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A re-examination of claims of aminoferrocene–graphene-based molecular magnets

Gayathri Athavan,¹ François-Xavier Coudert,² Robin. B. Bedford^{1*}

1. School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, U.K.
2. Chimie ParisTech, CNRS, Institut de Recherche de Chimie Paris, PSL University, Paris, France

Author to whom correspondence should be addressed: r.bedford@bristol.ac.uk

Abstract. A recent investigation claimed that graphene oxide (GO) modified by aminoferrocene gave a material that showed room temperature colossal superparamagnetic behaviour. The first step in the reported synthesis of aminoferrocene was the direct nitration of ferrocene. We show here, in accord with previous precedents, that the direct nitration of ferrocene by the nitronium ion does not occur under the conditions reported and therefore the material described previously cannot be based on aminoferrocene. Computational investigations undertaken herein show that the model used to account for the magnetic properties of the material results from an artefact of the GO model employed.

Following reports that graphene oxide (GO) and reduced graphene oxide show weak magnetism at room temperature,^{1,2} and that GO modified by aminoferrocene (**1**) shows tunable magnetic properties,³ El-Gendy and co-workers published an article describing colossal superparamagnetic behaviour at room temperature of GO⁴ modified by intercalation of aminoferrocene.⁵ Fig. 1. shows a redrawing⁶ of the published synthesis.⁵ The first step in the synthesis (step 1) is the direct nitration of ferrocene (**2**) by the nitronium ion – formed in a mixture of concentrated nitric and sulfuric acids – to give nitroferrocene **3**. We were surprised by this claim as the direct nitration of **2** to give **3** has long been reported to fail.⁷ Indeed, the authors cite that “nitration of ferrocene has been deemed un-attainable”, citing Woodward’s classic 1952 paper which explains why direct nitration fails.⁸ The failure of direct nitration is due to the fact that electrophilic aromatic substitutions of **2** fail when the electrophile is also strongly oxidising, since formation of the ferrocenium ion (**2**⁺) by oxidation of the iron centre from Fe(II) to Fe(III) occurs instead and prevents subsequent substitution.⁹ Consequently alternative, albeit typically low-yielding, synthetic approaches have been developed for **3** that do not rely on direct nitration.¹⁰⁻¹² Intrigued by the authors claims that they were able to produce **3** by direct nitration we decided to attempt to reproduce their methodology.

In the first attempt, we followed the reported experimental and slowly added ferrocene to the HNO₃/H₂SO₄ mixture in an ice bath at 0 °C. **CARE!** Addition of > 10 mg portions at a time led to spontaneous ignition, indeed as the reaction progressed even addition of this amount led to ignition. Within the first few seconds of the first addition, a blue coloration was observed, consistent with the formation of the ferrocenium ion [**2**]⁺, followed by a rapid change to green and then the formation of a brown-black mixture which remained throughout the rest of the addition. After ~ 50 mins we had added a total of ca. 200 mg of ferrocene. After a total of ~ 1 hour reaction time, the mixture was carefully diluted with water and the organic components were extracted with ethyl acetate. Removal of the solvent from this mixture under reduced pressure gave a low yield (28 mg) of a brown solid. Separately,

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the aqueous phase was neutralised and then extracted (ethyl acetate) yielding an orange, gum-like residue (21 mg). The colours of the residues are not consistent with formation of nitroferrocene which is purple.¹¹ Neither the ^1H or ^{13}C NMR spectra (see Supplementary Information, Figs. S2, S3, S5, S6) of the residues are consistent with the reported spectra of nitroferrocene.¹² The absence of nitroferrocene in the first fraction was further indicated by both IR spectroscopy (Figure S1), which showed no peaks at 1507 cm^{-1} for the nitro group stretch of nitroferrocene,¹¹ and ESI-MS (Figure S4) which showed no peaks at $m/z = 231$ consistent with the anticipated or reported mass spectrum of **3**.¹²

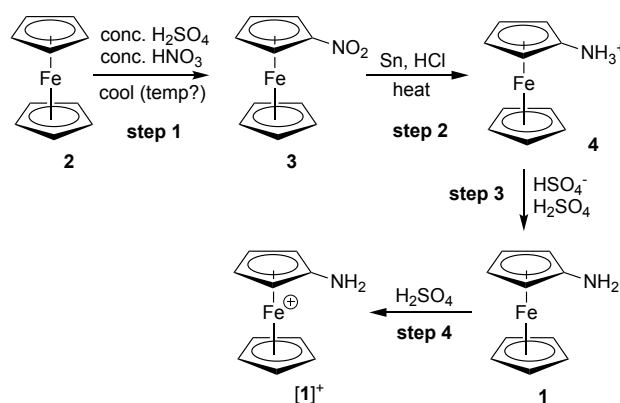


Fig. 1. Purported synthetic approach.⁵

Subsequently, on request, the authors kindly provided further information regarding their methodology that was not available in the publication,¹³ stipulating that the reaction was performed at $-80\text{ }^\circ\text{C}$ to $-30\text{ }^\circ\text{C}$ under an inert atmosphere. Accordingly, in our second attempt, we cooled the $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture under a nitrogen atmosphere to $-80\text{ }^\circ\text{C}$. This mixture was too viscous to stir at this temperature so we allowed the bath to warm to the point at which stirring could commence (ca. -50 to $-40\text{ }^\circ\text{C}$) and the bath was then maintained at this temperature for the addition of the ferrocene. In the first attempt we used a total of 190 mg of ferrocene, which yielded trace amounts ($\sim 4\text{ mg}$) of precipitated material in contrast with the authors' description that the product forms as a suspension and can be collected and washed.¹³ The rest of the material stayed in solution, the dark blue coloration (see Figure S10) of which was indicative of the formation of the ferrocenium ion 2^+ . The lack of reasonable amounts of isolable material may have been a consequence of the reduced scale of our attempt. So, for the third attempt we planned a reaction on the same scale as the authors, unfortunately, the addition of the first portion of ferrocene led to rapid thermal runaway and spontaneous ignition, at which point further attempts to reproduce the purported synthetic protocol(s) or variations on them were abandoned in the interest of safety.

We conclude, in line with previous investigations,^{7,8} that the direct nitration of ferrocene by the nitronium ion formed in concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ does not occur, instead the formation

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of the blue ferrocenium ion 2^+ is observed, accompanied by decomposition. Consequently, in our hands, and in line with all previous reports, the reaction shown in step 1 of the sequence shown in Fig. 1 fails, and therefore aminoferrocene **1** cannot be produced by this approach.

Fortunately, compound **1** can be readily made by multiple alternative approaches,¹⁴ or purchased from one of several commercial suppliers. It has been thoroughly spectroscopically, analytically and structurally characterised and indeed has had its single crystal X-ray structure determined twice.^{15,16} We recorded an IR spectrum of a genuine, commercial sample of **1** and this is shown in Figure S16; comparison with the IR spectrum reported shows that the material described is not **1**,⁵ similarly the reported X-ray powder diffraction does not fit that calculated for **1** (Fig. S18, determined using reported X-ray structural data for **1**).¹⁶ El-Gendy and co-workers describe the material as being in the oxidised, ferrocenium form 1^+ where, in direct contrast to the purported first step in Fig. 1, the sulfuric acid present has oxidised the ferrocene centre. A personal communication from the authors described the obtained material as brown,^{13,17} however ferrocenium ions would be expected to be typically blue or green. Indeed, a small-scale oxidation of **1** with concentrated H_2SO_4 gave a purple solution (Figure S12).

In addition to synthetic studies, we were also intrigued by the computational models obtained to explain the reported magnetic phenomena.⁵ Notwithstanding that aminoferrocene is not produced by the synthetic protocols, we undertook a re-examination of the computational findings reported by El-Gendy and co-workers on the nature of the intercalated aminoferrocene-GO material.⁵

Modelling GO, as produced by modifications of the Hummers' method,¹⁸ remains challenging. This is not least because of the heterogeneity of the GO structure, which contains hydroxyl, epoxy and carboxylic acid residues as the oxygenated groups formed during the oxidation of graphite, as captured by the Lerf-Klinowski model.¹⁹ In this model the carboxylic acid functions tend to localise at the edge of sheets while the rest tend to occur on sp^3 -hybridised carbons in the basal plane. While the Lerf-Klinowski model has been used to good effect in computational studies,²⁰ it tends to assume a random distribution of oxidised functionalities throughout the structure and this is open to question, not least because disruption of the sp^2 framework by oxidation means that proximate regions are more prone to subsequent oxidation.²¹ This leads to oxidised islands in otherwise unmodified seas of graphitic structure. Accordingly, more sophisticated models have been developed which capture these features.^{22,23}

Against this backdrop, a small, highly simplified ($C_{54}(OH)_7$) precursor model, **5**, with protonated epoxy groups as the sole O-containing functions was originally reported to describe the GO and its aminoferrocene adduct.⁵ Specifically, the precursor **5** had 6 protonated epoxy groups sitting over the centres of C_6 rings at the edges of the ring and a 7th sitting over the central C ring (Figure 2a).²⁴ The model was not capped with hydrogen atoms but retained unphysical open shell carbon atoms at its edge.²⁵ Two of these sheets were then arranged on either side of a dication of aminoferrocene (1^{2+} ; see below for discussion on the likely stability of this Fe(IV) structure) and then the structure was relaxed to give the unusual structure, **6**, shown in Fig. 2b with two free hydroxy radicals between 1^{2+} and the two GO

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sheets. The two GO layers bulge away from the aminoferrocene/hydroxyl radical region, hinting that the magnetic properties might be modulated by varying pressure.⁵ Importantly, partial electron-transfer from the Fe centre to the free hydroxy radicals appears to account for the metalization of the material and attendant magnetic properties.⁵ Free hydroxy radicals will not be present in the GO as prepared by the modified Hummers' method since these would have been removed during work-up or would have long since reacted directly with the GO.²⁶ Therefore, if they are indeed present in the intercalated structure, they presumably result from interaction of the GO layer with the intercalating aminoferrocene. We tested this hypothesis using the precursor model **5** previously described⁵ and subjecting it to geometry optimisation in isolation (PBE-d3bj/def2-TZVP). This led to extrusion of the central hydroxy radical (along with the migration of the remaining 6 hydroxyls to the periphery), as shown in Fig 2c.²⁷ This demonstrates that the extrusion of the free hydroxy radicals is simply an artefact resulting from the unphysical nature of the starting model **5**.

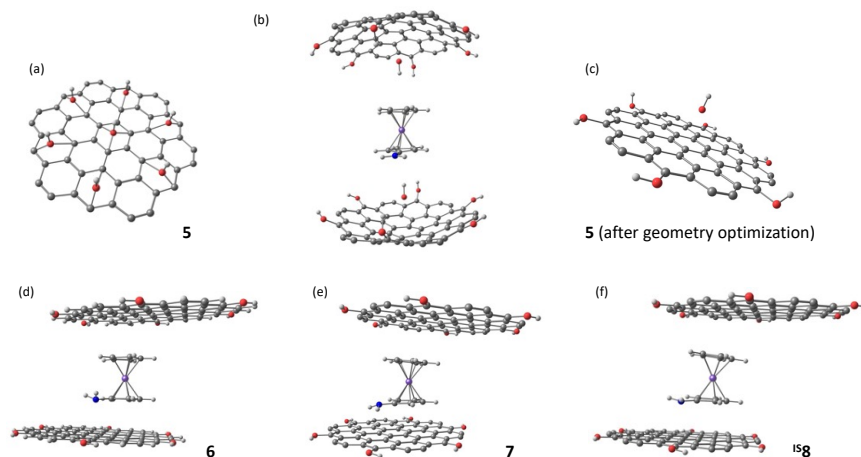


Figure 2. (a) The precursor model, **5**, used to represent GO prior to optimisation.⁵ (b) The model reported on relaxing a structure of $1^{2+}@[C_{54}(OH)_6OH]_2$.⁵ (c) The optimised structure **5** in the absence of aminoferrocene. (d) – (f) Structures **6** – **158** obtained on optimising $1^{n+}@[C_{54}(OH)_6]_2$ ($n = 0, 1$ and 2 respectively).

It is possible that the calculated bulging of the GO layers observed in Fig. 2(b) is a function of the presence of the aminoferrocene moiety, indeed this was suggested by El-Gendy and co-workers.⁵ Accordingly we modelled the interaction of aminoferrocene with optimised GO layers in the absence of free hydroxyl radicals. Geometry optimisation (PBE-d3bj/def2-SVP(def2-TZVP on Fe)) of three models (**6** – **158**; IS = intermediate spin) with intercalated **1**, **1**⁺ or **1**²⁺ (Fe(II), Fe(III) and Fe(IV), figure 2d – f respectively) gave structures that clearly show no bowing of the GO layers. Instead, the structures are largely unremarkable, formed by π -

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stacking of the cyclopentadienyl rings of the aminoferrocene moieties with the GO layers.²⁹ Separately, we also modelled both (i) chemically more realistic³⁰ hydrogenated version of **6** and **7** with H atoms added to the peripheral carbons (**9** and **10** respectively) and (ii) the effect of changing spin-state in **8**. Neither modification had a profound effect on the overall structure of the species obtained.²⁹

It should be noted, that when modelling varying oxidation states on ferrocenes, appropriate care must be spent on questioning the chemical likelihood of a given oxidation state under the conditions described. Looking at the oxidation states of the putative intercalating aminoferrocenes, **1** and **1⁺** are chemically reasonable under the conditions described by El-Gendy and co-workers,⁵ but the dication **1²⁺** is not. Ferrocene dications are remarkably rare due to their inherent extreme reactivity. To date, the only crystallographically characterised Fe(IV) ferrocene is $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{2+}$,^{31,32} which is extremely air- and moisture-sensitive and rapidly decomposes in organic solvents. Indeed, it can only be prepared and handled in anhydrous SO_2 and is produced by the oxidation of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]$ with powerful oxidising agents such as AsF_5 , SbF_5 , and ReF_6 . No such potent oxidising agents are present in the system reported by El-Gendy and co-workers:⁵ **1²⁺** would be highly unlikely to form under their conditions³³ and even if it did, it would not subsequently survive the reported reaction media.

In conclusion, inspired by the work of El-Gendy and co-workers we have re-examined key synthetic and computational aspects of their claims. We conclude that while the material produced by the authors may well display the interesting magnetic properties claimed, it is clearly not the material the authors claim it to be. Furthermore, the interesting results obtained by El-Gendy and co-workers in their computational studies are unfortunately simply a result of chemical artefacts brought about as a consequence of the choice of starting model employed.

Supplementary Material. Details of experimental procedures; spectroscopic details; computational methodology and .xyz coordinates of calculated structures.

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AUTHOR DECLARATIONS Conflict of Interest
The authors have no conflicts to disclose.

Author Contributions

Gayathri Athavan: conceptualization; methodology (synthetic studies); investigation (synthetic studies); validation; writing/original draft preparation; writing/review & editing. **François-Xavier Coudert:** conceptualization; writing/original draft preparation; writing/review & editing. **Robin B. Bedford:** conceptualization; data curation; funding acquisition; methodology (synthetic and computational studies) investigation (computational studies); supervision; validation; visualization; writing/original draft preparation; writing/review & editing.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material. The xyz coordinate files for the calculated structures, given in plain text in the supplementary material, are also freely available in the University of Bristol data repository, data.bris, with the identifier: XXXXX (to follow).

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17. It could be argued that any 1^+ produced by El-Gendy and co-workers was impure, indeed they now state in a personal communication, that the aminoferrocene produced by his method was not pure, but rather contained multiple products, not least due to the formation and subsequent reduction of some 1,1'-dinitroferrocene. It should be noted in this regard that 1,1'-dinitroferrocene is currently not known, see: S. Alexandr, P. P. Maurice, G. D. Whitener, and J. Arnold, "Synthesis, Structure, and Properties of 1,1'-Diamino- and 1,1'-Diazoferrocene," *Organometallics* **19**, 3978-3982 (2000).
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27. It should be noted that a frequency calculation reveals this structure to be a complex saddle point rather than a minimum on the potential energy surface (see Supporting Information for details), with imaginary stretches associated with several OH wagging processes, but this does not impact significantly upon the key conclusion.
28. It should be noted that this model for GO sheets precludes an accurate representation between intercalating species and oxygenated groups on the basal plane. Indeed, basal plane epoxide functions, which have not been included in the model, are known to undergo facile nucleophilic attack with primary amines (to which class aminoferrocene belongs), see: U. Sierra, E. Cuara, A. Mercado, E. Díaz-Barriga, A. Bahena, A. Cortés, J. P. Martínez, M. Solà and S. Fernández, "Efficient synthesis of amine-functionalized graphene oxide by ultrasound-assisted reactions and density functional theory mechanistic insight," *Appl. Nanosci.* **11**, 1637-1649 (2021).

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29. See supplementary information for full details.
30. An indication of the chemical instability of the structures **6** and **7** is highlighted by the substantial calculated gas-phase ΔG for their hydrogenation with 12 H₂ to give **9** (-980.9 kcal/mol) and **10** (-995.15 kcal/mol)
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