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► **To cite this version:**

Gayathri Athavan, François-Xavier Coudert, Robin B Bedford. A re-examination of claims of aminoferrocene-graphene-based molecular magnets. *Applied Physics Letters*, 2024, 124 (11), pp.111903. 10.1063/5.0202197. hal-04501138v2

HAL Id: hal-04501138

<https://hal.science/hal-04501138v2>

Submitted on 13 Mar 2024

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

Cite as: Appl. Phys. Lett. **124**, 111903 (2024); doi: [10.1063/5.0202197](https://doi.org/10.1063/5.0202197)

Submitted: 2 February 2024 · Accepted: 1 March 2024 ·

Published Online: 12 March 2024



View Online



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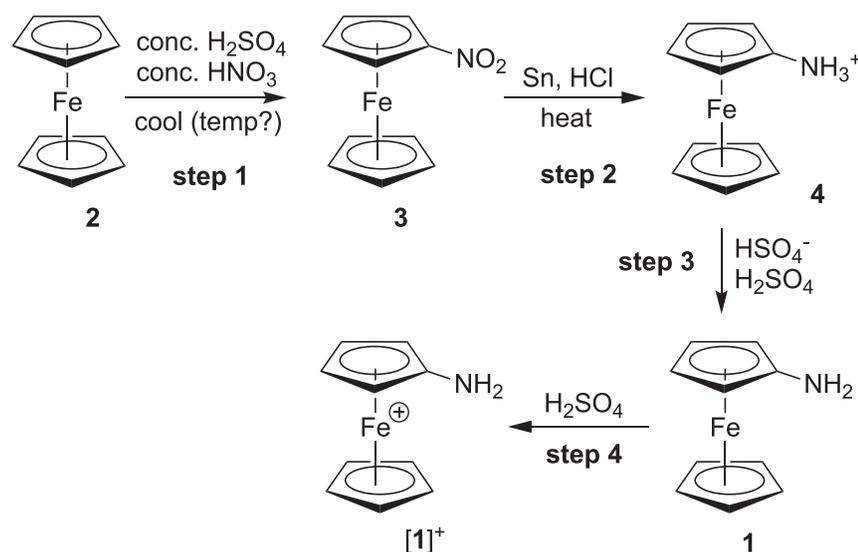
ABSTRACT

A recent investigation claimed that graphene oxide (GO) modified by aminoferrocene gave a material that showed room temperature colossal superparamagnetic behavior. 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 artifact of the GO model employed.

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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 behavior at room temperature of GO⁴ modified by intercalation of aminoferrocene.⁵ Figure 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 state 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 oxidizing, since formation of the ferrocenium ion (**2**⁺) by oxidation of the iron center 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 brownish-black mixture which remained throughout the rest of the addition. After ~50 min, we had added a total of ~200 mg of ferrocene. After a total of ~1 h 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, the aqueous phase was neutralized and then extracted (ethyl acetate) yielding an orange, gum-like residue (21 mg). The colors of the residues are not consistent with formation of nitroferrocene which is purple.¹¹ Neither the ¹H or ¹³C NMR spectra (see the supplementary material, 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 (Fig. S1), which showed no peaks at 1507 cm⁻¹ for the nitro group stretch of nitroferrocene,¹¹ and ESI-MS (Fig. S4) which showed

FIG. 1. Purported synthetic approach.⁵

no peaks at $m/z = 231$ consistent with the anticipated or reported mass spectrum of **3**.¹²

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 to -30°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°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 (~ -50 to -40°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 (~ 4 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 Fig. 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 that, in line with previous investigations,^{7,8} 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 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 characterized 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 Fig. 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 oxidized, ferrocenium form 1^+ where, in direct contrast to the purported first step in Fig. 1, the sulfuric acid present has oxidized the ferrocene center. 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 (Fig. 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

Modeling 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 localize 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 oxidized 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 oxidized 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 $[\text{C}_{54}(\text{OH})_7]$ 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 centers of C₆ rings at the edges of the ring and a 7th sitting over the central C ring [Fig. 2(a)].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. 2(b) with two free hydroxy radicals between 1^{2+} and the two GO 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 center 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 optimization in isolation (PBE-d3bj/def2-TZVP). This led to extrusion of the central hydroxy radical (along with the migration of the remaining six hydroxyls to the periphery), as shown in Fig. 2(c).²⁷ This demonstrates that the extrusion of the free hydroxy radicals is simply an artifact resulting from the unphysical nature of the starting model **5**.²⁸

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 modeled the interaction of aminoferrocene with optimized GO layers in the absence of free hydroxyl radicals. Geometry optimization

[PBE-d3bj/def2-SVP(def2-TZVP on Fe)] of three models (**6**—**8**; IS = intermediate spin) with intercalated 1 , 1^+ , or 1^{2+} [Fe(II), Fe(III), and Fe(IV); Figs. 2(d)–2(f), respectively] gave structures that clearly show no bowing of the GO layers. Instead, the structures are largely unremarkable, formed by π -stacking of the cyclopentadienyl rings of the aminoferrocene moieties with the GO layers (see the supplementary material). Separately, we also modeled both (i) chemically more realistic²⁹ 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 (see the supplementary material).

It should be noted that when modeling 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 1^{2+} is not. Ferrocene dications are remarkably rare due to their inherent extreme reactivity. To date, the only crystallographically characterized Fe(IV) ferrocene is $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{2+}$,^{30,31} which is extremely air- and moisture-sensitive and rapidly decomposes in organic solvents. Indeed, it can only be prepared and handled in anhydrous SO₂ and is produced by the oxidation of $[\text{Fe}(\text{C}_5\text{Me}_5)_2]$ with powerful oxidizing agents, such as AsF₅, SbF₅, and ReF₆. No such potent oxidizing agents are present in the system reported by El-Gendy and co-workers:⁵ 1^{2+} would be highly unlikely to form under their conditions³² 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

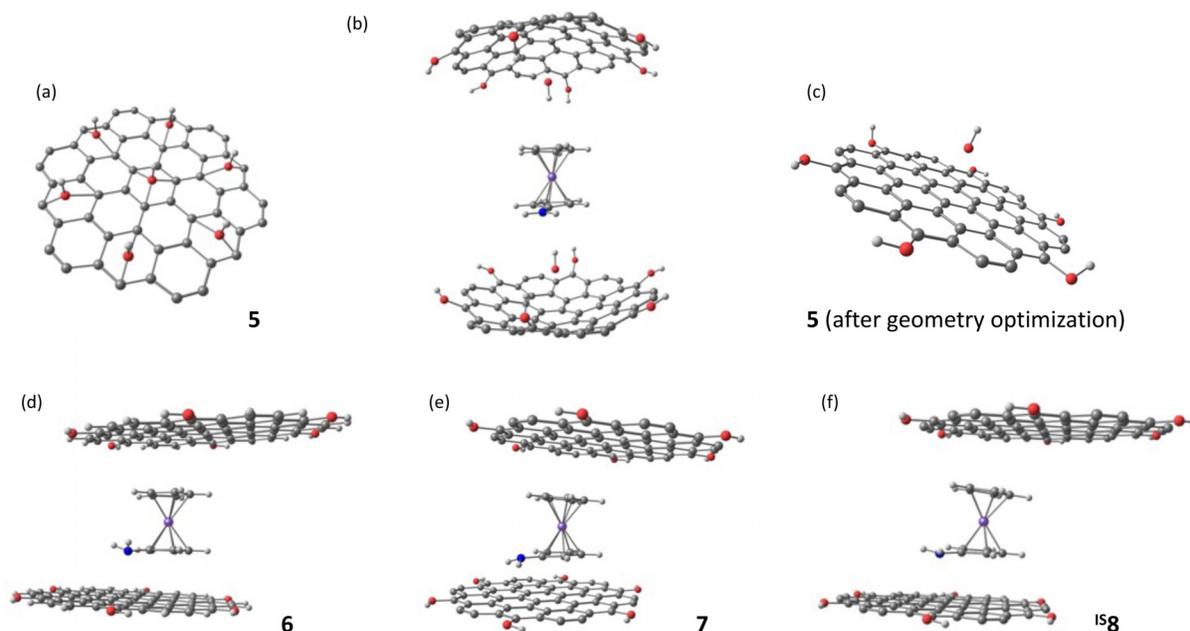


FIG. 2. (a) The precursor model, **5**, used to represent GO prior to optimization.⁵ (b) The model reported on relaxing a structure of $1^{2+} @ [\text{C}_{54}(\text{OH})_6 \cdot \text{OH}]_2$.⁵ (c) The optimized structure **5** in the absence of aminoferrocene. (d)–(f) Structures **6**–**8** obtained on optimizing $1^{n+} @ [\text{C}_{54}(\text{OH})_6]_2$ ($n = 0, 1, \text{ and } 2$, respectively).

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 artifacts brought about as a consequence of the choice of starting model employed.

See the supplementary material for details of experimental procedures; spectroscopic details; computational methodology; and xyz coordinates of calculated structures.

The authors gratefully acknowledge the UK Catalysis Hub for resources and support provided via our membership of the UK Catalysis Hub Consortium and funded by EPSRC Grant Nos. EP/R026939/1, EP/R026815/1, EP/R026645/1, EP/R027129/1, or EP/M013219/1 (biocatalysis). This work was carried out using the computational facilities of the Advanced Computing Research Centre, University of Bristol—<http://www.bristol.ac.uk/acrc/>.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Gayathri Athavan: Conceptualization (supporting); Investigation (equal); Methodology (equal); Writing – original draft (supporting); Writing – review & editing (supporting). **François-Xavier Coudert:** Conceptualization (supporting); Writing – original draft (supporting); Writing – review & editing (supporting). **Robin B. Bedford:** Conceptualization (lead); Data curation (lead); Funding acquisition (lead); Investigation (equal); Methodology (equal); Project administration (lead); Supervision (lead); Validation (equal); Visualization (equal); Writing – original draft (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material. In addition, the xyz coordinate files for the calculated structures are also available at the University of Bristol data repository, [data.bris](https://doi.org/10.5523/bris.mz85vyusop082j481j2ddl1rf), at <https://doi.org/10.5523/bris.mz85vyusop082j481j2ddl1rf>.

REFERENCES

- ¹A. Diamantopoulou, S. Glenis, G. Zolnierkiewicz, N. Guskos, and V. Likodimos, "Magnetism in pristine and chemically reduced graphene oxide," *J. Appl. Phys.* **121**, 043906 (2017).
- ²S. K. Sarkar, K. K. Raul, S. S. Pradhan, S. Basu, and A. Nayak, "Magnetic properties of graphite oxide and reduced graphene oxide," *Physica E* **64**, 78–82 (2014).
- ³M. Sakurai, P. Koley, and M. Aono, "Tunable magnetism of organometallic nanoclusters by graphene oxide on-surface chemistry," *Sci. Rep.* **9**, 14509 (2019).
- ⁴Rather than graphene, as described in the paper's title.
- ⁵Y. W. Getahun, F. S. Manciu, M. R. Pederson, and A. A. El-Gendy, "Room temperature colossal superparamagnetic order in aminoferrocene-graphene molecular magnets," *Appl. Phys. Lett.* **122**, 241903 (2023).
- ⁶Some chemical inaccuracies in the original representation have been removed.
- ⁷For discussion in selected textbooks: (a) R. W. Hoffmann, in *Comprehensive Organometallic Chemistry. The Synthesis, Reactions and Structures of Organometallic Compounds* edited by G. Wilkinson, F. G. A. Stone, and E. W. Abel. (Pergamon Press, Oxford, 1982), pp. 475–476; (b) D. Astruc, *Organometallic Chemistry and Catalysis* (Springer, Berlin, 2007), pp. 258; (c) J. F. Hartwig and J. P. Collman, *Organotransition Metal Chemistry: From Bonding to Catalysis* (University Science Books, New York, 2010), p. 120; (d) N. J. Long, *Metallocenes: An Introduction to Sandwich Complexes* (Blackwell Science, Oxford, 1998), p. 129.
- ⁸R. B. Woodward, M. Rosenblum, and M. C. Whiting, "A new aromatic system," *J. Am. Chem. Soc.* **74**, 3458–3459 (1952).
- ⁹The ferrocenium ion is too electron-deficient to undergo subsequent substitution reactions. Subsequently, decomposition may occur under the reaction conditions.
- ¹⁰H. Grubert and K. L. Rinehart, "Nitroferrocene," *Tetrahedron Lett.* **1**, 16–17 (1959).
- ¹¹J. F. Helling and H. Shechter, *Chem. Ind. (London)*, 1157 (1959).
- ¹²M. Herberhold and L. Haumaier, "Nitrosoferrocene," *Angew. Chem., Int. Ed. Engl.* **23**, 521–522 (1984).
- ¹³A. A. El-Gendy *et al.*, personal communication (2024).
- ¹⁴S. Sethi, P. K. Das, and N. Behera, "The chemistry of aminoferrocene, Fe(η^5 -C₅H₄NH₂)(η^5 -Cp): Synthesis, reactivity and applications," *J. Organomet. Chem.* **824**, 140–165 (2016).
- ¹⁵K. Heinze and M. Schlenker, "Main chain ferrocenyl amides from 1-aminoferrocene-1'-carboxylic acid," *Eur. J. Inorg. Chem.* **2004**, 2974.
- ¹⁶C. L. Perrine, M. Zeller, J. Woolcock, and A. D. Hunter, "Crystal structure of ferrocenyl amine," *J. Chem. Crystallogr.* **35**, 717–721 (2005).
- ¹⁷It could be argued that any I⁺ 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'-diazidoferrocene," *Organometallics* **19**, 3978–3982 (2000).
- ¹⁸G. Shao, Y. Lu, F. Wu, C. Yang, F. Zhong, and Q. Wu, "Graphene oxide: The mechanisms of oxidation and exfoliation," *J. Mater. Sci.* **47**, 4400–4409 (2012).
- ¹⁹A. Lerf, H. He, M. Forster, and J. Klinowski, "Structure of graphite oxide revisited," *J. Phys. Chem. B* **102**, 4477–4482 (1998).
- ²⁰A. Siklitskaya, E. Gacka, D. Larowska, M. Mazurkiewicz-Pawlicka, A. Malolepszy, L. Stobiński, B. Marciniak, A. Lewandowska-Andrałojć, and A. Kubas, "Lerf-Klinowski-type models of graphene oxide and reduced graphene oxide are robust in analyzing non-covalent functionalization with porphyrins," *Sci. Rep.* **11**, 7977 (2021).
- ²¹J. Yang, G. Shi, Y. Tu, and H. Fang, "High correlation between oxidation loci on graphene oxide," *Angew. Chem., Int. Ed.* **53**, 10190–10194 (2014).
- ²²R. C. Sinclair and P. V. Coveney, "Modeling nanostructure in graphene oxide: Inhomogeneity and the percolation threshold," *J. Chem. Inf. Model.* **59**, 2741–2745 (2019).
- ²³F. Mouhat, F.-X. Coudert, and M.-L. Bocquet, "Structure and chemistry of graphene oxide in liquid water from first principles," *Nat. Commun.* **11**, 1566 (2020).
- ²⁴We thank the El-Gendy and co-workers for kindly providing coordinate files on request.
- ²⁵More generally, the structure of optimised 5 represents a poor model of GO, with only one type of C-O functionality, namely, edge hydroxyls, no epoxide or carboxylic residues, and no sp³-hybridized carbons. In effect, the structure is best described as an edge-modified graphene layer rather than a GO layer. Even in the absence of the artificial extrusion of free hydroxyl radicals, this model cannot be reasonably used to draw any useful conclusions on the gross structure and interaction between GO sheets and intercalating species or indeed any fine detail on the electronic structure.
- ²⁶H.-S. Hsieh and R. G. Zepp, "Reactivity of graphene oxide with reactive oxygen species (hydroxyl radical, singlet oxygen, and superoxide anion)," *Environ. Sci.: Nano* **6**, 3734–3744 (2019).

²⁷It 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 the supplementary material for details), with imaginary stretches associated with several OH wagging processes, but this does not impact significantly upon the key conclusion.

²⁸It 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).

²⁹An 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).

³⁰M. Malischewski, M. Adelhardt, J. Sutter, K. Meyer, and K. Seppelt, "Isolation and structural and electronic characterization of salts of the decamethylferrocene dication," *Science* **353**, 678–682 (2016).

³¹The putative species **1**²⁺ would be expected to be both thermodynamically and kinetically far less stable due to the absence of the buttressing methyl residues.

³²Electrochemical studies on aminoferrocene support the Fe(II)/Fe(III) couple but show no evidence of Fe(IV), see: J. Věžník, M. Konhefr, L. Trnková, P. Skládal, and K. Lacina, "Elusive pK_a' of aminoferrocene determined with voltammetric methods in buffered and unbuffered systems and practical aspects of such experiments," *Electrochim. Acta* **318**, 534–541 (2019).