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Repurposing of oxazolone chemistry gaining access to functionalized graphene nanosheets in a top-down approach from graphite

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Solvent free 1,3-dipolar cycloaddition (1,3-DC) reactions between graphite flakes and mesoionic oxazolones were carried out by heating the resulting solid mixture at mild temperatures (70–120 °C). The direct functionalization and delamination of graphite flakes into few layers of graphene nanosheets was confirmed by micro-Raman and X-ray photoelectron spectroscopies, Scanning Transmission Electron Microscopy and thermogravimetric analysis. The 1,3-DC reactions of mesoionic dipole to model of graphene have been investigated with density functional theory exploring three different pathways: center, corner and edge; these theoretical calculations highlighted that the 1,3-DC reaction examined can proceed both through a concerted mechanism competing with a stepwise one involving a zwitterionic intermediate. The irreversible decarboxylation inherent the last step justify the high degree of functionalization experimentally observed, representing the training force of the process.

1. Introduction

Research into graphene, a single-atom thick nanomaterial with unprecedented properties, has generated enormous interest during recent years due to its tremendous potential applications,^{1–5} as electronic devices, selective sensors, functional composite materials, solar cells, energy storage or for biomedical use.^{6–8} Although its excellent properties endow graphene great potential, in many practical applications, its inertness nature, zero band gap, and non-dispersibility in solvents weaken its competitive strength in the synthesis of composites, semiconductors, sensors, etc. Moreover, the difficulty to produce high-quality graphene on a large scale limited its practical use. The functionalization of graphene is the key to achieve stable graphene dispersions leading to better processability for new materials, and to assist combination/incorporation with other classes of compounds to produce high performance multifunctional materials.^{9, 10} The most employed approaches for graphene modification involve the chemistry of graphene oxide¹¹ (GO), especially

esterification/amidation reactions at the carboxylic groups and the coupling of diazonium salts to the sp^2 network.^{12, 13} Other important approaches to fabricate functionalized graphene materials are the 1,3-dipolar cycloaddition (1,3-DC),^{14, 15} Bingel reaction,¹⁶ Diels–Alder reaction (DA),^{17, 18} among others^{19, 20} which directly take place on the graphene surface. These synthetic strategies are not avoid of drawbacks due to the low intrinsic reactivity of graphene, which is lower than that of other carbon nanoforms such as fullerene and carbon nanotubes, principally because of the absence of tension in the graphene basal planes. DA results the most investigated cycloaddition process since Haddon and co-workers have suggested that graphene can be used as either a diene or a dienophile for DA reactions.²¹ In 2013, for the first time, Seo *et al.* proposed DA protocol to access to functionalized graphene nanosheets in a top-down approach starting directly from graphite.²² More recently, modifications of graphite/graphene by DA reactions have been carried out using alternative protocols such as solvent free process²³ and retro-DA reaction.²⁴

To date, only the 1,3-DC reactions of azomethine ylides have been thoroughly investigated for the chemical manipulation of graphene^{14, 15} and no examples of graphite/graphene functionalization by mesoionic compounds as 1,3-dipole have been reported.

Oxazolones are versatile precursors in organic synthesis for the preparation of structurally complex amino acids and highly substituted heterocycles.^{25, 26} Oxazolones may act as electronic acceptors through the C5 or C2, as carbanions by deprotonation at C4, and also like mesoionic systems containing an azomethine ylide dipole. Their reactivity as

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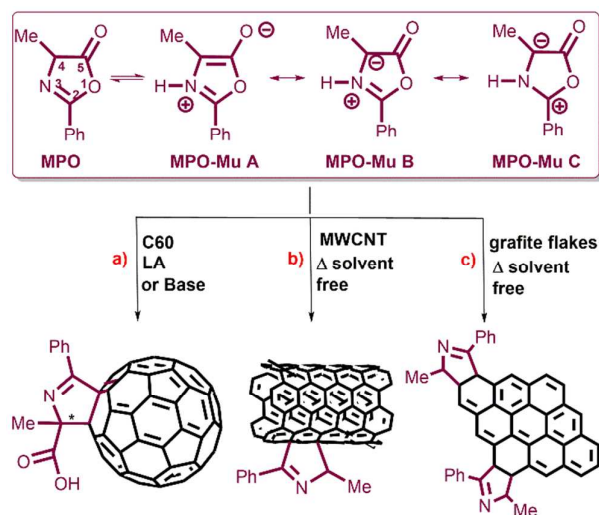


Fig. 1 Models of molecular structure of 4-methyl-2-phenyl oxazol-5-(4H)-one (MPO) and its Mu tautomers, and their undergoing into 1,3-DC. (a) Schematic representation of enantioselective cycloaddition of MPO-Mu onto C60 under organocatalysis or LA metal catalysis. (b) 1,3-DC reaction between MPO-Mu and MWCNT. (c) 1,3-DC of MPO-Mu with graphite flakes (GF) reported herein.

dipoles was exploited to functionalize carbon nanomaterials such as [60]fullerene and multiwalled carbon nanotubes (MWCNT) (Fig. 1).

The tautomerization of the oxazol-5-(4H)-one into its reactive mesoionic form (münchnone, Mu) has been promoted by heating, Lewis acid (LA) conditions and basic catalyst (Fig. 1).^{27, 28}

As a part of an ongoing program aimed at the functionalization of carbon nanomaterials we focused our interest on the direct delamination and functionalization of graphite into graphene exploiting the reactivity of oxazolones under heating in solvent free conditions. 4-Methyl-2-phenyl oxazolone (MPO) and 4-methyl-2-*p*-nitrophenyl oxazolone (MNPO) were selected as oxazolone substrates for their capability to react in solid/solid conditions.²⁸ Under heating, the isomerisation of oxazolones to münchnones triggers the cycloaddition process with the successive domino reactions of decarboxylation and final dehydration of 1:1 adduct.^{27, 28} We suppose that these features can be suited for the activation of graphite in a solid-solid 1,3-DC without the mechanical, thermal or chemical activation required in DA approaches.²²⁻²⁴

By comparing the results of our 1,3-DC with literature DA methods, the top-down approach applied in this work is mild (70–120 °C vs 160–220 °C) and efficient producing functionalized graphene nanosheets with a high degree of functionalization (2.1–4.6%). The structure, morphology and chemical composition of functionalized graphene materials were investigated by micro-Raman and X-ray photoelectron (XPS) spectroscopies, scanning transmission electron microscopy (STEM), and thermogravimetric analysis (TGA).

To shed light into this extraordinary reactivity and to predict the products and reaction sites an atomic-scale investigation of graphene functionalization with MPO was performed using DFT calculations.

2. Experimental section

2.1. Materials

Graphite flakes (GF), solvents and other reagents were purchased from Sigma Aldrich. MPO and MNPO were synthesized according to literature procedure.²⁹ Melting points were determined on a Kofler melting apparatus and are uncorrected. Merck Kieselgel 60F₂₅₄ plates were used for TLC and Merck silica gel 60 (0.063–0.100 mm) for column flash-chromatography.

2.2. Synthesis of G-MPO and G-MNPO

2.2.1. Entry 1, Table 1

MPO (500 mg) and GF (50 mg) were combined using a mortar and a pestle and the resulting powder was transferred into a glass ampoule. The reaction mixture was heated at 80 °C for 12 h. The mixture was cooled and the solid residue was washed for three times with methanol and dimethylformamide (1:1, 3 × 50 mL) and each time sonicated for 10 min and separated from the supernatant by centrifugation at 3500 rpm for 20 min. The effective elimination of unreacted dipole was monitored by NMR analysis of washing solvents. The residue was dried at 60 °C to give 50 mg of G-MPO1. From TGA analysis, under N₂ atmosphere, the amount of cycloadduct grafted to graphene was estimated to be ~3.5% wt.

2.2.2. Entries 2–4, Table 1

MPO (Mp: 38–39 °C)²⁸ or MNPO (Mp: 139–142 °C)³⁰ and GF, in the opportune w/w ratio (entries 2–4), were combined using a mortar and a pestle and the resulting powder was transferred into a glass ampoule. The reaction mixture was sonicated for 6 h at 70 °C, and then heated at 120 °C for 12 h. The mixture was cooled and subjected to workup procedure. From TGA analysis the amount of cycloadduct grafted to graphene was estimated to be ~2.1% wt, ~3.3% wt, and ~4.6% wt for G-MPO2, G-MNPO1, and G-MNPO2, respectively.

2.3. Characterization techniques

¹H-NMR spectra were obtained with a Varian 500 MHz spectrometer. The Fourier Transform Infrared (FTIR, Perkin Elmer Spectrum 100) spectra were collected, in Attenuated Total Reflectance (ATR) configuration, from 4000 to 450 cm⁻¹. The chemical composition and the bonding configurations of the samples were also investigated by means of XPS. The spectra were acquired at room temperature using a Thermo Scientific K-Alpha system, equipped with a monochromatic Al K α source (1486.6 eV) and an hemispherical analyser operating in constant-pass energy (CAE) mode. The pass-energy was set at 200 eV for survey scans and at 50 eV for the XPS core level spectra. A spot size diameter of about 400 μ m was adopted while surface charging effects were avoided using an electron flood gun. Raman spectra were carried out, in air at room temperature, using a Horiba XploRA spectrometer equipped with a confocal microscope and a Peltier-cooled charge-coupled detector (CCD). Spectra were excited using the 638 nm line from a solid state laser and integrated for 50 s, using a 50X microscope objective. In order to prevent laser induced damage or heating, measurements were carried out using a

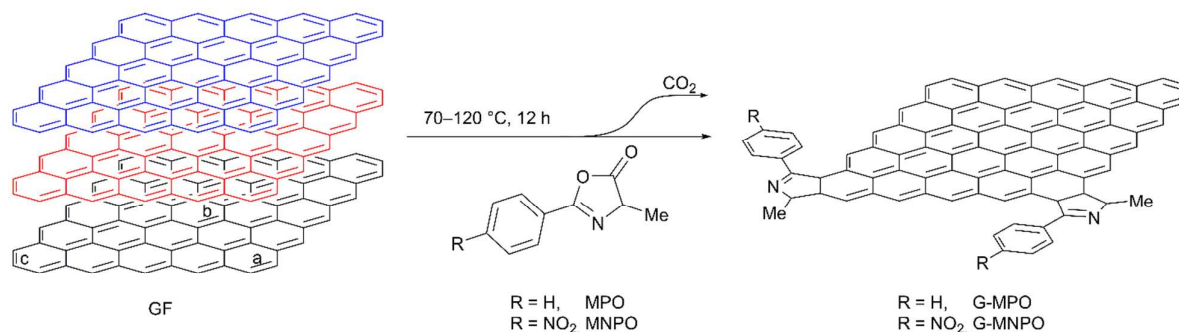


Fig. 2 Schematic representation of solvent free 1,3-DC reaction of MPO and MNPO on GF.

low laser power (2.5 mW on the illuminated area of 2.0 μm^2). Spectra from several random positions on each specimen were collected on account of the possible spatial non-homogeneity of the samples. To ensure reproducibility, experiments were performed in triplicate.

The morphology of graphene samples was analyzed using the Zeiss-Gemini 2 scanning electron microscope, operating, in transmission mode, at 30 kV and at a working distance of 4 mm. Some drops of the sample, dispersed in isopropanol ($\cong 0.5$ mg/mL) using the Sonics VCX 130 ultrasonic sonicator, were deposited on a 400 mesh holey-carbon coated copper grids and left to dry at room temperature for 3 h. TGA was performed by means of Perkin-Elmer Pyris TGA7, in the temperature range 50–800 °C. About 5 mg of each sample was, firstly, placed in a platinum pan and kept at 25 °C under a 60 mL/min N₂ flow until balance stabilization and subsequently heated with a scan rate of 10 °C/min under the same N₂ flux. Balance sensitivity was 0.1 μg . A baseline recorded in the same measurement conditions with empty platinum pan was subtracted from each thermogram before data analysis.

2.4. Computational details

Geometry optimizations of the critical points (reactants, transition structures and products) were studied at the (U)M06-2X level of theory^{31, 32}. For each geometry studied, calculation of harmonic vibrational frequencies was carried out, at the same level of theory, with the aim to characterize all structures as minima or transition state. For the minima, all the wavenumbers obtained are positive whereas transition state structures were found to have only one negative eigenvalue with the corresponding eigenvector involving the formation of the newly created bonds. Vibrational frequencies were calculated (1 atm, 298.15 K) for all optimized structures, at (U)M06-2X/6-31G(d) level of theory, and used, unscaled, to compute both ZPVE and thermal corrections at 298 K. The enthalpy and entropy changes were calculated from standard statistical thermodynamic formulas.³³ The intrinsic reaction coordinates^{34, 35} (IRC analysis) were also calculated to analyse the mechanism in detail for all the transition structures obtained at the same level of theory. All the optimizations were carried out by Berny's analytic gradient method³⁶ included in the Gaussian 09 software package.³⁷ In all the

cases, full geometry optimization was carried out without any symmetry constraints. The electronic structures of critical points were studied by the natural bond orbital³⁸ (NBO) method as implemented in Gaussian 09 suite.

3. Results and discussion

3.1. Chemistry

All 1,3-DC reactions were performed in solvent free conditions in a closed and sealed system using a glass ampoule at mild temperatures (70–120 °C) (Fig. 2). Moreover, the reactions were carried out under different experimental conditions such as graphite/dipole weight ratio (w/w), reaction temperature and sonication (Table 1). To increase the efficiency of 1,3-DC, GF and MPO or MNPO were firstly triturated in a mortar to a fine powder. In the first experiment the reaction was performed at 80 °C with a 1:10 GF/MPO weight ratio for 12 h (Table 1, entry 1). In order to completely remove the unreacted dipole, the reaction mixture was washed in sequence with different solvents, each time being sonicated and separated from the supernatant by centrifugation. The solid was then dried to constant weight under vacuum at 50 °C to constant weight and characterized. The graphene functionalization degree (loading %) was estimated in terms of weight loss by TGA upon heating a solid reaction product, from 100 °C to 700 °C under N₂ atmosphere (Fig. 3).

3.2. TGA characterization

Compared to GF, the TGA thermogram of G-MPO1 showed a great weight loss in the range 300–700 °C with a loading of 2.3% and 3.5% at 500 °C and 700 °C, respectively. The thermal stability of G-MPO1 at low temperatures is an unambiguous evidence of covalent grafting of organic groups on graphene sheets ruling out the presence of adsorbed organic compounds (TGA thermogram of physical mixture GF/MPO showed a great weight loss in the range 200–300 °C, data not shown). Moreover, the absence of adsorbed organic material was confirmed by the disappearance of characteristic azlactone absorption at 1818 cm^{-1} in IR spectra (data not shown). In order to facilitate the exfoliation of graphite and the efficiency of 1,3-DC process, the reaction mixture was subjected to sonication at 70 °C for 6 hours and then heated at 120 °C for

Table 1 Experimental conditions used in the synthesis of G-MPO and G-MNPO, with C, N, and O contents (%) obtained from XPS analysis

Entry	Experimental conditions	Sample	C 1s	N 1s	O 1s
1	GF/MPO=1/10, 80 °C, 12 h	G-MPO1	95.01	0.55	4.44
2	GF/MPO=1/10, 6 h))) ^a 70 °C; 120 °C, 12 h	G-MPO2	95.08	0.26	4.66
3	GF/MNPO=1/2, 6 h))) 70 °C; 120 °C, 12 h	G-MNPO1	82.92	1.61	15.47
4	GF/MNPO=1/10, 6 h))) 70 °C; 120 °C, 12 h	G-MNPO2	85.11	1.75	13.15
5	GF	GF	88.38	0.00	11.62

^a))) = sonication.

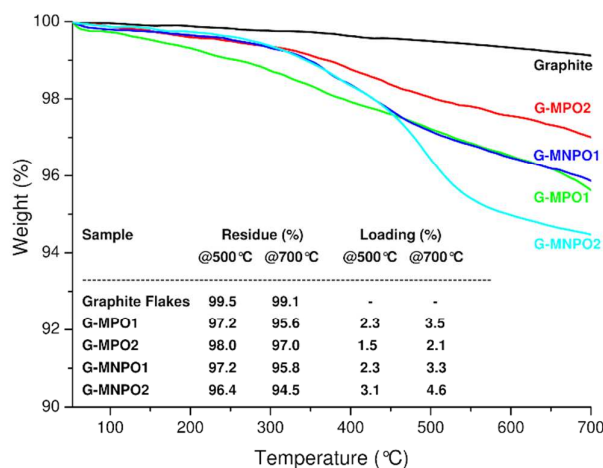


Fig. 3 TGA profiles of GF, G-MPO1, G-MPO2, G-MNPO1, and G-MNPO2, under a N₂ atmosphere. The inserted table reports the values, at 500 °C and 700 °C, of weight residue (%) and loading (%).

12 hours (Table 1, entries 2–4). We expect that the combined effects of temperature and sonication would promote the intercalation of oxazolones into graphite, expanding the graphite basal spacing and opening the avenues for the penetration of dipoles into the graphite crystals. The TGA profiles of G-MPO2, G-MNPO1, and G-MNPO2 revealed that the loading values are good for all experiments but no significant improvement in the efficiency of 1,3-DC was detected (Fig. 3). The efficiency of 1,3-DC reaction was maintained also in the case of oxazolone MNPO, despite its higher melting point respect to MPO. The 1,3-DC reaction of MNPO with GF (Table 1, entry 4) showed a good efficiency (4.5%@700 °C, Fig. 2). The loading was well preserved also lowering the graphite/dipole weight ratio from 1:10 to 1:2 (3.3%@700 °C, Fig. 3 and Table in Fig. 3, entry 3).

3.3. XPS analysis

Information about the types of functional groups grafted on the graphene surfaces were obtained carrying out XPS analysis. XPS results show that the graphene nanomaterials have different C, O and N contents on the basis of oxazolone

Table 2 C 1s XPS deconvolution fitting results. All values are in percent.

C 1s	C=C	C-H	C-N	C-O	C=O	$\pi-\pi^*$
Graphite	85.0	7.7	0.0	5.9	1.3	0.1
G-MPO2	83.4	4.6	6.8	4.3	0.8	0.1
G-MNPO2	68.5	11.0	12.2	6.0	2.0	0.3

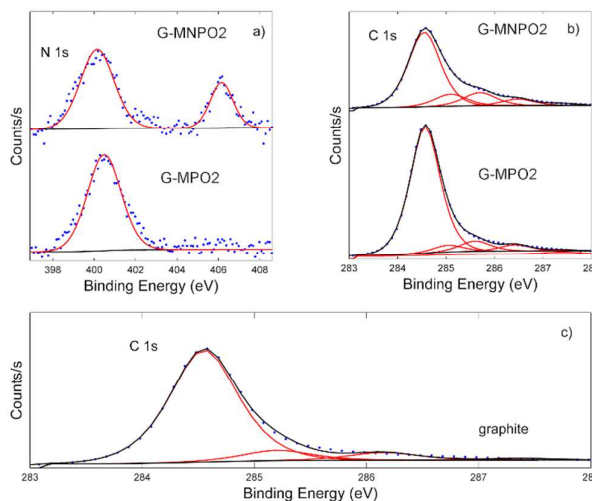


Fig. 4 N 1s and C 1s photoelectron deconvoluted lineshapes.

used (G-MPO series vs G-MNPO series, Table 1). The XPS data of G-MPO2 and G-MNPO2 samples, obtained in the same experimental conditions, were compared and discussed.

In particular, G-MNPO2 exhibits a relatively high amount of N (1.75%) and O (13.15%) as well as the lower C content (85.11%) with respect to the graphite (0.00% of N, 11.62% of O, and 88.38% of C) and the G-MPO2 sample (0.26% of N, 4.66% of O, and 95.08% of C).

As shown in Fig. 4, a change in the N 1s high resolution profiles occurs due to the additional presence of nitro group, absent in G-MPO2. The sample G-MNPO2 is dominated by two peaks at about 400 and 407 eV, representative of the formation of C=N functionality and of aromatic nitro groups, respectively. Otherwise, the G-MPO2 sample is characterized by only the contribution at 400 eV. Going from the sample G-MPO2 to G-MNPO2, the expected increase of the contribution centered at about 407 eV is observed (from 0% up to 28%). This behavior is accompanied by the decrease of the C=N percentage (from 100% down to 72%).

The C 1s bands were deconvoluted using six contributions: a main contribution at 284.5 eV attributed to C=C/C-C in the aromatic ring and four other contributions at higher binding energies corresponding to carbon atoms bonded to nitrogen (C-N) and oxygen in different surface functionalities (C-OH, C-O, C=O) centred at 285.2, 286.3, 288.7, and 288.9 eV, respectively (Fig. 4). The contribution at about 291.0 eV refers to $\pi-\pi^*$ bonds. The G-MPO2 and G-MNPO2 samples show only slight differences in terms of carbon-oxidized phases while, as expected, the percentage corresponding to C-N bonds increases in the G-MNPO2 sample (see Table 2).



Fig. 5 STEM images of (a) graphite, (b) few layers of graphene nanosheets of G-MPO2 sample and (c) folded graphene sheet of G-MNPO sample.

3.4. STEM analysis

Direct evidence of the effective occurrence of the exfoliation process was given by STEM analysis. All the samples showed homogeneously distributed exfoliated graphene layers.

In several portion of the samples various-dimensional transparent sheets stacked onto each other were observed, indicating the efficient functionalization and exfoliation of pristine graphite (whose morphology is shown in Fig. 5a) into a few layers of graphene nanosheets (Fig. 5b). Moreover, folded sheets were also observed (Fig. 5c). A thicknesses of about 2–3 nm was estimate in the G-MNPO samples. (see Fig S2, SI).

3.5. Raman spectroscopy investigations

The structure of G-MPO and G-MNPO was further investigated by micro-Raman spectroscopy. Since it probes a region much larger than that investigated by STEM, it is more representative of the overall samples structure. A comparison of all the Raman spectra is reported in Fig. 6. The spectra have been normalized to better reveal the band profiles changes. The graphene based-materials show, in the 1100–3000 cm^{-1} spectral region, four main peaks: the structural imperfections, due to the nanographene platform functionalization, D band (1350 cm^{-1}), the primary in-plane vibrational G mode (at about 1580 cm^{-1}), the G* band which appears in the 2400–2450 cm^{-1} region of the spectra and the second-order overtone 2D mode (at about 2690 cm^{-1}). The G* band is interpreted as a combination of a transverse optical and longitudinal acoustic phonon mode near the K point. This band results from double resonance Raman scattering processes and it is commonly denoted as D + D'.³⁹ Firstly, one can use Raman spectra to characterize the level of disorder in the samples, using the I_D/I_G peak intensities ratio. The estimated values are below 0.5, with no appreciable variation between the samples, indicating that the functionalization has a limited effect on the pristine graphite structure. The same behaviour is observed for the G mode peak position, which is located at about 1580 cm^{-1} for all the samples, with no shift.

On the other hand, information about the number of graphene layers can be derived from the I_G/I_{2D} peak intensities ratio, as well as their positions and shapes. In fact, because of added forces from the interactions between the graphene layers, the Raman spectrum will change from that of single-layer graphene, namely a splitting of the 2D peak, into an increasing

number of modes that can combine to give a wider, down-shifted, peak. Thus, the 2D band splitting of G-MPO2 sample indicates the presence of several (at least four) graphene layers. At variance, G-MNPO2 sample shows a single almost symmetric 2D peak, located at 2710 cm^{-1} , with a full width half maximum of about 65 cm^{-1} , i.e. in an intermediate position with respect to the 2D₁ (2683 cm^{-1}) and 2D₂ (2718 cm^{-1}) peak positions of the bulk graphite. Interestingly, the G-MNPO2 sample presents a I_G/I_{2D} ratio value of 0.2, significantly lower than both GF and G-MPO2 samples (1.5–1.4). The I_G/I_{2D} ratio value, the barely visible occurrence of the D band and the almost symmetric 2D band lineshape point out that the G-MNPO2 sample exfoliation process is rather effective to obtain a single layer-like functionalized graphene. In the other sample, Raman data suggest a simple delamination into a multiple (albeit few) layers of functionalized graphene nanosheets. All these evidences are in good agreement with literature data.^{40–42}

3.6. Computational studies

To further investigate the 1,3-DC of Mu to GF, and to rationalize and shed lights on the obtained results we explored the reactivity of MPO-Mu, chose as model, by first-principles calculations within the DFT framework. Graphene sheets were simulated by C₇₀H₂₂ polybenzenoid hydrocarbons consisting of 25 fused benzene rings (five in row and five in line), terminated by hydrogen atoms, presenting zigzag shape edges (Fig. 2).

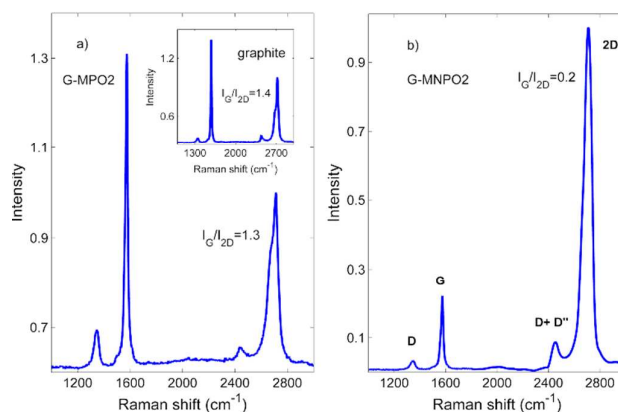


Fig. 6 Raman spectra of GF (insert), G-MPO2 and G-MNPO2.

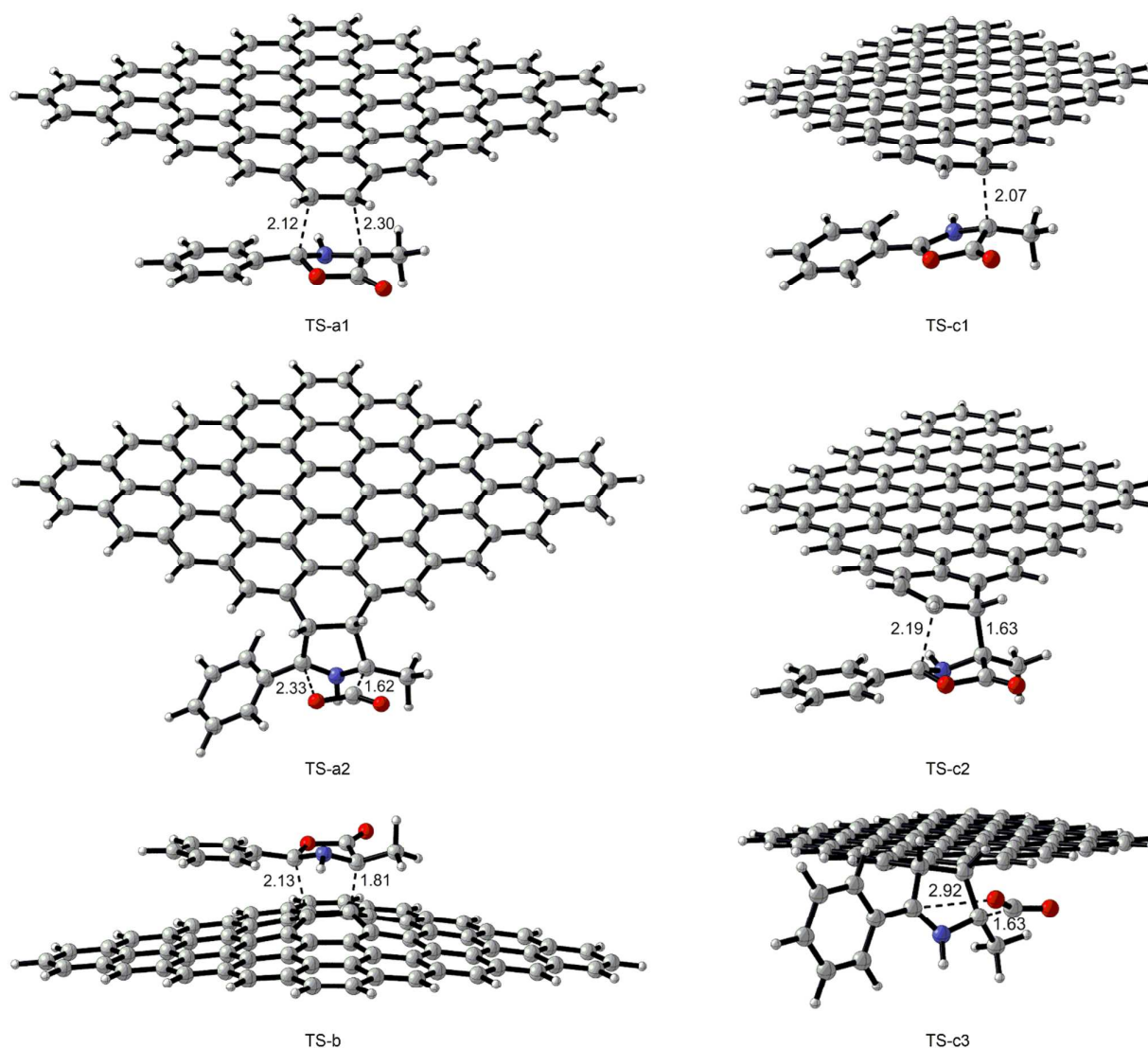


Fig. 7 Transition states optimized structures for the 1,3-DC reaction of MPO-Mu with GF. Distances are in Å. Carried out with CYLview.⁴³

Houk et Al. demonstrated that this 5×5 finite-size model provides reliable energetics for both interior and peripheral bonds and represents a good compromise for computational investigations.¹⁴ Although there are many types of double bonds in large graphene systems, we explored only three of them defined as corner (a), centre (b), and edge (c) (onwards defined as pathways a–c) (Fig. 2).

Because graphenes have a polyradical character and graphene models are more stable as open-shell singlet states,^{44–46} we performed unrestricted DFT calculations at M06-2X level of theory, that gives a mean error of 0.8 kcal/mol respect to the very well-performant CCSD(T) method,⁴⁷ with the 6-31G(d) basis set. Single point energy calculations were subsequently carried out on the optimized structures, at the same level of theory, with the larger basis set 6-311G(d,p). Ideally, the two zigzag double bonds a and c are indistinguishable when the graphene model approaches infinite but, because of the

simplified model, the 1,3-DC reaction on these two bonds differs in reactivity. Moreover, for the same reason, the double bonds b and c can lead to two regioisomeric products, but we have only considered the formation of a single regioisomer, choosing, especially for b, the one with less steric hindrance;⁴⁸ at the same time, we have considered only the *exo* approach because refined computational results showed that it is the preferred one.⁴⁹ However, preliminary computational studies conduct by us on pyrene (the simplest 2×2 model) confirmed both regio- and *exo/endo* selectivities here adopted (unpublished results). Finally, since Denis found that the presence of Stone-Wales translocations, 585 double vacancies, and 555-777 reconstructed double vacancies did not significantly change graphene reactivity,¹⁸ we have not considered the defects of graphene.

All transition states (TS-a–c), intermediates (I-a–c), and products structures (G-MPO-a,c) have been reported in Fig. 7

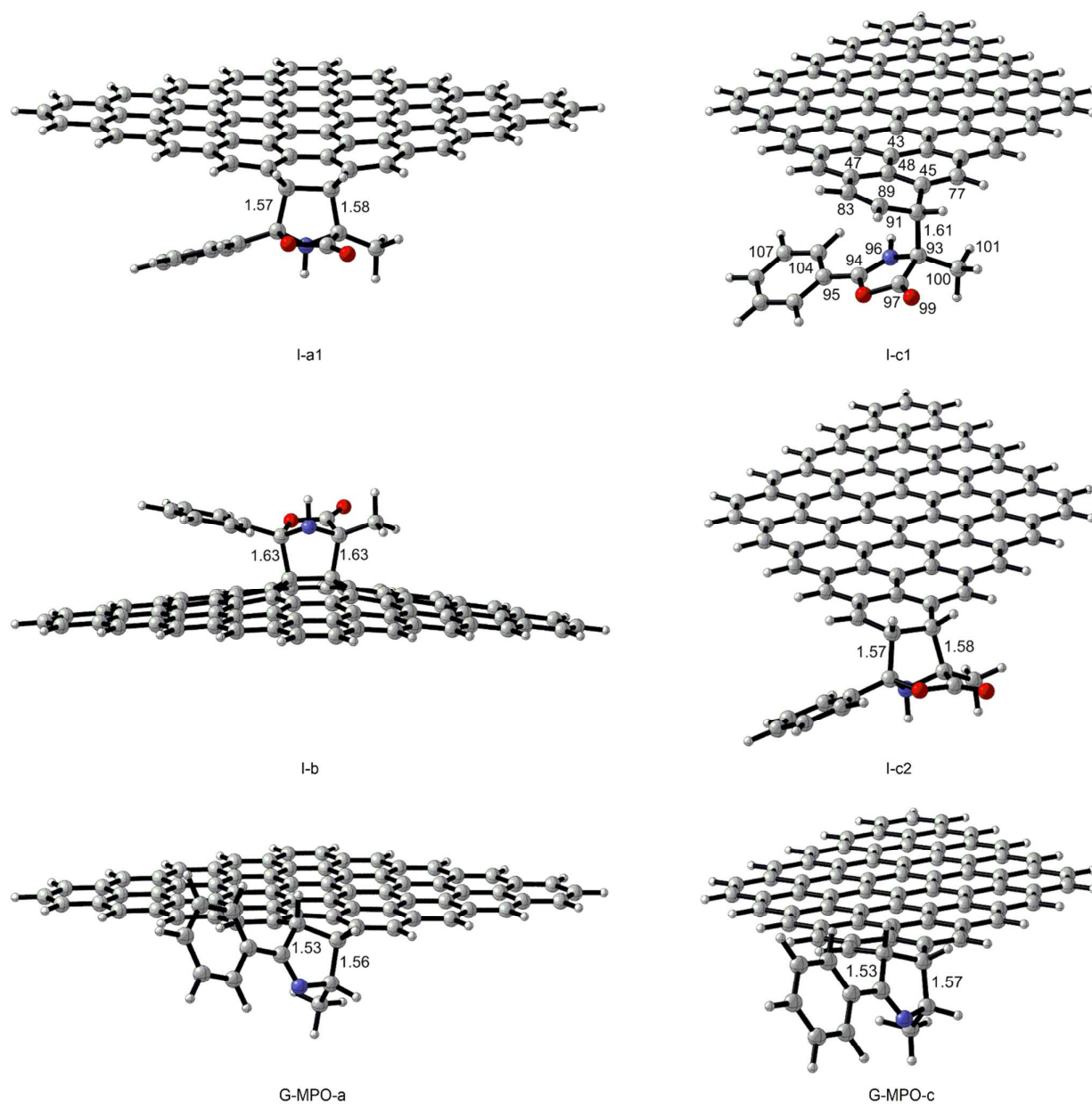


Fig. 8 Intermediates and products optimized structures for the 1,3-DC reaction of MPO-Mu with GF. Distances are in Å. Carried out with CYLview.⁴³

and 8, whereas their energetic and charge parameters have been summarized in Table 3, Fig. 9, and Table S1.

From a mechanistic standpoint, the formation of I-a1,b,c2 may be rationalised by two possible approaches, a stepwise mechanism and a concerted one. In our case, for pathways a,b we were able to localize only the concerted process whereas for pathway c only the stepwise one was successful. In principle, alternative mechanisms might also be envisaged for both cases, however all attempts to locate stationary points for reaction channels other than those herein reported were unsuccessful.

From Table 3 it is clear that pathway b is highly endergonic and

the formation of I-b can be ruled out; this behaviour was expected because the reaction on the interior double bond disrupts the aromaticity of four benzene rings. Pathway a is the only one that furnishes a 1,3-DC product energetically more stable than reagents and has an activation energy (TS-a1) of 2.87 kcal/mol higher than that of TS-c1 for pathway c (Fig. 9). On the contrary pathway c is slightly endergonic with an activation energy for the second step (TS-c2) of 3.41 kcal/mol higher than that of TS-a1. So, pathways a and c turn out to be competitive, with the second one highly reversible (ΔG inverse barriers of 7.41 and 15.15 kcal/mol for TS-c1 and TS-c2, respectively, compared to 27.89 kcal/mol for TS-a1).

The natural population analysis^{38,50} allows to evaluate the

Table 3. (U)M06-2X direct and inverse relative enthalpies (ΔH) (kcal/mol) and relative free energies (ΔG) (kcal/mol), and charge transfer (au) in terms of the residual charge of the MPO-Mu fragment in the transition state

Structure	Direct ΔH^a	Inverse ΔH^b	Direct ΔG^a	Inverse ΔG^b	NPA qCT (e)
TS-a1	-0.03	29.38	15.71	27.89	+0.18
TS-a2	21.74	29.78	20.74	41.60	—
TS-b	18.75	4.71	37.63	4.60	+0.32
TS-c1	-2.71	7.45	12.84	7.41	+0.47
TS-c2	12.51	15.00	19.12	15.15	+0.31
TS-c3	23.67	32.34	26.73	44.42	—
I-a1	-29.41	—	-12.18	—	—
I-b	14.04	—	33.04	—	—
I-c1	-10.16	—	5.43	—	+0.75
I-c2	-12.65	—	3.97	—	—
G-MPO-a	-37.45	—	-33.03	—	—
G-MPO-c	-21.32	—	-17.69	—	—

^aReferred to MPO-Mu + GF or corresponding I. ^bReferred to the corresponding products.

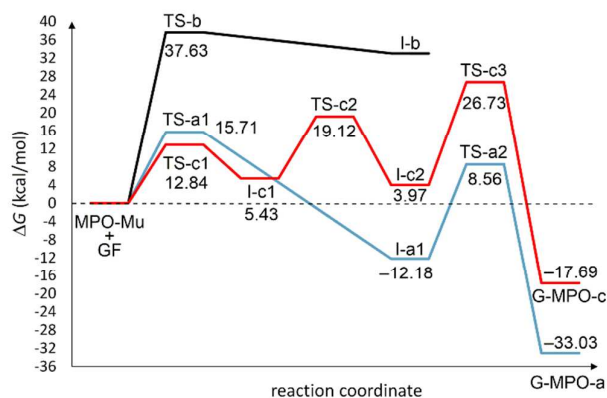


Fig. 9 Free energy profiles for the a-c pathways involved in the 1,3-DC of MPO-Mu with 5 × 5 GF model. All values are referred to MPO-Mu + GF.

charge transferred between the two reactants at the TSs geometry. The charge transfer in terms of the residual charge on the MPO-Mu, for all the optimized TSs involving the 1,3-DC process, is shown in Table 3. In all the cases the positive values are indicative of an electron flow from the HOMO of MPO-Mu to the LUMO of GF, in close agreement with Sustmann's type I dipolar cycloaddition rule (i.e. HOMO(dipole)-LUMO(dipolarophile) controlled reactions).⁵¹ Moreover this charge is more pronounced for the stepwise TS-c1 and reach its maximum for the zwitterionic intermediate I-c1 according to a nucleophilic addition of the negatively charged C4 carbon atom of MPO-Mu (Fig. 8, C93) to one of the carbon atoms belonging to the c double bond. In the I-c1 structure the positive charge is almost all concentrated to C93 atom (+0.72 e) whereas the negative one is principally spread on C83 and C89 atoms.

The zwitterionic intermediate I-c1 results stabilized by secondary orbital interactions. In fact, from the results of the secondary-order perturbation theory (SOPT) analysis of the Fock matrix in NBO basis, according to the definition of

delocalization energy given by Weinhold,^{52,53} and reported in Table 4, emerges that I-c1 is stabilized by a series of

Table 4. Secondary orbital interactions and delocalization energies for I-c1 as derived by the SOPT analysis

Bonds	Transition	Energy (kcal/mol)
C45-C47/C100-H101	$\pi \rightarrow \sigma^*$	0.18
C45-C85/C104-C107	$\pi \rightarrow \pi^*$	0.47
C83-C89/C93-C100	$\pi \rightarrow \sigma^*$	0.34
C83-C89/C94-C95	$\pi \rightarrow \pi^*$	0.52
C83-C89/C97-O99	$\pi \rightarrow \pi^*$	0.53
C89-H91/C97-O99	$\sigma \rightarrow \pi^*$	0.25
C97-O99/C83-C89	$\pi \rightarrow \pi^*$	0.16
C100-C101/C45-C77	$\sigma \rightarrow \pi^*$	0.14
C104-C107/C47-C85	$\pi \rightarrow \pi^*$	0.12
N96/C43-C48	$n \rightarrow \pi^*$	0.32
N96/C47-C85	$n \rightarrow \pi^*$	0.14
N96/C45-C77	$n \rightarrow \pi^*$	0.13
N96/C47-C85	$n \rightarrow \pi^*$	0.07

delocalizations of which the main are the $\pi \rightarrow \pi^*$ (0.47 kcal/mol) of the C45-C85 bonding orbital with the antibonding orbital of C104-C107 double bond and the two $\pi \rightarrow \pi^*$ (0.52 and 0.53 kcal/mol), due to the C83-C89 double bond with the antibonding orbitals of the C93-C100 and C97-O99 (Fig. 7, Table 4).

Considering that the nitrogen inversion is a fast event, at these operating temperatures, we have taken it in account and reported here only the most stable conformer.

Finally, we considered the decarboxylative process that conducts to products GMPO-a,c. The activation free energies, corresponding to the concerted loss of carbon dioxide from cycloadducts I-a1 and I-c2, of 20.74 and 22.76 kcal/mol, respectively, suggest that this is the slow step of the reaction. The irreversible character of decarboxylation and the stability of obtained products agree with the high grade of functionalization experimentally found.

The tautomerization of MPO to MPO-Mu is not yet fully clarified. An attempt to determine the free energy of activation for this process, based on 1,2-hydrogen shift mechanism, gave a result of 57.93 kcal/mol (see SI). Thus, the formation of the mesoionic compound must proceed through a more complex process.⁵⁴

Considering that the mesoionic MPO-Mu differ of +19.35 kcal/mol from the starting MPO tautomer, the outcome of the whole reaction is that in the case of pathway c the process is endoergonic of 1.66 kcal/mol whereas for the pathway a it is esoergonic of 13.68 kcal/mol. So, probably, the most expensive step could consist in the tautomerization reaction ($\Delta G^\ddagger > 25$ kcal/mol) justifying the temperature of almost 70 °C that it takes for the reaction to occur.

4. Conclusions

In summary, for the first time we have demonstrated that the solvent free 1,3-DC reaction of mesoionic compounds is an effective tool for the direct functionalization and delamination of graphite flakes into few layers of graphene nanosheets.

The procedure has been experimented by employing two differently substituted oxazolones and a high degree of functionalization (2.1–4.6%@700 °C) was obtained for both substrates under mild conditions (70–120 °C).

The graphite exfoliation efficiency depends upon the oxazolones substitution pattern. Raman data indicated that a single layer-like functionalized graphene was obtained using MNPO.

As inferred from theoretical calculations, the examined 1,3-DC reaction examined may proceed through a concerted mechanism (pathway a) competing with a stepwise one (pathway b) involving two transition states plus a zwitterionic intermediate. However, the last stage is irreversible and this behaviour is in accord with the high degree of functionalization experimentally observed and represents the training force of the process.

These results suggest a large scope of 1,3-DC between mesoionic compounds and graphite/graphene, and this strategy could be fruitfully extended to preformed Mu that, skipping the tautomerization process, should be more reactive.

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- 54 Experimental evidences indicate that several 1,3-DC of MPO with activated alkenes proceed at rt. Our results showed that 1,3-DC of MPO performed in solid/solid conditions were more effective than classical reactions in molecular solvent. The functionalization degree detected in the reaction performed in toluene at reflux for 12 h using a 1:10 GF/MPO weight ratio was 0.40%@500 °C and 0.93%@700 °C. Considering that no literature data are available, we have undertaken a comprehensive study to fully explain our results.