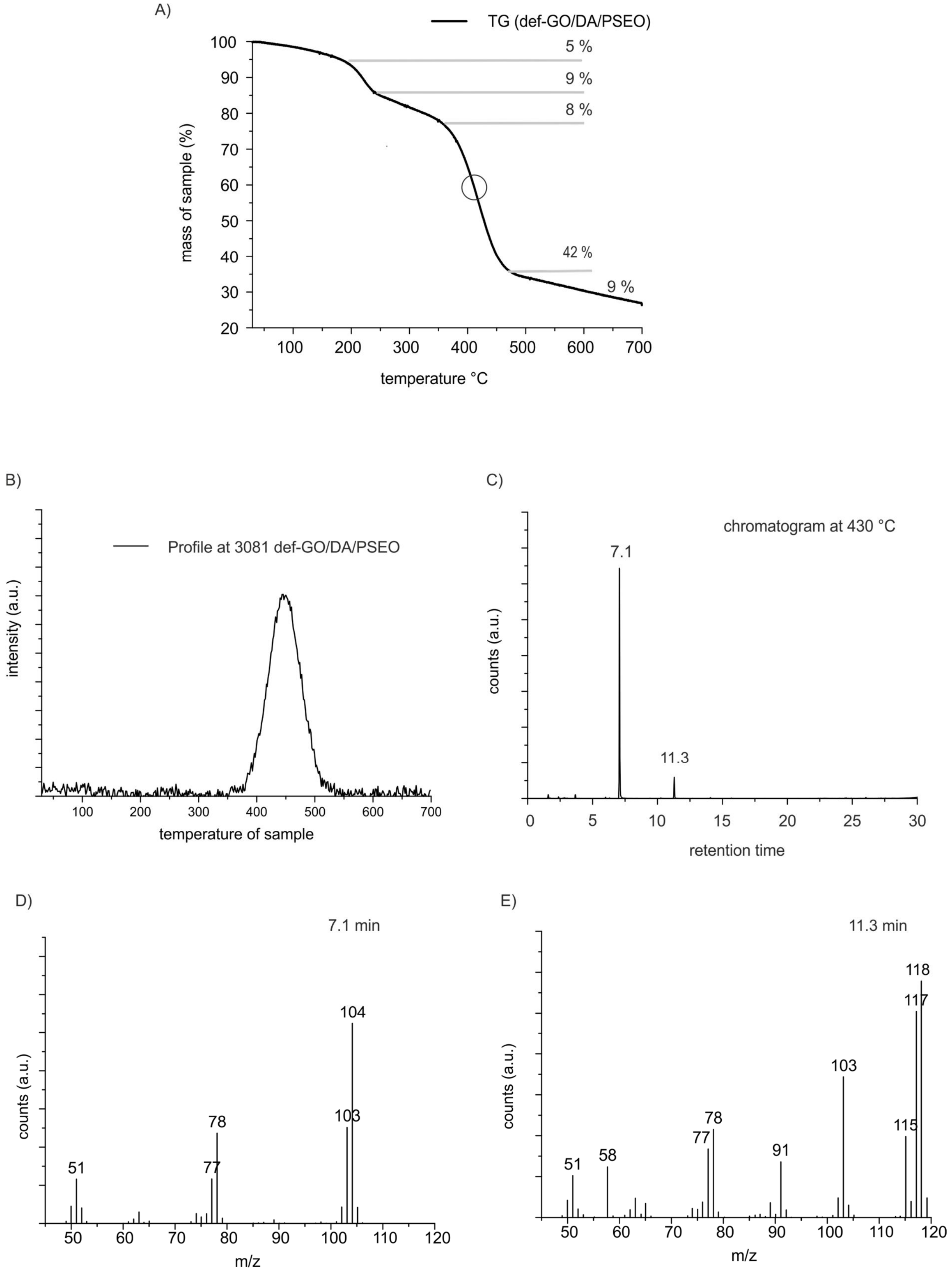

Figure S11. A) TGA of def-GO/DA between 30 °C and 700 °C and B) the temperature-profile of cleaved aromatic compounds identified by FTIR. C) Gas chromatogram of gases produced at 430 °C and MS spectra at D) 7.1 min and E) 11.3 min.

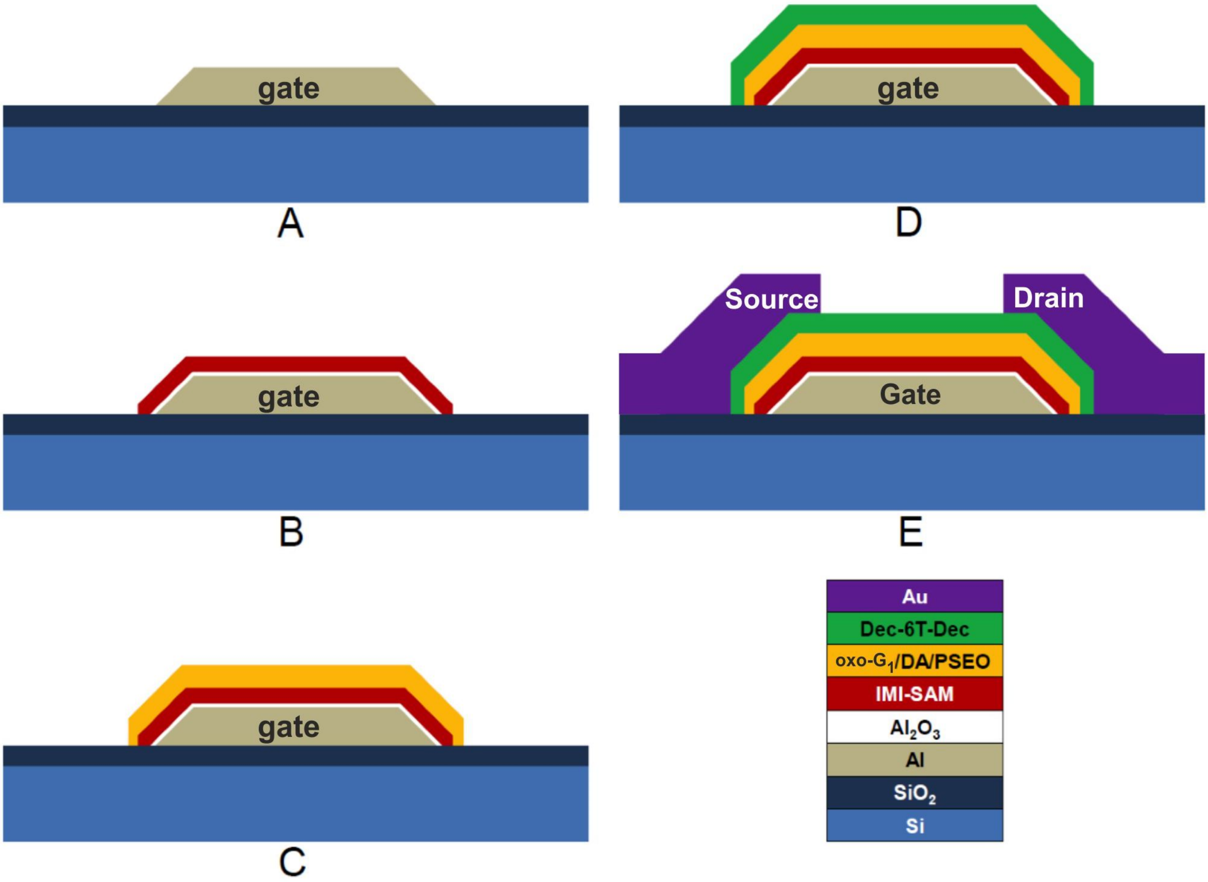

Figure S12. Fabrication process of the memory device. A) Patterning of the gate aluminum electrodes with shadow mask approach, followed by an oxygen plasma treatment to form the surface aluminum oxide layer. B) Self-assembly of the molecular monolayer IMI-PA by dip-coating. C) Spin-coating of the composite dispersion oxo-G_1/DA/PSEO. D) Thermal evaporation of the organic semiconductor with shadow mask approach. E) Patterning of the source and drain gold electrodes with shadow mask approach. The layered-structure legends are shown as well.

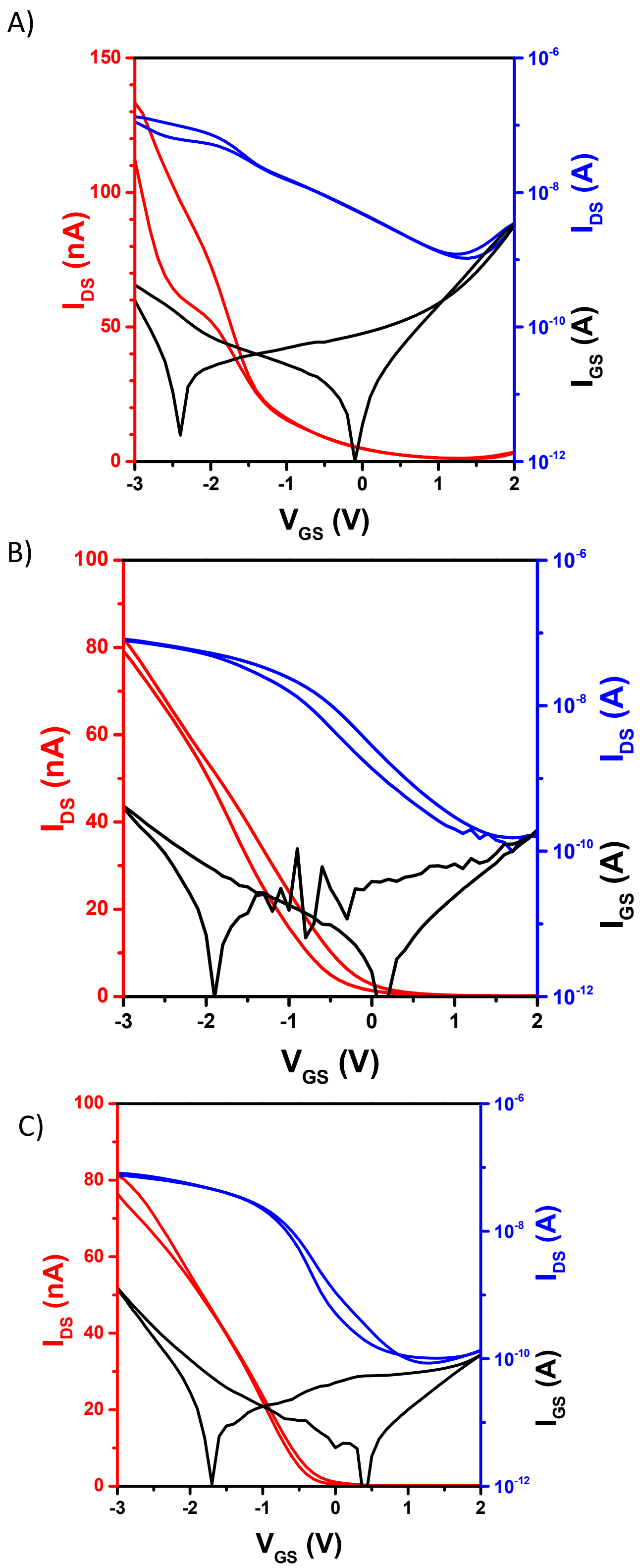

Figure S13. A) The transfer performance of the memory device based on def-GO/DA B) and C) The transfer performance of the memory device based on oxo-G_1/DA/PSEO. B) The spin-coating condition is 500 rpm for twice. V_{ds} = -1 V, channel length L = 20 μm, channel width W = 300 μm. C) The spin-coating condition is 500 rpm, and the gate dielectric is aluminum oxide without IMI-SAM molecule. V_{ds} = -1 V, channel length L = 30 μm, channel width W = 450 μm.

1. S. Eigler, F. Hof, M. Enzelberger-Heim, S. Grimm, P. Müller, A. Hirsch, *J. Phys. Chem. C* 2014, **118**, 7698-7704.
2. D. S. Wishart, C. G. Bigam, J. Yao, F. Abildgaard, H. J. Dyson, E. Oldfield, J. L. Markley and B. D. Sykes, *J. Biomol. NMR*, 1995, **6**, 135-140.
3. C. R. Morcombe and K. W. Zilm, *J. Magn. Reson.*, 2003, **162**, 479-486.
4. M. J. Frisch et al. *Gaussian 03 Revision E. 01*, Guassian Inc.: Pittisburgh, PA, 2004
5. L. B. Casabianca, M. A. Shaibat, W. W. Cai, S. Park, R. Piner, R. S. Ruoff, Y. Ishii, *J. Am. Chem. Soc.*, 2010, **132**, 5672-5676.
6. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
7. C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
8. P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222.
9. R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789–807.
10. M. Barfield, P. J. Fagerness, *J. Am. Chem. Soc.*, 1997, **119**, 8699−8711.
11. P. R. Srinivasan and R. L. Lichter, *J. Magn. Reson.*, 1977, **28**, 227-234.
12. M. Witanowski, L. Stefaniak, G. A. Webb, *Annu. Rep. NMR Spectrosc.*, e.d. G. A. Webb, Academic Press, London, 1993, **25**, 88.
13. S. Eigler, M. Enzelberger-Heim, S. Grimm, P. Hofmann, W. Kroener, A. Geworski, C. Dotzer, M. Rockert, J. Xiao, C. Papp, O. Lytken, H. P. Steinrück, P. Müller and A. Hirsch, *Adv. Mater.*, 2013, **25**, 3583-3587.
14. F. M. Koehler and W. J. Stark, *Acc. Chem. Res.*, 2013, **46**, 2297-2306.
15. S. Eigler and A. Hirsch, *Angew. Chem. Int. Ed.*, 2014, **53**, 7720-7738.