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Preparation of a ruthenium complex covalently bonded to multilayer graphene and its evaluation as a photocatalyst†‡

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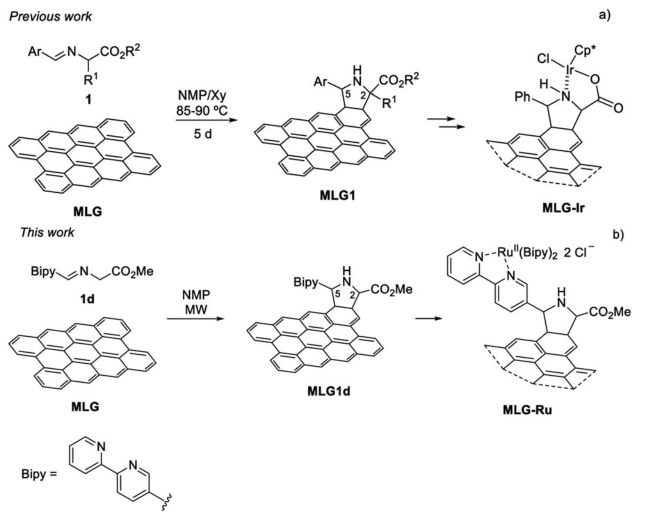
Multilayer graphene (**MLG**), obtained by mild sonication of graphite in NMP, was functionalised *via* 1,3-dipolar cycloaddition with azomethine ylides generated by thermal 1,2-prototropy from various imino esters. The microwave-assisted functionalisation took place in five hours at 100 °C. The resulting **MLG**, containing substituted proline-based amine functional groups, was characterized using XPS and showed a nitrogen loading three times that obtained for the same transformation performed for five days using convection-assisted heating. The preparation of the imino ester containing a bipyridine unit at the arylidene position allowed for the preparation of the corresponding functionalised **MLG**, which incorporated the ruthenium atom to achieve a heterogeneous **MLG-Ru** complex. This supported complex was tested, as a proof of concept, as a photocatalyst of the aerobic oxidative hydroxylation of 4-methoxyphenylboronic acid.

The association of transition metal catalysis with photocatalysis (known as metallaphotocatalysis)[1,2] gives access to unique very reactive intermediate species (impossible to generate using other protocols) under mild conditions. Versatility, modulation, scope and tolerance are also important features of these catalysed transformations. In addition, these processes are complementary to those traditionally used in the field of transition metal catalysis. The new frontiers of this area have been made to involve, among other features, ready access to robust and recoverable photocatalysts[3] in order to minimize costs and operational work, which would be very attractive from the industrial point of view.[4] Support materials to covalently bond the metal have been sought, and carbon materials constitute one of the preferred types of such materials nowadays. In this regard, graphene is a very useful and robust atomic-scale scaffold for the design of new nanomaterials. Due to the electrical, optical and mechanical properties of graphene,[5–10] functionalisation of these planar structures can produce many useful synergies.[11] Its covalent functionalisation, however, is not very simple because of its low reactivity. So, harsh reaction conditions (pressure, temperature, *etc.*) are usually required for this purpose. It is well known that the reactivity also depends on the type of graphene-based material used as a support,[12–14] and on the number of graphene layers.[15–17]

In most of the examples reported in the literature, multilayer graphene (**MLG**)[18] can be used as 4pi or 2pi components of [4 + 2] cycloadditions[19,20] in the presence of very reactive dienophiles or dienes, respectively. However, only [3 + 2] cycloadditions



Scheme 1 Synthesis of functionalised **MLG** from imino esters **1**.

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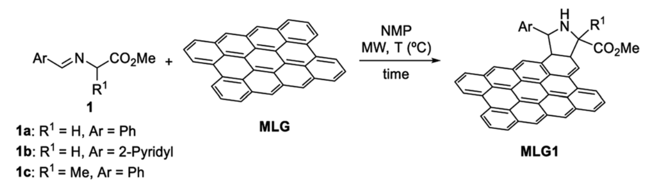
¶ This author contributed to the preparation of the pristine multilayer graphene suspensions.

involving fleeting azomethine ylides, generated *in situ via* the decarboxylation route (also called the Prato reaction),[21–23] have been found to allow the introduction of a secondary amine as a functional group.[24–32] This type of functionalisation takes place on the basal plane of the sheets and not on the edges, thus allowing a more complete exploitation of the support surface.[21] The synthesis of the graphene-based material often requires ultrasound-mediated dispersion (liquid exfoliation) of graphite in appropriate organic solvents such as pyridine[30] or *N*-methylpyrrolidone (NMP).[33,34] The reaction with a large excess of *N*-alkylglycines and the corresponding aldehyde in a multicomponent sequence at 130–180 °C for 3–5 days affords the prolinate-functionalised graphene. Our group reported the first thermal 1,2-prototropy of imino esters to **MLG**, achieved at 90 °C for 5 days and in a totally atom-economical process as no decarboxylation occurred during the generation of the intermediate azomethine ylide (Scheme 1a).[35]

In this contribution, the functionalisation of **MLG** using a 1,3-dipolar cycloaddition (1,3-DC) of azomethine ylides under microwave (MW)-assisted heating was studied and compared with the analogous process carried out using convection-assisted heating. With this strategy, it was possible to anchor a 2,2′-bipyridine unit to the ruthenium atom (Scheme 1b). The final goal of this metal-graphene-supported material was its application as a photocatalyst in a proof of concept.

The overall incorporation of nitrogen into pristine **MLG**,[36] under conventional heating (90 °C) in NMP after 5 days was 0.37% (ref. 35 and 37) (Table 1, entry 1). With this reference we started a microwave-assisted heating survey of reactions carried out for 5 h at the same temperature (Table 1, entry 2). Here, a notable increase in the functionalisation was observed (1.00% nitrogen content, with all such contents determined using thermogravimetric analysis) when only using 120 mg of the starting imino ester **1**, instead of 100 mg used per day in the mentioned convection-assisted heating. This value encouraged us to study the limit of the functionalisation of **MLG** under these conditions.[38,39]

Table 1 Optimization of 1,3-DC between MLG and 1a[a]

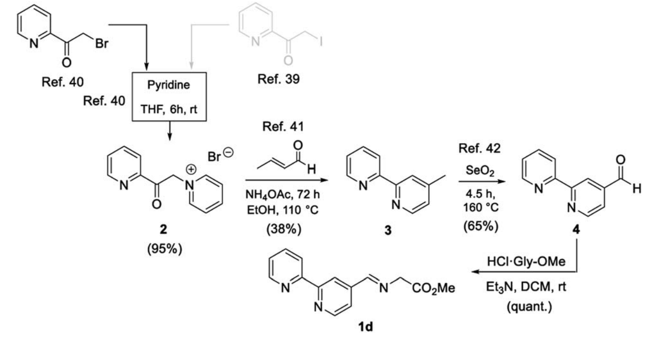


Ent.	1	Heating	T (°C)	t (h)	ML1	N^b (%)
1	**1a**	CH[c]	90	120	**MLG1a**	0.37 (ref. 35)
2	**1a**	MW	90	5	**MLG1a**	1.00
3	**1a**	**MW**	**100**	**5**	**MLG1a**	**1.45**
4	**1a**	MW	100	6	**MLG1a**	1.32
5	**1a**	MW	100	8	**MLG1a**	0.52
6	**1a**	MW	100	1	**MLG1a**	0.32
7	**1a**	MW	100	3	**MLG1a**	0.69
8	**1a**[d]	MW	100	5	**MLG1a**	1.38
9	**1a**[e]	MW	100	5	**MLG1a**	1.44
10	**1a**	MW	110	5	**MLG1a**	1.43
11	**1a**	MW	120	5	**MLG1a**	1.23
12	**1b**	MW	100	5	**MLG1b**	2.28
13	**1c**	MW	100	5	**MLG1c**	1.35

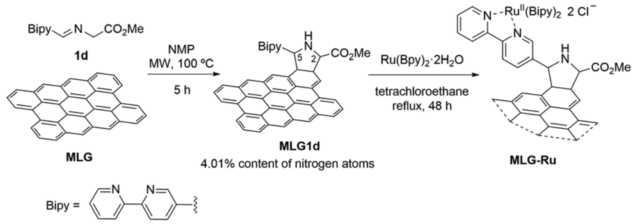
[a] A mass of 15 mg of graphene (in 50 mL of NMP), addition of imino ester 120 mg. [b] Determined from TG analysis. [c] CH = convection-assisted heating. Addition of 120 mg of imino ester per day. [d] A mass of 100 mg of imino ester **1a** was added. [e] A mass of 150 mg of imino ester **1a** was added.

When increasing the temperature to 100 °C, and keeping the reaction time at 5 h, the incorporation of nitrogen was 1.45% (Table 1, entry 3). After heating the reaction mixture for 6 or 8 h, a mass loss was detected (Table 1, entries 3 and 4). It seemed that the MW energy could induce some degradation of the organic material covalently bonded to the **MLG**. This result was observed in our previous research when allowing the reaction to proceed for more than 5 d. These reactions performed for 6 and 8 h were repeated three times and the results were essentially identical. Immediately, the reactions carried out for 1 and 3 h were analysed. In both cases, the extent of the organic functionalization was lower than that when the reaction was run for 5 h. So, neither longer reaction times (6 and 8 h) nor a shorter one (3 h) increased the nitrogen content during the functionalisation of **MLG** (Table 1, entries 4–7). Adding 100 mg of imino ester **1a** did not increase the functionalisation level (Table 1, entry 8). In addition, with 150 mg of imino ester **1a**, the incorporation of the nitrogen atoms was very similar to the transformation run using 100 mg of **1a** (Table 1, entry 9). Increasing the temperature to 120 °C, while keeping the reaction time at 5 h, was not beneficial for the reaction of graphene with imino ester **1a** (Table 1, entry 11). So, submitting a suspension of graphene in NMP (50 mL, 0.1 mg mL^{-1}), containing 120 mg of imino ester **1a**, to microwave irradiation (reaching 100 °C) for 5 h constituted the optimal set of reaction parameters to achieve a very good functionalisation of graphene.

These conditions were applied to another two imino esters just to test the reproducibility of this procedure. Specifically, the 2-pyridyl-substituted glycine-derived imino ester **1b** and its alanine analog **1c** were tested as azomethine ylide precursors in this 1,3-DC (Table 1, entries 12 and 13). For the reaction of substrate **1b**, the nitrogen content (2.28%) observed was less than double that observed for the same transformation run with

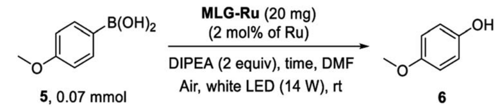


Scheme 2 Synthesis of imino ester 1d.



Scheme 3 Synthesis of functionalised **MLG-Ru** from **MLG1d**.

Table 2 Photocatalytic aerobic oxidative hydroxylation of 4-methoxyphenylboronic acid[a]



Ent.	DMF	[**5**][b]	*t* (h)	C. E.[c]	**6**[d] (%)	**6**[e] (%)
1	0.1 mL	0.70	36	—	nr	—
2	0.5 mL	0.14	36	—	nr	—
3	1.0 mL	0.07	36	—	45	40
4	1.5 mL	0.04	36	—	48	41
5	1.0 mL	0.07	72	—	94	88
6	1.0 mL	0.07	72	**MLG**[f]	nr	—
7	1.0 mL	0.07	72	**MLG1d**[g]	nr	—
8	1.0 mL	0.07	72	No **MLG-Ru**	nr	—
9	1.0 mL	0.07	72	Inert atm.	nr	—
10	1.0 mL	0.07	72	No DIPEA	nr	—
11	1.0 mL	0.07	72	Blue light	nr	—
12	1.0 mL	0.07	72	Darkness	nr	—
13	1.0 mL[h]	0.07	72	—	95	88

[a] A mass of 20 mg of **MLG-Ru**, in DMF, **5** (0.07 mmol), DIPEA (0.14 mmol), white LED light (14 W), and air atmosphere at room temperature. nr = no reaction. [b] In mol L^{-1}. [c] C. E. = control experiments. [d] Conversions determined from analysis of crude ^{1}H NMR spectra. [e] Isolated yield after flash chromatography. [f] **MLG** was used instead of **MLG-Ru**. [g] **MLG-1d** was used instead of **MLG-Ru**. [h] Recovered **MLG-Ru** from entry 5 was reused in a new reaction.

imino ester **1a** (compare entries 3 and 12 of Table 1). The alaninate **1c** afforded a slightly lower functionalisation (1.35%) in **MLG1c** (Table 1, entry 13), possibly due to a higher steric hinderance.

Once the microwave-assisted functionalisation was optimized, the synthesis of the 2,2′-bipyriridine-derived imino ester **1d** was undertaken. The chemical yield of aldehyde precursor **4** was extremely low,[40] so a modification of it was designed in order to obtain this aldehyde in large quantities and higher yields. For this purpose, reactions from several references were selected and combined, as shown in Scheme 2. 2-(Iodoacetyl) pyridine[40] was not used due to the waste material generated in this step. 2-(Bromoacetyl)pyridine[41] was used instead, affording cleanly the corresponding pyridinium salt **2**, in 82% yield, after treatment with pyridine at rt.[41] Bipyridine intermediate **3** was isolated in a 38% yield by reacting **2** with crotonaldehyde in the presence of ammonium acetate.[42] Aldehyde **4** was generated (65%) by subjecting **3** to a benzylic oxidation with selenium oxide, following the published procedure (Scheme 2).[43] Imino ester **1d** was formed quantitatively, after generation of the free base of Gly-OMe, in dichloromethane at rt[44] (Scheme 2).

The synthesis of the ruthenium-supported graphene photocatalyst (**MLG-Ru**) was performed by achieving a thermal 1,2-prototropy-mediated 1,3-DC between pristine graphene and **1d** under standard conditions, giving rise specifically to **MLG1d**, which incorporated 4.01% nitrogen atoms. In the second step, **MLG1d** was allowed to react with Ru(Bpy)$_2$Cl$_2\cdot$2H$_2$O complex in tetrachloroethane (40 mg of **MLG1d** in 20 mL) under reflux for 48 h[45] (Scheme 3). The amount of ruthenium, determined from an ICP analysis, was 0.80%, which revealed that approximately 60% of ruthenium atoms were coordinated by a bipyridine unit covalently bonded to **MLG**.

As a proof of concept, an evaluation of the catalytic activity of this heterogeneous **MLG-Ru** complex in the aerobic oxidative hydroxylation of arylboronic acids[46] was carried out. For this purpose, 4-methoxyphenylboronic acid (**5**, 10 mg, 0.07 mmol) was selected as the starting material to undergo this oxidation to the corresponding 4-methoxyphenol (**6**) with 20 mg of **MLG-Ru** complex (0.80%, 1.5×10^{-3} mmol, 2 mol% Ru), under an air atmosphere and irradiation with white LED light (14 W), and using diisopropylethylamine (DIPEA, 0.14 mmol, 2 equiv.) and DMF as solvent. Initially, very disappointing results were obtained when concentrated solutions of **5** (0.70 and 0.14 M) and **MLG-Ru** were employed (Table 2, entries 1 and 2). More diluted suspensions in DMF (0.07 and 0.04 M of **5**) afforded partial conversions at 36 h (Table 2, entries 3 and 4).[47] Perhaps, the low transparency of the most concentrated dense black suspensions impeded an efficient transmission of light to the reactive site. For this reason, the reaction was more sluggish than the published same reaction with Ru(Bpy)$_3$Cl$_2\cdot$2H$_2$O where an almost complete conversion at room temperature was observed at 72 h (Table 2, entry 5). The 0.07 M concentration was selected rather than 0.04 M because smaller amounts of DMF were required. Several control experiments were designed to demonstrate the necessity of all of the components involved. The absence of **MLG-Ru** catalyst (Table 2, entries 6–8), air (Table 2, entry 9), triethylamine (Table 2, entry 10), and white LED light (Table 2, entries 11 and 12) in each case yielded no reaction. As shown in the last entry of Table 2, we also tested the recycling of the heterogeneous catalyst under the standard conditions described in entry 5 of Table 2. The reaction was reproducible and the structure of the catalyst remained intact according to microscopy, XPS and ICP mass spectrometry analyses (see ESI‡).

In conclusion, the 1,3-DC of dispersed **MLG** and stabilized azomethine ylides **1**, originated from thermal 1,2-prototropy of imino esters, occurred under microwave irradiation in shorter reaction times (5 h *versus* 5 d) and with a final **MLG1** three times more functionalised than for the already published work.[35] To the best of our knowledge, this was the first time that this dipolar cycloaddition occurred with a total atom economy under microwave irradiation and it was the highest level of functionalisation of **MLG** achieved. The bipyridine unit was covalently bonded to the graphene and allowed for a complex to form with the ruthenium atom. The resulting heterogeneous catalyst acted as a photocatalyst in the aerobic oxidative hydroxylation of 4-methoxyphenylboronic acid and proceeded with a shorter reaction time than that needed for the reaction described in the original contribution.[46] This supported ruthenium catalyst was found (using TG, and TEM) to be robust and could be recycled in a second reaction batch. The catalytic efficiency of this heterogeneous supported complex offered slightly lower chemical yields for the mentioned oxidative hydroxylation than did the homogeneous reaction reported in the literature[46] using longer reaction times. The current reaction system showed an opacity to light, a drawback in our proof-of-concept experiment, but showed the advantage of the ability to separate and recycle the catalyst.

Author contributions

The manuscript was written and corrected through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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