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## Multilayer graphene functionalized through thermal 1,3-dipolar cycloadditions with imino esters. A versatile platform for supported ligands in catalysis

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Multilayer graphene (MLG), obtained by mild sonication of graphite in NMP or pyridine, was fully characterized via atomic force microscopy (AFM), transmission electron microscopy (TEM), Raman spectroscopy and X-ray photoemission spectroscopy (XPS). Then, it was functionalized via 1,3-dipolar cycloaddition with azomethine ylides generated by thermal 1,2-prototropy of various imino esters. The resulting MLG, containing substituted proline-based amine functions were characterized by XPS and presented a high nitrogen loading, ranging from 0.6 to 4.2 at.% depending on the imino ester used. Among these functionalized MLG a probe sample was subjected to the ester hydrolysis and used as a heterogeneous N,O-chelating ligand to coordinate iridium atomic centers. This supported complex was also characterized by XPS and its catalytic activity was tested in the hydrogen transfer reduction of acetophenone obtaining up to 85% yield. Furthermore, this catalyst could be recycled up to four times.

### Introduction

Due to electrical, optical and mechanical properties of graphene,<sup>[1][2][3][4]</sup> the functionalization of these few layer planar structures can produce many attractive synergies.<sup>[5]</sup> Although these features make graphene a potentially useful and robust atomic-scale scaffold for the design of new nanomaterials its covalent functionalization still remain a difficult task because of its low reactivity. As consequence, harsh reaction conditions (pressure, temperature, etc.) are commonly needed and this often limits the exploitation of the full potential of this type of chemistry. Moreover, the reactivity also depends on the type of graphene support,<sup>[6][7][8]</sup> and on the number of graphene layers.<sup>[9][10][11]</sup>

Typically, multilayer graphene (MLG)<sup>[12]</sup> can be used as 4 or 2 component of the [4+2] cycloadditions<sup>[13][14]</sup> in the presence of very reactive dienophiles or dienes, respectively. Besides, only [3+2] cycloadditions involving azomethine ylides, generated through the decarboxylation route,<sup>[15][16][17]</sup> allowed the introduction of a secondary amine as functional group.<sup>[18][19][20][21][22][23][24]</sup> Furthermore in this way, an extra functionality to the system was added, with a total atom economy in the process. This type of functionalization is known to mostly take place on the face of the sheets and not on the edges, thus allowing a more complete exploitation of the support surface.<sup>[15]</sup> Hence dipolar cycloaddition is a potentially useful approach for the preparation of MLG-based functional materials. Generally, in these type of reactions an ultrasound

mediated dispersion (liquid exfoliation) of graphene in suitable organic solvents as pyridine<sup>[24]</sup> or *N*-methylpyrrolidone (NMP)<sup>[25][26]</sup> is appropriate to react with large excesses of *N*-alkylglycines and the corresponding aldehyde in a multicomponent sequence, at 130-180 °C during 3-5 days, to give the desired proline functionalized graphene. With the aim to investigate new milder and versatile strategies that permit the structural modification of graphene nanomaterials, in this work we present a novel and convenient synthetic route to anchor stabilized azomethine ylides to MLG. Such method implies lower temperature than the usual (e.g. 85-95 °C against the 130-180 °C). Furthermore, this type of proline derivatized graphene nanomaterial can be used as ligand for the generation of a graphene supported metal complexes. As a proof of concept iridium complex immobilization is presented, which was evaluated as heterogeneous recyclable catalyst in the hydrogenation of acetophenone.

### Results and Discussion

The starting graphite was first heated at 930 °C in inert atmosphere in order to remove most of the oxygen functional groups, which could lead to undesired byproducts during the 1,3-DC. Exfoliation of graphene was performed in NMP and in pyridine, which are known to be good solvents for liquid exfoliation and are also compatible with the following chemical reaction. The exfoliated graphene was characterized by TEM, TG, AFM, and Raman spectroscopy (see SI). The isolated graphene nanomaterials consisted of few layers (MLG), what is in agreement with the literature.<sup>[15]</sup> The analysis also revealed that under this sonication method negligible functionalization by oxidizing radicals occurred.<sup>[27]</sup> 2D Region of the Raman

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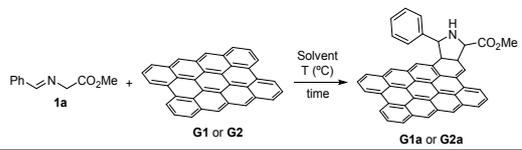
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spectrum for the MLG (sample **G1**) has a typical profile of few layers graphene materials (see SI).<sup>[28,29]</sup> Whereas 2D region for graphite is composed by 2D<sub>1</sub> and 2D<sub>2</sub> components with a peak intensity ratio 2D<sub>2</sub>/2D<sub>1</sub> close to 2, the 2D region for the MLG is much broader and it has a higher contribution from the lower frequency 2D<sub>1</sub> peaks.<sup>[28,29,30]</sup> Raman measurements have been done at different positions of the material to get useful information of 2D region.<sup>[31]</sup> The obtained data are in agreement with a MLG material with less than ten sheets (and more than four sheets) due to the higher contribution of the region below 2700 cm<sup>-1</sup> to the 2D peak.<sup>[29]</sup> AFM images are also in agreement with Raman results (see SI). Interestingly, the Raman spectrum for sample **G2a** is very similar to that for **G1** although it is blue-shifted, probably due to the functionalization reaction (the G band is shifted from 1586 cm<sup>-1</sup> to 1608 cm<sup>-1</sup>) (see SI). This shift blue of the G band has been reported for graphite oxide formation from graphite. It can be explained considering the existence of sp<sup>3</sup> carbon atoms on the edges that may create single-double bond alternation within extended sp<sup>2</sup> carbon areas.<sup>[32]</sup> This is in agreement with the functionalization achieved in this study.

Concerning the organic functionalization, the dispersed MLG **G1** (in pyridine) and **G2** (in NMP) were independently submitted to several conditions and solvents. In order to optimize the 1,3-DC with **1a**. Usually, 30 mL of this suspension were added to xylenes (50 mL) containing the target imino ester **1a**. The mixture of xylenes was employed as co-solvent because of its low cost and low toxicity, large temperature range and good dispersion achieved during the reaction. **G1** and **1a** were used as probe and were firstly studied (Table 1, entries 1-3) and the reaction resulted in the incorporation of 0.92 at.% of nitrogen (XPS evidence) or 0.34at.% (TG evidence) (Table 1, entry 1). Lower functionalization as determined by TG analyses is reasonable because the thermal treatment of covalently bonded groups on carbon materials, may produce the thermal decomposition of the lateral groups thus remaining the N heterocycle that can even be incorporated into the graphene layers. In fact, the thermal treatment of a carbon material modified with N-containing precursors is a method often used for N-doping in carbon materials.<sup>[33]</sup> Many reactive fleeting radical species could be formed, which reacted with MLG (Table 1). Higher functionalization (0.98 at.%) was observed (Table 1, entry 2) when double concentration of MLG was employed. The daily addition of a double amount of imino ester **1a** did not ameliorate the functionalization of **G1** (Table 1, entry 3). In all these previous experiments three different types of nitrogenated species were identified by XPS analysis, instead of the only one expected from the proline (see SI). Indeed, the expected pyrrolidinic nitrogen signal was flanked by two smaller peaks at 399.2 eV and 401.2 eV, related to amine and quaternary nitrogen groups, respectively.<sup>[34]</sup> So, blank experiments of both **G1** and **G2** were performed in order to investigate the possibility of some nitrogen contribution from the solvent. These two tests showed that **G2** was nitrogen-free (0.05 at.% approx.) but a notable residual 0.30 at.% of nitrogen was observed in **G1** case (Table 1, entries 4 and 5 and SI).

Further studies confirmed that the incorporation of the nitrogen occurred during the ultrasound-promoted exfoliation of the graphene in pyridine. Thus, we decided to avoid the use of pyridine and continued the study with **G2** and **1a**. These NMP dispersed samples displayed an incorporation of pure heterocyclic nitrogen of 1 at.%, after five days and independently of the temperature used (Table 1, entries 6 and 7). The evolution of the reaction course *versus* time was also analyzed, taking samples at different days during the reaction. As it can be deduced from Table 2 (entries 7-12) the increase of the percentage of nitrogen was negligible between the 5<sup>th</sup> and the 6<sup>th</sup> day, whilst more reaction time resulted in decomposition of **G2a**.

**Table 1** Optimization of 1,3-DC between **G1** or **G2** and **1a**.<sup>a</sup>



Ent.	Gx	T (°C)	t (d)	Gxa	N (%) <sup>b</sup>	N (%) <sup>c</sup>
1	<b>G1</b>	150-160	5	<b>G1a</b>	0.92	0.34
2 <sup>d</sup>	<b>G1</b>	150-160	5	<b>G1a</b>	0.98	0.36
3 <sup>e</sup>	<b>G1</b>	150-160	5	<b>G1a</b>	0.95	0.35
4 <sup>f</sup>	<b>G1</b>	150-160	5	---	0.30	0.11
5 <sup>f</sup>	<b>G2</b>	150-160	5	---	0.05	0.02
6	<b>G2</b>	150-160	5	<b>G2a</b>	1.00	0.37
7	<b>G2</b>	85-95	5	<b>G2a</b>	1.00	0.37
8	<b>G2</b>	85-95	1	<b>G2a</b>	0.33	0.12
9	<b>G2</b>	85-95	2	<b>G2a</b>	0.57	0.21
10	<b>G2</b>	85-95	4	<b>G2a</b>	0.80	0.30
11	<b>G2</b>	85-95	6	<b>G2a</b>	1.00	0.37
12	<b>G2</b>	85-95	10	<b>G2a</b>	0.26	0.10

<sup>a</sup> 0.3 mg of graphene (in 30 mL of pyridine or in NMP), xylene (50 mL), addition of imino ester (100-120 mg) each day. <sup>b</sup> Determined by XPS analysis. <sup>c</sup> Determined by TG analysis. <sup>d</sup> The concentration of the graphene suspension was twice higher. <sup>e</sup> Double amount of the imino ester **1a** (200 mg) was added per day. <sup>f</sup> These experiments were run in the absence of imino ester.

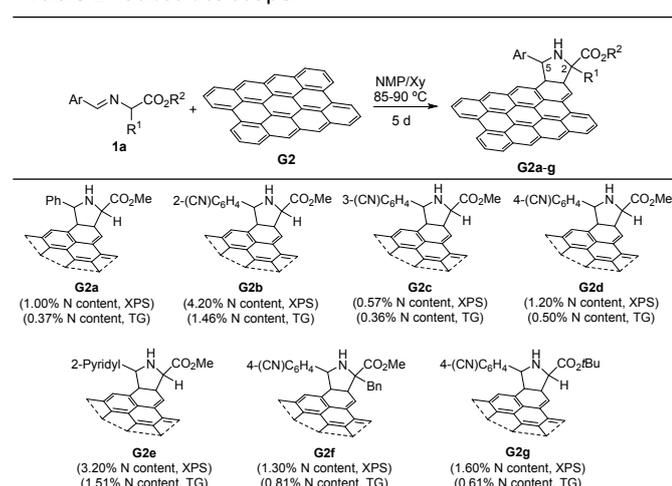
With the optimized reaction conditions in hand, we examined the scope of this thermal 1,3-DC employing the [1,2]-prototropy route for the generation of the reactive azomethine ylide **1** (Table 2). This study revealed that the reaction is compatible with a large library of structural motifs. In this regard, the presence of a cyano group in *o*-, *m*- and *p*-substituents was introduced to analyze the functionalization by subtractive-FTIR-ATR but this technique did not give the desired information. Furthermore the presence of heterocycles in the imino moiety was also tolerated as revealed the reaction performed with imino ester **1e**, obtained from 2-pyridylcarboxaldehyde, to afford **G2e** with a high nitrogen loading of 3.2 at.% (by XPS, Table 2). On the other hand, also the presence of hindered moieties in the imino ester, such as the benzylic group in  $\alpha$ -position, or a *tert*-butyl ester afforded very good results in terms of incorporation of nitrogen with 1.6 at.%

and 1.3 at.% for **G2f** and **G2g** respectively (Table 2). All functionalized MLG **G2a-G2g** were performed twice with a complete reproducibility.

All the **G2a-g** derivatives display a common peak comprised between 400.1 to 400.7 eV, respectively, corresponding to the proline nitrogen (see SI). A second peak appears in the case of **G2b-g** samples where another nitrogen is present in the cycloadduct, and its binding energy, respectively ranging from 399.4 and 399.8 eV, depends on the nature of the corresponding nitrogen. In every case, the area of the signals is coherent with the stoichiometry of the derivative (see SI). All the spectra present an almost negligible signal at around 401.0 eV due to some NMP adsorption.

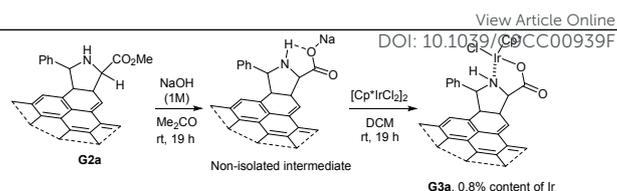
Concerning the stereoselectivity of the reaction, the relative configuration of C2 and C5 in the proline cycloadduct was not confirmed (Table 2). The normal trend of this mechanism predicts a 2,5-*cis* arrangement as a consequence of the existence of the intermediate W-shape 1,3-dipole,<sup>[35]</sup> but in many other examples, performed at higher temperatures (e.g. 150-160 °C), the presence of 2,5-*trans* arrangement was also favored.<sup>[35][36]</sup>

**Table 2** Substrate scope.<sup>a</sup>



<sup>a</sup> 0.3 mg of graphene (in 30 mL of NMP), xylene (50 mL), addition of imino ester (100-120 mg) each day, 100 °C, 5 d. Nitrogen content was determined by XPS analysis and represents the overall content.

These results pushed us to investigate the possibility of using this new type of functionalized MLG as metal centers support in the preparation of fine tunable heterogeneous catalysts. To this purpose **G2a** was used as heterogeneous ligand to prepare the iridium complex **G3a**. In this synthesis, **G2a** was firstly treated with sodium hydroxide (1 M, 1 mL/mg of **G2a**) in acetone (1 mL/mg of **G2a**) in order to hydrolyze the ester moiety and the resulting sodium salt was directly allowed to react with [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (0.5 mg/mg graphene) affording the desired complex **G3a**. In this new material, the proline cycloadduct behave as a N,O-chelating ligand and forms with the iridium center a stable five member ring (Scheme 1).<sup>[37]</sup> This new metallated MLG presented an Ir loading of 0.8% in mass (ICP- mass evidence).<sup>[38]</sup> This procedure was repeated three times obtaining identical **G3a** samples.



**Scheme 1** Synthesis of covalently bonded iridium-graphene complexes **G3a**.

N1s XPS of **G3a** displayed a principal peak at 402.2 eV, corresponding to a highly oxidized nitrogen, which is in agreement with a proline nitrogen coordinated to Ir centers. This signal is flanked by a second one, less intense, at 400.10 eV, that corresponds to some unreacted proline nitrogen. The ratio between the area of these two peaks allowed to estimate the yield of the coordination reaction to about 75%. An almost negligible signal at 401.2 eV due to some NMP adsorption on the MLG edges is also found. The presence in the sample of traces of NaCl, coming from the ester hydrolysis, prevents the iridium XPS characterization, as sodium shares the same spectral window of the highest intensity signal from iridium.

**G3a** was then evaluated in the Meerwein–Ponndorf–Verley (MPV) reduction of acetophenone through a hydrogen transfer from isopropyl alcohol, IPA, (Table 3).<sup>[39]</sup> The amount of iridium involved was about 0.12 mol%, corresponding to 40 mg of Ir-MLG. The amount of isopropyl was crucial because more diluted reaction mixture (using 3 mL of IPA per 1.5 mmol of acetophenone) only afforded a 22% yield after 1.5 d (Table 3, entry 2). However, the reaction performed with 1 mL of IPA led to a good conversion and yield (82%, Table 3, entry 3). In all the examples, the average of the recovery of the graphene hybrid material was  $\geq 90\%$  after careful centrifugation. Functionalized graphene **G2a** did not catalyze this reaction (Table 3, entry 1). Several cycles (up to four) with the same iridium catalyst **G3a** were performed (Table 3, entries 4-6). The maximum chemical yield of 1-phenylethanol was achieved diluting the reaction with 1.5 mL of IPA with 1.5 mmol of acetophenone and refluxing for 1.5 d (Table 3, entry 7). The recovered iridium-graphene complex was analyzed *via* ICP-Mass and no significant iridium leaching was detected, so 0.12 mol% of Ir can be considered the limit for the reaction completion and lower amounts afforded lower chemical yields. Entry 8 of Table 3 confirmed this fact. Here, the amount of the ketone was adjusted to the amount of functionalized MLG recovered from the reaction shown in entry 7 of Table 3. The experiments described in entries 3, 7 and 8 of Table 3 were performed up to three times demonstrating a reliable reproducibility for this process.<sup>[40][41]</sup>

**Table 3** Hydrogen transfer reduction of acetophenone.<sup>a</sup>

Entry	G	Cycle	G3 recov. (%)	Yield (%) <sup>b</sup>
1	<b>G2a</b> <sup>c</sup>	---	90	---
2	<b>G3a</b> <sup>d</sup>	---	90	22

3	<b>G3a</b>	1 <sup>st</sup>	92	82
4	<b>G3a<sup>e</sup></b>	2 <sup>nd</sup>	90	73
5	<b>G3a<sup>f</sup></b>	3 <sup>rd</sup>	91	52
6	<b>G3a<sup>g</sup></b>	4 <sup>th</sup>	89	32
7	<b>G3a<sup>h</sup></b>	1 <sup>st</sup>	92	85
8	<b>G3a<sup>h,i</sup></b>	2 <sup>nd</sup>	90	85

<sup>a</sup> See experimental section for details. <sup>b</sup> Determined <sup>1</sup>H NMR. <sup>c</sup> Pure **G2a** was used. <sup>d</sup> 3 mL of IPA were added instead of 0.5 mL. <sup>e</sup> 0.12 mol% of Ir/1.5 mmol of acetophenone was used. <sup>f</sup> 0.12 mol% of Ir/1.5 mmol of acetophenone was used. <sup>g</sup> 0.19 mol% of Ir/1.5 mmol of acetophenone was used. <sup>h</sup> 1.5 mL of IPA was added, warming for 1.5 d. <sup>i</sup> **G3a** recovered from entry 7/1.3 mmol of acetophenone/1.5 mL of IPA.

## Conclusions

The 1,3-DC of dispersed MLG and stabilized azomethine ylides originated from thermal 1,2-prototropy imino esters occurred in unexpected milder conditions than the reported ones for the analogous 1,3-DC with azomethine ylides generated *via* decarboxylative route. To the best of our knowledge, this is the first example of a graphene material functionalized *via* imino esters-based (1,3-DC). This is originated by the stability of the azomethine ylide. In addition, this ester moiety could be hydrolyzed and used as oxygen donor site to coordinate iridium centers, together with the proline nitrogen. This Ir-MLG was very efficient (more than the [Cp\*IrCl<sub>2</sub>]<sub>2</sub> itself and iridium complex anchored to fullerene<sup>[42]</sup>) in heterogeneous catalyst of the MPV reduction of acetophenone. **G3a** proved to be enough robust (no metal leaching was observed) to be recycled up to four times. All these set of transformations are highly reproducible. Considering the wide library of imines available for this type of reaction, this approach combines the possibility of a fine tune of the coordination sphere of the metal with the advantages of a graphene type heterogeneous support.

## Conflicts of interest

There are no conflicts to declare.

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